PHYSICAL REVIEW A, VOLUME 65, 052117

Model for dissipative quantum dynamics and nonlinear coupling: Lennard-Jones potential

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(Received 14 January 2002; published 8 May 2002)

In this paper a method is developed further that makes it possible to tailor the position dependence of the coupling strength between a system and a bath in a very flexible way. To do so, generalized raising/lowering operators from supersymmetric quantum mechanics are used, together with the Lindblad approach to dissipation. A one-dimensional numerical example illustrates the application of the method to a problem with polynomial position dependence, and the extension to problems of higher dimension is discussed.

DOI: 10.1103/PhysRevA.65.052117 PACS number(s): 03.65.Yz, 12.60.Jv

I. INTRODUCTION

Open system quantum dynamics is a rapidly developing field, which has applications in many areas of physics. It is impossible to give here a comprehensive overview, but among many others nuclear magnetic resonance spectroscopy [1], driven dissipative tunneling [2], and reactions on surfaces [3–5] should be mentioned. This paper will especially be concerned with the dynamics of open system density matrices within the dynamical semigroup–Lindblad [6–9] approach. Until recent years, most *Ansätze* had the serious limitation of being only applicable to a system-bath coupling bilinear in the coordinates. For many situations, aside from simple model systems, this is unphysical. For example, if the bath are the electronic and phononic degrees of freedom of a surface, then the coupling strength should decrease with the distance from the surface, and not increase. This situation is of special interest for catalytic reactions [5] as well as matter wave optics on atom chips [10]. An early attempt to account for this has been made in Ref. [11]. Recently, two suggestions have been made how to treat nonlinear coupling [12,13] more fundamentally. This paper will present further developments of one [13] of them. The time evolution of the reduced density matrix is governed by the Liouville–von Neumann equation [14]

$$\dot{\rho} = -\frac{i}{\hbar}[H,\rho] + \mathcal{L}_D[\rho], \tag{1}$$

where the dissipative Liouvillian $\mathcal{L}_D[\rho]$ describes the influence of the environment on the system. The most general dissipative functional that guarantees positivity of the evolution, i.e., the probabilistic interpretation of the matrix elements of ρ is the Lindblad functional [6]

$$\mathcal{L}_D[\rho] = \sum_{k=1}^{K} \gamma_k \left(V_k \rho V_k^\dagger - \frac{1}{2}[V_k^\dagger V_k, \rho]_+ \right). \tag{2}$$

A functional like this can be derived in several ways. One [15,16] employs second-order perturbation theory and the rotating wave approximation. In the case of an environment at 0 K this leads to a dissipative Liouvillian of Lindblad form. Another approach is to use the argument of complete positivity and then choose the operators V_k on the grounds of phenomenological reasoning. Both methods result in the *same* equation of motion, if an interaction Hamiltonian between system and bath of the form

$$H_{Int} = \sum_n \lambda_n a b_n^\dagger \tag{3}$$

is used, with a annihilation operator of the system, $b_n^\dagger$ creation operator of the bath, and the assumption that the bath is at 0 K. In this case one finds $V = a$. Dissipation of energy is thus naturally described by raising or lowering operators (RLOs). The use of Harmonic RLOs is then equivalent to a coupling, or interaction Hamiltonian, which is bilinear in the system and bath coordinates. In Sec. II of this paper the derivation of generalized RLOs, which allow to model a large variety of coupling strengths, is presented. Also two possibilities to extend the formalism to multidimensional problems are discussed. Section III presents a numerical example: the often used Lennard-Jones potential, which has seen in recent years a new revival in the field of Lennard-Jones liquids. Section IV gives a short summary of further properties of the RLOs, and Sec. V concludes this paper.

II. GENERALIZED RLOs

The general idea behind supersymmetric (SUSY) quantum mechanics (QM) is that not only the harmonic–oscillator Hamiltonian can be written as the “square” of some operator, $H = \hbar\omega b^\dagger b$, but others as well. We will denote harmonic RLOs by $b, b^\dagger$, and the generalized ones by a, $a^\dagger$, A, and $A^\dagger$. Here we will give only a short summary of those facts that are important for the problem at hand. More detailed introductions to SUSY QM and proofs can be found, e.g., in Ref. [17], and the excellent review paper of Cooper *et al.* [18]. Further, we will restrict ourselves to Hamiltonians of the standard form $H = p^2/2m + V(x)$. It can then be shown, that the operator that factorizes the Hamiltonian has the form

$$A = \phi(x) + \frac{\hbar}{\sqrt{2m}} \frac{d}{dx}, \tag{4}$$

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*Email address: mathias.nest@tc.pci.uni-heidelberg.de where the function $\phi(x)$ is called the superpotential and is related to the potential $V(x)$ by a Riccati differential equation,

$$V(x)=\phi^2(x)-\frac{\hbar}{\sqrt{2m}}\frac{d\phi}{dx}. \tag{5}$$

Equation (4) contains the implicit assumption that the potential V is shifted so that the energy of the ground state Ψ_0 vanishes. The general form of the generalized RLOs $A,A^\dagger$ is not surprising, if one considers that the kinetic-energy part of the Hamiltonian does not change (thus the term d/dx as in the harmonic case), so that the potential is just the square of ϕ, plus the commutator. It should be noted that the operators $A,A^\dagger$ no longer obey the standard Bose commutation relations. Instead,

$$[A^\dagger,A]=-\sqrt{\frac{2}{m}}\frac{d\phi}{dx}. \tag{6}$$

These operators will factorize the Hamiltonian: $H=A^\dagger A$. Next, we will need the so-called partner Hamiltonian H_p,

$$H_p\equiv AA^\dagger=A_p^\dagger A_p+E_0^{(p)}. \tag{7}$$

It is constructed by simply reversing the order of the RLOs. Of course, H_p can be rewritten in terms of a normal order product of RLOs, too. The only difference is now the additional constant $E_0^{(p)}$, because the zero-point energy was already fixed in the definition of H. The crucial point for our discussion is now that the eigenvalues of partner Hamiltonians are intimately connected. In fact, one can show that

$$E_{n+1}=E_n^{(p)}, \quad n=0,1,2,\ldots, \tag{8}$$

i.e., they are isospectral, with the exception that the ground state of H does not exist for H_p. Although the eigenfunctions of partner Hamiltonians are generally different, they are often quite similar. The reason for this is that the partner potentials are often (harmonic oscillator, Coulomb potential, Morse oscillator, etc. [18]), but not always, shape invariant,

$$V(x,\alpha)=V_p(x,f(\alpha))+R(\alpha). \tag{9}$$

This means their functional forms are the same, only the parameters have changed. And even for a large number of potentials that are not strictly shape invariant, at least very similar partner potentials are found.

Only in the case of the harmonic oscillator do these operators A *and* $A^\dagger$ coincide with exact RLOs. This is due to the fact of the equidistant eigenvalues. In the general case, one finds

$$A\Psi_n=(E_n-E_0)^{1/2}\Psi_{n-1}^{(p)}. \tag{10}$$

Therefore, the operator A lowers the quantum number n by one, and annihilates one node in the wave function. The difference to the harmonic case is that the new eigenfunction "belongs" to another Hamiltonian. But because of the (maybe approximate) shape invariance they are at least similar,

$$\Psi_n\approx\Psi_n^{(p)}, \tag{11}$$

and have the same number of nodes. This suggests the use of A and $A^\dagger$ as approximate RLOs. (A similar line of thought justifies the use of $A^\dagger$ as approximate raising operator [19].) In the remainder of this section we will show a fast and efficient way to derive them, and the following two sections will provide examples to show that they produce physically the most sensible results.

We found that the easiest derivation uses the ground-state wave function of H. There are a variety of methods to obtain Ψ_0; for example, the propagation in imaginary time method. Once the ground state is known, the superpotential is obtained via

$$\phi(x)=-\frac{\hbar}{\sqrt{2m}}\Psi_0'(x)/\Psi_0(x), \tag{12}$$

where the prime denotes differentiation with respect to x. And this is all that is needed for the derivation of the approximate RLOs.

At last it should be noted that A and $A^\dagger$ carry the unit "square root of energy." Usually, dimensionless operators are used ($H=\hbar\omega b^\dagger b$). This can be achieved by defining

$$a=\frac{A}{\sqrt{\hbar\omega}} \quad \text{and} \quad a^\dagger=\frac{A^\dagger}{\sqrt{\hbar\omega}}. \tag{13}$$

The choice of ω is not unambiguous for anharmonic problems. The choices of

$$\omega=(E_1-E_0)/\hbar$$

and

$$\omega=\sqrt{V''(x_0)/m}, \tag{14}$$

x_0 position of the minimum of the potential, both give good results.

The generalization of these results to several degrees of freedom can be done in different ways. A crude approximation could make the assumption that all degrees are independent. In this case, it is possible to write a two-dimensional operator as a sum of, e.g., a harmonic RLO and an RLO of exponential form [13]. But there is another possibility, which shall be presented now.

The RLOs $A,A^\dagger$ can be taken to be vectors of operators with elements

$$A_i=\frac{1}{\sqrt{2m}}\left(\frac{\partial}{\partial x_i}-\frac{\partial\Psi_0(x_1,\ldots,x_N)}{\partial x_i}\bigg/\Psi_0(x_1,\ldots,x_N)\right). \tag{15}$$

Thus, one finds a superpotential

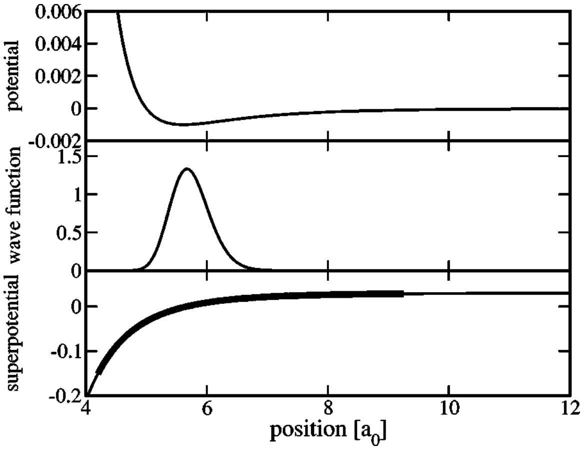

FIG. 1. Upper panel: Lennard-Jones potential [in units of the Hartree energy (E_H)]. Middle panel: ground-state wave function (units of $a_0^{-1/2}$), obtained by propagation in imaginary time. The derivative of it divided by the wave function leads (up to prefactors) to the superpotential, shown in the lower panel (in units of $E_H^{1/2}$). The thick line shows the part that was calculated numerically, the thin line shows the fit [Eq. (18)].

$$\phi_i(x_1, \ldots, x_N) = -\frac{1}{\sqrt{2m}} \frac{\partial \Psi_0(x_1, \ldots, x_N)}{\partial x_i} \Big/ \Psi_0(x_1, \ldots, x_N), \tag{16}$$

which depends on all coordinates. The Hamilton operator is then obtained by the scalar product $\vec{A}^\dagger \cdot \vec{A}$. This is a somewhat more accurate approach, but for numerical efficiency a fit of the numerically obtained superpotential to an analytic function is required, which can be quite difficult to obtain for the multidimensional case. An application of this is in preparation.

III. EXAMPLE

As a numerical example we have chosen the Lennard-Jones potential (Fig. 1)

$$V(x) = 4\epsilon\left[\left(\frac{s}{x}\right)^{12} - \left(\frac{s}{x}\right)^{6}\right] \tag{17}$$

with parameters $\epsilon = 10^{-3} E_H$, $s = 5a_0$, and $m = 5 \times 10^4 m_e$. Atomic units ($\hbar = m_e = a_0 = 1$) will be used from now on. This system has been chosen because it shows a polynomial decay for large x. The exponential case has already been discussed, also with other approaches, e.g., in Refs. [12,13]. Also, contrary to the Morse potential, and in accordance with most physically realistic potentials, it is not analytically treatable. To derive the approximate RLOs for this problem, the first thing to be done is to find the ground-state wave function. This has been done on a very fine grid in position space. Then the derivative [see Eq. (12)] has been calculated with the fast Fourier method, employing the identity $d/dx = ip$. For later application it is advantageous to fit $\phi(x)$ to an analytical expression. A least-squares fit gives

$$\phi(x) = c_1 - \frac{c_2}{c_3 + c_4 x^6 - c_5 x^{12}} \tag{18}$$

with parameters $c_1 = 0.03 E_H^{1/2}$, $c_2 = 995.7 E_H^{1/2}$, $c_3 = 25.29$, $c_4 = 1 a_0^{-6}$, and $c_5 = 1.094 \times 10^{-7} a_0^{-12}$. Please note that these are only four independent parameters, as c_4 is only used to obtain simpler units. The parameter ω [see Eq. (13)] was calculated from a harmonic approximation of the potential minimum. This concludes the derivation of a and $a^\dagger$.

These approximate RLOs can now be used to propagate the reduced density matrix with the Liouvillian of Eqs. (1) and (2), with $K = 1$ (one dissipative channel).

The interesting quantity now is the coupling strength between system and environment as a function of the position, e.g., the distance from a surface. It can be measured by the energy relaxation rate of a narrow Gaussian wave packet centered at x_0. The change of this rate with x_0 is then the desired quantity. There are two ways to perform this calculation. One is to propagate the density matrix for a short time, and monitor the change of $\langle H \rangle(t)$. This method was used in Refs. [13,19]. However, recently we found a better way, which does not require to actually perform a propagation. The derivative of the expectation value of the Hamiltonian can be computed directly:

$$\mathrm{Tr}\{H\dot{\rho}\} = \mathrm{Tr}\left\{ H\left[\gamma\left(a\rho a - \frac{1}{2}[a^\dagger a, \rho]_+ \right)\right]\right\} \tag{19}$$

$$= \gamma\omega \mathrm{Tr}\{a^\dagger a^\dagger a a \rho\} - \frac{\gamma}{\omega}\mathrm{Tr}\{H^2\rho\} \tag{20}$$

$$= \gamma\omega \mathrm{Tr}\left\{ a^\dagger \left(a a^\dagger - \sqrt{\frac{2}{m\omega^2}}\phi' \right) a\rho \right\} - \frac{\gamma}{\omega}\mathrm{Tr}\{H^2\rho\} \tag{21}$$

$$= -\gamma\sqrt{\frac{2}{m}}\mathrm{Tr}\{\phi' a \rho a^\dagger\}. \tag{22}$$

To come from Eq. (20) to Eq. (21) one has to apply the commutation relation (6). Equation (22) suggests yet another approach to anharmonic coupling strength functions. In principle this equation can be inverted, so that $\phi'(x_0)$ can be determined for arbitrary, given $\mathrm{Tr}\{H\dot{\rho}\}(x_0)$. This could turn out to be an easier and even more flexible way to determine the approximate RLOs, making the calculation of Ψ_0 unnecessary. A paper about this method is in preparation.

We implemented Eq. (22) with the initial condition

$$\rho(t=0) = |\Psi\rangle\langle\Psi|, \quad \Psi(x) \propto \exp\left(-\frac{(x-x_0)^2}{2\sigma^2} + ik_0 x \right), \tag{23}$$

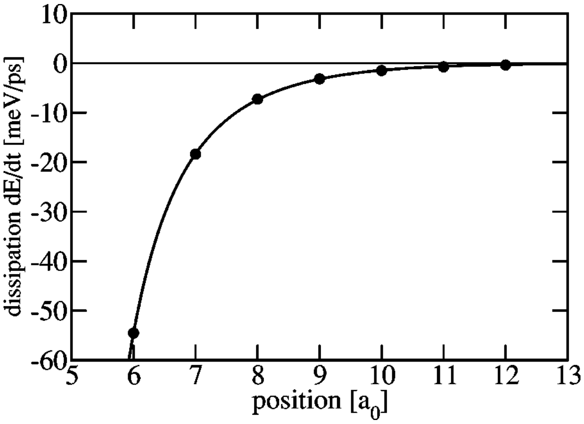

FIG. 2. Dissipation rate calculated by Eq. (22) (points), and fit [Eq. (24)] (line).

with $\sigma = 0.5 a_0$ and $\gamma = 1/500$ fs. The parameter k_0 was for each position x_0 adjusted, so that $\langle H \rangle = 2 \times 10^{-4} E_H$. As a result (see Fig. 2) we find a coupling strength function (again least-squares fit):

$$\frac{d}{dt} \langle H \rangle |_{x_0} = \frac{C_1}{C_2 - C_3 x_0^6 - C_4 x_0^{12}}, \tag{24}$$

with parameters $C_1 = 2.113 \times 10^6$ meV/ps, $C_2 = 8942$, $C_3 = 1 a_0^{-6}$, and $C_4 = 4.772 \times 10^{-7} a_0^{-12}$. Again, only three of them are independent. The parameters C_i depend on the parameters σ and k_0. The width of the wave function has to be chosen small enough so that the potential varies only slowly in that region, and large enough to prevent an unwanted broadening of the wave packet in momentum space. By definition, $k_0(x_0)$ was chosen to keep the total energy of the wave packet the same at different center positions. A coupling strength function that keeps the momentum expectation value constant instead could as well be used. It should be mentioned that Eqs. (18) and (24) have unphysical singularities, but they occur in regions that are, at least for this study, of no interest. Otherwise they could be shifted by small changes in the fit parameter, without significant deterioration of the quality of the fit.

To summarize, the approximate RLOs together with the Liouvillian of Eq. (2) lead to a position dependent coupling strength that imitates the polynomial form of the potential. The route of their derivation via the ground-state wave function can be followed also for potentials which are not analytically solvable, as for example those stemming from density functional theory studies.

IV. OTHER PROPERTIES

Other properties of these operators have been examined in earlier papers [5,19]. For the sake of completeness, we will give here a very short overview.

(a) Lifetimes of bound states. This dissipative model leads to lifetimes

$$\tau_n = \frac{\omega}{\gamma (E_n - E_0)}, \tag{25}$$

if one assumes for the moment that the RLOs were exact. This relation is a generalization of the well-known result for the harmonic oscillator $\tau_n = 1/(\gamma n)$. Numerical studies [13] have shown that Eq. (25) is indeed obeyed for the lifetimes of the lower bound states. The lifetime of the higher excited states are longer than expected.

(b) Quality of approximation. If one applies *(a)* to an energy eigenfunction $|n\rangle$ and compares the energy expectation value of the resulting wave function with the one of the next lower eigenfunction, one finds differences of typically between 1% and 5%, depending on the similarity of the partner potentials.

(c) Thermalization. The Liouvillian

$$\mathcal{L}[\rho] = \gamma \left(b \rho b^\dagger - \frac{1}{2} [b^\dagger b, \rho]_+ \right) + \delta \left(b^\dagger \rho b - \frac{1}{2} [b b^\dagger, \rho]_+ \right) \tag{26}$$

is used in Ref. [6] to describe a harmonic oscillator coupled bilinearly to a heat bath at temperature

$$T = \frac{\omega}{k_B \ln(\gamma/\delta)}. \tag{27}$$

Using the approximate RLOs for a model system representing an argon atom in front of a copper surface at 20 K, we found [19] that they lead to the relaxation to thermal equilibrium, too.

(d) Free to bound transitions. Because the approximate RLOs were derived using only discrete, bound states, it is not obvious that they are able to describe transitions between the free states in a continuum and bound states (“trapping”). In Ref. [13] we were able to show this by applying the dissipative Liouvillian of Eq. (2) to the inelastic scattering or adsorption of oxygen molecules on a platinum surface.

V. SUMMARY

The formalism of the description of dissipation with generalized RLOs was applied to the Lennard-Jones potential. It was found that the polynomial decay of the potential at large distances transforms into an analog position dependence of the coupling strength. The method can easily be adapted to other potentials in order to tailor coupling strength functions for different problems. There are different possibilities to extend the formalism to the multidimensional case, which still have to be explored.

ACKNOWLEDGMENTS

I would like to thank P. Saalfrank for numerous helpful discussions, and acknowledge financial support by the Deutsche Forschungsgemeinschaft.

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