Influence of phase-sensitive interaction on the decoherence process in molecular systems

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Abstract

The character of the interaction between an impurity vibrational mode and a heat bath leads to certain peculiarities in the relaxational dynamics of the excited states. We derive a non-Markovian equation of motion for the reduced density matrix of this system which is valid for initial, intermediate and kinetic stages of the relaxation. The linear phase-sensitive character of the interaction ensures the ultrafast disappearance of the quantum interference of the initially superpositional state and the effect of classical squeezing of the initially coherent state. On the other hand, the second power interaction induces a partial conservation of the quantum interference.

Keywords: decoherence, superposition, non-Markovian, vibronic wavepacket

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Motivation and model

Time-resolved experimental techniques [1] sometimes allow to detect quantum superpositional states in different physical systems [2,3]. Such states provide a basis for the possibility of applications like quantum computers [4]. Unfortunately, these interesting states inevitably decay due to the coupling with a heat bath containing many degrees of freedom [5]. Below we consider how the character of the coupling with the bath influences the dynamics of the superpositional state of the impurity vibrational mode. Describing this mode as a harmonic oscillator, one writes the interaction part of the Hamiltonian as

\[ H_I = \hbar \sum_{\xi} K(\omega\xi) \left( b_{\xi}^+ f(a, a^+) + b_{\xi} f^+(a, a^+) \right), \]

(1)

where the function \( K(\omega\xi) \) describes the intensity of the interaction between the vibronic mode and the bath mode operators \( b_{\xi} \). \( f(a, a^+) \) is a function of the vibronic mode operators. We consider two cases, namely \( f(a, a^+) = a + a^+ \), corresponding to the case of the linear phase-sensitive interaction, and \( f(a, a^+) = a^2 \) yielding a quadratic interaction in the rotating wave approximation. Below we are using “single” and “double” to indicate the baths with these two types of interactions.

Single bath

The first case describes the processes when system and bath are exchanging one quantum. Such a behavior is provided by the physical situation when the majority of the bath modes contributing to dephasing and thermalization of the system have approximately the same frequency \( \omega\xi \) as the system mode \( \omega \). Applying the formalism of the time evolution operator, and restricting to the second order cumulant expansion [6], we obtain the non-Markovian master equation [7] for the reduced density matrix \( \sigma \) of the impurity vibrational mode:
\[
\frac{\partial \sigma}{\partial t} = -i\omega [a^+ a, \sigma] + (\gamma_{n+1} + \tilde{\gamma}_n^*) [a\sigma, a^+ + a] \\
+ (\gamma_n^* + \tilde{\gamma}_n) [a^+ + a, \sigma a^+] \\
+ (\tilde{\gamma}_{n+1} + \gamma_n^*) [a^+ \sigma, a^+ + a] \\
+ (\tilde{\gamma}_n^* + \gamma_n) [a^+ + a, \sigma a].
\]  

We obtain four relaxation functions $\gamma$, which are shown in Fig. 1a. They originate from the correlations between the operators $a(t)$ and $a^+(t)$ of the system mode $\omega$ and the memory kernels of the bath, like $\langle b_\xi^+(0)b_{\xi'}(\tau) \rangle$, which appear in the second order cumulant expansion of the evolution operator. These coefficients are found to be time-dependent. $\gamma_{n+1}$ and $\gamma_n$ describe the situation when emission-like processes $\gamma_{n+1}$ prevail over the absorption-like processes $\gamma_n$, where $n$ denotes the number of quanta in the bath modes. The functions $\tilde{\gamma}_{n+1}$, $\tilde{\gamma}_n$ correspond to the reverse situation and are always small.

The evolution of the different initial states of the system was found [6] in analytical form for two cases, namely: the initial stage of relaxation, when all of the relaxation functions are linear in time, and for the kinetic stage of the relaxation, when the coefficients $\tilde{\gamma}_n$, $\tilde{\gamma}_{n+1}$ vanish, while $\gamma_n$, $\gamma_{n+1}$ become constants $\Gamma_1 n_1$ and $\Gamma_1(n_1 + 1)$, respectively. Here $n_1 = n(\omega)$ indicates the number of quanta in the bath mode at the system frequency. The analytical solution is based on the generating function formalism [6]. The approaches corresponding to the above stages are applied to the evolution of the superposition of two coherent states $|\alpha\rangle$ and $e^{i\phi} |\alpha\rangle$

\[
|\alpha, \phi\rangle = N^{-1} \left( |\alpha\rangle + e^{i\phi} |\alpha\rangle \right),
\]

where $N$ is the normalization constant, $|\alpha\rangle$ is obtained by displacement of the vacuum state $|0\rangle$ by $\alpha$ as $|\alpha\rangle = \exp(\alpha a^+ - \alpha^* a) |0\rangle$. The dependence of the probability
density $P$ on coordinate $Q$ and time is found to consist of classical and interference parts [7]:

$$P(Q, t) = P_{\text{class}}(Q, t) + P_{\text{int}}(Q, t). \quad (4)$$

The interference part behaves somewhat different under each approach, compare Fig. 1b. Nevertheless, energy relaxation of $P_{\text{class}}$ and decoherence of $P_{\text{int}}$ occur on different time scales, independent on the approach applied: The quantum interference $P_{\text{int}}$ disappears faster. The phase-sensitive character of the relaxation induces small oscillations of the broadening of the initially coherent wave packet [7].

**Double bath**

When the system interacts with a bath having the maximum of its mode density at twice the oscillator frequency, then processes occur in which the system loses 2 quanta and the bath obtains one quantum. The reverse processes are also allowed. To describe such a behavior we use $f(a,a^+) = a^2$ in the interaction Hamiltonian (1). The kinetic stage of the evolution of such a system follows the master equation

$$\frac{\partial \sigma}{\partial t} = -i\omega \left[ a^+ a, \sigma \right] + \Gamma_2(n_2 + 1) \left\{ \left[ a^2 \sigma, (a^+)^2 \right] + \left[ (a^+)^2, \sigma a^2 \right] \right\} + \Gamma_2 n_2 \left\{ \left[ (a^+)^2 \sigma, a^2 \right] + \left[ a^2, \sigma (a^+)^2 \right] \right\}, \quad (5)$$

where $\Gamma_2 = \pi K^2 g_2$ is the decay rate of the vibrational amplitude. Here, the number of quanta in the bath mode $n_2 = n(2\omega)$, the coupling function $K = K(2\omega)$, and the density of bath states $g_2 = g(2\omega)$ are evaluated at the double frequency of the selected oscillator.

Rewritten in the basis of eigenstates $|n\rangle$ of the unperturbed oscillator this master equation contains only linear combinations of such terms as $\sigma_{m,n} = \langle m | \sigma | n \rangle$, 

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\( \sigma_{m+2,n+2} \) and \( \sigma_{m-2,n-2} \). It ensures, in effect, a possibility to distinguish even and odd initial states of the system. The odd excited state \(|1\rangle\) cannot relax into the ground state \(|0\rangle\), but the even excited state \(|2\rangle\) can.

The evolution of the system after preparation under different initial conditions was simulated numerically. The equations of motion of the density matrix elements are integrated using a fourth order Runge-Kutta algorithm with stepsize control. To make the set of differential equations a finite one we restrict the number of levels by \( m, n \leq 20 \).

One of the representative examples is the behavior of the initially coherent state of the system. For comparison with the usual behavior we have used the time dependence of the mean value of the coordinate. One can see in Fig. 2a that the relaxation consists of two stages. The coordinate mean value of the usual system decreases with a constant rate during both stages. The same initial value of the system coupled to a double bath shows a fast decrement in the first stage and almost no decrement in the second.

The question about the influence of the type of the bath on the evolution of the superpositional state is of special importance. The simulation was made at a temperature of \( k_B T = 2\hbar \omega / \ln 3 \), corresponding to \( n(2\omega) = 0.5 \). To allow the comparison, we have simulated the evolution of the same superpositional states twice. The only difference was the type of the baths, namely single and double bath. The coordinate representation of the wave packets is presented in Fig. 2b and 2c. The same value of the relaxation \( \Gamma_1 = \Gamma_2 \) provides, however, different results. In the system coupled to the single bath the quantum interference disappears already during the first period, while the amplitude decreases only slightly. In the opposite case, the system coupled to the double bath leaves the interference almost unchanged, although a fast reduction of the amplitude occurs.
Therefore, the second system partially conserves the quantum superpositional state. The experimental investigation of systems displaying such properties [2] is necessary, both for extracting typical parameter ranges for theoretical models and for practical applications like quantum computation and quantum cryptography.

Conclusions
The character of the coupling with a heat bath plays a dominating role in the time evolution of different excited states of a vibrational mode. Linear coupling ensures the ultrafast decay of the interference part of the superpositional state. This result remains true even if different approaches are applied. The quadratic type of coupling gives the same time scales both for the amplitude and interference relaxations. Some initial coherent properties, like the distinction between even and odd levels, survive for long time scales.

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FIGURES

FIG. 1. (a) Time-dependent relaxation coefficients $\gamma_{n+1}$ (solid line), $\gamma_n$ (diamonds), $\tilde{\gamma}_{n+1}$ (boxes), $\tilde{\gamma}_n$ (crosses) of the master Eq. (2), calculated for a bath containing 60 modes in the range $[0, 6\omega]$, with coupling function $K(\omega \xi) \equiv 1$. (b) Time dependence of $P_{\text{int}}$ from Eq. (4), when the heat bath can be described with only two constants $\Gamma_1 = 0.25\omega$, $n_1 = 0.4$ for $\omega = 1$, $Q(t = 0) = 4$, $\phi = 0$. Crosses: derivation valid for the initial stage of the relaxation, solid line: result for the kinetic stage of the relaxation, diamonds: corresponding result obtained for the linear interaction in the rotating wave approximation $f(a, a^+) = a$.

FIG. 2. Difference between double and single baths. (a) Evolution of the coherent state: Mean value of the coordinate, for $Q(t = 0) = -2.2$. Diamonds: system coupled to the single bath, $\Gamma_1 = 0.15\omega$. Solid line: system coupled to the double bath, $\Gamma_2 = 0.5\omega$. (b) Time evolution of the superposition of coherent states with initial separation $2Q_0 = 8$ interacting with single bath (b) for $\omega = 1$, $\Gamma_1 = 0.005\omega$, $n(\omega) = 1.36$. (c) Same as (b), but for a double bath with $\Gamma_2 = 0.005\omega$, $n(2\omega) = 0.5$. 
relaxation coefficients

(a)

(b)

\[ \ln P_{int} \]

\[ \text{time} \]

\[ \text{time} \]
