Problem Sheet 12: The master equation approach in quantum physics: Numerical simulations of the Redfield equation (5 February 2019)

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Exercise 26. [18p] The Redfield equation.

In this exercise, we consider the energy transfer in a two-site system where the coupling between sites induces quantum features in energy transfer, while the coupling to thermal environments causes decoherence. We will employ the Redfield equation detailed below to simulate the energy transfer dynamics under environmental effects.

Each site is modeled by a two-level system consisting of electronic ground and excited states, denoted by $|g\rangle$ and $|e\rangle$, respectively. We assume that the initial excitation is localized at site 1, namely site 1 is in its excited state, while site 2 is in its ground state at time $t = 0$. The excitation of site 1 is transferred to site 2 and vice versa mediated by an electronic coupling J. Each site is coupled to an independent thermal bath modelled by quantum harmonic oscillators, which suppresses the coherent features in energy transfer dynamics without changing the number of electronic excitations within the system. The total Hamiltonian is modelled by $\hat{H} = \hat{H}_s + \hat{H}_e + \hat{H}_{s-e}$.

(i) $\hat{H}_s$ is the system Hamiltonian in the single excitation subspace

$$\hat{H}_s = \hbar\Omega_1 |1\rangle\langle 1| + \hbar\Omega_2 |2\rangle\langle 2| + \hbar J(|1\rangle\langle 2| + |2\rangle\langle 1|), \tag{1}$$

where $|1\rangle = |e_1\rangle \otimes |g_2\rangle$, $|2\rangle = |g_1\rangle \otimes |e_2\rangle$, and Ω_k denotes the energy level of site k. The system Hamiltonian satisfies $\hat{H}_s |\epsilon_k\rangle = \hbar\epsilon_k |\epsilon_k\rangle$, where ϵ_k denote the eigenvalues associated with eigenstates $|\epsilon_k\rangle = \psi_{k1}|1\rangle + \psi_{k2}|2\rangle$.

(ii) $\hat{H}_e$ is the environment Hamiltonian

$$\hat{H}_e = \sum_\xi \hbar\omega_\xi \left(\hat{b}^\dagger_{\xi,1}\hat{b}_{\xi,1} + \hat{b}^\dagger_{\xi,2}\hat{b}_{\xi,2}\right), \tag{2}$$

where $\hat{b}^\dagger_{\xi,k}$ and $\hat{b}_{\xi,k}$ denote the creation and annihilation operators, respectively, of the environmental mode with frequency ω_ξ, which is locally coupled to site k, as detailed below.

(iii) $\hat{H}_{s-e}$ is the interaction Hamiltonian between system and environment

$$\hat{H}_{s-e} = \sum_\xi \left[\hbar g_{\xi,1} |1\rangle\langle 1| \otimes \left(\hat{b}^\dagger_{\xi,1} + \hat{b}_{\xi,1}\right) + \hbar g_{\xi,2} |2\rangle\langle 2| \otimes \left(\hat{b}^\dagger_{\xi,2} + \hat{b}_{\xi,2}\right)\right], \tag{3}$$

where $g_{\xi,k}$ is the coupling between site k and environmental mode (ξ, k). We assume that the electronic energy levels are sufficiently higher in energy than the frequencies of the environmental modes, $\Omega_k \gg \omega_{\xi,k}$, such that the interaction Hamiltonian does not induce the transition between electronic ground and excited states, maintaining the number of electronic excitations.

The Born-Markov approximation leads to the Redfield equation shown below where the time evolution of the reduced system state is governed by

$$\frac{d}{dt}\rho^{\mathrm{eig}}_{kl}(t) = -i(\epsilon_k - \epsilon_l)\rho^{\mathrm{eig}}_{kl}(t) + \sum_{k'=1}^{2}\sum_{l'=1}^{2} R_{kl,k'l'}\rho^{\mathrm{eig}}_{k'l'}(t), \tag{4}$$

where $\rho^{\mathrm{eig}}_{kl}(t) = \langle\epsilon_k|\hat{\rho}_s(t)|\epsilon_l\rangle$ denote the elements of the reduced system state $\hat{\rho}_s(t)$ in the eigenbasis of $\hat{H}_s$. $R_{kl,k'l'}$ is the Redfield tensor describing decoherence

$$R_{kl,k'l'} = \Gamma_{l'l,kk'} + \Gamma^*_{k'k,ll'} - \delta_{ll'}\sum_{m=1}^{2}\Gamma_{km,mk'} - \delta_{kk'}\sum_{m=1}^{2}\Gamma^*_{lm,ml'}, \tag{5}$$

with $\delta_{kk'}$ denoting the Kronecker delta, defined by $\delta_{kk'} = 1$ if $k = k'$ and $\delta_{kk'} = 0$ otherwise. $\Gamma_{kl,k'l'}$ is defined by

$$\Gamma_{kl,k'l'} = \sum_{m=1}^{2} \langle\epsilon_k|m\rangle\langle m|\epsilon_l\rangle\langle\epsilon_{k'}|m\rangle\langle m|\epsilon_{l'}\rangle \pi\mathcal{J}_m(\epsilon_{l'} - \epsilon_{k'})[n(\epsilon_{l'} - \epsilon_{k'}) + 1], \tag{6}$$

where $n(\omega) = 1/(\exp(\hbar\omega/k_B T) - 1)$ is the Bose-Einstein distribution function at temperature T, and $\mathcal{J}_k(\omega) = \sum_\xi g^2_{\xi,k}\delta(\omega - \omega_\xi)$ is the spectral density, describing the spectrum of system-environmental couplings. For simplicity, we consider the Ohmic spectral density with a Lorentz-Drude cutoff function $\mathcal{J}_k(\omega) = \dfrac{2\lambda_k}{\pi}\dfrac{\omega\gamma_k}{\omega^2+\gamma_k^2}$, where $\lambda_k = \sum_\xi g_{\xi,k}^2\omega_\xi^{-1}$ quantifies the overall environmental coupling strength. Note that as $\epsilon_{l'} - \epsilon_{k'} \to 0$, $\mathcal{J}_m(0) \to 0$ and $n(0) \to \infty$, leading to $\mathcal{J}_m(0)(n(0)+1) \to \dfrac{2\lambda_k}{\pi}\dfrac{1}{(\hbar\gamma_k/k_B T)}$ in Eq. (6).

(a) [3p] Simulate the time evolution of the population of site 2, $\langle 2|\hat{\rho}_s(t)|2\rangle$, up to time $t = 1$ for the case that $\Omega_1 - \Omega_2 = 0$, $J = 100$, $\lambda_k = 0$, $\gamma_k = 50$, $(k_B T/\hbar) = 100$, and $\hat{\rho}_s(0) = |1\rangle\langle 1|$. Here the two sites have the same energy levels and they are decoupled from the environments, leading to a coherent energy transfer. Check the oscillatory features in population and coherence dynamics in the site basis, namely $\langle 1|\hat{\rho}_s(t)|1\rangle$ and $\langle 2|\hat{\rho}_s(t)|1\rangle$.

(b) [3p] Simulate the time evolution of the population of site 2 up to time $t = 1$ for the case that $\Omega_1 - \Omega_2 = 0$, $J = 100$, $\lambda_k = 10$, $\gamma_k = 50$, $(k_B T/\hbar) = 100$, and $\hat{\rho}_s(0) = |1\rangle\langle 1|$. Here the system is coupled to the thermal environments, leading to decoherence. Check the decay of the oscillatory features in system dynamics. Check that the two sites have the same population of 0.5 when saturated, which is due to the same energy levels, $\Omega_1 = \Omega_2$.

(c) [3p] Simulate the time evolution of the population of site 2 up to time $t = 1$ for the case that $\Omega_1 - \Omega_2 = 100$, $J = 100$, $\lambda_k = 10$, $\gamma_k = 50$, $(k_B T/\hbar) = 100$, and $\hat{\rho}_s(0) = |1\rangle\langle 1|$. Here site 1 has a higher energy level than site 2. Check that the population of site 2 becomes higher than that of site 1 when saturated. Check that the saturated value of the population of site 2 decreases as temperature increases.

(d) [3p] Simulate the time evolution of the negativity of the reduced system state $\hat{\rho}_s(t)$, defined by the sum of the negative eigenvalues of $\hat{\rho}_s(t)$. Consider the case that $\Omega_1 - \Omega_2 = 100$, $J = 100$, $\lambda_k = 1000$, $\gamma_k = 50$, $(k_B T/\hbar) = 100$, and $\hat{\rho}_s(0) = |1\rangle\langle 1|$, where the environmental coupling λ_k is stronger than the previous cases. The negativity implies that the Redfield equation can give rise to unphysical states, as a physical state should have non-negative eigenvalues. This is contrary to the Lindblad equations, where the reduced system state $\hat{\rho}_s(t)$ is positive semidefinite for all times.

(e) [3p] Here we consider the Redfield equation within the secular approximation, as an example of the Lindblad equation. In the interaction picture, the Redfield equation takes the form

$$\frac{d}{dt}\tilde{\rho}_{kl}^{\text{eig}}(t) = \sum_{k'=1}^{2}\sum_{l'=1}^{2} R_{kl,k'l'} \exp[i(\epsilon_k - \epsilon_l)t - i(\epsilon_{k'} - \epsilon_{l'})t]\tilde{\rho}_{k'l'}^{\text{eig}}(t), \tag{7}$$

where $\tilde{\rho}_{kl}^{\text{eig}}(t)$ denote the elements of the reduced system state in the interaction picture, defined by $\tilde{\rho}_{kl}^{\text{eig}}(t) = \rho_{kl}^{\text{eig}}(t)e^{i(\epsilon_k-\epsilon_l)t}$. The secular approximation is equivalent to neglecting the Redfield tensor elements $R_{kl,k'l'}$ satisfying $|(\epsilon_k - \epsilon_l) - (\epsilon_{k'} - \epsilon_{l'})| \neq 0$. Simulate the time evolution of the negativity of the reduced system state $\hat{\rho}_s(t)$ for the parameters in (d) and check that the negativity disappears. Simulate the time evolution of the population of site 2 with and without the secular approximation and check the differences in population dynamics.

(f) [3p] Here we consider a moderate environmental coupling strength, $J \approx \lambda_k$, which does not cause the negativity, but induces non-secular effects modulating system dynamics. Simulate the time evolution of the population of site 2 up to time $t = 1$ with and without the secular approximation for the case that $\Omega_1 - \Omega_2 = 0$, $J = 50$, $\lambda_k = 50$, $\gamma_k = 50$, $(k_B T/\hbar) = 100$, and $\hat{\rho}_s(0) = |1\rangle\langle 1|$. Check that disregarding non-secular terms results in different system dynamics.