Tutorial sheet 8

13. Evolution of a small quantum system in contact with a thermal reservoir

Consider a *closed* system $\mathcal{S}+\mathcal{R}$ consisting of a "small" quantum-mechanical system $\mathcal{S}$, with only few degrees of freedom or equivalently a low-dimensional Hilbert space, coupled to a "large" system, called environment—or reservoir, if it has infinitely many degrees of freedom, as we shall hereafter assume. The Hamiltonian of the total system is of the form

$$\hat{\mathsf{H}} = \hat{\mathsf{H}}_{\mathcal{S}} + \hat{\mathsf{H}}_{\mathcal{R}} + \hat{\mathsf{V}},$$

with $\hat{\mathsf{H}}_{\mathcal{S}}$ the free Hamiltonian of the small system and $\hat{\mathsf{H}}_{\mathcal{R}}$ that of the reservoir, while $\hat{\mathsf{V}}$ describes the interaction between $\mathcal{S}$ and $\mathcal{R}$. The eigenstates of $\hat{\mathsf{H}}_{\mathcal{S}}$ are denoted as $|i\rangle$, $|j\rangle\ldots$, with E_i, $E_j\ldots$ the corresponding energies.

As reservoir, we take an ensemble of harmonic oscillators labeled by an index λ, whose frequencies $\{\omega_\lambda\}$ span a large continuum encompassing the Bohr frequencies $\omega_{ki} \equiv (E_k - E_i)/\hbar$ (for $E_k > E_i$) of $\hat{\mathsf{H}}_{\mathcal{S}}$. Let $\hat{\rho}^{\mathcal{R}}$ denote the density operator of the free reservoir.

The total system is described by a density operator $\hat{\rho}(t)$. The purpose of this problem is to find a simplified evolution equation for the "reduced" density operator (cf. Sec. II.2.2 e in the lecture notes)

$$\hat{\rho}^{\mathcal{S}}(t) \equiv \mathrm{Tr}_{\mathcal{R}}\big(\hat{\rho}_{\mathrm{I}}(t)\big), \tag{1}$$

acting on the Hilbert space of $\mathcal{S}$, and obtained by integrating out ("tracing out") the degrees of freedom of the reservoir, where $\hat{\rho}_{\mathrm{I}}(t)$ will be defined in question **i.** below.

i. Preliminary: interaction picture

In the Dirac interaction picture with respect to the free evolution under $\hat{\mathsf{H}}_{\mathcal{S}} + \hat{\mathsf{H}}_{\mathcal{R}}$, the operators $\hat{\rho}(t)$, $\hat{\mathsf{V}}$ become $\hat{\rho}_{\mathrm{I}}(t)$, $\hat{\mathsf{V}}_{\mathrm{I}}(t)$.

Write down the expression of $\hat{\rho}_{\mathrm{I}}(t)$ as a function of $\hat{\rho}(t)$, as well as the analogous expression of the interaction term $\hat{\mathsf{V}}_{\mathrm{I}}(t)$ as a function of $\hat{\mathsf{V}}$. Which equation governs the time evolution of $\hat{\rho}_{\mathrm{I}}(t)$?

ii. Evolution of $\hat{\rho}_{\mathrm{I}}(t)$ over a short interval

Check that the integration of the evolution equation determined above between instants t and $t+\Delta t$ leads first to

$$\hat{\rho}_{\mathrm{I}}(t+\Delta t) = \hat{\rho}_{\mathrm{I}}(t) + \frac{1}{\mathrm{i}\hbar}\int_t^{t+\Delta t} \big[\hat{\mathsf{V}}_{\mathrm{I}}(t'), \hat{\rho}_{\mathrm{I}}(t')\big]\,\mathrm{d}t',$$

and equivalently to

$$\hat{\rho}_{\mathrm{I}}(t+\Delta t) = \hat{\rho}_{\mathrm{I}}(t) + \frac{1}{\mathrm{i}\hbar}\int_t^{t+\Delta t} \big[\hat{\mathsf{V}}_{\mathrm{I}}(t'), \hat{\rho}_{\mathrm{I}}(t)\big]\,\mathrm{d}t' + \frac{1}{(\mathrm{i}\hbar)^2}\int_t^{t+\Delta t} \left\{\int_t^{t'} \Big[\hat{\mathsf{V}}_{\mathrm{I}}(t'), \big[\hat{\mathsf{V}}_{\mathrm{I}}(t''), \hat{\rho}_{\mathrm{I}}(t'')\big]\Big]\,\mathrm{d}t''\right\}\mathrm{d}t'. \tag{2}$$

iii. Simplifying assumptions

Equation (2) is exact, but not very practical. To make progress, we need a few assumptions.

a) First, we assume that the reservoir is so large that it is not perturbed by its interaction with the small system, and additionally, that $\mathcal{R}$ is in a stationary state.

Show that these assumptions mean that the density operator for $\mathcal{R}$ always remains equal to its free value $\hat{\rho}^{\mathcal{R}}$, even in the interaction picture with respect to $\hat{\mathsf{H}}_{\mathcal{S}} + \hat{\mathsf{H}}_{\mathcal{R}}$, and that it is diagonal in a basis of eigenstates of $\hat{\mathsf{H}}_{\mathcal{R}}$. Give its expression in case $\mathcal{R}$ is in thermal equilibrium at temperature T (one then speaks of a thermal bath).

b) As second assumption, we take an interaction of the form $\hat{\mathsf{V}} = \hat{\mathsf{S}} \otimes \hat{\mathsf{R}}$, where $\hat{\mathsf{S}}$ acts on $\mathcal{S}$ only, and $\hat{\mathsf{R}}$ on $\mathcal{R}$ only. Additionally, we assume that the expectation value of $\hat{\mathsf{R}}$ in the stationary state $\hat{\rho}^{\mathcal{R}}$ vanishes. Give the interaction-picture representations of $\hat{\mathsf{S}}$ and $\hat{\mathsf{R}}$. Show that $\mathrm{Tr}_{\mathcal{R}}\big(\hat{\rho}^{\mathcal{R}}\,\hat{\mathsf{V}}_{\mathrm{I}}(t)\big) = 0$ at all times t.

Let $\kappa(t,t') \equiv \mathrm{Tr}_{\mathcal{R}}\big(\hat{\rho}^{\mathcal{R}}\,\hat{\mathsf{R}}_{\mathrm{I}}(t)\,\hat{\mathsf{R}}_{\mathrm{I}}(t')\big)$ be the autocorrelation function associated to the observable $\hat{\mathsf{R}}$. Show that $\kappa(t,t')$ actually only depends on $\tau \equiv t'-t$. It will thus henceforth be denoted as $\kappa(\tau)$.

c) We shall neglect correlations between $\mathcal{S}$ and $\mathcal{R}$, assuming that $\hat{\rho}_{\mathrm{I}}(t)$ factorizes at all times

$$\hat{\rho}_{\mathrm{I}}(t) \simeq \hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t) \otimes \hat{\rho}^{\mathcal{R}}. \tag{3}$$

In addition, we truncate Eq. (2), by replacing $\hat{\rho}_{\mathrm{I}}(t'')$ by $\hat{\rho}_{\mathrm{I}}(t)$ in the right-hand side, which amounts to performing a perturbative expansion up to second order (in the interaction $\hat{\mathsf{V}}$).

Show that these assumptions, as well as those made in **a)** and **b)**, allow you to derive from Eq. (2) the identity

$$\frac{\Delta\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)}{\Delta t} \equiv \frac{\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t+\Delta t)-\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)}{\Delta t} \simeq -\frac{1}{\hbar^2}\frac{1}{\Delta t}\int_t^{t+\Delta t}\left\{\int_t^{t'}\mathrm{Tr}_{\mathcal{R}}\Big(\Big[\hat{\mathsf{V}}_{\mathrm{I}}(t'),\big[\hat{\mathsf{V}}_{\mathrm{I}}(t''),\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)\otimes\hat{\rho}^{\mathcal{R}}\big]\Big]\Big)\,\mathrm{d}t''\right\}\mathrm{d}t'.$$

Check that the change of variables from t',t'' to $\tau \equiv t'-t'', t'$ transforms this equation into

$$\begin{aligned}\frac{\Delta\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)}{\Delta t} = -\frac{1}{\hbar^2}\int_0^{\Delta t}\frac{1}{\Delta t}\int_\tau^{t+\Delta t}\Big\{&\kappa(\tau)\big[\hat{\mathsf{S}}_{\mathrm{I}}(t')\,\hat{\mathsf{S}}_{\mathrm{I}}(t'-\tau)\,\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)-\hat{\mathsf{S}}_{\mathrm{I}}(t'-\tau)\,\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)\,\hat{\mathsf{S}}_{\mathrm{I}}(t')\big]\\ &+\kappa(-\tau)\big[\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)\,\hat{\mathsf{S}}_{\mathrm{I}}(t')\,\hat{\mathsf{S}}_{\mathrm{I}}(t'-\tau)-\hat{\mathsf{S}}_{\mathrm{I}}(t')\,\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)\,\hat{\mathsf{S}}_{\mathrm{I}}(t'-\tau)\big]\Big\}\,\mathrm{d}t'\,\mathrm{d}\tau.\end{aligned} \tag{4}$$

If Δt is much larger than the autocorrelation time τ_0 over which $\kappa(\tau)$ takes significant values, then we may replace the upper bound Δt of the integral over τ by $+\infty$, as well as the lower bound of the integral over t' by t instead of τ.

iv. Master equation in the basis of the energy eigenstates of the small system

Projecting now Eq. (4) over eigenstates $|a\rangle$, $|b\rangle$ of $\hat{\mathsf{H}}_{\mathcal{S}}$, show that it becomes the (generalized) master equation

$$\frac{\Delta(\rho_{\mathrm{I}}^{\mathcal{S}})_{ab}(t)}{\Delta t} = \sum_{c,d}\Gamma_{abcd}(t)\,(\rho_{\mathrm{I}}^{\mathcal{S}})_{cd}(t), \tag{5a}$$

with $(\rho_{\mathrm{I}}^{\mathcal{S}})_{ab}(t) \equiv \langle b\,|\,\hat{\rho}_{\mathrm{I}}^{\mathcal{S}}(t)\,|\,a\rangle$ and

$$\begin{aligned}\Gamma_{abcd}(t) \equiv -\frac{1}{\hbar^2}\int_0^{\infty}\frac{1}{\Delta t}\int_t^{t+\Delta t}\Big\{&\kappa(\tau)\Big[\delta_{bd}\sum_j(S_{\mathrm{I}})_{aj}(t')\,(S_{\mathrm{I}})_{jc}(t'-\tau)-(S_{\mathrm{I}})_{ac}(t'-\tau)\,(S_{\mathrm{I}})_{db}(t')\Big]\\ &+\kappa(-\tau)\Big[\delta_{ac}\sum_j(S_{\mathrm{I}})_{dj}(t'-\tau)\,(S_{\mathrm{I}})_{jb}(t')-(S_{\mathrm{I}})_{ac}(t')\,(S_{\mathrm{I}})_{db}(t'-\tau)\Big]\Big\}\,\mathrm{d}t'\,\mathrm{d}\tau,\end{aligned} \tag{5b}$$

where $(S_{\mathrm{I}})_{ab}(t) \equiv \langle b\,|\,\hat{\mathsf{S}}_{\mathrm{I}}(t)\,|\,a\rangle$. Check that the dependence on t' of all terms in the integrand is given by $\mathrm{e}^{\mathrm{i}(E_a-E_b+E_c-E_d)t'/\hbar}$, which makes the integral over t' trivial. This integral gives rise to a function f which only takes significant values when $(E_a-E_b+E_c-E_d) \ll \hbar/\Delta t$.

Write down the equation obeyed by the matrix elements $\rho_{ab}^{\mathcal{S}}(t) \equiv \langle b\,|\,\hat{\rho}^{\mathcal{S}}(t)\,|\,a\rangle$ of the reduced density operator in the Schrödinger picture. What can you say about the coefficients entering this equation?

v. Master equation for the populations of the small system

Give the equation governing the evolution of the diagonal elements $\rho_{aa}^{\mathcal{S}}(t)$, under the assumption that the small system has no Bohr frequency $|\omega_{cd}| \ll 1/\Delta t$ and using the localization property of the function f found above. What do you recognize?

Hint: One may rewrite $\kappa(\tau)$ using a complete set of eigenstates of $\hat{\mathsf{H}}_{\mathcal{R}}$ and the probability p_λ for the occupation of mode λ.