Chapter 2: Quantum Master Equations

I. THE LINDBLAD FORM

A. Superoperators and dynamical maps

The Liouville von Neumann equation is given by

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}\left[H, \rho\right].$$

(1)

We can define a superoperator $\mathcal{L}$ such that $\mathcal{L}\rho = -i/\hbar[H, \rho]$. It is called a superoperator because it is an object that acts on an operator and results in a new operator. If the Hamiltonian is time-independent, we may formally integrate the Liouville von Neumann equation and obtain

$$\rho(t) = \exp\left(\mathcal{L}t\right)\rho(0) \equiv \mathcal{V}(t)\rho(0),$$

(2)

where $\mathcal{V}$ is another superoperator that maps the density matrix from its initial form to its form at time t and therefore is called a dynamical map. It is related to the unitary evolution operator $U(t) = \exp(-iHt/\hbar)$ according to

$$\mathcal{V}(t)\rho(0) = U(t)\rho(0)U(t)^{\dagger}.$$

(3)

B. Quantum dynamical semigroups

Now let us include also interaction between the system of interest and its environment. In the following, we will use ρ_S for the reduced density operator for the system and $\mathrm{Tr}_E\{\rho\}$ for the partial trace over the environment. As the dynamics of the combination of system and environment is fully coherent, we have

$$\rho(t) = U(t)\rho(0)U(t)^{\dagger},$$

(4)

which after taking the trace over the environment on both sides results in

$$\rho_S(t) = \mathrm{Tr}_E\{U(t)\rho(0)U(t)^{\dagger}\}.$$

(5)

In many typical situations, the initial state between the system and the environment is a product state of the form

$$\rho(0) = \rho_S(0) \otimes \rho_E(0).$$

(6)

Then, we may again think of the right hand side of the previous equation to define a superoperator representing a dynamical map $\mathcal{V}(t)$, but now for S alone! Furthermore, we may use the following decompositions [1]

$$\rho_E(0) = \sum_\alpha \lambda_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \tag{7}$$

$$\mathcal{V}(t)\rho_S(0) = \sum_{\alpha\beta} W_{\alpha\beta}(t)\rho_S(0)W_{\alpha\beta}^\dagger(t), \tag{8}$$

where the operators $W_{\alpha\beta}$ act only on the Hilbert space of the system and are given by

$$W_{\alpha\beta}(t) = \sqrt{\lambda_\beta}\langle\psi_\alpha|U(t)|\psi_\beta\rangle. \tag{9}$$

From the completeness of the states $|\psi_\alpha\rangle$ on the Hilbert space of the environment, we may identify the relation

$$\sum_{\alpha\beta} W_{\alpha\beta}(t)W_{\alpha\beta}^\dagger(t) = 1_S, \tag{10}$$

from which follows

$$\text{Tr}\{\mathcal{V}(t)\rho_S(0)\} = \text{Tr}\{\rho_S\} = 1, \tag{11}$$

i.e., the dynamical map is trace-preserving. Moreover, it is completely positive, mapping a positive density matrix onto another positive density matrix [1].

In many important cases, we can make one further assumption on the dynamical map $\mathcal{V}(t)$. If correlations in the environment decay much faster than the timescale of the evolution in the system of interest, we may neglect memory effects describing how the system has previously interacted with the environment. This is also known as the Markov approximation. For example, consider a thermal state of the environment of the form

$$\rho_E = \sum_n \frac{1}{Z}\exp(-\beta E_n)|n\rangle\langle n|, \tag{12}$$

where $Z = \sum_n \exp(-\beta E_n)$ is the partition function, β is the inverse temperature and E_n is the energy of the state $|n\rangle$. Then, if the environment is large and its dynamics is fast enough, any energy exchanged with the system will quickly dissipate away to form a new thermal state with almost exactly the same temperature. Then, from the viewpoint of the system, the state of the environment will appear to be almost constant all the time.

Formally, we can express the consequences of the Markov approximation on the dynamical map as [1]

$$\mathcal{V}(t_1)\mathcal{V}(t_2) = \mathcal{V}(t_1 + t_2) \quad t_1, t_2 \leq 0. \tag{13}$$

Note that the constraint on the times being positive means that we can only piecewise propagate the system forward in time, i.e, the inverse of the dynamical map does usually not exist. This is in contrast to coherent dynamics, where there is an inverse operation corresponding to negative time arguments in the unitary evolution operator. Hence, while the dynamical maps of coherent systems form a group, the dynamical maps for open quantum systems only form a semigroup.

The generator of the semigroup is the Liouvillian $\mathcal{L}$, which is a generalization of the superoperator appearing on the right hand side of the Liouville von Neumann equation. One important consequence of this generalization is that the von Neumann entropy is no longer a conserved quantity. However, the Liouvillian has to fulfill the property of being the generator of a completely positive and trace-preserving dynamical map. In the following, we will see how the most general form of the Markovian master equation will look like.

C.   Most general form of the dynamics

Similar to the case of a closed quantum system, we can write the dynamical map of an open quantum system as an exponential of the generator of the semigroup,

$$\mathcal{V}(t) = \exp\left(\mathcal{L}t\right). \tag{14}$$

The superoperator $\mathcal{L}$ reduces to the one of the Liouville von Neumann equation in the case of purely coherent dynamics, but in general will have additional incoherent terms. Expanding the dynamical maps for short times τ, we obtain

$$\rho(t+\tau) = \mathcal{V}(\tau)\rho(t) = \left(1 + \mathcal{L}t\right)\rho(t) + O(\tau^2), \tag{15}$$

which in the limit $\tau \to 0$ yields a first-order differential equation known as a quantum master equation,

$$\frac{d}{dt}\rho(t) = \mathcal{L}\rho(t). \tag{16}$$

Let us now derive an explicit form for the master equation. For this, we need to define an operator basis $\{F_i\}$. The inner product for operators is defined as

$$\langle F_i, F_j \rangle \equiv \mathrm{Tr}\left\{F_i^\dagger F_j\right\}. \tag{17}$$

A complete orthonormal set consists of N^2 operators, where N is the Hilbert space dimension. It is convenient to choose one of the operators as proportional to the identity, i.e.,

$F_N^2 = 1/\sqrt{N}$ [1]. Then, all other operators are traceless. For example, in a two-level system, the remaining operators are proportional to the Pauli matrices.

We can now express the action of the dynamical map using this operator basis as

$$\mathcal{V}(t)\rho = \sum_{i,j=1}^{N^2} c_{ij}(t) F_i \rho F_j^\dagger, \tag{18}$$

where the coefficients $c_{ij}(t)$ is given by

$$c_{ij}(t) = \sum_{\alpha\beta} \langle F_i, W_{\alpha\beta}(t) \rangle \langle F_j, W_{\alpha\beta}(t) \rangle^* \tag{19}$$

with the operators $W_{\alpha\beta}$ defined as above. The coefficients $c_{ij}(t)$ form a postive matrix C, as for any N^2-dimensional vector v, we have [1]

$$v^\dagger C v = \sum_{\alpha\beta} \left| \left\langle \sum_i v_i F_i, W_{\alpha\beta}(t) \right\rangle \right|^2 \geq 0. \tag{20}$$

Inserting this expansion into the quantum master equation, we obtain

$$\mathcal{L}\rho = \lim_{\tau \to 0} \frac{\mathcal{V}(t)\rho - \rho}{\tau} \tag{21}$$

$$= \lim_{\tau \to 0} \left[\frac{1}{N} \frac{c_{N^2 N^2}(\tau) - N}{\tau} \rho + \frac{1}{\sqrt{N}} \sum_{i=1}^{N^2-1} \left(\frac{c_{iN^2}(\tau)}{\tau} F_i \rho + \frac{c_{N^2 i}(\tau)}{\tau} \rho F_i^\dagger \right) \right. \tag{22}$$

$$\left. + \sum_{i,j=1}^{N^2-1} \frac{c_{ij}(\tau)}{\tau} F_i \rho F_j^\dagger \right], \tag{23}$$

where we separated off all terms containing $F_{N^2 N^2} = \frac{1}{\sqrt{N}}$. As a next step, we define the following quantities

$$a_{ij} = \lim_{\tau \to 0} \frac{c_{ij}(\tau)}{\tau} \quad i,j = 1, \ldots, N^2 - 1 \tag{24}$$

$$F = \frac{1}{\sqrt{N}} \sum_{i=1}^{N^2-1} \lim_{\tau \to 0} \frac{c_{iN^2}(\tau)}{\tau} F_i \tag{25}$$

$$G = \frac{1}{2N} \lim_{\tau \to 0} \frac{c_{N^2 N^2}(\tau) - N}{\tau} + \frac{1}{2}(F^\dagger + F) \tag{26}$$

$$H = \frac{1}{2i}(F^\dagger - F). \tag{27}$$

Note that the operator H is Hermitian, although F is not because the coefficients c_{iN^2} are complex. Using these definitions, we find for the generator

$$\mathcal{L}\rho = -i[H, \rho] + \{G, \rho\} + \sum_{ij=1}^{N^2-1} a_{ij} F_i \rho F_j^\dagger. \tag{28}$$

Since the dynamical map is trace-preserving, the trace over quantum master equation has to vanish, i.e.,

$$\text{Tr}\left\{\mathcal{L}\rho\right\} = \text{Tr}\left\{\left(2G + \sum_{ij=1}^{N^2-1} a_{ij} F_i F_j^\dagger\right)\rho\right\} = 0, \tag{29}$$

from which we can read off that G has to be

$$G = -\frac{1}{2}\sum_{ij=1}^{N^2-1} a_{ij} F_i F_j^\dagger. \tag{30}$$

Substituting this result back into the quantum master equation, we obtain

$$\mathcal{L}\rho = -i[H,\rho] + \sum_{i,j=1}^{N^2-1} a_{ij}\left(F_i\rho F_j^\dagger - \frac{1}{2}\left\{F_j^\dagger F_i, \rho\right\}\right). \tag{31}$$

Finally, the matrix formed by the coefficients a_{ij} is again Hermitian and positive, so we can diagonalize it to obtain positive eigenvalues γ_i. Then, we find the most general form of a Markovian quantum master equation to be given by

$$\mathcal{L}\rho = -i[H,\rho] + \sum_{i=1}^{N^2-1} \gamma_i\left(A_i\rho A_i^\dagger - \frac{1}{2}\left\{A_i^\dagger A_i, \rho\right\}\right), \tag{32}$$

where the operators A_i are appropriate linear combinations of the operators F_i obtained from the diagonalization procedure. This form of the quantum master equation is known as the Lindblad form, as Lindblad first showed that the generator of a Markovian master equation has to be of that form [2].

The system Hamiltonian is contained in the Hermitian operator H, but the latter can also include additional terms coming from the interaction with the environment. Furthermore, the eigenvalues γ_i correspond to relaxation rates describing incoherent decay processes in the system. Typically, these decay processes will result in the system eventually reaching a stationary state characterized by $\frac{d}{dt}\rho = 0$. However, such a stationary state does not necessarily mean the absence of any dynamics: for example, a single realization of two-level system in a maximally mixed state might still violently jump between both levels! Only when the ensemble average is taken, the dynamics will vanish.

II.   THE QUANTUM OPTICAL MASTER EQUATION

A.   Weak-coupling approximation

In the following, we will consider a system S that is weakly coupled to a bath B. The Hamiltonian of the combined system is given by

$$H = H_S + H_B + H_I, \tag{33}$$

where H_S denotes the part of Hamiltonian only acting on S, H_B only acts on B, and H_I accounts for the interaction between the two. We first perform a unitary transformation $\rho = U(t)\rho'U(t)^\dagger$ into the interaction picture, i.e. (assuming $\hbar = 1$),

$$U(t) = \exp[-i(H_S + H_B)t]. \tag{34}$$

Inserting the transformed density matrix into the Liouville von Neumann equation, we obtain

$$\frac{d}{dt}\left(U(t)\rho'U(t)^\dagger\right) = -i[H, U(t)\rho'U(t)^\dagger], \tag{35}$$

which can be brought into the convenient form

$$\frac{d}{dt}\rho = -i[H_I(t), \rho]. \tag{36}$$

The interaction Hamiltonian is now time-dependent according to

$$H_I(t) = U^\dagger(t)H_I U(t) = \exp[i(H_S + H_B)t]H_I \exp[-i(H_S + H_B)t]. \tag{37}$$

We can formally integrate the Liouville von Neumann equation and obtain

$$\rho(t) = \rho(0) - i\int_0^t ds[H_I(s), \rho(s)]. \tag{38}$$

This expression can be inserted back into the Liouville von Neumann equation and after taking the trace over the bath, we arrive at [1]

$$\frac{d}{dt}\rho_S(t) = -\int_0^t ds \mathrm{Tr}_B\{[H_I(t), [H_I(s), \rho(s)]]\}, \tag{39}$$

where we have assumed that the initial state is such that the interaction does not generate any (first-order) dynamics in the bath, i.e.,

$$\mathrm{Tr}_B\{[H_I(t), \rho(0)]\} = 0. \tag{40}$$

So far, we have made little progress, as the right-hand side of the equation of motion still contains the density operator of the full system. To obtain a closed equation of motion for ρ_S only, we assume that the interaction is weak such that the influence on the bath is small. This is also known as the Born approximation. Then, we may treat the bath as approximately constant and write for the total density operator

$$\rho(t) = \rho_S(t) \otimes \rho_B. \tag{41}$$

Then, we obtain a closed integro-differential equation for the density operator ρ_S,

$$\frac{d}{dt}\rho_S(t) = -\int_0^t ds \, \mathrm{Tr}_B\{[H_I(t), [H_I(s), \rho_S(s) \otimes \rho_B]]\}. \tag{42}$$

Such an integro-differential equation is very difficult to handle as the dynamics at time t depends on the state of the system in all previous times. The equation of motion can be brought into a time-local form by replacing $\rho_S(s)$ by $\rho_S(t)$. As we will see later on, this is not really an approximation, but already implicit in the weak-coupling assumption. This step brings us to an equation known as the Redfield master equation [1],

$$\frac{d}{dt}\rho_S(t) = -\int_0^t ds \, \mathrm{Tr}_B\{[H_I(t), [H_I(s), \rho_S(t) \otimes \rho_B]]\}. \tag{43}$$

This equation is still a non-Markovian master equation and does not guarantee to conserve positivity of the density matrix due to approximations we have made.

B.   Markov approximation

To obtain a Markovian master equation, we first substitute s by $t - s$ in the integrand, which does not change the bounds of the integration. Then, we can understand the parameter s as indicating how far we go backwards in time to account for memory effects, which can be characteristic timescale τ_B, over which correlations in the bath decay. Under the Markov approximation, these memory effects are short-lived and therefore the integrand decays very quickly for $s \gg \tau_B$. Then, we may replace the upper bound of the integration by infinity, and obtain a Markovian master equation,

$$\frac{d}{dt}\rho_S(t) = -\int_0^\infty ds \, \mathrm{Tr}_B\{[H_I(t), [H_I(t - s), \rho_S(t) \otimes \rho_B]]\}. \tag{44}$$

The typical timescale of the dynamics generated by this master equation is characterized by τ_R, which is the relaxation time of the system due to the interaction with the bath. For the Markov approximation to be valid, this relaxation time has to be long compared to the bath correlation time, i.e, $\tau_R \gg \tau_B$. For quantum optical systems, τ_B is the inverse of the optical frequency, i.e., several inverse THz, while the lifetime of an optical excitation is in the inverse MHz range. Therefore, the Markov approximation is well justified in quantum optical systems.

The two approximation we have made so far are often grouped together as the Born-Markov approximation. However, they still do not guarantee that the resulting master equation generates a quantum dynamical semigroup and hence cannot be cast into a Lindblad form. For this, another approximation is necessary.

C.   Secular approximation

The secular approximation involves discarding fast oscillating terms in the Markovian master equation. It is therefore similar to the rotating-wave approximation (RWA) used in NMR and quantum optics. However, applying the RWA directly on the level on the interaction Hamiltonian can cause problems such as an incorrect renormalization of the system Hamiltonian [3]. The secular approximation (which is sometimes also called RWA), however, is carried out on the level of the quantum master equation.

To be explicit, let us write the interaction Hamiltonian in the form

$$H_I = \sum_\alpha A_\alpha \otimes B_\alpha, \tag{45}$$

where the Hermitian operators A_α and B_α only act on system and bath, respectively. Assume, we have already diagonalized the system Hamiltonian H_S, so we know its eigenvalues ε and its projectors onto eigenstates $\Pi(\varepsilon)$. Then, we can project the operators A_α on subspaces with a fixed energy difference ω [1],

$$A_\alpha(\omega) = \sum_{\varepsilon' - \varepsilon = \omega} \Pi(\varepsilon) A_\alpha \Pi(\varepsilon'). \tag{46}$$

As the eigenvectors of H_S form a complete set, we can recover A_α by summing over all frequencies,

$$\sum_\omega A_\alpha(\omega) = \sum_\omega A_\omega^\dagger = A_\alpha. \tag{47}$$

Then, we can write the interaction Hamiltonian as

$$H_I = \sum_{\alpha,\omega} A_\alpha(\omega) \otimes B_\alpha = \sum_{\alpha,\omega} A_\alpha(\omega)^\dagger \otimes B_\alpha^\dagger. \tag{48}$$

Using the relation

$$\exp(iH_s t) A_\alpha(\omega) \exp(-iH_s t) = \exp(-i\omega t) A_\alpha(\omega) \tag{49}$$

and its Hermitian conjugate, we can write the interaction Hamiltonian in the interaction picture as

$$H_I(t) = \sum_{\alpha,\omega} \exp(-i\omega t) A_\alpha(\omega) \otimes B_\alpha(t) = \sum_{\alpha,\omega} \exp(i\omega t) A_\alpha(\omega)^\dagger \otimes B_\alpha(t)^\dagger, \tag{50}$$

where we have introduced the interaction picture operators of the bath,

$$B_\alpha(t) = \exp(iH_B t) B_\alpha \exp(-iH_B t). \tag{51}$$

Inserting this expression into the Markovian master equation leads us to [1]

$$\frac{d}{dt}\rho = \int_0^\infty ds \mathrm{Tr}_B \left\{ H_I(t-s)\rho_S(t)\rho_B H_I(t) - H_I(t) H_I(t-s)\rho_S(t)\rho_B \right\} + \mathrm{H.c.} \tag{52}$$

$$= \sum_{\omega,\omega'} \sum_{\alpha\beta} e^{i(\omega'-\omega)t} \Gamma_{\alpha\beta}(\omega) \left[A_\beta(\omega)\rho_S(t) A_\alpha(\omega')^\dagger - A_\alpha(\omega')^\dagger A_\beta(\omega)\rho_S(t) \right] + \mathrm{H.c.}, \tag{53}$$

where we have used the one-sided Fourier transform of the bath correlation functions,

$$\Gamma_{\alpha\beta} = \int_0^\infty ds \exp(i\omega s) \mathrm{Tr}_B \left\{ B_\alpha(t)^\dagger B_\beta(t-s)\rho_B \right\}. \tag{54}$$

In the case where the state of the bath ρ_B is an eigenstate of the bath Hamiltonian H_B, the bath correlations do not depend on time.

The secular approximation is then referred to as the omission of all terms with $\omega' \neq \omega$, as these terms oscillate fast and average out. Again, in quantum optical systems, this comes from the fact that optical transition frequencies are much larger than the decay rates of excited states, i.e., $\tau_R \gg \tau_S$. Hence, we obtain

$$\frac{d}{dt}\rho = \sum_\omega \sum_{\alpha\beta} \Gamma_{\alpha\beta}(\omega) \left[A_\beta(\omega)\rho_S(t) A_\alpha(\omega)^\dagger - A_\alpha(\omega)^\dagger A_\beta(\omega)\rho_S(t) \right] + \mathrm{H.c.} \tag{55}$$

This master equation can now be cast into a Lindblad form. For this, we split real and imaginary parts of the coefficients $\Gamma_{\alpha\beta}$ according to

$$\Gamma_{\alpha\beta}(\omega) = \frac{1}{2}\gamma_{\alpha\beta}(\omega) + iS_{\alpha\beta}(\omega), \tag{56}$$

where the real part can be written as

$$\gamma_{\alpha\beta}(\omega) = \Gamma_{\alpha\beta}(\omega) + \Gamma_{\alpha\beta}(\omega)^* = \int_{-\infty}^{\infty} ds \exp(i\omega s)\langle B_\alpha(s)^\dagger B_\beta(0)\rangle \tag{57}$$

and forms a positive matrix [1]. Then, diagonlizing the coefficient matrix yields the Lindblad form for the dyanmics

$$\frac{d}{dt}\rho = -i\left[H_{LS}, \rho_S(t)\right] + \sum_{\omega,k} \gamma_k(\omega)\left(A_k(\omega)\rho_S A_k(\omega)^\dagger - \frac{1}{2}\left\{A_k(\omega)^\dagger A_k(\omega), \rho_S\right\}\right), \tag{58}$$

where the Lamb shift Hamiltonian H_{LS} commutes with the system Hamiltonian and hence results in a renormalization of the energy levels. This master equation is still expressed in the interaction picture, it can be transformed back to the Schrdinger picture by adding the system Hamiltonian H_S to the coherent part of the dynamics.

D.   Interaction with the radiation field

In the case of an atom interacting with the quantized radiation field, the Hamiltonian for the latter is given by a sum of harmonic oscillators,

$$H_B = \sum_{\vec{k}\lambda} \omega_{\vec{k}} a_{\vec{k}\lambda}^\dagger a_{\vec{k}\lambda}, \tag{59}$$

where λ is the polarization index [4]. If the wavelength of the radiation field is much larger than the spatial extent of the atomic wavefunction, the dominant interaction term is given by the electric dipole term,

$$H_I = -\vec{d}\vec{E}, \tag{60}$$

where $\vec{d}$ is the dipole operator of the atom and $\vec{E}$ is the quantized electric field,

$$\vec{E} = i\sum_{\vec{k}\lambda} \sqrt{\frac{h\omega_k}{V}}\vec{e}_\lambda\left(a_{\vec{k}\lambda} - a_{\vec{k}\lambda}\right). \tag{61}$$

We now assume the reference state of the bath, ρ_B is the vacuum without any photons. Then, we can use the following relations for the reservoir correlations [1]

$$\langle a_{\vec{k}\lambda} a_{\vec{k}'\lambda'} \rangle = \langle a_{\vec{k}\lambda}^\dagger a_{\vec{k}'\lambda'}^\dagger \rangle = \langle a_{\vec{k}\lambda}^\dagger a_{\vec{k}'\lambda'} \rangle = 0 \tag{62}$$

$$\langle a_{\vec{k}\lambda} a_{\vec{k}'\lambda'}^\dagger \rangle = \delta_{\vec{k}\vec{k}'} \delta_{\lambda\lambda'} \tag{63}$$

$$\sum_\lambda e_{\vec{k}\lambda}^i e_{\vec{k}\lambda}^j = \delta_{ij} - \frac{k_i k_j}{k^2}. \tag{64}$$

Using this, we find for the spectral correlation tensor

$$\Gamma_{ij} = \sum_{\vec{k}} \frac{\hbar \omega_k}{V} \left(\delta_{ij} - \frac{k_i k_j}{k^2} \right) \int_0^\infty ds \exp[-i(\omega_k - \omega)s]. \tag{65}$$

Going to the continuum limit, we can use

$$\frac{1}{V} \sum_{\vec{k}} \to \int \frac{dk}{(2\pi)^3} = \frac{1}{(2\pi)^3 c^3} \int_0^\infty d\omega_k \omega_k^2 \int d\Omega \tag{66}$$

$$\int d\Omega \left(\delta_{ij} - \frac{k_i k_j}{k^2} \right) = \frac{8\pi}{3} \delta_{ij}. \tag{67}$$

Fortunately, this means that the spectral correlation tensor is already in a diagonal form and we can directly obtain a Lindblad form for the master equation. For the s-integration, we make use of the relation

$$\int_0^\infty ds \exp[-i(\omega_k - \omega)s] = \pi \delta(\omega_k - \omega) + \mathrm{PV} \frac{1}{\omega_k - \omega}, \tag{68}$$

where PV denotes the Cauchy principal value. We can thus split the spectral correlation tensor into its real and imaginary part to obtain the decay rate and the Lamb shift, respectively. Note, however, that the expression for the Lamb shift is divergent as we have neglected relativistic effects that become relevant for large values of ω_k. Since it only gives a slight renormalization of the energy levels of the atom, we neglect it in the following. For simplicity, let us consider the case where we are interested in the transition between only two atomic levels differing by the frequency ω. Then, we finally arrive at the master equation in Lindblad form,

$$\frac{d}{dt} \rho = \gamma \left(\sigma_- \rho \sigma^+ - \frac{1}{2} \{ \sigma_+ \sigma_-, \rho \} \right), \tag{69}$$

where we have used the spontaneous emission rate

$$\gamma = \frac{4\omega d^2}{3\hbar c^3} \tag{70}$$

and the spin flip operators

$$\sigma_\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y). \tag{71}$$

The master equation can be solved by expanding it into Pauli matrices. The vector $\langle \vec{\sigma} \rangle$ is known as the Bloch vector and the equations of motion for its component decouple,

$$\frac{d}{dt}\langle \sigma_x \rangle = -\frac{\gamma}{2}\langle \sigma_x \rangle \tag{72}$$

$$\frac{d}{dt}\langle \sigma_y \rangle = -\frac{\gamma}{2}\langle \sigma_y \rangle \tag{73}$$

$$\frac{d}{dt}\langle \sigma_z \rangle = -\gamma(\langle \sigma_z \rangle + 1). \tag{74}$$

From this, we see that the off-diagonal elements of the density matrix decay exponentially with the rate $\gamma/2$, a phenomenon which is called decoherence. The z-component of the Bloch vector decays exponentially with the rate γ to a steady state of $\langle \sigma_z \rangle = -1$, i.e., the atom ends up in the state with lower energy.

E.   Resonance fluorescence

Let us assume now that in addition to the radiation field being in the vacuum state, there is a single mode that is being driven by an external laser. As the laser only affects a single mode, we can ignore its effect on the dissipative dynamics, i.e., the only consequence results from the Hamiltonian of the form

$$H_L = dE \cos(\omega t), \tag{75}$$

where we have assumed that the laser is on resonance with the atom. Denoting the two levels of the atom by $|g\rangle$, and $|e\rangle$, respectively, we can go into the rotating frame of the laser driving by making the unitary transformation

$$|e\rangle = \exp(i\omega t)|e\rangle. \tag{76}$$

Inserting back into the master equation, we see that the rotation exactly compensates the energy difference between $|e\rangle$ and $|g\rangle$, and the laser term becomes

$$H_L = \frac{dE}{2}[1 + \exp(2i\omega t)] \tag{77}$$

In the rotating wave approximation we neglect the fast oscillating term. Then, we can write the laser Hamiltonian as

$$H_L = \frac{\Omega}{2}(\sigma_+ + \sigma_-), \tag{78}$$

where we have introduced the Rabi frequency $\Omega = dE$. The total quantum master equation then reads

$$\frac{d}{dt}\rho = -i[H_L, \rho] + \gamma\left(\sigma_-\rho\sigma^+ - \frac{1}{2}\{\sigma_+\sigma_-, \rho\}\right). \tag{79}$$

The interesting aspect about this master equation is that it exhibits a competition between the coherent dynamics generated by the laser and the dissipative dynamics arising from the decay into the vacuum of the radiation field. As before, we can write the master equation as an equation of motion for the Bloch vector [1],

$$\frac{d}{dt}\langle\vec{\sigma}\rangle = G\langle\vec{\sigma}\rangle + \vec{b}, \tag{80}$$

using the matrix G and the vector $\vec{b}$ given by

$$G = \begin{pmatrix} -\gamma/2 & 0 & 0 \\ 0 & -\gamma/2 & -\Omega \\ 0 & \Omega & -\gamma \end{pmatrix}, \quad \vec{b} = \begin{pmatrix} 0 \\ 0 \\ -\gamma \end{pmatrix}, \tag{81}$$

respectively. This equation of motion is called the optical Bloch equation. Its stationary state $\langle\vec{\sigma}\rangle_s$ can be found from the condition $d/dt\langle\vec{\sigma}\rangle = 0$ and is given by

$$\langle\sigma_z\rangle_s = -\frac{\gamma^2}{\gamma^2 + 2\Omega^2} \tag{82}$$

$$\langle\sigma_+\rangle_s = \langle\sigma_-\rangle_s^* = -\frac{\Omega\gamma}{\gamma^2 + 2\Omega^2}. \tag{83}$$

Note that the population of the excited state,

$$p_e = \frac{1}{2}(1 + \langle\sigma_z\rangle_s) = \frac{\Omega^2}{\gamma^2 + 2\Omega^2} \tag{84}$$

is always less than $1/2$ even in the limit of strong driving, i.e., $\Omega \gg \gamma$. Thus, it is not possible to create population inversion in a two level system in the stationary state by coherent driving. The population will merely saturate at $p_e = 1/2$.

It is also interesting to look at the relaxation dynamics towards the stationary state. For this, we introduce another vector expressing the difference between the Bloch vector and the stationary solution [1], i.e.,

$$\delta\vec{\sigma} = \langle\vec{\sigma}\rangle - \langle\vec{\sigma}\rangle_s. \tag{85}$$

The dynamics of this vector is described by a homogeneous differential equation,

$$\frac{d}{dt}\delta\vec{\sigma} = G\delta\vec{\sigma}. \tag{86}$$

We find the eigenvalues of G to be

$$\lambda_1 = -\frac{\gamma}{2} \tag{87}$$

$$\lambda_{2/3} = -\frac{3}{4}\gamma \pm i\mu \tag{88}$$

where μ is given by

$$\mu = \sqrt{\Omega^2 - \left(\frac{\gamma}{4}\right)^2}. \tag{89}$$

Since all eigenvalues have negative real parts, all coefficients of the $\delta\vec{\sigma}$ vector will eventually decay and the stationary state $\langle\vec{\sigma}\rangle_s$ is reached. If the atom is initially in the state $|g\rangle$, the resulting dynamics is given by

$$p_e = \frac{\Omega^2}{\gamma^2 + 2\Omega^2}\left[1 - \exp\left(-\frac{3}{4}\gamma t\right)\left(\cos\mu t + \frac{3}{4}\frac{\gamma}{\mu}\sin\mu t\right)\right] \tag{90}$$

$$\langle\sigma_\pm\rangle = \mp\frac{\Omega\gamma}{\gamma^2 + 2\Omega^2}\left[1 - \exp\left(-\frac{3}{4}\gamma t\right)\left(\cos\mu t + \left\{\frac{\gamma}{4\mu} - \frac{\Omega^2}{\gamma\mu}\right\}\sin\mu t\right)\right]. \tag{91}$$

III. PROJECTION OPERATOR TECHNIQUES

A. Relevant and irrelvant part

While Markovian master equations have a broad range of applications, in some situations the assumption of rapidly decaying correlations in the environment is not valid. In particular, this is the case for isolated homogeneous quantum many-body systems, where the equilibration of local observables can only occur due to interaction with its surroundings. The complete dynamics is governed by the Liouville-von Neumann equation of the full system according to

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H, \rho] = \mathcal{L}(t)\rho. \tag{92}$$

Here, we aim at deriving a closed reduced dynamical equation for the subunit under consideration. This is done by introducing a projection superoperator $\mathcal{P}$ that projects onto the relevant part of the full density operator ρ [1]. The dynamics of the reduced system is no longer unitary, but described by

$$\mathcal{P}\frac{d}{dt}\rho = \mathcal{P}\mathcal{L}(t)\rho. \tag{93}$$

In many cases $\mathcal{P}$ defines a projection onto a tensor product state of one subsystem and a reference state ρ_E of the environment acoording to

$$\mathcal{P}\rho = \mathrm{Tr}_E\{\rho\} \otimes \rho_E. \tag{94}$$

However, it is also possible to generelize this approach to include correlations between system and environment [5]. For example, consider the case of a two-level system resonantly coupled to an environment consisting of two energy bands at the eigenenergies of the system. Then, we can introduce a projection superator given by

$$\mathcal{P}\rho = \sum_{\mu=1,2} \mathrm{Tr}\{\Pi_\mu\rho\} \frac{1}{n_\mu}\Pi_\mu, \tag{95}$$

where n is the number of levels in the energy band and the projectors Π_μ are given by

$$\Pi_\mu = \sum_{n_\mu} |\mu\rangle\langle\mu| \otimes |n_\mu\rangle\langle n_\mu|. \tag{96}$$

As these projectors act on both the system and the environment, the relevant part includes correlations between system and environment.

In order to obtain a closed equation for the relevant part, we define another projection superoperator $\mathcal{Q}$ projecting on the irrelevant part of the full density matrix ρ, i.e.,

$$\mathcal{Q}\rho = \rho - \mathcal{P}\rho, \tag{97}$$

leading to the dynamics described by

$$\mathcal{Q}\frac{d}{dt}\rho = \mathcal{Q}\mathcal{L}(t)\rho. \tag{98}$$

Being projection operators onto different parts of the system, $\mathcal{P}$ and $\mathcal{Q}$ have to satisfy the relations

$$\mathcal{P} + \mathcal{Q} = I \tag{99}$$

$$\mathcal{P}^2 = \mathcal{P} \tag{100}$$

$$\mathcal{Q}^2 = \mathcal{Q} \tag{101}$$

$$\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0, \tag{102}$$

where I is the identity operation. Then, we can derive a set of differential equations describing the dynamics,

$$\mathcal{P}\frac{d}{dt}\rho = \mathcal{P}\mathcal{L}(t)\mathcal{P}\rho + \mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho \tag{103}$$

$$\mathcal{Q}\frac{d}{dt}\rho = \mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho + \mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho. \tag{104}$$

B. The Nakajima-Zwanzig master equation

One possibility to tackle these equations is to formally solve the second equation for $\mathcal{Q}\rho$, resulting in

$$\mathcal{Q}\rho(t) = \int_{t_0}^{t} ds\, \mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho(s), \tag{105}$$

with an appropriate propagator $\mathcal{G}(t,s)$, while assuming factorizing initial conditions, i.e., $\mathcal{Q}\rho(t_0) = 0$. Inserting this solution for the irrelevant part into the differential equation for the relevant part leads to a closed integro-differential equation known as the Nakajima-Zwanzig equation [6, 7]. Although it allows for a systematic perturbation expansion its structure is usually very complicated because every order requires the integration over superoperators involving the complete history of $\mathcal{P}\rho$. Therefore, its applicability to many-body problems is rather limited.

C. The time-convolutionless master equation

A different approach tries to explicitly avoid the integral over the complete history by looking at the inverse of the time evolution. We replace the $\rho(s)$ in the above equation by

$$\rho(s) = G(t,s)(\mathcal{P} + \mathcal{Q})\rho(t), \tag{106}$$

where $G(t,s)$ is the backward propagator of the full system, i.e., the inverse of its unitary evolution. We then can write the solution of the irrelevant part as

$$\mathcal{Q}\rho(t) = \Sigma(t)(\mathcal{P} + \mathcal{Q})\rho(t), \tag{107}$$

where we have introduced the superoperator

$$\Sigma(t) = \int_{t_0}^{t} ds\, \mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}G(t,s). \tag{108}$$

We then move all occurrences of $\mathcal{Q}\rho(t)$ to the left-hand side. The superoperator $1 - \Sigma(t)$ may be inverted for small times or weak interactions with the irrelevant part [1], leading to

$$\mathcal{Q}\rho(t) = [1 - \Sigma(t)]^{-1}\mathcal{P}\rho(t). \tag{109}$$

Inserting this result into the differential equation for the relevant part yields

$$\mathcal{P}\frac{d}{dt}\rho(t) = \mathcal{P}\mathcal{L}(t)[1 - \Sigma(t)]^{-1}\mathcal{P}\rho(t).$$ (110)

Since this differential equation for the relevant part does not involve a convolution integral as in the Nakajima-Zwanzig equation, it is called the time-convolutionless (TCL) master equation [8].

The TCL generatior is defined as

$$\mathcal{K}(t) = \mathcal{P}\mathcal{L}(t)[1 - \Sigma(t)]^{-1}\mathcal{P}.$$ (111)

In order to perform a perturbation expansion of $\mathcal{K}(t)$ we rewrite $[1 - \Sigma(t)]^{-1}$ as a geometric series, allowing to write the TCL generator as

$$\mathcal{K}(t) = \sum_{n}\mathcal{P}\mathcal{L}(t)\Sigma(t)^{n}\mathcal{P} \equiv \sum_{n}\lambda^{n}\mathcal{K}_{n}(t),$$ (112)

where λ is the coupling constant in which the series expansion is performed. One may then use the definition of $\Sigma(t)$ and the series expansions of $\mathcal{G}(t,s)$ and $G(t,s)$ to compute the $\mathcal{K}_{n}$. In many situations, the odd terms of the series expansion vanish [1], and the leading term given by the second order expansion is

$$\mathcal{K}_{2} = \int_{t_0}^{t} ds\, \mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P},$$ (113)

leading to the second-order TCL master equation

$$\mathcal{P}\frac{d}{dt}\rho = \int_{t_0}^{t} ds\, \mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho.$$ (114)

In the interaction picture, it may be explicitely written as

$$\mathcal{P}\frac{d}{dt}\rho = -\int_{t_0}^{t} ds\, \mathcal{P}[H_I(t), [H_I(s), \mathcal{P}\rho]].$$ (115)

The second-order TCL master equation differs from the Nakajima-Zwanzig equation only by the density operator in the integral depending on t instead of s. If the projection operator describes a projection onto a product state between the system and a fixed state in the environment, it is identical to the Redfield equation that we have already encountered earlier.

IV. DECAY INTO TWO BANDS

We consider a two-level systems coupled to an environment consisting of two distinct energy bands. The system is described by the Hamiltonian

$$H = H_S + H_E + H_I. \tag{116}$$

The system Hamiltonian H_S is an ordinary two-level system with an energy difference of ΔE ,according to

$$H_S = \Delta E |e\rangle\langle e| = \Delta E \sigma_+ \sigma_-, \tag{117}$$

where we have set the energy of the ground state $|g\rangle$ to zero. For the energy bands of the environment, we assume a linear spectrum, i.e,

$$H_E = \sum_{n_1=1}^{N_1} \frac{\delta\varepsilon}{N_1} n_1 |n_1\rangle\langle n_1| + \sum_{n_2=1}^{N_2} \left(\Delta E + \frac{\delta\varepsilon}{N_2} n_2 \right) |n_2\rangle\langle n_2|, \tag{118}$$

where N_1 and N_2 are the total number of states in each band. The interaction Hamiltonian is given by

$$H_I = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \lambda_{n_1,n_2} \sigma_+ |n_1\rangle\langle n_2| + \text{H.c.}, \tag{119}$$

i.e., whenever the two-level system is de-excited, an excitation is created in the environment, and vice versa. The matrix elements $\lambda_{n1,n2}$ are random Gaussianly distributed variables with a variance λ^2. In the following, we assume a separation of energy scales according to $\Delta E \gg \delta E \gg \lambda$.

This model has some very interesting properties. First of all, the size of the environment is clearly finite, meaning that excitations in the environment may not decay fast enough and the Markov approximation may not be applicable. This is even further strengthened when taking into account that the interaction will lead to very strong correlations between system and environment. At the same time, the weak interaction naturally gives rise to a peturbative expansion.

We proceed by defining a correlated projection operator for the relevant part of the dynamics [5], according to

$$\mathcal{P}\rho = \text{Tr}\{\Pi_1\rho\} \frac{1}{N_1}\Pi_1 + \text{Tr}\{\Pi_2\rho\} \frac{1}{N_2}\Pi_2 = P_e \frac{1}{N_1}\Pi_1 + P_g \frac{1}{N_2}\Pi_2, \tag{120}$$

where we have introduced the projectors

$$\Pi_1 = \sum_{n_1=1}^{N_1} 1 \otimes |n_1\rangle\langle n_1| \tag{121}$$

$$\Pi_2 = \sum_{n_2=1}^{N_2} 1 \otimes |n_2\rangle\langle n_2| \tag{122}$$

and P_e and P_g denote the probability to find the two-level system in its excited or ground state, respectively. Because of conservation of probability, we have $P_g = 1 - P_e$, meaning that the relevant part of the dynamics consists of a single variable!

In the following, we will derive its equation of motion. The second order TCL master equation is given by

$$\mathcal{P}\frac{d}{dt}\rho = \int_0^t ds \mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho, \tag{123}$$

which in our case can be written as

$$\dot{P}_e \frac{1}{N_1}\Pi_1 + (1 - \dot{P}_e)\frac{1}{N_2}\Pi_2 = \int_0^t ds \, \mathrm{Tr}\left\{\Pi_1\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho\right\}\frac{1}{N_1}\Pi_1 + \mathrm{Tr}\left\{\Pi_2\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho\right\}\frac{1}{N_2}\Pi_2. \tag{124}$$

since the projection and the time derivative commute. Multiplying with Π_1 and taking the trace yields

$$\dot{P}_e = \int_0^t ds \, \mathrm{Tr}\left\{\Pi_1\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho\right\} \tag{125}$$

$$= -\int_0^t ds \, \mathrm{Tr}\left\{\Pi_1\left[H_I(t), \left[H_I(s), P_e\frac{1}{N_1}\Pi_1 + (1 - P_e)\frac{1}{N_2}\Pi_2\right]\right]\right\}. \tag{126}$$

Expanding the commutator and making use of the relation $\Pi_i\Pi_j = \delta_{ij}\Pi_i$ results in

$$\dot{P}_e = -\int_0^t ds \, \mathrm{Tr}\left\{P_e\frac{1}{N_1}\Pi_1 H_I(s)H_I(t) - (1 - P_e)\frac{1}{N_2}\Pi_1 H_I(t)H_I(s) + \mathrm{H.c.}\right\}. \tag{127}$$

We can now introduce two relaxation rates $\gamma_{1,2}$ describing the transition rates between the two bands. Specifically, we have

$$\gamma_i = \frac{1}{N_i}\int_0^t ds \sum_{n1}\langle n_1|H_I(s)H_I(t) + \mathrm{H.c}|n_1\rangle. \tag{128}$$

As the interaction Hamiltonian couples does not contain terms that leave the band index unchanged, we may write the matrix elements as

$$\langle n_1|H_I(s)H_I(t) + \text{H.c}|n_1\rangle = \sum_{n_2}\langle n_1|H_I(s)|n_2\rangle\langle n_2|H_I(t)|n_1\rangle + \text{c.c.}. \tag{129}$$

As we work in the interaction picture, we have

$$\langle n_1|H_I(s)|n_2\rangle\langle n_2|H_I(t)|n_1\rangle = \exp(i\omega_{12}s)\exp(-i\omega_{12}t)|\lambda_{n1,n2}|^2, \tag{130}$$

where we have introduced the transitions frequencies $\omega_{12} = \delta\varepsilon(n_1/N_1 - n_2/N_2)$. Using the statistical properties of the interaction Hamiltonian and performing the integration over s finally yields [9]

$$\gamma_i = \frac{2\lambda^2}{N_i}\sum_{n1,n2}\frac{\sin(\omega_{12}t)}{\omega_{12}}. \tag{131}$$

For the next step, we note that the sinc function appearing in the relaxation rates is a representation of the Dirac δ distribution, i.e.,

$$\pi\delta_t(\omega_{12}) = \lim_{t\to\infty}\frac{\sin(\omega_{12}t)}{\omega_{12}}. \tag{132}$$

Then, at large enough times and small enough couplings [10], we may approximate the rates by

$$\gamma_1 \approx \frac{2\pi\lambda^2}{N_1}\sum_{k,l}\delta(E_{n_1} - E_{n_2}) = 2\pi\lambda^2\frac{N_2}{\delta\varepsilon} \tag{133}$$

$$\gamma_2 \approx 2\pi\lambda^2\frac{N_1}{\delta\varepsilon}. \tag{134}$$

The equation of motion for the excited state probability then reads

$$\dot{P}_e = -(\gamma_2 + \gamma_1)P_e + \gamma_2. \tag{135}$$

Assuming the two-level system is initially in its excited state, the stationary state given by $P_e^s = \gamma_2/(\gamma_1 + \gamma_2)$ is approached in an exponential decay according to

$$P_e(t) = P_e^s + \frac{\gamma_1}{\gamma_1 + \gamma_2}\exp[-2(\gamma_1 + \gamma_2)t]. \tag{136}$$

This solution is in excellent agreement with numerical simulations of the full Schrdinger equation [11].

It is important to stress that this efficient description of such a complex system is only possible because our projection operator correctly captures the essential features of the

dynamics. If one choses a different projection operator, say, one without correlations between system and environments, according to

$$\mathcal{P}\rho = \text{Tr}_E\{\rho\} \otimes \rho_E, \tag{137}$$

then the second order TCL master equation no longer correctly describes the dynamics, as higher orders are divergent [11].

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[1] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).

[2] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).

[3] C. Fleming, N. I. Cummings, C. Anastopoulos, and B. L. Hu, J. Phys. A **43**, 405304 (2010).

[4] D. F. Walls and G. J. Milburn, *Quantum Optics* (Springer, Berlin, 1994).

[5] H.-P. Breuer, Phys. Rev. A **75**, 022103 (2007).

[6] S. Nakajima, Progr. Theo. Phys. **20**, 948 (1958).

[7] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).

[8] F. Shibata, Y. Takahashi, and N. Hashitsume, J. Stat. Phys. **17**, 171 (1977).

[9] H. Weimer, M. Michel, J. Gemmer, and G. Mahler, Phys. Rev. E **77**, 011118 (2008).

[10] F. Schwabl, *Quantum mechanics* (Springer, Berlin, Germany, 2010).

[11] H.-P. Breuer, J. Gemmer, and M. Michel, Phys. Rev. E **73**, 016139 (2006).