

# Introduction to open quantum systems: Markovian baths and the Lindblad equation

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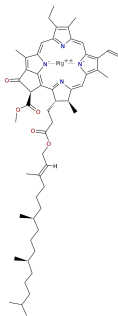
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# Outline

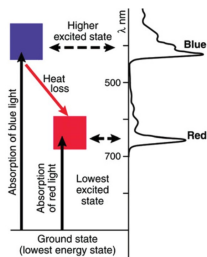
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# Motivation for OQS

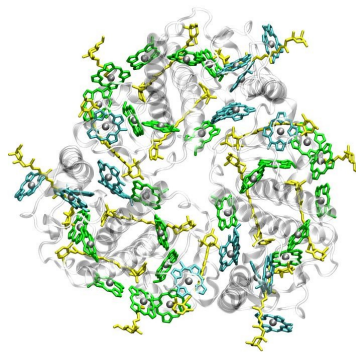
# Why do we need an open quantum system formalism?



Chlorophyll a

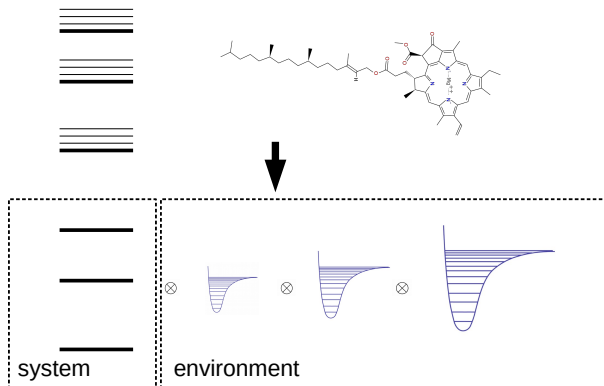


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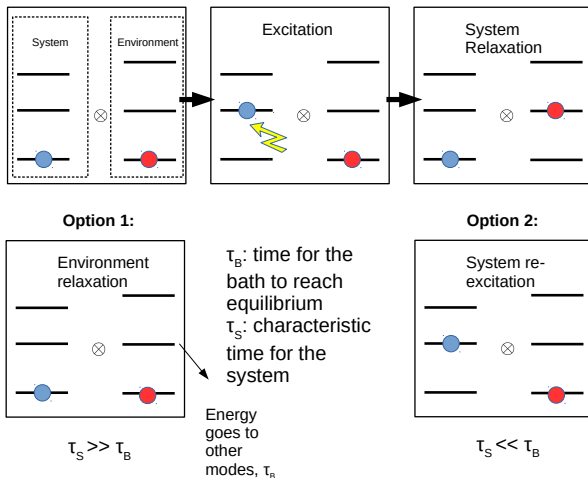


Light-harvesting complex

Aim: to develop dynamical descriptions of a subpartition of the entire system



# Classification of open quantum systems



# Classification of open quantum systems

**Markovian evolution:** An evolution which does not depend on the system's previous history, only on its present state. We have a memoryless bath.

**non-Markovian evolution:** An evolution which does depend on the system's previous history. The bath holds on to the excitations for a period long enough to return it to the system.

# Describing Markovian open quantum systems



## Where we are going

The evolution of a system coupled to a Markovian bath is given by the Lindblad-GKS equation:

$$\dot{\rho} = -i[H, \rho] + \sum_{i,\omega} \gamma_i(\omega) [F_i(\omega)\rho F_i^\dagger(\omega) - \frac{1}{2}\{F_i^\dagger(\omega)F_i(\omega), \rho\}_+] \quad (1)$$

where  $H$  is the system Hamiltonian and  $F_i$  are Hilbert space operators. This equation represents the evolution according to a **dynamical semigroup**, which ensures a physical evolution (**almost always**).

We present the microscopic derivation of this equation to evidence the physics behind it.

# A review of Hamiltonian evolution

We consider a single particle system described by a time-independent Hamiltonian  $H$  in a complete orthonormal basis  $|\phi_k\rangle$ . The dynamics are obtained by solving the Schrodinger equation:

$$\dot{\psi}(t) = -\frac{i}{\hbar}H\psi(t) \quad (2)$$

Also written as:

$$\psi(t) = e^{-iH(t-t_0)/\hbar}\psi(t_0) \equiv U(t, t_0)\psi(t_0) \quad (3)$$

If we want to know what the outcome of an experiment will be, we calculate the expectation value of the relevant operator:

$$\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle \quad (4)$$

# The density matrix

The density matrix formalism allows to obtain the same information as the wavefunction, and go beyond it by considering statistical ensembles of systems.

We want to:

- 1 Show how we recover all the same calculable quantities we obtain with the wavefunction.
- 2 How we can consider mixed states which have lost **coherence** between them.

# Equivalence between density matrix and wavefunction expectation values

Consider the projection operator  $\rho_{\text{pure}}(t) = |\psi(t)\rangle \langle\psi(t)|$  for some wavefunction  $|\psi(t)\rangle$ . Using  $(\sum_k |\phi_k\rangle \langle\phi_k| = \mathbf{1})$ , we have:

$$\begin{aligned}
 \langle\psi(t)|A|\psi(t)\rangle &= \sum_k \langle\psi(t)|\phi_k\rangle \langle\phi_k|A|\psi(t)\rangle \\
 &= \sum_k \langle\phi_k|[A|\psi(t)\rangle \langle\psi(t)|]|\phi_k\rangle \\
 &= \sum_k \langle\phi_k|A\rho_{\text{pure}}(t)|\phi_k\rangle \\
 &= \text{Tr}(A\rho_{\text{pure}}(t))
 \end{aligned} \tag{5}$$

$\text{Tr}(A\rho_{\text{pure}}(t))$  is equivalent to taking the expectation value, so that we can get the same information from the density matrix than the wavefunction.

## The density matrix: time evolution

The time evolution of the density matrix can be written as:

$$\begin{aligned}\rho(t) &= U(t, t_0)|\psi(t_0)\rangle\langle\psi(t_0)|U^\dagger(t, t_0) \\ &= U(t, t_0)\rho(t_0)U^\dagger(t, t_0)\end{aligned}\quad (6)$$

Using the chain rule (remembering  $U(t, t_0) = e^{-\frac{i}{\hbar}H(t-t_0)}$ ):

$$\begin{aligned}\dot{\rho}(t) &= \dot{U}(t, t_0)\rho(t_0)U^\dagger(t, t_0) + U(t, t_0)\rho(t_0)\dot{U}^\dagger(t, t_0) \\ &= -\frac{i}{\hbar}H\rho(t) + \rho(t)\frac{i}{\hbar}H = -\frac{i}{\hbar}[H\rho(t)]\end{aligned}\quad (7)$$

Liouville Von-Neumann equation

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H, \rho(t)]\quad (8)$$

## Describing statistical ensembles

**Pure state.** A wavefunction spanning two sites  $|1\rangle$  and  $|2\rangle$  equally is  $\psi = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ . Its corresponding density matrix is:

$$\rho_{\text{pure}} = \frac{1}{2}(|1\rangle\langle 1| + |1\rangle\langle 2| + |2\rangle\langle 1| + |2\rangle\langle 2|) \quad (9)$$

Notice the correlations between both sites.

**Mixed state.** We can alternatively consider a state of a mixed state, for example an ensemble of systems, some in site 1, some in site 2, with equal probability:

$$\rho = \frac{1}{2}(|1\rangle\langle 1| + |2\rangle\langle 2|) \quad (10)$$

This last density matrix cannot be written from a single wavefunction.

## Describing statistical ensembles

In general, we can define a mixed density matrix as:

$$\rho = \sum_{\psi} p_{\psi} |\psi\rangle \langle \psi| \quad (11)$$

for  $\sum_{\psi} p_{\psi} = 1$  and  $0 < p_{\psi} < 1$ . The density matrix is a Hermitian operator of trace 1. For a pure state:

$$\rho^2 = |\psi\rangle \langle \psi | \psi\rangle \langle \psi| = |\psi\rangle \langle \psi| = \rho \quad (12)$$

While for a mixed state:

$$\begin{aligned} \rho^2 &= \sum_{\psi, \psi'} p_{\psi} p_{\psi'} |\psi\rangle \langle \psi| |\psi'\rangle \langle \psi'| \\ &= \sum_{\psi} p_{\psi}^2 |\psi\rangle \langle \psi| \neq \rho \end{aligned} \quad (13)$$

## The partial trace

For a bipartite system  $A \otimes B$ , described by the density matrix  $\rho$ , the reduced density matrix of the subsystem  $A$  is obtained by the partial trace:

$$\rho_A = \text{Tr}_B(\rho) \quad (14)$$

$\rho_A$  only refers to the degrees of freedom of the  $A$  subsystem and contains the effect of the second subsystem  $B$ .

We now have the formalism to derive the master equation for a system coupled to a Markovian bath.



## The Lindblad equation

Consider a system (e.g. a particle with electronic levels) coupled to a thermal bath (i.e. vibrational modes, vacuum modes,...).

The first step is to separate the Hamiltonian:

$$H = H_S + H_B + H_I \quad (15)$$

The equations are more readily solved in the interaction picture:

$$\dot{\rho} = -\frac{i}{\hbar}[H_I(t), \rho] \quad (16)$$

where

$$H_I(t) = e^{\frac{i}{\hbar}(H_S+H_B)t} H_I e^{-\frac{i}{\hbar}(H_S+H_B)t} \quad (17)$$

## The reduced density matrix

Carrying out a formal integration of Liouville's equation:

$$\rho(t) = \rho(0) - \frac{i}{\hbar} \int_0^t ds [H_I(s), \rho(s)] \quad (18)$$

We reinsert this into Liouville's equation and take the partial trace to obtain the reduced density matrix for the system:

$$\begin{aligned} \dot{\rho}_s(t) &= -\frac{i}{\hbar} \text{Tr}_B [H_I(t), \rho(0)] - \frac{1}{\hbar^2} \int_0^t ds \text{Tr}_B [H_I(t), [H_I(s), \rho(s)]] \\ &= -\frac{1}{\hbar^2} \int_0^t ds \text{Tr}_B [H_I(t), [H_I(s), \rho(s)]] \end{aligned} \quad (19)$$

because we can set  $\text{Tr}_B [H_I(t), \rho(0)] = 0$ .

## the Born approximation

If we consider a chromophore dissipating energy inside a protein or a solvent, its perturbation on the environment will be minimal. That is, we can write that  $\rho(t) \approx \rho_S(t) \otimes \rho_B$  where  $\rho_B$  is the **equilibrium** density matrix for the bath. The entire time evolution is contained in  $\rho_S$  while the bath remains in thermal equilibrium. We then have:

$$\dot{\rho}_S(t) = - \int_0^t ds \text{Tr}_B [H_I(t), [H_I(s), \rho_S(s) \otimes \rho_B]] \quad (20)$$

The Born approximation involves a **weak coupling approximation**. A Markovian process depends only on the current state of the system, however, we still have the memory term  $\rho_S(s)$  on the RHS.

## The Markov approximation

We would like to make the equation time local  $\rho(s) \rightarrow \rho(t)$ . From equation (20) we see that  $\rho(t) - \rho(s) \propto \mathcal{O}(H_I^2)$  and so we can do the replacement which will incur in an error of  $\propto \mathcal{O}(H_I^4)$ .

$$\dot{\rho}_S(t) = - \int_0^t ds \text{Tr}_B[H_I(t), [H_I(s), \rho_S(t) \otimes \rho_B]] \quad (21)$$

and we make the variable change  $s = t - s'$

$$\dot{\rho}_S(t) = - \int_0^{t-s'} ds' \text{Tr}_B[H_I(t), [H_I(t - s'), \rho_S(t) \otimes \rho_B]] \quad (22)$$

## The Markov approximation

The previous integral is defined by the bath response time  $\tau_B$  and decays for times much larger than  $\tau_B$ . If  $\rho_S$  changes negligibly during  $\tau_B$ , we can let the integration limit go to  $\infty$ .

$$\dot{\rho}_S(t) = - \int_0^\infty ds' \text{Tr}_B[H_I(t), [H_I(t-s'), \rho_S(t) \otimes \rho_B]] \quad (23)$$

Now we have a time-local Markovian equation.

## The secular approximation

The last step consists of carrying out a secular (or rotating wave approximation) on the bath modes. As we will see, it consists of considering modes resonant (at exactly the same energy as) the system transitions. We consider a form of the interaction decomposed in the **system Hamiltonian eigenbasis**:

$$H_I = \sum_{\alpha, \omega} A_{\alpha}(\omega) \otimes B_{\alpha} \quad (24)$$

where  $\hbar\omega = E_S - E'_S$  is the difference between two eigenvalues of  $H_S$ . This is a very general form of the interaction.

## The secular approximation

We have:

$$[H_S, A_\alpha(\omega)] = -\omega A_\alpha(\omega) \quad (25)$$

which give in the interaction picture:

$$H_I(t) = \sum_{\alpha, \omega} e^{-i\omega t} A_\alpha(\omega) \otimes B_\alpha(t) \quad (26)$$

with  $B_\alpha(t) = e^{\frac{i}{\hbar} H_B t} B_\alpha e^{-\frac{i}{\hbar} H_B t}$ .

## Secular approximation

We can use the explicit form of the interaction to put into our Born-Markov equation:

$$\dot{\rho}_S(t) = - \int_0^\infty ds' \text{Tr}_B[H_I(t), [H_I(t-s'), \rho_S(t) \otimes \rho_B]] \quad (27)$$

We will make use of the two following equalities:

$$\begin{aligned} \langle B_\alpha(t) \rangle &= \text{Tr}_B(B_\alpha(t)\rho_B) = 0 \\ \Gamma_{\alpha\beta}(\omega) &= \int_0^\infty ds e^{i\omega s} \langle B_\alpha^\dagger B_\beta(t-s) \rangle \end{aligned} \quad (28)$$

The first one stems from the bath being at equilibrium. The second one is the Fourier transform of the bath autocorrelation function.



# Secular approximation

After some algebra, we obtain:

$$\begin{aligned} \dot{\rho}_S = & \sum_{\omega, \omega'} \sum_{\alpha, \beta} e^{i(\omega' - \omega)t} \Gamma_{\alpha\beta}(\omega) (A_\beta(\omega) \rho_S(t) A_\alpha^\dagger(\omega') - A_\alpha^\dagger(\omega') A_\beta(\omega) \rho_S(t) \\ & + h.c.) \end{aligned} \quad (29)$$

The secular approximation consists of choosing only boson modes which are resonant with the system transition. Thus we arrive at the final form of the equation:

$$\begin{aligned} \dot{\rho}_S = & \sum_{\omega} \sum_{\alpha, \beta} \Gamma_{\alpha\beta}(\omega) (A_\beta(\omega) \rho_S(t) A_\alpha^\dagger(\omega) - A_\alpha^\dagger(\omega) A_\beta(\omega) \rho_S(t) \\ & + h.c.) \end{aligned} \quad (30)$$

## Final form of the equation

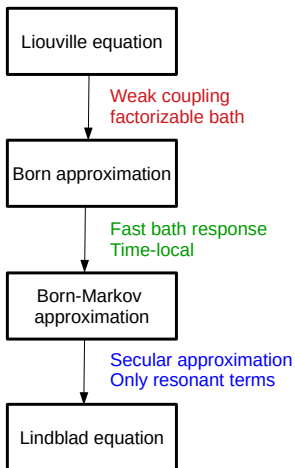
We first go back from the interaction picture to the Schrodinger picture. We get that:

$$\begin{aligned} \dot{\rho}_S = & -\frac{i}{\hbar}[H_S, \rho_S] + \sum_{\omega} \sum_{\alpha, \beta} \Gamma_{\alpha\beta}(\omega) (A_{\beta}(\omega) \rho_S(t) A_{\alpha}^{\dagger}(\omega) \\ & - A_{\alpha}^{\dagger}(\omega) A_{\beta}(\omega) \rho_S(t) + h.c.) \end{aligned} \quad (31)$$

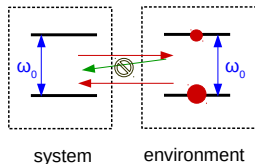
Finally, we use that  $\Gamma_{\alpha\beta}(\omega)$  is a positive semi-definite matrix and diagonalize to obtain:

$$\dot{\rho}_S = -i[H, \rho_S] + \sum_{i, \omega} \gamma_i(\omega) [F_i(\omega) \rho_S F_i^{\dagger}(\omega) - \frac{1}{2} \{F_i^{\dagger}(\omega) F_i(\omega), \rho_S\}_+] \quad (32)$$

# Summary



Give or take "arbitrary" amounts of energy and leave the bath unchanged.



Bath couples to eigenstates of  $H_S$

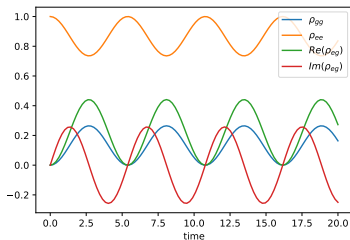
Energy given to the bath does not come back.

# Examples

# The two-level system

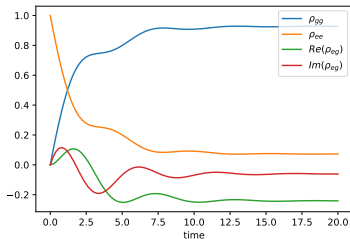
We look at the density matrix of a two-level system governed by the Hamiltonian  $H = \begin{bmatrix} 0 & V \\ V & E \end{bmatrix}$ . The density matrix

$\rho_S = \begin{bmatrix} \rho_{gg} & \rho_{ge} \\ \rho_{eg} & \rho_{ee} \end{bmatrix}$  has population of the levels along the diagonal and coherences between the levels on the off-diagonal.



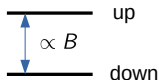
## Two-level system example

We add dissipation with the operator operator  $F_1 = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$ . The resulting dynamics show a decay to the ground state. We have a mixed state ( $\text{Tr}(\rho^2) = 0.99 < 1$ ).



# Relaxation in spins

Spin  $\frac{1}{2}$  in a magnetic field



Rotational frequency and Zeeman frequency match

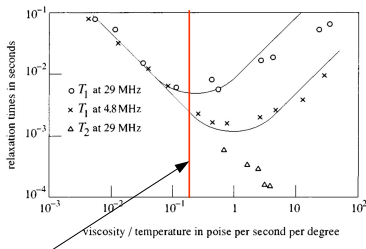


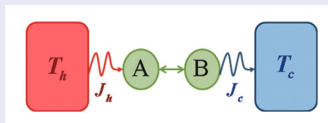
Figure: NMR and relaxation, Brian Cowan

The relaxation process is most efficient for resonant interaction between the rotational modes and the Zeeman frequency.

# Problems with local coupling

Local coupling, or coupling to non-diagonal states can lead to unphysical behavior. Global coupling (or coupling to the eigenstates of the system) fulfills the second law.

## Heat transport



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The Lindblad equation is a dynamical semigroup, and although the solution might seem physical (trace-preserving, completely positive), one should always keep in mind the physics, and (if possible), the microscopic model.



## Conclusions

- The Lindblad-GKS equation describes the evolution of a system coupled to a Markovian bath.
- It assumes that the bath is memoryless, and not perturbed by energy exchange with the system.
- The system is resonantly coupled to the bath, i.e. it only couples to modes which have the same energy as any difference between its eigenstates.

# References

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