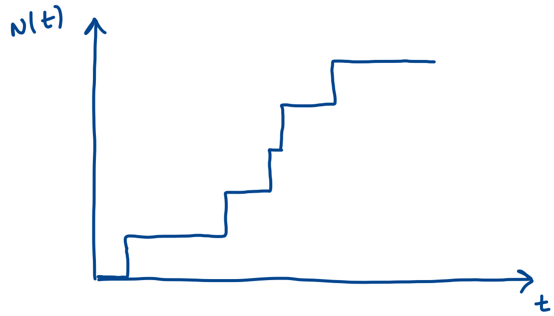
Lecture 4 – The master equation

Not all stochastic processes are continuous. Take for example an electric circuit where the current is low enough that charges arrive one by one, at random times. The number of charges that have arrived at time t, $N(t)$, will look something like this.



The curve is continous between certain jump processes (which in this case correspond to the arrival of a charge), which are discontinous. Here, of course, this is a consequence of the fact that $N(t)$ is an integer, the state space of the stochastic process $N(t)$ is discrete, and therefore there is no sense in which it can be continous. If the rate of arrival of charges becomes very large, we could maybe approximate the process by a continous curve, but this is not what we want here.

To describe such jump processes we still assume $x(t)$ is a Markov process, that therefore satisfies the Chapman-Kolmogorov

$$P(x,t \mid x_0 t_0) = \int dx' \; P(x t \mid x' t') \, P(x' t' \mid x_0 t_0)$$

and further assume that the transition probability only depends on time differences

$$P(x, t \mid x', t') = P_{t-t'}(x \mid x') = P_{\delta t}(x \mid x')$$

For a small δt,

$$P_{\delta t}(x|x') = (1-\gamma(x')\delta t)\,\delta(x-x') + w(x|x')\,\delta t + O((\delta t)^2)$$

where the transition rate $w(x|x')$ from $x' \to x$ satisfies $w(x|x)=0$, and the decay rate of state x' is $\gamma(x')$. We have also used that $P_{\delta t=0}(x|x') = \delta(x-x')$. To make sure that probability is conserved, we require

$$1 = \int P_{\delta t}(x|x')\,dx = 1 - \left[\gamma(x') - \int dx\, w(x|x')\right]\delta t + O((\delta t)^2)$$

Therefore

$$\gamma(x') = \int dx\, w(x|x') \qquad (\#)$$

Intuitively this makes sense: summing over all transitions away from the state x' gives us the decay rate out of the state x'.

Using these definitions, we have

$$P_{t+\delta t}(x|x_0) = \int dx'\, P_{\delta t}(x|x')\, P_t(x'|x_0)$$

$$= \int dx' \left[(1-\gamma(x')\,\delta t)\,\delta(x-x') + w(x|x')\,\delta t\right] P_t(x'|x_0)$$

$$= (1-\gamma(x)\,\delta t)\,P_t(x|x_0) + \delta t\int dx'\, w(x|x')\,P_t(x'|x_0)$$

Supressing the x_0 in the notation:

$$\frac{P_{t+\delta t}(x) - P_t(x)}{\delta t} = -\gamma(x)\,P_t(x) + \int dx'\, w(x|x')\,P_t(x')$$

which using # and taking $\delta t \to 0$ gives

$$\boxed{\frac{\partial P(x,t)}{\partial t} = \int dx' \left[w(x|x')\,P(x',t) - w(x'|x)\,P(x,t)\right]}$$

The master equation

If the state space is discrete $x = x_n$ with n an integer

$$\frac{\partial P_n}{\partial t} = \sum_m \Big[\underbrace{W_{nm} P_m(t)}_{\text{gain}} - \underbrace{W_{mn} P_n(t)}_{\text{loss}}\Big]$$

→ Master equation is a gain-loss equation for the probabilities P_n of different states n.

Note: We have assumed $W(x|x')$ (or W_{nm}) are independent of t. However, we can replace $W(x|x') \to W(x|x't)$ if we like in the master equation. We will not consider this case here.

We can write the discrete master equation in the matrix form

$$\frac{d\vec{P}}{dt} = \Gamma \vec{P}$$

where $(\vec{P})_n = P_n$ and

$$\Gamma_{nm} = W_{nm} - \delta_{nm} \sum_{n'} W_{n'n}$$

The formal solution can then be written

$$\vec{P}(t) = e^{\Gamma t} \vec{P}(0)$$

Note: Γ not necessarily symmetric and therefore left and right eigenvectors may be different.

$$\left.\begin{aligned} \Gamma \vec{v}_R &= \lambda \vec{v}_R \\ \vec{v}_L^{\,T} \Gamma &= \lambda' \vec{v}_L^{\,T} \end{aligned}\right\} \quad \begin{aligned} \vec{v}_L^{\,T} \Gamma \vec{v}_R &= \lambda\, \vec{v}_L \cdot \vec{v}_R \\ &= \lambda'\, \vec{v}_L \cdot \vec{v}_R \end{aligned}$$

and $\det(\Gamma - \lambda) = 0$

$\det(\Gamma^T - \lambda') = 0$
$= \det(\Gamma - \lambda')$

or $(\lambda - \lambda')\, \vec{v}_L \cdot \vec{v}_R = 0$

⇒ left and right eigenvalues the same and left and right eigenvectors with different eigenvalues orthogonal.

Properties of Γ

* $\Gamma_{nm} \geq 0$ if $n \neq m$ (transition probability positive)

* $\sum_n \Gamma_{nm} = 0$

The second one is a consequence of probability conservation, namely:

$$0 = \frac{d}{dt} \sum_n P_n = \sum_n \frac{dP_n}{dt} = \sum_n \Gamma_{nm} P_m \Rightarrow \sum_n \Gamma_{nm} = 0$$

The second of these conditions implies that if

$$\vec{v}_{0,L}^{T} = (1, 1, 1 \ldots, 1)$$

then

$$(\vec{v}_{0,L}^{T} \Gamma)_m = \sum_n \Gamma_{nm} = 0 \quad \text{for all } m$$

$\Rightarrow$ Γ has a left eigenvector with eigenvalue 0, and therefore also a right eigenvector $\vec{v}_0$ with eigenvalue 0: $\Gamma \vec{v}_0 = 0$

Since

$$\frac{d\vec{v}_0}{dt} = \Gamma \vec{v}_0 = 0$$

there is at least one stationary distribution.

Note: Assuming $\vec{v}_0$ is normalizable. There are some exceptions in infinite systems, such as a random walk where $P(x,t) \to 0$ as $t \to \infty$. $P(x,t) = \text{const}$ is an eigenvector but not normalizable.

Q: what would it mean if there are more than one eigenvectors with zero eigenvalue?

Long-time limit: As $t \to \infty$ all solutions of the master equation tend to the (or one of, if there are many) stationary solution.

(strictly true only for finite number of discrete states see e.g. van Kampen V.3 for details)

This is certainly true for systems that reach equilibrium; the equilibrium distribution then being an important example of a stationary solution.

Note: For physical systems this is somewhat the expected behavior. The master equation is however also used to describe non-physical systems, such as populations.

Detailed balance

A stationary solution satisfies $\frac{dP}{dt} = 0$ and therefore

$$\sum_m W_{nm} P_m^s = \sum_m W_{mn} P_n^s$$

A sufficient (but stronger) condition is that each term satisfies detailed balance

$$\boxed{W_{nm} P_m^{eq} = W_{mn} P_n^{eq}} \qquad (*)$$

This is generally valid in equilibrium, in time reversal symmetric systems.

Q: Does this make an intuitive sense?

To see this write:

$$P(x, t+\delta t\,;\, y, t) = P(x, t+\delta t \mid y, t)\, P_{eq}(y)$$
$$= P(y, t \mid x, t+\delta t)\, P_{eq}(x)$$

Using the transition probabilities this becomes

using time reversal

$$W_\tau(x|y)\,P_{eq}(y) = W_{-\tau}(y|x)\,P_{eq}(x) = W_\tau(y|x)\,P_{eq}(x)$$

which is the continuum form of detailed balance (*).

Pauli master equation

Suppose we have a quantum mechanical system with a set of states $\{|n\rangle\}$. These may be, for example, the states of electron localized on some site, in a quantum dot for example; it can be the different excitation states of an atom; etc. If we know the full Hamiltonian $\hat{H}$ then any state $|\psi\rangle$ will evolve in time according to the Schrödinger equation

$$i\partial_t |\psi\rangle = \hat{H}|\psi\rangle$$

Expanding the state $|\psi\rangle$ in $\{|n\rangle\}$, in general, the time dependent state will be $|\psi(t)\rangle = \sum_n c_n(t)\,|n\rangle$. The corresponding density matrix is

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)| = \sum_{n,m} c_n(t)\,c_m^*(t)\,|n\rangle\langle m|$$

The diagonal elements of $\hat{\rho}$ are probabilities $P_n = \rho_{nn} = \langle n|\hat{\rho}|n\rangle = |c_n(t)|^2$, while the off-diagonal elements $\rho_{nm} = c_n(t)\,c_m^*(t)$ are often called coherences, and they contain information about interference effects. Since $c_n(t)$ are in general complex there is no sense in which we can think of $\hat{\rho}_{nm}$ as probabilities. So, we can't obviously write down a master equation for quantum evolution. We will get back to this question later. Pauli was one of the people to think about this question, and made a first attempt. That attempt is far from perfect but it's occasionally useful. Now, I haven't read Pauli's paper on this (it's in some obscure source, and in german) but he could have argued something like this: The off-diagonal elements $\rho_{nm}(t)$ generally have rapidly oscillating phases. For example if $|n\rangle$ where eigenstates of $\hat{H}$ with $\hat{H}|n\rangle = \varepsilon_n |n\rangle$, then $c_n(t) = c_n(0)\, e^{-i\varepsilon_n t/\hbar}$ and therefore

$$\rho_{nm} = c_n(0)\, c_m^*(0)\, e^{-i(\varepsilon_n - \varepsilon_m)t/\hbar}.$$

This is the dynamics we would get in a closed quantum system, where everything that exist is the states $|n\rangle$ and interactions or couplings between them. But generally, the states $\{|n\rangle\}$ are embedded in another bigger system that we can call <u>the environment</u>. Effects of the environment can be complicated to incorporate exactly but we can try to think about in some kind of statistical or stochastic way. For the coherences, for example, we could write them as

$$\rho_{nm} = |\rho_{nm}|\, e^{-i\phi_{nm}(t)}$$

If the environment is interacting strongly with the system then one might expect $\phi_{nm}(t) \in [0, 2\pi)$ to fluctuate rapidly in time, and over some short time scale τ_ϕ become a random phase uniformly distributed in the interval $[0, 2\pi)$. In this case, the expected value of the coherences will be

$$\langle \rho_{nm} \rangle = |\rho_{nm}| \langle e^{i\phi_{nm}} \rangle$$

Here $\langle \rangle$ is the expectation value over the random varicbe ϕ_{nm}, not a quantum mechanical average (quantum average wouldn't make sense anyway, since ρ_{nm} is already a matrix element). Now

$$\langle e^{i\phi_{nm}} \rangle = \int_0^{2\pi} d\phi \, e^{i\phi} = 0$$

If this decoherence process is much faster than any time scale τ_s relevant to the dynamics of the system itself, i.e., $\tau_\phi \ll \tau_s$, then after every small interval Δt, which could in principle lead to build up of coherences, the environment will completely decohere it a way, Pauli said (I imagine, though maybe he used different words) and the density matrix $\hat{\rho}$ remains a diagonal matrix at all times, with the diagonal elements equal to the probability of being in state $|n\rangle$ at time t:

$$\hat{\rho}(t) = \begin{pmatrix} P_1(t) & & & 0 \\ & P_2(t) & & \\ & & \ddots & \\ 0 & & & P_n(t) \end{pmatrix}$$

OK, excellent, we now have only probabilities and could imagine writing down a master equation that coverns their time evolution. But we need the transition rates W_{nm}, how do we get them?

Here is where the physics comes in. We need to know and model what is driving the transitions between states. Generally this is some perturbation $\hat{V}$. Transitions between atomic levels are often induced by light, and then $\hat{V} \propto \vec{E}$ the electric field generated by the light. We then need to use time-dependent perturbation theory to calculate the effect of $\hat{V}$. Often people simply use <u>Fermi's golden rule</u> for the transition rates:

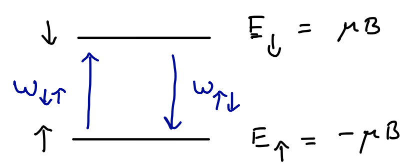
$$\boxed{W_{nm} = \frac{2\pi}{\hbar} |\langle n|\hat{V}|m\rangle|^2 \, \delta(E_n - E_m)}$$

Let's look at some examples of using the master equation. Here we focus on the master equation aspects. Calculating W_{nm} is in principle a quantum mechanical calculation so we can assume it has been done.

<u>Spin in a magnetic field</u>

$$H = -\mu \sigma_z B$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$



Master equation:

$$\begin{cases} \dfrac{dP_\uparrow}{dt} = W_{\uparrow\downarrow} P_\downarrow - W_{\downarrow\uparrow} P_\uparrow \\[2ex] \dfrac{dP_\downarrow}{dt} = W_{\downarrow\uparrow} P_\uparrow - W_{\uparrow\downarrow} P_\downarrow \end{cases}$$

In equilibrium we have

$$P_\sigma^{eq} = \frac{1}{Z} e^{-\beta E_\sigma} , \quad Z = \sum_\sigma e^{-\beta E_\sigma} = 2\cosh(\beta\mu B)$$

and

$$\frac{dP_\sigma}{dt} = 0 \quad \Rightarrow \quad W_{\uparrow\downarrow} e^{-\beta\mu B} = W_{\downarrow\uparrow} e^{+\beta\mu B} \equiv W_0$$

Now consider an ensemble of N spins.
The total number of spin up and down are then

$$N_\uparrow = N P_\uparrow \quad \text{and} \quad N_\downarrow = N P_\downarrow$$

The total magnetization is then $M = N_\uparrow - N_\downarrow$ and

$$M_{eq} = N\left(P_\uparrow^{eq} - P_\downarrow^{eq}\right) = N \frac{\sinh(\beta\mu B)}{\cosh(\beta\mu B)} = N\tanh(\beta\mu B)$$

$$\frac{dM}{dt} = N\frac{d}{dt}\left(P_\uparrow - P_\downarrow\right) = 2N\left(W_{\uparrow\downarrow}P_\downarrow - W_{\downarrow\uparrow}P_\uparrow\right)$$

That is

$$\frac{dM}{dt} = 2Nw_0\left(e^{\beta\mu B}P_\downarrow - e^{-\beta\mu B}P_\uparrow\right)$$

$$= 2Nw_0\left[\cosh(\beta\mu B)\underbrace{\left(P_\downarrow - P_\uparrow\right)}_{-M/N} + \sinh(\beta\mu B)\underbrace{\left(P_\downarrow + P_\uparrow\right)}_{=1}\right]$$

$$= -2w_0\left[M\cosh(\beta\mu B) - N\sinh(\beta\mu B)\right]$$

$$= -2w_0\cosh(\beta\mu B)\left[M - N\tanh(\beta\mu B)\right]$$

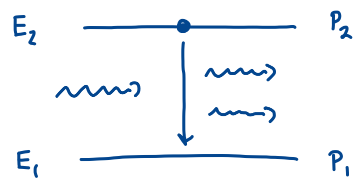
$$= -\gamma\left(M - M_{eq}\right) \qquad \text{where} \qquad \gamma = 2w_0\cosh(\beta\mu B)$$

This describes the relaxation towards equilibrium

$$M(t) = \underline{M_{eq} + \left(M(0) - M_{eq}\right)e^{-\gamma t}}$$

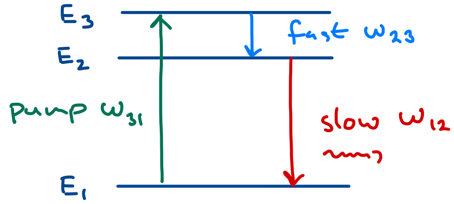
Population inversion and three-level laser

I assume you know (and probably better than me) the basic principle behind lasers. By establishing a population inversion in an atom, say, where in a ensemble of a large number of such atoms, more of them are in an excited state than in the ground state:



Once a population inversion is establishe, stimulated emission can take place that builds up a coherent source of light. (I'm skipping a lot of details, such as mirrors etc., but these are not essential for our discussion). Let us not discuss stimulated emission and coherent light now, but rather a simple master equation model of generating a population imbalance.

In the schematic picture above we only have two levels. In such two level systems in thermal equilibrium it's impossible to achieve a population inversion. But with three levels we can. To achieve population inversion we need some way of pumping the atoms from their lowest level E_1 to E_3. This could take place by light absorption or by other electrical or chemical means. Once the atom is in state E_3 a fast transition into a meta-stable state E_2 takes place. Once the atom is there, if we



wait long enough it will eventually decay to E_1 releasing a photon.

The fact that E_2 is meta-stable means that the rate $\omega_{12} \ll \omega_{23}, \omega_{31}$

The master equation describing the population dynamics is

$$\frac{dP_1}{dt} = \omega_{12} P_2 - \omega_{31} P_1$$

$$\frac{dP_2}{dt} = \omega_{23} P_3 - \omega_{12} P_2$$

$$\frac{dP_3}{dt} = \omega_{31} P_1 - \omega_{23} P_3$$

writing the probabilities as a vector $\vec{p} = (P_1, P_2, P_3)^T$, with T a transpose such that $\vec{p}$ is a column vector, we have

$$\frac{d\vec{p}}{dt} = T \vec{p} \qquad \text{with} \qquad T = \begin{pmatrix} -\omega_{31} & \omega_{12} & 0 \\ 0 & -\omega_{12} & \omega_{23} \\ \omega_{31} & 0 & -\omega_{23} \end{pmatrix}$$

Note that the sum over all columns $\sum_n T_{nm} = 0$ as required.

The formal solution of the above equation is as before

$$\vec{p}(t) = e^{Tt} \vec{p}(0)$$

If we take, as an example,

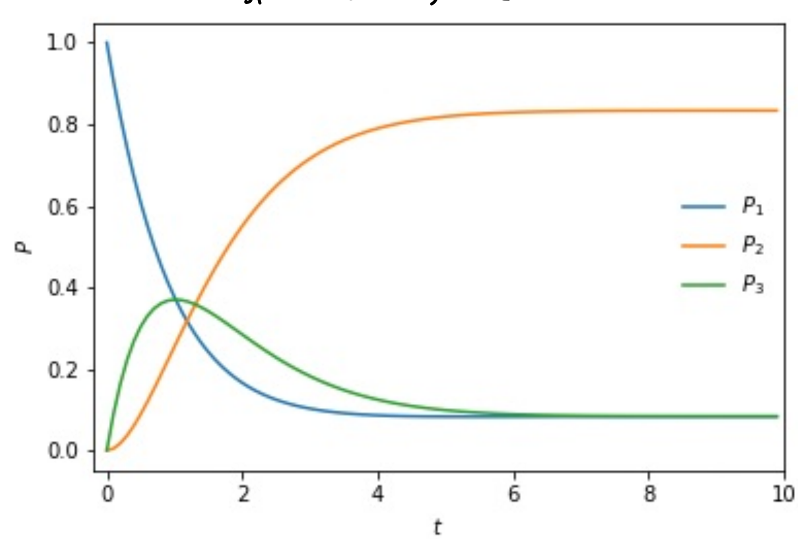
$\omega_{31} = \omega_{23} = 1$ and $\omega_{12} = 0.1$

$$\therefore T = \begin{pmatrix} -1 & 0.1 & 0 \\ 0 & -0.1 & 1 \\ 1 & 0 & -1 \end{pmatrix}$$

and initial conditions

$\vec{p}(0) = (1, 0, 0)$, we get:

$\omega_{31} = \omega_{23} = 1$; $\omega_{12} = 0.1$

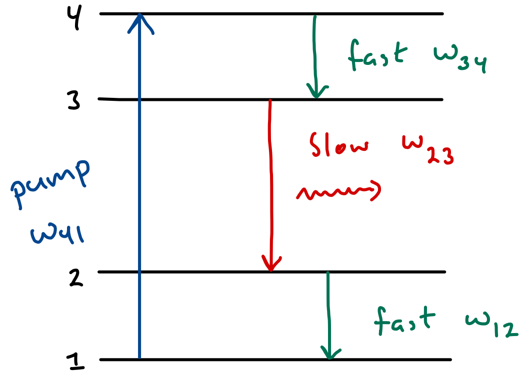


We see that at long times we approach a steady state with

$\vec{P}_s = (\frac{5}{60}, \frac{5}{6}, \frac{5}{60})$ with population inversion. This is the correct steady state, since

$$T \cdot \vec{P}_s = \begin{pmatrix} -1 & 0.1 & 0 \\ 0 & -0.1 & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} 5/60 \\ 5/6 \\ 5/60 \end{pmatrix} = \begin{pmatrix} -5/60 + 5/60 \\ -5/60 + 5/60 \\ 5/60 - 5/60 \end{pmatrix} = 0$$

We could have found this by diagonalizing T.


4
3
2
1
pump ω_{41}
fast ω_{34}
slow ω_{23}
fast ω_{12}