Markovian, non-Markovian processes and Master equations

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Overview

I. Derivation of the Classical Markovian Master equation
   i. Markovian Processes
   ii. Chapman Kolmogorov equation
   iii. Derivation of the Classical Master equation
   iv. Examples (Deterministic Processes, Fokker-Planck)
II. Derivation of the Non-Markovian Quantum Master equation
   i. Pauli equation
   ii. Van Hove equation
   iii. Solution by Zwanzig and Nakajima
   iv. The Fermi Golden Rule from the Markovian assumption

Markovian processes

- Process, with states: $z_i, i = 1,2, \dots$
  - Probability of state z_1 at time t_1: $\rho_1(z_1, t_1)$
  - Conditional probability: $\rho_2(z_2, t_2|z_1, t_1)$ and for z_n, t_n after:
    $z_{n-1}, z_{n-2}, \dots, z_1$, at $t_{n-1}, t_{n-2}, \dots, t_1$:
    $\rho_n(z_n, t_n|z_{n-1}, t_{n-1}, z_{n-2}, t_{n-2}, \dots, z_1, t_1)$;
- Markovian assumption:
  - Dependence only on the previous state:

$$\rho_n(z_n, t_n|z_{n-1}, t_{n-1}, z_{n-2}, t_{n-2}, \dots, z_1, t_1) = \rho_2\,(z_n, t_n|z_{n-1}, t_{n-1});$$

$$\Rightarrow \rho_3(z_3, t_3; z_2, t_2; z_1, t_1) = \rho_2(z_3, t_3|z_2, t_2)\,\rho_2(z_2, t_2|z_1, t_1)\rho_1(z_1, t_1);$$

Chapman- Kolmogorov equation

- Markovian assumption and integration over z_2:

$$\rho_3(z_3,t_3;z_1,t_1) = \int \rho_3(z_3,t_3;z_2,t_2;z_1,t_1)\,dz_2 = \int \rho_2(z_3,t_3|z_2,t_2)\rho_2(z_2,t_2|z_1,t_1)\rho_1(z_1,t_1)\,dz_2;$$

Chapman Kolmogorov equation:

$$\rho_2(z_3,t_3|z_1,t_1) = \int \rho_2(z_3,t_3|z_2,t_2)\rho_2(z_2,t_2|z_1,t_1)\,dz_2;$$

- Multiplying by ρ_1 and integrating over z_1:

Chapman- Kolmogorov equation for ρ_1:

$$\rho_1(z_3,t_3) = \int \rho_2(z_3,t_3|z_2,t_2)\rho_1(z_2,t_2)\,dz_2;$$

Master equation

- time evolution of the probability distribution ρ_1:
  i. Expansion of ρ_2 in τ short-time behaviour:
  $\rho_2(z, t+\tau|z'', t) = (1 - a(z,t)\tau)\delta(z - z'') + w(z, z'', t)\tau + O(\tau^2)$;

  ii. From the normalization of the density:
  $\int \rho_2(z, t+\tau|z'', t)\, dz = 1 \Rightarrow a(z', t) = \int w(z, z', t) dz$;

  iii. Using Chapman- Kolmogorov:
  $\rho_2(z, t+\tau|z', t')$ = $\int \rho_2(z, t+\tau|z'', t\,)\rho_2(z'', t\,|z', t'\,)\, dz''$=
$(1 - a(z,t)\tau)\; \rho_2(z, t\,|z', t'\,)$+$\tau \int w(z, z'', t)\rho_2(z'', t\,|z', t'\,)\, dz'' + O(\tau^2)$;

- Using ii. and taking the limit $\tau \to 0$:

$$\frac{\partial \rho_2(z,t\,|z',t')}{\partial t} = \int w(z,z'',t)\rho_2(z'',t\,|z',t')\,dz'' - \int w(z'',z,t)\rho_2(z,t\,|z',t')\,dz'';$$

- Multiplying by ρ_1(z´,t´) and integrating by z':

$$\frac{\partial \rho_1(z,t)}{\partial t} = \int w(z,z',t)\rho_1(z',t)\,dz' - \int w(z',z,t)\rho_1(z,t)\,dz';$$

- Discrete states:

$z \to n, \rho_1(z,t) \to \rho_n(t), w(z,z',t) \to w_{nn'}(t);$

- Discrete Master equation:

$$\partial_t \rho_n(t) = \sum_{n'} (w_{nn'}(t)\rho_{n'}(t) - w_{n'n}(t)\rho_{n'}(t));$$

- Ordering state-densities in a vector:

$$\partial_t \rho_\alpha(t) = \sum_{\alpha'} V_{\alpha\alpha'}\rho_{\alpha'}(t);$$

Liouville equation and deterministic processes

- Differential equation: $\dot{x} = f(x),\ x \in \mathbb{R}^n$;

$\rightarrow$ Define density: $\rho_2(z,t|x_0,t_0) \equiv \delta(z - x(t))$, with solution $x(t)$;

- Initial condition: $x(t_0) = x_0$;

$\rightarrow$ short time behaviour:

$$\rho_2(z,t+\tau|z',t') \equiv \delta(z - (z' - f(x)))$$
$$= \delta(z - z') - f(z')\frac{\partial}{\partial z}\delta(z - z')\tau + O(\tau^2);$$
$$\rightarrow w(z,z') = -f(z')\frac{\partial}{\partial z}\delta(z - z')\tau;$$
$$\Rightarrow a(z') = -\int f(z')\frac{\partial}{\partial z}\,\delta(z - z')d^n z = 0;$$

- Master equation:

$$\frac{\partial}{\partial z}\rho_1(z,t) = \int\left(-f(z')\frac{\partial}{\partial z}\ \delta(z-z')\right)\rho_1(z',t)d^n z' = -\frac{\partial}{\partial z}(f(z)\ \rho_1(z,t));$$

- For a Hamiltonian System:

$$z \equiv (p,q),\ \ \dot{z} = \left(-\frac{\partial H}{\partial q},\frac{\partial H}{\partial p}\right),$$

$$\Rightarrow\ \frac{\partial}{\partial z}\rho(p,q,t) = \frac{\partial H}{\partial q}\frac{\partial \rho}{\partial p} - \ \frac{\partial H}{\partial p}\frac{\partial \rho}{\partial q} \equiv \{H,\rho\};$$

A simple Fokker Planck equation

- Master equation:

$$\dot{\rho}_n = \alpha\rho_{n+1} + \beta\rho_{n-1} - (\alpha+\beta)\rho_n;$$

- Choosing a scale:

$-L \leq n \leq L$, with $L \gg 1$, $x \equiv \frac{n}{L}, \tilde{\Pi}(x,t) \equiv \rho_n(t)$;

- Thus:

$$\frac{\partial}{\partial t}\tilde{\Pi}(x,t) = \alpha\tilde{\Pi}\left(x+\frac{1}{L},t\right) + \beta\tilde{\Pi}\left(x-\frac{1}{L},t\right) - (\alpha+\beta)\tilde{\Pi}(x,t);$$

- Expanding in $\frac{1}{L}$:

$$\frac{\partial}{\partial t}\tilde{\Pi}(x,t) = (\alpha-\beta)\frac{1}{L}\frac{\partial}{\partial x}\tilde{\Pi}(x,t) + \frac{(\alpha+\beta)}{2}\frac{1}{L^2}\frac{\partial}{\partial^2 x}\tilde{\Pi}(x,t) + O\left(\frac{1}{L^3}\right);$$

$$\frac{\partial}{\partial t}\tilde{\Pi}(x,t) = (\alpha - \beta)\frac{1}{L}\frac{\partial}{\partial x}\tilde{\Pi}(x,t) + \frac{(\alpha + \beta)}{2}\frac{1}{L^2}\frac{\partial}{\partial x^2}\tilde{\Pi}(x,t) + O\left(\frac{1}{L^3}\right);$$

- Setting $\alpha = \beta = 1, \tau \equiv \frac{t}{L^2}$:

$$\frac{\partial}{\partial t}\tilde{\Pi}(x,t) = \frac{\partial}{\partial x^2}\tilde{\Pi}(x,t);$$

→Simplest Fokker-Planck equation;

- Describes Random Walk
- Solved by Gaussian dist.

$\hbar$=1

Quantum Master equation

Pauli´s Version of the QME:

- The Von Neumann equation and Liouville operator $\hat{L}$

$$i\frac{\partial}{\partial t}\hat{\rho} = [\hat{H}, \hat{\rho}] \equiv \hat{L}\hat{\rho};$$

$\Rightarrow$ formal solution: $\hat{\rho}\,(t) = e^{-i\hat{L}(t-t')}\hat{\rho}(t_0);$

in Heisenberg picture: $\hat{\rho}\,(t+\tau) = e^{-i\tau\hat{H}}\hat{\rho}(t)e^{i\tau\hat{H}};$

- Diagonal elements:

$$\rho_{mm}(t+\tau) = < m|e^{-i\tau\hat{H}}\hat{\rho}(t)e^{i\tau\hat{H}}|m >$$

$$= \sum_{n,l} < m|e^{-i\tau\hat{H}}|n >< n|\hat{\rho}(t)|l >< l|e^{i\tau\hat{H}}|m >;$$

$$\rho_{mm}(t+\tau) = < m|e^{-i\tau\hat{H}}\hat{\rho}(t)e^{i\tau\hat{H}}|m >$$

$$= \sum_{n,l} < m|e^{-i\tau\hat{H}}|n >< n|\hat{\rho}(t)|l >< l|e^{i\tau\hat{H}}|m > ;$$

- Pauli: → neglect off-diagonal elements:

$$\Rightarrow \ \rho_{mm}(t+\tau) = \sum_n < m|e^{-i\tau\hat{H}}|n >< n|\hat{\rho}(t)|n >< n|e^{i\tau\hat{H}}|m >$$

$$= \sum_n \rho_{nn}| < m|e^{-i\tau H}|n > |^2 \ ;$$

- Probabilities of the states: ρ_{mm} = P_m;

Pauli equation:

$$P_m(t+\tau) = \sum_n P_n| < m|e^{-i\tau\hat{H}}|n >|^2 \equiv \sum_n Q_{mn}(\tau)P_n(t);$$

Problem with Pauli equation:

$$P_m(t+\tau) = \sum_n Q_{mm}(\tau)P_n(t) = \sum_n Q_{mm}(-\tau)P_n(t) = P_m\ (t-\tau);$$

→ holds only, for constant probabilities

The Van Hove Method

- Perturbed Hamiltonian: $\hat{H}(t) = \hat{H}_0 + \lambda(t)\,\hat{W};$
- Looking again at diagonal elements:

$$P_m(t) = \sum_{n,l} < m|e^{-iHt}\ |n >< n|\hat{\rho}(0)|l >< l|e^{-iHt}|m >$$
$$= \sum_{n,l} | < m|e^{i(H_0+\lambda W)t}|n >|^2\ \rho_{nn}(0)$$
$$= \sum_{n} | < m|e^{i(H_0+\lambda W)t}|n >|^2\ P_{nn}(0);$$

($\hat{\rho}$ initially diagonal)

Zwanzig and Nakajimas solution of the QME

Idea:

i. Split the density Matrix into diagonal and off-diagonal parts to get two coupled equations

ii. Use a Green´s Function to solve one and plug into the other

iii. Simplify the expressions, using that the the perturbation is very small (Remark: up to now: system not necessarily Markovian, and thus more generally valid in this form)

iv. Make the Markovian assumption and derive the Fermi Golden Rule

i. Splitting the density matrix, by defining dioagonalization operator:

$$\hat{\rho} = \hat{\rho}_d + \hat{\rho}_{od} = \widehat{D}\hat{\rho} + (1 - \widehat{D})\hat{\rho};$$

ii. Applying $\widehat{D}$ and $(1 - \widehat{D})$ to the Von Neumann equation we get:

$$\partial_t \hat{\rho}_d = -i\, \widehat{D}\hat{L}\hat{\rho} = -\, i\, \widehat{D}\hat{L}\hat{\rho}_d - i\, \widehat{D}\hat{L}\hat{\rho}_{od};$$

$$\partial_t \hat{\rho}_{od} = -i \left(1 - \widehat{D}\right)\hat{L}\hat{\rho} = -\, i\, (1 - \widehat{D})\hat{L}\hat{\rho}_d - i\, (1 - \widehat{D})\hat{L}\hat{\rho}_{od};$$

iii. For differential equation of the type: $\partial_t x + \alpha x = f$;

solution given by: $x = x(0)\, e^{-\alpha t} + \int_0^t e^{-\alpha(t-t')} f(t')dt'$;

Using this on the equation for $\hat{\rho}_{od}$ we get:

$$\hat{\rho}_{od}(t) = e^{-i\,(1-\widehat{D})\hat{L}t}\hat{\rho}_{od}(0) - \int^{t} e^{-i\,(1-\widehat{D})\hat{L}(t-t')}\left(-i\,(1 - \widehat{D}\right)\hat{L}\hat{\rho}_d(t'))dt' ;$$

Plugging in to equation for $\hat{\rho}_d$:

$$\partial_t \hat{\rho}_d = -\, i\, \widehat{D}\hat{L}\hat{\rho}_d - \widehat{D}\hat{L} \int_0^t e^{-i\,(1-\widehat{D})\hat{L}(t-t')}\left(1 - \widehat{D}\right)\hat{L}\hat{\rho}_d(t')dt' ;$$

iv. Simplifications:

- $\widehat{D}\hat{L}\hat{\rho}_d = 0$;
- Define kernel K:

$$\partial_t \hat{\rho}_d = -\int_0^t \widehat{D}\left(\hat{L}_0 + \lambda \hat{L}_w\right) e^{-i\,(1-\widehat{D})(\hat{L}_0+\lambda\hat{L}_w)(t-t')}\left(\hat{L}_0 + \lambda \hat{L}_w\right)\hat{\rho}_d(t')dt'$$

$$\equiv -\int_0^t K(t-t')\hat{\rho}_d(t')dt';$$

- Considering $\lambda \to 0$:

$$K(t-t') = \widehat{D}\left(\hat{L}_0 + \lambda \hat{L}_w\right) e^{-i\,(1-\widehat{D})(\hat{L}_0+\lambda\hat{L}_w)(t-t')}\left(\hat{L}_0 + \lambda \hat{L}_w\right)$$

$$= \widehat{D}\left(\hat{L}_0 + \lambda \hat{L}_w\right) e^{-i\,(1-\widehat{D})\hat{L}_0(t-t')}\left(\hat{L}_0 + \lambda \hat{L}_w\right)$$

$$= \lambda^2 \hat{L}_w e^{-i\,\hat{L}_0(t-t')}\hat{L}_w;$$

- Define: $\widehat{M} = e^{-i(t-t')\widehat{H}_0}\,[\widehat{W}, \hat{\rho}_d]e^{i(t-t')\widehat{H}_0}$;
- \`Inserting ones´ and using $\widehat{H}_0|m> = \epsilon_m|m>$:

$$M_{mn} = e^{-i(t-t')\epsilon_m}(M_{mn}P_n - P_m M_{mn})\, e^{i(t-t')\epsilon_n};$$

- Diagonal elements:

$$
\begin{aligned}
< m|\partial_t \hat{\rho}_d|m > &= -\lambda^2 < m| \int_0^t [\widehat{W}, e^{-i(t-t')\hat{L}_0}[\widehat{W}, \hat{\rho}_d]]\, dt' \,|m > \\
&= -\lambda^2 \int_0^t \left(< m\middle|\widehat{W}\widehat{M}\middle|m >.-< m\middle|\widehat{M}\widehat{W}\middle|m >\right) dt' \\
&= -\lambda^2 \int_0^t \Sigma_n (W_{mn}M_{nm} - M_{mn}W_{nm}) dt' \\
&= -2\lambda^2 \int_0^t \Sigma_n |W_{mn}|^2 [P_n - P_m] \cos\big((t-t')(\epsilon - \epsilon')\big)\, dt';
\end{aligned}
$$

- More compact form:

$$\Omega_{mn}(t-t') \equiv |W_{mn}|^2 \cos\big((t-t')(\epsilon-\epsilon')\big);$$

$$\partial_t P_m = \int_0^t \Sigma_n (\Omega_{mn}(t-t')P_n - \Omega_{nm}(t-t')P_m) dt' \,;$$

iv. Markovian Quantum Master equation

- Non-Markovian

→ Bringing in Markovian assumption,

By: $corr(t,t') = 0$, for $t \neq t'$;

Or by simplifying: $\Omega_{mn}(t) = \delta(t) \int_0^t \Omega_{mn}(\tau) d\tau$;

- Master equation in interaction picture:

$$\partial_t P_m = -\lambda^2 \int_0^t \Sigma_n [(W_{mn} e^{-i(t-t')(\epsilon_n - \epsilon_m)} W_{nm}(P_m - P_n)$$

$$-\left(e^{-i(t-t')\epsilon_m} (W_{mn}P_n - P_m W_{mn}) e^{i(t-t')\epsilon_n}\right] dt' =$$

$$-\lambda^2 \Sigma_n \int_0^t \left[W_{mn}^I(t-t') W_{nm}^I(0)(P_m - P_n) - W_{mn}^I(t-t') W_{nm}^I(0)\big((P_n - P_m)\big]\right) dt';$$

- With the Markovian assumption:

$$\int_0^t W^I_{mn}(t-t')W^I_{nm}(0)(P_m(t)-P_n(t'))dt' =$$

$$(P_m(t)-P_n(t))\lim_{t\to\infty}\int_0^t W^I_{mn}(t-t')W^I_{nm}(0)dt' \,;$$

- Integrating over the exponentials:

$$\partial_t P_m(\mathrm{t}) = -\lambda^2 \Sigma_n (P_m(t)-P_n(t'))\lim_{t\to\infty}(\frac{|W_{mn}|^2}{i\omega_{nm}}(e^{-it\omega_{mn}} \text{-}\, e^{it\omega_{mn}}))$$

$$= 2\pi\lambda^2 \Sigma_n (P_m - P_n)|W_{mn}|^2 \lim_{t\to\infty}\left(\frac{\sin(\omega_{mn}t)}{\pi\omega_{mn}}\right);$$

- Taking the limit:

$$\partial_t P_m(\mathrm{t}) = 2\pi\lambda^2 \Sigma_n (P_n - P_m)|W_{mn}|^2 \delta(\epsilon_m - \epsilon_n)$$
$$= \Sigma_n \Omega_{\ mn} P_n - \Omega_{\ nm}\ P_m;$$

- The Fermi Golden Rule:

$$\Omega_{\ mn} = 2\pi\lambda^2 |W_{mn}|^2 \delta(\epsilon_m - \epsilon_n);$$

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