

# Lecture 3: Condensed-phase Quantum Dynamics

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## Outline

- \* system-bath model.
- \* cumulant expansion.
- \* Time-local Quantum Master equation:

Now we turn to consider quantum dynamics in condensed-phase systems:

\* difference in condensed-phase  $\Rightarrow$  environment, "bath", many DOFs.

\* system's Hamiltonian no longer well-defined.

\* model: phenomenological, focus on system;  $\swarrow$  fluctuations modulated by the environment.

$$H_S = H_S(t) = H_0 + \delta H(t).$$

microscopic model:

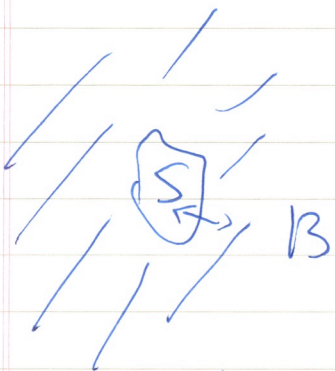
$$H = H_S + H_B + H_{SB}.$$

timeless

In this lecture series we focus on the microscopic model, but phenomenological models, such as Haken-Stroble-Reneker (HSR) model, are also quite effective and often provide a ~~better~~ <sup>good</sup> perspective to describe experiments.

\* system-bath model

The microscopic models <sup>are</sup> often based on a reduced system approach for open quantum systems:



$$H = H_S + H_B + H_{SB}$$

here we do not specify specifics.

The dividing "plane" of system & bath depends on the experiment, all <sup>instead</sup> observables only depend on the "system" part of the total system.

③

Because of the nature of the condensed phase,

we can not ~~also~~ explicitly specify the states of the vast DOFs in the bath,

therefore, a statistical treatment is

necessary  $\Rightarrow$  We must use density matrix.

$$\rho = \sum_i P_i |\phi_i\rangle\langle\phi_i|.$$

As we have mentioned, the time evolution of ~~the~~  $\rho$  follows the Liouville equation:

$$\dot{\rho} = \frac{-i}{\hbar} [H, \rho]$$

It is also easy to see that

$$\begin{aligned} \rho(t) &= \sum_i P_i |\phi_i(t)\rangle\langle\phi_i(t)| = \sum_i P_i \cdot U(t) \cdot |\phi_i(0)\rangle\langle\phi_i(0)| U^\dagger(t) \\ &= U^\dagger(t) \cdot \rho(0) \cdot U(t). \end{aligned}$$

So we can use what we learned before to calculate  $U(t)$  !!

Very often a "super-operator" notation is used, define

$\mathcal{L}$  is actually a rank-four tensor, i.e. transform a matrix to another matrix

$$\mathcal{L} \cdot \rho = [H, \rho]$$

i.e.  $\mathcal{L}$  takes commutators.

We then write

↑ very often

$$H^* \cdot \rho = [H, \rho]$$

$\mathcal{L}$  also used-

$$\dot{\rho} = \frac{-i}{\hbar} \mathcal{L} \cdot \rho$$

$$\rho(t) = e^{\frac{-i}{\hbar} \int_0^t \mathcal{L}(t') dt'} \cdot \rho(0)$$

In fact, we are not really interested in the total density matrix  $\rho(t)$ . All we care is the reduced-system density matrix.

← partial trace.

$$\text{Tr} : \text{trace} \\ = \sum_{i \in B} \langle i | \rho(t) | i \rangle$$

$$\sigma = \text{Tr}_B \rho(t)$$

Because  $\sigma$  gives all <sup>system's</sup> observables:

$$\langle A \rangle = \text{Tr} \sigma \cdot A$$

↑ defined in the system's space only  
i.e. boundaries of the system are defined by "the experiment" timeless

Thus, we want to calculate.

$$\sigma(t) = \text{Tr}_B \rho(t) = \text{Tr}_B \left\{ \exp\left\{ \frac{-i}{\hbar} \int_0^t dt' L(t') \right\} \cdot \rho(0) \right\}$$

Trace over bath states, partial trace -

this is actually an approximation

To carry on, we assume the system & bath

is initially in a product state:

↙ bath in thermal equilibrium.

$$\rho(0) = \sigma_0 \otimes \rho_b^{eq}$$

Using this approximated initial condition, we obtain

$$\sigma(t) = \text{Tr}_B \rho(t) = \text{Tr}_B \left\{ \exp\left[ \frac{-i}{\hbar} \int_0^t dt' L(t') \right] \cdot \rho_b^{eq} \right\} \cdot \sigma_0$$

$$= \left\langle \exp\left[ \frac{-i}{\hbar} \int_0^t dt' L(t') \right] \right\rangle_B \cdot \sigma_0$$

thermal average a super-operator !!

Note that we define  $\langle \cdot \rangle_B = \text{Tr}_B \{ \cdot \times \rho_b^{eq} \}$

"thermal average"

$$= \sum_{\bar{c} \in B} P_{\bar{c}} \times \langle \bar{c} | \cdot | \bar{c} \rangle$$

timeless

\* Cumulant expansion. ①

To perform the average, we introduce a very useful technique, cumulant expansion  
 $\Rightarrow$  average of exponential changes to exponential of averages.

Basic idea:  $\langle e^A \rangle \approx e^{\sum_{n=1}^{\infty} \frac{1}{n!} \times K_n \times \left(\frac{i}{\hbar}\right)^n}$

moments  
↓   ↓

$K_n$ : n-th order cumulants.

In our case:

$$\left\langle \exp_+ \left[ \frac{i}{\hbar} \int_0^t dt \cdot \mathcal{L}(t) \right] \right\rangle_B = e^{\sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{i}{\hbar}\right)^n K_n(t)}$$

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{i}{\hbar}\right)^n K_n(t) &= \ln \left\{ \left\langle \exp_+ \left[ \frac{i}{\hbar} \int_0^t dt \mathcal{L}(t) \right] \right\rangle_B \right\} \\ &\approx \ln \left\{ 1 - \frac{i}{\hbar} \int_0^t dt \mathcal{L}(t) + \frac{1}{2} \left(\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{L}(t_2) \mathcal{L}(t_1) \right. \\ &\quad \left. + \dots \right\}. \end{aligned}$$

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recall  $\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots$

$$\text{R.H.S.} = \ln \left\{ 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1 \underbrace{\langle \mathcal{L}(t_n) \dots \mathcal{L}(t_1) \rangle_B}_{\text{average here!!}} \right\}$$

$$\left(\frac{-i}{\hbar}\right) \cdot K_1^X(t) \left( = \left(\frac{-i}{\hbar}\right) \cdot \int_0^t dt \cdot \langle \mathcal{L}(t) \rangle \right.$$

$$\left. \frac{1}{2} \left(\frac{-i}{\hbar}\right)^2 K_2^X(t) \left( \begin{aligned} &+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \cdot \langle \mathcal{L}(t_2) \mathcal{L}(t_1) \rangle_B \\ &\ominus \frac{1}{2} \cdot \left(\frac{-i}{\hbar}\right)^2 \cdot \left[ \int_0^t dt \langle \mathcal{L}(t) \rangle \right]^2 \end{aligned} \right.$$

$$\left. + \left(\frac{-i}{\hbar}\right)^3 \dots \right)$$

Therefore, by compare term by term in the order of  $\left(\frac{-i}{\hbar}\right)^n$ ,

We obtain :

Super operator  $\rightarrow K_1^X(t) = \int_0^t dt \cdot \langle \mathcal{L}(t) \rangle_B$

$$K_2^X(t) = 2 \cdot \int_0^t dt_2 \int_0^{t_2} dt_1 \cdot \langle \mathcal{L}(t_2) \mathcal{L}(t_1) \rangle_B - \left[ K_1^X(t) \right]^2$$

\* second order is most useful

average over B, still an super operator in system's space.

timeless

(8)

if the bath fluctuations are Gaussian

Thus, the cumulant expansion yields

$$\langle \exp_{+} \left[ \frac{-i}{\hbar} \int_0^t \mathcal{L}(\tau) d\tau \right] \rangle_B \approx \exp \left[ \left( \frac{-i}{\hbar} \right) \cdot K_1^x(t) + \frac{1}{2} \left( \frac{-i}{\hbar} \right)^2 \cdot K_2^x(t) \right]$$

then higher cumulants are zero & this is exact!!

\* the second-order cumulant expansion approximation:

- ① effective a Gaussian fluctuation approx.
- ② better than direct 2<sup>nd</sup>-order ~~TDPT~~ TDPT.
- ③ valid for long times  $\rightarrow$ .

\* Quantum master equation:

Simple HSR model

Now we turn back to the evaluation of time-evolution of the density matrix.

Assume that  $H = \underbrace{H_S}_{\text{gen. bath.}} + \underbrace{H_B}_{\text{perturbation } V}$

Again, use the full Hamiltonian in the expansion is not effective, it it.



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necessary to adopt a interaction picture:

$$\rho(t) = U(t) \cdot \rho(s) U^\dagger(t)$$

$$= \underbrace{U_0(t) \cdot U_I(t) \cdot \rho(s) U_I^\dagger(t) U_0^\dagger(t)}_{\rho_I(t)}$$

$$= U_0(t) \cdot \rho_I(t) \cdot U_0^\dagger(t),$$

calculate  $\rho_I(t)$  using <sup>2nd order</sup> cumulant expansion:

$$\sigma_I(t) = \text{Tr}_B \rho_I(t) = \left\langle \exp \left[ \frac{-i}{\hbar} \int_0^t dt' L_I(t') \right] \right\rangle_B \cdot \sigma_0.$$

where  $L_I(t) \rho = V_I^\dagger(t) \cdot \rho = [V_I(t), \rho]$

$$V_I(t) = U_0^\dagger(t) \cdot H_{SI} \cdot U_0(t).$$

~~to get~~ <sup>Note that</sup> we assume the following about the system.

$$\textcircled{1} \rho(s) = \sigma_0 \otimes \rho_B^{\text{eq}}$$

$$\textcircled{2} \langle H_{SI} \rangle_B = 0$$

We then obtain:

$$\sigma_I(t) = \exp \left[ \left( \frac{-i}{\hbar} \right)^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \cdot \langle V_I^\dagger(t_2) V_I^\dagger(t_1) \rangle_B \right] \cdot \sigma_0$$

↑ superoperator in S.

such "exponential of superoperator" ~~would~~ would be very difficult to evaluate, we instead use a trick & write "the same equation" in ~~the~~ a differential form by taking derivatives on both sides.

$$\begin{aligned} \dot{\sigma}_I(t) &= \frac{d}{dt} \left[ e^{-\frac{1}{\hbar^2} K_2^X(t)} \cdot \sigma_0 \right] \\ &= -\frac{1}{\hbar^2} \cdot \frac{d}{dt} K_2^X(t) \cdot e^{-\frac{1}{\hbar^2} K_2^X(t)} \cdot \sigma_0 \\ &= -\frac{1}{\hbar^2} \int_0^t dt_1 \cdot \langle V_I^\dagger(t) V_I^\dagger(t_1) \rangle_B \cdot \sigma_I(t) \\ &= -\frac{1}{\hbar^2} \int_0^t dt_1 \cdot \text{Tr}_B \left\{ [V_I(t), [V_I(t_1), \sigma_I(t) \otimes \rho_B^{eq}]] \right\} \end{aligned}$$

back to the Schrodinger picture : ~~so~~.

system part only =  $e^{-\frac{i}{\hbar} H_S t}$ .

$$\sigma(t) = U_S(t) \cdot \sigma_I(t) \cdot U_S^\dagger(t)$$

$$\therefore \dot{\sigma}(t) = \left[ \frac{d}{dt} U_S(t) \right] \sigma_I(t) U_S^\dagger(t) + U_S(t) \sigma_I(t) \left[ \frac{d}{dt} U_S^\dagger(t) \right]$$

$$+ U_S(t) \cdot \dot{\sigma}_I(t) \cdot U_S^\dagger(t)$$

$$= -\frac{i}{\hbar} [H_S, \sigma(t)]$$

$U_S^\dagger(t) \cdot H_{SIB} \cdot U_S(t)$       $\sigma_I(t) = U_S^\dagger(t) \cdot \sigma(t) \cdot U_S(t)$

$$- \frac{i}{\hbar^2} \int_0^t dt' \cdot \text{Tr}_B \left\{ U_S(t') \cdot [V_I(t), [V_I(t'), U_S^\dagger(t') \cdot \sigma(t) \cdot U_S(t')] \cdot U_S(t) \right\}$$

driven by system-bath coupling

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$$= -\frac{i}{\hbar} [H_S, \sigma(t)] - \int_0^t dt' \cdot \text{Tr}_B \left\{ [H_{SIB}(t), [H_{SIB}(t-t), \sigma(t) \otimes \rho_B^{eq}]] \right\}$$

coherence

dissipative

This is a quantum master equation that governs the time evolution of a reduced-system density matrix.

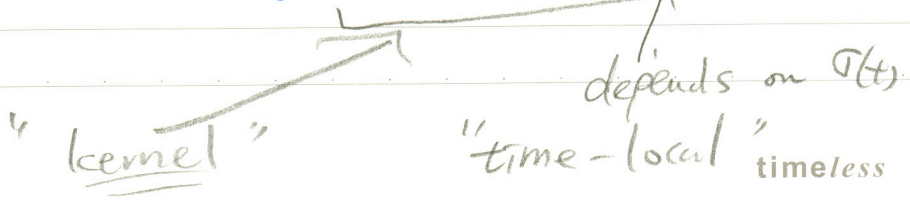
So far this is general for all possible system-bath couplings, It is instructive to assume a simple form of system bath coupling & inspect the form of the dissipative part:

The QME based on "small"  $H_{SB}$ , i.e. treat system-bath coupling  $H_{SB}$  as the perturbation.

$\Rightarrow V \equiv H_{SB}$

$\tau' = t - \tau$   
 $\downarrow d\tau' = -d\tau$

$$\begin{aligned} \dot{\sigma}(t) &= \frac{-i}{\hbar} [H_S, \sigma(t)] - \int_0^t d\tau \cdot \mathcal{T}_{\mathcal{B}} \left\{ [V, [V(\tau-t), \rho_b^{per} \otimes \sigma(t)]] \right\} \\ &= \frac{-i}{\hbar} [H_S, \sigma(t)] - \int_t^0 -d\tau' \mathcal{T}_{\mathcal{B}} \left\{ [V, [V(-\tau'), \sigma(t) \otimes \rho_b^{per}]] \right\} \\ &= \frac{-i}{\hbar} [H_S, \sigma(t)] - \int_0^t d\tau \cdot \mathcal{T}_{\mathcal{B}} \left\{ [V, [V(-\tau), \sigma(t) \otimes \rho_b^{per}]] \right\} \end{aligned}$$



to gain a better understanding of the QM, Let's ~~also~~ assume a simple model. (13)

$$H_{SB} = S \otimes B$$

↙ system operator
↖ bath operator,

$$\begin{aligned} \hookrightarrow H_{SB}(t) &= e^{\frac{i}{\hbar} H_S t} \cdot S \cdot e^{-\frac{i}{\hbar} H_S t} \otimes e^{\frac{i}{\hbar} H_B t} \cdot B \cdot e^{-\frac{i}{\hbar} H_B t} \\ &= S(t) \otimes B(t) \end{aligned}$$

The "kernel":

$$\text{Tr}_B \{ [V, [V(-\tau), \sigma(t) \otimes \rho_b^{eq}]] \}$$

$$= \text{Tr}_B \{ [S \cdot B, [S(-\tau) \cdot B(-\tau), \sigma(t) \otimes \rho_b^{eq}]] \}$$

trace over bath operators -  
invariant bath operators -

$$= \text{Tr}_B \{ \underbrace{S \cdot B \cdot S(-\tau) B(-\tau)} \cdot \sigma(t) \otimes \rho_b^{eq} - \underbrace{S B \cdot \sigma(t) \rho_b^{eq} \cdot S(-\tau) B(-\tau)} - \underbrace{S(-\tau) B(-\tau) \sigma(t) \cdot \rho_b^{eq} \cdot S \cdot B} + \underbrace{\sigma(t) \otimes \rho_b^{eq} \cdot S(-\tau) B(-\tau) \cdot S \cdot B} \}$$

$$= \langle B \cdot B(-\tau) \rangle_B \cdot S \cdot S(-\tau) \cdot \sigma(t) - \langle B(-\tau) B \rangle_B \cdot S \cdot \sigma(t) \cdot S(-\tau) - \langle B \cdot B(-\tau) \rangle_B \cdot S(-\tau) \cdot \sigma(t) \cdot S + \langle B(-\tau) B \rangle_B \cdot \sigma(t) \cdot S(-\tau) \cdot S$$

Collect bath part & system part

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Now all the bath influence to the quantum dynamics of the reduced-system density matrix is through the function

$\langle B(-\tau)B \rangle_B$  : time-correlation functions!!

In this formalism, only the time-correlations of both fluctuations affects the system's dynamics.

The TCFs actually represent the ~~time~~ statistical properties of the bath dynamics, and they play a central role in spectroscopy & statistical mechanics of non-equilibrium systems.

We will further explore the TCFs next week and continue the ~~discuss~~ discussion of their role in quantum relaxation theories.

When we learn about the Redfield theory  
 a little bit later, i.e. we will go  
 back to visit the QME as describe in  
 (p.13) when we discuss about Redfield theory.  
 (Yes, that is the Redfield relaxation tensor).

~~Next we~~

Let's summarize the main concepts introduced  
 in this lecture :

- \* system-bath model & reduced-system density matrix.
- \* cumulant expansion & Gaussian fluctuation model.
- \* quantum master equation.
- \* bath time-correlation functions — .

These will form the basis for all our  
 later discussions on condensed-phase quantum  
 dynamics & spectroscopy — .