Chap 7. Quantum Liouville Equation

1. Pure state : described by a wavefunction $|\psi(t)\rangle$

$$\text{Density operator : } \hat{\rho}(t) \equiv |\psi(t)\rangle\langle\psi(t)|$$

- Matrix representation :

  Expand by a basis set $\{|n\rangle\}$: $|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$

$$\Rightarrow \hat{\rho}(t) = \sum_n \sum_m \underbrace{c_n(t)c_m^*(t)}|n\rangle\langle m| \equiv \sum_n \sum_m |n\rangle \underbrace{\rho_{nm}(t)}_{\text{density matrix}}\langle m|$$

- Expectation value :

$$\langle \hat{A}(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle$$
$$= \sum_n \sum_m \rho_{nm}(t) A_{mn} = \mathrm{Tr}[\hat{\rho}(t)\hat{A}]$$

2. Mixed state : (statistical ensemble)

P_k = Probability of finding a system in state $|\psi_k(t)\rangle$

$$\hat{\rho}(t) \equiv \sum_k P_k |\psi_k(t)\rangle\langle\psi_k(t)|$$

$$\langle \hat{A}(t)\rangle = \sum_k P_k \langle\psi_k(t)|\hat{A}|\psi_k(t)\rangle = \mathrm{Tr}[\hat{\rho}(t)\hat{A}]$$

(same as the pure state case)

$$\rho_{nm}(t) = \langle n|\hat{\rho}(t)|m\rangle = \sum_k P_k \langle n|\psi_k(t)\rangle\langle\psi_k(t)|m\rangle$$

- Thermal equilibrium : (Boltzmann distribution)

$$P_k = e^{-\beta E_k}/Z \qquad \left[\begin{array}{l} \hat{H}|\psi_k\rangle = E_k|\psi_k\rangle \\ Z = \sum_k e^{-\beta E_k} = \mathrm{Tr}[e^{-\beta\hat{H}}] \end{array}\right]$$

$$\Rightarrow \hat{\rho}_{eq} = \sum_k \frac{e^{-\beta E_k}}{Z}|\psi_k\rangle\langle\psi_k| \quad \Leftrightarrow \quad \frac{e^{-\beta\hat{H}}}{Z} \text{ in basis } \{|\psi_k\rangle\}$$

• **<u>Time evolution</u>** : (Consider the pure state)

$$\frac{\partial}{\partial t}\hat{\rho}(t) = \frac{\partial}{\partial t}(|\psi(t)\rangle\langle\psi(t)|) = \left(\frac{\partial}{\partial t}|\psi(t)\rangle\right)\langle\psi(t)| + |\psi(t)\rangle\left(\frac{\partial}{\partial t}\langle\psi(t)|\right)$$

Time-dependent Schrodinger Eq. (& Hermite conjugate)

$$\frac{\partial}{\partial t}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\psi(t)\rangle \quad \& \quad \frac{\partial}{\partial t}\langle\psi(t)| = +\frac{i}{\hbar}\langle\psi(t)|\hat{H}$$

$\Rightarrow$ **Quantum Liouville Eq**

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}]$$

[Mixed state $\hat{\rho}(t)$ = linear combination of the pure state
$\Rightarrow$ extension of the above derivation involves only linear operations.
$\Rightarrow$ the same quantum Liouville Eq applies for the mixed state]

- **Example : 2-level system**

$$H = \begin{bmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{bmatrix} = \begin{bmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{bmatrix}, \qquad \rho(t) = \begin{bmatrix} \rho_{aa}(t) & \rho_{ab}(t) \\ \rho_{ba}(t) & \rho_{bb}(t) \end{bmatrix}$$

$$\frac{\partial}{\partial t}\rho(t) =$$

$$-\frac{i}{\hbar}\begin{bmatrix} V_{ab}\rho_{ba} - V_{ba}\rho_{ab} & (\varepsilon_a - \varepsilon_b)\rho_{ab} + V_{ab}(\rho_{bb} - \rho_{aa}) \\ (\varepsilon_b - \varepsilon_a)\rho_{ba} + V_{ba}(\rho_{aa} - \rho_{bb}) & V_{ba}\rho_{ab} - V_{ab}\rho_{ba} \end{bmatrix}$$

- Population (diagonal) $\Leftarrow$ Coherence (off-diagonal)
- Coherence $\Leftarrow$ (population difference) + $\Delta\varepsilon \times$ (self)

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Can be rewritten as :

$$\frac{\partial}{\partial t}\begin{bmatrix}\rho_{aa}\\ \rho_{bb}\\ \rho_{ab}\\ \rho_{ba}\end{bmatrix} = -\frac{i}{\hbar}\begin{bmatrix}0 & 0 & -V_{ba} & V_{ab}\\ 0 & 0 & V_{ba} & -V_{ab}\\ -V_{ab} & V_{ab} & \varepsilon_a-\varepsilon_b & 0\\ V_{ba} & -V_{ba} & 0 & \varepsilon_b-\varepsilon_a\end{bmatrix}\begin{bmatrix}\rho_{aa}\\ \rho_{bb}\\ \rho_{ab}\\ \rho_{ba}\end{bmatrix}$$

- **Liouville operator** (tetradic matrix, super-operator)

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

Matrix form of $\hat{\rho}$ $\Leftarrow$ $\hat{L}$ is specified by four indices

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{mn} &= -\tfrac{i}{\hbar}[(H\rho)_{mn} - (\rho H)_{mn}] = -\tfrac{i}{\hbar}\textstyle\sum_j (H_{mj}\rho_{jn} - \rho_{mj}H_{jn})\\ &\equiv -\tfrac{i}{\hbar}\textstyle\sum_{j,k} L_{mn,jk}\rho_{jk}\end{aligned}$$

$$L_{mn,jk} \equiv H_{mj}\delta_{nk} - \delta_{mj}H_{kn}$$

Reduced density operator

- System + Bath : $H = H_s(\mathbf{q}_s) + H_B(\mathbf{Q}_B) + V(\mathbf{q}_s, \mathbf{Q}_B)$
- Assume : $H_s|\psi_i\rangle = E_i|\psi_i\rangle$, $H_B|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$
- Abbreviate : $|\psi_i(\mathbf{q}_s)\rangle = |i\rangle$, $|\chi_a(\mathbf{Q}_a)\rangle = |a\rangle$
- Direct product $|ia\rangle = |i\rangle|a\rangle$ (Completeness $\sum_{i,a}|ia\rangle\langle ia| = 1$)

  Note : $|ia\rangle$ are not eigenfunctions of H because of V

  (though can be used for Tr calcs)

Expectation value :

$$\begin{aligned}\langle\hat{A}(\mathbf{q}_s, \mathbf{Q}_B)\rangle &= \mathrm{Tr}[\hat{\rho}(t)\hat{A}(\mathbf{q}_s, \mathbf{Q}_B)] \\ &= \sum_{i,a}\langle ia|\hat{\rho}(t)\hat{A}|ia\rangle = \sum_{i,a}\sum_{j,b}\langle ia|\hat{\rho}(t)|jb\rangle\langle jb|\hat{A}|ia\rangle\end{aligned}$$

If looking at a "system" quantity (depends only on $\mathbf{q}_s$)

$$\langle jb|\hat{A}(\mathbf{q}_s)|ia\rangle = \langle j|\hat{A}(\mathbf{q}_s)|i\rangle\langle b|a\rangle = \delta_{ab}\langle j|\hat{A}(\mathbf{q}_s)|i\rangle$$

$$\Rightarrow \langle \hat{A}(\mathbf{q}_s)\rangle = \sum_{i,j} \underbrace{\sum_a \langle ia|\hat{\rho}(t)|ja\rangle}\langle j|\hat{A}(\mathbf{q}_s)|i\rangle$$

<u>Reduced</u> density operator : $\hat{\sigma}(t) \equiv \underbrace{\mathrm{Tr_B}}\,\hat{\rho}(t) = \sum_a \langle a|\hat{\rho}(t)|a\rangle$

$$\sigma_{ij}(t) = \langle i|\mathrm{Tr_B}\hat{\rho}(t)|j\rangle = \sum_a \langle ia|\hat{\rho}(t)|ja\rangle$$

$$\Rightarrow \langle \hat{A}(\mathbf{q}_s)\rangle = \sum_{i,j} \sigma_{ij}(t)\hat{A}(\mathbf{q}_s)_{ji} = \mathrm{Tr_s}[\hat{\sigma}(t)\hat{A}(\mathbf{q}_s)]$$

Note : $\mathrm{Tr_B}$ possesses the properties of <u>projection</u> (Chap 5, p 9)

$\Rightarrow$ Projection partition method on the Liouville eq of $\hat{\rho}(t)$

$\Rightarrow$ <u>Reduced eq of motion</u> for $\hat{\sigma}(t)$