P4. Quantum Statistical Physics: Density Operator

- Quantum statistical physics combines quantum probability (for a quantum state, the probability for measuring a particular value for a physical quantity depends on the projection of the quantum state to the eigenstate of that quantity with that particular eigenvalue) with statistical probability: we do not know in which quantum state the system is; we have just a probability distribution. This probability distribution is represented by a (probability) density operator.

- Given some orthonormal basis $\{|i\rangle\}$ of the Hilbert space (the set of quantum states) of the system, we can expand an arbitrary quantum state as

$$|\psi\rangle = \sum c_i |i\rangle \quad , \quad \text{where} \quad c_i = \langle i|\psi\rangle$$

and an arbitrary density operator as

The matrix $\rho = [\rho_{ij}]$ is called the density matrix.

$$\hat{\rho} = \sum \rho_{ij} |i\rangle\langle j| \, , \quad \text{where} \quad \rho_{ij} = \langle i|\hat{\rho}|j\rangle$$

where c_i, ρ_{ij} are complex numbers. Since $\{|i\rangle\}$ is a complete orthonormal basis,

$$\langle i|j\rangle = \delta_{ij} \quad \text{and} \quad \sum_i |i\rangle\langle i| = \hat{1} \quad \text{(the identity operator).}$$

- An acceptable density operator satisfies three conditions:

1) $\hat{\rho} = \hat{\rho}^+$ (Hermitian) $\Rightarrow$ all eigenvalues p_α are real
2) $\langle\psi|\hat{\rho}|\psi\rangle \geq 0 \quad \forall |\psi\rangle$ (positive semi-definite) $\Rightarrow$ all $p_\alpha \geq 0$
3) $\mathrm{Tr}\,\hat{\rho} \equiv \sum_i \langle i|\hat{\rho}|i\rangle = \sum_\alpha p_\alpha = 1$

- Since $\hat{\rho}$ is Hermitian, $\exists$ complete set of orthogonal eigenstates $\{|\alpha\rangle\}$, where $\hat{\rho}$ is diagonal;

$$\hat{\rho} = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha| \qquad \text{Conditions 1-3} \Rightarrow 0 \leq p_\alpha \leq 1$$

- Interpretation: p_α is the probability that the system is in state $|\alpha\rangle$

$$\hat{\rho}|\alpha\rangle = \sum_\beta p_\beta |\beta\rangle \underbrace{\langle\beta|\alpha\rangle}_{\delta_{\beta\alpha}} = p_\alpha |\alpha\rangle$$

Pure State

- If we have perfect knowledge that the system is in a particular quantum state $|\psi\rangle$, i.e., $p_\psi = 1$, then

$$\hat{\rho} = |\psi\rangle\langle\psi| = \sum_{ij} c_i c_j^* |i\rangle\langle j| \qquad (4)$$

and we say that the system is in a <u>pure state</u> (although actually this is a statement about our knowledge of the system). For a pure state,

$$\hat{\rho}^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = \hat{\rho}$$

and $$\mathrm{Tr}\,\hat{\rho}^2 = \sum p_\alpha^2 = p_\psi^2 = 1 \qquad (5)$$

- For a non-pure state (i.e., imperfect knowledge about the quantum state of the system),

$$\mathrm{Tr}\,\hat{\rho}^2 = \sum p_\alpha^2 < 1 \qquad (6)$$

A non-pure state is called a <u>mixed state</u>.

Expectation Values

- The expectation value (combining quantum and statistical probability) of a physical quantity, whose operator is $\hat{O}$, is given by

$$\underline{\langle\hat{O}\rangle = \mathrm{Tr}\,\hat{\rho}\hat{O} = \mathrm{Tr}\,\hat{O}\hat{\rho}} = \sum_i \langle i|\hat{O}\hat{\rho}|i\rangle = \sum_{ij} \langle i|\hat{O}|j\rangle\langle j|\hat{\rho}|i\rangle = \sum_{ij} O_{ij}\rho_{ji} \qquad (7)$$

where O_{ij} are the matrix elements of $\hat{O}$ in the basis $\{|i\rangle\}$. In the $\hat{\rho}$ eigenbasis $\{|\alpha\rangle\}$,

$$\underline{\langle\hat{O}\rangle} = \sum_{\alpha\beta} \langle\alpha|\hat{O}|\beta\rangle\underbrace{\langle\beta|\hat{\rho}|\alpha\rangle}_{p_\alpha\delta_{\beta\alpha}} = \underline{\sum_\alpha p_\alpha \langle\alpha|\hat{O}|\alpha\rangle} \qquad (8)$$

and in the $\hat{O}$ eigenbasis $\{|a\rangle\}$, where O_a are the $\hat{O}$ eigenvalues

$$\underline{\langle\hat{O}\rangle} = \sum_{ab} \underbrace{\langle a|\hat{O}|b\rangle}_{O_b\delta_{ab}}\langle b|\hat{\rho}|a\rangle = \underline{\sum_a O_a \rho_{aa}} \qquad (9)$$

- <u>For a pure state</u>, $\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle = \sum c_i^* \langle i|\hat{O}|j\rangle c_j = \sum_{ij} c_i^* c_j O_{ij}$

or, from density matrix (4), $\langle\hat{O}\rangle = \mathrm{Tr}\,\hat{\rho}\hat{O} = \sum_{ikj} \underbrace{\langle i|c_k c_j^*|k\rangle}_{c_k c_j^* \delta_{ik}} \langle j|O|i\rangle = \sum_{ij} c_i c_j^* O_{ji} = \sum_{ij} c_i^* c_j O_{ij}$

Or, $\mathrm{Tr}\,\hat{\rho}\hat{O} = \sum_i \underbrace{\langle i|\psi\rangle}_{c_i}\langle\psi|\hat{O}|i\rangle = \langle\psi|\hat{O}|\psi\rangle$

Summary

	Quantum state	Density operator
expansion	$\vert\psi\rangle = \sum c_i \vert i\rangle$	$\hat{\rho} = \sum \rho_{ij} \vert i\rangle\langle j\vert$
coefficient	$c_i = \langle i\vert\psi\rangle$	$\rho_{ij} = \langle i\vert\hat{\rho}\vert j\rangle$
normalization	$\langle\psi\vert\psi\rangle = \sum \vert c_i\vert^2 = 1$	$\mathrm{Tr}\,\hat{\rho} = \sum_i \rho_{ii} = \sum_\alpha p_\alpha = 1$
operator expectation value	$\langle\hat{O}\rangle = \langle\psi\vert\hat{O}\vert\psi\rangle$	$\langle\hat{O}\rangle = \mathrm{Tr}\,\hat{O}\hat{\rho} = \sum_i \langle i\vert\hat{O}\hat{\rho}\vert i\rangle$