Phys. 528 Lecture 10

Quantum Statistics

In quantum stat. mech., the mean value of an observable is a double average, both quantum and statistical.

Suppose we have an ensemble of $\mathcal{N}$ quantum systems, with quantum states

$$|\psi^k(t)\rangle, \quad k = 1, 2, \ldots, \mathcal{N}.$$

Then

$$\langle \hat{Q}(t) \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \langle \psi^k(t) | \hat{Q} | \psi^k(t) \rangle$$

$$= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \langle \hat{Q} \rangle|_k$$

To describe both the quantum and statistical state of a system, we introduce the <u>density matrix</u>

$$\hat{\rho}(t) = \frac{1}{N} \sum_{k=1}^{N} |\psi^k(t)\rangle\langle\psi^k(t)|$$

1) <u>Properties of the density matrix:</u>

i) $\hat{\rho}^{+} = \hat{\rho}$

ii) $Tr\{\hat{\rho}\} = 1$

Proof: $$Tr\{\hat{\rho}\} = \frac{1}{N} \sum_{k=1}^{N} \sum_{n} \langle n|\psi^k\rangle\langle\psi^k|n\rangle$$

$$= \frac{1}{N} \sum_{k=1}^{N} \langle\psi^k|\psi^k\rangle = 1$$ ✓

iii) $P(u) = \langle u|\hat{\rho}|u\rangle$

Proof:
$$\langle u|\hat{\rho}|u\rangle = \frac{1}{N} \sum_{k=1}^{N} \langle u|\psi^k\rangle\langle\psi^k|u\rangle$$

$$= \frac{1}{N} \sum_{k=1}^{N} |\langle u|\psi^k\rangle|^2 = \frac{1}{N} \sum_{k=1}^{N} P_k(u)$$

iv) $\langle \hat{Q}(t) \rangle = \mathrm{Tr}\{ \hat{\rho}(t)\, \hat{Q} \}$

Proof: $\mathrm{Tr}\{ \hat{\rho}(t)\, \hat{Q} \} = \dfrac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_{n} \langle n | \psi^k(t) \rangle \langle \psi^k(t) | \hat{Q} | n \rangle$

$$= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_{n} \langle \psi^k(t) | \hat{Q} | n \rangle \langle n | \psi^k(t) \rangle$$

$$= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \langle \psi^k(t) | \hat{Q} | \psi^k(t) \rangle \qquad \checkmark$$

v) $i\hbar \dfrac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] \equiv \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$

Proof: $i\hbar \dfrac{d\hat{\rho}}{dt} = \dfrac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \Big\{ \Big(i\hbar \dfrac{d}{dt} | \psi^k(t) \rangle \Big) \langle \psi^k(t) |$

$$+ | \psi^k(t) \rangle\, i\hbar \frac{d}{dt} \langle \psi^k(t) | \Big\}$$

$$i\hbar \frac{d}{dt} | \psi^k(t) \rangle = \hat{H} | \psi^k(t) \rangle$$

$$-i\hbar \frac{d}{dt} \langle \psi^k(t) | = \langle \psi^k(t) | \hat{H}$$

$$i\hbar \frac{d\hat{\rho}}{dt} = \frac{1}{N} \sum_{k=1}^{N} \{ \hat{H} |\psi^k(t)\rangle\langle\psi^k(t)| - |\psi^k(t)\rangle\langle\psi^k(t)| \hat{H} \}$$

$$= \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = [\hat{H}, \hat{\rho}]$$ ✓

Note: this eq has the opposite sign of the usual Heisenberg eq. of motion for an operator!

2) Alternative expression

We can also write $\hat{\rho}$ as

$$\hat{\rho} = \sum_j P_j |\psi_j\rangle\langle\psi_j| ,$$

where the states $|\psi_j\rangle, |\psi_{j'}\rangle$ need not be orthogonal.

$$Tr\{\hat{\rho}\} = \sum_j P_j \sum_n \langle n|\psi_j\rangle\langle\psi_j|n\rangle = \sum_j P_j \sum_n \langle\psi_j|n\rangle\langle n|\psi_j\rangle$$

$$= \sum_j P_j \langle\psi_j|\psi_j\rangle = \sum_j P_j = 1$$ ✓

Eigenbasis Because $\hat{\rho}^{+} = \hat{\rho}$,

$\exists$ an orthonormal basis in which

$\hat{\rho}$ is diagonal

$$\hat{\rho} = \sum_i w_i |i\rangle\langle i| , \qquad \langle i|j\rangle = \delta_{ij}$$

3) Pure and mixed states

A pure state $|\psi\rangle$ has

$$\hat{\rho} = |\psi\rangle\langle\psi| .$$

$\langle \hat{Q} \rangle = \mathrm{Tr}\{\hat{\rho}\hat{Q}\} = \langle\psi|\hat{Q}|\psi\rangle$;

no statistical averaging. For a pure state,

$$\hat{\rho}^2 = \hat{\rho} .$$

Proof: $\hat{\rho}^2 = |\psi\rangle\underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi| = |\psi\rangle\langle\psi|$ ✓

As an example of a <u>mixed state</u>, consider

$$\hat{\rho} = P_1 |\psi_1\rangle\langle\psi_1| + P_2 |\psi_2\rangle\langle\psi_2|$$

$$\langle \hat{Q} \rangle = \mathrm{Tr}\{\hat{\rho}\hat{Q}\} = P_1 \langle\psi_1|\hat{Q}|\psi_1\rangle + P_2 \langle\psi_2|\hat{Q}|\psi_2\rangle$$

This is different than a <u>superposition of states</u>

$$|\psi\rangle = \sqrt{P_1}\, e^{i\theta_1} |\psi_1\rangle + \sqrt{P_2}\, e^{i\theta_2} |\psi_2\rangle$$

$$\begin{aligned}
\langle \hat{Q} \rangle = \langle\psi|\hat{Q}|\psi\rangle &= P_1 \langle\psi_1|\hat{Q}|\psi_1\rangle + P_2 \langle\psi_2|\hat{Q}|\psi_2\rangle \\
&+ \sqrt{P_1P_2}\, e^{i(\theta_1-\theta_2)} \langle\psi_2|\hat{Q}|\psi_1\rangle \\
&+ \sqrt{P_1P_2}\, e^{i(\theta_2-\theta_1)} \langle\psi_1|\hat{Q}|\psi_2\rangle
\end{aligned}$$

$$\begin{aligned}
\hat{\rho}' = |\psi\rangle\langle\psi| &= P_1 |\psi_1\rangle\langle\psi_1| + P_2 |\psi_2\rangle\langle\psi_2| \\
&+ \sqrt{P_1P_2}\, e^{i(\theta_1-\theta_2)} |\psi_1\rangle\langle\psi_2| \\
&+ \sqrt{P_1P_2}\, e^{i(\theta_2-\theta_1)} |\psi_2\rangle\langle\psi_1|
\end{aligned}$$

Matrix representation

$$\rho_{nm} = \langle n | \hat{\rho} | m \rangle$$

For the example $\hat{\rho} = P_1 |\psi_1\rangle\langle\psi_1| + P_2 |\psi_2\rangle\langle\psi_2|$,

$$\hat{\rho} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \begin{pmatrix} P_1 & 0 \\ 0 & P_2 \end{pmatrix}$$

For the example $\hat{\rho}' = |\psi\rangle\langle\psi|$,

$$\hat{\rho}' = \begin{pmatrix} P_1 & \sqrt{P_1 P_2}\, e^{i(\theta_1 - \theta_2)} \\ \sqrt{P_1 P_2}\, e^{i(\theta_2 - \theta_1)} & P_2 \end{pmatrix}$$

4) Entropy

In the eigenbasis,

$$S = -k_B \sum_{\mu} P(\mu) \ln P(\mu)$$

$$= -k_B \langle \ln P(\mu) \rangle$$

$$S = -k_B \operatorname{Tr}\{ \hat{\rho} \ln \hat{\rho} \}$$

For a pure state,

$$S = 0.$$