Lecture 18

Start quantum statistics proper (Ch 5)

Today, set up basic theory

Start: how to describe a quantum system?

Hamiltonian operator $\hat{H}$

Suppose ensemble of $\mathcal{N}$ systems

$\psi^k =$ wave function for system k

$k = 1$ to $\mathcal{N}$

Write $\psi^k = \psi^k(t, \tau)$

$t =$ time

$\tau = \{q_1 \ldots q_N\}$ coordinates

Schrodinger says:

$$H \psi^k = i\hbar \frac{d}{dt} \psi^k$$

Often convenient to express ψ in basis $\{\phi_n\}$:

$$\psi^k = \sum_n a_n^k \phi_n$$

Take $\phi_n = \phi_n(\tau)$ no time dependence

Get coefficient $a_n^k = \langle \phi_n | \psi^k \rangle = \int \phi_n^* \psi^k \, d\tau$

Require $\int |\psi^k|^2 d\tau = 1$

$$\Rightarrow \sum_n |a_n^k|^2 = 1$$

Interpret $|a_n^k|^2$ as probability that system k is in state ϕ_n

Can express Schr. Eqn as matrix relation:

$$i\hbar \dot{a}_n^k = i\hbar \int \phi_n^* \dot{\psi}^k(t)\, d\tau$$

$$= \int \phi_n^* \hat{H} \psi^k \, d\tau$$

$$= \int \phi_n^* \hat{H} \sum_m a_m^k \phi_m \, d\tau$$

$$\equiv \sum_m H_{nm} a_m^k$$

for $H_{nm} = \int \phi_n^* \hat{H} \phi_m \, d\tau$

$= \langle \phi_n | \hat{H} | \phi_m \rangle$

Now introduce key concept: density operator (= density matrix)

$$\rho_{mn}(t) \equiv \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k(t)\, a_n^k(t)^*$$

= ensemble average of $a_m a_n^*$

Then $\rho_{nn} = \langle |a_n|^2 \rangle$ = ensemble avg of quantum prob to be in state n

= overall prob to be in state n

Clearly $\sum_n \rho_{nn} = 1$

ρ_{mn} for $m \neq n$ = $\langle a_m a_n^* \rangle$ = "coherence"

Gives relationship between amplitudes to be in ϕ_m & ϕ_n

Say a bit more later

Clearly $\rho_{nm} = \rho_{mn}^*$; $\hat{\rho}$ is Hermitian operator

Now, suppose we are interested in quantity G described by Hermitian operator $\hat{G}$

Have $\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \int (\psi^k)^* \hat{G} \psi^k \, d\tau$

Combination of ensemble & quantum average

Can express in terms of density matrix:

Use $\psi^k = \sum_m a_m^k \phi_m$

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_k \sum_{m,n} a_n^{k*} a_m^k \underbrace{\int \phi_n^* \hat{G} \phi_m \, d\tau}_{\equiv G_{nm} = \langle \phi_n | \hat{G} | \phi_m \rangle}$$

$$= \sum_{m,n} G_{nm} \underbrace{\frac{1}{\mathcal{N}} \sum_k a_n^{k*} a_m^k}_{\rho_{mn}}$$

$$= \sum_{n,m} \rho_{mn} G_{nm}$$

$$= \sum_m [\hat{\rho}\hat{G}]_{mm} = \boxed{\mathrm{Tr}\, \hat{\rho}\hat{G}}$$

Tr = trace = sum of diagonal elements

So normalization $\sum_n \rho_{nn} = 1 = \text{Tr}\,\hat{\rho}$

If $\hat{\rho}$ not normalized, then

$$\langle G \rangle = \frac{\text{Tr}\,\hat{\rho}\hat{G}}{\text{Tr}\,\hat{\rho}}$$

Finally, consider time evolution of $\hat{\rho}$:

$$i\hbar \dot{\rho}_{mn} = \frac{1}{\mathcal{N}} \sum_k i\hbar \left[\dot{a}_m^k a_n^{k*} + a_m^k \dot{a}_n^{k*} \right]$$

$$= \frac{1}{\mathcal{N}} \sum_k \left\{ \left[\sum_l H_{ml} a_l^k \right] a_n^{k*} - a_m^k \left[\sum_l \underbrace{H_{nl}^*}_{= H_{ln}} a_l^{k*} \right] \right\}$$

$$= \sum_l H_{ml} \rho_{ln} - \sum_l \rho_{ml} H_{ln}$$

$$= (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn}$$

$$= [\hat{H}, \hat{\rho}]_{mn}$$

↳ comutator

So $\boxed{\dot{\hat{\rho}} = \frac{i}{\hbar}[\hat{\rho}, \hat{H}]}$

Compare classical

Phase space density

$$\dot{\rho} = [\rho, H] + \frac{\partial \rho}{\partial t}$$

↳ Poisson Bracket

See similarity

Argue that ρ = phase space density

and $\hat{\rho}$ = density operator

are analogous:

$\rho\{p,q\}$ ~ prob that system in state $\{p,q\}$

ρ_{nn} = prob that system in state n

Previously demanded that classical $\rho(t)$ is stationary

$\Rightarrow$ equilibrium state

Make same claim here:

In equilibrium, all averages $\langle G \rangle = \mathrm{Tr}\, \hat{\rho}\hat{G}$

should be independent of time

(if G indep time)

Requires $\hat{\rho}$ indep time

$$\Rightarrow \quad [\hat{\rho}, \hat{H}] = 0$$

But if $\hat{\rho}$ + $\hat{H}$ commute, then if we take

$\{\phi_n\}$ to be energy eigenstates

$$\hat{H}\phi_n = E_n \phi_n$$

Then $\{\phi_n\}$ will also be eigenstates of $\hat{\rho}$:

$$\hat{\rho}\phi_n = \rho_n \phi_n$$

or

$$\rho_{mn} = \langle \phi_m | \hat{\rho} | \phi_n \rangle = \rho_n \delta_{mn}$$

Choice of ρ_n depends on ensemble.

Simplest case:

All systems in ensemble have same state $\psi^k = \phi_l$ for some l

Then $\rho_n = \begin{cases} 1 & \text{if } n = l \\ 0 & \text{else} \end{cases}$

Say that system is in <u>pure state</u> ϕ_l

Don't really need stat mech to describe

More generally, system in many possible states ψ^l

Note that
$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_k a_m^k a_n^{k*}$$
$$= \frac{1}{\mathcal{N}} \sum_k \langle \phi_m | \psi^k \rangle \langle \psi^k | \phi_n \rangle$$

But in general $\rho_{mn} = \langle \phi_m | \hat{\rho} | \phi_n \rangle$

So
$$\hat{\rho} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} |\psi^k\rangle\langle\psi^k|$$

Suppose n_l systems in state ψ^l

Then have
$$\hat{\rho} = \sum_l \frac{n_l}{\mathcal{N}} |\psi^l\rangle\langle\psi^l|$$
$$\boxed{\hat{\rho} = \sum_l P_l |\psi^l\rangle\langle\psi^l|}$$

where P_l = prob to find system in state l

Pure state corresponds to $P_\ell = 1$ for some ℓ

Otherwise, have mixed state

Combination of quantum and classical uncertainty

QM: can't predict definite values for observables in a given quantum state

Classical: don't know for sure what quantum state is

Note that for stationary ensemble, must have

$$\hat{\rho} = \sum_n P_n |\phi_n\rangle\langle\phi_n|$$

for energy eigenstates ϕ_n

Ensembles:

Microcanonical:

$$P_n = \frac{1}{\Gamma} \quad \text{if} \quad E - \frac{\Delta}{2} \le E_n \le E + \frac{\Delta}{2}$$

$$= 0 \quad \text{else}$$

where Γ = # of states accessible

Once Γ determined, have $S = k_B \ln \Gamma$

Canonical:

$$P_n = C e^{-\beta E_n}$$

Get C from normalization

$$\mathrm{Tr}\,\hat{\rho} = \sum P_n = 1 \Rightarrow C = \frac{1}{\sum_n e^{-\beta E_n}} = \frac{1}{Q_N}$$

Then have

$$\hat{\rho} = \sum_n \frac{e^{-\beta E_n}}{Q_N} |\phi_n\rangle\langle\phi_n|$$

$$= \sum_n \frac{e^{-\beta \hat{H}}}{Q_N} |\phi_n\rangle\langle\phi_n|$$

$$= \frac{e^{-\beta \hat{H}}}{Q_N} \underbrace{\sum_n |\phi_n\rangle\langle\phi_n|}_{\text{Identity operator}}$$

So

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Q_N} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}}$$

To calculate expectation values, use

$$\langle G \rangle = \mathrm{Tr}\, \hat{\rho}\, \hat{G}$$

$$= \frac{\mathrm{Tr}\, \hat{G} e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

Compare classical

$$\langle G \rangle = \frac{\int G(p,q)\, e^{-\beta H}\, d\omega}{\int e^{-\beta H}\, d\omega}$$

See that trace over states is analogous to integral over phase space

Grand canonical ensemble:

Now number of particles varies

Introduce number operator $\hat{n}$

$$\hat{n}\,\psi^k = N_k\,\psi^k$$

for N_k = # of particles in system k

Then take

$$\hat{\rho} \propto e^{-\beta\hat{H} - \alpha\hat{n}}$$

$$= \frac{1}{\mathcal{Q}}\, e^{-\beta(\hat{H} - \mu\hat{n})}$$

for $$\mathcal{Q}(\mu, V, T) = \sum_{N,r} e^{-\beta(E_r - \mu N)}$$

$$= \mathrm{Tr}\, e^{-\beta(\hat{H} - \mu\hat{n})}$$

So ensemble average

$$\langle G \rangle = \frac{1}{\mathcal{Q}}\,\mathrm{Tr}\,\hat{G}\,e^{-\beta\hat{H}}\,e^{\beta\mu\hat{n}}$$

(assuming $[\hat{H}, \hat{n}] = 0$)

$$= \frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} e^{\beta\mu N}\,\mathrm{Tr}\,\hat{G}\,e^{-\beta\hat{H}}$$

$$= \frac{1}{\mathcal{Q}} \sum_{N} z^N \left[\langle G \rangle_N\, Q_N \right]$$

$$\hookrightarrow \langle G \rangle_N = \frac{\mathrm{Tr}\,\hat{G}\,e^{-\beta\hat{H}}}{Q_N}$$

= canonical average

Use $\mathcal{Q} = \sum_N z^N Q_N$:

$$\boxed{\langle G \rangle = \frac{\sum_N z^N \langle G \rangle_N Q_N}{\sum_N z^N Q_N}}$$

Next time, show a few examples!