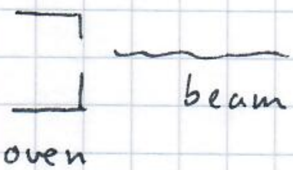
Density Matrix

See Sec. 3.4: Density operators and pure versus mixed ensembles

Situation 1: Consider spin-$\frac{1}{2}$ particle:



Let's say: Each particle is prepared in a superposition of spin-up and spin-~~superposition~~ down:

we have a fixed phase relation (coherent superposition)

$$|\Psi\rangle = c_+ |+\rangle + c_- |-\rangle$$

spin-up

spin-down

state ket of one particle: we have multiple particles and they are all described by the state ket $|\Psi\rangle$

Let spin point in direction $\hat{n}$.

Angle with z-axis described by (θ, ϕ).

$$\Rightarrow \quad \frac{c_+}{c_-} = \frac{\cos(\theta/2)}{e^{i\phi}\sin(\theta/2)}$$

Of course: $|c_+|^2 + |c_-|^2 = 1$ with
$|c_+|^2 = \cos^2(\frac{\theta}{2})$ and $|c_-|^2 = \sin^2(\frac{\theta}{2})$.

The description we have developed so far cannot describe a collection of atoms or electrons with random spin orientation.

Situation 2: Particles coming out of a hot oven with random spin orientation, i.e., no preferred direction.

We expect: 50% of the members of the ensemble are characterized by $|+\rangle$ and the remaining 50% by $|-\rangle$.

$$\left.\begin{array}{l} p_+ = 0.5 \\ \underbrace{p_-}_{\text{populations} \,\hat{=}\, \text{real numbers}} = 0.5 \end{array}\right\} \text{fractional populations for spin-up and spin-down, respectively.}$$

$\rightsquigarrow p_+ \neq |c_+|^2$ and $p_- \neq |c_-|^2$

(p_+ and p_- are more closely related to classical probability theory)

The discussion on the previous two pages shows that we are in need for a formalism that can treat ensembles.

$\hookrightarrow$ density matrices / operators

Density matrices

We will start with pure state.

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

looking ahead: here, just one state and $p=1$ (will be different for mixed state)

some state

Let $|\psi\rangle = \sum_n c_n |\varphi_n\rangle$

complete set of states

$$\Rightarrow \hat{\rho} = \sum_n \sum_m c_n c_m^* |\varphi_n\rangle\langle\varphi_m|$$

The matrix elements of $\hat{\rho}$ in the $\{|\varphi_n\rangle\}$ basis are:

$$\rho_{k\ell} = \langle\varphi_k|\hat{\rho}|\varphi_\ell\rangle$$

$$= \underbrace{\langle\varphi_k| \sum_n \sum_m c_n c_m^* |\varphi_n\rangle}_{\delta_{kn}} \underbrace{\langle\varphi_m|\varphi_\ell\rangle}_{\delta_{\ell m}}$$

$$= c_k c_\ell^*$$

A few properties that can be verified readily:

(i) $\hat{\rho}^2 = \hat{\rho}$

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

(iii) $\langle\hat{A}\rangle = Tr(\hat{A}\hat{\rho})$

expectation value

Let's look at each of these three properties:

(i) $\hat{\rho}^2 = |\psi\rangle\langle\underbrace{\psi|\psi}_{=1}\rangle\langle\psi| = |\psi\rangle\langle\psi| = \hat{\rho}$.

plugging in def. of $\hat{\rho}$, using $\hat{\rho}^2 = \hat{\rho}\hat{\rho}$.

(ii) $\mathrm{Tr}\,\hat{\rho} = \sum_k \rho_{kk} = \sum_k c_k c_k^* = \sum_k |c_k|^2 = 1$

evaluate in some basis

use result from above

(iii) $\langle \hat{A} \rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_m \sum_n c_m^* c_n \langle \varphi_m|\hat{A}|\varphi_n\rangle$

def. of $\langle\hat{A}\rangle$

expand ψ in basis

$$= \sum_m \sum_n \rho_{nm} A_{mn} = \sum_n \left(\sum_m \rho_{nm} A_{mn} \right)$$

use earlier result

rewrite in way 1

$$= \sum_m \left(\sum_n A_{mn} \rho_{nm} \right)$$

rewrite in way 2

$$= \mathrm{Tr}(\hat{\rho}\hat{A}) = \mathrm{Tr}(\hat{A}\hat{\rho})$$

Importantly: Properties (i), (ii), (iii) are independent of the basis chosen!

Also: $\hat{\rho}^{+} = \hat{\rho}$.

Eigenvalues of $\hat{\rho}$ are 1 and 0. ← all others

:

appears once

We will now look at mixed state.

For a mixed state, we define:

$$\hat{\rho} = \sum_i |\Psi_i\rangle \, p_i \, \langle\Psi_i|$$

$|\Psi_i\rangle$ are energy eigenstates of Hamiltonian $\hat{H}$

$\sum_i p_i = 1$

As before: Ψ_i can be expanded in terms of complete set of states:

$$|\Psi_i\rangle = \sum_n c_n^{(i)} \, |\varphi_n\rangle$$

the expansion coefficients for each of the energy eigenstates are distinct

$$\Rightarrow \quad \hat{\rho} = \sum_i \sum_n \sum_m c_n^{(i)} \left(c_m^{(i)}\right)^* p_i \, |\varphi_n\rangle\langle\varphi_m|$$

As in the pure case, we can evaluate $\hat{\rho}$ in any given basis. In the $\{|\varphi_n\rangle\}$ basis:

$$\rho_{kl} = \langle\varphi_k|\hat{\rho}|\varphi_l\rangle = \sum_i p_i \, c_k^{(i)} \left(c_l^{(i)}\right)^*$$

We can read off: $\rho_{kl} = \rho_{lk}^* \Rightarrow \hat{\rho}$ hermitian.

Since $\sum_n |c_n^{(i)}|^2 = 1$, we find:

$$\mathrm{Tr}(\hat{\rho}) = \sum_k \rho_{kk} = \sum_i p_i \underbrace{\sum_k |c_k^{(i)}|^2}_{1}$$

$$= \sum p_i$$

$$\Rightarrow \boxed{\mathrm{Tr}(\hat{\rho}) = 1}$$

(the same as in pure state case!)

Let's rewrite $\langle A \rangle$:

$$\langle \hat{A} \rangle = \sum_i p_i \langle \Psi_i | \hat{A} | \Psi_i \rangle$$

inserting two identities

$$= \sum_i \sum_{nm} p_i \underbrace{\langle \Psi_i | \varphi_n \rangle}_{(c_n^{(i)})^* \delta_{ni}} \underbrace{\langle \varphi_n | \hat{A} | \varphi_m \rangle}_{A_{nm}} \underbrace{\langle \varphi_m | \Psi_i \rangle}_{(c_m^{(i)}) \delta_{mi}}$$

rewriting $\rightarrow$ $= \sum_i \sum_{nm} p_i c_m^{(i)} (c_n^{(i)})^* A_{nm}$

reordering $\rightarrow$ $= \sum_{nm} \underbrace{\sum_i p_i c_m^{(i)} (c_n^{(i)})^*}_{\rho_{mn}} A_{nm}$

$$\Rightarrow \boxed{\langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho} \hat{A})}$$

(again, the same as in pure state case!)

However: $\hat{\rho}^2 \neq \hat{\rho}$ for mixed case!

Why? Work it out:

$$\hat{\rho}^2 = \sum_j \sum_i |\Psi^{(i)}\rangle p_i \underbrace{\langle \Psi^{(i)} | \Psi^{(j)}\rangle}_{\delta_{ij}} p_j \langle \Psi^{(j)}|$$

→ note: I'm making an assumption here. In general, the $\{|\Psi_j\rangle\}$ do not have to form orthonormal set.

$$= \sum_i |\Psi^{(i)}\rangle p_i^2 \langle\Psi^{(i)}|$$

Since $\sum_i p_i = 1$: $Tr(\hat{\rho}^2) = \sum_i p_i^2 < 1$ for a mixed state.

For "normal" operator: $\frac{d\hat{A}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{A}]$.

What about $\hat{\rho}$?

Let's work it out: $\frac{d}{dt}|\Psi^{(i)}\rangle = -\frac{i}{\hbar}\hat{H}|\Psi^{(i)}\rangle$

$$\Rightarrow \frac{d}{dt}\langle\Psi^{(i)}| = \frac{i}{\hbar}\langle\Psi^{(i)}|\hat{H}$$

using that $\hat{H}^+ = \hat{H}$

$$\Rightarrow \underbrace{\frac{d}{dt}\hat{\rho}}_{\text{def.}} = -\frac{i}{\hbar}\hat{H}\hat{\rho} + \frac{i}{\hbar}\hat{\rho}H$$

$$= \frac{d}{dt}\left(|\Psi^{(i)}\rangle\langle\Psi^{(i)}|\right)p_i$$

chain rule →

$$= \left[\left(\frac{d}{dt}|\Psi^{(i)}\rangle\right)\langle\Psi^{(i)}| + |\Psi^{(i)}\rangle\frac{d}{dt}\left(\langle\Psi^{(i)}|\right)\right]p_i$$

$$= -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]$$

So: $$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]$$

opposite to "normal" case!

or $$i\hbar\frac{\partial}{\partial t}\hat{\rho}(t) = -\left[\hat{\rho}(t),\hat{H}\right]$$

This equation of motion can be regarded as the quantum mechanical analog of Liouville's theorem in classical statistical mechanics:

$$\frac{\partial \rho_{classical}}{\partial t} = -\left[\rho_{classical}, H\right]$$

$\rho_{classical}$: density of representative points in phase space.

The analogy with classical statistical mechanics can be pushed further:

ensemble average

Quantum mechanically: $\langle\hat{A}\rangle = tr(\hat{\rho}\hat{A})$

Classically:

$$A_{\text{average}} = \frac{\int \rho_{\text{classical}}\, A(\vec{p},\vec{q})\, d\Gamma_{\vec{p},\vec{q}}}{\int \rho_{\text{classical}}\, d\Gamma_{\vec{p},\vec{q}}}$$

$d\Gamma_{\vec{p},\vec{q}}$: volume element in phase space

I use this analogy extensively when teaching Statistical Mechanics:

Classical statistical mechanics $\leftrightarrow$ quantum statistical mechanics

Example: Consider particle with magnetic moment $\frac{e\hbar}{2mc}$ subjected to uniform magnetic field in the z-direction.

$$\hat{H} = -\frac{e}{mc}\,\hat{\vec{S}}\cdot\vec{B} = -\frac{eB}{mc}\,\underbrace{\hat{S}_z}_{\text{eigenvalues are } \pm\frac{\hbar}{2}}$$

$$E = \mp\frac{eB}{2mc} \quad \left(\text{or } E_+ = -\hbar\omega/2 \text{ and } E_- = \hbar\omega/2\right)$$

$$\text{Let } \omega = \frac{eB}{mc} \implies E = \mp\hbar\omega/2$$

let $p_+ = e^{+\beta\hbar\omega/2}$ and $p_- = e^{-\beta\hbar\omega/2}$

you might recognize this as the canonical ensemble

then:

$$\hat{\rho} = \tilde{p}_+ |+\rangle\langle+| + \tilde{p}_- |-\rangle\langle-|$$

with $\tilde{p}_+ + \tilde{p}_- = 1$ $\longrightarrow$ $\left\{ \begin{array}{l} \tilde{p}_+ = p_+/(p_+ + p_-) \\ \tilde{p}_- = p_-/(p_+ + p_-) \end{array} \right\}$

It follows:

in $|+\rangle, |-\rangle$ basis

$$\rho = \begin{pmatrix} \tilde{p}_+ & 0 \\ 0 & \tilde{p}_- \end{pmatrix} = \frac{1}{Z}\begin{pmatrix} p_+ & 0 \\ 0 & p_- \end{pmatrix}$$

$$\text{Tr}\,\hat{\rho} = 1$$

$$\text{Tr}\,\hat{\rho}^2 = p_+^2 + p_-^2$$

High temperature limit:

The canonical ensemble becomes a completely random ensemble in which all energy eigenstates are equally populated.

Low temperature limit:

Canonical ensemble becomes a pure ensemble where only the ground state is populated.

Let us contrast the above with a quantum state $|\Psi\rangle$ of the form

$$|\Psi\rangle = c_+ |+\rangle + c_- |-\rangle$$

$$\Rightarrow \hat{\rho} = |\Psi\rangle\langle\Psi|$$

$$= \left(c_+ |+\rangle + c_- |-\rangle\right)\left(c_+^* \langle +| + c_-^* \langle -|\right)$$

$$= |c_+|^2 \, |+\rangle\langle +| + |c_-|^2 \, |-\rangle\langle -|$$

$$+ \underline{c_- c_+^*} \, |-\rangle\langle +| + \underline{c_+ c_-^*} \, |+\rangle\langle -|$$

"coherences"

$$\rho = \begin{pmatrix} |c_+|^2 & c_+ c_-^* \\ c_- c_+^* & |c_-|^2 \end{pmatrix}$$

in $|+\rangle, |-\rangle$ basis

how many "variables"?

c_+ has real & imaginary part.

c_- " " " " .

But : $|c_+|^2 + |c_-|^2 = 1$.

3 "variables" → one can be chosen as the overall phase of $|\Psi\rangle$

⇝ two independent quantities