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VI Quantum statistical physics

VI.1 The density operator

classical continuous system:
   probability density $\varrho(\vec{x}^N)$ on phase space
want to find quantum analog:
   density operator $\hat{\varrho}(t)$

$\varrho(\vec{x}^N)$	$\hat{\varrho}(t)$
function of phase space	operator on Hilbert space
$\varrho(\vec{x}^N)$ real	$\hat{\varrho}(t)$ hermitian
$\varrho(\vec{x}^N) \geq 0$	$\hat{\varrho}(t)$ positive semidefinite, i.e., $\langle\psi\|\hat{\varrho}(t)\|\psi\rangle \geq 0$ for all $\|\psi\rangle$
$\int d\vec{x}^N \varrho(\vec{x}^N) = 1$	$\mathrm{Tr}\, \hat{\varrho}(t) = 1$
$\langle f(\vec{x}^N)\rangle = \int d\vec{x}^N f(\vec{x}^N)\varrho(\vec{x}^N)$	$\langle \hat{O}\rangle = \mathrm{Tr}\, \hat{O}\hat{\varrho}(t)$

<u>Definition:</u> A hermitian, positive semidefinite operator $\hat{\varrho}$ with $\mathrm{Tr}\,\hat{\varrho} = 1$ is called a density operator.

<u>Representation in eigenbasis:</u>

$|\psi_i\rangle$ eigenvectors $\sum_i |\psi_i\rangle\langle\psi_i| = 1$

p_i eigenvalues

$$\Rightarrow \quad \hat{\varrho} = \sum_i |\psi_i\rangle p_i \langle\psi_i|$$

$\hat{\rho}$ hermitian $\Rightarrow$ p_i (exist and) are real
$\hat{\rho}$ positive semidefinite $\Rightarrow$ $p_i \geq 0$

$$1 = \mathrm{Tr}\,\hat{\rho} = \sum_j \langle\psi_j|\hat{\rho}|\psi_j\rangle = \sum_j \sum_i \langle\psi_j|\psi_i\rangle p_i \langle\psi_i|\psi_j\rangle$$
$$= \sum_i p_i$$

$\Rightarrow$ $p_i = \langle\psi_i|\hat{\rho}|\psi_i\rangle$ "probability to find state $|\psi_i\rangle$"

$$\langle\hat{O}\rangle = \mathrm{Tr}\,\hat{O}\hat{\rho} = \sum_j \langle\psi_j|\hat{O}\hat{\rho}|\psi_j\rangle$$
$$= \sum_j \sum_i \langle\psi_j|\hat{O}|\psi_i\rangle p_i \langle\psi_i|\psi_j\rangle = \sum_i p_i \langle\psi_i|\hat{O}|\psi_i\rangle$$

In eigenbasis $|o_i\rangle$ of operator $\hat{O}$:

$$\langle\hat{O}\rangle = \mathrm{Tr}\,\hat{O}\hat{\rho} = \sum_i \langle o_i|\hat{O}\hat{\rho}|o_i\rangle$$
$$= \sum_i \sum_j \langle o_i|\hat{O}|o_j\rangle \langle o_j|\hat{\rho}|o_i\rangle = \sum_i o_i \langle o_i|\hat{\rho}|o_i\rangle$$

$\Rightarrow$ $\langle o_i|\hat{\rho}|o_i\rangle$ probability to find state $|o_i\rangle$

$$\langle o_i|\hat{\rho}|o_i\rangle = \sum_j \langle o_i|\psi_j\rangle p_j \langle\psi_j|o_i\rangle$$
$$= \sum_j p_j |\langle o_i|\psi_j\rangle|^2$$

ensemble probability of state ψ_j

quantum mechanical overlap of states $|o_i\rangle$ and $|\psi_j\rangle$

two kinds of probabilities:

quantum mechanical probability

- $|\langle o_i|\psi_0\rangle|^2$
- fundamental uncertainty
- coherence important $\quad \sum_i \alpha_i |\psi_i\rangle$

statistical probability

- p_i
- our ignorance only - not fundamentally unknowable
- incoherent superposition of states

$$\sum_i |\psi_i\rangle p_i \langle\psi_i|$$

If there is no ~~principle~~ statistical uncertainty

$\Rightarrow$ one of the p_i is one, all other p_i are zero

$$\Rightarrow \quad \hat{\rho} = |\psi(t)\rangle\langle\psi(t)|$$

"pure state"

otherwise: "mixed state"

<u>Time evolution of a density operator</u>

individual state $\rightarrow$ Schrödinger equation

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

$$\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{\partial}{\partial t}\sum_i |\psi_i(t)\rangle p_i \langle\psi_i(t)|$$

$$= \sum_i \left(\frac{\partial}{\partial t}|\psi_i(t)\rangle\right) p_i \langle\psi_i(t)| + \sum_i |\psi_i(t)\rangle p_i \left(\frac{\partial}{\partial t}\langle\psi_i(t)|\right)$$

$$= \sum_i \frac{1}{i\hbar}\hat{H}|\psi_i(t)\rangle p_i \langle\psi_i(t)| + \sum_i \frac{-1}{i\hbar}|\psi_i(t)\rangle p_i \langle\psi_i(t)|\hat{H}$$

$$= \frac{1}{i\hbar}\hat{H}\sum_i |\psi_i(t)\rangle p_i \langle\psi_i(t)| - \frac{1}{i\hbar}\sum_i |\psi_i(t)\rangle p_i \langle\psi_i(t)|\hat{H}$$

$$= \frac{1}{i\hbar}\hat{H}\hat{\rho} - \frac{1}{i\hbar}\hat{\rho}\hat{H}$$

$$\Rightarrow i\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H},\hat{\rho}(t)] \equiv \hat{L}\,\hat{\rho}(t)$$

Liouville operator

~~In an eigenbasis $|E_i\rangle$ of the Hamiltonian:~~

$$\Rightarrow \hat{\rho}(t) = e^{-i\hat{L}t}\hat{\rho}(0) = e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)\,e^{\frac{i}{\hbar}\hat{H}t}$$

In an eigenbasis $|E_i\rangle$ of the Hamiltonian:

$$\hat{\rho}(t) = e^{-\frac{i}{\hbar}\hat{H}t}\sum_i |E_i\rangle\langle E_i|\,\hat{\rho}(0)\sum_j |E_j\rangle\langle E_j|\,e^{\frac{i}{\hbar}\hat{H}t}$$

$$= \sum_i\sum_j \langle E_i|\hat{\rho}(0)|E_j\rangle\, |E_i\rangle\langle E_j|\, e^{\frac{i}{\hbar}(E_j-E_i)t}$$

stationary state: $\hat{\rho}(t) = \hat{\rho}(0) \Rightarrow \langle E_i|\hat{\rho}(0)|E_j\rangle = 0$ for $E_i \neq E_j$

$\Rightarrow \hat{\rho}$ is diagonal in ~~the~~ some eigenbasis of $\hat{H}$

~~(if $\hat{H}$ [illegible])~~

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