Quantum Statistical Mechanics

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Pure and Mixed Ensembles

Let us consider spin 1/2 particles. In general, the state of the particle is given by

$$|\alpha\rangle = c_+|+\rangle + c_-|-\rangle.$$

If we describe an ensemble quantum mechanical, suppose that we have an physical system, 40% of $|\alpha\rangle$ 60% of $|\beta\rangle$. In order to deal with population probability, we introduce the concept of fractional population, such as

$$w_\alpha = 0.4, \quad w_\beta = 0.6.$$

Note that these two probabilities are essentially different.

Pure and Mixed Ensembles

- Pure ensemble: $|+\rangle$, $|-\rangle$, or $|\alpha\rangle$.
- Mixed ensemble: $\{w_+|+\rangle + w_-|-\rangle\}$ or $\{w_\alpha|\alpha\rangle + w_\beta|\beta\rangle\}$.

Because w is probability, they satisfy the normalization condition

$$\sum_i w_i = 1.$$

And, the ensemble average is given by

$$[A] = \sum_i w_i \langle i|A|i\rangle.$$

Note that the expectation value in quantum mechanics is

$$\langle A\rangle = \langle i|A|i\rangle.$$

Density Matrix

To cope with the ensemble average, we introduce the density matrix (operator) ρ as

$$\rho = \sum_i w_i |i\rangle\langle i|. \tag{1}$$

Then we have

$$\begin{aligned}
[A] &= \sum_i w_i \langle i|A|i\rangle & (2)\\
&= \sum_i w_i \langle i| \left(\sum_j |j\rangle\langle j| \right) A|i\rangle & (3)\\
&= \sum_i w_i \sum_j \langle j|A|i\rangle\langle i|j\rangle & (4)\\
&= \sum_j \langle j|A \left(\sum_i w_i |i\rangle\langle i| \right) |j\rangle & (5)\\
&= \sum_j \langle j|A\rho|j\rangle = \mathrm{Tr}(A\rho). & (6)
\end{aligned}$$

Pure Ensemble

A pure ensemble corresponds to $w_i = 1$ for some i and $w_i = 0$ for the others, and thus the density matrix is given by

$$\rho = |i\rangle\langle i|, \tag{8}$$

with no summation. Clearly, $\rho^2 = \rho$ and $\mathrm{Tr}(\rho) = 1$.
For instance, $|+\rangle$ for S_z with a spin 1/2 system,

$$\rho = |+\rangle\langle +| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} \tag{9}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{10}$$

Pure Ensemble: $|S_x;\pm\rangle$

For instance, $|+\rangle$ for S_x,

$$\rho = |S_x;+\rangle\langle S_x;+| = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)\frac{1}{\sqrt{2}}(\langle+| + \langle-|) \quad (11)$$

$$= \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}. \quad (12)$$

Mixed Ensemble

An incoherent mixture of a spin-up and down with the equal probability:

$$\rho = \frac{1}{2}|+\rangle\langle+| + \frac{1}{2}|-\rangle\langle-| \tag{13}$$

$$= \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}, \tag{14}$$

$$[S_x] = [S_y] = [S_z] = 0. \tag{15}$$

Another example of a partially polarized beam: $w(S_z;+) = 3/4$ and $w(S_x;+) = 1/4$.

$$\rho = \frac{3}{4}|+\rangle\langle+| + \frac{1}{4}\frac{1}{2}(|+\rangle + |-\rangle)(\langle+| + \langle-|) \tag{16}$$

$$= \begin{pmatrix} 7/8 & 1/8 \\ 1/8 & 1/8 \end{pmatrix}, \tag{17}$$

$$[S_x] = \frac{\hbar}{8}, \quad [S_y] = 0, \quad [S_z] = \frac{3\hbar}{8}. \tag{18}$$

Time Evolution of Ensembles (Density Matrix)

Density matrix is given by

$$\rho = \sum_i w_i |i\rangle\langle i|. \tag{19}$$

Then, time evolution of the matrix is

$$\frac{\partial \rho}{\partial t} = \sum_i w_i \left(\frac{\partial |i\rangle}{\partial t} \langle i| + |i\rangle \frac{\partial \langle i|}{\partial t} \right). \tag{20}$$

The time evolution of state ket with Hamiltonian is given by Schrödinger equation:

$$i\hbar \frac{\partial |i\rangle}{\partial t} = H|i\rangle, \quad -i\hbar \frac{\partial \langle i|}{\partial t} = \langle i|H. \tag{21}$$

Hence, we arrive at the quantum Liouville theorem

$$\frac{\partial \rho}{\partial t} = \sum_i w_i \frac{1}{i\hbar} \left(H|i\rangle\langle i| - |i\rangle\langle i|H \right) \tag{22}$$

$$= \frac{1}{i\hbar}(H\rho - \rho H) = \frac{1}{i\hbar}[H, \rho]. \tag{23}$$

Quantum Statistical Mechanics

The canonical distribution of a mixture of the energy state $|E_n\rangle$ with Boltzmann weights $exp(-\beta E_n)$. Hence, the density matrix ρ_{canon} is a diagonal form:

$$\rho_{canon} = \sum_n \frac{e^{-\beta E_n}}{Z} |E_n\rangle\langle E_n|, \tag{24}$$

where the partition function is

$$Z = \sum_n e^{-\beta E_n} = \sum_n \langle E_n|e^{-\beta H}|E_n\rangle \tag{25}$$

$$= \mathrm{Tr}\, e^{-\beta H}. \tag{26}$$

Note that

$$e^{-\beta H} = \sum_n |E_n\rangle e^{-\beta H} \langle E_n| = \sum_n |E_n\rangle e^{-\beta E_n} \langle E_n|. \tag{27}$$