Lecture 3: Mixed states and entangled states
Read:Gottfried & Yan, Chapter 1, 2.1, 2.2.

1   The density matrix

Quantum mechanical systems can be in states which cannot be described by wavefunctions. Such states are called the *mixed states*. The states described by wavefunctions are called *pure states*. Unlike the "statistical description" in classical mechanics which is essentially due to our insufficient knowledge of classical systems, even if we have complete knowledge of quantum systems, they still can be in the mixed state. This subtle point will be explained below. In this case, we need to use the concept of *density matrix* instead of wavefunctions.

A mixed state can be represented as an incoherent summation of orthonormal bases $|\Psi_i\rangle$'s as

$$\rho = \sum_i \rho_i |\Psi_i\rangle\langle\Psi_i|, \tag{1}$$

where ρ_i is the probability for the system in the state of Ψ_i, and Ψ_i's are the diagonal basis for ρ. ρ_i are called eigenvalues of the density matrix ρ. Please note that Eq. 1 is *not* the superposition of states $|\Psi_i\rangle$. There are no interference between different $|\Psi_i\rangle$'s.

If we measure an observable F, the distribution of measurement results in the mixed state described by ρ is the sum of those from individual pure states $|\Psi_i\rangle$ with the corresponding probability ρ_i. In other words, when performing measurements of F in the mixed states, we have two different steps of average.

1. For each eigenstate $|\Psi_i\rangle$ or ρ, we have the quantum mechanical statistical interpretation $\bar{F}_i = \langle\Psi_i|F|\Psi_i\rangle$. Generally speaking, the diagonal bases for ρ are not the eigenstates for F, in which $F = \sum_{ij} |\Psi_i\rangle\langle\Psi_j|F_{ij}$.

2. The second step is the usual statistical average over the probability distribution ρ_i, such that we have the expectation value of F as

$$\overline{F} = \sum_j \rho_j \bar{F}_j = \sum_j \rho_j \langle\Psi_j|F|\Psi_j\rangle, \tag{2}$$

which can further expressed in a formal way as

$$\overline{F} = \sum_j \rho_j\langle\Psi_j|F|\Psi_j\rangle = \sum_i\sum_j \rho_j\langle\Psi_i|\Psi_j\rangle\langle\Psi_j|F|\Psi_i\rangle = \sum_i \langle\Psi_i|\rho F|\Psi_i\rangle = \text{tr}\{\rho F\}. \tag{3}$$

Since ρ_i is the probability, it satisfies

$$\rho_i \geq 0, \quad \sum_i \rho_i = \text{tr}\rho = 1. \tag{4}$$

If there is one of ρ_i's equal to 1, say, $\rho_1 = 1$, and all other probabilities $\rho_i = 0 (i \neq 1)$, then $\rho = |\Psi_1\rangle\langle\Psi_1|$. It means that the system is in the pure state $|\Psi_1\rangle$, thus the pure state can also be represented by the density matrix. The trace of the square of ρ^2 satisfies the inequality of

$$\text{tr}\rho^2 = \sum_i \rho_i^2 \leq 1. \tag{5}$$

The equality is satisfied if ρ represents the pure state. In this case, $\rho^2 = \rho$, which is just a projection operator.

2 Density matrix in a general representation

Now we can use a general representation with orthonormal bases of $|\varphi\rangle$'s to represent the density matrix as

$$\rho = \sum_i \rho_i|\Psi_i\rangle\langle\Psi_i| = \sum_{i,a,b} \rho_i|\varphi_a\rangle\langle\varphi_a|\Psi_i\rangle\langle\Psi_i|\varphi_b\rangle\langle\varphi_b| = \sum_{ab}|\varphi_a\rangle\langle\varphi_b|\rho_{ab}, \tag{6}$$

where

$$\rho_{ab} = \langle\varphi_a|\rho|\varphi_b\rangle = \sum_i \rho_i\langle\varphi_a|\Psi_i\rangle\langle\Psi_i|\varphi_b\rangle. \tag{7}$$

The diagonal matrix elements $\rho_{aa} = \sum_i \rho_i|\langle\varphi_a|\Psi_i\rangle|^2$, which remains non-negative and can be interpreted as the probability for the system in the state of $|\varphi_a\rangle$. The off-diagonal matrix elements are generally complex valued. Since the trace is invariant under different bases, the expectation value of an observable F remains

$$\overline{F} = \text{tr}[\rho F] = \sum_{ab} \rho_{ab}F_{ba} = \sum_{ab} \rho_{ab}\langle\varphi_b|F|\varphi_a\rangle. \tag{8}$$

Exercise

I leave it as an exercise that you can directly obtain Eq. 8 starting from Eq. 2 by performing the transformation between bases.

3 Entropy

Next we define the *von Neumann entropy S* for a mixed state. Let us first recall how we define classical entropy S_{cl}. If there are a set of classical states with the probability distribution of ρ_i, the classical entropy is defined as $S_{cl} = k_B \sum \rho_i \ln \rho_i^{-1}$. Now for the mixed states described by the density matrix, in the diagonal representation $|\Psi_i\rangle$, we still define the *von Neumann*

entropy S

$$S = -k_B \sum_i \rho_i \ln \rho_i. \tag{9}$$

Formally, we can write a representation independent form as

$$S = -k_B \text{tr}[\rho \ln \rho]. \tag{10}$$

One question is how to define a logarithmic of an operator. Since all the eigenvalues of ρ are positive and smaller than 1, we can define

$$\ln \rho = \ln[1 - (1 - \rho)] = -\sum_{n=1}^{\infty} \frac{(1-\rho)^n}{n}. \tag{11}$$

For the pure state in which only one of ρ_i equals to 1 and all others probabilities are 0, thus $S_{pure} = 0$.

Exercise:

We can also prove that Eq. 9 reaches maximal if all the ρ_i are equal to each other. I leave it as an exercise, or, you can refer to Gottfried's book.

4 Entangled states

Generally speaking, for a large system with N-particles, in a pure state $\Psi(q_1, .., q_N)$. Let us ask what is the state that particle one is in? The answer is that the state of particle one cannot be described by a wavefunction, but in a mixed state.

Let us consider a system composed of two subsystems with coordinates q_1 and q_2 for each subsystem, respectively. Suppose the entire system is in a pure state $|\Psi_{12}\rangle$, and we use the coordinate representation in which the state is represented by the wavefunction $\Psi(q_1, q_2)$, and thus $\rho_{12} = |\Psi_{12}\rangle\langle\Psi_{12}|$. In the coordinate representation,

$$\langle q_1 q_2 | \rho_{12} | \acute{q_1} \acute{q_2} \rangle = \langle q_1 q_2 | \Psi_{12}\rangle\langle\Psi_{12}| \acute{q_1} \acute{q_2}\rangle = \Psi(q_1 q_2)\Psi^*(\acute{q_1}, \acute{q_2}). \tag{12}$$

However, the subsystem 1 is not in a pure state. It lives in the mixed state described by the density matrix ρ_1. It is defined as

$$\rho_1 = \text{tr}_2 \, \rho_{12}, \tag{13}$$

where tr_2 is a partial trace over the degree of freedom of particle 2. In the coordinate representation,

$$\langle q_1 | \rho_1 | \acute{q_1} \rangle = \int dq_2 \langle q_1 q_2 | \rho_{12} | \acute{q_1} q_2 \rangle = \int dq_2 \Psi(q_1 q_2)\Psi^*(\acute{q_1}, q_2). \tag{14}$$

Let us consider an operator A_1 that only depends on q_1 of the subsystem 1, i.e.,

$$\langle q_1 q_2 | A_1 | q_1' q_2' \rangle = \langle q_1 | A_1 | q_1' \rangle \delta(q_2 - q_2'). \tag{15}$$

Thus for the state of $|\Psi_{12}\rangle$, we have the expectation value of A_1 as

$$\begin{aligned}
\langle \Psi_{12} | A_1 | \Psi_{12} \rangle &= \int dq_1 dq_2 dq_1' dq_2' \, \langle \Psi_{12} | q_1 q_2 \rangle \langle q_1 q_2 | A_1 | q_1' q_2' \rangle \langle q_1' q_2' | \Psi_{12} \rangle \\
&= \int dq_1 dq_1' dq_2 \, \Psi^*(q_1, q_2) \langle q_1 | A_1 | q_1' \rangle \Psi(q_1', q_2) \\
&= \int dq_1 dq_1' \langle q_1 | A_1 | q_1' \rangle \langle q_1' | \rho_1 | q_1 \rangle \\
&= \mathrm{tr}_1(\rho_1 A_1). \tag{16}
\end{aligned}$$

Only if $|\Psi_{12}\rangle$ can be factorize into a product of $|\Psi_1\rangle \otimes |\Psi_2\rangle$ where $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are pure states for the subsystem 1 and 2, respectively, then $\rho_1 = |\Psi_1\rangle\langle\Psi_1|$ describing a pure state. In this case, there is no entanglement between subsystems 1 and 2. Otherwise, we say that subsystems 1 and 2 are *entangled*, and ρ_1 describes a mixed state for the subsystem 1.

In general, according to the Schmidt decomposition, for any $|\Psi_{12}\rangle$, it can always be decomposed as

$$|\Psi_{12}\rangle = \sum_{i=1}^{n} c_i |\Psi_{1,i}\rangle \otimes |\Psi_{2,i}\rangle, \tag{17}$$

where $|\Psi_{1,i}\rangle (i = 1, n)$ are orthogonal with each other for the subsystem 1, and so do $|\Psi_{2,i}\rangle (i = 1, n)$ for the subsystem 2. Then we have

$$\rho_1 = \sum_i \rho_i |\Psi_{1,i}\rangle \langle \Psi_{1,i}|, \tag{18}$$

with $\rho_i = |c_i|^2$. If there are more than one terms of $c_i \neq 0$, $\mathrm{tr}[\rho_1^2] = \sum_i |c_i|^4 < 1$, thus the subsystem 1 is in a mixed state.

Here I presen the proof of the theorem of Schmidt decomposition.

Theorem: *Consider two Hilbert spaces H_1 and H_2 for systems 1 and 2 with dimensions n_1 and n_2, respectively. Without loss of generality, we assume $n_1 \geq n_2$. The Hilbert space for the combined system is simply $H_1 \otimes H_2$. For any state of the combined system $|\Psi_{12}\rangle$ in $H_1 \otimes H_2$, we can always find a set of orthonormal states $|\Psi_{1,i}\rangle (i = 1, ...n_2)$ in H_1, and $|\Psi_{2,i}\rangle (i = 1, ..., n_2)$ in H_2, such that $|\Psi_{12}\rangle = \sum_{i=1}^{n_2} c_i |\Psi_{1,i}\rangle \otimes |\Psi_{2,i}\rangle$, where c_i is non-negative. The set of $|\Psi_{1,i}\rangle$ and $|\Psi_{2,i}\rangle$ are uniquely determined by the state $|\Psi_{12}\rangle$.*

Let us consider two general sets of orthonormal bases $|\alpha_i\rangle (i = 1, ...n_1)$ for space H_1, and $|\beta_i\rangle (i = 1, ...n_2)$ for space H_2, respectively. $|\Psi_{12}\rangle$ can always be expanded as

$$|\Psi_{12}\rangle = \sum_{i_1=1}^{n_1} \sum_{i_2=1}^{n_2} c_{i_1 i_2} |\alpha_{i_1}\rangle \otimes |\beta_{i_2}\rangle. \tag{19}$$

The coefficient c_{i_1,i_2} can be viewed as a rectangular $n_1 \times n_2$ matrix $M_{i_1,i_2} = c_{i_1,i_2}$.

According to the theorem in linear algebra of singular value decomposition, there always exist an $n_1 \times n_1$ unitary matrix U, and $n_2 \times n_2$ unitary matrix V such that

$$M = U \begin{bmatrix} \Sigma \\ 0 \end{bmatrix} V^T, \tag{20}$$

where Σ is a $n_2 \times n_2$ a positive semidefinite diagonal matrix, and 0 refers to a $(n_1 - n_2) \times n_2$ matrix with all elements 0. We use $c_i (i = 1, ..., n_2)$ to denote the diagonal element of Σ, $u_1, ..., u_{n_2}$ for the first n_2 columns of U, and $v_1, ..., v_{n_2}$ for the columns of V. Then we have $M = \sum_{i=1}^{n_2} c_i u_i v_i^T$, which means that

$$|\Psi_{12}\rangle = \sum_{i=1}^{n_2} c_i |u_i\rangle \otimes |v_i\rangle \tag{21}$$

where

$$|u_i\rangle = \sum_{j=1}^{n_1} U_{i,j} |\alpha_j\rangle, \quad |v_i\rangle = \sum_{j=1}^{n_1} V_{i,j} |\beta_j\rangle. \tag{22}$$

5 Two-particle interference

Let us consider an entangled two-particle state

$$\Psi(q_1, q_2) = c_1 u_1(q_1) v_1(q_2) + c_2 u_2(q_1) v_2(q_2), \quad |c_1|^2 + |c_2|^2 = 1. \tag{23}$$

Here we do not assume that $u_{1,2}$ are orthogonal, and neither do $v_{1,2}$. The two-body probability distribution is

$$\begin{aligned} \rho(q_1, q_2) &= |c_1|^2 |u_1(q_1)|^2 |v_1(q_2)|^2 + |c_2|^2 |u_2(q_1)|^2 |v_2(q_2)|^2 + I_2(q_1, q_2), \\ I_2(q_1, q_2) &= 2\text{Re}\Big\{ c_1 c_2^* u_1(q_1) u_2^*(q_1) v_1(q_2) v_2^*(q_2) \Big\}. \end{aligned} \tag{24}$$

The cross term $I_2(q_1, q_2)$ survives even if particles 1 and 2 are faraway from each other, i.e., $u_{1,2}$ do not have spatial overlap with $v_{1,2}$. Nevertheless if $v_{1,2}(q_2)$ are orthogonal to each other, in the reduced one-body density $\rho(q_1)$, the two-particle interference term I_2 vanishes after the integral of q_2.

If $v_{1,2}(q_2)$ are not orthogonal, then in the reduced one-body density

$$\rho(q_1) = |c_1| |u_1(q_1)|^2 + |c_2| |u_2(q_2)|^2 + 2\text{Re}[u_1^*(q_1) u_2(q_1) V], \tag{25}$$

where

$$V = \int dq_2 \; v_1(q_2) v_2^*(q_2). \tag{26}$$

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Thus particle 1 will show interference if the two states of particle 2 are not completely orthogonal.

6   Quantum statistical density matrix

In classical statistical mechanics, the equilibrium partition function is

$$Z = \sum_i \rho_i = \sum_i e^{-\beta E_i}, \tag{27}$$

where i is the index of the system configurations, E_i is the energy of the configuration i, and $\beta = 1/T$. From the partition function, we have $F = -\frac{1}{\beta}\ln Z$, from which we can obtain all the information of thermodynamics.

For a quantum statistical system, it is also connected to a heat bath, thus it is also in a mixed state. In the equilibrium, its density matrix is known

$$\rho = \frac{1}{Z}e^{-\beta H}, \tag{28}$$

$$Z = \mathrm{tr}\ e^{-\beta H}. \tag{29}$$

If we knew all the eigenstates $|\Psi_n\rangle$ of H, the density matrix and the partition function become $\rho_n = \frac{1}{Z}e^{-\beta E_n}$ and $Z = \sum_n e^{-\beta E_n}$. However, generally speaking, it is very difficult to solve the energy eigenstates for a many-body quantum mechanical systems. We have to use a convenient set of bases, which are often the tensor product of the bases of a single particle. And the single particle bases can either be chosen in momentum space bases or the coordinate bases. In a general many-body bases $|\varphi_i\rangle$, we have

$$\rho = \sum_{i,j} |\varphi_i\rangle\langle\varphi_j| \langle i|e^{-\beta H}|j\rangle$$

$$Z = \sum_i \langle i|e^{-\beta H}|i\rangle. \tag{30}$$

For the thermodynamic observable F,

$$\overline{F} = \sum_{ij} \langle i|F|j\rangle\langle j|e^{-\beta H}|i\rangle \tag{31}$$

Different from the classical case, $\langle j|e^{-\beta H}|i\rangle$ is not positive-definite, but in general complex. This is a major difficulty of quantum statistical problem.