8.333 Fall 2025 Recitations 9: Basic quantum statistical mechanics

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Some parts of this note largely follows the previous year's recitation by Sara Dal Cengio.

For a more comprehensive resource, see Ch. 6 of Mehran Kardar's *Statistical Physics of Particles* and Ch. 2 of David Tong's *Lectures on Statistical Physics*.

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1 Introduction to density matrix

1.1 Motivation

In classical statistical mechanics, we have always been considering an ensemble of microstates, such as a set of possible classical spins S, or a space of possible position and momentum q, p of a particle. How do we generalize this idea into the framework of quantum mechanics?

Let us first focus on the case of spins for simplicity. It is trivial when there is only a single state: we just write down the corresponding quantum state. For example, classical spins $S = \pm 1$ would correspond to quantum spins $|\uparrow\rangle, |\downarrow\rangle$. It becomes more tricky when it comes to an ensemble of states. How should we write down a "quantum state" with, let say, 50% spin up and 50% spin down? It may be tempting to write down

$$|\psi\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle \ , \tag{1}$$

so that if we measure the spin in the z-direction, we would indeed have 50% probability to measure spin up, and the same for spin down. However, it is crucial that quantum superposition is *not* the same as probabilistic mixture of states. In the above, $|\psi\rangle$ is still a single quantum state; in fact, it is the eigenstate

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle \ , \tag{2}$$

for spin in the x-direction, hence the result is not random at all if we measure in the x-direction. Randomness in measurement only arises because of the measurement basis we have chosen. Roughly speaking, we have asked the "wrong question" about the state! In below, such states are referred to as **pure states**.

Instead, the description of "50% spin up and 50% spin down" should be interpreted as the following: there is 50% probability that the state is *prepared* to be $|\uparrow\rangle$, and the same for $|\downarrow\rangle$. This is purely the classical uncertainty in the process of preparation, and has nothing to do with any quantum operations. It turns out that to describe this situation, it is useful to define the **density matrix**:

Definition 1.1: Density matrix

For an ensemble of pure states where there is probability p_i that the state $|\psi_i\rangle$ occurs for each i, the density matrix ρ is

$$\rho = \sum_i p_i |\psi_i\rangle \langle\psi_i| \,. \tag{3}$$

Importantly, since all the probabilities must sum to 1, i.e., $\sum_i p_i = 1$, we have

$$\mathrm{Tr}\ \rho = \mathrm{Tr}\left(\sum_i p_i |\psi_i\rangle \langle\psi_i|\right) = \sum_i p_i \langle\psi_i|\psi_i\rangle = \sum_i p_i = 1\,. \tag{4}$$

As an example, the above example should be described as

$$\rho = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow| \,, \tag{5}$$

or in the basis of $|\uparrow\rangle, |\downarrow\rangle$, the matrix form is

$$\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} . \tag{6}$$

As a comparison, for the state $|{\rightarrow}\rangle$, the density matrix is

$$\rho = |{\rightarrow}\rangle\langle{\rightarrow}| \tag{7}$$

$$= \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \tag{8}$$

$$= \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} , \tag{9}$$

which is indeed not the same as the previous density matrix.

1.2 Pure and mixed states

From the above discussion, we shall refer to the ordinary quantum states $|\psi\rangle$ as **pure states**, while refer to ensembles of pure states as **mixed states**. More precisely,

Definition 1.2: Pure and mixed states

A density matrix ρ represents a pure state if it can be written as

$$\rho = |\psi\rangle\langle\psi| \,, \tag{10}$$

for some state $|\psi\rangle$. Otherwise, it represents a mixed state.

Given a density matrix ρ, how do we know that whether it represents a pure state? It is perhaps not obvious by just staring at the matrix elements. Instead, we can look at the so-called **purity**:

$$\mathrm{Tr}\ \rho^2 = \sum_i p_i^2 \,. \tag{11}$$

Note that p_i^2 must be smaller than p_i unless $p_i = 0, 1$. With the normalization Tr $\rho = 1$, we see that the purity reaches maximum Tr $\rho^2 = 1$ if and only if one of the p_i's is 1 and all the others are 0, i.e., ρ is a pure state. In contrast, the purity reaches minimum when every state occurs with the same probability. If there are N pure states in the ensemble, we will have $p_i = 1/N$ and Tr $\rho^2 = 1/N$. This is referred to as the maximally mixed state.

1.3 Quantum mechanics with density matrix

To have a sense of how to work with density matrices in quantum mechanics, let us see how the typical quantities and equations are generalized to density matrices.

- **Expectation value**: For a pure state $|\psi\rangle$, the expectation value of an operator A is

$$\langle A\rangle = \langle\psi| A |\psi\rangle \,. \tag{12}$$

  For a mixed state, the above is further averaged over the ensemble of pure states. We have

$$\begin{aligned}\langle A\rangle &= \sum_i p_i \langle\psi_i| A |\psi_i\rangle &(13)\\ &= \mathrm{Tr}\left(\sum_i p_i |\psi_i\rangle\langle\psi_i| A\right) &(14)\\ &= \mathrm{Tr}\ \rho A \,. &(15)\end{aligned}$$

- **Measurement**: For simplicity we focus on non-degenerate eigenstates. For a pure state $|\psi\rangle$, the probability of measuring an eigenstate $|n\rangle$ is

$$P_n = |\langle n|\psi\rangle|^2 \,. \tag{16}$$

  For a mixed state, we again take the ensemble average and get

$$\begin{aligned}P_n &= \sum_i p_i |\langle n|\psi\rangle|^2 &(17)\\ &= \sum_i p_i \langle n|\psi_i\rangle\langle\psi_i|n\rangle &(18)\\ &= \langle n|\rho|n\rangle \,. &(19)\end{aligned}$$

  Interestingly, with density matrices we can now describe the state after a measurement but without knowing the measurement result. It is simply a *classical* mixture of the eigenstates $|n\rangle$ with probability P_n. Therefore, the density matrix ρ' after a measurement is

$$\rho' = \sum_n P_n |n\rangle\langle n| \,, \tag{20}$$

  where each P_n is determined from the previous equation.

- **Time evolution**: For a pure state $|\psi\rangle$, its time evolution (in the Schrödinger picture) is given by the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \,, \tag{21}$$

  where H is the Hamiltonian. The Hermitian conjugated version will also be useful:

$$-i\hbar\frac{\partial}{\partial t}\langle\psi| = \langle\psi| H \,. \tag{22}$$

  Now for a mixed state, the time evolution of its density matrix is

$$\begin{aligned}i\hbar\frac{\partial\rho}{\partial t} &= i\hbar\sum_i p_i \frac{\partial}{\partial t}\left(|\psi_i\rangle\langle\psi_i|\right) &(23)\\ &= i\hbar\sum_i p_i\left(\left(\frac{\partial}{\partial t}|\psi_i\rangle\right)\langle\psi_i| + |\psi_i\rangle\left(\frac{\partial}{\partial t}\langle\psi_i|\right)\right) &(24)\\ &= \sum_i p_i\left(H|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i| H\right) &(25)\\ &= H\rho - \rho H = [H,\rho] \,. &(26)\end{aligned}$$

  This looks very similar to the classical Liouville's equation. Indeed, it is consistent with the procedure of canonical quantization that replaces Poisson brackets with commutators.

This quantum version of Liouville's equation tells us how we should write down the density matrices for equilibrium statistical mechanics: ρ should be a function of the Hamiltonian H.

Example 1.1: Quantum canonical ensemble

Let us see how to write down the density matrix for canonical ensemble. First, the set of microstates with known energies E_i should correspond to the energy eigenstates $|\psi_i\rangle$ with the same energies. Assuming that each eigenstate $|\psi_i\rangle$ occurs with probability proportional to $e^{-\beta E_i}$, the density matrix is

$$\begin{aligned}\rho &= \sum_i \frac{e^{-\beta E_i}}{Z} |\psi_i\rangle \langle\psi_i| && (27)\\ &= \sum_i \frac{e^{-\beta H}}{Z} |\psi_i\rangle \langle\psi_i| && (28)\\ &= \frac{e^{-\beta H}}{Z}\,, && (29)\end{aligned}$$

which is indeed a function of H. The condition that Tr $\rho = 1$ implies that the **quantum partition function** Z should be

$$Z = \mathrm{Tr}\ e^{-\beta H} = \sum_i e^{-\beta E_i}\,, \tag{30}$$

which indeed agrees with the classical canonical partition function.

The other ensembles including the microcanonical and the grand canonical ensembles can be similarly expressed in terms of density matrices.

2 Density matrix in entanglement

Apart from ensembles of states, density matrices are also essential in understanding entanglement and subsystems in quantum mechanics. Let us start with a common misconception in entanglement. Suppose we have two particles A and B that are entangled in the state

$$|\psi\rangle_{AB} = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle_A \otimes |\downarrow\rangle_B + |\downarrow\rangle_A \otimes |\uparrow\rangle_B\right)\,. \tag{31}$$

This is the superposition of the up-down and down-up states. We could have also written more simply

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\,, \tag{32}$$

but the tensor product notation will be more helpful in below.

Now suppose we measure particle A. We will have equal probabilities to observe spin up or spin down for A, but the spin of B is fully determined by the measurement outcome and must be opposite to the spin of A due to the entanglement. It is somewhat common for beginners in quantum mechanics, including famous physicists in the early days, to claim the following: no matter which outcome we get, the measurement we performed seems to change "the state of B" (think about what this phrase exactly means in quantum mechanics) instantaneously, hence the change is faster than speed of light and quantum mechanics violates relativity...

We surely know that this cannot be true, but let us think more about what exactly happens to B due to the measurement. Suppose someone wants to gain information about B by measuring its spin. There are two cases:

- If B is measured *before* A is measured, the global quantum state has equal probabilities to collapse into up-down or down-up after the measurement of B, so there are also equal probabilities to observe B in spin up or down.
- If B is measured *after* A is measured, we already know that B has equal probabilities to be in the spin-up or the spin-down state due to the measurement of A. The measurement of B does not change its quantum state.

Therefore, it seems that no matter A is measured or not, the measurement probabilities for B are the same, so it seems that "the state of B" is actually not changed.

We can formalize the above statement using density matrices. First, after the measurement of A, B has 50% probability to be in state $|\uparrow\rangle$, and the same for state $|\downarrow\rangle$. Therefore, its density matrix is

$$\rho_B = \frac{1}{2} \left(|\uparrow\rangle_B \langle\uparrow|_B + |\downarrow\rangle_B \langle\downarrow|_B\right)\,. \tag{33}$$

The case before the measurement of A sounds more complicated. How should we describe the state of one particle in an entangled two-particle systems? The above discussion suggests that "the state of B" should also be described as a density matrix ρ_B, called a **reduced density matrix**. Let us think about what ρ_B should be. Consider the expectation value of an operator $\mathcal{O}_B$ that only acts on B. We should expect

$$\langle \mathcal{O}_B \rangle = \mathrm{Tr}_B \left(\rho_B \mathcal{O}_B \right) . \tag{34}$$

At the same time, the operator can be written as $I_A \otimes \mathcal{O}_B$ that acts on the full system. Then we have

$$\langle \mathcal{O}_B \rangle = \mathrm{Tr}_{AB} \left(\rho_{AB} (I_A \otimes \mathcal{O}_B) \right) . \tag{35}$$

How should we reduce Tr_{AB} to Tr_B? We need something called the **partial trace**. Let us consider a simple case: an operator $\mathcal{O} = \mathcal{O}_A \otimes \mathcal{O}_B$. Its trace is

$$\mathrm{Tr}_{AB}\ \mathcal{O} = (\mathrm{Tr}_A\ \mathcal{O}_A)(\mathrm{Tr}_B\ \mathcal{O}_B) = \mathrm{Tr}_B((\mathrm{Tr}_A\ \mathcal{O}_A)\mathcal{O}_B) . \tag{36}$$

Hence, we can write the partial trace

$$\mathrm{Tr}_A\ \mathcal{O} = (\mathrm{Tr}_A\ \mathcal{O}_A)\mathcal{O}_B , \tag{37}$$

such that

$$\mathrm{Tr}_{AB}\ \mathcal{O} = \mathrm{Tr}_B \left(\mathrm{Tr}_A\ \mathcal{O} \right) . \tag{38}$$

This can be generalized to linear combinations of tensor product operators since trace is a linear map, i.e., $\mathrm{Tr}(A+B) = \mathrm{Tr}\ A + \mathrm{Tr}\ B$. We finally see that

Definition 2.1: Partial trace and reduced density matrix

For a bipartite quantum system with components A and B, the partial trace over A is a linear map such that

$$\mathrm{Tr}_A\ (\mathcal{O}_A \otimes \mathcal{O}_B) = (\mathrm{Tr}_A\ \mathcal{O}_A)\mathcal{O}_B . \tag{39}$$

The result is an operator acting on B only.

The reduced density matrix of B is

$$\rho_B = \mathrm{Tr}_A\ \rho_{AB} , \tag{40}$$

where ρ_{AB} is the full density matrix for the whole system.

It turns out that the reduced density matrix ρ_B correctly produces all the measurement statistics, not only the expectation values. Therefore, it makes sense to treat ρ_B as "the state of B".

As an example, let us get our hands dirty compute ρ_B for our entangled *pure* state. First, the full density matrix is

$$\rho_{AB} = \frac{1}{2} \left(|{\uparrow}\rangle_A \otimes |{\downarrow}\rangle_B + |{\downarrow}\rangle_A \otimes |{\uparrow}\rangle_B \right) \left(\langle{\uparrow}|_A \otimes \langle{\downarrow}|_B + \langle{\downarrow}|_A \otimes \langle{\uparrow}|_B \right) . \tag{41}$$

To take the partial trace, we expand ρ_{AB} and take the partial trace term by term. Note that the cross term vanishes since, e.g., $\mathrm{Tr}\ |{\downarrow}\rangle \langle{\uparrow}| = 0$. Therefore,

$$\begin{aligned} \mathrm{Tr}_A\ \rho_{AB} &= \frac{1}{2} \left((\mathrm{Tr}_A\ \ |{\uparrow}\rangle_A \langle{\uparrow}|_A)(|{\downarrow}\rangle_B \langle{\downarrow}|_B) + (\mathrm{Tr}_A\ \ |{\downarrow}\rangle_A \langle{\downarrow}|_A)(|{\uparrow}\rangle_B \langle{\uparrow}|_B) \right) \qquad (42) \\ &= \frac{1}{2} \left(|{\uparrow}\rangle_B \langle{\uparrow}|_B + |{\downarrow}\rangle_B \langle{\downarrow}|_B \right) , \qquad (43) \end{aligned}$$

which is indeed exactly the same as the ρ_B after the measurement of A.

We see that even if the full system is a *pure* state, its subsystem can be a *mixed* state due to entanglement. We formalize this observation as a theorem without giving the proof:

Theorem 2.1: Entanglement and mixed states

For a bipartite system in a *pure* state, its components A and B are entangled if and only if their reduced density matrices ρ_A, ρ_B are mixed states.

Finally, we end this section with one more interesting example related to statistical mechanics.

Example 2.1: Thermofield double state

We have seen that the quantum canonical ensemble is given by a density matrix

$$\rho = \frac{e^{-\beta H}}{Z} = \frac{1}{Z}\sum_i e^{-\beta E_i} \left|\psi_i\right\rangle \left\langle\psi_i\right| \,, \tag{44}$$

where $|\psi_i\rangle$ are the set of energy eigenstates. Inspired by the above, can this mixed state also arise from a pure state of a larger system? It turns out that this is possible if we create two copies of the same system but with entanglement between them. Consider the **thermofield double state**

$$|TFD\rangle_{AB} = \frac{1}{\sqrt{Z}}\sum_i e^{-\beta E_i/2} \left|\psi_i\right\rangle_A \otimes \left|\psi_i\right\rangle_B \,. \tag{45}$$

The full density matrix is simply

$$\begin{aligned}
\rho_{AB} &= |TFD\rangle_{AB} \langle TFD|_{AB} && (46)\\
&= \frac{1}{Z}\sum_{ij} e^{-\beta E_i/2-\beta E_j/2} \left(|\psi_i\rangle_A \otimes |\psi_i\rangle_B\right)\left(\left\langle\psi_j\right|_A \otimes \left\langle\psi_j\right|_B\right) && (47)\\
&= \frac{1}{Z}\sum_{ij} e^{-\beta E_i/2-\beta E_j/2} |\psi_i\rangle_A \left\langle\psi_j\right|_A \otimes |\psi_i\rangle_B \left\langle\psi_j\right|_B && (48)
\end{aligned}$$

Now we compute the reduced density matrix ρ_B.

$$\begin{aligned}
\rho_B &= \mathrm{Tr}_A\ \rho_{AB} && (49)\\
&= \frac{1}{Z}\sum_{ij} e^{-\beta E_i/2-\beta E_j/2} \left(\mathrm{Tr}_A\ |\psi_i\rangle_A \left\langle\psi_j\right|_A\right)\left(|\psi_i\rangle_B \left\langle\psi_j\right|_B\right) && (50)\\
&= \frac{1}{Z}\sum_{ij} e^{-\beta E_i/2-\beta E_j/2} \delta_{ij} |\psi_i\rangle_B \left\langle\psi_j\right|_B && (51)\\
&= \frac{1}{Z}\sum_{i} e^{-\beta E_i} |\psi_i\rangle \langle\psi_i|_B \,, && (52)
\end{aligned}$$

which is indeed the same as the quantum canonical ensemble. As a fun fact, this state has been very important in describing, e.g., the Hawking temperature of a (two-sided) black hole.

3 From quantum to classical: where is the h?

In the above, we have seen that in quantum statistical mechanics, the partition function (in the canonical ensemble, for example) is

$$Z = \mathrm{Tr}\ e^{-\beta \hat{H}} \,. \tag{53}$$

Instead of spins, let us now think about one particle with 1D position and momentum. In classical statistical mechanics, the partition function is

$$Z = \int \frac{dq\,dp}{h} e^{-\beta H(q,p)} \,. \tag{54}$$

The quantum partition function should reduce back to the classical one, in a way that explains the strange $1/h$ factor in the classical one. However, the reduction is not obvious since in quantum mechanics, q, p cannot be simultaneously observed due to the uncertainty principle.

Here is the proper derivation. For simplicity, let us assume that the Hamiltonian has the simple form

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{q}) \,. \tag{55}$$

We can rewrite the trace into a sum over basis states. Without loss of generality, let us choose the position eigenstates and write

$$Z = \int dq\ \langle q|\, e^{-\beta(\hat{p}^2/2m+V(\hat{q}))}\, |q\rangle \,. \tag{56}$$

It is tempting to factorize the exponential into momentum and position parts, but this is not valid for operators! Instead, the Baker–Campbell–Hausdorff (BCH) formula tells us that

$$e^{\hat{A}}e^{\hat{B}} = e^{\hat{A}+\hat{B}+[\hat{A},\hat{B}]/2+\cdots} . \tag{57}$$

However, since $[\hat{q},\hat{p}] = i\hbar$, the correction terms are $O(\hbar)$ and can be ignored in the *classical* limit. Therefore, we can write

$$\begin{aligned} Z &\simeq \int dq \, \langle q| \, e^{-\beta\hat{p}^2/2m} e^{-\beta V(\hat{q})} \, |q\rangle \qquad (58)\\ &= \int dq \, e^{-\beta V(q)} \, \langle q| \, e^{-\beta\hat{p}^2/2m} \, |q\rangle \; . \qquad (59)\end{aligned}$$

There is still the operator $\hat{p}$, so we insert a complete set of momentum states and get

$$\begin{aligned} Z &= \int dq \, dp \, e^{-\beta V(q)} \, \langle q| \, e^{-\beta\hat{p}^2/2m} \, |p\rangle \, \langle p|q\rangle \qquad (60)\\ &= \int dq \, dp \, e^{-\beta(p^2/2m+V(q))} | \, \langle q|p\rangle \, |^2 \qquad (61)\\ &= \int \frac{dq \, dp}{h} e^{-\beta H(q,p)} \, , \qquad (62)\end{aligned}$$

where we have used the momentum wavefunction

$$\langle q|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipq/\hbar} \, . \tag{63}$$

This is indeed the classical partition function we are familiar with.