Intermediate Quantum Mechanics
Lecture 25 Notes (4/27/15)
Density Matrices I

Classical probability

- Up to now, we've only treated the case in which we definitely know the state of the system, for example, an electron in the state: $|\psi\rangle = \alpha\,|\uparrow\,\rangle + \beta\,|\downarrow\,\rangle$. We now want to treat the rather common situation in which the system is in a definite state but we don't know which one. We only know the probabilities that it is in various states. This type of probability is used in classical physics.

- Imagine a container with ten classical particles in it. In principle, we could know the states (position and momentum) of all ten of these classical particles. Then we would have complete knowledge of their states and the state of the system.

- Let's say though that we are "lazy" and don't want to try to determine the exact state. We can then use probability distributions to obtain some knowledge about the system. For example, if the container is not in a gravitational field (and also is not accelerating), the probability distribution of the position of each particle is uniform. Then we know the average position of a particle is the center point of the container and that, for example, the probability to be in the left half of the container is $1/2$. If we know the temperature, then we know that the average value of the square of the momentum is $\overline{p^2} = 3k_{B}T$.

- In the case of the air molecules in a room, it is not just a matter of being lazy. In a typical room there are about 10^{27} molecules. It is completely impossible to know the star of all 10^{27} molecules, nor would we want to. In this case, we must resort to using probability to describe the gas.

- If all we know is the probability for a system to be in various states, We estimate the average value of a kinematical quantity (position, momentum, angular momentum, energy) by weighting the average value of the quantity for each state by the probability of the state.

$$\overline{A} = \sum_i A_i P_i$$

- If the variable describing the state is continuous this would become an integral:

$$\overline{A} = \int A(x)\rho(x)\,dx$$

where $\rho(x)$ is the probability density.

Mixed states

- Just as for the classical case above, for a quantum system, we might not have complete knowledge of what state the system is in but only know the probabilities of it being in various states.

- An example of this is the polarization of the photons coming from the light source in your room. Every photon that makes up the light is in one of two definite polarization states. We can describe the polarization state of the photon in terms of two mutually perpendicular directions that are each perpendicular to the momentum of the photon. If the photon is moving in the z-direction, these could be the x and y polarization states. The light in your room consists of a huge number of photons (calculate it if you are interested) and you can't possibly know the polarization state of each photon. We then say that the light is unpolarized. That is, there are equal numbers of x and y polarized photons so that the average polarization is zero.

- Another case, might be where a friend gives us a system in a definite state but doesn't tell us which one but just the probabilities fro which states the system might be in. For example he might tells us there is a 70% probability that the state he gave us is $|\uparrow\,\rangle$ and a 30% probability that is is $|\downarrow\,\rangle$. Or, maybe he tells us there is a 50% probability that it is $|\uparrow\,\rangle$ and 50% probability that it is $|\rightarrow\,\rangle$. The state that we have is in a definite state but we don't know with certainty which one.

- In that case, we have a **mixed state**. Since we don't have complete knowledge of which state our friend gave us, our description of the state and our predictions for the results of any measurements on it must include this lack of knowledge. The way to do this is through the **density operator** or **density matrix**.

The density operator

- The density operator is defined by:

$$\hat{\rho} \equiv \sum_i P_i\,|\psi_i\rangle\langle\psi_i|$$

where $|\psi_i\rangle$ are the various states that our friend might have given us and P_i are the probabilities that our friend told us. Note that the probabilities must sum to one. $\sum_i P_i = 1$

- The $|\psi_i\rangle$ states might not be orthogonal. If we are to represent $\hat{\rho}$ as a matrix, we must select an orthonormal basis.

$$\hat{\rho} = \sum_{mn} \rho_{mn}\,|m\rangle\langle n|$$

where $|m\rangle$ and $|n\rangle$ are elements of a set of orthonormal basis vectors.

- We can find the matrix element of $\hat{\rho}$ in this basis by:

$$\rho_{mn} = \langle m|\hat{\rho}|n\rangle = \sum_i P_i\,\langle m\,|\,\psi_i\,\rangle\,\langle\psi_i\,|\,n\,\rangle$$

- Since $\hat{\rho}$ is a Hermitian operator, there is some basis in which its matrix representation is diagonal. The diagonal elements are then the probabilities that the system is in the corresponding basis state. The sum of the diagonal elements must then be one which means that the trace of the matrix must be one. As you

showed in a homework problem some time ago, the trace of a Hermitian matrix is independent of the basis chosen. Therefore, we always have:

$$\mathrm{Tr}\left(\hat{\rho}\right) \;=\; 1$$

If the trace of a matrix is not one, then it is not a density matrix.

- If we definitely know what state we have, then we say we have a pure state. That means the probability of one state is 100% and the probability of all other states is zero. In that case, in the diagonal representation, only one of the diagonal elements will be nonzero. For example:

$$\hat{\rho} \;\longrightarrow\; \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

- If a system has N dimensions and we only know is that there is equal probability that is one of the N basis states, then our lack of information about the state is maximal and we have a maximally mixed state. In that case, in the diagonal representation, all of the diagonal diagonal elements equal $1/N$. For example:

$$\hat{\rho} \;\longrightarrow\; \begin{pmatrix} 1/4 & 0 & 0 & 0 \\ 0 & 1/4 & 0 & 0 \\ 0 & 0 & 1/4 & 0 \\ 0 & 0 & 0 & 1/4 \end{pmatrix}$$

- We could also have a partially mixed state in which more than one of the diagonal elements are non zero but are not all equal.

Expectation values for a mixed state

- If we have a mixed state, then the expectation (average) value of an observable is given by weighing the expectation value for each state by the probability of that state.
$$\overline{A} \;=\; \sum_i P_i \left\langle \psi_i | \hat{A} | \psi_i \right\rangle$$

- In terms of the density operator:

$$\overline{A} \;=\; \sum_i P_i \left\langle \psi_i | \hat{A} | \psi_i \right\rangle \;=\; \sum_i \sum_{mn} P_i \left\langle \psi_i | n \right\rangle \left\langle n | \hat{A} | m \right\rangle \left\langle m | \psi_i \right\rangle$$

$$=\; \sum_{mn} \rho_{mn} A_{nm} \;=\; \mathrm{Tr}\left(\hat{\rho}\hat{A}\right)$$

- Since $\hat{\rho}\hat{A}$ is a Hermitian operator, its trace is independent of basis and we can calculate it in any orthonormal basis. Also, even if two operators don't commute, the trace of their product doesn't depend on the ordering.

$$\overline{A} \;=\; \mathrm{Tr}\left(\hat{\rho}\hat{A}\right) \;=\; \mathrm{Tr}\left(\hat{A}\hat{\rho}\right)$$

Thermodynamic Entropy

- In thermodynamics, entropy is a measure of the "disorder" of a system. The more states available to a system the higher the entropy. In terms of heat exchange and temperature, the change in entropy is given by:

$$dS = \frac{dQ}{T}$$

- If initially a gas is confined to part of a container and then allowed to expand adiabatically to fill the entire container, the change in entropy per molecule of the gas is given by:

$$\Delta S = k_B \ln(V_f/V_i)$$

  If the volume doubles, the change in entropy per molecule increase by $\Delta S = k_B \ln 2$ The entropy isproportional to the ln of the number of states available.

- The Second Law of Thermodynamics states that in any process the entropy of the system increases. This is probably the funniest law in all of physics. All other laws are absolute. In Newtonian mechanics, $F = ma$, no exceptions. In non-relativistic quantum mechanics, the time dependence of a state is given by the Schrodinger equation, no exceptions. In the case of the Second Law of Thermodynamics, obedience is optional. The correct statement of the law is that: In any process the entropy of the system probably increases.

- Consider again a box with ten particles. The probability is 1/2 that any one of the particles is in the left half of the box. The probability that all ten of the particles are in the left half of the box is $(1/2)^{10} \approx 10^{-3}$. If I were to take a photograph every second then in 1000 seconds, $\approx$ 15 minutes it would be likely that there would be one photograph will all of the particles in the left half of the box. That would violate the Second Law of Thermodynamics. If there were a hundred particles in the box, then the probability that all hundred were in the left half of the box would be $(10^{-3})^{10} = 10^{-30}$. Taking one photograph per second it would take about 10^{30} seconds to find all hundred particles in the left half of the box. There are about 10^7 seconds in a year and the universe has existed for about 10^{10} years, 10^{17} seconds. So we would half to wait for a time 13 orders of magnitude longer than the life of the universe to find all of the particle in the left half.

Information Entropy

- A related formulation of entropy is as a measure of the lack of information.

- Consider the situation in which there is a barrier such that all of the air is in one corner of a sealed room. An omniscient being would know the state of every air molecule and would know the exact state of the system. They would have complete information. If the gas is allowed to expand, the omniscient being would lose no information. They would still have complete information on the sate of every air molecule and therefore of the system. After the gas has expanded the information that it saws once all up in one corner is still there. If we were to reverse time and play the "movie" of the expansion backwards, all of the air would go back to the corner of the room.

4

- Since we're not omniscient, we lose information when the gas expands. When the gas is in the corner of the room we don't know where any molecule is in that corner but we do know that the probability is zero for finding it outside of the corner of the room. After the gas expands, there is now an equal probability for an air molecule to be anywhere in the room. Our entropy, lack of information has increased.

- The information contained in the system has not changed. The entropy of the system to an omniscient being is the same, $S = 0$ both before and after the expansion. The entropy for us depends on our lack of information. If someone else has more information about the system, then the entropy for them would be less.

- For a classical system, information entropy is given by:

$$S = -\sum_i P_i \log P_i$$

- If only one P_i is non-zero, we definitely know the state that the system is in and the entropy (lack of information) is zero. $S = 1 \log 1 = 0$

- If there is equal probability $1/n$ for the system to in any of n states and the probability to be in any state other than these n states is zero, then:

$$S = -\sum_{i=1}^{n} \frac{1}{n} \log(1/n) = \sum_{i=1}^{n} \frac{1}{n} \log n = \log n$$

- We may the log to any base, but if we choose base 2, then $S = \log_2 n$ is the number of bits of information that we lack.

- For a system with a total of N possible states, the maximum entropy is when the system has equal probability of being in any of the N states. $S_{\text{max}} = \log N$

Entropy of a quantum system

- For a quantum system, the formula corresponding to $S = -\sum_i P_i \log P_i$ is:

$$S = -\operatorname{Tr}(\hat{\rho} \log \hat{\rho})$$

- Here $\log \hat{\rho}$ is a function of the operator, $\hat{\rho}$. It is given by the log power series. In the basis in which $\hat{\rho}$ is diagonal,

$$\log \hat{\rho} \longrightarrow \begin{pmatrix} \log p_1 & \cdot & & \cdot & \cdot \\ \cdot & \log p_2 & \cdot & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot \end{pmatrix}$$

- As for the classical case, if the system is definitely in one state, then $S = 1 \log 1 = 0$

- If there is equal probability $1/n$ for the system to in any of n states and the probability to be in any state other than these n states is zero, then: $S = \log n$. As an example, in the two dimensional case of electron spin, the diagonalized

density matrix for maximal entropy is:

$$\hat{\rho} \longrightarrow \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

The entropy is then:

$$S = -\operatorname{Tr}\left(\hat{\rho}\log\hat{\rho}\right) \longrightarrow -\operatorname{Tr}\begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}\begin{pmatrix} \log(1/2) & 0 \\ 0 & \log(1/2) \end{pmatrix} = \log 2$$