Physics Through Problem Solving XXVII: Density Matrix

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In this issue we shall solve some short problems on density matrix.

INTRODUCTION

Consider a quantum system in the state $|\psi\rangle$. If A is an observable, the expectation value of A is given by

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle \tag{1}$$

where $\hat{A}$ is the quantum mechanical operator for A. Here onwards we shall omit the hat and use the same symbol for both the observable and its quantum operator. We understand $\langle A \rangle$ as a quantum mechanical average of an observable quantity A, if the system is in the state $|\psi\rangle$. That is, the average value of A obtained, when the system is repeatedly prepared in the state $|\psi\rangle$ and A is measured.

Now consider the following. There is a two state system, with states given by $|\psi_1\rangle$ and $|\psi_2\rangle$. And suppose we do not know for sure in which state the system is – $|\psi_1\rangle$ or $|\psi_2\rangle$. We only know the *probabilities* p_1 and p_2 that the system is in the states $|\psi_1\rangle$ and $|\psi_2\rangle$ respectively ($p_1 + p_2 = 1$). What is the expectation value of A in this case?

If you think it is $\langle \psi | A | \psi \rangle$, with $|\psi\rangle = p_1|\psi_1\rangle + p_2|\psi_2\rangle$ (it seems the 'natural' thing to do!), you are wrong! Superpositions like this do not describe a system which is *either* in the state $|\psi_1\rangle$ *or* in the state $|\psi_2\rangle$, but a system which is *simultaneously in both the states* $|\psi_1\rangle$ *and* $|\psi_2\rangle$. The system we are considering *cannot* be represented by a single wavefunction or state vector like $|\psi_1\rangle$ or $|\psi_2\rangle$, or any of their linear superposition. This kind quantum states which cannot be represented by state vectors are known as 'statistical mixtures', or 'mixed states'.

The quantum states that can be represented by state vectors are called 'pure states'. These are the states that we study in quantum mechanics, when we are not concerned with statistics. But when we deal with a statistical mixture described above, we have to specify it with a set of pure states and the corresponding probabilities. We can neatly pack this information in a matrix, known as 'Density Matrix', usually denoted by ρ. And the density matrix completely specifies a mixed state, just as a state vector completely specifies a pure state.

Let us come back to the question we started with. It is not difficult to find the expectation value of A for the situation described above. If the system is in the state $|\psi_1\rangle$ the expectation value of A is $\langle\psi_1|A|\psi_1\rangle$, which obviously has a probability p_1. Similarly the expectation value is $\langle\psi_2|A|\psi_2\rangle$ with a probability p_2. So the average expectation value is (expectation value of expectation values!)

$$\langle A\rangle = p_1\langle\psi_1|A|\psi_1\rangle + p_2\langle\psi_2|A|\psi_2\rangle \qquad (2)$$

We can readily generalize the above result - consider a system which can be in states $|\psi_i\rangle$ with probabilities p_i, where $i = 1, 2, 3, \ldots n$, and $\{|\psi_i\rangle\}$ forms a complete orthonormal basis for the system Hilbert space. The expectation value of observable A is

$$\begin{aligned}\langle A\rangle &= \sum_{i=1}^{n} p_i\langle\psi_i|A|\psi_i\rangle \\ &= \mathrm{tr}(\rho A)\end{aligned} \qquad (3)$$

where the operator ρ, know as the *density operator* or *density matrix* is given by

$$\rho = \sum_{i=1}^{n} p_i|\psi_i\rangle\langle\psi_i| \qquad (4)$$

Since p_i's are probabilities, $0 \leq p_i \leq 1$ and $\sum_{i=1}^{n} p_i = 1$.

We are also interested in what value we obtain for an observable A when we perform a measurement. For a pure state ψ (normalized) it is one of the eigenvalues of A, say a_i, with the probability $|\langle a_i|\psi\rangle|^2$, where $|a_i\rangle$ is the normalized eigenstate for the eigenvalue a_i. Now consider a mixture given by a density matrix ρ. The probability that this measurement yields the value a_i is

$$P(A = a_i) = \langle a_i|\rho|a_i\rangle \qquad (5)$$

The derivations of the relations (3) and (5) are simple and can be found in any statistical mechanics text book, and so are the following important properties of a density matrix, which we just state here.

The diagonal elements of ρ are probabilities and therefore

$$0 \leq \rho_{ii} \leq 1 \qquad (6)$$

The density matrix is Hermitian:

$$\rho^\dagger = \rho \qquad (7)$$

It has unit trace:

$$\mathrm{tr}(\rho) = 1 \qquad (8)$$

For a pure state

$$\mathrm{tr}(\rho^2) = 1 \tag{9}$$

For a mixed state

$$\mathrm{tr}(\rho^2) < 1 \tag{10}$$

For a canonical ensemble in thermal equilibrium

$$\rho = \frac{e^{-\beta H}}{\mathrm{tr}(e^{-\beta H})} \tag{11}$$

where $\beta = 1/k_B T$ and H is the Hamiltonian operator. The time evolution of the density matrix is given by

$$i\hbar\frac{\partial \rho}{\partial t} = [\rho, H] \tag{12}$$

which is known as Liouville-von Neumann equation, and can be considered as the generalization of Schrödinger equation for systems in mixed states.

Now we turn to solving some simple problems

PROBLEMS AND SOLUTIONS

Problem 1. Consider a spin-1/2 system and the eigenbasis of the operator S_z (i.e., z-component of angular momentum). Write the density matrices for the following and calculate the traces. $|a\rangle, |b\rangle$ are eigenstates of S_z for the eigenvalues $\pm\hbar/2$

(a) The pure state given by $|\psi\rangle = c_1|a\rangle + c_2|b\rangle$; c_1, c_2 are two complex numbers such that $|\psi\rangle$ is normalized, i.e., $|c_1|^2 + |c_2|^2 = 1$

(b) The mixed state specified as : $|a\rangle$ with probability 2/3, $|b\rangle$ with probability 1/3

Solution

(a) We have the general definition in equation (4). Here we have only one state, $|\psi\rangle$, with $p = 1$. Thus

$$\begin{aligned}\rho &= |\psi\rangle\langle\psi| \\ &= (c_1|a\rangle + c_2|b\rangle)(c_1^*\langle a| + c_2^*|\langle b|) \\ &= |c_1|^2|a\rangle\langle a| + c_1^* c_2|b\rangle\langle a| + c_1 c_2^*|a\rangle\langle b| + |c_2|^2|b\rangle\langle b|\end{aligned} \tag{13}$$

In doing the above algebra with bras and kets it is important to remember to maintain the order, because $|b\rangle\langle a| \neq |a\rangle\langle b|$ and so on. Now let us write ρ above in matrix form (in the basis $\{|a\rangle, |b\rangle\}$):

$$\begin{aligned}\rho &= \begin{pmatrix}\langle a|\rho|a\rangle & \langle a|\rho|b\rangle \\ \langle b|\rho|a\rangle & \langle b|\rho|b\rangle\end{pmatrix} \\ &= \begin{pmatrix}|c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2\end{pmatrix}\end{aligned} \tag{14}$$

In evaluating the matrix elements above we have used (13) and the orthonormality of $|a\rangle$ and $|b\rangle$. Thus $\mathrm{tr}(\rho) = |c_1|^2 + |c_2|^2$, which is 1, as assumed in the beginning. The matrix diagonal elements are positive and lie between 0 and 1, and $\rho^\dagger = \rho$. Since the system is in a pure, we must have $\mathrm{tr}(\rho^2) = 1$. The reader can take the square of the matrix ρ and check the trace is $|c_1|^4 + 2|c_1c_2|^2 + |c_2|^4 = (|c_1|^2 + |c_2|^2)^2 = 1$.

(b) In this case we have two states $|a\rangle$ and $|b\rangle$ with respective probabilities 2/3 and 1/3, and therefore

$$\rho = \frac{2}{3}|a\rangle\langle a| + \frac{1}{3}|b\rangle\langle b|$$

In matrix form

$$\begin{aligned}\rho &= \begin{pmatrix} \langle a|\rho|a\rangle & \langle a|\rho|b\rangle \\ \langle b|\rho|a\rangle & \langle b|\rho|b\rangle \end{pmatrix} \\ &= \begin{pmatrix} 2/3 & 0 \\ 0 & 1/3 \end{pmatrix}\end{aligned}$$

Once again $\mathrm{tr}(\rho) = 1$ and $\rho^\dagger = \rho$. But now the system is in a mixed sate, and therefore $\mathrm{tr}(\rho^2) = 4/9 + 1/9 = 5/9 < 1$.

Problem 2. In the above problem, find the expectation value of S_z in the pure and the mixed states.

Solution

For the pure state

$$\begin{aligned}\langle S_z\rangle &= \langle\psi|S_z|\psi\rangle \\ &= (c_1^*\langle a| + c_2^*|\langle b|)S_z(c_1|a\rangle + c_2|b\rangle) \\ &= (c_1^*\langle a| + c_2^*|\langle b|)(c_1S_z|a\rangle + c_2S_z|b\rangle) \\ &= (c_1^*\langle a| + c_2^*|\langle b|)\frac{\hbar}{2}(c_1|a\rangle - c_2|b\rangle) \\ &= \frac{\hbar}{2}(|c_1|^2 - |c_2|^2)\end{aligned}$$

We have used above $S_z|a\rangle = (\hbar/2)|a\rangle$, $S_z|b\rangle = (-\hbar/2)|b\rangle$. For the mixed state

$$\begin{aligned}\langle S_z\rangle &= \mathrm{tr}(\rho S_z) \\ &= \mathrm{tr}\left\{\begin{pmatrix} 2/3 & 0 \\ 0 & 1/3 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right\} \\ &= \frac{\hbar}{6}\end{aligned}$$

Next we consider a slightly more complex problem.

Problem 3. Consider a spin-1 system and the eigenbasis of the operator J_z. Write the density matrix for the system in the mixed state: states $|a\rangle$, $(|a\rangle + |b\rangle)/\sqrt{2}$ and $(|b\rangle + |c\rangle)/\sqrt{2}$, each with probability 1/3. $|a\rangle$, $|b\rangle$, and $|c\rangle$ are the normalized eigenstates of J_z for the three eigenvalues $\hbar, 0$ and $-\hbar$ respectively. Find the expectation value and the variance of J_z.

Solution

$$\rho = \frac{1}{3}|a\rangle\langle a| + \frac{1}{3}\cdot\frac{1}{2}(|a\rangle + |b\rangle)(\langle a| + \langle b|) + \frac{1}{3}\cdot\frac{1}{2}(|b\rangle + |c\rangle)(\langle b| + \langle c|)$$
$$= \frac{1}{6}\{3|a\rangle\langle a| + 2|b\rangle\langle b| + |c\rangle\langle c| + |a\rangle\langle b| + |b\rangle\langle a| + |b\rangle\langle c| + |c\rangle\langle b|\} \tag{15}$$

In matrix form

$$\rho = \begin{pmatrix} \langle a|\rho|a\rangle & \langle a|\rho|b\rangle & \langle a|\rho|c\rangle \\ \langle b|\rho|a\rangle & \langle b|\rho|b\rangle & \langle b|\rho|c\rangle \\ \langle c|\rho|a\rangle & \langle c|\rho|b\rangle & \langle c|\rho|c\rangle \end{pmatrix} = \frac{1}{6}\begin{pmatrix} 3 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 1 \end{pmatrix} \tag{16}$$

As we expect, the diagonal elements of ρ are between 0 and 1, $\rho^\dagger = \rho$, $\mathrm{tr}(\rho) = 1$ and $\mathrm{tr}(\rho^2) = 1/2 < 1$.

The operator J_z in its own eigenbasis is given by

$$J_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

And the expectation value

$$\langle J_z\rangle = \mathrm{tr}(\rho J_z) = \mathrm{tr}\left\{\frac{1}{6}\begin{pmatrix} 3 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 1 \end{pmatrix}\hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right\} = \frac{\hbar}{3}$$

And

$$\langle J_z^2\rangle = \mathrm{tr}(\rho J_z^2) = \mathrm{tr}\left\{\frac{1}{6}\begin{pmatrix} 3 & 1 & 0 \\ 1 & 2 & 0 \\ 0 & 1 & 1 \end{pmatrix}\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\right\} = \frac{2\hbar^2}{3}$$

which gives the variance

$$\mathrm{Var}(J_z) = \langle J_z^2\rangle - \langle J_z\rangle^2 = \frac{2\hbar^2}{3} - \frac{\hbar^2}{9} = \frac{5\hbar^2}{9}$$

Problem 4. For the system in problem 3, what is the probability that a measurement of J_z will result in a value $\hbar$?

Solution

To get the value $\hbar$, the system has to be found in the state $|a\rangle$. Using the relation in equation (5)

$$P(J_z = \hbar) = \langle a|\rho|a\rangle$$

Substituting for ρ from equation (15) we readily get

$$P(J_z = \hbar) = \frac{1}{2}$$

which you can see that is the first diagonal element in the matrix for ρ in equation (16). From the same logic you can see that the other two diagonal elements, 1/3 and 1/6, are the probabilities for getting $J_z = 0$ and $J_z = -1$. In general the diagonal elements of density matrix give the probabilities of finding the system in the basis states - which you can readily see by comparing the equation (5) and the form the diagonal elements of ρ.