

Physics 342 Lecture 39

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Well, this is it; the final quantum mechanics lecture. I wish I could have delivered it under different circumstances, given you a bow-tie tying course, but alas. Nevertheless, I hope you have enjoyed the course and have even learned a little bit.

In this final lecture on the density matrix, we're going to do some examples and derive a useful expression for the density matrix in a particular limit. As an example, let's go back to our spin- $1/2$ buddies and construct the density matrix for a collection of spin- $1/2$ particles. Let's say that we have a partially polarized beam for which ~~is~~ a fraction 0.75 are polarized in the $+S_z$ direction and 0.25 of the sample are polarized along the $+S_x$ direction. So, our density matrix is

$$\rho = \frac{3}{4} |\uparrow_z\rangle\langle\uparrow_z| + \frac{1}{4} |\uparrow_x\rangle\langle\uparrow_x|$$

Now, this is perfectly fine, but let's re-express this in the orthonormal basis of z spin up and down. To do this, we exploit the fact that

$$|\uparrow_z\rangle\langle\uparrow_z| + |\downarrow_z\rangle\langle\downarrow_z| = 1 \text{ and eigenstates of } \hat{S}_x \text{ can be expressed as: } |\uparrow_x\rangle = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle + |\downarrow_z\rangle), |\downarrow_x\rangle = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle - |\downarrow_z\rangle).$$

Then, our density matrix is:

$$\rho = \frac{3}{4} |\uparrow\rangle\langle\uparrow| + \frac{1}{4} \cdot \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} (|\uparrow\rangle + |\downarrow\rangle) (\langle\uparrow| + \langle\downarrow|)$$

$$\begin{aligned}
 &= \frac{3}{4} |\uparrow\rangle\langle\uparrow| + \frac{1}{8} |\uparrow\rangle\langle\uparrow| + \frac{1}{8} |\uparrow\rangle\langle\downarrow| + \frac{1}{8} |\downarrow\rangle\langle\uparrow| + \frac{1}{8} |\downarrow\rangle\langle\downarrow| \\
 &= \frac{7}{8} |\uparrow\rangle\langle\uparrow| + \frac{1}{8} |\uparrow\rangle\langle\downarrow| + \frac{1}{8} |\downarrow\rangle\langle\uparrow| + \frac{1}{8} |\downarrow\rangle\langle\downarrow|.
 \end{aligned}$$

Here, we have dropped the z subscript $\frac{1}{2}$ as all of these spin states are eigenstates of \hat{S}_z . Now, we can write this as an explicit 2×2 matrix, just reading off the coefficients of the terms in this representation of the density matrix:

$$\rho = \begin{pmatrix} \frac{7}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} \end{pmatrix}. \text{ Note that indeed } \text{tr} \rho = 1.$$

$$\text{Additionally } \rho^2 = \begin{pmatrix} \frac{7}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} \end{pmatrix} \begin{pmatrix} \frac{7}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} \end{pmatrix} = \begin{pmatrix} \frac{50}{64} & \frac{8}{64} \\ \frac{8}{64} & \frac{2}{64} \end{pmatrix} = \begin{pmatrix} \frac{25}{32} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{32} \end{pmatrix}.$$

Note that $\rho^2 \neq \rho$, so this is not a pure state, as expected. Further, the $S^{(1)}$ entropy is:

$$S^{(1)} = \text{tr}(\rho - \rho^2) = \text{tr} \left[\begin{pmatrix} \frac{7}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} \end{pmatrix} - \begin{pmatrix} \frac{25}{32} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{32} \end{pmatrix} \right] = 1 - \frac{26}{32} = \frac{3}{16} \neq 0,$$

again demonstrating that this is not a pure state. What about the von Neumann entropy? We need to calculate

$$S_{\text{vN}} = -\text{tr}(\rho \ln \rho) = -\sum_i \rho_{ii}^{(\text{diag})} \ln \rho_{ii}^{(\text{diag})}, \text{ when the density}$$

matrix is expressed in diagonal form. When diagonal, the density matrix elements that are non-zero are just its eigenvalues; hence another way to express the von Neumann entropy is:

$$S_{\text{vN}} = -\sum_i \lambda_i \ln \lambda_i, \text{ where } \{\lambda_i\} \text{ are the eigenvalues}$$

of the density matrix. We can find the eigenvalues with the old trick that $\det \rho = \lambda_1 \lambda_2$, $\text{tr} \rho = \lambda_1 + \lambda_2$. As $\text{tr} \rho = 1$, $\lambda_2 = 1 - \lambda_1$, so $\det \rho = \lambda(1 - \lambda)$. The determinant of this matrix is:

$$\det \rho = \begin{vmatrix} \frac{7}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} \end{vmatrix} = \frac{7}{64} - \frac{1}{64} = \frac{3}{32}, \text{ so the eigenvalues}$$

satisfy: $\lambda^2 - \lambda + \frac{3}{32} = 0$. Then, $\lambda = \frac{1}{2} \pm \frac{1}{2} \sqrt{1 - \frac{3}{8}} = \frac{1}{2} \pm \frac{1}{2} \sqrt{\frac{5}{8}}$. Using this result, we find

$$\begin{aligned} S_{\text{vN}} &= - \left(\frac{1}{2} + \frac{1}{2} \sqrt{\frac{5}{8}} \right) \ln \left(\frac{1}{2} + \frac{1}{2} \sqrt{\frac{5}{8}} \right) - \left(\frac{1}{2} - \frac{1}{2} \sqrt{\frac{5}{8}} \right) \ln \left(\frac{1}{2} - \frac{1}{2} \sqrt{\frac{5}{8}} \right) \\ &= -\frac{1}{2} \ln \left[\frac{1}{4} - \frac{5}{32} \right] + \frac{1}{2} \sqrt{\frac{5}{8}} \ln \left[\frac{1 - \sqrt{\frac{5}{8}}}{1 + \sqrt{\frac{5}{8}}} \right] \end{aligned}$$

$\approx 0.33532\dots$, which is indeed non-zero and positive.

For a final exercise this semester, let's formulate the property of thermal equilibrium in this quantum statistical language. If a system is in thermal equilibrium, as studied in Physics 202 or perhaps Physics 351, the most important property is that the system is time-independent. Individual components or particles of the system might still have non-trivial dynamics (like the air molecules in the room), but in aggregate, all of those little, microscopic fluctuations average out to statis in a large ensemble. Hence, the density matrix is time independent:

$$\frac{d\rho}{dt} = 0, \text{ or } \rho \text{ commutes with the Hamiltonian: } [\hat{H}, \rho] = 0.$$

Further, as the density matrix is constant, the total energy

of the system (the internal energy) is also constant. With N particles in the system, the average energy per particle is:

$$\langle H \rangle = \text{tr}(\rho H) = \sum_i g_{ii} E_i = \text{constant}.$$

Note that because $[\hat{H}, \rho] = 0$, we can choose a basis in which the density matrix and Hamiltonian are simultaneously diagonalized, hence the simple sum over ~~the~~ eigenenergies E_i weighted by probability $g_{ii} = w_i$.

The final quality we enforce in thermal equilibrium is more subtle. We will assume that entropy is maximized for a given total energy in equilibrium. I won't discuss this in detail, but recall that thermal equilibrium means that ~~no~~^{net} heat (i.e., energy) can be transferred from the system to the environment; otherwise, it wouldn't be in equilibrium. Entropy is a measure of the energy per unit temperature; namely

$$dS = \frac{dQ}{T}, \text{ where } dQ \text{ is the work}$$

done by the system and T is its temperature. Thus, if $dQ = 0$ in thermal equilibrium, then so too must $dS = 0$. Thus, entropy is extremized in equilibrium, and the second law of thermodynamics identifies that extremum to be a maximum.

So, in thermal equilibrium, we have:

$$1) \frac{dS}{dt} = 0, \quad 2) \sum_i g_{ii} E_i = \text{constant}, \quad 3) dS = 0,$$

$$\text{and also } \text{tr} \rho = \sum_i g_{ii} = 1.$$

With these constraints, we would like to determine the entries of the diagonalized density matrix (its eigenvalues in an arbitrary basis), p_{ii} . We do this with the method of Lagrange multipliers. First, we identify all of our constraints which are required:

$$-\sum_i p_{ii} E_i = \text{constant} \Rightarrow \sum_i \delta p_{ii} E_i = 0, \text{ where } \delta p_{ii} \text{ is its variation.}$$

$$-dS_{vN} = 0 = \delta \sum_i p_{ii} \ln p_{ii} = \sum_i \delta p_{ii} (\ln p_{ii} + 1)$$

$$-\text{tr } \rho = \text{constant} \Rightarrow \sum_i \delta p_{ii} = 0.$$

Now, we sum together the constraints, weighted by the Lagrange multipliers β and γ :

$$\sum_i \delta p_{ii} \left[(\ln p_{ii} + 1) + \beta E_i + 1 \cdot \gamma \right] = 0.$$

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 $\delta S_{vN} = 0$ $\langle H \rangle = \text{const}$ $\text{tr } \rho = 1$

For this to vanish for arbitrary variation δp_{ii} , each term in the sum must be 0:

$$\ln p_{ii} + 1 + \beta E_i + \gamma = 0, \text{ or that } p_{ii} = e^{-\gamma-1} e^{-\beta E_i}.$$

Now, using the normalization of the trace of ρ , we can solve for γ :

$$\text{tr } \rho = 1 = \sum_i p_{ii} = e^{-\gamma-1} \sum_i e^{-\beta E_i}, \text{ or that } e^{\gamma+1} = \sum_i e^{-\beta E_i}.$$

You might recognize this as the thermodynamic partition function and the elements of the density

matrix is the canonical ensemble:

$$p_{ii} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \equiv \frac{1}{Z} e^{-\beta E_i}, \text{ where } Z = \sum_i e^{-\beta E_i} \text{ is the partition function.}$$

Everything we can possibly ask about our system is encoded in the partition function, and in thermodynamics, the ~~the~~ Lagrange multiplier β is identified with inverse temperature: $\beta = 1/k_B T$, where k_B is the Boltzmann constant.

Now, you can go to town with the partition function, but I want to connect it to something we were recently introduced to: the path integral. First, note that the partition function is compactly expressed in a basis independent way as:

$$Z = \text{tr}(e^{-\beta \hat{H}}), \text{ where } \hat{H} \text{ is the Hamiltonian.}$$

Recall that the path integral was

$Z = \int [dx] e^{\frac{iS[x]}{\hbar}}$. Though I have used the same letter, Z , to denote them, the partition function and path integral are not the same. Right? I mean, the path integral has an imaginary number and the action, not Hamiltonian, in the exponent.

Well, let's look at this exponent more carefully. The exponent in the path integral is:

$$\frac{i}{\hbar} \int_0^T dt \left[\frac{m}{2} \dot{x}^2 - V(x) \right] = \frac{iS[x]}{\hbar}.$$

Now, let's see if we can massage the path integral into a form like the partition function. I'm going to do something really crazy: let's complexify time t , introducing a new coordinate $\tau = it$. Thus, the integration measure is: $dt = -i d\tau$. Further, we have to account for the time derivative in the kinetic energy. Note that

$$\dot{x} = \frac{dx}{dt} = i \frac{dx}{d\tau}, \text{ so that the kinetic energy is}$$

modified to: $\frac{m}{2} \dot{x}^2 \rightarrow -\frac{m}{2} \left(\frac{dx}{d\tau}\right)^2 \equiv -\frac{m}{2} \dot{x}^2$, where now $\dot{}$ means derivative wrt τ .

With these identifications, the factor in the exponent becomes:

$$\frac{i}{\hbar} S[x] = \frac{i}{\hbar} \int_0^{-i\tau} (-i) d\tau \left[-\frac{m}{2} \dot{x}^2 - V(x) \right] = -\frac{1}{\hbar} \int_0^{-i\tau} d\tau H(x, \dot{x}),$$

where $H(x, \dot{x})$ is the Hamiltonian (albeit with weird coordinates).

~~Now, assuming that the~~

Now, the path integral with imaginary time is:

$$Z(\tau = it) = \int [dx] e^{-\frac{1}{\hbar} \int_0^{-i\tau} d\tau H(x, \dot{x})}$$

Further, by completeness of the eigenstates of the Hamiltonian, the imaginary time path integral can be re-expressed in terms of eigenvalues of the Hamiltonian. The path integral sums over every possible state/trajectory between two points, but this sum in position space can be re-organized into a sum over all energy eigenstates, as the position and energy bases are both complete. Hence the sum over paths is also just a sum, or trace over energy eigenstates:

$$Z = \int [dx] e^{-\frac{i}{\hbar} \int_0^T dt H(x, \dot{x})} = \text{tr} \left(e^{-\frac{\hat{H} T}{\hbar}} \right), \text{ where } \hat{H} \text{ is}$$

now the Hamiltonian operator. Now, we see that the parameter $\beta = T/\hbar$, where \hbar is Planck's reduced constant and T is the "time" over which we integrate.

Hence, "time" is inversely related to temperature, in the thermodynamic representation. So, I really mean it when I say that the path integral is everything; the path integral is life.

Thank you again for a wonderful semester and I hope to see you (in person!) in the fall.

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