LECTURE 29:

Friday, April 03, 2020

Theorem 0.0.1 (Spectral Theorem for a General Quantum State)**.** *Suppose we have a quantum state W with $Wkt\psi_n = p_n |\psi_n\rangle$ and $\langle\psi_n|\psi_m\rangle = \delta_{nm}$ and $\sum_n |\psi_n\rangle\langle\psi_n| = 1$. This means that $\{|\psi_n\rangle\}$ is an eigenbasis of the Hilbert space to the state W. This means we can write*

$$W = \sum_n p_n |\psi_n\rangle\langle\psi_n|$$

where $0 \le p_n \le 1$ and $\sum_n p_n = 1$, which follows from $\mathrm{Tr}(W) = 1$.

In this framework, what do we mean by expectation value?

$$\begin{aligned}\langle A\rangle = \mathrm{Tr}(WA) &= \mathrm{Tr}\left(\sum_n p_n |\psi_n\rangle\langle\psi_n| A\right) \\ &= \sum_n p_n \mathrm{Tr}(|\psi_n\rangle\langle\psi_n| A) \\ &= \sum_n p_n \sum_m \langle\psi_m|\psi_n\rangle\langle\psi_n| A |\psi_m\rangle \\ &= \sum_n p_n \underbrace{\langle\psi_n|A|\psi_n\rangle}_{\text{objective indeterminacy}}\end{aligned}$$

The term objective indeterminacy is something that is new in quantum mechanics. The value of this matrix element causes the result to not necessarily be deterministic. The p_n give subjective ignorance, a sense that we have not measured the state carefully enough. This is because the original state that we worked with is not pure.

The entropy of a state is a measure of our subjective ignorance plus, in quantum mechanics, the objective indeterminacy. Classicaly, the entropy is bounded by $-\infty \le S \le k_B \ln\left(\int_\Gamma \frac{\mathrm{d}p\mathrm{d}q}{h}\right) = +\infty$ if $\Gamma = \mathbb{R}^2$. In quantum mechanics, however, $0 \le S \le k_B \ln(\dim\mathcal{H}) = +\infty$ if $\mathcal{H} = L^2(\mathbb{R})$. The interesting thing is that the entropy cannot get arbitrarily small, it's bounded below by 0. This looks a lot like it has something to do with the third law of thermodynamics. For quantum mechanics, we can prove this:

$$W\ln(W) = \sum_n p_n \ln(p_n) |\psi_n\rangle\langle\psi_n|$$

This implies

$$S = -k_B \mathrm{Tr}(W\ln(W)) = -k_B \sum_n p_n \ln(p_n)$$

If we have maximal knowledge about the system, then we have minimal entropy. Maximal knowledge means that $p_n = \delta_{n,n_0}$ (we know the system is exactly in one pure state). This makes $S = 0$ since $1\ln(1) = 0\ln(0) = 0$. Conversely, if we have minimal knowledge, we have maximal entropy. In that case, $p_n = \frac{1}{N}$ where $N = \dim\mathcal{H}$. If so, then

$$S = -k_B \sum_{n=1}^N \frac{1}{N}\ln\left(\frac{1}{N}\right) = -k_B \ln\left(\frac{1}{N}\right) = k_B\ln(N) = k_B\ln(\dim\mathcal{H})$$

which is infinite if the Hilbert space square-integrable over the reals.

0.1 The Quantum Canonical Ensemble

By analogy with the classical case, we can reasonably guess that the quantum canonical state is given by

$$W = \frac{1}{Z}e^{=\beta H}$$

Note that this is an operator, since H is an operator. The partition function must be

$$Z = \mathrm{Tr}\big(e^{-\beta H}\big)$$

Since H is self-adjoint (and hopefully compact) its eigenvalues are real and its eigenvectors form an orthonormal basis of Hilbert space:

$$H\left|n\right\rangle = E_n \left|n\right\rangle$$

such that $\left|n\right\rangle$ is an energy eigenvector. This corresponds to a pure energy eigenstate $\left|n\right\rangle\left\langle n\right|$ with the corresponding eigenvalue E_n. The fact that this basis is orthonormal means $\langle n|m\rangle = \delta_{nm}$ and $H = \sum_n E_n \left|n\right\rangle\left\langle n\right|$. This is the spectral theorem for (compact) operators.

Since the canonical state is a function of H, it is diagonal in the same basis as H. Therefore,

$$\begin{aligned} Z = \mathrm{Tr}\big(e^{-\beta H}\big) &= \sum_n \left\langle n\right| e^{-\beta H} \left|n\right\rangle \\ &= \sum_n \left\langle n\right| e^{-\beta E_n} \left|n\right\rangle \\ &= \sum_n e^{-\beta E_n} \end{aligned}$$

It could happen that the Hamiltonian is degenerate. If we have degenerate eigenstates of H, we can (if we want) sum over the energy levels, but then we need to explicitly multiply back the degeneracy:

$$Z = \sum_n e^{-\beta E_n} = \sum_l \Omega(l) e^{-\beta E_l}$$

where l is an energy level and $\Omega(l)$ is the degeneracy of the level.

0.1.1 Thermal Averages

$$\langle A\rangle = \langle A, W\rangle = \mathrm{Tr}(AW) = \sum_n \left\langle n\right| AW \left|n\right\rangle$$

where $\left|n\right\rangle$ is the energy eigenbasis and W is the canoical state. Then we get that

$$\begin{aligned} \langle A\rangle &= \sum_n \left\langle n\right| A e^{-\beta E_n} \frac{1}{Z} \left|n\right\rangle \\ &= \sum_n p_n \langle n|A|n\rangle \end{aligned}$$

The matrix element is agains a measure of objective indeterminacy while the p_n factors are a measure of subjective ignorance.