

## 4.10: Quantal Statistical Mechanics

How shall we define a partition function for quantal systems? A reasonable first guess is that

$$Z(T, \text{parameters}) = \sum_{\text{all quantal states}} e^{-\beta E}. \quad [\text{first guess}]$$

This guess runs into problems immediately. Most quantal states are not energy eigenstates, so it's not clear how to interpret " $E$ " for such states. Another difficulty—harder to see—arises because there are many more quantal states than classical states, so the guess above is in some sense counting too many states. It's hard to see how it could have the correct classical limit. (Indeed, a mathematical investigation of the above guess would reveal that it doesn't even have the correct thermodynamic limit—if you were to calculate the Helmholtz free energy from the above guess, the resulting  $F(T, V, N)$  would increase far faster than linearly with system size.) A second guess might be

$$Z(T, \text{parameters}) = \sum_{\text{all energy eigenstates}} e^{-\beta E}. \quad [\text{second guess}]$$

This avoids the problem of how to interpret  $E$  for non-energy eigenstates, but there still seems to be an over-counting of states in the case of an energy degeneracy: If two energy eigenstates are separate in energy by any amount, no matter how small, those two energy eigenstates will contribute two terms to the above sum. But if the energy separation vanishes, then all linear combinations of the two states are also energy eigenstates, and each of this infinite number of combinations will enter into the sum.

Finally we arrive at a workable definition for quantal partition function, namely

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenbasis } n} e^{-\beta E_n}. \quad (4.10.1)$$

Note that this is a sum over an *energy eigenbasis*, not over energy eigenvalues. These two sums differ through degeneracy: If  $E_6 = E_5$ , then two equal terms enter into the sum. More formally: if  $N(m)$  is the degeneracy of eigenvalue  $m$ , that is, the number of linearly independent states with energy  $E_m$ , then

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenvalues } m} N(m) e^{-\beta E_m}. \quad (4.10.2)$$

The above argument has a strange, *ex post facto* character: We define the quantal partition function not from first principles, but to insure that it has properties that we consider desirable (namely, that it avoids subtle interpretation issues, it possesses the expected classical limit, and it has desirable behavior at level crossings). Linear combinations of energy eigenstates are quantal states just as legitimate as energy eigenstates, so why do we ignore them in the sum? The argument reminds me of politics at its worst: "I'm going to pass this law because I want it, even though I can't support it with any rationale." The resulting definition of partition function is strange in that it seems to select the energy eigenbasis as some sort of God-given basis, "better" than any other basis. In fact, the result is not as bad as it seems. It turns out (see problem 4.2) that our definition can be rephrased in a basis-independent manner as

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenbasis } n} e^{-\beta E_n} = \sum_{\text{any basis } j} \langle j | e^{-\beta \hat{H}} | j \rangle. \quad (4.10.3)$$

If you don't know what it means to exponentiate the Hamiltonian operator  $\hat{H}$ , don't worry. For this book—and for most practical calculations—the most effective definition is the form on the left. The point is simply that the definition of partition function *can* be cast into the basis-independent form on the right. The energy eigenbasis is *not* special.

In this chapter we have often found, first, results about probabilities, and second, connections to thermodynamics. This section has so far dealt with only the second element. What do these results imply for probabilities? I will often say things like "The probability of having energy  $E_m$  is

$$\frac{N(m) e^{-\beta E_m}}{Z}."$$

On the face of it, this statement is absurd, because most of the microstates aren't energy eigenstates so they don't have any energy at all. What I mean is "If the energy is measured, the probability of finding energy  $E_m$  is

$$\frac{N(m) e^{-\beta E_m}}{Z}."$$

I will often use the first statement rather than the long and formal second statement. I do so, however, fully realizing that the first statement is wrong and that I use it just as convenient shorthand for the second statement. You may use this shorthand too, as long as you don't mean it.

The ultimate source of such problems is that the English language was invented by people who did not understand quantum mechanics, hence they never produced concise, accurate phrases to describe quantal phenomena. In the same way, the ancient phrase "Search the four corners of the Earth" is still colorful and practical, and is used today even by those who know that the Earth isn't flat.

Similarly, I will often say "The probability of being in the energy eigenstate  $\eta_n(x_1, \dots, x_N)$  with energy  $E_n$  is

$$\frac{e^{-\beta E_n}}{Z}."$$

But what I really mean is "If the microstate is projected onto a basis which includes the energy eigenstate  $\eta_n(x_1, \dots, x_N)$ , then the probability of projecting onto that state is

$$\frac{e^{-\beta E_n}}{Z}."$$

#### 4.2 The trace

Show that for any operator  $\hat{A}$ , the "trace" of  $\hat{A}$ , defined as

$$\text{trace}\{\hat{A}\} \equiv \sum_{\text{any basis } j} \langle j | \hat{A} | j \rangle, \quad (4.10.4)$$

is independent of basis. What is the trace in terms of the matrix representation of the operator?

#### 4.3 Entropy in the canonical ensemble

From the partition function (4.61), one can find the free energy  $F$  and hence the entropy  $S$ . Show that the entropy obtained in this manner equals

$$S(T) = -k_B \sum_n p_n \ln p_n, \quad (4.10.5)$$

where

$$p_n = \frac{e^{-\beta E_n}}{Z(T)} \quad (4.10.6)$$

is the probability that the system is in its  $n$ th energy eigenstate (using the shorthand mentioned above). This expression for the entropy is particularly useful in information theory. (Clue: Work forward from  $S = -\partial F / \partial T$  and backwards from equation (4.65) to meet at the middle.)

#### 4.4 Entropy in the microcanonical ensemble

[You must work the previous problem before working this one.] What are the state probabilities  $p_n$ , analogous to (4.66), for an system in the microcanonical ensemble? Devise a suitable quantal replacement for the microcanonical definition of entropy (2.7). Cast your replacement into the form of a function of the microcanonical probabilities  $p_n$ . Is formula (4.65) correct in the microcanonical ensemble?

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