10.5.2: The canonical ensemble

In analogy to the classical canonical ensemble, the quantum canonical ensemble is defined by

$$\rho = e^{-\beta H}$$
$$f(E_i) = e^{-\beta E_i}$$

Thus, the quantum canonical partition function is given by

$$\begin{aligned} Q(N,V,T) &= \mathrm{Tr}(e^{-\beta H}) \\ &= \sum_i e^{-\beta E_i} \end{aligned}$$

and the thermodynamics derived from it are the same as in the classical case:

$$\begin{aligned} A(N,V,T) &= -\frac{1}{\beta}\ln Q(N,V,T) \\ E(N,V,T) &= -\frac{\partial}{\partial\beta}\ln Q(N,V,T) \\ P(N,V,T) &= \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q(N,V,T) \end{aligned}$$

etc. Note that the expectation value of an observable A is

$$\langle A\rangle = \frac{1}{Q}\mathrm{Tr}(Ae^{-\beta H})$$

Evaluating the trace in the basis of eigenvectors of H (and of ρ), we obtain

$$\begin{aligned} \langle A\rangle &= \frac{1}{Q}\sum_i \langle E_i|Ae^{-\beta H}|E_i\rangle \\ &= \frac{1}{Q}\sum_i e^{-\beta E_i}\langle E_i|A|E_i\rangle \end{aligned}$$

The quantum canonical ensemble will be particularly useful to us in many things to come.