Chapter 11

The Quantum Microcanonical Distribution

At first blush, it seems we can define the microcanonical distribution for a quantum system just as classically. Define the density operator by

\[ \rho(H) = \frac{1}{\Omega(E)} \delta(E - H), \]  

(11.1)

where \( H \) is the Hamiltonian operator, so in terms of the eigenvectors and eigenvalues of the Hamiltonian,

\[ H|E_l, k\rangle = E_l|E_l, k\rangle, \]

(11.2)

\( k \) corresponding to eigenvalues of other observables compatible with the Hamiltonian, we write the \( \delta \) function as [cf. Eq. (4.42)]

\[ \delta(E - H) = \sum_{l,k} |E_l, k\rangle \delta(E - E_l) \langle E_l, k|. \]

(11.3)

Now the density operator has unit trace, which is the statement of the conservation of probability,

\[ \text{Tr} \rho = 1, \]

(11.4)

which implies that the structure function satisfies

\[ \Omega(E) = \text{Tr} \delta(E - H) = \sum_l \delta(E - E_l) \sum_k \langle E_l, k|E_l, k\rangle = \sum_l g_l \delta(E - E_l). \]

(11.5)

Here we have used the fact that the states are represented by orthonormal vectors,

\[ \langle E_l, k|E_{l'}, k'\rangle = \delta_{ll'} \delta_{kk'}. \]

(11.6)
and \( g_l \), the degeneracy, is the number of states with energy \( E_l \).

Now consider two independent systems, so \( H = H_1 + H_2 \), and so

\[
\Omega(E) = \text{Tr} \, \delta(E - H_1 - H_2) = \sum_{l,m} g_1, l g_2, m \delta(E - E_l^{(1)} - E_m^{(2)})
\]

\[
= \text{Tr} \sum_{l,m,k_1,k_2} |E_l^{(1)}, k_1 \rangle |E_m^{(2)}, k_1 \rangle \delta(E - E_l^{(1)} - E_m^{(2)}) \langle E_l^{(1)}, k_1 | \langle E_m^{(2)}, k_2 |
\]

\[
= \text{Tr} \int dE_1' \sum_{l,k_1} |E_l^{(1)}, k_1 \rangle \delta(E_1' - E_l^{(1)}) \langle E_l^{(1)} | \times \sum_{m,k_2} |E_m^{(2)}, k_2 \rangle \delta(E - E_1' - E_m^{(2)}) \langle E_m^{(2)} | = \int dE_1' \Omega_1(E_1') \Omega_2(E - E_1'),
\]

which is the same convolution law as seen classically. However these definitions of \( \rho \) and \( \Omega(E) \) are not satisfactory, because the spectrum of the Hamiltonian is in general discrete, so for example,

\[
\Omega(E) = \begin{cases} 
0 & \text{if } E \neq E_l, \text{ for all } l, \\
\infty & \text{if } E = E_l.
\end{cases}
\]

Therefore, we need to average over a small energy range.

### 11.1 Smallness of energy spacings

We need to appreciate how closely the energy levels are spaced. Consider a system in a large box. The Schrödinger equation for a particle of mass \( m \) in a one-dimensional box of length \( a \) is

\[
-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x),
\]

which for boundaries at \( x = 0 \) and \( x = a \), is subject to the boundary conditions

\[
\psi(0) = \psi(a) = 0.
\]

Thus

\[
\psi(x) = A \sin \frac{n\pi}{a} x, \quad n = 1, 2, \ldots,
\]

and the energy levels are

\[
E_n = \frac{\hbar^2 n^2 \pi^2}{2m a^2},
\]

so the typical energy spacing is

\[
\Delta E = \frac{\hbar^2 \pi^2}{2ma^2}.
\]
Suppose we consider a proton, of mass approximately $mc^2 = 1 \text{ GeV} = 10^9 \text{ eV}$, in a box of size $a = 1 \text{ cm}$. The unit conversion factor is
\[ \hbar c \approx 2 \times 10^{-5} \text{ eV cm}, \quad (11.14) \]
so
\[ \Delta E \approx 10^{-18} \text{ eV}, \quad (11.15) \]
which is a very small energy, indeed. Such discreteness in the energy is practically imperceptible.

### 11.2 Smoothed MC distribution

So we can introduce a very small energy scale $\epsilon$ which is very large compared to the level spacing, but tiny on a macroscopic scale. Then, we define the density operator by
\[ \rho_\epsilon = \frac{1}{\Omega_\epsilon} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \delta(E' - H). \quad (11.16) \]

Then $\text{Tr} \rho_\epsilon = 1$ gives the smoothed structure function
\[ \Omega_\epsilon(E) = \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \text{Tr} \delta(E' - H) = \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \Omega(E'), \quad (11.17) \]
which is the number of states with energy between $E - \epsilon/2$ and $E + \epsilon/2$.

Now consider a compound system, $H = H_1 + H_2$, and consider the density operator for subsystem 1:
\[
\rho_1 = \text{Tr} \rho_\epsilon = \frac{1}{\Omega_\epsilon(E)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \text{Tr}_2 \delta(E' - H_1 - H_2) \\
= \frac{1}{\Omega_\epsilon(E)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \Omega_2(E' - H_1) \\
= \frac{\Omega_2(E - H_1)}{\Omega_\epsilon(E)}. \quad (11.18)
\]
The spectral resolution of this
\[ \rho_1 = \sum_{jk} |E_j^{(1)},k\rangle \frac{\Omega_2(E - E_j^{(1)})}{\Omega_\epsilon(E)} \langle E_j^{(1)},k|, \quad (11.19) \]
means that $\Omega_2(E - E_j^{(1)}/\Omega_\epsilon(E)$ is the probability of finding system 1 is the state $(E_j^{(1)},k)$, and the probability of finding system 1 in any $E_j^{(1)}$ state
\[ g_j \frac{\Omega_2(E - E_j^{(1)})}{\Omega_\epsilon(E)} \quad (11.20) \]
However, the averaging process has spoiled the convolution property given in Eq. (11.7). To fix this problem, let us divide the energy into discrete bins, $E = n\epsilon$, where by energy $E$ we refer to all energies between $(n - \frac{1}{2})\epsilon$ and $(n + \frac{1}{2})\epsilon$. Then because $\Omega_\epsilon(E)$ is the number of states in the $E$ bin, we have

$$\Omega_\epsilon(E) = \sum_{E'} \Omega_{1\epsilon}(E')\Omega_{2\epsilon}(E - E'),$$

(11.21)

where the summand is the number of states corresponding to a particular partitioning of the energy between the two subsystems. The general convolution law is, if $H = \sum_j H_j$,

$$\Omega_\epsilon(E) = \sum_{\{E_l\}} \delta_{E,E'} \prod_l \Omega_{l\epsilon}(E_l).$$

(11.22)

As previously, we assume that all energies are nonnegative. (This is just a choice of the zero of energy, assuming energies are bounded below.) Then we define the partition function by a discrete Laplace transform,

$$\chi(\alpha) = \sum_E e^{-\alpha E} \Omega_\epsilon(E),$$

(11.23)

so again for a compound system

$$\chi(\alpha) = \sum_{E,(E_l)} e^{-\alpha E} \delta_{E,E'} \prod_l \Omega_{l\epsilon}(E_l)$$

$$= \sum_{\{E_l\}} \prod_l e^{-\alpha E_l} \Omega_{l\epsilon}(E_l) = \prod_l \sum_{E_l} e^{-\alpha E_l} \Omega_{l\epsilon}(E_l)$$

$$= \prod_l \chi_l(\alpha),$$

(11.24)

the expected product law.

Again, we seek an asymptotic expansion for $\Omega$. For this we first recall

$$\frac{1}{2\pi i} \oint_{\gamma} \frac{dz}{z} z^n = \delta_{n0},$$

(11.25)

where $\gamma$ is any closed contour which encircles the origin once in the positive (CCW) sense. That is, the integral is zero for any integer $n$, positive or negative, except for $n = 0$. Then, because we are now measuring $E$ in integer multiples of $\epsilon$, this is the same as

$$\frac{1}{2\pi i} \oint_{\gamma} \frac{dz}{z} e^{(E-E')/\epsilon} = \delta_{EE'}.$$

(11.26)

Next, let $z = e^{\alpha\epsilon}$, so $dz/z = \epsilon d\alpha$, and

$$\delta_{EE'} = \frac{\epsilon}{2\pi i} \int_{\gamma} e^{(E-E')/\epsilon} d\alpha e^{\alpha(E-E')}.$$

(11.27)
where because
\[
\alpha = \frac{1}{\epsilon} \ln z = \frac{1}{\epsilon} [\ln R + i\theta],
\] (11.28)
if we choose \(\gamma\) to be a circle of radius \(R\), \(A = \frac{\ln R}{\epsilon}\). As \(\epsilon \to 0\), the endpoints of the finite path recede to \(\pm i\infty\).

So now we have, from the convolution formula (11.22)
\[
\Omega_\epsilon(E) = \sum_{\{E_i\}} \delta_{E, \sum_l E_l} \prod_l \Omega_\epsilon(E_l)
= \frac{\epsilon}{2\pi i} \int d\alpha \sum_{\{E_l\}} e^{\alpha (E - \sum_l E_l)} \prod_l \Omega_\epsilon(E_l)
= \frac{\epsilon}{2\pi i} \int d\alpha e^{\alpha E} \prod_l \chi_l(\alpha)
= \frac{\epsilon}{2\pi i} \int_{A - i\pi\epsilon}^{A + i\pi\epsilon} d\alpha e^{\alpha E} \chi(\alpha),
\] (11.29)
the exact analog of the classical formula (9.23).

The asymptotic saddle-point analysis goes through just as before, with the result
\[
\Omega_\epsilon(E) \sim \frac{\epsilon e^{\beta E} \chi(\beta)}{\sqrt{2\pi(\ln \chi)'(\beta)}},
\] (11.30)
where \(\beta\) is the unique positive real root of
\[
(\ln \chi)'(\beta) = -E.
\] (11.31)
[The fact that the path of integration is finite is immaterial, since the significant contributing region is very near the saddle point,
\[
\frac{\Delta \beta}{\beta} \sim \frac{1}{\sqrt{N}},
\] (11.32)
so as long as
\[
\frac{\pi}{\epsilon} \gg \frac{\beta}{\sqrt{N}}, \quad \text{or} \quad \epsilon \ll \pi \sqrt{N kT},
\] (11.33)
the endpoints are irrelevant.]

The probability that the system 1 is in a particular state with energy \(E_j^{(1)}\) is from Eq. (11.19)
\[
\frac{\Omega_\epsilon^{(N-1)}(E - E_j^{(1)})}{\Omega_\epsilon^{(N)}(E)} \sim \frac{e^{-\beta E_j^{(1)}}}{\chi_1(\beta)},
\] (11.34)
so the density operator for system 1 is
\[
\rho_1 = \sum_{jk} |E_j^{(1)}, k\rangle e^{-\beta E_j^{(1)}} \chi_1(\beta) \langle E_j^{(1)}, k|
= \frac{e^{-\beta H_1}}{\chi_1(\beta)},
\] (11.35)
which is the canonical distribution, with
\[
\chi_1(\beta) = \text{Tr} e^{-\beta H_1} = \sum_j g_j e^{-\beta E_j^{(1)}}, \quad (11.36)
\]
which is consistent with
\[
\chi(\alpha) = \sum_E e^{-\alpha E} \Omega_\epsilon(E), \quad (11.37)
\]
where \(\Omega_\epsilon(E)\) is the number of states with energy \(E\).