3.1   Density matrices

Quantum systems are described by wave functions and eigenvalues, solutions of the Schrödinger equation. We shall show for the one-dimensional harmonic oscillator how exactly the probabilities of quantum physics combine with the statistical weights in the Boltzmann distribution, before moving on to more general problems.

3.1.1   The quantum harmonic oscillator

The one-dimensional quantum mechanical harmonic oscillator, which consists of a particle of mass m in a potential

$$V(x) = \frac{1}{2}m\omega^2 x^2,$$

is governed by the Schrödinger equation

$$H\psi_n^{\text{h.o.}} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \right) \psi_n^{\text{h.o.}} = E_n \psi_n^{\text{h.o.}}. \qquad (3.1)$$

procedure `harmonic-wavefunction`
input x
$\psi_{-1}^{\text{h.o.}}(x) \leftarrow 0$ (unphysical, starts recursion)
$\psi_0^{\text{h.o.}}(x) \leftarrow \pi^{-1/4}\exp\left(-x^2/2\right)$ (ground state)
for $n = 1, 2, \ldots$ **do**
$\left\{ \quad \psi_n^{\text{h.o.}}(x) \leftarrow \sqrt{\frac{2}{n}}x\psi_{n-1}^{\text{h.o.}}(x) - \sqrt{\frac{n-1}{n}}\psi_{n-2}^{\text{h.o.}}(x) \right.$
output $\{\psi_0^{\text{h.o.}}(x), \psi_1^{\text{h.o.}}(x), \ldots\}$
———

Algorithm 3.1 `harmonic-wavefunction`. Eigenfunctions of the one-dimensional harmonic oscillator (with $\hbar = m = \omega = 1$).

In general, the wave functions $\{\psi_0, \psi_1, \ldots\}$ satisfy a completeness condition

$$\sum_{n=0}^{\infty} \psi_n^*(x)\psi_n(y) = \delta(x - y),$$

where $\delta(x - y)$ is the Dirac δ-function, and form an orthonormal set:

$$\int_{-\infty}^{\infty} \mathrm{d}x \; \psi_n^*(x)\psi_m(x) = \delta_{nm} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{otherwise} \end{cases}, \qquad (3.2)$$

where δ_{nm} is the discrete Kronecker δ-function. The wave functions of the harmonic oscillator can be computed recursively[1] (see Alg. 3.1 (`harmonic-wavefunction`)). We can easily write down the first few of them, and verify that they are indeed normalized and mutually orthogonal, and that $\psi_n^{\text{h.o.}}$ satisfies the above Schrödinger equation (for $m = \hbar = \omega = 1$) with $E_n = n + \frac{1}{2}$.

[1]In most formulas in this chapter, we use units such that $\hbar = m = \omega = 1$.

In thermal equilibrium, a quantum particle occupies an energy state n with a Boltzmann probability proportional to $\mathrm{e}^{-\beta E_n}$, and the partition function is therefore

$$Z^{\mathrm{h.o.}}(\beta) = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n} = \mathrm{e}^{-\beta/2} + \mathrm{e}^{-3\beta/2} + \mathrm{e}^{-5\beta/2} + \cdots$$

$$= \mathrm{e}^{-\beta/2}\left(\frac{1}{1 - \mathrm{e}^{-\beta}}\right) = \frac{1}{\mathrm{e}^{\beta/2} - \mathrm{e}^{-\beta/2}} = \frac{1}{2\sinh(\beta/2)}. \quad (3.3)$$

The complete thermodynamics of the harmonic oscillator follows from eqn (3.3). The normalized probability of being in energy level n is

$$\left\{\begin{array}{c}\text{probability of being}\\\text{in energy level } n\end{array}\right\} = \frac{1}{Z}\,\mathrm{e}^{-\beta E_n}.$$

When it is in energy level n (see Fig. 3.2), a quantum system is at a position x with probability $\psi_n^*(x)\psi_n(x)$. (The asterisk stands for the complex conjugate; for the real-valued wave functions used in most of this chapter, $\psi^* = \psi$.) The probability of being in level n at position x is

$$\left\{\begin{array}{c}\text{probability of being}\\\text{in energy level } n\\\text{at position } x\end{array}\right\} = \frac{1}{Z}\,\mathrm{e}^{-\beta E_n}\psi_n(x)\psi_n^*(x). \quad (3.4)$$

This expression generalizes the Boltzmann distribution to quantum physics. However, the energy levels and wave functions are generally unknown for complicated quantum systems, and eqn (3.4) is not useful for practical computations. To make progress, we discard the information about the energy levels and consider the (diagonal) density matrix

$$\pi(x) = \left\{\begin{array}{c}\text{probability of being}\\\text{at position } x\end{array}\right\} \propto \rho(x, x, \beta) = \sum_n \mathrm{e}^{-\beta E_n}\psi_n(x)\psi_n^*(x),$$

as well as a more general object, the nondiagonal density matrix (in the position representation)

$$\left\{\begin{array}{c}\text{density}\\\text{matrix}\end{array}\right\} : \rho(x, x', \beta) = \sum_n \psi_n(x)\mathrm{e}^{-\beta E_n}\psi_n^*(x'), \quad (3.5)$$

which is the central object of quantum statistics. For example, the partition function $Z(\beta)$ is the trace of the density matrix, i.e. the sum or the integral of its diagonal terms:

$$Z(\beta) = \mathrm{Tr}\,\rho = \int \mathrm{d}x\,\rho(x, x, \beta). \quad (3.6)$$

We shall compute the density matrix in different settings, and often without knowing the eigenfunctions and eigenvalues. For the case of the harmonic oscillator, however, we have all that it takes to compute the density matrix from our solution of the Schrödinger equation (see Alg. 3.2 (`harmonic-density`) and Fig. 3.3). The output of this program will allow us to check less basic approaches.
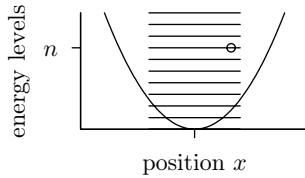
Fig. 3.2 A quantum particle at position x, in energy level n. The density matrix only retains information about positions.