Chapter 4. Using Quantum Mechanics on Simple Systems

Free particle Hamiltonian:

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (V=0) \]

Schrödinger equation:

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = E \Psi \]

Solutions:

\[ \Psi^\pm(x) = e^{\pm ikx}, \quad k = \left( \frac{2mE}{\hbar^2} \right)^{1/2} \quad \text{(plane wave)} \]

\[ E = \frac{(\hbar k)^2}{2m}, \quad p = \pm k\hbar \quad \text{(not quantized)} \]

Particle in a 1D box:

\[ V(x) = 0, \quad 0 \leq x \leq L \]
\[ = \infty, \quad x < 0, \text{and} \quad x > L \]

Schrödinger eqn. (inside the well):

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = E \Psi \]
Solutions:

$$\Psi(x) = A e^{+ikx} + B e^{-ikx} = C \cos kx + D \sin kx$$

where we used $$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$ and $$A, B, C, D$$ are (complex) coefficients to be determined.

Verification:

$$rhs = E\Psi = \left(\frac{k^2 \hbar^2}{2m}\right)\Psi$$

$$lhs = -\left(\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2} (C \cos kx + D \sin kx)$$

$$= -\left(\frac{\hbar^2}{2m}\right)(-Ck^2 \cos kx - Dk^2 \sin kx)$$

$$= \left(\frac{\hbar^2 k^2}{2m}\right)(C \cos kx + D \sin kx)$$

$$rhs = lhs$$, it is a solution. We have used $$\frac{d \sin kx}{dx} = k \cos kx$$, $$\frac{d \cos kx}{dx} = -k \sin kx$$.

Acceptable solutions and quantization:

Since $$V - E > 0$$, the probability for finding the particle outside the well has to be zero.
So the boundary conditions:

\[ \Psi = 0 \quad \text{at } x \leq 0 \text{ and } x \geq L \]

Impose the boundary conditions:

\[ \Psi(x) = C \cos kx + D \sin kx \]

At \( x = 0 \), \( 0 = \Psi'(0) = C \)
At \( x = L \), \( 0 = \Psi(L) = D \sin kL \)

So \( kL = n\pi \), \( n = 1, 2, ... \) \( (n \neq 0) \)

\[ E_n = \frac{(kh)^2}{2m} = \frac{(n\pi h)^2}{2mL^2} = \frac{(nh)^2}{8mL^2}, \]

Energy is quantized because the motion is restricted.

Normalization:

\[ \Psi_n = D \sin \left( \frac{n\pi x}{L} \right) \quad D \text{ is undetermined.} \]

\[ 1 = \int \Psi_n^* \Psi_n \, dx \]

\[ = \int_0^L D^2 \sin^2 \left( \frac{n\pi x}{L} \right) \, dx \]

\[ = D^2 \left( \frac{x}{2} - \frac{L}{4n\pi} \sin \left( \frac{2n\pi x}{L} \right) \right)_0^L = D^2 \frac{L}{2} \]
where we have used \( \sin^2 x = (1 - \cos 2x) / 2 \). So, \( D = \sqrt{2} / L \) and normalized wavefunction:

\[
\Psi_n = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)
\]

Wavefunction \( \Psi_n \) and probability density \( |\Psi_n|^2 \)

Example: Probability for finding a particle between \( x=0 \) and \( x=l \) inside a box of 1.0 nm length (assuming in its ground state).

The probability for finding the particle in \((0,l)\) is

\[
P = \int_0^l \Psi_n^* \Psi_n \, dx
\]

\[
= \left( \frac{2}{L} \right) \int_0^l \sin^2 \left( \frac{n\pi x}{L} \right) \, dx
\]

\[
= \left( \frac{2}{L} \right) \left[ \frac{x}{2} - \frac{L}{4n\pi} \sin \left( \frac{2n\pi x}{L} \right) \right]_0^l
\]

\[
= \left( \frac{2}{L} \right) \left( \frac{l}{2} - \frac{L}{4n\pi} \sin \left( \frac{2n\pi l}{L} \right) \right)
\]
when $l = 0.1$ nm
when $l = 0.2$ nm
when $l = 0.5$ nm
when $l = 1.0$ nm

Properties of the solution

Zero-point energy, lowest energy level, $n = 1$:

$$E_1 = \frac{h^2}{8mL^2} \quad (> 0) \quad \text{(quantum effect)}$$

ZPE, a quantum effect, is due to restriction of motion.

Energy separation

$$\Delta E_{n\rightarrow n+1} = \frac{[(n+1)^2 - n^2]h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2}$$

$\Delta E \rightarrow 0$ as $m$ or $L$ increases (correspondence principle: QM approaches CM with heavy mass, high energy).

Example: An electron is in a 1D box with $L = 1.0$ nm. Calc. zero-point energy and photon frequency for $1 \rightarrow 2$ transition.

$$E_1 = \frac{h^2}{8m_eL^2}$$
\[ \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8(9.1 \times 10^{-31} \text{ kg})(1.0 \times 10^{-9} \text{ m})^2} = 6.03 \times 10^{-20} \text{ J} \]

\[ \Delta E_{1 \rightarrow 2} = \frac{(2 \times 1 + 1)\hbar^2}{8mL^2} = 3E_1 = 1.81 \times 10^{-19} \text{ J} \]

\[ \nu = \frac{\Delta E}{h} = \frac{1.81 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 2.73 \times 10^{14} \text{ s}^{-1} \]

Orthogonality:

\[ \int \Psi_1^* \Psi_2 dx = \left( \frac{2}{L} \right) \int_0^L \sin \frac{\pi x}{L} \sin \frac{2\pi x}{L} dx \]

\[ = 2 \left( \frac{2}{L} \right) \int_0^L \sin \frac{\pi x}{L} \sin \frac{\pi x}{L} \cos \frac{\pi x}{L} dx \]

\[ = \left( \frac{4}{L} \right) \int_0^L \sin^2 \frac{\pi x}{L} d \left( \sin \frac{\pi x}{L} \right) \frac{L}{\pi} \]

\[ = \left( \frac{4}{3\pi} \right) \sin^3 \frac{\pi x}{L} \bigg|_0^L = 0 \]

Nodal structure: The \( n \)th state has \((n-1)\) nodes.

\[ \Psi = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) = 0 \quad \text{at} \quad \frac{n\pi x}{L} = m\pi, \ m = 1, 2, .. \]

Positions of the node: \( x = mL/n \) and \( 0 < x < L \)
Average position and momentum

\[ \langle x \rangle = \int_{0}^{L} x |\Psi_n(x)|^2 dx = \frac{2}{L} \int_{0}^{L} x \sin^2 \frac{n\pi x}{L} dx = \frac{2L^2}{L} = \frac{L}{2} \]

At the middle of the box! Here, we have used the formula:

\[ \int x \sin^2 \alpha x dx = \frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} \]

\[ \langle p \rangle = \frac{2}{L} \int_{0}^{L} \sin \frac{n\pi x}{L} (-i\hbar \frac{d}{dx}) \sin \frac{n\pi x}{L} dx \]

\[ = -\frac{2}{L} i\hbar \int_{0}^{L} \sin \frac{n\pi x}{L} d \sin \frac{n\pi x}{L} \]

\[ = -\frac{i\hbar}{L} \left[ \sin^2 \frac{n\pi x}{L} \right]_0^L = 0 \]

Average momentum is zero!

**Particle in a two-dimensional box:**

\[ V(x, y) = 0, \quad 0 \leq x \leq L_1, 0 \leq y \leq L_2 \]

\[ = \infty, \quad \text{otherwise} \]

Schrödinger eqn.:

\[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi = E \Psi \]
Separation of variables:

\[ \Psi(x, y) = \Psi^x(x) \Psi^y(y) \]

Differentiate the wavefunction

\[ \frac{\partial^2 \Psi}{\partial x^2} = \Psi^y \frac{d^2 \Psi^x}{dx^2}, \quad \frac{\partial^2 \Psi}{\partial y^2} = \Psi^x \frac{d^2 \Psi^y}{dy^2}, \]

so the Schrödinger eqn becomes

\[ -\frac{\hbar^2}{2m} \left( \frac{\Psi^y}{\Psi^x} \frac{d^2 \Psi^x}{dx^2} + \frac{\Psi^x}{\Psi^y} \frac{d^2 \Psi^y}{dy^2} \right) = E \Psi^x \Psi^y \]

Divide by \( \Psi^x \Psi^y \):

\[ -\frac{\hbar^2}{2m} \left( \frac{1}{\Psi^x} \frac{d^2 \Psi^x}{dx^2} + \frac{1}{\Psi^y} \frac{d^2 \Psi^y}{dy^2} \right) = E \]

So, we can write two separated equations:

\[ -\frac{\hbar^2}{2m} \left( \frac{1}{\Psi^x} \frac{d^2 \Psi^x}{dx^2} \right) = E^x, \]
\[ -\frac{\hbar^2}{2m} \left( \frac{1}{\Psi^y} \frac{d^2 \Psi^y}{dy^2} \right) = E^y \]

where \( E = E^x + E^y \), and the solutions are
\[
\Psi_{n_1}^x(x) = \left(\frac{2}{L_1}\right)^{1/2} \sin\left(\frac{n_1 \pi x}{L_1}\right),
\]

\[
\Psi_{n_2}^y(y) = \left(\frac{2}{L_2}\right)^{1/2} \sin\left(\frac{n_2 \pi y}{L_2}\right)
\]

Energy:

\[
E_{n_1, n_2} = \left[\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2\right] \frac{\hbar^2}{8m}, \quad n_1, n_2 = 1, 2, \ldots
\]

If \( L_1 = L_2 = L \),

\[
E_{n_1, n_2} = \frac{(n_1^2 + n_2^2)\hbar^2}{8mL^2}
\]

Degeneracy: different wavefunctions with the same energy.

\[
E_{1,2} = E_{2,1} = \frac{5\hbar^2}{8mL^2}
\]

Their wavefunctions are different:

\[
\Psi_{1,2} = \left(\frac{2}{L}\right) \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right)
\]

\[
\Psi_{2,1} = \left(\frac{2}{L}\right) \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right)
\]