Chapter 4. Using Quantum Mechanics on Simple Systems

Free particle Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad (V=0)$$

Schrödinger equation:

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

Solutions:

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

$$E = \frac{(\hbar k)^2}{2m}, \qquad p = \pm k\hbar \qquad \text{(not quantized)}$$

Particle in a 1D box:

$$V(x) = 0, \quad 0 \le x \le L$$
$$= \infty, \quad x < 0, and\ x > L$$

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:

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

$$\begin{aligned} lhs &= -\left(\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}(C\cos kx + D\sin kx) \\ &= -\left(\frac{\hbar^2}{2m}\right)(-Ck^2\cos kx - Dk^2\sin kx) \\ &= \left(\frac{\hbar^2 k^2}{2m}\right)(C\cos kx + D\sin kx) \end{aligned}$$

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 <u>boundary conditions</u>:

$$\Psi = 0 \qquad \text{at } x \le 0 \text{ and } x \ge L$$

Impose the boundary conditions:

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

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

So $kL = n\pi$, $n = 1, 2, \ldots \qquad (n \neq 0)$

$$E_n = \frac{(k\hbar)^2}{2m} = \frac{(n\pi\hbar)^2}{2mL^2} = \frac{(nh)^2}{8mL^2},$$

Energy is quantized because the motion is restricted.

<u>Normalization:</u>

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

$$\begin{aligned}
1 &= \int \Psi_n^* \Psi_n dx \\
&= \int_0^L D^2 \sin^2\left(\frac{n\pi x}{L}\right) dx \\
&= D^2\left(\frac{x}{2} - \frac{L}{4n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right)\Bigg|_0^L = D^2\frac{L}{2}
\end{aligned}$$

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 Ψ_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

$$\begin{aligned} P &= \int_0^l \Psi_n^* \Psi_n dx \\ &= \left(\frac{2}{L}\right) \int_0^l \sin^2\left(\frac{n\pi x}{L}\right) dx \\ &= \left(\frac{2}{L}\right) \left[\frac{x}{2} - \frac{L}{4n\pi} \sin\left(\frac{2n\pi x}{L}\right)\right]_0^l \\ &= \left(\frac{2}{L}\right) \left(\frac{l}{2} - \frac{L}{4n\pi} \sin\left(\frac{2n\pi l}{L}\right)\right) \end{aligned}$$

$= 0.0064 \qquad \textit{when}\ l = 0.1\,\text{nm}$

$= 0.048 \qquad \textit{when}\ l = 0.2\,\text{nm}$

$= 0.50 \qquad \textit{when}\ l = 0.5\,\text{nm}$

$= 1.00 \qquad \textit{when}\ l = 1.0\,\text{nm}$

Properties of the solution

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

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

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

Energy separation

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

$\Delta E \to 0$ 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 $1 \to 2$ transition.

$$E_1 = \frac{h^2}{8m_e L^2}$$

$$= \frac{(6.626\times10^{-34}\,Js)^2}{8(9.1\times10^{-31}kg)(1.0\times10^{-9}m)^2} = 6.03\times10^{-20}\,J$$

$$\Delta E_{1\to2} = \frac{(2\times1+1)h^2}{8mL^2} = 3E_1 = 1.81\times10^{-19}\,J$$

$$\nu = \frac{\Delta E}{h} = \frac{1.81\times10^{-19}\,J}{6.626\times10^{-34}\,Js} = 2.73\times10^{14}\,s^{-1}$$

<u>Orthogonality:</u>

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

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

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

$$= \left(\frac{4}{3\pi}\right)\sin^3\frac{\pi x}{L}\Big|_0^L = 0$$

<u>Nodal structure:</u> The nth state has (n-1) nodes.

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

Positions of the node: $x = mL/n$ and $0 < x < L$

Average position and momentum

$$\langle x \rangle = \int_0^L x|\Psi_n(x)|^2 dx = \frac{2}{L}\int_0^L x\sin^2\frac{n\pi x}{L}dx = \frac{2}{L}\frac{L^2}{4} = \frac{L}{2}$$

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

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

$$\langle p \rangle = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\left(-i\hbar\frac{d}{dx}\right)\sin\frac{n\pi x}{L}dx$$

$$= -\frac{2}{L}i\hbar\int_0^L \sin\frac{n\pi x}{L}d\sin\frac{n\pi x}{L}$$

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

Average momentum is zero!

Particle in a two-dimensional box:

$$\begin{aligned} V(x,y) &= 0, \qquad 0 \le x \le L_1, 0 \le y \le L_2 \\ &= \infty, \qquad otherwise \end{aligned}$$

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

$$\frac{\partial^2\Psi}{\partial x^2} = \Psi^y \frac{d^2\Psi^x}{dx^2}, \qquad \frac{\partial^2\Psi}{\partial y^2} = \Psi^x \frac{d^2\Psi^y}{dy^2},$$

so the Schrödinger eqn becomes

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

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:

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

If $L_1 = L_2 = L$,

$$E_{n_1,n_2} = \frac{(n_1^2 + n_2^2)h^2}{8mL^2}$$

<u>Degeneracy</u>: different wavefunctions with the same energy.

$$E_{1,2} = E_{2,1} = \frac{5h^2}{8mL^2}$$

Their wavefunctions are different:

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

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