SOLUTIONS TO THE SCHRÖDINGER EQUATION

Free particle and the particle in a box

Schrödinger equation is a 2nd-order diff. eq.

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x)$$

We can find two independent solutions $\phi_1(x)$ and $\phi_2(x)$
The general solution is a linear combination

$$\psi(x)=A\phi_1(x)+B\phi_2(x)$$

A and B are then determined by <u>boundary conditions</u> on $\psi(x)$ and $\psi'(x)$.

Additionally, for physically reasonable solutions we require that $\psi(x)$ and $\psi'(x)$ be continuous function.

(I) <u>Free particle</u> $V(x) = 0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}=E\psi(x)$$

Define $k^2=\frac{2mE}{\hbar^2}$ or $E=\frac{\hbar^2k^2}{2m}$

$$V(x)=0,\quad E=\frac{p^2}{2m}\quad\Rightarrow\quad p^2=\hbar^2k^2\quad\Rightarrow\quad \boxed{p=\hbar k}$$

de Broglie $p=\frac{h}{\lambda}\quad\Rightarrow\quad \boxed{k=\frac{2\pi}{\lambda}}$

The wave eq. becomes $$\frac{\partial^2\psi(x)}{\partial x^2} = -k^2\psi(x)$$

with solutions $$\psi(x) = A\cos(kx) + B\sin(kx)$$

Free particle $\Rightarrow$ no boundary conditions

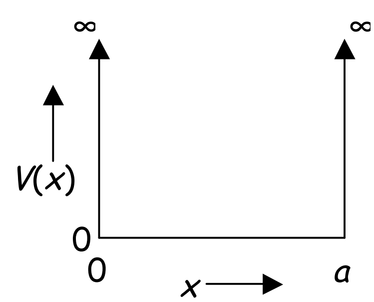
$\Rightarrow$ <u>any</u> *A* and *B* values are possible, any $E = \frac{\hbar^2k^2}{2m}$ possible

So any wavelike solution (traveling wave or standing wave) with any wavelength, wavevector, momentum, and energy is possible.

(II) <u>Particle in a box</u>

$V(x) = \infty \quad (x < 0,\ x > a)$

$V(x) = 0 \quad (0 \le x \le a)$



Particle can't be anywhere with $V(x) = \infty$

$$\Rightarrow \quad \psi(x < 0,\ x > a) = 0$$

For $0 \le x \le a$, Schrödinger equation is like that for free particle.

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = -k^2\psi(x)$$ with same definition

$$k^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad E = \frac{\hbar^2k^2}{2m}$$

again with solutions $\psi(x) = A\cos(kx) + B\sin(kx)$

But this time there are boundary conditions!

Continuity of $\psi(x)$ $\Rightarrow$ $\psi(0) = \psi(a) = 0$

(i) $\psi(0) = A\cos(0) + B\sin(0) = 0 \Rightarrow A = 0$

(ii) $\psi(a) = B\sin(ka) = 0$

Can't take *B* = 0 (no particle anywhere!)

Must have $\sin(ka) = 0 \Rightarrow ka = n\pi$ *n* = 1, 2, 3,...

$\Rightarrow$ <u>*k* is not continuous</u> but takes on discrete values $k = \dfrac{n\pi}{a}$

Thus integer evolves naturally !!

So solutions to the Schrödinger equation are

$$\boxed{\psi(0 \le x \le a) = B\sin\left(\frac{n\pi x}{a}\right) \qquad n = 1,2,3,\ldots}$$

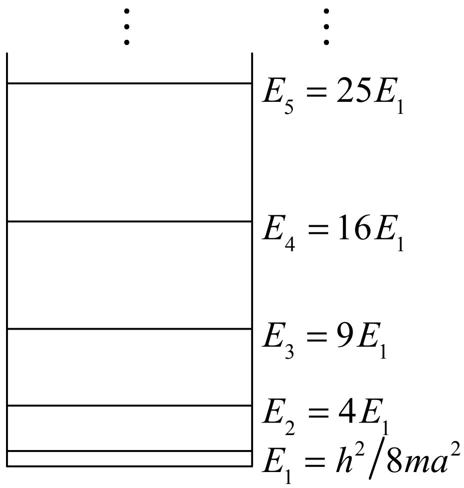
These solutions describe different stable (time-independent or "stationary") states with energies

$$E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad \boxed{E_n = \frac{n^2 h^2}{8ma^2}}$$

Energy is quantized!! And the states are labeled by a quantum number *n* which is an integer.

Properties of the stationary states

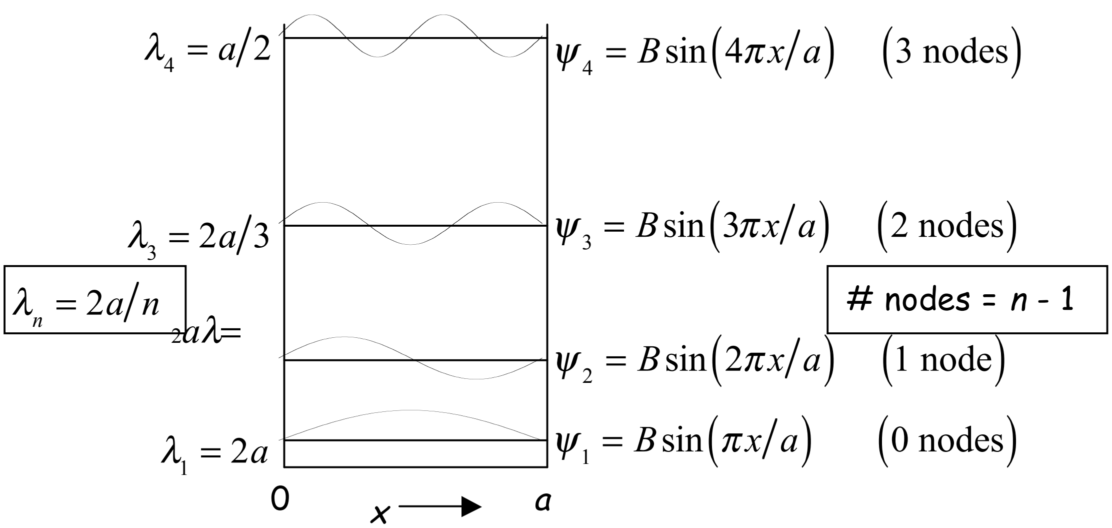
(a) The energy spacing between successive states gets progressively larger as *n* increases



$$E_{n+1} - E_n = \left[(n+1)^2 - n^2\right]\frac{h^2}{8ma^2}$$

$$\boxed{E_{n+1} - E_n = (2n+1)E_1}$$

(b) The wavefunction $\psi(x)$ is sinusoidal, with the number of nodes increased by one for each successive state



(c) The energy spacings increase as the box size decreases.

$$E \propto \frac{1}{a^2}$$

We've solved some simple quantum mechanics problems! The P-I-B model is a good approximation for some important cases, e.g. pi-bonding electrons on aromatics.

Electronic transitions shift to lower energies as molecular size increases !