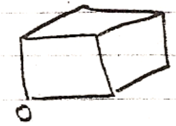
- **Translation 3D Box**

Particle in a Three-dimensional box



cube of length L

$V(x,y,z) = 0$ within box

$V(x,y,z) = \infty$ outside box

Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\,\psi(x,y,z)$$

assume form $\boxed{\psi(x,y,z) = X(x)\,Y(y)\,Z(z)}$

substitute in

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}\right) = EXYZ$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) = E$$

we are using separation of variables to solve

we assume

$$\boxed{E = E_x + E_y + E_z}$$

and get three analogous equations like

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 X}{\partial x^2}\right) = E_x X$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Y}{\partial y^2} = E_y Y$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Z}{\partial z^2} = E_z Z$$

~~each of these cases~~

Each of these of the same form as particle in one-dimensional box

$$E_x = \frac{h^2}{8mL^2} n_x^2$$

$$X(x) = \left(\frac{2}{L}\right)^{1/2} \sin(n_x \pi x / L)$$

3 sets of solutions

so

$$E_{n_x, n_y, n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

simplify if all sides same length L

$$\Psi_{n_x, n_y, n_z} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \cdot \sin\left(\frac{n_z \pi z}{L}\right)$$

note that $\Psi_{1,2,3}$ | $\Psi_{2,1,3}$ $\Psi_{3,2,1}$

$\Psi_{1,3,2}$ $\Psi_{2,3,1}$ $\Psi_{3,1,2}$ are all same energy

all have different spatial orientation in terms of most probable location of particle but have same energy

$$E_{1,2,3} = \frac{h^2}{8mL^2}\left(1^2 + 2^2 + 3^2\right)$$

diff Ψ give same E

wavefunction are <u>degenerate</u>

<u>degeneracy</u> - possession of same energy by different wavefunctions

As E larger - greater degeneracy - more combinations give same E

- Example: Consider 1e⁻ orbitals — degeneracy

energy ↑	4s 4p 4d 4f	$4^2 = 16$
	3s 3p 3d	$3^2 = 9$
	2s 2p	$2^2 = 4$
	1s	$1^2 = 1$