Particle in 2-D Square-Well Potential

Hamiltonian $$\widehat{H} = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar}{2m}\frac{\partial^2}{\partial y^2} = \widehat{H}_x + \widehat{H}_y$$

$$\widehat{H} \cdot \psi(x,y) = E_n \cdot \psi(x,y)$$

$$\psi(x,y) = \psi(x) \cdot \psi(y)$$

$$E_n = E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

ψ is a product of the eigenfunctions of the parts of $\hat{H}$

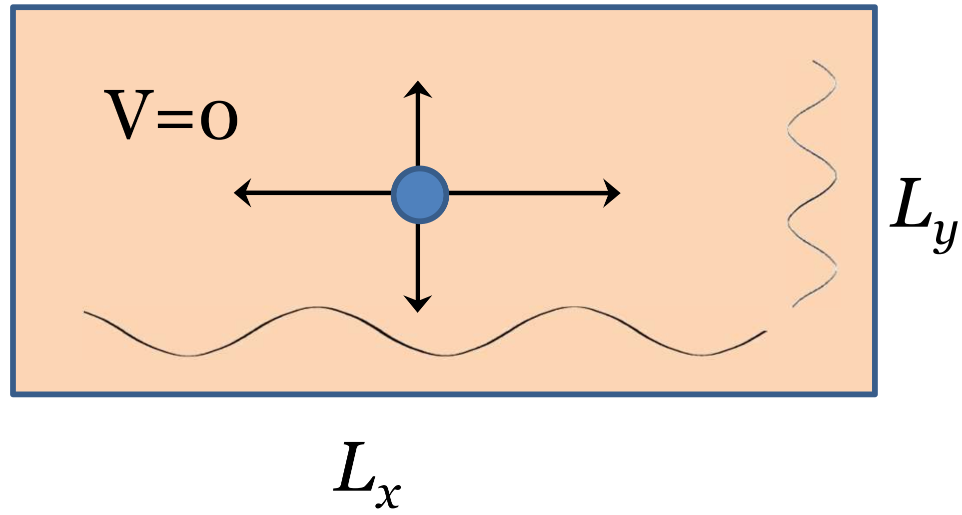
E is sum of the eigenvalues of the parts of $\hat{H}$

Particle in 2-D Square-Well Potential

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$

$$= \sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x \cdot \sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$

$$= \frac{2}{\sqrt{L_x L_y}}\sin\frac{n\pi}{L_x}x \cdot \sin\frac{n\pi}{L_y}y$$

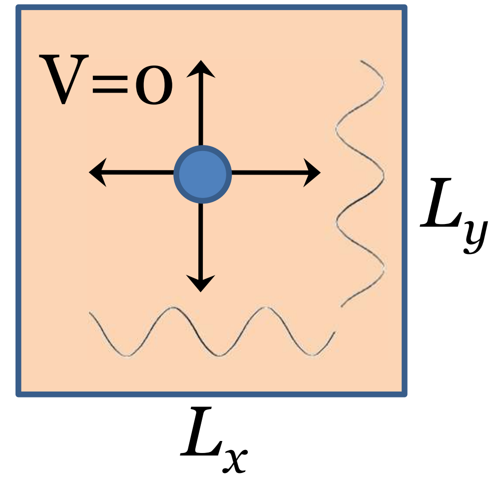


$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2}$$

$$= \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \quad n_x, n_y = 1,2,3,4\ldots$$

Particle in 2-D Square-Well Potential



Square Box
$\Rightarrow L_x = L_y = L$

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$

$$= \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x\cdot\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}y$$

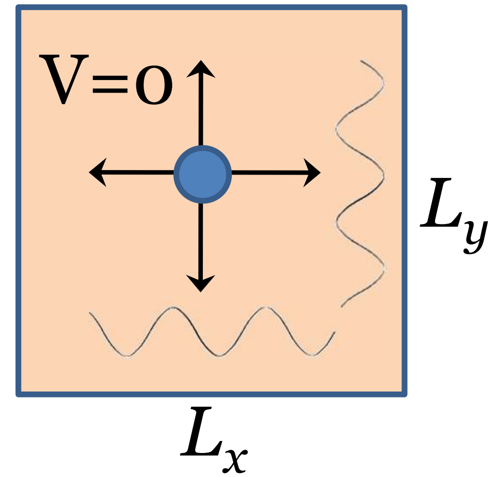
$$= \frac{2}{L}\sin\frac{n\pi}{L}x\cdot\sin\frac{n\pi}{L}y$$

$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

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

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right) \quad n_x, n_y = 1,2,3,4\ldots$$

Particle in 2-D Square-Well Potential



$$\psi_{1,2} = \psi_1 \cdot \psi_2 = \frac{2}{L} \sin\frac{\pi}{L}x \cdot \sin\frac{2\pi}{L}y$$

$$E_{1,2} = E_1 + E_2 = \frac{5h^2}{8mL^2}$$

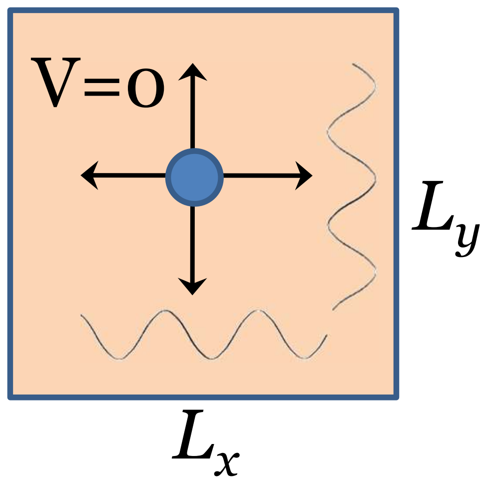
Square Box
$\Rightarrow L_x = L_y = L$

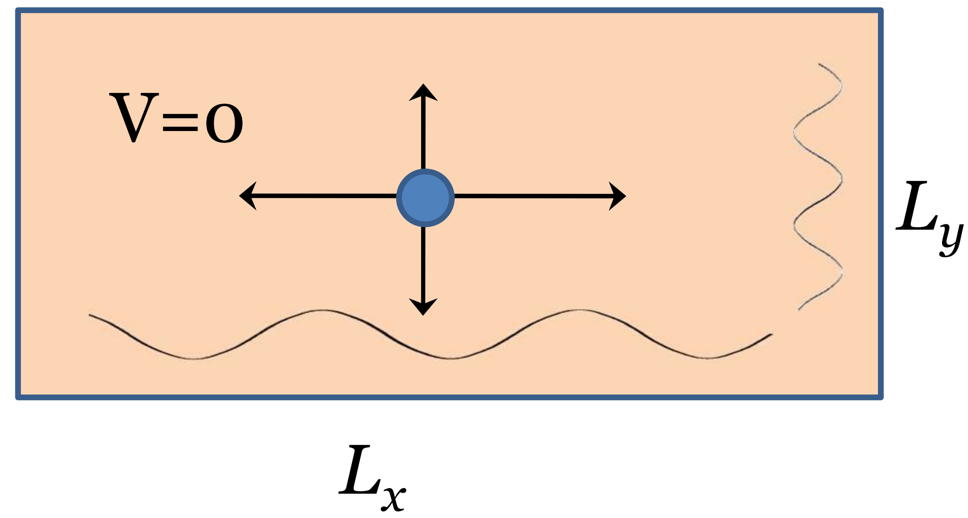
$$\psi_{2,1} = \psi_2 \cdot \psi_1 = \frac{2}{L} \sin\frac{2\pi}{L}x \cdot \sin\frac{\pi}{L}y$$

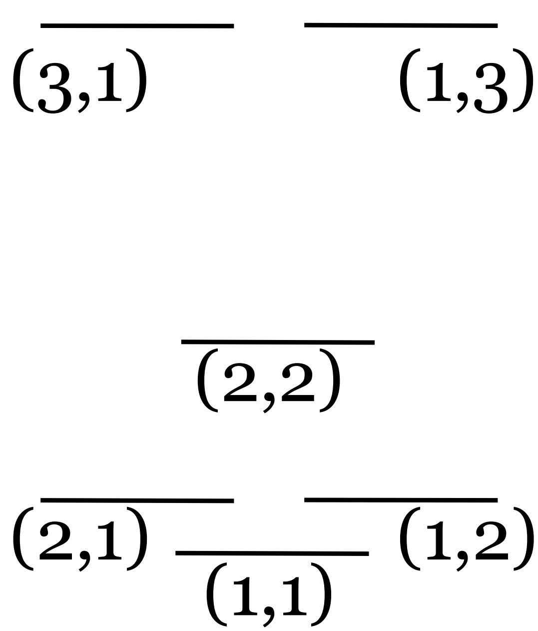
$$E_{2,1} = E_2 + E_1 = \frac{5h^2}{8mL^2}$$

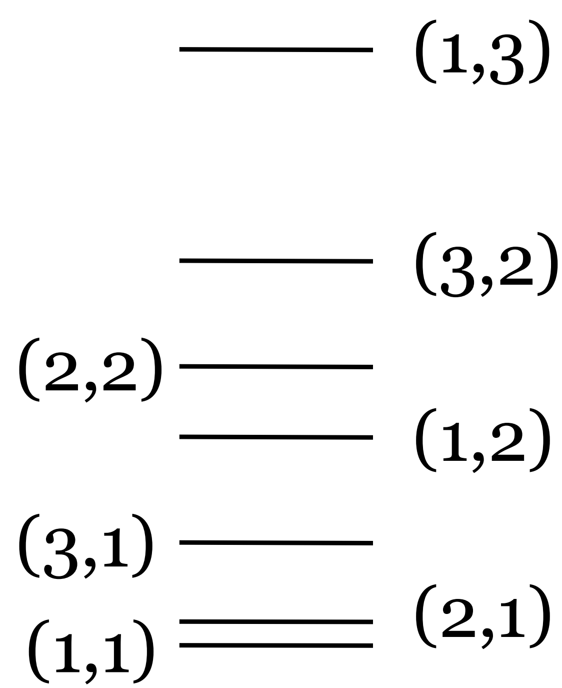
$E_{1,2} = E_{2,1} \Rightarrow \psi_{1,2}$ and $\psi_{2,1}$ are degenerate wavefunctions

Particle in 2-D Square-Well Potential – Symmetry

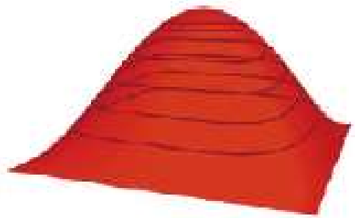


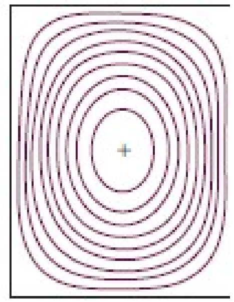


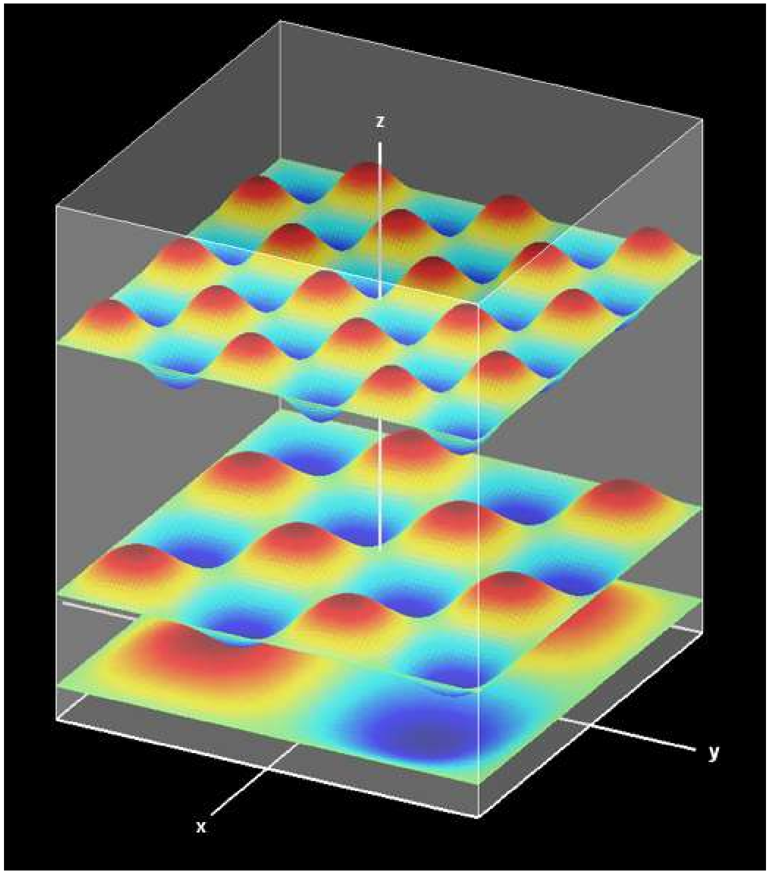


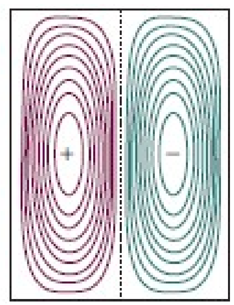


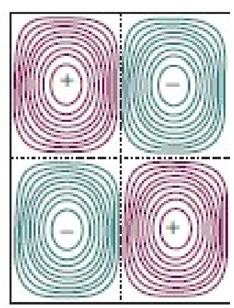
Particle in a 2-D Well – Wavefunctions











Number of nodes = n_x+n_y-2

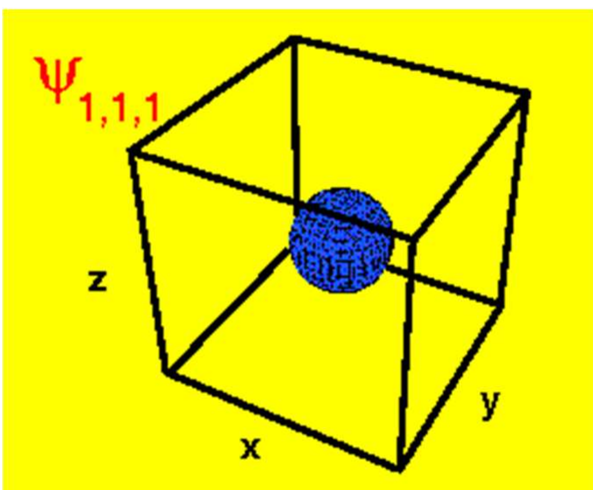
Particle in a 3D-Box

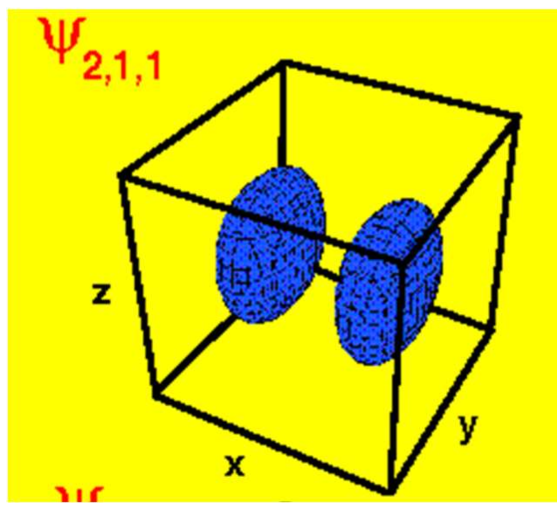
$$\psi(x,y,z)=\psi(x)\cdot\psi(y)\cdot\psi(z)$$

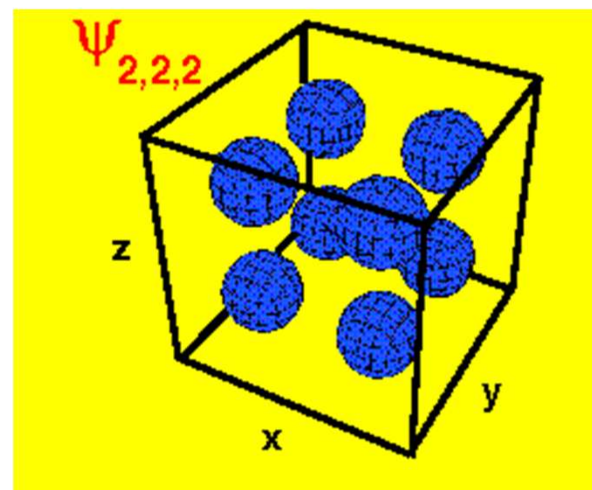
$$=\sqrt{\frac{2}{L_x}}\sin\frac{n_x\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n_y\pi}{L_y}y\cdot\sqrt{\frac{2}{L_z}}\sin\frac{n_z\pi}{L_z}z$$

$$E_{n_x,n_y,n_z}=E_{n_x}+E_{n_y}+E_{n_z}$$

$$=\frac{n_x^2h^2}{8mL_x^2}+\frac{n_y^2h^2}{8mL_y^2}+\frac{n_z^2h^2}{8mL_z^2}\quad n_x,n_y,n_z=1,2,3,4\ldots$$

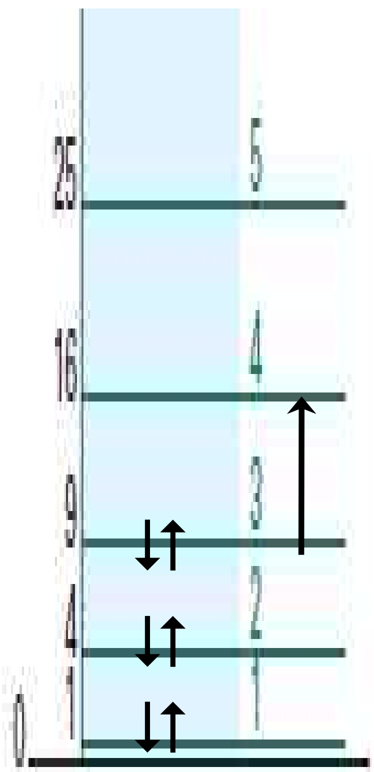






Particle in a Box – Application in Chemistry

Hexatriene is a linear molecule of length 7.3 Å
It absorbs at 258 nm
Use particle in a box model to explain the results.



Six π electron fill lower three levels

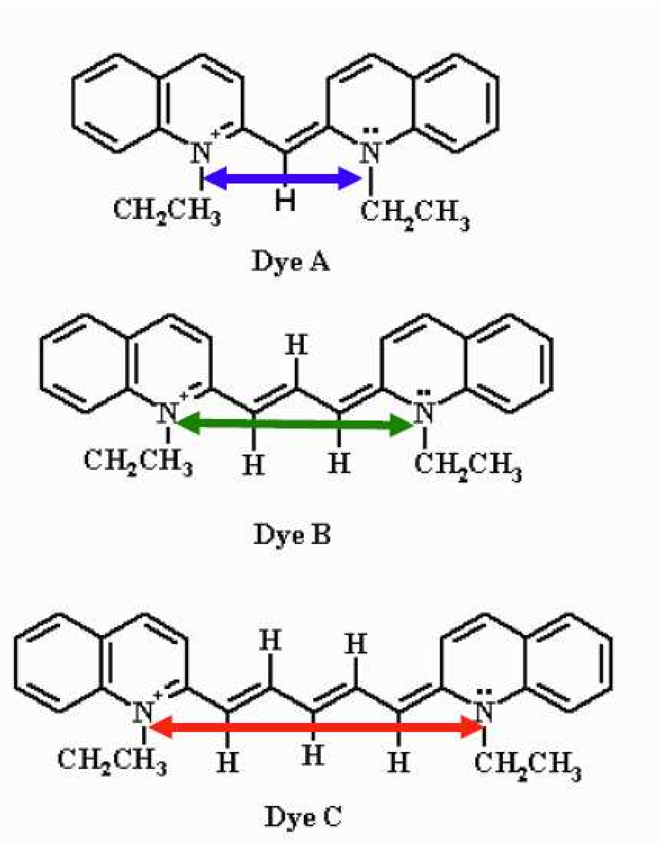
$$\Delta E = E_f - E_i = \left(n_f^2 - n_i^2\right)\frac{h^2}{8mL^2} = \frac{hc}{\lambda}$$

$$\lambda = \frac{8mL^2c}{h}\left(n_f^2 - n_i^2\right) \approx 251\text{nm}$$

Agrees well with the experimental value of 258 nm
Particle in a box is a good model

Particle in a Box – Application in Chemistry

Electronic spectra of conjugated molecules

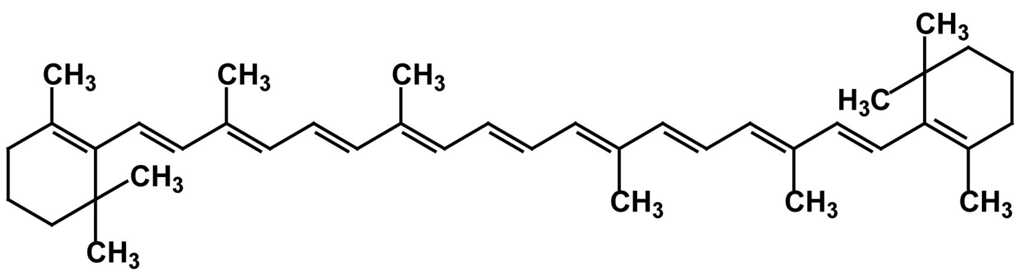


$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} \quad \Rightarrow \quad \lambda \propto L^2$$

Increase in bridge length increase the emission wavelength.

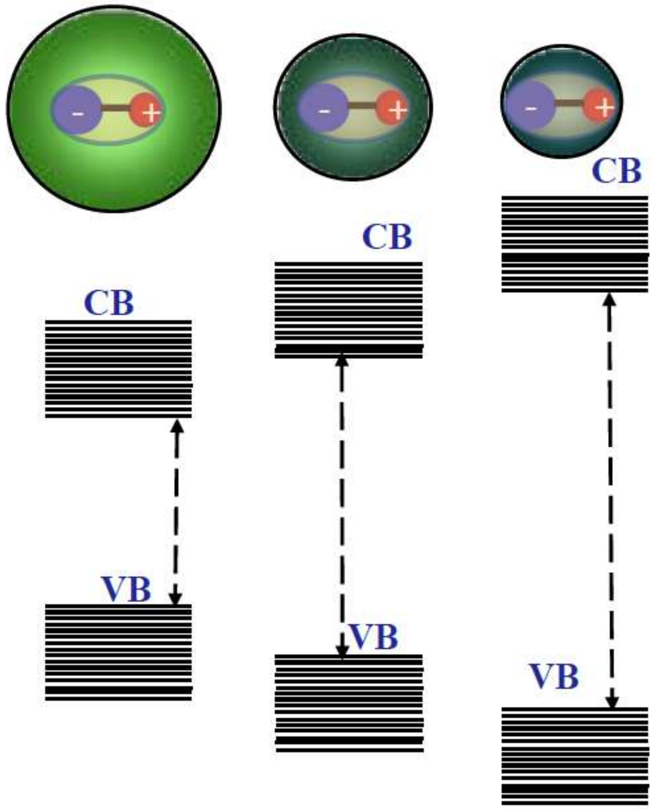
Predicts correct trend and gets the wavelength almost right.

Particle in a box is a good model



B-carotene is orange because of 11 conjugated double bonds

Particle in a Box – Application in nano-science



Band gap changes due to confinement, and so does the color of emitted light

Quantum Dots have a huge application in chemistry, biology, and materials science for photoemission imaging purpose, as well as light harvesting/energy science

What have we learnt?

Formulate a correct Hamiltonian (energy) Operator H

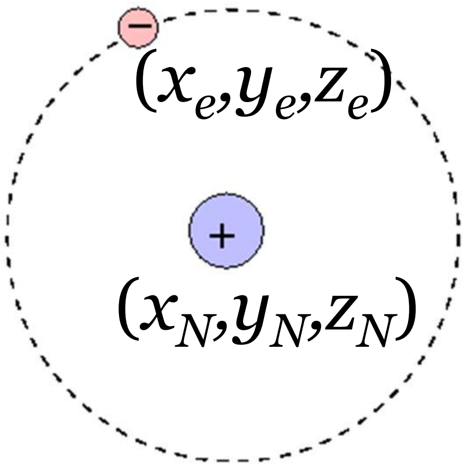
Solve TISE $H\Psi = E\,\Psi$ by separation of variables and intelligent trial wavefunction

Impose boundary conditions for eigenfunctions and obtain Quantum numbers

Eigenstatesor Wavefunctions: Should be "well behaved" - Normalization of Wavefunction

Probabilities and Expectation Values

Hydrogen Atom



Two particle central-force problem

Completely solvable – a rare example!

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{N\text{-}e}$$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_o}\frac{Z_N Z_e e^2}{r_{eN}}$$

$$\nabla_N^2 = \frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2} \qquad \nabla_e^2 = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

$$r_{eN} = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$

Hydrogen Atom

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_o}\frac{Z_N Z_e e^2}{r_{eN}}$$

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}$$

with $Z_N = Z \quad Z_e = 1$ and $\frac{1}{4\pi\varepsilon_o} = Q$

Schrodinger Equation

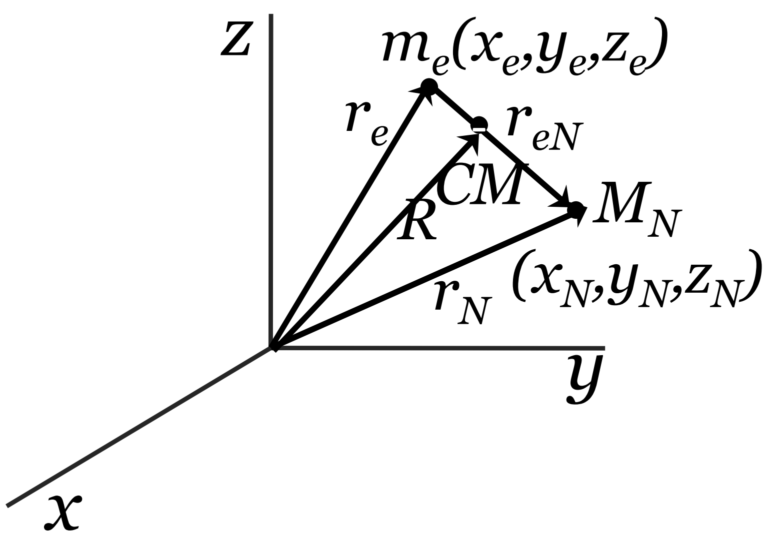
$$\left[-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right]\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

$$\Psi_{Total} = \Psi(x_N, y_N, z_N, x_e, y_e, z_e)$$

Hydrogen Atom: Relative Frame of Reference

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right)\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

Separation of $\hat{\boldsymbol{H}}$ into Center of Mass and Internal co-ordinates



$$x = x_e - x_N$$

$$y = y_e - y_N$$

$$z = z_e - z_N$$

$$r_e = \sqrt{\left(x_e^2 + y_e^2 + z_e^2\right)}$$

$$r_N = \sqrt{\left(x_N^2 + y_N^2 + z_N^2\right)}$$

$$r = r_{eN} = r_e - r_N$$

$$= \sqrt{\left(x^2 + y^2 + z^2\right)}$$

$$X = \frac{m_e x_e + m_N x_n}{m_e + m_N}$$

$$Y = \frac{m_e y_e + m_N y_n}{m_e + m_N}$$

$$Z = \frac{m_e z_e + m_N z_n}{m_e + m_N}$$

$$R = \frac{m_e r_e + m_N r_N}{m_e + m_N}$$

Hydrogen Atom: Relative Frame of Reference

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{QZe^2}{r_{eN}}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

$$\Downarrow$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

where $M=m_e+m_N$ and $\mu=\dfrac{m_e m_N}{m_e+m_N}$

Checkout Appendix-1

Hydrogen Atom: Separation to Relative Frame

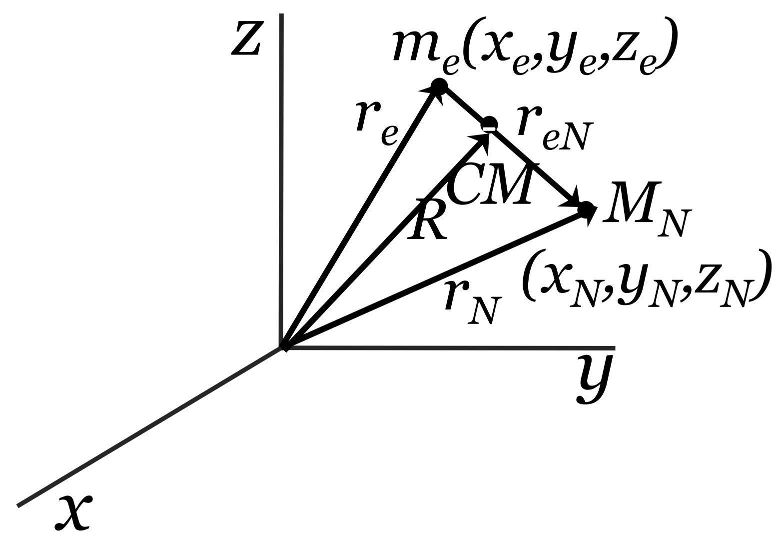
Appendix-1

Hydrogen atom has two particles the nucleus and electron with co-ordinates x_N, y_N, z_N and x_e, y_e, z_e

The potential energy between the two is function of relative co-ordinates $x=x_e-x_N$, $y=y_e-y_N$, $z=z_e-z_N$

$$r = ix + jy + kz$$

$$x = x_e - x_N, y = y_e - y_N, z = z_e - z_N$$



$$R = iX + jY + kZ$$

$$X = \frac{m_e x_e + m_N x_n}{m_e + m_N}, Y = \frac{m_e y_e + m_N y_n}{m_e + m_N}, Z = \frac{m_e z_e + m_N z_n}{m_e + m_N}$$

Hydrogen Atom: Separation to Relative Frame

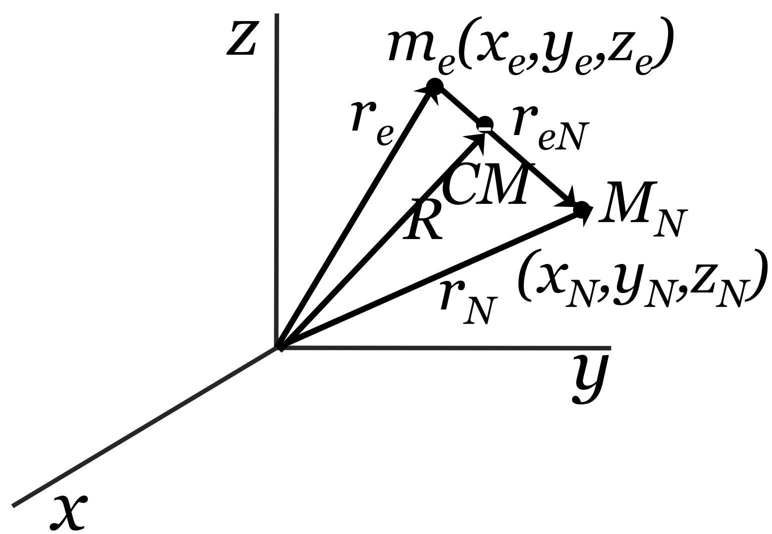
Appendix-1

$$R = \frac{m_e r_e + m_N r_N}{m_e + m_N}$$

$$r = r_{eN} = r_e - r_N$$

$$r_e = R - \frac{m_N}{m_e + m_N} r$$

$$r_N = R - \frac{m_e}{m_e + m_N} r$$



Hydrogen Atom: Separation to Relative Frame

Appendix-1

$$T = \frac{1}{2} m_e \left|\dot{r}_e\right|^2 + \frac{1}{2} m_N \left|\dot{r}_N\right|^2$$

$$T = \frac{1}{2} m_e \left(\dot{R} - \frac{m_N}{m_e + m_N} \dot{r} \right) \cdot \left(\dot{R} - \frac{m_N}{m_e + m_N} \dot{r} \right)$$

$$+ \frac{1}{2} m_e \left(\dot{R} - \frac{m_e}{m_e + m_N} \dot{r} \right) \cdot \left(\dot{R} - \frac{m_e}{m_e + m_N} \dot{r} \right)$$

$$T = \frac{1}{2} (m_e + m_N) \left|\dot{R}\right|^2 + \frac{1}{2} \left(\frac{m_e m_N}{m_e + m_N} \right) \left|\dot{r}\right|^2$$

$$\dot{r}_e = \frac{dr_e}{dt}$$

$$\dot{r}_N = \frac{dr_N}{dt}$$

$$\dot{r} = \frac{dr}{dt}$$

$$\dot{R} = \frac{dR}{dt}$$

$T = \frac{1}{2} M \left|\dot{R}\right|^2 + \frac{1}{2} \mu \left|\dot{r}\right|^2$ where $M = m_e + m_N$ and $\mu = \frac{m_e m_N}{m_e + m_N}$

Hydrogen Atom: Separation to Relative Frame

Appendix-1

$$T = \frac{1}{2} M \left|\dot{R}\right|^2 + \frac{1}{2} \mu \left|\dot{r}\right|^2$$

$$T = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu}$$

In the above equation the first term represent the kinetic energy of the center of mass (CM) motion and second term represents the kinetic energy of the relative motion of electron and

$$H = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu} - \frac{Z_N \cdot Z_e}{r}$$

$$\widehat{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{Z_N \cdot Z_e}{r}$$

Hydrogen Atom: Separation of CM motion

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

$$\widehat{H}=\widehat{H}_N+\widehat{H}_e \qquad \Psi_{Total}=\chi_N\cdot\psi_e \qquad E_{Total}=E_N+E_e$$

$$-\frac{\hbar^2}{2M}\nabla_R^2=\widehat{H}_N \qquad -\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}=\widehat{H}_e$$

$$\boxed{\widehat{H}_N\chi_N=\left(-\frac{\hbar^2}{2M}\nabla_R^2\right)\chi_N=E_N\chi_N}$$

Free particle!
Kinetic energy of the atom

$$E_N=\frac{\hbar^2k^2}{2M}$$