Part V

Applying Quantum Mechanics

Previous lecture

- Schrodinger equation in 3D

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

- Using separation of variables by taking $\psi(x,y,z)=X(x)Y(y)Z(z)$
- Form of potential for separation of variables technique to be applicable

$$V(x,y,z)=V_1(x)+V_2(y)+V_3(z)$$

Examples:

$$\textit{Free particle} \quad V(x,y,z)=constant=0$$

$$\textit{Particle in a 3D rectangular box with potential being } \infty \textit{ outside}$$

$$\textit{3D harmonic oscillator } V(x,y,z)=\frac{1}{2}m\omega_1^2x^2+\frac{1}{2}m\omega_2^2y^2+\frac{1}{2}m\omega_3^2z^2$$

Previous lecture: Separation of variables technique ....

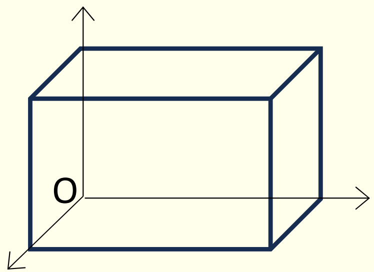
- Schrodinger equation is separated for each variable

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}+V_1(x)X(x)=E_xX(x) \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}+V_2(y)Y(y)=E_yY(y) \qquad -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2}+V_3(z)Z(z)=E_zZ(z)$$

- Total energy of the system $E = E_x + E_y + E_z$

➢ Free particle $\psi(x,y,z) = Ce^{i(k_xx+k_yy+k_zz)} = Ce^{i\vec{k}.\vec{r}}$; $\vec{p} = \hbar\vec{k}$; $E = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$

➢ Particle in a rectangular box of size $L_x \times L_y \times L_z$ with one corner at the origin and three faces on the xy, yz and zx planes



$$\psi(x,y,z) = \sqrt{\frac{8}{L_xL_yL_z}};\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)\sin\left(\frac{n_z\pi}{L_z}z\right); \quad E = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

Previous lecture

- Angular momentum in spherical coordinates

$$L_x = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right] \quad L_y = i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right] \quad L_z = -i\hbar\frac{\partial}{\partial\phi}$$

- Eigenfunctions $\Phi(\phi)$ of L_z

$$L_z\Phi(\phi) = -i\hbar\frac{\partial\Phi}{\partial\phi} = \lambda\Phi(\phi) \qquad gives \qquad \Phi(\phi) = Ce^{i\left(\frac{\lambda}{\hbar}\right)\phi}$$

- Boundary condition $\Phi(\phi + 2\pi) = \Phi(\phi)$ gives $\lambda = m_z\hbar$ $\quad (m_z = 0, \pm1, \pm2, \dots\dots)$
- Normalization is done over $0 \le \phi \le 2\pi$ and gives normalized wavefunctions

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_z\phi} \qquad (m_z = 0, \pm1, \pm2, \dots\dots)$$

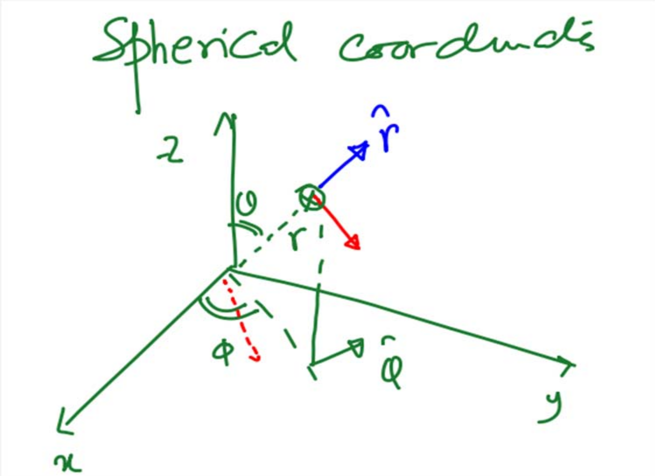
- For a particle mass m free to move on a ring of radius R

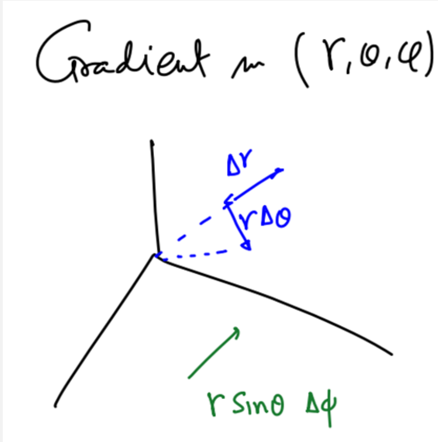
$$H = \frac{L_z^2}{2mR^2} = -\frac{\hbar^2}{2mR^2}\frac{d^2}{d\phi^2} \;\; ; \;\; H\psi(\phi) = E\psi(\phi) \;\; gives \;\; E = \frac{m_z^2\hbar^2}{2mR^2} \; with \; \psi(\phi) = \Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_z\phi}$$

Lecture 29

Schrödinger equation for
3D spherically symmetric potentials
(i) Normalization using spherical Polar coordinates
(ii) The hydrogen atom

Describing classical motion using spherical coordinates: The kinetic energy and the angular momentum





$$\hat{r} = \sin\theta\cos\phi\hat{x} + \sin\theta\sin\phi\hat{y} + \cos\theta\hat{z}$$

$$\hat{\theta} = \cos\theta\cos\phi\hat{x} + \cos\theta\sin\phi\hat{y} - \sin\theta\hat{z}$$

$$\hat{\phi} = -\sin\phi\hat{x} + \cos\phi\hat{y}$$

$$\vec{v} = \dot{r}\hat{r} + r\dot{\theta}\hat{\theta} + r\sin\theta\dot{\phi}\hat{\phi}$$

$$v^2 = \dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2$$

$$\vec{p} = m\dot{r}\hat{r} + mr\dot{\theta}\hat{\theta} + mr\sin\theta\dot{\phi}\hat{\phi}$$

$$\vec{L} = \vec{r} \times \vec{p} = mr^2\dot{\theta}\hat{\phi} - mr^2\sin\theta\dot{\phi}\hat{\theta}$$

$$KE = \frac{p^2}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

Angular momentum operator and Kinetic energy operator in spherical coordinates

$$\boldsymbol{L}^2 = \boldsymbol{L}_x^2 + \boldsymbol{L}_y^2 + \boldsymbol{L}_z^2$$

$$= -\hbar^2\left[\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right]^2 - \hbar^2\left[-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right]^2 - \hbar^2\frac{\partial^2}{\partial\phi^2}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Kinetic energy operator

$$\frac{\vec{\boldsymbol{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\boldsymbol{L}^2}{2mr^2}$$

$$\begin{aligned}&\textit{Kinetic energy due to radial motion}\\ &+\ \textit{kinetic energy due to motion in angular directions}\end{aligned}$$

Schrödinger equation for radially symmetric (no angular dependence) potentials and separation of variables

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

OR

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{2mr^2}L^2(\theta,\phi)\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

- Since the potential depends only on r, the wavefunction can be written as

$$\psi(r,\theta,\phi)=R(r)Q(\theta,\phi)$$

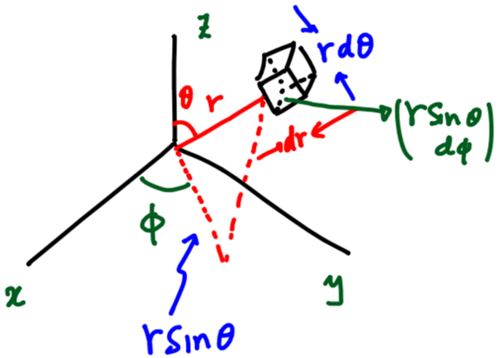
- Here $Q(\theta,\phi)$ are the eigenfunctions of total and z-component of angular momentum

$$L^2(\theta,\phi)Q_{l,m_z}(\theta,\phi)=-\frac{\hbar^2}{2m}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Q_{l,m_z}=l(l+1)\hbar^2Q_{l,m_z}$$

$$L_zQ_{l,m_z}=m_z\hbar Q_{l,m_z}\qquad -l\le m_z\le l$$

Normalization of wavefunction using spherical coordinates

Spherical polar coordinates



$0 \leq r < \infty$

$0 \leq \theta \leq \pi$

$0 \leq \phi \leq 2\pi$

Volume element

$$dV = dr \times r\,d\theta \times r\sin\theta\, d\phi$$

$$= r^2 dr \sin\theta\, d\theta\, d\phi$$

$0 \leq \theta \leq \pi$

$0 \leq r < \infty$

$0 \leq d\phi \leq 2\pi$

$$dV = r^2 dr\, d(\cos\theta)\, d\phi$$

$-1 \leq \cos\theta \leq 1$

$$\int_0^\infty dr\, r^2 |R(r)|^2 \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi |Q(\theta,\phi)|^2 = 1$$

$$\int_0^\infty dr\, r^2 |R(r)|^2 \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi |Q(\theta,\phi)|^2 = 1$$

Some eigenfunctions of the angular momentum operators

$$l = 0 \quad m_z = 0 \ (s \text{ orbital})$$

$$Q_{00} = constant$$

$$l = 1 \quad m_z = -1, 0, +1 \ (p \text{ orbitals})$$

$$Q_{1\pm1}(\theta,\phi) = C\sin\theta e^{\pm i\phi} \qquad Q_{10}(\theta,\phi) = C\cos\theta$$

$$l = 2 \qquad m_z = -2, -1, 0, +1, +2 \ (d \text{ orbitals})$$

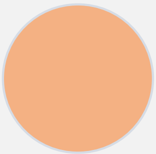
$$Q_{2\pm2}(\theta,\phi) = \mathrm{C}\sin^2\theta e^{\pm 2i\phi} \qquad Q_{2\pm1}(\theta,\phi) = C\sin\theta\cos\theta e^{\pm i\phi}$$

$$Q_{20}(\theta,\phi) = C(3\cos^2\theta - 1)$$

Assignment problem: Find normalization constants for each of these wavefunctions

Polar plots of angular momentum eigenfunctions

Show the orbital by drawing a line of length
equal to the value of the eigenfunction at the given (θ, ϕ)



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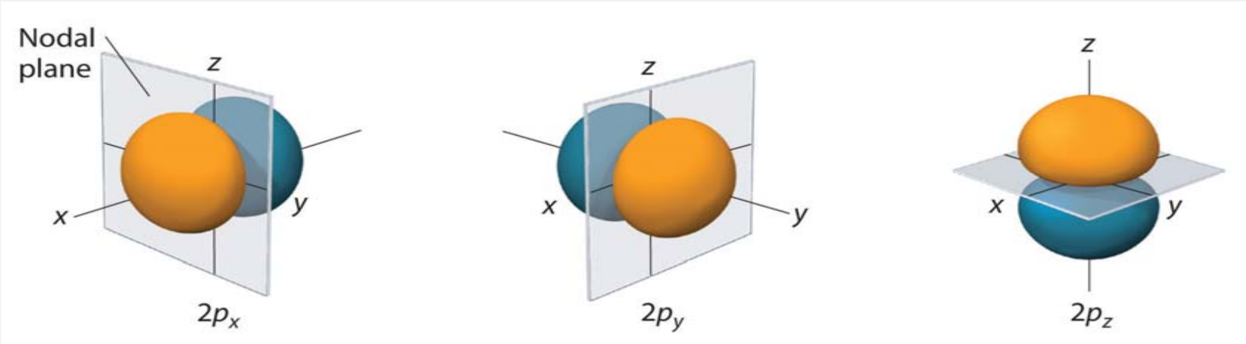


$Q_{00} = constant$

$p_x = Csin\theta cos\phi$
$= Q_{1+1}(\theta, \phi) + Q_{1-1}(\theta, \phi)$

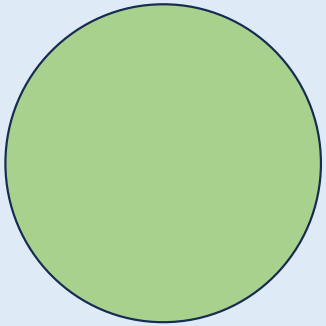
$p_y = Csin\theta sin\phi$
$= Q_{1+1}(\theta, \phi) - Q_{1-1}(\theta, \phi)$

$p_z = Ccos\theta$
$= Q_{10}(\theta, \phi)$

SHAPE OF THE ORBITAL

Probability density plots for angular momentum eigenfunctions

Show the shape of the orbital by drawing a line of length equal to square of the eigenfunction at the given (θ, ϕ)



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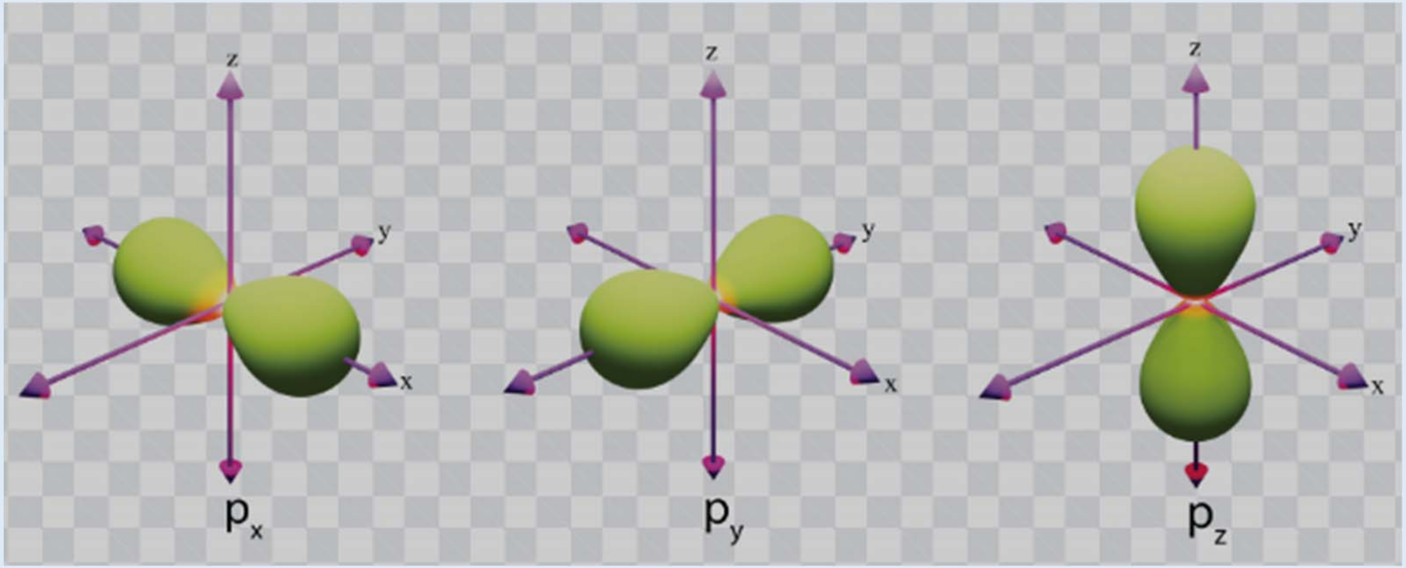


Schrödinger equation for radially symmetric potentials ....

- With $L^2(\theta,\phi)Q_{lm_z}(\theta,\phi) = l(l+1)\hbar^2 Q_{lm_z}$ The Schrödinger equation for $R(r)$ becomes

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l(r)}{dr}\right) + \left(\frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right)R_l(r) = ER_l(r)$$

- This is to be solved with the boundary conditions

$$R(0) = finite \text{ and } R(\infty) = 0$$

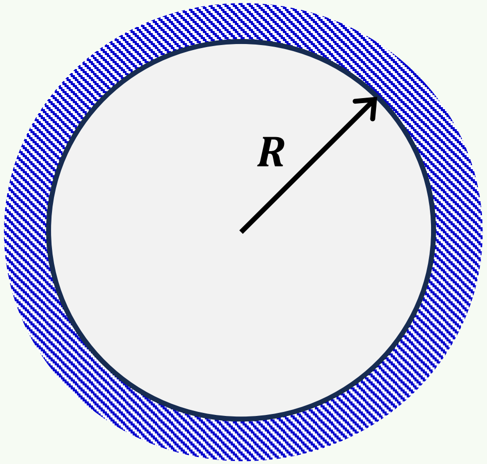
- For simplifying the equation take $u(r) = rR(r)$ or equivalently $R(r) = u(r)/r$ so that (Assignment problem)

$$-\frac{\hbar^2}{2m}\frac{d^2u_l(r)}{dr^2} + \left(\frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right)u_l(r) = Eu_l(r)$$

- Boundary conditions on $u(r)$

$$u_l(0) = 0 \text{ and } u_l(\infty) = 0$$

Solution for a spherical box for $l = 0$
(connection with quantum dot spectrum; lecture 27)



The potential

$$V(r) = \begin{cases} 0 & r < R \\ \infty & r \geq R \end{cases}$$

Schrödinger equation for $l = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{n0}(r)}{dr^2} = E u_{n0}(r)$$

Boundary condition and solution

$$u_{n0}(0) = 0 \qquad u_{n0}(R) = 0$$

$$u_{n0}(r) = C\sin\left(\frac{n\pi}{R}r\right) \qquad E_{n0} = \frac{\hbar^2\pi^2}{2mR^2}n^2$$

Solution for the hydrogen-like atoms ($l = 0$)

- The Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2u_{n0}(r)}{dr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}u_{n0}(r) = Eu_{n0}(r)$$

- For bound states $E < 0$ ($E = -|E|$) and the boundary conditions are

$$u_{n0}(0) = 0 \qquad u_{n0}(\infty) = 0$$

- In the limit $r \to \infty$

$$\frac{\hbar^2}{2m}\frac{d^2u_{n0}(r)}{dr^2} - |E|u_{n0}(r) = 0 \quad \text{and therefore} \quad u_{n0}(r \to \infty) = e^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$$

- In the limit of $r \to 0$ the solution is of the form

$$u_{10}(r) = Cre^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$$

and satisfies the Schrödinger equation and the boundary condition $u_{10}(0) = 0$

Solution for the hydrogen-like atoms ($\boldsymbol{l = 0}$)

- Substitute $\boldsymbol{u_{10}(r) = Cre^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}}$ in the Schrödinger equation to get lowest energy

$$\boldsymbol{E_1 = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2}}$$

- The ground-state wavefunction is

$$\boldsymbol{\psi_{10}(r,\theta,\phi) = R_{10}(r) = Ce^{-Zr/a_0}}$$

with

$$\boldsymbol{a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = Bohr\ radius}$$

Higher state solution for the hydrogen-like atoms ($\boldsymbol{l = 0}$)

- For higher energy states, take the solution to be of the form to satisfy

$$u_{n0}(r) = Crf_{n-1}(r)e^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$$

with $f_{n-1}(r)$ being a polynomial of degree $(n-1)$

- Substitute in the Schrödinger equation to get the energy

$$E_n = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2} \times \frac{1}{n^2}$$

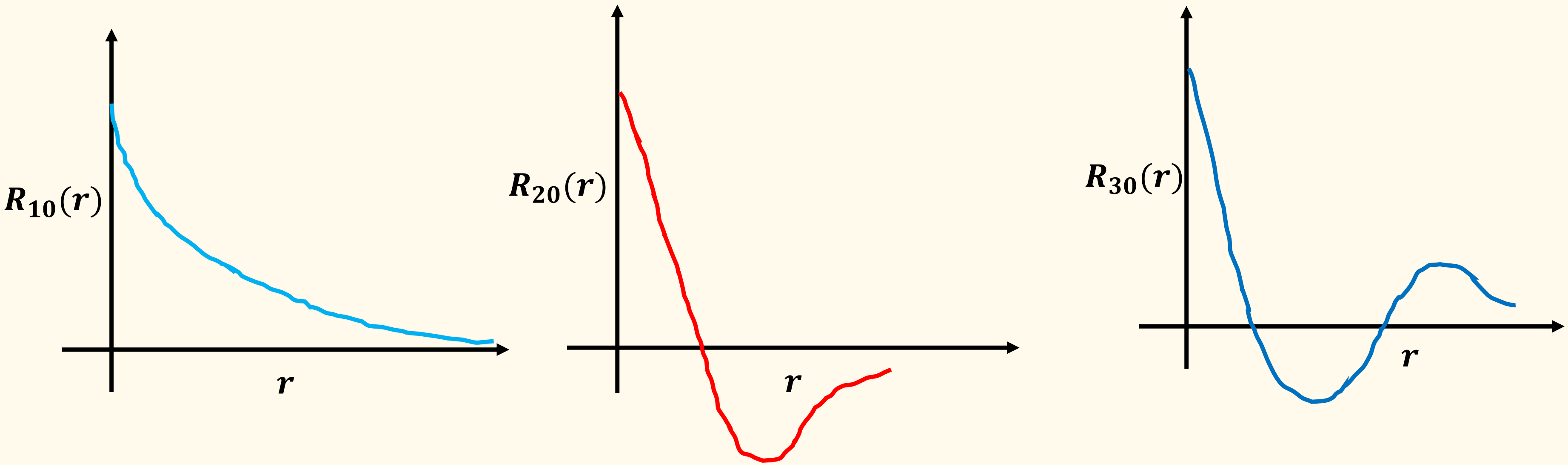
and the coefficients of the polynomial $f_{n-1}(r)$

- The wavefunction is

$$\psi_{n0}(r,\theta,\phi) = R_{n0}(r) = Cf_{n-1}(r)e^{-Zr/na_0}$$

- The wavefunction is spherically symmetric and has $(n-1)$ nodes

The first three wavefunctions for $\boldsymbol{l = 0}$ (these are called $\boldsymbol{s}$ orbitals)

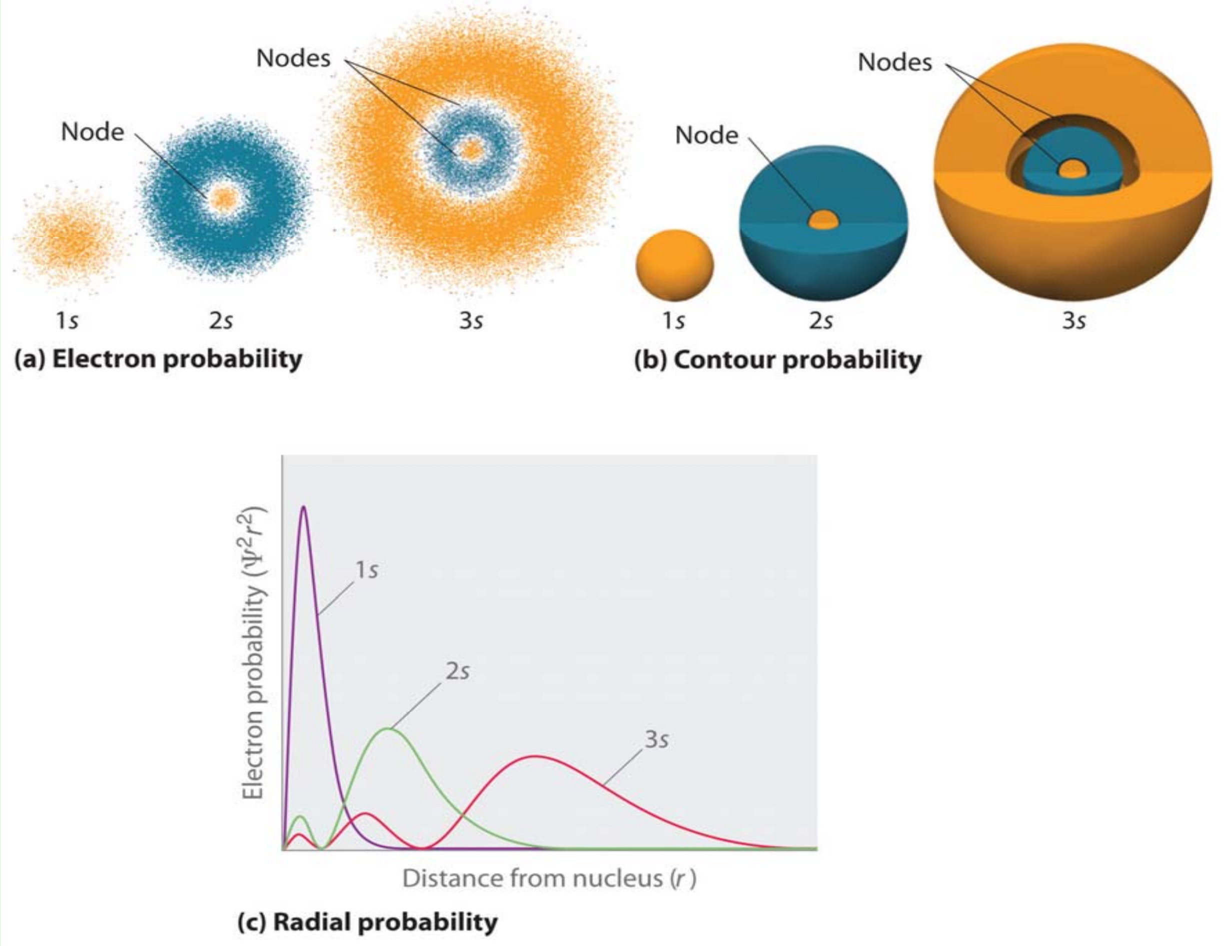


$R_{10}(r) = C_1 e^{-Zr/a_0}$

$R_{20}(r) = C_2\left(2 - \frac{Zr}{a_0}\right) e^{-2Zr/a_0}$

$R_{30}(r) = C_3\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-3Zr/a_0}$

Radial Probability density $r^2 R_{n0}^2$ for the first three $l = 0$ wavefunctions



Solution for the hydrogen-like atoms ($\boldsymbol{l \neq 0}$)

- The Schrödinger equation for $\boldsymbol{l \neq 0}$

$$-\frac{\hbar^2}{2m}\frac{d^2u_{nl}(r)}{dr^2}+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{Ze^2}{4\pi\epsilon_0 r}u_{nl}(r)=Eu_{nl}(r)$$

- For bound states $\boldsymbol{E<0}$ $(\boldsymbol{E=-|E|})$ and the boundary conditions are

$$u_{nl}(0)=0 \qquad u_{nl}(\infty)=0$$

- In the limit $r \to \infty$

$$\frac{\hbar^2}{2m}\frac{d^2u_{nl}(r)}{dr^2}-|E|u_{nl}(r)=0 \quad \text{and therefore} \quad u_{nl}(r\to\infty)=e^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$$

- In the limit of $\boldsymbol{r \to 0}$ the solution is of the form

$$u_{n=l+1\,l}(r)=\mathrm{C}r^{l+1}e^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$$

and satisfies the Schrödinger equation and the boundary condition

$$u_{n=l+1\,l}(0)=0$$

Solution for the hydrogen-like atoms ($\boldsymbol{l \neq 0}$)

- Substitute $u_{n=l+1\,l}(r) = Cr^{l+1}e^{-\sqrt{\frac{2m|E|}{\hbar^2}}r}$ in the Schrödinger equation to get lowest energy for a given $\boldsymbol{l}$

$$E_{l+1} = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2} \times \frac{1}{(l+1)^2}$$

- The lowest energy wavefunction for a given $\boldsymbol{l}$ is

$$\psi_{n=l+1\,l\,m_z}(r,\theta,\phi) = R_{n=l+1\,l}(r)Q_{lm_z}(\theta,\phi) = Cr^l e^{-Zr/(l+1)a_0}Q_{lm_z}(\theta,\phi)$$

with

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = Bohr\ radius$$

Lowest energy eigenfunction for $\boldsymbol{l = 1}$ state

$$\psi_{n=2\; l=1\; m_z}(r,\theta,\phi) = R_{n=2\; l=1}(r)Q_{l=1 m_z}(\theta,\phi) = Cre^{-Zr/2a_0}Q_{l=1m_z}(\theta,\phi)$$

$$\psi_{210} = C\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$$

$$\psi_{21\pm1} = C\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta e^{\pm i\phi}$$

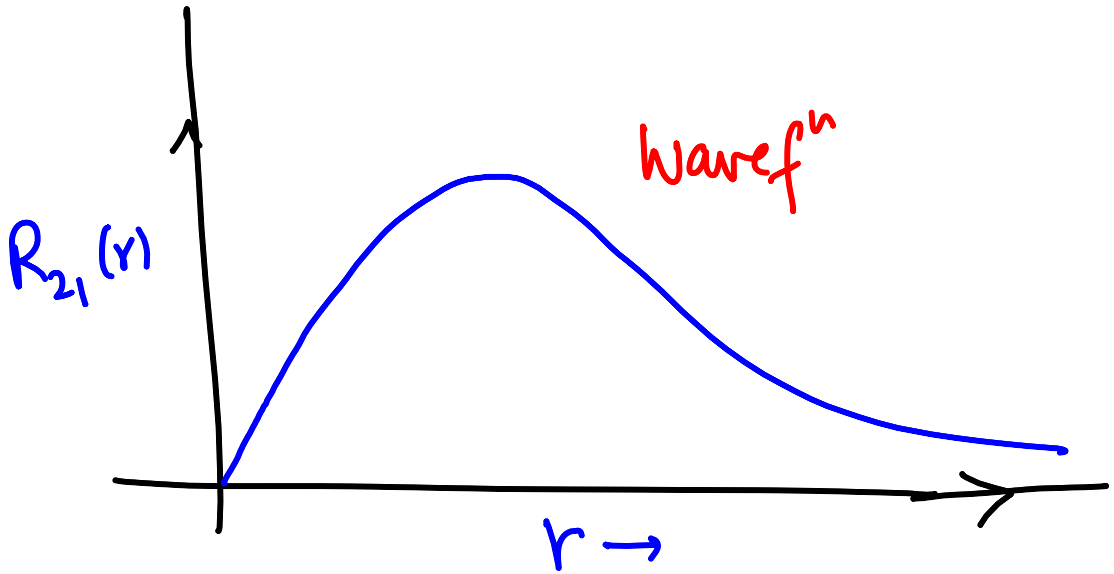
$$E_{n=2,l=1} = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2}\times\frac{1}{2^2}$$

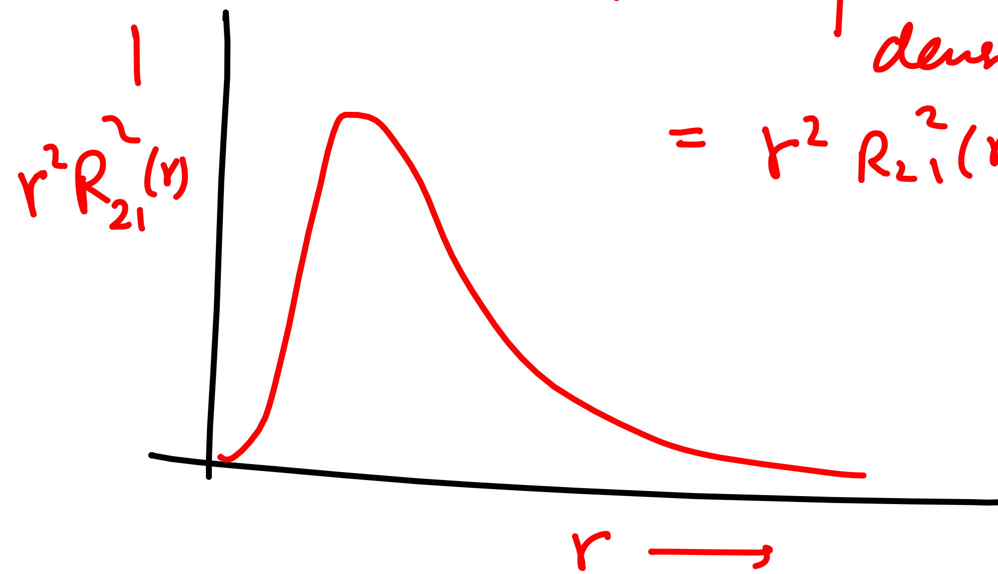
Note that

$$E_{n=2,l=1} = E_{n=2,l=0}$$

$R_{n=2,\,l=1}(r)$ for hydrogen-like atoms

$$R_{n=2,\,l=1} = C\, r\, e^{-Zr/2a_0}$$





radial prob. density $= r^2 R_{21}^2(r)$

$$E_{n=2,\,l=0} = E_{n=2,\,l=1}$$

Energy depends only on 'n'.

(θ, ϕ) variation of $p_x = Q_{1+1} + Q_{1-1}$ (not an eigenf^n of L_z but an eigenf^n of L^2)

$p_y = Q_{1+1} - Q_{1-1}$

$p_z = Q_{10}$