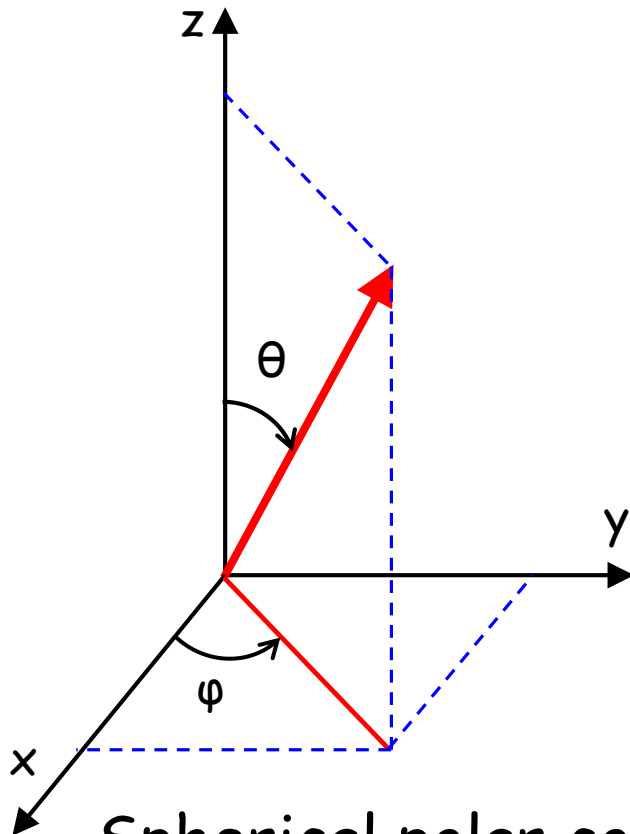


QM for the hydrogen atom

Schrödinger eq. for the hydrogen atom

$$\hat{H} = \frac{p^2}{2m} + V(r)$$

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



$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\frac{\partial}{\partial x} = \sin \theta \cos \phi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \phi \frac{\partial}{\partial \theta} - \frac{1 \sin \phi}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = \sin \theta \sin \phi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \phi \frac{\partial}{\partial \theta} + \frac{1 \cos \phi}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \cos \theta \frac{\partial}{\partial r} - \frac{1}{r} \sin \theta \frac{\partial}{\partial \theta}$$

Spherical polar coordinates

Transformation of the Schrödinger eq.

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \Lambda \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda \quad \Lambda = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\end{aligned}$$

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

Plugging-in $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

Multiplying the both sides by $-\frac{2m}{\hbar^2} \frac{r^2}{RY}$

Separation of variables

$$\frac{\hbar^2}{2m} \left[\frac{1}{R} \left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} \right) + \{E - V(r)\} \right] = -\frac{\Lambda Y}{Y} = \lambda \text{ (constant)}$$

depends the only r

depends θ and ϕ

$$-\frac{\hbar^2}{2m} \left\{ \frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} - \frac{\lambda}{r^2} R(r) \right\} + V(r)R(r) = ER(r)$$

$$\Lambda Y(\theta, \phi) - \lambda Y(\theta, \phi) = 0$$

Plugging-in $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \left(\lambda - \frac{\nu}{\sin^2 \theta} \right) \Theta(\theta) = 0$$

$$\frac{\partial^2}{\partial \phi^2} \Phi(\phi) - \nu \Phi(\phi) = 0$$

Solutions to the Eigenvalue eqs. for φ and θ

$$\frac{\partial^2}{\partial \phi^2} \Phi(\phi) + \nu \Phi(\phi) = 0$$

$$\Phi(\phi) = C \exp(i \nu^{1/2} \phi)$$

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

$$\nu^{1/2} = m \quad (m = 0, \pm 1, \pm 2, \dots)$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad (m = 0, \pm 1, \pm 2, \pm 3 \dots)$$

Magnetic quantum number

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \left(\lambda - \frac{\nu}{\sin^2 \theta} \right) \Theta(\theta) = 0$$

Replacing θ and ν by

$$\nu = m^2 \quad (m = 0, \pm 1, \pm 2, \dots)$$
$$z = \cos \theta$$

$$m = 0 \quad \frac{d}{dz} \left((1 - z^2) \frac{dP(z)}{dz} \right) + \lambda P(z) = 0 \quad \text{Legendre's differential eq.}$$

Solution $P(z) \rightarrow P'_\ell(z)$

$$P'_\ell(z) = \sum_\ell a_\ell z^\ell \quad \text{finite term} \quad a_{\ell+2} = \frac{\ell(\ell+1) - \lambda}{(\ell+1)(\ell+2)} a_\ell \quad \text{Recursion formula}$$

To avoid $P'_\ell(z) = \sum_\ell a_\ell z^\ell \rightarrow \infty \Rightarrow \ell(\ell+1) = \lambda$

$$P_\ell(z) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dz^\ell} (z^2 - 1)^\ell$$

Rigorous solutions
= Legendre polynomial

$$m \neq 0 \quad P_\ell^m(z) = (1 - z^2)^{\frac{m}{2}} \frac{d^m}{dz^m} P_\ell(z)$$

Associated
Legendre function

$$P_\ell(z) = \sum_\ell a_\ell z^\ell \Rightarrow \frac{d^m}{dz^m} P_\ell(z) \quad \text{Polynomial}$$

To avoid $P_\ell(z) = \sum_\ell a_\ell z^\ell \rightarrow \infty \Rightarrow \ell(\ell+1) = \lambda$

If $m > \ell \Rightarrow P_\ell^m(z) = 0$

$\Rightarrow m = 0, \pm 1, \pm 2, \pm 3 \dots, \pm \ell \quad \lambda = \ell(\ell+1) \quad \ell \geq m$

Rewriting $Y(\theta, \phi) \rightarrow Y_\ell^m(\theta, \phi)$

Eigen function: $Y_\ell^m(\theta, \phi) = N_\ell^m P_\ell^m(\cos \theta) \exp(im\phi)$

Normalization $\Rightarrow N_\ell^{\pm m} \left\{ \frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!} \right\}^{\frac{1}{2}}$

$$\left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} Y_\ell^m(\theta, \phi) = -\ell(\ell + 1) Y_\ell^m(\theta, \phi)$$

$$-\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} Y_\ell^m(\theta, \phi) = \ell(\ell + 1) \hbar^2 Y_\ell^m(\theta, \phi)$$

$= \hat{L}^2$

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \ell(\ell + 1) \hbar^2 Y_\ell^m(\theta, \phi) \quad \ell \text{ Angular momentum quantum number}$$

$$\hat{L}_z Y_\ell^m(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} Y_\ell^m(\theta, \phi) = m\hbar Y_\ell^m(\theta, \phi)$$

$$m = 0, \pm 1, \pm 2, \pm 3 \dots, \pm \ell \quad \text{Magnetic quantum number}$$



Memo: Angular momentum and rigid motor model

Radial direction

$$-\frac{\hbar^2}{2m} \left\{ \frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} - \frac{\ell(\ell+1)}{r^2} R(r) \right\} + V(r)R(r) = ER(r)$$

$$V(r) = -\frac{Ze^2}{r} \quad R(r) = \frac{1}{r} \chi(r), \quad \rho = \alpha r$$

$$\chi''(\rho) + \left\{ \frac{2mE}{\hbar^2} \frac{1}{\alpha^2} + Ze^2 \frac{2m}{\hbar^2 \alpha} \frac{1}{\rho} \right\} \chi(\rho) - \frac{\ell(\ell+1)}{\rho^2} \chi(\rho) = 0$$

$$\alpha^2 = -\frac{8mE}{\hbar^2}, \quad N = \frac{2mZe^2}{\alpha \hbar^2}$$

$$\chi''(\rho) + \left\{ \frac{N}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} \right\} \chi(\rho) = 0$$

$$R(r) \rightarrow 0$$

$$\chi(\rho) = e^{-\frac{\rho}{2}} \rho^\ell \sum_{\mu} a_{\mu} \rho^{\mu} \quad a_{\mu+1} = \frac{N - (\ell + \mu + 1)}{2(\mu + 1)(\ell + 1) + \mu(\mu + 1)} a_{\mu}$$

$$\chi(\rho) \rightarrow 0, \quad |\chi(\rho)|^2 : \text{Integrable} \quad (\rho \rightarrow \infty)$$

$$\Rightarrow \quad \boxed{N = \ell + \mu + 1} \quad \Rightarrow \quad N = n \geq 1 \quad n = 1, 2, 3, \dots$$

Principle quantum number

$$\Rightarrow \quad \ell = n - 1 - \mu \quad \Rightarrow \quad \ell = 1, 2, \dots, n - 1$$

Solution:

$$\chi(\rho) = A_{n\ell} e^{-\frac{\rho}{2}} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) \quad L_{n+\ell}^{2\ell+1}(\rho) \quad \text{Associated Laguerre polynomial}$$

$$\alpha^2 = -\frac{8mE}{\hbar^2}, \quad N = \frac{2mZe^2}{\alpha\hbar^2}$$

$$\Rightarrow \quad E_n = -\frac{mZ^2e^4}{2\hbar^2} \cdot \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Total wave functions

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell}^m(\theta, \phi)$$

determined by three quantum numbers

$$\begin{array}{l} n = 1, 2, 3, \dots \quad \rightarrow \quad \ell = 0, 1, 2, \dots, (n-1) \\ \ell = 0, 1, 2, \dots, (n-1) \quad \rightarrow \quad m = 0, \pm 1, \pm 2, \dots, \pm \ell \end{array}$$

$$n = 1, 2, 3, \dots$$

Principle quantum number

- ✓ Determines total energy that is conserved and quantized.
cf. planetary motion

$$\ell = 0, 1, 2, \dots, (n-1)$$

Angular momentum
quantum number

- ✓ Gives quantization of angular momentum magnitude.

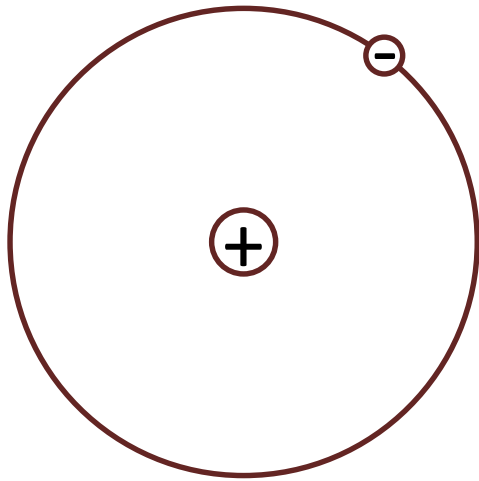
$$m = 0, \pm 1, \pm 2, \pm 3 \dots, \pm \ell$$

Magnetic quantum number

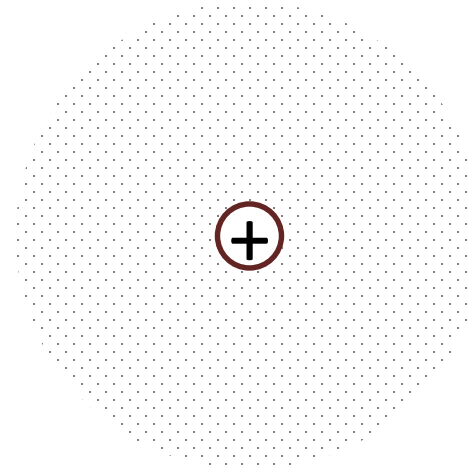
$$(2\ell + 1)$$

- ✓ Gives quantization of angular momentum direction.
orientation

Principle quantum number



Bohr model

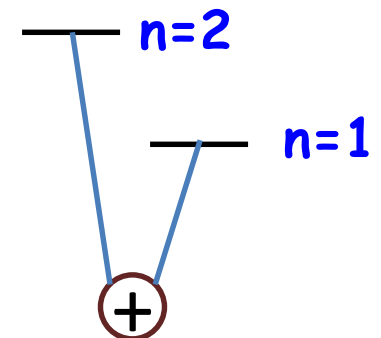


Quantum mechanics

Principle quantum number $n = 1, 2, 3, \dots$

The main energy level (shell) occupied by the electron.

Average distance from the nucleus.



Quantization of energy!!

Angular momentum quantum number

Angular momentum quantum number

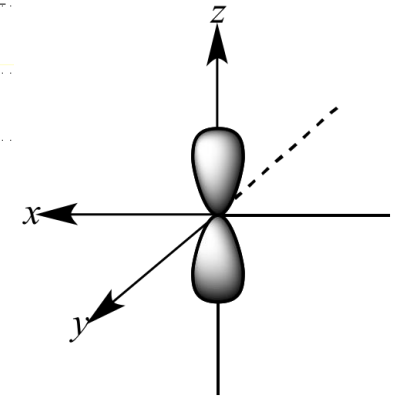
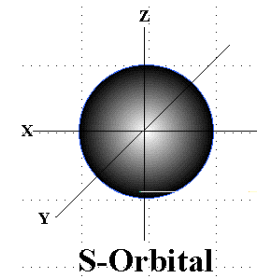
$$\ell = 0, 1, 2, \dots, (n-1)$$

Shape of the orbitals

$n=1 \Rightarrow \ell=0$ s orbital

$n=2 \Rightarrow \ell=0, 1$ $\ell=0$ s orbital

$\ell=1$ p orbital



$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} (-V + E) - \frac{\ell(\ell+1)}{r^2} \right] R = 0$$

$$E = KE_{Radial} + KE_{Orbital} + V$$

$$\Rightarrow \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[KE_{Radial} + KE_{Orbital} - \frac{\ell(\ell+1)}{2mr^2} \right] R = 0$$

$$\Rightarrow KE_{Orbital} = \frac{\ell(\ell+1)}{2mr^2} \quad \Rightarrow KE_{Orbital} = \frac{L^2}{2mr^2} \quad KE_{Orbital} = \frac{1}{2} m v_{orb}^2 \quad L = m v_{orb} r$$

$$\Rightarrow L = \sqrt{\ell(\ell+1)} \hbar \quad \mathbf{L: Angular momentum}$$

Quantization of angular momentum magnitude!!

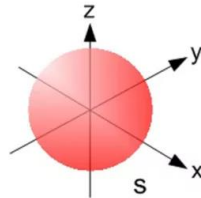
Magnetic quantum number

Magnetic quantum number

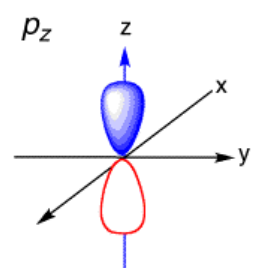
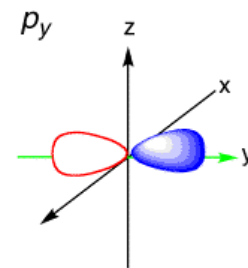
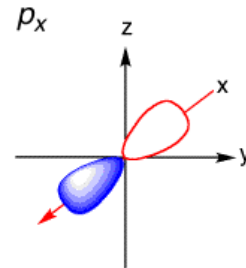
$$m_\ell = -\ell \dots 0 \dots +\ell$$

Orientation of an orbital around the nucleus.

$$\ell = 0 \Rightarrow m_\ell = 0$$



$$\ell = 1 \Rightarrow m_\ell = -1, 0, 1$$

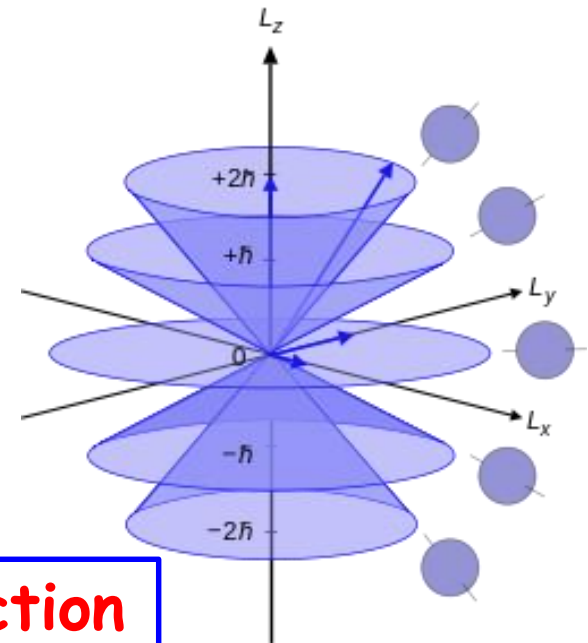


The three p orbitals are aligned along perpendicular axes

The projection of the angular momentum in an arbitrarily-chosen direction, conventionally L_z ,
The magnitude of the angular momentum in the z direction, is given by the formula: $L_z = m\hbar$

$$\Rightarrow \cos \theta = \frac{L_z}{L} = \frac{m}{\sqrt{\ell(\ell+1)}}$$

Space quantization



Quantization of angular momentum direction

Angular momentum

$$\vec{L} = \vec{r} \times \vec{p} = L_x \cdot \hat{i} + L_y \cdot \hat{j} + L_z \cdot \hat{k}$$

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = -i\hbar \left(-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = -i\hbar \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = \hat{L} \cdot \hat{L} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Angular momentum

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = i\hbar \hat{L}_z$$

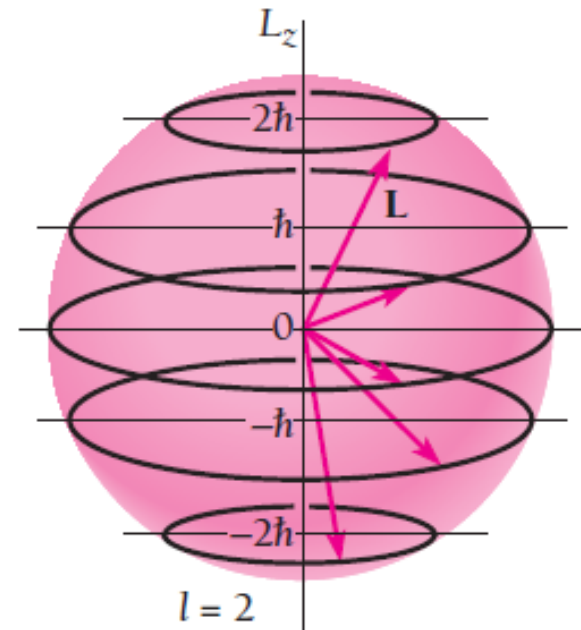
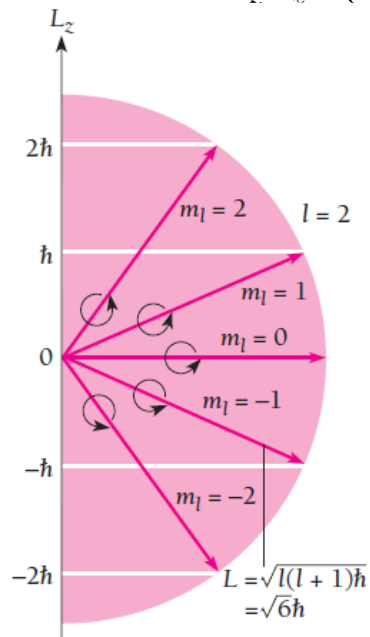
$$[\hat{L}_y, \hat{L}_z] = \hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z = i\hbar \hat{L}_y$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \ell(\ell + 1)\hbar^2 Y_\ell^m(\theta, \phi)$$

$$\hat{L}_z Y_\ell^m(\theta, \phi) = m\hbar Y_\ell^m(\theta, \phi)$$



Electron probability density

✓ No definite orbits

1. Only relative probabilities for finding electron at various locations.

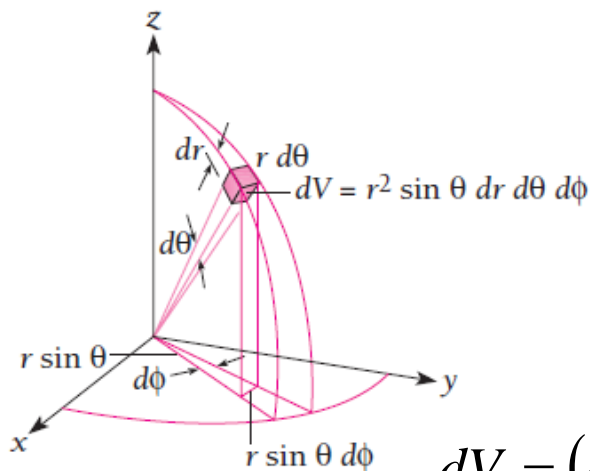
2. $|\psi|^2$ is independent of time and varies from place to place.

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\Rightarrow |\psi|^2 = |RY|^2 = |R|^2|\Theta|^2|\Phi|^2$$

$$|\Phi|^2 = A^2 e^{-im\phi} e^{+im\phi} = A^2$$

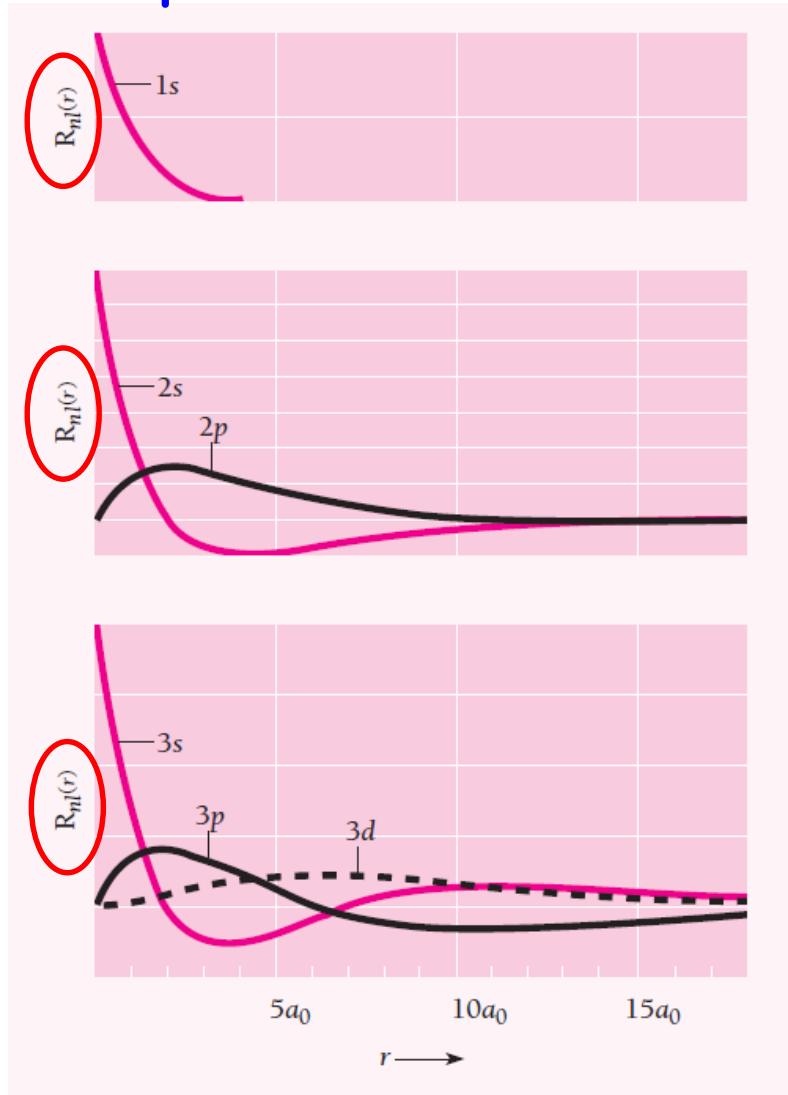
$|R|^2$ Depends on r , and combination of n and ℓ .



$$dV = (dr)(rd\theta)(r \sin \theta d\phi) = r^2 \sin \theta dr d\theta d\phi$$

Radial part of the wave function and the probability of finding the electron

Radial part of the wave function



Probability of finding the electron

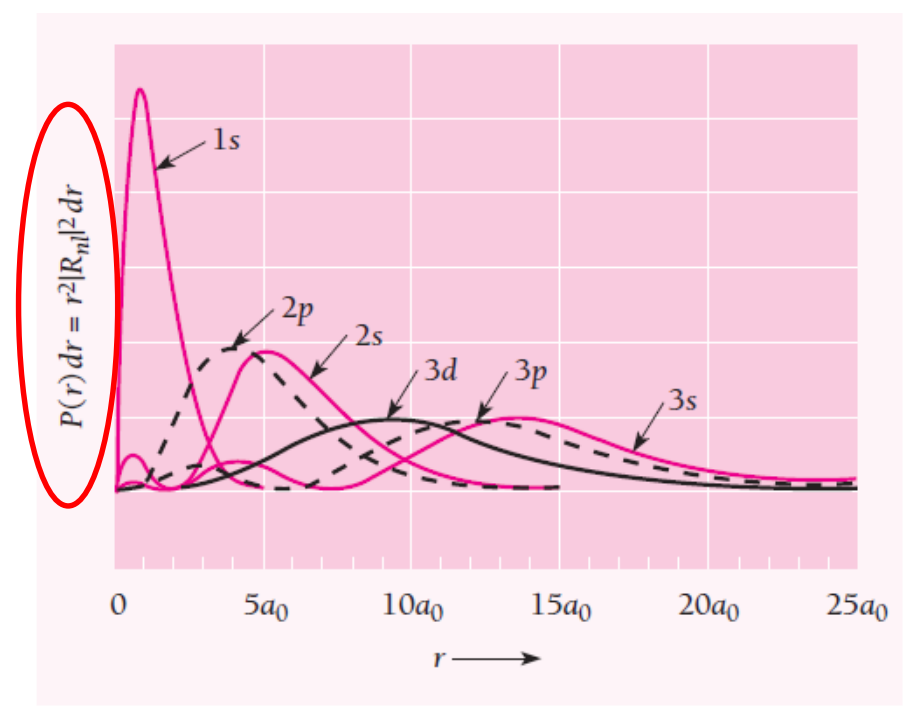
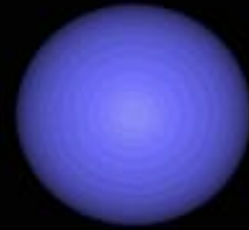


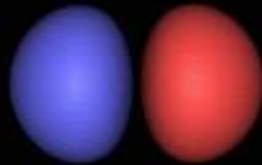
Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2,$ and 3^*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

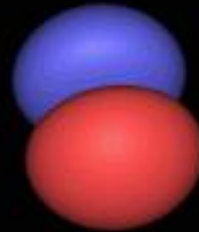
*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.



s



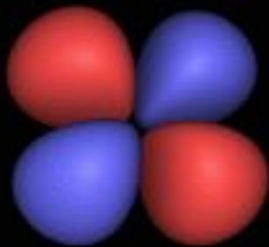
p_x



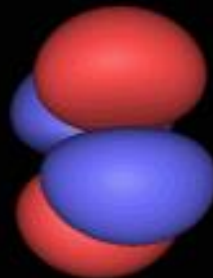
p_y



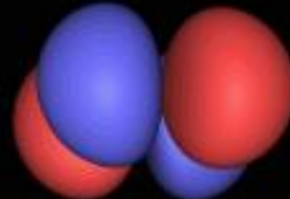
p_z



d_{xy}



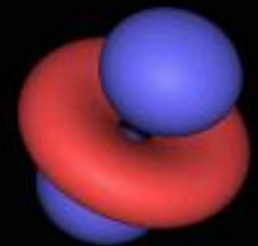
d_{xz}



d_{yz}



d_{x² - y²}



d_{z²}

The identity of an atom

Electrons are not circulating but exist as waves around the nuclei. If you try to forcefully ascertain where the particles of electrons are, you will be able to find them somewhere around the atomic nucleus. However, it is only a matter of seeing the result that the reaction of observation act occurs somewhere..

If you want to think that it is the position of the particle, that is fine, but the electron is not there from the beginning. As a result of the observation, the spread waves converged to a narrow range. The position is stochastically determined.

We are thinking that atoms are real particles, something like a mass. Actually, however, we call the spread of waves around the atomic nucleus as atoms. It is like calling "the phenomenon that the air flows" as "wind", and the existence of atoms is just a phenomenon, just as there is no entity in the "wind".