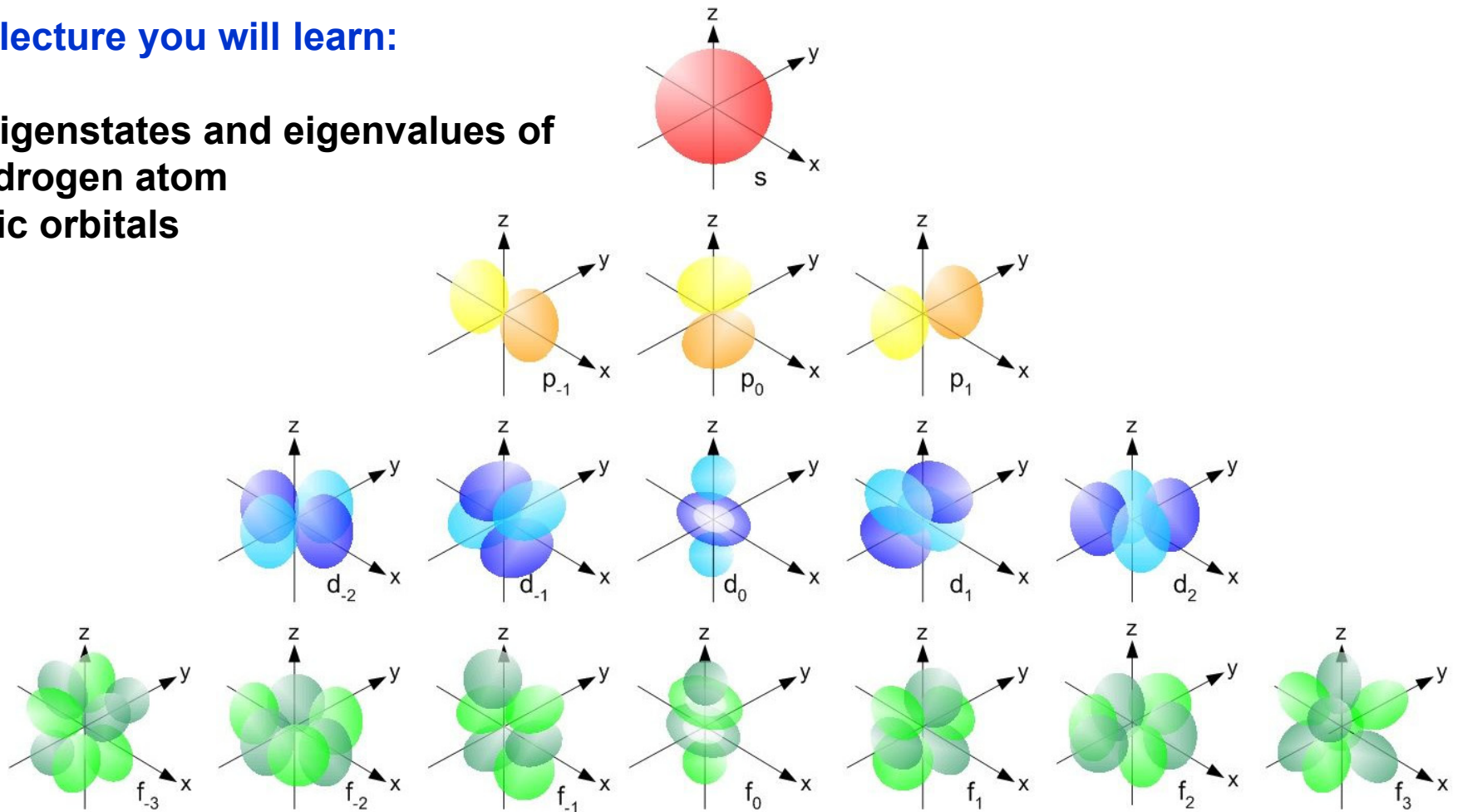


# Lecture 26

## The Hydrogen Atom

In this lecture you will learn:

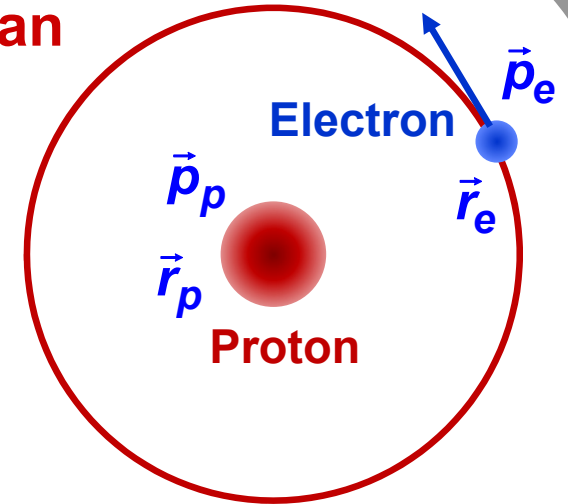
- The eigenstates and eigenvalues of the Hydrogen atom
- Atomic orbitals



## The Hydrogen Atom: Hamiltonian

The Hamiltonian is:

$$\hat{H} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \underbrace{\frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}_e - \hat{\vec{r}}_p|}}_{\text{Coulomb potential}}$$



Proton is ~1837 times more massive than the electron

The only non-zero commutation relations are:

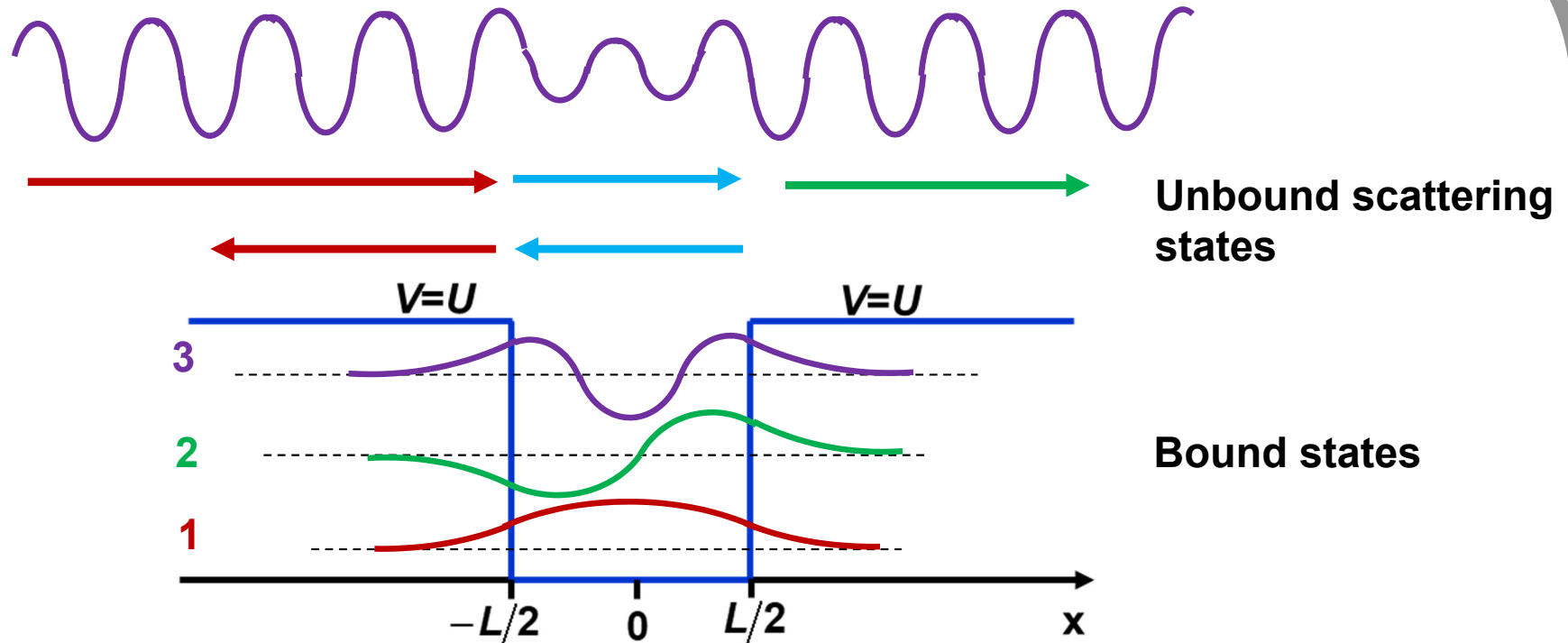
$$\left[ r_e^j, p_e^k \right] = i\hbar\delta^{j,k} \quad \left[ r_p^j, p_p^k \right] = i\hbar\delta^{j,k}$$

What we are looking for are the eigenfunctions and eigenvalues of this Hamiltonian:

$$\langle \vec{r}_e, \vec{r}_p | \hat{H} | \psi \rangle = E \psi(\vec{r}_e, \vec{r}_p)$$

How do we find  $\psi(\vec{r}_e, \vec{r}_p)$  ?

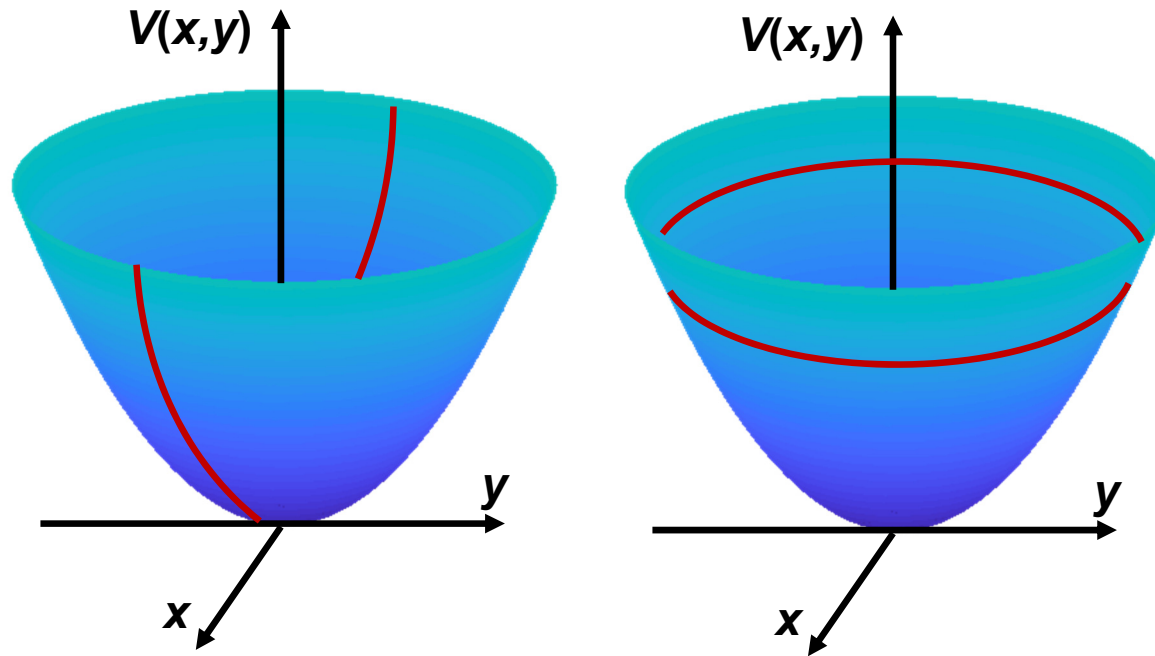
## The Finite Potential Well Problem in 1D: Lessons Learnt



### The 1D finite potential well - lessons learnt:

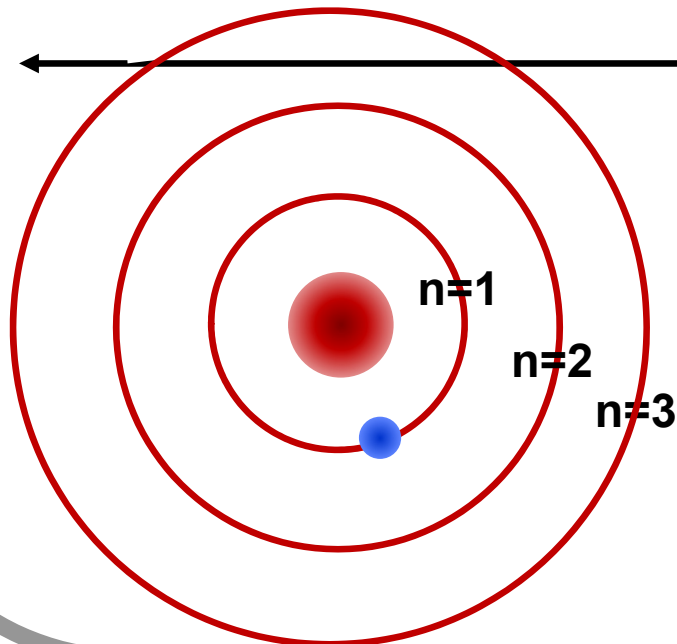
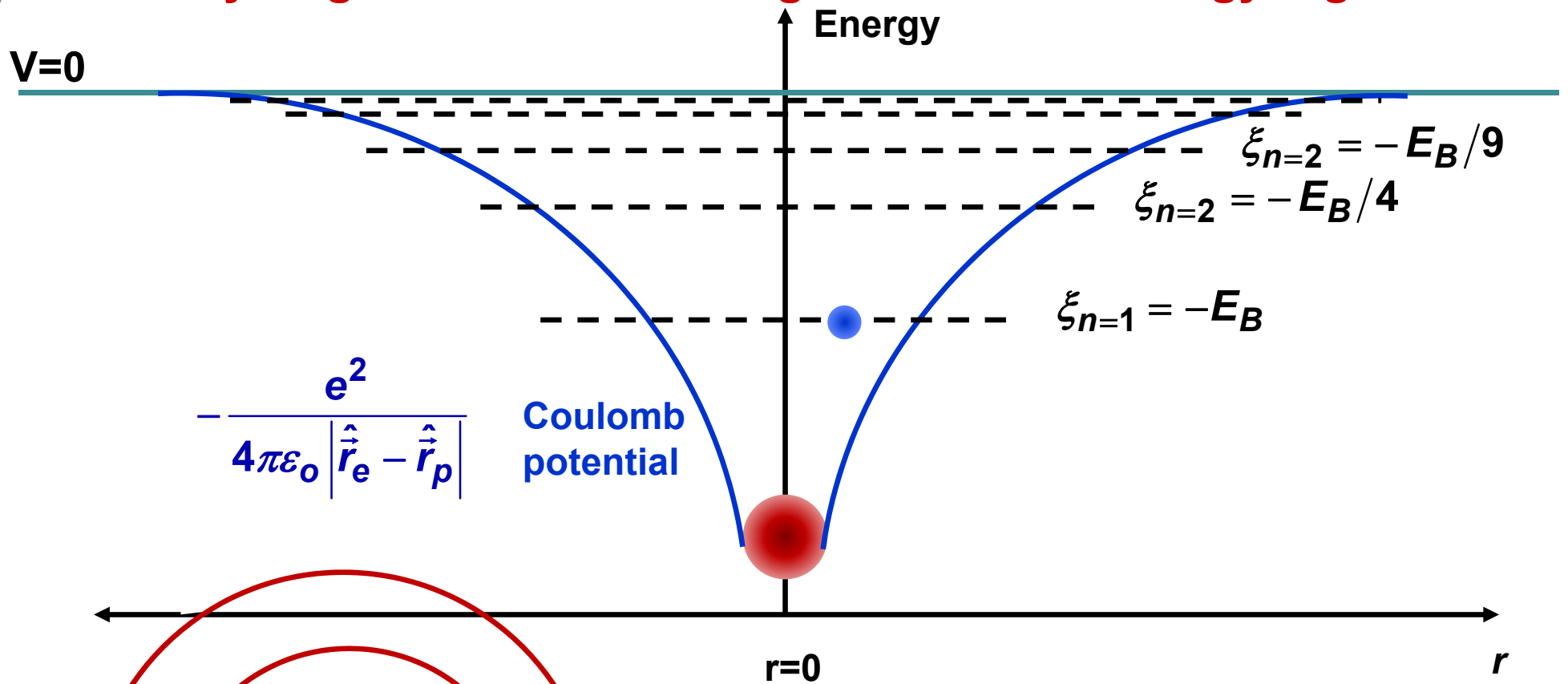
- 1) A finite potential well has discrete bound states
- 2) There are always unbound continuum of scattering states
- 3) The bound states decay exponentially away from the potential well in the **classically forbidden region** where the bound state energy eigenvalue  $E$  is smaller than the potential  $V(x)$

## The 2D SHO: Lessons Learnt



- The energy eigenstates can be chosen to be also angular momentum eigenstates
- Two kinds of energy eigenstates are possible:
  - i) Those with a net angular momentum
  - ii) Those with no net angular momentum
- The lowest energy state had no angular momentum and its energy was solely due to oscillatory motion

# The Hydrogen Atom: Bound Eigenstates and Energy Eigenvalues



The actual wavefunctions of bound states will look nothing like these rings!

$$\xi_n = -\frac{E_B}{n^2} = -\frac{13.6 \text{ eV}}{n^2} \quad \{n = 1, 2, 3, \dots\}$$

## The Hydrogen Atom: New Coordinates

The Hamiltonian is:

$$\hat{H} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \frac{e^2}{4\pi\epsilon_0 |\hat{r}_e - \hat{r}_p|}$$

Define **center of mass** and **relative** coordinates as:

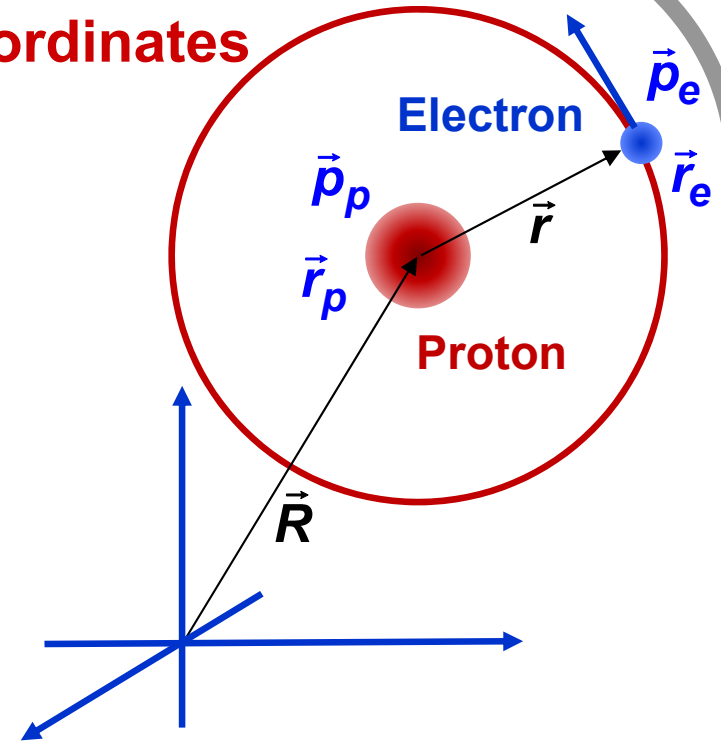
$$\left. \begin{aligned} \hat{R} &= \frac{m_e \hat{r}_e + m_p \hat{r}_p}{M} \approx \hat{r}_p \\ \hat{r} &= \hat{r}_e - \hat{r}_p \end{aligned} \right\} M = m_e + m_p$$

Define **center of mass** and **relative** momenta as:

$$\left. \begin{aligned} \hat{Q} &= \hat{p}_e + \hat{p}_p \\ \hat{p} &= \frac{m_p \hat{p}_e - m_e \hat{p}_p}{M} = \mu \left[ \frac{\hat{p}_e}{m_e} - \frac{\hat{p}_p}{m_p} \right] \approx \hat{p}_e \end{aligned} \right\} \mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e m_p}{M} \approx m_e$$

The only non-zero commutation relations are:

$$[r^j, p^k] = i\hbar \delta^{j,k} \quad [R^j, Q^k] = i\hbar \delta^{j,k}$$



## The Hydrogen Atom: Hamiltonian in New Coordinates

The Hamiltonian is:

$$\hat{H} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}_e - \hat{\vec{r}}_p|}$$

In the new coordinates the Hamiltonian is:

$$\hat{H} = \frac{\hat{Q}^2}{2M} + \frac{\hat{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|}$$

The only non-zero commutation relations are:

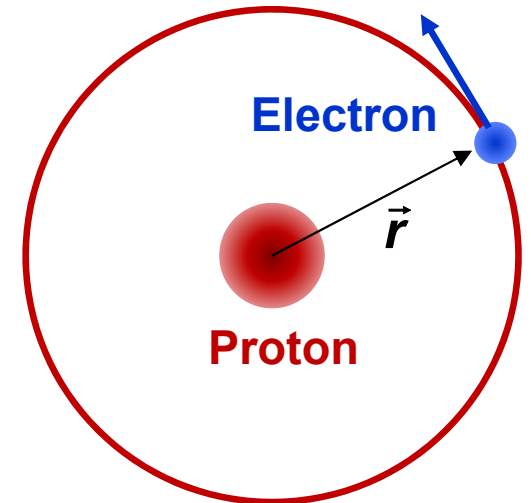
$$[r^j, p^k] = i\hbar\delta^{j,k} \quad [R^j, Q^k] = i\hbar\delta^{j,k}$$

$$\begin{aligned} \vec{p} &\Leftrightarrow \frac{\hbar}{i} \nabla_{\vec{r}} \\ \vec{Q} &\Leftrightarrow \frac{\hbar}{i} \nabla_{\vec{R}} \end{aligned}$$

What we are looking for are the eigenfunctions and eigenvalues of this Hamiltonian:

$$\langle \vec{r}, \vec{R} | \hat{H} | \psi \rangle = E\psi(\vec{r}, \vec{R})$$

How to find  $\psi(\vec{r}, \vec{R})$  ?



## The Hydrogen Atom: Hamiltonian

$$\hat{H} = \frac{\hat{Q}^2}{2M} + \frac{\hat{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|}$$

$$\Rightarrow \langle \vec{r}, \vec{R} | \hat{H} | \psi \rangle = E \psi(\vec{r}, \vec{R})$$

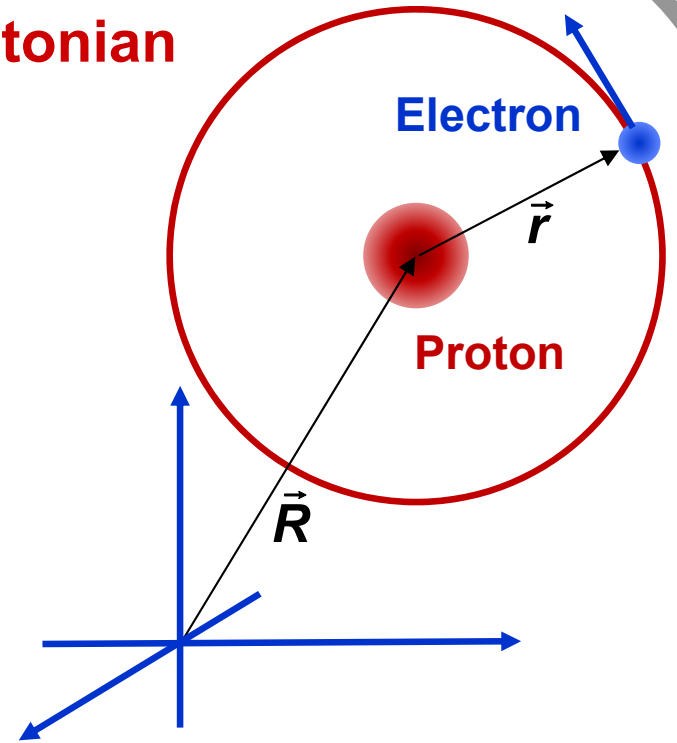
$$\Rightarrow \left[ -\frac{\hbar^2 \nabla_{\vec{R}}^2}{2M} - \frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \psi(\vec{r}, \vec{R}) = E \psi(\vec{r}, \vec{R})$$

We assume a product wavefunction in the center of mass and relative coordinates:

$$\psi(\vec{r}, \vec{R}) = \phi(\vec{R}) \chi(\vec{r}) = \frac{e^{i\vec{k} \cdot \vec{R}}}{\sqrt{V}} \chi(\vec{r})$$

$$\Rightarrow \left[ -\frac{\hbar^2 \nabla_{\vec{R}}^2}{2M} - \frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \psi(\vec{r}, \vec{R}) = E \psi(\vec{r}, \vec{R})$$

$$\Rightarrow \left[ \frac{\hbar^2 \mathbf{k}^2}{2M} - \frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \chi(\vec{r}) = E \chi(\vec{r})$$





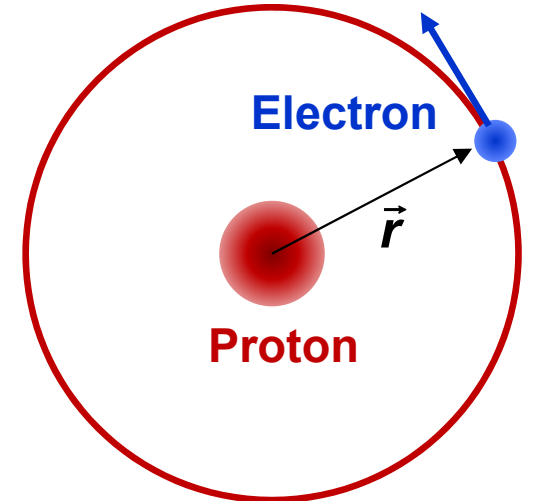
## The Hydrogen Atom: Eigenvalue Equation

$$\left[ -\frac{\hbar^2 \nabla_{\vec{R}}^2}{2M} - \frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \psi(\vec{r}, \vec{R}) = E \psi(\vec{r}, \vec{R})$$

$$\Rightarrow \left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \chi(\vec{r}) = \left( E - \frac{\hbar^2 k^2}{2M} \right) \chi(\vec{r})$$

$$\Rightarrow \left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \chi(\vec{r}) = \xi \chi(\vec{r}) \quad \left\{ \xi = E - \frac{\hbar^2 k^2}{2M} \right.$$

The eigenvalue equation that we need to solve



Given that:

$$\begin{aligned} \mu &\approx m_e & \hat{\vec{r}} &= \hat{\vec{r}}_e - \hat{\vec{r}}_p \\ \hat{\vec{p}} &\approx \hat{\vec{p}}_e \end{aligned}$$

the above eigenvalue equation is essentially the Schrodinger equation of an electron in the potential of a proton assuming that the proton was held fixed at the origin

## Relative Motion Hamiltonian and Relative Angular Momentum

$$\left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] \chi(\vec{r}) = \xi \chi(\vec{r})$$

In operator form, the eigenvalue equation becomes :

$$\hat{H}' |\chi\rangle = \left[ \frac{\hat{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right] |\chi\rangle = \xi |\chi\rangle$$

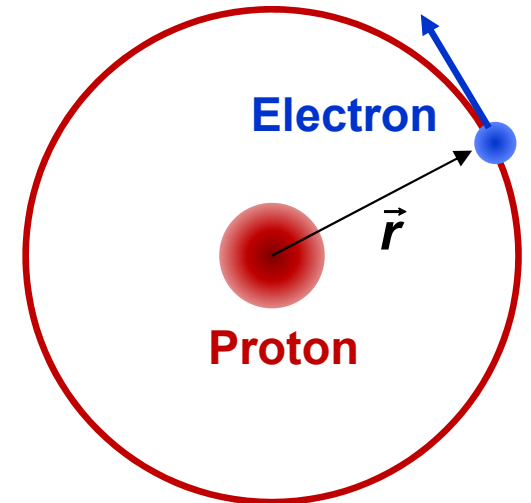
↑  
Relative motion  
Hamiltonian

Relative angular momentum:

$$\hat{L} = \hat{\vec{r}} \times \hat{\vec{p}}$$

The relative angular momentum operators commute with the relative Hamiltonian and the full Hamiltonian:

$$[\hat{H}', \hat{L}^2] = [\hat{H}', \hat{L}_z] = 0 \quad [\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = 0$$

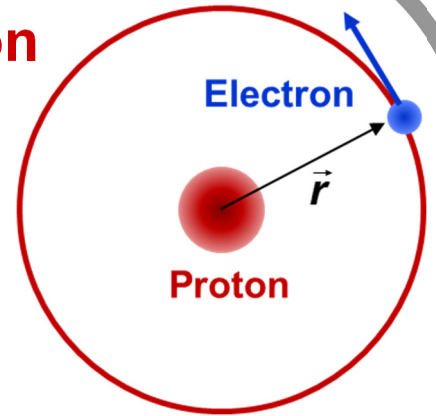


This means that the relative angular momentum eigenstates could also be the energy eigenstates!!

## The Hydrogen Atom: Eigenvalue Equation

Change to spherical coordinates:

$$\left\{ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|} \right\} \chi(\vec{r}) = \xi \chi(\vec{r})$$



$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \chi(r, \theta, \phi) = \xi \chi(r, \theta, \phi)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \chi(r, \theta, \phi) = \xi \chi(r, \theta, \phi)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{2\mu r^2} [\tilde{L}^2] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \chi(r, \theta, \phi) = \xi \chi(r, \theta, \phi)$$

$\tilde{L}^2$

Let the wavefunction be:

$$\chi(r, \theta, \phi) = f_\ell(r) Y_\ell^m(\theta, \phi) \quad \left\{ \begin{array}{l} [\tilde{L}^2] Y_\ell^m(\theta, \phi) = \ell(\ell+1) \hbar^2 Y_\ell^m(\theta, \phi) \end{array} \right.$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{2\mu r^2} [\tilde{L}^2] - \frac{e^2}{4\pi\epsilon_0 r} \right\} f_\ell(r) Y_\ell^m(\theta, \phi) = \xi f_\ell(r) Y_\ell^m(\theta, \phi)$$

## The Hydrogen Atom: The Radial Eigenvalue Equation

We have:

$$\chi(r, \theta, \phi) = f_\ell(r) Y_\ell^m(\theta, \phi)$$

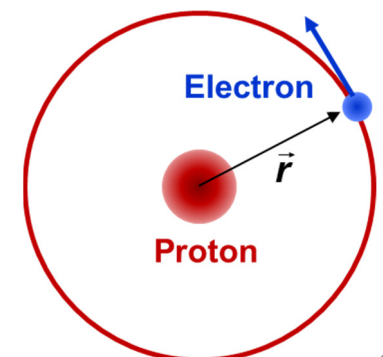
$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{2\mu r^2} [\tilde{L}^2] - \frac{e^2}{4\pi\epsilon_0 r} \right\} f_\ell(r) Y_\ell^m(\theta, \phi) = \xi f_\ell(r) Y_\ell^m(\theta, \phi)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right\} f_\ell(r) = \xi f_\ell(r)$$

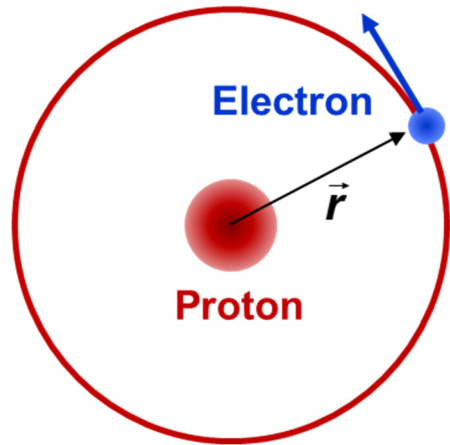
The above equation does not depend on the z-component of the angular momentum whose eigenvalue is “ $m$ ”, and therefore the energy  $\xi$  also does not depend on “ $m$ ”

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right\} f_\ell(r) = \xi f_\ell(r)$$

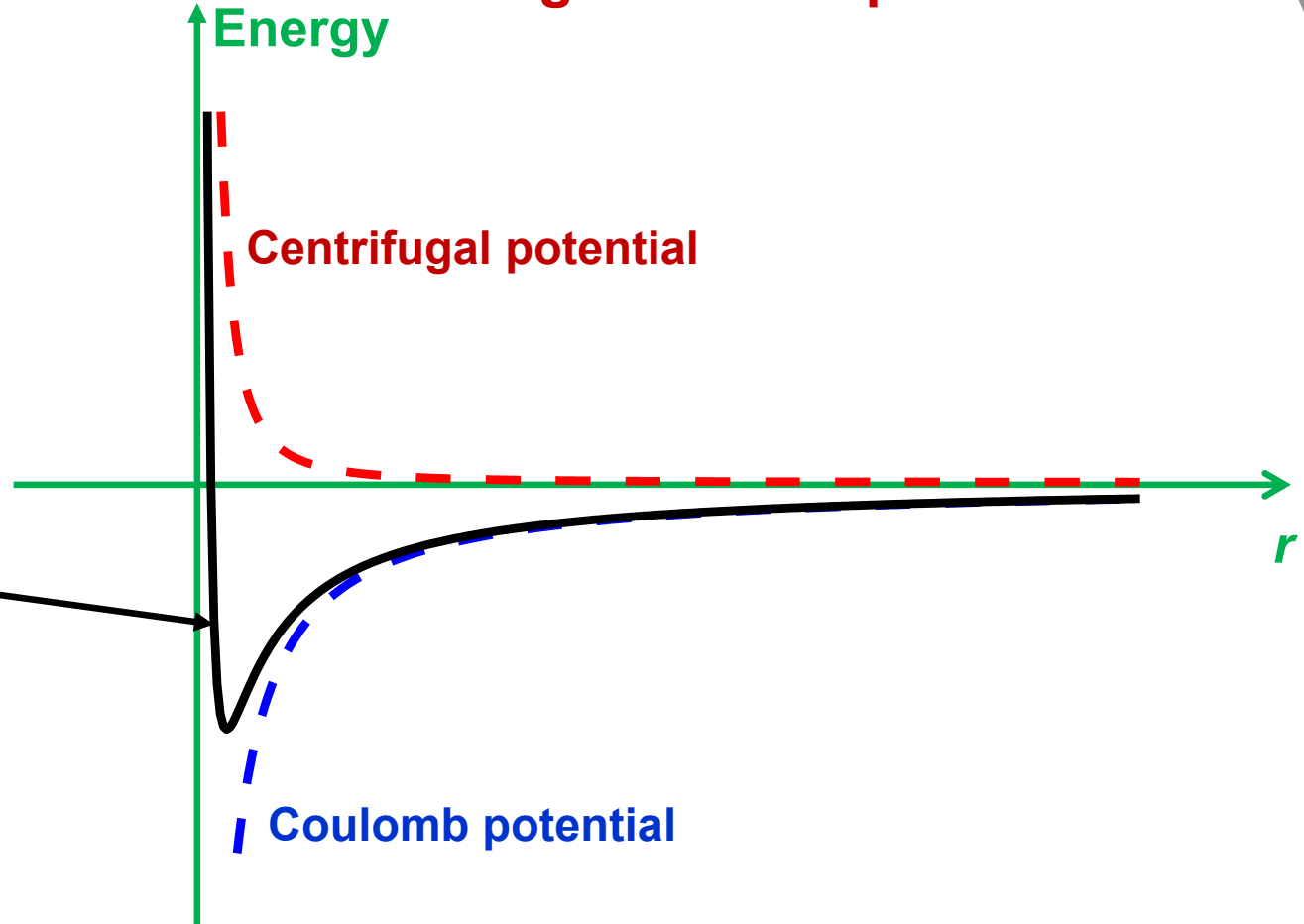
The radial equation



# The Hydrogen Atom: The Radial Eigenvalue Equation



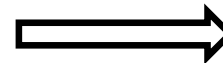
The effective radial potential well



$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}}_{\text{Effective Centrifugal potential}} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{\text{Coulomb potential}} \right\} f_\ell(r) = \xi f_\ell(r)$$

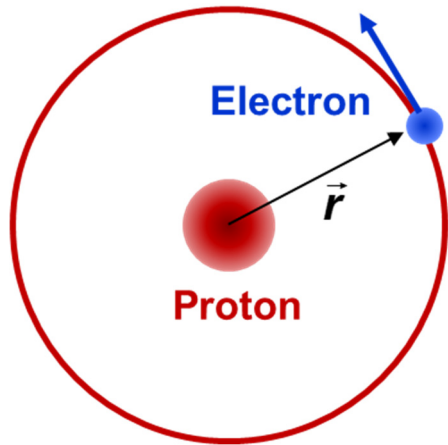
**Effective Centrifugal potential**

**Coulomb potential**

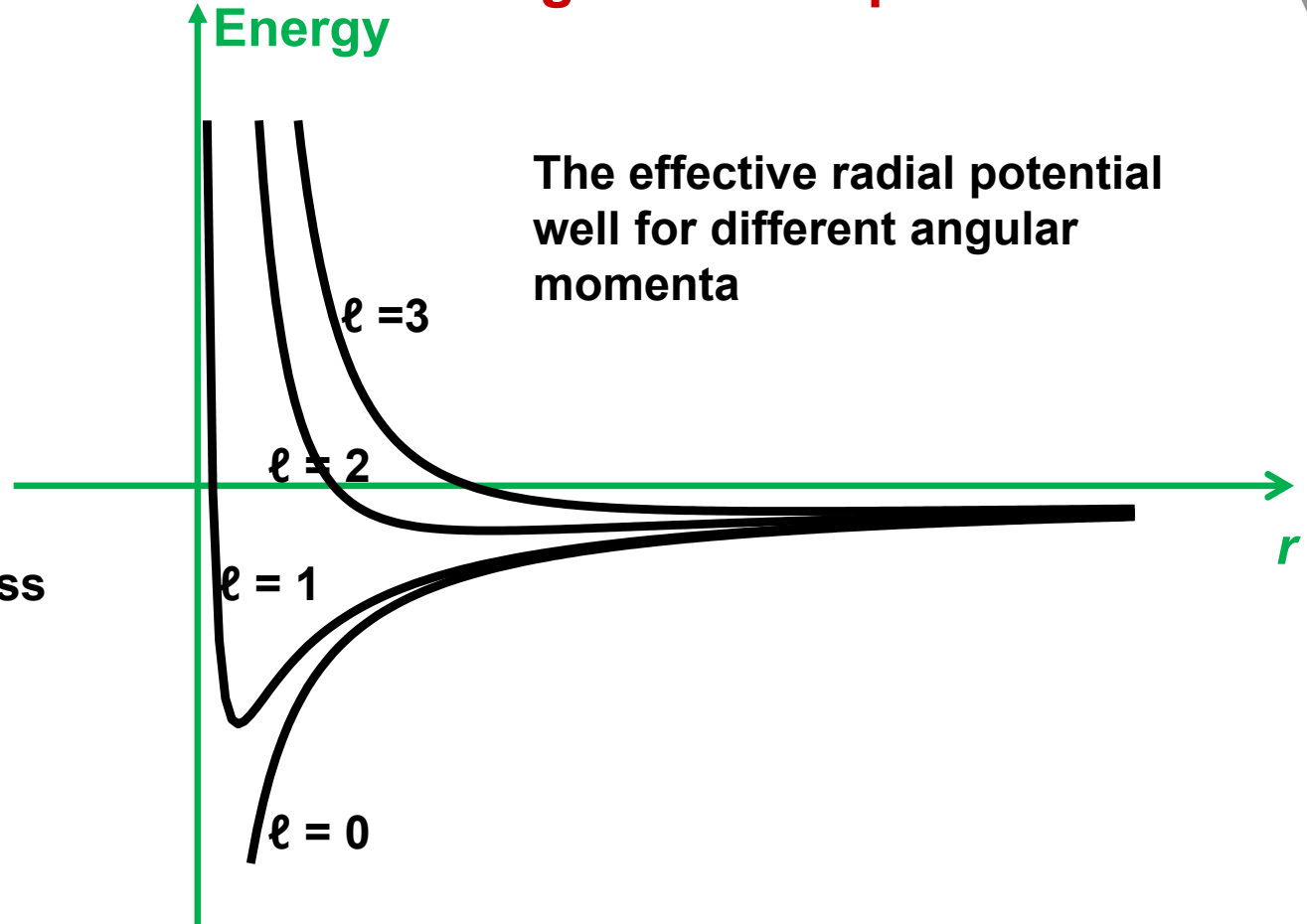


The effective radial potential consists of two parts

# The Hydrogen Atom: The Radial Eigenvalue Equation



We expect  $f_\ell(r)$  to have less and less weight near the origin as  $\ell$  becomes larger and larger !



The effective radial potential well for different angular momenta

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}}_{\text{Effective Centrifugal potential}} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{\text{Coulomb potential}} \right\} f_\ell(r) = \xi f_\ell(r)$$

Effective Centrifugal potential

Coulomb potential

# The Hydrogen Atom: The Radial Eigenvalue Equation Solutions

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right\} f_l(r) = \xi f_l(r)$$

Define a length parameter as:  $a_B = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.53 \text{ Angstroms} \longrightarrow \text{Bohr Radius}$

Solutions can be written as:

$$f_{n,l}(r) = A_{n,l} e^{-\frac{r}{na_B}} \left( \frac{2r}{na_B} \right)^\ell L_{(n-1)-\ell}^{2\ell+1} \left( \frac{2r}{na_B} \right)$$

Associated Laguerre polynomials

$$\xi_n = -\frac{e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{\hbar^2}{2\mu n^2 a_B^2} = -\frac{E_B}{n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

Solution only possible if:  
 $n = 1, 2, 3, \dots$   
 $l < n \quad \{ l = 0, 1, 2, \dots, (n-1) \}$

$$a_B = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \longrightarrow \text{Bohr Radius}$$

$$E_B = \frac{e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2} \longrightarrow \text{Rydberg energy or Bohr energy} = 13.6 \text{ eV}$$

# The Hydrogen Atom: Eigenstates and Energy Eigenvalues

$$\left\{ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{r}|} \right\} \chi(\vec{r}) = \xi \chi(\vec{r})$$

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

$$\xi_n = -\frac{E_B}{n^2} = -\frac{13.6}{n^2}$$

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

**Radial quantum number**

For every value of  $n$  :

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

**Azimuthal quantum number**

For every value of  $\ell$  :

$$m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell$$

**Magnetic quantum number**

Note that the energy of the electron only depends on the radial quantum number  $n$

*Different values of  $n$  correspond to different energy shells*

The degeneracy of the  $n$ -th energy shell is:  $\sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$

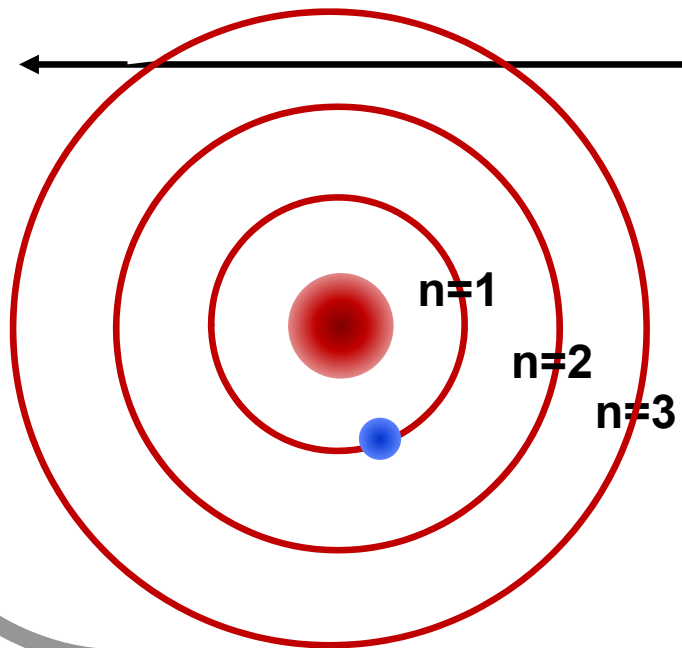
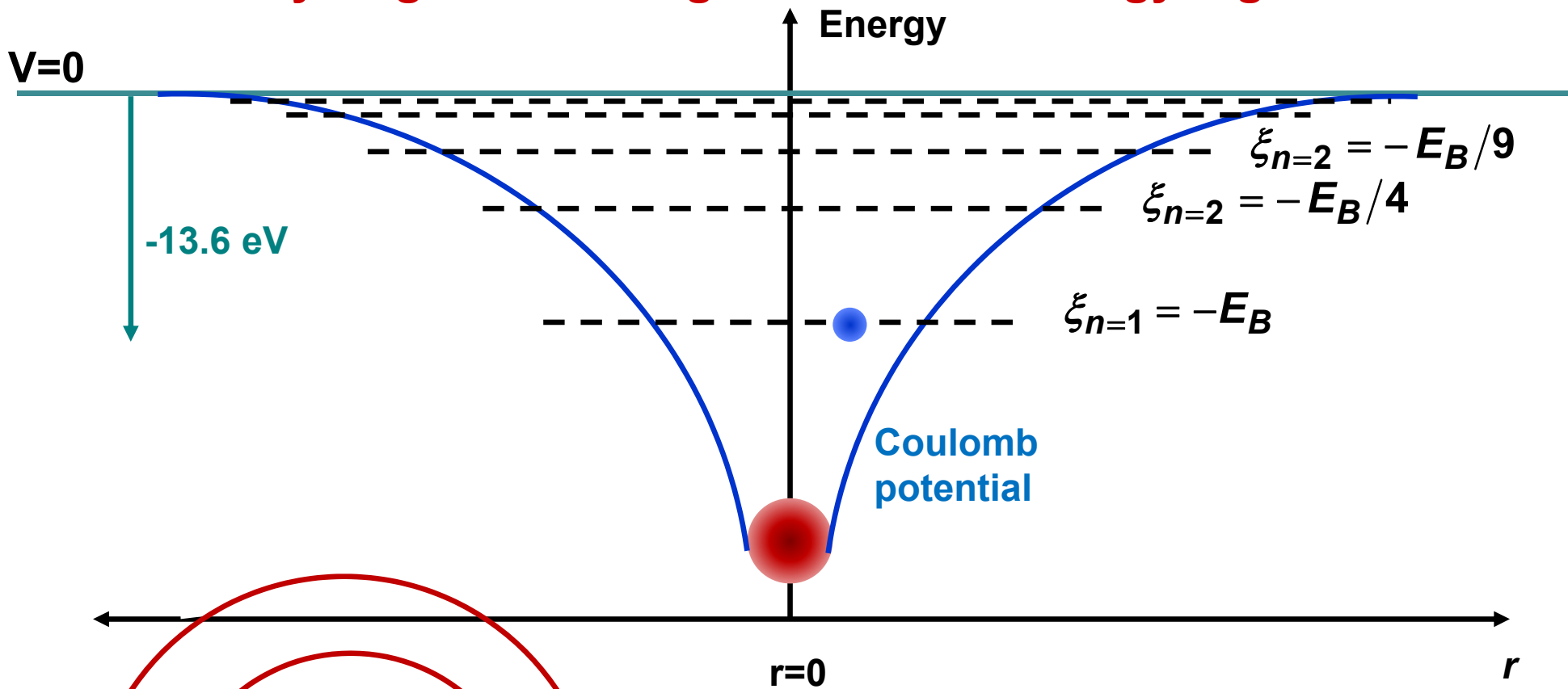
$\ell = 0$      $1$      $2$      $3$     .....

s    p    d    f    .....

**States with different values of  $\ell$  (irrespective of the values of  $n$  or  $m$ ) are called sub-shells or orbitals, and are labeled by alphabets**



# The Hydrogen Atom: Eigenstates and Energy Eigenvalues



$$\xi_n = -\frac{E_B}{n^2} = -\frac{13.6 \text{ eV}}{n^2} \quad \{n = 1, 2, 3, \dots\}$$

Shell	Orbital	Degen.	Wavefunction
<b>n=1</b>	<b>ℓ=0: 1s</b>	<b>2ℓ+1=1</b>	$\chi_{n=1,\ell=0,m=0}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_B}\right)^{3/2} e^{-\frac{r}{a_B}}$
<b>n=2</b>	<b>ℓ=0: 2s</b>	<b>2ℓ+1=1</b>	$\chi_{n=2,\ell=0,m=0}(\vec{r}) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(2 - \frac{r}{a_B}\right) e^{-\frac{r}{2a_B}}$
<b>n=2</b>	<b>ℓ=1: 2p</b>	<b>2ℓ+1=3</b>	$\chi_{n=2,\ell=1,m=0}(\vec{r}) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(\frac{r}{a_B}\right) e^{-\frac{r}{2a_B}} \cos \theta$
			$\chi_{n=2,\ell=1,m=\pm 1}(\vec{r}) = \mp \frac{1}{\sqrt{64\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(\frac{r}{a_B}\right) e^{-\frac{r}{2a_B}} \sin \theta e^{\pm i\phi}$
<b>n=3</b>	<b>ℓ=0: 3s</b>	<b>2ℓ+1=1</b>	$\chi_{n=3,\ell=0,m=0}(\vec{r}) = \frac{1}{\sqrt{162\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(6 - 4\left(\frac{r}{a_B}\right) + \frac{4}{9}\left(\frac{r}{a_B}\right)^2\right) e^{-\frac{r}{3a_B}}$
<b>n=3</b>	<b>ℓ=1: 3p</b>	<b>2ℓ+1=3</b>	$\chi_{n=3,\ell=1,m=0}(\vec{r}) = \frac{1}{27\sqrt{2\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(\frac{r}{a_B}\right) \left(4 - \frac{2}{3}\left(\frac{r}{a_B}\right)\right) e^{-\frac{r}{3a_B}} \cos \theta$
			$\chi_{n=3,\ell=1,m=\pm 1}(\vec{r}) = \mp \frac{1}{27\sqrt{4\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(\frac{r}{a_B}\right) \left(4 - \frac{2}{3}\left(\frac{r}{a_B}\right)\right) e^{-\frac{r}{3a_B}} \sin \theta e^{\pm i\phi}$
<b>n=3</b>	<b>ℓ=2: 3d</b>	<b>2ℓ+1=5</b>	???

# The Hydrogen Atom: Bound Eigenstates

Normalization:

$$\int d^3\vec{r} |\chi_{n,\ell,m}(r,\theta,\phi)|^2 = \int d^3\vec{r} |f_{n,\ell}(r) Y_\ell^m(\theta,\phi)|^2 = 1$$

Orthogonality:

$$\int d^3\vec{r} \chi_{n',\ell',m'}^*(r,\theta,\phi) \chi_{n,\ell,m}(r,\theta,\phi) = \delta_{n,n'} \delta_{\ell,\ell'} \delta_{m,m'}$$

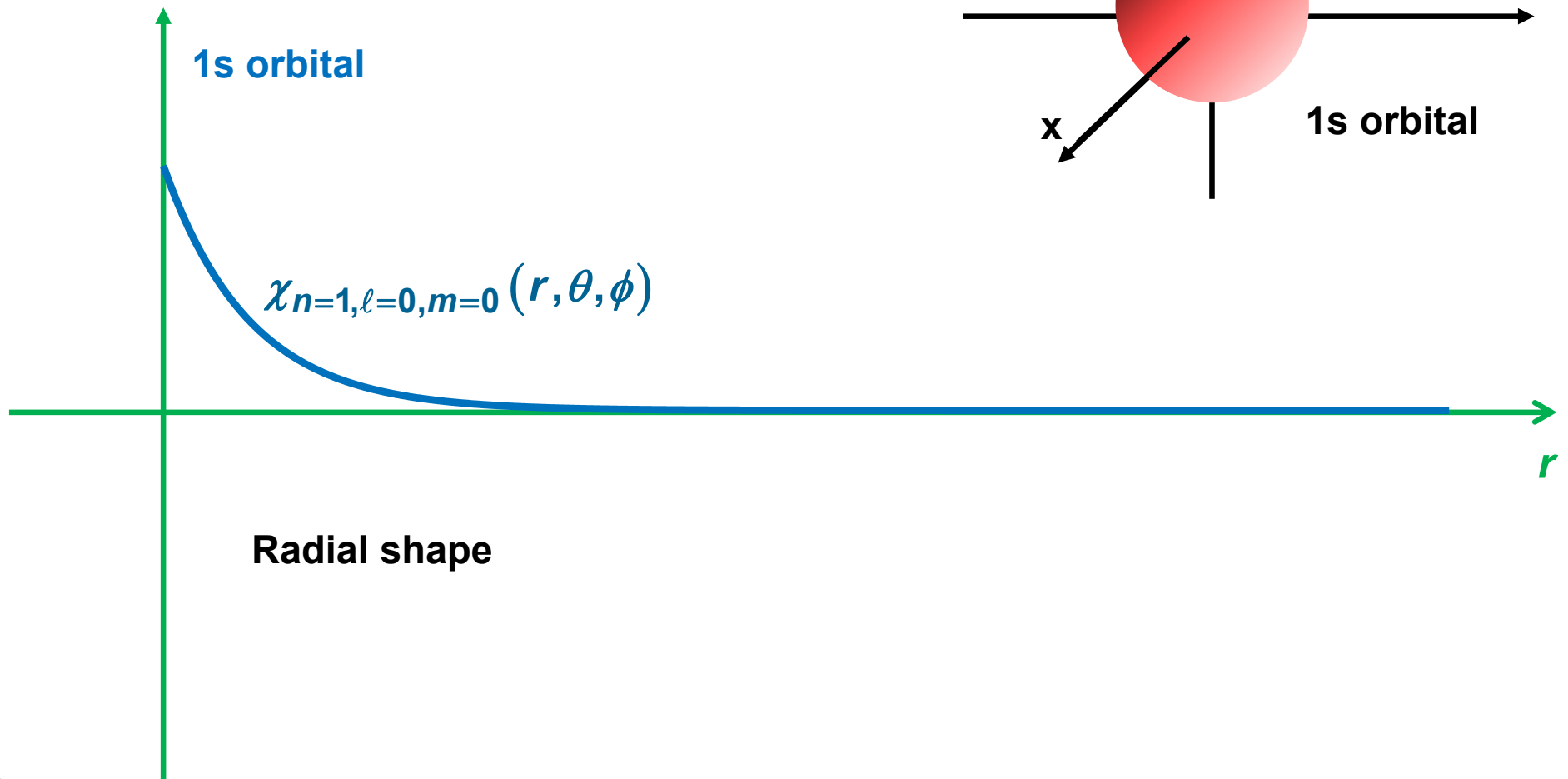
Radial probability distribution:

$$\int d^3\vec{r} |\chi_{n,\ell,m}(r,\theta,\phi)|^2 = \int_0^\infty dr \underbrace{\int_0^\pi r d\theta \int_0^{2\pi} r \sin\theta d\phi}_{P_{n,\ell,m}(r)} |\chi_{n,\ell,m}(r,\theta,\phi)|^2 = 1$$

$$\Rightarrow \int_0^\infty dr P_{n,\ell,m}(r) = 1$$

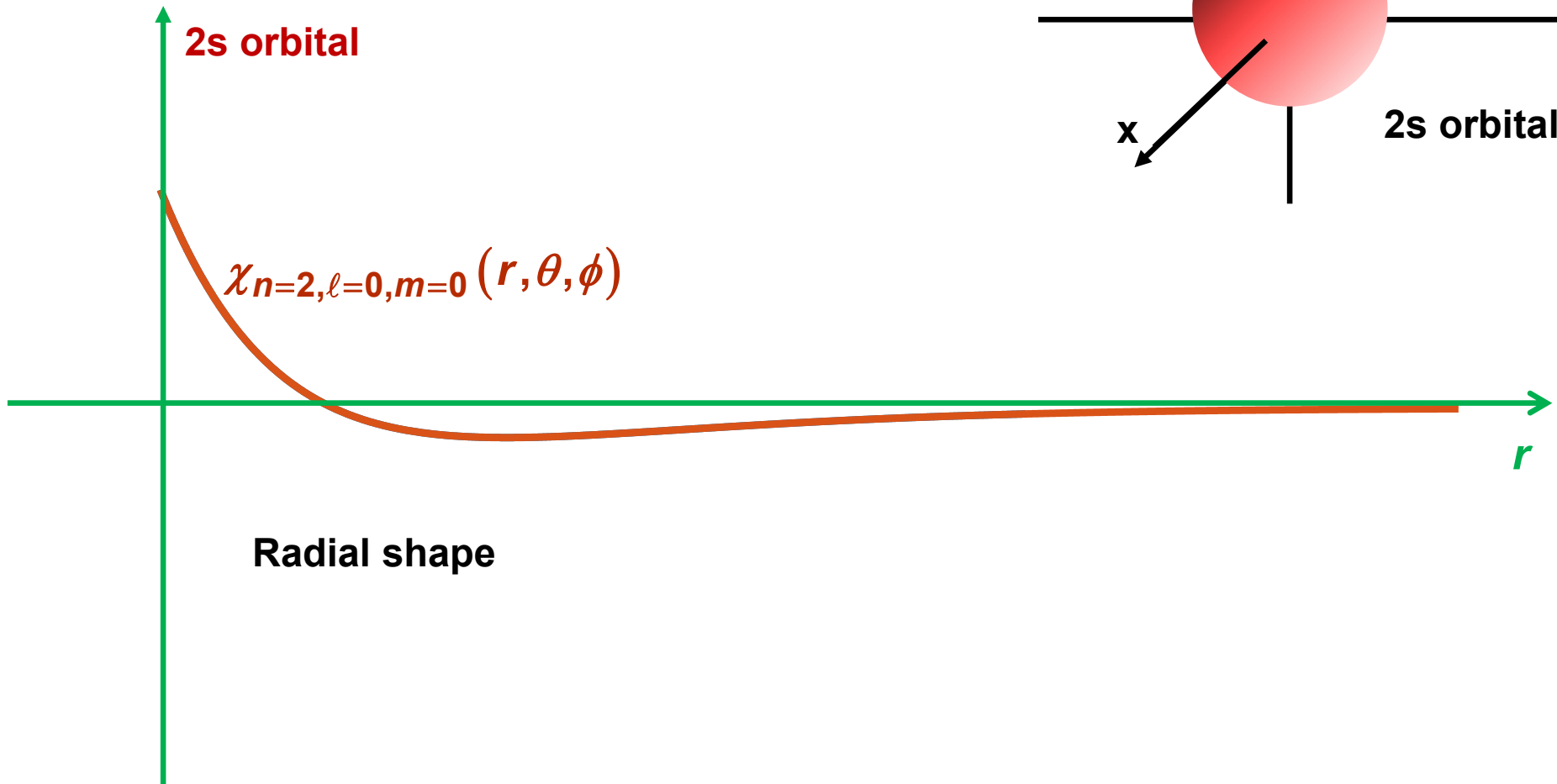
# The Hydrogen Atom: 1s Orbital

$$\chi_{n=1,l=0,m=0}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_B} \right)^{3/2} e^{-\frac{r}{a_B}}$$



## The Hydrogen Atom: 2s Orbital

$$\chi_{n=2,\ell=0,m=0}(\vec{r}) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(2 - \frac{r}{a_B}\right) e^{-\frac{r}{2a_B}}$$

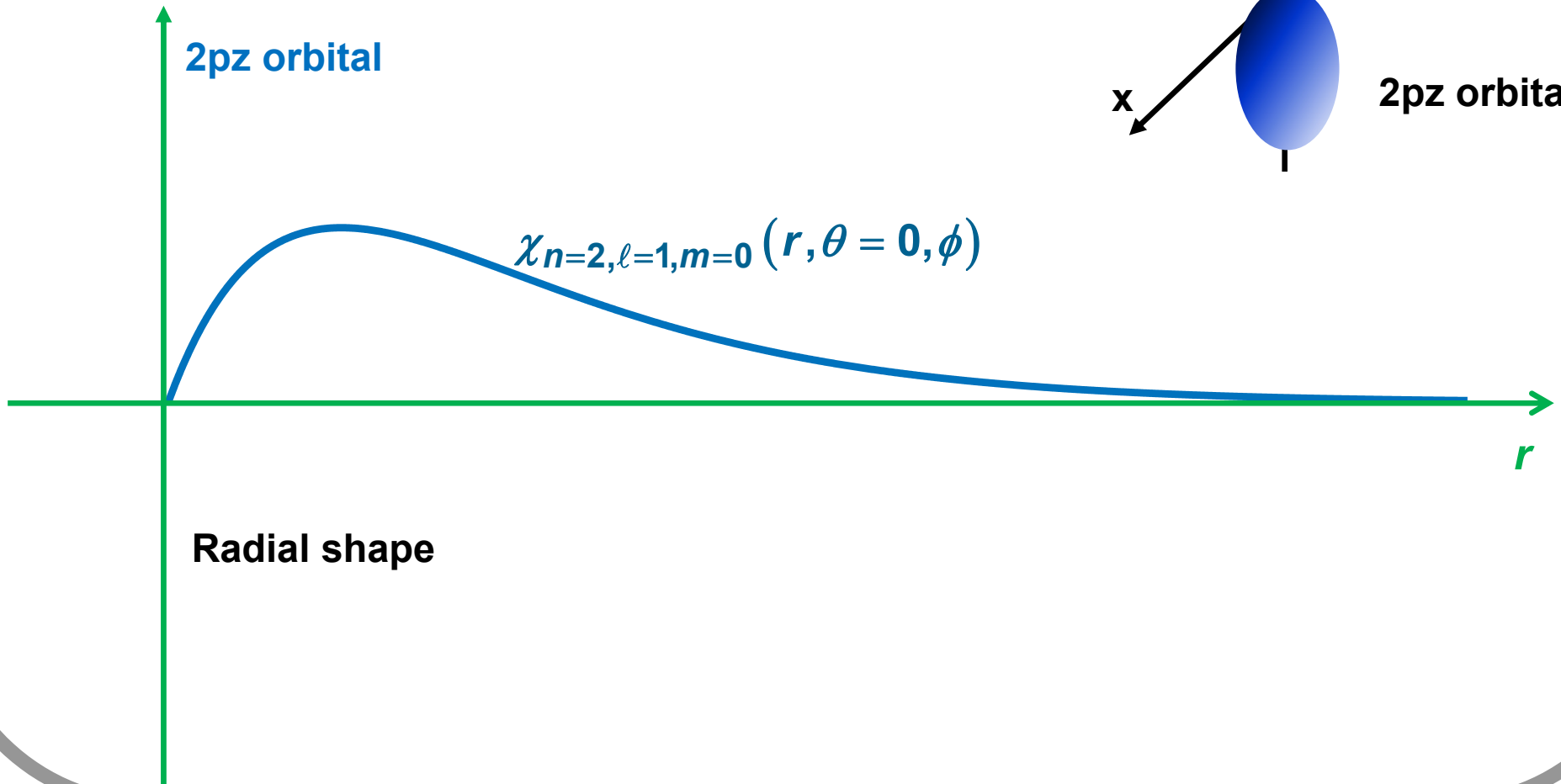
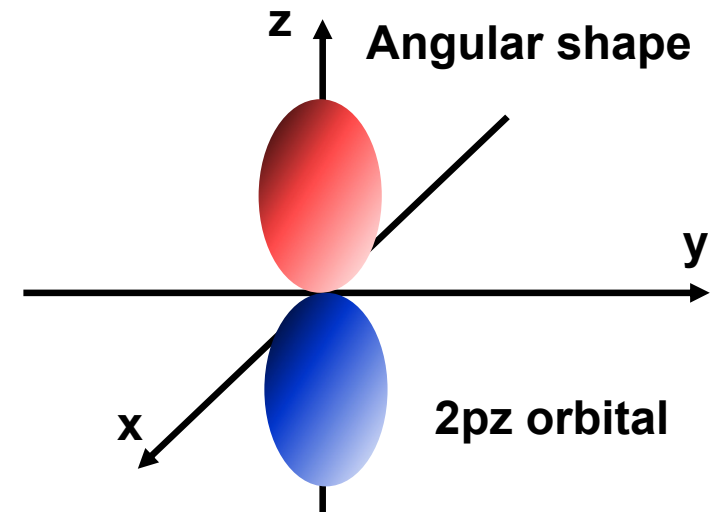


# The Hydrogen Atom: 2pz Orbital

Consider the 2p orbitals; there are three of them

The 2pz Orbital:

$$\chi_{n=2,\ell=1,m=0}(\vec{r}) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_B}\right)^{3/2} \left(\frac{r}{a_B}\right) e^{-\frac{r}{2a_B}} \cos\theta$$



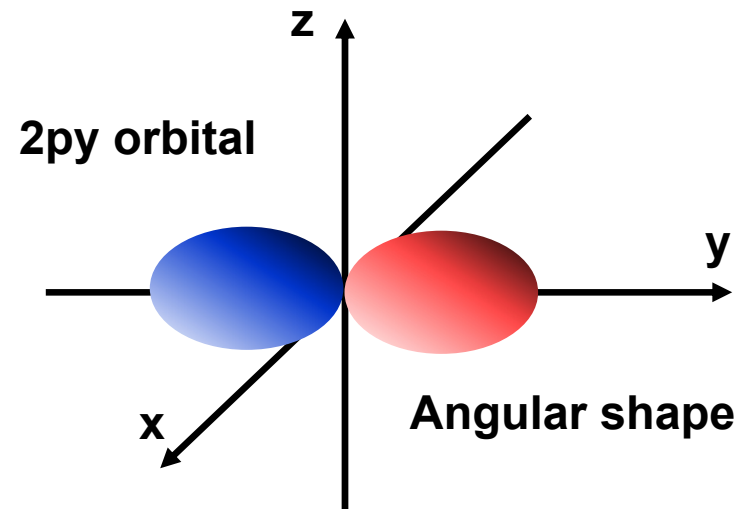
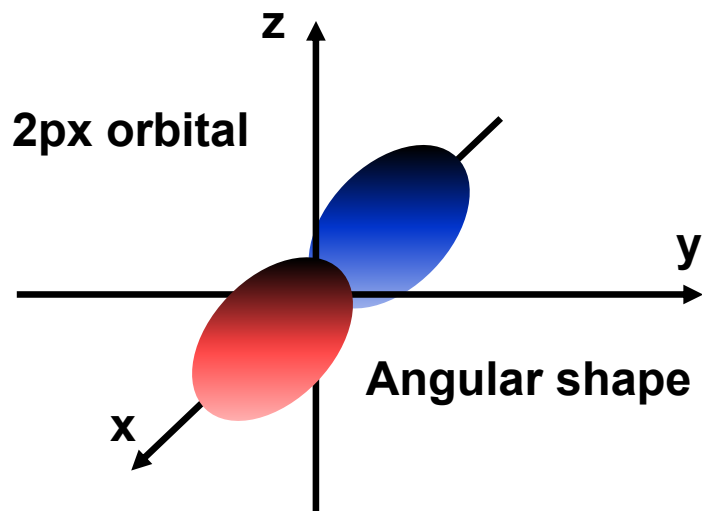
## The Hydrogen Atom: 2px and 2py Orbitals

2px Orbital:

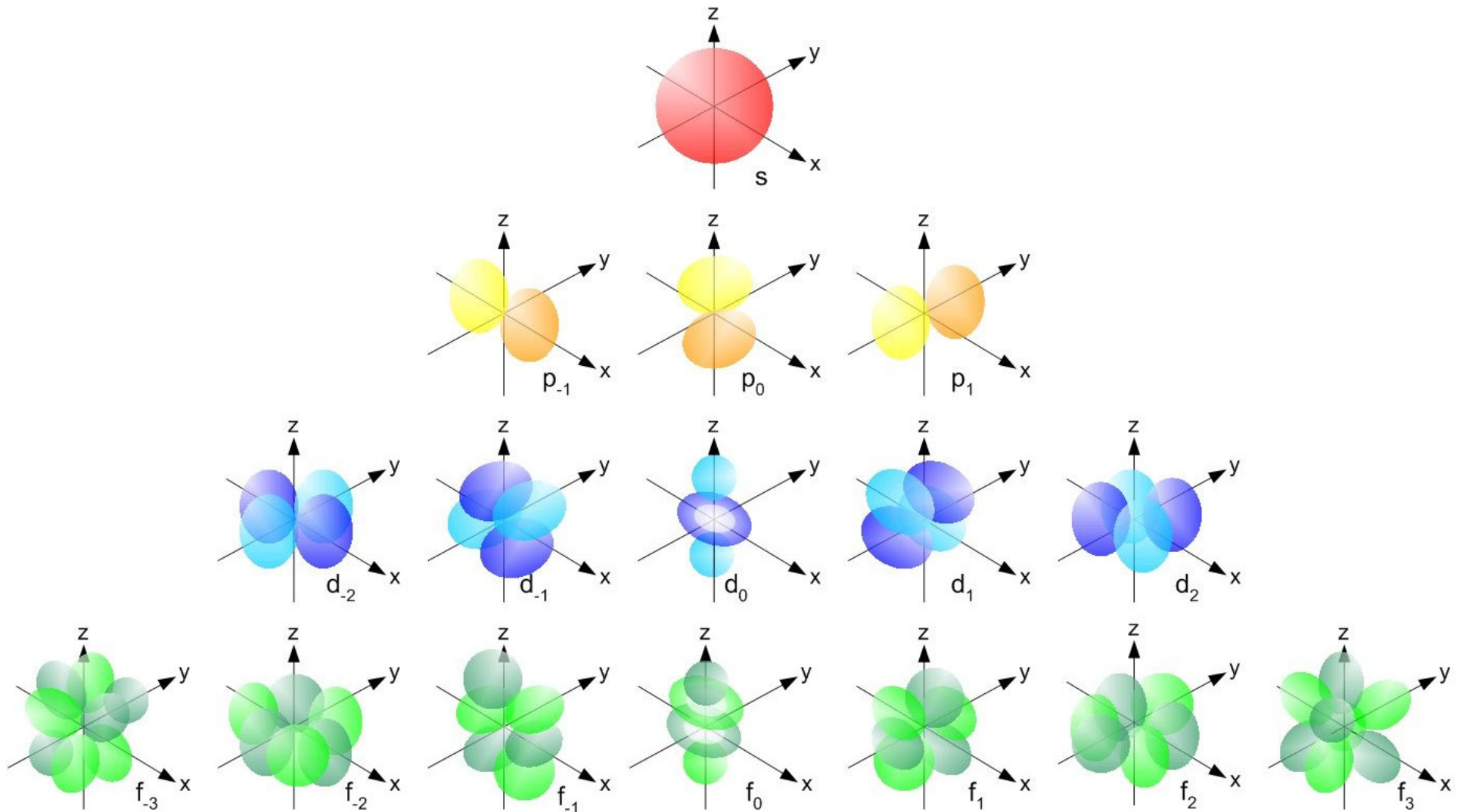
$$\begin{aligned}\chi_{n=2,\ell=1,p_x}(\vec{r}) &= \frac{1}{\sqrt{2}} \left[ -\chi_{n=2,\ell=1,m=+1}(\vec{r}) + \chi_{n=2,\ell=1,m=-1}(\vec{r}) \right] \\ &= \frac{1}{\sqrt{32\pi}} \left( \frac{1}{a_B} \right)^{3/2} \left( \frac{r}{a_B} \right) e^{-\frac{r}{2a_B}} \sin\theta \cos\phi\end{aligned}$$

2py Orbital:

$$\begin{aligned}\chi_{n=2,\ell=1,p_y}(\vec{r}) &= \frac{i}{\sqrt{2}} \left[ -\chi_{n=2,\ell=1,m=+1}(\vec{r}) - \chi_{n=2,\ell=1,m=-1}(\vec{r}) \right] \\ &= \frac{1}{\sqrt{32\pi}} \left( \frac{1}{a_B} \right)^{3/2} \left( \frac{r}{a_B} \right) e^{-\frac{r}{2a_B}} \sin\theta \sin\phi\end{aligned}$$

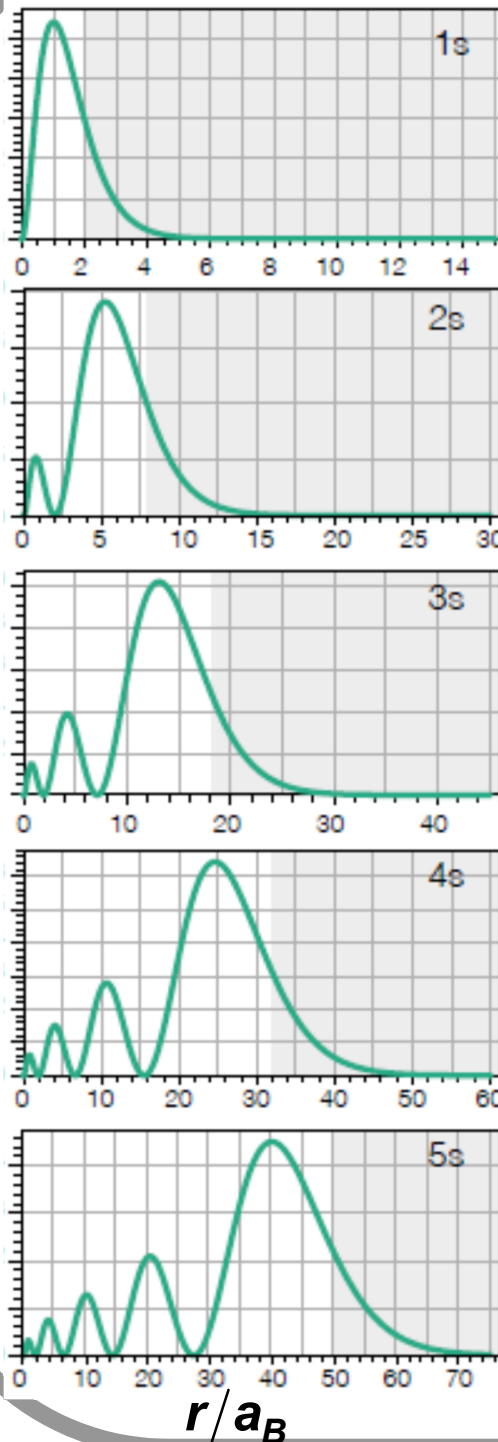


# The Hydrogen Atom: Angular Shapes of s, p, d, and f Orbitals





## Radial Probability Distributions for s ( $\ell = 0$ ) Orbitals for different $n$



$$\int d^3\vec{r} |\chi_{n,\ell,m}(r,\theta,\phi)|^2$$

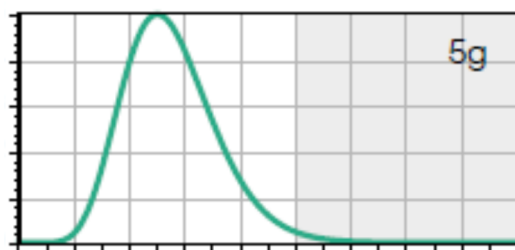
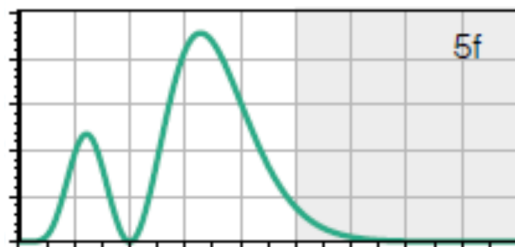
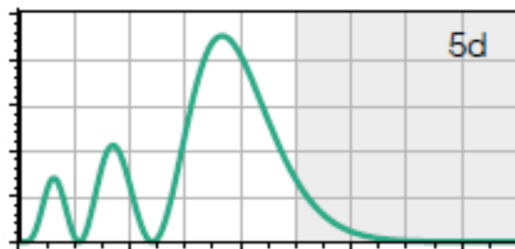
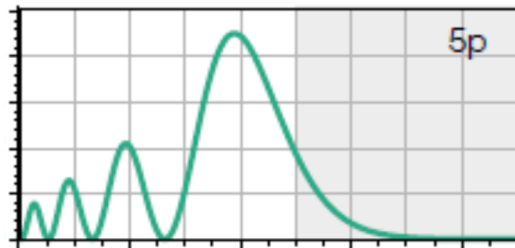
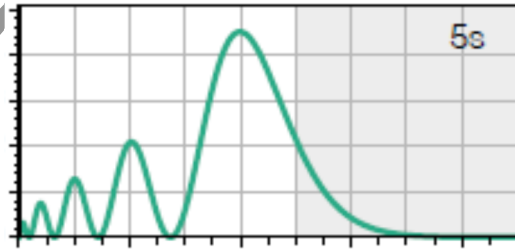
$$= \int_0^\infty dr \int_0^\pi r d\theta \int_0^{2\pi} r \sin\theta d\phi |\chi_{n,\ell,m}(r,\theta,\phi)|^2 = 1$$

$$\Rightarrow \int_0^\infty dr P_{n,\ell,m}(r) = 1$$

- Wavefunctions extend further out in the radial direction as  $n$  increases
- Wavefunctions gets more nodes in the radial direction as  $n$  increases
- Gray shaded regions are the **classically forbidden region** where the energy eigenvalue is less than the potential  $V(r)$

Classically forbidden region:  $r > 2n^2 a_B$

## Radial Probability Distributions for n=5 Shell for different $\ell$



$r/a_B$

$$\int d^3\vec{r} |\chi_{n,\ell,m}(r,\theta,\phi)|^2$$

$$= \int_0^\infty dr \int_0^\pi r d\theta \int_0^{2\pi} r \sin\theta d\phi |\chi_{n,\ell,m}(r,\theta,\phi)|^2 = 1$$

$$\Rightarrow \int_0^\infty dr P_{n,\ell,m}(r) = 1$$

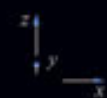
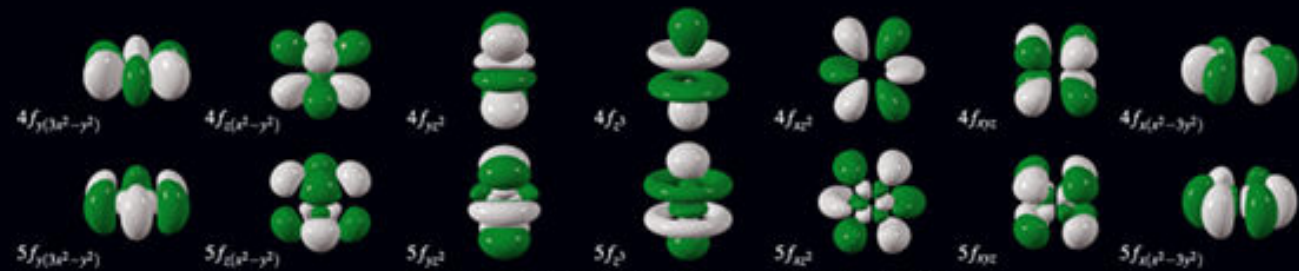
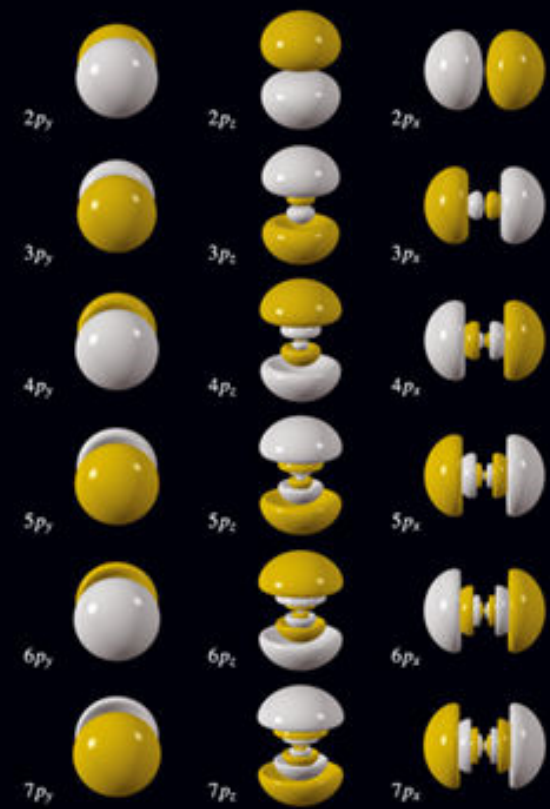
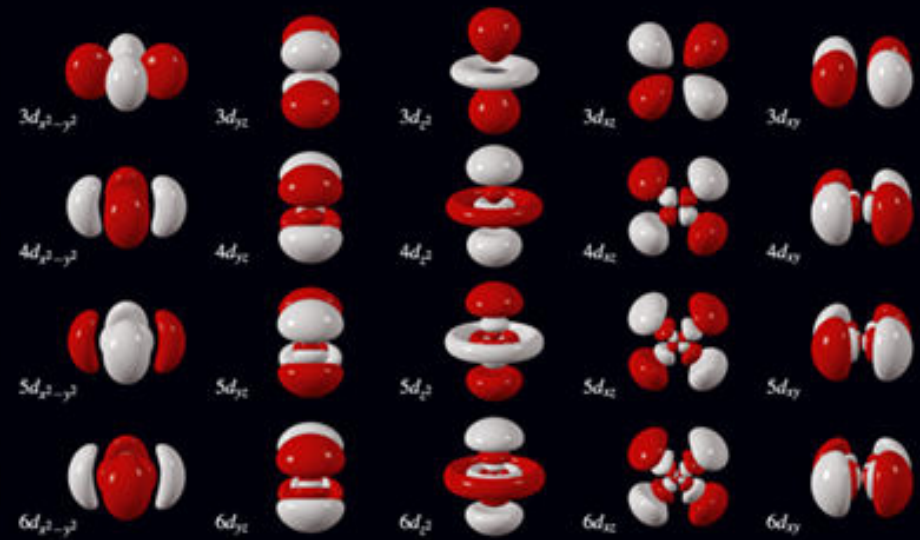
- Wavefunctions extend further out in the radial direction as  $\ell$  decreases
- Wavefunctions get more nodes in the radial direction as  $\ell$  decreases
- Gray shaded regions are the classically forbidden region where the energy eigenvalue is less than the potential  $V(r)$

Classically forbidden region:  $r > 2n^2 a_B$

# The Orbitron gallery of atomic orbitals



1s  
2s  
3s  
4s  
5s  
6s  
7s



## The Hydrogen Atom: Summary

The full Hamiltonian was:

$$\hat{H} = \frac{\hat{Q}^2}{2M} + \frac{\hat{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 |\hat{\vec{r}}|}$$

It had the following eigenstates:

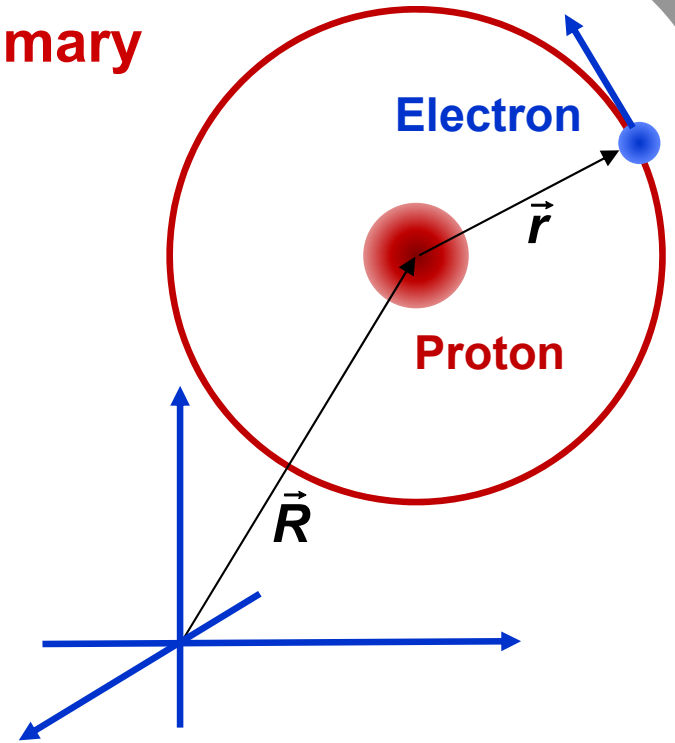
$$\begin{aligned} \hat{H}|\psi\rangle &= E|\psi\rangle \\ \Rightarrow \langle \vec{r}, \vec{R} | \hat{H} | \psi \rangle &= E\psi(\vec{r}, \vec{R}) \end{aligned}$$

We wrote the eigenfunctions as:

$$\psi_{\vec{k},n,l,m}(\vec{r}, \vec{R}) = \phi_{\vec{k}}(\vec{R}) \chi_{n,l,m}(\vec{r}) = \frac{e^{i\vec{k}\cdot\vec{R}}}{\sqrt{V}} \chi_{n,l,m}(\vec{r})$$

The corresponding eigenenergies were:

$$\begin{aligned} \hat{H}|\psi_{\vec{k},n,l,m}\rangle &= E_{\vec{k},n,l,m}|\psi_{\vec{k},n,l,m}\rangle \\ E_{\vec{k},n,l,m} &= \frac{\hbar^2 k^2}{2M} + \xi_{n,l} = \frac{\hbar^2 k^2}{2M} - \frac{E_B}{n^2} \end{aligned}$$



## The Hydrogen Atom CSCO: Adding Spin

Each electron can have spin up and spin down , so we write the quantum states as:

$$|\psi_{\vec{k},n,l,m}\rangle \otimes |z \uparrow\rangle$$

$$|\psi_{\vec{k},n,l,m}\rangle \otimes |z \downarrow\rangle$$

Orbital/spatial part

Spin part

The complete CSCO for the Hydrogen atom then becomes:

$$\hat{H} \quad \hat{L}^2 \quad \hat{L}_z \quad \hat{S}^2 \quad \hat{S}_z$$

