PHYS 2D
DISCUSSION SECTION

2012/5/30

- Quiz this Friday

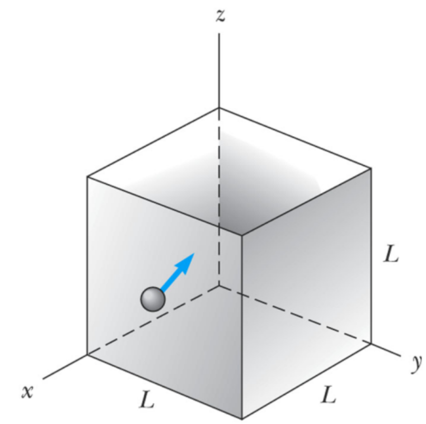
- QM in 3D (math really)

More Realistic QM

- Our world is 3 dimensional
- Must use 3 coordinates

- Study 2 cases:
  - Particle in a 3D box
    - -Essentially the same thing
  - Hydrogen atom
    - -Spherical coordinates, very different

Particle in a 3D box



- Choose Cartesian coordinates x, y, z
- Schrodinger's equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t)+U(x,y,z)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}$$

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

- Separation of variables 1:
- $\Psi(x,y,z,t)=\psi(x,y,z)\phi(t)$
- Yields $-\frac{\hbar^2}{2\text{m}}\nabla^2\psi(x,y,z)+U(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$
- $\phi(t)=\exp(-i\omega t)$, $E=\hbar\omega$

Particle in a 3D box

- Separation of variables 2:
- $\psi(x,y,z)=\psi_1(x)\psi_2(y)\psi_3(z)$
- Dividing by $\psi(x,y,z)$ yields

$$\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_1(x)}\frac{\partial^2\psi_1(x)}{\partial x^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_2(y)}\frac{\partial^2\psi_2(y)}{\partial y^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_3(z)}\frac{\partial^2\psi_3(z)}{\partial z^2}\right)=E=Const$$

- Each part must be independent of coordinates, so

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2}=E_1\psi_1(x) \qquad -\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2}=E_2\psi_2(y) \qquad -\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2}=E_3\psi_3(z)$$

$$\mathrm{E}_1+\mathrm{E}_2+\mathrm{E}_3=\mathrm{E}=\mathrm{Constant}$$

Particle in a 3D box

- We have essentially three 1D problems

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2} = E_1\psi_1(x) \quad -\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2} = E_2\psi_2(y) \quad -\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2} = E_3\psi_3(z)$$

- $\psi_1 = A\sin k_1 x = A\sin[(n_1\pi/L)x]$
- $\psi_2 = B\sin k_2 y = B\sin[(n_2\pi/L)y]$
- $\psi_3 = C\sin k_3 z = C\sin[(n_3\pi/L)z]$
- $E_1 = \frac{n_1{}^2\pi^2\hbar^2}{2mL^2} \quad E_2 = \frac{n_2{}^2\pi^2\hbar^2}{2mL^2} \quad E_3 = \frac{n_3{}^2\pi^2\hbar^2}{2mL^2}$

- $E = E_1 + E_2 + E_3$

Particle in a 3D box

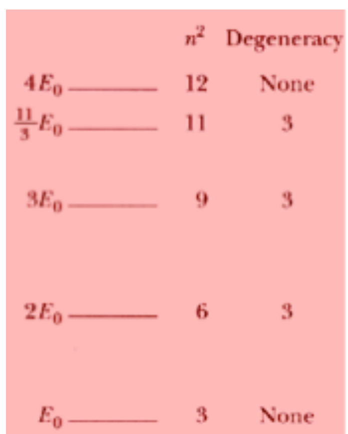
- $\Psi(x,y,z,t)=\psi(x,y,z)\phi(t)=\psi_1(x)\psi_2(y)\psi_3(z)\phi(t)$
  - $\Psi(\vec{r},t)=\psi(\vec{r})\, e^{-i\frac{E}{\hbar}t} = A\,[\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$
- Normalization: $1 = \iiint_{x,y,z} P(r)dx\, dydz$
  - $\Rightarrow A = \left[\frac{2}{L}\right]^{\frac{3}{2}}$ and $\Psi(\vec{r},t)= \left[\frac{2}{L}\right]^{\frac{3}{2}} [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$
- $k_i=n_i\pi/L$
- Need 3 "quantum numbers" $n_1 n_2 n_3$ to specify a state

Particle in a 3D box

- Degeneracy: If different sets of (n_1, n_2, n_3) correspond to the same E, they are said to be degenerate states

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2); \quad n_i = 1,2,3\ldots\infty, n_i \neq 0$$

$$\text{Ground State Energy } E_{111} = \frac{3\pi^2\hbar^2}{2mL^2}$$



(2,2,2)
(3,1,1)
(2,2,1)
(2,1,1)
(1,1,1)

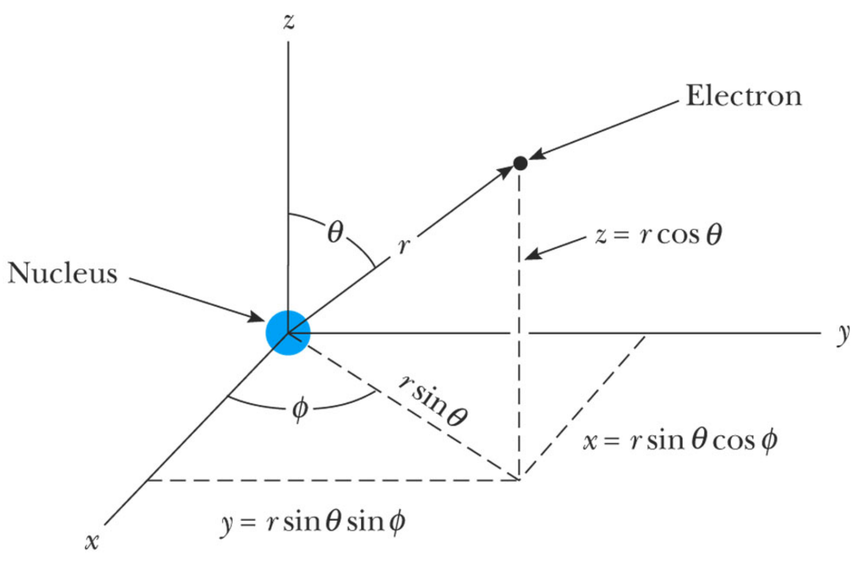
Hydrogen atom

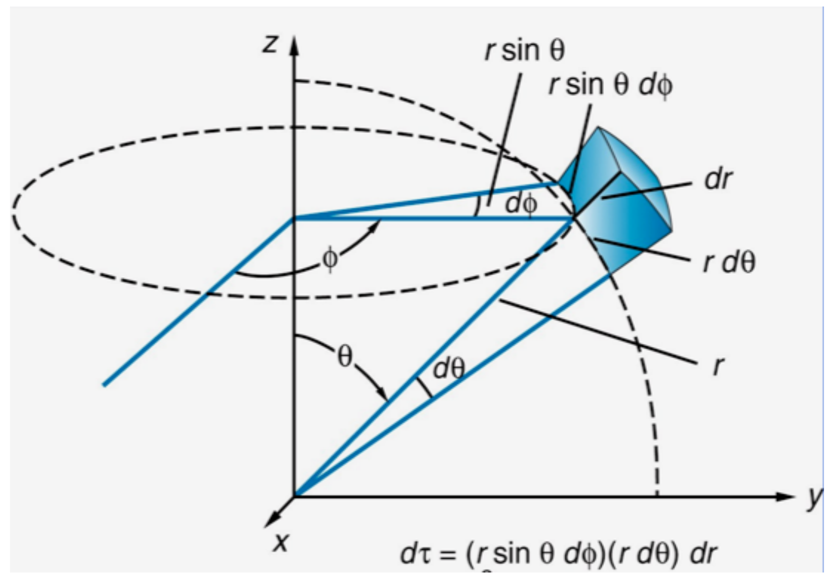
- $$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t)+U(x,y,z)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}$$
- Want to find wave function of the electron
- Wave function can be described using any 3D coordinate system
- U(x,y,z)~1/r
- The system is spherically symmetric: a positive charge at the center
- More natural to use spherical coordinates (r, θ, ϕ) than Cartesian coordinates (x, y, z)
- The differential equation is very different
- So the wave functions also look very different

Steps to finding the wave function

- To find the wave function, method is still the same:
- Write out the form of the differential equation
- Separation of variables, $\Psi(r,\theta,\phi,t)=R(r)\Theta(\theta)\Phi(\phi)T(t)$
- Separate the equation into 4 parts
- Solve each part
- The 3 spatial parts will each give a quantum number
- Combine all 4 parts and normalize

Spherical coordinates





$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\varphi = \arctan\left(\frac{y}{x}\right)$$
$$\theta = \arccos\left(\frac{z}{r}\right)$$

Volume Element dV

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

Schrodinger's equation

- $$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial^2 \phi}$$
- Multiply Schrodinger's equation by $-2m/\hbar^2$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi(r,\theta,\phi)}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi(r,\theta,\phi)}{\partial^2 \phi} + \frac{2m}{\hbar^2}(E-U(r))\psi(r,\theta,\phi) = 0$$

$$U(r) = \frac{kZe^2}{r}$$

Separation of variables

- $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial^2\phi}+\frac{2m}{\hbar^2}(E-U(r))\psi(r,\theta,\phi)=0$$

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

$$\frac{\partial\Psi(r,\theta,\phi)}{\partial r}=\Theta(\theta).\Phi(\phi)\frac{\partial R(r)}{\partial r}$$
$$\frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Phi(\phi)\frac{\partial\Theta(\theta)}{\partial\theta}$$
$$\frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Theta(\theta)\frac{\partial\Phi(\phi)}{\partial\phi}$$

- Multiply by $r\sin^2\theta/(R\Theta\Phi)$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})=0$$

Φ(ϕ)

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})=0$$

- Φ(ϕ) is the first the be separated
- The rest of the equation does not depend on ϕ, so $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}$ is some constant
- Periodic boundary condition: $\Phi(\phi+2\pi)=\Phi(\phi)$
- $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}=-(m_l)^2$, $\Phi(\phi)\sim\exp(im_l\phi)$
- Boundary condition $\Phi(\phi+2\pi)=\Phi(\phi)$ is satisfied

Θ(θ) & R(r)

- Now that we've dealt with Φ(ϕ)

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}+\frac{2\mathrm{m}r^2\sin^2\theta}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})=0$$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mathrm{m}r^2\sin^2\theta}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})=\mathrm{m}_l^2$$

- Divide by $\sin^2\theta$ and separate r & θ terms

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mathrm{m}r^2}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})=\frac{\mathrm{m}_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

- Some smart guy solved the θ differential equation and found that solutions exist only when
- $$\mathrm{LHS}=\mathrm{const}=\mathrm{RHS}=l(l+1)$$

Separated equations

- After separation, we have

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta) = 0 \ldots\ldots(2)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r}) - \frac{l(l+1)}{r^2}\right]R(r) = 0 \ldots(3)$$

- All solved by smart people (Legendre, Laguerre)

$\Theta(\theta)$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta)=0$$

- Solutions are called associated Legendre polynomials $P_l^m(\cos\theta)$
- Solutions exist only when $l=0, 1, 2, \ldots$
- Also require $m_l=-l, -l+1, -l+2, \ldots, 0, \ldots, l-2, l-1, l$
- Ex. $l=3$, $m_l=-3, -2, -1, 0, 1, 2, 3$

R(r)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2mr^2}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})-\frac{l(l+1)}{r^2}\right]R(r)=0$$

- Solutions are called associated Laguerre functions
- Solutions exist only when E>0 (continuous states) or

$$\mathrm{E}=-\frac{\mathrm{ke}^2}{2\mathrm{a}_0}\left(\frac{1}{n^2}\right);a_0=\frac{\hbar^2}{mke^2}=\text{Bohr Radius}$$

(bound states)

- $n=1, 2, 3, \ldots, \infty$
- Happens to be what Bohr predicted
- Also require $l=0, 1, 2, \ldots, n-1$

Quantum numbers

- 3D problem has 3 quantum numbers
  - Each set of 3 q-#'s specify a state
- In hydrogen the set is (n, l, m_l)
  - n goes from 0 to ∞, l is restricted by n, m_l is restricted by l
- Ex. If n=2, l=0/1, m_0=0, m_1=-1/0/1
  - 1 possible state with n=1: (1,0,0)
  - 4 possible states with n=2: (2,0,0) & (2,1,-1/0/1)
  - 9 possible states with n=3
  - N^2 possible states with n=N

The wave functions

- Denote m_l as m
- $\Phi(\phi)=\Phi_m(\phi)\sim\exp(im\phi)$
- $\Theta(\theta)=\Theta_{l,m}(\theta)\sim P_l^m(\cos\theta)$
- $R(r)=R_{n,l}(r)$
- $T(t)\sim\exp(-iEt/\hbar)$

$$\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta)=0\ldots\ldots(2)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r})-\frac{l(l+1)}{r^2}\right]R(r)=0\ldots.(3)$$

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$

ℓ	m_ℓ	$Y_{\ell m_l}(\theta,\phi)=\Theta_{\ell m_l}(\theta)\Phi_{m_l}(\phi)$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	±1	$\mp(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta-1)$
2	±1	$\mp(15/8\pi)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	±2	$(15/32\pi)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

Wave function for hydrogen

- $\Psi(r,\theta,\phi,t)=R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_{m}(\phi)T(t)$

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

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$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$

ℓ	m_ℓ	$Y_{\ell m_l}(\theta,\phi)=\Theta_{\ell m_l}(\theta)\Phi_{m_l}(\phi)$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	±1	$\mp(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta-1)$
2	±1	$\mp(15/8\pi)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	±2	$(15/32\pi)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

- We can look at for example the ground state

$$\psi_{100} = R_{10}(r)Y_0^0(\theta,\phi) \qquad |\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3}e^{-2Zr/a_0}$$

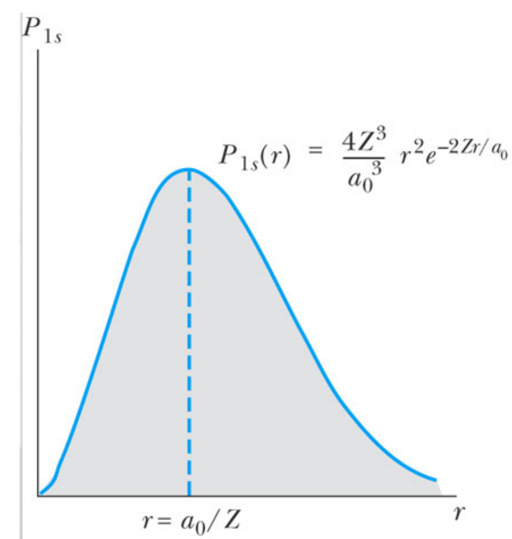
The ground state

- $|\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0}$ is spherically symmetric

- We can define the radial probability distribution

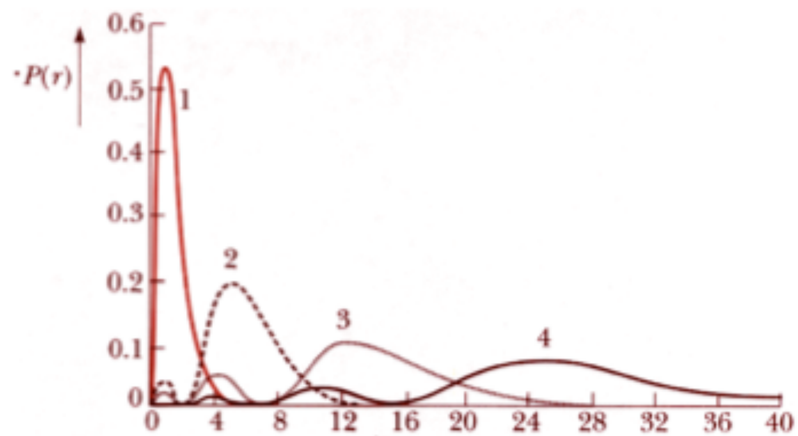
$$P(r)dr = |\psi|^2 \, 4\pi r^2 dr$$

- This is the probability the electron will be found at a distance [r, r+dr] from the nucleus



- All the l=m=0 states are spherically symmetric

n	l	m_l	$R(r)=$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a}$
2	0	0	$\frac{1}{2\sqrt{2}a_0^{3/2}}(2-\frac{r}{a_0})e^{-\frac{r}{2a_0}}$
3	0	0	$\frac{2}{81\sqrt{3}a_0^{3/2}}(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2})e^{-\frac{r}{3a_0}}$



The excited states

- Orbitals