

IX. Quantum Theory of the Hydrogen Atom

- It is a $U(r)$ problem [everything from Ch. VIII carries over]
- $U(r) \sim -\frac{1}{r}$
- This is essential for understanding matter (atoms, molecules, solids)
- Pictures of atomic orbitals

A. $U(r) \propto -\frac{1}{r}$ is a very special case

$$\text{Radial Eq. } \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} (E - U(r))R = \overbrace{\ell(\ell+1)}^{\lambda} R$$

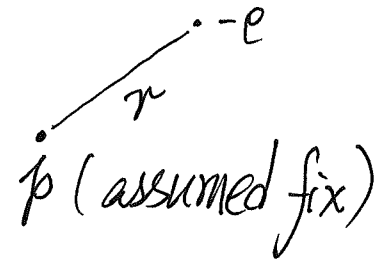
$$\text{OR } \boxed{\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(E - U(r) - \underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}} \right) R = 0} \quad (1)$$

- $\ell=0$ one problem, $\ell=1$ another problem, etc. c.f. $\frac{L^2}{2mr^2}$ in classical mechanics
- Each $\ell \Rightarrow$ an eigenvalue problem (1) for central force problems
- Hydrogen: Nucleus (proton) + 1 electron

nucleus mass \gg electron mass m_e
(assume nucleus fixed at origin)

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r} \propto -\frac{1}{r} \quad (2)$$

[negative is important] (attractive)



- Hydrogen-like ions : A nucleus plus one electron

He^+ : Nucleus + Ze ($Z=2$) charge and 1 electron

$$U(r) = - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (3)$$

$Z \equiv$ atomic number

[lines up elements in periodic table]

- Accounting for finite mass of proton (nucleus of hydrogen)

▪ Center of mass + relative motion

free motion

[not our focus]

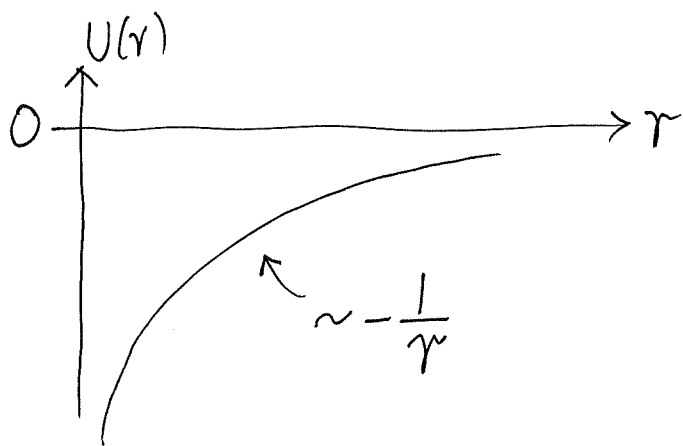
m_e replaced by reduced mass μ

$$\frac{1}{\mu} = \underbrace{\frac{1}{m_e}}_{\text{big}} + \underbrace{\frac{1}{m_p}}_{\text{small term}}$$

μ is slightly different from m_e

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + U(r) \quad (4)$$

↑
reduced mass



\therefore Bound states have $E < 0$

[There are $E > 0$ solutions to TISE, but we only discuss bound states.]

Eq. (1) can be solved by the Series Solution Method (see Appendix)

Key Features of solutions to:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2mr^2} \right) R = 0 \quad (5)$$

- $R(r)$ must be well-behaved [e.g. can't diverge]
- Generally $R_{nl}(r) \leftrightarrow E_{nl}$ (any $U(r)$)
- $U(r) \sim -\frac{1}{r}$ shows additional features

$$l=0 \quad R_{10} \quad R_{20} \quad R_{30} \quad R_{40} \quad \dots$$

$$l=1 \quad R_{21} \quad R_{31} \quad R_{41} \quad \dots$$

$$l=2 \quad R_{32} \quad R_{42} \quad \dots$$

$$l=3 \quad R_{43} \quad \dots$$

$$\vdots$$

For well-behaved $R_{nl}(r)$
in solving Eq. (5)

Pattern
of
 E_{nl}

$$E_{10}$$

$$\parallel$$

$$\boxed{E_1}$$

$$[n=1]$$

$$E_{20}$$

$$\parallel$$

$$E_{21}$$

$$\parallel$$

$$\boxed{E_2}$$

$$[n=2]$$

$$E_{30}$$

$$\parallel$$

$$E_{31}$$

$$\parallel$$

$$E_{32}$$

$$\parallel$$

$$\boxed{E_3}$$

$$[n=3]$$

$$E_{40}$$

$$\parallel$$

$$E_{41}$$

$$\parallel$$

$$E_{42}$$

$$\parallel$$

$$E_{43}$$

$$\parallel$$

$$\boxed{E_4}$$

$$[n=4]$$

$$E_n = \frac{-me^4}{2 \cdot (4\pi\epsilon_0)^2 \hbar^2} \cdot \frac{1}{n^2}$$

depends
only on n
(not on l)

-13.6 eV

$$\blacksquare \quad E_{n0} = E_{n1} = E_{n(l=n-1)} = E_n = \frac{-me^4}{32\pi^2\epsilon_0^2\hbar^2} \cdot \frac{1}{n^2}$$

due to $-\frac{1}{r}$ form [not expected based on $U(r)$]

▪ Schrödinger (1926) obtained E_n by solving his Schrödinger Equation

▪ Same E_n as in Bohr's (1913) model of hydrogen atom

▪ Schrödinger didn't need ad hoc rules as Bohr needed

▪ Schrödinger only needed his Equation AND Well-behaved ψ (B.C.'s)

▪ Higher degeneracy than simply $U(r)$

Each n , $l = 0, 1, 2, \dots, n-1$

then each l , $m_l = l, l-1, \dots, 0, \dots, -l+1, -l$

} Different states all
} have energy E_n

For E_n , degeneracy = $\sum_{l=0}^{n-1} (2l+1) = n^2$ [Note: We ignored "spin" here]

Labels and Degeneracy

$n=1$ (E_1)

$l=0$

1s orbital

Degeneracy
[ignoring spin]

1

Degeneracy
[including spin]

2

$n=2$ (E_2)

$l=0$

2s orbital

1

} 4

8

$l=1$

2p orbital

3

$n=3$ (E_3)

$l=0$

3s orbital

1

} 9

18

$l=1$

3p orbital

3

$l=2$

3d orbital

5

$n=4$ (E_4)

$l=0$

4s orbital

1

} 16

32

$l=1$

4p orbital

3

$l=2$

4d orbital

5

$l=3$

4f orbital

7

o
o
o

$l=0$	R_{10}	R_{20}	R_{30}	R_{40}	\dots
	[1s]	[2s]	[3s]	[4s]	
$l=1$		R_{21}	R_{31}	R_{41}	\dots
		[2p]	[3p]	[4p]	
$l=2$			R_{32}	R_{42}	\dots
			[3d]	[4d]	
$l=3$				R_{43}	\dots
				[4f]	
\vdots					

For well-behaved $R_{nl}(r)$

Labelling
"nl"

Getting close to what you
learned in chemistry
courses.

E_{10}	E_{20}	E_{30}	E_{40}
E_{21}	E_{31}	E_{41}	
E_{32}	E_{42}		
E_{43}			
E_1	E_2	E_3	E_4
[n=1]	[n=2]	[n=3]	[n=4]

$$E_n = \frac{-me^4}{2 \cdot (4\pi\epsilon_0)^2 \hbar^2} \cdot \frac{1}{n^2}$$

depends only on n (not on l)

-13.6 eV

$$\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi)$$

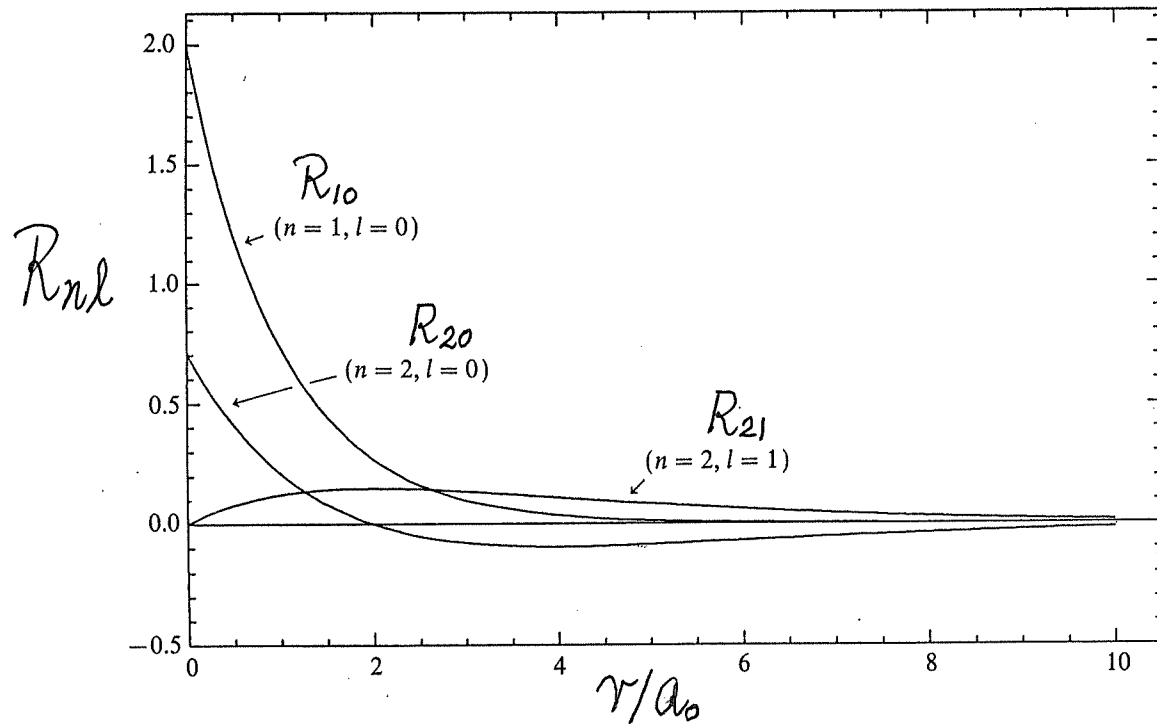
Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2,$ and 3^*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^3} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^3} e^{-r/a_0}$ Ψ_{100}
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^3} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^3} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$ Ψ_{200}
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^3} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^3} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$ Ψ_{210}
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^3} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^3} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$ Ψ_{211} and Ψ_{21-1}
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^3} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^3} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$ Ψ_{300}
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^3} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^3} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$ Ψ_{310}
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^3} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^3} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$ Ψ_{311} and Ψ_{31-1}
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$ Ψ_{320}
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$ Ψ_{321} and Ψ_{32-1}
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^3} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$ Ψ_{322} and Ψ_{32-2}

$$U(r) \Rightarrow \underbrace{Y_{lm_l}(\theta, \phi)}_{\text{Angular part}} \underbrace{R_{nl}(r)}_{\text{Radial part [due to } U \sim \frac{1}{r}]} \underbrace{\Psi_{nlm_l}(r, \theta, \phi)}_{\text{Total wave function}}$$

Bohr radius: $a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{m_e e^2} = 5.292 \times 10^{-11} \text{ m} = 0.5292 \text{ \AA}$ appears naturally

A few $R_{nl}(r)$ [see table for functional form]



- R_{20}, R_{21} extend further in r (further from the nucleus) than R_{10}

- $R_{nl}(r)$ are real functions
- $R_{nl}(r)$ is the part of ψ with r in it
- a_0 sets the length scale of an atom, thus atomic physics, and molecules, and solids!
- \sim few \AA [separation between atoms in molecules and solids]

B. How to visualize $\Psi_{nlm_l}(r, \theta, \phi)$ and use the QM results?

Think like a physicist!

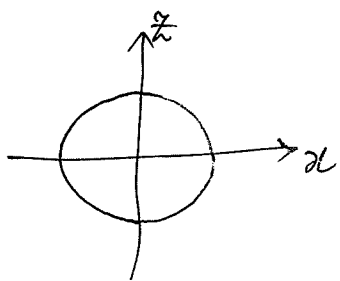
$$\Psi_{nlm_l}(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{governs radial dependence}} \cdot \underbrace{Y_{lm_l}(\theta, \phi)}_{\text{governs angular dependence}}$$

[how big r away] [which direction is bigger]

Example: $\Psi_{100}(r, \theta, \phi)$ [1S]

$$Y_{00}(\theta, \phi) = \text{constant} \frac{1}{\sqrt{4\pi}}$$

Polar Plot

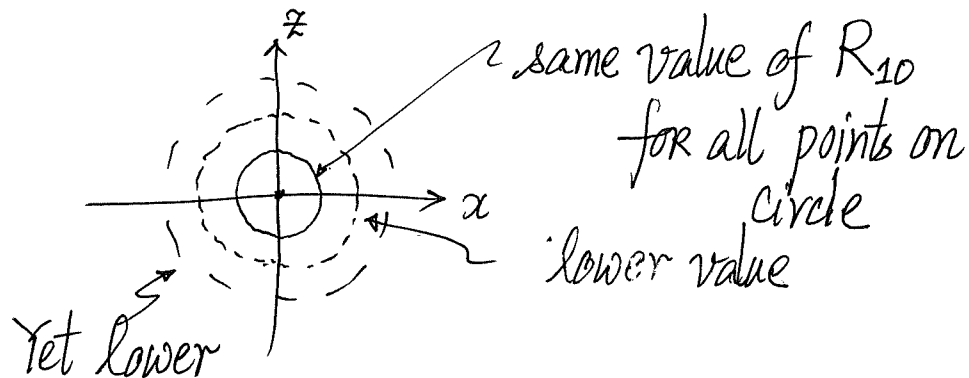
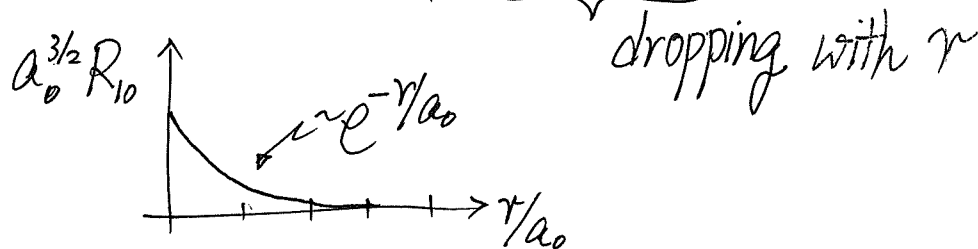


Meaning



every direction
has same value
[no preferred direction]

$$R_{10}(r) = \frac{1}{a_0^{3/2}} \frac{1}{\sqrt{\pi}} e^{-r/a_0}$$

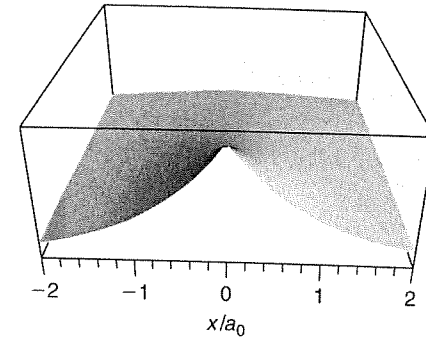
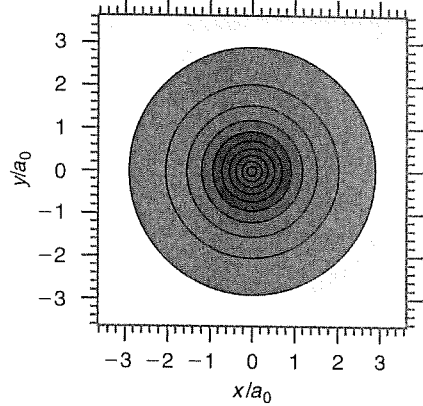


Now multiply the pictures together \Rightarrow how $\Psi_{100}(r, \theta, \phi)$ looks like

- Spherical stuff, biggest at origin, exponentially dropping as r goes out, tiny when $r \gg a_0$

Adding third axis to show Ψ_{100}

1s



1s

Contour plot of $\Psi_{100}(r, \theta, \phi)$

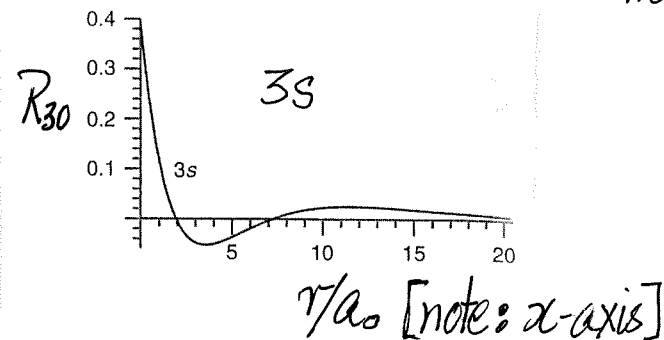
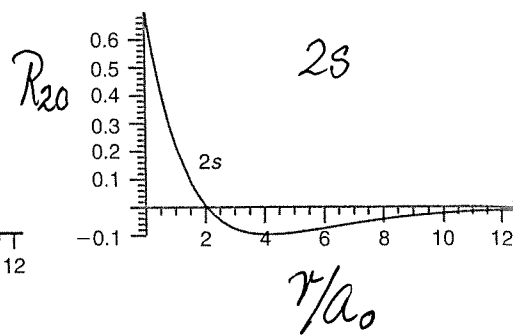
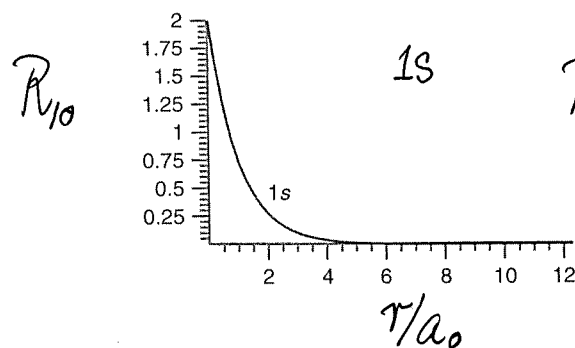
[same value of Ψ on a contour]

[value drops for outer contours]

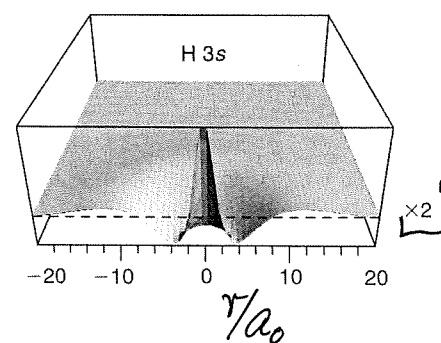
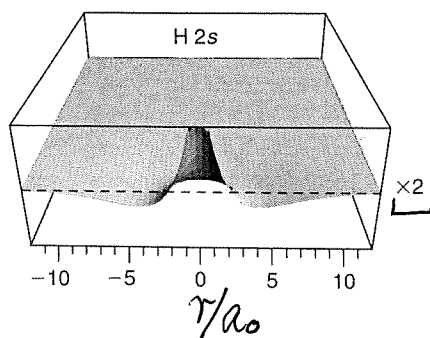
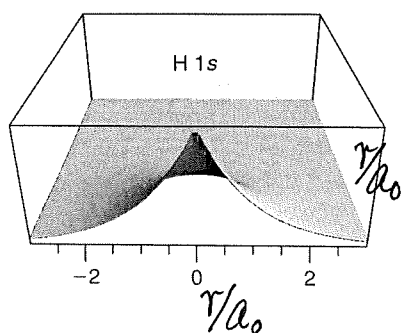
[Whole picture: Rotate about an axis through origin]

This is the most important (simplest also) atomic orbital for H-atom because the only electron lives there. Thus hydrogen 1s is involved in chemistry (forming bond), e.g. H_2 molecule

$\Psi_{200}(r, \theta, \phi)$ and $\Psi_{300}(r, \theta, \phi)$ [Same $Y_{00}(\theta, \phi) = \text{isotropic}$ (各向同性)]
no direction dependence



[Multiply them by Y_{00} give a sphere with circular contours of constant ψ]



Blow up to see clearly

Three-dimensional perspective plots of the 1s, 2s, and 3s orbitals. The dashed lines indicate the zero of amplitude for the wave functions. The "x2" refers to the fact that the amplitude of the wave function has been multiplied by 2 to make the subsidiary maxima apparent. The horizontal axis shows radial distance in units of a_0 .

[Pictures taken from Engel, "Quantum Chemistry and Spectroscopy"]

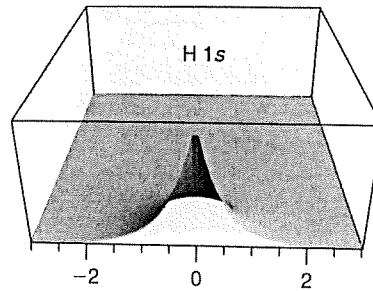
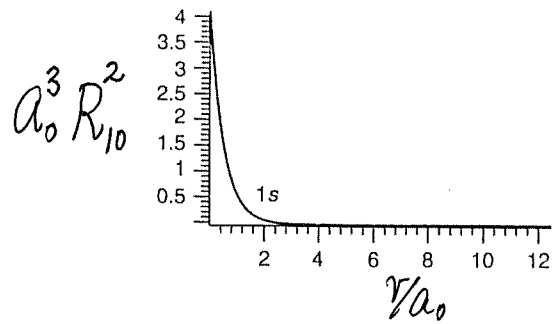
Student A: From pictures of Ψ_{100} , Ψ_{200} , Ψ_{300} , they all have its biggest value at $r=0$ [the nucleus position], does it mean that the electron has the largest probability to be found at $r=0$? I learned from Bohr that it is out there some distance a_0 away. What's wrong?

Good Question!

Idea in the answer is useful in different subjects, e.g. solid state physics, liquid state physics, statistical physics.

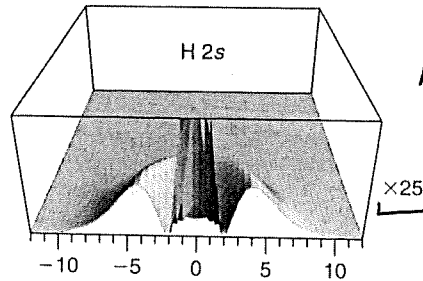
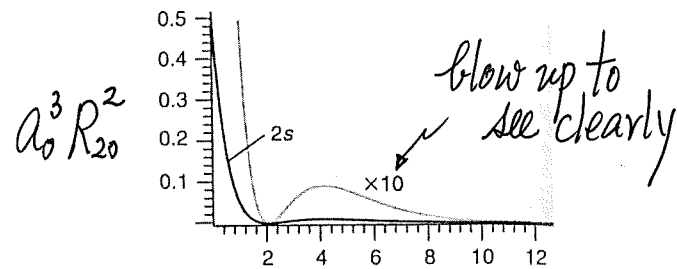
Two points in the answer.

Point 1: Should study $|\psi_{nlm_l}(r, \theta, \phi)|^2$ (Born)



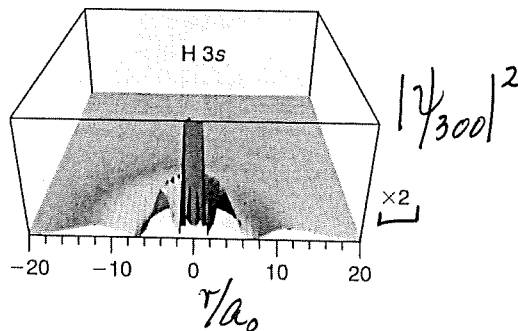
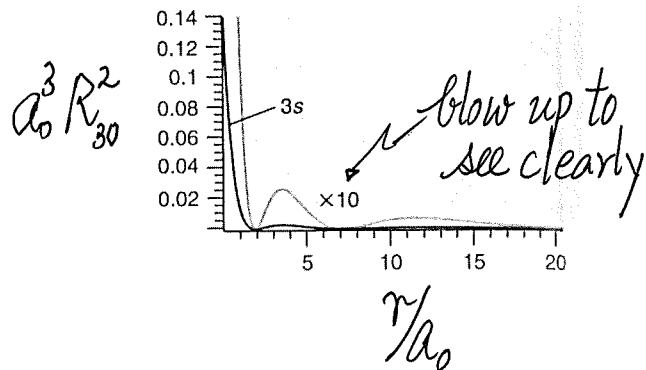
$|\psi_{100}|^2$

Probability Density



$|\psi_{200}|^2$

But Student A's question remains.



$|\psi_{300}|^2$

3D perspective plots of the square of the wave functions for the orbitals indicated. The numbers on the axes are in units of a_0 . The "x25" refers to the fact that the amplitude of the wave function has been multiplied by 25 to make the subsidiary maxima apparent.

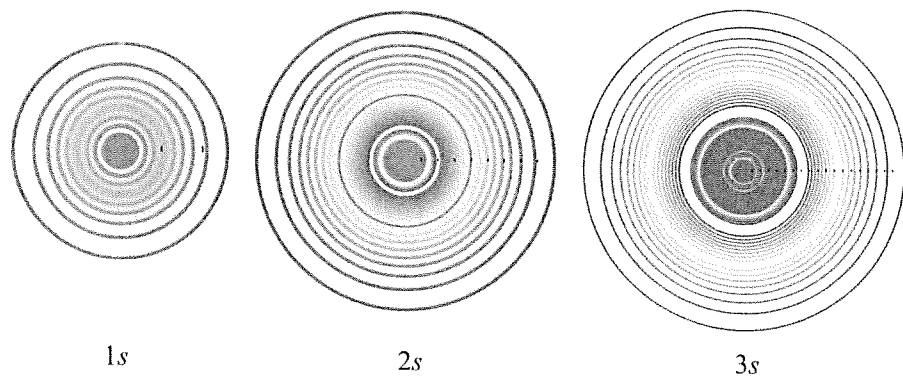
Bonus: Note that 2s has a part near $r \approx 0$ [quite close to nucleus] [useful in next course]

Other ways of showing $|\psi|^2$

Contour Plots of $|\psi_{100}|^2, |\psi_{200}|^2, |\psi_{300}|^2$

[dots are distances in a_0]

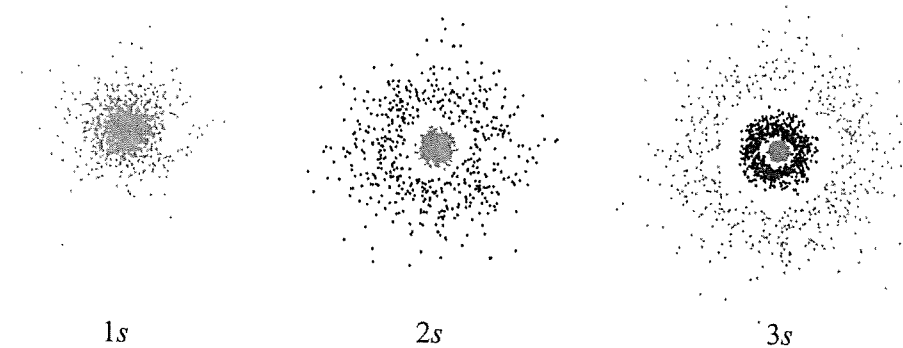
Contours enclosed 10%, 20%, ..., 90% probability



1s

2s

3s



1s

2s

3s

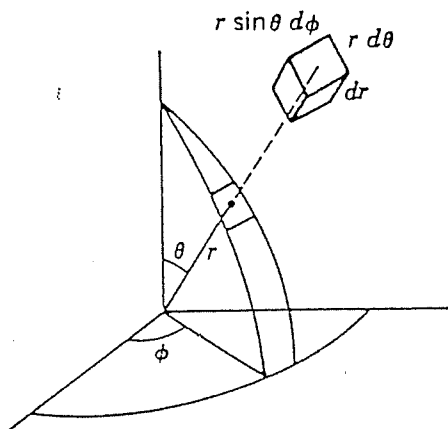
Using dots (density of dots is proportional to probability of finding the electron in that region)

[x-z cut]

Point 2: See what exactly is the quantity in question

Born: $|\psi_{nlm_e}(r, \theta, \phi)|^2 d\tau = |\psi_{nlm_e}(r, \theta, \phi)|^2 \underbrace{r^2 \sin\theta dr d\theta d\phi}_{\text{volume element in spherical coordinates}}$

Volume element $d\tau$ in spherical polar coordinates.



$$= |\psi_{nlm_e}(r, \theta, \phi)|^2 r^2 dr \cdot \underbrace{d\Omega}_{\text{solid angle element}}$$

= Prob. of finding electron in volume element $d\tau$ located at \vec{r} from origin

• Question 1: What is the probability of finding electron at a position \vec{r} ?

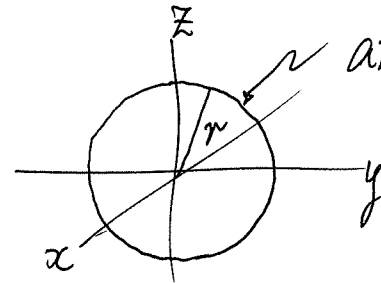
Bad Question, because \vec{r} is a continuous variable!

▪ Question 2: What is the probability of finding electron at exactly r away from nucleus, regardless of the direction?

▪ Don't care about direction

▪ A better question, but still

not good enough! The surface is too thin!



anywhere on surface of sphere is OK

[doesn't matter where!]

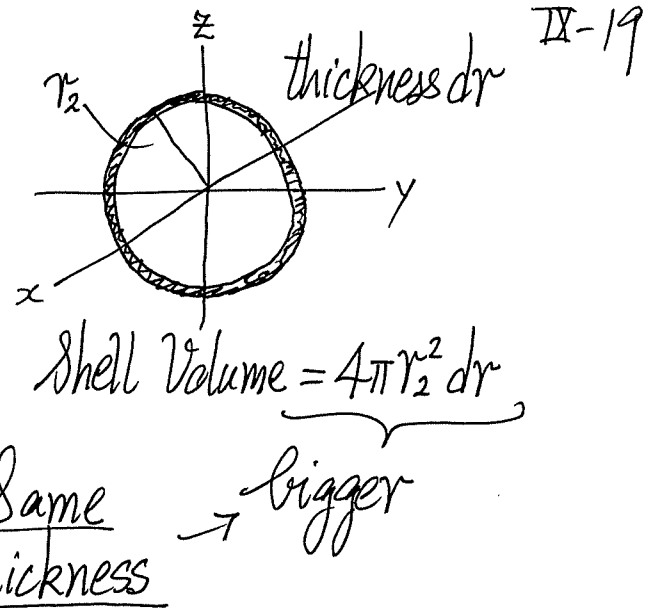
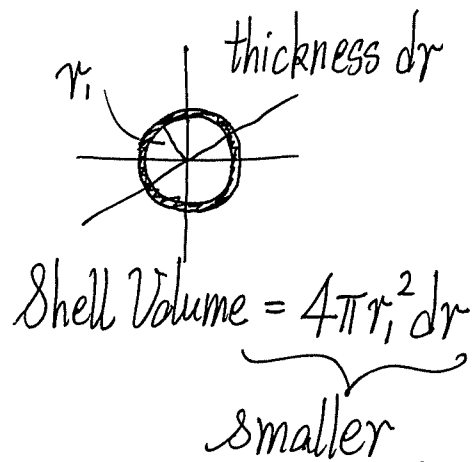
▪ Question 3: What is the probability of find the electron in the spherical shell that is exactly r away from nucleus with thickness dr ? [Implicit in question: regardless of direction]

This is The Question behind the layman's version

"How far is the electron from nucleus?"

▪ Dimension (3D) matters

Volume of spherical shell
grows as $4\pi r^2 dr$



Answer to Question 3

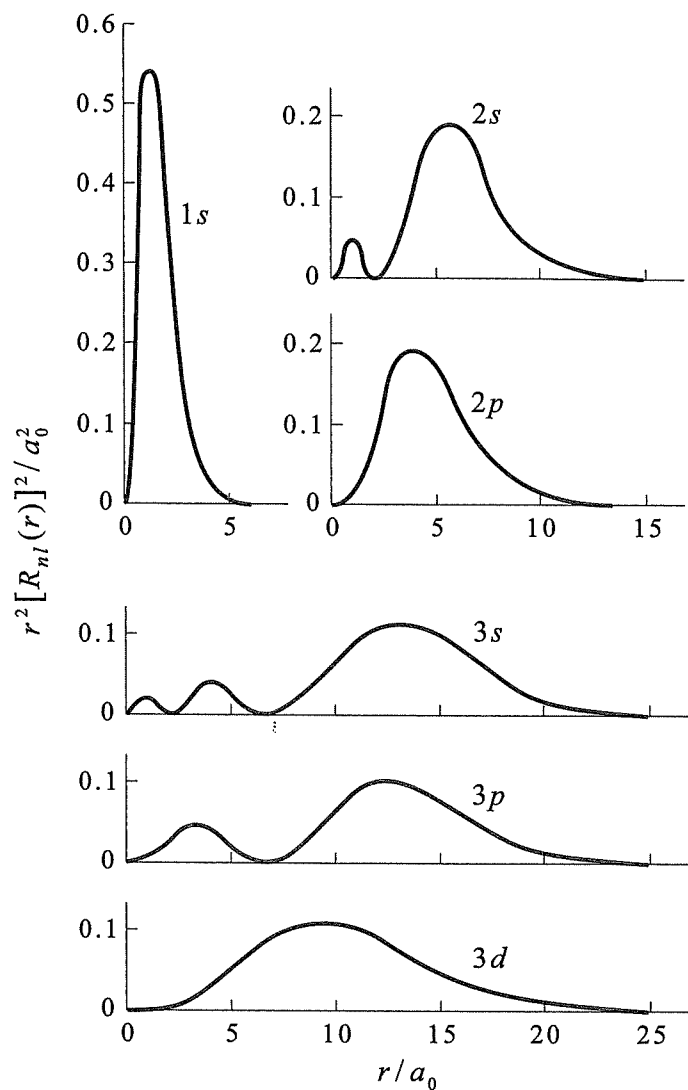
$$\begin{aligned}
 P(r) dr &= r^2 dr \underbrace{\int_0^{2\pi} d\phi \int_0^\pi d\theta}_{\text{regardless of direction}} |\psi_{nlm_e}(r, \theta, \phi)|^2 \sin\theta \\
 &= r^2 |R_{nl}(r)|^2 dr \underbrace{\int_0^{2\pi} d\phi \int_0^\pi d\theta |Y_{lm_e}(\theta, \phi)|^2 \sin\theta}_1 \quad \text{[this is how } Y_{lm_e} \text{ are normalized]} \\
 &= r^2 |R_{nl}(r)|^2 dr
 \end{aligned}$$

Question 3's
quantity

∴

$$P(r) = r^2 |R_{nl}(r)|^2 \equiv \text{Radial Probability Distribution Function}$$

$$P(r) = r^2 [R_{nl}(r)]^2 \quad (\text{Washed angular information away})$$



1s: peaks at $r = a_0$ (Bohr said must be)
 QM: Most probable at $r = a_0$
 to be at $r = a_0$ (can be elsewhere)

2s: peaks at $r = 5.24 a_0$ [Not Bohr's $4a_0$]

2p: peaks at $r = 4a_0$ [Bohr said must be $r = 4a_0$]

o
o
o

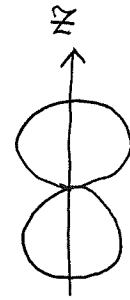
3d: peaks at $r = 9a_0$ [Bohr said must be $r = 9a_0$]

QM: Most probable there (can be elsewhere)

C. How about p and d orbitals?

(i) Angular Part

p orbitals $l=1 \Rightarrow Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$



- Y_{10} is real
- directional along z
- p_z orbital

$$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$$

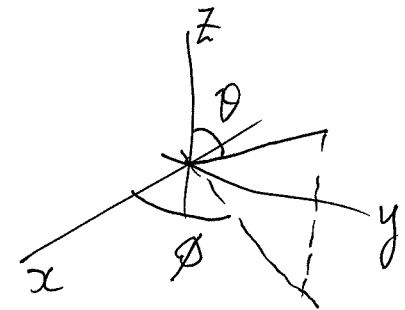
$$Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}$$

} complex [they are not p_x, p_y yet]

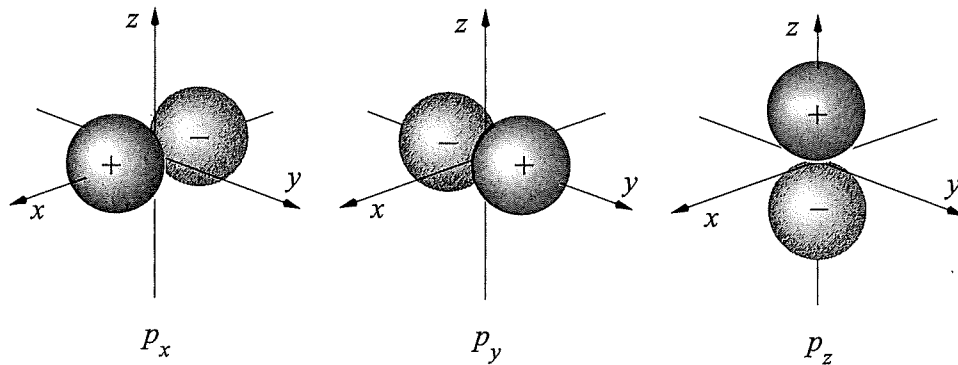
- Useful and practical to combine them into real directional functions

$$\frac{1}{\sqrt{2}} (Y_{1-1} - Y_{11}) \equiv p_x = \sqrt{\frac{3}{4\pi}} \underbrace{\sin\theta \cos\phi}_{\text{in } x\text{-direction}}$$

$$\frac{i}{\sqrt{2}} (Y_{1-1} + Y_{11}) \equiv p_y = \sqrt{\frac{3}{4\pi}} \underbrace{\sin\theta \sin\phi}_{\text{in } y\text{-direction}}$$



p_x, p_y, p_z are orthonormal [$\because Y_{10}, Y_{11}, Y_{1,-1}$ are orthonormal]
 real functions [identical shape but along different directions]



These are the p_x, p_y, p_z
 in Chemistry courses.

[No $R_{nl}(r)$ yet]

Three-dimensional polar plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 1$

Optional ($l=2$: d orbitals[†]) Y_{20} (real), Y_{21} , Y_{2-1} , Y_{22} , Y_{2-2} (complex)

$$d_{z^2} \equiv Y_{20} = \sqrt{\frac{5}{16\pi}} \underbrace{(3 \cos^2 \theta - 1)}_{P_2(\cos \theta)}$$

$$d_{xz} \equiv \frac{1}{\sqrt{2}} (Y_{2-1} - Y_{21}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi$$

$$d_{yz} = \frac{i}{\sqrt{2}} (Y_{2-1} + Y_{21}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}} (Y_{22} + Y_{2-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$$

$$d_{xy} = \frac{1}{\sqrt{2}i} (Y_{22} - Y_{2-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi$$

orthonormal

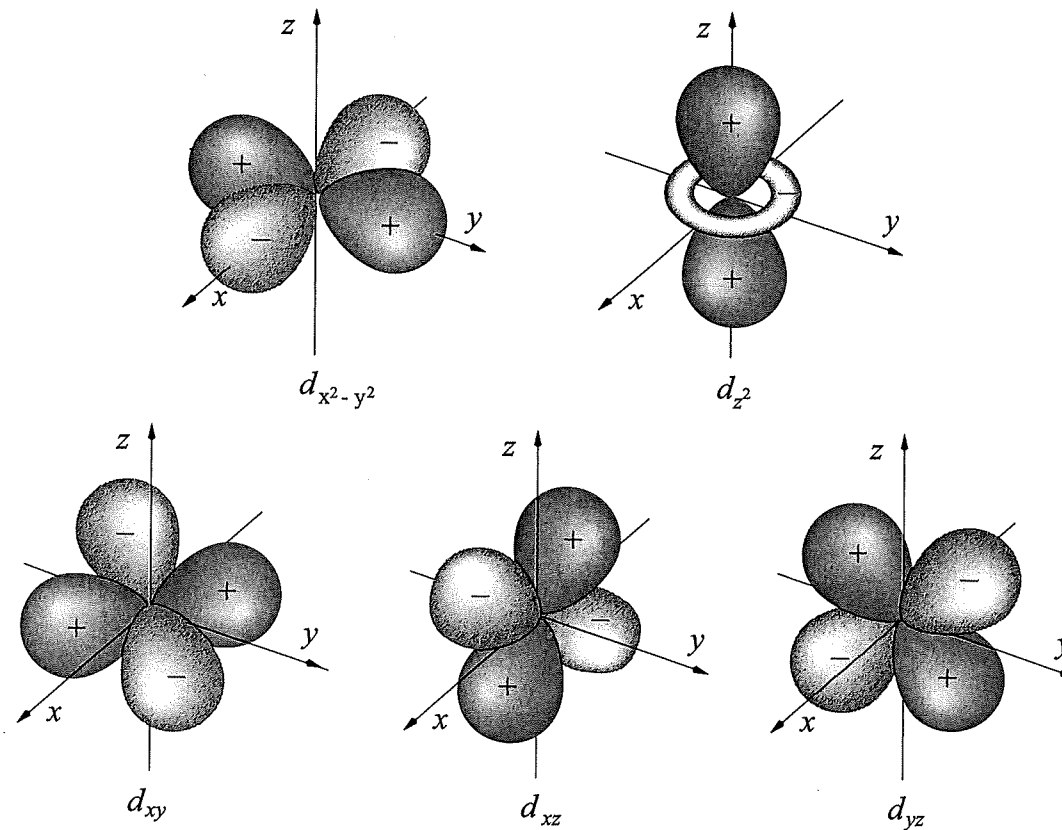
different angular dependence

all real

$Y_{\ell m}$ can be combined to form real functions

[†] Useful for understanding magnetic materials.

The d orbitals

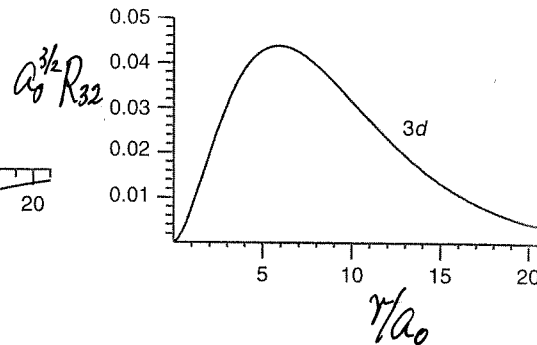
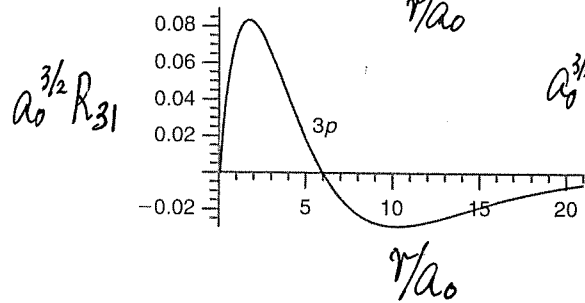
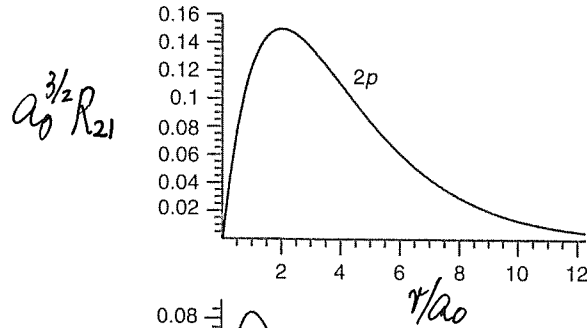


Three-dimensional plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 2$. Such plots show the directional character of these orbitals but are not good representations of the shape of these orbitals because the radial functions are not included.

Recall: There is a radial $R_{n2}(r)$ to multiply into them to get the "nd" states
e.g. (3d states)

(ii) Radial Part

2p requires $R_{21}(r)$, 3p requires $R_{31}(r)$, 3d requires $R_{32}(r)$



Multiply (in mind)

into p_x, p_y, p_z

[$2p_x, 2p_y, 2p_z$]

[$3p_x, 3p_y, 3p_z$]

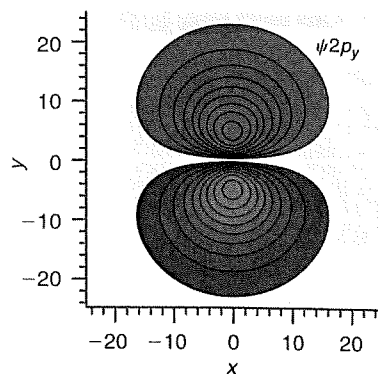


Multiply (in mind)

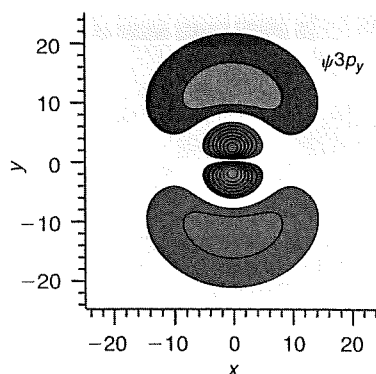
into the five d-orbitals

[five 3d orbitals]

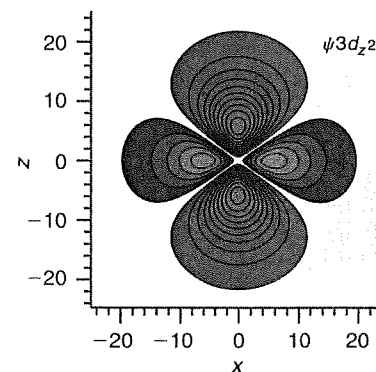
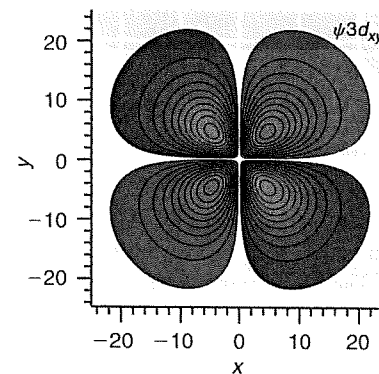
A 2p orbital



A 3p orbital



Two 3d orbitals

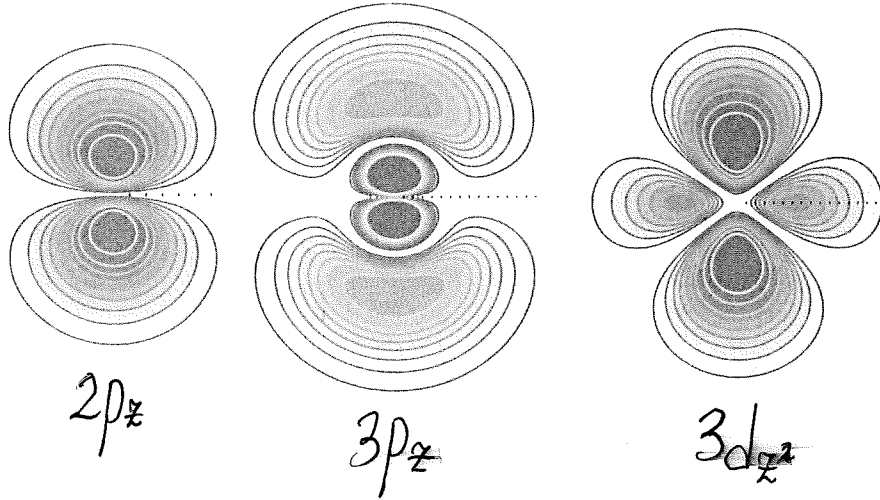


[Same as $2p_z$ ($3p_z$) if "y-axis" is "z-axis"]

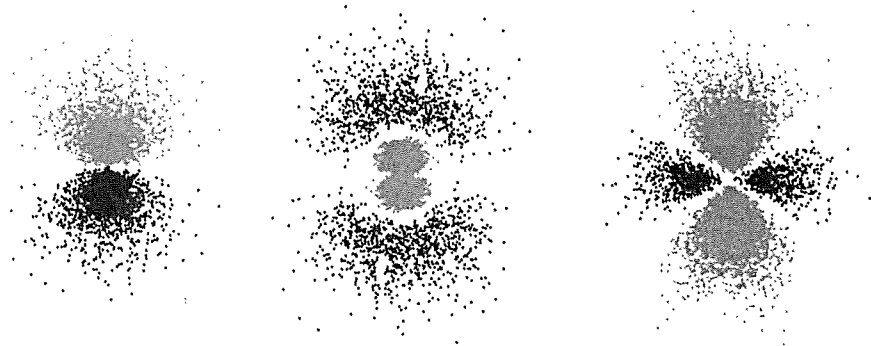
[Figures taken from Engel's "Quantum Chemistry and Spectroscopy"]

(iii) Probability density $|\Psi|^2$

[Take real wavefunctions and square them] (Similar shape)



Contours enclosing 10%, ..., 90%
of probability

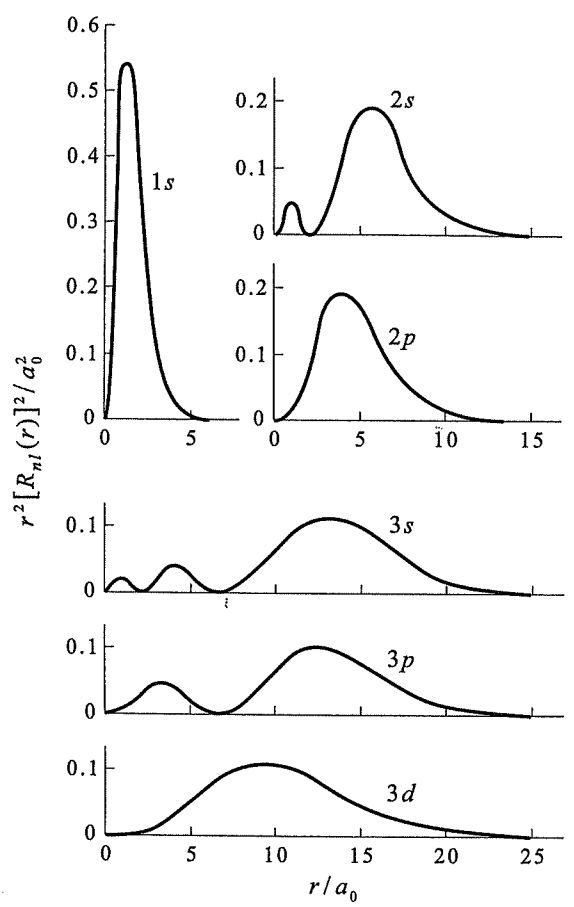


Using dots

Probability density plots in a planar cross section of some hydrogen atomic orbitals. The density of the dots is proportional to the probability of finding the electron in that region.

(iv) How far away is the electron? $P(r) =$ Radial prob. distribution function

$P(r) = r^2 [R_{nl}(r)]^2$ (Washed angular information away)



1s: peaks at $r = a_0$ (Bohr said must be)

QM: Most probable at $r = a_0$ to be at $r = a_0$ (can be elsewhere)

2s: peaks at $r = 5.24 a_0$ [Not Bohr's $4 a_0$]

2p: peaks at $r = 4 a_0$ [Bohr said must be $r = 4 a_0$]

⋮

3d: peaks at $r = 9 a_0$ [Bohr said must be $r = 9 a_0$]

QM: Most probable there (can be elsewhere)