4E : The Quantum Universe

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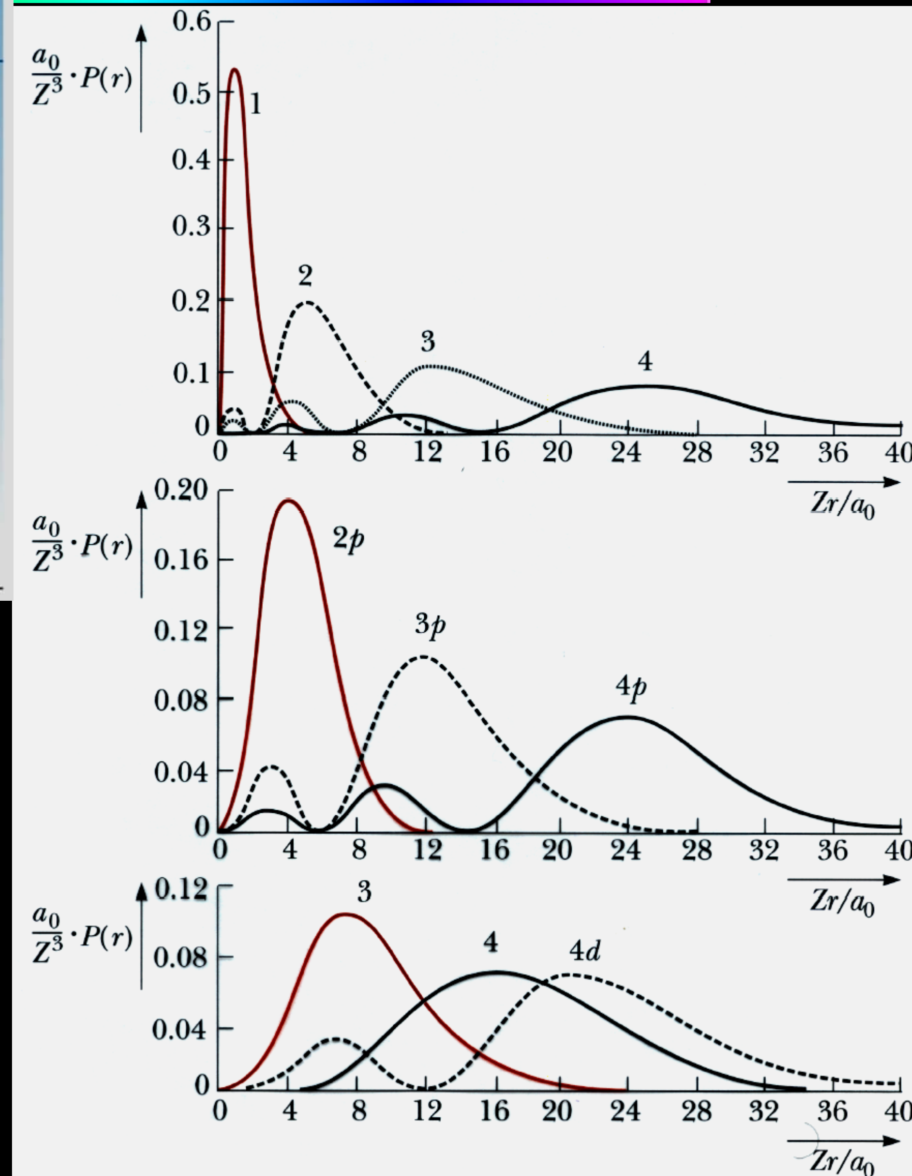
Radial Probability Distribution P(r)= $r^2R(r)$

TABLE 7-2 Radial functions for hydrogen

$n=1$	$l=0$	$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$
$n=2$	$l=0$	$R_{20} = \frac{1}{\sqrt{2a_0^3}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$
	$l=1$	$R_{21} = \frac{1}{2\sqrt{6a_0^3}}\frac{r}{a_0}e^{-r/2a_0}$
$n=3$	$l=0$	$R_{30} = \frac{2}{3\sqrt{3a_0^3}}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$
	$l=1$	$R_{31} = \frac{8}{27\sqrt{6a_0^3}}\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right)e^{-r/3a_0}$
	$l=2$	$R_{32} = \frac{4}{8\sqrt{30a_0^3}}\frac{r^2}{a_0^2}e^{-r/3a_0}$



Because P(r)=r^2R(r); No matter what R(r) is for some n,

The prob. Of finding electron inside the nucleus = 0 !!

Normalized Spherical Harmonics & Structure in H Atom

TABLE 7-1 Spherical harmonics

$l = 0$	$m = 0$	$Y_{00} = \sqrt{\dfrac{1}{4\pi}}$
$l = 1$	$m = 1$	$Y_{11} = -\sqrt{\dfrac{3}{8\pi}} \sin\theta\, e^{i\phi}$
	$m = 0$	$Y_{10} = \sqrt{\dfrac{3}{4\pi}} \cos\theta$
	$m = -1$	$Y_{1-1} = \sqrt{\dfrac{3}{8\pi}} \sin\theta\, e^{-i\phi}$
$l = 2$	$m = 2$	$Y_{22} = \sqrt{\dfrac{15}{32\pi}} \sin^2\theta\, e^{2i\phi}$
	$m = 1$	$Y_{21} = -\sqrt{\dfrac{15}{8\pi}} \sin\theta \cos\theta\, e^{i\phi}$
	$m = 0$	$Y_{20} = \sqrt{\dfrac{5}{16\pi}} (3\cos^2\theta - 1)$
	$m = -1$	$Y_{2-1} = \sqrt{\dfrac{15}{8\pi}} \sin\theta \cos\theta\, e^{-i\phi}$
	$m = -2$	$Y_{2-2} = \sqrt{\dfrac{15}{32\pi}} \sin^2\theta\, e^{-2i\phi}$

Excited States (n>1) of Hydrogen Atom : Birth of Chemistry !

Features of Wavefunction in θ & ϕ :

Consider $n = 2,\ l = 0 \ \Rightarrow \psi_{200} =$ Spherically Symmetric (last slide)

Excited States (3 & each with same E_n) :

ψ_{211}, ψ_{210} , ψ_{21-1} are all 2p states

$$\psi_{211} = R_{21} Y_1^1 = \left(\frac{1}{\pi}\right) \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Z}{8}\right)\left(\frac{r}{a_0}\right) e^{\frac{-Zr}{a_0}} .\sin\theta . e^{i\phi}$$

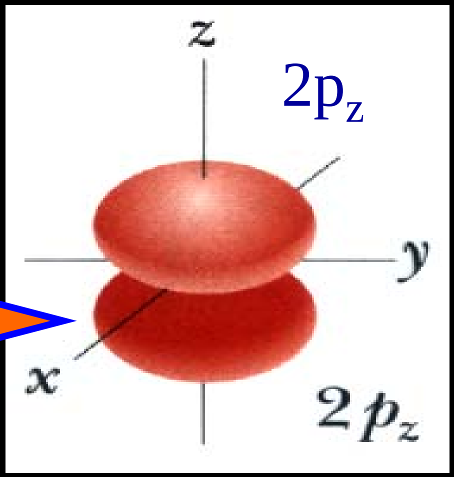
$\boxed{|\psi_{211}|^2 = |\psi^*_{211}\psi_{211}| \ \propto \sin^2\theta}$ Max at $\theta = \frac{\pi}{2}$, min at $\theta = 0$; Symm in ϕ

What about (n=2, ℓ=1,$m_l = 0$)

$\psi_{210} = R_{21}(r)\ Y_1^0(\theta,\phi)$;

$Y_1^0(\theta,\phi) \propto \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$;

Function is max at θ=0, min at $\theta = \frac{\pi}{2}$



We call this $2p_z$ state because of its extent in z

Excited States (n>1) of Hydrogen Atom : Birth of Chemistry !

Remember Principle of Linear Superposition

for the TISE which is basically a simple differential equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi$$

Principle of Linear Superposition $\Rightarrow$ If ψ_1 *and* ψ_2 are sol. of TISE

then a "designer" wavefunction made of linear sum

$\psi' = a\psi_1 + b\psi_2$ is also a sol. of the diff. equation !

To check this, just substitute ψ' in place of ψ

& convince yourself that

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi' + U\psi' = E\psi'}$$

The diversity in Chemistry and Biology DEPENDS

on this superposition rule

Designer Wave Functions: Solutions of S. Eq !

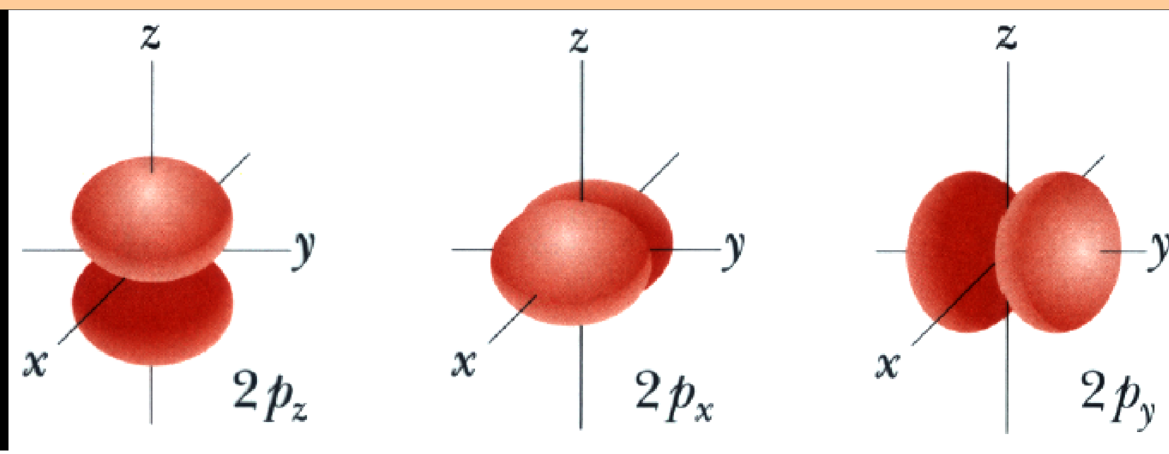
Linear Superposition Principle means allows me to "cook up" wavefunctions

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}\left[\psi_{211} + \psi_{21-1}\right]$$ ......has electron "cloud" oriented along x axis

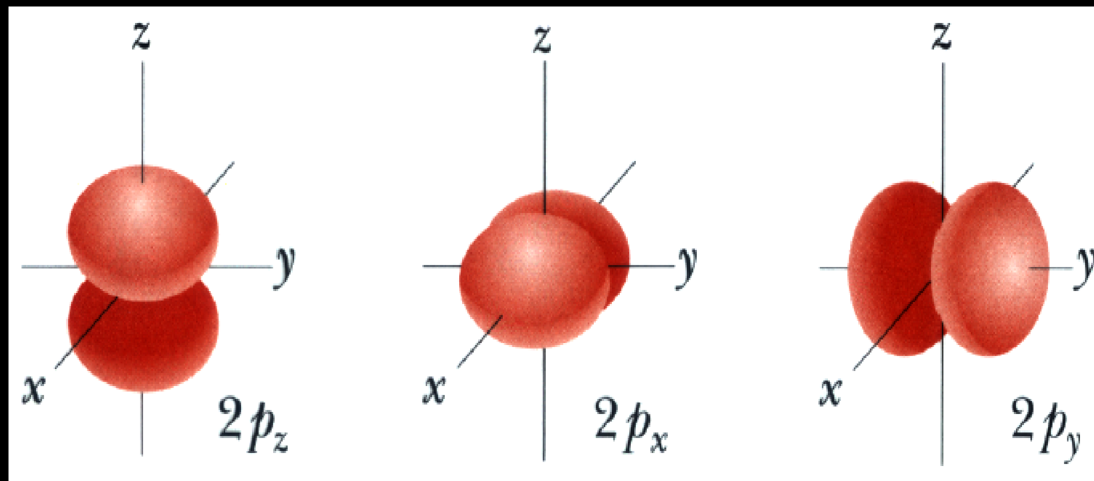
$$\psi_{2p_y} = \frac{1}{\sqrt{2}}\left[\psi_{211} - \psi_{21-1}\right]$$ ......has electron "cloud" oriented along y axis

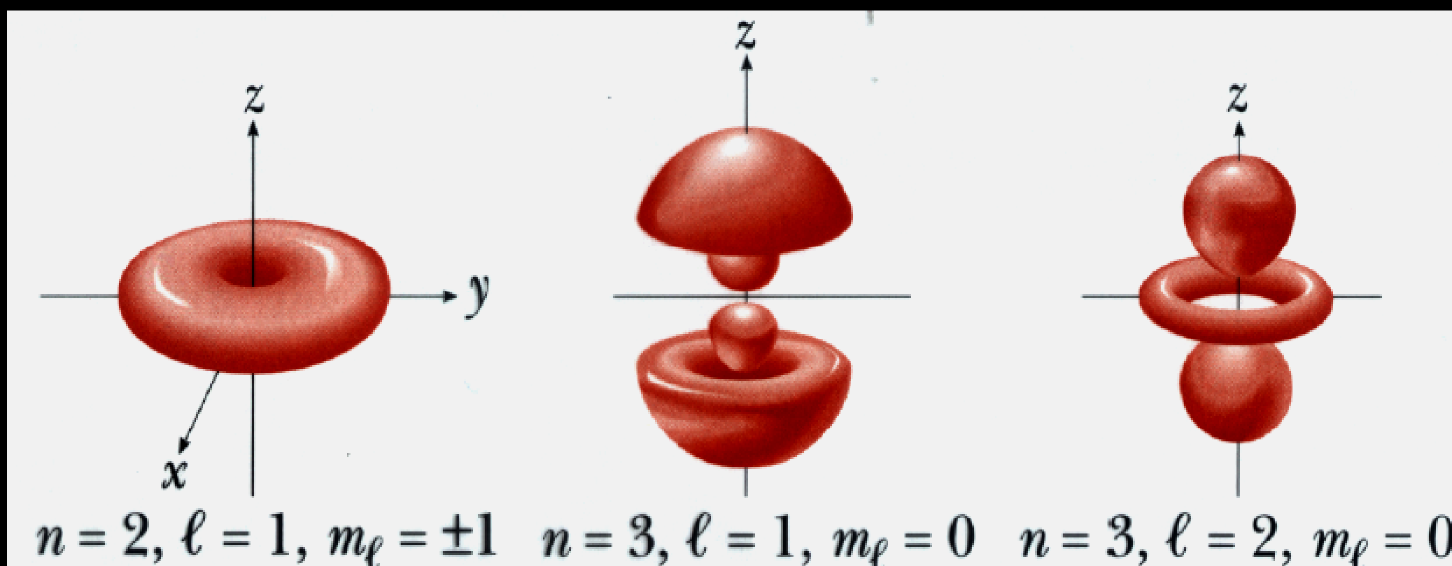
So from 4 solutions $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1} \rightarrow 2s, 2p_x, 2p_y, 2p_z$

Similarly for n=3 states ...and so on ...can get very complicated structure in θ & ϕ.......which I can then mix & match to make electrons "most likely" to be where I want them to be !



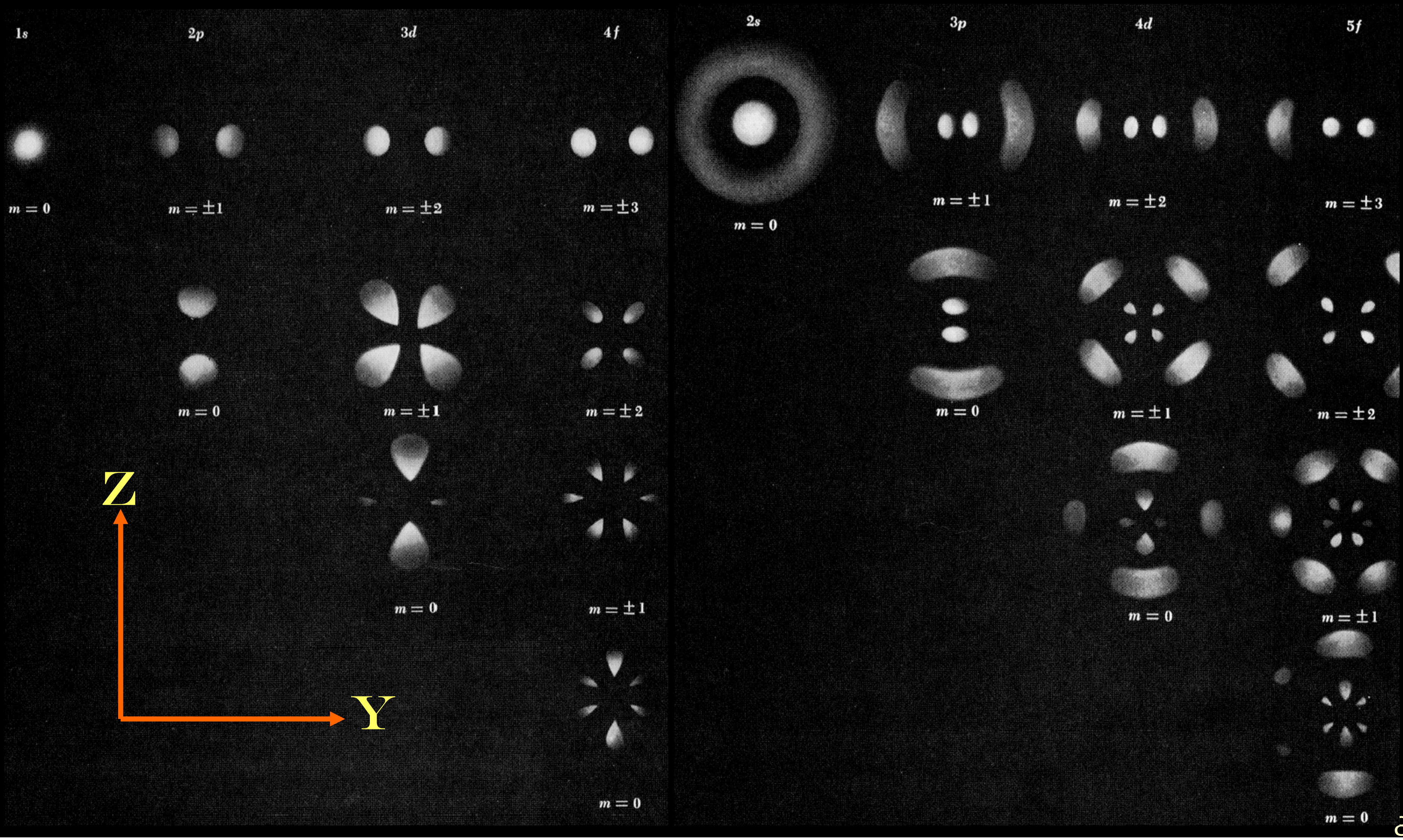
Designer Wave Functions: Solutions of S. Eq !



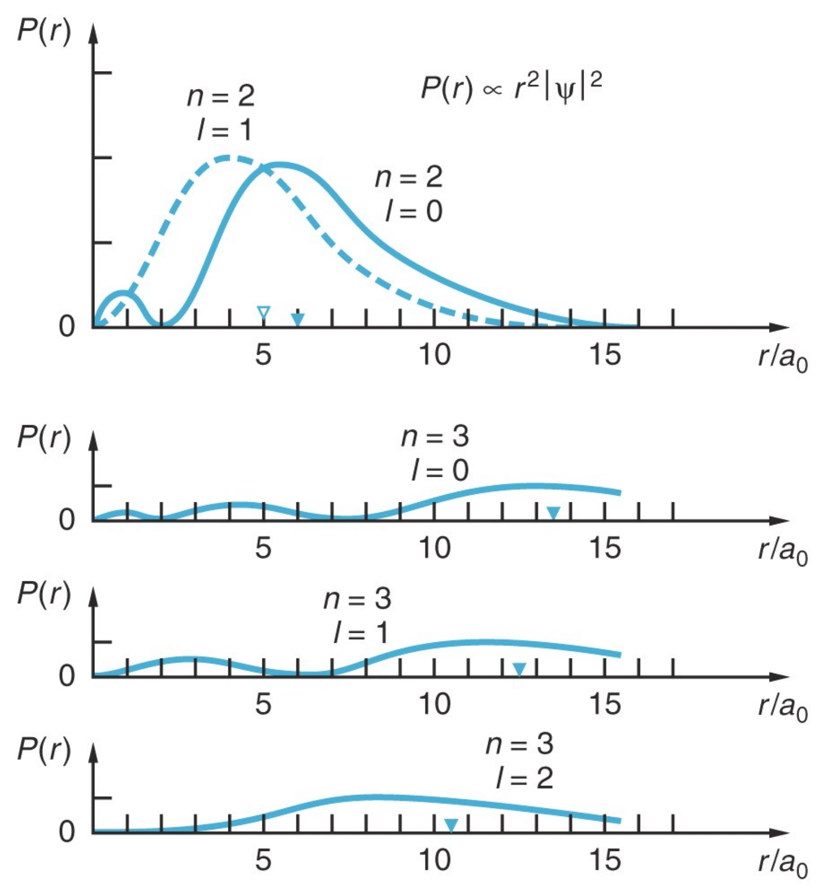


Cross Sectional View of Hydrogen Atom prob. densities in r,θ,ϕ
Birth of Chemistry (Can make Fancy Bonds→ Overlapping electron "clouds")

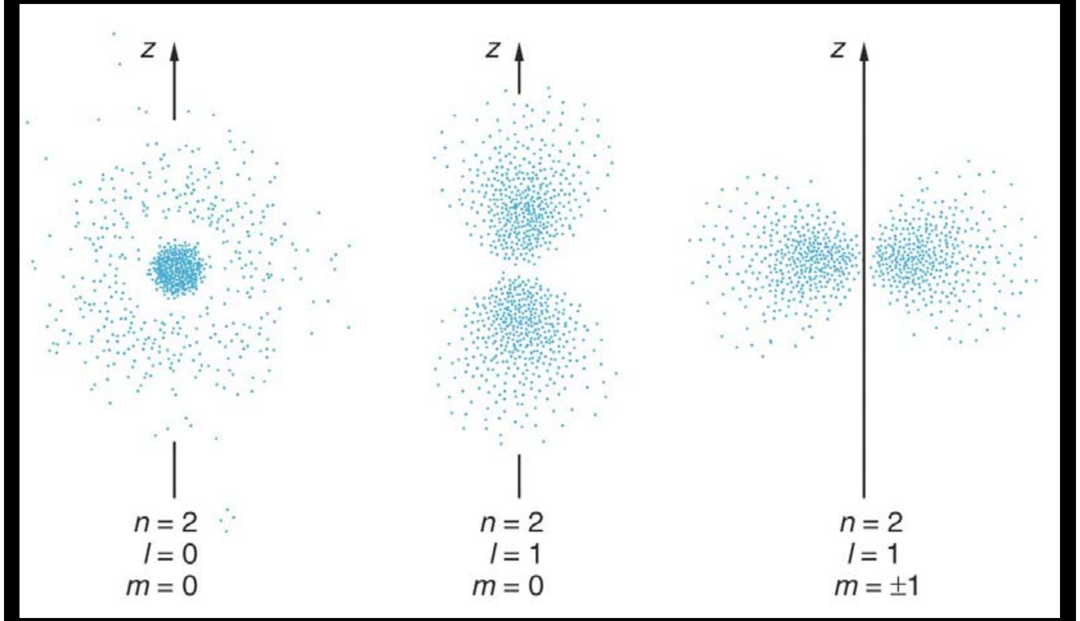
What's the electron "cloud" : Its the Probability Density in r, θ,ϕ space!



More Radial Probabilities P(r) Vs. r/a_0



Net Prob. densities for n=2 states



spherically symmetric

dumbbell

Doughnut (toroid)

Radiative Transitions: An Impromptu Discussion

- Concepts
  - Write and use the wavefunctions which arise as solutions of the time-dependent Schrodinger equation
  - Use concept of linear superposition of time-dependent wavefunctions
  - Calculate expectation value for <x>, when is it time-dependent?

- See slides (posted) from Lecture 27 (See also Modern Physics by Beiser, chapter 6, sections 8-9, page 214. Text available from the E-reserve page as pdf files