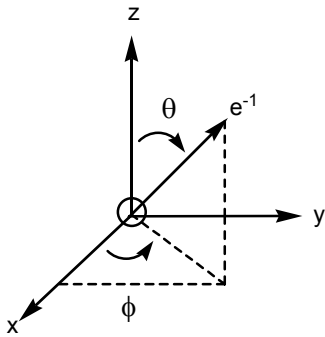


## Atoms – 09 update-- start with single electron: H-atom



3-D problem - free move in x, y, z  
 - easier if **change coord. systems:**  
 Cartesian  $\rightarrow$  Spherical Coordinate  
 $(x, y, z) \rightarrow (r, \theta, \phi)$

Reason:  $V(r) = -Ze^2/|r|$  depend - separation not orientation  
electrostatic potential – basis of chemistry

Note: (if proton fixed at 0,0,0 then  $|r|=x^2+y^2+z^2$ )

$\mathbf{r} = (x_e - x_p)\mathbf{i} + (y_e - y_p)\mathbf{j} + (z_e - z_p)\mathbf{k}$  --vector

$|r| = [(x_e - x_p)^2 + (y_e - y_p)^2 + (z_e - z_p)^2]^{1/2}$  --length (scalar)

Goal – separate variables  $V(r) \rightarrow x,y,z$  mixed  
 – no problem for K.E. – **T already separated**

First step–formal: reduce from 6-coord:  $x_e, y_e, z_e$  &  $x_p, y_p, z_p$   
 to 3-internal coordinates. Eliminate center of mass

whole atom:  $\mathbf{R} = \mathbf{X} + \mathbf{Y} + \mathbf{Z}$   $\mathbf{X} = (m_e x_e + m_p x_p) / (m_e + m_p)$  . . etc.  
 this normalizes the position – correct for mass

for H-atom these are almost equal to:  $x_p, y_p, z_p$

but process is general – move equal mass – issue

other 3 coord: relative  $x = x_e - x_p$  etc. ideal for  $V(r)$

Problem separates,  $V = V(r)$  only depend on internal coord.

$$H\Psi = [-\hbar^2/2M \nabla_R^2 + -\hbar^2/2\mu \nabla_r^2 + V(r)] \Psi(R,r) = E\Psi$$

$$M = m_e + m_p$$

$$\mu = m_e \cdot m_p / (m_e + m_p)$$

$\Psi(R,r) = \Xi(R) \psi(r) \rightarrow$  product wave function separates  
summed  $H$  like before (eg.3-D p.i.b.)

i.e. Operate  $H$  on  $\Psi(R,r)$  and operators pass through  
 $R$  and  $r$  dependent terms,  $\Xi(R)$  and  $\psi(r)$ , to give:

*left side:* *right side =*  $E \{ \Xi(R) \psi(r) \}$

$$\boxed{(-\hbar^2/2M)\psi(r)\nabla_R^2\Xi(R)} \text{ and } \boxed{\Xi(R)[(-\hbar^2/2\mu)\nabla_r^2+V(r)]\psi(r)}$$

so divide through by  $\Psi(R,r) = \Xi(R) \psi(r)$  and results  
 are independent ( $R$  and  $r$ )  $\rightarrow$  sum equal constant,  $E$

R-dependent equation:  $(-\hbar^2/2M)(1/\Xi(R))\nabla_R^2\Xi(R) = E_T$

Motion (T) of whole atom – free particle -not quantized -ignore

r-dependent equation:  $(1/\psi(r))[-\hbar^2/2\mu)\nabla_r^2+V(r)]\psi(r) = E_{\text{int}}$   
relative (internal) coord. here we let  $E = E_T + E_{\text{int}}$

internal equation simplified by conversion:  $x,y,z \rightarrow r,\theta,\phi$

result internal:  $\boxed{H(r)\psi(r) = [(-\hbar^2/2\mu)\nabla_r^2 - Ze^2/r]\psi(r) = E_{\text{int}}\psi(r)}$

(idea – potential only depends on  $r$ ,  
 so other two coordinates,  $\phi,\theta$  –only contribute K.E.)

$$\nabla_{r,\theta,\phi}^2 = 1/r^2\{\partial/\partial r(r^2\partial/\partial r)+[1/\sin\theta]\partial/\partial\theta(\sin\theta\partial/\partial\theta) + [1/\sin^2\theta]\partial^2/\partial\phi^2\}$$

Easy to separate  $\phi$  dependence

set up  $H\psi = E\psi$ , multiply  $r^2\sin^2\theta$ ,  $\phi$  only in 1 term

$$\begin{aligned} [(-\hbar^2/2\mu)\nabla_{r,\theta,\phi}^2 - Ze^2/r] \psi(r,\theta,\phi) = \\ (-\hbar^2/2\mu r^2)\{\partial/\partial r(r^2\partial/\partial r)+ [1/\sin\theta]\partial/\partial\theta(\sin\theta\partial/\partial\theta) + \\ [1/\sin^2\theta]\partial^2/\partial\phi^2\}\psi(r,\theta,\phi) - Ze^2/r \psi(r,\theta,\phi) = E_{\text{int}} \psi(r,\theta,\phi) \end{aligned}$$

$$(-\hbar^2/2\mu) \sin^2\theta \{ \partial/\partial r (r^2 \partial/\partial r) + [1/\sin\theta] \partial/\partial\theta (\sin\theta \partial/\partial\theta) \} \psi(r,\theta,\phi) + \partial^2 \psi(r,\theta,\phi) / \partial \phi^2 - [r^2 \sin^2\theta (Z)e^2/r] \psi(r,\theta,\phi) = r^2 \sin^2\theta E_{\text{int}} \psi(r,\theta,\phi)$$

$$(-\hbar^2/2\mu) \{ \sin^2\theta \partial/\partial r (r^2 \partial/\partial r) + \sin\theta \partial/\partial\theta (\sin\theta \partial/\partial\theta) - r^2 \sin^2\theta (E_{\text{int}} + Ze^2/r) \} \psi(r,\theta,\phi) = - \partial^2 / \partial \phi^2 \psi(r,\theta,\phi)$$

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

$$(-\hbar^2/2\mu) \{ \sin^2\theta \partial/\partial r (r^2 \partial/\partial r) + \sin\theta \partial/\partial\theta (\sin\theta \partial/\partial\theta) - r^2 \sin^2\theta (E_{\text{int}} + Ze^2/r) \} R(r) \Theta(\theta) \Phi(\phi) = - \partial^2 / \partial \phi^2 R(r) \Theta(\theta) \Phi(\phi)$$

Recall  $\partial^2 / \partial \phi^2$  only operate on  $\Phi(\phi)$  part, rest pass through

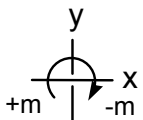
$$\Phi(\phi) (-\hbar^2/2\mu) \{ \sin^2\theta \partial/\partial r (r^2 \partial/\partial r) + \sin\theta \partial/\partial\theta (\sin\theta \partial/\partial\theta) - r^2 \sin^2\theta (E_{\text{int}} + Ze^2/r) \} R(r) \Theta(\theta) = - R(r) \Theta(\theta) \partial^2 / \partial \phi^2 \Phi(\phi)$$

divide through as before by  $\Psi(r,\theta,\phi)$

$$[R(r)\Theta(\theta)]^{-1} (-\hbar^2/2\mu) \{ \sin^2\theta \partial/\partial r (r^2 \partial/\partial r) + \sin\theta \partial/\partial\theta (\sin\theta \partial/\partial\theta) - r^2 \sin^2\theta (E_{\text{int}} + Ze^2/r) \} R(r) \Theta(\theta) = - [\Phi(\phi)]^{-1} \partial^2 / \partial \phi^2 \Phi(\phi) = \text{const.}$$

right side (red) independent of left side, so must be constant

a) Let  $\Phi$  part equal constant,  $m^2$ :  $\partial^2 / \partial \phi^2 \Phi(\phi) = -m^2 \Phi(\phi)$



rotation about z-axis

$$\Phi(\phi) = e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots$$

b) Can similarly separate  $\Theta(\theta) \rightarrow$  *but arithmetic messier*  
 1<sup>st</sup> divide through by  $\sin^2\theta$  (separate r and  $\theta$  terms)

$$[\mathbf{R}(r)\Theta(\theta)]^{-1}(-\hbar^2/2\mu)\{ \partial/\partial r(r^2\partial/\partial r)+(\sin\theta)^{-1}\partial/\partial\theta(\sin\theta \partial/\partial\theta) - r^2(E_{\text{int}} + Ze^2/r)\} \mathbf{R}(r)\Theta(\theta) = m^2/\sin^2\theta$$

Note 1<sup>st</sup> and 3<sup>rd</sup> terms have r but middle only  $\theta$ , separates

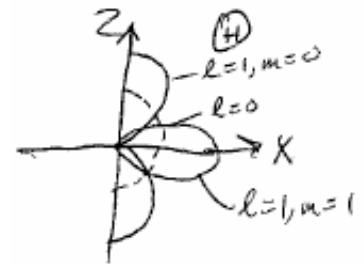
$$[\Theta(\theta)]^{-1}(-\hbar^2/2\mu)\{ (\sin\theta)^{-1}\partial/\partial\theta(\sin\theta \partial/\partial\theta)-m^2/\sin^2\theta\}\Theta(\theta) = -[\mathbf{R}(r)]^{-1}(-\hbar^2/2\mu)\{ \partial/\partial r(r^2\partial/\partial r) r^2 -(E_{\text{int}} + Ze^2/r)\} \mathbf{R}(r) = \text{const.}$$

Resulting equation:

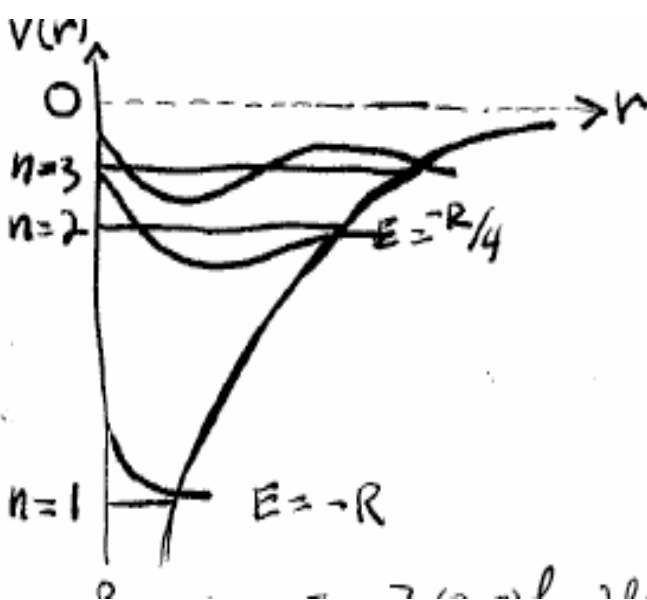
$$(-\hbar^2/2\mu)\{ (\sin\theta)^{-1}\partial/\partial\theta(\sin\theta \partial/\partial\theta)-m^2/\sin^2\theta\}\Theta(\theta) = l(l+1) \Theta(\theta)$$

LeGendre polynomial:  $\Theta_{lm}(\theta) = P_\ell^{m}(\cos \theta) \quad \ell = 0, 1, 2, \dots$

$\ell = 0$	$-\sqrt{2}/2$
$\ell = 1 \quad m = 0$	$-(3/2)^{1/2} \cos \theta$
$\ell = 1 \quad m = \pm 1$	$-(3/4)^{1/2} \sin \theta$
$\ell = 2 \quad m = 0$	$-(5/8)^{1/2} (3 \cos^2\theta - 1)$
$\ell = 2 \quad m = \pm 1$	$-(15/4)^{1/2} (\sin \theta \cos \theta)$
$\ell = 2 \quad m = \pm 2$	$-(15/16)^{1/2} (\sin^2\theta) \dots$



c) Radial function messier yet but must fit B.C.



$r \rightarrow \infty \Rightarrow R_{n\ell}(r) \rightarrow 0$   
 (must be integrable)  
 exponential decay,  
 penetrate potential  
 $\sim e^{-\alpha r}$  damp (r always +)

Must be orthogonal  
 this works when fct.  
 oscillate (wave-like)  
 power series will do

## Associated LaGuerre Polynomial

$$R_{n\ell} = [\text{const}] (2\sigma/n)^\ell L_{n+\ell}^{2\ell+1} (2\sigma/n)e^{-\sigma/n} \quad \sigma = Zr/a_0$$

$$n = 1, 2, 3, \dots \quad \ell = 0, 1, 2, \dots n-1, \quad \ell \geq |m|$$

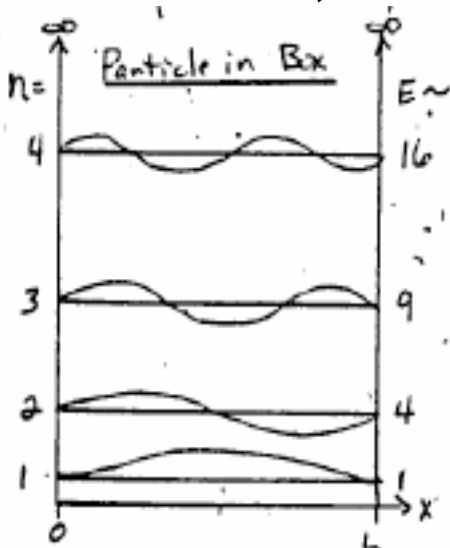
$n = 1, \ell = 0$	$\sim e^{-\sigma}$
$n = 2 \quad \ell = 0$	$\sim (2 - \sigma)e^{-\sigma/2}$
$n = 2 \quad \ell = 1$	$\sim \sigma e^{-\sigma/2}$
$n = 3 \quad \ell = 0$	$\sim (1 - 2\sigma/3 + 2\sigma^2/27)e^{-\sigma/3}$
$n = 3 \quad \ell = 1$	$\sim (\sigma - \sigma^2/6)e^{-\sigma/3}$
$n = 3 \quad \ell = 2$	$\sim \sigma^2 e^{-\sigma/3} \dots$

Note:  $n$  restricts  $\ell$  ( $\leq n-1$ ) and  $\ell$  restricts  $|m|$  ( $\leq \ell$ )

### Comparison of potentials

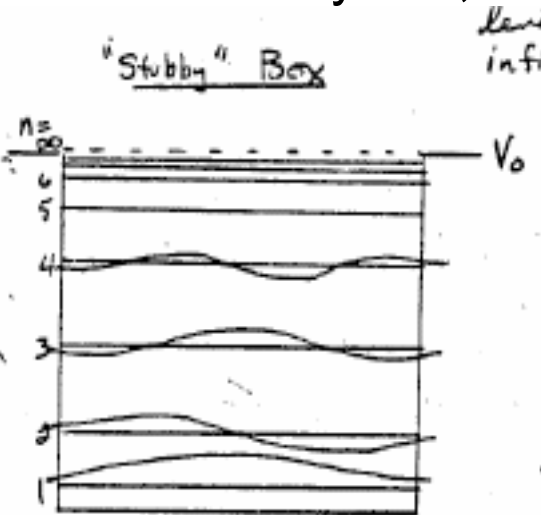
- when potential not infinite, **levels collapse**,
- when sides not infinite and vertical  
**w/f penetrates potential wall**

Particle in box;



E-levels expand  
 $\Delta E \sim n$

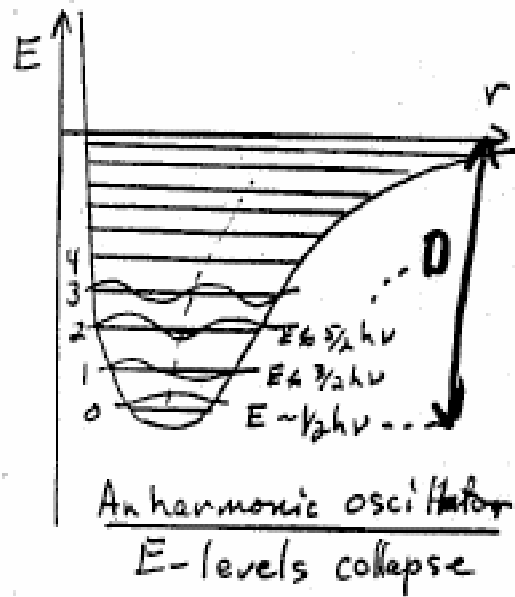
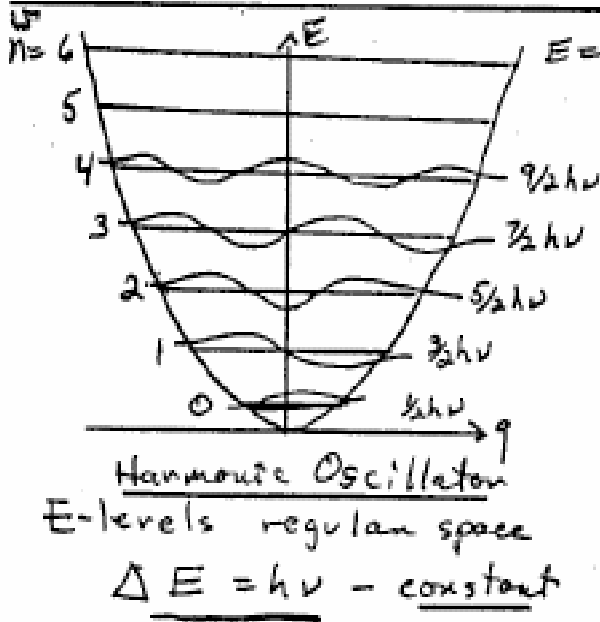
Stubby box;



At top, E-levels collapse

Harmonic oscillator;

Anharmonic oscillator



For finite potential, levels collapse, wavefct penetrate wall

H-atom

Solutions drawn are for  $\ell = 0$

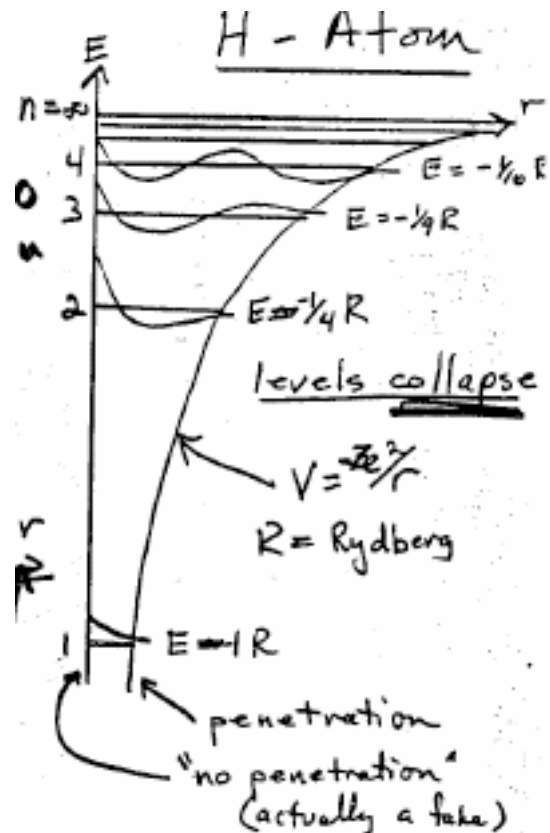
higher  $\ell$ , less nodes

If rotate this around

$r = 0$ , get a symmetric well and shapes look a little like harmonic oscillator shapes

since potential "bends over,"  $V=0$  at  $r=\infty$ , get collapse of Levels as  $n \rightarrow \infty$

Energy vary with nodes and curvature as before



These functions can be combined

$$\psi(r,\theta,\phi) = R_{n\ell}(r) \Theta_{\ell}^{|m|}(\theta) \Phi_m(\phi)$$

Note: only  $R_{n\ell}$  depend on  $r$  as does  $V(r)$

Energy will not depend on  $\theta, \phi$  for H-atom

Often separate as  $Y_{\ell m}(\theta, \phi) = \Theta_{\ell}^{|m|}(\theta) \Phi_m(\phi)$

$\Rightarrow$  these are eigenfunctions of Angular Momentum

recall :  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ ,  $L^2 \sim -\hbar^2 \nabla_r^2$ ,  $L_z = xp_y - yp_x$ ,  $L_z = -i\hbar \partial/\partial \phi$

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

$$L_z Y_{\ell m}(\theta, \phi) = m\hbar Y_{\ell m}$$

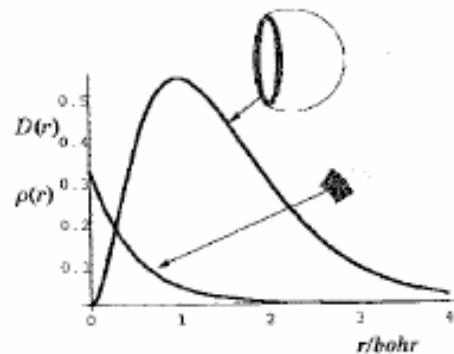
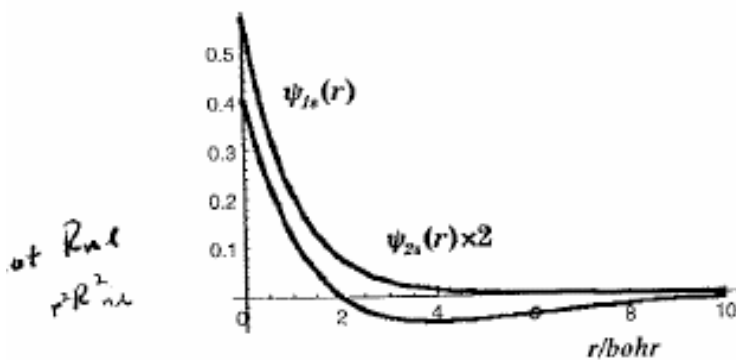
This is source of familiar orbitals,  $\ell = 0, 1, 2, 3, \dots$  or s, p, d, f

Solving  $R_{n\ell}$  equation

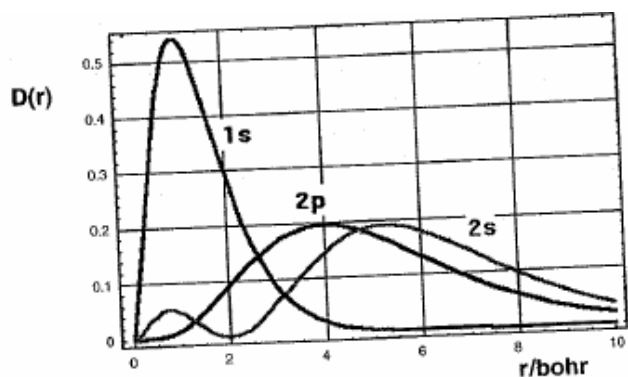
$$E_n = -Z^2 e^2 \mu / 2\hbar^2 n^2$$

$\rightarrow$  exactly Bohr solution (must be, since works)

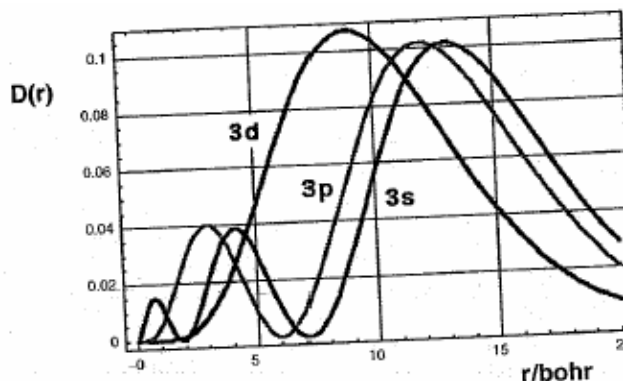
<b>Familiar:</b>	$n = 1$	$\ell = 0$	$m = 0$	– 1s
	$n = 2$	$\ell = 0$	$m = 0$	– 2s
		$\ell = 1$	$m = 0, \pm 1$	– 2p (2p <sub>0</sub> +2p <sub><math>\pm 1</math></sub> )
	$n = 3$	$\ell = 0$	$m = 0$	– 3s
		$\ell = 1$	$m = 0, \pm 1$	– 3p
		$\ell = 2$	$m = 0, \pm 1, \pm 2$	– 3d (3d <sub>0</sub> , 3d <sub><math>\pm 1</math></sub> , 3d <sub><math>\pm 2</math></sub> )



Note: 1s decays, 2s has node  $\rightarrow$  (2- $\sigma$ ) term, 2p starts at 0



Note: 2s node makes dip in probability ( $e^-$  density)



Note: # radial nodes (in  $R_{n\ell}$ ) decrease with  $\ell$ , i.e. # =  $n - \ell - 1$

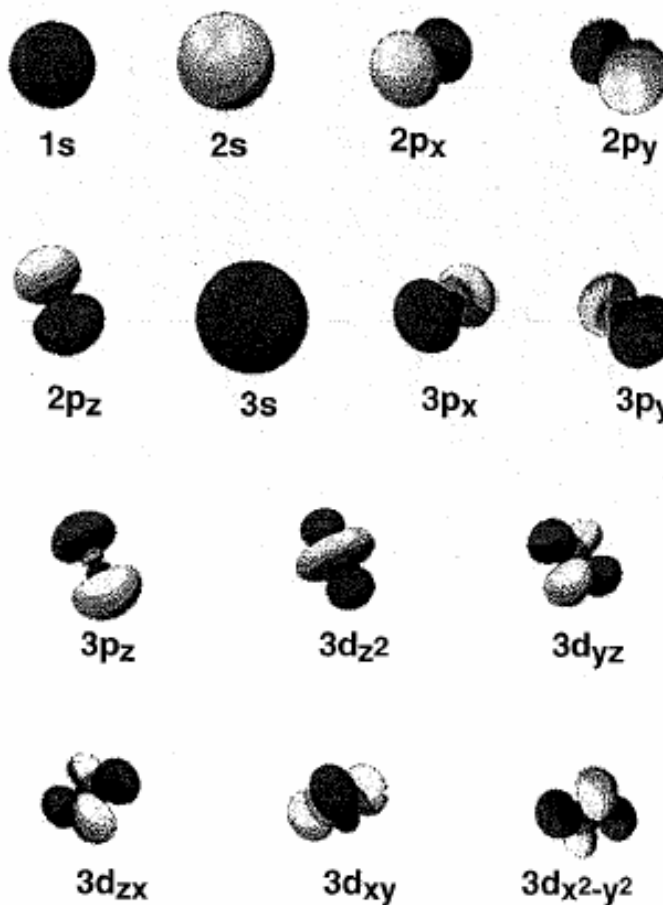
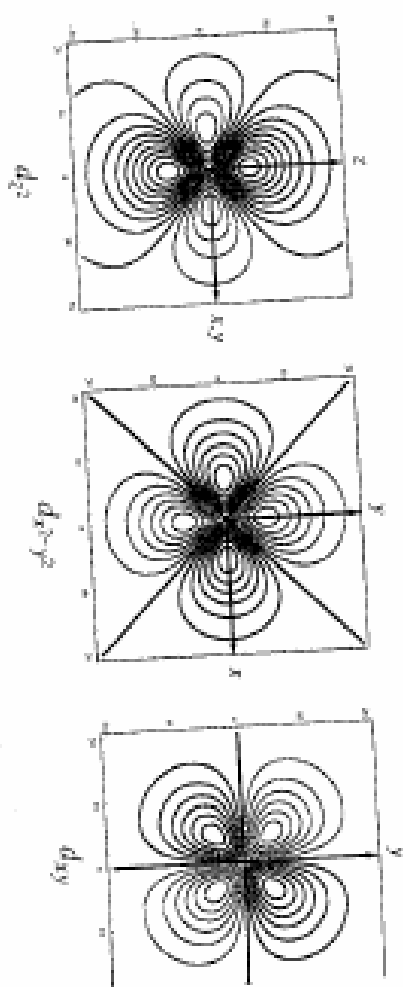


Figure 7.10 ► Hydrogenic atomic orbitals.

Angular functions have no radial value --> just surface, combine with radial function to get magnitude or  $e^-$  density, Best represented as a contour map or probability surface

Real orbitals, take linear combinations of  $\pm m$  values, eliminate  $i$  dependent terms, get  $x, y, z$  functions

Cartesian form:  $e^{im\phi} + e^{-im\phi} = \cos\phi + i\sin\phi + \cos\phi - i\sin\phi \sim x$

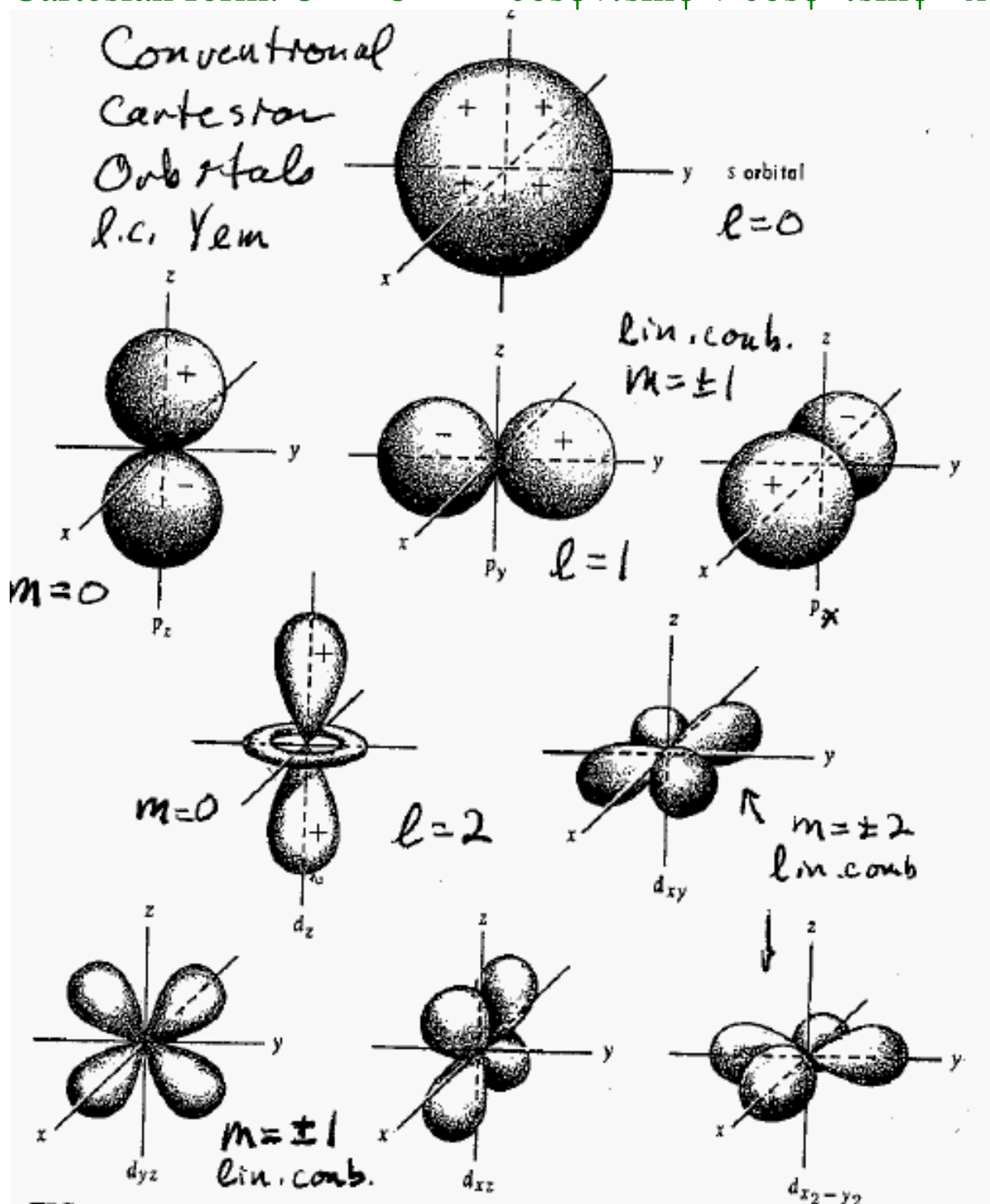


FIGURE 2-11 Angular portions of  $\psi$ . Note that since  $f_{lm}$  is independent of  $n$ , all  $s$  orbitals ( $1s, 2s, \dots$ ) have the same shape, all  $p$  orbitals ( $2p, 3p, \dots$ ) have the same shape, etc., and differ only in size.

**TABLE 7.1 ▶ Real Hydrogenic Orbitals in Atomic Units**

$$\psi_{1s} = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr}$$

$$\psi_{2s} = \frac{Z^{3/2}}{2\sqrt{2\pi}} \left(1 - \frac{Zr}{2}\right) e^{-Zr/2}$$

$$\psi_{2p_z} = \frac{Z^{5/2}}{4\sqrt{2\pi}} z e^{-Zr/2} \quad \psi_{2p_x}, \psi_{2p_y} \text{ analogous}$$

$$\psi_{3s} = \frac{Z^{3/2}}{81\sqrt{3\pi}} (27 - 18Zr + 2Z^2r^2) e^{-Zr/3}$$

$$\psi_{3p_z} = \frac{\sqrt{2} Z^{5/2}}{81\sqrt{\pi}} (6 - Zr) z e^{-Zr/3} \quad \psi_{3p_x}, \psi_{3p_y} \text{ analogous}$$

$$\psi_{3d_{z^2}} = \frac{Z^{7/2}}{81\sqrt{6\pi}} (3z^2 - r^2) e^{-Zr/3}$$

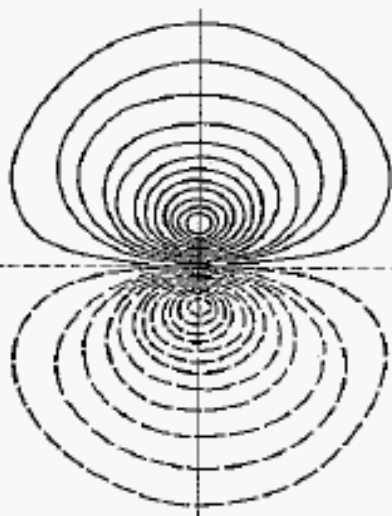
$$\psi_{3d_{zx}} = \frac{\sqrt{2} Z^{7/2}}{81\sqrt{\pi}} zx e^{-Zr/3} \quad \psi_{3d_{yz}}, \psi_{3d_{xy}} \text{ analogous}$$

$$\psi_{3d_{x^2-y^2}} = \frac{Z^{7/2}}{81\sqrt{\pi}} (x^2 - y^2) e^{-Zr/3}$$

# Contour Plots

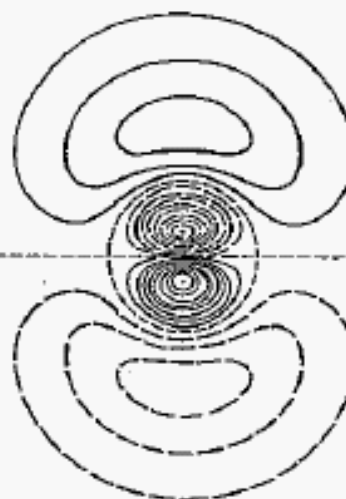
Shapes of Canonical AOs

radial node effect on p-orbital <sup>27</sup>



$n=2$

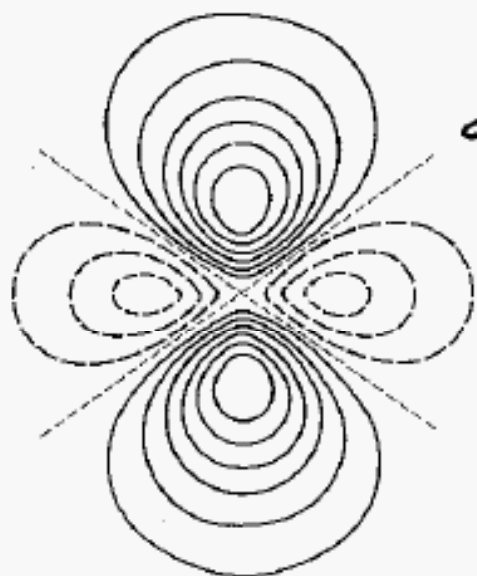
$(2p_0) = (2p_z)$   
 $(2p_1') = (2p_x)$   
 $(2p_1'') = (2p_y)$



$n=3$

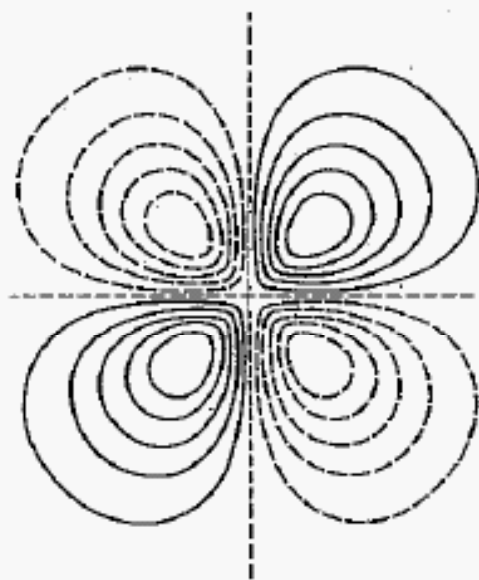
$(3p_0) = (3p_z)$   
 $(3p_1') = (3p_x)$   
 $(3p_1'') = (3p_y)$

odd under  
inversion



even  
d-orb.

$(3d_0) = (3d_{z^2} - r^2)$



$(3d_1') = (3d_{xz}), (3d_1'') = (3d_{yz})$   
 $(3d_2') = (3d_{x^2 - y^2}), (3d_2'') = (3d_{xy})$

**Radial function effect** represented by contours, each line represents lower e- density – sign change makes node between lobes or radially (e.g. see top, 3p vs. 2p)

Linear comb. of degenerate orbitals also solutions  
**H-atom** – show effect of mixing s and p orbitals:

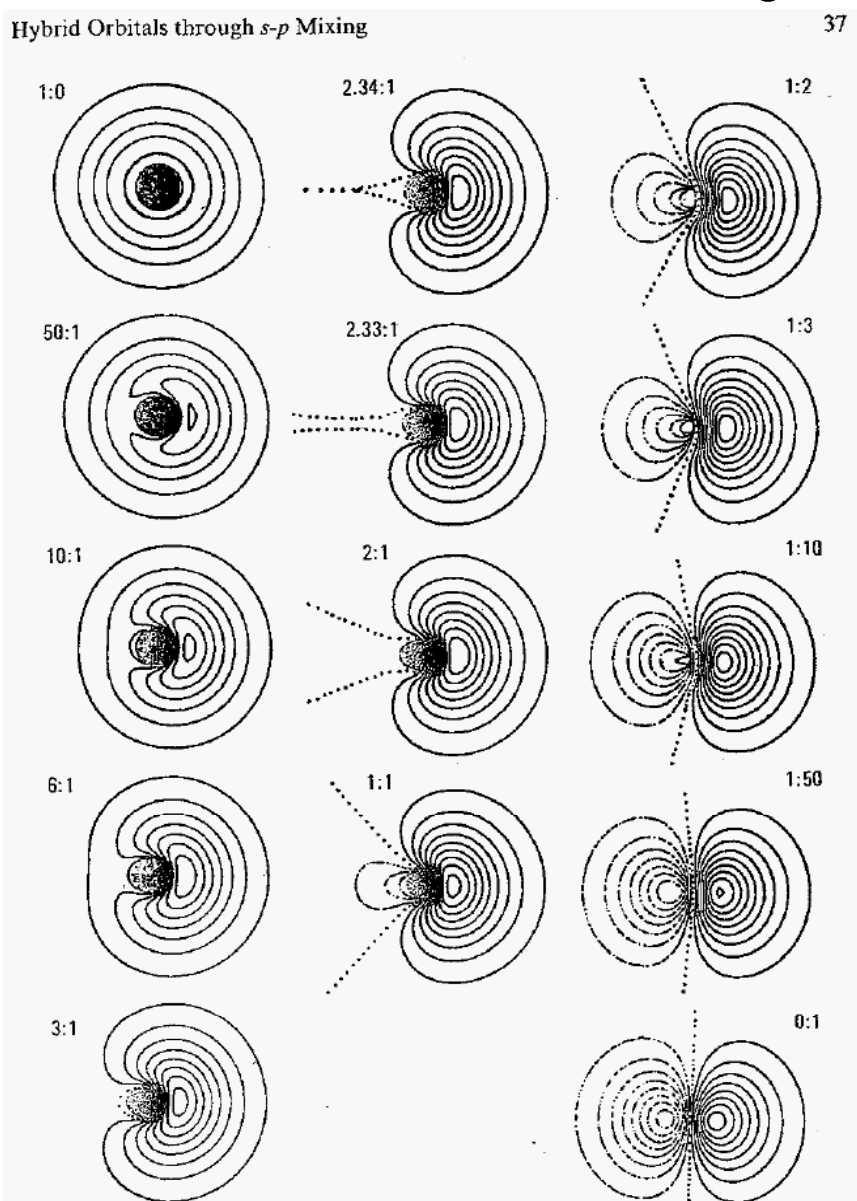


Figure 2-11. Contour plots ( $\psi = \text{constant}$ ) of mixtures of (*s*) and (*p*) atomic orbitals showing the ratios  $A^2 : B^2$ . In these plots solid, dotted, and dashed lines denote regions where  $\psi > 0$ ,  $\psi = 0$ , and  $\psi < 0$ , respectively. The absolute value of the smallest value of  $\psi$  is  $0.05 \text{ Bohr}^{-3/2}$  and  $\Delta\psi$  has the same value. (Courtesy of Dr. K. Ruedenberg.)

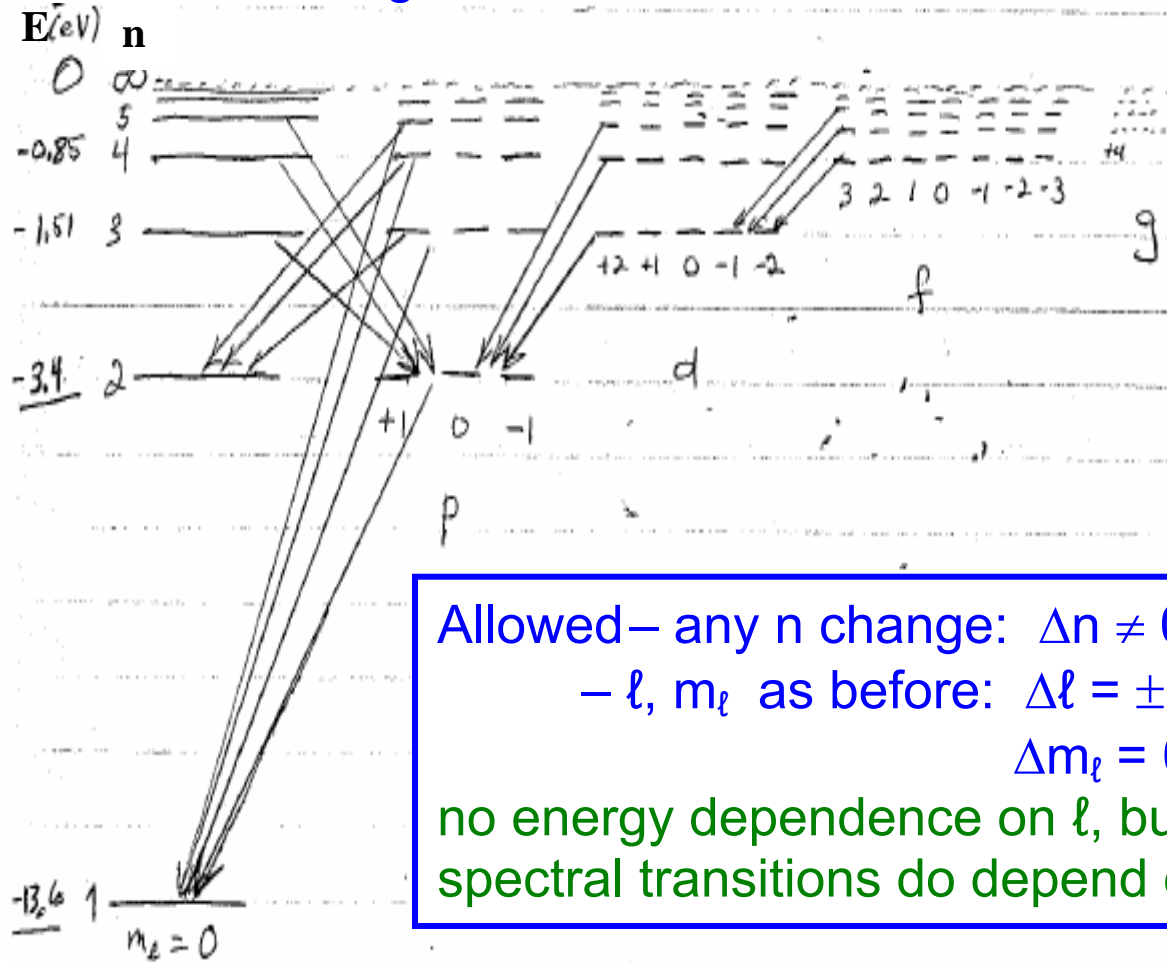
**Hybrids** – linear comb. of s and p – **orient for bonding**

$sp \rightarrow 2$  orbitals / opposite direction,  $(s \pm p)$  are  $180^\circ$

$sp^2 \rightarrow 3$  orbitals / in plane /  $120^\circ$  apart

$sp^3 \rightarrow 4$  orbitals / 4 vertices of tetrahedron ( $109^\circ$ )

## Energy level diagram – H-atom



Spectral transitions match Balmer series

but also must account for  $\Theta, \Phi$  functions

**Allowed**  $\rightarrow$  selection rules (see box)

$n \rightarrow n' = 1$  – **Lyman** must start p orbital  $\rightarrow$  end 1s

$n \rightarrow n' = 2$  – **Balmer** must start d or s orbital  $\rightarrow$  end 2p  
 or start in p orbital  $\rightarrow$  end in 2s etc.

Test with Zeeman effect –  $m_\ell \beta H = E'$  add E from field