V. From Atoms to Solids

- Atoms → Molecules → Solids
- How atoms form bonds (useful ideas in understanding solids)
- Ideas in Handling multi-electron atoms (carried over to solids)
- From LCAO (linear combinations of atomic orbitals) to TBM (Tight-Binding Model)
- What is hybridization? (sp, sp^2, sp^3)
- ETBM (Empirical TBM)
- Wannier Functions (localized basis formed by combining Bloch functions)

A. Pictures of the Simplest Atomic States

- Hydrogen atom is the Only exactly solvable QM atomic problem!
  - 1-electron problem (that's why we want to reduce solid's problem to 1-electron problems)
  - H-atom $\psi_{n\ell m_\ell}(\vec{r}) = \psi_{n\ell m_\ell}(r,\theta,\phi)$ [No spin consideration]

$$= \underbrace{R_{n\ell}(r)} \cdot \underbrace{Y_{\ell m_\ell}(\theta,\phi)} \qquad (1)$$

associated Laguerre Polynomials

spherical harmonics (here for all $U(r)$) gives ANGULAR (directional) dependence (general)

{ specific to H-atom (not general)
{ related to how far atomic states reach out from nucleus (general)

$$P(r) \sim r^2 |R_{n\ell}(r)|^2$$

H-atom states

$$\psi_{nlm_l}(r;\theta,\phi) = R_{nl}(r)\cdot Y_{lm_l}(\theta,\phi) \quad \text{[in spherical coordinates]}$$

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

$U(r) \Rightarrow \underbrace{\Phi(\phi)\quad\Theta(\theta)}_{Y_{lm_l}(\theta,\phi)} \qquad \underbrace{R(r)}_{R_{nl}(r)\ \left[\text{due to } U = \frac{-e^2}{4\pi\varepsilon_0 r}\right]} \qquad \underbrace{\psi(r,\theta,\phi)}_{\psi_{nlm_l}(r,\theta,\phi)}$

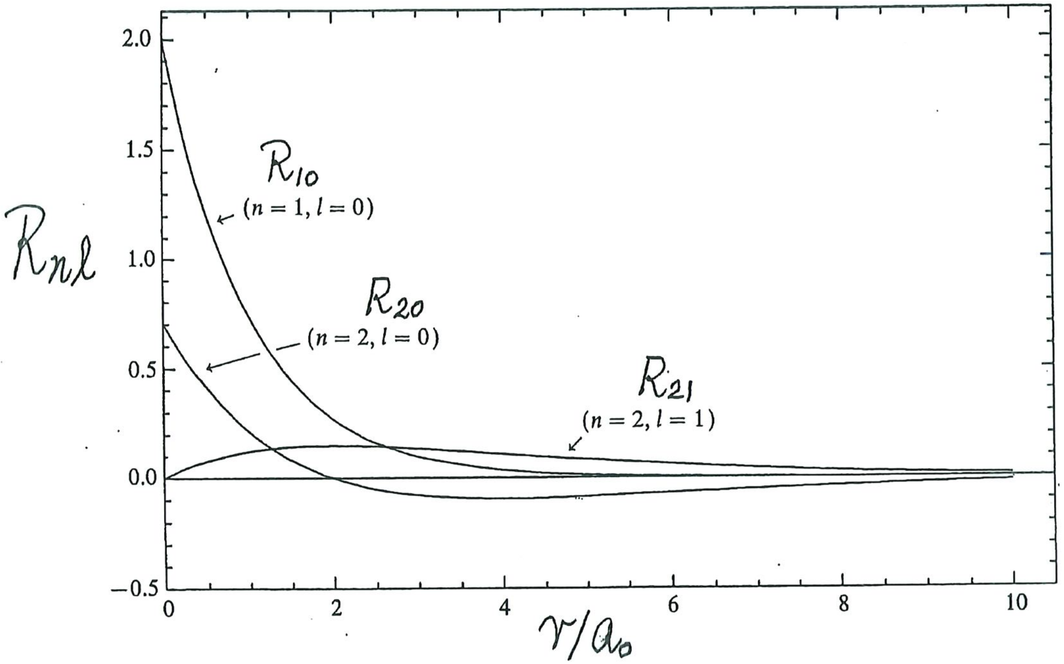
Bohr radius: $a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2} = 5.292\times10^{-11}\,\text{m} = 0.5292\,\text{Å}$ appears naturally (roughly "half Angström")

- $\underbrace{\text{s-state}}_{l=0,\ m_l=0}$ has no directional dependence

$Y_{00}(\theta,\phi)$ = constant (no θ, ϕ dependence)

with $R(r) \sim e^{-r/a_B}$ for 1s ; $\sim e^{-r/2a_B}$ (with wiggling in r at small r) for 2s;

$\sim e^{-r/3a_0}$ (with more wiggling in r at small r) for 3s; ...

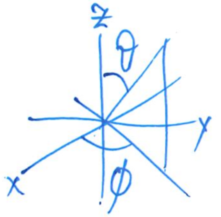


- Bohr radius sets the length scale of atomic states (atomic orbitals)
- ~Å
- also sets the length scale in molecules, solids (lattice constant)
- (see figure) R_{20}, R_{21} extend farther in r than R_{10}

Visualizing $\psi_{100}(r,\theta,\phi)$ (1s)

Only directional information

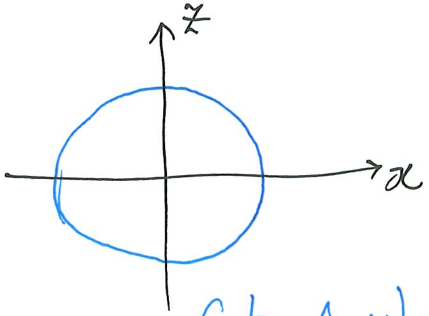
$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$



Pick any (θ,ϕ), make a "dot" of "length" $\frac{1}{\sqrt{4\pi}}$ from origin

⇒ It is a spherical surface

(This is the Polar Plot of $Y_{00}(\theta,\phi)$)



OR x-y OR y-z

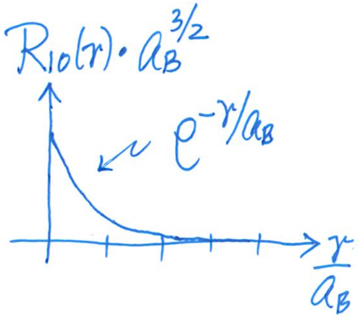
Cut of spherical surface at y=0

(This is why s-state is like a ball)

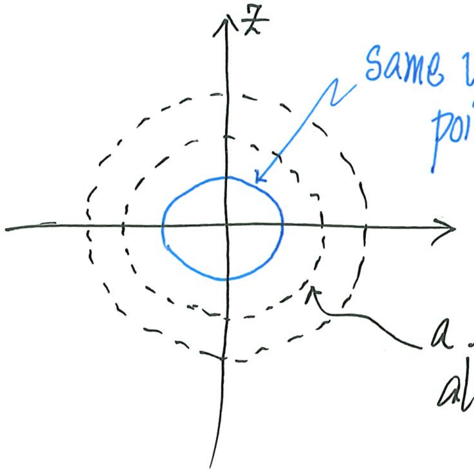
$$\psi_{100}(\vec{r}) = \frac{1}{a_B^{3/2}}\frac{1}{\sqrt{\pi}}\, e^{-r/a_0} \cdot \left(\frac{1}{\sqrt{4\pi}}\right) \leftarrow Y_{00}(\theta,\phi)$$

With radial information

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



Contour Plot

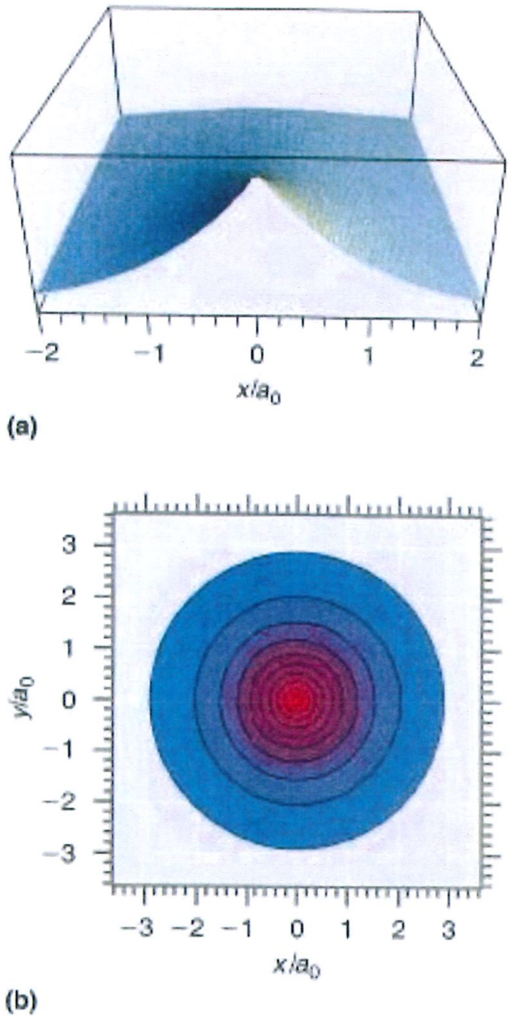


same value of R_{10} for all points on contour

a lower value for all points on contour

Formally, need 4D plots

Side view, add third axis for values of ψ_{100}

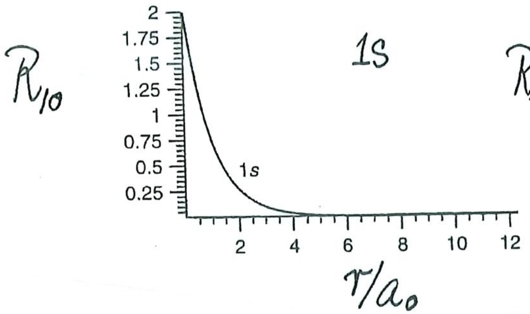


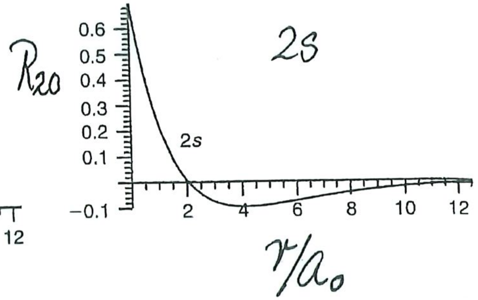
(a) 3D perspective and **(b)** contour plot of $\psi_{100}(r)$. Red and blue contours correspond to the most positive and least positive values of the wave function, respectively.

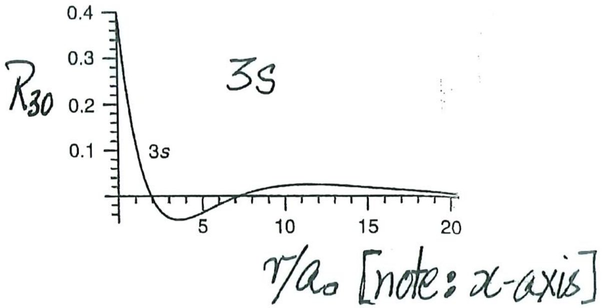
(indicating wavefunction is decaying from nucleus)

Engel, Quantum Chemistry and Spectroscopy

Contour Plots







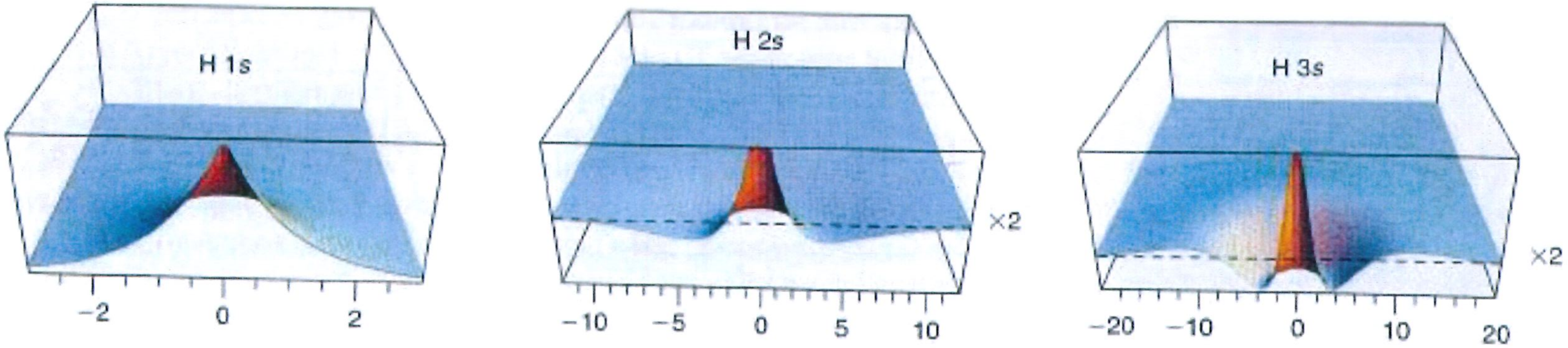
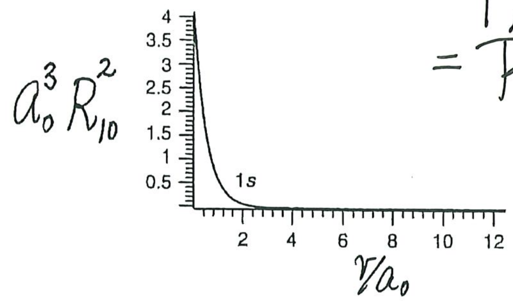


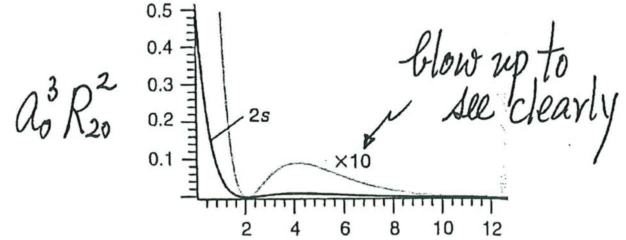
FIGURE 9.5

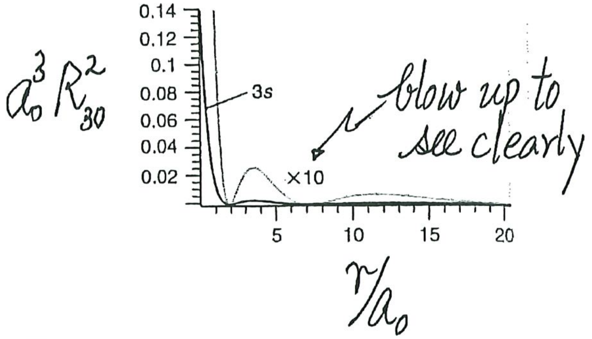
Three-dimensional perspective plots of the 1*s*, 2*s*, and 3*s* orbitals. The dashed lines indicate the zero of amplitude for the wave functions. The "×2" refers to the fact that the amplitude of the wave function has been multiplied by 2 to make the subsidiary maxima apparent. The horizontal axis shows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

From Engel

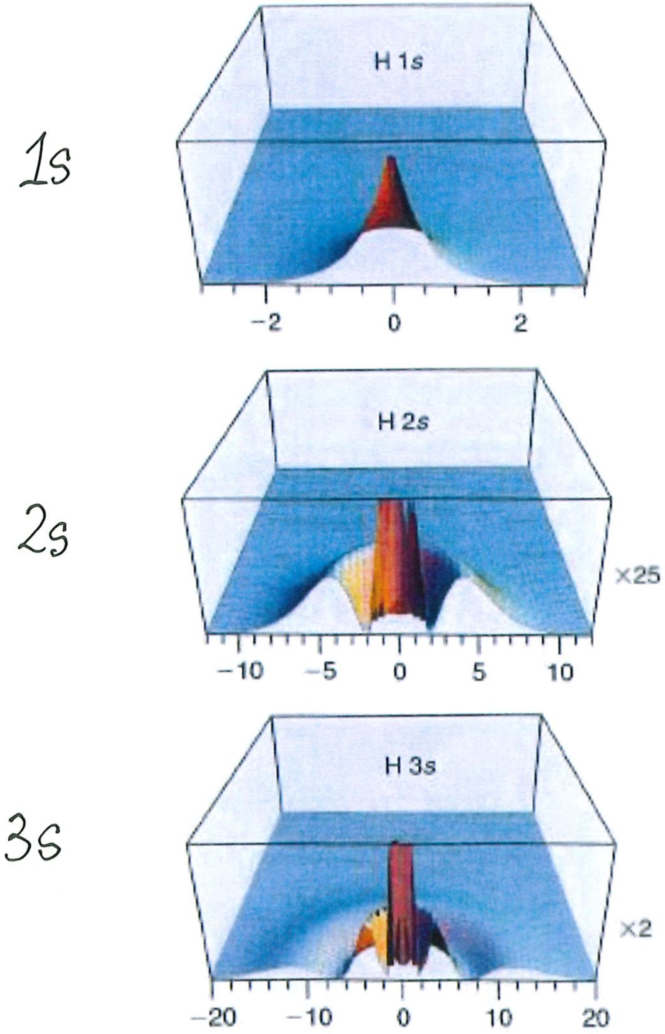
Born: Should study $|\psi|^2$ = Probability Density







<u>Bonus</u>: Note that 2s has a part near $r \approx 0$ [quite close to nucleus]

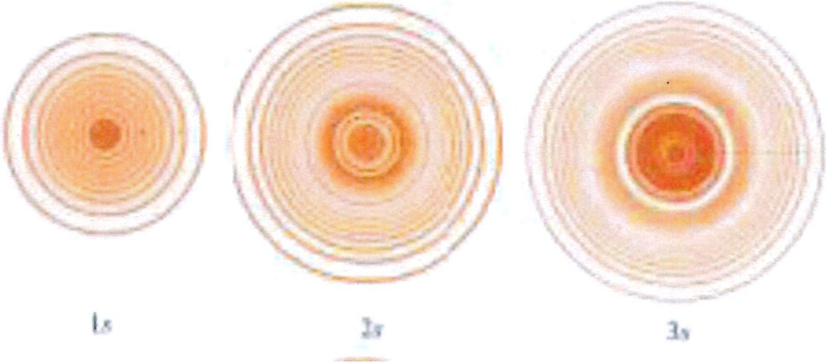


From Engel

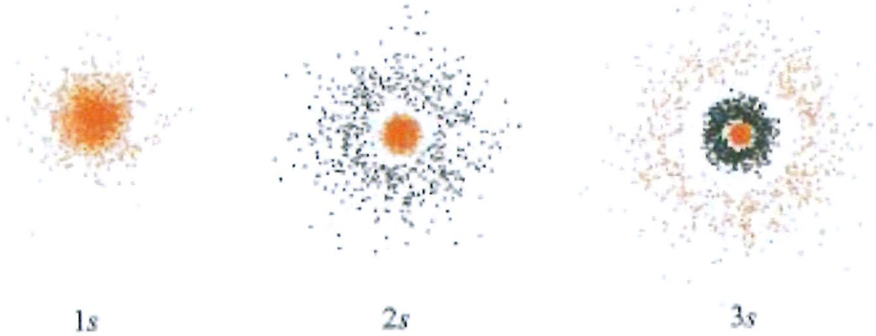
3D perspective plots of the square of the wave functions for the orbitals indicated. The numbers on the axes are in units of a_0. The "×25" refers to the fact that the amplitude of the wave function has been multiplied by 25 to make the subsidiary maxima apparent.

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

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



Wavefunction squared
(probability density)
Contour plots (Contours enclosing 10%, 20%, ..., 90% probability)



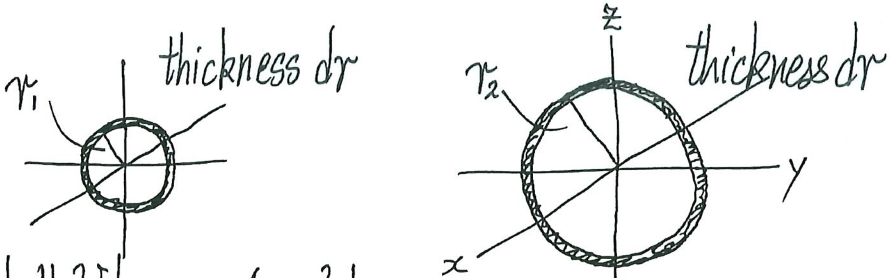
McQuarrie, “Quantum Chemistry”

← Using dots (density of dots is proportional to probability of finding the electron in that region)
[x-z cut, or equivalent]

But 4D Plots (r, θ, ϕ) then gives $\psi(r,\theta,\phi)$ OR $|\psi(r,\theta,\phi)|^2$ are too complicated

- "How far is the electron from the nucleus? Regardless of direction".

What is the prob. of find the electron in a spherical shell of thickness dr that is exactly r away from the nucleus? This is $P(r)\,dr$.



$\underbrace{\text{Shell Volume} = 4\pi r_1^2\, dr}_{\text{smaller}}$ $\qquad$ $\underbrace{\text{Shell Volume} = 4\pi r_2^2\, dr}_{\text{bigger}}$

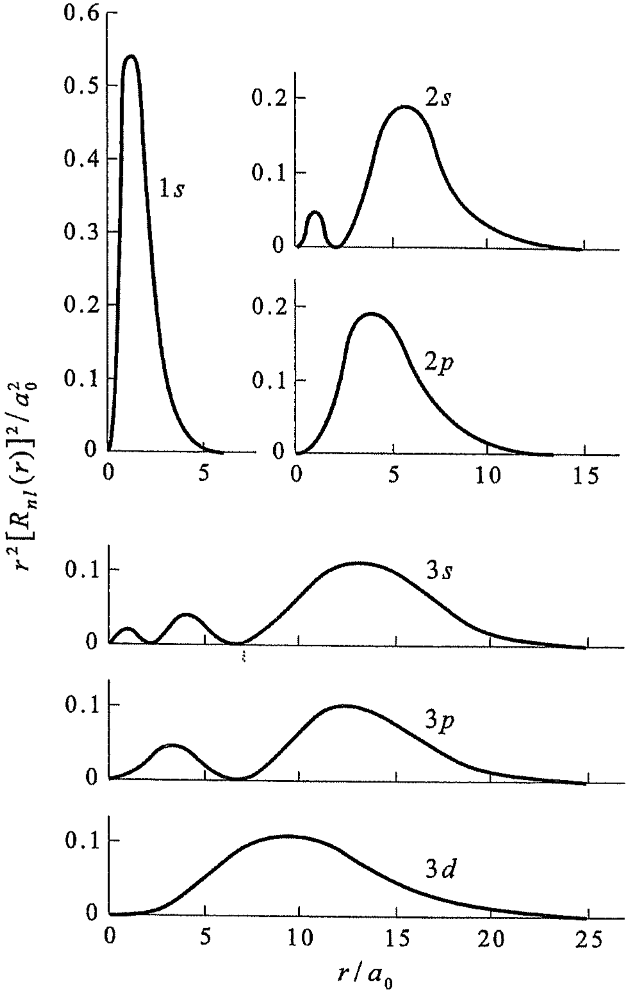
smaller ← Same thickness → bigger

$$P_{n\ell}(r) = \overline{r^2}\,|R_{n\ell}(r)|^2 \qquad (2)$$

= Radial Probability Distribution Function

a "$r^2 dr$" factor enters

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



1s: $\underbrace{\text{peaks at } r = a_0}_{\text{QM: Most probable to be at } r=a_0 \text{ (can be elsewhere)}}$ (Bohr said must be at $r = a_0$)

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

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

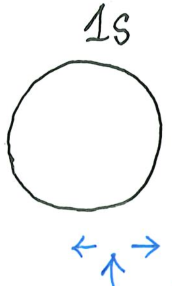
⋮

3d: $\underbrace{\text{peaks at } r = 9a_0}_{\text{QM: Most probable there (can be elsewhere)}}$ [Bohr said must be $r = 9a_0$]

Started to see the "shell structure"

Take-Home Message

- Pictures have solid QM foundation; artistic way of presenting QM results
- Only with QM knowledge



has better meaning

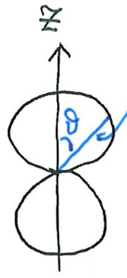
showing extent (spatial extent) that ψ ($|\psi|^2$, $P(r)$) is appreciable!

ψ is not zero (though small)

p states $\ell=1,\ m_\ell = 1, 0, -1$

Angular Part

p orbitals $\ell=1$ $\Rightarrow$ $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$
$= p_z \quad (3)$



length $= |\cos\theta|$

Polar Plot

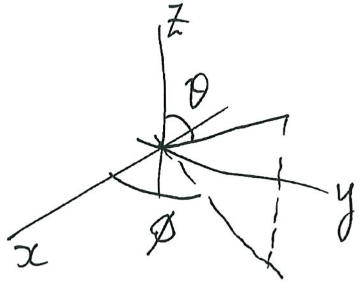
- Y_{10} is real
- directional along z
- p_z orbital

$$\left.\begin{aligned} Y_{11} &= -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \\ Y_{1-1} &= \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} \end{aligned}\right\} \text{complex [they are not } p_x, p_y \text{ yet]}$$

- Useful and practical to combine them into real directional functions

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

$$\frac{i}{\sqrt{2}}(Y_{1-1} + Y_{11}) \equiv p_y = \sqrt{\frac{3}{4\pi}}\underbrace{\sin\theta\sin\phi}_{\text{in } y\text{-direction}} \qquad (5)$$

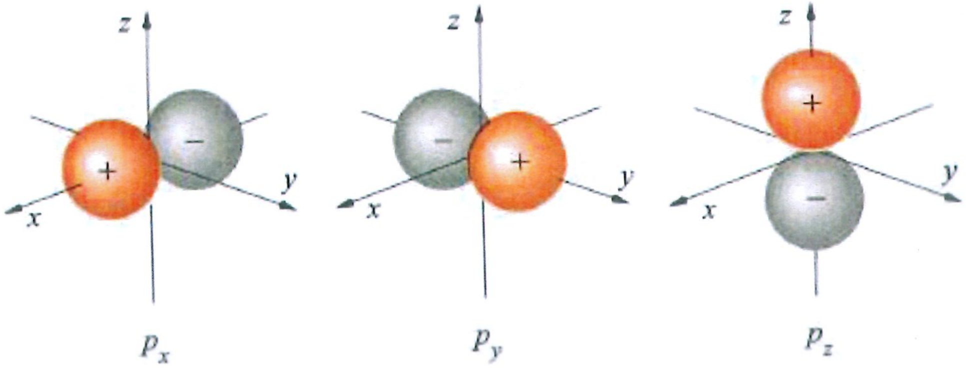


(real)

Polar Plots of p_x, p_y, p_z

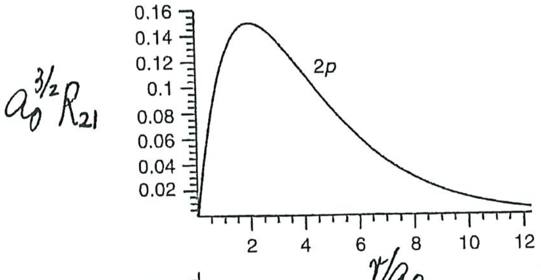
Only directional information

($\pm$ sign: sign of real angular functions)

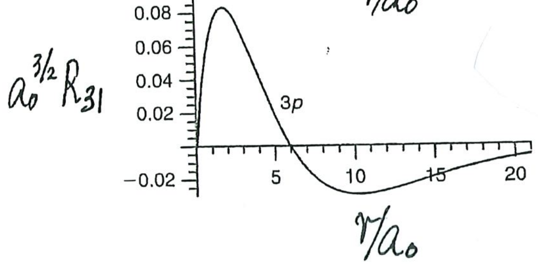


Radial Part

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



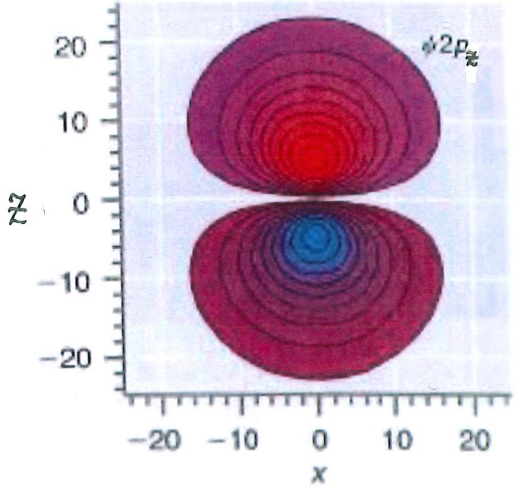
← Multiply this into p_x, p_y, p_z gives ψ_{2p_x}, ψ_{2p_y}, ψ_{2p_z}

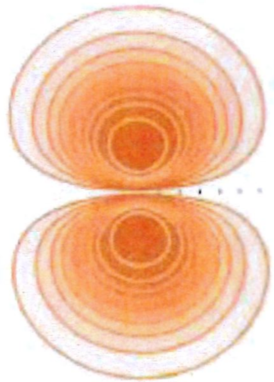


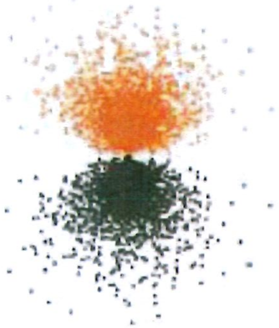
← Multiply this into p_x, p_y, p_z gives ψ_{3p_x}, ψ_{3p_y}, ψ_{3p_z}

ψ_{2p_z}

Ways to represent $|\psi_{2p_z}|^2$



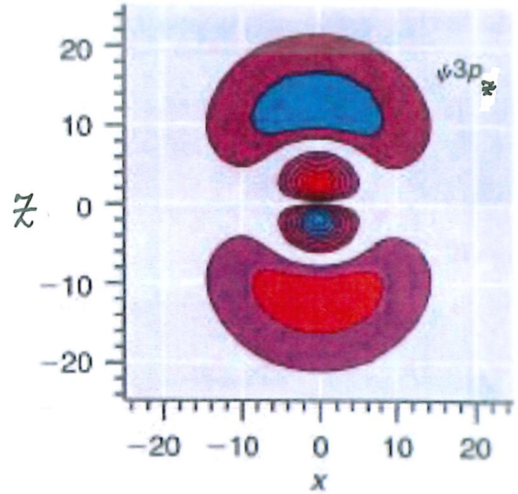


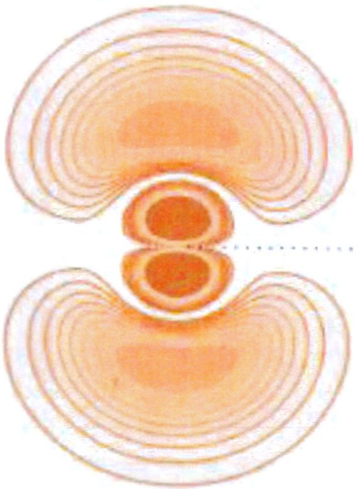


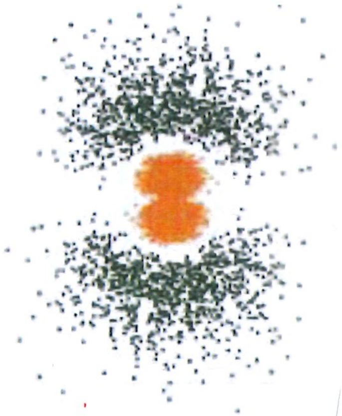
(rotating about $\hat{z}$-axis gives full picture)

ψ_{3p_z}

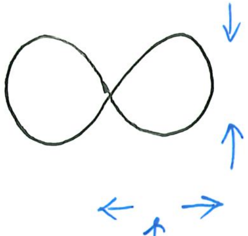
Ways to represent $|\psi_{3p_z}|^2$







Take-Home Message

- When you see  for p-states, it embedded much QM results

spatial extent where ψ_p (or $|\psi_p|^2$) is appreciable

and extents are different for ψ_{2p} and ψ_{3p}

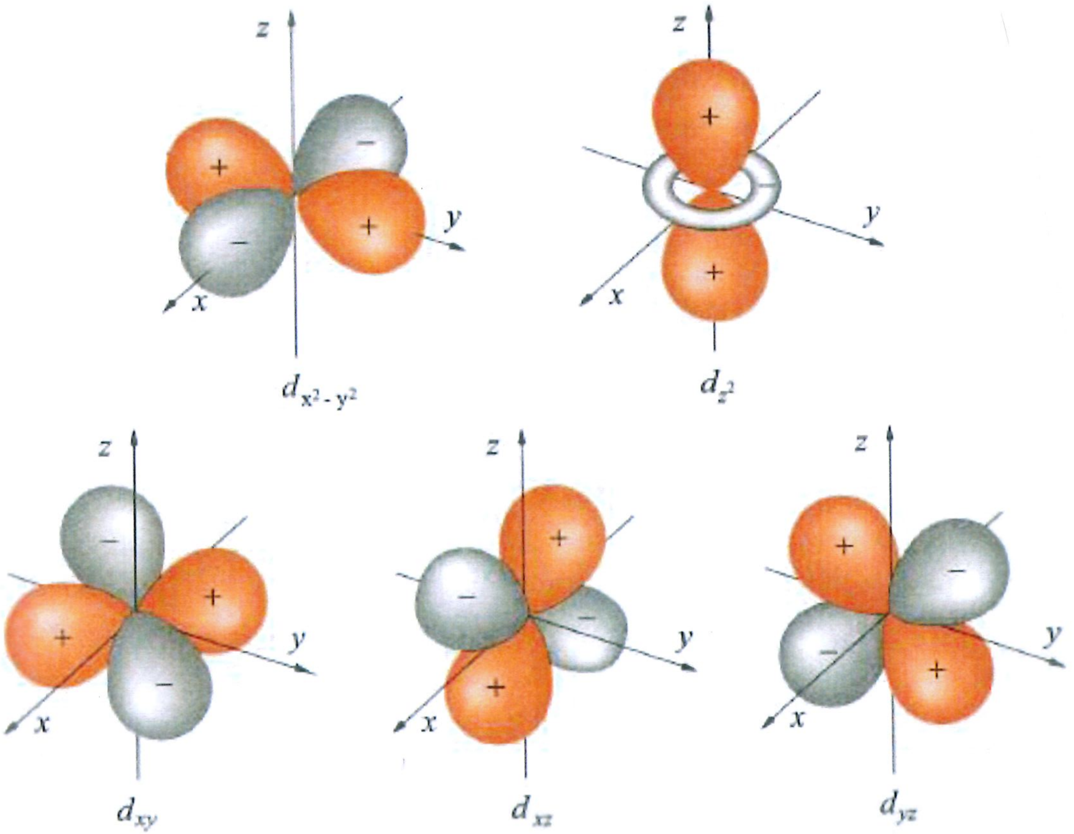
Optional ($\ell=2$: d orbitals[†]) Y_{20} (real), Y_{21}, Y_{2-1}, Y_{22}, Y_{2-2} (complex)

$$\left.\begin{aligned}
d_{z^2} &\equiv Y_{20} = \sqrt{\frac{5}{16\pi}}\,\underbrace{(3\cos^2\theta-1)}_{P_2(\cos\theta)} \\
d_{xz} &\equiv \frac{1}{\sqrt{2}}\left(Y_{2-1}-Y_{21}\right) = \sqrt{\frac{15}{4\pi}}\,\sin\theta\cos\theta\cos\phi \\
d_{yz} &= \frac{i}{\sqrt{2}}\left(Y_{2-1}+Y_{21}\right) = \sqrt{\frac{15}{4\pi}}\,\sin\theta\cos\theta\sin\phi \\
d_{x^2-y^2} &= \frac{1}{\sqrt{2}}\left(Y_{22}+Y_{2-2}\right) = \sqrt{\frac{15}{16\pi}}\,\sin^2\theta\cos2\phi \\
\underbrace{d_{xy}}_{\text{orthonormal}} &= \frac{1}{\sqrt{2}\,i}\left(Y_{22}-Y_{2-2}\right) = \sqrt{\frac{15}{16\pi}}\,\underbrace{\sin^2\theta\sin2\phi}_{\text{different angular dependence}}
\end{aligned}\right\}\text{ all real} \qquad (6)$$

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

[†] Useful for understanding magnetic materials, transition metals.

Polar Plots



$d_{x^2-y^2}$ d_{z^2}

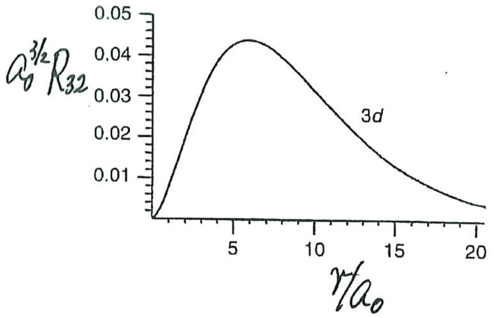
d_{xy} d_{xz} d_{yz}

(the five real angular functions ($l=2$))

$n=3$

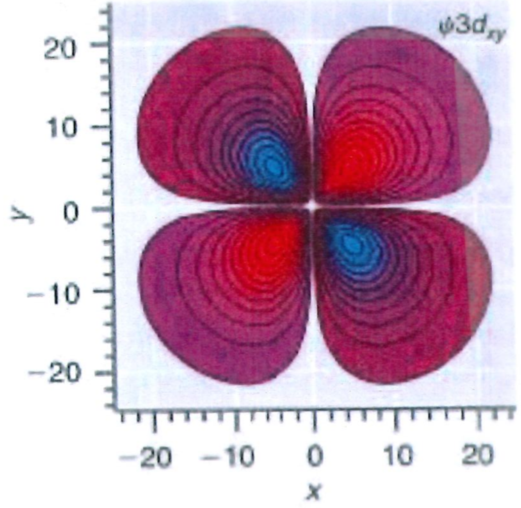
3d

We need to multiply these d-states into $R_{32}(r)$

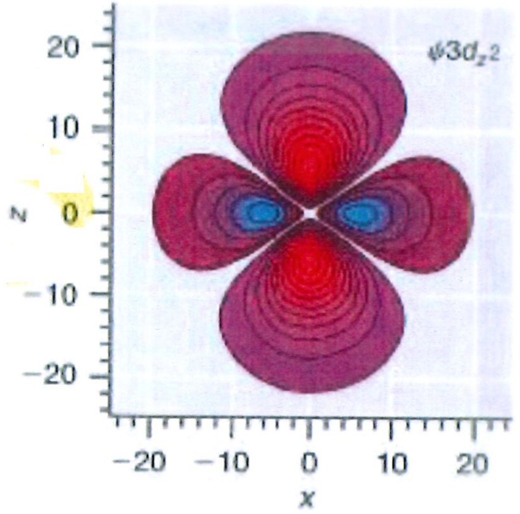


Multiply (in mind)
into the five d-orbitals
[five 3d orbitals]

$\psi_{3d_{xy}}$

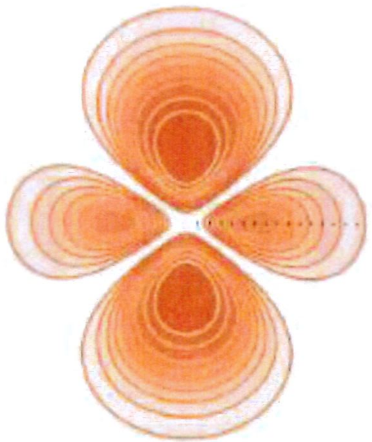


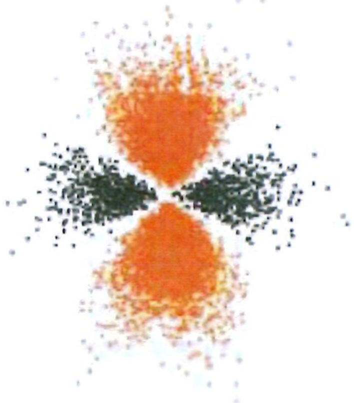
$\psi_{3d_{z^2}}$



Wavefunction
(x-z cut)

Ways to represent $|\psi_{3d_{z^2}}|^2$





Remarks

- d-states will be useful in a class of materials called diluted magnetic semiconductors (DMS)

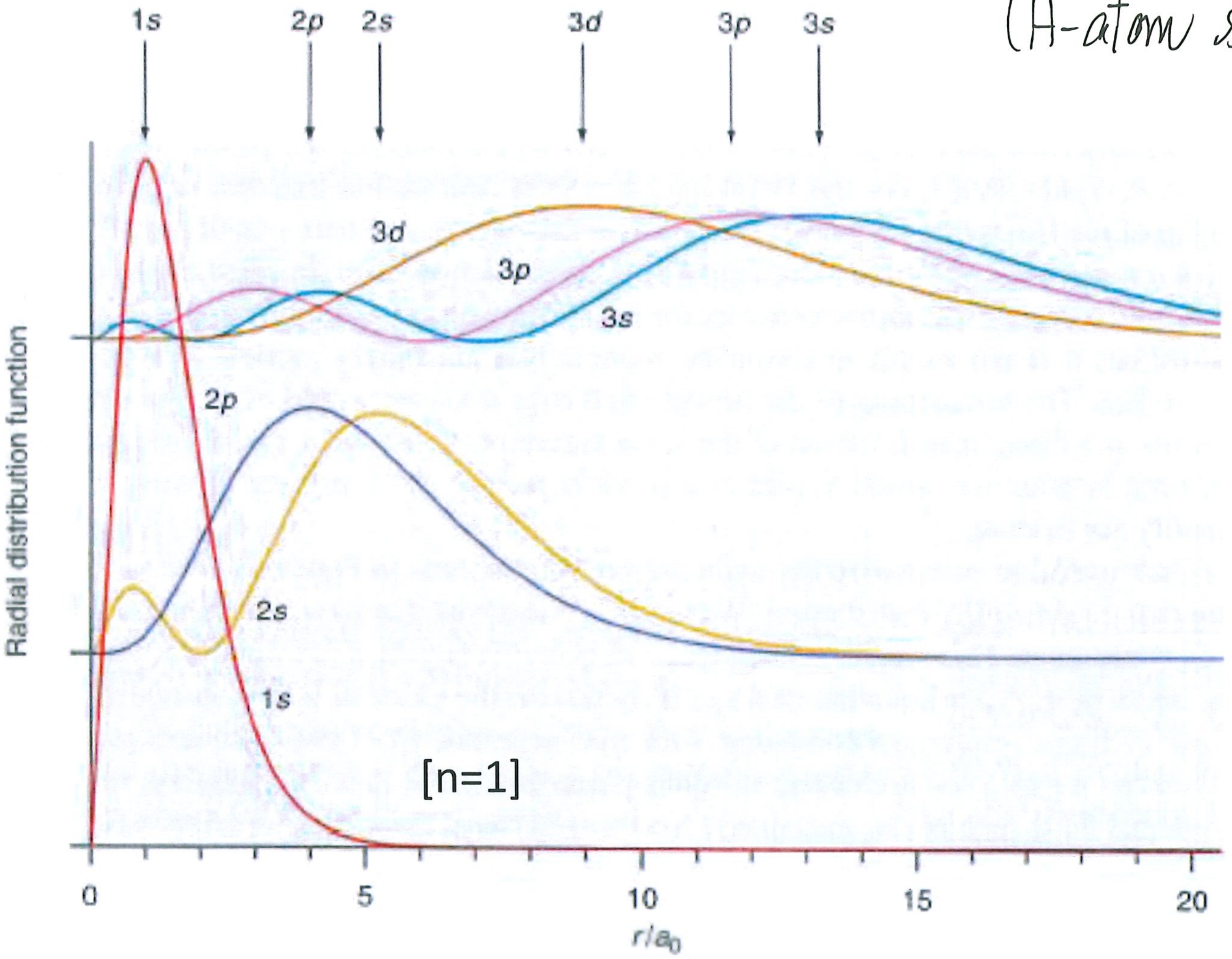
  magnetic (d electrons)

  e.g. CdMnTe (substitute some Cd in CdTe by Mn)

  Combine advantages of semiconducting materials and magnetic property

P(r) = Radial probability distribution function

(H-atom states)



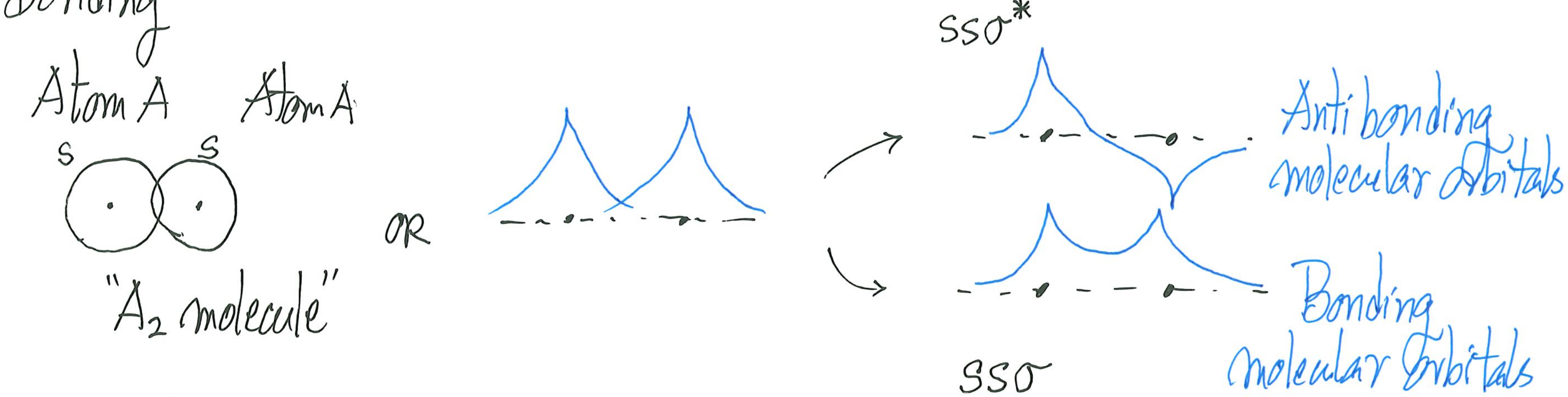
[n=3] (x-axis shifted upward for clarity)

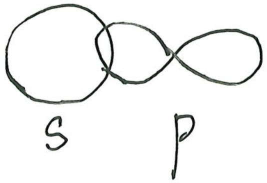
[n=2] (x-axis shifted upward for clarity)

[n=1]

Summary

- ○ , ∞ s and p states
- Useful even for atoms (≠ hydrogen) (Why? A big question!)
- Bonding





spσ bond

What do these pictures imply/mean?