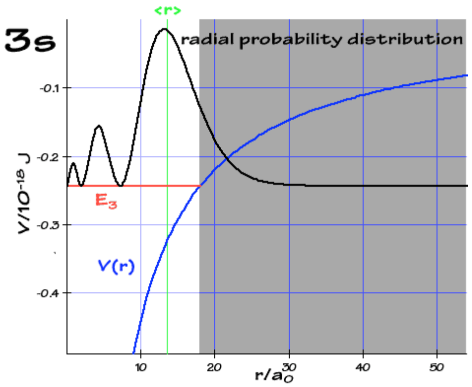
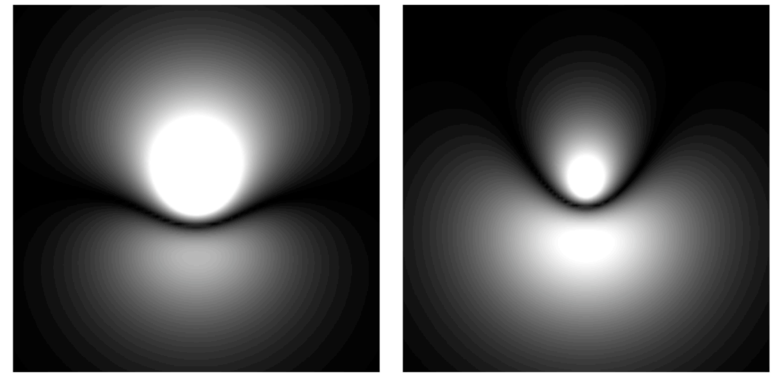
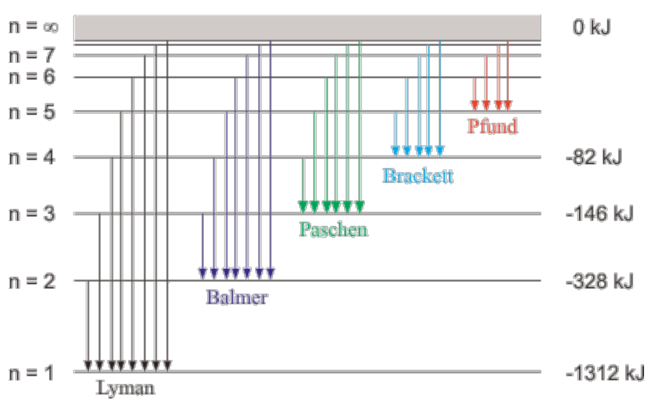
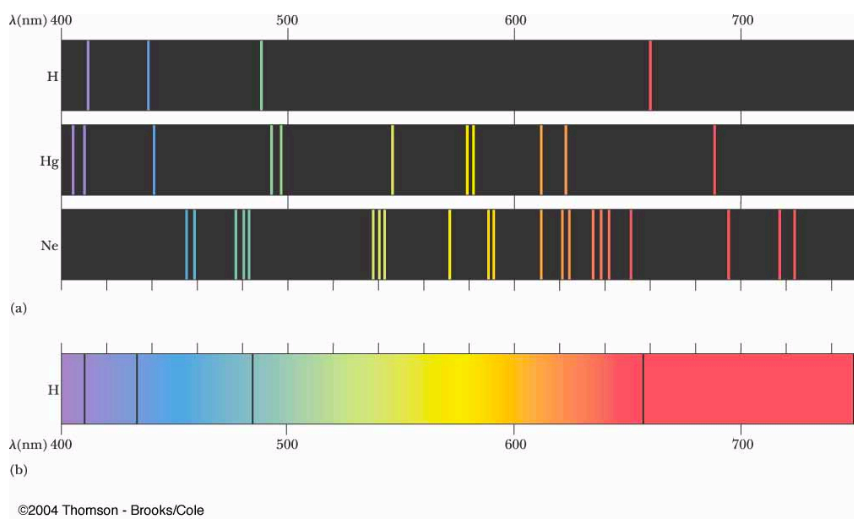




The H atom: The radial wave function (more)

Reading: McIntyre 8.5-8.6





Back to radial wave functions

- The power series we found is an associated Laguerre polynomial, and we multiply by the asymptotic forms we found.

$$R_{n\ell}(r) = N_{n,\ell} r^{\ell} e^{-Zr/na_0} \sum_{j=0}^{j_{\max}} c_j \left(2Zr / na_0\right)^j$$

$$R_{n\ell}(r) = N_{n,\ell} r^{\ell} e^{-Zr/na_0} \underbrace{L_{n+\ell}^{2\ell+1}\left(2Zr / na_0\right)}_{\text{Assoc. Laguerre polynomial of this argument}}$$

Polynomial of order jmax = n-el-1

- Then we normalize. So what is the condition associated with *R* that normalizes the probability?

Full Wave Function: orthonormality

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$$

- Orthonormal over all space

$$\langle n_1\ell_1 m_1 | n_2 \ell_2 m_2 \rangle = \delta_{n_1 n_2}\delta_{\ell_1\ell_2}\delta_{m_1 m_2}$$

$$\int_0^{2\pi}\int_0^{\pi}\left(Y_{\ell_1}^{m_1}(\theta,\phi)\right)^* Y_{\ell_2}^{m_2}(\theta,\phi)\underbrace{\sin\theta\, d\theta\, d\phi}_{?} = \delta_{\ell_1\ell_2}\delta_{m_1 m_2}$$

$$\int_0^{\infty} R_{n_1\ell_1}^*(r) R_{n_2\ell_2}(r)\underbrace{r^2\, dr}_{?} = \delta_{\ell_1\ell_2}\delta_{n_1 n_2}$$

This factor of r^2 from the volume element is important

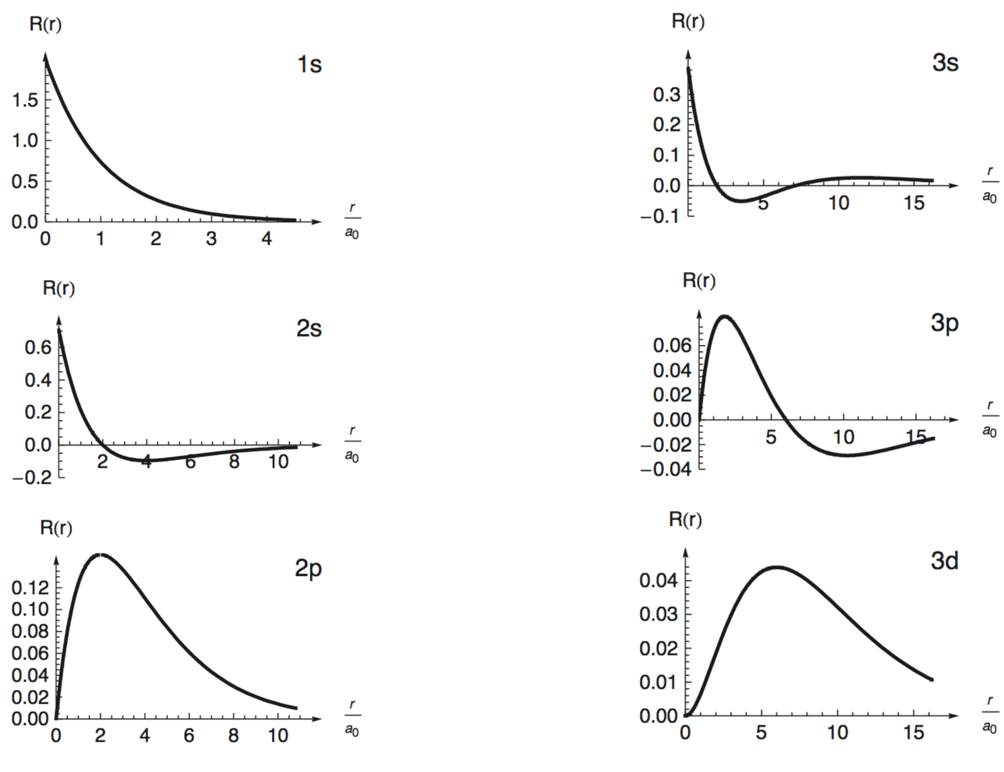
$$R_{n\ell}(r) = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right\}^{1/2} e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1}(2Zr/na_0)$$

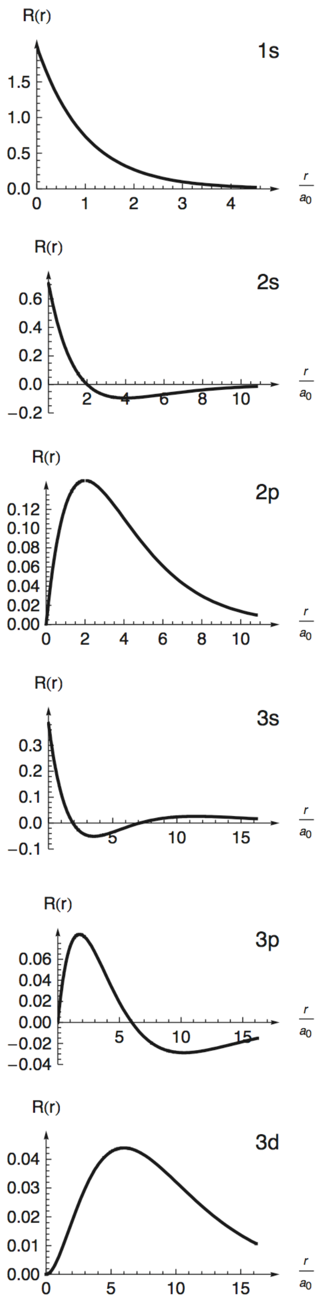
Back to radial wave functions

And here is the radial wave function:

$$R_{n\ell}(r) = -\left\{ \left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1}(2Zr/na_0)$$

Notice the nodes and maxima;
You will examine these for yourselves in a worksheet.





Radial wave functions

- Here are more of them. Know where to look them up.
- Exponential at large r : decay length depends on energy.
- Power law at small r: non zero at origin only for s states
- Poly of order n-el-1
- Fits into the box!

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

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

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

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

$$R_{31}(r) = \frac{4\sqrt{2}}{9}\left(\frac{Z}{3a_0}\right)^{3/2} \frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

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

Full wave function

$$\left|n\ell m\right\rangle$$

- What is the action of these operators on the full solution?

$$H\left|n\ell m\right\rangle = ?$$

$$L^2\left|n\ell m\right\rangle = ?$$

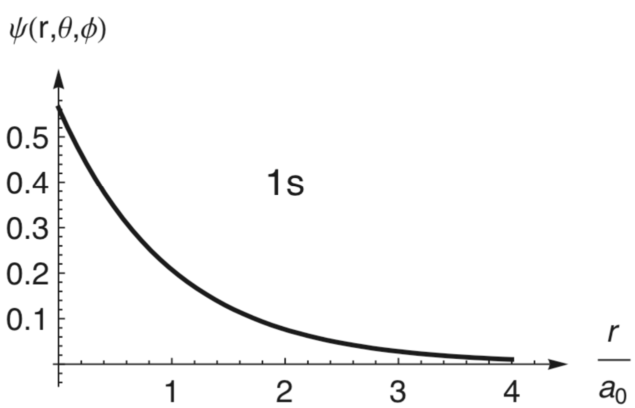
$$L_z\left|n\ell m\right\rangle = ?$$

- Do these operators commute?

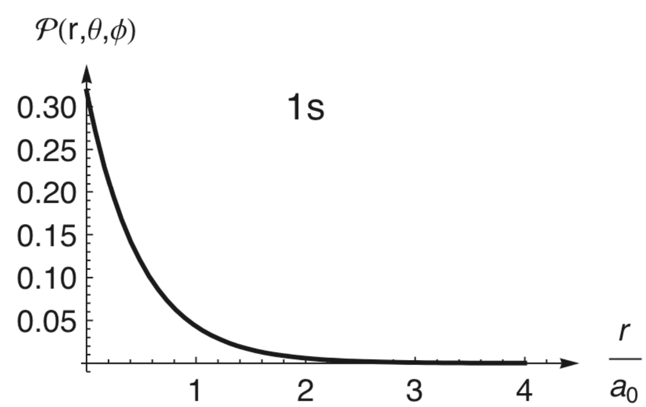
Probability density

- Define $$\mathcal{P}(r,\theta,\phi) = \left|\psi_{n\ell m}(r,\theta,\phi)\right|^2$$ $$= \left|R_{n\ell}(r)Y_\ell^m(\theta,\phi)\right|^2$$

a)

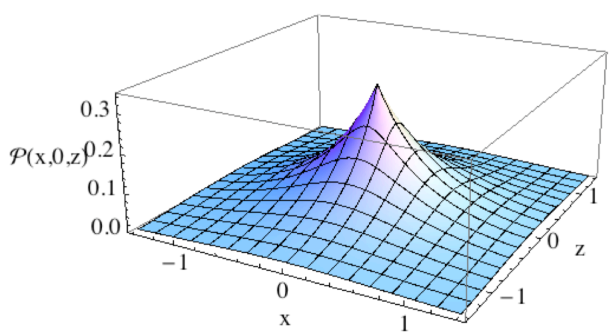


b)



1 s state is spherically symmetric

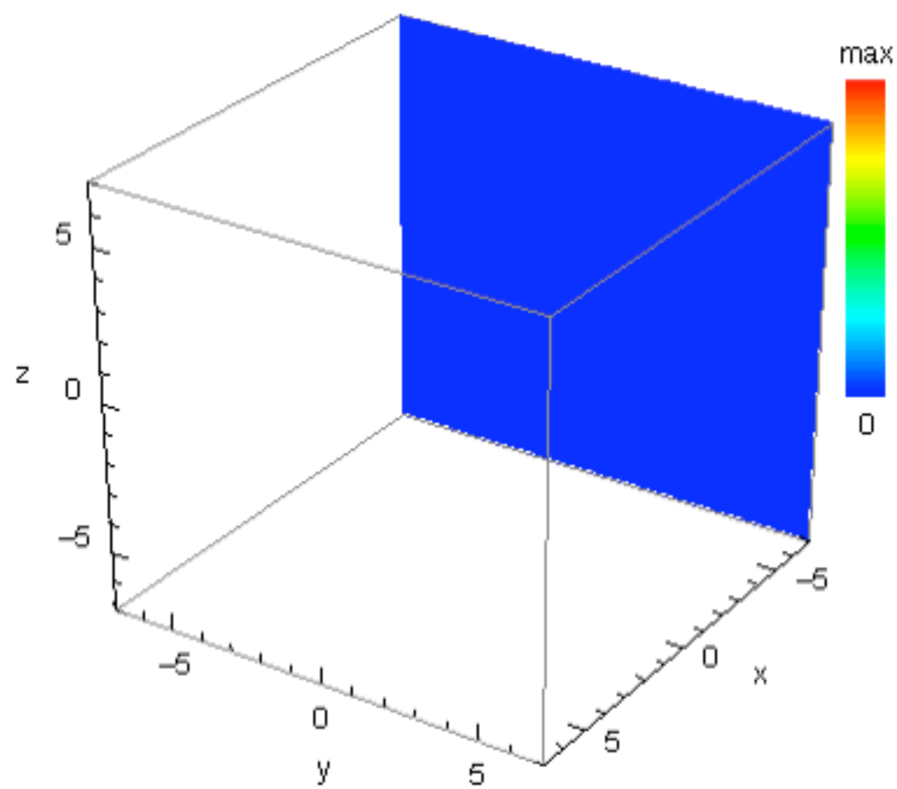
(a)

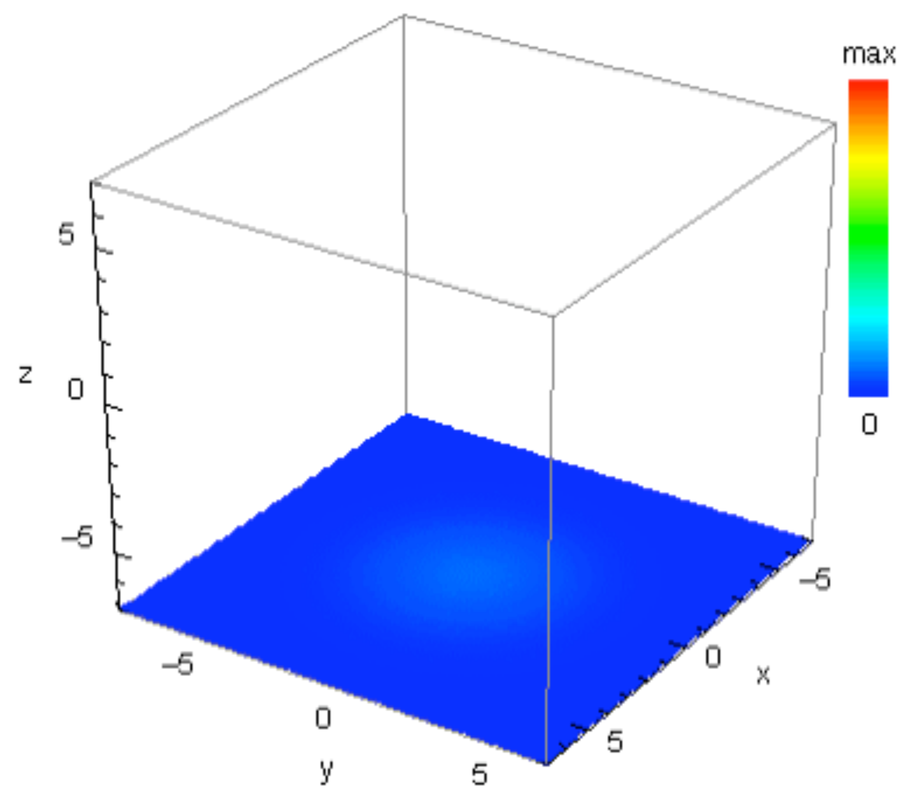


(b)

Visualizing probabilities in 3-d

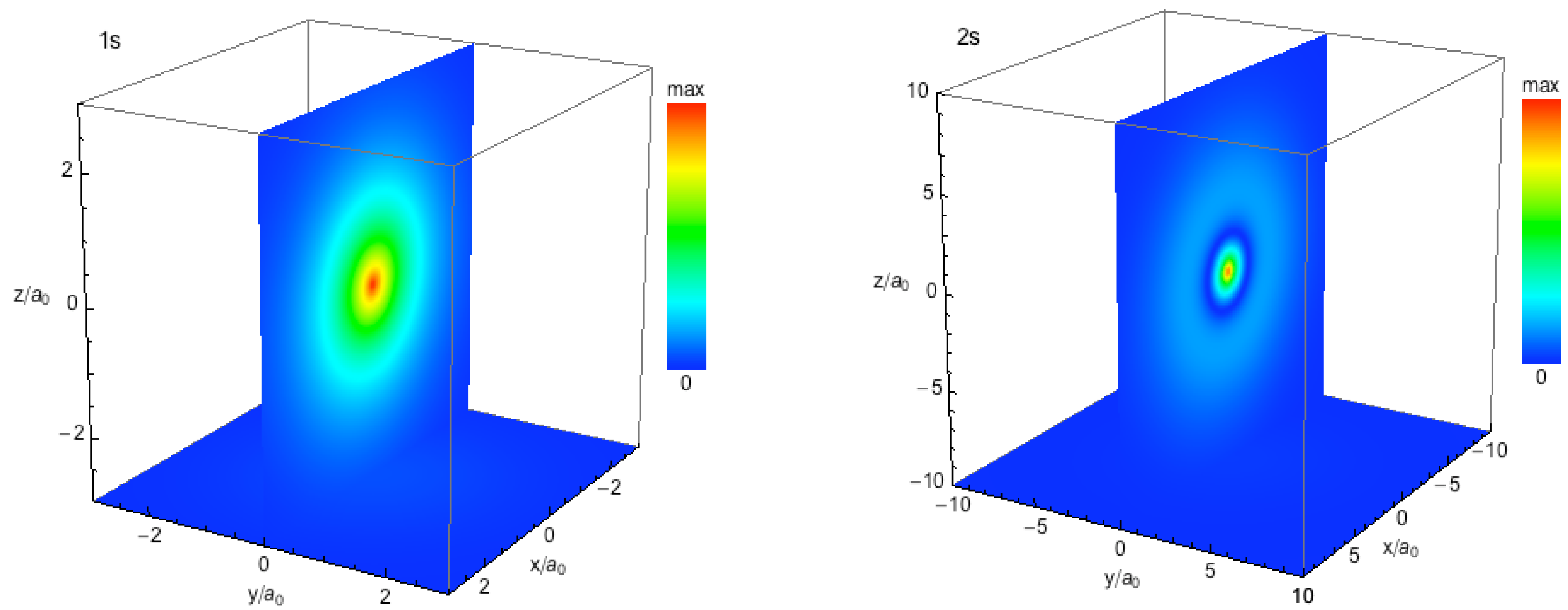
- In 3-d, we don't have another axis to plot probability as height. We MUST use color! We can access that color by looking at slices in the various planes. Which state is this?





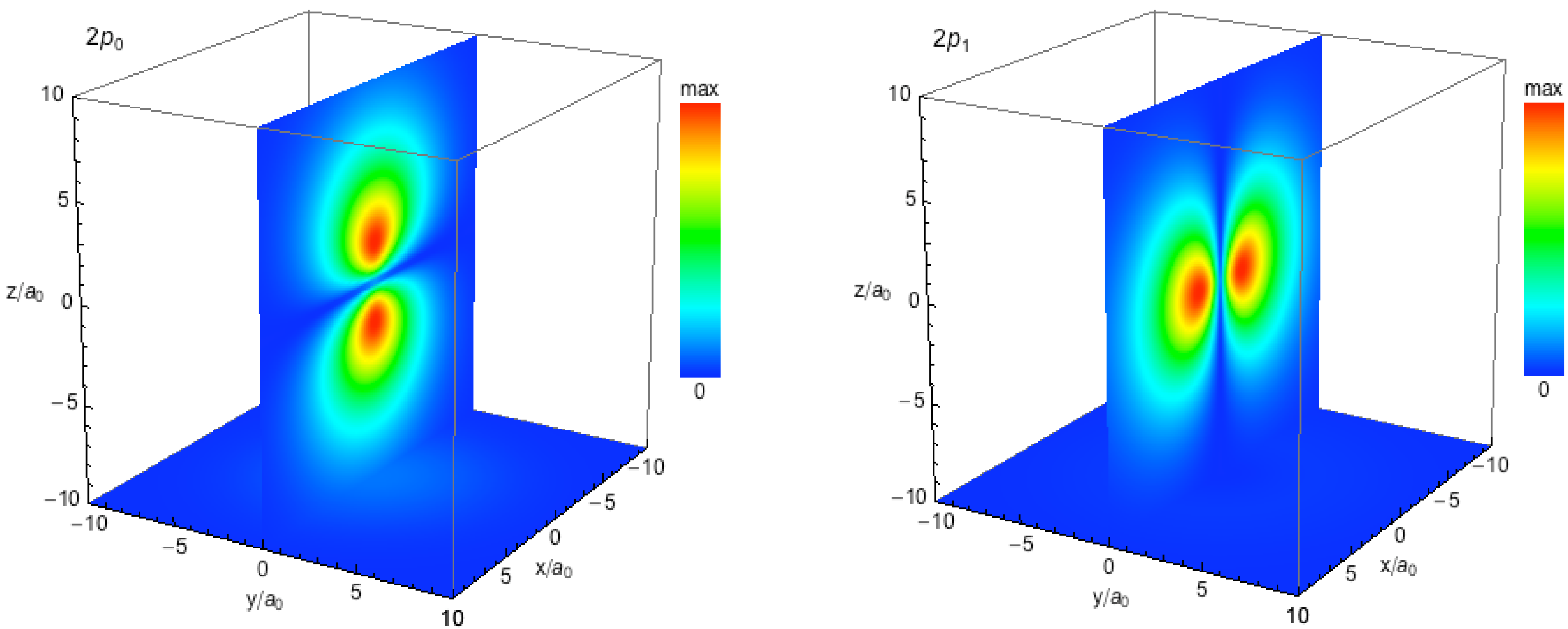
s- states

- What additional structure does the radial wave function impose that you can't see from the Ylms?



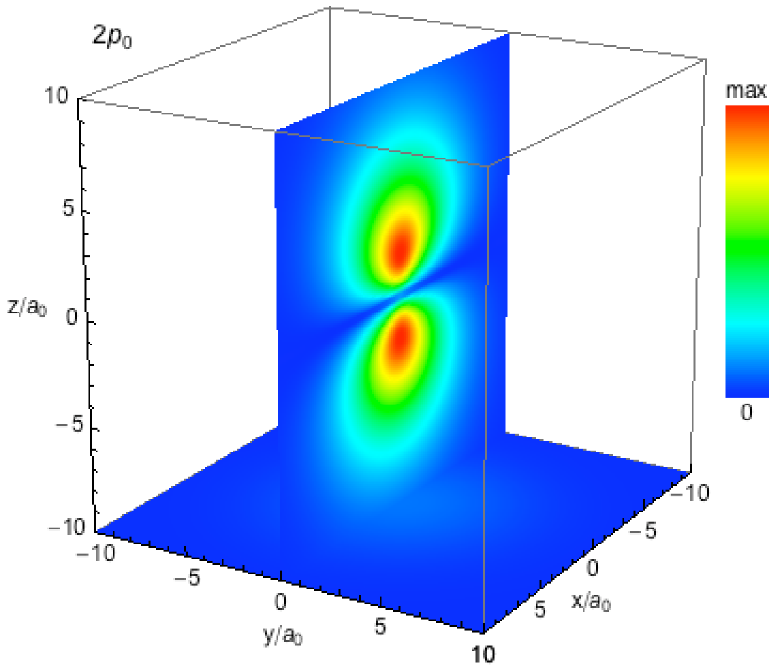
p- states

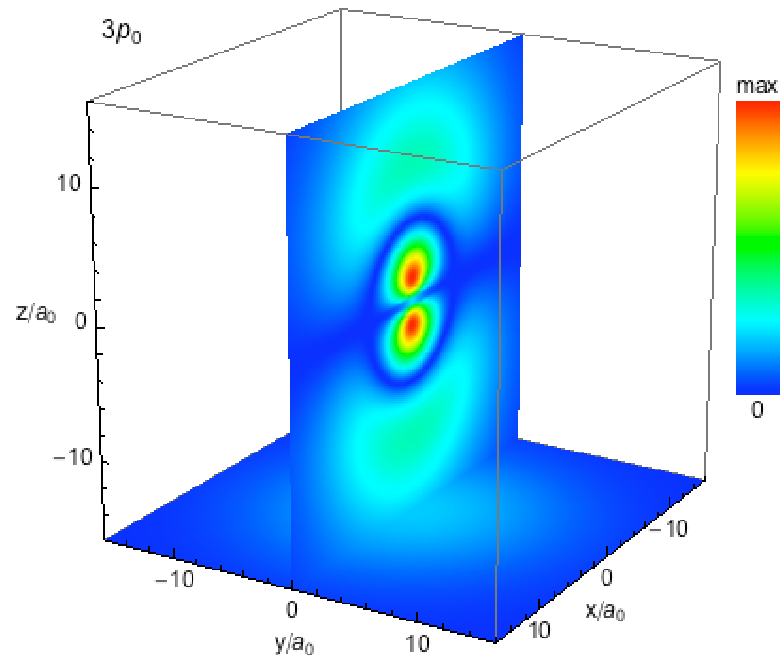
- What additional structure does the radial wave function impose that you can't see from the Ylms?



p- states

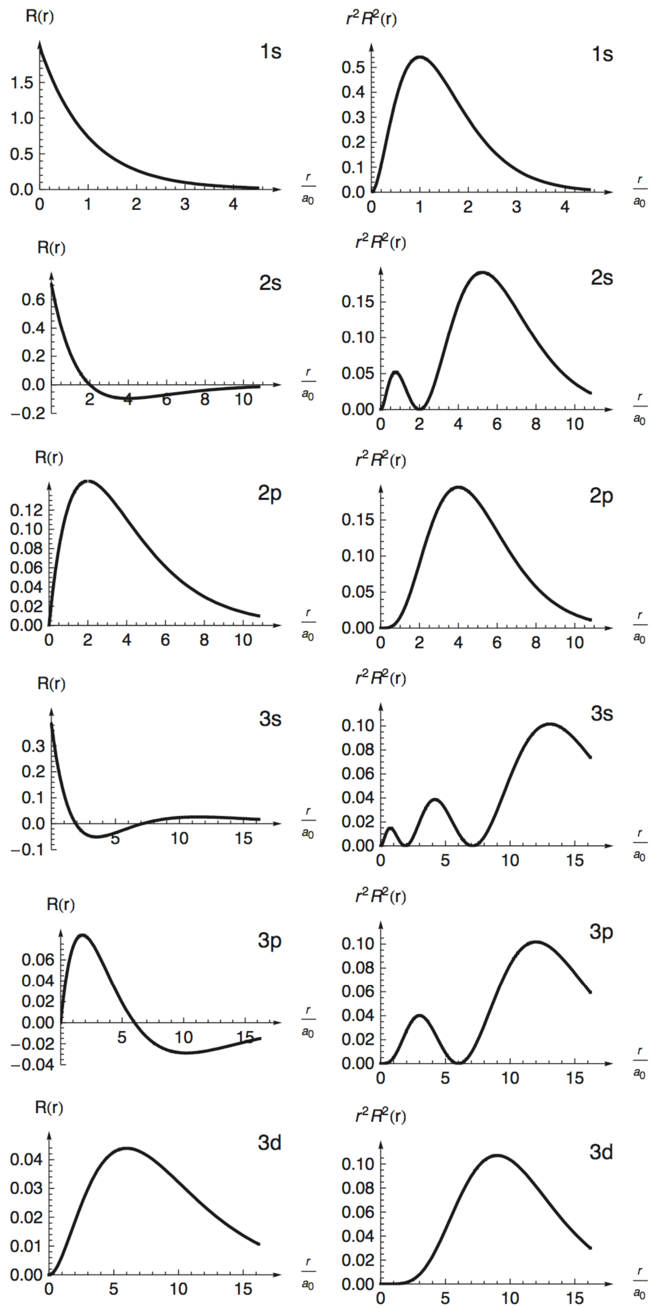
- What additional structure does the radial wave function impose that you can't see from the Ylms?





Visualizing probabilities in 3-d

- There is a Mathematica worksheet that will allow you to generate a similar plot for any state. The final visualization step is unfortunately computationally intense, and can take up to 5 minutes to generate one plot. Let's see what we can learn …



Radial wave functions

- Plot on the right is the radial probability distribution (see next page).

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

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

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

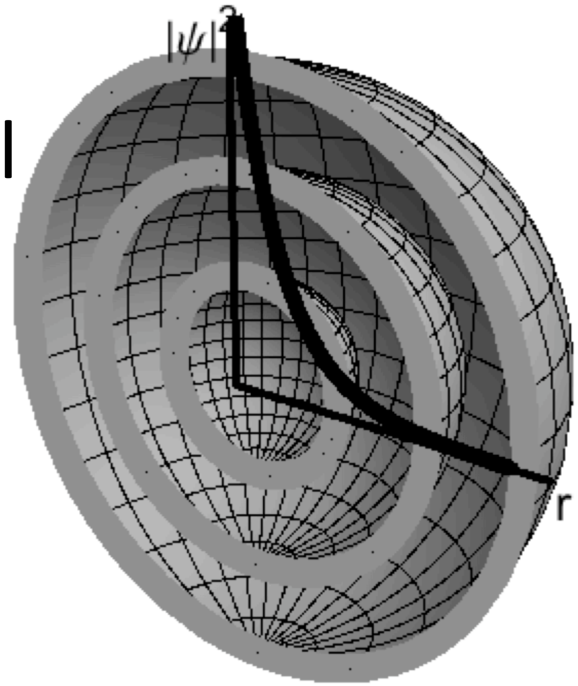
$$R_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{3/2}\left[1-\frac{2Zr}{3a_0}+\frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9}\left(\frac{Z}{3a_0}\right)^{3/2}\frac{Zr}{a_0}\left(1-\frac{Zr}{6a_0}\right)e^{-Zr/3a_0}$$

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

Shell probabilities

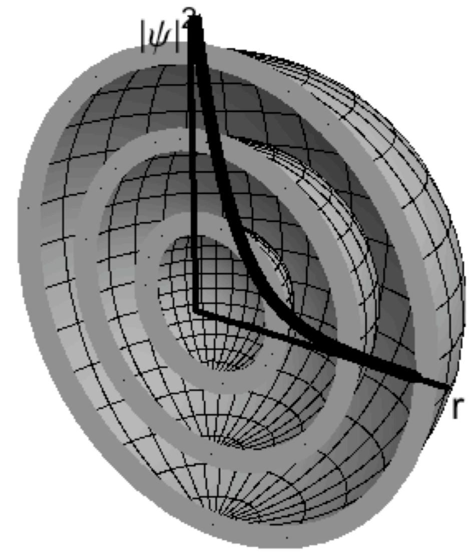
- Suppose we wish to calculate (for example), the number of electrons in a particular volume
- Sometimes, that volume is a shell centered on the origin
- The volume of the shell is weighted by r^2, so we define a "radial probability density" that takes account of this weighting



$$\mathcal{P}_{shell} = r^2 \left|R_{n\ell}\right|^2 dr$$

Shell probabilities

- It is necessary to use this “radial probability density” that takes account of this weighting to calculate quantities such as



$$\langle n\ell m|r|n\ell m\rangle = \langle r\rangle$$

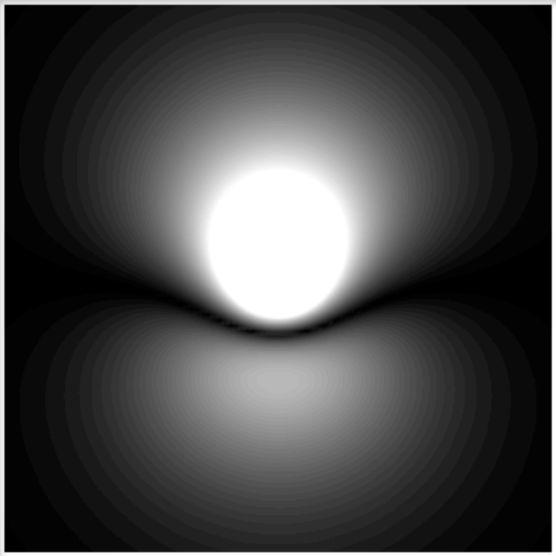
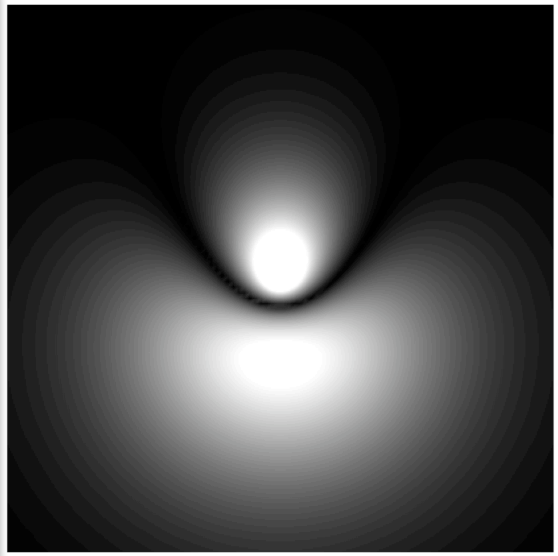
$$\langle n\ell m|V|n\ell m\rangle = \frac{-Ze^2}{4\pi\varepsilon_0}\langle n\ell m|\frac{1}{r}|n\ell m\rangle = \frac{-Ze^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle$$

Now you investigate

- Use Mathematica to draw radial wave functions, radial probability distributions and look for patterns
- Calculate some average quantities.

H atom wave functions as a basis set

- 1s-2p hybrid and 2s-2p hybrid

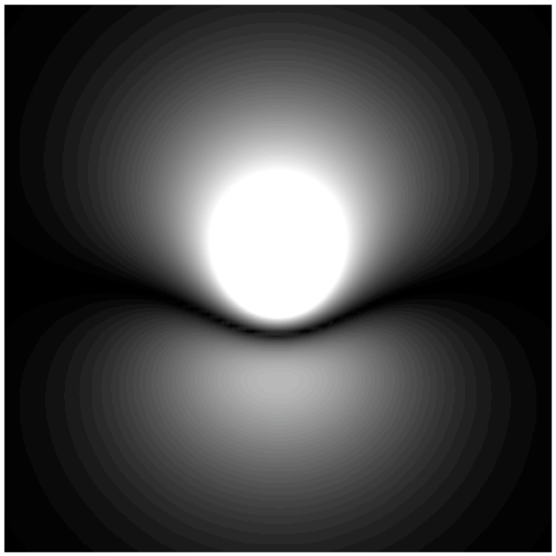
Time evolution of this state - radiation

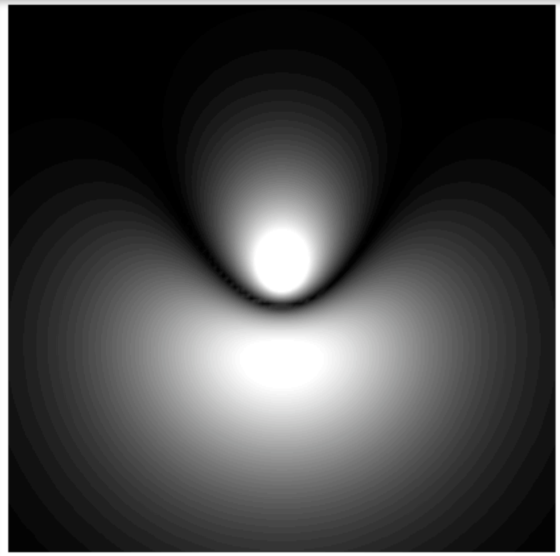
$$\psi(r,\theta,\phi,t) = \frac{1}{\sqrt{2}}\psi_{100}(r,\theta,\phi)e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\psi_{210}(r,\theta,\phi)e^{-iE_2t/\hbar}$$

$$= \frac{1}{\sqrt{2\pi a_0^3}} e^{-iE_1t/\hbar}\left(e^{-r/a_0} + \frac{z}{4\sqrt{2}a_0} e^{-r/2a_0} e^{-i\omega_{21}t} \right)$$

H atom wave functions as a basis set

- 1s-2p hybrid and 2s-2p hybrid (BOOK error)





No time evolution of this state – static dipole – more electron density at –z. (Stark effect)

$$\psi(r,\theta,\phi,t)=\tfrac{1}{\sqrt{2}}\psi_{200}(r,\theta,\phi)e^{-iE_2t/\hbar}+\tfrac{1}{\sqrt{2}}\psi_{210}(r,\theta,\phi)e^{-iE_2t/\hbar}$$

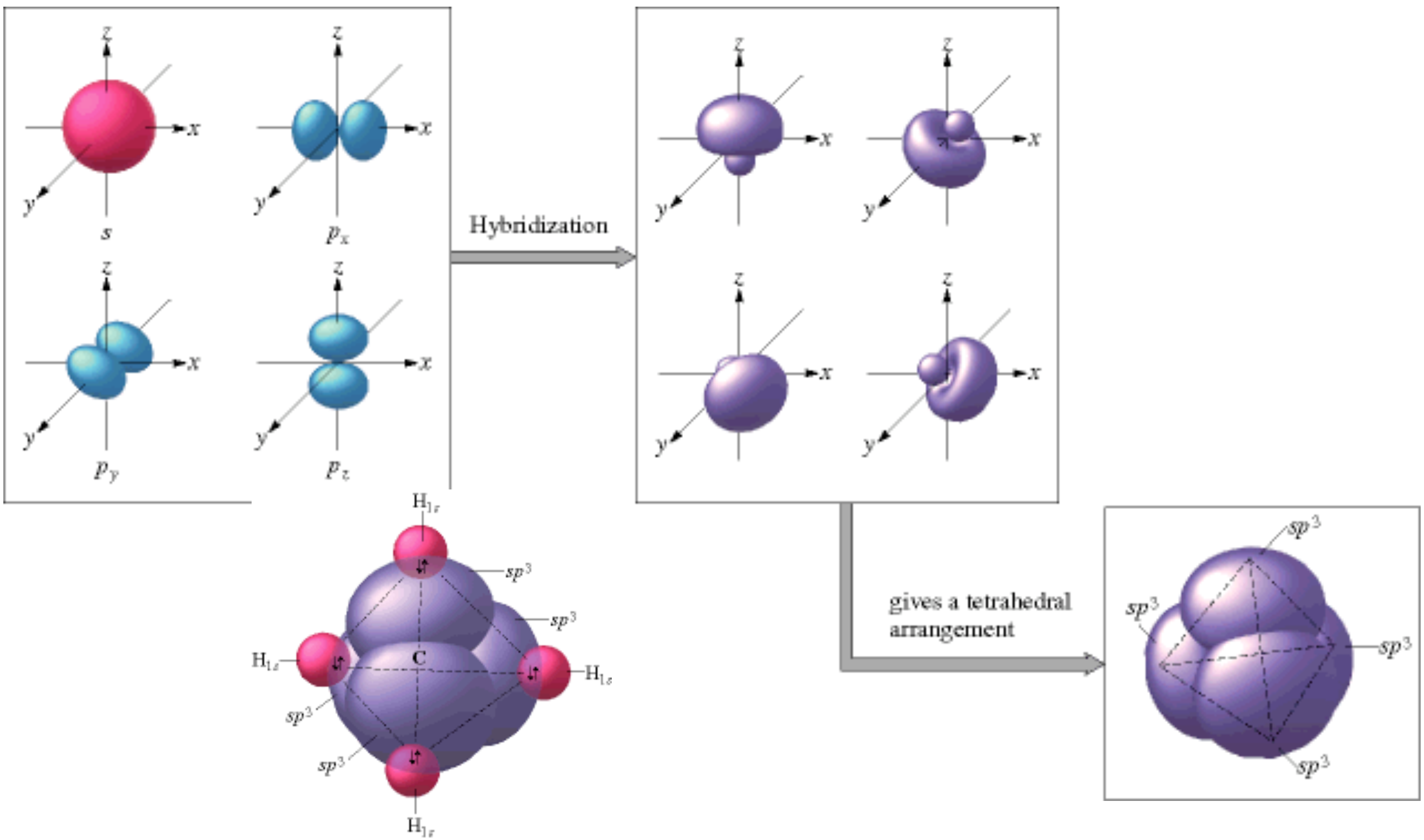
$$=\frac{1}{4\sqrt{\pi a_0^3}}e^{-iE_2t/\hbar}\left(\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}+\frac{z}{2a_0}e^{-r/2a_0}\right)$$

H atom wave functions as a basis set

- Hybrid orbitals: the orbitals that describe bonds are often superpositions of the eigenstates we have just described. Discuss the orbitals of $C_{diamond}$ and $C_{graphite}$
- This is very important in molecular orbital theory. We consider the molecular orbital of the H_2 molecule as a linear superposition of the H atom wave functions of the two constituent H atoms – leads to bonding and antibonding. A similar construct is the basis for considering solids as "giant molecules".

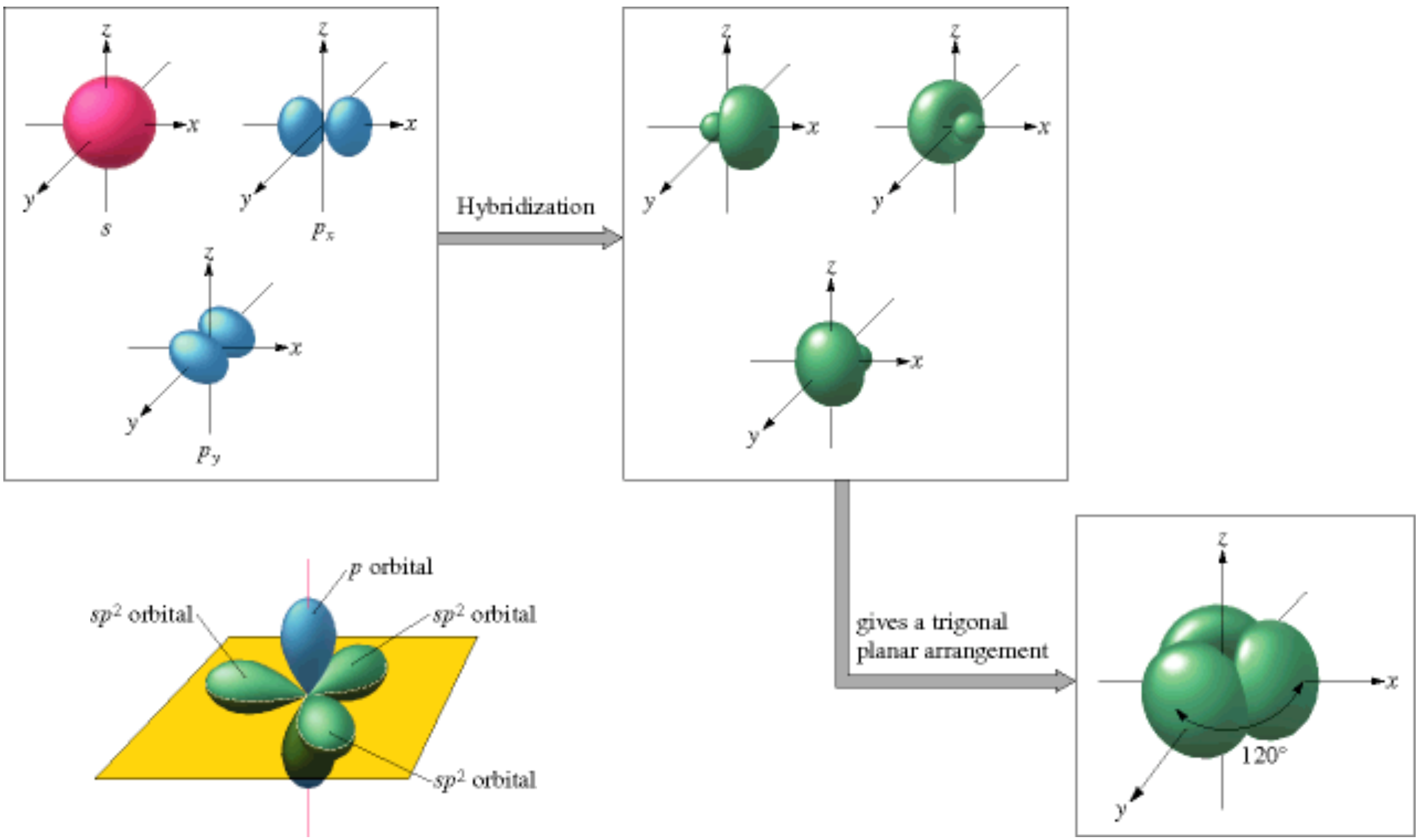
H atom wave functions as a basis set

- sp^3 hybrids: Carbon diamond (this is just Ylms in this depiction)
- www.mcat45.com/content/valence-bond-theory



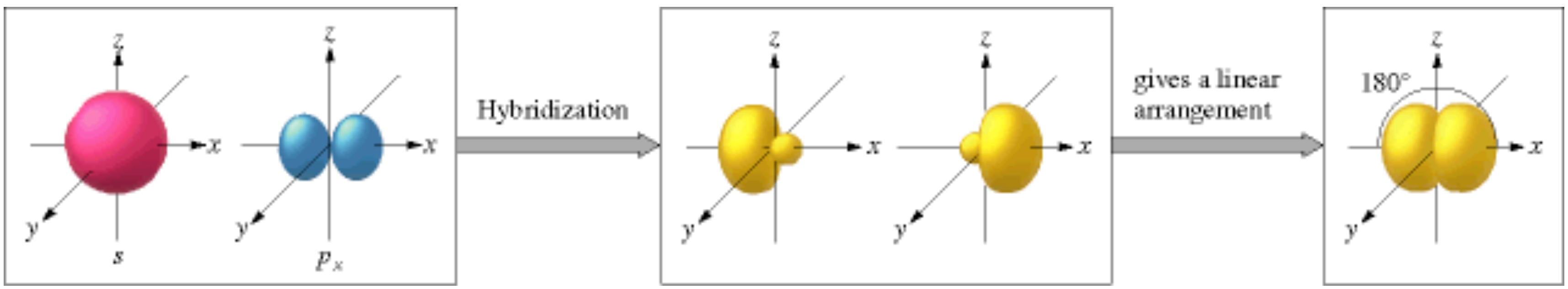
H atom wave functions as a basis set

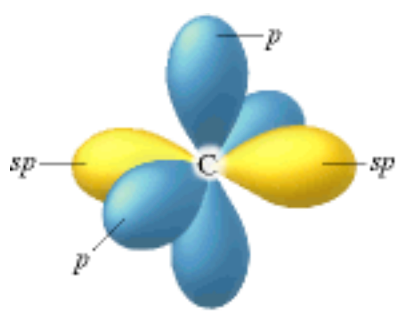
- sp^2 hybrids: Carbon graphite (this is just Ylms in this depiction)
- www.mcat45.com/content/valence-bond-theory



H atom wave functions as a basis set

- sp hybrids: alkynes (this is just Ylms in this depiction)
- www.mcat45.com/content/valence-bond-theory





Summary

- The fact that the series must be a finite polynomial is what (mathematically) leads to a maximum (and integer) value of *n*, and restricts *el*.
- The radial wave functions depend on *n* and *el*, but the energy depends only on *n* - degeneracy Write form of E_n
- We pull out the asymptotic dependencies of the wave function (power law at small *r* and exp decay at large *r*); what remains is an associated Laguerre polynomial.
- Probabilities, radial probability, normalization