

How about the ground state wave function?

Remember:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho) \quad u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad \rho \equiv \kappa r$$

*(Note: A blue arrow points from  $u(\rho)$  to  $R(r) = u(r)/r$  in the original image.)*

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We start with  $n=1$ , the lowest energy (i.e. the most negative). Since  $n = j_{\max} + l + 1$ , then  $l=0, j_{\max}=0$ . Then

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi)$$

with  $R_{10}(r) = \frac{c_0}{a} e^{-r/a}$  because  
the polynomial has only a  
constant  $c_0$ .

$$Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$$

*(Note: A blue arrow points from this equation to  $Y_0^0$  in the equation above.)*

We then **normalize**, which means we fix the value of  $c_0$  :

$$\int_0^{\infty} |R_{10}|^2 r^2 dr = \frac{|c_0|^2}{a^2} \int_0^{\infty} e^{-2r/a} r^2 dr = |c_0|^2 \frac{a}{4} = 1$$

The very final result for the ground state of an electron in a  $H$  atom is:

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

which, amazingly, is remarkably **simple**.

Consider now the **excited states**, starting with  **$n=2$** :

$$E_2 = \frac{-13.6 \text{ eV}}{4}$$

$$= -3.4 \text{ eV}$$

Because  $n = j_{\max} + l + 1$ , then  $n=2$  allows for  $l=0, j_{\max}=1$  or  $l=1 (m=1,0,-1), j_{\max}=0$ . Thus, degeneracy is 4 (in general, degeneracy is  $n^2$ ).

This will be the 2s and three 2p's orbitals.

(2) If  $l=0, j_{\max}=1$ , then  $c_{j_{\max}+1}=c_2=0$ .

Use  $c_1 = [2(j+l+1-n)/(j+1)(j+2l+2)] c_0$  with  $n=2, j=0$  (because  $c_0$  means  $j=0$ ) and  $l=0$ , and you get  $c_1 = -c_0$  so the polynomial becomes  $v(\rho)=c_0(1-\rho)$  with  $c_0$  again used to normalize.

$$Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$$

$$R_{20}(r) = \frac{c_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

The factors 2 arise from  $\rho = (1/an)r$  with  $n=2$ .

(3) If  $l=1, j_{\max}=0$ , you get  $c_{j_{\max}+1}=c_1=0$  so the polynomial is only  $c_0$ , as for the ground state.

Use the general formula  $R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho)$  with  $l=1$  and  $n=2$ .

$$R_{21}(r) = \frac{c_0}{4a^2} r e^{-r/2a}$$

$$\rho = (1/2a)r \\ \text{with } n=2$$

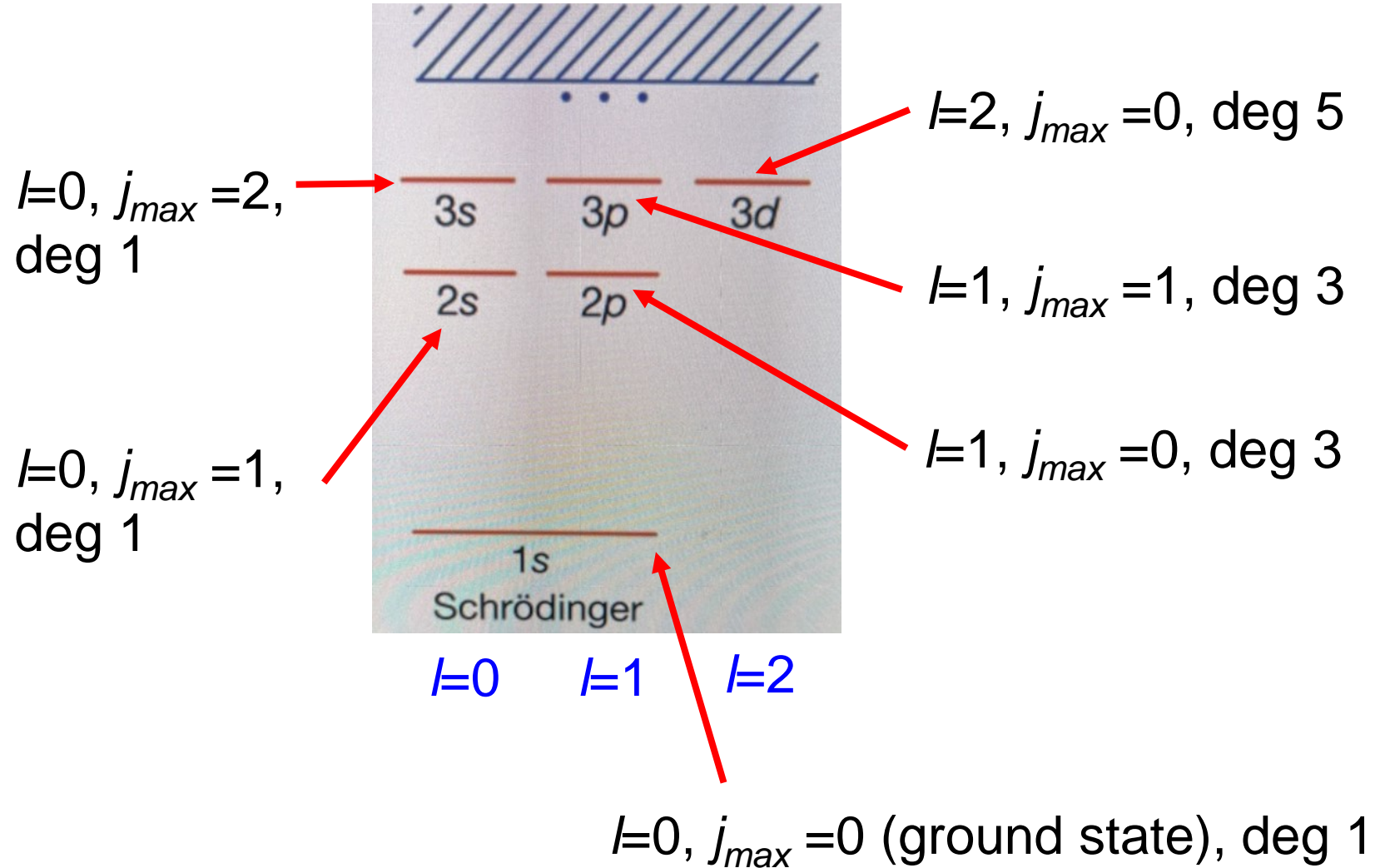
The front factor comes from  $\rho^2/r = (r/2a)^2/r$ .

The spherical harmonics are:

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$$

**Visually:** the familiar levels of the H-atom arise from playing with  $l$  and  $j_{max}$



In general, the polynomials  $v(\rho)$  are called **associated Laguerre polynomials**

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad \rho = (1/na) r$$

and there are tables with these polynomials.

Putting all together, for arbitrary  $(n,l,m)$  the normalized wave functions are:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l \left[ L_{n-l-1}^{2l+1}(2r/na) \right] Y_l^m(\theta, \phi)$$

$$R_{nl}(r)$$

$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a}\right) \left(\frac{r}{a}\right)^2 \exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$$

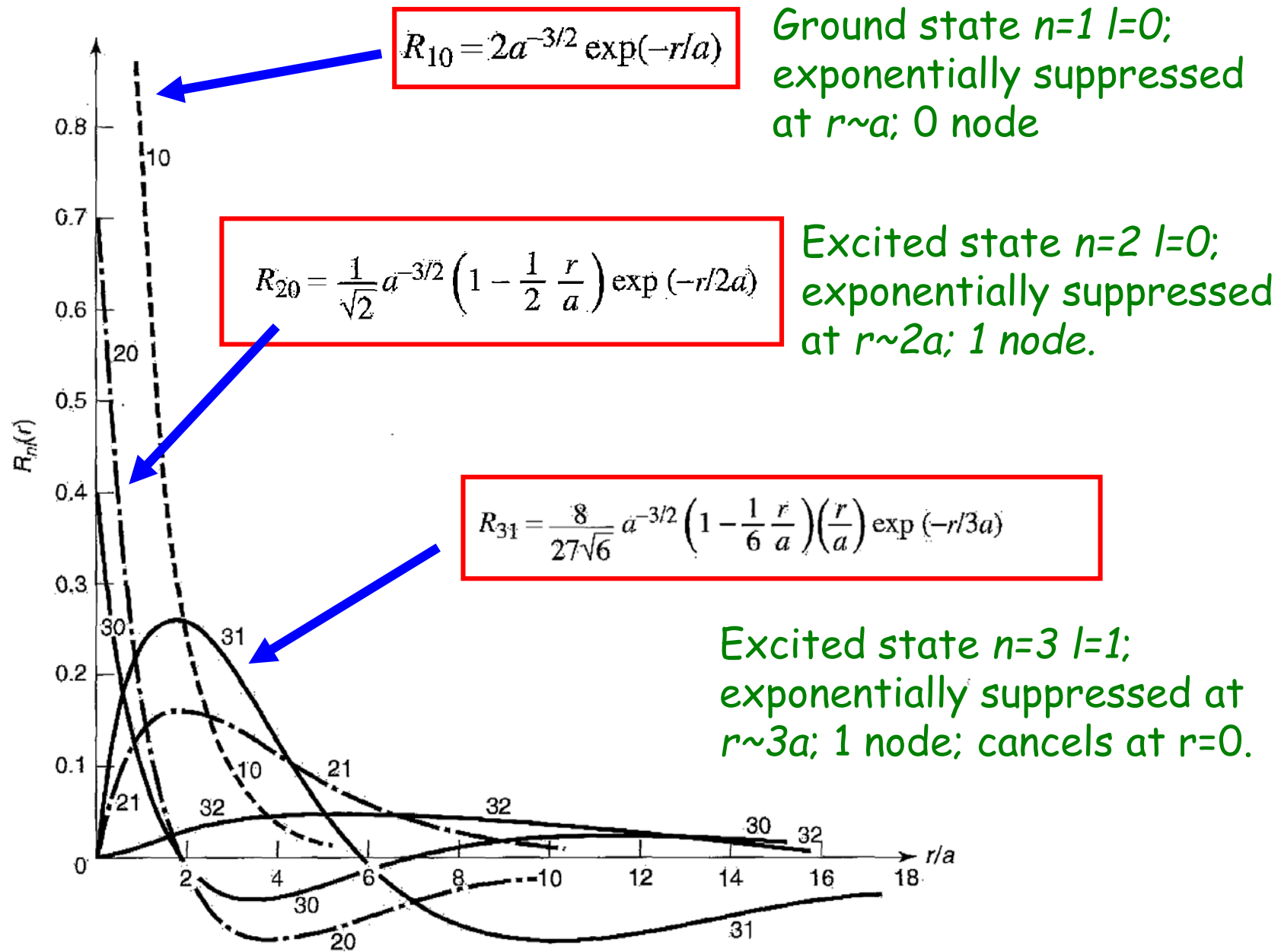
Only  $l=0$  are nonzero at the center  $r=0$ , as it happened in the spherical well.

3 nodes

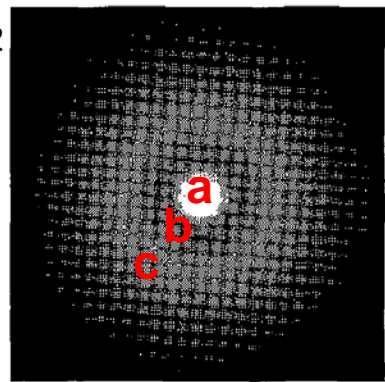
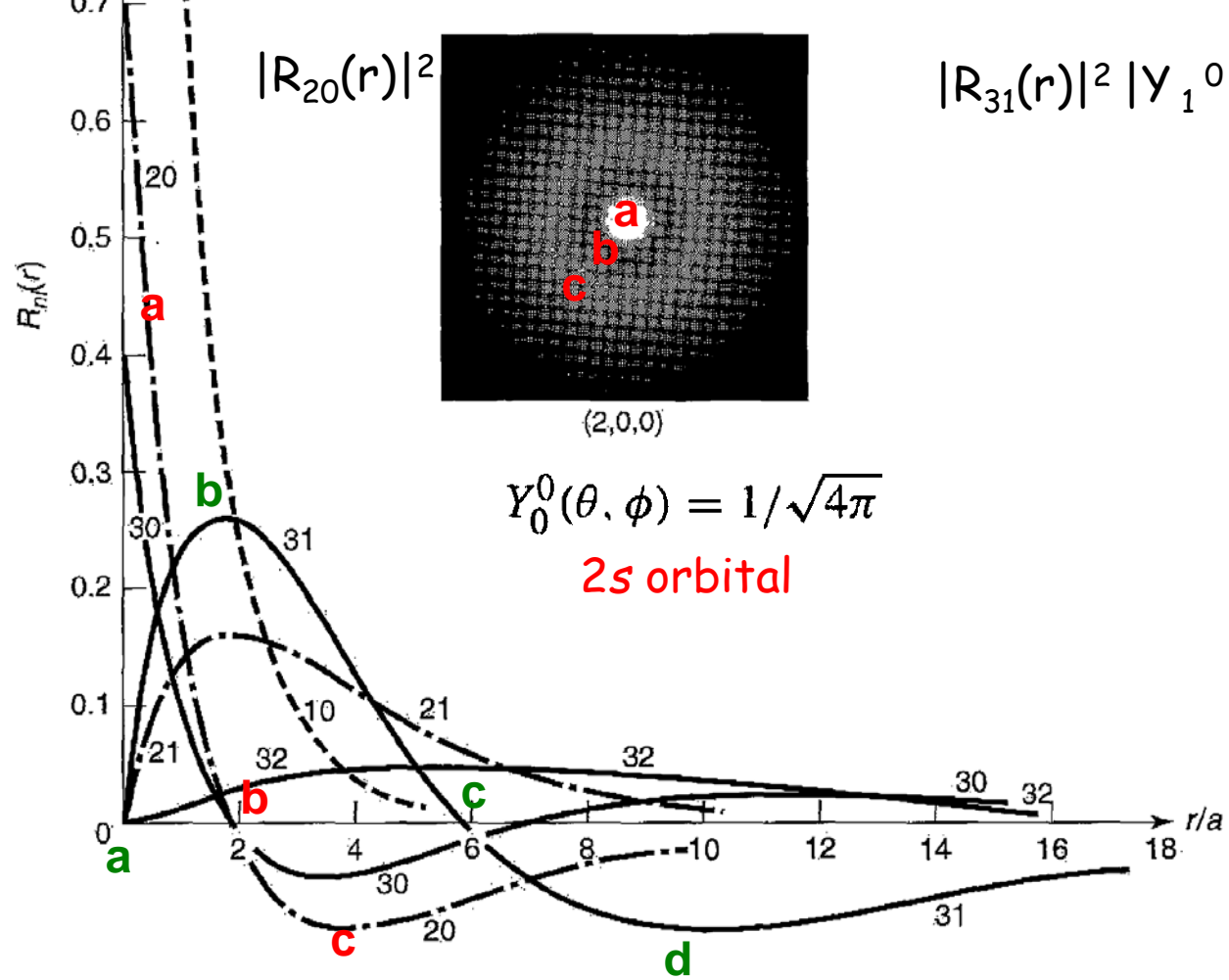
2 nodes

1 nodes

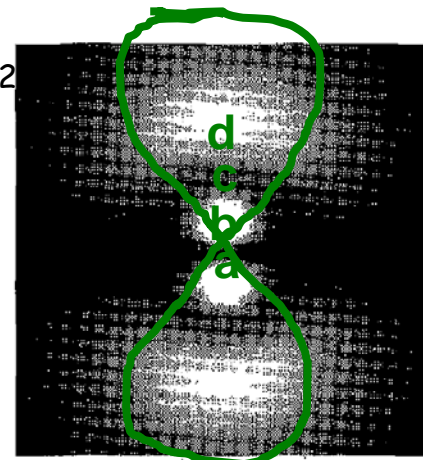
0 nodes





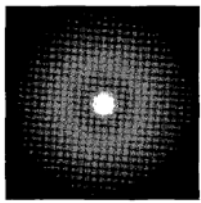


$|R_{31}(r)|^2 |Y_1^0|^2$

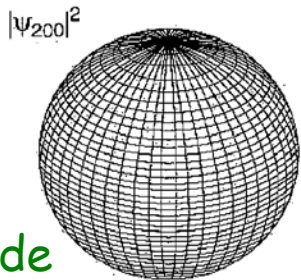


$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$   
**3p<sub>z</sub> orbital**

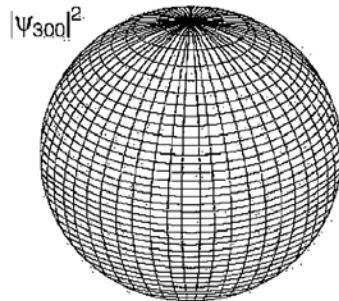
$(3,1,0)$



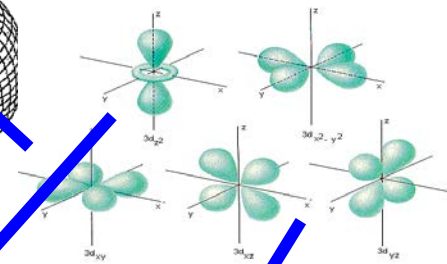
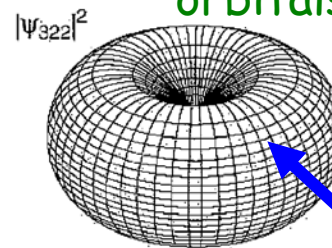
2s orbital  
1 node inside



3s orbital, 2 nodes inside

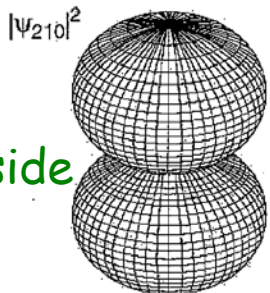


By linear combinations you recover the canonical 3d orbitals of textbooks

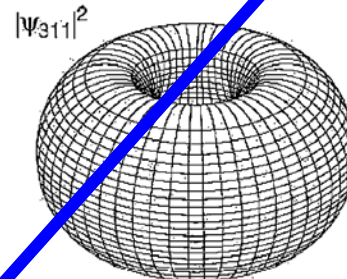
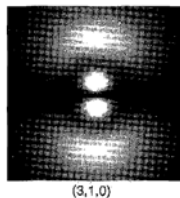
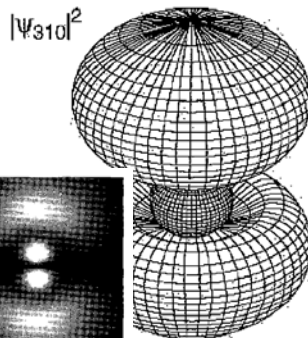


$l=2, m=-2,-1,0,1,2$

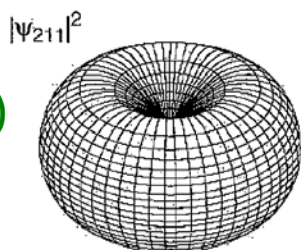
3p<sub>z</sub> orbital, 1 node inside



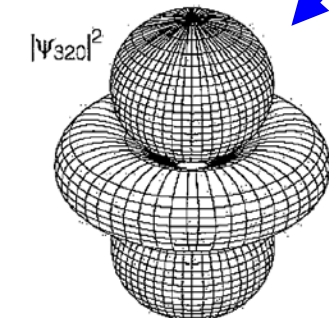
2p<sub>z</sub> orbital  
0 nodes inside



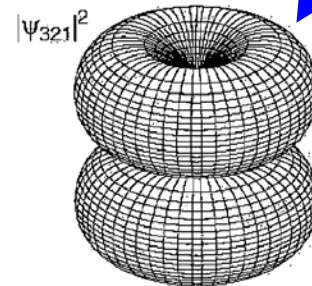
3(p<sub>x</sub>+ip<sub>y</sub>)  
orbital, 1 node



2(p<sub>x</sub>+ip<sub>y</sub>)  
orbital



3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> orbital,  
0 node inside



linear combination  
of canonical 3d  
orbitals d<sub>xz</sub> and d<sub>yz</sub>

And as usual, the wave functions are **orthonormal**:

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta dr d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

Because of  
radial  
equation.

Because of  
spherical  
harmonics.