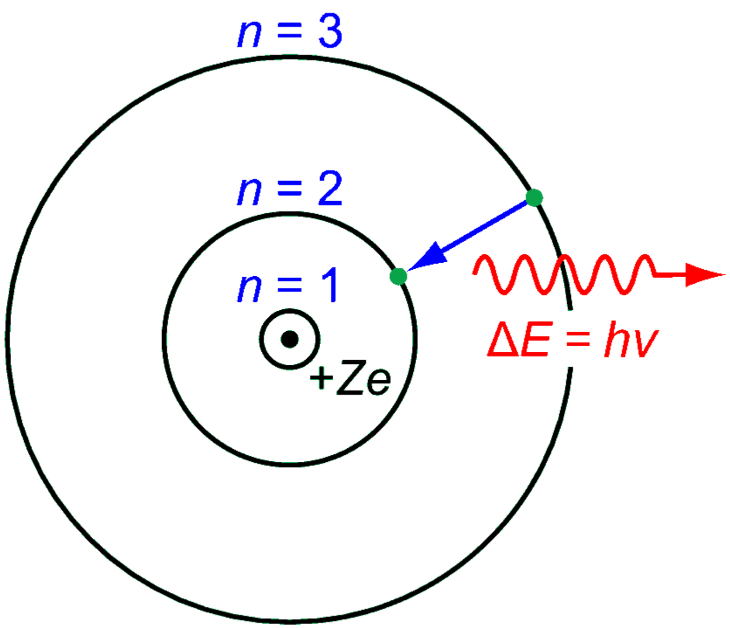
THE HYDROGEN ATOM

General Chemistry I, Lecture Series 6

Pengxin Liu

Reading:
OGB8 §5.1, YY §2.3

The first: Bohr Model

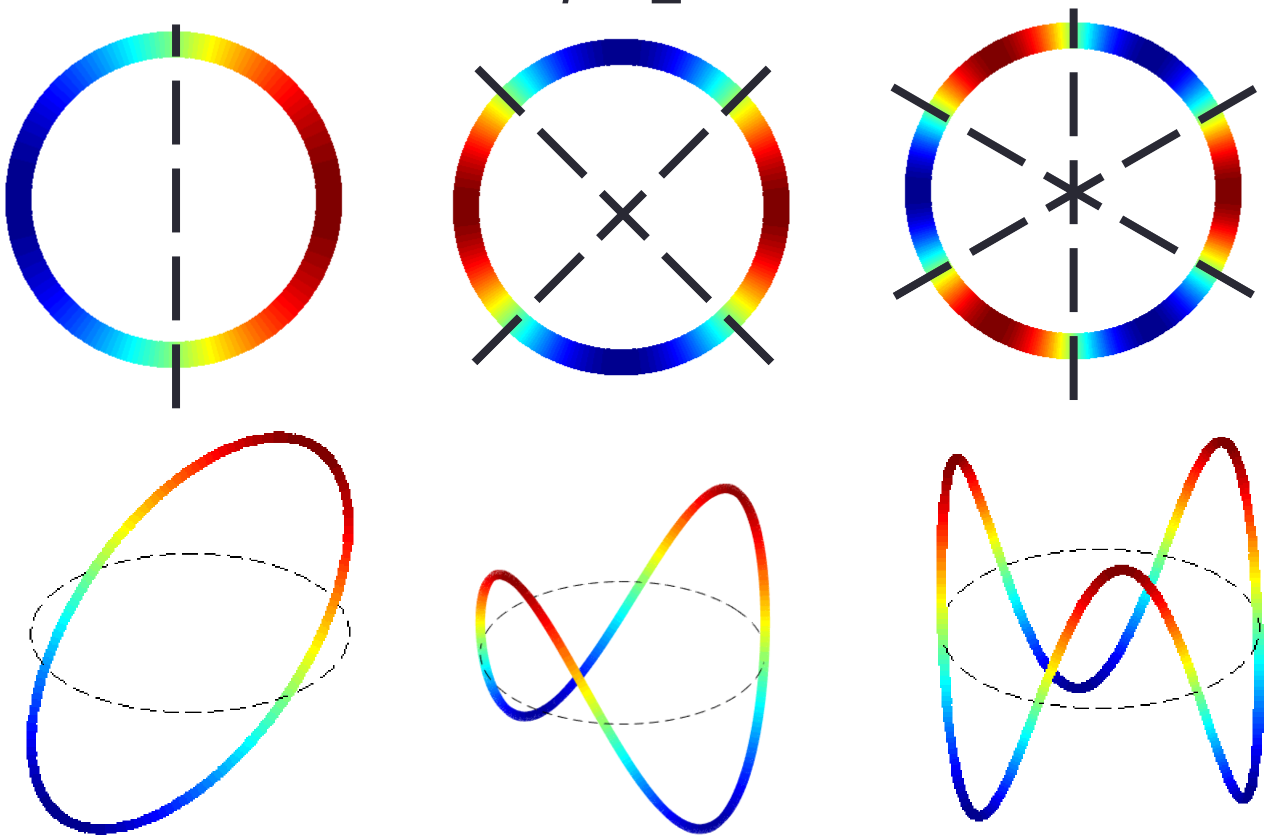


Old Quantum theory

- The electron orbits the nucleus. Each orbit is a circle specified by an angular momentum $L = nh/2\pi$ ($n \in \mathbb{N}$).
- The electron is stable in these orbits, but gains or loses energy when jumping between the orbits.

The second: Standing Wave Model

$l = 1$ $l = 2$ $l = 3$



de Broglie wave

$2\pi r = \lambda$

$2\pi r = 2\lambda$

$2\pi r = 3\lambda$

The third: Schrodinger equation

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

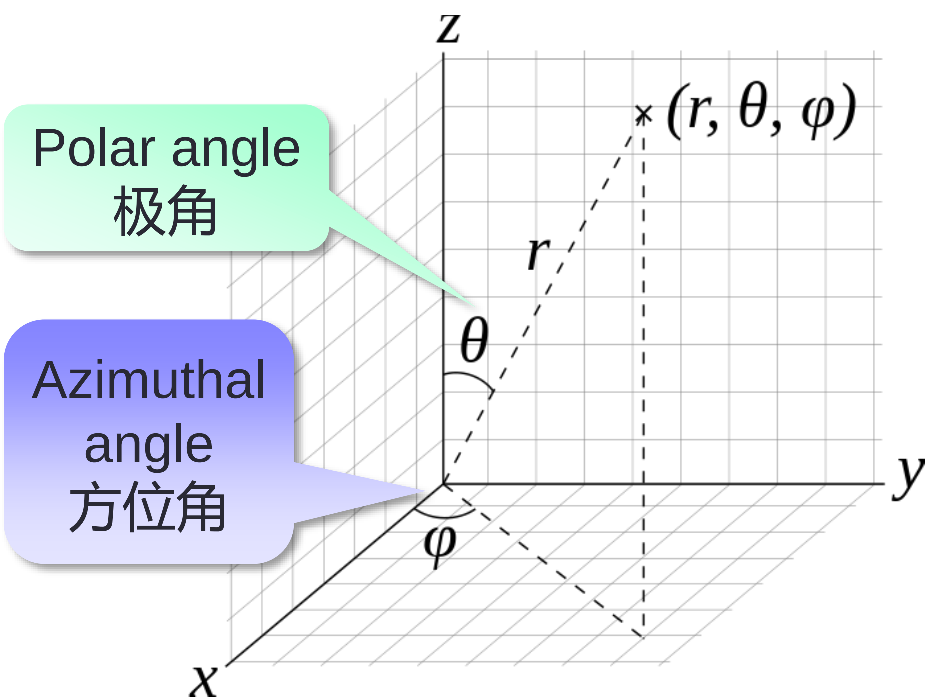
$$-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\cdot - V\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

Spherical Polar Coordinates
球极坐标

$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = rcos\theta$$



Wave function of hydrogen atom

General solution

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

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

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

$$Y_{lm}(\theta, \phi) = (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\phi}$$

Outline

- Atomic orbitals: Appearance
  - Quantum number
  - Oscillations in 1D, 2D and 3D
  - Shape of H atomic orbitals

- Atomic orbitals: Size
  - Most probable radius r_{mp}

The Three Quantum Numbers

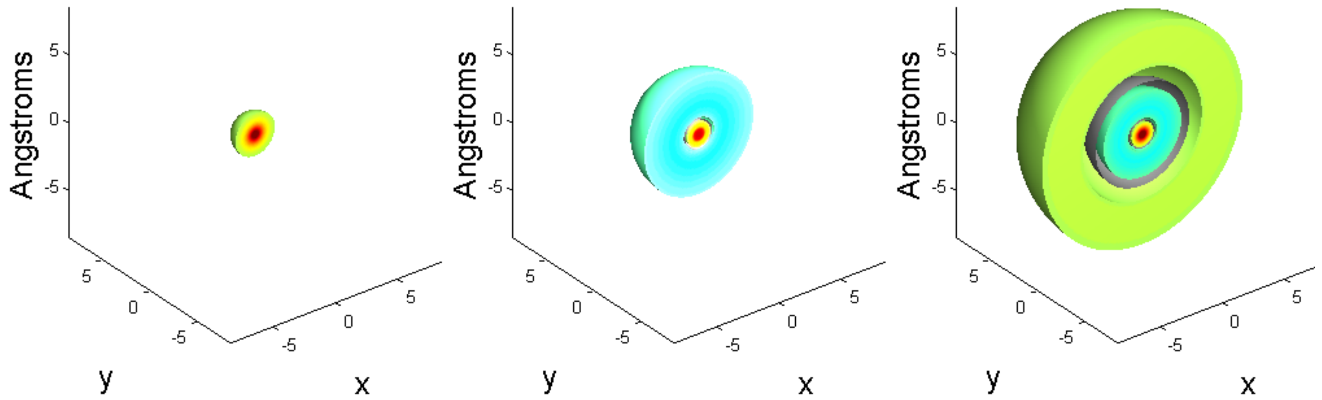
- **The Principal Quantum Number 主量子数 (n)**

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

The Three Quantum Numbers

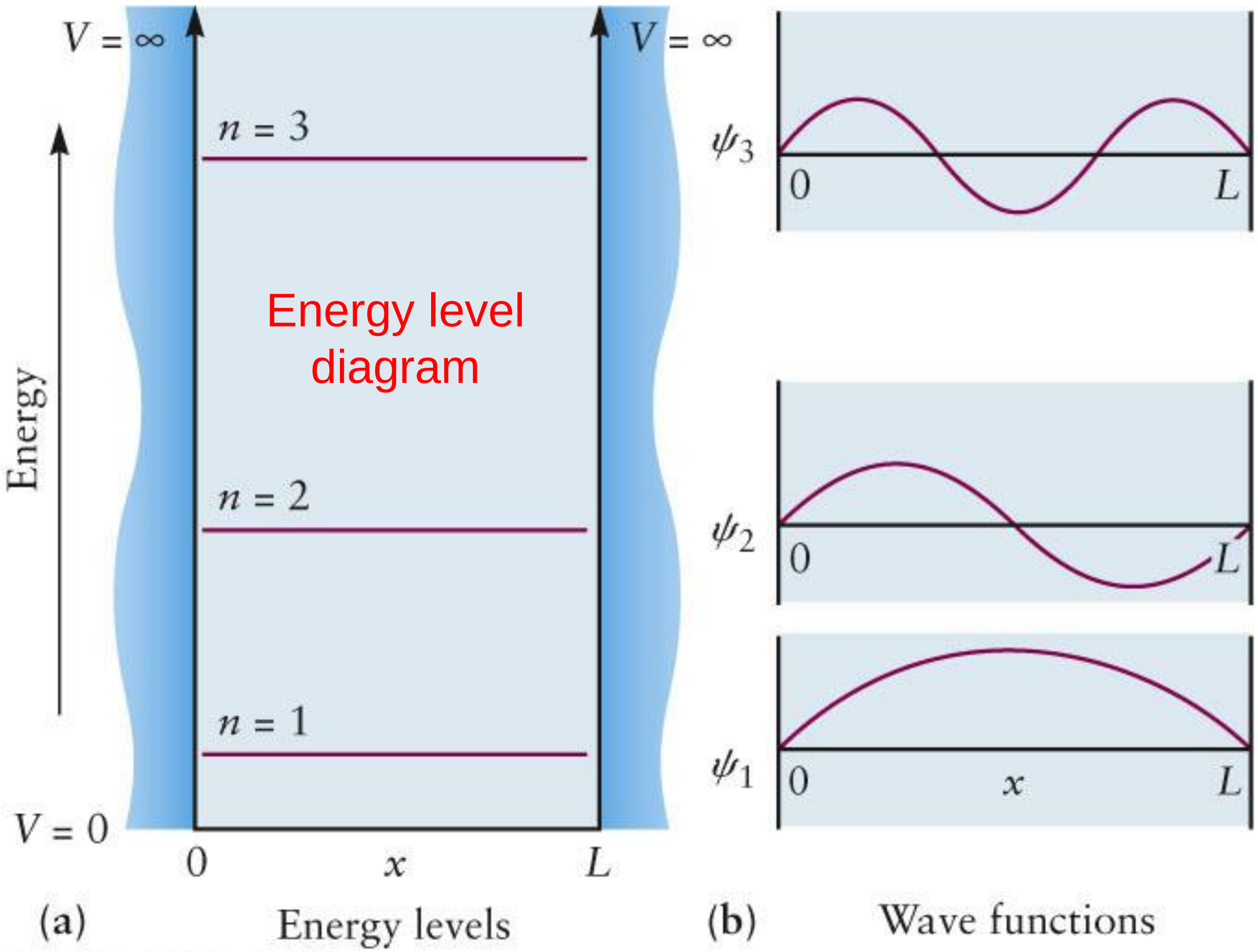
- **The Principal Quantum Number 主量子数 (n):** One of three quantum numbers that tells the the energy of the electron and the average distance of an electron from the nucleus

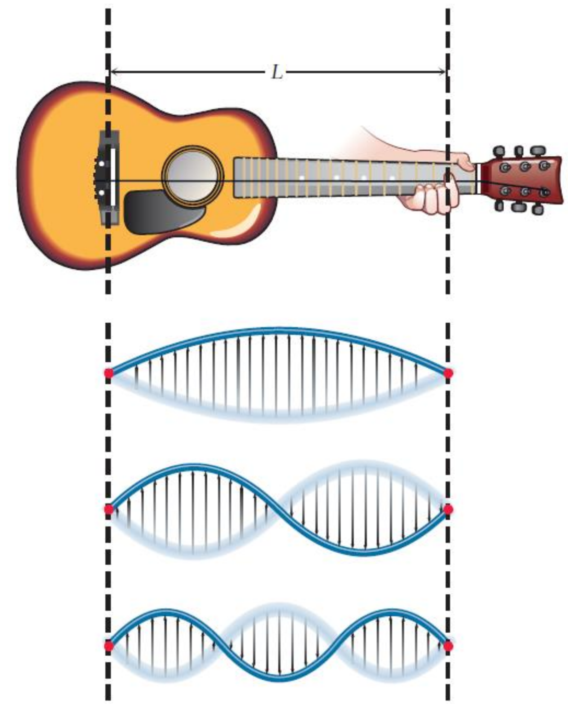
- n= 1, 2, 3, 4, ...



n in 1D Standing Wave

The n^{th} Wave function: $\psi_n(x) \propto \sin\left(n\pi\frac{x}{L}\right)$, n = number of nodes + 1.

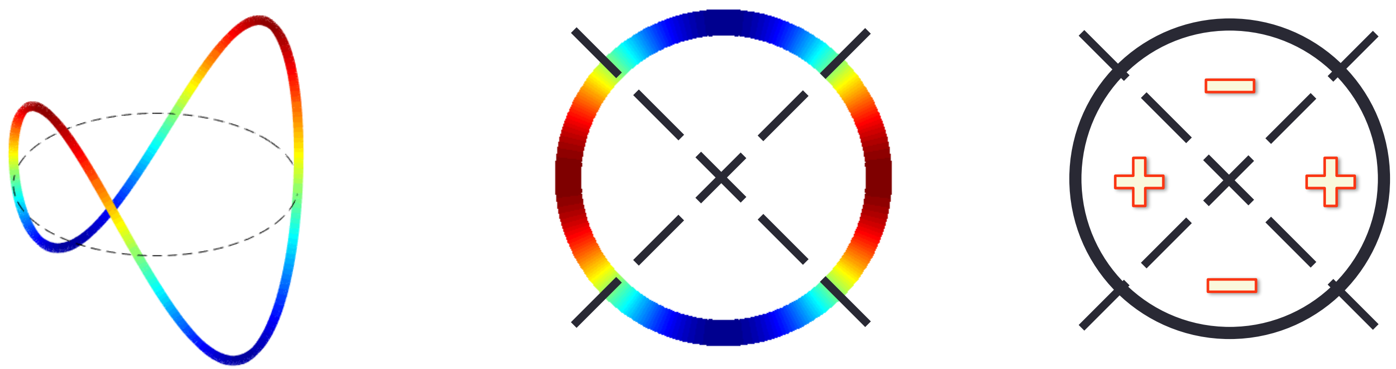




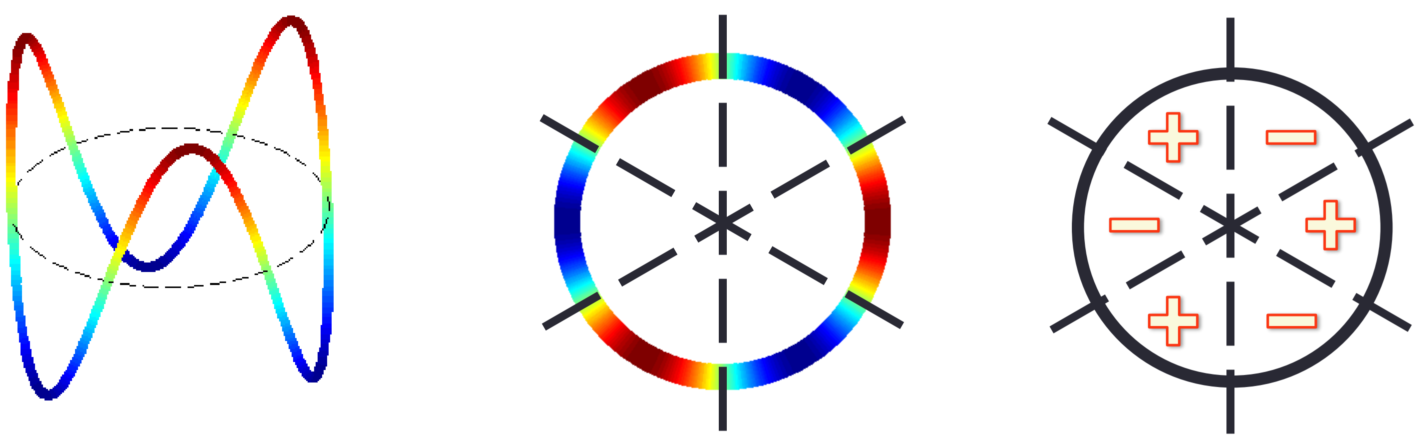
n in 1D circular Standing Wave

$2\pi r = \lambda$

$2\pi r = 2\lambda$

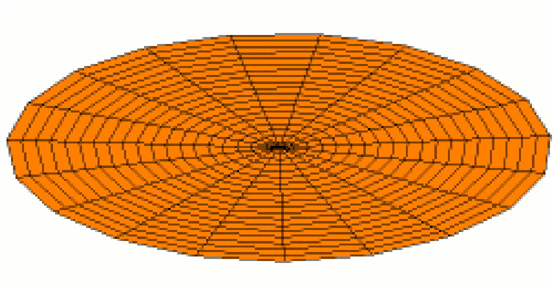


$2\pi r = 3\lambda$

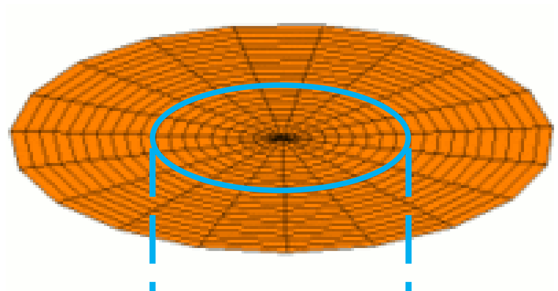


n in oscillations of a Round Plate

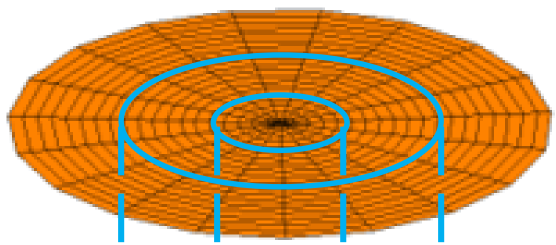
No nodes



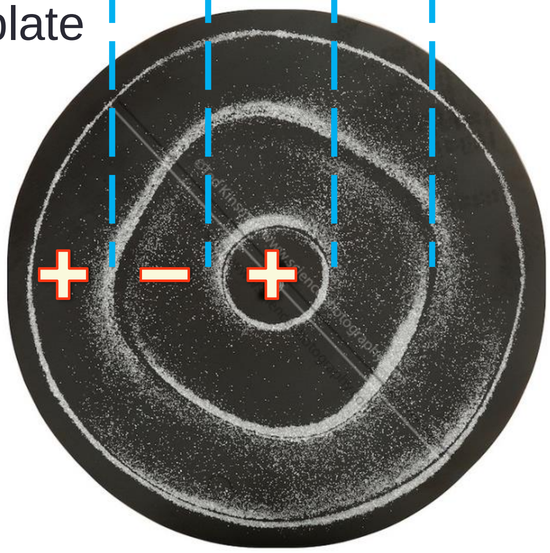
1 nodal ring
(radial node)



2 nodal rings



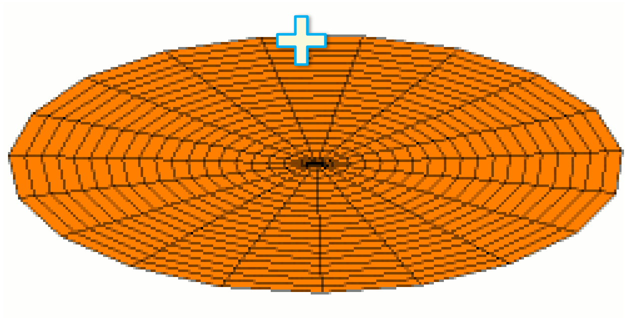
Top view of
sand on plate

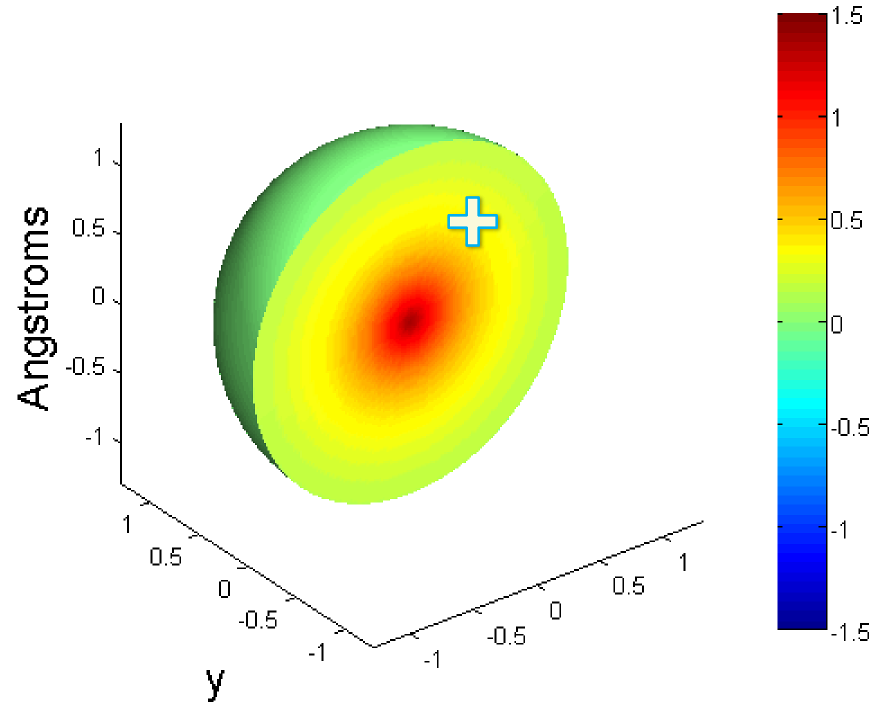


The 1*s* Wave in 3D

No nodes.

$n = 1, l = 0 \Longrightarrow 1s$

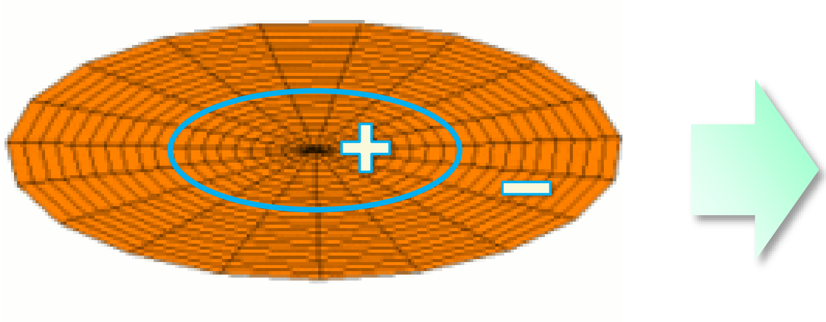


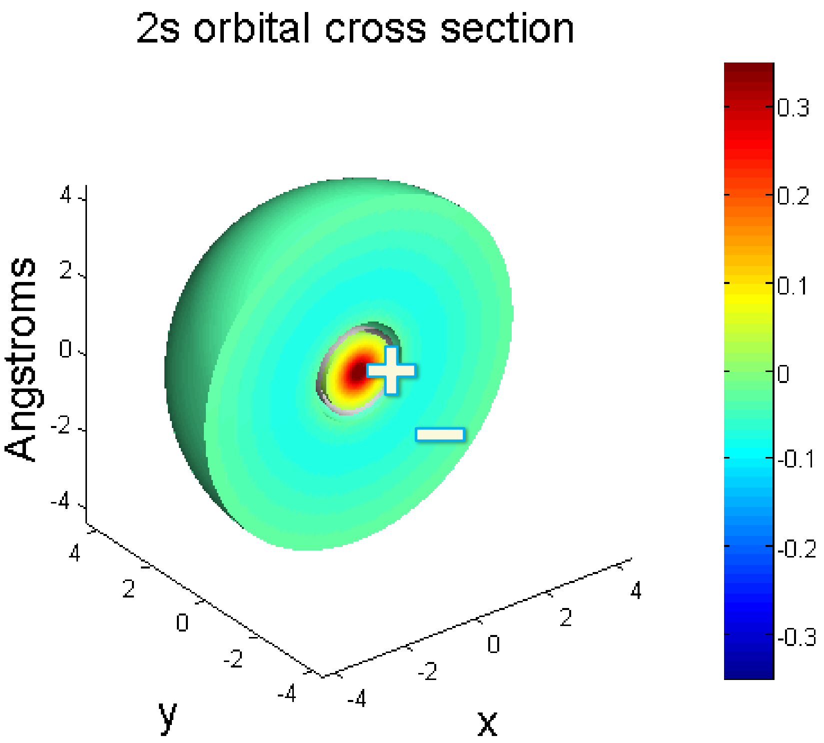


The 2*s* Wave in 3D

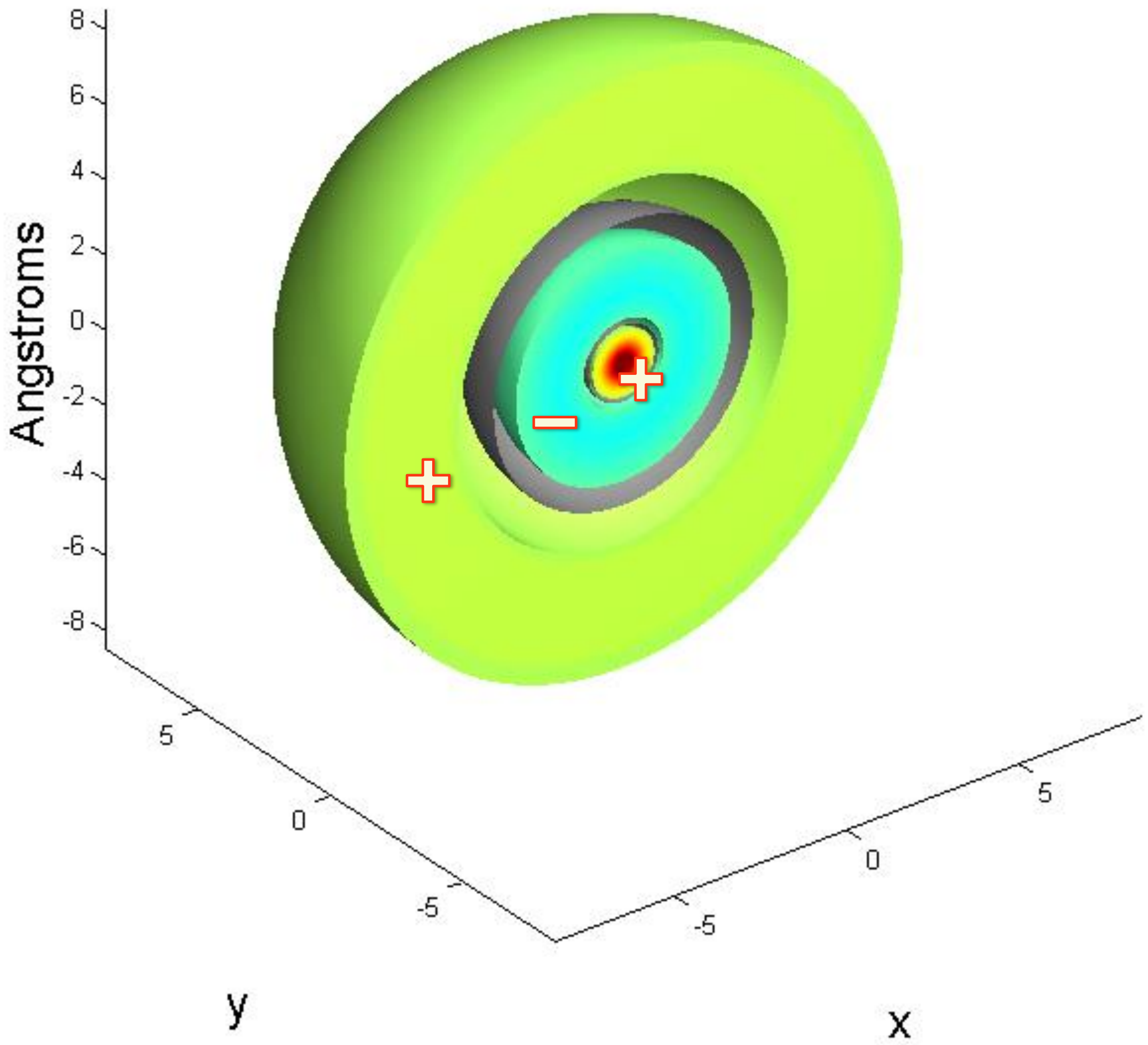
1 nodal sphere (radial node)

$n = 2, l = 0 \Longrightarrow 2s$

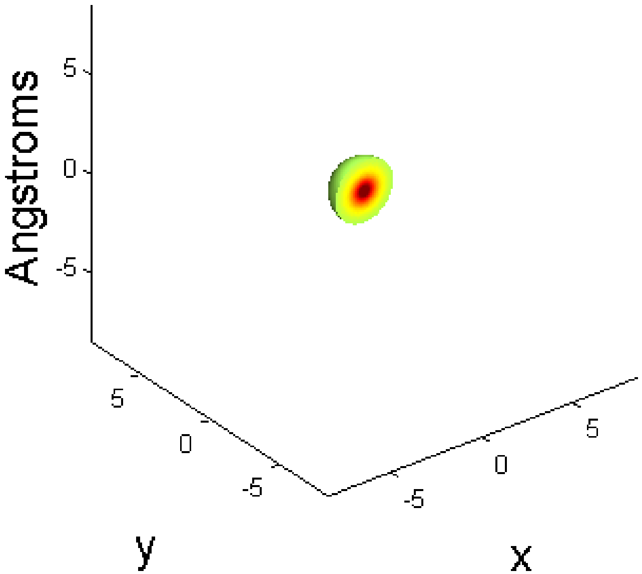




The 3s Orbital

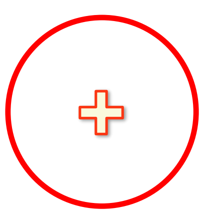


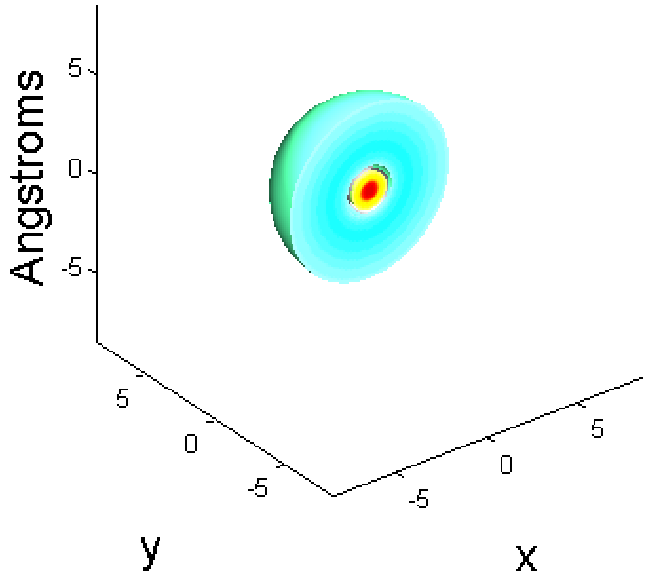
Comparison of 1*s*, 2*s*, 3*s* Orbitals



1*s*

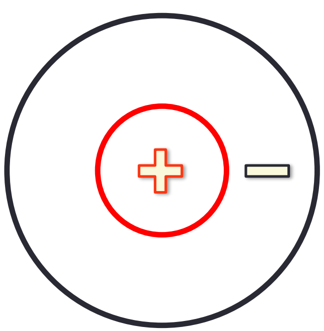
n = 1, *l* = 0.

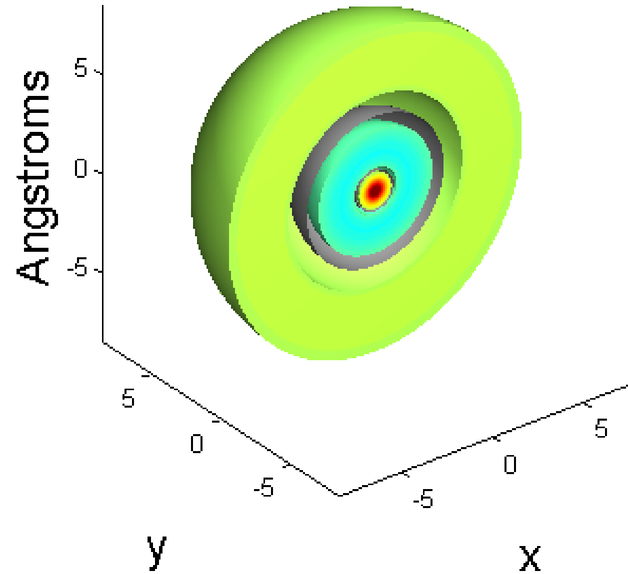




2*s*

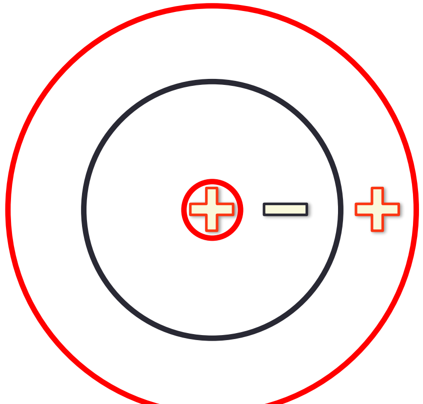
n = 2, *l* = 0.





3*s*

n = 3, *l* = 0.



Wave function of hydrogen atom

General solution

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

$$R_{nl}(r) \;\; = \;\; - \left[\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2} \left(\frac{2r}{na_0} \right)^l e^{-r/na_0} \, L_{n+l}^{2l+1}(2r/na_0)$$

$$Y_{lm}(\theta,\phi) \;\; = \;\; (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos\theta)\, e^{im\phi}$$

The Three Quantum Numbers

- **The Azimuthal(Angular) Quantum Number 角(动量)量子数 (l):** One of three that describes the shape of the region of space occupied by an electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

- l = 0,1,.,2, 3,..(n−1)

- n = 1, l = 0 (s)
- n = 2, l = 0, 1 (s, p)
- n = 3, l = 0, 1, 2 (s, p, d)

- s, p, d, f, g, h, i

The Three Quantum Numbers

- **The Magnetic Quantum Number 磁量子数 (m):** One of three that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field. The allowed values of m depend on the value of l: m can range from −l to l in integral steps:

- m = −l, −l+1, ... 0, ... l−1, l

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

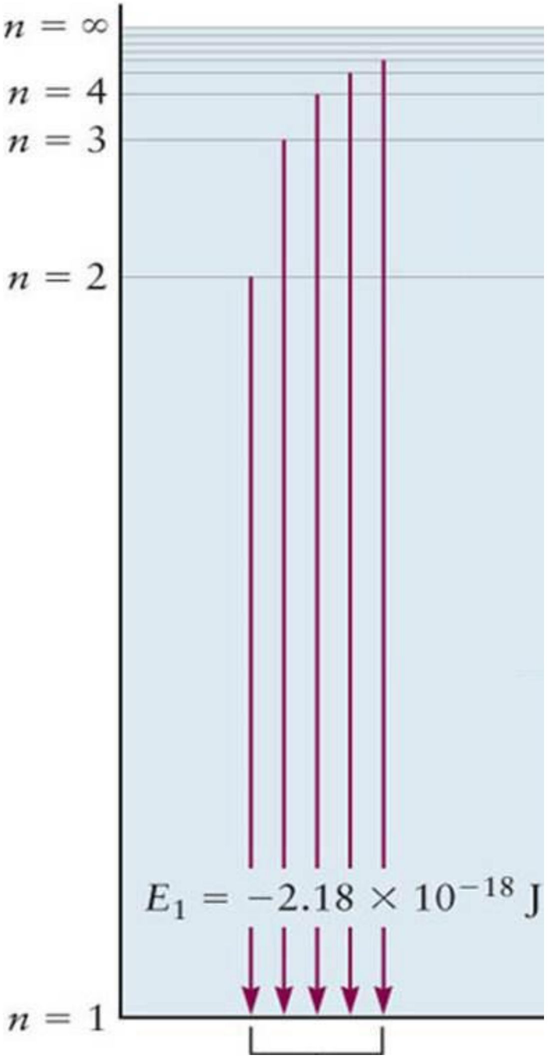
The Three Quantum Numbers

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

An orbital with quantum numbers n and l has l angular nodes and n-l-1 radial nodes, giving a total of n-1 nodes. An angular node is defined by a plane. A radial node is defined by a spherical surface.

Orbital Energy

Bohr, OGB8 p.143

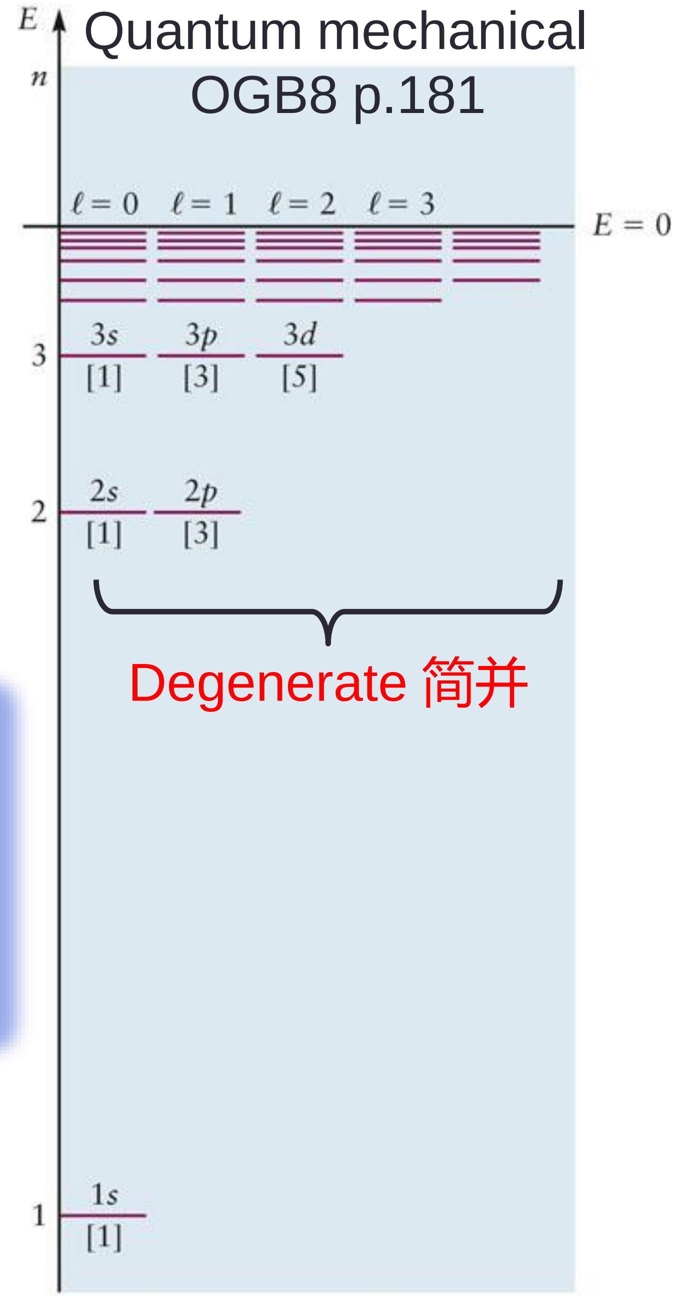


$$E_n = -\frac{\mathrm{Ry}}{n^2},$$

$$\mathrm{Ry} = 2.18\times10^{-18}\ \mathrm{J}$$

$$= 13.6\ \mathrm{eV}$$

Quantum mechanical OGB8 p.181



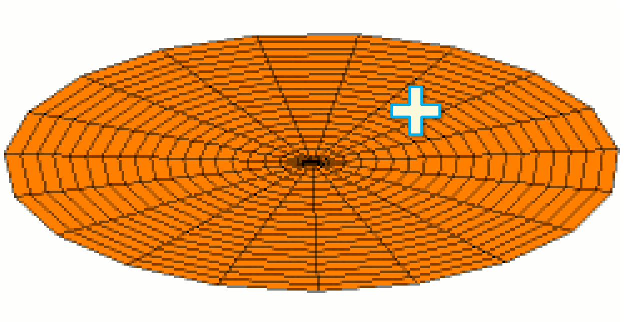
Degenerate 简并

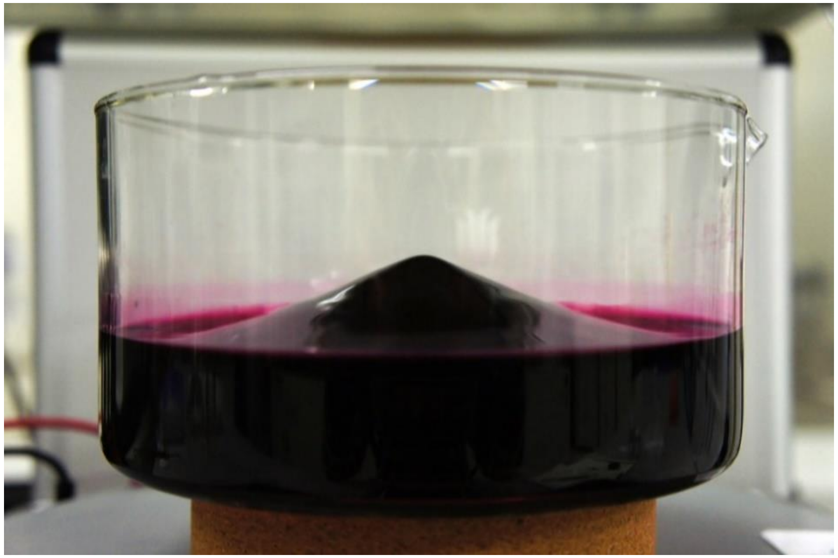
Outline

- Atomic orbitals: Appearance
  - Quantum number
  - Oscillations in 1D, 2D and 3D
  - Shape of H atomic orbitals

- Atomic orbitals: Size
  - Most probable radius r_{mp}

The 1s Wave





主量子数
Principal quantum number n = Total number of nodes + 1

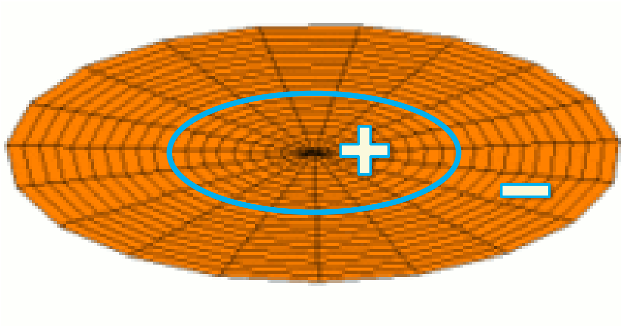
角(动量)量子数
Angular quantum number l = Number of angular nodes

$l = 0, 1, 2, 3\ldots \Rightarrow s, p, d, f\ldots$

No nodes.

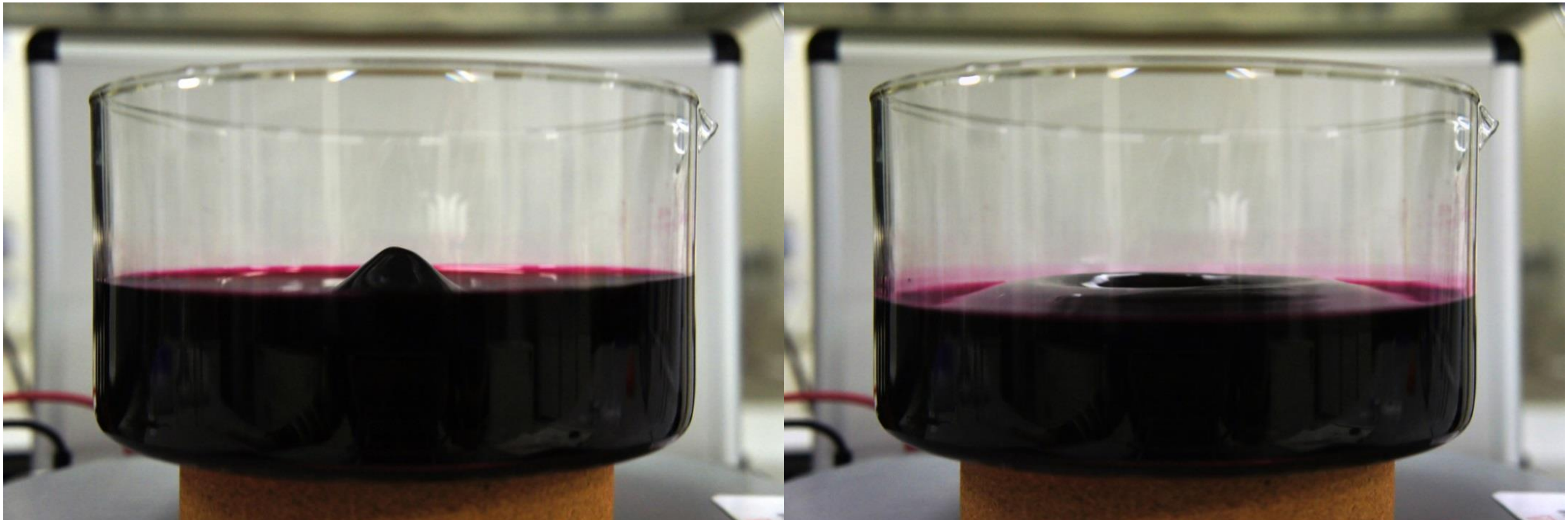
$n = 1, l = 0 \Rightarrow 1s$

The 2*s* Wave

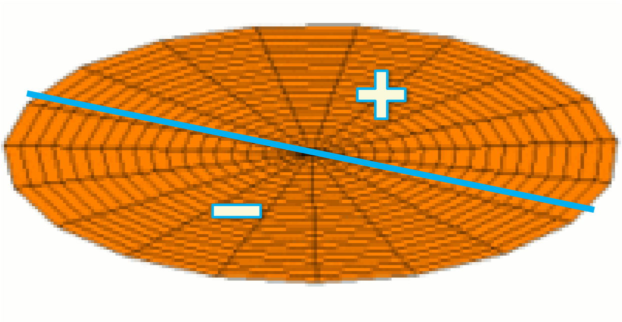


1 nodal ring (radial node)

$n = 2, l = 0 \Longrightarrow 2s$

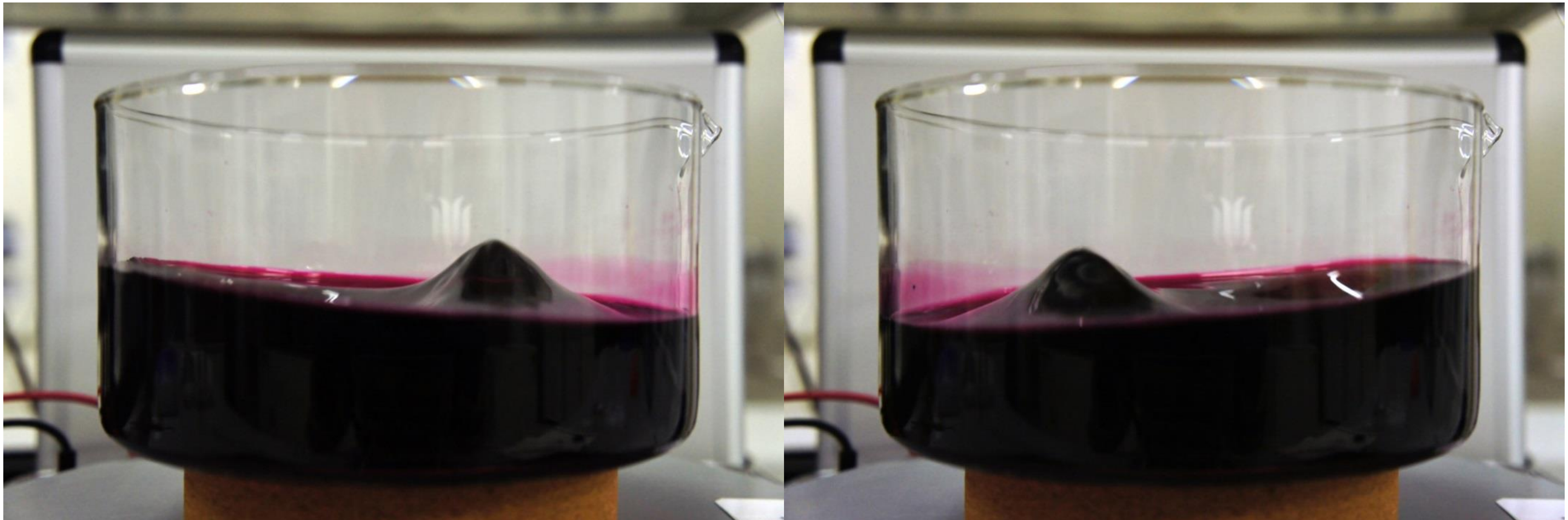


The 2*p* Wave

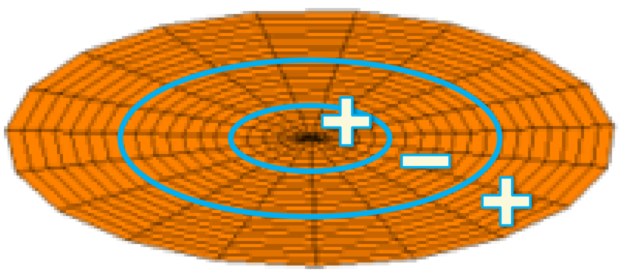


1 nodal line (angular node)

$n = 2, l = 1 \implies 2p$

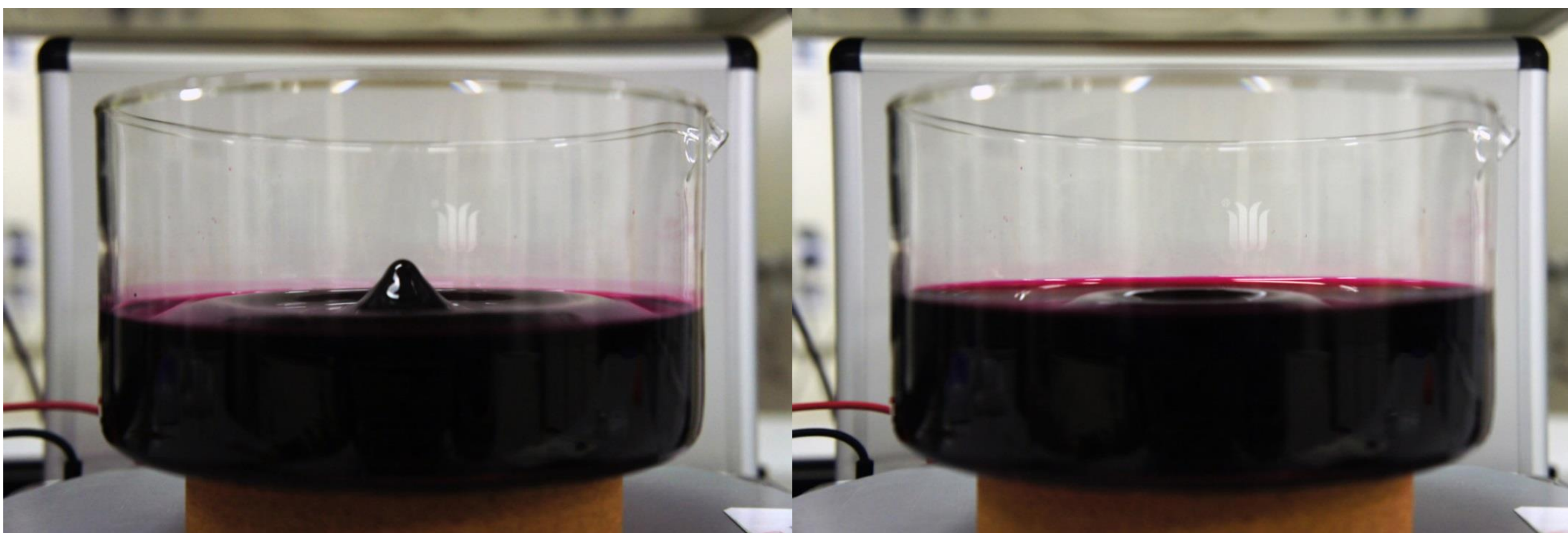


The 3s Wave

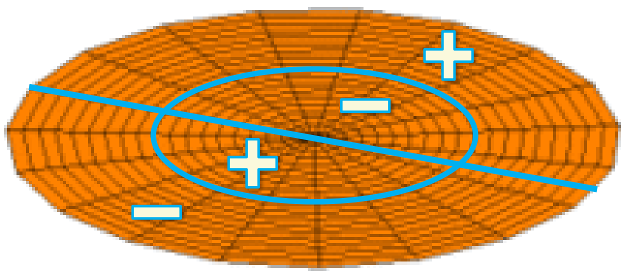


2 nodal rings (radial nodes)

$n = 3$, $l = 0$ $\Longrightarrow$ 3s



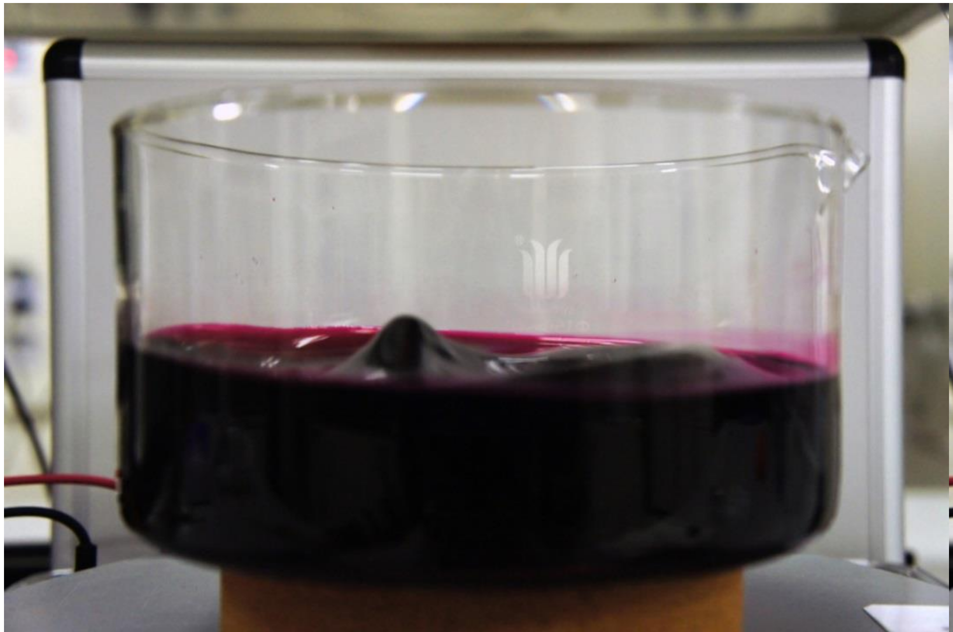
The 3*p* Wave

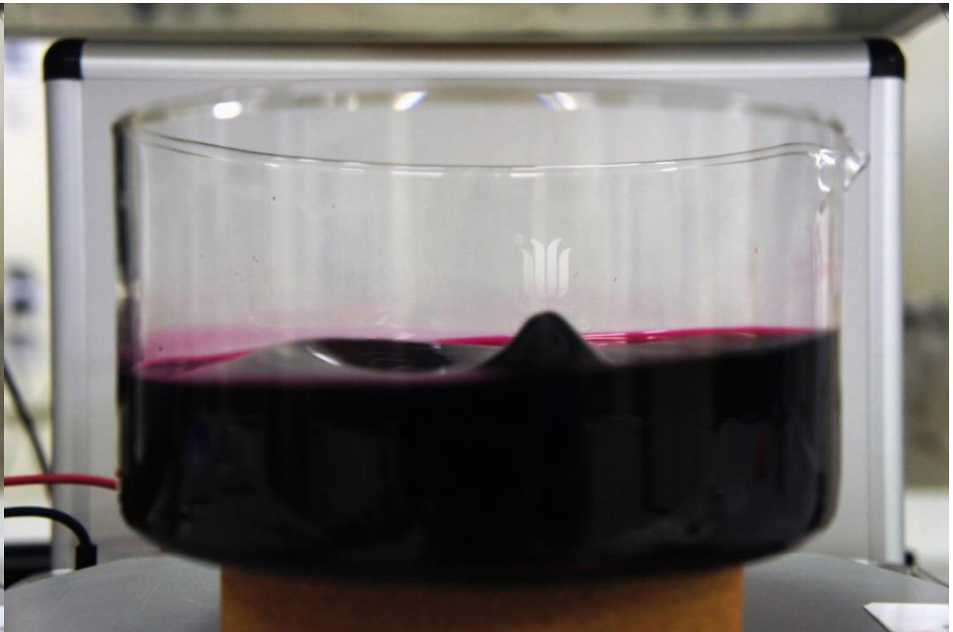


1 nodal ring (radial node)

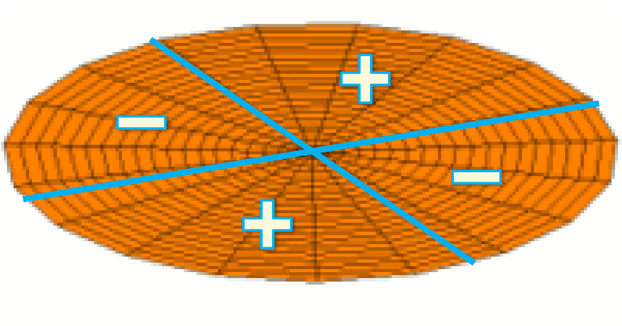
1 nodal line (angular node)

$n = 3, l = 1 \implies 3p$



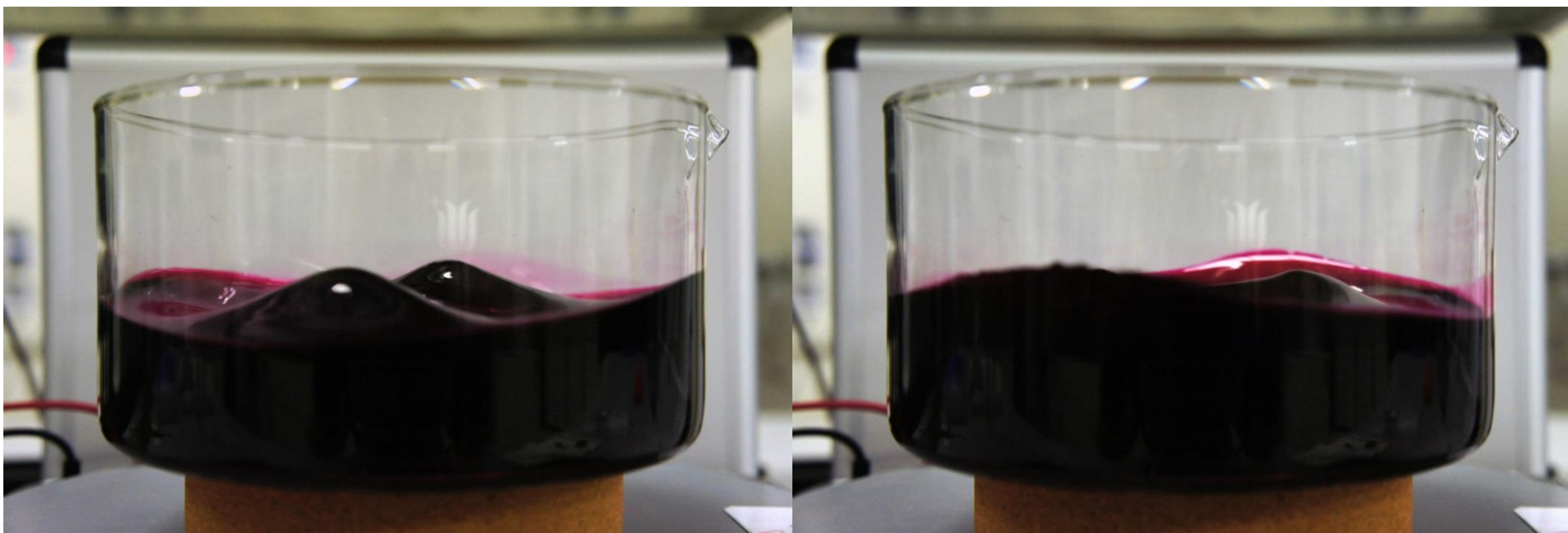


The 3*d* Wave



2 nodal lines (angular nodes)

$n = 3, l = 2 \implies 3d$



Outline

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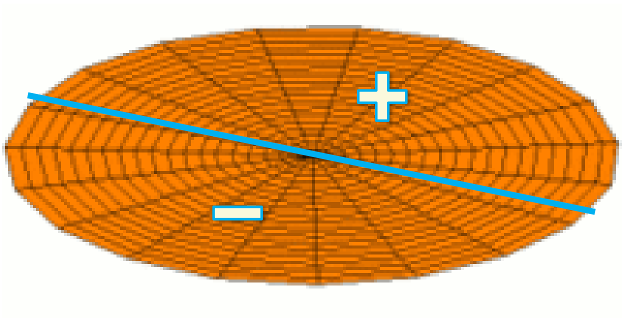
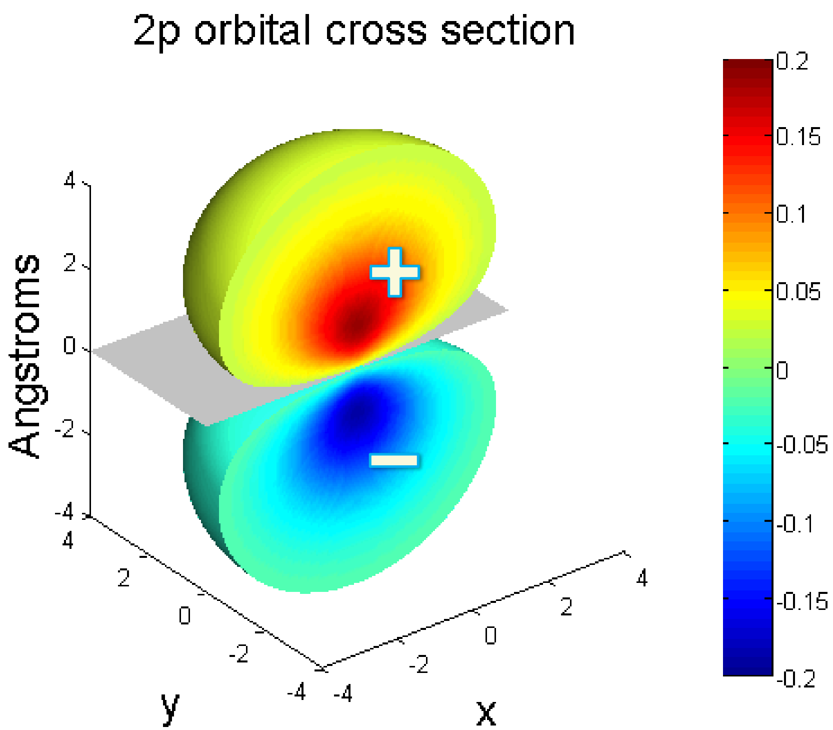
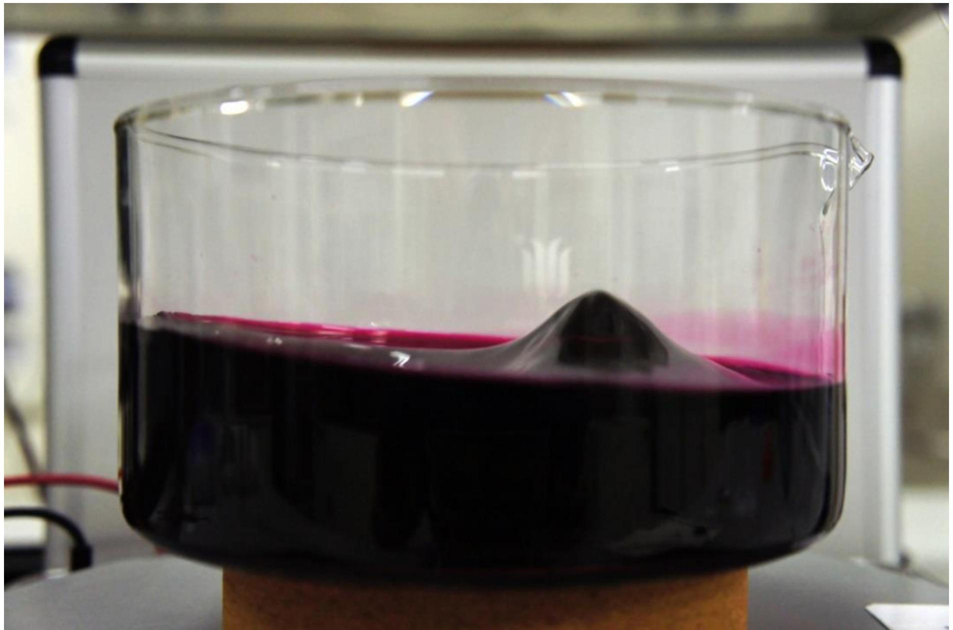
The 2*p* Wave in 3D



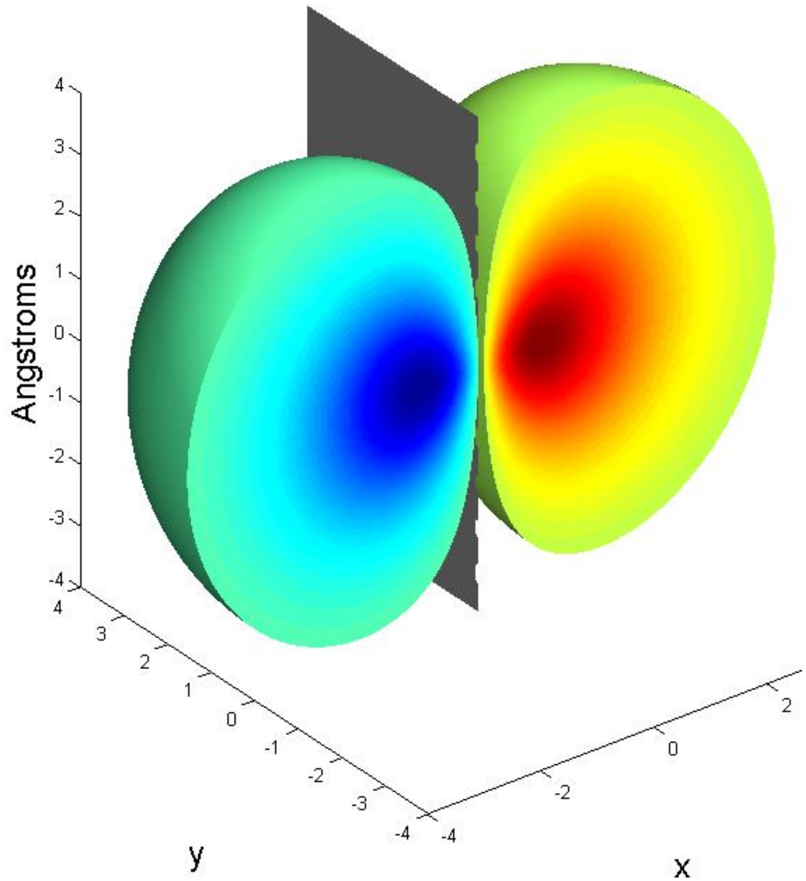




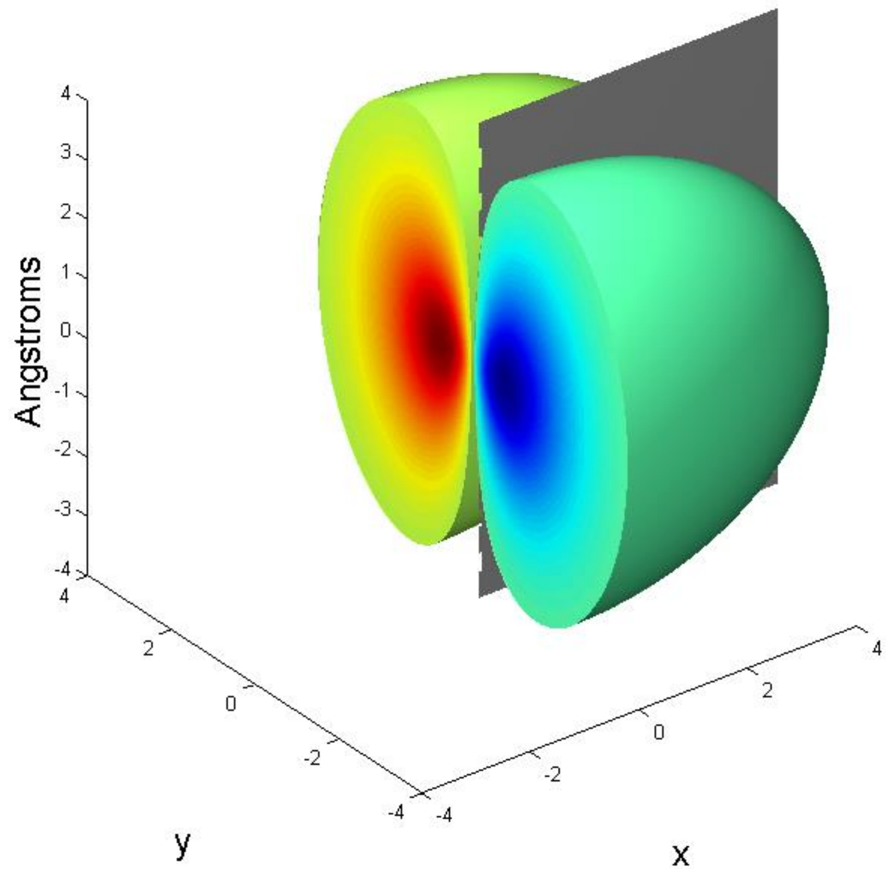
1 nodal plane (angular node)

$n = 2, l = 1 \implies 2p$

The $2p_x$ and $2p_y$ Orbitals

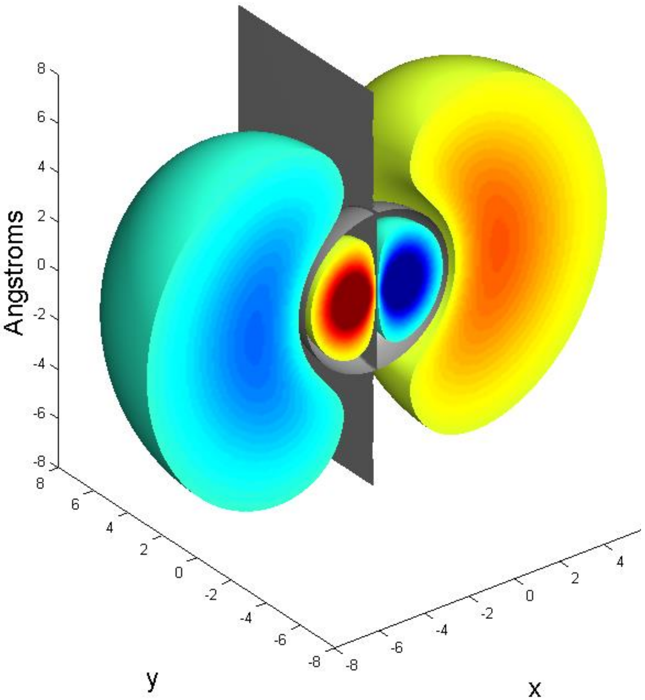


$2p_x$

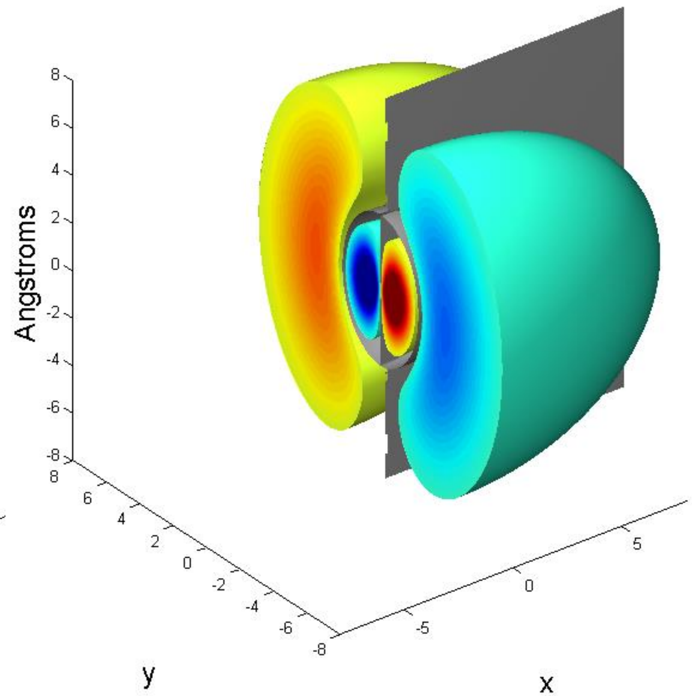


$2p_y$

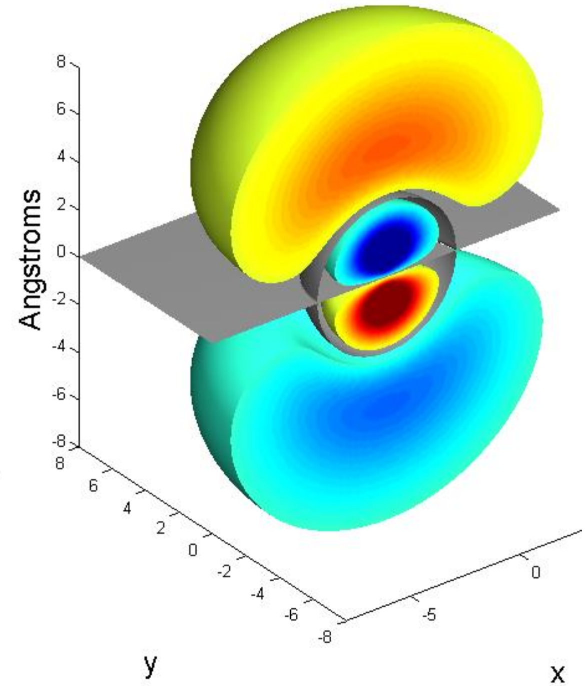
The 3*p* Orbitals



$3p_x$

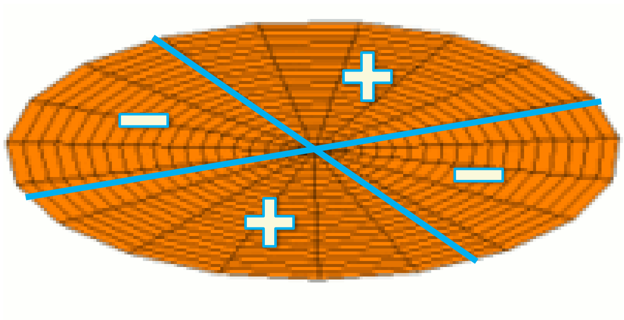


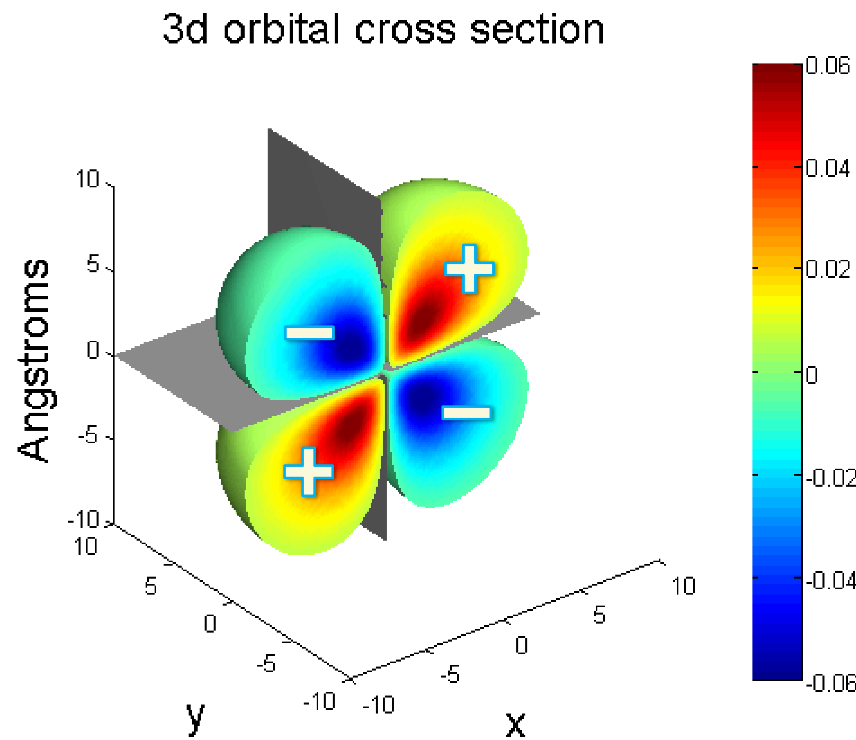
$3p_y$



$3p_z$

The 3*d* Wave in 3D

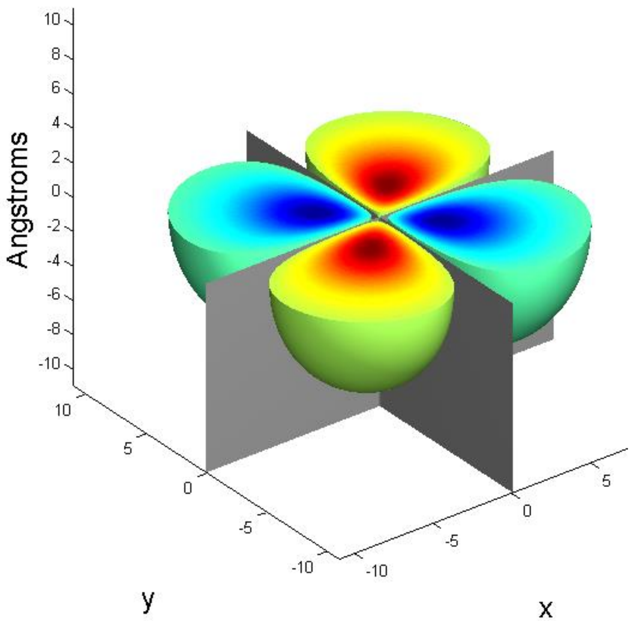




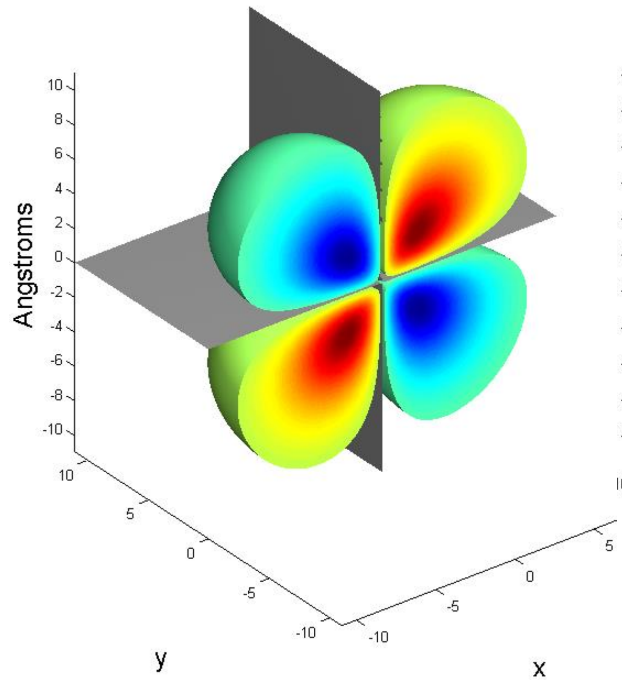
2 nodal planes (angular nodes)

n = 3, l = 2 $\Longrightarrow$ 3d

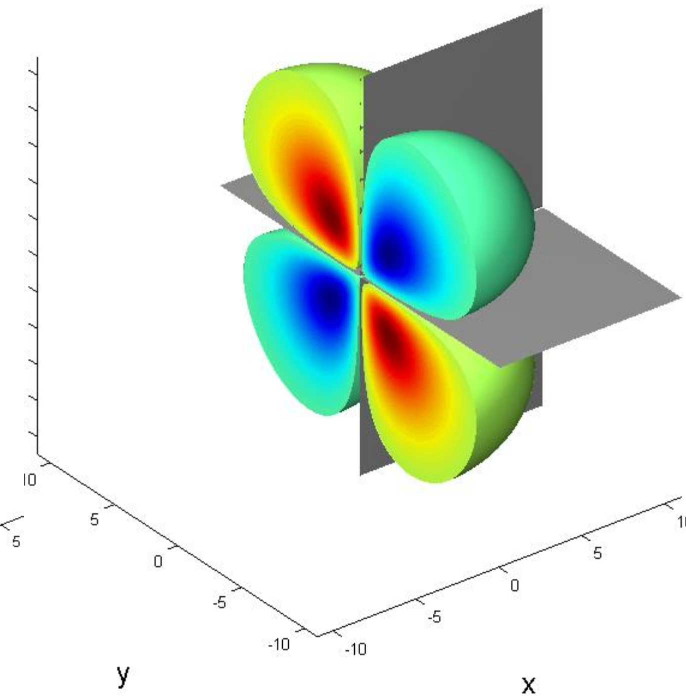
The 3*d* Orbitals (1)



$3d_{xy}$

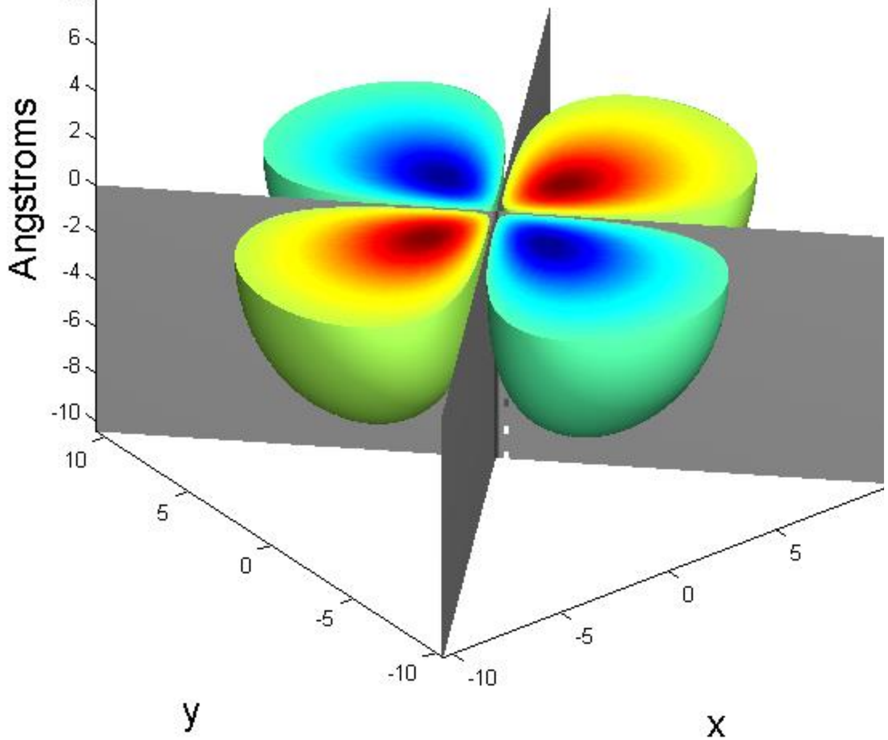


$3d_{xz}$

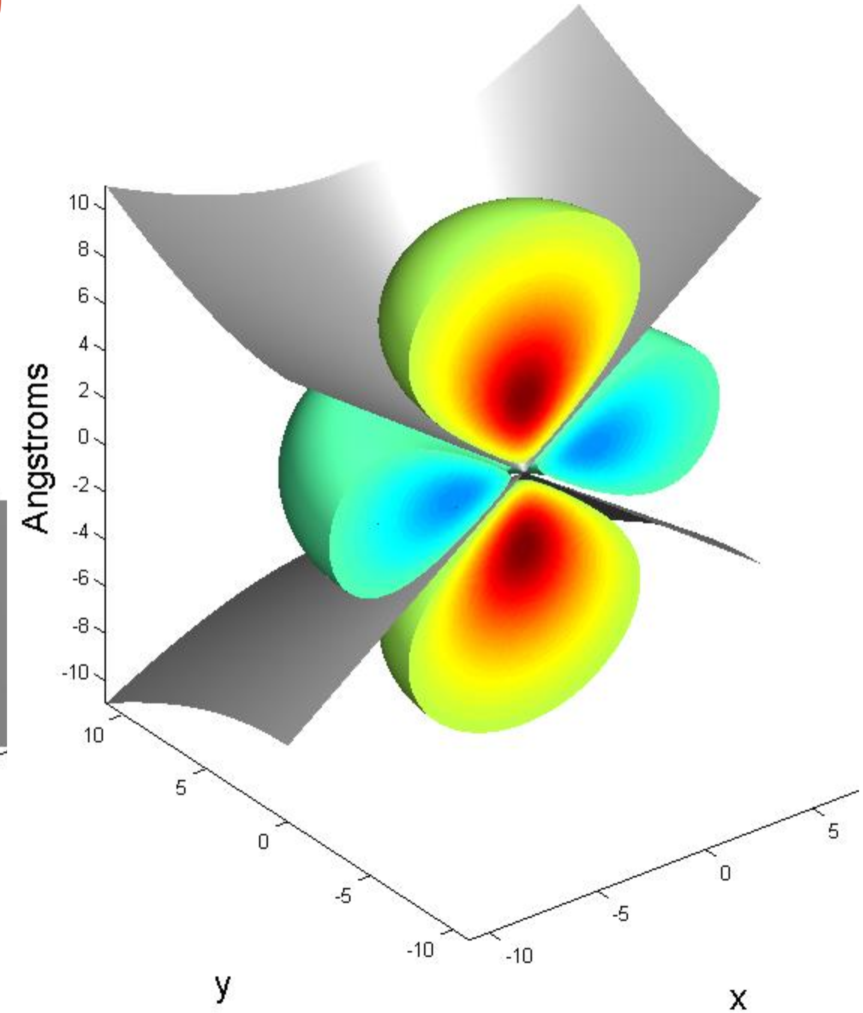


$3d_{yz}$

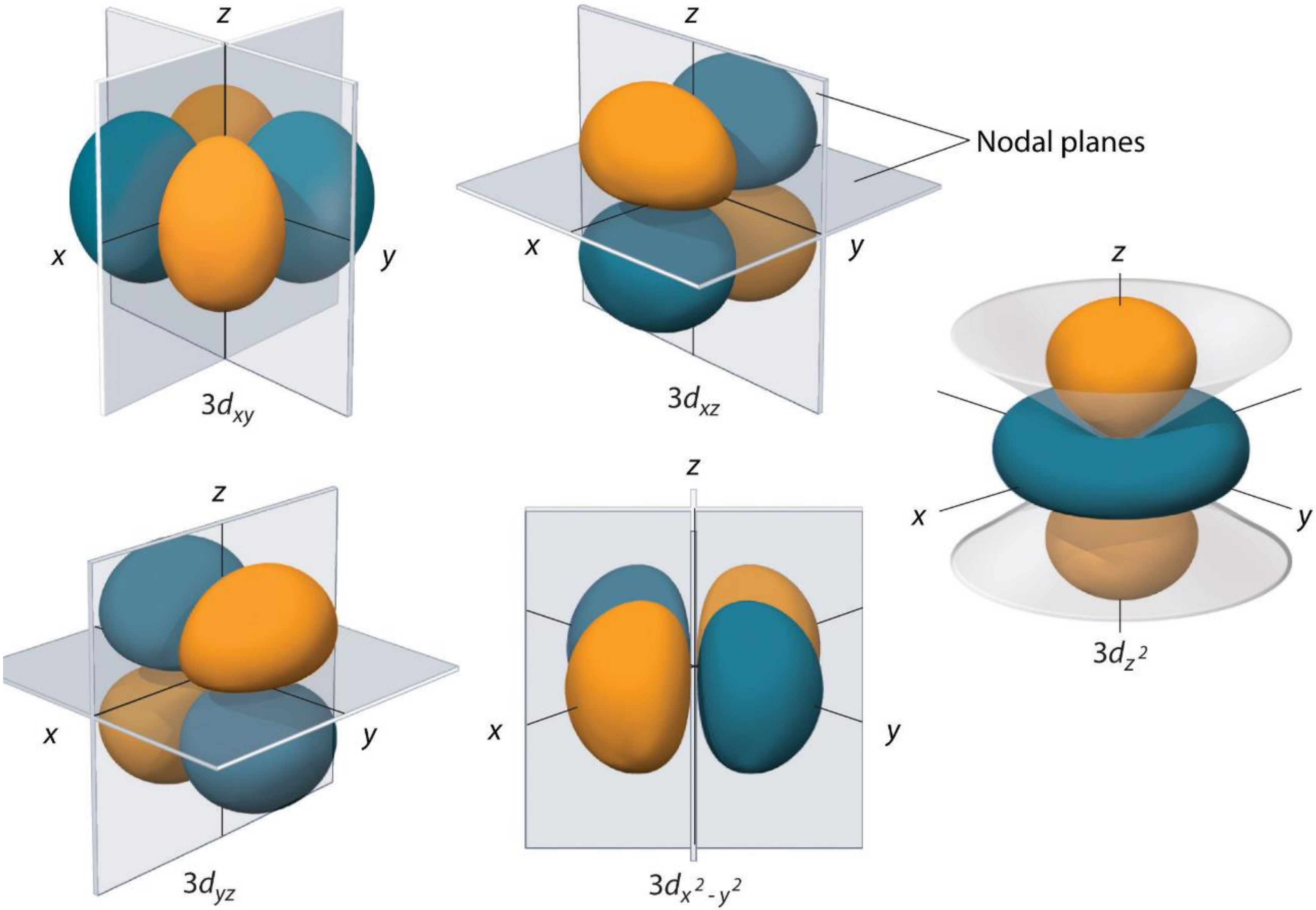
The 3*d* Orbitals (2)



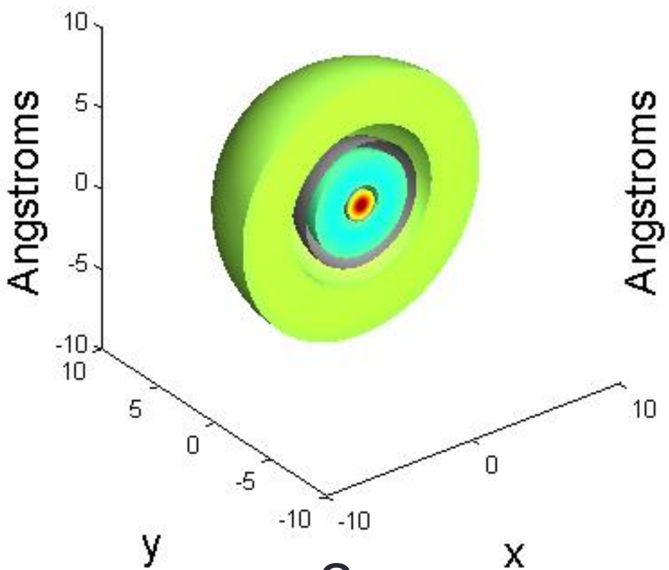
$3d_{x2-y2}$



$3d_{z2}$

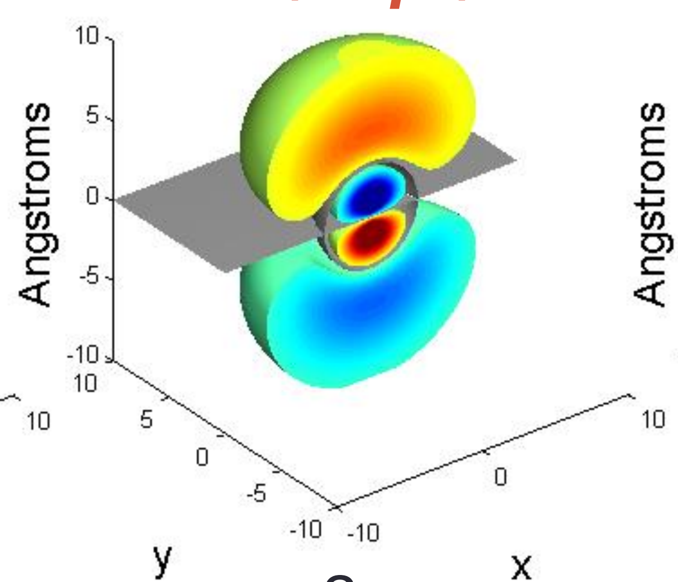

z
x
y
3d_xy
z
x
y
Nodal planes
3d_xz
z
x
y
3d_z²
z
x
y
3d_yz
z
x
y
3d_x²-y²

Comparison of 3*s*, 3*p*, 3*d* Orbitals



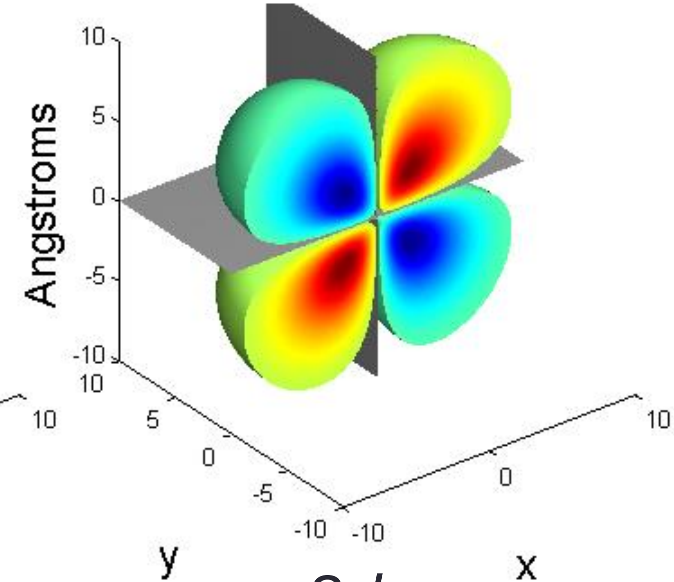
$3s$

n = 3, l = 0.



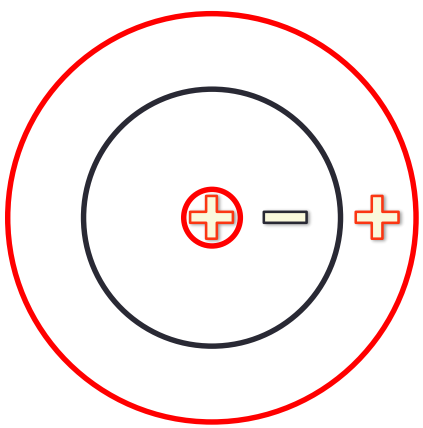
$3p_z$

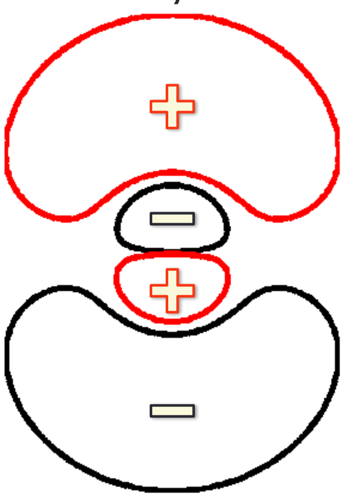
n = 3, l = 1.

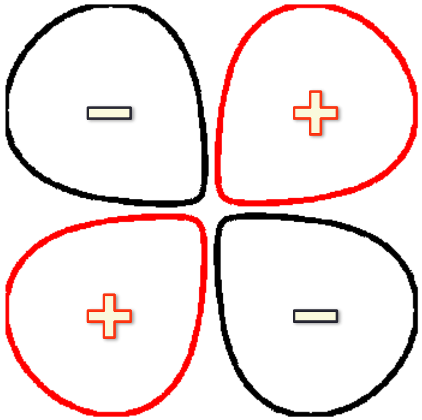


$3d_{xz}$

n = 3, l = 2.







Outline

- Atomic orbitals: Appearance
  - Quantum number
  - Oscillations in 1D, 2D and 3D
  - Shape of H atomic orbitals

- Atomic orbitals: Size
  - Most probable radius r_{mp}

Wave function of hydrogen atom

General solution

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

$$R_{nl}(r) \quad = \quad -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]^{1/2} \left(\frac{2r}{na_0}\right)^l e^{-r/na_0}\, L_{n+l}^{2l+1}(2r/na_0)$$

$$Y_{lm}(\theta,\phi) \quad = \quad (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\phi}$$

Particular solution

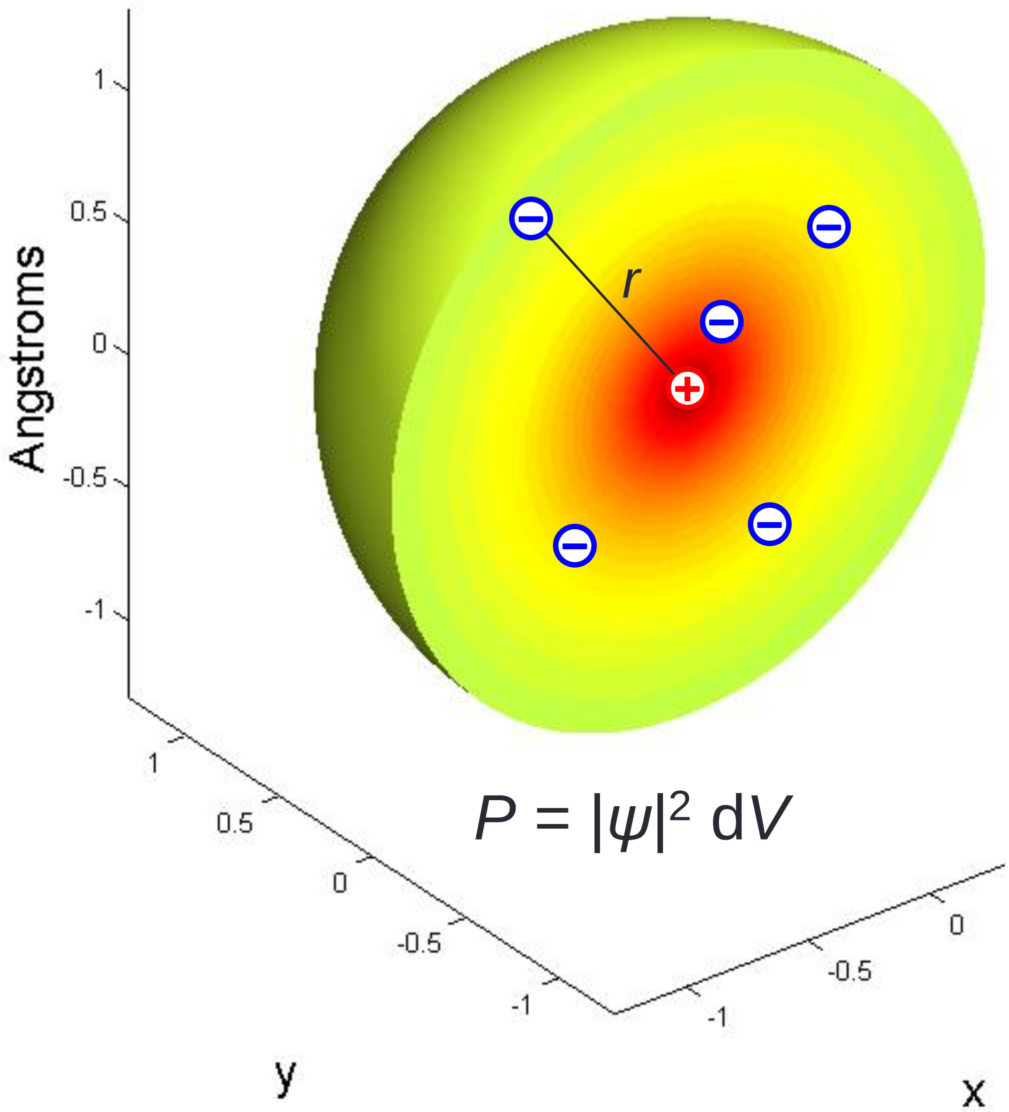
TABLE 5.2

Angular and Radial Parts of Wave Functions for One-Electron Atoms

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n\ell}(r)$
$\ell = 0$: $Y_s = \left(\frac{1}{4\pi}\right)^{1/2}$	$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-\sigma)$
	$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\sigma)\exp(-\sigma/2)$
	$R_{3s} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27 - 18\sigma + 2\sigma^2)\exp(-\sigma/3)$
$\ell = 1$: $Y_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$	$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma\exp(-\sigma/2)$
$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\sigma - \sigma^2)\exp(-\sigma/3)$
$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$\ell = 2$: $Y_{d_{z^2}} = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2\exp(-\sigma/3)$
$Y_{d_{xz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$	
$Y_{d_{yz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$	
$Y_{d_{xy}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$	
$Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$	

$$\sigma = \frac{Zr}{a_0} \qquad a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.529 \times 10^{-10}\ \text{m}$$

Wave Function of the 1*s* Orbital

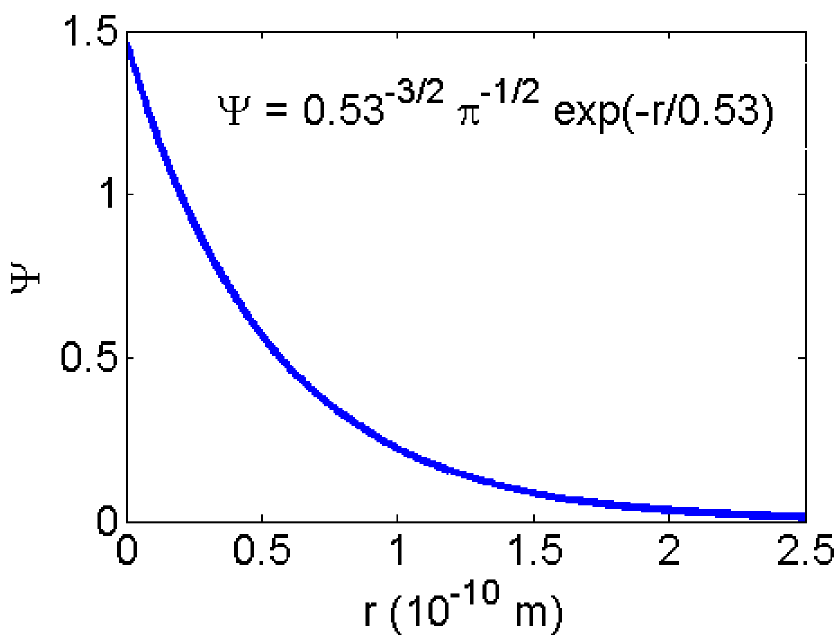


$P = |\psi|^2 \, dV$

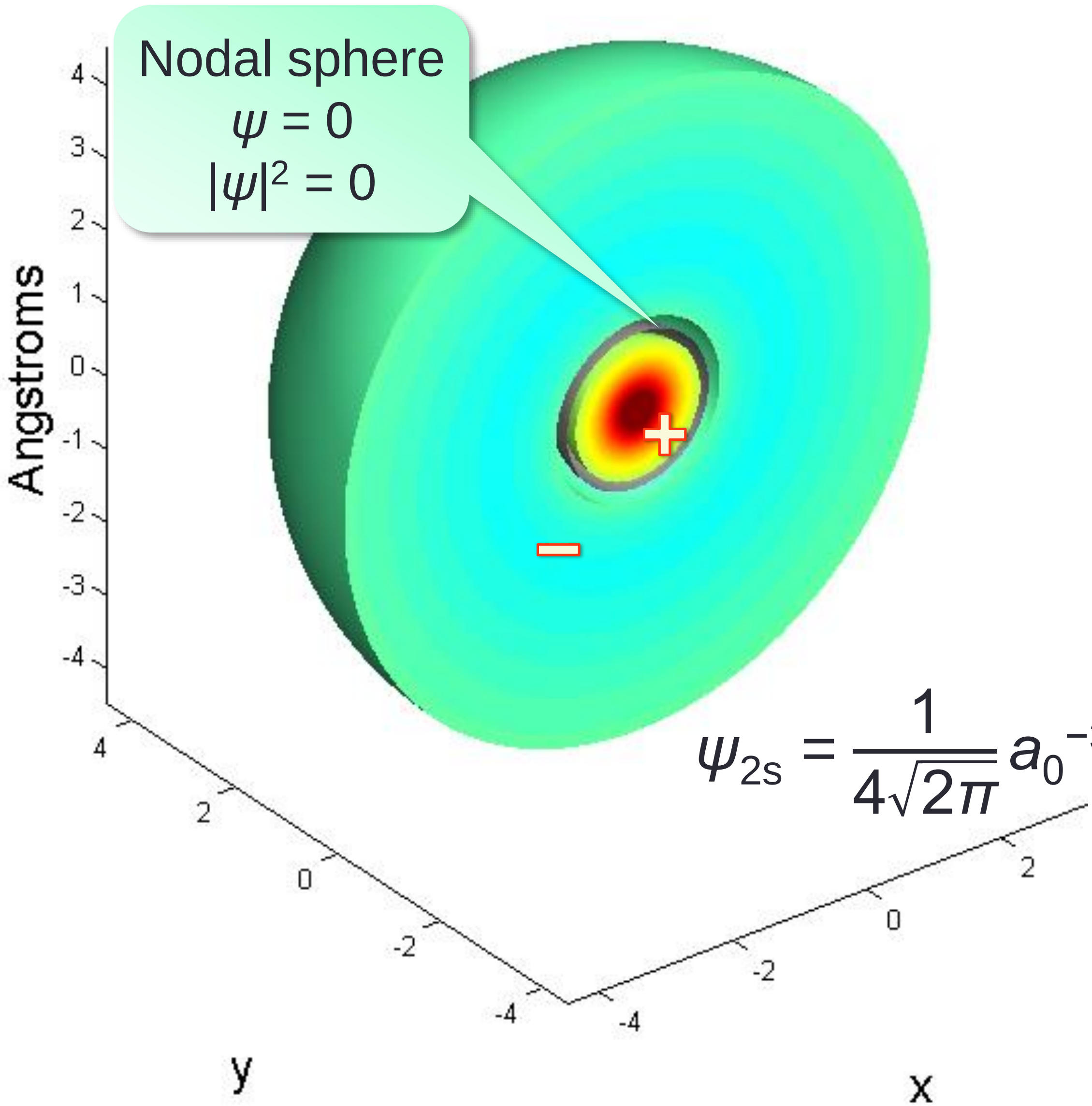
$$\psi_{1s} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} \cdot \exp\left(-\frac{r}{a_0}\right)$$

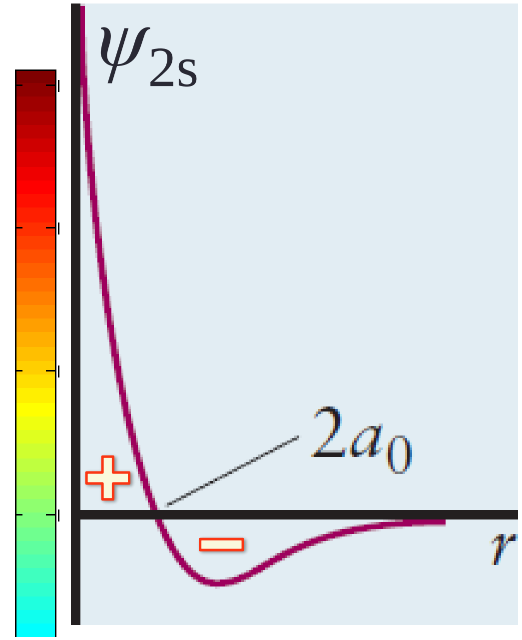
Bohr radius a_0 = 53 pm = 0.53 Å

1 Ångstrom = 10^{-10} m



Wave Function of the 2*s* Orbital





$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \cdot \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$

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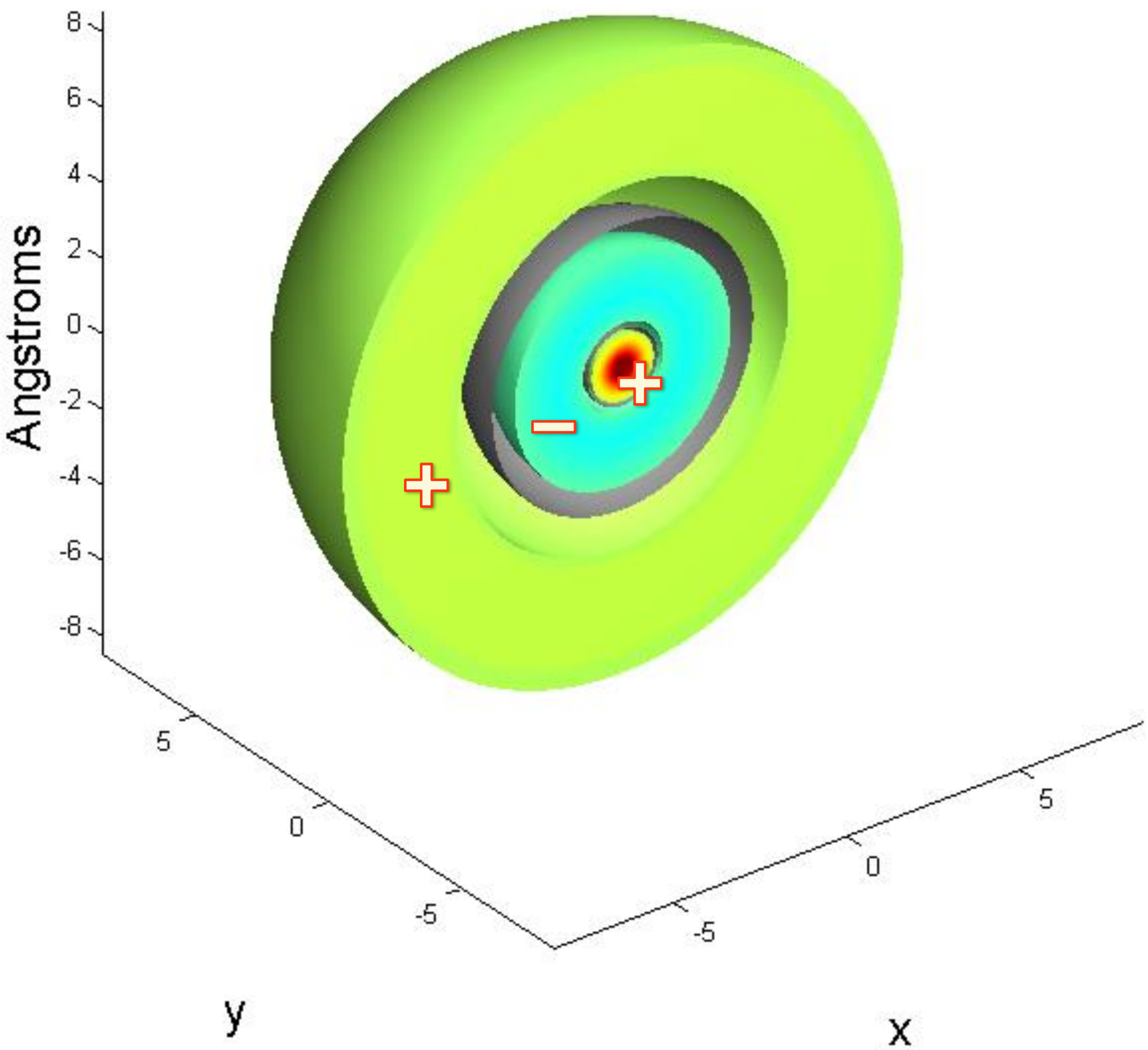
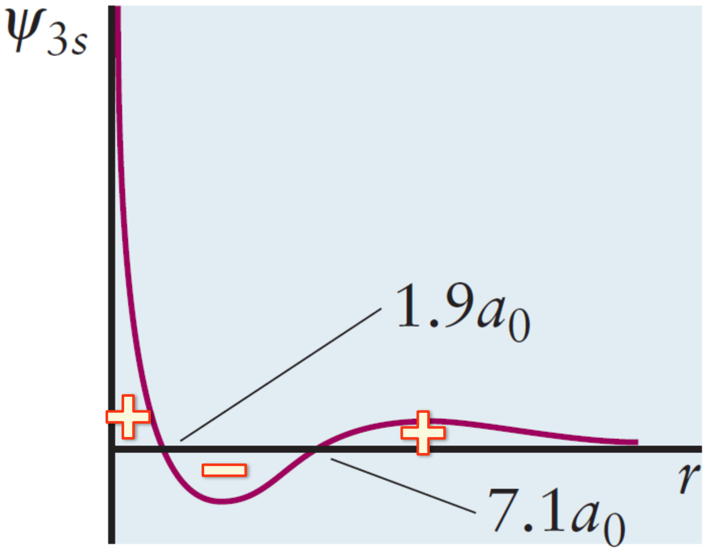
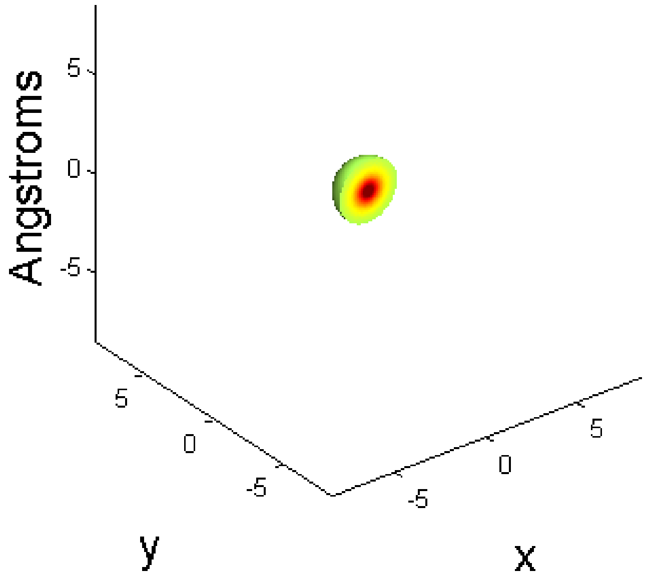
The 3s Orbital



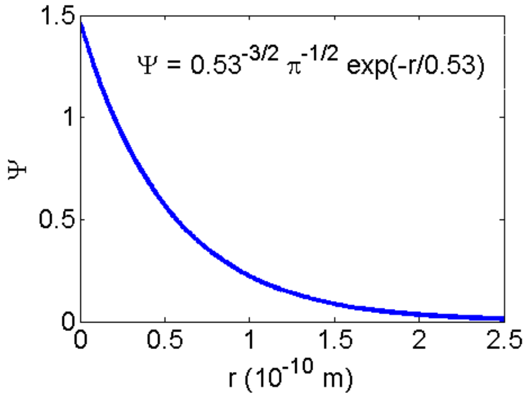


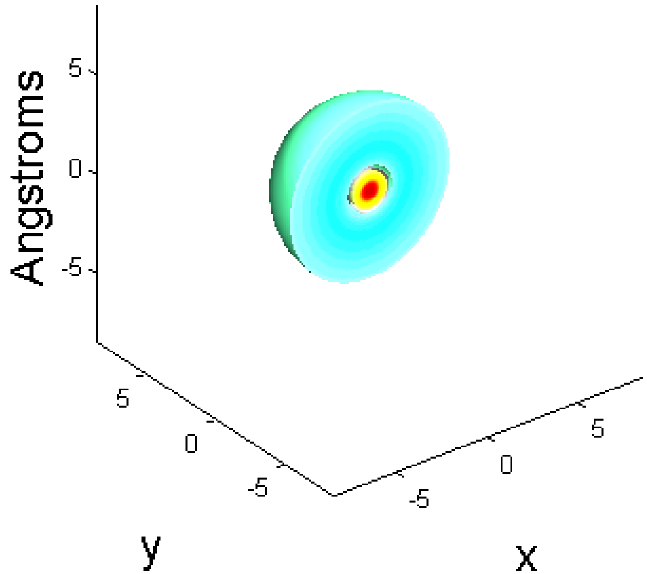
Comparison of 1*s*, 2*s*, 3*s* Orbitals



1*s*

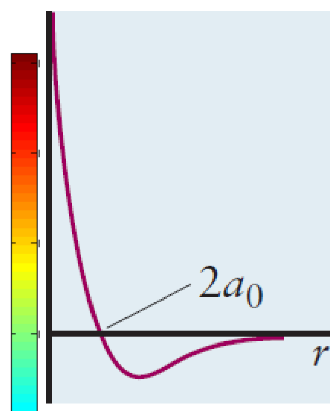
n = 1, l = 0.

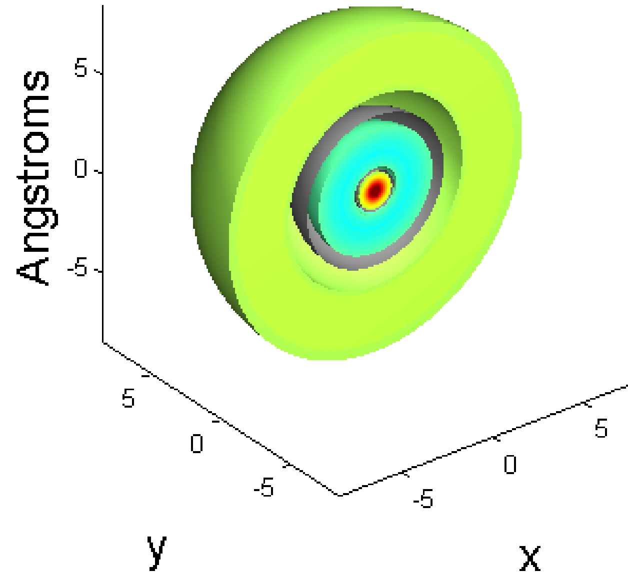




2*s*

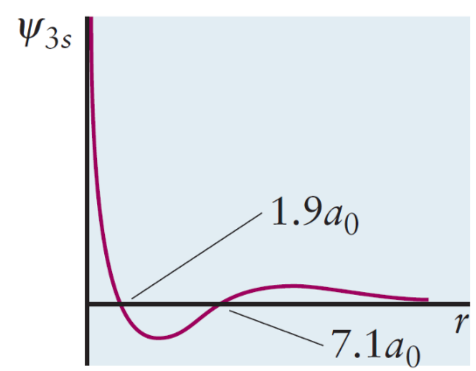
n = 2, l = 0.





3*s*

n = 3, l = 0.



Spherical Shell

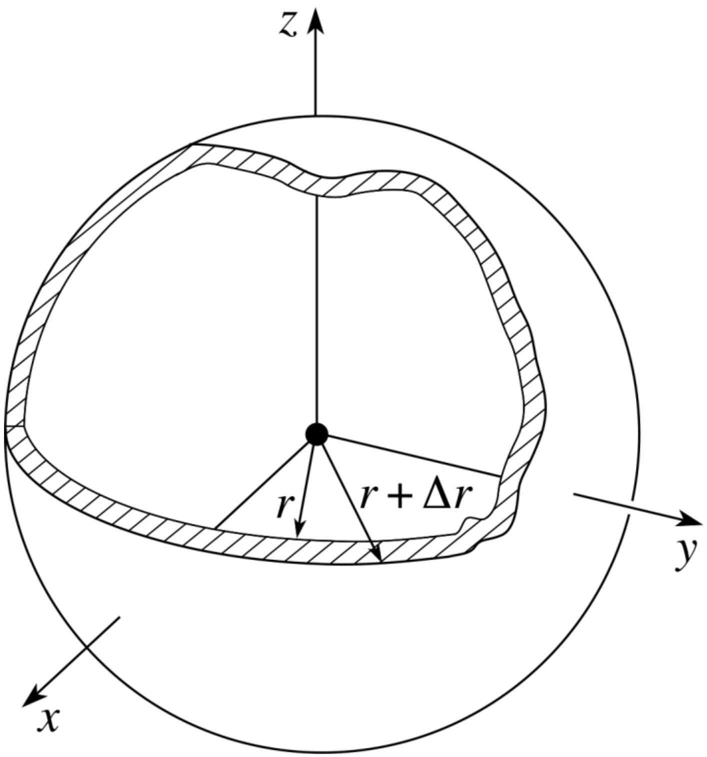


TABLE 5.2

Angular and Radial Parts of Wave Functions for One-Electron Atoms

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n\ell}(r)$
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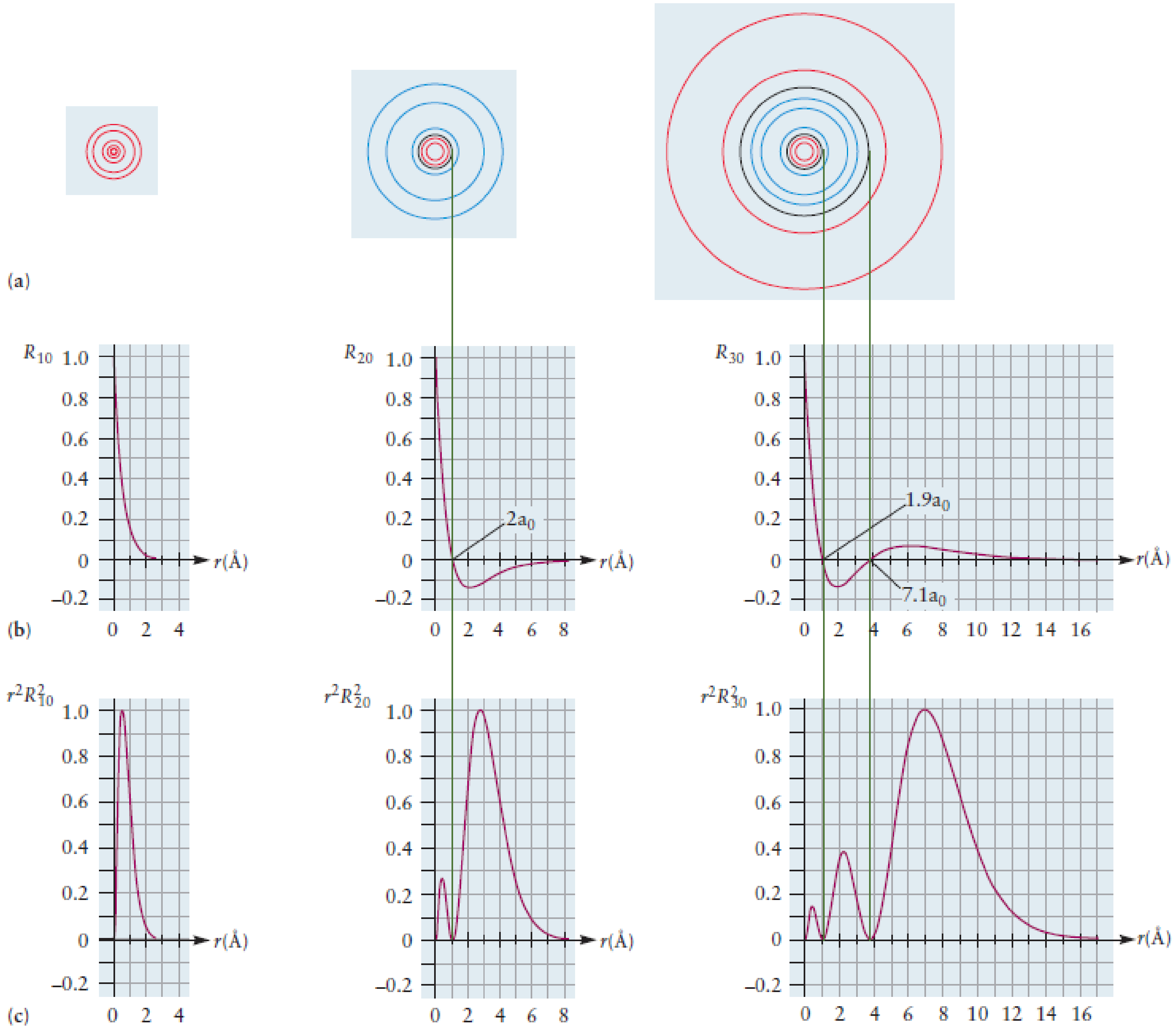
$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)\exp(-\sigma/3)$
$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	

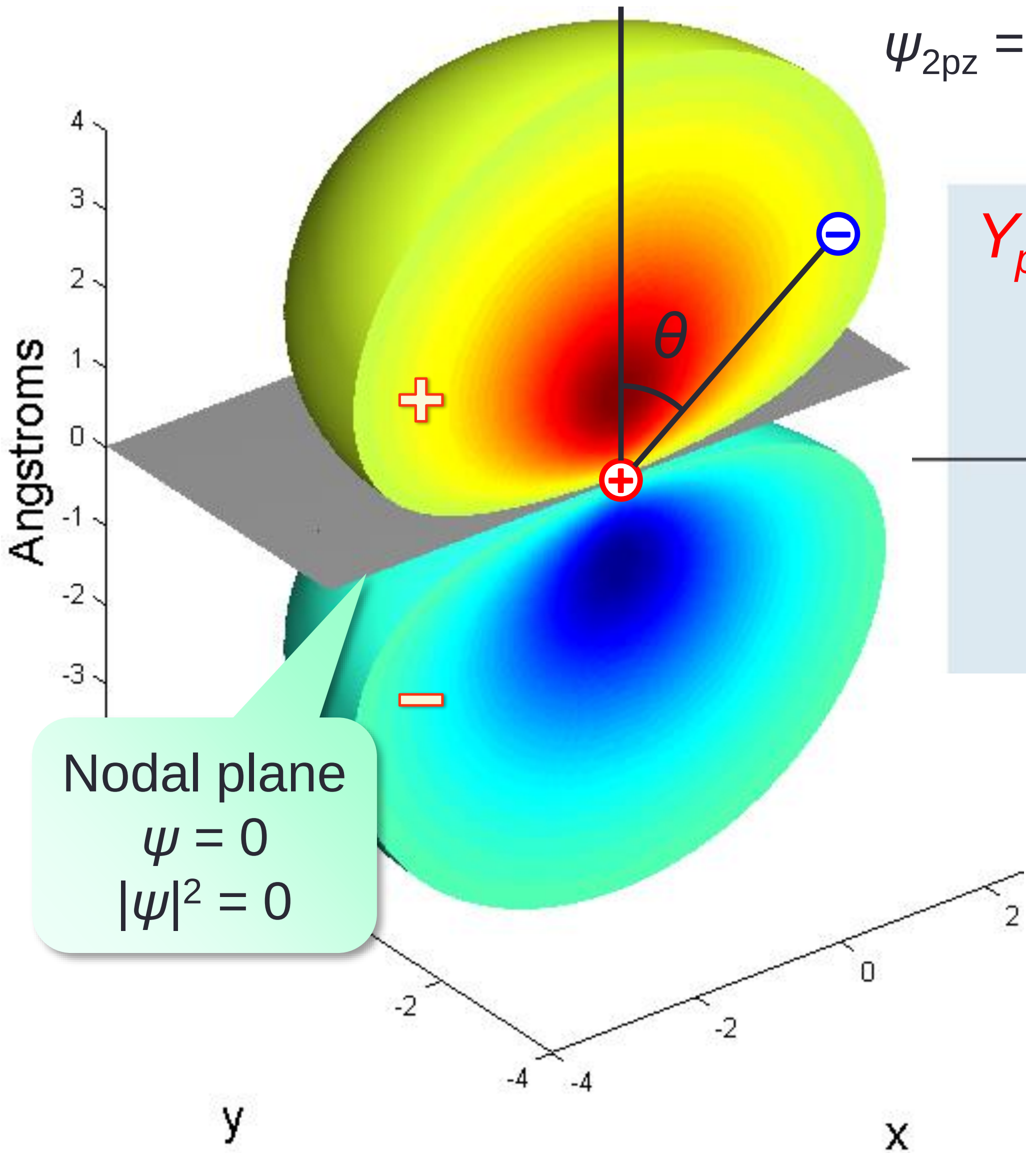
$$A = 4\pi r^2$$
$$dV = A\,dr = 4\pi r^2 dr$$

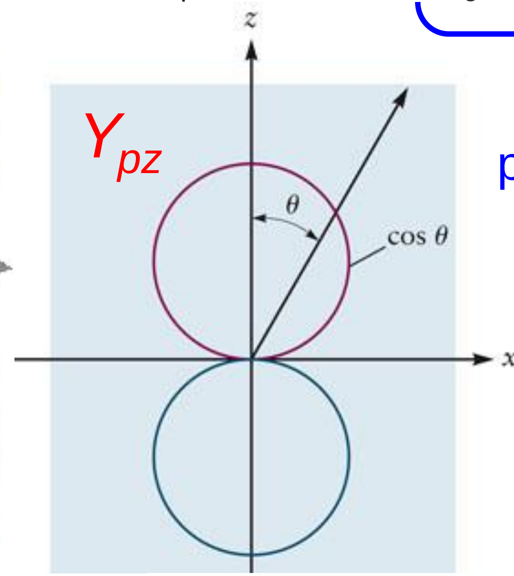
$$P = |\psi|^2\, dV = R^2 Y^2\, dV$$
$$= R^2 \cdot \frac{1}{4\pi} \cdot 4\pi r^2 dr$$
$$= r^2 R^2\, dr$$

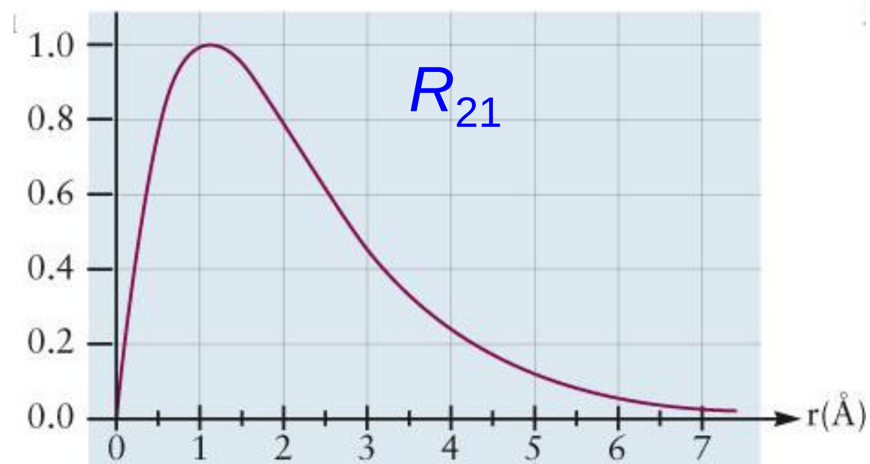

(a)
R10
1.0
0.8
0.6
0.4
0.2
0
–0.2
r(Å)
(b)
0 2 4
R20
2a0
0 2 4 6 8
R30
1.9a0
7.1a0
0 2 4 6 8 10 12 14 16
r2R210
(c)
r2R220
r2R230

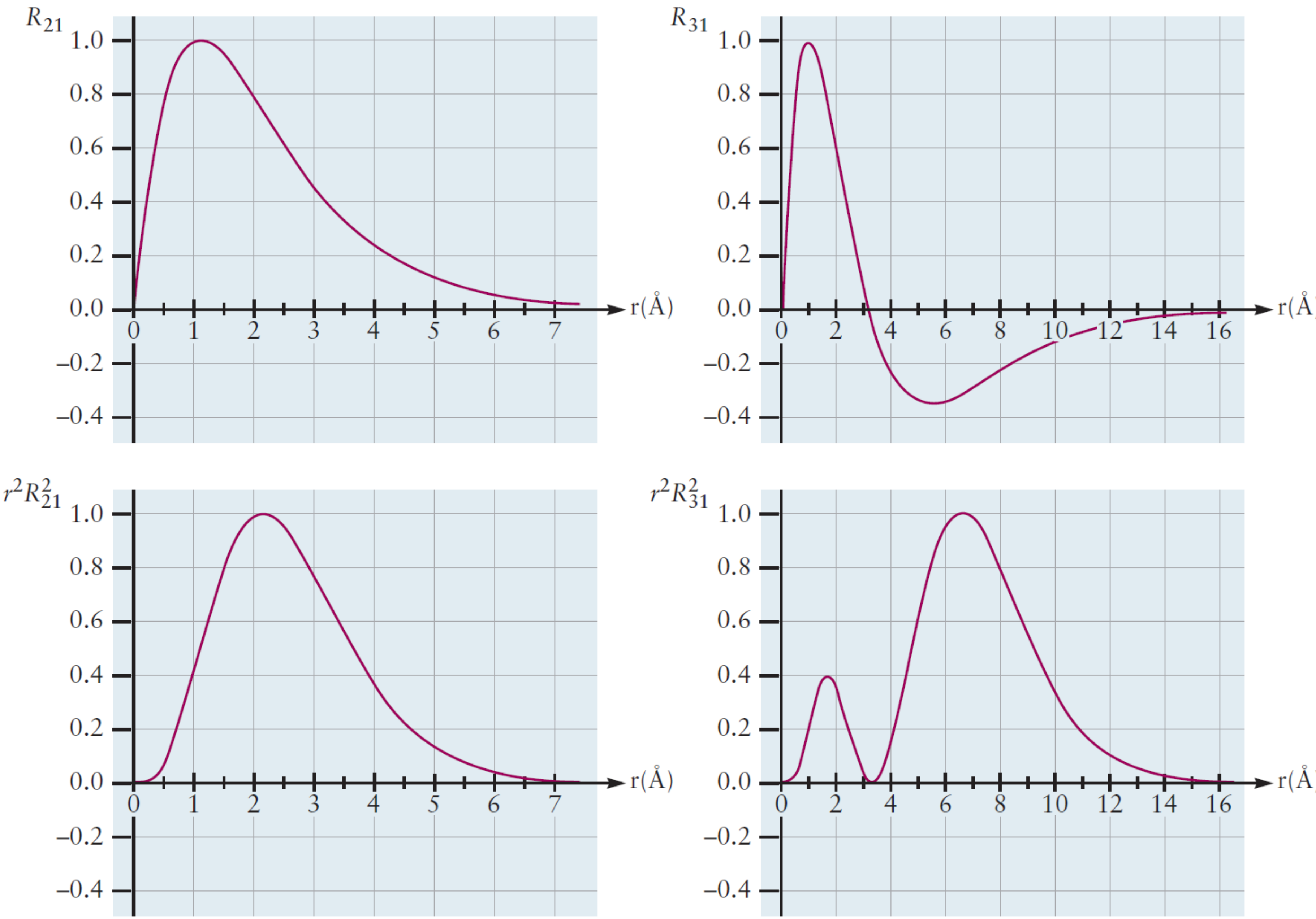
Wave Function of the 2p_z Orbital

$$\psi_{2pz} = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \cdot \underbrace{\frac{r}{a_0}\exp\left(-\frac{r}{2a_0}\right)}_{\text{Radial part, } R_{21}} \cdot \underbrace{\cos\theta}_{\text{Augular part, } Y_{pz}}$$





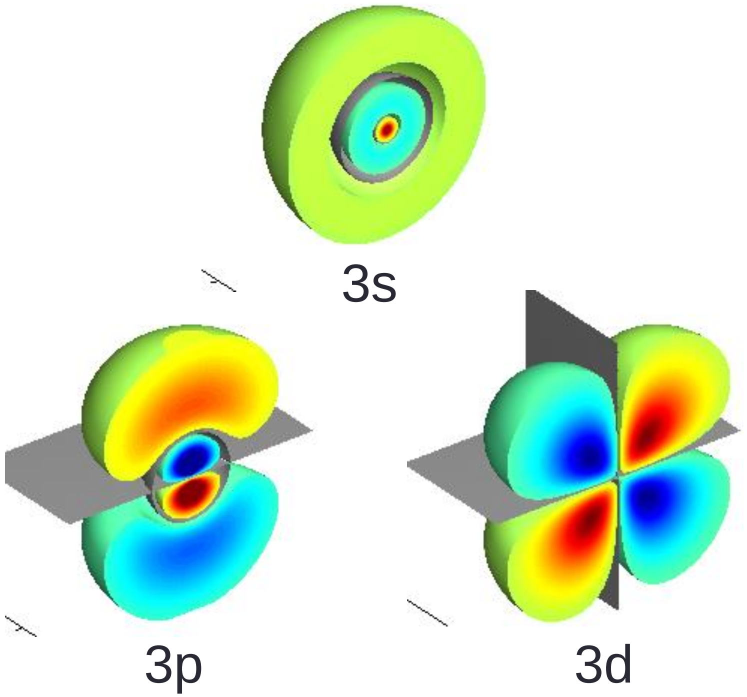


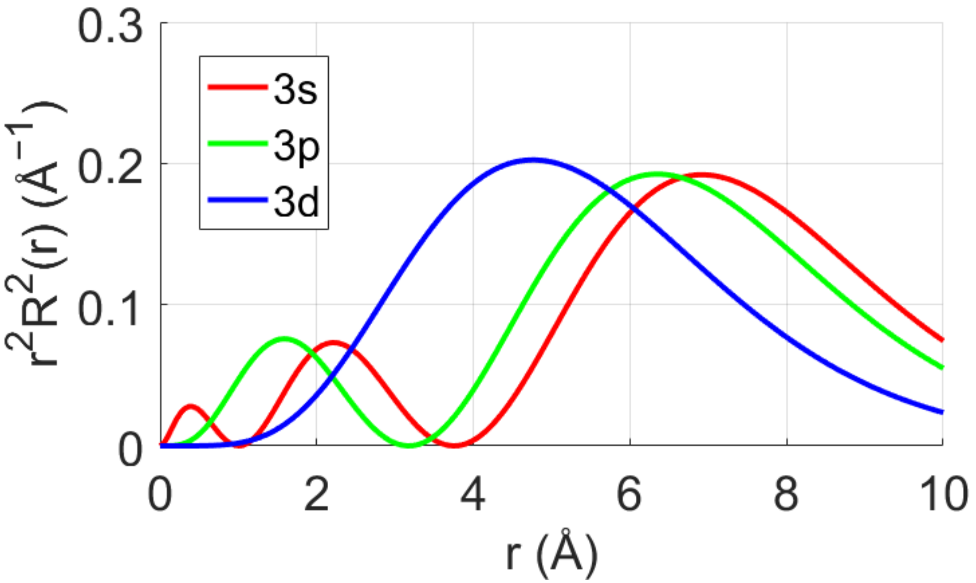


R_{21}
R_{31}
$r^2R_{21}^2$
$r^2R_{31}^2$
1.0
0.8
0.6
0.4
0.2
0.0
–0.2
–0.4
0 1 2 3 4 5 6 7
0 2 4 6 8 10 12 14 16
r(Å)

Radial Distribution

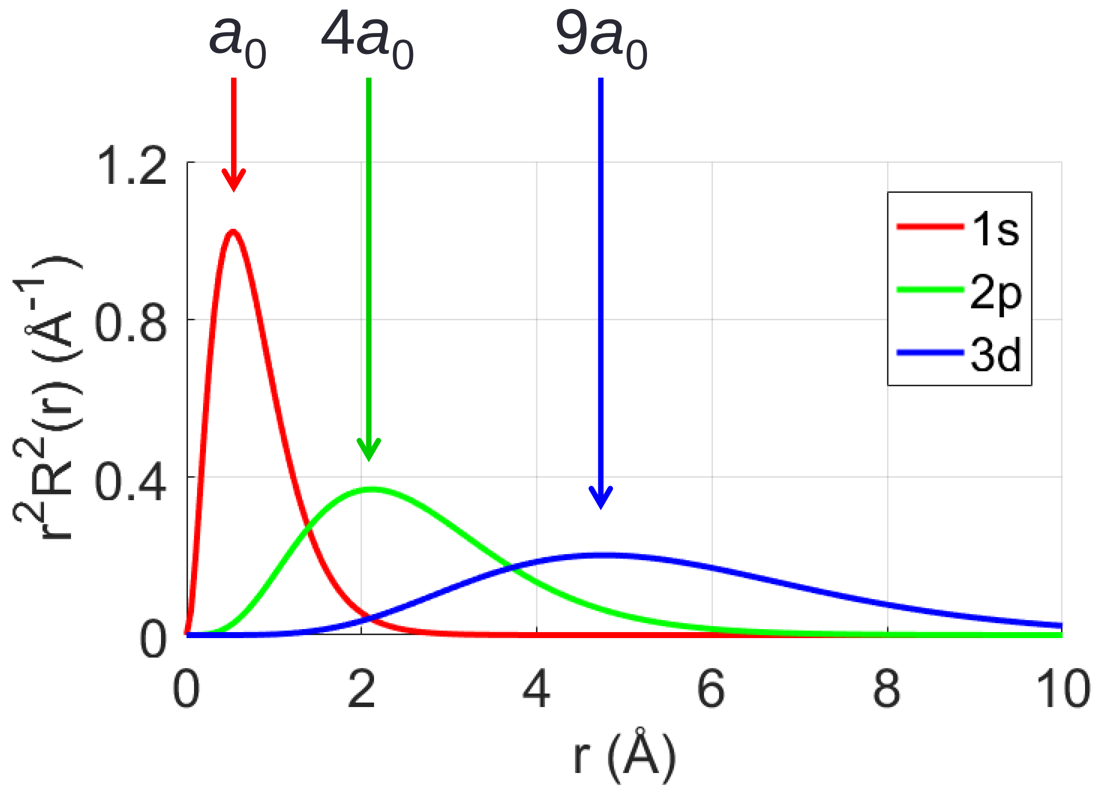
For H atom,
$r(3s) > r(3p) > r(3d)$





Orbital Radius

Most probable radius r_{mp}



Plot $r^2R^2(r)$ vs. r

For Bohr Model: $r_n = n^2a_0$

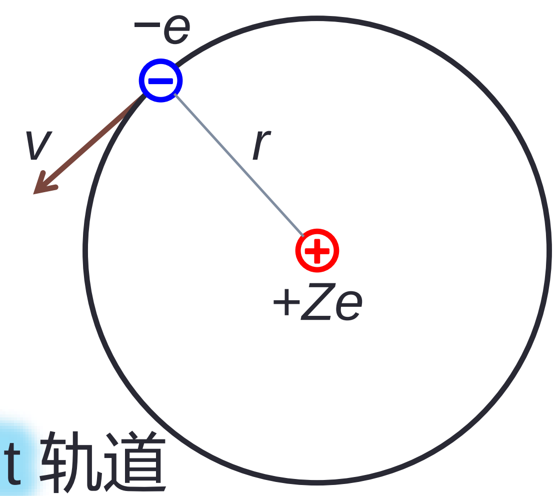
For 1s, 2p, 3d, …: $r_{mp,n} = n^2a_0$

Old *vs*. New Quantum Theory

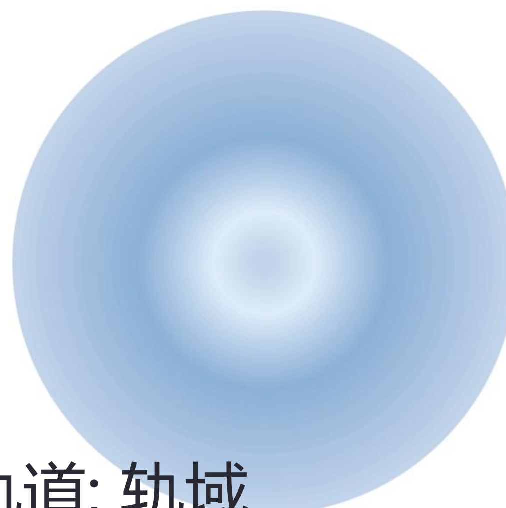
Niels Bohr
(Copenhagen, Cambridge,
1885–1962)

VS

Erwin Schrödinger
(Zürich, 1887–1961)



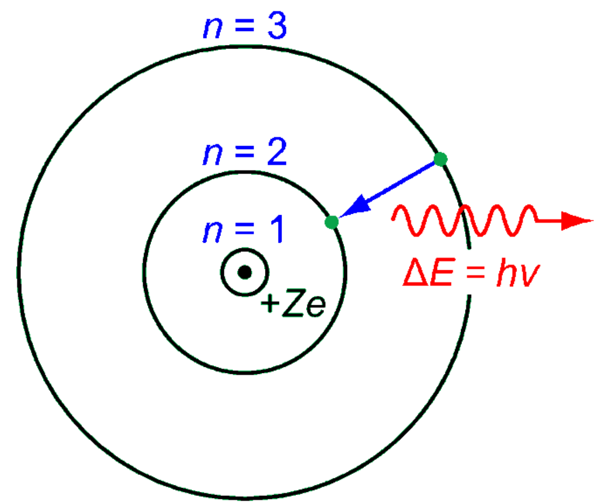
Orbit 轨道



Orbital 轨道; 轨域

Orbital Angular Momentum

$$L = \sqrt{l(l+1)} \cdot h/2\pi \approx l \cdot h/2\pi$$



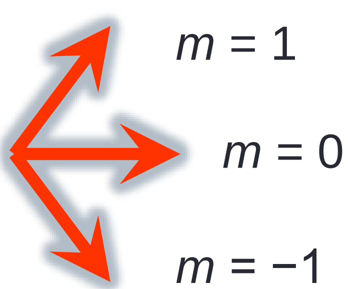
$L_n = nh/2\pi$
in two dimensions

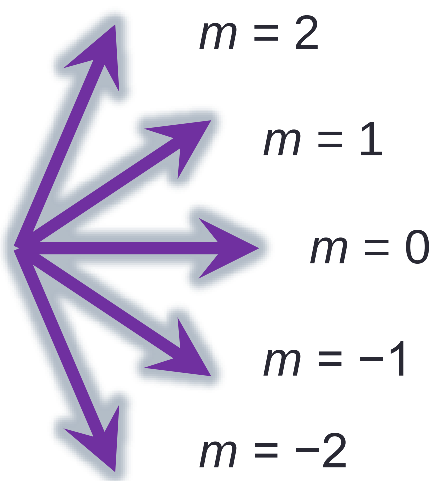
For 1*s*, 2*s* orbitals: $l = 0$, $L = 0$.

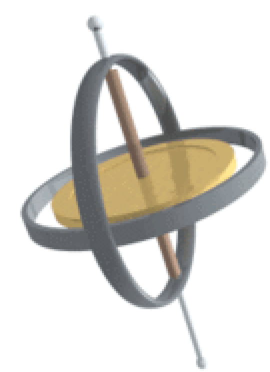
For 2*p*, 3*p* orbitals: $l = 1$, $L = \sqrt{2}\,\hbar$,
L can take 3 orientations.

For 3*d*, 4*d* orbitals: $l = 2$, $L = \sqrt{6}\,\hbar$,
L can take 5 orientations.

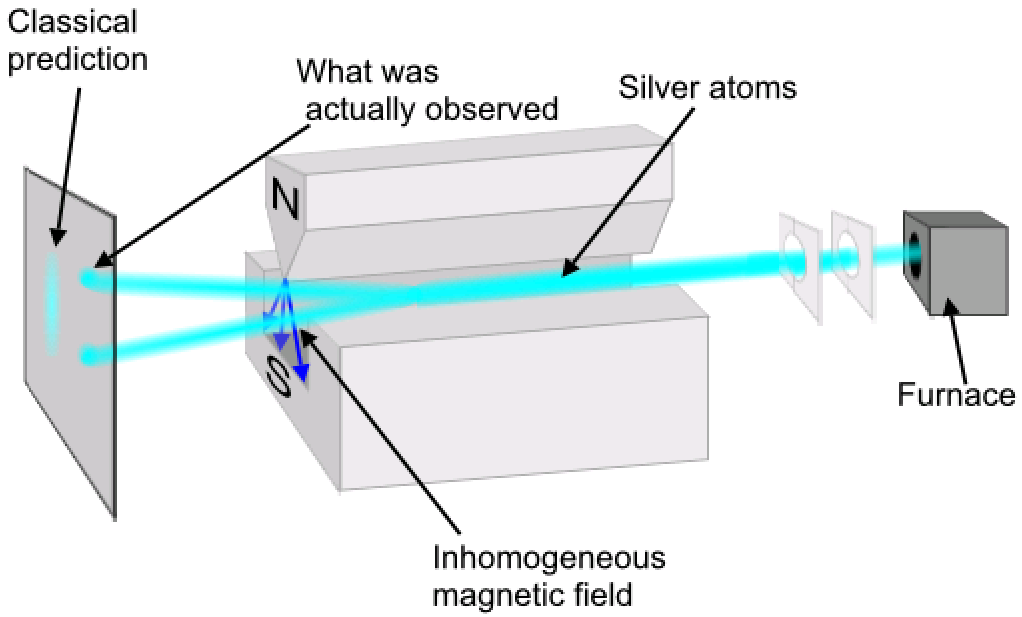
磁量子数
Magnetic quantum number *m*



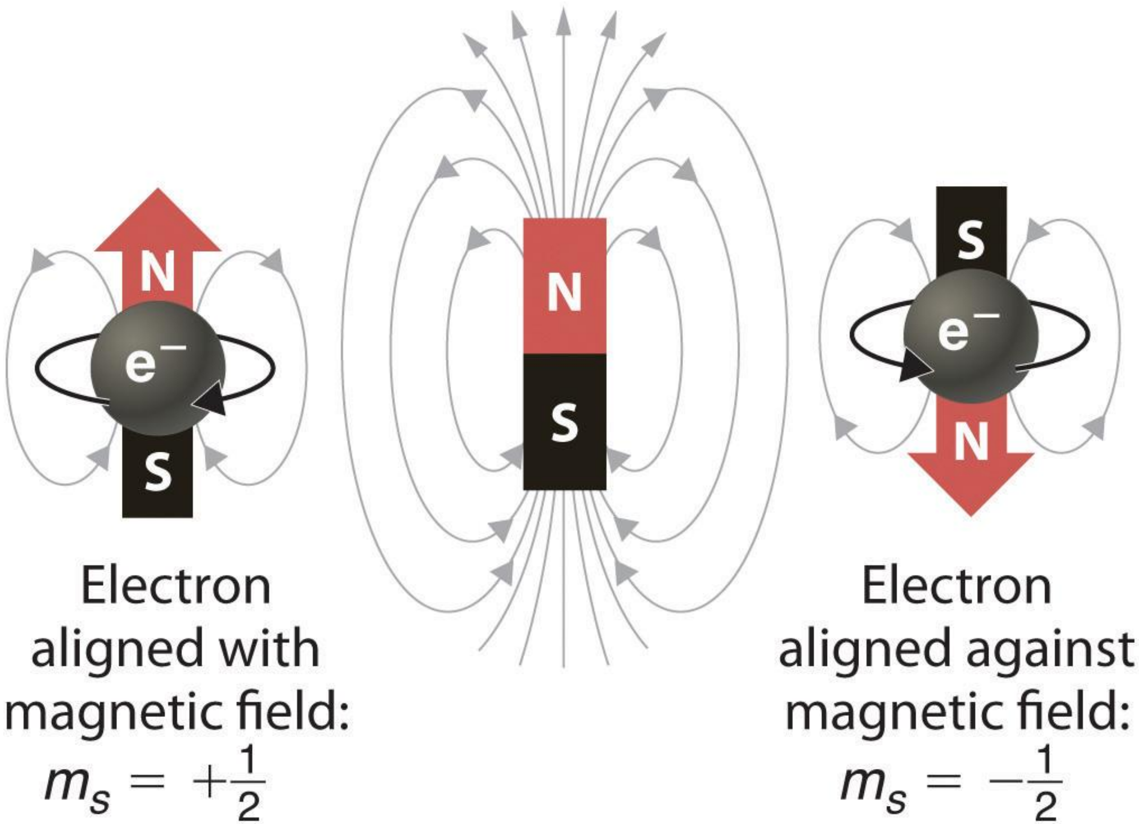




The fourth Quantum Number



The fourth Quantum Number



Summary

Principal quantum number n = Total number of nodes + 1

n = 1, 2, 3, …

Angular momentum quantum number l = Number of nodal planes

l = 0, 1, 2, …, $n - 1$.

$$E_n = -\frac{13.6\ \text{eV}}{n^2}$$

For 1*s*, 2*p*, 3*d*, …: $r_{\text{mp},n} = n^2 a_0$

2*s*, 3*s*, 2*p* exhibit penetration effect.

Midterm 1 on Wednesday Oct. 30th