

# The Schrödinger equation in spherical coordinates.

For most realistic potentials, the Schrödinger equation in Cartesian coordinates is not soluble by using the separation of the wave function in three independent wave functions. For example, for the electromagnetic interaction between an electron and a proton, the potential is:

$$V(x, y, z) = -\frac{ke^2}{\sqrt{x^2 + y^2 + z^2}} = -\frac{ke^2}{r} = V(r)$$

Transformation to a spherical coordinate system.

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

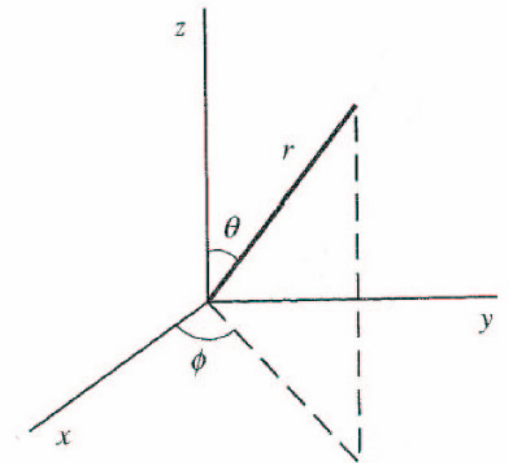
$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

The Schrödinger equation is then:

$$\left[ -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2mr^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(r) \right] \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$



Now, the new equation in spherical coordinates is separable.

A set of three new quantum numbers appears. But now, the quantum numbers are not fully independent one another.

## Separation of variables

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Diese Gleichung kann durch einen Separationsansatz gelöst werden. Mit  $\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$  erhalten wir

$$\begin{aligned} & \frac{-\hbar^2}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + 2mr^2(V(r) - E) \\ & - \frac{\hbar^2}{Y(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) = 0. \end{aligned} \quad (7)$$

Hier wurde erst  $R(r)Y(\theta, \phi)$  in 6 eingesetzt und dann durch  $R(r)Y(\theta, \phi)$  dividiert. Da die Gleichung 7 für alle  $r, \theta$  und  $\phi$  gilt, müssen die erste und zweite Zeile der linken Seite für sich jeweils konstant sein. Wir setzen die zweite Zeile einer Konstanten gleich, die wir  $L^2$  nennen:

$$\frac{\hbar^2}{Y(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) = -L^2. \quad (8)$$

Diese Konstante  $L^2$  setzen wir jetzt anstatt des Winkelteils in Gleichung 7 ein

$$-\frac{\hbar^2}{2mr^2 R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + V(r) + \frac{L^2}{2mr^2} - E = 0. \quad (9)$$

# Separation of variables

- The Schrödinger equation for the hydrogen atom involves Coulomb potential  $-ke^2/r$ . Since this is a central potential (it has spherical symmetry) the equation can be separated in different independent equations when it is expressed in spherical coordinates.

RADIAL

$$\frac{-\hbar^2}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + 2mr^2(V(r) - E)$$

ANGULAR

$$-\frac{\hbar^2}{Y(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) = 0.$$

RADIAL

= -L<sup>2</sup>

ANGULAR

= -L<sup>2</sup>

$$\frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2}$$

$$+ \frac{L^2}{\hbar^2} \sin^2 \theta - \frac{\sin \theta}{P(\theta)} \frac{d}{d\theta} \left[ \sin \theta \frac{dP(\theta)}{d\theta} \right]$$

= 0

$$\psi(r, \theta, \phi) = \boxed{R(r)} \cdot \boxed{P(\theta)} \cdot \boxed{F(\phi)}$$

## Separation of variables: Solution of angular components

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Zur Lösung des Winkelteils machen wir eine weitere Separation:  $Y(\theta, \phi) = P(\theta)F(\phi)$ .

$$\frac{\hbar^2}{\sin \theta P(\theta)} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial P(\theta)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\hbar^2}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} = -L^2. \quad (12)$$

Wiederum müssen beide Summanden für sich konstant sein:

$$\frac{\hbar^2}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} = -m_l^2 \hbar^2 \quad (13)$$

$$\frac{1}{P(\theta)} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial P(\theta)}{\partial \theta} \right) - \frac{m_l^2}{\sin^2 \theta} = -\frac{L^2}{\hbar^2}. \quad (14)$$

Gleichung 13 hat Lösungen der Form

$$F(\phi) \propto e^{im_l \phi}. \quad (15)$$

Wir werden später erfahren, welche Werte  $m_l$  annehmen kann.

Um Gleichung 14 zu lösen, machen wir die Variablensubstitution  $x = \cos \theta$ . Das führt auf

$$(1 - x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[ \frac{L^2}{\hbar^2} - \frac{m_l^2}{1 - x^2} \right] P = 0. \quad (16)$$

Dies sind für  $m_l = 0$  die Legendreschen Differentialgleichungen und für  $m_l \neq 0$  die assoziierten Legendreschen Differentialgleichungen. Die Gleichungen haben Lösungen für  $L^2/\hbar^2 = l(l+1)$ . Die Lösungen dieser Gleichung sind die Legendre-Polynome oder assoziierten Legendre-Polynome ( $m_l \neq 0$ )  $P_{l,m_l}(\cos \theta)$ . Die möglichen Werte von  $l$  sind  $|m_l|, |m_l| + 1, |m_l| + 2, \dots$

# Solution of the angular part of the Schrödinger equation.

2. The solution of every independent equation gives rise to a different quantum number.

$$\boxed{\frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2} = C} \xrightarrow{\text{General solution}} F(\phi) = Ae^{c\phi} \quad + \quad \xrightarrow{\text{Azimuth boundary condition}} F(\phi) = F(\phi + 2\pi) \Rightarrow \xrightarrow{\text{Azimuth solution}} \begin{aligned} F(\phi) &= Ae^{im_l\phi} \\ m_l &= \text{integer} \\ c &= -m_l^2 \end{aligned}$$

$$\boxed{-m_l^2} + \boxed{\frac{L^2}{\hbar^2} \sin^2 \theta - \frac{\sin \theta}{P(\theta)} \frac{d}{d\theta} \left[ \sin \theta \frac{dP(\theta)}{d\theta} \right]} = 0 \xrightarrow{\text{General solution}} \begin{aligned} &\text{This equation has a solution, only when:} \\ &\text{The solution are Legendre polynomial} \end{aligned} \quad \left\{ \begin{aligned} \frac{L^2}{\hbar^2} &= l(l+1) \\ \frac{L^2}{\hbar^2} - m_l^2 &\geq 0; l > |m_l| \end{aligned} \right.$$

$$P_{m_l}^l(x) = \frac{(-1)^m}{2^l l!} (1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l,$$

$$x = \cos \theta$$

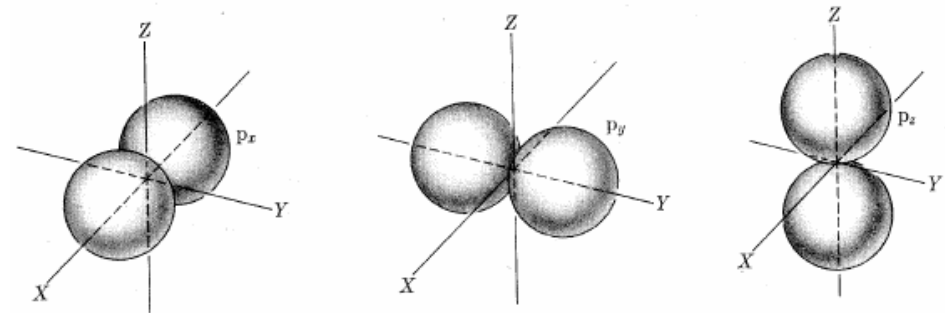
The solution of the angular part of the electronic wave function for the hydrogen atom are Spheric Harmonic

$$Y_{l,m_l}(\theta, \phi) = \boxed{P(\theta)} \cdot \boxed{F(\phi)} = \boxed{P_{m_l}^l(\cos \theta)} \boxed{e^{im_l\phi}} \quad \begin{aligned} &l \text{ Positive integers} \\ &|m_l| < l \end{aligned}$$

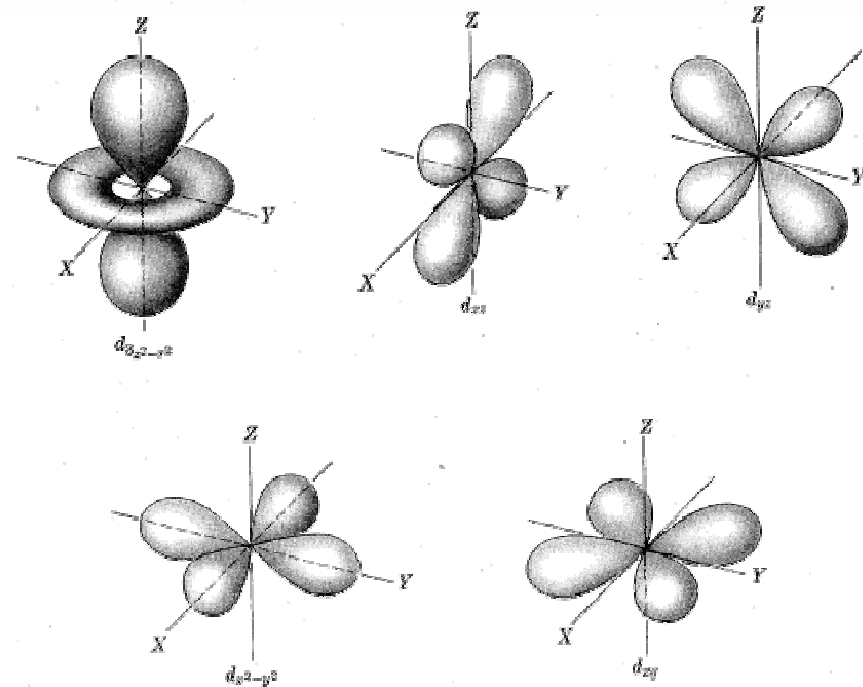
# The angular wave functions

**TABLE H-1**  
**SOLUTIONS TO THE ANGULAR PART OF THE**  
**SCHRÖDINGER EQUATION.**

$\ell$	$m_\ell$	$Y_{\ell, m_\ell}(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	1	$\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
2	1	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$
2	2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$
3	0	$\sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
3	1	$\sqrt{\frac{21}{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{i\phi}$
3	2	$\sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{2i\phi}$
3	3	$\sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{3i\phi}$

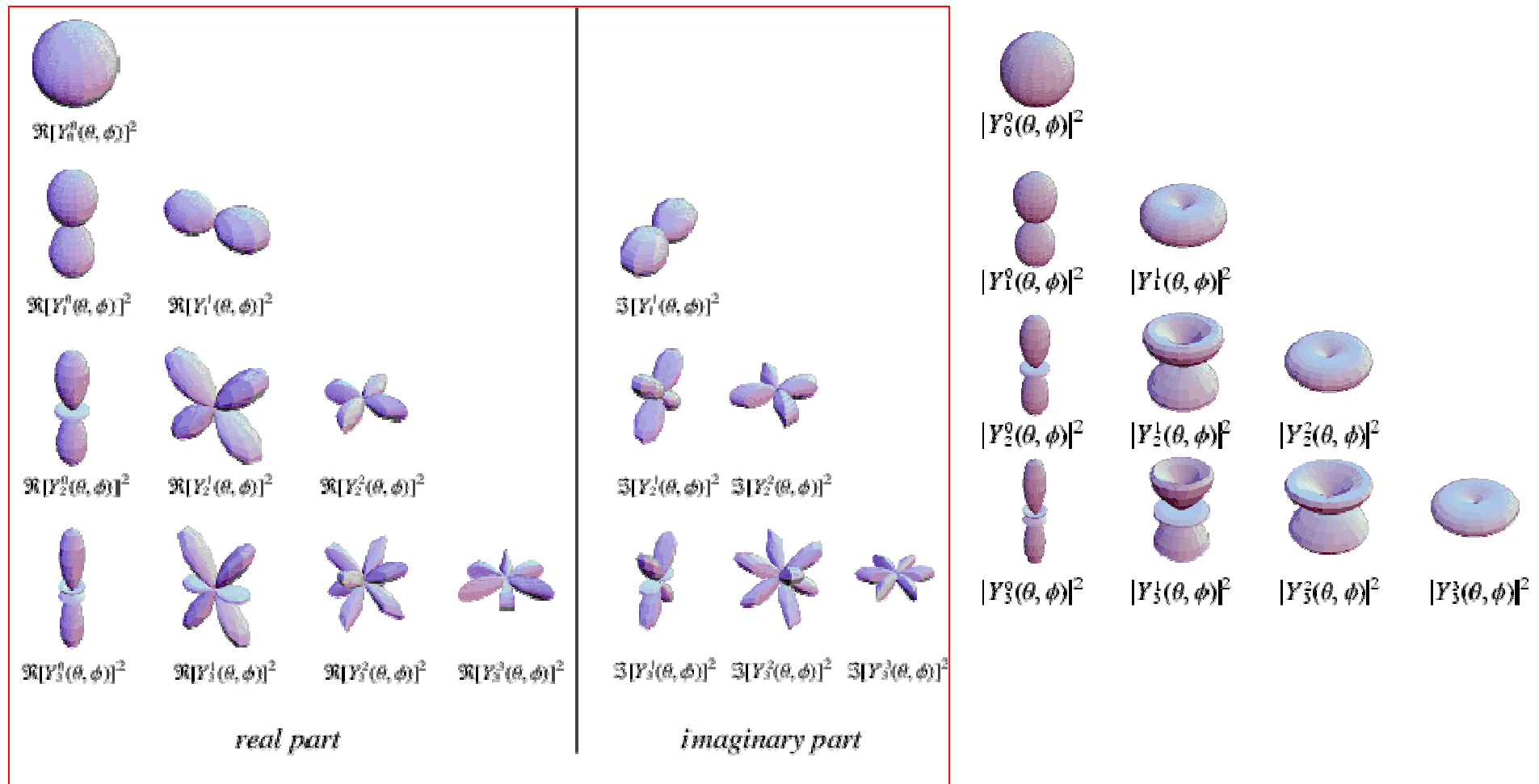


**Abb. 3-10.** Winkelwellenfunktionen für p-Zustände ( $l = 1$ ).



**Abb. 3-11.** Winkelwellenfunktionen für d-Zustände ( $l = 2$ ).

# Spherical Harmonics



# Solution of the radial part of the Schrödinger equation.

## RADIAL

$$\frac{-\hbar^2}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + 2mr^2(V(r) - E) = -l(l+1) \cdot \hbar^2$$

General solution

This equation has a set of solutions, each a polynomial series with the form of an exponential times a polynomial of r:

$$R(r) = e^{-r/na_0} g(x) = e^{-r/na_0} r^l L_n$$

The solutions have the form of associated Laguerre polynomials  $L_{n,l}$ , which only exist when n,l are integer numbers and  $n \geq l$

The energy of each solution can be obtained by solving the radial Schrödinger equation

$$E_n = -\frac{\alpha^2 mc^2}{2n^2} = -\frac{13,6eV}{n^2}$$

Which is the same expression that the obtained by the Bohr model of the atom.

Energy

0

$$-\frac{E_R}{4^2}$$

$$-\frac{E_R}{3^2}$$

$$-\frac{E_R}{2^2}$$

$$-\frac{E_R}{1^2}$$

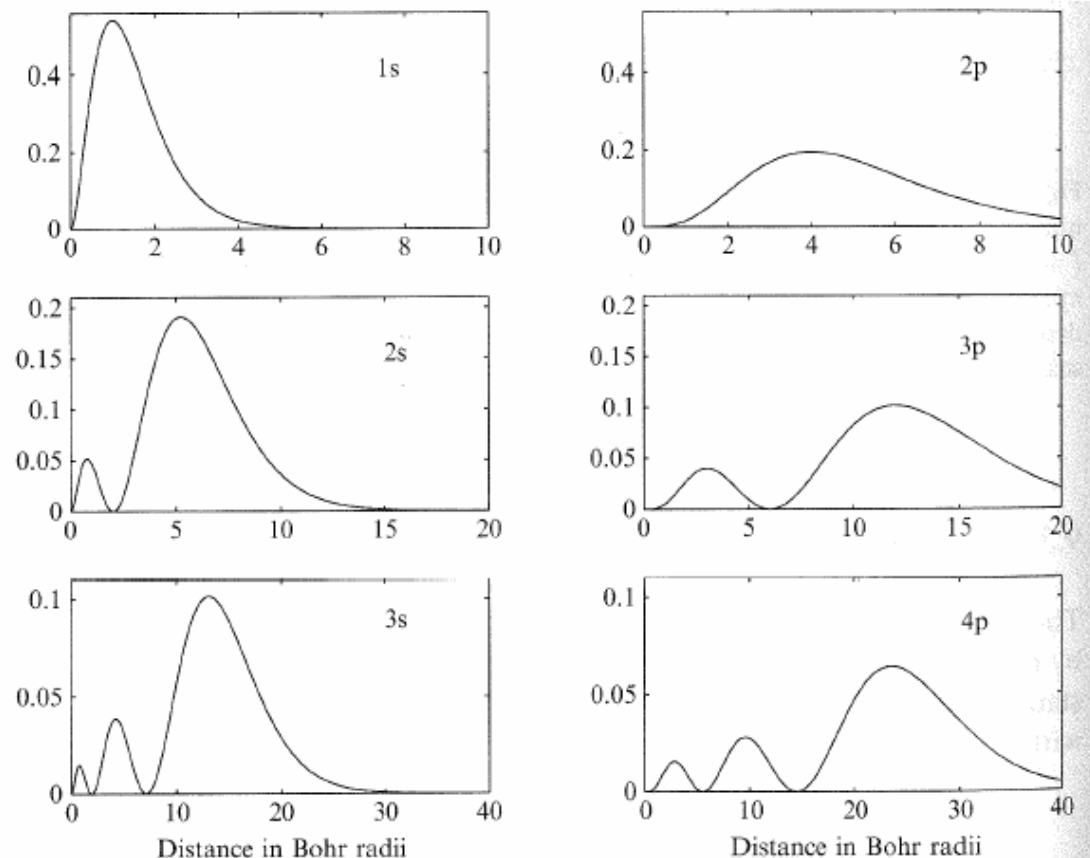


# The radial wave function and probability densities.

**TABLE H-2**  
**RADIAL WAVE FUNCTIONS.**

$n$	$\ell$	$R_{n,\ell}$
1	0	$\frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$
2	0	$\frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$
2	1	$\frac{1}{\sqrt{24a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$
3	0	$\frac{2}{\sqrt{27a_0^3}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{8}{27\sqrt{6a_0^3}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$
3	2	$\frac{4}{81\sqrt{30a_0^3}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

Note: The number of nodes depend not only on  $n$ , but on  $\ell$ . The magnetic quantum number  $m_\ell$  does not have any effect on the radial probability.



**Fig. 9.5** Radial probability densities for the 1s, 2s, 3s, 2p, 3p and 4p states of the hydrogen atom. Note that the unit of distance is the Bohr radius  $a_0$  and that a different scale is used for states with a different number of radial nodes.

# The hydrogen wave functions.

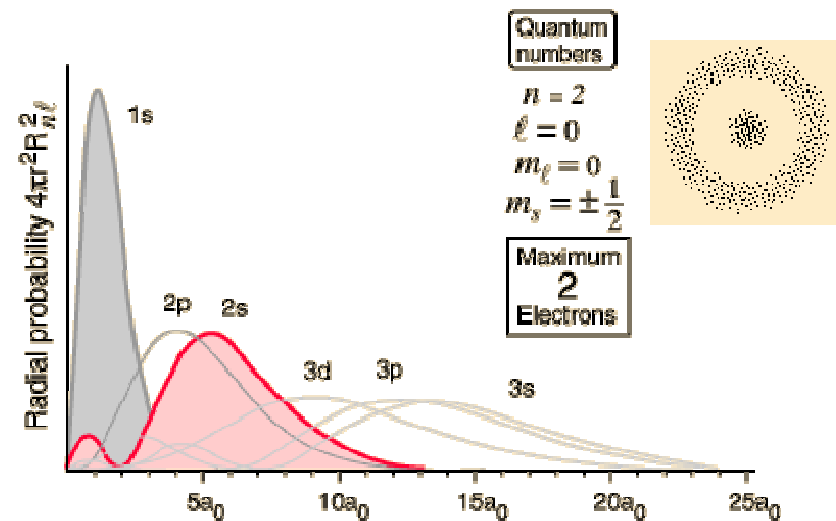
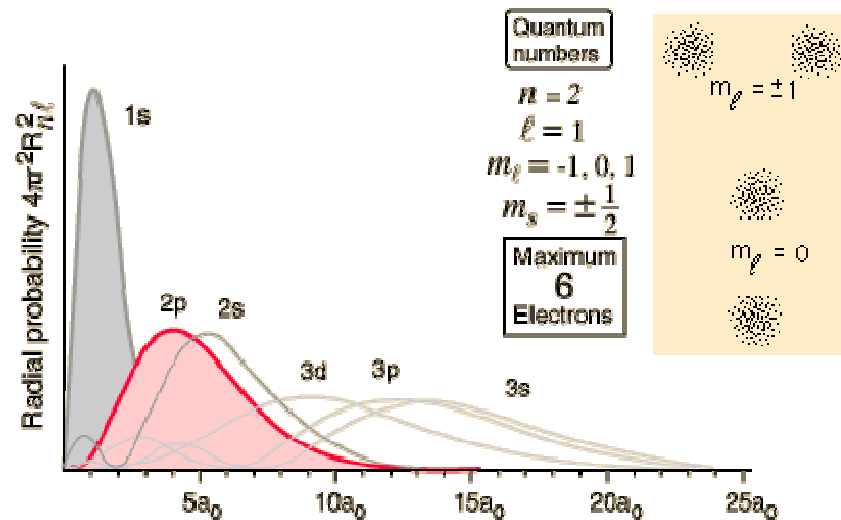
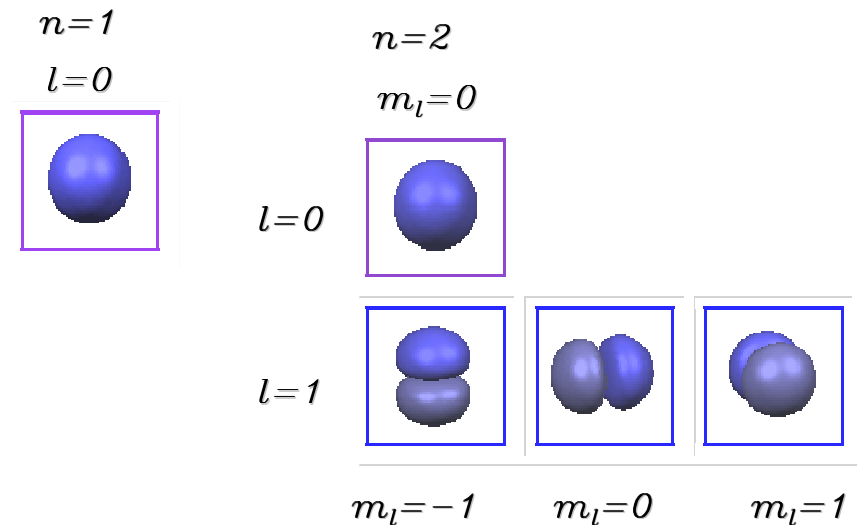
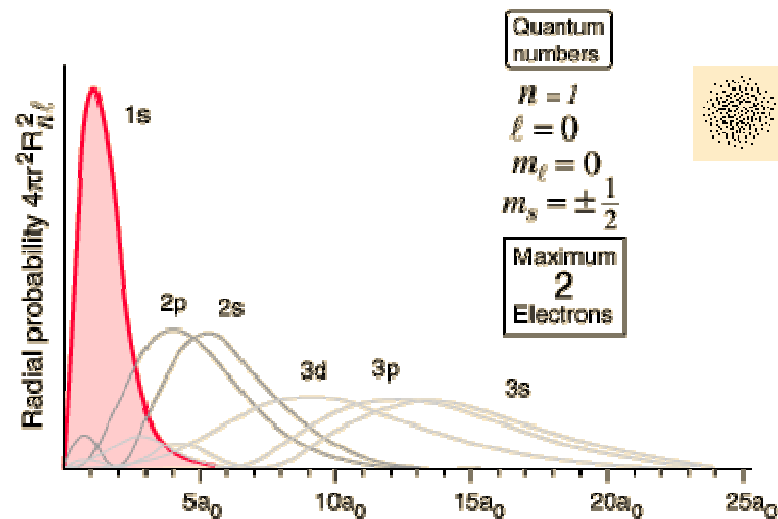
**TABLE 8-1**  
**HYDROGEN ATOM WAVE FUNCTIONS.**

Spectroscopic Notation	$\psi_{n,\ell,m_\ell}(r,\theta,\phi)$
1s	$\psi_{1,0,0} = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2s	$\psi_{2,0,0} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0}$
2p ( $m_\ell=0$ )	$\psi_{2,1,0} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left( \frac{r}{a_0} \right) e^{-r/2a_0} \cos\theta$
2p ( $m_\ell=+1$ )	$\psi_{2,1,1} = \frac{1}{8\sqrt{\pi} a_0^{3/2}} \left( \frac{r}{a_0} \right) e^{-r/2a_0} \sin\theta e^{i\phi}$
2p ( $m_\ell=-1$ )	$\psi_{2,1,-1} = \frac{1}{8\sqrt{\pi} a_0^{3/2}} \left( \frac{r}{a_0} \right) e^{-r/2a_0} \sin\theta e^{-i\phi}$

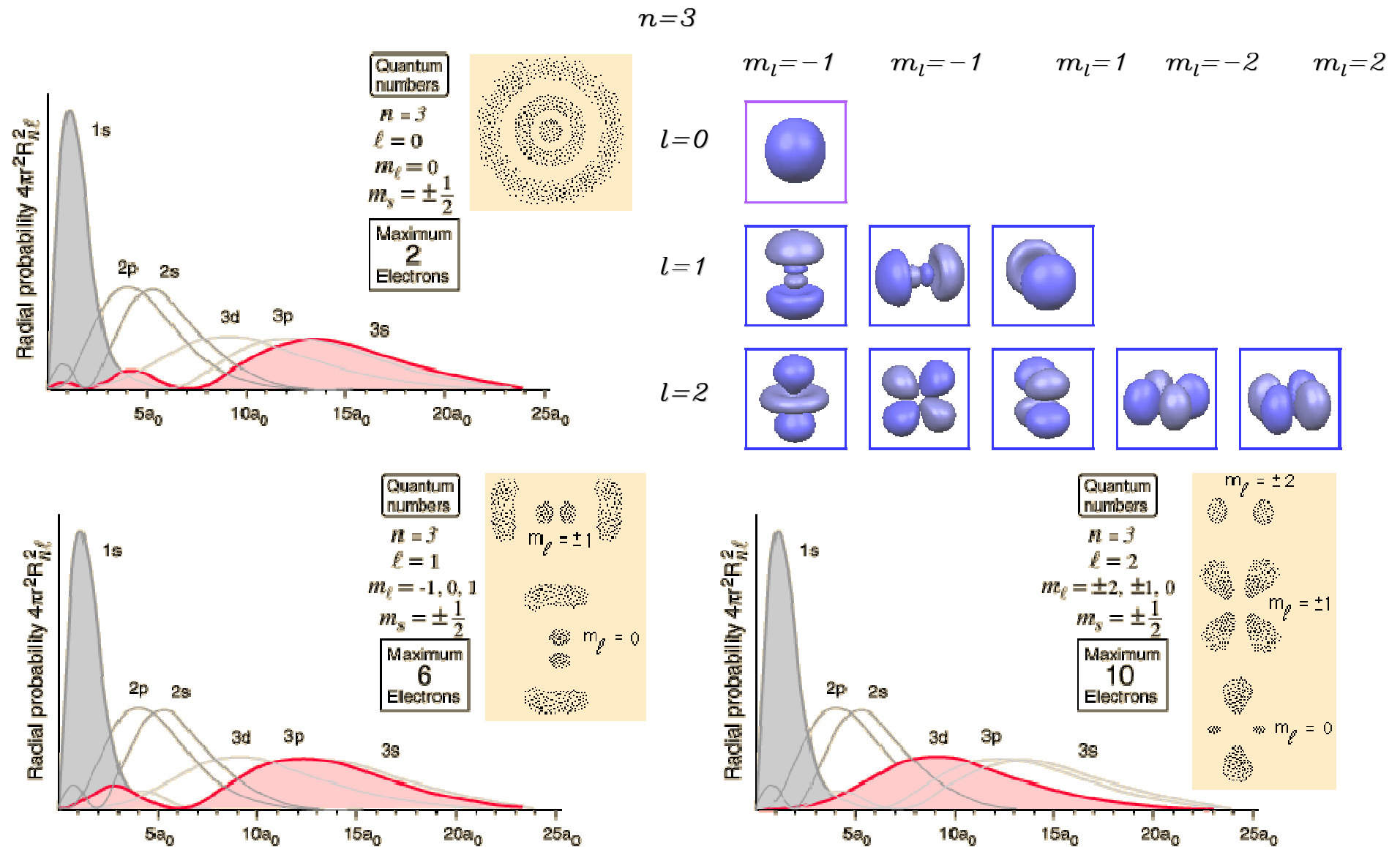
$$\psi(r, \theta, \phi) = R(r) \cdot P(\theta) \cdot F(\phi)$$

3s	$\psi_{3,0,0} = \frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left( 27 - \frac{18r}{a_0} + \frac{2r^2}{a_0^2} \right) e^{-r/3a_0}$
3p ( $m_\ell=0$ )	$\psi_{3,1,0} = \frac{2}{81\sqrt{2\pi} a_0^{3/2}} \left( \frac{6r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \cos\theta$
3p ( $m_\ell=+1$ )	$\psi_{3,1,1} = \frac{1}{81\sqrt{\pi} a_0^{3/2}} \left( \frac{6r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin\theta e^{i\phi}$
3p ( $m_\ell=-1$ )	$\psi_{3,1,-1} = \frac{1}{81\sqrt{\pi} a_0^{3/2}} \left( \frac{6r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin\theta e^{-i\phi}$
3d ( $m_\ell=0$ )	$\psi_{3,2,0} = \frac{1}{81\sqrt{6\pi} a_0^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0} (3\cos^2\theta - 1)$
3d ( $m_\ell=+1$ )	$\psi_{3,2,1} = \frac{1}{81\sqrt{\pi} a_0^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin\theta \cos\theta e^{i\phi}$
3d ( $m_\ell=-1$ )	$\psi_{3,2,-1} = \frac{1}{81\sqrt{\pi} a_0^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin\theta \cos\theta e^{-i\phi}$
3d ( $m_\ell=+2$ )	$\psi_{3,2,2} = \frac{1}{162\sqrt{\pi} a_0^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin^2\theta e^{2i\phi}$
3d ( $m_\ell=-2$ )	$\psi_{3,2,-2} = \frac{1}{162\sqrt{\pi} a_0^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin^2\theta e^{-2i\phi}$

# The probability densities for the Hydrogen atom



# The probability densities for the Hydrogen atom



# Quantum numbers for the Hydrogen atom

The hydrogen atom solution requires finding solutions to the separated equations which obey the constraints on the wavefunction. The solution to the radial equation can exist only when a constant which arises in the solution is restricted to integer values. This gives the principal quantum number  $n$ :

$$R(r) \xrightarrow{\text{Solution exists if and only if ...}} n = 1, 2, 3 \dots$$

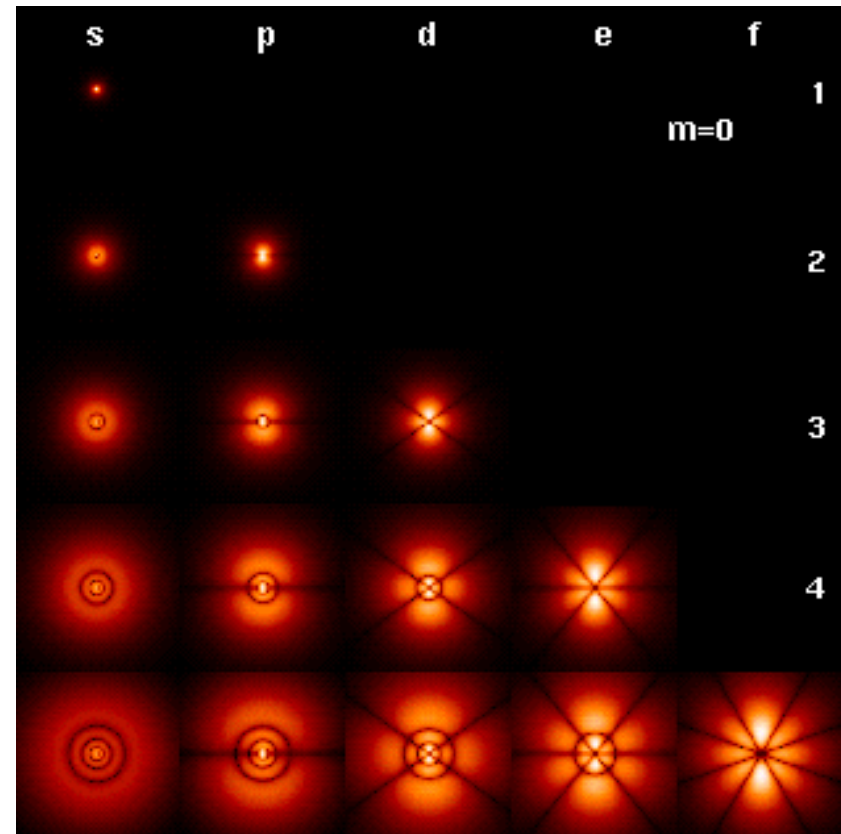
Similarly, a constant arises in the colatitude equation which gives the orbital quantum number  $\ell$

$$P(\theta) \xrightarrow{\text{Solution exists if and only if ...}} \ell = 0, 1, 2, 3, \dots, n-1$$

Finally, constraints on the azimuthal equation give what is called the magnetic quantum number  $m_\ell$ :

$$F(\phi) \xrightarrow{\text{Solution exists if and only if ...}} m_\ell = -\ell, -\ell+1, \dots, +\ell$$

"sharp"	s	$\ell = 0$	<i>For example, if <math>n=2, \ell=1</math>, the state is designated 2p</i>
"principal"	p	$\ell = 1$	
"diffuse"	d	$\ell = 2$	
"fundamental"	f	$\ell = 3$	



The higher  $n$  the state the larger it extends in space.

The number of nodal spheres increases as  $n-l$

The number of nodal planes increases as  $l-1$

# Electronic levels and quantum numbers in the hydrogen atom

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## *Summary of Allowed Combinations of Quantum Numbers*

$n$	$l$	$m$	Subshell Notation	Number of Orbitals in the Subshell	Number of Electrons Needed to Fill Subshell	Total Number of Electrons in Subshell
1	0	0	1s	1	2	2
2	0	0	2s	1	2	
2	1	1,0,-1	2p	3	6	8
3	0	0	3s	1	2	
3	1	1,0,-1	3p	3	6	
3	2	2,1,0,-1,-2	3d	5	10	18
4	0	0	4s	1	2	
4	1	1,0,-1	4p	3	6	
4	2	2,1,0,-1,-2	4d	5	10	
4	3	3,2,1,0,-1,-2,-3	4f	7	14	32

# The orbital angular momentum

From the radial equation we get that:

$$\frac{-\hbar^2}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + 2mr^2(V(r) - E) = -l(l+1) \cdot \hbar^2$$

The equation represents the one dimensional equation of a particle under an effective potential given by:

$$V_{\text{eff}}(r) = -\frac{ke^2}{r} + \frac{l(l+1)\hbar^2}{2mr^2}$$

The potential represents the electrostatic attraction of opposite charges plus a centrifugal potential  $L^2/2mr^2$ . Thus, the separation constant is the orbital angular momentum. The electron, in spite of not having a well defined orbit, has an orbital degree of freedom which is represented by a vector  $\mathbf{L}$ .

The magnitude of  $\mathbf{L}$  is:  $|\vec{L}| = \sqrt{l(l+1)}\hbar$

The electronic orbital has associated an angular momentum  $\vec{L}$ . The Schrödinger equations only fix their modulus and projection along the z axis. The other two components remain thus undetermined.

**“The absolute value of the orbital angular momentum  $L^2$  and its projection in the z axis can be measured simultaneously”**

From the angular equation we get that

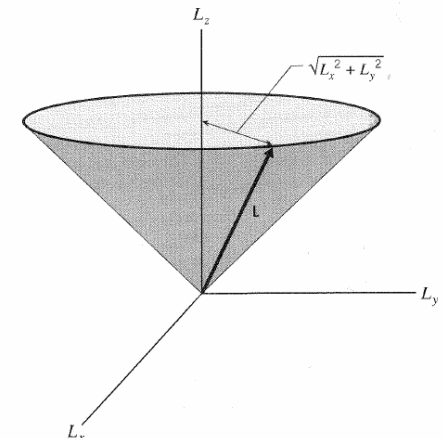
$$-m_l^2 + \frac{L^2}{\hbar^2} \sin^2 \theta - \frac{\sin \theta}{P(\theta)} \frac{d}{d\theta} \left[ \sin \theta \frac{dP(\theta)}{d\theta} \right] = 0$$

The equation angular momentum projection along the z-axis

must be an integer number times of  $\hbar$

so that  $L \cos \theta = m_l \hbar$

The angular momentum  $\vec{L}$  can only have a discrete set of latitude angles, so that the component along the z axis is the magnetic quantum number  $m_l$



# The orbital quantum number

1 The angular momentum of every level is given by the quantum number  $l$

$$-L^2 = -l(l+1) \cdot \hbar^2$$

$$L = \sqrt{l(l+1)} \cdot \hbar$$

2 The squared angular momentum is discrete in integer values of  $l$ .

3 The degeneracy of the angular momentum is  $n$

4 The parity of the wave function depend on  $l$ :

$l=0, 2, 4, \dots$  even wave function

$l=1, 3, 5, \dots$  Odd wave function

5  $l$  also determines the number of nodal planes. This an the parity is important for the selection rules of electronic transitions.

6  $l$  fix the modulus of the angular momentum, but not its orientation!

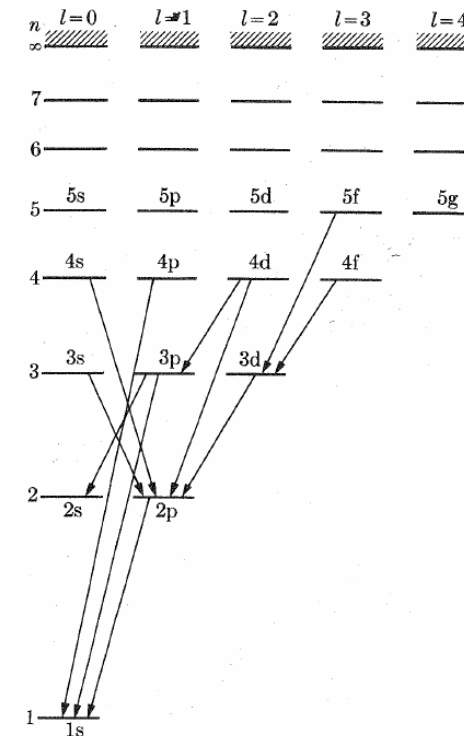
7 The Bohr model of the atom set that the angular momentum was an integer number of  $\hbar$ <sup>2</sup>  
What is wrong?

This is true in the z component  $L_z$

		n=1	n=2	n=3	n=4
s -- sharp	$l=0$	1s	2s	3s	4s
p -- principal	$l=1$		2p	3p	4p
d -- diffuse	$l=2$			3d	4d
f -- fundamental	$l=3$				4f
g	$l=4$	beyond this point, the notation just follows the alphabet			
h	$l=5$				
...					

8 The orbital quantum number sets the selection rules of electronic transitions

$$\Delta l = \pm 1$$





# The magnetic quantum number

1  $l$  fix the modulus of the angular momentum, but not its orientation!

2 The Bohr model of the atom set that the angular momentum was an integer number of

What is wrong?

$$L_z = m_l \hbar$$

This is true in the z component

3 Both, the modulus  $L$  and the z component  $L_z$  are defined. The orientation of the angular momentum can not be defined due to the uncertainty principle. Other ways, we would have well defined orbits.

4  $m_l$  determines the azimuth shape of the wave function. Given a specific orbital shape, with an associated angular momentum, specifies the orientation in space, such that the z component of the angular momentum is a discrete number of  $\hbar$ .

5 The larger is the modulus of  $m_l$  the more distant will be the electronic charge from the z axis. For  $m_l=0$ , the wave function is around the z axis. The z component of the angular momentum will be along the perpendicular plane, the x-y plane.

5 For  $m_l$  different than 0, there is a net component of the angular momentum around a direction of space. Since it corresponds to a charge in a circular movement, it produces a net magnetic field.

