

Quantum Theory of the Hydrogen Atom

Schrodinger equation for electron in three dimensions:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

The potential energy U here is the electric potential energy

Electric potential
energy

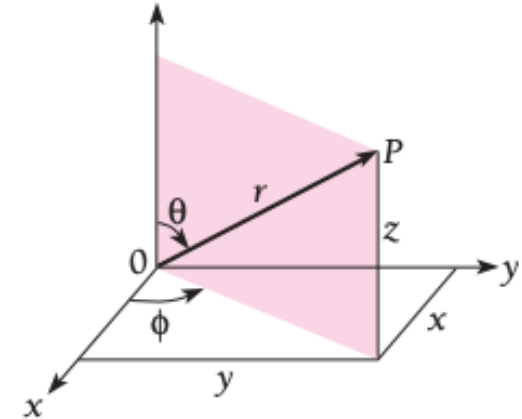
$$U = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right)$$

$$+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

Hydrogen atom

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0$$



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

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

$$z = r \cos \theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1} \frac{z}{r} \quad (\text{Polar angle})$$

$$\phi = \tan^{-1} \frac{y}{x} \quad (\text{Azimuthal angle})$$

Quantum Theory of the Hydrogen Atom

Separation of variables

Hydrogen-atom
wave function

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r} = \Theta \Phi \frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \phi^2} = R \Theta \frac{d^2 \Phi}{d\phi^2}$$

$$\begin{aligned} \frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \\ + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0 \end{aligned}$$

Quantum Theory of the Hydrogen Atom



$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}$$

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2$$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right)$$

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1)$$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l+1)$$

Quantum Theory of the Hydrogen Atom



Equation for Φ

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \quad m_l = 0, \pm 1, \pm 2, \dots \quad \dots\dots\dots(1)$$

Equation for Θ

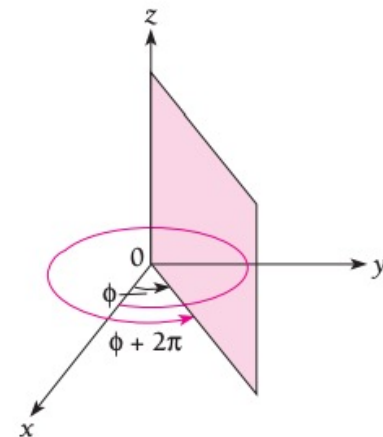
$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta} \right] \Theta = 0 \quad \dots\dots\dots(2)$$

Equation for R

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots\dots\dots(3)$$

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2} \right) = \frac{E_1}{n^2} \quad n = 1, 2, 3, \dots$$

$$\Phi(\phi) = Ae^{im_l\phi} \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l$$



Quantum Theory of the Hydrogen Atom

- Schrödinger equation has been separated into three ordinary second-order differential equations [Eq (1), (2), and (3)], each containing only one variable.
- Φ must be single valued at a given point in space, which means m_ℓ can take values 0 or a positive or a negative integer
- Eq. for Θ has a solution only if ℓ is an integer greater than or equal to $|m_\ell|$. For each value of ℓ , m_ℓ can take $(2\ell + 1)$ discrete values.
- Note that $\ell(\ell + 1)$ shows up in radial Eq. for R, it turns out, from standard differential equations, that R can be solved only for $n \geq (\ell + 1)$

Principal quantum number

$$n = 1, 2, 3, \dots$$

Orbital quantum number

$$l = 0, 1, 2, \dots, (n - 1)$$

Magnetic quantum number

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

Quantization of Orbital Angular Momentum



$$\mathbf{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

Using Eq 1 and Eq 2, we can write the following

$$L = \sqrt{l(l+1)} \hbar \quad (l = 0, 1, 2, \dots, n-1)$$

$$L_z = m_l \hbar \quad (m_l = 0, \pm 1, \pm 2, \dots, \pm l)$$

Table 41.1 Quantum States of the Hydrogen Atom

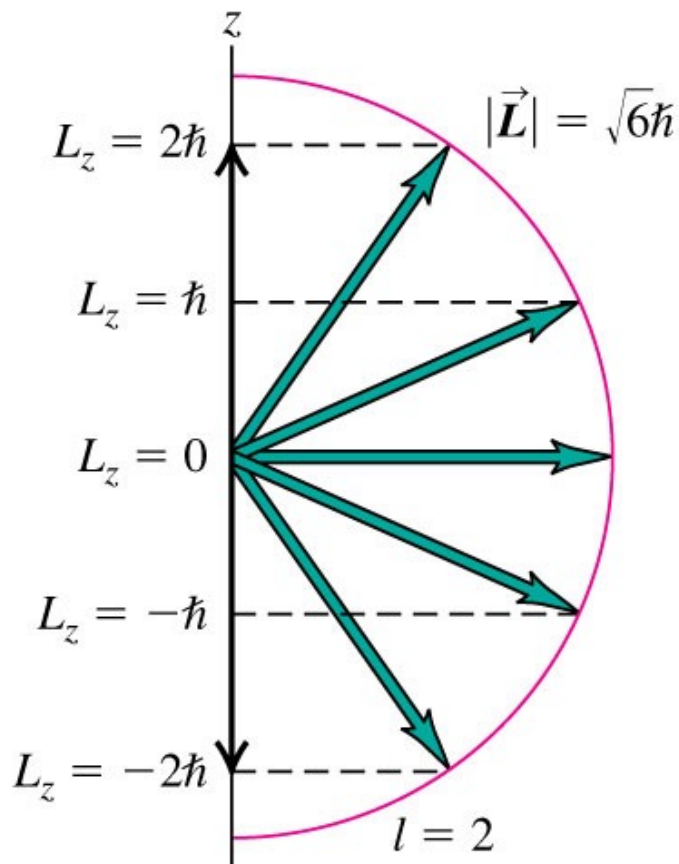
n	l	m_l	Spectroscopic Notation	Shell
1	0	0	1s	K
2	0	0	2s	L
2	1	-1, 0, 1	2p	
3	0	0	3s	M
3	1	-1, 0, 1	3p	
3	2	-2, -1, 0, 1, 2	3d	
4	0	0	4s	N

and so on

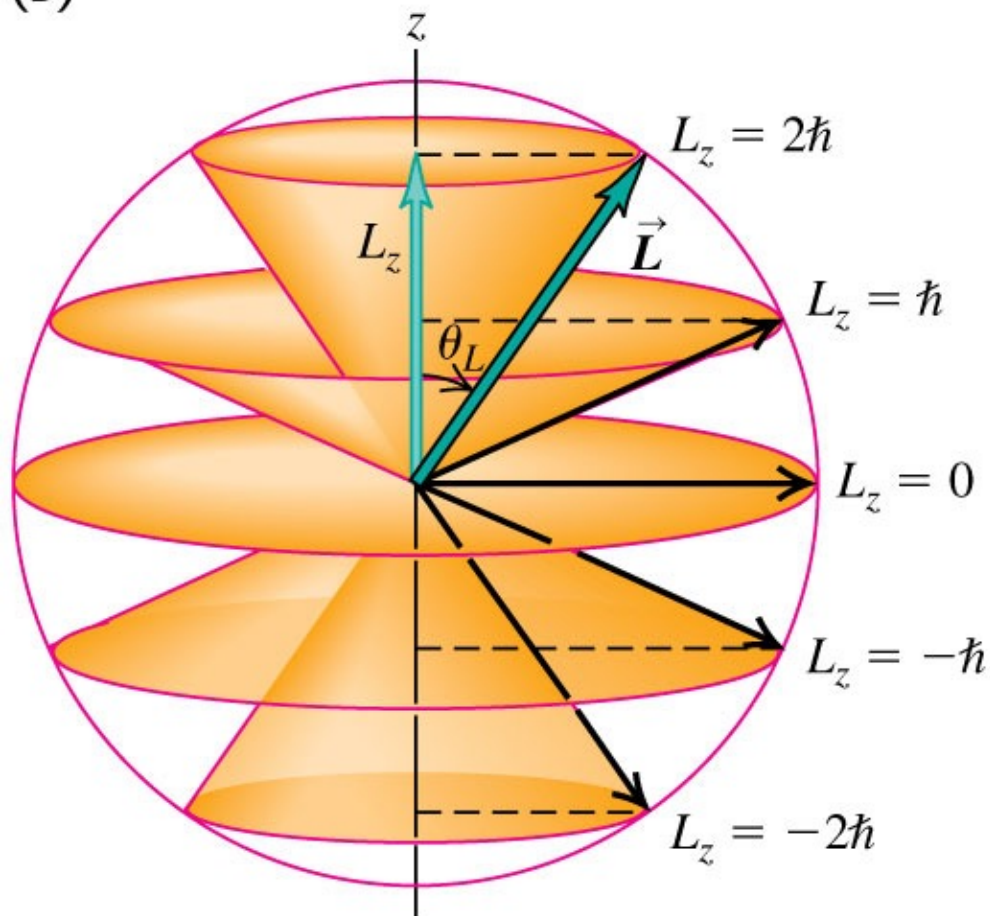
Quantization of Orbital Angular Momentum



(a)

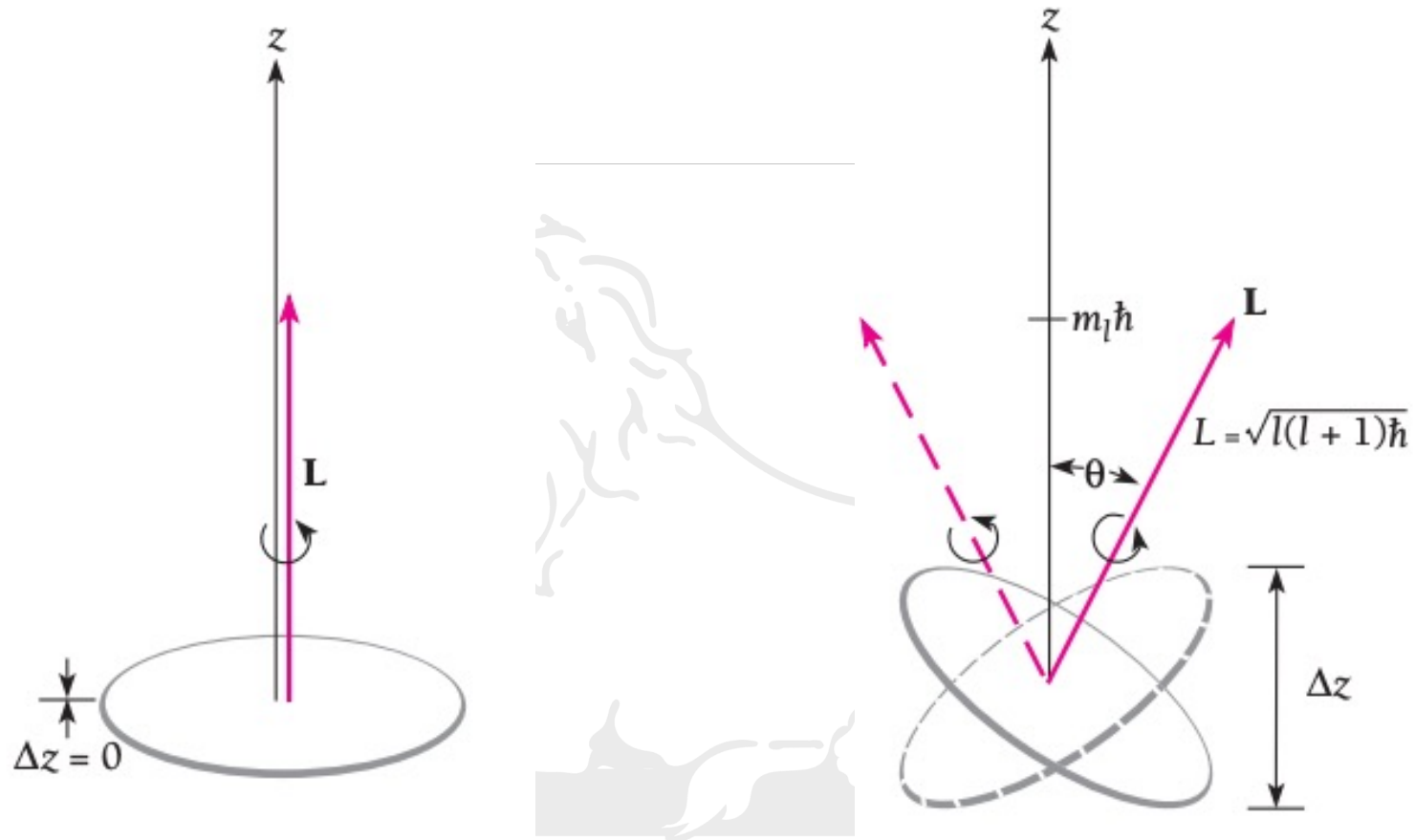


(b)



Number of possible orientations of \mathbf{L} in a magnetic field is $(2\ell + 1)$, which means orbital angular momentum is space quantized

Why is only one component of L quantized?



L can not be fixed in space rather specified in such a way that its projection L_z is $m_l \hbar$ **(built-in uncertainty in the z -coordinate of electron)**

Normalized wave functions of the Hydrogen Atom

Table 6.1 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	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

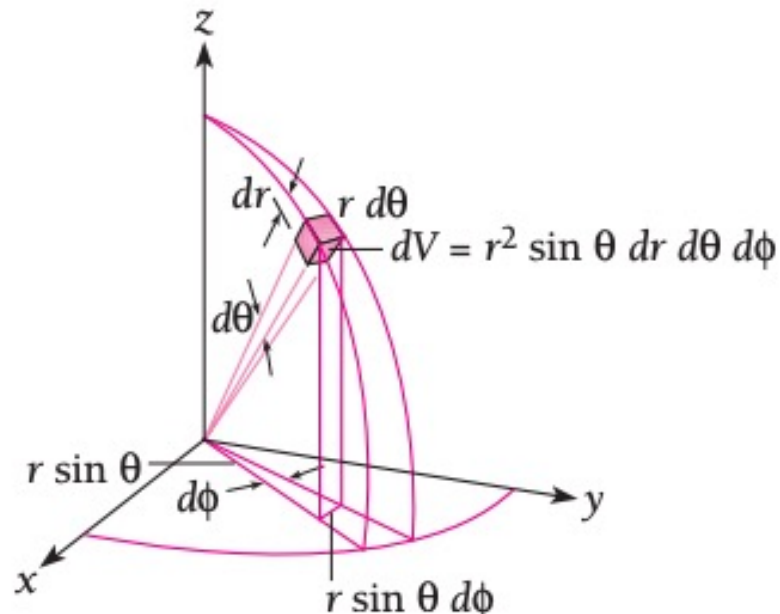
*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

Electron Probability density

Volume element

$$dV = (dr) (r d\theta) (r \sin \theta d\phi)$$

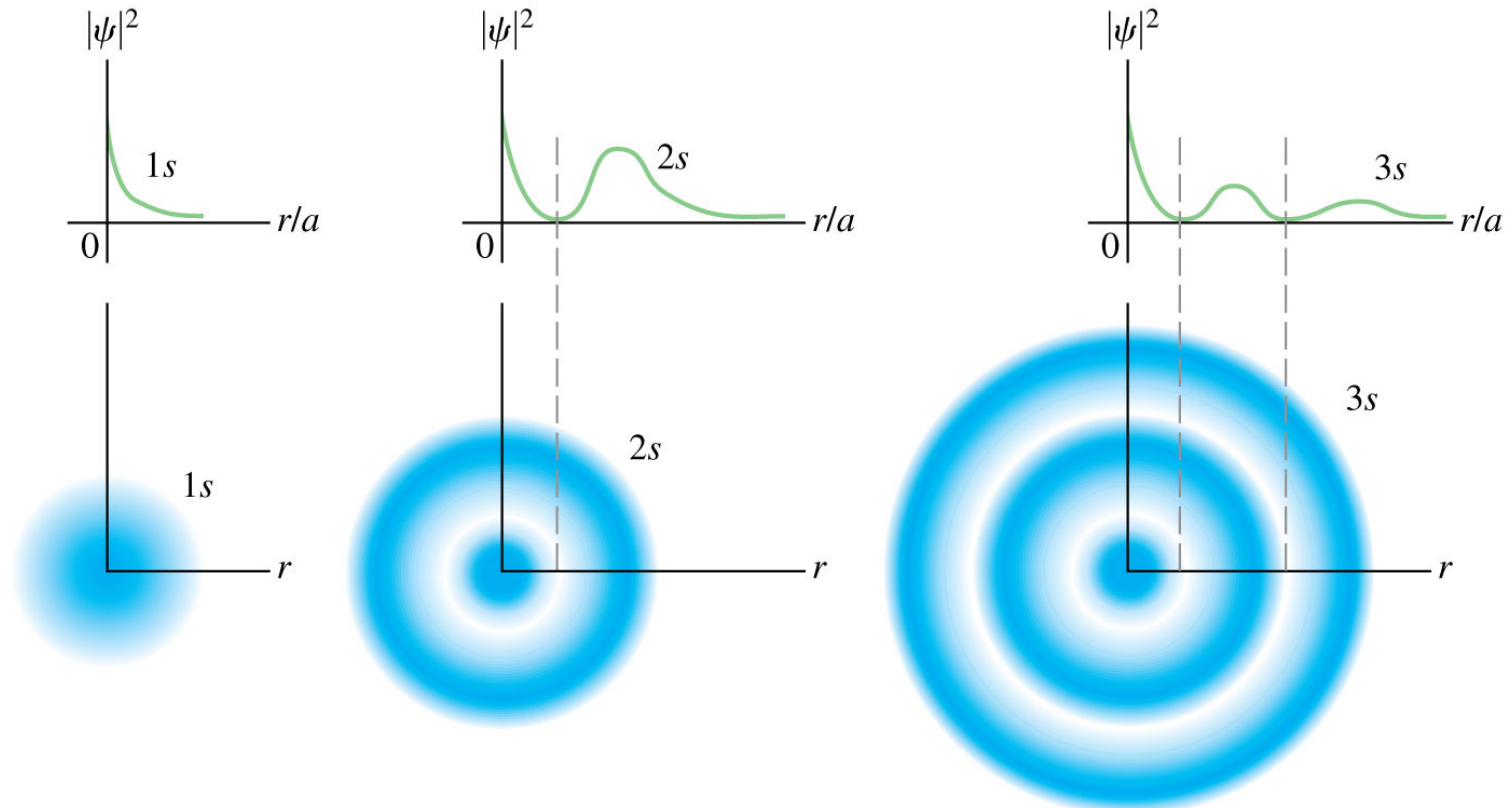
$$= r^2 \sin \theta dr d\theta d\phi$$



$$P(r) dr = r^2 |R|^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi$$

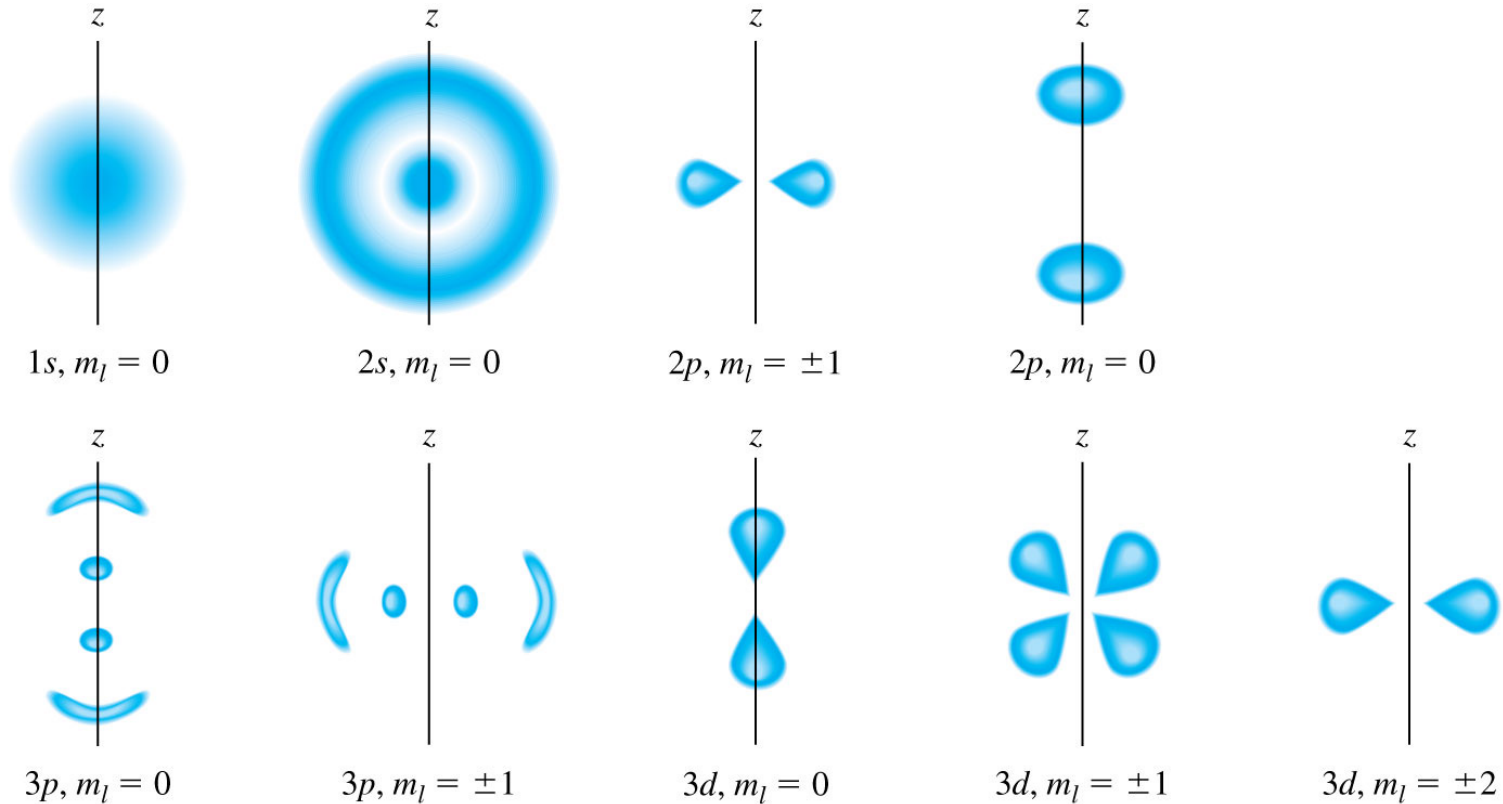
$$= r^2 |R|^2 dr$$

The hydrogen atom: Probability distributions



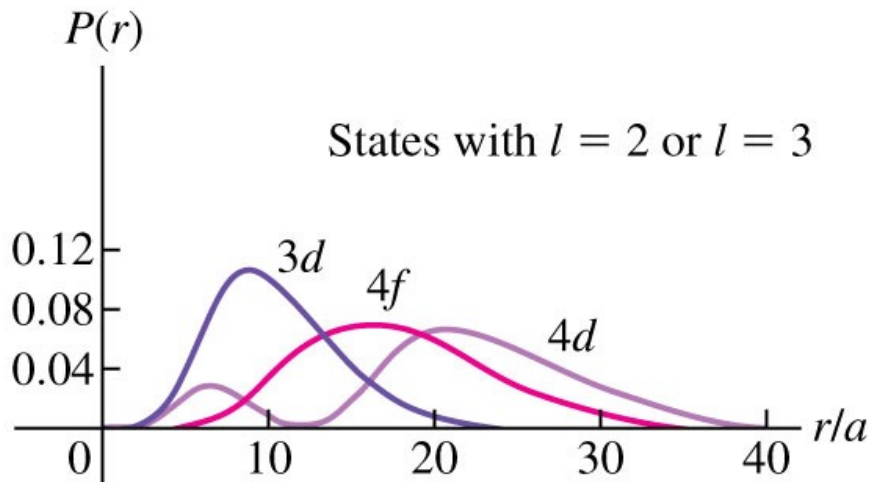
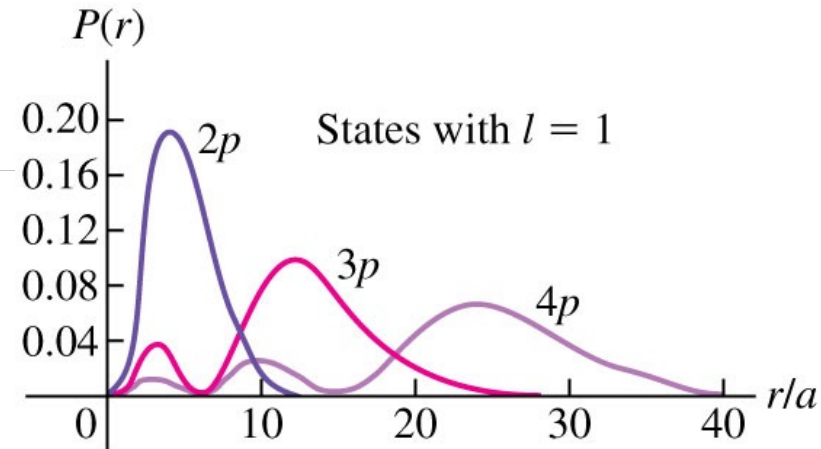
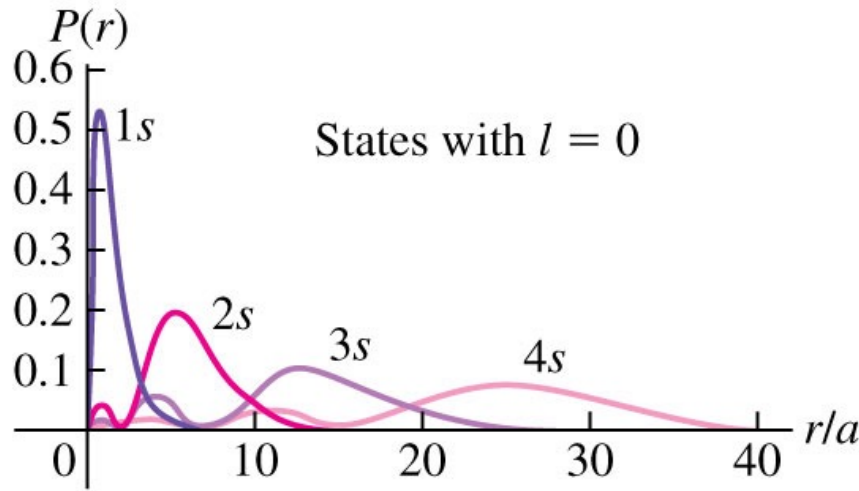
States of the hydrogen atom with $l = 0$ (zero orbital angular momentum) have spherically symmetric wave functions that depend on r but not on θ or ϕ . These are called s states.

The hydrogen atom: Probability distributions



States of the hydrogen atom with nonzero orbital angular momentum, such as p states ($l = 1$) and d states ($l = 2$), have wave functions that are *not* spherically symmetric.

The hydrogen atom: Degeneracy



Hydrogen atom states with the same value of n but different values of l and m_l are degenerate (have the same energy).

Questions on hydrogen atom

Q1: Find the ground-state electron energy E_1 using the radial wave function $R(r)$ that corresponds to $n = 1$ and $l = 0$

[Ans: $E_1 = -\frac{\hbar^2}{2ma_0^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}$ **]**

Q2: Using ground state wavefunction of hydrogen atom, calculate the most probable distance of the electron from the nucleus.

[Ans: $r = a_0$]

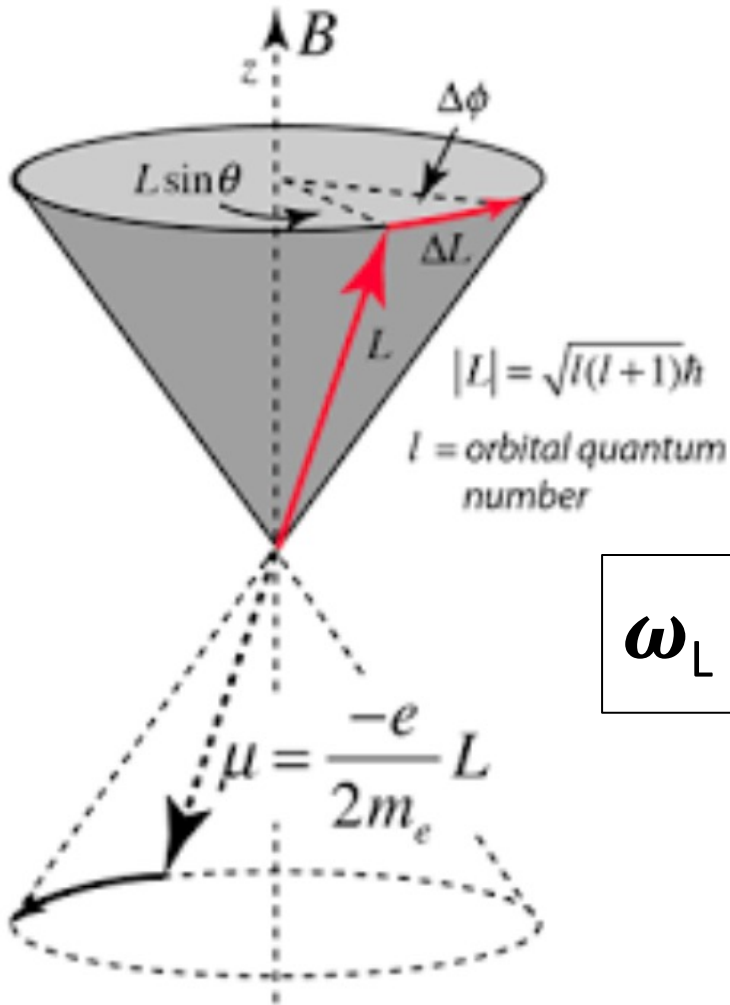
Q3: Calculate the probability that the electron on the ground state of hydrogen atom will be found outside the first Bohr radius.

[Ans: 67.7 %]

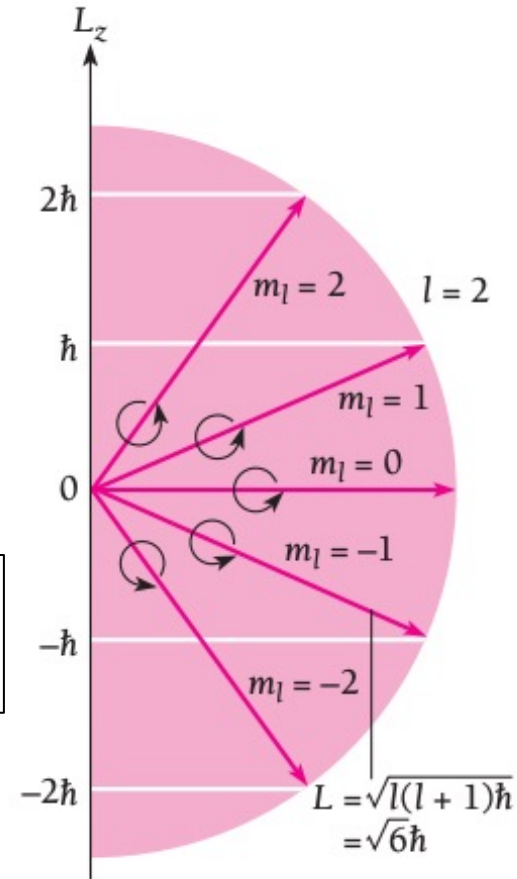
Q4: Calculate the most probable distance of the electron from the nucleus in the ground state of hydrogen atom and compare this with the average distance.

[Ans: $\langle r \rangle = 3/2 a_0$]

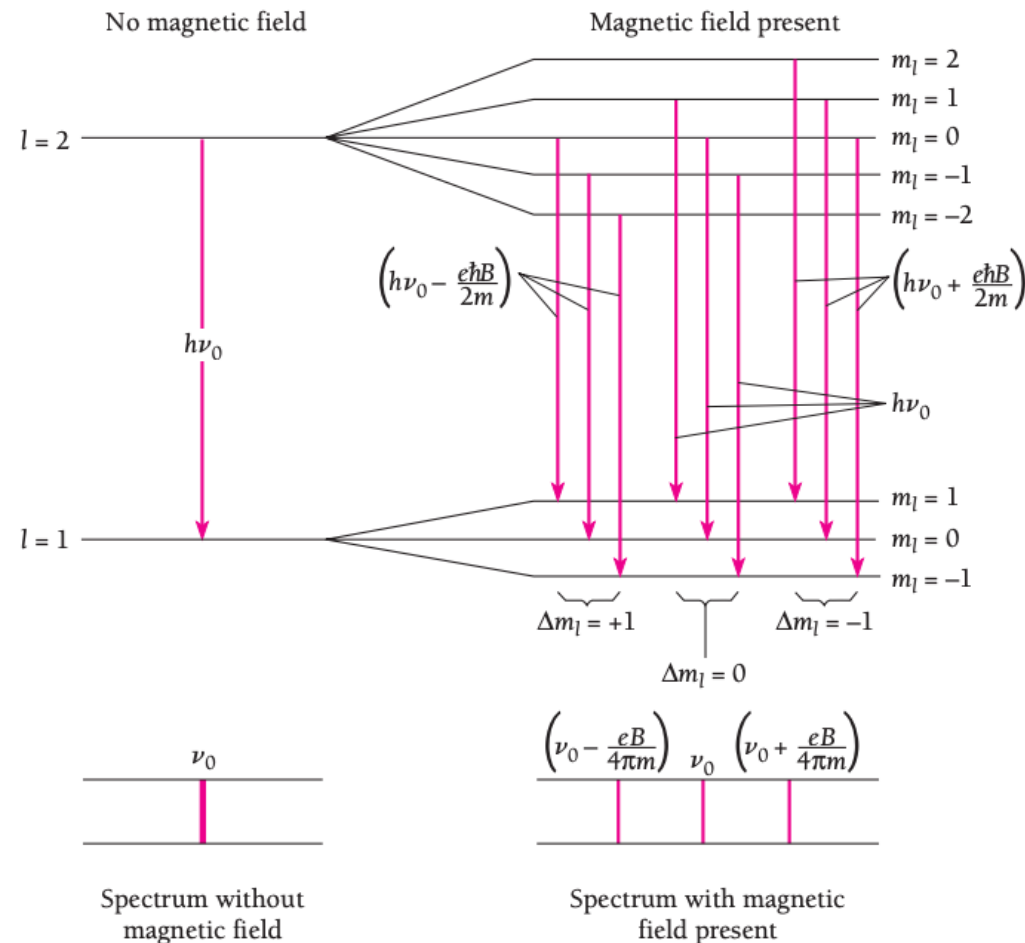
Space quantization of atoms (Larmor's precession)



$$\omega_L = \frac{e}{2m} B$$



Zeeman effect (Nobel Prize in 1902)



- The splitting of spectral lines into a number of polarized components by a magnetic field
- The spacing of the lines depends on the magnitude of the magnetic field

Selection rules

$$\Delta l = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

Normal Zeeman effect

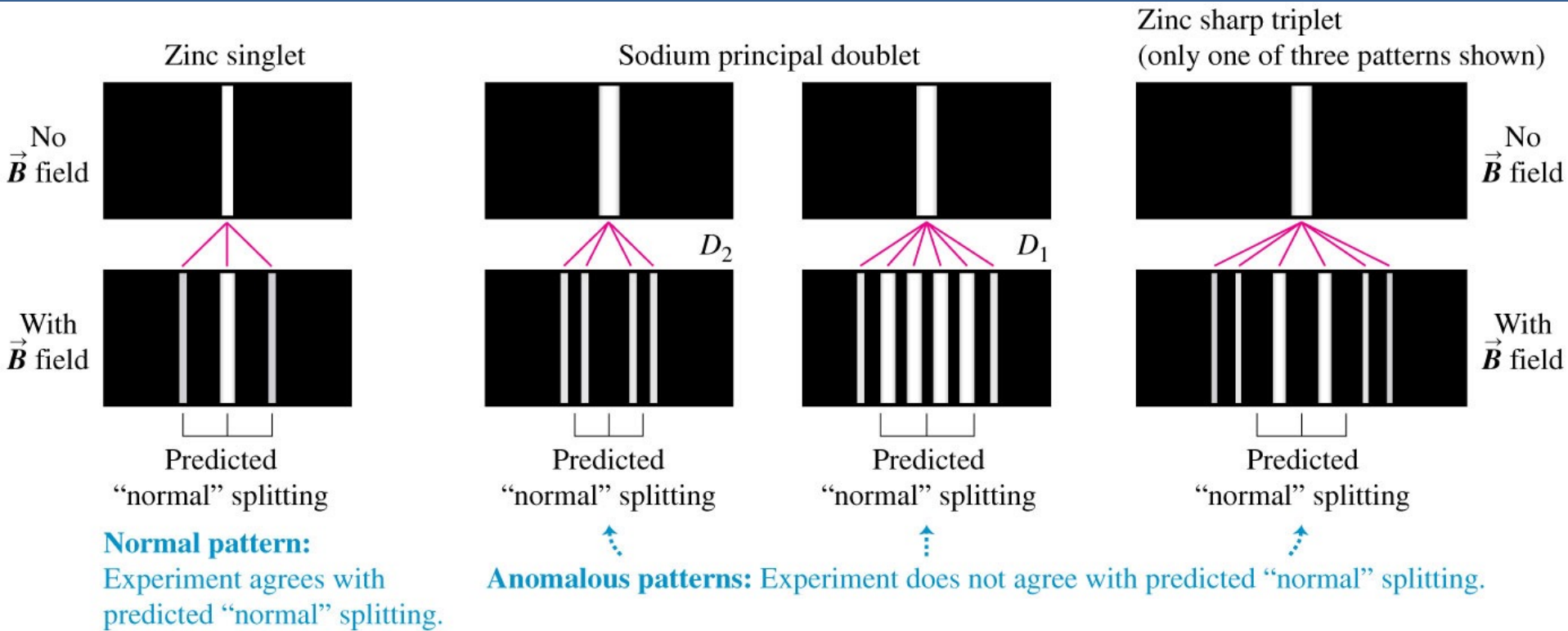
$$\nu_1 = \nu_0 - \mu_B \frac{B}{h} = \nu_0 - \frac{e}{4\pi m} B$$

$$\nu_2 = \nu_0$$

$$\nu_3 = \nu_0 + \mu_B \frac{B}{h} = \nu_0 + \frac{e}{4\pi m} B$$

$$U = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B} = \frac{eB}{2m_e} L_z = \hbar \omega_L m_\ell$$

Normal and Anomalous Zeeman effect



Failure of quantum theory of atoms developed so far:

- Fines structure of the first line of Balmer series (H_α line)
- Anomalous Zeeman effect (D_1 and D_2 components of Na doublet show four and six lines in the Zeeman pattern)

Electron Spin

“Every electron has an intrinsic angular momentum, called spin, whose magnitude is the same for all electrons. Associated with this angular momentum is a magnetic moment.”

Spin angular
momentum

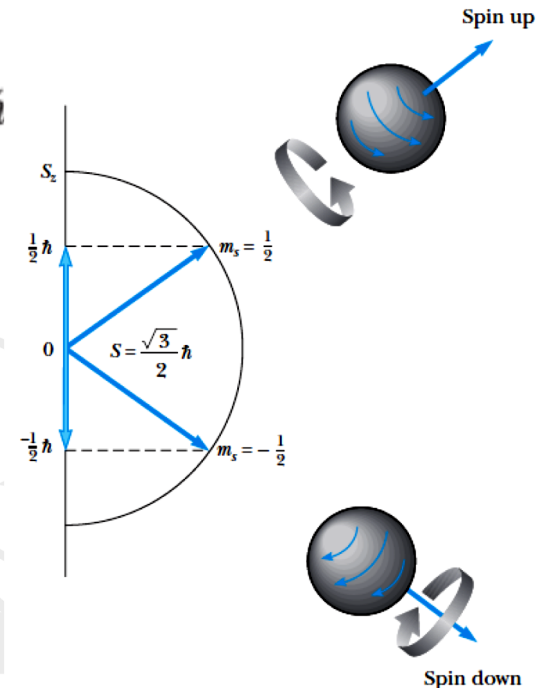
z component of
spin angular
momentum

Spin magnetic
moment

$$S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

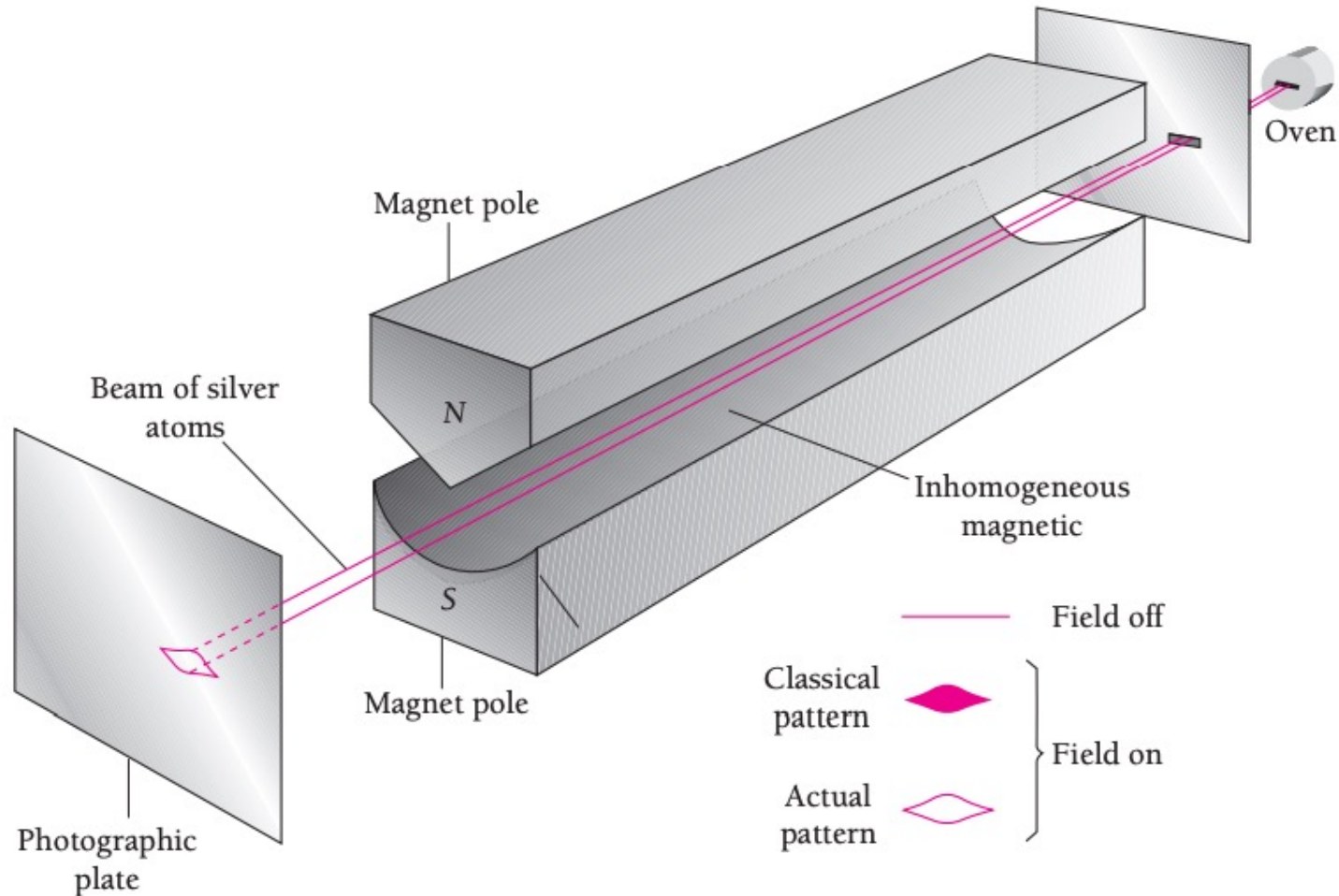
$$S_z = m_s\hbar = \pm \frac{1}{2}\hbar$$

$$\mu_s = -\frac{e}{m}S$$



The quantum number s describes the spin angular momentum of the electron. The only value s can have, $s = 1/2$

Electron spin and the Stern-Gerlach experiment



Classically, all orientations should be present in a beam of Ag atoms. It was found that the initial beam split into two distinct parts that correspond to the two opposite spin orientations in the magnetic field permitted by space quantization

Vector model of atom

Total atomic
angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

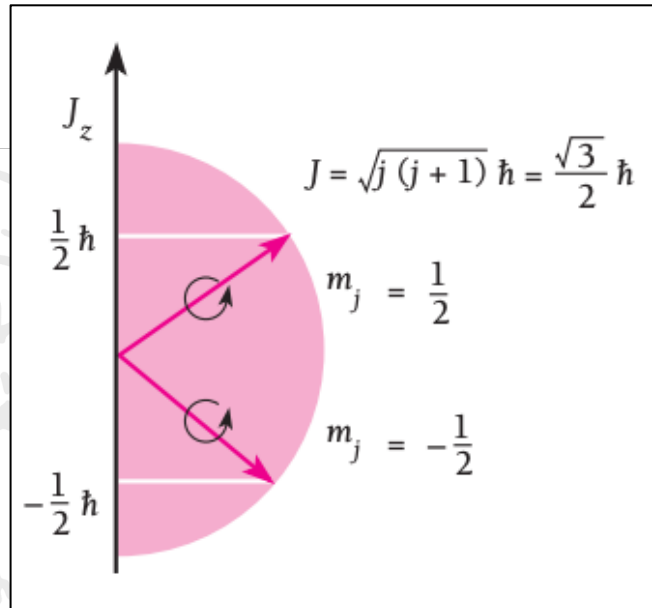
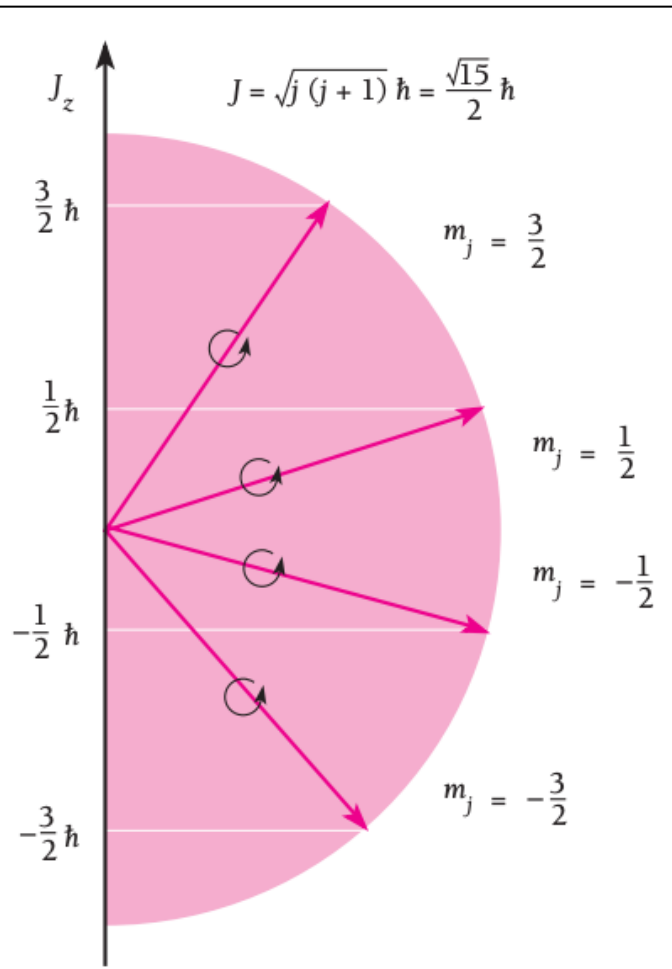
$$J = \sqrt{j(j+1)}\hbar \quad j = l + s = l \pm \frac{1}{2}$$

$$J_z = m_j \hbar \quad m_j = -j, -j+1, \dots, j-1, j$$

Spin magnetic
moment

$$\boldsymbol{\mu}_s = -\frac{e}{m} \mathbf{S}$$

Space quantization of total angular momentum for $\ell = 1$



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

$$L_z = M_L\hbar$$

$$S = \sqrt{S(S+1)}\hbar$$

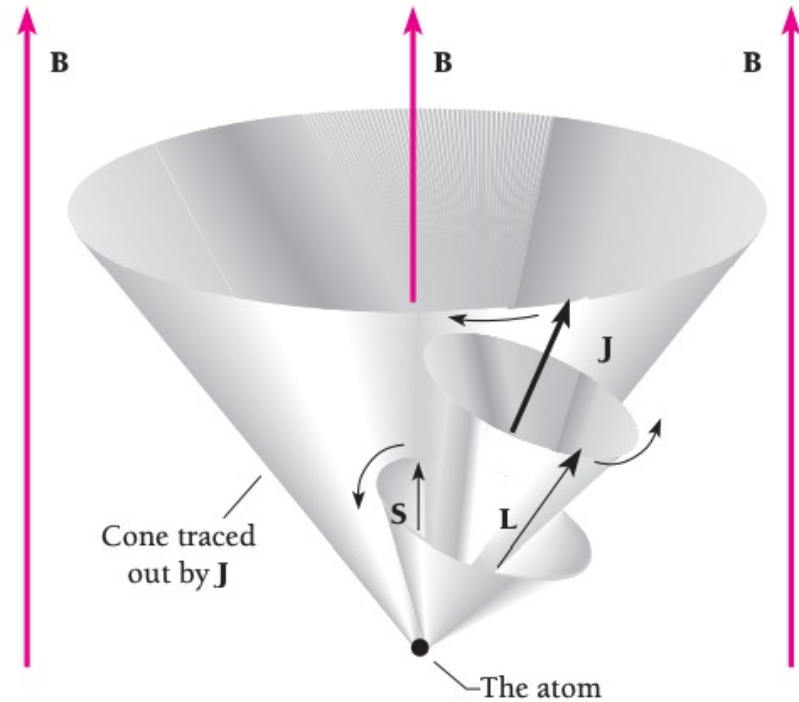
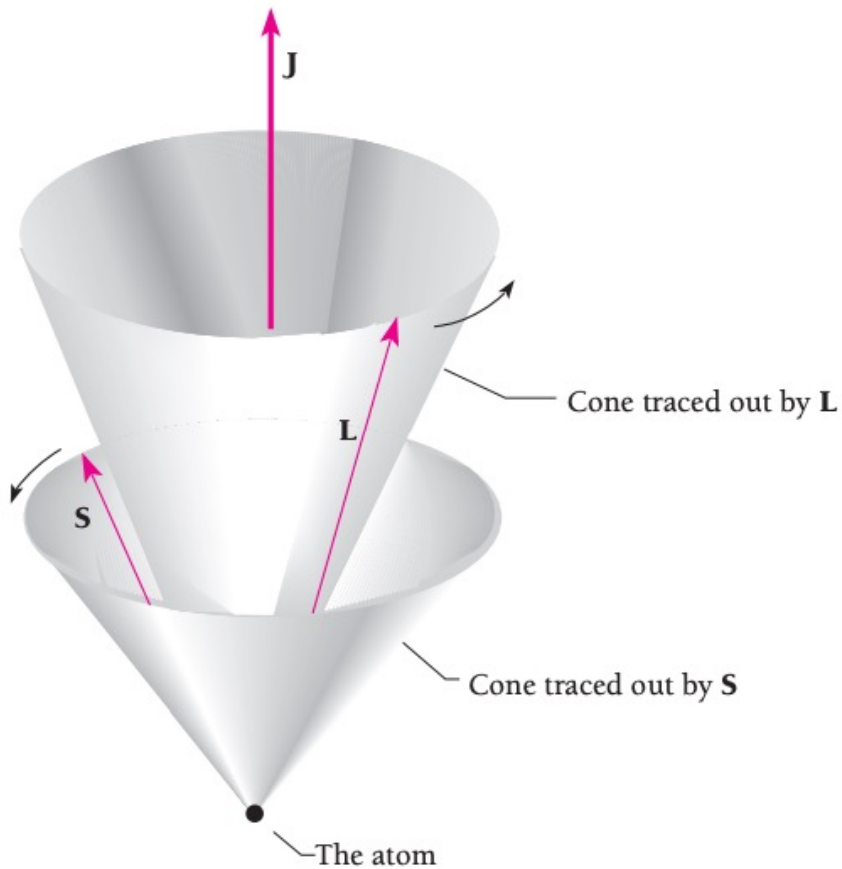
$$S_z = M_S\hbar$$

$$J = \sqrt{J(J+1)}\hbar$$

$$J_z = M_J\hbar$$

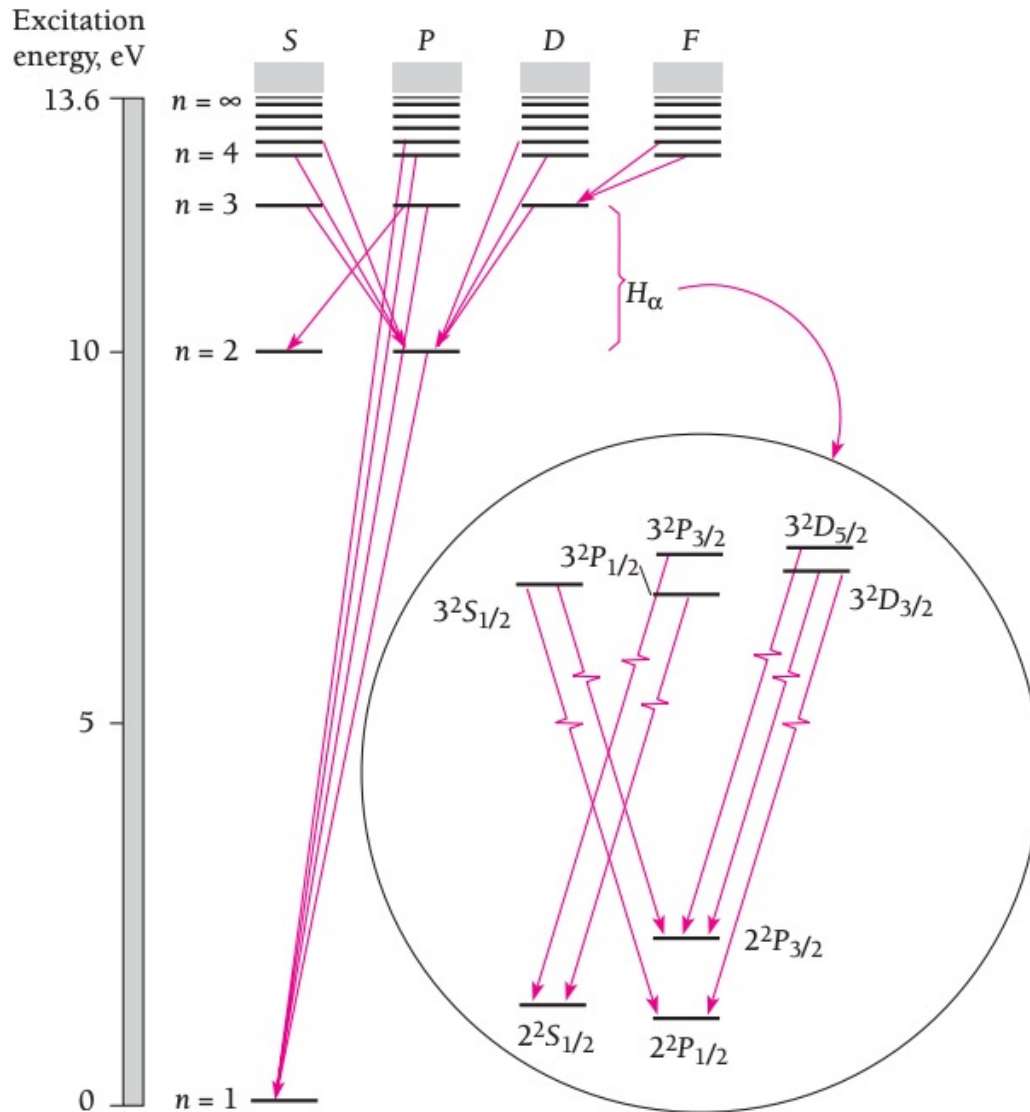
In the absence of magnetic field, the total angular momentum J is conserved in both magnitude and direction, and L and S precess around the resultant J .

Vector model of atom (L-S coupling)



- In the presence of magnetic field \mathbf{B} , \mathbf{J} precesses about the direction of \mathbf{B} while \mathbf{L} and \mathbf{S} continue precessing about \mathbf{J} .
- The precession of \mathbf{J} about \mathbf{B} gives rise to the anomalous Zeeman effect, since different orientations of \mathbf{J} involve slightly different energies in the presence of \mathbf{B} .

Fine structure of H_α line in hydrogen atom



- Selection rules for a single electron atom

$$\Delta n = \text{anything}$$

$$\Delta l = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

$$\Delta m_s = 0$$

$$\Delta m_j = 0, \pm 1$$

$$\Delta j = 0, \pm 1$$

- Selection rules make sure photon carries away one unit of angular momentum, \hbar
- The spin-orbit coupling splits $n = 3$ and $n = 2$ levels into sublevels of different j and transitions between ($n = 3 \rightarrow n = 2$) sublevels lead to seven closely spaced components

