

Angular Momentum,
Spin,
Zeeman Effect, Fine Structure,
and
Spectroscopic Notation

Townsend Ch 6.2-6.5

The Full Angular Solutions – Spherical Harmonics

The θ and φ solutions can now be combined

$F_{lm}(\theta, \varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi)$ and when normalized, yields the Spherical Harmonics:

$$Y_l^m = \left(\frac{2l+1}{4\pi} \right) \frac{(l-m)!}{(l+m)!} \Theta_l^m(\cos \theta) e^{im\varphi}$$

The orthonormality relation is: $\iint Y_l^m Y_{l'}^{m'} \sin \theta d\theta d\varphi = \delta_{ll'} \delta_{mm'}$

l	m	$Y_{lm}(\varphi, \theta)$
0	0	$(4\pi)^{-1/2}$
1	0	$(3/4\pi)^{1/2} \cos \theta$
1	1	$-(3/8\pi)^{1/2} \sin \theta e^{i\varphi}$
2	0	$(5/16\pi)^{1/2} (3 \cos^2 \theta - 1)$

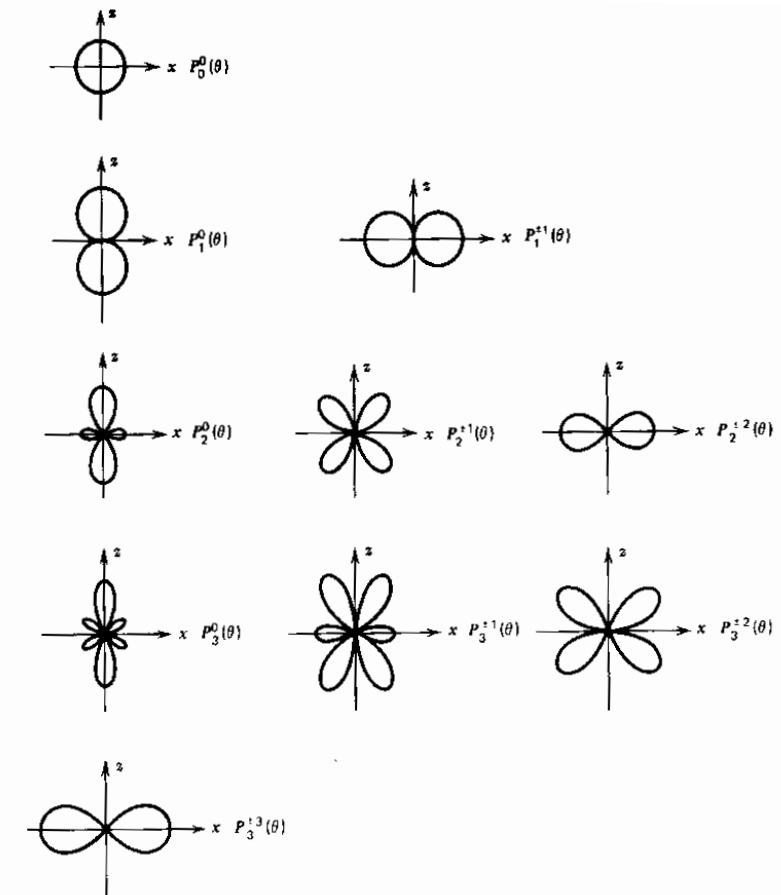


Fig. 12-3. Shapes of the associated Legendre polynomials as a function of θ , the angle between the z -axis and the equatorial plane, denoted here by the x -axis.

Notes on Quantum Angular Momentum

In classical physics, the angular momentum of a particle is defined as:

$$\vec{L} = \vec{r} \times \vec{p};$$

so $L_x = yp_z - zp_y$, $L_y = zp_x - xp_z$, and $L_z = xp_y - yp_x$,

Rewriting in terms of operators:

$$L_{x,op} = y \frac{\hbar}{i} \frac{\partial}{\partial z} - z \frac{\hbar}{i} \frac{\partial}{\partial y}; L_{y,op} = z \frac{\hbar}{i} \frac{\partial}{\partial x} - x \frac{\hbar}{i} \frac{\partial}{\partial z}, L_{z,op} = x \frac{\hbar}{i} \frac{\partial}{\partial y} - y \frac{\hbar}{i} \frac{\partial}{\partial x}$$

Converting to spherical coordinates yields $L_{z,op} = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$

$$L_{x,op} = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) ; \text{ and } L_{y,op} = \frac{\hbar}{i} \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

Quantum Angular Momentum

If we evaluate the operator in spherical coordinates for the square of the angular momentum, $L_{op}^2 = L_{x,op}^2 + L_{y,op}^2 + L_{z,op}^2$ we find that it is equal to:

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

which is related to the angular part of the Schrodinger Equation,

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right) = \frac{L_{op}^2 \Psi}{2mr^2}$$

Classically, this is the rotational kinetic energy.

Remember our solution to the angular term produced

$$L_{op}^2 \Psi = l(l+1)\hbar^2 \Psi, \text{ or } |\vec{L}| = \sqrt{l(l+1)}\hbar$$

From which we know that the the magnitude of the angular momentum is quantized.

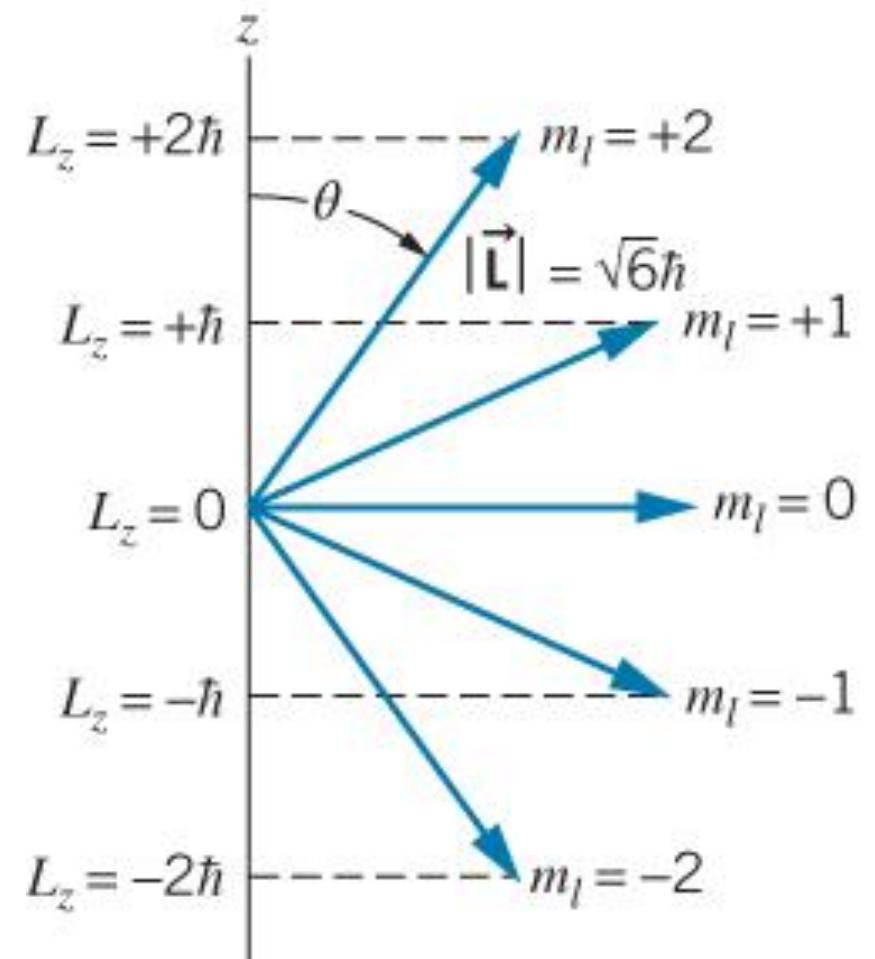
Quantum Angular Momentum

It can be shown that $[L_{op}^2, L_{z,op}] = 0$, therefore it is possible to simultaneously find eigenfunctions of the total angular momentum and the z-component of the angular momentum.

$$L_{op}^2 \Psi = l(l+1)\hbar^2 \Psi$$

$$L_{z,op} \Psi = m_l \hbar \Psi$$

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



Magnetic Moment and Angular Momentum

We again make a classical analogy to get started on quantum mechanical properties.

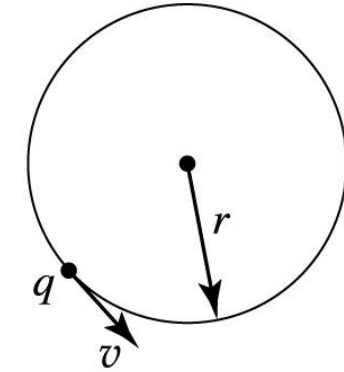


Figure 6.10 copyright 2009 University Science

If a particle of charge q , mass m and speed v circulates with radius r , it forms a current loop with average current $I = q/T$ where $T = 2\pi r/v$.

The magnetic moment of a current loop is $\mu = IA$,

$$\text{so } \mu = \frac{qv}{2\pi r} \pi r^2 = \frac{qvr}{2}.$$

But wait, we also know that $\vec{L} = \vec{r} \times \vec{p} = mrv\hat{L}$ so

$$\vec{\mu} = \frac{q}{2m} \vec{L}$$

State Energy in a Magnetic Field

If a system with a magnetic moment is placed in a magnetic field, the energy of interaction will be:

$$-\mu \cdot \vec{B} = -\frac{q}{2m} \vec{L} \cdot \vec{B}$$

so for a field along the z axis a term will be added to the Hamiltonian:

$$H_B \sim \frac{qB}{2m} L_{z,op}$$

The energy of the eigenfunction is therefore expected to shift by:

$$\Delta E_B = \frac{qB}{2m} m_l \hbar = \mu_B B m_l$$

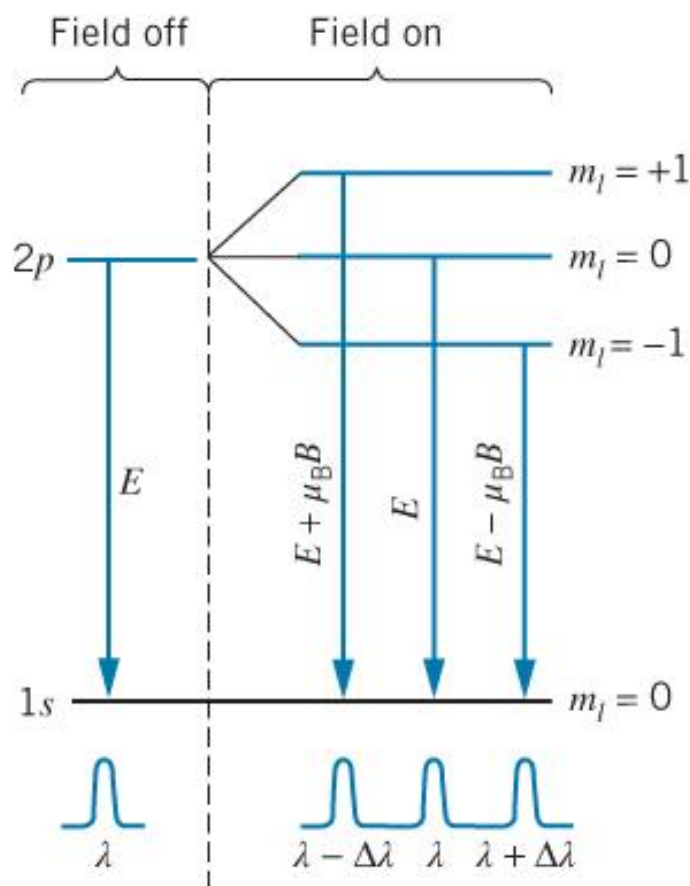
where $\mu_B = \frac{e\hbar}{2m} \approx 5.79 \times 10^{-5} \text{ eV/T}$ is called the Bohr magneton.

Zeeman Effect

The energy of a magnetic dipole assumes discrete energies associated with the magnetic moment.

$$\Delta E_B = -\vec{\mu} \cdot \vec{B} = -\mu_{L,z}B = -m_l\mu_B B$$

Where $\mu_B = \frac{e\hbar}{2m_e} = 5.8 \times 10^{-5} \frac{eV}{T}$



For $B=1$ T (strong!)

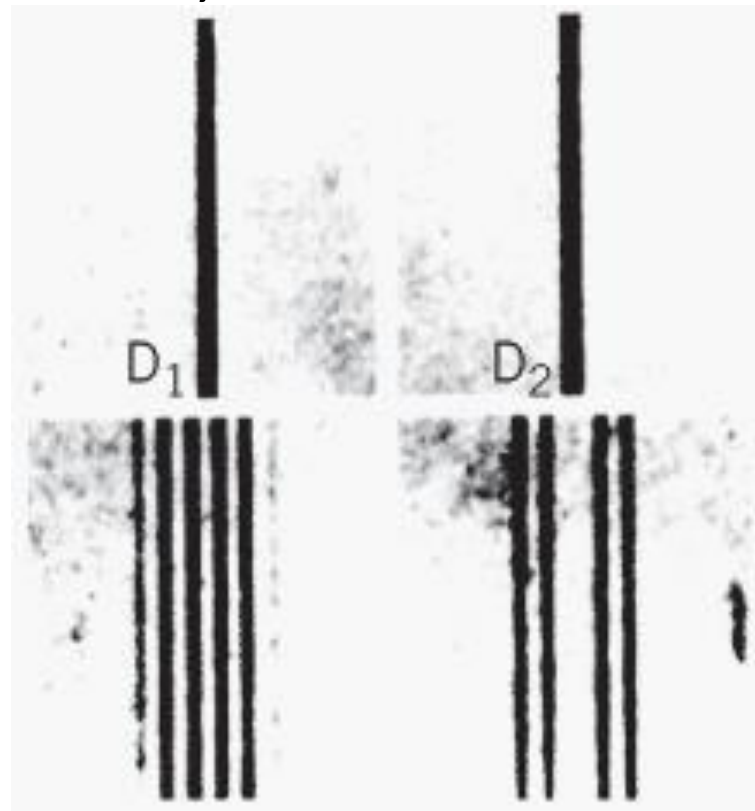
$$\Delta E \sim 10^{-4} \text{ eV}$$

And $\frac{\Delta\lambda}{\lambda} = \frac{\lambda^2}{hc} \Delta E \sim 0.03 \text{ nm}$ out of about 600 nm for a typical optical transition.

(This is a hard experiment, and Zeeman did it with a much weaker field in the 1890's. He shared the 1902 Nobel prize for his spectroscopic work.)

Anomalous Zeeman Effect

- Our theory so far predicts that a magnetic field will split a spectral line into an odd number of shifted lines.
- Instead, Zeeman observed this:



The theory is missing something.

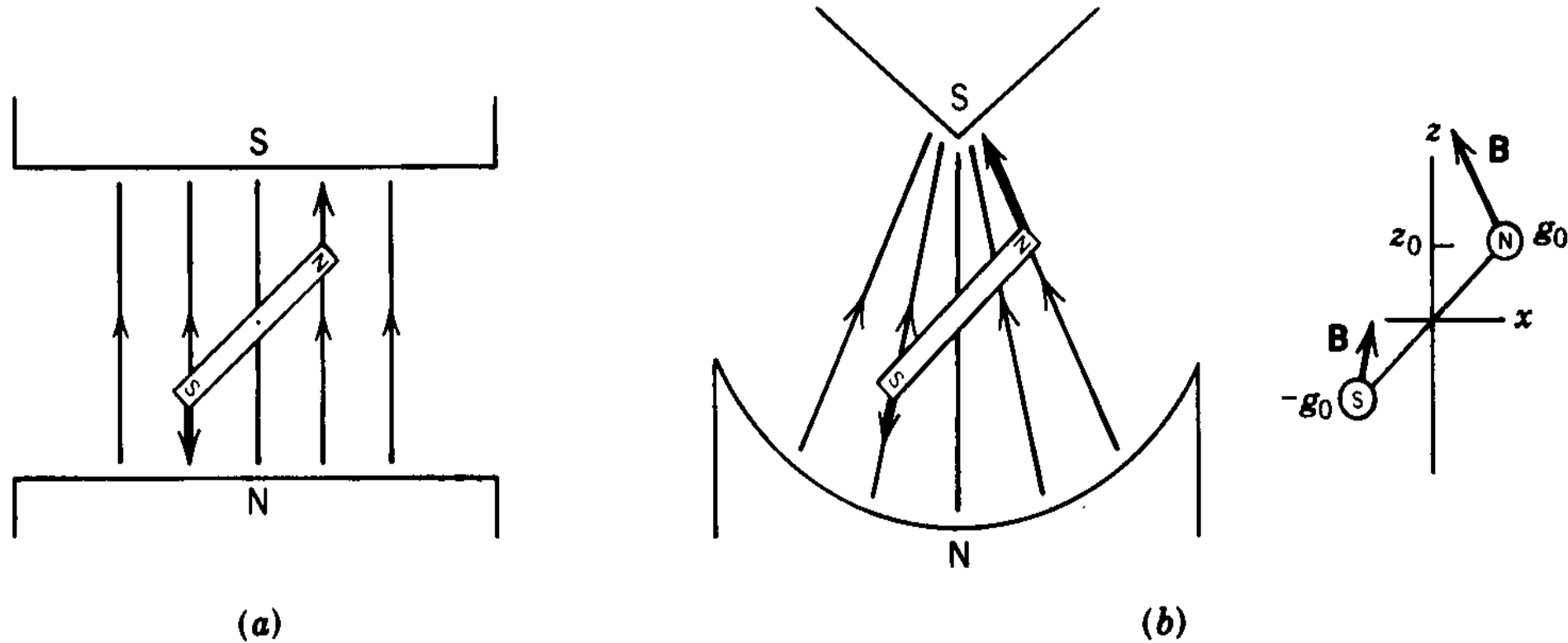
The anomalous Zeeman effect in sodium. (Top) The so-called sodium D-lines, a close-lying doublet of wavelengths 589.0 and 589.6 nm in the absence of a magnetic field. (Bottom) Splitting of the lines into six and four components in a magnetic field. This image was photographed by Pieter Zeeman in 1897.

The Stern-Gerlach Experiment

- The Stern-Gerlach experiment enables the separation of atoms in a beam into different magnetic dipole moments.
- A uniform magnetic field exerts a torque on a dipole, but no net translational force.
- A dipole in a non-uniform field experiences a net force.

Figure 8-9

Forces on the poles of a magnet in a uniform field and in a nonuniform field. The field gradient exerts a net force on the magnet in the second case.



Dipole (N and S poles) at different locations in a non-uniform field

$$B_z(N) = B_{z0} + z_0 \frac{\partial B_z}{\partial z} \text{ and}$$

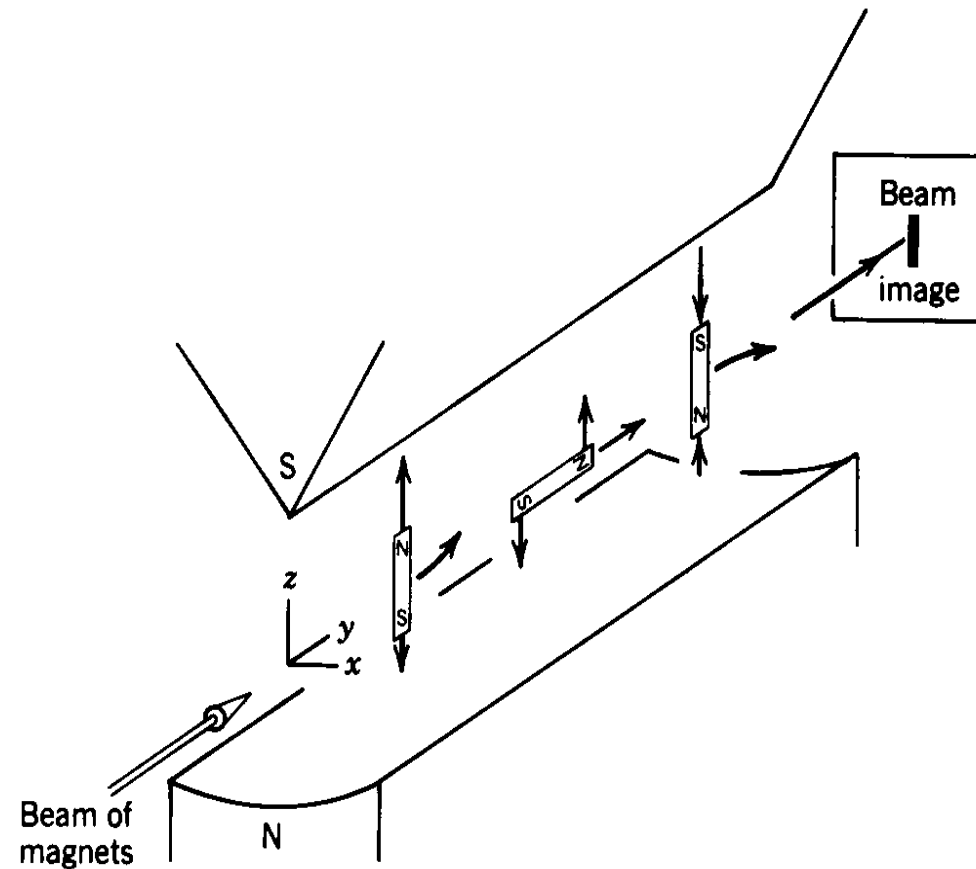
$$B_z(S) = B_{z0} - z_0 \frac{\partial B_z}{\partial z}$$

Assigning pole strengths $\pm g_0$ to the dipole,

$$F_z \cong g_0(B_z(N) - B_z(S)) = 2g_0z_0 \frac{\partial B_z}{\partial z} = \mu_z \frac{\partial B_z}{\partial z}$$

Figure 8-10

Deflection of a beam of classical magnets in a nonuniform magnetic field.

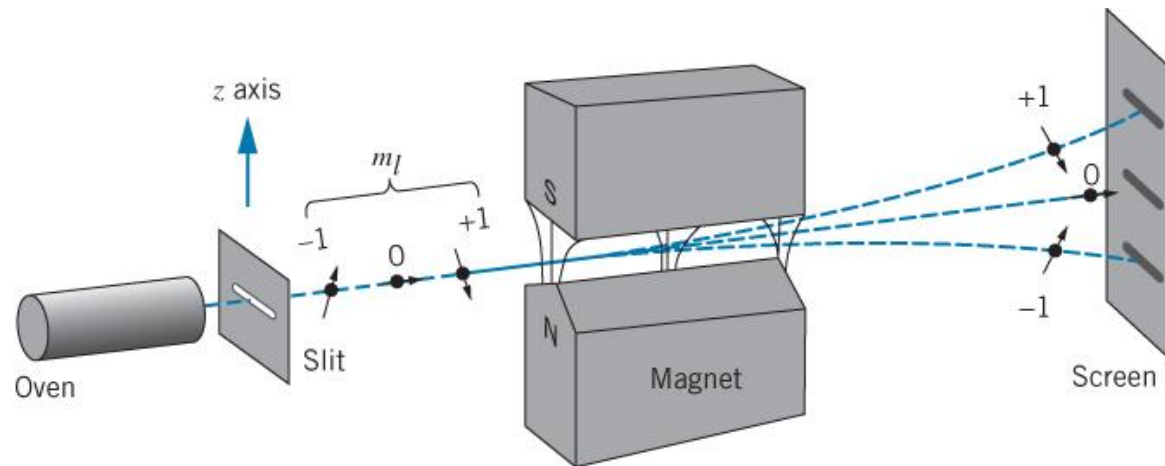


For a force $F_z = \mu_z \frac{\partial B_z}{\partial z}$, we can estimate the deflection of the beam Δz after it passes along the length of the magnet gap.

$$\Delta z = \frac{1}{2} a_z t^2 \text{ with } a_z = \frac{\mu_z}{M} \frac{\partial B_z}{\partial z} \text{ and } t = \frac{x}{v_x}$$

$$\text{and estimating } v_x = \sqrt{\frac{3k_B T}{M}} \quad \Delta z = \frac{1}{2} \mu_z \frac{\partial B_z}{\partial z} \frac{x^2}{6k_B T}$$

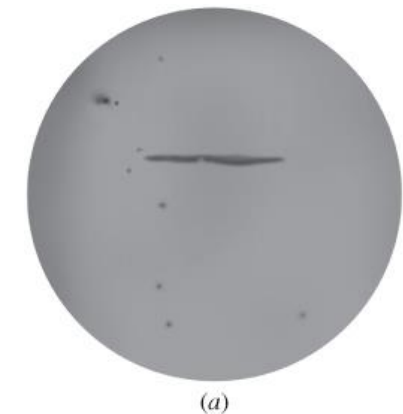
The Stern-Gerlach Experiment: Observation



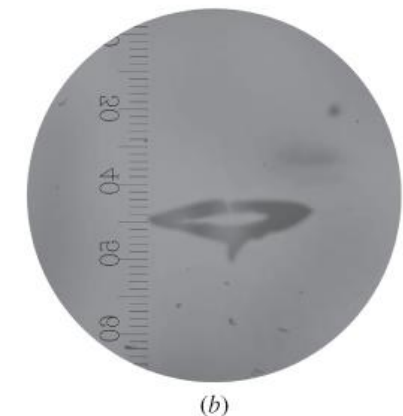
Theory so far predicts that Ag atoms passing perpendicular to a B field gradient will not be deflected. They are deflected into two lines.

From deflection magnitude and Zeeman spectra: $\mu_e \approx \mu_B$

No B field →



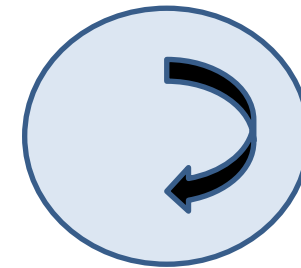
B field →



Pauli proposed that the observed experimental structure could arise if the a new two-valued degree of freedom could be assigned to the electron itself.

Maybe the electron is spinning.

Imagine a ball of spinning charge:



Classical radius: $r_e = \frac{q^2}{\epsilon_0 m_e c^2}$

If we use the classical radius, we find that the edge of the electron must spin at 10x the speed of light.

A full quantum theory is required.

Electron Magnetic Moment

The observed splittings imply that the electron has a magnetic moment.

A new spin quantum number m_s was proposed to explain the experiments. The intrinsic **spin** angular momentum is \vec{S}

where $|\vec{S}| = \sqrt{s(s+1)}\hbar$

and $S_z = m_s\hbar$ and $m_s = -s, \dots, s$ in integer steps

($2s + 1$ allowed values)

m_s must be two-valued (Stern-Gerlach Exp.) and does not appear to have a term with $\mu=0$, so it was proposed that

$$s = 1/2 \text{ and}$$

$$m_s = -1/2 \text{ or } +1/2$$

Two independent indices m_l and m_s are used to specify states according to the z component of **L** and **S**.

Electron Spin Magnetic Moment

The electron magnetic moment can be found from the splittings, but also can be derived from first principles (too hard for this course).

$$\vec{\mu}_s = -\frac{q_e}{m} \vec{S}$$

(Note that this relation differs by a factor of two from the angular momentum – moment relation.)

$$\Delta E = -\vec{\mu}_s \cdot \vec{B} = -\mu_{s_z} B$$

Quantum State and Optical Terminology

- We can describe the possible electronic states of an electron in hydrogen by listing the quantum numbers (n, l, m_l, m_s) , where
 - $m_l(m_s)$ is the projection of L (S) on the z axis.
 - $m_l < (l(l+1))^{1/2}$ and $m_s = +$ or $- \frac{1}{2}$.
- Spectroscopic notation was developed before quantum numbers were understood and described the *appearance* of some spectral lines.
- The levels with $n=1, 2, 3, 4$ are listed with that number since it is a good measure of the transition energies.
- The angular momentum quantum number is specified using s, p, d, f, g for $l=0, 1, 2, 3, 4$.

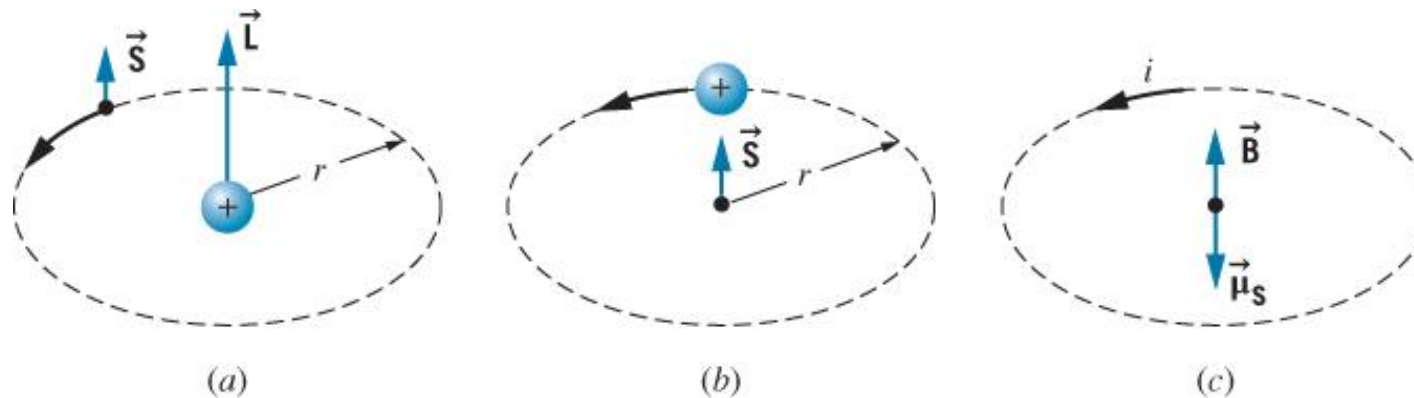
(s =sharp, p =principal, d =diffuse, f =fundamental, g and h are notes to follow f .)

Total angular momentum

- We now have two sources of magnetic moment and consequent energy shift.
- We are tempted to think that they are just two effects that are independent of one another, but no, it is more complicated.
- The two magnetic moments are coupled. (Orbital angular momentum creates a magnetic field that defines a z-direction for the spin moment (and vice versa).)
- Because \vec{L} and \vec{S} are coupled, they interact with an external magnetic field in such a way that the total angular momentum: $\vec{J} = \vec{L} + \vec{S}$ is a conserved quantity

Fine Structure

- The spin of the electron also gives rise to energy splitting of lines due to the magnetic field induced by the angular momentum of the proton around the electron.



- The magnetic field due to the orbiting proton can be estimated semi-classically.

$$B = \frac{\mu_0 i}{2r} \sim \frac{\mu_0}{2r} \frac{ev}{2\pi r}$$

And taking $mvr = L = n\hbar$ (where n is the primary quantum number)

$$\Delta E = 2\mu_B B \sim \mu_0 m e^8 / (256\pi^4 \epsilon_0^3 \hbar^4 n^5)$$

$$\Delta E \cong mc^2 \alpha^4 / n^5 \approx 10^{-5} eV$$

Where $\alpha = e^2 / 4\pi\epsilon_0 \hbar c = 1/137$.

Total angular momentum

The total angular momentum (J) is the vector sum of the orbital and electron angular momenta (spin).

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

The total angular momentum is conserved in all interactions (and not necessarily L or S individually). The total angular momentum has the value:

$$|J| = \sqrt{j(j+1)}\hbar \text{ with possible values}$$
$$j = |l-s|, |l-s|+1, |l-s|+2, \dots, |l+s|$$

and with $j_z = m_z\hbar$

Spectroscopic notation

In spectroscopic notation we label the value of the total angular momentum quantum number j with a subscript following the letter code for orbital angular momentum.

As an example: The notation $3p_{3/2}$ denotes a single electron in the $n=3, l=1, j=3/2$ state.

Spectroscopic notation can also be used to describe the state of an atom with more than one electron. The angular momentum and spin are the sum for all the electrons in the system.

As an example: The notation $3P_{1/2}$ can denote a sodium atom with its electron in the $n=3, l=1, j=1/2$ state. The electrons in the filled shells are paired off in such a way that the total angular momentum and spin are zero.

Spectroscopic notation example

What is the total angular momentum and its z-component for an electron in the ground state of hydrogen? And what is its spectroscopic notation?

$$l = 0, s = 1/2$$

so j can only have the value

$$j = l + s = 1/2 \text{ and therefore}$$

$$m_j = +1/2 \text{ or } -1/2.$$

The spectroscopic notation is thus $1s_{1/2}$

$$\text{The total angular momentum is } |J| = \sqrt{j(j+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

Example 2

What are the possible values for the total angular momentum for an electron in an $n=4$, p state?

$l = 1$ and $s = 1/2$ so

$j=3/2$ or $1/2$ and

$$J = \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} \hbar = \frac{\sqrt{3}}{2} \hbar$$

with $J_z = \pm 1/2$ or

$$J = \sqrt{\frac{3}{2} \left(\frac{3}{2} + 1 \right)} \hbar = \frac{\sqrt{15}}{2} \hbar$$

with $J_z = \pm \frac{3}{2}, \pm \frac{1}{2}$

Spectroscopic notation is therefore:

$4p_{1/2}$ or $4p_{3/2}$

Summary

- Orbital angular momentum gives rise to an orbital magnetic moment
 - The energy shift of states due to magnetic moment interaction with external field is observed as the Zeeman effect
- Electron spin also gives rise to a magnetic moment
 - Evidence for electron spin of $\frac{1}{2}$ unit is found from the Anomalous Zeeman and Stern-Gerlach experiments (even splittings)
 - Fine structure spectroscopic energy shifts indicate that the spin and orbital magnetic moments interact with one another.
- The total spin and orbital angular momentum couple to one another so that the total angular momentum $\vec{J} = \vec{L} + \vec{S}$, with $|J| = \sqrt{j(j+1)}\hbar$ with possible values $j = |l - s|, |l - s| + 1, |l - s| + 2, \dots, |l + s|$ and with $j_z = m_z\hbar$.
- Spectroscopic Notation