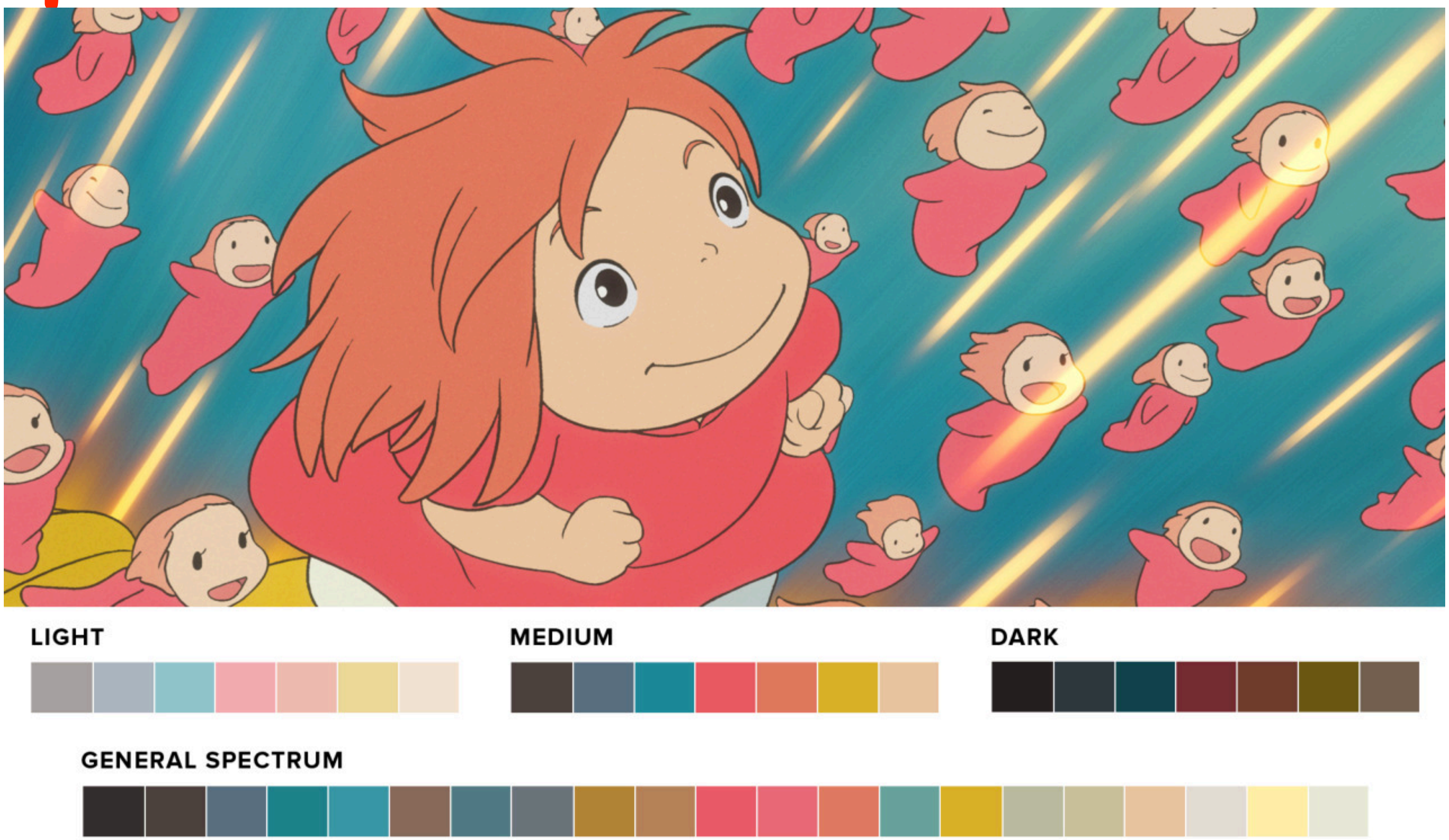
Atomic Physics

Chapter 4 Fine structures of Atoms



4.1Magnetic moment of electron

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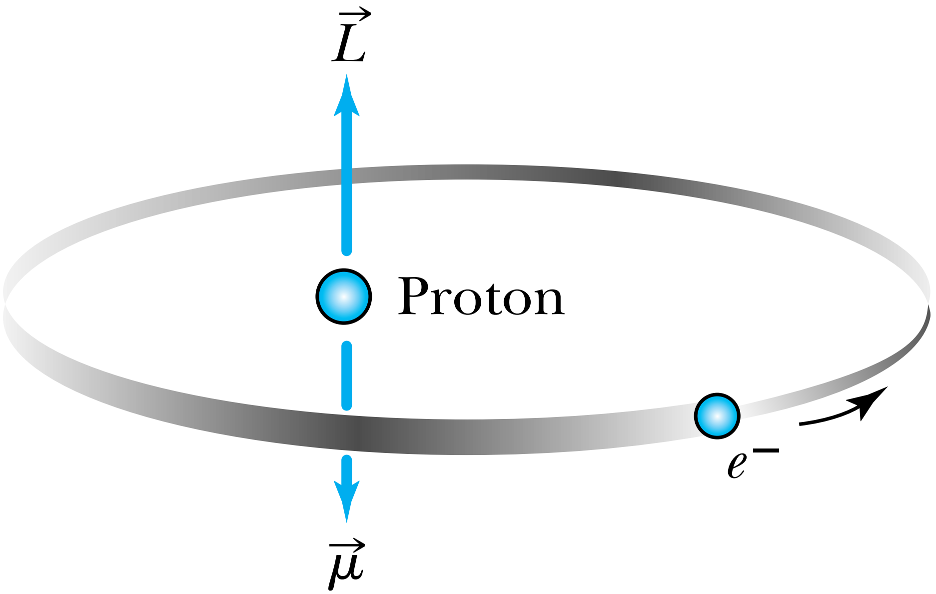
As a rough model, think of an electron circulating around the nucleus as a circular current loop. The current loop has a magnetic moment

$$\mu = IA = \frac{q}{T}A = \frac{-e\pi r^2}{2\pi r/v} = \frac{-erv}{2} = -\frac{e}{2m}L$$



where L=mvr is the magnitude of the orbital angular momentum.

Magnetic moment of electron

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Both the magnetic moment and angular momentum are vectors so that

$$\vec{\mu} = -\frac{e}{2m}\vec{L}$$

Gyromagnetic ratio

$$\gamma = \frac{e}{2m}$$

In classical electromagnetism, if a magnetic dipole having a magnetic moment, is placed in an external magnetic field, the dipole will experience a torque

$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

which aligns the dipole with the magnetic field.

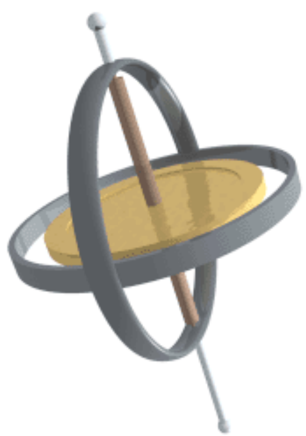
Magnetic moment of electron

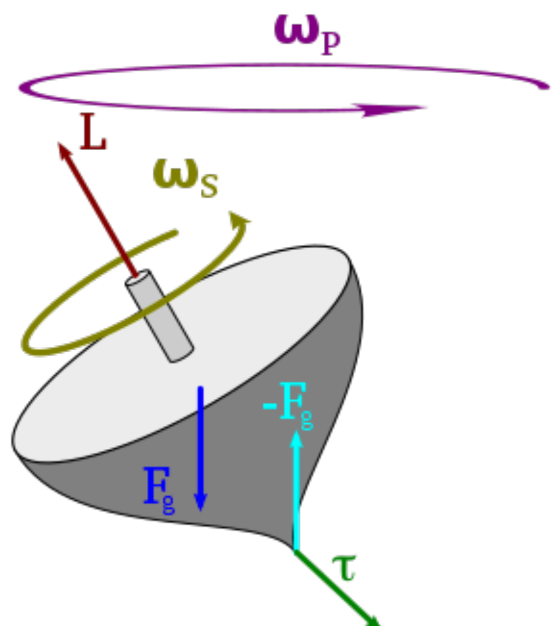
The dipole also has a potential energy in the field given by

$$V_B = -\vec{\mu} \cdot \vec{B}$$

According to classical physics, if the system can change its potential energy, the magnetic moment will align itself with the external magnetic field to minimize energy.

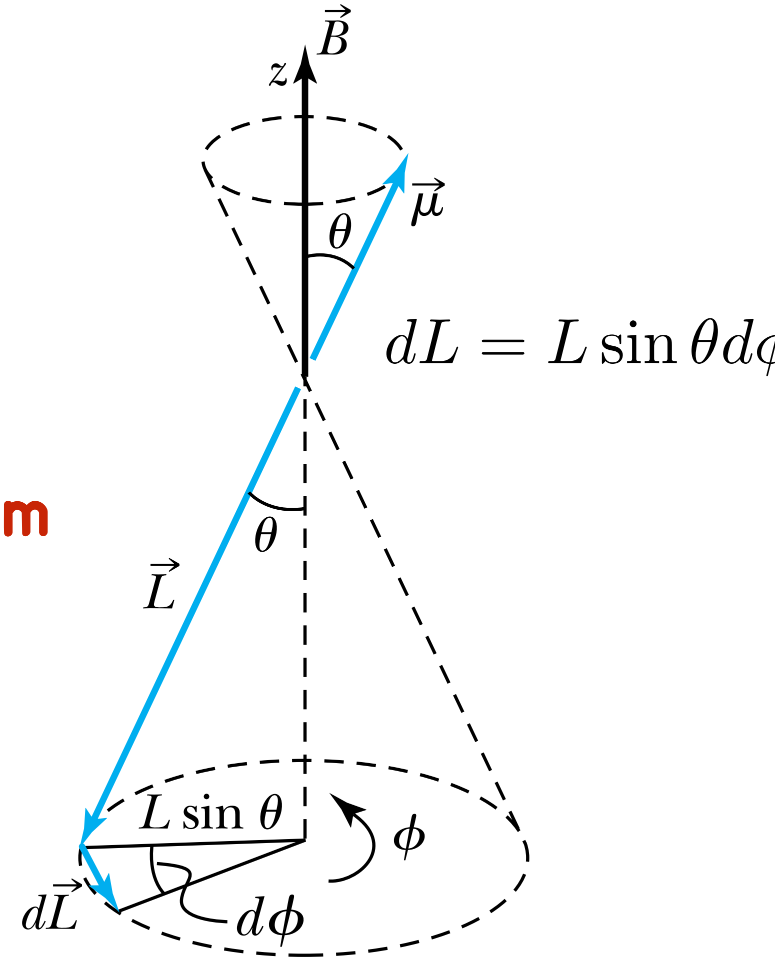
Precession in gravitational field





Magnetic moment of electron

An atom with magnetic moment in an external magnetic field has Larmor precession.



Precessional frequency

$$\omega_L = \frac{d\phi}{dt} = \frac{1}{L\sin\theta}\frac{dL}{dt}$$

Newton's second law in angular form

$$\vec{\tau} = \frac{d\vec{L}}{dt}$$

So

$$\omega_L = \left(\frac{e}{2m\mu\sin\theta}\right)\mu B\sin\theta = \frac{eB}{2m}$$

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Orbit angular momentum operator

$$\hat{L} = \hat{r} \times \hat{p}$$

The components of orbit angular moment

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

The square of orbit angular momentum operator

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Magnetic moment of electron

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Eigenstate and eigenvalue

$$\hat{Q}f = \lambda f$$

f is the eigenstate and λ is the corresponding eigenvalue.

The eigenstate and eigenvalue of orbit angular moment

$$\hat{L}^2 Y_{lm} = L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

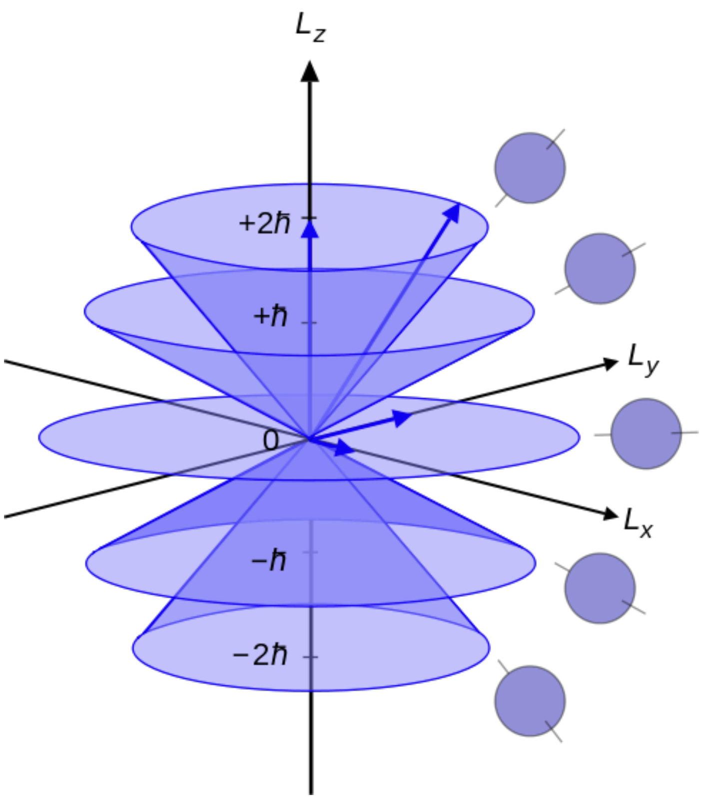
$$\hat{L}_z Y_{lm} = m_l \hbar Y_{lm}$$

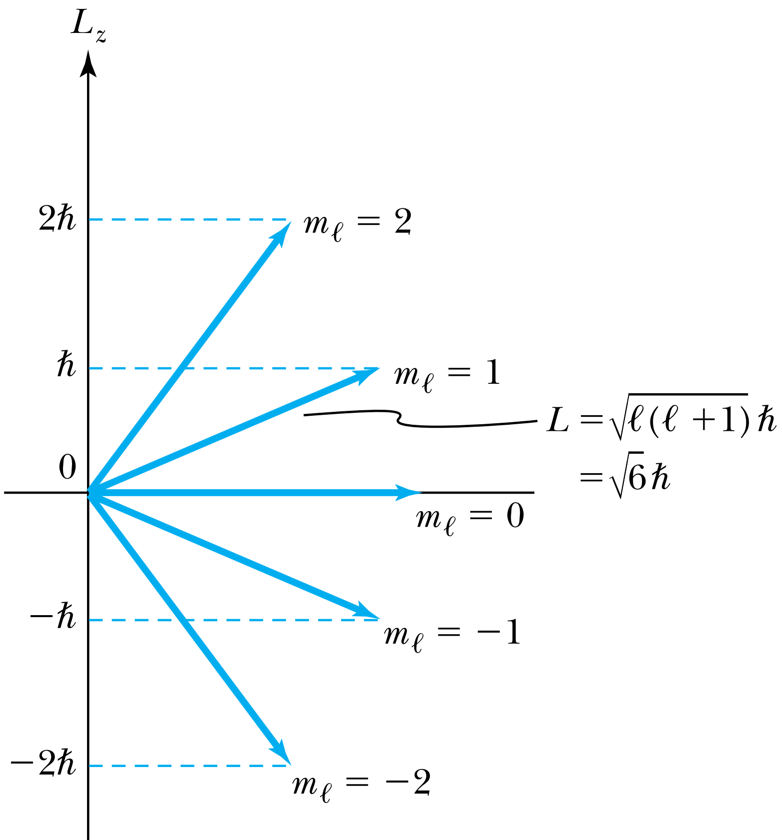
l is the quantum number of orbit angular momentum

m_l is the magnetic quantum number

Magnetic moment of electron

$n = 1, 2, 3, 4, \dots$	Integer
$l = 0, 1, 2, 3, \dots, n-1$	Integer
$m_l = -l, -l+1, \dots, 0, 1, \dots, l-1, l$	Integer





Magnetic moment of electron

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Magnetic moment operator

$$\hat{\vec{\mu}} = -\frac{e}{2m}\hat{\vec{L}}$$

$$\hat{\mu}_z = -\frac{e}{2m}\hat{L}_z$$

The eigenvalue of magnetic moment

$$\mu_l = -\frac{e\hbar}{2m}\sqrt{l(l+1)}$$

$$\mu_z = -\frac{e\hbar}{2m}m_l$$

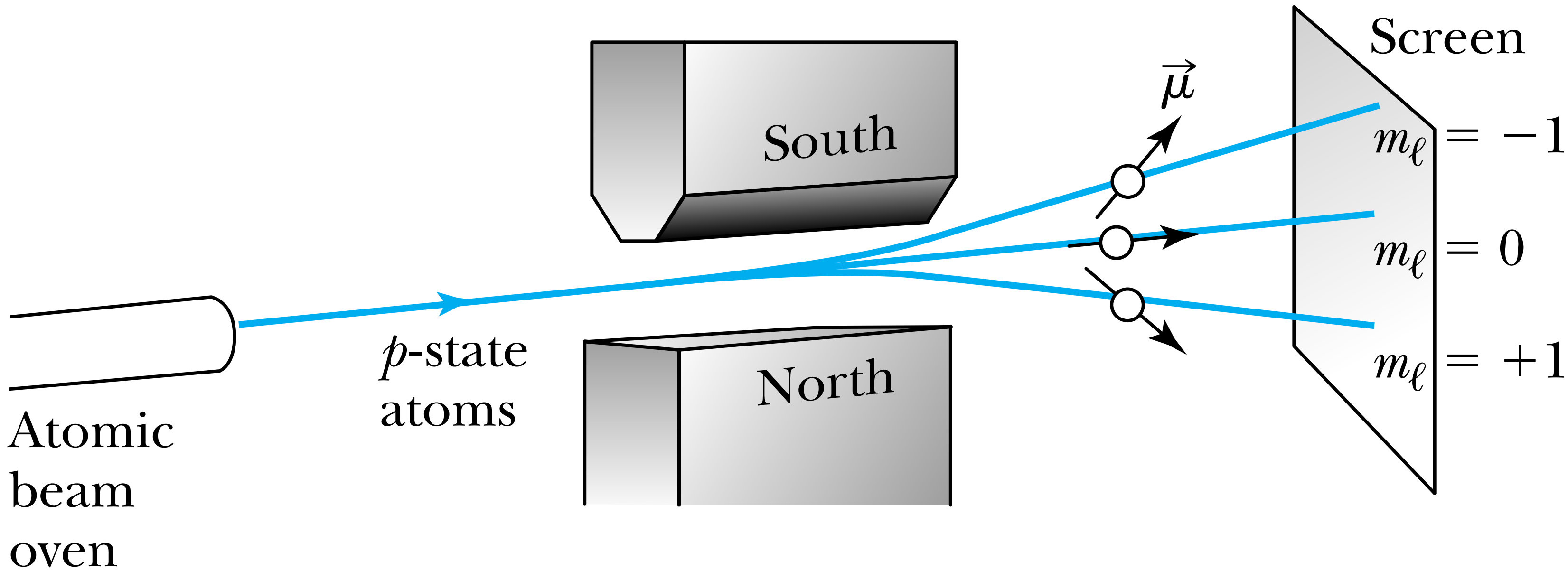
Bohr magneton

$$\mu_B = \frac{e\hbar}{2m}$$

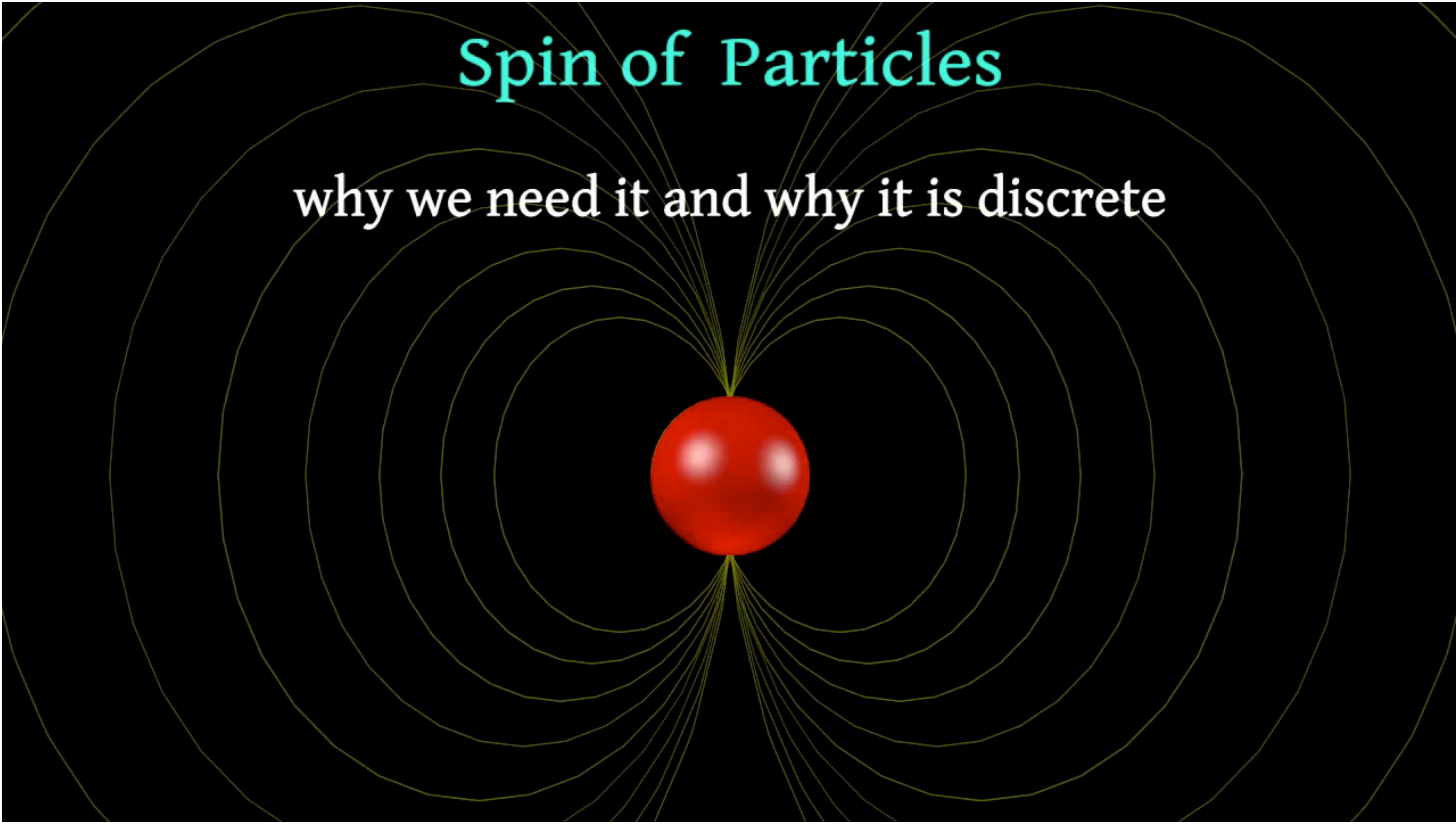
The energy of the orbiting electron in a magnetic field

$$E_B = -\mu_z B = \mu_B m_l B$$

In 1922 O. Stern and W. Gerlach reported the results of an experiment that clearly showed evidence for space quantization.



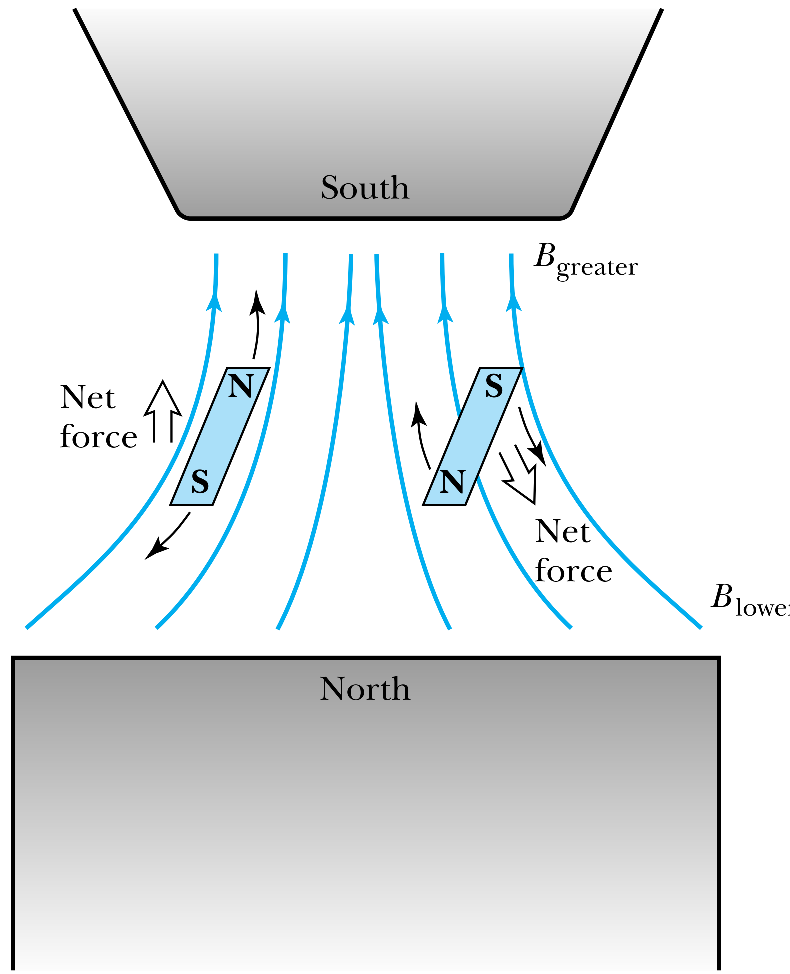
Stern-Gerlach experiment



Stern-Gerlach experiment

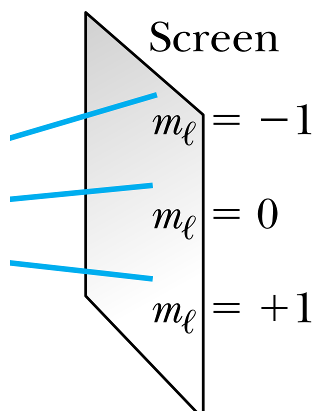
If an external magnetic field is inhomogeneous, the force on the particles is

$$F_z = -\frac{dE_B}{dz} = \mu_z \frac{dB}{dz}$$

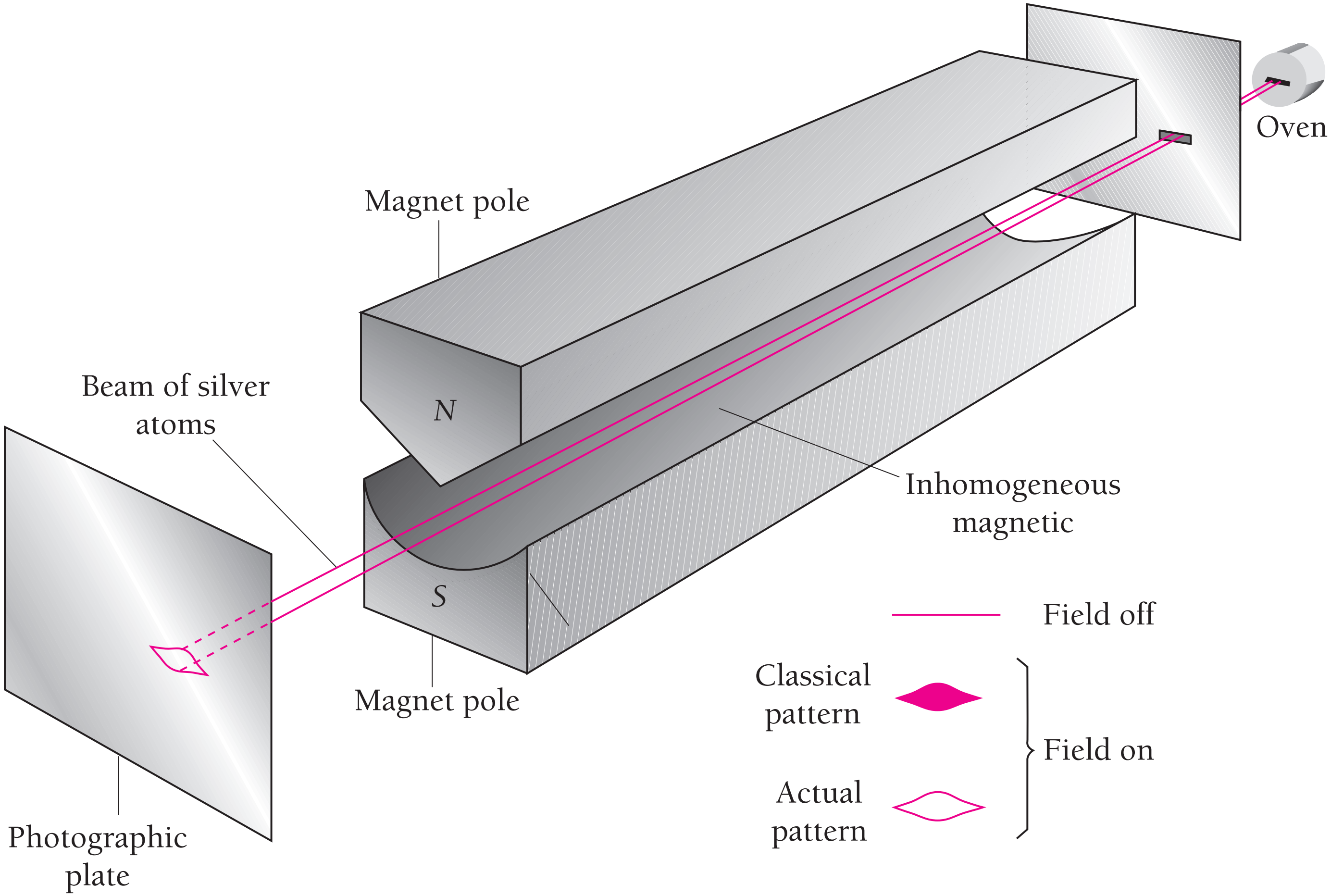


When l=1

$$\mu_z = -1,\ 0,\ 1\mu_B$$

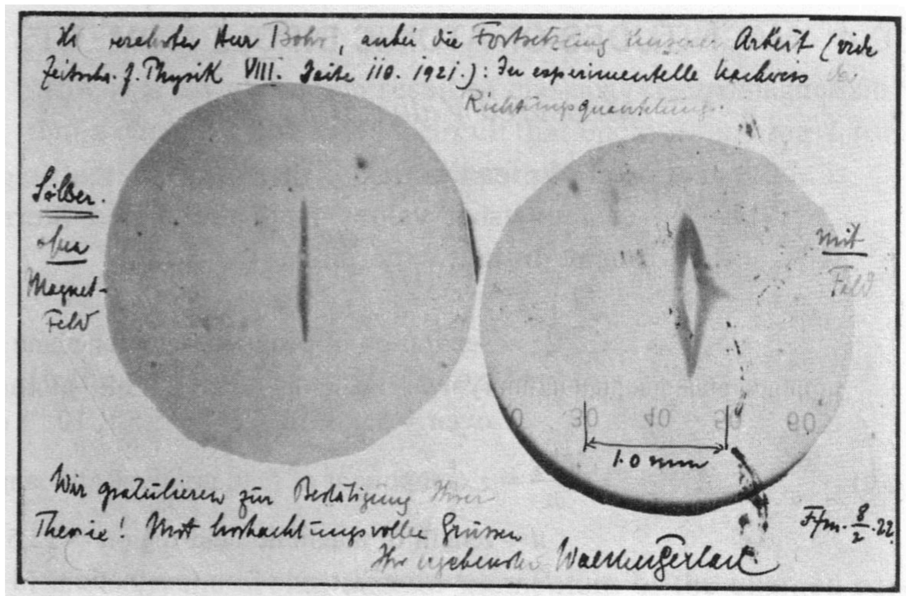


Stern-Gerlach experiment



Stern-Gerlach experiment

Stern and Gerlach performed their experiment with silver atoms and observed two distinct lines, not three.



This was clear evidence of space quantization, although the number of m_l states is always odd and should have produced an odd number of lines if the space quantization were due to the magnetic quantum number m_l.

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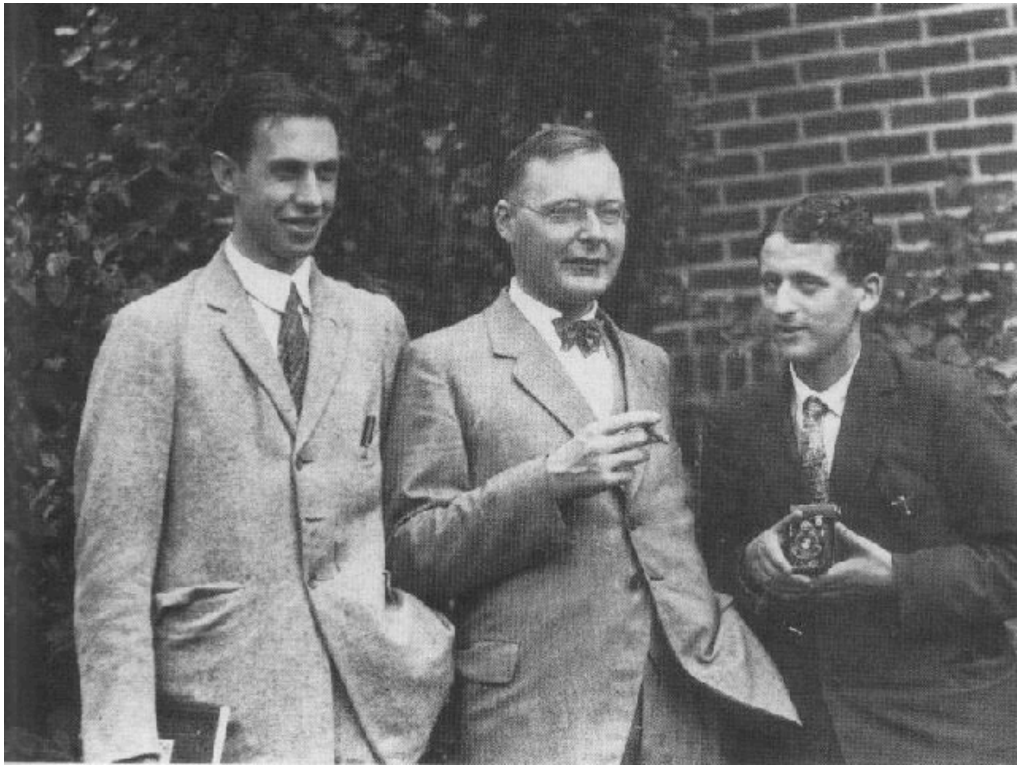
In 1925 Samuel Goudsmit and George Uhlenbeck, two young physics graduate students in Holland, proposed that the electron must have an intrinsic angular momentum and therefore a magnetic moment



Intrinsic Spin

In order to achieve the angular momentum needed, Paul Ehrenfest showed that the surface of the spinning electron (or electron cloud) would have to be moving at a velocity greater than the speed of light!

If such an intrinsic angular momentum exists, we must regard it as a purely quantum-mechanical result.

To explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an intrinsic spin quantum number

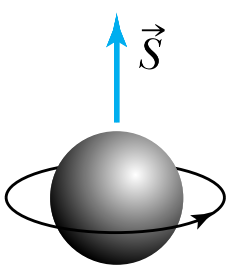
$$s = 1/2$$

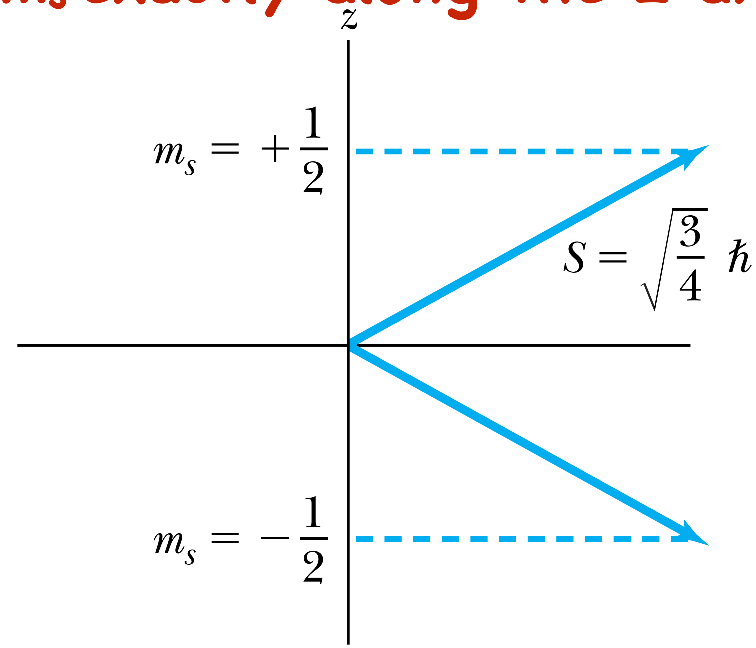
Intrinsic Spin

The magnetic spin quantum number m_s has only two values

$$m_s = \pm 1/2$$

The electron's spin will be oriented either "up" or "down" in a magnetic field, and the electron can never be spinning with its magnetic moment m_s exactly along the z axis





Intrinsic Spin

The intrinsic spin angular momentum

$$|\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$$

The magnetic moment of intrinsic spin

$$\vec{\mu}_s = -g_s \mu_B \vec{S}/\hbar = -2\mu_B \vec{S}/\hbar$$

where g_s is the Lande factor and

$$g_s = 2$$

The z component of spin magnetic moment

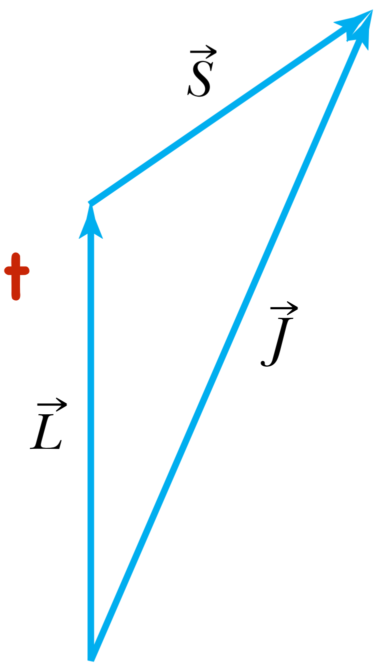
$$\mu_{s,z} = -2m_s\mu_B$$

where

$$m_s = \pm 1/2$$

If an atom has an orbital angular momentum and a spin angular momentum, these angular momenta combine to produce a total angular momentum,

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



Because L, L_z, S, and S_z are quantized, the total angular momentum and its z component J_z are also quantized

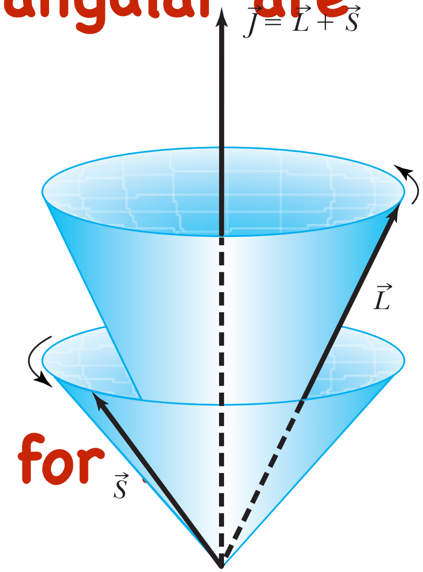
$$J = \sqrt{j(j+1)}\hbar$$

$$J_z = m_j \hbar$$

Because m_l is integral and m_s is half-integral, m_j will always be half-integral.

Total angular momentum of single electron

The quantization of the magnitudes of various angular are all similar,



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

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

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

The total angular momentum quantum number for single electron can only have the values,

$$j=l\pm s$$

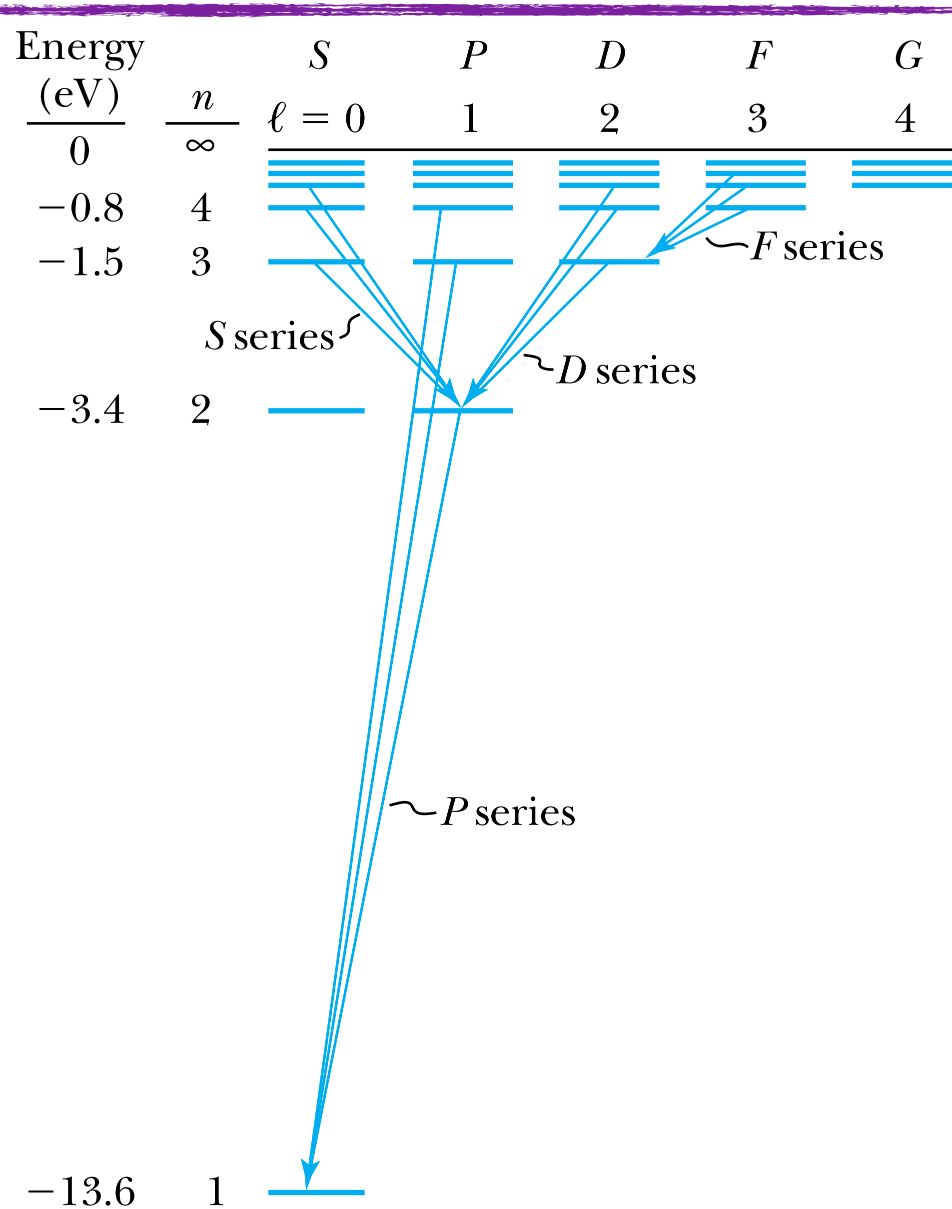
$$=l\pm\frac{1}{2}$$

The notation commonly used to describe these states

$${}^{2S+1}L_J \qquad L=0,1,2,3,\ldots$$

$$=S,P,D,F,\ldots$$

Total angular momentum of single electron



Total magnetic moment

The total magnetic moment is,

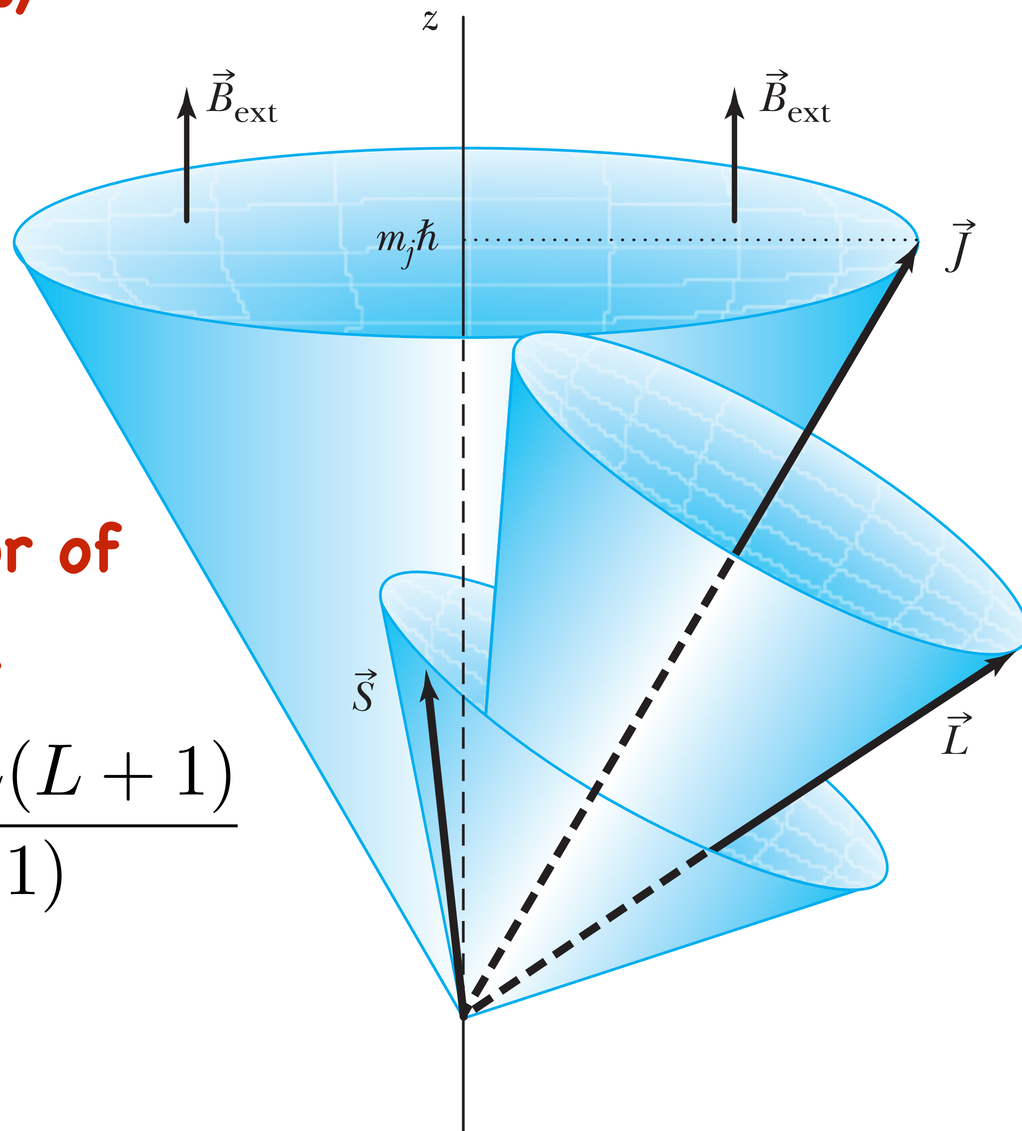
$$\vec{\mu}_j = \vec{\mu}_l + \vec{\mu}_s,$$
$$= -g_j \mu_B \vec{J}/\hbar$$

and,

$$\mu_{j,z} = -g_j m_j \mu_B$$

where, g_j is the Lande factor of total angular momentum and

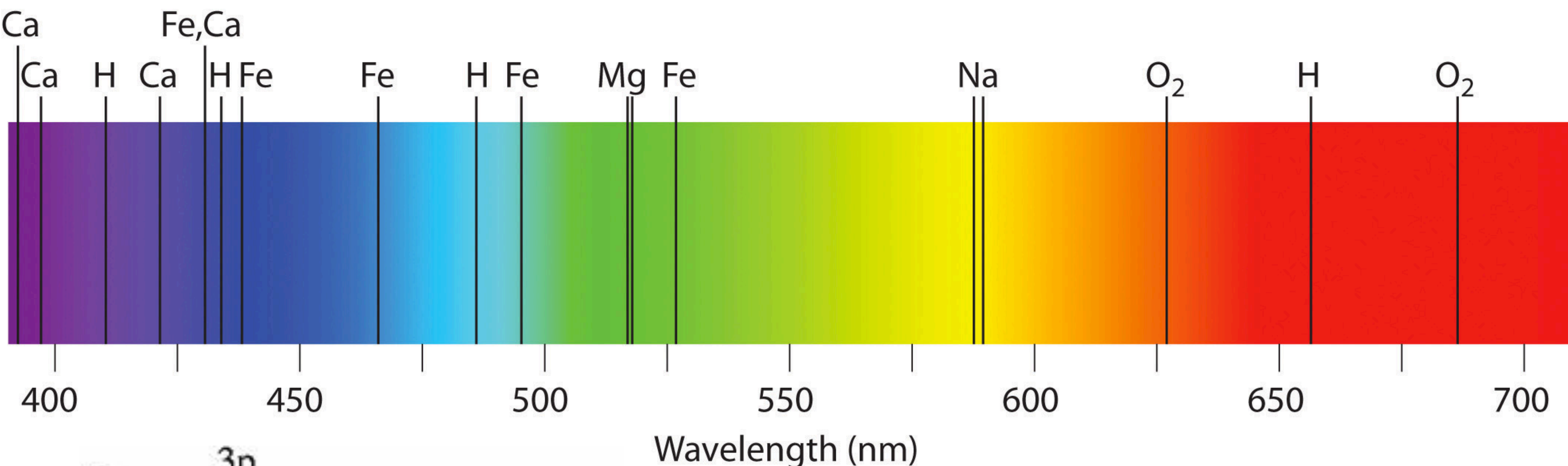
$$g_j = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$
$$= \frac{3}{2} + \frac{\hat{S}^2 - \hat{L}^2}{2\hat{J}^2}$$

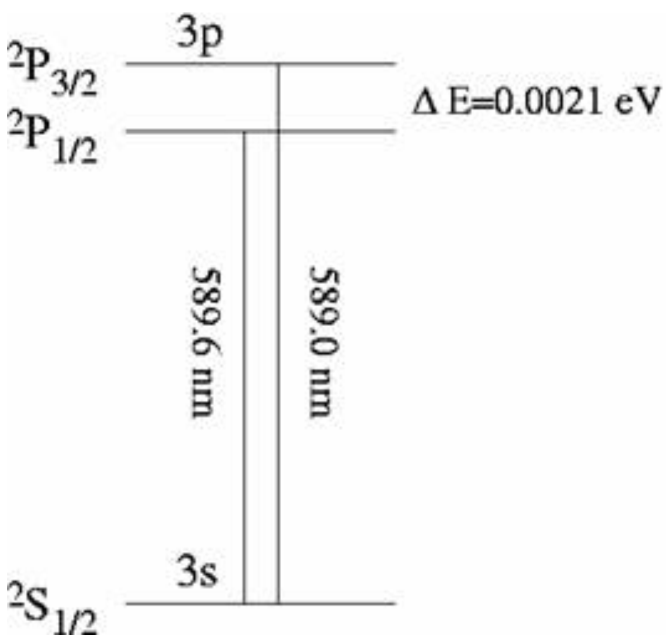


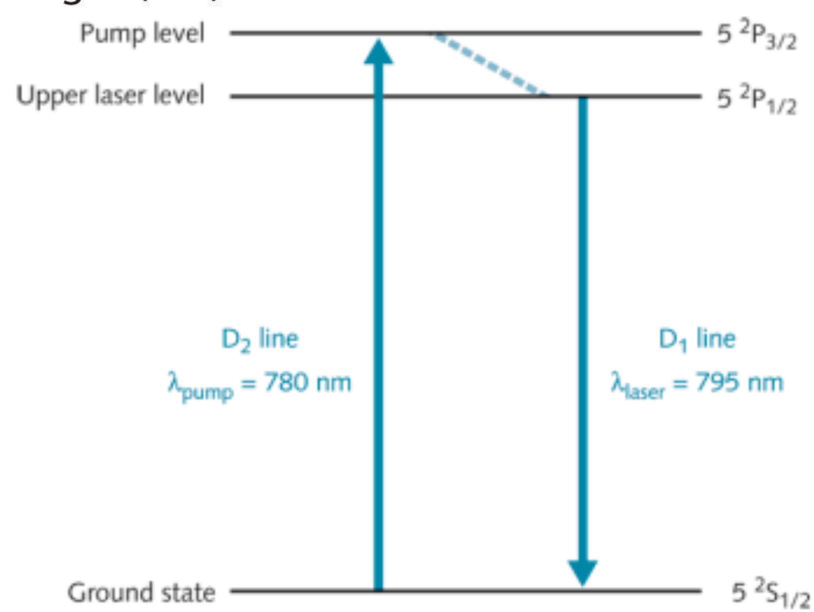
Lande factor of different state

States	g_j	$m_j g_j$
$^2S_{1/2}$	2	±1
$^2P_{1/2}$	2/3	±1/3
$^2P_{3/2}$	4/3	±2/3, ±6/3
$^2D_{3/2}$	4/5	±2/5, ±6/5
$^2D_{5/2}$	6/5	±3/5, ±9/5, ±15/5

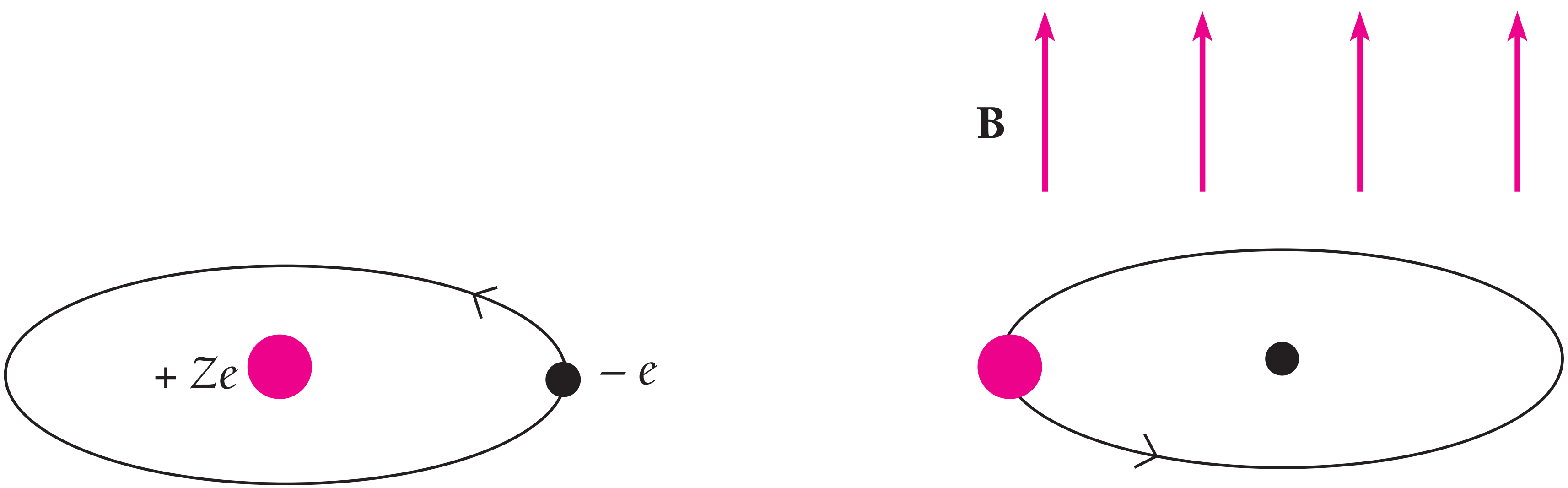
4.5 Spin-orbit coupling







This classical picture indicates that the orbiting proton creates a magnetic field at the position of the electron.



Spin-orbit coupling

An electron moving through an electric field E experiences an effective magnetic field B given by

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E}$$

Since, the electric field is

$$\vec{E} = \frac{1}{e}\frac{\partial V}{\partial r}\frac{\vec{r}}{r}$$

We have

$$\vec{B} = \frac{1}{m_e c^2}\frac{1}{er}\frac{\partial V}{\partial r}\vec{L}$$

The potential of the electron's magnetic moment with the orbital field gives

$$U = -\vec{\mu}_s\cdot\vec{B}$$

$$= g_s\mu_B\frac{1}{m_e c^2 er}\frac{\partial V}{\partial r}\vec{L}\cdot\vec{S}$$

Spin-orbit coupling

With Coulomb potential and relativistic correction that arises because we are calculating the magnetic field in a frame of reference that is not stationary but rotates as the electron moves about the nucleus,

$$U = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{2m_e^2c^2r^3}\vec{L}\cdot\vec{S}$$

The expectation value of this potential gives an energy change of ,

$$E_{so} = \frac{1}{8\pi\varepsilon_0 m_e^2c^2}\langle\frac{1}{r^3}\rangle\langle\vec{L}\cdot\vec{S}\rangle$$

The expectation value of spin-orbit coupling

$$\langle \vec{L} \cdot \vec{S} \rangle = \frac{j(j+1) - l(l+1) - s(s+1)}{2} \hbar^2$$

The expectation value of radii

$$\langle \frac{1}{r^3} \rangle = \frac{Z^3}{n^3 l(l+1/2)(l+1) a_1^3}$$

Thus the spin-orbit interaction produces a shift in energy of

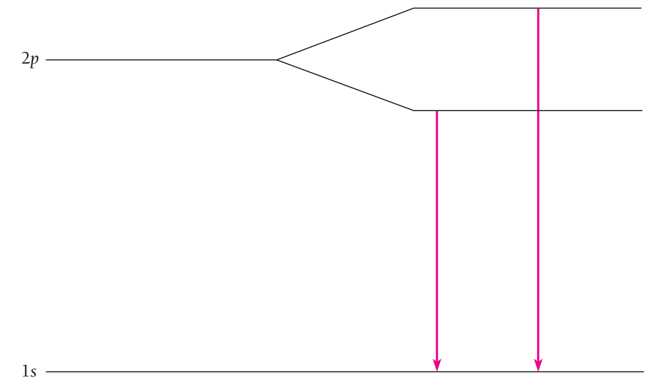
$$E_{so} = \frac{Z^4 e^2 \hbar^2}{16\pi\varepsilon_0 m_e^2 c^2 a_1^3} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l+1/2)(l+1)}$$

A single electron has s =1/2 so, for each l, its total angular momentum quantum number j has two possible values:

$$j = l \pm \frac{1}{2}$$

We find that the energy interval between these levels:

$$\Delta E_{so} = \frac{Z^4 e^2 \hbar^2}{8\pi\varepsilon_0 m_e^2 c^2 a_1^3} \frac{1}{n^3 l(l+1)} = \frac{(\alpha Z)^4}{2n^3 l(l+1)} E_0$$

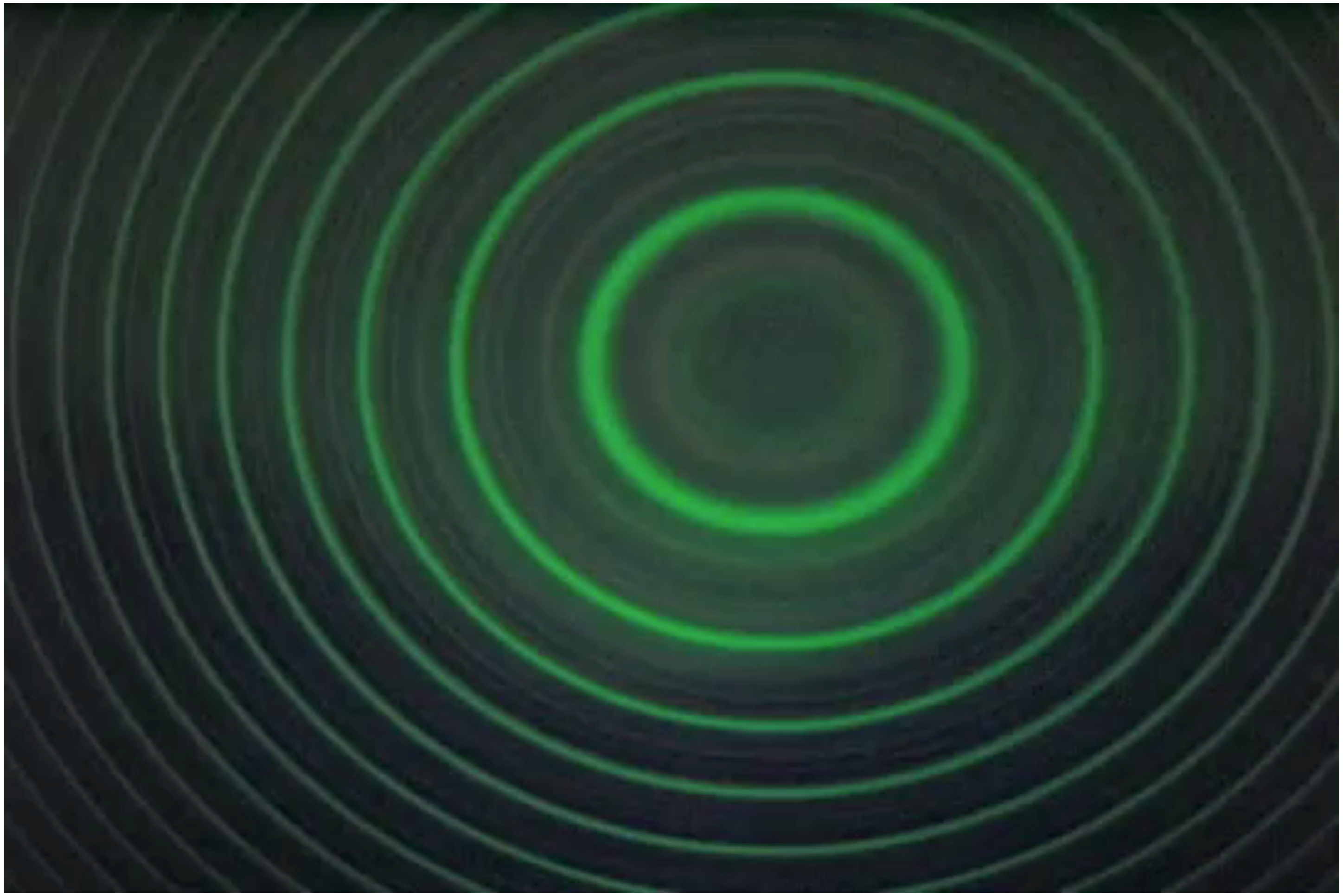


The energy interval of 2p state of hydrogen

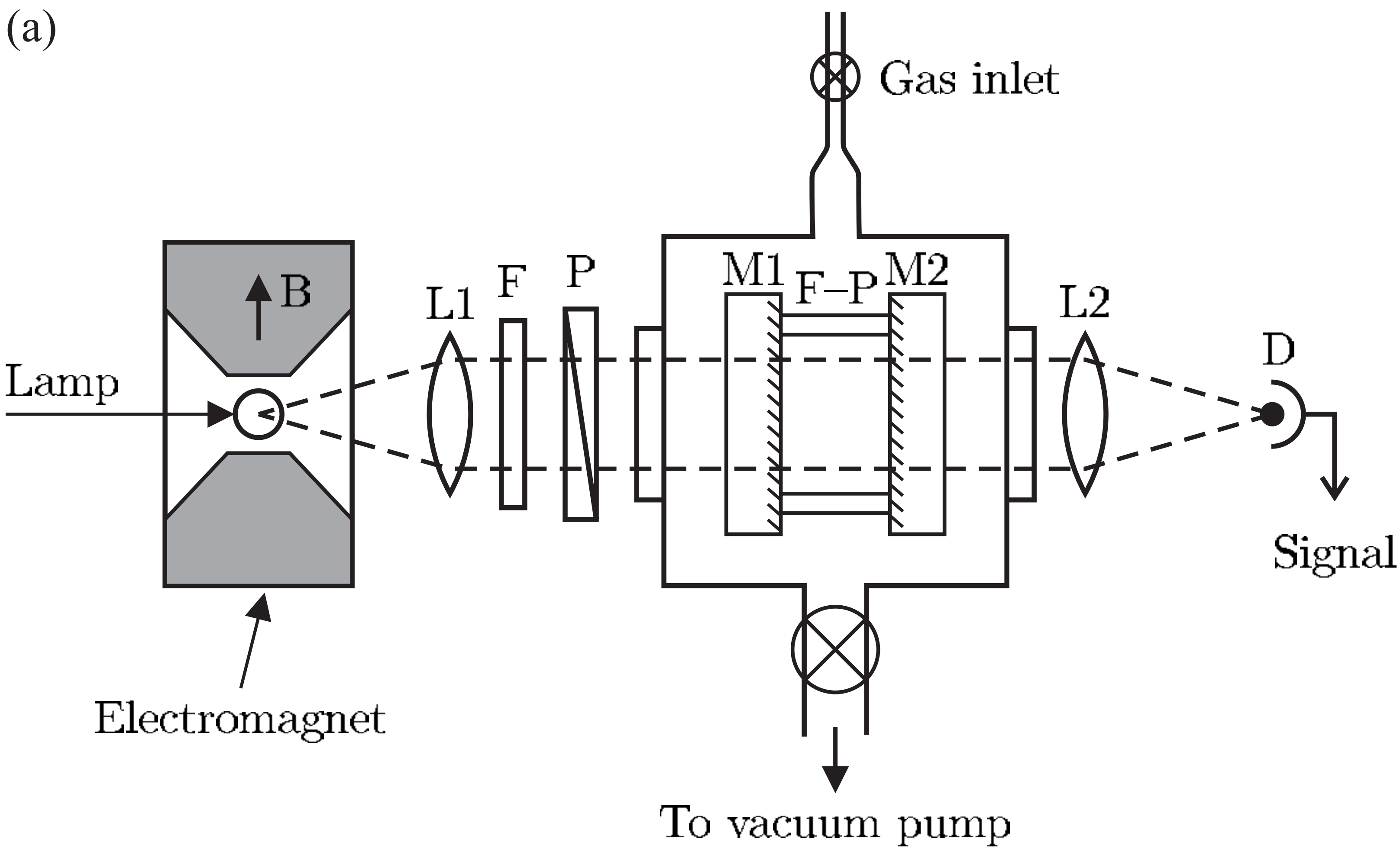
$$\Delta E_{so} = 4.53 \times 10^{-5}\ \text{eV}$$

4.6Zeeman effect

1896, Pieter Zeeman found that the splitting of spectral lines by a magnetic field



Zeeman effect



Zeeman effect

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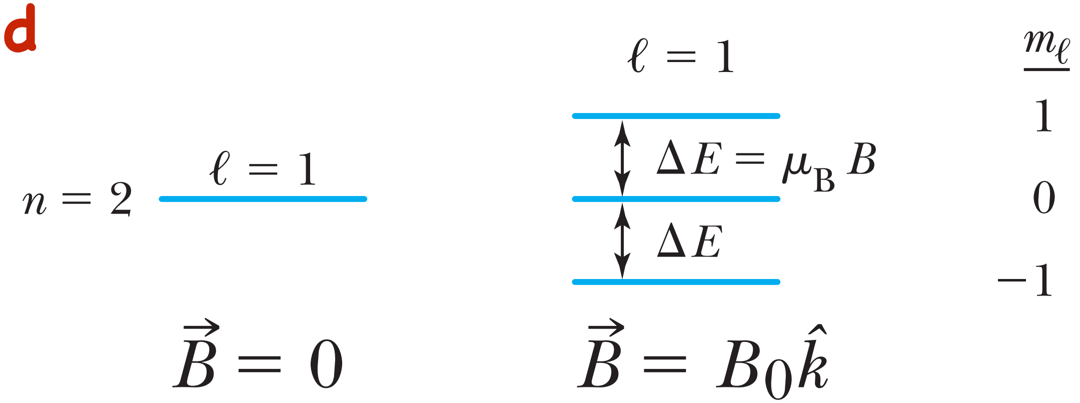
In a magnetic field, then, the energy of a particular atomic state depends on the value of m_l as well as on that of n

$$E_B = -\mu_z B = \mu_B m_l B$$

Each (degenerate) atomic level of given l is split into 2l+1 different energy states according to the value of m_l

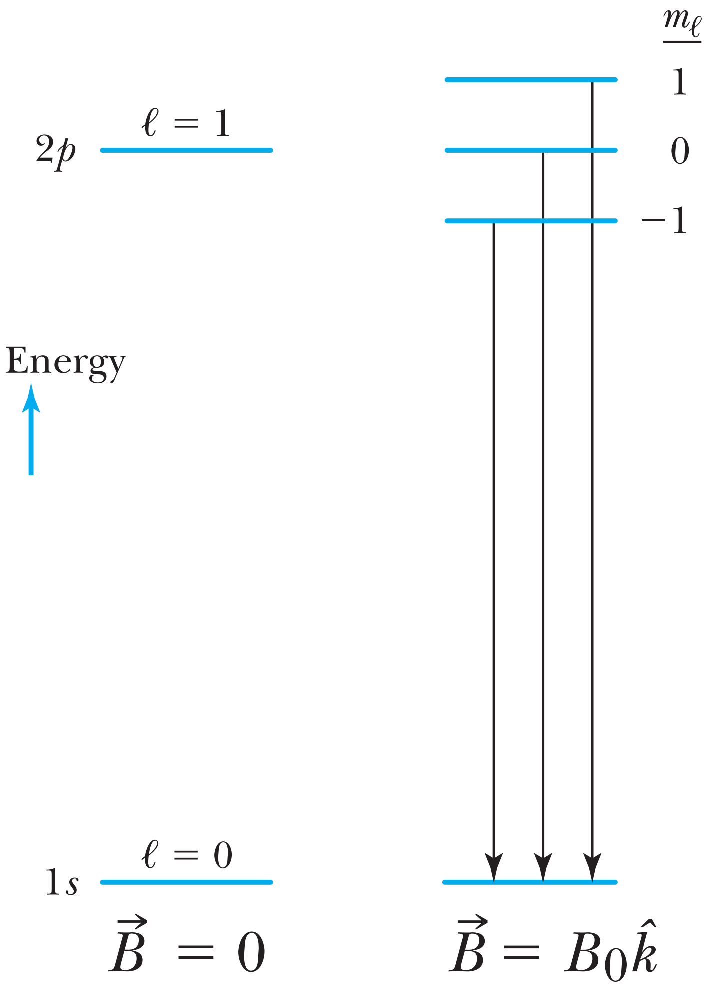
The energy degeneracy of a given nl level is removed by a magnetic field



If the degenerate energy of a state is given by E_0, the three different energies in a magnetic field B for a l=1 state are

$$E = E_0,\ E_0 \pm \mu_B B$$

m_ℓ	Energy
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



Zeeman effect

Because m_l can have the 2l+1 values, a state of given orbital quantum number l is split into 2l+1 substates that differ in energy by $\mu_B B$ when the atom is in a magnetic field.

However we expect a spectral line from a transition between two states of different l to be split into only three components for selection rules

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

due to the spin of phonon as one.

The normal Zeeman effect consists of the splitting of a spectral line of frequency into three components whose frequencies are

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

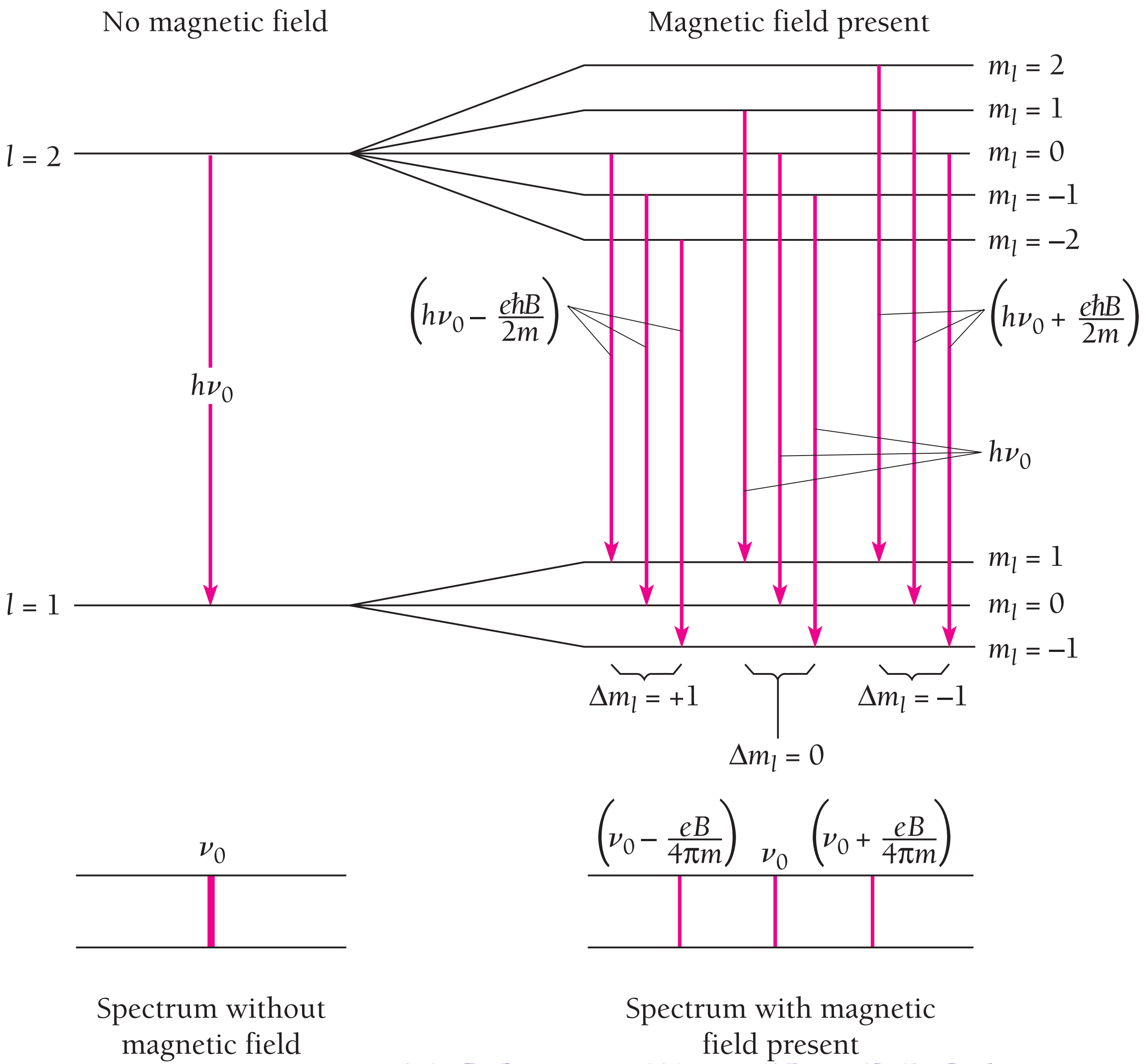
$$\nu_2 = \nu_0$$

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

where, the Larmor frequency is defined as

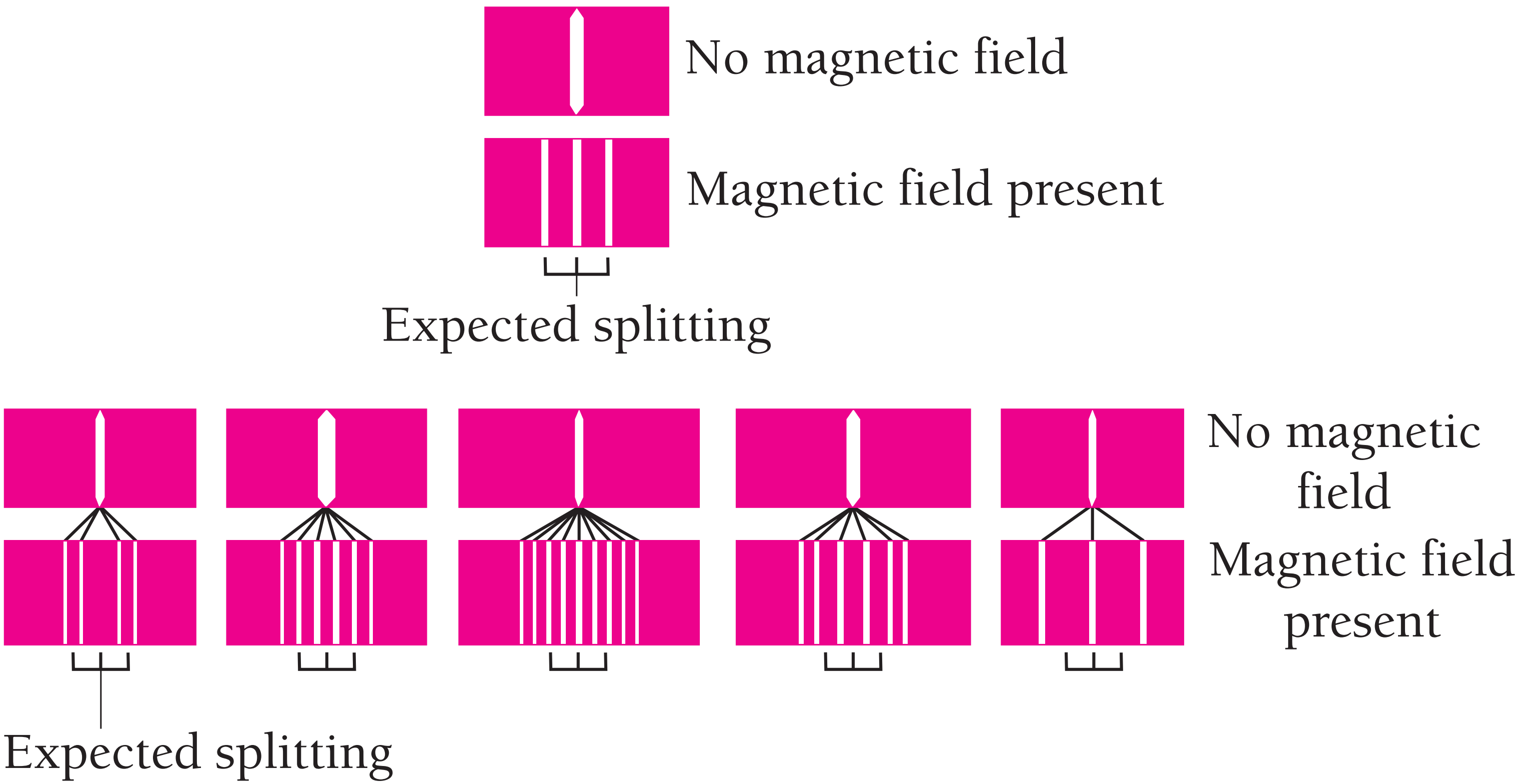
$$\nu_L = \frac{\omega_L}{2\pi} = \frac{e}{4\pi m}B(\mathrm{T}) = 14B(\mathrm{T})\ \mathrm{GHz}$$

Zeeman effect



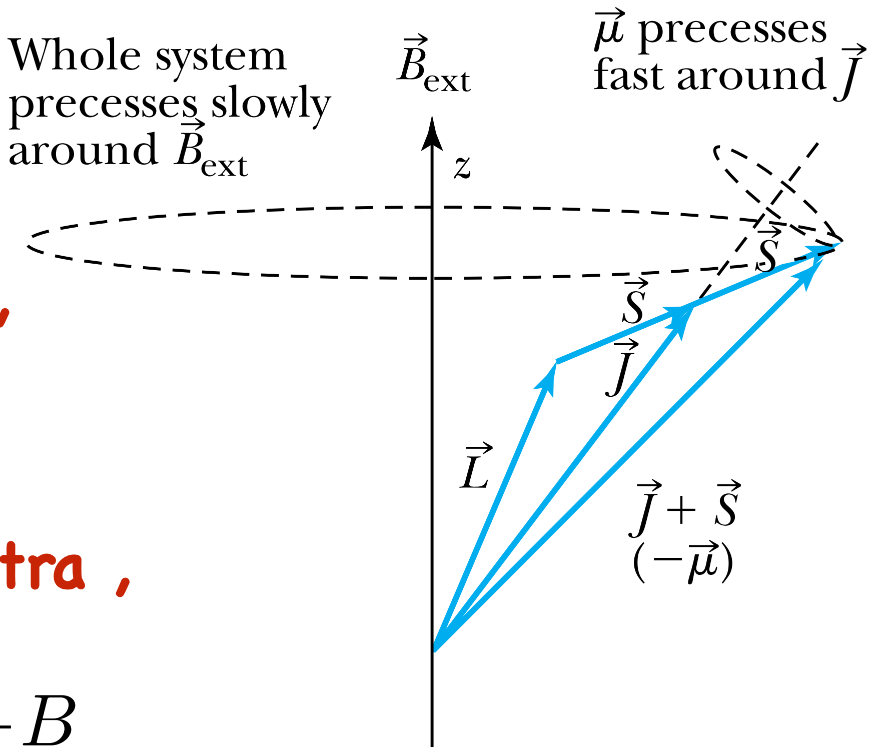
Anomalous Zeeman effect

Soon after the discovery of this effect by Zeeman in 1896, it was found that often more than three closely spaced optical lines were observed.



We shall see that the anomalous effect depends on the effects of electron intrinsic spin.

$$\vec{\mu}_j = \vec{\mu}_l + \vec{\mu}_s,$$
$$= -g_j \mu_B \vec{J}/\hbar$$



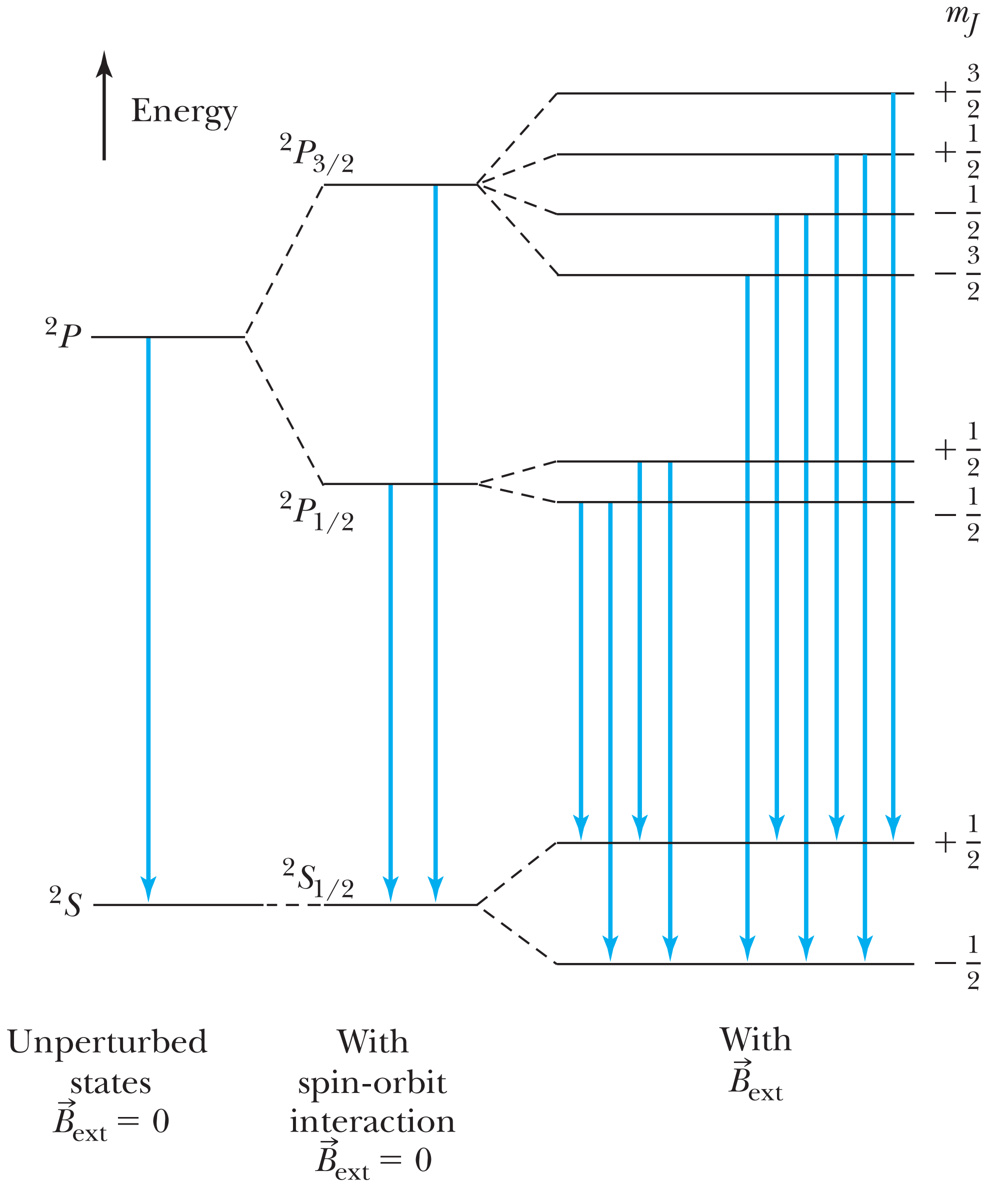
The energy in magnetic field is,

$$E_B = g_j m_j \mu_B B$$

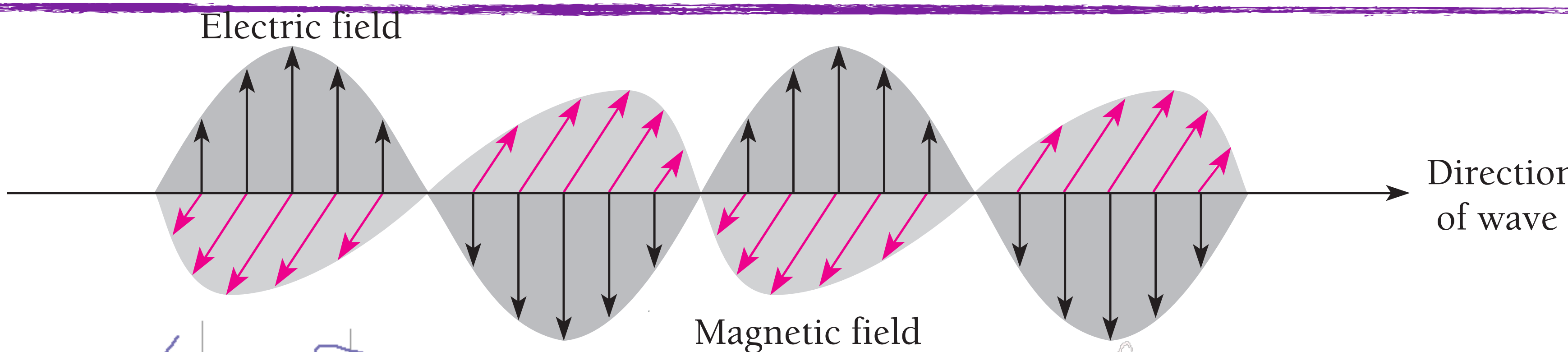
The frequency of splitting spectra ,

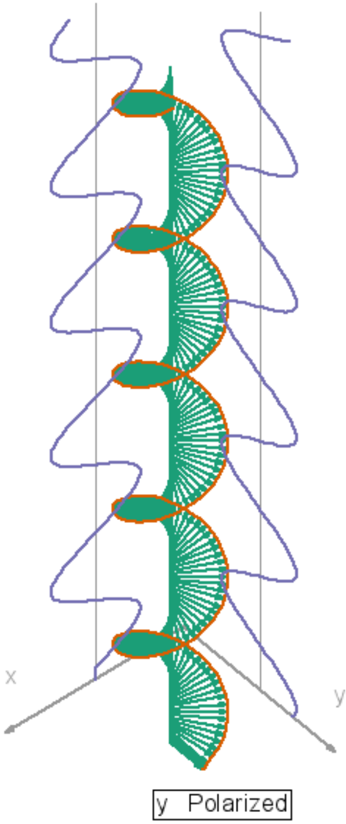
$$\nu = \nu_0 + (m_2 g_2 - m_1 g_1)\frac{e}{4\pi m}B$$

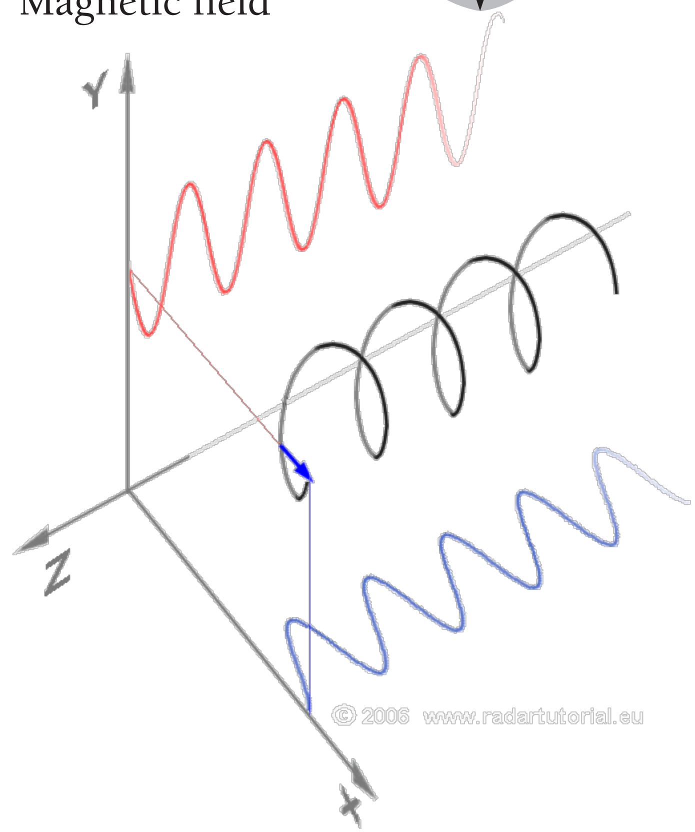
Anomalous Zeeman effect



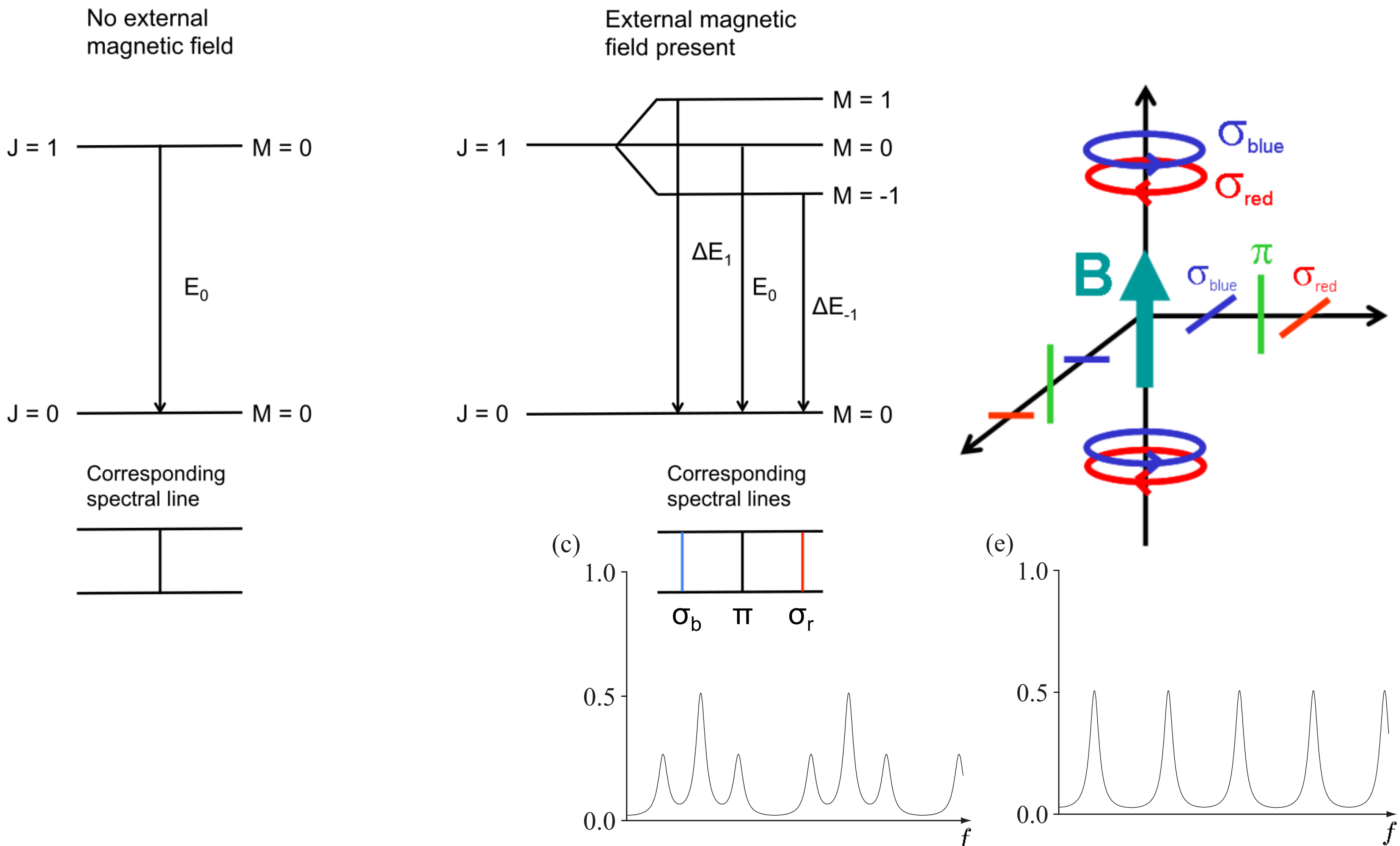
Polarization of light







Polarization of Zeeman effect



Polarization of Zeeman effect

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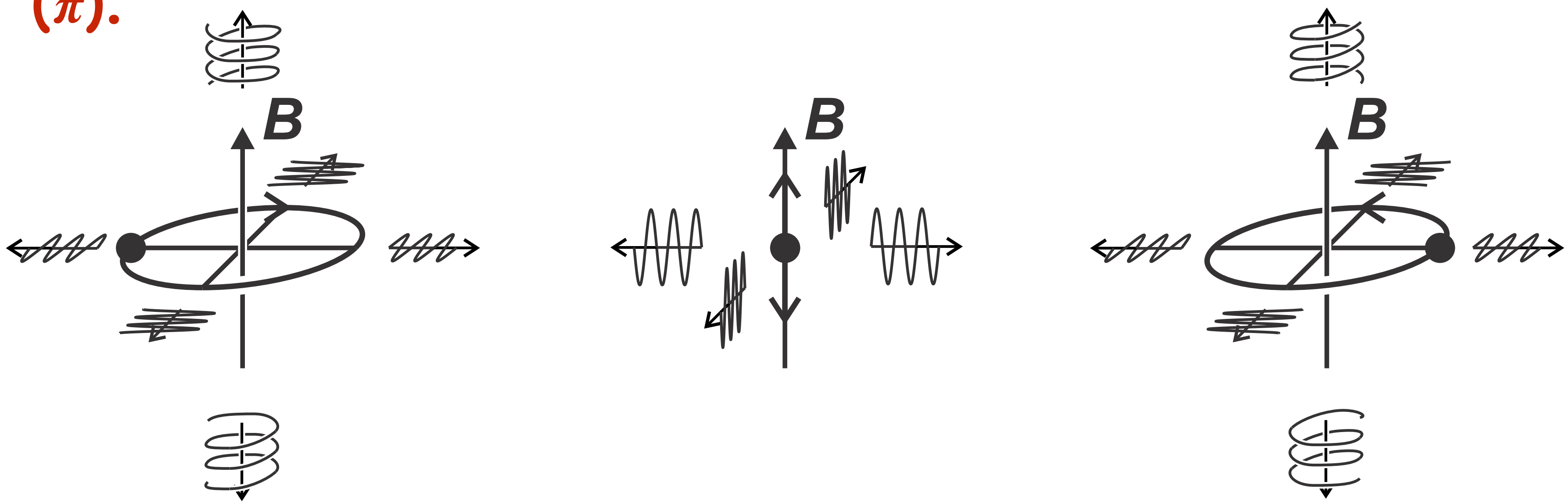
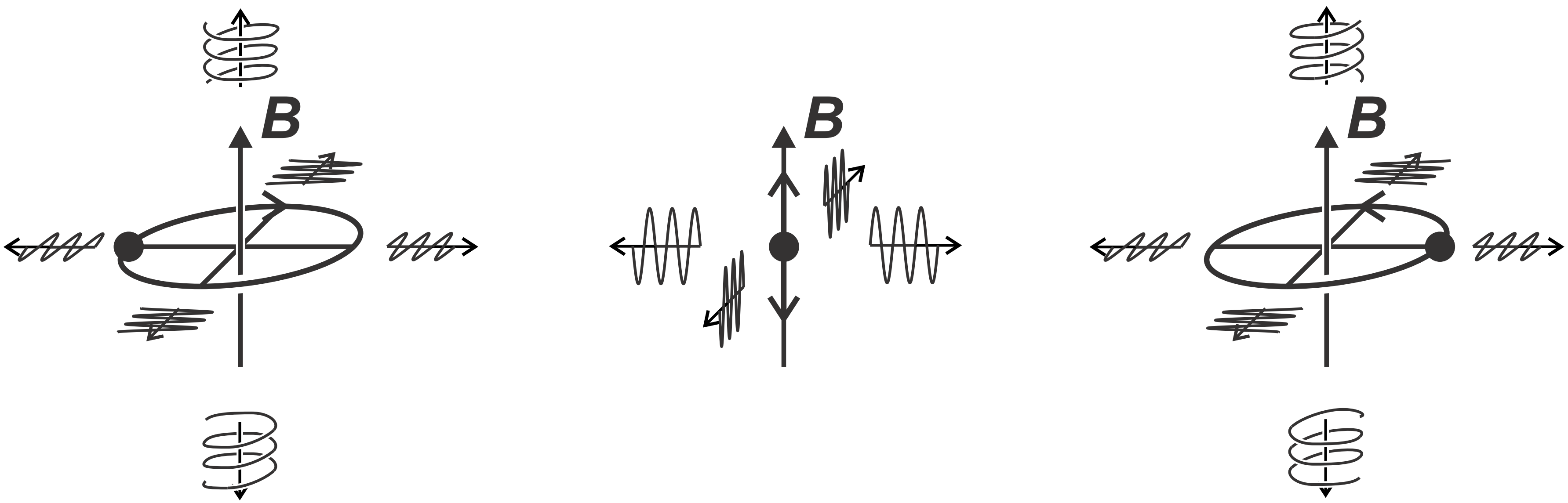
$\Delta M_J=0$ corresponds to an infinitesimal dipole oscillating parallel to the magnetic field. No quanta are emitted in the direction of the magnetic field. The light emitted perpendicular to the magnetic field is linearly polarized (π).



σ^- (ΔM_J = -1) π (ΔM_J = 0) σ^+ (ΔM_J = +1)

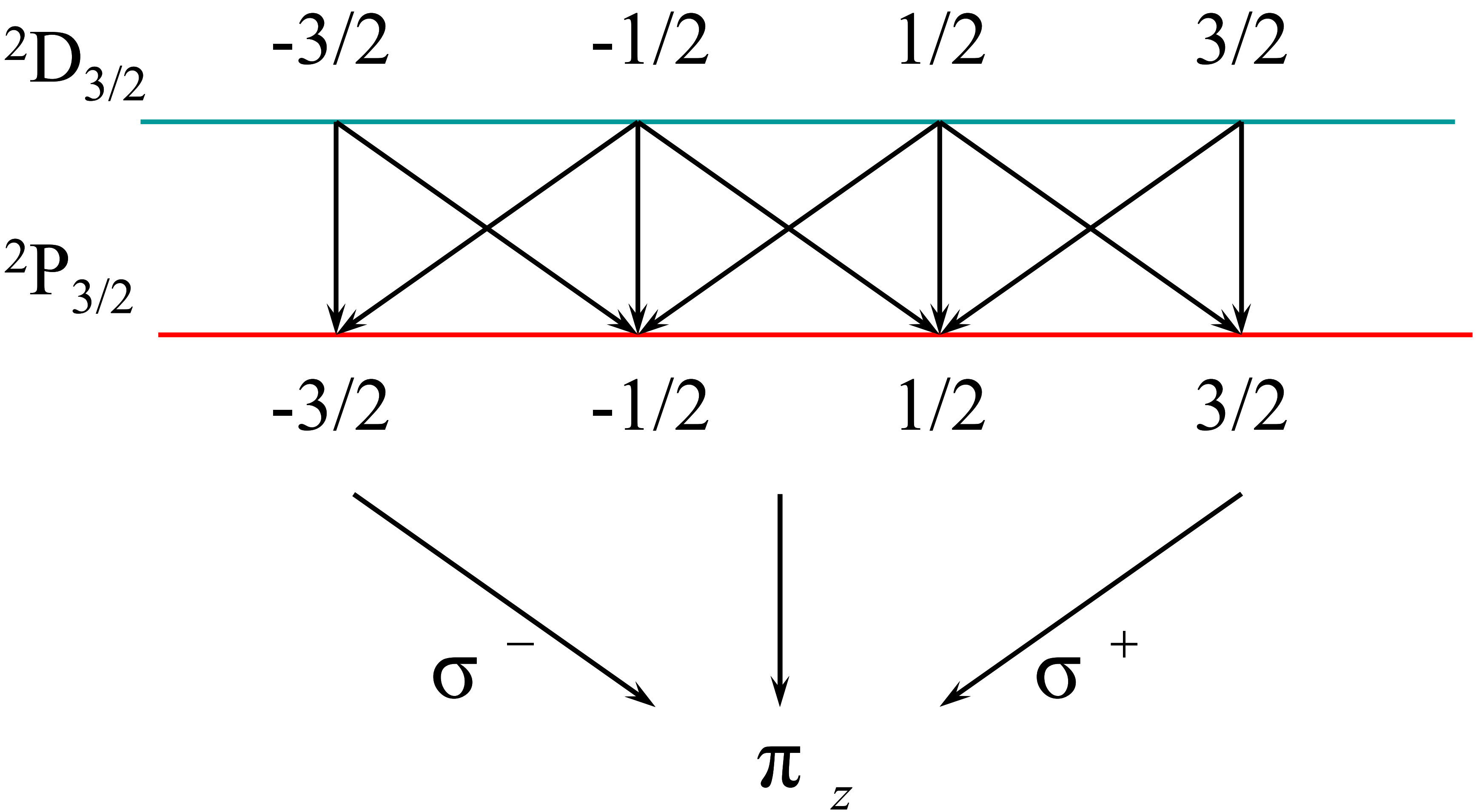
Polarization of Zeeman effect

$\Delta M_J=1$ corresponds to two parallel dipoles oscillating with a phase difference of 90^0 . The superposition of the two dipoles produces a circulating current (σ^+, σ^-).



σ^- ($\Delta M_J = -1$) π ($\Delta M_J = 0$) σ^+ ($\Delta M_J = +1$)

Grotrian Diagram



The Physics of Atoms and Quanta

12.1, 12.3, 12.5, 13.1, 13.2, 13.3, 13.4

1. Treat the hydrogen atom as a one-dimensional entity of length $2a_0$ and determine the electron's minimum kinetic energy.

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Solution:

$$K_{\min} = \frac{\hbar^2}{2m\ell^2} = \frac{(\hbar c)^2}{2mc^2\ell^2}$$

$$= \frac{(197\ \text{eV}\cdot\text{nm})^2}{(2)(0.511 \times 10^6\ \text{eV})(2 \times 0.0529\ \text{nm})^2} = 3.4\ \text{eV}$$

2. An atom in an excited state normally remains in that state for a very short time (10^{-8}s) before emitting a photon and returning to a lower energy state. The "lifetime" of the excited state can be regarded as an uncertainty in the time t associated with a measurement of the energy of the state. This, in turn, implies an "energy width," namely, the corresponding energy uncertainty ΔE. Calculate (a) the characteristic "energy width" of such a state and (b) the uncertainty ratio of the frequency $\Delta f/f$ if the wavelength of the emitted photon is 300 nm.

Solution: (a)

$$\Delta E \geq \frac{\hbar}{2\,\Delta t} = \frac{6.58 \times 10^{-16}\ \text{eV}\cdot\text{s}}{(2)(10^{-8}\ \text{s})} = 3.3 \times 10^{-8}\ \text{eV}$$

Solution: (b)

(b) The frequency is found to be

$$f = \frac{c}{\lambda} = \frac{3 \times 10^{8}\ \text{m/s}}{300 \times 10^{-9}\ \text{m}} = 10^{15}\ \text{Hz}$$

The uncertainty Δf is

$$\Delta f = \frac{\Delta E}{h} = \frac{3.3 \times 10^{-8}\ \text{eV}}{4.136 \times 10^{-15}\ \text{eV}\cdot\text{s}} = 8 \times 10^{6}\ \text{Hz}$$

The uncertainty ratio of the frequency $\Delta f/f$ is

$$\frac{\Delta f}{f} = \frac{8 \times 10^{6}\ \text{Hz}}{10^{15}\ \text{Hz}} = 8 \times 10^{-9}$$

3. Find the quantized energy levels of an electron constrained to move in a one-dimensional atom of size 0.1 nm.

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Solution:

$$E_n = n^2 \frac{h^2}{8m\ell^2} = n^2 \frac{h^2c^2}{8mc^2\ell^2}$$

$$= n^2 \frac{(1239.8\ \text{eV}\cdot\text{nm})^2}{(8)(0.511\times 10^6\ \text{eV})(0.1\ \text{nm})^2}$$

$$= n^2(38\ \text{eV})$$

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4. Determine the expectation values for x, x^2, p, and p^2 of a particle in an infinite square well for the first excited state.

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Solution:

$$\langle x\rangle_{n=2} = \frac{2}{L}\int_0^L x\ \sin^2\left(\frac{2\pi x}{L}\right)\ dx = \frac{L}{2}$$

$$\langle x^2\rangle_{n=2} = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{2\pi x}{L}\right)\ dx = 0.32L^2$$

$$\langle p\rangle_{n=2} = -\frac{4i\hbar}{L^2}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\cos\left(\frac{2\pi x}{L}\right)\ dx = 0$$

4.Determine the expectation values for x, x^2, p, and $p^2$of a particle in an infinite square well for the first excited state.

Solution:

$$\langle p^2\rangle_{n=2} = \frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)\sin\left(\frac{2\pi x}{L}\right)\,dx$$

$$= (-i\hbar)^2\frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(\frac{2\pi}{L}\frac{d}{dx}\right)\cos\left(\frac{2\pi x}{L}\right)\,dx$$

$$= -(-\hbar^2)\frac{8\pi^2}{L^3}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\,dx$$

$$= \frac{4\pi^2\hbar^2}{L^2}$$

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5.What are the possible quantum numbers for the state $n=4$ in atomic hydrogen?

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Solution:

n	ℓ	m_ℓ
4	0	0
4	1	−1, 0, 1
4	2	−2, −1, 0, 1, 2
4	3	−3, −2, −1, 0, 1, 2, 3

6. What is the value of the Bohr magneton? Use that value to calculate the energy difference between the $m_l=0$ and $m_l=1$ components in the 2p state of atomic hydrogen placed in an external field of 2.00 T ?

6. What is the value of the Bohr magneton? Use that value to calculate the energy difference between the m_l=0 and m_l=1 components in the 2p state of atomic hydrogen placed in an external field of 2.00 T ?

Solution: The Bohr magneton is determined to be

$$\mu_B = \frac{e\hbar}{2m}$$

$$= \frac{(1.602 \times 10^{-19}\,\mathrm{C})(1.055 \times 10^{-34}\,\mathrm{J \cdot s})}{2\,(9.11 \times 10^{-31}\,\mathrm{kg})}$$

$$\mu_B = 9.27 \times 10^{-24}\,\mathrm{J/T}$$

$$\Delta E = (9.27 \times 10^{-24}\,\mathrm{J/T})(2.00\,\mathrm{T}) = 1.85 \times 10^{-23}\,\mathrm{J}$$

$$= 1.16 \times 10^{-4}\,\mathrm{eV}$$

7. Show that an energy difference of $2*10^{-3}$eV for the 3p subshell of sodium accounts for the 0.6nm splitting of a spectral line at 589.3 nm.

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Solution: since

$$E = \frac{hc}{\lambda} \qquad |\Delta\lambda| = \frac{\lambda^2}{hc}|\Delta E|$$

$$|\Delta\lambda| = \frac{(589.3\ \mathrm{nm})^2(2\times 10^{-3}\,\mathrm{eV})}{1.240\times 10^3\ \mathrm{eV}\cdot\mathrm{nm}} = 0.6\ \mathrm{nm}$$

8. If the spin-orbit splitting of the $3P_{3/2}$ and $3P_{1/2}$ states of sodium is 0.0021 eV, what is the internal magnetic field causing the splitting?

8. If the spin-orbit splitting of the $3P_{3/2}$ and $3P_{1/2}$ states of sodium is 0.0021 eV, what is the internal magnetic field causing the splitting?

Solution:

$$\Delta E = g_s\left(\frac{e\hbar}{2m}\right)\frac{\hbar}{\hbar}B = \frac{e\hbar}{m}B$$

Then

$$B = \frac{m\Delta E}{e\hbar} = \frac{(9.11\times10^{-31}\,\mathrm{kg})(0.0021\,\mathrm{eV})}{(1.6\times10^{-19}\,\mathrm{C})(6.58\times10^{-16}\,\mathrm{eV\cdot s})}$$

$$= 18\ \mathrm{T}$$