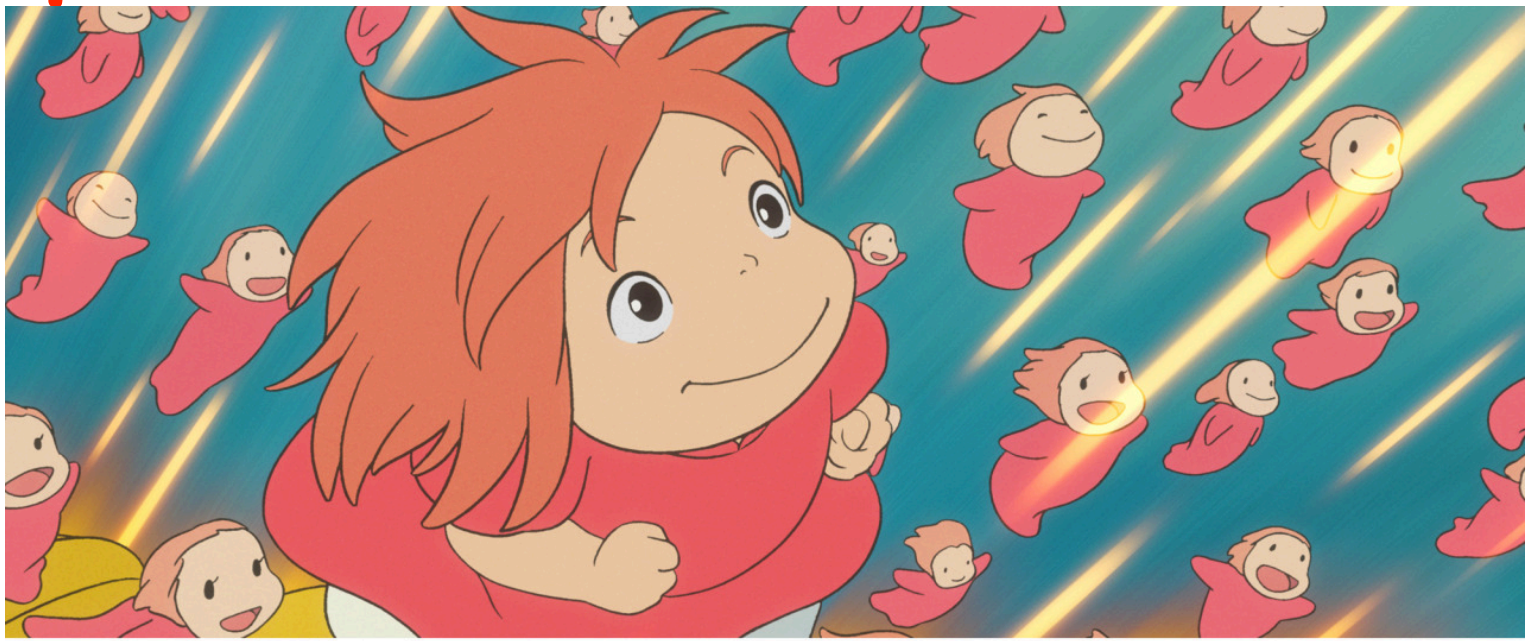
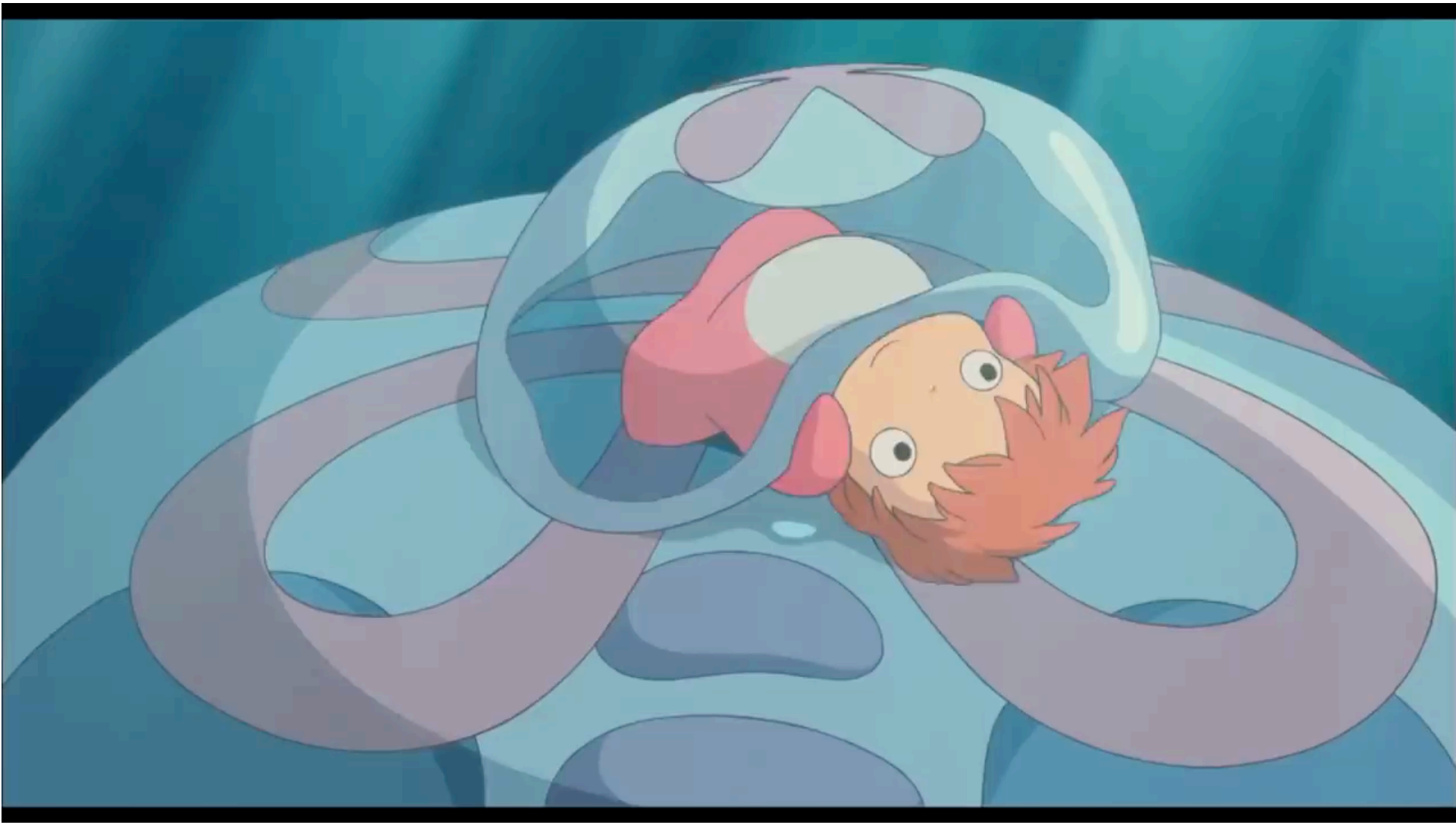
# Atomic Physics

## Chapter 4 Fine structures of Atoms





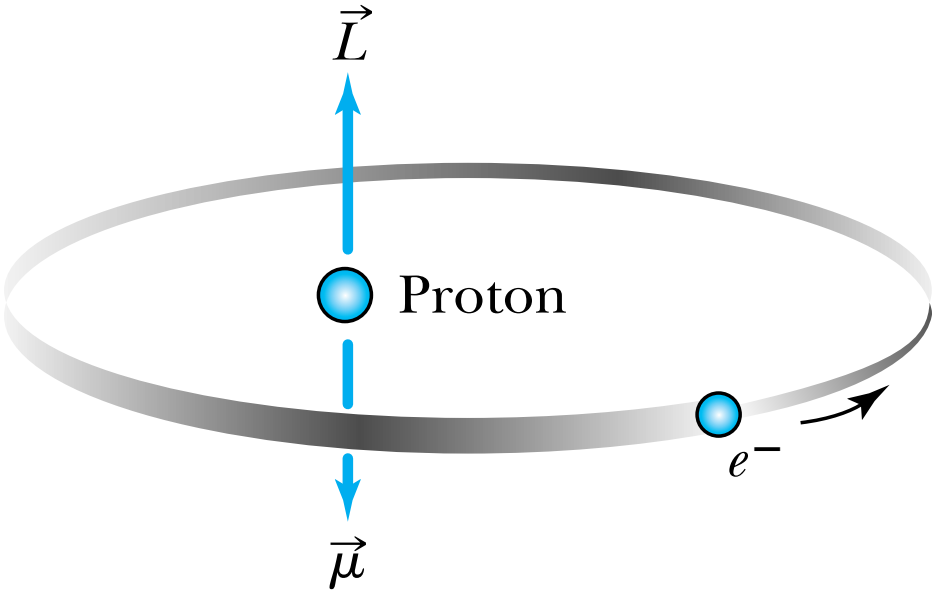
# 4.1Magnetic moment of electron



# 4.1Magnetic moment of electron

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

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.

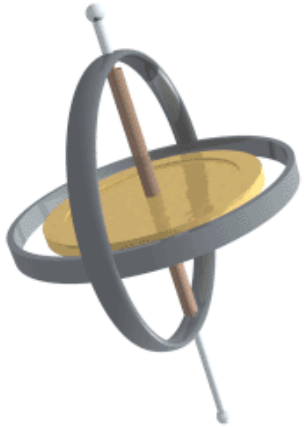
# Magnetic moment of electron

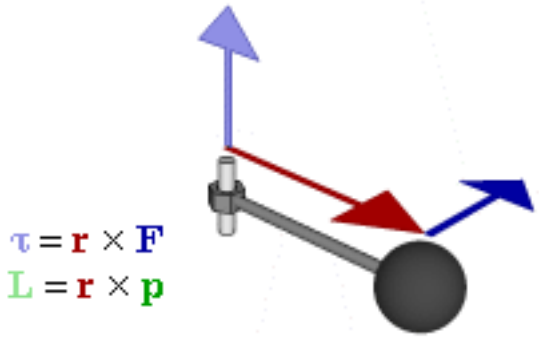
The dipole also has a potential energy in the field given by

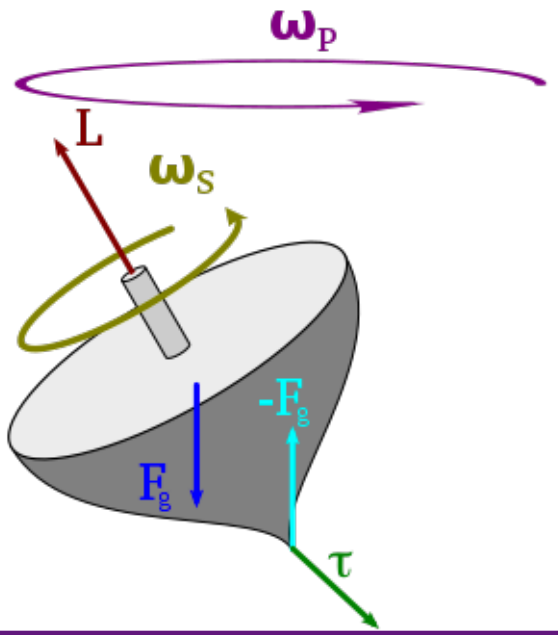
$$V_B = -\vec{\mu} \cdot \vec{B}$$

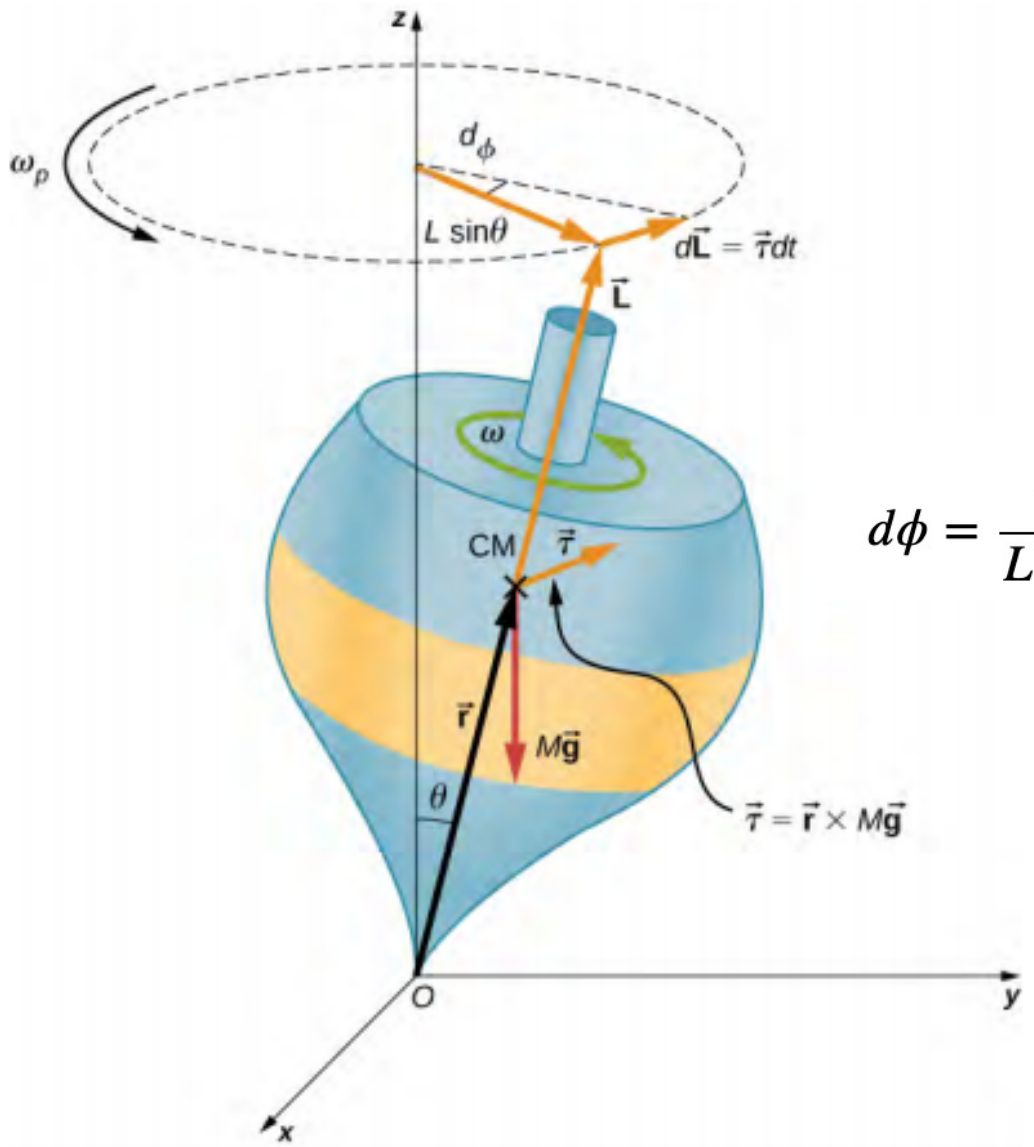
According to classical physics, if the system can change its potential energy, the magnetic moment will align itself with the external magnetic field to minimize energy.

Precession in gravitational field








$$\tau = rMg\sin\theta.$$

$$dL = rMg\sin\theta dt.$$

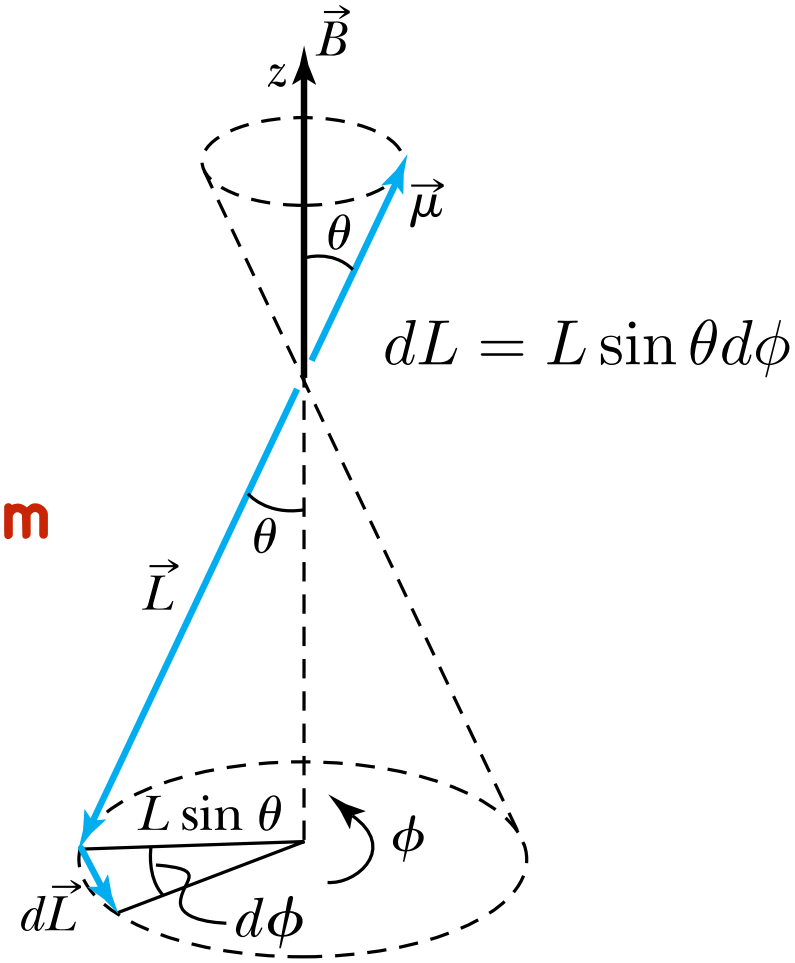
$$d\phi = \frac{dL}{L\sin\theta} = \frac{rMg\sin\theta}{L\sin\theta}dt = \frac{rMg}{L}dt.$$

$$\omega_P = \frac{d\phi}{dt},$$

$$\omega_P = \frac{rMg}{L}.$$

# 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**

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

# Magnetic moment of electron

## 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

The expectation value of the square of the angular momentum L is therefore

$$\left\langle \boldsymbol{L}^2 \right\rangle = \int \psi^* \hat{L}^2 \psi \, \mathrm{d}\tau = l(l+1)\hbar^2$$

For the absolute value of the angular momentum we obtain

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

The expectation value of $L_z$ is

$$\langle L_z \rangle = m\hbar.$$

# Magnetic moment of electron

If the operators $L_x$ or $L_y$ are applied to the wave function, one can prove that $\psi$ is not an eigenfunction of $L_x$, i.e.,

$$\hat{L}_x \psi \neq m_x \psi.$$

The same is true for $L_y$. For their square summation operator,

$$\left(\hat{L}_x^2 + \hat{L}_y^2\right)\psi = \left[l(l+1) - m^2\right]\hbar^2\psi.$$

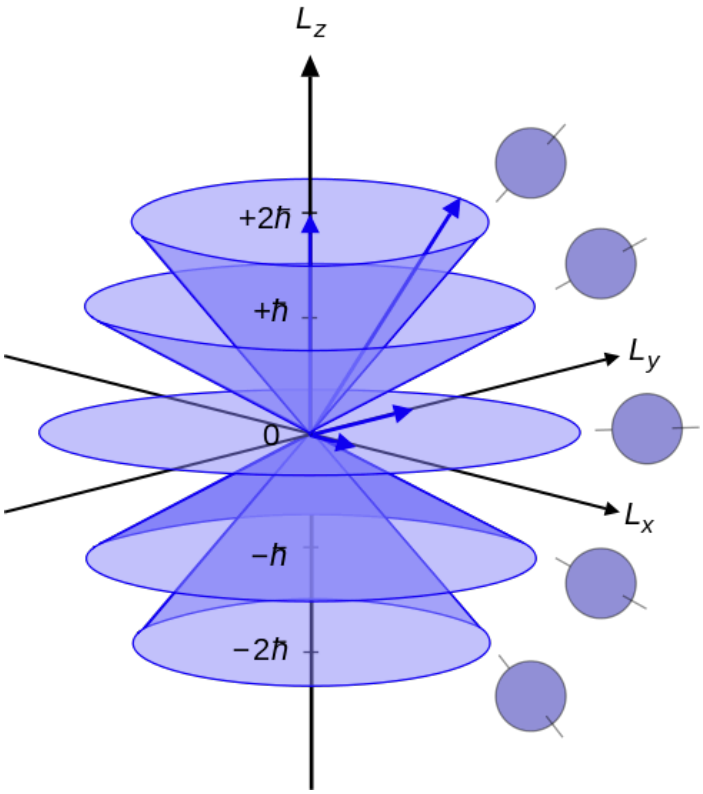
| $l$ | $m$ | Name | Degree of degeneracy |
|---|---|---|---|
| 0 | 0 | $s$ | 1 |
| 1 | $-1, 0, +1$ | $p$ | 3 |
| 2 | $-2$ to $+2$ | $d$ | 5 |
| 3 | $-3$ to $+3$ | $f$ | 7 |
| 4 | $-4$ to $+4$ | $g$ | 9 |
| 5 | $-5$ to $+5$ | $h$ | 11 |

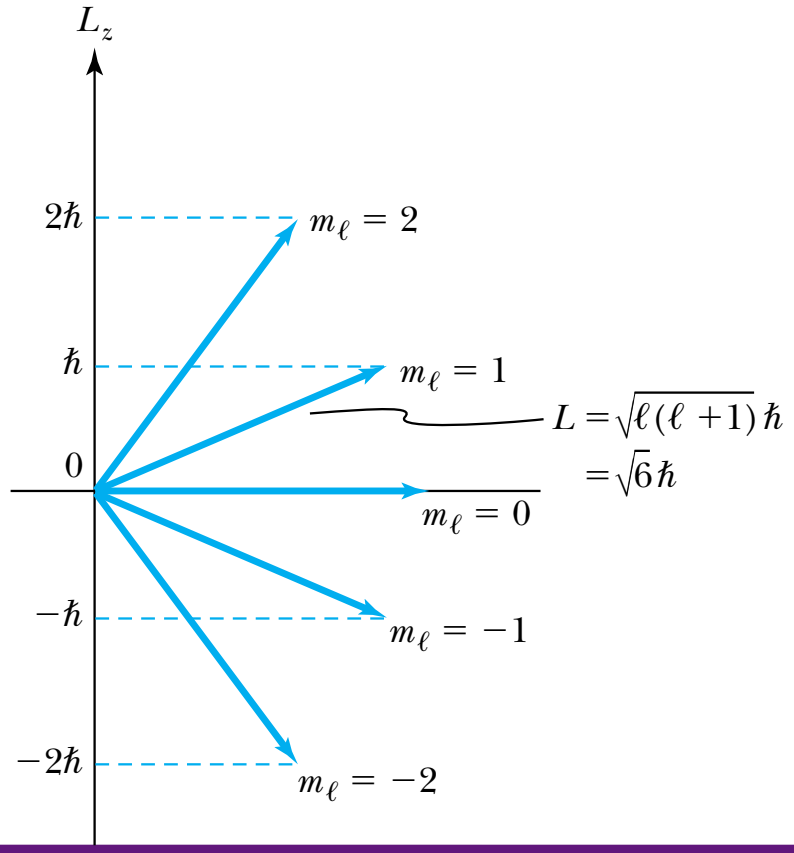
# Magnetic moment of electron

$$n = 1, 2, 3, 4, \ldots \qquad \text{Integer}$$

$$l = 0, 1, 2, 3, \ldots, n-1 \qquad \text{Integer}$$

$$m_l = -l, -l+1, \ldots, 0, 1, \ldots, l-1, l \qquad \text{Integer}$$



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

| $n$ | $\ell$ | $m_\ell$ |
|---|---|---|
| 4 | 0 | 0 |
| 4 | 1 | $-1, 0, 1$ |
| 4 | 2 | $-2, -1, 0, 1, 2$ |
| 4 | 3 | $-3, -2, -1, 0, 1, 2, 3$ |

# 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

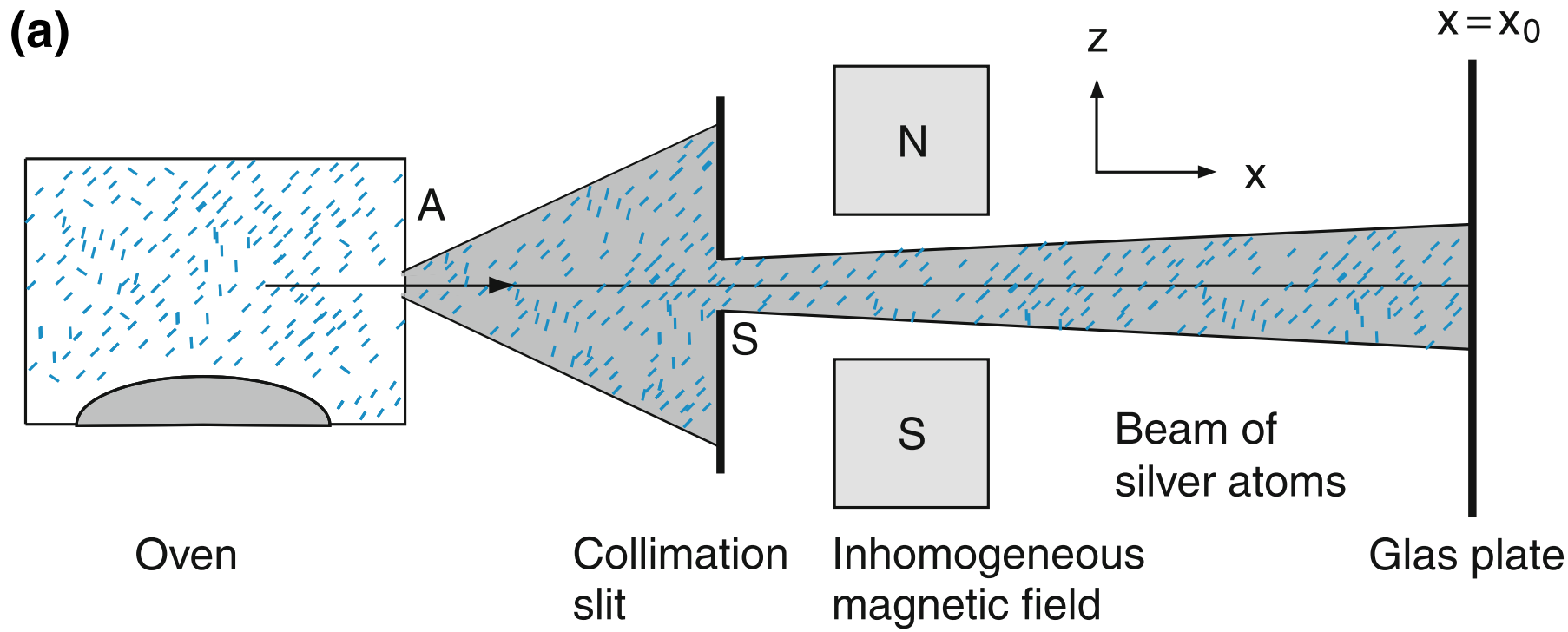
$$\mu_B = \frac{e\hbar}{2m}$$

## The energy of the orbiting electron in a magnetic field

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

# Stern-Gerlach experiment

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



# Stern-Gerlach experiment

They started in 1919 and after many unsuccessful efforts and following improvements to their beam apparatus, the two researchers were finally rewarded with an unexpected result in 1921

They chose as test objects silver atoms because these atoms could be detected on a glass plate, where they condensate and form a thin layer with an optical transparency depending on the thickness of the layer and therefore the number of incident atoms.

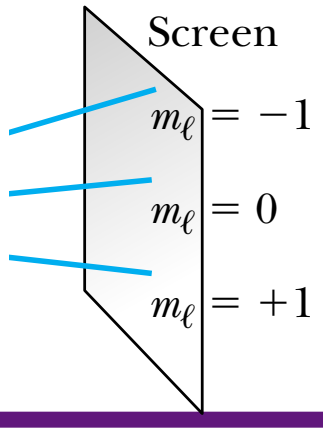
# Stern-Gerlach experiment

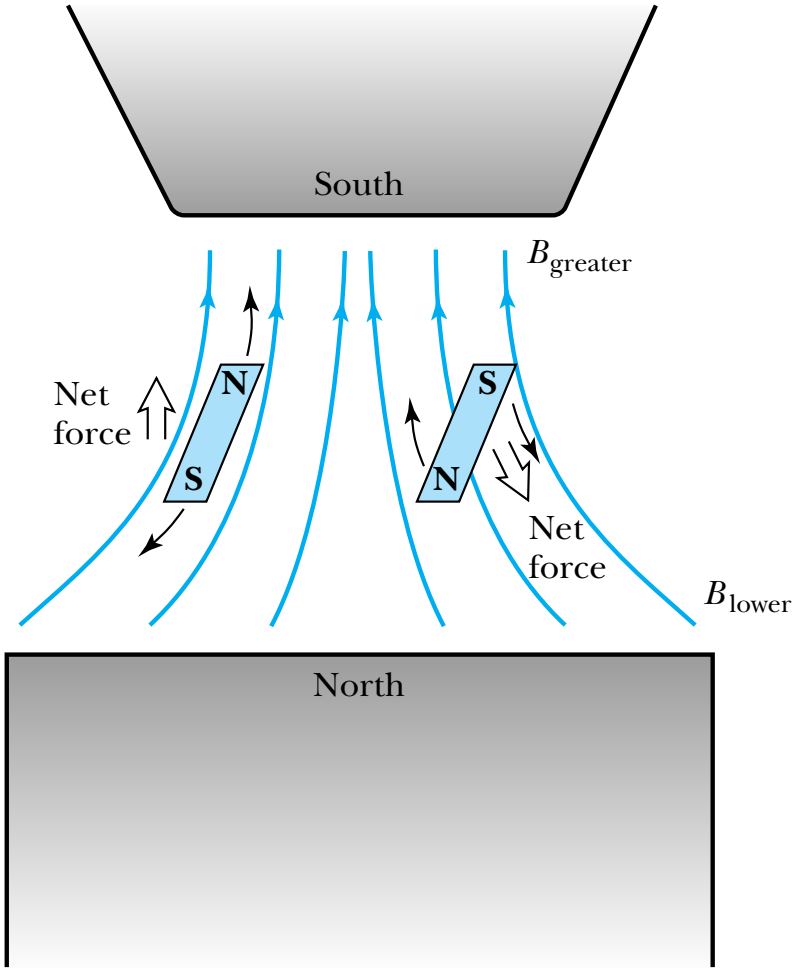
If an external magnetic field is inhomogeneous, the force on the particles is

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

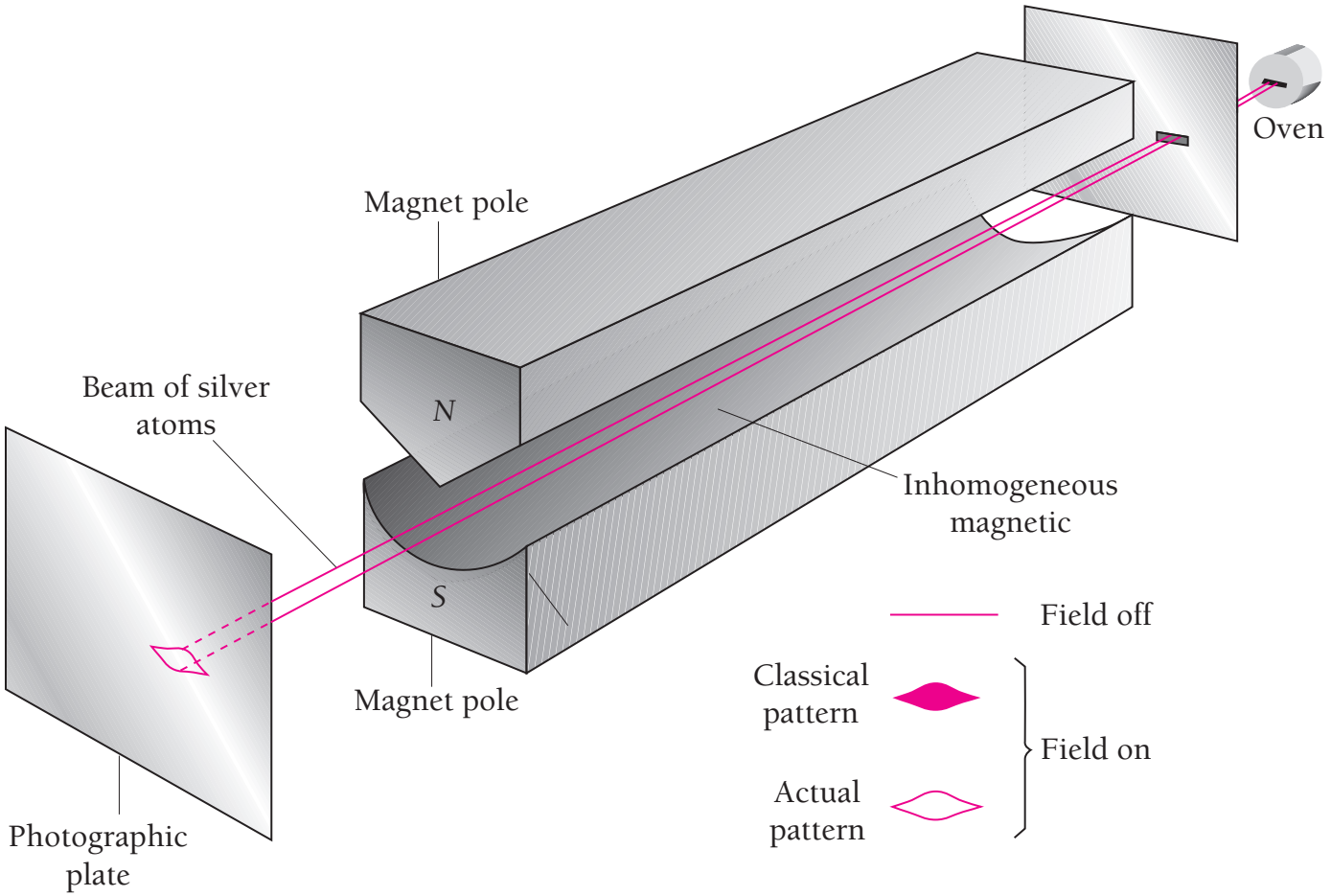
When l=1

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



# Stern-Gerlach experiment



# Stern-Gerlach experiment

The acceleration of the atom along the z direction is

$$a_z = F_z/m.$$

The separation of the atom along the z direction due to this acceleration is

$$d = a_z t^2/2.$$

The time that the atom spends within the inhomogeneous field is

$$t = \Delta x/v_x$$

where ?Δx is the length of the inhomogeneous field, and $v_x$ is the constant speed of the atom within the field. The separation d is therefore found from

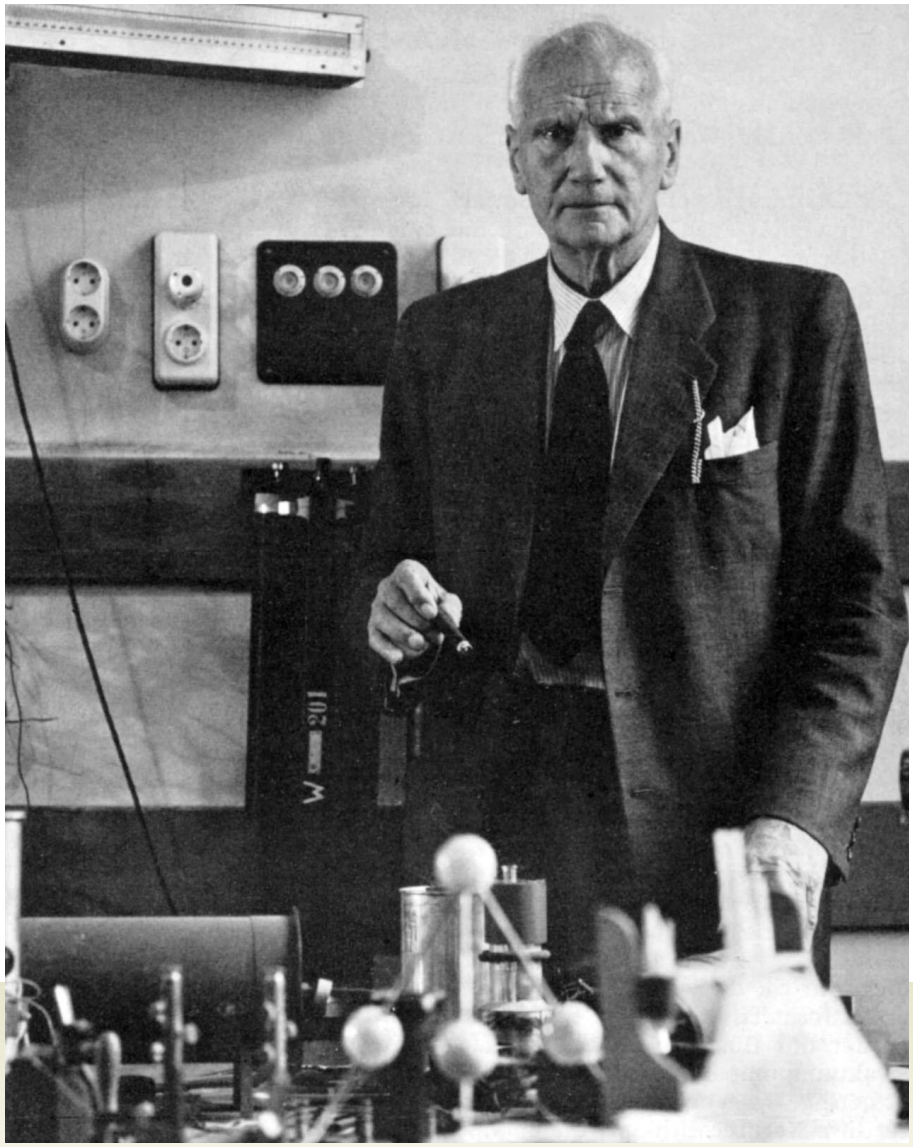
$$d = \frac{1}{2}a_z t^2 = \frac{1}{2}\left(\frac{F_z}{m}\right)t^2 = \frac{1}{2m}\left(\mu_z \frac{dB}{dz}\right)\left(\frac{\Delta x}{v_x}\right)^2$$

$$\frac{1}{2}m\langle v_x^2\rangle = \frac{3}{2}kT.$$

# Stern-Gerlach experiment

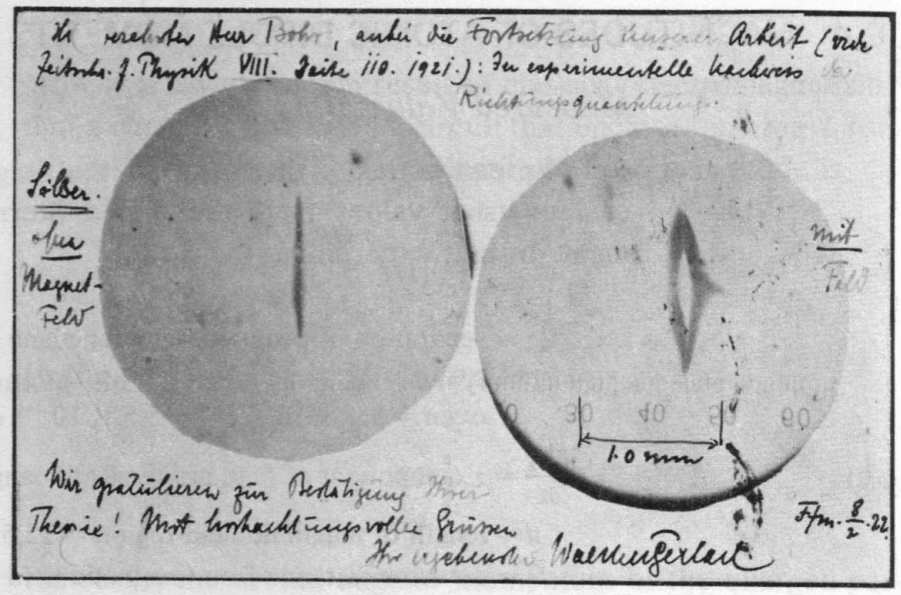


# Stern-Gerlach experiment



# 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 $m_l$.

# Reactions to the Stern–Gerlach Experiment

Through their clever experimental arrangement Stern and Gerlach not only demonstrated *ad oculos* [for the eyes] the space quantization of atoms in a magnetic field, but they also proved the quantum origin of electricity and its connection with atomic structure.

**—*Arnold Sommerfeld* (1868–1951)**

The most interesting achievement at this point is the experiment of Stern and Gerlach. The alignment of the atoms without collisions via radiative [exchange] is not comprehensible based on the current [theoretical] methods; it should take more than 100 years for the atoms to align. I have done a little calculation about this with [Paul] Ehrenfest. [Heinrich] Rubens considers the experimental result to be absolutely certain.

**—*Albert Einstein* (1879–1955)**

More important is whether this proves the existence of space quantization. Please add a few words of explanation to your puzzle, such as what's really going on.

**—*James Franck* (1882–1951)**

I would be very grateful if you or Stern could let me know, in a few lines, whether you interpret your experimental results in this way that the atoms are oriented only parallel or opposed, but not normal to the field, as one could provide theoretical reasons for the latter assertion.

**—*Niels Bohr* (1885–1962)**

This should convert even the nonbeliever Stern.

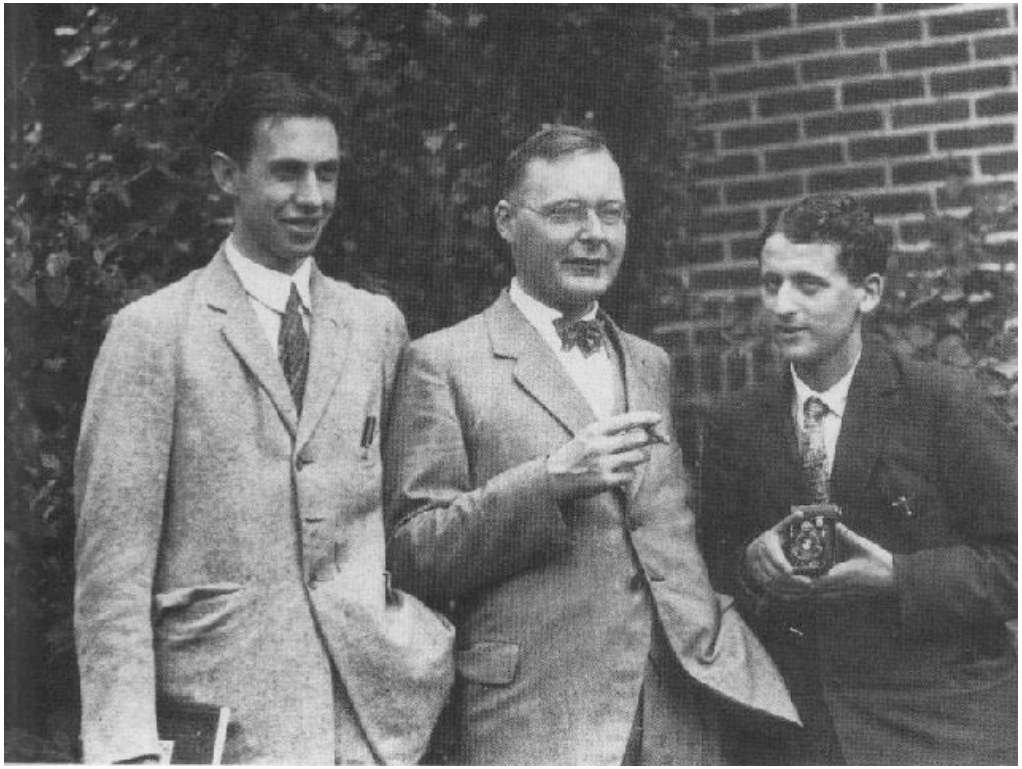
**—*Wolfgang Pauli* (1900–58)**

As a beginning graduate student back in 1923, I . . . hoped with ingenuity and inventiveness I could find ways to fit the atomic phenomena into some kind of mechanical system. . . . My hope to [do that] died when I read about the Stern–Gerlach experiment. . . . The results were astounding, although they were hinted at by quantum theory. . . . This convinced me once and for all that an ingenious classical mechanism was out and that we had to face the fact that the quantum phenomena required a completely new orientation.

**—*Isidor I. Rabi* (1898–1988)**

# 4.3 Intrinsic Spin

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

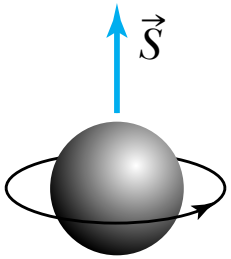
$$s = 1/2$$

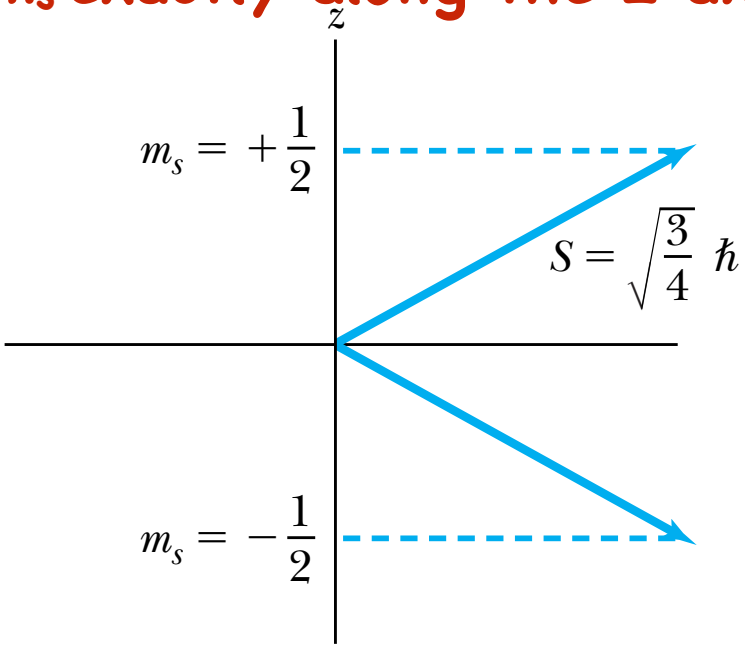
# Intrinsic Spin

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

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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

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

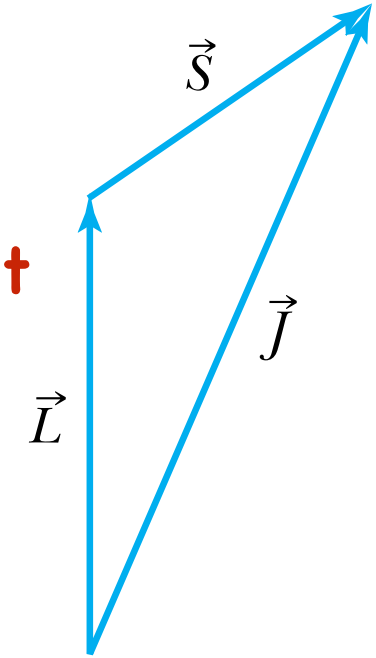
where

$$m_s = \pm 1/2$$

# Total angular momentum of single electron

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.

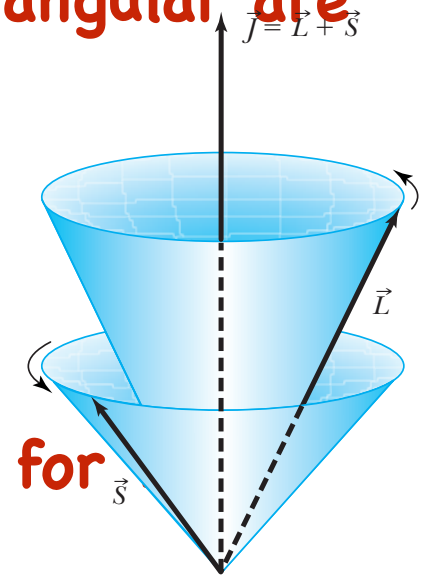
# Total angular momentum of single electron

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,

$$j = l \pm s$$

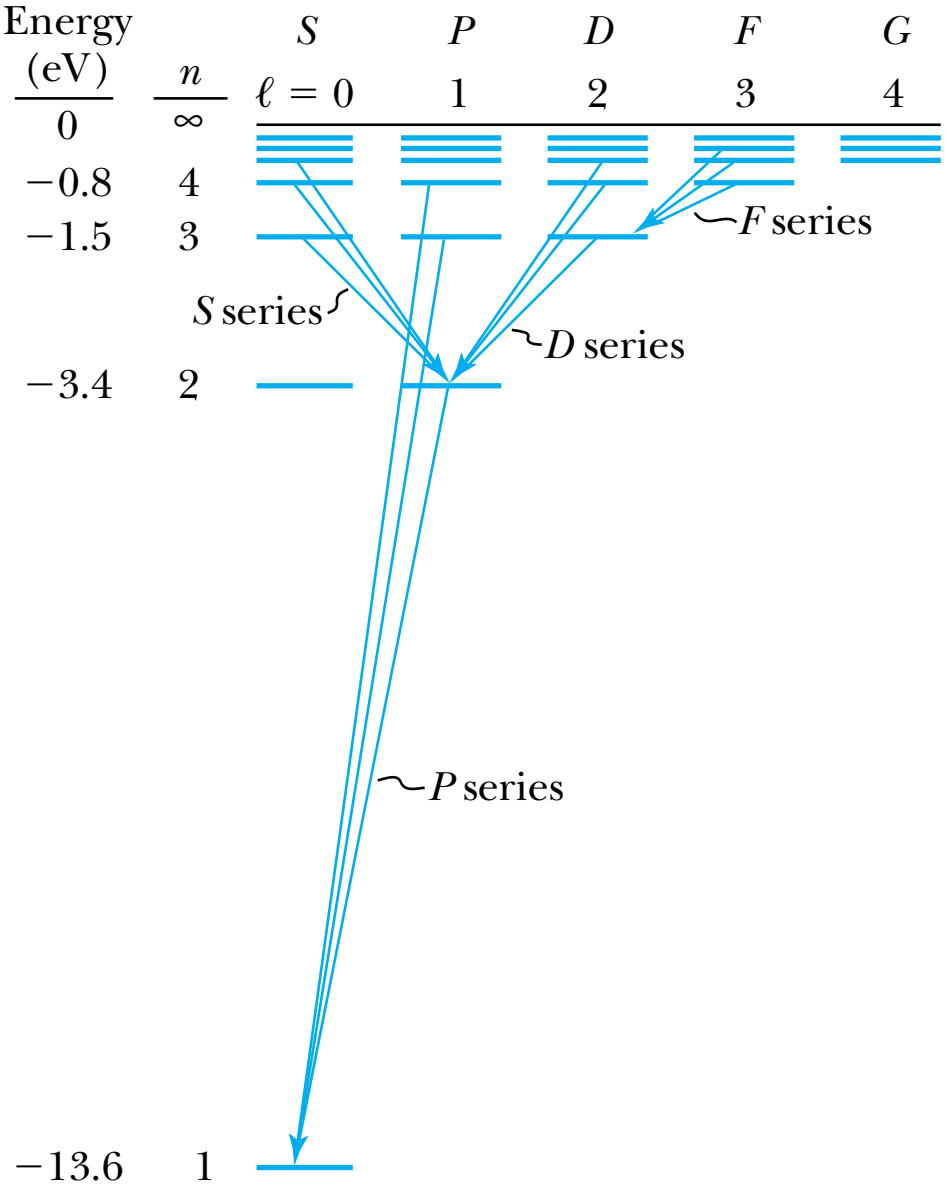
$$= l \pm \frac{1}{2}$$

The notation commonly used to describe these states

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

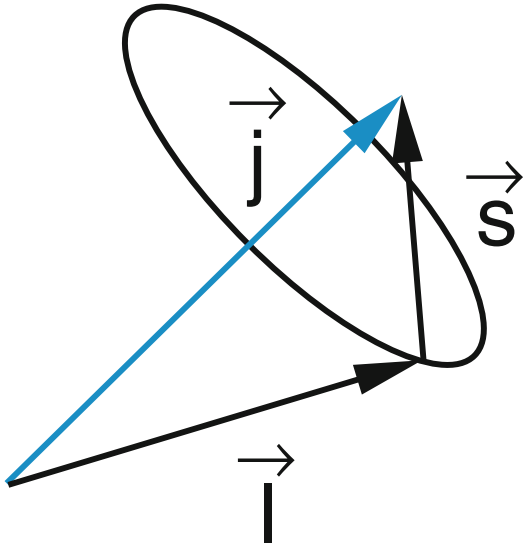
$$= S, P, D, F, \ldots$$

# Total angular momentum of single electron



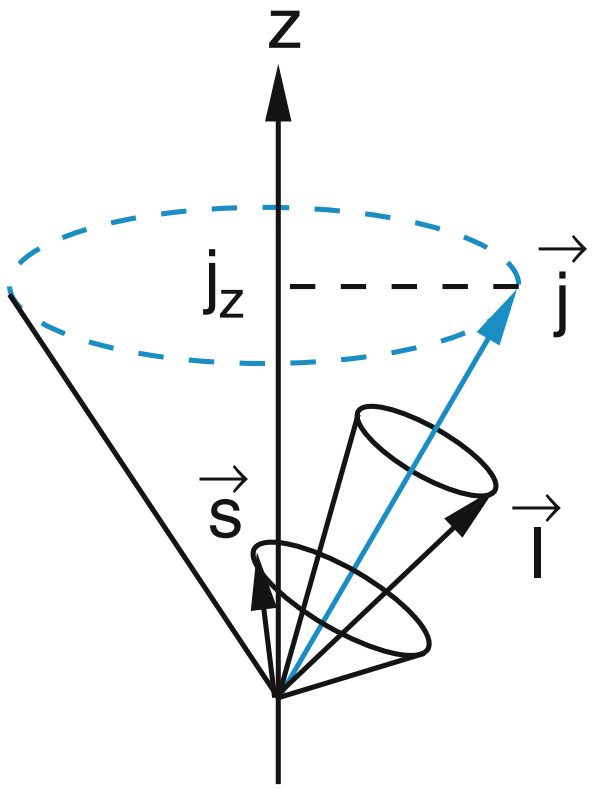
# Total magnetic moment

Without a magnetic field, the total angular momentum j = l + s of the electron in a Coulomb field (central force field) is constant, which means that its orientation in space and its absolute value are constant, independent of time.



# Total magnetic moment

In an external homogeneous magnetic field B = {0, 0, $B_z$}, the magnetic moment $\mu_j$, and therefore j, precess around the field axis with constant components $\mu_z$ and $j_z$



# Total magnetic moment

If the coupling between orbital angular momentum and spin is stronger than the coupling of $\mu_l$ and $\mu_s$ to the external field. The spin-orbit coupling is still valid and the absolute value |j| of the total angular momentum

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s} \quad \text{with} \quad |\boldsymbol{j}| = \sqrt{j(j+1)}h$$

is conserved in the external magnetic field. Its direction is, however, no longer space-fixed because the magnetic moment $\mu_j = \mu_l + \mu_s$, which is related to j, experiences a torque

$$\boldsymbol{D} = \boldsymbol{\mu}_j \times \boldsymbol{B}.$$

# Total magnetic moment

The magnetic moments of orbital motion and spin of the electron are:

$$\boldsymbol{\mu}_l = -(\mu_B/\hbar)\boldsymbol{l} \quad \text{and} \quad \boldsymbol{\mu}_s = -g_s(\mu_B/\hbar)\boldsymbol{s}.$$

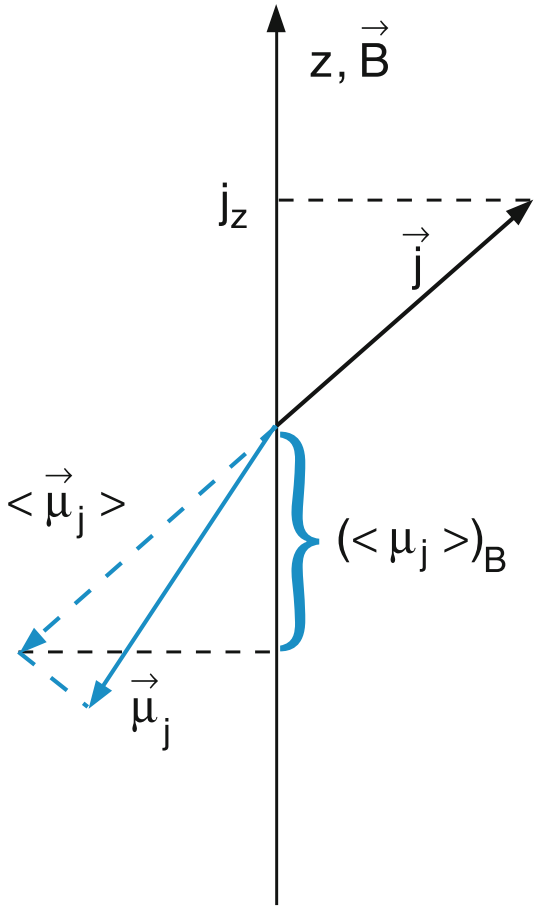
Because of the Lande factor $g_s \approx 2$ for the spin moment $\mu_s$, the total magnetic moment

$$\boldsymbol{\mu}_j = \boldsymbol{\mu}_l + \boldsymbol{\mu}_s = -(\mu_B/\hbar)(\boldsymbol{l} + g_s\boldsymbol{s})$$

is for l > 0 no longer parallel to the total angular momentum j = l + s!

# Total magnetic moment

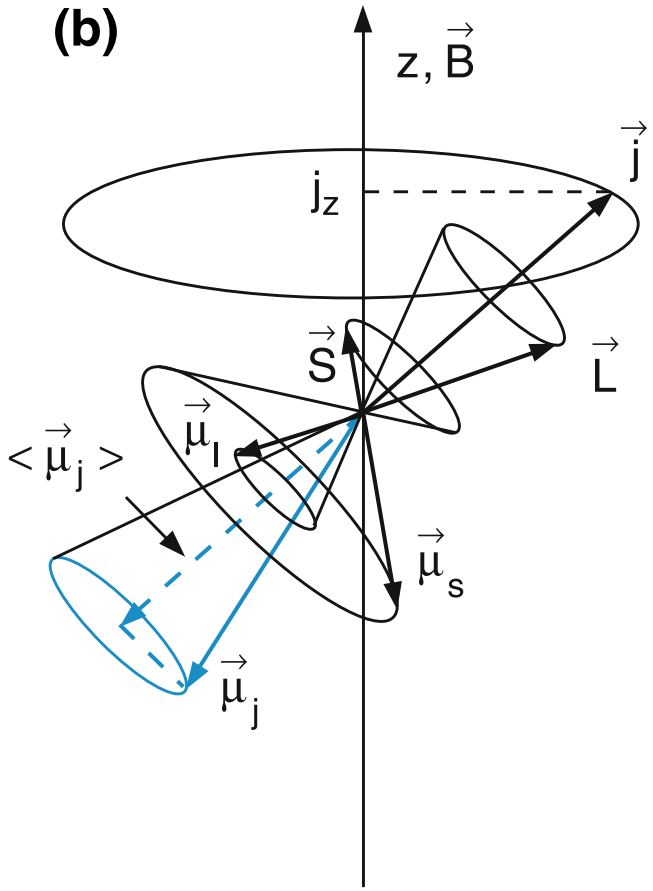
Without an external field the absolute value and the direction of j is constant in time. Since the vector s precesses around the axis of the internal magnetic field produced by the orbital movement of the electron and $\mu_j$ is not parallel to j, $\mu_j$ has to precess around the direction of the space-fixed vector j. The time average $\langle\mu_j\rangle$ of $\mu_j$ is then the projection of $\mu_j$ onto j.



# Total magnetic moment

This gives

$$\langle \boldsymbol{\mu}_j \rangle = \frac{\boldsymbol{\mu}_j \cdot \boldsymbol{j}}{|\boldsymbol{j}|^2}\boldsymbol{j} = -\frac{e}{2m_e}\left(\frac{\boldsymbol{l}\cdot\boldsymbol{j}}{|\boldsymbol{j}|^2} + g_s\frac{\boldsymbol{s}\cdot\boldsymbol{j}}{|\boldsymbol{j}|^2}\right)\boldsymbol{j}.$$



# Total magnetic moment

From j = l + s follows

$$l \cdot j = \frac{1}{2}[j^2 + l^2 - s^2]$$

$$= \frac{1}{2}[j(j+1) + l(l+1) - s(s+1)]\hbar^2$$

and similar from l = j – s:

$$s \cdot j = \frac{1}{2}[j(j+1) + s(s+1) - l(l+1)]\hbar^2.$$

We can therefore write for the component of $\langle \mu_j \rangle$ in the direction of j with $g_s \approx 2$

$$\langle \boldsymbol{\mu}_j \rangle_j = -\frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \mu_B \vec{j} = -g_j \mu_B \vec{j}$$

# Total magnetic moment

The Lande factor $g_j$ is defined here as

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$

For s = 0 (pure orbital magnetism) it follows j = l and we obtain $g_j$ =1. For l=0 (pure spin magnetism) is j=s and therefore $g_j \approx 2$.

In the z direction,

$$\langle \mu_j \rangle_z = -m_j g_j \mu_B$$

$$\Delta E_{m_j} = -\langle \mu_j \rangle_z B = m_j g_j \mu_B B.$$

$\vec{j}$

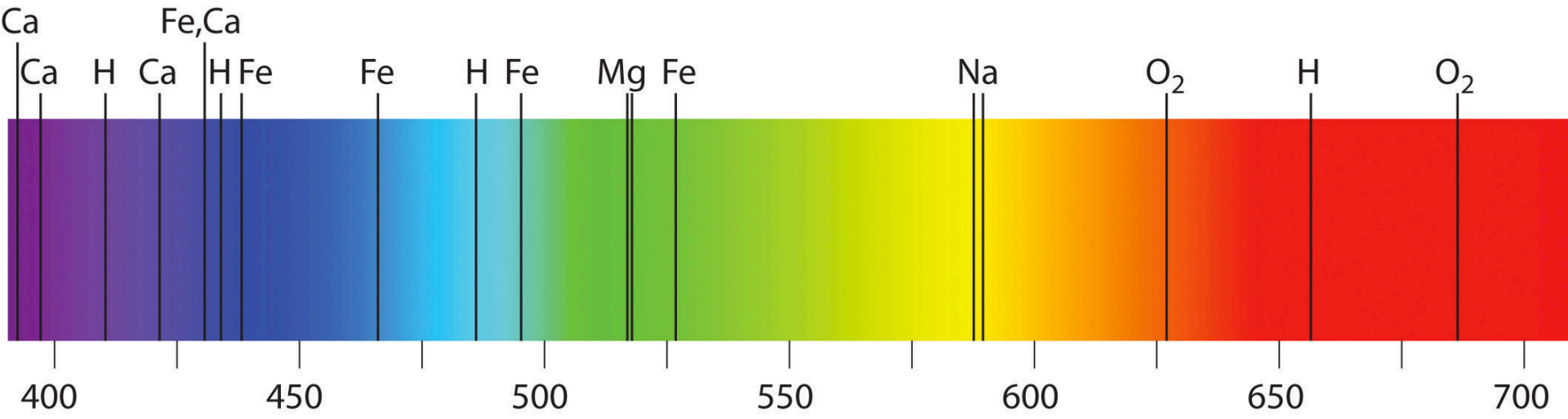
# Total magnetic moment

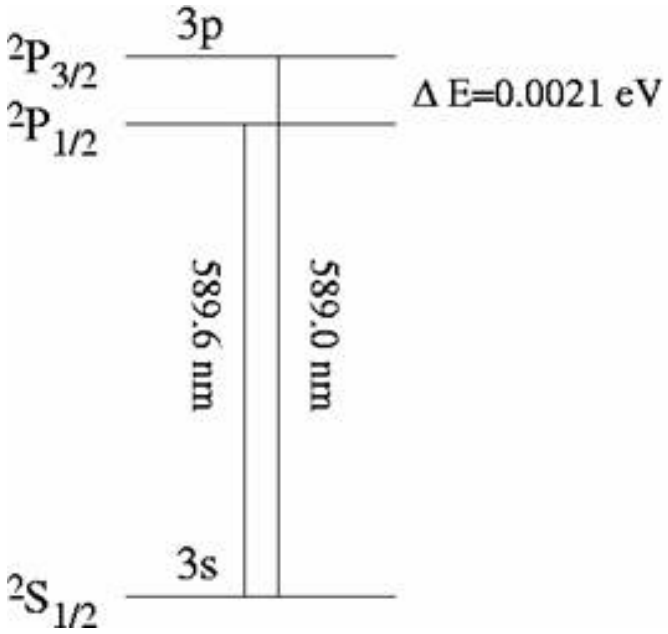
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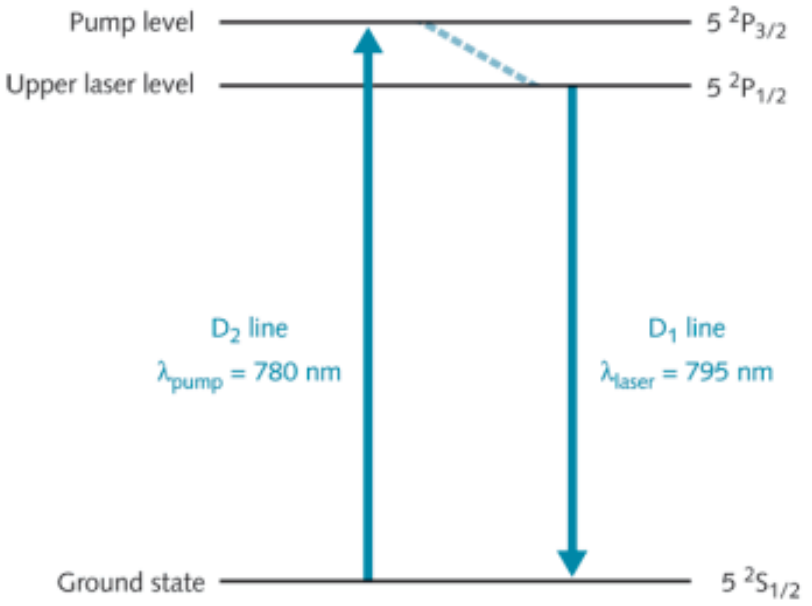
## Lande factor of different state

| 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

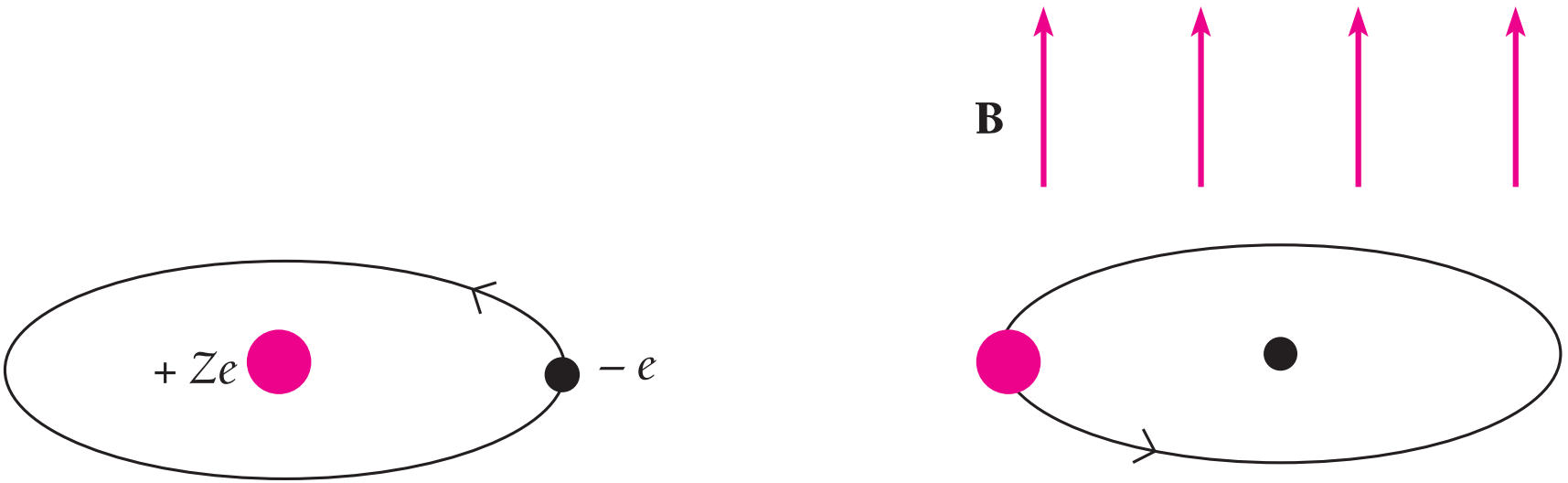


# Spin-orbit coupling

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 ,

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

# Spin-orbit coupling

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**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**

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

# Spin-orbit coupling

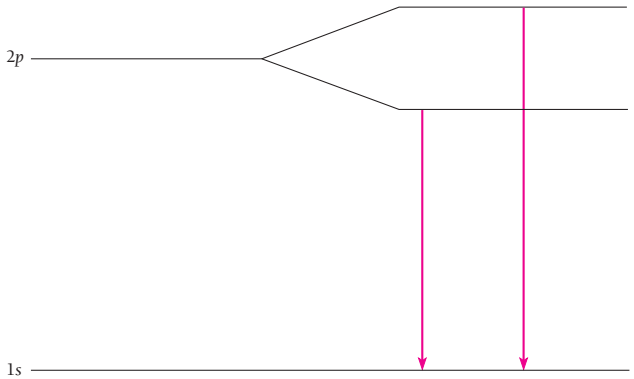
A single electron has s =1/2 so, for each l, its total angular momentum quantum number j has two possible values:

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

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

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

# The relativistic hydrogen model

The form of the Hamiltonian with relativistic corrections to order $v^2/c^2$ is

$$H = \frac{p^2}{2\mu} + V(r) - \frac{p^4}{8\mu^3 c^2} + \frac{1}{2\mu^2 c^2}\frac{1}{r^2}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S} + \frac{\hbar^2}{8\mu^2 c^2}\nabla^2 V(r).$$

The first two terms are the classical Hamiltonian.

The third term is a relativistic correction to the energy.

The fourth term is the spin-orbit interaction energy for l ≥ 1 electrons, which includes a relativistic correction to the electromagentic potential. The final term is a correction called the Darwin term for l= 0electrons

# The relativistic hydrogen model

We can use the perturbation theory to calculate these corrections

$$\frac{\Delta E_1}{E_n} = -\frac{(Z\alpha)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+1/2}\right],$$

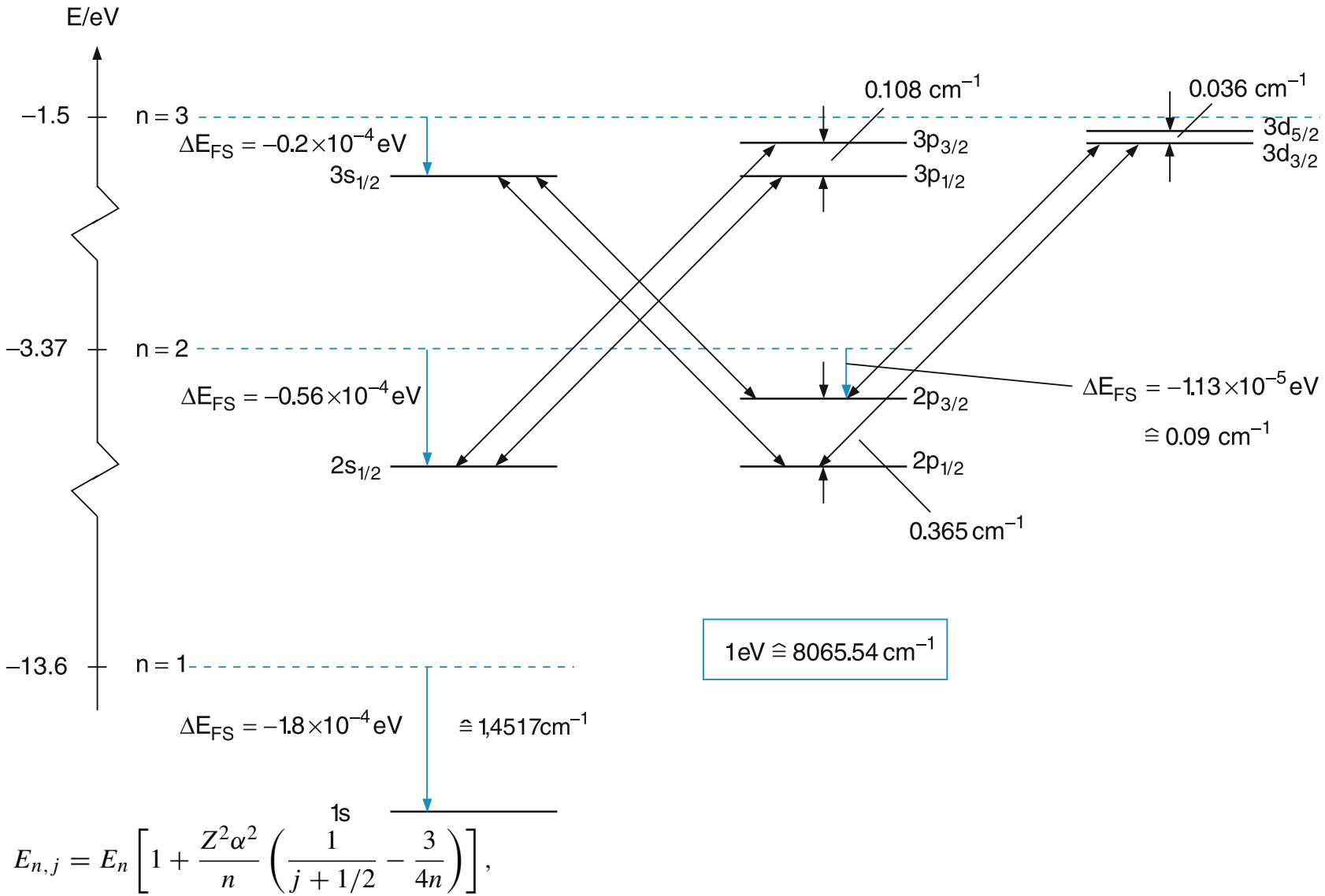
$$\frac{\Delta E_2}{E_n} = -\frac{(Z\alpha)^2}{n}\left[\frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+1/2)(l+1)}\right] \qquad l \neq 0,$$

$$\frac{\Delta E_3}{E_n} = -\frac{(Z\alpha)^2}{n} \qquad l = 0,$$

Following the addition of the three correction terms, the energy for an electron in state nj can be expressed

$$E_{nj} = E_n\left(1 + \Delta E_{nj}\right) = E_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right],$$

# Hydrogen fine structure spectrum




$$E_{n,j} = E_n\left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right],$$

# Hyperfine structure

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The nuclei spin

$$|\boldsymbol{I}| = \sqrt{I(I+1)}\hbar$$

The projection of I onto the z-axis is

$$I_z = m_I \hbar \quad \text{with} \quad -I \leq m_I \leq +I.$$

A magnetic moment is connected with the nuclear spin

$$\mu_{\mathrm{N}} = \gamma_{\mathrm{K}} I.$$

The unit of the nuclear magnetic moment is the nuclear magneton

$$\mu_{\mathrm{K}} = \frac{e}{2m_{\mathrm{p}}}\hbar = \frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\mu_{\mathrm{B}} = \frac{\mu_{\mathrm{B}}}{1836}$$

$$= 5.05 \times 10^{-27}\,\mathrm{JT}^{-1}$$

# Hyperfine structure

The magnetic moment of any atomic nucleus can be written in units of the nuclear magneton as

$$\mu_{\mathrm{N}} = \gamma_{\mathrm{K}} I = g_{\mathrm{N}} \frac{\mu_{\mathrm{K}}}{\hbar} I,$$

The where the dimensionless factor $g_N$ is called the nuclear g-factor.

The magnetic moment of the proton is $\mu_I$(p) = 2.79$\mu_K$ and is determined by the movements and charges of the three quarks (u,u,d) inside the proton.

# Hyperfine structure

The nuclear magnetic moment gives two contributions to the shift and splitting of energy levels of the atomic electrons:

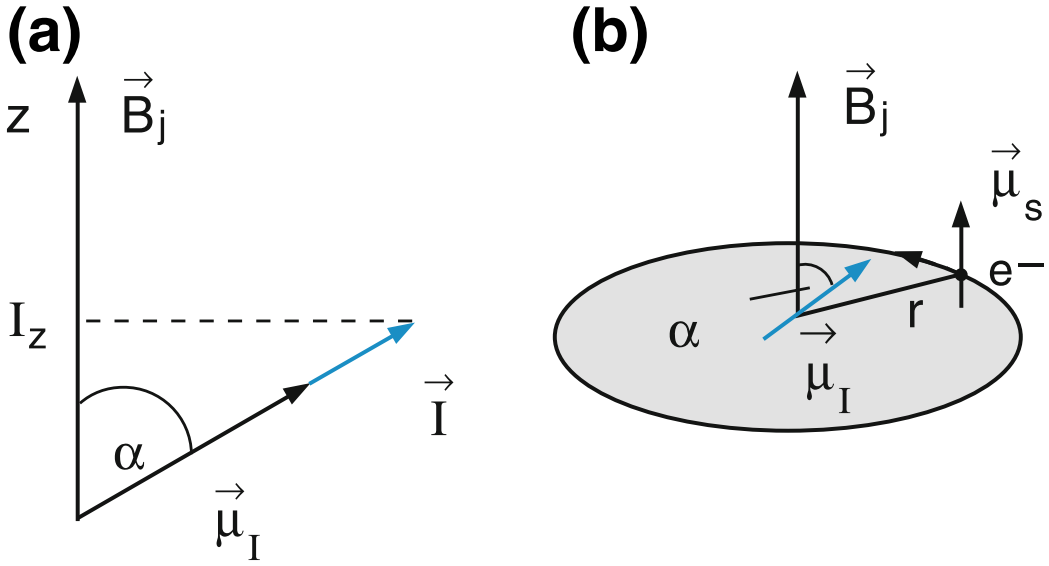
a) The interaction of the nuclear magnetic moment $\mu_N$ with the magnetic field produced by the electrons at the nucleus (Zeeman effect of $\mu_N$ in the internal magnetic field produced by the electrons).

b) The interaction of the electronic magnetic moment $\mu_j$ with the nuclear moment $\mu_N$ (magnetic dipole-dipole interaction).

# Hyperfine structure

The potential energy of the nuclear magnetic moment $\mu_N$ in the magnetic field produced by the electron at the location of the nucleus is

$$E_{\text{pot}}(I, j) = -\boldsymbol{\mu}_{\text{N}} \cdot B_{\text{int}} = -|\boldsymbol{\mu}_{\text{N}}| B_j \cos(\angle \boldsymbol{j}, \boldsymbol{I}).$$




$E_{HFS} = -\vec{\mu}_I \cdot \vec{B}_j$

$\vec{B} = \vec{B}(\vec{\mu}_s, \vec{\mu}_I, r)$

# Hyperfine structure

Introducing the total angular momentum F = j+I of the atom as the vector sum of the total electronic angular momentum j = l + s and the nuclear spin I, we obtain

$$\cos\angle(\boldsymbol{j},\boldsymbol{I}) = \frac{\boldsymbol{j}\cdot\boldsymbol{I}}{|\boldsymbol{j}||\boldsymbol{I}|}$$
$$= \frac{1}{2}\frac{F(F+1) - j(j+1) - I(I+}{\sqrt{j(j+1)I(I+1)}}.$$

The hyperfine energy of the H atom is then

$$\Delta E_{\mathrm{HFS}} = \frac{A}{2}[F(F+1) - j(j+1) - I(I+1)],$$

where the hyperfine constant

$$A = \frac{g_{\mathrm{N}}\mu_{\mathrm{K}}B_j}{\sqrt{j(j+1)}}$$

# Hyperfine structure

Each energy level $E_{n,j,l}$, splits into hyperfine components, due to the interaction between nuclear magnetic moment and electronic magnetic moments. The energy of these components is

$$E_{\mathrm{HFS}} = E_{n,l,j} + \frac{1}{2}A[F(F+1) - j(j+1) - I(I+1)].$$

For the H atom, with a proton as the nucleus, the experiments give the values

$$I = 1/2, \quad g_I = +5.58 \Rightarrow (\mu_{\mathrm{N}})_z = \pm 2.79\mu_{\mathrm{K}}$$

# Hyperfine structure

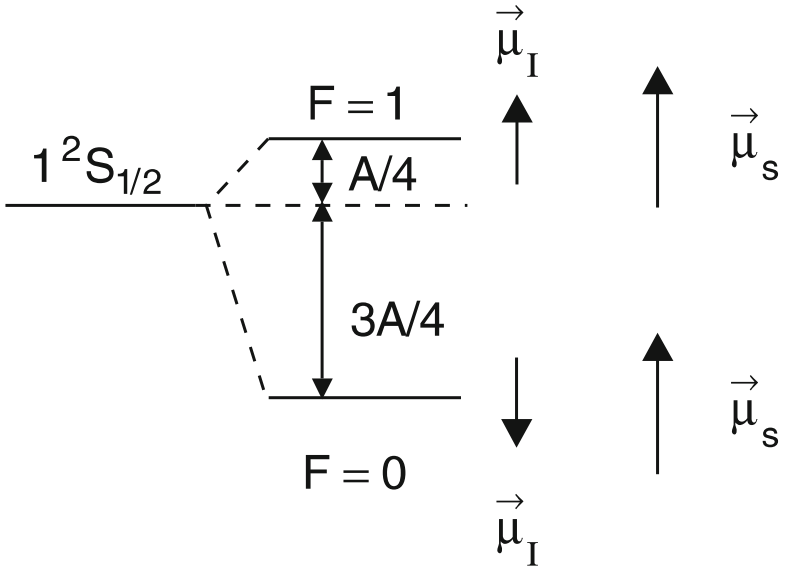
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For the ground state $^2S_{1/2}$ is j = 1/2, I = 1/2 ⇒ F = 0 or F = 1.

This gives the two hyperfine components

$$E_{\mathrm{HFS}}(F=0) = E_{1,0,1/2} - \frac{3}{4}A$$

$$E_{\mathrm{HFS}}(F=1) = E_{1,0,1/2} + \frac{1}{4}A,$$




with the separation

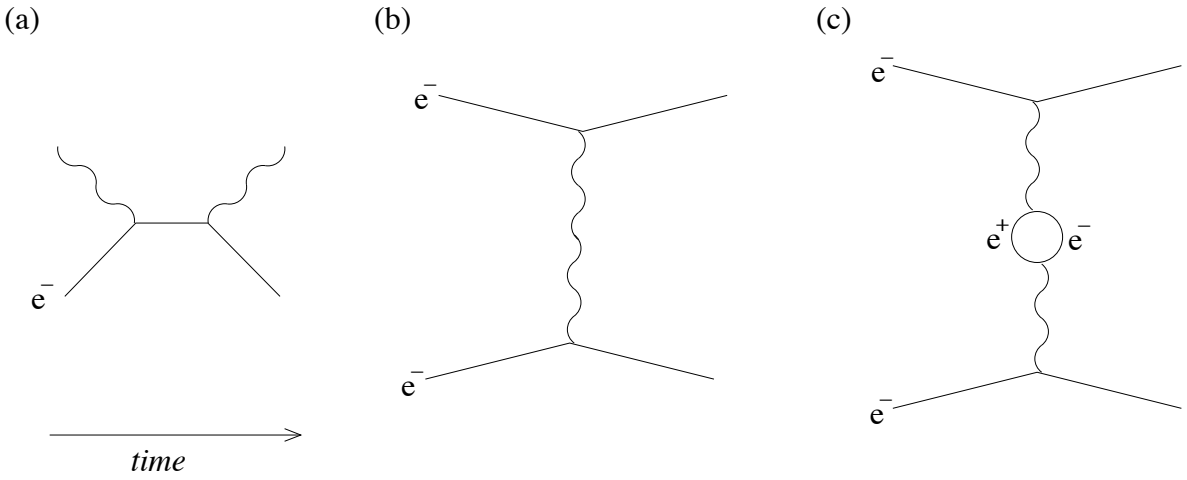
$$\Delta E = A = 5.8 \cdot 10^{-6}\,\mathrm{ev}$$

and

$$\Delta\lambda = 21\ \mathrm{cm}$$

# Lamb shift

The virtual particles are the carriers of the "force" by which particles interact with one another.




The energy corrections, based upon the lowest order radiative corrections are

$$\frac{\Delta E_{n0}}{E_n} = -\frac{8\alpha}{3\pi}\frac{(Z\alpha)^2}{n}\left[\frac{19}{13} + K_{n0}\right]$$

for s state.

# Mass polarization correction

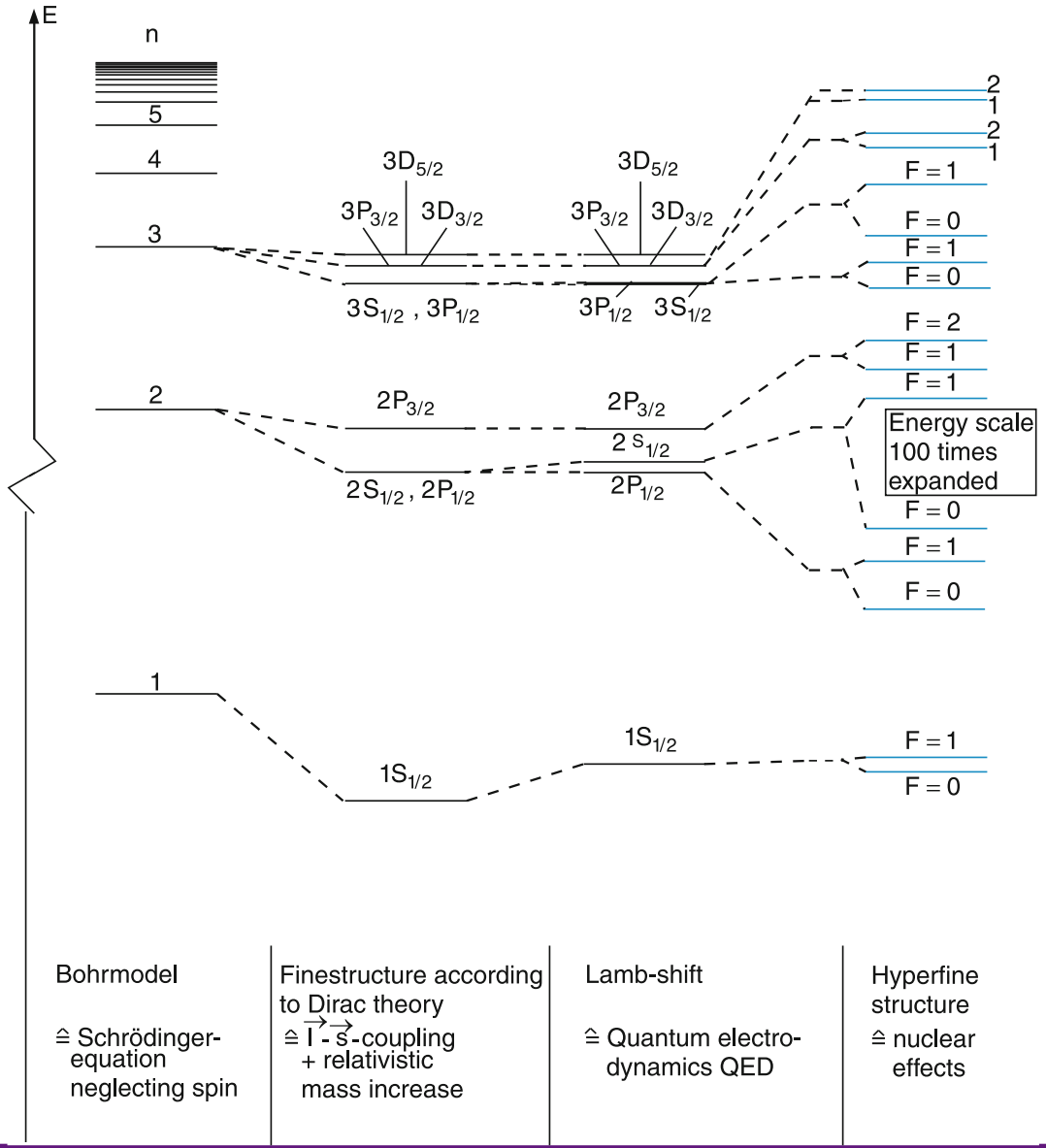
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**The different proton distributions of the isotopes for a given atom or ion will produce unique energy shifts. For multi-electron atoms, the interaction term is known as the mass polarization correction.**

$$\frac{\Delta E}{E_n} = -\frac{4}{5} A^{2/3} \frac{r_0^2}{a_\mu^2} \frac{Z^2}{n} = -\frac{4}{5} A^{2/3} \frac{r_0^2 \mu^2 c^2}{\hbar^2} \frac{(Z\alpha)^2}{n} \qquad l = 0,$$

| Interaction Energy | Fractional Correction | $\Delta E/E_n$ |
|---|---|---|
| Fine structure | $Z^2\alpha^2/n^2$ | $5 \times 10^{-5}\, Z^2/n^2$ |
| Lamb shift | $Z^2\alpha^3/n$ | $4 \times 10^{-7}\, Z^2/n$ |
| Hyperfine structure | $(m_e/m_p)(\mu/m_e)^2 Z\alpha^2/n$ | $3 \times 10^{-8}\, (\mu/m_e)^2 Z/n$ |
| Mass polarization | $A^{2/3}(r_0^2\mu^2c^2/\hbar^2)Z^2\alpha^2/n$ | $5 \times 10^{-10}\, A^{2/3} Z^2/n$ |

# Complete Description of H



# 4.6Zeeman effect

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



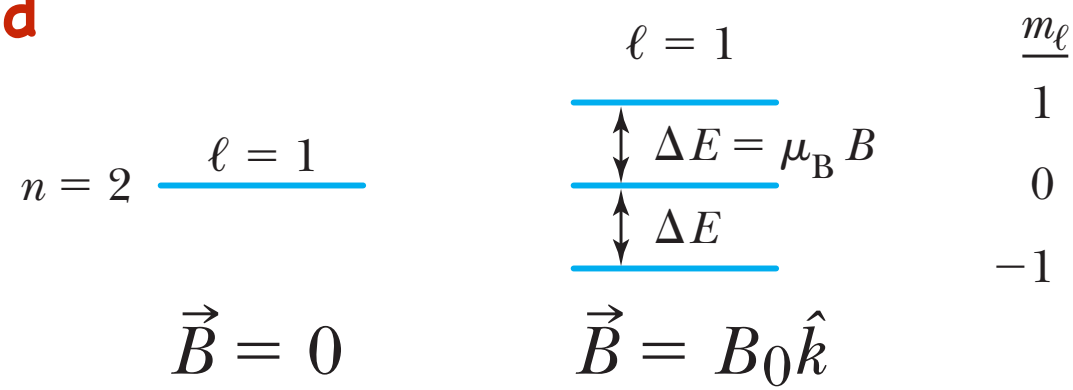
# Zeeman effect

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

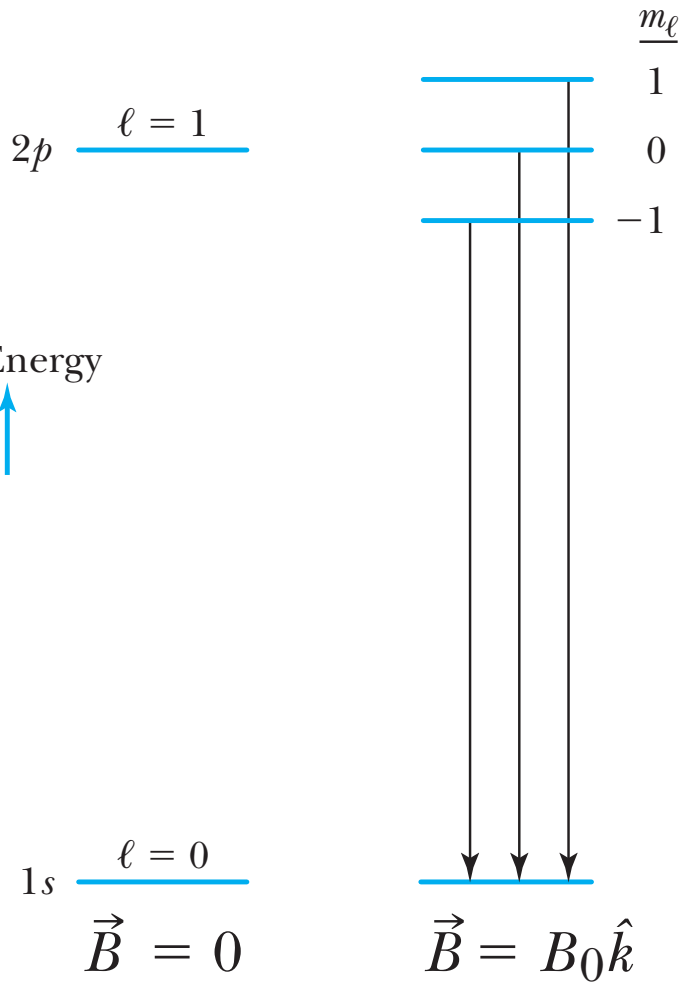


# Zeeman effect

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

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

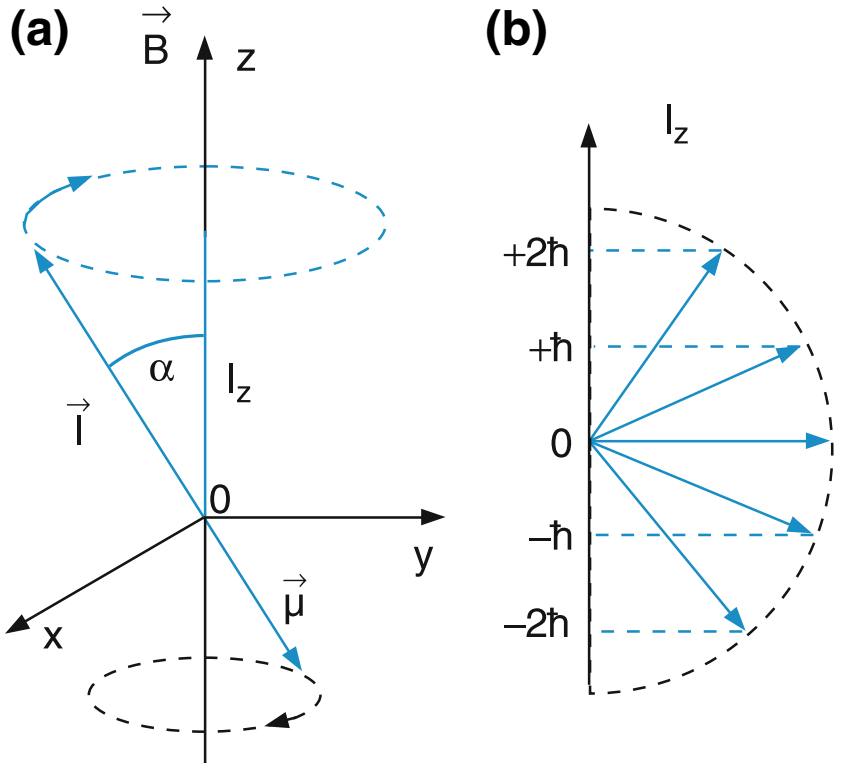
| $m_\ell$ | Energy |
|---|---|
| 1 | $E_0 + \mu_B B$ |
| 0 | $E_0$ |
| −1 | $E_0 - \mu_B B$ |



# Zeeman effect

(a) Classical model of orbital angular momentum precessing around the field axis.

(b) Possible orientations of l and projections m[?] in the quantum mechanical description



# 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.

# Zeeman effect

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

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

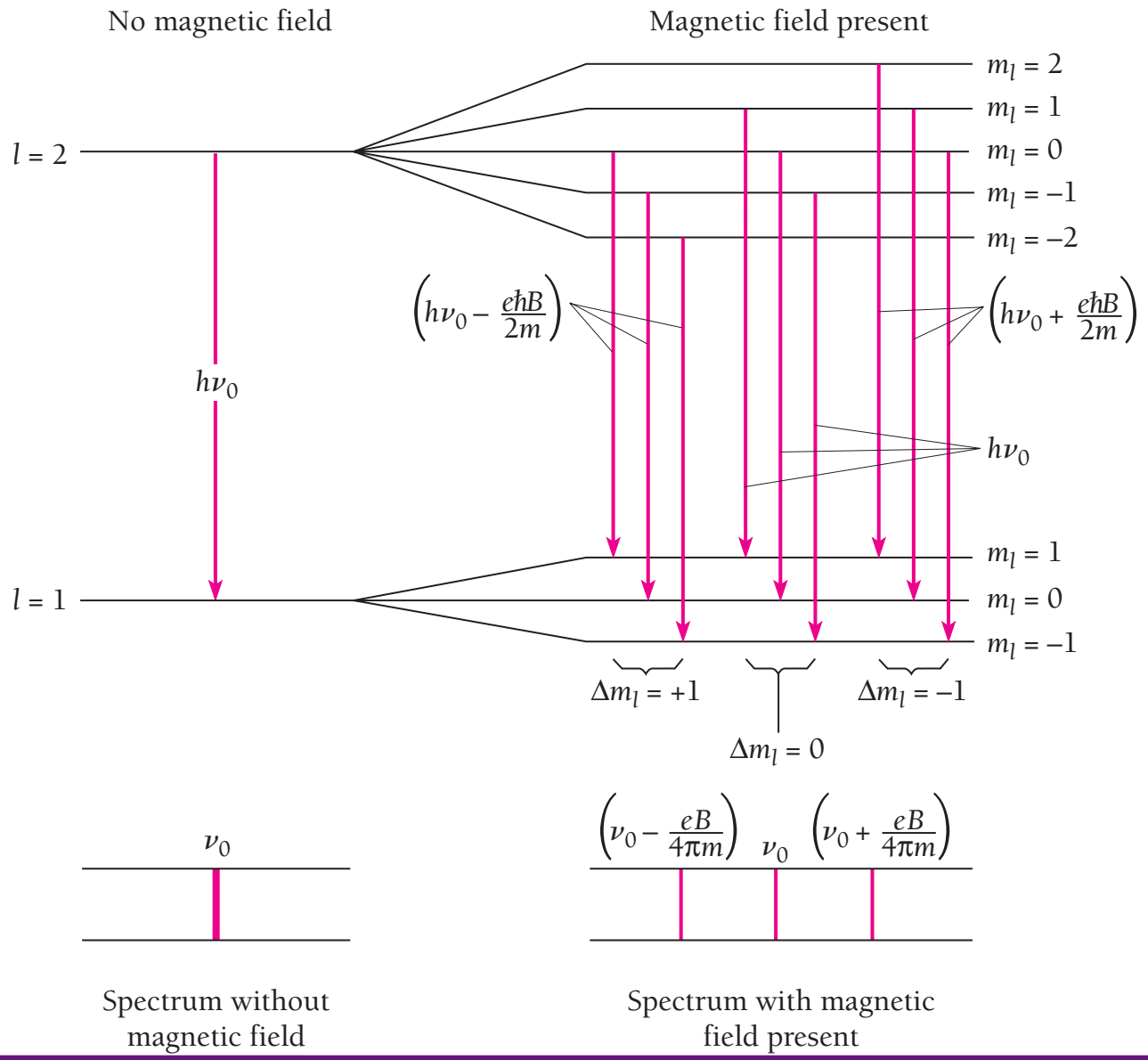
$$\nu_2 = \nu_0$$

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

where, the Larmor frequency is defined as

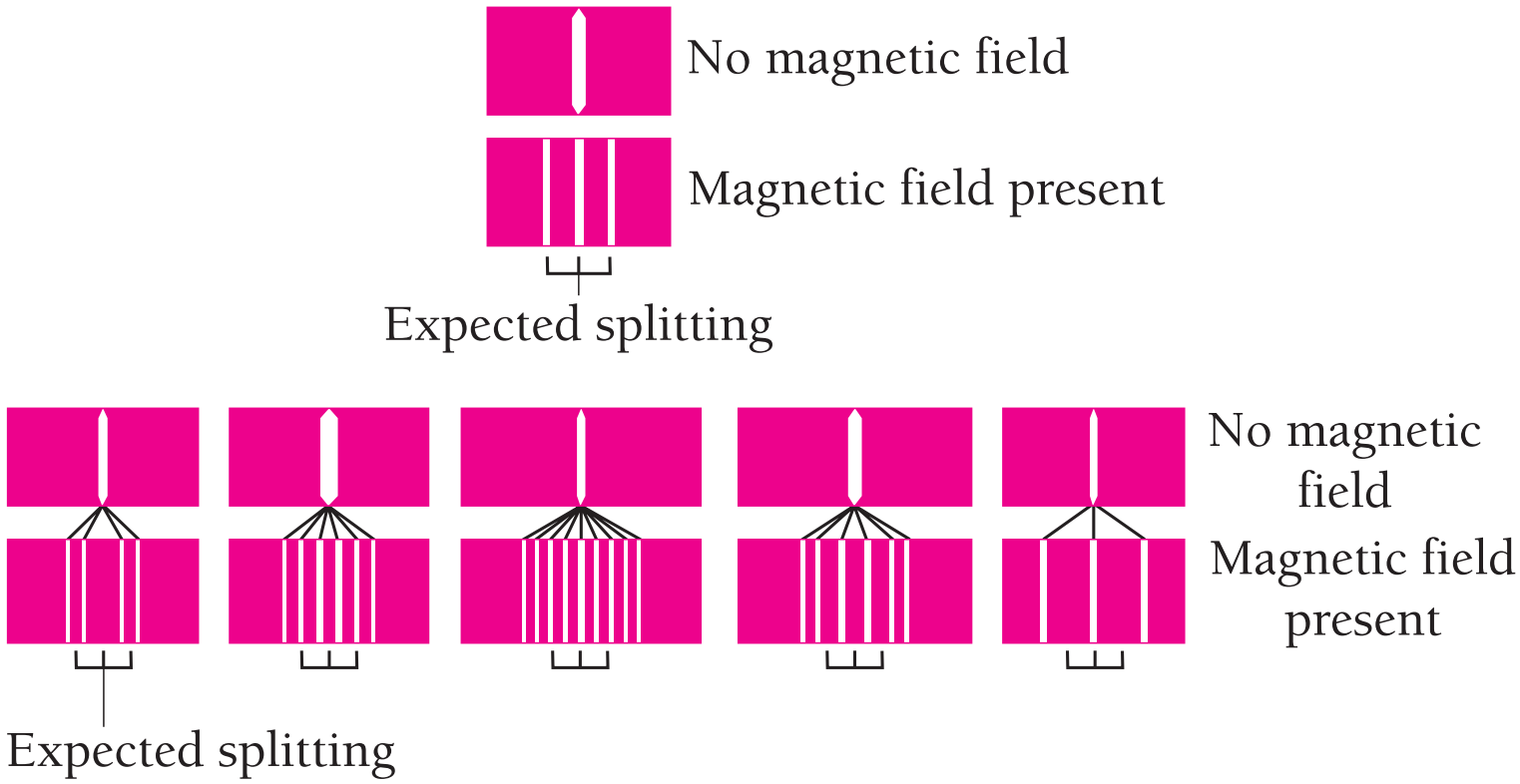
$$\nu_L = \frac{\omega_L}{2\pi} = \frac{e}{4\pi m} B(\mathrm{T}) = 14 B(\mathrm{T})\ \mathrm{GHz}$$

# Zeeman effect



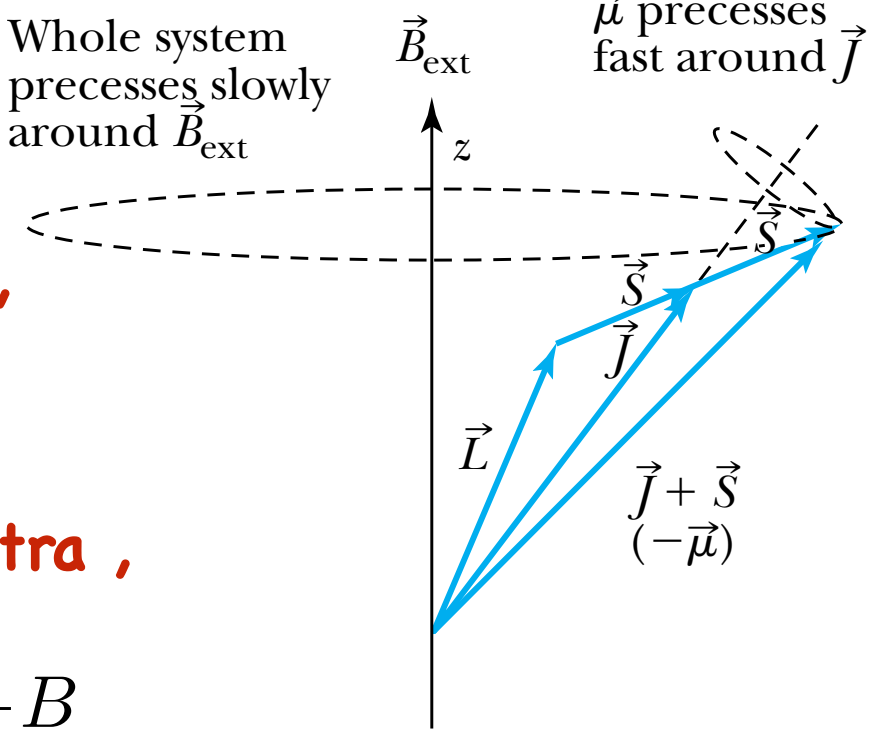
# Anomalous Zeeman effect

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,

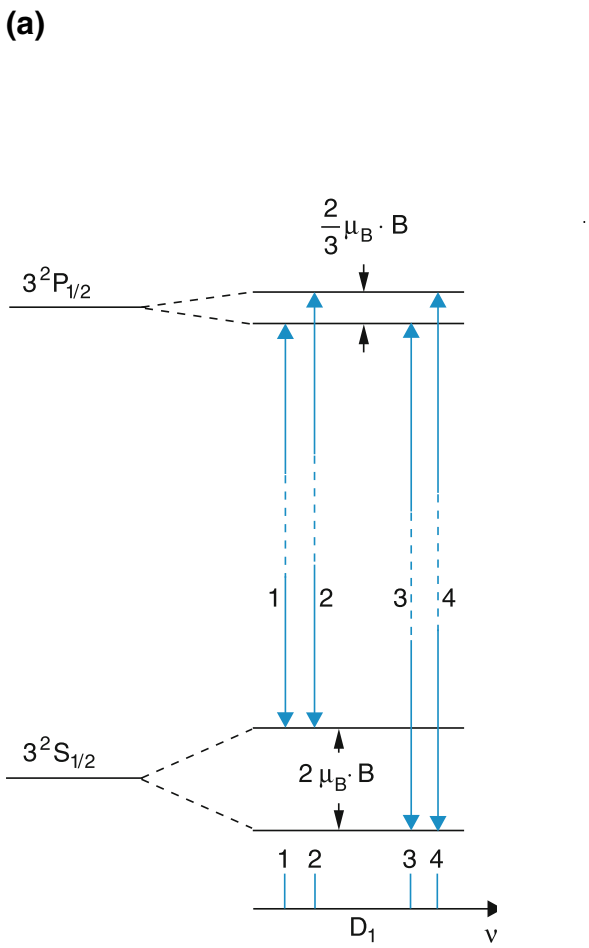
$$E_B = g_j m_j \mu_B B$$

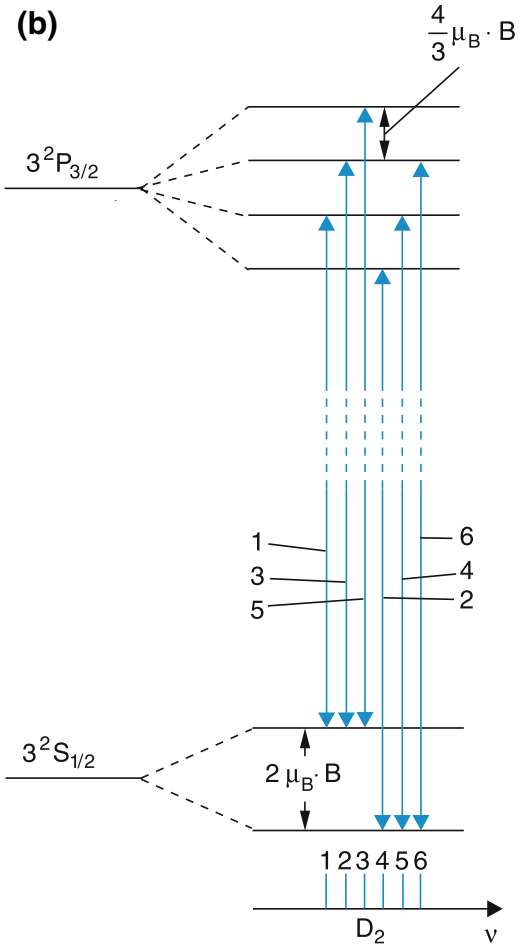
The frequency of splitting spectra ,

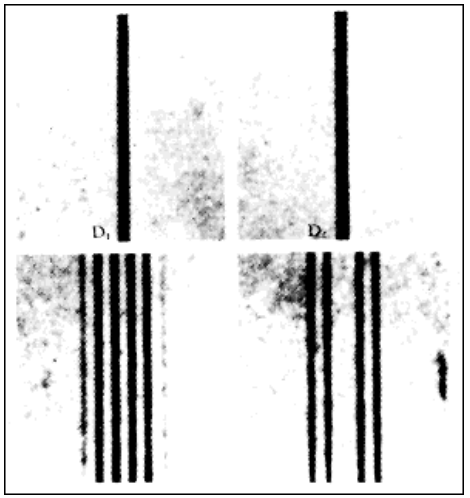
$$\nu = \nu_0 + (m_2 g_2 - m_1 g_1)\frac{e}{4\pi m} B$$

# Anomalous Zeeman effect

## The Zeeman pattern of the two D-lines in the sodium spectrum

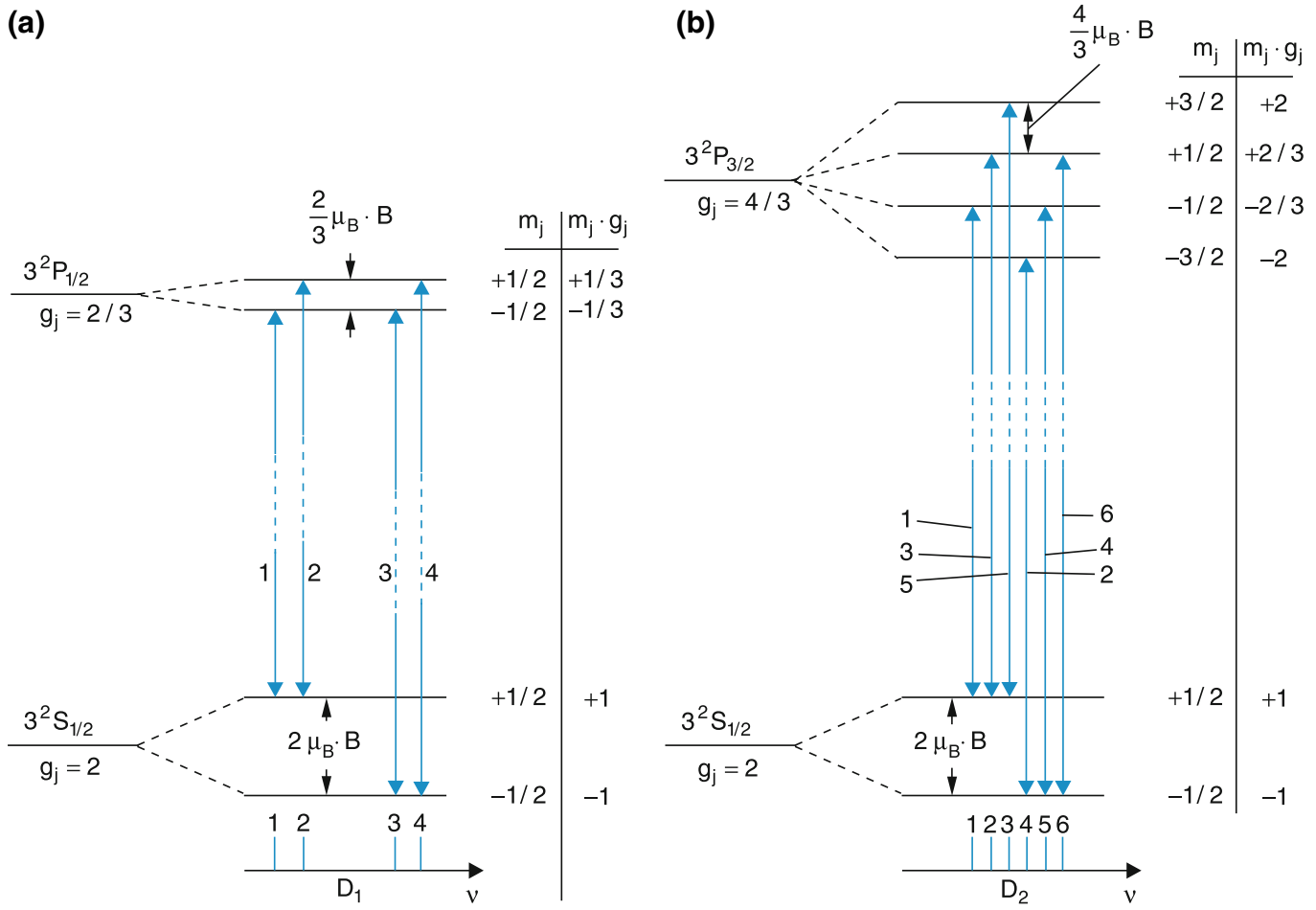


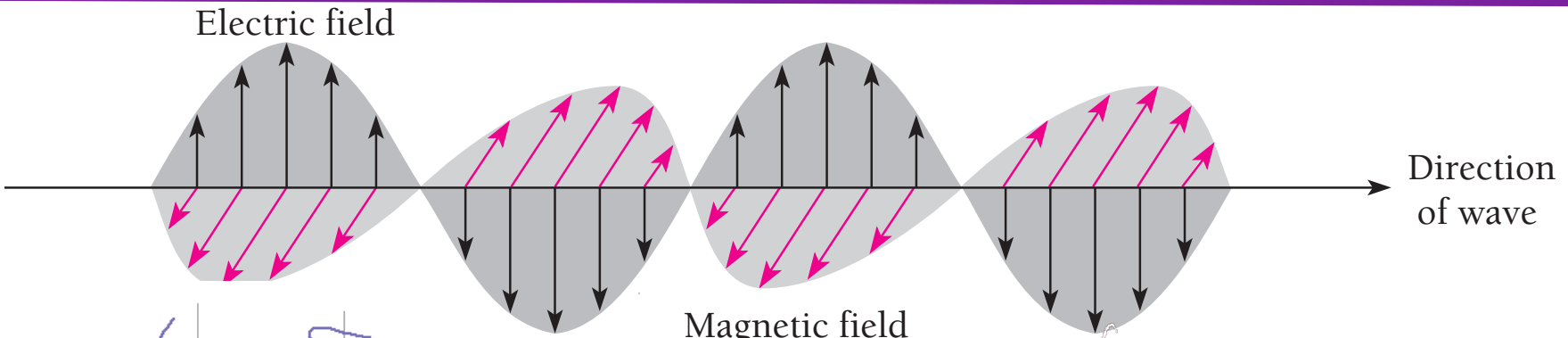



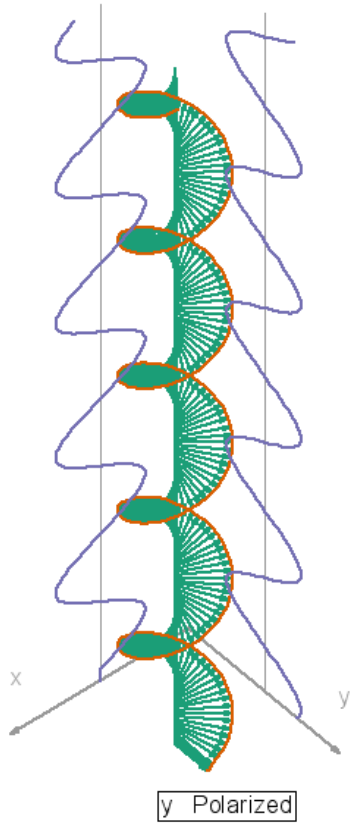
# Anomalous Zeeman effect

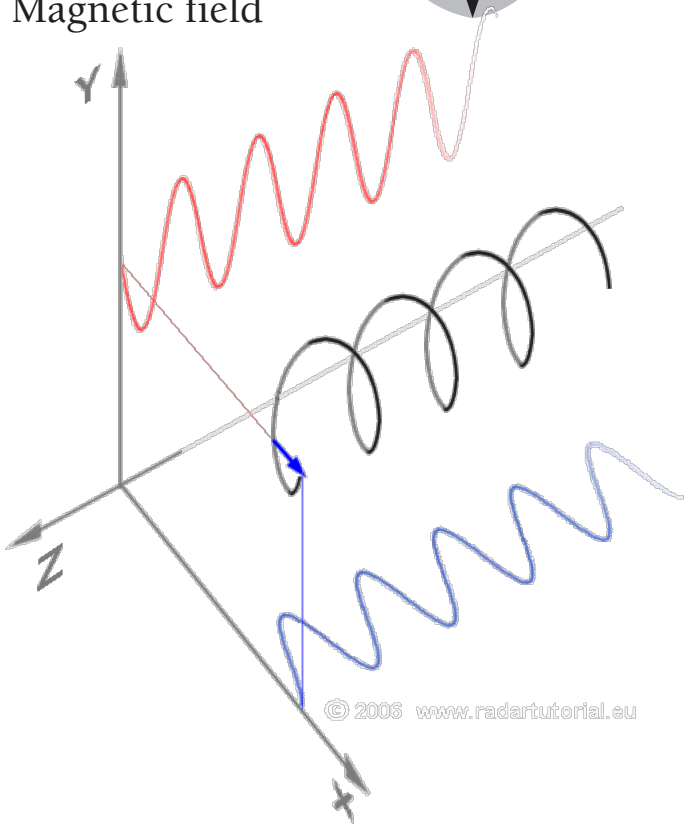
## The Zeeman pattern of the two D-lines in the sodium spectrum



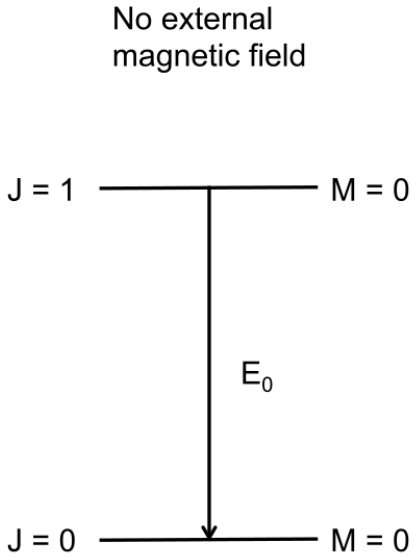
# Polarization of light

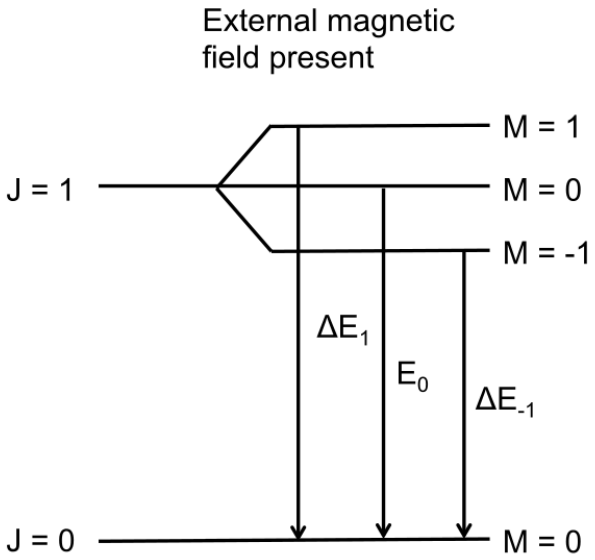


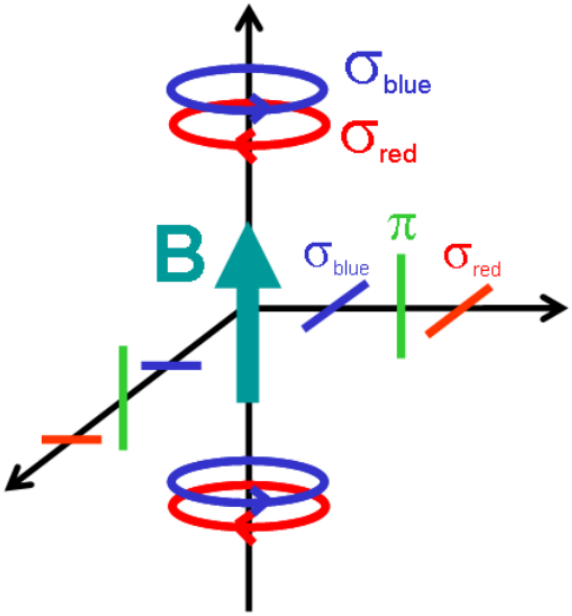



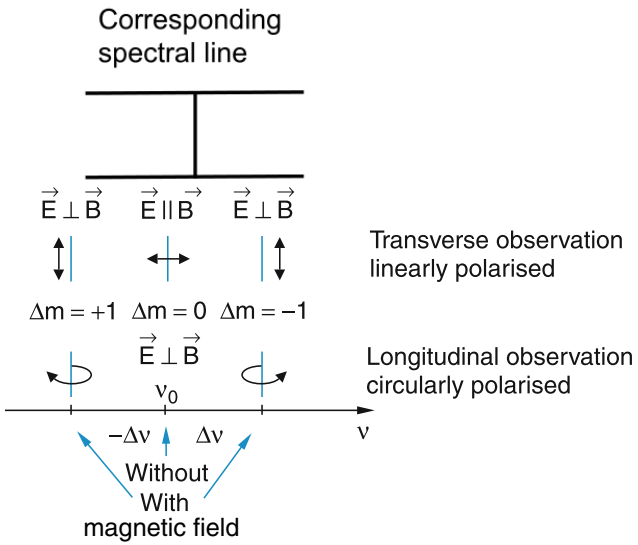



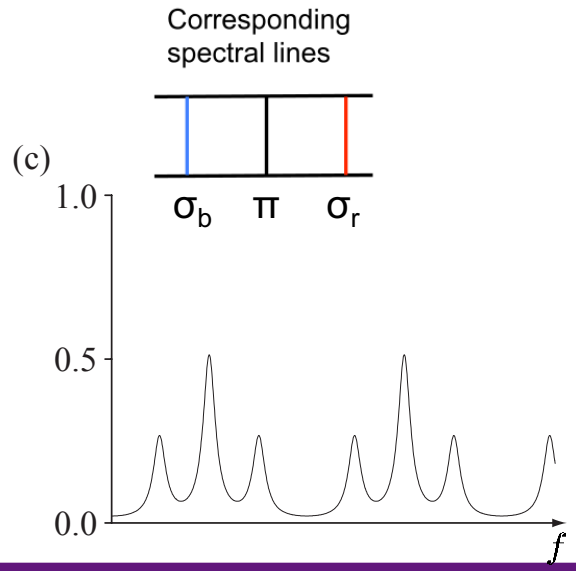
# Polarization of Zeeman effect

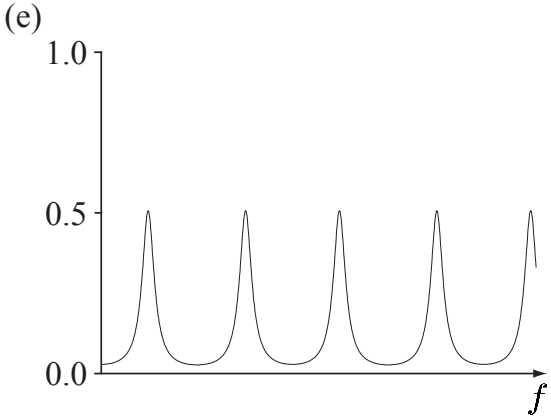


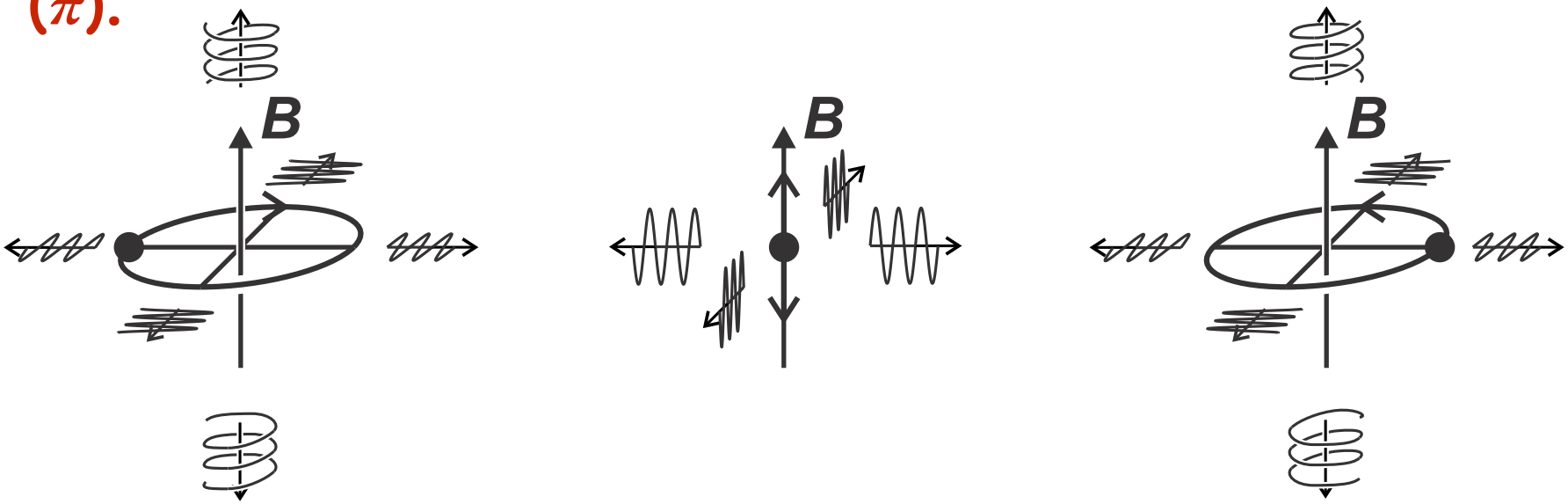



# Polarization of Zeeman effect

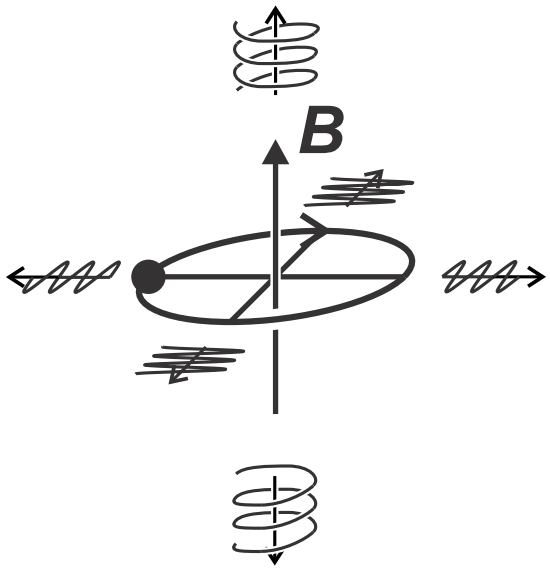
$\Delta M_J=0$ corresponds to an infinitesimal dipole oscillating parallel to the magnetic field. No quanta are emitted in the direction of the magnetic field. The light emitted perpendicular to the magnetic field is linearly polarized ($\pi$).



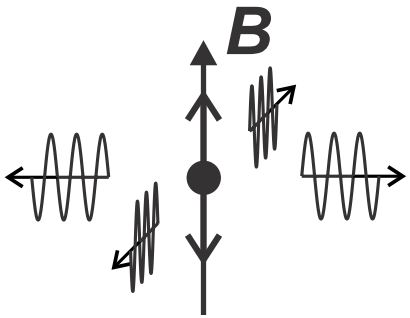

$\sigma^-$ ($\Delta M_J = -1$) $\pi$ ($\Delta M_J = 0$) $\sigma^+$ ($\Delta M_J = +1$)

# Polarization of Zeeman effect

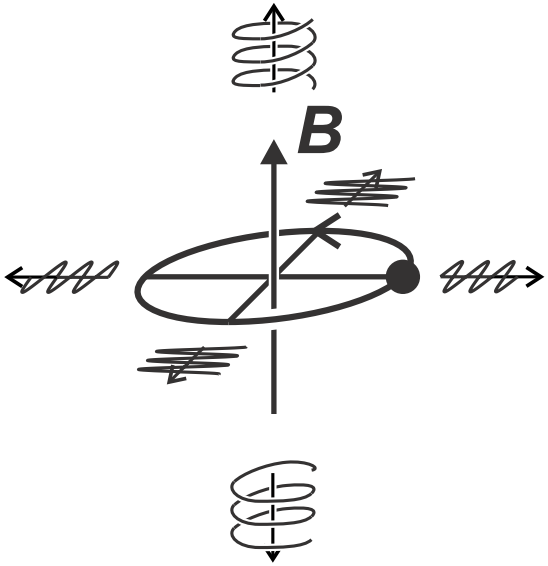
$\Delta M_J=1$ corresponds to two parallel dipoles oscillating with a phase difference of $90^0$ . The superposition of the two dipoles produces a circulating current ($\sigma^+$, $\sigma^-$).




$\sigma^-$ ($\Delta M_J$ = -1)




$\pi$ ($\Delta M_J$ = 0)



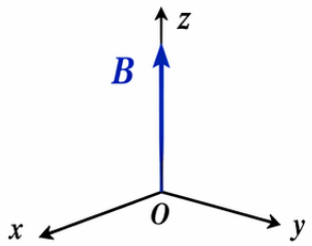

$\sigma^+$ ($\Delta M_J$ = +1)

# Polarization of Zeeman effect

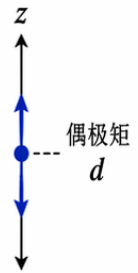
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## ① 偶极模式

$B \parallel z$



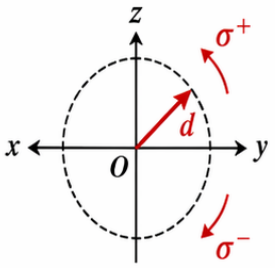

**$\pi$ 分量，$\Delta m = 0$**




$d_\pi(t) = d_0 \hat{z} \cos\omega t$

沿 $z$（$\parallel B$）方向
上下振动

**$\sigma^\pm$ 分量，$\Delta m = \pm 1$**

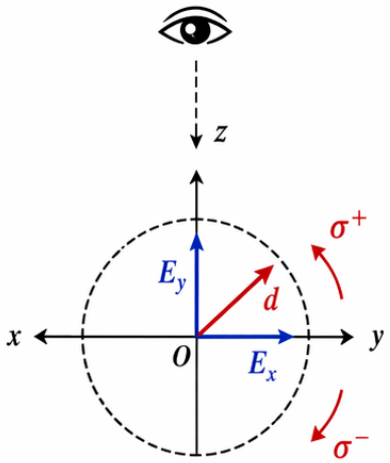



$d_{\sigma^\pm}(t) = d_0(\hat{x}\cos\omega t \pm \hat{y}\sin\omega t)$

在 $xy$ 平面内做圆周旋转
（从 $+z$ 方向看）

## ② 沿磁场方向观察（$n \parallel B$）

观察方向 $n \parallel B \parallel z$（从 $+z$ 方向观察）



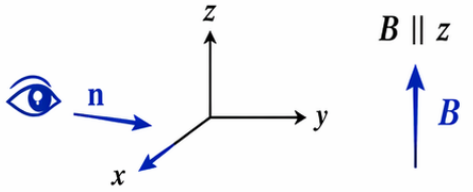

$E_x$、$E_y$ 为两个正交电场分量
等幅，相差 90°

结果：
$\sigma^+$ / $\sigma^-$ → 左/右圆偏振
（从观察者方向看）

**$\pi$ 分量：**
$d \parallel n$（沿 $z$），无横向分量
→ 不可见

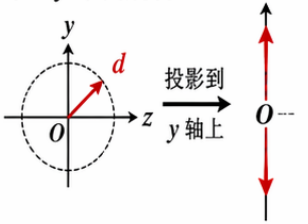
## ③ 垂直磁场方向观察（$n \perp B$）

观察方向 $n \parallel x \perp B$（从 $+x$ 方向观察）




**$\sigma^+$ / $\sigma^-$ 分量：**

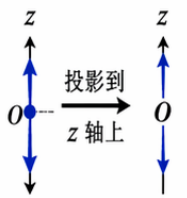
在 $xy$ 平面旋转




投影后仅剩
固定方向
振动
↓
线偏振，
偏振方向
$\perp B$（沿 $y$）

**$\pi$ 分量：**

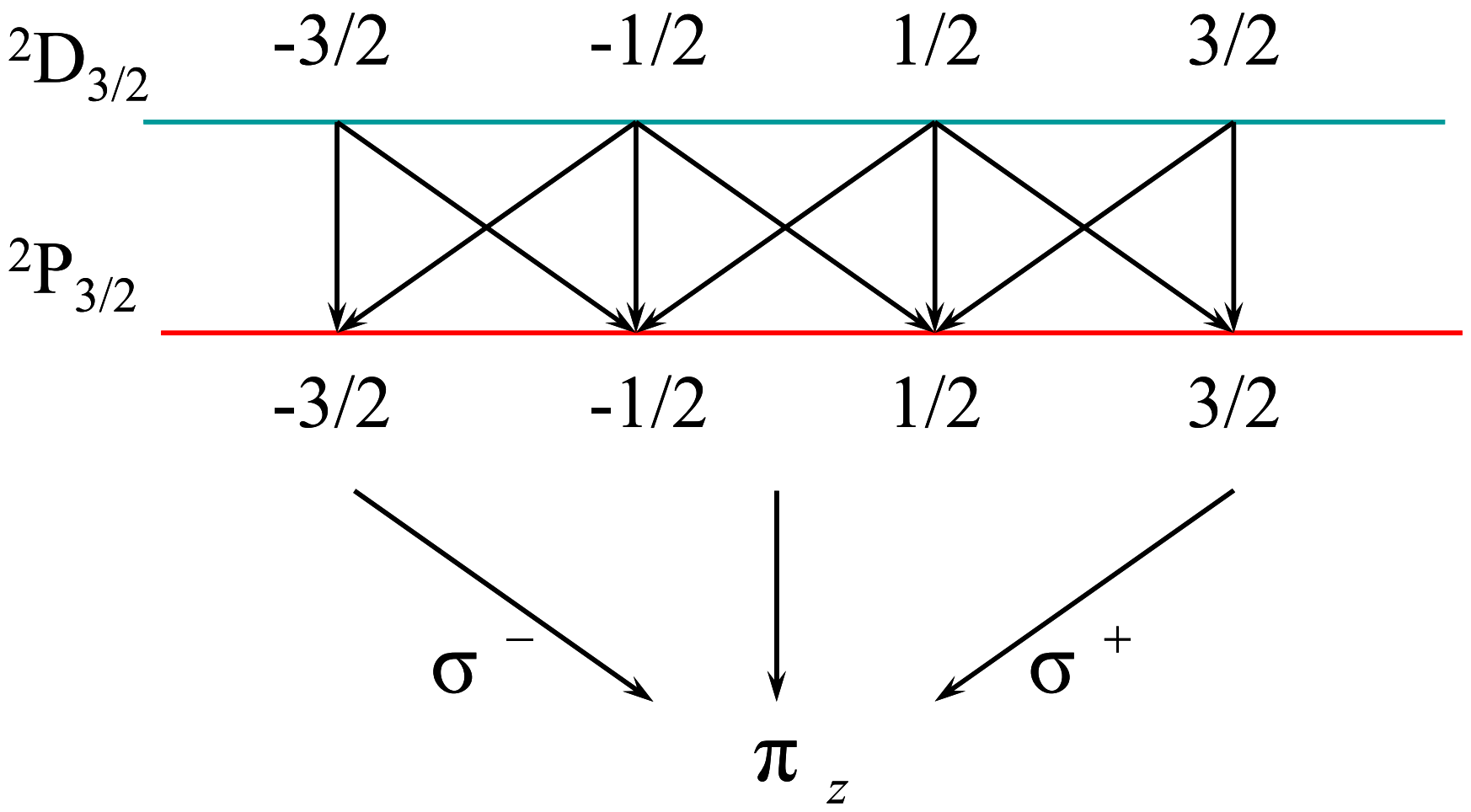
沿 $z$（$\parallel B$）
上下振动




可见
↓
线偏振，
偏振方向
$\parallel B$（沿 $z$）

**总结：** 沿 $B$ 看：$\sigma^\pm$ → 左/右圆偏振，$\pi$ 不可见；垂直 $B$ 看：$\sigma^\pm$ → 线偏振（$\perp B$），$\pi$ → 线偏振（$\parallel B$）。

# Grotrian Diagram



# Paschen-Back effect

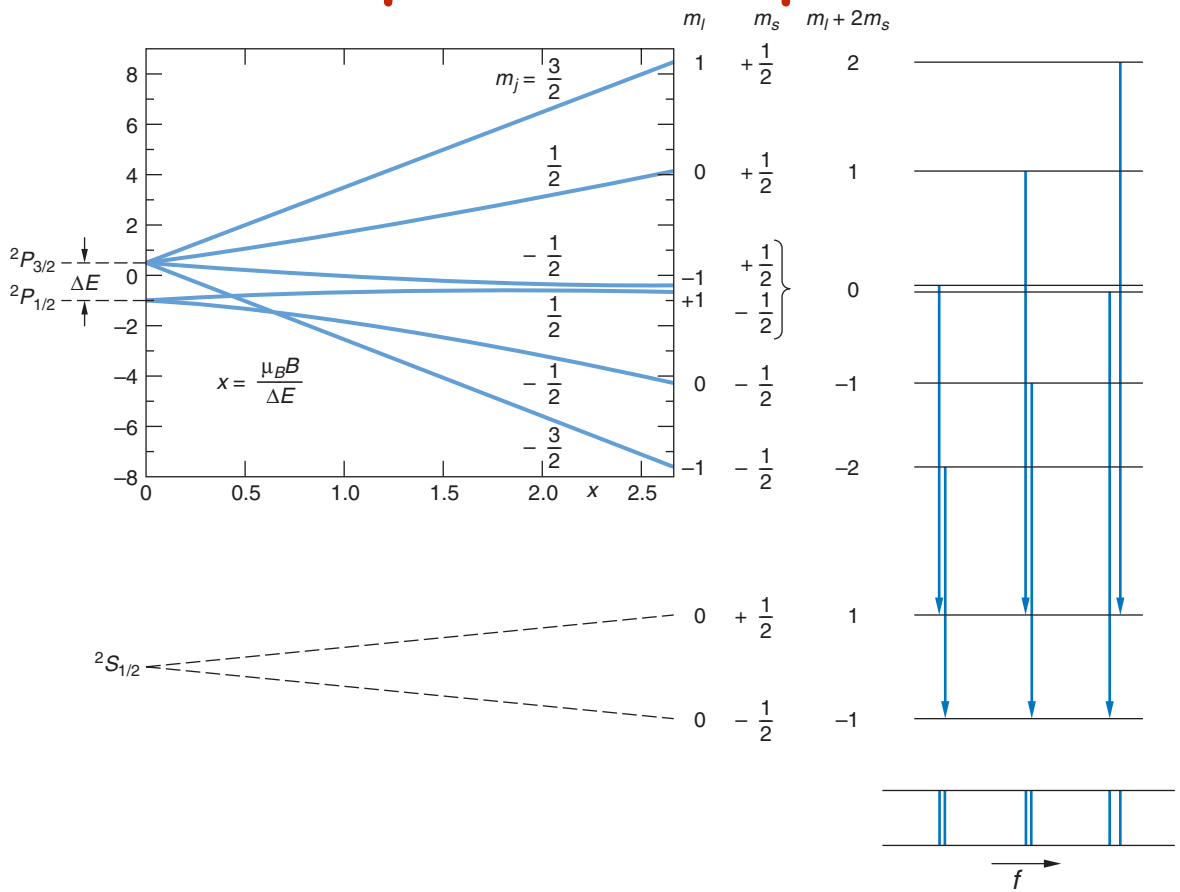
If the external magnetic field is sufficiently large, the Zeeman splitting is greater than the fine-structure splitting. If B is large enough so that we can neglect the fine-structure splitting, the Zeeman splitting is given by

$$\Delta E = (m_\ell + 2m_s)\left(\frac{e\hbar B}{2m_e}\right) = (m_\ell + 2m_s)\mu_B B$$

The splitting is then similar to the normal Zeeman effect and only three lines are observed. This behavior in large magnetic fields is called the Paschen-Back effect after its discoverers, F. Paschen and E. Back.

# Paschen-Back effect

The basic reason for the change in the appearance of the anomalous effect as B increases is that the external magnetic field overpowers the spin-orbit effect.

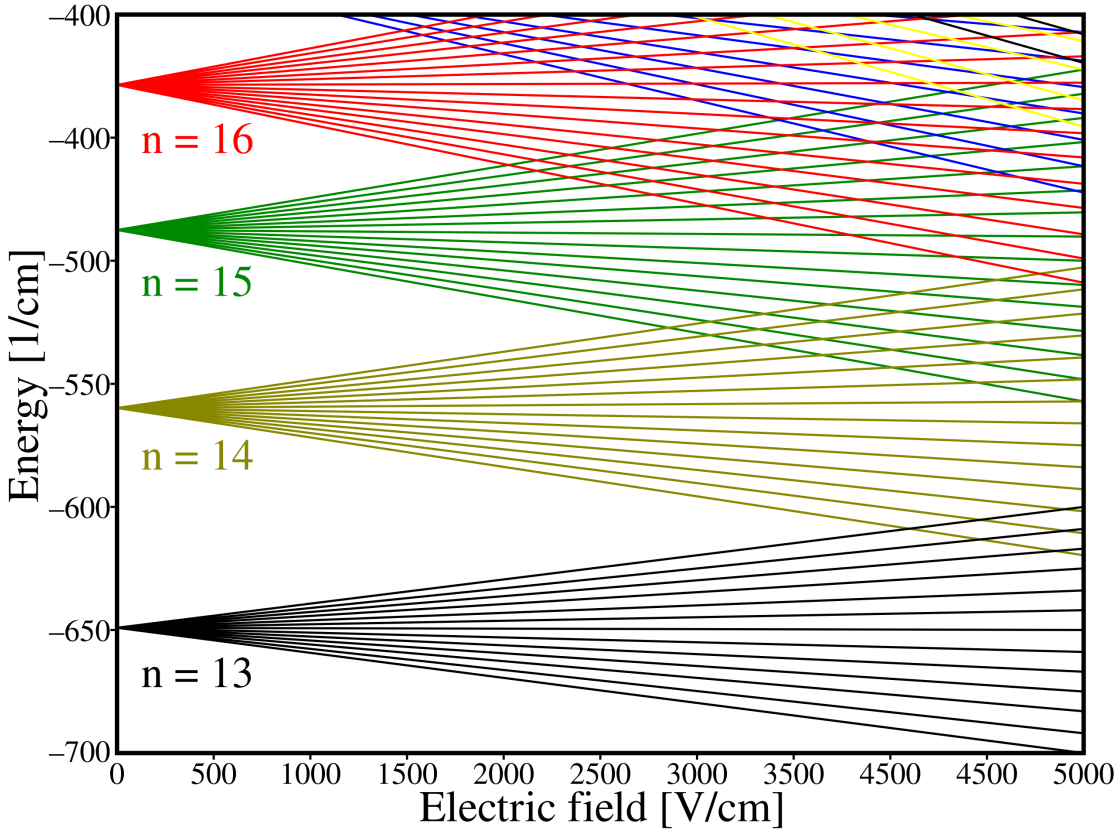


# Stark effect



# Stark effect

The Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field.



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# The Physics of Atoms and Quanta

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

# Exercise class

1. What are the possible quantum numbers for the state n=3 in atomic hydrogen?

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

**Solution:**

| $n$ | $\ell$ | $m_\ell$ |
|---|---|---|
| 4 | 0 | 0 |
| 4 | 1 | $-1, 0, 1$ |
| 4 | 2 | $-2, -1, 0, 1, 2$ |
| 4 | 3 | $-3, -2, -1, 0, 1, 2, 3$ |

2. 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 4.00 T ?

2. 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

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

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

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

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

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

# Exercise class

3. 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.

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

Solution: since

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

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

4. If the spin-orbit splitting of the $3P_{3/2}$ and $3P_{1/2}$ states of sodium is 0.0063 eV, what is the internal magnetic field causing the splitting?

4. 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

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

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

5. Examine the Zeeman spectrum produced by hydrogen atoms initially in the n=2 state when electron spin is taken into account without spin-orbit interaction, assuming the atoms to be in a magnetic field of magnitude B=1.00 T

5. Examine the Zeeman spectrum produced by hydrogen atoms initially in the n?=2 state when electron spin is taken into account without spin-orbit interaction, assuming the atoms to be in a magnetic field of magnitude B=1.00 T

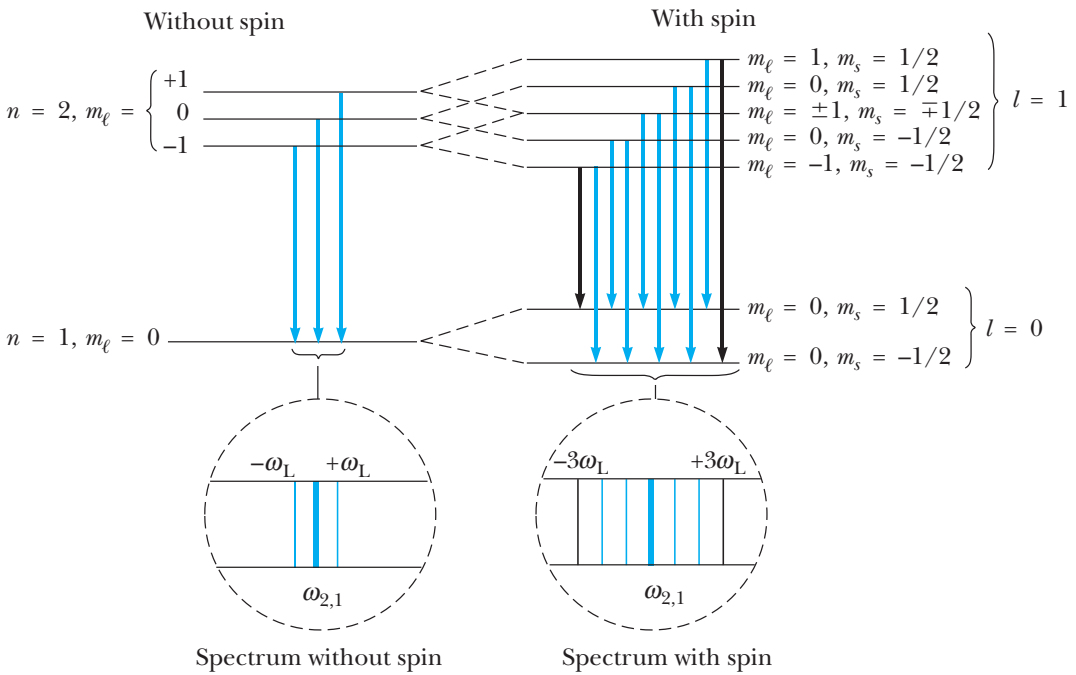
We calculate the magnetic energy

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} = \frac{e}{2m_e} B\{L_z + gS_z\} = \frac{e\hbar}{2m_e} B(m_\ell + gm_s)$$

and

$$\mu_B B = (9.27\times10^{-24}\,\mathrm{J/T})(1.00\,\mathrm{T}) = 9.27\times10^{-24}\,\mathrm{J} = 5.79\times10^{-5}\,\mathrm{eV}$$

5. Examine the Zeeman spectrum produced by hydrogen atoms initially in the n=2 state when electron spin is taken into account without spin-orbit interaction, assuming the atoms to be in a magnetic field of magnitude B=1.00 T



6. An atom with the states $^3F_3$ and $^3G_4$ is placed in a weak magnetic field. Draw the energy levels and indicate the possible allowed transitions between the two states

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