Chapter 11

Atoms and Molecules

Hydrogen Atom

First order theory

$$H = \frac{\vec{P}^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$Z = 1$ hydrogen atom

⇒ the problem is exactly soluable.

$\psi_{n,\ell,m_\ell}(\vec{r})$ simultaneous eigenstate of H, $\vec{L}^2$, L_z

with eigenvalues $E_n = -\frac{1}{2} m_e c^2 (Z\alpha)^2 \frac{1}{n^2}$, $\ell(\ell+1)\hbar^2$, $m_\ell \hbar$ respectively

$$\downarrow$$

$$[H, \vec{L}^2] = 0$$

$$[H, L_z] = 0$$

$$[\vec{L}^2, L_z] = 0$$

Remarks.

This is a central force problem

In a central force problem $E_{n,\ell}$

$\downarrow$

energy is a function of n and ℓ

only for Coulomb potential E is a function of n only.

$n > \ell$, $m_\ell = -\ell, -\ell+1, \cdots, \ell$

number of degeneracy

$$= \sum_{\ell=0}^{n} (2\ell+1) = n^2$$

Example $n = 3$, $\begin{array}{ccc} \ell = 0, & 1, & 2 \\ \downarrow & \downarrow & \\ 1 & 3 & 5 \end{array}$ $1+3+5 = 9 = 3^2$

Corrections .

Reduced mass effect

2 body problem ⟶ 1 body problem

$m_e \longrightarrow \underset{\downarrow}{\mu}$ reduced mass

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M_p} \Rightarrow \mu = \frac{{}_e M_p}{M_p + m_e} \cong m_e \left(1 - \frac{m_e}{M_p}\right)$$

$$= 1 - 5.4 \cdot 10^{-4}$$

The correction can be taken care of by $m_e \to \mu$

There is another correction to the kinetic energy
↓
relativistic correction.

$$K = \sqrt{\vec{p}^2 c^2 + (m_e c^2)^2} - m_e c^2$$

$$\simeq \frac{\vec{p}^2}{2m_e} - \frac{1}{8}\underset{\downarrow}{\frac{(\vec{p}^2)^2}{m_e^3 c^2}} + \cdots$$

$$H_1 = -\frac{1}{8}\frac{\langle \vec{p}^2 \rangle^2}{m^3 c^2}$$

$$H_0 = \underset{\downarrow}{\frac{\vec{p}^2}{2\mu}} + H_1 - \frac{Ze^2}{r} = H_0 + H_1$$

reduced mass

Existence of fine structure
↓
the existence of electron spin.

$\Rightarrow$ spin - orbit interaction.

$$H_2 = \frac{1}{2m^2c^2}\frac{Ze^2}{r^3}\vec{S}\cdot\vec{L}$$

$$\Rightarrow H = H_0 + H_1 + H_2$$

A rough estimate of H_1 and H_2 can be made using the Bohr model

$\Rightarrow$ $\underline{H_1 \; , \; H_2 \;\; << \;\; H_0}$

by a order $\sim (0.53 \cdot 10^{-4}) Z^2$ for H_1

H_2 is in the same order of magnitude

$\Rightarrow$ perturbation theory (method) can be used to calculate the correction. (A brief discussion of the perturbation method is given in Appendix A)

Look at the spin-orbit interaction.

$$\psi_{n,\ell,m_\ell}(\vec{r}) \longrightarrow \psi_{n,\ell,m_\ell}(\vec{r}) \underset{\substack{\downarrow \\ \text{spin wave function}}}{\chi_{m_s}}$$

With $H = H_0$ only

ψ_{n,ℓ,m_ℓ,m_s} $\rightarrow$ are simultaneous eigenfunction of $H_0, \vec{L}^2, L_z, \vec{S}^2, S_z$

Any linear combinations of ψ_{n,ℓ,m_ℓ,m_s} with the same n are still eigenfunction of H_0 with eigenvalue E_n.

One set of these linear combinations are

ψ_{n,ℓ,j,m_j} which are simultaneous eigenstate of $H_0, \vec{L}^2, \vec{J}^2, \vec{S}^2, J_z$ respectively

Number of state ψ_{n,ℓ,m_ℓ,m_s} with same n, ℓ

$$\underset{\substack{\downarrow \\ m_s \text{ can} \\ \text{be } \pm\frac{1}{2}}}{2} \, (\underset{\substack{\downarrow \\ \text{different } m_\ell}}{2\ell+1})$$

Number of ψ_{n,ℓ,j,m_j} with same n, ℓ

j can be $\ell + \frac{1}{2}$ $\quad m_j$ has $\underline{\qquad}$ $2j+1$ state

$2(\ell+\frac{1}{2})+1$

$\ell - \frac{1}{2}$ $\quad 2(\ell-\frac{1}{2})+1$

$\Rightarrow \quad 2\ell + 2 + 2\ell = 2(2\ell+1)$ state

$\{\psi_{n,\ell,j,m_j}\}$ are rearrangement of $\{\psi_{n,\ell,m_\ell,m_s}\}$

The reason for choosing $\{\psi_{n,\ell,j,m_j}\}$ to calculate the energy shift.

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

$$\vec{J}^2 = \vec{L}^2 + 2\vec{L}\cdot\vec{S} + \vec{S}^2$$

$$\vec{S}\cdot\vec{L} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

ψ_{n,ℓ,j,m_j} are eigenstate of $H_0 + H_1 + H_2$

$\Rightarrow$ $j = \ell + \frac{1}{2}$, $j = \ell - \frac{1}{2}$ has slightly different eigen

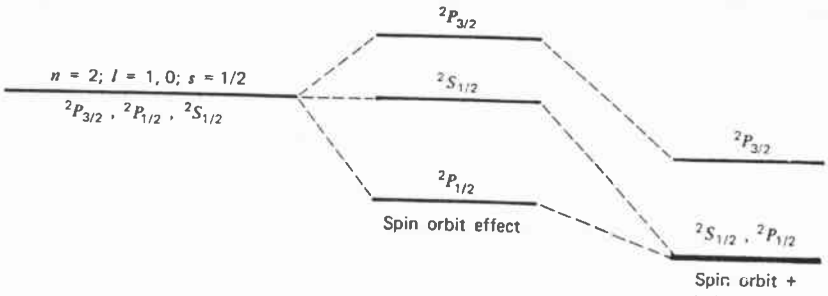
$\Rightarrow$ fine structure

Notation $\underset{\underset{n=2}{\downarrow}}{2}\, S_{1/2} \rightarrow j = \frac{1}{2}$

$n = 2, \quad \ell = 0, \quad j = \frac{1}{2}$

ℓ	0	1	2	...
	s	p	d	....

In the following figure, we present the splitting of the $n = 2$ level



Splitting of the $n = 2$ levels by (1) the spin-orbit coupling (which leaves the S state unaffected) and (2) the relativistic effect. The final degeneracy of the $^2S_{1/2}$ and $^2P_{1/2}$ states is actually lifted by quantum electrodynamic effects. The tiny upward shift of the $^2S_{1/2}$ state is called the Lamb shift.

Note: the $2P_{1/2}$ and $2S_{1/2}$ degeneracy

More careful discussion, using the relativistic Dirac equation does not alter this result.

Lamb shift

Lamb and Retherford 1947
↓
experimentally discovered that there is a tiny splitting of the two levels.

theoretical calculation based on quantum electrodynamics.
~ 1975

Theoretical
1057.916 ± 0.010 MHz
1057.864 ± 0.014 MHz

Experimental
1057.893 ± 0.020 MHz
1057.862 ± 0.020 MHz

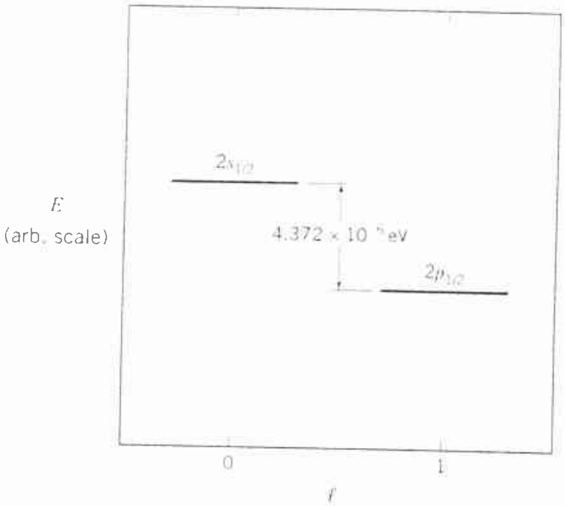


FIGURE 8-20 The Lamb shift in hydrogen. The spin–orbital interaction gives corrections to the energy levels in the hydrogen atom that depend only on the quantum numbers n and j. The $2s_{1/2}$ and the $2p_{1/2}$ states of hydrogen have the same energy after applying this correction. The gyromagnetic factor (g) of the electron is slightly greater than 2 so that a component of spin angular momentum of $g\hbar/2$ contributes more to the electron magnetic moment than a component of orbital angular momentum $\hbar$. This causes the $2s_{1/2}$ state to have a slightly higher energy than the $2p_{1/2}$ state. The factor g can be calculated to many decimal places so that the measurement of the energy difference of the $2s_{1/2}$ and $2p_{1/2}$ states provides a precision test of quantum electrodynamics.

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編號： 11-6
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It is very important that this problem should receive further experimental and theoretical attention. When an accuracy of comparison of 0.1 megacycle per second has been reached, it will mean that the energy separations of the $2s$ and $2p$ states of hydrogen agree with theory to a precision of a few parts in 10^9 of their binding energy or that the exponent in Coulomb's law of force is 2 with comparable accuracy.

Willis E. Lamb, Jr.

Now put the hydrogen atom in a weak magnetic field

So far, we are doing the perturbation theory to first order in H_1 and H_2

We have studied the problem without an external magnetic field.

With an external magnetic field $\vec{B}$, there is an additional term to the Hamiltonian

$$H_3 = \frac{e}{2mc}(\underset{\downarrow}{\vec{L}+2\vec{S}})\cdot\vec{B}$$

lead to the anomalous Zeeman effect

Magnetic field is "weak"

$H_3 \ll H_2$

In this case $\underset{\downarrow}{H} = \frac{p^2}{2\mu} - \frac{Ze^2}{r} + H_1 + H_2$

unperturbed Hamiltonian

H_3 is treated as perturbation.

Straightforward perturbation calculation ⇒ figures given in next page

↓

give a complete account for the Zeeman effect.

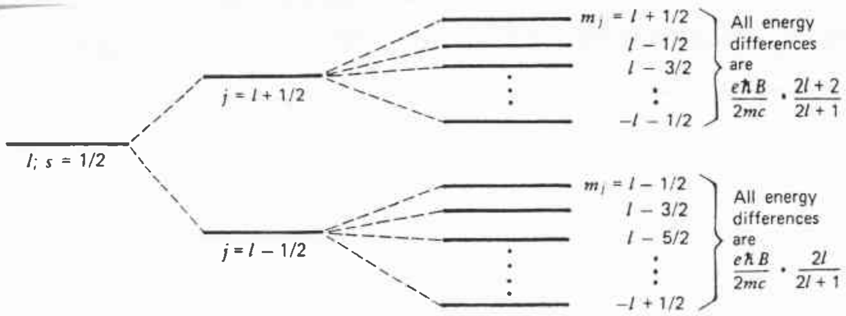


Figure 17-2. General representation of anomalous Zeeman effect.

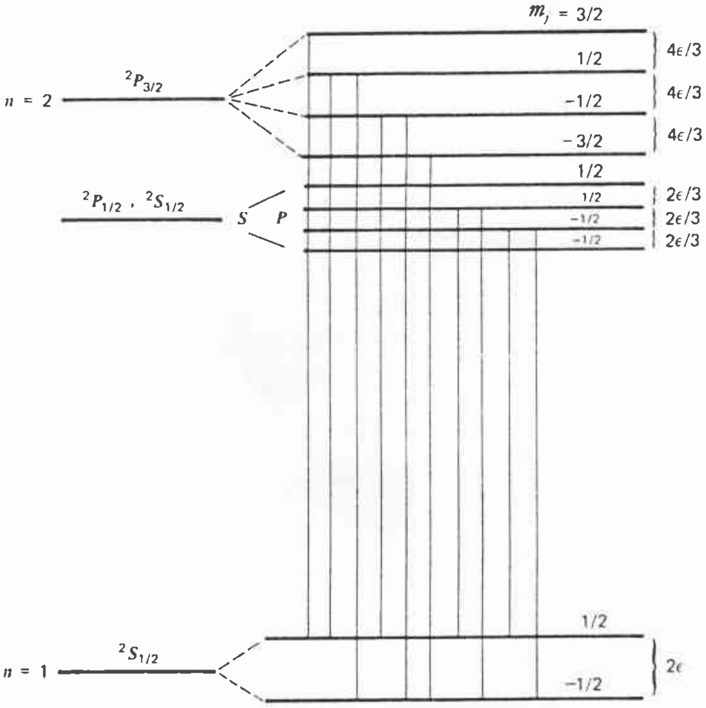


Figure 17-3. Zeeman effect in hydrogen, ϵ represents the energy $e\hbar B/2mc$. The transitions for which $l = 1$, $\Delta m = 1, 0, -1$ are drawn in the figure. The location of the unperturbed states is given by Fig. 17-1.

Hyperfine structure

Proton has spin

$$\vec{\mu}_p = \frac{e g_p}{2M_p c} \underset{\substack{\downarrow \\ \text{proton spin}}}{\vec{I}} \qquad g_p = 5.56$$

Note, Since $M_p \gg m_e$

$$\downarrow$$

$$\mu_p \ll \mu_e$$

The magnetic moment of proton will produce a magnetic field around it.

The $\underset{\substack{\downarrow \\ \propto \vec{I}}}{\text{field}}$ will interact with the magnetic moment of $\underset{\propto \vec{S}}{\text{electron}}$

Interaction Hamiltonian $\propto \vec{S}\cdot\vec{I}$

(similar to $\vec{L}\cdot\vec{S}$ coupling with $\vec{L}$ replaced by $\vec{I}$)

Define $\vec{F} = \vec{S} + \vec{I}$

Since both proton and electron have spin $\frac{1}{2}$

$F = 0$ or 1

⇒ The interaction Hamiltonian will lead to an energy difference between $F=1$ (excited state) and $F=0$ (ground state) ⇒ $\Delta E = \frac{4}{3}\, 5.56 \,\frac{1}{1840}\,\frac{1}{(137)^4}\,(m_e c^2)$

$= h\nu = h\frac{c}{\lambda}$ ⇒ $\lambda = 21$ cm

From an analysis of the intensity of the 21 cm radiation received ⇒ astronomers can learn
the density distribution of neutral hydrogen in interstellar space
the motion and temperature of gas clouds containing hydrogen.

Real Hydrogen Atom

Reduced Mass Effect

$$\mu = \frac{m_e m_p}{m_e + m_p} \longrightarrow \mu$$

deuterium

Without $\vec{B}$ field

Total Angular Momentum

With $\vec{B}$ field

Zeeman effect

Dirac Equation

Hyperfine

Lamb - shift

g - 2

The Hydrogen Atom.

A hydrogen atom consists of a proton and an electron held together by the electrostatic attraction between them

$$E = \frac{\vec{P}_e^{\,2}}{2m_e} + \frac{\vec{P}_p^{\,2}}{2m_p} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

($Z = 1$ for hydrogen
$Z \rightarrow$ nuclear charge
for hydrogen-like atom)

$$r = |\vec{r}_e - \vec{r}_p|$$

$$\Rightarrow \quad H = -\frac{\hbar^2}{2m}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + \underset{\displaystyle -\frac{Ze^2}{4\pi\epsilon_0 r}}{\underset{\parallel}{V(r)}}$$

Define
$$\vec{R} = \frac{m_e\vec{r}_e + m_p\vec{r}_p}{m_e + m_p} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

$$\vec{r} = \vec{r}_e - \vec{r}_p = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\frac{\partial\psi}{\partial x_e} = \frac{\partial\psi}{\partial X}\frac{\partial X}{\partial x_e} + \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial x_e}$$

$$= \frac{m_e}{m_e + m_p}\frac{\partial\psi}{\partial X} + \frac{\partial\psi}{\partial x}$$

Similar expression for $\frac{\partial\psi}{\partial x_p}, \frac{\partial\psi}{\partial y_e}, \frac{\partial\psi}{\partial z_e}, \frac{\partial\psi}{\partial y_e}, \cdots$ can be obtained.

Define
$$\underset{\underset{\displaystyle \mu}{\parallel}}{m} = \frac{m_e m_p}{m_e + m_p} \quad \Rightarrow \quad \nabla_e = \frac{m}{m_p}\nabla_R + \nabla$$

↳ reduced mass

$$\nabla_p = \frac{m}{m_e}\nabla_R - \nabla$$

↳ with respect to $\vec{r}$

$$H = -\frac{\hbar^2}{2m_e}\left(\frac{m}{m_p}\nabla_R + \nabla\right)^2 - \frac{\hbar^2}{2m}\left(\frac{m}{m_e}\nabla_R - \nabla\right)^2 + V(r)$$

$$= -\frac{\hbar^2}{2m_e}\left[\frac{m^2}{m_p^2}\nabla_R^2 + \frac{m}{m_p}(\nabla_R\nabla + \nabla\nabla_R) + \nabla^2\right]$$
$$- \frac{\hbar^2}{2m_p}\left[\frac{m^2}{m_e^2}\nabla_R^2 - \frac{m}{m_e}(\nabla_R\nabla + \nabla\nabla_R) + \nabla^2\right] + V(r)$$

$$\Rightarrow \quad H = -\frac{\hbar^2}{2(m_e + m_p)}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The time independent Schrodinger equation becomes

$$\left(-\frac{\hbar^2}{2(m_e + m_p)}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(\vec{r}, \vec{R}) = \phi(\vec{R})\,u(\vec{r})$$

Again carry out the seperation of variable.

Ansatz $\psi(\vec{r}, \vec{R}) = \phi(\vec{R})\, u(\vec{r})$

Substitute into above equation

$$\Rightarrow \quad \frac{-\hbar^2}{2(m_e+m_p)}\, u\, \nabla_R^2 \phi - \frac{\hbar^2}{2m}\, \phi\, \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} u\phi = E_t\, u\phi$$

Divide by $u\phi$

$$-\frac{\hbar^2}{2(m_e+m_p)\phi} \nabla_R^2 \phi - \frac{\hbar^2}{2mu} \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} = E_t$$

We group together the r and the R dependent terms and equal them to the same constant

$$\frac{-\hbar^2}{2(m_e+m_p)\phi} \nabla_R^2 \phi = E_c = \frac{\hbar^2}{2mu} \nabla^2 u + \frac{Ze^2}{4\pi\epsilon_0 r} + E_t$$

Define $E = E_t - E_c$

$$\Rightarrow \quad -\frac{\hbar^2}{2(m_e+m_p)} \nabla_R^2 \phi = E_c\, \phi$$

$\downarrow$

the solution is a plane wave
describing the motion of the center of mass
this part is of no interest to us

$$-\frac{\hbar^2}{2m} \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} u = E u$$

$\downarrow$

Schrodinger equation of a particle
moving in a fixed central potential
except that the electron mass have
been replaced by the reduced mass

⇒ This seperation is sometimes referred to as the reduction of a two-body problem to a single-one-body problem. [We have carried out similar procedure in Chapter 1]

We follow "Basic Quantum Mechanics" by K. Ziock P. 73-77]

$$\left[\; m = \frac{m_e m_p}{m_e + m_p} \sim m_e \quad \text{since } m_p \sim 1836\, m_e \;\right]$$

Normal Zeeman Effect

External Magnetic Field

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

$\vec{\mu}$ magnetic dipole moment

$\vec{\mu}$ using classical model

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

$$\mu = iA$$

$$i = \frac{e}{T} = e\,\frac{v}{2\pi r}$$

$$\mu = \frac{ev}{2\pi r}\pi r^2 = \frac{1}{2}evr$$

$$L = \underset{m_e}{\underset{\shortparallel}{\mu_e}}\, vr$$

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

$$V_M = \frac{e}{2m_e}\vec{L} \cdot \vec{B}$$

$$H = H_0 + \underbrace{\frac{e}{2m_e}\vec{L} \cdot \vec{B}}_{H'}$$

Take $\vec{B} = B_0\vec{k}$

$$H' = \frac{e}{2m_e}L_z B_0$$

$H_0\psi_0 = E_0\psi_0$;

$\psi + \psi_0$

$$H\psi = (H_0 + H')(\psi_0 + \psi') = E\psi$$

$$= (E_0 + E')(\psi_0 + \psi')$$

Perturbation

$$H_0\psi_0 = E_0\psi_0$$

$$H'\psi_0 = E'\psi_0$$

$$\Delta E = \frac{e}{2m_e} L_z B$$

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

magnetic quantum number

odd number of lines   odd

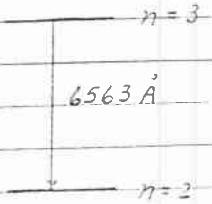
equal space

Chapter 10

Many - Electron Atoms

New inputs (i) electron spin
(ii) exclusion principle

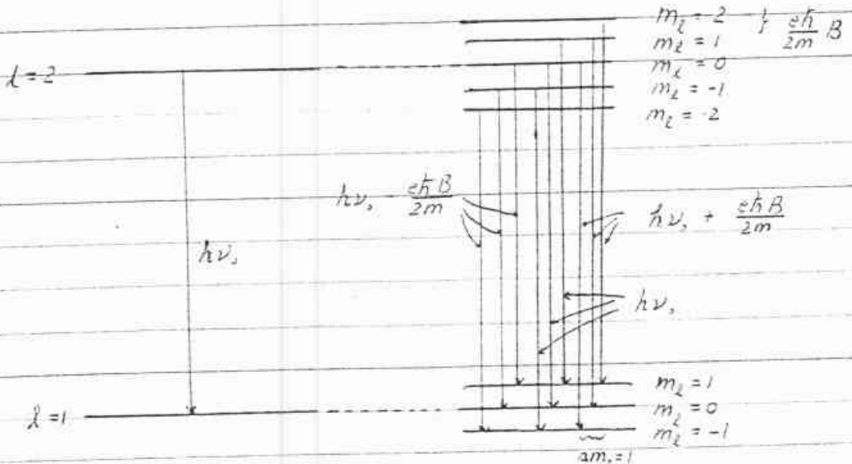
Experimental fact that many spectral lines actually consist of two seperate lines that are very close together ⇒ fine structure



→ first line of the Balmer series of hydrogen

Actually , there are 2 lines 1.4 Å apart

Normal Zeeman effect



Without magnetic field

With magnetic field

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

⇒ splitting of a spectral line of ν_0 into three components whose frequencies are

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

$$\nu_2 = \nu_0$$

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

Anomalous Zeeman effect

(i) 4, 6 or even more components may appear

(ii) even when 3 components are present their spacing may not agree with the above prediction.

1921 Compton suggested that the electron might be a spinning particle.

1925 Goudsmit and Uhlenbeck proposed

(i) the electron possesses an intrinsic angular momentum independent of any orbital momentum it might have

(ii) associated with this angular momentum, a certain magnetic moment

$\vec{S}$ operator

$[\hat{S}_x , \hat{S}_y] = i\hbar \hat{S}_z$ and cyclic permutation

$\Rightarrow [\vec{S}^2 , S_z] = 0$

S_z has two possible eigenvalue $\pm \frac{1}{2} \hbar = m_s \hbar$

S^2 has eigenvalue $\sqrt{\frac{3}{4}\hbar^2}$

$\frac{1}{2}(1+\frac{1}{2})\hbar^2$

$$\vec{\mu}_s = - \frac{e}{m} \vec{S} = - \underset{\llcorner\, g\text{-factor}}{g} \frac{e}{2m} \vec{S}$$

1928 Dirac → theory of electron ⇒ $g = 2$

↓

predict electron must have just the intrinsic angular momentum and magnetic moment attributed to them by Goudsmit and Uhlenbeck

Stern-Gerlach experiment

A magnetic dipole with magnetic moment $\vec{\mu}$ in a magnetic field $\vec{B}$ will have a potential energy

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

In an inhomogeneous magnetic field along z direction

$$\vec{B} = B(z) \hat{k}$$

$$\Rightarrow \quad V = - \mu_z B(z)$$

$$= g \frac{e}{2m} S_z B(z)$$

$$F_z = - \frac{\partial V}{\partial z} = - g \frac{e}{2m} m_s \hbar \frac{\partial B(z)}{\partial z}$$

Experimental set up.

Anomalous Zeeman Effect

Fine Structure

↓

spin

spin magnetic moment

Stern - Gerlach experiment $S^2 = (\frac{1}{2})(\frac{1}{2}+1)\hbar^2$

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

electron has spin and spin magnetic moment

$$\vec{\mu}_s = -g\frac{e}{2m}\vec{S}$$

Spin orbit interaction

↓

fine structure

$$\underset{\substack{\downarrow \\ \text{magnetic} \\ \text{moment}}}{\vec{\mu}} = \underset{\substack{\downarrow \\ \text{orbital}}}{\vec{\mu}} + \underset{\substack{\downarrow \\ \text{spin}}}{\vec{\mu}_s}$$

External $\vec{B}$ field

↓

both terms contributes

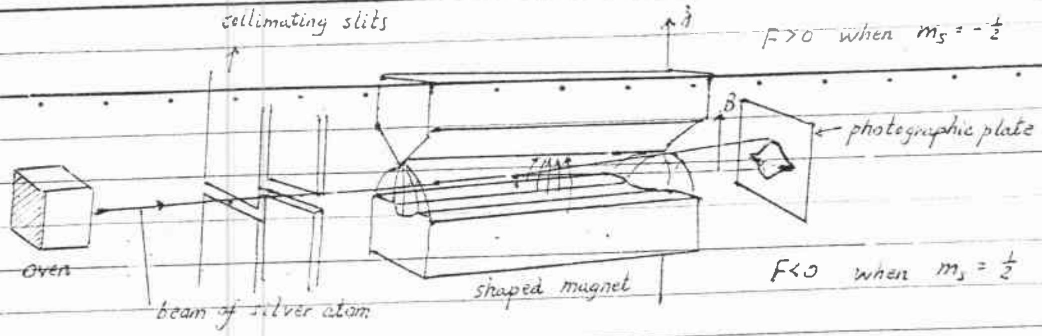
↓

explain the anomalous Zeeman effect.

Spin is independent of orbital motion

$$[\vec{L}, \vec{S}] = 0$$

$$[S_i, S_j] = \epsilon_{ijk} S_k$$



Field off ——

field on classical pattern 

actual pattern 

Spin - orbit coupling

Electron has spin ⇒ it has magnetic dipole moment $-\frac{e}{m}\vec{S}$

Look at the problem in the electron rest system

Proton is circling about the electron, it will produce a magnetic field $\vec{B}$ at the origin.

Direction of $\vec{B}$ is parallel to $\vec{L}$
orbital angular momentum

Magnitude of $\vec{B}$ is given by

$$B = \frac{\mu_0 i}{2r} \quad \text{obtained from Ampere's law}$$

$$= \frac{\mu_0 \nu e}{2r} = \frac{\mu_0 \frac{\omega}{2\pi} e}{2r} = \mu_0 \frac{\omega e}{2r \cdot 2\pi}$$

$$= \frac{\mu_0}{4\pi r^3} e r^2 \omega = \frac{\mu_0 \varepsilon_0 e^2}{4\pi\varepsilon_0 r^3} \frac{1}{e} \frac{mr^2\omega}{m}$$

$$V_e = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad \frac{dV_e}{dr} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$B = \frac{1}{c^2} \frac{1}{r} \frac{dV}{dr} \cdot \frac{1}{e} \frac{L}{m}$$

$$\Rightarrow \quad \vec{B} = \frac{1}{emc^2} \frac{1}{r} \frac{dV_e}{dr} \vec{L}$$

Potential due to magnetic interaction

$$V_m = -\vec{\mu}_s \cdot \vec{B} = \frac{e}{m} \frac{1}{emc^2} \frac{1}{r} \frac{dV_e}{dr} \vec{S} \cdot \vec{L} = \frac{1}{mc^2} \frac{1}{r} \frac{dV_e}{dr} \vec{S} \cdot \vec{L}$$

The above result is calculated in the electron rest system, which is not an inertial frame of reference.

Transform into the center of mass system of the atom

$$V_m = \frac{1}{2}\frac{1}{m^2c^2}\frac{1}{r}\frac{dV_e}{dr}\vec{S}\cdot\vec{L}$$

↳ Thomas factor

The interaction is known as the spin-orbit interaction

The total Hamiltonian of the hydrogen atom

$$H = \underbrace{\frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}}_{H_0} + \underbrace{\frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0 r^3}}_{H_1}\vec{S}\cdot\vec{L}$$

Order of magnitude estimate:

$$\frac{H_1}{H_0} \sim \frac{\frac{e^2}{2m^2c^2}\frac{\hbar^2}{4\pi\epsilon_0 a^3}}{\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a}}$$ $m \simeq \mu$, a = Bohr radius

$$\sim \left(\frac{\hbar}{mc}\right)^2\frac{1}{a^2} \sim 10^{-5} - 10^{-4} \ll 1$$

⇒ fine structure

Total angular momentum.

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

$[\vec{L}, \vec{S}] = 0 \Rightarrow [L_i, S_j] = 0$ for $i, j = x, y, z$

since $\vec{L}$ depends on spatial coordinates, $\vec{S}$ does not

$[J_x, J_y] = [L_x + S_x, L_y + S_y] = [L_x, L_y] + [S_x, L_y] + [L_x, S_y]$
$+ [S_x, S_y] = i\hbar L_z + i\hbar S_z$
$= i\hbar J_z$

Same argument $\Rightarrow [J_y, J_z] = i\hbar J_x$, $[J_z, J_x] = i\hbar J_y$

$m_j = m_\ell + m_s$

Example, $\ell = 1$, $s = \frac{1}{2}$
↳ for one electron, this is always the case.

m_ℓ	m_s	m_j
1	$\frac{1}{2}$	$\frac{3}{2}$
1	$-\frac{1}{2}$	$\frac{1}{2}$
0	$\frac{1}{2}$	$\frac{1}{2}$
0	$-\frac{1}{2}$	$-\frac{1}{2}$
-1	$\frac{1}{2}$	$-\frac{1}{2}$
-1	$-\frac{1}{2}$	$-\frac{3}{2}$

$m_j = \frac{3}{2} \Rightarrow j = \frac{3}{2}$ exists it should have 4 states with $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
$\psi_{3/2, 3/2}$, $\psi_{3/2, 1/2}$, $\psi_{3/2, -1/2}$, $\psi_{3/2, -3/2}$

$\psi_{3/2, 3/2} \rightarrow Y_{1,1}(\theta, \phi)\chi_+$

$\psi_{3/2, 1/2} \rightarrow$ linear combination of $Y_{1,1}(\theta, \phi)\chi_- + Y_{1,0}(\theta, \phi)\chi_+$

$\psi_{3/2, -1/2} \rightarrow$ linear combination of $Y_{1,0}(\theta, \phi)\chi_- + Y_{1,-1}(\theta, \phi)\chi_+$

$\psi_{3/2, -3/2} \rightarrow Y_{1,-1}(\theta, \phi)\chi_-$

Two states are left $\Rightarrow$ they corresponds to $j = \frac{1}{2}$ with $m_j = \frac{1}{2}, -\frac{1}{2}$.

$\psi_{1/2, 1/2} \rightarrow$ linear combination of $Y_{1,1}(\theta, \phi)\chi_- + Y_{1,0}(\theta, \phi)\chi_+$

$\psi_{1/2, -1/2} \rightarrow$ linear combination of $Y_{1,0}(\theta, \phi)\chi_- + Y_{1,-1}(\theta, \phi)\chi_+$

The possible j value $= \ell + \frac{1}{2}$, $\ell - \frac{1}{2}$

The result is of general validity. This can be seen from considering the number of states

$l \rightarrow (2l+1)$ state $\quad m_s = \pm \frac{1}{2}$

$\Rightarrow$ there are $2(2l+1)$ state

$$j = l + \tfrac{1}{2} \Rightarrow 2j+1 = 2l+2 \text{ states}$$
$$j = l - \tfrac{1}{2} \Rightarrow 2j+1 = \underline{2l} \text{ states}$$
$$2(2l+1) \text{ states}$$

$$H_0 = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$[H_0, \vec{L}^2] = [H_0, L_z] = [H_0, S_z] = 0$$
$$[L^2, L_z] = [L^2, S_z] = 0$$
$$[L_z, S_z] = 0$$

n
$l = 0, 1, 2, \cdots n-1$
$m_l = -l, -l+1, \cdots l-1, l$
$m_s = -\frac{1}{2}, +\frac{1}{2}$

Stationary states can be chosen to be also eigenstates of $\vec{L}^2$, $\vec{L}_z$, and S_z
$\Rightarrow$ stationary states are eigenstates of H_0, $\vec{L}^2$, L_z, S_z with eigenvalues E_n, $l(l+1)\hbar^2$, $m_l\hbar$, $m_s\hbar$ respectively. These states are labelled by four quantum numbers n, l, m_l, m_s
States with the same n will have the same energy E_n

$$[H_0, \vec{L}^2] = [H_0, \vec{J}^2] = [H_0, J_z] = 0$$
$$[\vec{J}^2, J_z] = [\vec{J}^2, \vec{L}^2] = 0$$
$$[\vec{L}^2, J_z] = 0$$

n
$l = 1, 2, \cdots n-1$
$j = l - \frac{1}{2}, \ l - \frac{1}{2}$ +
$m_j = -j, -j+1, \cdots j-1, j$

Stationary states can be chosen to be also eigenstates of $\vec{L}^2$, $\vec{J}^2$ and J_z
$\Rightarrow$ stationary states are eigenstates of H_0, $\vec{L}^2$, $\vec{J}^2$, and J_z with eigenvalues E_n, $l(l+1)\hbar^2$, $j(j+1)\hbar^2$, $m_j\hbar$ respectively. These states are labelled by four quantum number n, l, j, m_j

$$\vec{J} \cdot \vec{S} = J_x S_x + J_y S_y + J_z S_z$$
$$= \frac{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}{2}$$

$$\Rightarrow [H_0 + H_1, \vec{L}^2] = [H_0 + H_1, \vec{J}^2] = [H_0 + H_1, J_z] = 0$$
$$[\vec{J}^2, J_z] = [\vec{J}^2, \vec{L}^2] = 0$$
$$[\vec{L}^2, J_z] = 0$$

Stationary states are eigenstates of $H = H_0 + H_1$, $\vec{L}^2$, $\vec{J}^2$ and J_z with eigenvalues $E_n + \frac{1}{2m^2c^4} \frac{e^2}{4\pi\epsilon_0} \langle \frac{1}{r^3} \rangle_{nl} \frac{j(j+1) - l(l+1) - s(s+1)}{2} \hbar^2$, $l(l+1)\hbar^2$, $j(j+1)\hbar^2$, $m_j\hbar$ respectively

$l = 0$

m_l	m_s	m_j
0	$\frac{1}{2}$	$\frac{1}{2}$
0	$-\frac{1}{2}$	$-\frac{1}{2}$

$\Rightarrow j = \frac{1}{2}$ $\quad l = 0$ the only possible j value is $\frac{1}{2}$. (remember j must be positive)

Notation

$$l = \begin{array}{cccccccc} 0 & 1 & 2 & 3 & 4 & 5 & \cdots \\ S & P & D & F & G & H & \cdots \end{array} \qquad n\, l_J$$

Example

$n = 3$, $\quad l = 0$ $\quad j$ must be $\frac{1}{2}$ $\qquad 3S_{1/2}$

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

These two states has the same energy $\quad E_3 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\cdot\frac{1}{9} = -\frac{13.6}{9}\,eV$

$n = 2$, $\quad l = 0$ $\quad j$ must be $\frac{1}{2}$ $\qquad 2S_{1/2}$

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

These two states have the same energy $\quad E_2 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\,\frac{1}{4} = -\frac{13.6}{4}\,eV$

$n = 2$, $\quad l = 1$ $\quad j$ can be $\frac{3}{2}$ $\qquad 2P_{1/2}$

$m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

These four states have the same energy

$$E_2 + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\hbar^2 \left\langle \frac{1}{r^3} \right\rangle_{\substack{nl \\ \frac{3}{2}\frac{1}{2}}} \frac{\frac{3}{2}(\frac{3}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)}{2}$$

use the wave function obtained in last chapter

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{1}{n^3a^3\,l(l+1)(l+\frac{1}{2})} = \frac{1}{8a^3\,1(2)(\frac{3}{2})}$$

Thus its energy is

$$\frac{-me^4}{32\pi^2\epsilon_0^2\hbar^2}\cdot\frac{1}{4} + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\hbar^2\frac{1}{48a^3}$$

$$-\frac{13.6}{4}\,eV$$

a = Bohr radius

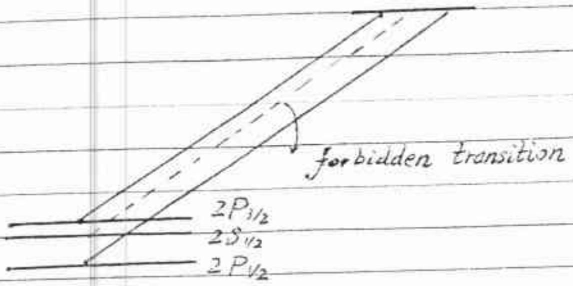
$n = 2$ $\quad l = 1$ $\quad j$ can be $\frac{1}{2}$ $\qquad 2P_{1/2}$

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

These two states have the same energy

$$E_2 + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\hbar^2\left\langle\frac{1}{r^3}\right\rangle_{\substack{nl \\ \frac{1}{2}\frac{1}{2}}} \frac{\frac{1}{2}(\frac{1}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)}{2}$$

$$= -\frac{13.6}{4}\,eV - \frac{1}{2m^2c^2}\cdot\frac{e^2}{4\pi\epsilon_0}\cdot\hbar^2\frac{1}{24a^3}$$



Selection rules : $\Delta l = \pm 1$
$\Delta j = 0, \pm 1$

$$\left.\begin{array}{l} 3S_{1/2} \longrightarrow 2P_{3/2} \\ 3S_{1/2} \longrightarrow 2P_{1/2} \end{array}\right\}$$ two lines close to each other => fine structure

Anomalous Zeeman effect

$$H = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0 r^3}\vec{S}\cdot\vec{L}$$

$$\vec{\mu} = -\frac{\mu_B}{\hbar}[\vec{L}+2\vec{S}]$$

Remember $\frac{d}{dt}\langle O\rangle = \frac{1}{i\hbar}\langle[O, H]\rangle$

If $[\hat{O}, \hat{H}]=0$ then $\hat{O}$ is constant of motion

(i) $[\vec{L}^2, H] = 0$ ⇒ the magnitude of $\vec{L}$ is constant of motion

$$[\vec{L}^2, S_xL_x+S_yL_y+S_zL_z]=0$$

Because $[\vec{L}^2, L_x] = [\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0$
$[L_i, S_j] = 0$ for all possible i, j

(ii) Same argument ⇒ $[\vec{S}^2, H] = 0$ ⇒ the magnitude of $\vec{S}$ is constant of motion

(iii) $[J_x, S_xL_x+S_yL_y+S_zL_z]$

$= [L_x, S_xL_x+S_yL_y+S_zL_z] + [S_x, S_xL_x+S_yL_y+S_zL_z]$

$= S_y[L_x, L_y] + S_z[L_x, L_z] + [S_x, S_y]L_y + [S_x, S_z]L_z$

$= S_y i\hbar L_z - S_z i\hbar L_y + i\hbar S_z L_y - i\hbar S_y L_z = 0$

Similar $[J_y, \vec{L}\cdot\vec{S}] = [J_z, \vec{L}\cdot\vec{S}] = 0$

⇒ $[\vec{J}, H] = 0$

$\vec{J}$ is a constant of motion

(iv) $[L_x, S_xL_x+S_yL_y+S_zL_z]$

$= S_y[L_x, L_y] + S_z[L_x, L_z]$

$= i\hbar S_yL_z - i\hbar L_yS_z = i\hbar(\vec{S}\times\vec{L})_x = i\hbar(\vec{J}\times\vec{L})_x$

Same argument ⇒ $[L_y, S_xL_x+S_yL_y+S_zL_z] = i\hbar(\vec{J}\times\vec{L})_y$
$[L_z, S_xL_x+S_yL_y+S_zL_z] = i\hbar(\vec{J}\times\vec{L})_z$

$$\frac{d\langle \vec{L} \rangle}{dt} = \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0 r^3}\langle \vec{J} \times \vec{L} \rangle$$

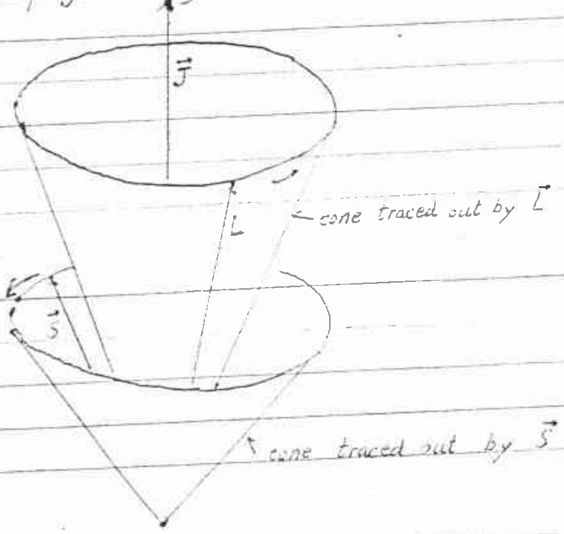
It has the form $\frac{d\langle \vec{L} \rangle}{dt} = \vec{\omega} \times \langle \vec{L} \rangle$

$\vec{L}$ process about $\vec{J}$, the projection of $\vec{L}$ along $\vec{J}$ is constant of motion.

(v) Same argument $\Rightarrow$ $\frac{d\langle \vec{S} \rangle}{dt} = \vec{\omega} \times \langle \vec{S} \rangle$

$\vec{S}$ process about $\vec{J}$, the projection of $\vec{S}$ along $\vec{J}$ is constant of motion

$\Rightarrow$



$\vec{\mu} = -\frac{\mu_B}{\hbar}[\vec{L} + 2\vec{S}]$

$\vec{\mu}$ is not along $\vec{J}$, but precess about it.

The time averaged $\langle \vec{\mu} \rangle$ is along $\vec{J}$ with magnitude

$$\mu_J = |\vec{\mu}|\frac{\vec{\mu}\cdot\vec{J}}{|\vec{\mu}||\vec{J}|} = -\frac{\mu_B}{\hbar}\frac{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})}{|\vec{J}|}$$

If an external $\vec{B}$ field (weak) is applied along z direction

weak $\Rightarrow$ magnetic potential energy $\ll$ spin-orbit interaction

the magnetic potential energy

$$= -\mu_J \underbrace{\hat{J}}_{\text{unit vector along } \vec{J}} \cdot \vec{B}$$

$$= \mu_J \frac{J_z}{|\vec{J}|} B = \frac{\mu_B B}{\hbar}\frac{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})}{\vec{J}^2} J_z$$

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

$$\langle \Delta E \rangle_{jlm_j} = \frac{\mu_B B}{\hbar}\frac{[3j(j+1) - l(l+1) + s(s+1)]\hbar^2}{2j(j+1)\hbar^2} m_j\hbar = \mu_B B g m_j$$

$$\underset{\llcorner \text{ Lande g factor}}{g} = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

分類：
編號：10-12
總號：

magnetic field produced by the magnetic moment of the proton leads to hyperfine interaction

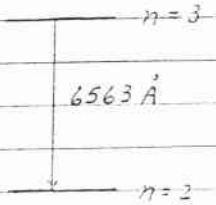
分類：
編號： 10-1
總號：

Chapter 10

Many - Electron Atoms

New inputs : (i) electron spin
(ii) exclusion principle

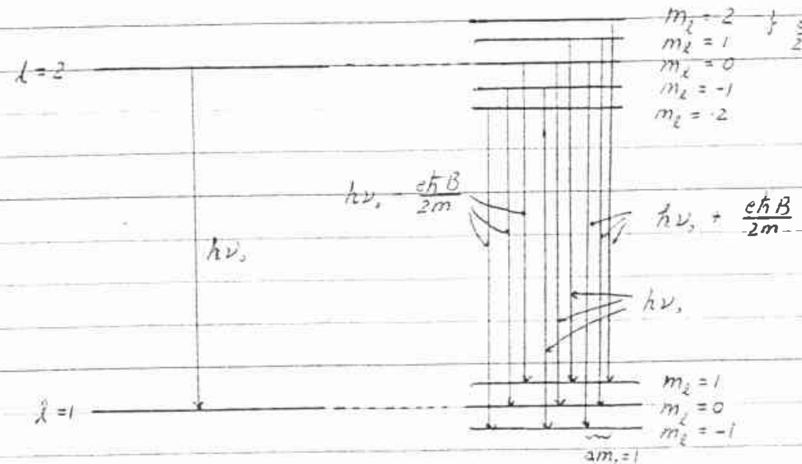
Experimental fact that many spectral lines actually consist of two seperate lines that are very close together ⇒ fine structure



→ first line of the Balmer series of hydrogen

Actually , there are 2 lines 1.4 Å apart

Normal Zeeman effect



Without magnetic field — With magnetic field

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

⇒ splitting of a spectral line of ν_0 into three components whose frequencies are

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

$$\nu_2 = \nu_0$$

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

Anomalous Zeeman effect

(i) 4, 6 or even more components may appear
(ii) even when 3 components are present their spacing may not agree with the above prediction.

1921 Compton suggested that the electron might be a spinning particle

1925 Goudsmit and Uhlenbeck proposed
(i) the electron possesses an intrinsic angular momentum independent of any orbital momentum it might have
(ii) associated with this angular momentum, a certain magnetic moment

$\vec{S}$ operator

$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z$ and cyclic permutation

$\Rightarrow [\vec{S}^2, S_z] = 0$

S_z has two possible eigenvalue $\pm \frac{1}{2}\hbar = m_s \hbar$

S^2 has eigenvalue $\sqrt{\frac{3}{4}\hbar^2}$

$\frac{1}{2}(1+\frac{1}{2})\hbar^2$

$$\vec{\mu}_s = -\frac{e}{m}\vec{S} = -g\frac{e}{2m}\vec{S}$$

$\hookrightarrow$ g-factor

1928 Dirac → theory of electron ⇒ $g = 2$

predict electron must have just the intrinsic angular momentum and magnetic moment attributed to them by Goudsmit and Uhlenbeck

Stern-Gerlach experiment

A magnetic dipole with magnetic moment $\vec{\mu}$ in a magnetic field $\vec{B}$ will have a potential energy

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

In an inhomogeneous magnetic field along z direction

$$\vec{B} = B(z)\,\hat{k}$$

$$\Rightarrow V = -\mu_z B(z)$$

$$= g\frac{e}{2m} S_z B(z)$$

$$F_z = -\frac{\partial V}{\partial z} = -g\frac{e}{2m} m_s \hbar \frac{\partial B(z)}{\partial z}$$

Experimental set up.

Anomalous Zeeman Effect

Fine Structure

↓

spin

spin magnetic moment

Stern - Gerlach experiment

$$S^2 = (\tfrac{1}{2})(\tfrac{1}{2}+1)\hbar^2$$
$$S_z = \pm\tfrac{1}{2}$$

electron has spin and spin magnetic moment

$$\vec{\mu}_s = -g\frac{e}{2m}\vec{S}$$

Spin orbit interaction

↓

fine structure

$$\underset{\substack{\downarrow\\ \text{magnetic}\\ \text{moment}}}{\vec{\mu}} = \underset{\substack{\downarrow\\ \text{orbital}}}{\vec{\mu}} + \underset{\substack{\downarrow\\ \text{spin}}}{\vec{\mu}_s}$$

External $\vec{B}$ field

↓

both terms contributes

↓

explain the anomalous Zeeman effect.

Spin is independent of orbital motion

$$[\vec{L}, \vec{S}] = 0$$

$$[S_i, S_j] = \epsilon_{ijk} S_k$$

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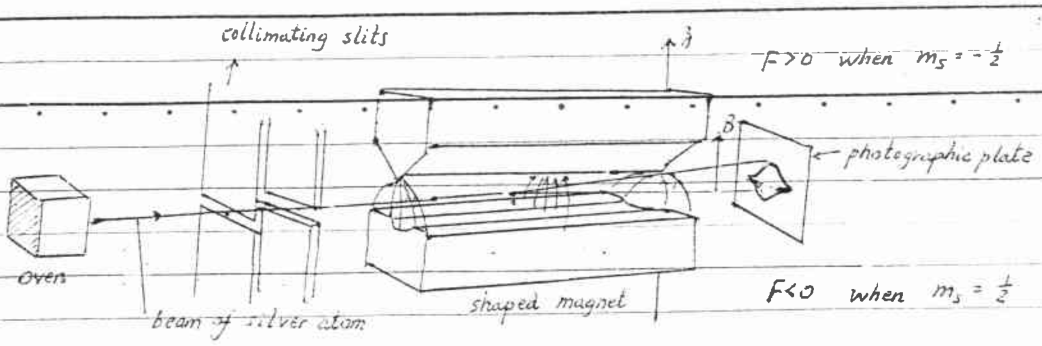
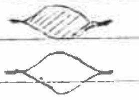


Field off —

field on classical pattern

actual pattern



Spin - orbit coupling

Electron has spin ⇒ it has magnetic dipole moment $-\frac{e}{m}\vec{S}$

Look at the problem in the electron rest system

Proton is circling about the electron, it will produce a magnetic field $\vec{B}$ at the origin.

Direction of $\vec{B}$ is parallel to $\underset{\substack{\uparrow \\ \text{orbital angular momentum}}}{\vec{L}}$

Magnitude of $\vec{B}$ is given by :

$$B = \frac{\mu_0 i}{2r} \quad \text{obtained from Ampere's law}$$

$$= \frac{\mu_0 \nu e}{2r} = \frac{\mu_0 \frac{\omega}{2\pi} e}{2r} = \mu_0 \frac{\omega e}{2r \cdot 2\pi}$$

$$= \frac{\mu_0}{4\pi r^3} e r^2 \omega = \frac{\mu_0 \epsilon_0 e^2}{4\pi\epsilon_0 r^3} \frac{1}{e} \frac{mr^2\omega}{m}$$

$$V_e = -\frac{e^2}{4\pi\epsilon_0 r} \qquad \frac{dV_e}{dr} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$B = \frac{1}{c^2}\frac{1}{r}\frac{dV}{dr} \cdot \frac{1}{e} \frac{L}{m}$$

$$\Rightarrow \quad \vec{B} = \frac{1}{emc^2}\frac{1}{r}\frac{dV_e}{dr}\vec{L}$$

Potential due to magnetic interaction

$$V_m = -\vec{\mu}_s \cdot \vec{B} = \frac{e}{m} \cdot \frac{1}{emc^2} \frac{1}{r} \frac{dV_e}{dr} \vec{S}\cdot\vec{L} = \frac{1}{mc^2} \cdot \frac{1}{r}\frac{dV_e}{dr}\vec{S}\cdot\vec{L}.$$

The above result is calculated in the electron rest system, which is not an inertial frame of reference.

Transform into the center of mass system of the atom

$$V_m = \frac{1}{2}\,\frac{1}{m^2c^2}\,\frac{1}{r}\,\frac{dV_e}{dr}\,\vec{S}\cdot\vec{L}$$

$\frac{1}{2}$ ↳ Thomas factor

The interaction is known as the spin-orbit interaction

The total Hamiltonian of the hydrogen atom

$$H = \underbrace{\frac{\vec{p}^{\,2}}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}}_{H_0} + \underbrace{\frac{1}{2m^2c^2}\,\frac{e^2}{4\pi\epsilon_0 r^3}}_{H_1}\,\vec{S}\cdot\vec{L}$$

Order of magnitude estimate :

$$\frac{H_1}{H_0} \sim \frac{\frac{e^2}{2m^2c^2}\,\frac{\hbar^2}{4\pi\epsilon_0 a^3}}{\frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0 a}} \qquad m \simeq \mu,\quad a = \text{Bohr radius}$$

$$\sim \left(\frac{\hbar}{mc}\right)^2 \frac{1}{a^2} \sim 10^{-5} - 10^{-4} \ll 1$$

⇒ fine structure

Total angular momentum

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

$[\vec{L}, \vec{S}] = 0 \Rightarrow [L_i, S_j] = 0$ for $i, j = x, y, z$

since $\vec{L}$ depends on spatial coordinates, $\vec{S}$ does not

$$[J_x, J_y] = [L_x + S_x, L_y + S_y] = [L_x, L_y] + [S_x, L_y] + [L_x, S_y] + [S_x, S_y] = i\hbar L_z + i\hbar S_z = i\hbar J_z$$

Same argument $\Rightarrow [J_y, J_z] = i\hbar J_x$, $[J_z, J_x] = i\hbar J_y$

$m_j = m_\ell + m_s$

Example, $\ell = 1$, $s = \frac{1}{2}$

↳ for one electron, this is always the case.

m_ℓ	m_s	m_j
1	$\frac{1}{2}$	$\frac{3}{2}$
1	$-\frac{1}{2}$	$\frac{1}{2}$
0	$\frac{1}{2}$	$\frac{1}{2}$
0	$-\frac{1}{2}$	$-\frac{1}{2}$
-1	$\frac{1}{2}$	$-\frac{1}{2}$
-1	$-\frac{1}{2}$	$-\frac{3}{2}$

$m_j = \frac{3}{2} \Rightarrow j = \frac{3}{2}$ exists it should have 4 states with $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

$\psi_{3/2, 3/2}$, $\psi_{3/2, 1/2}$, $\psi_{3/2, -1/2}$, $\psi_{3/2, -3/2}$

$\psi_{3/2, 3/2} \longrightarrow Y_{1,1}(\theta, \phi)\chi_+$

$\psi_{3/2, 1/2} \longrightarrow$ linear combination of $Y_{1,1}(\theta, \phi)\chi_- + Y_{1,0}(\theta, \phi)\chi_+$

$\psi_{3/2, -1/2} \longrightarrow$ linear combination of $Y_{1,0}(\theta, \phi)\chi_- + Y_{1,-1}(\theta, \phi)\chi_+$

$\psi_{3/2, -3/2} \longrightarrow Y_{1,-1}(\theta, \phi)\chi_-$

Two states are left $\Rightarrow$ they corresponds to $j = \frac{1}{2}$ with $m_j = \frac{1}{2}, -\frac{1}{2}$.

$\psi_{1/2, 1/2} \longrightarrow$ linear combination of $Y_{1,1}(\theta, \phi)\chi_- + Y_{1,0}(\theta, \phi)\chi_+$

$\psi_{1/2, -1/2} \longrightarrow$ linear combination of $Y_{1,0}(\theta, \phi)\chi_- + Y_{1,-1}(\theta, \phi)\chi_+$

The possible j value $= \ell + \frac{1}{2}$, $\ell - \frac{1}{2}$

The result is of general validity. This can be seen from considering the number of states.

$l \rightarrow (2l+1)$ state $\quad m_s = \pm\frac{1}{2}$

$\Rightarrow$ there are $2(2l+1)$ state

$$j = l + \tfrac{1}{2} \Rightarrow 2j+1 = 2l+2 \text{ states}$$
$$j = l - \tfrac{1}{2} \Rightarrow 2j+1 = \underline{2l} \text{ states}$$
$$2(2l+1) \text{ states}$$

$$H_0 = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$[H_0, \vec{L}^2] = [H_0, L_z] = [H_0, S_z] = 0$$
$$[L^2, L_z] = [L^2, S_z] = 0$$
$$[L_z, S_z] = 0$$

n
$l = 0, 1, 2, \cdots n-1$
$m_l = -l, -l+1, \cdots l-1, l$
$m_s = -\frac{1}{2}, +\frac{1}{2}$

Stationary states can be chosen to be also eigenstates of $\vec{L}^2$, $\vec{L}_z$, and S_z
$\Rightarrow$ stationary states are eigenstates of H_0, $\vec{L}^2$, L_z, S_z with eigenvalues E_n, $l(l+1)\hbar^2$, $m_l\hbar$, $m_s\hbar$ respectively. These states are labelled by four quantum numbers n, l, m_l, m_s
States with the same n will have the same energy E_n

$$[H_0, \vec{L}^2] = [H_0, \vec{J}^2] = [H_0, J_z] = 0$$
$$[\vec{J}^2, J_z] = [\vec{J}^2, \vec{L}^2] = 0$$
$$[\vec{L}^2, J_z] = 0$$

n
$l = 1, 2, \cdots n-1$
$j = l+\frac{1}{2}, l-\frac{1}{2}$ *
$m_j = -j, -j+1, \cdots j-1, j$

Stationary states can be chosen to be also eigenstates of $\vec{L}^2$, $\vec{J}^2$ and J_z
$\Rightarrow$ stationary states are eigenstates of H_0, $\vec{L}^2$, $\vec{J}^2$, and J_z with eigenvalues E_n, $l(l+1)\hbar^2$, $j(j+1)\hbar^2$, $m_j\hbar$ respectively. These states are labelled by four quantum number n, l, j, m_j

$$\vec{J}\cdot\vec{S} = J_x S_x + J_y S_y + J_z S_z$$
$$= \frac{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}{2}$$

$$\Rightarrow [H_0 + H_1, \vec{L}^2] = [H_0 + H_1, \vec{J}^2] = [H_0 + H_1, J_z] = 0$$
$$[\vec{J}^2, J_z] = [\vec{J}^2, \vec{L}^2] = 0$$
$$[\vec{L}^2, J_z] = 0$$

Stationary states are eigenstates of $H = H_0 + H_1$, $\vec{L}^2$, $\vec{J}^2$ and J_z with eigenvalues $E_n + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r^3}\right\rangle_{nl}\frac{j(j+1) - l(l+1) - s(s+1)}{2}\hbar^2$, $l(l+1)\hbar^2$, $j(j+1)\hbar^2$, $m_j\hbar$ respectively

$\ell = 0$

m_ℓ	m_s	m_j
0	$\frac{1}{2}$	$\frac{1}{2}$
0	$-\frac{1}{2}$	$-\frac{1}{2}$

$\Rightarrow j = \frac{1}{2}$ $\ell = 0$ the only possible j value is $\frac{1}{2}$. (remember j must be positive)

Notation

$\ell =$ 0 1 2 3 4 5 ⋯ $n\,\ell_J$

S P D F G H ⋯

Example

$n = 3$, $\ell = 0$ j must be $\frac{1}{2}$ $3S_{1/2}$

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

These two states has the same energy $E_1 = -\frac{me^4}{32\pi^2\epsilon^2\hbar^2}\cdot\frac{1}{9} = -\frac{13.6}{9}\,eV$

$n = 2$, $\ell = 0$ j must be $\frac{1}{2}$ $2S_{1/2}$

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

These two states have the same energy $E_2 = -\frac{me^4}{32\pi^2\epsilon^2\hbar^2}\frac{1}{4} = -\frac{13.6}{4}\,eV$

$n = 2$. $\ell = 1$ j can be $\frac{3}{2}$ $2P_{1/2}$

$m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

These four states have the same energy

$$E_2 + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\hbar^2 \left\langle \frac{1}{r^3}\right\rangle_{\substack{n\ell\\ 2\,1}} \frac{\frac{3}{2}(\frac{3}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)}{2}$$

use the wave function obtained in last chapter

$$\left\langle \frac{1}{r^3}\right\rangle_{n\ell} = \frac{1}{n^3a^3\,\ell(\ell+1)(\ell+\frac{1}{2})} = \frac{1}{8a^3\,1(2)(\frac{3}{2})}$$

Thus its energy is

$$\frac{-me^4}{32\pi^2\epsilon_0^2\hbar^2}\cdot\frac{1}{4} + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0^2}\hbar^2\frac{1}{48a^3}$$

$$-\frac{13.6}{4}\,eV$$

$a =$ Bohr radius

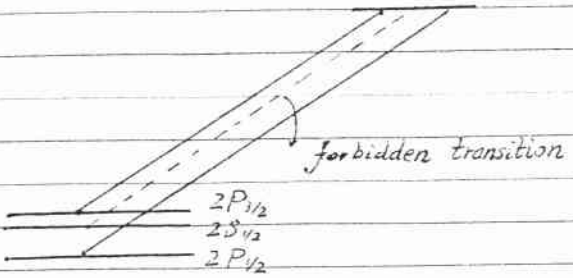
$n = 2$ $\ell = 1$ j can be $\frac{1}{2}$ $2P_{1/2}$

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

These two states have the same energy

$$E_2 + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0}\hbar^2\left\langle\frac{1}{r^3}\right\rangle_{\substack{n\ell\\ 2\,1}}\frac{\frac{1}{2}(\frac{1}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)}{2}$$

$$= -\frac{13.6}{4}\,eV - \frac{1}{2m^2c^2}\cdot\frac{e^2}{4\pi\epsilon_0}\cdot\hbar^2\,\frac{1}{24a^3}$$



Selection rules : $\Delta l = \pm 1$

$\Delta j = 0, \pm 1$

$$\left.\begin{array}{l} 3S_{1/2} \longrightarrow 2P_{3/2} \\ 3S_{1/2} \longrightarrow 2P_{1/2} \end{array}\right\}$$ two lines close to each other => fine structure

Anomalous Zeeman effect

$$H = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0 r^3}\vec{S}\cdot\vec{L}$$

$$\vec{\mu} = -\frac{\mu_B}{\hbar}[\vec{L}+2\vec{S}]$$

Remember $\frac{d}{dt}\langle O\rangle = \frac{1}{i\hbar}\langle[O,H]\rangle$

If $[\hat{O},\hat{H}]=0$ then $\hat{O}$ is constant of motion

(i) $[\vec{L}^2, H] = 0 \Rightarrow$ the magnitude of $\vec{L}$ is constant of motion

$$[\vec{L}^2, S_xL_x+S_yL_y+S_zL_z]=0$$

Because $[\vec{L}^2, L_x] = [\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0$

$[L_i, S_j] = 0$ for all possible i, j

(ii) Same argument $\Rightarrow [\vec{S}^2, H] = 0 \Rightarrow$ the magnitude of $\vec{S}$ is constant of motion

(iii) $[J_x, S_xL_x+S_yL_y+S_zL_z]$

$$= [L_x, S_xL_x+S_yL_y+S_zL_z] + [S_x, S_xL_x+S_yL_y+S_zL_z]$$

$$= S_y[L_x,L_y] + S_z[L_x,L_z] + [S_x,S_y]L_y + [S_x,S_z]L_z$$

$$= S_y\, i\hbar L_z - S_z\, i\hbar L_y + i\hbar S_z L_y - i\hbar S_y L_z = 0$$

Similar $[J_y, \vec{L}\cdot\vec{S}] = [J_z, \vec{L}\cdot\vec{S}] = 0$

$\Rightarrow [\vec{J}, H] = 0$

$\vec{J}$ is a constant of motion

(iv) $[L_x, S_xL_x+S_yL_y+S_zL_z]$

$$= S_y[L_x,L_y] + S_z[L_x,L_z]$$

$$= i\hbar S_yL_z - i\hbar L_yS_z = i\hbar(\vec{S}\times\vec{L})_x = i\hbar(\vec{J}\times\vec{L})_x$$

Same argument $\Rightarrow [L_y, S_xL_x+S_yL_y+S_zL_z] = i\hbar(\vec{J}\times\vec{L})_y$

$[L_z, S_xL_x+S_yL_y+S_zL_z] = i\hbar(\vec{J}\times\vec{L})_z$

$$\frac{d\langle \vec{L}\rangle}{dt} = \frac{1}{2m^2c^2}\frac{e^2}{4\pi\epsilon_0 r^3}\langle \vec{J}\times\vec{L}\rangle$$

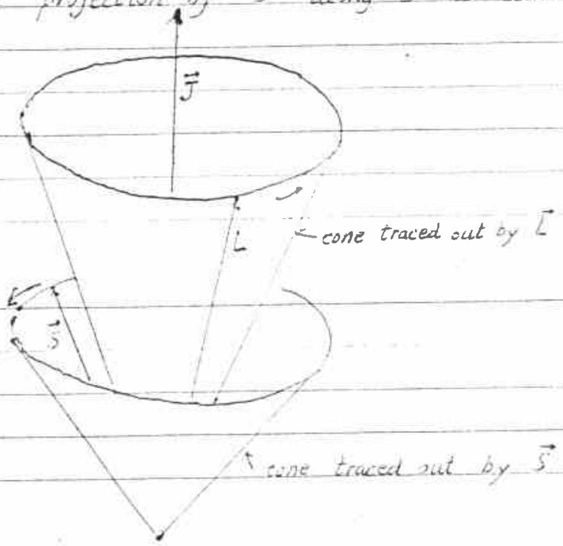
It has the form $\frac{d\langle \vec{L}\rangle}{dt} = \vec{\omega}\times\langle\vec{L}\rangle$

$\vec{L}$ process about $\vec{J}$, the projection of $\vec{L}$ along $\vec{J}$ is constant of motion.

(v) Same argument $\Rightarrow$ $\frac{d\langle \vec{S}\rangle}{dt} = \vec{\omega}\times\langle\vec{S}\rangle$

$\vec{S}$ precess about $\vec{J}$, the projection of $\vec{S}$ along $\vec{J}$ is constant of motion.

$\Rightarrow$



$$\vec{\mu} = -\frac{\mu_B}{\hbar}[\vec{L}+2\vec{S}]$$

$\vec{\mu}$ is not along $\vec{J}$, but precess about it.

The time averaged $\langle\vec{\mu}\rangle$ is along $\vec{J}$ with magnitude

$$\mu_J = |\vec{\mu}|\frac{\vec{\mu}\cdot\vec{J}}{|\vec{\mu}||\vec{J}|} = -\frac{\mu_B}{\hbar}\frac{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})}{|\vec{J}|}$$

If an external $\vec{B}$ field (weak) is applied along z direction
the magnetic potential energy

weak $\Rightarrow$ magnetic potential energy $\ll$ spin-orbit interaction

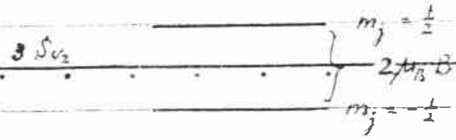
$$= -\mu_J \underbrace{\hat{J}}_{\text{unit vector along } \vec{J}}\cdot\vec{B}$$

$$= \mu_J\frac{J_z}{|\vec{J}|}B = \frac{\mu_B B}{\hbar}\frac{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})}{J^2}J_z$$

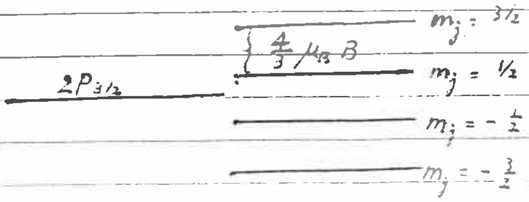
$$\vec{L}^2 + 2\vec{S}^2 + 3\vec{L}\cdot\vec{S} = \vec{L}^2+2\vec{S}^2 + \frac{3}{2}(\vec{J}^2-\vec{L}^2-\vec{S}^2) = \frac{1}{2}(3\vec{J}^2-\vec{L}^2+S^2)$$

$$\langle\Delta E\rangle_{jlm_j} = \frac{\mu_B B}{\hbar}\frac{[3j(j+1)-l(l+1)+s(s+1)]\hbar^2}{2j(j+1)\hbar^2}m_j\hbar = \mu_B B g m_j$$

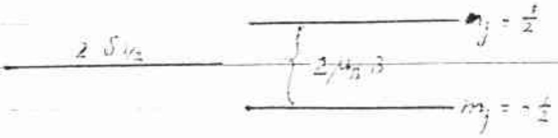
$$\underbrace{g}_{\text{Landé g factor}} = 1+\frac{j(j+1)-l(l+1)-s(s+1)}{2j(j+1)}$$



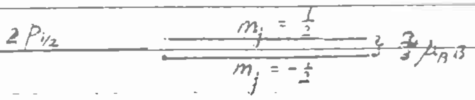
$$g = 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) - 0(0+1) + \frac{1}{2}(\frac{1}{2}+1)}{2\cdot\frac{1}{2}(\frac{1}{2}+1)} = 2$$



$$g = 1 + \frac{\frac{3}{2}(\frac{3}{2}+1) - 1(1+1) + \frac{1}{2}(\frac{1}{2}+1)}{2\cdot\frac{3}{2}(\frac{3}{2}+1)} = \frac{4}{3}$$



g is the same as that for $3S_{1/2}$



$$g = 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) - 1(1+1) + \frac{1}{2}(\frac{1}{2}+1)}{2\cdot\frac{1}{2}(\frac{1}{2}+1)}$$

$$= \frac{2}{3}$$

Additional correction

(i) Relativistic correction

K.E. (kinetic energy) in the center of mass frame $|\vec{P}_e^*| = |\vec{P}_p^*| = |\vec{P}^*|$

$$\frac{\vec{P}_e^{*2}}{2m} + \frac{\vec{P}_p^{*2}}{2M} = \frac{\vec{P}^{*2}}{2\mu} \qquad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

$$\rightarrow \sqrt{\vec{P}_e^{*2}c^2 + m^2c^4} - mc^2 + \frac{\vec{P}_p^{*2}}{2M} = mc^2\left(1 + \frac{\vec{P}_e^{*2}c^2}{m^2c^4}\right)^{\frac{1}{2}} - m^2c^2 + \frac{\vec{P}_p^{*2}}{2M}$$

$$\cong \frac{\vec{P}^{*2}}{2m} - \frac{1}{8}\frac{(\vec{P}^{2})^2}{m^4c^2} + \frac{\vec{P}^{*2}}{2M} = \frac{\vec{P}^{*2}}{2\mu} - \frac{1}{8}\frac{(\vec{P}^{2})^2}{m^3c^2}$$

↳ relativistic correction term

(ii) Hyperfine interaction

Proton has spin $\frac{1}{2}$ ⇒ magnetic moment $\mu_p = g_p \frac{e}{2M_p}\vec{S}$

↳ mass of proton

⇒ this magnetic moment will produce a magnetic field around it

⇒ interaction between the magnetic dipole moment of electron and the

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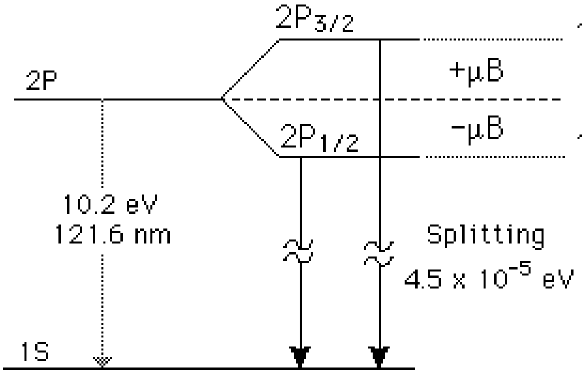
總號：

magnetic field produced by the magnetic moment of the proton leads to ...

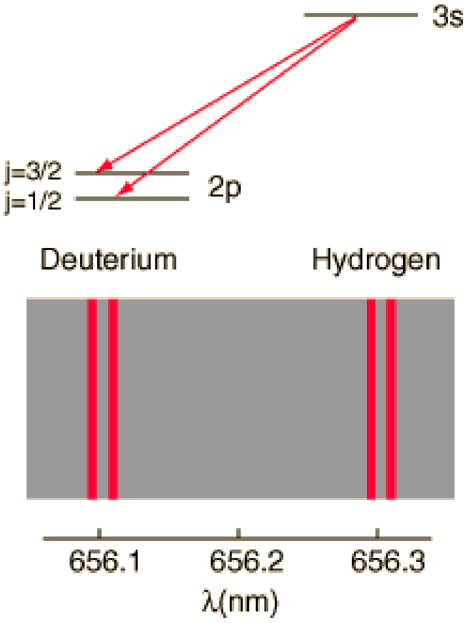
hyperfine interaction

Hydrogen Fine Structure

When the spectral lines of the hydrogen spectrum are examined at very high resolution, they are found to be closely-spaced doublets. This splitting is called fine structure and was one of the first experimental evidences for electron spin.



The small splitting of the spectral line is attributed to an interaction between the electron spin S and the orbital angular momentum L. It is called the spin-orbit interaction.



The familiar red H-alpha line of hydrogen is a single line according to the Bohr theory. The straight application of the Schrodinger equation to the hydrogen atom gives the same result. If you calculate the wavelength of this line using the energy expression from the Bohr theory, you get 656.11 nm for hydrogen, treating the nucleus as a fixed center. If you use the reduced mass, you get 656.47 nm for hydrogen and 656.29 nm for deuterium. The difference between the hydrogen and deuterium lines is about 0.2 nm and the splitting of each of them is about 0.016 nm, corresponding to an energy difference of about 0.000045 eV. This corresponds to an internal magnetic field on the electron of about 0.4 Tesla.

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Examination of fine structure by saturation spectroscopy

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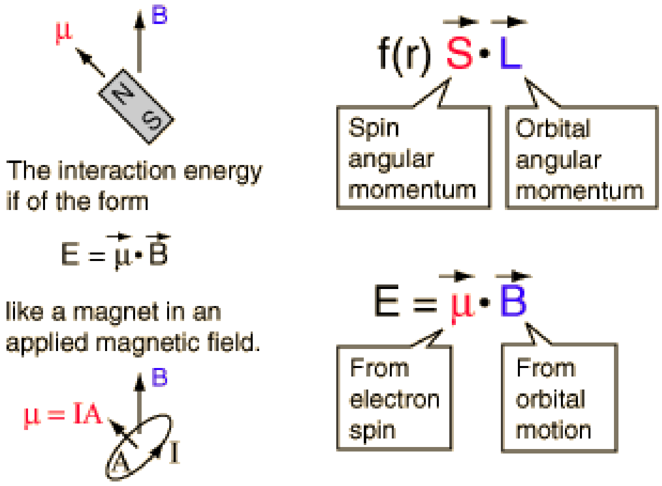
Spin-Orbit Interaction

The energy levels of atomic electrons are affected by the interaction between the electron spin magnetic moment and the orbital angular momentum of the electron. It can be visualized as a magnetic field caused by the electron's orbital motion interacting with the spin magnetic moment. This effective magnetic field can be expressed in terms of the electron orbital angular momentum. The interaction energy is that of a magnetic dipole in a magnetic field and takes the form



When atomic spectral lines are split by the application of an external magnetic field, it is called the Zeeman effect. The spin-orbit interaction is also a magnetic interaction, but with the magnetic field generated by the orbital motion of an electron within the atom itself. It has been described as an "internal Zeeman effect".

Spin-orbit splitting in sodium

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Effective Magnetic Field of Orbit

The magnetic field in the electron frame of reference arising from the orbital motion is

$$B = \frac{\mu_0 Zev}{4\pi r^2}$$

Assuming a circular orbit, the angular momentum is mrv, so this field can be expressed in terms of the orbital angular momentum L:

$$B = \frac{\mu_0 Ze\vec{L}}{4\pi m_e r^3}$$

For a hydrogen electron in a 2p state at a radius of 4x the Bohr radius, this translates to a magnetic field of about 0.3 Tesla. This is fairly consistent with the splitting of levels observed in the hydrogen fine structure.

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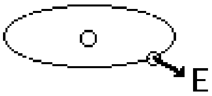
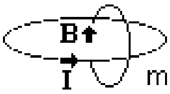
Magnetic Field in Electron Frame

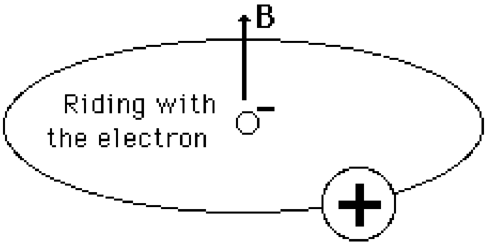


In the lab frame, the electron sees an electric field from the nucleus, but if you ride with the electron, you see a magnetic field caused by the relative motion of the nucleus.



The magnetic field at the center of a circular current loop is

$$B = \frac{\mu_0 I}{2r}$$



The effective current from the motion of a nucleus in a circular orbit is

$$I = \frac{\Delta Q}{\Delta t} = \frac{Zev}{2\pi r}$$

The effective magnetic field at the electron is then

$$B = \frac{\mu_0 Zev}{4\pi r^2}$$

Magnetic field of current loop

Express in terms of angular momentum

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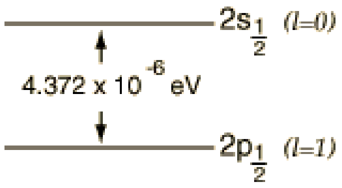
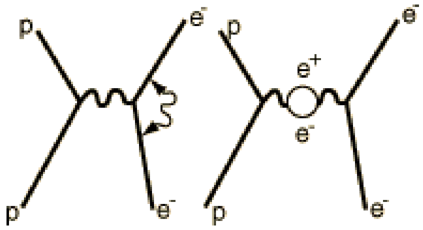
The Lamb Shift

According to the hydrogen Shrodinger equation solution, the energy levels of the hydrogen electron should depend only on the principal quantum number n. In 1951, Willis Lamb discovered that this was not so - that the 2p(1/2) state is slightly lower than the 2s(1/2) state resulting in a slight shift of the corresponding spectral line (the Lamb shift).

It might seem that such a tiny effect would be deemed insignificant, but in this case that shift probed the depths of our understanding of electromagnetic theory.





At the heart of the process is the exchange force by which charges interact by the exchange of photons (the exchange force model of the electromagnetic force). There can be a self interaction of the electron by exchange of a photon as sketched in the Feynman diagram at left. This "smears out" the electron position over a range of about 0.1 fermi (Bohr radius = 52,900 fermis). This causes the electron spin g-factor to be slightly different from 2. There is also a slight weakening of the force on the electron when it is very close to the nucleus, causing the 2s electron (which has penetration all the way to the nucleus) to be slightly higher in energy than the 2p(1/2) electron.

When we say the that the penetration of the 2s electron closer to the nucleus leads to an energy higher than that of the 2p, this sounds directly contradictory to the situation with multi-electron atoms. There the penetration of the 2s closer to the nucleus means that it has penetrated inside the 1s electrons and therefore feels a stronger attraction to the positive nucleus, leading to a lower energy level (it takes more energy to remove the 2s from the atom than the 2p). But in the case of the hydrogen atom, there is only one electron, so there is none of the shielding from inner electrons when it is in the 2s or 2p excited states. The effect

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on the energy levels has an entirely different origin, modeled by quantum electrodynamics. In the absence of this effect, the 2s and 2p would have identical energies since there is no shielding by the presence of other electrons. The "self-interaction" of the electron when it is near the proton causes the effective "smearing" of the electron charge so that its attraction to the proton is slightly weaker than it otherwise would have been. This means it has encountered an interaction which makes it slightly less tightly bound than a 2p electron, hence higher in energy.

Microwave measurement of the Lamb shift.	Significance of the Lamb shift

Saturation spectroscopy measurement of the Lamb shift.

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Measurement of the Lamb Shift

While the Lamb shift is extremely small and difficult to measure as a splitting in the optical or uv spectral lines, it is possible to make use of transitions directly between the sublevels by going to other regions of the electromagnetic spectrum. Willis Lamb made his measurements of the shift in the microwave region. He formed a beam of hydrogen atoms in the 2s(1/2) state. These atoms could not directly take the transition to the 1s(1/2) state because of the selection rule which requires the orbital angular momentum to change by 1 unit in a transition. Putting the atoms in a magnetic field to split the levels by the Zeeman effect, he exposed the atoms to microwave radiation at 2395 MHz (not too far from the ordinary microwave oven frequency of 2560 MHz).

Then he varied the magnetic field until that frequency produced

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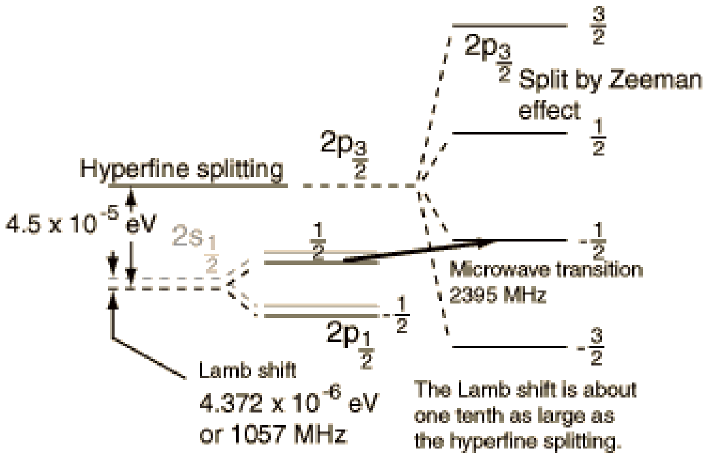

transitions from the 2p(1/2) to 2p(3/2) levels. He could then measure the allowed transition from the 2p(3/2) to the 1s(1/2) state. He used the results to determine that the zero-magnetic field splitting of these levels correspond to 1057 MHz. By the Planck relationship, this told him that the energy separation was 4.372 E-6 eV.

Saturation spectroscopy measurement of the Lamb shift.

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Significance of the Lamb Shift

When the Lamb shift was experimentally determined, it provided a high precision verification of theoretical calculations made with the quantum theory of electrodynamics. These calculations predicted that electrons continually exchanged photons, this being the mechanism by which the electromagnetic force acted. The effect of the continuous emission and absorption of photons on the electron g-factor could be calculated with great precision.

The tiny Lamb shift, measured with great precision, agreed to many decimal places with the calculated result from quantum

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electrodynamics. The measured precision gives us the electron spin g-factor as $$g=2.002319304386$$	et al., Sec 18.4.
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Zeeman effect

From Wikipedia, the free encyclopedia

The **Zeeman effect** (🔊 /ˈzeɪmən/; IPA: [ˈzeːmɑn]), named after the Dutch physicist Pieter Zeeman, is the effect of splitting a spectral line into several components in the presence of a static magnetic field. It is analogous to the Stark effect, the splitting of a spectral line into several components in the presence of an electric field. Also similarly to the Stark effect, transitions between different components have, in general, different intensities, with some being entirely forbidden (in the dipole approximation), as governed by the selection rules.

Since the distance between the Zeeman sub-levels is a function of the magnetic field, this effect can be used to measure the magnetic field, e.g. that of the Sun and other stars or in laboratory plasmas. The Zeeman effect is very important in applications such as nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, magnetic resonance imaging (MRI) and Mössbauer spectroscopy. It may also be utilized to improve accuracy in atomic absorption spectroscopy. A theory about the magnetic sense of birds assumes that a protein in the retina is changed due to the Zeeman effect.[1]

When the spectral lines are absorption lines, the effect is called **inverse Zeeman effect**.

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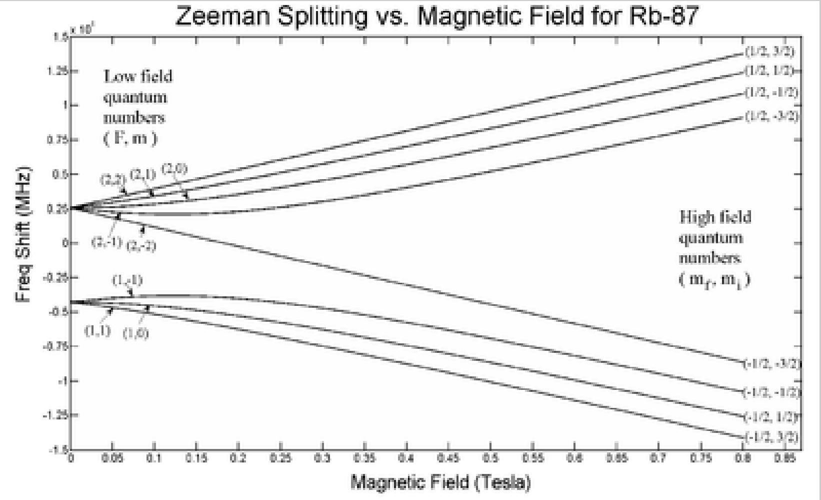


Zeeman splitting of the 5s level of Rb-87, including fine structure and hyperfine structure splitting. Here F = J + I, where I is the nuclear spin. (for Rb-87, I = 3/2)

Nomenclature

Historically, one distinguishes between the "normal" and an **anomalous Zeeman effect** that appears on transitions where the net spin of the electrons is not 0, the number of Zeeman sub-levels being even instead of odd if there's an uneven number of electrons involved. It was called "anomalous" because the electron spin had not yet been discovered, and so there was no good explanation for it at the time that Zeeman observed the effect.

At higher magnetic fields the effect ceases to be linear. At even higher field strength, when the strength of the external field is comparable to the strength of the atom's internal field, electron coupling is disturbed and the spectral lines rearrange. This is called the **Paschen-Back effect**.

In the modern scientific literature, these terms are rarely used, with a tendency to use just the "Zeeman effect".

Theoretical presentation

The total Hamiltonian of an atom in a magnetic field is

$$H = H_0 + V_M,$$

where H_0 is the unperturbed Hamiltonian of the atom, and V_M is perturbation due to the magnetic field:

$$V_M = -\vec{\mu} \cdot \vec{B},$$

where $\vec{\mu}$ is the magnetic moment of the atom. The magnetic moment consists of the electronic and nuclear parts, however, the latter is many orders of magnitude smaller and will be neglected here. Therefore,

$$\vec{\mu} = -\mu_B g \vec{J}/\hbar,$$

where μ_B is the Bohr magneton, $\vec{J}$ is the total electronic angular momentum, and g is the Landé g-factor. The operator of the magnetic moment of an electron is a sum of the contributions of the orbital angular momentum $\vec{L}$ and the spin angular momentum $\vec{S}$, with each multiplied by the appropriate gyromagnetic ratio:

$$\vec{\mu} = -\mu_B (g_l \vec{L} + g_s \vec{S})/\hbar,$$

where $g_l = 1$ and $g_s \approx 2.0023192$ (the latter is called the anomalous gyromagnetic ratio; the deviation of the value from 2 is due to Quantum Electrodynamics effects). In the case of the LS coupling, one can sum over all electrons in the atom:

$$g\vec{J} = \left\langle \sum_i (g_l \vec{l_i} + g_s \vec{s_i}) \right\rangle = \left\langle (g_l \vec{L} + g_s \vec{S}) \right\rangle,$$

where $\vec{L}$ and $\vec{S}$ are the total orbital momentum and spin of the atom, and averaging is done over a state with a given value of the total angular momentum.

If the interaction term V_M is small (less than the fine structure), it can be treated as a perturbation; this is the Zeeman effect proper. In the Paschen-Back effect, described below, V_M exceeds the LS coupling significantly (but is still small compared to H_0). In ultrastrong magnetic fields, the magnetic-field interaction may exceed H_0, in which case the atom can no longer exist in its normal meaning, and one talks about Landau levels instead. There are, of course, intermediate cases which are more complex than these limit cases.

Weak field (Zeeman effect)

If the spin-orbit interaction dominates over the effect of the external magnetic field, $\vec{L}$ and $\vec{S}$ are not separately conserved, only the total angular momentum $\vec{J}=\vec{L}+\vec{S}$ is. The spin and orbital angular momentum vectors can be thought of as precessing about the (fixed) total angular momentum vector $\vec{J}$. The (time-)"averaged" spin vector is then the projection of the spin onto the direction of $\vec{J}$:

$$\vec{S}_{avg} = \frac{(\vec{S}\cdot\vec{J})}{J^2}\vec{J}$$

and for the (time-)"averaged" orbital vector:

$$\vec{L}_{avg} = \frac{(\vec{L}\cdot\vec{J})}{J^2}\vec{J}.$$

Thus,

$$\langle V_M \rangle = \frac{\mu_B}{\hbar}\vec{J}(g_L\frac{\vec{L}\cdot\vec{J}}{J^2} + g_S\frac{\vec{S}\cdot\vec{J}}{J^2})\cdot\vec{B}.$$

Using $\vec{L}=\vec{J}-\vec{S}$ and squaring both sides, we get

$$\vec{S}\cdot\vec{J} = \frac{1}{2}(J^2+S^2-L^2) = \frac{\hbar^2}{2}[j(j+1)-l(l+1)+s(s+1)],$$

and: using $\vec{S}=\vec{J}-\vec{L}$ and squaring both sides, we get

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

Combining everything and taking $J_z=\hbar m_j$, we obtain the magnetic potential energy of the atom in the applied external magnetic field,

$$\begin{aligned} V_M &= \mu_B B m_j \left[g_L\frac{j(j+1)+l(l+1)-s(s+1)}{2j(j+1)} + g_S\frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)} \right] \\ &= \mu_B B m_j \left[1 + (g_S-1)\frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)} \right], \\ &= \mu_B B m_j g_j \end{aligned}$$

where the quantity in square brackets is the Landé g-factor g_J of the atom ($g_L = 1$ and $g_S \approx 2$) and m_j is the z-component of the total angular momentum. For a single electron above filled shells $s = 1/2$ and $j = l \pm s$, the Landé g-factor can be simplified into:

$$g_j = 1 \pm \frac{g_S - 1}{2l+1}$$

Example: Lyman alpha transition in hydrogen

The Lyman alpha transition in hydrogen in the presence of the spin-orbit interaction involves the transitions

$$2P_{1/2} \to 1S_{1/2} \text{ and } 2P_{3/2} \to 1S_{1/2}.$$

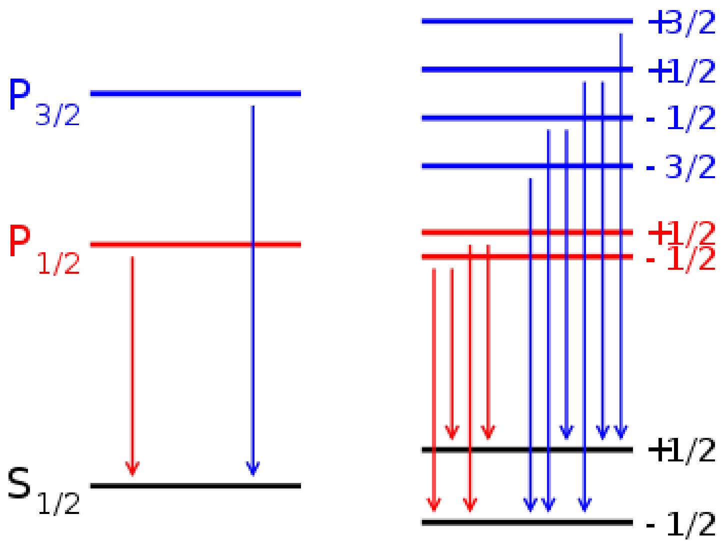
In the presence of an external magnetic field, the weak-field Zeeman effect splits the 1S$_{1/2}$ and 2P$_{1/2}$ states into 2 levels each ($m_j = 1/2, -1/2$) and the 2P$_{3/2}$ state into 4 levels ($m_j = 3/2, 1/2, -1/2, -3/2$). The Landé g-factors for the three levels are:

$g_J = 2$ for $1S_{1/2}$ (j=1/2, l=0)

$g_J = 2/3$ for $2P_{1/2}$ (j=1/2, l=1)

$g_J = 4/3$ for $2P_{3/2}$ (j=3/2, l=1).

Note in particular that the size of the energy splitting is different for the different orbitals, because the g$_J$ values are different. On the left, fine structure splitting is depicted. This splitting occurs even in the absence of a magnetic field, as it is due to spin-orbit coupling. Depicted on the right is the additional Zeeman splitting, which occurs in the presence of magnetic fields.



Strong field (Paschen-Back effect)

The Paschen-Back effect is the splitting of atomic energy levels in the presence of a strong magnetic field. This occurs when an external magnetic field is sufficiently large to disrupt the coupling between orbital ($\vec{L}$) and spin ($\vec{S}$) angular momenta. This effect is the strong-field limit of the Zeeman effect. When $s = 0$, the two effects are equivalent. The effect was named after the German physicists Friedrich Paschen and Ernst E. A. Back.

When the magnetic-field perturbation significantly exceeds the spin-orbit interaction, one can safely assume $[H_0, S] = 0$. This allows the expectation values of L_z and S_z to be easily evaluated for a state $|\psi\rangle$. The energies are simply:

$$E_z = \langle\psi| \left(H_0 + \frac{B_z \mu_B}{\hbar}(L_z + g_s S_z) \right) |\psi\rangle = E_0 + B_z \mu_B (m_l + g_s m_s).$$

The above may be read as implying that the LS-coupling is completely broken by the external field. However m_l and m_s are still "good" quantum numbers. Together with the selection rules for an electric dipole transition, i.e., $\Delta s = 0, \Delta m_s = 0, \Delta l = \pm 1, \Delta m_l = 0, \pm 1$ this allows to ignore the spin degree of freedom altogether. As a result, only three spectral lines will be visible, corresponding to the $\Delta m_l = 0, \pm 1$ selection rule. The splitting $\Delta E = B \mu_B \Delta m_l$ is *independent* of the unperturbed energies and electronic configurations of the levels being considered. It should be noted that in general (if $s \neq 0$), these three components are actually groups of several transitions each, due to the residual spin-orbit coupling.

In general, one must now add spin-orbit coupling and relativistic corrections (which are of the same order, known as 'fine structure') as a perturbation to these 'unperturbed' levels. First order perturbation theory with these fine-structure corrections yields the following formula for the Hydrogen atom in the Paschen-Back limit:[2]

$$E_{z+fs} = E_z + \frac{\alpha^2}{2n^3}\left[\frac{3}{4n} - \left(\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)}\right)\right]$$

Intermediate field for j = 1/2

In the magnetic dipole approximation, the Hamiltonian which includes both the hyperfine and Zeeman interactions is

$$\begin{aligned} H &= hA\vec{I}\cdot\vec{J} - \mu\cdot\vec{B} \\ H &= hA\vec{I}\cdot\vec{J} - \mu_B(g_J\vec{J} + g_I\vec{I})\cdot\vec{B} \end{aligned}$$

To arrive at the Breit-Rabi formula we will include the hyperfine structure (interaction between the electron's spin and the magnetic moment of the nucleus), which is governed by the quantum number $F \equiv |\vec{F}| = |\vec{J} + \vec{I}|$, where $\vec{I}$ is the spin angular momentum operator of the nucleus. Alternatively, the derivation could be done with J only. The constant A is known as the zero field hyperfine constant and is given in units of Hertz. μ_B is the Bohr magneton. $\hbar\vec{J}$ and $\hbar\vec{I}$ are the electron and nuclear angular momentum operators. g_J and g_F can be found via a classical vector coupling model or a more detailed quantum mechanical calculation to be:

$$\begin{aligned} g_J &= g_L\frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_S\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \\ g_F &= g_J\frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I\frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)} \end{aligned}$$

As discussed, in the case of weak magnetic fields, the Zeeman interaction can be treated as a perturbation to the $|F, m_f\rangle$ basis. In the high field regime, the magnetic field becomes so large that the Zeeman effect will dominate, and we must use a more complete basis of $|I, J, m_I, m_J\rangle$ or just $|m_I, m_J\rangle$ since I and J will be constant within a given level.

To get the complete picture, including intermediate field strengths, we must consider eigenstates which are superpositions of the $|F, m_F\rangle$ and $|m_I, m_J\rangle$ basis states. For $J = 1/2$, the Hamiltonian can be solved analytically, resulting in the Breit-Rabi formula. Notably, the electric quadrapole interaction is zero for $L = 0$ ($J = 1/2$), so this formula is fairly accurate.

To solve this system, we note that at all times, the total angular momentum projection $m_F = m_J + m_I$ will be conserved. Furthermore, since $J = 1/2$ between states m_J will change between only $\pm 1/2$. Therefore, we can define a good basis as:

$$|\pm\rangle \equiv |m_J = \pm 1/2, m_I = m_F \mp 1/2\rangle$$

We now utilize quantum mechanical ladder operators, which are defined for a general angular momentum operator L as

$$L_{\pm} \equiv L_x \pm iL_y$$

These ladder operators have the property

$$L_{\pm}|L,m_L\rangle = \sqrt{(L \mp m_L)(L \pm m_L + 1)}|L,m_L \pm 1\rangle$$

as long as m_L lies in the range $-L, \ldots\ldots, L$ (otherwise, they return zero). Using ladder operators $J_{\pm}$ and $I_{\pm}$ We can rewrite the Hamiltonian as

$$H = hAI_zJ_z + \frac{hA}{2}(J_+I_- + J_-I_+) - \mu_B B(g_J J_z + g_I I_Z)$$

Now we can determine the matrix elements of the Hamiltonian:

$$\begin{aligned}\langle\pm|H|\pm\rangle &= -\frac{1}{4}A - \mu_B B g_I m_F \pm \frac{1}{2}(hAm_F - \mu_B B(g_J - g_I)) \\ \langle\pm|H|\mp\rangle &= \frac{1}{2}hA\sqrt{(I + 1/2)^2 - m_F^2}\end{aligned}$$

Solving for the eigenvalues of this matrix, (as can be done by hand, or more easily, with a computer algebra system) we arrive at the energy shifts:

$$\begin{aligned}\Delta E_{F=I\pm1/2} &= -\frac{h\Delta W}{2(2I+1)} + \mu_B g_I m_F B \pm \frac{h\Delta W}{2}\sqrt{1 + \frac{2m_F x}{I+1/2} + x^2} \\ x &\equiv \frac{\mu_B B(g_J - g_I)}{h\Delta W} \qquad \Delta W = A\left(I + \frac{1}{2}\right)\end{aligned}$$

where ΔW is the splitting (in units of Hz) between two hyperfine sublevels in the absence of magnetic field B,

x is referred to as the 'field strength parameter' (Note: for $m = -(I + 1/2)$ the square root is an exact square, and should be interpreted as $+(1 - x)$). This equation is known as the **Breit-Rabi formula** and is useful for systems with one valence electron in an s ($J = 1/2$) level.[3][4]

Note that index F in $\Delta E_{F=I\pm1/2}$ should be considered not as total angular momentum of the atom but as *asymptotic total angular momentum*. It is equal to total angular momentum only if $B = 0$ otherwise eigenvectors corresponding different eigenvalues of the Hamiltonian are the superpositions of states with different F but equal m_F (the only exceptions are $|F = I + 1/2, m_F = \pm F\rangle$).

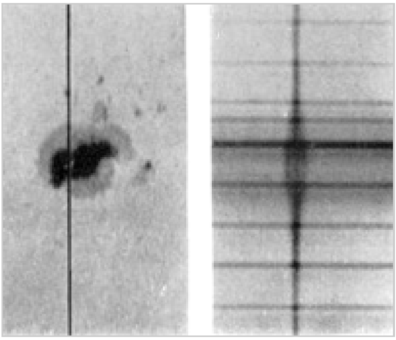
Applications

Astrophysics

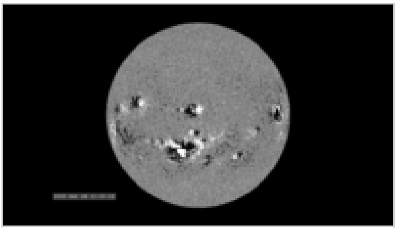
George Ellery Hale was the first to notice the Zeeman effect in the solar spectra, indicating the existence of strong magnetic fields in sunspots. Such fields can be quite high, on the order of .1 Tesla or higher. Today, the Zeeman effect is used to produce magnetograms showing the variation of magnetic field on the sun.

See also

- Magneto-optic Kerr effect
- Voigt effect
- Faraday effect
- Cotton-Mouton effect
- Polarization spectroscopy
- Zeeman energy



Zeeman effect on a sunspot spectral line



Solar magnetogram

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2. ^ Griffiths, David J. (2004). *Introduction to Quantum Mechanics* (2nd ed.). Prentice Hall. p. 247. ISBN 0-13-111892-7. OCLC 40251748 (//www.worldcat.org/oclc/40251748) .
3. ^ Woodgate, *Elementary Atomic Structure*, section 9.
4. ^ first appeared in G. Breit and I. Rabi, Phys. rev. 38, 2082 (1931).

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External links

- Zeeman Effect Apparatus Manufacturer (http://www.holmarc.com/zeeman_effect_apparatus.html)

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Dirac Equation

Relativistic, applies gauge invariance

Non-relativistic limit ⇒ Pauli equation

$\vec{S}$, $g = 2$

1928 -1930 prediction of e^+

$\uparrow$

positron

$\downarrow$

anti particle