Zeeman effect in Na, Cd, and Hg

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(Date: January 13, 2012)

Abstract:

In 1897, Pieter Zeeman observed the splitting of the atomic spectrum of cadmium (Cd) from one main line to three lines. Such a splitting of lines is called the normal Zeeman effect. According to the oscillation model by Hendrik Lorentz, the Zeeman splitting arises from the oscillation of charged particles in atoms. The discovery of the Zeeman effect indicates that the charged particles are electrons. In 1897 - 1899, J.J. (Joseph John) Thomson independently found the existence of electrons from his explorations on the properties of cathode rays.

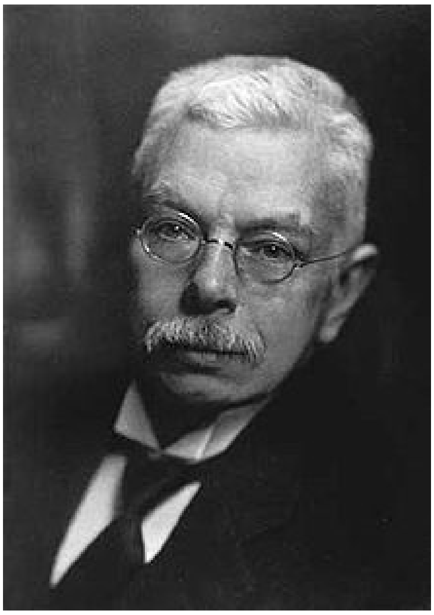
There are few atoms showing the normal Zeeman effect. In contrast, many atoms shows anomalous Zeeman effects. For the spectra of sodium (Na). for example, there are two D-lines (yellow) in the absence of the magnetic field. When the magnetic field is applied, each line is split into four and six lines, respectively. Although Zeeman himself observed the spectra of Na, he could not find the splitting of the D lines in the presence of the magnetic field because of the low resolution of his spectrometer. The electron configuration of Na is similar to that of hydrogen. There is one electron outside the closed shell. Instead, he chose Cd for his experiment and found the normal Zeeman effect (three lines). In the electron configuration of Cd, there are two electrons outside the closed shell. The three lines observed in Cd was successfully explained in terms of the Lorentz theory. It seems that the choice of Cd by Zeeman is fortunate to the development of atomic physics. If Zeeman found the anomalous Zeeman effect in Na by using spectrometer with much higher resolution, Lorentz might have some difficulty in explaining such a complicated phenomenon. In fact, only the quantum mechanics can explain the normal Zeeman effect, the anomalous Zeeman effect, and the Paschen-Back effect (Zeeman effect in an extremely large magnetic field). Here we note that the Fabry-Perot interferometer (which is used for the measurement of Zeeman effect in our laboratory), designed in 1899 by C. Fabry and A. Perot, represents a significant improvement over the Michelson interferometer.

In our Advanced laboratory [Senior Laboratory (Phys.427, Phys.429) and Graduate Laboratory (Phys.527)], students (both undergraduate and graduate students) are supposed to do the experiment for the Zeeman splitting of mercury (Hg), using an equipment consisting of magnetic field, Hg light source, polarizer, Fabry-Perot Etalon, CCD camera, and computer. The normal Zeeman splitting is observed in Hg. The electron configuration of Hg is similar to that of Cd, where two electrons are outside the closed shell. The

introduction of such new techniques may lead to clear visualization of the Zeeman effect in the laboratory class.

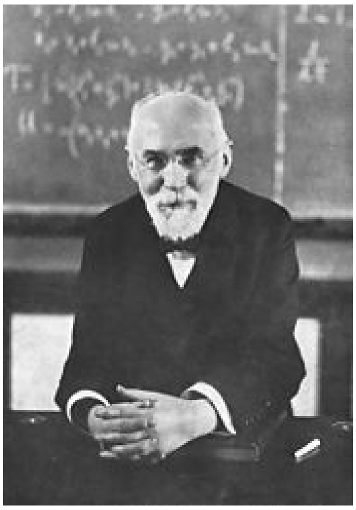
In this lecture note, we present both classical and quantum mechanical theories on the Zeeman effect. (1) Lorenz theory, (2) the Zeeman effect of Na using quantum mechanics, (3) the Zeeman effect of Cd and Hg. These notes will be helpful to understanding the Zeeman effect from a view point of quantum mechanics. "The atomic spectra are sort of voices which can be heard from the quantum world."

Pieter Zeeman (25 May 1865 – 9 October 1943) was a Dutch physicist who shared the 1902 Nobel Prize in Physics with Hendrik Lorentz for his discovery of the Zeeman effect.



http://en.wikipedia.org/wiki/Pieter_Zeeman

Hendrik Antoon Lorentz (18 July 1853 – 4 February 1928) was a Dutch physicist who shared the 1902 Nobel Prize in Physics with Pieter Zeeman for the discovery and theoretical explanation of the Zeeman effect. He also derived the transformation equations subsequently used by Albert Einstein to describe space and time.



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1. Orbital angular momentum and its magnetic moment of one electron

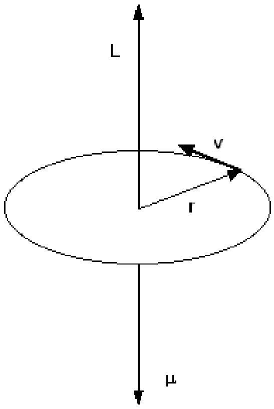

Fig.1 Orbital (circular) motion of electron with mass m and a charge –*e*. The direction of orbital angular momentum *L* is perpendicular to the plane of the motion (*x*-*y* plane).

The orbital angular momentum of an electron (charge –*e* and mass *m*) *L* is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (m\mathbf{v}) \text{, or } L_z = mvr \ .$$

According to the de Broglie relation, we have

$$p(2\pi r) = \frac{h}{\lambda} 2\pi r = nh\,,$$

where p (= mv) is the momentum ($p = \frac{h}{\lambda}$), n is integer, h is the Planck constant, and λ is the wavelength.

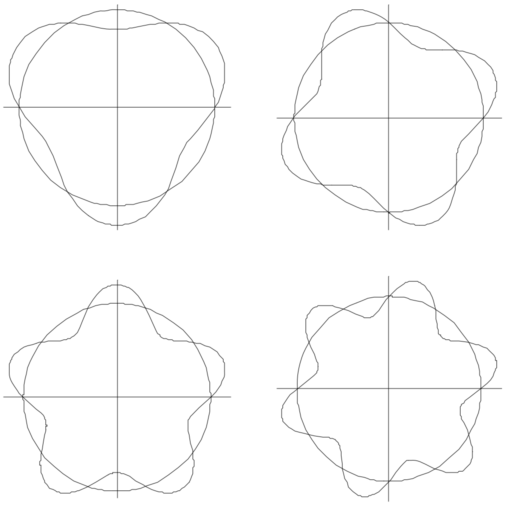

Fig. 2 Acceptable wave on the ring (circular orbit). The circumference should be equal to the integer n (=1, 2, 3,…) times the de Broglie wavelength λ. The picture of fitting the de Broglie waves onto a circle makes clear the reason why the orbital angular momentum is quantized. Only integral numbers of wavelengths can be fitted. Otherwise, there would be destructive interference between waves on successive cycles of the ring.

Then the angular momentum L_z is described by

$$L_z = pr = mvr = \frac{nh}{2\pi} = n\hbar\,.$$

The magnetic moment of the electron is given by

$$\mu_z = \frac{1}{c} I_\theta A,$$

where c is the velocity of light, $A = \pi r^2$ is the area of the electron orbit, and I_θ is the current due to the circular motion of the electron. Note that the direction of the current is opposite to that of the velocity because of the negative charge of the electron. The current I_θ is given by

$$I_\theta = -\frac{e}{T} = -\frac{e}{(2\pi r/v)} = -\frac{ev}{2\pi r},$$

where T is the period of the circular motion. Then the magnetic moment is derived as

$$\mu_z = \frac{1}{c} I_\theta A = -\frac{evr}{2c} = -\frac{e}{2mc} L_z = -\frac{e\hbar}{2mc}\frac{L_z}{\hbar} = -\frac{\mu_B}{\hbar} L_z \quad (e > 0),$$

where μ_B ($= \frac{e\hbar}{2mc}$) is the Bohr magneton. $\mu_B = 9.27400915 \times 10^{-21}$ emu. emu=erg/Oe. Since $L_z = n\hbar$, the magnitude of orbital magnetic moment is $n\mu_B$.

2. Spin angular momentum and its magnetic moment

The spin magnetic moment is given by

$$\boldsymbol{\mu}_S = -\frac{2\mu_B}{\hbar}\mathbf{S},$$

where $\boldsymbol{S}$ is the spin angular momentum.
In quantum mechanics, the above equation is described by

$$\hat{\mu} = -\frac{2\mu_B}{\hbar}\hat{S},$$

using operators (Dirac). When $\hat{S} = \frac{\hbar}{2}\hat{\sigma}$, we have $\hat{\mu} = -\mu_B\hat{\sigma}$. The spin angular momentum is described by the Pauli matrices (operators)

$$\hat{S}_x = \frac{\hbar}{2}\hat{\sigma}_x, \ \hat{S}_y = \frac{\hbar}{2}\hat{\sigma}_y \ \hat{S}_z = \frac{\hbar}{2}\hat{\sigma}_z.$$

Using the basis,

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

we have

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The commutation relations are valid;

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \ [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, \ [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y.$$

The resultant magnetic moment of an electron is given by

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}).$$

3. Magnetic moment of atom

We consider an isolated atom with incomplete shell of electrons. The orbital angular momentum ***L*** and spin angular momentum ***S*** are given by

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2 + \mathbf{L}_3 + ..., \ \mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + ...$$

The total angular momentum ***J*** is defined by

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

The total magnetic moment $\boldsymbol{\mu}$ is given by

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}).$$

The Landé g-factor is defined by

$$\boldsymbol{\mu}_J = -\frac{g_J \mu_B}{\hbar}\mathbf{J},$$

where

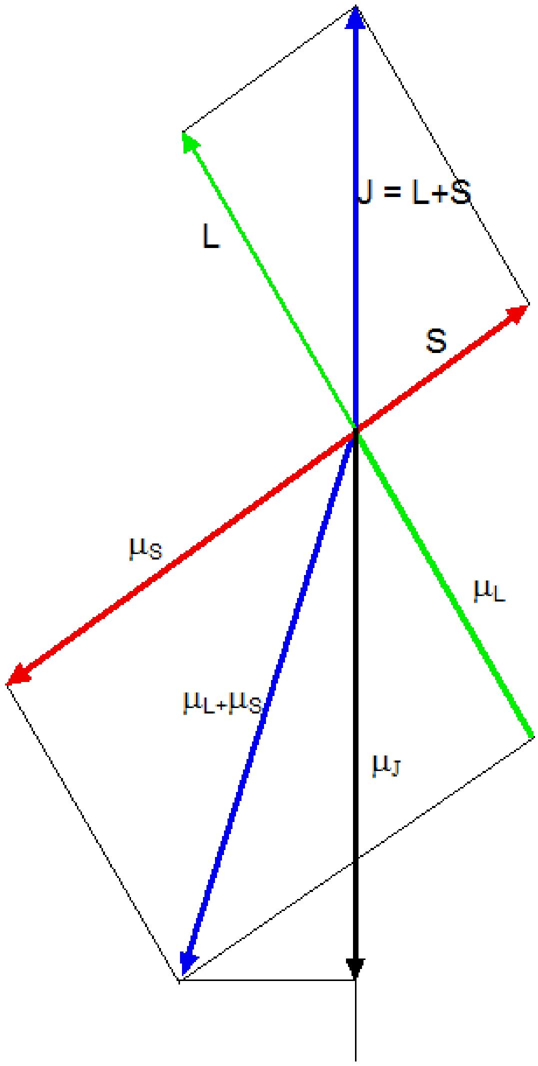

Fig.3 Basic classical vector model of orbital angular momentum (***L***), spin angular momentum (***S***), orbital magnetic moment ($\boldsymbol{\mu}_L$), and spin magnetic moment ($\boldsymbol{\mu}_S$). ***J*** (= ***L*** + ***S***) is the total angular momentum. $\boldsymbol{\mu}_J$ is the component of the total magnetic moment ($\boldsymbol{\mu}_L + \boldsymbol{\mu}_S$) along the direction (-*J*).

Suppose that

$$\mathbf{L} = a\mathbf{J} + \mathbf{L}_\perp \text{ and } \mathbf{S} = b\mathbf{J} + \mathbf{S}_\perp,$$

where *a* and *b* are constants, and the vectors $\mathbf{S}_\perp$ and $\mathbf{L}_\perp$ are perpendicular to ***J***.

Here we have the relation $a + b = 1$, and $\mathbf{L}_\perp + \mathbf{S}_\perp = 0$. The values of *a* and *b* are determined as follows.

$$a = \frac{\mathbf{J}\cdot\mathbf{L}}{\mathbf{J}^2}, \quad b = \frac{\mathbf{J}\cdot\mathbf{S}}{\mathbf{J}^2}.$$

Here we note that

$$\mathbf{J}\cdot\mathbf{S} = (\mathbf{L}+\mathbf{S})\cdot\mathbf{S} = \mathbf{S}^2 + \mathbf{L}\cdot\mathbf{S} = \mathbf{S}^2 + \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2}{2} = \frac{\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2}{2},$$

or

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

using the average in quantum mechanics. The total magnetic moment $\boldsymbol{\mu}$ is

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) = -\frac{\mu_B}{\hbar}[(a+2b)\mathbf{J} + (L_\perp + 2S_\perp)].$$

Thus we have

$$\boldsymbol{\mu}_J = -\frac{\mu_B}{\hbar}(a+2b)\mathbf{J} = -\frac{\mu_B}{\hbar}(1+b)\mathbf{J} = -\frac{g_J\mu_B}{\hbar}\mathbf{J},$$

with

$$g_J = 1 + b = 1 + \frac{\mathbf{J}\cdot\mathbf{S}}{\mathbf{J}^2} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

((Note))
The spin component is given by

$$\mathbf{S} = b\mathbf{J} + \mathbf{S}_\perp = (g_J - 1)\mathbf{J} + \mathbf{S}_\perp,$$

with $b = g_J - 1$. The de Gennes factor is defined by

$$\frac{(g_J-1)^2\mathbf{J}^2}{\hbar^2}=(g_J-1)^2J(J+1)\,.$$

In ions with strong spin-orbit coupling the spin is not a good quantum number, but rather the total angular momentum , ***J*** = ***L***+***S***. The spin operator is described by

$$\mathbf{S}=(g_J-1)\mathbf{J}\,.$$

4. Spin-orbit interaction in an electron around the nucleus (SI units)

The electron has an orbital motion around the nucleus. This also implies that the nucleus has an orbital motion around the electron. The motion of nucleus produces an orbital current. From the Biot-Savart's law, it generates a magnetic field on the electron.

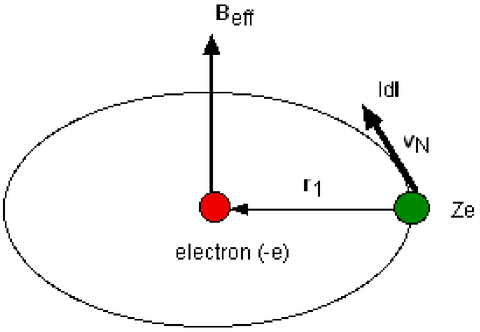

Fig.4 Simple model for the spin-orbit interaction. The orbital current due to the circular motion of the nucleus (with velocity $\mathbf{v}_N$ and charge *Ze*) produces an magnetic field at the center where the electron is located.

The current *I* due to the movement of nucleus (charge *Ze*, *e*>0) is given by

$$Id\mathbf{l}=Ze\mathbf{v}_N\,,$$

where $\mathbf{v}_N$ is the velocity of the nucleus and $\frac{d\mathbf{l}}{dt}=\mathbf{v}_N$. Note that

$$Id\mathbf{l}=\frac{\Delta q}{\Delta t}d\mathbf{l}=\Delta q\frac{d\mathbf{l}}{dt}=Ze\mathbf{v}_N\,.$$

The effective magnetic field at the electron at the origin is

$$\mathbf{B}_{eff} = \frac{\mu_0 I}{4\pi} \frac{d\mathbf{l} \times \mathbf{r}_1}{r_1^3}, \qquad \mathbf{v}_N = v\mathbf{e}_\theta ,$$

where v is the velocity of the electron. Then we have

$$\mathbf{B}_{eff} = \frac{Ze\mu_0}{4\pi} \frac{\mathbf{v}_N \times \mathbf{r}_1}{r_1^3} = \frac{Ze\mu_0}{4\pi} \frac{v\mathbf{e}_\theta \times \mathbf{r}_1}{r_1^3} .$$

Since $\mathbf{r}_1 = -\mathbf{r}$, $\mathbf{B}_{eff}$ can be rewritten as

$$\mathbf{B}_{eff} = \frac{Ze\mu_0}{4\pi} \frac{\mathbf{v}_N \times \mathbf{r}_1}{r_1^3} = \frac{Ze\mu_0}{4\pi} \frac{v\mathbf{e}_\theta \times \mathbf{r}_1}{r_1^3} ,$$

or

$$\mathbf{B}_{eff} = -\frac{Ze\mu_0}{4\pi} \frac{v\mathbf{e}_\theta \times \mathbf{r}}{r^3} = \frac{Ze\mu_0 v}{4\pi} \frac{\mathbf{e}_\theta \times \mathbf{r}}{r^2} = \frac{Ze\mu_0 v}{4\pi} \frac{\mathbf{e}_z}{r^2} = \frac{Ze\mu_0 v}{4\pi} \frac{\mathbf{e}_z}{r^2} = \frac{Ze\mu_0 mrv}{4\pi mr^3} \mathbf{e}_z .$$

The Coulomb potential energy is given by

$$V_c(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r}, \qquad \frac{dV_c(r)}{dr} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2} .$$

Thus we have

$$\begin{aligned} \mathbf{B}_{eff} &= \frac{Ze\mu_0 mrv}{4\pi mr^3} \mathbf{e}_z = \frac{Ze^2 \mu_0}{4\pi mer^3} L_z \mathbf{e}_z \\ &= \frac{1}{mer} \frac{Ze^2 \varepsilon_0 \mu_0}{4\pi\varepsilon_0 r^2} L_z \mathbf{e}_z = \frac{1}{mec^2 r} \frac{dV_c(r)}{dr} L_z \mathbf{e}_z \end{aligned} .$$

where

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}, \quad \text{and} \qquad L_z = mvr$$

Then we get

$$\mathbf{B}_{eff} = \frac{1}{mec^2} \frac{1}{r} \frac{dV_c(r)}{dr} L_z \mathbf{e}_z ,$$

where L_z is the *z*-component of the orbital angular momentum, $L_z = mvr$.
The spin magnetic moment is given by

$$\boldsymbol{\mu}_s = -\frac{2\mu_B}{\hbar}\mathbf{S}.$$

The Zeeman energy is given by

$$\begin{aligned} H_{LS} &= -\frac{1}{2}\boldsymbol{\mu}_s \cdot \mathbf{B}_{eff} = -\frac{1}{2}\left(-\frac{2\mu_B}{\hbar}\mathbf{S}\right)\cdot\left(\frac{1}{mec^2}\frac{1}{r}\frac{dV_c(r)}{dr}\mathbf{L}\right) \\ &= \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV_c(r)}{dr}\mathbf{S}\cdot\mathbf{L} = \xi(\mathbf{S}\cdot\mathbf{L}) \end{aligned}$$

((Thomas correction))

Thomas factor 1/2, which represents an additional relativistic effect due to the acceleration of the electron. The electron spin, magnetic moment, and spin-orbit interaction can be derived directly from the Dirac relativistic electron theory. The Thomas factor is built in the expression.

$$H_{LS} = \xi \mathbf{S}\cdot\mathbf{L},$$

with

$$\xi = \left\langle \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV_c(r)}{dr} \right\rangle = \frac{1}{2}Z\left(\frac{e}{mc}\right)^2 \frac{1}{4\pi\varepsilon_0}\left\langle \frac{1}{r^3} \right\rangle_{av}.$$

When we use the formula

$$\left\langle r^{-3}\right\rangle = \frac{Z^3}{n^4 a_0{}^3 l(l+1/2)(l+1)},$$

the spin-orbit interaction constant ξ is described by

$$\begin{aligned}\xi &= \frac{e^2 Z^4}{2m^2c^2n^4(4\pi\varepsilon_0)a_0{}^3 l(l+1/2)(l+1)} \\ &= \frac{m^3e^8Z^4}{2m^2c^2n^4\hbar^6(4\pi\varepsilon_0)^4 l(l+1/2)(l+1)} \quad , \\ &= \frac{me^8Z^4}{2c^2n^4\hbar^6(4\pi\varepsilon_0)^4 l(l+1/2)(l+1)}\end{aligned}$$

where

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.52917720859 \text{ Å}.$$

(Bohr radius) (from NIST physics constants)

The energy level (negative) is given by

$$|E_n| = \frac{Z^2e^2}{8\pi\varepsilon_0 n^2 a_0} = \frac{mZ^2e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = \frac{1}{2}mc^2\frac{\alpha^2Z^2}{n^2}.$$

The ratio $\hbar^2\xi/|E_n|$ is

$$\frac{\hbar^2\xi}{|E_n|} = \frac{e^4Z^2}{c^2n^2\hbar^2 l(l+1/2)(l+1)} = \frac{(\alpha Z)^2}{n^2}\frac{1}{l(l+1/2)(l+1)},$$

with

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137.036} = 7.2973525698 \times 10^{-3}$$

ξ can be also expressed by

$$\xi = \frac{(\alpha Z)^2}{n^2\hbar^2}\frac{|E_n|}{l(l+1/2)(l+1)} = \frac{(\alpha Z)^4}{2n^4\hbar^2}mc^2\,\frac{1}{l(l+1/2)(l+1)}$$

Then we have

$$\begin{aligned} H_{LS} &= \frac{\xi}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) = \frac{\xi\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)] \\ &= \frac{(\alpha Z)^4}{4n^4}mc^2\,\frac{[j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)} \end{aligned},$$

((Note)) For $l = 0$ the spin-orbit interaction vanishes and therefore $\xi = 0$ in this case.

5. Separation of 3p and 3s energy levels in Na

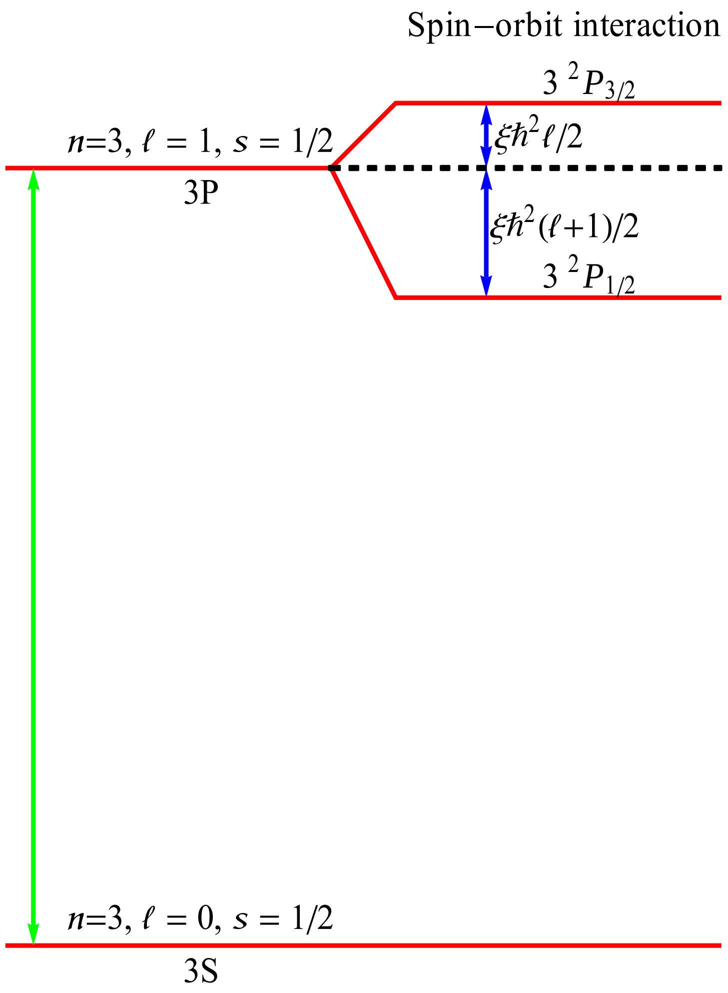

Fig.12 Energy levels of Na with and without spin-orbit interaction. The 3P level is slightly different from the 3S level. The 3P level is split into 3 $^2P_{3/2}$ (4 degeneracies) and 3 $^2P_{1/2}$ (3 degeneracies) due to the spin-orbit interaction.

The well known bright doublet which is responsible for the bright yellow light from a sodium lamp may be used to demonstrate several of the influences which cause splitting of the emission lines of atomic spectra. The transition which gives rise to the doublet is from the 3*p* to the 3*s* level, levels which would be the same in the hydrogen atom. The fact that the 3s (orbital quantum number l = 0) is lower than the 3*p* (l = 1) is a good example of the dependence of atomic energy levels on angular momentum. The 3s electron penetrates the 1*s* shell more and is less effectively shielded than the 3*p* electron, so the 3*s* level is lower (more tightly bound). The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum . The 3*p* level is split into states with total angular momentum j = 3/2 and j = 1/2 by the magnetic energy of the electron spin in the presence of the internal magnetic field caused by the orbital motion. This effect is called the spin-orbit effect. In the presence of an additional externally applied magnetic field, these levels are further split by the magnetic interaction, showing dependence of the energies on the z-component of the total angular momentum. This splitting gives the Zeeman effect for sodium.

When the wavefunctions for electrons with different orbital quantum numbers are examined, it is found that there is a different amount of penetration into the region occupied by the 1*s* electrons. This penetration of the shielding 1*s* electrons exposes them to more of the influence of the nucleus and causes them to be more tightly bound, lowering their associated energy states. In the case of Na with two filled shells, the 3s electron penetrates the inner shielding shells more than the 3p and is significantly lower in energy.

6. The states of 3 $^2S_{1/2}$, 3 $^2P_{3/2}$, and 3 $^2P_{1/2}$ in Na

The electron configuration of Na is given by

Na: $(1s)^2(2s)^2(2p)^6(3s)$

The inner 10 electrons can be visualized to form a spherically symmetrical electron cloud. We are interested in the excitation of the 11-th electron from 3s to a possible higher state.

(a) The 3s state

For the electron with 3s state (l = 0, s = 1/2),

$$D_0 \times D_{1/2} = D_{1/2}$$

Thus we have j = 1/2 (the degeneracy 2). The state is described by 3 $^2S_{1/2}$ (or simply $^2S_{1/2}$). Here we use the notation of $n\ ^{2S+1}L_j$ where n is the principal quantum number, s is the spin number, l is the orbital angular momentum, and j is the resultant angular momentum.

$$|j = 1/2, m = 1/2\rangle = |m_l = 0, m_s = 1/2\rangle$$

$$|j = 1/2, m = -1/2\rangle = |m_l = 0, m_s = -1/2\rangle$$

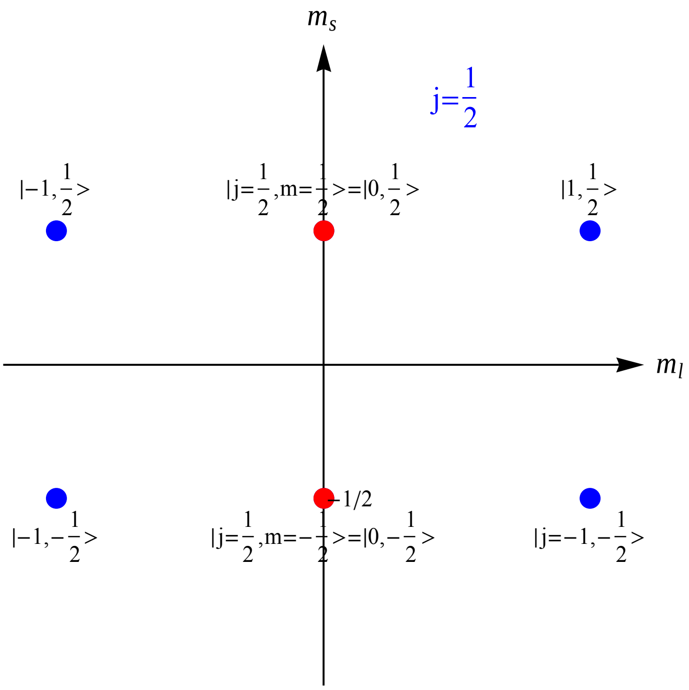

Fig.13 $\left|j=\frac{1}{2},m\right\rangle$. ($l$ = 0). m = 1/2. m = -1/2. The recursion relation to obtain the Clebsch-Gordan coefficients.

(b) The 3*p* state

For the electron with 3p state ($l = 1$, $s = 1/2$), we have

$$D_1 \text{ x } D_{1/2} = D_{3/2} + D_{1/2}$$

Thus we have j = 3/2 (the degeneracy 4) and j = 1/2 (degeneracy 2). These states are described by 3 $^2P_{3/2}$ (j = 3/2) and 3 $^2P_{1/2}$ (j = 1/2).

Note that

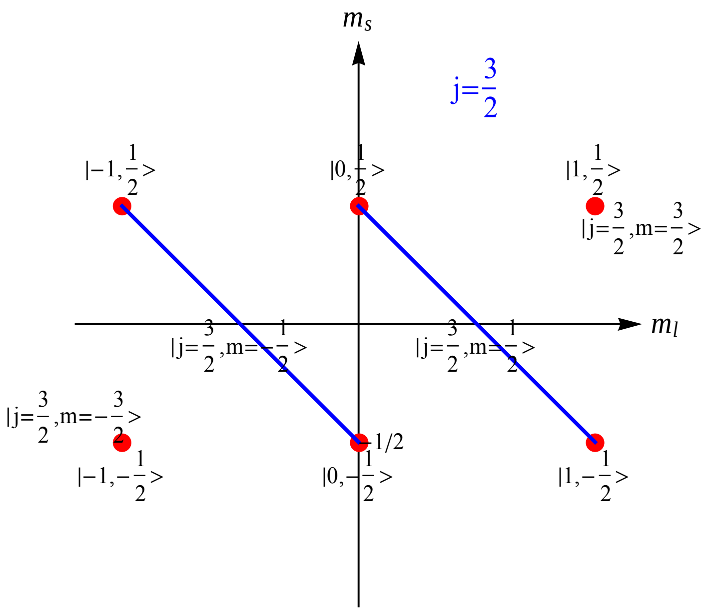

Fig.14 $\left| j=\frac{3}{2},m\right\rangle$. ($l$ = 1). The recursion relation to obtain the Clebsch-Gordan coefficients.

The Clebsch-Gordon coefficients can be calculated using the Mathematica.

(i) For j = 3/2 (3 $^2P_{3/2}$),

$$\left| j=3/2,m=-3/2\right\rangle =\left| m_l=-1,m_s=-1/2\right\rangle$$

$$\left| j=3/2,m=-1/2\right\rangle =\sqrt{\frac{2}{3}}\left| m_l=0,m_s=-1/2\right\rangle +\frac{1}{\sqrt{3}}\left| m_l=-1,m_s=1/2\right\rangle$$

$$\left| j=3/2,m=1/2\right\rangle =\frac{1}{\sqrt{3}}\left| m_l=1,m_s=-1/2\right\rangle +\sqrt{\frac{2}{3}}\left| m_l=0,m_s=1/2\right\rangle$$

$$\left| j=3/2,m=3/2\right\rangle =\left| m_l=1,m_s=1/2\right\rangle$$

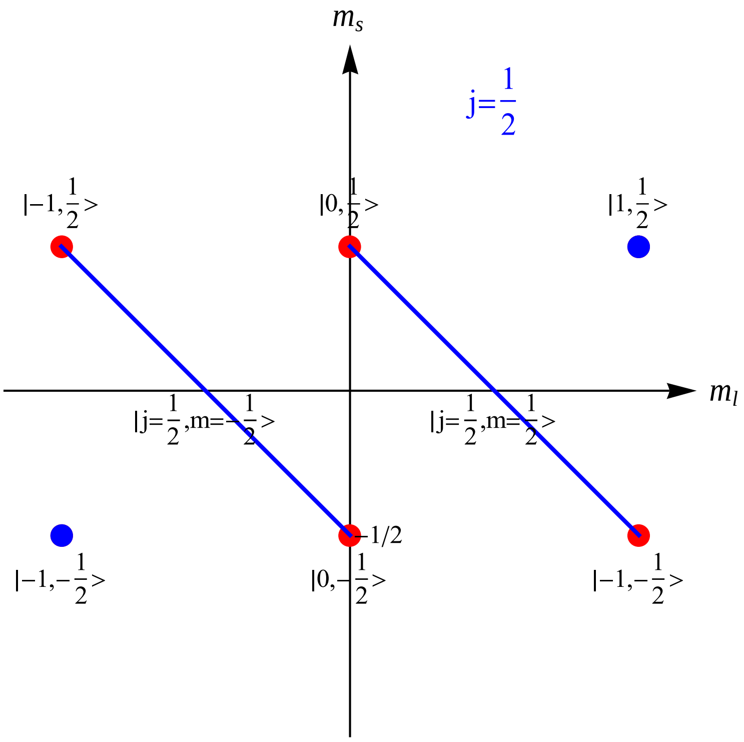

Fig.15 $\left|j=\frac{1}{2},m\right\rangle$. l = 1. The recursion relation to obtain the Clebsch-Gordon coefficients.

(ii) For j = 1/2 ($3\ ^2P_{1/2}$),

$$\left|j=1/2,m=-1/2\right\rangle=\frac{1}{\sqrt{3}}\left|m_l=0,m_s=-1/2\right\rangle-\sqrt{\frac{2}{3}}\left|m_l=-1,m_s=1/2\right\rangle$$

$$\left|j=1/2,m=1/2\right\rangle=\sqrt{\frac{2}{3}}\left|m_l=1,m_s=-1/2\right\rangle-\frac{1}{\sqrt{3}}\left|m_l=0,m_s=1/2\right\rangle$$

(c) *g* factors

The Lande *g*-factor is defined by

$$g_J = \frac{3}{2} + \frac{s(s+1) - l(l+1)}{2j(j+1)}$$

(see the Appendix)

Table

Term	j	l	S	g_J
$3\,^2P_{3/2}$	3/2	1	1/2	4/3
$3\,^2P_{1/2}$	1/2	1	1/2	2/3
$3\,^2S_{1/2}$	1/2	0	1/2	2

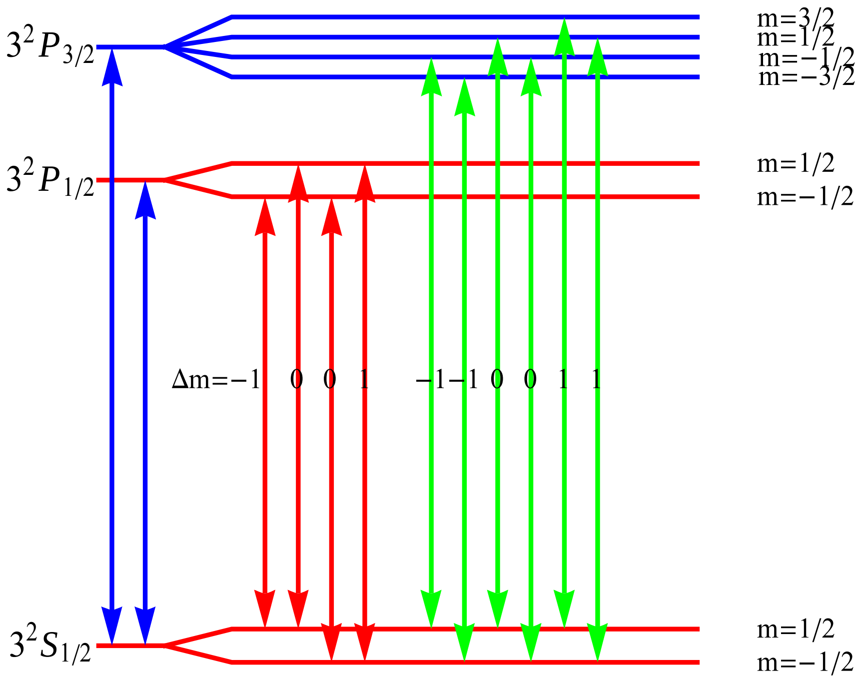

Fig.7 Schematic diagram of energy levels in Na ($n = 3$) with and without magnetic field B. The splitting of energy levels occurs due to the spin-orbit interaction and the Zeeman effect.

The wavelength of sodium D lines is given by

$\lambda = 589.6$ nm (3 $^3P_{1/2}$ - 3 $^3S_{1/2}$).

$\lambda = 589.0$ nm (3 $^3P_{3/2}$ - 3 $^3S_{1/2}$).

The sodium D lines correspond to the 3p → 3s transition. In the absence of a magnetic field *B*, the spin orbit interaction splits the upper 3p state into 3 $^2P_{3/2}$ and 3 $^2P_{1/2}$ terms separated by 17 cm^{-1}. The lower 3 $^2S_{1/2}$ has no spin-orbit interaction.

8. Quantum mechanics for system with one electron

(a) Spin orbit interaction

The spin-orbit interaction serves to remove the *l* degeneracy of the eigenenergies of hydrogen atom. If the spin-orbit interaction is neglected, energies are dependent only on *n* (principal quantum number). In the presence of spin-orbit interaction (*n*, *l*, *s* = 1/2; *j*, *m*) are good quantum numbers. Energies are dependent only on (*n*, *l*, *j*).

We introduce a new Hamiltonian given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{LS},$$

$$\hat{J} = \hat{L} + \hat{S},$$

$$\hat{H}_{LS} = \xi \hat{L} \cdot \hat{S} = \frac{1}{2}\xi(\hat{J}^2 - \hat{L}^2 - \hat{S}^2),$$

The Hamiltonian $\hat{H}_0$ commutes with all the components of $\hat{L}$ and $\hat{S}$.

$$[\hat{H}_0, \hat{\mathbf{L}}^2] = [\hat{H}_0, \hat{L}_z^2] = [\hat{H}_0, \hat{L}_z],$$

$$[\hat{H}_0, \hat{S}^2] = [\hat{H}_0, \hat{S}_z^2] = [\hat{H}_0, \hat{S}_z],$$

$$[\hat{H}_0, \hat{H}_{LS}] = \hat{0},$$

or

$$[\hat{H},\hat{H}_0]=\hat{0},$$

$$[\hat{H},\hat{S}_z]\neq\hat{0},$$

and

$$[\hat{H},\hat{L}_z]\neq\hat{0}.$$

Thus we conclude that

$|\psi\rangle$ is the simultaneous eigenket of the mutually commuting observables$\{\hat{H}_0, \hat{L}^2, \hat{S}^2, \hat{J}^2,$ and $\hat{J}_z\}$.

$$\hat{H}_0|\psi\rangle=E_n^{(0)}|\psi\rangle,$$

$$\hat{L}^2|\psi\rangle=\hbar^2 l(l+1)|\psi\rangle,$$

$$\hat{S}^2|\psi\rangle=\hbar^2 s(s+1)|\psi\rangle,$$

$$\hat{J}|\psi\rangle=\hbar^2 j(j+1)|\psi\rangle,$$

$$\hat{J}_z|\psi\rangle=\hbar m|\psi\rangle.$$

We consider the hydrogen atom problem with the spin orbit interaction. The eigenket $|\psi\rangle$ is expressed by $|n,l,s;j,m\rangle$. The angular part of this eigenket is

$$|j,m\rangle=|l,s;j,m\rangle,$$

with

$$s=1/2, j=l\pm 1/2,$$

where

$$D_l \times D_{1/2} = D_{j=l+\frac{1}{2}} + D_{j=l-\frac{1}{2}}.$$

The spin-orbit interaction is given by

$$H_{LS} = \xi \hat{L}\cdot\hat{S} = \frac{\xi}{2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2],$$

$$\begin{aligned} H_{LS}|j,m\rangle &= \xi\hat{L}\cdot\hat{S}|j,m\rangle \\ &= \frac{\xi}{2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2]|j,m\rangle \\ &= \frac{\xi}{2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2]|j,m\rangle \\ &= \frac{\xi}{2}\hbar^2[j(j+1) - l(l+1) - 3/4]|j,m\rangle \end{aligned}$$

(a) For $j = l + 1/2$,

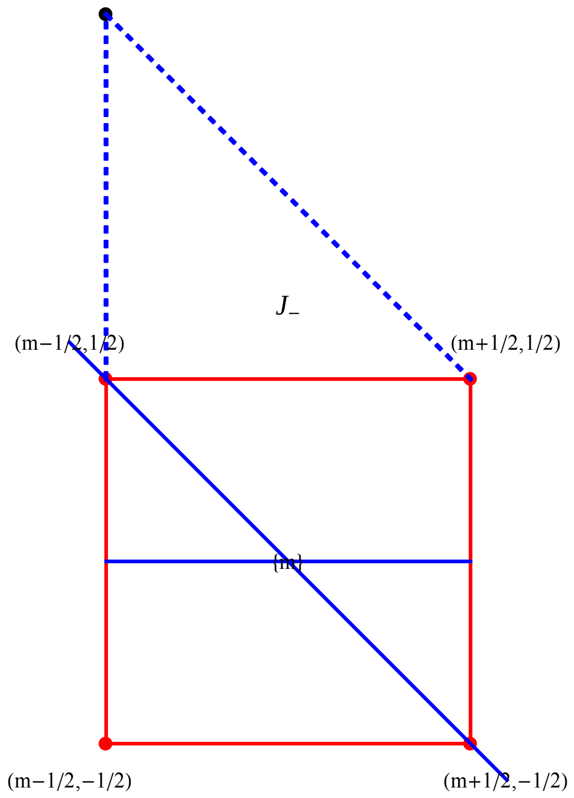

Fig.17 $\left| j=l+\frac{1}{2},m \right\rangle$. The recursion relation to obtain the Clebsch-Gordan coefficients.

$$\hat{H}_{LS}\left| j=l+1/2,m \right\rangle = E_{LS}\left| j=l+1/2,m \right\rangle,$$

with

$$E_{LS}=\frac{\xi}{2}\hbar^2[(l+1/2)(l+3/2)-l(l+1)-3/4]=\frac{\xi}{2}\hbar^2 l\,.$$

We note that

$$\left| j = l + 1/2, m \right\rangle = \sqrt{\frac{l+m+1/2}{2l+1}} \left| m_l = m - 1/2, m_s = 1/2 \right\rangle$$
$$+ \sqrt{\frac{l-m+1/2}{2l+1}} \left| m_l = m + 1/2, m_s = -1/2 \right\rangle$$

The expectation values of $\hat{L}_z$ and $\hat{S}_z$ are obtained as follows.

$$\hat{L}_z \left| j = l + 1/2, m \right\rangle = \hbar \sqrt{\frac{l+m+1/2}{2l+1}} (m - 1/2) \left| m_l = m - 1/2, m_s = 1/2 \right\rangle$$
$$+ \hbar \sqrt{\frac{l-m+1/2}{2l+1}} (m + 1/2) \left| m_l = m + 1/2, m_s = -1/2 \right\rangle$$

$$\left\langle j = l + 1/2, m \right| \hat{L}_z \left| j = l + 1/2, m \right\rangle = \hbar \begin{pmatrix} \sqrt{\frac{l+m+1/2}{2l+1}} & \sqrt{\frac{l-m+1/2}{2l+1}} \end{pmatrix} \begin{pmatrix} \sqrt{\frac{l+m+1/2}{2l+1}} (m-1/2) \\ \sqrt{\frac{l-m+1/2}{2l+1}} (m+1/2) \end{pmatrix}$$
$$= \hbar \left[\frac{l+m+1/2}{2l+1} (m - 1/2) + \frac{l-m+1/2}{2l+1} (m + 1/2) \right]$$
$$= \frac{\hbar 2lm}{2l+1}$$

Similarly,

$$\hat{S}_z \left| j = l + 1/2, m \right\rangle = \hbar \sqrt{\frac{l+m+1/2}{2l+1}} (1/2) \left| m_l = m - 1/2, m_s = 1/2 \right\rangle$$
$$+ + \hbar \sqrt{\frac{l-m+1/2}{2l+1}} (-1/2) \left| m_l = m + 1/2, m_s = -1/2 \right\rangle$$

$$\left\langle j = l + 1/2, m \right| \hat{S}_z \left| j = l + 1/2, m \right\rangle = \hbar \left[\frac{l+m+1/2}{2l+1} (1/2) - \frac{l-m+1/2}{2l+1} (1/2) \right]$$
$$= \frac{\hbar m}{2l+1}$$

Then we have

$$\langle j = l + 1/2, m | \hat{L}_z + 2\hat{S}_z | j = l + 1/2, m \rangle = \hbar m (1 + \frac{1}{2l + 1})$$

(b) For $j = l$ -1/2

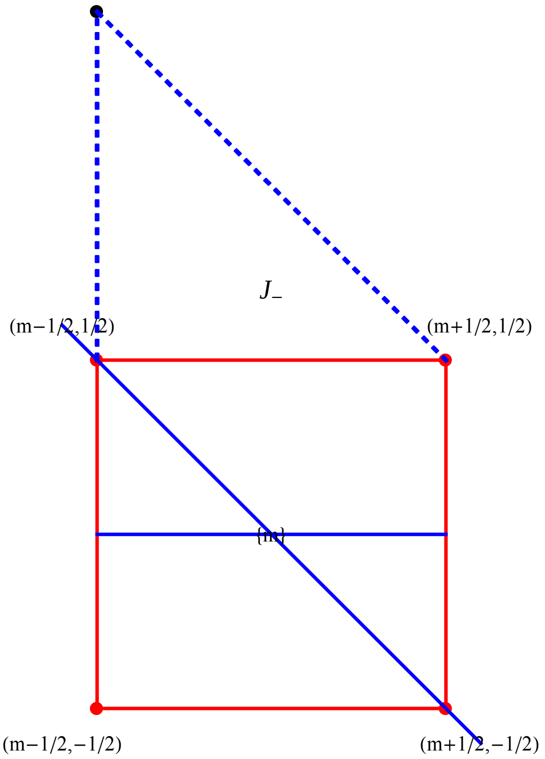

Fig.18 $J = l - \frac{1}{2}$. The recursion relation to obtain the Clebsch-Gordan coefficients.

$$\hat{H}_{LS} | j = l - 1/2, m \rangle = E_{LS} | j = l - 1/2, m \rangle,$$

with

$$E_{LS} = \frac{\xi}{2} \hbar^2 [(l - \frac{1}{2})(l + \frac{1}{2}) - l(l + 1) - \frac{3}{4}] = -\frac{\xi}{2} \hbar^2 (l + 1),$$

$$\left|\, j = l - 1/2, m \right\rangle = -\sqrt{\frac{l - m + 1/2}{2l + 1}} \left| m_l = m - 1/2, m_s = 1/2 \right\rangle + \sqrt{\frac{l + m + 1/2}{2l + 1}} \left| m_l = m + 1/2, m_s = -1/2 \right\rangle$$

or

$$\hat{H}_{LS} \left|\, j = l - 1/2, m \right\rangle = -\frac{\xi}{2} \hbar^2 (l + 1) \left|\, j = l - 1/2, m \right\rangle .$$

The expectation value of $\hat{L}_z$ and $\hat{S}_z$

$$\begin{aligned} \left\langle j = i - 1/2, m \right| \hat{L}_z \left|\, j = i - 1/2, m \right\rangle &= \hbar \left[\frac{l - m + 1/2}{2l + 1} (m - 1/2) + \frac{l + m + 1/2}{2l + 1} (m + 1/2) \right] \\ &= \frac{2\hbar m (l + 1)}{2l + 1} \end{aligned}$$

$$\begin{aligned} \left\langle j = l - 1/2, m \right| \hat{S}_z \left|\, j = l - 1/2, m \right\rangle &= \hbar \left[\frac{l - m + 1/2}{2l + 1} (1/2) - \frac{l + m + 1/2}{2l + 1} (1/2) \right] \\ &= -\frac{\hbar m}{2l + 1} \end{aligned}$$

Then we have

$$\left\langle j = l - 1/2, m \right| \hat{L}_z + 2\hat{S}_z \left|\, j = l - 1/2, m \right\rangle = \hbar m \left(1 - \frac{1}{2l + 1}\right) .$$

In summary, the energy shift due to the spin-orbit interaction is given by

$$\Delta E = E_{LS} = \frac{\xi}{2} \hbar^2 l, \qquad \text{for } j = l+1/2,$$

$$\Delta E = E_{LS} = -\frac{\xi}{2} \hbar^2 (l + 1), \qquad \text{for } j = l\text{-}1/2,$$

$$\hat{H}_{LS} = \begin{pmatrix} \frac{\xi}{2} \hbar^2 l & 0 \\ 0 & -\frac{\xi}{2} \hbar^2 (l + 1) \end{pmatrix}$$

under the basis of $|\, j = l + 1/2, m\rangle$ and $|\, j = l - 1/2, m\rangle$,

where

$$\frac{\hbar^2 \xi}{|E_n|} = \frac{e^4 Z^2}{c^2 n^2 \hbar^2 l(l+1/2)(l+1)} = \frac{(\alpha Z)^2}{n^2} \frac{1}{l(l+1/2)(l+1)},$$

or

$$\hbar^2 \xi = R\alpha^2 \frac{Z^4}{n^4} \frac{1}{l(l+1/2)(l+1)}.$$

(b) Zeeman effect in a system with a single electron such as Na

The magnetic moment is given by a sum of the orbital magnetic moment and spin magnetic moment as

$$\hat{\boldsymbol{\mu}} = -\frac{\mu_B}{\hbar}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}),$$

where $\mu_B = \dfrac{e\hbar}{2 m_e c}$ (>0) is the Bohr magneton. The Zeeman energy is given by

$$\hat{H}_B = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = \frac{\mu_B}{\hbar}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} = \frac{\mu_B}{\hbar}(\hat{\mathbf{J}} + \hat{\mathbf{S}}) \cdot \mathbf{B} = \frac{\mu_B B}{\hbar}(\hat{J}_z + \hat{S}_z),$$

for ***B***//z. We now calculate

$$\begin{aligned}\hat{H}_B |\, j = l + 1/2, m\rangle = {} & \frac{\mu_B B}{\hbar}(\hat{L}_z + 2\hat{S}_z)\sqrt{\frac{l+m+1/2}{2l+1}}\,|m_l = m - 1/2, m_s = 1/2\rangle \\ & + \frac{\mu_B B}{\hbar}(\hat{L}_z + 2\hat{S}_z)\sqrt{\frac{l-m+1/2}{2l+1}}\,|m_l = m + 1/2, m_s = -1/2\rangle\end{aligned}$$

or

$$\hat{H}_B|\,j=l+1/2,m\rangle=\mu_B B(m+\frac{1}{2})\sqrt{\frac{l+m+1/2}{2l+1}}|m_l=m-1/2,m_s=1/2\rangle$$
$$+\mu_B B(m-\frac{1}{2})\sqrt{\frac{l-m+1/2}{2l+1}}|m_l=m+1/2,m_s=-1/2\rangle$$

Noting that

$$\hat{H}_{LS}|\,j=l+1/2,m\rangle=E_{LS}|\,j=l+1/2,m\rangle,$$

we have

$$(\hat{H}_{LS}+\hat{H}_B)|\,j=l+1/2,m\rangle=[\frac{\xi}{2}l\hbar^2+\mu_B B(m+\frac{1}{2})]\sqrt{\frac{l+m+1/2}{2l+1}}]|m_l=m-1/2,m_s=1/2\rangle$$
$$+[\frac{\xi}{2}l\hbar^2+\mu_B B(m-\frac{1}{2})]\sqrt{\frac{l-m+1/2}{2l+1}}|m_l=m+1/2,m_s=-1/2\rangle$$

Similarly,

$$\hat{H}_B\left|\,j=l-\frac{1}{2},m\right\rangle=-\frac{\mu_B B}{\hbar}(\hat{L}_z+2\hat{S}_z)\sqrt{\frac{l-m+1/2}{2l+1}}|m_l=m-1/2,m_s=1/2\rangle$$
$$+\frac{\mu_B B}{\hbar}(\hat{L}_z+2\hat{S}_z)\sqrt{\frac{l+m+1/2}{2l+1}}|m_l=m+1/2,m_s=-1/2\rangle$$

or

$$\hat{H}_B\left|\,j=l-\frac{1}{2},m\right\rangle=-\mu_B B(m+\frac{1}{2})\sqrt{\frac{l-m+1/2}{2l+1}}|m_l=m-1/2,m_s=1/2\rangle$$
$$+\mu_B B(m-\frac{1}{2})\sqrt{\frac{l+m+1/2}{2l+1}}|m_l=m+1/2,m_s=-1/2\rangle$$

or

$$(\hat{H}_{LS}+\hat{H}_B)|\,j=l-1/2,m\rangle=[\frac{\xi}{2}(l+1)\hbar^2-\mu_B B(m+\frac{1}{2})]\sqrt{\frac{l-m+1/2}{2l+1}}|m_l=m-1/2,m_s=1/2\rangle$$
$$+[-\frac{\xi}{2}(l+1)\hbar^2+\mu_B B(m-\frac{1}{2})]\sqrt{\frac{l+m+1/2}{2l+1}}|m_l=m+1/2,m_s=-1/2\rangle$$

Note that

$$\left\langle j=l+\frac{1}{2},m\right| = \sqrt{\frac{l+m+1/2}{2l+1}}\left\langle m_l=m-1/2,m_s=1/2\right| + \sqrt{\frac{l-m+1/2}{2l+1}}\left\langle m_l=m+1/2,m_s=-1/2\right|$$

$$\left\langle j=l-\frac{1}{2},m\right| = -\sqrt{\frac{l-m+1/2}{2l+1}}\left\langle m_l=m-1/2,m_s=1/2\right| + \sqrt{\frac{l+m+1/2}{2l+1}}\left\langle m_l=m+1/2,m_s=-1/2\right|$$

Then the matrix elements of $\hat{H}_{LS}+\hat{H}_B$ in the basis $\{\left|j=l+1/2,m\right\rangle, \left|j=l-1/2,m\right\rangle\}$ can be obtained as

$$\begin{array}{c|cc} & \left|j=l+1/2,m\right\rangle & \left|j=l-1/2,m\right\rangle \\ \left\langle j=l+\frac{1}{2},m\right| & \frac{\xi}{2}l\hbar^2+\mu_B Bm(1+\frac{1}{2l+1}) & -\frac{\mu_B B\sqrt{(l+1/2)^2-m^2}}{2l+1} \\ \left\langle j=l-\frac{1}{2},m\right| & -\frac{\mu_B B\sqrt{(l+1/2)^2-m^2}}{2l+1} & -\frac{\xi}{2}(l+1)\hbar^2+\mu_B Bm(1-\frac{1}{2l+1}) \end{array}$$

for the same *l* and *m*. The eigenvalues of this matrix are given by

$$\lambda_1=\mu_B Bm-\frac{\xi\hbar^2}{4}-\frac{1}{4}\sqrt{4\mu_B{}^2B^2+8\mu_B Bm\xi\hbar^2+\xi^2(2l+1)^2\hbar^4}\ ,$$

$$\lambda_2=\mu_B Bm-\frac{\xi\hbar^2}{4}+\frac{1}{4}\sqrt{4\mu_B{}^2B^2+8\mu_B Bm\xi\hbar^2+\xi^2(2l+1)^2\hbar^4}\ .$$

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9. Zeeman effect in Na

We now consider the D lines of Na.

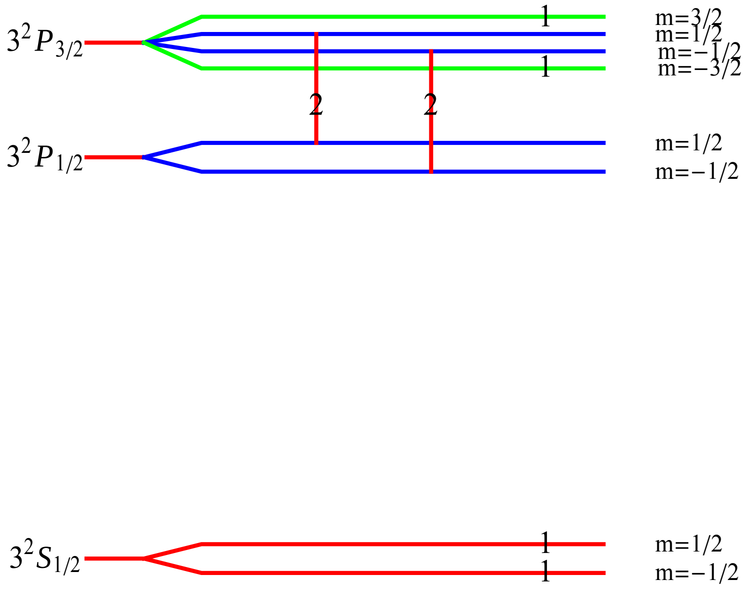

Fig.19 Energy levels for Na in the presence of weak magnetic field. In the presence of a strong magnetic field, the states $\left|j=3/2, m=\pm 1/2\right\rangle$ in 3 $^2P_{3/2}$ $\left|j=1/2, m=\pm 1/2\right\rangle$ in 3 $^2P_{1/2}$ are no loner eigenstate. The appropriate linear combination of $\left|j=3/2, m=\pm 1/2\right\rangle$ in 3 $^2P_{3/2}$ and $\left|j=1/2, m=\pm 1/2\right\rangle$ in 3 $^2P_{1/2}$ for the same m (= ±1/2) becomes eigenstates of $\hat{H}_{LS}+\hat{H}_B$.

(a) ***l* = 1**

The mixed state of $3^2P_{3/2}$ (j = 3/2, l = 1, s = 1/2), and $3^2P_{1/2}$ (j = 1/2, l = 1, s = 1/2) is the eigenstate.

$$\begin{array}{c|cc} & \left|j=\frac{3}{2},m\right\rangle & \left|j=\frac{1}{2},m\right\rangle \\ \left\langle j=\frac{3}{2},m\right| & \frac{\xi}{2}\hbar^2+\mu_B Bm\frac{4}{3} & -\frac{\mu_B B\sqrt{\frac{9}{4}-m^2}}{3} \\ \left\langle j=\frac{1}{2},m\right| & -\frac{\mu_B B\sqrt{\frac{9}{4}-m^2}}{3} & -\xi\hbar^2+\mu_B Bm\frac{2}{3} \end{array}$$

with $m = \pm 1/2$, where the factors 4/3 and 2/3 of the Zeeman terms correspond to the g factors for ${}^2P_{3/2}$ and ${}^2P_{1/2}$, respectively. The eigenvalue can be obtained from the eigenvalue problem for the (2 x 2) matrix. We get

$$E_2(m) = E(3p) + \mu_B Bm - \frac{\xi\hbar^2}{4} - \frac{1}{4}\sqrt{4\mu_B{}^2 B^2 + 8\mu_B Bm\xi\hbar^2 + 9\xi^2\hbar^4}\ ,$$

for $m = \pm 1/2$, and

$$E_4(m) = E(3p) + \mu_B Bm - \frac{\xi\hbar^2}{4} + \frac{1}{4}\sqrt{4\mu_B{}^2 B^2 + 8\mu_B Bm\xi\hbar^2 + 9\xi^2\hbar^4}\ ,$$

for $m = \pm 1/2$. We note that $\left| j = \frac{3}{2}, m = \pm\frac{3}{2} \right\rangle$ is the eigenket of $\hat{H}_{LS} + \hat{H}_B$, where

$$(\hat{H}_{LS} + \hat{H}_B)\left| j = \frac{3}{2}, m = \frac{3}{2} \right\rangle = (\frac{\xi}{2}\hbar^2 + 2\mu_B B)\left| j = \frac{3}{2}, m = \frac{3}{2} \right\rangle,$$

with

$$E_5 = E(3p) + \frac{\xi}{2}\hbar^2 + 2\mu_B B \quad ,$$

for $m = 3/2$,

and

$$(\hat{H}_{LS} + \hat{H}_B)\left| j = \frac{3}{2}, m = -\frac{3}{2} \right\rangle = (\frac{\xi}{2}\hbar^2 - 2\mu_B B)\left| j = \frac{3}{2}, m = -\frac{3}{2} \right\rangle,$$

with

$$E_3 = E(3p) + \frac{\xi}{2}\hbar^2 - 2\mu_B B\,,$$

for m = -3/2.

(b) *j* = 1/2, *l* = 0, *s* = 1/2

$\left| j = 1/2, m = \pm\frac{1}{2} \right\rangle$ is the eigenket of $\hat{H}_{LS} + \hat{H}_B$,

with the eigenvalue

$$E_1(m) = E(3s) + 2\mu_B Bm,$$

for $m = \pm\frac{1}{2}$.

10. Paschen-Back effect in Na

The Paschen-Back effect is the splitting of atomic energy levels in the presence of a strong magnetic field. This effect is the strong-field limit of the Zeeman effect. The effect was named after the German physicists Friedrich Paschen and Ernst E. A. Back.

In the limit of strong magnetic field *B*, the energy levels of Na are strongly dependent on the magnetic field, and are given by

$$E_1(m = \frac{1}{2}) = E(3s) + \mu_B B,$$

$$E_1(m = -\frac{1}{2}) = E(3s) - \mu_B B,$$

$$E_2(m = \frac{1}{2}) = E(3p) - \frac{\xi\hbar^2}{4},$$

$$E_2(m = -\frac{1}{2}) = E(3p) - \frac{\xi\hbar^2}{4} - \mu_B B,$$

$$E_3 = E(3p) + \frac{\xi}{2}\hbar^2 - 2\mu_B B,$$

$$E_4(m=\frac{1}{2}) = E(3p) - \frac{\xi\hbar^2}{4} + \mu_B B\,,$$

$$E_4(m=-\frac{1}{2}) = E(3p) - \frac{\xi\hbar^2}{4}\,,$$

$$E_5 = E(3p) + \frac{\xi}{2}\hbar^2 + 2\mu_B B\,.$$

((**Mathematica**))
We use

$\mu_B = 1$, $\hbar = 1$
E(3p) - E(3s)= -7. $\xi = 1$.

for the calculation using the Mathematica.

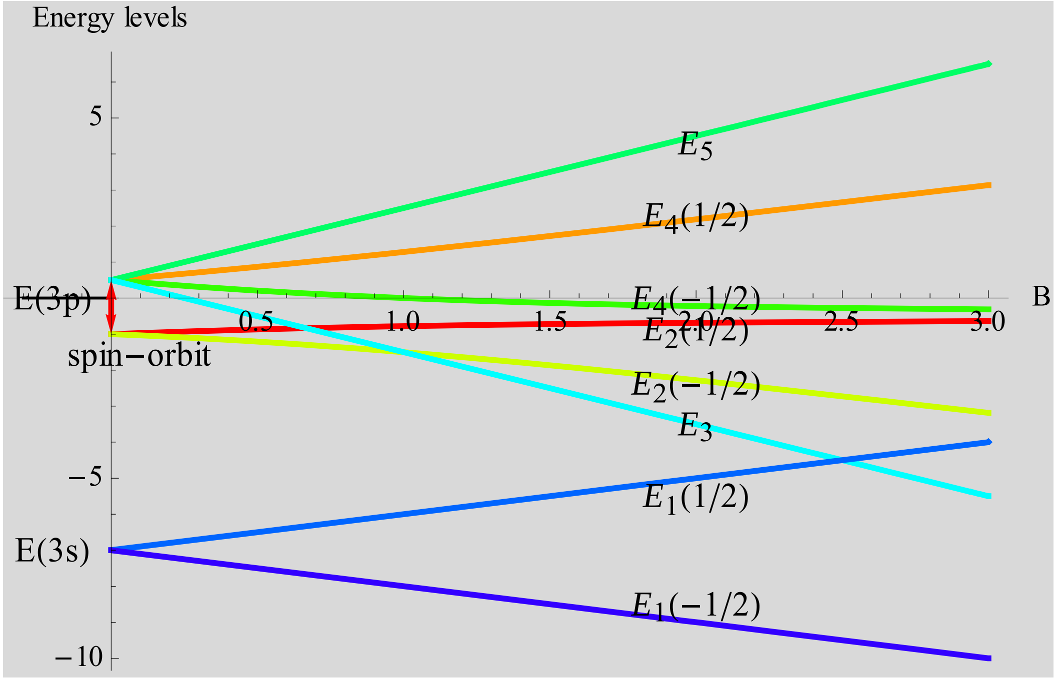

Fig.20 Splitting of energy levels of Na in a magnetic field B (anomalous Zeeman effect).

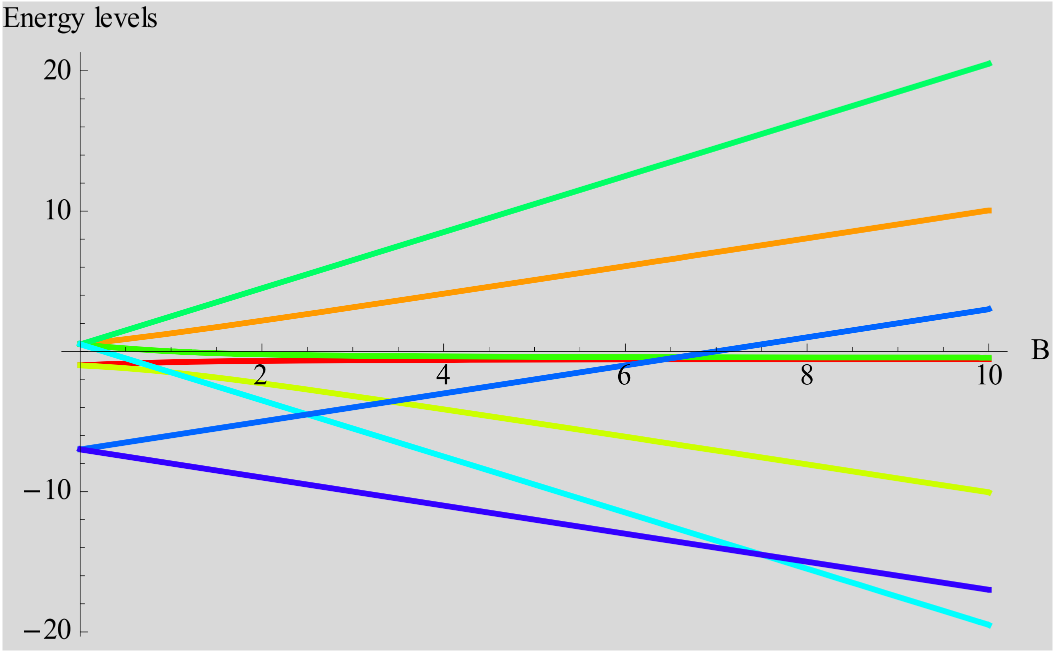

Fig.21

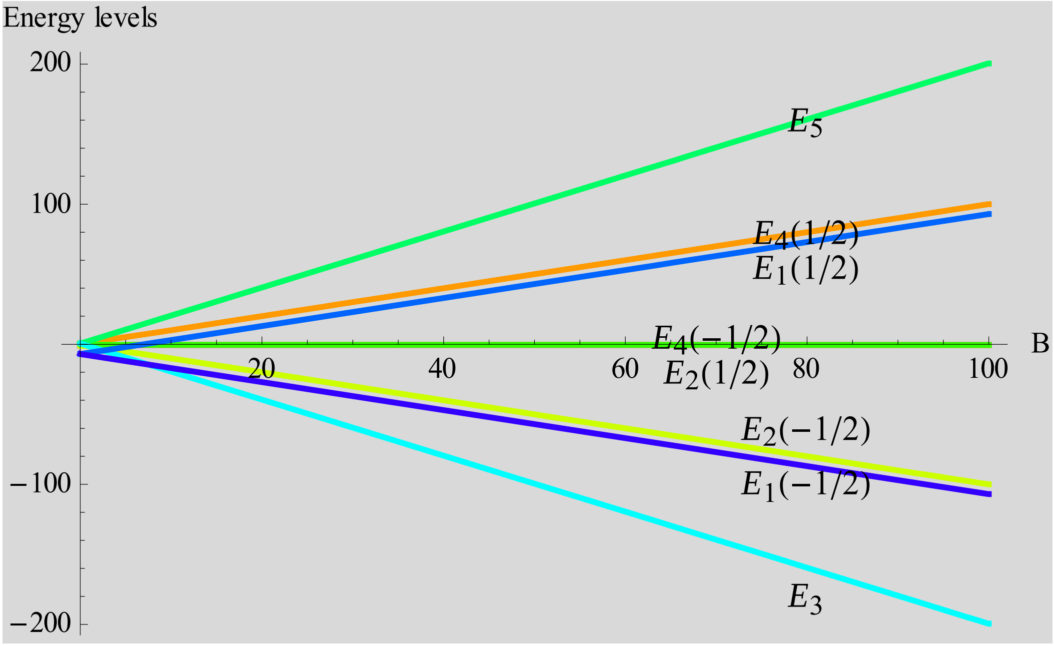

Fig.22 Paschen-Back effect. Zeeman splitting in the very large magnetic field for Na.

11. Paschen-Back effect in Na; quantum mechanical treatment

Suppose that an extremely strong magnetic field is applied for the case of Na. The Zeeman term of the Hamiltonian is much significant compared to the spin-orbit interaction. in this case, the Hamiltonian H is simply given by

$$\hat{H}_B = \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B$$

in the presence of the magnetic field along the *z* axis.

(1) 3p states

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

$$\hat{H}_B|m_l, m_s\rangle_{3p} = \mu_B B(m_l + 2m_s)|m_l, m_s\rangle_{3p}$$

$|m_l, m_s\rangle_{3p}$ is the eigenket of $\hat{H}_B$ with the eigenvalue $\mu_B B(m_l + 2m_s)$.

$|m_l, m_s\rangle_{3p}$ ($m_l = 1, 0, -1$, $m_s = 1/2, -1/2$).

(2) 3s states

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

$$\hat{H}_B|m_l, m_s\rangle_{3s} = \mu_B B(m_l + 2m_s)|m_l, m_s\rangle_{3s}$$

$|m_l, m_s\rangle_{3s}$ is the eigenket of $\hat{H}_B$ with the eigenvalue $\mu_B B(m_l + 2m_s)$.

$|m_l, m_s\rangle_{3s}$ ($m_l = 0$, $m_s = 1/2, -1/2$).

In the extremely high magnetic fields, the energy levels of 3s and 3p states split into five levels. The difference between adjacent energy levels is the same and is equal to $\mu_B B$.

Table

Energy (μ_BB)	Eigenkets	
2	$\left\|1,1/2\right\rangle_{3p}$	
1	$\left\|0,1/2\right\rangle_{3p}$	$\left\|0,1/2\right\rangle_{3s}$
0	$\left\|1,-1/2\right\rangle_{3p}$	$\left\|-1,1/2\right\rangle_{3p}$
-1	$\left\|0,-1/2\right\rangle_{3p}$	$\left\|0,-1/2\right\rangle_{3s}$
-2	$\left\|-1,-1/2\right\rangle_{3p}$	

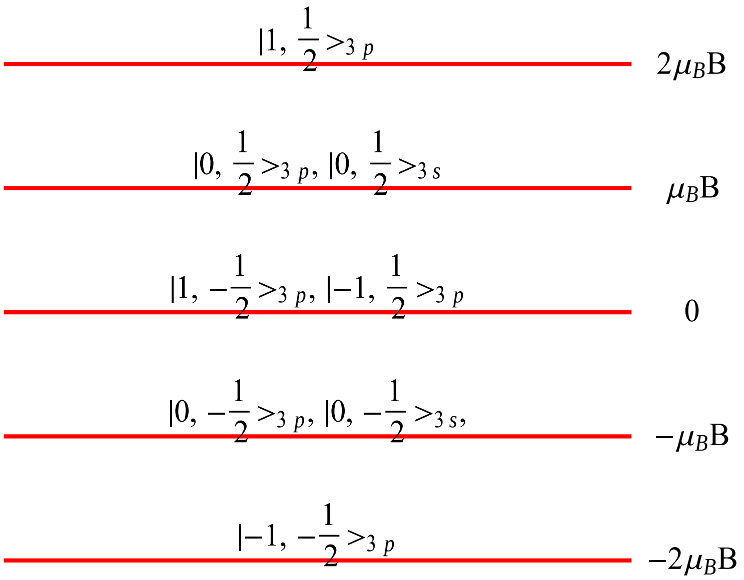

Fig. The level splitting of Na for the Pashen-Back effect. $\left|m_l, m_s\right\rangle_{3p}$ is the eigenket for 3*p* states (6, states; m_l = 1, 0, -1, m_s = 1/2, -1/2). $\left|m_l, m_s\right\rangle_{3s}$ is the eigenket for 3s states (2 states; m_l = 0, m_s = 1/2, -1/2).

---

12. Zeeman splitting in Cd

The electron configuration of Cd is given by (Kr) $4d^{10}$ $5s^2$. This is similar to the outer electron configuration of He but also of Hg.

(a) 5s5s

D_0 x D_0 = D_0 $\quad\quad$ $l = 0$

$D_{1/2}$ x $D_{1/2} = D_1 + D_0$ $s = 1, s = 0$

$l = 0$ and $s = 1$

D_0 x $D_1 = D_1$ $j = 1$

$5\,^3S_1$

$l = 0$ and $s = 0$

D_0 x $D_0 = D_0$ $j = 0$

$5\,^1S_0$

(b) 5s5p

D_1 x $D_0 = D_1$ $l = 1$

$D_{1/2}$ x $D_{1/2} = D_1 + D_0$ $s = 1, s = 0$

$l = 1$ and $s = 1$

D_1 x $D_1 = D_2 + D_1 + D_0$

$j = 2$ $5\,^3P_2$

$j=1$ $5\,^3P_1$

$j = 0$ $5\,^3P_0$

$l = 1$ and $s = 0$

D_1 x $D_0 = D_1$ $j = 1$

$\underline{5\,^1P_1 \qquad (g = 1)}$

(c) 5s5d

D_2 x $D_0 = D_2$ $l = 2$

$D_{1/2}$ x $D_{1/2} = D_1 + D_0$ $s = 1, s = 0$

$l = 2$ and $s = 1$

D_2 x $D_1 = D_3 + D_2 + D_1$

$j = 3$ $5\,^3D_3$

$j = 2$ $5\,^3D_2$

$j = 1$ $5\,^3D_1$

$l = 2$ and $s = 0$

$D_2 \times D_0 = D_2$ $j = 2$

$\underline{5\,^1D_2 \quad (g = 1)}$

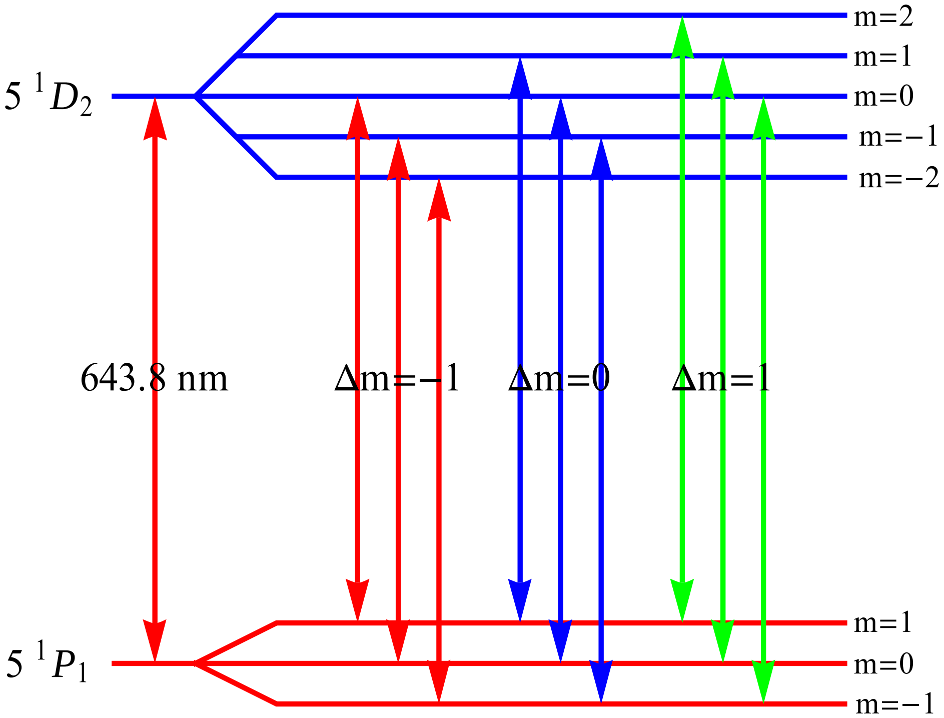

Fig.23 Schematic diagram for the Zeeman splitting in Cd. 643.8 nm. $g = 1$ for $5\,^1D_2$ ($j = 2$, $l = 2$, $s = 0$) and $5\,^1P_1$ ($j = 1$, $l = 1$, $s = 0$).

We can observe the normal Zeeman effect in the red spectral line of Cd (643.8 nm). It corresponds to the transition

$$5\,^1D_2\ (j = 2, l = 2, s = 0) \rightarrow 5\,^1P_1\ (j = 1, l = 1, s = 0).$$

In the presence of the magnetic field, the $5\,^1D_2$ level splits into 5 Zeeman components and the $5\,^1P_1$ level splits into 3 Zeeman component. The optical transitions between these levels are only possible in the form of electrical dipole radiation. The following selection rules apply for the magnetic quantum number m of the states involved;

$\Delta m = \pm 1$ for σ components,

$\Delta m = 0$ for π components,

Thus we observe three spectral lines

---

10. Energy levels in Hg: system with two electrons

The neutral mercury (Hg) atom in its ground state has 80 electrons in the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$ in which the n = 1, 2, 3, 4, and 5 electrons form an inert core for two 6s valence electrons. The optical emission spectrum of Hg results from transitions of the two valence electrons between various excited two-electron configurations. The Hg spectrum therefore has many features in common with the two-electron helium system.

$^{2S+1}L_J$

Orbital angular momentum

$D_{l1} \text{ x } D_{1/2} = D_{l1+l2} + \ldots.. + D_{|l1-l2|}$

Spin:

$D_{1/2} \text{ x } D_{1/2} = D_1 + D_0$

(a) 6s6s

$l = 0$ and $l = 0 \rightarrow$ $D_0 \text{ x } D_0 = D_0$

$l = 0$ and $s = 1$

$D_0 \text{ x } D_1 = D_1$

$j = 1$ $6\ {}^3S_1$

$l = 0$ and $s = 0$

$D_0 \text{ x } D_0 = D_0$
$j = 0$ $6\ {}^1S_0$

(b) 6s6p

$l = 0$ and $l = 1 \rightarrow$ $D_0 \text{ x } D_1 = D_1$

$l = 1$ and $s = 1$

$D_1 \text{ x } D_1 = D_2 + D_1 + D_0$

$j = 2$ $6\ {}^3P_2$ ($g = 3/2$).
$j = 1$ $6\ {}^3P_1$
$j = 0$ $6\ {}^3P_0$

$l = 1$ and $s = 0$

$D_1 \text{ x } D_0 = D_1$
$j = 1$ $6\ {}^1P_1$

(c) 6s6d

$l = 0$ and $l = 2 \rightarrow$ $D_0 \text{ x } D_2 = D_2$

$l = 2$ and $s = 1$

$D_2 \text{ x } D_1 = D_3 + D_2 + D_1$

$j = 3$ $6\ {}^3D_3$
$j = 2$ $6\ {}^3D_2$
$j = 1$ $6\ {}^3D_1$

$l = 2$ and $s = 0$
$D_2 \text{ x } D_0 = D_2$
$j = 2$ $6\ {}^1D_2$

(d) 6s7s

$l = 0$ and $l = 0 \rightarrow$ $D_0 \times D_0 = D_0$

$l = 0$ and $s = 1$

$D_0 \times D_1 = D_1$

$j = 1$ $7\,^3S_1$ ($g = 2$)

$l = 0$ and $s = 0$

$D_0 \times D_0 = D_0$

$j = 0$ $7\,^1S_0$

(e) 6s7p

$l = 0$ and $l = 1 \rightarrow$ $D_0 \times D_1 = D_1$

$l = 1$ and $s = 1$

$D_1 \times D_1 = D_2 + D_1 + D_0$

$j = 2$ $7\,^3P_2$
$j = 1$ $7\,^3P_1$
$j = 0$ $7\,^3P_0$

$l = 1$ and $s = 0$

$D_1 \times D_0 = D_1$
$j = 1$ $7\,^1P_1$

(f) 6s7d

$l = 0$ and $l = 2 \rightarrow$ $D_0 \times D_2 = D_2$

$l = 2$ and $s = 1$

$D_2 \times D_1 = D_3 + D_2 + D_2$

$j = 3$	$7\ ^3D_3$
$j = 2$	$7\ ^3D_2$
$j = 1$	$7\ ^3D_1$

$l = 2$ and $s = 0$

$D_2 \times D_0 = D_2$

$j = 2$	$7\ ^1D_1$

---

11. Zeeman splitting in Hg

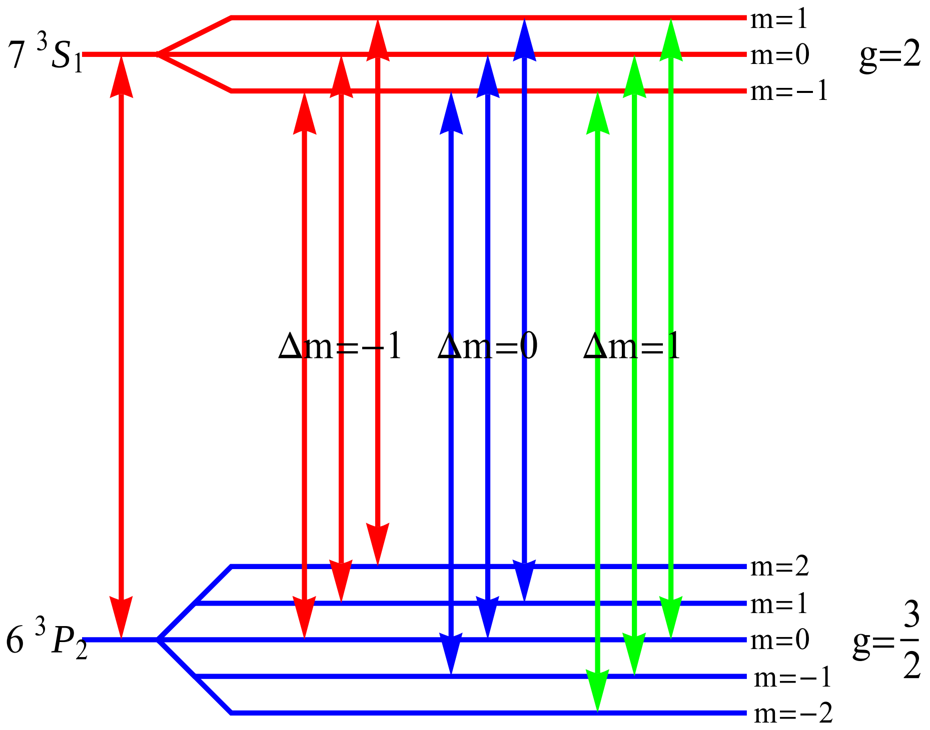

Fig.24 Schematic diagram for the Zeeman splitting in Hg. 546.07 nm (Green line). $7\ ^3S_1$ (6s7s). $6\ ^3P_2$ (6s6p). $7\ ^3S_1$ ($j = 1$, $l = 0$, $s = 1$) and $6\ ^3P_2$ ($j = 2$, $l = 1$, $s = 1$).

The Hg green line corresponds to the transition from $7\ ^3S_1$ to $6\ ^3P_2$.

The state of the $7\ ^3S_1$ level is described by

$|j_2 = 1, m_2\rangle$ (j_2= 1, s_2= 1, l_2 = 0, g_2= 2)

with m_2 = 1, 0, and -1. The state of 6 $^3P_2$ level is described by

$|j_1 = 2, m_1\rangle$ (j_1 = 2, s_1= 1, l_1= 1, g_1= 3/2)

with m_1 = 2, 1, 0, -1, and -2. According to the selection rule (Δm = 1, 0, and -1), there are 9 lines.

$\Delta m = \pm 1$ (6 lines): σ lines.

$\Delta m = 0$ (3 lines): π lines.

12. Evaluation of observed wavelenghts

$E_2 = E_{20} + g_2 \mu_B m_2 B$, for 7 $^3S_1$ level

$E_1 = E_{10} + g_2 \mu_B m_1 B$ for 6 $^3P_2$ level

The energy separation is given by

$$\Delta E_{12} = E_2 - E_1 = \Delta E_{12}{}^0 + \mu_B B(m_2 g_2 - m_1 g_1)$$

with

$\Delta m = m_2 - m_1$ = -1, 0, or 1.

m_2 =1, 0, -1. m_1 = 2, 1, 0, -1, -2.

g_2=2 g_1 = 3/2

Here we note that

$$\Delta E_{12} = h\frac{c}{\lambda_{12}}, \qquad \Delta E_{12}{}^{0} = h\frac{c}{\lambda_{12}{}^{0}}$$

Then we have

$$\left(\frac{1}{\lambda_{12}} - \frac{1}{\lambda_{12}{}^{0}}\right) = \frac{\lambda_{12}{}^{0} - \lambda_{12}}{\lambda_{12}\lambda_{12}{}^{0}} = \frac{1}{2\pi c\hbar}\mu_B B(m_2 g_2 - m_1 g_1)$$

or

$$\frac{\lambda_{12}{}^{0} - \lambda_{12}}{\lambda_{12}\lambda_{12}{}^{0}} \approx \frac{-\Delta\lambda_{12}}{\left(\lambda_{12}{}^{0}\right)^2} = \frac{1}{2\pi c\hbar}\mu_B B(m_2 g_2 - m_1 g_1)$$

or

$$\frac{\Delta\lambda_{12}}{\left(\lambda_{12}{}^{0}\right)^2} = \frac{1}{2\pi c\hbar}\mu_B B(-2m_2 + m_1\frac{3}{2})$$

where

$$\frac{1}{2\pi c\hbar}\mu_B = 4.66865 \times 10^{-5} \ (\mathrm{Oe^{-1}cm^{-1}})$$

and

$\lambda_{12}{}^{0}$ = 546.07 nm (Green)

We note that

$$f(m_1, m_2) = (-2m_2 + m_1\frac{3}{2})$$

takes discrete values of 3/2, 1, 1/2, 0, -1/2, -1, and -3/2.

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APPENDIX

A.1. Paschen-Back effect in Na

Mathematica calculation

Calculation of Matrix element for the Zeeman effect

Eigenvalue problem for the Zeeman effect

```
Clear["Global`*"];
```

$$\mathrm{M1}=\left\{\left\{\frac{\xi\hbar^2}{2}\,l+\mu B\,B\,m\left(1+\frac{1}{2\,l+1}\right),\ -\frac{\mu B\,B\sqrt{(l+1/2)^2-m^2}}{2\,l+1}\right\},\right.$$
$$\left.\left\{-\frac{\mu B\,B\sqrt{(l+1/2)^2-m^2}}{2\,l+1},\ -\frac{\xi\hbar^2}{2}\,(l+1)+\mu B\,B\,m\left(1-\frac{1}{2\,l+1}\right)\right\}\right\};$$

```
eq1 = Eigensystem[M1] // Simplify;
```

The eigenvalues;

```
λ1 = eq1[[1, 1]]
```

$$B\,m\,\mu B-\frac{\xi\,\hbar^2}{4}-\frac{1}{4}\sqrt{4\,B^2\,\mu B^2+8\,B\,m\,\mu B\,\xi\,\hbar^2+(\xi+2\,l\,\xi)^2\,\hbar^4}$$

```
λ2 = eq1[[1, 2]]
```

$$\frac{1}{4}\left(4\,B\,m\,\mu B-\xi\,\hbar^2+\sqrt{4\,B^2\,\mu B^2+8\,B\,m\,\mu B\,\xi\,\hbar^2+(\xi+2\,l\,\xi)^2\,\hbar^4}\right)$$

The eigenvectors:

```
ψ1 = eq1[[2, 1]]
```

$$\left\{\frac{2\,B\,\sqrt{1+4\,l+4\,l^{2}-4\,m^{2}}\;\mu B}{4\,B\,m\,\mu B+(1+2\,l)\left((1+2\,l)\,\xi\,\hbar^{2}+\sqrt{4\,B^{2}\,\mu B^{2}+8\,B\,m\,\mu B\,\xi\,\hbar^{2}+(\xi+2\,l\,\xi)^{2}\,\hbar^{4}}\right)},\ 1\right\}$$

```
ψ1 = eq1[[2, 2]] // FullSimplify
```

$$\left\{\frac{2\,B\,\sqrt{(1+2\,l)^{2}-4\,m^{2}}\;\mu B}{4\,B\,m\,\mu B+(1+2\,l)\left((1+2\,l)\,\xi\,\hbar^{2}-\sqrt{4\,B^{2}\,\mu B^{2}+8\,B\,m\,\mu B\,\xi\,\hbar^{2}+(\xi+2\,l\,\xi)^{2}\,\hbar^{4}}\right)},\ 1\right\}$$

A.2 Zeeman splitting for Na

Here we discuss the eigenvalue problem in more detail.

$j = 3/2$, $l = 1$, $s = 1/2$

Clebsch-Gordan coefficient

$$\left|j=\frac{3}{2}, m=\frac{3}{2}\right\rangle = \left|l=1, m_l=1\right\rangle\left|\uparrow\right\rangle$$

$$\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|l=1, m_l=1\right\rangle\left|\downarrow\right\rangle + \sqrt{\frac{2}{3}}\left|l=1, m_l=0\right\rangle\left|\uparrow\right\rangle$$

$$\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|l=1, m_l=0\right\rangle\left|\downarrow\right\rangle + \frac{1}{\sqrt{3}}\left|l=1, m_l=-1\right\rangle\left|\uparrow\right\rangle$$

$$\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle = \left|l=1, m_l=-1\right\rangle\left|\downarrow\right\rangle$$

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

Clebsch-Gordan coefficient;

$$\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle=\sqrt{\frac{2}{3}}\left|l=1,m_l=1\right\rangle\left|\downarrow\right\rangle-\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle$$

$$\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle=\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle-\sqrt{\frac{2}{3}}\left|l=1,m_l=-1\right\rangle\left|\uparrow\right\rangle$$

Note that

$$\begin{pmatrix}\left|l=1,m_l=1\right\rangle\left|\downarrow\right\rangle\\ \left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle\end{pmatrix}=\begin{pmatrix}\sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}}\\ -\frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}}\end{pmatrix}\begin{pmatrix}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle\\ \left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle\end{pmatrix}$$

$$\begin{pmatrix}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle\\ \left|l=1,m_l=-1\right\rangle\left|\uparrow\right\rangle\end{pmatrix}=\begin{pmatrix}\frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}}\\ -\sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}}\end{pmatrix}\begin{pmatrix}\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle\\ \left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle\end{pmatrix}$$

The Hamiltonian is expressed by

$$H=\xi\mathbf{L}\cdot\mathbf{S}+\frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)+\frac{\mu_B}{\hbar}(L_z+2S_z)B\,.$$

We need to calculate $H\left|j,m>\right\rangle$ with j = 1/2 ($m=\pm1/2$) and j = 3/2 (m = ±3/2, ±1/2).

$$\begin{aligned}H_{Zeeman}\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle&=\frac{\mu_B}{\hbar}B(L_z+2S_z)\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle-\frac{\mu_B}{\hbar}B(L_z+2S_z)\sqrt{\frac{2}{3}}\left|l=1,m_l=-1\right\rangle\left|\uparrow\right\rangle)\\&=-\mu_B B\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle\\&=-\frac{\mu_B B}{3}(\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle+\sqrt{2}\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle)\end{aligned}$$

$$H_{spin-orbit}\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle=-\xi\hbar^2\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle$$

$$
\begin{aligned}
H_{Zeeman}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle &= \frac{\mu_B}{\hbar}B(L_z+2S_z)\sqrt{\frac{2}{3}}\left|l=1,m_l=1\right\rangle\left|\downarrow\right\rangle-\frac{\mu_B}{\hbar}B(L_z+2S_z)\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle \\
&= -\mu_B B\frac{1}{\sqrt{3}}\left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle \\
&= -\mu_B B\frac{1}{\sqrt{3}}(-\frac{1}{\sqrt{3}}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle \\
&= -\frac{\mu_B B}{3}(-\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle+\sqrt{2}\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle
\end{aligned}
$$

$$
H_{spin-orbit}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle=-\xi\hbar^2\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle
$$

$$
\begin{aligned}
H_{Zeeman}\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle &= \frac{\mu_B}{\hbar}B(L_z+2S_z)\left|l=1,m_l=-1\right\rangle\left|\downarrow\right\rangle \\
&= -2\mu_B B\left|l=1,m_l=-1\right\rangle\left|\downarrow\right\rangle=-2\mu_B B\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle
\end{aligned}
$$

$$
H_{spin-orbit}\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\mu_B\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle=\frac{1}{2}\xi\hbar^2\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle
$$

$$
\begin{aligned}
H_{zeeman}\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle &= \frac{\mu_B}{\hbar}B(L_z+2S_z)(\sqrt{\frac{2}{3}}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle+\frac{\mu_B}{\hbar}B(L_z+2S_z)\frac{1}{\sqrt{3}}\left|l=1,m_l=-1\right\rangle\left|\uparrow\right\rangle) \\
&= -\mu_B B\sqrt{\frac{2}{3}}\left|l=1,m_l=0\right\rangle\left|\downarrow\right\rangle \\
&= -\mu_B B\sqrt{\frac{2}{3}}(\frac{1}{\sqrt{3}}\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle) \\
&= -\frac{\mu_B B}{3}(\sqrt{2}\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle+2\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle)
\end{aligned}
$$

$$
H_{spin-orbit}\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\mu_B\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle=\frac{1}{2}\xi\hbar^2\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle
$$

$$H_{zeeman}\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle=\frac{\mu_B}{\hbar}B(L_z+2S_z)(\frac{1}{\sqrt{3}}\left|l=1,m_l=1\right\rangle\left|\downarrow\right\rangle+\frac{\mu_B}{\hbar}B(L_z+2S_z)\sqrt{\frac{2}{3}}\left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle)$$

$$=\mu_B B\sqrt{\frac{2}{3}}\left|l=1,m_l=0\right\rangle\left|\uparrow\right\rangle$$

$$=\mu_B B\sqrt{\frac{2}{3}}(-\frac{1}{\sqrt{3}}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle$$

$$=\frac{\mu_B B}{3}(-\sqrt{2}\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle+2\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle)$$

$$H_{spin-orbit}\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\mu_B\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle=\frac{1}{2}\xi\hbar^2\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle$$

$$H_{Zeeman}\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle=\frac{\mu_B}{\hbar}B(L_z+2S_z)\left|l=1,m_l=1\right\rangle\left|\uparrow\right\rangle$$

$$=2\mu_B B\left|l=1,m_l=1\right\rangle\left|\uparrow\right\rangle=2\mu_B B\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle$$

$$H_{spin-orbit}\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle=\frac{\xi}{2}(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)\mu_B\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle=\frac{1}{2}\xi\hbar^2\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle$$

Then we have

$$H\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle=(2\mu_B B+\frac{1}{2}\xi\hbar^2)\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle$$

$$H\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle=(\frac{2}{3}\mu_B B+\frac{1}{2}\xi\hbar^2)\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3}\mu_B B\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle$$

$$H\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle=(-\frac{2}{3}\mu_B B+\frac{1}{2}\xi\hbar^2)\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3}\mu_B B\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle$$

$$H\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle=(-2\mu_B B+\frac{1}{2}\xi\hbar^2)\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle$$

$$H\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle=(-\xi\hbar^2+\frac{1}{3}\mu_B B)(\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3}\mu_B B\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle$$

$$H\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle=(-\xi\hbar^2-\frac{\mu_B B}{3})\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3}\mu_B B\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle$$

From this, we find that

$\left|j=\frac{3}{2},m=\frac{3}{2}\right\rangle$ is the eigenket of H with the energy $(2\mu_B B+\frac{1}{2}\xi\hbar^2)$.
$\left|j=\frac{3}{2},m=-\frac{3}{2}\right\rangle$ is the eigenket of H with the energy $(-2\mu_B B+\frac{1}{2}\xi\hbar^2)$.

There are two subspaces of the matrices for the basis of $\{\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle$, $\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle$, and $\{\left|j=\frac{3}{2},m=-\frac{1}{2}\right\rangle$, $\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle\}$

(i) For the basis of $\{\left|j=\frac{3}{2},m=\frac{1}{2}\right\rangle$, $\left|j=\frac{1}{2},m=\frac{1}{2}\right\rangle$,

$$H_{sub1}=\begin{pmatrix} \frac{2}{3}\mu_B B+\frac{1}{2}\xi\hbar^2 & -\frac{\sqrt{2}}{3}\mu_B B \\ -\frac{\sqrt{2}}{3}\mu_B B & \frac{1}{3}\mu_B B-\xi\hbar^2 \end{pmatrix}$$

((Mathematica))

```
Clear["Global`*"];
```

```
m = 1 / 2;
```

$$\mathrm{M1} = \begin{pmatrix} \frac{\xi \hbar^2}{2} + \mu B\, B \frac{4\, m}{3} & -\frac{\mu B\, B}{3}\sqrt{\frac{9}{4} - m^2} \\ -\frac{\mu B\, B}{3}\sqrt{\frac{9}{4} - m^2} & -\xi \hbar^2 + \mu B\, B \frac{4\, m}{3} \end{pmatrix};$$

```
eq1 = Eigensystem[M1] // Simplify
```

$$\left\{\left\{\frac{1}{12}\left(8\, B\, \mu B - 3\, \xi\, \hbar^2 - \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}\right), \frac{1}{12}\left(8\, B\, \mu B - 3\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}\right)\right\}, \left\{\left\{\frac{-9\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}}{4\sqrt{2}\, B\, \mu B}, 1\right\}, \left\{-\frac{9\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}}{4\sqrt{2}\, B\, \mu B}, 1\right\}\right\}\right\}$$

```
E1 = eq1[[1, 1]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$-\xi\, \hbar^2 + \frac{2\, \mu B\, B}{3} - \frac{4\, \mu B^2\, B^2}{27\, \left(\xi\, \hbar^2\right)} + O[B]^4$$

```
E2 = eq1[[1, 2]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\frac{\xi\, \hbar^2}{2} + \frac{2\, \mu B\, B}{3} + \frac{4\, \mu B^2\, B^2}{27\, \xi\, \hbar^2} + O[B]^4$$

```
ψ1 = eq1[[2, 1]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\left\{\frac{2\sqrt{2}\, \mu B\, B}{9\, \xi\, \hbar^2} - \frac{16\, \left(\sqrt{2}\, \mu B^3\right)\, B^3}{729\, \left(\xi^3\, \hbar^6\right)} + O[B]^4, 1\right\}$$

```
ψ2 = eq1[[2, 2]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\left\{-\frac{9\, \left(\xi\, \hbar^2\right)}{2\, \left(\sqrt{2}\, \mu B\right)\, B} - \frac{2\, \left(\sqrt{2}\, \mu B\right)\, B}{9\, \left(\xi\, \hbar^2\right)} + \frac{16\sqrt{2}\, \mu B^3\, B^3}{729\, \xi^3\, \hbar^6} + O[B]^4, 1\right\}$$

(ii) For the basis of $\{\left| j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle, \left| j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle\}$

$$H_{sub2} = \begin{pmatrix} -\frac{2}{3}\mu_B B + \frac{1}{2}\xi\hbar^2 & -\frac{\sqrt{2}}{3}\mu_B B \\ -\frac{\sqrt{2}}{3}\mu_B B & -\frac{1}{3}\mu_B B - \xi\hbar^2 \end{pmatrix}$$

((**Mathematica**))

```
Clear["Global`*"];
```

```
m = -1 / 2;
```

$$M1 = \begin{pmatrix} \frac{\xi \hbar^2}{2} + \mu B\, B \frac{4\, m}{3} & -\frac{\mu B\, B}{3}\sqrt{\frac{9}{4} - m^2} \\ -\frac{\mu B\, B}{3}\sqrt{\frac{9}{4} - m^2} & -\xi \hbar^2 + \mu B\, B \frac{4\, m}{3} \end{pmatrix};$$

```
eq1 = Eigensystem[M1] // Simplify
```

$$\left\{\left\{\frac{1}{12}\left(-8\, B\, \mu B - 3\, \xi\, \hbar^2 - \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}\right),\ \frac{1}{12}\left(-8\, B\, \mu B - 3\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}\right)\right\},\ \left\{\left\{\frac{-9\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}}{4\sqrt{2}\, B\, \mu B}, 1\right\}, \left\{-\frac{9\, \xi\, \hbar^2 + \sqrt{32\, B^2\, \mu B^2 + 81\, \xi^2\, \hbar^4}}{4\sqrt{2}\, B\, \mu B}, 1\right\}\right\}\right\}$$

```
E1 = eq1[[1, 1]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$-\xi\, \hbar^2 - \frac{2\, \mu B\, B}{3} - \frac{4\, \mu B^2\, B^2}{27\, \left(\xi\, \hbar^2\right)} + O[B]^4$$

```
E2 = eq1[[1, 2]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\frac{\xi\, \hbar^2}{2} - \frac{2\, \mu B\, B}{3} + \frac{4\, \mu B^2\, B^2}{27\, \xi\, \hbar^2} + O[B]^4$$

```
ψ1 = eq1[[2, 1]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\left\{\frac{2\sqrt{2}\, \mu B\, B}{9\, \xi\, \hbar^2} - \frac{16\left(\sqrt{2}\, \mu B^3\right) B^3}{729\left(\xi^3\, \hbar^6\right)} + O[B]^4, 1\right\}$$

```
ψ2 = eq1[[2, 2]] // Series[#, {B, 0, 3}] & // Simplify[#, {ξ > 0, ℏ > 0}] &
```

$$\left\{-\frac{9\left(\xi\, \hbar^2\right)}{2\left(\sqrt{2}\, \mu B\right) B} - \frac{2\left(\sqrt{2}\, \mu B\right) B}{9\left(\xi\, \hbar^2\right)} + \frac{16\sqrt{2}\, \mu B^3\, B^3}{729\, \xi^3\, \hbar^6} + O[B]^4, 1\right\}$$

Appendix

Zeeman splitting in Ca

Normal Zeeman effect

The electron configuration of Ca is given by $1s^2\ 2s^2p^6\ 3s^2p^6\ 4s^2$.

(a) 4s4s

$D_0 \times D_0 = D_0$ $\quad l = 0$

$D_{1/2} \times D_{1/2} = D_1 + D_0$ $\quad s = 1, s = 0$

$l = 0$ and $s = 1$

$D_0 \times D_1 = D_1$ $\quad j = 1$

$4\ {}^3S_1$

$l = 0$ and $s = 0$

$D_0 \times D_0 = D_0$ $\quad j = 0$

$4\ {}^1S_0$

(b) 4s4p

$D_1 \times D_0 = D_1$ $\quad l = 1$

$D_{1/2} \times D_{1/2} = D_1 + D_0$ $\quad s = 1, s = 0$

$l = 1$ and $s = 1$

$D_1 \times D_1 = D_2 + D_1 + D_0$

$j = 2$ $\quad 4\ {}^3P_2$ $\quad (g = 3/2)$

$j=1$ $\quad 4\ {}^3P_1$ $\quad (g = 3/2)$

$j = 0$ $\quad 4\ {}^3P_0$

$l = 1$ and $s = 0$

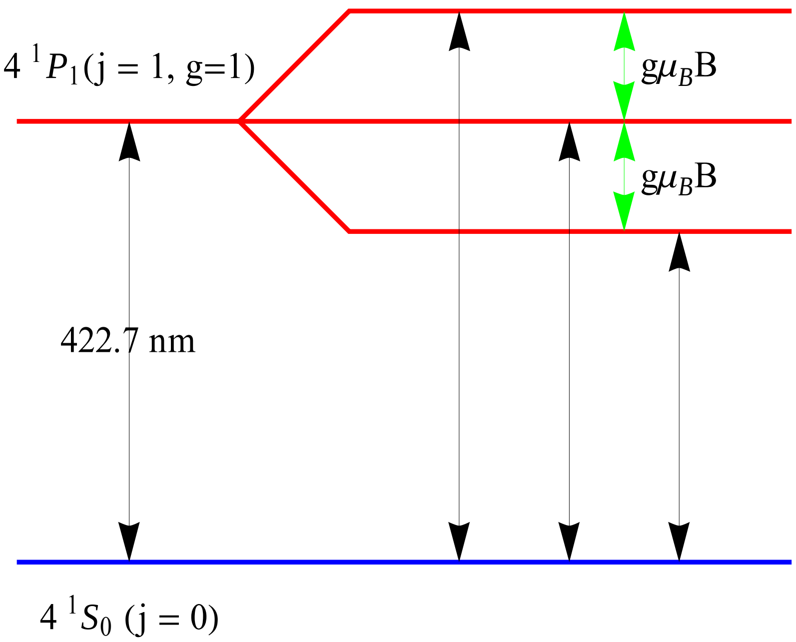
$D_1 \times D_0 = D_1$ $\quad j = 1$

$4\ {}^1P_1$

((White))

H.E. White, Introduction to atomic spectra (McGraw-Hill, NY 1934).

$\lambda = 422.6$ nm between $4\ {}^1S_0$ ($l = 0, s = 0, j = 0$) and $4\ {}^1P_1$ ($l = 1, s = 0, j = 1$; $g = 1$)


$4\,^1P_1$(j = 1, g=1)
gμ_BB
gμ_BB
422.7 nm
$4\,^1S_0$ (j = 0)