# Zeeman effect <br> Masatsugu Sei Suzuki <br> Department of Physics, SUNY at Binghamton <br> (Date March 18, 2015) 


#### 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 Dlines (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 $(\mathrm{Hg})$, 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

## 1. Introduction

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 Dlines (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.

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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."

## 2. History: explanation of the normal Zeeman effect

(a) The discovery of the normal; Zeeman effect

The explanation for the atomic spectra is due to the oscillation of charged particles inside atoms. There was no positive evidence that the particle should be an electron. The experimental evidence for the atomic spectra due to an electron was found by Pieter Zeeman in 1897. He observed splitting of Cd lines into three components (normal Zeeman
effect) when an external magnetic field $B$ is applied. He showed that the angular frequency of these lines are given by

$$
\omega=\omega_{0}, \quad \omega=\omega_{0}+\omega_{L}, \quad \omega=\omega_{0}-\omega_{L}
$$

where $\omega_{0}$ is the angular frequency in the absence of $B$. The angular frequency $\omega_{L}$ is given by

$$
\omega_{L}=\frac{e B}{2 m c}=\frac{1}{2} \omega_{c},
$$

where $-e$ is the charge of electron (we assume that $e>0$ ) and $m$ is the mass of electron.
In 1897, Hendrik Lorentz presented a theoretical interpretation for the observation by Zeeman. The Zeeman effect is the splitting of the energy levels of an atom when it is placed in an external magnetic field. The splitting occurs because of the interaction of the magnetic moment $\boldsymbol{\mu}$ of the atom with the magnetic field $\boldsymbol{B}$ slightly shifts the energy of the atomic levels by an amount,

$$
\Delta \varepsilon=-\boldsymbol{\mu} \cdot \boldsymbol{B}
$$

The magnetic moment $\mu_{\mathrm{L}}$ of electron can be expressed by

$$
\boldsymbol{\mu}_{L}=-\frac{\mu_{B}}{\hbar} \boldsymbol{L}
$$

where $\boldsymbol{L}$ is the orbital angular momentum, $\mu_{\mathrm{B}}$ is the Bohr magneton of electron, and $\hbar$ is the Planck's constant,

$$
\mu_{B}=\frac{e \hbar}{2 m c}
$$



Fig. $\quad$ Schematic diagram. $B=0$.


Fig. Schematic diagram, where a magnetic field is applied along the $z$ axis.

## (b) Oscillation model of Lorentz

We consider a particular orbit, in which the particle is rotating around the $z$ axis with angular frequency $\pm \omega_{0}$, where $+\omega_{0}$ indicates the counterclockwise (CCW) rotation, and $-\omega_{0}$
indicates clockwise (CW) rotation. If we view the atoms in the $z$ direction, we will obtain light that is circularly polarized with the electric vector rotating in the same direction as the electron.


## Fig.

If we view it normal to the $z$ axis, the electric field that reaches us will depend only on the projection of the electron motion on the axis normal to the viewing. The projection of circular motions on such an axis is simple harmonic motion. So that the light viewed in a direction parallel to the plane of motion will be polarized in a direction normal to the direction of viewing and parallel to the plane of electron motion.

Viewed from the z axis $(\mathrm{B}=0)$

Circulary polarized [2 modes ( $x-y$ plane) $]$


Fig. Viewed from the $z$ axis. $B=0$. There are two modes (circularly polarized, $x y$ plane).

## Viewed from the $x-y$ plane



Fig. $\quad$ Viewed from the $x-y$ plane. $B=0$. There are three modes at $\omega=\omega_{0} .2$ modes (linearly polalized, $x y$ plane) and 1 mode (linearly polarized, $z$ axis).

## (c) Magnetic field along the $\boldsymbol{z}$ axis: $\boldsymbol{B} \neq \mathbf{0}$.

In the presence of an external magnetic field along the $z$ axis, the components of the motion in the $z$ direction are left unchanged, while the components of motion in the $x y$ plane are altered. Those atoms with counterclockwise orbits will have their frequencies of rotation in the xy plane increased by $\omega_{L}$, while clockwise orbits will have their frequencies decreased by $\omega_{L}$, where

$$
\omega_{L}=\frac{\omega_{c}}{2}
$$

with

$$
\omega_{c}=\frac{e B}{m c} \quad \text { (Larmor angular frequency). }
$$



Fig. Schematic diagram for the classical explanation of the normal Zeeman effect.

When viewed along the $z$ axis (the direction of the magnetic field), the radiated line will therefore split into two lines, with opposite circular polarization. The electrons moving in the $z$ direction cannot radiate in the $z$ direction; as a result, there will be no un-deviated lines in the light emitted in the $z$ direction.

Viewed from the z axis
No linearly polarized (z)


Fig. Viewed from the $z$ axis. $B \neq 0$.

If the atom is viewed normal to the $z$ direction, then there will be un-deviated line, produced by electrons which move in the $z$ direction. This will be polarized in the $z$ direction. The components of electron motion in the $x y$ plane will produce two deviated lines, each linearly polarized in a direction normal to $z$.

Viewed from the xy plane


Fig. Viewed from the $x y$ plane.

## 3. Experimental configuration



Fig. $\boldsymbol{B} / /$ z. Isometric depiction of the polarization in the longitudinal and transverse Zeeman effect. Longitudinal observation (parallel to the field $\boldsymbol{B}$ ). No $\pi$-line can be observed. Transverse observation (perpendicular to the field $\boldsymbol{B}$ ). Three linearly polarized beams are seen. One $(\pi)$ is parallel to the field $\boldsymbol{B}$. Two others $(\sigma)$ are perpendicular to the field $\boldsymbol{B}$. The magnetic field $\boldsymbol{B}$ is along the $z$ direction.

In 1896 Zn observed that the transition lines split when the field is applied. The "Zeeman effect" is the energy shift of atomic states due to the coupling of the electron orbital angular momentum to the external magnetic field. The normal Zeeman effect occurs when there is no effect from the spin magnetic moment. The energy shift in the presence an external magnetic field can be observed by the wavelength shift of the radiation emitted in atomic transitions between these states


Fig. Normal Zeeman effect in Cd. Schematic diagram for the Zeeman splitting in Cd . 643.8 nm . $g=1$ for $5{ }^{1} \mathrm{D}_{2}(j=2, l=2, s=0)$ and $5{ }^{1} \mathrm{P}_{1}(j=1, l=1, s=0) . \Delta m=0$ for linearly polarized light $(\pi) . \Delta m=1$ for the right-hand circularly polarized light $\left(\sigma^{+}\right) . \Delta m=-1$ for the left-circularly polarized light $\left(\sigma^{-}\right)$. Normal Zeeman effect: transversal and longitudinal observation of the splitting of the red 643.847 nm Cdline in the magnetic field showing the normal Zeeman effect. The definition of $\Delta m$ is as followed. $\Delta m=$ the value of $m$ for the lower state minus the value of $m$ for the upper state. The light is emitted when the state of electron changes from the upper state to the lower state. The Landé $g$ factor is $g=1$ for both $5^{1} \mathrm{D} 2$ and $5{ }^{1} \mathrm{P}_{1}$.

The selection rule for the transition due to the electric dipole moment
A transition in which $m^{\prime}=m+1$ results in the right-hand circularly polarized light, at least for a wave going in the $z$ direction, while $m^{\prime}=m-1$ yields a wave of opposite polarization; right-hand circularly polarized light.

For light which is emitted normal to the $z$ axis (transverse configuration, along the $x$ axis), the polarization will be linear in any transition in which the change of $m$ is defined. A transition in which $\Delta m=0$ can produce only light which is polarized in the $z$ direction,
while if $\Delta m= \pm 1$ must be linearly polarized to the $z$ direction. See the discussion in the section for the selection rule for the radiation due to the electric dipole moment.

## Longitudinal

If the radiation is viewed along the direction of the magnetic field, then only $x$ and $y$ can appear in the matrix element $D_{\mathrm{fi}}$, so that the transition with $\Delta m=0$ does not contribute to this line. The transition with


Fig. Longitudinal observation for the transition with $\Delta m= \pm 1 . \boldsymbol{k}$ is the wavevector of light, propagating along the magnetic field direction. The lights are right-hand and left-hand circularly polarized $\left(\sigma^{+}, \sigma^{-}\right)$.

## Transverse

If the light is viewed normal to the magnetic field, say in the $x$ direction, then it can be polarized either the $z$ or in the $y$ direction. In a transition in which $\Delta m=0$, we see that the matrix element of the electric dipole moment $D_{\text {fi }}$ is along the $z$ axis. This means that the transition with $\Delta m=0$ leads to the light polarized in the $z$ direction, which propagates in the $x$ direction. electric polarization vector should be parallel to the $z$ axis. The net result is that the line is split into three parts; first a linearly polarized light with the polarization along the $z$ axis. Second, two parts polarized in the direction normal to the $z$ axis. The transition with $\mathrm{Dm}=1$ leads to the right-hand circularly polarized light, while $\mathrm{Dm}=-1$ yields the left-hand circularly polarized light. As a result, only two lines appear along the direction of the magnetic field.


Fig. Transverse observation for the transition with $\Delta m=0 . . \boldsymbol{k}$ is the wavevector of light (linearly polarized, $\pi$ ), propagating along the magnetic field direction. The polarization vector is parallel to the magnetic field $\boldsymbol{B}$.


Fig. Transverse observation for the transition with $\Delta m= \pm 1 . . \boldsymbol{k}$ is the wavevector of light (linearly polarized, $\sigma^{ \pm}$), propagating along the magnetic field direction. The polarization vector is perpendicular to the magnetic field $\boldsymbol{B}$ and the wavevector $\boldsymbol{k}$.

## ((Normal Zeeman effect in Cd))

The Hamiltonian due to the Zeeman energy is given by

$$
\hat{H}=-\hat{\boldsymbol{\mu}}_{J} \cdot \boldsymbol{B}=\frac{g_{J} \mu_{B}}{\hbar} \hat{\boldsymbol{J}} \cdot \boldsymbol{B}=\frac{g_{J} \mu_{B} B}{\hbar} \hat{J}_{z}
$$

$$
\begin{array}{ll}
\hat{H}|j, m\rangle=\frac{g_{J} \mu_{B} B}{\hbar} \hat{J}_{z}|j, m\rangle=g_{J} \mu_{B} m B|j, m\rangle \\
E_{2}=E_{20}+g_{2} \mu_{B} m_{2} B, & \text { for } 5{ }^{1} \mathrm{D}_{2} \text { level } \\
E_{1}=E_{10}+g_{2} \mu_{B} m_{1} B & \text { for } 5{ }^{1} \mathrm{P}_{1} \text { level }
\end{array}
$$

where

$$
\begin{aligned}
& m_{2}=2,1,0,-1,-2, \quad m_{1}=1,-1, \\
& g_{2}=1, \quad g_{2}=1 .
\end{aligned}
$$

The energy separation is given by

$$
\begin{aligned}
\Delta E_{12} & =E_{2}-E_{1} \\
& =\Delta E_{12}^{0}+\mu_{B} B\left(m_{2} g_{2}-m_{1} g_{1}\right) \\
& =\Delta E_{12}^{0}+\mu_{B} B\left(m_{2}-m_{1}\right)
\end{aligned}
$$

with

$$
\Delta E_{12}{ }^{0}=\frac{h c}{\lambda(643.85 \mathrm{~nm})}
$$

Then we have three lines with

$$
m_{2}-m_{1}= \pm 1,0
$$

## 5. Zeeman effect for $\mathrm{Na} D$ lines: Separation of $3 p$ and 3 s energy levels due to spin -orbit interaction

Spin-orbit interaction


Fig. 12 Energy levels of Na with and without spin-orbit interaction. The 3P level is slightly different from the 3 S level. The 3 P level is split into $3{ }^{2} \mathrm{P}_{3 / 2}(4$ degeneracies) and $3{ }^{2} \mathrm{P}_{1 / 2}$ ( 3 degeneracies) due to the spin-orbit interaction. The Lande $g$-factor is $g=4 / 3$ for into $3^{2} \mathrm{P}_{3 / 2}, g=2 / 3$ for into $3^{2} \mathrm{P}_{1 / 2}$, and $g=$ 2 for into $3{ }^{2 S} \mathrm{P}_{1 / 2}$


Fig. Zeeman effect of the Na D lines ( 589.0 nm and 589.6 nm ). The Landé g-factors for $3{ }^{2} \mathrm{P}_{3 / 2}, 3{ }^{2} \mathrm{P}_{1 / 2}$, and $3{ }^{2} \mathrm{~S}_{1 / 2}$ are denoted in Fig.

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 3 s (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 3 s 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 3 s electron penetrates the inner shielding shells more than the $3 p$ and is significantly lower in energy.

## 6. Lande $\boldsymbol{g}$-factor in Na

The Lande $g$-factor is given by

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

The total angular momentum $\boldsymbol{J}$ 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. Basic classical vector model of orbital angular momentum ( $\boldsymbol{L}$ ), spin angular momentum $(\boldsymbol{S})$, orbital magnetic moment $\left(\boldsymbol{\mu}_{\mathrm{L}}\right)$, and spin magnetic moment $\left(\boldsymbol{\mu}_{\mathrm{S}}\right) . \boldsymbol{J}(=\boldsymbol{L}+\boldsymbol{S})$ is the total angular momentum. $\boldsymbol{\mu}_{\mathrm{J}}$ is the component of the total magnetic moment $\left(\boldsymbol{\mu}_{\mathrm{L}}+\boldsymbol{\mu}_{\mathrm{S}}\right)$ along the direction ( $-J$ ).

Suppose that

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

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

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.

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

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 $\mu$ is

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

Thus we have

$$
\boldsymbol{\mu}_{J}=-\frac{\mu_{B}}{\hbar}(a+2 b) \mathbf{J}=-\frac{\mu_{B}}{\hbar}(1+b) \mathbf{J}=-\frac{g_{J} \mu_{B}}{\hbar} \mathbf{J},
$$

with

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

7. The states of $3^{2} S_{1 / 2}, 3^{2} \mathbf{P}_{3 / 2}$, and $3^{2} \mathbf{P}_{1 / 2}$ in Na The electron configuration of Na is given by
$\mathrm{Na}:(1 \mathrm{~s})^{2}(2 \mathrm{~s})^{2}(2 \mathrm{p})^{6}(3 \mathrm{~s})$

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 3 s to a possible higher state.

## (a) The 3s state

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

$$
\begin{aligned}
& D_{0} \times D_{1 / 2}=D_{1 / 2} \\
& |j, m\rangle \text { where } j=1 / 2(m=1 / 2,-1 / 2)
\end{aligned}
$$

Thus we have $j=1 / 2$ (the degeneracy 2). The state is described by $3{ }^{2} \mathrm{~S}_{1 / 2}$ (or simply ${ }^{2} \mathrm{~S}_{1 / 2}$ ). Here we use the notation of $n{ }^{2 S+1} L_{j}$ 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.

$$
\begin{aligned}
& |j=1 / 2, m=1 / 2\rangle=\left|m_{l}=0, m_{s}=1 / 2\right\rangle \\
& |j=1 / 2, m=-1 / 2\rangle=\left|m_{l}=0, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$



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

## (b) The $3 p$ state

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

$$
\mathrm{D}_{1} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{3 / 2}+\mathrm{D}_{1 / 2}
$$

or

$$
\begin{aligned}
& \left|j=\frac{3}{2}, m\right\rangle, \text { where } m=3 / 2,1 / 2,-1 / 2,-3 / 2 \\
& \left|j=\frac{1}{2}, m\right\rangle, \text { where } m=1 / 2,-1 / 2
\end{aligned}
$$

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

Note that


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

The Clebsch-Gordon coefficients can be calculated using the Mathematica.
(i) $\operatorname{For} j=3 / 2\left(3{ }^{2} \mathrm{P}_{3 / 2}\right)$,

$$
\begin{aligned}
& |j=3 / 2, m=-3 / 2\rangle=\left|m_{l}=-1, m_{s}=-1 / 2\right\rangle \\
& |j=3 / 2, m=-1 / 2\rangle=\sqrt{\frac{2}{3}}\left|m_{l}=0, m_{s}=-1 / 2\right\rangle+\frac{1}{\sqrt{3}}\left|m_{l}=-1, m_{s}=1 / 2\right\rangle \\
& |j=3 / 2, m=1 / 2\rangle=\frac{1}{\sqrt{3}}\left|m_{l}=1, m_{s}=-1 / 2\right\rangle+\sqrt{\frac{2}{3}}\left|m_{l}=0, m_{s}=1 / 2\right\rangle \\
& |j=3 / 2, m=3 / 2\rangle=\left|m_{l}=1, m_{s}=1 / 2\right\rangle
\end{aligned}
$$



Fig. $\quad\left|j=\frac{1}{2}, m\right\rangle . l=1$. The recursion relation to obtain the Clebsch-Gordon coefficients.
(ii) $\operatorname{For} j=1 / 2\left(3^{2} \mathrm{P}_{1 / 2}\right)$,

$$
\begin{aligned}
& |j=1 / 2, m=-1 / 2\rangle=\frac{1}{\sqrt{3}}\left|m_{l}=0, m_{s}=-1 / 2\right\rangle-\sqrt{\frac{2}{3}}\left|m_{l}=-1, m_{s}=1 / 2\right\rangle \\
& |j=1 / 2, m=1 / 2\rangle=\sqrt{\frac{2}{3}}\left|m_{l}=1, m_{s}=-1 / 2\right\rangle-\frac{1}{\sqrt{3}}\left|m_{l}=0, m_{s}=1 / 2\right\rangle
\end{aligned}
$$

(c) $g$ factors

The Lande $g$-factor is defined by

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

Table

| Term | $j$ | $l$ | $S$ | $g_{J}$ |
| :--- | :--- | :--- | :--- | :--- |
| $3{ }^{2} \mathrm{P}_{3 / 2}$ | $3 / 2$ | 1 | $1 / 2$ | $4 / 3$ |
| $3{ }^{2} \mathrm{P}_{1 / 2}$ | $1 / 2$ | 1 | $1 / 2$ | $2 / 3$ |
| $3{ }^{2} \mathrm{~S}_{1 / 2}$ | $1 / 2$ | 0 | $1 / 2$ | 2 |



Fig. $\quad$ Schematic diagram of energy levels in $\mathrm{Na}(n=3)$ 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

$$
\begin{aligned}
& \lambda=589.6 \mathrm{~nm}\left(3{ }^{3} \mathrm{P}_{1 / 2}-3{ }^{3} \mathrm{~S}_{1 / 2}\right) . \\
& \lambda=589.0 \mathrm{~nm}\left(3{ }^{3} \mathrm{P}_{3 / 2}-3{ }^{3} \mathrm{~S}_{1 / 2}\right) .
\end{aligned}
$$

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

## 8. Anomalous Zeeman effect in Na

The Hamiltonian due to the Zeeman energy is given by

$$
\begin{array}{cc}
\hat{H}=-\hat{\boldsymbol{\mu}}_{J} \cdot \boldsymbol{B}=\frac{g_{J} \mu_{B}}{\hbar} \hat{\boldsymbol{J}} \cdot \boldsymbol{B}=\frac{g_{J} \mu_{B} B}{\hbar} \hat{J}_{z} \\
\hat{H}|j, m\rangle=\frac{g_{J} \mu_{B} B}{\hbar} \hat{J}_{z}|j, m\rangle=g_{J} \mu_{B} m B|j, m\rangle & \\
E_{3}=E_{30}+g_{3} \mu_{B} m_{2} B, & \text { for } 3{ }^{2} \mathrm{P}_{3 / 2} \text { level } \\
E_{2}=E_{20}+g_{2} \mu_{B} m_{2} B, & \text { for } 3{ }^{2} \mathrm{P}_{1 / 2} \text { level } \\
E_{1}=E_{10}+g_{1} \mu_{B} m_{1} B & \text { for } 3{ }^{2} \mathrm{~S}_{1 / 2} \text { level }
\end{array}
$$

where

$$
\begin{aligned}
& m_{3}=3 / 2,1 / 2,-1 / 2,-3 / 2, \quad m_{2}=1 / 2,-1 / 2, \quad m_{1}=1 / 2,-1 / 2, \\
& g_{3}=\frac{4}{3}, \quad g_{2}=\frac{2}{3}, \quad g_{1}=2
\end{aligned}
$$

The energy separation is given by

$$
\begin{aligned}
& \Delta E_{13}=E_{3}-E_{1}=\Delta E_{13}{ }^{0}+\mu_{B} B\left(m_{3} g_{3}-m_{1} g_{1}\right) \\
& \Delta E_{12}=E_{2}-E_{1}=\Delta E_{12}^{0}+\mu_{B} B\left(m_{2} g_{2}-m_{1} g_{1}\right)
\end{aligned}
$$

with

$$
\Delta E_{13}{ }^{0}=\frac{h c}{\lambda(589.0 \mathrm{~nm})}, \quad \Delta E_{12}{ }^{0}=\frac{h c}{\lambda(589.6 \mathrm{~nm})}
$$

Then we have

$$
\begin{array}{ll}
m_{3} g_{3}-m_{1} g_{1}=-5 / 3,-1,-1 / 3,1 / 3,1,5 / 3 & \text { around } 589.0 \mathrm{~nm} \\
m_{2} g_{2}-m_{1} g_{1}=-3 / 2,-4 / 3,4 / 3,2 / 3 & \text { around } 589.6 \mathrm{~nm}
\end{array}
$$

where

$$
m_{3}-m_{1}= \pm 1,0, \quad m_{2}-m_{1}= \pm 1,0
$$



Fig. Zeeman splitting of the $\mathrm{Na} D$ lines in $B=3 T .[1 / \lambda(589.0 \mathrm{~nm})-1 / \lambda(589.6 \mathrm{~nm})]=$ $17.28 \mathrm{~cm}^{-1}$.


Fig. H. White, Introduction to Atomic Spectra

## 8. Spin orbit interaction for one electron system

We introduce a new Hamiltonian given by

$$
\hat{H}=\hat{H}_{0}+\hat{H}_{L S},
$$

The total angular momentum J is the addition of the orbital angular momentum and the spin angular momentum,

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

The spin-orbit interaction is defined by

$$
\hat{H}_{L S}=\xi \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}=\xi \frac{1}{2}\left(\hat{\boldsymbol{J}}^{2}-\hat{\boldsymbol{L}}^{2}-\hat{\boldsymbol{S}}^{2}\right) .
$$

where

$$
\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}}=i \hbar \hat{\boldsymbol{L}}, \quad \hat{\boldsymbol{S}} \times \hat{\boldsymbol{S}}=i \hbar \hat{\boldsymbol{S}}
$$

The unperturbed Hamiltonian $\hat{H}_{0}$ commutes with all the components of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$.

$$
\begin{aligned}
& {\left[\hat{H}_{0}, \hat{\boldsymbol{L}}^{2}\right]=\left[\hat{H}_{0}, \hat{L}_{z}^{2}\right]=\left[\hat{H}_{0}, \hat{L}_{z}\right]=0,} \\
& {\left[\hat{H}_{0}, \hat{\boldsymbol{S}}^{2}\right]=\left[\hat{H}_{0}, \hat{S}_{z}^{2}\right]=\left[\hat{H}_{0}, \hat{S}_{z}\right]=0,}
\end{aligned}
$$

and

$$
\left[\hat{H}_{0}, \hat{J}_{z}\right]=\left[\hat{H}_{0}, \hat{L}_{z}+\hat{S}_{z}\right]=0
$$

We note that

$$
\begin{aligned}
{\left[\hat{H}_{0}, \hat{H}_{L S}\right] } & =\left[\hat{H}_{0}, \xi \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}\right] \\
& =\left[\hat{H}_{0}, \xi\left(\hat{L}_{x} \hat{S}_{x}+\hat{L}_{y} \hat{S}_{y}+\hat{L}_{z} \hat{S}_{z}\right)\right] \\
& =0
\end{aligned}
$$

Then we have

$$
\left[\hat{H}_{0}, \hat{\boldsymbol{J}}^{2}-\hat{\boldsymbol{L}}^{2}-\hat{\boldsymbol{S}}^{2}\right]=0
$$

or

$$
\left[\hat{H}_{0}, \hat{\boldsymbol{J}}^{2}\right]=0
$$

We also note that

$$
\begin{aligned}
{\left[\hat{\boldsymbol{J}}^{2}, \hat{\boldsymbol{L}}^{2}\right] } & =\left[\hat{\boldsymbol{L}}^{2}+\hat{\boldsymbol{S}}^{2}+2 \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{\boldsymbol{L}}^{2}\right]=2\left[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{\boldsymbol{L}}^{2}\right]=0 \\
{\left[\hat{\boldsymbol{J}}^{2}, \hat{\boldsymbol{S}}^{2}\right] } & =\left[\hat{\boldsymbol{L}}^{2}+\hat{\boldsymbol{S}}^{2}+2 \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{\boldsymbol{S}}^{2}\right]=2\left[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{\boldsymbol{S}}^{2}\right]=0 \\
{\left[\hat{\boldsymbol{J}}^{2}, \hat{J}_{z}\right] } & =\left[\hat{\boldsymbol{L}}^{2}+\hat{\boldsymbol{S}}^{2}+2 \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{L}_{z}+\hat{S}_{z}\right] \\
& =2\left[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{L}_{z}+\hat{S_{z}}\right]=0 \\
& =-2\left[\hat{L}_{z}, \hat{L}_{x}\right] \hat{S}_{x}+2\left[\hat{L}_{y}, \hat{L}_{z}\right] \hat{S}_{y}-2 \hat{L}_{x}\left[\hat{S}_{z}, \hat{S}_{x}\right]+2 \hat{L}_{y}\left[\hat{S}_{y}, \hat{S}_{z}\right] \\
& =-2 i \hbar \hat{L}_{y} \hat{S}_{x}+2 i \hbar \hat{L}_{x} \hat{S}_{y}-2 i \hbar \hat{L}_{x} \hat{S}_{y}+2 i \hbar \hat{L}_{y} \hat{S}_{x} \\
& =0
\end{aligned}
$$

Thus we conclude that $|\psi\rangle$ is the simultaneous eigenket of the mutually commuting observables $\left\{\hat{H}_{0}, \hat{\boldsymbol{L}}^{2}, \hat{\boldsymbol{S}}^{2}, \hat{\boldsymbol{J}}^{2}\right.$, and $\left.\hat{\boldsymbol{J}}_{z}\right\}$.

$$
\begin{aligned}
& \hat{H}_{0}|\psi\rangle=E_{n}^{(0)}|\psi\rangle \\
& \hat{\boldsymbol{L}}^{2}|\psi\rangle=\hbar^{2} l(l+1)|\psi\rangle \\
& \hat{\boldsymbol{S}}^{2}|\psi\rangle=\hbar^{2} s(s+1)|\psi\rangle
\end{aligned}
$$

$$
\begin{aligned}
& \hat{\boldsymbol{J}}^{2}|\psi\rangle=\hbar^{2} j(j+1)|\psi\rangle \\
& \hat{J}_{z}|\psi\rangle=\hbar m|\psi\rangle
\end{aligned}
$$

The eigenket can be described by

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

Note that the expression of the state can be formulated using the Clebsch-Gordan coefficient (which will be discussed later). The value of $j$ is related to $l$ and $s(=1 / 2)$ as

$$
j=l+s=l+\frac{1}{2}, \quad j=l-s=l-\frac{1}{2}
$$

When the spin orbit interaction is the perturbation Hamiltonian, we can apply the degenerate theory for the perturbation theory.

$$
\begin{aligned}
\hat{H}_{L S}|j, m ; l, s\rangle & =\frac{\xi}{2}\left(\hat{\boldsymbol{J}}^{2}-\hat{\boldsymbol{L}}^{2}-\hat{\boldsymbol{S}}^{2}\right)|j, m ; l, s\rangle \\
& =\frac{\xi \hbar^{2}}{2}[j(j+1)-l(l+1)-s(s+1)|j, m ; l, s\rangle \\
& =E_{S O}{ }^{(1)}|j, m ; l, s\rangle
\end{aligned}
$$

where

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

with $s=1 / 2$. Here we note that

$$
\begin{aligned}
\xi & =\frac{e^{2}}{2 m_{e}{ }^{2} c^{2}}\left\langle\frac{1}{r^{3}}\right\rangle_{a v} \\
& =\frac{e^{2}}{2 m_{e}{ }^{2} c^{2}} \frac{1}{l(l+1 / 2)(l+1) n^{3} a_{B}{ }^{3}} \\
& =\frac{1}{2} m_{e} c^{2} \frac{\alpha^{4}}{\hbar^{2}} \frac{1}{l(l+1 / 2)(l+1) n^{3}}
\end{aligned}
$$

where

$$
\left\langle\frac{1}{r^{3}}\right\rangle_{a v}=\frac{1}{l(l+1 / 2)(l+1) n^{3} a_{B}^{3}} .
$$

with

$$
a_{B}=\frac{\hbar^{2}}{m_{e} e^{2}}, \quad \alpha=\frac{e^{2}}{\hbar c}
$$

Then we have

$$
\begin{aligned}
E_{\text {SO }}{ }^{(1)} & =\frac{\xi \hbar^{2}}{2}[j(j+1)-l(l+1)-s(s+1) \\
& =\frac{1}{4} m_{e} c^{2} \alpha^{4} \frac{[j(j+1)-l(l+1)-s(s+1)]}{n^{3} l(l+1 / 2)(l+1)} \\
& =\frac{1}{2} m_{e} c^{2} \frac{\alpha^{4}}{n^{3}} \frac{\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{2 l(l+1 / 2)(l+1)}
\end{aligned}
$$

When $j=l+\frac{1}{2}$

$$
E_{\text {SO }}{ }^{(1)}=\frac{1}{2} m_{e} c^{2} \frac{\alpha^{4}}{n^{3}} \frac{l}{2 l(l+1 / 2)(l+1)}
$$

When $j=l-\frac{1}{2}$

$$
E_{s o}{ }^{(1)}=\frac{1}{2} m_{e} c^{2} \frac{\alpha^{4}}{n^{3}} \frac{-(l+1)}{2 l(l+1 / 2)(l+1)}
$$



$$
l=0
$$

## Spin-orbit interaction

Fig. The degenerate states with the same $l(\neq 0)$ are separated into the energy level with $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$ due to the spin-orbit interaction. The state with $l=0$ (sstate) remains unchanged. $\delta=\frac{1}{2} m_{e} c^{2} \frac{\alpha^{4}}{n^{3}} \frac{1}{2 l(l+1 / 2)(l+1)}$ depends on $n$ and $l$.

## 9. Eigenstates for $\boldsymbol{j}=\boldsymbol{l}+\mathbf{1} / \mathbf{2}$,



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

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

with

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

We note that

$$
\begin{aligned}
|j=l+1 / 2, m\rangle & =\sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

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

$$
\begin{gathered}
\hat{L}_{z}|j=l+1 / 2, m\rangle=\hbar \sqrt{\frac{l+m+1 / 2}{2 l+1}}(m-1 / 2)\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
+\hbar \sqrt{\frac{l-m+1 / 2}{2 l+1}}(m+1 / 2)\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle \\
\langle j=l+1 / 2, m| \hat{L}_{z}|j=l+1 / 2, m\rangle=\hbar\left(\sqrt{\frac{l+m+1 / 2}{2 l+1}} \sqrt{\frac{l-m+1 / 2}{2 l+1}}\right)\left(\sqrt{\frac{l+m+1 / 2}{2 l+1}}(m-1 / 2)\right. \\
\left.\sqrt{\frac{l-m+1 / 2}{2 l+1}}(m+1 / 2)\right) \\
\end{gathered} \begin{aligned}
& \hbar\left[\frac{l+m+1 / 2}{2 l+1}(m-1 / 2)+\frac{l-m+1 / 2}{2 l+1}(m+1 / 2)\right] \\
& =\frac{\hbar 2 l m}{2 l+1}
\end{aligned}
$$

Similarly,

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

Then we have

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

## 10. Eigenstates for $\boldsymbol{j}=\boldsymbol{l} \mathbf{- 1 / 2}$



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

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

with

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

$$
\begin{aligned}
|j=l-1 / 2, m\rangle & =-\sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

or

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

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

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

Then we have

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

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

$$
\begin{aligned}
& \Delta E=E_{L S}=\frac{\xi}{2} \hbar^{2} l, \quad \text { for } j=l+1 / 2, \\
& \Delta E=E_{L S}=-\frac{\xi}{2} \hbar^{2}(l+1), \quad \text { for } j=l-1 / 2,
\end{aligned}
$$

$$
\hat{H}_{L S}=\left(\begin{array}{cc}
\frac{\xi}{2} \hbar^{2} l & 0 \\
0 & -\frac{\xi}{2} \hbar^{2}(l+1)
\end{array}\right)
$$

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

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

or

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

## 11. Pachen-Back effect

We consider the Hamitonian given by

$$
\hat{H}=\hat{H}_{0}+\frac{\xi \hbar^{2}}{2} \frac{1}{\hbar^{2}} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}+\mu_{B} B \frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)
$$

The matrix of $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ under the basis of $\left|m_{l}=m-\frac{1}{2}, m_{s}=\frac{1}{2}\right\rangle$ and $\left|m_{l}=m+\frac{1}{2}, m_{s}=-\frac{1}{2}\right\rangle$, is obtained as

$$
\frac{2}{\hbar^{2}} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}=\left(\begin{array}{cc}
\left(m-\frac{1}{2}\right) & \sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} \\
\sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} & -\left(m+\frac{1}{2}\right)
\end{array}\right)
$$

We note that

$$
\frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)\left|m_{l}=m-\frac{1}{2}, m_{s}=\frac{1}{2}\right\rangle=\left(m+\frac{1}{2}\right)\left|m_{l}=m-\frac{1}{2}, m_{s}=\frac{1}{2}\right\rangle
$$

$$
\frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)\left|m_{l}=m+\frac{1}{2}, m_{s}=-\frac{1}{2}\right\rangle=\left(m-\frac{1}{2}\right)\left|m_{l}=m-\frac{1}{2}, m_{s}=\frac{1}{2}\right\rangle
$$

So we have the matrix of $\frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)$ under the basis of $\left|m_{l}=m-\frac{1}{2}, m_{s}=\frac{1}{2}\right\rangle$ and $\left|m_{l}=m+\frac{1}{2}, m_{s}=-\frac{1}{2}\right\rangle$, as

$$
\frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)=\left(\begin{array}{cc}
m+\frac{1}{2} & 0 \\
0 & m-\frac{1}{2}
\end{array}\right)
$$

Thus the resulting matrix is given by

$$
\begin{aligned}
\frac{\xi \hbar^{2}}{4}\left(\frac{2}{\hbar^{2}} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}\right)+\mu_{B} B \frac{1}{\hbar}\left(L_{z}+2 S_{z}\right)= & \frac{\xi \hbar^{2}}{4}\left(\begin{array}{cc}
\left(m-\frac{1}{2}\right) & \sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} \\
\sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} & -\left(m+\frac{1}{2}\right)
\end{array}\right) \\
& +\mu_{B} B\left(\begin{array}{cc}
m+\frac{1}{2} & 0 \\
0 & m-\frac{1}{2}
\end{array}\right)
\end{aligned}
$$

We solve the eigenvalue problem.

$$
\frac{\xi \hbar^{2}}{4}=\frac{1}{2} \alpha, \quad \beta=\mu_{B} B
$$

The matrix (2x2) is given by
$A=\frac{\alpha}{2}\left(\begin{array}{cc}\left(m-\frac{1}{2}\right) & \sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} \\ \sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)} & -\left(m+\frac{1}{2}\right)\end{array}\right)+\beta\left(\begin{array}{cc}m+\frac{1}{2} & 0 \\ 0 & m-\frac{1}{2}\end{array}\right) ;$
or

$$
A=\frac{\alpha}{2}\left(\begin{array}{cc}
m-\frac{1}{2} & k \\
k & -\left(m+\frac{1}{2}\right)
\end{array}\right)+\beta\left(\begin{array}{cc}
m+\frac{1}{2} & 0 \\
0 & m-\frac{1}{2}
\end{array}\right)
$$

where for simplicity we use

$$
k=\sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)}
$$

The eigenvalues are

$$
\begin{aligned}
& \lambda_{1}=-\frac{\alpha}{4}+\beta m+\frac{1}{2} \sqrt{\left.\alpha^{2}\left(l+\frac{1}{2}\right)^{2}+2 \alpha \beta m+\beta^{2}\right)} \\
& \lambda_{2}=-\frac{\alpha}{4}+\beta m-\frac{1}{2} \sqrt{\left.\alpha^{2}\left(l+\frac{1}{2}\right)^{2}+2 \alpha \beta m+\beta^{2}\right)}
\end{aligned}
$$

We introduce the ratio $\zeta$ as

$$
\varsigma=\frac{\beta}{\alpha} .
$$

Then we have

$$
\lambda_{1}=\frac{\alpha}{4}\left(-1+4 \varsigma m+\frac{1}{2} \sqrt{\left.\left(l+\frac{1}{2}\right)^{2}+2 \varsigma m+\varsigma^{2}\right)}\right.
$$

and

$$
\lambda_{2}=\frac{\alpha}{4}\left(-1+4 \varsigma m-\frac{1}{2} \sqrt{\left.\left(l+\frac{1}{2}\right)^{2}+2 \varsigma m+\varsigma^{2}\right)}\right.
$$

For $\varsigma \ll 1$,

$$
\begin{aligned}
& \lambda_{1}=\frac{\alpha}{2} l+\beta m \frac{2 l+2}{2 l+1} \\
& \lambda_{2}=-\frac{\alpha}{2}(l+1)+\beta m \frac{2 l}{2 l+1}
\end{aligned}
$$

For $\varsigma \gg 1$,

$$
\lambda_{1}=\alpha \varsigma\left(m+\frac{1}{2}\right)=\beta\left(m+\frac{1}{2}\right), \quad \lambda_{2}=\alpha \varsigma\left(m-\frac{1}{2}\right)=\beta\left(m-\frac{1}{2}\right)
$$


((Mathematica))

Clear["Global`*"]; rule1 $=\left\{\sqrt{\mathrm{k}^{2}+\mathrm{m}^{2}} \rightarrow \mathrm{~L}+\frac{1}{2}\right\}$;
rule $2=\left\{k \rightarrow \sqrt{\left(L-m+\frac{1}{2}\right)\left(L+m+\frac{1}{2}\right)}\right\} ;$
$A 1=\frac{\alpha}{2}\left(\begin{array}{cc}m-\frac{1}{2} & k \\ k & -\left(m+\frac{1}{2}\right)\end{array}\right)+\beta\left(\begin{array}{cc}m+\frac{1}{2} & 0 \\ 0 & \left(m-\frac{1}{2}\right)\end{array}\right) ;$
eq1 = Eigensystem[A1];
$\lambda 1$ = eq1 [ [1, 2] ] /. rule1 /. rule2 // Simplify [\#, L > 0] \& $\frac{1}{4}\left(-\alpha+4 m \beta+\sqrt{(\alpha+2 L \alpha)^{2}+8 m \alpha \beta+4 \beta^{2}}\right)$
$\lambda 2$ = eq1 [ [1, 1] ] /. rule1 /. rule2 // Simplify[\#, L > 0] \&
$-\frac{\alpha}{4}+m \beta-\frac{1}{4} \sqrt{(\alpha+2 L \alpha)^{2}+8 m \alpha \beta+4 \beta^{2}}$
$\lambda 11=\lambda 1 / .\{\beta \rightarrow \zeta \alpha\} / /$ Simplify $[\#, \alpha>0] \&$
$\frac{1}{4} \alpha\left(-1+4 m \zeta+\sqrt{1+4 L+4 L^{2}+8 m \zeta+4 \zeta^{2}}\right)$
$\lambda 22=\lambda 2 / .\{\beta \rightarrow \zeta \alpha\} / /$ Simplify $[\#, \alpha>0] \&$
$-\frac{1}{4} \alpha\left(1-4 m \zeta+\sqrt{1+4 L+4 L^{2}+8 m \zeta+4 \zeta^{2}}\right)$
Series [ $111,\{\zeta, 0,2\}] / / S i m p l i f y[\#, 2 L+1>0] \&$ $\frac{L \alpha}{2}+\frac{2(1+L) m \alpha \zeta}{1+2 L}+\frac{\left(1+4 L+4 L^{2}-4 m^{2}\right) \alpha \zeta^{2}}{2(1+2 L)^{3}}+0[\zeta]^{3}$

Series[ 22 , \{̧, 0, 2\}] // Simplify[\#, $2 L+1>0] \&$

$$
-\frac{1}{2}(1+L) \alpha+\frac{2 L m \alpha \zeta}{1+2 L}-\frac{\left(\left(1+4 L+4 L^{2}-4 m^{2}\right) \alpha\right) \zeta^{2}}{2(1+2 L)^{3}}+0[\zeta]^{3}
$$

## 12. 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

$$
\hat{\boldsymbol{\mu}}=-\frac{\mu_{B}}{\hbar}(\hat{\boldsymbol{L}}+2 \hat{\boldsymbol{S}})
$$

where $\mu_{B}=\frac{e \hbar}{2 m_{e} c}(>0)$ is the Bohr magneton. The Zeeman energy is given by

$$
\hat{H}_{B}=-\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B}=\frac{\mu_{B}}{\hbar}(\hat{\boldsymbol{L}}+2 \hat{\boldsymbol{S}}) \cdot \boldsymbol{B}=\frac{\mu_{B}}{\hbar}(\hat{\boldsymbol{J}}+\hat{\boldsymbol{S}}) \cdot \boldsymbol{B}=\frac{\mu_{B} B}{\hbar}\left(\hat{J}_{z}+\hat{S}_{z}\right),
$$

for $\boldsymbol{B} / / \mathrm{z}$. We now calculate

$$
\begin{aligned}
\hat{H}_{B}|j=l+1 / 2, m\rangle & =\frac{\mu_{B} B}{\hbar}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) \sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\frac{\mu_{B} B}{\hbar}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

or

$$
\begin{aligned}
\hat{H}_{B}|j=l+1 / 2, m\rangle & =\mu_{B} B\left(m+\frac{1}{2}\right) \sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\mu_{B} B\left(m-\frac{1}{2}\right) \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

Noting that

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

we have

$$
\begin{aligned}
\left(\hat{H}_{L S}+\hat{H}_{B}\right)|j=l+1 / 2, m\rangle & \left.\left.=\left[\frac{\xi}{2} l \hbar^{2}+\mu_{B} B\left(m+\frac{1}{2}\right)\right] \sqrt{\frac{l+m+1 / 2}{2 l+1}}\right] m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\left[\frac{\xi}{2} l \hbar^{2}+\mu_{B} B\left(m-\frac{1}{2}\right)\right] \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

Similarly,

$$
\begin{aligned}
\hat{H}_{B}\left|j=l-\frac{1}{2}, m\right\rangle= & -\frac{\mu_{B} B}{\hbar}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\frac{\mu_{B} B}{\hbar}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) \sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

or

$$
\begin{aligned}
\hat{H}_{B}\left|j=l-\frac{1}{2}, m\right\rangle & =-\mu_{B} B\left(m+\frac{1}{2}\right) \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\mu_{B} B\left(m-\frac{1}{2}\right) \sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

or

$$
\begin{aligned}
\left(\hat{H}_{L S}+\hat{H}_{B}\right)|j=l-1 / 2, m\rangle & =\left[\frac{\xi}{2}(l+1) \hbar^{2}-\mu_{B} B\left(m+\frac{1}{2}\right)\right] \sqrt{\frac{l-m+1 / 2}{2 l+1}}\left|m_{l}=m-1 / 2, m_{s}=1 / 2\right\rangle \\
& +\left[-\frac{\xi}{2}(l+1) \hbar^{2}+\mu_{B} B\left(m-\frac{1}{2}\right)\right] \sqrt{\frac{l+m+1 / 2}{2 l+1}}\left|m_{l}=m+1 / 2, m_{s}=-1 / 2\right\rangle
\end{aligned}
$$

Note that

$$
\begin{aligned}
& \left\langle j=l+\frac{1}{2}, m\right|=\sqrt{\frac{l+m+1 / 2}{2 l+1}}\left\langle m_{l}=m-1 / 2, m_{s}=1 / 2\right|+\sqrt{\frac{l-m+1 / 2}{2 l+1}}\left\langle m_{l}=m+1 / 2, m_{s}=-1 / 2\right| \\
& \left\langle j=l-\frac{1}{2}, m\right|=-\sqrt{\frac{l-m+1 / 2}{2 l+1}}\left\langle m_{l}=m-1 / 2, m_{s}=1 / 2\right|+\sqrt{\frac{l+m+1 / 2}{2 l+1}}\left\langle m_{l}=m+1 / 2, m_{s}=-1 / 2\right|
\end{aligned}
$$

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

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

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

$$
\begin{aligned}
& \lambda_{1}=\mu_{B} B m-\frac{\xi \hbar^{2}}{4}-\frac{1}{4} \sqrt{4 \mu_{B}^{2} B^{2}+8 \mu_{B} B m \xi \hbar^{2}+\xi^{2}(2 l+1)^{2} \hbar^{4}}, \\
& \lambda_{2}=\mu_{B} B m-\frac{\xi \hbar^{2}}{4}+\frac{1}{4} \sqrt{4 \mu_{B}^{2} B^{2}+8 \mu_{B} B m \xi \hbar^{2}+\xi^{2}(2 l+1)^{2} \hbar^{4}} .
\end{aligned}
$$

## 13. Zeeman effect in $\mathbf{N a}$

We now consider the D lines of Na .


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

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

$$
\left.\begin{array}{r}
\left|j=\frac{3}{2}, m\right\rangle
\end{array}\left|j=\frac{1}{2}, m\right\rangle\right)
$$

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

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

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

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

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

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

with

$$
E_{5}=E(3 p)+\frac{\xi}{2} \hbar^{2}+2 \mu_{B} B
$$

for $m=3 / 2$,
and

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

with

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

for $m=-3 / 2$.
(b) $\quad j=1 / 2, l=0, s=1 / 2$

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

with the eigenvalue

$$
E_{1}(m)=E(3 s)+2 \mu_{B} B m,
$$

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

## 14. 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

$$
\begin{aligned}
& E_{1}\left(m=\frac{1}{2}\right)=E(3 s)+\mu_{B} B, \\
& E_{1}\left(m=-\frac{1}{2}\right)=E(3 s)-\mu_{B} B, \\
& E_{2}\left(m=\frac{1}{2}\right)=E(3 p)-\frac{\xi \hbar^{2}}{4}, \\
& E_{2}\left(m=-\frac{1}{2}\right)=E(3 p)-\frac{\xi \hbar^{2}}{4}-\mu_{B} B, \\
& E_{3}=E(3 p)+\frac{\xi}{2} \hbar^{2}-2 \mu_{B} B, \\
& E_{4}\left(m=\frac{1}{2}\right)=E(3 p)-\frac{\xi \hbar^{2}}{4}+\mu_{B} B, \\
& E_{4}\left(m=-\frac{1}{2}\right)=E(3 p)-\frac{\xi \hbar^{2}}{4}, \\
& E_{5}=E(3 p)+\frac{\xi}{2} \hbar^{2}+2 \mu_{B} B .
\end{aligned}
$$

## ((Mathematica))

We use

$$
\begin{aligned}
& \mu_{\mathrm{B}}=1, \hbar=1 \\
& E(3 \mathrm{p})-E(3 \mathrm{~s})=-7 . \xi=1 .
\end{aligned}
$$

for the calculation using the Mathematica.


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


Fig.


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

## 15. 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

$$
\hat{H}_{B}=\frac{\mu_{B}}{\hbar}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) B
$$

in the presence of the magnetic field along the $z$ axis.
(1) 3 p states

$$
\begin{aligned}
& l=1, \mathrm{~s}=1 / 2 . \\
& \hat{H}_{B}\left|m_{l}, m_{s}\right\rangle_{3 p}=\mu_{B} B\left(m_{l}+2 m_{s}\right)\left|m_{l}, m_{s}\right\rangle_{3 p}
\end{aligned}
$$

$\left|m_{l}, m_{s}\right\rangle_{3 p}$ is the eigenket of $\hat{H}_{B}$ with the eigenvalue $\mu_{B} B\left(m_{l}+2 m_{s}\right)$.

$$
\left|m_{l}, m_{s}\right\rangle_{3 p} \quad\left(m_{1}=1,0,-1, m_{\mathrm{s}}=1 / 2,-1 / 2\right)
$$

(2) 3 s states

$$
\begin{aligned}
& l=0, \mathrm{~s}=1 / 2 \\
& \hat{H}_{B}\left|m_{l}, m_{s}\right\rangle_{3 s}=\mu_{B} B\left(m_{l}+2 m_{s}\right)\left|m_{l}, m_{s}\right\rangle_{3 s}
\end{aligned}
$$

$\left|m_{l}, m_{s}\right\rangle_{3 s}$ is the eigenket of $\hat{H}_{B}$ with the eigenvalue $\mu_{B} B\left(m_{l}+2 m_{s}\right)$.

$$
\left|m_{l}, m_{s}\right\rangle_{3 s} \quad\left(m_{l}=0, m_{\mathrm{s}}=1 / 2,-1 / 2\right)
$$

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

Table

Energy ( $\mu_{\mathrm{B}} \mathrm{B}$ )
2
1
0
$-1$
-2

## Eigenkets

$|1,1 / 2\rangle_{3 p}$
$|0,1 / 2\rangle_{3 p} \quad|0,1 / 2\rangle_{3 s}$
$|1,-1 / 2\rangle_{3 p} \quad|-1,1 / 2\rangle_{3 p}$
$|0,-1 / 2\rangle_{3 p} \quad|0,-1 / 2\rangle_{3 s}$
$|-1,-1 / 2\rangle_{3 p}$

$$
\begin{array}{cc}
\frac{\mid 1, \frac{1}{2}>_{3 p}}{} & 2 \mu_{B} \mathrm{~B} \\
\left|0, \frac{1}{2}>_{3 p},\right| 0, \frac{1}{2}>_{3 s} & \mu_{B} \mathrm{~B} \\
\frac{\left|1,-\frac{1}{2}>_{3 p},\right|-1, \frac{1}{2}>_{3 p}}{} & 0 \\
\left|0,-\frac{1}{2}>_{3 p},\right| 0,-\frac{1}{2}>_{3 s}, & -\mu_{B} \mathrm{~B} \\
\mid-1,-\frac{1}{2}>_{3 p} & -2 \mu_{B} \mathrm{~B}
\end{array}
$$

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

## 16. Zeeman splitting in $\mathbf{C d}$

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

## (a) 5 s 5 s

$$
\begin{array}{ll}
\mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0} & l=0 \\
\mathrm{D}_{1 / 2} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{1}+\mathrm{D}_{0} & s=1, s=0 \\
l=0 \text { and } s=1 & \\
\mathrm{D}_{0} \times \mathrm{D}_{1}=\mathrm{D}_{1} & j=1
\end{array}
$$

$$
5^{3} \mathrm{~S}_{1}
$$

$$
l=0 \text { and } s=0
$$

$$
\mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0} \quad j=0
$$

## $5^{1} \mathrm{~S}_{0}$

## (b) $\quad 5 \mathbf{s 5 p}$

$\begin{array}{ll}\mathrm{D}_{1} \times \mathrm{D}_{0}=\mathrm{D}_{1} & l=1 \\ \mathrm{D}_{1 / 2} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{1}+\mathrm{D}_{0} & s=1, s=0\end{array}$
$l=1$ and $s=1$

$$
\mathrm{D}_{1} \times \mathrm{D}_{1}=\mathrm{D}_{2}+\mathrm{D}_{1}+\mathrm{D}_{0}
$$

$$
j=2
$$

$$
5^{3} \mathrm{P}_{2}
$$

$$
j=1
$$

$$
5^{3} \mathrm{P}_{1}
$$

$$
j=0
$$

$$
5^{3} \mathrm{P}_{0}
$$

$l=1$ and $s=0$

$$
\mathrm{D}_{1} \times \mathrm{D}_{0}=\mathrm{D}_{1}
$$

$$
j=1
$$


(c) 5 s 5 d

$$
\begin{array}{ll}
\mathrm{D}_{2} \times \mathrm{D}_{0}=\mathrm{D}_{2} & l=2 \\
\mathrm{D}_{1 / 2} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{1}+\mathrm{D}_{0} & s=1, s=0 \\
& \\
l=2 \text { and } s=1 &
\end{array}
$$

$$
\mathrm{D}_{2} \times \mathrm{D}_{1}=\mathrm{D}_{3}+\mathrm{D}_{2}+\mathrm{D}_{1}
$$

$$
\begin{aligned}
& j=3 \\
& j=2 \\
& j=1
\end{aligned}
$$

$l=2$ and $s=0$

$$
\mathrm{D}_{2} \times \mathrm{D}_{0}=\mathrm{D}_{2}
$$

$5^{3} \mathrm{D}_{3}$
$5^{3} \mathrm{D}_{2}$
$5^{3} \mathrm{D}_{1}$
$j=2$
$5^{{ }^{1} \mathrm{D}_{2}} \quad(g=1)$


Fig. $\quad$ Schematic diagram for the Zeeman splitting in Cd. $643.8 \mathrm{~nm} . g=1$ for $5^{1} \mathrm{D}_{2}$ $(j=2, l=2, s=0)$ and $g=1$ for $5{ }^{1} \mathrm{P}_{1}(j=1, l=1, s=0)$.

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

$$
5{ }^{1} \mathrm{D}_{2}(j=2, l=2, s=0) \rightarrow 5{ }^{1} \mathrm{P}_{1}(j=1, l=1, s=0) .
$$

In the presence of the magnetic field, the $5{ }^{1} \mathrm{D}_{2}$ level splits into 5 Zeeman components and the $5{ }^{1} \mathrm{P}_{1}$ 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;

$$
\Delta m= \pm 1 \quad \text { for } \sigma \text { components }
$$

$$
\Delta m=0 \quad \text { for } \pi \text { components, }
$$

Thus we observe three spectral lines

## 17. Energy levels in $\mathbf{H g}$ : system with two electrons

The neutral mercury $(\mathrm{Hg})$ atom in its ground state has 80 electrons in the configuration $1 \mathrm{~s}^{2} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{6} 3 \mathrm{~s}^{2} 3 \mathrm{p}^{6} 3 \mathrm{~d}^{10} 4 \mathrm{~s}^{2} 4 \mathrm{p}^{6} 4 \mathrm{~d}^{10} 4 \mathrm{f}^{4} 5 \mathrm{~s}^{2} 5 \mathrm{p}^{6} 5 \mathrm{~d}^{10} 6 \mathrm{~s}^{2}$ in which the $n=1,2,3,4$, and 5 electrons form an inert core for two 6 s 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 twoelectron helium system.

$$
{ }^{2 S+1} L_{J}
$$

Orbital angular momentum

$$
\mathrm{D}_{l 1} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{l 1+l 2}+\ldots . .+\mathrm{D}_{|11-12|}
$$

Spin:
$\mathrm{D}_{1 / 2} \times \mathrm{D}_{1 / 2}=\mathrm{D}_{1}+\mathrm{D}_{0}$

## (a) 6 s 6 s

$$
l=0 \text { and } l=0 \rightarrow \quad \mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0}
$$

$$
l=0 \text { and } s=1
$$

$$
\begin{aligned}
& \mathrm{D}_{0} \times \mathrm{D}_{1}=\mathrm{D}_{1} \\
& j=1
\end{aligned} \quad 6^{3} \mathrm{~S}_{1}
$$

$$
\begin{aligned}
& l=0 \text { and } s=0 \\
& \quad \begin{array}{l}
\mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0} \\
j=0
\end{array} \\
& \quad 6{ }^{1} \mathrm{~S}_{0}
\end{aligned}
$$

(b) $6 s 6 p$
(c) $6 s 6 d$

$$
\begin{aligned}
& l=0 \text { and } l=2 \rightarrow \quad \mathrm{D}_{0} \times \mathrm{D}_{2}=\mathrm{D}_{2} \\
& l=2 \text { and } s=1 \\
& \mathrm{D}_{2} \times \mathrm{D}_{1}=\mathrm{D}_{3}+\mathrm{D}_{2}+\mathrm{D}_{1} \\
& j=3 \\
& j=2 \\
& j=1
\end{aligned}
$$

$$
l=2 \text { and } s=0
$$

$$
\mathrm{D}_{2} \times \mathrm{D}_{0}=\mathrm{D}_{2}
$$

$$
j=2
$$

$$
6{ }^{1} \mathrm{D}_{2}
$$

(d) 6 s 7 s

$$
\begin{aligned}
& l=0 \text { and } l=0 \rightarrow \quad \mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0} \\
& l=0 \text { and } s=1
\end{aligned}
$$

$$
\mathrm{D}_{0} \times \mathrm{D}_{1}=\mathrm{D}_{1}
$$

$$
\begin{aligned}
& l=0 \text { and } l=1 \rightarrow \quad \mathrm{D}_{0} \times \mathrm{D}_{1}=\mathrm{D}_{1} \\
& l=1 \text { and } s=1 \\
& \mathrm{D}_{1} \times \mathrm{D}_{1}=\mathrm{D}_{2}+\mathrm{D}_{1}+\mathrm{D}_{0} \\
& l=1 \text { and } s=0 \\
& \begin{array}{l}
\begin{array}{l}
\mathrm{D}_{1} \times \mathrm{D}_{0}=\mathrm{D}_{1} \\
j=1
\end{array} \quad 6{ }^{1} \mathrm{P}_{1}
\end{array}
\end{aligned}
$$


(e) $6 s 7 p$
$l=0$ and $l=1 \rightarrow \quad \mathrm{D}_{0} \times \mathrm{D}_{1}=\mathrm{D}_{1}$
$l=1$ and $s=1$

$$
\begin{array}{ll}
\mathrm{D}_{1} \times \mathrm{D}_{1}=\mathrm{D}_{2}+\mathrm{D}_{1}+\mathrm{D}_{0} \\
& \\
j=2 & 7^{3} \mathrm{P}_{2} \\
j=1 & 7^{3} \mathrm{P}_{1} \\
j=0 & 7^{3} \mathrm{P}_{0}
\end{array}
$$

$$
l=1 \text { and } s=0
$$

$$
\mathrm{D}_{1} \times \mathrm{D}_{0}=\mathrm{D}_{1}
$$

$$
j=1
$$

$$
7{ }^{1} \mathrm{P}_{1}
$$

(f) $\quad 6 \mathrm{~s} 7 \mathrm{~d}$

$$
l=2 \text { and } s=0
$$

$$
\mathrm{D}_{2} \times \mathrm{D}_{0}=\mathrm{D}_{2}
$$

$$
\begin{aligned}
& l=0 \text { and } l=2 \rightarrow \\
& \mathrm{D}_{0} \times \mathrm{D}_{2}=\mathrm{D}_{2} \\
& l=2 \text { and } s=1 \\
& \mathrm{D}_{2} \times \mathrm{D}_{1}=\mathrm{D}_{3}+\mathrm{D}_{2}+\mathrm{D}_{2} \\
& \begin{array}{ll}
j=3 & 7^{3} \mathrm{D}_{3} \\
j=2 & 7^{3} \mathrm{D}_{2} \\
j=1 & 7^{3} \mathrm{D}_{1}
\end{array}
\end{aligned}
$$

$$
\begin{aligned}
& l=0 \text { and } s=0 \\
& \mathrm{D}_{0} \times \mathrm{D}_{0}=\mathrm{D}_{0} \\
& j=0 \quad 7^{1} \mathrm{~S}_{0}
\end{aligned}
$$

$$
j=2 \quad 7^{1} \mathrm{D}_{1}
$$

## 18. Zeeman splitting in $\mathbf{H g}$



Fig. $\quad$ Schematic diagram for the Zeeman splitting in Hg .546 .07 nm (Green line). $7{ }^{3} \mathrm{~S}_{1}(6 \mathrm{~s} 7 \mathrm{~s}) \cdot 6{ }^{3} \mathrm{P}_{2}(6 \mathrm{~s} 6 \mathrm{p}) \cdot 7{ }^{3} \mathrm{~S}_{1}(j=1, l=0, s=1)$ and $6{ }^{3} \mathrm{P}_{2}(j=2, l=1, s=$ 1).

The Hg green line corresponds to the transition from $7{ }^{3} \mathrm{~S}_{1}$ to $6^{3} \mathrm{P}_{2}$.

The state of the $7{ }^{3} \mathrm{~S}_{1}$ level is described by

$$
\left|j_{2}=1, m_{2}\right\rangle \quad\left(j_{2}=1, s_{2}=1, l_{2}=0, g_{2}=2\right)
$$

with $m_{2}=1,0$, and -1 . The state of $6{ }^{3} \mathrm{P}_{2}$ level is described by

$$
\left|j_{1}=2, m_{1}\right\rangle \quad\left(j_{1}=2, s_{1}=1, l_{1}=1, g_{1}=3 / 2\right)
$$

with $m_{1}=2,1,0,-1$, and -2 . According to the selection rule $(\Delta m=1,0$, and -1$)$, there are 9 lines.

$$
\begin{array}{ll}
\Delta m= \pm 1(6 \text { lines }): & \sigma \text { lines. } \\
\Delta m=0(3 \text { lines }): & \pi \text { lines. }
\end{array}
$$

## 20. Evaluation of observed wavelenghts

$$
\begin{array}{ll}
E_{2}=E_{20}+g_{2} \mu_{B} m_{2} B, & \text { for } 7^{3} \mathrm{~S}_{1} \text { level } \\
E_{1}=E_{10}+g_{2} \mu_{B} m_{1} B & \text { for } 6^{3} \mathrm{P}_{2} \text { level }
\end{array}
$$

The energy separation is given by

$$
\Delta E_{12}=E_{2}-E_{1}=\Delta E_{12}{ }^{0}+\mu_{B} B\left(m_{2} g_{2}-m_{1} g_{1}\right)
$$

with

$$
\begin{aligned}
& \Delta m=m_{2}-m_{1}=-1,0, \text { or } 1 . \\
& m_{2}=1,0,-1 . \\
& m_{1}=2,1,0,-1,-2 . \\
& g_{2}=2
\end{aligned} g_{1}=3 / 2.2 .
$$

Here we note that

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

Then we have

$$
\left(\frac{1}{\lambda_{12}}-\frac{1}{\lambda_{12}^{0}}\right)=\frac{\lambda_{12}{ }^{0}-\lambda_{12}}{\lambda_{12} \lambda_{12}^{0}}=\frac{1}{2 \pi c \hbar} \mu_{B} B\left(m_{2} g_{2}-m_{1} g_{1}\right)
$$

or

$$
\frac{\lambda_{12}^{0}-\lambda_{12}}{\lambda_{12} \lambda_{12}^{0}} \approx \frac{-\Delta \lambda_{12}}{\left(\lambda_{12}^{0}\right)^{2}}=\frac{1}{2 \pi c \hbar} \mu_{B} B\left(m_{2} g_{2}-m_{1} g_{1}\right)
$$

or

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

where

$$
\frac{1}{2 \pi c \hbar} \mu_{B}=4.66865 \times 10^{-5}\left(\mathrm{Oe}^{-1} \mathrm{~cm}^{-1}\right)
$$

and

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

We note that

$$
f\left(m_{1}, m_{2}\right)=\left(-2 m_{2}+m_{1} \frac{3}{2}\right)
$$

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

## REFERENCES

E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1991).
H.E. White, Introduction to Atomic Spectra, McGraw-Hill, New York, 1934).
G. Herzberg, Atomic Spectra \& Atomic Structure (Dover Publications, New York, 1944).
D. Bohm, Quantum Theory (Englewood Cliffs, NJ, Prentice Hall, 1951).
J.J. Sakurai, Modern Quantum Mechanics, Revised Edition (Addison-Wesley, Reading, MA, 1994).
D.H. Goldstein and E. Collett, Polarized light, 2nd-edition (Marcel Dekker, Inc., 1993, New York). p. 353.
J.F. Mulligan, :Who are Fabry and Perot?",Am. J. Phys. 66, 797 (1998).

## APPENDIX

## A. Paschen-Back effect in Na

## Mathematica calculation

Calculation of Matrix element for the Zeeman effect
Eigenvalue problem for the Zeeman effect

$$
\begin{aligned}
& \text { Clear["Global`*"]; } \\
& M 1=\left\{\left\{\frac{\xi \hbar^{2}}{2} 1+\mu B B m\left(1+\frac{1}{2 l+1}\right),-\frac{\mu B B \sqrt{(1+1 / 2)^{2}-m^{2}}}{2 l+1}\right\},\right. \\
& \left.\left\{-\frac{\mu \mathrm{B} \mathrm{~B} \sqrt{(1+1 / 2)^{2}-\mathrm{m}^{2}}}{21+1},-\frac{\xi \hbar^{2}}{2}(1+1)+\mu \text { B B m }\left(1-\frac{1}{21+1}\right)\right\}\right\} ; \\
& \text { eq1 = Eigensystem [M1] // Simplify; }
\end{aligned}
$$

The eigenvalues;

$$
\begin{aligned}
& \lambda 1=\operatorname{eq} 1[[\mathbf{1}, \mathbf{1}]] \\
& \mathrm{Bm} \mu \mathbf{B}-\frac{\xi \hbar^{2}}{4}-\frac{1}{4} \sqrt{4 \mathrm{~B}^{2} \mu \mathbf{B}^{2}+8 \mathrm{Bm} \mu \mathbf{B} \xi \hbar^{2}+(\xi+2 \mathrm{l} \xi)^{2} \hbar^{4}} \\
& \lambda 2=\operatorname{eq} 1[[\mathbf{1}, \mathbf{2}]] \\
& \frac{1}{4}\left(4 \mathrm{Bm} \mu \mathbf{B}-\xi \hbar^{2}+\sqrt{4 \mathbf{B}^{2} \mu \mathbf{B}^{2}+8 \mathrm{Bm} \mu \mathbf{B} \xi \hbar^{2}+(\xi+2 \mathbf{l} \xi)^{2} \hbar^{4}}\right)
\end{aligned}
$$

The eigenvectors:

$$
\begin{aligned}
& \psi 1=e q 1[[2,1]] \\
& \left\{\frac{2 B \sqrt{1+4 l+41^{2}-4 m^{2}} \mu \mathrm{~B}}{4 \mathrm{Bm} \mu \mathrm{~B}+(1+2 \mathrm{l})\left((1+2 \mathrm{l}) \xi \hbar^{2}+\sqrt{4 \mathrm{~B}^{2} \mu \mathrm{~B}^{2}+8 \mathrm{Bm} \mu \mathrm{~B} \xi \hbar^{2}+(\xi+2 \mathrm{l} \xi)^{2} \hbar^{4}}\right)}, 1\right\} \\
& \psi \mathbf{1}=\text { eq1 }[[2,2]] / / \text { FullSimplify } \\
& \left\{\frac{2 \mathrm{~B} \sqrt{(1+2 \mathrm{l})^{2}-4 \mathrm{~m}^{2}} \mu \mathrm{~B}}{4 \mathrm{Bm} \mu \mathrm{~B}+(1+2 \mathrm{l})\left((1+2 \mathrm{l}) \xi \hbar^{2}-\sqrt{4 \mathrm{~B}^{2} \mu \mathrm{~B}^{2}+8 \mathrm{Bm} \mu \mathrm{~B} \xi \hbar^{2}+(\xi+2 \mathrm{l} \xi)^{2} \hbar^{4}}\right)}, 1\right\}
\end{aligned}
$$

## B. Zeeman splitting for Na

Here we discuss the eigenvalue problem in more detail.
$j=3 / 2, l=1, s=1 / 2$
Clebsch-Gordan coefficient

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

$j=1 / 2, l=1, s=1 / 2$
Clebsch-Gordan coefficient;

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

Note that

$$
\begin{aligned}
& \binom{\left|l=1, m_{l}=1\right\rangle|\downarrow\rangle}{\left|l=1, m_{l}=0\right\rangle|\uparrow\rangle}=\left(\begin{array}{cc}
\sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}} \\
-\frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}}
\end{array}\right)\binom{\left.j=\frac{1}{2}, m=\frac{1}{2}\right\rangle}{\left.j=\frac{3}{2}, m=\frac{1}{2}\right\rangle} \\
& \binom{\left|l=1, m_{l}=0\right\rangle|\downarrow\rangle}{\left|l=1, m_{l}=-1\right\rangle|\uparrow\rangle}=\left(\begin{array}{cc}
\frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} \\
-\sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}}
\end{array}\right)\binom{\left.j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle}{\left.j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle}
\end{aligned}
$$

The Hamiltonian is expressed by

$$
H=\xi \mathbf{L} \cdot \mathbf{S}+\frac{\mu_{B}}{\hbar}(\mathbf{L}+2 \mathbf{S}) \cdot \mathbf{B}=\frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right)+\frac{\mu_{B}}{\hbar}\left(L_{z}+2 S_{z}\right) B
$$

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

$$
\begin{aligned}
H_{\text {Zeeman }}\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle & \left.=\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \frac{1}{\sqrt{3}}\left|l=1, m_{l}=0\right\rangle|\downarrow\rangle-\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \sqrt{\frac{2}{3}}\left|l=1, m_{l}=-1\right\rangle|\uparrow\rangle\right) \\
& =-\mu_{B} B \frac{1}{\sqrt{3}}\left|l=1, m_{l}=0\right\rangle|\downarrow\rangle \\
& =-\frac{\mu_{B} B}{3}\left(\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle+\sqrt{2}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle\right) \\
H_{\text {spin-orbit }}\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle & =\frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right)\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle=-\xi \hbar^{2}\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
H_{\text {Zeeman }}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle & =\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \sqrt{\frac{2}{3}}\left|l=1, m_{l}=1\right\rangle|\downarrow\rangle-\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \frac{1}{\sqrt{3}}\left|l=1, m_{l}=0\right\rangle|\uparrow\rangle \\
& =-\mu_{B} B \frac{1}{\sqrt{3}}\left|l=1, m_{l}=0\right\rangle|\uparrow\rangle \\
& =-\mu_{B} B \frac{1}{\sqrt{3}}\left(-\frac{1}{\sqrt{3}}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle\right. \\
& =-\frac{\mu_{B} B}{3}\left(-\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle+\sqrt{2}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle\right. \\
H_{\text {spin-orbit }}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle & =\frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right)\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle=-\xi \hbar^{2}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
H_{\text {Zeeman }}\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle & =\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right)\left|l=1, m_{l}=-1\right\rangle|\downarrow\rangle \\
& =-2 \mu_{B} B\left|l=1, m_{l}=-1\right\rangle|\downarrow\rangle=-2 \mu_{B} B\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle \\
H_{\text {spin-orbit }}\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle & =\frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right) \mu_{B}\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle=\frac{1}{2} \xi \hbar^{2}\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
H_{\text {zeeman }}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle & =\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right)\left(\sqrt{\frac{2}{3}}\left|l=1, m_{l}=0\right\rangle|\downarrow\rangle+\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \frac{1}{\sqrt{3}}\left|l=1, m_{l}=-1\right\rangle|\uparrow\rangle\right) \\
& =-\mu_{B} B \sqrt{\frac{2}{3}}\left|l=1, m_{l}=0\right\rangle \downarrow \downarrow \\
& =-\mu_{B} B \sqrt{\frac{2}{3}}\left(\frac{1}{\sqrt{3}}\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle\right) \\
& =-\frac{\mu_{B} B}{3}\left(\sqrt{2}\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle+2\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle\right) \\
H_{\text {spin-orbit }}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle & =\frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right) \mu_{B}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle=\frac{1}{2} \xi \hbar^{2}\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
H_{\text {zeeman }}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle & =\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right)\left(\frac{1}{\sqrt{3}}\left|l=1, m_{l}=1\right\rangle|\downarrow\rangle+\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right) \sqrt{\frac{2}{3}}\left|l=1, m_{l}=0\right\rangle|\uparrow\rangle\right) \\
& =\mu_{B} B \sqrt{\frac{2}{3}}\left|l=1, m_{l}=0\right\rangle|\uparrow\rangle \\
& =\mu_{B} B \sqrt{\frac{2}{3}}\left(-\frac{1}{\sqrt{3}}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle\right. \\
& =\frac{\mu_{B} B}{3}\left(-\sqrt{2}\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle+2\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle\right) \\
H_{\text {spin-orbit }}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle= & \frac{\xi}{2}\left(\mathbf{J}^{2}-\mathbf{L}^{2}-\mathbf{S}^{2}\right) \mu_{B}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle=\frac{1}{2} \xi \hbar^{2}\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
H_{\text {Zeeman }}\left|j=\frac{3}{2}, m=\frac{3}{2}\right\rangle & =\frac{\mu_{B}}{\hbar} B\left(L_{z}+2 S_{z}\right)\left|l=1, m_{l}=1\right\rangle|\uparrow\rangle \\
& =2 \mu_{B} B\left|l=1, m_{l}=1\right\rangle|\uparrow\rangle=2 \mu_{B} B\left|j=\frac{3}{2}, m=\frac{3}{2}\right\rangle
\end{aligned}
$$

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

Then we have

$$
\begin{aligned}
& H\left|j=\frac{3}{2}, m=\frac{3}{2}\right\rangle=\left(2 \mu_{B} B+\frac{1}{2} \xi \hbar^{2}\right)\left|j=\frac{3}{2}, m=\frac{3}{2}\right\rangle \\
& H\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle=\left(\frac{2}{3} \mu_{B} B+\frac{1}{2} \xi \hbar^{2}\right)\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3} \mu_{B} B\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle \\
& H\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle=\left(-\frac{2}{3} \mu_{B} B+\frac{1}{2} \xi \hbar^{2}\right)\left|j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3} \mu_{B} B\left|j=\frac{1}{2}, m=-\frac{1}{2}\right\rangle \\
& H\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle=\left(-2 \mu_{B} B+\frac{1}{2} \xi \hbar^{2}\right)\left|j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle \\
& H\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle=\left(-\xi \hbar^{2}+\frac{1}{3} \mu_{B} B\right)\left(\left|j=\frac{1}{2}, m=\frac{1}{2}\right\rangle-\frac{\sqrt{2}}{3} \mu_{B} B\left|j=\frac{3}{2}, m=\frac{1}{2}\right\rangle\right.
\end{aligned}
$$

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

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

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

$$
H_{\text {sub } 1}=\left(\begin{array}{cc}
\frac{2}{3} \mu_{B} B+\frac{1}{2} \xi \hbar^{2} & -\frac{\sqrt{2}}{3} \mu_{B} B \\
-\frac{\sqrt{2}}{3} \mu_{B} B & \frac{1}{3} \mu_{B} B-\xi \hbar^{2}
\end{array}\right)
$$

((Mathematica))

## Clear["Global`*"];

m = 1/2;

$$
M 1=\left(\begin{array}{cc}
\frac{\xi \hbar^{2}}{2}+\mu B B \frac{4 m}{3} & -\frac{\mu B B}{3} \sqrt{\frac{9}{4}-m^{2}} \\
-\frac{\mu B B}{3} \sqrt{\frac{9}{4}-m^{2}} & -\xi \hbar^{2}+\mu B B \frac{4 m}{3}
\end{array}\right) ;
$$

## eq1 = Eigensystem [M1] // Simplify

$$
\begin{aligned}
& \left\{\left\{\frac{1}{12}\left(8 \mathbf{B} \mu \mathbf{B}-3 \xi \hbar^{2}-\sqrt{32 \mathbf{B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}\right),\right.\right. \\
& \left.\quad \frac{1}{12}\left(8 \mathbf{B} \mu \mathbf{B}-3 \xi \hbar^{2}+\sqrt{32 \mathbf{B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}\right)\right\}, \\
& \left.\left\{\left\{\frac{-9 \xi \hbar^{2}+\sqrt{32 \mathbf{B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}}{4 \sqrt{2} \mathbf{B} \mu \mathbf{B}}, 1\right\},\left\{-\frac{9 \xi \hbar^{2}+\sqrt{32 \mathbf{B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}}{4 \sqrt{2} \mathbf{B} \mu \mathbf{B}}, 1\right\}\right\}\right\}
\end{aligned}
$$

E1 = eq1[ [1, 1] ] // Series[\#, $\{B, 0,3\}] \& / / \operatorname{Simplify[\# ,~}\{\xi>0, \hbar>0\}] \&$ $-\xi \hbar^{2}+\frac{2 \mu \mathbf{B B}}{3}-\frac{4 \mu \mathbf{B}^{2} \mathrm{~B}^{2}}{27\left(\xi \hbar^{2}\right)}+0[\mathrm{~B}]^{4}$

$$
\begin{aligned}
& \text { E2 = eq1 }[[1,2]] / / \text { Series }[\#,\{B, 0,3\}] \& / / \operatorname{Simplify}[\#,\{\xi>0, \hbar>0\}] \& \\
& \frac{\xi \hbar^{2}}{2}+\frac{2 \mu B B}{3}+\frac{4 \mu B^{2} B^{2}}{27 \xi \hbar^{2}}+0[B]^{4} \\
& \psi 1=\text { eq1 }[[2,1]] / / \text { Series }[\#,\{B, 0,3\}] \& / / \operatorname{Simplify}[\#,\{\xi>0, \hbar>0\}] \& \\
& \left\{\frac{2 \sqrt{2} \mu B B}{9 \xi \hbar^{2}}-\frac{16\left(\sqrt{2} \mu B^{3}\right) B^{3}}{729\left(\xi^{3} \hbar^{6}\right)}+0[B]^{4}, 1\right\} \\
& \psi 2=\operatorname{eq1}[[2,2]] / / \operatorname{Series}[\#,\{B, 0,3\}] \& / / \operatorname{Simplify}[\#,\{\xi>0, \hbar>0\}] \& \\
& \left\{-\frac{9\left(\xi \hbar^{2}\right)}{2(\sqrt{2} \mu B) B}-\frac{2(\sqrt{2} \mu B) B}{9\left(\xi \hbar^{2}\right)}+\frac{16 \sqrt{2} \mu B^{3} B^{3}}{729 \xi^{3} \hbar^{6}}+0[B]^{4}, 1\right\}
\end{aligned}
$$

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

$$
H_{\text {sub } 2}=\left(\begin{array}{cc}
-\frac{2}{3} \mu_{B} B+\frac{1}{2} \xi \hbar^{2} & -\frac{\sqrt{2}}{3} \mu_{B} B \\
-\frac{\sqrt{2}}{3} \mu_{B} B & -\frac{1}{3} \mu_{B} B-\xi \hbar^{2}
\end{array}\right)
$$

((Mathematica))

## Clear["Global`*"];

$m=-1 / 2 ;$

$$
M 1=\left(\begin{array}{cc}
\frac{\xi \hbar^{2}}{2}+\mu B B \frac{4 m}{3} & -\frac{\mu B B}{3} \sqrt{\frac{9}{4}-m^{2}} \\
-\frac{\mu B B}{3} \sqrt{\frac{9}{4}-m^{2}} & -\xi \hbar^{2}+\mu B B \frac{4 m}{3}
\end{array}\right) ;
$$

eq1 = Eigensystem[M1] // Simplify

$$
\begin{aligned}
& \left\{\left\{\frac{1}{12}\left(-8 \mathbf{B} \mu \mathbf{B}-3 \xi \hbar^{2}-\sqrt{32 \mathrm{~B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}\right),\right.\right. \\
& \left.\quad \frac{1}{12}\left(-8 \mathbf{B} \mu \mathbf{B}-3 \xi \hbar^{2}+\sqrt{32 \mathrm{~B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}\right)\right\}, \\
& \left.\left\{\left\{\frac{-9 \xi \hbar^{2}+\sqrt{32 \mathrm{~B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}}{4 \sqrt{2} \mathbf{B} \mu \mathbf{B}}, 1\right\},\left\{-\frac{9 \xi \hbar^{2}+\sqrt{32 \mathrm{~B}^{2} \mu \mathbf{B}^{2}+81 \xi^{2} \hbar^{4}}}{4 \sqrt{2} \mathbf{B} \mu \mathbf{B}}, 1\right\}\right\}\right\}
\end{aligned}
$$

E1 = eq1 [ [1, 1] ] // Series[\#, $\{B, 0,3\}] \& / / \operatorname{Simplify[\# ,~}\{\xi>0, \hbar>0\}]$ \& $-\xi \hbar^{2}-\frac{2 \mu \mathrm{BB}}{3}-\frac{4 \mu \mathrm{~B}^{2} \mathrm{~B}^{2}}{27\left(\xi \hbar^{2}\right)}+0[\mathrm{~B}]^{4}$

$$
\begin{aligned}
& \text { E2 = eq1 }[[1,2]] / / \text { Series }[\#,\{B, 0,3\}] \& / / \text { Simplify }[\#,\{\xi>0, \hbar>0\}] \& \\
& \frac{\xi \hbar^{2}}{2}-\frac{2 \mu B B}{3}+\frac{4 \mu B^{2} B^{2}}{27 \xi \hbar^{2}}+0[B]^{4} \\
& \psi 1=\text { eq1 }[[2,1]] / / \text { Series }[\#,\{B, 0,3\}] \& / / \text { Simplify }[\#,\{\xi>0, \hbar>0\}] \& \\
& \left\{\frac{2 \sqrt{2} \mu B B}{9 \xi \hbar^{2}}-\frac{16\left(\sqrt{2} \mu B^{3}\right) B^{3}}{729\left(\xi^{3} \hbar^{6}\right)}+0[B]^{4}, 1\right\} \\
& \psi \mathbf{2}=\operatorname{eq1}[[2,2]] / / \operatorname{Series}[\#,\{B, 0,3\}] \& / / \operatorname{Simplify}[\#,\{\xi>0, \hbar>0\}] \& \\
& \left\{-\frac{9\left(\xi \hbar^{2}\right)}{2(\sqrt{2} \mu B) B}-\frac{2(\sqrt{2} \mu B) B}{9\left(\xi \hbar^{2}\right)}+\frac{16 \sqrt{2} \mu B^{3} B^{3}}{729 \xi^{3} \hbar^{6}}+0[B]^{4}, 1\right\}
\end{aligned}
$$

