

Atoms

- 1 Early atomic physics
- 2 The Schrödinger equation as a wave equation
- 3 Quantum mechanics
- 4 Atoms with many electrons

Addition of angular momenta

Quantum mechanics

- Stern-Gerlach experiment
- Spin of the electron
- Dirac notation
- Spin-orbit coupling
- **Addition of angular momenta**
- Anomalous Zeeman effect
- Hyperfine interaction
- Selection rules for elm. dipole transitions
- Autler-Townes splitting

Addition of angular momenta 1

Torque $\vec{\tau}$ that acts on a magnetic moment $\vec{\mu}$ in a magnetic field \vec{B}

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

a torque acting on an angular momentum leads to a precession movement

$$\frac{d\vec{L}}{dt} = \vec{\tau} \quad \text{and} \quad \frac{d\vec{S}}{dt} = \vec{\tau}$$

mechanical examples ([Kreisel.mp4](#) and [Präzession.mp4](#))

$$L_z \neq 0$$



$$L_z \approx 0$$



Addition of angular momenta 1

Comment 1

At the minimum of the potential energy, a magnetic moment is aligned parallel to the magnetic field.

If the magnetic moment is not parallel to the magnetic field, then there is a torque that turns the magnetic moment in the direction of the magnetic field.

The first equation outlined in red gives the torque that acts on a magnetic moment in a magnetic field.

The vector of the torque is perpendicular to the plane which is defined by the direction of the magnetic field and the direction of the magnetic moment.

In mechanics, the torque is defined by the vector product $\vec{r} \times \vec{F}$.

The vector r points from the center of rotation to the acting force F .

Addition of angular momenta 1

Comment 2

With an angular momentum, the torque leads to a precession movement.

The derivation of the angular momentum with respect to time equals the torque, as shown by the formulas outlined in red.

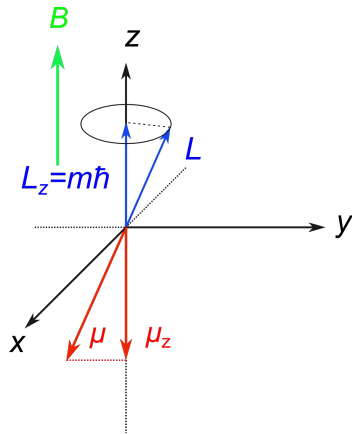
The two videos show the precession of a gyroscope and a rotating wheel due to the force of weight.

The z-direction is defined by the direction of the gravitational force.

The first video shows the precession when the angular momentum is large along the z-direction.

The second video shows the precession when the angular momentum is close to zero along the z-direction.

Addition of angular momenta 2



The magnetic moment of the orbital angular momentum

$$\vec{\mu}_L = -\mu_B \frac{\vec{L}}{\hbar}$$

magnetic moment of the spin of the electron

$$\vec{\mu}_s = -g\mu_B \frac{\vec{S}}{\hbar}$$

angular velocity of the precession due to e.g.

$$\frac{d\vec{L}}{dt} = \vec{\mu} \times \vec{B}$$

$$\omega_p = \frac{\mu_B B}{\hbar}$$

Addition of angular momenta 2

Comment 1

The figure shows the orbital angular momentum with its magnetic moment in a magnetic field B which defines the quantization axis.

A similar figure could be plotted for the spin.

Since the magnetic moment is antiparallel to the angular momentum (compare the box equations), the uncertainty of the component of the magnetic moment perpendicular to the magnetic field is infinite, as with the angular momentum, i.e. the perpendicular component of the magnetic moment can point in any direction.

When many magnetic moments are considered, there is no magnetization perpendicular to the applied magnetic field because the perpendicular moments add up to zero.

The sketch shows that there is always an angle between the magnetic field and the magnetic moment.

Addition of angular momenta 2

Comment 2

Hence there is always a torque and a precession motion of the angular momentum.

The formula underlined in red indicates the precession frequency.

The precession frequency does not depend on the angle between the magnetic moment and the magnetic field.

$$\frac{d}{dt} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = -\frac{\mu_B}{\hbar} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix} = -\frac{\mu_B}{\hbar} \begin{pmatrix} L_y B \\ -L_x B \\ 0 \end{pmatrix}$$

With $L_x = L_{\perp} \cos \omega_p t$ and $L_y = L_{\perp} \sin \omega_p t$ results the underlined equation $\omega_p = \frac{\mu_B B}{\hbar}$.

Addition of angular moment 3

Spin-orbit coupling

$$\hat{H}_{SL} = \xi \frac{\hat{\vec{s}} \cdot \hat{\vec{L}}}{\hbar^2}$$

$$\frac{d\vec{s}}{dt} = \vec{\mu}_s \times \vec{B}_L \quad \text{and} \quad \frac{d\vec{L}}{dt} = \vec{\mu}_L \times \vec{B}_s$$

L_z and s_z no longer have eigenvalues

Conservation of angular momentum

Internal torques **cannot** change the total angular momentum



(Drehimpulserhaltung.mp4)

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

Addition of angular momenta 3

Comment 1

The formula outlined in red shows the Hamiltonian of the spin-orbit coupling.

Due to the spin-orbit coupling, the spin experiences a torque that is caused by the magnetic field of the orbit.

The orbital angular momentum experiences a torque that comes from the magnetic field of the spin.

Both the magnetic field of the orbit and the spin change constantly, so that no quantization directions can be defined by means of these magnetic fields.

It turns out that there is no longer any quantization direction for orbital angular momentum and spin.

Addition of angular momenta 3

Comment 2

It is known from classical mechanics that internal torques cannot change the total angular momentum.

The video shows this effect for the vertical angular momentum.

At the beginning of the experiment, the swivel chair is at rest and the angular momentum of the wheel is horizontal.

If the rotating wheel is turned so that the angular momentum points in the vertical direction, then this angular momentum is compensated by a corresponding counter-rotating movement of the chair.

If the wheel axle is rotated by 180° , the chair rotates in the opposite direction.

Addition of angular momenta 3

Comment 3

The total angular momentum in the vertical direction is always zero.

For the other components of the angular momentum, the earth's angular momentum must be taken into account. However, this is so great that no effect can be observed if the axis of rotation of the wheel is changed.

The formula framed in red gives the addition of orbital angular L momentum and spin s to the total angular momentum J .

The total angular momentum from orbit and spin is usually denoted by the letter J .

Although no vector component of \vec{L} and \vec{S} can be determined due to the spin-orbit coupling, the orbital angular momentum and spin do not lose their meaning.

In particular, the length of these vectors $\hbar\sqrt{\ell(\ell+1)}$ and $\hbar\sqrt{s(s+1)}$ is still well defined!

Addition of angular momenta 4

The eigenvalue equations for the total angular momentum are

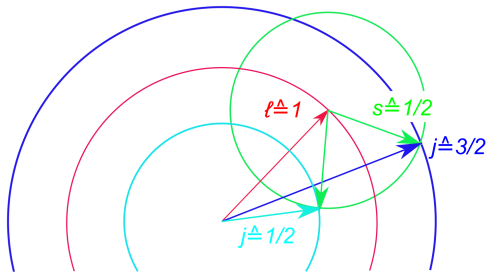
$$\begin{aligned}\hat{J}^2 |j, m_j\rangle &= j(j+1)\hbar^2 |j, m_j\rangle \\ \hat{J}_z |j, m_j\rangle &= m_j\hbar |j, m_j\rangle\end{aligned}$$

The quantum number j has the values

$$j = |\ell - s|, |\ell - s| + 1, \dots, \ell + s$$

and the quantum number m_j

$$m_j = -j, -j + 1, \dots, +j - 1, +j$$



Addition of angular momenta 4

Comment 1

In quantum mechanics, the angular momentum is defined by the eigenvalue equation for the square of the angular momentum and the eigenvalue equation for the z component of the angular momentum.

The total angular momentum must also satisfy the eigenvalue equations of angular momentum.

The eigenvalue equations can be formulated quite generally with the Dirac notation of the quantum states.

The eigenstates of the total angular momentum $|j, m_j\rangle$ are given by a sum of the products of the spherical harmonics and 2-tuples, i.e. by the eigenstates of the free orbital angular \vec{L} momentum and the free spin \vec{S} .

Exact knowledge of these sums is not required in this lecture.

Addition of angular momenta 4

Comment 2

The symbolic Dirac notation is sufficient for the eigenstates of the total angular momentum.

The equations outlined in red indicate the eigenvalue equations of the total angular momentum.

The message of the eigenvalue equations is important: The total angular momentum is a vector with the length $\hbar\sqrt{j(j+1)}$ and the projection $m_j\hbar$ on the z-axis.

The vectors of orbital angular momentum and spin can be added to the total angular momentum like normal vectors.

The figure shows the addition of a spin $s = 1/2$ to an orbital angular momentum with the quantum number $\ell = 1$.

Addition of angular momenta 4

Comment 3

The radius of the red circle corresponds to the length of the orbital angular momentum vector $\hbar\sqrt{\ell(\ell+1)} = \hbar\sqrt{2}$ and the radius of the green circle corresponds to the length of the spin vector $\hbar\sqrt{s(s+1)} = \hbar\sqrt{\frac{3}{4}}$.

The dark blue circle corresponds to an angular momentum length to the quantum number $j = 3/2$.

The light blue circle corresponds to the angular momentum length of the quantum number $j = 1/2$.

The addition of the angular momentum with the quantum number $\ell = 1$ and $s = 1/2$ results from the intersections of the green circle with the dark blue and light blue circles.

Addition of angular momenta 4

Comment 4

The orientation of the total angular momentum is irrelevant as long as no quantization direction is specified.

Therefore the vectors only point to two of the intersection points.

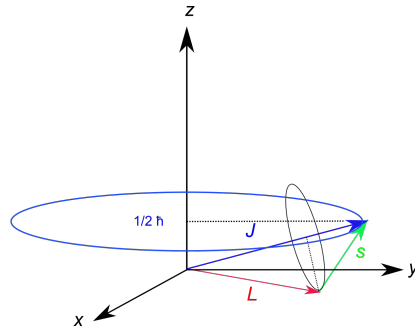
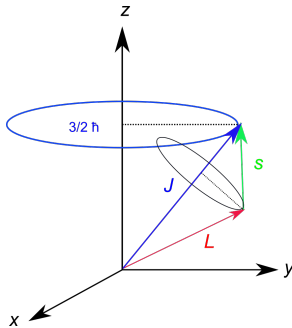
The points of intersection with the red circle are not taken into account because the total angular momentum quantum number j only increases in steps of one from $|\ell - s|$ to $\ell + s$.

Likewise, the quantum number m_j varies in steps of one between $-j$ and $+j$, since $m_j = m_\ell + m_s$.

The two formulas underlined in red next to the figure give the general rules for the quantum numbers j and m_j when adding orbital angular momentum and spin.

Addition of angular momenta 5

addition of the angular momenta $\ell = 1$ and $s = 1/2$ to
 $j = 3/2$ and $m_j = 3/2$ or $j = 3/2$ and $m_j = 1/2$



Addition of angular momenta 5

Comment 1

The figure illustrates the addition of $\ell = 1$ and $s = 1/2$ to $j = 3/2$ when a quantization direction is defined for the total angular momentum.

The total angular momentum vector lies on a conical surface, which is determined by the eigenvalue for J_z .

The figures show the case that the eigenvalue of the z-component has the value $+3/2 \hbar$ or $+1/2 \hbar$.

Since the internal magnetic fields couple the magnetic moments of the orbit and the spin to form the total angular momentum, orbital angular momentum and spin are located on conical surfaces around the direction of the total angular momentum, which is indicated by the black ellipse.

Addition of angular momenta 5

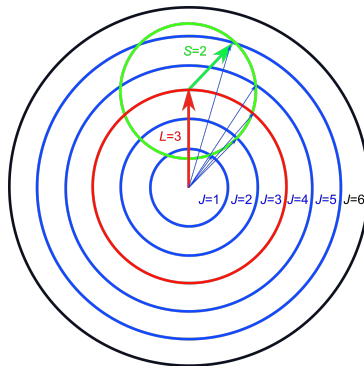
Comment 2

Although the coordinates of the vectors of orbital angular momentum and spin can no longer be determined, the orientation of these vectors in space is not completely arbitrary but limited by the conical surfaces around the total angular momentum.

However, the direction of \vec{J} is not a quantization direction for \vec{L} and \vec{S} .

Addition of angular momenta 6

addition of the orbital angular momentum $L = 3$ and the spin $S = 2$



$$|L - S| \leq J \leq L + S$$

Addition of angular momenta 6

Comment

The rules for adding angular momentum apply in general.

The figure shows the addition of an angular momentum with the quantum number $L = 3$ and a spin with the quantum number $S = 2$.

The total angular momentum J varies in steps of one in the limits $|L - S|$ and $L + S$, i.e. between $J = 1$ and 5.

Addition of angular momenta 7

notation of hydrogen orbitals

$$n^{2s+1}\ell_j$$

1st excited p orbital

$$\underline{2^2p_{\frac{1}{2}}} \quad \text{and} \quad 2^2p_{\frac{3}{2}}$$

due to spin-orbit coupling

$$E(2^2p_{\frac{1}{2}}) < E(2^2p_{\frac{3}{2}})$$

Addition of angular momenta 7

Comment 1

An orbital of the hydrogen atom is fully characterized by the specification of the principal quantum number n , the orbital angular momentum quantum number ℓ and the total angular momentum quantum number j .

The formula framed in red indicates the notation of an atomic orbital of the hydrogen atom.

The notation begins with the principal quantum number n .

The so-called multiplicity $2s + 1$ of the orbital due to the spin is given as the upper index.

For a single spin, the multiplicity is 2.

This is called a doublet.

Addition of angular momenta 7

Comment 2

Then follows with ℓ the quantum number of the orbital angular momentum, which is denoted by the letters *s*: $\ell = 0$, *p*: $\ell = 1$, *d*: $\ell = 2$, *f*: $\ell = 3$ etc.

The lower index indicates the quantum number of the total spin j .

As an example, the notation of the first excited *p* orbital of the hydrogen atom is shown.

The energy of the state $j = 1/2$ is smaller than the energy of the state $j = 3/2$, since the spin and orbital angular momentum of an electron is preferably aligned antiparallel.

Addition of angular momenta 8

Hamilton operator of the spin-orbit coupling

$$\hat{H}_{sL} = \xi \frac{\hat{\mathbf{s}} \cdot \hat{\mathbf{L}}}{\hbar^2}$$

with

$$\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{s}})^2 = \hat{L}^2 + \hat{s}^2 + 2\hat{\mathbf{s}}\hat{\mathbf{L}} \quad \rightarrow \quad \hat{\mathbf{s}}\hat{\mathbf{L}} = \frac{1}{2} \left(\hat{J}^2 - \hat{L}^2 - \hat{s}^2 \right)$$

is

$$\hat{\mathbf{s}} \cdot \hat{\mathbf{L}} |\ell, s, j, m_j\rangle = \frac{\hbar^2}{2} (j(j+1) - \ell(\ell+1) - s(s+1)) |\ell, s, j, m_j\rangle$$

and the eigenvalues of \hat{H}_{sL} are

$$E_{j,\ell,s} = \frac{\xi}{2} (j(j+1) - \ell(\ell+1) - s(s+1))$$

Addition of angular momenta 8

Comment

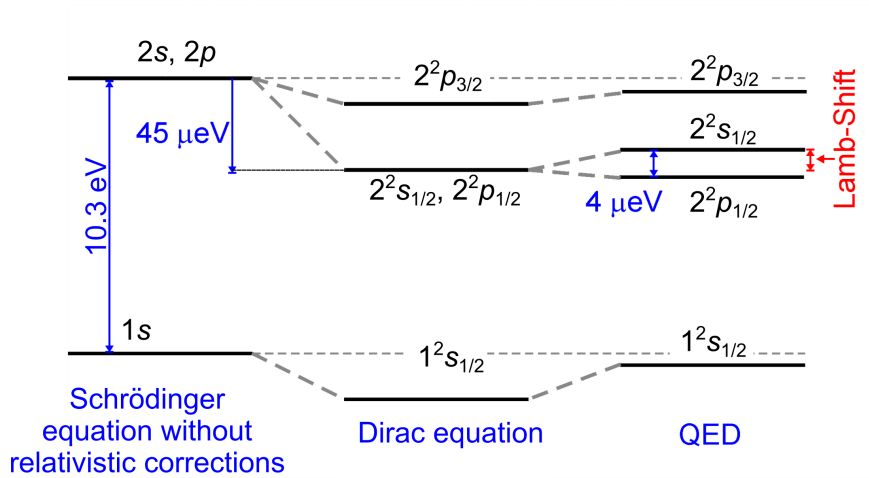
Now the energy eigenvalues for the Hamilton operator of the spin-orbit coupling can be calculated.

With the red underlined formula for the square of the total angular momentum vector, the eigenvalues for the scalar product of spin and orbital angular momentum can be expressed by the known eigenvalues for the squares of the angular momenta.

The formula outlined in red gives the energy eigenvalues for the Hamilton operator of the spin-orbit coupling.

Addition of angular momenta 9

ground state and first excited states of the Hydrogen atom



Addition of angular momenta 9

Comment 1

The figure shows the ground state and the first excited orbitals of the hydrogen atom with the principal quantum number $n = 2$.

The energy level diagram on the left gives the result of an experiment if the spectral resolution is not sufficient to resolve the so-called fine structure of the first excited states.

The second energy level diagram shows the result of Dirac's relativistic Schrödinger equation, which agrees perfectly with the experiment.

A special prediction of the Dirac theory is that the $2s_{1/2}$ orbital has exactly the same energy as the $2p_{1/2}$ orbital.

Addition of angular momenta 9

Comment 2

Since 1927, the experimental challenge for the experimenters was to increase the resolution of the measurements to such an extent that this prediction of the Dirac theory could also be experimentally verified.

Using a normal hydrogen spectral lamp, the spectral width (essentially Doppler broadening) of the transitions is so large that even the spin-orbit splitting can hardly be resolved.

In 1947 W.E. Lamb and R.C. Retherford succeeded to resolve the energy difference between $2s_{1/2}$ and $2p_{1/2}$ by a combination of microwave resonance and optical spectroscopy.

Since then, this energy difference has been called the Lamb shift.

Addition of angular momenta 9

Comment 3

Willis Eugene Lamb was awarded the Nobel Prize in Physics in 1955 for "for his discoveries concerning the fine structure of the hydrogen spectrum".

He shared the Nobel Prize with Polycarp Kusch who received the Nobel Prize for "for his precision determination of the magnetic moment of the electron".

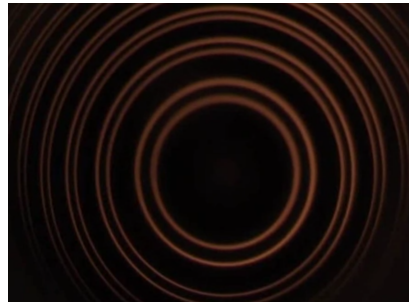
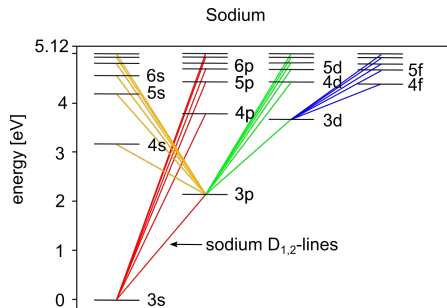
The measurement of the Lamb shift and the measurement of the g-factor of the electron are important tests of quantum electrodynamics (QED), i.e. the techniques used to solve the time-dependent Schrödinger equation for the electromagnetic interaction.

Addition of angular momenta 10

splitting of the Sodium D line (atomic number of sodium $Z = 11$)

$$D_1 : 3^2s_{1/2} \rightarrow 3^2p_{1/2} \quad (\lambda = 589.5924 \text{ nm})$$

$$D_2 : 3^2s_{1/2} \rightarrow 3^2p_{3/2} \quad (\lambda = 588.9951 \text{ nm})$$



$$\Delta E = E(3^2p_{3/2}) - E(3^2p_{1/2}) \approx 2 \text{ meV}$$

Addition of angular momenta 10

Comment 1

The atomic number of the sodium atom is $Z = 11$

10 of the electrons result in the stable noble gas configuration of the neon atom.

These electrons have a large binding energy and cannot be excited with visible light.

The 11th electron is the weakly bound valence electron that occupies the 3s orbital in the ground state.

The figure on the left shows the energy level scheme when the valence electron of the sodium atom is excited.

The right figure shows the fine structure splitting of the sodium D-line, which is observed with a Fabry-Perot interferometer.

Addition of angular momenta 10

Comment 2

The sodium D-line is caused by the transition between the 3s orbital in the ground state and the excited 3p orbital, which is split into two components by the spin-orbit coupling.

The sodium D₁ line corresponds to the transition between the $3s_{1/2}$ orbital and the $3p_{1/2}$ orbital.

The wavelength of the transition is 589.5923 nm.

The sodium D₂ line corresponds to the transition between the $3s_{1/2}$ orbital and the $3p_{3/2}$ orbital.

The wavelength of the transition is 588.9951 nm.

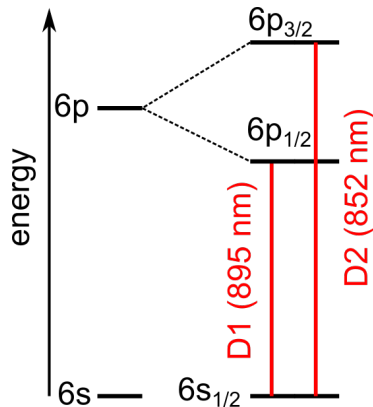
Addition of angular momenta 10

Comment 3

The difference in wavelength results in an energy difference between the $3p_{1/2}$ and the $3p_{3/2}$ orbital of about 2 meV.

The spin-orbit coupling in the sodium atom is 44 times stronger than in the hydrogen atom.

Addition of angular momenta 11



Caesium ($Z = 55$)

Fine structure splitting of the 6p orbital

$6p_{1/2} \leftrightarrow 6p_{3/2}$

$$\begin{aligned} \Delta E_{6p_{3/2} \leftrightarrow 6p_{1/2}} &= \frac{hc}{852 \text{ nm}} - \frac{hc}{895 \text{ nm}} \\ &= 70 \text{ meV} \end{aligned}$$

Addition of angular momenta 11

Comment

The figure shows the doublet splitting of the D line for the caesium atom.

The atomic number of caesium is $Z = 55$.

54 electrons form the stable configuration of the noble gas xenon.

The 55th electron occupies the 6s orbital in the ground state.

With the wavelengths of 895 nm and 852 nm of the two D-lines, the energy of the doublet splitting of the 6p orbital can be calculated.

The result is a value of 70 meV.

As expected, the strength of the spin-orbit coupling increases with the atomic number.

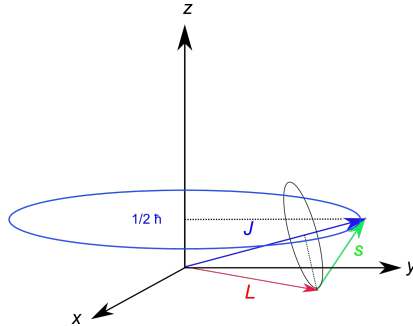
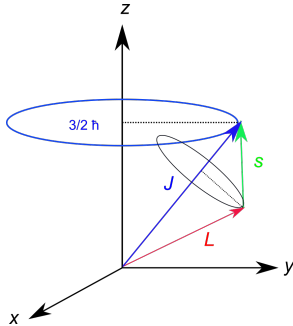
Anomalous Zeeman effect

Quantum mechanics

- Stern-Gerlach experiment
- Spin of the electron
- Dirac notation
- Spin-orbit coupling
- Addition of angular momenta
- **Anomalous Zeeman effect**
- Hyperfine interaction
- Selection rules for elm. dipole transitions
- Autler-Townes splitting

Anomalous Zeeman effect 0

addition of angular momenta



Anomalous Zeeman effect 0

Comment 1

The figure shows again the addition of orbital angular momentum and spin to the total angular momentum.

The Zeeman effect shows that the vector addition of the angular momentum is not fictional.

Although the vector components of orbital angular momentum and spin can no longer be specified, these vectors lie on conical surfaces around the total angular momentum.

The magnetic moment of the orbit and the spin are proportional to the orbital angular momentum and the spin.

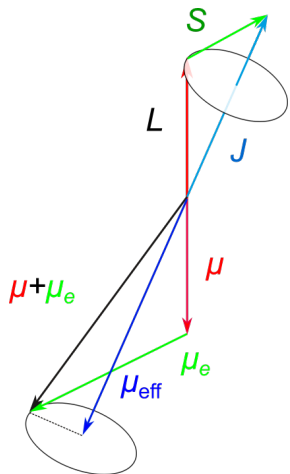
Anomalous Zeeman effect 0

Comment 2

Since the exact position of orbital angular momentum and spin on the conical surfaces cannot be fixed and fluctuate around the total angular momentum \vec{J} , the components of the magnetic moments that are perpendicular to the total angular momentum are on average zero.

Only the projection of the magnetic moments in the direction of the total angular momentum is effective for the Zeeman effect.

Anomalous Zeeman effect 1



magnetic moment of the orbit

$$\underline{\vec{\mu}} = -\mu_B \frac{\vec{L}}{\hbar}$$

magnetic moment of the spin

$$\underline{\vec{\mu}_e} = -g\mu_B \frac{\vec{S}}{\hbar}$$

effective magnetic moment

$$\underline{\vec{\mu}_{eff}} = -g_{j,\ell,s}\mu_B \frac{\vec{J}}{\hbar}$$

Landé g-factor :

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

Anomalous Zeeman effect 1

Comment 1

The figure shows the projection of the magnetic moments onto the direction of the total angular momentum vector.

Since the proportionality factors between angular momentum and magnetic moment are different for orbital angular momentum and spin, the total magnetic moment is not parallel to the total angular momentum.

For the magnetic moment only the projection on the direction of the total angular momentum is effective.

The effective magnetic moment is proportional to the total angular momentum.

The resulting g-factor is called the Landé g-factor.

The equation outlined in red shows the formula that results for the Landé g factor when calculating the projection.

Anomalous Zeeman effect 1

Comment 2

The sum of the magnetic moments of spins and orbital angular momentum $\vec{\mu}$ is

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

and the projection on the direction of the total angular momentum \vec{J}

$$\mu_{\text{eff}} = \frac{\vec{\mu} \cdot \vec{J}}{J} = -\frac{\mu_B}{\hbar} \frac{(\vec{L} + 2\vec{S}) \cdot \vec{J}}{J} = -\frac{\mu_B}{\hbar} \frac{(\vec{L} + 2\vec{S}) \cdot (\vec{L} + \vec{S})}{J} = -\frac{\mu_B}{\hbar} \frac{(\vec{L}^2 + 2\vec{S}^2 + 3\vec{L} \cdot \vec{S})}{J}$$

With $\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$ is the projection on the direction of \vec{J}

$$\mu_{\text{eff}} = -\frac{\mu_B}{\hbar} \frac{(3\vec{J}^2 - \vec{L}^2 + \vec{S}^2)}{2J} \rightarrow \vec{\mu}_{\text{eff}} = \mu_{\text{eff}} \frac{\vec{J}}{J} = -\frac{\mu_B}{\hbar} \frac{3\vec{J}^2 - \vec{L}^2 + \vec{S}^2}{2J^2} \vec{J}$$

Anomalous Zeeman effect 2

$$\ell = 0$$

$$g_{j=s, \ell=0, s} = \frac{3}{2} - \frac{\ell(\ell+1) - s(s+1)}{2j(j+1)} = 2$$

$$s = 0$$

$$g_{j=\ell, \ell, s=0} = \frac{3}{2} - \frac{\ell(\ell+1) - s(s+1)}{2j(j+1)} = 1$$

$$^2p_{1/2} \text{ orbital: } \ell = 1, s = 1/2 \text{ and } j = 1/2$$

$$g_{j=1/2, \ell=1, s=1/2} = \frac{3}{2} - \frac{\ell(\ell+1) - s(s+1)}{2j(j+1)} = \frac{2}{3}$$

$$^2p_{3/2} \text{ orbital: } \ell = 1, s = 1/2 \text{ and } j = 3/2$$

$$g_{j=3/2, \ell=1, s=1/2} = \frac{3}{2} - \frac{\ell(\ell+1) - s(s+1)}{2j(j+1)} = \frac{4}{3}$$

Anomalous Zeeman effect 2

Comment

This page shows some examples

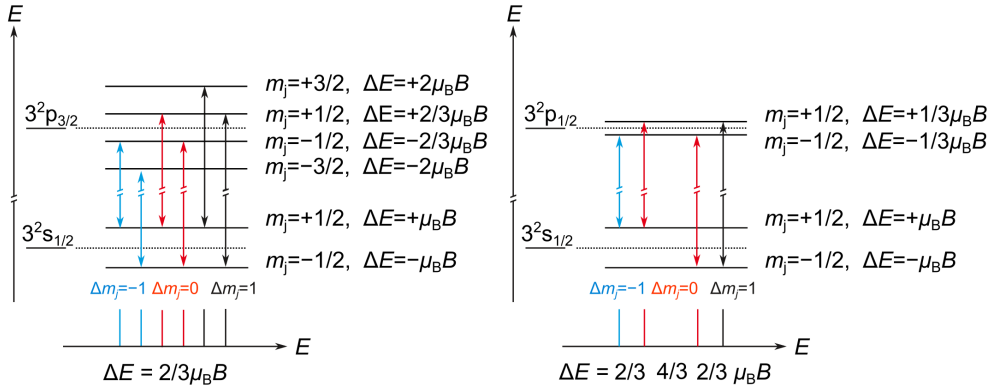
The g-factor 2 results for a pure spin.

The g-factor 1 results for a pure orbital angular momentum.

For the two components of the spin-orbit doublet, the g-factors $2/3$ ($j = 1/2$) and $4/3$ ($j = 3/2$) result for the p orbital.

Anomalous Zeeman effect 3

Zeeman effect of the sodium D lines



Anomalous Zeeman effect 3

Comment 1

With these g-factors one can determine the Zeeman splitting of the sodium D-lines.

The left figure shows the transition $3^2s_{1/2} \leftrightarrow 3^2p_{3/2}$ with the wavelength $\lambda = 588.9951 \text{ nm}$.

The right figure shows the transition $3^2s_{1/2} \leftrightarrow 3^2p_{1/2}$ with the wavelength $\lambda = 589.5924 \text{ nm}$.

For the ground state, which has no orbital angular momentum, the g-factor is 2.

The level with the m_j quantum number $+1/2$ shifts by $+\mu_B \cdot B$ to larger energies and the level with the m_j quantum number $-1/2$ shifts by $-\mu_B \cdot B$ to lower energies.

Anomalous Zeeman effect 3

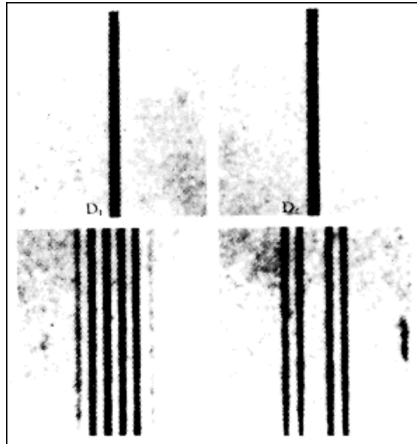
Comment 2

For the excited $3^2p_{1/2}$ level with the g-factor $2/3$, the corresponding shift of the energy levels in the magnetic field is only $\pm \frac{1}{3}\mu_B \cdot B$, while the shifts for the $3^2p_{3/2}$ level are $\Delta E = \pm \frac{2}{3}\mu_B \cdot B$ and $\pm 2\mu_B \cdot B$.

With the selection rule $\Delta m_j = 0, \pm 1$ the transitions and the splitting of the spectral lines in the magnetic field result as shown in the figures.

Anomalous Zeeman effect 4

Pieter Zeeman (1896): Zeeman splitting of the Sodium D lines



Anomalous Zeeman effect 4

Comment

The figure shows once again the historic measurement by Pieter Zeeman for the sodium D lines in a magnetic field (Nobel Prize 1902).

The theory of the anomalous Zeeman effect agrees fully with these measurements.

Anomalous Zeeman effect 5

Zeeman effect of the green spectral line of Mercury

$$\underline{7\ ^3S_1 [6s^1, 7s^1] \leftrightarrow 6\ ^3P_2 [6s^1, 6p^1] \quad \lambda = 546,1\text{ nm}}$$

Landé g-factor :

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

Landé g-factors

$$\begin{aligned} {}^3S_1 (S=1, L=0, J=1) : \quad g_{J,L,S} &= 2 \\ {}^3P_2 (S=1, L=1, J=2) : \quad g_{J,L,S} &= 1.5 \end{aligned}$$

Anomalous Zeeman effect 5

Comment 1

As a second example of an anomalous Zeeman effect the Zeeman splitting of the green spectral line of a mercury spectral lamp is considered.

For the mercury atom there are two valence electrons and the spins of the two electrons can add up to $S = 0$ or $S = 1$.

When the green spectral line is emitted, an excited electron passes from the 7s orbital to the 6p orbital.

The line underlined in red specifies the transition.

(Only one electron is excited while the other remains in the 6s ground state.)

Anomalous Zeeman effect 5

Comment 2

The electron configurations are given in square brackets.

The notation $7^3S_1 [6s^1, 7s^1]$ means that a s-electron with the principal quantum number $n = 6$ and a s-electron with the principal quantum number $n = 7$ form together the quantum state with the total spin $S = 1$.

The multiplicity $2s + 1$ has the value three and one speaks of a triplet state.

Since both electrons have no orbital angular momentum, the total orbital angular momentum of the two electrons also has the quantum number $L = 0$.

The total angular momentum of this electron configuration thus has the quantum number $J = 1$.

Anomalous Zeeman effect 5

Comment 3

The notation $6^3P_2 [6s^1, 6p^1]$ means that a s-electron with the principal quantum number $n = 6$ and a p-electron also with the principal quantum number $n = 6$ form a quantum state with the total spin $S = 1$.

Since one electron has no orbital angular momentum and the other has an orbital angular momentum with the quantum number $\ell = 1$, the quantum number $L = 1$ results for the total orbital angular momentum.

The spin and the orbital angular momentum of this quantum state are coupled to the total angular momentum with the quantum number $J = 2$.

In the notation of the quantum states of electron configurations with several electrons, the angular momenta are indicated by capitalized letters.

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Comment 4

The formula for the Landé g-factor can also be used when there are several electrons involved.

For this purpose, the lower-case quantum numbers of the original formula are replaced by capital letters that describe the total spin, the total orbital angular momentum and the total angular momentum of the electron configuration.

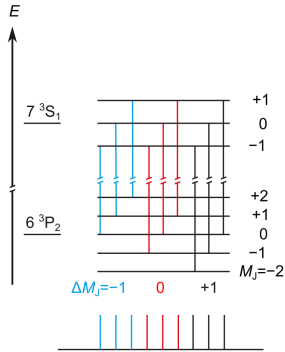
This results in the formula outlined in red for the Landé g-factor.

This formula can be used to calculate the g-factors that are required for the green spectral line.

For the 3S_1 the g-factor has the value 2, as can be expected for a pure spin state.

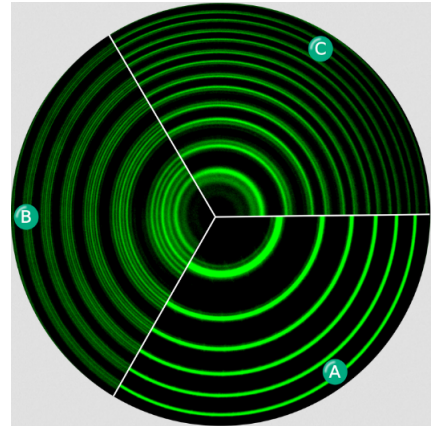
For the 3P_2 the g-factor has the value 1.5, since with $S = 1$ for the spin and $L = 1$ for the orbital angular momentum, the second term of the Landé formula results in zero.

Anomalous Zeeman effect 6



energetic distance of the Zeeman lines

$$\Delta E = \frac{1}{2} \mu_B B$$



Anomalous Zeeman effect 6

Comment 1

The left figure shows the energy level diagram with the Zeeman splitting and the expected electrical dipole transitions.

The selection rule $\Delta M_J = \pm 1$ results in light that is perpendicular polarized to the magnetic field, i.e. the vector of the electric field is perpendicular to the direction of the magnetic field.

The selection rule $\Delta M_J = 0$ leads to parallel polarized light.

The right figure shows again the measurement of the spectral line with a Fabry-Perot interferometer.

Area A shows the green spectral line when no magnetic field is applied.

Region B shows the Zeeman splitting when no polarizing filter is used.

Anomalous Zeeman effect 6

Comment 2

Some lines of the spectrum are difficult or impossible to see.

Area C shows the spectrum when a polarizer perpendicular to the magnetic field is used.

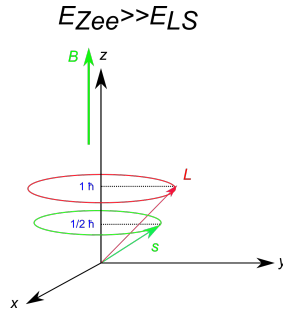
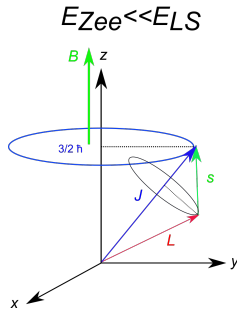
The inner three rings, which are polarized parallel to the magnetic field, are extinguished by the polarizer.

Usually the anomalous Zeeman effect is observed.

The normal Zeeman effect can only be observed when the spins of the electrons add up to zero.

Anomalous Zeeman effect 7

Paschen-Back effect: $\mu_B B \gg |\xi|$



eigenvalues of the Zeeman Hamilton operator when spin-orbit coupling is negligible

$$E_{Zee} = m\mu_B B + 2m_s\mu_B B$$

Anomalous Zeeman effect 7

Comment 1

The spin-orbit coupling can be neglected if the external magnetic field is much stronger than the internal magnetic fields.

In astronomical measurements of stars and galaxies, very strong magnetic fields are usually observed.

The magnetic moments of orbital angular momentum and spin precess independently of one another around the external magnetic field.

The figure on the left shows the case in which the orbital angular momentum and spin are coupled to the total angular momentum, while the figure on the right shows the case in which the orbital angular momentum and spin move independently about the external magnetic field.

Anomalous Zeeman effect 7

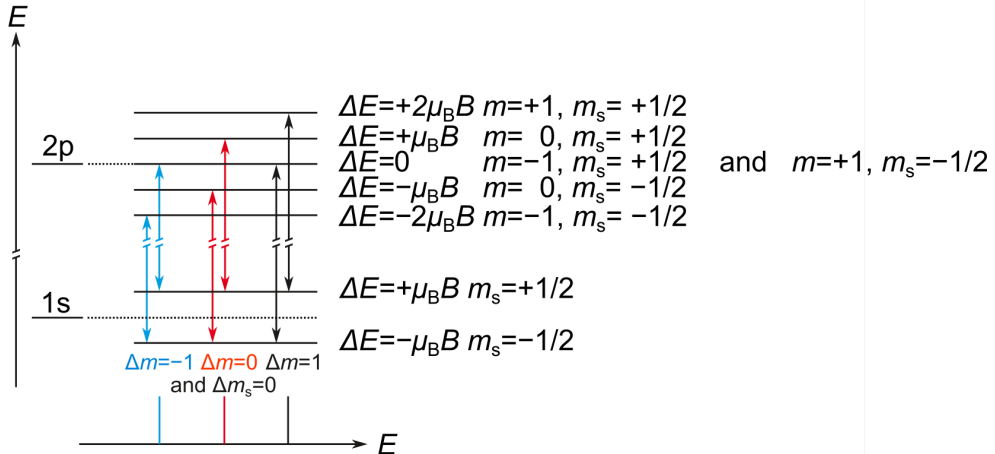
Comment 2

When the spin-orbit coupling is broken by the external magnetic field, the magnetic energy is simply the sum of the Zeeman energy of the orbital angular momentum and the spin.

The formula outlined in red gives the energy eigenvalues of the Zeeman operator of the orbital angular momentum and of the spin.

Anomalous Zeeman effect 8

Paschen-Back effect of the hydrogen atom



Anomalous Zeeman effect 8

Comment

The figure shows the Zeeman splitting of the ground state and the first excited state of the hydrogen atom in a strong magnetic field.

The figure also shows the permitted electrical dipole transitions.

The electric dipole operator does not affect the spin of the electrons.

Therefore, the spin quantum number does not change with an electrical dipole transition.

The spectral line splits into three components in a magnetic field.

This corresponds to the normal Zeeman effect.

The normal Zeeman effect can be observed when the spins of the electrons add up to zero, or the spin has no influence because it is not coupled to the orbital angular momentum and cannot influence the electrical dipole transition.

Revision

Summary in Questions

1. Due to spin-orbit coupling spin and orbital angular momentum are coupled together and form the total angular momentum. Explain the rules for the addition of two angular momenta.
2. Give the eigenvalue equation of the total angular momentum. Use the Dirac notation.
3. Give the eigenvalue equation of the spin-orbit Hamiltonian and its eigenvalues.
4. Give the magnetic moment due to the total angular momentum.
5. Describe the meaning of the Landé g-factor.