# Atoms

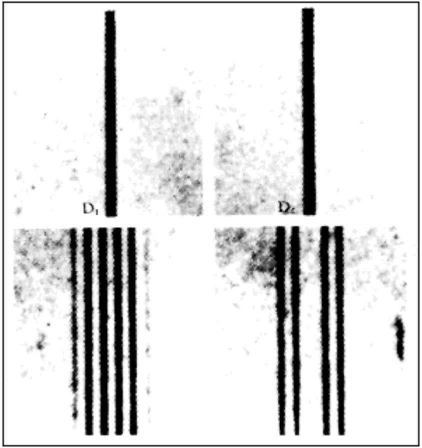
# Normal Zeeman

# The Schrödinger equation as a wave equation

- Schrödinger equation
- Box potential
- Harmonic oscillator
- Orbital angular momentum
- Rotation of a diatomic molecule
- Schrödinger equation of the hydrogen atom
- Normal Zeeman effect
- Dia- and paramagnetism

# Normal Zeeman effect 1

Pieter Zeeman (1896): splitting of the sodium D lines in a strong magnetic field



# Normal Zeeman effect 1 Comment

The Zeeman effect describes the splitting of spectral lines in a magnetic field.

The figure shows the historical measurement of Pieter Zeeman in 1896.

The doublet of the yellow sodium line is split into many components when a magnetic field is applied.

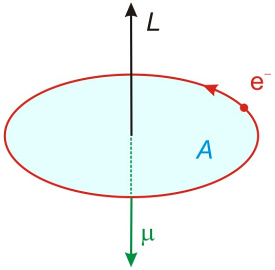
The D1 line ($\lambda$ = 589.5924 nm) is split into four components and the D2 line ($\lambda$ = 588.9951 nm) into six components. (One spectral line of D2 is nearly missing in the photo.)

In contrast to the notation of Pieter Zeeman, today the line with the longer wavelength is called the D1 line, while the line with the shorter wavelength is called the D2 line.

# Normal Zeeman effect 2

the orbital motion of the electron leads to a magnetic moment

$$\boxed{\mu = AI}$$




$$I = -\frac{e}{T} = -e\frac{v}{2\pi r}$$

$$\mu = \pi r^2 \cdot \frac{-ev}{2\pi r} = -\frac{e\,r\,v}{2} = -\frac{e\,r m\,v}{2m}$$

$$\boxed{\mu = -\frac{eL}{2m} = -\frac{e\hbar L}{2m\hbar} = -\mu_B \frac{L}{\hbar}}$$

# Normal Zeeman effect 2 Comment 1

The motion of an electron around the nucleus creates an electrical current.

According to the Ampere law, this current leads to a magnetic field.

This magnetic field can be traced back to a magnetic moment caused by the orbital movement of the electron.

The formula outlined in red gives the classic definition of the magnetic moment.

The current multiplied by the area $A$ enclosed by the current gives the magnetic moment, i.e. $\mu = I \cdot A$.

Due to the wave-particle dualism, all types of orbits that are compatible with the wave function are allowed.

# Normal Zeeman effect 2 — Comment 2

The figure shows a circular path that was used in Bohr's model of the atom.

The probability that the electron will move in a circular orbit is small, but a circular orbit is certainly not forbidden.

Hence, the circular orbit can be used to study the effects.

The first underlined equation gives the current due to an electron.

$T$ denotes the period of rotation.

The rotation period results from the quotient of the circumference and the speed of the electron.

The equation outlined in red gives the magnetic moment of the orbit.

# Normal Zeeman effect 2 Comment 3

The magnetic moment is proportional to the angular momentum.

Since the angular momentum is measured in units of $\hbar$, the equation is expanded with $\hbar$.

The constants before the quotient of angular momentum and $\hbar$ are combined to form Bohr's magneton.

# Normal Zeeman effect 3

Bohr's magneton

$$\boxed{\mu_B = \frac{e\hbar}{2m} = 9.274 \cdot 10^{-24}\,\mathrm{J/T} = 9.274 \cdot 10^{-24}\,\mathrm{Am}^2 = 5.8 \cdot 10^{-5}\,\frac{\mathrm{eV}}{\mathrm{T}}}$$

potential energy of a magnetic moment $\vec{\mu}$ in a homogeneous $\vec{B}$-field is

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

Hamilton Operator (replace $\vec{p}$ by $-i\hbar\nabla$ and thereby $\vec{L}$ by $\hat{\vec{L}}$)

$$\boxed{\hat{H}_{Zee} = \mu_B \frac{\hat{\vec{L}}}{\hbar}\vec{B}}$$

# Normal Zeeman effect 3 Comment 1

Bohr's magneton is the fundamental quantity that determines the magnetism caused by electrons.

The numerical values of Bohr's magneton are outlined in red in the first line.

The equation underlined in red gives the potential energy of a magnetic moment in a magnetic field.

The potential energy is smallest when the magnetic moment is aligned parallel to the magnetic field.

The potential energy is part of the Hamilton function and the Hamilton function becomes the Hamilton operator when the momentum of the electron is replaced by the momentum operator $-i\hbar\nabla$.

# Normal Zeeman effect 3 — Comment 2

This turns the orbital angular momentum of the electron into the angular momentum operator.

This contribution of the Hamilton operator is called the Zeeman operator.

The equation outlined in red gives the Zeeman operator, which must be included in the Schrödinger equation when a magnetic field is present.

Although the discussion started with a very particular orbit of the electron, the result is general.

# Normal Zeeman effect 4

eigenvalue equation ($B$ defines the $z$-direction and with $\hat{L}_z Y_{\ell,m} = m\hbar Y_{\ell,m}$)

$$\hat{H}_{Zee} Y_{\ell,m} = \mu_B \frac{\hat{L}_z}{\hbar} B Y_{\ell,m} = m \mu_B B Y_{\ell,m}$$

energy eigenvalues

$$\boxed{E_{Zee} = m\mu_B B}$$

and $m = 0, \pm 1, \pm 2, ....$

# Normal Zeeman effect 4 — Comment

The eigenvalue equation of the Zeeman operator is very simple when the magnetic field is applied along the z-direction or the magnetic field defines the z-direction.

In this case the eigenvalue equation of the Zeeman operator is proportional to the eigenvalue equation of the z-component of the angular momentum.

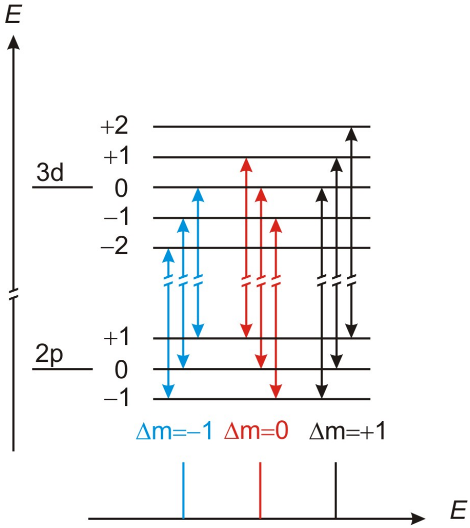
The eigenfunctions are the spherical harmonics.

The equation outlined in red shows the eigenvalues of the Zeeman operator.

Independent of the details of the atomic eigenstates, the shift of the energy is determined by the quantum number $m$ of the angular momentum.

The quantum number $m$ is therefore sometimes also called the magnetic quantum number.

# Normal Zeeman effect 5




splitting of the spectral line

$$\Delta m = -1: \quad \Delta E = -\mu_B B$$
$$\Delta m = 0: \quad \Delta E = 0$$
$$\Delta m = +1: \quad \Delta E = +\mu_B B$$

in 3 components

# Normal Zeeman effect 5 — Comment 1

The figure shows the splitting of a 2p and a 3d orbital.

The 2p orbital is split into three components.

The 3d orbital is split into five components.

The arrows indicate the allowed electrical dipole transitions.

The selection rules for electrical dipole transitions are $\Delta\ell = \pm 1$ and $\Delta m = 0, \pm 1$.

The figure shows that the transition between the 2p and 3d orbitals should split into three spectral lines in a magnetic field.

This result does not agree with the observation of Pieter Zeeman.

# Normal Zeeman effect 5 Comment 2

Since the analysis of Hendrik Lorentz of the Zeeman effect in 1897 predicted a splitting into three spectral lines, a threefold splitting of spectral lines in a magnetic field is called the normal Zeeman effect.

Zeeman’s original observation is somewhat anomalous. A splitting of spectral lines in more or less than three lines is therefore called the anomalous Zeeman effect.

It is obvious that the Schrödinger theory is not complete at the current state of the discussion.

What is missing is the intrinsic magnetic moment of the electron, which is independent of the orbital motion.

The intrinsic magnetic moment of the electron is related to an intrinsic angular momentum of the electron called the spin of the electron.

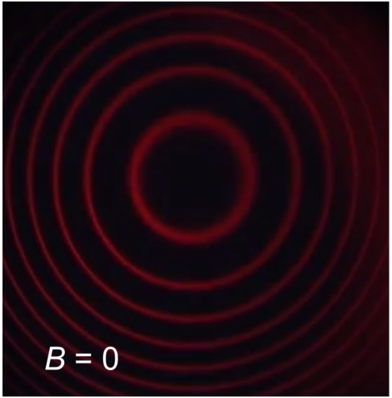
# Normal Zeeman effect 5 Comment 3

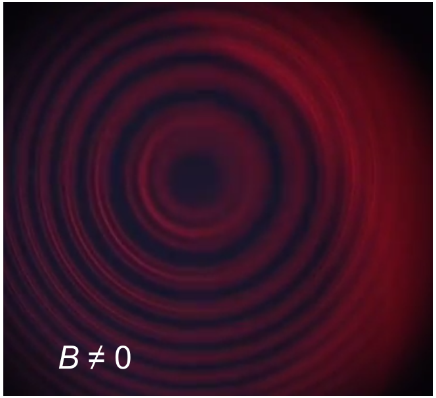
The fact that the electron has a magnetic moment and its own angular momentum was first demonstrated in 1922 with the “Stern-Gerlach experiment”.

However, the attempt to understand the magnetic moment of the electron in the context of classical physics leads to absolutely unrealistic results.

# Normal Zeeman effect 6

Zeeman effect of the red Cadmium line ($\lambda = 643.8$ nm)




(ZeemanCdLinie.mp4)

# Normal Zeeman effect 6 Comment

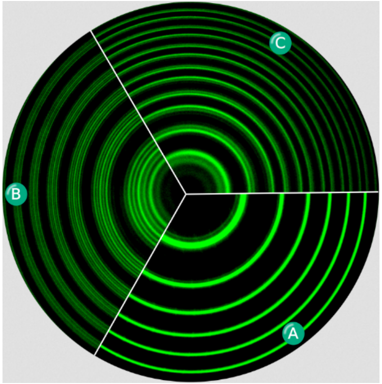
The splitting of spectral lines into three components when a magnetic field is applied can be observed in nature.

The video shows the splitting of the red Cadmium line.

The measurement with a Fabry-Perot interferometer clearly shows a split into three lines.

# Normal Zeeman effect 7

Zeeman effect of the green Mercury line ($\lambda = 546.1$ nm)




(ZeemanGüneHgLinie.mp4)

# Normal Zeeman effect 7 Comment 1

The video shows the Zeeman splitting of the green Mercury spectral line.

The resolution of the interferometer in the video is low, giving the impression that the green spectral line is also split into three components.

The figure shows the measurement with a better Fabry-Perot interferometer.

The resolution of the experiment is much greater.

The green spectral line splits into 9 components.

Region A shows the rings when no magnetic field is applied.

The region B shows the rings when a magnetic field is applied.

Only 7 of the expected rings are clearly visible.

# Normal Zeeman effect 7 Comment 2

A polarization filter is used in area C, which blocks the light from the inner three rings.

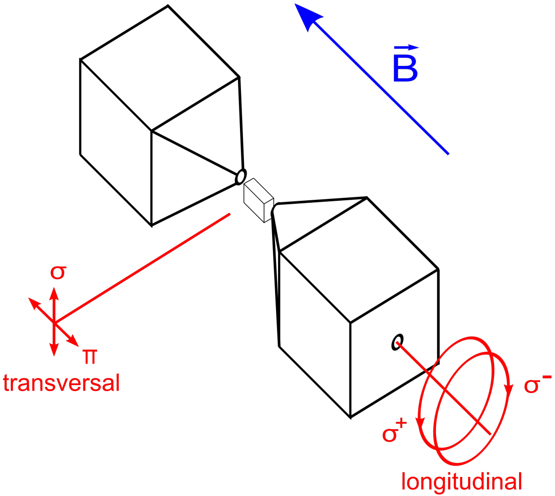
For this purpose, the polarization filter is set so that only light can pass that is polarized perpendicular to the direction of the magnetic field.

The light of the inner three rings is obviously polarized parallel to the direction of the magnetic field.

The same effect can also be observed for the red Cadmium line.

Since the spectrum of the red Cadmium line agrees with the theory at hand, one can conclude that the selection rule $\Delta m = \pm 1$ leads to light polarized perpendicular to the magnetic field, while transitions that follow the selection rule $\Delta m = 0$ are polarized parallel to the magnetic field.

# Normal Zeeman effect 8




(Circularpolarization.mp4)

# Normal Zeeman effect 8 Comment 1

The sketch shows the experimental setup.

π describes the polarization of light in which the electric field of the wave oscillates parallel to the magnetic field.

σ describes the polarization of light in which the electric field oscillates perpendicular to the magnetic field.

If the light is observed parallel to the magnetic field, it is circularly polarized.

The video shows that a phase shift of π/2 between two mutually perpendicular components of the electric field leads to circular polarization.

# Dia- and Paramagnetism

# The Schrödinger equation of the H-atom

- Schrödinger equation
- Box potential
- Harmonic oscillator
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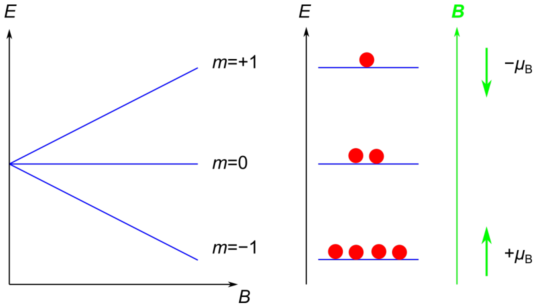
- Normal Zeeman effect
- Dia- and paramagnetism

# Dia- and paramagnetism 1

**paramagnetism**: magnetic moment due to the orbital angular momentum

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




The paramagnetic moment results from the thermal average

$$\boxed{\mu_{para} = \langle \mu_L \rangle}$$

# Dia- and paramagnetism 1 Comment 1

The equation outlined in red gives the operator of the magnetic moment.

If the applied magnetic field defines the z-direction, then the eigenvalues for the operator of the magnetic moment can easily be given.

The left figure shows the splitting of a quantum state with the orbital angular momentum $\ell = 1$.

If there are many atoms, then the thermal occupation of the energy levels can be calculated using the Boltzmann factor.

A magnetic moment can be assigned to each energy level according to the magnetic quantum number $m$.

# Dia- and paramagnetism 1 Comment 2

In the figure, the thermal occupation of the energy levels is indicated by red dots and the magnetic moment by green arrows.

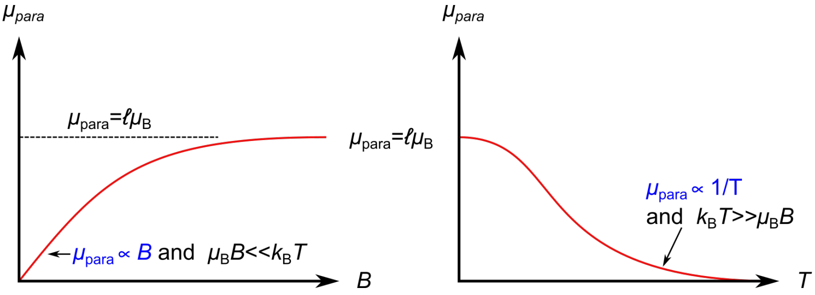
The total magnetic moment of the atoms is obtained by adding up the magnetic moments of all atoms.

If the total magnetic moment is divided by the number of atoms, the result is an averaged magnetic moment per atom, which is aligned parallel to the magnetic field.

The magnitude of the magnetic moment depends on the strength of the magnetic field and the temperature.

This phenomenon is called paramagnetism.

# Dia- and paramagnetism 2




**the paramagnetic moment is** (in thermal equilibrium)

- proportional to the strength of $B$: $\mu_{para} \propto B$, as long as $k_B T >> \mu_B B$
- proportional to the reciprocal temperature: $\mu_{para} \propto 1/T$, as long as $k_B T >> \mu_B B$ (Curie-law)

# Dia- and paramagnetism 2 Comment 1

The paramagnetic moment is determined by the ratio between the thermal energy $k_B T$ and the magnetic energy, since $\mu_\mathrm{B} B$ determines the energy of the Zeeman splitting.

The left figure shows the variation of the paramagnetic moment as a function of the applied magnetic field $B$.

The paramagnetic moment is zero when the magnetic field is zero.

As long as the magnetic energy is smaller than the thermal energy, the increase in the magnetic moment is proportional to the magnetic field strength.

If the magnetic energy is much greater than the thermal energy, only the ground state is occupied and the paramagnetic moment reaches its maximum value $\mu_\mathrm{para} = \ell \mu_\mathrm{B}$.

# Dia- and paramagnetism 2 — Comment 2

The paramagnetic moment is saturated in strong magnetic fields.

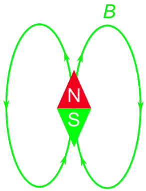
The figure on the right side shows the temperature dependence of the paramagnetic moment.

The paramagnetic moment begins with the maximum value at low temperatures and decreases with increasing temperature, since more and more energy levels are occupied with smaller or even antiparallel magnetic moments.

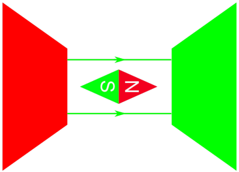
If the thermal energy is much greater than the magnetic energy, the temperature dependence of the paramagnetic moment is given by Curie's law.

The paramagnetic moment is proportional to $T^{-1}$.

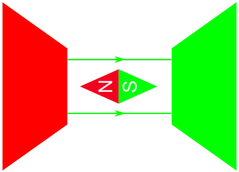
# Dia- and paramagnetism 3




paramagetism




diamagnetism




(ParamagnetischerSauerstoff.mp4)

# Dia- and paramagnetism 3 — Comment 1

The left figure shows a macroscopic magnetic moment.

A magnetic moment has a magnetic north and a south pole.

The magnetic field lines start at the magnetic north pole and end at the south pole.

The upper figure on the right shows the behavior of a paramagnetic moment between the poles of a magnet.

The paramagnetic moment is oriented parallel to the magnetic field of the magnet.

Since there is a force of attraction between opposing magnetic poles, there is a force that holds the paramagnetic moment in the field of the magnet.

The video shows an experiment with liquid nitrogen and liquid oxygen.

# Dia- and paramagnetism 3 Comment 2

The boiling temperature of $N_2$ is 77 K and the boiling temperature of $O_2$ is 90 K.

A pair of magnets with a small gap between them is cooled in liquid nitrogen.

Nothing special happens when the pair of magnets is pulled out of the liquid nitrogen.

When the cold magnet pair is immersed in liquid oxygen, a droplet of oxygen is held between the magnets when they are removed from the liquid oxygen.

$O_2$ is paramagnetic while $N_2$ is diamagnetic.

In diamagnetism, the magnetic moment of the atoms is oriented antiparallel to the magnetic field.

This is shown in the second figure on the right.

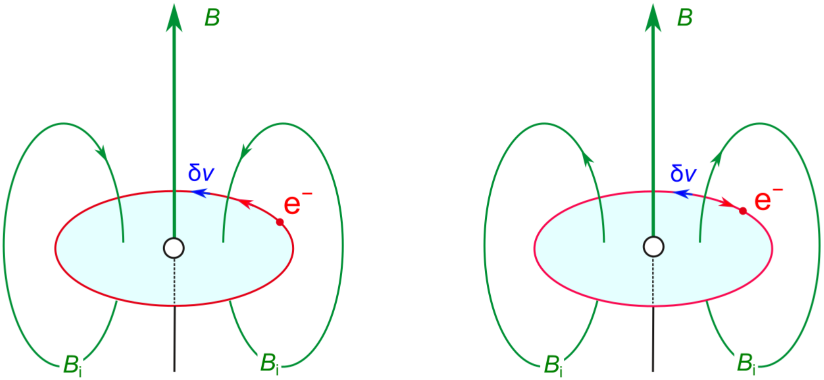
# Dia- and paramagnetism 3 Comment 3

Since there is a repulsive force between magnetic poles of the same type, no diamagnetic moment can be held between the poles of a magnet.

The $N_2$ molecule is diamagnetic.

# Dia- and paramagnetism 4

**diamagnetism**: magnetic moment due to Lenz's law (1834)



# Dia- and paramagnetism 4 — Comment 1

The figures illustrate the reason for the diamagnetic moment.

Lenz's law states that a current is induced which counteracts the change in the magnetic flux when a magnetic field is applied.

The figure illustrates the effect for a circular orbit of an electron.

The speed of the electron is indicated by a red arrow.

The closed magnetic field lines $B_\mathrm{i}$ indicate the internal magnetic field of an atom that is caused by the motion of the electron according to Ampere's law.

The magnetic field $\vec{B}$ denotes an external magnetic field that is turned on.

The blue vectors $\delta\vec{v}$ indicate the speed change of the electron due to Lenz's law.

# Dia- and paramagnetism 4 Comment 2

In the left figure, the magnetic flux through the electron's path is reduced by the applied magnetic field.

Therefore the speed of the electron has to be increased to compensate for the effect.

In the right figure, the magnetic flux is increased by the applied magnetic field and the speed of the electron has to be reduced to compensate for the effect.

The direction of the induced magnetic moment is opposite to the applied magnetic field in both cases.

# Dia- and paramagnetism 4 Comment 3

The induced diamagnetic moment is much smaller than the paramagnetic moment.

If the paramagnetic moments compensate each other because the electrons rotate in opposite directions, the diamagnetic moment remains.

# Dia- and paramagnetism 5

change of the centrifugal force $F_v$ due to $\delta v$

$$\frac{\delta F_v}{\delta v} = \frac{d}{dv}\left(\frac{mv^2}{r}\right) = \frac{2mv}{r} \quad \text{and} \quad \underline{\delta F_v = \frac{2mv}{r}\delta v}$$

the change of the centrifugal force due to $\delta v$ is compensated by the Lorentz force $F_L = evB$

$$\delta F_v = F_L \quad \rightarrow \quad \frac{2mv\delta v}{r} = evB$$

and

$$\boxed{\delta v = \frac{erB}{2m}}$$

# Dia- and paramagnetism 5 — Comment

When a magnetic field is applied, the speed of the electron must change due to Lenz's law.

The reaction of the centrifugal force to the change in speed $\delta v$ is given by the underlined equation.

The change in centrifugal force must be compensated for by the Lorentz force.

This results in the formula outlined in red for the change in speed as a function of the magnetic field.

($e$ denotes the elementary charge, i.e. $\approx +1.6 \cdot 10^{-19}$ As and the forces their absolute values.)

# Dia- and paramagnetism 6

magnetic moment of a charge on a circular orbit

$$\boxed{\mu = -\frac{erv}{2}}$$

with

$$\boxed{\delta v = \frac{erB}{2m}}$$

is the response of the magnetic moment due the applied magnetic field

$$\underline{\delta\mu = -\frac{er\delta v}{2} = -\frac{e^2 r^2}{4m} B}$$

# Dia- and paramagnetism 6 Comment

With the formula for the magnetic moment of an electron on a circular path, the induced diamagnetic moment in a magnetic field results.

This result for a circular path can be generalized for any path that is described by a wave function.

The square of the radius $r$ has to be replaced by the mean value, which can be calculated with the wave function.

As with the circular path, only the component of $r$ that is perpendicular to the magnetic field has to be taken into account.

# Dia- and paramagnetism 7

the diamagnetic moment is

$$\boxed{\vec{\mu}_{\mathrm{dia}} = -\frac{e^2}{4m}\langle \vec{r}_{\perp}^{\,2}\rangle \vec{B}}$$

- induced by the $\vec{B}$ field
- it is proportional to the area of the atom / molecule perpendicular to $\vec{B}$
- it is independent of the temperature
- and it is always antiparallel to the direction of the $\vec{B}$-field

# Dia- and paramagnetism 7 Comment 1

The formula outlined in red shows the exact result for the magnetic moment.

Like the paramagnetic moment, the diamagnetic moment is also induced by a magnetic field.

Without a magnetic field there is no paramagnetic or diamagnetic moment.

The diamagnetic moment increases with the diameter of an atom and the number of electrons.

In molecules, the diamagnetic moment depends on the direction of the magnetic field in relation to the molecular coordinates.

In contrast to the paramagnetic moment, the diamagnetic moment is almost independent of temperature.

# Dia- and paramagnetism 7 — Comment 2

For the paramagnetic moment the relevant energy scale is given by the magnetic energy $\mu_B B$.

This energy scale is usually comparable to the thermal energy scale $k_B T$.

The relevant energy scale for the diamagnetic moment is given by the excitation energy of the electronic eigenstates.

These energies are much larger than the thermal energy and the influence of the thermal excitation on the diamagnetic moment is usually negligible.

Due to Lenz's law, the diamagnetic moment always points in the opposite direction of the applied magnetic field, while the paramagnetic moment is parallel to the applied magnetic field.

# Atoms

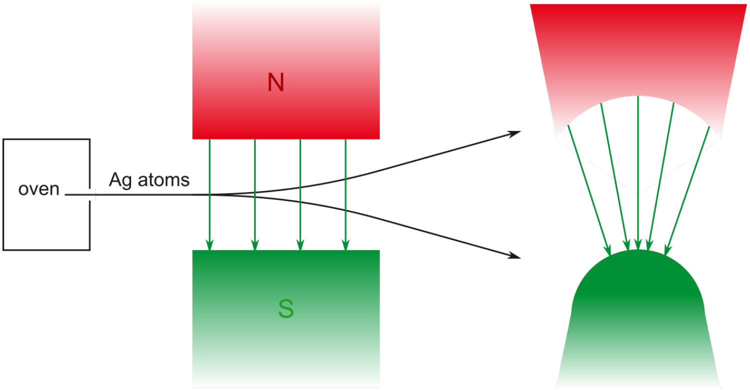
# Stern-Gerlach-Exp.

# Quantum mechanics and the spin of the electron

- Stern-Gerlach experiment
- Spin of the electron
- Spin-orbit coupling
- Addition of angular momenta
- anomalous Zeeman effect
- Hyperfine interaction
- Selection rules for elm. dipole transitions

# Stern-Gerlach experiment 1

In the Stern-Gerlach experiment an atom beam made of Ag atoms passes through a inhomogeneous magnetic field (Otto Stern and Walther Gerlach 1922)



# Stern-Gerlach experiment 1 Comment 1

An important Bohr postulate is that the angular momentum of the electrons is quantized in units of $\hbar$.

This postulate follows in Bohr's model of the atom from the fact that the energy of the electron in the hydrogen atom is quantized.

The Zeeman effect shows that the projection of the angular momentum onto the direction of the magnetic field is also quantized.

The directional quantization of angular momentum and the related magnetic moment follows easily from the Schrödinger equation but not at all from Bohr's model of the atom.

# Stern-Gerlach experiment 1 — Comment 2

Therefore in the time before the Schrödinger equation, the direction quantization was an astonishing effect that Otto Stern and Walter Gerlach wanted to investigate independent of optical spectroscopy with an atomic beam experiment in 1921 and 1922.

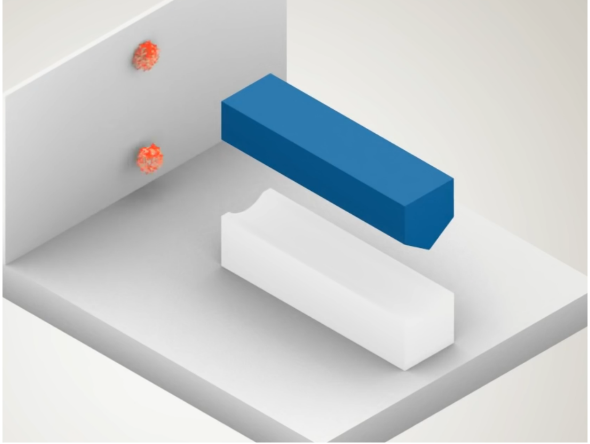
The figure shows a sketch of the famous experiment.

A beam of Silver atoms is guided through an inhomogeneous magnetic field.

The inhomogeneity of the magnetic field is determined by the shape of the magnet's pole pieces.

With this experimental set-up, Stern and Gerlach observed that the beam of the silver atoms splits into two partial beams after the inhomogeneous magnetic field.

# Stern-Gerlach experiment 2



(SternGerlachexperiment.mp4)

# Stern-Gerlach experiment 2 Comment

The video shows an animation of the experiment with both classical magnetic moments and a magnetic moment, which has two setting options with regard to the direction of the magnetic field.

# Stern-Gerlach experiment 3

force on a magnetic moment in an inhomogeneous magnetic field

$$\underline{\vec{F} = (\vec{\mu}\,\nabla)\vec{B}}$$

simplifying assumptions are $\vec{B} \parallel \hat{z}$ and $\frac{\partial B}{\partial z} \neq 0$

$$F_z = \mu_z \frac{\partial B}{\partial z}$$

- with a classical magnetic moment, all orientations in relation to the directions of the magnetic field are possible, i.e. $\mu_z = |\vec{\mu}| \cos\theta$.
- With Schrödinger's angular momentum theory, the z-component is quantized according to the *m* quantum number.

# Stern-Gerlach experiment 3 — Comment 1

The underlined equation indicates the force on a magnetic moment in an inhomogeneous magnetic field.

The formula results when $\nabla$ is applied to the potential energy $E_{pot} = -\vec{\mu}\vec{B}$, because the force due to the potential energy is $\vec{F} = -\nabla E_{pot}$.

The formula is simplified if the magnetic field is only aligned along the z-direction and only the partial derivative of the magnetic field according to the z-coordinate differs from zero.

Since a classic magnetic moment can have all orientations with respect to the z-direction, no beam splitting is to be expected.

In Schrödinger's theory, the angular momentum is quantized along the z-direction and a beam splitting is not surprising.

# Stern-Gerlach experiment 3 Comment 2

The twofold splitting of the atomic beam shows directly that there are two setting options for the magnetic moment of the silver atoms in relation to the magnetic field.

In fact, it has long been assumed that the electron must have a magnetic moment and that this moment must have two possible attitudes in relation to the magnetic field.

Reasons for this assumption are the doublet splitting of the spectral lines of the alkali metals, the doublet splitting of the characteristic X-rays and the Zeeman splitting of the spectral lines of the alkali metals into an even number of lines.

# Stern-Gerlach experiment 3 — Comment 3

In fact, in 1924, Nils Bohr was able to explain the periodic table of the elements by assuming that the electron must have a double quantum number.

However, these findings raised many questions.

The directional quantization of angular momentum and magnetic moment has been shown experimentally, but the reason for this was completely unclear.

The intrinsic angular momentum of an electron can easily be explained, if one imagines the electron as a charged sphere that rotates around an axis.

The experiments show that the magnetic moment of the electron must be in the range of a Bohr magneton $\mu_B$.

# Stern-Gerlach experiment 3 Comment 4

However, this assumption leads to a value in the range of $10^{-13}$ m for the radius of the electron sphere, which is by far too large and cannot agree with Rutherford's scattering experiments.

The problems were finally solved in 1927 by Paul Dirac.

# Spin

# 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

# Spin of the electron 1

relativistic energy-momentum relation

$$\boxed{E^2 - c^2\vec{p}^{\,2} = m_0^2 c^4}$$

$$-i\hbar\frac{\partial\psi}{\partial x} = p_x\psi \quad \text{and} \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

and

$$E^2 - c^2\vec{p}^{\,2} = m_0^2 c^4 \quad \rightarrow \quad (E^2 - c^2\vec{p}^{\,2})\psi = m_0^2 c^4\psi$$

Klein-Gordon equation

$$\underline{\hbar^2\frac{\partial^2\psi}{\partial t^2} - c^2\hbar^2\nabla^2\psi = m_0^2 c^4\psi}$$

# Spin of the electron 1 Comment

The equation outlined in red gives the relativistic energy-momentum relationship of a particle with no potential energy.

The Klein-Gordon equation results when energy and momentum are replaced by the corresponding partial derivatives of the wave function.

In 1926, however, the Klein-Gordon equation was not accepted as the wave equation of matter waves, since in this differential equation the number of particles is not a conserved quantity.

The Klein-Gordon equation is a second order differential equation.

Paul Dirac solved this problem by reducing the Klein-Gordon equation to a set of first-order differential equations.

# Spin of the electron 2

Dirac equation for a free particle with no potential energy

$$i\hbar\frac{\partial\psi}{\partial t} = (c\vec{\alpha}\hat{\vec{p}} + \beta m_0 c^2)\psi$$

the Klein-Gordon equation results when the Dirac equation is applied twice

the coefficients $\vec{\alpha}$ and $\beta$ must meet the conditions

$$\boxed{\begin{aligned} \alpha_i\alpha_j + \alpha_j\alpha_i &= 2\delta_{ij} \\ \alpha_i\beta + \beta\alpha_i &= 0 \\ \beta^2 &= 1 \end{aligned}}$$

the coefficients $\alpha_{i=x,y,z}$ and $\beta$ are $4 \times 4$-matrices formed by Pauli matrices

# Spin of the electron 2 — Comment

The underlined equation is the Dirac equation of a relativistic electron with no potential energy.

The Klein-Gordon equation results when the operators on the left and right side of the Dirac equation are applied twice.

This only works if the coefficients $\alpha_i$ and $\beta$ are $4 \times 4$ matrices that meet the conditions outlined in red.

These matrices are formed by the Pauli matrices.

This makes the calculation very extensive and tedious, so that the Dirac theory cannot be discussed in more detail in this lecture.

# Spin of the electron 3

Pauli matrices

$$\boxed{\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

spin of the electron

$$\underline{\hat{\vec{s}} = \frac{\hbar}{2} \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}}$$

# Spin of the electron 3 Comment 1

The formulas framed in red give the Pauli matrices.

The intrinsic angular momentum of the electron is called spin and it turns out in the context of the Dirac theory that the electron's spin is described by the Pauli matrices.

The underlined equation gives the operator of the spin.

In contrast to the orbital angular momentum, the spin operator is not a differential operator that acts on spatial coordinates.

The vector components of the spin operator are proportional to the Pauli matrices.

The operator of the spin does not act on spatial coordinates and consequently has nothing to do with a rotating sphere of charge.

# Spin of the electron 3 — Comment 2

The spin is consequently not caused by a rotating charged sphere.

There is no experiment in which a finite radius of the electron could be proven.

# Spin of the electron 4

z-component of the spin

$$\boxed{\hat{s}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

eigenvalue equations of the z-component

$$\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = +\frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

# Spin of the electron 4 Comment 1

Schrödinger’s wave mechanics defines angular momentum using differential operators that lead to eigenvalue equations that determine the vector of the orbital angular momentum.

These eigenvalue equations are now the key to generalizing wave mechanics to quantum mechanics.

The essence of generalization can be illustrated using the spin.

In quantum mechanics, a physical quantity is called angular momentum if it fulfills the eigenvalue equations of angular momentum.

The equation outlined in red gives the z-component of the spin operator.

# Spin of the electron 4 — Comment 2

The following two matrix equations give the eigenvalue equation of the z component.

The eigenstates of the spin are obviously the 2-tuples $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

# Spin of the electron 5

square of the spin

$$\boxed{\hat{\vec{s}}^{\,2} = \left(\frac{\hbar}{2}\right)^2 (\sigma_x^2 + \sigma_y^2 + \sigma_z^2)} \quad \text{with} \quad \sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

the 2-tuple $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are the eigenstates of $\hat{\vec{s}}^{\,2}$ and

$$\underline{\hat{\vec{s}}^{\,2} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\left(\frac{1}{2} + 1\right)\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}$$

quantum numbers of the spin

$$\boxed{s = \frac{1}{2} \qquad \text{and} \qquad m_s = \pm\frac{1}{2}}$$

# Spin of the electron 5 Comment

The first equation outlined in red gives the operator for the square of the spin.

The square of each Pauli matrix gives the unit matrix.

Therefore the 2-tuples $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are also eigenstates of the squared spin operator.

The underlined equation shows that the eigenvalue 3/4 $\hbar^2$ can be written with the spin quantum number $s = 1/2$ like the eigenvalue of the squared orbital angular momentum.

The formulas outlined in red indicate the quantum numbers of the spin.

# Spin of the electron 6

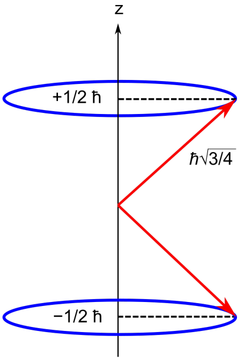
$s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$

magnetic moment of the electron

$$\boxed{\vec{\mu}_e = -g\mu_B\vec{s}/\hbar}$$

g-factor of the electron

$$g = 2.00231930436256(35)$$



# Spin of the electron 6 — Comment 1

The vector of the spin is determined with the eigenvalues of the spin operator underlined in red.

The figure shows the vector of the spin, which, like the vector of the orbital angular momentum, lies on conical surfaces.

The z-component of the vector has the length $\pm\frac{1}{2}\hbar$.

The length of the vector is $\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar = \sqrt{\frac{3}{4}}\hbar$.

Like the orbital angular momentum, the electron spin is connected to a magnetic moment.

The equation outlined in red gives the formula that results from the Dirac equation for the magnetic moment of the electron.

# Spin of the electron 6 Comment 2

Except for the g-factor, this formula corresponds to the formula for the magnetic moment of the orbital angular momentum.

The Dirac theory gives the exact value $g = 2$ for the g-factor of the electron.

In 1927 the results of the Dirac equation agreed exactly with the measurements of the spectra of the hydrogen atom.

Therefore, similar to Wien's radiation formula, the question arose whether the Dirac theory is actually exact, or whether it is only an approximation.

Great efforts have been made to measure the spectra of the hydrogen atom and the magnetic moment of the electron as precisely as possible.

During the 1940s it became clear that the Dirac equation is an approximation.

# Spin of the electron 6 — Comment 3

The formula underlined in red gives the currently known value of the g-factor of the electron.

The g-factor is determined experimentally up to 12 digits behind the decimal point.

This accuracy is also achieved when calculating the g-factor in the context of quantum electrodynamics.

Experiment and theory match perfectly.

The solution of the time-dependent Schrödinger equation is only possible approximately.

In the case of electromagnetic interaction, the procedure is called quantum electrodynamics and particularly successful.

# Dirac notation

# 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

# Dirac notation 1

Dirac notation for quantum states

$$\boxed{|1^{\text{st}}\,\text{quantum number},\quad 2^{\text{nd}}\,\text{quantum number}, \ldots\rangle}$$

spin eigenstates

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \to \underline{|1/2, +1/2\rangle} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \to \underline{|1/2, -1/2\rangle}$$

orbital angular momentum eigenstates

$$Y_{\ell,m}(\theta, \varphi) \quad \to \quad \underline{|\ell, m\rangle}$$

eigenstate of the hydrogen atom

$$R_{n,\ell}(r)\,Y_{\ell,m}(\theta, \varphi) \quad \to \quad \underline{|n, \ell, m\rangle}$$

# Dirac notation 1 Comment

Dirac discovered that quantum states are not only determined by wave functions.

The 2-tuples of the spin eigenstates are also quantum states.

Dirac therefore introduced an abbreviated notation for quantum states, which is outlined in red in the first line.

The symbol $|...\rangle$ is called a “ket”.

This is a special brac**ket** that encloses the quantum numbers.

The following lines give examples of the use of the short notation.

# Dirac notation 2

eigenvalue equation of the spin

$$\boxed{\begin{aligned}\hat{\vec{s}}^{\,2}\,|s, m_s\rangle &= s(s+1)\hbar^2\,|s, m_s\rangle \\ \hat{s}_z\,|s, m_s\rangle &= m_s\hbar\,|s, m_s\rangle\end{aligned}}$$

eigenvalue equation of the orbital angular momentum with the Dirac notation

$$\hat{\vec{L}}^2 Y_{\ell,m}(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y_{\ell,m}(\theta,\varphi) \quad \rightarrow \quad \boxed{\hat{\vec{L}}^2\,|\ell, m\rangle = \ell(\ell+1)\hbar^2\,|\ell, m\rangle}$$

$$\hat{L}_z Y_{\ell,m}(\theta,\varphi) = m\hbar Y_{\ell,m}(\theta,\varphi) \quad \rightarrow \quad \boxed{\hat{L}_z\,|\ell, m\rangle = m\hbar\,|\ell, m\rangle}$$

# Dirac notation 2 — Comment

The boxed formulas give the eigenvalue equations of the spin using the Dirac notation and the same symbolic notation for the eigenvalue equations of the orbital angular momentum.

# Dirac notation 3

time independent Schrödinger equation of the hydrogen atom
(abbreviation: $\psi_{n,\ell,m}(\vec{r},t) = R_{n,\ell}(r)Y_{\ell,m}(\theta,\varphi)e^{-iE_n t/\hbar}$)

$$\hat{H}\psi_{n,\ell,m}(\vec{r},t) = E_n\psi_{n,\ell,m}(\vec{r},t) \quad \rightarrow \quad \boxed{\hat{H}\,|n,\ell,m\rangle = E_n\,|n,\ell,m\rangle}$$

normalization of the wave function

$$\underline{\int_V \psi^*_{n,\ell,m}(\vec{r},t)\psi_{n,\ell,m}(\vec{r},t)dV = 1}$$

the “bra”

$$\psi^*_{n,\ell,m}(\vec{r},t) \quad \rightarrow \quad \boxed{\langle n,\ell,m|}$$

$$\int_V \psi^*_{n,\ell,m}(\vec{r},t)\psi_{n,\ell,m}(\vec{r},t)dV = 1 \quad \rightarrow \quad \boxed{\langle n,\ell,m|n,\ell,m\rangle = 1}$$

# Dirac notation 3 Comment

The Schrödinger equation of the hydrogen atom can also be formulated using the Dirac notation.

The wave function is abbreviated with the ket $|n, \ell, m\rangle$.

The equation underlined in red gives the integral for the normalization of the wave function.

Dirac introduced the “ bra ” symbol for the complex conjugate wave function $\psi^*_{n,\ell,m}$.

The equation outlined in red gives the bra of the quantum state $\psi^*_{n,\ell,m}(\vec{r})$.

The last equation framed in red gives the short notation for the integral.

The symbol $\langle n, \ell, m|n, \ell, m\rangle$ is called a **bracket** and abbreviates the integral.

# Dirac notation 4

expectation value e.g. $\langle x \rangle$

$$\langle x \rangle = \int_V \psi^*_{n,\ell,m}(\vec{r},t)\, x\, \psi_{n,\ell,m}(\vec{r},t)\, dV$$

Dirac notation

$$\boxed{\langle x \rangle = \langle n,\ell,m |\, x \,| n,\ell,m \rangle}$$

# Dirac notation 4 Comment

Sometimes one likes to calculate the average of a physical quantity.

The example shows the integral for calculating the mean value of the coordinate $x$.

The mean value over the wave function of a physical quantity is called the expectation value of the physical quantity.

The expectation value can be determined by measuring many similar quantum systems.

When examining a single quantum system, the measurement must be carried out several times and the result averaged.

The equation outlined in red gives the abbreviated form of the integral in Dirac notation for the expectation value of the coordinate $x$.

# Spin-Orbit Coupling

# Quantum mechanics

- Stern-Gerlach experiment
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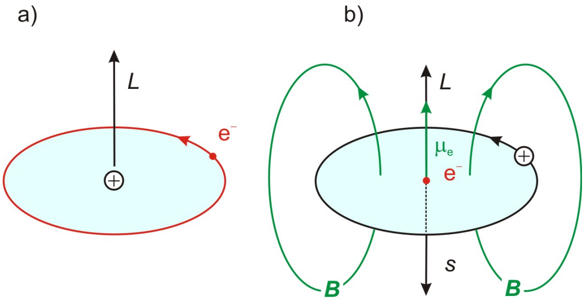
# Spin-orbit coupling 1

the magnetic moment of the electron aligns itself in the magnetic field that is created by the movement of the electron around the nucleus



# Spin-orbit coupling 1 — Comment 1

The left figure shows the movement of an electron around the nucleus on a circular orbit.

Although the electron can also travel through other orbits on its way around the atomic nucleus, a circular path is used in the following for the sake of simplicity.

A circular orbit is unlikely, but not forbidden either.

The potential energy of the magnetic moment of the electron in the magnetic field of a circular orbit can easily be calculated.

In order to finally get the Hamilton operator of the spin-orbit coupling, orbital angular momentum and spin have to be replaced by their operators.

# Spin-orbit coupling 1 — Comment 2

The illustration on the right shows the same movement.

The reference system is now attached to the electron, i.e. the electron is at rest and the nucleus is in motion.

The electron is surrounded by a ring current that creates a magnetic field according to Ampere’s law.

# Spin-orbit coupling 2

Magnetic field $B$ in the center of a circular current $I$

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

Current caused by a nucleus with atomic number $Z$ on a circular orbit around the electron

$$I = \frac{Zev}{2\pi r}$$

$$B = \mu_0 \frac{Zev}{4\pi r^2} = \mu_0 \frac{Zev}{4\pi r^2} \frac{rm}{rm} = \mu_0 \frac{Ze}{4\pi r^3 m} L$$

with Bohr's magneton $\mu_B = \frac{e\hbar}{2m}$ results $\boxed{B = \mu_0 \frac{Z\mu_B}{2\pi r^3} \frac{L}{\hbar}}$

# Spin-orbit coupling 2 Comment

The first underlined equation gives the magnetic field in the center of a ring-current $I$.

The second underlined equation gives the current due to the movement of the nucleus with the atomic number $Z$ around the electron.

The resulting formula for the magnetic field $B$ can be expanded with the product $r\,m$.

$m$ denotes the mass of the electron.

The magnetic field is proportional to the orbital angular momentum of the electron, since the speed of the nucleus around the electron is equal to the speed of the electron around the nucleus.

The formula outlined in red results when the constants are combined to form Bohr’s magneton.

# Spin-orbit coupling 3

potential energy of the magnetic moment $\mu_e$ of the electron in the magnetic field, which is caused by the atomic nucleus

$$E_{pot} = -\vec{\mu}_e \vec{B} \quad \text{with} \quad B = \mu_0 \frac{Z\mu_B}{2\pi r^3} \frac{L}{\hbar}$$

and

$$\boxed{\vec{\mu}_e = -g\mu_B \vec{s}/\hbar}$$

$$\underline{E_{pot} = g\mu_B^2 \frac{\mu_0}{2\pi} \frac{Z}{r^3} \frac{\vec{s}\vec{L}}{\hbar^2}}$$

Hamilton operator of the spin-orbit coupling

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

# Spin-orbit coupling 3 Comment 1

With the formula for the potential energy of a magnetic moment in the magnetic field and with the magnetic moment of an electron, the formula underlined in red results for the potential energy of the spin-orbit coupling.

The Hamilton operator of the spin-orbit coupling results when the orbital angular momentum and spin of the electron are replaced by the orbital angular momentum operator and the spin operator.

The prefactor is abbreviated with the letter $\xi$ and is usually determined experimentally.

# Spin-orbit coupling 3 — Comment 2

The prefactor of the underlined formula written in green is correct except for a factor of 1/2.

The underlined equation agrees with the Dirac equation if the additional factor 1/2 is included.

The combination of Bohr’s atomic model with the quantization rules of Schrödinger obviously allows almost exact results to be achieved.

In contrast to the Dirac equation, Bohr’s atomic model enables a very intuitive description of quantum physics, which is obviously not completely misleading.

# Spin-orbit coupling 4

formula of the spin-orbit coupling constant

$$\underline{\xi = g\mu_B^2 \frac{\mu_0}{4\pi} \frac{Z}{r^3}}$$

estimation with the Bohr radius

$$r_n = \frac{a_B}{Z} n^2$$

$$\underline{\xi \propto \frac{Z^4}{n^6}}$$

# Spin-orbit coupling 4 Comment

The formula underlined in red shows the exact result for the coupling constant of the spin-orbit coupling $\xi$.

If the radius of the Bohr orbits is used, it turns out that the coupling constant increases with the fourth power of the atomic number $Z$ and decreases with the sixth power of the principal quantum number $n$.

The effect of the atomic number $Z$ is overestimated because the influence of the shielding of the atomic charge due to other electrons is not taken into account.

The experimental data show that the strength of the spin-orbit coupling increases strongly with the atomic number.

If the atomic number is greater than $Z = 70$, then the energy of the spin-orbit coupling is greater than the energy of the electrical repulsive force between the electrons.

# Revision

# Summary in Questions 1

1. Give the Zeeman Hamilton operator.
2. Give the eigenvalue equation of the Zeeman Hamilton operator.
3. Sketch the level-splitting of a p orbital in a magnetic field.
4. Give the magnetic moments of the Zeeman levels.
5. Explain the difference between para- and diamagnetism.
6. Give the paramagnetic moment for $T \to 0$.
7. Give the temperature dependence of the paramagnetic moment when $k_B T >> \mu_B B$.
8. Sketch and explain the temperature dependence of the paramagnetic moment.

# Summary in Questions 2

9. Write down the Pauli matrices.

10. Calculate the squares of the Pauli matrices.

11. Sketch the possible orientations of the spin vector.

12. Which quantum numbers describe the spin of the electron and which numerical values do these quantum numbers have?

13. Explain the Dirac notation for quantum states.

14. Write down the eigenvalue equations for the spin in Dirac notation.

15. Use the Dirac notation to write down the eigenvalue equations of the orbital angular momentum.

# Summary in Questions 3

16. What is meant by spin-orbit coupling?

17. Write down the Hamilton operator of the spin-orbit coupling.

18. Why does the strength of the spin-orbit coupling increase strongly with the atomic number?

19. Why does the strength of the spin-orbit coupling decrease with increasing principal quantum number?

20. Give the magnetic moment due to the orbit of the electron.

21. Give the magnetic moment due to the spin of the electron.

22. Explain why spin and orbital angular momentum align antiparallel.