Atoms

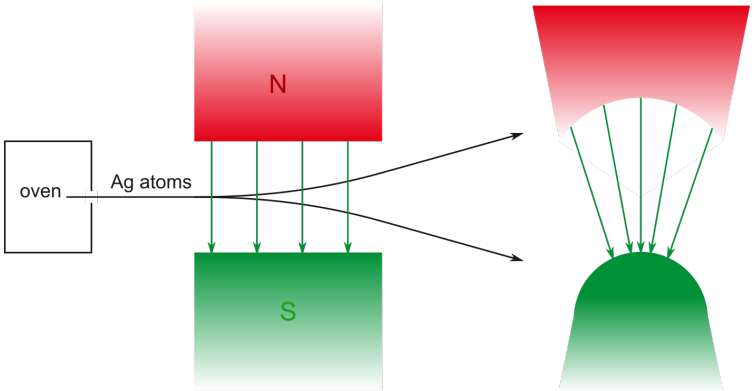
Stern-Gerlach-Exp.

Quantum mechanics

- 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
- Autler-Townes splitting

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 result of Bohr's theory of the atom is that the angular momentum of the electrons is quantized in units of $\hbar$.

This emerges from comparing Bohr's theory with the results of optical spectroscopy of the hydrogen atom.

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.

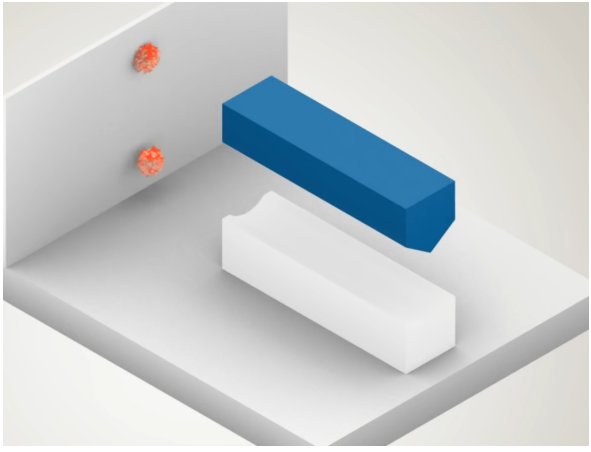
The figure shows a sketch of the famous experiment.

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 polepieces of the magnet.

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

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

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. $\mu_z = |\vec{\mu}| \cos\theta$, and a beam splitting is not expected at all.
- A beam of silver atoms is split into two components.

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

e.g. $F_x = \mu_x \partial_x B_x + \mu_y \partial_x B_y + \mu_z \partial_x B_z$. With 4th Maxwell-equation without current and without a dynamic electric field, i.e. $\nabla \times \vec{B} = 0$ or explicitly $\partial_x B_y = \partial_y B_x$ and $\partial_x B_z = \partial_z B_x$ one finds the red underlined equation.

The formula is simplified if the magnetic field is only aligned along the z-direction and only the partial derivative of the magnetic field for 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.

Stern-Gerlach experiment 3

Comment 2

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

The twofold splitting of the atom beam shows directly that there is a twofold quantization for the magnetic moment of the silver atoms.

In fact, it has long been suspected that the electron must have a magnetic moment and that this moment has a twofold direction quantization.

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 has a twofold quantum number.

However, these findings raised many questions.

The direction quantization of angular momentum and magnetic moment has been shown experimentally, but the reason for this was not known.

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 Bohr's magneton μ_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

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Spin of the electron 1

relativistic energy-momentum relation

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

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

and

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

Klein-Gordon equation

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

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 β must meet the conditions

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

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

Spin of the electron 2

Comment 1

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 α_i and β are 4×4 matrices that meet the conditions outlined in red.

These matrices are formed by the Pauli matrices (next slide)

$$\alpha_{i=x,y,z} = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}.$$

Spin of the electron 2

Comment 2

This leads to a lot of math.

However, few conclusions from Dirac's theory are really important unless one wants to become a specialist in relativistic quantum mechanics.

Spin of the electron 3

Pauli matrices

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

spin operator of the electron

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

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.

The underlined equation gives the operator of the spin.

The Pauli matrices multiplied by $\hbar/2$ are the components of the spin operator.

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

The spin operator does not act on spatial coordinates and therefore has nothing to do with an electrically charged rotating sphere.

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 operator

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

eigenvalue equations of $\hat{s}_z$

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

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

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 an 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 operator 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 operator

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

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

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

quantum numbers of the spin operator

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

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

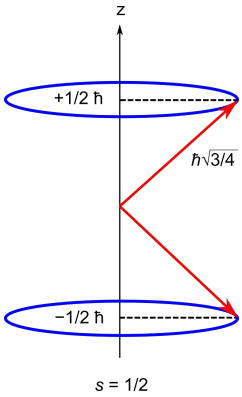
$$s = \frac{1}{2} \quad \text{and} \quad m_s = \pm\frac{1}{2}$$

magnetic moment of the electron

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

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, i.e. when solving the time-dependent Schrödinger equation.

Experiment and theory match perfectly.

Dirac notation

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Dirac notation 1

Dirac notation for quantum states

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

spin eigenstates

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

orbital angular momentum eigenstates

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

eigenstate of the hydrogen atom

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

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

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

eigenvalue equation of the orbital angular momentum with the Dirac notation

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

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

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 of $\psi_{n,\ell,m}(\vec{r},t) = R_{n,\ell}(r)Y_{\ell,m}(\theta,\varphi)e^{-iE_n t/\hbar} \rightarrow |n,\ell,m\rangle$)

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

normalization of the wave function

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

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 **bra**c**ket** 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

$$\langle x \rangle = \langle n,\ell,m|\, x\, |n,\ell,m\rangle$$

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

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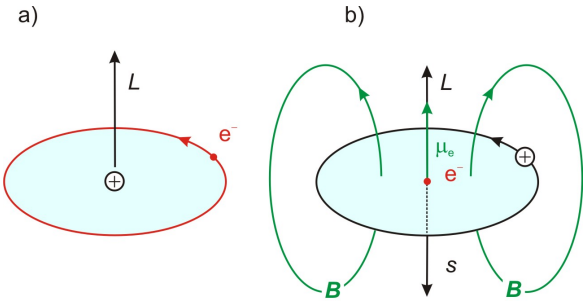
Spin-orbit coupling 1

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 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 1

Comment 2

The potential energy of the magnetic moment of the electron in this magnetic field 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 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

$$B = \mu_0 \frac{Z\mu_B}{2\pi r^3} \frac{L}{\hbar}$$

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 μ_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

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

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

Hamilton operator of the spin-orbit coupling

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

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 ξ 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

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

estimation with the Bohr radius

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

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

Spin-orbit coupling 4

Comment

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

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. Write down the Pauli matrices.
2. Calculate the squares of the Pauli matrices.
3. Sketch the possible orientations of the spin vector.
4. Which quantum numbers describe the spin of the electron and which numerical values do these quantum numbers have?
5. Explain the Dirac notation for quantum states.
6. Write down the eigenvalue equations for the spin in Dirac notation.

Summary in Questions 2

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

8. What is meant by spin-orbit coupling?

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

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

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

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

Summary in Questions 3

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

14. Explain why the interaction energy of the spin-orbit coupling is smallest when the orbital angular momentum and the spin are aligned antiparallel.