5: Spin and the fine structure

Objectives

In this chapter we recall the experimental evidences of the existence of spin in atomic physics. Spin is a genuinely quantum-mechanical concept, despite the term spin being reminiscent of classical spinning.

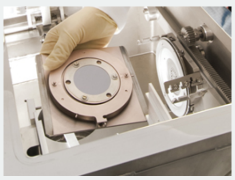
The fine structure of the spectrum was observed already in the beginning of the 20th century, but to explain it's origin theoretically, a relativistic treatment of the electron was necessary.

Prerequisites

Magnetic moment and its connection with angular momentum. The force and energy of a current loop or a magnetic moment in an external magnetic field. Chapter 3.

The Stern-Gerlach Experiment and the spin

Animation



This webpage offers a two word explanation of spin. Check out the spin tab with an animated video showing basic concepts of spin. You can also find some additional information on application of spin in technology.

http://www.toutestquantique.fr

The experiment of Stern and Gerlach, performed in 1921, was intended to look at the magnetic moment of atoms. As it is known, a magnetic momentum arises from current loops, or from charges circulating in a closed orbits, and it is still considered to be true, that a magnetic moment of a particle or a system is always proportional to its angular momentum. The hypothesis that macroscopic magnetism is also a consequence of microscopic circular atomic currents originates from Ampère.

Therefore the experiment was intended to investigate also the angular momentum of the atoms. Stern and Gerlach used silver atoms, that were evaporated from a furnace then after collimating and blending slits they obtained an atomic beam, which passed through an **inhomogeneous magnetic field**. The field of the specially shaped magnets was such that it pointed mainly to one direction, let this be the z direction. Stern and Gerlach experienced that the field caused a splitting of the atomic beam traveling originally say in the yy direction, into two beams, deviating in direction of $\mathbf{z}$ and $-\mathbf{z}$. The silver atoms are electrically neutral, therefore the bending of the atoms could not be attributed to the magnetic Lorentz force, and actually there is no such effect if the magnetic field is homogeneous. The reason of the deviation was that the atoms possessed a magnetic dipole moment, so they behaved like a magnetic needle, or a small coil and therefore the magnetic field acted on them by the force $\mathbf{F}=-\operatorname{grad}(\mathbf{mB})$, which had predominantly a z component $F_z=-\mathfrak{m}_z\frac{\partial B_z}{\partial z}$, as it was known from electromagnetism. We see that $\frac{\partial B_z}{\partial z}\neq 0$ i.e. inhomogeneity is necessary for the force to appear. This force is the reason why the silver atoms deviate from their original direction, and the amount of deviation must be proportional to the z component of the force.

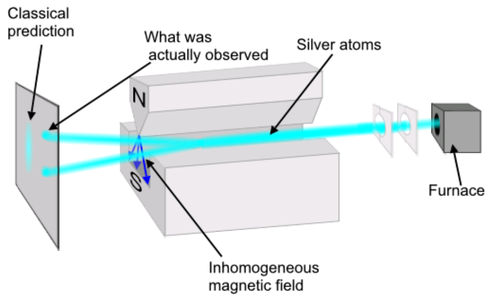
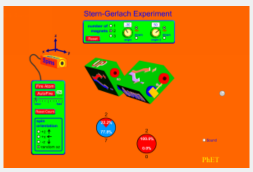


Figure 5.1: Experimental setup of the Stern-Gerlach experiment.
http://en.Wikipedia.org/wiki/File:Stern-Gerlach_experiment.PNG

Animation



The classic Stern-Gerlach Experiment shows that atoms have a property called spin. Spin is a kind of intrinsic angular momentum, which has no classical counterpart. When the z-component of the spin is measured, one always gets one of two values: spin up or spin down.

http://phet.colorado.edu/en/simulation/stern-gerlach

We may think that the different atoms arriving into the interaction region have all possible directions of their magnetic moment, and therefore the atoms deviate in several directions depending on their $\mathfrak{m}_z$, and one obtains a continuous distribution of deviation direction. As this was not the case, and only two definitely distinct directions were observed, this proved that there must have been a kind of quantization of the direction of the magnetic momentum of the atom, and as it was supposed also in the angular momentum of the atom, which was the reason of the magnetism in particles consisting of charged constituents. The quantization of angular momentum was already known to a certain extent, but only an odd number of possibilities was predicted. According to A. Sommerfeld who already extended the old quantum model of Bohr at that time, the quantum number ℓ existed and in case of $\ell = 1$, the three possibilities of the magnetic quantum number: $m = 0, \pm 1$ was expected, instead of the observed two. What was even worse, it was known already from the spectroscopy of Ag, that its ground state is an ss state with $\ell = 0$, so the electron has no orbital angular momentum, and therefore one does not expect magnetic momentum either.

Figure 5.2:

As it turned out a few years later, the splitting was due to a new degree of freedom of atomic particles, namely the spin, which is the intrinsic angular momentum of particles, not connected with their motion in space, rather it is a kind of rotation of the particle itself, like the spinning of a ball. Although there are strong arguments that this simple picture cannot be valid, one can still visualize the spin of a particle in that way. The discovery did come from spectroscopy, S. Goudsmit and G. Uhlenbeck, the young students of P. Ehrenfest in Leiden recognized in 1926 that the fine spectrum of the H atom can be explained if one assumes that the electron possesses this intrinsic angular momentum, and

$$\mathfrak{m} = \gamma \mathbf{S} \quad (5.1)$$

where $\mathbf{S}$ is the mechanical angular momentum, which – if measured in a certain, say the z direction – can take only the two possible values $\hbar/2$ and $-\hbar/2$. This explained the result of the Stern Gerlach experiment, where only the valence electron has angular momentum, and it is a spin momentum, the angular momenta of all the other electrons add up to zero.

In view of angular momentum theory in quantum mechanics this means that the operator S_z has only two eigenstates and eigenvalues, with $m_s = \frac{1}{2}$, and $m_s = -\frac{1}{2}$, corresponding to the two discrete eigenvalues:

$$S_z \chi^+ = \frac{\hbar}{2} \chi^+, \quad S_z \chi^- = -\frac{\hbar}{2} \chi^- \quad (5.2)$$

The quantum number characterizing the total angular momentum (corresponding to ℓ) is denoted here by s, and from the analogy with the theory of angular momentum one obtains that $s = \frac{1}{2}$, as $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$, and for the eigenvalue of $\mathbf{S}^2$ we have $s(s+1)$:

$$\mathbf{S}^2 \chi^\pm = \hbar^2 s(s+1) \chi^\pm = \hbar^2 \frac{3}{4} \chi^\pm \quad (5.3)$$

Einstein de Haas experiment

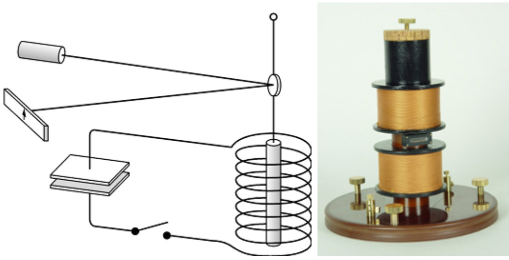


Figure 5.3: Schematic and the real setup of the Einstein-de-Haas experiment.
http://www.techniklexikon.net/d/einstein-de-haas-versuch/einstein-de-haas-versuch.htm
http://www.histodid.uni-oldenburg.de/forschung/aktuelles.htm

This was the only experiment performed by A. Einstein, and he did it in collaboration with W. J. de Haas in 1914. In the apparatus, a cylindrical iron rod was suspended on a torsion thread. Magnetization of the rod was achieved by a coil surrounding the rod with current in. Letting the current through the coil caused the cylinder to rotate by some small angle. The rotation was measured by light reflection from a mirror fixed to the sample. The effect can be explained theoretically by the fact that the magnetic moments of the atoms of the iron, being oriented in the direction of the external magnetic field, cause a change in the atomic mechanical moments – the magnetic moment *M* of an atom is proportional to the resultant angular momentum *J*, that is, $M = \gamma J$, where γ is the gyromagnetic ratio. On the basis of the law of the conservation of angular momentum, the total angular momentum of a body must remain unchanged, and upon magnetization the body therefore acquires an angular impulse (very small in magnitude) that is inverse with respect to the axis of magnetization.

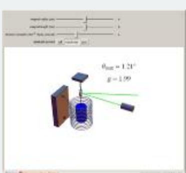
As we know now that the orbital angular momentum of the electrons in iron is zero, the reason is spin. As it is known from classical electrodynamics, in the case of a circular currents the coefficient between the magnetic and angular momentum is

$$\mathfrak{m} = \frac{q}{2m}\mathbf{L} \quad (5.4)$$

Interestingly in the case of spin angular momentum the coefficient giving the magnetic moment is twice

$$\mathfrak{m} = \frac{q}{m}\mathbf{S} \quad (5.5)$$

Animation



Einstein had long contemplated Ampère’s conjecture in 1820 that magnetism is caused by circulation of electric charge. This Demonstration describes a technologically updated version of the original Einstein–de Haas experiment. The current is large enough to create a magnetic field strong enough to saturate the cylinder’s magnetization in either direction. If Ampère was right, this should create an angular displacement of the magnet.

http://demonstrations.wolfram.com/EinsteinDeHaasEffect/

Spin orbit coupling and fine structure

The derivation of the energy levels for the Coulomb potential was based on the Schrödinger equation, which did not contain spin. In reality, there exist small corrections to the level structure, due to the so called spin-orbit coupling. This leads to a fine structure of the spectrum, which could be observed already in the beginning of the 20th century before the advent of modern quantum mechanics. The exact formulation of how the spin and angular momenta are coupled to each other is a difficult mathematical problem, and it necessitates a relativistic treatment of the electron. Therefore we explain here this effect by hand-waving arguments.

In the coordinate system of the electron circulating around the nucleus the proton is moving around the electron therefore in addition to the electric field there must be also a magnetic field. According to the Biot-Savart law, or more generally from Ampère’s law $(\operatorname{rot} \mathbf{B} = \mu_0 \mathbf{J})$ the field emerging from the motion of the proton is

$$\mathbf{B}=\frac{\mu_0}{4\pi}\frac{Zq_0}{m_0}\frac{\mathbf{L}}{r^3} \quad (5.6)$$

This magnetic field also interacts with the intrinsic magnetic moment of the electron, stemming from its spin, and causes an additional energy shift $\Delta E=-\mathfrak{m}\mathbf{B}=\frac{\mu_0}{4\pi}\frac{Zq_0^2}{m_0}\frac{\mathbf{s}\cdot\mathbf{L}}{r^3}$. Going back to the laboratory frame, the rest frame of the proton, an additional factor of $1/2$ arises this is due to an effect called Thomas precession, and it's reason is the **circular** motion of the two frames with respect to each other. The result of spin-orbit interaction is an energy shift

$$\Delta E=-\mathfrak{m}\mathbf{B}=\frac{\mu_0}{4\pi}\frac{Zq_0^2}{2m_0}\frac{\mathbf{S}\cdot\mathbf{L}}{r^3}=\frac{Ze_0^2}{2m_0c^2}\frac{\mathbf{S}\cdot\mathbf{L}}{r^3} \quad (5.7)$$

where the last equality comes from the definition $e_0^2=q_0^2/4\pi\epsilon_0$ and $\epsilon_0\mu_0=c^{-2}$. We note again that this result can be deduced strictly from the relativistic quantum mechanical equation of the electron, the famous Dirac equation, which we will not considered here. The operator product $\mathbf{S}\cdot\mathbf{L}$ can be calculated as follows. First, one defines the total angular momentum:

$$\mathbf{J}=\mathbf{L}+\mathbf{S} \quad (5.8)$$

which is a conserved quantity in a central field, in contrast to $\mathbf{L}$ or $\mathbf{S}$ separately. We square this sum and obtain

$$\mathbf{J}^2=(\mathbf{L}+\mathbf{S})^2=\mathbf{L}^2+\mathbf{S}^2+2\mathbf{LS} \quad (5.9)$$

as $\mathbf{L}$ and $\mathbf{S}$ are commuting operators. Then

$$\mathbf{LS}=\frac{1}{2}\left(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2\right) \quad (5.10)$$

As the eigenvectors of the Hamilton operator are eigenvectors of all the three operators $\mathbf{J}^2$, $\mathbf{L}^2$, and $\mathbf{S}^2$, with the respective eigenvalues $\hbar^2 j(j+1), \hbar^2 l(l+1), \hbar^2 s(s+1)$, the energy correction due to the spin orbit interaction is

$$\Delta E=\frac{\beta}{2}(j(j+1)-l(l+1)-s(s+1)) \quad (5.11)$$

where the spin-orbit coupling strength is given by

$$\beta=\frac{Ze_0^2}{2m_0c^2}\frac{\hbar^2}{r^3}=\frac{\mu_0}{4\pi}\frac{Zq_0^2}{2m_0}\frac{\hbar^2}{r^3} \quad (5.12)$$

If we want to find explicitly the effect of this term we have to calculate its expectation value in a state ψ_{nlm}. In order to do so, we have to calculate the following integral with the eigenfunctions $\psi_{nlm}(\mathbf{r})=\frac{u_{nl}(r)}{r}Y_\ell^m(\theta,\phi)$

$$\int\psi_{nlm}^*(\mathbf{r})\frac{1}{r^3}\psi_{nlm}(\mathbf{r})d^3\mathbf{r}=\int_0^\infty\frac{u_{nl}^2(r)}{r^2}\frac{1}{r^3}r^2dr=\int_0^\infty\frac{u_{nl}^2(r)}{r^3}dr \quad (5.13)$$

with the radial functions $u_{nl}(r)$ determined in the previous section. The integration with respect to the angular variables gives unity, in view of the normalization of the spherical harmonics. The integration can be done using the properties of the Laguerre polynomials, or by some other tricks and yields the result $\frac{2Z^3}{a_0^3n^3l(l+1)(2l+1)}$ which gives

$$\beta(n,l)=\frac{Z^4e_0^2}{2m_0c^2}\hbar^2\frac{1}{a_0^3n^3l(l+1/2)(l+1)} \quad (5.14)$$

Another contribution to the fine structure of the H atom comes from the relativistic correction to the kinetic energy. In relativity the kinetic energy of a particle is

$$E_{kin}=\sqrt{m_0^2c^4+c^2p^2}-m_0c^2=m_0c^2\sqrt{1+\frac{p^2}{m_0^2c^2}}-m_0c^2\approx\frac{p^2}{2m_0}-\frac{p^4}{8c^2m_0^3} \quad (5.15)$$

where the approximation is valid up to second order in p/m_0c. The first term is the ordinary nonrelativistic kinetic energy, while the second one is the correction. Now – as it is customary in quantum mechanics we – consider this term as an operator, and calculate its expectation value in the $\psi_{nlm}(\mathbf{r})$ states. To this end we apply the operator $P^4=\hbar^4\Delta^2=\hbar^4\nabla^4$ and calculate

$$\Delta E_r=-\frac{\hbar^4}{8c^2m_0^3}\int\psi_{nlm}^*(\mathbf{r})\nabla^4\psi_{nlm}(\mathbf{r})d^3\mathbf{r}=-E_{nr}\frac{Z^2\alpha^2}{n}\left(\frac{3}{4n}-\frac{1}{l+1/2}\right) \quad (5.16)$$

Here α is the **fine structure constant** introduced by A. Sommerfeld

$$\alpha=\frac{q_0^2}{4\pi\epsilon_0}\frac{1}{\hbar c}=\frac{e_0^2}{\hbar c}=7.297\times10^{-3}=\frac{1}{137} \quad (5.17)$$

which is a dimensionless quantity, playing an important role in atomic physics and in quantum electrodynamics.

In order to obtain the total correction one has to add the two terms yielding

$$E_{nj} = E_n \left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \quad (5.18)$$

Importantly the same result is obtained from Dirac's exact relativistic theory in second order in p/m_0c.

As a result the ground state energy of the H atom, where $n = 1$, $j = 1/2$ is lowered by , and a similar shift is valid for all the ss states. Additionally there is a splitting with respect to the nonrelativistic result, causing the fine structure in the observed lines. Namely for a given ll one has two possible *j*-s, $j = l + 1/2$ and $j = l - 1/2$, except for $l = 0$. The splitting between the $2p_{3/2}$ and the $2p_{1/2}$ levels is $\Delta E = 4.6 \times 10^{-6}\mathrm{eV}$. Corresponding to a difference in wave number $\Delta\bar{\nu} = 0.37\ \mathrm{cm}^{-1}$.

Animation

We can investigate the relativistic energy levels for Hydrogen atom with this interactive animation. The fine-structure constant can be conceptually changed from 0 to its actual value, or equivalently the speed of light c from ∞ to 1 (meaning $3 \cdot 10^8\ \mathrm{m/s}$), to show the transition from nonrelativistic to relativistic energies for quantum numbers $n = 1, 2$ and 3.

http://demonstrations.wolfram.com/RelativisticEnergyLevelsForHydrogenAtom/

Hyperfine structure

A more refined spectroscopic investigation revealed that even the fine structure components of the H atom are split into two subcomponents and a similar doublet structure was observed in several other atoms. It turned out, that this splitting was due the interaction of the magnetic moment of the nucleus, and the electrons.

In the case of the H atom the simple picture is the following. The proton has a magnetic moment just like the electron. If the two magnetic momenta are antiparallel, then a magnetic attraction appears so the energy will be lower than for parallel moments. So these two possibilities lead to an extra splitting of the $1s$ ground state, and a smaller splitting of other states, as well.

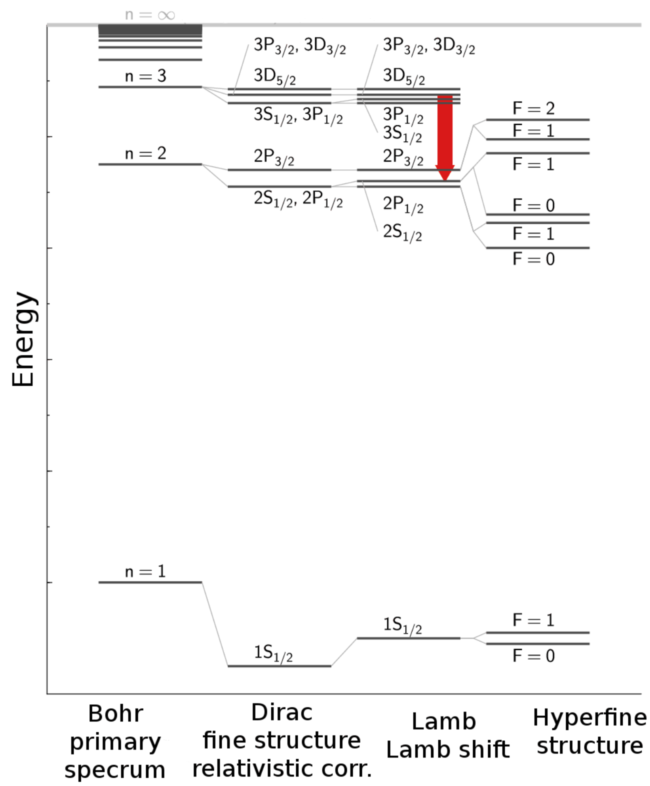


Figure 5.4: The hierarchy of energy shifts of the spectra of hydrogen-like atoms as a result of relativistic corrections. The first column shows the primary spectrum. The second column shows the fine structure from relativistic corrections. The third column includes corrections due quantum electrodynamics and the fourth column includes interaction terms with nuclear spin The H-α line, particularly important in the astronomy, is shown in red