Atoms

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

Hydrogen atom

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

Schrödinger equation of the hydrogen atom 6

radial wave functions

$$\boxed{R_{n,\ell}(r) = f_{n,\ell}(r) \cdot e^{-r/na_B}}$$

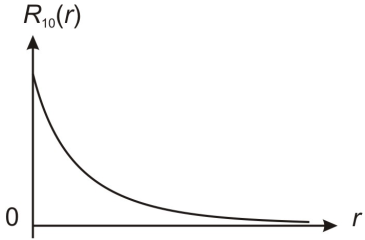
$f_{n,\ell}(r)$ denotes a polynomial which is determined by the quantum numbers n and ℓ

for $n = 1$ and $\ell = 0$ is the radial wave function an exponential function

$$R_{10}(r) \propto e^{-r/a_B}$$

and

$$\boxed{E_1 = -13.6\,\text{eV}}$$



Schrödinger equation of the hydrogen atom 6 Comment 1

Now the radial wave functions have to be considered.

The radial wave function is the product of an exponential function and a polynomial.

This is reminiscent of the harmonic oscillator solution.

The polynomials are well known in mathematics and are called Laguerre polynomials.

The polynomials depend on the quantum number n and ℓ.

The formula outlined in red provides the general solution to the radial Schrödinger equation. It results from the product of a polynomial and an exponential function. The decay length of the exponential is a multiple of Bohr’s radius.

Schrödinger equation of the hydrogen atom 6 Comment 2

The radial wave function of the ground state is a simple exponential function.

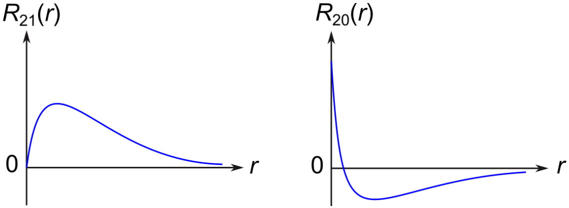
The solution of the Schrödinger equation shows that the decay length of the exponential function is given by the Bohr radius.

The numerical value -13.6 eV results for the energy of the ground state, which agrees perfectly with the experimental result.

Therefore, the principal quantum number takes on the value $n = 1$ and there is no rotational energy i.e. $\ell = 0$.

Schrödinger equation of the hydrogen atom 7

for $n = 2$ there is one s orbital and three p orbitals



$$\underline{R_{21}(r) \propto r\, e^{-r/2a_B}} \quad \text{and} \quad E_2 = -\frac{13.6\,\text{eV}}{2^2}$$

$$\underline{R_{20}(r) \propto \left(1 - \frac{r}{2a_B}\right) e^{-r/2a_B}} \quad \text{and} \quad E_2 = -\frac{13.6\,\text{eV}}{2^2}$$

Schrödinger equation of the hydrogen atom 7 Comment 1

If one increases the angular momentum to $\ell = 1$, one finds a solution of the Schrödinger equation, if one multiplies the exponential function with the distance r between electron and proton.

Due to the centrifugal force the radial wave function vanishes for $r \to 0$.

The first underlined equation gives the result of the calculation.

The decay length of the exponential function is twice the Bohr radius and the energy is equal to $-13.6/2^2$.

This is the energy of the first excited state with the principal quantum number $n = 2$.

$\ell = 1$ denotes a p orbital and there are three eigenfunctions with $m = -1, 0, +1$.

Schrödinger equation of the hydrogen atom 7 Comment 2

If ℓ is reduced to zero for an s-electron, the radial wave function must start at $r = 0$ with a finite value.

Since the energy due to the angular momentum is zero, the energy of the radial movement has to be increased by adding a node to the standing wave.

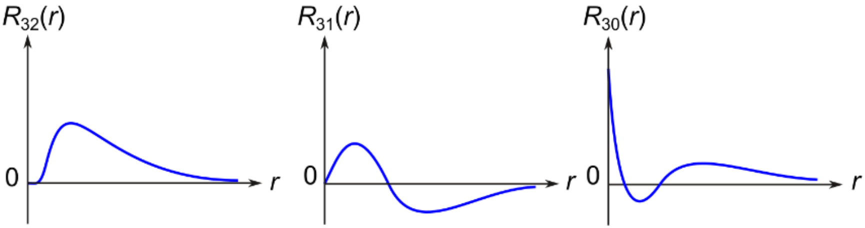
The second underlined equation shows the polynomial that results from solving the Schrödinger equation.

The energy of the s orbital is the same as that of the p orbital, i.e. $E_{\text{n}=2} = -13.6/2^2$ eV.

Both the s- and the p orbital have the same energy.

Schrödinger equation of the hydrogen atom 8

for $n = 3$ there is one s orbital, three p orbitals and five d orbitals



$R_{32}(r) \propto r^2 e^{-r/3a_B}$ and $\boxed{E_3 = -\frac{13.6\,\mathrm{eV}}{3^2}}$

$R_{31}(r) \propto \frac{r}{a_B}\left(1 - \frac{r}{6a_B}\right) e^{-r/3a_B}$ and $R_{30}(r) \propto \left(27 - \frac{18r}{a_B} + \frac{2r^2}{a_B^2}\right) e^{-r/3a_B}$

Schrödinger equation of the hydrogen atom 8 Comment 1

If the angular momentum is increased to $\ell = 2$, one can start with the underlined wave equation.

The exponential function is multiplied by r^2.

The solution of the Schrödinger equation shows that the decay length of the exponential function is given by $3a_\mathrm{B}$.

The formula outlined in red gives the energy of this wave function.

The principal quantum number of this solution is $n = 3$ and the energy of the orbital is $-13.6/3^2$ eV.

Schrödinger equation of the hydrogen atom 8 Comment 2

If ℓ is reduced to 1, the radial energy has to be increased by adding a node.

The radial wave function has to start at zero, since the effective potential for $r \to 0$ becomes strongly repulsive.

The solution of the Schrödinger equation is the wave function R_{31} and the energy is also $-13.6/3^2$ eV.

For the s-electron the radial wave function has to start with a finite value for $r = 0$ and a second node has to be added to increase the radial energy.

The wave function R_{30} is the solution and the energy is also $-13.6/3^2$ eV.

Schrödinger equation of the hydrogen atom 9

probability to find the electron within the volume *dV* is

$$\underline{\psi(\vec{r})\psi(\vec{r})^{*}dV}$$

volume element in spherical coordinates

$$\underline{dV = r^{2}dr\sin\theta d\theta d\varphi}$$

probability when using spherical coordinates

$$\boxed{\psi\psi^{*}dV = r^{2}R_{n,\ell}^{2}dr\cdot Y_{\ell,m}Y_{\ell,m}^{*}\sin\theta d\theta d\varphi}$$

usually $\underline{r^{2}R_{n,\ell}^{2}}$ is plotted

Schrödinger equation of the hydrogen atom 9 Comment

The first underlined equation gives the probability of finding the electron in the volume element dV.

The second underlined equation gives the volume element when spherical coordinates are used.

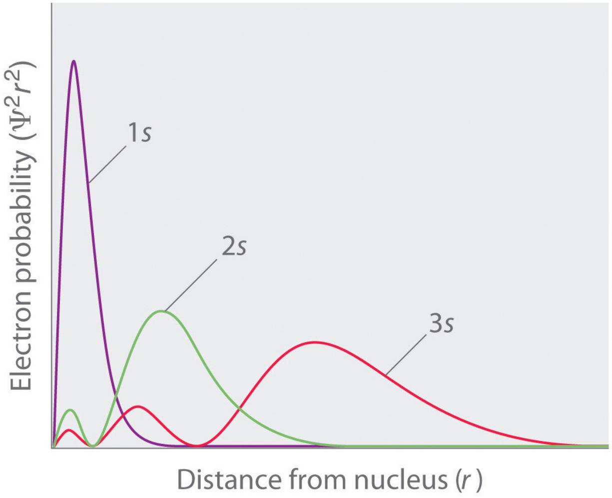
The equation outlined in red gives the probability of finding the electron of the hydrogen atom in the specified volume element.

The part of the formula written in gray gives the probability that the position vector $\vec{r}$ points in the direction determined by the angles θ and φ.

The part of the formula written in blue gives the probability that the distance between the proton and electrons is r.

The last underlined equation gives the radial probability density of the electron.

Schrödinger equation of the hydrogen atom 10

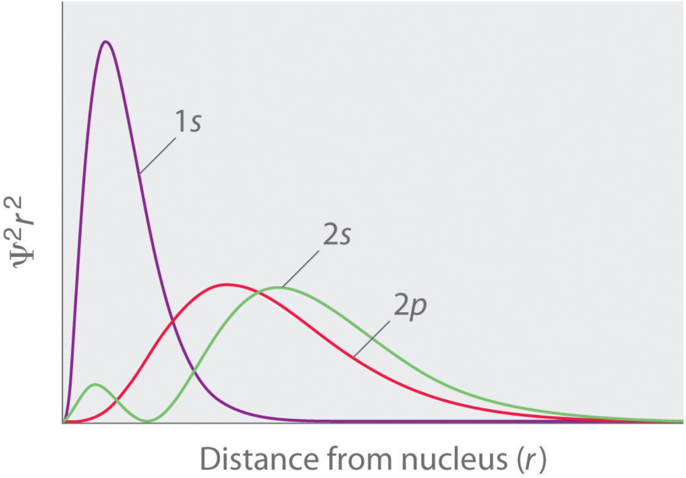


Schrödinger equation of the hydrogen atom 10 Comment

The figure shows the radial probability density of the ground state and the first and second excited s orbital.

The decay length of the exponential function is $1a_B$ for $n = 1$, $2a_B$ for $n = 2$ and $3a_B$ for $n = 3$.

Schrödinger equation of the hydrogen atom 11



Schrödinger equation of the hydrogen atom 11 Comment

The figure compares the radial probability density for the ground state and the s and p orbital of the first excited state.

The maximum of the probability density of the 2s orbital is somewhat shifted to larger *r* values than for the 2p orbital.

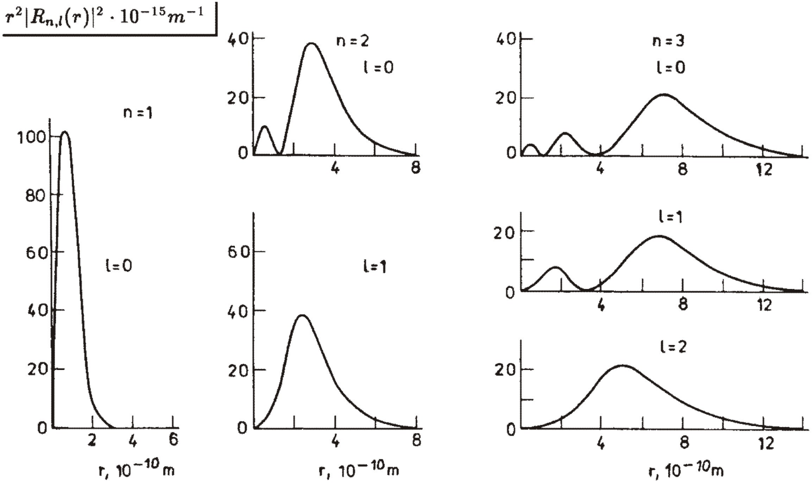
This effect becomes more pronounced with increasing *n* quantum number.

This is shown in the following figure.

In the s orbital, all of the energy is due to the radial movement, while in the other orbitals a fraction of the energy is due to the rotational movement.

The more energy there is in the radial movement, the further the maximum of the wave function shifts away from the atomic nucleus.

Schrödinger equation of the hydrogen atom 12



Schrödinger equation of the hydrogen atom 12 Comment

The figure compares the radial probability density of the ground state and the first and second excited states.

Perhaps it is instructive to compare these results with the prediction of Bohr's model of the atom. The radii of Bohr's orbits are $r_n = a_\mathrm{B} \cdot n^2$.

For $n \geq 2$, the probability of finding the electron is mainly enclosed by the Bohr radius.

Only for $n = 1$ does the maximum of the probability density lie at a value greater than that corresponding to the Bohr radius.

Schrödinger equation of the hydrogen atom 13

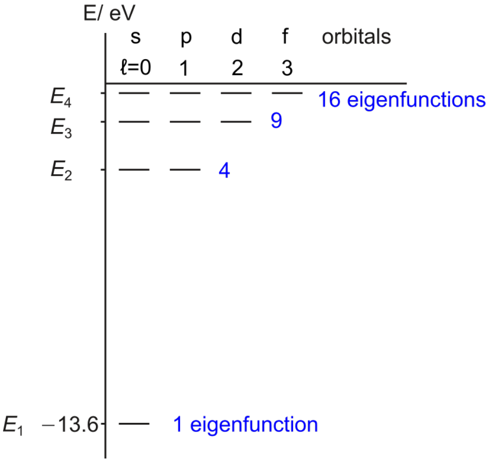
energy eigenvalues:
(in agreement with experiment)

$$\boxed{E_n = -13.6\,\mathrm{eV}\frac{1}{n^2}}$$

and $n = 1, 2, \ldots$

angular momentum

$$\boxed{\ell < n}$$



Schrödinger equation of the hydrogen atom 13 Comment 1

On this page I summarize the results of the Schrödinger equation for the hydrogen atom.

The Hamilton operator contains the kinetic energy of the electron and the potential energy due to the movement in the electric field of the nucleus.

The first equation outlined in red gives the total energy, which is in perfect agreement with the experimental results of Balmer, Lyman, Paschen, etc.

The new information obtained from the Schrödinger equations concerns the angular momentum ℓ of the electron and, above all, the knowledge of the electron wave function.

The figure shows the resulting energy level diagram.

Schrödinger equation of the hydrogen atom 13 Comment 2

There are many more energy levels than would be expected from Bohr’s atomic model.

If these energy levels are shifted slightly, one can quite easily get the energy level scheme of the alkali metals and recognize the energy levels of the side series, the principal series, the diffuse series, and the fourth forth series.

Then it is quite clear that one likes to fall back on the old notation of the energy terms s, p, d, f in order to characterize the quantum number of the orbital angular momentum of the electron.

In contrast to the energy levels of the alkali metals, the energy levels of the hydrogen atom have the same energy with the same principal quantum number. (If you take a closer look, small energy shifts can also be observed in the hydrogen atom.)

Schrödinger equation of the hydrogen atom 13 Comment 3

The reason for this is the $1/r$ dependence of the potential energy of the electron in the electric field of the proton.

In the case of the valence electron of an alkali metal, the electrical potential is not only determined by the nucleus, but also by the shielding of the atomic nucleus by the core electrons and deviates from the $1/r$ dependence.

The energy of the valence electron therefore depends not only on the principal quantum number n but also on the angular momentum quantum number ℓ.

Normal Zeeman

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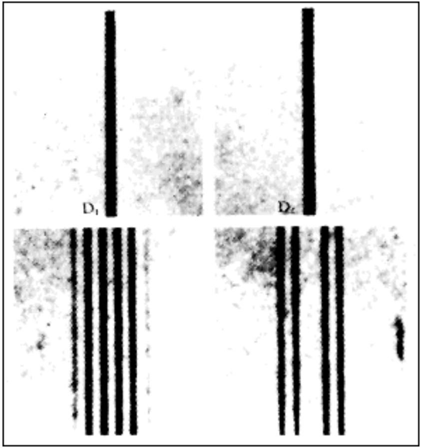
Normal Zeeman effect 1

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.

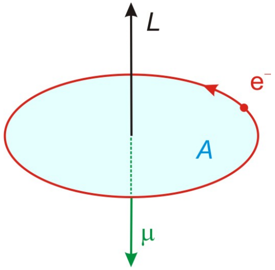
One line is split into six components while the other is split into four components.

The splitting is proportional to the strength of the applied magnetic field.

Normal Zeeman effect 2

the orbital motion of the electron leads to a magnetic moment

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



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

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

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

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 are combined to Bohr's magneton μ_B.

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 $-\mathrm{i}\hbar\nabla$.

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.

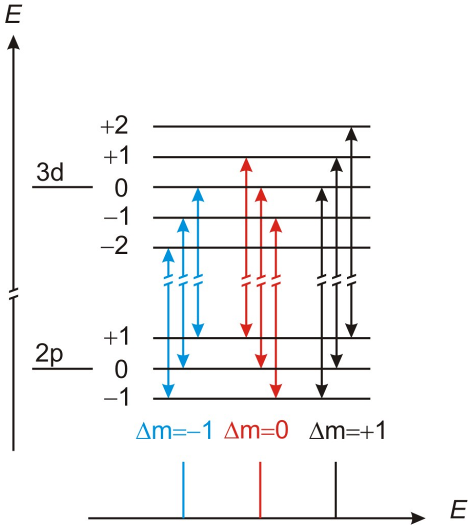
The eigenfunctions are the spherical harmonics.

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



selection rules for electrical dipole transitions

$$\Delta\ell = \pm 1$$

$$\Delta m = 0, \pm 1$$

splitting of the spectral line in 3 components

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

$$\Delta m = 0: \quad \Delta E = 0$$

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

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.

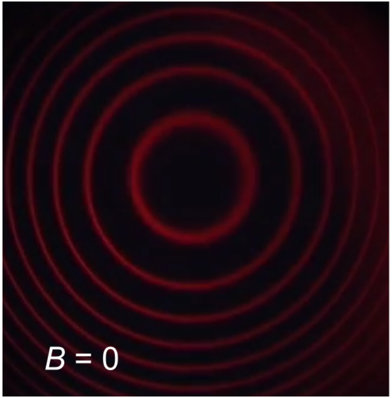
Normal Zeeman effect 5 Comment 3

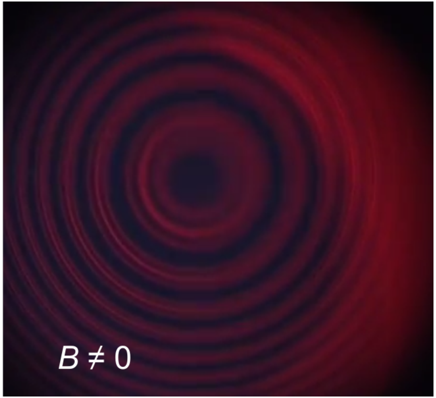
The fact that the electron has a magnetic moment and its own angular momentum was first demonstrated in 1922 with the “Stern-Gerlach experiment”.

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

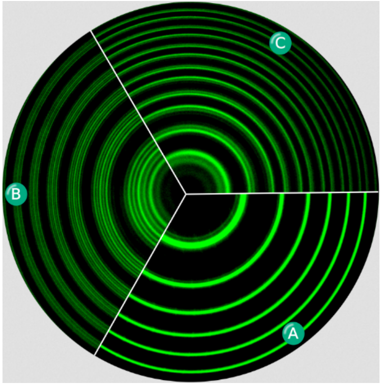
The splitting of spectral lines into three components when a magnetic field is applied can be observed in nature.

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.

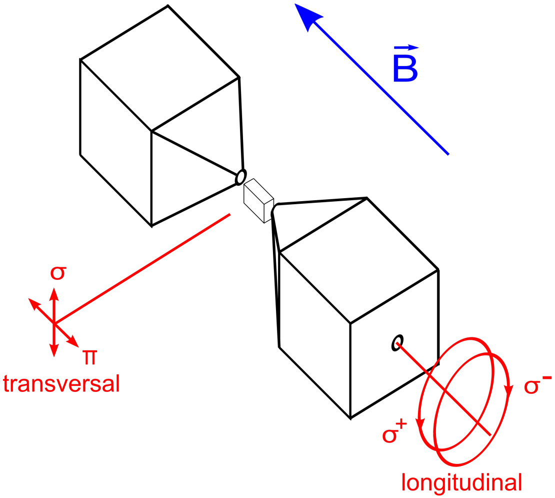
For this purpose, the polarization filter is set so that only light can pass that is polarized perpendicular to the direction of the magnetic field.

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

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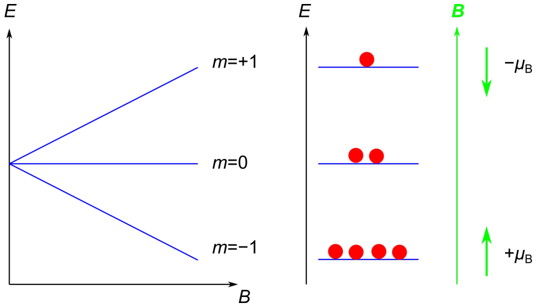
Dia- and paramagnetism 1

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.

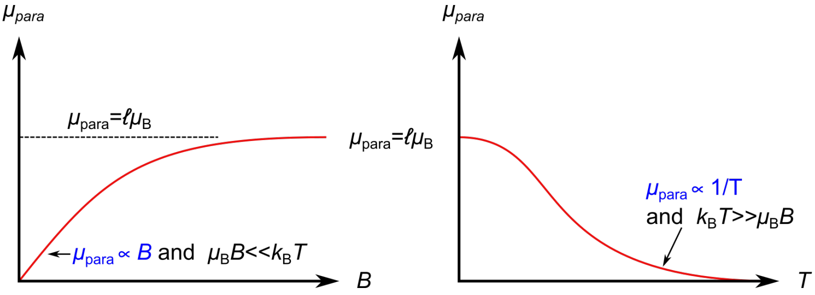
The total magnetic moment of the atoms is obtained by adding up the magnetic moments of all atoms.

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.

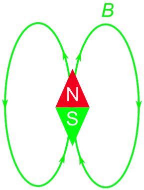
The figure on the right side shows the temperature dependence of the paramagnetic moment.

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.

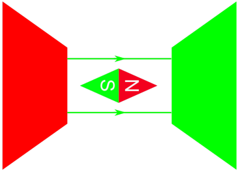
If the thermal energy is much greater than the magnetic energy, the temperature dependence of the paramagnetic moment is given by Curie’s law.

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

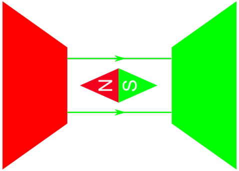
Dia- and paramagnetism 3



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

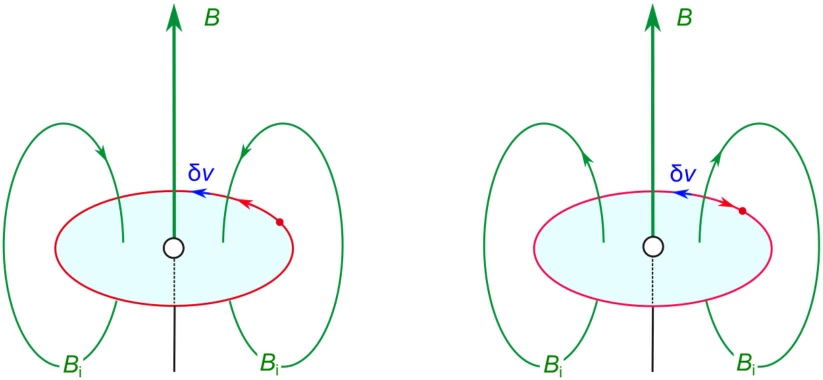
Comment 3

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 through an area 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_i indicate the internal magnetic field of an atom that is caused by the motion of the electron according to Ampere's law.

Rule of the right hand: The thumb points parallel to the speed of the electron. The other fingers point in the opposite direction of the magnetic field due to the negative sign of the charge.

Dia- and paramagnetism 4 Comment 2

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.

In the left figure, the magnetic flux through the area enclosed by the electron orbit 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 δv

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

the change of the centrifugal force due to δv 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 δv is given by the underlined equation.

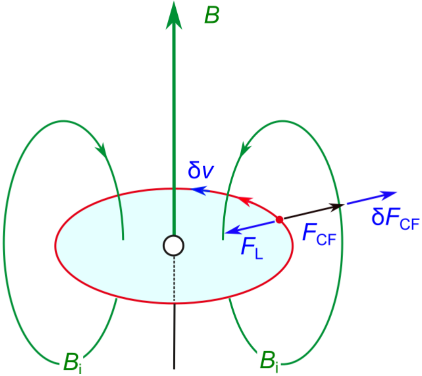
Assuming that the electron's orbit does not change due to the applied magnetic field, the change in centrifugal force must be compensated for by the Lorentz force.

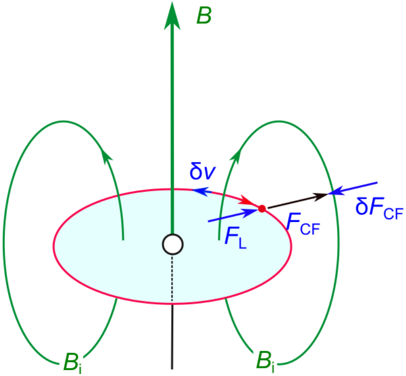
The compensation is illustrated in the following figure.

This effect 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





Dia- and paramagnetism 7

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 7 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 8

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 8 Comment 1

The formula outlined in red shows the exact result for the magnetic moment, although the derivation is anything but exact.

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 8 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.

Revision

Summary in Questions 1

1. Give the quantum numbers which characterize an orbital of the hydrogen atom.
2. Give all quantum number of an orbital with the main quantum number $n = 3$.
3. Sketch the radial wave functions with the quantum numbers $n = 4, \ell = 3$ and $n = 4, \ell = 0$.
4. Give arguments for these plots.
5. Sketch the radial probability density for the quantum numbers $n = 4, \ell = 0$.
6. Show that the wave function e^{-r/a_B} is a solution of the Schrödinger equation of the hydrogen atom.
7. Calculate the numerical value of the corresponding eigenvalue.

Summary in Questions 2

8. Give the Zeeman Hamilton operator.
9. Give the eigenvalue equation of the Zeeman Hamilton operator.
10. Sketch the level-splitting of a p orbital in a magnetic field.
11. Give the magnetic moments of the Zeeman levels.
12. Explain the difference between para- and diamagnetism.
13. Give the paramagnetic moment for $T \to 0$.
14. Give the temperature dependence of the paramagnetic moment when $k_\mathrm{B}T >> \mu_\mathrm{B}B$.