Atoms

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

Hyperfine interaction

Quantum mechanics

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

Hyperfine interaction 1

magnetic moment of proton and neutron

$$\boxed{\vec{\mu}_p = +g_p \mu_N \frac{\vec{I}}{\hbar}} \quad \text{and} \quad \boxed{\vec{\mu}_n = +g_n \mu_N \frac{\vec{I}}{\hbar}}$$

- $\hat{\vec{I}}$ denotes the spin of the nucleons with the quantum numbers $I = 1/2$ and $M_I = \pm 1/2$
- $\mu_\mathrm{N} = \frac{e\hbar}{2m_\mathrm{p}}$ denotes the nuclear magneton

$$\mu_\mathrm{N} = \frac{m_\mathrm{e}}{m_\mathrm{p}}\mu_\mathrm{B} = \frac{0.511\,\mathrm{MeV}}{938.272\,\mathrm{MeV}}\mu_\mathrm{B} = 5.45 \cdot 10^{-4}\,\mu_\mathrm{B} \quad \text{and} \quad \mu_\mathrm{B} = 5.8 \cdot 10^{-5}\,\frac{\mathrm{eV}}{\mathrm{T}}$$

- $g_\mathrm{p} = +5.585694702(17)$ is the g-factor of the proton
- $g_\mathrm{n} = -3.82608545(90)$ is the g-factor of the neutron

most nuclei have a magnetic moment

Hyperfine interaction 1 Comment 1

The magnetic moment of the nucleons, i.e. of the proton and neutron, is, like the magnetic moment of the electron, proportional to the spin.

The spin of the nucleons has the quantum numbers $I = 1/2$ and $M_I = \pm 1/2$.

The formula of the nuclear magneton corresponds to the formula of Bohr's magneton.

The mass of the electron is replaced by the mass of the proton.

The nuclear magneton is therefore much smaller than Bohr's magneton.

In contrast to the electron, the g-factor of the nucleons deviates strongly from the value 2.

Hyperfine interaction 1 Comment 2

The g-factor of the proton is positive and the magnetic moment is aligned parallel to the spin.

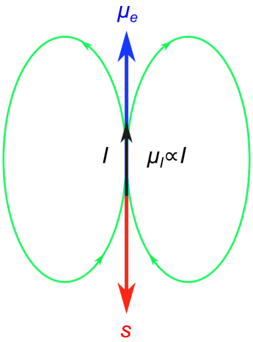
The g-factor of the neutron is negative and the magnetic moment is antiparallel to the spin.

The nucleons consist of many charged particles, which cause the magnetic moment through their motion and their intrinsic magnetic moments.

Since the nucleons are magnetic, it is not surprising that most atomic nuclei also have a magnetic moment.

Hyperfine interaction 2

- the interaction between magnetic moments decreases strongly with distance
- only s electrons reach the atomic nucleus and cause a strong hyperfine interaction



Fermi contact interaction (1930):

hyperfine interaction of s electrons

$$\boxed{\hat{H}_{Is} = A\frac{\hat{\vec{I}}\,\hat{\vec{s}}}{\hbar^2}}$$

constant A for the 1s orbital of the hydrogen $\underline{A = 5.88\,\mu\text{eV}} \rightarrow A/h = 1420\,\text{MHz}$

Hyperfine interaction 2 Comment 1

As long as the atomic nuclei are spherical, the hyperfine interaction is only caused by the magnetic moments of the atomic nucleus and the electrons.

The magnetic dipole interaction between the atomic nucleus and the magnetic moment of the electron spin is proportional to $1/r^3$ and therefore decreases very strongly with the distance.

If the electron has an orbital angular momentum, it is pushed away from the nucleus by centrifugal force and the direct dipole interaction between the magnetic moments of the nucleus and the electron spin is very small.

The interaction between the magnetic moment of the electron orbit and the magnetic moment of the atomic nucleus is also small.

Hyperfine interaction 2

Comment 2

If the electron has no orbital angular momentum, then its orbit runs directly through the atomic nucleus.

The magnetic dipole interaction then becomes very large.

However, this does not lead to an infinitely strong interaction, since the electron is only in the atomic nucleus for a very short time.

At $\approx 10^{-15}$ m, the radius of the atomic nucleus is much smaller than the radius of an s orbital of $\approx 10^{-10}$ m.

This magnetic interaction was investigated by Enrico Fermi in 1930.

In doing so, he found the Hamilton operator outlined in red.

Hyperfine interaction 2

Comment 3

Since the interaction only takes place in the atomic nucleus, it has since been called Fermi contact interaction.

Like the spin-orbit coupling, the Fermi contact interaction is determined by the scalar product of two angular momentum operators.

In the case of spin-orbit coupling, it is the scalar product of spin and orbital angular momentum of the electron.

In the case of the Fermi contact interaction, it is the scalar product of the nuclear and electron spin.

If two electrons occupy an orbital, the magnetic moments of the electrons are aligned antiparallel to one another.

Hyperfine interaction 2 Comment 4

The Fermi contact interaction of the electrons is compensated in this case.

The Fermi contact interaction only occurs when there are unpaired electrons.

The figure illustrates the Fermi contact interaction.

The black arrow shows the magnetic moment of the atomic nucleus, which in most cases is aligned parallel to the nuclear spin.

The green lines indicate the magnetic field lines that are caused by the nuclear magnetic moment.

The red and blue arrows indicate the electron’s spin and magnetic moment.

Hyperfine interaction 2 Comment 5

In the minimum of the potential energy, the magnetic moment of the electron aligns itself parallel to the magnetic field, so that in the ground state the spin of the electron and the spin of the atomic nucleus are aligned antiparallel to each other.

The coupling constant A of the Fermi contact interaction therefore has a positive value.

The last line gives the coupling constant for the hydrogen atom in the ground state.

Hyperfine interaction 3

$$\underline{\hat{H}_{Is} = A\frac{\hat{\vec{I}}\,\hat{\vec{s}}}{\hbar^2}} \quad \rightarrow \quad \text{total spin} \quad \boxed{\vec{F} = \vec{I} + \vec{s}}$$

with the coupled quantum states of the hyperfine interaction $|F, M_F, I, s\rangle$ one can write the eigenvalue equation of the Fermi contact interaction

$$\hat{H}_{Is}\,|F, M_F, I, s\rangle = \frac{A}{2\hbar^2}\left(\hat{\vec{F}}^2 - \hat{\vec{I}}^2 - \hat{\vec{s}}^2\right)|F, M_F, I, s\rangle = E(F, M_F, I, s)\,|F, M_F, I, s\rangle$$

energy eigenvalues

$$E(F, M_F, I, s) = \frac{A}{2}\left(F(F+1) - I(I+1) - s(s+1)\right)$$

hyperfine splitting in the ground state of hydrogen $I = 1/2$, $s = 1/2 \quad \rightarrow \quad F = 0, 1$

$$\underline{\Delta E = E(F=1) - E(F=0) = A} \quad \text{and} \quad A/h = 1420\,\text{MHz}$$

Hyperfine interaction 3 Comment

The Fermi contact interaction couples the nuclear spin with the electron spin to form a total spin, denoted by the letter F.

As with the spin-orbit coupling, the Hamilton operator of the Fermi contact interaction can be transformed in such a way that only the squares of the angular momentum operators appear.

The energy eigenvalues can then easily be written down.

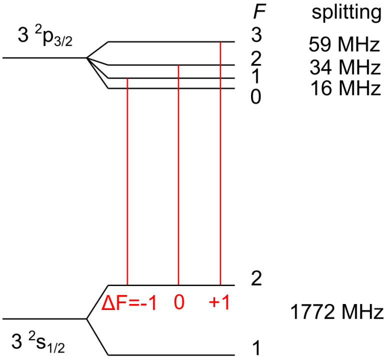
The ground state of the hydrogen atom splits into a hyperfine doublet.

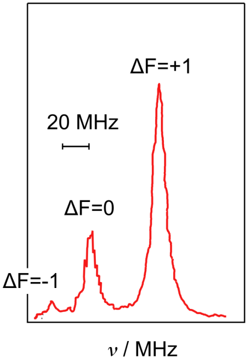
The ground state has the quantum number $F = 0$ and the excited state has the quantum number $F = 1$.

The excitation energy is equal to the coupling constant of the Fermi contact interaction.

Hyperfine interaction 4

hyperfine splitting of the sodium D2 line





Hyperfine interaction 4 Comment 1

The figure shows the hyperfine splitting of the sodium D2 line.

The valence electron in the 3s orbital is excited into the state $3^2\mathrm{p}_{3/2}$ state.

The quantum number of the nuclear spin of the sodium nucleus is $I = 3/2$.

The electron spin and the nuclear spin add in the ground state to the total angular momentum $F = 1, 2$.

Due to the hyperfine interaction, the angular momentum $j = 3/2$ of the electrons in the excited p orbital and the nuclear spin add up to $F = 0, 1, 2, 3$.

The hyperfine splitting of the $3^2\mathrm{s}_{1/2}$ ground state is comparable to the hyperfine splitting of the hydrogen atom.

Hyperfine interaction 4 Comment 2

The hyperfine splitting of the $3^2p_{3/2}$ state is very much smaller, since a p-electron cannot reach the nucleus and there is no direct Fermi-contact interaction.

The measurement of the hyperfine splitting was carried out with a tunable laser aimed at a beam of sodium atoms.

The laser beam is aligned perpendicular to the sodium atom beam in order to avoid the Doppler shift of the spectral lines.

The sodium atoms begin to emit when excited by the laser and the fluorescence is measured as a function of the laser frequency.

Selection rules

Quantum mechanics

- Stern-Gerlach experiment
- Spin of the electron
- Dirac notation
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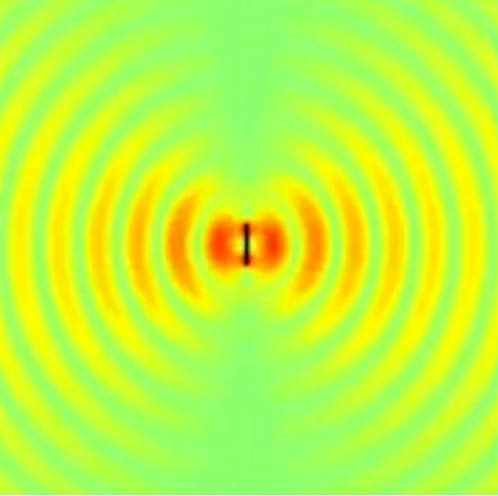
- Selection rules for elm. dipole transitions
- Autler-Townes splitting

Selection rules for elm. dipole transitions 1

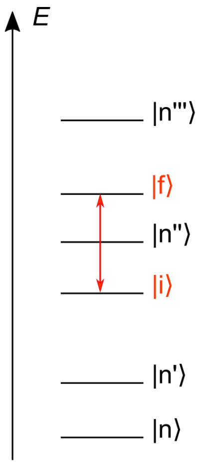


(DipolAntenne.mp4)

Selection rules for elm. dipole transitions 1 Comment

The animation shows again the emission of an electromagnetic wave by a pulsating electric dipole as it can be calculated with the classical theory of Heinrich Hertz (1886).

Selection rules for elm. dipole transitions 2



Paul Dirac (1927): Fermi's golden rule

$$\boxed{W_{i\to f} = \frac{2\pi}{\hbar} |\langle f|\hat{H}'|i\rangle|^2 \rho(E_f)}$$

- $\hat{H}'$: time-independent part of a perturbation operator with sinusoidal time dependence
- $\rho(E_f)$: density of states, i.e. number of quantum states in the energy interval dE

electric dipole radiation $\underline{|\langle f|\hat{H}'|i\rangle|^2 \propto |\vec{E}\langle f|e\vec{r}|i\rangle|^2}$

Selection rules for elm. dipole transitions 2 Comment 1

In quantum physics, photons are emitted or absorbed during the transitions between two quantum states.

The figure shows an energy level scheme with a transition between an initial state $|i\rangle$ and an final state $|f\rangle$.

The transition probability was calculated by Paul Dirac in 1927.

The formula outlined in red shows the result of Paul Dirac’s calculation.

The formula for the transition probability became famous as Fermi’s golden rule.

The transition is caused by a disturbance with a sinusoidal time dependence.

Selection rules for elm. dipole transitions 2 Comment 2

The Hamilton operator $\hat{H}^{'}$ is the time-independent part of the perturbation operator, i.e. all except $\sin(\omega t)$.

The transition probability also depends on the density of states of the final states, i.e. the number of quantum states in the energy interval dE around the energy E_f.

For electric dipole radiation, the transition matrix element $\langle f | \hat{H}^{'} | i \rangle$ is proportional to the amplitude of the electric field of the electromagnetic wave $\vec{E} \sin(\omega t)$ causing the transition and the expectation value of the electric dipole operator $e\vec{r}$.

Fermi's golden rule can be used as long as the energy of the perturbation, i.e. $< \hat{H}' >$, is small compared to the line width $\Delta E = \hbar \Delta \omega$ of the transition.

Selection rules for elm. dipole transitions 3

$$\boxed{\langle f | e\vec{r} | i \rangle}$$

electric dipole moment $\underline{e\vec{r}}$

with $|i\rangle := \varphi_i(\vec{r})$ and $\langle f| := \varphi_f^*(\vec{r})$

$$\underline{\langle f | e\vec{r} | i \rangle := \int_V \varphi_f^*(\vec{r}) e\vec{r} \varphi_i dV}$$

the frequency of the transition equals the frequency of the oscillating electric field

$$\boxed{\omega_{if} = \frac{E_i - E_f}{\hbar} = \frac{E_{if}}{\hbar}}$$

Selection rules for elm. dipole transitions 3 Comment 1

The formula outlined in red shows the matrix element $\langle f \,|\, e\vec{r} \,|\, i \rangle$ for the electric dipole moment $e\vec{r}$ with the Dirac notation.

Under the quantum states $|i\rangle$ and $|f\rangle$ one can imagine, for example, the solutions of the time-independent Schrödinger equation for an atom.

The formula underlined in red shows the integral of the matrix element.

The formula outlined in red indicates the frequency of the transition between the initial state and the final state.

This frequency is also the frequency of the oscillating electric field.

Selection rules for elm. dipole transitions 3 Comment 2

Before starting to calculate the transition probability, it is useful to know whether the matrix element can have a numerical value other than zero.

For this purpose there are selection rules which, depending on the quantum number, indicate whether a transition can take place or whether the transition is forbidden.

Selection rules for elm. dipole transitions 4

$$\boxed{\vec{E}\,\langle f|\,e\vec{r}\,|i\rangle}$$

- maximal transition probability when $\vec{E} \parallel \vec{r}$
- zero transition probability when $\vec{E} \perp \vec{r}$

one can rearrange $\vec{E}\,\vec{r}$ if the atom is in a homogeneous magnetic field

$$\vec{E}\,\vec{r} = E_x x + E_y y + E_z z = \underline{(E_x - iE_y)\frac{1}{2}(x + iy) + (E_x + iE_y)\frac{1}{2}(x - iy) + E_z z}$$

$$= \frac{1}{2}E_x x + \frac{1}{2}E_y y + \frac{i}{2}E_x y - \frac{i}{2}E_y x + \frac{1}{2}E_x x + \frac{1}{2}E_y y - \frac{i}{2}E_x y + \frac{i}{2}E_y x + E_z z$$

Selection rules for elm. dipole transitions 4 Comment 1

The formula outlined in red shows that the polarization of the emitted or absorbed radiation is determined by the electrical dipole moment.

The probability of absorption and emission is maximal when the electric field is polarized parallel to the electric dipole moment, but zero when the electric field and the dipole moment are perpendicular to each other.

It is known that the spectral lines of an atom in the magnetic field split into components that are linearly polarized parallel to the magnetic field and into components that are circularly polarized perpendicular to the magnetic field.

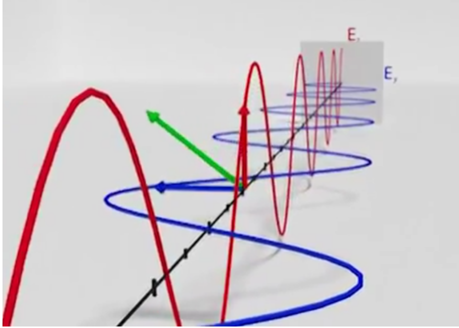
This can be described by transforming the scalar product as shown by the formula underlined in red.

Selection rules for elm. dipole transitions 4 Comment 2

The electric field of the light wave can be split into a linear part that is polarized parallel to the z-axis, and into two circularly polarized light waves perpendicular to the z-axis.

Selection rules for el. dipole transitions 5

$$\vec{E} = \vec{E}_x \pm i\vec{E}_y = (\vec{E}_{0x} \pm i\vec{E}_{0y})e^{i(\vec{k}\vec{r}-\omega t)}$$



(Circularpolarization.mp4)

Selection rules for elm. dipole transitions 5 Comment

The underlined equation gives the wave function of a wave whose electric field is polarized in the xy plane.

The animation shows the effect of a phase shift between the x and y components of the electric field.

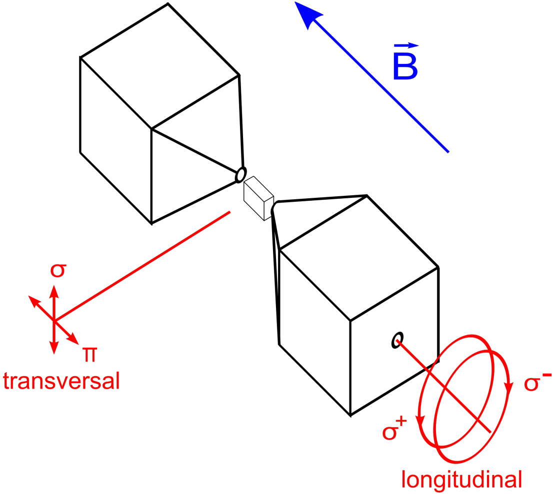
The wave is linearly polarized when the phase shift is 0°.

If the phase shift is 90°, then the wave is circularly polarized.

The decomposition of the scalar product $\vec{E}\vec{r}$ is adapted to the situation of an atom in a magnetic field.

In a crystal lattice, for example, it can make sense to look at $E_x x$, $E_y y$ and $E_z z$ separately.

Selection rules for el. dipole transitions 6



Selection rules for elm. dipole transitions 6 Comment

The illustration shows the Zeeman effect again.

The quantization direction, i.e. the z-direction, is defined by the direction of the magnetic field.

The light is polarized perpendicular to the magnetic field.

However, the light is circularly polarized in the direction of the magnetic field.

Selection rules for el. dipole transitions 7

electric dipole moment and spherical harmonics

$$x + iy = r \sin\theta \cos\varphi + i \sin\theta \sin\varphi = r \sin\theta e^{+i\varphi} \propto rY_{1,+1}(\theta, \varphi)$$

and

$$x - iy = r \sin\theta \cos\varphi - i \sin\theta \sin\varphi = r \sin\theta e^{-i\varphi} \propto rY_{1,-1}(\theta, \varphi)$$

and

$$z = r \cos\theta \propto rY_{10}(\theta, \varphi)$$

$$\boxed{\begin{gathered} E_z z \propto E_z r Y_{1,0} \\ (E_x \mp iE_y)(x \pm iy) \propto (E_x \mp iE_y) r Y_{1,\pm 1} \end{gathered}}$$

Selection rules for elm. dipole transitions 7 Comment 1

The coordinates *x, y, z* can be combined to form spherical harmonics with quantum number $\ell = 1$.

The scalar product of the electric field and the electric dipole moment can be expressed in terms of spherical harmonics.

The formulas outlined in red summarize the results of the conversion.

The first line shows the linear polarization along the z-axis.

This is known as π polarization.

The second line shows the polarization perpendicular to the z-axis.

This is known as σ polarization.

Selection rules for elm. dipole transitions 8

$$\underline{\langle f | e\vec{r} | i \rangle}$$

selection rule for the spin

$$\boxed{\Delta m_s = 0}$$

the electric dipole moment $e\vec{r}$ cannot act on the spin

$$|s, m_s = +1/2\rangle \hat{=} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } |s, m_s = -1/2\rangle \hat{=} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Selection rules for elm. dipole transitions 8 Comment

The essence of the selection rules becomes particularly clear when one considers the electron spin.

The electric dipole moment cannot change the quantum states of the spin, so that the matrix element underlined in red can only deviate from zero if the spin quantum numbers for the initial and final state are the same.

This results in the selection rule outlined in red for the spin quantum number m_s.

Selection rules for elm. dipole transitions 9

$$\underline{\langle f|\, e\vec{r}\,|i\rangle}$$

selection rules with the wave functions of the hydrogen atom

$$\langle f| \hat{=} R_{n',\ell'}(r)Y^*_{\ell',m'}(\theta,\varphi) \quad \text{and} \quad |i\rangle \hat{=} R_{n,\ell}(r)Y_{\ell,m}(\theta,\varphi)$$

$$\underline{\langle f|\, e\vec{r}\,|i\rangle} = e\int R_{n',\ell'}(r)rR_{n,\ell}(r)r^2dr \underline{\int Y^*_{\ell',m'}(\theta,\varphi)Y_{1,0 \text{ or } \pm 1}(\theta,\varphi)Y_{\ell,m}(\theta,\varphi)\sin\theta d\theta d\varphi}$$

mathematical detail $Y_{1,n=0 \text{ or } \pm 1}Y_{\ell,m} = aY_{\ell-1,m+n} + bY_{\ell,m+n} + cY_{\ell+1,m+n}$

orthogonality of spherical harmonics

$$\boxed{\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} Y^*_{\ell',m'}(\theta,\varphi)Y_{\ell,m}(\theta,\varphi)\sin\theta d\theta d\varphi = \delta_{\ell',\ell}\delta_{m',m}}$$

Selection rules for elm. dipole transitions 9 Comment 1

The matrix element of the electric dipole moment for the wave functions of the hydrogen atom or more general for single atomic orbitals is fundamental for all selection rules.

The integral of the matrix element is divided into an integral over the distance r to the center and an integral over the angles θ and φ.

The radial integral is only a prefactor which has to be calculated.

The selection rules for the orbital angular momentum result from the angle-dependent integral.

There is a small mathematical detail that needs to be considered: The product of two spherical harmonics can be written as the sum of spherical harmonics.

Selection rules for elm. dipole transitions 9 Comment 2

The shaded area shows the decomposition of the product $Y_{1,n} Y_{\ell,m}$.

It decomposes into the sum of the spherical harmonics $Y_{\ell-1,n+m}$, $Y_{\ell,n+m}$ and $Y_{\ell+1,n+m}$.

The numbers *a*, *b* and *c* are Clebsch-Gordon coefficients.

(see table of Clebsch-Gordon coefficients https://en.wikipedia.org/wiki/Table_of_Clebsch-Gordan_coefficients)

With the orthogonality relation of the spherical harmonics result the selection rules for the quantum numbers of the orbital angular momentum.

Selection rules for elm. dipole transitions 10

selection rules for the quantum numbers of the orbital angular momentum

- selection rule for the ℓ-quantum number

$$\boxed{\Delta\ell = \pm 1}$$

- selection rule for the m-quantum number

$$\boxed{\Delta m = 0, \pm 1}$$

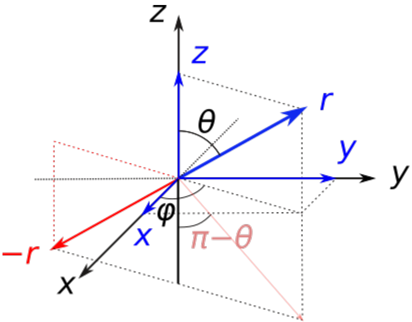
Selection rules for elm. dipole transitions 10 Comment

The matrix element is only different from zero if the quantum numbers ℓ’ equals $\ell \pm 1$ and m’ equals m or $m \pm 1$.

Astonishingly, the matrix elements with $\ell' = \ell$ are always zero.

Selection rules for elm. dipole transitions 11

Inversion (parity)



$\underline{\theta \to \pi - \theta \quad \text{and} \quad \varphi \to \varphi + \pi}$

$$\boxed{Y_{\ell,m}(\pi - \theta, \varphi + \pi) = (-1)^{\ell} Y_{\ell,m}(\theta, \varphi)}$$

selection rule for the ℓ-quantum number

$$\boxed{\Delta\ell = \pm 1}$$

$$\int Y^{*}_{\ell',m'}(\pi - \theta, \varphi + \pi) Y_{\ell=1,m=0,\pm1}(\pi - \theta, \varphi + \pi) Y_{\ell,m}(\pi - \theta, \varphi + \pi) \sin\theta d\theta d\varphi$$

$$= (-1)^{\ell'+1+\ell} \int Y^{*}_{\ell',m'}(\theta, \varphi) Y_{\ell=1,m=0,\pm1}(\theta, \varphi) Y_{\ell,m}(\theta, \varphi) \sin\theta d\theta d\varphi$$

Selection rules for elm. dipole transitions 11 Comment 1

The above discussion is not sufficient for the selection rule of the orbital angular momentum quantum number ℓ.

For the selection rule of the orbital angular momentum quantum number ℓ, the inversion of the coordinate system must also be taken into account.

The figure shows the inversion of the vector $\vec{r}$ when using spherical coordinates.

The vector $\vec{r}$ is first mirrored on the xy-plane and then rotated by 180 ° around the z-axis.

If you insert the corresponding red underlined angles into the spherical harmonic, you get the formula outlined in red.

Selection rules for elm. dipole transitions 11 Comment 2

When inverting the coordinate system, the spherical harmonic must be multiplied by the factor $(-1)^\ell$.

During the inversion, the complex exponential function $e^{im\varphi}$ changes by $(-1)^m$ ($e^{im(\varphi+\pi)} = (-1)^m e^{im\varphi}$) and the polynomial, which is formed from sine and cosine functions, changes by $(-1)^{\ell+m}$.

The last line shows how the inversion of the coordinate system affects the angle-dependent part of the matrix element.

The integrals on both sides of the equation are identical.

The integration over the angle φ is not changed by the addition of π, since the complex exponential function is a periodic function and the integral extends from 0 to 2π.

Selection rules for elm. dipole transitions 11 Comment 3

The integration over the angle θ has to be considered more closely.

With the substitution $y = \pi - \theta$ one has

$$\int_{\theta=0}^{\pi} f(\pi - \theta) \sin \theta d\theta = -\int_{y=\pi}^{0} f(y) \sin y dy = \int_{y=0}^{\pi} f(y) \sin y dy$$

On the left and right side there are the same integrals and the prefactor $(-1)^{\ell'+1+\ell}$ must result in 1 if the integrals should not be zero.

This results in the selection rule outlined in red for the ℓ quantum number.

In the case of an electrical dipole transition, the orbital angular momentum quantum number changes by ± 1.

Selection rules for el. dipole transitions 12

a) Selection rules for a single electron without spin-orbit coupling

the photon carries an intrinsic angular momentum $\pm\hbar$ therefore

$$\boxed{\Delta\ell = \pm 1}$$

π polarization

$$\boxed{\Delta m = 0}$$

σ polarization

$$\boxed{\Delta m = \pm 1}$$

Selection rules for elm. dipole transitions 12 Comment 1

This page summarizes the selection rules for electric dipole radiation for a single electron.

These selection rules are fundamental because one photon is emitted or absorbed with electric dipole radiation, and the matrix element can always be traced back to that of a single electron, even if an atom contains many electrons.

These selection rules become plausible when one considers that the photon has an intrinsic angular momentum of $\hbar$.

When a photon is emitted or absorbed, the angular momentum quantum number must always change by one.

Since the π polarization is related to the spherical harmonics $Y_{1,0}$, the result is the selection rule $\Delta m = 0$.

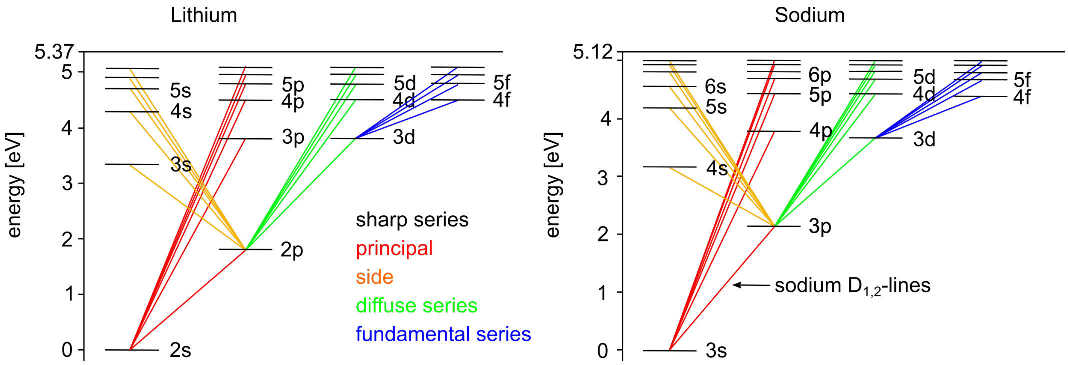
Selection rules for elm. dipole transitions 12 Comment 2

The *m*-quantum number does not change with the π polarization.

The last boxed formula gives the selection rule for σ polarization.

The *m*-quantum number changes by ± 1, since the σ polarization is related to the spherical harmonic $Y_{1,\pm 1}$.

Selection rules for el. dipole transitions 13



Selection rules for elm. dipole transitions 13 Comment

The figure shows once again the energy level scheme of Lithium and Sodium.

The observed series confirm the selection rule $\Delta\ell = \pm 1$.

Selection rules for el. dipole transitions 14

b) Selection rules for a single electron with spin-orbit coupling

the photon carries an angular momentum $\pm\hbar$

$$\boxed{\Delta\ell = \pm 1}$$

quantum number of the total angular momentum j

$$\boxed{\Delta j = 0, \pm 1}$$

π polarisation

$$\boxed{\Delta m_j = 0}$$

σ polarisation

$$\boxed{\Delta m_j = \pm 1}$$

Selection rules for elm. dipole transitions 14 Comment

The spin and the angular momentum of the orbit couple due to the spin-orbit coupling to the total angular momentum j.

The selection rule $\Delta\ell = \pm 1$ remains valid.

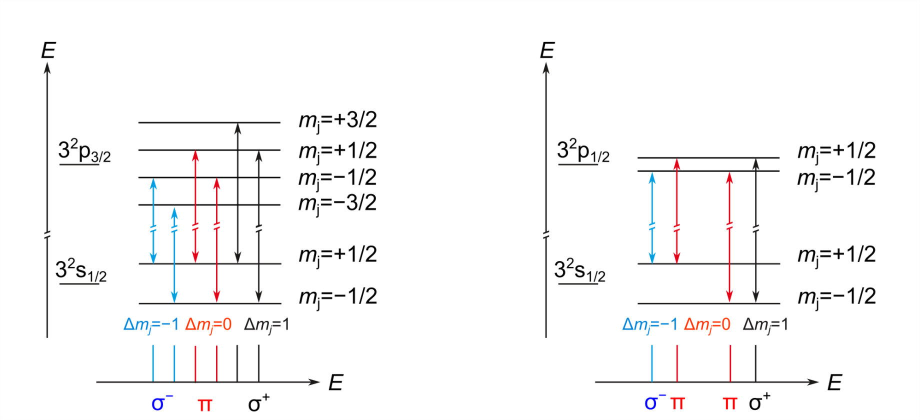
In addition there are the selection rules for to total angular momentum.

For the total angular momentum, the transition with $\Delta j = 0$ is also possible.

The selection rules for the m_j quantum number are $\Delta m_j = 0$ for π polarization and $\Delta m_j = \pm 1$ for σ polarization.

Selection rules for elm. dipole transitions 15

Zeeman effect of the Sodium D lines



Selection rules for elm. dipole transitions 15 Comment 1

To illustrate these selection rules the figure shows again the Zeeman effect of the Sodium D-lines.

The left figure shows the selection rule $\Delta j = \pm 1$ and the right figure the selection rule $\Delta j = 0$.

The colours indicate the σ^+, σ^- and π polarisation of the transitions according to the $\Delta m_j = \pm 1, 0$ selection rule.

Selection rules for elm. dipole transitions 15 Comment 2

In the following some transitions are to be considered in more detail.

First, let's look at the transition $|^2\mathrm{s}_{1/2}, \mathrm{m_j} = +1/2\rangle \rightarrow |^2\mathrm{p}_{3/2}, \mathrm{m_j} = +3/2\rangle$.

The wave functions are

$$|^2\mathrm{s}_{1/2}, \mathrm{m_j} = +1/2\rangle \hat{=} Y_{00} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|^2\mathrm{p}_{3/2}, \mathrm{m_j} = +3/2\rangle \hat{=} Y_{11} \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

Between these quantum states only the component Y_{1-1} of the electric dipole operator is possible (σ^+ polarization) and the matrix element is proportional to

$$\int Y^*_{0,0} Y_{1,-1} Y_{1,+1} \sin\theta d\theta d\varphi.$$

Selection rules for elm. dipole transitions 15 Comment 3

Second, consider the transition $|^2s_{1/2}, m_j = +1/2\rangle \rightarrow |^2p_{1/2}, m_j = +1/2\rangle$.

The wave functions are

$$|^2s_{1/2}, m_j = +1/2\rangle \hat{=} Y_{00} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|^2p_{1/2}, m_j = +1/2\rangle \hat{=} \sqrt{2/3} Y_{1,1} \begin{pmatrix} 0 \\ 1 \end{pmatrix} - \sqrt{1/3} Y_{1,0} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

(see table of Clebsch-Gordon coefficients https://en.wikipedia.org/wiki/Table_of_Clebsch-Gordan_coefficients)

Between these quantum states only the component Y_{10} of the electric dipole operator is possible (π polarization) and the matrix element is proportional to

$$\sqrt{1/3} \int Y^*_{0,0} Y_{1,0} Y_{1,0} \sin\theta d\theta d\varphi.$$

Selection rules for el. dipole transitions 16

c) Selection rules for electron configurations with many electrons

Parity

$$\underline{\sum_{\text{n}} \ell_{\text{n}}^{(\text{i})} - \sum_{\text{n}} \ell_{\text{n}}^{(\text{f})} = \pm 1}$$

selection rules for quantum numbers of the total angular momentum *J*

$$\boxed{\Delta J = 0, \pm 1} \qquad \text{but not} \qquad \boxed{J = 0 \leftrightarrow J = 0}$$

π polarization

$$\boxed{\Delta M_J = 0}$$

σ polarization

$$\boxed{\Delta M_J = \pm 1}$$

Selection rules for elm. dipole transitions 16 Comment 1

If one considers an atom with many electrons, the orbital angular momentum and the spins of the electrons add up to a total angular momentum of the electron configuration.

The total angular momentum is denoted by the capital letter J.

Since one photon has to be absorbed or emitted in the case of electrical dipole radiation, the most basic selection rule is given by the first underlined equation.

The selection rule states that the sum over the orbital angular momenta of all electrons of the initial and final configuration must differ by one.

In particular, this selection rule states that there can be no electric dipole transitions within an electron configuration.

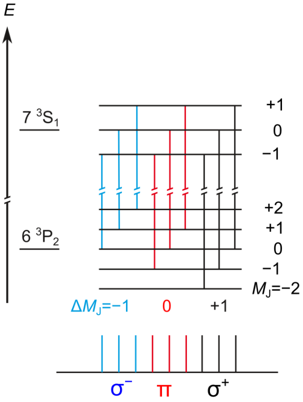
Selection rules for elm. dipole transitions 16 Comment 2

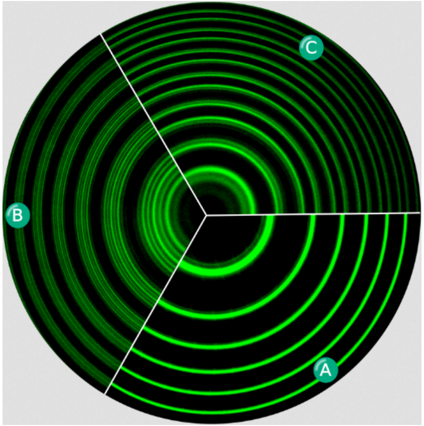
The selection rules for the total angular momentum J are similar to the selection rules for a single electron with spin-orbit coupling.

But there is one big difference:

If the total angular momentum of the initial and final state is zero, no electrical dipole transition is possible.

Selection rules for elm. dipole transitions 17





Selection rules for elm. dipole transitions 17 Comment

As an example for the application of the selection rules, the figure on the left shows the Zeeman effect of the green mercury line again.

The Zeeman effect is observed with a Fabry-Perot interferometer in a transverse configuration.

In area C of the image the lines of π polarization are not visible due to a polarization filter aligned perpendicular to the direction of the magnetic field.

Selection rules for el. dipole transitions 18

d) Additional selection rules if the spin-orbit coupling is negligible

If the atomic number is less than $Z \approx 50$, the influence of the spin-orbit coupling is small. The spins of the electrons add up to the total spin S and the orbital angular momenta of the electrons add up to the total orbital angular momentum L

Parity

$$\underline{\sum_{\mathrm{n}} \ell_{\mathrm{n}}^{(\mathrm{i})} - \sum_{\mathrm{n}} \ell_{\mathrm{n}}^{(\mathrm{f})} = \pm 1}$$

Selection rule for the total spin

$$\boxed{\Delta S = 0}$$

Selection rule of the total orbital angular momentum

$$\boxed{\Delta L = 0, \pm 1} \qquad \text{but not} \qquad \boxed{L = 0 \leftrightarrow L = 0}$$

Selection rules for elm. dipole transitions 18 Comment 1

If the influence of the spin-orbit coupling in an electron configuration with many electrons is small, orbital angular momentum and electron spins add up independently of one another to form a total orbital angular momentum *L* and a total spin *S*.

The first selection rule for the orbital angular momenta of the electrons underlined in red is still valid.

The second selection rule says that the electric dipole moment cannot influence the electron spin.

The spin quantum numbers of the initial and final state must be the same.

Selection rules for elm. dipole transitions 18 Comment 2

The third selection rule is the usual selection rule for the orbital angular momentum.

But there is a small difference to the case of a single electron: If there are many electrons also $\Delta L = 0$ is possible.

However, an electric dipole transition is not possible if the total orbital angular momentum of the initial and final state is zero.

Since the spin-orbit coupling can never be completely neglected, the selection rules for the total angular momentum J remain valid.

Selection rules for el. dipole transitions 19

e) Selection rules for hyperfine splittings

the quantum number of the total angular momentum, which results from the addition of the angular momentum of the electron configuration *J* and the nuclear spin *I*, is denoted by the capital letter *F*.

$\boxed{\Delta F = 0, \pm 1}$ but not $\boxed{F = 0 \leftrightarrow F = 0}$

π polarization

$$\boxed{\Delta M_F = 0}$$

σ polarization

$$\boxed{\Delta M_F = \pm 1}$$

the selection rules $\Delta\ell = \pm 1$ and $\Delta J = 0, \pm 1$ but not $J = 0 \leftrightarrow J = 0$ remain valid

Selection rules for elm. dipole transitions 19 Comment

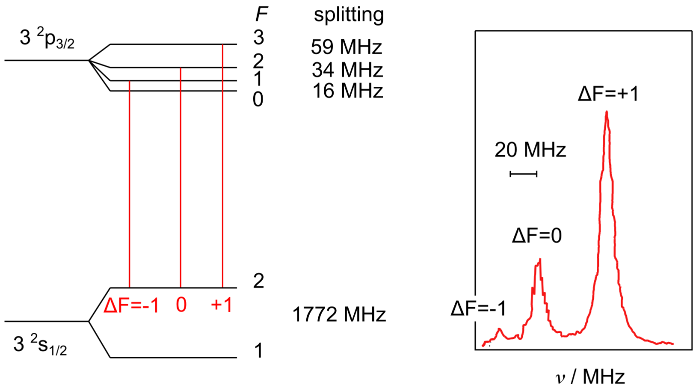
If the nuclear spin is added to the total angular momentum of the electron configuration, the resulting total angular momentum is denoted by the capital letter F.

The selection rules for the hyperfine quantum number F are similar to the selection rule for the total angular momentum of the electron configuration J.

In addition, the selection rules in the previous sections must be met.

Selection rules for elm. dipole transitions 20

hyperfine splitting of the sodium D2 line

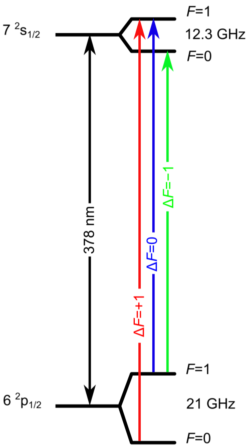


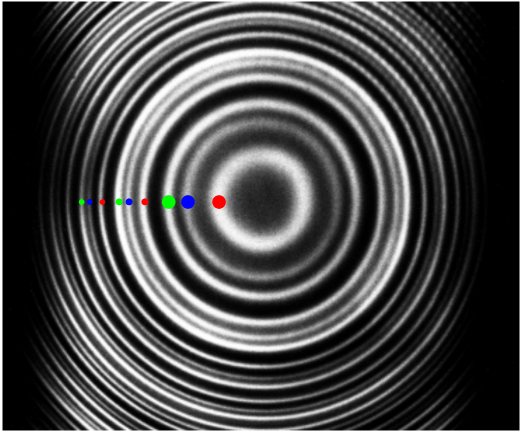
Selection rules for elm. dipole transitions 20 Comment

The hyperfine transitions observed for the sodium D2 line confirm the selection rules discussed above.

Selection rules for elm. dipole transitions 21

Hyperfine splitting Thallium





Selection rules for elm. dipole transitions 21 Comment 1

The energy level diagram shows the excitation of the valence electron of thallium (electron configuration [Xe] $4f^{14}5d^{10}6s^{2}6p^{1}$, see experiment in our lab).

The transitions between the ground state $6\,^2p_{1/2}$ and the excited state $7\,^2s_{1/2}$ obey the selection rules $\Delta j = 0$ and $\Delta\ell = \pm 1$.

The nuclear spin of thallium is 1/2 and the quantum numbers of the total angular momentum are either $F = 0$ or $F = 1$.

The permitted dipole transitions are marked in red, blue and green.

The transition F $= 0 \leftrightarrow F = 0$ is forbidden.

If both the beginning and the end state have no total angular momentum, then no photon can be emitted or absorbed, since the photon has an intrinsic angular momentum of $\hbar$.

Selection rules for elm. dipole transitions 21 Comment 2

The figure shows a recording of the spectral line with a Fabry-Perot interferometer.

The rings show a triplet structure, represented by three dots in red, blue and green according to the transitions shown in the energy level diagram.

The diameter difference of the rings is roughly proportional to the frequency difference $\Delta\nu$ of the spectral lines.

Revision

Summary in Questions

1. Give the magnetic moments of the proton and the neutron.
2. Calculate the ratio between the magnetic moment of the electron and the magnetic moment of the proton.
3. Write down the Hamilton operator of the Fermi contact interaction.
4. Give the selection rule for the ℓ-quantum number.
5. Give the selection rule for the m-quantum number and explain how this quantum number influences the polarization of the radiation.
6. Give the selection rule for the spin quantum numbers.
7. Give the selection rules for the quantum numbers of the total angular momentum.