

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

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

- $\vec{I}$ denotes the spin of the nucleons with the quantum numbers $I = 1/2$ and $M_I = \pm 1/2$
- $\mu_N = \frac{e\hbar}{2m_p}$ denotes the nuclear magneton

$$\mu_N = \frac{m_e}{m_p} \mu_B = \frac{0.511 \text{ MeV}}{938.272 \text{ MeV}} \mu_B = 5.45 \cdot 10^{-4} \mu_B \quad \text{and} \quad \mu_B = 5.8 \cdot 10^{-5} \frac{\text{eV}}{\text{T}}$$

- $g_p = +5.585694702(17)$ is the g-factor of the proton
- $g_n = -3.82608545(90)$ 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.

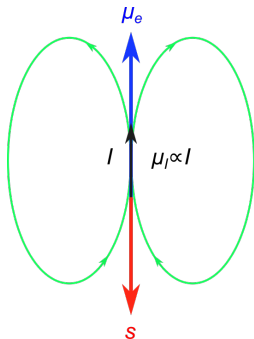
The nucleons consist of many charged particles, which cause the magnetic moment through their motion and their intrinsic magnetic moments.

Although the neutron does not carry an electrical charge, it is formed by charged particles that produce the total spin and magnetic moment of the neutron.

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

$$\hat{H}_{Is} = A \frac{\hat{I} \cdot \hat{S}}{\hbar^2}$$

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

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.

Hyperfine interaction 2

Comment 4

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

$$\hat{H}_{Is} = A \frac{\hat{\vec{I}} \cdot \hat{\vec{S}}}{\hbar^2} \rightarrow \text{total spin } \boxed{\vec{F} = \vec{I} + \vec{S}}$$

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

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

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

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

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.

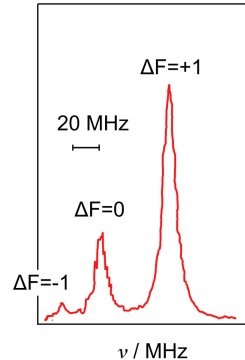
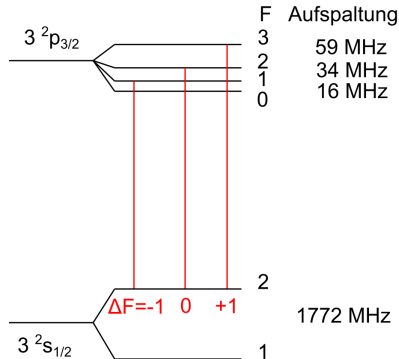
The ground state of the hydrogen atom splits into a hyperfine doublet.

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 $3^2p_{3/2}$ 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 $3^2s_{1/2}$ 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.

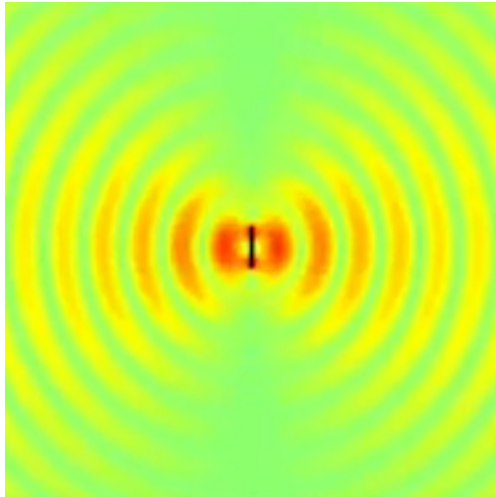
The sodium atoms begin to emit when excited by the laser and the fluorescence is measured as a function of the laser frequency.

Selection rules

Quantum mechanics

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

Selection rules for elm. dipole transitions 1



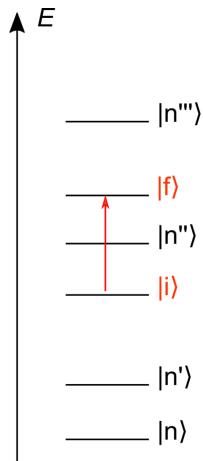
(DipolAntenne.mp4)

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

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

- $\hat{H}'$: time-independent part of a perturbation operator with sinusoidal time dependence
- $\rho(E_{i \rightarrow f})$: density of states, i.e. number of quantum states which contribute to the transition $i \rightarrow f$

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

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, e.g. $\hat{H}' = \vec{d}\vec{E}$ when the complete perturbation is $\vec{d}\vec{E}\sin(\omega t)$.

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 $\vec{d} = e\vec{r}$.

In this case, Fermi's Golden Rule describes the absorption or the stimulated emission (when $E_f < E_i$) of electromagnetic radiation and the rule can be used as long as the energy of the disturbance, i.e. $\langle \hat{H}' \rangle$, is small compared to the natural linewidth $\Delta E = \hbar\Delta\omega$ of the transition caused by spontaneous emission.

The transition probability also depends on the density of states of the final states, i.e. the number of quantum states which are involved in the transition $i \rightarrow f$.

Selection rules for elm. dipole transitions 3

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

electric dipole moment $e\vec{r}$

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

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

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

$$\omega_{i \rightarrow f} = \frac{E_f - E_i}{\hbar} = \frac{E_{i \rightarrow f}}{\hbar}$$

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.

In the range of the uncertainty relation, this frequency must also be the frequency of the oscillating electric field.

Selection rules for elm. dipole transitions 3

Comment 2

Before the transition probability is actually calculated, it is helpful to know whether the transition matrix element is zero or not.

For this purpose there are selection rules which show whether a transition can take place or not.

Selection rules for elm. dipole transitions 4

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

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

it is helpful to rearrange $\vec{E}\vec{r}$

$$\begin{aligned} \vec{E}\vec{r} &= E_x x + E_y y + E_z z = \underbrace{(E_x - iE_y) \frac{1}{2}(x + iy) + (E_x + iE_y) \frac{1}{2}(x - iy) + E_z z}_{\substack{= \frac{1}{2}E_x x + \frac{1}{2}E_y y + \frac{i}{2}E_x y - \frac{i}{2}E_y x + \frac{1}{2}E_x x + \frac{1}{2}E_y y - \frac{i}{2}E_x y + \frac{i}{2}E_y x + E_z z}} \end{aligned}$$

Selection rules for elm. dipole transitions 4

Comment 1

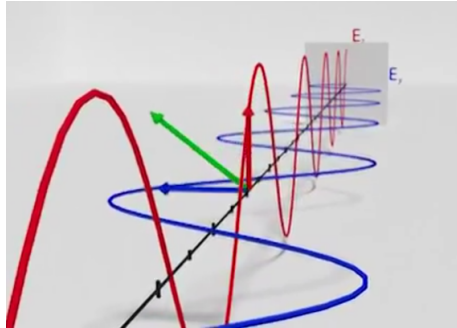
The formula outlined in red shows that the polarization of the emitted or absorbed radiation is determined by the electrical dipole moment.

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.

Since it is known that atoms can absorb and emit circularly polarized electromagnetic waves, it is helpful to rearrange $\vec{E}\vec{r}$ so that the circular polarization of the radiation is present in the formula.

Selection rules for el. dipole transitions 5

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



(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.

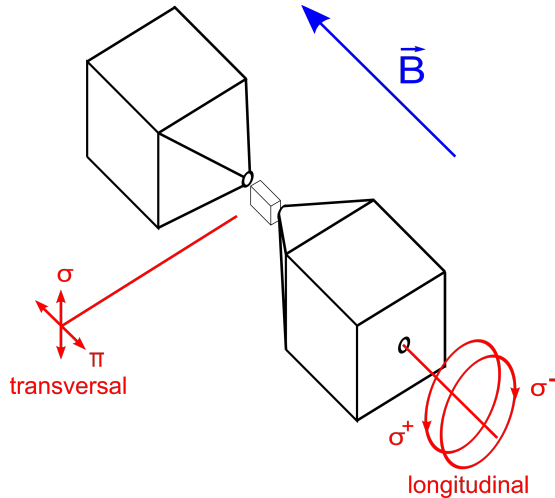
The animation shows the effect of a phase shift between the x and y components of the electric field.

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 or, more generally, for an atom in an axial symmetric field.

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 linearly polarized when observed perpendicular to the magnetic field and circularly polarized when observed along the direction of the magnetic field.

Selection rules for el. dipole transitions 7

electric dipole moment and spherical harmonics

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

and

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

and

$$z = r \cos \theta \propto r Y_{1,0}(\theta, \varphi)$$

$$E_z z \propto E_z r Y_{1,0}$$

$$(E_x \mp iE_y)(x \pm iy) \propto (E_x \mp iE_y) r Y_{1,\pm 1}$$

Selection rules for elm. dipole transitions 7

Comment

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

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

selection rule for the spin

$$\Delta m_s = 0$$

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

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

selection rules with the wave functions of the hydrogen atom

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

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

mathematical detail $Y_{1,n=0 \text{ or } \pm 1} Y_{\ell,m} = a Y_{\ell-1,m+n} + b Y_{\ell,m+n} + c Y_{\ell+1,m+n}$

orthogonality of spherical harmonics

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

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 follow from the angle-dependent integral.

Therefore, the quantum numbers of the angular momenta are important not only to specify the atomic eigenstates but also to characterize the transition probability between the eigenstates.

Selection rules for elm. dipole transitions 9

Comment 2

To evaluate the angle-dependent integral, two mathematical points must be taken into account.

First: The product of two spherical harmonics can be written as the sum of spherical harmonics.

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 $Y_{\ell+1,n+m}$.¹

The decomposition describes the addition of an angular momentum with the quantum number $\ell = 1$ and an angular momentum with the quantum number ℓ .

¹(The numbers a , b and c are Clebsch-Gordan coefficients. Table of Clebsch-Gordan coefficients
https://en.wikipedia.org/wiki/Table_of_Clebsch-Gordan_coefficients)

Selection rules for elm. dipole transitions 9

Comment 3

The product $Y_{1,n}Y_{\ell,m}$ corresponds to a sum of the total momentum states with the quantum numbers $j = \ell - 1$, $j = \ell$ and $j = \ell + 1$.²

Second: The spherical harmonics are orthogonal functions, as indicated by the formula outlined in red.

It is obvious that the integral of the transition probability is non-zero only when the selection rule $\Delta\ell = \ell' - \ell = 0$ or ± 1 is satisfied.

² $\vec{j} = \vec{\ell}_1 + \vec{\ell}_2$ with $\ell_1 = 1$ and $\ell_2 = \ell$

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

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

- but not!

$$\Delta\ell = 0$$

- selection rule for the m -quantum number

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

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.

The physical reason is that the photon always adds or carries away an angular momentum $\hbar$. Therefore ℓ has to change by ± 1 .

(The mathematical reason is the inversion symmetry. When the coordinate system is reversed, the numerical value of the transition integral does not change.

However, the spherical harmonics change according to $Y_{\ell,m} \rightarrow (-1)^{\ell} Y_{\ell,m}$

Selection rules for el. dipole transitions 11

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

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

π polarization

$$\Delta m = 0$$

σ polarization

$$\Delta m = \pm 1$$

Selection rules for elm. dipole transitions 11

Comment

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

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

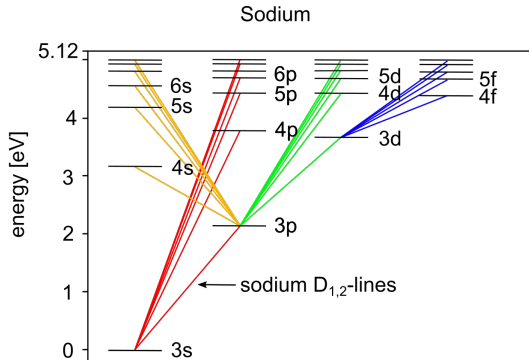
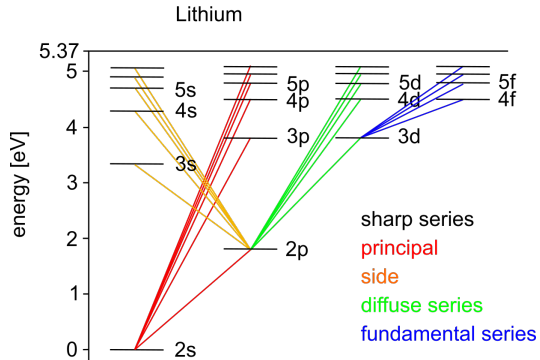
Since the π polarization is related to the spherical harmonics $Y_{1,0}$, the result is the selection rule $\Delta m = 0$.

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 12



Selection rules for elm. dipole transitions 12

Comment

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

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

Selection rules for el. dipole transitions 13

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

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

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

quantum number of the total angular momentum j

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

π polarisation

$$\Delta m_j = 0$$

σ polarisation

$$\Delta m_j = \pm 1$$

Selection rules for elm. dipole transitions 13

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.

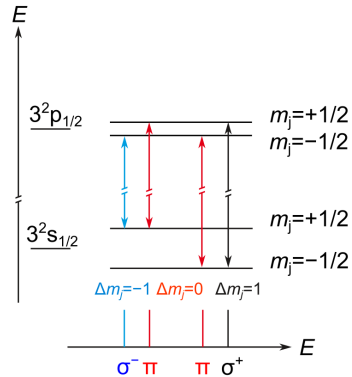
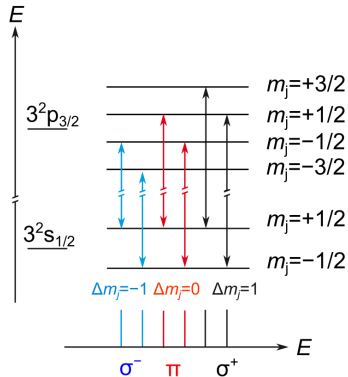
In addition there are the selection rules for total angular momentum.

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 14

Zeeman effect of the Sodium D lines



Selection rules for elm. dipole transitions 14

Comment

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 el. dipole transitions 15

c) Selection rules for electron configurations with many electrons

selection rule for the ℓ quantum numbers

$$\sum_n \ell_n^{(i)} - \sum_n \ell_n^{(f)} = \pm 1$$

selection rules for quantum numbers of the total angular momentum J

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

but not

$$J = 0 \leftrightarrow J = 0$$

π polarization

$$\Delta M_J = 0$$

σ polarization

$$\Delta M_J = \pm 1$$

Selection rules for elm. dipole transitions 15

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 15

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 el. dipole transitions 16

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**

Selection rule for the ℓ quantum numbers

$$\sum_n \ell_n^{(i)} - \sum_n \ell_n^{(f)} = \pm 1$$

Selection rule for the total spin

$$\Delta S = 0$$

Selection rule of the total orbital angular momentum

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

but not

$$L = 0 \leftrightarrow L = 0$$

Selection rules for elm. dipole transitions 16

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 16

Comment 2

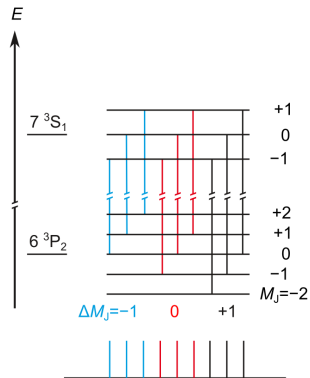
The third selection rule is the usual selection rule for the orbital angular momentum.

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 elm. dipole transitions 17



The green spectral line of Mercury

$$\underline{7^3S_1 [6s^1, 7s^1] \leftrightarrow 6^3P_2 [6s^1, 6p^1] \quad \lambda = 546,1 \text{ nm}}$$

- Parity: $\Delta \ell = \pm 1$
- Spin: $\Delta S = 0$
- Orbit: $\Delta L = \pm 1$
- total angular momentum: $\Delta J = \pm 1$
- magnetic quantum number:
 $\Delta M_J = 0, \pm 1$

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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 transition of the green spectral line of mercury satisfies the selection rules.

However, the atomic number of mercury is $Z = 80$ and the spin-orbit coupling is not small.

Therefore, there are many transitions that only satisfy the selection rules for the total angular momentum J .

Selection rules for el. dipole transitions 18

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 .

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

but not

$$F = 0 \leftrightarrow F = 0$$

π polarization

$$\Delta M_F = 0$$

σ polarization

$$\Delta M_F = \pm 1$$

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 18

Comment

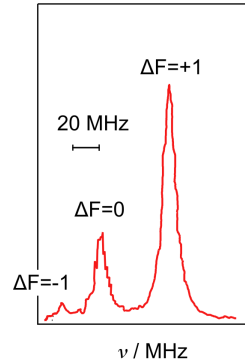
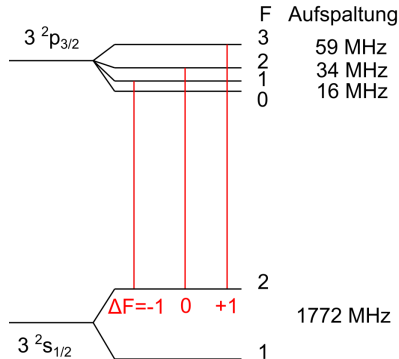
If the nuclear spin is added to the total angular momentum of the electron configuration, the resulting total angular momentum is denoted by the capital letter F .

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.

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hyperfine splitting of the sodium D2 line



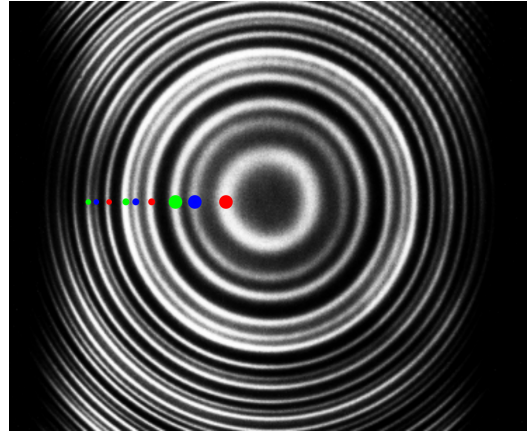
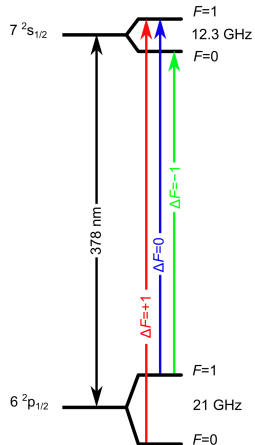
Selection rules for elm. dipole transitions 19

Comment

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

Selection rules for elm. dipole transitions 20

Hyperfine splitting Thallium



Selection rules for elm. dipole transitions 20

Comment 1

The energy level diagram shows the excitation of the valence electron of thallium (electron configuration $[\text{Xe}] 4f^{14}5d^{10}6s^26p^1$, 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 20

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.