

## 21. Time dependent perturbation theory

Next we start to analyse the perturbations when the perturbation operator depends explicitly on time

$$\hat{H}' = \hat{H}'(t) .$$

The total Hamilton operator

$$\hat{H} = \hat{H}_0 + \hat{H}(t)$$

depends now on time and that means that the total energy of a given system is not conserved (see § 26). For that reason there are no energy level changes or splittings, but there appear transitions between different energy levels (radiation or absorption).

**21.1 General solution of Schrödinger equation without perturbation.** At first we analyse the solutions without perturbation. We have eigenvalue problem for  $\hat{H}_0$

$$\hat{H}_0 \psi_n = E_n \psi_n ,$$

and we assume that it is solved. Then the possible energy values are, for example

$$E_1, E_2, \dots$$

and the corresponding stationary eigenfunctions are

$$\psi_1, \psi_2, \dots .$$

The general solution of the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi$$

is an arbitrary linear combination

$$\Psi(\vec{r}, t) = \sum c_n e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) ,$$

where  $c_1, c_2, \dots$  are some constants.

**21.2 General solution for the time dependent perturbation.** Next we assume, that from some moment, for example, from  $t = 0$  to our system starts to act some time dependent perturbation  $\hat{H}'(t)$ . We have to solve the next equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}(t) \Psi ,$$

where

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$$

Since for  $t < 0$  the solution is expressed as an above given linear combination, we start to search the solution in form

$$\Psi(\vec{r}, t) = \sum c_n(t) e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) ,$$

where coefficients  $c_n(t)$  depend on time.

Of course, now we get some differential equation for  $c_n(t)$ . Calculating separately both sides of Schrödinger equation, we have

$$i\hbar \frac{\partial \Psi}{\partial t} = \sum_n e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) (E_n c_n(t) + i\hbar \frac{d c_n(t)}{d t}) ,$$

$$(\hat{H}_0 + \hat{H}'(t)) \Psi = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} (E_n + \hat{H}'(t)) \psi_n(\vec{r}) .$$

Equalizing, we get

$$i\hbar \sum_n \frac{d c_n(t)}{d t} e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} \hat{H}'(t) \psi_n(\vec{r}) .$$

Multiplying from left to  $\psi_m^*(\vec{r})$  and integrating, we get the following equation

$$i\hbar \frac{d c_m(t)}{d t} e^{-\frac{i}{\hbar} E_m t} = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} H'_{mn} ,$$

where

$$H'_{mn} = \int \psi_m^* \hat{H}'(t) \psi_n dV = \langle \psi_m | \hat{H}'(t) | \psi_n \rangle$$

are the matrix elements of perturbation operator (which, of course, now depend on time).

Finally we move the exponent from left to the right side. Denoting

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} ,$$

we write the equations for  $c_m(t)$  in its final form

$$i\hbar \frac{d c_m(t)}{d t} = \sum_n e^{i \omega_{mn} t} H'_{mn} c_n(t) ,$$

where  $m = 1, 2, \dots$

The last system of equations is exact and applicable for all perturbations (small ones and large ones), since we have made no additional restrictions.

**21.3 Small time dependent perturbation.** Next we assume that  $\hat{H}'(t)$  is some small perturbation. We expand coefficients  $c_n(t)$  as series

$$c_n(t) = c_n^0 + c_n^1 + c_n^2 + \dots ,$$

where each next term is of one order of value smaller than the previous one. Small perturbation means, that nonzero matrix elements  $H'_{mn}$  are of the same order of value, as  $c_n^1$ . Substituting coefficients and equating the terms with the same order of value, we get the next equations

$$i\hbar \frac{d c_m^0}{d t} = 0 ,$$

$$i\hbar \frac{d c_m^1}{d t} = \sum_n e^{i\omega_{mn} t} H'_{mn} c_n^0 ,$$

$$i\hbar \frac{d c_m^2}{d t} = \sum_n e^{i\omega_{mn} t} H'_{mn} c_n^1 ,$$

...

From the first equation it follows that

$$c_m^0 = \text{const.}$$

Therefore choosing  $c_m^0$  we are able to calculate step by step other coefficients  $c_n^1$ ,  $c_n^2$ , ... .

**21.4 First order approximation.** At first we start to analyse the situation, when before the perturbation starts to act ( $t < 0$ ) our system was in some stationary state with energy  $E_n$ . Therefore we assume, that

$$c_n^0 = 1 ,$$

and other coefficients  $c_m^0 = 0$  ( $m \neq n$ ).

The equations for the first approximation then are

$$i\hbar \frac{d c_m^1}{d t} = e^{i\omega_{mn} t} H'_{mn} ,$$

and the simple integration gives

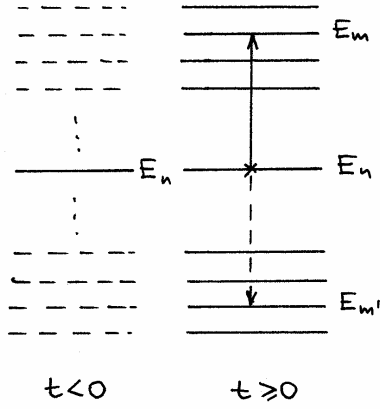
$$c_m^1 = \frac{1}{i\hbar} \int_0^t e^{i\omega_{mn} \tau} H'_{mn} d\tau .$$

Since  $H'_{mn} = H'_{mn}(t)$ , it is not possible to integrate without knowing the exact forms of these matrix elements.

Note! In textbooks the expression, given above, is frequently written as

$$c_m^1 = \frac{1}{i\hbar} \int_0^t e^{i\omega_{mn} t} H'_{mn} d t ,$$

which is mathematically not quite correct (we integrate to  $t$  over the same  $t$ ). Therefore we have denoted the time under the integral by different letter  $\tau$ .



From the above given integrals we get one interesting and important conclusion. If our system is in some stationary state with energy  $E_n$ , then after the time dependent perturbation is applied there open the possibilities for transitions to other states with energies  $E_m$  ( $E_m > E_n$  or  $E_m < E_n$ ) if  $c_m^1 \neq 0$ . The probability of transition  $n \rightarrow m$  depends on  $|c_m^1|^2$ .

**21.5 Harmonic perturbation.** Next we specify the perturbation operator  $\hat{H}'(t)$ . We assume that the perturbation is harmonic with some frequency  $\omega$  (for example, the external electromagnetic wave with frequency  $\omega$  and wavelength  $\lambda$ ) and write  $\hat{H}'(t)$  as

$$\hat{H}'(t) = \hat{h} e^{-i\omega t} + \hat{h}^+ e^{i\omega t},$$

where  $\hat{h}$  is some time independent operator. Matrix elements of our perturbation operator are

$$H'_{mn} = h_{mn} e^{-i\omega t} + h_{mn}^+ e^{i\omega t},$$

where  $h_{mn} = \langle \varphi_m | \hat{h} | \varphi_n \rangle = (h_{nm}^+)^*$ . In order to find  $c_m^1$  one must calculate the integral

$$c_m^1 = \frac{1}{i\hbar} \int_0^t (e^{i(\omega_{mn}-\omega)\tau} h_{mn} + e^{i(\omega_{mn}+\omega)\tau} h_{mn}^+) d\tau.$$

These integrals are quite elementary:

$$\int_0^t e^{i(\omega_{mn} \mp \omega)\tau} d\tau = \frac{e^{i(\omega_{mn} \mp \omega)\tau}}{i(\omega_{mn} \mp \omega)} \Big|_0^t = \frac{e^{i(\omega_{mn} \mp \omega)t} - 1}{i(\omega_{mn} \mp \omega)}.$$

Therefore the final result is

$$c_m^1 = -\frac{1}{\hbar} \left( h_{mn} \frac{e^{i(\omega_{mn}-\omega)t} - 1}{\omega_{mn} - \omega} + h_{mn}^+ \frac{e^{i(\omega_{mn}+\omega)t} - 1}{\omega_{mn} + \omega} \right).$$

Next we start to calculate the probabilities  $|c_m^1|^2$  of transitions  $n \rightarrow m$ , but before it we give some general remarks. Usually the frequency  $\omega$  is quite large (in the visible light case, for example  $\omega \sim 10^{15}$  1/s), and therefore for  $\omega \neq \pm \omega_{mn}$  both summands are very small, but if  $\omega \rightarrow \omega_{mn}$  (and  $\omega_{mn} > 0$ ), the first summand is large and the second summand is small and it should be omitted. Therefore, in that case one may analyse the first summand only. Since  $\omega_{mn} = (E_m - E_n)/\hbar$ , then in the case of  $\omega_{mn} > 0$  there is some induced transition from some low energy level to some

higher energy level and the system absorbs from external radiation one photon with the frequency  $\omega = \omega_{mn}$ . But when  $\omega_{mn} < 0$  we get induced (stimulated) radiation. Now the first summand is small and the second one large. The frequency of external radiation equals to  $\omega = -\omega_{mn}$ .

Next we analyse the absorption of radiation ( $\omega_{mn} > 0$ ). Omitting in  $c_m^1$  the second summand, we have

$$c_m^1 = -\frac{h_{mn}}{\hbar} \frac{e^{i(\omega_{mn}-\omega)t} - 1}{\omega_{mn} - \omega}.$$

The corresponding transition probability is

$$\begin{aligned} |c_m^1|^2 &= \frac{|h_{mn}|^2}{\hbar^2} \frac{(e^{i(\omega_{mn}-\omega)t} - 1)(e^{-i(\omega_{mn}-\omega)t} - 1)}{(\omega_{mn} - \omega)^2} = \frac{2|h_{mn}|^2}{\hbar^2} \frac{(1 - \cos(\omega_{mn} - \omega)t)}{(\omega_{mn} - \omega)^2} = \\ &= \frac{4|h_{mn}|^2}{\hbar^2} \frac{\sin^2 \frac{(\omega_{mn} - \omega)t}{2}}{(\omega_{mn} - \omega)^2}. \end{aligned}$$

Let us analyse the result more closely. Transition probability depends on the modulus square  $|h_{mn}|^2$  of matrix element  $h_{mn}$  and also from the rapidly oscillating function of frequency  $\omega$

$$\frac{\sin^2 \frac{(\omega_{mn} - \omega)t}{2}}{(\omega_{mn} - \omega)^2},$$

which is mainly nonzero near  $\omega = \omega_{mn}$ . Since the perturbation is small, the transition probability becomes essential after longer time intervals (theoretically, if  $t \rightarrow \infty$ ). Next we demonstrate that in the limit  $t \rightarrow \infty$  the transition probability is proportional to time and we have the resonance transition, where  $\omega = \omega_{mn}$ .

To prove it, we use the following definition of  $\delta$ -function

$$\delta(x) = \lim_{A \rightarrow \infty} \frac{\sin^2 Ax}{\pi Ax^2},$$

which in our case gives

$$\lim_{t \rightarrow \infty} \frac{\sin^2 \frac{\omega_{mn} - \omega}{2} t}{\pi \frac{(\omega_{mn} - \omega)^2}{4} t} = \delta\left(\frac{\omega_{mn} - \omega}{2}\right) = 2\delta(\omega_{mn} - \omega).$$

Therefore, for quite long time intervals we have

$$P_{mn} = \lim_{t \rightarrow \infty} |c_m^1|^2 = \frac{2\pi |h_{mn}|^2 t}{\hbar^2} \delta(\omega_{mn} - \omega) .$$

**21.6 Transition probability per unit time.** Since the transition probability is proportional to time, we usually talk about transition probability per unit time

$$\frac{dP_{mn}}{dt} = \frac{2\pi |h_{mn}|^2}{\hbar^2} \delta(\omega_{mn} - \omega) .$$

From here it follows that the transition takes place if frequency  $\omega = \omega_{mn}$ , which is the resonance frequency and the probability is proportional to  $|h_{mn}|^2$  (and it also gives the intensity of corresponding spectral line).

Instead of frequency one must use energy. Then

$$\frac{dP_{mn}}{dt} = \frac{2\pi |h_{mn}|^2}{\hbar} \delta(E_m - E_n - \hbar\omega) ,$$

which means that  $E_m = E_n + \hbar\omega$  .

It is obvious, that analyzing similarly the radiation processes, we get

$$\frac{dP_{mn}}{dt} = \frac{2\pi |h_{mn}^+|^2}{\hbar} \delta(E_m - E_n + \hbar\omega) .$$

In the next paragraph we take a more closer look to radiation processes and derive the selection rules for spectral transitions.

## 22. Radiation transitions, selection rules

**22.1 Perturbation due to the external electromagnetic field.** Assume, that on atom there acts some monochromatic electromagnetic wave (for example light wave), which has the electric field strength

$$\vec{E} = \vec{E}_0 \cos(\omega t - \vec{k} \cdot \vec{r}) .$$

Since the atomic diameter ( $d \sim 10^{-10} m$ ) is small, comparing the wave length of light (in the case of visible light  $\lambda \sim 10^{-7} m$ ), the quantity  $\vec{k} \cdot \vec{r} = kr \cos\alpha = 2\pi r \cos\alpha / \lambda$  in atomic region does not practically change and we therefore take  $\vec{k} \cdot \vec{r}$  to be constant (dipole approximation). In that case  $\vec{k} \cdot \vec{r}$  is some phase constant and we for simplicity take it equal to zero. Electrical field strength then changes harmonically with frequency  $\omega$

$$\vec{E} = \vec{E}_0 \cos \omega t .$$

Connecting the starting point of our coordinate system with nucleus, the electrical potential of a given external field is

$$\phi(\vec{r}) = -\vec{r} \cdot \vec{E} .$$

(Indeed, if  $\phi(\vec{r}) = -(xE_x + yE_y + zE_z)$ , then from  $\vec{E} = -\text{grad } \phi(\vec{r})$  we obtain the above given field strength.)

If we assume that electrical field is directed along the z-axis:  $\vec{E} = (0, 0, E)$ , then

$$\phi(z) = -z \cdot E = -z E_0 \cos \omega t ,$$

and it gives to electron the additional energy

$$\Delta U(t) = -e\phi(z) = e z E_0 \cos \omega t .$$

The last expression gives us the following time dependent perturbation operator

$$\hat{H}'(t) = e z E_0 \cos \omega t = \frac{e z E_0}{2} (e^{i\omega t} + e^{-i\omega t}) ,$$

which in turn gives us

$$\hat{h} = \hat{h}^+ = \frac{e z E_0}{2} .$$

**22.2 Transition probability.** In induced transitions, both, for  $\omega = \omega_{mn}$  and also for  $\omega = -\omega_{mn}$  the transition probabilities are expressed via the matrix elements of z, as follows

$$\frac{d P_{mn}}{d t} = \frac{\pi e^2 E_0^2}{\hbar^2} |z_{mn}|^2 ,$$

where

$$z_{mn} = \langle \psi_m | z | \psi_n \rangle = \int \psi_m^* z \psi_n dV .$$

Directing the field along the x- or y-axis, we analogically obtain

$$\frac{d P_{mn}}{d t} = \frac{\pi e^2 E_0^2}{\hbar^2} |x_{mn}|^2 , \quad \frac{d P_{mn}}{d t} = \frac{\pi e^2 E_0^2}{\hbar^2} |y_{mn}|^2 .$$

It means that the transition probabilities are directly connected with matrix elements of radius vector  $\vec{r} = (x, y, z)$

$$\vec{r}_{mn} = (x_{mn}, y_{mn}, z_{mn}) .$$

It is obvious that the transition is possible (allowed) only in cases, where  $\vec{r}_{mn} \neq 0$ . If  $\vec{r}_{mn} = 0$ , the transition probability is equal to zero and there are no such transition. Therefore the

investigation of matrix elements  $\vec{r}_{mn}$  gives us information which transitions are possible and which ones are forbidden. The restrictions on transitions are called the selection rules.

The radiation transitions, we analyze here, are usually called the dipole transitions, since the selection rules depend on the matrix elements  $\vec{d}_{mn} = e\vec{r}_{mn}$  of dipole moment

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

In addition to the dipole radiation there are another ones: electrical quadrupole, magnetical dipole and other ones which depend on the corresponding system parameters. Since these have intensities which are five to six orders of magnitude smaller from dipole radiation, we do not analyse then here.

**22.3 Radiation transitions.** From the elementary radiation theory, given in 1917 by A. Einstein, it follows that for induced radiation the probabilities are connected as follows

$$\frac{dP_{mn}}{dt} = B_{mn} \rho(\omega) = B_{nm} \rho(\omega) = \frac{dP_{nm}}{dt},$$

where  $\rho(\omega)$  is the intensity of external radiation and  $B_{mn} = B_{nm}$  is the probability of inner (induced) transitions (up and down). We have derived the same result from quantum mechanics

$$\frac{dP_{mn}}{dt} = \frac{\pi e^2 E_0^2}{\hbar^2} |z_{mn}|^2 = \frac{dP_{nm}}{dt},$$

since  $|z_{mn}|^2 = |z_{nm}|^2$ . As  $E_0^2$  characterizes the intensity of external radiation, we have, that the probability of atomic transitions

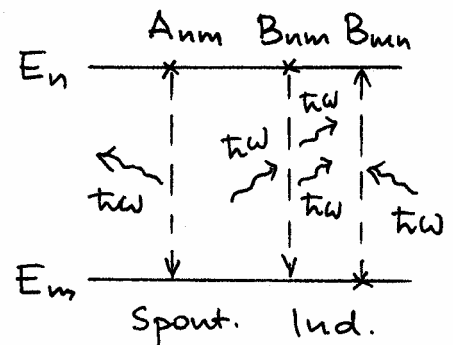
$$B_{mn} = B_{nm} \approx |z_{mn}|^2.$$

Therefore, quantum mechanics gives us the prescription to calculate Einstein coefficients.

Einstein theory gives also the relation between spontaneous and induced transitions

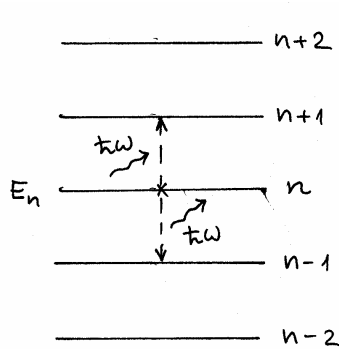
$$A_{nm} = \frac{2\pi\hbar\omega^3}{c^2} B_{mn}.$$

Therefore the calculation of matrix elements of coordinates allows also to analyze the spontaneous radiation (the mean life of excited states, for example).





**Example 1. Harmonic oscillator.** In the case of harmonic oscillator the selection rules are determined by the matrix elements of  $x$ -coordinate



$$x_{mn} = \langle \psi_m | x | \psi_n \rangle .$$

Using the results of §6 it follows that

$$x_{mn} \neq 0, \quad \text{iff} \quad m = n \pm 1 .$$

From that it is obvious that transitions are allowed between neighbouring levels. In radiation the possible transitions are  $n \rightarrow n-1$  and in absorbing  $n \rightarrow n+1$ . In the first case energy  $\hbar\omega$  is radiated, in the second case the same energy is absorbed.

In conclusion: harmonic oscillator always radiates and absorbs energy, which is equal to  $\hbar\omega$  (Planck's energy quantum).

**Example 2. Atomic transitions.** Next we analyse transitions in atoms, when there is transition from the state  $|nlm\sigma\rangle$  with energy  $E_{nl}$  to the state  $|n'l'm'\sigma'\rangle$  with energy  $E_{n'l'}$ . Since the transition probabilities are determined by the matrix elements of  $x$ ,  $y$  and  $z$ , it is easy to verify that the spin projection on transitions cannot change. Indeed, if we write the states as

$$|nlm\sigma\rangle = \psi_{nlm}(r, \theta, \varphi) Y_{1/2\sigma} ,$$

$$|n'l'm'\sigma'\rangle = \psi_{n'l'm'}(r, \theta, \varphi) Y_{1/2\sigma'} ,$$

we, for example, for  $x_{ij}$  have

$$x_{ij} = \langle n'l'm'\sigma' | x | nlm\sigma \rangle = \left( \int \psi_{n'l'm'}^* x \psi_{nlm} dV \right) Y_{1/2\sigma'}^* Y_{1/2\sigma} .$$

From the orthonormality of spin functions:  $Y_{1/2\sigma'}^* Y_{1/2\sigma} = \delta_{\sigma'\sigma}$  it follows, that in all transitions  $\sigma' = \sigma$ . Therefore it remains to calculate the matrix elements

$$x_{ij} = \int \psi_{n'l'm'}^* x \psi_{nlm} dV$$

and analogically

$$y_{ij} = \int \psi_{n'l'm'}^* y \psi_{nlm} dV \quad \text{and} \quad z_{ij} = \int \psi_{n'l'm'}^* z \psi_{nlm} dV .$$

As follows, we demonstrate that from these integrals we get the following selection rules for spectral transitions

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1 .$$

Next we start to calculate integrals. In all cases we must calculate three integrals, over  $r$ ,  $\theta$  and  $\varphi$ , because

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi) .$$

In spherical coordinates we have

$$x = r \sin \theta \cos \varphi, \quad y = r \sin \theta \sin \varphi, \quad z = r \cos \theta .$$

To simplify calculations it is useful instead of  $x$  and  $y$  take the new variables

$$\xi = x + iy = r \sin \theta e^{i\varphi}, \quad \eta = x - iy = r \sin \theta e^{-i\varphi},$$

since now  $\xi, \eta$  and  $z$  are expressed via the spherical functions  $Y_{lm}(\theta, \varphi)$ , and we may next use the properties of spherical functions. The result is

$$\xi = -\sqrt{\frac{8\pi}{3}} r Y_{11}(\theta, \varphi), \quad \eta = \sqrt{\frac{8\pi}{3}} r Y_{1-1}(\theta, \varphi), \quad z = \sqrt{\frac{4\pi}{3}} r Y_{10}(\theta, \varphi).$$

Next we must calculate the following types of integrals

$$(\xi_{ij}, \eta_{ij}, z_{ij}) = \alpha \int_0^\infty R_{n'l'}(r) R_{nl}(r) r^3 dr \cdot \int_{4\pi} Y_{l'm'} Y_{lm} Y_{lm} d\Omega,$$

where  $\alpha$  is correspondingly  $-\sqrt{8\pi/3}$ ,  $\sqrt{8\pi/3}$  or  $\sqrt{4\pi/3}$ .

At first, we find the integrals over the variables  $\theta$  and  $\varphi$ , which are to be integrated over the total solid angle.

Starting from the matrix elements of  $z$ -coordinate, we must calculate the integral

$$\int Y_{l'm'} Y_{10} Y_{lm} d\Omega.$$

Using the relation between spherical functions (§ 17 Example 6), we get

$$Y_{10} Y_{lm} = \alpha_z Y_{l+1m} + \beta_z Y_{l-1m}$$

(we do not write here the exact values of  $\alpha_z$  and  $\beta_z$ , since we are interested mainly in selection rules). Using these relations, we have

$$\int_{4\pi} Y_{l'm'} Y_{10} Y_{lm} d\Omega = \alpha_z \int_{4\pi} Y_{l'm'} Y_{l+1m} d\Omega + \beta_z \int_{4\pi} Y_{l'm'} Y_{l-1m} d\Omega.$$

From the orthonormality of spherical functions, we get, that the result is nonzero, iff

$$m' = m \quad \text{and} \quad l' = l \pm 1,$$

or otherwise written

$$\Delta l = \pm 1, \quad \Delta m = 0.$$

In the case of matrix elements of  $\xi$  and  $\eta$  we must calculate the integrals

$$\int Y_{l'm'} Y_{1\pm 1} Y_{lm} d\Omega,$$

which using

$$Y_{l\pm 1} Y_{lm} = \alpha_{\pm} Y_{l+1m\pm 1} + \beta_{\pm} Y_{l-1m\pm 1} ,$$

give

$$\int Y_{l'm'} Y_{l\pm 1} Y_{lm} d\Omega = \alpha_{\pm} \int Y_{l'm'} Y_{l+1m\pm 1} d\Omega + \beta_{\pm} \int Y_{l'm'} Y_{l-1m\pm 1} d\Omega .$$

From those integrals it follows that the result is nonzero, iff

$$m' = m \pm 1 \quad \text{ja} \quad l' = l \pm 1 ,$$

or

$$\Delta l = \pm 1 , \quad \Delta m = \pm 1 .$$

In conclusion we derived the general selection rules for dipole transitions

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

(all other dipole transitions are forbidden).

These selection rules are the most general ones, since for the quantum number  $n$  there are no restrictions, because the integrals

$$\int_0^{\infty} R_{n'l\pm 1} R_{nl} r^3 dr$$

are for every  $n$  and  $n'$  nonzero (the radial functions always overlapped and their product is nonzero). From these integrals of course depend the intensities of corresponding spectral lines.

Condition  $\Delta l = \pm 1 , \quad \Delta m = 0$  means, that the radiation along the  $z$ -axis is linearly polarized, the radiation along the  $x$ - and  $y$ -plane has circular polarization ( $\Delta l = \pm 1 , \quad \Delta m = \pm 1$ ).

In many cases we use the total angular momentum

$$\vec{J} = \vec{L} + \vec{s} ,$$

but the selection rules for  $l$  and  $m$  remain the same. Since spin projection does not change, we get the selection rules

$$\Delta j = \pm 1 , \quad \Delta m_j = 0 , \pm 1 .$$

Since in general  $j = l \pm 1/2$ , the rule  $\Delta l = \pm 1$  allows also the transition

$$\Delta j = 0 ,$$

(the same  $j$  give different  $l$  values (for example  $j = l + 1/2$  and  $j = (l+1) - 1/2$ )).

## 23. Fine structure of atomic levels

The investigation of many-electron atoms is very complicated and there are no analytical solutions which give us electrons energy levels. In §32 we shall see that even for He atom there are no analytical solution at all and we must try to use different approximations in order to find energies and states of that atom. In this paragraph we analyse the structure of energy levels in atoms which have one valence electron. The first approximation is to use the so-called one electron approximation.

In the H-atom case (one electron) we get, that in the Coulomb field ( $U(r) \sim 1/r$ ) the energies and wave functions are

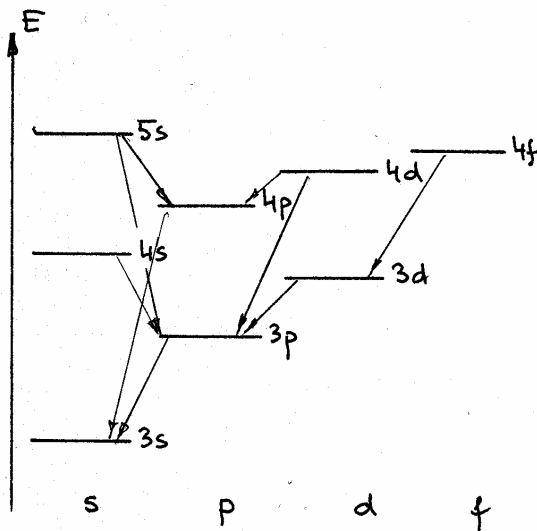
$$E = E_n, \quad \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

(moreover we get the exact expressions for energies and wave functions).

In other cases the field acting on electron is not the Coulomb field, but as a first approximation we can assume, that the potential energy, acting on each electron, is central symmetric  $U = U(r)$ . Then the energies and wave functions are

$$E = E_{nl}, \quad \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

(of course, now we do not have exact expressions for energies and radial functions, but know only the general dependence on quantum numbers). That approximation seems quite naive, but it gives us qualitative explanation for the periodic table of elements and for that reason it is usable, at least as the first approximation.



Here we use it for atoms, which in outer shell have only one valence electron (as Li, Na, K, ...). In one electron approximation we assume that the potential energy of that valence electron is central symmetric (it “moves” far from nucleus and other electrons which are in inner shells). The ground state of that valence electron is some ns state. For Na, as an example, there are in total 11 electrons, ten of them are in K (1s states) and L shells (2s and 2p states), and the 11-th one is in M shell, its ground state is 3s state. It has possible excited states 3p, 4s, 4p and so on (see the energy levels diagram, where also the possible spectral transitions are given).

**23.1 L-S coupling.** In real atoms the structure of energy levels is more complicated than we obtain from one electron approximation. There are more interactions between the electrons than the electrical one we discussed before. As we know, electron has spin and the corresponding magnetic moment, on the other hand it interacts with the magnetic moment which is due to the orbital angular momentum. Next we analyse what effects the latter interaction causes. Of course,

magnetic forces are in general quite weak and therefore the changes in energy levels are quite small and gives us the so-called fine structure of energy levels.

As follows, we analyse the fine structure of atomic energy levels in atoms with one valence electron. In that case we instead of one energy level obtain usually two close lying levels.

Due to the orbital “motion” electron has magnetic moment

$$\vec{\mu} = -\frac{e}{2M} \vec{L} ,$$

due to spin it has magnetic moment

$$\vec{\mu}_s = -\frac{e}{M} \vec{s} .$$

The interaction between the magnetic momenta gives additional energy

$$\Delta U \sim \vec{\mu} \cdot \vec{\mu}_s \sim \vec{L} \cdot \vec{s} .$$

Since it depends on orbital angular momentum and spin (intrinsic angular momentum) and for that reason it is called L-S coupling or spin-orbital coupling.

If we add the spin-orbital coupling, we must add to the Hamilton operator the following additional term

$$\hat{H}' = \beta \vec{L} \cdot \vec{s}$$

(for simplicity we omit the operator marks). Since the classical physics do not give the correct expression for  $\beta$  (see §29), we do not specify it here, but since magnetical forces are in general weak, we assume that the additional term may be considered as a small perturbation.

Hamiltonian operator is now

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta + U(r) + \beta \vec{L} \cdot \vec{s} .$$

**23.2 States in the case of L-S coupling.** Next we see, that stationary states are not determined with the help of principal, orbital and magnetic quantum numbers, since now the conserved quantity is total angular momentum

$$\vec{J} = \vec{L} + \vec{s} .$$

Next we find the quantities that commute with Hamilton operator and describe states in the case of L-S coupling. We see, that these quantities are  $\vec{J}^2$  and  $\hat{J}_z = \hat{L}_z + \hat{s}_z$ , and also  $\vec{L}^2$  and  $\vec{s}^2$ . At first we remind the commutation relations for some known operators

$$\begin{aligned} [\hat{J}_x, \hat{J}_y] &= i\hbar \hat{J}_z , & [\hat{J}_y, \hat{J}_z] &= i\hbar \hat{J}_x , & [\hat{J}_z, \hat{J}_x] &= i\hbar \hat{J}_y , \\ [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z , & [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x , & [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y , \\ [\hat{s}_x, \hat{s}_y] &= i\hbar \hat{s}_z , & [\hat{s}_y, \hat{s}_z] &= i\hbar \hat{s}_x , & [\hat{s}_z, \hat{s}_x] &= i\hbar \hat{s}_y , \end{aligned}$$

orbital and spin operators mutually commute

$$[\hat{L}_i, s_j] = 0 .$$

From these relations it follows, that

$$[(\vec{L} \cdot \vec{s}), \vec{L}^2] = 0 \quad \text{and} \quad [(\vec{L} \cdot \vec{s}), \vec{s}^2] = 0 ,$$

from which we have

$$[(\vec{L} \cdot \vec{s}), \vec{J}^2] = 0 .$$

Direct calculation gives that  $\hat{L}_z$  and  $\hat{s}_z$  separately do not commute with  $(\vec{L} \cdot \vec{s})$ , but their sum commutes

$$[(\vec{L} \cdot \vec{s}), \hat{J}_z] = 0 .$$

Indeed,

$$[(\vec{L} \cdot \vec{s}), \hat{L}_z] = \hat{s}_x [\hat{L}_x, \hat{L}_z] + \hat{s}_y [\hat{L}_y, \hat{L}_z] = i\hbar (-\hat{s}_x \hat{L}_y + \hat{s}_y \hat{L}_x) ,$$

$$[(\vec{L} \cdot \vec{s}), \hat{s}_z] = \hat{L}_x [\hat{s}_x, \hat{s}_z] + \hat{L}_y [\hat{s}_y, \hat{s}_z] = i\hbar (-\hat{s}_y \hat{L}_x + \hat{s}_x \hat{L}_y) .$$

Also with Hamilton operator commute operators  $\vec{L}^2$  ja  $\vec{s}^2$ . In conclusion we get

$$[\hat{H}, \hat{J}^2] = [\hat{H}, \hat{J}_z] = [\hat{H}, \vec{L}^2] = [\hat{H}, \vec{s}^2] = 0 .$$

In the case of the L-S coupling, therefore, in addition to the energy these four quantities are also determined and the physical state is now characterized by the following quantum numbers

$$|n j m_j l s\rangle ,$$

where  $m_j$  characterizes the projection of the total angular momentum. If we analyse one electron states, then  $s=1/2$  and it is not usually added, but considering many electron states the total spin must be also specified.

For one electron states we from adding angular momenta have, that if orbital quantum number is  $l$  the total angular momentum is

$$j = l \pm 1/2$$

(if  $l = 0$ , then of course  $j = 1/2$ ). It means that previous energy levels  $E_{nl}$  in general split to two levels ( $l+1/2$  and  $l-1/2$  levels).

Next we find the corresponding energies, assuming that in the case of L-S coupling the perturbation is small. In order to take in consideration the L-S coupling we must find the eigenvalues of  $(\vec{L} \cdot \vec{s})$ . For that we take squares of both sides of  $\vec{J} = \vec{L} + \vec{s}$

$$\hat{J}^2 = \hat{L}^2 + \hat{s}^2 + 2(\vec{L} \cdot \vec{s}) ,$$

which gives

$$(\vec{L} \cdot \vec{s}) = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{s}^2) .$$

In the state  $|n j m_j l s\rangle$  all these quantities are determined, therefore

$$(\vec{L} \cdot \vec{s}) = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) .$$

For  $j = l + 1/2$  we get

$$(\vec{L} \cdot \vec{s}) = \frac{\hbar^2}{2} l$$

and for  $j = l - 1/2$  we get

$$(\vec{L} \cdot \vec{s}) = -\frac{\hbar^2}{2} (l+1) .$$

These results gives the following energies if the L-S coupling is assumed:

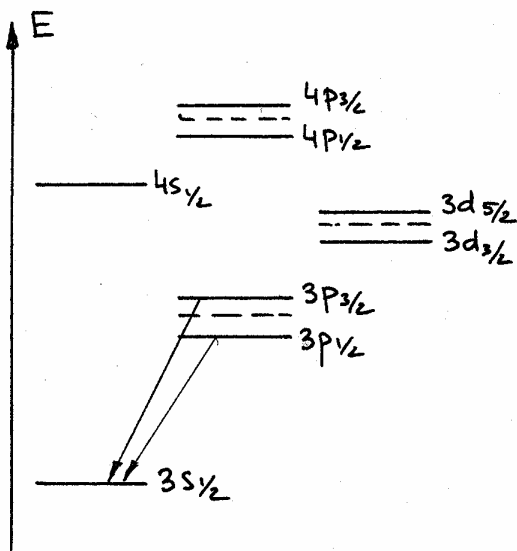
$$j = l + 1/2, \quad E_{nl} + \frac{\beta \hbar^2}{2} l ,$$

$$j = l - 1/2, \quad E_{nl} - \frac{\beta \hbar^2}{2} (l+1) .$$

In the L-S coupling case to the notation of states s, p, d, ... the lower index, which denotes the total angular momentum, is usually added. So we get states, as

$$s_{1/2}, p_{1/2}, p_{3/2}, d_{3/2}, d_{5/2}, \dots ,$$

which all have different energies.



As an example, we give the modified level structure for Na, where the L-S coupling is added (dotted lines give levels without L-S coupling).

All the s-levels remain the same, but other levels split to two close lying levels. The more interesting result here is, that the Na yellow doublet lines with the corresponding wave length 5890 Å and 5896 Å, are due to the transitions  $3p_{3/2} \rightarrow 3s_{1/2}$ ,  $3p_{1/2} \rightarrow 3s_{1/2}$ .

In conclusion: due to the L-S coupling we have fine structure of energy levels, since the splitting of levels is very small (approximately  $10^{-5} eV$ ).

Since the fine structure is in general quite complicated to find, we restrict ourselves to one valence electron case. In the He atom case when there is two electrons, we must take their total spin (which is zero or one). The energy levels are now triplets or singlets. Other cases are even more complicated.

**23.3 Fine structure of hydrogen atom levels.** Similarly to the previous case we must take into account the L-S coupling also in the hydrogen atom. But here is the situation different, since we in addition to the L-S coupling must take into consideration other physical effects (which we discuss in §28 ja §29, using the relativistic Dirac equation): mass dependence from velocity (in H-atom the electron is more close to the proton and has greater velocity) and also the specific contact interaction.

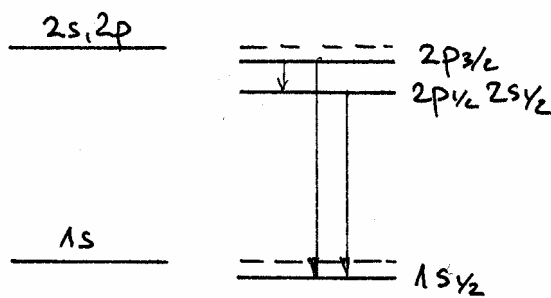
Fine structure gives the following energy levels for H-atom

$$E_{nj} = -\frac{R\hbar}{n^2} \left( 1 + \frac{\alpha^2}{n^2} \left( \frac{2n}{2j+1} - \frac{3}{4} \right) \right),$$

where the constant  $\alpha = be^2 / \hbar c$  is called the fine structure constant. Since

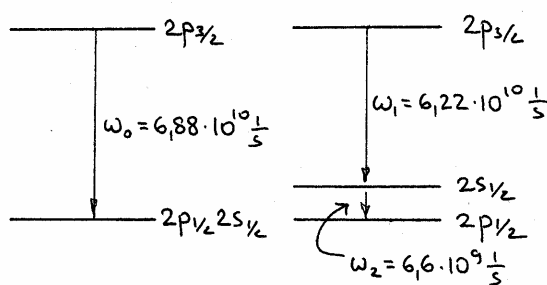
$$\alpha = \frac{be^2}{\hbar c} \approx 0,00728 \approx \frac{1}{137}$$

and energy corrections are proportional to its square, the order of energy corrections is  $10^{-5} eV$ .



As an illustration we consider the levels 1s, 2s ja 2p. The fine structure gives us new levels  $1s_{1/2}$ ,  $2s_{1/2}$ ,  $2p_{1/2}$ ,  $2p_{3/2}$ . Since the energy now depends on total angular momentum, the levels  $2s_{1/2}$  and  $2p_{1/2}$  have the same energy. The comparison of levels are drawn on the left. As we see there are arise new possible spectral lines, which are from transitions  $2p_{3/2} \rightarrow 2s_{1/2}$ ,

$2p_{3/2} \rightarrow 1s_{1/2}$  and  $2p_{1/2} \rightarrow 1s_{1/2}$ .



The more detailed analysis of hydrogen levels demonstrates, that the levels  $2s_{1/2}$  and  $2p_{1/2}$  do not have the exactly same energy, but the energy of  $2s_{1/2}$  level lies a little bit higher (approximately one tenth of the difference between  $2p_{3/2}$  and  $2p_{1/2}$ ). The real structure of  $n = 2$  levels is given on the left figure. Since the energy of  $2s_{1/2}$  level is different

from the energy of  $2p_{1/2}$  level, we have the new spectral transition  $2s_{1/2} \rightarrow 2p_{1/2}$  which has the wave length 28 cm.

The difference of energies between  $2s_{1/2}$  and  $2p_{1/2}$  levels is called Lamb shift. It is explained in quantum electrodynamics and is due to the so called vacuum polarization (sea of virtual electron-positron pairs and virtual photons which act mainly on s-states).

**23.4 Hyperfine structure of H-atom levels.** If we try to systematically analyse the electron interactions in atoms, we in addition to magnetic forces, treated before must also consider how



the magnetic momentum of nucleous (in H-atom proton) acts on electron. Hydrogen nucleous – proton – has spin  $1/2$ , and magnetic momentum

$$\vec{\mu}_t = \gamma \vec{s}_t .$$

Instead of Bohr’s magneton we have there nuclear magneton (electron mass is changed to the proton mass)

$$\mu_t = \frac{e\hbar}{2M_p} .$$

Proton’s magnetic moment is greater that the nuclear magneton (so called anomalous magnetic moment) and equals

$$\mu_p = 2,79 \mu_t .$$

Since it is three orders of magnitude less than Bohr’s magneton, it is logical to assume that its effects on energy levels are very small. The energy levels shift is in the same order, as the Lamb shift and is called the hyperfine structure of H-atom.

We give only some remarks of hyperfine splitting, and as an example, analyse the splitting of ground level (1s-level). Now the orbital quantum and magnetic quantum numbers are equal to zero, we must take into account only the interaction between electron’s and proton’s magnetic momenta. It gives additional hamiltonian

$$\hat{H}' = \kappa \vec{\mu}_t \cdot \vec{\mu}_s = \delta (\vec{s}_t \cdot \vec{s}_e) .$$

It is similar to the L-S coupling term, where instead of the orbital angular momentum, there is nuclear spin.

The states are determined by the total spin  $\vec{s} = \vec{s}_t + \vec{s}_e$ , which has values

$$s = 1 \quad \text{and} \quad s = 0 .$$

Therefore we get triplet (  $s = 1$  ) and singlet (  $s = 0$  ) levels. The corresponding shifts of levels are proportional to eigenvalues of operator  $(\vec{s}_t \cdot \vec{s}_e)$ . Since

$$(\vec{s}_t \cdot \vec{s}_e) = \frac{1}{2} (\vec{s}^2 - \vec{s}_t^2 - \vec{s}_e^2) ,$$

we get, that

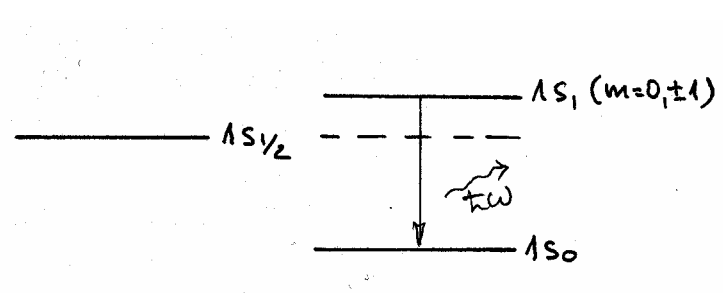
$$\text{for } s = 1 \quad (\vec{s}_t \cdot \vec{s}_e) = \frac{\hbar^2}{4} \quad \text{and for } s = 0 \quad (\vec{s}_t \cdot \vec{s}_e) = -\frac{3\hbar^2}{4} .$$

It means that the triplet level shifts up by  $\delta \hbar^2 / 4$  and the singlet level shifts by  $3\delta \hbar^2 / 4$  down (see figure).

Transition  $1s_1 \rightarrow 1s_0$  gives us the “cosmic” wave legth known from radioastronomy

$$\lambda = 21,121 \text{ cm} .$$

(The difference between the hyperfine levels is of the same order as the Lamb shift.)



## 24. Zeeman effect

In 1896 P. Zeeman discovered that in an external magnetic field the spectral lines of atoms are splitting, instead of one previous spectral line there arise some close lying spectral lines. Depending on the number of lines we have normal or anomalous Zeeman effect. If instead of one spectral line there are three lines, it is called normal Zeeman effect, since it was in principle possible to explain using classical electrodynamics. If instead of one spectral line we had even number of lines (two, four, ...), it is called anomalous Zeeman effect, since it had no explanation in classical physics. Since spectral lines are formed by transitions between energy levels, it means that in external magnetic fields energy levels of atoms must split due to the additional magnetic energy. We previously analysed different simple models that explain some special cases, here we give the more thorough explanation of Zeeman effect.

**24.1 Weak magnetic field.** We start with the weak magnetic field case, which means that the additional energy which is due to the external magnetic field is less than the energy difference due to the L-S coupling. The latter also means that we must use the states which are labelled by the quantum numbers  $n, j, m_j, l, s$

$$\psi_{n j m_j} = |n j m_j l s\rangle .$$

If there are no external field these states are eigenstates of the Hamilton operator  $\hat{H}_0$

$$\hat{H}_0 \psi_{n j m_j} = E_{nj}^0 \psi_{n j m_j} ,$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2M} \Delta + U(r) + \beta \vec{L} \cdot \vec{s} .$$

As we in §18 demonstrated, in external magnetic field the following perturbation

$$\hat{H}' = \frac{e}{2M} (\vec{L} + 2\vec{s}) \cdot \vec{B} = \frac{e}{2M} (\vec{J} + \vec{s}) \cdot \vec{B} ,$$

where  $\vec{J} = \vec{L} + \vec{s}$  is the total angular momentum, is added.

Therefore we must solve the eigenvalue problem

$$(\hat{H}_0 + \hat{H}') \psi = E_{nj} \psi .$$

If  $\hat{H}'$  is a small perturbation, then the first order correction to energy ( $E_{nj} = E_{nj}^0 + \Delta\varepsilon$ ) is

$$\Delta\varepsilon = \langle n j m_j | \hat{H}' | n j m_j \rangle .$$

Now we had a problem, since the state  $|n j m_j\rangle$  is not an eigenstate of the perturbation operator and therefore the direct calculation of its diagonal elements is impossible and we need to show some inventiveness.

We, as usually, assume that the external magnetic field is homogeneous, Then we must calculate matrix elements

$$\langle njm_j | \vec{K} | njm_j \rangle = \langle njm_j | \vec{J} + \vec{s} | njm_j \rangle$$

of the operator

$$\vec{K} = \vec{J} + \vec{s} .$$

Our states  $|njm_j\rangle$  are eigenstates of  $\vec{J}$ , but not for  $\vec{s}$  (spin projection is not determined).

Since we calculate matrix elements in the subspace of total angular momentum  $|njm_j\rangle$ , we try to find an operator  $\hat{G}$ , which satisfies

$$\hat{G} \hat{J} = \hat{J} + \hat{s}$$

(projects  $\vec{J}$  along  $\vec{K} = \vec{J} + \vec{s}$ ). Next we demonstrate that such operator indeed exists and find it by direct calculation.

First we multiply the above given expression from right to operator  $\hat{J}$

$$\hat{G} \hat{J}^2 = \hat{J}^2 + (\hat{s} \cdot \hat{J}) .$$

In the sub-space of states  $|njm_j\rangle$  we instead of  $\hat{J}^2$  may write  $\hbar^2 j(j+1)$ , and therefore

$$\hat{G} = 1 + \frac{\hat{s} \cdot \hat{J}}{\hbar^2 j(j+1)} .$$

Next we calculate  $\hat{s} \cdot \hat{J}$  and use the fact that  $\hat{J}^2$  and also  $\hat{L}^2$  and  $\hat{s}^2$  are determined. We write  $\hat{J} = \hat{L} + \hat{s}$  as

$$\hat{J} - \hat{s} = \hat{L}$$

and take the square of both sides

$$\hat{J}^2 - 2(\hat{J} \cdot \hat{s}) + \hat{s}^2 = \hat{L}^2 .$$

From here

$$\hat{J} \cdot \hat{s} = \frac{1}{2} (\hat{J}^2 + \hat{s}^2 - \hat{L}^2) .$$

Since all the quantities on right are determined in state  $|njm_j\rangle$ , we can write that

$$\hat{J} \cdot \hat{s} = \frac{\hbar^2}{2} (j(j+1) + s(s+1) - l(l+1)) .$$

Now it is obvious, that operator  $\hat{G}$  in the given subspace is equal to some number. Denoting  $\hat{G} = g$ , we have

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} .$$

$g$  is called the Lande factor.

Next we calculate the energy corrections. Taking magnetic field along the z-axis  $\vec{B} = (0, 0, B)$ , the perturbation operator is

$$\hat{H}' = \frac{eB}{2M}(\hat{J}_z + \hat{s}_z) .$$

Since

$$\hat{J}_z + \hat{s}_z = g \hat{J}_z ,$$

then

$$\hat{H}' = \frac{egB}{2M} \hat{J}_z$$

and the correction to energy is

$$\Delta\varepsilon = \langle njm_j | \hat{H}' | njm_j \rangle = \frac{e\hbar g B}{2M} m_j$$

$$(\hat{J}_z | njm_j \rangle = \hbar m_j | njm_j \rangle).$$

In conclusion: in weak external magnetic field every level  $E_{nj}^0$  is splitting to  $2j+1$  levels, which have energies equal to

$$E_{njm_j} = E_{nj}^0 + \frac{e\hbar g B}{2M} m_j ,$$

where  $m_j = +j, \dots, -j$ .

Let us analyse our result more closely. If we have one electron states, then

$$j = l \pm 1/2$$

and therefore the total angular momentum  $j$  is half-odd integer ( $1/2, 3/2, 5/2, \dots$ ) and  $2j+1$  is an even number. It means that instead of one level  $E_{nj}^0$  we in magnetic field have even number of close lying energy levels  $E_{njm_j}$ . It is also important that the distance between these levels depends on Lande factor  $g$ , which for each  $l$  is different. For that reason the splitting of levels with the same  $j$ , but different  $l$  is also different (for example  $p_{3/2}$  and  $d_{3/2}$ ).

The next table gives Lande factors for  $j = l \pm 1/2$  ( $s = 1/2$ ).

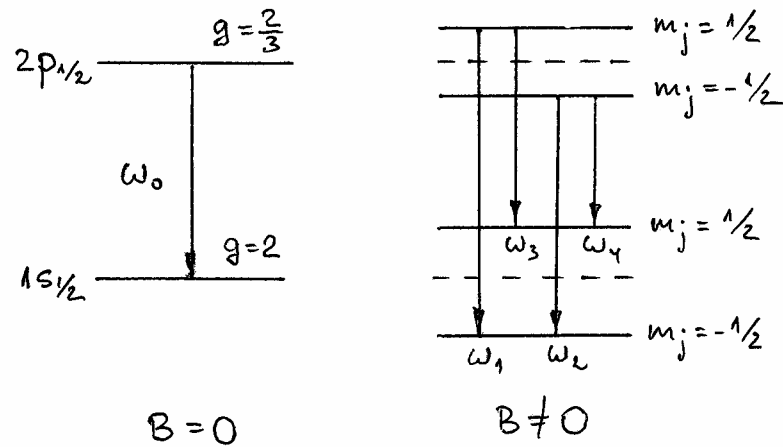
**Table.**

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
$g$	2	2/3	4/3	4/5	6/5

It is possible to demonstrate that in spectral transitions (using selection rules) we always get even number of spectral lines (anomalous Zeeman effect).

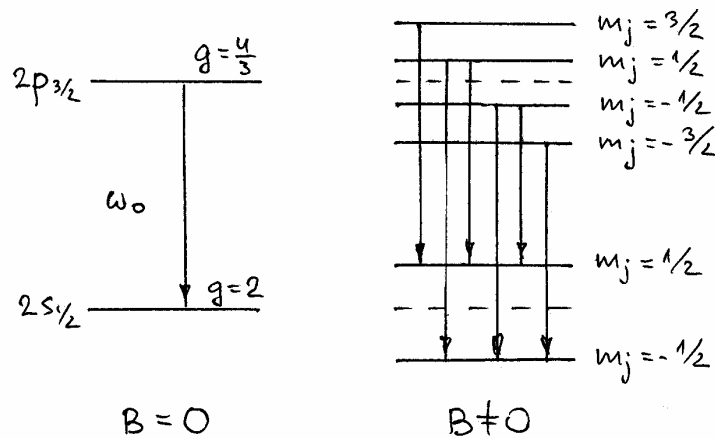
We omit the detailed analysis of spectral transitions and give some examples.

**Example 1.** Take the transition  $2p_{1/2} \rightarrow 1s_{1/2}$  in hydrogen atom (or transition  $(n+1)p_{1/2} \rightarrow ns_{1/2}$  in some alcali metal). We draw the energy levels without magnetic field and in the presence of magnetic field.



Both levels split to two close lying levels, but distance between them is different (Lande factors  $2/3$  and  $2$ ). The selection rules give us four close lying spectral lines with frequencies  $\omega_1, \omega_2, \omega_3$  and  $\omega_4$ .

**Example 2.** Transitions  $2p_{3/2} \rightarrow 2s_{1/2}$  (or analogically  $2p_{3/2} \rightarrow 1s_{1/2}$ ).



Instead of one spectral line we get six close lying lines.

From the above given one may conclude that in weak fields there exists only the anomalous Zeeman effect, but it is not true in general. There exist both possibilities. We treated before the case of one valence electron. But if in the outer shell there are more electrons and due to their mutual interaction their angular momenta and spins are added separately (the mostly existing case), then that shell is characterized with total angular momentum and total spin

$$\vec{L} = \sum_i \vec{L}_i, \quad \vec{s} = \sum_i \vec{s}_i.$$

Total angular momentum now is  $\hat{J} = \hat{L} + \hat{s}$ . As a final result we get the same formula for energy corrections and energy levels split to  $2j+1$  levels. Lande factor is expressed as above, but  $\vec{L}$  is total orbital angular momentum and  $\vec{s}$  total spin.

Now there is possibility, that the total spin of whole outer shell is equal to zero ( $s = 0$ ). In that case

$$\hat{J} = \hat{L} \quad \text{ja} \quad g = 1$$

and there is  $2l+1$  splitted levels (odd number of levels) and independently on  $l$  the energy difference between levels is the same. The result is normal Zeeman effect, as our trivial cases treated in previous paragraphs (zero spin case, example 3 in §20). Examples are the singlet terms in Zn, Cd, and others, where total spin of outer shell is equal to zero.

The second special case where we get normal Zeeman effect, is when the total angular momentum is equal to zero  $\vec{L} = 0$  and  $\vec{s} \neq 0$ , but has some even value. Now

$$\vec{J} = \vec{s} \quad \text{ja} \quad g = 2 .$$

Concluding the weak field case we explain of how to know whether the magnetic field is weak or not. We assumed that in the weak field case the difference between the splitted levels  $\Delta\varepsilon$  is less that the difference between fine structure levels  $E_{nj} - E_{nj'}$ . Taking  $\Delta\varepsilon \approx e\hbar B / 2M = \mu_B B$ , we get the following condition

$$\mu_B B < |E_{nj} - E_{nj'}| .$$

It allows to evaluate, if the magnetic field is indeed weak.

As an example we get the hydrogen levels  $2p_{3/2}$  and  $2p_{1/2}$ . The difference between the levels is a little bit greater than  $10^{-5}$  eV, therefore we take

$$|E_{2p_{3/2}} - E_{2p_{1/2}}| \approx 10^{-5} \text{ eV} .$$

If we take Bohr's magneton in electronvolts to Tesla

$$\mu_B = 9,27 \cdot 10^{-24} \frac{J}{T} \approx 6 \cdot 10^{-5} \frac{eV}{T} ,$$

we may say that magnetic fields  $B < 0,1$  T are weak fields.

**24.2 Strong magnetic fields.** Next we shall show that in strong magnetic field there exists only normal Zeeman effect. If in the weak field there is anomalous Zeeman effect then in the strong field it goes over to the normal Zeeman effect. That phenomenon is called Paschen-Back effect.

However, we had analysed it before in one example, let us do it once more. The perturbation hamiltonian remains the same

$$\hat{H}' = \frac{e}{2M} (\vec{L} + 2\vec{s}) \cdot \vec{B} ,$$

but now we do not express it via the total angular momentum. The reason is, that in strong fields the additional energy, connected with magnetic field are much greater than the difference between fine structure levels and therefore we do not take the L-S coupling into account. Therefore the starting hamiltonian, we use now, is

$$\hat{H}_0 = -\frac{\hbar^2}{2M} \Delta + U(r)$$

Now the states have certain angular momentum, its projection and certain spin projection

$$\hat{H}_0 \psi_{nlm\sigma} = E_{nl}^0 \psi_{nlm\sigma} .$$

The state  $\psi_{nlm\sigma}$  may be presented as

$$\psi_{nlm\sigma} \equiv |nlm\sigma\rangle = \psi_{nlm}(r, \theta, \varphi) Y_{l/2\sigma} .$$

The perturbation operator is the same, as before

$$\hat{H}' = \frac{eB}{2M} (\hat{L}_z + 2\hat{s}_z) .$$

Now it is quite trivial to calculate its diagonal matrix elements, since in the state  $|nlm\sigma\rangle$

$$\hat{L}_z |nlm\sigma\rangle = \hbar m |nlm\sigma\rangle ,$$

$$\hat{s}_z |nlm\sigma\rangle = \hbar \sigma |nlm\sigma\rangle .$$

Therefore the energy corrections are

$$\Delta\varepsilon = \langle nlm\sigma | \hat{H}' | nlm\sigma \rangle = \frac{e\hbar B}{2M} (m + 2\sigma) .$$

Depending on the spin projection we have  $2l+1$  corrections

$$\sigma = +1/2 \quad \Delta\varepsilon_+ = \mu_B B (m + 1) \quad m = +l, \dots, 0, \dots, -l ,$$

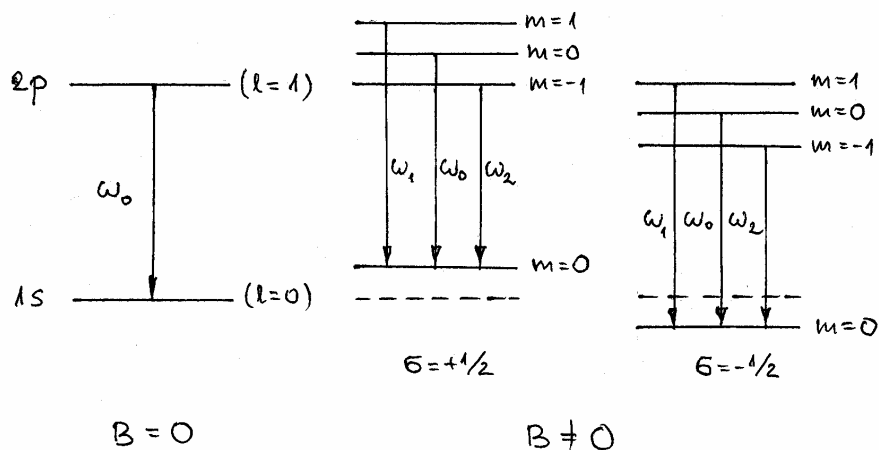
$$\sigma = -1/2 \quad \Delta\varepsilon_- = \mu_B B (m - 1) \quad m = +l, \dots, 0, \dots, -l .$$

(That result was already derived in §18 using Pauli equation.)

Since in spectral transitions spin projection does not change, there are separate transitions between the  $\sigma = +1/2$  states and between the  $\sigma = -1/2$  states. As a result we always have normal Zeeman effect since  $g = 1$ .

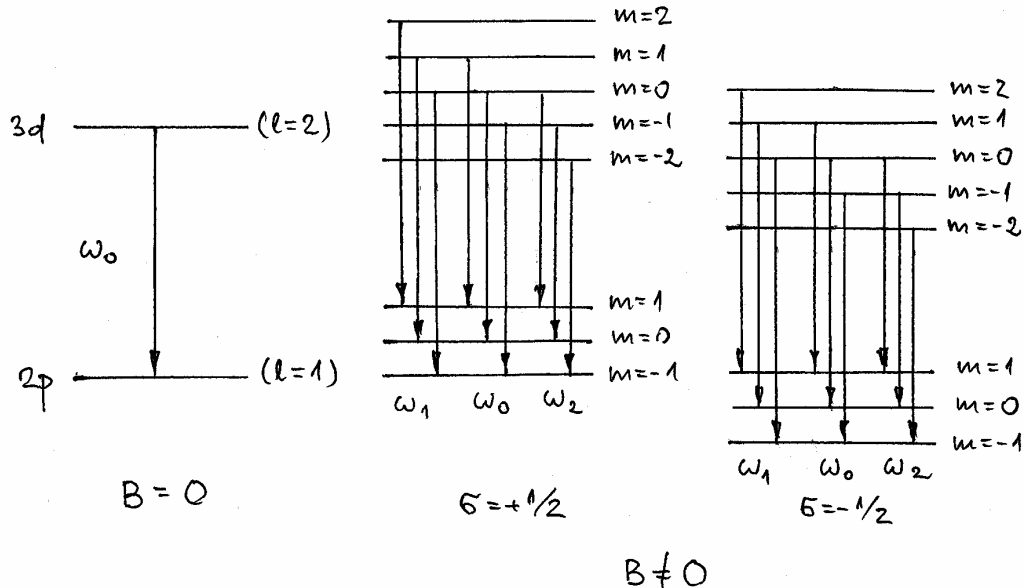
To demonstrate that we always have three spectral lines, we give two special examples.

**Example 3.** Transition  $2p \rightarrow 1s$  (or  $2p \rightarrow 2s$ ). (The same is given in §18.)



Energy levels for  $\sigma = +1/2$  and  $\sigma = -1/2$  are given separately. Selection rules  $\Delta l = \pm 1$  and  $\Delta m = 0, \pm 1$  give three spectral lines (the same for  $\sigma = +1/2$  and for  $\sigma = -1/2$ ).

**Example 4.** Transition  $3d \rightarrow 2p$ . Not there are more splitted levels, but the result is the same – three spectral lines.



From selection rules  $\Delta l = \pm 1$  and  $\Delta m = 0, \pm 1$  there are 9 possible transitions, but only 3 different spectral lines.

## 25. Dia- and paramagnetism of atoms

Here we give a short discussion about the magnetism of atoms. In an external magnetic field matter acquires some magnetic moment, which is directed along the external magnetic field or in opposite direction and depending on it we correspondingly call para- and diamagnetism (we do not talk here about ferromagnetism, which is connected with certain solids).

Next we shall analyse the behaviour of atoms (in gases or liquids) in an external magnetic field and take into account both – orbital magnetic moment and spin magnetic moment. External magnetic field we take along the z-axis

$$\vec{B} = (0, 0, B)$$

and use vector potential

$$\vec{A} = \frac{1}{2}(-yB, xB, 0) .$$

Now we take the full hamiltonian (add also the term with vector potential square)

$$\hat{H} = \hat{H}_0 + \frac{eB}{2M}(\hat{L}_z + 2\hat{s}_z) + \frac{e^2 B^2}{4M}(x^2 + y^2) ,$$



where  $\hat{H}_0$  describes electron when there are no external magnetic field present.

The additional term we consider as an electrons total magnetic moment's  $\mu_z$  energy in an external field  $\Delta U = -\mu_z B$ . From the last expression the total magnetic moment of an atom is

$$\mu_z = -\frac{e}{2M}(\hat{L}_z + 2\hat{s}_z) - \frac{e^2 B}{4M}(x^2 + y^2) \equiv \mu'_z + \mu''_z .$$

The first term does not depend on magnetic field, the second one depends. We show that the first term gives paramagnetism, the second one diamagnetism.

Let us analyse the first magnetic moment

$$\mu'_z = -\frac{e}{2M}(\hat{L}_z + 2\hat{s}_z) \equiv -\frac{e}{2M}(\hat{J}_z + \hat{s}_z) .$$

We already analysed it in Zeeman effect paragraph in weak and strong field cases. Here we analyse only the weak field case where the states are determined by the total angular momentum -  $|njm_j\rangle$ . As we have already demonstrated there are  $2j+1$  different values

$$\mu'_z = -\frac{eg\hbar}{2M} m_j , \quad m_j = +j, \dots, -j ,$$

where  $g$  is Lande factor. (That result may be generalised to the case where  $l$  is the total angular momentum of electron shell and  $s$  is its total spin.

The given magnetic moment always generates paramagnetism. We must analyse the behaviour of atoms in the case of thermodynamic equilibrium at some temperature  $T$ . The probability that the magnetic moment's projection is  $\mu_z$  depends on its energy  $E_i = -\mu_z B$  and is given by the Boltzmann distribution

$$P_i \sim e^{-\frac{E_i}{kT}} .$$

From the Boltzmann distribution it follows that the probability of states with negative energy ( $E_i < 0$ ) is always greater than the probability of states with positive energy and therefore the states with negative energy are preferred. To states with negative energy there correspond magnetic moments directed along the magnetic field ( $\mu_z > 0$ ) and therefore the total magnetic moment is also directed along the magnetic field and we get paramagnetism.

The most important in paramagnetism is that there take part both – the orbital magnetic momentum and spin magnetic momentum. Since the analog of orbital magnetic momentum in classical physics is the orbiting electron, called by Ampere the atomic current, and its magnetic moment, there are great difference between classical and quantum physics, since diamagnetism in classical physics is connected with atomic currents. By quantum mechanics it gives us paramagnetism. It is interesting to know, that in electrodynamics it is proved that in classical physics matter has no magnetic properties at all!

Next we analyse which physics is connected with the second term

$$\mu_z'' = -\frac{e^2 B}{4M} (x^2 + y^2) .$$

Here the diagonal matrix elements of magnetic moment are the mean values of  $x^2 + y^2$ , therefore

$$\mu_z'' = -\frac{e^2 B}{4M} \langle x^2 + y^2 \rangle .$$

Due to the minus sign it is always antiparallel to the magnetic field and therefore leads to diamagnetism. Since the mean value of  $x^2 + y^2$  is positive, diamagnetism is present in all atoms, but when there is paramagnetism also present, paramagnetism is always dominating, since the diamagnetic part is in all atoms smaller.

Next we evaluate the order of magnitude of atomic magnetism. In the paramagnetics case the magnetic moment is of the same order of magnitude as Bohr's magneton

$$\mu_z' \approx \mu_B \approx 10^{-23} \text{ J/T} .$$

In order to evaluate the diamagnetic term we take

$$\mu_z'' = \frac{e^2 B}{4M} r^2 ,$$

where  $r^2$  is the square of atomic radius. If we assume that, et  $\mu_z'' \ll \mu_z'$ , we get the inequality

$$\frac{e^2 B}{4M} r^2 \ll \mu_B ,$$

from which

$$B \ll \frac{2M\mu_B}{e^2 r^2} \approx 10^5 \text{ T} .$$

From the latter inequality it is obvious that for each practically realizable magnetic field the diamagnetic effect compared to the paramagnetic effect is insignificant.

Diamagnetism appeared in atoms if there is even number of electrons and their magnetic moments compensate each other ( $j = 0$ ) (in other words, when paramagnetism is absent). One example is He, where in ground state  $L = 0$  and  $s = 0$ . Diamagnetic moment is

$$\mu_z'' = -\frac{e^2 B}{4M} (\langle x_1^2 + y_1^2 \rangle + \langle x_2^2 + y_2^2 \rangle) .$$

Since the ground state has spherical symmetry, then for both electrons  $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle r^2 \rangle / 3$  and we get

$$\mu_z'' = -\frac{e^2 \langle r^2 \rangle}{3M} B .$$

A detailed calculation gives that diamagnetic permeability of He is equal to  $\chi = -1,87 \cdot 10^{-6}$ , which is in good accordance with the experimental result  $\chi = -1,88 \cdot 10^{-6}$ .