Chapter 2
STRUCTURE AND PROPERTIES OF ATOMS

2.1 Introduction

A set of elementary particles, protons, neutrons and electrons build an atom. The atom is a new quality.

Our model in this chapter is the *isolated atom*, the atom that does not treat into interactions with its environment. This is, of course, an abstraction. It can be a good approach, if the interactions are weak. A low pressure gas is a good realisation of the isolated atom.

2.2 The hydrogen atom

The hydrogen atom is the simplest atom. Therefore we begin with it the study of the atoms.

2.2.1 The structure of the hydrogen atom

The description of the hydrogen atom with quantum mechanics is not very complicate. The solution of the Schrödinger equation

$$\hat{H}\psi = E\psi \qquad (2.1)$$

is relatively easy. Here $\hat{H}$ is the Hamilton (energy) operator, ψ is the eigenfunction (a wave function), E is the energy eigenvalue. This atom consists of two particles: a proton and an electron (Fig. 2.1).
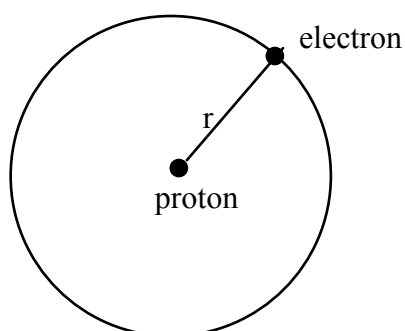

Fig. 2.1

The calculations are simpler using polar coordinates (Fig. 2.2) instead of Cartesian ones. The polar coordinates are as follows: r is the radius, φ is the polar angle, θ is the azimuthal angle.

For the solution of Eq. 2.1 the following form is assumed:

$$\psi(r, \varphi, \theta) = R(r)Y(\varphi, \theta) \qquad (2.2)$$

The Hamilton operator is the sum of the kinetic (T) and potential (V) energy operators:

$$\hat{H} = \hat{T} + \hat{V} \qquad (2.3)$$

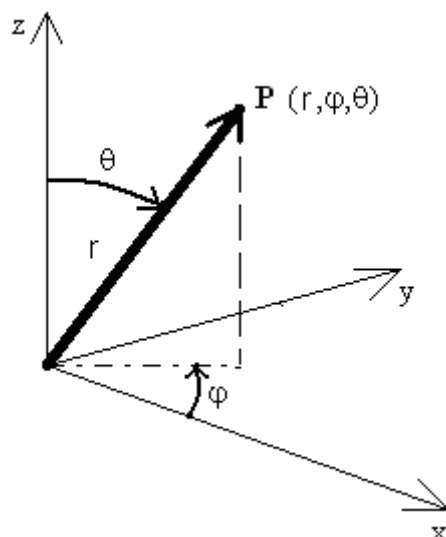The $\hat{V}$ acts simply by multiplication with the potential energy.

Fig. 2.2

The potential energy of the charged system is

$$V = -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r} \qquad (2.3)$$

e is the absolute value of the electron charge (1.602176×10^{-19}As), ε_0 is the permittivity of vacuum (8.85419×10^{-12}AsV^{-1}m^{-1}). The kinetic energy operator is

$$\hat{T} = -\frac{\hbar^2}{2m_e}\left(\hat{T}_r + \hat{T}_{\varphi,\theta}\right) - \frac{\hbar^2}{2m_p}\hat{T}_p \qquad (2.4)$$

The first term is the kinetic energy of the electron (m_e is its mass, 9.10938×10^{-31}kg) is divided into to parts: the r dependent one represents the translation, the second one the rotation; the second term is the kinetic energy operator of the proton (its mass is m_p, 1.67262×10^{-27}kg).

According to the Born-Oppenheimer approximation (adiabatic approximation) the movement of the electron is much faster than that of the proton (take into account the mass rate: $m_p/m_e \approx 1850$). Therefore the proton can be regarded as a particle fixed in space and therefore second term of Eq. 2.4 is negligible.

Substituting Eqs. 2.2, 2.3 and 2.4 into Eq. 2.1 we have

$$Y(\varphi,\theta)\left[-\frac{\hbar^2}{2m_e}\hat{T}_r + \hat{V}\right]R(r) - \frac{\hbar^2}{2m_e}R(r)\hat{T}_{\varphi,\theta}[Y(\varphi,\theta)] = ER(r)Y(\varphi,\theta) \qquad (2.5)$$

The r depending and the φ and θ dpending parts of this equation are separable:

$$\frac{1}{R(r)}\left[-\frac{\hbar^2}{2m_e}\hat{T}_r + \hat{V}\right]R(r) = \frac{\hbar^2}{2m_e}\frac{1}{Y(\varphi,\theta)}\hat{T}_{\varphi,\theta}[Y(\varphi,\theta)] - E \qquad (2.6)$$

The first step of the solution of such kind differential equations is easy. If the variables are separated, both sides of Eq. 2.6 are equal to the same constant. However, the solution of these differential equations is complicate. The solution of Eq. 2.5 results the energy *eigenvalues*

$$E_n = -\frac{e^4 m_e}{32\pi^2\varepsilon_o^2\hbar^2 n^2} = -hc\frac{R_H}{n^2} \tag{2.7}$$

i.e. the electron energy is *quantized,* it depend on the *quantum number n*, the *principal quantum number*. The *quantization* of the energy means, that only their discrete values are allowed, these are called *energy levels.* R_H is the Rydberg constant for hydrogen atom (109737 cm^{-1}).

The *eigenfunctions* of Eq. 2.5, called also *orbitals,* are complicate:

$$\psi(n,l,m) = N_{n,l,m}\frac{1}{r}R_n^l\left(\frac{2r}{na_o}\right)Y_l^m(\varphi,\theta) \tag{2.8}$$

with the Bohr radius

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{m_e e^2} = 52.9177 \text{pm} \tag{2.9}$$

$N_{n,l,m}$ is a *normalization factor* to fulfil the request the normalization to 1:

$$\int\psi^*\psi d\tau = 1 \tag{2.10}$$

The functions R and Y are found in Table 2.1.

The quantum numbers *n, l* and *m* are

n	principle quantum number	*n*=1,2,3,... , all positive integers
l	angular moment quantum number	*l*= 0,1,2,...,*n*-1
m	magnetic quantum number	-*l*,-*l*+1,...,0,...,*l*-1,*l*

The *electron states (orbitals)* of the hydrogen atom are *degenerated*: the same energy belongs to several eigenfunctions, since only the principal quantum number determines the energy.

Electron orbitals with the same *n* build an electron *shell*, orbitals with the same *n* and *l* build a *subshell*. Shells are labelled with capitals:

n =	1	2	3	4	5	6	etc.
label	K	L	M	N	O	P	etc.

Subshells are labelled by (some special) small letters:

l =	0	1	2	3	4	5	etc.
label	s	p	d	f	g	h	etc.

There exist a special angular moment of the electron, form its nature, the spin (see Chapter 1).

If the principal quantum number of a shell is n, the possible maximal number of electrons on this shell is $2n^2$.

Table 2.1
Eigenfunctions (orbitals) of the hydrogen atom

n	l	m	factor	r function	θ function	φ function	alternative φ function	orbital name
1	0	0		R_1				1s
2	0	0	$\sqrt{2}$	$R_2 (2-\rho)$				2s
2	1	0	$\sqrt{2}$	$R_2 \rho$	$\cos\theta$			$2p_z$
2	1	+1		$R_2 \rho$	$\sin\theta$	$\exp(+i\varphi)$	$\cos\varphi$	$2p_x$
2	1	-1		$R_2 \rho$	$\sin\theta$	$\exp(-i\varphi)$	$\sin\varphi$	$2p_y$
3	0	0	$2/\sqrt{3}$	$R_3 (27-18\rho+2\rho^2)$				3s
3	1	0	$\sqrt{2}$	$R_3 (6\rho-\rho^2)$	$\cos\theta$			$3p_z$
3	1	+1		$R_3 (6\rho-\rho^2)$	$\sin\theta$	$\exp(+i\varphi)$	$\cos\varphi$	$3p_x$
3	1	-1		$R_3 (6\rho-\rho^2)$	$\sin\theta$	$\exp(-i\varphi)$	$\sin\varphi$	$3p_y$
3	2	0	$1/\sqrt{6}$	$R_3 \rho^2$	$3\cos^2\theta -1$			d_{z^2}
3	2	+1		$R_3 \rho^2$	$\sin\theta \cos\theta$	$\exp(+i\varphi)$	$\cos\varphi$	d_{xz}
3	2	-1		$R_3 \rho^2$	$\sin\theta \cos\theta$	$\exp(-i\varphi)$	$\sin\varphi$	d_{zy}
3	2	+2	$1/\sqrt{2}$	$R_3 \rho^2$	$\sin^2\theta$	$\exp(+i2\varphi)$	$\cos2\varphi$	$d_{x^2-y^2}$
3	2	-2	$1/\sqrt{2}$	$R_3 \rho^2$	$\sin^2\theta$	$\exp(-i2\varphi)$	$\sin2\varphi$	d_{xy}

$$R_1 = \frac{1}{\sqrt{\pi}} a_o^{-3/2} \exp(-\rho)$$

$$R_2 = \frac{1}{8\sqrt{\pi}} a_o^{-3/2} \exp(-\rho/2) \qquad \rho = \frac{r}{a_o}$$

$$R_3 = \frac{1}{81\sqrt{\pi}} a_o^{-3/2} \exp(-\rho/3)$$

The surfaces where the orbitals have zero value are called *nodal surfaces*. Looking the form of functions in Table 2.1 it is clear that the nodal surfaces depend on r, φ and θ functions:

- R_1, R_2 and R_3 functions have only one nodal surface in the infinity, the polynomials have $n-l-1$ nonzero solutions; since the points with the same r value build a sphere, an orbital has $n-l$ spheric nodal surfaces, one of them is in the infinity;

- although the points with common θ build a cone, $\sin\theta$ is zero at 0° or 180° but according to the definition this is neither a plane nor a surface, only the z axis; $\cos\theta$ is zero at 90° and define nodal plane or cone(s) (see e.g. the $\psi(3,2,0)$ function); the total number of conic nodal surfaces is $l - |m|$;

- the points with common polar angle φ build planes; $\sin\varphi=0$ defines the xz plane, while $\cos\varphi=0$ the yz one; the number of planar nodal surfaces is $|m|$.

Summing up the nodal surfaces of an orbital we have for the sum $n-1$. The shapes of the orbitals of hydrogen atoms are presented in Fig. 2.3.
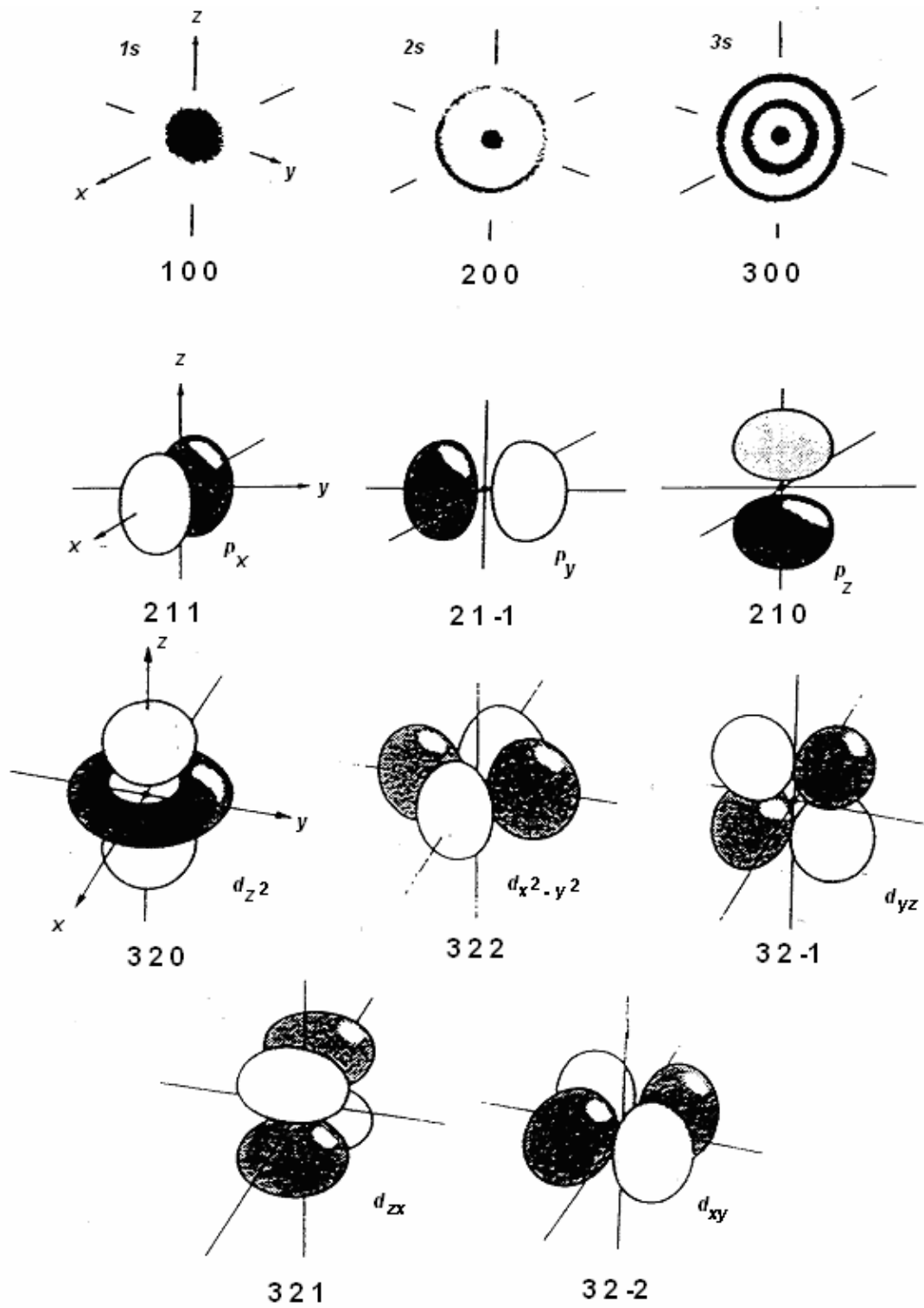
Fig. 2.3

It is interesting to denote, that the electrons have *finite charge densities at the place of the nucleus* (e. g. *s* electrons, see Table 2.1 and Fig. 2.3.

2.2.2 Angular and magnetic moments of the hydrogen atom

The energy levels of the hydrogen atom are degenerated. If an external electric (**E**) or magnetic (**B**) field acts on the atom, the levels split (the direction of the external field is regarded always as z). Vectors in this case can be defined by their absolute value and their z component.

The eigenfunction of the square of the *orbital angular moment operator* ($\hat{\mathbf{l}}$) act on the angular part of the energy eigenfunction

$$\hat{\mathbf{l}}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m \tag{2.11}$$

Therefore we have for the absolute value of the orbital angular moment operator

$$l = \sqrt{l(l+1)}\hbar = l^* \hbar \tag{2.12}$$

The z component of **l** has the same eigenfunction as $\hat{\mathbf{l}}^2$, so

$$\hat{l}_z Y_l^m = m\hbar Y_l^m \tag{2.13}$$

The possible values of l_z are

$$l_z = m\hbar \tag{2.14}$$

Both l and l_z are quantified, therefore both the absolute value of the orbital angular moment (by l)and its direction (by m) are quantified.

If e.g. l=3, then $l^*=\sqrt{12}$, and the possible values of m are 3, 2, 1, 0, -1, -2 and -3. The corresponding angles are calculated like

$$\alpha = \arccos\left(\frac{m}{l^*}\right)$$

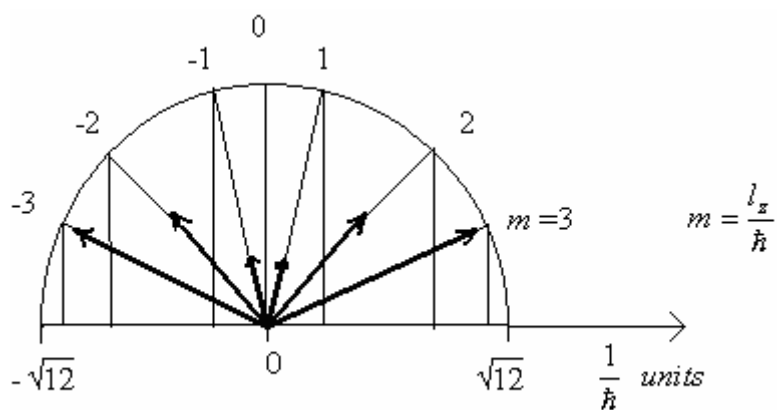Fig. 2.4 and Table 2.2 introduce the results.

Fig. 2.4

Table 2.2
The possible directions and relative values of l_z if $l=3$

m	$\dfrac{l_z}{\hbar}$	angle (**B**, **l**)
3	$\dfrac{\sqrt{3}}{2}$	30.0º
2	$\dfrac{1}{\sqrt{3}}$	54.7º
1	$\dfrac{1}{\sqrt{12}}$	73.2º
0	0	90.0º
-1	$\dfrac{1}{\sqrt{12}}$	106.8º
-2	$\dfrac{1}{\sqrt{3}}$	125.3º
-3	$\dfrac{\sqrt{3}}{2}$	150.0º

The *orbital magnetic moment* is (see Eq. 1.28)

$$m = -\mu_B l^* \tag{2.15}$$

and its z component is like Eq. 2.15

$$m_z = -\mu_B m \tag{2.16}$$

The *spin angular moment* (see Eqs. 1.24 and 1.25) is similarly determinable knowing the eigenvalue equation

$$\hat{s}^2 \varphi(\sigma) = s(s+1)\hbar \varphi(\sigma) \tag{2.17}$$

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with the "spin coordinate" σ, the spin quantum number s and the eigenfunction φ. The eigenvalues of s are

$$s = \sqrt{s(s+1)}\hbar = s^*\hbar \qquad (2.18)$$

the only value of the quantum number s is $1/2$. The eigenvalues of the z component of the spin is determined with the help of Eq. 2.11,

$$\hat{s}_z \varphi(\sigma) = m_s \hbar \varphi(\sigma) \qquad (2.19)$$

and its absolute value is

$$s_z = m_s \hbar \qquad (2.20)$$

Since $-s \leq m_s \leq +s$, the *spin magnetic quantum number* has only two values: -1/2 and +1/2. The corresponding magnetic spin moment is

$$m_s = -2\mu_B s^* \qquad (2.21)$$

and its z component has the form

$$m_{s,z} = -2\mu_B m_s \qquad (2.22)$$

The *total angular moment of the electron* is the sum of the orbital angular moment and the spin:

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \qquad (2.23)$$

Solving the eigenvalue equation of $\hat{\mathbf{j}}^2$ we have

$$j = \sqrt{j(j+1)}\hbar = j^*\hbar \quad (j = l + s) \qquad (2.24)$$

j is the *total angular moment quantum number*. For the z component we have

$$j_z = m_j \hbar \qquad \left(-j \leq m_j \leq +j\right) \qquad (2.25)$$

and m_j is the corresponding magnetic quantum number. Of course, the magnetic moments can be also calculated, similarly to Eqs. 2.16 and 2.17.

The *nuclear spin (*if it exists, see Section 1.4.1) has the eigenvalue equation

$$\hat{\mathbf{I}}^2 \psi = I(I+1)\hbar^2 \psi \qquad (2.26)$$

with *I,* the *nuclear spin quantum number.* The absolute value of the nuclear spin is

$$I = \sqrt{I(I+1)}\hbar = I^*\hbar \qquad \text{for hydrogen } I = \frac{1}{2} \qquad (2.27)$$

The z component of the nuclear spin has the eigenvalues

$$I_z = M_I \hbar \qquad \left(-I \leq M_I \leq +I\right) \qquad (2.28)$$

For hydrogen $M_I = -\frac{1}{2}, +\frac{1}{2}$. The corresponding *nuclear magnetic moment* has the eigenvalues

$$M_I = g_p \mu_N I^*$$ (2.29)

g_p is the Landé factor of the proton, its z component is

$$M_{I,z} = g_p \mu_N M_I$$ (2.30)

Table 2.3. gives a general survey on the electron moments.

Table 2.3.
Electron moments, a survey.

Variable	Nomination [1]	Equation [2]
Mechanic moment operator vector	$\hat{\mathbf{o}}$	
Eigenvalue equation		$\hat{\mathbf{o}}^2 \psi = o(o+1)\hbar^2 \psi$
Moment vector	$\mathbf{o}$	
Absolute value	o	$o = \sqrt{o(o+1)}\hbar = o^*\hbar$
Quantum number	o	
z component operator	$\hat{\mathbf{o}}_z$	$\hat{\mathbf{o}}_z \psi = m\hbar\psi$
Magnetic quantum number	m	
Absolute value	o_z	$o_z = m\hbar$
Magnetic moment operator vector	$\hat{\mathbf{q}}$	
Eigenvalue equation		$\hat{\mathbf{q}}^2 \psi = \alpha^2 \mu_B^2 o(o+1)\psi$
Moment vector	$\mathbf{q}$	
Absolute value	q	$q = \alpha\mu_B o^*$
z component operator	$\hat{\mathbf{q}}_z$	
Eigenvalue equation		$\hat{\mathbf{q}}_z \psi = \alpha\mu_B m\psi$
Absolute value	q_x	$q_z = \alpha\mu_B m$

[1] Orbital angular moments are labelled with **l;**
orbital magnetic moments are labelled with **m;**
spin angular moments are labelled with **s;**
spin magnetic moments are labelled with **m_s.**
Eigenfunction for orbital moments is Y_m^l;
eigenfunction for spin moments is labelled with φ.

[2] α is for orbital electron moments -1,
for spin electron moments -2.

2.2.3 Selection rules for the hydrogen spectrum

The necessary conditions for the generation of the hydrogen spectrum are

- energy difference between the ground and excited states; this difference is equal to the energy of the photon:

$$\Delta E = E_i - E_j = h\nu \tag{2.31}$$

- the transition moment vector (Eq. 1.46) is not zero:

$$\mathbf{P} = \int \psi_i^* \Delta\mathbf{p}\psi_j \, d\tau \neq 0 \tag{2.32}$$

The change in the dipole moment is in the case of one electron

$$\Delta\mathbf{p} = -e\Delta\mathbf{r} \tag{2.33}$$

Its Cartesian components of Eq. 2.33 are

$$\Delta p_x = -e\Delta r \sin\theta \cos\varphi \tag{2.34}$$
$$\Delta p_y = -e\Delta r \sin\theta \sin\varphi \tag{2.35}$$
$$\Delta p_z = -e\Delta r \cos\theta \tag{2.36}$$

The space element is

$$d\tau = r^2 \sin\theta \, d\varphi d\theta dr \tag{2.37}$$

Considering Eqs. 2.34-2.37 we have for the components of the transition moment vector

$$P_x = -e\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_i^*(r,\varphi,\theta)\psi_j(r,\varphi,\theta)r^2 \Delta r \sin^2\theta \cos\varphi \, d\varphi d\theta dr \tag{2.38}$$

$$P_y = -e\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_i^*(r,\varphi,\theta)\psi_j(r,\varphi,\theta)r^2 \Delta r \sin^2\theta \sin\varphi \, d\varphi d\theta dr \tag{2.39}$$

$$P_x = -e\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_i^*(r,\varphi,\theta)\psi_j(r,\varphi,\theta)r^2 \Delta r \sin\theta \cos\theta \, d\varphi d\theta dr \tag{2.40}$$

The part of the integrands depending on the angle coordinates determine the zero (or non-zero) values of the transition moment vector.

Integrating with respect to θ from 0 to π
        all integer powers of $\sin\theta$ the result non-zero,
        for the even powers of $\cos\theta$ the result is non-zero,
        for its odd powers the result is zero.
Integrating with respect to φ from 0 to 2π
        even powers of $\sin\varphi$ the result non-zero,

for its odd powers the result is zero,
even powers of $\cos \varphi$ result non-zero,
for odd powers of $\cos \varphi$ the result result zero.

For excitation of the hydrogen atom from the 1s state (100) to the 2s state (200) the angular function part of the Eqs. 2.38-2.40 (see Table 2.1 for the eigenfunctions)

for the x component: $\sin^2\theta\cos\varphi$ the integral is zero
for the y component: $\sin^2\theta\sin\varphi$ the integral is zero
for the z component: $\sin\theta\cos\theta$ the integral is zero

there is no transition. It should be so, since $\Delta l = 0$.

For excitation of the hydrogen from the 1s state (100) to the $2p_X$ state (211) the angle function part of the Eqs. 2.38-2.40 (see Table 2.1 for the eigenfunctions)

for the x component: $\sin^3\theta\cos^2\varphi$ the integral is non-zero
for the y component: $\sin^3\theta\sin\varphi\cos\varphi$ the integral is zero
for the z component: $\sin^2\theta\cos\theta\cos\varphi$ the integral is zero

therefore the direction of the transition is x.

Similarly, one can find for the transition for 1s state to $2p_y$ one, this direction is y, for the transition for 1s state to $2p_Z$ one the direction is z.
The general result for the *selection rules* is

$$\Delta l = \pm 1$$
$$\Delta n \neq 0$$

The first rule allows the transition. The second one is necessary for having energy difference between the ground and the excited states of hydrogen. If Δn=0, transition does not exist.

2.2.4 The electronic spectrum of the hydrogen atom

The hydrogen atom can be excited in an electric arc or with discharges. According to Eq. 2.7 the necessary wavenumber of the *spectral line* is

$$\tilde{\nu} = \frac{\Delta E}{hc} = R_H \left(\frac{1}{n_j^2} - \frac{1}{n_i^2} \right) \qquad n_i > n_j \qquad (2.41)$$

The corresponding spectral lines can be ranged into *series*. In a given series the n_j quantum number does not change, i.e. this is the ground state. The distance between the neighbouring lines decreases and there is a limit of such a series at $n_i \rightarrow \infty$ and therefore

$$\tilde{\nu}_{\lim it} = T_j = \frac{R_H}{n_j^2} \qquad (2.42)$$

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The T_i like expressions are called *spectral terms*. The wavenumber of the spectral line is the difference between such kind terms.

The most important spectral line series of the hydrogen atom are listed in Table 2.4., Fig. 2.5 introduces the electronic spectrum of the hydrogen atom, and the series are also shown (the positions of the lines are given in wavelengths)

Table 2.4
The spectral series of the hydrogen atom

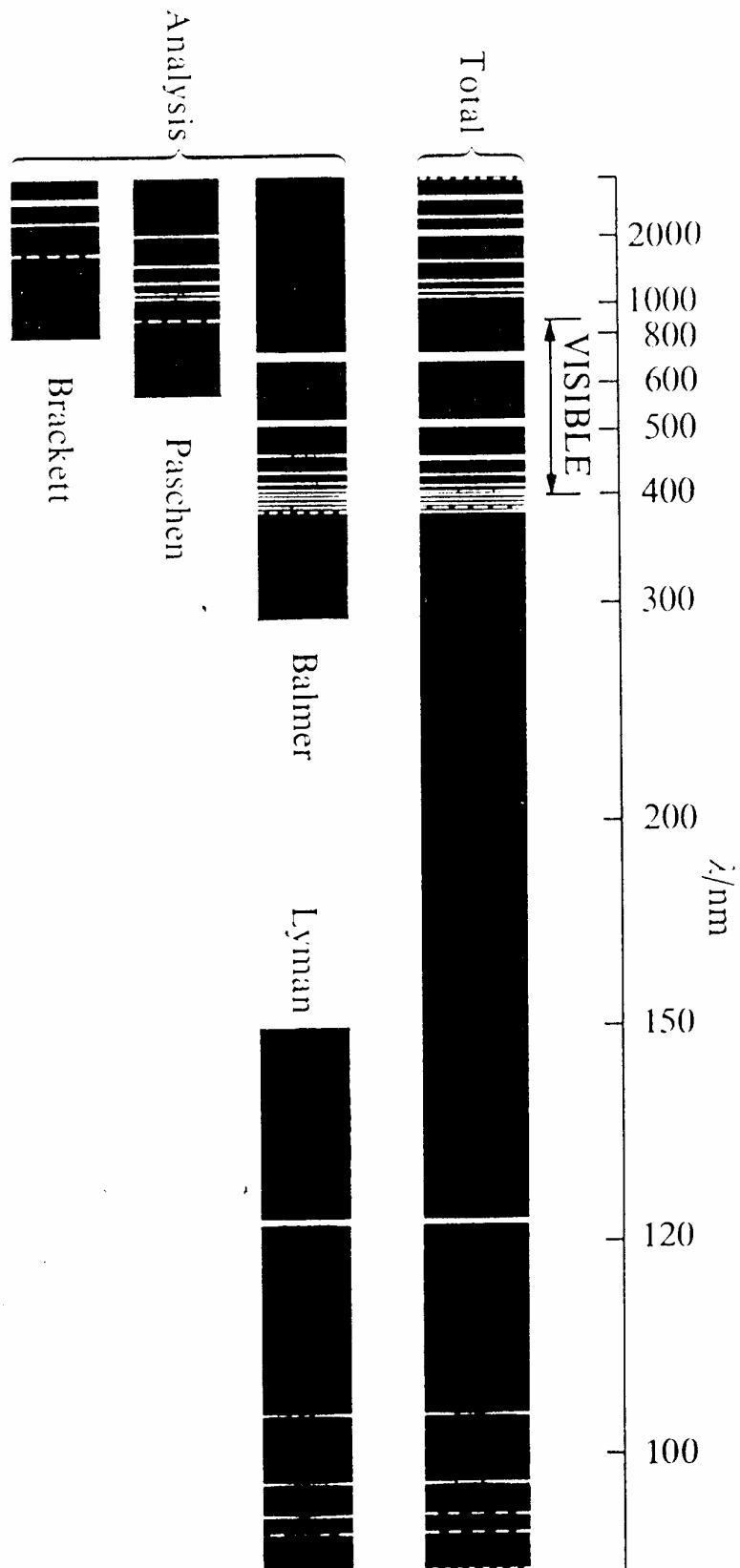| n_i	name of the series	spectral region
1	Lyman	ultraviolet (UV)
2	Balmer	visible (VIS)
3	Paschen	infrared (IR)
4	Brackett	infrared
5	Pfundt	infrared

Fig. 2.5

2.3 Many-electron atoms

If the atomic number is greater than one, more than one electron move around the nucleus. These electrons do not move independently. There are electric and magnetic interactions between the individual electrons of the electron cloud.

Hydrogenic atoms (or ions) have only one electron on their external shell. For these atoms the hydrogen model is a good approximation.

All other atoms are far from this model, their description is very complicate.

2.3.1 Hydrogenic atoms

Extending Eq. 2.7 to these atoms we have

$$E_n = -\frac{z^2 hc R_H}{n^2} = -hc\frac{R_z}{n^2} \tag{2.43}$$

where R_z is the Rydberg constant for the atom with atomic number z.

Practically, comparing this eqution with the data of the measured spectra, it is rigorously not valid. The positions (wavenumbers) of the lines can be describe with the equation

$$\tilde{v} = R_z\left[\frac{1}{(n_j - a_j)^2} - \frac{1}{(n_i - a_i)^2}\right] \tag{2.44}$$

In some cases one have to substitute two different but very close numbers for the constants a_j and a_i to describe the real positions of the spectral lines. The bands described by Eq. 2.44 build series with constant n_j. Becouse of the corrections also $n_j > n_i$ is possible.

Alkali metal atoms with one s electron on their external shell approach quite well the hydrogenic atom model. The most important spectral series of the alkali metal atoms are listed in Table 2.5.

Table 2.5
Spectral series of alkali metal atoms

name of the series	n_j	n_i
*p*rincipal	4	>4
*s*harp	4	>4
*d*iffuse	4	>4
*f*undamental	3	>3

2.3.2 Other many-electron atoms

Strong electron interactions exist in open (not absolutely closed) electron shells and clouds. The Hamilton operator of a many-electron system can be written in the following form:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla^2 - \sum_i \frac{ze^2}{r_i} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \qquad (2.45)$$

the sums are extended over all electrons, r_i is the electron-nucleus distance, r_{ij} is the electron-electron one. The first term in Eq. 2.45 is the kinetic energy operator (∇ is the nabla operator), the second is the potential energy of the electron-nucleus interactions, while the third one gives the same for the electron-electron interactions. The atomic energy of these atoms depends also on the angular moment quantum number *l*.

The quantum mechanical calculations resulted the following energy level series for the subshells:

$$E_{1s} < E_{2s} < E_{2p} < E_{3s} < E_{3p} < E_{4s} < E_{3d} < E_{4p} < E_{5s}... \qquad (2.46)$$

According to *Hund's rule* the atom in its ground state adopts the greatest possible number of unpaired electrons.

The electron configuration of the atoms is labelled with giving the value of the principal quantum number, the letter for the orbital angular quantum number *l*, and its superscript is the number of electrons in the subshell, e.g. the electron configuration of the sulfur atom in its ground state is $1s^2 2s^2 p^6 3s^2 p^4$. Labelling the orbitals with squares and the spin directions with arrows, we have

1s	2s	2p	2p	2p	3s	3p	3p	3p
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑

The *moments of the many- electron atoms* are the vector sums of the individual moments.

The *total orbital angular moment of all the electrons* is

$$\mathbf{L} = \sum_i \mathbf{l}_i \qquad (2.47)$$

Similarly to the Eq. 2.13 we have for the absolute value of this orbital angular momentum for all electrons

$$L = \sqrt{L(L+1)}\hbar = L^*\hbar \qquad (2.48)$$

For two electrons $\mathbf{L} = \mathbf{l_1} + \mathbf{l_2}$ and also for more electrons one have to add them as vectors. There exists also the corresponding magnetic quantum number M_L, like Eq. 2.15. The states with different values of L are labelled with capitals (like the subshells according to l):

$L =$	0	1	2	3	4	5	etc.
label	S	P	D	F	G	H	etc.

The *spin vector for all electrons* of the atom is also the vector sum of the individual spin vectors:

$$\mathbf{S} = \sum_i \mathbf{s}_i \qquad (2.49)$$

and its absolute value is

$$S = \sqrt{S(S+1)}\hbar = S^*\hbar \qquad (2.50)$$

S is the *spin orbital quantum number* of all electrons. For two electrons S = 1 or 0. The z component of $\mathbf{S}$ is determined by the magnetic quantum number for all electrons M_S, like Eq. 2.20.

The calculation of the *total angular moment for all electrons* $\mathbf{J}$ depends on the type of interactions. Two types of electron-electron interactions exist:

A. electrostatic interactions
B. magnetic (spin-orbital) interactions

If the atomic number z < 30 then A>B, case ①, (for Zn z=30)
if the atomic number z ≥ 30 then B>A, case ②.

① This is the *Russel-Sounders* or *ls coupling*. The total angular moment for all electrons is the vector sum of $\mathbf{L}$ and $\mathbf{S}$:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \qquad (2.51)$$

and

$$J = \sqrt{J(J+1)}\hbar = J^*\hbar \qquad J = L+S, L+S-1, ..., |L-S| \qquad (2.52)$$

Its z component is

$$J_z = M_J\hbar \qquad -J \le M_J \le +J \qquad M_J = M_L + M_S \qquad (2.53)$$

The quantity

$$\begin{aligned} \iota &= 2S+1 \qquad (L \ge S, \text{usually}) \\ \iota &= 2L+1 \qquad (L < S, \text{very rarely}) \end{aligned} \qquad (2.54)$$

is the *multiplicity* of the state. The names of the states are: if $\iota=1$ this is a singlet state, if $\iota=2$ this is a doublet one, if $\iota=3$ this is a triplet one, etc.

② This is a *jj coupling*. The total angular moment for all electrons is the sum of the total angular moments of the individual electrons:

$$\hat{\mathbf{J}} = \sum_i \hat{\mathbf{j}}_i \quad \text{for two electrons:} \quad J = j_1 + j_2, j_1 + j_2 - 1, ..., |j_1 - j_2| \qquad (2.55)$$

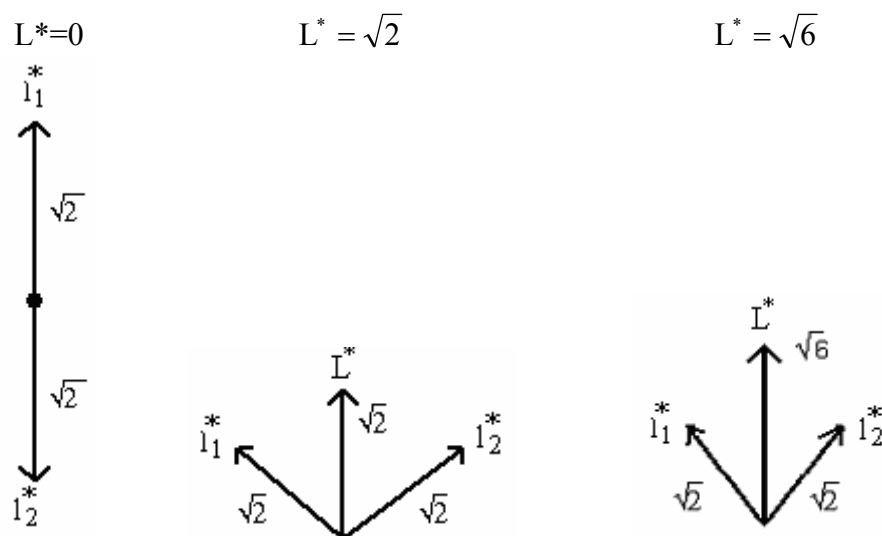*Example:* the electron states of two *p* electrons, *ls* coupling.
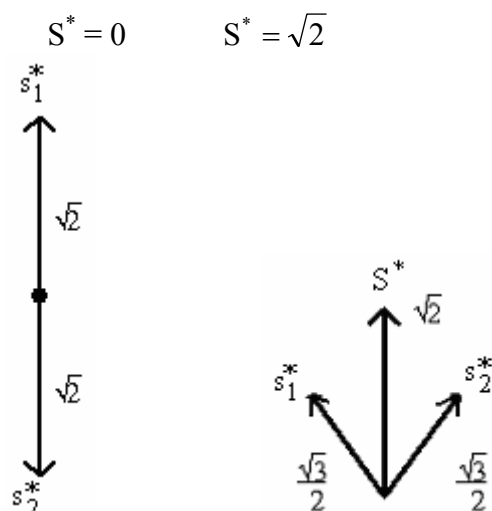The individual quantum numbers:

<div align="center">

first electron   second electron

</div>

$$l_1 = 1 \quad l_1^* = \sqrt{2} \quad s_1 = \frac{1}{2} \quad s_1^* = \frac{\sqrt{3}}{2} \qquad l_2 = 1 \quad l_2^* = \sqrt{2} \quad s_2 = \frac{1}{2} \quad s_2^* = \frac{\sqrt{3}}{2}$$

The quantum numbers for all electrons:

$$L = 0, 1, 2 \qquad L^* = 0, \sqrt{2}, \sqrt{6} \qquad S = 0, 1 \qquad S^* = 0, \sqrt{2}$$

The possible vector sums of the angular moments and spins are (in $\hbar$ units):

$$S^* = 0 \qquad S^* = \sqrt{2}$$

The combination of the orbital and spin moments is not arbitrary. Symmetric orbital moments (L is even, in our case L=0,2) can be combinated only with antisymmetric spin moments (the electron spins have opposite directions, in our case S=0) and antisymmetric orbital moments L is odd (in our case L=1) can be combinated with symmetric spin moments (the spin moments are parallel, in our case S=1).

 The possible combinations of the two moments are L=0 & S=0, L=1 & S=1, L=2 & S=0.

 The effect of the interactions are the following. Labelling of the states: label of the total orbital angular moment, its left superscript is value of the multiplicity ι, its right subscript is the value of total angular quantum number J).

the angular moment	S		P		D
electrostatic interaction	^1S		^3P		^1D
magnetic interaction (spin-orbit interaction)	$^1S_0$	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$
external magnetic field (possible values of M_J)	0	0	-1,0,1	-2,-1,0,1,2	-2,-1,0,1,2

The possible vector sums are as follows (for $^1S_0$ both vector terms are zero):

40
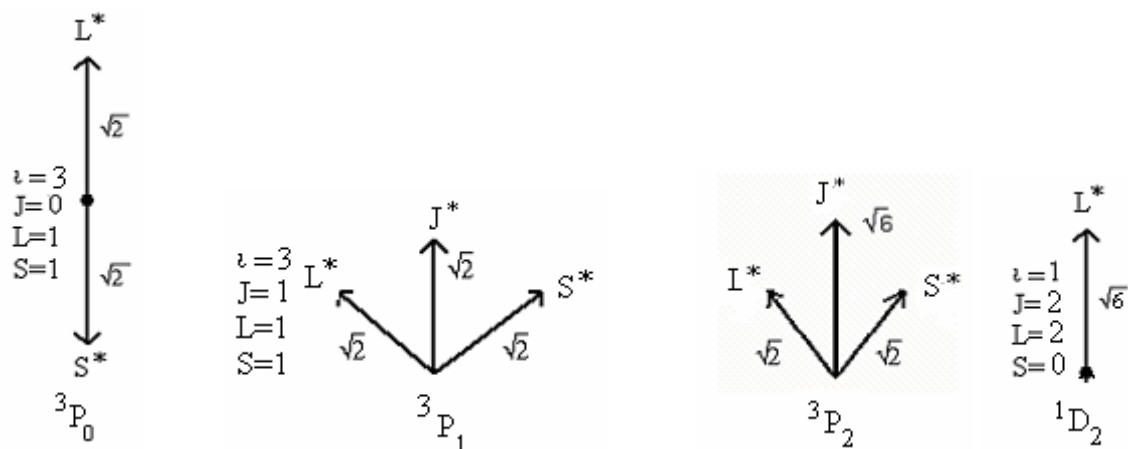
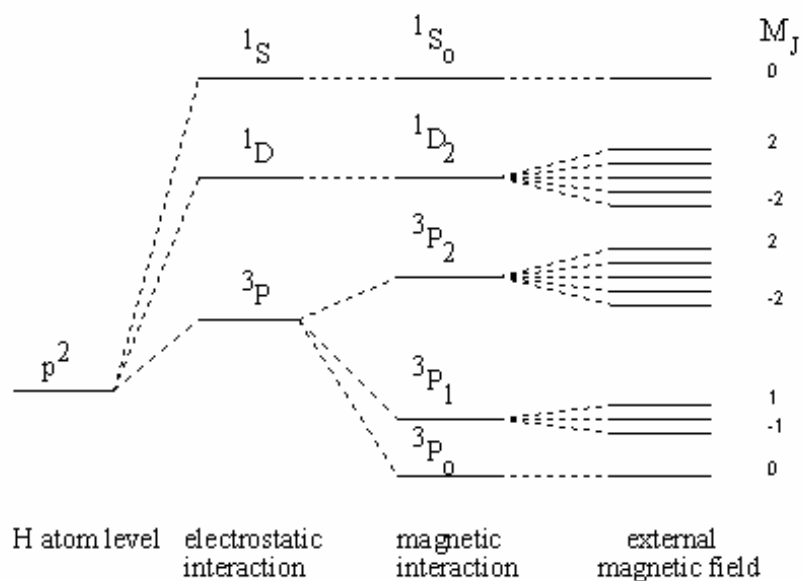According to this example the energy levels are shown in Fig. 2.6.

Fig. 2.6

2.3.3 Interaction with external magnetic field

The energy of the electron states (E_0, without interactions) depends on the electrostatic interactions (on J*) and in the presence of weak or modest magnetic fields B on M_J:

$$E = E_o + \frac{1}{2} A(J^*)^2 + g\mu_B M_J B \tag{2.56}$$

$\underline{A}$ is a coupling constant, g is the Landé factor:

$$g = 1 + \frac{(J^*)^2 + (S^*)^2 - (L^*)^2}{2(J^*)^2} \tag{2.57}$$

The electronic levels split according to M_J quantum number (see e.g. Fig. 2.6) to $2M_J+1$ levels. This effect is the *Zeeman effect.*

The *Landé factor of a free electron* is ($l = 0$, $s = \frac{1}{2}$, $j = \frac{1}{2}$, $l^* = 0$, $s^* = \frac{\sqrt{3}}{2}$, $j^* = \frac{\sqrt{3}}{2}$) applying Eq. 2.57 g = 2.

In the case of strong magnetic field the magnetic interactions dominate (*jj* coupling):

$$E = E_o + AM_L M_S + g(M_L + 2M_S)B \tag{2.58}$$

This very strong splitting is the *Paschen-Back effect.*

The energy levels of the nucleus splits similarly in magnetic field:

$$E = E_o - g_N \mu_N M_I B \tag{2.59}$$

The splitting of the energy levels in external magnetic field is important in the methods of nuclear magnetic resonance and electron spin (paramagnetic) resonance.

2.3.4 Interaction with external electric field

In external electric field (E) the electronic energy levels also split but according to the equation

$$E = E_o + \frac{1}{2} E^2 \left[a + 2b \left(M_J^2 - \frac{1}{3} (J^*)^2 \right) \right] \tag{2.60}$$

a and b are constant. In this *Stark effect* the levels splits only according the absolute values since the M_J quantum number is squared. The levels split to M_J+1 ones.

2.3.5 Interpretation of the electronic spectra

The *emission* of the photon is either *spontaneous* or *induced* (see Section 1.2). The excitation with photons is called *absorption* (Fig. 2.7). Beside the photon absorption (optical excitation) the excitation is possible with electric energy, with collisions and with thermal energy.

E_i^* excited state

absorption   emission
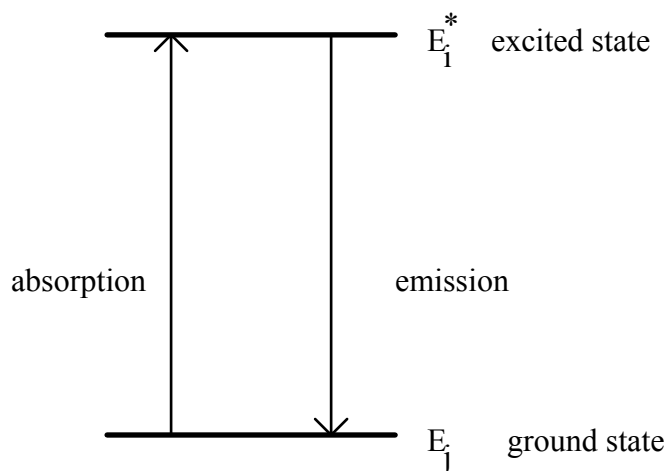
E_j ground state

Fig. 2.7

The absorption and the emission is possible if the transition moment is not zero. Table 2.5 shows the selection rules for one-electron and for many-electron atoms. These selection rules are strictly only for electrostatic interactions valid. If the magnetic (spin-orbit) coupling is strong, the $\Delta S > 0$ is also possible.

We shall studied the structure of the spectrum of a many-electron atom on the example of potassium. The potassium is a hydrogenic atom. Its electron state is $1s^2 2s^2 p^6 3s^2 p^6 4s$. The atom has a closed Ar configuration and only one electron on the outside (valence) shell.

Table 2.6
Selection rules for one- and many-electron atoms

quantum number	one-electron	many-electron
Δn	$\neq 0$	
Δl or ΔL	± 1	$0, \pm 1$
Δs or ΔS	0	0
Δj or ΔJ	$0, \pm 1$	$0, \pm 1$
Δm_j or ΔM_J	$0, \pm 1$	$0, \pm 1$

Therefore the characteristic quantum numbers are: $L = l = 0$, $S = s = \dfrac{1}{2}$, $\iota = 2$, $J = j = \dfrac{1}{2}$.
The possible spectral series are (see Section 2.3.1, Table 2.5 and Fig. 2.8):

sharp series $\quad\quad$ $S \rightarrow P$ $\quad\quad$ $^2S_{1/2} \rightarrow {}^2P_{1/2}, {}^2P_{3/2}$ $\quad\quad$ $\Delta J = 0, +1 \quad \Delta L = +1$

principal series $\quad$ $P \rightarrow S$ $\quad\quad$ $^2P_{1/2}, {}^2P_{3/2} \rightarrow {}^2S_{1/2}$ $\quad\quad$ $\Delta J = -1, 0 \quad \Delta L = -1$

diffuse series $\quad\;$ $D \rightarrow P$ $\quad\quad$ $^2D_{3/2} \rightarrow {}^2P_{3/2}, {}^2P_{1/2}$ $\quad\quad$ $\Delta J = -1, 0 \quad \Delta L = -1$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $^2D_{5/2} \rightarrow {}^2P_{3/2}$ $\quad\quad\quad$ $\Delta J = -1 \quad\quad \Delta L = -1$

fundamental series $\;$ $F \rightarrow D$ $\quad\quad$ $^2F_{5/2} \rightarrow {}^2D_{5/2}, {}^2D_{3/2}$ $\quad\quad$ $\Delta J = -1, 0 \quad \Delta L = -1$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $^2F_{7/2} \rightarrow {}^2D_{5/2}$ $\quad\quad\quad$ $\Delta J = -1 \quad\quad \Delta L = -1$

The line of the sharp and the principal series split into 2 lines (doublets), those of the diffuse and the fundamental series split into three lines (triplets). $\Delta L = 0$ transition does not appear, since only one electron is in the valence shell in excited state. The addition of the orbital angular and spin angular moment to the total angular moment is similar like in the case of the example in Section 2.3.2.

Fig. 2.8 presents the term diagram (Grotrian diagram) of the potassium spectrum. You can find the transitions of the mentioned series, the lines of the series and their sum, the electronic emission spectrum.

Generally the interpretation is very difficult. In the case of *jj* coupling the theoretical interpretation is quite impossible.

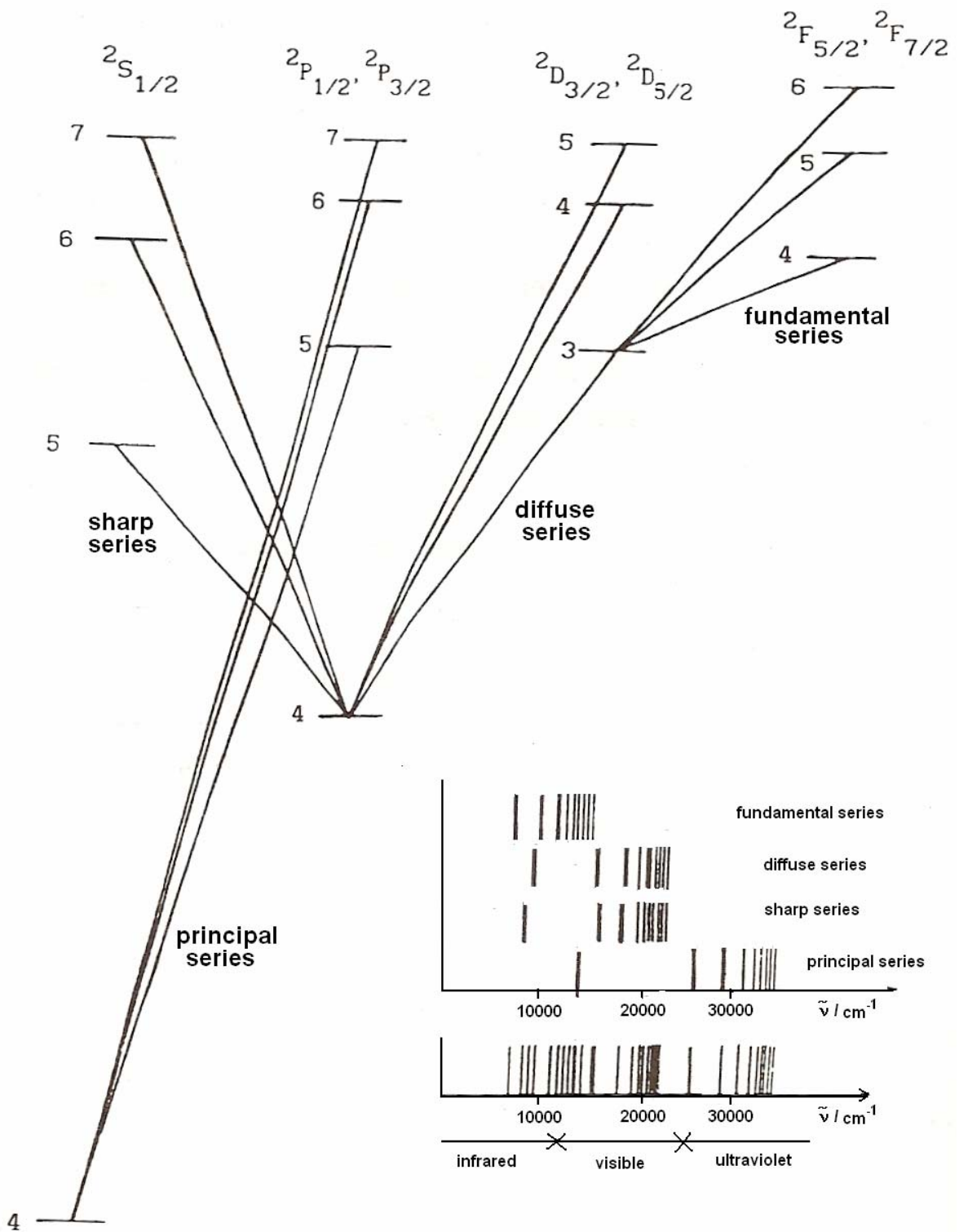If the atom will be ionized the resulted ion has an absolutely different spectrum.

Fig. 2.8

2.3.6 The measurement of the atomic spectra

Fig. 2.9 shows the scheme of an *emission spectrometer.* The computer controls the system and stores the measured data. The excited sample emits the spectrum. The monochromator resolves the spectrum, the computer controls the monochromator by stepwise turning the grating (see Section 1.5). The detector detects the optical signal and transforms it into electric one. The electronics under the control of the computer forms the signal and transfers it to the computer (data acquisition).
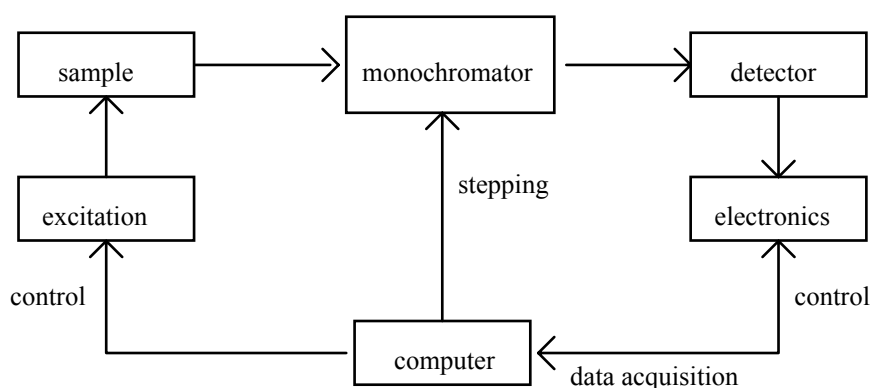

Fig. 2.9

Fig. 2.10 is the scheme of an *absorption spectrometer*. The difference between the emission and the absorption spectrometer (with monochomator) in the sample handling. At the emission spectrometer the sample is the light source, here is the sample passive and a light source transilluminates it. The transmitted light will be detected. The control and the data acquisition is like at the emission spectrometer. Mostly double-beam absorption spectrometers are applied, i.e. the sample and the reference are parallelly measured, the absorption of the sample is related to the that of the reference.
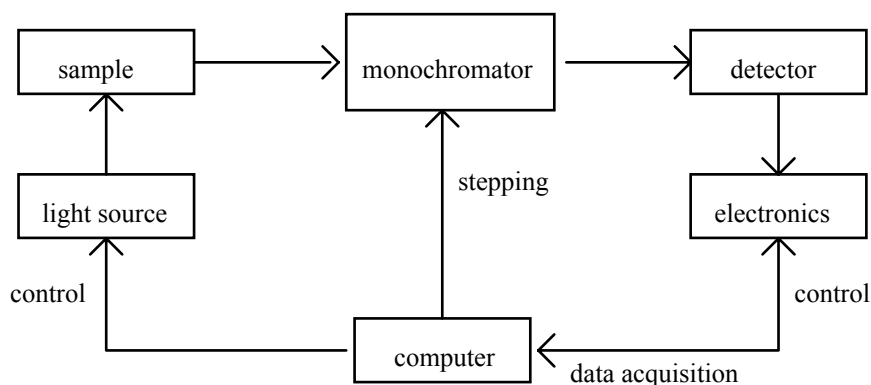

Fig. 2.10

Light sources
  -emission: the sample itself , atomic emission spectroscopy, AES
      - - in a graphite furnace;
      - - in electric arc;
      - - in flame (gas torch), developed to flame photometry;

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- - in electric spark;
- - excitation in discharging tubes, developed inductively coupled plasma spectroscopy, ICP, the most developed method;
- - excitation with electron beam.
- *absorption: atomic absorption spectroscopy, AAS*
- - tungsten or halogen lamp in the visible region;
- - SiC bar in the infrared region;
- - ceramic bar in the IR region;
- - high pressure mercury lamp in the far IR region;
- - low pressure D_2 discharging lamp in the UV region;
- - high pressure Xe lamp for fluorescence spectra;
- - selective discharging lamps for selective measurements.

monochromator (see Section 1.5): it resolves the spectrum using a (reflecting) grating or a prism, that is transparent in the investigated region (or a Fourier transform spectrometer is used).

detector: transforms the optical signal to electric one.
- photocell, photodiode, photodiode array, photomultiplier (PMT: photo-multiplier tube), photoelement in the UV and VIS regions, CCD (charge-coupled device);
- thermoelement in the VIS and IR regions;
- piezoelectric crystal, Golay cell (IR, far IR);
- chilled semiconductor detectors (IR, near IR).

electronics: signal elaboration (signal difference for double-beam spectrometers, amplitude or phase modulation, amplification), digital computer, printer and plotter.

The spectral information:
- *frequency*, i.e. position of the line;
- *intensity,* i.e. area of the line;
- *profile or shape* of the line.

Applications of the atomic spectra: mostly quantitative and qualitative chemical analysis, rarely physics (theory of atomic structure).

2.4 Ions

This chapter deals beside the atomic ions also with the molecular ions.

2.4.1 Ionization

The generation of positive ions is called *ionisation,* e.g. the ionization of the neutral atom A is

$$A - e^- = A^+ \qquad\qquad (2.61)$$

The *external* (outside) *ionization* is the removing of an electron from the outmost (valence) shell of the atom. *Internal* (inner) *ionization* is the removing of an electron from the core (inner electron shells) of the atom.

The *electron gain* is the building of a negative (or more negative) ion by receiving an electron:

$$A + e^- = A^-$$
$$A^- + e^- = A^{2-}$$
(2.62)

The *ionization energy* of an atom (I) is the necessary energy to remove an electron from an atomic (molecular) orbital. Table 2.7 contains the first (lowest) and second ionization energies of some atoms.

Table 2.7
First and second ionization energies of some atoms (kJ mol^{-1})

atom	I_1	I_2	atom	I_1	I_2
H	1312.0	-	Li	513.3	7298.0
Li	513.3	7298.0	Be	899.4	1757.1
Na	495.8	4562.4	B	800.6	2427.0
K	418.8	3051.4	C	1086.2	2352.0
Rb	403.0	2632.1	N	1402.3	2856.1
Cs	375.5	2420.0	O	1313.9	3388.2
			F	1681.0	3374.0
			Ne	2080.6	3952.2

In the first column of the periodic table the first ionization energies decrease with the increasing atomic number since the valence shell is more and more far away form the nucleus and the core electron shell shields the nuclear charge. The same is the situation with the second ionisation energy that is higher since the removed electron is attracted by the positive ion. In the first row the first ionization energy increases since the nucleus became more and more positive; the second ionization energy has a jump from Li to Be since at the Li the electron must be removed form a closed shell, otherwise the tendency is the smilar to the first ionization.

The *electron affinity* (A) is the energy gain that we get if an electron is absorbed by an atom or a molecule. The ionization energies of the negative ions are equal with opposite sign to the electron affinity of the corresponding ion, e. g. for the oxygen atom:

$$I(O^-) = -A(O)$$
(2.63)

Table 2.8 contain the electron affinities for the first and the second electrons.

The hydrogen has very low electron affinity, fluorine and chlorine have higher ones and here is the maximum. The heavier halogens have lower and lower electron affinities. There were not found data in the literature for the second electron affinities of halogens. The electron affinities of the first row elements do not show a tendency.

Several methods exist for the ionization of atoms (A) and molecules (M). The most important methods are here listed.

Table 2.8
Electron affinities of some atoms (kJ mol^{-1})

atom	A_1	A_2	atom	A_1	A_2
H	72.8		Li	59.8	
F	322.0		Be	-18.0	
Cl	348.7		B	23.1	
Br	324.5		C	122.5	
I	295.3		N	-7.0	
At	270.5		O	140.9	-844.0
			F	322.2	
			Ne	-29.0	

1. *Collision in vacuum with high energy electrons.* This is a partly inelastic scattering (Section 1.2). The reactions of the process are (A atom, M molecule)

$$A + e^- = A^+ + 2e^- \qquad (2.64)$$

$$M + e^- = M^+ + 2e^- \qquad (2.65)$$
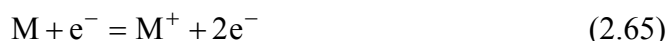
This is a widely applied method in mass spectroscopy, the *electron impact (EI) ionization.* During this ionization also the generation of negative ions is possible, e. g.

$$ABC + e^- = AB^- + C \qquad (2.66)$$

2. *Ionization with photons* (inelastic scattering with particle change). If the photon energy is higher than the ionization energy of the atom (molecule) the atom (molecule) will be ionized:

$$A + h\nu = A^+ + e^- \qquad (2.67)$$

In the spectrum at the frequency of the photon there is a break: the spectral line density increases and approaches a limit, at higher frequencies a diffuse region appears. This method is applied in the photoelectron spectroscopy (see Subsections 3.6.6 and 4.5.1).

3. *Penning ionization.* The atom A excited with photon absorption transfers its energy to atom B with collision (partly inelastic scattering). If the transferred energy is high enough the atom B will be ionized:

$$A^* + B = A + B^+ + e^- \qquad (2.68)$$

4. *Dissociative ionization.* The atom A excited with photon absorption collides with the molecule BC. The following reaction proceeds:

$$A^* + BC = AC^+ + B + e^- \qquad (2.69)$$

5. *Ionization through collision.* The excited atom A collides with atom B. The result is

$$A^* + B = A^+ + B + e^- \qquad (2.70)$$

or

$$A^* + B = A^+ + B^- \qquad (2.71)$$

6. *Associative ionization*. The excited atom A associates with atom B to a molecular ion:

$$A^* + B = AB^+ + e^- \qquad (2.72)$$

7. *Auger effect.* After an internal ionization there is an electron gap at an internal electron shell. This gap will be filled by an electron jump form a higher level. The energy difference between the two states can resulted in the emission of an X-ray photon or to a second ionization: to the emission of a second photon. The latter is the Auger effect (see also Subsection 4.5.2).

8. *Chemical ionization (CI)*. This is a special method for the ionization of molecules. A high velocity molecular ion (let us denote it with X^+) collides with the molecule M. The possible reaction are:

$$X^+ + M = X + M^+ \qquad (2.73)$$

$$X^+ + M = XM^+ \qquad (2.74)$$

If X contains hydrogen atoms (XH) then the reaction

$$XH^+ + M = X + MH^+ \qquad (2.75)$$

is also possible. The method is applied in the mass spectroscopy (Subsection 3.8).

9. *Fast atomic bombardment (FAB)*. This is also a special method for the ionization of molecules. The molecules are bombarded with high velocity atom or ion radiation (Ar, Xe, Cs^+). The method is applied in the mass spectroscopy (Subsection 3.8) and in the secondary ion emission spectroscopy (Subsection 4.5.3).

2.4.2 Interactions of ions

The interaction of ions with electromagnetic waves is similar to those of the neutral atoms. Similarly, spectral line series appear in the emission and absorption spectra of the ions. Both electric and magnetic fields act on the ions:

$$\mathbf{F} = Q\mathbf{E} \qquad (2.76)$$

$$\mathbf{F} = Q\mathbf{v} \times \mathbf{B} \qquad (2.77)$$

$\mathbf{F}$ is the acting force, $\mathbf{v}$ is the velocity of the ion. With the help of these equations the ions can be directly detected. Using the Lorentz force (Eq. 2.77) with constant $\mathbf{B}$ the particles can be separated by their velocities. Having the same Q charge (e.g. electrons) and different

velocities the particles are detectable with the same (in the space fixed) detector. They come after one other, according their velocity. This is the "time-of-flight" (TOF) detection method.

Changing the magnetic induction, particles with different velocity can be directed to the detector. This method is important in the mass spectroscopic (Subsections 3.8 and 4.5.3), and in the different electron spectroscopic methods (Subsections 3.6.6, 4.,4.4, 4.5.2).