

Chapter 3

STRUCTURE AND PROPERTIES OF MOLECULES

The *molecule* is a set of atoms those are in strong chemical connection to one another building a new substance.

There are three types of the strong interactions between atoms:

1. Several atoms give the same number of electrons for the system. These electrons belong to the full system, they are *delocalized*. They move practically without resistance in the system of atoms. This is the way of the building the *metal bond*, or the electron system of benzene ring.

2. One of the interacting atoms has low first ionization energy (e. g. an alkali metal), the second one has high electron affinity (e.g. a halogen element, Section 2.4.1). The electron transfer from the first atom to the second is easy. In this way an ion pair is formed. The two ions with opposite charges attract each other: we have an *ionic bond*. Only electrostatic forces act here.

3. If both interacting atoms have open valence shells they share a part of their valence electrons and an electron pair builds a chemical bond. This is a *covalent bond*. If a molecule (the donor) has a non-bonded electron pair in his valence shell and there is an other molecule (the acceptor) that has electron pair gap, a covalent bond may form. The non-bonded electron pair builds the bond. This is a *dative bond*.

The shared electron pairs now belong to the molecule and they move on *molecular orbitals* (MO). If the probability of the electron pair in the environment of the two atoms is not equal, the bond is a *polar bond*. If the electrons belong to more than two atoms we have *delocalized orbitals*.

The molecules with covalent bonds contain finite number of atoms with the exclusion of polymers. Ionic and metal bonds occur mostly in crystals.

Our model is in this chapter the isolated molecule. If the interaction of the molecule with the environment is negligible then our model describes the system quite well.

3.1 The molecular symmetry

3.1.1 Symmetry elements and symmetry operations

An object is called *symmetric* if there exists an operation that brings the object in a position that is *equivalent* to the starting one. These operations are called *symmetry operations*, the positions are *equivalent configurations*. The equivalent configurations are indistinguishable. Symmetry operations belong to the *symmetry elements* of the object. The possible symmetry elements of molecules are listed in Table 3.1.

Turning a cube around an axis perpendicular to the center of one of its faces, there are four equivalent configurations during a 360° rotation: at 90° , 180° , 270° and 360° degrees. This axis is a tetragir, C_4 . The corresponding operations are C_4^1 , C_4^2 and C_4^3 . The 360° (0°) rotation is an operation that restores the original configuration (zero operation). This operation is called identity.

A water molecule has a digir that crosses the oxygen atom and halves the HOH angle (Fig. 3.1).

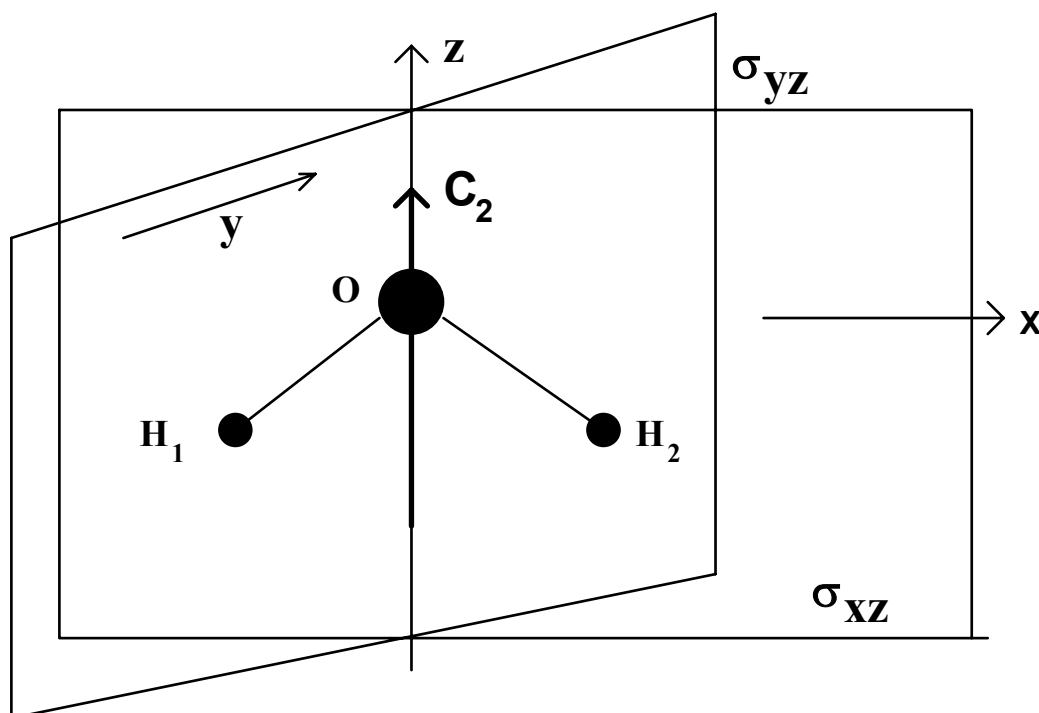


Fig. 3.1

Table 3.1
Symmetry elements and symmetry operations of molecules

Symmetry element		Symmetry operation	
Name	Notation	Name	Notation
<i>gir</i> : <i>n</i> -fold rotation axis, e.g. digir, trigir, tetragir, etc.	C_n	<i>n</i> -fold rotation	C_n^p $p=1,2,\dots,n-1$
<i>giroide</i> : <i>n</i> -fold rotation-reflection axis, e.g. trigiroide, tetragiroide, etc.	S_n	<i>n</i> -fold rotation together with a horizontal reflection	S_n^p $p=1,2,\dots,n-1$
<i>plane of symmetry</i> (mirror plane)	$\sigma \equiv S_1$	reflection	σ
<i>center of symmetry</i>	$i \equiv S_2$	inversion	i
<i>identity</i>	$E \equiv C_1$	zero operation	E or I

The water molecule has, besides, two mirror planes: the plane of the molecule and the plane perpendicular to it and that crosses the digir.

The next formation in Fig. 3.2 has a tetragiroide.

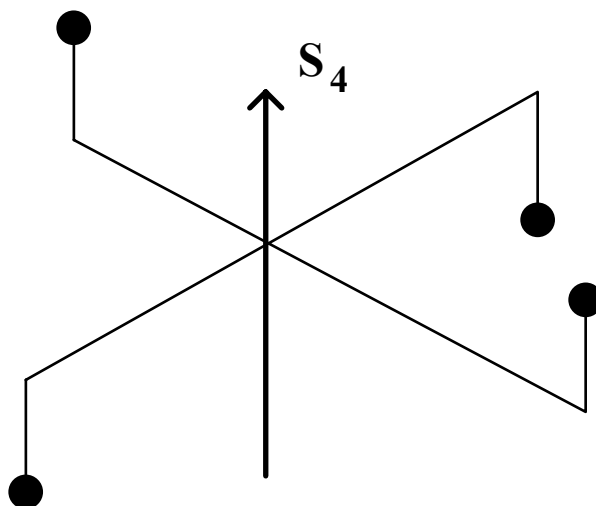


Fig. 3.2

The methane molecule has a very high symmetry. It has also tetragiroides, these are the bisectors of two HCH angles, see Fig. 3.3.

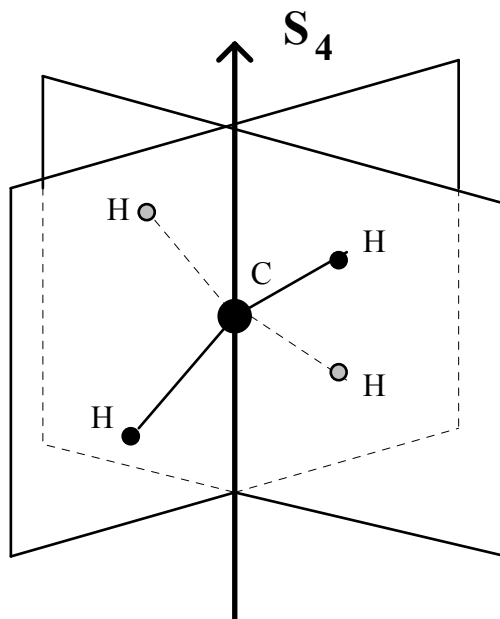


Fig. 3.3

The trans conformer of the hydrogen peroxide has a symmetry center (see Fig. 3.4) and also a digir perpendicular to the molecular plane at the center of inversion.

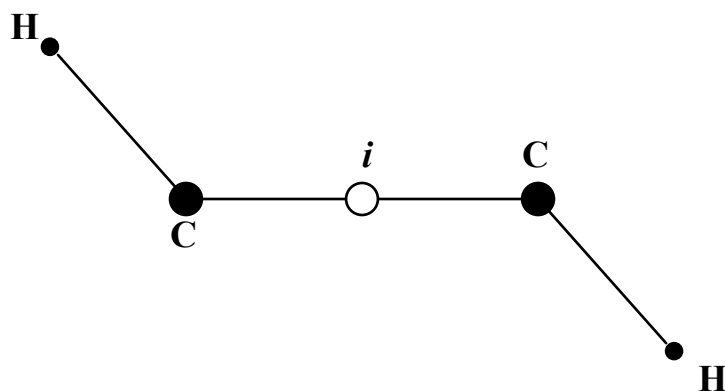


Fig. 3.4

3.1.2 Point groups

The symmetry operations build *algebraic groups*. It is necessary to define an *group operation* between the elements of an algebraic group. This operation is for the groups of symmetry operations the execution of the symmetry operations one after the other.

A group G has to satisfy the following requirements (X , Y and Z are group elements).

1. The group is closed for the group operation, i. e. the result of the operation is always an element of the group.

2. It has an unit element E that does not change the other elements in the group operation:

$$E \times X = X \times E = X \quad (3.1)$$

3. An inverse element belongs to each group element. If

$$X \times Y = E \quad (3.2)$$

then X is the inverse element of Y and vice versa:

$$Y = X^{-1} \quad \text{and} \quad X = Y^{-1} \quad (3.3)$$

4. The operation is associative:

$$(A \times B) \times C = A \times (B \times C) \quad (3.4)$$

Two elements of a group are *conjugates* of one another if

$$Y = Z \times X \times Z^{-1} \quad \text{i.e.} \quad X = Z \times Y \times Z^{-1} \quad (3.5)$$

A set of the group elements that are conjugated each other builds a *class* of the group.

The groups of the symmetry operations are called *point groups* since these operations are defined on sets of points, in our case on sets of atoms.

Table 3.2 contains the symmetry elements and notation of the most important point groups.

Table 3.2
Symmetry elements and notations of important point groups

notation	symmetry elements
C_i	E and i
C_s	E and σ
C_n $n=1,2,3,\dots$	E and C_n
C_{nv} $n=1,2,3,\dots,\infty$	E, C_n and n σ that intersect each other in the n -fold gir (σ_v)
C_{nh} $n=1,2,3,\dots$	E, C_n and one σ perpendicular to C_n (σ_h)
D_n $n=1,2,3,\dots$	E, C_n and n C_2 perpendicular to C_n
D_{nh} $n=1,2,3,\dots,\infty$	E, C_n , σ_h , n σ_v and n C_2 perpend. to C_n , in σ_h and σ_v planes
D_{nd} $n=1,2,3,\dots$	like D_{nh} but the n C_2 are bisectors of the σ_v planes
S_{2n} $n=2,3,\dots$	E and S_{2n}
O, O_h	octahedral groups
T, T_d , T_h	tetrahedral groups

3.1.3 Representations of point groups

The symmetry elements of water are illustrated on Fig. 3.1. According to Table 3.2 this molecule belongs to point group C_{2v} . Considering Table 3.1 its symmetry operations are: E, C_{2z} , σ_{xz} (the molecular plane) and σ_{yz} . Table 3.3 contains all possible products of the symmetry operations of this group.

Table 3.3
Products of the symmetry operations in the point group C_{2v}

First→ Second↓	E	C_{2z}	σ_{xz}	σ_{yz}
E	E	C_{2z}	σ_{xz}	σ_{yz}
C_{2z}	C_{2z}	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_{2z}
σ_{yz}	σ_{yz}	σ_{xz}	C_{2z}	E

Substituting the symmetry operations by numbers or matrices one can find sets of numbers or matrices that give true results (the number or matrix product corresponds to symmetry operation product). These number or matrix sets are called *representations* of the group. The matrices of the least order (if it is one, we have numbers) are called *irreducible representations* of the group. Irreducible representations are called *symmetry species* in the spectroscopic science.

Table 3.4

Character table (irreducible representations) of the point group C_{2v}

Classes of symmetry operations → Irreducible representation↓	E	C_{2z}	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

The number of representations of a group is equal to the number of its classes. An irreducible representation (Γ_i) is a line of the in the *character table matrix* (Table 3.4 for the point group C_{2v}) An element in this line is the *character* of the symmetry operation in the symmetry species in question, χ_{ij} (i^{th} species, j^{th} operation).

Generally, the irreducible representations are labelled with Γ . For point groups, however, the following symbols are applied.

- A if the most important gir has a character +1;
- B if the most important gir has a character -1;
- E the dimension of representations is 2, all the elements of this line are traces of a 2×2 matrix;
- F, T if the dimension of the symmetry species is 3;
- G, etc. further according to the alphabet.

The indexing of these symbols is as follows.

Superscripts:

- ' the important mirror plane has character +1;
- " the important mirror plane has character -1.

Subscripts:

- 1, 2, 3, ... denotes simply the order of the symmetry species according to the permutation of the numbers;
- g the inversion has character +1;
- u the inversion has character -1.

The character table of the point group C_{2v} is presented in Table 3.5 applying this notation.

Table 3.5

Character table of the point group C_{2v}

Symmetry operation→ Irreducible representation↓	E	C_{2z}	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The symmetry operations transform the atoms into new positions. The equation of transformation of *proper operations* (or giro operations, like E and C_n) is (rotation around the z axis, φ is the angle of rotation, $2\pi p/n$, see Table 3.1):

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} \quad (3.6)$$

For *improper operations* (or giroide operations, i.e. σ , i and S_n) the equation of transformation is (rotation around the z axis followed by a reflection on the plane perpendicular to it):

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} \quad (3.7)$$

The traces of these transformation matrices characterize the operations, since they are independent of the coordinate system, they are the *characters of the symmetry operations*, χ_j (j-th symmetry operation). The summary of Eqs. 3.6 and 3.7 gives the general expression

$$\chi_j = \pm 1 + 2 \cos \left(2\pi \frac{p}{n} \right) \quad p = 1, 2, \dots, n-1 \quad (3.8)$$

The symmetry of the molecules is important in the description of the molecular orbitals and in the interpretation of the molecular spectra.

3.2 The electronic structure of the molecules

3.2.1 Construction of molecular orbitals

We shall study the electronic structure of the molecule using the Born-Oppenheimer *adiabatic approach*. That means, our starting-point is like in the case of the atoms. According to the approach the motion of the electrons is very quick in comparison with those of the nuclei. Therefore the motion of the nuclei can be neglected in this approach. One can regard them as in space fixed bodies during the electron motions.

Applying this approach and neglecting relativistic effects, the Hamilton operator of a molecule has the form

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla^2 + \sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{r_{ij}} - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{\alpha=1}^N \sum_{\beta>\alpha}^N \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} \quad (3.9)$$

Z is the atomic number, N is the number of atoms, n is the number of electrons in the molecule, r is the distance of the particles. The first term in Eq. 3.9 is the kinetic energy operator for the electrons, the second is their mutual potential (Coulombian repulsion) energy, the third one is the electron-nucleus (attraction) potential energy and the last term is the nucleus-nucleus (repulsion) potential energy (a new member in comparison with the atomic Hamiltonian), ∇ is the nabla operator. Considering our approach, the last term is constant.

The quantum-mechanical description of the molecule is more complicated than that of the atoms. The exact solution of their Schrödinger equation for molecule is only for the H_2^+ ion (three particles) possible. Therefore additional approaches are necessary.

1. The wavefunction of the molecule is the product of the molecular orbital functions that depend only on the Cartesian coordinates and the spin coordinates;

2. Pauli's principle is satisfied by determinant wavefunctions;

3. The *model of independent particles* is used, i.e. each particle has its own orbital function that depends only on its own coordinates;

4. The Hartree-Fock method is applied in its Roothaan representation for the practical determination of the orbital functions, i.e. the orbital functions are expanding into series according to *basic functions*. In first approach this is a linear combination of the basic functions. The number of these functions is at least equal to the number of the orbitals. The higher the number of the basic functions, the better the approach. The coefficients of the linear combination are determined by finding the minimal energy of the molecule.

The *self consistent field (SCF)* method is used to get iteratively the minimal energy. Using initial values of coefficients, the energy is calculated. Applying this new energy, new coefficients can be calculated. This method is repeated, until it converges to the prescribed limit (difference in energy between the two last steps).

A simple choice for basic function is the application of the atomic orbitals (Hartree-Fock-Roothaan, HFR method). Therefore this method is called *linear combination of atomic orbitals (LCAO)*, sometimes the LCAO-SCF acronym is used to express the method of the solution, or since the results are molecular orbitals (MO), LCAO-MO is also applied.

3.2.2 The symmetry of molecular orbitals

In Subsection 3.1 we dealt with the molecular symmetry. The molecular orbitals have also symmetry. The orbital functions are either *symmetric* (their sign does not change) under the effect of a symmetry operation or they change their sign and are *antisymmetric*. If +1 stands in the character table for the χ_{ij} character, the symmetry operation does not change the sign of the function, otherwise, if it is -1, the sign of the function changes.

As an example we shall investigate the water molecule. As we know already, this molecule belongs to the point group C_{2v} (Subsection 3.1). For the character table see Table 3.5. The molecular orbitals of water are presented in Fig. 3.5.

The molecular orbitals are denoted with the label of their symmetry species but lower case letters are used. Capital letters are used for the symmetry species for the wave function of the total molecule. Molecular orbitals belonging to the same symmetry species are numbered with beginning from the orbital of lowest energy. This number appears as a coefficient. The five molecular orbitals of the water molecule are $1a_1$, $2a_1$, $1b_1$, $3a_1$ and $1b_2$. The three a_1 orbitals preserve the original symmetry of the molecule, the b_1 orbital is antisymmetric to the yz plane, the b_2 one is antisymmetric to the xz plane. In Fig. 3.5 the dark shade denotes the positive regions, the white one the negative regions of the functions. The energy values in this figure are results of LCAO-MO calculations. (1 eV = 96.475 kJ mole⁻¹).

The electron configuration of the water molecule is $1a_1^2 2a_1^2 1b_1^2 3a_1^2 1b_2^2$. The superscript denotes the number of electrons on the orbital. Orbitals belonging to the same symmetry species build an *electron shell*. A shell is closed if it contains the possible maximal number of electrons. A molecule has closed shell if all their shells are close.

In general, the determination of the symmetry of the molecular wavefunction is difficult. If, however, the molecule has closed shell, its wavefunction belongs to the symmetry species that preserve the molecular symmetry. For the water molecule the wave function is labelled by 1A_1 , where the upper left index is the multiplicity of the configuration (a closed molecular shell has zero total spin quantum number, therefore the multiplicity is 1). Removing one electron the symmetry of the molecular wavefunction changes to 2B_2 .

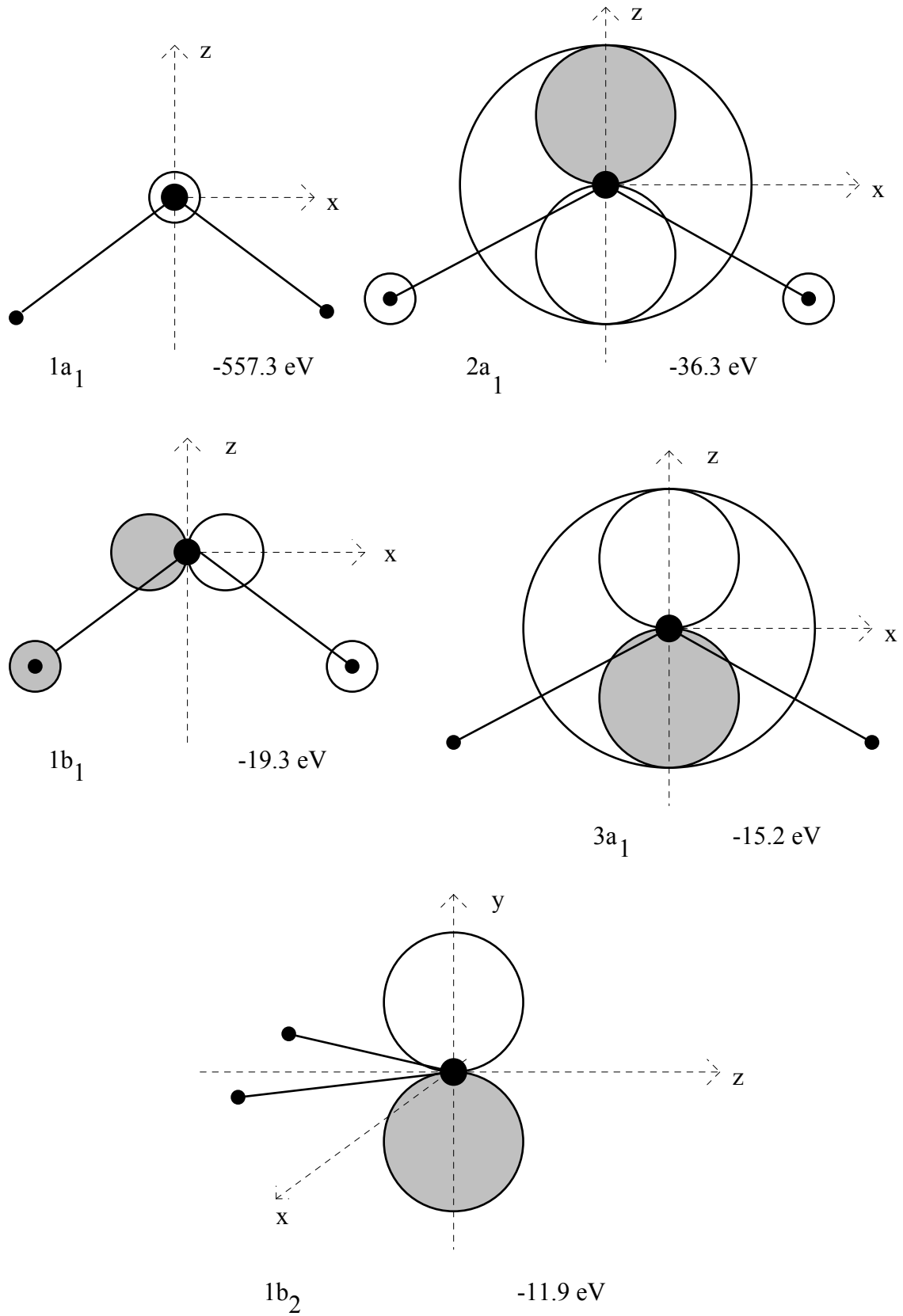


Fig. 3.5

3.2.3 Localized molecular orbitals

The molecular orbitals in Fig. 3.5 are not suitable for the demonstration of the spatial distribution of the electronic structure. This later is, however, important for the chemist. Namely, these orbitals are *delocalized*, i.e. they expand to the entire molecule. The linear combinations of independent molecular orbitals belonging to the same symmetry species, are equivalent. However, there exist orbitals (linear combinations of the molecular orbitals) that are localized in the space. Since they are linear combinations of the delocalized orbitals there is no reason to speak about their energies. Orbital energies belong only to molecular orbitals that are results of quantum chemical calculations. Fig. 3.6 gives the shapes of the localized orbitals of the water molecule.

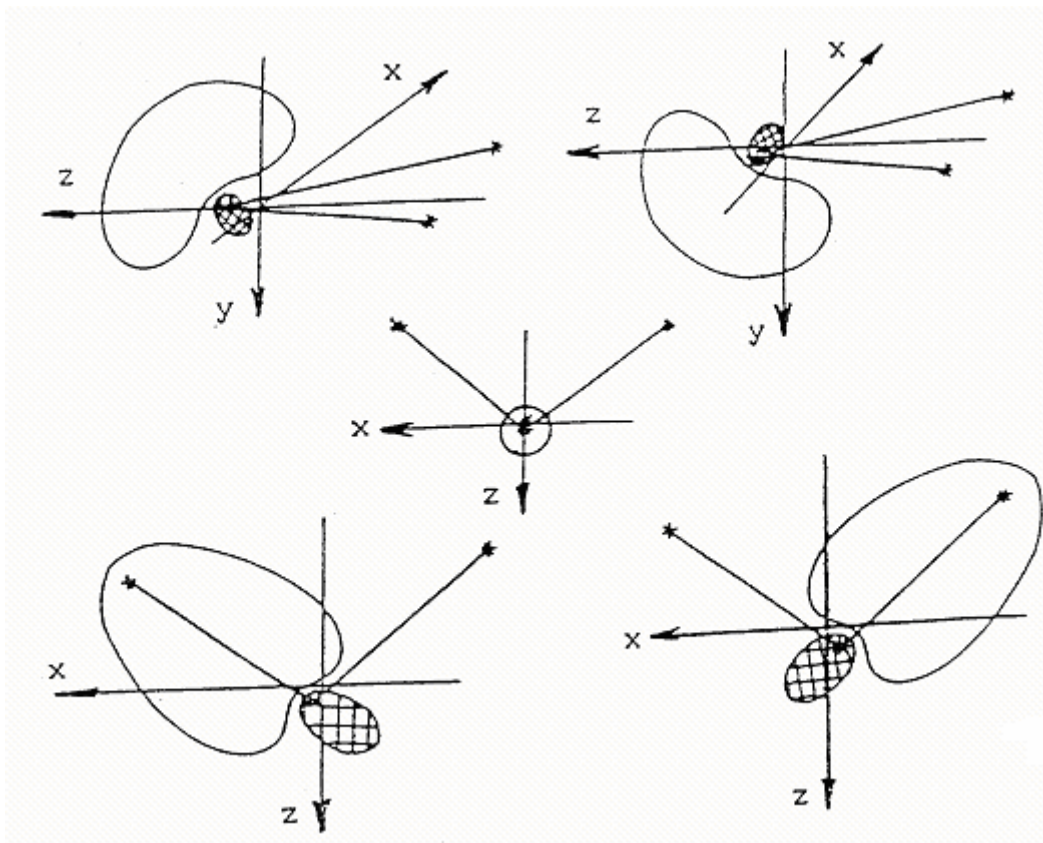


Fig. 3.6

Examining the localized orbitals in Fig. 3.6 the tetrahedral formation of the four electron pairs around the closed shells of the oxygen atom is well observable. The binding orbitals are less localized than the non-binding orbitals. The $1a_1$ orbital remains unchanged, i.e. localized.

The $1s$ orbitals of the hydrogen atoms and the $2s$, $2p_x$ and $2p_y$ orbitals of the oxygen atom create the chemical bonds ($2a_1$ and $1b_1$). There exist also true delocalized molecular orbitals, e.g. those of the aromatic rings. Here is difficult to form localized orbitals.

3.3 The covalent bond

3.3.1 The characteristics of the covalent bond

Several factors influence the formation of the molecular orbitals.

1. The first term of the Eq. 3.9 Hamilton operator corresponds the kinetic energy of the molecule. The smaller is the free space of the electron, the higher is its kinetic energy.

2. The second term of Eq. 3.9 is the electron-electron repulsion. The corresponding force acts increasing the electron-electron distances.

3. The third term of Eq. 3.9 is the electron-nucleus attraction. The corresponding Coulombian force is the only attractive force that acts on the electrons.

4. The fourth term is the nucleus-nucleus repulsion. This effect plays important role in the formation of the equilibrium geometry of the molecule.

5. The spin-spin interaction of the electrons. Electrons with the same (parallel) spin "repulse", try to move away from one another, electrons with opposite (antiparallel) spin "attract", try to come nearer to one another. This phenomenon corresponds to Pauli's principle and to Hund's rule. Pauli's principle is valid also for molecular orbitals and plays important role in their formation, i.e. it influences the structure of the molecule.

The results of the effects are: the *localized electron pairs* try

- to avoid one another;
- to expanding to the most possible area;
- to become as close as possible to the nucleus.

The equilibrium geometry is the result of these three effects.

If the electron clouds of two atoms come nearer and nearer, the formation of a molecular orbital becomes possible. The molecular orbital is forming during the mixing of the atomic orbitals. The mixing of the atomic orbitals is called *hybridization*. The measure of this mixing is the *overlap integral*:

$$S_{12} = \int \psi_1^* \psi_2 d\tau \quad (3.10)$$

ψ_1 and ψ_2 are the atomic orbitals. The greater this overlap and the nearer the energy levels of the two atomic orbitals, the greater the grade of their mixing. The two extreme cases are:

- There is no mixing of atomic orbitals in the orbital $1a_1$ of the water molecule (see Fig. 3.5).
- The two atomic orbitals take part with the same ratio in the molecular orbital (e.g. the HH bond in H_2 created by the 1s orbitals of the H atoms).

During the nearing of the two atomic orbitals two molecular orbitals are formed:

- One of them has an orbital energy that is lower than the energies of the atomic orbitals. It is localized to the small area between the two atoms, its electron density is high, this is the *bonding orbital*.
- The other molecular orbital has higher energy than that of any atomic orbital. It has a nodal surface (Section 2.1.1), its electron density in the interatomic area is low, this is the *antibonding orbital*.

Fig 3.7 presents the relative energy levels of the molecular orbitals created between the atoms A and B as functions of their energy difference, and as functions of the overlap integral. If the energy difference between the two atomic orbitals increases, then the energy level of the antibonding orbital decreases and approaches the higher atomic energy level. At the same time the energy of the bonding orbital increases and approaches the lower atomic energy level. An increasing overlap increases the energy difference of these two molecular orbitals (see Fig. 3.7)

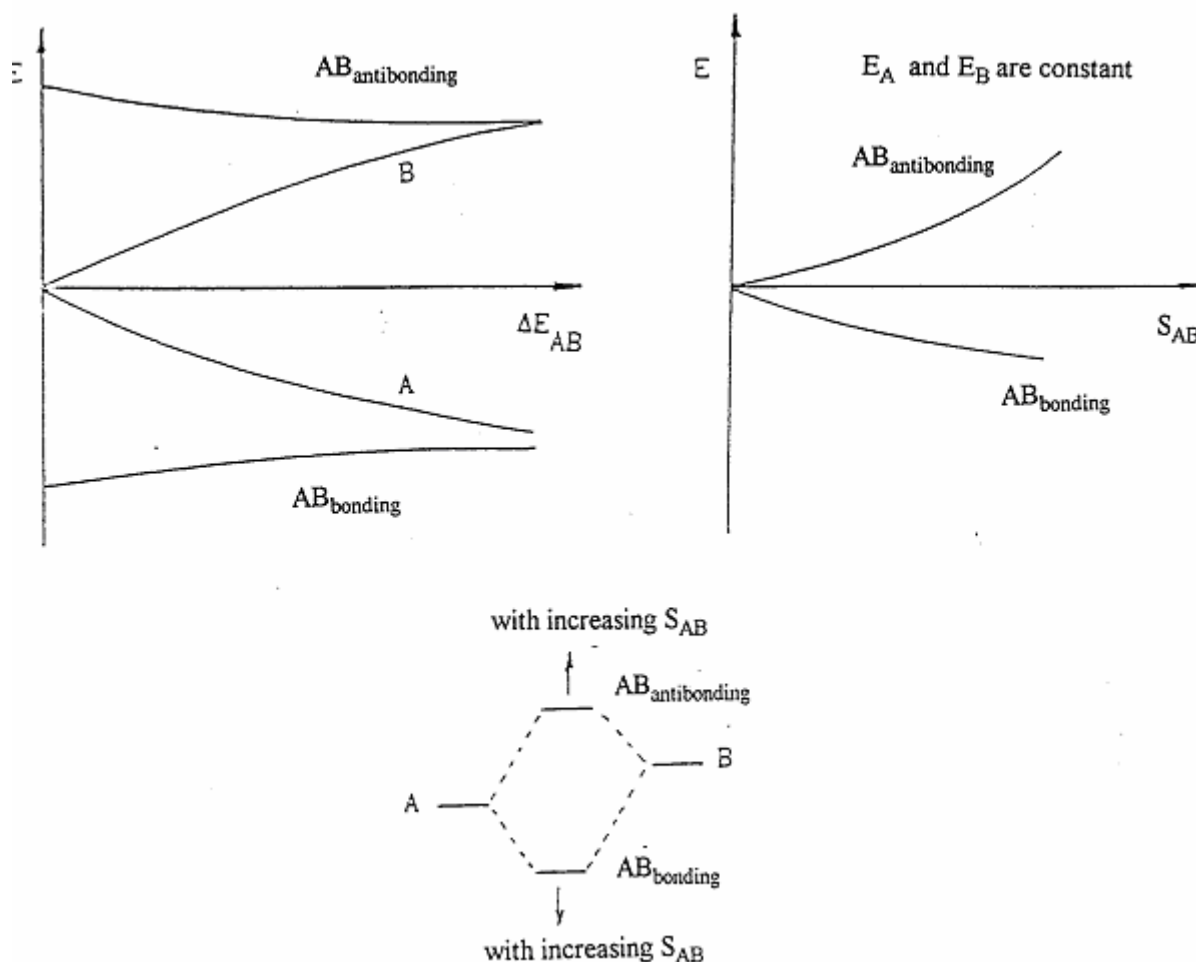


Fig. 3.7

This model is a very good approach for the formation of molecules if only s atomic orbitals take part in the bond. The more atomic orbitals with nearly the same energy level combine in the bond, the greater the deformation of the original atomic orbitals. The description of the molecular orbitals is possible only as linear combination of several atomic orbitals. If only elements with atomic number lower than 10 take part in the molecule, the deformation of the atomic orbitals is small.

There is not necessary to have an electron pair for building a bond. In the H_2^+ molecule ion the bond is formed only by one electron.

The attractive force between the interatomic electron cloud and the atomic cores is greater than the repulsive force between the atomic cores. This is the fundamental reason of the formation of chemical bonds.

The intramolecular electron affinity of the atoms is characterized by the *electronegativity*. Under several definitions the widely used if that of Mullikan:

$$X = \frac{1}{2}(I + A) \quad (3.11)$$

I is the ionization energy, A is the electronegativity of the atom (Section 2.4.1).

The atoms at the first part of the periodic table having high electronegativity (Tables 2.6 and 2.7) like carbon, nitrogen and oxygen can mobilize even two or three electrons to fill their valence electron shell. The second and third bonds are weaker than the first one since the interatomic area is occupied by the electron pair of the first bond (repulsion). A multiple bond

needs atomic orbitals of appropriate orientation (p or d orbitals) that energy level is not very high.

3.3.2 The structure of two-atomic molecules

The two-atomic molecules are the simplest. Therefore we investigate their structure at first.

The point group of molecules consisting of two equivalent atoms is the point group $D_{\infty h}$, i.e. the molecules have cylindrical symmetry, infinite number of equivalent configurations are possible during the rotations around the C_{∞} axis (see Table 3.6). Besides the C_{∞} the symmetry elements of this group are an S_{∞} giroid in the same axis as C_{∞} , a symmetry center, infinite number of digirs perpendicular to C_{∞} , infinite number of vertical mirror planes and a mirror plane perpendicular to C_{∞} .

Table 3.6
The character table of the point group $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi} \dots$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi} \dots$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_u^+	1	1	1	-1	-1	-1
Σ_g^-	1	1	-1	1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_g	2	$2 \cos \varphi$	0	2	$-2 \cos \varphi$	0
Π_u	2	$2 \cos \varphi$	0	-2	$2 \cos \varphi$	0
Δ_g	2	$2 \cos \varphi$	0	2	$-2 \cos \varphi$	0
Δ_u	2	$2 \cos \varphi$	0	-2	$2 \cos \varphi$	0

The molecular orbitals of the hydrogen molecule are created from the orbitals $1s_A$ and $1s_B$ of the two hydrogen atoms:

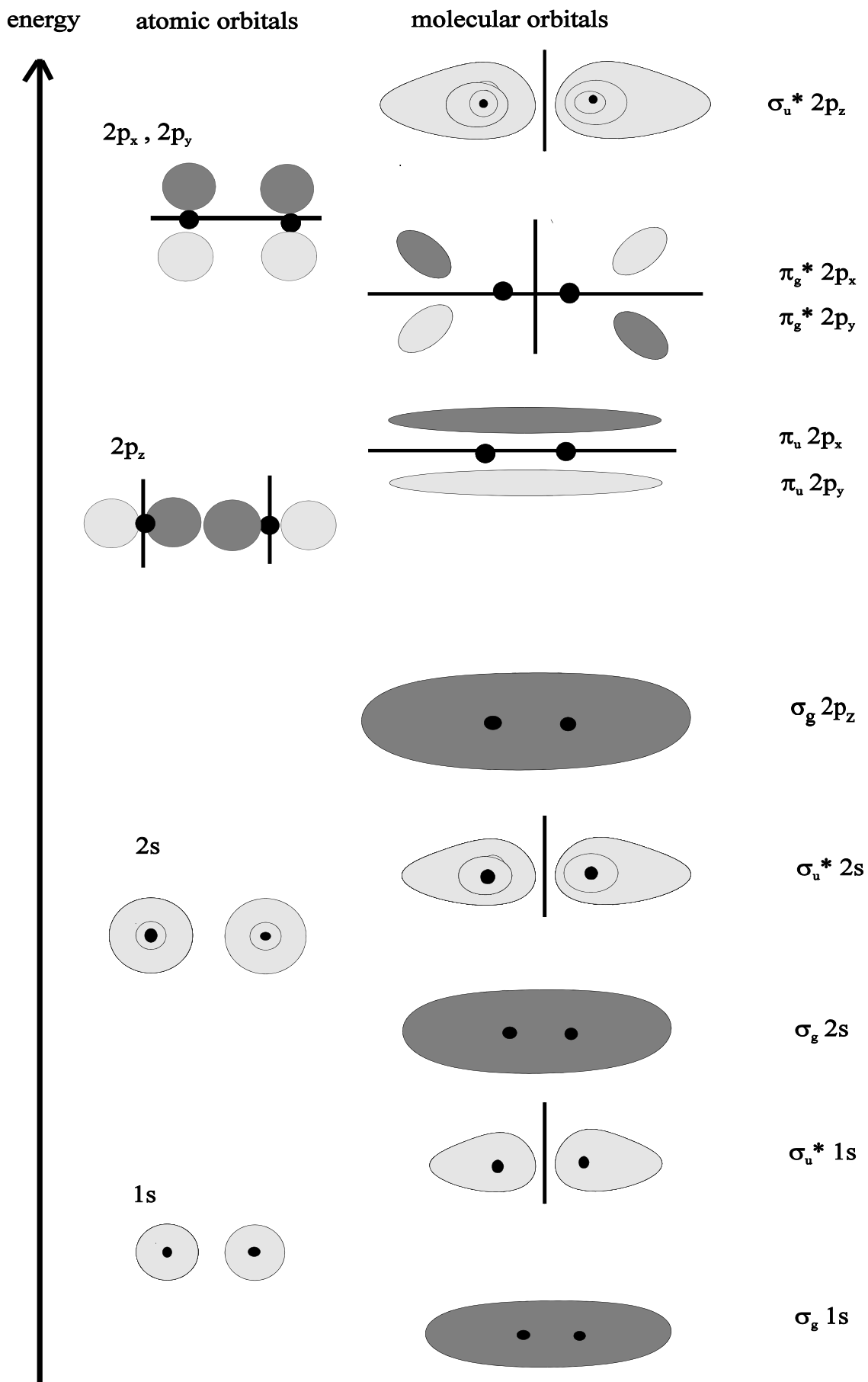


Fig. 3.8

$$\begin{array}{ll} \text{species} & \text{molecular orbital} \\ \Sigma_g^+ & \sigma_g = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \end{array} \quad (3.12)$$

$$\begin{array}{ll} \Sigma_u^+ & \sigma_u^* = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \end{array} \quad (3.13)$$

Considering the molecular orbital σ_g the electron density on the atoms decreases in comparison to the isolated atoms but increases in the interatomic area (see the electron densities on the orbital in Fig. 3.8). The orbital energy of this orbital increases with increasing atomic distance. It is a bonding orbital, the ground state of the hydrogen atom and belongs to the Σ_g^+ symmetry species.

Considering the molecular orbital σ_u^* the electron density in the interatomic area is low, it has a nodal surface perpendicular to the atom-atom line. Its energy decreases with increasing atomic distance (see Fig. 3.8). This is an antibonding orbital, belonging to the symmetry species Σ_u^+ .

The notation of the molecular orbitals corresponds to its symmetry species in the $D_{\infty h}$ point group: they are either σ or π orbitals. The shapes of the molecular orbitals of X_2 type molecules and their relative energy levels are shown in Fig. 3.8. The atoms lie in the z direction. The x and the y axes are perpendicular to it, the molecular orbitals are formed from the $2p_x$ and the $2p_y$ orbitals and therefore they are degenerated. The molecular orbitals are labelled with names of the species and the atomic orbital.

Most of the X_2 molecules have the energy level order as in Fig. 3.8. The order of the orbitals is the result of measurements and they are interpreted with the help of quantum-mechanical calculations. The molecular orbitals having the same symmetry may mix, especially if their energy levels are close. For example, the $\sigma_g 2s$ and the $\sigma_g 2p_z$ orbitals of the nitrogen molecule interact and the result is their withdrawing.

3.3.3 Hybridization

A molecular orbital is called *hybrid orbital* if an atom takes part in it with more than one orbitals. The measure of the hybridization is the participation ratio of the individual atomic orbitals in the wavefunction of the molecular orbital. The hybridization is possible only in the case of σ orbitals, s , p and d orbitals may take part in them.

During the hybridization the central atom contacts n equivalent atoms or atom groups. This results in n equivalent orbitals that arrange symmetrically in the space and determine the structure of the molecule.

The hybridization of the carbon atom is a well-known example. The ground state of the C atom is $1s^2 2s^2 2p^2$ (3P_0). If one $2s$ electron transits to a $2p$ orbital (according to Hund's rule) then the electron configuration changes to $1s^2 2s 2p^3$ (5S_2). This configuration is suitable to build in the space symmetric, equienergetic orbitals. All the orbitals have the same weight in each hybrid orbital. The hybrid orbitals are orthogonal each to the other, i.e. their overlap integrals (Eq. 3.10) are zero. The four hybrid orbitals of the carbon atom determine a tetrahedron. The four orbitals belonging to the 5S_2 state are:

$$\psi_1 = \frac{1}{2} [\chi(2s) + \chi(2p_x) + \chi(2p_y) + \chi(2p_z)] \quad (3.14)$$

$$\psi_2 = \frac{1}{2}[\chi(2s) + \chi(2p_x) - \chi(2p_y) - \chi(2p_z)] \quad (3.15)$$

$$\psi_3 = \frac{1}{2}[\chi(2s) - \chi(2p_x) + \chi(2p_y) - \chi(2p_z)] \quad (3.16)$$

$$\psi_4 = \frac{1}{2}[\chi(2s) - \chi(2p_x) - \chi(2p_y) + \chi(2p_z)] \quad (3.17)$$

χ denotes the atomic orbitals.

The methane molecule contains a central carbon atom and four connecting hydrogen atoms. The molecule - a typical example for the hybridization - has tetrahedral structure. Two theoretical ways exist for the construction of the methane molecule from 1 carbon and 4 hydrogen atoms.

1. The carbon atom will be excited (the necessary energy is called promotional energy) and then combined with the four hydrogen atoms (during this process the promotional energy will be recovered).

2. The carbon atom will be combined with the hydrogen atoms and the methane molecule is built in its excited state since the 5S_2 (hybrid orbital) state has lower energy.

The Eqs. 3.14-3.17 describe the sp^3 hybridization. Similar hybridizations occur for C_2H_4 (sp^2) and C_2H_2 (sp).

From the viewpoint of the molecular orbital theory the hybridization means the transformation to other, equivalent orbitals.

The four orbitals (Eqs. 3.14-3.17) are equivalent as long as the four substituents are equivalent. If the four substituents are not equivalent, the symmetry gets damaged and the participation of the four atomic orbitals is no more equivalent in the hybrid orbitals.

The hybridization is also important for the complex molecules of transition metals (see Section 3.3.5). The hybrid orbitals generated from the d orbitals of the central metal atom determine the symmetry of the molecule. E. g. the spd^2 hybrid orbitals determine a square structure, a trigonal bipyramide belongs to the spd^3 orbitals, etc.

3.3.4 Delocalized systems

We mentioned the phenomenon of the delocalization at the σ bonded molecules. The organic compounds with *conjugated double bonds* are special case of the double bonded molecules. The second bonds are π bonds. The delocalization of the electrons in the conjugated double bonded systems spreads over several atoms. The energy levels of these orbitals are high over those of the σ orbitals. Therefore the σ - π separation is a good approach in the study of the π systems.

The simplest method for the calculation of the π orbital level is the Hückel method. The restrictions of this method are:

1. All overlap integrals are zero

$$S_{ij} = 0 \quad i \neq j \quad (3.18)$$

$$S_{ij} = 1 \quad i = j \quad (3.19)$$

2. The matrix elements H_{ij} (see quantum mechanics and quantum chemistry)

$$H_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau \quad (3.20)$$

that are built during the solution of the Schrödinger equation are

$$H_{ij} = \alpha \text{ if } i \text{ and } j \text{ belongs to the same atom (Coulomb integral) (3.21)}$$

$$H_{ij} = \beta \text{ if } i \text{ and } j \text{ belong to neighbour atoms (resonance integral) (3.22)}$$

$$H_{ij} = 0 \text{ in all other cases (3.23)}$$

The constant α characterizes the quality of the atom, the constant β characterizes the quality of neighbour atoms.

Both α 's and β 's are negative, the absolute values of α 's are greater. The energy eigenvalue equation in his general form is

$$|\mathbf{H} - E\mathbf{S}| = 0 \quad (3.24)$$

\mathbf{H} is the Hamilton matrix (from H_{ij} elements), \mathbf{S} the overlap matrix (S_{ij} elements).

Applying this equation in the framework of the Hückel theory for the ethylene molecule we have

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad (3.25)$$

The rows and the columns correspond the carbon atoms. The results are

$$\begin{aligned} E_1 &= \alpha + \beta && \text{for the bonding } \pi \text{ orbital} \\ E_2 &= \alpha - \beta && \text{for the antibonding } \pi \text{ orbital} \end{aligned}$$

Similar equations can be written for compounds with conjugated π orbitals. The method was extended also for heterocyclic systems (EHT = extended Hückel theory). The constants for the Coulomb and resonance integrals are in the case of the neighbouring atoms X and Y

$$\alpha_X = \alpha + h_X\beta \quad (3.26)$$

$$\beta_{XY} = k_{XY}\beta \quad (3.27)$$

h and k are constant characterizing the atoms X and their pair XY, respectively. The constants for nitrogen are: $h_N=0.5$ and $k_{CN}=1$.

The energy levels are usually expressed with the α and β parameters of the carbon atom. The results for the benzene molecule are

$$\begin{aligned} E_1 &= \alpha - 2\beta \\ E_2 &= E_3 = \alpha - \beta \\ E_4 &= E_5 = \alpha + \beta \\ E_6 &= \alpha + 2\beta \end{aligned}$$

There are two degenerated energy levels. The six electrons taking part in the π bonds occupy the three lowest levels: E_4 , E_5 and E_6 . The average energy for the π orbitals of benzene would be $6 \times (\alpha + \beta) = 6\alpha + 6\beta$, while the calculated energy is $4 \times (\alpha + \beta) + 2 \times (\alpha + 2\beta) = 6\alpha + 8\beta$. The calculated energy is with 2β lower then the assumed. Since $\beta \approx -75 \text{ kJ} \cdot \text{mole}^{-1}$, the *delocalization energy* of benzene is $2\beta \approx -150 \text{ kJ} \cdot \text{mole}^{-1}$.

The Hückel method could interpret the aromaticity with the delocalization energy. This method gives a good order for the π orbital energies. Two of these orbitals are very important in the organic chemistry. The electron density on the *highest occupied molecular orbital* (HOMO) is nearly proportional to the reactivity in electrophilic reactions. A similar role plays in nucleophilic reactions the *lowest unoccupied molecular orbital* (LUMO). These limit levels

play also important role in the development of the chemical and spectroscopic properties of the molecule.

The fast progress in computer technology enlarged the possibilities of the quantum chemistry for the calculation of the molecular orbitals energies, the molecular energy and the molecular geometry (see Section 3.11.4). The new ab initio methods are post-Hartree-Fock methods that take into consideration also the interactions that are neglected in the framework of the HF method. If atoms with atomic number more than 10 are found in the molecule the d orbitals may play role in the formation of the chemical bonds. The participation of d orbitals complicates fairly the calculations.

3.3.5 Complex compounds of the transition metals

The knowledge of the complex compounds of the transition metals is important since several catalysts and coenzymes belong to these compounds. Since the d orbitals of the transition metals participate in the chemical bond, the description of these molecules is more complicate than that of the organic compounds. Therefore a simple model giving a good approach is very useful here.

The oldest but also nowadays acceptable model is given by Bethe's crystal field theory. According to this model the ligands with their negative charges (ion or dipole) connect the central ion (having positive charge). This bond is relatively weak. Therefore the structure of the central ion plays decisive role in the formation of the molecular structure. Let us imagine a free positive ion surrounding with negative ions as it is in an ionic crystal. The electric field effects of the crystal field, the spin-orbital interaction and the internal magnetic field effect take also part in the Hamilton operator of the molecule.

The discussion of the complexes with 3d orbitals is the simplest. Here we shall not deal with the complex molecules containing nd ($n > 3$) and nf orbitals since their discussion is considerably complicate.

In the case of $n=3$ the maximal value of the total angular momentum quantum number is $l=2$. So the possible number of the d orbitals is 5 (see Fig. 2.3). These 5 orbitals are degenerated as long as an external electric or magnetic field does not act on the ion.

There are several complex molecules of transition metals with six equivalent ligands connecting the central ion, they are sp^3d^2 hybrids. The six ligands are arranged in octahedral form, belonging to the O_h point group (Table 3.7). Table 3.7 contains also the symmetry species of transformation properties of each d orbitals (see Section 2.2.1). The angle depending parts of the d orbital functions determine their symmetry. The $3d_{x^2-y^2}$ and the $3d_{z^2}$ (transforming like $3z^2 - r^2$) are symmetrical to the xy, xz and yz ($3\sigma_h$) mirror planes and are also symmetrical to the x, y and z digirs ($3C_2$), therefore they belong to the symmetry species E_g . The three other d orbitals, d_{xy} , d_{xz} and d_{yz} are symmetric to the six axis-axis bisectors ($6C_2$) and to the mirror planes determined by a bisector and an axis ($6\sigma_d$) and to the inversion (i). Therefore they belong to T_{2g} . Watch the symmetry of the orbitals on Fig. 2.3! (The label T of the point group is equivalent to the label F).

Table 3.7

The character table of the point group O_h (octahedral group)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	coordinates
-------	---	--------	--------	--------	--------	---	--------	--------	-------------	-------------	-------------

A _{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A _{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A _{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E _g	2	-1	0	0	2	2	0	-1	2	0	$x^2 - y^2, 3z^2 - r^2$
E _u	2	-1	0	0	2	-2	0	1	-2	0	
T _{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T _{2g}	3	0	1	-1	-1	3	-1	0	-1	1	xy, xz, yz
T _{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x, y, z
T _{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

The originally five times degenerated energy level splits into two groups. The ligands connecting to the central ion are positioned on the coordinate axes. The t_{2g} orbitals (orbitals are labelled similarly to their symmetry species only small letters are used) are situated *between* the coordinate axes, while the e_g orbitals are *centred on* them. Therefore the ligands repulse the e_g orbitals, so their energy is higher than that of the t_{2g} ones.

The energy difference between these two orbital groups depends above all on the electric field generated by the ligands. The experimentally measured splitting is denoted by Δ (Section 3.6.2).

The crystal field theory gives the order of the orbital energies but only as expressions, their values are not calculable.

The measure of the splitting in octahedral crystal field is labelled by $10Dq$. Using the experimental data the Dq becomes calculable (q is the ratio of two matrix elements, D is a coefficient in the description of the crystal field). The shift of the band system by the ligands is not considered. Therefore the average energy of the d orbitals is always 0 d . The splitting is influenced by two effects:

1. The crystal field (metal ion - ligand, d orbital symmetry) effect.
2. The mutual repulsion of the d electrons.

If the first effect is stronger, we have a *strong crystal field*, if the second one is stronger, we have a *weak crystal field*.

In a strong crystal field the electrons occupy the energy levels according to the increasing energy. Therefore the t_{2g} orbitals are occupied at first, and the e_g ones only later. The energy of the t_{2g} orbitals is $4Dq$ lower than average, while that of the e_g orbitals is $6Dq$ higher than average. The t_{2g} orbitals are the bonding ones, the e_g 's are the antibonding ones. See the stabilization energies in Table 3.8!

Table 3.8
Stabilization energies in the strong octahedral crystal field
and the symmetries of the ground state

Configuration of the central ion	Orbital configuration of the crystal field	Symmetry of the crystal field	Stabilization energy (Dq)
d^1	t_{2g}	${}^3T_{2g}$	4
d^2	t_{2g}^2	${}^3T_{1g}$	8

d^3	t_{2g}^3	${}^4A_{2g}$	12
d^4	t_{2g}^4	${}^3T_{1g}$	16
d^5	t_{2g}^5	${}^2T_{2g}$	20
d^6	t_{2g}^6	${}^1A_{2g}$	24
d^7	$t_{2g}^6e_g$	2E_g	18
d^8	$t_{2g}^6e_g^2$	${}^3A_{2g}$	12
d^9	$t_{2g}^6e_g^3$	2E_g	6

The situation is more complicate in weak crystal fields. The repulsion of the electrons split the orbitals into several levels. Sometimes these levels are very close. The electrons occupy the orbitals according Hund's rule. At first all orbitals are occupied by one electron. After the occupation of all orbitals in this way the second electrons join stepwise the first ones with opposite spins.

Octahedral complexes with weak and strong crystal fields differ in the case of d^4 , d^5 , d^6 and d^7 configurations.(Fig. 3.9 shows the situation).

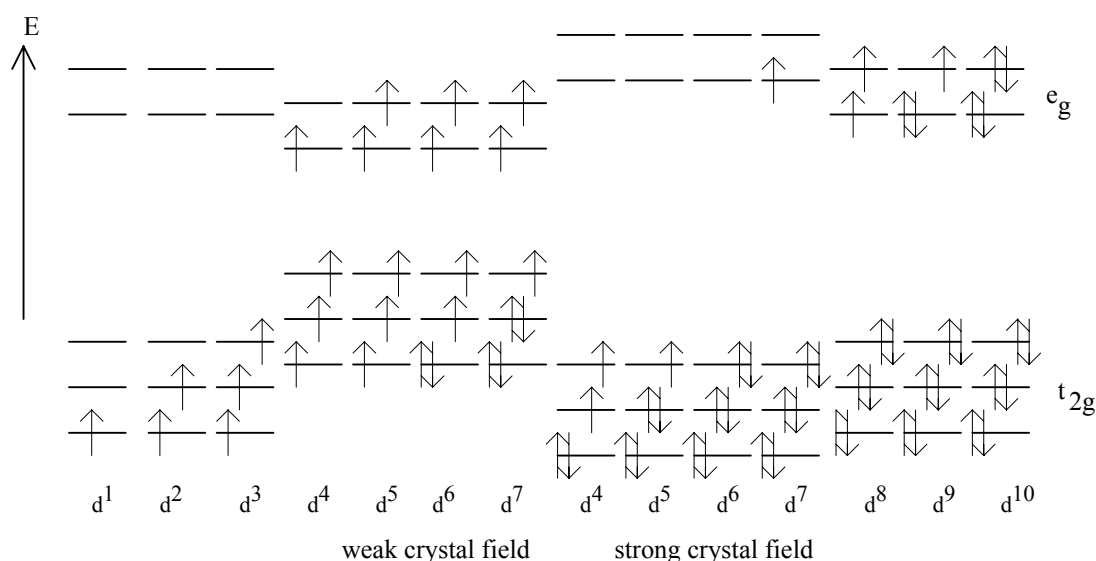


Fig. 3.9

The group spin quantum numbers of the mentioned configurations are for weak crystal fields high, they are *high spin states*. For strong crystal fields the group spin quantum number is in these cases low, they are *low spin states*. These two types of states are distinguishable by magnetic measurements (Section 3.9.1).

The *ligand field theory* is the application of the molecular orbital theory to transition metal complexes. It is very useful if the ligand-metal bond is covalent (e.g. MnO_4^- , $Fe(CN)_6^{2-}$, metal carbonyls, π complexes, etc.). The advances of the method are the better qualitative description

of the molecule and the quantitative energy values. Most of these methods use semiempirical quantum-chemical models.

Fig. 3.10 presents the term diagram (the splitting of the energy levels) in octahedral strong crystal fields. Here the crystal field effect (metal-ligand interaction) is dominated. In octahedral weak crystal fields the electron-electron interaction dominates (Fig. 3.11).

Both strong and weak crystal fields are extreme cases. The real complexes stand between these two models, they crystal fields are more strong or more weak.

In the case of nd ($n > 3$) and nf orbitals it is necessary to modify this simple model. The spin-orbital interactions play important role in these cases.

The *Jahn-Teller effect* is important for transition metal complexes. If an electron state of a symmetric polyatomic molecule is degenerated, the nuclei of the atoms move to come into an asymmetric electron state. In this way the degenerated state splits. The system will be stabilized by the combination of the electron orbitals with vibrational modes (Section 3.5.3). This is not valid for linear molecules and for spin caused degenerations.

Octahedral complexes (e.g. $\text{Fe}(\text{CN})_6^{2-}$) can be distorted by the Jahn-Teller effect in two forms: into prolate (stretched) or into oblate (compressed) octahedron, according to the symmetry of the coupled vibrational mode (the first case occurs more frequently). The Jahn-Teller effect is observable also in the electronic spectra of the transition metal complexes (Section 3.6.2). The spectral bands split or broaden.

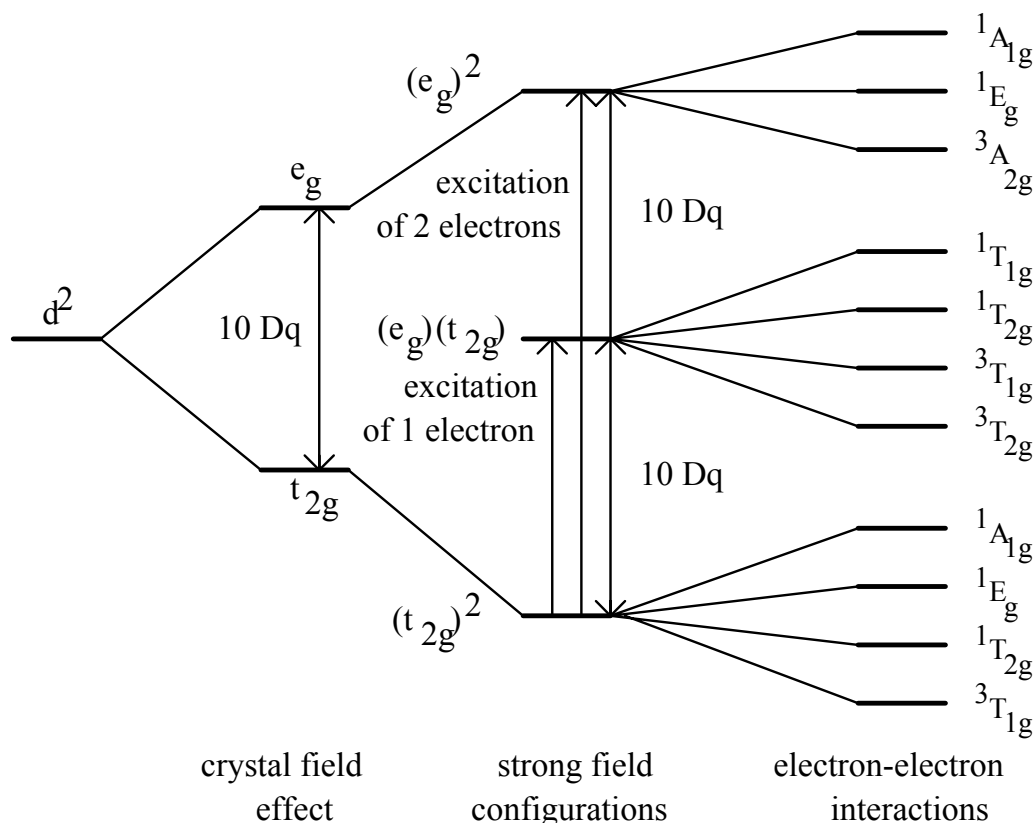


Fig. 3.10

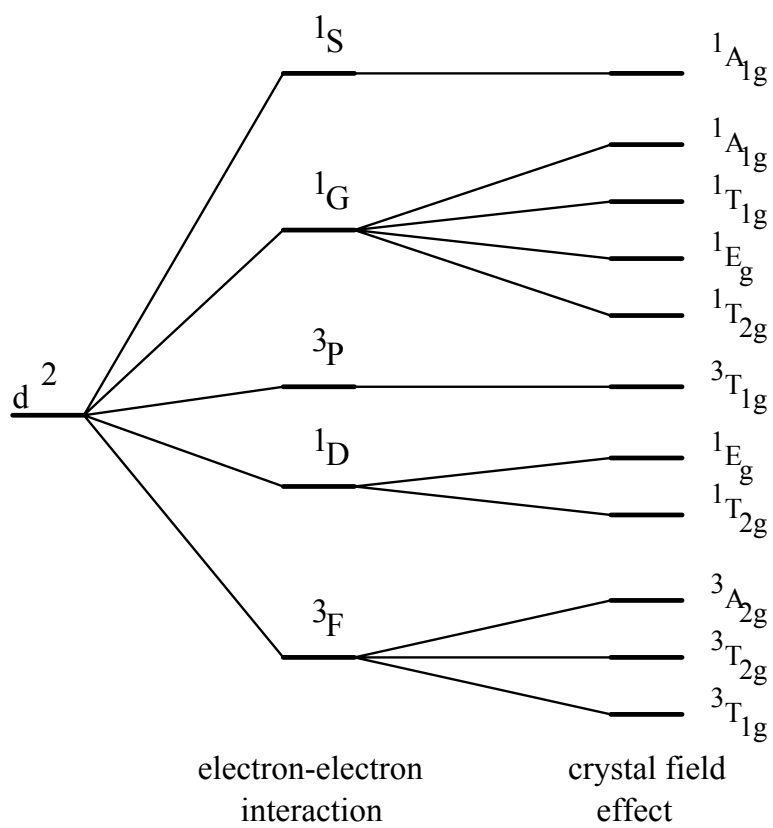


Fig. 3.11