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1. ELEMENTARY QUANTUM CHEMISTRY

1.1 PRINCIPLES OF QUANTUM MECHANICS

Discrete character of some physical quantities (energy, linear momentum, angular momentum, etc.) causes that in quantum mechanics these quantities cannot be described by continuous functions. Appropriate mathematical representatives of physical quantities, adopting continuous and discrete values, are **operators**. The operator is a function defined on the set of functions.

The principles of quantum mechanics, as the only successful physical theory applicable to microobjects, are based on several postulates the validity of which has been proved by agreement of theoretical predictions with experimental results. (There is a different number of quantum-mechanical postulates cited in the literature.)

Postulate 1. An arbitrary n-th state of a physical microobject can be fully described by a **wave (state) function** Ψ_n. The wave function depends only on spatial coordinates, spin variables X_k and time t: $\Psi_n = |\Psi_n> = \Psi_n(X_k,t)$, where X_k stands for the set of coordinates defined by the position vector r_k and the spin projection s_k.

In terms of mathematics, the wave function belongs to the function of complex variable forming the **Hilbert space**. The Hilbert space is: a) linear; b) metric; c) of infinite dimension; d) complete; e) separable. Thus the wave function is quadratically integrable and it has to form a complete set. A physical meaning of the normalized wave function is that the expression $|\Psi(X_k;t)|^2\, dX_k = \Psi^*(X_k;t)\, \Psi(X_k;t)\, dX_k$ represents the probability of finding of k-th particle at the volume element dr_k around r_k with the spin projection s_k at the time t ($dX_k = dr_k\, ds_k$). After the integration over the whole space the probability should be a unity, i.e., $\int \Psi^*(X_k;t)\, \Psi(X_k;t)\, dX_k = <\Psi(X_k;t)|\Psi(X_k;t> = 1$.

Postulate 2. Every physical quantity A has associated a linear hermitian operator $\hat{A}$; the possible values of the quantity A correspond to the eigenvalues a_n of the operator $\hat{A}$. They are given by the **characteristic equation**

$$\hat{A}\, \Psi_n(x) = a_n\, \Psi_n(x) \qquad [1]$$

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TABLE 1
Quantum-mechanical operators of single particle.[a]

Quantity	Symbol	Classical formula	Operator
Coordinates	$\hat{r}$		
	$\hat{x}$	x	x
	$\hat{y}$	y	y
	$\hat{z}$	z	z
Linear momentum	$\hat{p}$		
	$\hat{p}_x$	$m\, dx/dt$	$-i\hbar\, \partial/\partial x$
	$\hat{p}_y$	$m\, dy/dt$	$-i\hbar\, \partial/\partial y$
	$\hat{p}_z$	$m\, dz/dt$	$-i\hbar\, \partial/\partial z$
Angular momentum	$\hat{l}$		
	$\hat{l}_x$	$yp_z - zp_y$	$-i\hbar(y\, \partial/\partial z - z\, \partial/\partial y)$
	$\hat{l}_y$	$zp_x - xp_z$	$-i\hbar(z\, \partial/\partial x - x\, \partial/\partial z)$
	$\hat{l}_z$	$xp_y - yp_x$	$-i\hbar(x\, \partial/\partial y - y\, \partial/\partial x)$
Spin [b]	$\hat{s}$		
	$\hat{s}_x$	none	$(\hbar/2)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
	$\hat{s}_y$	none	$(\hbar/2)\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$
	$\hat{s}_z$	none	$(\hbar/2)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
Time	$\hat{t}$	t	t
Kinetic energy	$\hat{T}$	$p^2/2m$	$-(\hbar^2/2m)\nabla^2$
Electrostatic potential energy	$\hat{V}$	$e^2/4\pi\varepsilon_0 r$	$e^2/4\pi\varepsilon_0 r$
Dipole moment	$\hat{d}$		
	$\hat{d}_x$	qx	qx
	$\hat{d}_y$	qy	qy
	$\hat{d}_z$	qz	qz

[a] This is the Schrödinger representation of operators.
[b] Pauli matrices σ_i are defined through $\hat{s}_i = (\hbar/2)\sigma_i$.

Let us recall that eigenvalues of the hermitian operator are real, that is to say they form either a discrete set of numbers - discrete spectrum, or they change continuously within a definite interval - continuous spectrum. The eigenfunctions form an orthonormal set. In the case of degenerate eigenvalues ($a_n = a_m$) the corresponding eigenfunctions are not necessarily orthogonal but in all case they can be orthogonalized. The form of important quantum-mechanical operators is shown in Table 2. According to the correspondence principle every classical physical quantity (a function of coordinates and momenta) can be transformed to corresponding quantum-mechanical counterparts by substituting all coordinates and momenta for the respective operators. Such an approach fails for quantities which have no classical analogue (e.g., the spin).

Postulate 3. The time dependence of the state of a microobject is given by the **time-dependent Schrödinger equation**

$$\hat{H}\,\Psi(x;t) = i\hbar\,[\partial\Psi(x;t)/\partial t] \qquad [2]$$

where $\hat{H}$ is the **Hamilton operator** (**Hamiltonian**) standing for the operator of the total energy of the system. In the case of $\hat{H}$ independent of time the above equation has a solution in the form

$$\Psi(x;t) = \psi(x)\,e^{-iEt/\hbar} \qquad [3]$$

where the amplitudal function $\psi(x)$ obeys the **stationary Schrödinger equation**

$$\hat{H}\,\psi(x) = E\,\psi(x) \qquad [4]$$

and E being the total energy of the system. **Stationary states** possess the following properties:

1. the probability density of finding the system in the given point of space does not depend on time;
2. the mean values of physical quantities, the operators of which do not depend on time, are time-independent;
3. the probability that the measurement of the quantity A would yield just the value of a_n is time-independent.

It should be mentioned that the Schrödinger equation cannot be derived from other physical principles; this belongs to principal postulates of quantum mechanics only.

Postulate 4. The mean (average) value of the physical quantity A in the state Ψ of the system is

$$\langle A\rangle = [\int \Psi^*(x;t)\,\hat{A}\,\Psi(x;t)\,dx]/[\int \Psi^*(x;t)\,\Psi(x;t)\,dx] =$$
$$= \langle\Psi|\hat{A}|\Psi\rangle/\langle\Psi|\Psi\rangle \qquad [5]$$

The denominator of the above expression adopts a unity value for the normalized wave functions.

Postulate 5. The wave function has to be antisymmetric (symmetric) with respect to the transposition of fermions (bosons). Fermions are particles of half-valued spin (e.g., electrons) whereas bosons have an integer spin (e.g., photons) in units of $\hbar$.

A collection of important statements of quantum mechanics is presented bellow without exact proofs; they can be found in textbooks of quantum mechanics (1-13).

1. The commutating operators

$$[\hat{A},\hat{B}]_- = \hat{A}\hat{B} - \hat{B}\hat{A} = \hat{0} \qquad [6]$$

have a common set of eigenfunctions, so that it holds true

$$\hat{A}\ \Psi_n = a_n\ \Psi_n \qquad [7]$$

$$\hat{B}\ \Psi_n = b_n\ \Psi_n \qquad [8]$$

The difference in measurement of physical quantities A and B described by the same wave function Ψ_n is zero: $\Delta A = 0$, $\Delta B = 0$, so that these quantities can be simultaneously and precisely determined. Contrariwise, the non-commutating operators have no common wave function and the difference in measurement of physical quantities fulfils the **Heisenberg relation**

$$\Delta A\ \Delta B \geq (1/2)\ \langle[\hat{A},\hat{B}]^2\rangle^{1/2} \qquad [9]$$

2. The operator of linear momentum does not commutate with the corresponding coordinate

$$[\hat{r}_k,\hat{p}_j]_- = \hat{r}_k\hat{p}_j - \hat{p}_j\hat{r}_k = i\hbar\delta_{kj} \qquad [10]$$

This means that both these quantities (for example x and p_x) cannot be simultaneously measured exactly.

3. The components of the angular momentum (orbital $\hat{l}$ and spin $\hat{s}$) fulfil the relationships

$$[\hat{l}_x,\hat{l}_y]_- = i\hbar\hat{l}_z \qquad [11]$$

$$[\hat{l}_y,\hat{l}_z]_- = i\hbar\hat{l}_x \qquad [12]$$

$$[\hat{l}_z,\hat{l}_x]_- = i\hbar\hat{l}_y \qquad [13]$$

This implies that the simultaneous determination of all components of angular momentum is impossible.

4. The operator of square of angular momentum

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \qquad [14]$$

obeys the commutation relationship

$$[\hat{l}^2,\hat{l}_\alpha]_- = \hat{0} \qquad [15]$$

for α = x, y and z; therefore the quadrat of the angular momentum $\hat{l}^2$ and one of the component (say $\hat{l}_z$) can be measured simultaneously. They have a common set of eigenfunctions $\Psi = |l,m_l>$

$$\hat{l}^2 \; |l,m_l> = l(l+1)\hbar^2 \; |l,m_l> \qquad [16]$$

$$\hat{l}_z \; |l,m_l> = m_l \; \hbar \; |l,m_l> \qquad [17]$$

The quantum numbers l and m_l are bound by the condition $-l \le m_l \le l$ and l can adopt half-valued or integer values. Hereafter the notation according to Table 2 is used for angular momenta.

TABLE 2

List of angular momenta operators.[a]

Angular momentum	Operator	Quantum number	Eigenvalue
One-electron			
- orbital	$\hat{l}^2$	l	$l(l + 1)\hbar^2$
	$\hat{l}_z$	m_l	$m_l\hbar$
- spin	$\hat{s}^2$	s	$s(s + 1)\hbar^2$
	$\hat{s}_z$	m_s	$m_s\hbar$
- total	$\hat{j}^2$	j	$j(j + 1)\hbar^2$
	$\hat{j}_z$	m_j	$m_j\hbar$
Many-electron			
- orbital	$\hat{L}^2$	L	$L(L + 1)\hbar^2$
	$\hat{L}_z$	M_L	$M_L\hbar$
- spin	$\hat{S}^2$	S	$S(S + 1)\hbar^2$
	$\hat{S}_z$	M_S	$M_S\hbar$
- total	$\hat{J}^2$	J	$J(J + 1)\hbar^2$
	$\hat{J}_z$	M_J	$M_J\hbar$
Nuclear			
- total [b]	$\hat{I}^2$	I	$I(I + 1)\hbar^2$
	$\hat{I}_z$	M_I	$M_I\hbar$
Total	$\hat{F}^2$	F	$F(F + 1)\hbar^2$
	$\hat{F}_z$	M_F	$M_F\hbar$

[a] Rules for the vector addition are:

$$\hat{L} = \sum_k \hat{l}_k, \; \hat{S} = \sum_k \hat{s}_k, \; \hat{j}_k = \hat{l}_k + \hat{s}_k, \; \hat{J} = \sum_k \hat{j}_k = \hat{L} + \hat{S}, \; \hat{F} = \hat{J} + \hat{I}$$

[b] Total nuclear angular momentum is simply denoted as nuclear spin. In reality, it consists of orbital and spin contributions of individual nucleons.

5. The time development of the arbitrary operator $\hat{A}$ is described as

$$(d\hat{A}/dt) = (\partial\hat{A}/\partial t) + (1/i\hbar)[\hat{A},\hat{H}]_- \qquad [18]$$

If the operator $\hat{A}$ does not depend explicitly on time $(\partial\hat{A}/\partial t) = \hat{0})$ and commutates with the Hamiltonian $\hat{H}$ of the system, $[\hat{A},\hat{H}]_- = \hat{0}$, then the mean value $\langle A\rangle$ is conserved $(d\hat{A}/dt = \hat{0}$, $\langle A\rangle = \text{const.})$ and the quantity A becomes an integral of motion. As a consequence:

a) for time-independent Hamiltonian the energy E obeys a conservation law, since $[\hat{H},\hat{H}]_- = \hat{0}$;

b) the time change of the linear momentum is

$$(d\hat{p}_x/dt) = (1/i\hbar)\ [\hat{p}_x,\hat{H}]_- = -\ (\partial\hat{V}/\partial x) \qquad [19]$$

(Ehrenfest theorem), i.e. in the homogeneous potential field $(\partial\hat{V}/\partial x = \hat{0})$ the linear momentum vector p obeys the conservation law;

c) the time change of the angular momentum is

$$(d\hat{l}_z/dt) = (1/i\hbar)\ [\hat{l}_z,\hat{H}]_- = -\ [x(\partial\hat{V}/\partial y) - y(\partial\hat{V}/\partial x)] \qquad [20]$$

so that in isotropic (central symmetric) potential field the angular momentum vector l obeys the conservation law;

d) the time change of parity is

$$(d\hat{P}/dt) = (1/i\hbar)\ [\hat{P},\hat{H}]_- = (1/i\hbar)\ [\hat{P},\hat{V}]_- \qquad [21]$$

so that in the central symmetric potential field the state parity obeys the conservation law. The parity operator is defined by the relationship

$$\hat{P}\ \Psi(x,y,z;t) = \Psi(-x,-y,-z;t) = \epsilon_p\ \Psi(x,y,z;t) \qquad [22]$$

and its eigenvalues are $\epsilon_p = \pm 1$.

6. The eigenfunctions of a hermitian operator, corresponding to an observable A, form a **complete set**. This implies that an arbitrary normalized wave function Ψ can be expressed in form of an infinite series

$$\Psi = \sum_i c_i\ \Psi_i \qquad [23]$$

where $\{\Psi_i\}$ is a complete set of eigenfunctions of the operator $\hat{A}$, $\hat{A}\ \Psi_i = a_i\ \Psi_i$. The mean value of the operator $\hat{A}$ is a state described by the wave function Ψ is

$$\langle A\rangle = \sum_i c_i^*\ c_i\ a_i = \sum_i |c_i|^2\ a_i \qquad [24]$$

The complex coefficients $c_i = \langle\Psi_i|\Psi\rangle$ determine the probability $W_i = |c_i|^2$ so that the result of measurement of quantity A would be the eigenvalue a_i of the corresponding operator A.

7. The eigenfunction of the operator of the positional vector $\hat{r}(x,y,z)$ is represented by the **Dirac delta function**

$$\hat{r}\ \delta(x,y,z) = r_0\ \delta(x,y,z) \qquad [25]$$

which vanishes in all points of the space except in the point of measurement $r(x,y,z) = r_0(x_0,y_0,z_0)$. The Dirac function has many important properties, for example

$$\delta(-x) = \delta(x) \qquad [26]$$

$$\int_{-\infty}^{+\infty} f(x)\ \delta(x - a)\ dx = f(a) \qquad [27]$$

$$\int_{-\infty}^{+\infty} \delta(x - x_0)\ dx = 1 \qquad [28]$$

$$x\ \delta(x) = 0 \qquad [29]$$

8. The mean value of the Hamiltonian $\hat{H}$ through the normalized wave function Φ is the upper estimate of the lowest eigenvalue E_0

$$<H> = <\Phi|\hat{H}|\Phi> = \sum_i c_i^* c_i E_i \geq E_0 \qquad [30]$$

which represents the statement of the **Rayleigh-Ritz variational principle**.

9. The **virial theorem** links together the mean value of the kinetic energy <T> and the potential energy <V>, $\hat{V} = \hat{V}(x,y,z)$, at the eigenstates of the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$

$$2<T> = <r.\nabla V> \qquad [31]$$

In the case of a Coulomb potential $V \sim 1/r$ it holds true that

$$2<T> = -<V> \qquad [32]$$

In diatomic molecules the virial theorem adopts the form of

$$2<T> + <V> = R(\partial<E>/\partial R) = 0 \qquad [33]$$

where the total molecular energy <E> is a function of internuclear separation R.

10. The **superposition principle** states that if the functions $\Psi_1(x), \Psi_2(x),\ldots,\Psi_n(x)$ represent the possible wave functions of the system, then the function

$$\Psi(x) = \sum_i c_i \Psi_i(x) \qquad [34]$$

belongs to possible wave functions, too. This statement follows from the use of linear operators in the quantum mechanics.

11. The eigenfunctions $|s,m_s>$ of the operator of electron spin obey the relationships

$$\hat{s}_z\ |s,m_s\rangle = m_s\hbar\ |s,m_s\rangle \qquad [35]$$

$$\hat{s}^2\ |s,m_s\rangle = s(s+1)\hbar^2\ |s,m_s\rangle \qquad [36]$$

for the quantum numbers $s = 1/2$ and $m_s = \pm 1/2$ ($-s \le m_s \le +s$). For the eigenfunctions the following notation was introduced: $|s = 1/2, m_s = 1/2\rangle = \alpha(\xi)$, $|s = 1/2, m_s = -1/2\rangle = \beta(\xi)$, where ξ is a formal continuous variable enabling to write the normalization conditions in the form

$$\int \alpha^*(\xi)\ \alpha(\xi)\ d\xi = 1 \qquad [37]$$

$$\int \beta^*(\xi)\ \beta(\xi)\ d\xi = 1 \qquad [38]$$

$$\int \alpha^*(\xi)\ \beta(\xi)\ d\xi = 0 \qquad [39]$$

$$\int \beta^*(\xi)\ \alpha(\xi)\ d\xi = 0 \qquad [40]$$

The wave function of a particle of zero spin $\Psi(r_k,s_k=0;t)$ is a scalar quantity. As the spin variable (projection into a certain direction) has only finite number of discrete values, the wave function of a particle of non-zero spin forms a set differing only in the spin index. A two-component wave function of an electron is termed the **spinor**

$$\Psi(r,s;t) = \begin{pmatrix} \phi_+(r,t) \\ \phi_-(r,t) \end{pmatrix} = \phi_+(r,t)\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \phi_-(r,t)\begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad [41]$$

where the spatial function $\phi_+(r,t)$ corresponds to $m_s = +1/2$ and the function $\phi_-(r,t)$ to $m_s = -1/2$. Elementary spin functions may be written as

$$\alpha(\xi) = |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad [42]$$

$$\beta(\xi) = |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad [43]$$

and it is obvious that they obey the relationships $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$. These functions, however, are not eigenfunctions of the operators $\hat{s}_x$ and $\hat{s}_y$ (operators $\hat{s}_x$ and $\hat{s}_y$ do not commutate with $\hat{s}_z$), as

$$\hat{s}_x\ \alpha = (\hbar/2)\ \beta \qquad [44]$$

$$\hat{s}_x\ \beta = (\hbar/2)\ \alpha \qquad [45]$$

$$\hat{s}_y\ \alpha = (i\hbar/2)\ \beta \qquad [46]$$

$$\hat{s}_y\ \beta = -(i\hbar/2)\ \alpha \qquad [47]$$

The operators of spin have properties analogous to those of orbital angular momentum. The operator of an angular momentum can be understood as an operator of infinitesimal rotations (13). The spin operator, however, does not act on the continuous variable but on the discrete one; therefore the corresponding infinitesimal rotation should be imagined as the rotation of the whole coordinate system. It is useless to imagine the spin as a rotation of the particle along its axis. For example, the H_2 molecule in its ground state has zero spin but it rotates around the molecular axis - it possesses a quantized rotation momentum and exhibits the rotation spectra. In passing to macroscopic bodies ($\hbar \rightarrow 0$) the spin properties disappear so that there is no a classical interpretation of the spin. On the contrary, the rotation momentum increases ($L \rightarrow \infty$), so that the product $L\hbar$ adopts for macroscopic bodies a definite value.

12. The **Hellmann-Feynman theorem** states that the forces acting to atomic nuclei in the stationary states are given by

$$(\partial E/\partial x_A) = F_x^{(A)} \qquad [48]$$

where $F_x^{(A)}$ is the component of a force acting to the A-th nucleus. Such an expression was known even in the classical physics but, now the function $E(\ldots,x_A,\ldots)$ should be obtained by a quantum-mechanical approach. In an equivalent formulation it is

$$<(\partial\Psi/\partial R)|\hat{H}|\Psi> = 0 \qquad [49]$$

13. The **Kramers theorem** states that in the system of odd electrons, the Hamiltonian of which is invariant to time reversal, the electronic levels are at least doubly degenerate. Let us consider the time-reversal operator $\hat{K}$ of the N-electron system in

$$\hat{K} = \prod_{j=1}^{N} (-i\sigma_{yj})\, K_0 \qquad [50]$$

where $\hat{K}_0$ is the operator altering the orbital part of the wave function to its complex conjugate

$$\hat{K}_0\, \Psi(r) = \Psi^*(r) \qquad [51]$$

and σ_{yj} is the Pauli spin matrix altering the spin function of j-th electron from α to β and *vice versa*

$$\sigma_{yj} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_j \qquad [52]$$

Then it holds true that

$$\hat{K}^2 = \hat{K}\,\hat{K} = (-1)^N \qquad [53]$$

If the wave function Ψ describes a stationary state of energy E, then the function $\hat{K}\Psi$ describes a state of the same energy. When the functions Ψ and $\hat{K}\Psi$ differ only in the phase factor, i.e.

$$\hat{K}\ \Psi = c\ \Psi \qquad [54]$$

with $|c| = 1$, then both the states are identical. When time reversal is applied to both sides of eq. [39], we get

$$\hat{K}^2\ \Psi = \hat{K}\ c\ \Psi = |c|^2\ \Psi = \Psi \qquad [55]$$

The above result holds only for odd N; therefore in systems with an odd number of electrons the states Ψ and $\hat{K}\Psi$ should be different, and thus the Kramers theorem is proven.

1.2 APPROXIMATE METHODS OF QUANTUM MECHANICS

1.2.1 Perturbation Theory for Stationary States

The perturbation theory for stationary (time-independent) states is used to calculate the eigenvalues E_n and eigenfunctions $|\Psi_n>$ of the Hamiltonian $\hat{H}$, which can be written in the form

$$\hat{H} = \hat{H}^0 + \hat{H}' \qquad [56]$$

i.e.,

$$\hat{H}\ |\Psi_n> = E_n\ |\Psi_n> \qquad [57]$$

The perturbation theory is applicaple under these conditions:

1. A hermitian operator $\hat{H}^0$ comprises the dominant part of the Hamiltonian, the solutions of which are already known

$$\hat{H}^0\ |\phi_i> = E_i^0\ |\phi_i> \qquad [58]$$

so that E_i^0 are the eigenvalues and $|\phi_i>$ the eigenfunctions of the **unperturbed Hamiltonian** $\hat{H}^0$.

2. The operator $\hat{H}'$ - **perturbation** - comprises the rest of the total Hamiltonian. The perturbation should be small in comparison with the eigenvalues of $\hat{H}^0$; this is expressed by the condition

$$|\ <\phi_i|\hat{H}'|\phi_j>\ | \ll |E_i^0 - E_j^0| \qquad [59]$$

3. The wave function $|\Psi_n>$ to be found obeys an **intermediate normalization** condition, i.e.

$$<\phi_i|\Psi_n> = 1 \qquad [60]$$

for the known unperturbed function $|\phi_i>$ which yields the best approximation to the perturbed function $|\Psi_n>$.

4. When the perturbation is switched off, the limitting conditions have to be fulfilled

$$\lim_{\hat{H}'\to 0} |\Psi_n\rangle = |\phi_i\rangle \qquad [61]$$

$$\lim_{\hat{H}'\to 0} E_n = E_i^0 \qquad [62]$$

Hereafter the subscript n will be omitted for the clarity, but the derived formulas will be valid for any state of the system.

First, we search for the shift of energy as an effect of the perturbation. The starting point is the characteristic equation

$$(\hat{H}^0 + \hat{H}')|\Psi\rangle = E\,|\Psi\rangle \qquad [63]$$

which after multiplying from the left side by ϕ_i^* and the integration yields

$$0 = \langle\phi_i|\hat{H}^0|\Psi\rangle + \langle\phi_i|\hat{H}'|\Psi\rangle - E\langle\phi_i|\Psi\rangle =$$

$$= E_i^0\langle\phi_i|\Psi\rangle + \langle\phi_i|\hat{H}'|\Psi\rangle - E\langle\phi_i|\Psi\rangle \qquad [64]$$

Since $\hat{H}^0$ is a hermitian operator, we may write

$$\langle\phi_i|\,\hat{H}^0 = \langle\phi_i|\,E_i^0 \qquad [65]$$

Using the intermediate normalization $\langle\phi_i|\Psi\rangle = 1$ we arrive at the relationship

$$E = E_i^0 + \langle\phi_i|\hat{H}'|\Psi\rangle \qquad [66]$$

Second, we search for the expression of the perturbed wave function. Again we start from the characteristic equation [63] in a modified form

$$(\epsilon - \hat{H}^0)|\Psi\rangle = (\hat{H}' + \epsilon - E)|\Psi\rangle \qquad [67]$$

where ϵ is an arbitrary number (the reference energy level). By introducing an inverse operator we get

$$|\Psi\rangle = (\epsilon - \hat{H}^0)^{-1}\,(\hat{H}' - \epsilon - E)|\Psi\rangle \qquad [68]$$

Now we introduce a projection operator $\hat{P}$ as an effect of which the perturbation is switched off

$$\hat{P}\,|\Psi\rangle = |\phi_i\rangle \qquad [69]$$

(The projection operators are to be hermitian, $\hat{P}^+ = \hat{P}$, and idempotent, $\hat{P}^2 = \hat{P}$. They transform a basis of any linear vector space to its subspace.) Eq. [69] may be transcribed as

$$|\Psi\rangle = |\phi_i\rangle + (\hat{1} - \hat{P})|\Psi\rangle \qquad [70]$$

which, after substitution of $|\Psi\rangle$ for [68], yields the formula

$$|\Psi\rangle = |\phi_i\rangle + (\hat{1} - \hat{P})(\epsilon - \hat{H}^0)^{-1}(\hat{H}' + \epsilon - E)|\Psi\rangle \qquad [71]$$

appropriate one for an iterative solution. The final expression may be written as

$$|\Psi> = \sum_{n=0}^{\infty} \{(\hat{1} - \hat{P})(\epsilon - \hat{H}^0)^{-1}(\hat{H}' + \epsilon - E)\}^n |\phi_i> \qquad [72]$$

The number ϵ has been arbitrary. By an appropriate choice we obtain two basic forms of the perturbation theory.

1. At $\epsilon = E$ the Brillouin-Wigner perturbation theory is obtained

$$|\Psi> = \sum_{n=0}^{\infty} \{(\hat{1} - \hat{P})(E - \hat{H}^0)^{-1} \hat{H}'\}^n |\phi_i> \qquad [73]$$

2. At $\epsilon = E_i^0$ we arrive at the Rayleigh-Schrödinger perturbation theory

$$|\Psi> = \sum_{n=0}^{\infty} \{(\hat{1} - \hat{P})(E_i^0 - \hat{H}^0)^{-1}(\hat{H}' + E_i^0 - E)\}^n |\phi_i> \qquad [74]$$

which has broader applications. A disadvantage of the Brillouin-Wigner perturbation theory is represented by the fact that the denominator depends upon the final energy value; this requires an iterative solution of equations.

The form of the projection operator $\hat{P}$ can be found by taking into account property that unperturbed wave functions $|\phi_i>$ form a complete orthonormal set, so that the following expansion is applicable

$$|\Psi> = \sum_j c_j |\phi_j> = |\phi_i> + \sum_{j\neq i} c_j |\phi_j> \qquad [75]$$

in which $c_j = <\phi_j|\Psi>$ and $c_i = 1$. Then it is

$$(\hat{1} - \hat{P})|\Psi> = \sum_{j\neq i} c_j |\phi_j> = \{ \sum_{j\neq i} |\phi_j><\phi_j| \}|\Psi> \qquad [76]$$

In order to calculate the coefficients c_j the following procedure can be applied. By multiplying eq. [67] form the left side by ϕ_j^*, after integration we get

$$\epsilon<\phi_j|\Psi> - <\phi_j|\hat{H}^0|\Psi> = <\phi_j|\hat{H}'|\Psi> + (\epsilon - E)<\phi_j|\Psi> \qquad [77]$$

and after some manipulations we obtain

$$(\epsilon - E_j^0)c_j = <\phi_j|\hat{H}'|\phi_i> + \sum_{k\neq i} <\phi_j|\hat{H}'|\phi_k>c_k + (\epsilon - E)c_j \qquad [78]$$

In the case of non-zero difference $(\epsilon - E_j^0)$ the final formula is obtained

$$c_j = 1/(\epsilon - E_j^0) \left\{<\phi_j|\hat{H}'|\phi_i> + \sum_{k\neq i} <\phi_j|\hat{H}'|\phi_k>c_k + (\epsilon - E)c_j\right\} \qquad [79]$$

This formula is suitable for an iterative solution.

TABLE 3

Formulas of the second-order Rayleigh-Schrödinger perturbation theory.

Energy $E^{(n)}$	Wave function $\Psi^{(n)}$
$E^{(0)} = E_i^0$	$\Psi^{(0)} = \vert\phi_i>$
$E^{(1)} = E^{(0)} + H'_{ii}$	$\Psi^{(1)} = \Psi^{(0)} + \sum_{j\neq i} [H'_{ji}/(E_i^0 - E_j^0)]\vert\phi_j>$
$E^{(2)} = E^{(1)} +$	$\Psi^{(2)} = \Psi^{(1)} - \sum_{j\neq i} [H'_{ii}H'_{ji}/(E_i^0 - E_j^0)^2]\vert\phi_j> +$
$+ \sum_{j\neq i} [H'_{ij}H'_{ji}/(E_i^0 - E_j^0)]$	$+ \sum_{j\neq i} \sum_{k\neq i} [H'_{jk}H'_{ki}/(E_i^0 - E_j^0)(E_i^0 - E_k^0)]\vert\phi_j>$

The usual requirement of the perturbation theory is the contributions of the higher order to be lower in absolute value than the contributions of preceeding orders; this is the first condition of forming the members of a convergent series.

Explicit formulas for energy and the wave function up to the second order of the Rayleigh-Schrödinger perturbation theory are collected in Table 3.

1.2.2 Perturbation Theory for Degenerate States

Within the framework of the Rayleigh-Schrödinger perturbation theory the energy levels are very often degenerate. In such a case the term $(\epsilon - E_j^0) = E_i^0 - E_j^0 = 0$ and it cannot be used in role of the denominator in eq. [78]. Therefore an alternative formulation of the perturbation theory is necessary for the degenerate states.

As a starting point again the formula [63] can serve; by multiplying from the left side by ϕ_l^*, after integration we get

$$(E_l^0 - E)<\phi_l|\Psi> + <\phi_l|\hat{H}'|\Psi> = 0 \qquad [80]$$

The wave function $|\Psi>$ is expanded in the form of

$$|\Psi> = c_i|\phi_i> + c_j|\phi_j> + \sum_{k\neq i,j} c_k\,|\phi_k> \qquad [81]$$

where $|\phi_i>$ and $|\phi_j>$ are the degenerate wave functions of the same energy value $E_i^0 = E_j^0$; the expanding coefficients are $c_k = <\phi_k|\Psi>$. By substitution to the eq. [62] the following relationship is obtained

$$(E_l^0 - E)c_l + <\phi_l|\hat{H}'|\phi_i>c_i + <\phi_l|\hat{H}'|\phi_j>c_j = -\sum_{k\neq i,j} c_k<\phi_l|\hat{H}'|\phi_k> \qquad [82]$$

This equation is fulfilled for arbitrary index l, so that for degenerate state (l = i = j) we arrive at the system of equations

$$(E_i^0 - E + \langle\phi_i|\hat{H}'|\phi_i\rangle)c_i + \langle\phi_i|\hat{H}'|\phi_j\rangle c_j = -\sum_{k\neq i,j} c_k\langle\phi_i|\hat{H}'|\phi_k\rangle$$

$$\langle\phi_j|\hat{H}'|\phi_i\rangle c_i + (E_j^0 - E + \langle\phi_j|\hat{H}'|\phi_j\rangle)c_j = -\sum_{k\neq i,j} c_k\langle\phi_j|\hat{H}'|\phi_k\rangle \qquad [83]$$

In the first-order perturbation theory (in the first iteration) the right side can be simply neglected. In the other words we search for such a combination of degenerate functions $|\phi_i\rangle$ and $|\phi_j\rangle$ that makes the perturbation $\hat{H}'$ to be diagonal. Notice, that an arbitrary linear combination of degenerate functions belongs to the set of eigenfunctions of the unperturbed Hamiltonian $\hat{H}^0$. Thus the system of equations [65] is transformed to a system of linear equations for energy E and the combination coefficients c_i and c_j

$$\begin{pmatrix} H'_{ii} + E_i^0 - E; & H'_{ij} \\ H'_{ji} & ; H'_{jj} + E_j^0 - E \end{pmatrix}\begin{pmatrix} c_i \\ c_j \end{pmatrix} = 0 \qquad [84]$$

Here the matrix elements $H'_{ij} = \langle\phi_i|\hat{H}'|\phi_j\rangle$ have been introduced. In the case of strict degeneracy it is $E_i^0 = E_j^0$ so that for the shift of energy $\Delta E = E - E_i^0$, as an effect of the perturbation, the characteristic equation is obtained

$$(H' - \Delta E\ I)C = 0 \qquad [85]$$

where I is a unit matrix. Its solution is obtained for the zero value of the determinant

$$det\ (H' - \Delta E\ I) = 0 \qquad [86]$$

and it leads to different roots ΔE_d (d is the degree of degeneracy that determines the dimension of matrix H'). The final expression for the energy shift, as an effect of the perturbation, is

$$E^{(1)} = E_i^0 + \Delta E_d \qquad [87]$$

This means that due to the perturbation the degeneracy disappears: the degenerate level is split into sublevels of different energy. The effect of the perturbation to energy values is shown in Fig. 1.

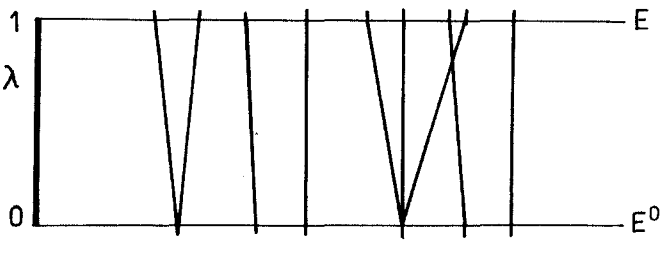

Fig. 1. Effect of perturbation to the spectrum of Hamiltonian.

The perturbation theory is often formulated on the basis of the Hamiltonian

$$\hat{H}(\lambda) = \hat{H}^0 + \lambda\hat{H}' \qquad [88]$$

where λ is the parameter ranging between $0 \le \lambda \le 1$; when the perturbation is switched on parameter λ adopts value of 1. The main reason of introducing the parameter λ lies in its utilization in distinguishing various orders of the perturbation theory as explained below.

The eigenvalues $E_n(\lambda)$ and eigenfunctions $\Psi_n(\lambda)$ of the Hamiltonian $\hat{H}(\lambda)$ may be expanded into a power series

$$E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \qquad [89]$$

$$\Psi_n(\lambda) = \phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + \ldots \qquad [90]$$

They may be used in the Schrödinger equation

$$\hat{H}(\lambda)\ |\Psi_n(\lambda)\rangle = E_n(\lambda)\ |\Psi_n(\lambda)\rangle \qquad [91]$$

By comparing coefficients standing at individual powers of λ, i.e. at λ^0, λ^1, λ^2, etc., we obtain a set of equations

$$\hat{H}^0|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(0)}\rangle, \text{ for } \lambda^0 \qquad [92]$$

$$\hat{H}^0|\phi_n^{(1)}\rangle + \hat{H}'|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(1)}\rangle + E_n^{(1)}|\phi_n^{(0)}\rangle, \text{ for } \lambda^1 \qquad [93]$$

$$\hat{H}^0|\phi_n^{(2)}\rangle + \hat{H}'|\phi_n^{(1)}\rangle = E_n^{(0)}|\phi_n^{(2)}\rangle + E_n^{(1)}|\phi_n^{(1)}\rangle + E_n^{(2)}|\phi_n^{(0)}\rangle, \text{ for } \lambda^2 \qquad [94]$$

This set may be utilized in deriving formulas in which the higher-order contributions of the perturbation theory recurrently depend upon lower-order terms.

1.2.3 Linear Variation Method

We are looking for the solution of the Schrödinger equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$ by considering the wave function $|\Psi\rangle$ in the form of a restricted linear combination of known basis set functions $|\phi_i\rangle$

$$|\Psi\rangle \approx |\Phi\rangle = \sum_i^n c_i\ |\phi_i\rangle \qquad [95]$$

The mean energy value is given by the relationship

$$\langle E\rangle = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \frac{\sum_i\sum_j c_i^* c_j \langle\phi_i|\hat{H}|\phi_j\rangle}{\sum_i\sum_j c_i^* c_j \langle\phi_i|\phi_j\rangle} = \frac{c^+ H c}{c^+ S c} \qquad [96]$$

where **c** is a column vector of coefficients c_i, **c** is a row vector of coefficients c_i^* (hermitian conjugate), **H** is a matrix of integrals $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$ and **S** is the overlap integral matrix of elements $S_{ij} = \langle\phi_i|\phi_j\rangle$. From the variational principle [30] it follows that the mean value will be the upper estimate of the lowest eigenvalue E_0 of the Hamiltonian

$$\langle E\rangle = f(c_1, c_2, \ldots, c_n) \geq E_0 \qquad [97]$$

Now the problem could be formulated as evaluation of coefficients c_i which minimize the energy functional $\langle E\rangle$. In an alternative formulation the energy functional $E = f(c_1, c_2, \ldots, c_n) = \langle\Phi|\hat{H}|\Phi\rangle$ should be minimized at the boundary condition $\langle\Phi|\Phi\rangle = 1$. In this case the method of Lagrangian multipliers is applicable: such a Lagrangian multiplier ε is chosen so that the functional

$$F(c_1, c_2, \ldots, c_n) = \langle\Phi|\hat{H}|\Phi\rangle - \varepsilon\langle\Phi|\Phi\rangle = \sum_i \sum_j (H_{ij} - \varepsilon S_{ij}) c_i^* c_j \qquad [98]$$

adopts the minimum value. The condition of the minimum is $(\partial F/\partial c_i^*) = 0$ for all i = 1, 2, ..., n; this yields a homogeneous system of linear equations for the coefficients c_i

$$\sum_j^n (H_{ij} - \varepsilon S_{ij}) c_j = 0 \qquad [99]$$

or in the matrix form

$$(\mathbf{H} - \varepsilon\mathbf{S})\mathbf{c} = 0 \qquad [100]$$

This system of equations has the non-trivial solutions for zero determinant

$$det(\mathbf{H} - \varepsilon\mathbf{S}) = 0 \qquad [101]$$

The above equation serves for determination of the unkown Lagrangian multiplier ε. The second condition of the minimum $(\partial F/\partial c_j) = 0$ for all j = 1, 2, ..., n yields exactly the same result. By multiplying the eq. [100] from the left side by non-zero vector $\mathbf{c}^+$ we arrive at the relationship

$$(\mathbf{c}^+\mathbf{H}\mathbf{c})(\mathbf{c}^+\mathbf{S}\mathbf{c})^{-1} = \varepsilon \qquad [102]$$

so that the Lagrangian multiplier is just the energy of the system: $\varepsilon = \langle E\rangle$. Since [99] is an algebraic equation of n-th order with respect to ε, it has, in general, n roots. The ground-state energy equals to the minimum root: $E = min\{\varepsilon_n\}$.

The basis set extension n → n' leads to systematic changes in eigenvalues E_n. Hylleraas, Udheim and McDonald (14,15) prooved a **separation theorem**, according to which any basis set extension may lead only to lowering of energy eigenvalues (see Fig. 2)

$$E^{(n)}(c_1,\dots,c_n) \geq E^{(n+1)}(c_1,\dots,c_n,c_{n+1}) \geq E_0 \qquad [103]$$

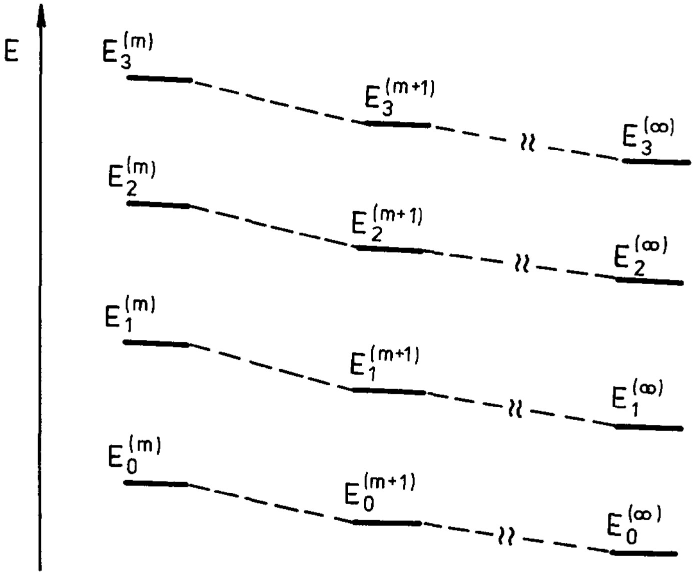

Fig. 2. Changes in energies of states by the basis set extension in the variational method.

Therefore the following limitting relationships hold true

$$\lim_{n\to\infty} |\Phi\rangle = |\Psi\rangle \qquad [104]$$

$$\lim_{n\to\infty} E(c_1,c_2,\dots,c_n) = E_0 \qquad [105]$$

The above criteria are often used in testifying the basis sets in *ab initio* methods.

1.2.4 Nonlinear Variation Method

The trial wave function $|\Phi\rangle = f(p_1,p_2,\dots,p_n)$ dependent on the set of variational parameters $\{p_n\}$ may be chosen in a more complicated, nonlinear form. Such a function has to fulfil all the requirements placed to the wave functions. In the above method a set of parameters $(p_1^0, p_2^0, \dots, p_n^0)$ is searched for so that the mean value of the system energy becomes minimum

$$\langle E\rangle = f(p_1,p_2\dots,p_n) = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \qquad [106]$$

Such a value represents the upper estimate of the ground-state energy E_0 for the given type of trial function. In processing at digital computers one of the numerous minimization procedures is used. It is of advantage when analytical formula for the energy gradient is known, i.e. the vector $G(\partial E/\partial p_1, \partial E/\partial p_2, \ldots, \partial E/\partial p_n)$. The variational method may be adapted to determine the excited states, too. The corresponding trial wave function, however, should be orthogonal to the ground-state wave function as well as to all wave functions of lower in energy excited states.

1.2.5 Partitioning Method

This method serves for decomposition of a high-dimensional secular equation to matrix equations of lower dimension. We start from the transcription of matrix equation (H - EI)C to blocks of lower dimension

$$\begin{pmatrix} H^{AA} & ; & H^{AB} \\ H^{BA} & ; & H^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} = E \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} \qquad [107]$$

which is equivalent to a couple of matrix equations

$$H^{AA}\mathbf{a} + H^{AB}\mathbf{b} = E\,\mathbf{a} \qquad [108]$$

$$H^{BA}\mathbf{a} + H^{BB}\mathbf{b} = E\,\mathbf{b} \qquad [109]$$

As far as a non-singular resolvent $R = (EI - H^{BB})^{-1}$ does exit, the second equation enables to express the vector **b**

$$\mathbf{b} = (EI - H^{BB})^{-1}\, H^{BA}\, \mathbf{a} \qquad [110]$$

Then we can solve the equation

$$H^{eff}\, \mathbf{a} = E\, \mathbf{a} \qquad [111]$$

for the matrix of effective Hamiltonian

$$H^{eff} = H^{AA} + H^{AB}\, (EI - H^{BB})^{-1}\, H^{BA} \qquad [112]$$

Such a system of equations can be solved by an iterative procedure. In the case of non-orthogonal basis set we stand at the problem of (H - ES)C = 0 and the solution may be found in a similar way (moreover the terms including overlap integrals appear).

1.2.6 Method of Effective Hamiltonian

The exact Hamiltonian $\hat{H}$ defines a Hilbert space which can be partitioned into a subspace S of exact solutions, which we are interested in, and an orthogonal subspace $S^{\perp}$ of remaining states. We can introduce the corresponding projection operators: $\hat{P} \in S$ and $\hat{Q} \in S^{\perp}$ satisfying the properties of $\hat{P}^2 = \hat{P}$, $\hat{Q}^2 = \hat{Q}$ and $\hat{P} + \hat{Q} = \hat{1}$.

The Hamiltonian $\hat{H}$ may be transformed by a similarity transformation U to the form

$$\hat{\mathcal{H}} = U^{-1}\ \hat{H}\ U = \hat{P}_0\ \hat{\mathcal{H}}\ \hat{P}_0 + \hat{Q}_0\ \hat{\mathcal{H}}\ \hat{Q}_0 \qquad [113]$$

that enables a separation of subspaces $S_0(\hat{P}_0)$ and $S_0^{\perp}(\hat{Q}_0 = \hat{1} - \hat{P}_0)$. The effective Hamiltonian is introduced under constraints

$$\hat{H}^{eff} = \hat{P}_0\ \hat{\mathcal{H}}\ \hat{P}_0 \qquad [114]$$

and it has exactly the same spectrum of eigenvalues in the model subspace S_0 as the complete Hamiltonian $\hat{H}$ in the subspace S.

For the subsequent considerations we introduce the similarity transformation in the form

$$U = \hat{P}(\hat{P}_0\hat{P}\hat{P}_0)^{-\nu} + \hat{Q}(\hat{Q}_0\hat{Q}\hat{Q}_0)^{-\nu} \qquad [115]$$

and the wave operator $\hat{\Omega} = \hat{P}(\hat{P}_0\hat{P}\hat{P}_0)^{-1}$ which transforms the wave functions Ψ_0 from the model space S_0 into wave functions Ψ of the subspace S of exact solutions: $\Psi = \hat{\Omega}\ \Psi_0$. Now by the appropriate choice of ν we obtain:

1. according to Okubo (16) $\nu = 0$, and

$$\hat{H}^{eff} = (\hat{P}_0\hat{P}\hat{P}_0)^{-1}\hat{P}\hat{H}\hat{P}_0 = \hat{\Omega}^{+}\hat{H}\hat{P}_0 \qquad [116]$$

2. according to des Cloizeaux (17) $\nu = 1/2$, and

$$\hat{H}^{eff} = (\hat{P}_0\hat{P}\hat{P}_0)^{-1/2}\hat{P}\hat{H}\hat{P}(\hat{P}_0\hat{P}\hat{P}_0)^{-1/2} = (\hat{\Omega}^{+}\hat{\Omega})^{-1/2}\hat{\Omega}^{+}\hat{H}\hat{\Omega}(\hat{\Omega}^{+}\hat{\Omega})^{-1/2} \qquad [117]$$

3. according to Bloch (18) $\nu = 1$, and

$$\hat{H}^{eff} = \hat{P}_0\hat{H}\hat{P}(\hat{P}_0\hat{P}\hat{P}_0)^{-1} = \hat{P}_0\hat{H}\hat{\Omega} \qquad [118]$$

The commutation relationship $[\hat{H},\hat{P}]_- = \hat{0}$ and the properties of the wave operator imply a general (canonical) operator equation for $\hat{\Omega}$ (19) in the form

$$\hat{H}\hat{\Omega} = \hat{\Omega}\hat{H}\hat{\Omega} \qquad [119]$$

which is equivalent to $[\hat{H},\hat{\Omega}]_-\ \hat{\Omega} = \hat{0}$. By introducing a reduced wave operator $\hat{X} = \hat{Q}_0\hat{\Omega}$ we may arrive at the equation

$$\hat{Q}_0(\hat{1} - \hat{X})\hat{H}(\hat{1} + \hat{X})\hat{P}_0 = 0 \qquad [120]$$

which can be solved by an iterative way. The above procedure is implicitly based on the variational principle for the wave functions instead of standard methods exploiting the Rayleigh-Ritz variational principle for energy.

As far as the perturbation theory is concerned, the Hamiltonian $\hat{H}$ is split into $\hat{H} = \hat{H}^0 + \hat{H}'$ and it holds true that

$$(\hat{H}^0 + \hat{H}')\hat{\Omega} = \hat{\Omega}\hat{H}^0 + \hat{\Omega}\hat{H}'\hat{\Omega} \qquad [121]$$

$$[\hat{H}^0,\hat{X}]_- = -\hat{Q}_0(\hat{1} - \hat{X})\hat{H}'(\hat{1} + \hat{X})\hat{P}_0 \qquad [122]$$

Having known the solutions of the Schrödinger equation for unperturbed Hamiltonian, $\hat{H}^0|\phi_i\rangle = E_i^0|\phi_i\rangle$, we obtain an implicit operator equation for $\hat{X}$

$$\hat{X} = \sum_{i\in S_0} \hat{Q}_0(E_i^0 - \hat{H}^0)^{-1}(\hat{1} - \hat{X})\hat{H}'(\hat{1} + \hat{X})|\phi_i\rangle\langle\phi_i| \qquad [123]$$

which may be solved by an iterative procedure. The above method represents a generalization of the Rayleigh-Schrödinger perturbation theory.

1.3 SYMMETRY IN QUANTUM MECHANICS

Symmetry in quantum mechanics and consequently in quantum chemistry is of an extraordinary importance. Generally speaking, symmetry expresses a specific property of spatial anisotropy of material objects and thus it is closely related to the angular momentum.

Every microparticle (atom, ion molecule, molecular ion) has its own symmetry which is reflected to the symmetry of the corresponding wave function. Therefore the energy levels, the spectral transitions and also chemical reactions are subjects of symmetry rules. Moreover, the use of symmetry makes the practical quantum chemistry more easy as it permits the reduction of evaluation of matrix elements, arrangement of matrix representation of operators into a block-diagonal form and finally the lowering of computing time.

We have no space here to deal with symmetry in details; only the basic principles and necessary conclusions are breafly presented below. To study this subject in more details we can recommend a number of excellent monographs (20-42).

1.3.1 Symmetry of Molecules

The nature of the molecular symmetry lies in the existence of symmetry operations (transformations of coordinates of nuclei) which transforms the molecule into nuclear configuration identical with an initial one. The symmetry elements (axis, plane, inversion centre) remain unchanged. Molecules belong to the category of point groups of symmetry as all the symmetry operations have at least one point in common. This point does not necessarily be identified with any atom of the molecule.

The most important properties of symmetry point groups are collected in Table 4.

TABLE 4

Elementary terms in theory of the symmetry point group.

Term	Property	Note
Symmetry operation $\hat{R}_k$		Inverse operator $\hat{R}_k^{-1}$
$\hat{E}$ $(\hat{I})$	identity	$\hat{E}$
$\hat{C}_n$	rotation about angle $2\pi/n$	$\hat{C}_n^{n-k}$ for $\hat{C}_n^k$
$\hat{\sigma}$ $(\hat{\sigma}_h, \hat{\sigma}_v, \hat{\sigma}_d)$	mirror plane	$\hat{\sigma}$
$\hat{i}$ $(\hat{S}_2)$	inverse centre	$\hat{i}$
$\hat{S}_n = \hat{\sigma}_h \hat{C}_n$	rotation followed by the mirror plane	$\hat{S}_n^{n-k}$ for $\hat{S}_n^k$
Properties of the symmetry group G of order h		
product	$\hat{R}_i\hat{R}_j = \hat{R}_k$	$\hat{R}_i, \hat{R}_j, \hat{R}_k \in G$
associativity	$\hat{R}_i(\hat{R}_j\hat{R}_k) = (\hat{R}_i\hat{R}_j)\hat{R}_k$	
identity property	$\hat{R}_k\hat{E} = \hat{E}\hat{R}_k = \hat{R}_k$	
inversion property	$\hat{R}_k\hat{R}_k^{-1} = \hat{R}_k^{-1}\hat{R}_k = \hat{E}$	$\hat{R}_k, \hat{R}_k^{-1} \in G$
Class T of the group G		
set of operators which fulfil the property	$\hat{R}_i = \hat{R}_s^{-1}\hat{R}_j\hat{R}_s$	$\hat{R}_i, \hat{R}_j \in T$, $\hat{R}_s \in G$
Representation Γ of the group G		
existence of transformation matrices	$\hat{R}_k \Rightarrow A(R_k)$	for $k \in \langle 1,h \rangle$
acting to the basis $(f_1,\ldots,f_l\rangle$	$\hat{R}_k f_m = \sum_{n=1} [A(R_k)]_{nm} f_n$	for $k \in \langle 1,h \rangle$ and $m \in \langle 1,l \rangle$
properties of matrices	$A(R_k)A(R_j) = A(R_i)$	if $\hat{R}_k\hat{R}_j = \hat{R}_i$ for $k \in \langle 1,h \rangle$
dimension of the representation	l = dimension of **A**	
equivalent representations	$B(R_k) = U^{-1}A(R_k)U$	U - unitary matrix $k \in \langle 1,h \rangle$

The symmetry point groups are classified as shown in Table 5. There are several algorithms of how to determine the symmetry point group for molecules. One of them is given by Fig. 3.

A set of matrices $A(R_k)$, transforming coordinates in the same way as the symmetry operators $\hat{R}_k$, forms a **representation** Γ of the group G. The representation is **reducible**, Γ_r, when by the same similarity transformation U a block-diagonal (bd) form of matrices $A(R_k)$ is obtained

$$A_{bd}(R_k) = U^{-1}A(R_k)U \qquad [124]$$

TABLE 5

Symmetry point groups of molecules.

Type Symbol	Symmetry operations $\hat{R}_k$	Order h of group	Number of IR	Note
Nonaxial				
C_1	$\hat{E}$	1	1	C
C_s	$\hat{E}, \hat{\sigma}$	2	2	$C_{1h} = C_{1v} = S_1$
C_i	$\hat{E}, \hat{i}$	2	2	S_2
Axial				
- cyclic				
C_n	$\hat{E}, \hat{C}_n$	n	n	n = 2, 3, ...
S_{2n}	$\hat{E}, \hat{C}_n, \hat{S}_{2n}$	2n	2n	$S_6 = C_{3i}$
- noncyclic				
C_{nh}	$\hat{E}, \hat{C}_n, \hat{\sigma}_h, \hat{S}_n$	2n	2n	
C_{nv}	$\hat{E}, \hat{C}_n, n\hat{\sigma}_v$	2n	(n + 3)/2 (n + 6)/2	for odd n, for even n;
- dihedral				
D_n	$\hat{E}, \hat{C}_n, n\hat{C}_2'$	2n	(n + 3)/2 (n + 6)/2	for odd n, for even n, $D_2 = V$;
D_{nh}	$\hat{E}, \hat{C}_n, n\hat{C}_2', \hat{S}_n,$ $\hat{\sigma}_h, n\hat{\sigma}_v$	4n	n + 3 n + 6	for odd n, for even n, $D_{2h} = V_h$
D_{nd}	$\hat{E}, \hat{C}_n, n\hat{C}_2', n\hat{\sigma}_d,$ $\hat{S}_{2n}$	4n	n + 3	$D_{nd} = S_{2nd}, D_{2d} = V_d$
- linear				
$C_{\infty v}$	$\hat{E}, \hat{C}_\infty, \infty\hat{\sigma}_v$	∞	∞	
$D_{\infty h}$	$\hat{E}, \hat{C}_\infty, \infty\hat{\sigma}_v,$ $\hat{S}_\infty, \infty\hat{C}_2'$	∞	∞	
Cubic				
T	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2$	12	4	
T_h	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2,$ $4\hat{S}_6, 3\hat{\sigma}_v$	24	8	$T_h = C_i \times T$
T_d	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2,$ $3\hat{S}_4, 6\hat{\sigma}_d$	24	5	regular tetrahedron
O	$\hat{E}, 4\hat{C}_3, 3\hat{C}_4, 6\hat{C}_2$	24	5	
O_h	$\hat{E}, 4\hat{C}_3, 3\hat{C}_4, 6\hat{C}_2,$ $3\hat{S}_4, 4\hat{S}_6, 3\hat{\sigma}_h, 6\hat{\sigma}_d$	48	10	regular octahedron

TABLE 5 (Continued)

Type Symbol	Symmetry operations $\hat{R}_k$	Order h of group	Number of IR	Note
Icosahedral				
I	$\hat{E}$, $6\hat{C}_5$, $10\hat{C}_3$, $15\hat{C}_2$	60	5	
I_h	$\hat{E}$, $6\hat{C}_5$, $10\hat{C}_3$, $15\hat{C}_2$, $12\hat{S}_{10}$, $10\hat{S}_6$, $15\hat{\sigma}$	120	10	regular icosahedron

The reducible representation consists of **irreducible** components. The decomposition of a reducible representation into irreducible ones may be written as

$$\Gamma_r = \sum_\alpha n_\alpha \Gamma_\alpha \qquad [125]$$

where n_α is a multiplicity of unequivalent irreducible representations. Their orders obey the relationship

$$l_r = \sum_\alpha n_\alpha l_\alpha \qquad [126]$$

where l_α is the dimension of α-th block A_α in A_{bd}. The matrix elements of irreducible representations (IR) satisfy the orthogonality condition

$$\sum_k^h [A_\alpha(R_k)]_{\mu\nu} [A_\beta(R_k)]_{\lambda\sigma} = h(l_\alpha l_\beta)^{-1/2} \delta_{\alpha\beta}\, \delta_{\mu\lambda}\, \delta_{\nu\sigma} \qquad [127]$$

The irreducible representations are fully characterized by their **characters**

$$\chi_\alpha(R_k) = Tr\{A_\alpha(R_k)\} = \sum_i^{l_\alpha} [A_\alpha(R_k)]_{ii} \qquad [128]$$

for k = 1, 2, ..., h. The characters form an ordered set of traces of transformation matrices and they are orthogonal one to another

$$\sum_k^h \chi_\alpha(R_k)\, \chi_\beta(R_k) = h\, \delta_{\alpha\beta} \qquad [129]$$

The multiplicity n_α of irreducible representation Γ_α in the reducible representation Γ_r is given by the formula

$$n_\alpha = (1/h) \sum_k^h \chi_\alpha(R_k)\, \chi_r(R_k) \qquad [130]$$

The irreducible representations (IR) possess several important properties of which the following are noticeable:

1. number of nonequivalent IR of the group equals to the number of its classes;

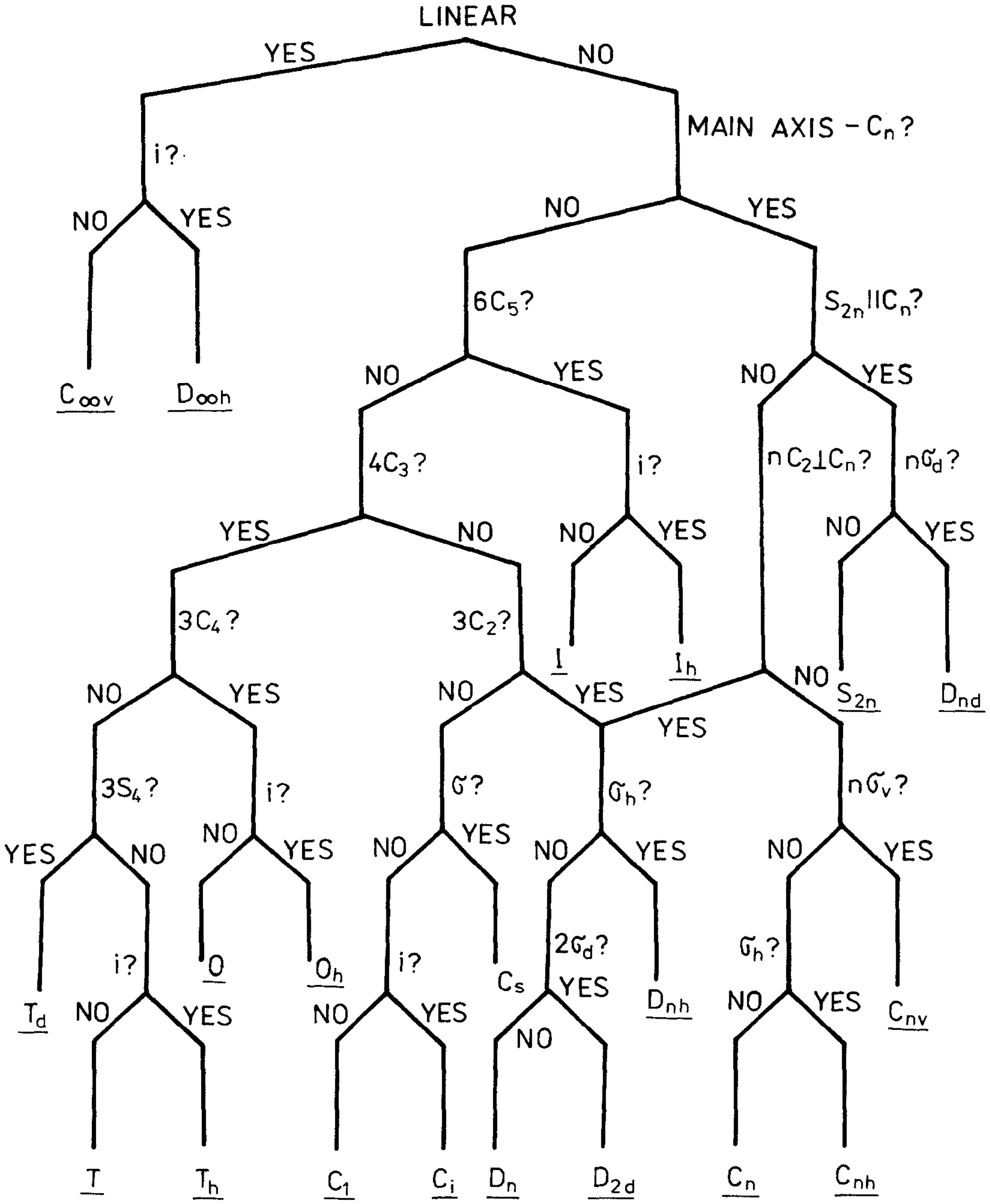

Fig. 3. Algorithm for determination of the symmetry point group of a molecule.

TABLE 6
Mulliken classification of irreducible representations.

Representation Γ_α [a]	Name	Property $\chi_\alpha(R_k) = m$	
		$\hat{R}_k$	m
A	one-dimensional	$\hat{C}_n$	+1
B	one-dimensional	$\hat{C}_n$	-1
E	two-dimensional		
T(F)	three-dimensional		
G	four-dimensional		
H	five-dimensional		
A'	symmetric	$\hat{\sigma}_h$	+1
A''	antisymmetric	$\hat{\sigma}_h$	-1
A_g	even (gerade)	$\hat{i}$	+1
A_u	odd (ungerade)	$\hat{i}$	-1
$A_1(\Sigma^+)$, $E_1(\Pi)$	symmetric	$\hat{\sigma}_v$	+1
$A_2(\Sigma^-)$, $E_2(\Delta)$	antisymmetric	$\hat{\sigma}_v$	-1
A_3, $E_3(\Phi)$		specific properties	

[a] For linear groups ($C_{\infty v}$ and $D_{\infty h}$) the notation in brackets (Σ^+, Σ^-, Π, Δ, Φ) is used.

2. sum of quadrats of dimensions of IR equals to the order h of the group;
3. dimensions l_α of IR are divisors of the order h of the group;
4. a unit (totally symmetric) IR belongs to the set of IRs; its characters are units.

The irreducible representations are denoted as shown in Table 6. The capital letters (A, B, E, T, or Σ, Π, Δ, Φ) are used to characterize the symmetry of electronic states whereas small letters (a, b, e, t, or σ, π, δ, ϕ) denote the symmetry of molecular orbitals or normal vibrations. Characters of irreducible representations are tabulated in numerous monographs and therefore only a few of them are collected in Table 7.

From the above relationships an important formula may be derived

$$\hat{\eta}^{(\alpha)} f_m = (l_\alpha/h) \{\sum_k^h \chi_\alpha(R_k) \hat{R}_k\} f_m = f_m^{(\alpha)} \qquad [131]$$

This means that a function $f_m^{(\alpha)}$ belonging to a given irreducible representation α is obtained as an effect of action of a projection operator $\hat{\eta}^{(\alpha)}$ to any member of the basis - the generator f_m. The construction of such a projection operator is obvious from [131]. It is used in generating a set of symmetry (group) orbitals for molecular orbital methods or symmetry coordinates in the theory of vibration spectra.

In practical applications an important role is played by the direct product of representations. Let us consider a basis set $(f_1, f_2, \ldots, f_m)$ of m-dimensional representation $A(R_k)$ and the basis set $(g_1, g_2, \ldots, g_n)$ of n-dimensional representation $B(R_k)$. The products $f_i g_j$ form a basis set of new representation $C(R_k)$ having dimension m x n; this corresponds to a direct (tensor) product of matrices $A(R_k)$ and $B(R_k)$

$$C(R_k) = A(R_k) \otimes B(R_k) \qquad [132]$$

The direct product (DP) embraces these important properties:

1. DP is commutative, $A \otimes B = B \otimes A$;
2. DP of two diagonal matrices is again a diagonal matrix;
3. DP of two unit matrices is again a unit matrix;
4. DP of two unitary matrices is again a unitary matrix;
5. character of a DP of two representations, $\Gamma_\gamma = \Gamma_\alpha \otimes \Gamma_\beta$, equals to a product of corresponding characters

$$\chi_\gamma(R_k) = \chi_\alpha(R_k)\ \chi_\beta(R_k) \qquad [133]$$

6. DP of two irreducible representations is, in general, a reducible representation which may be expressed in the form of the sum of irreducible representations

$$\Gamma_\alpha \otimes \Gamma_\beta = \Gamma_r = \sum_\epsilon n_\epsilon\ \Gamma_\epsilon \qquad [134]$$

7. DP of two irreducible representations can be decomposed to a symmetric component, $[C(R_k)]_+$, and antisymmetric one, $[C(R_k)]_-$

$$A(R_k) \otimes B(R_k) = [C(R_k)]_+ + [C(R_k)]_- \qquad [135]$$

The following rules hold for the direct product of irreducible representations:

1. for the representation A
   - $A \otimes A = A$
   - $A \otimes B = B$
   - $A \otimes E_k = E_k$
   - $A \otimes T = T$
2. for the representation B
   - $B \otimes B = A$ for all groups except D_2 and D_{2h};
   - $B \otimes B = B$ for groups D_2 and D_{2h} if their numerical indices are different;

TABLE 7

Characters of irreducible representations of most frequent groups.

Order Group Γ_i	Classes of symmetry operations									
h = 4										
C_{2v}	E	C_2	σ_v	σ_v'						
A_1	+1	+1	+1	+1						
A_2	+1	+1	-1	-1						
B_1	+1	-1	+1	-1						
B_2	+1	-1	-1	+1						
h = 8										
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$					
D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$					
D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$					
A_1	+1	+1	+1	+1	+1					
A_2	+1	+1	+1	-1	-1					
B_1	+1	-1	+1	+1	-1					
B_2	+1	-1	+1	-1	+1					
E	+2	0	-2	0	0					
h = 16										
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1
E_g	+2	0	-2	0	0	+2	0	-2	0	0
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1
E_u	+2	0	-2	0	0	-2	0	+2	0	0
h = 24										
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$					
O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$					
A_1	+1	+1	+1	+1	+1					
A_2	+1	+1	+1	-1	-1					
E	+2	-1	+2	0	0					
T_1	+3	0	-1	+1	-1					
T_2	+3	0	-1	-1	+1					

TABLE 7 (Continued)

Order Group Γ_i	Classes of symmetry operations									
h = 48										
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
A_{2g}	+1	+1	−1	−1	+1	+1	−1	+1	+1	−1
E_g	+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
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_u	+2	−1	0	0	+2	−2	0	+1	−2	0
T_{1u}	+3	0	−1	+1	−1	−3	−1	0	+1	+1
T_{2u}	+3	0	+1	−1	−1	−3	+1	0	+1	−1
h = ∞										
$C_{\infty v}$	E	$2C_\infty^\varphi$	...	$\infty\sigma_v$						
Σ^+	+1	+1	...	+1						
Σ^-	+1	+1	...	−1						
Π	+2	$2\cos\varphi$	...	0						
Δ	+2	$2\cos 2\varphi$	...	0						
Φ	+2	$2\cos 3\varphi$	...	0						
...			...							
$D_{\infty h}$	E	$2C_\infty^\varphi$	...	$\infty\sigma_v$	i	$2S_\infty^\varphi$	...	$\infty C_2'$		
Σ_g^+	+1	+1	...	+1	+1	+1	...	+1		
Σ_g^-	+1	+1	...	−1	+1	+1	...	−1		
Π_g	+2	$2\cos\varphi$	...	0	+2	$-2\cos\varphi$	...	0		
Δ_g	+2	$2\cos 2\varphi$	...	0	+2	$+2\cos 2\varphi$	...	0		
Φ_g	+2	$2\cos 3\varphi$	...	0	+2	$-2\cos 3\varphi$	...	0		
...			...				...			
Σ_u^+	+1	+1	...	+1	−1	−1	...	−1		
Σ_u^-	+1	+1	...	−1	−1	−1	...	+1		
Π_u	+2	$2\cos\varphi$	...	0	−2	$+2\cos\varphi$	...	0		
Δ_u	+2	$2\cos 2\varphi$	...	0	−2	$-2\cos 2\varphi$	...	0		
Φ_u	+2	$2\cos 3\varphi$	...	0	−2	$+2\cos 3\varphi$	...	0		
...			...				...			

TABLE 8
Irreducible components of direct products of degenerate representations.

G_n[a]	Note		$\Gamma_i \backslash$	Γ_1	Γ_2	Γ_3	Γ_4
3	$+S_6$	E	Γ_1	$A_1,(A_2),E$;			
4	$+D_{2d}$	B	Γ_1	A;			
	$-D_{4d}$	E	Γ_2	E;	$A_1,(A_2),B_1,B_2$;		
5	$+S_{10}$	E_1	Γ_1	$A_1,(A_2),E_2$;			
		E_2	Γ_2	E_1,E_2;	$A_1,(A_2),E_1$;		
6	$-S_6$	B	Γ_1	A;			
	$-D_{6d}$	E_1	Γ_2	E_2;	$A_1,(A_2),E_2$;		
		E_2	Γ_3	E_1;	B_1,B_2,E_1;	$A_1,(A_2),E_2$;	
7		E_1	Γ_1	$A_1,(A_2),E_2$;			
		E_2	Γ_2	E_1,E_3;	$A_1,(A_2),E_3$;		
		E_3	Γ_3	E_2,E_3;	E_1,E_2;	$A_1,(A_2),E_1$;	
8	$+D_{4d}$	B	Γ_1	A;			
	$-D_{8d}$	E_1	Γ_2	E_3;	$A_1,(A_2),E_2$;		
		E_2	Γ_3	E_2;	E_1,E_3;	$A_1,(A_2),B_1,B_2$;	
		E_3	Γ_4	E_1;	B_1,B_2,E_2;	E_1,E_3;	$A_1,(A_2),E_2$
Linear		Σ	Γ_1	Σ;			
		Π	Γ_2	Π;	$\Sigma^+,(\Sigma^-),\Delta$;		
		Δ	Γ_3	Δ;	Π,Φ;	$\Sigma^+,(\Sigma^-),\Gamma$;	
Cubic		E	Γ_1	$A_1,(A_2),E$;			
		T_1	Γ_2	T_1,T_2;	$A_1,E,(T_1),T_2$;		
		T_2	Γ_3	$(T_1),T_2$;	A_2,E,T_1,T_2;	$A_1,E,(T_1),T_2$;	
I,I_h		T_1	Γ_1	$A,(T_1),H$;			
		T_2	Γ_2	G,H;	$A,(T_2),H$;		
		G	Γ_3	T_2,G,H;	T_1,G,H;	$A,(T_1+T_2),G,H$;	
		H	Γ_4	T_1,T_2,G,H;	T_1,T_2,G,H;	$T_1,T_2,G,2H$;	(T_1+T_2+G), $A,G,2H$;

[a] Groups $G_n = C_n, C_{nh}, C_{nv}, D_n, D_{nh}, D_{nd}$ and S_n.

TABLE 9
Irreducible components of direct products of degenerate representations for D_{6d} and S_{12} groups.

B	B	E_1	E_2	E_3	E_4	E_5
B	A;					
E_1	E_5;	A_1,(A_2),E_2;				
E_2	E_4;	E_1,E_3;	A_1,(A_2),E_4;			
E_3	E_3;	E_2,E_4;	E_1,E_5;	A_1,(A_2),B_1,B_2;		
E_4	E_2;	E_3,E_5;	B_1,B_2,E_2;	E_1,E_5;	A_1,(A_2),E_4;	
E_5	E_1;	B_1,B_2,E_4;	E_3,E_5;	E_2,E_4;	E_1,E_3;	A_1,(A_2),E_2

B ⊗ E = E

3. for upper indices g and u
g ⊗ g = g
u ⊗ u = g
g ⊗ u = u

4. for upper indices ' and ''
' ⊗ ' = '
'' ⊗ '' = '
' ⊗ '' = ''

5. for numerical indices standing at A and B
1 ⊗ 1 = 1
2 ⊗ 2 = 1
1 ⊗ 2 = 2 for all groups except D_2 and D_{2h};
1 ⊗ 2 = 3
2 ⊗ 3 = 1
1 ⊗ 3 = 2 for groups D_2 and D_{2h};

6. The direct product of degenerate representations obeys rules specific for a given group. The groups C_n, C_{nh}, C_{nv}, D_n, D_{nh}, D_{nd} and S_n have common rules for the given n. Eventual exceptions are explicitly marked in Tables 8 and 9. The antisymmetic components are presented there in parentheses.

Using the direct product of irreducible representations the symmetry of the electronic wave function composed of molecular orbitals may be determined. The irreducible representation of the determinantal function $\Phi^{el} = \hat{A} \{ \prod_{i}^{n} \phi_i \}$ is given by the formula

$$\Gamma_{\Phi} = \Gamma_{\phi_1} \otimes \Gamma_{\phi_2} \otimes \dots \otimes \Gamma_{\phi_n} \qquad [136]$$

This implies that the electronic state of a molecule having completely filled occupied MOs) always is totally symmetric.

The direct product of irreducible representations can be used in simplifying the calculation of observables. The physical quantity F has its matrix elements of the corresponding operator $F_{ij} = \langle\Psi_i|\hat{F}|\Psi_j\rangle$ non-zero only in the case when the direct product of irreducible representations of wave functions Ψ_i and Ψ_j, $\Gamma_i \otimes \Gamma_j$, contains a representation of the operator $\hat{F}$

$$\Gamma_i \otimes \Gamma_j = \Gamma_r = \Gamma_F + \sum_{\epsilon} \Gamma_\epsilon \qquad [137]$$

(Γ_ϵ are the remaining components of the reducible representation Γ_r). As a consequence of this property the characteristic equation often is decomposed to a set of equations of lower dimension. Having known the symmetry of the wave functions and that of the transition moment operator one can derive the selection rules for spectral transitions; this is a great advantage since the form of the wave functions is not necessary to known.

For multidimensional irreducible representations the **Wigner-Eckart theorem** is often utilized; this serves for decomposition of a matrix element of a tensor operator $\hat{V}(\Gamma\gamma)$ corresponding to γ-component of multidimensional representation Γ

$$\langle\Gamma_1\gamma_1|\hat{V}(\Gamma\gamma)|\Gamma_2\gamma_2\rangle = \langle\Gamma_1|\hat{V}(\Gamma)|\Gamma_2\rangle\,\langle\Gamma_1\gamma_1,\Gamma\gamma|\Gamma_2\gamma_2\rangle \qquad [138]$$

The numerical coefficient $\langle\Gamma_1\gamma_1,\Gamma\gamma|\Gamma_2\gamma_2\rangle$, often denoted as $C^{\Gamma_1\Gamma\Gamma_2}_{\gamma_1\gamma\gamma_2}$, does not depend upon the form of the operator $\hat{V}(\Gamma\gamma)$ but only on its symmetry properties and the symmetry of wave functions. It is referred to as the **Clebsh-Gordan coefficient** evaluable by recurrent formulas; often it is tabulated is specialized monographs. The integral $\langle\Gamma_1|V(\Gamma)|\Gamma_2\rangle$ is termed the **reduced matrix element** and it is independent of γ_1, γ and γ_2 components. Its value is accessible from experimental data or it may be evaluated in a theoretical way. The Wigner-Eckart theorem enables a reduction of a large number of matrix elements to a small number of more fundamental quantities.

The Clebsh-Gordan coefficients (vector coupling coefficients)

$$\langle l_1m_1,l_2m_2|LM\rangle = C^{l_1l_2L}_{m_1m_2M} = C(L,M|l_1,m_1,l_2,m_2) = C(l_1l_2L;m_1m_2) \qquad [139]$$

are used in expressing the eigenstates of the total angular momentum and its projection via eigenstates of angular momenta $|l_1m_1\rangle$ and $|l_2m_2\rangle$ of subsystems

$$|L,M,l_1,l_2\rangle = \sum_{m_1,m_2} \langle l_1m_1,l_2m_2|LM\rangle\;|l_1m_1\rangle\;|l_2m_2\rangle \qquad [140]$$

They are interrelated to Wigner 3j-symbols as

$$\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix} = (-1)^{l_1-l_2-M} (2L + 1)^{-1/2} \langle l_1m_1,l_2m_2|LM\rangle \qquad [141]$$

The 3j-symbol is evaluated as

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3}[(j_1 + j_2 - j_3)!\ (j_1 - j_2 + j_3)!$$

$$(-j_1 + j_2 + j_3)!\ (j_1 + m_1)!\ (j_1 - m_1)!\ (j_2 + m_2)!\ (j_2 - m_2)!$$

$$(j_3 + m_3)!\ (j_3 - m_3)!\ /(j_1 + j_2 + j_3 + 1)!]^{1/2} \sum_{k=0} (-1)^k/[k!$$

$$(j_1 + j_2 - j_3 - k)!\ (j_1 - m_1 - k)!\ (j_3 - j_2 + m_1 + k)!$$

$$(j_3 - j_1 - m_2 + k)!] \qquad [142]$$

In the relativistic theory when the spin-orbit interaction is taken into account the states of half-valued quantum number J are decribed by two-components spinors. These in symmetry transformations have no ordinary representations but doubled. The **double groups** have been introduced for this purpose: they contain an additional symmetry operation $\hat{Q}$ which means a rotation by angle 2π, but $\hat{Q} \neq \hat{E}$. Every symmetry operation $\hat{R}_k$ in the ordinary group has its additional member $\hat{Q}\hat{R}_k$ within the double group. Some important double groups fully characterized by their characters are presented in Table 10.

The symmetry properties are widely exploited in the quantum chemistry. The principle is utilized that the operator of an arbitrary observable is invariant with respect to all symmetry operations or, in the other words, the operator $\hat{F}$ of a physical quantity commutates with the symmetry operators

$$[\hat{F},\hat{R}_i]_- = \hat{F}\hat{R}_i - \hat{R}_i\hat{F} = \hat{0} \qquad [143]$$

For this reason such a set of eigenfunctions exists which is common for these operators. In the special case it holds true that

$$\hat{H}\ \Psi_k = E_k\ \Psi_k \qquad [144]$$

$$\hat{R}_i\ \Psi_k = c_i\ \Psi_k \qquad [145]$$

where Ψ_k are eigenfunctions of the Hamiltonian corresponding to energy eigenvalues and $c_i = \pm 1$. If an eigenvalue E_k is d-fold degenerate (having number of d different wave functions Ψ_{k1}, Ψ_{k2}, etc.), then also the function

$$\Psi'_{kl} = \hat{R}_i\ \Psi_{kl} = \sum_{j=1} a^i_{lj}\ \Psi_{kj} = \sum_{j=1} \langle\Psi_{kl}|\hat{R}_i|\Psi_{kj}\rangle\ \Psi_{kj} \qquad [146]$$

belongs to eigenfunctions of the Hamiltonian and it yields the same

TABLE 10

Characters of irreducible representations of some double groups.

Order Group Γ_i	Classes of symmetry operations							
h = 16								
C'_{4v}	E	Q	C_4	C_4^3	C_2	$2\sigma_v$	$2\sigma_d$	
			C_4^3Q	C_4Q	C_2Q	$2\sigma_vQ$	$2\sigma_dQ$	
D'_4	E	Q	C_4	C_4^3	C_2	$2C'_2$	$2C''_2$	
			C_4^3Q	C_4Q	C_2Q	$2C'_2Q$	$2C''_2Q$	
D'_{2d}	E	Q	S_4	S_4^3	C_2	$2C'_2$	$2\sigma_d$	
			S_4^3Q	S_4Q	C_2Q	$2C'_2Q$	$2\sigma_dQ$	
$A_1(\Gamma_1)$	+1	+1	+1	+1	+1	+1	+1	
$A_2(\Gamma_2)$	+1	+1	+1	+1	+1	-1	-1	
$B_1(\Gamma_3)$	+1	+1	-1	-1	+1	+1	-1	
$B_2(\Gamma_4)$	+1	+1	-1	-1	+1	-1	+1	
$E_1(\Gamma_5)$	+2	+2	0	0	-2	0	0	
$E'_1(\Gamma_6)$	+2	-2	$+\sqrt{2}$	$-\sqrt{2}$	0	0	0	
$E'_2(\Gamma_7)$	+2	-2	$-\sqrt{2}$	$+\sqrt{2}$	0	0	0	
h = 48								
T'_d	E	Q	$4C_3$	$4C_3^2$	$3C_2$	$3S_4$	$3S_4^3$	$6\sigma_d$
			$4C_3Q$	$4C_3^2Q$	$3C_2Q$	$3S_4Q$	$3S_4^3Q$	$6\sigma_dQ$
O'	E	Q	$4C_3$	$4C_3^2$	$3C_2$	$3C_4$	$3C_4^3$	$6C'_2$
			$4C_3Q$	$4C_3^2Q$	$3C_2Q$	$3C_4Q$	$3C_4^3Q$	$6C'_2Q$
$A_1(\Gamma_1)$	+1	+1	+1	+1	+1	+1	+1	+1
$A_2(\Gamma_2)$	+1	+1	+1	+1	+1	-1	-1	-1
$E_1(\Gamma_3)$	+2	+2	-1	-1	+2	0	0	0
$T_1(\Gamma_4)$	+3	+3	0	0	-1	+1	+1	-1
$T_2(\Gamma_5)$	+3	+3	0	0	-1	-1	-1	+1
$E'_1(\Gamma_6)$	+2	-2	+1	-1	0	$+\sqrt{2}$	$-\sqrt{2}$	0
$E'_2(\Gamma_7)$	+2	-2	+1	-1	0	$-\sqrt{2}$	$+\sqrt{2}$	0
$G'(\Gamma_8)$	+4	-4	-1	+1	0	0	0	0

eigenvalue E_k. In this way each symmetry operator $\hat{R}_i$ generates a transformation matrix $A(R_i)$ of the order n. The set of these matrices forms a representation of the symmetry point group of the molecule. The representations obey the following properties:

1. all representations are unitary, $A^{-1} = A^{+}$ because of the orthogonality of eigenfunctions Ψ_{kl};
2. the dimension of the representation equals to the degree of degeneracy of the corresponding eigenvalue E_k;
3. the representations having basis set formed of nondegenerate eigenvalues are irreducible.

Thus, every energy level of a molecule has a corresponding irreducible representation of the molecular symmetry point group. The symmetrized wave functions $\Psi^{(\alpha)}$ of an irreducible representation Γ_α may be obtained by acting the operator $\hat{\eta}^{(\alpha)}$ to any wave function Ψ_i (the generator) according to formula [131].

As an example, the symmetric orbitals of NH_3 will be constructed. The symmetry point group C_{3v} has the following characters of irreducible representations

h = 6	Classes of operations			Basis set functions
Γ	E	$2C_3$	$3\sigma_v$	f_m
A_1	+1	+1	+1	z, $x^2+y^2+z^2$, z^2
A_2	+1	+1	−1	
E	+2	−1	0	(x,y), (x^2-y^2,xy), (xz,yz)

(Notice some properties: order $h = 1^2(A_1) + 1^2(A_2) + 1^2(E) = 1^2 + 1^2 + 2^2 = 6$; number of classes = 3.) The valence basis set consists of these atomic orbitals: $(1s)_{H1}$, $(1s)_{H2}$, $(1s)_{H3}$, $(2s)_N$, $(2p_x)_N$, $(2p_y)_N$ and $(2p_z)_N$. Let $(1s)_{H1}$ be a generator of symmetric functions. According to [131] the unnormalized symmetry function is

$$f_1^u(a_1) = \{1.\hat{E} + 1.\hat{C}_3^1 + 1.\hat{C}_3^2 + 1.\hat{\sigma}_1 + 1.\hat{\sigma}_2 + 1.\hat{\sigma}_3\}(1s)_{H1} =$$
$$= 2[(1s)_{H1} + (1s)_{H2} + (1s)_{H3}] \qquad [147]$$

which after the normalization gives

$$f_1(a_1) = (1/\sqrt{3})[(1s)_{H1} + (1s)_{H2} + (1s)_{H3}] \qquad [148]$$

The same result is obtained when $(1s)_{H2}$ or $(1s)_{H3}$ are used in the role of generators. Other symmetry functions of the representation a_1 are represented by net atomic orbitals of the nitrogen atom: $f_2(a_1) = (2s)_N$ and $f_3(a_1) = (2p_z)_N$. This follows directly from character tables where the central atom orbitals are directly associated with definite irreducible representations. (This is valid only at conventional orientation of symmetry elements: the z-axis being the rotational axis of the highest order.) The same result, however, is obtained by using generators $(2s)_N$ and $(2p_z)_N$, respectively.

Next one symmetry function results from the operation

$$\begin{aligned} f_4^u(e) &= \{2.\hat{E} - 1.\hat{C}_3^1 - 1.\hat{C}_3^2 + 0.\hat{\sigma}_1 + 0.\hat{\sigma}_2 + 0.\hat{\sigma}_3\}(1s)_{H1} = \\ &= 2(1s)_{H1} - (1s)_{H2} - (1s)_{H3} \end{aligned} \tag{149}$$

which after the normalization yields

$$f_4(e) = (1/\sqrt{6})[2(1s)_{H1} - (1s)_{H2} - (1s)_{H3}] \tag{150}$$

The second component of this two-dimensional representation is obtained in a similar way, using the generator $(1s)_{H2}$, namely

$$f_5^u(e) = 2(1s)_{H2} - (1s)_{H3} - (1s)_{H1} \tag{151}$$

This function, however, is not orthogonal to $f_4(e)$ so that the Schmidt orthogonalization procedure and subsequent normalization should be applied yielding

$$f_5(e) = (1/\sqrt{2})[(1s)_{H2} - (1s)_{H3}] \tag{152}$$

By applying the generator $(1s)_{H3}$ the third function $f(e)$ may be obtained, but this is linearly dependent on $f_4(e)$ and $f_5(e)$ so that it should be omitted.

The last two symmetric functions are represented by an arbitrary linear combination of net atomic orbitals $(2p_x)_N$ and $(2p_y)_N$, e.g., $f_6(e) = (2p_x)_N$ and $f_7(e) = (2p_y)_N$.

When the symmetry functions are known

$$\begin{pmatrix} f_1(a_1) \\ f_2(a_1) \\ f_3(a_1) \\ f_4(e) \\ f_5(e) \\ f_6(e) \\ f_7(e) \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} & 0 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} (1s)_{H1} \\ (1s)_{H2} \\ (1s)_{H3} \\ (2s)_N \\ (2p_z)_N \\ (2p_x)_N \\ (2p_y)_N \end{pmatrix} \tag{153}$$

then one can proceed in construction of the Fock operator matrix

$$F = \begin{pmatrix} F_{11} & F_{12} & F_{13} & 0 & 0 & 0 & 0 \\ F_{12} & F_{22} & F_{23} & 0 & 0 & 0 & 0 \\ F_{13} & F_{23} & F_{33} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & F_{44} & F_{45} & F_{46} & F_{47} \\ 0 & 0 & 0 & F_{45} & F_{55} & F_{56} & F_{57} \\ 0 & 0 & 0 & F_{46} & F_{56} & F_{66} & F_{67} \\ 0 & 0 & 0 & F_{47} & F_{57} & F_{67} & F_{77} \end{pmatrix} \tag{154}$$

which keeps the block-diagonal form.

1.3.2 Reduction of Matrix Elements

This paragraph is concerned with an appropriate expression for the vibronic matrix elements V^{r}_{kl} and V^{rs}_{kl} in the basis set of degenerate electronic wave functions |k> and |l>. The operator parts

$$\frac{\partial \hat{V}_{eN}}{\partial Q_r} = V^{\cdot}\begin{pmatrix} \Gamma_r \\ \gamma_r \end{pmatrix} \qquad [155]$$

$$\frac{\partial^2 \hat{V}_{eN}}{\partial Q_r \partial Q_s} = V^{\cdot\cdot}\begin{pmatrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{pmatrix} \qquad [156]$$

are classified according to the irreducible representations, Γ_r, and their components, γ_r, within the symmetry group G_0. A similar classification is used for wave functions $\left| \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \right\rangle$ and $\left| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle$. Thus the Wigner-Eckart theorem states

$$V^{r}_{kl} = \left\langle \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \middle| V^{\cdot}\begin{pmatrix} \Gamma_r \\ \gamma_r \end{pmatrix} \middle| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle = N \left\langle \begin{matrix} \Gamma_l & \Gamma_r \\ \gamma_l & \gamma_r \end{matrix} \middle| \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \right\rangle X(\Gamma_k \Gamma_l ; \Gamma_r > \qquad [157]$$

The reduced matrix element $X(\Gamma_k \Gamma_l ; \Gamma_r) = X_{\Gamma_r}$ depends only on Γ; it does not depend on the γ components of the multidimensional representation. The Clebsh-Gordan coefficients $\left\langle \begin{matrix} \Gamma_k & \Gamma_l \\ \gamma_k & \gamma_l \end{matrix} \middle| \begin{matrix} \Gamma_r \\ \gamma_r \end{matrix} \right\rangle$ couple the angular momenta of $\left| \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \right\rangle$ and $\left| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle$ to yield the angular momentum of $\left| \begin{matrix} \Gamma_r \\ \gamma_r \end{matrix} \right\rangle$, so that

$$\left| \begin{matrix} \Gamma_r \\ \gamma_r \end{matrix} \right\rangle = \sum_{\gamma_k , \gamma_l} \left\langle \begin{matrix} \Gamma_k & \Gamma_l \\ \gamma_k & \gamma_l \end{matrix} \middle| \begin{matrix} \Gamma_r \\ \gamma_r \end{matrix} \right\rangle \left| \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \right\rangle \left| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle \qquad [158]$$

holds.

The Clebsh-Gordan coefficients are proportional to the 3j-symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3}(2j_3 + 1)^{-1/2} \left\langle \begin{matrix} j_1 & j_2 \\ m_1 & m_2 \end{matrix} \middle| \begin{matrix} j_3 \\ -m_3 \end{matrix} \right\rangle \qquad [159]$$

which possess important symmetry properties and are easily evaluable.

As a consequence of [157], the replacement theorem is valid: if two operators, say $\hat{V}^{\cdot}$ and $\hat{W}^{\cdot}$, are of the same symmetry (i.e. they are of the same type with respect to an angular momentum), then both are reduced by the same Clebsh-Gordan coefficient C

$$V^{r}_{kl} = C\, X_r \qquad [160]$$

$$W^{r}_{kl} = C\, Y_r \qquad [161]$$

This implies a proportionality of

$$V^{r}_{kl} = W^{r}_{kl}(X_r/Y_r) \tag{162}$$

(the method of operator equivalents). An angular momentum operator may be chosen in the role of W^{r}_{kl}. Thus the transformation properties of spherical harmonics $Y_{j,m}(\vartheta,\varphi)$ (see later) are sufficient in evaluating the integrals [161]. Table 11 shows real combinations Y^R of spherical harmonics that enable the symmetry classification in terms of cartesian components. Since they are listed in all character tables, the classification of $\left|\begin{matrix}r\\ Y\end{matrix}\right\rangle$ in terms of angular momenta quantum numbers (j,m) is straightforward. In some cases two or more sets of cartesian components (say $x^2 - y^2$, xy, xz or yz in D_3) belong to the same multidimensional irreducible representation so that a linear combination of them should be considered. Hence, the symmetry descent technique is applicable.

TABLE 11

Real linear combinations, Y^R, of spherical harmonics, $Y_{j,m}$.

j	Y^R	Symmetry properties
0	$Y_{0,0}$	$x^2 + y^2 + z^2$
1	$(i/\sqrt{2})(Y_{1,1} + Y_{1,-1})$	y
	$-(1/\sqrt{2})(Y_{1,1} - Y_{1,-1})$	x
	$Y_{1,0}$	z
2	$Y_{2,0}$	z^2
	$(i/\sqrt{2})(Y_{2,1} + Y_{2,-1})$	yz
	$-(1/\sqrt{2})(Y_{2,2} + Y_{2,-2})$	$x^2 - y^2$
	$-(i/\sqrt{2})(Y_{2,2} - Y_{2,-2})$	xy

In order to illustrate the above consideration, let us evaluate the coupling coefficients for the doubly degenerate E term within the O group. The real basis functions are

$$z^2 \quad \ldots \left|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = Y_{2,0} \tag{163}$$

$$x^2 - y^2 \ldots \left|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle = (Y_{2,2} + Y_{2,-2})/\sqrt{2} \tag{164}$$

The only non-zero 3j-symbols are $\begin{pmatrix}2 & 2 & 2\\ m_1 & m_2 & m_3\end{pmatrix}$ with $m_1 = m_2 + m_3$.

For $m_i = 0$, 2 or -2 the coefficients adopt a value of $a = (2/35)^{1/2}$ except $\begin{pmatrix}2 & 2 & 2\\ 0 & 0 & 0\end{pmatrix} = -(2/35)^{1/2} = -a$. Therefore

$$\left\langle\begin{matrix}E & E\\ \vartheta & \vartheta\end{matrix}\,\middle|\,\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = (-1)^2\begin{pmatrix}2 & 2 & 2\\ 0 & 0 & 0\end{pmatrix} = -a \qquad [165]$$

and similarly

$$\left\langle\begin{matrix}E & E\\ \epsilon & \epsilon\end{matrix}\,\middle|\,\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = \left\langle\begin{matrix}E & E\\ \vartheta & \epsilon\end{matrix}\,\middle|\,\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle = \left\langle\begin{matrix}E & E\\ \epsilon & \vartheta\end{matrix}\,\middle|\,\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = a \qquad [166]$$

The normalized coupling coefficients are $c_i = Na_i$ where the normalization factor is

$$N = \left[\sum_i (a_i)^2\right]^{1/2} \qquad [167]$$

and i runs over the single component γ or over all components of the irreducible representation. Conventionally, $c = 1/\sqrt{2}$ for the former case.

Because of the renormalization, the same result is obtained using the Racah V-coefficients, Clebsh-Gordan coefficients or Wigner 3j-symbols. The coupling coefficients have been tabulated in specialized monographs (37,43-45).

It must be mentioned that the same coupling coefficients are obtained for isomorphous groups (e.g. for O and T_d, C_{nv} and D_n, etc.). Moreover, the coupling coefficients for direct product groups ($T_h = C_i \otimes T$, $O_h = C_i \otimes O$, etc.) can be expressed by multiplying the coupling coefficients of the respective subgroups.

For the doubly degenerate electronic state ($\Gamma_k = \Gamma_l = E$), the relevant matrix elements for the cubic groups become

$$\begin{pmatrix} \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \vartheta\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \vartheta\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \\ \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \vartheta\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \vartheta\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \end{pmatrix} = \begin{pmatrix} -X_e/\sqrt{2} \;; & 0 \\ 0 \;; & X_e/\sqrt{2}\end{pmatrix} = X_e C_3 \qquad [168]$$

$$\begin{pmatrix} \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \epsilon\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \epsilon\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \\ \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \epsilon\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}e\\ \epsilon\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \end{pmatrix} = \begin{pmatrix} 0 \;; & X_e/\sqrt{2} \\ X_e/\sqrt{2} \;; & 0\end{pmatrix} = X_e C_2 \qquad [169]$$

$$\begin{pmatrix} \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}a\\ \cdot\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \vartheta\end{matrix}\middle| V^{\cdot}\begin{pmatrix}a\\ \cdot\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \\ \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}a\\ \cdot\end{pmatrix} \middle|\begin{matrix}E\\ \vartheta\end{matrix}\right\rangle & \left\langle\begin{matrix}E\\ \epsilon\end{matrix}\middle| V^{\cdot}\begin{pmatrix}a\\ \cdot\end{pmatrix} \middle|\begin{matrix}E\\ \epsilon\end{matrix}\right\rangle \end{pmatrix} = \begin{pmatrix} X_a \;; & 0 \\ 0 \;; & X_a\end{pmatrix} = X_a C_1 \qquad [170]$$

with

$$C_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \ldots a_1 \tag{171}$$

$$C_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \ldots e_\varepsilon \tag{172}$$

$$C_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \ldots e_\vartheta \tag{173}$$

This set may be completed by

$$C_4 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \qquad \ldots a_2 \tag{174}$$

Therefore,

$$V^{(1)} = C_2 X_e Q_{e\varepsilon} + C_3 X_e Q_{e\vartheta} \tag{175}$$

is valid for groups in which the symmetrized direct product is $[E \otimes E] = A_1 + E$ (e.g. for cubic groups). For the remaining groups with $[E \otimes E] = A_1 + B_1 + B_2$ (e.g. for D_{4h}), the expression

$$V^{(1)} = C_2 X_{b_1} Q_{b_1} + C_3 X_{b_2} Q_{b_2} \tag{176}$$

holds.

In the reduction of quadratic matrix elements V_{kl}^{rs}, the operator part $V^{\cdot\cdot}\begin{pmatrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{pmatrix}$ represents a component of the basis set that is obtained by a direct product $\Gamma_r \otimes \Gamma_s$. Its representation is, in general, reducible. The decomposition of the operator part may be performed according to the Wigner formula

$$\left| \begin{matrix} \Gamma_r \\ \gamma_r \end{matrix} \right\rangle \left| \begin{matrix} \Gamma_s \\ \gamma_s \end{matrix} \right\rangle = \sum_{\Gamma_i, \gamma_i} \left\langle \begin{matrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{matrix} \middle| \begin{matrix} \Gamma_i \\ \gamma_i \end{matrix} \right\rangle |\Gamma_r \Gamma_s \; \Gamma_i \gamma_i > \tag{177}$$

where the summations run over all Γ_i representations and their γ_i components are contained in the direct product

$$\Gamma_r \otimes \Gamma_s = \Gamma_{red} = \sum_i \Gamma_i \tag{178}$$

Therefore

$$\begin{aligned} \left\langle \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \middle| V^{\cdot\cdot}\begin{pmatrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{pmatrix} \middle| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle &= \sum_{\Gamma_i, \gamma_i \in \Gamma_r \otimes \Gamma_s} \left\langle \begin{matrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{matrix} \middle| \begin{matrix} \Gamma_i \\ \gamma_i \end{matrix} \right\rangle \cdot \\ \cdot \left\langle \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \middle| Y(\Gamma_r \Gamma_s \Gamma_i \gamma_i) \middle| \begin{matrix} \Gamma_l \\ \gamma_l \end{matrix} \right\rangle &= X(\Gamma_k, \Gamma_l; \Gamma_r \Gamma_s) \sum_{\Gamma_i, \gamma_i} \left\langle \begin{matrix} \Gamma_r & \Gamma_s \\ \gamma_r & \gamma_s \end{matrix} \middle| \begin{matrix} \Gamma_i \\ \gamma_i \end{matrix} \right\rangle \cdot \\ \cdot \left\langle \begin{matrix} \Gamma_l & \Gamma_i \\ \gamma_l & \gamma_i \end{matrix} \middle| \begin{matrix} \Gamma_k \\ \gamma_k \end{matrix} \right\rangle & \end{aligned} \tag{179}$$

is valid.

For example, in cubic groups the reduction proceeds as

$$\left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| V^{\cdot\cdot}\begin{pmatrix}e & e\\ \vartheta & \vartheta\end{pmatrix} \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = \sum_{\substack{\Gamma=a_1,a_2,e\\ \gamma_e=\vartheta,\varepsilon}} \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}\Gamma\\ \gamma\end{matrix}\right\rangle \cdot$$

$$\cdot \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(ee\Gamma_{\gamma}) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}a_1\\ \cdot\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(eea_1\cdot) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle +$$

$$+ \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}a_2\\ \cdot\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(eea_2\cdot) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle +$$

$$+ \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \vartheta\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(eee\vartheta) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle +$$

$$+ \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \varepsilon\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(eee\varepsilon) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = \left\langle \begin{matrix}e & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \vartheta\end{matrix}\right\rangle \left\langle \begin{matrix}E & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle \cdot$$

$$\cdot\ X(EE;ee) = \left(\frac{-1}{\sqrt{2}}\right)\left(\frac{-1}{\sqrt{2}}\right) X_{ee} = \frac{1}{2} X_{ee} \qquad [180]$$

Capital letters denote the symmetry of electronic states and small letters that of vibrational modes.

The important finding is that the integral

$$\left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| V\begin{pmatrix}a_1 & e\\ \cdot & \vartheta\end{pmatrix} \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle = \left\langle \begin{matrix}a_1 & e\\ \cdot & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \vartheta\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(a_1ee\vartheta) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle +$$

$$+ \left\langle \begin{matrix}a_1 & e\\ \cdot & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \varepsilon\end{matrix}\right\rangle \left\langle \begin{matrix}E\\ \vartheta\end{matrix} \middle| Y(a_1ee\varepsilon) \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle =$$

$$= \left\langle \begin{matrix}a_1 & e\\ \cdot & \vartheta\end{matrix} \middle| \begin{matrix}e\\ \vartheta\end{matrix}\right\rangle \left\langle \begin{matrix}E & e\\ \vartheta & \vartheta\end{matrix} \middle| \begin{matrix}E\\ \vartheta\end{matrix}\right\rangle X(EE;a_1e) = 1 \cdot \left(\frac{-1}{\sqrt{2}}\right) X_{ae} \qquad [181]$$

and its analogues are non-zero, a fact which used to be overlooked.

Analogously, the cubic matrix element V_{kl}^{rst} is reduced as

$$\left\langle \begin{matrix}\Gamma_k\\ \gamma_k\end{matrix} \middle| V^{\cdot\cdot}\begin{pmatrix}\Gamma_r & \Gamma_s & \Gamma_t\\ \gamma_r & \gamma_s & \gamma_t\end{pmatrix} \middle| \begin{matrix}\Gamma_l\\ \gamma_l\end{matrix}\right\rangle = \sum_{\Gamma_i\gamma_i\in\Gamma_r\otimes\Gamma_s} \left\langle \begin{matrix}\Gamma_r & \Gamma_s\\ \gamma_r & \gamma_s\end{matrix} \middle| \begin{matrix}\Gamma_i\\ \gamma_i\end{matrix}\right\rangle \cdot$$

$$\cdot \left\langle \begin{matrix}\Gamma_k\\ \gamma_k\end{matrix} \middle| Z\left(\Gamma_r\Gamma_s\begin{bmatrix}\Gamma_i\\ \gamma_i\end{bmatrix} \begin{matrix}\Gamma_t\\ \gamma_t\end{matrix}\right) \middle| \begin{matrix}\Gamma_l\\ \gamma_l\end{matrix}\right\rangle = \sum_{\Gamma_i\gamma_i\in\Gamma_r\otimes\Gamma_s} \left\langle \begin{matrix}\Gamma_r & \Gamma_s\\ \gamma_r & \gamma_s\end{matrix} \middle| \begin{matrix}\Gamma_i\\ \gamma_i\end{matrix}\right\rangle \cdot$$

$$\cdot \sum_{\Gamma_j\gamma_j\in\Gamma_i\otimes\Gamma_t} \left\langle \begin{matrix}\Gamma_i & \Gamma_t\\ \gamma_i & \gamma_t\end{matrix} \middle| \begin{matrix}\Gamma_j\\ \gamma_j\end{matrix}\right\rangle \left\langle \begin{matrix}\Gamma_k\\ \gamma_k\end{matrix} \middle| Y\left(\Gamma_r\Gamma_s\Gamma_t\begin{bmatrix}\Gamma_j\\ \gamma_j\end{bmatrix}\right) \middle| \begin{matrix}\Gamma_l\\ \gamma_l\end{matrix}\right\rangle =$$

$$= \sum_{\Gamma_i\gamma_i} \left\langle \begin{matrix}\Gamma_r & \Gamma_s\\ \gamma_r & \gamma_s\end{matrix} \middle| \begin{matrix}\Gamma_i\\ \gamma_i\end{matrix}\right\rangle \sum_{\Gamma_j\gamma_j} \left\langle \begin{matrix}\Gamma_i & \Gamma_t\\ \gamma_i & \gamma_t\end{matrix} \middle| \begin{matrix}\Gamma_j\\ \gamma_j\end{matrix}\right\rangle \left\langle \begin{matrix}\Gamma_l & \Gamma_j\\ \gamma_l & \gamma_j\end{matrix} \middle| \begin{matrix}\Gamma_k\\ \gamma_k\end{matrix}\right\rangle \cdot$$

$$\cdot\ X(\Gamma_k\Gamma_l;\Gamma_r\Gamma_s\Gamma_t) \qquad [182]$$

1.4 ONE-ELECTRON APPROXIMATION

1.4.1 Many-Electron Systems

According to the principles of quantum mechanics the wave function $\Psi(X_k;t)$ carries complete information on the state of a physical microobject. Its shape is determined by solving the corresponding Schrödinger equation for the given Hamiltonian of the system.

The final task of the quantum-mechanical approach, as a rule, is not to obtain the exact form of the wave function (which, in most cases, is not of any physical meaning). The problem that is solved is the computation of the average value of a physical quantity <A>. Then we can apply the following analysis.

The arbitrary hermitian operator adopts the general form

$$\hat{A} = \hat{A}_0 + \sum_i \hat{A}_i + (1/2!)\sum_{i,j}{}' \hat{A}_{ij} + (1/3!)\sum_{i,j,k}{}' \hat{A}_{ijk} + \ldots =$$
$$= \hat{A}^{(0)} + \hat{A}^{(1)} + \hat{A}^{(2)} + \hat{A}^{(3)} + \ldots \qquad [183]$$

where individual terms are represented by particle-less, $\hat{A}^{(0)}$, one-particle, $\hat{A}^{(1)}$, two-particle, $\hat{A}^{(2)}$, or multi-particle, $\hat{A}^{(n)}$, operators. It should be recalled that common quantum-mechanical operators do not have more than two-particle terms. With this limitation, the task can be formulated as the search for such mathematical representatives which carry all the substantial information on the state of the microobject from the viewpoint of calculation of the average value of two-particle operators. Such representatives for the n-particle system are the **density functions** (frequently called the density matrices).

A generalized two-particle density function is defined by the relationship

$$\rho_2(X_1,X_2;X_1',X_2') = [n(n-1)/k] \int \Psi(X_1,X_2,\ldots,X_n)\, \Psi^*(X_1',X_2',\ldots,X_n)\, dX_3\ldots dX_n \qquad [184]$$

where according to Löwdin (46) the numerical constant is k = 2! while McWeeny (47) introduced k = 1 as the factor. Hereafter we assume the value of k = 1. With the use of a two-particle density function the two-particle operator has the average value of

$$<A^{(2)}> = \int \Psi^* \,[(1/2!) \sum_{i,j}^{n}{}' \hat{A}_{ij}]\, \Psi \, dX = [n(n-1)/2!] \int \Psi^* \hat{A}_{12} \Psi \, dX =$$
$$= (k/2!) \int \{\hat{A}_{12}(X_1,X_2)\, \rho_2(X_1,X_2;X_1',X_2')\}_{X_1'=X_1,X_2'=X_2} \, dX_1 \, dX_2 \qquad [185]$$

where the convention is that the operator does not act on primed indices which prior to integration are put equal to the non-primed ones.

A generalized one-particle density function is defined in a similar manner

$$\rho_1(X_1;X_1') = n \int \Psi(X_1,X_2,\ldots,X_n)\, \Psi^*(X_1',X_2,\ldots,X_n)\, dX_2\ldots dX_n \tag*{[186]}$$

which fulfils the following relationship

$$[(n-1)/k]\; \rho_1(X_1;X_1') = \int \rho_2(X_1,X_2;X_1',X_2')\, dX_2 \tag*{[187]}$$

The average value of the one-particle operator can be expressed as

$$<A^{(1)}> = \int \Psi^* \; (\sum_i^n \hat{A}_i)\; \Psi\, dX = n \int \Psi^* \; \hat{A}_1 \; \Psi\, dX =$$

$$= \int \{\hat{A}_1(X_1)\; \rho_1(X_1;X_1')\}_{X_1'=X_1}\, dX_1 \tag*{[188]}$$

The physical meaning of the density functions is as follows: The expression $\rho_1(X_1;X_1)dX_1$ means the probability that the particle occurs in the vicinity of the point r_1 with the spin s_1, multiplied by the number of particles wherein all the other particles are located in arbitrary positions assuming arbitrary permissible spin orientations. Expression $\rho_2(X_1,X_2;X_1,X_2)dX_1dX_2$ is proportional to the probability of occurence of the first particle in the vicinity of r_1 with the spin s_1 and at the same time of the second particle around r_2 with the spin s_2, other particles occupy arbitrary positions with arbitrary spin projections.

Spinless density functions are obtained by integrating over spin variables

$$P_2(r_1,r_2;r_1',r_2') = \int \{\rho_2(X_1,X_2;X_1',X_2')\}_{s_1'=s_1,s_2'=s_2}\, ds_1\, ds_2 \tag*{[189]}$$

$$P_1(r_1;r_1') = \int \{\rho_1(X_1;X_1')\}_{s_1'=s_1}\, ds_1 \tag*{[190]}$$

Their physical meaning is like that described above but differs in the fact that the particles assume arbitrary spins. For example, the last function (expressing the probability of occurence of the electron at the volume element around the point r_1 irrespective of its spin) is measurable in röntgenographic experiments.

Density functions enable considerable simplification of the transfer of information for microobjects like atoms and molecules. For example, in the case of a many-electron atom the limitation to 10 values for each variable coordinate means the numerical table $P_2(r_1,r_2;r_1',r_2')$ has 10^6 values only.

In a system of n identical particles the transposition operator can be defined through

$$\hat{T}_{ij} = \begin{pmatrix} 1 & \ldots & i & \ldots & j & \ldots & n \\ 1 & \ldots & j & \ldots & i & \ldots & n \end{pmatrix} \tag*{[191]}$$

which when acting on the wave function $\Psi(X_1,\dots,X_i,\dots,X_j,\dots X_n)$ yields

$$\hat{T}^2\Psi = \hat{T}\,(\epsilon_T\Psi) = \epsilon_T^2\Psi = \Psi \qquad [192]$$

From the above it follows that $\epsilon^2 = 1$ or $\epsilon = \pm 1$. This result means that the wave function for identical particles is either symmetric or antisymmetric with respect to arbitrary transposition of the particles. Since every permutation can be expressed in the form of the product of transpositions

$$\hat{P} = \begin{pmatrix} 1 & 2 & \dots & n \\ p_1 & p_2 & \dots & p_n \end{pmatrix}^{P} = \prod_k \hat{T}_{i_k j_k} \qquad [193]$$

then the wave function of a system of identical particles is always either symmetric, $\hat{P}\Psi = \Psi$, or antisymmetric, $\hat{P}\Psi = (-1)^p\Psi$, p being the number of transpositions - the parity of permutation.

One of the quantum-mechanical postulates says that the wave function of fermions (systems of half-valued spin such as electrons) must be **antisymmetric**. As a consequence, the generalized density function describing electrons is also antisymmetric

$$\rho_2(X_2,X_1;X_1',X_2') = -\,\rho_2(X_1,X_2;X_1',X_2') \qquad [194]$$

In the case of diagonal matrix elements

$$\rho_2(X_1,X_1;X_1',X_1') = 0 \qquad [195]$$

The physical meaning of the above result is that at short distances a very strong correlation comes into effect, which holds the particles with equal spin apart from each other (Fermi correlation). This conclusion is the equivalent of the **Pauli exclusion principle**.

1.4.2 Electron Configuration

The one-electron approximation is based on the separation of coordinates of individual electrons; the motions of individual electrons are taken as independent - uncorrelated. In this approximation the state of every electron is characterized by a one-electron wave function - the **spinorbital**

$$\psi_k(X_k) = \phi_k(r_k)\ \eta_k(s_k) \qquad [196]$$

It consists of the orbital part $\phi_k(r_k)$ depending on the positional vector r_k (spatial variables) and the spin function $\eta_k(s_k)$. The spin function is denoted as α for the spin projection $m_{sk} = +1/2$

and β for $m_{sk} = -1/2$. The spinorbitals represent a basis set in the Hilbert vector space. The set of individual states - **electron configuration** - is characterized by an antisymmetrized product of spinorbitals

$$\Phi_u(1,2,\ldots,n) = \hat{A}_n \prod_k^n \psi_k(X_k) = (n!)^{-1/2} \sum_\sigma^{n!} (-1)^{p(\sigma)} \hat{P}_\sigma \prod_k^n \psi_k(X_k) \quad [197]$$

where $\hat{A}_n$ is the antisymmetrization operator securing the fundamental property of a system of fermions - the antisymmetry with respect to the arbitrary transposition of electrons, $\hat{P}_\sigma$ is the permutation operator acting on the electron coordinates X_k, $p(\sigma)$ is its parity and the sum over the index σ runs over all the possible permutations including the identical one.

The antisymmetrized product of spinorbitals is called the **determinantal function** since it can be written in the form of the **Slater determinant**

$$\Phi_u(1,2,\ldots,n) = (n!)^{-1/2} \, det \begin{pmatrix} \psi_1(X_1) & \psi_2(X_1) & \ldots & \psi_n(X_1) \\ \psi_1(X_2) & \psi_2(X_2) & \ldots & \psi_n(X_2) \\ \ldots & \ldots & & \ldots \\ \psi_1(X_n) & \psi_2(X_n) & \ldots & \psi_n(X_n) \end{pmatrix} \quad [198]$$

The Slater determinant shows such a notable property that its value is zero, when two spinorbitals are identical. Thus, such a situation does not represent any electronic state which matches well with the Pauli exclusion principle.

Mathematical formulation of the one-electron approximation is represented by the expression of the electronic wave functions through a single determinantal function $\Psi_u^{el} = \Phi_u$. Different electron configurations can be considered through the selection of the number n out of the total number m of the one-electron functions. From the properties of the Hilbert space it follows that the electronic wave function may be expressed through the series

$$\Psi_i^{el} = \lim_{u \Rightarrow \infty} \sum_u C_{iu} \Phi_u \quad [199]$$

where C_{iu} are the expansion coefficients. The passage from the one-electron approximation to the multi-determinantal expansion [199] is referred to as the **configuration interaction**. In the case of degenerate states and the open-shell systems there is a definite minimum number of determinantal functions whose linear combination guarantees the proper spatial and spin symmetry of the resulting wave function.

1.4.3 Matrix Elements of Operators

Let us consider a couple of electron configurations characterized by their normalized determinantal functions

$$\Phi_u = \hat{A}_n \prod_k^n \psi_k^u \qquad [200]$$

$$\Phi_v = \hat{A}_n \prod_l^n \psi_l^v \qquad [201]$$

In general, the non-orthogonality integrals

$$\mathrm{D}_{kl}^{uv} = \langle \psi_k^u | \psi_l^v \rangle \qquad [202]$$

may differ from zero for $k \neq l$. **Generalized minors** (algebraic complements) with respect to the matrix D^{uv} of non-orthogonality integrals may be defined as follows: The first-order minor $D^{uv}(k_1,l_1)$ is a determinant of the matrix of order $(n-1)$ which is obtained by omitting the row k_1 and the column l_1 in the matrix D^{uv} with the sign $(-1)^{k_1+l_1}$. The second-order minor $D^{uv}(k_1k_2|l_1l_2)$ is a determinant of the matrix of order $(n-2)$ created by omitting the rows k_1, k_2 and the columns l_1, l_2 in the matrix D^{uv}. Its basic sign is $(-1)^{k_1+k_2+l_1+l_2}$ for ordered index sequences $k_1 < k_2$ and $l_1 < l_2$. Thus, it is an antisymmetric function in every set of its indices which means the subsequent multiplication by the factor $\varepsilon(k_1,k_2)\cdot\varepsilon(l_1,l_2)$ where $\varepsilon(i,j) = +1$ for $i < j$ and $\varepsilon(i,j) = -1$ for $i > j$.

By decomposing the determinantal function through permutation operators Löwdin has shown (46) that the arbitrary operator $\hat{A}$ (in the sum of particle-less, one-particle and two-particle terms)

$$\hat{A} = \hat{A}^{(0)} + \hat{A}^{(1)} + \hat{A}^{(2)} = \hat{A}_0 + \sum_i \hat{A}_i + (1/2)\sum_{i,j}{}' \hat{A}_{ij} \qquad [203]$$

yields the following **transition matrix elements** between two electron configurations

$$\langle \Phi_u | \hat{A} | \Phi_v \rangle = A_0 D^{uv} + \sum_{k_1,l_1} \langle \psi_{k_1}^u | \hat{A}_1 | \psi_{l_1}^v \rangle D^{uv}(k_1|l_1) +$$

$$+ (1/2) \sum_{k_1,k_2,l_1,l_2} \langle \psi_{k_1}^u \psi_{k_2}^u | \hat{A}_{12} | \psi_{l_1}^v \psi_{l_2}^v \rangle D^{uv}(k_1k_2|l_1l_2) \qquad [204]$$

If the matrix of non-orthogonality integrals D^{uv} is not singular, i.e. the determinant D^{uv} is non-zero

$$D^{uv} = \langle \Phi_u | \Phi_v \rangle = det\{\mathrm{D}^{uv}\} \neq 0 \qquad [205]$$

then there exists an inverse matrix $(\mathrm{D}^{-1})^{uv}$ to the matrix D^{uv} and for the minors

$$D^{uv}(k_1|l_1) = D^{uv}\,(D^{-1})^{uv}_{l_1,k_1} \qquad [206]$$

$$D^{uv}(k_1k_2|l_1l_2) =$$

$$= D^{uv}[(D^{-1})^{uv}_{l_1,k_1}(D^{-1})^{uv}_{l_2,k_2} - (D^{-1})^{uv}_{l_1,k_2}(D^{-1})^{uv}_{l_2,k_1}] \qquad [207]$$

The relationship [204] is widely used e.g., in configuration interaction, when calculating the probability of spectroscopic transitions, when calculating the orbitals with the use of Hartree-Fock method and when evaluating the mean value of observables.

Within the one-electron approximation the density functions fulfil the relationship

$$\rho_1(X_1;X_1') = \rho(1,1') \qquad [208]$$

$$\rho_2(X_1,X_2;X_1',X'_2) = (1/2)[\rho(1,1')\rho(2,2') - \rho(1,2')\rho(2,1')] \qquad [209]$$

where

$$\rho(1,2) = \sum_{k,l} \psi_k^*(1)\,\psi_l(2)\,(D^{-1})^{uu}_{l,k} \qquad [210]$$

is the **Fock-Dirac density matrix** (originally defined for orthogonal spinorbitals) with the properties of projection operators

$$\rho^2 = \rho, \quad \text{and} \quad Tr(\rho) = n \qquad [211]$$

This means that if the electronic wave function Ψ_i^{el} is approximated exclusively by single determinantal function Φ_u then the density functions of higher orders can be expressed through the first-order density function. The condition of

$$\rho_1\,\rho_1 = \rho_1 \qquad [212]$$

is a necessary and sufficient one for the reduction of the electronic wave function to a single-determinantal function. Then, for the mean value of the operator $\hat{A}$

$$\langle A\rangle_u = \langle\Phi_u|\hat{A}|\Phi_u\rangle = A_0 + \int \hat{A}_1\,\rho(1,1')\,dX_1 +$$

$$+ (1/2)\int \hat{A}_{12}\,[\rho(1,1')\rho(2,2') - \rho(1,2')\rho(2,1')]\,dX_1\,dX_2 \qquad [213]$$

In the special case of an orthogonal basis set of one-electron functions we get

$$D^{uv} = \langle\Phi_u|\Phi_v\rangle = det\{D^{uv}\} = \delta_{u,v} \qquad [214]$$

and the expression for the mean value of the operator $\hat{A}$ adopts the form

$$\langle A\rangle_u = \langle\Phi_u|\hat{A}|\Phi_u\rangle = A_0 + \sum_k^n \langle\psi_k|\hat{A}_1|\psi_k\rangle +$$

$$+ (1/2)\sum_{k,l}[\langle\psi_k\psi_l|\hat{A}_{12}|\psi_k\psi_l\rangle - \langle\psi_k\psi_l|\hat{A}_{12}|\psi_l\psi_k\rangle] \qquad [215]$$

1.4.4 Hartree-Fock Equations

Calculation of one-electron functions is based on the variational method. The mean value of the spinless Hamiltonian $\hat{H}_0$ in the Born-Oppenheimer approximation (see Chapter 2.2), i.e. the total molecular energy, is

$$\langle E\rangle_i = \langle\Phi_i|\hat{H}_0|\Phi_i\rangle = V_{NN} + \sum_{k}^{n} \langle\psi_k(1)|\hat{h}(1)|\psi_k(1)\rangle +$$

$$+ (1/2)\sum_{k,l}^{n} [\langle\psi_k(1)\psi_l(2)|\hat{g}(1,2)|\psi_k(1)\psi_l(2)\rangle -$$

$$- \langle\psi_k(1)\psi_l(2)|\hat{g}(1,2)|\psi_l(1)\psi_k(2)\rangle] \qquad [216]$$

where the one-electron and two-electron operators are denoted as

$$\hat{h} = \hat{h}(1) = -(\hbar^2/2m_e)\nabla_1^2 - (e^2/4\pi\epsilon_0)\sum_{A}^{N} Z_A\, r_{1A}^{-1} \qquad [217]$$

$$\hat{g} = \hat{g}(1,2) = (e^2/4\pi\epsilon_0)\, r_{12}^{-1} \qquad [218]$$

$$V_{NN} = (e^2/4\pi\epsilon_0)\sum_{A<B} Z_A\, Z_B\, r_{AB}^{-1} \qquad [219]$$

The orbitals to be calculated should be linearly independent, though not necessarily orthonormal. It is possible to find an optimum set of orbitals minimizing the total energy of the system and then to do their orthonormalization. The corresponding one-electron functions when orthogonalized are changed by a constant factor. The molecular energy, however, stays invariant. That is why without detriment to its general validity it can be assumed that the orbitals form an orthonormal set. Then we have n^2 orthonormality conditions, under which the functional

$$F = E_i - \sum_{k,l} \lambda_{kl}\, \langle\psi_k|\psi_l\rangle \qquad [220]$$

assumes a stationary value. The coefficients λ_{kl} represent the Lagrangian multipliers that are to be calculated. The variational condition $\delta F = 0$ after some manipulations yields

$$\delta F = \sum_{k}^{n} \langle\delta\psi_k(1)|\left\{[\hat{h} + \sum_{l\neq k}^{n}(\hat{J}_l - \hat{K}_l)]]|\psi_k(1)\rangle - \sum_{l}^{n} \lambda_{kl}|\psi_l(1)\rangle\right\} +$$

$$+ \sum_{k}^{n} \left\{\langle\psi_k(1)|[\hat{h} + \sum_{l\neq k}^{n}(\hat{J}_l^{*} - \hat{K}_l^{*})] - \sum_{l}^{n} \lambda_{lk}\langle\psi_l(1)|\right\}|\delta\psi_k(1)\rangle = 0 \qquad [221]$$

where the following notation has been used

$$\hat{J}_l\ |\psi_k(1)\rangle = \langle\psi_l(2)|\hat{g}|\psi_k(1)\psi_l(2)\rangle \qquad [222]$$

$$\langle\psi_k(1)|\ \hat{J}_l^{*} = \langle\psi_k(1)\psi_l(2)|\hat{g}|\psi_l(2)\rangle \qquad [223]$$

for the Coulomb operator and

$$\hat{K}_l \; |\psi_k(1)\rangle = \langle\psi_l(2)|\hat{g}|\psi_l(1)\psi_k(2)\rangle \qquad [224]$$

$$\langle\psi_k(1)| \; \hat{K}_l^* = \langle\psi_l(1)\psi_k(2)|\hat{g}|\psi_l(2)\rangle \qquad [225]$$

for the **exchange operator**. Since the variations $|\delta\psi_k(1)\rangle$ and $\langle\delta\psi_k(1)|$ are linearly independent (as they belong to dual spaces), then each term in parentheses is individually equal to zero

$$[\hat{h} + \sum_{l \neq k}^{n} (\hat{J}_l - \hat{K}_l)]|\psi_k(1)\rangle - \sum_{l}^{n} \lambda_{lk} \; |\psi_l(1)\rangle = 0 \qquad [226]$$

$$\langle\psi_k(1)|[\hat{h} + \sum_{l \neq k}^{n} (\hat{J}_l^* - \hat{K}_l^*)] - \sum_{l}^{n} \lambda_{lk} \; \langle\psi_l(1)| = 0 \qquad [227]$$

Because of the hermicity of operators $\hat{h}$, $\hat{J}_l$ and $\hat{K}_l$ the following condition is obtained

$$\sum_{l}^{n} |\psi_l(1)\rangle \; [\lambda_{kl} - \lambda_{lk}^*] = 0 \qquad [228]$$

or $\lambda_{kl} = \lambda_{kl}^*$ so that the Lagrangian multipliers represent the elements of a hermitian matrix. The system of equations that serves to determine the orbitals then adopts the form

$$\hat{F}_k \; |\psi_k\rangle = \sum_{l}^{n} \lambda_{kl} \; |\psi_l\rangle \qquad [229]$$

for $k = 1, 2, \ldots, n$. These equations are the familiar **Hartree-Fock equations** in which the **Fock operator** is defined as

$$\hat{F}_k = \hat{h} + \sum_{l \neq k}^{n} (\hat{J}_l - \hat{K}_l) = \hat{h}(1) + \hat{V}_k(1) \qquad [230]$$

The physical meaning of the one-electron approximation is thus the description of the motion of every electron in the averaged effective field of the other electrons

$$\hat{V}_k(1) = \sum_{l \neq k}^{n} (\hat{J}_l - \hat{K}_l) \qquad [231]$$

The exchange operator is non-zero only for the electrons with identical spin orientation

$$\hat{K}_l \; |\psi_k(1)\rangle = \langle\phi_l(2)|\hat{g}|\phi_l(1)\phi_k(2)\rangle \; \langle\eta_l(2)|\eta_k(2)\rangle \; |\eta_l(1)\rangle \qquad [232]$$

since $\langle\eta_l(2)|\eta_k(2)\rangle = \delta_{m_{sk}, m_{sl}}$. Exchange integrals occur always with an inverse sign with respect to the Coulomb integral; henceforth this decreases the repulsive interaction energy between electrons of parallel spin. Furthemore, this means that they represent a definite type of correlation of electron motion having parallel spin (Fermi correlation).

Now let us make use of the determinantal form of the function $|\Phi_i>$. By applying the arbitrary unitary transformation U to the set of spinorbitals $\{\psi_k\}$ we obtain a new basis set $\{\psi'_k\} = U\ \{\psi_k\}$ and a new determinantal function $|\Phi'_i>$ differing from the original one not more than by its sign

$$|\Phi'_i> = det\{U\}\ |\Phi_i> = \pm\ |\Phi_i> \qquad [233]$$

so that the molecular energy $E_i = <\Phi_i|\hat{H}_0|\Phi_i> = <\Phi'_i|\hat{H}_0|\Phi'_i>$ remains unchanged. The unitary transformation U may be chosen also in such an advantageous manner that it makes the matrix L of Lagrangian multipliers λ_{kl} to be diagonal

$$U^T\ L\ U = E \qquad [234]$$

where E is the diagonal matrix of orbital energies ϵ_k. Then the Hartree-Fock equations assume the form of a pseudocharacteristic problem

$$\hat{F}_k\ |\psi_k> = \epsilon_k\ |\psi_k> \qquad [235]$$

for k = 1, 2, ..., n.

Hartree-Fock equations represent the system of integro-differential equations that can be solved by an iterative procedure. The trial set of orbitals is used for the construction of the Fock operator and from the pseudocharacteristic problem a new estimate of orbitals is obtained. The procedure is repeated until self-consistency occurs (self-consistent field procedure). The above method forms the basis of the contemporary computational methods of quantum chemistry.

1.4.5 Density Functional Theory

The alternative approach to the many-electron Schrödinger equation, namely the Density-Functional Theory (DF), was introduced by Hohenberg, Kohn and Sham (48,49) and preceded by the works of Thomas (50), Fermi (51), Slater (52,53) and Gáspár (54). The DFT starts with the ground state one-electron density $\rho(1)$ as a fundamental variable, which has one-to-one correspondence (to within a constant) with the external potential of the electrons. The density also gives the total number of electrons, n, which then implies that the total energy of the many-electron system is a functional of $\rho(1)$, and furthermore, the total energy functional has a minimum equal to the ground state energy of the system. This leads to the conclusion that the ground state density $\rho(1)$ unequivocally determines the entire Hamiltonian (55).

The electronic energy of a system (a function of the density $\rho(1)$) may be decomposed as

$$E^{el}[\rho] = E_1[\rho] + E_C[\rho] + E_{xc}[\rho] \qquad [236]$$

with the one-electron term

$$E_1[\rho] = \int \rho(1)\ \hat{h}_1\ dX_1 \qquad [237]$$

a two-electron Coulomb term with Hartree potential $\hat{V}_C(1)$ of the charge density

$$E_C[\rho] = (1/2) \int \rho(1)\ \hat{V}_C(1)\ dX_1 =$$

$$= (1/2) \int \rho(1)\ [\int \rho(2)\ \hat{g}_{12}\ dX_2]\ dX_1 \qquad [238]$$

and the exchange-correlation term $E_{xc}[\rho]$ which contains all the remaining contributions. We point out that the first term is defined as the kinetic energy of n non-interacting electrons in an effective potential $\hat{V}_{eff}$. Due to this definition there remains a substantial part of the kinetic energy included in the term $E_{xc}[\rho]$.

The variational principle applied to this electronic energy expression under the constraint of electron conservation now leads to the following self-consistent one-electron like equations

$$\{\hat{T}_e(1) + \hat{V}_{eff}(1)\}\ \psi_i(1) = \epsilon_i\ \psi_i(1) \qquad [239]$$

with

$$\hat{V}_{eff}(1) = \hat{V}_{eN}(1) + \hat{V}_C(1) + \hat{V}_{xc}(1) \qquad [240]$$

and

$$\rho(1) = \sum_i n_i\ \psi_i(1)\ \psi_i^*(1) = \sum_i n_i\ |\psi_i(1)|^2 \qquad [241]$$

where n_i is the occupation number of the one-electron levels. The last term in the effective potential $\hat{V}_{eff}(1)$ is the functional derivative of the exchange and correlation energy

$$\hat{V}_{xc}(1) = \partial E_{xc}[\rho]/\partial\rho(1) \qquad [242]$$

Using these expressions an alternative formula for the electronic energy stands

$$E^{el}[\rho] = \sum_i n_i\epsilon_i - (1/2) \int \rho(1)\ \hat{V}_C(1)\ dX_1 -$$

$$- \int \rho(1)\ \hat{V}_{xc}(1)\ dX_1 + E_{xc}[\rho] \qquad [243]$$

which does not contain an explicit reference to the kinetic energy.

The system of equations [236] - [243] is not closed until a formula is found for the unknown functional $E_{xc}[\rho]$. It turns out, however, that there exist accurate approximations to this functional and even the simplest one is very useful in making computational methods effective but still reasonably accurate, especially for large or infinite electron systems.

This approach to the many-electron problem deserves a closer discussion, especially as compared to the Hartree-Fock (HF) and multi-configuration Hartree-Fock (MCHF) or configuration interaction (CI) approaches. The one-electron equations [239] look even simpler than the corresponding HF equations, [230] and [235]. This is an artifact since the many-body effects (neglected in HF but included in CI) are only transferred to the unknown functional $E_{xc}[\rho]$. The one-electron eigenfuctions and eigenvalues [239] do not correspond to those of HF, and they are often regarded as auxiliary quantities yielding the charge density and the kinetic energy contribution. However, for the highest occupied level of a many-electron system it can be shown that the bare DFT eigenvalue equals the ionization energy; the more localized the orbitals are, the more their eigenvalues deviate from ionization energies.

Making use of the properties of a homogeneous electron gas the useful **Local-Density Approximation** (LDA) to the exchange and correlation of a many-electron system can be defined.

The exchange is usually defined in terms of the HF approximation separating the whole functional into two contributions

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \qquad [244]$$

where the first term, which is called the exchange energy, is a consequence of the antisymmetry of the electronic wave function. The second term includes the correlation energy, i.e., the many-body effects.

The homogeneous electron gas is defined by its density ρ or the density parameter

$$r_s = (3/4\pi\rho)^{1/3} \qquad [245]$$

which is the radius of the spherical volume occupied by one electron. Using this expression, the (average) exchange energy per electron is

$$\epsilon_x(\rho) = -\frac{3}{4}\,\hat{v}_x(\rho) = -\frac{3}{4}\,(3\rho/\pi)^{1/3} = -\,0.458/r_s \qquad [246]$$

(in atomic units) which is obtained analytically by integrating over the wave vector up to the Fermi level.

The correlation energy for the homogeneous electron gas is more laborious to evaluate and various approximations have been proposed (56). The two leading terms in the high-density expansion for the ground state are (57)

$$\epsilon_c(\rho) = 0.0311 \ln r_s - 0.048 \qquad [247]$$

(in atomic units).

The LDA approximation for the inhomogeneous electron gas yields

$$E_{xc}[\rho] = \int \rho(1) \, [\epsilon_x(\rho) + \epsilon_c(\rho)] \, dX_1 \qquad [248]$$

This is an unambiguous approximation that does not contain any adjustable parameters, as is often misunderstood. Though neglecting the long range effects of density variation, the LDA has shown unexpected successful applicability to electron systems from free atoms to solid matter.

1.5 FREE ATOM

1.5.1 Electron Configuration of a Free Atom

The wave function of an atom with a single electron can be described in the form of corresponding atomic spinorbital characterized by a set of quantum numbers (n,l,m_l,m_s) of the form

$$\psi(n,l,m_l,m_s) = R_{n,l}(r) \, Y_{l,m_l}(\vartheta,\varphi) \, \eta(m_s) \qquad [249]$$

where $R_{n,l}$ is the radial part of the atomic orbital, Y_{l,m_l} its angular part and $\eta(m_s)$ is the spin variable function. For the d^n electron configuration it is sufficient to specify only the quantum numbers m_{li} and m_{si} only, since the values n_i and l_i are in common for all the spinorbitals ψ_i.

From atomic spinorbitals, various Slater determinants can be formed (determinantal functions, configuration functions) Φ_k, representing eigenfunctions of the projection operators of the total orbital angular momentum $\hat{L}_z = \sum_i \hat{l}_{zi}$ and of the projection of total spin $\hat{S}_z = \sum_i \hat{s}_{zi}$. Then

$$\hat{L}_z\Phi_k = \hbar M_{lk}\Phi_k \qquad [250]$$

$$\hat{S}_z\Phi_k = \hbar M_{sk}\Phi_k \qquad [251]$$

With the use of linear combinations of determinantal functions

$$\Psi(L,M_L,S,M_S) = \sum_k c_k\Phi_k \qquad [252]$$

wave functions can also be constructed which are the eigenfunctions of the operators $\hat{L}^2$ and $\hat{S}^2$

$$\hat{L}^2\Psi(L,M_L,S,M_S) = \hbar^2 L(L + 1)\Psi(L,M_L,S,M_S) \qquad [253]$$

$$\hat{S}^2\Psi(L,M_L,S,M_S) = \hbar^2 S(S + 1)\Psi(L,M_L,S,M_S) \qquad [254]$$

TABLE 12
Determinantal functions of the d^2 configuration.[a]

M_S M_L	1	0		-1
4		$\Phi_1=\vert 2^+,2^-\vert$		
3	$\Phi_2=\vert 2^+,1^+\vert$	$\Phi_3=\vert 2^+,1^-\vert$	$\Phi_4=\vert 2^-,1^+\vert$	$\Phi_5=\vert 2^-,1^-\vert$
2	$\Phi_6=\vert 2^+,0^+\vert$	$\Phi_7=\vert 2^+,0^-\vert$	$\Phi_8=\vert 2^-,0^+\vert$	$\Phi_{10}=\vert 2^-,0^-\vert$
		$\Phi_9=\vert 1^+,1^-\vert$		
1	$\Phi_{11}=\vert 1^+,0^+\vert$	$\Phi_{13}=\vert 1^+,0^-\vert$	$\Phi_{14}=\vert 1^-,0^+\vert$	$\Phi_{17}=\vert 1^-,0^-\vert$
	$\Phi_{12}=\vert 2^+-1^+\vert$	$\Phi_{15}=\vert 2^+,-1^-\vert$	$\Phi_{16}=\vert 2^-,-1^+\vert$	$\Phi_{18}=\vert 2^-,-1^-\vert$
0	$\Phi_{19}=\vert 2^+,-2^+\vert$	$\Phi_{21}=\vert 2^+,-2^-\vert$	$\Phi_{22}=\vert 2^-,-2^+\vert$	$\Phi_{26}=\vert 2^-,-2^-\vert$
	$\Phi_{20}=\vert 1^+,-1^+\vert$	$\Phi_{23}=\vert 1^+,-1^-\vert$	$\Phi_{24}=\vert 1^-,-1^+\vert$	$\Phi_{27}=\vert 1^-,-1^-\vert$
		$\Phi_{25}=\vert 0^+,0^-\vert$		
-1	$\Phi_{28}=\vert 0^+,-1^+\vert$	$\Phi_{30}=\vert 0^-,-1^+\vert$	$\Phi_{31}=\vert 0^+,-1^-\vert$	$\Phi_{34}=\vert 0^-,-1^-\vert$
	$\Phi_{29}=\vert 1^+,-2^+\vert$	$\Phi_{32}=\vert 1^-,-2^+\vert$	$\Phi_{33}=\vert 1^+,-2^-\vert$	$\Phi_{35}=\vert 1^-,-2^-\vert$
-2	$\Phi_{36}=\vert 0^+,-2^+\vert$	$\Phi_{37}=\vert 0^-,-2^+\vert$	$\Phi_{38}=\vert 0^+,-2^-\vert$	$\Phi_{40}=\vert 0^-,-2^-\vert$
		$\Phi_{39}=\vert -1^+,-1^-\vert$		
-3	$\Phi_{41}=\vert -1^+,-2^+\vert$	$\Phi_{42}=\vert -1^-,-2^+\vert$	$\Phi_{43}=\vert -1^+,-2^-\vert$	$\Phi_{44}=\vert -1^-,-2^-\vert$
-4		$\Phi_{45}=\vert -2^+,-2^-\vert$		

[a] Spinorbital a^+ has the spin $\alpha(m_s = +1/2,\ m_l = a)$, spinorbital b^- has the spin $\beta(m_s = -1/2,\ m_l = b)$.

Computation can be done by solving the homogeneous system of linear equations

$$\sum_k c_k\, [L^2_{kj} - \hbar^2 L(L + 1)\delta_{kj}] = 0 \quad \text{for } L^2_{kj} = \langle\Phi_k|\hat{L}^2|\Phi_j\rangle \qquad [255]$$

$$\sum_k c_k\, [S^2_{kj} - \hbar^2 S(S + 1)\delta_{kj}] = 0 \quad \text{for } S^2_{kj} = \langle\Phi_k|\hat{S}^2|\Phi_j\rangle \qquad [256]$$

The wave functions $\Psi(L,M_L,S,M_S)$ may also be obtained with projection operators

$$\hat{P}_S = \prod_{K\neq S} \frac{\hat{S}^2 - \hbar^2 K(K + 1)}{\hbar^2[S(S + 1) - K(K + 1)]} \qquad [257]$$

$$\hat{P}_L = \prod_{N\neq L} \frac{\hat{L}^2 - \hbar^2 N(N + 1)}{\hbar^2[L(L + 1) - N(N + 1)]} \qquad [258]$$

or by shift operators

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \qquad [259]$$

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \qquad [260]$$

For the electron configuration $d^\alpha s^\beta p^\gamma$ the number of different determinantal functions $\Phi(M_L,M_S)$ is equal to $\binom{10}{\alpha}\binom{2}{\beta}\binom{6}{\gamma}$. The system wave functions $\Psi(L,M_L,S,M_S)$ with definite values of the quantum numbers L and S, forms the **electron term** designated by the symbol T(L)

L	0	1	2	3	4	5	...
T(L)	S	P	D	F	G	H	...

The left upper index on the term symbol is the spin multiplicity, i.e. the number m = 2S + 1 expressing the degree of spin degeneracy $^mT(L)$. Total degeneracy of the term is the number d = (2L + 1)(2S + 1). The presence of electron interaction in a free atom is manifest by formation of terms which are further split into multiplets due to the spin-orbit interaction. In the presence of an external field the degeneracy of the energy levels is removed.

For the d^2 electron configuration, $\binom{10}{2}$ = 45 different determinantal functions $\Phi(M_L,M_S)$ can be created with the values $-4 \leq M_L \leq +4$ and $-1 \leq M_S \leq +1$ as listed in Table 12. From the above determinantal functions, the wave functions $\Psi(L,M_L,S,M_S)$ of individual terms $^1S(L = 0,\ S = 0,\ d = 1)$, $^3P(L = 1,\ S = 1,\ d = 9)$, $^1D(L = 2,\ S = 0,\ d = 5)$, $^3F(L = 3,\ S = 1,\ d = 21)$ and $^1G(L = 4,\ S = 0,\ d = 9)$ can be formed. They are expressed in Table 13.

1.5.2 Energies of Atomic Terms

To determine the atomic term energies it is necessary to exexpress the matrix elements of the electronic Hamiltonian

$$\hat{H}^{eff} = \sum_i \hat{h}_i + \sum_{i<j} \hat{g}_{ij} \qquad [261]$$

in the basis set of wave functions $\Psi(L,M_L,S,M_S)$. Since the wave functions are composed of the determinantal functions $\Phi(M_L,M_S)$ and further of the spinorbitals ψ_i, then the computation is reduced to the determination of one-electron and two-electron integrals

$$<i|\hat{h}|i'> = <\psi_i(1)|(-\hbar^2/2m_e)\nabla_1^2 - \sigma_{SI}Z_A/r_1|\psi_{i'}(1)> \qquad [262]$$

TABLE 13
Wave functions $\Psi(L,M_L,S,M_S)$ of the individual terms of the d^2 configuration.

Term	L	M_L	S	M_S	Function
^1G	4	4	0	0	Φ_1
	4	3	0	0	$1/\sqrt{2}(\Phi_3-\Phi_4)$
	4	2	0	0	$1/\sqrt{14}(\sqrt{3}\Phi_7-\sqrt{3}\Phi_8+2\sqrt{2}\Phi_9)$
	4	1	0	0	$1/\sqrt{14}(\Phi_{15}-\Phi_{16}+\sqrt{6}\Phi_{13}-\sqrt{6}\Phi_{14})$
	4	0	0	0	$1/\sqrt{70}(\Phi_{21}-\Phi_{22}+4\Phi_{23}-4\Phi_{24}+6\Phi_{25})$
	4	-1	0	0	$1/\sqrt{14}(\Phi_{33}-\Phi_{32}+\sqrt{6}\Phi_{31}-\sqrt{6}\Phi_{30})$
	4	-2	0	0	$1/\sqrt{14}(\sqrt{3}\Phi_{38}-\sqrt{3}\Phi_{37}+2\sqrt{2}\Phi_{39})$
	4	-3	0	0	$1/\sqrt{2}(\Phi_{43}-\Phi_{42})$
	4	-4	0	0	Φ_{45}
^1F	3	3	1	1	Φ_2
	3	3	1	0	$1/\sqrt{2}(\Phi_3+\Phi_4)$
	3	3	1	-1	Φ_5
	3	2	1	1	Φ_6
	3	2	1	0	$1/\sqrt{2}(\Phi_7+\Phi_8)$
	3	2	1	-1	Φ_{10}
	3	1	1	1	$1/\sqrt{5}(\sqrt{3}\Phi_{12}+\sqrt{2}\Phi_{11})$
	3	1	1	0	$1/\sqrt{10}(\sqrt{3}\Phi_{15}+\sqrt{3}\Phi_{16}+\sqrt{2}\Phi_{13}+\sqrt{2}\Phi_{14})$
	3	1	1	-1	$1/\sqrt{5}(\sqrt{3}\Phi_{18}+\sqrt{2}\Phi_{19})$
	3	0	1	1	$1/\sqrt{5}(\Phi_{19}+2\Phi_{20})$
	3	0	1	0	$1/\sqrt{10}(\Phi_{21}+\Phi_{22}+2\Phi_{23}+2\Phi_{24})$
	3	0	1	-1	$1/\sqrt{5}(\Phi_{26}+2\Phi_{27})$
	3	-1	1	1	$1/\sqrt{5}(\sqrt{3}\Phi_{29}+\sqrt{2}\Phi_{28})$
	3	-1	1	0	$1/\sqrt{10}(\sqrt{3}\Phi_{32}+\sqrt{3}\Phi_{33}+\sqrt{2}\Phi_{30}+\sqrt{2}\Phi_{31})$
	3	-1	1	-1	$1/\sqrt{5}(\sqrt{3}\Phi_{35}+\sqrt{2}\Phi_{34})$
	3	-2	1	1	Φ_{36}
	3	-2	1	0	$1/\sqrt{2}(\Phi_{37}+\Phi_{38})$
	3	-2	1	-1	Φ_{40}

TABLE 13 (Continued)

Term	L	M_L	S	M_S	Function
	3	-3	1	1	Φ_{41}
	3	-3	1	0	$1/\sqrt{2}(\Phi_{42}+\Phi_{43})$
	3	-3	1	-1	Φ_{44}
^3P	1	1	1	1	$1/\sqrt{5}(\sqrt{3}\Phi_{11}-\sqrt{2}\Phi_{12})$
	1	1	1	0	$1/\sqrt{10}(\sqrt{3}\Phi_{13}+\sqrt{3}\Phi_{14}-\sqrt{2}\Phi_{15}-\sqrt{2}\Phi_{16})$
	1	1	1	-1	$1/\sqrt{5}(\sqrt{3}\Phi_{17}-\sqrt{2}\Phi_{18})$
	1	0	1	1	$1/\sqrt{5}(\Phi_{20}-2\Phi_{19})$
	1	0	1	0	$1/\sqrt{10}(\Phi_{23}+\Phi_{24}-2\Phi_{21}-2\Phi_{22})$
	1	0	1	-1	$1/\sqrt{5}(\Phi_{27}-2\Phi_{26})$
	1	-1	1	1	$1/\sqrt{5}(\sqrt{3}\Phi_{28}-\sqrt{2}\Phi_{29})$
	1	-1	1	0	$1/\sqrt{10}(\sqrt{3}\Phi_{30}+\sqrt{3}\Phi_{31}-\sqrt{2}\Phi_{32}-\sqrt{2}\Phi_{33})$
	1	-1	1	-1	$1/\sqrt{5}(\sqrt{3}\Phi_{34}-\sqrt{2}\Phi_{35})$
^1D	2	2	0	0	$1/\sqrt{7}(\sqrt{2}\Phi_{7}-\sqrt{2}\Phi_{8}-\sqrt{3}\Phi_{9})$
	2	1	0	0	$1/\sqrt{14}(\sqrt{6}\Phi_{15}-\sqrt{6}\Phi_{16}-\Phi_{13}+\Phi_{14})$
	2	0	0	0	$1/\sqrt{14}(2\Phi_{21}-2\Phi_{22}+\Phi_{23}-\Phi_{24}-2\Phi_{25})$
	2	-1	0	0	$1/\sqrt{14}(\sqrt{6}\Phi_{33}-\sqrt{6}\Phi_{32}-\Phi_{31}+\Phi_{30})$
	2	-2	0	0	$1/\sqrt{7}(\sqrt{2}\Phi_{38}-\sqrt{3}\Phi_{33}-\sqrt{2}\Phi_{37})$
^1S	0	0	0	0	$1/\sqrt{5}(\Phi_{21}-\Phi_{22}-\Phi_{23}+\Phi_{24}+\Phi_{25})$

$$<ij|\hat{g}|i'j'> = \sigma_{SI}<\psi_i(1)\psi_j(2)|1/r_{12}|\psi_{i'}(1)\psi_{j'}(2)> \qquad [263]$$

where the conversion factor for the SI unit system is $\sigma_{SI} = e^2/4\pi\epsilon_0$. The atomic spinorbitals consist of the radial part $R_{n_i l_i}(r_i)$ dependent on the distance r_i of the electrons from the nucleus A, the angular part $Y_{l_i m_{l_i}}(\vartheta_i,\varphi_i)$ and the spin part $\eta_{si}(m)$ with the projection $\eta(1/2) = \alpha$ and $\eta(-1/2) = \beta$.

Spherical harmonics are defined as (Table 14)

$$Y_{k,m}(\vartheta,\varphi) = (-1)^m\left[\frac{2k+1}{4\pi}\,\frac{(k-m)!}{(k+m)!}\right]^{1/2} P_l(\cos\vartheta)e^{im\varphi} \qquad [264]$$

for m ≥ 0 and

$$Y_{k,m}(\vartheta,\varphi) = (-1)^m [Y_{k,-m}]^* \qquad [265]$$

for m < 0. The associate Legendre polynomials are

$$P_k^m(x) = \frac{1}{2^k k!} (1-x^2)^{m/2} \frac{d^{k+m}}{dx^{k+m}} (x^2 - 1)^k \qquad [266]$$

and Legendre polynomials are

$$P_k(x) = \frac{1}{2^k k!} \frac{d^k}{dx^k} (x^2 - 1)^k \qquad [267]$$

TABLE 14

Normalized spherical harmonic functions $Y_{l,m_l}(\vartheta,\varphi)$.

l	m_l	Y_{l,m_l}
0	0	$1/\sqrt{4\pi}$
1	0	$\sqrt{3/4\pi}\ \cos\vartheta$
1	±1	$\mp\sqrt{3/8\pi}\ \sin\vartheta\ \exp(\pm i\varphi)$
2	0	$\sqrt{5/16\pi}\ (2\cos^2\vartheta - \sin^2\vartheta)$
2	±1	$\mp\sqrt{15/8\pi}\ \cos\vartheta\ \sin\vartheta\ \exp(\pm i\varphi)$
2	±2	$\sqrt{15/32\pi}\ \sin^2\vartheta\ \exp(\pm 2i\varphi)$
3	0	$\sqrt{7/16\pi}\ (2\cos^3\vartheta - 3\cos\vartheta\ \sin^2\vartheta)$
3	±1	$\mp\sqrt{21/64\pi}\ (4\cos^2\vartheta\sin\vartheta - \sin^3\vartheta)\ \exp(\pm i\varphi)$
3	±2	$\sqrt{105/32\pi}\ \cos\vartheta\ \sin^2\vartheta\ \exp(\pm 2i\varphi)$
3	±3	$\mp\sqrt{35/64\pi}\ \sin^3\vartheta\ \exp(\pm 3i\varphi)$
4	0	$3/\sqrt{256\pi}\ (35\cos^4\vartheta - 30\cos^2\vartheta + 3)$
4	±1	$\mp\sqrt{45/64\pi}\ \sin\vartheta\ (7\cos^3\vartheta - 3\cos\vartheta)\ \exp(\pm i\varphi)$
4	±2	$\sqrt{45/128\pi}\ \sin^2\vartheta(7\cos^2\vartheta - 1)\ \exp(\pm 2i\varphi)$
4	±3	$\mp\sqrt{315/64\pi}\ \sin^3\vartheta\ \cos\vartheta\ \exp(\pm 3i\varphi)$
4	±4	$\sqrt{315/512\pi}\ \sin^4\vartheta\ \exp(\pm 4i\varphi)$

For a one-electron integral, due to the orthonormality of the angular and spin parts of atomic spinorbitals

$$\langle i|\hat{h}|i'\rangle = \left[\int_0^\infty R^*_{n_i l_i}(r_1)\hat{h}_1 R_{n_{i'}, l_{i'}}(r_1) r_1^2\, dr_1\right] \delta_{m_{li}, m_{li'}} \delta_{m_{si}, m_{si'}} =$$

$$= U_i \delta_{m_{li}, m_{li'}} \delta_{m_{si}, m_{si'}} \qquad [268]$$

Here we have made use of identity of the quantum numbers $n_i = n_{i'}$ and $l_i = l_{i'}$.

For expressing the two-electron integrals it is advantageous to expand the operator $1/r_{12}$ into the basis of spherical harmonic functions $Y_{k,m}(\vartheta,\varphi)$ or the Legendre polynomials $P_k(\cos\gamma_{12})$

$$1/r_{12} = \sum_{k=0}^{\infty} [4\pi/(2k + 1)](r_<^k/r_>^{k+1}) \sum_{m=-k}^{+k} Y_{k,m}(\vartheta_1,\varphi_1)Y_{k,m}(\vartheta_2,\varphi_2) =$$

$$= \sum_{k=0}^{\infty} (r_<^k/r_>^{k+1})P_k(\cos\gamma_{12}) \qquad [269]$$

The expression $r_<^k/r_>^{k+1}$ is equal to the function r_1^k/r_2^{k+1} for $r_1 < r_2$ and the function r_2^k/r_1^{k+1} for $r_1 > r_2$ so that we can use the notation $r_< = min\{r_1,r_2\}$ and $r_> = max\{r_1,r_2\}$. The argument of the Legendre polynomial is $\cos\gamma_{12} = \cos\vartheta_1\cos\vartheta_2 + \sin\vartheta_1\sin\vartheta_2\cos(\varphi_1-\varphi_2)$. After integrating over the spin and angular parts of the spinorbitals, the two-electron integral can be expressed in the form

$$<ij|\hat{g}|i'j'> = \delta_{m_{si},m_{si'}} \delta_{m_{sj},m_{sj'}} \delta_{(m_{li}+m_{lj}),(m_{li'}+m_{lj'})} \cdot$$

$$\cdot \sum_{k=0}^{\infty} c^k(l_i,m_{li},l_{i'},m_{li'})\ c^k(l_j,m_{lj},l_{j'},m_{lj'}) \cdot$$

$$\cdot\ R^k(n_i,l_i,n_j,l_j,n_{i'},l_{i'},n_{j'},l_{j'}) \qquad [270]$$

Here, the integral over the radial functions is defined as

$$R^k_{iji'j'} = R^k(n_i,l_i,n_j,l_j,n_{i'},l_{i'},n_{j'},l_{j'}) =$$

$$= \sigma_{SI} \int_0^{\infty}\int_0^{\infty} (r_<^k / r_>^{k+1})\ R^*_{n_i,l_i}(r_1)\ R^*_{n_j,l_j}(r_2)\ R_{n_{i'},l_{i'}}(r_1) \cdot$$

$$\cdot\ R_{n_{j'},l_{j'}}(r_2)\ r_1^2\ r_2^2\ dr_1 dr_2 \qquad [271]$$

The integrals over the angular parts of spinorbitals can be expressed, e.g., as follows

$$c^k(l,m,l',m') = \left(\frac{4}{2k+1}\right)^{1/2} \int_0^{\infty}\int_0^{\infty} Y^*_{l,m}(\vartheta,\varphi)\ Y_{k,m-m'}(\vartheta,\varphi) \cdot$$

$$\cdot\ Y_{l',m'}(\vartheta,\varphi)\ \sin\vartheta\ d\vartheta\ d\varphi = \left(\frac{2}{2k+1}\right)^{1/2} \int_0^{\infty} P_l^m(\cos\vartheta) \cdot$$

$$\cdot\ P_k^{m-m'}(\cos\vartheta)\ P_{l'}^{m'}(\cos\vartheta)\ \sin\vartheta\ d\vartheta \qquad [272]$$

The above coefficients are independent of the atom concerned and their values for atomic d orbitals are listed in Table 15. The advantage of expression [270] rests in the fact that the sum over the index k is reduced to several non-zero terms, only. Now for the Coulomb integral J_{ij} and the exchange integral K_{ij}

TABLE 15
The values of the coefficients $c^k(l_i,m_{li},l_j,m_{lj})$.

l_i	l_j	m_{li}	m_{lj}	c^0	c^1	c^2
2	2	±2	±2	1	$-\sqrt{4/49}$	$\sqrt{1/441}$
2	2	±2	±1	0	$\sqrt{6/49}$	$-\sqrt{5/441}$
2	2	±2	0	0	$-\sqrt{4/49}$	$\sqrt{15/441}$
2	2	±1	±1	1	$\sqrt{1/49}$	$-\sqrt{16/441}$
2	2	±1	0	0	$\sqrt{1/49}$	$\sqrt{30/441}$
2	2	0	0	1	$\sqrt{4/49}$	$\sqrt{36/441}$
2	2	±2	∓2	0	0	$\sqrt{70/441}$
2	2	±2	∓1	0	0	$-\sqrt{35/441}$
2	2	±1	∓1	0	$-\sqrt{6/49}$	$-\sqrt{40/441}$

$$\hat{J}_{ij} = \langle ij|g|ij\rangle = \sum_{k=0} a^k(l_i,m_{li},l_j,m_{lj})\; F^k(n_i,l_i,n_j,l_j) \qquad [273]$$

$$K_{ij} = \langle ij|\hat{g}|ji\rangle = \sum_{k=0} b^k(l_i,m_{li},l_j,m_{lj})\; G^k(n_i,l_i,n_j,l_j) \qquad [274]$$

where the radial integrals of the type

$$F^k(n_i,l_i,n_j,l_j) = R^k_{ijij} \qquad [275]$$

$$G^k(n_i,l_i,n_j,l_j) = G^k_{ijji} \qquad [276]$$

are called **Slater-Condon parameters**. The coefficients a^k and b^k are

$$a^k(l_i,m_{li},l_j,m_{lj}) = c^k(l_i,m_{li},l_i m_{li})\; c^k(l_j,m_{lj},l_j,m_{lj}) \qquad [277]$$

$$b^k(l_i,m_{li},l_j,m_{lj}) = |c^k(l_i,m_{li},l_j,m_{lj})|^2 \qquad [278]$$

Sometimes, the functions F_k are used instead of the parameters F^k

$$F_0 = F^0 \qquad [279]$$

$$F_2 = F^2/49 \qquad [280]$$

$$F_4 = F^4/441 \qquad [281]$$

In crystal field theory, as a rule, the **Racah parameters** are used, defined by the relationships

$$A = F_0 - 49F_4 \qquad [282]$$

$$B = F_2 - 5F_4 \qquad [283]$$

$$C = 35F_4 \qquad [284]$$

TABLE 16

The energies of the individual terms of d^n configurations.

d^n	Energy *via* Racah parameters
d^2	$E(^3F) = A - 8B$
	$E(^3P) = A + 7B$
	$E(^1G) = A + 4B + 2C$
	$E(^1D) = A - 3B + 2C$
	$E(^1S) = A + 14B + 7C$
d^3	$E(^4F) = 3A - 15B$
	$E(^4P) = 3A$
	$E(^2H) = 3A - 6B + 3C$
	$E(^2G) = 3A - 11B + 3C$
	$E(^2F) = 3A + 9B + 3C$
	$E(^2D) = 3A + 5B + 5C \pm [193B^2 + 8BC + 4C^2]^{1/2}$
	$E(^2P) = 3A - 11B + 3C$
d^4	$E(^5D) = 6A - 21B$
	$E(^3H) = 6A - 17B + 4C$
	$E(^3G) = 6A - 12B + 4C$
	$E(^3F) = 6A - 5B + (11/2)C \pm (3/2)[68B^2 + 4BC + 4C^2]^{1/2}$
	$E(^3D) = 6A - 5B + 4C$
	$E(^3P) = 6A - 5B + (11/2)C \pm (1/2)[912B^2 - 24BC + 9C^2]^{1/2}$
	$E(^1I) = 6A - 15B + 6C$
	$E(^1G) = 6A - 5B + (15/2)C \pm (1/2)[708B^2 - 12BC + 9C^2]^{1/2}$
	$E(^1F) = 6A + 6C$
	$E(^1D) = 6A + 9B + (15/2)C \pm (3/2)[144B^2 + 8BC + C^2]^{1/2}$
	$E(^1S) = 6A + 10B + 10C \pm (1/2)[193B^2 + 8BC + 4C^2]^{1/2}$
d^5	$E(^6S) = 10A - 35B$
	$E(^4G) = 10A - 25B + 5C$
	$E(^4F) = 10A - 13B + 7C$
	$E(^4D) = 10A - 18B + 5C$
	$E(^4P) = 10A - 28B + 7C$
	$E(^2I) = 10A - 24B + 8C$
	$E(^2H) = 10A - 22B + 10C$
	$E(^2G_a) = 10A - 13B + 8C$
	$E(^2G_b) = 10A - 3B + 10C$
	$E(^2F_a) = 10A - 9B + 8C$
	$E(^2F_b) = 10A - 25B + 10C$
	$E(^2D_a) = 10A - 4B + 10C$
	$E(^2D_{b,c}) = 10A - 3B + 11C \pm 3[57B^2 + 2BC + C^2]^{1/2}$
	$E(^2P) = 10A + 20B + 10C$
	$E(^2S) = 10A - 3B + 8C$

TABLE 17

The energies of the individual terms of d^n configurations.

d^n	Energy *via* Slater-Condon parameters
d^2	$E(^3F) = F_0 - 8F_2 - 9F_4$
	$E(^3P) = F_0 + 7F_2 - 84F_4$
	$E(^1G) = F_0 + 4F_2 + F_4$
	$E(^1D) = F_0 - 3F_2 + 36F_4$
	$E(^1S) = F_0 + 14F_2 + 126F_4$
d^3	$E(^4F) = 3F_0 - 15F_2 - 72F_4$
	$E(^4P) = 3F_0 - 147F_4$
	$E(^2H) = 3F_0 - 6F_2 - 12F_4$
	$E(^2G) = 3F_0 - 11F_2 + 13F_4$
	$E(^2F) = 3F_0 + 9F_2 - 87F_4$
	$E(^2D) = 3F_0 + 5F_2 + 3F_4 \pm [193F_2^2-1650F_2F_4+8325F_4^2]^{1/2}$
	$E(^2P) = 3F_0 - 6F_2 - 12F_4$
d^4	$E(^5D) = 6F_0 - 21F_2 - 189F_4$
	$E(^3H) = 6F_0 - 17F_2 - 69F_4$
	$E(^3G) = 6F_0 - 12F_2 - 94F_4$
	$E(^3F) = 6F_0 - 5F_2 -(153/2)F_4 \pm(1/2)[612F_2^2-4860F_2F_4+20025F_4^2]^{1/2}$
	$E(^3D) = 6F_0 - 5F_2 - 129F_4$
	$E(^3P) = 6F_0 - 5F_2 -(153/2)F_4 \pm(1/2)[912F_2^2-9960F_2F_4+38025F_4^2]^{1/2}$
	$E(^1I) = 6F_0 - 15F_2 - 9F_4$
	$E(^1G) = 6F_0 - 5F_2 - (13/2)F_4 \pm(1/2)[708F_2^2-7500F_2F_4+38025F_4^2]^{1/2}$
	$E(^1F) = 6F_0 - 48F_4$
	$E(^1D) = 6F_0 + 9F_2-(153/2)F_4\pm(1/2)[1296F_2^2-10440F_2F_4+30825F_4^2]^{1/2}$
	$E(^1S) = 6F_0 + 10F_2 + 6F_4 \pm(1/2)[3088F_2^2-26400F_2F_4+133200F_4^2]^{1/2}$
d^5	$E(^6S) = 10F_0 - 35F_2 - 315F_4$
	$E(^4G) = 10F_0 - 25F_2 - 190F_4$
	$E(^4F) = 10F_0 - 13F_2 - 180F_4$
	$E(^4D) = 10F_0 - 18F_2 - 225F_4$
	$E(^4P) = 10F_0 - 28F_2 - 105F_4$
	$E(^2I) = 10F_0 - 24F_2 - 90F_4$
	$E(^2H) = 10F_0 - 22F_2 - 30F_4$
	$E(^2G_a) = 10F_0 - 13F_2 - 145F_4$
	$E(^2G_b) = 10F_0 - 3F_2 - 155F_4$
	$E(^2F_a) = 10F_0 - 9F_2 - 165F_4$
	$E(^2F_b) = 10F_0 - 25F_2 - 15F_4$
	$E(^2D_a) = 10F_0 - 4F_2 - 120F_4$
	$E(^2D_{b,c}) = 10F_0 - 3F_2 - 90F_4 \pm(1/2)[513F_2^2-4500F_2F_4+20700F_4^2]^{1/2}$
	$E(^2P) = 10F_0 + 20F_2 - 240F_4$
	$E(^2S) = 10F_0 - 3F_2 - 195F_4$

As an example, let us express the energy of the ^3F term of the d^2 electron configuration. According to Table 12 and 13 the wave function of the ^3F term assumes, for example, the following possible form

$$\Psi(3,3,1,1) = \Phi_2 = |2^+,1^+| \qquad [285]$$

The corresponding energy is

$$E(^3F) = \langle\Phi_2|\hat{H}^{el}|\Phi_2\rangle = 2U_d + J_{21} - K_{21} =$$
$$= 2U_d + F_0 - 8F_2 - 9F_4 = 2U_d + A - 8B \qquad [286]$$

The energies of individual d^n term configurations are listed in Table 16 (expressed with the help of Racah parameters) and Table 17 (expressed through Slater-Condon parameters). It is necessary to add the term nU_{dd} to all the energies. The relative energies of the configurations d^{10-n} are the same as the energies of the configurations d^n.

1.5.3 Spin-Orbit Interaction in Atoms

The spin-orbit interaction (SOI) is described by the one-electron operator

$$\hat{h}^{so} = \frac{e^2}{8\pi\epsilon_0^2 m_e^2 c^2} \sum_i Z_A r_i^{-3}\, \hat{s}_i.\hat{l}_i = \sum_i \xi(r_i)\, \hat{s}_i.\hat{l}_i \qquad [287]$$

This operator has non-zero off-diagonal matrix elements in the basis set of wave functions $\Psi(L,M_L,S,M_S)$, as it does not commutate with the operators $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$ and $\hat{S}_z$. For the atoms with low Z_A, however, off-diagonal matrix elements of the operator $\hat{h}^{so}$ are small. Thus the effect of SOI can be approximated by the diagonal matrix elements.

The operators $\hat{J}^2$ and $\hat{J}_z$ of the total angular momentum $J = L + S$ commutate both with the electronic Hamiltonian $\hat{H}^{el}$ and $\hat{h}^{so}$, i.e. they have the set of eigenfunctions $\Psi(J,M_J)$ in common. To express the diagonal matrix elements of the operator $\hat{h}^{so}$ the relationship

$$\hat{S}.\hat{L} = (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)/2 \qquad [288]$$

can be used.

Both the operators $\hat{S}.\hat{L}$ and $\sum_i \hat{s}_i\hat{l}_i$ have identical matrix elements. Further, the functions $\xi(r_i)$ are constant within the given electron configuration; they are denoted as $\xi_{n,l}$. Then the SOI contribution to the energy of the atomic term, as specified in first order perturbation theory, assumes the form

$$E^{so} = \hbar^2\xi_{n,l}[J(J + 1) - L(L + 1) - S(S + 1)]/2 \qquad [289]$$

For each atomic term of the given configuration (characterized by the quantum numbers L and S) the energy contributions are obtained, corresponding to the possible values of the quantum number $J \in \langle |L - S|, L + S\rangle$. Thus, the term is split into a set of $m = 2S + 1$ different energy levels called the **multiplet**. Individual terms of the multiplet differ according to value of J - designated by the right subscript standing by the symbol of the term $^{m}T(L)_J$. The difference in the energies of the successiie multiplet levels is

$$\Delta E = E_{J+1} - E_J = \hbar^2 \xi_{n,l}(J + 1) \qquad [290]$$

i.e., it is proportional to the quantum number $J' = J + 1$ of the level with higher energy (Landé interval rule).

1.6 CRYSTAL FIELD THEORY

The influence of the inhomogeneous electrostatic field defined by the charges and electric dipoles of the ligands is manifested in the splitting of the electronic levels of the central atom (local Stark effect). The crystal field theory studies the influence of the ligand electrostatic field upon the electronic states of the central atom.

The original crystal field theory comprises three simplifications:

1) the ligands are taken as point chatges or electric dipoles;
2) the energy of the interelectron repulsion in the complex is identified with the repulsion energy in a free atom;
3) the radial pasrt of the atomic orbitals is unchanged upon formation of the complex.

The interaction operator of the electrons of the central atom with the corresponding electrostatic ligand field (crystal field) is

$$\hat{V}^{cf} = \sum_i^n \sum_L^N \frac{-eq_L}{4\pi\varepsilon_0 |r_i - R_L|} = \sigma_{SI} \sum_i^n \sum_L^N \frac{q_L^0}{r_{iL}} = \sum_i^n \hat{v}_i \qquad [291]$$

where q_L^0 is the absolute value of the ligand's charge expressed in terms of elementary charge (assuming that the ligands L are negative ions). The basic influence of the ligand upon the electron states of the central atom is the splitting of its terms (removal of degeneracy). For computation of the energy of electronic states the operator $\hat{V}^{cf}$ is to be added to the one-electron part of the electronic Hamiltonian $\hat{H}^{el}$. Computational procedure can be matched according to the relative value of the members $\hat{V}^{cf}$, $\hat{V}_{ee}$ and $\hat{h}^{so}$.

1.6.1 Splitting of d-Levels in the Crystal Field

The pure effect of the crystal field can be studied in a one-electron atom. Let us consider a central atom with one d-electron whose ground electronic state characterizes the orbitally degenerate term ^2D. It is sufficient to index the basis set wave functions with the quantum number m_l of atomic spinorbitals $(-2 \le m_l \le 2)$. When using the degenerate perturbation theory (Section 1.2.2) the contributions to the energy of the term, due to the effect of the crystal field, can be determined from the 5-th order secular equation

$$det\{v_{ij} - \epsilon\delta_{ij}\} = 0 \qquad [292]$$

Matrix elements v_{ij} are defined by the relationship

$$v_{ij} = \langle\psi_i|\hat{V}_1|\psi_j\rangle = \sigma_{SI} \sum_{L}^{N} q_L^0 \langle\psi_i|r_{1L}^{-1}|\psi_j\rangle \qquad [293]$$

for i,j = -2, -1, 0, 1, 2. The operator r_{1L}^{-1} is expanded into the basis set of Legendre polynomials according to the relationship [269]. Thus, the expression

$$v_{ij} = \sum_{L}^{N} q_L^0 \sum_{k=0}^{\infty} F_k(R_L)\, \Theta_{i,j}^k(\vartheta_L,\varphi_L) \qquad [294]$$

is obtained, where the integral composed of the radial parts of spinorbitals is of the form

$$F_k(R_L) = \sigma_{SI} \left\{ \frac{1}{R_L^{k+1}} \int_0^{R_L} r^k [R_{n,2}(r)]^2\, r^2\, dr + \right.$$

$$\left. + R_L^k \int_{R_L}^{\infty} \frac{1}{r^{k+1}} [R_{n,2}(r)]^2\, r^2\, dr \right\} \qquad [295]$$

The function $F_k(R_L)$ should not be misunderstood as the modified Slater-Condon parameters F_k introduced by the relationships [279] - [281].

The integral comprising the angular parts of the orbitals

$$\Theta_{i,j}^k(\vartheta_L,\varphi_L) = \int_0^{\pi}\int_0^{2\pi} Y_{2,i}(\vartheta,\varphi)\, Y_{2,j}(\vartheta,\varphi)\, P_k(cos\gamma_{1L})\, sin\vartheta\, d\vartheta\, d\varphi \qquad [296]$$

can be transformed for d-orbitals into the form

$$\Theta_{i,j}^k(\vartheta_L,\varphi_L) = A_{ij}\, Y_{4,i-j}(\vartheta_L,\varphi_L)\, \delta_{k,4} + B_{ij}\, Y_{2,i-j}(\vartheta_L,\varphi_L)\, \delta_{k,2} +$$

$$+ D_{ij}\, Y_{0,i-j}(\vartheta_L,\varphi_L)\, \delta_{k,0} \qquad [297]$$

where the following coefficients appear

$$A_{ij} = (-1)^j\, 5\sqrt{4\pi}\, C^{224}_{-ji}\, C^{224}_{00}/27 \qquad [298]$$

$$B_{ij} = (-1)^j \sqrt{4\pi}\, C^{222}_{-ji}\, C^{222}_{00}/\sqrt{5} \qquad [299]$$

$$D_{ij} = (-1)^j\, 5\sqrt{4\pi}\, C^{220}_{-ji}\, C^{220}_{00} = \sqrt{4\pi}\, \delta_{ij} \qquad [300]$$

The coefficients A_{ij}, B_{ij} and D_{ij} are defined through the tabulated Clebsch-Gordan coefficients $C^{l_1, l_2, L}_{m, m_1, M_2}$ known from the theory of the addition of angular momenta (see Section 1.3.1); they are listed in Table 18.

TABLE 18
The values of the coefficients A_{ij} and B_{ij} in the matrix elements of the crystal field potential.

	$63/\sqrt{4\pi}\ A_{ij}$					$35/\sqrt{4\pi}\ B_{ij}$				
i j	2	1	0	-1	-2	2	1	0	-1	-2
2	1	$-\sqrt{5}$	$\sqrt{15}$	$-\sqrt{35}$	$\sqrt{70}$	$-\sqrt{20}$	$\sqrt{30}$	$-\sqrt{20}$	0	0
1	$\sqrt{5}$	-4	$\sqrt{30}$	$-\sqrt{40}$	$\sqrt{35}$	$-\sqrt{30}$	$\sqrt{5}$	$\sqrt{5}$	$-\sqrt{30}$	0
0	$\sqrt{15}$	$-\sqrt{30}$	6	$-\sqrt{30}$	$\sqrt{15}$	$-\sqrt{20}$	$-\sqrt{5}$	$\sqrt{20}$	$-\sqrt{5}$	$-\sqrt{20}$
-1	$\sqrt{35}$	$-\sqrt{40}$	$\sqrt{30}$	-4	$\sqrt{5}$	0	$-\sqrt{30}$	$\sqrt{5}$	$\sqrt{5}$	$-\sqrt{30}$
-2	$\sqrt{70}$	$-\sqrt{35}$	$\sqrt{15}$	$-\sqrt{5}$	1	0	0	$-\sqrt{20}$	$\sqrt{30}$	$-\sqrt{20}$

The advantage of the notation [294] rests in the fact that it contains only three non-zero terms for the series k = 0, 2 and 4

$$v_{ij} = \sum_{L}^{N} q_L^0 \,[F_4(R_L)\, Y_{4,i-j}(\vartheta_L,\varphi_L)\, A_{ij} + F_2(R_L)\, Y_{2,i-j}(\vartheta_L,\varphi_L)\, B_{ij} + {}$$
$$+ F_0(R_L)\, Y_{0,i-j}(\vartheta_L,\varphi_L)\, \sqrt{4\pi}\, \delta_{ij}] \qquad [301]$$

Final expressions for the independent part of the v_{ij} matrix elements are listed in Table 19.

The above procedure may be applied also to f-electrons, taking into account L = 3, so that the interaction matrix [293] with v_{ij} elements is of the 7-th order. The integrals [296] comprising the angular part of f-orbitals $\theta^k_{i,j}(\vartheta_L,\varphi_L)$ contain spherical harmonics up to the 6-th order, $Y_{6,i-j}$, and consequently the expansion [294] consists of four non-zero terms (k = 0, 2, 4 and 6). Final expressions for the independent part of the v_{ij} elements are given in Table 20.

TABLE 19

Matrix elements v_{ij} for d-electrons.[a]

$$
\begin{aligned}
\langle 0|\hat{V}|0\rangle &= \sum_L q_L\{F_0 + (1/7)(2\cos^2\vartheta_L - \sin^2\vartheta_L)F_2 + \\
&\quad + (1/28)(35\cos^4\vartheta_L - 30\cos^2\vartheta_L + 3)F_4\} \\
\langle \pm1|\hat{V}|\pm1\rangle &= \sum_L q_L\{F_0 + (1/14)(2\cos^2\vartheta_L - \sin^2\vartheta_L)F_2 + \\
&\quad - (1/42)(35\cos^4\vartheta_L - 30\cos^2\vartheta_L + 3)F_4\} \\
\langle \pm2|\hat{V}|\pm2\rangle &= \sum_L q_L\{F_0 - (1/7)(2\cos^2\vartheta_L - \sin^2\vartheta_L)F_2 + \\
&\quad + (1/168)(35\cos^4\vartheta_L - 30\cos^2\vartheta_L + 3)F_4\} \\
\langle 2|\hat{V}|1\rangle &= \sum_L q_L\{\cos\vartheta_L \sin\vartheta_L \exp(i\varphi_L)[-(3/7)F_2 + \\
&\quad + (5/4\sqrt{7})(7\cos^2\vartheta_L - 3)F_4]\} \\
\langle 2|\hat{V}|0\rangle &= \sum_L q_L\{(1/7\sqrt{6})\sin^2\vartheta_L \exp(2i\varphi_L) \\
&\quad [-3F_2 + (5/4)(7\cos^2\vartheta_L - 1)F_4]\} \\
\langle 2|\hat{V}|-1\rangle &= \sum_L q_L\{(5/12)\sin^3\vartheta_L \cos\vartheta_L \exp(3i\varphi_L)F_4\} \\
\langle 2|\hat{V}|-2\rangle &= \sum_L q_L\{(5/24)\sin^4\vartheta_L \exp(4i\varphi_L)F_4\} \\
\langle 1|\hat{V}|0\rangle &= \sum_L q_L\{(\sqrt{6}/14)\cos\vartheta_L \sin\vartheta_L \exp(i\varphi_L) \\
&\quad [-F_2 - (1/30)(7\cos^2\vartheta_L - 3)F_4]\} \\
\langle 1|\hat{V}|-1\rangle &= \sum_L q_L\{(1/14)\sin^2\vartheta_L \exp(2i\varphi_L) \\
&\quad [-3F_2 - (5/3)(7\cos^2\vartheta_L - 1)F_4]\}
\end{aligned}
$$

[a] $F_n = F_n(R_L)$.

TABLE 20

Matrix elements v_{ij} for f-electrons.[a]

$$
\begin{aligned}
\langle 0|\hat{V}|0\rangle &= \sum_L q_L\{F_0 + (2/15)(3\cos^2\vartheta_L - 1)F_2 + (1/44)(35\cos^4\vartheta_L - \\
&\quad -30\cos^2\vartheta_L + 3)F_4 + (25/1716)(231\cos^6\vartheta_L - 315\cos^4\vartheta_L - \\
&\quad +105\cos^2\vartheta_L - 5)F_6\} \\
\langle \pm1|\hat{V}|\pm1\rangle &= \sum_L q_L\{F_0 + (1/10)(3\cos^2\vartheta_L - 1)F_2 + (1/264)(35\cos^4\vartheta_L - \\
&\quad -30\cos^2\vartheta_L + 3)F_4 - (25/2288)(231\cos^6\vartheta_{,} - 315\cos^4\vartheta_L + \\
&\quad +105\cos^2\vartheta_L - 5)F_6\}
\end{aligned}
$$

TABLE 20 (Continued)

$$\begin{aligned}
<\pm2|\hat{V}|\pm2> &= \sum_L q_L\{F_0-(7/264)(35\cos^4\vartheta_L-30\cos^2\vartheta_L+3)F_4+(5/1144)\cdot\\
&\quad\cdot(231\cos^6\vartheta_L-315\cos^4\vartheta_L+105\cos^2\vartheta_L-5)F_6\}
\end{aligned}$$

$$\begin{aligned}
<\pm3|\hat{V}|\pm3> &= \sum_L q_L\{F_0-(1/6)(3\cos^2\vartheta_L-1)F_2+(1/88)(35\cos^4\vartheta_L-\\
&\quad-30\cos^2\vartheta_L+3)F_4-(5/6864)(231\cos^6\vartheta_L-315\cos^4\vartheta_L+\\
&\quad+105\cos^2\vartheta_L-5)F_6\}
\end{aligned}$$

$$\begin{aligned}
<3|\hat{V}|2> &= \sum_L q_L(1/\sqrt{6})\exp(-i\varphi_L)\sin\vartheta_L\cos\vartheta_L\{-F_2+(5/22)(7\cos\ \vartheta_L^2-\\
&\quad-3)F_4-(35/1144)(33\cos^4\vartheta_L-30\cos^2\vartheta_L+5)F_6\}
\end{aligned}$$

$$\begin{aligned}
<3|\hat{V}|1> &= \sum_L q_L(\sqrt{15}/2)\exp(-2i\varphi_L)\sin^2\vartheta_L\{-(1/15)F_2+(1/22)\cdot\\
&\quad\cdot(7\cos^2\vartheta_L-1)F_4-(35/3432)(33\cos^4\vartheta_L-18\cos^2\vartheta_L+1)F_6\}
\end{aligned}$$

$$\begin{aligned}
<3|\hat{V}|0> &= \sum_L q_L(7\sqrt{5}/44)\exp(-3i\varphi_L)\sin^3\vartheta_L\cos\vartheta_L\{F_4-(5/26)\cdot\\
&\quad\cdot(11\cos^2\vartheta_L-3)F_6\}
\end{aligned}$$

$$\begin{aligned}
<3|\hat{V}|-1> &= \sum_L q_L(7\sqrt{15}/88)\exp(-4i\varphi_L)\sin^4\vartheta_L\{(1/3)F_4-(5/26)\cdot\\
&\quad\cdot(11\cos^2\vartheta_L-1)F_6\}
\end{aligned}$$

$$<3|\hat{V}|-2> = \sum_L q_L(385\sqrt{6}/2288)\exp(-5i\vartheta_L)\sin^5\vartheta_L\cos\vartheta_L F_6$$

$$<3|\hat{V}|-3> = \sum_L q_L\{-(385\sqrt{6}/2288)\exp(-5i\varphi_L)\sin^5\vartheta_L\cos\vartheta_L F_6\}$$

$$\begin{aligned}
<2|\hat{V}|-2> &= \sum_L q_L(35/88)\exp(-4i\varphi_L)\sin^4\vartheta_L\{(1/3)F_4+(3/13)\cdot\\
&\quad\cdot(11\cos^2\vartheta_L-1)F_6\}
\end{aligned}$$

$$\begin{aligned}
<1|\hat{V}|-1> &= -\sum_L q_L\exp(-2i\varphi_L)\sin^2\vartheta_L\{(1/5)F_2+(5/66)(7\cos^2\vartheta_L-1)\cdot\\
&\quad\cdot F_4+(175/2288)(33\cos^4\vartheta_L-18\cos^2\vartheta_L+1)F_6\}
\end{aligned}$$

$$\begin{aligned}
<1|\hat{V}|0> &= -\sum_L q_L\sqrt{3}\exp(-i\varphi_L)\sin\vartheta_L\cos\vartheta_L\{(1/15)F_2+(5/132)\cdot\\
&\quad\cdot(7\cos^2\vartheta_L-3)F_4+(175/3432)(33\cos^4\vartheta_L-30\cos^2\vartheta_L+5)F_6\}
\end{aligned}$$

$$\begin{aligned}
<2|\hat{V}|1> &= \sum_L q_L\sqrt{10}\exp(-i\varphi_L)\sin\vartheta_L\cos\vartheta_L\{(-1/10)F_2-(1/33)\cdot\\
&\quad\cdot(7\cos^2\vartheta_L-3)F_4+(35/2288)(33\cos^4\vartheta_L-30\cos^2\vartheta_L+5)F_6\}
\end{aligned}$$

$$\begin{aligned}
<2|\hat{V}|0> &= \sum_L q_L\sqrt{30}/6)\exp(-i\varphi_L)\sin^2\vartheta_L\{-(1/5)F_2-(1/44)\cdot\\
&\quad\cdot(7\cos^2\vartheta_L-1)F_4+(35/572)(33\cos^4\vartheta_L-18\cos^2\vartheta_L+1)F_6\}
\end{aligned}$$

$$\begin{aligned}
<2|\hat{V}|-1> &= \sum_L q_L(7\sqrt{10}/44)\exp(-3i\varphi_L)\sin^3\vartheta_L\cos\vartheta_L\{(1/3)F_4+\\
&\quad+(15/52)(11\cos^2\vartheta_L-3)F_6\}
\end{aligned}$$

---

[a] $F_n = F_n(R_L)$.

As an example we calculate the splitting of the ^2D term of the electron configuration d^1 for the central atom in an octahedral field. Using the polar coordinates for individual ligands, according to Figs. 1 and 2 of Appendix 2, then

$$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R \qquad [302]$$

$$\vartheta_1 = \vartheta_2 = \vartheta_3 = \vartheta_4 = \pi/2, \; \vartheta_5 = \vartheta_6 = \pi \qquad [303]$$

$$\varphi_1 = 0, \; \varphi_2 = \pi/2, \; \varphi_3 = \pi, \; \varphi_4 = 3\pi/2 \qquad [304]$$

$$v_{2,2} = v_{-2,-2} = q[6F_0(R) + F_4(R)/6] \qquad [305]$$

$$v_{1,1} = v_{-1,-1} = q[6F_0(R) - 2F_4(R)/3] \qquad [306]$$

$$v_{0,0} = q[6F_0(R) + F_4(R)] \qquad [307]$$

$$v_{2,-2} = v_{-2,2} = 5qF_4(R)/6 \qquad [308]$$

After introduction of the substitutions

$$E_0 = 6qF_0(R) \qquad [309]$$

$$\Delta = 5qF_4(R)/3 \qquad [310]$$

the matrix of the integrals v_{ij} can be expressed

$$v = E_0 I + \frac{\Delta}{10} \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad [311]$$

By solving the secular equation [292] we arrive at the roots

$$\epsilon_{1,2,3} = E_0 - (4/10)\Delta = q[6F_0(R) - 2F_4(R)/3] = \epsilon(T_{2g}) \qquad [312]$$

$$\epsilon_{4,5} = E_0 + (6/10)\Delta = q[6F_0(R) + F_4(R)] = \epsilon(E_g) \qquad [313]$$

with the corresponding wave functions for the triply degenerate term T_{2g}

$$\Psi_1 = -i(d_2 - d_{-2})/\sqrt{2} = d_{xy} \qquad [314]$$

$$\Psi_2 = -(d_1 - d_{-1})/\sqrt{2} = d_{xz} \qquad [315]$$

$$\Psi_3 = i(d_1 + d_{-1})/\sqrt{2} = d_{yz} \qquad [316]$$

while those of the double degenerate term E_g are

$$\Psi_4 = d_0 = d_{z^2} \qquad [317]$$

$$\Psi_5 = (d_2 + d_{-2})/\sqrt{2} = d_{x^2-y^2} \qquad [318]$$

The energy difference is

$$\epsilon(E_g) - \epsilon(T_{2g}) = \Delta = 10Dq \qquad [319]$$

The strength of the crystal field is expressed through the parameter Δ (or 10Dq) (Fig. 4).

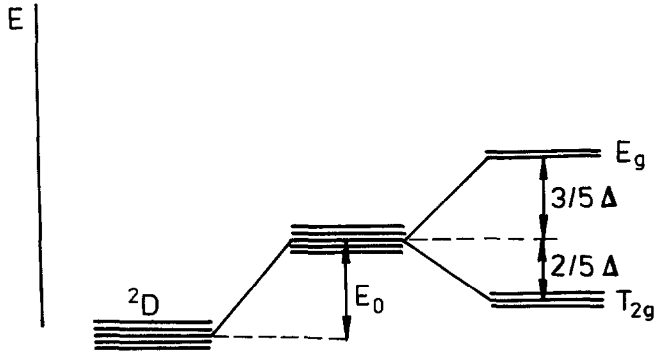

Fig. 4. The splitting of atomic term ^2D in the octahedral ligand field.

In an analogous way the energies of terms with complexes of other symmetries can be expressed (Table 21).

1.6.2 Weak Crystal Field

For electron configurations with more than one d-electrons the scheme for the possible terms and splittings in the ligand field is more complicated due to the interelectronic repulsion. If the influence of the ligand field is much weaker than the interelectronic repulsion ($\hat{V}_{ee} > \hat{V}^{cf} > \hat{h}^{so}$), then the atomic terms can be classified according to the quantum number L and the effect of the crystal field $\hat{V}^{cf}$ can be determined as a perturbation with the use of degenerate perturbation theory. The ground electronic state in the weak crystal field model will be the term of the maximum spin multiplicity (high-spin complexes).

For quantitative computations it is important to determine the matrix elements of the operator $\hat{V}^{cf}$ in the basis set of the wave functions $\Psi(L,M_L,S,M_S)$ of the corresponding atomic term. Since it is satisfactory that the operator $\hat{V}^{cf}$ does not operate over spin variables, then the wave functions of the above term differ in the index M_L. Then the respective matrix elements are first expressed through the determinantal functions $\Phi(M_L,M_S)$

$$V_{M_L,M'_L} = <\Psi(L,M_L,S,M_S|\hat{V}^{cf}|\Psi(L',M'_L,S',M'_S> =$$

$$= \sum_{i,j} c_i\ c_j\ <\Phi_i(M_L,M_S)|\hat{V}^{cf}|\Phi_j(M'_L,M'_S)> \qquad [320]$$

TABLE 21

Energies of the d-level splitting in various fields.

System	Symmetry	N	Energy
MX_6	O_h	6	$\varepsilon(T_{2g}) = q[F_0(R) - (2/3)F_4(R)] =$
			$= E_0 - (2/5)\Delta$
			$\varepsilon(E_g) = q[F_0(R) + F_4(R)] = E_0 + (3/5)\Delta$
			$E_0 = 6qF_0(R)$
			$\Delta = (5/3)qF_4(R)$
MX_4	T_d	4	$\varepsilon(E) = q[4F_0(R) - (4/9)F_4(R)] =$
			$= E_0 - (3/5)\Delta$
			$\varepsilon(T_2) = q[4F_0(R) + (8/27)F_4(R)] =$
			$= E_0 + (2/5)\Delta$
			$E_0 = 4qF_0(R)$
			$\Delta = (20/27)qF_4(R)$
MX_4Y_2	D_{4h}	6	$\varepsilon(E_g) = E_0 - (2/5)\Delta - D_s + 4D_t$
			$\varepsilon(B_{2g}) = E_0 - (2/5)\Delta + 2D_s - D_t$
			$\varepsilon(A_{1g}) = E_0 + (3/5)\Delta - 2D_s - 6D_t$
			$\varepsilon(B_{1g}) = E_0 + (3/5)\Delta + 2D_s - D_t$
			$E_0 = q[4F_0(R_X) + 2F_0(R_Y)]$
			$\Delta = (5/3)qF_4(R_X)$
			$D_s = (2/7)q[F_2(R_X) - F_2(R_Y)]$
			$D_t = (2/21)q[F_4(R_X) - F_4(R_Y)]$
MX_4	D_{4h}	4	$\varepsilon(E_g) = E_0 - (6/35)\Delta - D_s$
			$\varepsilon(B_{2g}) = E_0 - (16/35)\Delta + 2D_s$
			$\varepsilon(A_{1g}) = E_0 + (9/35)\Delta - 2D_s$
			$\varepsilon(B_{1g}) = E_0 + (19/35)\Delta + 2D_s$
			$E_0 = 4qF_0(R)$
			$\Delta = (5/3)qF_4(R)$
			$D_s = (2/7)qF_2(R)$

The matrix elements between determinantal functions can be evaluated with the use of Slater rules (see Chapter 4) according to which for identical determinantal functions $\Phi_A(\psi_1,\psi_2,\ldots,\psi_n)$ created from the spinorbitals ψ_k

$$\langle\Phi_A|\hat{V}^{cf}|\Phi_A\rangle = \sum_k \langle\psi_k|\hat{V}^{cf}|\psi_k\rangle \qquad [321]$$

For the determinants $\Phi_A(\psi_1,\ldots,\psi_k,\ldots,\psi_n)$ and $\Phi_B(\psi_1,\ldots,\psi_{k'},\ldots,\psi_n)$ differing only by a single spinorbital then

$$\langle\Phi_A|\hat{V}^{cf}|\Phi_B\rangle = (-1)^p \langle\psi_k|\hat{V}^{cf}|\psi_{k'}\rangle \qquad [322]$$

where p is the number of transpositions in the spinorbitals yielding the maximum coincidence in the spinorbital arrangement. The other cases yield zero matrix elements for the one-electron operator $\hat{V}^{cf}$.

As an example, let us evaluate the effect of the crystal field upon the splitting of the ^3F term of the d^2 electron configuration. The necessary expressions for the wave functions $\Psi(3,M_L,1,1)$ can be evaluated, for example, as follows

$$\begin{aligned} V_{1,3} &= \langle\Psi(3,1,1,1)|\hat{V}^{cf}|\Psi(3,3,1,1)\rangle = \sqrt{3}\,\langle\Phi_{12}|\hat{V}^{cf}|\Phi_2\rangle/\sqrt{5} + \\ &+ \sqrt{2}\,\langle\Phi_{11}|\hat{V}^{cf}|\Phi_2\rangle/\sqrt{5} = \sqrt{3}\,\langle\Phi(2^+;-1^+)|\hat{V}^{cf}|\Phi(2^+;1^+\rangle/\sqrt{5} + \\ &+ \sqrt{2}\,\langle\Phi(1^+;0^+|\hat{V}^{cf}|\Phi(2^+;1^+)\rangle/\sqrt{5} = \\ &= \sqrt{3}\,v_{-1,1}/\sqrt{5} + \sqrt{2}\,(-1)^1 v_{0,2}/\sqrt{5} \end{aligned} \qquad [323]$$

using also the expressions for determinantal functions according to Table 12. As the ^3F term shows 7-times degeneracy, the 7-th order secular equation can be compiled as follows from degenerate perturbation theory

$$det\{V_{M_L,M_L'} - \epsilon\delta_{M_L,M_L'}\} = 0 \qquad \text{for} \quad M_L,M_L' \in \langle -3;3\rangle \qquad [324]$$

In the case of an octahedral crystal field the corresponding matrix V assumes the form

$$V = \begin{pmatrix} V_{3,3} & 0 & 0 & 0 & V_{-3,1} & 0 & 0 \\ 0 & V_{2,2} & 0 & 0 & 0 & V_{-2,2} & 0 \\ 0 & 0 & V_{1,1} & 0 & 0 & 0 & V_{-3,1} \\ 0 & 0 & 0 & V_{0,0} & 0 & 0 & 0 \\ V_{-3,1} & 0 & 0 & 0 & V_{1,1} & 0 & 0 \\ 0 & V_{-2,2} & 0 & 0 & 0 & V_{2,2} & 0 \\ 0 & 0 & V_{-3,1} & 0 & 0 & 0 & V_{3,3} \end{pmatrix} =$$

$$= 2E_0 I + \frac{\Delta}{10} \begin{pmatrix} -3 & 0 & 0 & 0 & \sqrt{15} & 0 & 0 \\ 0 & 7 & 0 & 0 & 0 & -5 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & \sqrt{15} \\ 0 & 0 & 0 & -6 & 0 & 0 & 0 \\ \sqrt{15} & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & -5 & 0 & 0 & 0 & 7 & 0 \\ 0 & 0 & \sqrt{15} & 0 & 0 & 0 & -3 \end{pmatrix} \qquad [325]$$

The solution of the secular equation [324] results in the roots

$$\epsilon_1 = V_{0,0} \qquad [326]$$

$$\epsilon_{2,3} = V_{2,2} \pm V_{-2,2} \qquad [327]$$

$$\epsilon_{4,5,6,7} = \left[(V_{1,1} + V_{3,3}) \pm \sqrt{(V_{1,1} - V_{3,3})^2 + 4(V_{-3,1})^2}\right]/2 \qquad [328]$$

The energy of the ^3F term in octahedral ligand field can be obtained in the form

$$\epsilon_3(^3A_{2g}) = 2E_0 + 6\Delta/5 = q\,[12F_0(R) + 2F_4(R)] \qquad [329]$$

$$\epsilon_{2,4,5}(^3T_{2g}) = 2E_0 + \Delta/5 = q\,[12F_0(R) + F_4(R)/3] \qquad [330]$$

$$\epsilon_{1,6,7}(^3T_{1g}) = 2E_0 - 3\Delta/5 = q\,[12F_0(R) - F_4(R)] \qquad [331]$$

where the substitutions [309] and [310] have been used. Thus, the atomic term ^3F is split into three terms due to the effect of an octahedral crystal field; $^3T_{1g}$ is the ground state.

Similarly, the splitting of the other d^2 configuration terms, in an octahedral crystal field, can be expressed as

- ^1D term: $\epsilon_{1,2}(^1E_g) = 2E_0 + 12\Delta/35$ [332]

  $\epsilon_{3,4,5}(^1T_{2g}) = 2E_0 - 8\Delta/35$ [333]

- ^3P term: $\epsilon_{1,2,3}(^3T_{1g}) = 2E_0$ [334]

- ^1G term: $\epsilon_1(^1A_{1g}) = 2E_0 + 2\Delta/5$ [335]

  $\epsilon_{2,3}(^1E_g) = 2E_0 + 2\Delta/35$ [336]

  $\epsilon_{4,5,6}(^1T_{1g}) = 2E_0 + \Delta/5$ [337]

  $\epsilon_{7,8,9}(^1T_{2g}) = 2E_0 - 13\Delta/35$ [338]

- ^1S term: $\epsilon_1(\ A_{1g}) = 2E_0 - 13\Delta/35$ [339]

The splitting of individual terms is a linear function of the crystal field strength parameter Δ. When Δ is higher, the terms of a different slope may cross and then the weak crystal field model is applicable no more.

In practice, the configurations d^n and d^{10-n} have mutually inverse term splitting diagrams. In case of weak crystal field, this rule is also valid for configurations d^n and d^{5-n}. For example, the ground state ^4F of the d^3 configuration also has three components, similarly to the state ^3F of the d^2 configuration. These components, however, are arranged in reverse order $\epsilon(^4A_{2g}) < \epsilon(^4T_{2g}) < \epsilon(^4T_{1g})$.

1.6.3 Strong Crystal Field

In the opposite limit when the ligand influence upon the central atom state is strong, prevailing over the interelectronic repulsion($\hat{V}^{cf}>\hat{V}_{ee}>\hat{h}^{so}$),the atomic states characterized by the quantum number L are losing their significance. We speak about removal of the orbital coupling among the electrons. In this case, every atom is influenced by the crystal field more than by other electrons of the central atom.

In the strong crystal field model, the energies of the d-electrons in the crystal field are first calculated, while inter-electron repulsion is incorporated afterwards into computation of the electronic states.

The respective computational procedure will be demonstrated on the electron configuration d^2. In an octahedral crystal field, the atomic d-orbitals are split into two energy levels $t_{2g}(d_{xy},d_{xz},d_{yz})$ and $e_g(d_{z^2},d_{x^2-y^2})$. For two d-electrons the electron configurations $(t_{2g})^2$, $(t_{2g})^1(e_g)^1$ and $(e_g)^2$ can be formed. The respective symmetrized wave functions can be obtained as a result of action of the symmetrization operator (see Section 1.3.1) upon the determinantal wave functions of the singlet $^1\Phi$ and and triplet $^3\Phi$ states. These atomic terms are further split due to the interelectronic repulsion. The splitting energy is obtained by evaluating the matrix elements of the operator $\hat{V}_{ee}$ in the basis set of symmetrized term functions.

For example, for the electron repulsion contribution to the energy of the term $^3A_{2g}$ of the electron configuration $(e_g)^2$

$$\begin{aligned}
E(^3A_{2g}) &= \langle e_g^2, {}^3A_{2g}|\hat{V}_{ee}|e_g^2, {}^3A_{2g}\rangle = \\
&= \langle\Phi(d^+_{z^2},d^+_{x^2-y^2})|\hat{V}_{ee}|\Phi(d^+_{z^2},d^+_{x^2-y^2})\rangle = \\
&= \langle d_{z^2},d_{x^2-y^2}|\hat{g}|d_{z^2},d_{x^2-y^2}\rangle - \langle d_{z^2},d_{x^2-y^2}|\hat{g}|d_{x^2-y^2},d_{z^2}\rangle = \\
&= \langle d_0d_2|\hat{g}|d_0d_2\rangle + \langle d_0d_2|\hat{g}|d_0d_{-2}\rangle + \langle d_0d_{-2}|\hat{g}|d_0d_2\rangle + \\
&+ \langle d_0d_{-2}|\hat{g}|d_0d_{-2}\rangle - \langle d_0d_2|\hat{g}|d_2d_0\rangle - \langle d_0d_2|\hat{g}|d_{-2}d_0\rangle - \\
&- \langle d_0d_{-2}|\hat{g}|d_2d_0\rangle - \langle d_0d_{-2}|\hat{g}|d_{-2}d_0\rangle = \\
&= F_0 - 8F_2 - 9F_4 = A - 8B \qquad [340]
\end{aligned}$$

Here Slater rules (see Chapter 4) were used for the calculation of the matrix elements of the two-electron operator $\hat{V}_{ee}$ between determinantal functions as well as the decomposition of one-electron wave functions $d_{z^2} = d_0$ and $d_{x^2-y^2} = (d_2 + d_{-2})/\sqrt{2}$ through atomic orbitals. Similarly, the splitting for the other terms can be evaluated (Table 22).

TABLE 22
Energies of the d^2-configuration terms at the strong crystal field.

Configuration	Crystal field splitting	Term	Electron repulsion splitting
$(t_{2g})^2$	$2E_0 - (4/5)\Delta$	$^3T_{1g}$	A - 5B
		$^1A_{1g}$	A + 10B + 5C
		^1E_g	A + B + 2C
		$^1T_{2g}$	A + B + 2C
$(t_{2g})^1(e_g)^1$	$2E_0 + (1/5)\Delta$	$^3T_{2g}$	A - 8B
		$^3T_{1g}$	A + 4B
		$^1T_{2g}$	A + 2C
		$^1T_{1g}$	A + 4B + 2C
$(e_g)^2$	$2E_0 + (6/5)\Delta$	$^3A_{2g}$	A - 8B
		$^1A_{1g}$	A + 8B + 4C
		^1E_g	A + 2C

The strong crystal field model requires that the splitting due to interelectronic repulsion is much lower than the energy difference between individual configurations. For example, for the $E(^3T_{2g}) = 15B + 5C \ll \Delta$. In the opposite case, the $^3T_{1g}$ term of the $(t_{2g})^2$ configuration interacts strongly with the $^3T_{1g}$ term of the $(t_{2g})^1(e_g)^1$ configuration and thus the strong crystal field approximation cannot be used.

1.6.4 Improvements and Limits of the Crystal Field Theory

Intermediate Crystal Field.

As a consequence of the predominance of various types of interactions, ground states in the strong field can differ from those in the weak one. For example, for the d^6 configuration, in the weak field the ground state is $^5T_{2g}:(t_{2g})^4(e_g)^2$, while in the strong field the ground state is $^1A_{1g}:(t_{2g})^6$. Symmetry requirements, however, lead to the conclusion that both the number and the type of the states in these cases must be equal and that there must exist a continuous transition from one to another.

If for a d^n configuration in a field of a given symmetry a state ${}^{2S+1}\Gamma_i$ only appears once, its energy and wave function are equal in the weak and strong field. If, however, for the configuration under study, several states of the same symmetry and multiplicity originate, their mutual interaction must be taken into account via a configuration interaction (see Chapter 4). If, in the system, there exist two states ${}^{2S+1}\Gamma_i$ approaching each other with increasing field strength, they might to cross each orher; then as a consequence, the configuration interaction brings about 'repulsion' of these states (no crossover occurs). Configuration interaction may be derived using the strong crystal field wave functions as used by Tanabe and Sugano or from weak crystal field functions as in the procedure of Orgel. It is obvious, that when configuration interaction is included among all terms of the given multiplicity and symmetry, then in both cases we arrive at an equal result.

Spin-Orbit Coupling.

As a consequence of the interaction between electron spins and their angular momenta the spin degeneracy of the state uder study usually is decreased. This degeneracy, however, is not completely removed in the case of an odd number of electrons, for which there exists at least a two-fold spin degeneracy (Kramer's theorem). The spin-orbit interaction contributes to Hamiltonian with the term

$$\hat{h}^{so} = \xi_{n,d} \sum_i \hat{l}'_i \cdot \hat{s}_i \qquad [341]$$

where $\hat{l}'_i$ is the quantity analogous to the orbital angular momentum $\hat{l}_i$ in a free atom (with spherically symmetric potential). Here we assume that the effect of deviation from spherical symmetry can be included in the parameter $\xi_{n,d}$. Similarly, it can be written

$$\hat{h}^{so} = \lambda \hat{L}'.\hat{S} \qquad [342]$$

where for λ

$$\lambda = \frac{1}{M_L M_s} \sum_i \xi_{n,d}\, m_{li} m_{si} \qquad [343]$$

The spin-orbit interaction energy is then proportional to expressions of the type

$$h_{ab} = \langle\Psi_a|\hat{h}^{so}|\Psi_b\rangle \qquad [344]$$

which can be decomposed into the product of orbital and spin component. Since the components of the vector $\hat{s}_i$ in an octahedral group transform as the irreducible representation T_{1g}, then the component of the vector $\hat{l}'_i$ must be transformed in the same way since the operator $\hat{h}^{so}$ is a fully symmetric operator (see Section 1.3.1). Thus the orbital part of the integral [344] is equal to zero, if the direct product of representations $\Gamma_a \otimes \Gamma_b$ does not contain the representation T_{1g}.

Important conclusions follow from the above requirement: in the field of octahedral symmetry, spin-orbit interaction cannot cause splitting and energy changes in the states A_{1g}, E_g and A_{2g}. However, the states T_{1g} and T_{2g} can be split through the spin-orbit coupling. Mixing of states differing in multiplicity occurs only when they differ in spin quantum number S by the value of $\Delta S = \pm 1$ (only then the spin part of the integral [344] is non-zero).

The influence of the electrostatic field upon the spin-orbit interaction is formally manifest only in the changed selection rules for non-zero matrix elements of the operator $\hat{h}^{so}$ if the parameter $\xi_{n,d}$ is not evaluated theoretically but obtained from experimental data. Though this leads to the inclusion of the anisotropy of the electrostatic field into the parameter $\xi_{n,d}$. This procedure, however, is not fully reasonable since the electrostatic field contributes to the perturbation operator by the term

$$\lambda' = \sum_i \xi_{n,d} \hat{l}'_i \cdot \hat{s}_i \qquad [345]$$

Thus the raison d'etre for the commonly used procedure to evaluate the spin-orbit interaction decreases with increasing crystal field strength as well as with the elements of the second and third transition metal series.

f-Electrons.

Fundamental specific features of the term splitting of the f-electrons includes the considerable screening of these electrons by by external s, p and d electrons, and therefore exerts the crystal field less influence upon these electrons. Thus with f-electrons the weak crystal field is usually applied when its influence is less than the interelectronic repulsion as well as the spin-orbit interaction. In this case it is necessary to start with the free ion state considering both interelectronic repulsion as well as the spin-orbit interaction which splits states of definite L and S according to the value of the quantum number J.

For example for one f-electron ($L = 3$, $S = 1/2$), including the spin-orbit interaction, two states $^2F_{5/2}$ and $^2F_{7/2}$ are obtained in which, within the framework of the given approximation, the crystal field effect can be separately considered.

Applicability.

Crystal field theory is based upon the idea of electrostatic nature of ligand influence through point charges or dipoles. Such an idea idea automatically excludes the possibility of studying all the phenomena dependent on the electronic structure of ligands, as as well as the nature of the central atom - ligand interaction including the π-bond formation and the chelate effect.

The theory explains just the properties of coordination compounds which are based on the electronic structure of the central atom under the influence of the ligands. These properties include the electron absorption spectra in both the visible and UV region (d-d and f-f transitions), as well as magnetic susceptibility, ESR spectra (excluding hyperfine structure), the effects of internal assymetry, stability in solution and so on.

1.7 EMPIRICAL MODELS

1.7.1 Ligand Field Theory

In crystal field theory the overlap integral between the central atom and ligand orbitals is neglected. The more elaborate concepts, abbreviated as ligand field theory (LFT), account for these effects (81). The characteristic feature of the LFT approach is that a basis set of symmetrized functions (group orbitals) is considered; these orbitals correspond to individual irreducible representations γ of the molecular point group of symmetry. The molecular orbitals can then be written in the form of a linear combination of central atom orbitals χ_γ^M and ligand group orbitals

$$\phi_\gamma = a_M \chi_\gamma^M + a_L \vartheta_\gamma^L = N(\chi_\gamma^M + \lambda \sum_i^L \sum_\mu c_{i\mu}^\gamma A_\mu^i) \qquad [346]$$

The coefficients $c_{i\mu}^\gamma$ forming the group orbitals may be evaluated using group theory. The basis set on the central atom is usually restricted to the valence d-orbitals but sometimes the ns- or np-orbitals are also included in the basis set. Ligands are characterized only by donor atom ns-orbitals and np-orbitals and eventually by hybrid atomic orbitals. The symmetry orbitals [346] obey the secular equation

$$det \begin{pmatrix} H_{MM} - \epsilon_\gamma; & H_{ML} - \epsilon_\gamma G_{ML} \\ H_{ML} - \epsilon_\gamma G_{ML}; & H_{LL} - \epsilon_\gamma \end{pmatrix} = 0 \qquad [347]$$

where $H_{MM} = \langle\chi_\gamma^M|\hat{H}|\chi_\gamma^M\rangle$ and analogously H_{ML} and H_{LL} are the matrix elements of the one-electron effective Hamiltonian; $G_{ML} = \langle\chi_\gamma^M|\chi_\gamma^L\rangle$ is the group overlap integral. Although this equation can be exactly solved, we will apply an approximate solution leading to the pseudopotential approach in the subspace of the central atom orbitals.

A strongly polar bond is formed through coordination of a ligand to the central atom. In other words, the diagonal matrix elements H_{MM} and H_{LL} differ substantially so that the eigenvalues ϵ_γ will be predominantly determined by values of the diagonal elements. Where $H_{LL} \approx \epsilon_\gamma$ we arrive at the approximate solution of [347] in the form

$$\epsilon_\gamma = H_{LL} - (H_{ML} - H_{LL}\, G_{ML})^2/(H_{MM} - H_{LL}) \qquad [348]$$

which corresponds to the energy of the bonding orbital

$$\phi_\gamma \approx \vartheta_\gamma^L \qquad [349]$$

Analogously, where $H_{MM} \approx \epsilon_\gamma$ we obtain

$$\epsilon_\gamma^* = H_{MM} + (H_{ML} - H_{MM}\, G_{ML})^2/(H_{MM} - H_{LL}) \qquad [350]$$

and the corresponding antibonding orbital is

$$\phi_\gamma^* = (1 - G_{ML}^2)^{-1/2}(\chi_\gamma^M - G_{ML}\, \vartheta_\gamma^L) \qquad [351]$$

With the assumption that the ϕ_γ and ϕ_γ^* orbitals represent in a good approximation the Hartree-Fock functions, the following relationships are fulfilled

$$\hat{F}\, |\phi_\gamma^*\rangle = \epsilon_\gamma^*\, |\phi_\gamma^*\rangle \qquad [352]$$

$$\hat{F}\, |\phi_\gamma\rangle = \epsilon_\gamma\, |\phi_\gamma\rangle \qquad [353]$$

Substituting [351] into [352] and using [353] we obtain

$$\hat{F}\, |\chi_\gamma^M\rangle + (\epsilon_\gamma^* - \epsilon_\gamma)G_{ML}\, |\chi_\gamma^L\rangle = \epsilon_\gamma^*\, |\chi_\gamma^M\rangle \qquad [354]$$

which can be rewritten into the characteristic form

$$(\hat{F} + \hat{V}^{lf})\, |\chi_\gamma^M\rangle = \epsilon_\gamma^*\, |\chi_\gamma^M\rangle \qquad [355]$$

where the following pseudopotential has been introduced (82,83)

$$\hat{V}^{lf}\, \chi_\gamma^M(1) = (\epsilon_\gamma^* - \epsilon_\gamma)\int [\chi_\gamma^M(2)]^*\, \vartheta_\gamma^L(2)\, dV_2\, \vartheta_\gamma^L(1) \qquad [356]$$

The pseudopotential $\hat{V}^{lf}$ is a totally symmetric operator and plays a similar role to the $\hat{V}^{cf}$ potential in crystal field theory.

The application of ligand field theory is exemplified using an octahedral complex with a d-orbital basis set classified according to the irreducible representations: e_g (shortly e) and t_{2g} (shortly t). The equation [354] implies

$$\varepsilon_e^* = \langle d_e^M|\hat{F}|d_e^M\rangle + G_e^2(\varepsilon_e^* - \varepsilon_e) \qquad [357]$$

$$\varepsilon_t^* = \langle d_t^M|\hat{F}|d_t^M\rangle + G_t^2(\varepsilon_t^* - \varepsilon_t) \qquad [358]$$

We can take into account the form of the Fock operator diagonal matrix elements

$$F_{ii} = U_i^M + \sum_j (J_{ij} - K_{ij}) - \sigma_{SI} \sum_L Z_L^C/r_{L1} \qquad [359]$$

where the last term represents the crystal field potential $\hat{V}^{cf}$. Then an approximate formula is obtained

$$\Delta\varepsilon = \varepsilon_e^* - \varepsilon_t^* = \langle d_e^M|\hat{V}|d_e^M\rangle - \langle d_t^M|\hat{V}|d_t^M\rangle + G_e^2(\varepsilon_e^* - \varepsilon_e) - G_t^2(\varepsilon_t^* - \varepsilon_t) =$$

$$= 10Dq + \varepsilon_{ML}^0(G_e^2 - G_t^2) \qquad [360]$$

where we assume that $\varepsilon_e^* - \varepsilon_e \approx \varepsilon_t^* - \varepsilon_t = \varepsilon_{ML}^0$. For small values of the overlap integrals (low degree of covalency) the orbitals responsible for low energy electronic transitions, ϕ_γ^*, are practically pure atomic d-orbitals. In this limit the picture of crystal field theory is obtained. An important conclusion follows from equation [360]: the splitting of the d-levels by the crystal field (Δ = 10Dq) is not given by a simple difference in orbital energies $\Delta\varepsilon$. This result is often ignored in comparison of SCF results with parameters obtained by crystal field theory.

The equation [360] may be modified by expressing the group overlap integrals through common diatomic overlap integrals $G_e^2 = 3S^2(\sigma,d_\sigma)$ and $G_t^2 = 4S^2(\pi,d_\pi)$ so that

$$\Delta\varepsilon = 10Dq + \varepsilon_{ML}^0[3S^2(\sigma,d_\sigma) - 4S^2(\pi,d_\pi)] \qquad [361]$$

In the majority of complexes the σ overlap integrals are greater than those of the π type, so that the correction to the 10Dq value by the ligand field positive.

A more detailed analysis of the secular equation [347] leads to the following observation. When using the Wolfsberg-Helmholtz approximation for the off-diagonal matrix elements

$$H_{ML} = (1/2)\ K\ (H_{MM} + H_{LL})\ G_{ML} \qquad [362]$$

the solutions of [348] and [350] are obtained in the form of

$$\varepsilon_\gamma = H_{LL} - G_{ML}^2\ H_{MM}^2\ /(H_{MM} - H_{LL}) \qquad [363]$$

$$\varepsilon_\gamma^* = H_{MM} - G_{ML}^2\ H_{LL}^2\ /(H_{MM} - H_{LL}) \qquad [364]$$

where K = 2.0 has been used. The energy shift (increase) of the central atom orbitals $\Delta E_M^* = \varepsilon_\gamma - H_{MM}$ as well as that (decrease) of the orbitals $\Delta E_L = \varepsilon_\gamma - H_{LL}$ is proportional to the square of the group overlap integral G_{ML}^2. On the other hand, solution of the secular equation [347] yields the condition

$$\epsilon_\gamma + \epsilon_\gamma^* = (H_{MM} + H_{LL} - 2H_{ML}G_{ML})/(1 - G_{ML}^2)$$

$$= (H_{MM} + H_{LL})(1 - K\,G_{ML}^2)/(1 - G_{ML}^2) \qquad [365]$$

According to the matrix trace, it is also valid that

$$\epsilon_\gamma + \epsilon_\gamma^* = H_{MM} + H_{LL} \qquad [366]$$

This condition is fulfilled only if the Wolfsberg-Helmholtz constant, K = 1. If K ranges between 1 and 2, the sum $\epsilon_\gamma + \epsilon_\gamma^*$ is less negative than $H_{MM} + H_{LL}$ by an increment depending on the overlap integrals. Then the decrease in energy of the bonding orbitals is lower than the increase of the energy of the antibonding orbitals, $-\Delta E_L < \Delta E_M$, so that small changes in the overlap integrals may alter the energies of the antibonding orbitals. Since the splitting of the central atom orbitals due to the ligand field is given by energy differences between antibonding MOs, then it must also depend on values of these overlap integrals. The correct deternation of H_{MM} and H_{LL} is of great importance, especially if their dependence on the charge distribution in a molecule is considered. The charge distribution influences the radial part of the atomic orbitals (orbital exponents) and therefore also the values of the overlap integrals. Although this effect is of secondary importance in comparison with the correct determination of the H_{MM} and H_{LL} values, it follows from relationships [363 - 364] that ϵ_γ^* values will be influenced more significantly than ϵ_γ as $H_{LL}^2 \gg H_{MM}^2$.

1.7.2 Angular Overlap Method

The Angular Overlap Method (AOM) (84 - 87) utilizes a decomposition of the group overlap integrals G_{ML} into a radial part, S_{ML}^*, and an angular part, F_λ^1

$$G_{ML} = F_\lambda^1\, S_{ML}^* \qquad [367]$$

The radial part S_{ML}^* is a function of the radial properties of the atomic orbitals and the interatomic distance. The angular part F_λ^1 characterizes the geometry of the coordination polyhedron and depends only on the mutual orientation of the overlapping orbitals of the central atom (with azimuthal quantum number 1) and ligand orbital of λ-symmetry. The parameter λ denotes the component of the angular momentum of the molecular orbital with respect to the linkage of atoms

λ	0	1	2	3 ...
type	σ	π	δ	φ ...

The equation [364] demonstrates that an increase of energy of the central atom orbitals ΔE_M is proportional to the square of the group overlap integral. Using a factorization it may be rewritten

$$\Delta E_M = \epsilon^*_\gamma - H_{MM} = e_\lambda \, (F^1_\lambda)^2 \tag{368}$$

where

$$e_\lambda = (S^*_{ML})^2 \, H^2_{LL}/(H_{MM} - H_{LL}) \tag{369}$$

represents a function that does not depend on the angular properties. Since all the d-orbitals for the given central atom have the same value of H_{MM}, then the parameter e_λ for a given ligand and constant interatomic distance becomes constant.

The radial part of the overlap integrals S^*_{ML} represents an angularly independent overlap consisting of net diatomic overlap integrals, e.g. $S(\sigma,d_\sigma)$, $S(\pi,d_\pi)$ and $S(\delta,d_\delta)$. The overlap integrals between orbitals in a given orientation can be expressed through a projection of the net diatomic overlap integrals in the direction of a bond. The coordinate systems for the central atom (x,y,z) and a ligand (x',y',z') are described in Appendix 2. The polar coordinates of the i-th ligand in the coordinate system of the central atom are denoted as r_i, ϑ_i, φ_i. We can put $r_i = 1$ because the distance occurs only in the factor F^1_λ. The p-orbital transformation can be carried out using the Euler matrix A_p

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = A_p \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \tag{370}$$

and the transformation of the d-orbitals using the matrix A_d

$$\begin{pmatrix} z^2 \\ yz \\ xz \\ xy \\ x^2-y^2 \end{pmatrix} = A_d \begin{pmatrix} (z^2)' \\ (yz)' \\ (xz)' \\ (xy)' \\ (x^2-y^2)' \end{pmatrix} \tag{371}$$

The Euler transformation matrix is

$$A_p = \begin{pmatrix} C_\vartheta C_\varphi; & -S_\varphi; & S_\vartheta C_\varphi \\ C_\vartheta S_\varphi; & C_\varphi; & S_\vartheta S_\varphi \\ -S_\vartheta; & 0; & C_\vartheta \end{pmatrix} \tag{372}$$

where the substitution $C_k = cos(k)$ and $S_k = sin(k)$ are used. Similarly the transformation matrix A_d for d-functions is expressed as follows

$$A_d = \begin{pmatrix} (1 + 3C_{2\vartheta})/4; & 0; & -S_{2\vartheta}\sqrt{3}/2; & 0; & (1 - C_{2\vartheta})\sqrt{3}/4 \\ S_{\varphi}S_{2\vartheta}\sqrt{3}/2; & C_{\varphi}C_{\vartheta}; & S_{\varphi}C_{2\vartheta}; & -C_{\varphi}S_{\vartheta}; & -S_{\varphi}S_{2\vartheta}/2 \\ C_{\varphi}S_{2\vartheta}\sqrt{3}/2; & -S_{\varphi}C_{\vartheta}; & C_{\varphi}C_{2\vartheta}; & S_{\varphi}S_{\vartheta}; & -C_{\varphi}S_{2\vartheta}/2 \\ S_{2\varphi}(1 - C_{2\vartheta})\sqrt{3}/4; & C_{2\varphi}S_{\vartheta}; & S_{2\varphi}S_{2\vartheta}/2; & C_{2\varphi}C_{\vartheta}; & S_{2\varphi}(3 + C_{2\vartheta})/4 \\ C_{2\varphi}(1 - C_{2\vartheta})\sqrt{3}/4; & -S_{2\varphi}S_{\vartheta}; & C_{2\varphi}S_{2\vartheta}/2; & -S_{2\varphi}C_{2\vartheta}; & C_{2\varphi}(3 + C_{2\vartheta})/4 \end{pmatrix} \qquad [373]$$

For ML_L type oordination compounds the energy changes may be determined from the simple formula

$$\Delta E_M = \sum_{A=1}^{N} e_{\lambda}^{A} \, (F_{\lambda}^{1})_{A}^{2} \qquad [374]$$

Values of the $(F_{\lambda}^{1})_{A}^{2}$ coefficients to calculate ΔE_M in complexes of various symmetry are listed in Table 23 (73, 88). In the case of unequivalent ligands a combination of various rows may be used.

When applied to octahedral$_6$ ML complexes the individual ligand polar coordinates ϑ_i and φ_i should be calculated by considering their localization in space. Then using formulas [371] and [374] we obtain

$$\Delta E_M(d_{z}2) = \Delta E_M(d_{x}2_{-y}2) = 3e_{\sigma} + 3e_{\delta} = E^{*}(e_{g}) \qquad [375]$$

$$\Delta E_M(d_{xy}) = \Delta E_M(d_{xz}) = \Delta E_M(d_{yz}) = 4e_{\pi} + 2e_{\delta} = E^{*}(t_{2g}) \qquad [376]$$

and the splitting in the octahedral field is given by

$$E^{*}(e_{g}) - E^{*}(t_{2g}) = 3e_{\sigma} - 4e_{\pi} + e_{\delta} \qquad [377]$$

For a trans-octahedral complex MA_2B_4 of D_{4h} symmetry we can use $(F_{\lambda}^{1})_{A}^{2}$ values tabulated for the square planar complex ML_4 (four ligands B are in the x-y plane) and the ML_2 system (two ligands A are in the z-axis). In this way

$$\Delta E_M(d_{z}2) = 2e_{\sigma}^{A} + e_{\sigma}^{B} + 3e_{\delta}^{B} \qquad [378]$$

$$\Delta E_M(d_{xz}) = \Delta E_M(d_{yz}) = 2e_{\pi}^{A} + 2e_{\pi}^{B} + 2e_{\delta}^{B} \qquad [379]$$

$$\Delta E_M(d_{xy}) = 2e_{\delta}^{A} + 4e_{\pi}^{B} \qquad [380]$$

$$\Delta E_M(d_{x}2_{-y}2) = 2e_{\delta}^{A} + 3e_{\sigma}^{B} + e_{\delta}^{B} \qquad [381]$$

The e_{λ} parameters for a given type of complex can be obtained theoretically but those values are too rough due to many approximations introduced. Therefore only the semiempirical version is used with parameters e_{λ} fitting the experimental data (Table 24).

TABLE 23

Angular overlap integrals $(F_\lambda^1)^2$ in the AOM method.

System		Type	Irreducible representation of an orbital				
			d_{z^2}	d_{yz}	d_{xz}	d_{xy}	$d_{x^2-y^2}$
ML	$C_{\infty v}$		σ^+	π	π	δ	δ
		e_σ	1	0	0	0	0
		e_π	0	1	1	0	0
		e_δ	0	0	0	1	1
ML_2	$D_{\infty h}$		σ_g^+	π_g	π_g	δ_g	δ_g
		e_σ	2	0	0	0	0
		e_π	0	2	2	0	0
		e_δ	0	0	0	2	2
ML_3	D_{3h}		a_1'	e''	e''	e'	e'
		e_σ	3/4	0	0	9/8	9/8
		e_π	0	3/2	3/2	3/2	3/2
		e_δ	9/4	3/2	3/2	3/8	3/8
ML_4	D_{4h}		a_{1g}	e_g	e_g	b_{2g}	b_{1g}
		e_σ	1	0	0	0	3
		e_π	0	2	2	4	0
		e_δ	3	2	2	0	1
ML_4	C_{3v}		a_1	e	e	e	e
		e_σ	7/4	0	0	9/8	9/8
		e_π	0	5/2	5/2	3/2	3/2
		e_δ	9/4	3/2	3/2	11/8	11/8
ML_5	C_{4v}		a_1	e	e	b_2	b_1
		e_σ	2	0	0	0	3
		e_π	0	3	3	4	0
		e_δ	3	2	2	1	2
ML_5	D_{3h}		a_1'	e''	e''	e'	e'
		e_σ	11/4	0	0	9/8	9/8
		e_π	0	7/2	7/2	3/2	3/2
		e_δ	9/4	3/2	3/2	19/8	19/8
ML_6	O_h		e_g	t_{2g}	t_{2g}	t_{2g}	e_g
		e_σ	3	0	0	0	3
		e_π	0	4	4	4	0
		e_δ	3	2	2	2	3

According to one assumption of the AOM the ratio e_π/e_σ should be the same as $(S_\pi/S_\sigma)^2$ when only overlap with ligand p-orbitals (or corresponding hybrid orbitals) is considered. The calculations show, however, that such an assumtion is not always fulfilled. For example, in the square $[CuCl_4]^{2-}$ there is $e_\pi/e_\sigma = 0.16$ whereas $(S_\pi/S_\sigma)^2 = 0.26$.

TABLE 24
Typical values of e_λ parameters (in units of 10^3 cm^{-1}).[a]

Ligand	Cr(III)		Co(III)		Ni(II)	
	e_σ	e_π	e_σ	e_π	e_σ	e_π
OH^-	9.0	2.0	9.6	4.5		
CN^-	8.5	-0.3	12.1	0.4		
H_2O	7.5	1.4	6.6	1.1	2.0	
F^-	7.4	1.7				
en	7.3	0	7.9	0	4.0	0
NH_3	7.0	0	7.8	0	3.6	0
NCS^-	6.4	0.4			3.8	0.1
py	5.8	-1.0	6.1	-0.7	4.3	0.1
Cl^-	5.5	0.9	6.3	1.3	1.7	-0.3
Br^-	4.9	0.6			1.2	-0.6
I^-	4.3	0.6				

a) Taken from $[ML_4L'_2]$ complexes (89, 90).

Some problems arise when transferability of the e_λ parameters from one complex to another is considered. For example, for the complex $[Cr(py)_4X_2]^+$ e_π is negative for the pyridine ligand if we assume that the e_λ parameters for $X^- = F^-$, Cl^- and Br^- are the same as in the complex $[Cr(NH_3)_4X_2]^+$. The theoretical expression for e_λ [369] assumes only a positive value.

In order to improve the AOM method d-s and d-p mixing (hybridization) of central atom orbitals has been considered. Consequently, the set of e_λ parameters is enlarged to include values of e_{ds}, $e_{dp\sigma}$ and $e_{dp\pi}$ (91, 92). The d-s mixing is important in systems of tetragonal symmetry (stabilization of d_{z^2} orbital) whereas d-p mixing is significant in tetrahedral systems.

Using the Wolfsberg-Helmholtz approximation in [350] we obtain

$$e_\lambda = (S^*_{ML})^2[(K_\lambda/2 - 1)H_{MM} + K_\lambda H_{LL}/2]^2/(H_{MM} - H_{LL}) \qquad [382]$$

For σ bonds the usual value $K_\sigma = 1.67$ and for π bonds $K_\pi = 2.0$. Then the e_λ parameters exhibit the following trends.

1. With increasing interatomic distance R_{M-L} values of overlap integrals decrease and thus the e_λ parameters decrease. The ratio e_σ/e_π increases with increasing R_{M-L} as S_π decreases more sharply than S_σ.

2. With increasing central atom proton number Z (an increase

of $|H_{MM}|$) values of e_σ and e_π increase as the denominator in [382] decreases. For the π bond the numerator is practically constant because $K_\pi \approx 2$. For the σ bond ($K_\sigma \approx 1.67$) the numerator will also decrease. Therefore the ratio e_σ/e_π will decrease.

3. With decreasing effective charge of the ligand (increase of $|H_{LL}|$) values of e_σ and e_π will decrease because the denominator of [382] increases. The increase of $|H_{LL}|$ causes greater changes in values of e_π relative to e_σ so the ratio e_σ/e_π will decrease.

A more elaborate parametrization scheme of the AOM has been proposed through a cellular approach (93). The ligand field potential $\hat{V}^{lf}$ (i.e. the crystal field potential modified to covalency) may be introduced through [356]. It may be divided into a superposition of contributions from a set of N nonoverlapping cells, so that its matrix elements in the d-orbital basis set are

$$v_{ij} = \langle\psi_i|\hat{V}^{lf}|\psi_j\rangle = \sum_{c=1}^{N} \langle\psi_i|\hat{v}_c|\psi_j\rangle \qquad [383]$$

As $v^c_{ij} = \langle\psi_i|\hat{v}_c|\psi_j\rangle$ form hermitian matrices v_c, these may be diagonalized to e_c ones using a unitary transformation

$$R_c\ v_c\ R_c^+ = e_c \qquad [384]$$

with matrices R_c determined by the molecular geometry only. Thus the new basis set $|\psi^c_k\rangle$ obtained by a transformation of the original d-orbitals $|\psi_i\rangle$

$$|\psi^c_k\rangle = \sum_{i=1}^{5} R^c_{ki}\ |\psi_i\rangle \qquad [385]$$

defines the AOM parameters as

$$e^c_k = \langle\psi^c_k|\hat{v}_c|\psi^c_k\rangle \qquad [386]$$

so that the fundamental equation of the AOM may be rewritten to

$$v_{ij} = \sum_{c=1}^{N} \sum_{k=1}^{5} (R^c_{ik})^+\ R^c_{kj}\ e^c_k \qquad [387]$$

For d-orbitals the matrix v_{ij} has $5(5 + 1)/2 = 15$ independent elements and there are 5N AOM parameters e^c_k ($k = 1, 5$; $c = 1, N$). In metal complexes usually $N \geq 4$ and thus the set of AOM parameters needs additional constraints to be reduced below 15. As the ligand field potential is energy dependent and reflects the whole electron density around the central atom, it may have contributions also from 'empty cells'. For example, in square ML_4 complexes there is a contribution of e-parameters associated with empty cells localized above and below the molecular plane. This, however, is equivalent to the d-s mixing concept in the extended ligand field theory.

In summary, the angular overlap method is based on a realistic physical model. The method is simple to calculate and is very frequently used to interpret the electron spectra of coordination compounds (90).

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2. THE NATURE OF THE CHEMICAL BOND

The chemical bond as a phenomenon has its origin in the electrostatic interaction of the moving atomic nuclei and electrons. Its description and better understanding requires the use of a specific apparatus based on the principles of quantum mechanics as the only successful physical theory applicable to microparticles. The prediction quality of the present theory depends on three factors: the interactions respected when postulating the Hamiltonian, the flexibility of the trial wave function and the procedure used for solving (in principle only an approximate one) of the corresponding Schrödinger equation for a molecule. The hierarchized approximation diagram at first separates the motion of the nuclei from that of the electrons, thus leading to the concept of an adiabatic potential. This concept enables the combination of the electronic theory of chemical bond with molecular spectroscopy, statistical thermodynamics and chemical kinetics as well as with the theory of molecular structure and chemical reactivity. The idea of an electron moving in the electric field of nuclei and of the rest of electrons leads to the one-electron approximation. This forms the basis for deriving the contemporary computational methods of quantum chemistry. It was the method of configuration interaction that enabled one to take into account the mutual correlation of the electronic motion. The intrinsic angular momentum of an electron - the spin - in the nonrelativistic approach is taken for an external parameter of the theory, that is manifest in the symmetrical properties of the wave function.

2.1 MOLECULAR HAMILTONIAN

2.1.1 Isolated Molecule

Molecules (molecular ions) can be taken for the systems of atomic nuclei and electrons interacting with each other. Since the range of strong interactions among protons and neutrons does not exceed the dimensions of a nucleus (10^{-15} m), then the only interactions of interest from the view-point of the object of chemical studies are represented by electromagnetic interactions.

Atomic nuclei and electrons, in a satisfactory approximation, can be described by point charges obeying the Coulomb law. The terms of the internal potential energy in an isolated molecule are

1. mutual electrostatic repulsion of atomic nuclei

$$V_{NN} = \sigma_{SI} \sum_{A<B} Z_A Z_B / r_{AB} \tag{1}$$

2. mutual electrostatic repulsion of electrons

$$V_{ee} = \sigma_{SI} \sum_{i<j} 1/r_{ij} \tag{2}$$

3. electrostatic attraction of atomic nuclei and electrons

$$V_{eN} = \sigma_{SI} \sum_{i} \sum_{A} Z_A / r_{iA} \tag{3}$$

In the above expressions:

Z_A- electric charge of the nucleus expressed in the units of the elementary charge e (i.e. the proton number of the nucleus),

r_{AB}, r_{ij}, r_{iA} - the distances between the charges (nucleus - nucleus, electron - electron and electron - nucleus),

$\sigma_{SI} = e^2/4\pi\epsilon_0$ - the conversion factor to SI units (ϵ_0 is the permittivity of vacuum. (The values of these physical constants are summarized in Appendix 1.)

Atomic nuclei and electrons are in permanent motion so that they have their own internal kinetic energy (T_N and T_e), independent of the external energy of translation of a molecule as a whole. The internal kinetic energy of every particle (nucleus, electron) depends on its mass, and thus, for different nuclides is dependent on the nucleon number of a nucleus. The presence of various numbers of neutrons in atomic nuclei is manifest in the molecular properties that depend explicitly on the kinetic energy of the nuclei (such as rotation and vibration spectra).

In an isolated molecule the spin-independent nonrelativistic Hamiltonian (total energy operator) is written

$$\hat{H}_0 = \hat{T} + \hat{V} \tag{4}$$

The kinetic energy operator is

$$\hat{T} = \hat{T}_N + \hat{T}_e = \sum_A (\hat{p}_A)^2/2m_A + (1/2m_e)\sum_i (\hat{p}_i)^2 \tag{5}$$

and the total potential energy operator is

$$\hat{V} = V_{NN} + V_{ee} + V_{eN} \tag{6}$$

Individual terms of $\hat{V}$ were defined by relationships [1] through [3].

As a rule, the Hamiltonian $\hat{H}_0$ is satisfactory for a basic description of the chemical bond in molecules. However, there are cases which cannot be described using this type of Hamiltonian (the effect of external fields, some effects of the special theory of relativity, effects of quantum electrodynamics, etc.).

In several cases, the atomic nuclei cannot be viewed as point charges, but rather as a system of charges and currents. The interaction energy of such a system with an external electromagnetic field **A** can be expressed through the multipole expansion

$$E_{elmg} = q\Phi_0 - d.E_0 - \bar{\mu}.B_0 - (1/6)\sum_{k,l} Q_{kl}(\partial E_l/\partial x_k)_0 - \ldots \qquad [7]$$

where 0 means the origin of the coordinate system (e.g. at the centre of the gravity); and

Φ - electrostatic potential of the external field,

E - vector of the electric field intensity (its cartesian components are E_x, E_y, E_z), whereby $E = - \nabla\Phi - \partial A/\partial t$,

B - vector of the magnetic induction, $B = \nabla \times A$,

q - total electric charge of the system,

d - electric moment of the dipole (dipole moment)

$\bar{\mu}$ - moment of the magnetic dipole (magnetic moment),

Q_{kl} - components of the electric quadrupole tensor Q.

The advantage of such an expansion (which is of general validity) lies in the fact that in many practical cases it is satisfactory to restrict its expansion to several of the lowest multipoles, only. The static electric dipole moment of atomic nuclei is equal to zero (1). A non-zero electric quadrupole moment means that the nuclear charge does not possess spherical symmetry; this can be represented by the distribution of charge in the shape of an ellipsoid. The components of the electric quadrupole tensor are defined as

$$Q_{kl} = \int \rho(3x_k x_l - \delta_{kl}r^2)\, dV \qquad [8]$$

where ρ is the charge density. According to [7] nuclei with a non-zero quadrupole moment interact with the electric field gradient $(\partial E_l/\partial x_k)$; this gradient can also be generated by the electronic structure of a molecule. This effect is demonstrated for example in Nuclear Quadrupole Resonance - NQR. The Electric multipole is non-zero only for definite values of the angular momentum of a nucleus, and as a consequence, nuclei with angular momentum $|I| = 0$, or $|I| = (1/2)\hbar$ (that is the frequent case) show zero static electric quadrupole moment.

The total angular momentum I of a nucleus is the vector sum of the angular momenta of all the nucleons (protons and neutrons), and further consists of the orbital angular momentum and intrinsic (spin) angular momentum. Ground states of atomic nuclei assume low values of I which provide evidence that both the motion of nucleons and that of their spins are such that the majority of angular momenta vectors cancel each other.

The nuclear angular momentum is the raison d'etre of the magnetic moment

$$\bar{\mu}_A = \gamma_A I = g_A \beta_N I/\hbar \qquad [9]$$

where $\beta_N = e\hbar/2m_p$ is the nuclear magneton,

g_A - spectroscopic resolution factor (nuclear g-factor)

γ_A - nuclear gyromagnetic ratio.

The interaction of the nuclear magnetic moment with the external magnetic field comes into effect in Nuclear Magnetic Resonance - NMR.

2.1.2 Effect of External Magnetic Field

The electromagnetic field is described by the scalar $\Phi(\mathbf{r},t)$ and the vector $\mathbf{A}(\mathbf{r},t)$ potential. Usually, the so-called coulombic calibration *div*$\mathbf{A}$ = $\nabla.\mathbf{A}$ = 0 is postulated for it. The spin-independent nonrelativistic Hamiltonian of a molecule in the presence of an external electromagnetic field assumes the form

$$\hat{H}_{elmg} = \sum_{\alpha}^{N+n} [(\hat{\mathbf{p}}_\alpha - q_\alpha \mathbf{A}_\alpha)^2/2m_\alpha + q_\alpha \Phi_\alpha] + \sum_{\alpha<\beta}^{N+n} q_\alpha q_\beta/4\pi\epsilon_0 r_{\alpha\beta} =$$

$$= \hat{H}_0 + \sum_{\alpha}^{N+n} [q_\alpha \Phi_\alpha - (q_\alpha/m_\alpha)\mathbf{A}_\alpha \cdot \hat{\mathbf{p}}_\alpha + (q_\alpha^2/2m_\alpha)(\mathbf{A}_\alpha)^2] \qquad [10]$$

This relationship is simplified in the case of the pure electrostatic field, or of a pure magnetostatic field

$$\hat{H}_{elmg} = \hat{H}_0 + \hat{H}_{els}(B \Rightarrow 0) + \hat{H}_{mg}(E \Rightarrow 0) \qquad [11]$$

The changes in the system energy due to an external electrostatic field are called by the comprehensive name, the **'Stark effect'**. For the electrostatic potential of the field with intensity E oriented along z-axis, it is $\Phi(\mathbf{r}) = -|E|z$. Then the electrostatic Hamiltonian of the electron is

$$\hat{H}_{els} = q_e \Phi_e = e|E|z \qquad [12]$$

and can be used for computation of the energies of bound states according to perturbation theory. In the first-order perturbation theory the linear Stark effect, while in the second-order one the quadratic Stark effect are distinguished. A specific example of the Stark effect is represented by the crystal field of ligands on energy levels of a central atom in coordination compounds. The corresponding electrostatic Hamiltonian assumes the form

$$\hat{H}_{els} = q_e\Phi_e = -(e/4\pi\varepsilon_0)\sum_{i}^{n}\sum_{l}^{m} q_L/r_{iL} \qquad [13]$$

where m is the number of ligands, q_L being their effective charges.

Let the external magnetic field be homogeneous, given by the vector potential $A = (1/2)B \times r$. Since it holds true that $B \times r.\hat{p} = B.r \times \hat{p} = B.\hat{l}$ (where $\hat{l} = r \times \hat{p}$ is the orbital angular momentum operator), then the magnetic part of the Hamiltonian for the electrons ($q = -e$) assumes the form

$$\hat{H}_{mg} = (e/2m_e)\sum_{i}^{n} B.\hat{l}_i + (e^2/8m_e)\sum_{i}^{n} (B \times r_i)^2 \qquad [14]$$

The first term (designated $\hat{H}_e^{l-B}$) describes the effects of orbital paramagnetism in the states with non-zero angular momentum. In the second-order perturbation theory, this term also yields the contribution to diamagnetism. The dominating diamagnetic contribution is given by the second term of $\hat{H}_{mg}$. The interaction $\hat{H}_e^{l-B}$ leads to the shift of energy levels of atoms (or molecules) in the magnetic field referred to as the **normal Zeeman effect.** The description of the latter is correct if carried out through $\hat{H}_e^{l-B}$ only in extremely strong external magnetic fields B. The relationship [14] does not account for a very important spin-orbit interaction, which to a decisive extent, predetermines the energy levels in weak external fields.

2.1.3 Inclusion of the Spin

The existence of spin (intrinsic angular momentum of a particle) does not follow from the Schrödinger equation, because the spin does not have any classical macroscopic analogue. Furthemore, this is the reason why the substitution of the classical terms of the Hamilton function to the quantum-mechanical operators does not lead to the concept of spin.

Since the electron has two possible spin states ($s_z = \pm\hbar/2$), Pauli proposed to describe the electron, not by a scalar wave function, but with the use of a two-component spinor. The corresponding stationary Schrödinger equation has a matrix form

$$\begin{pmatrix} \hat{H}_0 & 0 \\ 0 & \hat{H}_0 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \qquad [15]$$

and two equivalent solutions in the absence of an external magnetic field. With an external magnetic field present, the Hamiltonian assumes the form of the sum of both the spin-independent and spin-dependent parts

$$\hat{H}(r,s) = \hat{H}_0(r) + \hat{H}_e^{s-B} \qquad [16]$$

The additional spin-dependent part of the Hamiltonian is determined by the interaction energy of the magnetic moment $\bar{\mu}$ with the external field B

$$\hat{H}_e^{s-B} = - \bar{\mu}.B = \beta\underline{\hat{\sigma}}.B = \beta(\hat{\sigma}_x B_x + \hat{\sigma}_y B_y + \hat{\sigma}_z B_z) =$$

$$= \beta \begin{pmatrix} B_z & ;\ B_x - iB_y \\ B_x + iB_y; & -B_z \end{pmatrix} = \beta|B| \begin{pmatrix} \cos\vartheta & ;\ \sin\vartheta\ e^{i\varphi} \\ \sin\vartheta\ e^{i\varphi}; & -\cos\vartheta \end{pmatrix} \qquad [17]$$

where the relationships between the cartesian and polar coordinates $B_x = |B|\ \sin\vartheta\ \cos\varphi$, $B_y = |B|\ \sin\vartheta\ \sin\varphi$, $B_z = |B|\ \cos\vartheta$ were used. (Pauli spin matrices $\hat{\sigma}_x$, $\hat{\sigma}_y$, $\hat{\sigma}_z$ are described in Section 1.1) The solution of the corresponding characteristic equation is represented by the eigenvalues

$$E_{\pm} = E_0 \pm \beta|B| \qquad [18]$$

(E_0 is the eigenvalue of the spin-independent Hamiltonian $\hat{H}_0$) and a couple of spinors $\underline{\psi}_+$ and $\underline{\psi}_-$. For example, the spinor

$$\underline{\psi}_+(0) = \begin{pmatrix} \cos(\vartheta/2)\ e^{-i\varphi/2} \\ \sin(\vartheta/2)\ e^{+i\varphi/2} \end{pmatrix} \qquad [19]$$

corresponds to the spin oriented along the field B and its time evolution is

$$\underline{\psi}_+(t) = \underline{\psi}_+(0)\ e^{-iE_+ t/\hbar} \qquad [20]$$

While the angle ϑ is constant over the time, for the angle φ the following time dependence holds true

$$\varphi = (e/m_e)|B|t \qquad [21]$$

Therefore in an external magnetic field the direction of spin rotates with angular velocity

$$\omega = - 2\mu|B|/\hbar \qquad [22]$$

around the direction of the external magnetic filed. This precession can be used for the determination of the magnetic moments $\bar{\mu}$ of microparticles from the angular velocity value ω obtained by measurement and from the known magnetic induction B.

The relationship (17) can be generalized for several particles

$$\hat{H}_e^{s-B} = \sum_i (e/m_e)\mathrm{B}\cdot\hat{s}_i \qquad [23]$$

and the resulting interaction term of the electrons with the magnetic field will be

$$\hat{H}_e^{l-B} + \hat{H}_e^{s-B} = (e/2m_e)\sum_i^n \mathrm{B}\cdot(\hat{l}_i + 2\hat{s}_i) = (\beta/\hbar)\sum_i^n \mathrm{B}\cdot(\hat{j}_i + \hat{s}_i) \qquad [24]$$

(The addition of angular momenta is presented in Section 1.1). Finally, by summing up the orbital and spin angular momenta of individual particles we obtain

$$\hat{H}_e^{J-B} = \hat{H}_e^{L-B} + \hat{H}_e^{S-B} = (\beta/\hbar)\mathrm{B}\cdot(\hat{L} + 2\hat{S}) = (\beta/\hbar)\mathrm{B}\cdot(\hat{J} + \hat{S}) \qquad [25]$$

2.1.4 Relativistic Terms

In the special theory of relativity, the Hamilton function of a particle adopts the form

$$H = (m_0^2c^4 + p^2c^2)^{1/2} \qquad [26]$$

or

$$(H/c)^2 - m_0^2c^2 - p^2 = 0 \qquad [27]$$

Its operator form is termed the Klein-Gordon equation. Its transformation into a linear operator form (making the 'root') was achieved by Dirac (2) by introducing the operators $\hat{\gamma}_n$ (n = 1, 2, 3 and 4) with such properties so that the expression

$$(\hat{H}/c + \sum_n^3 \hat{\gamma}_n\hat{p}_n + \hat{\gamma}_4 m_0 c)(\hat{H}/c - \sum_n^3 \hat{\gamma}_n\hat{p}_n - \hat{\gamma}_4 m_0 c) = 0 \qquad [28]$$

was transformed into [27]. The operators $\hat{\gamma}_n$ fulfil the anticommutation relationships

$$[\hat{\gamma}_n,\hat{\gamma}_m]_+ = \hat{\gamma}_n\hat{\gamma}_m + \hat{\gamma}_m\hat{\gamma}_n = 0, \text{ for } m \neq n, \ \hat{\gamma}_n^2 = 1 \qquad [29]$$

They can be represented by square matrices of the dimension 4 x 4, such as

$$\hat{\gamma}_n = \begin{pmatrix} 0 & \hat{\sigma}_n \\ \hat{\sigma}_n & 0 \end{pmatrix}, \text{ for } n = 1, 2, 3; \quad \hat{\gamma}_4 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad [30]$$

where $\hat{\sigma}_n$ are the Pauli spin matrices and I is the unit matrix of the dimension 2 x 2. Then the **Dirac relativistic equation** for a free particle is

$$\{\hat{H} - c\sum_{n}^{3} \hat{\gamma}_n\hat{p}_n - \hat{\gamma}_4 m_0c^2\}\underline{\Psi} = 0 \qquad [31]$$

The operators $\hat{\gamma}_n$ cause the wave function $\underline{\Psi}$ to be viewed upon as a **four-component spinor**. The properties of the operators $\hat{\gamma}_n$ take into account the spin properties of the fermions (such as electrons) so that the existence of spin is seen as a natural consequence of the special theory of relativity, as explained later. The time development of the system is described by the substitution $\hat{H} \Rightarrow i\hbar(\partial/\partial t)$ and the stationary state by the substitution $\hat{H} \Rightarrow E$, similar to the Schrödinger equation.

In the presence of an external electromagnetic field $(\Phi,\mathbf{A})$ substitutions of $\hat{\mathbf{p}} \Rightarrow \hat{\mathbf{p}} - q\mathbf{A}$ and $\hat{H} \Rightarrow \hat{H} - q\Phi$ are useful. Thus, the relativistic equation for the four-component spinor $\underline{\Psi}$ is

$$\{c\sum_{n}^{3} \hat{\gamma}_n(\hat{p}_n - qA_n) + \hat{\gamma}_4 m_0c^2 + q\Phi - \hat{H}\}\underline{\Psi} = 0 \qquad [32]$$

Then the relativistic (four-component) Hamiltonian of the j-th particle can be written as

$$\hat{H}^{(j)} = c\hat{\underline{\gamma}}^{(j)}\hat{\mathbf{P}}^{(j)} + m_0^{(j)}c^2\hat{\gamma}_4^{(j)} + q^{(j)}\Phi^{(j)} \qquad [33]$$

where the generalized linear momentum is $\hat{\mathbf{P}} = \hat{\mathbf{p}} - q\mathbf{A}$. If representations of the operators $\hat{\gamma}_n$ through the Pauli matrices $\hat{\sigma}_n$ are used (see Section 1.1), then the equation [32] may be rewritten into the form

$$\begin{pmatrix} I(q\Phi + m_0c^2); & c\hat{\underline{\sigma}}\cdot\hat{\mathbf{P}} \\ c\hat{\underline{\sigma}}\cdot\hat{\mathbf{P}} & ; I(q\Phi - m_0c^2) \end{pmatrix} \begin{pmatrix} \underline{\psi}_u \\ \underline{\psi}_l \end{pmatrix} = \hat{H} \begin{pmatrix} \underline{\psi}_u \\ \underline{\psi}_l \end{pmatrix} \qquad [34]$$

where $\underline{\psi}_u$ (upper) and $\underline{\psi}_l$ (lower) are two-component spinors

$$\underline{\Psi} = \begin{pmatrix} \underline{\psi}_u \\ \underline{\psi}_l \end{pmatrix} \qquad [35]$$

The solution of this system of equations can be found with the use of the partitioning technique (see Section 1.2.5). The result valid for the stationary spinor $\underline{\psi}_u$ (by $\hat{H} \Rightarrow E$) is

$$\{(q\Phi + m_0c^2)I + c^2\hat{\underline{\sigma}}\cdot\hat{\mathbf{P}}[(E - q\Phi + m_0c^2)I]^{-1}\,\hat{\underline{\sigma}}\cdot\hat{\mathbf{P}}\}\underline{\psi}_u = E\underline{\psi}_u \qquad [36]$$

It can be further modified with the use of the substitution $\hat{k} = [(E + m_0c^2 - q\Phi)I]^{-1}$ and the identity $(\hat{\underline{\sigma}}\cdot\mathbf{a})(\hat{\underline{\sigma}}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b} + i\hat{\underline{\sigma}}\cdot(\mathbf{a} \times \mathbf{b})$ fulfilled for the vectors $\mathbf{a} = \hat{\mathbf{P}}$ and $\mathbf{b} = \hat{k}\hat{\mathbf{P}}$ commuting with $\hat{\underline{\sigma}}$. In this way, the relativistic equation

$$\{(q\Phi + m_0c^2)I + c^2(\hat{P}.\hat{k}\hat{P}) + ic^2\hat{\underline{\sigma}}.(\hat{P} \times \hat{k}\hat{P})\}\psi_u = E\psi_u \qquad [37]$$

can be obtained; it is still an exact relativistic equation whose advantage is only its two-component form.

When the magnetic field is applied, the scalar potential vanishes ($\Phi = 0$) and the vector potential is not a function of time ($\partial\mathbf{A}/\partial t = 0$). Now a satisfactory approximation may be introduced by assuming that the particle's energy E does not differ substantially from the rest energy m_0c^2. This may be considered as a nonrelativistic limit or the first estimate of E in an iterative solution of equation [37]. Within this approximation $\hat{k} \approx 1/(2m\ c^2)$. With the use of further modification of the vector product $\hat{P} \times \hat{P} = (\hat{p} - q\mathbf{A}) \times (\hat{p} - q\mathbf{A}) = q\hat{p} \times \mathbf{A} = i\hbar q\nabla \times \mathbf{A} = i\hbar q\mathbf{B}$ we get

$$\{(1/2m_0)(\hat{p} - q\mathbf{A})^2 - (q\hbar/2m_0)\hat{\underline{\sigma}}.\mathbf{B}\}\psi_u = (E - m_0c^2)\psi_u \qquad [38]$$

which, in fact, is a form of the **Pauli nonrelativistic equation** for the two-component spinor ψ_u. Subtraction of the rest energy can be secured either by considering the kinetic energy $E' = E - m_0c^2$ or by selecting the phase of the wave function $\psi_u' = exp(-im_0c^2t/\hbar)\psi_u$. For the electron charge ($q = -e$) a correct derivation of the proportionality coefficient between the magnetic moment and spin angular momentum is obtained

$$\bar{\mu} = -(e\hbar/2m_e)\hat{\underline{\sigma}} = -\beta\hat{\underline{\sigma}} = -(e/m_e)\hat{\mathbf{s}} = -(g\beta/\hbar)\hat{\mathbf{s}} \qquad [39]$$

Here β is the Bohr magneton and g = 2 the 'theoretical' value of the electronic g-factor. (Because of an anomalous magnetic moment of the electron $\mu = 1.001\ 16\ \beta$ the precise value of the electronic g-factor is g = 2.0023. This deviation originates in the contribution from virtual electron-positron pairs, as explained by quantum electrodynamics. The g-factors of nucleons deviate considerably from the spin value as a consequence of strong interactions with the meson field.)

For the interaction energy of the magnetic moment $\bar{\mu}$ with the external magnetic field B:

$$\hat{H}^{s-B}_{e\cdot} = -\bar{\mu}.\mathbf{B} = (g\beta/\hbar)\hat{\mathbf{s}}.\hat{\mathbf{B}} = (g\beta/2)\hat{\underline{\sigma}}.\mathbf{B} \qquad [40]$$

The exact relativistic equation [37] may be approximated in several ways. One yields the result (3)

$$\hat{H}_{app} = \hat{P}^2/2m_0 + q\Phi - (q\hbar/2m_0)\hat{\underline{\sigma}}.\mathbf{B} - \hat{P}^4/8m_0^3c^2 + \\ + (q\hbar/8m_0^2c^2)(\hat{\underline{\sigma}}.\hat{P} \times \mathbf{E} - \hat{\underline{\sigma}}.\mathbf{E} \times \hat{P} - \hbar\nabla.\mathbf{E}) \qquad [41]$$

which is the approximate two-component Hamiltonian for electron motion ($q = -e$) in an electromagnetic field including the relativistic correction of the order $1/c^2$.

Generalization of the relativistic Hamiltonian for a system of charged particles with mutual interaction is very complicated. This is necessary since some other factors must be taken into account. First, the interaction of moving charges depends on their velocity. Second, the moving charged particle contributes to the vector potential (it induces an additional magnetic field). This is the reason why the complete relativistic Hamiltonian for a molecule has not so far been derived (this area, however, is still the subject of scientific activity).

For a two-particle system the relativistic Hamiltonian contains the additional interaction term I_{12}, which by considering the dependence of interaction of two charges on their velocities has the approximate form (4)

$$I_{12} = (q_1 q_2/8\pi\epsilon_0 c^2)[v_1 \cdot v_2/r_{12} + (v_1 \cdot r_{12})(v_2 \cdot r_{12})/r_{12}^3] \qquad [42]$$

For its operator form the substitution $v_n \Rightarrow c\hat{\gamma}_n$ is introduced. Then for a system of charged particles the relativistic **Darwin-Breit Hamiltonian** is obtained

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} + q_1 q_2/4\pi\epsilon_0 r_{12} -$$

$$- (q_1 q_2/8\pi\epsilon_0)[r_{12}^{-1}\,\hat{\gamma}^{(1)} \cdot \hat{\gamma}^{(2)} + r_{12}^{-3}\,(\hat{\gamma}^{(1)} \cdot r_{12})(\hat{\gamma}^{(2)} \cdot r_{12})] \qquad [43]$$

Decomposition of this four-dimensional Hamiltonian into the two-dimensional approximate Hamiltonian of the type [41] is rather complicated. It leads, however, to acquisition of new interaction terms enabling the classification and interpretation of a series of fine effects that are well known in molecular spectroscopy (ESR, NMR, ENDOR, etc.) (5).

Table 1 presents the classification of interactions in molecules. The relationships for individual terms of the Hamiltonian are summarized in Table 2. In the available literature the most frequently used metric systems are the Gauss system of units (CGSE, CGSM) or the atomic system of units (a.u.). Therefore the transformation coefficients between these systems of units and SI system of units are also given.

Thus, it can be concluded, that the Hamiltonian of a molecule can be written in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_{ext} + \hat{H}_{int} \qquad [44]$$

TABLE 1
Types of interaction in molecules.

Quantity	q	Z	Q	I_N	s	l	B
Electron charge q	V_{ee}						
Nuclear charge Z	V_{eN}	V_{NN}					
Nuclear quadrupole moment Q	$\hat{H}^{q-Q}_{eN}$						
Nuclear spin I_N			$\hat{H}^{Q-I}_{NN}$	$\hat{H}^{I-I}_{NN}$			
Electron spin s				$\hat{H}^{s-I}_{eN}$	$\hat{H}^{s-s}_{ee}$		
Electron angular momentum l				$\hat{H}^{l-I}_{eN}$	$\hat{H}^{l-s}_{ee}$	$\hat{H}^{l-l}_{ee}$	
Magnetic field B				$\hat{H}^{I-B}_{N}$	$\hat{H}^{s-B}_{e}$	$\hat{H}^{l-B}_{e}$	$\hat{H}^{B}_{e}$
Electric field Φ	$\hat{H}^{q-\Phi}_{e}$	$\hat{H}^{Z-\Phi}_{N}$			$\hat{H}^{s-E}_{e}$		

The term $\hat{H}_0$ embraces the kinetic energy of the particles (both of nuclei and electrons) as well as the electrostatic potential energy between them. The second term comprises all interactions of the system with the external electromagnetic field. The last term reflects all the interactions among the particles inside the system that are not of electrostatic nature. These interactions cover the spin properties of electrons and nuclei that come into effect, e.g. in spin-orbit and spin-spin interaction. $\hat{H}_{int}$ can comprise the effects of quantum electrodynamics (such as the correction with respect to the radiation of charged particles - Lamb shift) and also partly some other effects of the theory of relativity (such as increase of particle's mass with its velocity and the Darwin correction for definite size of particles).

TABLE 2

Hamiltonian terms in a molecule [a]

No	Operator	Unit system factor		
		SI	Gauss	a.u.
A) Nonrelativistic terms				
1. Kinetic energy of nuclei	$\hat{T}_N = -\sum_A (1/2m_A)\nabla_A^2$	$\hbar^2$	$\hbar^2$	m_e
2. Kinetic energy of electrons	$\hat{T}_e = -(1/2)\sum_i \nabla_i^2$	$\hbar^2/m_e$	$\hbar^2/m_e$	1
3. Electrostatic repulsion of nuclei	$\hat{V}_{NN} = \sum_{A<B} Z_A Z_B/r_{AB}$	$e^2/4\pi\epsilon_0$	e^2	1
4. Electrostatic repulsion of electrons	$\hat{V}_{ee} = \sum_{i<j} 1/r_{ij}$	$e^2/4\pi\epsilon_0$	e^2	1
5. Electrostatic electron-nuclear attraction	$\hat{V}_{eN} = -\sum_i \sum_A Z_A/r_{iA}$	$e^2/4\pi\epsilon_0$	e^2	1
6. Electrostatic interaction of nuclear quadrupole moment - electron charge	$\hat{H}_{eN}^{q-Q} = -(1/2)\sum_i \sum_A r_{iA}^{-5} \mathbf{R}_{iA} Q_A \mathbf{R}_{iA}$	e	e	1
B) Relativistic corrections independent both of the spins and the field				
7. Kinetic energy correction	$\hat{T}_e(2) = -(1/8)\sum_i \nabla_i^4$	$\hbar^4/m_e^3c^2$	$\hbar^4/m_e^3c^2$	$1/c^2$
8. Electron-nuclear Darwin term	$\hat{H}_{eN} = (\pi/2)\sum_i \sum_A Z_A \delta(\mathbf{R}_{iA})$	$4\beta^2$	$4\beta^2$	$1/c^2$
9. Electron-electron Darwin term	$\hat{H}_{ee} = -\pi \sum_{i<j} \delta(\mathbf{R}_{ij})$	$4\beta^2$	$4\beta^2$	$1/c^2$
10. Electron-electron orbital interaction	$\hat{H}_{ee}^{1-1}(1) = (1/2) \sum_{i<j} [r_{ij}^{-1}\nabla_i\cdot\nabla_j - r_{ij}^{-3}(\mathbf{R}_{ij}\cdot\nabla_i)(\mathbf{R}_{ij}\cdot\nabla_j)]$	$4\beta^2$	$4\beta^2$	$1/c^2$
11. Electron-electron orbital interaction	$\hat{H}_{ee}^{1-1}(2) = (1/4) \sum_{i<j} r_{ij}^{-3}(\mathbf{R}_{ij}\cdot\nabla_j - \mathbf{R}_{ij}\cdot\nabla_i)$	$4\beta^2$	$4\beta^2$	$1/c^2$
12. Electron-electron orbital interaction	$\hat{H}_{ee}^{1-1}(3) = \pi \sum_{i<j} \delta(\mathbf{R}_{ij})(\mathbf{R}_{ij}\cdot\nabla_i - \mathbf{R}_{ij}\cdot\nabla_j)$	$4\beta^2$	$4\beta^2$	$1/c^2$

TABLE 2 (Continued)

		Unit system factor		
No	Operator	SI	Gauss	a.u.
C) Terms dependent on the electron spin				
13. Spin-orbit interaction of electrons (spin - own orbital)	$\hat{H}_{ee}^{s-l}(1) = -(ig'/4)\sum_{j}\sum_{A} Z_A[k_0(R_{jA})]^2$ $r_{jA}^{-3}\, s_j \cdot (R_{jA}\, x\, \nabla_j)$	$4\beta^2$	$4\beta^2$	$1/c^2$
14. Spin-orbit interaction of electrons (spin--other orbital)	$\hat{H}_{ee}^{s-l}(2) = i\sum_{j\neq k} r_{jk}^{-3}\, s_j \cdot (R_{jk}\, x\, \nabla_k)$	$4\beta^2$	$4\beta^2$	$1/c^2$
15. Spin-orbit interaction of electrons	$\hat{H}_{ee}^{s-l}(3) = (ig'/4)\sum_{j\neq k} r_{jk}^{-3}\, s_j \cdot R_{jk}\, x\, \nabla_j$	$4\beta^2$	$4\beta^2$	$1/c^2$
16. Spin-spin interaction of electrons (dipolar term)	$\hat{H}_{ee}^{s-s}(1) = \sum_{i<j}[r_{ij}^{-3}\, s_i \cdot s_j -$ $- 3r_{ij}^{-5}(s_i \cdot R_{ij})(s_j \cdot R_{ij})]$	$4\beta^2$	$4\beta^2$	$1/c^2$
17. Spin-spin interaction of electrons (contact term)	$\hat{H}_{ee}^{s-s}(2) = -(8\pi/3)\sum_{i<j} s_i \cdot s_j\, \delta(R_{ij})$	$4\beta^2$	$4\beta^2$	$1/c^2$
D) Terms dependent on the nuclear spin				
18. Nuclear dipole-dipole interaction	$\hat{H}_{NN}^{I-I}(1) = (1/4)\sum_{A<B} g_A g_B[r_{AB}^{-3}\, I_A \cdot I_B -$ $- 3r_{AB}^{-5}(I_A \cdot R_{AB})(I_B \cdot R_{AB})]$	$4\beta_N^2$	$4\beta_N^2$	
19. Nuclear spin-spin interaction	$\hat{H}_{NN}^{I-I}(2) = (1/8)\sum_{i}\sum_{A,B} g_A g_B[k_0(R_{Ai})]$ $r_{iA}^{-3} r_{iB}^{-3}[(I_A \cdot I_B)(R_{iA} \cdot R_{iB}) - (I_A \cdot R_{iA})(I_B \cdot R_{iB})]$			
20. Orbital hyperfine interaction	$\hat{H}_{eN}^{l-I}(1) = -(i/2)\sum_{i}\sum_{A} g_A[k_0(R_{jA})]$ $r_{jA}^{-3}(R_{jA}\, x\, \nabla_j) \cdot I_A$	$4\beta_N\beta$	$4\beta_N\beta$	
21. Orbital hyperfine correction	$\hat{H}_{eN}^{l-I}(2) = (i/4)\sum_{j}\sum_{A} g_A[k_0(R_{jA})]^3$ $\nabla_j^2\, r_{jA}^{-3}(R_{jA}\, x\, \nabla_j) \cdot I_A$			
22. Nuclear quadrupole interaction	$\hat{H}_{NN}^{Q-I} = \sum_{A} Q_A/[2I_A(2I_A-1)]\sum_{i}[r_{iA}^{-3}\, I_A^2 -$ $- 3r_{iA}^{-5}(R_{iA} \cdot I_A)^2]$	$e^2/4\pi\epsilon_0$	e^2	1

TABLE 2 (Continued)

No	Operator	Unit system factor SI	 Gauss	 a.u.
E) Terms dependent on both the nuclear and electron spins				
23. Dipolar hyperfine interaction	$\hat{H}_{eN}^{s-I}(1) = -(g/4)\sum_i \sum_A g_A[k_0(r_{iA})]$ $[r_{iA}^{-3}\, s_i \cdot I_A - 3r_{iA}^{-5}(s_i \cdot R_{iA})(I_A \cdot R_{iA})]$	$4\beta_N\beta$	$4\beta_N\beta$	
24. Fermi contact hyperfine interaction	$\hat{H}_{eN}^{s-I}(2) = (2\pi g'/3)\sum_i \sum_A g_A s_i \cdot I_A\, \delta(R_{iA})$	$4\beta_N\beta$	$4\beta_N\beta$	
25. Spin-orbit hyperfine correction	$\hat{H}_{eN}^{s-I}(3) = (g'/8)\sum_i \sum_{A\neq B} g_A Z_B[k_0(r_{iA})]^2$ $r_{iA}^{-3} r_{iB}^{-3}[(R_{iA} \cdot R_{iB})(s_i \cdot I_A)-(s_i \cdot R_{iB})(I_A \cdot R_{iA})]$			
26. Spin-orbit hyperfine correction	$\hat{H}_{eN}^{s-I}(4) = (1/4)\sum_{i\neq j} \sum_A g_A\, r_{ij}^{-3}\, r_{iA}^{-3}$ $[(R_{ji} \cdot R_{jA})(s_i \cdot I_A) - (R_{ji} \cdot I_A)(R_{jA} \cdot s_i)]$			
27. Spin-orbit hyperfine correction	$\hat{H}_{eN}^{s-I}(5) = (g'/8)\sum_{i\neq j} \sum_A g_A\, r_{ij}^{-3}\, r_{iA}^{-3}$ $[(R_{ji} \cdot R_{iA})(s_i \cdot I_A) - (s_i \cdot R_{iA})(I_A \cdot R_{ji})]$			
F) Terms dependent on magnetic field				
28. Orbital Zeeman interaction	$\hat{H}_e^{l-B}(1) = -(i/2)\sum_j (r_j\, x\, \nabla_j) \cdot B$	2β	2β	$1/c$
29. Orbital Zeeman correction	$\hat{H}_e^{l-B}(2) = -(i/4)\sum_j [k_0(r_j)]^3 \nabla_j^2 (r_j x \nabla_j) \cdot B$			$1/c^3$
30. Diamagnetic term	$\hat{H}_e^{B} = (1/8)\sum_i [B^2 r_i^2 - (B \cdot r_i)^2]$	e^2	$e^2/m_e c^2$	$1/c^2$
G) Terms dependent on electric field				
31. Interaction nuclear charge - electric potential	$\hat{H}_N^{Z-\Phi} = \sum_A Z_A \Phi^A$	e	e	1
32. Interaction electron charge - electric potential	$\hat{H}_e^{q-\Phi} = -\sum_i \Phi^i$	e	e	1
33. Energy shift by field	$\hat{H}_e^{E} = (1/8)\sum_i \nabla_i \cdot E^i$			$1/c^2$

TABLE 2 (Continued)

No	Operator	Unit system factor SI	Unit system factor Gauss	Unit system factor a.u.
H) Terms dependent on the electron spin and magnetic field				
34. Electron spin Zeeman term	$\hat{H}_e^{s-B}(1) = (g/2)\sum_i s_i\cdot B$	2β	2β	$1/c$
35. Electron spin Zeeman correction	$\hat{H}_e^{s-B}(2) = -(g/2)\sum_i \nabla_i^2\, s_i\cdot B$			$1/c^3$
36. Spin-orbit Zeeman gauge correction	$\hat{H}_e^{s-B}(3) = (g'/8)k_0^2 \sum_i \sum_A Z_A r_{iA}^{-3}$ $[(R_{iA}\cdot r_i)(s_i\cdot B) - (s_i\cdot r_i)(r_i\cdot B)]$			$1/c^3$
37. Spin-orbit Zeeman gauge correction	$\hat{H}_e^{s-B}(4) = (g'/8)\sum_{i\neq j} r_{ij}^{-3}$ $[(R_{ij}\cdot r_i)(s_i\cdot B)-(s_i\cdot B)-(s_i\cdot r_i)(R_{ji}\cdot B)]$			$1/c^3$
38. Spin-orbit Zeeman gauge correction	$\hat{H}_e^{s-B}(5) = (1/2)\sum_{i\neq j} r_{ij}^{-3}$ $[(R_{ij}\cdot r_j)(s_i\cdot B) - (s_i\cdot r_j)(R_{ij}\cdot B)]$			$1/c^3$
I) Terms dependent on the nuclear spin and magnetic field				
39. Nuclear Zeeman interaction	$\hat{H}_N^{I-B}(1) = (1/2)\sum_A g_A I_A\cdot B$	$2\beta_N$	$2\beta_N$	
40. Nuclear Zeeman correction	$\hat{H}_N^{I-B}(2) = (k_0/4)\sum_i \sum_A g_A r_{iA}^{-3}$ $[(r_i\cdot R_{iA})(I_A\cdot B) - (r_i\cdot I_A)(R_{iA}\cdot B)]$			
J) Terms dependent on the electron spin and electric field				
41. Interaction electron spin - - electric field	$\hat{H}_e^{s-E} = -(i/8)\sum_j s_j\cdot(E^j \times \nabla_j - \nabla_j \times E^j)$			$1/c^2$

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[a] The symbols used: β - Bohr magneton (in the Gauss system $\beta = e\hbar/2m_ec$), β_N - nuclear magneton (in the Gauss system $\beta_N = e\hbar/2m_pc$), $R_{ij} = r_i - r_j$, $r_{ij} = |R_{ij}|$ is separation of particles, $\delta(R_{ij})$ - Dirac function, $g = 2(1 + g_1)$ is electronic Zeeman g-factor, $g' = 2(1 + 2g_1)$ is electronic spin-orbital g-factor, $k_0 = (1 + \Phi_{int}e/2m_ec^2)^{-1} \approx 1$ is correction to internal electrostatic field of particles, B - homogeneous magnetic field. Spins s_i and I_A of particles are in units of $\hbar$.

2.2 BORN-OPPENHEIMER APPROXIMATION

2.2.1 Classification of Molecular Motions

It is known that energy is a scalar quantity representing a quantitative measure of motion of every massive object. A definite numerical value of this energy corresponds to a definite state of motion of an object. The molecular state of motion can be decomposed into five contributions.

1. **Translational motion** of a molecule as a whole is characterized by three degrees of freedom with a non-quantizied positive value of kinetic energy that does not yield any information on its internal properties. By considering a coordinate system at the centre of gravity the translational motion can be separated from other types of motion. (In the relativistic theory such a separation is only approximate.)
2. **Rotational motion** of a molecule as a whole is characterized by three (in the case of linear molecules, by two) degrees of freedom.
3. **Vibrational motion** of atomic nuclei is characterized by 3N-6 (in case of linear molecules by 3N-5) degrees of freedom.
4. **Orbital motion** and the electron **spin** in the molecule.
5. The **nuclear spin** of individual nuclei having non-zero magnetic moment.

In an isolated molecule, the mutual electrostatic interaction of the moving nuclei and the electrons is in equilibrium and is associated with a discrete (quantized) value of the **internal energy**. We can speak about a stationary energetic state of a molecule if the value of its internal energy is time independent (constant. The stationary state with the minimum value of this internal energy is referred to as the ground energy state. The other energy states are excited states.

A substantial part of the molecular internal energy results from the orbital motion of the electrons, the motions of nuclei about their equilibrium positions and the rotational motion of the molecule as a whole about three axes. The energy range of these contributions to the molecular internal energy can be estimated as follows.

In classical physics the energy of rotational motion is expressed as $E = L^2/2I$ where L is the angular momentum, I being the moment of inertia. If the molecule has mass M and its 'length' is d, then the moment of inertia can be estimated as $I = Md^2$. The minimum possible change of the angular momentum ΔL equals $\hbar$ (reduced Planck constant). Therefore the minimum variation of the rotational energy ΔE_{rot} is

$$\Delta E_{rot} = (\Delta L^2)/2Md^2 = h^2/2Md^2 \tag{45}$$

which after substituting appropriate values in a molecular range yields $\Delta E_{rot} \fallingdotseq 1 - 10^2$ J mol^{-1}.

Analogously, the electronic orbital motion (along a closed curve) can be estimated as $\Delta E_{el} = 10^5 - 10^6$ J mol^{-1}. Here M must be substituted by the electronic mass and d for the length of a molecule since the electron does not leave the molecule.

The change in energy due to molecular vibrations may be estimated through the relationship

$$\Delta E_{rot} : \Delta E_{vib} : \Delta E_{el} = (1/M) : (1/\mu) : (1/m_e) \tag{46}$$

where μ is the reduced mass of a subsystem of vibrating nuclei. After evaluating the above expression we obtain $\Delta E_{vib} = 10^3 - 10^4$ J mol^{-1}.

A discrete energy state of a molecule corresponds to a definite superposition of electronic, vibrational and rotational motion. Since the contributions of individual types of motion to the total internal energy of a molecule usually differ by several orders of magnitude, then in a suitable approximation they can be taken as independent. One can imagine that within the framework of the given electronic state several vibrational states are possible while within a definite vibrational state there exist several rotational states of a molecule.

The total Hamiltonian $\hat{H}$ of an isolated molecule in the non-relativistic approximation does not contain any spin variables. The wave function, however, is a parametric function of spin variables $\Psi = \Psi(R, r; [I], [s])$. Hereafter a simplified notation of $\Psi = \Psi(R, r)$ will be used. Then the non-relativistic Schrödinger equation for a free molecule assumes the form

$$\{\hat{T}_N(R) + \hat{T}_e(r) + \hat{V}(R,r) - W_\nu\}\Psi(R,r) = 0 \tag{47}$$

where W_ν is the total internal energy of the ν-th stationary state of a molecule. A dependence on nuclear coordinates (R), electronic coordinates (r) and both, nuclear and electronic coordinates (R,r) is shown for individual operators. The above relationship represents a second-order partial differential equation with the number of variables equal to 3(N + n), where N is the number of nuclei and n is of electrons. Its exact solution in the form of analytical functions can be obtained only for two-body systems (such as hydrogen atom, and He^+, Li^{2+} ions). Very precise numerical solutions have been obtained for three-body systems (He, Li^+, H_2^+). For many-body systems the mathematical formulation of the problem (construction of the Schödinger equation) is not complicated but its numerical solution encounters extreme difficulties. Thus, the task will be to find such approximate methods to solve the Schrödinger equation enabling one to determine the molecular wave function Ψ_1 and the ground-state energy W_1 to a sufficient degree of precision (according to the nature of the physical or chemical phenomenon under study). It has proved advantageous to formulate the above scheme in such a manner that, if required, one can pass from a less exact solution to a more sophisticated one.

In principle, one proceeds according to a certain hierarchized approximation scheme, within whose framework, a separation of variables especially is concerned. The levels of simplification introduced can be divided into three groups:

1. separation of nuclear motions from those of electrons (adiabatic or Born-Oppenheimer approximation);
2. substitution of the local interelectron interaction, expressed by the terms representing potential energy $1/(r_i - r_j)$ by a definite average, expressed by the additive function of r_i and r_j (neglect of electron correlation - one-electron approximation which leads to the molecular orbital method);
3. substitution of the one-electron function spreading over the whole molecule by the finite linear combination of analytic one-centre functions (LCAO approximation in the molecular orbital method).

2.2.2 Separation of Electron and Nuclear Motion

We shall try to find the wave function $\Psi_\nu(R,r)$ of the ν-th stationary molecular state in the form of a series

$$\Psi_\nu(R,r) = \sum_{i=0}^{\infty} f_{\nu,i}\, \Psi_i(r;[R]) \qquad [48]$$

The electronic wave functions $\Psi_i(r;[R])$ depend explicitly upon electronic coordinates (r) and in a parametric way upon nuclear coordinates (fixed values of [R]). The expanding coeffficents $f_{\nu,i}(R)$ depend only on nuclear coordinates and represent the vibrational functions. Expression [48] represents an exact expansion of the wave function into the basis set of other (known) functions in the Hilbert space. That means that so far we have not introduced any approximation if all the terms in the above series are considered (there is infinite number of them). In practical calculations, however, we are able, as a rule, to include in the series only a finite number of terms. Let us note that the basis set functions $\Psi_i(r;[R])$, in fact, can be arbitrary. Usually we proceed so that these functions satisfy the characteristic equation

$$\{\hat{T}_e(r) + \hat{V}(R,r) - E_i(R)\}\ \Psi_i(r;[R]) = 0 \qquad [49]$$

This is for two reasons. For the first, the functions $\Psi_i(r;[R])$ obtained by solving the equation [49], as a rule, represent a good approximation to the molecular wave function Ψ_ν, thus it is satisfactory to include the only term in the series [48]. In case this is not applicable for the description of the given physical or chemical problem, it is still possible to include into the series several terms that, as a consequence, enable one to approximate the wave function to an arbitrary level of precision. For the second, the equation [49] again has the form of the Schrödinger equation having a physical model. The nuclei in the above model can be taken for static (frozen) or infinitely heavy ($m_A \Rightarrow \infty$) when their kinetic energy vanishes, $T_N(R) \Rightarrow 0$.

A simple train of thoughts shows that a model such as this can be operational. Here we are taking into account that the mass of the nuclei is several-times more than that of the electron, at least 1836-times (representing the ratio m_p/m_e for hydrogen) more. In electron - nuclear interaction both the particles are exposed to the same force. Then according to Newton's second law, the electron acquires a much higher acceleration (due to its lesser mass) than the nucleus, and thus, its velocity will be several times (10^3 to 10^4) higher than that of the nucleus. The slow moving nuclei then generates the electrostatic field in which the electrons move much faster. Their motion is therefore fast enough to be able to follow the changes in configuration of the nuclei. On the other hand, the atomic nuclei are exposed to such fast fluctuations of the electrostatic field of electrons that they obey its average.

Let us now come back to the analytic form of the Schrödinger equation for a molecule. Having replaced [48] into eq. [47] with the use of algebraic transformations, we arrive at the system of differential equations (6)

$$\{\hat{T}_N(R) + E_i(R) - W_\nu\}\ f_{\nu,i}(R) = -\sum_j \hat{G}_{ij}(R)\ f_{\nu,j}(R) \qquad [50]$$

for i = 0, 1, ...where the non-adiabatic coupling operator

$$\hat{G}_{ij}(R) = \int \Psi_i^*(r;[R])\ \hat{T}_N(R)\ \Psi_j(r;[R])\ dr -$$

$$- \sum_{A=1}^{N} (\hbar^2/2m_A) \int \Psi_i^*(r;[R])\ \{\nabla_A\ \Psi_j(r;[R])\}\ dr\ \nabla_A \qquad [51]$$

has been introduced. The system of equations [48] through [51] is exact. Its solution can be realized according to the scheme

$$[49] \Rightarrow \left\{ \begin{array}{l} E_i(R) \\ \Psi_i(r;[R]) \Rightarrow [51] \Rightarrow \hat{G}\ \ (R) \end{array} \right\} \Rightarrow [50] \Rightarrow \left\{ \begin{array}{l} W_\nu \\ f_{\nu,i}(R) \end{array} \right.$$

$$\downarrow$$

$$[48] \Rightarrow \Psi_\nu(R,r)$$

The above non-adiabatic calculations were carried out for very systems (diatomic molecules and ions H_2^+, H_2), only. The difficulty rests in the fact that the equations [49] and [50] represent a very complicated system of integro-differential equations for functions of several variables. Though these equations were formulated as early as in the thirties, their exact solutions were not found until the seventies, when more powerful computers became available.

In an effort to simplify these equations [50] their right hand side may be neglected (set equal to zero). This, however, represents the phenomenon called the **Born-Oppenheimer approximation** leading to the following dynamic equations for nuclear motion

$$\{\hat{T}_N(R) + E_i(R) - E_{i,\mu}\}\ f_{i,\mu}(R) = 0 \qquad [52]$$

for individual sets of $\mu = 0, 1, \ldots$ and $i = 0, 1, \ldots$ Their solutions cover the energy values $E_{i,\mu}$ and vibration functions $f_{i,\mu}(R)$. The computational scheme is modified as follows

$$[49] \Rightarrow \left\{ \begin{array}{l} E_i(R) \\ \Psi_i(r;[R]) \Rightarrow [52] \Rightarrow \end{array} \right. \left\{ \begin{array}{l} E_{i,\mu} \\ f_{i,\mu}(R) \Rightarrow \ \Psi_{i,\mu} = f_{i,\mu}\ \Psi_i(r;[R]) \end{array} \right.$$

This approximation has the following consequences. In the non-adiabatic theory the exact wave function Ψ_ν and the characteristic value of the total energy W_ν of the ν-the stationary state resulted from a superposition of electronic motion and vibration-rotational motion of the nuclei. In the Born-Oppenheimer approximation the following items (Fig. 1) were separately specified:

1. **electronic states** described by the wave functions $\Psi_i(r;[R])$ with the corresponding total energy $E_i(R)$;
2. **vibration-rotational states** described by the wave functions $f_{i,\mu}(R)$ with the corresponding energy values $E_{i,\mu}$ within the framework of the electronic state under study.

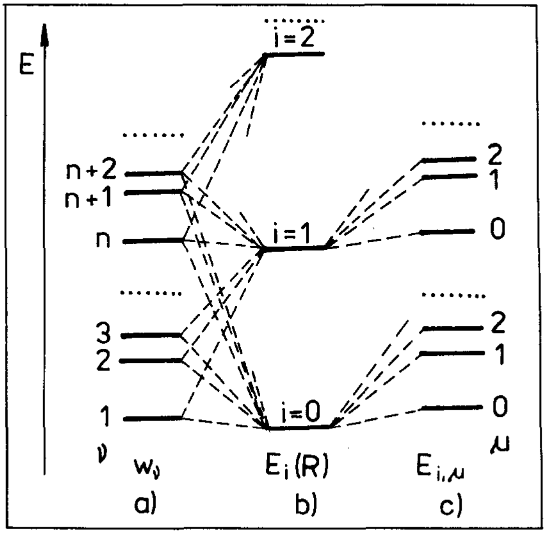

Fig. 1. Relationship among characteristic states: a) non-adiabatic theory; b) electronic states within Born-Oppenheimer approximation; c) vibration-rotational states for a given electronic state.

Born-Oppenheimer approximation is satisfactory if the mutual coupling of a couple of electronic states through the vibration-rotational states is weak, i.e. if

$$- \int f^*_{i,\mu}(R)\ \hat{G}_{ij}(R)\ f_{j,\lambda}(R)\ dR \ll |E_{i,\mu} - E_{j,\lambda}| \text{ for } i \neq j \qquad [53]$$

In connection with the study of the chemical bond in molecules this condition is usually satisfied. However, several cases are known where the Born-Oppenheimer approximation fails (e.g. including the dynamic Jahn-Teller effect). Then we must consider more terms in the expansion of the molecular wave function.

2.2.3 Adiabatic Potential

The function $E_i(R)$ appearing in the dynamic equations for nuclear motion [52] describes a kind of the potential energy. That is why it is referred to as an **adiabatic potential** (or frequently the energy hypersurface). This is defined as the total molecular energy in the case of static nuclei so that it is a function of nuclear coordinates regarded as parameters. It is obtained in a theoretical way by solving the Schödinger equation for electronic motion [49]. This is unknown within the non-adiabatic theory as no single term of the exact Schödinger equation [50] describes the potential energy. An intermediate approximation standing between the non-adiabatic theory and the Born-Oppenheimer approximation is represented by the **adiabatic approximation**. It arises from the neclect of off-diagonal terms $\hat{G}_{ij}$ so that the diagonal corrections to nuclear motion $\hat{G}_{ii}$ are used to modify the adiabatic potential: $E_i(R) + \hat{G}_{ii}(R)$.

As the wave function $\Psi_i(r,[R])$ is not explicitly dependent upon nuclear coordinates R, the operator $\hat{V}_{NN}(R)$ does not act on the latter, and thus

$$\frac{\langle\Psi_i|\hat{V}_{NN}|\Psi_i\rangle}{\langle\Psi_i|\Psi_i\rangle} = V_{NN}(R) \qquad [54]$$

which represents the classical expression for electrostatic Coulomb repulsion of the nuclei. Then the Schrödinger equation [49] can be transcribed into the form

$$\frac{\langle\Psi_i|\hat{T}_e(r) + \hat{V}_{ee}(r) + \hat{V}_{eN}(R,r)|\Psi_i\rangle}{\langle\Psi_i|\Psi_i\rangle} = E_i^{el}(R) = E_i(R) - V_{NN}(R) \qquad [55]$$

Here we have used decomposition of the total potential energy operator into the part reflecting internuclear repulsion $\hat{V}_{NN}(R)$, interelectronic repulsion $\hat{V}_{ee}(r)$ and the electron-nuclear attraction $\hat{V}_{eN}(R,r)$. Equation [55] is called the **electronic Schödinger equation** and can be transformed into the form

$$\hat{H}^{el}\ |\Psi_i(r,[R])\rangle = E_i^{el}(R)\ |\Psi_i(r,[R])\rangle \qquad [56]$$

Its eigenvalue is represented by the **electronic energy** E_i^{el}. Thus it can be concluded that the adiabatic potential $E_i(R)$ consists of two terms:

1. nuclear repulsion energy $V_{NN}(R)$ which is always positive and independent of the electronic state;
2. electronic energy $E_i^{el}(R)$ characterizing the electronic state of a molecule.

Thus, it is

$$E_i(R) = V_{NN}(R) + E_i^{el}(R) \qquad [57]$$

In a nonlinear molecule the adiabatic potential depends on

(3N-6) coordinates. It can be represented by a surface in the multidimensional space. Usually, equienergetic curves for a couple of variables are shown at fixed values of the other variables (a section of an energy hypersurface) as exemplified in Fig. 2.

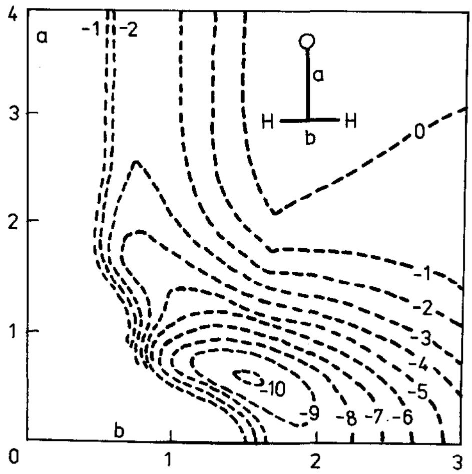

Fig. 2. A cut of the adiabatic potential surface for the water molecule. The equienergetic lines (eV) are shown for an approach of oxygen atom (^1D) state to H_2 molecule.

Let us recall that the electronic state does not represent a real (observable) state of a molecule. It is the electron-vibration-rotational state of a molecule which is admissible. Within the framework of the Born-Oppenheimer approximation the energy state of a molecule can be taken for a vibration-rotational one within the given electronic state. That means that the wave functions $\Psi_{i,\mu}$ and the energies $E_{i,\mu}$ represent, to a certain extent, an approximation (sufficient, as a rule) to the molecular states Ψ_ν and observable energies E_ν accessible within the framework of the non-adiabatic theory.

Energy levels of the vibration-rotational states $E_{i,\mu}$ are usually marked on the adiabatic potential curve of a given electronic state. The energy $E_{0,0}$ corresponds to the ground molecular state. The difference in the energy level of the minimum of the adiabatic potential and the $E_{0,0}$ value is called the correction to zero-point vibration (ZPV correction). In some cases, the vibrational levels are also supplemented by an amplitude function $f_{i,\mu}$ which yields the vibrational amplitude a^2 by means of $a^2/2 = \langle f|R^2|f\rangle - \langle f|R|f\rangle^2$.

The adiabatic potential is one of the most important concepts in chemical physics. It represents the fundamental element of molecular spectroscopy, chemical kinetics and theory of the chemical bond. Information on the characteristic features of adiabatic potential come not only from theoretical computational methods but also from experimental techniques of molecular spectroscopy, chemical thermodynamics and kinetics, non-Boltzmann experiments of molecular beams, etc. The relationship of the characteristics of adiabatic potential to various experimental methods is illustrated by Fig. 3.

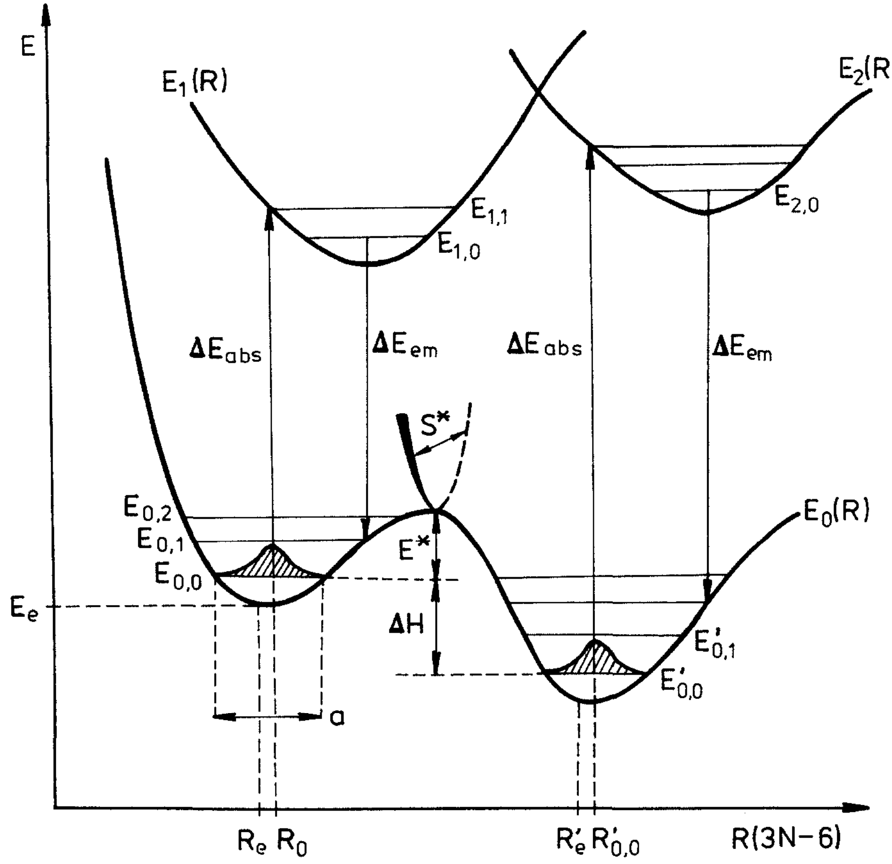

Fig. 3. Relationship between parameters of adiabatic potential and observable quantities: structural characteristics - R_0; spectroscopic characteristics - a, ΔE_{abs}, ΔE_{em}; thermodynamic characteristics - ΔH; kinetic characteristics - E^*, S^*.

When compiling the vibrational Hamiltonian of a polyatomic molecule it is advantageous instead of cartesian coordinates of displacement

$$\Delta\vec{\rho}_A = \vec{\rho}_A - \vec{\rho}_0 = \vec{i}\Delta x_A + \vec{j}\Delta y_A + \vec{k}\Delta z_A \qquad [58]$$

($\vec{\rho}_A$ is the instantaneous position of the nucleus A, $\vec{\rho}_0$ being its equilibrium position) to use the valence force coordinates {q}.

The valence force coordinates can be of two different types:

1) Valence coordinates Δr_A are connected with a change of bond length

$$\Delta r_A = \vec{e}_A \cdot (\vec{\rho}_A - \vec{\rho}_0) \qquad [59]$$

where $\vec{e}_A$ is the unit vector directed along the bond (Fig. 4).

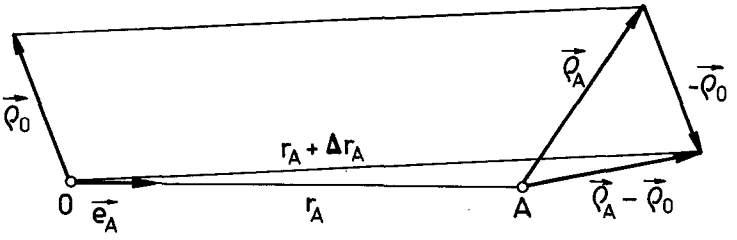

Fig. 4. The relation between cartesian and valence coordinates.

2) Deformation coordinates $\Delta\varphi_{AB}$ describing changes in bond angles (Fig. 5)

$$\Delta\varphi_{AB} = \frac{\cos\varphi_{AB}\vec{e}_B - \vec{e}_A}{r_B \sin\varphi_{AB}} \cdot \vec{\rho}_B + \frac{\cos\varphi_{AB}\vec{e}_A - \vec{e}_B}{r_A \sin\varphi_{AB}} \cdot \vec{\rho}_A + $$

$$+ \frac{(r_B - r_A\cos\varphi_{AB})\vec{e}_B + (r_A - r_B\cos\varphi_{AB})\vec{e}_A}{r_A r_B \sin\varphi_{AB}} \cdot \vec{\rho}_0 \qquad [60]$$

The transformations above can be expressed in matrix form

$$\{q\} = S\{\rho\} \qquad [61]$$

where {q} is the column vector of linearly independent valence force coordinates of dimension m = 3N - 6 (for linear molecule m = = 3N - 5), {ρ} is the column vector of cartesian displacements of

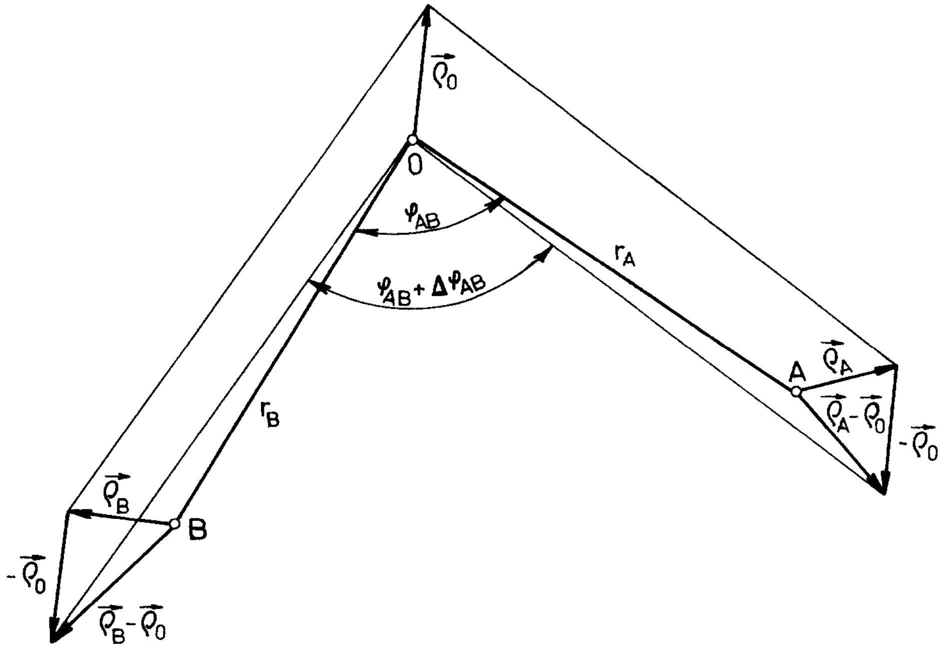

Fig. 5. The relation between cartesian and deformation coordinates.

dimension 3N and S is the transformation matrix of dimension 3N *x* m. Similarly, the transformation of the nuclei's linear momentum can be performed

$$\{\hat{p}\} = S^T\{\hat{\pi}\} \qquad [62]$$

where $\{\hat{p}\}$ is the column vector of the linear momenta operators expressed in cartesian coordinates and $\{\pi\}$ is the column vector of linear momenta operators in valence force coordinates.

The vibrational Hamiltonian in terms of valence force coordinates assumes the form, in the harmonic approximation,

$$\hat{H}_v = \frac{1}{2}\sum_{k,l}(G_{kl}\hat{\pi}_k\hat{\pi}_l + F_{kl}q_kq_l) \qquad [63]$$

where G_{kl} are matrix elements of the kinematic (Wilson) matrix

$$G = SM^{-1}S^T \qquad [64]$$

The diagonal matrix M^{-1} is formed by the elements $1/m_A$ where m_A is the mass of nucleus A. The force constants F_{kl} express the curvature of the adiabatic potential E(q) in equilibrium geometry

$$F_{kl} = [\partial E(q)/\partial q_k\partial q_l]_0 \qquad [65]$$

To obtain the solution of the Schrödinger equation for vibrational motion

$$\hat{H}_v\theta_v = E_v\theta_v \tag*{[66]}$$

it is useful to perform a transformation, such that both the kinetic and potential energy will be expressed only through the sum of the square terms $\hat{\pi}_k^2$ and q_k^2. The coordinates in which the matrices G and F are diagonal, are called the normal coordinates {Q} and are defined by the square transformation matrix L

$$\{q\} = L\{Q\} \tag*{[67]}$$

The corresponding linear momentum operators are transformed as follows

$$\{\pi\} = (L^{-1})^T\{\hat{\Pi}\} \tag*{[68]}$$

For unambiguous determination of the matrix L we require that the matrix G be transformed to a unit matrix I, so that the following relationships are fulfilled

$$L^{-1}G(L^{-1})^T = I \tag*{[69]}$$

$$L^TFL = \Lambda \tag*{[70]}$$

where Λ is a diagonal matrix. The above conditions can be expressed in the form of a matrix equation

$$(GF - \Lambda)L = 0 \tag*{[71]}$$

leading ultimately to a secular equation

$$det(GF - \Lambda) = 0 \tag*{[72]}$$

the solution of which furnishes eigenvalues λ_i of the diagonal matrix Λ. These in turn, when substituted into equation [71] determine the transformation matrix L.

The vibrational Hamiltonian would assume, after such transformation, the form

$$\hat{H}_v = \frac{1}{2}\sum_i (\hat{\Pi}_i^2 - \lambda_i Q_i^2) \tag*{[73]}$$

The total vibrational function $\theta = \prod_i \chi_i(Q_i)$ as well as the energy $E = \sum_i \epsilon_i$ are made up of contributions from normal vibrations. In this manner a set of characteristic equations is obtained

$$(\hat{\Pi}_i + \lambda_i Q_i)\chi_i = \epsilon_i\chi_i \tag*{[74]}$$

describing a harmonic oscillator. Energy eigenvalues represent then the solution of these differential equations

$$\epsilon_i = h\nu_i(v_i + 1/2) \tag*{[75]}$$

where $\nu_i = \sqrt{\lambda_i}/2\pi$ is an eigenfunction of the oscillator and v_i the vibrational quantum number ($v_i = 0,1,2,\ldots$).

The vibrational functions have the form

$$\chi_j(Q) = Q_0^{-1/2} exp(-\xi^2/2)\ H_i(\xi) \qquad [76]$$

for the argument $\xi = Q/Q_0$ where $Q_0 = (h/m\nu_0)^{1/2}$. The corresponding Hermitean polynomials of n-th order are

$$H_n(\xi) = (-1)^n(2^n\ n!\ \sqrt{\pi})^{-1/2}\ e^{\xi^2}(d^n/d\xi^n)\ e^{-\xi^2} \qquad [77]$$

In cases whereby eigenvalue ε_i is d_i-times degenerate, we obtain, by solving the equation for the harmonic oscillator with dimension d_i,

$$\varepsilon_i = h\nu_i(v_i + d_i/2) \qquad [78]$$

The total energy of vibrational motion of the molecule

$$E_v = h \sum_i{}' \nu_i(v_i + d_i/2) \qquad [79]$$

the sum being performed only over different eigenfrequencies.

If the cubic terms $\sum_{k,l,m} [\partial^3 E(q)/\partial q_k \partial q_l \partial q_m]_0$ of the Taylor series is included into the adiabatic potential, then the approximate solution of the Schrödinger equation for nuclear motion in the anharmonic approximation yields the vibrational energy in the form $\varepsilon_i = h\nu_i(v_i + 1/2) + h\nu_i x_i(v_i + 1/2)^2$. In such a case ν_i denotes the harmonic frequency and x_i the anharmonicity constant. (In reality, analysis of vibrational spectra is carried out, expect in the case of simple molecules, in the harmonic oscillaror approximation.)

The secular equation [72] can be simplified (expressed by lower dimension equations) on the basis of symmetry coordinates, corresponding to the respective irreducible representations of the symmetry point group of the molecule (Section 1.3.1).

The secular equation $det(GF - \Lambda) = 0$ can be solved for three sets of different starting conditions.

1) If the geometry of the molecule and the atomic weights are known (i.e. the matrix G), as well as the force constants F_{kl}, we can calculate λ_i and hence also the vibrational frequencies.

2) Knowing the molecular structure and vibrational frequencies, we can determine the force constants.

3) From known force constants and frequencies the molecular geometry can be determined.

2.4 UTILIZATION OF THE ADIABATIC POTENTIAL

2.4.1 Properties of the Adiabatic Potential

The Born-Oppenheimer approximation assigns to each electronic state Ψ_i of an arbitrary N-atomic system an adiabatic potential $E_i(Q) = E_i(Q_1,Q_2,\dots Q_{3N-6})$, giving the system's energy as the function of 3N - 6 (3N - 5 in linear molecules) independent nuclear coordinates Q_A. Atomic configurations at local minima of the adiabatic potential curve correspond to equilibrium geometry of the system, which in turn characterizes the respective molecular structure.

In order to be able to give a total description of the molecular structure we need as the minimum requirement the following information:

1) precisely localized adiabatic potential minima for each, especially the ground, electronic states;

2) curvature of the adiabatic potential at a local minimum, in other words the knowledge of force constants $F_{KL} = (\partial^2 E_i/\partial Q_K \partial Q_L)$;

3) heights of energy barriers separating the local minima.

In addition, if we want to tackle chemical kinetics we need to know the curvature of the adiabatic potential in the saddle points of energy barriers or, if collision theory is to be applied, the shape of the entire hypersurface.

Geometric parameters of the local minimum at the adiabatic potential curve determines the molecular geometry. The adiabatic potential curve can feature more than one minimum - these minima correspond to isomers of the molecule, and are separated by energy barriers high enough to ensure relative stability of individual isomers. In Rouvray's terms (6) isomers are understood as chemical individuals represented by identical molecular formula, but showing differences in certain properties over periods of time long enough for differences to be measurable. Muetterties contends (7) that in order for isomers to become experimentally separable, their lifetime should exceed 10^{-2} s. Bersuker (8) considers two isomers distinguishable when the energy difference between the local minimum and the lowest neighbouring barrier ΔE conforms to $\Delta E \geq 2h\nu$, ν being the vibration frequency in the minimum. Flat minima, separated by low energy barriers defy static interpretation of equilibrium geometry, a dynamic model of nonrigid (fluxional) molecules is called for.

The equilibrium geometry is in terms of adiabatic potential defined by structural parameters R_e, belonging to the respective minimum. The parameters represent internuclear distances in free molecules (Fig. 6). From the experimental point of view the situation is more complex owing to the fact that at each above-zero temperature the vibration-rotation parameters are observed averaged over all states. The averaging is performed by weight factors w_i, given by the Boltzmann distribution law

$$w_i = \frac{g_i \, exp(-E_i/kT)}{\sum_j g_j \, exp(-E_j/kT)} \qquad [80]$$

where E_i is energy of the i-th state, g_i the multiplicity of its degeneracy, k the Boltzmann constant and T the temperature. Even at absolute zero the observed experimental values are averaged over all vibrations of the vibrational ground state. This is due to the fact that even at absolute zero temperature the molecule has, according to the Heisenberg's uncertainity principle, a non-zero vibration energy.

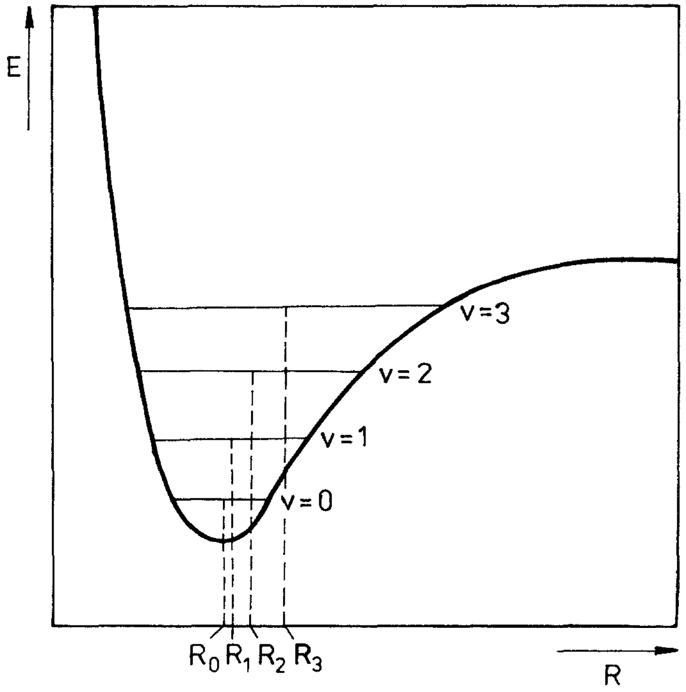

Fig. 6. Various types of interatomic distances.

The construction of adiabatic potential curve involves a series of calculations of Schrödinger equation for electronic motions localized in fields of the selected sets of stationary es are incrementally varied depends on the type of study the adiabatic potential is set up for. Thus for stereochemical and spectral studies the knowledge of adiabatic potential in the vicinity of a local minimum usually suffices, whilst for kinetic and thermodynamic studies assymptotical behaviour of the potential at each dissociation limit as well as the shape of saddle points between the minima must be known. The precision with which such adiabatic potential is eventually obtained is limited by the selected step size. Increasing the number of steps, needed for e.g. a multidimensional adiabatic potential leads to an explosive growth of calculations times. For an n-dimensional adiabatic potential x^n Schrödinger equations have to be solved, where x equals the number of steps in one direction (the number being the same for each direction). Thus for instance in a nonlinear five-atomic molecule we get $n = 3N - 6 = 9$ dimensions, and at 10 steps in each direction we need 10^9 calculations.

Starting from the listed values of adiabatic potential we arrive at an analytical expression by fitting the free parameters on the energy at selected discrete nuclear configurations. For this the method of choice is usually the least-square method with linear or non-linear regression. Analytical functions must be flexible enough to preserve the fidelity to the adiabatic potential in the entire required area.

Even granting many simplifications involved in the solution of the Schrödinger equation for electron motions (LCAO approximation, finite number of basis set functions, incomplete CI calculations, neglecting the relativistic effects, and some integrals in semi-empirical methods) calculations of adiabatic potential curves remain limited to small molecules. In case of bigger molecules only cross-section of energy hypersurfaces are accessible (9, 10), or studies are carried out only at selected geometries, varying only one degree of freedom (6 - 18).

The adiabatic potential curve of a diatomic molecule is well described by a Morse potential

$$E(R) = D_e \{1 - exp[-a(R - R_e)]\}^2 \qquad [81]$$

where D_e is the dissociation energy, or the Dunham potential

$$E(\xi) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \ldots) \qquad [82]$$

$\xi = (R - R_e)/R_e$ being the relative coordinates, a_0, a_1, $a_2, \ldots$ constant coefficients.

In studies of elementary chemical reactions various empirical forms of adiabatic potential are being used, the best known amongst which is the LEPS (London-Eyring-Polanyi-Sato) potential (19). It is based on the physical expression of the interaction in the three-atomic systems and has the form

$$E = \{Q_{AB} + Q_{BC} + Q_{CA} - (1/\sqrt{2})[(\alpha_{AB} - \alpha_{BC})^2 + (\alpha_{BC} - \alpha_{CA})^2 + (\alpha_{CA} - \alpha_{AB})^2]^{1/2}\}/\{1 + S^2\} \qquad [83]$$

The diatomic parameters Q_{AB} and α_{AB} are derived from the dissociation curves, the shape of which is determined by the Morse potential of the bonding (E_{AB}) and antibonding state (E^*_{AB}) of a diatomic molecule

$$E_{AB} = \frac{Q_{AB} + \alpha_{AB}}{1 + S^2_{AB}} = D_e\{exp[-2a(R - R_e)] - 2exp[-a(R - R_e)]\} \qquad [84]$$

$$E^*_{AB} = \frac{Q_{AB} - \alpha_{AB}}{1 - S^2_{AB}} = D_e\{exp[-2a(R - R_e)] + 2exp[-a(R - R_e)]\} \qquad [85]$$

whence S_{AB} stands for an empirical parameter. The adiabatic potential can also be expressed in the form of a Taylor series, running over vibration coordinates

$$E(Q) = E_0 + \frac{1}{2}\sum_{k,l} F_{kl}Q_kQ_l + (1/3!)\sum_{k,l,m} F_{klm}Q_kQ_lQ_m \qquad [86]$$

where F_{kl} and F_{klm} are quadratic and cubic force constants. Nevertheless hypersurfaces defined in the above manner only describe well the immediate vicinity of equilibrium geometries; at dissociation limits they fail even when 4-th order terms are included. This drawback can be partly overcome by developing (20, 21) the series along relative coordinates $\tau = (R - R_e)/R$, an operation which markedly improves the regression and the stability of expanding coefficients.

Murrell (22-26) suggested that the analytical forms of adiabatic potential can be expressed by the function

$$E = \sum_{A<B} E_{AB} + \sum_{A<B<C} E_{ABC} + \sum_{A<B<C<D} E_{ABCD} + \cdots \qquad [87]$$

where E_{AB} are contributions from the diatomic interactions (usually in the form of an extended Morse potential), E_{ABC} corrections related to the three-atomic interactions (a polynome assuring the correct limit behaviour), E_{ABCD} the four-atomic (usually negligibly small) contributions.

Clementi (27-37) applied the pair interaction potential, a potential based on the interaction model of point charges.

In spite of much effort of numerous workers in the field the problem of obtaining analytical form of adiabatic potential for polyatomic systems with any satisfactory precision still remains a challenge. Fig. 7 depicts the calculation scheme applicable for stereochemical, thermodynamic, spectroscopic and kinetic parameters of molecules. Strictly speaking, all calculations based on the adiabatic potential concept and concerning an isolated molecule are limited (except when interactions with the environment are explicitly included) to the state of ideal gas.

Stationary points of an adiabatic potential can be obtained by solving the system of equations

$$(\partial E/\partial Q_k) = 0 \qquad (k = 1, 2, 3, \ldots, 3N - 6) \qquad [88]$$

A still better resolution between the stationary points allows the matrix of force constants

$$F_{kl} = [\partial^2 E/(\partial Q_k \partial Q_l)]_0 \qquad [89]$$

While the minima at the energy hypersurface possess only positive eigenvalues of force constant matrix, saddle points, featuring a single negative eigenvalue of force constant matrix, have for this reason the meaning of transition states or activated complexes.

The contemporary approach to stationary points at energy hypersurfaces makes use of direct, geometry optimizing gradient method, which does not require the explicit knowledge of adiabatic potential curves. The optimization procedure itself consists of a two-step repeating cycle, consisting of:

1) Determination of energy gradient components in a given point of adiabatic potential. The gradients are accessible through either analytical formulas, or by numerical methods.

2) Recurrent approximation of coordinates of the sought after stationary point by iterative optimization technique, selected in such a way that it suits the problem in question.

Unfortunately none of the optimization procedures can furnish a criterion for determining the number of stationary points of a given hypersurface. The only more or less safe approach to localization of stationary points appears to be the systematic variation of starting structures. Such studies can involve rather extensive calculations, as illustrated by the optimization of conformation of N-acetyl-N-methylamides of amino acids, which required 20 000 starting structures (38).

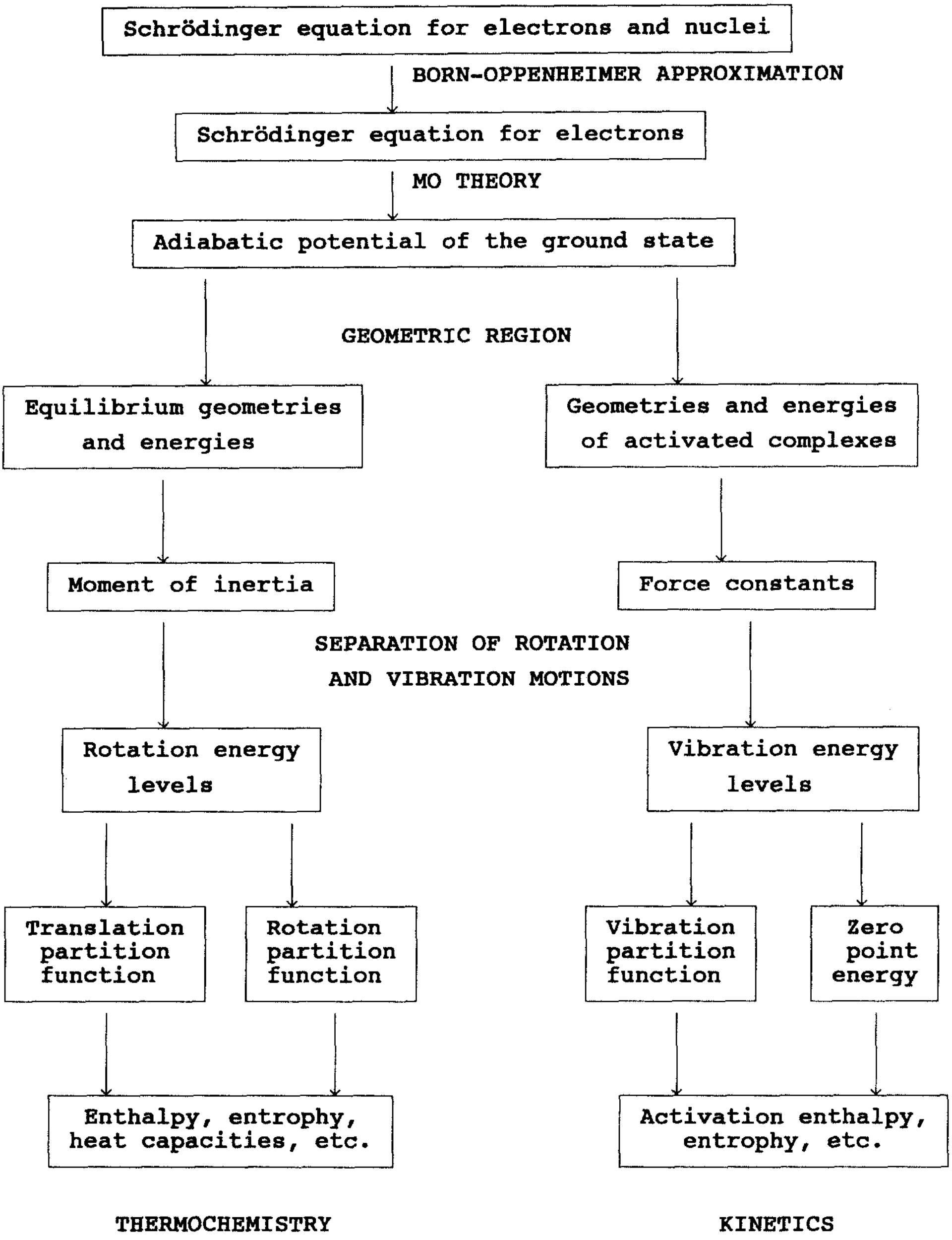

Fig. 7. The scheme of the calculation procedure of stereochemical, thermodynamic, spectoscopic and kinetic charasteristics of molecules.

Adiabatic potential curves are often made along curved lines and assumed to represent reaction pathways or coordinates. Nevertheless these lines have no physical meaning. Their shape may depend on the coordinate system and is not necessarily related to classical trajectories (39, 40) obtained by solving Lagrange motion equations which are, at least in a classical approach, physically meaningful.

The advantage of the concept of reaction coordinate lies in the fact that it does not, in contrast to classical trajectories, presuppose the actual knowledge of the analytical form of adiabatic potential. In addition, the concept of reaction coordinates enables one to systematically determine the geometry of activated complexes and products and thus to facilitates the search for stationary points of the adiabatic potential. Reaction coordinates also plays a specific role in problems concerning the tunneling effect and in the dynamics of chemical reactions.

One defines the reaction coordinate as the pathway along the steepest slope at energy hypersurface and connecting reactants and products. Fukui (41) suggested that reaction coordinate be defined as a curve leading from reactants to products via an activated complex, and being at the same time orthogonal to energetically equipotential hyperplanes. Under such conditions one is led to a homogeneous system of equations for the shift of coordinates ΔQ_k between two points as the reaction coordinate

$$\Delta Q_k = a \sum_l \frac{\partial^2 E(Q)}{\partial Q_k \partial Q_l} \Delta Q_l \qquad [88]$$

where the constant a defines the step size. The solution of the system of equations leads to the secular problem for the force constant matrix $F_{kl} = \partial^2 E(Q)/\partial Q_k \partial Q_l$, the direction of motion being determined by its eigenvector. As it turned out (42) the reaction pathway defined in such a manner depended on the selection of coordinates. This dependence can be removed by introducing the mass weighted coordinates (43-46).

$$q_k = \sqrt{m_k}\, Q_k \qquad [89]$$

Apart from the steepest descent path the minimum energy path is often selected (47-49), along which the energy of the system is minimized by optimizing other coordinates for a series of fixed values of a single geometrical parameter. The procedure allows to set up two different reaction pathways, one starting from reactants, the other starting from products (chemical hysteresis)

(50 - 52). The resulting route also depends on the selection of a fixed parameter (53) and can even be discontinuous, or it can bypass the activated complex (50 - 58).

The concept of reaction coordinates can portray the fate of reactants after they have reached the activated complex and also thereafter, a fact that justifies its application. The theory of absolute reaction rates, statistical in nature, does not require any route to be specified as it allows in principle any route, provided it leads from reactants to products.

2.4.2 Thermodynamic and Kinetic Parameters

Quantum chemical calculations of thermodynamic parameters are an offspring of the combination of quantum chemistry and statistical thermodynamics. In a system in thermal equilibrium thermodynamic parameters can be expressed in terms of the partition function Q, defined as

$$Q = \sum_i g_i \, exp\{-(\epsilon_i - \epsilon_0)/kT \qquad [90]$$

the summation running over all quantum states of the system, ϵ_0 represents the zero-point energy and helps overcome the ambiguities in energy scale selection. The respective thermodynamic functions are defined as follows

$$H^0_T = H^0_0 + RT^2(\partial lnQ/\partial T)_p \qquad \text{(standard enthalpy)} \qquad [91]$$

$$S^0_T = Rln(Q/N_A) + RT(\partial lnQ/\partial T)_p \qquad \text{(standard entrophy)} \qquad [92]$$

$$G^0_T = H^0_0 - RTln(Q/N_a) \qquad \text{(standard Gibbs energy)} \qquad [93]$$

$$C^0_p = 2RT(\partial lnQ/\partial T)_p + RT^2(\partial^2 lnQ/\partial^2 T)_p \qquad \text{(standard heat capacity)} \qquad [94]$$

where H_0 is the standard enthalpy at zero degrees, defined as the system's energy E_0 corrected for the zero point vibrations (ZPV correction)

$$E_{ZPV} = \frac{1}{2} N_A \sum_i h\nu_i \qquad [94]$$

ν_i being harmonic vibration frequencies, the summation includes all vibrational degrees of freedom.

Strictly speaking calculation of a partition function should involve summation over all quantum states of the system. Usually however, we resort to simplifications, the principal among them being the assumption of separability of molecular motions allowing also the separation of the expression for the total partition function Q into a product of translation (Q_t), vibration (Q_v), rotation (Q_r), electron excitation (Q_e) and nuclear spin (Q_N) functions

$$Q = Q_tQ_vQ_rQ_eQ_N \qquad [95]$$

In doing so we also assume that for electronic states the vibration and rotation function remains the same; nuclear spin partition function is usually neglected ($Q_N = 1$) (59,60).

The standard translation partition function Q_t uses the potential box to calculate energy levels of a molecule

$$Q_t = (2\pi MkT)^{3/2}RT/h^3 \qquad [96]$$

where M is the molecular weight. Results obtained in a potential box inevitable suffers the loss of precision when transferred to other types of reaction vessels.

Rotation partition function is usually an approximation of a rigid rotator

$$Q_r = \frac{1}{\sigma}\left\{ \frac{8\pi^2IkT}{h^2} + \frac{1}{3} + \frac{1}{15}\,\frac{h^3}{8\pi^2IkT} + \frac{4}{315}\left(\frac{h^2}{8\pi^2IkT}\right)^2\right\} \qquad [97]$$

for linear molecule, and

$$Q_r = \frac{(\pi I_AI_BI_C)^{1/2}}{\sigma}\left(\frac{8\pi^2kT}{h^2}\right)^{3/2} \qquad [98]$$

for non-linear molecule; here I, I_A... represent the principal moments of inertia, σ the symmetry number defining the number of indistinguishable positions a molecule can assume by simple rotation. The symmetry number can be elaborated from the group theory; its value corresponds to the order of the rotation subgroup belonging to the molecular symmetry point group (59).

Extending the above logistic further we express the vibration partition function by an approximation of a harmonic oscillator (61)

$$Q_v = \prod_i \frac{1}{1 - exp(-h\nu_i/kT)} \qquad [99]$$

ν being harmonic frequencies of standard vibration modes.

The electronic partition function can be written as

$$Q_e = \sum_i g_i exp\{-(E_i - E_0)/kT\} \qquad [100]$$

where g_i is the order of degeneracy of the i-th electronic state and E_i its energy above that of the ground state E_0. If the energy difference is large enough (a condition often fulfilled in coordination compounds) the partition function Q_e equals the statistical weight of the ground electronic state. By approximating partition function by a rigid rotator and harmonic oscillator we neglect the centrifugal distortion effects, anharmonicity of vibrations and also vibration-rotation interactions. For diatomic molecules these deficiencies are sometimes corrected (59, 60) and although general correction expressions are available even for bigger molecules (62, 63), their use makes calculations too unwieldy. An important contribution to the value of thermodynamic functions comes from the internal free or retarded rotation respectively. A partition function for a free symmetric rotator is available

$$Q_r = \frac{(8\pi^2 I_m kT)^{1/2}}{h\sigma_m} \qquad [101]$$

wherein σ_m stands for the symmetry number of internal rotator and I_m for the reduced moment of inertia, defined as

$$I_m = I_m^0 \left\{ 1 - I_m^0 \left[\frac{\lambda_{m_A}^2}{I_A} + \frac{\lambda_{m_B}^2}{I_B} + \frac{\lambda_{m_C}^2}{I_C} \right] \right\} \qquad [102]$$

I_m is the moment of inertia of a rotating group with respect to the axis of rotation, λ_{m_A}, λ_{m_B}, λ_{m_C} direction cosines of angles between main molecular axes and the rotation axis.

The potential energy of the retarded internal rotation is usually approximated by the Fourier series

$$V = \frac{1}{2} \sum_k V_k[1 - cos(kn\alpha)] \qquad [103]$$

in which n designates the number of minima at the plot of the retarding potential against the rotation angle α in the interval $0 - 2\pi$. Actually though we can determine at most the first two constants of the series (64, 65), a feat achievable by standard methods of quantum chemistry (66).

To calculate equilibrium constants let us consider a chemical reaction

$$\sum_i^N \nu_i A_i = 0 \qquad [104]$$

in a state of equilibrium, characterized by an equilibrium constant

$$K_p = \prod_{i=1}^N p_i^{\nu_i} \qquad [105]$$

Since

$$ln K_p = - \Delta G_T^0/RT \qquad [106]$$

and also

$$G_T^0 = H_0^0 - RT ln(Q/N_A) \qquad [107]$$

we arrive at an expression for K_p

$$K_p = \prod_{i=1}^{N} (Q/N_A)^{\nu_i} exp(-\Delta H_0^0/RT) \qquad [108]$$

in which ν_i are stoichiometric coefficients, positive for products and negative for reactants.

In such a manner we can calculate the equilibrium constant, provided we know the respective partition functions Q_i of the participating species. Calculations of this sort have become a matter of routine for small (predominantly organic) systems. There were already a number of attempts to calculate equilibrium parameters for coordination compounds, such as for instance the equilibrium of the tetrahedral-square interconversion in a series of tetrahalogenated complexes of the first transition row of elements (67).

The formula for the rate constants of a reaction as given by the theory of activated complex reads as

$$k = \kappa (kT/h) K^{\neq} \qquad [109]$$

where $K^{\neq}$ is the equilibrium constant of the formation of activated complex from reactants and κ a statistical factor (transmission coefficient). The statistical factor is in fact the number of different symmetry operations leading to the identical activated complex and involving equivalent motions of atomic systems or their equivalents (55). Other authors define the transmission coefficient (43, 56) as the number of symmetrically equivalent activated complexes; the number must be multiplied by two when going from symmetric reactants to an unsymmetrical complex, and divided by two if symmetries are reversed.

We see that in fact the activated complex theory reduces the problem of rate constant calculations to calculation of the equilibrium constant $K^{\neq}$ for the process of formation of activated complex from the reactants, i.e. to a problem we have already dealt with. There is however a difference to our earlier explications of the problem, concerning the exclusion of one vibrational degree of freedom of the activated complex (an active vibration leading to products) on account of the complex's motion along the reaction pathway and represented by the partition function kT/h (68,69).

The match between the calculated and experimental values of reaction rate constants is satisfactory in the series of simple reactions, except when the reactions proceed at very low temperatures. In these cases the quantum mechanical tunneling effect is thought to come strongly into play. The effect is often corrected for by applying the Wigner correction (70), which assumes a parabolic shape of the potential barrier

$$\Gamma = 1 - \frac{1}{24}\left(\frac{h\nu^{\neq}}{kT}\right) \qquad [110]$$

$\nu^{\neq}$ being the imaginary frequency of the normal mode of decay of the activated complex. If this value, accessible by the correct vibrational analysis of the activated complex, is not available, it can be approximated by the second derivative of the curvature $A^{\neq}$ of the adiabatic potential (43, 71-73)

$$(\nu^{\neq})^2 = A^{\neq}/(4\pi^2M) \qquad [111]$$

where M is the reduced mass.The correction factor Γ enters the reaction rate equation as a multiplication factor.

2.4.3 Molecular Mechanics

The molecular mechanics belongs to the class of empirical methods based on the assumption that a set of analytic formulas can be used in representing the adiabatic potential (74). Within the framework of valence coordinates (R - bond lengths, ϑ - bond angles and ω - torsion angles) the adiabatic potential E is expressed as

$$E = V_R + V_\vartheta + V_\omega + V_{int} \qquad [112]$$

where V_R stands for the valence potential, V_ϑ - deformation potential, V_ω - torsion potential and V_{int} - interaction terms. The harmonic functions are used in the first approximation to these potentials, namely

$$V_R = (1/2) \sum_i F^R_{ii}\, \Delta R_i^2 \qquad [113]$$

$$V_\vartheta = (1/2) \sum_i F^\vartheta_{ii}\, \Delta\vartheta_i^2 \qquad [114]$$

$$V_\omega = (1/2) \sum_i F^\omega_{ii}\, \Delta\omega_i^2 \qquad [115]$$

with displacement coordinates from the equilibrium ones

$$\Delta R_i = R_i - R_i^0 \qquad [116]$$

$$\Delta\vartheta_i = \vartheta_i - \vartheta_i^0 \qquad [117]$$

$$\Delta\omega_i = \omega_i - \omega_i^0 \qquad [118]$$

The higher order corrections include, for example, the anharmonic terms

$$V_{RRR} = F^{RRR}\ \Delta R_i^3 \qquad [119]$$

and interaction contributions, e.g.

$$V_{R\vartheta} = (1/2)\ F^{R\vartheta}\ \Delta R\ \Delta\vartheta \qquad [120]$$

$$V_{\vartheta\omega} = F^{\vartheta\omega}\ \Delta\vartheta\ \Delta\omega \qquad [121]$$

$$V_{\vartheta\vartheta\omega} = F^{\vartheta\vartheta\omega}\ \Delta\vartheta\ \Delta\vartheta'\ \Delta\omega \qquad [122]$$

The equilibrium coordinates (R_i^0, ϑ_i^0 and ω_i^0) as well as the force constants (F^R,F^ϑ, F^ω, F^{RRR}, $F^{R\vartheta}$, etc.) are taken for the empirical parameters characteristic for a given type of chemical bond and transferable from one molecule to another having similar types of bonds. As an example, in alkanes, the values of $c^R = 71.94$, $F^R = 4.60$, $R^0 = 1.113$ and $F'^R = -2.0$ are used to parametrize the valence potential

$$V_R = c^R\ F^R\ \Delta R^2(1 + F'^R\ \Delta R) \qquad [123]$$

Analogously, $c^\vartheta = 0.021914$, $F^\vartheta = 0.320$, $\vartheta^0 = 109.4$ and $F'^\vartheta = 7.0 \times 10^{-8}$ define the deformation potential

$$V_\vartheta = c^\vartheta\ F^\vartheta\ \Delta\vartheta^2(1 + F'^\vartheta\ \Delta\vartheta^4) \qquad [124]$$

The interaction terms involve also the other types of corrections, e.g. the dipole-dipole interactions

$$V_d = [d_i d_j/(4\pi\varepsilon_0 R_{ij}^3)](cos\beta - 3\ cos\alpha_i cos\alpha_j] \qquad [125]$$

with β - angle of dipoles, α_i - an angle of the dipole d_i relative to the linkage R_{ij}. The van der Waals interactions may be covered by the Lennard-Jones type 6-12 potential

$$V_w = \varepsilon[(R^0/R)^{12} - 2(R^0/R)^6] \qquad [126]$$

where ε is the deepth of the energy minimum, or the Buckingham type potential

$$V_w = [\varepsilon/(1 - 6/\alpha)]\{(6/\alpha)exp[\alpha/(1 - R/R^0)] - (R_0/R)^6\} \qquad [127]$$

Having postulated the analytic form of the adiabatic potential, an energy minimization procedure is applied to reach the total energy minimum from which the equilibrium geometry is read off. The procedure is fast enough to be applied on personal computers and therefore it becomes very popular, especially in combination with geometry visualization programs. Among numerous verions of molecular mechanics (MUB1, MUB2, MM1, MM2, MM3, EAS, CFF-3) the MM2 version is often applied.

2.5 JAHN-TELLER EFFECT

There is an abundant literature concerning the Jahn-Teller effect and related phenomena; various aspects of this topic have been summed up in excellent reviews (75 - 82). Unfortunately, many confusions, misunderstandings and inadequate terminology also can be met in some publications. In trying to rederive the basic equations for the adiabatic potential surface in the presence of (pseudo) degeneracy, both the variation and perturbation methods may be used. It must be noted that they produce different results if nondegenerate, pseudodegenerate or strictly degenerate states are considered. This fact is of great importance. Evidently, a smooth transition must exist between the case of degenerate and pseudodegenerate states, so that the Jahn-Teller effect and the pseudo Jahn-Teller effect should be explained on a common base. Nevertheless, the former has been formulated in a truncated basis set of degenerate electronic states using the 1st order perturbation theory. The latter, on the other hand, used to be explained by the 2nd order perturbation theory (the so called second-order effect) in a complete (infinite) basis set of electronic wave functions (82). The variational formulation, restricting only to the first excited state of an appropriate symmetry, is also known (76). Thus there is need for a more general formulation of vibronic coupling, and the approach outlined by Özkan and Goodman (83) seems to be an appropriate solution of the problem. This section closely resembles their proposal based on the partitioning method.

Another problem originates in the fact that a multimode vibronic coupling should be considered in higher orders of the theory; at least the a_1 mode is to be included beginning with the second order. Therefore the analytic forms of the adiabatic potential surface need a rederivation. Finally, some structural transitions should be either included or deleted from the Jahn-Teller mechanism, and the symmetry descent concept is useful along these lines.

2.5.1 Vibronic Coupling

Let us consider the Schrödinger equation for a molecule: $\hat{H}\Psi = E\Psi$. Its solution may be performed through the following steps:

1) construction of the molecular Hamiltonian;

2) expression of the molecular wave function in a suitable form;

3) application of the matrix partitioning method to reduce the dimensionality of the characteristic problem;

4) introduction of specific approximations that allow the solution of the problem.

The construction of the molecular Hamiltonian $\hat{H}$ is straightforward since it consists of the kinetic energy $\hat{T}$ of all nuclei and electrons and the potential energy $\hat{V}$ of all electrostatic interactions

$$\hat{H}(r,Q) = \hat{T} + \hat{V} = \hat{T}_N(Q) + \hat{T}_e(r) + \hat{V}_{NN}(Q) + \hat{V}_{ee}(r) + \hat{V}_{eN}(r,Q) \qquad [128]$$

$\hat{T}_N$ being the nuclear kinetic energy, $\hat{T}_e$ - the kinetic energy of electrons, $\hat{V}_{NN}$ - the internuclear repulsion, $\hat{V}_{ee}$ - the interelectronic repulsion and $\hat{V}_{eN}$ - the electron-nuclear attraction.

The wave function Ψ depends on all electron coordinates r_i and also on nuclear coordinates Q^0_j. Its exact expression in the Hilbert space is made possible by the expansion of

$$\Psi(r,Q) = \sum_{k=0}^{\infty} f_k(Q)\ \Phi_k(r;[Q^0]) \qquad [129]$$

where the basis set is represented by electronic wave functions $\Phi_k(r;[Q^0])$ for fixed nuclear coordinates Q^0_j, and the expansion coefficients $f_k(Q)$ are the nuclear (vibration) functions. The electronic wave functions are orthonormal and they obey the electronic Schrödinger equation

$$\{\hat{T}_e + \hat{V} - E_k\}\Phi_k(r;[Q]) = 0 \qquad [130]$$

However it is not necessarily fulfilled since

$$\hat{H}^{el}_{kl} = \langle\Phi_k|\hat{T}_e + \hat{V}|\Phi_l\rangle_r = E^0_k\ \delta_{kl} + H'_{kl} \qquad [131]$$

represents a matrix element of the electronic Hamiltonian

$$\hat{H}^{el} = \hat{T}_e + \hat{V} \qquad [132]$$

(it is non-zero, for example, for a couple of degenerate electronic states). Usually $[Q^0]$ is a configuration of nuclei in which $E_k[Q]$ displays a minimum value: $E_k[Q^0] = E^0_k$.

By substituting [129] into the molecular Schrödinger equation

$$\sum_k \hat{H}|\Phi_k\rangle\ f_k = E \sum_k |\Phi_k\rangle\ f_k \qquad [133]$$

which - after multiplication from the left side by $\langle\Phi_l|$ and integration over electronic coordinates - yields the following set of differential equations

$$\sum_k \langle\Phi_l|\hat{H}|\Phi_k\rangle_r\ f_k = E\ f_l \qquad \text{for}\quad l = 1,\ 2,\ \ldots \qquad [134]$$

where

$$\langle\Phi_l|\hat{H}|\Phi_k\rangle_r\ f_k = [\hat{T}_N(Q)\ \delta_{lk} + H^{el}_{lk} + \hat{G}_{lk}(Q)]\ f_k \qquad [135]$$

The non-adiabatic coupling operator

$$\hat{G}_{lk}(Q) = \langle\Phi_l|\hat{T}_N(Q)|\Phi_k\rangle_r - \sum_A^N (\hbar^2/m_A)\,\langle\phi_l|\nabla_A|\Phi_k\rangle_r\,\nabla_A \qquad [136]$$

arises from the operations

$$\{\hat{T}_N(Q)\}(f\Phi) = -\sum_A^N (\hbar^2/2m_A)\,\nabla_A^2\,(f\Phi) =$$

$$= -\sum_A^N (\hbar^2/2m_A)(\Phi\nabla_A^2 f + 2\nabla_A\Phi\nabla_A f + f\nabla_A^2\Phi) \qquad [137]$$

Thus the exact Schrödinger equation for nuclear motion may be rewritten in the form

$$\{\hat{T}_N 1 + \hat{H} - E1\}f = 0 \qquad [138]$$

with the interaction matrix elements

$$\hat{H}_{lk}(Q) = \hat{H}^{el}_{lk} + \hat{G}_{lk}(Q) \qquad [139]$$

This system of equations is of infinite dimension; therefore it can be solved by the partitioning technique.

The complete space of solutions is split into two subspaces: the one S_a covers a limited number of solutions which we are interested in and the other S_b contains the excited states. Fig. 8 shows three most important cases: non-degenerate, pseudodegenerate, and strictly degenerate states within the subspace S_a. With this partitioning Eq. [138] becomes

$$\begin{pmatrix} \hat{H}_{aa} + (\hat{T}_N - E)1_a & ; \hat{H}_{ab} \\ \hat{H}_{ba} & ; \hat{H}_{bb} + (\hat{T}_N - E)1_b \end{pmatrix} \begin{pmatrix} f_a \\ f_b \end{pmatrix} = 0 \qquad [140]$$

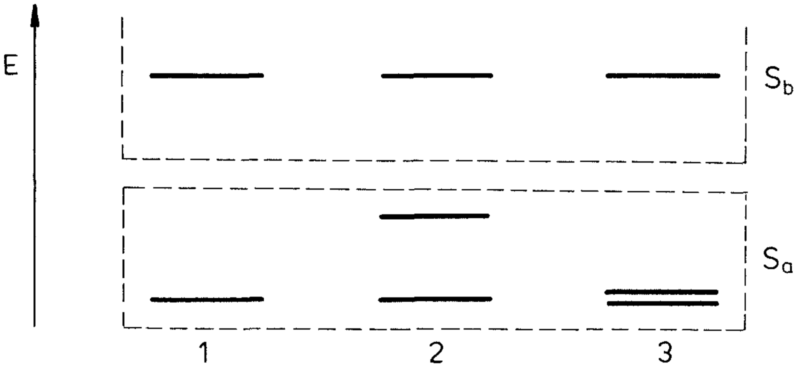

Fig. 8. Partitioning of states into strongly coupled subspace S_a and weakly coupled subspace of excited states S_b: 1 - nondegenerate state; 2 - pseudodegenerate states; 3 - strictly degenerate states.

Here f_a and f_b are column vectors, 1_a and 1_b unit matrices and $\hat{H}_{aa}$, $\hat{H}_{ab}$, $\hat{H}_{ba}$ and $\hat{H}_{bb}$ are the submatrices of the given order. From the second equation for submatrices, one can express

$$f_b = \hat{R}_{bb}\hat{H}_{ba}f_a \qquad [141]$$

using the resolvent

$$\hat{R}_{bb} = (E1_b - \hat{T}_N 1_b - \hat{H}_{bb})^{-1} \qquad [142]$$

Thus the solution of [49] may be found in the form of

$$\hat{H}^{eff}_{aa} f_a = E\ f_a \qquad [143]$$

for the effective Hamiltonian in the subspace S_a of strongly coupled functions

$$\hat{H}^{eff}_{aa} = \hat{T}_N 1_a + U_{aa} = \hat{T}_N 1_a + \hat{H}_{aa} + \hat{H}_{ab}\hat{R}_{bb}\hat{H}_{ba} \qquad [144]$$

Equation [143] is of principal significance since it is still the exact Schrödinger equation for nuclear motion in an applicable form.

In order to express the resolvent, the following formula should be applied to square matrices A and B

$$(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1} = A^{-1} + A^{-1}BA^{-1} +$$
$$+ A^{-1}BA^{-1}B(A - B)^{-1} + \ldots = A^{-1}\sum_{p=0}^{\infty}(BA^{-1})^p \qquad [145]$$

Hence,

$$\hat{R}_{bb} = [(E^0 1_b - E^0_b) - (\hat{T}_N 1_b - \epsilon 1_b + H'_{bb} + \hat{G}_{bb})]^{-1} \qquad [146]$$

may be written in various degrees of approximation, viz.

$$\hat{R}^{(0)}_{bb} = 0 \qquad [147]$$

$$\hat{R}^{(1)}_{bb} = (E^0 1_b - E^0_b)^{-1} \qquad [148]$$

$$\hat{R}^{(2)}_{bb} = \hat{R}^{(1)}_{bb} + (E^0 1_b - E^0_b)^{-1}(\hat{T}_N 1_b - \epsilon 1_b + \hat{H}'_{bb} + \hat{G}_{bb}).$$
$$.(E^0 1_b - E^0_b)^{-1} \qquad [149]$$

where

$$\epsilon = E - E^0 \qquad [150]$$

is a pure vibration energy. The partitioning [146] guarantees that [148] is a good approximation to the resolvent since the second term in parentheses practically vanishes (B → 0).

Also the electron interaction may be expressed in the form of a Taylor series

$$H^{el}_{kl} = E^0_k\ \delta_{kl} + H'_{kl} = E^0_k\ \delta_{kl} + H^{(1)}_{kl} + H^{(2)}_{kl} + \ldots \qquad [151]$$

where

$$H_{kl}^{(1)} = \sum_{r} \langle\Phi_{k}^{0}|[\partial(\hat{T}_{e} + \hat{V})/\partial Q_{r}]_{0}|\Phi_{l}^{0}\rangle \, \Delta Q_{r} \quad [152]$$

$$H_{kl}^{(2)} = \frac{1}{2} \sum_{r,s} \langle\Phi_{k}^{0}|[\partial^{2}(\hat{T}_{e} + \hat{V})/\partial Q_{r}\partial Q_{s}]_{0}|\Phi_{l}^{0}\rangle \, \Delta Q_{r}\Delta Q_{s} \quad [153]$$

etc. The operator $\hat{T}_e$ may be omitted here since it is not a function of nuclear coordinates Q_r. For the same reason $\hat{V}$ becomes reduced to $\hat{V}_{NN} + \hat{V}_{eN}$ only. The summations run over all internal displacement coordinates ΔQ_r (usually symmetric coordinates measured relative to Q^0).

At this point, approximate expressions of [134] may be formulated. The usual treatment is to neglect the non-adiabatic coupling tems by setting $\hat{G}_{kl} \to 0$. Thus the interaction matrix elements $\hat{H}_{kl} \to \hat{H}_{kl}^{el}$ represent the potential energy in the Schrödinger equation [138] for nuclear motion. In the limiting case of frozen nuclei ($\hat{T}_N \to 0$), the eigenvalues of H_{kl}^{el} become the total energy (because $\varepsilon \to 0$) and they represent the adiabatic potential surface.

Five important cases may be distinquished within the Born-Oppenheimer approximation (Table 3) in which the adiabatic potential surface originates:

1) The zeroth-order approximation to the resolvent [147] corresponds to the truncated basis set ($S_b \to 0$). If $\dim(S_a) = 1$, a non-degenerate state is under consideration. The adiabatic potential is simply $U_{kk} = E_k^0$, i.e. it is solution of the electronic Schrödinger equation [130]. In addition, if diagonal matrix elements $\hat{G}_{kk}(Q)$ are considered within the adiabatic approximation, the modified adiabatic adiabatic potential $U_{kk} = E_k^0 + \hat{G}_{kk}(Q)$ is obtained.

2) If $\dim(S_a) > 1$ within the truncated basis set and $E_k^0 \approx E_l^0$, the case of pseudodegenerate states is considered. The adiabatic potential is obtained by solving the secular equation

$$\det\{U_{kl} - E\,\delta_{kl}\} = 0 \quad [154]$$

with

$$U_{kl} = E_k^0\,\delta_{kl} + H_{kl}^{(1)} + H_{kl}^{(2)} + \ldots \quad [155]$$

This solution follows from application of the variation method.

3) If $E_k^0 = E_l^0$ holds within the truncated basis set, the strict degeneracy of electronic states occurs; usually twofold to fivefold degeneracy comes into consideration. The adiabatic potential may again be obtained from [154]. This formulation is consistent with the results of the 1st-order perturbation theory for degenerate states.

TABLE 3
Origin of the adiabatic potential.

Case	*dim*(S_a)	*dim*(S_b)	$R^{(n)}$	Interaction matrix elements	
Non degenerate state	1	0	$R^{(0)}$	$U_{kk} = E_k^0$	(a)
				$U_{kk} = E_k^0 + \hat{G}_{kk}(Q)$	(b)
Pseudodegenerate states within truncated basis set	1	0	$R^{(0)}$	$U_{lk} = E_k^0\delta_{lk} + H_{lk}^{(1)}$	(c)
Degenerate states within truncated basis set	d	0	$R^{(0)}$	$U_{lk} = E_0^0\delta_{lk} + \hat{H}_{lk}^{(1)} + \hat{H}_{lk}^{(2)}$	(d)
Ground state weakly coupled with excited states	1	∞	$R^{(1)}$	$U_{kk} = E_k^0 + \sum_{j\in N_b} \hat{H}_{kj}^{(1)} \cdot \hat{H}_{jk}^{(1)}/(E_k^0 - E_j^0)$	(e)
(Pseudo)degenerate states weakly coupled with excited states	d	∞	$R^{(1)}$	$U_{lk} = E_k^0\delta_{lk} + H_{lk}^{(1)} + H_{lk}^{(2)} + \sum_{j\in N_b} H_{lk}^{(1)} \cdot H_{jk}^{(1)}/(E_k^0 - E_j^0)$	(f)

a) Born-Oppenheimer approximation.

b) Adiabatic approximation.

c) Consistent with the variation method; pseudo Jahn-Teller effect.

d) Consistent with the first-order perturbation theory; Jahn-Teller effect or Renner-Teller effect.

e) Consistent with the second-order perturbation theory; pseudo Jahn-Teller effect.

f) General theory of vibronic coupling.

4) If dim(S_a) = 1 and the complete basis set is considered, i.e. dim(S_b) → ∞, weak coupling of the ground state with the excited states is taken into account. The resolvent in the form of [58] yields

$$U_{kk} = E_k^0 + \sum_{j\in S_b} H_{kj}^{(1)} H_{jk}^{(1)}/(E_k^0 - E_j^0) \tag{156}$$

This formulation is consistent with the result of the second-order perturbation theory for the energy (the first-order wave function).

5) A more general case appears if dim(S_a) > 1 and weak coupling with excited states is considered via $\hat{R}_{bb}^{(1)}$. Thus

$$U_{kl} = E^{0}_{k}\delta_{kl} + H^{(1)}_{kl} + H^{(2)}_{kl} + \ldots + \sum_{j\in S_b} H^{(1)}_{kj}\, H^{(1)}_{jl}/(E^{0}_{k} - E^{0}_{j}) \qquad [157]$$

This formula is applicable for both degenerate and pseudodegenerate states. The formulation of [157] allows consideration of the Jahn--Teller effect, the pseudo Jahn-Teller effect and the Renner-Teller effect on a common basis in an arbitrary degree of approximation and the basis-set dimension.

Let us consider the Eq.[154] in which the concept of the adiabatic potential surface originates. If the diagonal matrix elements are arranged in ascending order, $U_{11} < U_{22} < \ldots$, the non-zero off--diagonal elements cause at least one eigenvalue to fulfil the inequality $E_1 < U_{11}$. This result follows from the well known separation theorem (84). A proof for the 2x2 problem is trivial since

$$2E_{1,2} = U_{11} + U_{22} \pm [(U_{11} - U_{22})^2 + 4U^2_{12}]^{1/2} \qquad [158]$$

Jahn and Teller have found (85, 86) that it is valid for any non-linear molecule

$$H^{(1)}_{kl} = \sum_{r} \langle\Phi^{0}_{k}|[\partial(\hat{V}_{NN} + \hat{V}_{eN})/\partial Q_r]_0|\Phi^{0}_{l}\rangle\, \Delta Q_r \neq 0 \qquad [159]$$

so that at least one vibrational mode Q_r exists for which the irreducible repersentation $\Gamma(Q_r)$ is contained in the symmetrized direct product of wave functions

$$[\Gamma_k \otimes \Gamma_l] = \Gamma_{red} = \Gamma(Q_r) + \ldots \qquad [160]$$

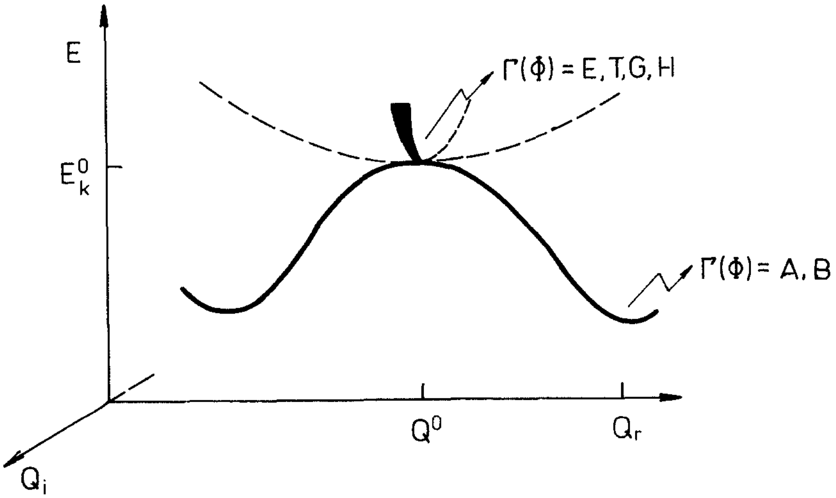

Fig. 9. Energy (symmetry) lowering along vibronic active coordinate Q_r.

(condition for the non-zero $\langle r_k | r(Q_r) | r_l \rangle$ type matrix element). This finding excludes the existence of an extremum at the point Q^0 of electron degeneracy (Fig. 9). Accordingly, the Jahn-Teller theorem may be formulated as:

The electronic wave function corresponding to the minimum of the adiabatic potential cannot be orbitally degenerate (except in linear geometry); or a non-linear polyatomic configuration with a degenerate electronic state has a non-zero energy gradient and thus no energy minimum (it is unstable).

The theorem can be proved by looking at all point groups and their irreducible representations, taking into account the rules for the direct product of multidimensional irreducible representations (87). A more general proof of the Jahn-Teller theorem can be found in (75, 88, 89).

Three effects based on the Jahn-Teller theorem can be distinguished (Fig. 10).

1) The Jahn-Teller effect arises from the strict degeneracy at the reference geometry of a non-linear molecule as a consequence of $H_{kl}^{(1)} \neq 0$. Consequently, a symmetry descent with respect to Q^0 proceeds, and the electron degeneracy is removed. It has been termed the first-order effect although some second-order terms $H_{kl}^{(2)}$ adopt non-zero values; they are responsible for the stabilization of the respective geometry.

2) The Renner-Teller effect take place for linear polyatomic molecules where $H_{kl}^{(1)} = 0$. It has a consequence of the fact that the distortion modes Σ^- and Π are absent within $[\Pi \otimes \Pi] = \Sigma^+ + \Delta$, etc. As the $H_{kl}^{(2)}$ adopt a leading role, it has been termed the second-order effect. Depending on the value of $H_{kl}^{(2)}$, a bending of the linear molecule may occur.

3) The pseudo Jahn-Teller effect occurs for pseudodegenerate states. Either

$$E_{kk}^{(2)} = \sum_{j \in S_b} H_{kj}^{(1)} H_{jk}^{(1)} / (E_k^0 - E_j^0) \neq 0 \qquad [161]$$

or

$$H_{kl}^{(1)} \neq 0 \text{ , } E_k^0 < E_l^0 \qquad [162]$$

are responsible for its existence. It has been termed the second-order effect, according to the use of the 2nd-order perturbation theory.

The usual procedure is to apply a Taylor expansion for the adiabatic potential

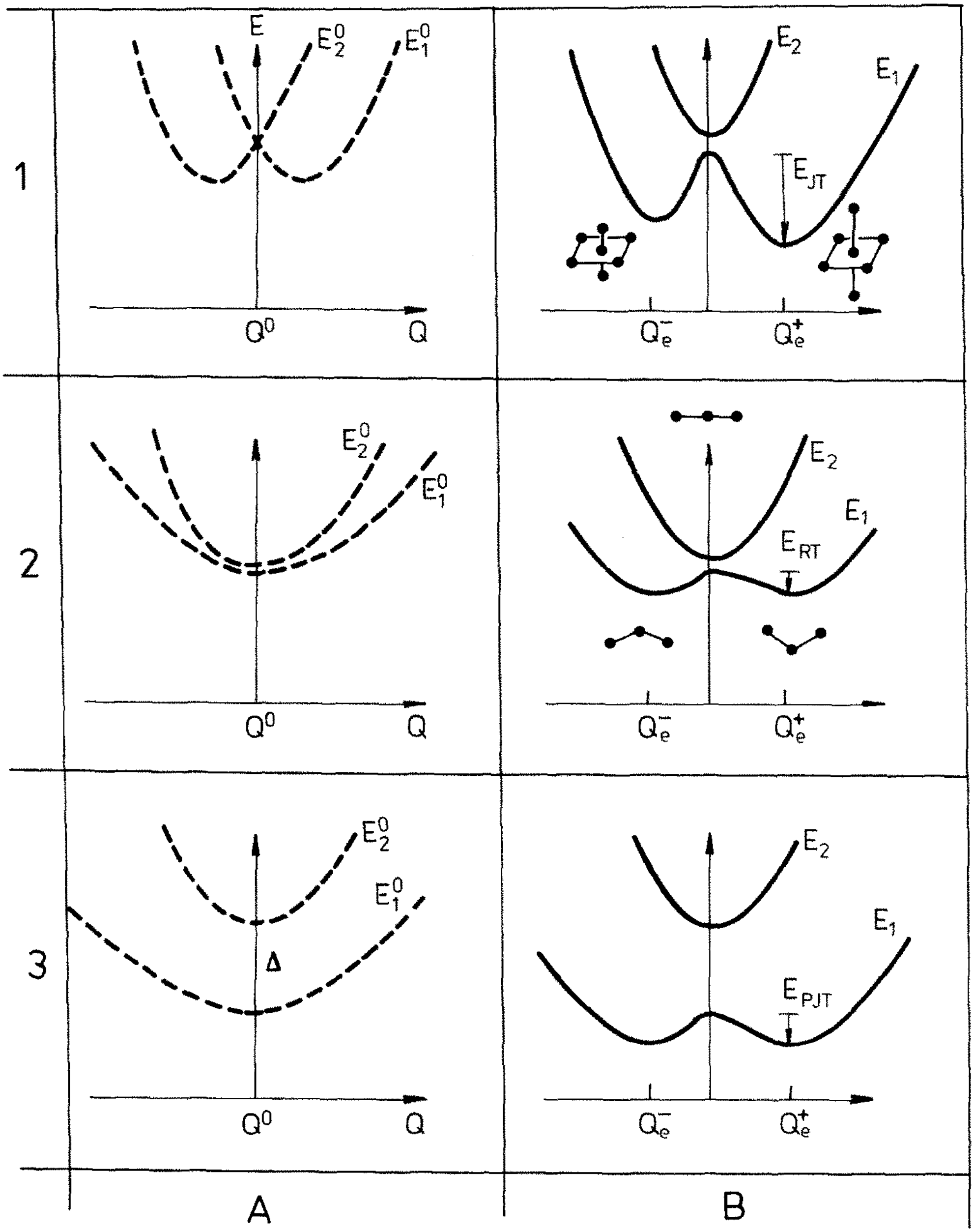

Fig. 10. Three effects of vibronic interactions: 1 - Jahn-Teller effect; 2 - Renner-Teller effect; 3 - pseudo Jahn-Teller effect; A - before interaction, B - after interaction.

$$E(\ldots Q_i \ldots) = E^0 + K_1Q_1 + K_2Q_2 + (1/2)\ K_{11}Q_1^2 + K_{12}Q_1Q_2 + \\ + (1/2)\ K_{22}Q_2^2 + \ldots \qquad [163]$$

where the gradient components

$$K_i = (\partial E/\partial Q_i)_0 = \langle\Phi_0|[\partial(\hat{V}_{NN} + \hat{V}_{eN})/\partial Q_i]_0|\Phi_0\rangle = F_i + X_i \qquad [164]$$

vanish at the extremum point Q^0, so that the pure nuclear term, F_i, and the electron-nuclear term, X_i, are cancelled. The second derivatives

$$K_{ij} = [\partial^2 E/\partial Q_i \partial Q_j]_0 = \langle\Phi_0|[\partial^2(\hat{V}_{NN} + \hat{V}_{eN})/\partial Q_i \partial Q_j]_0|\Phi_0\rangle + \\ + [\partial^2 E_{00}^{(2)}/\partial Q_i \partial Q_j]_0 \qquad [165]$$

represent the harmonic force constants. The last term originates in the weak coupling with excited states and it gives a negative contribution to K_{ij} (83). Higher-order force constants like K_{ijk} and K_{ijkl} describe the anharmonicity effects. Equation [163] is only applicable for the non-degenerate electronic states near the reference configuration Q^0. A better description is obtained in relative coordinates.

The occurence of electron degeneracy brings two effects. First, the molecular Hamiltonian is invariant with respect to arbitrary symmetry operations, so that the adiabatic potential belongs to the totally symmetric representation (A-type or Σ-type). Therefore, only certain combinations of Q_iQ_j or $Q_iQ_jQ_k$ are allowed for symmetry coordinates and they must span the totally symmetric representation. Secondly, the interaction matrix U

$$U_{kl} = E^0_{kl}\delta_{kl} + H^{(1)}_{kl} + H^{(2)}_{kl} + \ldots = E'_{kl}\delta_{kl} + V_{kl} \qquad [166]$$

has a scalar part

$$E'_k = E^0_k + \sum_r K_rQ_r + (1/2)\sum_{r,s} K_{rs}Q_rQ_s + \ldots \qquad [167]$$

and a non-scalar part

$$V_{kl} = V^{(1)}_{kl} + V^{(2)}_{kl} + \ldots = \sum_r \langle\Phi^0_k|[\partial\hat{V}_{eN}/\partial Q_r]_0|\Phi^0_l\rangle\Delta Q_r + \\ + (1/2)\sum_{r,s} \langle\Phi^0_k|[\partial^2\hat{V}_{eN}/\partial Q_r \partial Q_s]_0|\Phi^0_l\rangle\Delta Q_r\Delta Q_s + \ldots \qquad [168]$$

The scalar part yields the usual (harmonic) Taylor expansion of the adiabatic potential, where the force constants occur. The non-scalar part may be reduced according to the Wigner-Eckart theorem to

$$V^{r}_{kl} = <\Phi^{0}_{k}|[\partial\hat{V}_{eN}/\partial Q_{r}]_{0}|\Phi^{0}_{l}> = X(\Gamma_{k}\Gamma_{l};\ \Gamma_{r}) \left\langle \begin{matrix}\Gamma_{l} & \Gamma_{r}\\ \gamma_{l} & \gamma_{r}\end{matrix} \middle| \begin{matrix}\Gamma_{k}\\ \gamma_{k}\end{matrix} \right\rangle N \qquad [169]$$

where $X(\Gamma_k\Gamma_l;\Gamma_r) = X_{\Gamma r}$, is the reduced matrix element (considered as a parameter or the vibronic constant) and the Clebsh-Gordan coefficients have been tabulated (N is a conventional normalization factor). The reduction of a quadratic term, V^{rs}_{kl}, needs a succesive decomposition of the operator part, $[\partial^2\hat{V}_{eN}/\partial Q_r\partial Q_s]_0$, according to the Wigner formula

$$\left| \begin{matrix}\Gamma_{r} & \Gamma_{s}\\ \gamma_{r} & \gamma_{s}\end{matrix} \right\rangle = \sum_{\Gamma,\gamma} \begin{pmatrix}\Gamma_{r} & \Gamma_{s} & \Gamma\\ \gamma_{r} & \gamma_{s} & \gamma\end{pmatrix} |\Gamma_{r}\Gamma_{s}\Gamma_{\gamma}> \qquad [170]$$

where the 3j-symbols (or Wigner coefficients) in parentheses also have been tabulated. The summations run over all Γ and γ contained in the reducible representation of the direct product $\Gamma_r \otimes \Gamma_s$.

Thus $V^{(2)}$ is the scalar convolution of two second-rank tensors, their components forming the basis of the $\Gamma_r \otimes \Gamma_s$ direct product.

In this way, the non-scalar part forms a symmetric matrix **V**; its elements are a linear function of vibronic constants X and nuclear displacements ($Tr\{\mathbf{V}\} = 0$). Its eigenvalues ϵ'

$$det\{V_{kl} - \epsilon'\delta_{kl}\} = 0 \qquad [171]$$

represent a vibronic correction to the harmonic form of the adiabatic potential

$$E_k = E'_k + \epsilon'_k \qquad [172]$$

This correction is responsible for the warping of the adiabatic potential surface near the nuclear configuration with electron degeneracy. The analytic form of the adiabatic potential surface becomes a non-linear (not only polynomial) function of nuclear displacements in which potential constants of two kinds occur. The force constants K_i, K_{ii}, K_{iik}, etc. contain the pure nuclear term F_i, F_{ii}, F_{iik}, etc. as well as the electron-nuclear (vibronic) term X_i, X_{ii}, X_{iik}, etc. The vibronic constants X_i, X_{ii},X_{iik}, etc. enter into the vibronic correction term ϵ'. They determine a warping of the adiabatic potential surface and they can couple vibration modes of different symmetry, e.g. X_{ij} for $i \neq j$.

With the exception of icosahedral groups, only three basic types of vibronic coupling are possible:

1) the three-mode coupling T-$(a_1 + e + t_2)$ for cubic groups (T_d, T_h, T, O_h and O) with triply degenerate electronic terms;

2) the three-mode coupling E-$(a_1 + b_1 + b_2)$ for groups D_{4h}, C_{4v}, C_{4h}, C_4, S_4, D_{2d}, etc., where $E \otimes E = A_1 + A_2 + B_1 + B_2$ holds;

3) the two-mode coupling $E-(a_1 + e)$ for the remaining groups with doubly degenerate electronic terms.

Usually the a_1 mode (the totally symmetric coordinate Q_1) is deleted from consideration since it has no influence in the linear approximation of $V_{kl}^{(1)}$. In quadratic approximation, however, this mode couples with other vibronic active modes.

In order to illustrate the behaviour of $E-(a_1 + e)$ coupling, let us consider the displacements $Q_1(a_{1g})$, $Q_2(e_g)$ and $Q_3(e_g)$. From Section 1.3.2 it follows that

$$V = V^{(1)} + V^{(2)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} [X_e Q_2 + X_{ae} Q_1 Q_2 + X_{ee} Q_2 Q_3/\sqrt{2}] +$$

$$+ \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} [X_e Q_3 + X_{ae} Q_1 Q_3 + X_{ee}(Q_2^2 - Q_3^2)/(2\sqrt{2})] \qquad [173]$$

The quadratic part

$$V^{(2)} = V^{(2)}[a + e, a + e] + V^{(2)}[t,t] + V^{(2)}[a + e, t] =$$

$$= \frac{1}{2} \sum_{r=1}^{3} \sum_{s=1}^{3} V^{rs}[a + e, a + e] \Delta Q_r \Delta Q_s +$$

$$+ \frac{1}{2} \sum_{r=4}^{15} \sum_{s=4}^{15} V^{rs}[t,t] \Delta Q_r \Delta Q_s + \frac{1}{2} \sum_{r=1}^{3} \sum_{s=4}^{15} V^{rs}[a+e, t] \Delta Q_r \Delta Q_s \qquad [174]$$

includes the first term only. The second term is not considered within $E_g-(a_{1g} + e_g)$ coupling model. The last term vanishes exactly by the symmetry. In this way, the number of 2x15x15x2 = 900 quadratic integrals, V_{kl}^{rs}, becomes reduced to 16 non-zero elements.

Since the potential matrix U adopts the form of (definition of the matrix C_1, C_2 and C_3 see in the Section 1.3.2)

$$U = E^0 1 + H^{(1)} + H^{(2)} = E' 1 + V^{(1)} + V^{(2)} = c_1 C_1 + c_2 C_2 + c_3 C_3 \qquad [175]$$

its eigenvalues are

$$E = c_1 \pm [(c_2^2 + c_3^2)/2]^{1/2} \qquad [176]$$

The vibronic correction to the adiabatic potential yields

$$\epsilon' = \pm [(X_e + X_{ae} Q_1)^2 (Q_2^2 + Q_3^2)/2 + X_{ee}^2 (Q_2^2 + Q_3^2)/16 +$$

$$+ X_{ee}(X_e + X_{ae} Q_1) Q_3 (3Q_2^2 - Q_3^2)/(2\sqrt{2})]^{1/2} \qquad [177]$$

With the polar coordinates

$$\rho = (Q_2^2 + Q_3^2)^{1/2} \qquad [178]$$

$$\varphi = arctg(Q_2/Q_3) \qquad [179]$$

and the substitutions

$$A = X_e/\sqrt{2} \qquad [180]$$

$$B = X_{ee}/4 \qquad [181]$$

$$Z = X_{ae}/\sqrt{2} \qquad [182]$$

for vibronic constants, the analytic form of the adiabatic potential surface is

$$E_1(Q_1,\rho,\varphi) = E^0 + (1/2)\, K_{aa}Q_1^2 + (1/2)\, K_{ee}\rho^2 \pm \rho[(A + ZQ_1)^2 + \\ + B^2\rho^2 - 2(A + ZQ_1)B\rho\, cos(3\varphi)]^{1/2} \qquad [183]$$

In graphic representation, a "Mexican-hat" potential with warping is obtained (Fig. 11).

This result is valid for an arbitrary molecular system with E-(a_1 + e) coupling. Important examples are:

1) the octahedron (O_h) with tetragonal distortions;
2) the tetrahedron (T_d);
3) the cube of O_h symmetry;
4) the triangle of D_{3h} symmetry;
5) the antiprism of D_{3d} symmetry;
6) the linear system with $X_e = 0$ (Renner-Teller effect) where $\varepsilon' = \pm\ |X_{ee}|\rho^2$.

Since the above potential [183] includes the vibrational part to the second order and the vibronic corrections to the second order as well, it is called [2/2]-potential within the E-(a_1 + e) coupling.

The second type of vibronic coupling E-(a_1 + b_1 + b_2) is characterized by $Q_1(a_{1g})$, $Q_2(b_1)$ and $Q_3(b_2)$ modes and it yields

$$V = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} [(X_2 + X_{12}Q_1)Q_2] + \\ + \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} [(X_3 + X_{13}Q_1)Q_3] \qquad [184]$$

so that the vibronic correction is (90 - 92)

$$\varepsilon' = \pm\ [(X_2 + X_{12}Q_1)^2Q_2^2/2 + (X_3 + X_{13}Q_1)^2Q_3^2/2]^{1/2} \qquad [185]$$

Finally, the last type of vibronic coupling is T-(a_1 + e + t_2); it operates over six coordinates $Q_1(a_{1g})$, Q_2 and $Q_3(e_g)$, Q_4, Q_5 and $Q_6(t_{2g})$ for the octahedral reference configuration. The corresponding matrix elements V_{ij} are listed in Table 4 and the vibration corrections to the adiabatic potential ε' are obtained as eigenvalues of this 3x3 matrix.

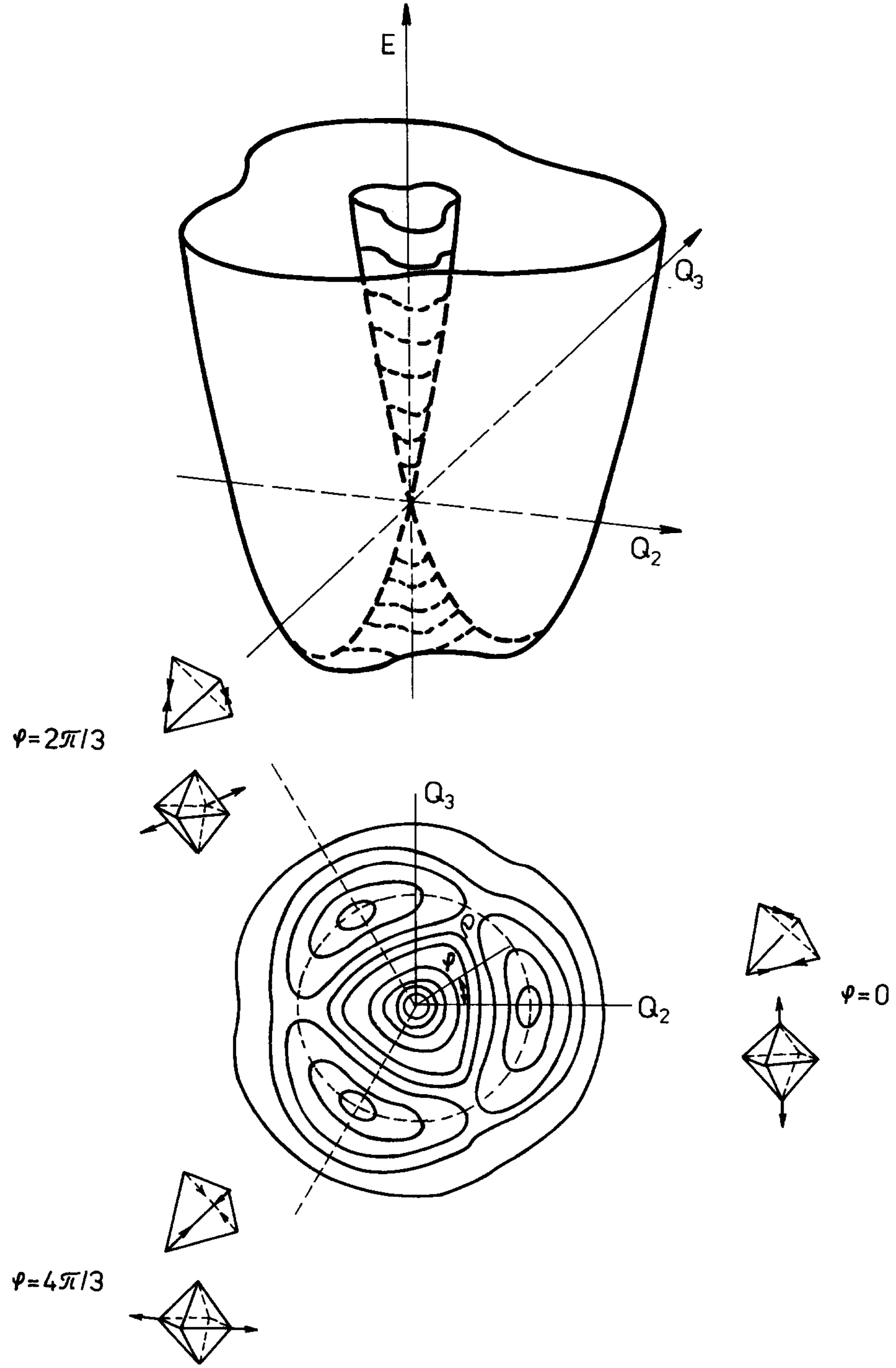

Fig. 11. Representation of the adiabatic potential surface for the E-e vibronic coupling.

Table 4 summarizes the expressions for the vibronic matrix elements V_{ij}, which all correspond to the [2/2]-type of the adiabatic potential.

TABLE 4

Vibronic matrix elements of the [2/2] complexity.

Type of coupling	Active vibrations	$V_{kl} = V_{lk}$
$T-(a_1+e+t_2)$	$Q_1(a_{1g}), Q_2(e_g),$ $Q_3(e_g), Q_4(t_{2g}),$ $Q_5(t_{2g}), Q_6(t_{2g})$	$V_{11} = X_e(Q_3-\sqrt{3}Q_2)/2+X_{ee}(Q_2^2-Q_3^2-2\sqrt{3}Q_2Q_3)/2+X_{ae}Q_1(Q_3-3\sqrt{3}Q_2)/2+X_{tt}(-2Q_4^2+Q_5^2+Q_6^2)/\sqrt{6}$ $V_{12} = X_tQ_6-X_{et}Q_3Q_6+X_{tt}Q_4Q_5+X_{at}Q_1Q_6$ $V_{13} = X_tQ_5+X_{et}Q_5(Q_3+\sqrt{3}Q_2)/2+X_{at}Q_1Q_5+X_{tt}Q_4Q_6$ $V_{22} = X_e(Q_3+\sqrt{3}Q_2)+X_{ee}(Q_2^2-Q_3^2+2\sqrt{3}Q_2Q_3)/2+X_{ae}Q_1(Q_3+3\sqrt{3}Q_2)/2+X_{tt}(Q_4^2-2Q_5^2+Q_6^2)/\sqrt{6}$ $V_{23} = X_tQ_4+X_{et}Q_4(Q_3-\sqrt{3}Q_2)/2+X_{at}Q_1Q_4+X_{tt}Q_5Q_6$ $V_{33} = -X_eQ_3-X_{ee}(Q_2^2-Q_3^2)+X_{tt}(Q_4^2+Q_5^2-2Q_6^2)/\sqrt{6}-X_{ae}Q_1Q_3$
$E-(a_1+b_1+b_2)$	$Q_1(a_{1g}), Q_2(b_1),$ $Q_3(b_2)$	$V_{11} = -V_{22} = (X_{13}Q_1-X_3)Q_3/\sqrt{2}$ $V_{12} = (X_2-X_{12}Q_1)Q_2/\sqrt{2}$
$E-(a_1+e)$	$Q_1(a_{1g}), Q_2(e_g),$ $Q_3(e_g)$	$V_{11} = -V_{22} = -[X_{ae}Q_1Q_3+X_{ee}(Q_2^2-Q_3^2)/(2\sqrt{2})]/\sqrt{2}+X_eQ_3/\sqrt{2}$ $V_{12} = (X_{ae}Q_1Q_2+X_{ee}Q_2Q_3/\sqrt{2})/\sqrt{2}+X_eQ_2/\sqrt{2}$

2.5.2 Approximations to E - (a_1 + e) Vibronic Coupling

Works dealing with the static Jahn-Teller effect usually are based on the adiabatic potential in which only the single mode E-e coupling is considered. Within this more approximative approach, the coupling constants X_{ae} is ommited and the [2/2] potential is simplified to

$$E = E^0 + (1/2)\ K_{aa}Q_1^2 + (1/2)\ K_{ee}\rho^2 \pm$$
$$\pm\ \rho[A^2 + B^2\rho^2 - 2AB\rho\ cos(3\varphi)]^{1/2} \qquad [186]$$

The ways of determining the potential parameters K_{aa}, K_{ae}, A and B, as well as the Jahn-Teller radius ρ_0, are discussed elsewhere (75, 76, 80). The last formula differs from [183] only by the substitution of $A_1 + ZQ$ for A. Notice that $Z \approx X_{ae}$ should be considered as an observable that differs from $B \approx X_{ee}$ (unlike the assumption of Coffman (93)).

Several authors (80, 94, 95) have tried to introduce a third-order term

$$K^{(3)} = K_{eee}(3Q_2^2Q_3 - Q_3^3) = -\ K_{eee}\rho^3 cos(3\varphi) \qquad [187]$$

where the constant K_{eee} has a dimension of energy per volume. This term is also responsible for warping the "Mexican-hat" -type potential. The corresponding [3/1] potential

$$E = E^0 + (1/2)\ K_{ee}\rho^2 \pm A\rho - K_{eee}\rho^3 cos(3\varphi) \qquad [188]$$

has extreme points (three absolute minima and three saddle points) for a angular coordinates $\varphi = n\pi/3$ ($n = 1, 2, 3$), which are analogous to Eq. [186].

A more complex [3/2] potential within E-e coupling model was considered by Goodenough (96) in the form of

$$E = E^0 + (1/2)\ K_{ee}\rho^2 - K_{eee}\rho^3 cos(3\varphi) \pm$$
$$\pm\ \rho[A^2 + B^2\rho^2 - 2AB\rho\ cos(3\varphi)]^{1/2} \qquad [189]$$

Its counterpart within the more sophisticated $E-(a_1 + e)$ coupling scheme is

$$E = E^0 + (1/2)K_{aa}Q_1^2 + (1/2)K_{ee}\rho^2 +$$
$$+\ K_{aaa}Q_1^3 + K_{aee}Q_1\rho^2 - K_{eee}\rho^3 cos(3\varphi) \pm$$
$$\pm\ \rho[(A + ZQ_1)^2 + B^2\rho^2 - 2(A + ZQ_1)B\rho\ cos(3\varphi)]^{1/2} \qquad [190]$$

The necessity to include a cubic term $K^{(3)}$ was discussed elsewhere (94). Only certain combinations of K_{ijk} are possible since the molecular Hamiltonian spans the totally symmetric representation (a_1 or σ^+) of the symmetry point group G_0. The method outlined by Goodenough (166) may be used in determining $K^{(3)}$ or higher-order terms.

Finally, Englman (75) presented the third-order vibronic correction in the form of

$$V^{(3)} = \frac{\sqrt{6}}{8}\,(Q_2^2 + Q_3^2)\begin{pmatrix} -Q_3 & Q_2 \\ Q_2 & Q_3 \end{pmatrix} X_{eee} \qquad [191]$$

The corresponding [3/3] potential within the E-e coupling scheme is

$$E = E^0 + (1/2)K_{ee}\rho^2 - K_{eee}\rho^3 cos(3\varphi)\ \pm$$

$$\pm\ \rho[(A + C\rho^2)^2 + B^2\rho^2 - 2(A + C\rho^2)B\rho\ cos(3\varphi)]^{1/2} \qquad [192]$$

where $C = X_{eee}\sqrt{6}/8$. No additional warping is obtained by the third-order vibronic correction, and a formal analogy with [190] is evident.

With the results of Section 1.3.2 a complete third-order vibronic term can be obtained

$$V^{(3)} = C_2\left\{X_{aae}Q_1^2Q_2/2 + X_{aee}Q_1Q_2Q_3/\sqrt{2} + (\sqrt{2} + 1)X_{eee}Q_2(Q_2^2 + Q_3^2)/12\right\} +$$

$$+\ C_3\left\{X_{aae}Q_1^2Q_3/2 + X_{aee}Q_1(Q_2^2 - Q_3^2)/(2\sqrt{2}) +\right.$$

$$\left.+\ (\sqrt{2} + 1)X_{eee}Q_3(Q_2^2 + Q_3^2)/12\right\} \qquad [193]$$

Thus the vibronic matrix becomes

$$V = V^{(1)} + V^{(2)} + V^{(3)} =$$

$$= \sqrt{2}C_2[A_1Q_2 + 2A_2Q_2Q_3] + \sqrt{2}C_3[A_1Q_3 + A_2(Q_2^2 - Q_3^2)] =$$

$$= A_1\begin{pmatrix} -Q_3 & Q_2 \\ Q_2 & Q_3 \end{pmatrix} + A_2\begin{pmatrix} -(Q_2^2 - Q_3^2); & 2Q_2Q_3 \\ 2Q_2Q_3 & ;(Q_2^2 - Q_3^2) \end{pmatrix} \qquad [194]$$

with

$$A_1 = \frac{1}{\sqrt{2}}\left[X_e + X_{ae}Q_1 + X_{aae}Q_1^2/2 + (\sqrt{2} + 1)X_{eee}(Q_2^2 - Q_3^2)/12\right] \qquad [195]$$

$$A_2 = \frac{1}{2\sqrt{2}}\left[\frac{1}{\sqrt{2}}X_{ee} + \frac{1}{\sqrt{2}}X_{aee}Q_1\right] \qquad [196]$$

The vibronic correction is

$$\varepsilon' = \pm\ \{(A_1Q_2 + 2A_2Q_2Q_3)^2 + [A_1Q_3 + A_2(Q_2^2 - Q_3^2)]^2\}^{1/2} =$$

$$= \pm\ \rho[A_1^2 + A_2^2\rho^2 - 2A_1A_2\rho\ cos(3\varphi)]^{1/2} \qquad [197]$$

so that the adiabatic potential adopts the final form of

$$E = E^0 + K_{aa}Q_1^2/2 + K_{ee}\rho^2/2 + K_{aaa}Q_1^3 + K_{aee}Q_1\rho^2 - K_{eee}\rho^3 cos(3\varphi)\ \pm$$

$$\pm\ \rho[A_1^2 + A_2^2\rho^2 - 2A_1A_2\rho\ cos(3\varphi)]^{1/2} \qquad [198]$$

The last expression represents the most general formula for the [3/3] potential within the E-(a_1 + e) coupling scheme. It contains 5 force constants and 6 vibronic constants combined into A_1 and A_2 terms. With various approximations for A_1 and A_2, the all the simplified formulas may be obtained.

A_1 is constant in first-order, a function $A_1 = f(Q_1)$ in second-order and a function $A_1 = f(Q_1,\rho)$ in third-order. Similarly, A_2 vanishes in first-order, it is constant in second-order and a function $A_2 = = f(Q_1)$ in third-order. If the admixture of the a_1 mode is switched off, within the E-e coupling scheme, A_1 is constant in the first- and second-order and a function $A_1 = f(\rho)$ in the third-order, as presented in Table 5.

TABLE 5
Various analytic formulas for adiabatic potential surface.

Coupling	Potential[a)]	A_1	A_2	Formula
E_g-e_g	[2/1]	const.	0	-
	[3/1]	const.	0	[188]
	[2/2]	const.	const.	[186]
	[3/2]	const.	const.	[189]
	[3/3]	$f(\rho)$	const.	[191]
E_g-(a_{1g} + e_g)	[2/1]	const.	0	-
	[3/1]	const.	0	-
	[2/2]	$f(Q_1)$	const.	[183]
	[3/2]	$f(Q_1)$	const.	[190]
	[3/3]	$f(Q_1,\rho)$	$f(Q_1)$	[198]

a) The potential of [m/n] type results from combination of degrees of expansion in force (m) and vibronic (n) constants, respectively.

Restricting to ourselves to Q_1 = const., the behaviour of the $E(Q_2,Q_3;[Q_1])$ potential is similar to the "Mexican hat" - function with warping. Fig. 12 shows a plot of the function

$$E = C_0 + K_2\rho^2 + K_3U -$$
$$- [(A + C\rho^2)^2\rho^2 + B^2\rho^4 + 2(A + C\rho^2)BU]^{1/2} \qquad [199]$$

with $U = 3Q_2^2Q_3 - Q_3^3 = -\rho\ cos(3\varphi)$ in various degrees of complexity. The following conclusions may be drawn from it:

1) The linear vibronic constant A is responsible for a valley on the adiabatic potential surface at the Jahn-Teller radius ρ_0.

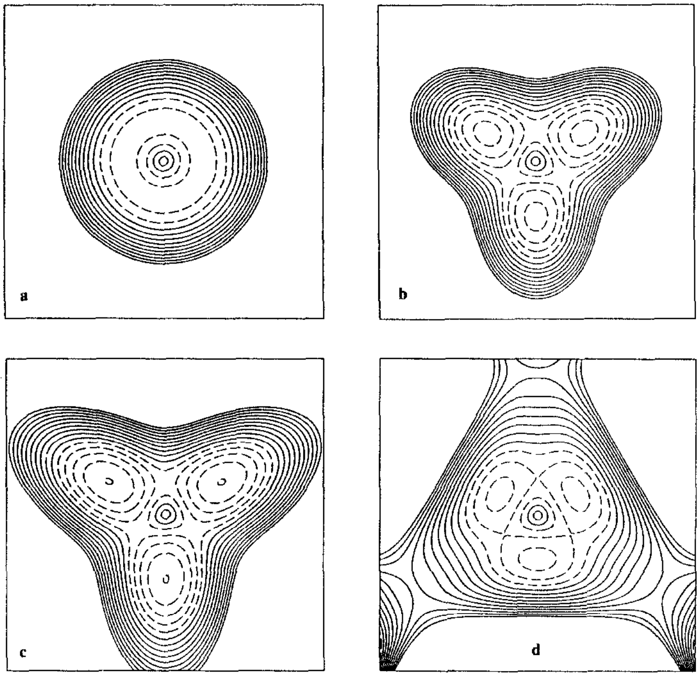

Fig. 12. Computer plot of the adiabatic potential surface $E(Q_2,Q_3;[Q_1])$ in various degrees of complexity ($C_0 = 0.05$, $K_2 = 20.0$, $A = 3.0$): a - [2/1] type with $B = C = K_3 = 0$; b - [2/2] type with $B = 6.0$, $C = K_3 = 0$; c - [2/3] type with $B = 6.0$, $C = 10.0$, $K_3 = 0$; d - [3/3] type with $B = 6.0$, $C = 10.0$, $K_3 = 40.0$.

Within the [2/1] approximation, $\rho_0 = AK_2/2$ holds.

2) The quadratic vibronic constant B yields an additional warping with three minima and three saddle points. They are localized at $\rho_0 = A/(2K_2 \pm 2B)$ and $\varphi_0 = n\pi/3$ ($n = 1, 2, 3$).

3) The cubic vibronic constant C magnifies the value of A so that the Jahn-Teller radius ρ_0 increases. Simultaneously the slope of the adiabatic potential is changed as seen from difference between isoenergy lines.

4) The cubic vibration constant K_3 describes the anharmonicity effects. Notice, that both the quadratic and cubic approximations give in incorrect behaviour for larger displacements from the reference configuration; they are applicable only for small displacements as shown by Fig. 13.

Various types of vibronic coupling in various degrees of complexity are compared in Table 6.

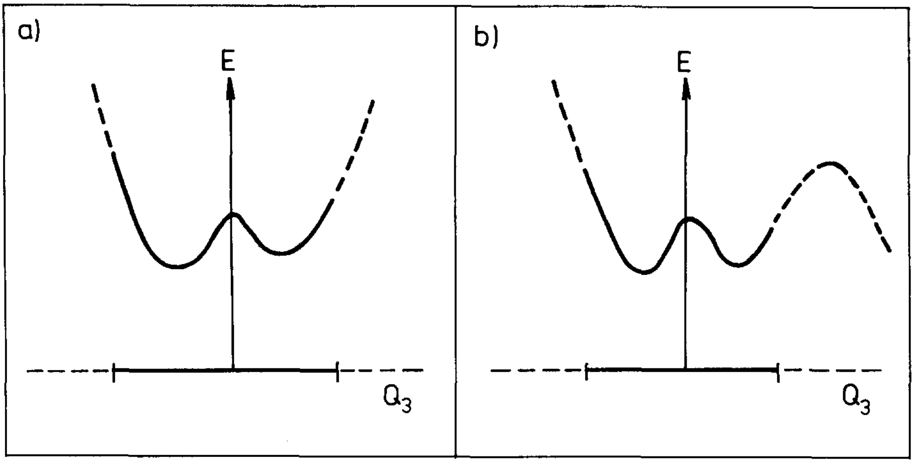

Fig. 13. Cut of the adiabatic potential surface $E(Q_2,Q_3;[Q_1])$: a - for [2/2] potential; b - for [3/3] potential.

TABLE 6

The dependence of number of adiabatic potential surface constants on the type of vibronic interaction.

Vibronic interaction	Force constants			Vibronic constants		
	linear $m = 1$	harmonic $m = 2$	cubic $m = 3$	linear $n = 1$	quadratic $n = 2$	cubic $n = 3$
Case 1						
T-e, T-t_2	0	1	1	1	1	1
T-(e+t_2)	0	2	3	2	3	4
T-(a_1+e+t_2)	1	3	6	2	5	9
T-(a_1+2e+t_2)	1	5	12	3	9	19
T-(a_1+e+2t_2)	1	5	13	3	9	19
T-(a_1+2e+2t_2)	1	7	21	4	14	34
Case 2						
E-b_1, E-b_2	0	1	0	1	0	1
E-(b_1+b_2)	0	2	0	2	0	4
E-(a_1+b_1+b_2)	1	3	3	2	2	4
E-(a_1+b_1+2b_2)	1	5	5	3	3	13
E-(a_1+2b_1+b_2)	1	5	5	3	3	13
E-(a_1+2b_1+2b_2)	1	7	7	4	4	24
Case 3						
E-e	0	1	1	1	1	1
E-(a_1+e)	1	2	3	1	2	3
E-(a_1+2e)	1	4	8	2	3	7

2.5.3 Symmetry Descent Concept

The determination of distortion routes for coordination polyhedra due to the Jahn-Teller effect represents the subject of numerous papers. The usual treatment is to investigate the analytic form of the adiabatic potential generated by the first-order perturbation theory. In terms of the above language, the eigenvalues of

$$U_{kl} = E_k^0\delta_{kl} + H_{kl}^{(1)} + H_{kl}^{(2)} \qquad [200]$$

are analysed.

Some authors, on the other hand (97 - 99), applied the group theoretical approach to this problem; it is based on the symmetry properties of the Jahn-Teller active vibrational mode. Unfortunately, these studies have also been restricted to the first-order perturbation theory. This section exploits an entirely different treatment. The correlation among symmetry point groups is investigated for individual Jahn-Teller active systems from the viewpoint of the pertinent electronic state.

The Jahn-Teller theorem implies the following consequences:

1) With the exception of two atomic linear systems, the equilibrium geometry (characterized by vanishing gradient components $K_i =$ $= 0$ and positive force constants $K_{ij} > 0$) corresponds to the nondegenerate electronic state S_N (thus being of A or B type).

2) The nondegenerate electronic state, stable with respect to the nuclear configuration (molecular geometry), arises by splitting the degenerate state S_D (being of E or T type, eventually of G or H type).

3) The splitting of the degenerate electronic state S_D is accompanied by a decrease of symmetry, i.e. some symmetry elements vanish.

In other words, the Jahn-Teller distortion causes a descent in the symmetry $G^0 \rightarrow G^n$ and the original electronic state $S_D(G^0)$ is split yielding the nondegenerate term $S_N(G^n)$. The symbol G^0 marks the symmetry point group of the reference system. A symmetry descent generates the n-th level subgroup G^n. For the first-level subgroup $G^1 \subset G^0$ holds, the second-level subgroup satisfies the relation $G^2 \subset G^1 \subset G^0$, etc. An important relation is valid among the group orders $\mathcal{O}$.

$$\mathcal{O}(G^0) = m_1\mathcal{O}(G^1) = m_1m_2\mathcal{O}(G^2) = \dots \qquad [201]$$

The integer multiplicator m_i is equal to the number of equivalent configurations within the subgroup G^0 to which the reference group

G^{n-1} can distort. This number corresponds to the competent minimum points of the adiabatic potential surface.

These considerations may be summarized as follows (Fig. 14):

1) The symmetry elements of the perturbed geometry form a subgroup G^n of the reference system: $G^n \subset G^0$.

2) The irreducible representation $\Gamma(S_n)$ describing the electronic state in the "perturbed" geometry G^n originates from the splitting of the multidimensional irreducible configuration, $\Gamma(S_D^0)$, which corresponds to the actual degenerate electronic state in the reference geometry G^0.

3) The stable equilibrium geometry corresponds to the nondegenerate electronic state, $S_N(G^n)$, described by the one-dimensional irreducible representation $\Gamma(S_N)$. Otherwise the system continues in symmetry descent.

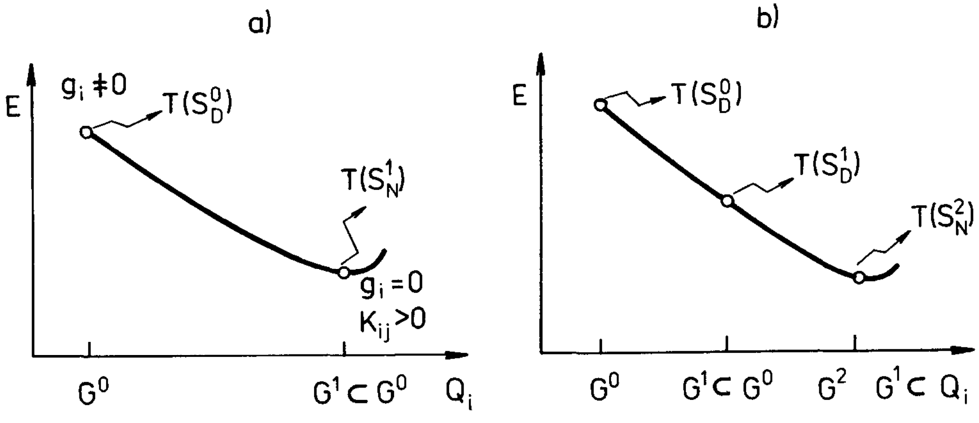

Fig. 14. Possible routes of the Jahn-Teller distortions: a - single stage process; b - double stage process.

The results of the group-theoretical analysis of all molecular symmetry point groups have been summarized elsewhere (100, 101). The procedure is illustrated for the symmetry group O_h in Fig. 15. This group contains 6 multidimensional irreducible representations (E_g, E_u, T_{1g}, T_{2g}, T_{1u}, T_{2u}) and has 24 subgroups. The distortion route depends on the actual electronic state. For example, the electronic term T_{2g} is split into B_{2g} and E_g terms of D_{4h}, or into A_{1g} and E_g terms of D_{3d} subgroup at the first-level. The remaining first-level subgroups (O, T_d, T_h) cause no be split to give nondegenerate states (the corresponding subgroups are given in parentheses): $B_2(D_4)$, $A_1(D_3)$, $B_2(D_{2d})$, B_{1g}, B_{2g} and $B_{3g}(D_{3h})$, $A_g(S_6)$, $A_1(C_{3v})$, A_g and $B_g(C_{2h})$. Analogously, at the third level the symmetry decrease yields: B_1, B_2 and $B_3(D_2)$, $A(C_3)$, B_1 and $B_2(C_{2v})$, $B_g(C_{2h})$, A and $B(C_2)$, $A_g(C_i)$, A' and A"(C_s). At the fourth-level only a single nondegenerate electronic term is possible: $B(C_2)$.

The restriction to the so-called Jahn-Teller active vibrations yields the distorted geometries D_{3d} and D_{4h} in accordance with earlier investigations (97, 98, 102); the present approach is more general.

On the basis of the above results, the geometrical rearrangement $T_d \rightarrow D_{4h}$ is not allowed by the Jahn-Teller effect since D_{4h} is not a correlating subgroup of the tetrahedron. The order of the D_{4h} group equals to 16 and the order of T_d is 24, so that the condition [201] is not fulfilled. Analogously the transition $D_{3h} \rightarrow C_{4v}$ should be excluded from the Jahn-Teller mechanism since $C_{4v} \notin D_{3h}$ (Fig. 16).

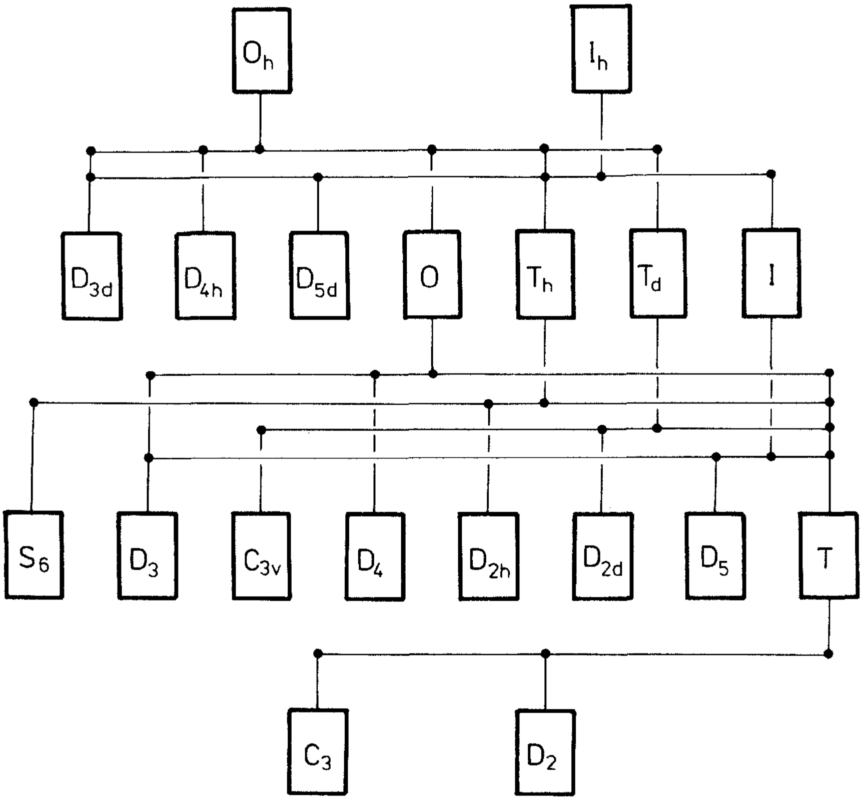

Fig. 15. Symmetry descent of the point groups to their subgroups.

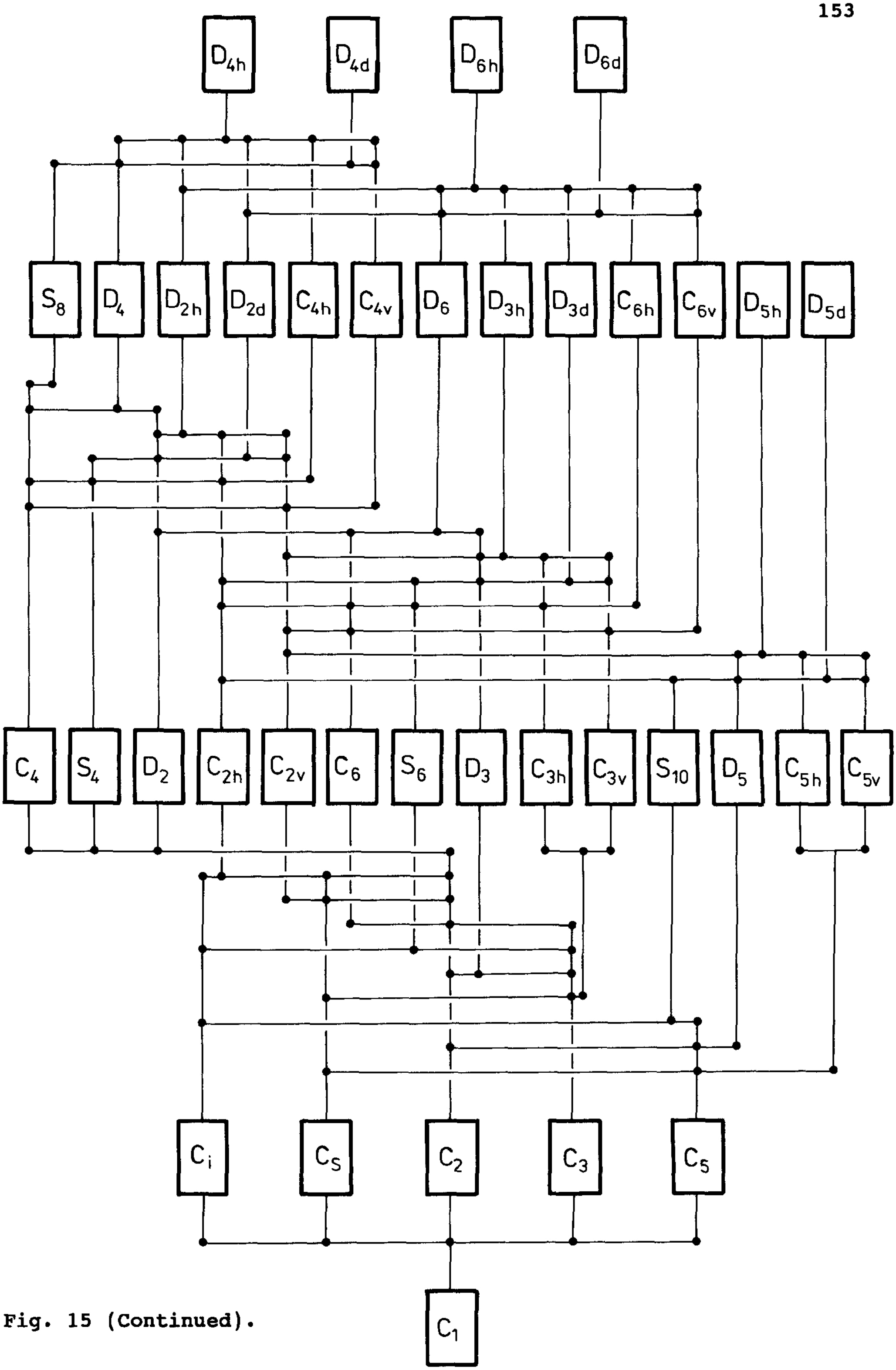

Fig. 15 (Continued).

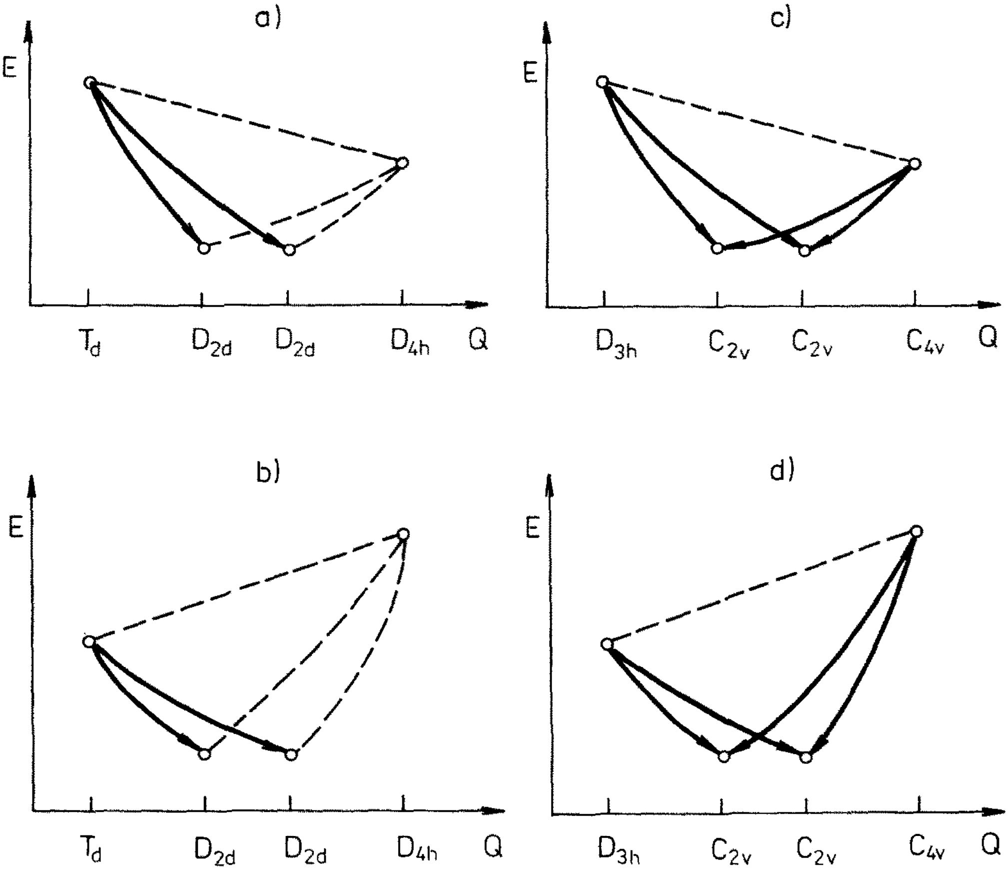

Fig. 16. Forbidden (---) and allowed (——) Jahn-Teller distortions for $T_d \rightarrow D_{4h}$ (a,b) and $D_{3h} \rightarrow C_{4v}$ (c,d) geometric rearrangements.

For the symmetry-descent concept, an important question becomes relevant: Which molecular geometry should be considered as reference for operating the Jahn-Teller effect? For example, the octahedral geometry with T-type electronic state can split into O, T_h, T_d, D_{3d} or D_{4h} first-level subgroups. If the corresponding electronic state still remains degenerate, the symmetry descent continues to the second-, third- or fourth-level subgroups. One possible pathway of distortion is shown in Fig. 17 for the descent from cubic symmetry via the tetragonal pattern. The central atom effect (the proton number influence of the central atom, as well as oxidation and spin state of the complex) and the ligand field effect represent important factors that determine the final ground-state geometry of the system. The vibronic coupling in hexacoordinate

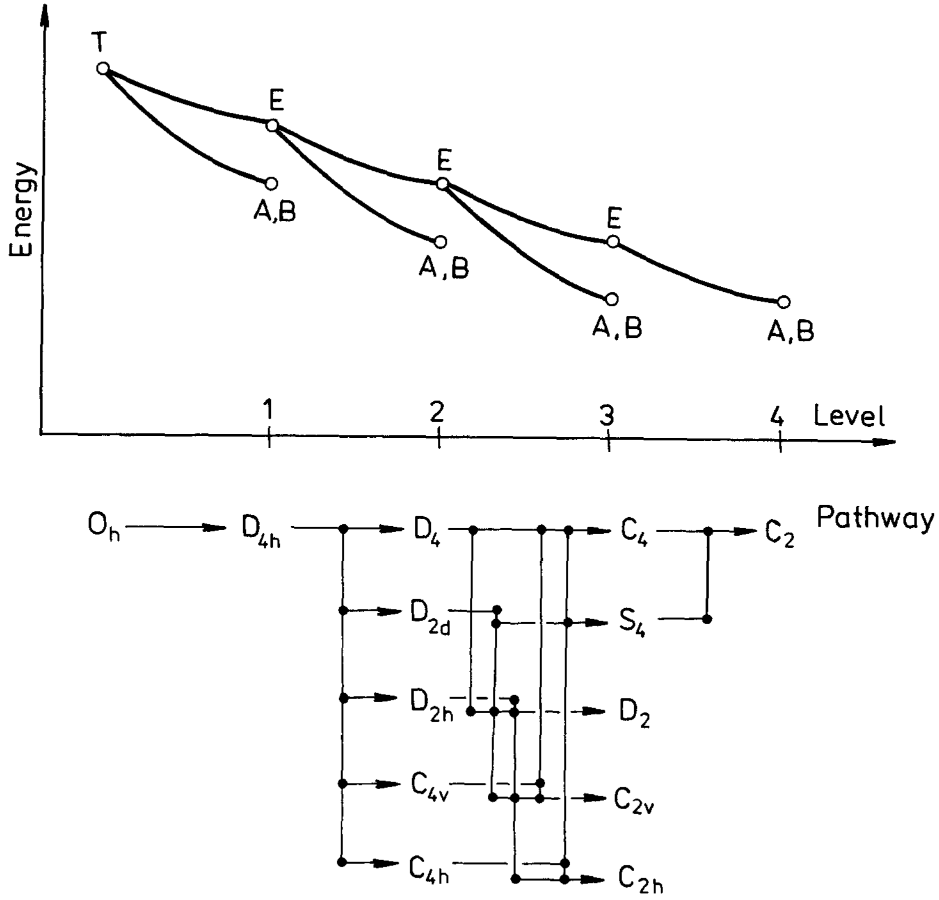

Fig. 17. Tetragonal route for symmetry descent of O_h group.

systems may refer to $T_{2g}-(a_{1g} + e_g + t_{2g})$ type within the group O_h, to $E-(a_1 + b_1 + b_2)$ type within the group D_4, to $E-(a_1 + e)$ type within the group C , etc.

Liehr (99) postulated that the vibronic coupling operates in the presence of electronic degeneracy within the group of the highest symmetry (maximum group order). Nevertheless, no proof of this theorem has been presented. On the contrary, quantum-chemical calculations showed (92) that the vibronic coupling should be considered within the reference group of the minimum symmetry (minimum group order) where the electronic state is still degenerate. For example, a better description of the adiabatic potential is obtained for certain MX_6^q systems if either $E_g - (a_{1g} + e_g)$ coupling within the group D_{3d} or $E_g-(a_1 + b_1 + b_2)$ coupling within the group D_{4h} are considered instead of $T_{2g} - (a_{1g} + e_g)$ within the group O_h.

2.5.4 Calculation of Vibronic Constants

There are two methods of evaluating the Jahn-Teller coupling constants. The former is based on their direct evaluation on various levels of complexity, namely

1) the electrostatic model of van Vleck (103);
2) crystal (ligand) field approach (104 - 106);
3) angular overlap model (AOM) (79, 107 - 109);
4) analysis of LCAO contributions (110, 111);
5) analytical derivatives within LCAO approach (112).

The latter method is based on a least-squares fitting of the numerical map of the adiabatic potential to the analytic form (89-92, 112, 113) and is applicable in an arbitrary degree of complexity.

The calculation of any Jahn-Teller coupling constant can be carried out via the evaluation of matrix elements

$$c^{\Gamma}_{\gamma} = \left\langle \Phi^{\Gamma_1}_{\gamma_1} \left\| \left[\partial\hat{V}/\partial Q^{\Gamma}_{\gamma} \right]_0 \right| \Phi^{\Gamma_1}_{\gamma_1} \right\rangle \qquad [202]$$

having the appropriate symmetry-adapted wave functions Φ^{Γ}_{γ} , $\Phi^{\Gamma_1}_{\gamma_1}$; Q^{Γ}_{γ} are symmetry coordinates corresponding to the γ-component of the Γ irreducible representation and

$$\frac{\partial\hat{V}}{\partial Q^{\Gamma}_{\gamma}} = \sum_{n=1}^{N} \frac{\partial\hat{V}}{\partial r_n} \frac{\partial r_n}{\partial Q^{\Gamma}_{\gamma}} \qquad [203]$$

where r_n stands for the generic coordinate (R_n, ϑ_n, φ_n) of the n-th ligand.

Within the approximation of the crystal field theory, the Jahn-Teller coupling constants may be evaluated in a simple way. For example, in the case of E-e vibronic coupling in octahedral MX_6 complexes (104, 105)

$$A = \left(\frac{\partial V_{22}}{\partial Q_3} \right)_0 = - \frac{2\sqrt{3}}{7} q \left\{ \frac{\partial}{\partial R} [F_2(R) + (5/12)F_4(R)] \right\}_{R=R_0} \qquad [204]$$

$$B = \left(\frac{\partial^2 V_{11}}{\partial Q_2^2} \right)_0 = - \frac{2}{7} q \left\{ \frac{\partial^2}{\partial R^2} [F_2(R) + (5/12)F_4(R)] \right\}_{R=R_0} \qquad [205]$$

where $R_k(R_0)$ are the crystal field integrals defined by Eq. [295] of Chapter 1; R_0 is the reference M-X distance and q - the effective ligand charge.

More sophisticated results were obtained by the angular-overlap method (79, 107 - 109). The formula [202] may be rewritten in the form

$$c^{\Gamma}_{\gamma} = \sum_{\lambda,\omega} \sum_{n=1}^{N} \frac{\partial}{\partial r_n} \left[e_{\lambda n} F_{\lambda\omega}(\Phi_i, X_n)\ F_{\lambda\omega}(\phi_j, X_n) \right] \frac{\partial r_n}{\partial Q^{\Gamma}_{\gamma}} \qquad [206]$$

where $F_{\lambda\omega}(\Phi_i, X_n)$ is the angular-overlap factor at a given M-X_n distance; $e_{\lambda n}$ is the radial parameter; λ indicates the bonding symmetry (σ, π, δ); ω specifies the particular orbital and r_n is defined in Eq. [203].

It follows from Eq. [206] that the Jahn-Teller coupling constants related to the stretching vibrational modes are functions of $\partial e_{\lambda n}/\partial R$ while those related to the bending modes are simply functions of $e_{\lambda n}$; $F_{\lambda\omega}$ depends upon the bond length R and angular coordinates ϑ and φ, respectively.

The quadratic Jahn-Teller coupling constants can be easily obtained by introducing second derivatives into [202] and [206]. The results of d^x systems for a number of symmetries were published by Bacci (79, 107, 108) and Warren (109). The vibronic coupling constants can be expressed through a limited number of parameters in the framework of AOM. It is possible to calculate e_λ and its derivatives theoretically, but better results are obtained with e_λ derived from experiments. Their derivatives can be evaluated numerically. The coupling constants related to the stretching modes are less accurate than those related to the bending modes, because of the uncertainty about their derivatives. Calculation of force constants remains problematic since only approximate values can be reached for less-simple systems.

Nikiforov and coworkers (110, 111) tried to evaluate Jahn--Teller coupling constants of 3d transition metals in the cluster approximation by using a semiempirical MO LCAO approach.

A qualitatively new treatment was proposed by Dixon (113), who fitted the electronic energies to polynomial functions of displacement coordinates. In the works (90 - 92, 114) authors independently elaborated the method of evaluation of Jahn-Teller coupling and force constants using a non-linear least-squares fitting of total energy of the system. This treatment consists of two steps. First, the numerical map of adiabatic potential surface values should be calculated by any quantum-chemical method. Then, the least-squares method is applied in order to fit the numerical map, $E^c(Q_i)$, to the analytic form. Actually, the set of approximate values, $E^a(Q_i)$, is produced so that the function

$$F = \sum_i w_i^2 \left[E^c(Q_i) - E^a(Q_i)\right]^2 \qquad [207]$$

adopts a minimum value. The values of $E^a(Q_i)$ are calculated by Eq.

[190] for a trial set of potential (i.e.coupling and force) constants. The statistical weights were chosen in accordance with the metric weighting concept

$$w_i = \left[\sum_i Q_k^2 \right]^{-1/2} \qquad [208]$$

where Q_k is a set of displacement coordinates for the given adiabatic potential surface point. The established minimization procedure, in general, is based on a non-linear optimization (Newton--Raphson and/or Fletcher-Powell algorithm were used). In order to accelerate a convergence, the process may be split into two, linear and nonlinear optimizations. Another simplification of the problem consists in considering only selected cuts of the adiabatic potential surface (e.g. only D_{4h} distortions of ML_6 systems). This may lead to a simpler, purely polynomial form of the adiabatic potential that can be fitted by the linear optimization only (115). The quality of regression is measured by statistical characteristics (e.g. standard deviations of individual potential constants, the correlation coefficient, the discrepancy R-factor).

The above method was systematically applied to adiabatic potential surface of some hexahalo and tetrahalo complexes of the first transition metal row and led to the following conclusions (90 - 92).

1) Inclusion of the totally symmetric vibration mode manifests itself in a significant contribution to the values of the corresponding vibronic constants. Thus, its importance is clearly demonstrated.

2) The e_g vibration modes are much softer than the a_{1g} ones according to the calculated force constants: $K_{ee} < K_{aa}$. This fact may play an important role in deformations in the solid-state systems.

3) The Jahn-Teller distortions calculated from these constants are small when compared with distortions found for solid-state complexes. It indicates that solid-state influence may prevail over the net Jahn-Teller effect.

4) Calculated tetragonal distortions and stabilization energies in systems with triple electron degeneracy are much lower in comparison with analogous complexes with double electron degeneracy.

5) Higher distortions and stabilization energies occur in M(III) complexes compared to analogous M(II) systems. All the characteristics calculated are also functions of the polarity of metal-ligand bonds, spin multiplicity and proton number of the central atom.

2.5.5 Dynamic Jahn-Teller Effect

The adiabatic potential in an analytic form may be used in equations for nuclear motion. The solutions of these equations have been obtained in E-e, T-t_2 and T-(e + t_2) approximations to the vibronic coupling, respectively.

The nuclear motions may be classified as a radial motion along the coordinate ρ, and an angular motion along the coordinate φ. The radial motion has been considered in the harmonic approximation, having the energy $E_n = h\nu_\rho(n + 1/2)$ with the vibrational quantum number n = 0, 1, 2, ... The energy of the angular rotation is given by $E_m = m^2(h\nu_\rho)^2/4E_{JT}$ where m = ±1/2, ±3/2, ... stands for the rotational quantum number and E_{JT} is the Jahn-Teller stablization energy, which, within the E-e approximation is expressed as $E_{JT} = A^2/2K_{ee}$. The total energy expression is then

$$W_{nm} = -E_{JT} + h\nu_\rho(n + 1/2) + h^2\nu_\rho^2 m^2/4E_{JT} \qquad [209]$$

When the second-order terms are incuded, the solution becomes very complicated. O'Brien (95) considered the second-order terms as a small perturbation of the ground vibrational state. The angular motion contains some admixtures to pure rotational motion and its equation is

$$\{-a \frac{\partial^2}{\partial\varphi^2} + b\, cos(3\varphi) - E_m\}\, f_m(\varphi) = 0 \qquad [210]$$

where $a = \hbar^2/3M\rho_0^2 \approx (h\nu_\rho)^2/E_{JT}$ and $b = B\rho_0{}^2$.

Another procedure has been proposed by Bersuker (8, 116, 117) who applied variation functions of the type

$$f(\rho,\varphi) = N\, (\rho/\rho_0)^{1/2}\, exp[v\, cos(3\varphi) - (u/2)(\rho/\rho_0 - 1)^2]f_1 \qquad [211]$$

with parameters u and v (N being the normalization factor). The function f_1 accounts for the tunnelling splitting of three degenerate energy levels for individual energy minima to a pair of A_1 and E vibronic levels, i.e.

$$f_1(E) = \left\{ \begin{matrix} cos(\varphi/2) \\ sin(\varphi/2) \end{matrix} \right\} \qquad [212]$$

$$f_1(A_1) = cos(3\varphi/2) \qquad [213]$$

Perturbation theory may be applied to describe an interactions among energy minima, each of them characterized by the adiabatic potential. The solution leas to a tunnelling among individual energy minima through the energy barriers. The initial (unperturbed) wave functions in the minima (m) of the adiabatic potential are expressed through a product of the electronic wave function $\Phi_m(r;[Q_m^0])$ and the nuclear vibrational function $f_{m\mu}(Q_m)$

$$\Psi_{m\mu}^0(r,Q) = \Phi_m(r;[Q_m^0])\ f_{m\mu}(Q_m) \qquad [214]$$

The total molecular wave function is then a linear combination of the particular wave functions corresponding to each minimum

$$\Psi_{n\mu}(r,Q) = \sum_{m=1}^{p} C_{mn}\ \Psi_{m\mu}^0(r,Q) \qquad [215]$$

for n = 1, 2, ... p (p being the number of energy minima). By solving the secular equation

$$det\ \{H_{mn}^{\mu} - \epsilon_{\mu} S_{mn}^{\mu}\} = 0 \qquad [216]$$

for matrix elements $H_{mn}^{\mu} = <\Psi_{m\mu}^0|\hat{H}|\Psi_{n\mu}^0>$ and $S_{mn}^{\mu} = <\Psi_{m\mu}^0|\Psi_{n\mu}^0>$ we get the total energy

$$W_{\mu} = -\ E_{JT} + \sum_j h\nu_j(n_j + 1/2) + \epsilon_{\mu} \qquad [217]$$

In the case of E-e vibronic coupling (p = 3) the roots of the secular equation are

$$\epsilon_{\mu}(E) = -H_{12}^{\mu}/(1 - S_{12}^{\mu}) \qquad [218]$$

$$\epsilon_{\mu}(A_1) = 2H_{12}^{\mu}/(1 + 2S_{12}^{\mu}) \qquad [219]$$

Finally the tunnelling splitting is (Fig. 18)

$$\delta_{\mu} = \epsilon_{\mu}(A_1) - \epsilon_{\mu}(E) = 2H_{12}^{\mu}/(1 + 2S_{12}^{\mu})(1 - S_{12}^{\mu}) \qquad [220]$$

The above perturbation treatment is applicable under the constraint that the tunnelling splitting is much lower than the vibrational quantum in the minimum of the adiabatic potential, i.e., $\delta \ll h\nu$.

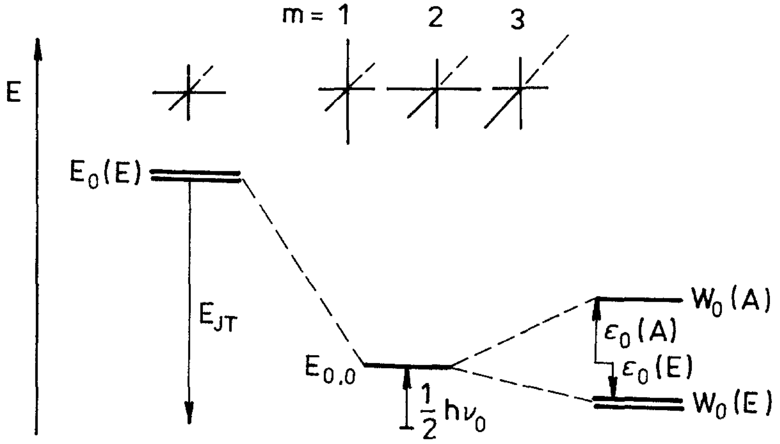

Fig. 18. Tunnelling splitting in systems with E-e vibronic coupling.

2.6 BOUND STATES OF MOLECULES

2.6.1 Physical Origin of the Chemical Bond

In the Born-Oppenheimer approximation, the bound molecular state is interpreted as a vibration-rotational state corresponding to a minimum on the adiabatic potential surface which is characterized by finite geometric parameters. Among the bound molecular the chemical bond and the intermolecular interactions may be distinguished. The former is the raison d'etre of the existence of molecules, molecular ions, radicals, complex compounds and crystals, including metals and chemisorbates on surfaces, whereas the latter covers hydrogen bonds, van der Waals complexes, clathrates, solvated particles, etc.

The most frequently used criteria for differentiating between the chemical bond and intermolecular interactions are the stabilization energy and the range of interaction. In fact, from both the viewpoint of stabilization energy and from the range of interactions there is no well defined boundary between the chemical bond and intermolecular interactions (Table 7). Both cases of the system stabilization have something in common: the existence of a minimum on the adiabatic potential surface as a consequence of electrostatic interactions in the system.

TABLE 7

Comparison of stabilization energies.

Chemical bond		Intermolecular interactions	
System	Energy (kJ mol^{-1})	System	Energy (kJ mol^{-1})
$Cl-O_2$	17	$H_2 \cdots H_2$	0.3
NO_2-NO_2	57	$O_2 \cdots O_2$	1.1
Li-Li	105	$I_2 \cdots I_2$	12.1
H-H	458		
N-N	940		

A substantially more important criterion for distinguishing between the chemical bond and intermolecular interactions is that chemical behaviour ist manifest largely in chemical reactivity. One can speak of a chemical bond if such a bound system is formed whose individual subsystems have lost their chemical individuality. In terms of its chemical behaviour a chemically bound system differs from its possible subsystems. While the chemical bond can be taken for the raison d'etre for molecules, the intermolecular interactions are usually the cause of existence of condensed phases. Individual subsystems bound due to intermolecular interactions retain partially their chemical individuality and chemical properties. Moreover, the chemical bond, as a rule, shows directional character in space and possesses a saturation property.

The first serious attempt to explain the physical nature of the chemical bond was represented by the Heitler-London computation on the hydrogen molecule. This approach, in fact, represents a simple application of the Valence-Bond (VB) method (see Section 4.3). The molecular wave function is of the form

$$ {}^{1,3}\Psi^{VB}(1,2) = (2 \pm 2\langle\phi_A|\phi_B\rangle^2)^{-1/2}[\phi_A(1)\phi_B(2) \pm \phi_B(1)\phi_A(2)] \qquad [221] $$

where the positive sign corresponds to the singlet state and the negative sign to the triplet state; $\phi(i)$ stands for an atomic orbital (1s) of the hydrogen atom. This approach, however, was just a qualitative description of the dominating factors responsible for the formation of a chemical bond (the calculated dissociation energy of 2.9 eV is too low in comparison with the experimental value of 4.7 eV).

Later, the Heitler-London procedure was made more precise with application of a more flexible spatial part of the wave function. For example, the wave function

$$ \begin{aligned} {}^{1}\Psi_{+}^{VB}(1,2) = {} & N_{+}\{[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] + \\ & + \lambda\ [\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)]\} \end{aligned} \qquad [222] $$

enables an optimum weighing of covalent and ionic terms. In principle, the variational method was applied, which guarantees an upper estimate of the system energy, i.e., the increase of the number of variational parameters can only result in the decrease of the total molecular energy (and thus, to increased dissociation energy). Variational functions show a complicated nonlinear form (power series with exponential factor) with a large number of terms.

The exact computations for small molecules were aimed at deciding whether the Born-Oppenheimer and adiabatic approximation are relevant (i.e. the determination of both, the diagonal $\hat{G}_{ii}$ and off-diagonal $\hat{G}_{ij}$ corrections to nuclear motion) as well as whether the nonrelativistic approach is correct (i.e. the estimate of relativistic corrections). Also an absolute coincidence of the theory with experimental data needed to be verified, thereby indicating the soundness of the quantum mechanics to molecules.

The most precise computations of Kolos and Wolniewicz (118, 119) were based on electron correlation functions of the type

$$\Psi(r_1,r_2) = e^{-k(\xi_1+\xi_2)} \sum_{l,m,n,p,q} C_{lmnpq}(\xi_1^l\eta_1^m\xi_2^n\eta_2^p \pm \xi_1^n\eta_1^p\xi_2^l\eta_2^m)r_{12}^q \qquad [223]$$

where $\xi = (r_1 + r_2)/R_{AB}$ and $\eta = (r_1 - r_2)/R_{AB}$. The dissociation energy value (36 117.4 cm^{-1}) is in a full agreement with the corresponding experimental reading (36 117.3 ± 1.0 cm^{-1}). (Precision of the experimental value is limited by the natural broadening of spectral lines.) Some other characteristics of the hydrogen molecule were also obtained from exact computational procedures.

More detailed analysis of individual contributions to the dissociation energy has shown that the diagonal corrections to nuclear motion ($\hat{G}_{ii}$ in the adiabatic approximation) can be significant for light nuclei while the off-diagonal ones ($\hat{G}_{ij}$ in the non-adiabatic theory) are negligible (Table 8). As the mass of the nuclei increases the role of diagonal corrections decreases, hence, in most cases, the Born-Oppenheimer approximation can be accepted for heavier nuclei.

TABLE 8

Dissociation energies of small molecules.[a]

Particle	State	Approximation			Experiment
		B-O	Adiabatic	None	
H_2^+	$^2\Sigma_g^+$	21375.9	21379.1	21379.3	
H_2	$X^1\Sigma_g^+$	36112.2	36118.0	36117.4	36117.3 ± 1.0
	$B^1\Sigma_u^+$	28211.4	28167.3		28169.2
	$a^3\Sigma_g^+$	23293.4	23297.4		23299.1
	$E^1\Sigma_g^+$	19200.4	19200.4		19207.8
HD	$^1\Sigma$	36401.5	36405.7	36402.9	36400.5
D_2	$^1\Sigma_g^+$	36745.6	36748.3	36748.0	36748.9

[a] Energies are given through wave-numbers (cm^{-1}).

The value of relativistic corrections to the dissociation energy of H_2^+ and H_2 systems is low (+0.11 or -0.5 cm^{-1}). Relativistic effects, however, are strongly dependent on the proton number Z. The dominant contribution to relativistic energy is due to the inner electronic shells, which can be seen from the relationship

$$\hat{T}_e(2) = -(1/8m_e^3c^2) \sum_i^n (\hat{p}_i)^4 \qquad [224]$$

since the electrons of the inner shells have a higher linear momentum. Due to the increase in relativistic corrections with Z there is doubt about whether the perturbation theory is applicable for Z > 30: $\hat{T}_e(2)$ does not represent a small perturbation any more (Table 9). In this case it is neccessary to formulate the equations for the calculation of the molecular energy by means of the variational method.

TABLE 5

Relativistic correction E_{rel} to ground-state energy of atoms (E_h).

Atom	E_{rel}	$\epsilon(1s)$	$\epsilon(2s)$	$\epsilon(2p)$	$\epsilon(3s)$	$\epsilon(3p)$	$\epsilon(4s)$	$\epsilon(3d)$
Be	-0.002	-0.002	-0.0002					
Ne	-0.131	-0.107	-0.014	-0.011				
Mg	-0.295	-0.228	-0.034	-0.031	-0.001			
Ar	-1.761	-1.221	-0.235	-0.257	-0.025			
Ca	-2.799	-1.885	-0.381	-0.429	-0.051	-0.051	-0.003	
Zn	-15.919	-9.909	-2.285	-2.802	-0.368	-0.447	-0.015	-0.100

To understand better the phenomena accompanying the formation of the chemical bond, the consequences resulting from the quantum-mechanical virial theorem can be used. At the energy minimum as well as in the dissociation limit the total energy gradient vanishes, $\partial E/\partial R = 0$, so that the virial theorem (see Section 1.1.1) assumes the form $2\bar{T} + \bar{V} = 0$. As the sum of the kinetic energy of the electrons $\bar{T}$ and the potential energy $\bar{V}$ yields the total molecular energy, it is

$$\bar{E} = \bar{T} + \bar{V} = -\bar{T} = \bar{V}/2 \qquad [225]$$

This is fulfilled for the equilibrium geometry of a molecule as well as for free atoms. Thus, we can arrive at the expression for the binding energy of the H_2 molecule as follows

$$E_b = 2\bar{E}(H) - \bar{E}(H_2) = -2\bar{T}(H) + \bar{T}(H_2) = [2\bar{V}(H) - \bar{V}(H_2)]/2 > 0 \qquad [226]$$

From the above it is evident that the formation of the chemical bond is accompanied by:

1. an increase of the positive value of the electronic kinetic energy, since $\overline{T}(H_2) > 2\overline{T}(H)$;

2. a simultaneous decrease of the negative value of the total potential energy, as $\overline{V}(H_2) < 2\overline{V}(H)$.

The decrease by 4.7 eV (which is the value of the dissociation energy) of the total energy accompanying formation of the chemical bond in the H_2 molecule requires an increase of the electronic kinetic energy by the same value as well as the decrease of the total potential energy by 9.4 eV. Since the potential energy consists of

$$\overline{V} = \overline{V}_{NN} + \overline{V}' = \overline{V}_{NN} + \overline{V}_{ee} + \overline{V}_{eN} \, , \qquad [227]$$

whereby the terms expressing internuclear repulsion $\overline{V}_{NN}$ and interelectronic repulsion $\overline{V}_{ee}$ are always positive (except for $R \Rightarrow 0$ when $\overline{V}_{NN} = 0$), the decrease of $\overline{V}$ upon the bond formation is accompanied by a deep decrease of the electron-nuclear attraction $\overline{V}_{eN}$. At the equilibrium geometry of the hydrogen molecule (R_0 = 74.1 pm) the value of V_{NN} = 19.4 eV appears. Hence the decrease of $\overline{V}'$ upon bond formation should be 9.4 + 19.4 = 28.8 eV.

The formation of the chemical bond is connected with the increase of electronic kinetic energy and - in-parallel - with increased electron-nuclear attraction (having negative contribution to the total energy). In other words, electrons are accelerated by synergic effect of several atomic nuclei. This is possible only as a result of increased electron density in the internuclear region. Thus, the chemical bond is based on the collectivization principle of electron motion.

From the above examples it can be seen that the stabilization of the chemical bond is strongly dependent upon the electronic energy of the system. It can be concluded that:

1. chemical bond theory should be based on consideration of electron motion;

2. stabilization of the bound molecular state is caused exclusively by the forces of electrostatic nature;

3. the classical electrostatic theory fails but the quantum-mechanical approach is useful in computing the stationary charge distribution in systems of electrons and atomic nuclei.

However, it was proved by Hellman and Feynman that if for a certain configuration of nuclei the electron density has been calculated (by solving the corresponding Schödinger equation) then the forces acting upon nuclei can be found with the use of classical laws of electrostatic theory. Thus the quantum-mechanical computation enables determination of the specific distribution of electronic charge in the stationary state of the system under study. The stability of the molecular system, however, results from only the mutual electrostatic interactions among charged particles in motion.

The practical calculations in studying the bound states of molecules are based on an hierarchized scheme of approximations as summarized in Table 10.

TABLE 10

Basic approximations in the theory of chemical bond.

	Approximation		
Feature	nonadiabatic	Born-Oppenheimer	one-electron
Wave function	molecular $\Psi_\nu = \sum_i f_{\nu i} \Psi_i^{el}$	electronic $\Psi_i^{el} = \sum_u C_{iu} \Phi_u$	determinantal $\Phi_u = \hat{A}_n \prod_k \psi_k(X_k)$
Energy operator	nonrelativistic Hamiltonian	electronic Hamiltonian $\hat{H}^{el}$	Fock operator $\hat{F}$
Characteristic equation	molecular Schrödinger	electronic Schrödinger	Hartree-Fock equations
Energy eigenvalues	energy of electron-vibration-rotation states W_ν	electronic energy and adiabatic potential $E_i = E_i^{el} + V_{NN}$	orbital energy ϵ_k
Calculation method	off-diagonal corrections	configuration interaction	self-consistent field
Physical model	moving nuclei	frozen nuclei	effective field of electrons

2.6.2 Specific Features of Coordination Bond

There is a lot of space in the literature devoted to the classification of chemical bonds. This effort, however, is formal and usually does not properly reflect the physical aspects of the chemical bond. If, on the other hand, we carry on our attempt for classification, it will prove necessary to specify the characteristic features through which individual types of bonds will be distinguished.

In genealogic understanding, for the coordination (donor - acceptor) bond such a connection of atoms is taken in which one partner appears as the donor of an electron pair, the other being the acceptor. As an example, the creation of the complex ion $Fe^{2+} + 6CN^- \Rightarrow [Fe(CN)_6]^{4-}$ can be valid. Such a formulation of the concept, however, meets many obstacles. For example in a series of particles BH_4^-, CH_4 and NH_4^+ only BH_4^- and NH_4^+ are taken to contain a coordination bond. In fact, however, the electronic structures of all three particles do not differ except for the fact that the proton number of the central atom is changed. Here the boron atom is the acceptor of electrons on formation of BH_4^- while the nitrogen atom represents the electron donor on formation of NH_4^+. Another example casting doubt upon the genealogic interpretation of the donor-acceptor bond is represented by the reaction of LiH with H_2O. An elementary reaction step in the development of dihydrogen is $H^- + H^+ \Rightarrow H_2$, a textbook-like example of a nonpolar covalent bond, though the origin of the bonding electrons would allow its interpretation as a donor-acceptor bond.

In a more detailed analysis of the properties of coordination compounds a donor-acceptor bond can be both, covalent (more or less polar) and ionic (strongly polar), single or multiple localized or delocalized (Table 11). Coordination compounds, however, represent a rich group of substances with specific features.

TABLE 11

Basic classification of chemical bonds.

Type of bond - property	Type of bond - property
Valent - formed of radicals - homolytic splitting $X^{\bullet} + Y^{\bullet} \leftrightarrow X\text{-}Y$	Coordination (donor-acceptor) - creation from donor and acceptor - heterolytic splitting $A + B: \leftrightarrow A\text{-}B$
Covalent - low polarity - formed of radicals $X^{\bullet} + Y^{\bullet} \leftrightarrow X\text{-}Y$	Ionic (electrovalent) - high polarity - formed of ions $A^+ + B^- \leftrightarrow A\text{-}B$
Single (σ) - formed on line connecting atoms	Multiple (π, δ) - formed out of the line connecting atoms
Localized - concentrated between atomic pair - tendency to additivity - transferability of local characteristics	Delocalized - spread over more atoms - nonadditivity - nontransferability

1. The atomic configuration (molecular geometry) of a coordination compound is characterized by having its central atom M surrouded by a group of ligands (or by a polydentate ligand) L, so that for the mononuclear complexes a general formula $[ML_n]^q$ can be written (q is the electric charge of the complex). This property of coordination compounds, as a rule, is reflected by a high symmetry of the chromophore $\{MD_n\}$ (central atom surrounded by the donor atoms D of ligands L). Fractional occupation of the one-electron levels in high symmetry can result in the existence of **degenerate electronic states** which manifest themselves in electronic lability such as the Jahn-Teller effect.

2. Transition metals may exist in various oxidation states and the polarity of the M-L bond can also vary over a wide interval, bringing about, as a consequence, a decrease in characteristic features of local bonding parameters such as bonding energies, bond lengths, stretching vibration frequencies, dipole moments, electric polarizabilities, magnetic susceptibilities, etc.

3. The electrostatic potential of the ligands causes a local Stark effect leading to the **splitting of degenerate d-levels** (or f-levels) of the central atom. Since the electronic levels after splitting are close in energy, the coordination compounds with partly filled d (or f) orbitals show characteristic **spectral and magnetic properties**. In parallel, there appears the possibility of coexistence of several spin states (low-spin and high-spin complexes).

4. In many cases the ligand entering the complex behaves as a discrete structural unit showing a change in electronic structure only in the vicinity of the donor atom (formation of a new chemical bond). However, there are numerous groups of complex-formation reactions whose characteristic feature is a substantial change in the electronic structure of the ligands. This effect yields the basis for **electronic activation** of ligands (increase of their reactivity for a certain type of chemical reaction. There operates a **mutual influence of ligands** mediated through the central atom in coordination compounds; this manifests itself in static (structural spectral, thermodynamic) as well as in dynamic (mostly kinetic) properties.

5. For heavier transition metals of higher Z the **relativistic effects** become significant. Among them spin-orbit splitting as well as orbital relaxation (expansion and/or contraction) play an important role.

6. Orbitals of higher angular momenta (d and f) possess some

unique properties among which is their tendency to be localized; the probability function, $|\psi|^2 dV$, adopts significant values only in a limited region of the molecular framework. Consequently, the electronic spectra (the d-d transitions) and photoelectron spectra (the d ionizations) of coordination compounds display a high portion of the relaxation energy.

The stereochemistry of coordination compounds is also uniquely rich:

1. There is a plethora of possible spatial arrangements of nuclei.

2. Coordination variability is not confined to the coordination compounds as a group, but is typical for structures with the same central atom as well.

3. Some central atoms show the tendency to form distorted polyhedra, forcing identical ligands to assume different metal--ligand distances.

4. Coordination compounds display novel, unique types of isomerism.

5. In some coordination compounds unsaturated organic ligands are bound by π-bonds, such as in $K[Pt(C_2H_4)Cl_3].H_2O$, ferrocene, etc.

6. Coordination compounds are prone to form auxiliary oriented bonds with atoms of abutting complexes. These bonds can be of the metal-ligand-metal, or of the metal-metal type. Such bonds arise even in nontypical bridging ligands, for instance in the tetramer $Pt(CH_3)_4$ with octahedral coordination around all Pt atoms.

7. Coordination compounds often spans the class of non-rigid molecules which exbitit internal motions of nuclei other than pure vibrational motions; they lead to structural dynamics paasing from one nuclear configuration to identical one through a transition state. Temperature dependence of this nuclear dynamics has been termed the fluxionality.

Isomers are chemical individuals possessing identical molecular formula, but differing in some physico-chemical properties, and stable within certain time interval. In coordination compounds we distinguish the following basic types of isomerisms:

1. Stereoisomerism - shown by compounds with different spatial arrangement of ligands around the central atom, such as the tetrahedral and square configuration of MX_4 chromophore, *cis* and *trans*-configuration of MX_2Y_2 or MX_4Y_2 complexes, *mer*- and *fac*-configuration in complexes of the type MX_3Y_3 and so on.

2. Distortion isomerism - manifests itself by the different degree of deformation of the coordination polyhedron. Especially prone to this type of isomerism are complexes affected by the Jahn-Teller effect.

3. Configuration isomerism - arising on account of different possible coordination number, e.g. 6 and 4+2.

4. Coordination isomerism - based on different possible ligand arrangements in the respective coordination spheres, such in $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(CN)_6][Cr(NH_3)_6]$.

5. Ionization isomerism - observable in complexes having two types of ions in the molecules which can alternatively occupy the coordination sphere (e.g. $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4.Br_2]Cl_2$). This gives rise to different ionization in solutions.

6. Hydration isomerism - a phenomenon akin to the ionization isomerism. It is based on the fact that water molecules can be variously distributed between the inner and outer sphere of the complex, as in $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

7. Optical isomerism - occurs in compounds without either the centre or plane of symmetry. In such cases parts of the molecules behave as objects and their mirror image, and show optical rotation of opposite signs.

8. Bonding isomerism - emanates from the difference in ways ligands bind to the central atom, for instance

M-CN (cyano complexes)	M-NC (isocyano complexes)
M-OCN (cyanate complexes)	M-NCO (isocyanate complexes)
M-SCN (thiocyanate complexes)	M-NCS (isothiocyanate complexes)

9. Ligand isomerism - isomerism in ligands around the central atom, as in $[CoCl_2(A)_2]Cl$, where A represents a bidentate ligand, for instance the 1,2-diaminopropane or isomeric trimethylene-diamine.

10. Co-ligand isomerism - existence of complexes with simple ligands and a product of their nucleophylic reaction in the coordination sphere, e.g. $[Cu(dmpz)_2(NCO)_2]$ and $[Cu(dmpz.NCO)_2]$, dmpz - dimethylpyrazole.

11. Bridge-bond isomerism - a different bridging in binuclear complexes, as in $[Cu_2(bipyO)_2Cl_4]$.

The above classical classification has often been criticized as confusing and overlapping (120, 121). There are examples where a complex shows two types of isomerism, e.g. geometric and optical. In addition the classification does account for rotational isomerism, possible by rotating parts of the complex around formally single bonds, and the existence of conformers. It has been suggested that the class of stereoisomers be split to inversion and rotation isomers, where inversion isomers are those that can be inter converted by inversion of at least one atom, a process that engenders cleavage and formation of several bonds. Rotation isomers on the other hand are interconverted by rotation around a single bond (conformers, rotamers, conformation isomers). Energy barriers between such isomers are as a rule too low for isomers to be resolved at all but very low temperatures.

Mutual influence of ligands in coordination compounds is usually understood as the change of bonding properties of M - X_i bonds in the ground state of compounds of the type MX_nL elicited by an exchange of the ligand L. Such ligand exchange has 'static' consequences on the one hand (spectral, structural, thermodynamic), and the so called 'dynamic' consequences, which concern predominantly kinetic properties of compounds in question. While in the first case we speak of 'an influence', in the second case we deal with an 'effect', such as e.g. the *trans*- effect, discovered by Chernyaiev (122, 123).

The very early theory that dealt with mutual influencing of ligands was the polarization theory of *trans*-influence (124), which assumed the formation of an induced dipole in a ligand in *trans*-position to the substituent L, the influence having been mediated by the central atom. Exclusively electrostatic character of the interaction between ligands, assumed by the theory, has been its weakest point, since the *trans*-effect was often observed with central atoms having ligands connected by bonds with high degree of covalent character.

Syrkin (125) tried to account for the effect of mutual influencing of ligands by assuming a rehybridization of orbitals of the central atom, whereby the p-character of such orbitals decreased as a consequence of higher covalent character of M - L bond with respect to the M - X bond.

Another approach to the problem (126, 127) asserted that a dative π-bond has been formed between the transition metal and the ligand. However, such approach failed to explain large *trans*-effect of ligands such as H^- and CH_3^-, which cannot act as π-acceptors.

Yatsimirskii (128 - 130) introduced the term 'undirected influence', manifesting itself on and assume three-centre M - L - X orbital, and which allowed for other effects at different L-M-X angles as well. Such were, for instance, the *cis*-effect (angle L-M-

X = = 90°), the *trans* effect (angle L-M-X = 180°), as well as additional effects observable at other angles in the molecular fragment. The analysis of nodal points in such three-centre MO (131, 132) allowed some qualitative conclusions concerning the *trans* and *cis* effect.

The first quantitative theory of mutual influencing of ligands has been presented by Nefedov and collaborators (133 - 138); it was based formally on the perturbation theory of localized molecular orbitals. The authors showed that the *trans*-effect of ligands correlated with characteristics of the M - X bond , such as population of bonding overlap and nuclear charge. Those characteristics could then serve as quantitative parameters of the bond strength of the M - X bond, and indeed of the influence of the ligand L in position *trans* to X.

The concept of *trans* and *cis* effects in understanding of mutual interactions between ligands has been extended to encompass also the equatorial-axial interaction (139, 140). The term describes collective interactions among ligands in the equatorial plane on the one hand and axially bonded ligands on the other. Studies of the adiabatic potential of complexes $[CuX_6]^q$ ($X = H_2O, F^-, Cl^-, Br^-$) (114, 141) revealed that interactions between ligands have a through-bond character, mediated by the central atom.

2.7 SYMMETRY IN CHEMICAL REACTIONS

The role of molecular symmetry in affecting the course of chemical reactions was recognized already by Mulliken (142), Schuler (143) and others (144, 145) authors utilizing the correlation methods.

The most successful in this respect have become rules formulated by Woodward and Hoffmann (146-149), although similar approach had earlier been taken by Coulson and Longuett-Higgins (150, 151), Fukui (152, 153) and Dewar (154). It was Bader (155) who first pointed out the possibility of explicit utilization of symmetry invoked restrictions to chemical reactivity; in his case the transformations of an activated complex to products by a monomolecular reaction were involved.

Mechanisms of monomolecular reactions were also studied by Salem (156) and Pearson (157-159). In contrast to the method of correlation diagrams which assessed the feasibility of a reaction by evaluating the correlation between the symmetry of electronic states of reactants and those of the products, the theory of activated complex and monomolecular reactions examined the system's symmetry in a single point on the reaction coordinate. Pearson was able to extend (160-162) the approach so that it encompassed bimolecular reactions as well; he applied the perturbation theory to clarify the principle of the conservation of orbital symmetry in chemical reactions (163).

2.7.1 Woodward-Hoffmann Rules

When we analyze elementary steps of a chemical reaction, we discover that the reaction mechanism can be roughly classified into two groups:

1) concerted reactions, which take place in a single elementary act. The plot of total energy against the reaction coordinate does not show any extreme, that is in no point at the reaction coordinate having

$$\partial E/\partial Q = 0 \qquad [228]$$

2) Nonconcerted reactions, designated also as step-wise reactions, and taking place as a sequence of elementary steps. The energy of the system reaches along the reaction coordinate the corresponding number of extremal points.

The whole reaction can be thus split up to a series of elementary steps, each of which obeys the symmetry rules. The overall process however, as defined the stoichiometry, does not conform to symmetry rules. Consequently the system is allowed to change geometry in extremal points.

Let us consider a concerted elementary reactions of arbitrary molecularity, and following the reaction coordinate shown in Fig. 19. Each point at the curve represents a definite configuration $R \equiv (R_1, R_2, \ldots R_N)$ of nuclei of a pseudomolecule, composed of atoms of reactants, and represented by a definite point group of symmetry $G(R)$.

The electronic states of such pseudomolecules are in the Born-Oppenheimer approximation represented by an adiabatic potential. Let us now examine a thermal reaction of closed-shell reactants. Let us define a reaction coordinate as a series of configurations leading from reactants to products along the energetically most favourable pathway on the energy hypersurface of the ground electronic state. Now consider a small shift of nuclei from the parent configuration Q_0 to a new configuration $Q = Q_0 + \delta Q$. Each such a shift can in our analysis be represented by the sum of shifts corresponding to normal modes of the pseudomolecules. The Hamiltonian of the reacting system can be expanded to a Taylor series

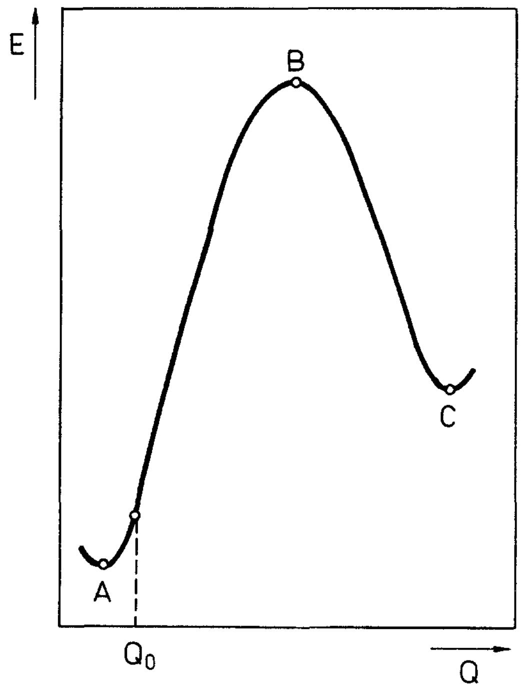

Fig. 19. The dependence of energy of the system upon the reaction coordinate: A - reactants; B - activated complex; C - products.

$$\hat{H} = \hat{H}_0 + [\partial\hat{V}/\partial Q]_0\ \delta Q + (1/2)\ [\partial^2\hat{V}/\partial Q^2]_0\ \delta Q^2 + \ldots \qquad [229]$$

The potential energy $\hat{V}$ comprises the energy of mutual interaction of nuclei $\hat{V}_{NN}$ and that of the electrons-nuclei interaction $\hat{V}_{eN}$. Kinetic energy of electron and their mutual repulsion can be neglected in the series, since neither is a function of nuclear coordinates in the first approximation. The requirement that the system Hamiltonian must be totally symmetric towards any symmetry operation of the pseudomolecules rules that operators δQ and $(\partial V/\partial Q)_0$ belong to the same representation of the symmetry point group. The operator δQ^2 being totally symmetric, the operator $(\partial^2 V/\partial Q^2)_0$ too has to belong to a totally symmetric representation, since only then their direct product will be totally symmetric, too. The second order perturbation theory for δQ gives for the energy of the ground electronic state of the system

$$E = E_0 + \delta Q\langle\Psi_0|\partial\hat{V}/\partial Q|\Psi_0\rangle + (1/2)\delta Q^2\langle\Psi_0|\partial^2\hat{V}/\partial Q^2|\Psi_0\rangle +$$

$$+ \delta Q^2\sum_{k=1}^{\infty}\langle\Psi_0|\partial\hat{V}/\partial Q|\Psi_k\rangle^2/(E_0 - E_k) = E_0 + E^{(1)} + E^{(2)} + E^{(2')}\ldots [230]$$

The perturbed wave function expressed with the first order precision in Q then reads

$$|\Psi\rangle = |\Psi_0\rangle + \delta Q \sum_{k=1}^{\infty} (E_0 - E_k)^{-1} \langle\Psi_0|\partial\hat{V}/\partial Q|\Psi_k\rangle\ |\Psi_k\rangle \qquad [231]$$

Notwithstanding the fact that the expression holds true only for small displacements around Q, it can still be generalized, since Q_0 can arbitrarily selected along the reaction coordinate, and thus the entire reaction coordinate can be represented by a series of incremental changes δQ.

Qualitative assessment of integrals in [230] is facilitated by by the well-known group theory rule (Section 1.2.1), according to which the integral is non-zero only if the sub integral function contains a totally symmetric representation.

Since in any extreme of the adiabatic potential

$$\partial E/\partial Q = 0 \qquad [232]$$

the linear term $E^{(1)}$ in [230] equals zero irrespective of the system's symmetry. Complications arise when Ψ_0 belongs to a degenerate representation, potentially distorted by the Jahn-Teller effect. From the point of view of chemical reactivity this, however, is hardly of interest, and we shall assume that Ψ_0 belongs to a nondegenerate irreducible representation.

The direct product of nondegenerate representations always retains the total symmetry and consequently $\Gamma_0 \otimes \Gamma_0$ is a totally symmetric representation. In order that the $E^{(1)}$ term in [230] be nonzero in both ascending and descending region of the reaction coordinate the operator $(\partial V/\partial Q)$ and thus also δQ have to be totally symmetric. Such symmetry analysis allowed Pearson to formulate the first selection rule:

1. With the exception of extremes at the adiabatic potential curve all reaction coordinates Q belong to the totally symmetric representation of the symmetry point group of the reacting system.

Even though the totally symmetric nuclear motion can change bond angles and distances, it cannot alter the symmetry group of the system. This rule does not hold true for extremal points of the reaction coordinate, in which the normal mode can be orthogonal to the reaction coordinate. Accordingly then the entire reaction coordinate between the extremal points belongs to the same symmetry point group.

Integral $\langle\Psi_0|\partial^2V/\partial Q^2)|\Psi_0\rangle$ assumes non-zero values since, as has already been shown, operator $(\partial^2V/\partial Q^2)$ is totally symmetric. The integral represents the force constant resisting the nuclear motion from the parent Q_0 nuclear configuration taking place along the reaction coordinate Q, $|\Psi_0|^2$ the probability of the occurrence of electrons.

The last term in equation [230] $E^{(2')}$ gauges the change of energy the system experiences due to redistribution of its electrons. The summation runs over electron excited states of the Q_0 configuration. The wave function, however, would change only if the electron redistribution elicited by changed nuclear configuration is energetically favourable. Salem designates this energy-lowering effect (163) relaxibility of the system along the reaction coordinate. Its denominator being negative the whole term $E^{(2')}$ is negative and as such responsible for lowering of energy barriers of the reaction, provided the integral $\langle\Psi_0|\partial^2V/\partial Q^2)|\Psi_k\rangle$ is non-zero. The total symmetry of operator $(\partial^2V/\partial Q^2)$ requires that wave functions Ψ_0 and Ψ_k be of the same symmetry. As has been demonstrated by Fukui and by other authors (152, 164, 165), it is significant that the integral reaches sufficiently large values only for low lying Ψ_k excited states. This allows us to formulate the second symmetry rule:

2. Only reaction whose low lying excited electron states retains the symmetry of the ground state have acceptable activation energy. Changes in electron density during excitation must be consistent with the corresponding nuclear motions.

Reactions conforming to the symmetry rules are called **symmetry allowed. Symmetry forbidden** on the other hand are reactions slowed by excessive activation energies as a consequence of the absence of suitable low lying excited states along the reaction coordinate.

The precision of equation [230] ends with the second order of δQ, a fact that also holds true for the symmetry considerations. For practical application we are forced to accept further simplifications. One of them is the assumption that MO LCAO wave functions are taken for exact solutions of the system's Hamiltonian $\hat{H}_0$. As long as we are interested in symmetry properties of the system, this assumption is acceptable. It must be realized however that the inclusion of configuration interaction may alter the ground state symmetry.

Another simplification we often resort to has a more drastic character - in the equation [230] we restrict ourselves to several lowest lying excited states instead of summing over all possible excited states. This is permissible as it can be shown that contributions form the latter converge sufficiently fast to $|E_0 - E_k|$

since the value of integral $\langle\Psi_0|\partial^2V/\partial Q^2)|\Psi_k\rangle$ is inversely proportional to the difference $E_0 - E_k$.

For practical purpose we simplify the MO theory by substituting symmetry of the product of molecular orbitals ϕ_i and ϕ_f for the symmetry of the product of wave functions Ψ_0 and Ψ_k, where ϕ_i (ϕ_f) are occupied molecular orbitals in the respective ground (excited) state. The electron transfer from ϕ_i to ϕ_f engenders the redistribution of electrons density in the molecule. In the region of positive overlap of ϕ_i and ϕ_f the electron density increases, in the region of negative overlap decreases; positively charge nuclei move toward the higher electron density region, defining thus the reaction coordinate with the same symmetry as that of $\Gamma_i \otimes \Gamma_f$.

Consider a reaction the detailed reaction mechanism of which is unknown. Bonding situation of a pseudomolecule along the reaction coordinate varies with the changing MO. The greatest changes are to be expected in molecular orbitals involved in creation/cleavage of bonds. It is these molecular orbitals that we concern ourselves with in analyzing the symmetry-induced restrictions. In doing so we must not forget that canonical MOs are the solution of the secular equation and in MO LCAO are formed from atomic orbitals of the respective atoms. That means that for construction of MO of both reactants and products we utilize the same basis set of atomic orbitals. Let us assume, for simplicity sake, that the reaction involves the change of only one bond, and hence of only one corresponding molecular orbital. The system before reaction is described by the wave function Ψ_0, the final state by the wave function Ψ. The relationship between these wave functions defines with the first order in δQ precision the equation [231], whereby its second term can be considered to represent the correction of the starting Ψ_0 as a response to the changed bonding situation. Symmetry rules then restrict us to such combinations of wave functions Ψ_0 and Ψ_k that belong to the same irreducible representation of the symmetry point group of the system. In other words, wave functions Ψ_0 and Ψ_k must be of the same symmetry.

Within the MO method the wave functions Ψ_k are constructed in the form of Slater determinants formed of the corresponding spin orbitals. Let the molecular orbital ϕ_a represents the bond changed in the course of reaction. Further let MO ϕ_a of the parent system corresponds to MO ϕ_b of the changed bonding situation. Applying all the simplifications we are concerned only with ϕ_a and ϕ_b. Now in order for the reaction to be symmetry allowed the MO ϕ_a has to have the same symmetry as MO ϕ_b of the product, since only then the wave function Ψ_0 would correlate with Ψ_k. We are now in the position to formulate the principle of conservation of orbital symmetry:

Concerted reactions in which orbital symmetries in reactants and products are conserved proceed easily.

In symmetry allowed reaction electrons are transferred from the highest occupied molecular orbital (HOMO) of reactants ϕ_i to the lowest unoccupied MO (LUMO) of products ϕ_j. The orbitals in question have the same symmetry and their overlap integral is positive. Owing to the negative value of the last term in equation [230] such overlap would decrease the energy of the system and keep the energy barrier at acceptable value. The HOMO-LUMO charge transfer will however be effective only if directed towards electronegative atoms. In such case the absolute value of denominator in the last term of [230] would be small, and hence the stabilization effect of the charge transfer large.

The principle of conservation of orbitals symmetry has been allied by its originators Woodward-Hoffmann and numerous other authors to many organic reactions. Pearson and others (155-163) applied it to reactions of inorganic systems; the rules were later extended to important catalytic reactions as well (166-173). The principle of conservation of orbitals symmetry has since become an important tool in investigating chemical reactivity.

When applying the principle of conservation of orbital symmetry to coordination compounds we have to realize that due to spin-orbit interaction characteristic for them it no longer makes sense to classify separately orbital and spin angular momenta. The reaction taking place in such systems can thus involve change in spin state ($\Delta S = = \pm 1$) and violate at the same time the principle of conservation of orbital symmetry. Nevertheless, the symmetry of the wave function (total angular momentum) is conserved.

2.7.2 Frontier Orbital Theory

According to the perturbation theory properties of frontier orbitals are the principal factor affecting the course of chemical reaction. In the preceding chapter we showed that the last term in equation [230] was responsible for the lowering of activation energy. Simple MO theory allows us to rewrite it to

$$E^{(2)} = 2\delta Q \sum_{i}^{occ} \sum_{p}^{vir} \frac{\langle\phi_i|\partial\hat{V}/\partial Q|\phi_p\rangle}{\epsilon_p - \epsilon_i} \qquad [233]$$

where ϕ_i (ϕ_p) are occupied (unoccupied) MO, ϵ_i (ϵ_p) the corresponding orbital energies. HOMO and LUMO are the closest at energy scale and we can safely assume the biggest stabilization would emanate from their interaction.

For a bimolecular reaction the Eq. [233] can be rewritten (174, 175) to

$$E^{(2)} = 2\delta Q \sum_{i}^{occ} \sum_{p'}^{vir} \frac{<\phi_i|\partial\hat{V}/\partial Q|\phi_{p'}>^2}{\epsilon_{p'} - \epsilon_i} +$$

$$+ 2\delta Q^2 \sum_{i'}^{occ} \sum_{p}^{vir} \frac{<\phi_{i'}|\partial\hat{V}/\partial Q|\phi_p>^2}{\epsilon_p - \epsilon_{i'}} \qquad [234]$$

where primed indices characterize one, and simple indices the other reactant. Since δQ has to be totally symmetric coordinate, only those terms in [234] would assume nonzero values, for which ϕ_i and $\phi_{p'}$, or $\phi_{i'}$ and ϕ_p have the same symmetry.

Consider an interaction between a doubly occupied HOMO of particle A and an unoccupied LUMO of particle B (Fig. 20). The interaction creates two novel orbitals of compound particle (pseudomolecule) AB, whereby energy of the bonding orbital would decrease, that of the antibonding orbital would increase. In absolute value the increase of energy of antibonding orbital is bigger than the stabilization of the bonding orbital (174). If both new orbitals should be doubly occupied, the energy of the pseudomolecule AB would rise, meaning that the particles would repel each other. The activation energy would thereby remain acceptably low only if the delocalization stabilization is large, i.e. the strength of the HOMO-LUMO interaction is directly proportional to their overlap and indirectly proportional to the energy gap between them. Based on

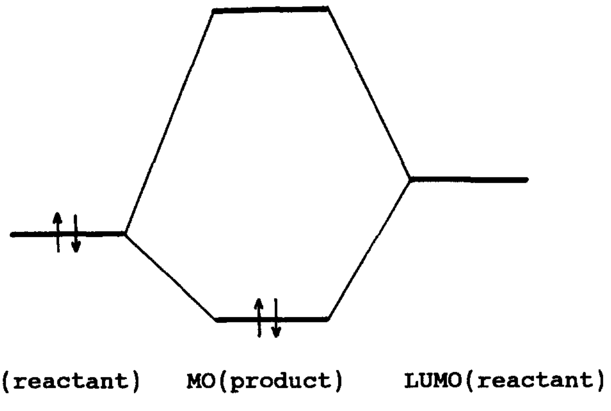

Fig. 20. The scheme of HOMO-LUMO interaction.

such reasoning additional rules have been formulated, allowing qualitative assessment of the forbideness or allowedness of reactions. These are the following:

1) In our assessment we restrict ourselves to HOMOs and LUMOs, as their overlap furnishes the crucial contribution to the total energy of the system. As the reactants approach each other a stabilizing interaction between HOMO(A)-LUMO(B) and vice versa takes place, involving a charge transfer $A \rightleftarrows B$.

2) Frontier orbitals must have suitable geometry in order that their overlap be effective.

3) The interacting HOMO and LUMO must not lie too far apart on energy scale ($\Delta E < 6$eV). If symmetry considerations prevent frontier orbital from interacting, their role can be assumed by other orbitals, provided the energy difference is not too large.

4) HOMO and LUMO must correspond to broken and newly created bonds respectively. This holds true if both orbitals are bonding in both regions. In case they are antibonding the requirement is reversed.

If no pair of orbitals conforming to the above conditions can be found the reaction is forbidden. The rules are based on the perturbation theory and apply only for early stages of the reaction; further along the reaction coordinate symmetry can be changed, an event sufficiently rare to render the above rules practicable.

The reaction may involve a radical as one of the reactants. Its SOMO (singly occupied MO) takes over the role of HOMO or LUMO, or both, depending on the energy gap between the closed-shell orbitals (176) and SOMO of the respective reactants.

2.7.3 Catalysis of Symmetry Forbidden Reactions

Although conservation of orbital symmetry itself does not suffice to promote chemical reactions, symmetry forbidden reaction practically do not proceed. Any reaction proceeds spontaneously, provide its maximum work is positive. The maximum work is therefore called also the chemical affinity of reaction. Practical utility of a reaction however does not depend on its thermodynamic feasibility alone, but largely on the reaction rate. The reaction rate is closely related to the activation energy of the reaction. Surprisingly, even a simple MO theory succeeds in describing clearly the effect activation energy exerts on the course of chemical reaction. This fact unmistakably reflects the extraordinary importance of symmetry properties of molecular orbitals in assessing the possible course of reaction. The necessary condition for a low activation energy of a reaction is the conservation of symmetry of occupied orbitals. Ideally, bonding molecular orbitals of reactants and products possess the same symmetry - they correlate. Such situation invokes no symmetry imposed restrictions and having low activation energies they are called **symmetry allowed**. Now if bonding orbitals of reactants correlate with antibonding or nonbonding orbitals of products, symmetry considerations renders such reactions improbable, with the concomitant high activation energy. In other words, such reactions are **symmetry forbidden**. We must note here that critical symmetry correlations only concern molecular orbitals with different occupational numbers. The molecular system responds in such a way as to maximally conserve bonding properties (e.g. symmetry correlation of bonding MOs). Drastic changes in bonding situation implies high activation energies and such processes are under usual experimental conditions improbable. There are however chemical or physical agents (excitation, ionization, catalysis) capable of reestablishing normal bonding conditions and hence of lifting symmetry imposed restrictions.

Let us now consider a chemical reaction $A \rightarrow B$, for which we have set up a correlation diagram shown in Fig. 21a. Symmetry properties are indicated by S (symmetric) and A (antisymmetric) respectively. In addition, antibonding orbitals are indicated by an asterix. As it is, the shown reaction is symmetry forbidden, owing to the correlation of the bonding $\Psi_{2A}(S)$ orbitals and an unoccupied antibonding $\Psi^{*}_{3B}(S)$ orbital, and an unoccupied antibonding orbital $\Psi^{*}_{3A}(A)$ with the occupied bonding $\Psi_{2B}(A)$ orbitals. In other words, the ground state of A correlates with the excited state of B. If the reaction is to proceed in spite of high activation energy, the product arisen would have to have the $\Psi^{2}_{1B}(S)\ \Psi^{0}_{2B}(A)\ \Psi^{2}_{3B}(S)\ \Psi^{0}_{4B}(A)$ configuration. Excitation energy of this state makes up a substantial part of the total activation energy.

Symmetry imposed restrictions in such a reaction can be overcome either by excitation, ionization or by catalytic action of transition metals (167, 172, 173, 177-179).

a) *Excitation*

If the system A enters the reaction in the excited state $\Psi^{2}_{1A}(S)\ \Psi^{0}_{2A}(S)\ \Psi^{*2}_{3A}(A)\ \Psi^{*0}_{4A}(A)$, the transformation $A^{*} \rightarrow B$ involves electron transfer from an antibonding to a bonding orbital, a transport that would lower the systems energy. Electron population

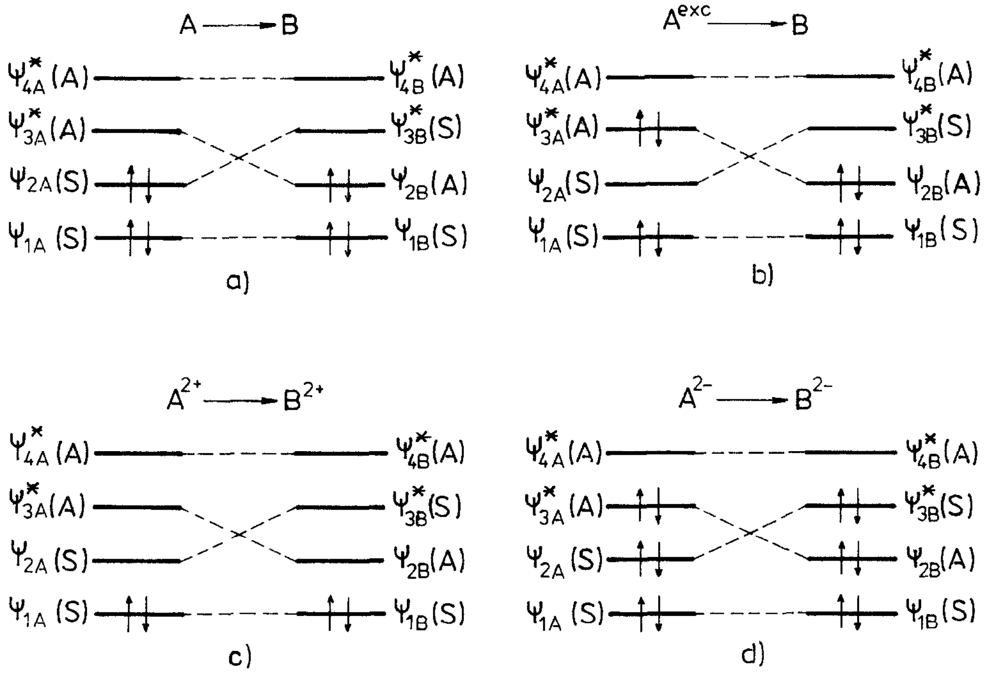

Fig. 21. Correlation diagram of the reaction: a) A → B type; b) A^{exc} → B type; c) $A^{2+} \rightarrow B^{2+}$ type; d) $A^{2-} \rightarrow B^{2-}$ type.

of the system A has by excitation become capable of creating a bonding situation in the bonding band of the system B; symmetry correlations occupied orbitals with unoccupied MOs have been removed (Fig. 21.b).

b) *Ionization*

1) Reaction $A^{2+} \longrightarrow B^{2+}$

Compound A enters the reaction as a cation, possessing the configuration $\Psi_{1B}^{2}(S)\ \Psi_{2B}^{0}(S)\ \Psi_{3B}^{*0}(A)\ \Psi_{4B}^{*0}(A)$. As it appears from inspection of Fig. 21c, critical correlations $\Psi_{2A}(S) \rightarrow \Psi_{3B}(S)$ and $\Psi_{3A}(A) \rightarrow \Psi_{2B}(A)$ are under such conditions not operative, the ground state of A correlates with the ground state of B^{2+} and energy barrier of the reaction is lowered.

2) Reaction $A^{2-} \longrightarrow B^{2-}$

The reactant A^{2-} has the electron configuration $\Psi_{1B}^{2}(S)\ \Psi_{2B}^{2}(S)\ \Psi_{3B}^{*2}(A)\ \Psi_{4B}^{*0}(A)$. The correlation diagram (Fig. 21d) shows that by populating the antibonding orbital Ψ_{3A}^{*} by an electron pair removes the symmetry forbidden correlation between the filled bonding and vacant antibonding molecular orbitals. Once again the ground state of A^{2-} corresponds to that of B^{2-}, so that we can expect a lower energy barrier of the reaction.

c) *Catalytic effect of transition metals*

Numerous important and symmetry forbidden chemical reactions proceed smoothly when catalyzed by transition element catalysts. Such significant change in reactivity is the consequence of electron density redistribution, and the corollary change in symmetry of the filled molecular orbitals coordinated to a transition element. Processes made feasible in this way are called **catalytically allowed**. In view of the growing practical importance of such reactions the interest in their theoretical study has attracted a lot of attention (177-184). MO of ligands interact with orbitals of the transition element of suitable symmetry, bringing about a redistribution of electron density between the particles and eventually a donor-acceptor bond. In this manner can a bonding π orbital of an olefin ligand furnish electrons to unfilled orbitals of the transition metal (donor bond), whilst the antibonding π^* orbital accepts electrons from its filled orbitals (acceptor bond). In such a donor-acceptor interaction only the symmetry of participating orbitals counts (Fig. 22).

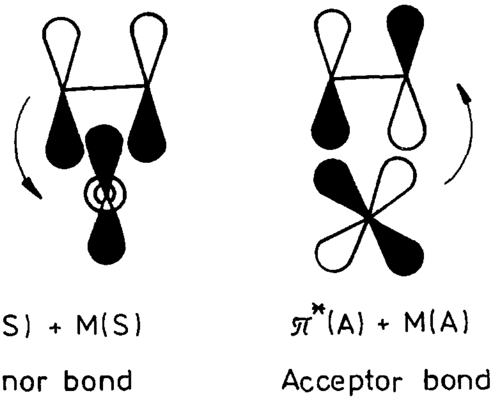

Fig. 22. The scheme of donor-acceptor interaction transition metal--reactant.

Both the donor and acceptor interaction lessens the bonding of the coordinated ligands. The mutual electron exchange, as described above, diminishes the effect the bond order of the ligand and reshuffles its electron structure not unlike an excitation does. Indeed, reactions of in such a way coordinated ligands resemble those of an excited state. An extreme example is the symmetry-restricted electron transfer from filled orbitals of the transition element to vacant antibonding π^* orbitals of the ligand. As a consequence, ligands enriched by electron from the central atom behave like anion radicals (one electron transfer) L^-, or as a dianion L^{2-} (electron pair transfer) respectively. An opposite extreme occurs when occupancy of transition metal orbitals allows only for a donor interactions. In such a case ligands assume the character of a cation radical L^+ , or a dication L^{2+}.

Let us now analyze a situation depicted in Fig. 23. The reaction in question is a symmetry-forbidden A ⟶ B process, taking place in the presence of a transition element. The correlation $\Psi_{2A}(S) \longrightarrow \Psi_{3B}(S)$ that would otherwise render the process symmetry forbidden has been weakened by electron redistribution towards the ligands orbitals by their interaction with those of the central atom. The latter provides an unfilled orbital of suitable symmetry for an interaction with the bonding $\Psi_{2A}(S)$ orbital, taking away some of its electron density. At the same time electron density in $\Psi^*_{3A}(A)$ grows as a consequence of its interaction with a filled antisymmetric orbital of the transition element. Both reactants, in fact two ligands, bind to the central atom, each in its own way.

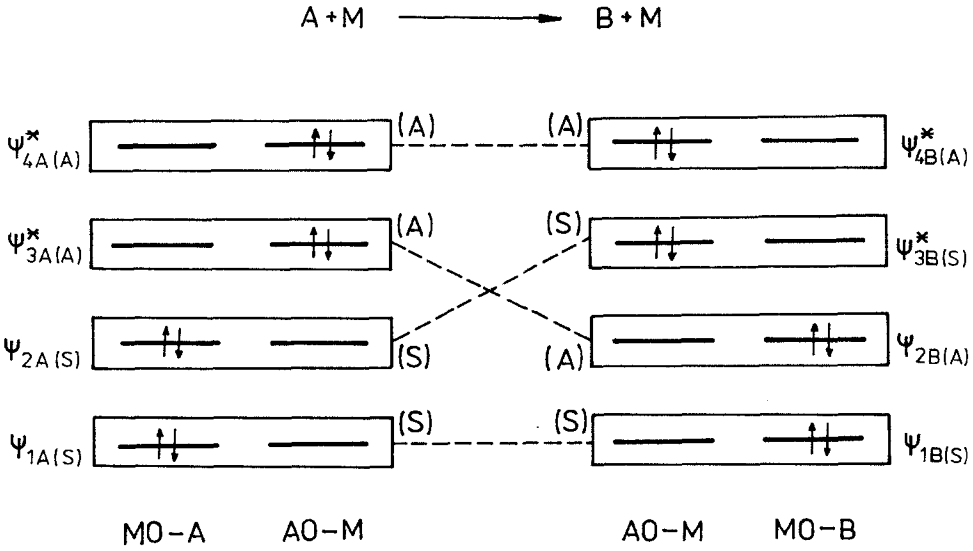

Fig. 23. Correlation diagram of the reaction A → B in the presence of transition metal.

Electron pair exchange is the result of reshuffling of valence electrons of the transition metal ($S^0A^2 \longrightarrow A^0S^2$); orbitals are designated according to their symmetry. Redistribution of electrons is an essential prerequisite for preservation of coordination bonds. In ligands a partial mixing of ground and excited state takes place, shifting the character of the species to the latter. This is a characteristic feature of coordination linkages in catalytically allowed reactions. Growing electron population in the Ψ^*_{3A} orbital decreases the bonding order in the ligand and facilitates bonding in the system B (Ψ_{2B}). Reduced electron population of Ψ_{2A} has similar effect (Fig. 23).

In conclusion we may say that the role of coordination bonds in catalytically allowed reactions lies in creating new bonding conditions and thus in lifting the symmetry-imposed restrictions by mixing of ground and excited states of the ligand as a consequence of coordination to the central atom.

2.7.4 Topological Approach

The topological approach (185, 186) tries to simplify the problem of chemical reactivity by concentrating on essentials. The crucial facts can be summarized as follows:

1) In a chemical reaction bonds get broken and new ones are created, a process in which bond lengths undergo far greater changes then either bond or dihedral angles.

2) The same result yields also the analysis of force constants of valence and deformation vibrations.

3) Bonding parameters are well transferable between similar molecular moieties.

4) Transformations of canonical molecular orbitals to orthogonal localized orbitals usually wipe out matrix elements between atoms not directly bonded by a chemical bond.

The topological method takes into account these facts and

a) utilizes basis set of orthogonal hybrid atomic orbitals;

b) neglects interaction between orbitals at the same centre;

c) neglects interactions between indirectly bonded atoms;

d) it expresses broken and created bonds as a linear combination of hybrid atomic orbitals of reactants χ_{ir} and products χ_{ip}

$$\varphi_i = \cos\alpha_i \, \chi_{ir} + \sin\alpha_i \, \chi_{ip} \qquad [235]$$

In this manner the adiabatic potential curve becomes a simple function of trigonometric functions at reaction centres and can accordingly be easily mapped and reaction coordinates calculated.

The topological method harbours several advantages, among them:

a) reduction by two orders of magnitude the amount of necessary calculations;

b) the matrix of force constant can be directly calculated by explicit derivation of simple trigonometric functions;

c) reaction coordinates show neither discontinuities nor chemical hysteresis;

d) reduced amount of calculations allows treatment of bigger systems.

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3. MOLECULAR ORBITAL THEORY

The majority of the present apparatus of quantum chemistry is derived from molecular orbital theory. The nodus operandi of this group of methods involves the expansion of one-electron wave functions - molecular orbitals into a basis set of one-centre analytic functions - referred to as the LCAO approximation. The expansion coefficients are determined by the iterative solution of Roothaan equations. For the open-shell systems, there exist several alternative procedures (UHF, RHF, LHP). Different computational procedures can be classified into four basic groups according to the degree of approximation introduced, namely: *ab initio* methods, non-empirical methods, methods using zero differential overlap approximation, and last, but not least, effective Hamiltonian methods. For compounds containing heavy atoms it is important to cover some relativistic effects. When performing molecular orbital calculations, two basic steps are distinguished: the calculation of integrals from basis set functions and the self-consistent field procedure. Computational algorithms are applied in such a manner that, as a rule, they yield the so-called canonical molecular orbitals diagonalizing, as a result, the matrix of Lgrangian multipliers. They show one important property - they are transformed according to individual irreducible representations of the molecular symmetry point group permitting their effective use for the semi-quantitative description of ionized and excited molecular states. An alternative solution of the Hartree-Fock equations is represented by localized MOs enabling the description of collective molecular properties in the form of additive contributions of two-electron covalent bonds, lone pairs, etc. The construction of strictly localized MOs is connected with the hybridization concept - formation of one-centre orbitals having directional properties.

3.1 LCAO APPROXIMATION

3.1.1 Charge Density Bond-Order Matrix

The LCAO approximation is based on the linear expansion of molecular orbitals $|\phi_k\rangle$ into the basis set of other (known) one-center functions $|\vartheta_i\rangle$

$$|\phi_k\rangle = \sum_i^m C_{ki}\ |\vartheta_i\rangle \qquad [1]$$

As a rule, this basis set is formed of atomic orbitals, and hence the name linear combination of atomic orbitals. (The basis set may consist of arbitrary one-centre functions, localized for instance in the middle of the chemical bond.)

For the column vector of molecular spinorbitals in matrix form one can write

$$\{\psi\} = \begin{pmatrix} \{\psi^\alpha\} \\ \{\psi^\beta\} \end{pmatrix} = \begin{pmatrix} \alpha\ \{\phi^\alpha\} \\ \beta\ \{\phi^\beta\} \end{pmatrix} = \begin{pmatrix} \alpha\ \mathbf{C}^\alpha; & 0 \\ 0 & ;\ \beta\ \mathbf{C}^\beta \end{pmatrix} \begin{pmatrix} \{\vartheta^\alpha\} \\ \{\vartheta^\beta\} \end{pmatrix} \qquad [2]$$

where α and β represent the spin functions, $\mathbf{C}^\eta$ is the square matrix composed of LCAO coefficients and $\{\vartheta^\eta\}$ is the column vector of basis set functions for $\eta = \alpha$ or β. The operator which secures a selection of n-electron configurations $\{\psi_u\}$ from the set of m molecular spinorbitals $\{\psi\}$ can be represented by a selection matrix J of dimension n x 2m

$$\{\psi_u\} = \mathbf{J}\ \{\psi\} = \begin{pmatrix} \mathbf{J}^\alpha; & 0 \\ 0 & ;\ \mathbf{J}^\beta \end{pmatrix} \begin{pmatrix} \{\psi^\alpha\} \\ \{\psi^\beta\} \end{pmatrix} = \begin{pmatrix} \alpha\ \mathbf{J}^\alpha\ \mathbf{C}^\alpha; & 0 \\ 0 & ;\ \beta\ \mathbf{J}^\beta\ \mathbf{C}^\beta \end{pmatrix} \begin{pmatrix} \{\vartheta^\alpha\} \\ \{\vartheta^\beta\} \end{pmatrix} \qquad [3]$$

Matrix J originates by omitting all zero rows of the diagonal matrix M of the occupation numbers of molecular spinorbitals; it fulfils the following relationships

$$\mathbf{J}^T\mathbf{J} = \mathbf{M} \qquad [4]$$

$$\mathbf{J}\mathbf{J}^T = \mathbf{I} \qquad [5]$$

Matrix M has properties of a projection operator, i.e. $\mathbf{M}^2 = \mathbf{M}$ and $Tr\{\mathbf{M}\} = n$. Matrices M and J may be exemplified by

$$\mathbf{M} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \qquad \mathbf{J} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

Then for the matrix of non-orthogonality integrals it holds true that

$$\mathbf{D}^{uu} = \langle\{\psi_u\}|\{\psi_u\}^+\rangle = \begin{pmatrix} \mathbf{J}^\alpha\mathbf{C}^\alpha\mathbf{S}^\alpha\mathbf{C}^{\alpha+}\mathbf{J}^{\alpha+}; & 0 \\ 0 & ;\ \mathbf{J}^\beta\mathbf{C}^\beta\mathbf{S}^\beta\mathbf{C}^{\beta+}\mathbf{J}^{\beta+} \end{pmatrix} \qquad [6]$$

where $\mathbf{S}^\eta = \langle\{\vartheta^\eta\}|\{\vartheta^\eta\}^+\rangle$ is a matrix of overlap integrals of basis set functions. Orthogonality of the spin functions is the cause of zero off-diagonal blocks of the matrix $\mathbf{D}^{uu}$. Then by substituting into the definition for the Fock-Dirac density matrix the following expression can be obtained

$$\rho(1,2) = \{\psi_u(1)\}^+(D^{-1})^{uu}\{\psi_u(2)\} =$$

$$= \alpha(1)\{\vartheta^\alpha(1)\}^+P^\alpha\{\vartheta^\alpha(2)\}\alpha(2) + \beta(1)\{\vartheta^\beta(1)\}^+P^\beta\{\vartheta^\beta(2)\}\beta(2) \quad [7]$$

where the square **charge-density (bond-order) matrices**

$$P^\alpha = C^{\alpha+}J^{\alpha+}(J^\alpha C^\alpha S^\alpha C^{\alpha+}J^{\alpha+})^{-1}J^\alpha C^\alpha$$

$$P^\beta = C^{\beta+}J^{\beta+}(J^\beta C^\beta S^\beta C^{\beta+}J^{\beta+})^{-1}J^\beta C^\beta \quad [8]$$

have been introduced in the basis set of atomic orbitals for α and β spins, respectively. These matrices comply with the properties of projection operators in the non-orthogonal space of the metrics S^η

$$P^\eta S^\eta P^\eta = P^\eta \quad [9]$$

$$Tr\{S^\eta P^\eta\} = n_\eta \quad [10]$$

whereby $n_\alpha + n_\beta = n$ holds. In the case of the orthogonal molecular spinorbitals the matrix D^{uu} is reduced to unit one I, so that a simplified relationship is satisfied

$$P^\eta = C^{\eta+}J^{\eta+}J^\eta C^\eta = C^{\eta+}M^\eta C^\eta \quad [11]$$

Since the basis set functions are independent of the spin indices, it can be further written that $\{\vartheta^\alpha\} = \{\vartheta^\beta\} = \{\vartheta\}$ and $S^\alpha = S^\beta = S$. With the use of the Fock-Dirac density matrix the mean value of the operator $\hat{A}$ in the LCAO approximation can be written as follows

$$<A>_u = <\Phi_u|\hat{A}|\Phi_u> = A_0 + \sum_{i,k}^{m} <\vartheta_i(1)|\hat{A}_1|\vartheta_k(1)>(P^\alpha_{ik} + P^\beta_{ik}) +$$

$$+ (1/2)\sum_{i,j,k,l}^{m} <\vartheta_i(1)\vartheta_j(2)|\hat{A}_{12}|\vartheta_k(1)\vartheta_l(2)> \times$$

$$\times [(P^\alpha_{ik} + P^\beta_{ik})(P^\alpha_{jl} + P^\beta_{jl}) - P^\alpha_{il}P^\alpha_{jk} - P^\beta_{il}P^\beta_{jk}] \quad [12]$$

Within the LCAO approximation the total molecular energy is

$$E_u = V_{NN} + \sum_{i,k}^{m} P^\alpha_{ki}\{h_{ik} + (1/2)\sum_{j,l}^{m}[(P^\alpha_{lj} + P^\beta_{jl})(ik|jl) - P^\alpha_{lj}(il|jk)]\} +$$

$$+ \sum_{i,k}^{m} P^\beta_{ki}\{h_{ik} + (1/2)\sum_{j,l}^{m}[(P^\alpha_{lj} + P^\beta_{lj})(ik|jl) - P^\beta_{lj}(il|jk)]\} =$$

$$= V_{NN} + (1/2)\sum_{i,k}^{m}[P^\alpha_{ki}(h_{ik} + F^\alpha_{ik}) + P^\beta_{ki}(h_{ik} + F^\beta_{ik})] \quad [13]$$

where the following abbreviations have been used

$$F^{\eta}_{ik} = h_{ik} + \sum_{j,l}^{m} [(P^{\alpha}_{lj} + P^{\beta}_{lj})(ik|jl) - P^{\eta}_{lj}(il|jk)] \qquad [14]$$

for the Fock-matrix elements,

$$h_{ik} = <\vartheta_k(1)|\hat{h}(1)|\vartheta_k(1)> = <i|\hat{h}|k> \qquad [15]$$

for one-electron bare integrals (they represent the energy of electrons in the field of nuclei) and

$$(ik|jl) = <ij|\hat{g}|kl> = <\vartheta_i(1)\vartheta_j(2)|\hat{g}(1,2)|\vartheta_k(1)\vartheta_l(2)> \qquad [16]$$

for two-electron repulsion integrals. These four-centre two-electron integrals satisfy the relationships

$$\begin{aligned}(ab|cd) &= (ab|dc) = (ba|cd) = (ba|dc) = \\ &= (cd|ab) = (cd|ba) = (dc|ab) = (dc|ba)\end{aligned} \qquad [17]$$

Let us recall that up to now no restrictions were placed upon one-electron functions, with respect for example, to orthogonality and normalization. The eventual non-orthogonality of the molecular orbitals taken into account in the definition of matrices P^{η}.

3.1.2 Roothaan Method for Closed-Shell Systems

In closed-shell systems the number of electrons with α spin coincides with those having β spin: $n_{\alpha} = n_{\beta} = n/2$. Similarly, the set of molecular orbitals for α and β spins is identical $\{\phi^{\alpha}\} = \{\phi^{\beta}\} = \{\phi\}$. For the matrices defined in the above paragraph it is true that $C^{\alpha} = C^{\beta} = C$, $F^{\alpha} = F^{\beta} = F$ and $P^{\alpha} = P^{\beta} = (1/2)P$. The expression for electronic energy of a closed-shell molecule can be written in the following form

$$E^{el} = (1/2)\sum_{i,k}^{m} P_{ki}(h_{ik} + F_{ik}) \qquad [18]$$

where the Fock matrix has the elements

$$F_{ik} = h_{ik} + \sum_{j,l}^{m} P_{lj}[(ik|jl) - (1/2)(il|jk)] \qquad [19]$$

In the case of orthogonal molecular orbitals the total bond-order matrix is given by the relationship

$$P = P^{\alpha} + P^{\beta} = 2C^{+}J^{+}JC = 2C^{+}MC \qquad [20]$$

The variational condition for computation of the LCAO matrix C is represented by the stationarity of the functional

$$\mathcal{F} = E^{el} - 2\sum_{a,b}^{m} \lambda_{ab} <\phi_a|\phi_b> \qquad [21]$$

where λ_{ab} are the Lagrangian multipliers (that must be derived) respecting the orthonormality conditions for molecular orbitals. First, the functional F is decomposed through the LCAO coefficients

$$F = 2 \sum_{i,k,\mu}^{m} C^{*}_{\mu k} M_{\mu\mu} C_{\mu i}\{h_{ik} +$$

$$+ \sum_{j,l,\nu}^{m} C^{*}_{\nu l} M_{\nu\nu} C_{\nu j}[(ik|jl) - (1/2)(il|jk)]\} -$$

$$- \sum_{a,b,p,q}^{m} C^{*}_{ap} S_{pq} C_{bq} \lambda_{ab} \qquad [22]$$

The stationary condition is

$$\delta F = \sum_{k,\mu}^{m} (\partial F/\partial C^{*}_{\mu k})\delta C^{*}_{\mu k} + \sum_{i,\mu}^{m} (\partial F/\partial C_{\mu i})\delta C_{\mu i} = 0 \qquad [23]$$

Since all the variations are independent, every summation term is separately zero. By performing prescribed operations with permitted re-indexing we can obtain

$$(\partial F/\partial C^{*}_{\mu k}) = 2\sum_{i}^{m} M_{\mu\mu} C_{\mu i} h_{ik} +$$

$$+ 4\sum_{i}^{m} M_{\mu\mu} C_{\mu i} \sum_{j,l,\nu}^{m} C^{*}_{\nu l} M_{\nu\nu} C_{\nu j} [(ik|jl) - (1/2)(il|jk)] -$$

$$- 2\sum_{b,q}^{m} S_{kq} C_{bq} \lambda_{\mu b} = 0 \qquad [24]$$

or

$$M_{\mu\mu} \sum_{i}^{m} C_{\mu i} F_{ik} = \sum_{b,q}^{m} S_{kq} C_{bq} \lambda_{\mu b} \qquad [25]$$

for all the values of the indices μ and k. Let us notice that the elements of the occupation number matrix **M** are either 0 or 1, so that in the matrix form

$$\mathbf{FC}^{+} = \mathbf{SC}^{+}\mathbf{L}$$

$$\mathbf{CF} = \mathbf{LCS} \qquad [26]$$

where **F**, **S** and **L** are hermitian matrices. Only the occupied molecular orbitals (for $M_{\mu\mu} = 1$) are determined by energetic criteria since the strict matrix equivalent of [25] is $\mathbf{FC}^{+}\mathbf{M} = \mathbf{SC}^{+}\mathbf{L}$. The unoccupied orbitals are bound only by orthonormality conditions.

The matrix equations derived above do not have a unambiguous solution with respect to the LCAO matrix **C**. The number of the unknown LCAO coefficients in matrix **C** is m x m while the number of the unknown Lagrangian multipliers in the hermitian matrix L is m(m + 1)/2. However, at our disposal is just m(m + 1)/2 linear independent equations [26] and m(m + 1)/2 equations expressing the orthonormality of the orbitals

$$\mathrm{CSC}^+ = \mathrm{I} \qquad [27]$$

Thus m(m - 1)/2 additional conditions must be found to eneble unambiguous determination of the molecular orbitals. For this purpose the unitary transformation U can be used. This transforms the set of molecular orbitals $\{\phi\}$ into another set $\{\phi'\}$

$$\{\phi\} = \mathrm{C}\ \{\vartheta\} = \mathrm{U}\ \{\phi'\} = \mathrm{UC}'\{\vartheta\} \qquad [28]$$

whereby the molecular energy stays unchanged. The unitary transformation U can be selected in such a way that the matrix of Lagrangian multipliers is diagonalized

$$\mathrm{U}^+\mathrm{LU} = \mathrm{E} \qquad [29]$$

where E is the diagonal matrix of the orbital energies of the molecular orbitals. Using the properties of the unitary matrix $\mathrm{UU}^+ = \mathrm{I}$ eq. [26] may be rewritten as

$$\mathrm{FC}^+\mathrm{U} = \mathrm{SC}^+\mathrm{UU}^+\mathrm{LU} \qquad [30]$$

$$\mathrm{FC}'^+ = \mathrm{SC}'^+\mathrm{E} \qquad [31]$$

The new LCAO matrix of the coefficients $\mathrm{C}' = \mathrm{U}^+\mathrm{C}$ corresponds with the so-called **canonical molecular orbitals**. The **Roothaan equations** [31] derived above can be solved using an iterative procedure - SCF (Self-Consistent Field) method (1).

Transformation into the form of the characteristic equation assumes that the overlap integral matrix is non-singular. Then S can be diagonalizad by an orthogonal matrix **X**

$$\mathbf{X}^T\mathrm{S}\mathbf{X} = \mathcal{S} \qquad [32]$$

which enables the determination of the matrices $\mathrm{S}^{1/2}$ and $\mathrm{S}^{-1/2}$, as

$$\mathrm{S}^{\mathrm{p}} = \mathbf{X}\mathcal{S}^{\mathrm{p}}\mathbf{X}^T \qquad [33]$$

Using Löwdin orthogonalization (2) then

$$(\mathrm{CS}^{1/2})(\mathrm{S}^{1/2}\mathrm{C}^+) = \mathrm{I} \qquad [34]$$

$$(\mathrm{CS}^{1/2})(\mathrm{S}^{-1/2}\mathrm{FS}^{-1/2})(\mathrm{S}^{1/2}\mathrm{C}^+) = \mathrm{E} \qquad [35]$$

By introducing substitutions of

$$\mathrm{V} = \mathrm{S}^{1/2}\mathrm{C}^+ \qquad [36]$$

$$\mathrm{F}' = \mathrm{S}^{-1/2}\mathrm{FS}^{-1/2} \qquad [37]$$

it may be written

$$V^{+}V = I \tag{38}$$

$$V^{+}F'V = E \tag{39}$$

The last equation means that the unitary matrix V makes the hermitian matrix F'diagonal. The LCAO coefficients may be obtained by the reverse transformation

$$C = V^{+}S^{-1/2} \tag{40}$$

It is not the matrix C which represents the invariant solution of the equations for the calculation of molecular orbitals, but the bond-order matrix P. It follows from the fact that the molecular energy can be expressed as a function of m(m + 1)/2 unknown elements of the matrix P and moreover, also m(m + 1)/2 Lagrangian multipliers are left to be found. Since we have at disposal m(m + 1)/2 equations for the P matrix elements

$$P^{\alpha}SP^{\alpha} = P^{\alpha} \tag{41}$$

then the rest of the m(m + 1)/2 equations must be found to connect the matrices F, P^{α} and L together. As shown by Löwdin (3), the respective equations are as follows

$$F = SP^{\alpha}LP^{\alpha}S \tag{42}$$

or in another form

$$P^{\alpha} = FP^{\alpha} = P^{\alpha}LP^{\alpha} \tag{43}$$

The interpretation of the above result is as follows: the Fock matrix belongs to the subspace defined by the projection operator P^{α} in an non-orthogonal space with metrics S. From the modified equation $(I - SP^{\alpha})FP^{\alpha} = 0$ at canonical fixation $MCLC^{+}M^{+} = E$ the Roothaan equations $FC^{+}M = SC^{+}E$ can be obtained.

3.1.3 Unrestricted Hartree-Fock Method

The method presented here serves for the computation of molecular orbitals in the LCAO form for an open-shell system. It is based on the assumption that the molecular orbitals for α spins are independent of those showing β spins. The unrestricted Hartree-Fock method (UHF) used to be named the spin-polarized Hartree-Fock method or DODS (Different Orbitals for Different Spins) method.

The above method represents a simple extension of the Roothaan procedure known for the closed-shell systems. Some quantities assume different values according to the spin index: $n_{\alpha} \neq n_{\beta}$, $\{\phi^{\alpha}\} \neq \{\phi^{\beta}\}$, $C^{\alpha} \neq C^{\beta}$, $F^{\alpha} \neq F^{\beta}$ and $P^{\alpha} \neq P^{\beta}$. The expression for the total molecular energy of an open-shell system is given by the formula [13]. The variational condition for the computation of the LCAO matrices $\mathbf{C}^{\alpha}$ and $\mathbf{C}^{\beta}$ is represented by the stationary property of the functional

$$F = E - \sum_{a,b}^{m} (\lambda_{ab}^{\alpha} \langle \phi_a^{\alpha} | \phi_b^{\alpha} \rangle + \lambda_{ab}^{\beta} \langle \phi_a^{\beta} | \phi_b^{\beta} \rangle) \qquad [44]$$

Since the orbitals for α spins and β spins are taken to be mutually independent, then the condition $\delta F = 0$ leads to a couple of matrix equations (4,5)

$$\mathbf{F}^{\eta}\mathbf{C}^{\eta +} = \mathbf{S}\mathbf{C}^{\eta +}\mathbf{L}^{\eta} \qquad [45]$$

for $\eta = \alpha, \beta$. For the canonical molecular orbitals the two equations above can be transformed into the form of a pseudo-characteristic equation

$$\mathbf{F}^{\alpha}\mathbf{C}^{\alpha +} = \mathbf{S}\mathbf{C}^{\alpha +}\mathbf{E}^{\alpha}$$

$$\mathbf{F}^{\beta}\mathbf{C}^{\beta +} = \mathbf{S}\mathbf{C}^{\beta +}\mathbf{E}^{\beta} \qquad [46]$$

These **UHF equations** are interrelated through the total bond-order matrix

$$\mathbf{P} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta} \qquad [47]$$

appearing in the definition of the Fock matrices $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$ [14]. The procedure for solving the UHF equations can be expressed by the scheme

$$\mathbf{h} \Rightarrow \mathbf{F}^{(0)} \left\{ \begin{array}{l} \mathbf{C}^{\alpha} \Rightarrow \mathbf{P}^{\alpha} \\ \mathbf{C}^{\beta} \Rightarrow \mathbf{P}^{\beta} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} \mathbf{F}^{\alpha} \Rightarrow \mathbf{C}^{\alpha} \Rightarrow \ldots \\ \mathbf{F}^{\beta} \Rightarrow \mathbf{C}^{\beta} \Rightarrow \ldots \end{array} \right.$$
$$[11] \quad [14] \quad [46] \quad [11]$$

For an open-shell system the **spin density matrix** can be defined

$$\mathbf{P}^{\mathrm{s}} = \mathbf{P}^{\alpha} - \mathbf{P}^{\beta} \qquad [48]$$

While the charge-density (bond-order) matrix $\mathbf{P}$ is used for analyzing the charge distribution over a molecule, the spin density matrix $\mathbf{P}^{\mathrm{s}}$ is important in the analysis of the spatial distribution of the unpaired electrons.

The UHF method applied to the case of a closed-shell system system ($n_{\alpha} = n_{\beta}$) becomes identical with the ordinary Roothaan method for closed-shell systems. However, the UHF method can also yield a result differing from that given by Roothaan closed-shell method. A typical example is represented by the description for dissociation of a closed-shell molecule (for example H_2) into radidicals (2H); here the UHF method is fully applicable instead of the Roothaan closed-shell one.

The determinantal function ${}^{UHF}\Phi_u$ obtained by the UHF method fulfils the requirement that it is an eigenfunction of the spin component operator $\hat{S}_z$; it is not, however, an eigenfuction of the $\hat{S}^2$ operator (except for the case of the maximum possible spin multiplicity). It can be shown that in general the UHF function is composed of several components, each of them being a pure spin state

$$ {}^{UHF}\Phi_u = \sum_{m=0}^{n} C_{s'+m}\, \Phi_{s'+m} \qquad [49] $$

where $s' = (n_\alpha - n_\beta)/2$ and the net spin function $\Phi_{s'+m}$ having the spin multiplicity $2(s' + m) + 1$ is an eigenfunction of the $\hat{S}^2$ operator. According to definition, the net spin state $|S,M_S\rangle$ obeys the relation of $\hat{S}^2\ |S,M_S\rangle = \hbar^2\ S(S + 1)\ |S,M_S\rangle$. Then the equation of $\{\hat{S}^2 - \hbar^2 S(S + 1)\}|S,M_S\rangle$ represents an annihilation of state $|S,M_S\rangle$ by the projection operator $\hat{O}_S = \hat{S}^2 - \hbar^2 S(S + 1)$. Therefore it is possible to annihilate the contributions of higher multiplicities using the projection operator

$$ \hat{O}_S = \prod_{K\neq S} \frac{\hat{S}^2 - K(K + 1)\hbar^2}{S(S + 1)\hbar^2 - K(K + 1)\hbar^2} \qquad [50] $$

The expression

$$ \hat{O}_S\ \Phi_u = \Phi_S \qquad [51] $$

annihilates all the undesirable components of the spin K (i.e. with the spin multiplicity 2K + 1) from the UHF function Φ_u conserving the component Φ_S with the spin S (of the spin multiplicity 2S + 1). The denominator of the projection operator ensures that the projection component Φ_S stays unchanged. The projection of a pure spin state (annihilation of the undesired components) can be performed in every iteration of the SCF procedure or after its completion.

3.1.4 Restricted Hartree-Fock Method

This represents an alternative method for computation of the molecular orbitals in the LCAO form for open-shell systems. It is based on the assumption that the system can be described by the wave function as follows

$$ {}^{RHF}\Psi = \hat{A}\ (\Phi_c\ \Phi_o) \qquad [52] $$

where Φ_c is the product function of closed shells (representing the configuration of n_1 orbitals occupied by electron pairs of mutually opposite spins) while Φ_o is the product function of open shells (representing the non-degenerate configuration of n_2 orbitals occupied by single electrons with α spins). This is where the name of the method (Restricted Hartree-Fock: RHF) comes from. The principal difference between RHF and UHF methods is illustrated in Fig. 1.

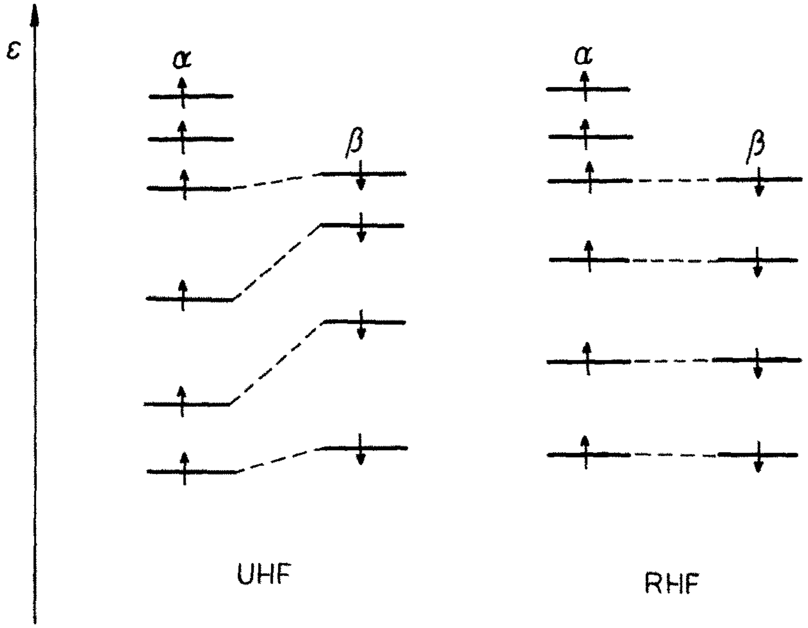

Fig. 1. Comparison of orbital energies in UHF and RHF methods.

The RHF functions corresponds to a pure spin state, i.e. they are the eigenfunctions of the operator $\hat{S}^2$. The one-determinantal UHF function provides a correct description of the system only for a limited number of simple cases. Mostly, the RHF function must be written in the form of a fixed linear combination of several determinantal functions so that it is the eigenfunction not only of the operators $\hat{H}_0$, $\hat{L}_z$ and $\hat{S}_z$ but also of the operators $\hat{L}^2$ and $\hat{S}^2$.

For the number of electrons in the RHF approach the following relationships hold true

$$n = \nu_1 n_1 + \nu_2 n_2 = 2n_1 + n_2 = n_\alpha + n_\beta$$

$$n_\alpha = n_1 + n_2$$

$$n_\beta = n_1 \qquad [53]$$

with the coefficients $\nu_1 = 2$ and $\nu_2 = 1$ assuming the meaning of the orbital occupation numbers for closed and open shells.

For the multi-determinantal RHF function, the molecular energy (in the case of orthonormal molecular orbitals) can be written

$$\begin{aligned} E^{el} = {} & \nu_1\Big[\sum_i^{n_1}\langle i|\hat{h}|i\rangle + (1/2)\nu_1\sum_{i,j}^{n_1}(\langle ij|\hat{g}|ij\rangle - (1/2)\langle ij|\hat{g}|ji\rangle)\Big] + \\ & + \nu_2\Big[\sum_k^{n_2}\langle k|\hat{h}|k\rangle + (1/2)\nu_2\sum_{k,l}^{n_2}(a\langle kl|\hat{g}|kl\rangle - (1/2)b\langle kl|\hat{g}|lk\rangle)\Big] + \\ & + \nu_1\ \nu_2\Big[\sum_i^{n_1}\sum_k^{n_2}(\langle ik|\hat{g}|ik\rangle - (1/2)\langle ik|\hat{g}|ki\rangle)\Big] \end{aligned} \qquad [54]$$

Now the coefficient ν_2 attains the meaning of a fractional occupation number of an open level being defined as a ratio of the number of electrons lying in an open level n_2 to the total number of the orbitals m_2 in an open shell: $\nu_2 = 2f = n_2/m_2$. Thus $0 < \nu_2 <$ < 2 or $0 < f < 1$. The coefficients a and b depend on the Coulomb and exchange electron interaction in an open shell for the definite definite electronic state and they can differ for various states of the same electron configuration. The values of the coefficients f, a and b for some common cases are listed in Table 1.

In atoms, however, the energy formula may be rewritten by utilizing the supermatrices formalism in which the vector coupling coefficients $J_{\lambda\mu\nu}$ and $K_{\lambda\mu\nu}$ occur; λ denotes the symmetry elements. The constants $J_{\lambda\mu\nu}$ and $K_{\lambda\mu\nu}$ differ from case to case; they are characteristics of the state and configuration of the atom under consideration. They were tabulated for p^n and sp^n configurations (6) and for those involving d-orbitals in (7).

The expression for the molecular energy is obtained as the average over the electronic Hamiltonian $\hat{H}^{el}$ at the definite spin-free density functions (formulas [69] through [70] of Chapter 1) respecting the multideterminantal form of the wave function (8)

$$E^{el} = Tr\{\hat{h}P_1 + (1/2)\hat{g}P_2\}$$

The occupation number matrices can be expressed in a very simple manner obeying the convention as follows. Let us arrange the vector of molecular orbitals in the order of the closed-shell, open-shell and virtual orbitals

TABLE 1

Numerical constants for the RHF method.

Configuration of open shell	Electronic state	Constant f	a	b	Note
$\Phi(\phi_n\alpha)$	$^2\Psi = \Phi$	1/2	1	2	
$\Phi_1(\phi_1\alpha,\phi_2\alpha)$	$^3\Psi = \Phi_1$	1/2	1	2	
$\Phi_2(\phi_1\beta,\phi_2\beta)$	$^3\Psi = \Phi_2$	1/2	1	2	
$\Phi_3(\phi_1\alpha,\phi_2\beta)$	$^3\Psi = (\Phi_3+\Phi_4)/\sqrt{2}$	1/2	1	2	
$\Phi_4(\phi_1\beta,\phi_2\alpha)$	$^1\Psi = (\Phi_3-\Phi_4)/\sqrt{2}$	1/2	1	-2	
$\Phi_1(\phi_1\alpha,\phi_1\beta,\phi_2\alpha)$	$^2\Psi = (\Phi_1+\Phi_2)/\sqrt{2}$	3/4	8/9	8/9	degeneracy
$\Phi_2(\phi_1\alpha,\phi_2\alpha,\phi_2\beta)$	$^2\Psi' = (\Phi_1-\Phi_2)/\sqrt{2}$	3/4	8/9	8/9	
Configurations π^n or δ^n of diatomic molecules					
$\Phi(\pi_1\alpha)$	$^2\Pi = \Phi$	1/4	0	0	or $^2\Delta$
$\Phi_1(\pi_1\alpha,\pi_2\alpha)$	$^3\Sigma^- = \Phi_1$	1/2	1	2	
$\Phi_2(\pi_1\beta,\pi_2\beta)$	$^3\Sigma^- = \Phi_2$	1/2	1	2	
$\Phi_3(\pi_1\alpha,\pi_2\beta)$	$^3\Sigma^- = (\Phi_3+\Phi_4)/\sqrt{2}$	1/2	1	2	
$\Phi_4(\pi_1\beta,\pi_2\alpha)$	$^1\Sigma^+ = (\Phi_3-\Phi_4)/\sqrt{2}$	1/2	1	-2	
$\Phi_5(\pi_1\alpha,\pi_1\beta)$	$^1\Delta = (\Phi_5+\Phi_6)/\sqrt{2}$	1/2	1/2	0	or $^1\Gamma$
$\Phi_6(\pi_2\alpha,\pi_2\beta)$	$^1\Delta' = (\Phi_5-\Phi_6)/\sqrt{2}$	1/2	1/2	0	
$\Phi_1(\pi_1\alpha,\pi_1\beta,\pi_2\alpha)$	$^2\Pi = (\Phi_1+\Phi_2)/\sqrt{2}$	3/4	8/9	8/9	or $^2\Delta$
$\Phi_2(\pi_1\alpha,\pi_2\alpha,\pi_2\beta)$	$^2\Pi' = (\Phi_1-\Phi_2)/\sqrt{2}$	3/4	8/9	8/9	
Configurations p^n of atoms					
p^1	^2P	1/6	0	0	
p^2	^3P	1/3	3/4	3/2	
	^1D	1/3	9/20	-3/10	
	^1S	1/3	0	-3	
p^3	^4S	1/2	1	2	
	^2D	1/2	4/5	4/5	
	^2P	1/2	2/3	0	
p^4	^3P	2/3	15/16	9/8	
	^1D	2/3	69/80	27/40	
	^1S	2/3	3/4	0	
p^5	^2P	5/6	24/25	24/25	

$$\{\phi\} = \begin{pmatrix} \{\phi^c\} \\ \{\phi^o\} \\ \{\phi^v\} \end{pmatrix} = \left(\begin{array}{c} \text{closed} \\ \hline \text{open} \\ \hline \text{virtual} \end{array} \right) \{\vartheta\} = C\,\{\vartheta\} \qquad [55]$$

Then the diagonal occupation number matrices are

$$M_1 = \begin{pmatrix} I & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$M_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & I & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$M^c = \nu_1 M_1$$

$$M^o = \nu_2 M_2$$

$$M^\alpha = M_1 + M_2$$

$$M^\beta = M_1$$

$$M = M^\alpha + M^\beta = M^c + M^o = \nu_1 M_1 + \nu_2 M_2 \qquad [56]$$

Using them the bond-order matrices may be expressed as

$$P_1 = C^+ M_1 C$$

$$P_2 = C^+ M_2 C$$

$$P^c = C^+ M^c C$$

$$P^o = C^+ M^o C$$

$$P^\alpha = C^+ M^\alpha C$$

$$P^\beta = C^+ M^\beta C$$

$$P = \nu_1 P_1 + \nu_2 P_2 = P^c + P^o = P^\alpha + P^\beta = C^+ M C \qquad [57]$$

Finally, the spin density matrix is

$$P^s = P^\alpha - P^\beta = P^o = C^+ M^o C \qquad [58]$$

The orthonormality conditions for molecular orbitals hold true

$$C S C^+ = I \qquad [59]$$

as well as the projection properties of density matrices in the non-orthogonal space

$$P_1 S P_1 = P_1$$

$$P_2 S P_2 = P_2$$

$$P_1 S P_2 = 0 \qquad [60]$$

There exist several non-trivial procedures for the computation of LCAO coefficients using the minimization of the total energy at the constraint of their orthonormality. One starts at the transcription of the electronic energy as follows (9)

$$E^{el} = \sum_{p,q}^{m} h_{pq}(P^{c}_{pq} + P^{o}_{pq}) + (1/2) \sum_{p,q,r,s}^{m} [(P^{c}_{pq}\, P^{c}_{rs} + P^{c}_{pq}\, P^{o}_{rs} + P^{o}_{pq}\, P^{c}_{rs}) \times$$

$$\times\, G_{pq,rs} + P^{o}_{pq}\, P^{o}_{rs}(G_{pq,rs} - G'_{pq,rs}) \qquad [61]$$

where the repulsion integrals supermatrices are defined as

$$G_{pq,rs} = (pq|rs) - (1/4)[(ps|qr) + (pr|qs)] \qquad [62]$$

$$G'_{pq,rs} = (1 - a)(pq|rs) - [(1 - b)/4][(pr|qs) + (ps|qr)] \qquad [63]$$

These supermatrices have their specific symmetry properties which become advantageous when using computers. They yield the following electron interaction matrices

$$\mathrm{G}_{pq} = \sum_{r,s}^{m} G_{pq,rs}(P^{c}_{rs} + P^{o}_{rs}) \qquad [64]$$

$$\mathrm{G}'_{pq} = \sum_{r,s}^{m} G'_{pq,rs}\, P^{o}_{rs} \qquad [65]$$

The LCAO coefficients to be found, minimizing the total energy, represent solutions of two coupled equations

$$\sum_{q}^{m} (h_{pq} + \mathrm{G}_{pq})C_{ip} = \sum_{q}^{m} S_{pq}\left(\sum_{j}^{n_1} C_{jq}\, \lambda_{ji}/M_{ii} + \sum_{l}^{n_2} C_{lq}\, \lambda_{li}/M_{ii}\right)$$

$$\sum_{q}^{m} (h_{pq} + \mathrm{G}_{pq} - \mathrm{G}'_{pq})C_{kq} = \sum_{q}^{m} S_{pq}\left(\sum_{j}^{n_1} C_{jq}\, \lambda_{jk}/M_{kk} + \sum_{l}^{n_2} C_{lq}\, \lambda_{kl}/M_{kk}\right) \qquad [66]$$

Molecular orbitals can be subjected to such a unitary transformation which eliminates the off-diagonal Lagrangian multipliers λ_{li} (the term closed shell - closed shell) and λ_{kl} (the term open shell - open shell). Such a transformation, however, does not eliminate the off-diagonal multipliers λ_{li} and λ_{jk} (the terms closed shell - open shell). Nevertheless, a pseudosecular form of SCF equations can be derived by transforming the coupling (closed shell - open shell) terms to the left side of eq. [66]. For this purpose new square matrices are intruduced

$$R^{c}_{pq} = [1/(2n_1 - n_2)] \sum_{u,w}^{m} (S_{pu}\, P^{c}_{uw}\, \mathrm{G}'_{wq} + \mathrm{G}'_{pu}\, P^{c}_{uw}\, S_{wq}) \qquad [67]$$

$$R^{o}_{pq} = [1/(2n_1 - n_2)] \sum_{u,w}^{m} (S_{pu}\, P^{o}_{uw}\, \mathrm{G}'_{wq} + \mathrm{G}'_{pu}\, P^{o}_{uw}\, S_{wq}) \qquad [68]$$

The resulting RHF equations adopt the form of a pseudo-characteristic equation

$$F^{c}C^{+} = SC^{+}E^{c} \qquad [69]$$

$$\mathbf{F}^{o}\mathbf{C}^{+} = \mathbf{S}\mathbf{C}^{+}\mathbf{E}^{o} \qquad [70]$$

where the Fock operator has the following matrix elements

$$F^{c}_{pq} = h_{pq} + G_{pq} + R^{o}_{pq} \qquad [71]$$

$$F^{o}_{pq} = h_{pq} + G_{pq} - G'_{pq} + R^{c}_{pq} \qquad [72]$$

Roothaan (10) originally presented another formulation for the SCF equations for the RHF method in which both the closed-shell and open-shell orbitals represent a solution of the only characteristic equation. Such SCF equations, however, may yield an energy which is not invariant with respect to unitary transformations of the orbitals. This can lead to undesirable discontinuities of the adiabatic potential when considering a different symmetry of the nuclear configuration.

Another formulation of the SCF equations based on the properties of projection operators was developed by McWeeny (6,11). It is based on an alternative expression for the electronic energy of a molecule

$$E^{el} = (1/2)Tr\{\nu_1\mathbf{P}_1(\mathbf{h} + \mathbf{F}_1) + \nu_2\mathbf{P}_2(\mathbf{h} + \mathbf{F}_2)\} =$$

$$= (1/2)\sum_{K=1}^{2} \nu_K Tr\{\mathbf{P}_K(\mathbf{h} + \mathbf{F}_K)\} \qquad [73]$$

where

$$\mathbf{F}_1 = \mathbf{h} + \nu_1\mathbf{J}[P_1] - (1/2)\nu_1\mathbf{K}[P_1] + \nu_2\mathbf{J}[P_2] - (1/2)\nu_2\mathbf{K}[P_2] \qquad [74]$$

$$\mathbf{F}_2 = \mathbf{h} + \nu_1\mathbf{J}[P_1] - (1/2)\nu_1\mathbf{K}[P_1] + \nu_2 a\mathbf{J}[P_2] - (1/2)\nu_2 b\mathbf{K}[P_2] \qquad [75]$$

Here, the following notation has been used for elements of matrices $\mathbf{J}[P_\mu]$, $\mathbf{K}[P_\mu]$ and $\mathbf{h}$

$$J[P_\mu]_{pq} = \sum_{r,s}^{m} (P_\mu)_{rs}\ (pq|rs) \qquad [76]$$

$$K[P_\mu]_{pq} = \sum_{r,s}^{m} (P_\mu)_{rs}\ (ps|rq) \qquad [77]$$

$$h_{pq} = \langle p|\hat{h}|q\rangle \qquad [78]$$

Then, for the variation of the total energy

$$\delta E = Tr\{\nu_1\mathbf{F}_1\delta\mathbf{P}_1 + \nu_2\mathbf{F}_2\delta\mathbf{P}_2\} = \sum_{K=1}^{2} \nu_K\ Tr\{\mathbf{F}_K\ \delta\mathbf{P}_K\} \qquad [79]$$

whereby we have made use of the property $Tr\{\mathbf{P}_1\mathbf{J}[P_2]\} = Tr\{\mathbf{P}_2\mathbf{J}[P_1]\}$ and similarly for the matrix $\mathbf{K}[P]$.

For further manipulations it is advantageous to consider an orthonormal basis set of atomic orbitals which fulfil the relationships

$$P_1P_1 = P_1$$

$$P_2P_2 = P_2$$

$$P_1P_2 = 0 \qquad [80]$$

The orthonormalization can be performed using the Löwdin transformation $C = C'S^{1/2}$, so that it is $CC^+ = I$ instead of the original condition $C'SC'^+ = I$.

The projector P_1 projects onto a subspace of a closed shell while the projector P_2 onto that of an open shell, so that there exists a projector P_3 projecting onto a subspace of unoccupied molecular orbitals

$$P_3 = I - P_1 - P_2 \qquad [81]$$

When applying variation for the bonding condition $P_KP_K - P_K = 0$ after respective modifying we arrive at the RHF condition for one closed and one open shell of the following form

$$P_1(\nu_1F_1 - \nu_2F_2)P_2 = 0$$

$$P_1F_1P_3 = 0$$

$$P_2F_2P_3 = 0 \qquad [82]$$

In considering a general combination of several closed and open shells (K = 1, 2, ..., N) then the general RHF equations are

$$P_K(\nu_KF_K - \nu_LF_L)P_L = 0$$

$$P_KF_KP_Z = 0 \qquad [83]$$

for K, L = 1, 2, ... N. The projector out of the subspace of occupied orbitals is

$$P_Z = I - \sum_K^N P_K \qquad [84]$$

These equations can be transformed into the characteristic problem by the following transformation. First an effective model Hamiltonian is introduced

$$H_{eff} = \sum_K a_K(P_K + P_Z)F_K(P_K + P_Z) +$$

$$+ \sum_{K<L} b_{KL}(P_K + P_L)(\nu_KF_K - \nu_LF_L)(P_K + P_L) \qquad [85]$$

(a_K and b_{KL} are numerical coefficients). It may be proven that the effective Hamiltonian fulfils the commutation equation

$$H_{eff}P_K - P_KH_{eff} = 0 \qquad [86]$$

which is completely equivalent to the relationships [83]. Using the canonical constraints the numerical coefficients are

$$a_K = 1/N \qquad [87]$$

$$b_{KL} = 1/N(\nu_K - \nu_L) \text{ for } K < L \qquad [88]$$

With another choice of coefficients a_K and b_{KL} the eigenvectors of the effective Hamiltonian stay invariant but the eigenvalues are shifted. For this reason the eigenvalues ϵ_k do not have the meaning of orbital energies within the framework of the RHF method. Unlike the UHF method, they cannot be used to approximate ionization energies (violation of Koopmans theorem).

By using the identity $P_K = C^+M_KC$ and introducing the diagonal matrix $E_K = M_kCH_{eff}C^+M_K$ we obtain

$$H_{eff}C^+M_K = C^+E_K \qquad [89]$$

The last equation serves for the computation of the LCAO coefficients in the general RHF method using the orthonormal basis set of atomic orbitals. Using the back Löwdin transformation $C = C'S^{1/2}$ the general RHF equations in the non-orthogonal basis set are obtained

$$H'_{eff}C'^+M_K = SC'^+E_K \qquad [90]$$

where $H'_{eff} = S^{1/2}H_{eff}S^{1/2}$.

During the iterative process for solving the RHF equations the eigenvectors c may be identified as follows: if for the projection it is $P_Kc^+ \approx c^+$, then c belongs to the K-th shell; in the opposite case of $P_Kc^+ \approx 0$ the eigenvector c belongs to another shell.

3.1.5 Half-Electron Method

This is a simplified version of the RHF method for the approximate computation of open-shell systems. The above method was developed by Longuet-Higgins and Pople (12) - hence the abbreviations for the method: LHP method.

The wave function Ψ is approximated by the only determinantal function

$$^{LHP}\Psi = \Phi_u = \hat{A}\{(\phi_1\alpha)(\phi_1\beta)\cdots(\phi_{n_1}\alpha)(\phi_{n_1}\beta)(\phi_{n_1+1}\alpha)\cdots(\phi_{n_2}\alpha)\} \qquad [91]$$

The LCAO coefficients may be calculated by solving the modified Roothaan equations [26], i.e.

$$FC^+ = SC^+E \qquad [92]$$

with matrix elements of the Fock operator of the form similar to that of the closed-shell systems [19]

$$F_{ik} = h_{ik} + \sum_{j,l}^{m} P^{h}_{lj}[(ik|jl) - (1/2)(il|jk)] \qquad [93]$$

The charge density (bond-order) matrix is subject to modification, having a form similar to that in the RHF method [57]

$$P^{h} = \nu_1 P_1 + \nu_2 P_2 = C^{+}MC \qquad [94]$$

with the coefficients in the occupation number matrix [56]

$$M = \nu_1 M_1 + \nu_2 M_2 \qquad [95]$$

assuming values $\nu_1 = 2$ and $\nu_2 = 1$. The spin density matrix is

$$P^{spin} = C^{+}M_2C \qquad [96]$$

3.2 AB INITIO APPROACH

Here the term *ab initio* involves the Hartree-Fock method for computation of molecular orbitals in the LCAO approximation. Some authors, however, termed as *ab initio* all non-empirical calculations over the range of the one-electron approximation, thus including the electron correlation (CI, VB, GVB methods, etc.).

In the above method no other simplifying assumptions are used with the exception of postulating the basis set of analytic functions (as a rule, atomic orbitals are concerned). The MO LCAO SCF calculations are performed according to the Roothaan equation, which were derived from the variational principle (Section 3.1). For that very reason, the quality of the calculation can be judged from the value of the energy obtained: increasing the basis set size can only lead to a decrease of the energy. The minimum (attainable limit) energy is denoted as the **Hartree-Fock limit**.

3.2.1 Basis Sets

The procedures for constructing the basis set of the analytic functions for atoms (ions) are well known. Atomic orbitals are searched in the form of a linear combination

$$\vartheta_\lambda = \sum_{\mu}^{m_\lambda} c_{\lambda\mu}\, \chi_\mu \qquad [97]$$

According to the length m_λ of the expansion and the type of primitive functions (PF) the following types of the basis sets can be distinguished:

1. **Minimum basis set** (single-zeta: SZ) represents a system of functions, in which every orbital is simulated by a single PF. For example, for an oxygen atom a SZ basis set is (1s, 2s, $2p_x$, $2p_y$, $2p_z$). Since the PF are not orthogonal, they can combine with each other: the optimum 1s orbital resulting from the energy minimization contains an admixture from both the s-type PFs:
$\vartheta(1s) = c_1\chi(1s) + c_2\chi(2s)$.

2. **Double-zeta basis set** (DZ) contains every occupied atomic orbital expanded over two PFs

$$\vartheta_\lambda = c_\lambda\chi_\lambda + c'_\lambda\chi'_\lambda \qquad [98]$$

The corresponding primitive functions have equal angular parts $Y_{l,ml}(\vartheta,\varphi)$ and different radial parts $R_{nl}(r)$ and $R'_{nl}(r)$ differing in their orbital exponent ζ:
$\vartheta(1s) = c_1\chi(1s) + c'_1\chi'(1s) + c_2\chi(2s) + c'_2\chi'(2s)$.
Higher ζ value corresponds to the inner (more compact) component while lower ζ to a more diffuse component (Fig. 2).

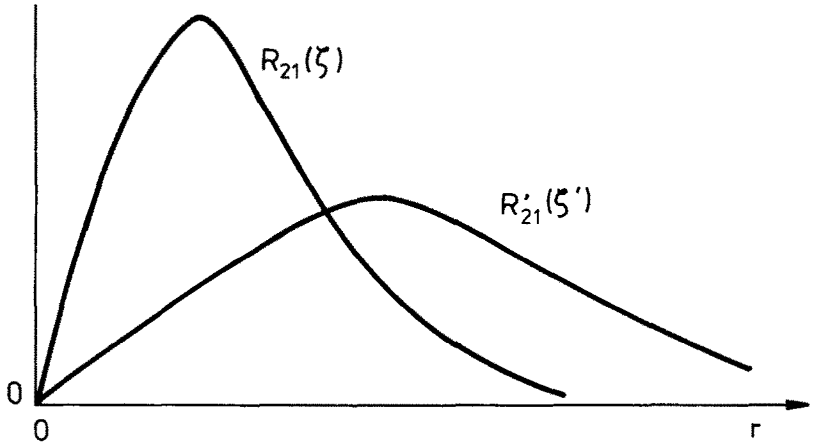

Fig. 2. Radial parts $R(r) = r\, exp(-\zeta r)$ for the 2p type primitive functions in the DZ basis set.

3. **Valence-split basis set** (VS) represents a compromise between the DZ and SZ basis sets. For the valence electrons, the split DZ functions are used while for the core electrons, the single-component SZ functions are taken: $\vartheta(1s) = c_1\chi(1s) + c_2\chi(2s) + c'_2\chi'(2s)$.

4. **Extended basis set** (poly-zeta: PZ) where the expansion of every occupied orbital contains more PFs: orbitals of a given quantum number n also contain PFs of different n (13). For example, for an oxygen atom the PZ basis set assumes the form

$$\vartheta_1(1s) = c_{1,1}\chi_1(1s) + c_{1,2}\chi_2(1s) + \\ + c_{1,3}\chi_3(2s) + c_{1,4}\chi_4(2s) + c_{1,5}\chi_5(2s) + c_{1,6}\chi_6(2s)$$

$$\vartheta_2(2s) = c_{2,1}\chi_1(1s) + c_{2,2}\chi_2(1s) + \\ + c_{2,3}\chi_3(2s) + c_{2,4}\chi_4(2s) + c_{2,5}\chi_5(2s) + c_{2,6}\chi_6(2s)$$

$$\vartheta_3(2p_x) = c_{3,7}\chi_7(2p_x) + c_{3,8}\chi_8(2p_x) + c_{3,9}\chi_9(2p_x) + c_{3,10}\chi_{10}(2p_x)$$

$$\vartheta_4(2p_y) = c_{4,7}\chi_7(2p_y) + c_{4,8}\chi_8(2p_y) + c_{4,9}\chi_9(2p_y) + c_{4,10}\chi_{10}(2p_y)$$

$$\vartheta_5(2p_z) = c_{5,7}\chi_7(2p_z) + c_{5,8}\chi_8(2p_z) + c_{5,9}\chi_9(2p_z) + c_{5,10}\chi_{10}(2p_z)$$

By increasing the dimension m_i of the basis set one can arrive at a value of the energy approaching the Hartree-Fock limit.

When calculating single atoms the object of the optimization is represented by the expansion coefficients of the primitive functions $c_{\lambda,\mu}$ (linear parameters) and orbital exponents ζ_μ (non-linear parameters). For open shell systems, the RHF version of the Hartree-Fock method is the only method to be used. The value of the atomic energy obtained this way is usually tested for the satisfaction of the virial theorem (see Section 1.1).

The basis sets for molecules correspond to a simple superposition of atomic basis sets. The expansion coefficients of the primitive functions in a molecule are re-optimized for the creation of molecular orbitals

$$\phi_i = \sum_{\nu}^{m} c_{i\nu}\chi_\nu \qquad [99]$$

The expansion coefficients of the atomic orbitals for the bases denoted as STO-nG and CGTF are left fixed, while the molecular orbitals searched in the form of an LCAO expansion

$$\phi_i = \sum_{\lambda}^{m} c'_{i\lambda}\vartheta'_\lambda \qquad [100]$$

A similar procedure is applied in the semiempirical all-valence methods (e.g. EHT) if DZ or PZ basis sets are used.

As a rule, for *ab initio* calculations for molecules the diffuse, polarization and bond functions are added.

Diffuse functions (D) are those, whose principal quantum number is greater than for occupied atomic orbitals of the ground state. For example, the diffuse function for the Cu atom is the 4p orbital. The localization of the maximum for the radial part of the diffuse function often extends beyond the atomic covalent radius.

Polarization functions (P) correspond to such PFs, whose azimuthal quantum number is larger than for the occupied atomic orbitals of the ground state of the atom. For example, polarization functions for the hydrogen atom are 2p, 3p, 3d, ... orbitals while those for the copper atom are f, g, etc. orbitals. Polarization functions do not alter the energy values of a free atom, and thus, they cannot be determined from computations for atoms. However, they exert significant influence upon the quality of the MO calculations for molecules. The notation of the basis set (4s 2p 1d /2s 1p) for a water molecule means DZ+P basis containing 4 functions of s-type, 2 sets of p-functions (p_x, p_y, p_z) and one set of d- functions ($d_{x^2-y^2}$, $d_{3z^2-r^2}$, d_{xz}, d_{yz} and d_{xy}) for an oxygen atom followed by 2 functions of s-type and 1 set of the p-functions for the hydrogen atom (heavy atoms are denoted first, while light hydrogen atoms follow the slash).

Bond functions (B) are not centred at atomic nuclei but in such positions as the centre of a chemical bond. They improve the results for molecular characteristics in the equilibrium geometry. On the other hand, however, they cause difficulties when evaluating the dissociation energy of the molecule.

Acoording to their analytical form, two basic types of PF are known: Slater-type orbitals and Gaussian orbitals.

Slater-Type Orbitals (STO) have the radial part as follows

$$R_{\zeta,n}(r) = [(2n^*)!]^{-1/2} (2\zeta)^{n^*+1/2} r^{n^*-1} e^{-\zeta r} \qquad [101]$$

with a positive orbital exponent ζ and effective principal quantum number n^*. These functions, in contrast to hydrogen atom functions, are nodeless and are not orthogonal to each other. STOs STOs can be expressed in the form of a finite linear combination of exponential functions

$$\chi(\zeta,n',i,j,k) = N r^{n'-1} x^i y^j z^k e^{-\zeta r} \qquad [102]$$

Orbital exponents for SZ-STO may be evaluated from the empirical relationship

$$\zeta = (Z - \sigma)/n^* \qquad [103]$$

where the screening constant σ determines the effective charge of a given nucleus $Z^* = Z - \sigma$. The values of σ and n^* have been tabulated by Slater (14) or Burns (15).

In *ab initio* calculations the orbital exponents ζ are taken for adjustable parameters evaluated by minimization of atomic energies. In small molecules they undergo re-optimization (for small basis sets). If the molecular geometry is changed significantly then their re-optimization is again required. For extended basis sets there is no need for re-optimization of the exponents. Basis set extension is often more efficient (economizing computational time) than the re-optimization of the exponents.

Gauss-type functions (GTF) have as their radial part

$$R_{\zeta,n'}(r) = [(2^{2n'+3/2})/(2n' - 1)!!\sqrt{2})]^{1/2}\ \zeta^{(2n'+1)/4}\ r^{n'-1}\ e^{-\zeta r^2} \qquad [104]$$

Another common expression for the GTF is

$$\chi_{\alpha ijk} = \left[(\pi/2\alpha)^{3/2} \frac{(2i - 1)!!\ (2j - 1)!!\ (2k - 1)!!}{2^{2(i + j + k)}\ \alpha^{(i + j + k)}} \right]^{-1/2} x^i\ y^j\ z^k\ e^{-\alpha r^2} \qquad [105]$$

with a positive orbital exponent α, whereby i, j, k $\geq$ 0 are integers. Such functions are not characterized by the principal quantum number. Their angular dependence is given by powers of cartesian coordinates. For example, i = j = k = 0 corresponds to s-type functions. In comparison with STOs, the GTFs show some characteristic features:

1. the calculation of two-electron integrals (ij|kl) using GTF is much faster;

2. the behaviour of the GTF both close to the nuclei and distant from the nucleus is poor (Fig. 3), so that a larger number of GTFs

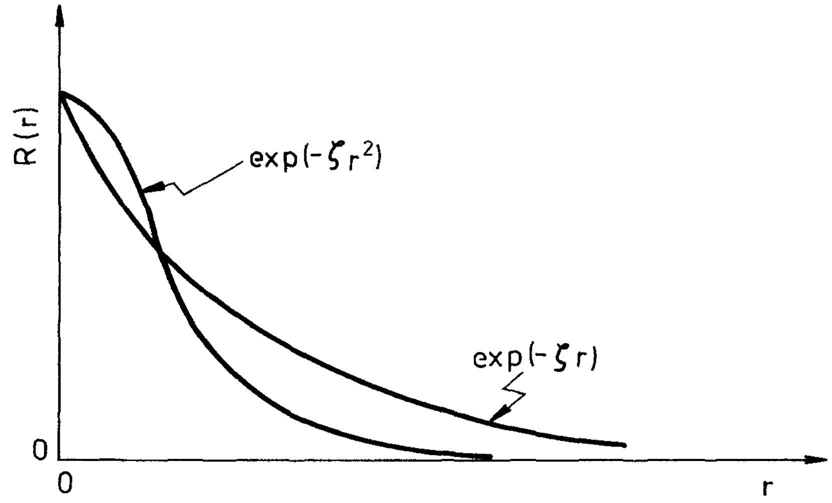

Fig. 3. Radial parts of STO and GTF.

than STOs should be included in the orbital expansion. This follows from the fact that it is not the Gauss function but the exponential which represents a solution of the Schrödinger equation for the central field potential. Near the nucleus GTF do not fulfil the condition $[(\partial\chi/\partial r_{1A})/\chi] = -Z_A$ (for $r_{1A} \Rightarrow 0$) and in the asymptotic region ($r_{1A} \Rightarrow \infty$) their drop is too steep.

When using the GTF basis set for molecules, one of three possible alternatives is usually followed.

1. Atomic orbitals $\{\vartheta_\lambda\}$ are expressed in the form of an expansion over GTFs $\{\chi_\mu\}$. The exponents of the primitive functions ζ_μ and expansion coefficients $c_{\lambda\mu}$ are optimized in order to yield the minimum energy of the free atom. The GTFs obtained serve as the basis for molecular orbital calculations. The expansion coefficients $c_{\lambda\mu}$ derived from the calculations for atoms are not used for molecules; they are completely re-optimized to form molecular orbitals. This procedure involves MO calculations in the so-called uncontracted GTF basis, representing a procedure analogous to that used with the PZ-STO basis set.

2. A group of contracted Gaussian-tupe functions (CGTF) is formed $\{\vartheta'_\lambda\}$ based on SCF calculations for atoms. By contraction is understood an intuitive restriction of the original expansion for every atomic orbital to a fixed combination of PFs, $\vartheta \Rightarrow \vartheta'$. The expansion coefficients $c_{\lambda\mu}$ within every CGTF stay unchanged when entering the molecule. MO calculation deals with the LCAO coefficients $c'_{i\lambda}$. The number of variation parameters is thus significantly reduced (as well as that of the two-electron integrals necessary for energy enery calculation in each iteration of the SCF procedure) with loss of quality in the result. In Table 2 an example of basis set contraction can be found. The contraction is denoted in square brackets, e.g. (7s 3p/3s) ⇒ [4s 2p/2s], eventually as (1234)(5)(6)(7);(12)(1)/(12)(1) or (4,1,1,1;2,1/2,1). If every PF brings a contribution to only one orbital, we speak of the **segmented basis set** of CGTF.

Two empirical rules are usually used in contraction:

a. primitive functions which reach the valence region (usually the mostly diffuse components of the individual orbitals) are left uncontracted;

b. primitive functions yielding a significant contribution to different AOs with substantially differing weights relative to other PFs are left uncontracted. In the general contraction scheme a definite PF can contribute to several CGTFs (16).

TABLE 2

Example of contraction of s-functions for nitrogen atom.[a]

Exponents	Expansion coefficients of GTF							
of GTF	PZ-GTF		SZ-GTF		DZ-GTF			
	ϑ_1(1s)	ϑ_2(2s)	ϑ'_1(1s)	ϑ'_2(2s)	ϑ'_1	ϑ'_2	ϑ'_3	ϑ'_4
1619.0	0.0059	-0.0013	0.0059	-	0.0059	-	-	-
248.7	0.0424	-0.0096	0.0424	-	0.0424	-	-	-
57.75	0.1820	-0.0422	0.1820	-	0.1820	-	-	-
16.36	0.4570	-0.1326	0.4570	-	0.4570	-	-	-
5.081	0.4412	-0.1897	0.4412	-	-	1	-	-
0.7797	0.0342	0.5077	-	0.5077	-	-	1	-
0.2350	-0.0089	0.6151	-	0.6151	-	-	-	1

[a] Various notations:
Minimal basis set [2s...] = (12345)(67) = (5,2;...)
Valence-split set [3s...] = (12345)(6)(7) = (5,1,1;...)
Double-zeta set [4s...] = (1234)(5)(6)(7) = (4,1,1,1;...)
Uncontracted set [7s...] = (1)(2)(3)(4)(5)(6)(7)

3. STOs are simulated in the form of a fixed expansion over several GTFs. We speak of the STO-nG basis set. Expansion coefficients are derived using the least-squares method and they are fixed during the molecular orbital calculations. The number of expansion terms ranges from n = 3 to 6. Sometimes the valence orbitals are subject to decontraction. Under the latter it is understood that the most diffuse primitive function (having the minimum exponent) is left uncontracted. As an example the 4-31G basis can serve, which represents a valence-split basis set. The addition of polarization functions is marked with an asterisk, e.g. 6-31G*.

For computation with GTFs some alternative procedures were proposed. In one of them, the orbital exponents are generated by a geometric series

$$\zeta_k = \alpha\, \beta^k \qquad [106]$$

for k = 1, 2, ..., m so that for the given symmetry type (s, p, d) only the two parameters α and β are optimized. Another approach is based on the manipulation of the Gaussian lobe functions (GLF) where higher order functions for $l \geq 1$ are simulated by a linear combination of s-type gaussians situated out of the symmetry centre of the simulated orbital (Fig. 4). Calculations with the use of GLF yield results similar to those based on cartesian GTFs.

The selection of the basis set in the *ab initio* calculations represents a critical step determining both the quality and the

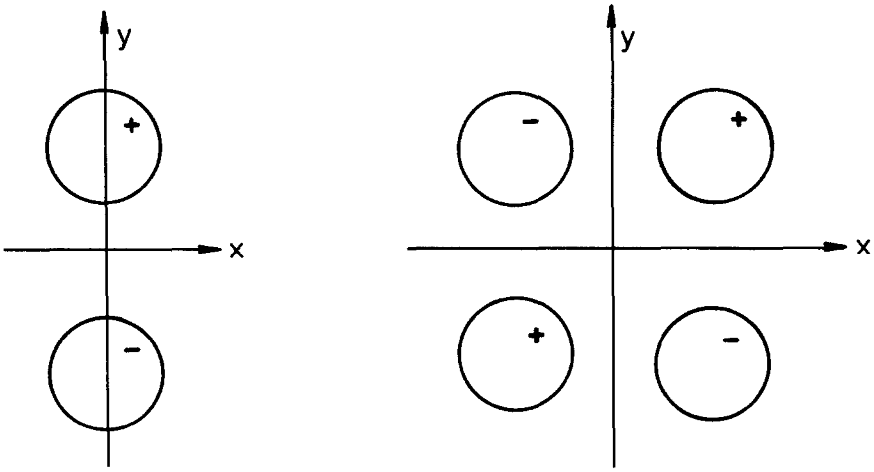

Fig. 4. Representation of p_y and d_{xy} orbitals by GFL.

price of molecular orbital calculations. *Ab initio* calculations are tedious mainly for the reason of calculation and manipulation with a large number of two-electron integrals whose number grows enormously when enlarging the basis set (Table 3). The predictability of *ab initio* calculations is excellent if an adequate basis set is used (and eventually the correlation effects are taken into account via configuration interaction) respecting the nature of the problem under study. However, *ab initio* calculations in extended basis sets

TABLE 3

Basis set dependence for water molecule.[a]

Basis set size	Number of functions m	Number of integrals M	Energy E/E_h
(2s1p/1s)	7(SZ)	406	-75.70545
(4s2p/2s)	14(DZ)	5565	-75.00530
(4s3p/2s)	17	11781	-76.01997
(5s4p/3s)	23	38226	-76.02384
(4s3p1d/2s1p)	29	94830	-76.05954
(5s4p1d/3s1p)	35	198765	-76.06309
(5s4p2d/3s1p)	41	371091	

[a] Number of nonequivalent two-electron integrals (ij|kl) is $M = (m^4 + 2m^3 + 3m^2 + 2m)/8$. It is evaluated for 6 d-functions (xx, yy, zz, xz, yz, xy) of which only 5 are linearly independent d-orbitals and the last one has the symmetry of an s-function.

TABLE 4
Recommended basis set size for ab initio calculations.

Property	Size	Note
Molecular geometry	SZ	for dihedral angles and pyramidal structures DZ+P
Barriers to rotation	SZ	also DZ+P
Ion and dipole interactions, hydrogen bonds	SZ	
NMR and ESR parameters	SZ,DZ	
Electron spectra, ionization energies	SZ,DZ	for Rydberg states DZ+P
Force constants	DZ	
Reaction energies	DZ	for anions DZ+P+D
Barriers of inversion	DZ+P	
One-electron properties	DZ+P	
Polarizability	PZ+2P	
Weak intermolecular interactions	PZ+P+D	

are so time consuming, that as a rule we must try to find a compromise between the quality and the price of the calculations. From this viewpoint the situation is illustrated in Table 4 reflecting a certain experience with the selection of the basis sets (17-19).

In general, the necessity to use balanced basis sets is is respected, meaning that in the molecule, individual atomic basis sets are either minimum, valence-split, double-zeta, or poly-zeta (sufficiently large). Sometimes a scaling technique is used when transferring the basis sets to the molecules. This involves a multiplication of the orbital exponents by an empirically determined numerical factor. For example, the exponent of the hydrogen 1s orbital is multiplied by the factor 1.2 for STOs and by 1.44 for GTFs. Polarization functions are added to large basis sets only (DZ or better quality). For transition metals the diffusion functions (3d with a small exponent and 4p) are important, especially if negative ions are concerned. An overview of some frequently used basis sets is listed in Table 5.

In the basis set of primitive functions a certain number of one-electron and two-electron integrals must be calculated. For MO calculations the following types of integrals are necessary:

TABLE 5

Selected basis sets of GTF and CGTF quality.

Atom	Size	Author [a]	Recommended contraction [b]
H, He	(1s)-(10s)	Huzinaga	SZ: (3s)/[1s] DZ: (4s)/[2s] TZ: (5s)/[3s]
Li-Ne	(6s3p)-(11s7p)	Huzinaga	DZ: (8s4p)/[4s,2p]
	(9s5p)	Huzinaga	VS: [3s2p] TZ: [5s,3p]
	(10s6p)	Huzinaga	
	(11s7p)	Huzinaga et al.	PZ: [6s4p]
	(2s1p)-(8s4p)	Whitman et al.	
	(7s3p)	Roos et al.	
	(4s2p)-(13s9p)	van Duijneveldt	SZ: (6s3p)/[2s1p]
	(6s3p)-(7s4p)	Tatewaki et al.	SZ: [2s1p]
Na-Ar	(9s5p)-(12s9p)	Huzinaga	DZ: (11s7p)/[6s4p] (12s9p)/[7s5p]
	(12s9p)	Veillard	
	(10s6p)	Roos et al.	
Na-Ca	(9s6p)-(13s7p)	Sakai et al.	SZ: [3s2p]
K-Zn	(12s6p4d)	Roos et al.	VS+D: [5s4p2d] DZ: [8s4p2d]
	(9s5p3d)	Roos et al.	
	(14s9p5d)	Wachters	
Sc-Zn	(12s6p3d)- -(13s7p4d)	Tatewaki et al.	SZ: [4s2p1d]
Sc-Cu	(15s8p5d)	Basch et al.	SZ: [4s2p1d]
	(13s7p5d)	Hyla-Krispin et al.	
Y-Ag	(14s8p7d)	Hyla-Krispin et al.	
	(17s11p8d)	Huzinaga	

[a] References (20-36).

[b] Recommended contraction according to (18,19).

1. overlap integrals which, in general, are two-centre

$$S_{i_A j_B} = \langle \chi_i^A(1) | \chi_j^B(1) \rangle \tag{107}$$

2. kinetic integrals, which are also maximum two-centre

$$T_{i_A j_B} = -(\hbar^2/2m_e) \langle \chi_i^A(1) | \nabla_1^2 | \chi_j^B(1) \rangle \tag{108}$$

3. nuclear attraction integrals which are three-centre

$$V^C_{i_A j_B} = \sigma_{SI} \; Z_C \; \langle \chi_i^A(1) | r_{1C}^{-1} | \chi_j^B(2) \rangle \tag{109}$$

4. electron repulsion integrals which are four-centre

$$\langle i_A j_B | \hat{g} | k_C l_D \rangle = \sigma_{SI} \; \langle \chi_i^A(1) \chi_j^B(2) | r_{12}^{-1} | \chi_k^C(1) \chi_l^D(2) \rangle \tag{110}$$

A number of efficient algorithms has been developed (37,38) for the evaluation of these three-fold or six-fold integrals. The numerical complexity of the calculation depends above all on the type of primitive functions used. Evaluation of the integrals from GTF are efficient especially using the **product theorem**, according to which the product of two Gaussians centred at the points A and B yields a new Gaussian centred at the point P situated on the line connecting A and B

$$G(\alpha_1,A)\,G(\alpha_2,B) = k\,G(\alpha_2,\,P) \qquad [111]$$

This enables one to reduce the computation of four-centre integrals tp two-centre ones, while that of two-centre integrals is reduced to one-centre ones. When evaluating two-electron integrals it is useful to apply the following rules:

1. integrals which for symmetry reasons are identically equal to zero are not taken into account;
2. integrals whose value does not reach the threshold defined beforehand (10^{-8} to 10^{-11} a.u.) are neglected;
3. integrals whose value, for symmetry reasons, is repeated are evaluated and stored in external memory media (magnetic tape or disc) only once.
4. Two-electron integrals are stored to external memory media either in the conventional form (pq|rs) or in the supermatrix form, i.e. $G_{pq,rs}$ and $G'_{pq,rs}$, respectively.

3.2.2 Self-Consistent Field Procedure

The SCF procedure for solving the Roothaan equations is accompanied with a number of subsequent steps which have the following order (9,37-39).

1. **Construction of the one-electron operator matrix.** The matrix h is formed from the one-electron integrals T_{pq} and V_{pq}. This is utilized in each cycle of the SCF procedure to form Fock matrix F (F^o and F^c for the RHF approach or F^α and F^β for the UHF approach). The symmetric matrices are usually kept in a linear array in the sequence of the upper or lower triangle.

2. **Determination of the transformation matrix.** As far as the Löwdin transformation of the matrix F is used, the overlap integral matrix S should be diagonalized, i.e. $X^T SX = \mathcal{S}$. Then the symmetric matrix $S^{-1/2}$ is calculated as $S^{-1/2} = X\mathcal{S}^{-1/2}X^T$. An appropriate transformation matrix may also be obtained by the formula $U = \mathcal{S}^{-1/2}X^T$. For this purpose more effective algorithms are currently known.

3. **First estimate of LCAO coefficients.** This step is critical to secure the convergence of the SCF procedure since the trial vectors $C^{(0)}$ of the pseudocharacteristic equation have some qualitative relation to the final vectors (from the point of view of symmetry

properties). The following alternatives may be used:

a) the use of zero trial vectors $C^{(0)} = 0$;

b) the solution of the pseudocharacteristic equation for the bare-nucleus Hamiltonian, i.e. $hC^T = SC^TE$. The matrix h may be substituted for another one-electron model Hamiltonian, for example the Hamiltonian of the Extended Hückel Theory;

c) for extended basis sets one can use the SCF results obtained for restricted basis sets;

d) LCAO coefficients of inner shells may be taken for SCF results of free atoms. A localized bonding model may mimic the valence shells where the valence MOs describe two-centre bonds;

e) some programs utilize the FSGO approach or addition of molecular fragments;

f) for coordination compounds ($CuCl_4^{2-}$, $H_3N.BH_3$) the trial vector may be composed of individual subsystems (Cu^{2+} + $4Cl^-$, NH_3 + BH_3);

g) in a subsequent geometry of the same molecule one can start the SCF procedure from the final vectors of the preceeding geometry, if the symmetry of the system was not changed;

h) for excited states the occupations of individual MOs may be altered. The Schmidt orthogonalization of trial vectors $C^{(0)}$ is performed, if necessary.

4. **Determination of the bond-order matrix.** The eigenvectors are used to calculate the bond-order matrix $P = C^TMC$ (P^o and P^c for the RHF approach, P^α and P^β for the UHF approach). The elements of the diagonal matrix of the occupation numbers M are specified on input or are determined according to the lowest eigenvalues of the pseudocharacteristic equation.

5. **Determination of the electron interaction matrix.** The two-electron integrals are read in groups from an external memory unit and the matrix of two-electron interaction G (plus G' for open-shell system) is formed. Integrals stored in the usual form of (pq|rs) are put into different parts of the matrix G, e.g. to G_{pq}, G_{rs}, G_{ps}, G_{qr}, G_{pr} and G_{qs}. Integrals stored in the supermatrix $\mathcal{G}_{pq,rs}$ and $\mathcal{G}'_{pq,rs}$ are put only into the G_{pq} elements of the matrix G. Individual computer programs mainly mainly at this stage. This stép is rather tedious since it requires manipulation of all the two-electron integrals (their number is of the order of m^4).

6. **Determination of the Fock matrix.** The matrices h, G (and eventually G') are used to form the Fock matrix F (F^c and F^o for the RHF approach, F^α and F^β for the UHF approach). The RHF approach, moreover, needs the matrices R^o and R^c.

7. **Evaluation of electronic energy.** In order to see the convergence of the SCF procedure it is advantageous to separately tabulate the one-electron part and the two-electron part of the electronic energy, as well as the total molecular energy.

8. **Transformation of the pseudocharacteristic problem to the characteristic equation.** The Fock matrix F is transformed to $\mathrm{F}' = \mathrm{U}\mathrm{F}\mathrm{U}^T$ according to one of the following possibilities:

a) the Löwdin orthogonalization is used, i.e. $\mathrm{U} = \mathrm{S}^{-1/2}$;

b) the transformation matrix is $\mathrm{U} = S^{-1/2}\mathrm{X}^T$;

c) the symmetrized functions (Appendix 4) are used. The set of nonorthogonal symmetrized functions $\{\sigma\}$ is defined by a transformation $\{\sigma\} = \underline{\Gamma}\,\{\vartheta\}$. The corresponding overlap matrix S_0 is

$$\mathrm{S}_0 = \{\sigma\}\,\{\sigma\}^T = \underline{\Gamma}\,\{\vartheta\}\,\{\vartheta\}^T\,\underline{\Gamma}^T = \underline{\Gamma}\,\mathrm{S}\,\underline{\Gamma}^T \qquad [112]$$

and it adopts a block-diagonal form. It can be transformed to a diagonal form (in the first iteration) according to individual blocks as

$$\mathrm{X}_0^T\,\mathrm{S}_0\,\mathrm{X}_0 = S_0 \qquad [113]$$

where S_0 is a diagonal matrix. Then the rows of the matrix U,

$$\mathrm{U} = S_0^{-1/2}\,\mathrm{X}_0^T\,\underline{\Gamma} \qquad [114]$$

represent the functions transforming according to individual irreducible representations of the molecular point group of symmetry, since

$$\mathrm{U}\,\mathrm{S}\,\mathrm{U}^T = S_0^{-1/2}\,\mathrm{X}_0^T\,\underline{\Gamma}\,\mathrm{S}\,\underline{\Gamma}^T\,\mathrm{X}_0\,S_0^{-1/2} = S_0^{-1/2}\,\mathrm{X}_0^T\,\mathrm{S}_0\,\mathrm{X}_0\,S_0^{-1/2} =$$

$$= S_0^{-1/2}\,S_0\,S_0^{-1/2} = \mathrm{I} \qquad [115]$$

The transformation

$$\mathrm{F}' = \mathrm{U}\,\mathrm{F}\,\mathrm{U}^T = S_0^{-1/2}\,\mathrm{X}_0^T\,\underline{\Gamma}\,\mathrm{F}\,\underline{\Gamma}^T\,S_0^{-1/2} \qquad [116]$$

yields a block-diagonal matrix for individual irreducible representations which significantly simplifies the situation in the diagonalization of matrices of higher dimension;

d) to transform the Fock matrix one can use the eigenvectors of the previous iteration: $\mathrm{U} = \mathrm{C}^{(i-1)}$. In this case the F matrix is expressed in the basis set of molecular orbitals (still not self-consistent), and thus it has small off-diagonal elements. The Jacobi algorithm will be most efficient for its diagonalization. Its effectiveness increases with the number of iterations as the F' matrix approaches the form of the diagonal one (at self-consistency it is diagonal).

9. **Solution of the characteristic equation.** The eigenvalues E and eigenvectors V result from equation $F'V = VE$. The matrix F' is to be diagonalized for this purpose; the time required for this process is proportional to m^3 (m is the basis set size). Individual programs differ from one another in this step. Some of the common procedures follow:

a) The full spectrum of eigenvalues and a complete set of the eigenvectors are calculated using, for example, the Jacobi algorithm. The threshold of diagonalization can vary with the number of iterations because less precise values are sufficient at the beginning of the procedure.

b) During the SCF procedure only those eigenvectors corresponding to occupied MOs need be derived; the sub-matrix V_{occ} (of the order m x n') of occupied MOs is used in constructing the P matrix. The occupied orbitals are usually attributed to the lowest eigenvalues ϵ_k. Thus it is sufficient only to determine the lowest part of the spectrum of eigenvalues ϵ_k^{occ} and the corresponding eigenvectors V_{occ}. For this purpose effective algorithms were outlined. Such an approach is very effective in extended basis sets when $n' \ll m$.

c) In small basis sets (including semiempirical all-valence methods) the number of unoccupied orbitals is lower than the number of occupied orbitals: $m - n' < m$. In this case it is more advantageous to determine the upper part of the spectrum of eigenvalues ϵ_k^{vir} and the corresponding eigenvectors V_{vir} of the dimension $(m - n') \times m$. They can equivalently be used in constructing the P matrix.

d) Since the Fock matrix changes slowly during the SCF procedure, some diagonalization algorithms utilize the result of the previous iteration to accelerate the calculation.

10. **Back transformation of eigenvectors.** For the back transformation of the orthogonal matrix V to the LCAO matrix $C = V^T U$ one can use (see point 8):

a) $U = S^{-1/2} = X\mathcal{S}^{-1/2}X^T$

b) $U = \mathcal{S}^{-1/2}X^T$

c) $U = \mathcal{S}^{-1/2}\ X_0^T\ \underline{\Gamma}$

d) $U = C^{(i-1)}$

Usually the matrix $C^T = U^T V$ is kept in the computer memory.

11. **Selection of occupied MOs.** In the first step, the eigenvectors ϵ_k are ordered according to their values. This step is

usually incorporated in the diagonalization algorithms. The corresponding rows of the C matrix (columns of the C^T matrix) are ordered in the same manner, so that the corresponding occu- occupation number diagonal matrix has its first n' elements equal to 1 and the remaining elements are zero (n' = n/2 for the closed shell system, n' = n_α or n_β for the UHF approach and n' = n_1 or $n_1 + n_2$ for the RHF approach). Such a selection is violated in

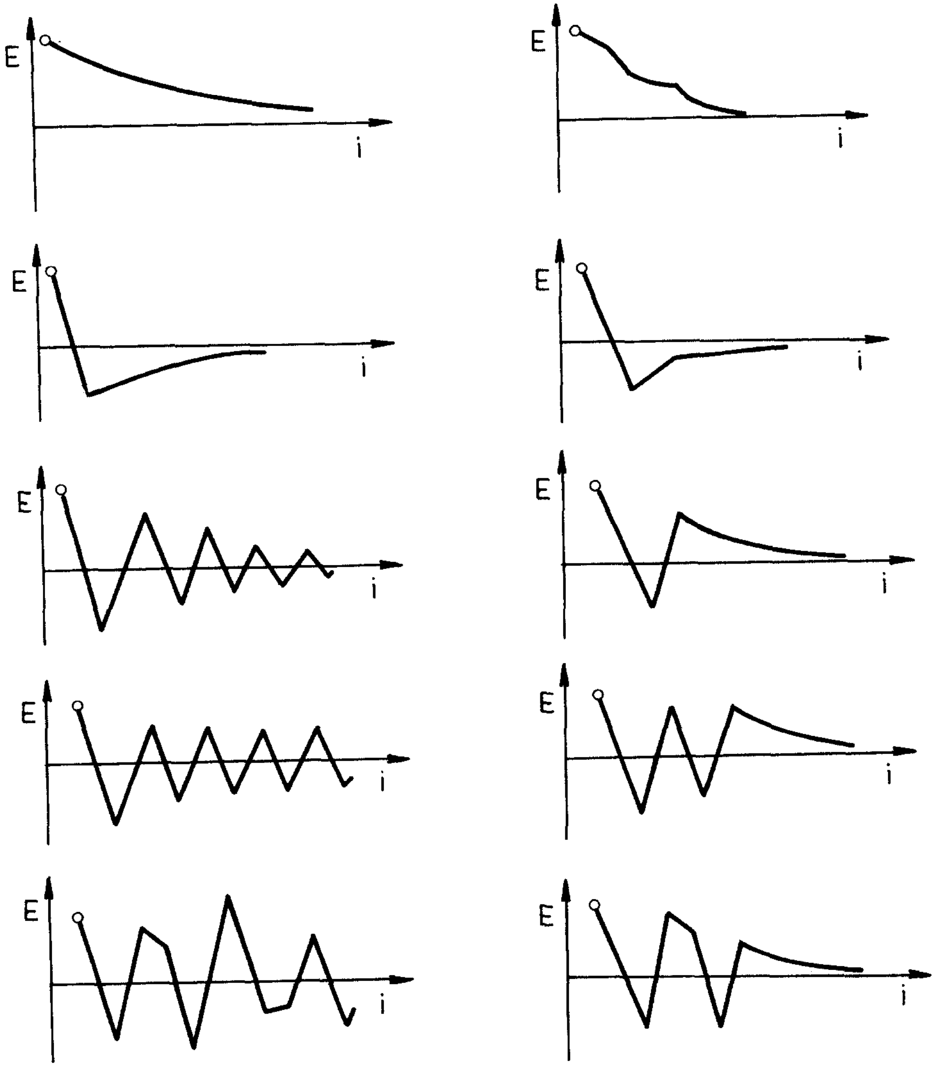

Fig. 5. Various types of convergence of SCF procedure. a - without extrapolation or damping, b - with extrapolation or damping; i - number of iterations.

the RHF approach when the open level orbital is not necessarily of the order $n_1 + 1$, but corresponds to an orbital energy ϵ_p^o for $p \le n_1 + n_2$. From time to time the position of an open level p can change during the SCF procedure. For the proper selection of open level, special criteria have been proposed. One of them (9) compares the overlap integral of the trial vector with p-th eigenvector: the open level is attributed to the first eigenvector c_p^o yielding an overlap integral greater than $1/\sqrt{2}$.

12. Convergence test. Several criteria are used for this purpose; they are based on testing the difference of a certain quantity calculated in two subsequent iterations. The testing quantities cover: total energy, two-electron and one-electron part of the total energy, full spectrum of orbital energies, all elements of matrices **F**, **P** or **C** (the strength of the convergence criterion increases in this order). The SCF procedure is completed when:

a) the convergence criterion is fulfilled;

b) the iteration limit is exceeded;

c) the time limit has expired (a restart is possible);

d) divergence appears and attempts to correct this are not successful.

An appropriate convergence criterion is represented by the absolute values of the off-diagonal matrix elements of the **F** matrix in the MOs basis set. The total molecular energy can vary depending on the number of iterations (Fig. 5).

13. Extrapolation of eigenvectors. In order to accelerate convergence of the SCF procedure (and reduce computing time) some extrapolation techniques are useful. Usually three LCAO matrices of two subsequent iterations are processed according to the scheme:

iteration	trial vectors	resulting vectors	extrapolated vectors
i	$C^{(i)}$ ⇒	$C^{(i+1)}$	
i+1	$C^{(i+1)}$ ⇒	$C^{(i+2)}$ ⇒	C'

a) The Aitken extrapolation method is based on the assumption of a geometric decrease of error for every matrix element. It provides

$$C'_{kl} = [C_{kl}^{(i+2)} C_{kl}^{(i)} - C_{kl}^{(i+1)} C_{kl}^{(i+1)}]/[C_{kl}^{(i+2)} - 2C_{kl}^{(i+1)} + C_{kl}^{(i)}] \quad [117]$$

b) The spiral method (6) yields

$$\mathbf{b}' = (\alpha - 2\beta + \gamma)^{-1}[\alpha\mathbf{b}^{(i)} - 2\beta\mathbf{b}^{(i+1)} + \gamma\mathbf{b}^{(i+2)}] \quad [118]$$

with

$$\alpha = [\mathbf{b}^{(i+2)} - \mathbf{b}^{(i+1)}]^T [\mathbf{b}^{(i+2)} - \mathbf{b}^{(i+1)}] \quad [119]$$

$$\beta = [\mathbf{b}^{(i+2)} - \mathbf{b}^{(i+1)}]^T [\mathbf{b}^{(i+1)} - \mathbf{b}^{(i)}] \quad [120]$$

$$\gamma = [\mathbf{b}^{(i+1)} - \mathbf{b}^{(i)}]^T [\mathbf{b}^{(i+1)} - \mathbf{b}^{(i)}] \quad [121]$$

The column vector **b** consists of all the LCAO coefficients of the occuied MOs. The extrapolation is successful only when the matrices $C^{(i)}$, $C^{(i+1)}$ and $C^{(i+2)}$ are convergent and the corresponding eigenvectors are of the same phase. Since the molecular energy is invariant to the substitution of $\phi_i \to -\phi_i$, the signs of the LCAO coefficients in the individual MOs should be checked before the extrapolation.

14. Damping technique. If the energy oscillates during the SCF procedure or is divergent, convergence may be secured by interpolation or using the damping technique

$$C' = \lambda C^{(i)} + (1 - \lambda) C^{(i+1)} \text{ for } E^{(i)} < E^{(i+1)} \quad [122]$$

$$C' = (1 - \lambda) C^{(i)} + \lambda C^{(i+1)} \text{ for } E^{(i)} > E^{(i+1)} \quad [123]$$

The damping parameter is chosen from the range $0 < \lambda < 1$; usually it is $\lambda = 0.7 - 0.9$. To use the damping procedure the individual MOs should be in the same phase.

15. Level shifting procedure. The SCF procedure is usually divergent when the HOMO and LUMO frontier orbitals are close in energy. In such a case the occupation of these levels may change and thus the total molecular energy oscillates (it corresponds to different sheets of the adiabatic potential). In these situations the level shifting procedure might be successful (40); this is based on the fact that the LUMO does not contribute to the rotal molecular energy at self-consistency. For this reason an artificial increase by a positive amount λ of the LUMO energy can only lead to a decrease in the total molecular energy. The undesired admixtures of LUMO into the molecular energy are filtered out. Within this process the Fock operator matrix is expressed in the basis set of MOs: $F' = C^{(i-1)} F C^{(i-1)T}$. Then the diagonal matrix element of the undesired level is shifted by the value of λ ($F'_{aa} \Rightarrow F'_{aa} + \lambda$) and the resulting matrix undergoes Jacobi diagonalization. The eigenvectors are processed in the usual manner. According to this procedure the polarization energy decreases; it is given by the perturbation formula as

$$E^{(2)}_{\mathrm{pol}} = \sum_{i}^{occ} \sum_{a}^{vir} [\langle i|\hat{F}|a\rangle^2]/[\epsilon_i - (\epsilon_a + \lambda)] \quad [124]$$

so that the system obeys the Brillouin theorem better, which is equivalent to the Hartree-Fock equations (see Chapter 4). The transformation of F to F' requires knowledge of all eigenvectors including those for virtual MOs.

16. Construction of the bond-order matrix. In addition to the definition $P = C^T MC$ it is possible to exploit the ordering of individual MOs according to their orbital energies. If MOs are ordered according to increased orbital energies, an incomplete matrix mutiplication can be done

$$P_{pq} = \sum_{i}^{n'} C_{ip} C_{iq} \qquad [125]$$

or

$$P = C^T_{occ}\, C_{occ} = U^T\, V_{occ}\, V^T_{occ}\, U \qquad [126]$$

One can use an alternative relationship in the case that only the virtual MOs were determined

$$P = C^T C - C^T_{vir} C_{vir} = U^T (I - V_{vir} V^T_{vir}) U \qquad [127]$$

When extrapolation or damping are used the matrix P is constructed from the new matrix C'. Sometimes the extrapolation or damping are applied to the matrix P instead of the matrix C. Since the matrix P is symmetric, this process requires fewer mathematical operations.

The damping method has also been proposed in such a form that assumes the following relationships hold true

$$\begin{aligned} P' &= \lambda P^{(i)} + (1 - \lambda) P^{(i+1)} = \\ &= P^{(i+1)} + \lambda [P^{(i)} - P^{(i+1)}] = P + \lambda\, \Delta P \end{aligned} \qquad [128]$$

$$\begin{aligned} F' &= \lambda F^{(i)} + (1 - \lambda) F^{(i+1)} = \\ &= F^{(i+1)} + \lambda [F^{(i)} - F^{(i+1)}] = F + \lambda\, \Delta F \end{aligned} \qquad [129]$$

The expression for the electronic energy within the UHF approach then adopts the form of

$$\begin{aligned} E^{el} &= (1/2)\, Tr\{(P'^{\alpha} + P'^{\beta}) h + P'^{\alpha} F'^{\alpha} + P'^{\beta} F'^{\beta}\} = \\ &= (1/2)\, Tr\{[(P^{\alpha} + P^{\beta}) h + P^{\alpha} F^{\alpha} + P^{\beta} F^{\beta}] + \\ &+ \lambda [(\Delta P^{\alpha} + \Delta P^{\beta}) h + \Delta P^{\alpha} F^{\alpha} + P^{\alpha} \Delta F^{\alpha} + \Delta P^{\beta} F^{\beta} + P^{\beta} \Delta F^{\beta}] + \\ &+ \lambda^2 [\Delta P^{\alpha} \Delta F^{\alpha} + \Delta P^{\beta} \Delta F^{\beta}]\} \end{aligned} \qquad [130]$$

The optimum value of the λ parameter may be found from the stationary condition $(\partial E^{el}/\partial\lambda) = 0$ which implies

$$\lambda = - (1/2)[Tr\{(\Delta P^{\alpha} + \Delta P^{\beta})h + \Delta P^{\alpha}F^{\alpha} + P^{\alpha}\Delta F^{\alpha} + \Delta P^{\beta}F^{\beta} + P^{\beta}\Delta F^{\beta}\}]/ \\ / [Tr\{\Delta P^{\alpha}\Delta F^{\alpha} + \Delta P^{\beta}\Delta F^{\beta}\}] \qquad [131]$$

The λ parameter determined in this way is used only for damping matrix P if $0 < \lambda < 1$ is true. For the evaluation of λ, nine symmetric matrices are needed within the UHF approach (namely h, ΔP^{α}, ΔP^{β}, ΔF^{α}, ΔF^{β}, P^{α}, P^{β}, F^{α} and F^{β}) and five symmetric matrices for closed shell systems (h, ΔP, ΔF, P and F). These matrices, however, occupy less space than six square matrices C (three for closed shell system) used in the three-point extrapolation. The Fock matrix is evaluated twice - before the damping $F^{(i)}$ and after the damping from the new matrix P'. Practical experience with this process at the semiempirical level shows that it is capable to secure the convergence of the SCF procedure in cases where simpler approaches fail.

17. **Continuation of the SCF procedure.** The steps 5 to 16 are repeated. When the convergence criterion is satisfied, it is useful to do one iteration more without the extrapolation, damping and level shifting. Now the complete spectrum of eigenvalues and corresponding eigenvectors are evaluated.

Depending on the quality of the initial approximation from 10 to 20 iteration should be done. For transition metal complexes it is difficult to find an appropriate guess of C and, as a rule, the number of iterations is 40 or more. As an example, carbonyl complexes of transition metals show bad convergence. Usually the SCF procedure meets with difficulties for geometries at the dissociation of chemical bonds or in cases of crossing of two sheets of the adiabatic potential.

The SCF procedure just described leads to a stationary state of a molecule but there is no guarantee that the given state is the ground state. For most organic molecules this alternative situation rarely appears but for inorganic complexes may be frequent. Therefore we recommend performing the SCF procedure for several alternative MO occupations and the state of lowest energy is accepted as the ground state. In the case of energy levels lying close to one another, configuration interaction may alter their order.

For *ab initio* calculations of the electronic structure of molecules a large number of computer programs has been developed. Among them the program POLYATOM (version II) and its derivatives IBMOL and PHANTOM, program GAUSSIAN 70 and its innovated versions

76, 80, 82, systems ASTERIX, MUNICH, MOLECULE, SUPERMOLECULE, ALCHEMY, HONDO5, HONDO7, GAMESS, etc. should be mentioned. These programs represent software of high level and all have been developed for decades by a group of authors in different institutes and countries. The programs are written in FORTRAN-IV or FORTRAN-77 languague and their length is from 10^4 to 10^5 cards (HONDO5 - 22 000, GAMESS - 42 000, GAUSSIAN 80 - 110 000 cards). In manipulation with two-electron integrals they often utilize machine languague to increase their efficiency (subroutines of read/ write operations to disks and other frequent operations are written in ASSEMBLER). The programs are followed by packages for the calculation of molecular observables. Some are available from exchange institutes (41,42).

Recently *ab initio* programs have been rewritten to run at personal computers (e.g. MICROMOLE system). This development is of the principal importance since good quality calculations may be performed on the table overnight.

Ab initio programs exclusively utilize the atomic system of units - a.u. (see Appendix 1) where the Bohr radius a_0 is the unit of length (bohr) and the double value of the ionization energy of hydrogen atom E_h serves for the unit of energy (hartree).

3.3 NON-EMPIRICAL METHODS

With this abbreviation we understand calculation methods within the one-electron approximation utilizing certain approximations either in the Hamiltonian or wave function. These methods are derived from the Hartree-Fock equations or Roothaan equations in the LCAO approximation. The calculations are usually carried out using the self-consistent field (SCF) method.

3.3.1 Floating Spherical Gaussian Orbitals

This method (abbreviated FSGO) is based on the approximation of each occupied MO by a single spherical gaussian function

$$\phi_i \approx \chi_i = (2/\pi\rho_i^2)^{3/4}\ exp[-(R - R_i)^2/\rho_i^2] \qquad [132]$$

The parameter ρ_i is interrelated to the orbital exponent of GTF α_i as follows

$$\alpha_i = 1/\rho_i^2 \qquad [133]$$

and it has a meaning of the orbital radius. By integrating one can prove that approximately 74 % of the electron density is situated inside the sphere of radius ρ_i (43). The above orbitals for the closed-shell system directly represent traditional electron pairs of the Lewis valence theory. The electronic wave function within this approximation is given by a single Slater determinant

$$\Psi_0^{el} = \Phi_0 = N_0\ \hat{A}_n\{\phi_1(1)\alpha\ \phi_1(2)\beta\ \ldots\phi_n(2n-1)\alpha\ \phi_n(2n)\beta)\} \qquad [134]$$

Since the orbitals are non-orthogonal, the normalization factor is

$$1/N_0 = [(2n!)]^{1/2}\ det\{S\} \qquad [135]$$

where S is an overlap matrix of elements

$$S_{ij} = \langle\phi_i|\phi_j\rangle \qquad [136]$$

If the overlap matrix is non-singular, then an inverse matrix S^{-1} exists and thus the electronic energy in the non-orthogonal basis set, according to formulas [84] - [87] of Chapter 1, may be expressed as

$$E^{el} = 2\sum_{i,k}^{n/2} \langle i|\hat{h}|k\rangle S_{ki}^{-1} + \sum_{i,j,k,l}^{n/2} (ik|kl)[2S_{ij}^{-1}\ S_{kl}^{-1} - S_{il}^{-1}\ S_{jk}^{-1}] =$$

$$= f(R_1,\rho_1,\ldots,R_n,\rho_n) \qquad [137]$$

This is a non-linear function of orbital centres R_i and orbital radii ρ_i. In order to minimize the molecular energy one of numerous methods of minimization can be used. It is possible to show that FSGOs fulfil the virial theorem as well as the Hellmann-Feynman theorem (Appendix 2).

In comparison with standard *ab initio* methods the FSGO procedure involves some specific features.

1. The FSGO method utilizes an **absolute minimum basis set** in which every orbital is occupied. For example, in the water molecule the FSGO basis set covers only 5 spherical GTFs whereas the minimum basis set for an *ab initio* calculation consists of 7 cartesian GTFs or 13 spherical GLFs. As virtual orbitals are omitted in the FSGO method, the subsequent application of configuration interaction is impossible.
2. The position of the GTF is optimized in contrast to *ab initio* basis sets which are fixed at the atomic nuclei.
3. The FSGO method does not utilize the self-consistent field procedure but the direct minimization of the molecular energy in the non-orthogonal basis set of one-electron functions.

The molecular energy within the FSGO approach is only 82 - 85 % of the Hartree-Fock (SCF) energy. In its most simple form the method does not correctly describe the lone electron pairs, π-bonds and inner shells (except the K-shell). For instance, in optimizing the energy of the water molecule the lone pairs exhibit a tendency to coalesce; this, however, leads to the singularity of overlap matrix S. The above defect is avoided by postulating a minimum separation of centres of gaussians (usually 0.1 - 0.2 a_0). Since FSGOs have no nodal planes, they cannot describe π-bonds. For this purpose a pair of banana-type bonds is used instead of $\sigma + \pi$ bonds (e.g. in ethene molecule) or three banana-type bonds instead of $\sigma + 2\pi$ bonds (in ethyne). The inner shells (L and M) are simulated by a tetrahedral configuration of four gaussians. Again it is necessary *a priori* to prohibit their natural tendency to coalesce.

Substantial improvement of the FSGO method has been achieved by considering the double-zeta basis set

$$\phi_i = c_{i1}\chi_{i1}(R_i,\rho_{i1}) + c_{i2}\chi_{i2}(R_i,\rho_{i2}) = N_i(\chi_{i1} + \lambda_i\chi_{i2}) \qquad [138]$$

The corresponding primitive functions are centered at the same point R_i. The number of parameters to be optimized is increased to 4 for each orbital (R_i, λ_i, ρ_{i1} and ρ_{i2}). The molecular energy, however, decreases substantially and it reaches 95 % of the Hartree-Fock energy.

Other modifications of the FSGO method utilize ellipsoidal Gauss-type functions instead of spherical ones. Pseudopotential versions have also been developed to simulate the inner shells. There exist versions of SCF calculations in which the molecular orbitals are expressed in the form of a linear combination of FSGOs. An important field of application of the FSGO method is represented by the method of molecular fragments (44).

The FSGO calculations may be performed by specific programs (45,46) or using standard *ab initio* programs having options for an automatic optimization of the basis set (exponents of FSGOs) and molecular geometry (positions of FSGOs). The FSGOs non-centered at nuclei may be introduced through fictitious atoms having zero electrostatic charge on the 'nucleus' at the given site.

3.3.2 Pseudopotential Methods

These methods are appropriate for studying the electronic structure of molecules containing heavy atoms. The pseudopotential methods utilize the fact that only valence electrons take part in the chemical bond whereas the inner atomic shells are only slightly influenced by bond formation. With this assumption calculations of the electronic structure of molecules can be done in the valence basis set only, whereas the core (inner-shell electrons and the atomic nucleus) of individual atoms are approximated through a nonlocal effective potential - pseudopotential. Although the pseudopotential method was outlined as early as the beginning of quantum mechanics (47,48), only in the eighties it has found a broader and theoretically advanced application.

Herring (49) introduced the plane wave method for valence electrons, which are orthogonal to all spherical core wave functions, when studying the electronic structure of crystals. As an effect of the orthogonalization, a complicated and physically difficult to interpret problem arose. Slater (50) utilized the spherical symmetry of the core function by introducing the Orthogonalized Plane Wave (OPW) method; this, however, demanded the potential outside the atomic region to be constant. In an important development Phillips and Kleinman (51) used a symmetric combination of plane waves, orthogonal to core plane waves, in the role of the basis set. These authors have described the basic conditions leading to the separation of the valence and core electrons. In the seventies the number of papers dealing with pseudopotential techniques grew rapidly (52 - 82). Finally the general theory of hermitian pseudopotentials was outlined; it is applicable both to molecules and the solid state.

Let us consider a hermitian Hamiltonian for valence electrons, $\hat{H}_v$, and let us determine the basis set for orthonormal orbitals $\{\phi_c\}$ belonging to the core subspace. The problem is reduced to minimization of the energy functional

$$E_v = \langle\phi_v|\hat{H}_v|\phi_v\rangle \qquad [139]$$

for the normalized valence orbital ϕ_v that fulfils the orthogonality condition with respect to all core orbitals

$$\langle\phi_v|\phi_c\rangle = 0 \qquad [140]$$

This condition limites the core subspace to which the valence orbitals $|\phi_v\rangle$ do not belong. Therefore one can define a projection operator $\hat{P}$ (hermitian and idempotent) in the form

$$\hat{P} = \sum_c |\phi_c\rangle\langle\phi_c| \qquad [141]$$

which satisfies the relationship

$$\hat{P}\,|\phi_c\rangle = |\phi_c\rangle \qquad [142]$$

Then the complementary projector $\hat{Q} = \hat{1} - \hat{P}$ yields

$$\hat{Q}\,|\phi_c\rangle = (\hat{1} - \hat{P})\,|\phi_c\rangle = 0 \qquad [143]$$

The valence orbital $|\phi_v\rangle$ may be specified as

$$|\phi_v\rangle = \hat{Q}\ |\phi_p\rangle = (\hat{1} - \hat{P})\ |\phi_p\rangle \qquad [144]$$

The orthogonality condition [140] is satisfied for an arbitrary pseudoorbital $|\phi_p\rangle$ and its arbitrary variation. The function $|\phi_p\rangle$ is not necessarily orthogonal to the core orbitals, i.e. $\langle\phi_c|\phi_p\rangle \neq \neq 0$. The problem of minimization of E_v is transcribed as

$$E_v = \langle\hat{Q}\ \phi_p|\hat{H}_v|\hat{Q}\ \phi_p\rangle \qquad [145]$$

at the normalization condition for $|\phi_v\rangle$, i.e.

$$\langle\hat{Q}\ \phi_p|\hat{Q}\ \phi_p\rangle = 1 \qquad [146]$$

The variation of $\delta\phi_p$ leads to the equation

$$\langle\delta\phi_p|\hat{Q}\ \hat{H}_v\ \hat{Q}|\phi_p\rangle - \epsilon_v\langle\delta\phi_p|\hat{Q}|\phi_p\rangle = 0 \qquad [147]$$

where ϵ_v is a Lagrangian multiplier. Since the variation $\delta\phi_p$ is arbitrary, then

$$\{\hat{Q}\hat{H}_v\hat{Q} - \epsilon_v\hat{Q}\}|\phi_p\rangle = 0 \qquad [148]$$

This is equivalent to the equation

$$\{\hat{H}_v + \hat{V}_R^{GPK}\}|\phi_p\rangle = \epsilon_v|\phi_p\rangle \qquad [149]$$

where a **generalized Phillips-Kleinman pseudopotential** has been introduced

$$\hat{V}_R^{GPK} = \hat{P}\hat{H}_v\hat{P} - \hat{H}_v\hat{P} - \hat{P}\hat{H}_v + E_v\hat{P} \qquad [150]$$

It follows from the characteristic equation [149] that the Lagrangian multiplier $\epsilon_v = E_v$ represents an eigenvalue of the pseudo-Hamiltonian

$$\hat{H}_{PS} = \hat{H}_v + \hat{V}_R^{GPK} = (\hat{1} - \hat{P})\hat{H}_v(\hat{1} - \hat{P}) + E_v\hat{P} \qquad [151]$$

so that

$$\hat{H}_{PS}\ |\phi_p\rangle = E_v|\phi_p\rangle \qquad [152]$$

The form of the pseudo-Hamiltonian [151] is not appropriate as an effect of application of projection operators: it contains not only one-electron and two-electron operators but, as a consequence, also multielectron integrals. For this reason an **effective Hamiltonian** $\hat{H}_v^{eff}$ is introduced in which the projection is applied only to the one-electron part of the operator $\hat{H}_v$

$$\hat{H}_v^{eff} = \sum_i^{n_v} -(\hbar^2/2m_e)\nabla_i^2 + \sum_A^N \hat{W}_{PS}^A(i) + \sum_{i<j}^{n_v} \sigma_{SI}\ r_{ij}^{-1} \qquad [153]$$

It is advantageous to write the **effective pseudopotential** for atom A in the form of

$$\hat{W}^A_{PS}(i) = -\sigma_{SI}\, Z^c_A\, r^{-1}_{Ai} + \hat{W}^A_R(i) \qquad [154]$$

because in the limiting case of $r \to \infty$ we obtain $\hat{W}^A_{PS}(i) \to -\sigma_{SI} Z^c_A r^{-1}_{Ai}$ (Z^c_A is the core charge).

The direct calculation of the pseudopotential meets with limitations which make such an approach too complicated. The valence pseudoorbitals may be chosen in the form of a linear combination of valence orbitals and core orbitals

$$\phi_p = \phi_v + \sum_c a_c \phi_c \qquad [155]$$

where a_c are the combination coefficients calculated by the variational method. The above pseudopotential functions obey eq. [148].

The following problems complicate the direct theoretical approach.

1. The core orbitals should be known in order to determine an effective Hamiltonian $\hat{H}_{PS}$.

2. The pseudopotential is a function of pseudoorbitals ϕ_p so that an iterative procedure must be used:

a) the solution of the Hartree-Fock equations for core orbitals

$$\hat{H}_c|\phi_c\rangle = E_c|\phi_c\rangle \qquad [156]$$

b) an estimate of the energy E_v and the construction of the pseudo-Hamiltonian $\hat{H}_{PS}$;

c) diagonalization of the matrix of the pseudo-Hamiltonian and determination of the lowest eigenvalue E_v. This cycle is repeated until self-consistency is achieved.

More advantageous is the semiempirical approach in which the valence pseudoorbitals ϕ_p and the corresponding pseudopotentials $\hat{W}^A_{PS}$ are constructed from the known atomic energy values. Such pseudopotentials are constructed in an analytical form (Table 6) and are then used to calculate the electronic structure of the molecules. In this way, changes in the atomic core, upon the bond formation, are neglected (Frozen Core Approximation) (55).

The valence pseudoorbitals ϕ_p are solutions of the pseudopotential equation [152]. They have to exactly fit the valence orbitals ϕ_v in the valence region and vanish in the core region (Fig. 6). The pseudoorbitals may be calculated by minimization of the functional (53,54)

$$F = \langle\phi_p - \phi_v|\phi_p - \phi_v\rangle_{Rc} \qquad [157]$$

Most frequently the form of the pseudoorbitals is chosen through a linear combination of Gauss-type or Slater functions

TABLE 6

Analytical forms of pseudopotentials.

No	Function	Ref.
1	$W = -\sigma_{SI}Z^c/r$ for $r > R_c$ $W = \infty$ for $r < R_c$ 'hard-core'	(74)
2	$W = -\sigma_{SI}Z^c/r$ for $r > R_c$ $W = -\sum_l A_l\hat{P}_l$ for $r < R_c$ 'Abarenkov-Heine'	(75-77)
3	$W = -\sigma_{SI}Z^c/r - \sum_l (A_l + B_l r)\hat{P}_l$ 'linear cut-off'	(78)
4	$W = -\sigma_{SI}Z^c/(r + c/r^2)$ for $r > R_c$ $W = A\,exp(-ar)$ for $r < R_c$	(79,80)
5	$W = -\sigma_{SI}Z^c/r + \sum_l (B_l/r^2)\hat{P}_l$	(81)
6	$W = Cr^2 + C_0$	(82)
7	$W = -\alpha_d/[2(r^2 + d^2)^2] - \alpha_q/[2(r^2 + d^2)^3] - 1/r +$ $+ \sum_l A_l r^p\,exp(-\xi_l r^q)$	(73)
8	$W = -\sigma_{SI}Z^c/r + \sum_l \hat{P}_l(B_{1l}/r + B_{2l}/r^2)$	(70)
9	$W = -\sigma_{SI}Z^c/r + [A_1 exp(-\alpha_1 r) + A_2 exp(-\alpha_2 r^2)]/r$	(68)
10	$W = -\sigma_{SI}Z^c/r - [exp(-\alpha_1 r) + exp(-\alpha_2 r)]/r$	(70)
11	$W = -\sigma_{SI}Z^c/r + \sum_l \hat{P}_l(C_1/r^2 + C_2 r^2)exp(-\alpha r^2)$	(70)
12	$W = -\sigma_{SI}Z^c/r - \sum_l C_l r^{n_l} exp(-\alpha_l r^2)$	(56,71)
13	$W = -\sigma_{SI}Z^c/r - \sum_l C_l r^{n_l} exp(-\alpha_l r)$	(56,71)

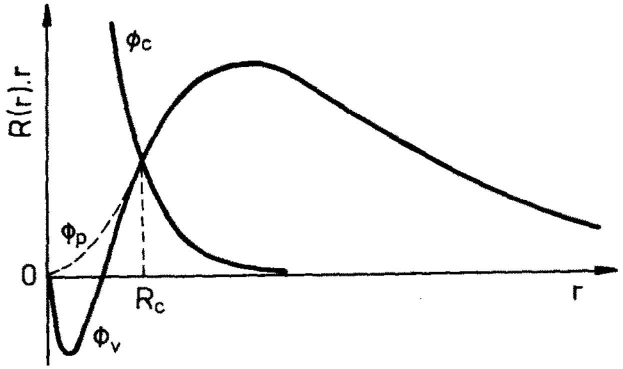

Fig. 6. Radial part of the pseudoorbital ϕ_p, valence orbital ϕ_v and core orbital ϕ_c.

$$\phi_p = \sum_i c_i \chi_i \qquad [158]$$

By substituting into [157] and taking into account the orthogonality condition we arrive at the set of linear equations

$$\sum_j (\langle\chi_i|\chi_j\rangle_{R_c} - \lambda\langle\chi_i|\chi_j\rangle)c_j = \langle\chi_i|\chi_v\rangle_{Rc} \qquad [159]$$

where λ is a Lagrangian multiplier close to zero because the orbitals ϕ_p and ϕ_v are practically the same in the region $R > R_c$. The index R_c means that the integration is carried out in the region outside the core subspace: $R > R_c$. The value of R_c is chosen as the crossing point between the radial parts of the valence orbitals ϕ_v and the most outer core orbital of the same symmetry (Fig. 6). Although the choice of R_c is rather arbitrary, the shape of the pseudoorbital is not very sensitive to R_c value. Eq. [159] is solved by an interative procedure.

It is useful to introduce a semilocal form of the operator $\hat{W}_R^A(i)$ into the effective pseudopotential [154]

$$\hat{W}_R^A(i) = \sum_i \hat{W}_{R,l}^A(i)\ \hat{P}_l \qquad [160]$$

which contains only a limited number of adjustable parameters. The operator $\hat{P}_l$ is a projector into l-th subspace of spherical harmonics

$$\hat{P}_l = \sum_{m=-l}^{+l} |Y_{lm}\rangle\langle Y_{lm}| \qquad [161]$$

The operators $\hat{W}_{R,l}^A(i)$ are specified in an analytical form (Table 6). The corresponding parameters are determined in such a way that in the pseudoorbitals ϕ_p basis set, the effective pseudo-Hamiltonian [153] yields the best agreement with the experimental or theoretical valence orbital energies obtained by *ab initio* calculations.

Pseudopotential methods are most effective for compounds having a large number of core electrons. Here, however, it is necessary to include some relativistic effects. For this reason pseudopotential versions which include relativistic effects into the pseudopotential operators have been developed (65,66). The calculations are performed in the relativistic pseudoorbital basis set.

The effectiveness of the pseudopotential method lies in the fact that the number of necessary two-electron integrals is greatly reduced; this is important for heavy atoms. The approximations introduced, however, mean that the pseudopotential calculations are less exact than the full *ab initio* approach for the given type of basis set.

As a consequence of the frozen core approximation the results become worse with increasing bond polarity because in this situation the core orbitals are influenced more by bond formation. This can be improved by considering the pseudopotentials to be dependent on the oxidation state of the atom in the molecule. The errors increase with increasing number of valence electrons as a consequence of the higher polarizability of the atoms at the right side of the periodic table. The above errors originate in the frozen core approximation and partially disappear when some of the core electrons are included into the calculation.

Despite these difficulties the pseudopotential methods are very effective for coordination compounds. They enable the use of extended valence orbital basis sets which, with the limited speed and capacity of existing computers, can lead to results superior to those obtained by *ab initio* calculations with small basis sets.

3.3.3 Xα Method

This method closely resembles the density functional theory outlined in paragraph 1.4.5. The electronic energy of a molecule can, within the Hartree-Fock method (or one-electron approximation), be written as

$$E^{el} = E_1 + E_{12} \qquad [162]$$

where the one-electron term is

$$E_1 = \sum_i^m n_i \langle \psi_i | \hat{h} | \psi_i \rangle \qquad [163]$$

and the two-electron term

$$E_{12} = \int \rho_2(1,2;1,2)\ \hat{g}_{12}\ dX_1\ dX_2 = E_c + E_x \qquad [164]$$

consists of the Coulomb term

$$E_c = (1/2) \int \rho(1)\ \hat{V}_c(1)\ dX_1 = (1/2) \sum_{i,j}^m n_i\ n_j\ J_{ij} \qquad [165]$$

and the **exchange-correlation term**

$$E_x = (1/2) \int \rho(1)\ \hat{V}_x(1)\ dX_1 = (1/2) \sum_{i,j}^m n_i\ n_j\ K_{ij} \qquad [166]$$

The density functions obey the relationship

$$\rho_2(1,2;1,2) = (1/2)[\rho(1;1)\ \rho(2;2) - \rho(1;2)\ \rho(2;1)] \qquad [167]$$

where the one-particle Fock-Dirac density matrix is expanded through the **natural orbitals**

$$\rho(1) = \sum_i n_i \; \psi_i(1) \; \psi_i^*(1) \qquad [168]$$

so that ψ_i are eigenfunctions and $n_i \in <0, 1>$ the eigenvalues of ρ.

The Coulomb potential has the form

$$\hat{V}_c = \int \rho(2) \; \hat{g}_{12} \; dX_2 = \sum_j^m n_j <\psi_j(2)|\hat{g}_{12}|\psi_j(2)> = \sum_j^m n_j \; \hat{J}_j(1) \qquad [169]$$

and the potential of the exchange-correlation hole is

$$\hat{V}_x = \int \rho_x(1;2) \; \hat{g}_{12} \; dX_2 =$$

$$= - [\sum_j n_j <\psi_i(1)\psi_j(2)|\hat{g}_{12}|\psi_j(1)\psi_i(2)>]/[\psi_i^*(1)\psi_i(1)] \qquad [170]$$

For the exchange-correlation hole it holds true

$$\rho_x(1;2) = [2\rho_2(1,2;1,2)/\rho(1)] - \rho(2) \qquad [171]$$

Within this symbolism the Hartree-Fock equations may be rewritten into the form

$$\{\hat{h}(1) + \hat{V}_c(1) + \hat{V}_x(1)\}\psi_i(1) = \epsilon_i \psi_i(1) \qquad [172]$$

Recall that in the Hartree-Fock method, the potential acting on the electron is non-local (formed of a sum of local one-electron potentials differing for each electron). In an appropriate approximation the non-local potential of an atom may be substituted for a local one. Such an approximation is used within the framework of the $X\alpha$ method.

According to Slater (83) the exchange-correlation term $\hat{V}_x(1)$ is substituted for a weighted mean value

$$\hat{V}_{xi}(1) \Rightarrow [\hat{V}_{xi}(1)]_{av} = - [\sum_{i<j} n_i \; n_j \; <\psi_i(1)\psi_j(2)|\hat{g}_{12}|\psi_j(1)\psi_i(2)>]/$$

$$/ \; [\sum_k n_k \; \psi_k^*(1)\psi_k(1) \;] \qquad [173]$$

(indices i, j and k have the same spin). For such a statistical approximation the exact analytical solution is known for a free-electron gas

$$[\hat{V}_{xi}(1)]_{av} = - \sigma_{SI} \; [(81/8\pi) \; \rho(1)]^{1/2} \qquad [174]$$

The basic approximation of the $X\alpha$ method is represented by the following assumption for the exchange-correlation potential

$$\hat{V}_{xi}(1) \Rightarrow \hat{V}_{X\alpha}(1) = \alpha \; [\hat{V}_{xi}(1)]_{av} = - \sigma_{SI} \; \alpha \; [(81/8\pi) \; \rho(1)]^{1/3} \qquad [175]$$

The numerical factor $2/3 < \alpha < 1$ is regarded as an adjustable parameter which depends upon the atomic number Z of the atom. (In the original derivation Slater assumed $\alpha = 1$ whereas in an alternative approach (85,86) $\alpha = 2/3$.) Several methods to determine the parameter α have been so far proposed (84). The values obtained by minimizing the difference in the atomic energy between the Xα method and Hartree-Fock method have found broad application. For open- shell systems the energy is averaged over the individual multiplets of the given electron configuration (87); this approach is known as the hyper-Hartree-Fock method (HHF). Values of α are tabulated in literature (88,89).

In the Xα method, the electronic energy is

$$E(X\alpha) = \sum_{i}^{m} n_i\langle i|\hat{h}|i\rangle + (1/2)\int \rho(1)\ \hat{V}_c(1)\ dX_1 + $$

$$+ (1/2) \int \rho(1)\ \hat{U}_{X\alpha}(1)\ dX_1 \qquad [176]$$

where

$$\hat{U}_{X\alpha} = (3/2)\ \hat{V}_{X\alpha} \qquad [177]$$

For the spin-polarized version another expression is used

$$E_x = (1/2) \sum_{s}^{\alpha,\beta} \int \rho_s(1)\ \hat{U}^{(s)}_{X\alpha}(1)\ dX_1 \qquad [178]$$

where

$$\hat{U}^{(s)}_{X\alpha} = (3/2)\ \hat{V}^{(s)}_{X\alpha} = - \sigma_{SI}\ (3/2)\ \alpha\ [(81/4\pi)\ \rho_s(1)]^{1/3} \qquad [179]$$

and ρ_s is a charge density for the spin $s = \alpha$ or β. The spin-polarized (p) and spin-unpolarized (u) versions do not differ substantially except for the case of the hydrogen atom for which $\rho^p_\alpha = \rho$ and $\rho^p_\beta = 0$, whereas $\rho^u_\alpha = \rho^u_\beta = \rho/2$ and $\alpha^p = 2^{-1/3}\alpha^u$.

The eigenvalues of the characteristic equation fulfil an important relationship

$$[\partial E(X\alpha)/\partial n_i] = \langle i|\hat{h}|i\rangle + \langle i|\hat{V}_c|i\rangle + (2/3)\langle i|\hat{U}_{X_a}|i\rangle = \epsilon_i \qquad [180]$$

for $0 \le n_i \le 1$. This indicates that ϵ_i values differ substantially from the orbital energies within the Hartree-Fock method. For example, the ionization energy within the Xα method is given by the formula

$$I_k(X\alpha) = - \langle k|\hat{h}|k\rangle - \langle k|\hat{V}_c|k\rangle - \langle k|\hat{U}_{X_a}|k\rangle =$$

$$= - \epsilon_k - (1/2)\langle k|\hat{V}_{X\alpha}|k\rangle \qquad [181]$$

whereas the Koopmans theorem within the Hartree-Fock method predicts $I_k = - \epsilon_k$. An unusual feature of the Xα method is the possibility to obtain the lowest (stationary) value of the energy for fractional occupation numbers of spinorbitals. Such a situation is characteristic of the Fermi statistics when the Fermi distribution law is valid

$$n_i = 1/[exp(\epsilon_i - \epsilon_F)/kT + 1]$$

For the ground state (T = 0) we obtain

$$n_i = \begin{cases} 1 & \text{for } \epsilon_i < \epsilon_F \\ 0 & \text{for } \epsilon_i > \epsilon_F \\ \in (0;\ 1) & \text{for } \epsilon_i = \epsilon_F \end{cases}$$

where ϵ_F is a constant (Fermi level). The fractional occupation of the energy levels contributes to the entropy at T = 0 which manifests itself, for example, in the magnetic properties. For the first transition metal row elements (Ti - Ni) the highest occupied orbitals (3d and 4s) have approximately the same energy. The $X\alpha$ method often yields the lowest atomic energy for a fractional occupation of these orbitals (83,84).

Applications of the $X\alpha$ method for atoms are derived from the iterative solution of the radial Schrödinger equation for the spherical potential

$$\{-(\hbar^2/2m_e)d^2/dr^2 + l(l + 1)\hbar^2/2r^2 + \hat{V}(r) - E_{nl}\}\ P_{nl}(r) = 0 \qquad [182]$$

The charge density is given by the formula

$$\rho(r) = (1/4\pi r^2) \sum_{n,l} w_{nl}\ [P_{nl}(r)]^2 \qquad [183]$$

where w_{nl} is the degeneracy of the subshell characterized by the quantum numbers n and l. The spherical potential may be expressed as follows

$$\hat{V}(r) = \sigma_{SI}\ \{ -Z/r + (1/r)\int_0^r 4\pi r'^2\ \rho(r')\ dr' + \int_r^\infty 4\pi r'\ \rho(r')\ dr' - \alpha\ [(81/8\pi)\ \rho(r)]^{1/3}\} \qquad [184]$$

Another approach is based on the expansion of the charge density via atomic orbitals χ_{nlm} (90)

$$\rho(1) = \sum_{n,l} N_{nl}\ \rho_{nl}(1) = \sum_{n,l} N_{nl} \sum_{m=-l}^{+l} \chi_{nlm}^2(1)/(2l + 1) \qquad [185]$$

where N_{nl} are the occupation numbers of the subshells. This approach leads to an iterative solution of the equation

$$\hat{H}_{X\alpha}^{eff} |\chi_{nlm}\rangle = \epsilon_{nl}\ |\chi_{nlm}\rangle \qquad [186]$$

where the one-electron effective Hamiltonian is

$$\hat{H}_{X\alpha}^{eff} = \hat{h}(1) + \hat{V}_c(1) + \hat{V}_{X\alpha}(1) \qquad [187]$$

For applications of the Xα method to molecules several variants have been outlined. Some are discussed below.

1. **Cellular methods** are based on the expansion of one-electron functions ψ_i into the numeric-analytical basis set

$$\psi_i^k = \sum_L C_L^{ik} R_l^k(r) Y_L(\vartheta,\varphi) \qquad [188]$$

where L = (l,m) is the set of angular quantum numbers, Y_L are analytical spherical harmonic functions, C_L^{ik} are expanding coefficients, $R_l^k(r)$ is a numerical solution of the radial Schrödinger equation [182] for the k-th cell. Within this group of methods some additional assumptions are presumed; they differ from each other in the way they split the whole integration space into individual cells, namely:

a) The **Scattered-Wave** (SW) or **Multiple-Scattering** (MS) version operates either with the muffin-tin (MT) approximation for spherical cells or with angular corrections to the non-muffin-tin (NMT) potential (91-93);

b) The **Linear Muffin-Tin Orbital** (LMTO) version utilizes basis set functions independent to the eigenvalue ϵ_i (94);

c) The **Variation-cellular** version applies a minimization of discontinuities at the sphere boundaries (95);

d) The **Overlapping Sphere** version considers the sphere radii and heights of the cylindric parts of the overlap as variational parameters (96).

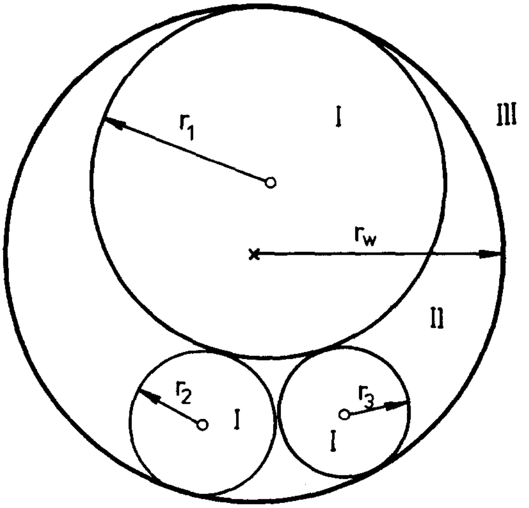

Fig. 7. Watson and atomic spheres in the Xα-SW-MT method.

In the widely used Xα-SW method the molecular space is split into three regions (Fig. 7):

a) atomic spheres of radii b_j centerd on atoms (I);

b) a region over the Watson sphere that separates a molecule from the remaining space (III);

c) a region between the atomic spheres and the Watson sphere (II). Such decomposition is also applied to the one-electron functions ψ_i. Within the muffin-tin approximation the spherical potential is postulated inside the atomic spheres whereas it is constant, $\bar{V}_{II}$, outside the spheres. In this approximation the one-electron functions have the form

$$\psi_j^I(r) = \sum_L C_L^j R_L^j(\epsilon;r) Y_L(r), \text{ for } 0 < r < b_j$$

$$\psi^{II}(r) = \sum_j \sum_L A_L^j k_l^{(1)}(\kappa r_j) Y_L(r_j) + \sum_L A_L^w i_l(\kappa r_w) Y_L(r_w), \text{ for } \epsilon < \bar{V}_{II}$$

$$\psi^{II}(r) = \sum_j \sum_L A_L^j n_l(\kappa r_j) Y_L(r_j) + \sum_L A_L^w j_l(\kappa r_w) Y_L(r_w), \text{ for } \epsilon > \bar{V}_{II}$$

$$\psi^{III}(r) = \sum_j \sum_L C_L^w R_l^w(\epsilon;r) Y_L(r), \text{ for } b_w < r < \infty \qquad [189]$$

where the index w represents the Watson sphere, $\kappa = |\epsilon - V_{II}|^{1/2}$, $k_l^{(1)}$ are the modified spherical Hankel functions of the first kind, n_l - the spherical Neumann functions, i_l - the modified spherical Bessel functions and j_l - spherical Bessel functions. The one-electron functions ψ_i must be continuous (with continuous first derivatives), which is secured by the boundary conditions at the contacts of the spheres. These conditions lead to a system of equations for determining the coefficients C_L^j and A_L^j which can be solved by an iterative procedure.

2. The **expansion methods** are based upon specification of the one-electron functions in the form

$$\psi_i = \sum_k \sum_{n,L} C_{nL}^{ik} \chi_{nL}^k \qquad [190]$$

which leads to Roothaan-like equations for determining C_{nL}^{ik} coefficients.

In the **Discrete-Variation Method** (DVM) the basis set functions $\{\chi\}$ are defined with a discrete set of points $\{r_k\}$, whereby a matrix of deviations is minimized (98,99)

$$\chi_{ij} = \sum_k w_k <\psi_i(r_k)|\hat{H}_{X\alpha}^{eff} - \epsilon|\psi_j(r_k)> \qquad [191]$$

Here w_k are the weighing factors of trial points r_k. The solution of the characteristic equation

$$det \{H_{ij} - \epsilon S_{ij}\} = 0 \qquad [192]$$

is represented by a spectrum of orbital energies ϵ, which is utilized in the interpretation of photoelectron spectra. The matrix elements

$$H_{ij} = \sum_k w_k <\psi_i(r_k)|\hat{H}^{eff}_{X\alpha}|\psi_j(r_k)> \qquad [193]$$

$$S_{ij} = \sum_k w_k <\psi_i(r_k)|\psi_j(r_k)> \qquad [194]$$

are evaluated in a numerical way by using cubature formulas. The calculation of a large number of six-fold integrals to high precision becomes a serious problem. It may be simplified by expanding the charge density into the basis set of auxiliary (usually analytical, spherically symmetric) functions

$$\rho(r) = \sum_\mu b_\mu B_\mu(r) \qquad [195]$$

Now the Coulomb potential $\hat{V}_c$ can be expressed analytically by using B_μ functions so that, in the subsequent step, one can effectively determine the matrix elements H_{ij} by a numerical integration. The number of points necessary for such a procedure ranges between 10^3 to 10^5, or more.

The **LCAO version** of the Xα method (90,100) utilizes Slater or Gauss-type orbitals as basis set functions $\{\chi\}$. The form of the exchange potential $\hat{V}_{X\alpha} \approx \rho^{1/3}$, however, does not allow the calculation of its matrix elements in an analytical way. This problem is avoided by introducing a set of auxiliary analytical functions $\{A_\mu\}$ and $\{B_\mu\}$ which are used to mimic the charge density and the exchange-correlation potential, e.g.

$$\rho(r) = \sum_\nu a_\nu A_\nu(r) - \alpha [(81/8\pi) \rho(r)]^{1/3} \approx \sum_\mu b_\mu B_\mu(r) \qquad [196]$$

The coefficients a_ν and b_μ are obtained by the least-squares method for a small number of trial points in each cycle of the SCF procedure. Then the matrix elements of the one-electron effective Hamiltonian

$$H_{ij} = <\chi_i|\hat{H}^{eff}_{X\alpha}|\chi_j> \qquad [197]$$

are expressed analytically through the integrals of χ_i, A_ν and B_μ functions. The results obtained in this way are sensitive to the type and extent of the atomic orbital basis set.

In the Xα method the theory of the **transition state** (TS) plays an important role (83,84). According to this concept the ionization energy of a closed shell is equal to

$$I_k = \{E(n_k - 1) - E(n_k)\}_{n_k=2} =$$

$$= - [\partial E(X\alpha)/\partial n_k]_{n_k^t=3/2} + O_3 \approx - \{\epsilon_k\}_{n_k^t=3/2} \qquad [198]$$

and the ionization energy of an open level is

$$I_k = \{E(n_k - 1) - E(n_k)\}_{n_k=1} =$$

$$= - [\partial E(X\alpha)/\partial n_k]_{n_k^t=1/2} + O_3 \approx - \{\epsilon_k\}_{n_k^t=1/2} \qquad [199]$$

The corrections O_3 are of the third order when considering a Taylor expansion of the energy. This case corresponds to a generalization of the Koopmans theorem for the Xα method: the ionization energy is given by a value of $-\epsilon_k$ in the hypothetical TS state of fractional occupation number $n_k^t = n_k - 1/2$. Analogously the excitation energy may be expressed as

$$\Delta E_{i\to a} = \{E(n_i - 1,\ n_a + 1) - E(n_i,n_a)\} = \{\epsilon_a - \epsilon_i\}_t + O_3 \qquad [200]$$

for occupation numbers in the TS equal to $n_i^t = n_i - 1/2$ and $n_a^t = n_a + 1/2$. This approximation has found application in practical calculations since the errors in the calculation of $\{\epsilon_a - \epsilon_i\}_t$ are much lower than those in the calculation of total molecular energies.

The main advantage of the Xα method is the simplicity of its algorithm and, usually, the lower cost in computer time compared to *ab initio* methods. This non-empirical method often yields results comparable with the double-zeta basis set of an *ab initio* approach. Therefore it is exclusively used for compounds of the heavy elements like OsO_4, UF_6^-, $Re_2Cl_8^{2-}$, $Pt(CN)_4^{2-}$, etc. The Xα method has also been corrected for relativistic effects.

An important feature of the Xα method is the fact that both the occupied and unoccupied orbitals of the n-electron system feel the potential of the remaining (n-1) electrons. This is the main difference with respect to the Hartree-Fock method in which the virtual orbitals are not properly determined properly. This is the reason for the successful description of excitation and ionization energies using the concept of the transition state. The advantages of the Xα method also include the rigorous validity of the virial theorem as well as the Hellmann-Feynman theorem regardless of the value of the α parameter.

A drawback of the Xα method is the fact that the energy functional does not correspond to the wave function used. For this reason applications of Xα method are usually limited to energy properties only. Also the α parameter is not chosen unambigously. Some approximate versions of the $X\alpha$ method contain additional inadequate assumptions. For example, the geometry of the water molecule is predicted to be linear when using the $X\alpha$-SW-MT method but this, evidently, is an artifact of the muffin-tin approximation.

3.3.4 NEMO and Fenske-Hall Method

Nonempirical methods of molecular orbitals (NEMO) are based on the Roothaan equations for MO-LCAO-SCF calculations. Instead of the rigorous *ab initio* approach these method utilize some simplifications and approximations for matrix elements of the Fock operator; the reason for this is to reduce the type and number of two-electron integrals.

The **Ruedenberg approximation** starts from the expansion of an arbitrary i-th atomic orital centered at the atom A into a complete orthogonal basis set centered at another atom of the molecule

$$\vartheta_i^A = \sum_{p}^{\infty B} a_{ip}\, \vartheta_p^B \qquad [201]$$

The orthonormality condition fulfilled at each centre implies that

$$a_{ip} = <\vartheta_i^A|\vartheta_p^B> = S_{i,p}^{A,B} \qquad [202]$$

Then the matrix element of the one-electron operator $\hat{M}$ is given exactly in the complete basis set as

$$<\vartheta_i^A|\hat{M}|\vartheta_j^B> = \sum_{p}^{\infty A} S_{p,j}^{A,B} <\vartheta_i^A|\hat{M}|\vartheta_p^A> = \sum_{q}^{\infty B} S_{i,q}^{A,B} <\vartheta_j^B|\hat{M}|\vartheta_q^B> \qquad [203]$$

According to Ruedenberg (101) the following approximation is possible in the minimum basis set

$$<\vartheta_i^A|\hat{M}|\vartheta_j^B> = (1/2)[\sum_{p}^{A} S_{p,j}^{A,B} <\vartheta_i^A|\hat{M}|\vartheta_p^A> + \sum_{q}^{B} S_{i,q}^{A,B} <\vartheta_j^B|\hat{M}|\vartheta_q^B>] \qquad [204]$$

Within this approximation the two-electron integral is expressed as

$$(i_A j_B|k_C l_D) = (1/4)[\sum_{p}^{A} \sum_{s}^{D} S_{p,j}^{A,B} S_{s,k}^{D,C} (i_A p_A|s_D l_D) +$$

$$+ \sum_{p}^{A} \sum_{r}^{C} S_{p,j}^{A,B} S_{r,l}^{C,D} (i_A p_A|k_C r_C) + \sum_{q}^{B} \sum_{r}^{C} S_{q,i}^{B,A} S_{r,l}^{C,D} (q_B j_B|k_C r_C) +$$

$$+ \sum_{q}^{B} \sum_{s}^{D} S_{q,i}^{B,A} S_{s,k}^{D,C} (q_B j_B|s_D l_D)] \qquad [205]$$

Using the Ruedenberg approximation the four-centre and three-centre integrals may be expressed through the two-centre and one-centre ones. As pointed out by Ruttink (102) such an approximation yields a result which is invariant with respect to rotation of the axes of the local coordinate system. This approximation, moreover, does not depend on the hybridization of the atomic orbitals (i.e. on a unitary transformation at the given centre).

The **Mulliken approximation** may be considered as a special case of the Ruedenberg approximation

$$<\vartheta_i^A|\hat{M}|\vartheta_j^B> = (1/2)[\sum_p^A S_{p,j}^{A,B} <\vartheta_i^A|\hat{M}|\vartheta_p^A>\delta_{ip} + \sum_q^B S_{i,q}^{A,B} <\vartheta_j^B|\hat{M}|\vartheta_q^B>\delta_{jq}]$$

$$= (1/2)S_{i,j}^{A,B}[<\vartheta_i^A|\hat{M}|\vartheta_i^A> + <\vartheta_j^B|\hat{M}|\vartheta_j^B>] \qquad [206]$$

Within this approximation the two-electron integral becomes expressed as

$$(i_A j_B|k_C l_D) = (1/4)\ S_{i,j}^{A,B}\ S_{k,l}^{C,D}\ [(i_A i_A|k_C k_C) + (i_A i_A|l_D l_D) +$$

$$+ (j_B j_B|k_C k_C) + (j_B j_B|l_D l_D)] \qquad [207]$$

In the Mulliken approximation only the two-centre and one-centre integrals occur; they are of the Coulomb type $(i_A i_A|k_B k_B)$ only. Their number is equal to m^2 in the basis set of m orbitals. The Mulliken approximation yields the result which is invariant with respect to rotation of the axes of the local coordinate system but dependent on the hybridization.

The **Fenske-Hall method** assumes the one-electron Fock operator in the form (104-196)

$$\hat{F} = \hat{T}(1) + \sum_C^N \hat{W}_C(1) \qquad [208]$$

which means that the electron density is associated with a certain centre, $\hat{T}(1)$ is the kinetic energy term. Within this approximation the diagonal matrix elements of the Fock operator become

$$F_{i_A i_A} = <i|\hat{T} + \hat{W}_A|i> + \sum_{C\neq A}^N <i|\hat{W}_C|i> = \varepsilon_i^A + \sum_{C\neq A}^N <i|\hat{W}_C|i> \qquad [209]$$

where the orbital energy of the i-th atomic orbital for the mean electron configuration of atom A is

$$\varepsilon_i^A = <i|\hat{h}|i> + \sum_k^{m_A} n_k^A(J_{ik} - K_{ik}) =$$

$$= <i|\hat{T}|i> + \sigma_{SI}<i|Z_A/r_{A1}|i> + \sum_{k\neq i}^{m_A} n_k^A\ G_{ik} + (n_i^A - 1)G_{ii} \qquad [210]$$

Expressions for averaged energies of the electron interaction G_{ij} have been published by Slater (107); they can be easily calculated by an analytical integration of STOs. The term $<i_A|\hat{W}_C|i_A>$ describes the influence of the remaining centres (nuclei and electrons) and is approximated by point charges as

$$<i_A|\hat{W}_C|i_A> = -\sigma_{SI}(q_C^0/R_{AC}) \qquad [211]$$

where the effective atomic charge (in units of e) is given by the formula

$$q_C^0 = Z_C - \sum_i^C n_i^C \qquad [212]$$

In molecules, the Mulliken orbital populations are the n_i^C values; they are calculated by population analysis of the occupied molecular orbitals. After these substitutions, the diagonal matrix elements of the Fock operator adopt the simple form

$$F_{i_A i_A} = \epsilon_i^A - \sigma_{SI}\sum_{C\neq A}^{N}(q_C^0/R_{AC}) \qquad [213]$$

For the off-diagonal matrix elements one can write

$$F_{i_A j_B} = <i_A|\hat{T} + \hat{W}_A|j_B> + <i_A|\hat{T} + \hat{W}_B|j_B> - <i_A|\hat{T}|j_B> +$$

$$+ \sum_{C\neq A,B}^{N} <i_A|\hat{W}_C|j_B> \qquad [214]$$

Using the Mulliken approximation the three-centre integrals $<i_A|\hat{W}_C|j_B>$ are decomposed and by introducing the point-charge approximation we obtain

$$F_{i_A j_B} = S_{i_A j_B}(\epsilon_i^A + \epsilon_j^B) - T_{i_A j_B} -$$

$$- (1/2)\, S_{i_A j_B} \sum_{C\neq A,B}^{N} \sigma_{SI}\, q_C^0(1/R_{AC} + 1/R_{BC}) \qquad [215]$$

where the overlap and kinetic integrals are calculated by the analytical integration of STOs. Finally, as a consequence of the orthogonality of atomic orbitals at the given atom, we obtain

$$F_{i_A j_A} = <i_A|\hat{T} + \hat{W}_A|j_A> + \sum_{C\neq A}^{N} <i_A|\hat{W}_C|j_A> =$$

$$= (\epsilon_i^A - \sigma_{SI}\sum_{C\neq A}^{N} q_C^0/R_{AC})\delta_{ij} = 0 \qquad [216]$$

This molecular orbital method is performed by an iterative solution.of the Roothaan equations

$$FC^T = SC^TE \qquad [217]$$

because the matrix elements of the Fock operator depend on the result of the population analysis of the molecular orbitals through the q_C^0 values. The analytical function basis set is usually represented by single-zeta STOs for inner core electrons and double-zeta STOs for valence electrons. This method belongs to the most simple and relatively little time-consuming versions of MO-LCAO-SCF calculations.

3.4 METHODS OF ZERO DIFFERENTIAL OVERLAP

This numerous group of quantum-chemical calculation methods is based on the Roothaan equations for molecular-orbital calculations in the LCAO approximation. Instead of *ab initio* calculations, heavy approximations and simplifications are used as follows (108-112).

1. The methods only operate in the valence basis set of atomic orbitals so that the nuclear charges $q_A = eZ_A$ are substituted for core charges eZ_A^c. The number Z_A^c means the number of valence electrons in the free atom.

2. Atomic orbitals are of the Slater type (STO) and are usually of the single-zeta quality.

3. A complete or partial zero differential overlap approximation is used

$$\vartheta_i(1)\ \vartheta_j(1)\ dV_1 = [\vartheta_i(1)]^2\ \delta_{ij}\ dV_1 \qquad [218]$$

4. Some components of the matrix elements of the Fock operator are not evaluated from the basis set functions but are taken as parameters determined in a semiempirical fashion.

5. Additional approximations are introduced for certain types of integrals.

3.4.1 ZDO Approximation

The differential overlap of a couple of atomic orbitals ϑ_i and ϑ_j has the meaning of the probability of finding the k-th electron in the volume element dV common for these orbitals; it is

$$D_{ij}(k)\ dV_k = \vartheta_i(k)\ \vartheta_j(k)\ dV_k \qquad [219]$$

In the Zero Differential Overlap (ZDO) approximation it is assumed that D_{ij} vanishes for $i \neq j$. Consequently the integrals containing D_{ij} are neglected for $i \neq j$. Within this approximation the molecular integrals are reduced to only the following types:

a) overlap integrals

$$S_{i_A j_B} = \langle\vartheta_i^A|\vartheta_j^B\rangle = \int D_{ij}(1)\ dV_1 = \delta_{ij} \qquad [220]$$

b) kinetic integrals

$$T_{i_A j_B} = -(\hbar^2/2m_e)\ \langle\vartheta_i^A|\nabla_1^2|\vartheta_j^B\rangle \qquad [221]$$

whereby the operator ∇_1^2 transforms the function $\vartheta_j(1)$ before the integration thus yielding an overlap integral;

c) electron-nuclear attraction integrals

$$V^C_{i_A j_B} = \sigma_{SI}\, Z^c_C \langle \vartheta^A_i | r^{-1}_{1C} | \vartheta_B \rangle = \sigma_{SI}\, Z^c_C \int r^{-1}_{1C}\, D_{ij}(1)\, dV_1 =$$

$$= V^C_{i_A i_A}\, \delta_{ij} \qquad [222]$$

which are either one-centre (C = A) or two-centre (C ≠ A);

d) electron repulsion integrals

$$(i_A j_B | k_C l_D) = \sigma_{SI} \iint r^{-1}_{12}\, D_{ij}(1)\, D_{kl}(2)\, dV_1\, dV_2 =$$

$$= (i_A i_A | k_C k_C)\, \delta_{ij}\, \delta_{kl} = J^{AC}_{ik}\, \delta_{ij}\, \delta_{kl} \qquad [223]$$

which are either one-centre or two-centre; their number is only m^2 which represents a significant reduction with respect to the original number of m^4.

As a consequence of the ZDO approximation the Roothaan equations adopt the form

$$F^{\eta} C^{\eta T} = C^{\eta T} E^{\eta} \qquad [224]$$

where $\eta = \alpha$ or β for the open-shell system in the UHF approach. For the closed-shell system it is sufficient only to consider $\eta = \alpha$. The above expression means that the matrix of LCAO coefficients C directly makes the Fock operator matrix diagonal. The normalization condition for the matrix of LCAO coefficients is simplified to

$$CC^T = I \qquad [225]$$

For the matrix elements of the one-electron core operator it holds true:

a) diagonal terms are

$$h^c_{i_A i_A} = U^A_i - \sum_{C \neq A}^{N} V^C_{i_A i_A} \qquad [226]$$

where the one-centre part of the kinetic and potential energy is

$$U^A_i = T_{i_A i_A} - V^A_{i_A i_A} \qquad [227]$$

b) off-diagonal one-centre terms are equal to zero

$$h^c_{i_A j_A} = 0 \qquad [228]$$

c) off-diagonal two-centre terms (resonance integrals) are approximated through the overlap integral matrix (which in this case only is not taken in the ZDO approximation)

$$h^{c}_{i_A j_B} = T_{i_A j_B} \approx \beta^{t}_{AB} S_{i_A j_B} \qquad [229]$$

The adjustable parameters β^{t}_{AB} are regarded as functions of the atomic pair (A, B) and of the type of interaction t (σ or π). Sometimes a functional dependence on the interatomic distance R_{AB} is considered for them.

The matrix elements of the Fock operator are

$$F^{\eta}_{i_A i_A} = h^{c}_{i_A i_A} + \sum_{i} (P^{\alpha}_{jj} + P^{\beta}_{jj})(i_A i_A|jj) - P^{\eta}_{i_A i_A}(i_A i_A|i_A i_A) \qquad [230]$$

$$F^{\eta}_{i_A j_A} = - P^{\eta}_{i_A j_A} (i_A i_A|j_A j_A) \qquad [231]$$

$$F^{\eta}_{i_A j_B} = h^{c}_{i_A j_B} - P^{\eta}_{i_A j_B} (i_A i_A|j_B j_B) \qquad [232]$$

They represent a substantial simplification relative to the *ab initio* approach. The ZDO equations derived above, however, are not used in practical calculations. Usually an additional requirement is applied, namely the invariance of the total molecular energy by coordinate transformation (rotation); this leads to certain restrictions for integrals $V^{C}_{i_A i_A}$ and $(i_A i_A|j_B j_B)$ which must be averaged over the azimuthal quantum number (l) of the atomic orbital.

According to subsequent assumptions three basic classes of ZDO methods are distinguished:

1. methods of CNDO type (also PPP for π-electron systems);
2. methods of INDO type (also MINDO, EMZDO, MCZDO and SINDO);
3. methods of NDDO type (also MNDO, PNDO and LNDO).

These methods will be discussed in the forthcoming paragraphs. For open-shell systems they are applied only within the UHF approach.

3.4.2 Principles of Semiempirical Parametrization

The neglect of differential overlap represents a heavy simplification of the two-electron part of the Fock operator which should be carefully balanced by an appropriate modification of the one-electron operator $\hat{h}^{c}$. For this purpose a semiempirical parametrization is used.

Let us start from the atomic energy formula

$$E_A = \sum_{i}^{occ} U^{A}_{i} + \sum_{i<j}^{occ} (J_{ij} - K_{ij}) \qquad [233]$$

from which the ionization energy I^{A}_{i} or the electron affinity A^{A}_{i} may be expressed as functions of integrals U^{A}_{i}, J_{ij} and K_{ij}. The experimental values of these quantities are known from atomic spectroscopy where, if necessary, an extrapolation technique may also be used. This procedure enables one to evaluate 'spectral' values of integrals U_i^A and some one-centre repulsion integrals. The data obtained in this way depend strongly on the choice of the reference electron configuration and thus different values of these quantities can be found in the literature. It must be mentioned that the spectral values differ substantially from the theoretical data obtained by direct integration over the basis set functions. From time to time a scaling approach is applied: the theoretical integrals are multiplied by an empirically obtained reduction factor. The spectral values, moreover, include a part of the correlation energy.

The use of spectral parameters for certain integrals to evaluate matrix elements of the Fock operator will be successful only if the true electron configuration of an atom in the molecule does not substantially differ from the reference electron configuration of the free atom. This condition is fulfilled well in hydrocarbons where the valence state of the carbon atom is retained in a large series of similar compounds. On the contrary, coordination compounds of transition metals exhibit great variability of the relevant electron configurations. For this reason a universal parametrization for such elements is not available.

The one-centre electron repulsion integrals (ac|bd) may be expressed (Laplace-Neumann expansion) through radial integrals R^k_{acbd} and angular coefficients obtained by a combination of Clebsch-Gordan coefficients (see Section 2.2)

$$(ac|bd) = \sum_k^{\infty} R^k_{acbd}\ c^k(l_a m_a, l_c m_c)\ c^k(l_b m_b, l_d m_d) \qquad [234]$$

The radial integrals of the Coulomb and exchange type

$$R^k_{abab} = F^k_{ab}$$

$$R^k_{abba} = G^k_{ab} \qquad [235]$$

are called the Slater-Condon parameters (SCP); they are available from the analysis of atomic spectra (113).

The mean energy value of the electron configuration $s^x p^y d^z f^w$ may be written in the form (107)

$$E(s^x p^y d^z f^w) = xU_s + yU_p + zU_d + wU_f + (1/2)x(x - 1)G_{ss} +$$
$$+ (1/2)y(y - 1)G_{pp} + (1/2)z(z - 1)G_{dd} + (1/2)w(w - 1)G_{ff} + xyG_{sp} +$$
$$+ xzG_{sd} + xwG_{sf} + yzG_{pd} + ywG_{pf} + zwG_{df} \qquad [236]$$

The electronic interaction terms are averaged for individual values of the azimuthal quantum number l and they consists of Coulomb and exchange integrals (114)

$$J_{ss} = F^0_{ss}$$

$$J_{pp} = F^0_{pp} - (4/125)F^2_{pp}$$

$$K_{pp} = (3/25)F^2_{pp}$$

$$J_{dd} = F^0_{dd} - (4/441)F^2_{dd} - (4/441)F^4_{dd}$$

$$K_{dd} = (5/98)F^2_{dd} + (5/98)F^4_{dd}$$

$$J_{sp} = F^0_{sp}$$

$$K_{sp} = (1/3)G^1_{sp}$$

$$J_{sd} = F^0_{sd}$$

$$K_{sd} = (1/5)G^2_{sd}$$

$$J_{pd} = F^0_{pd}$$

$$K_{pd} = (2/15)G^1_{pd} + (3/35)G^3_{pd}$$

$$\mathcal{G}_{ss} = J_{ss} = F^0_{ss}$$

$$\mathcal{G}_{pp} = J_{pp} - (2/5)K_{pp} = F^0_{pp} - (2/25)F^2_{pp}$$

$$\mathcal{G}_{dd} = J_{dd} - (4/9)K_{dd} = F^0_{dd} - (2/63)F^2_{dd} - (2/63)F^4_{dd}$$

$$\mathcal{G}_{ff} = F^0_{ff} - (4/195)F^2_{ff} - (2/143)F^4_{ff} - (100/5577)F^6_{ff}$$

$$\mathcal{G}_{sp} = J_{sp} - (1/2)K_{sp} = F^0_{sp} - (1/6)G^1_{sp}$$

$$\mathcal{G}_{sd} = J_{sd} - (1/2)K_{sd} = F^0_{sd} - (1/10)G^2_{sd}$$

$$\mathcal{G}_{sf} = F^0_{sf} - (1/14)G^3_{sf}$$

$$\mathcal{G}_{pd} = J_{pd} - (1/2)K_{pd} = F^0_{pd} - (1/15)G^1_{pd} - (3/70)G^3_{pd}$$

$$\mathcal{G}_{pf} = F^0_{pf} - (3/70)G^2_{pf} - (2/63)G^4_{pf}$$

$$\mathcal{G}_{df} = F^0_{df} - (3/70)G^1_{df} - (2/105)G^3_{df} - (5/231)G^5_{df} \qquad [237]$$

Using the formula [236] the ionization energies may be written as

$$-I^A_s = E(s^x p^y d^z f^w) - E(s^{x-1} p^y d^z f^w) =$$

$$= U^A_s + (x - 1)\mathcal{G}_{ss} + y\mathcal{G}_{sp} + z\mathcal{G}_{sd} + w\mathcal{G}_{sf}$$

$$\begin{aligned}
-I_p^A &= E(s^x p^y d^z f^w) - E(s^x p^{y-1} d^z f^w) = \\
&= U_p^A + xG_{sp} + (y - 1)G_{pp} + zG_{pd} + wG_{pf} \\
-I_d^A &= E(s^x p^y d^z f^w) - E(s^x p^y d^{z-1} f^w) = \\
&= U_d^A + xG_{sd} + yG_{pd} + (z - 1)G_{dd} + wG_{df} \\
-I_f^A &= E(s^x p^y d^z f^w) - E(s^x p^y d^z f^{w-1}) = \\
&= U_f^A + xG_{sf} + yG_{pf} + zG_{df} + (w - 1)G_{ff}
\end{aligned} \tag*{[238]}$$

and analogously the electron affinities are

$$\begin{aligned}
-A_s^A &= E(s^{x+1} p^y d^z f^w) - E(s^x p^y d^z f^w) = U_s^A + xG_{ss} + yG_{sp} + zG_{sd} + wG_{sf} \\
-A_p^A &= E(s^x p^{y+1} d^z f^w) - E(s^x p^y d^z f^w) = U_p^A + xG_{sp} + yG_{pp} + zG_{pd} + wG_{pf} \\
-A_d^A &= E(s^x p^y d^{z+1} f^w) - E(s^x p^y d^z f^w) = U_d^A + xG_{sd} + yG_{pd} + zG_{dd} + wG_{df} \\
-A_f^A &= E(s^x p^y d^z f^{w+1}) - E(s^x p^y d^z f^w) = U_f^A + xG_{sf} + yG_{pf} + zG_{df} + wG_{ff}
\end{aligned} \tag*{[239]}$$

Further the Mulliken orbital electronegativities, defined as $X_i^A = (I_i^A + A_i^A)/2$, may be expressed

$$\begin{aligned}
-X_s^A &= U_s^A + [(x_i + x_a - 1)G_{ss} + (y_i + y_a)G_{sp} + \\
&\quad + (z_i + z_a)G_{sd} + (w_i + w_a)G_{sf}]/2 \\
-X_p^A &= U_p^A + [(x_i + x_a)G_{sp} + (y_i + y_a - 1)G_{pp} + \\
&\quad + (z_i + z_a)G_{pd} + (w_i + w_a)G_{pf}]/2 \\
-X_d^A &= U_d^A + [(x_i + x_a)G_{sd} + (y_i + y_a)G_{pd} + \\
&\quad + (z_i + z_a - 1)G_{dd} + (w_i + w_a)G_{df}]/2 \\
-X_f^A &= U_f^A + [(x_i + x_a)G_{sf} + (y_i + y_a)G_{pf} + \\
&\quad + (z_i + z_a)G_{df} + (w_i + w_a - 1)G_{ff}]/2
\end{aligned} \tag*{[240]}$$

where x_i (x_a) are the occupation numbers in the reference electron configuration for the ionization (affinity) process. Finally the quantities $Y_i^A = I_i^A - A_i^A$ may be expressed as

$$\begin{aligned}
Y_s^A &= G_{ss} \\
Y_p^A &= G_{pp} \\
Y_d^A &= G_{dd} \\
Y_f^A &= G_{ff}
\end{aligned} \tag*{[241]}$$

TABLE 7
Reference electron configurations $d^zs^xp^y$.

Process	z	x	y
Process for p-elements			
$I_s(s^xp^y \Rightarrow s^{x-1}p^y)$		2	$Z^c - 2$
$I_p(s^xp^y \Rightarrow s^xp^{y-1})$		2	$Z^c - 2$
$A_s(s^xp^y \Rightarrow s^{x+1}p^y)$		1	$Z^c - 1$
$A_p(s^xp^y \Rightarrow s^xp^{y+1})$		2	$Z^c - 2$
First process for d-elements			
$I_s(d^{z-1}s^1p^0 \Rightarrow d^{z-1}s^0p^0)$	$Z^c - 1$	1	0
$I_p(d^{z-1}s^0p^1 \Rightarrow d^{z-1}s^0p^0)$	$Z^c - 1$	0	1
$I_d(d^{z-1}s^1p^0 \Rightarrow d^{z-2}s^1p^0)$	$Z^c - 1$	1	0
$A_s(d^zs^0p^0 \Rightarrow d^zs^1p^0)$	Z^c	0	0
$A_p(d^zs^0p^0 \Rightarrow d^zs^0p^1)$	Z^c	0	0
$A_d(d^{z-1}s^1p^0 \Rightarrow d^zs^1p^0)$	$Z^c - 1$	1	0
Second process for d-elements			
$I_s(d^{z-2}s^2p^0 \Rightarrow d^{z-2}s^1p^0)$	$Z^c - 2$	2	0
$I_p(d^{z-2}s^1p^1 \Rightarrow d^{z-2}s^1p^0)$	$Z^c - 2$	1	1
$I_d(d^{z-2}s^2p^0 \Rightarrow d^{z-3}s^2p^0)$	$Z^c - 2$	2	0
$A_s(d^{z-1}s^1p^0 \Rightarrow d^{z-1}s^2p^0)$	$Z^c - 1$	1	0
$A_p(d^{z-1}s^1p^0 \Rightarrow d^{z-1}s^1p^1)$	$Z^c - 1$	1	0
$A_d(d^{z-1}s^1p^0 \Rightarrow d^zs^1p^0)$	$Z^c - 1$	1	0

Values of G_{is} are accessible from various electron exchange processes, viz.

$$G_{sp} = I_s^A(s^xp^yd^zf^w \rightarrow s^{x-1}p^yd^zf^w) - I_s^{A+}(s^xp^{y-1}d^zf^w \rightarrow s^{x-1}p^{y-1}d^zf^w) =$$

$$= I_p^A(s^xp^yd^zf^w \rightarrow s^xp^{y-1}d^zf^w) - I_p^{A+}(s^{x-1}p^yd^zf^w \rightarrow s^{x-1}p^{y-1}d^zf^w) \qquad [242]$$

In processing these formulae, the reference electron configuration must first be chosen. Relevant examples are shown in Table 7.

The relationships above represent the basis for the semiempirical parametrization of the CNDO type methods (which contain only the monopole F^0 contributions) and INDO type methods (with a complete set of non-zero multipole G^n and F^n contributions in the Laplace-Neumann expansion of the repulsion integrals).

Basis set of STO functions. Explicit knowlege of the analytical form of the atomic orbitals is necessary for the evaluation of overlap integrals and some repulsion integrals. The following basis sets are frequently used.

1. **Slater AOs** (14) have orbital exponents calculated with $\zeta_{nl} = (Z - \sigma_{nl})/n^*$ where the screening constants σ_{nl} are:

$\sigma_{1s} = 0.3(K - 1)$

$\sigma_{2s} = \sigma_{2p} = 0.85K + 0.35(L - 1)$

$\sigma_{3s} = \sigma_{3p} = K + 0.85L + 0.35(M_{sp} - 1)$

$\sigma_{3d} = K + L + M_{sp} + 0.35(M_d - 1)$

$\sigma_{4s} = \sigma_{4p} = K + L + 0.85M + 0.35(N_{sp} - 1)$

$\sigma_{4d} = \sigma_{4f} = K + L + M + 0.35(N_{df} - 1)$

$\sigma_{5s} = \sigma_{5p} = K + L + M + 0.85N + 0.35(O_{sp} - 1)$

$\sigma_{5d} = \sigma_{5f} = K + L + M + N + 0.35(O_{df} - 1)$

$\sigma_{6s} = \sigma_{6p} = K + L + M + N + 0.85O + 0.35(P_{sp} - 1)$

$\sigma_{6d} = \sigma_{6f} = K + L + M + N + O + 0.35(P_{df} - 1)$

Here, K, L, M_{sp}, ... is the number of electrons in the shell or subshell. The characteristic feature of these AOs is the attribution of the common orbital exponent to a group of orbitals (ns, np) and (nd, nf). The value of $\zeta_{1s}^{H} = 1.2$ is usually used for the hydrogen atom in molecules. The fractional effective quantum number n^* is given as

n	1	2	3	4	5	6
n^*	1.0	2.0	3.0	3.7	4.0	4.2

This definition, however, complicates the evaluation of integrals. In this case the radial part of the orbital may be approximated by a pair of primitive functions having the closest higher and lower integer quantum number. For example, for $n^* = 3.7$ it is

$$R_4(r) = Nr^{2.7}exp(-Z^*r/3.7a_0) \approx N'(0.3r^2 + 0.7r^3)exp(-Zr/3.7a_0) \qquad [243]$$

where the normalization factor is N' = 1.012 845 31.

2. **Burns AOs** (15) possess another definition for the screening constants and have an integer effective quantum number equal to the principal one. They reproduce better the results of the atomic SCF calculations.

3. **Clementi-Raimondi AOs** (115,116) were obtained by atomic SCF calculations. They, however, are unknown for virtual AOs.

4. **Zerner-Gouterman** exponents (114,117) for atoms Sc through Zn describe better transition metals in their valence state.

5. Extended basis sets of DZ or PZ type have been published by a group of authors (118-122). They describe better the radial dependence of transition metal atom d-orbitals (Fig. 8).

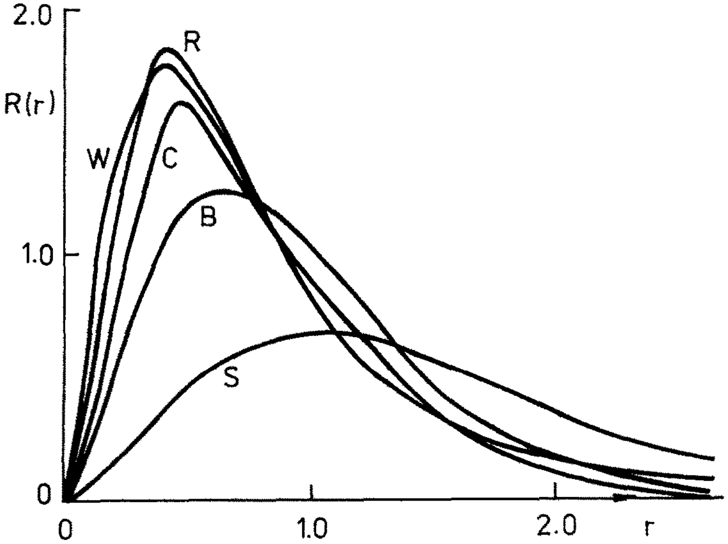

Fig. 8. 3d-orbital radial parts for the iron atom ($3d^6 4s^2$ configuration). R - Richardson AO, W - Watson AO, C - Clementi AO, B - Burns AO, S - Slater AO.

6. In semiempirical methods, STO function exponents may be regarded as adjustable parameters and may be obtained by calibration to selected molecular properties.

7. STO function exponents (e.g. Slater or Burns) may be scaled using a universal scaling factor λ_{nl} dependent on the principal and the azimuthal quantum numbers.

Expression of repulsion integrals. Only one-centre and two-centre repulsion integrals are considered in methods utilizing the ZDO approximation. These integrals shoud be mutually proportional as follows from the limiting conditions:

$$\text{a)} \lim_{R_{AB}\to 0} J_{i_A j_B} = \overline{(J_{i_A i_A}, J_{j_B j_B})} \qquad [244]$$

i.e. at short distances the bicentric integral should be transformed to the mean value of the one-centre integrals;

b) $\lim\limits_{R_{AB}\to\infty} J_{i_A j_B} = \sigma_{SI}/R_{AB}$ [245]

i.e. at long distances the value of the two-centre integral corresponds to the classical formula for coulombic repulsion of two point charges.

The use of theoretical values for the one-centre integrals is consistent with the theoretical integration of two-centre J_{ij}. The use of spectroscopic values for one-centre integrals requires certain approximations for the two-centre integrals J_{ij}. For this purpose several formulae have been proposed; the most frequently used approximations are according to:

a) Mataga and Nishimoto (123,124)

$$J_{ij} = \sigma_{SI}/(R_{AB} + a) \qquad [246]$$

where

$$a = 2\sigma_{SI}/(J_{ii} + J_{jj}) \qquad [247]$$

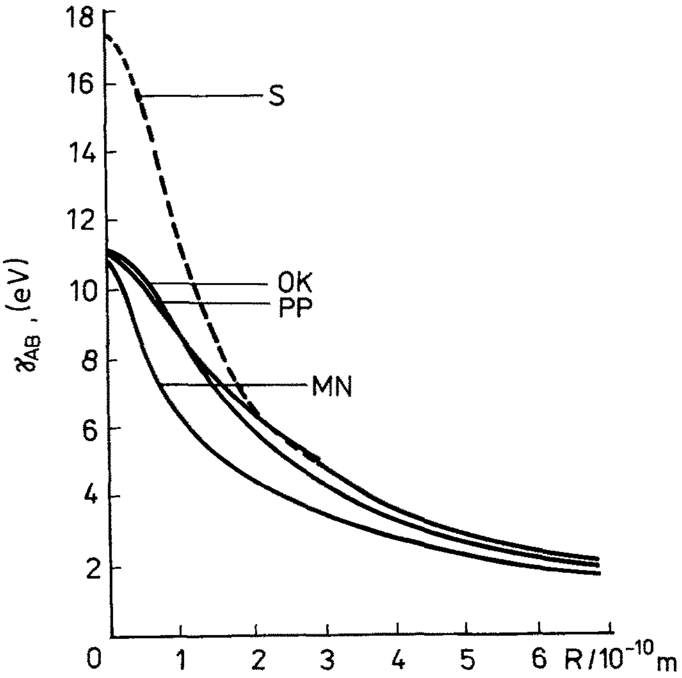

Fig. 9. Plot of repulsion integral $\gamma_{AB}(R)$ *vs* R for two carbon atoms. S - theoretical value using Slater AOs; OK - Ohno-Klopman approximation; PP - Pariser-Parr approximation; MN - Mataga-Nishimoto approximation.

b) Ohno (125)

$$J_{ij} = \sigma_{SI}/(R_{AB}^2 + a^2)^{1/2} \qquad [248]$$

c) Klopman (126)

$$J_{ij} = \sigma_{SI}/[R_{AB}^2 + (\sigma_{SI}/4)(1/J_{ii} + 1/J_{jj})^2]^{1/2} \qquad [249]$$

The Pariser-Parr approximation is also utilized for π-electron systems in the PPP method (127,128). The mutual relationship of these approximations is illustrated in Fig. 9.

Approximation of attraction integrals. The interaction energy of an electron situated on an atomic orbital ϑ_i^A with the neutral atom C consists of the attraction energy to atomic core Z_A^C and the energy of interelectronic repulsion (Fig. 10)

$$(i_Ai_A|C) = -V^C_{i_Ai_A} + \sum_k^C n_k^C[(i_Ai_A|k_Ck_C) - (1/2)(i_Ak_C|i_Ak_C)] \qquad [250]$$

where n_k^C are the atomic orbital occupation numbers of atom C. For the electron configuration $s^xp^yd^zf^w$ in the ZDO approximation it is true that

$$(i_Ai_A|C) = -V^C_{i_Ai_A} + xJ^{AC}_{is} + yJ^{AC}_{ip} + zJ^{AC}_{id} + wJ^{AC}_{if} \qquad [251]$$

Since the penetration integral $(i_Ai_A|C)$ is usually very small, we can neglect it to obtain

$$V^C_{i_Ai_A} = xJ^{AC}_{is} + yJ^{AC}_{ip} + zJ^{AC}_{id} + wJ^{AC}_{if} \qquad [252]$$

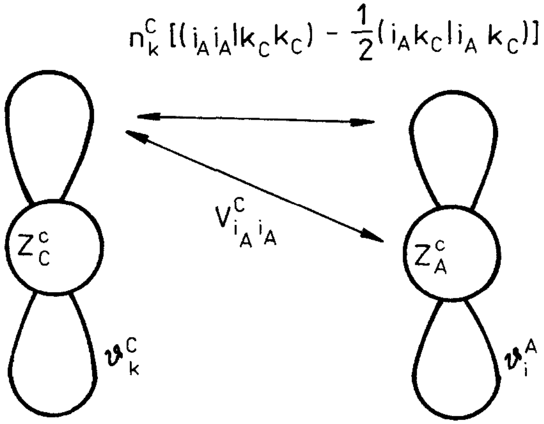

Fig. 10. Schematic representation of the penetration interaction.

In the special case of the mean electron configuration $(ns,np)^{x+y}$, which is the usual assumption of the CNDO and INDO methods,

$$V^{C}_{i_A i_A} = (x + y)J^{AC}_{is} = Z^{c}_{C}\, J^{AC}_{is} \qquad [253]$$

and for the configuration $(3d)^{z}(4s,4p)^{x+y}$ it holds true

$$V^{C}_{i_A i_A} = (x + y)J^{AC}_{is} + [Z^{c}_{C} - (x + y)]J^{AC}_{id} \qquad [254]$$

This approximation can be modified for partial inclusion of penetration effects, viz.

$$V^{C}_{i_A i_A} = Z^{c}_{C}[(1 - \omega)J^{AC}_{is} + \omega\, f_1(R_{AC},\zeta_A)] \qquad [255]$$

where the parameter ω represents the degree of penetration and f_1 is an empirical function. The more difuse functions (2p or 4s orbitals) exhibit a higher penetration effect relative to the more localized orbitals (2s or 3d AOs).

The attraction integrals may be evaluated by direct integration over STOs. Better results, however, were obtained using approximate formulae probably as an effect of compensation of errors introduced by ZDO approximation.

Repulsion of atomic core. The total energy term

$$V_{NN} = \sum_{A<B}^{N} W_{AB} \qquad [256]$$

substantially influences the calculation of equilibrium geometries. In all-valence methods

$$W_{AB} = Z^{c}_{A}\, Z^{c}_{B}\, f_2(R_{AB}) \qquad [257]$$

where the repulsion potential is

$$f_2(R_{AB}) = \sigma_{SI}/R_{AB} \qquad [258]$$

The electronic energy of a molecule is strongly affected by the ZDO approximation. Such an energy defect should be compensated by an appropriate choice of the empirical potential W_{AB}. One frequently used approximation is

$$W_{AB} = Z^{c}_{A}\, Z^{c}_{B}\, J^{AB} \qquad [259]$$

and for transition metal elements

$$W_{ML} = Z^{c}_{L}\, (xJ^{ML}_{ss} + yJ^{ML}_{ps} + zJ^{ML}_{ds}) \qquad [260]$$

The empirical function $f_2(R_{AB})$ is specifically defined for certain calculation methods.

Expression of resonance integrals. The resonance integrals h^{c}_{ij} substantially influence the energy of the chemical bond. A detailed theoretical analysis leads to the conclusion that this integral is proportional to the interference density, which is a measure of the electron transfer into the interbond region upon bond formation. In methods utilizing the ZDO approximation these integrals are expressed in a semiempirical way, only. Most frequently their proportionality to overlap integrals is exploited. The common formulae are of the following type

$$h^C_{i_A j_B}(I) = (1/2)K_t(\beta^0_A + \beta^0_B)S_{ij} \qquad [261]$$

and

$$h^C_{i_A j_B}(II) = -K_{AB}(I^A_i + I^B_j)S_{ij} \qquad [262]$$

3.4.3 CNDO Method

This method (Complete Neglect of Differential Overlap: CNDO) utilizes all consequences of the ZDO approximation. In order to secure the invariance of the total energy by rotation of the coordinate system, two additional assumptions are made:

a) integrals of electron repulsion are averaged over orbitals at the given centre

$$(i_A i_A | j_B j_B) \approx \bar{J}^{AB}_{ss} = \gamma_{AB} \qquad [263]$$

b) electron-nuclear attraction integrals are averaged as

$$V^C_{i_A i_A} \approx V^C_A \qquad [264]$$

The requirement of invariance of the molecular energy demands an averaging process only over the azimuthal quantum number (l) so that it is possible to consider charge densities $D_{ii}(1)$ and $D_{jj}(2)$ with different atomic orbital radial parts.

Individual versions of the CNDO method differ from one another in these details:

a) expression of U^A_i integrals and choice of the reference electron configuration;

b) evaluation of integrals γ_{AA} and γ_{AB};

c) expression of averaged integrals V^C_A;

d) choice of exponents of Slater-type orbitals ζ^A_i;

e) expression of resonance integrals and calibration of adjustable parameters;

f) expression of the V_{NN} potential for repulsion of atomic core.

The best known versions of the CNDO method are briefly characterized in Table 8 and are discussed in more detail below.

Parametrization of CNDO/1 method for atoms H through F (129) utilizes the integrals U_i^A expressed via a mean value of the ionization energy I_i^A

$$U_i^A = -I_i^A - (Z_A^c - 1)\gamma_{AA} \qquad [265]$$

The integrals γ_{AA}, γ_{AB} and V_A^C are evaluated by a direct integration over valence s-orbitals of the Slater type

$$\gamma_{AB} = \sigma_{SI} \int\int r_{12}^{-1} [s_A(1)]^2 [s_B(2)]^2 \, dV_1 \, dV_2 \qquad [266]$$

$$V_A^C = \sigma_{SI} Z_A^c \int r_{1C}^{-1} [s_A(1)]^2 \, dV_1 \qquad [267]$$

The resonance integrals are used in the form $h_{ij}^c(I)$ according to formula [261] with the proportionality constant $K_t = 1.0$. The atomic parameters β_A^0 for the H - F elements were calibrated in such a way so that the best agreement was obtained with orbital energies derived from *ab initio* calculations of small molecules.

A modified version of the CNDO/1 method has been proposed by Brown and Burden (130).

CNDO/2 version for s-p elements utilizes, instead of the CNDO/1 version, the following expressions for the integrals

$$V_A^C = Z_C^c \gamma_{AC} \qquad [268]$$

$$U_i^A = -X_i^A - (Z_A^c - 1/2)\gamma_{AA} \qquad [269]$$

The orbital Mulliken electronegativity X_i^A is taken as an empirical parameter determined from spectroscopic data. The values of the CNDO/2 parameters are given in Table 9.

According to Santry and Segal (132), the parametrization of elements Na through Cl has options for different basis set size: s-p, s-p-d and s-p-d' (of more diffuse d-functions). The values of the β_A^0 parameters for the Na - Cl atoms were obtained by scaling the values of β_B^0 known for atoms Li - F according to the formula

$$\beta_A^0 = \beta_B^0(U_{3s}^A + U_{3p}^A)/(U_{2s}^B + U_{2p}^B) \qquad [270]$$

In the expression [261] for the resonance integrals, the proportionality factor is $K_t = 0.75$ if the pair of atoms A and B spans the interval Na - Cl; elsewhere $K_t = 1.0$.

This method has been modified by Santry (133) to CNDO/2B version and also by Mislow et al. (134). The extensions of this type of parametrization to other elements have been carried out by Hase and Schweig (135) and Scharfenberg (136).

CNDO/2 method for d-elements differentiates between two types of orbitals $T_i^A = S, D$ according to their principal quantum number.

TABLE 8

Various versions of the CNDO method.

No	Authors	Atoms	Type	Calibration	Ref.
A) CNDO/1 versions					
1	Pople-Segal	H-F	S	$\Delta\epsilon$, C	(129)
2	Brown-Burden	H,C-F	S	d	(130)
B) CNDO/2 versions for p-elements					
3	Pople-Segal	H-F	S	from CNDO/1	(131)
4	Santry-Segal	Na-Cl	S,(D)	scaling	(132)
5	Hase-Schweig	Ge-Br	S	R, d, I	(135)
6	Scharfenberg	I	S	R, d	(136)
C) CNDO/2 versions for d-elements					
7	Clack et al.	Sc-Cu	S,D	$\Delta\epsilon$, C	(137)
8	Ruette-Ludena	Mo	S,D	R, ΔH	(139)
9	Blyholder	Ni	S,D	R, ΔH	(140)
10	Kai-Nishimoto	Mn-Cu	S,D	scaling	(141)
11	Sérafini et al.	Cr,Fe,Ni	S,D	q	(142),(143)
12	Freund et al.	Cr-Ni	S,P,D	q	(144),(145)
13	Baetzold	Na,Ca,Cu,Ag, Pd,Cd,Au	S,D	R, ΔH, I	(146)
D) CNDO/S versions					
14	del Bene-Jaffé	H-F	S	ΔE	(147)-(150)
15	Singerman-Jaffé	S	S,(D)		(151)
16	Rajtzmann et al.	H-Cl,Ga-Br, Ti-Cu,Zr-Ag	S		(152),(153)
E) Other versions					
17	Brown-Robby	H-Cl	S		(154)
18	Fischer-Kollmar	H,C	S	ΔH	(155)
19	Höjer-Meza	H-Ca,Ga-Br	S	$\Delta\epsilon$,d,ΔH,I	(156),(157)
20	Bhattacharyya	H-Br,I	S,D		(158)-(160)
21	Sakaki et al.	Cr,Mn,Pd, Ir-Hg			(161)-(163)
22	Deb-Coulson	F,Cl,Br,I	S	scaling	(165)
23	Sichel-Whitehead	H-F,Si-Cl, Ge-Br,Sn-I	S	ΔH	(166)-(168)
24	Todello	C-F,Cl,Br, Ti-Cu,Zr-Ag	S	none	(169)
25	Böhm-Gleiter	H-Br	S,P,D	R	(177)
F) Quasirelativistic CNDO/1 version					
26	Boča	H-118	S,P,D,F	R	(172)

[a] Calibration quantities: $\Delta\epsilon$ - difference in orbital energy, C - LCAO matrix, d - dipole moment, R - equilibrium geometry, I - ionization energy, ΔH - heat of formation, q - atomic charges, ΔE - excitation energy.

TABLE 8 (Continued)

No	Parameters [b]					
	U	V	γ_{AA}	γ_{AB}	ζ	β_{AB}
A) CNDO/1 versions						
1	I,γ(AA)	TI	TI	TI	Sl	β(S)
2	AP	TI	TI	TI	Sl	Pople
B) CNDO/2 versions for p-elements						
3	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S)
4	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S),K
5	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S),K
6	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S),K
C) CNDO/2 versions for d-elements						
7	X,γ(AA)	γ(AC)	TI	TI	ZG,B	β(S),β(D)
8	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S)
9	X,γ(AA)	γ(AC)	TI	TI	Sl	β(S),β(D)
10	X,γ(AA)	γ(AC)	TI	TI	ZG	β(S),β(P),β(D)
11	X,γ(AA)	γ(AC)	TI	TI	ZG	β(S),β(P),β(D)
12	X,γ(AA)	γ(AC)	TI	TI	AP	β(S),β(P),β(D)
13	X,γ(AA)	γ(AC)	TI	TI	CR	β(S)
D) CNDO/S versions						
14	X,γ(AA)	γ(AC)	SP	M,P	Sl	β(S),K
15	X,γ(AA)	γ(AC)	SP	M	Sl,B	β(S),K
16	X,γ(AA)	γ(AC)	TI/S	M,O	Sl	β(S)
E) Other versions						
17	I	1/R(AC)	TI/S	1/R(AB)	Sl,B	K
18	I,γ(AA)	γ(AC),OK	TI	TI	Sl	I,K
19	I,γ(AA)	γ(AC)	TI	TI	CR	β(S)
20	I,γ(AA)	γ(AC)	TI/S	M	CR	I,K
21	I,γ(AA)	γ(AC)	P	O	B	I,K
22	TI	γ(AC)	TI	TI	SZ	β(S)
23	SP	γ(AC)	SP	M,O,TI	Sl	β(S)
24	SP	TI	TI	TI	SE	
25	SP	γ(AC),OK	TI/S	OK	B	I
F) Quasirelativistic CNDO/1 version						
26	I,γ(AA)	γ(AC)	TI	TI	PL	ζ,K

[b] Integrals: TI - theoretical, AP - adjustable parameters, SP - spectral values, M - Mataga approximation, O - Ohno approximation, P - Pariser approximation, TI/S - scaling of theoretical integrals. Exponents: Sl - Slater, B - Burns, CR - Clementi-Raimondi, ZG - Zerner-Gouterman, DZ - double-zeta, SZ - single-zeta, SE - semiempirical, AP - adjustable parameters, PL - Pyykkö-Lohr.

TABLE 9

CNDO/2 parameters for p-elements. [a]

Z	A	X_s^A	X_p^A	X_d^A	ζ^A	$-\beta_A^0$
A) Pople-Segal (131)						
1	H	7.176			1.200	9.0
3	Li	3.106	1.258		0.650	9.0
4	Be	5.946	2.563		0.975	13.0
5	B	9.594	4.001		1.300	17.0
6	C	14.051	5.572		1.625	21.0
7	N	19.316	7.275		1.950	25.0
8	O	25.390	9.111		2.275	31.0
9	F	32.272	11.080		2.600	39.0
B) Santry-Segal (132)						
11	Na	2.804	1.302	0.150	0.733	7.720
12	Mg	5.125	2.052	0.162	0.950	9.447
13	Al	7.771	2.995	0.224	1.167	11.301
14	Si	10.033	4.133	0.337	1.383	13.065
15	P	14.033	5.464	0.500	1.600	15.070
16	S	17.650	6.989	0.713	1.817	18.150
17	Cl	21.591	8.708	0.977	2.033	22.330
C) Boča						
30	Zn	4.547	1.452		1.509	7.0
D) Hase-Schweig (138)						
32	Ge	11.435	4.080		1.527	10.0
33	As	13.335	5.345		1.702	13.0
34	Se	16.315	7.100		1.878	16.0
35	Br	19.630	8.400		2.054	22.0
E) Scharfenberg (136)						
53	I	17.704	6.423		2.5015	14.0
F) Santry (133)						
14	Si	9.0	4.5			8.5
15	P	11.2	5.2			10.0
16	S	13.0	6.4			11.5
17	Cl	16.0	7.0			12.2

[a] Parameters X and β in eV.

The 3d orbitals are classified as orbitals of the D-type whereas the 4s and 4p orbitals are of the S-type. Then the one-centre integrals are of the $\gamma_{AA}(S,S)$, $\gamma_{AA}(S,D)$, $\gamma_{AA}(D,D)$, $\beta_A^0(S)$ and $\beta_A^0(D)$ type and the two-centre integrals are of the $\gamma_{AB}(S,S)$, $\gamma_{AB}(S,D)$, $\gamma_{AB}(D,S)$, $\gamma_{AB}(D,D)$, $V_A^C(S)$, $V_A^C(D)$, $V_B^C(S)$ and $V_B^C(D)$ type. If the reference electron configuration of a transition metal is $(3d)^{n-2}$ $(4s,4p)^2$, then the integrals U_i^A are given by formulae

$$U_{4s}^A = -X_{4s}^A - \gamma_{AA}(S,S) - (Z_A^c - 3/2)\gamma_{AA}(S,D) \qquad [271]$$

$$U_{4p}^A = -X_{4p}^A - \gamma_{AA}(S,S) - (Z_A^c - 3/2)\gamma_{AA}(S,D) \qquad [272]$$

$$U^A_{3d} = -X^A_{3d} - 2\gamma_{AA}(S,D) - (Z^c_A - 5/2)\gamma_{AA}(D,D) \qquad [273]$$

Choosing another reference electron configuration $(3d)^z (4s,4p)^{x+y}$, after analysis of the atomic spectra, one can obtain different values of X^A_i. Therefore the CNDO parametrization for transition metals possesses an additional degree of freedom represented by the occupation numbers n^A_k of the atomic orbitals.

The two-centre repulsion integrals are evaluated by direct integration over atomic s-orbitals with their radial parts dependent on the true principal quantum number (n) and the orbital exponent ζ_{nl}, viz.

$$\gamma_{AB}(S,D) = \sigma_{SI} \int\int r^{-1}_{12} [\vartheta^A_{4s}(r_1,\zeta^A_{4s})]^2 [\vartheta^B_{3s}(r_2,\zeta^B_{3d})]^2 \, dr_1 \, dr_2 \qquad [274]$$

Neglecting penetration integrals, an approximate expression for the integrals $V^C_A(S)$ and $V^C_A(D)$ is obtained. For the electron configuration $(3d)^{n-2}(4s,4p)^2$, i.e. $x + y = 2$, we obtain

$$V^C_A(T^A_i) = (Z^c_C - 2) \, \gamma_{AC}(T^A_i,D) + 2\gamma_{AC}(T^A_i,S) \qquad [275]$$

if the atom C is of D-type, and

$$V^C_A(T^A_i) = Z^c_C \, \gamma_{AC}(T^A_i,S) \qquad [276]$$

if the atom C is of S-type.

The parametrization of the CNDO/2 method according to Clack et al. (137) for atoms Sc through Cu (Table 10) exploits the semi-empirical values of $\beta^0_A(S)$ and $\beta^0_A(D)$ determined for two different basis sets: with exponents according to Zerner and Gouterman or according to Burns.

A modified parametrization for atoms Mn through Cu has been proposed by Kai and Nishimoto (141) who applied a scaling procedure

$$\beta^0_A(S) = a \, X^A_{4s} + b \qquad [277]$$

$$\beta^0_A(P) = \beta^0_A(S) \, X^A_{4p}/X^A_{4s} \qquad [278]$$

Some other types of parametrization are presented in Tables 10 and 11.

The CNDO/2 version of Freund et al. (144,145) explicitly differentiates among S, P and D types of integrals. This progress was motivated mainly by the fact that the vacant 4p orbitals differ substantially from occupied 4s orbitals for transition metals. The values of U^A_i depend on the reference electron configuration and two sets have been proposed:

a) for the configuration $3d^{n-2}4s^2$

TABLE 10

CNDO/2 parameters for d-elements. [a]

Z	A	X_s^A	X_p^A	X_d^A	ζ_S^A	ζ_D^A	$-\beta_S^0$	$-\beta_D^0$
A) **Clack et al.** (137)								
21	Sc	3.657	0.558	3.793	1.230	2.020	2.0	15.0
22	Ti	3.770	0.690	4.140	1.300	2.183	7.0	18.0
23	V	3.822	0.777	4.475	1.300	2.330	12.0	21.0
24	Cr	3.909	0.876	4.822	1.320	2.470	17.0	23.0
25	Mn	3.983	0.975	5.157	1.360	2.600	22.0	25.0
26	Fe	4.120	1.062	5.504	1.370	2.722	26.0	27.0
27	Co	4.170	1.16	5.839	1.423	2.830	29.0	28.0
28	Ni	4.306	1.26	6.182	1.473	2.960	32.0	29.0
29	Cu	4.567	1.347	6.520	1.482	3.080	35.0	30.0
B) **Blyholder** (140)								
28	Ni	4.3	1.3	10.0	1.8	2.5	6.0	10.0
C) **Ruette-Ludena** (139)								
42	Mo	3.93	0.71	4.53	0.7375	1.243	5.85	5.85

[a] Parameters X and β in eV.

TABLE 11

Modified CNDO/2 parameters for d-elements.

Z	A	ζ_s^A	ζ_p^A	ζ_d^A	$-\beta_s^0$	$-\beta_p^0$	$-\beta_d^0$
A) **Kai-Nishimoto** (141)							
25	Mn	1.360	1.360	2.600	16.1	3.94	25.0
26	Fe	1.370	1.370	2.722	16.9	4.36	27.0
27	Co	1.423	1.423	2.830	17.1	4.76	28.0
28	Ni	1.473	1.473	2.960	17.9	5.22	29.0
29	Cu	1.482	1.482	3.080	19.3	5.69	30.0
B) **Sérafini et al.** (143)							
24	Cr	1.320	0.400	2.480	18.0	14.0	24.0
26	Fe	1.370	0.425	2.722	23.0	16.0	29.0
28	Ni	1.473	0.450	2.960	25.0	18.0	31.0
C) **Freund et al.** (145)							
24	Cr	1.225	0.150	1.355	3.0	3.0	7.0
25	Mn	1.325	0.388	1.499	4.0	4.0	8.0
26	Fe	1.375	0.413	1.780	6.0	6.0	9.0
27	Co	1.475	0.438	1.930	5.0	5.0	10.0
28	Ni	1.530	0.400	2.180	5.0	5.0	10.0

$$U_{4s}^A = -X_{4s}^A - \gamma_{AA}(S,S) - (Z_A^c - 3/2)\,\gamma_{AA}(S,D) \qquad [279]$$

$$U_{4p}^A = -X_{4p}^A - 2\gamma_{AA}(S,P) - (Z_A^c - 5/2)\,\gamma_{AA}(P,D) \qquad [280]$$

$$U_{3d}^A = -X_{3d}^A - 2\gamma_{AA}(S,D) - (Z_A^c - 5/2)\,\gamma_{AA}(D,D) \qquad [281]$$

b) for the configuration $3d^{n-1}4s^1$

$$U^A_{4s} = -X^A_{4s} - (1/2)\gamma_{AA}(S,S) - (Z^c_A - 1)\ \gamma_{AA}(S,D) \qquad [282]$$

$$U^A_{4p} = -X^A_{4p} - \gamma_{AA}(S,P) - (Z^c_A - 3/2)\ \gamma_{AA}(P,D) \qquad [283]$$

$$U^A_{3d} = -X^A_{3d} - \gamma_{AA}(S,D) - (Z^c_A - 3/2)\ \gamma_{AA}(D,D) \qquad [284]$$

The stability order of these configurations $E(s^xp^yd^z)$ alters in passing from Mn to Fe. For elements Sc - Mn the configuration $3d^{n-2}4s^2$ is the most stable whereas for elements Fe - Cu the configuration $3d^{n-1}4s^1$ is the most stable. The integrals V^C_A are given by an approximate formula [252]. In this version the orbital exponents are regarded as adjustable parameters and together with the $\beta^0_A(T^A_i)$ parameters they were calibrated to atomic charges and differences in orbital energies obtained by *ab initio* calculations and pseudopotential calculations for transition metal carbonyls.

The CNDO/S method of del Bene and Jaffé (147-150) has been parametrized to be capable to reproduce the excitation energies (electronic spectra) of molecules. It is combined with the limited configuration interaction. This method closely resembles the PPP version developed for the π-electron systems. Its characteristic feature is a semiempirical parametrization of one-centre repulsion integrals which are determined by the difference of the mean ionization energy and electron affinity values

$$\gamma_{AA} = \bar{I}^A - \bar{A}^A \qquad [285]$$

The two-centre repulsion integrals are expressed using Pariser-Parr approximation, by a model of uniformly charged spheres or by Mataga-Nishimoto approximation. The proportionality factor in the formula for resonance integrals $h^C_{ij}(I)$ depends on the type of chemical bond: $K_\sigma = 1.0$ and $K_\pi = 0.585$.

The method above has been extended to third-row elements (151) as well as transition metals (152,153). It was shown that the spectroscopic values for the Coulomb integrals J_{ii} may be reproduced by scaling the theoretical integrals obtained by direct integration over Slater AOs

$$(J_{ij})_{sp} = \lambda_{nl}\ (ii|jj) \qquad [286]$$

The CNDO version of Tondello (169) operates with spectroscopic values for the U^A_i integrals. For this purpose the averaged atomic configuration energies of adjacent oxidation states (A^0, A^+ and A^{2+} for transition metals and A^-, A^0 and A^+ for s-p elements) are considered. The exponents of the STO are also deduced from them so that they are regarded as semiempirical parameters. The Mulliken approximation (170) is used to express the off-diagonal matrix elements.

The **CNDO version of Böhm and Gleiter** (171) for atoms H through Br differentiates among three types of spheres: T_i^A = S, P and D. In order to secure rotational invariance the method uses averaged values of the one-centre repulsion integrals

$$\gamma_{AA}(T_i^A,T_j^A) = [\gamma_{AA}(T_i^A,T_i^A) + \gamma_{AA}(T_j^A,T_j^A)]/2 \qquad [287]$$

The theoretical integrals obtained by a direct integration over the Burns atomic orbitals are scaled by the factor $\lambda_i^A(T^A)$. The two-centre repulsion integrals are expressed using the Ohno-Klopman formula. The spectroscopic values for U_i^A published by Sichel and Whiteheat (166) and DiSipio et al. (172) are used. Values of U_d^A have been extrapolated as

$$U_d^A = [(U_s^A + U_p^A)/(I_s^A + I_p^A)]\ I_d^A \qquad [288]$$

The values of U_{3d}^A for atoms Na through Cl, as well as values for U_{4s}^A and U_{4p}^A for atoms Sc through Zn were scaled by factors of 0.80, 0.80 and 0.75, respectively. The ionization energies have been taken from publications of Pople and Beveridge (108), Levison and Perkins (157), Ballhausen and Gray (173) and Moore (113).

The integrals V_A^C partly include the penetration effect and are expressed by a formula similar to those of Fischer and Kollmar

$$V_A^C = Z_C^c\{\omega_A\gamma_{AC} + (1 - \omega_A)(R_{AC}^2 + 1/\zeta_A^2)^{-1/2}[(\lambda_A + \lambda_B)/2]^{2/3}\} \qquad [289]$$

which is the weighted average of the Ohno-Klopman formula and CNDO/2 formula for two-centre repulsion integrals. The parameter $\omega_A = \zeta_A/(\zeta_H n_A)$ represents the degree of penetration dependent on the relative AO diffusion.

The atomic core repulsion is given by an empirical potential

$$W_{AB} = Z_A^C\ Z_B^C\ \gamma_{AB}[1 + exp(-\alpha_A R_{AB}) + exp(-\alpha_B R_{AB})]f_{eff} \qquad [290]$$

where the parameters α_A and f_{eff} are calibrated to equilibrium geometries of the diatomic molecules.

The resonance integrals are expressed by a rather complicated formula

$$h_{ij}^C = A_{ij}\ I_{ij}(R_{AB})\ M_{ij}(R_{AB}) \qquad [291]$$

where A_{ij} is the weighted mean value of ionization energies, $I_{ij}(R)$

is the interference function proportional to factor $(1 - S_{ij}^2)S_{ij}$ and M_{ij} is the direction dependent (orientation) function reflecting the polarization of AOs in the bonding region. The functions I_{ij} and M_{ij} contain specific parameters dependent on the type of the chemical bond (δ, π, δ).

Other versions of the CNDO method are characterized in Table 8. Nonempirical vesions of the CNDO method (174-176) have also been proposed and utilise extended basis sets of PZ-STO functions.

Quasirelativistic (177) and relativistic versions for heavy atoms will be discussed in Section 3.6.

3.4.4 INDO Method

This method (Intermediate Neglect of Differential Overlap: INDO) represents a natural extension of the CNDO method. The extension lies in the inclusion of all one-centre repulsion integrals. The matrix elements of the Fock operator in the INDO method are (108-112)

$$F^{\eta}_{i_A i_A} = h^{C}_{i_A i_A} + \sum_{k,l}^{A} [(P^{\alpha}_{k_A l_A} + P^{\beta}_{k_A l_A})(i_A i_A|k_A l_A) - P^{\eta}_{k_A l_A}(i_A k_A|i_A l_A)] +$$

$$+ \sum_{C \neq A} \sum_{k}^{C} (P^{\alpha}_{k_A k_A} + P^{\beta}_{k_A k_A})(i_A i_A|k_C k_C) \qquad [292]$$

$$F^{\eta}_{i_A j_A} = \sum_{k,l}^{A} [(P^{\alpha}_{k_A l_A} + P^{\beta}_{k_A l_A})(i_A j_A|k_A l_A) - P^{\eta}_{k_A l_A}(i_A l_A|k_A j_A)] \qquad [293]$$

$$F^{\eta}_{i_A j_B} = h^{C}_{i_A j_B} - P^{\eta}_{i_A j_B}(i_A i_A|j_B j_B) \qquad [294]$$

Classification of the one-centre repulsion integrals used in the INDO method is given in Table 12. These integrals are not calculated by direct integration over STOs but they are composed of Slater-Condon parameters the values of which are known from atomic spectroscopy. Their values were published by Slater (107), Hinze and Jaffé (178), Tondello et al. (179) or Anno and Teruya (180, 181), Liška et al. (182), Stevenson and Burkey (185), Galasso (187) and Gordon (188).

In the s-p basis set the following expressions hold true for non-zero repulsion integrals

$$/1/ \quad J_{ss} = (ss|ss) = F^{0}_{ss} \qquad [295]$$

$$/6/ \quad J_{sp} = (ss|p_i p_i) = F^{0}_{sp} \qquad [296]$$

$$/3/ \quad J_{pp} = (p_i p_i|p_i p_i) = F^{0}_{pp} + (4/25)F^{2}_{pp} \qquad [297]$$

/6/ $J_{pp'} = (p_ip_i|p_jp_j) = F^0_{pp} - (4/25)F^0_{pp}$ [298]

/12/ $K_{pp} = (sp_i|sp_i) = (1/3)G^1_{sp}$ [299]

/12/ $K_{pp'} = (p_ip_j|p_ip_j) = (3/25)F^0_{pp}$ [300]

The numbers in slashs represent the multiplicity of the formula, i.e. alltogether 40 non-zero cases. In the d-s-p basis set there exist 232 non-zero repulsion integrals, forming 13 groups according to their value, which cannot be expressed through Slater-Condon parameters (SCP). The total number of non-zero integrals equals 735; they form 58 groups according to the same value (183).

The semiempirical parametrization of the INDO method closely resembles the CNDO approach. Using SCPs the expression for the energy of an electron configuration (ns^xnp^y) may be written as

$$E(A;\ ns^xnp^y) = xU^A_{ns} + yU^A_{np} + (x + y)(x + y - 1)F^0/2 -$$

$$- xyG^1_{sp}/6 - y(y - 1)F^2_{pp}/25 \qquad [301]$$

where F^0 is an averaged value of the F^0_{ss}, F^0_{sp} and F^0_{pp} parameters

TABLE 12

Classification of integrals in the INDO method.

Characteristic	Basis set size		
	s	s-p	d-s-p
A) Statistics			
number of orbitals	1	4	9
number of integrals	1	156	6561
non-zero integrals	1	40	753
number of classes	1	6	58
B) Radial parts			
$\gamma(S,S)$	F^0_{ss}	$F^0_{ss},F^0_{sp},F^0_{pp}$	$F^0_{ss},F^0_{sp},F^0_{pp}$
$\gamma(S,D)$			F^0_{sd},F^0_{pd}
$\gamma(D,D)$			F^0_{dd}
spectral available		F^2_{pp},G^1_{sp}	$F^2_{pp},F^2_{pd},F^2_{dd},F^4_{dd},G^1_{sp},$ $G^1_{pd},G^2_{sd},G^3_{pd}$
not SCP type			$R^1_{sppd},R^2_{sppd},R^2_{sddd}$

TABLE 13

Expression of U-integrals in the INDO method.

Atom	U_i^A	Correction Δ_i^A [a] INDO/1	INDO/2
H,Li,Na	U_s^A	-	-
	U_p^A	-	$G_{sp}^1/12$
Be,Mg	U_s^A	-	$G_{sp}^1/12$
	U_p^A	$G_{sp}^1/6$	$G_{sp}^1/4$
B-F Al-Cl	U_s^A	$-G_{sp}^1(Z_A^C-2)/6$	$G_{sp}^1(Z_A^C-3/2)/6$
	U_p^A	$G_{sp}^1/3 - F_{pp}^2(Z_A^C-3)2/25$	$G_{sp}^1/3 + F_{pp}^2(Z_A^C-5/2)2/25$

[a] $U_i^A(\text{INDO}) = U_i^A(\text{CNDO}) + \Delta_i^A$

usually is taken for $\gamma_{AA}(S,S)$ integral of the CNDO method. The U_i^A integrals are similar to those of the CNDO method with a correction Δ_i^A dependent on the SCP values (Table 13).

In the s-p valence basis set the matrix elements of the Fock operator are simplified as

$$F^{\eta}_{i_A i_A} = U_i^A + \sum_k^A [(P^{\alpha}_{k_A k_A} + P^{\beta}_{k_A k_A})J^{AA}_{ik} - P^{\eta}_{k_A k_A} K^{AA}_{ik}] + \\ + \sum_{C \neq A} [V_A^C + \sum_k^C (P^{\alpha}_{k_C k_C} + P^{\beta}_{k_C k_C})\gamma_{AC}] \qquad [302]$$

$$F^{\eta}_{i_A j_A} = 2(P^{\alpha}_{i_A j_A} + P^{\beta}_{i_A j_A})K^{AA}_{ij} - P^{\eta}_{i_A j_A}(K^{AA}_{ij} + J^{AA}_{ij}) \qquad [303]$$

$$F^{\eta}_{i_A j_B} = h^C_{i_A j_B} - P^{\eta}_{i_A j_B}\gamma_{AB} \qquad [304]$$

The most important versions of the INDO method will be discussed in more detail. Their review is given in Table 14.

INDO/2 method for s-p elements closely resembles the CNDO/2 parametrization so that only the set of Slater-Condon parameters F_{pp}^2 and G_{sp}^1 is added. Their values according to various sources are listed in Table 15. The versions of Galasso (187) and Gordon et al. (188) utilize the modified parameters X_i^A, ζ_i^A and β_A^0.

MINDO method for s-p elements (Modified INDO) is characterized by a different way to express the resonance integrals; they are calibrated to the heat of formation of the molecules. Since parame-

TABLE 14

Various versions of the INDO method.

No	Authors	Atoms	Expression of h^{c}_{ij} [a]	Ref.
A) INDO/2 versions for p-elements				
1	Pople et al.	H-F	as CNDO/1	(184)
2	Stevenson-Burkey	Na-Cl	as CNDO/2-B	(185)
3	Benson-Hudson	C-F,Si-Cl	as CNDO/1 or CNDO/2-B	(186)
4	Deb-Coulson	F,Cl,Br,I	scaling	(165)
5	Galasso	C-F,S,Cl,Br,I	scaling	(187)
6	Gordon et al.	Na-Cl	scaling	(188)
7	Kaufman-Predney	Na-Cl	as CNDO/2	(189)
8	van Catlege	H-F	I, A	(190)
B) MINDO version for p-elements				
9	MINDO/1	H-F	I, K'(AB), K''(AB)	(191)
10	MINDO/2	H-F	I, K(AB)	(193),(194)
11	MINDO/3	H-Cl	I, K(AB)	(195)
C) INDO versions for d-elements				
12	Clack	Sc-Cu	as CNDO/2	(197)
13	Boča-Pelikán	Sc-Cu	as CNDO/2	(199),(200)
14	Fantucci-Valenti	Sc-Cu	as CNDO/2	(198)
15	Bacon-Zerner	H-Ca, Sc-Cu	as CNDO/2	(201)
16	Zerner et al.	Ca-Zn	as CNDO/2	(202)
17	Böhm-Gleiter	H-K, Ca-Zn	I	(171)
18	Van der Lugt		I	(203)
19	Blair-Webb	Pt,Cl	U, K(AB)	(204)
20	Oleari et al.		I	(205)-(208)
D) Quasirelativistic INDO/1 version				
21	Boča	H-118	ζ, K	(223)

[a] Expressions through: I - ionization energy, A - electron affinity, U - atomic potential, ζ - orbital exponents.

ters $\gamma_{AA} = F^0$ are taken from spectroscopic data, then the two-centre integrals are not evaluated theoretically but are approximated through Onho-Klopman formula. This class of methods covers MINDO/1 (191), SPINDO/1 (192), MINDO/2 (193, 194) and MINDO/3 (195) versions. In the last version the atomic parameters U^A_s, U^A_p, J^{AA}_{ss}, J^{AA}_{pp}, K^{AA}_{sp}, and K^{AA}_{pp}, are determined from spectroscopic data using the approach of Oleari et al. (172, 196). The STO exponents are regarded as adjustable parameters and together with diatomic parameters α_{AB} and K_{AB}, are calibrated to the experimental values of heat of formation and equilibrium geometries of the small molecules.

INDO/2 method for d-elements utilizes the corresponding CNDO/2 approach with corrections by values of the Slater-Condon parameters

$$U^A_i(\mathrm{INDO/2}) = U^A_i(\mathrm{CNDO/2}) + \Delta^A_i(\mathrm{SCP}) \qquad [305]$$

TABLE 14 (Continued)

No	Parameters [b]					
	U	SCP	V	γ_{AA}	γ_{AB}	ζ
A) INDO/2 versions for p-elements						
1	X,SCP	Sl	γ(AC)	TI	TI	Sl
2	X,SCP	Ex	γ(AC)	TI	TI	Sl
3	X,SCP	HJ	γ(AC)	TI	TI	Sl
4	TI	TI	γ(AC)	TI	TI	SZ
5	X,SCP	SE,TI	γ(AC)	TI	TI	CR
6	X,SCP	Ex	γ(AC)	TI	TI	AP
7	X,SCP	Ex	γ(AC)	TI	TI	Sl
8	X,SCP	Sl	γ(AC)	Sp	TI/S	Sl
B) MINDO version for p-elements						
9	Sp	Sp	γ(AC)	Sp	OK	Sl
10	Sp	Sp	γ(AC)	Sp	OK	Sl
11	Sp	Sp	γ(AC)	Sp	OK	AP
C) INDO versions for d-elements						
12	X,SCP	Ol	γ(AC)	TI	TI	ZG
13	X,SCP	AT+TI	γ(AC)	TI	TI	ZG
14	Sp	HJ	γ(AC)	Sp	MN	ZG
15	I,SCP	HJ	γ(AC)	TI	TI	Sl ZG
16	I,SCP	Ol	γ(AC)	Sp	MN	ZG
17	Sp	HJ,Ol	γ(AC)+OK	TI/S	OK	B
18	I,SCP	Sp	Ap	TI	Ap	CR,DZ
19	I,SCP	TI	γ(AC)	TI	TI	SZ
20	Sp	Sp	γ(AC)	Sp	1/R	DZ
D) Quasirelativistic INDO/1 version						
21	I,SCP	TI	γ(AC)	TI	TI	PL

[b] Slater-Condon parameters according to: HJ - Hinze-Jaffé, Ol - Oleari et al., AT - Anno-Teruya, Sl - Slater, Sp - own spectral values, TI - theoretical integration, Ex - extrapolated values, SE - semiempirical values. Approximate expressions: MN - Mataga-Nishimoto, OK - Ohno-Klopman, Ap - own functions. Other symbols are the same as in Table 8.

where

$$\Delta_s^A = (Z_A^c - 3/2)\, G_{sd}^2/10 \qquad [306]$$

$$\Delta_p^A = G_{sp}^1/6 + (Z_A^c - 3/2) G_{pd}^1/15 + G_{pd}^3(3/70) \qquad [307]$$

$$\Delta_d^A = G_{sd}^2/5 + (Z_A^c - 5/2) F_{dd}^2(2/63) + F_{dd}^4(2/63) \qquad [308]$$

Only the Coulomb (ii|jj) and exchange (ij|ij) one-centre integrals are considered so that the rotational invariance of the method is not achieved in the d-s-p basis set. This deffect, however, is not serious. The SCP values according to various sources are given in Table 16.

TABLE 15
Slater-Condon parameters for p-elements.

Atom		Slater (107) Stevenson (185)	Hinze-Jaffé (178)	Galasso (187)	Gordon (188)
A) Parameters F^2_{pp} (eV)					
3	Li	1.3568			
4	Be	2.4251	2.6562		
5	B	3.5485	3.4807		
6	C	4.7269	4.5097	6.3700	
7	N	5.9605	6.4592	7.8394	
8	O	7.2492	6.9024	9.0277	
9	F	8.5929	(8.058)	10.3634	
11	Na	1.1866			1.9579
12	Mg	1.8318	3.2730		2.4680
13	Al	2.4685	1.6024		2.9411
14	Si	3.2777	2.2626		3.4951
15	P	3.7912	2.9476		4.1229
16	S	4.4872	4.5376	5.9301	4.7672
17	Cl	5.2094	(5.277)	6.6842	5.4826
35	Br			6.0446	
54	I			5.2354	
B) Parameters G^1_{sp} (eV)					
3	Li	2.5036			
4	Be	3.8284	3.8279		
5	B	5.4220	5.4012		
6	C	7.2843	6.8975	9.3733	
7	N	9.4154	8.9580	11.0039	
8	O	11.815	11.8148	12.7306	
9	F	14.484	(13.388)	14.5536	
11	Na	2.1216			3.5005
12	Mg	2.8018	2.4763		3.7750
13	Al	3.6546	3.3589		4.3543
14	Si	4.6575	4.8121		5.2186
15	P	5.8025	1.0478		6.3102
16	S	7.6011	3.0755	8.5173	7.5285
17	Cl	8.5078	(2.864)	9.4913	8.95440
35	Br			8.4035	
54	I			7.1057	

A rotational invariant version (199,200) is obtained by considering all one-centre repulsion integrals in the d-s-p basis set. Since the radial integrals R^1_{sppd}, R^2_{sppd} and R^2_{sddd} are not available from the spectroscopic data (they do not occur in formulae for energies of atomic terms) an extrapolation was used, to obtain

$$R^1_{sppd} = (R^1_{sppd}/G^1_{pd})_{theor}\ (G^1_{pd})_{spec} \qquad [309]$$

$$R^2_{sppd} = (R^2_{sppd}/G^2_{sd})_{theor}\ (G^2_{sd})_{spec} \qquad [310]$$

$$R^2_{sddd} = (R^2_{sddd}/G^2_{sd})_{theor}\ (G^2_{sd})_{spec} \qquad [311]$$

The necessary theoretical (theor) values for these integrals have been evaluated by direct integration over PZ-STOs in the valence basis set of Richardson et al. (120,121). The spectroscopic (spec) parameters were taken from data of Anno and Teruya for the $d^{n-2}s^1p^1$ electron configurations of neutral atoms. The radial integrals obtained in this way are listed in Table 17.

INDO/1 version of Bacon and Zerner (202) for elements from H through Cu is based on the evaluation of U_i^A integrals using the ionization energies I_i^A and SCPs. Both relevant electron configurations are considered for transition metals. The version has been modified by Zerner et al. (191) by evaluating the one-centre integrals F^0 from spectroscopic data (INDO/S approach). The two-centre repulsion integrals are expressed through a modified Mataga-Nishimoto formula

$$\gamma_{AB} = \sigma_{SI}\ f/[R_{AB} + 2\sigma_{SI}f/(\gamma_{AA} + \gamma_{BB})] \qquad [312]$$

with the screening constant f = 1.2. The mixing of two relevant reference electron configurations for transition metals is also taken into account in this version.

Other INDO versions for transition metals have been proposed by Böhm and Gleiter (171), van der Lugt (203), Blair and Webb (204), Oleari et al. (205-208), Ross (209,210), Blomquist et al. (211), DeBrouckére et al. (212) and Ziegler (213,214).

An MCZDO method (154) is known with corrections to the potential of the crystal lattice (215), a SINDO method (216) and an EMZDO method (217) spanning the class of the INDO approach.

INDO versions for f-block elements (lanthanoides) have been developed by Clack and Warren (218), Farning and Fitzpatrick (219), Le-Min et al. (220,221) and Culberson et al. (222). In the last version Slater-type orbitals of double-zeta quality have been used with parameters (exponents and weights) generated by the best fit to the set of $\langle r\rangle$, $\langle r^2\rangle$ and $\langle r^3\rangle$ values promoted by a numerical Dirac-Fock relativistic atomic program.

A quasirelativistic INDO/1 version applicable to all elements (including superheavy atoms) will be described in Section 3.6.1.

TABLE 16

Slater-Condon parameters for d-elements.

Atom				Parameter (cm^{-1}) [b]							
Z	A	q	[a]	F^2_{dd}	F^4_{dd}	G^2_{sd}	F^2_{pd}	G^1_{pd}	G^3_{pd}	G^1_{sp}	F^2_{pp}
21	Sc	0	HJ	28420	9702	5475	2380	2730	7840	8232	
		1		36113	22491	6090	8470	5700	735	24729	
		0	AT	29500	14600	5870	11000	5650	2210	12100	5000
		1		36100	22700	6090	8470	5700	651	24700	
		0	AT*			6680	11000	5650	2210	12100	
		1								24700	
22	Ti	0	HJ	37730	20727	7670	8015	4890	6370	6276	
		1		39053	14112	9060	15190	6750	7840	21825	
		0	To	37485	24255	7750	15750	5250	3185	6600	5500
		1		42875	27783	10000	17500	6750	4116	7200	8750
		0	AT	44900	29700	6200	13700	7320	10300	13100	
		1		51900	36100	7600	10200	5120	1690	23900	
		0	AT*	45200	27600	2520	13700	7320	10300	13100	
		1				10800	13800	5990	938	23900	
23	V	0	HJ	36603		9065	27510	17535	27930	10854	
		1		47089	30870	9710	13370	4650	8820		
		0	To	43855	28444	8250	17500	5700	3454	7050	6000
		1		49245	31972	10500	21000	7200	4385	7650	9250
		0	AT	50800	35400	6240	11200	5180	1710	15100	
		1		43700	27100	7940	11500	4880	2440	25100	
		0	AT*	56000	34300	8310	11200	5180	1710	15100	
		1		67100	42200	8130	16700	5000	3640	25100	
24	Cr	0	HJ	46697	36162	7310	1225	45	3430	30960	
		1		51499	35721	8735	16065	7245	14210		
		0	To	50225	32634	7900	19250	6150	3748	7500	6500
		1		55615	36162	10500	21000	7650	4679	8100	9750
		0	AT	63500	36800	5220	11400	5580	297	14400	
		1		52500	32000	6600	12800	4680	4380		
		0	AT*	63200	37900	7930	11400	5580	297	14400	
25	Mn	0	HJ	55909	42777	5960	7595	13710		8523	
		1		23520	59094	6510		24900	2940		
		0	To	56595	36823	9000	19250	6600	4018	7950	7000
		1		61985	40351	9500	22750	8100	4949	8550	10250
		0	AT	66000	37900	6110	8010	1240	4970	18900	
		1		57100	35600	7880	11800	4810	3560	28000	
		0	AT*	67300	42000	6550	7810	5100	2450	18900	
		1		77400	48700	10300	18700	7130	3510	28000	
26	Fe	0	HJ	58310	33516	6425	7385	225	8820	12234	
		1		66689	49833	7955	11165	3915	7350		
		0	To	62965	41013	8000	12250	7050	4312	8400	7500
		1		68355	44541	9000	22750	8550	5218	9000	10750
		0	AT	61000	38400	6640	5020	2450	3520	16300	
		1		61400	42400	7810	10300	4050	4560	27800	
		0	AT*	72100	46000	11200	10300	2350	88	16300	
		1		83400	53100	9170	17400	6180	5660	27800	
27	Co	0	HJ	68992	52479	5715	7035	2385			
		1		44394		18785	12355				
		0	To	69335	45202	8500	17500	7500	4581	8850	8000
		1		74725	48730	10500	24500	9000	5488	9450	11250
		0	AT	64500	48100	6340	6290	3170	2260	22700	
		1		65900	44200	7830	12700	4380	3070	14200	
		0	AT*	77400	50500	3070	12100	2860	7150	22700	
		1		88100	56700	9390	17900	5870	4950	14200	

TABLE 16 (Continued)

Atom				Parameter (cm^{-1}) [b]							
Z	A	q	[a]	F^2_{dd}	F^4_{dd}	G^2_{sd}	F^2_{pd}	G^1_{pd}	G^3_{pd}	G^1_{sp}	F^2_{pp}
28	Ni	0	HJ	79821	53361	6695	4550	3000	3920		
		1		80213	53802	7705	11970	3570	7840		
		0	To	75705	49392	9500	12250	7950	4875	9300	8500
		1		81095	52920	10000	15750	9450	5757	9900	11750
		0	AT	79800	53300	6700	6050	3010	3250	19400	
		1		82400	58300	7620	12700	4560	4190		
		0	AT*	77600	53100	9780	8570	3080		19400	
29	Cu	0	HJ				11025	5865	8575	23436	
		1		84280	58212	14470	5565	3990	5145	21	
		0	To	82075	53581	10000	16800	8400	5145	9750	9000
		1		87465	57109	11500	19250	9900	6027	10350	12250
		0	AT	85980	57965	4460	10700	5620	6930	20700	
		1		92800	59800	9040	15600	4960	7350	31700	
		0	AT*			4460	10700	5620	6930	20700	
		1		92800	61800	8500	18500	5230	6270	31700	

[a] HJ - Hinze-Jaffé (178) using total regression to configurations d^n, $d^{n-1}s^1$, $d^{n-1}p^1$, $d^{n-2}s^2$, $d^{n-2}s^1p^1$ and $d^{n-2}p^2$; To - Tondello et al. (179); AT - Anno-Teruya (180) for energetically lowest configurations; AT* - Anno-Teruya (180) for configurations $d^{n-2}s^1p^1$.

[b] 1 eV ≈ 8066 cm^{-1}.

TABLE 17

Parameters of rotational invariant INDO method.

Atom			Ratio [a]			Extrapolated integral/eV		
Z	A	q	R^1_{sppd}/G^1_{pd}	R^2_{sppd}/G^2_{sd}	R^2_{sddd}/G^2_{sd}	R^1_{sppd}	R^2_{sppd}	R^2_{sddd}
21	Sc	0	1.7953	0.4787	1.0112	1.2576	0.3965	0.8374
22	Ti	0	1.9637	0.4793	0.9745	1.7821	0.1497	0.3044
		1	1.8336	1.2182	0.9574			
23	V	0	2.1544	0.4475	0.9420	1.3836	0.4611	0.9705
		1	1.9183	1.2809	0.8936			
24	Cr	0	2.3447	0.4273	0.9029	1.6221	0.4201	0.8876
		1	2.0020	1.3431	0.8284			
25	Mn	0	2.5363	0.4073	0.8650	1.6037	0.3308	0.7025
		1	2.1137	1.3556	0.7673			
26	Fe	0	2.7451	0.3799	0.8255	0.7996	0.5275	1.1462
		1	2.2059	1.3877	0.7128			
27	Co	0	2.9001	0.3867	0.7904	1.0284	0.1472	0.3008
		1	2.2721	1.4381	0.6617			
28	Ni	0	3.0381	0.3919	0.7631	1.1599	0.4752	0.9253
		1	2.3525	1.4616	0.6151			
29	Cu	0	3.2568	0.3555	0.7212	2.2693	0.1966	0.3988
		1	2.4271	1.4816	0.5745			

[a] According to (199) for Richardson AOs.

3.4.5 NDDO and MNDO method

This method utilizing the ZDO approximation is characterized by the feature that all types of one-centre $(i_A j_A|k_A l_A)$ repulsion integrals and two-centre $(i_A j_A|k_B l_B)$ Coulomb-type integrals are exactly taken into account. This is the origin of the abbreviation NDDO: Neglect of Diatomic Differential Overlap.

Within this approximation the matrix elements of the Fock operator become

$$F^{\eta}_{i_A i_A} = h^{c}_{i_A i_A} + \sum_{C\neq A} \sum^{C}_{k,l} (P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A i_A|k_C l_C) + \\ + \sum^{A}_{k,l} [(P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A i_A|k_A l_A) - P^{\eta}_{kl}(i_A l_A|i_A k_A)] = \\ = F^{\eta}_{i_A i_A}(\mathrm{INDO}) + \sum_{C\neq A} \sum^{C}_{k,l} (P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A i_A|k_C l_C) \qquad [313]$$

$$F^{\eta}_{i_A j_A} = h^{c}_{i_A j_A} + \sum_{C\neq A} \sum^{C}_{k,l} (P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A j_A|k_C l_C) + \\ + \sum^{A}_{k,l} [(P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A j_A|k_A l_A) - P^{\eta}_{kl}(i_A l_A|j_A k_A)] = \\ = F^{\eta}_{i_A j_A}(\mathrm{INDO}) + \sum_{C\neq A} [V^{C}_{i_A j_A} + \sum^{C}_{k,l} (P^{\alpha}_{kl} + P^{\beta}_{kl})(i_A i_A|k_C l_C)] \qquad [314]$$

$$F^{\eta}_{i_A j_B} = h^{c}_{i_A j_B} - \sum^{A}_{k} \sum^{B}_{l} P^{\eta}_{k_A l_B}(i_A k_A|j_B l_B) \qquad [315]$$

In the s-p atomic orbital basis set the terms $F^{\eta}_{i_A i_A}$ and $F^{\eta}_{i_A j_B}$ may be simplified in their INDO part since the one-centre repulsion integrals are only of the Coulomb $(ii|jj)$ and exchange $(ij|ij)$ type. Instead of the CNDO and INDO method there are 22 different bicentric NDDO integrals in the valence s-p basis set. Neglecting the penetration effects the following approximation is usually accepted

$$V^{C}_{i_A j_A} = - Z^{c}_{C}\ (i_A j_A|s_C s_C) \qquad [316]$$

The integrals U^{A}_{i} are taken from the INDO method.

The principles of the NDDO method have been formulated by Pople at al. (224) and the method developed by various authors (225-228). In these version the two-centre repulsion integrals are evaluated by direct integration over the STOs.

MNDO method (Modified Neglect of Diatomic Overlap) (229) is a version of the NDDO method that utilizes a semiempirical way to evaluate the two-centre repulsion integrals. These integrals are calculated by considering electric multipoles in a mutual interaction:

$$(i_A k_A | j_B l_B) = \sum_{l_1} \sum_{l_2} \sum_{m} [M^A_{l_1 m}, M^B_{l_2 m}] \qquad [317]$$

where M^A_{lm} is the multipole moment of the charge distribution $e[\vartheta^A_i(1)\vartheta^A_k(1)]$, the subscripts l and m specifying the order and orientation of the multipoles. Each multipole is represented by an appropriate configuration of 2^l point charges of magnitude $e/2^l$, with charge separations D_l. The interaction between two multipoles is then calculated by applying the formula

$$[M^A_{l_1 m}, M^B_{l_2 m}] = \frac{e^2}{2^{l_1+l_2}} \sum_{i=1}^{2l_1} \sum_{j=1}^{2l_2} f_l(R_{ij}) \qquad [318]$$

where R_{ij} denotes the distance between the point charges i and j in the interacting configurations at atoms A and B. The function $f_l(R_{ij})$ stands for any semiempirical expression which behaves properly in the limits $R_{AB} \Rightarrow \infty$ and $R_{AB} \Rightarrow 0$. With a minimal sp basis set for the valence electrons, there are only four configurations to be considered: the differential overlap D_{ss} is an electric monopole, D_{sp} is a dipole, D_{pp} a linear (diagonal) quadrupole and $D_{pp'}$ is a square (off-diagonal) quadrupole. The charge separation in the dipole configuration is d_1 and that in the quadrupole configuration is d_2.

The resulting value of the integral is evaluated using the Dewar-Sabelli-Klopman formula of [294] type

$$f_l(R_{ij}) = [R_{ij}^2 + (\rho^A_{l_1} + \rho^B_{l_2})^2]^{1/2} \qquad [319]$$

and Mataga-Nishimoto approximation

$$f_l(R_{ij}) = [R_{ij} + 1/(\rho^A_{l_1} + \rho^B_{l_2})]^{-1} \qquad [320]$$

With an s-p basis set, both functions make use of three additive terms ρ_l for each element which are characteristic of monopole, dipole, and quadrupole (l = 0, 1, 2). These are chosen to yield the correct one-centre limit for the interaction between two monopoles J^{AA}_{ss}, K^{AA}_{sp} and K^{AA}_{pp}. The set of optimized atomic parameters is U^A_s, U^A_p, $\zeta^A_s = \zeta^A_p$, β^A_s, β^A_p and α_A values (Table 18). The α_A parameter occurs in the approximation for the attraction integrals $V^C_{i_A j_A}$

$$V^C_{i_A j_A} = -Z^C_C(i_A j_A | s_C s_C) + f_2(R_{AC}, \alpha_A, \alpha_C) \qquad [321]$$

and for the empirical potential W_{AB} for expression of atomic core repulsion

$$W_{AB} = Z_A^c\, Z_B^c\, (s_As_A|s_Bs_B)[1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}] \qquad [322]$$

with a slight modification for the pairs N-H and O-H

$$W_{XH} = Z_X^c\, Z_H^c\, (s_Xs_X|s_Hs_H)[1 + R_{XH}e^{-\alpha_X R_{XH}} + e^{-\alpha_H R_{XH}}] \qquad [323]$$

Finally

$$h^c_{i_A j_B} = S_{i_A j_B}(\beta_i^A + \beta_j^B)/2 \qquad [324]$$

The MNDO parameters are calibrated through the heats of formation, equilibrium geometries, dipole moments and ionization energies of the organic molecules.

TABLE 18

MNDO parameters for some elements.[a]

Z	A	Parameters				
		U_s^A	U_p^A	$\zeta_s^A=\zeta_p^A$	$-\beta_s^A$	$-\beta_p^A$	α_A
1	H	-11.906		1.332	6.989		2.544
5	B	-34.547	-23.122	1.507	8.252	8.252	2.135
6	C	-52.280	-39.206	1.788	18.985	7.934	2.546
7	N	-71.932	-57.172	2.256	20.496	20.496	2.861
8	O	-99.643	-77.797	2.700	32.688	32.688	3.160
9	F	-131.071	-105.782	2.848	48.290	36.508	3.420

Z	A	d_1	d_2	ρ_0	ρ_1	ρ_2
1	H			0.560345		
5	B	0.506893	0.430113	0.679822	0.539446	0.476128
6	C	0.427284	0.362563	0.588660	0.430254	0.395734
7	N	0.338616	0.287325	0.529751	0.337322	0.324853
8	O	0.282894	0.240043	0.466882	0.275822	0.278628
9	F	0.268138	0.227522	0.425492	0.243849	0.255793

[a] Parameters U and β in eV, α in Å^{-1}, d and ρ in Å.

The MNDO method has been further modified (248) and named the **Austin Model 1** (AM1). The principal change is applied to the core repulsion function

$$W_{AB} = Z_A^c\, Z_B^c\, (s_As_A|s_Bs_B)[1 + F(A) + F(B)] \qquad [325]$$

where

$$F(A) = exp(-\alpha_A R_{AB}) + \sum_i K_i^A\, exp[L_i^A\, (R_{AB} - M_i^A)^2] \qquad [326]$$

and analogously for F(B). The new set of parameters K_i^A, L_i^A and M_i^A

(see Table 19) provides a serious improvement yielding realistic results for molecular geometries, heats of formation, rotational barriers, ionization energies and dipole moments of the organic molecules. The main gains are the ability of AM1 to reproduce hydrogen bonds and the promise of better estimates of activation energies for reactions.

TABLE 19

AM1 parameters.

Parameter	Element			
	H	C	N	O
U_s	-11.396	-52.029	-71.860	-97.830
U_p		-39.614	-57.168	-78.262
ζ_s	1.188	1.807	2.315	3.108
ζ_p		1.685	2.158	2.524
$-\beta_s$	6.174	15.716	20.299	29.273
$-\beta_p$		7.719	18.239	29.273
α	2.882	2.648	2.947	4.455
K_1	0.122796	0.011355	0.025251	0.280962
K_2	0.005090	0.045924	0.028953	0.081430
K_3	-0.018336	-0.020061	-0.005806	
K_4		-0.001260		
L_1	5.000	5.000	5.000	5.000
L_2	5.000	5.000	5.000	7.000
L_3	2.000	5.000	2.000	
L_4		5.000		
M_1	1.200	1.600	1.500	0.847918
M_2	1.800	1.850	2.100	1.445071
M_3	2.100	2.050	2.400	
M_4		2.650		

The MNDO version has been reparametrized in order to take into account the correlation effects. This **MNDOC method** (230) utilizes the second-order Brillouin-Wigner perturbation theory.

LNDO/S method (Local Neglect of Differential Overlap) (231) applies the ZDO approximation to two-centre repulsion integrals in the local coordinate system instead of the molecular one. This version represents an extension of the CNDO/S and INDO/S approachs and has been used with success to calculate the excitation energies in hydrocarbons.

PNDO method (Partial Neglect of Differential Overlap) (112, 232) differentiates among two-centre repulsion integrals in the local coordinate system. A special procedure was proposed for the parametrization of one-centre integrals.

Yonezava (233,234) utilizes the Mulliken approximation for repulsion integrals side by side with the semiempirical parametrization of one-centre integrals.

The NDDO method initiated the appearance of a set of similar methods among which included: IRDO (Intermediate Retention of Differential Overlap) (235), DRINDO (Dipole Retained INDO) (236), NNDO (Neglect of Non-neighbour Diatomic Overlap) (237,238), PDDO (Projection of Diatomic Differential Overlap) (239-241), LEDO (Limited Expansion of Diatomic Overlap) (242), PRDDO (Partial Retention of Diatomic Differential Overlap) (243,244) and VRDDO (Variable Retention of Diatomic Differential Overlap) (245,246). In this development a non-empirical approach is preferred; it simulates the *ab initio* calculations by a substantial reduction of the enormous number of two-centre repulsion integrals.

3.4.6 Comparison of NDO Methods

There are three basic groups of all-valence methods which deal with the ZDO approximation: CNDO, INDO and NDDO. Each of them comprises numerous versions differing one from another mainly in the semiempirical parametrization. There is no doubt that the number of methods utilizing the ZDO approximation will continue to grow. Therefore it is necessary do discuss specific advantages of individual types of methods.

The main motivation of these NDO methods lies in the reduction the large number of two-electron repulsion integrals; this is connected with finding a compromise between sophistication and time consumption of the respective method. The CNDO method is formally compatible with the Mulliken approximation for the repulsion integrals and the NDDO method is compatible with the Ruedenberg approximation. By orthogonalization of the basis set the CNDO method is exact in the first-order and the NDDO method in the second-order expansion of the overlap integral matrix. Whereas the CNDO method is rather fast, the NDDO method is slower in evaluation and manipulation of a higher number of repulsion integrals. If there are m valence orbitals at each centre and the number of atoms in a molecule is N, then the number of repulsion integrals is given by the following estimate

method	one-centre	two-centre
CNDO	N	N(N - 1)/2
INDO	M.N	N(N - 1)/2
NDDO	M.N	M.N(N - 1)/2

where $M = [m(m + 1)/2][m(m + 1)/2 + 1]/2 = (m^4 + 2m^3 + 3m^2 + 2m)/8$. If $m = 4$ and $N = 50$, then we obtain 1226, 3975 and 70125 repulsion integrals to be considered within the CNDO, INDO and NDDO methods, respectively. Therefore the CNDO and INDO integrals can be kept in fast memory whereas NDDO integrals must be stored on the external (slow) memory medium.

A comparison of different NDO methods from the viewpoint of their time consumption and precision is given in Fig. 11.

The use of the INDO method is preferred to study those molecular properties which depend on the one-centre exchange

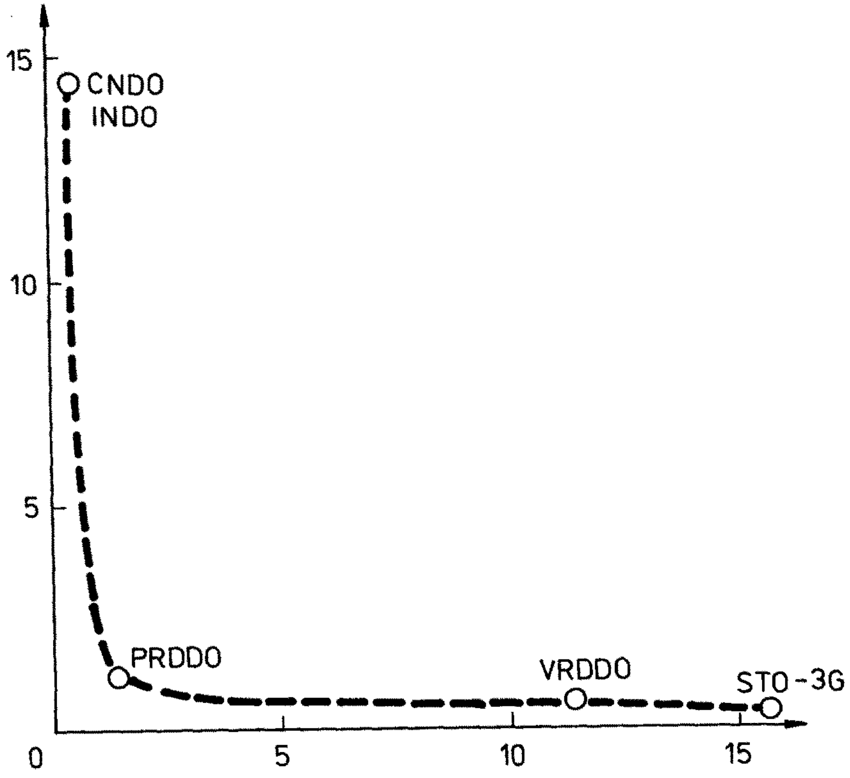

Fig. 11. Relative error *vs* relative CPU-time cost for some SCF methods.

interaction. For example, the INDO method correctly differentiates between the singlet and triplet state of the O_2 molecule, octahedral $[NiF_6]^{4-}$ complex, etc. For this reason the INDO method is recommended for coordination compounds of high symmetry (having degenerate energy levels).

In semiempirical parametrization three basic approaches are known:

a) analysis of atomic spectra;
b) scaling of theoretical integrals and an extrapolation;
c) adjustment of parameters to the selected molecular properties.

The **analysis of atomic spectra** may be complicated by the fact that not all the energy levels (according to atomic structure theory (107)) are determined or correctly interpreted. The missing data influence the value of the mean energy of the electron configuration and subsequently also the values of the parameters derived such as U_i^A, F^0, G^1_{sp}, F^2_{pp}, etc. This problem becomes serious for the third-row and for the transition metal elements. Analysis of atomic spectra is not capable of giving information about some radial integrals (for d-s-p elements) which are not of the SCP type. The resulting parameters implicitly include the electron correlation effects, the influence of inner shells as well as relativistic effects. This fact makes the subsequent application of the configuration interaction rather problematic.

One of the most important property of spectroscopic parameters is represented by their configurational dependence. This means that the values deduced for the parameters depend on the choice of the reference electron configuration and oxidation states of the atoms or ions. This problem is important for transition metal elements. For this reason, there are further attempts to take the configurational dependence of the semiempirical parameters into account in the calculation of molecular electronic structure (248).

The **scaling of the theoretical integrals** is based on the fact that the one-centre integrals in the STO basis set can simply be evaluated by explicit formulas (248). For example, the kinetic integral $T_{ii} = \zeta^2[2l(l + 1) + n]/[2n(2n - 1)]$ (in units of hartree), the attraction integral is $V^A_{ii} = Z^c_A \zeta/n$ and the two-electron integrals are $(ns\ ns|ns\ ns) = \zeta\ k_n$, where the constant factors $k_1 = 5/8$, $k_2 = 93/256$, $k_3 = 793/3072$, $k_4 = 26333/13107$ and $k_5 = 43191/262144$. Then the theoretical dependence of U_i^A on ζ_i^A is a quadratic function and F^0 is a linear function of ζ. Either the STO exponents or the theoretical values of integrals may be scaled.

Adjustment of the parameters to selected molecular properties (e.g., the MINDO/3 or MNDO approach) may yield excellent results in a series of similar (mostly organic) compounds. In this approach, however, the original physical meaning of some quantities can be lost. For example, the optimized MINDO/3 exponents of STOs exhibit certain anomalies: $\zeta_s^O > \zeta_s^F$, $\zeta_p^O > \zeta_p^F$, $\zeta_s^P > \zeta_s^S$ or $\zeta_p^P > \zeta_p^S$. These trends are inadequate from the viewpoint of the screening of the nuclear charge $\zeta = (Z - \sigma)/n^*$. The use of a larger set of adjustable parameters is compicated by the fact that a change of one parameter, by a non-linear optimization of the multidimensional calibration function, alters the values of the remaining parameters in a way which cannot be predicted (195).

A review of the applicability of the NDO methods is presented in Table 20.

TABLE 20
Applications of NDO methods.

Property	Useful method
1. Molecular geometry	MINDO/3, MNDO, CNDO, INDO, AM1
2. Heat of formation	MINDO/3, MNDO, AM1 some versions of CNDO, INDO
3. Conformational analysis	PCILO, MINDO/3, MNDO, AM1
4. Weak intermolecular interactions, hydrogen bonds	PCILO, CNDO, AM1
5. Reactivity: qualitatively quantitatively	EHT MINDO/3, CNDO , MNDO, AM1
6. Ionization energies (in Koopmans approximation)	MINDO/3, MNDO, CNDO, INDO, AM1
7. Electronic spectra	CNDO/S, INDO/S, MNDOC
8. Dipole moments	CNDO, INDO, MINDO/3, MNDO, AM1
9. ESCA parameters	CNDO, MINDO/3
10. NMR parameters	CNDO, INDO, MINDO/3
11. ESR parameters	INDO
12. Separation of different spin states	INDO
13. Molecules consisting heavy atoms	Quasirelativistic CNDO, INDO, REX
14. Spin-orbit splitting	Relativistic CNDO, REX

Comparison of the applicability of the various NDO versions to reproduce molecular properties is rather problematical. Each version is successful in reproducing at least one characteristic (as a rule the one which was selected for calibration of the semisemiempirical parameters); this is a basic condition for publication of the method. In general, the INDO method is regarder to be more sucessful than the CNDO method while the NDDO (MNDO) method is more sophisticated than the INDO approach. However, the number of parameters increases in this order so that new problems of their proper balance appear.

3.5 EXTENDED HÜCKEL METHOD

This all-valence semiempirical method (abbreviated as EHT: Extended Hückel Theory or MWH: Mulliken-Wolfsberg-Helmholtz) is very simple and popular. It is an extension of the method developed by E. Hückel as early as in 1930 which was applicable to the aromatic compounds (250-258).

The method is based on the one-electron effective Hamiltonian

$$\hat{H} = \sum_{p}^{n} \hat{h}_p^{eff} \qquad [327]$$

In this method the electron repulsion is not explicitly expressed but is included implicitly in the semiempirical parameters used for evaluation of the matrix elements of the effective operator $\hat{h}^{eff}$. The diagonal matrix elements (Coulomb integrals) are given through the ionization energy of the valence orbitals

$$H_{i_A i_A} = <\vartheta_i^A(1)|\hat{h}_1^{eff}|\vartheta_i^A(1) = - I_i^A \qquad [328]$$

and the off-diagonal matrix elements (resonance integrals) are proportional to overlap integral and to a mean value of the diagonal matrix elements

$$H_{i_A j_B} = f(S_{i_A j_B}, H_{i_A i_A}, H_{j_B j_B}) \qquad [329]$$

according to one of the following approximations:

a) according to Wolfsberg and Helmholtz (259)

$$H_{ij} = (1/2)\ K\ S_{ij}(H_{ii} + H_{jj}) \qquad [330]$$

where the proportionality constant $K \in <1;\ 2>$, usually $K = 1.75$;

b) according to Ballhausen and Gray (260)

$$H_{ij} = -\ K\ S_{ij}\ (H_{ii}\ H_{jj})^{1/2} \qquad [331]$$

c) according to Yeranos (261)

$$H_{ij} = 2K\, S_{ij}\, H_{ii}\, H_{jj} / (H_{ii} + H_{jj}) \qquad [332]$$

d) according to Cusachs (262)

$$H_{ij} = (1/2)\, S_{ij}\, (2 - |S_{ij}|)(H_{ii} + H_{jj}) \qquad [333]$$

The matrix of LCAO coefficients C is in the EHT method obtained by solving the matrix equation

$$H\, C^{T} = S\, C^{T}\, E \qquad [334]$$

and the electronic energy is given by the formula

$$E^{el} = \sum_{i,j}^{m} P_{ij}\, H_{ij} = \sum_{\mu}^{occ\,\alpha} \epsilon_{\mu} + \sum_{\mu}^{occ\,\beta} \epsilon_{\mu} \qquad [335]$$

The overlap integrals are calculated using SZ-STOs and for valence d-orbitals using DZ-STOs.

In the role of parameters the ionization energies of valence orbitals occur: VSIP - Valence State Ionization Potential, VSIE - Valence State Ionization Energy, VOIP - Valence Orbital Ionization Potential, VOIE - Valence State Ionization Energy. Constant values of these parameters are used in the EHT version; they are obtained by analysis of atomic spectra. For example, the VOIE value for the transition from state T_a^q to T_b^{q+1} of atom A is (263)

$$\mathrm{VOIE} = E_{av}(A;T_b^{q+1}) - E_{av}(A;T_a^q) + I^A(q) \qquad [336]$$

where the energies of electron configurations E_{av} are averaged over all multiplets and $I^A(q)$ is the ionization energy of the atomic ground state (or of the ion A^{q+}). Selected values of H_{ii} parameters are collected in Table 21.

TABLE 21

Parameters of the EHT method (eV).

Atom		Ionization energy		Atom		Ionization energy		
Z	A	I_s^A	I_p^A	Z	A	I_s^A	I_p^A	I_d^A
1	H	13.6		24	Cr	8.66	5.24	11.22
5	B	15.2	8.5	25	Mn	8.36	5.06	11.59
6	C	21.4	11.4	26	Fe	9.10	5.32	12.6
7	N	26.0	13.4	27	Co	9.21	5.29	13.18
8	O	32.2	14.8	28	Ni	8.86	4.90	12.99
9	F	40.0	18.1	42	Mo	8.34	5.24	10.50
15	P	18.6	14.0	74	W	8.26	5.17	10.37
16	S	20.0	13.3	75	Re	9.36	5.96	12.66
17	Cl	26.3	14.2	78	Pt	9.01	5.47	12.59
35	Br	24.0	12.3					

Substantial improvement of the ETH method is obtained by iterative versions (IEHT - Iterative Extended Hückel Theory). In these methods the VOIE are considered as functions of the effective atomic charge q_A^0 and eventually of the orbital population n_i^A, viz.

a) according to Hinze and Jaffé (264) for atoms H - Ar

$$\mathrm{VOIE}(A,i) = a_i^A + b_i^A\, q_A^0 + c_i^A (q_A^0)^2 \qquad [337]$$

b) according to Cusachs and Reynolds (265-267)

$$\mathrm{VOIE}(A,i) = a_i^A + b_i^A\, q_A^0 + c_i^A\, n_i^A \qquad [338]$$

for atoms Li - Cl (Table 22) and

$$\mathrm{VOIE}(H,1s)\ /\mathrm{eV} = -13.6 - 26.93\, q_H^0 - 13.97\, (q_H^0)^2 + 0.121\, (q_H^0)^3 \qquad [339]$$

for the hydrogen atom;

c) according to Basch et al. (251-253) for atoms Ti - Cu (Table 23)

$$\mathrm{VOIE}(A,i;T) = a_i^{A,T} (q_A^0)^2 + b_i^{A,T}\, q_A^0 + c_i^{A,T} \qquad [340]$$

In this last version, which is configurational dependent, a linear interpolation is used for transition metal elements, namely

$$- H_{dd} = (1 - n_s^A - n_p^A)\mathrm{VOIE}(A,d;d^n) + n_s^A\, \mathrm{VOIE}(A,d;d^{n-1}s^1) + n_p^A\, \mathrm{VOIE}(A,d;d^{n-1}p^1) \qquad [341]$$

$$- H_{ss} = (2 - n_s^A - n_p^A)\mathrm{VOIE}(A,s;d^{n-1}s^1) + (n_s^A - 1)\mathrm{VOIE}(A,s;d^{n-2}s^2) + n_p^A\, \mathrm{VOIE}(A,s;d^{n-2}s^1p^1) \qquad [342]$$

$$- H_{pp} = (2 - n_s^A - n_p^A)\mathrm{VOIE}(A,p;d^{n-1}s^1) + (n_p^A - 1)\mathrm{VOIE}(A,p;d^{n-2}p^2) + n_p^A\, \mathrm{VOIE}(A,p;d^{n-2}s^1p^1) \qquad [343]$$

TABLE 22

VOIP parameters according to Cusachs and Reynolds (248 - 250).

Atom		Parameter (eV)					
Z	A	a_s^A	b_s^A	c_s^A	a_p^A	b_p^A	c_p^A
3	Li	6.50	4.30	1.10	3.90	4.30	0.30
4	Be	11.50	7.20	1.30	6.70	7.20	0.70
5	B	17.00	9.80	1.50	9.60	9.80	1.00
6	C	22.90	11.90	1.70	12.90	11.90	1.50
7	N	29.30	13.70	1.90	16.30	13.70	1.90
8	O	36.20	15.29	2.10	19.90	12.09	2.30
9	F	43.60	16.20	2.30	23.80	16.20	2.80
14	Si	17.88	8.16	1.56	8.85	8.16	0.95
15	P	20.21	9.41	1.02	11.16	9.41	0.42
16	S	26.15	9.70	2.43	13.62	9.70	1.12
17	Cl	30.30	10.34	2.98	15.52	10.36	1.13

TABLE 23

VOIE parameters for d-elements (251 - 253).[a]

Atom			Parameter (10^3 cm^{-1})								
			VOIE(3d)			VOIE(4s)			VOIE(4p)		
Z	A		a	b	c	d	e	f	g	h	i
21	Sc	C	23.2	37.5	49.7	46.1	53.8	60.8	26.1	34.9	31.9
22	Ti	A	17.15	18.45	18.45	9.3	9.3	9.3	7.8	7.8	7.8
		B	60.85	77.85	76.75	50.4	58.5	55.0	35.6	48.9	48.9
		C	27.4	44.6	55.4	48.6	57.2	66.0	26.9	35.9	34.4
23	V	A	15.8	14.0	14.0	8.55	8.55	8.55	7.45	7.45	7.45
		B	68.0	87.0	87.3	54.15	62.95	57.55	45.45	50.85	50.85
		C	31.4	51.4	61.4	51.0	60.4	70.6	27.7	36.8	36.4
24	Cr	A	14.75	9.75	9.75	8.05	8.05	8.05	7.25	7.25	7.25
		B	74.75	95.95	96.95	57.55	66.85	60.45	47.55	52.85	52.85
		C	35.1	57.9	67.7	53.2	63.3	74.7	28.4	37.8	38.1
25	Mn	A	14.1	5.5	5.5	7.6	7.6	7.6	7.2	7.2	7.2
		B	80.8	105.0	106.0	60.9	70.3	63.8	49.3	55.2	55.2
		C	38.6	64.1	74.3	55.3	65.9	78.3	29.2	38.8	39.4
26	Fe	A	13.8	13.8	13.8	7.35	7.35	7.35	7.3	7.3	7.3
		B	86.2	101.5	101.9	63.85	73.05	67.35	50.8	57.8	57.8
		C	41.9	70.0	81.2	57.3	68.3	81.4	29.9	39.7	40.3
27	Co	A	13.85	13.85	13.85	7.25	7.25	7.25	7.55	7.55	7.55
		B	91.15	106.25	105.55	66.65	75.25	71.35	51.95	60.65	60.65
		C	44.8	75.6	88.4	59.1	70.5	84.0	30.7	40.7	40.8
28	Ni	A	14.2	14.2	14.2	7.35	7.35	7.35	7.95	7.95	7.95
		B	95.5	110.7	108.2	69.05	77.05	75.65	52.85	63.75	63.75
		C	47.6	80.9	95.9	60.8	72.3	86.0	31.4	41.6	40.9
29	Cu	A	15.05	15.05	15.05	7.6	7.6	7.6	8.45	8.45	8.45
		B	98.95	114.65	109.75	71.3	78.1	80.3	53.55	67.15	67.15
		C	50.30	86.00	103.75	62.3	74.0	87.6	32.1	42.6	40.6
30	Zn	C					75.3	88.6		43.5	39.9

[a] Electron configurations: a - d^n, b - $d^{n-1}s^1$, c - $d^{n-1}p^1$, d - $d^{n-1}s^1$, e - $d^{n-2}s^2$, f - $d^{n-2}s^1p^1$, g - $d^{n-1}p^1$, h - $d^{n-2}p^2$, i - $d^{n-2}s^1p^1$. 1 eV ≈ 8066 cm^{-1}.

The dependence of the diagonal matrix elements of the effective Hamiltonian on the effective charge and orbital population requires an iterative solution to eq. [334] until self-consistency. Therefore this method is abbreviated as SCC (Self-Consistent Charge) or SCCC (Self-Consistent Charge and Configuration) method.

In the novel parametrization initiated by Anno and Sakai (271-273) the following expression is used

$$- H_{ii} = \mathrm{VOIE}(A,i;d^z s^x p^y) = B_1 + B_2 x + B_3 y + B_4 x^2 + B_5 xy + B_6 y^2 + + B_7 z + B_8 xz + B_9 yz + B_{10} z^2 + (B_{11} + B_{12} x + B_{13} y + B_{14} z) Z_A + + B_{15} Z_A^2 \qquad [344]$$

where the values of B_1 through B_{15} parameters have been calculated for a whole period of elements. These parameters have been published for electron configurations:

a) $K^2 2s^x 2p^y$ of elements Be - F (272)

b) $K^2 L^8 3s^x 3p^y$ of elements Mg - Cl (274)

c) $K^2 L^8 3s^2 3p^6 3d^z 4s^x 4p^y$ of elements Sc - Cu (271)

d) $K^2 L^8 M^{18} 4s^x 4p^y$ of elements Zn - Kr (275)

e) $K^2 L^8 M^{18} 4s^2 4p^6 4d^z 5s^x 5p^y$ of elements Y - Cd (276)

f) $K^2 L^8 M^{18} 4s^2 4p^6 4d^{10} 5s^x 5p^y$ of elements Ag - Xe (277)

g) $K^2 L^8 M^{18} N^{32} 5s^2 5p^6 5d^z 6s^x 6p^y$ of elements Hf - Bi (278).

The Extended Hückel method and its iterative versions are frequently used to study coordination compounds. The method contributed to the formulation of the Woodwaard-Hoffmann rules which can be used in predicting the courses of various organic and inorganic reactions. On the other hand, the method exhibits some drawbacks, among which the absence of the interelectronic repulsion is critical: the method is not capable of reproducing many important properties, namely those dependent on the exchange interaction. For this purpose some additional corrections to electron repulsion have been proposed (279).

In its original formulation the Hückel method assumes a σ-π separability, according to which the electronic Hamiltonian $\hat{H}^{el}$ is split into $\hat{H}_\sigma$ and $\hat{H}_\pi$ components

$$\hat{H}_\sigma = \sum_i^{n_\sigma} \{-(\hbar^2/2m_e)\nabla_i^2 - \sigma_{SI} \sum_A^N Z_A/r_{iA}\} + \sigma_{SI} \sum_i^{n_\sigma} \sum_{<j}^{n_\sigma} (1/r_{ij}) \qquad [345]$$

$$\hat{H}_\pi = \sum_k^n \hat{h}_k^{core} + \sigma_{SI} \sum_{k<l}^{n} \sum^{n} (1/r_{kl}) \qquad [346]$$

for k, l $\in$ $<n_\sigma + 1, n>$ running over π-electrons. The one-electron operator $\hat{h}_k^{core}$ involves the effective potential, given by the nuclei, inner-shell electrons and σ-electrons, which acts to the π electron

$$\hat{h}_k^{core} = -(\hbar^2/2m_e)\nabla_k^2 - \sigma_{SI} \sum_A^N Z_A/r_{kA} + $$

$$+ \sigma_{SI} \sum_i^{n_\sigma} (\langle i|r_{12}^{-1}|ik\rangle - \langle i|r_{12}^{-1}|ki\rangle) \qquad [347]$$

Accordingly the total electronic energy consists of E_σ and E_π contributions

$$E^{el} = E_\sigma + E_\pi = \langle\Phi_\sigma|\hat{H}_\sigma|\Phi_\sigma\rangle + \langle\Phi_\pi|\hat{H}_\pi|\Phi_\pi\rangle \qquad [348]$$

where Φ_σ and Φ_π are the determinantal, mutually orthogonal, wave functions corresponding to σ and π molecular orbitals, respectively.

The HMO method is purely empirical and based on these assumptions:

a) all diagonal matrix elements h_{ii} of the effective Hamiltonian $\hat{H}_\pi$ are set to α quantities;

b) the off-diagonal matrix elements h_{ij} for adjaced p-orbitals (adjaced atoms) equal to β quantities and the rest of them is put zero;

c) overlap integrals are neglected.

Within these approximations, the secular equation is solved to yield the energies and LCAO coefficients of π-molecular orbitals.

Various versions of the HMO method differ one from another in specifying the choice of α and β integrals and their eventual dependence on the atomic charge or orbital population.

3.6 INCLUSION OF RELATIVISTIC EFFECTS

3.6.1 Dominant Relativistic Terms

The inclusion of relativistic effects into the MO-LCAO-SCF celculations of the molecules is important when studying the molecules consisting of heavy atoms.

Basic equation for relativistic quantum chemistry is the Dirac equation: equation [32] of Chapter 2. For a single electron in the central potential field V(r)

$$\{c \sum_{n=1}^{3} \hat{\gamma}_n \hat{p}_n + \hat{\gamma}_4 m_e c^2 + eV(r)\}\psi_1 = \epsilon\, \psi_1 \qquad [349]$$

or simply

$$\hat{h}_1\, \psi_1 = \epsilon\, \psi_1 \qquad [350]$$

where ψ_1 is a four-component spinor. For many-electron systems a relativistic Hartree-Fock approximation is applied in which the wave function is approximated by a single Slater determinant formed of one-particle four-component spinors

$$\Psi = \hat{A}' \{ \prod_{i}^{n} \psi_i(i) \} = |\psi_1(1)\ \psi_2(2)\ \ldots\ \psi_n(n)| \qquad [351]$$

The electronic Hamiltonian has the form of

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i<j} \sigma_{SI}\, r_{ij}^{-1} \qquad [352]$$

so that one-electron relativistic effects are exactly covered whereas the interelectron repulsion is taken in the nonrelativistic limit. The **Dirac-Fock method** is based on these assumptions so that the following equation has to be solved

$$\hat{H}\ \underline{\Psi} = E\ \underline{\Psi} \qquad [353]$$

The non-relativistic limit is obtained by a simple substitution of the speed of light in the Dirac Hamiltonian for $c \to \infty$. The above method may be extended by considering additional relativistic terms according to Table 3 of Chapter 2. According to (280), the dominant relativistic corrections in heavier many-electron systems are represented by the kinetic energy correction proportional to $\hat{p}_i^4$, the spin-orbit interaction and the Darwin term. The Darwin corrections appear by decomposition of the four-component Dirac equation into the two-component form, when the electron cannot be considered as a point charge but rather as a diffuse charge cloud of definite size.

The principal atomic relativistic effects are the relativistic contraction of orbitals, the spin-orbit splitting and the indirect relativistic expansion of diffuse orbitals (281).

1. **Relativistic Contraction.** In hydrogen-like atoms, the probability function maximum for the 1s electron is localized at a distance $\langle r\rangle_{max}$ from the nucleus which is proportional to the Bohr radius a: $\langle r\rangle_{max} = an^2/Z$. The Bohr radius $a = 4\pi\epsilon_0\hbar^2/me^2 = a_0(m_e/m)$ depends on the electron mass m which is a function of its velocity v according to the Einstein formula $m_e = m\ /[1 - (v/c)^2]^{1/2}$. For Z = 80 (Hg atom) an estimate of the radial velocity at the 1s orbital is $\langle v_r\rangle = \langle 1s|v_r|1s\rangle \approx 0.58$ c so that the electron mass is $m \approx 1.23\ m_e$. As a consequence of the greater electron mass the Bohr radius decreases and thus the mean orbital radius contracts due to relativistic effects (in the given example by 23 %). The remaining orbitals, orthogonal to 1s, will also contract because

$$\int_0^\infty R_{1s}(r)\ R_{ns}(r)\ r^2\ dr = 0 \qquad [354]$$

requires a shift of the nodal planes towards the nucleus. The p-orbitals and the inner d-orbitals contract in an analogous way. The contraction of the subshell $p_{1/2}$ is comparable to that of the $s_{1/2}$ orbital whereas the subshell $p_{3/2}$ is subject to less contraction.

2. **Spin-Orbit Splitting.** Within the relativistic approach the orbital angular momentum $\mathbf{l}$ and the spin angular momentum $\mathbf{s}$ cannot be separately considered but only coupled in the total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$. The corresponding quantum number j differen-

tiates between the electron subshells $p_{1/2}$ and $p_{3/2}$, $d_{3/2}$ and $d_{5/2}$, etc. The subshell splitting (e.g. energy difference of $p_{1/2}$ and $p_{3/2}$ levels) is a relativistic effect and can adopt values of several eV for heavy atoms. Whereas the lower energy subshell $p_{1/2}$ may be occupied by two electrons, the $p_{3/2}$ subshell may be occupied by four electrons.

3. **Indirect Relativistic Expansion.** The d- and f-electrons possess high angular momenta and thus occur near the nucleus only with low probability. Since the s- and p-electrons undergo relativistic contraction of the corresponding shell, then the screening of the nuclear charge becomes larger. Therefore the d- and f-electrons feel a weaker nuclear attraction and consequently the corresponding shells are expanded (energetically destabilized). The mutual relationship between the relativistic contraction and expansion is illustrated in Fig. 12.

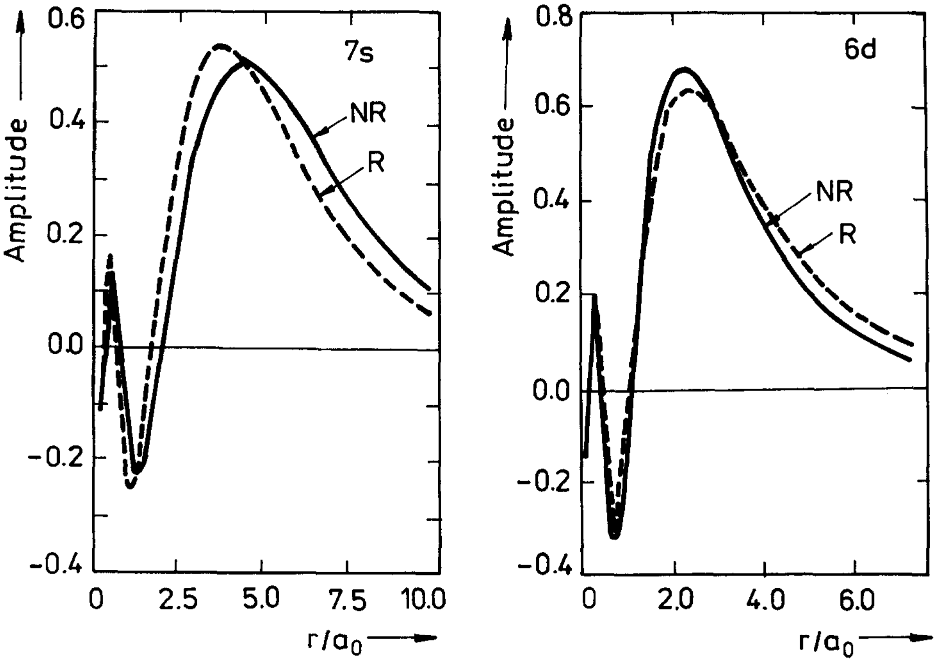

Fig. 12. Radial relativistic contraction of the 7s orbital and expansion of the 6d orbital for the uranium atom. R - relativistic calculation; NR - nonrelativistic one.

The one-electron four-component wave function in the central potential field has the form

$$\psi^{(4)}_{nkm}(r,\vartheta,\varphi) = \begin{pmatrix} g_{nk}(r) \ \chi^{(2)}_{km}(\vartheta,\varphi) \\ if_{nk}(r) \ \chi^{(2)}_{-km}(\vartheta,\varphi) \end{pmatrix} \qquad [355]$$

where g(r) and f(r) are the radial functions obeying the normalization condition

$$\int_0^\infty [g^2(r) + f^2(r)]\, r^2\, dr = 1 \qquad [356]$$

The functions $\chi^{(2)}_{km}$ are two-component spinors which may be expressed through (complex) normalized spherical harmonics Y_{l,m_l}

$$\chi^{(2)}_{km} = \begin{pmatrix} C(j,m;l,m - 1/2,1/2,+1/2)\ Y_{l,m-1/2} \\ C(j,m;l,m + 1/2,1/2,-1/2)\ Y_{l,m+1/2} \end{pmatrix} \qquad [357]$$

for quantum numbers $k = \pm(j + 1/2)$ and $l = j \pm 1/2$ by the constraint $m = m_j = m_l + m_s$. The necessary Clebsh-Gordan coefficients $C(j,m;l - m_s,1/2,m_s)$ are given in Table 24.

TABLE 24

Selected Clebsh-Gordan coefficients.

j	m_s	$C(j,m;l,m - m_s,1/2,m_s)$
$l + 1/2$	$1/2$	$[(l + m + 1/2)/(2l + 1)]^{1/2}$
$l - 1/2$	$1/2$	$-[(l - m + 1/2)/(2l + 1)]^{1/2}$
$l + 1/2$	$-1/2$	$[(l - m + 1/2)/(2l + 1)]^{1/2}$
$l - 1/2$	$-1/2$	$[(l - m + 1/2)/(2l + 1)]^{1/2}$

The common set of eigenfunctions of operators $\hat{l}^2$, $\hat{s}^2$, $\hat{j}^2$ and $\hat{j}_z$ depends on the relativistic quantum numbers k and m_j

$$\hat{l}^2\ |\chi_{km}\rangle = l(l + 1)\ \hbar^2\ |\chi_{km}\rangle \qquad [358]$$

$$\hat{s}^2\ |\chi_{km}\rangle = (3/4)\ \hbar^2\ |\chi_{km}\rangle \qquad [359]$$

$$\hat{j}^2\ |\chi_{km}\rangle = j(j + 1)\ \hbar^2\ |\chi_{km}\rangle \qquad [360]$$

$$\hat{j}_z\ |\chi_{km}\rangle = m_j\ \hbar\ |\chi_{km}\rangle \qquad [361]$$

The mutual relationship among the quantum numbers is given in Table 25.

Relativistic *ab initio* calculations for diatomic molecules begin with generation of a numerical basis set by solving the radial part of the Dirac equation; the molecular integrals are then calculated by a numerical integration (282).

TABLE 25
Relationships among quantum numbers for relativistic AOs.

Quantum number	Atomic orbital s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
l	0	1	1	2	2	3	3
j	1/2	1/2	3/2	3/2	5/2	5/2	7/2
k	-1	+1	-2	+2	-3	+3	-4

The Dirac-Fock method for molecules (283) is covered by numerous approximate versions; some will be discussed below.

1. The **One-Centre Expansion** (OCE) method is applicable to hydrides of the XH_n type. It is based on expansion of the proton potential around the heavy centre X (280)

$$r_H^{-1} = \sum_{l=0}^{\infty} (r_<^{l})/(r_>^{l+1})\ P_l(\cos \vartheta_X) \qquad [362]$$

where P_l are associated Legendre polynomials; $r_<$ and $r_>$ are the lower and upper component relative to r_H (see Chapter 2). The method is successful in the reproduction of equilibrium interatomic distances and harmonic force constants. Some valence orbital energy illustrative calculations are compiled in Table 26.

TABLE 26
Ionization energies I (eV), Dirac-Fock orbital energies ϵ (eV) and their relativistic changes.

Atom	Ionization energy I_1	I_2	Orbital energy ns	$(n-1)d_{5/2}$	$\epsilon_{rel}/\epsilon_{nr}$ ns	$(n-1)d_{5/2}$
Cu	7.72	20.29	6.66	12.91	1.03	0.97
Ag	7.57	21.48	6.45	13.65	1.08	0.93
Au	9.22	20.5	7.94	11.67	1.32	0.82

2. **Relativistic Pseudopotential Methods** (65,284) link together the advantages of effective core potentials and SCF calculations in the valence basis set with partial inclusion of relativistic effects. The method is useful in studying compounds of the heaviest elements such as UF_6.

3. The **Dirac-Slater method** (DS) is a relativistic modification of the Xα method. In the DS-Xα-DVM version the basis set functions $\chi_j(r_k)$ are represented by relativistic symmetry orbitals which are

obtained by a linear combination of the four-component AOs of different atoms (285,286). In the DS-Xα-SW version the wave functions obey the integral equation (287)

$$\psi(r) = \int G(r,r')\,[V(r') - V_{II}]\,\psi(r')\,dr' \qquad [363]$$

where the Green function G(r,r') is defined by the Dirac-type equation

$$\{c\sum_{n=1}^{3} \hat{\gamma}_n\hat{p}_n + \hat{\gamma}_4 m_e c^2 - \epsilon\}G(r,r') = -I\,\delta(r - r') \qquad [364]$$

and the muffin-tin potential (see Section 3.3.3) is given as

$$V(r) = \sum_j V_j^I(r_j) + V^{II} + V_w(r_w) \qquad [365]$$

4. The **Relativistic Extended Hückel** method (REX) considers a doubled basis set with Slater-type orbitals having different exponents for $s_{1/2} = s$, $p_{1/2} = \bar{p}$, $p_{3/2} = p$, $d_{3/2} = \bar{d}$, $d_{5/2} = d$, $f_{5/2} = \bar{f}$ and $f_{7/2} = f$ subshells (288-290). The set of exponents was obtained from the formula $\zeta_i^A = (n_i + 1/2)/<r_i>$ or $\zeta_i^A = n_i/r_i^{max}$ with r_i representing calculated Dirac-Fock atomic values (291). The diagonal matrix elements of the one-electron effective Hamiltonian are approximated by values for the atomic orbital energies obtained from atomic Dirac-Fock calculations. A Full list of these parameters is reproduced in Table 27. The off-diagonal matrix elements are expressed by standard EHT approximations dependent on the overlap integrals and diagonal matrix elements. Calculation of the overlap integrals is carried out in the usual (real) basis set of l-functions (real spherical harmonics) and then a transformation is applied into the basis set of complex spinors using appropriate Clebsh- Gordan coefficients. In practical calculations a quaternionic storage mode is used (292) which allows a reduction of the memory requirements.

More elaborate versions use a relativistic double-zeta basis set which is important for valence d- and f-orbitals (293-296). These were derived from the best fit of the Dirac-Fock charge density (in a numerical form) by DZ-STOs. An iterative version of the REX method has also been proposed; all these facilities have been integrated into the computer program ITEREX (292).

The resulting wave function of REX or ITEREX methods is four-component.

5. The **Quasirelativistic CNDO/1 and INDO/1 Methods** (177,223,297) are based on the assumption that the dominant relativistic effect is represented by the orbital relaxation (expansion and/or contrac-

tion) as exemplified by Fig. 13 for the platinum atom. In these versions spin-orbit coupling is switched off. Orbital relaxation is treated through the set of parameters: orbital exponents ζ_i^A and Dirac-Fock orbital energies ϵ_i^A. These parameters are taken from the REX method and averaged over the spin-orbit components as

$$\zeta_l = [l\ \zeta_{l-1/2} + (l + 1)\zeta_{l+1/2}]/(2l + 1) \qquad [366]$$

$$\epsilon_l = [l\ \epsilon_{l-1/2} + (l + 1)\epsilon_{l+1/2}]/(2l + 1) \qquad [367]$$

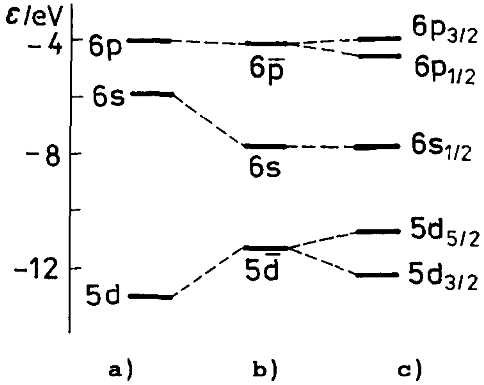

Fig. 13. Calculated orbital energies for a Pt atom: a - non-relativistic Hartree-Fock, b - averaged (quasirelativistic), c - relativistic Dirac-Fock.

The parametrization of this class of methods utilizes the following expression for the atomic potential

$$U_i^A = - I_i^A + G_{ii}^{AA} - \sum_j N_j^A G_{ij}^{AA} \qquad [368]$$

with ionization potentials given through atomic orbital energies

$$I_i^A = - \epsilon_i^A \qquad [369]$$

Then the diagonal matrix elements of the one-electron part of the Fock operator are

$$H_{i_A i_A} = U_i^A - \sum_{C \neq A} Z_C^C N_j^C G_{ij}^{AC} \qquad [370]$$

where N_j^C is the occupation number of the i-th shell (reference electron configuration) and G_{ij}^{AC} stands for the mean interelectronic repulsion between shells i and j. At the CNDO level only the monopole F^0 terms contribute to G_{ij}^{AA} whereas at the INDO levels the exact contribution of the corresponding Slater-Condon parameters F^k and G^k is considered. The necessary one-electron and two-electron integrals are calculated by a direct integration over STOs.

TABLE 27

Parameters of REX and relativistic CNDO/1 methods.

		Orbital exponents						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
		1s						
1 H	$1s^1$	1.0						
2 He	$1s^2$	1.618						
		2s	$2\bar{p}$	2p				
3 Li	$2s^1$	0.645						
	$2p^1$		0.524	0.524				
4 Be	$2s^2$	0.944						
	$2s^12p^1$		0.875	0.875				
5 B	$2s^22p^1$	1.265	1.134	1.134				
6 C	$2s^22p^2$	1.577	1.435	1.434				
7 N	$2s^22p^3$	1.886	1.729	1.728				
8 O	$2s^22p^4$	2.194	2.020	2.017				
9 F	$2s^22p^5$	2.501	2.308	2.303				
10 Ne	$2s^22p^6$	2.807	2.595	2.588				
		3s	$3\bar{p}$	3p				
11 Na	$3s^1$	0.833						
	$3p^1$		0.611	0.611				
12 Mg	$3s^2$	1.078						
	$3s^13p^1$		0.863	0.861				
13 Al	$3s^23p^1$	1.349	1.020	1.018				
14 Si	$3s^23p^2$	1.592	1.257	1.254				
15 P	$3s^23p^3$	1.821	1.481	1.476				
16 S	$3s^23p^4$	2.042	1.696	1.689				
17 Cl	$3s^23p^5$	2.258	1.907	1.897				
18 Ar	$3p^23p^6$	2.471	2.114	2.102				
		4s	$4\bar{p}$	4p	$3\bar{d}$	3d		
19 K	$4s^1$	0.861						
	$4p^1$		0.672	0.670				
	$3d^1$				0.364	0.364		
20 Ca	$4s^2$	1.071						
	$4s^14p^1$		0.895	0.891				
	$4s^13d^1$				1.872	1.865		
21 Sc	$4s^23d^1$	1.143			2.072	2.067		
	$4s^14p^13d^1$		0.954	0.950				

TABLE 27
(Continued)

		Orbital energies (eV)						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
		1s						
1 H	$1s^1$	13.606						
2 He	$1s^2$	24.980						
		2s	$2\bar{p}$	2p				
3 Li	$2s^1$	5.343						
	$2p^1$		3.499	3.499				
4 Be	$2s^2$	8.417						
	$2s^1 2p^1$		5.631	5.631				
5 B	$2s^2 2p^1$	13.468	8.431	8.428				
6 C	$2s^2 2p^2$	19.391	11.073	11.065				
7 N	$2s^2 2p^3$	26.253	13.847	13.829				
8 O	$2s^2 2p^4$	34.080	16.784	16.745				
9 F	$2s^2 2p^5$	42.885	19.901	19.828				
10 Ne	$2s^2 2p^6$	52.677	23.207	23.083				
		3s	$3\bar{p}$	3p				
11 Na	$3s^1$	4.962						
	$3p^1$		2.977	2.975				
12 Mg	$3s^2$	6.897						
	$3s^1 3p^1$		4.170	4.164				
13 Al	$3s^2 3p^1$	10.734	5.713	5.698				
14 Si	$3s^2 3p^2$	14.844	7.594	7.563				
15 P	$3s^2 3p^3$	19.306	9.564	9.508				
16 S	$3s^2 3p^4$	24.145	11.647	11.555				
17 Cl	$3s^2 3p^5$	29.378	13.857	13.716				
18 Ar	$3p^2 3p^6$	35.010	16.201	15.995				
		4s	$4\bar{p}$	4p	$3\bar{d}$	3d		
19 K	$4s^1$	4.028						
	$4p^1$		2.603	2.597				
	$3d^1$				1.580	1.580		
20 Ca	$4s^2$	5.342						
	$4s^1 4p^1$		3.577	3.561				
	$4s^1 3d^1$				3.228	3.226		
21 Sc	$4s^2 3d^1$	5.753			9.145	9.124		
	$4s^1 4p^1 3d^1$		3.728	3.739				

TABLE 27
(Continued)

		Orbital exponents						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
22 Ti	$4s^2 3d^2$	1.203			2.338	2.332		
	$4s^1 4p^1 3d^2$		1.004	0.998				
23 V	$4s^2 3d^3$	1.257			2.577	2.568		
	$4s^1 4p^1 3d^2$		1.048	1.040				
24 Cr	$4s^1 3d^5$	1.186			2.488	2.474		
	$4p^1 3d^5$		0.894	0.889				
25 Mn	$4s^2 3d^5$	1.357			3.011	2.998		
	$4s^1 4p^1 3d^5$		1.123	1.113				
26 Fe	$4s^2 3d^6$	1.404			3.216	3.200		
	$4s^1 4p^1 3d^5$		1.155	1.144				
27 Co	$4s^2 3d^7$	1.450			3.416	3.396		
	$4s^1 4p^1 3d^7$		1.186	1.174				
28 Ni	$4s^2 3d^8$	1.494			3.613	3.588		
	$4s^1 4p^1 3d^8$		1.215	1.203				
29 Cu	$4s^1 3d^{10}$	1.380			3.532	3.493		
	$4p^1 3d^{10}$		0.989	0.980				
30 Zn	$4s^2 3d^{10}$	1.580			3.998	3.963		
	$4s^1 4p^1 3d^{10}$		1.267	1.251				
31 Ga	$4s^2 4p^1 3d^{10}$	1.838	1.327	1.309	4.439	4.406		
32 Ge	$4s^2 4p^2 3d^{10}$	2.057	1.569	1.544	4.851	4.817		
33 As	$4s^2 4p^3$	2.258	1.783	1.751				
34 Se	$4s^2 4p^4$	2.449	1.981	1.942				
35 Br	$4s^2 4p^5$	2.633	2.169	2.124				
36 Kr	$4s^2 4p^6$	2.811	2.350	2.298				
		5s	$5\bar{p}$	5p	$4\bar{d}$	4d		
37 Rb	$5s^1$	0.992						
	$5p^1$		0.782	0.772				
	$4d^1$				0.515	0.516		
38 Sr	$5s^2$	1.205						
	$5s^1 5p^1$		1.010	0.994				
	$5s^1 4d^1$				1.611	1.594		
39 Y	$5s^2 4d^1$	1.306			1.799	1.785		
	$5s^2 5p^1$		1.097	1.077				
40 Zr	$5s^2 4d^2$	1.382			2.069	2.050		
	$5s^2 5p^1 4d^1$		1.162	1.139				

TABLE 27
(Continued)

Z	Configuration	Orbital energies (eV)						
		s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
22 Ti	$4s^2 3d^2$	6.086			10.824	10.786		
	$4s^1 4p^1 3d^2$		3.877	3.863				
23 V	$4s^2 3d^3$	6.383			12.315	12.256		
	$4s^1 4p^1 3d^2$		3.977	3.951				
24 Cr	$4s^1 3d^5$	5.739			8.654	8.572		
	$4p^1 3d^5$		3.196	3.181				
25 Mn	$4s^2 3d^5$	6.923			15.003	14.882		
	$4s^1 4p^1 3d^5$		4.106	4.120				
26 Fe	$4s^2 3d^6$	7.176			16.258	16.095		
	$4s^1 4p^1 3d^5$		4.204	4.168				
27 Co	$4s^2 3d^7$	7.421			17.474	17.260		
	$4s^1 4p^1 3d^7$		4.261	4.221				
28 Ni	$4s^2 3d^8$	7.661			18.662	18.385		
	$4s^1 4p^1 3d^8$		4.310	4.266				
29 Cu	$4s^1 3d^{10}$	6.661			13.276	12.906		
	$4p^1 3d^{10}$		3.395	3.374				
30 Zn	$4s^2 3d^{10}$	8.126			20.977	20.537		
	$4s^1 4p^1 3d^{10}$		4.394	4.343				
31 Ga	$4s^2 4p^1 3d^{10}$	11.818	5.702	5.604	32.025	31.488		
32 Ge	$4s^2 4p^2 3d^{10}$	15.523	7.417	7.236	44.049	43.391		
33 As	$4s^2 4p^3$	19.397	9.143	8.858				
34 Se	$4s^2 4p^4$	23.477	10.926	10.516				
35 Br	$4s^2 4p^5$	27.782	12.787	12.226				
36 Kr	$4s^2 4p^6$	32.321	14.736	13.996				
		5s	$5\bar{p}$	5p	$4\bar{d}$	4d		
37 Rb	$5s^1$	3.811						
	$5p^1$		2.470	2.447				
	$4d^1$				1.625	1.627		
38 Sr	$5s^2$	4.932						
	$5s^1 5p^1$		3.317	3.263				
	$5s^1 4d^1$				2.944	2.935		
39 Y	$5s^2 4d^1$	5.479			6.331	6.274		
	$5s^2 5p^1$		3.557	3.489				
40 Zr	$5s^2 4d^2$	5.859			7.977	7.875		
	$5s^2 5p^1 4d^1$		3.716	3.636				

TABLE 27
(Continued)

		Orbital exponents						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
41 Nb	$5s^1 4d^4$	1.358			2.127	2.100		
	$5s^1 5p^1 4d^3$		1.218	1.191				
42 Mo	$5s^1 5d^5$	1.405			2.347	2.315		
	$5p^1 4d^5$		1.089	1.064				
43 Tc	$5s^2 4d^5$	1.558			2.705	2.674		
	$5s^1 5p^1 4d^5$		1.311	1.276				
44 Ru	$5s^1 4d^7$	1.488			2.744	2.702		
	$5s^1 5p^1 4d^6$		1.351	1.312				
45 Rh	$5d^1 4d^8$	1.525			2.929	2.882		
	$5p^1 4d^8$		1.162	1.127				
46 Pd	$5s^1 5p^1 4d^8$	1.961						
	$5p^1 4d^9$		1.180	1.144				
	$4d^{10}$				2.944	2.876		
47 Ag	$5s^1 4d^{10}$	1.594			3.224	3.285		
	$5p^1 4d^{10}$		1.196	1.157				
48 Cd	$5s^2 4d^{10}$	1.781			3.588	3.594		
	$5s^1 5p^1 4d^{10}$		1.483	1.428				
49 In	$5s^2 5p^1 4d^{10}$	2.018	1.499	1.445	3.885	3.890		
50 Sn	$5s^2 5p^2 4d^{10}$	2.218	1.732	1.664	4.162	4.107		
51 Sb	$5s^2 5p^3$	2.399	1.933	1.853				
52 Te	$5s^2 5p^4$	2.568	2.117	2.025				
53 I	$5s^2 5p^5$	2.731	2.289	2.198				
54 Xe	$5s^2 5p^6$	2.888	2.454	2.339				
		6s	$6\bar{p}$	6p	$5\bar{d}$	5d		
55 Cs	$6s^1$	1.068						
	$6p^1$		0.866	0.842				
	$5d^1$				0.793	0.796		
56 Ba	$6s^2$	1.279						
	$6s^1 6p^1$		1.097	1.059				
	$6s^1 5d^1$				1.879	1.842		
57 La	$6s^2 5d^1$	1.377			1.920	1.889		
	$6s^1 6p^1 5d^1$		1.184	1.137				
		6s	$5\bar{p}$	5p	$5\bar{d}$	5d	$4\bar{f}$	4f
58 Ce	$6s^2 5p^6 5d^1 4f^1$	1.398	3.205	3.066	1.952	1.919	4.342	4.576

TABLE 27
(Continued)

		Orbital energies (eV)						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
41 Nb	$5s^1 4d^4$	5.593			7.008	6.866		
	$5s^1 5p^1 4d^3$		3.837	3.747				
42 Mo	$5s^1 5d^5$	5.770			8.206	8.003		
	$5p^1 4d^5$		3.176	3.118				
43 Tc	$5s^2 4d^5$	6.679			12.510	12.225		
	$5s^1 5p^1 4d^5$		4.016	3.906				
44 Ru	$5s^1 4d^7$	6.074			10.605	10.251		
	$5s^1 5p^1 4d^6$		4.085	3.966				
45 Rh	$5d^1 4d^8$	6.208			11.823	11.377		
	$5p^1 4d^8$		3.287	3.218				
46 Pd	$5s^1 5p^1 4d^8$	9.224						
	$5p^1 4d^9$		3.314	3.243				
	$4d^{10}$				9.267	8.702		
47 Ag	$5s^1 4d^{10}$	6.453			14.313	13.646		
	$5p^1 4d^{10}$		3.338	3.226				
48 Cd	$5s^2 4d^{10}$	7.658			20.089	19.290		
	$5s^1 5p^1 4d^{10}$		4.281	4.127				
49 In	$5s^2 5p^1 4d^{10}$	10.790	5.478	5.214	28.090	27.132		
50 Sn	$5s^2 5p^2 4d^{10}$	13.883	7.008	6.568	36.362	35.220		
51 Sb	$5s^2 5p^3$	17.070	8.535	7.892				
52 Te	$5s^2 5p^4$	20.390	10.099	9.223				
53 I	$5s^2 5p^5$	23.860	11.719	10.580				
54 Xe	$5s^2 5p^6$	27.487	13.404	11.968				
		6s	$6\bar{p}$	6p	$5\bar{d}$	5d		
55 Cs	$6s^1$	3.490						
	$6p^1$		2.329	2.279				
	$5d^1$				1.768	1.771		
56 Ba	$6s^2$	4.440						
	$6s^1 6p^1$		3.105	2.991				
	$6s^1 5d^1$				3.625	3.582		
57 La	$6s^2 5d^1$	4.888			6.477	6.350		
	$6s^1 6p^1 5d^1$		3.315	3.175				
		6s	$5\bar{p}$	5p	$5\bar{d}$	5d	$4\bar{f}$	4f
58 Ce	$6s^2 5p^6 5d^1 4f^1$	4.968	31.583	28.613	6.501	6.364	14.732	14.449

TABLE 27
(Continued)

		Orbital exponents						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
59 Pr	$6s^2 5p^6 4f^3$	1.345	3.189	3.038			4.138	4.090
	$6s^2 5p^6 5d^1 4f^2$				1.979	1.944		
60 Nd	$6s^2 5p^6 4f^4$	1.363	3.262	3.100			4.361	4.308
	$6s^2 5p^6 5d^1 4f^3$				2.001	1.963		
61 Pm	$6s^2 5p^6 4f^5$	1.382	3.334	3.161			4.565	4.506
	$6s^2 5p^6 5d^1 4f^4$				2.019	1.979		
62 Sm	$6s^2 5p^6 4f^6$	1.399	3.405	3.219			4.755	4.689
	$6s^2 5p^6 5d^1 4f^5$				2.035	1.992		
63 Eu	$6s^2 5p^6 4f^7$	1.417	3.474	3.276			4.936	4.862
	$6s^2 5p^6 5d^1 4f^6$				2.046	2.002		
64 Gd	$6s^2 5p^6 5d^1 4f^7$	1.520	3.636	3.429	2.056	2.009	5.429	5.364
65 Tb	$6s^2 5p^6 4f^9$	1.451	3.612	3.387			5.275	5.185
	$6s^2 5p^6 5d^1 4f^8$				2.062	2.012		
66 Dy	$6s^2 5p^6 4f^{10}$	1.468	3.680	3.441			5.437	5.337
	$6s^2 5p^6 5d^1 4f^9$				2.066	2.014		
67 Ho	$6s^2 5p^6 4f^{11}$	1.485	3.749	3.494			5.595	5.485
	$6s^2 5p^6 5d^1 4f^{10}$				2.066	2.012		
68 Er	$6s^2 5p^6 4f^{12}$	1.502	3.817	3.547			5.750	5.628
	$6s^2 5p^6 5d^1 4f^{11}$				2.065	2.008		
69 Tm	$6s^2 5p^6 4f^{13}$	1.519	3.886	3.599			5.902	5.767
	$6s^2 5p^6 5d^1 4f^{12}$				2.060	2.001		
70 Yb	$6s^2 5p^6 4f^{14}$	1.536	3.955	3.651			6.051	5.903
	$6s^2 5p^6 5d^1 4f^{13}$				2.052	1.992		
71 Lu	$6s^2 5p^6 5d^1 4f^{14}$	1.666	4.124	3.810	2.041	1.979	6.482	6.355
		6s	$6\bar{p}$	6p	$5\bar{d}$	5d		
72 Hf	$6s^2 5d^2$	1.760			2.353	2.273		
	$6s^1 6p^1 5d^2$		1.486	1.371				
73 Ta	$6s^2 5d^3$	1.841			2.598	2.504		
	$6s^1 6p^1 5d^3$		1.557	1.426				
74 W	$6s^2 5d^4$	1.915			2.811	2.705		
	$6s^1 6p^1 5d^4$		1.621	1.474				
75 Re	$6s^2 5d^5$	1.984			3.005	3.056		
	$6s^1 6p^1 5d^5$		1.680	1.518				
76 Os	$6s^2 5d^6$	2.049			3.187	3.058		
	$6s^1 6p^1 5d^6$		1.733	1.555				

TABLE 27
(Continued)

		Orbital energies (eV)						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
59 Pr	$6s^2 5p^6 4f^3$	4.674	29.243	26.249			9.089	8.782
	$6s^2 5p^6 5d^1 4f^2$				6.491	6.346		
60 Nd	$6s^2 5p^6 4f^4$	4.739	30.135	26.894			10.045	9.666
	$6s^2 5p^6 5d^1 4f^3$				6.455	6.304		
61 Pm	$6s^2 5p^6 4f^5$	4.803	30.998	27.500			10.855	10.398
	$6s^2 5p^6 5d^1 4f^4$				6.400	6.242		
62 Sm	$6s^2 5p^6 4f^6$	4.865	31.843	28.077			11.551	11.009
	$6s^2 5p^6 5d^1 4f^5$				6.328	6.165		
63 Eu	$6s^2 5p^6 4f^7$	4.926	32.679	28.632			12.154	11.518
	$6s^2 5p^6 5d^1 4f^6$				6.242	6.075		
64 Gd	$6s^2 5p^6 5d^1 4f^7$	5.438	37.340	32.700	6.144	5.973	20.111	19.349
65 Tb	$6s^2 5p^6 4f^9$	5.047	34.343	29.695			13.136	12.284
	$6s^2 5p^6 5d^1 4f^8$				6.035	5.862		
66 Dy	$6s^2 5p^6 4f^{10}$	5.107	35.179	30.209			13.536	12.559
	$6s^2 5p^6 5d^1 4f^9$				5.917	5.741		
67 Ho	$6s^2 5p^6 4f^{11}$	5.167	36.022	30.713			13.833	12.770
	$6s^2 5p^6 5d^1 4f^{10}$				5.789	5.612		
68 Er	$6s^2 5p^6 4f^{12}$	5.227	36.874	31.210			14.184	12.923
	$6s^2 5p^6 5d^1 4f^{11}$				5.654	5.477		
69 Tm	$6s^2 5p^6 4f^{13}$	5.287	37.739	31.700			14.443	13.020
	$6s^2 5p^6 5d^1 4f^{12}$				5.512	5.335		
70 Yb	$6s^2 5p^6 4f^{14}$	5.348	38.618	32.186			14.666	13.066
	$6s^2 5p^6 5d^1 4f^{13}$				5.362	5.188		
71 Lu	$6s^2 5p^6 5d^1 4f^{14}$	6.055	44.241	36.951	5.207	5.035	23.274	21.519
		6s	$6\bar{p}$	6p	$5\bar{d}$	5d		
72 Hf	$6s^2 5d^2$	6.522			6.730	6.409		
	$6s^1 6p^1 5d^2$		3.915	3.593				
73 Ta	$6s^2 5d^3$	6.912			8.122	7.640		
	$6s^1 6p^1 5d^3$		4.005	3.691				
74 W	$6s^2 5d^4$	7.257			9.470	8.814		
	$6s^1 6p^1 5d^4$		4.170	3.767				
75 Re	$6s^2 5d^5$	7.573			10.808	9.962		
	$6s^1 6p^1 5d^5$		4.267	3.828				
76 Os	$6s^2 5d^6$	7.867			12.149	11.098		
	$6s^1 6p^1 5d^6$		4.351	3.877				

TABLE 27
(Continued)

Z	Configuration	Orbital exponents						
		s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
77 Ir	$6s^2 5d^7$	2.111			3.360	3.220		
	$6s^1 6p^1 5d^7$		1.784	1.590				
78 Pt	$6s^1 5d^9$	2.071			3.415	3.245		
	$6s^1 6p^1 5d^8$		1.835	1.621				
79 Au	$6s^1 5d^{10}$	2.124			3.581	3.398		
	$6p^1 5d^{10}$		1.633	1.428				
80 Hg	$6s^2 5d^{10}$	2.286			3.843	3.670		
	$6s^1 6p^1 5d^{10}$		1.926	1.676				
81 Tl	$6s^2 6p^1 5d^{10}$	2.520	1.848	1.620	4.108	3.945		
82 Pb	$6s^2 6p^2 5d^{10}$	2.718	2.115	1.849	4.351	4.341		
83 Bi	$6s^2 6p^3$	2.898	2.338	2.040				
84 Po	$6s^2 6p^4$	3.067	2.538	2.211				
85 At	$6s^2 6p^5$	3.229	2.724	2.369				
86 Rn	$6s^2 6p^6$	3.384	2.900	2.517				
		7s	$7\bar{p}$	7p	$6\bar{d}$	6d		
87 Fr	$7s^1$	1.266						
	$7p^1$		1.015	0.930				
	$6d^1$				0.888	0.904		
88 Ra	$7s^2$	1.490						
	$7s^1 7p^1$		1.269	1.140				
	$7s^1 6d^1$				1.857	1.779		
89 Ac	$7s^2 6d^1$	1.630			1.896	1.828		
	$7s^1 7p^1 6d^1$		1.392	1.236				
90 Th	$7s^2 6d^2$	1.742			2.142	2.056		
	$7s^1 7p^1 6d^2$		1.333	1.178				
		7s	$6\bar{p}$	6p	$6\bar{d}$	6d	$5\bar{f}$	5f
91 Pa	$7s^2 6p^6 6d^1 5f^2$	1.699	3.803	3.350	2.023	1.941	3.624	3.524
92 U	$7s^2 6p^6 6d^1 5f^3$	1.728	3.907	3.425	2.062	1.975	3.866	3.761
93 Np	$7s^2 6p^6 6d^1 5f^4$	1.756	4.008	3.496	2.093	2.000	4.081	3.969
94 Pu	$7s^2 6p^6 5f^6$	1.681	4.048	3.492			4.059	3.911
	$7s^2 6p^6 6d^1 5f^5$				2.117	2.019		
95 Am	$7s^2 6p^6 5f^7$	1.704	4.142	3.553			4.259	4.104
	$7s^2 6p^6 6d^1 5f^6$				2.136	2.032		
96 Cm	$7s^2 6p^6 6d^1 5f^7$	1.838	4.297	3.689	2.149	2.041	4.639	4.507

TABLE 27
(Continued)

Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
77 Ir	$6s^2 5d^7$	8.146			13.503	12.229		
	$6s^1 6p^1 5d^7$		4.425	3.917				
78 Pt	$6s^1 5d^9$	7.734			12.201	10.700		
	$6s^1 6p^1 5d^8$		4.492	3.950				
79 Au	$6s^1 5d^{10}$	7.937			13.430	11.667		
	$6p^1 5d^{10}$		3.697	3.351				
80 Hg	$6s^2 5d^{10}$	8.926			17.689	15.637		
	$6s^1 6p^1 5d^{10}$		4.606	3.998				
81 Tl	$6s^2 6p^1 5d^{10}$	12.223	5.751	4.804	24.341	21.937		
82 Pb	$6s^2 6p^2 5d^{10}$	15.416	7.486	5.984	30.988	28.192		
83 Bi	$6s^2 6p^3$	18.672	9.211	7.107				
84 Po	$6s^2 6p^4$	22.037	10.976	8.216				
85 At	$6s^2 6p^5$	25.528	12.803	9.328				
86 Rn	$6s^2 6p^6$	29.156	14.705	10.450				
		7s	$7\bar{p}$	7p	$6\bar{d}$	6d		
87 Fr	$7s^1$	3.611						
	$7p^1$		2.337	2.188				
	$6d^1$				1.724	1.738		
88 Ra	$7s^2$	4.523						
	$7s^1 7p^1$		3.065	2.743				
	$7s^1 6d^1$				2.917	2.872		
89 Ac	$7s^2 6d^1$	5.186			4.882	4.694		
	$7s^1 7p^1 6d^1$		3.366	2.951				
90 Th	$7s^2 6d^2$	5.699			6.068	5.733		
	$7s^1 7p^1 6d^2$		3.594	3.095				
		7s	$6\bar{p}$	6p	$6\bar{d}$	6d	$5\bar{f}$	5f
91 Pa	$7s^2 6p^6 6d^1 5f^2$	5.410	34.965	25.982	5.203	4.962	7.950	7.348
92 U	$7s^2 6p^6 6d^1 5f^3$	5.506	36.548	26.795	5.245	4.987	9.444	8.697
93 Np	$7s^2 6p^6 6d^1 5f^4$	5.602	38.064	27.522	5.248	4.977	10.830	9.932
94 Pu	$7s^2 6p^6 5f^6$	5.139	36.482	25.567			8.103	7.100
	$7s^2 6p^6 6d^1 5f^5$				5.221	4.941		
95 Am	$7s^2 6p^6 5f^7$	5.205	37.764	26.045			9.134	7.960
	$7s^2 6p^6 6d^1 5f^6$				5.171	4.883		
96 Cm	$7s^2 6p^6 6d^1 5f^7$	5.897	42.455	29.379	5.099	4.807	14.614	13.218

TABLE 27
(Continued)

Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
		Orbital exponents						
97 Bk	$7s^26p^65f^9$	1.748	4.329	3.667			4.623	4.452
	$7s^26p^66d^15f^8$				2.157	2.045		
98 Cf	$7s^26p^65f^{10}$	1.770	4.422	3.722			4.792	4.613
	$7s^26p^66d^15f^9$				2.161	2.045		
99 Es	$7s^26p^65f^{11}$	1.792	4.515	3.775			4.956	4.768
	$7s^26p^66d^15f^{10}$				2.160	2.040		
100 Fm	$7s^26p^65f^{12}$	1.815	4.608	3.826			5.115	4.916
	$7s^26p^66d^15f^{11}$				2.155	2.032		
101 Md	$7s^26p^65f^{13}$	1.838	4.702	3.876			5.269	5.061
	$7s^26p^66d^15f^{12}$				2.145	2.019		
102 No	$7s^26p^65f^{14}$	1.861	4.797	3.925			5.419	5.200
	$7s^26p^66d^15f^{13}$				2.130	2.002		
103 Lr	$7s^26p^66d^15f^{14}$	2.041	4.964	4.073	2.109	1.980	5.722	5.527
		7s	$7\bar{p}$	7p	$6\bar{d}$	6d		
104	$7s^26d^2$	2.171			2.467	2.297		
	$7s^17p^16d^2$		1.854	1.489				
105	$7s^26d^3$	2.287			2.729	2.530		
	$7s^17p^16d^3$		1.966	1.548				
106	$7s^26d^4$	2.397			2.949	2.726		
	$7s^17p^16d^4$		2.071	1.600				
107	$7s^26d^5$	2.501			3.145	2.900		
	$7s^17p^16d^5$		2.172	1.646				
108	$7s^26d^6$	2.603			3.325	3.061		
	$7s^17p^16d^6$		2.270	1.688				
109	$7s^26d^7$	2.703			3.494	3.211		
	$7s^17p^16d^7$		2.367	1.725				
110	$7s^26d^8$	2.802			3.654	3.354		
	$7s^17p^16d^8$		2.464	1.759				
111	$7s^26d^9$	2.901			3.808	3.490		
	$7p^16d^{10}$		2.423	1.648				
112	$7s^26d^{10}$	3.001			3.957	3.621		
	$7s^17p^16d^{10}$		2.662	1.818				
113	$7s^27p^16d^{10}$	3.214	2.456	1.666	4.190	3.880		
114	$7s^27p^26d^{10}$	3.405	2.749	1.892	4.403	4.104		
115	$7s^27p^36d^{10}$	3.584	2.995	2.078	4.601	4.307		

TABLE 27
(Continued)

		Orbital energies (eV)						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
97 Bk	$7s^26p^65f^9$	5.340	40.323	26.893			11.073	9.532
	$7s^26p^66d^15f^8$				5.013	4.720		
98 Cf	$7s^26p^65f^{10}$	5.409	41.615	27.272			11.993	10.254
	$7s^26p^66d^15f^9$				4.912	4.619		
99 Es	$7s^26p^65f^{11}$	5.479	42.924	27.626			12.887	10.937
	$7s^26p^66d^15f^{10}$				4.798	4.508		
100 Fm	$7s^26p^65f^{12}$	5.550	44.256	27.957			13.755	11.583
	$7s^26p^66d^15f^{11}$				4.673	4.388		
101 Md	$7s^26p^65f^{13}$	5.622	45.618	28.267			14.601	12.194
	$7s^26p^66d^15f^{12}$				4.538	4.261		
102 No	$7s^26p^65f^{14}$	5.696	47.014	28.557			15.425	12.770
	$7s^26p^66d^15f^{13}$				4.395	4.127		
103 Lr	$7s^26p^66d^15f^{14}$	6.738	53.227	32.758	4.242	3.985	22.375	19.452
		7s	$7\bar{p}$	7p	$6\bar{d}$	6d		
104	$7s^26d^2$	7.443			5.641	5.121		
	$7s^17p^16d^2$		4.225	3.320				
105	$7s^26d^3$	8.076			6.889	6.090		
	$7s^17p^16d^3$		4.475	3.415				
106	$7s^26d^4$	8.675			8.088	6.994		
	$7s^17p^16d^4$		4.701	3.489				
107	$7s^26d^5$	9.260			9.271	7.863		
	$7s^17p^16d^5$		4.915	3.547				
108	$7s^26d^6$	9.841			10.454	8.712		
	$7s^17p^16d^6$		5.122	3.594				
109	$7s^26d^7$	10.427			11.646	9.550		
	$7s^17p^16d^7$		5.326	3.633				
110	$7s^26d^8$	11.024			12.851	10.381		
	$7s^17p^16d^8$		5.532	3.664				
111	$7s^26d^9$	11.636			14.074	11.208		
	$7p^16d^{10}$		4.916	3.374				
112	$7s^26d^{10}$	12.269			15.316	12.032		
	$7s^17p^16d^{10}$		5.961	3.711				
113	$7s^27p^16d^{10}$	16.004	7.223	4.103	20.731	16.890		
114	$7s^27p^26d^{10}$	19.632	9.674	5.015	26.020	21.561		
115	$7s^27p^36d^{10}$	23.334	12.131	5.867	31.361	26.238		

TABLE 27
(Continued)

		Orbital exponents						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
116	$7s^2 7p^4 6d^{10}$	3.754	3.216	2.242	4.788	4.497		
117	$7s^2 7p^5$	3.920	3.422	2.391				
118	$7s^2 7p^6$	4.081	3.617	2.528				
		8s	$8\bar{p}$	8p	$7\bar{d}$	7d		
119	$8s^1$	1.634						
	$8p^1$		1.265	0.987				
	$7d^1$				0.970	1.030		
120	$8s^2$	1.851						
	$8s^1 8p^1$		1.554	1.141				
	$8s^1 7d^1$				1.641	1.616		

The expression for the resonance integrals is as simple as possible

$$H_{i_A j_B} = (1/2)\ S_{ij}\ (\beta_i^A + \beta_j^B)\ K_{AB} \qquad [371]$$

with an approximation of

$$\beta_i^A = -\zeta_i^A / n_i^A \qquad [372]$$

(in eV) and the universal scaling factor $K_{AB} = 1.4$. The last quantity may depend upon atomic electronegativities, viz.

$$K_{AB} = \chi_A / \chi_B \geq 1 \qquad [373]$$

(so called variable scaling approach).

The resulting wave function is single-component and the method is as fast as the common CNDO or INDO versions.

An important feature of this class of methods is that the CNDO or INDO formulas depend explicitly on the reference electron configuration $s^x p^y d^z f^w$ (numbers N_i^A). This should be consistent with the configuration used in the derivation of parameters (ζ_i^A and I_i^A). The choice of the reference electron configuration should be carefully performed. For example, in trying to study planar Pd(II) and Pt(II) complexes, it must be remembered that such complexes behave like d^8 systems. Thus the consistent reference electron configurations must be $4d^8 5s^2$ and $5d^8 6s^2$ and not the experimental $4d^{10}$ and $5d^9 6s^1$, respectively. Similarly, hexacoordinate Cu(II)

TABLE 27
(Continued)

		Orbital energies (eV)						
Z	Configuration	s	$\bar{p}$	p	$\bar{d}$	d	$\bar{f}$	f
116	$7s^27p^46d^{10}$	27.158	14.670	6.694	36.797	30.966		
117	$7s^27p^5$	31.128	17.324	7.509				
118	$7s^27p^6$	35.258	20.116	8.320				
		8s	$8\bar{p}$	8p	$7\bar{d}$	7d		
119	$8s^1$	4.322						
	$8p^1$		2.498	2.067				
	$7d^1$				1.680	1.727		
120	$8s^2$	5.218						
	$8s^18p^1$		3.204	2.369				
	$8s^17d^1$				2.230	2.273		

complexes are typical d^9 systems, and therefore the $3d^94s^2$ reference configuration must be used instead of the experimental free-atom state of $3d^{10}4s^1$. If such a set of parameters is not at one's disposal from direct Dirac-Fock calculations, an interpolation can be used, as exemplified by Fig. 14 for first transition metal series (223).

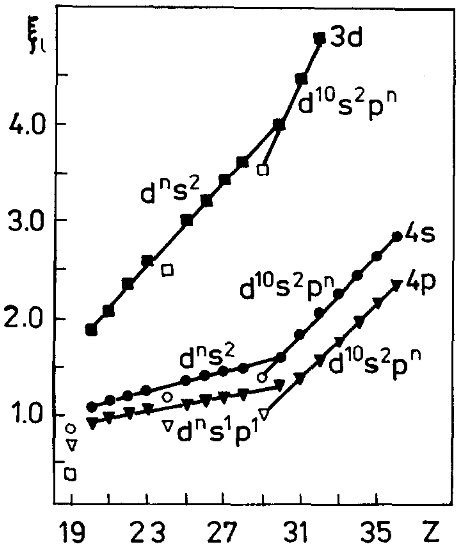

Fig. 14. Averaged exponents of Slater-type orbitals for fourth-row atoms.

6. **The Relativistic CNDO/1 Method** (298,299) integrates the progress of the REX method with that of the quasirelativistic CNDO/1 version. This method includes spin-orbit splitting in the same way as the REX method, through a set of parameters.

Within the Condon-Shortley phase convention used below the complex spherical harmonics can be composed of real angular momentum functions $Y^{\pm}_{l,m_l}$ as

$$Y_{l,m_l} = (-1)^{(m_l + |m_l|)/2}[(1 + \delta_{m_l,0})/2]^{1/2}[Y^{+}_{l,m_l} + i\ sign(m_l)\ Y^{-}_{l,m_l}] \qquad [374]$$

The alternative Fano-Racah convention $Y'_{l,m_l} = i^{l}\ Y_{l,m_l}$ has been used in the ITEREX program (292). Then the spherical spinors may be expressed as

$$\chi^{(2)}_{km} = \begin{pmatrix} C^{-}_{j,m}\ Y_{l,m-1/2} \\ C^{+}_{j,m}\ Y_{l,m+1/2} \end{pmatrix} = \begin{pmatrix} D_1\ Y^{+}_{l,m_l} + D_3\ Y^{-}_{l,m_l} \\ D_2\ Y^{+}_{l,m_l} + D_4\ Y^{-}_{l,m_l} \end{pmatrix} \qquad [375]$$

with the D-coefficients defined by

$$D_1(j,l,m) = C^{-}_{j,m}\ [(1 + \delta_{m,+1/2})/2]^{1/2}\ (-1)^{[m-1/2+|m-1/2|]/2} \qquad [376]$$

$$D_2(j,l,m) = C^{+}_{j,m}\ [(1 + \delta_{m,-1/2})/2]^{1/2}\ (-1)^{[m+1/2+|m+1/2|]/2} \qquad [377]$$

$$D_3(j,l,m) = sign(m - 1/2)\ D_1 \qquad [378]$$

$$D_4(j,l,m) = sign(m + 1/2)\ D_2 \qquad [379]$$

In summary, the atomic spinors need usual (real) angular momentum functions $Y^{\pm}_{l,m_l}$ and the appropriate Clebsh-Gordan coefficients $C^{\pm}_{j,m}$ (or the corresponding D-coefficients) for their construction.

The four-component atomic spinors

$$\underline{\Psi}^{(4)}_{nkm} = \begin{pmatrix} f^{(2)}_{nkm} \\ (1/2m_e c)\ \underline{\sigma}\ \cdot\hat{p}\ f^{(2)}_{nkm} \end{pmatrix} \qquad [380]$$

are constructed from the two-component functions

$$f^{(2)}_{nkm}(r,\vartheta,\varphi) = R_{n\zeta}(r)\ \chi^{(2)}_{km}(\vartheta,\varphi) \qquad [381]$$

with the radial part in the form of a Slater-type orbital

$$R_{n\zeta}(r) = [(2\zeta)^{2n+1}/(2n)!]^{1/2}\ r^{n-1}\ exp(-\zeta r) \qquad [382]$$

Hence $\underline{\sigma}$ is the vector of Pauli matrices and $\hat{p}$ is the linear momentum operator. The overlap integral between two atomic spinors centered at atoms A and B is

$$S_{AB} = <\Psi_A^{(4)}|\Psi_B^{(4)}> = <f_A^{(2)}|f_B^{(2)}> + (1/4m_e^2c^2)\ <f_A^{(2)}|\hat{p}^2|f_B^{(2)}> \qquad [383]$$

Because $1/(4m_e^2c^2) \approx 10^{-5}$ a.u., the second term over the lower component functions can be omitted. For the same reason the one-electron part of the Fock operator contains only the integrals over the upper component functions

$$\begin{aligned} H_{AB} &= <\Psi_A^{(4)}|\hat{h}|\Psi_B^{(4)}> \approx <f_A^{(2)}|\hat{h}|f_B^{(2)}> = \\ &= <C^-_{j_A m_A}\ Y_{l_A,m_A-1/2}\ R_A|\hat{h}|C^-_{j_B m_B}\ Y_{l_B,m_B-1/2}\ R_B> + \\ &+ <C^+_{j_A m_A}\ Y_{l_A,m_A+1/2}\ R_A|\hat{h}|C^+_{j_B m_B}\ Y_{l_B,m_B+1/2}\ R_B> \qquad [384] \end{aligned}$$

Now it is seen that the one-electron integrals over atomic spinors can be expressed through integrals evaluated in the real orbital basis set with appropriate exponents. Then the real and imaginary parts of H_{AB} are composed as

$$\begin{aligned} Re(H_{AB}) &= D_{1A}\ D_{1B}\ <R_A\ Y_A^+|\hat{h}|R_B\ Y_B^+> + D_{3A}\ D_{3B}\ <R_A\ Y_A^-|\hat{h}|R_B\ Y_B^-> + \\ &+ D_{2A}\ D_{2B}\ <R_A\ Y_A^+|\hat{h}|R_B\ Y_B^+> + D_{4A}\ D_{4B}\ <R_A\ Y_A^-|\hat{h}|R_B\ Y_B^-> \qquad [385] \end{aligned}$$

$$\begin{aligned} Im(H_{AB}) &= D_{1A}\ D_{3B}\ <R_A\ Y_A^+|\hat{h}|R_B\ Y_B^-> - D_{3A}\ D_{1B}\ <R_A\ Y_A^-|\hat{h}|R_B\ Y_B^+> + \\ &+ D_{2A}\ D_{4B}\ <R_A\ Y_A^+|\hat{h}|R_B\ Y_B^-> - D_{4A}\ D_{2B}\ <R_A\ Y_A^-|\hat{h}|R_B\ Y_B^+> \qquad [386] \end{aligned}$$

where $<R_A\ Y_A^{\pm}|\hat{h}|R_B\ Y_B^{\pm}>$ are calculated in real (l) orbital basis set.

The remaining integrals to be considered within the CNDO approach are the two-centre Coulomb integrals over s-functions

$$G_{ij}^{AB} = <s_i^A\ s_j^B|r_{12}^{-1}|s_i^A\ s_j^B> \qquad [387]$$

Since the s-functions are always real, the Coulomb integral matrix does not need any transformation.

The Fock operator matrix in the relativistic CNDO method is

$$F_{ii} = H_{ii} - P_{ii}G_{ii} + \sum_j P_{jj}G_{ij} \qquad [388]$$

$$F_{ik} = H_{ik} - P_{ki}\ G_{ik} \qquad [389]$$

with the charge density matrix

$$P_{ik} = \sum_{\mu} C_{i\mu}^*\ N_{\mu}\ C_{\mu k} \qquad [390]$$

defined using coefficients $C_{\mu k}$ of the linear combination of atomic spinorbitals and the occupation numbers N_{μ} of molecular spin-orbitals having values of 0 or 1.

For open shell system the formulation above is consistent with the spin-unrestricted Hartree-Fock approach (different orbitals for different spin). The Roothaan equations for obtaining the combination coefficient matric C are

$$\mathbf{F}\mathbf{C}^{+} = \mathbf{C}^{+}\mathbf{E} \qquad [391]$$

Notice, the matrices **H**, **P** and **F** are complex hermitian, **C** is complex unitary, **G** is real symmetric (s-functions only) and **E** is real diagonal. The diagonalization matrix returned from the eigenproblem routines is $\mathbf{Z} = \mathbf{C}^{+}$.

Since the relativistic approach utilizes a doubled basis set, $M_R = 2M$, the corresponding complex matrices need $4N^2$ space, i.e., 8 times more than the real (nonrelativistic) matrices of M^2 size. Possible hermicity reduces the desired space twice and the quaternionic storage mode by another factor of two. If M^3 was the rate determining step for a nonrelativistic SCF procedure, the relativistic calculation would need $M_R^3 = 8M^3$ time, i.e., 8 times more CPU time. For this reason the relativistic CNDO method needs a generation higher computer equipment than the comparable non-relativistic versions.

3.6.2 Spin-Orbit Interaction

The spin-orbit interaction (SOI) operator in one-electron atoms is obtained from the Dirac equation in the form

$$\hat{h}^{so} = -\,(e/2m_e^2c^2)\; r^{-1}\,[\partial V(r)/\partial r]\;\hat{\mathbf{s}}.\hat{l} = \xi\;\hat{\mathbf{s}}.\hat{l} \qquad [392]$$

where $V(r) = eZ_A/4\pi\epsilon_0 r$ is the Coulomb potential determined by the nuclear charge. This equation defines the spin-orbit coupling constant ξ for a single-electron atom. For many-electron atoms the potential V(r) is understood as a superposition of the coulombic interactions of the nucleus and all the remaining electrons with the given electron (300-302). This potential is no longer generated by a point charge and its partial derivative is unknown.

If the whole magnetic interaction of a many-electron atom includes relativistic terms containg spin and orbital coordinates, then according to Table 3 of Chapter 2

$$\hat{V}_{mg} = [\hat{H}_{ee}^{s-l}(1)]_A + \hat{H}_{ee}^{s-l}(2) + \hat{H}_{ee}^{s-l}(3) + \hat{H}_{ee}^{s-s}(1) =$$

$$= \sum_i \hat{h}_{Ai}^{so} + \sum_{i\neq j}(\hat{h}'^{so}_{ji} + \hat{h}_{ji}^{so}) + \sum_{i\neq j}\hat{h}_{ij}^{ss} \qquad [393]$$

where

$$\hat{h}_{Ai}^{so} = K\; Z_A\; r_{Ai}^{-3}\;\hat{\mathbf{s}}_i.\hat{l}_i \qquad [394]$$

is the SOI term of the type 'spin - own orbital' in the Coulomb field;

$$\hat{h}'^{so}_{ji} = -\ 2\ K\ r_{ij}^{-3}\ (R_{ij} \ x\ \hat{p}_i).\hat{s}_j \qquad [395]$$

is the SOI term of the type 'spin - other orbital' (interaction of the spin magnetic moment of the j-th electron with the orbital angular momentum of the i-th electron);

$$\hat{h}^{so}_{ji} = -\ K\ r_{ij}^{-3}\ (R_{ij} \ x\ \hat{p}_i).\hat{s}_i \qquad [396]$$

is the SOI term of the type 'spin - own orbital' for i-th electron in the Coulomb field of the j-th electron;

$$\hat{h}^{ss}_{ij} = K[r_{ij}^{-3}\ \hat{s}_i.\hat{s}_j - 3r_{ij}^{-5}(\hat{s}_i.R_j)(\hat{s}_j.R_{ij})] \qquad [397]$$

is the spin-spin interaction term for electrons (dipole-dipole interaction of spin magnetic moments). The factor K includes all the physical constants in the given system of units (in SI units it is $K_{SI} = \sigma_{SI}/2m_e^2c^2 = e^2/8\pi\epsilon_0 m_e^2 c^2$). The expressions above have been derived by Bethe and Salpeter (303) from the Breit equation and Slater (304) from the classical analogy.

The relationship [393] can be simplified for an atom having a single open shell lying above several closed shells; then the spin-orbit coupling constant may be defined exactly through

$$\hat{V}_{mg} = \xi_c \sum_i^{o} \hat{l}_i.\hat{s}_i + \sum_{i\neq j}^{o} \hat{h}'_{ji} + \sum_{i\neq j}^{o} \hat{h}^{ss}_{ij} \qquad [398]$$

where o means summation over electrons of the open levels only. To derive this expression we take into account the fact that summation over electrons of the closed shells yields a zero contribution to the first and third terms of [393]. The second term has been analyzed by Elliot (305) who pointed out that the interaction of an electron of the open shell with electrons of the closed shell may be considered as an effective one-particle spin-orbit potential. The nuclear potential is screened by this term and thus the value of the spin-orbit coupling constant decreases. The quantity ξ_c is a constant within the given electron configuration and the subscript c denotes that the mutual interaction of electrons of outer shells is not included in the spin-orbit coupling constant.

Horie (306) found that part of the mutual SOI of open-shell electrons can also be considered as a one-electron SOI and arrived at the relationship

$$\hat{V}_{mg} = \xi' \sum_i^{o} \hat{l}_i.\hat{s}_i + [\sum_{i\neq j}^{o} \hat{h}'_{ji} - (\xi' - \xi_c)\sum_i^{o} \hat{l}_i.\hat{s}_i + \sum_{i\neq j}^{o} \hat{h}^{ss}_{ij}] \qquad [399]$$

where the constant ξ' also includes the effective screening of the nuclear potential by the outer electrons. This constant is defined in such a way that the terms in square brackets do not have the one-electron part anymore. Blume and Watson (301,302) were successful in expressing ξ_c through radial integrals available from Hartree-Fock wave functions.

The SOI coupling constants can be determined by including the operator $\hat{V}_{mg}$ into the electronic Hamiltonian. Its eigenvalues may be compared with the experimentally recorded splitting of the spectroscopic terms. Such an approach is necessary when the SOI is comparable to the interelectronic repulsion and thus the LS coupling applicable no more. In this approach the matrix elements of the dipole-dipole interaction of the spin magnetic moments must be evaluated side by side with those describing the spin - other orbital interaction. There are several publications on this topic (306-310) in which formulae for these integrals have been tabulated. The above method, however, seems to be too complicated for more complex electron configurations.

Usually it is assumed that $\hat{V}_{mg}$ is much lower in energy than the interelectronic repulsion (LS coupling scheme is possible). Within this approximation the splitting of a multiplet obeys the Landé interval rule (see Section 1.5.3). The effect of spin-spin interactions is often neglected.

For practical purposes the one-electron effective SOI operator of the A-th atom adopts the form

$$\hat{V}_A^{so} = \sum_i^A \xi_{i,nl}^A \hat{l}_i \cdot \hat{s}_i \qquad [400]$$

Using the above expression the energy terms available from atomic spectroscopy have been analyzes and semiempirical values for the SOI coupling constants $\xi_{i,nl}^A$ have been derived for all electron configurations of atoms Be through Br (311).

Summation of the above terms is considered for molecules (312). The energy eigenvalues are determined by the secular equation (the CI method - see Chapter 4)

$$det\{H_{uv} - E \langle\Phi_u|\Phi_v\rangle\} = 0 \qquad [401]$$

where matrix elements of the Hamiltonian between determinantal wave functions consist of an electronic term and the spin-orbit term

$$H_{uv} = \langle\Phi_u|\hat{H}^{el}|\Phi_v\rangle + H_{uv}^{so} \qquad [402]$$

Matrix elements of the SOI operator between determinantal wave functions are expressed as

$$H^{so}_{uv} = \langle \Phi_u | \sum_A \sum_i^A \xi^A_{i,nl} \hat{l}^A_i \cdot \hat{s}_i | \Phi_v \rangle = (-1)^p \langle \psi_i | \sum_A \xi^A_{nl} \hat{l}^A \cdot \hat{s} | \psi_j \rangle \qquad [403]$$

for the case of determinantal wave functions differing only in a single spinorbital $\psi_i \neq \psi_j$; p is the number of transpositions which transfer the functions ψ_i and ψ_j to the same place in the Slater determinant. The diagonal matrix elements between determinantal functions are

$$H^{so}_{uu} = \sum_i^{occ} \langle \psi_i | \sum_A \xi^A_{nl} \hat{l}^A \cdot \hat{s} | \psi_i \rangle \qquad [404]$$

For closed shells the individual components cancel because the integrals for $m_s = +1/2$ and $m_s = -1/2$ have the same absolute values but different signs. Therefore only electrons of open shells contribute to diagonal matrix elements of the SOI operator.

In order to evaluate H^{so}_{uv} integrals, LCAO expansion of the molecular orbitals is required

$$\phi_i = \sum_r^m C_{ir} \vartheta_r \qquad [405]$$

Then the molecular spinorbitals are $\psi_i = \phi_i \eta_i$ with η_i representing the formal spin function. Then we obtain expressions for the matrix elements

$$H^{so}_{uu} = \sum_r^m \sum_i^{occ} (c'_{ir})^2 H'_{ri,ri} \qquad [406]$$

$$H^{so}_{uv} = (-1)^p \sum_r^m \sum_s^m c'_{ir} c'_{js} H'_{ri,sj} \qquad [407]$$

with abbreviation of

$$H'_{ri,sj} = \langle \vartheta_r \eta_i | \sum_A \xi^A_{nl} \hat{l}^A \cdot \hat{s} | \vartheta_s \eta_j \rangle \qquad [408]$$

For the closed-shell system the number of electrons is $n = 2n_\alpha$ and then

$$c'_{ir} = C_{i,r}, \quad \eta_r = \alpha \quad \text{for } r \leq n/2 \qquad [409]$$

$$c'_{ir} = C_{i,r-n/2}, \quad \eta_r = \beta \quad \text{for } r > n/2. \qquad [410]$$

As the effective spin-orbit coupling constant ξ^A_{nl} is proportional to r^{-3}_{Ai}, only the one-centre integrals are considered in many cases. They may be evaluated by considering the identity

$$\hat{l}^A \cdot \hat{s} = \hat{l}^A_z \hat{s}_z + (\hat{l}^A_+ \hat{s}_- + \hat{l}^A_- \hat{s}_+) \qquad [411]$$

where the angular momenta shift operators are

$$\hat{l}^A_\pm = \hat{l}^A_x \pm i \hat{l}^A_y \qquad [412]$$

$$\hat{s}^A_\pm = \hat{s}^A_x \pm i \hat{s}^A_y \qquad [413]$$

Such a substitution allows a simple expression for the matrix elements $H'_{rk,sl}$ in the form

$$H'_{rk,sl} = H^{z}_{rk,sl} + H^{+}_{rk,sl} + H^{-}_{rk,sl} \qquad [414]$$

The imaginary parts of $H^{\pm}_{rk,sl}$ cancel. Then the following steps are applied:

1. decide the non-zero matrix elements, i.e.

$$\begin{aligned} G^{z}_{rk,sl} &= 0 \text{ except } k \le n/2 \text{ and } l \le n/2, \\ &\qquad \text{or } k > n/2 \text{ and } l > n/2 \\ G^{+}_{rk,sl} &= 0 \text{ except } k > n/2 \text{ and } l \le n/2 \\ G^{-}_{rk,sl} &= 0 \text{ except } k \le n/2 \text{ and } l > n/2 \end{aligned} \qquad [415]$$

2. introduction of auxiliary discrete functions

$$\begin{aligned} A_k &= +1/2 \text{ for } k \le n/2 \\ A_k &= -1/2 \text{ for } k > n/2 \\ B_{\mu,\nu} &= 1 \text{ for } \vartheta_r = \mu \text{ and } \vartheta_s = \nu \\ B_{\mu,\nu} &= 0 \text{ elsewhere;} \end{aligned} \qquad [416]$$

3. evaluation of non-zero matrix elements in the s-p-d atomic orbital basis set

$$\begin{aligned} G^{z}_{rk,sl} = i\hbar^2\, A_k\{\xi^{A}_{(p),kl}(B_{y,x} - B_{x,y}) + \xi^{A}_{(d),kl}[(B_{yz,xz} - B_{xz,yz}) + \\ + 2(B_{xy,x^2-y^2} - B_{x^2-y^2,xy})]\} \end{aligned} \qquad [417]$$

$$\begin{aligned} G^{\pm}_{rk,sl} = \hbar^2\, A_k\{\xi^{A}_{(p),kl}[(B_{x,z} - B_{z,x}) \pm i(B_{y,z} - B_{z,y})] + \\ + \xi^{A}_{(d),kl}[\sqrt{3}(B_{xz,z^2} - B_{z^2,xz}) + (B_{x^2-y^2,xz} - B_{xz,x^2-y^2}) + \\ + (B_{xz,yz} - B_{yz,xz}) \pm i[\sqrt{3}(B_{yz,z^2} - B_{z^2,yz}) + \\ + (B_{xy,xz} - B_{xz,xy}) + (B_{yz,x^2-y^2} - B_{x^2-y^2,yz})]]\} \end{aligned} \qquad [418]$$

These rules can easily be programmed on digital computers.

In a detailed study of molecular electronic structure spin-orbit splitting often plays a dominant role in the theoretical interpretation of experimental data. This research has been stimulated by the development of photoelectron spectroscopy in last few decades, since the photoelectron spectra of molecules containing heavy atoms exhibit considerable spin-orbit splitting. Some studies will be discussed below.

Manne et al. (313) included the SOI operator into the extended Hückel method. They applied an approach where after completion of the iterative procedure, the matrix representation of the SOI operator has been diagonalized in the molecular spinorbital basis set. Such an approach allows application of the Koopmans theorem even in the case of strong spin-orbit splitting. Moreover, it may be implemented also to other MO-LCAO-SCF methods (314).

A semiempirical model for SOI inclusion in molecular ions has been developed by Berkosky el al. (315). These authors took into account explicit dependence of the SOI coupling constants upon effective atomic charges in molecules, including metal complexes.

Bird and Day (316) applied perturbation theory to the results of MO-LCAO-SCF calculations in order to include the SOI effect. Perturbation theory has been used in a number of semi-empirical calculations for the interpretation of small molecule photoelectron spectra (315-319).

Numerous experimental data produced by photoelectron spectroscopy represent a good basis for testing the various methods for inclusin of the SOI effect.

3.7 MOLECULAR ORBITAL PROPERTIES

3.7.1 Canonical Molecular Orbitals

The Hartree-Fock equations

$$\hat{F}\{\phi\} = L\ \{\phi\} \qquad [419]$$

have an infinite number of solutions $\{\phi\}$, $\{\phi'\}$, $\{\phi''\}$, etc., which transform, one to another, by unitary matrices U', U'', etc.

$$\{\phi\} = U'\{\phi'\} = U''\{\phi''\} = \ldots \qquad [420]$$

All these solutions produce the same determinantal wave function and thus the same value for the electronic energy. For an unambiguous choice of molecular orbitals $\{\phi\}$ some additional conditions should be imposed (320). One possibility leads to **canonical molecular orbitals**. These orbitals are fixed with the condition that the Lagrangian multiplier matrix L is diagonal

$$U^{+}\ L\ U = E \qquad [421]$$

In this basis the Hartree-Fock equations adopt the usual form

$$\hat{F}\ |\phi_{\nu}> = \epsilon_{\nu}\ |\phi_{\nu}> \qquad [422]$$

The density function $\rho_{\nu} = \phi^{*}_{\nu}\phi_{\nu}$ meanins the probability of finding an electron, in the orbital ϕ_{ν}, in the volume element dV. Since this function is spread over the whole molecular framework, we speak ab ut delocalized molecular orbitals.

The Fock operator $\hat{F}$ is invariant with respect to all symmetry operations $\hat{R}_k$ of the molecular symmetry so that the following commutation relation is true

$$[\hat{F},\hat{R}_k]_- = \hat{F}\,\hat{R}_k - \hat{R}_k\,\hat{F} = 0 \qquad [423]$$

Therefore there exists a set of eigenfunctions, common to both operators, represented by canonical molecular orbitals: these are transformed according to individual irreducible representations of the molecular point group symmetry. The above property of these canonical MOs is useful in interpreting the excitation and ionization of molecules. This is conditioned by the requirement that the electronic wave functions in the ground, excited and ionized states should transform according to irreducible representations of the molecular. The canonical MOs obey this rquirement.

The electronic energy of a neutral closed-shell system may be written in the form

$$E^0 = \sum_i^{occ} [2h_{ii} + \sum_j^{occ} (2J_{ij} - K_{ij})] = \sum_i^{occ} (h_{ii} + \epsilon_i) \qquad [424]$$

where the integrals are expressed in the molecular orbital basis set and the orbital energy is given as

$$\epsilon_i = h_{ii} + \sum_j^{occ} (2J_{ij} - K_{ij}) \qquad [425]$$

Similarly, for the energy of a molecular cation we have

$$E_k^+ = \sum_{i \neq k} [2h_{ii} + \sum_{j \neq k} (2J_{ij} - K_{ij}) + h_{kk} + \sum_{i \neq k} (2J_{ik} - K_{ik}) \qquad [426]$$

With the assumption that there is no orbital relaxation when passing from the neutral to the ionized system, we arrive at the expression

$$E_k^+ = \sum_i^{occ} [2h_{ii} + \sum_j^{occ} (2J_{ij} - K_{ij})] - [h_{kk} + \sum_j^{occ} (2J_{kj} - K_{kj}) =$$

$$= E^0 - \epsilon_k \qquad [427]$$

The subscript k means the orbital from which the electron has been removed. Then the ionization energy is given as

$$I_k^0 = E_k^+ - E^0 = - \epsilon_k \qquad [428]$$

The last equation represents statement of the **Koopmans theorem** (321) acording to which the ionization energy is given by the negative value of the corresponding orbital energy. The above statement neglests many important effects among which orbital relaxation and the electrostatic correlation energy predominate.

1. **Orbital relaxation** manifests itself in a decrease of the molecular cation energy from compensation of the electron hole created by the ionization. For this reason relaxation energy always decreases the $-\epsilon_k$ value by the term Δ_k^r. Its evaluation is possible using the ΔSCF approach

$$I_k^{SCF} = (E_k^+)_{SCF} - (E^0)_{SCF} = - \epsilon_k + \Delta_k^r \qquad [429]$$

where the energies of the molecular cation and neutral molecule are evaluated by an independent SCF calculation. Because the ionized system has open shells, the energy E_k^+ is calculated to a different degree of approximation (UHF, RHF, LHP). The relaxation energy is relatively low (about 1 eV) for ionization of strongly delocalized orbitals (e.g., in conjugated hydrocarbons or aromatics) where the electron hole is spread over the whole molecular skeleton. With ionization of strongly localized orbitals (e.g., transition metal 3d-orbitals) the relaxation energy reaches 10 - 20 eV. In these cases Koopmans theorem is applicable no more. However, the ΔSCF calculation is not advantageous because it requires an additional SCF calculation for each level which has to be done with high accuracy.

2. The **electrostatic correlation energy** decreases the value of the electronic energy for both the neutral and ionized system but to a different extent. The substantial part of the correlation energy is inversely proportional to the energy separation of the HOMO and LUMO: $|\epsilon_{HOMO} - \epsilon_{LUMO}|$. Since in the molecular cation, as a rule, this difference is larger than in the neutral system, the correlation energy becomes smaller. Simultaneously, the number of electrons is smaller so that the correlation energy has a reduced number of terms. For this reason correlation energy increases the $-\epsilon_k$ values by the term Δ_k^c. Consequently the ΔSCF calculation may yield values for ionization energies which are lower relative to experimental data.

The ionization of the closed level in an open-shell system of the spin multiplicity m leads to two final states of different spin multiplicity: $m' = m \pm 1$.

Koopmans theorem corresponds to the statement that both electrons in the doubly occupied molecular orbital contribute equally to the molecular energy and thus they have the same binding energy. In the other words this assumption means that the interelectronic repulsion within the orbital, changes linearly with the change of occupation number n_i from 2 to 1 and 0. This is illustrated in Fig. 15 by the stright line (denoted as a). In reality such a dependence is non-linear (curve b) which rationalizes deviations from Koopmans theorem.

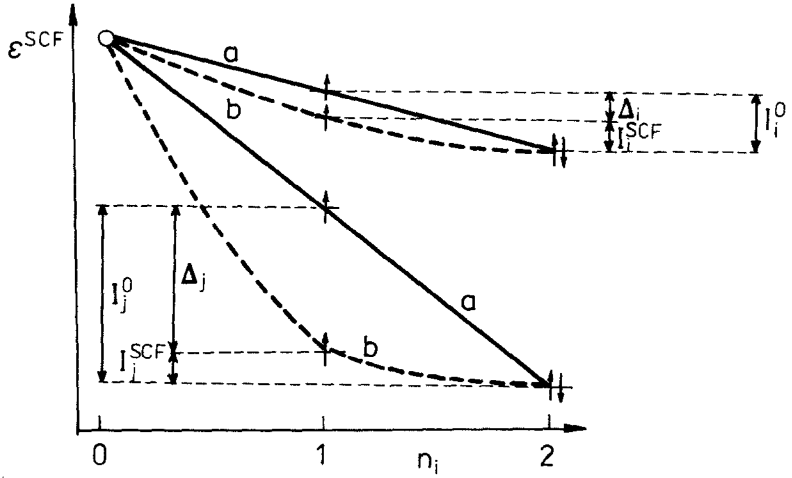

Fig. 15. Demonstration of a paradoxical violation of the Koopmans theorem; n_i - occupation number.

Koopmans theorem is limited not only quantitatively but also qualitatively as explained below. If the relaxation energies have altered order relative to the orbital energies

$$\epsilon_i - \epsilon_j < \Delta_j - \Delta_i \qquad [430]$$

the ionization energy order is interchanged

$$I_i^{SCF} > I_j^{SCF} \qquad [431]$$

This represents a paradox with respect to the Koopmans statement

$$I_i^0 = -\epsilon_i < I_j^0 = -\epsilon_j \qquad [432]$$

according to which ionization of the lower energy orbital is more favourable than ionization of the higher energy orbital. Thus the electron configuration $(\phi_j)^1(\phi_i)^2$ is more stable than $(\phi_j)^2(\phi_i)^1$ despite the relationship $\epsilon_j < \epsilon_i$. The condition [430] appears when (322):

a) there is a small difference in orbital energies;

b) there is a large value for the interelectronic repulsion J_{jj} for the lower energy orbital;

c) these is a small value for the interelectronic repulsion J_{ii} for the higher energy orbital;

d) there is a large value of the interatomic Coulomb potential Madelung term).

The above paradox may be such that the singly occupied orbital is bonding whereas the doubly occupied is its antibonding counterpart.

In order to calculate the excitation energies we first put down the energies of the individual excited states. For example, the energy of the singlet and triplet excited state obtained via the i → a transitions is

$$ {}^{1,3}E(\Phi_i^a) = \sum_{j\neq i} [2h_{ii} + \sum_{k\neq i}(2J_{jk} - K_{jk})] + [h_{ii} + \sum_{j\neq i}(2J_{ij} - K_{ij})] + $$

$$ + [h_{aa} + \sum_{j\neq i}(2J_{ja} - K_{ja})] + J_{ia} \pm K_{ia} \qquad [433] $$

Then the excitation energy is

$$ {}^{1,3}E(\Phi_i^a) - E^0 = \epsilon_a - \epsilon_i - (J_{ia} - K_{ia}) \pm K_{ia} \qquad [434] $$

and the singlet-triplet separation is

$$ {}^{1}E(\Phi_i^a) - {}^{3}E(\Phi_i^a) = 2K_{ia} \qquad [435] $$

Since the exchange integral is always positive, the energy of the lowest triplet state is always lower than the energy of the lowest excited singlet state; this matches well with Hund rules. Note that methods neglecting electron exchange interaction fail in these predictions.

The formulae for the ionization and excitation energies in various approximations are collected in Table 28.

Molecular orbital calculations can be substantially simplified when an appropriate transformation of the atomic orbital basis set is used. One possibility is the use of **symmetry orbitals**. They are defined by a linear combination of atomic orbitals $\{\vartheta\}$ of appropriate symmetry

$$ \{f\} = \gamma \ \{\vartheta\} \qquad [436] $$

Each symmetry orbital $f_m^{(\alpha)}$ is transformed according to an irreducible representation Γ_α of the molecular symmetry point group (Section 1.3.1). In this basis set the characteristic equation adopts the block-diagonal form. For ML_n coordination compounds the symmetry orbitals either contain net central atom atomic orbitals or ligand orbitals. Symmetry orbitals consisting only of ligand components are named **group orbitals**. Then the canonical MOs are given by a linear combination of group orbitals and central atom orbitals of the same symmetry. Effective algorithms for the

TABLE 28
Energy quantities the in one-electron approximation.[a]

Quantity	Approach	
	RHF	LHP
A) Ionization energy ^{m}I to state of spin multiplicity m		
$^{2}I_{i}$	$-\epsilon_{i}$	
$^{1}I_{i}$	$-\epsilon_{i}-(3/2)K_{im}$	$-\epsilon_{i}-(3/2)K_{im}$
$^{3}I_{i}$	$-\epsilon_{i}+(1/2)K_{im}$	$-\epsilon_{i}+(1/2)K_{im}$
$^{1}I_{m}$	$-\epsilon_{m}-(1/2)K_{mm}$	$-\epsilon_{m}-(1/2)K_{mm}$
B) Electron affinity ^{m}A to state of spin multiplicity m		
$^{2}A_{i}$	ϵ_{a}	
$^{1}A_{i}$	$\epsilon_{m}+(1/2)J_{mm}$	$\epsilon_{m}+(1/2)J_{mm}$
C) Excitation energy		
$^{1}\Delta_{i\Rightarrow a}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}+2K_{ia}$	
$^{3}\Delta_{i\rightarrow a}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}$	
$^{2}\Delta_{i\rightarrow a}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}-2K_{im}+2K_{am}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}+2K_{ia}$
$^{4}\Delta_{i\rightarrow a}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}+2K_{im}+2K_{ma}$	$\epsilon_{a}-\epsilon_{i}-J_{ia}-(1/2)K_{ma}-(1/2)K_{im}$
$^{2}\Delta_{m\rightarrow a}$	$\epsilon_{a}-\epsilon_{m}-J_{ma}+(3/2)K_{ma}+(1/2)J_{mm}$	$\epsilon_{a}-\epsilon_{m}-J_{ma}+(1/2)K_{ma}+(1/2)J_{mm}$
$^{4}\Delta_{i\rightarrow m}$	$\epsilon_{m}-\epsilon_{i}-J_{im}+(3/2)K_{im}+(1/2)J_{mm}$	$\epsilon_{m}-\epsilon_{i}-J_{im}+(1/2)K_{im}+(1/2)J_{mm}$

[a] Levels are marked as follows: i - doubly occupied MO, m - singly occupied MO, a - unoccupied MO.

generation of symmetry orbitals are incorporated into many programs for MO-LCAO-SCF calculations.

Pople (323) pointed out that the molecular wave function and electronic energy remain invariant by an arbitrary linear combination applied to the sub-set of occupied MOs. For example, in N_2 molecule a combination of the σ orbital and two π orbitals yields three equivalent orbitals, called the banana (bent) bonds. The axial symmetry of the molecular wave function remains unchanged. Similarly a combination of canonical MOs in the F_2 molecule yields three equivalent one-centre orbitals (lone electron pairs) at each atom.

3.7.2 Localized Molecular Orbitals

Such molecular orbitals may be constructed for which individual probability functions ρ_ν adopt significant values only in the limited region of the molecular framework. These localized molecular orbitals (LMO) correspond to intuitive chemical concepts (e.g., the Lewis approach) - the formation of two-electron covalent bonds, lone electron pairs, etc. The LMOs permit the analysis of the mean values for many molecular observables (binding energies, dipole moments, diamagnetic susceptibilities, electric polarizabilities, etc.) in the form of contributions from molecular fragments.

The various methods for the construction of localized MOs are reviewed in Table 29. Some are discussed in more detail below.

TABLE 29
Methods for defining localized molecular orbitals.

Type	Authors	Localization criterion
A) Methods of internal localization		
1. Exclusive LMOs	Boys-Foster (328,329)	$f(r_{12}) = r_{12}^2$
2. Energetic LMOs	Edmiston-Ruedenberg (330-333)	$f(r_{12}) = r_{12}^{-1}$
3. Charge LMOs	von Niessen (335)	$f(r_{12}) = \delta(r_{12})$
B) Methods of external localization		
1. Equivalent LMOs	Lennard-Jones, Pople-Hall (334,342)	unitary transformation of canonical MOs
2. Population LMOs	Magnasco-Perico (343) Weinstain-Paunz (346)	maximization of local populations
3. Projected LMOs	Polák (345,346) Robby (347)	minimization of projection norm
4. Direct LMOs	Daudey (348)	Brillouin theorem
5. Strictly localized or semi-localized MOs	Boča (349,350)	modified Roothaan equations

1. **Methods of internal localization** are based on the modified Hartree-Fock equations; they retain the SCF energy unchanged in the given basis set and Hamiltonian approximation. The intrinsic localized MOs obey the equation

$$(\hat{F} + \hat{L}^{(f)})|\phi_i\rangle = \epsilon\ |\phi_i\rangle \qquad [437]$$

where

$$\hat{L}^{(f)} = \rho\ \hat{L}\ \rho \qquad [438]$$

is an integral localization operator, ρ - spinless Fock-Dirac density matrix and $\hat{L}$ - an arbitrary one-electron operator that defines the localization. The equations above have been generalized for non-orthogonal LMOs (326,327) as well as for the MC-SCF approach (336-341). They were modified (324-327) for the description of the solid state in the form

$$(\hat{F}_A + \hat{W}_A^{ps})\ |\phi_i^A\rangle = \epsilon_i^A\ |\phi_i^A\rangle \qquad [439]$$

with a non-local pseudopotential

$$\hat{W}_A^{ps} = \hat{v}_A - \rho\ \hat{L}_A\ \rho \qquad [440]$$

Here $\hat{F}_A$ is the Fock operator for electrons localized at the A-th centre and $\hat{v}_A = \hat{F} - \hat{F}_A$ is the environmental potential.

In calculation of intrinsic localized MOs the following function

$$D = \sum_i \langle ii|f(r_{12})|ii\rangle \qquad [441]$$

is minimized. The monotonous separation function $f(r_{12})$ is chosen in a specific way.

2. **Methods of external localization** are based on additional assumptions about the form of the orbitals. These orbitals, as a rule, do not reach the SCF level of energy. They are specified in the form of a parametric function (for example, a limited linear combination of orbitals of two centres) and the unknown parameters are determined by energy minimization.

3. **Methods of molecular fragments** (44), separated electron groups (351), atoms in molecules or molecules in molecules (352-354) exploit the transferability of LMOs from one molecule to another having similar bonds. Among them the most elaborate is the DIM (Diatomics in Molecules) method (355).

Hybrid atomic orbitals (HAO) introduced by Pauling (356) represent an appropriate basis of one-centre functions to develop chemical concepts in the theory of the chemical bond. HAOs $\{h_i^A\}$ are defined by an orthogonal transformation of the real atomic orbitals $\{\vartheta_k^A\}$ at the given atom A

$$\{h^A\} = B_A\ \{\vartheta^A\} \qquad [442]$$

where the transformation matrix B_A fulfils the orthogonality condition

$$B_A B_A^T = I \qquad [443]$$

The resulting one-centre functions have directional properties. Instead of pure atomic orbitals the HAOs have their centre of mass of the electron density situated out of the nucleus. Therefore it is possible to define a direction for the HAO through the vector connecting the nucleus with the centre of mass of the electron density of the HAO under consideration. From the geometric point of view HAOs are chosen to be situated along covalent bonds, i.e. the directional vectors of a pair of HAOs will be colinear. However, there are examples known where the real (and orthogonal) HAOs cannot be oriented along the bond directions (for example in cyclopropane, P_4 molecule, etc.) so that deviation of the HAOs from the bond direction must be introduced.

The HAO directional properties enable one to construct strictly localized (two-centre) molecular orbitals. Therefore the hybridization concept is associated with the study of the collective (additive) properties of molecules in their ground electronic state.

The numerous methods for construction of these HAOs may be classified as follows:

a) criteria involving the projection of LMOs from MO LCAO SCF wave functions (346,347,357-359);

b) geometric criteria (356,360-362);

c) maximum overlap criterion (363-374);

d) other energetic criteria (375).

According to Kimball (362) construction of equivalent HAOs can be based on group theory. The set of equivalent HAOs {h} forms an irreducible representation of the molecular point group. By applying individual symmetry operations to the appropriate generator h_i new functions (symmetry orbitals) {h'} are formed; they form a basis of an irreducible representation. The result of the projection (Section 1.3.1) is given by the linear combination

$$\{h'\} = \mathbf{A} \{h\} \qquad [444]$$

and the decomposition of the reducible representation to irreducible components has the form

$$\Gamma_h = \sum_k n_k \Gamma_{h'k} \qquad [445]$$

The set of central atom orbitals $\{\vartheta\}$ can be divided into subsets which span the basis of certain irreducible representations. Therefore the decomposition of the reducible representation Γ_ϑ is

$$\Gamma_\vartheta = \sum_l n_l \Gamma_{\vartheta l} \qquad [446]$$

If all the multiplicities fulfil the condition $n_l \geq n_k$, then such a subset $\{\vartheta'\}$ exists for which the following relationship is true

$$\Gamma_{\vartheta'} = \sum_k n_k \Gamma_{\vartheta k} \qquad [447]$$

and each element of ϑ'_j transforms exactly as one of the functions h'_j. In other words, the expression [444] represents a linear combination of hybrid atomic orbitals from which net atomic orbitals of the central atom result. As far as the transformation matrix **A** is determined then the inverse matrix $\mathbf{B} = \mathbf{A}^{-1}$ defines the hybridization matrix

$$\{h\} = \mathbf{A}^{-1} \{h'\} = \mathbf{B} \{\vartheta'\} \qquad [448]$$

Results of the group theoretical approach for determining equivalent HAOs are presented in Table 30.

In order to calculate the hybrid atomic orbitals in polyatomic molecules without any symmetry the maximum overlap criterion can be used. The general solution of the problem is given by the Extended Maximum Overlap Approximation (EMOA) method (372-374). This method is based on an expression for the molecular binding energy ε in the form of two-centre increments

$$\varepsilon = \sum_{\nu}^{N} E_\nu = (1/2) \sum_{A,B} \sum_{i}^{A} \sum_{j}^{B} E_{ij}^{AB} (1 - \delta_{A,B}) \delta_{f(A,i),f(B,j)} \qquad [449]$$

where the particular binding energies E_{ij}^{AB} are proportional to weighted overlap integrals of bonding HAOs

$$E_{ij}^{AB} = K_t^{AB} \langle h_i^A | h_j^B \rangle \qquad [450]$$

The discrete topological function $f(A,i) = \nu$ describes the bonding model (electronic structure formula) of a molecule; their values are equal to the ordering numbers of the chemical bonds: $\nu = 1, 2, 3, \ldots$ The proportionality constants K_t^{AB} are regarded as semi-empirical parameters transferable from one molecule to another; they are determined for the pair of atoms (A, B) and the type of chemical bond ($t = \sigma, \pi, \delta$). They may be obtained by calibration to binding energies of small molecules.

TABLE 30

Equivalent hybrid atomic orbitals according to group analysis.

Coord. number	Group	Spatial arrangement	Hybridization of orbitals		
			σ	strong π	weak π
2	$D_{\infty h}$	linear	sp	p^2d^2	-
			dp	p^2d^2	-
	C_{2v}	bent	p^2	d(pd)	d(sd)
			ds	d(pd)	p(pd)
			d^2	d(pd)	p(spd)
3	D_{3h}	regular triangle	sp^2	pd^2	d^2
			dp^2	pd^2	d^2
			d^2s	pd^2	p^2
			d^3	pd^2	p^2
	C_{2v}	triangle	dsp	pd^2	(pd)d
	C_{3v}	trigonal pyramid	p^3	-	$(sd)d^4$
			d^2p	-	$(sd)p^2d^2$
4	T_d	tetrahedron	sp^3	d^2	d^3
			d^3s	d^2	p^3
	D_{4h}	square	dsp^2	d^3p	-
			d^2p^2	d^3p	-
	C_{3v}	irregular tetrahedron	d^2sp	-	d
			dp^3	-	s
			d^3p	-	s
	C_{4v}	tetragonal pyramid	d^4	d	(sp)p
5	D_{3h}	trigonal bipyramid	dsp^3	d^2	d^2
			d^3sp	d^2	p^2
	C_{4v}	tetragonal pyramid	d^2sp^2	d	pd^2
			d^4s	d	p^3
			d^2p^3	d	sd^2
			d^4p	d	sp^2
	D_{5h}	regular pentangle	d^3p^2	pd^2	-
	C_{5v}	pentagonal pyramid	d^5	-	$(sp)p^2$
6	O_h	octahedron	d^2sp^3	d^3	-
	D_{3h}	trigonal prism	d^4sp	-	p^2d
			d^5p	-	p^2s
	D_{3d}	trigonal antiprism	d^3p^3	-	sd
		mixed type	d^3sp^2		
			d^5s		
			d^4p^2		

TABLE 30 (Continued)

Coord. number	Group	Spatial arrangement	Hybridization of orbitals		
			σ	strong π	weak π
7	C_{3v}	structure of ZrF_7^{3-}	d^3sp^3	-	d^2
			d^5sp	-	p^2
	C_{2v}	structure of TaF_7^{2-}	d^4sp^2	-	dp
			d^4p^3	-	ds
			d^5p^2	-	ps
8	V_d	dodecahedron	d^4sp^3	d	-
	D_{4d}	antiprism	d^5p^3	-	s
	C_{2v}	planar centered prism	d^5sp^2	p	-

The optimum hybrid atomic orbitals are determined by the maximization of the molecular binding energy which leads to a system of matrix equations for individual centres

$$B_A = (D_A D_A^T)^{-1/2} D_A \qquad [451]$$

with

$$(D_A)_{ik} = \sum_{B\neq A}^{N} \sum_{j}^{B} \sum_{l}^{B} \langle \vartheta_k^A | \vartheta_l^B \rangle (B_A)_{jl} K_t^{AB} \delta_{f(A,i),f(B,j)} \qquad [452]$$

3.7.3 Distribution of Electron Density

The electron density $\rho(R)$ in the point R of the molecule is calculated as the mean value of the one-electron charge density operator

$$\rho(R) = \langle \Psi_0^{el} | \sum_{p}^{n} \delta(R - r_p) | \Psi_0^{el} \rangle = \sum_{i,j}^{m} P_{ij} \vartheta_i(R) \vartheta_j(R) \qquad [453]$$

where δ is the Dirac function. Redistribution of the electron density upon bond formation can be studied by the Roux function (377)

$$\Delta(R) = \rho(R) - \sum_{A}^{N} \rho_A(R) \qquad [454]$$

where $\rho_A(R)$ represents a hypothetical electron distribution caused by setting the free atom A into the corresponding molecular site. The difference between the electron density in the molecule and the sum of atomic electron densities should be calculated for each point of space. Graphically this function is represented by contour diagrams in important planes of the molecule. The properties of the function $\Delta(\mathbf{R})$ have been discussed by Rosenfeld (378).

Within the MO-LCAO approximation the total electron charge may be divided into spatially localized one-centre and two-centre terms

$$n = \sum_{i,j}^{m} P_{ij}\, S_{ij} = \sum_{A,B}^{N} \sum_{i}^{A} \sum_{j}^{B} \sum_{\nu} C^{A}_{\nu i}\, C^{A}_{\nu j}\, M_{\nu\nu}\, S^{AB}_{ij} \qquad [455]$$

where P_{ij} are the elements of the charge density - bond order matrix expressed through the LCAO coefficient matrix $\mathbf{C}$ and molecular orbitals occupation numbers $M_{\nu\nu}$. In the **Mulliken population analysis** (379) the charge distribution is described via the the following quantities.

1. **Net populations** characterize the one-centre contributions, namely:

a) net orbital population

$$n^{A}_{i} = P^{AA}_{ii} \qquad [456]$$

b) net atomic population

$$n_{A} = \sum_{i}^{A} n^{A}_{i} \qquad [457]$$

c) net atomic charge (in units of *e*)

$$q'_{A} = Z_{A} - n_{A} \qquad [458]$$

2. **Overlap populations** characterize two-centre contributions:

a) interorbital overlap population

$$n^{AB}_{ij} = 2\, P^{AB}_{ij}\, S^{AB}_{ij} \qquad [459]$$

b) interatomic overlap population

$$n_{AB} = \sum_{i}^{A} \sum_{j}^{B} n^{AB}_{ij} \qquad [460]$$

3. **Gross populations** represent the sum of the net populations and one half of the overlap populations:

a) gross orbital population

$$N^{A}_{i} = n^{A}_{i} + (1/2) \sum_{B} \sum_{j}^{B} n^{AB}_{ij} = P^{AA}_{ii} + \sum_{B} \sum_{j}^{B} P^{AB}_{ij}\, S^{AB}_{ij} \qquad [461]$$

b) gross atomic population

$$N_{A} = \sum_{i}^{A} N^{A}_{i} \qquad [462]$$

c) gross (effective) atomic charge (in units of *e*)

$$q^{0}_{A} = Z_{A} - N_{A} \qquad [463]$$

More detailed distribution of the electronic charge within the ν-th molecular orbital can be described by using partial net orbital populations

$$n_i^A(\nu) = M_{\nu\nu} \, (C_{\nu i}^A)^2 \qquad [464]$$

and partial overlap populations

$$n_{ij}^{AB}(\nu) = 2 \, M_{\nu\nu} \, C_{\nu i}^A \, C_{\nu j}^B \, S_{ij}^{AB} \qquad [465]$$

The critical point of the Mulliken population analysis is represented by the definition of the gross orbital population: the overlap population is equally distributed between two centres which is reasonable only in non-polar diatomic molecules. The Mulliken population analysis cannot exclude the observation of negative electron densities and also atomic orbital electron populations greater than 2.0. The results of this population analysis are not invariant with respect to the transformation of the basis set functions. The net orbital population n_i^A contribution is always attributed to the A-th centre although corresponding electron density maximum may lie in the region of another atom especially in the case of diffuse functions (380,381).

In reality, no physical criterion exists for the unambiguous definition of the effective atomic charge in molecules (the effective atomic charge is not an observable). Among a large number of different definitions for effective atomic charge, a few examples will be mentioned below.

1. Postulation of an additional criterion for unequal division of the overlap population betwen the centres: modified population analysis according to Löwdin (382), Jug (383) or others (384-389).
2. Introduction of certain integration principles according to which the electron density is summed up in the atomic region, such as the Politzer method (390), mid-plane method (391) and similar approaches (392-394).
3. Exclusion of the overlap population which may be obtained by an asymmetric orthogonalization of the AOs basis set in the molecule or by the neglect of differential overlap applied in CNDO, INDO and NDDO methods.

Population analysis for multideterminantal wave functions has been proposed by Karo (395).

The overlap population resulting from the Mulliken population analysis is often correlated with the strength of the chemical bond. Another quantity of this kind is represented by the Wiberg (bond-strength) index defined as (396)

$$W_{AB} = \sum_{i}^{A} \sum_{j}^{B} (P_{ij}^{AB})^2 \qquad [466]$$

Notice, $P_{ij} = 2\, P_{ij}^{\alpha}$ is used for a closed-shell system and $P_{ij}^{\alpha} = P_{ij}^{\beta} + P_{ij}^{\beta}$ for an open-shell system. The above index adopts values aroun 1.0 for the single bond, 2.0 for the double bond and 3.0 for the triple bond. It should be modified when dealing with the relativistic atomic spinorbital basis set. In the latter case the bond-order index is defined as (299)

$$B_{AB} = 2 \sum_{i}^{A} \sum_{j}^{B} (P_{ij}^{AB})^2 \qquad [467]$$

In studying donor-acceptor interactions in coordination compounds it is possible to define specific criteria which characterize the charge distribution, for example the σ-donor and π-acceptor index. They may be introduced using the partial net orbital populations $n_i^A(\nu)$. For example, for the π-acceptor ability of a diatomic ligand XY (dinitrogen molecule) coordinated linearly to a central atom, the π-acceptor index has been defined as (397)

$$X(\pi_A) = \sum_{A}^{X,Y} \sum_{i}^{A} \sum_{\nu \in \Gamma_e}^{occ} n_i^A(\nu) \qquad [468]$$

where the summation runs over only molecular orbitals (ν) of specific symmetry (irreducible representation Γ_e).

Electric moments represent another set of characteristics describing the charge distribution in molecules. The operator of the electric multipole moment of k-th order $\xi^{(k)}$ of a system consisting of M charged particles with the position vectors r_μ and electric charges q_μ is defined as a tensor (398)

$$\hat{\xi}^{(k)}_{\alpha\beta\ldots\omega} = \sum_{\mu}^{M} q_\mu\, (-1)^k (k!)^{-1}\, r_\mu^{2k+1}\, (\partial/\partial r_{\mu\alpha})\, (\partial/\partial r_{\mu\beta}) \ldots (\partial/\partial r_{\mu\omega})\, r_\mu^{-1} \qquad [469]$$

where the subscripts α, β, ..., ω denote one of the cartesian coordinates (X, Y, Z). The tensor $\xi^{(k)}$ has, in general, 2k + 1 independent components but this number can be by considering the symmetry properties of the system under study. The lowest electric multipole moments (2^n-poles) are:

a) scalar of the electric monopole - the charge of the system $q = \xi^{(0)}$;

b) vector of the electric dipole - the dipole moment of the system $d = \xi^{(1)}$;

c) tensor of the electric quadrupole - the quadrupole moment of the system $Q = \xi^{(2)}$;

d) tensor of the electric octupole - the octupole moment of the system $O = \xi^{(3)}$;

e) tensor of the electric hexadecapole - the hexadecapole moment of the system $H = \xi^{(4)}$.

Quantum-chemical calculations of molecular electric moments are used:

a) for testing the approximate molecular wave function by comparison of calculated and experimentally established values of the lowest electric moments;

b) to estimate the interaction energy of molecules when the separation between them is larger than their size (when the overlap of full molecular wave functions is negligible);

c) to characterize intramolecular charge distribution.

The **electric dipole** operator is given by

$$\hat{d} = \sum_{\mu}^{M} q_{\mu}\, r_{\mu} = |e|\ \Big(\sum_{A}^{N} Z_A\, R_A - \sum_{p}^{n} r_p\Big) \qquad [470]$$

where R_A is the positional vector of the A-th nucleus and r_p that of p-th electron with respect to the reference coordinate system. By shifting the origin of the coordinate system with the vector R_0 then $r_{\mu} = r'_{\mu} + R_0$ and the following relationship is true for the dipole moment

$$\langle d\rangle = \langle\Psi|\sum_{\mu}^{M} q_{\mu}\, r_{\mu}|\Psi\rangle = \langle\Psi|\sum_{\mu}^{M} q_{\mu}\, r'_{\mu}|\Psi\rangle + R_0 \sum_{\mu}^{M} q_{\mu} \qquad [471]$$

Thus the dipole moment of the molecule is invariant with respect to the shift of the origin of the coordinate system only in the case when the total charge of the molecule is equal to zero.

Within the Born-Oppenheimer approximation the mean value of the molecular dipole moment $\langle d\rangle$ can be written in the form of a sum of the electronic term $\langle d^{el}\rangle$ and the term induced by the nuclear point charges $|e|Z_AR_A$. The electronic contribution within the MO-LCAO-SCF approach is

$$\langle d^{el}\rangle = -|e| \sum_{p}^{n} \langle\Psi_0^{el}|r_p|\Psi_0^{el}\rangle =$$

$$= -|e| \sum_{\nu}^{occ} \langle\phi_{\nu}|r_1|\phi_{\nu}\rangle = -|e| \sum_{i,j}^{m} P_{ij}\ \langle\vartheta_i|r_1|\vartheta_j\rangle =$$

$$= -|e| \sum_{A,B}^{N} \sum_{i}^{A} \sum_{j}^{B} P_{ij}^{AB}\ (R_A\ S_{ij}^{AB} + \langle\vartheta_i^A|r'_1|\vartheta_j^B\rangle) \qquad [472]$$

where a local coordinate system is introduced (Fig. 16) with origin at the midpoint of the interatomic separation R_{AB}, so that

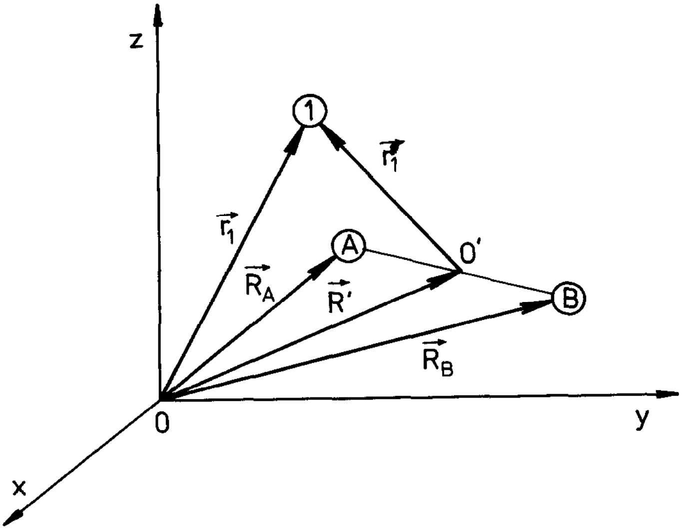

Fig. 16. Coordinate systems for the transformation of the molecular dipole moment.

$$r_1 = r_1' + (R_A + R_B)/2 \qquad [473]$$

Then the total molecular dipole moment is composed of:

a) contributions of elementary dipoles $|e|R_A q_A^0$ induced by effective atomic charges

$$q_A^0 = Z_A - \sum_B^N \sum_i^A \sum_j^B P_{ij}^{AB} S_{ij}^{AB} \qquad [474]$$

(using the Mulliken population analysis these charges are identical with gross atomic charges);

b) contributions of momentum integrals of the first order $<\vartheta_i^A|r_1'|\vartheta_j^B>$ in the atomic orbital basis set calculated in the local coordinate systems.

In the case of the electronic wave function constructed from strictly localized molecular orbitals, the electronic part of the dipole moment is given by the contributions from individual two-centre chemical bonds and lone electron pairs: $<\phi_\nu|r_1|\phi_\nu>$. This result explaines the success of the method of additivity of molecular dipole moments.

The dipole moment represents a sensitive criterion for testing the molecular wave function, since the molecular dipole moment is given by two terms of high value but opposite sign. Therefore a relatively small change in the electronic contribution causes a significant change in the value of the molecular dipole moment. For example, one of the drastic consequences of the ZDO approximation is the neglect of contributions of polar π-bonds to the molecular dipole moment.

Within the Born-Oppenheimer approximation the components of the tensor of the **electric quadrupole moment** of the molecule are given by the relationship

$$<Q_{\alpha\beta}> = |e| \ (1/2) \ [\sum_{A}^{N} Z_A(3R_{A\alpha} \ R_{A\beta} - R_A^2 \ \delta_{\alpha\beta}) - \\ - \sum_{p}^{n} <\Psi_0^{el}|(3r_{p\alpha} \ r_{p\beta} - r_p^2 \ \delta_{\alpha\beta})|\Psi_0^{el}>] \qquad [475]$$

where α and β represent cartesian coordinates. The quadrupole moment tensor may be transformed to its main axes using a similarity transformation

$$Q' = U^T \ Q \ U \qquad [476]$$

where the components in the main axes Q'_{XX}, Q'_{YY} and Q'_{ZZ} represent observable physical quantities (370,371). As the quadrupole moment is given by two terms of high value but opposite sign, it is also a sensitive criterion for testing the molecular wave functions (400).

The **electrostatic potential** $V^{es}(R)$ at a point R in the vicinity of an atomic or molecular system having an electronic density $\rho(r)$ is given by (401)

$$V^{es}(R) = \sum_{A} Z_A|R_A - R|^{-1} - \int \rho(R')|R' - R|^{-1} \ dR' \qquad [477]$$

where Z_A is the charge on nucleus A, located at R_A. The two terms on the right side correspond to the nuclear and electronic contributions to the potential; they have opposite signs and accordingly opposite effects. The electrostatic potential is exactly equal in magnitude to the electrostatic (coulombic) interaction energy between the static charge distribution of the system and a positive unit point charge located at R. It obeys exactly the Poisson's equation

$$\nabla^2 \ V^{es}(R) = 4\pi \ \rho(R) \qquad [478]$$

The total molecular energy can be ralated to the electrostatic potential by

$$E = (1/2) \sum_{A} (Z_A V_A^0 - \int_0^{Z_A} \left[Z'_A \left(\frac{\partial V_A^0}{\partial Z'_A} \right) - V_A^0 \right]_n dZ'_A \qquad [479]$$

where

$$V_A^0 = \sum_{B \neq A} Z_B|R_B - R_A|^{-1} - \int \rho(R)|R - R_A|^{-1} \ dR' \qquad [480]$$

is the electrostatic potential at nucleus A, which includes contributions from other nuclei as well as the n electrons.

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4. ELECTRON CORRELATION

By accounting for electron correlation the artifacts of the one-electron approximation are overcome. One possibility how to include correlation efects is the use of correlation functions explicitly dependent upon the interelectronic distances. Configuration interaction (CI) and the subsequently derived MC SCF and pair correlation theories, as well as the VB and GVB methods, have won wide application. In the above methods the determinantal functions basis set is generated by electronic excitations from the ground-state wave function. Modern approachs include the many-body perturbation theory (MBPT), the coupled cluster approach (CCA) and the Green function technique (GFT). These methods operate operate on the molecular spinorbital basis set using creation and annihilation operators. The resulting algebraic relationships are obtained with a diagrammatic technique.

Even calculations on the Hartree-Fock level are accompanied by numerical difficulties. They are performed on efficient computers but despite their time requirement they produce data which can only be taken for semi-quantitative. Taking into account electron correlation, the time requirement is increased. For this price, however, data are obtained which are capable of decribing the majority of molecular characteristics. Electron correlation should be taken into account especially when calculating the enthalpy of formation, activation energy, dissociation energy, ionization and excitation energy, electron affinity and weak intermolecular interactions. To a considerable extent the equilibrium and rate constant values are determined by correlation effects so that they assume a central position in the theoretical quantitative study of the majority of chemical problems.

4.1 CORRELATION ENERGY

In Section 2.2 we noted that the basic approximation in the theory of the chemical bond, molecular spectroscopy and chemical kinetics is the Born-Oppenheimer approximation enabling one to consider the multi-electron wave function $\Psi(1,2,\ldots,n)$ in the field of the frozen nuclei. The one-electron (Hartree-Fock) approximation is quite a rough description for the system where the probability density for the simultaneous occurrence of two electrons with opposite spins at definite locations is simply given by the product of the probability densities for the individual independent electrons. The electron repulsion term proportional to the factor r_{12}^{-1} requires a mutual correlation for electron motion. The neglect of electron correlation causes a defect in the electronic energy referred to as **correlation energy**. The correlation energy for a specific electronic state of the system, $|\Psi\rangle$, is defined as the difference between the eigenvalue of the Hamiltonian (as a rule, it is the non-relativistic Hamiltonian $\hat{H}_0$ in the Born-Oppenheimer approximation) and its average in the Hartree-Fock approximation for the corresponding determinantal function $|\Phi\rangle$

$$E_{corr} = \langle\Psi|\hat{H}_0|\Psi\rangle - \langle\Phi|\hat{H}_0|\Phi\rangle \qquad [1]$$

With the exception of very simple molecules neither the Hartree-Fock limit energy nor the exact (non-relativistic) energy are accessible for polyatomic molecules from *ab initio* calculations . Thus correlation energy computations contain a systematic error (Fig. 1). (The definition of correlation energy for excited states is problematic, since the Hartree-Fock limit energy is not precisely determined.) Since the one-determinantal (Hartree-Fock) function $|\Phi\rangle$ as well as the exact wave function $|\Psi\rangle$ satisfy the virial theorem then for correlation energy

$$E_{corr} = - \langle T\rangle_{corr} = (1/2)\ \langle V\rangle_{corr} \qquad [2]$$

so that the correlation error in the potential energy is, apart from the sign, twice as much as the correlation error in the kinetic energy.

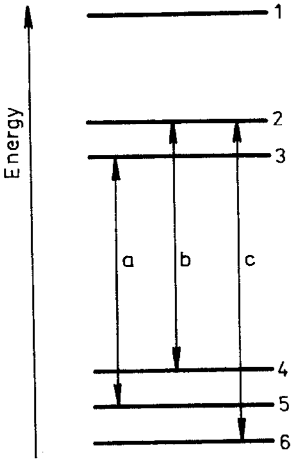


Fig. 1. Energy scale related to the correlation energy.
1 - SCF calculation in the minimum basis set;.
2 - near Hartree-Fock level;
3 - Hartree-Fock limit;
4 - extended CI;
5 - exact non-relativistic energy;
6 - experiment;
a - usual definition of the correlation energy;
b - practical estimate of the correlation energy;
c - experimental value for the correlation energy.

While the relative value for the correlation energy is small, representing about a 1 % correction with respect to the Hartree-Fock energy, its absolute value is large. Very often it is one or even more orders of magnitude higher than the reaction heat and activation energy values of chemical processes. There exist some reactions for which the approximate conservation of correlation energy can be considered (1); it is necessary that the number of electron pairs as well as the spatial distribution of neighbouring pairs be conserved. However, there are also processes known where there is a substantial change in the correlation energy. Among these latter processes are included electron excitation and electron ionization. In the description of weak intermolecular interactions, when dispersion forces are considered, an extraordinary important role is played by correlation effects.

Curves for the adiabatic potential at the SCF level, at larger deviations from equilibrium geometry, show substantial deviation from experiment. Very often, for infinitely separated nuclei, the SCF energy is more than twice the energy of the isolated atoms. For an F_2 molecule the sign of the dissociation energy at the SCF level is even negative (Fig. 2). These artifacts of the one-electron approximation vanish when correlation effects are included.

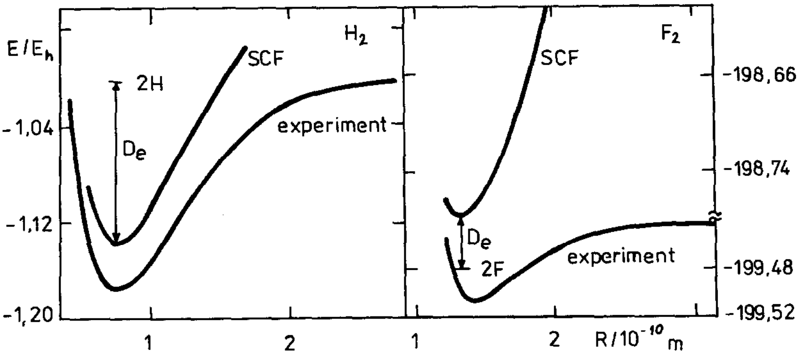


Fig. 2. Curves for the adiabatic potential for H_2 and F_2 molecules.

The methods used for solving the correlation problem where explicit functions of the $\vartheta(r_{12})$ type are considered, have found only limited use for systems with a small number of electrons. These methods have historically been derived from the fundamental work of Hylleraas (2). They were used especially for He (2-7), Li (8,9) and Be (10,11) atoms (Table 1).

TABLE 1

Atomic calculations with electron correlation functions.

Atom	Energy (E_h)	Number of terms	Ref.
He	-2.902 44		[2]
	-2.903 209	34	[3]
	< -2.903 723 7	80	[4,5]
	> -2.903 746 7		
	-2.903 724 375	1078	[6,7]
	(-2.903 72)	exper.	
Li	-7.476 07	10	[8]
	-7.478 025	60	[9]
	(-7.478 06)	exper.	
Be	-14.666 54	107	[11]
	(-14.666 7)	exper.	

For the He atom Hylleraas (2) used a wave function of the type

$$\Psi(r_1,r_2) = m\, e^{-ks/2} \sum_{l,m,n} C_{lmn}\, k^{l+m+n}\, s^l\, t^m\, u^n \qquad [3]$$

with elliptic coordinates $s = r_1 + r_2$, $r = r_2 - r_1$ and $u = r_{12}$. Later the method was modified by Kinoshita (4,5) who considered the wave function in the form of a series having 80 terms. The most precise calculations were done by Pekeris (6,7) in perimetric coordinates

$$u = k(r_2 + r_{12} - r_1)/2 \qquad [4]$$

$$v = k(r_1 + r_{12} - r_2)/2 \qquad [5]$$

$$w = k(r_1 + r_2 - r_{12}) \qquad [6]$$

with the wave function

$$\Psi(r_1,r_2) = e^{-(u+v+w)} \sum_{l,m\,n} C_{lmn}\, L_l(u)\, L_m(v)\, L_n(w) \qquad [7]$$

having 1078 terms, $L_n(w)$ being the normalized Laguerre polynomials of the n-th order.

Precise calculations for the H_2 molecule (12) were based on the correlation functions according to formula [223] of Chapter 2. They yielded the dissociation energy (36 117.4 cm^{-1}) which is in full agreement with the experimental value (36 117.3 ± 1.0 cm^{-1}).

4.2 VARIATIONAL CONFIGURATION INTERACTION

In the one-electron approximation the one-electron function basis set is used, represented by the molecular spinorbitals. molecular spinorbitals. A determinental function Φ_u is associated with every electron configuration taking into account the collective property of a system of electrons (fermions), i. e. the antisymmetry with respect to transposition of electron coordinates. Determinantal functions form the basis set in the Hilbert space giving rise to the possibility of exact expression of the many-electron wave function in the form of a CI series

$$\Psi^{el}(1,2,\ldots,n) = \sum_u^{\infty} a_u \, \Phi_u \qquad [8]$$

While in the one-electron approximation $\Psi_u^{el} \approx \Phi$, with independent particles, the electron correlation effects were neglected, they may be taken into account by inclusion of configuration interactio.

In the variational Configuration Interaction (CI) method the coefficients in the CI expansion are evaluated by the linear variational method (Section 1.2.3). Its principle rests on the construction of matrix elements of the electronic Hamiltonian $H_{uv}^{CI} = \langle\Phi_u|\hat{H}^{el}|\Phi_v\rangle$ and on the non-orthogonality integrals $S_{uv}^{CI} = \langle\Phi_u|\Phi_v\rangle$. By solving the characteristic equation

$$(H^{CI} - ES^{CI})\{a\} = 0 \qquad [9]$$

the column vector {a} of the expansion coefficients is obtained; this corresponds to an eigenvalue E of the secular equation having a meaning of the electronic energy.

The variational CI is of general use for atoms and molecules as well as for systems with closed shells and open shells, for ground and excited states and for geometries close and from the equilibrium atomic configuration.

The configuration interaction can be performed as the next step following the SCF procedure (when the molecular orbitals are known) or after GVB or MC SCF methods. Unlikely to MC SCF method, the number of the CI series terms is extremely large (of the order 10^3 to 10^5). For this reason configuration interaction represents an exacting numerical problem.

Substantial simpification of the CI procedure can be achieved by utilizing the molecular symmetry. For this purpose it is useful to consider the spin-adapted configuration functions representing the eigenvalues of the operator $\hat{S}_z$ and $\hat{S}^2$; this is obtained by a simple linear combination of the several (as a rule two or three) determinantal functions with combination coefficients known from the symmetry requirements, similarly as in the RHF method.

In an analogous way, **symmetry-adapted configuration functions** are introduced representing eigenfunctions of the operators $\hat{L}_z$ and $\hat{L}^2$.

Note that orbitals obtained using the SCF procedure usually have random phases. This is not important for orbitals belonging to one-dimensional irreducible representations. The symmetry adaptation of configuration functions, however, does depend upon the selection of phases of orbitals which belong to multidimensional irreducible representation. For example, if a pair of orbitals should be transformed as (x,y) but in fact, are transformed as (x,-y), then the configuration function will not have the correct symmetry. Therefote it is necessary to obtain correct phase for orbitals to be used in the CI calculation.

A very important property resulting from symmetry is the fact that matrix elements of H^{CI}_{uv} are zero if the configuration functions Φ_u and Φ_v belong to different irreducible representations of the symmetry point group of molecule. Due to the above property the H^{CI} matrix can be arranged into block-diagonal form. (For this purpose it is more advantageous if the RHF orbitals are processed, since the orbitals do not possess the desired symmetry properties.)

Characteristic equation can be solved separately for the blocks corresponding to individual symmetry types. Very often the H^{CI} matrix contains only some 20 % non-zero elements, so that its arrangement into block-diagonal form can substantially decrease the requirements placed upon numerical computer processing.

Moreover, the symmetry adapted configuration functions are automatically orthogonal to all other configuration functions of a different symmetry type. Then, on the basis of the separation theorem (Section 1.2.3) an upper limit for the excited state energy can be estimated, being the energy value of the lowest state within its relevant symmetry type. The above estimate does not require explicit calculation of all the lower states of another symmetry.

The number of determinantal functions which can be obtained for the basis set of m orbitals for a state with n electrons with total spin S is calculated according to the Weyls formula

$$N = (2S + 1)/(m + 1) \begin{pmatrix} m + 1 \\ n/2 - S \end{pmatrix} \begin{pmatrix} m + 1 \\ n/2 + S + 1 \end{pmatrix} \qquad [10]$$

For $m \gg n \gg S$ the above number can be roughly approximated as $N \approx n^{-2}(2me/n)^n$, where e is natural logarithm base.

If configuration interaction is performed on all the determinantal (configuration) functions produced at specifc m and n this is referred to as **complete** CI. In the case of a **limited** CI calculation either the orbital basis is reduced from m to m' (omitting several highest virtual MOs) or only several types of determinantal functions are included in the CI series. In the case of a fixed MO basis the determinental functions can be classified as monoexcited Φ_i^a (if the i-th occupied spinorbital is replaced by virtual a), biexcited Φ_{ij}^{ab} (if substituting a pair of virtual orbitals for a pair of occupied), triexcited, tetraexcited, etc. In many applications into the CI series only the monoexcited and biexcited configurations are included. Very seldomly are triexcitations and tetraexcitations included and very rarely configurations from higher excitations. Monoexcited and biexcited configurations yield about 90% of the correlation energy.

For a complete CI calculation the solution of the characteristic equation is invariant with respect to an arbitrary unitary transformation applied to the molecular orbital basis set so that the symmetry and spin adaptation of the configuration functions can be omitted.

For a limited CI calculation this invariant property is lost. Thus, the question of convergence of the CI expansion is emphasized, i.e. the number of CI terms which, in a given molecular orbital basis set, secures a certain degree of accuracy of the CI wave function (e.g. the percentage of the correlation energy covered).

Alternatively the **natural orbitals** (NO) rather than molecular orbitals can be used in the CI method. Such orbitals were introduced by Löwdin (13) as the eigenfunctions of the first-order spin-free density function $P_1(r';r)$. The corresponding eigenvalues are the non-integer occupation numbers of the natural orbitals. NOs have the advantage that they provide a much faster convergence of the CI series compared with canonical MOs (Table 2). The density functions, however, are only known after performing the configuration interaction, so that special features of NOs are losing their umerical effect.

TABLE 2
Convergence of the CI method using MOs or NOs.[a]

Per-cent of E_{corr}	Number of configuration functions MO	NO
50	87	32
60	140	50
70	220	79
80	351	147
90	617	362
95	944	697
98	1410	1213
99	1760	1652
100	4120	4120

[a] For H_2O molecule (15).

One way to overcome these troubles is by using the method of **itarative orbitals** (INO) (14).

When implementing configuration interaction the following steps must be taken (15,16):

1. selection of the proper atomic orbital basis set $\{\vartheta\}$ and computation of the one-electron and two-electron integrals in this basis for the given molecular geometry;
2. calculation of the molecular orbitals $\{\phi\}$ using the SCF procedure and transformation of the integrals from the atomic orbital basis set into the molecular orbital basis set;
3. selection and construction of the set of symmetry and spin adapted configuration functions suitable for the description of the electronic state under study; calculation of the respective H^{CI}_{uv} matrix elements from the configuration functions;
4. computation of the lowest, E_0, or several lowest eigenvalues and of the corresponding eigenvectors of the matrix H^{CI};
5. construction of the reduced density functions P_1 and P_2 from the known eigenvectors $\{a_0\}$ as well as mean values of the one-electron, $\hat{A}^{(1)}$, and two-electron, $\hat{A}^{(2)}$, operators for observables. Calculations may be accompanied by construction of the reduced transition functions from the eigenvectors $\{a_i\}$ and $\{a_j\}$ to determine the transition moments between two electronic states Ψ_i and Ψ_j.

Both the one-electron and two-electron integrals is the mole- molecular orbital basis set have to be known to obtain matrix elements H^{CI}_{uv}. Canonical MOs obtained via the SCF procedure are orthogonal, which helps to simplify the matter. In some cases (such as GVB) orthonormalization of the one-electron function must be carried out. For this purpose either the modified Schmidt orthogonalization procedure or the Löwdin symmetry orthogonalization method is used.

In the following transformations into the molecular orbitals basis set

$$\langle i|\hat{h}|j\rangle = \sum_{p,q}^{m} C_{ip}^{*}\, C_{jq}\, \langle p|\hat{h}|q\rangle \qquad [11]$$

$$\langle ij|\hat{g}|kl\rangle = \sum_{p,q,r,s}^{m} C_{ip}^{*}\, C_{jq}\, C_{kr}^{*}\, C_{ls}\, \langle pq|\hat{g}|rs\rangle \qquad [12]$$

the latter represents an extremely exacting numerical problem. In fact, it is necessary to calculate as many as m^4 two-electron integrals $\langle ij|\hat{g}|kl\rangle$, each representing the result of four-fold summation and containing m^4 terms. This results in the process being dependent on the basis set size to the power of m^8. Fortunately, this process contains redundant operations, which can be eliminated by successive application of four summations

$$\langle pq|\hat{g}|rl\rangle = \sum_{s=1}^{m} C_{ls}\, \langle pq|\hat{g}|rs\rangle \qquad [13]$$

$$\langle pq|\hat{g}|kl\rangle = \sum_{r=1}^{m} C_{kr}\, \langle pq|\hat{g}|rl\rangle \qquad [14]$$

$$\langle pj|\hat{g}|kl\rangle = \sum_{q=1}^{m} C_{jq}\, \langle pq|\hat{g}|kl\rangle \qquad [15]$$

$$\langle ij|\hat{g}|kl\rangle = \sum_{p=1}^{m} C_{ip}\, \langle pj|\hat{g}|kl\rangle \qquad [16]$$

A successive transform such as this is dependent on the dimension of the basis set to the power of m^5, which, compared to the original m^8 process represents a substantial simplification. Further simplification can be achieved using the symmetry properties (by dividing individual transformations into blocks according to irreducible representations).

The matrix elements H_{uv}^{CI} are given by the general expression [204] of Chapter 1

$$H_{uv}^{CI} = \sum_{i,j}^{m} \langle i|\hat{h}|j\rangle\, D^{uv}(i|j) + (1/2) \sum_{i,j,k,l}^{m} \langle ij|\hat{g}|kl\rangle\, D^{uv}(ij|kl) \qquad [17]$$

where $D^{uv}(i|j)$ and $D^{uv}(ij|kl)$ are the generalized minors formed of the matrix of non-orthogonality integrals $D_{kl}^{uv} = \langle \psi_k^u | \psi_l^v \rangle$ in the molecular spinorbital basis set. In the orthogonal basis set of

TABLE 3

Slater rules for matrix elements of the electronic Hamiltonian.[a]

Determinantal functions	One-electron term $H_{uv}^{(1)} = <\Phi_u\|\hat{H}^{(1)}\|\Phi_v>$	Two-electron term $H_{uv}^{(2)} = <\Phi_u\|\hat{H}^{(2)}\|\Phi_v>$
1. Determinants are equivalent		
$\Phi_u = \|\psi_1\psi_2\cdots\psi_n\|$ $\Phi_v = \|\psi_1\psi_2\cdots\psi_n\|$	$\sum_i <i\|\hat{h}\|j>$	$\sum_{i<j} [<ij\|\hat{g}\|ij> -$ $- <ij\|\hat{g}\|ji>\delta_{\eta(i),\eta(j)}]$
2. Determinants differ in one spinorbital $\psi_k \neq \psi_k'$		
$\Phi_u = \|\psi_1\cdots\psi_k\cdots\psi_n\|$ $\Phi_v = \|\psi_1\cdots\psi_k'\cdots\psi_n\|$	$<k\|\hat{h}\|k'>$	$\sum_i [<ik\|\hat{g}\|ik'> -$ $- <ik\|\hat{g}\|k'i>\delta_{\eta(i),\eta(k')}\cdot$ $\cdot\ \delta_{\eta(i),\eta(k')}]$
3. Determinants differ in two spinorbitals $\psi_k \neq \psi_k'$ and $\psi_j \neq \psi_j'$		
$\Phi_u = \|\psi_1\cdots\psi_k\cdots\psi_j\cdots\psi_n\|$ $\Phi_v = \|\psi_1\cdots\psi_k'\cdots\psi_j'\cdots\psi_n\|$	0	$<ik\|\hat{g}\|k'j'> -$ $- <ik\|\hat{g}\|j'k'>\delta_{\eta(k),\eta(j')}\cdot$ $\cdot\ \delta_{\eta(j),\eta(k')}$
4. Determinants differ in more than two spinorbitals		
	0	0

[a] Matrix elements of the Hamiltonian are $H_{uv}^{CI} = H_{uv}^{(1)} + H_{uv}^{(2)}$.

molecular spinorbitals, **Slater rules** can be applied with great advantage to evaluate the matrix elements H_{uv}^{CI} (Table 3). The common transcription valid for Slater rules (17) in the molecular spinorbital basis set is given by

$$H_{uv}^{CI} = \sum_i^m Q_i <i|\hat{h}|i'> + \sum_{i,j}^m Q_{ij}(<ij|\hat{g}|i'> - <ij|\hat{g}|j'i'>) \qquad [18]$$

where for the numerical coefficients it holds true that

$$Q_{ij\ldots} = \begin{cases} 1, \text{ if } k = k' \text{ for all } k \neq i,j,\ldots \\ 0, \text{ elsewhere} \end{cases} \qquad [19]$$

and $Q_0 = 0$ if $\Phi_u \neq \Phi_v$. The determinantal functions

$$\Phi_u = \hat{A}\{\psi_1\psi_2\cdots\psi_n\} = |1,2,\ldots,n| \qquad [20]$$

$$\Phi_v = \hat{A}\{\psi_1'\psi_2'\cdots\psi_n'\} = |1',2',\ldots,n'| \qquad [21]$$

are arranged so that maximum coincidence in the arrangement of the spinorbitals is achieved, i.e. $\psi_i = \psi_i'$ for the maximum number of i-values. For computer calculations, at present, several efficient algorithms serve to yield the matrix elements H_{uv}^{CI} among symmetry adapted and spin adapted functions (15,16).

The structure of the H^{CI} matrix follows from the Slater rules. For the matrix elements H_{uv}^{CI} differing by only one spinorbital

$$H_{uv}^{CI} = \langle\Phi_u(k\rightarrow k')|\hat{H}^{el}|\Phi_v\rangle =$$

$$= \langle k|\hat{h}|k'\rangle + \sum_i (\langle ik|\hat{g}|ik'\rangle - \langle ik|\hat{g}|k'i\rangle) = \langle k|\hat{F}|k'\rangle \qquad [22]$$

If the one-electron functions $|k\rangle$ and $|k'\rangle$ represent the canonical molecular orbitals obtained by solving the Hartree-Fock (Roothaan) equations, then the relationship

$$\langle k|\hat{F}|k'\rangle = \epsilon_k \, \delta_{k,k'} \qquad [23]$$

is true; consequently the matrix elements [22] all are zero. The above result represents the contents of the **Brillouin theorem**, which, as a rule, is formulated as follows: the matrix elements of a one-electron Hamiltonian between configuration functions of the ground and monoexcited states are zero. It then follows that monoexcited configurations do not influence the ground-state energy. In combination with the doubly excited configurations the CI is influenced by the monoexcited configurations.

The general rule to reduce the number of CI matrix elements is based on the property that operators commuting with the Hamiltonian share the same eigenfunctions. Then, if the wave function Ψ is connected with a definite symmetry, orbital angular momentum, spin angular momentum, etc., then every configuration function $\Phi_u$contributing to the CI expansion of Ψ must show the same symmetry, orbital angular momentum, spin, etc. For example, for the ground state $^1\Sigma_g^+$ of a H_2 molecule the configuration $(1\sigma_g)^2$ cannot be combined with the configuration $(1\sigma_g)^1(1\sigma_u)^1$ besause the latter is of different symmetry. The configuration $(1\sigma_u)^1(2\sigma_u)^1$ can contribute to the CI expansion, whereby the symmetrized combination for the singlet state

$$\Phi_u = (|1\sigma_u^+,2\sigma_u^-| - |1\sigma_u^-,2\sigma_u^+|)/\sqrt{2} \qquad [24]$$

should be used; the positive sign combination for the triplet state again disappear.

The solution of the characteristic equation [9] of high order (10^3 - 10^5) represents is a complicated numerical problem. Usually we operate in an orthogonal basis set of configuration functions. The existing computers do not allow one to retain the high-dimensional H^{CI} matrix in the fast memory, so that the standard diagonalization algorithms cannot be used. Special numerical procedures have been developed to find the eigenvalues and eigenvectors of the H^{CI} matrix stored in an external storage (magnetic tape or disc).

At present, algorithms are often used which enable implementation of configuration interaction direct from the set of molecular integrals $\langle i|\hat{h}|j\rangle$ and $\langle ij|\hat{g}|kl\rangle$. This method is referred to as the CIMI (Configuration Interaction from Molecular Integrals) (18). Another version of the CI - the vector method - also does not require the construction, manipulation and diagonalization of the high-dimensional H^{CI} matrix (19).

4.3 VALENCE BOND METHOD

The Valence Bond (VB) method appeared as an extension of the Heitler-London approach applied to the hydrogen molecule. The development of the method was based on idea that the chemical bond is formed as a consequence of spin pairing; the corresponding electrons singly occupy valence orbitals of the respective atoms in the molecule.

The VB method utilizes the atomic orbitals basis set $\{\vartheta\}$ which, in general, is non-orthogonal. In this basis set the configuration functions are constructed

$$\Phi_u(X_1,X_2,\ldots,X_n) = \hat{A}\{\Omega_u(r_1,r_2,\ldots,r_n)\ \Theta_u(s_1,s_2,\ldots,s_n)\} \qquad [25]$$

with different spin components $\Theta_u(s_1,s_2,\ldots,s_n)$ coupled into the total spin S of the system and with the orbital component

$$\Omega_u(r_1,r_2,\ldots,r_n) = \phi_1(r_1)\ \phi_2(r_2)\ \ldots\ \phi_n(r_n) \qquad [26]$$

Then the electronic wave function of the molecule is written in the form of the VB expansion

$$\Psi^{VB} = \sum_u a_u\ \Phi_u \qquad [27]$$

which is formally analogous to the variational CI. In the VB method, however, neither a reference configurational function nor the corresponding Hartree-Fock energy occur and thus the correlation energy is not defined. The effects of the electron correlation are implicitly included into the VB method.

The coefficients of the linear combination are obtained via the variational method by solving the characteristic equation

$$(H^{VB} - ES^{VB})\{a\} = 0 \qquad [28]$$

where the matrix elements of the electronic Hamiltonian are $H_{uv}^{VB} = \langle\Phi_u|\hat{H}^{el}|\Phi_v\rangle$ and the non-orthogonality integrals are $S_{uv}^{VB} = \langle\Phi_u|\Phi_v\rangle$.

When the orbital component Ω_u of the configuration function Φ_u contains only different singly occupied atomic orbitals, we speak of a **covalent structure** instead of the **ionic structure** in which doubly occupied atomic orbitals also occur.

The principal problem of the VB method rests in evaluation of the matrix elements H_{uv}^{VB} and S_{uv}^{VB} in the non-orthogonal atomic orbital basis set. Within the constraint of basis set orthogonality the calculations become much simpler but the problem of the contruction of the high-dimensional H^{VB} matrix still remains open.

It is useful to exploit the relationship between the VB method and the theory of the symmetric group (20). The spin functions form a basis set of 2^n-dimensional representation of the symmetry group of permutations where the number n of singly occupied orbitals is used to construct the configuration functions. The spin function basis set may be selected in such a way so that the reducible representation of the group splits into irreducible components of lower dimension. One can then rewrite the characteristic equation into a block-diagonal form so that the problem is reduced to characteristic equations of lower dimension.

The full CI in the molecular orbital basis set (in LCAO form) is completely equivalent to the VB method in the same atomic orbital basis set. Then the configuration functions of the MO method Φ^{MO} and the VB method Φ^{VB} are interrelated by a unitary transformation

$$\{\Phi^{VB}\} = U\ \{\Phi^{MO}\} \qquad [29]$$

and the CI coefficients by the relationship

$$\{a^{VB}\} = U^{-1}\ \{a^{MO}\} \qquad [30]$$

so that the wave function is

$$\Psi = \{\Phi^{MO}\}^T\ \{a^{MO}\} = \{\Phi^{VB}\}^T\ U^{-1}\ U\ \{a^{VB}\} = \{\Phi^{VB}\}^T\ \{a^{VB}\} \qquad [31]$$

As an example of the VB calculation the LiH molecule is selected. The calculation consists of these steps:

1. Basis set selection. The minimum basis set is represented by four (m = 4) atomic orbitals: ϑ_1(Li,1s), ϑ_2(Li,2s), ϑ_3(Li,2p$_z$) and ϑ_4(H,1s).
2. Integral evaluation. In the above basis set m(m + 1)/2 = 10 one-electron integrals $\langle\vartheta_r|\hat{h}|\vartheta_s\rangle$, 10 overlap itegrals $\langle\vartheta_r|\vartheta_s\rangle$ and

55 two-electron integrals $<\vartheta_r\vartheta_s|\hat{g}|\vartheta_t\vartheta_u>$ should be calculated.

3. Construction of spin-adapted configuration functions. According to the Weyls formula [10] there are N = 20 possible configuration functions for the basis set size m = 4, number of electrons n = 4 and the total spin S = 0. For example, the first spin-adapted function Φ_1 corresponding to the electron configuration $(\vartheta_1)^2(\vartheta_2)^1(\vartheta_4)^1$ is $\Phi_1 = \hat{A}\{\vartheta_1\alpha, \vartheta_2\alpha, \vartheta_1\beta, \vartheta_4\beta\} + \hat{A}\{\vartheta_1\alpha, \vartheta_4\alpha, \vartheta_1\beta, \vartheta_2\beta\}$.

4. Construction of matrix elements of H^{VB} and S^{VB}. In the spin-adapted basis set the respective matrix elements are constructed. They may be expressed in terms of integrals calculated in the atomic orbital basis set by means of formula [204] of Chapter 1 in non-orthogonal space.

5. Solution of characteristic equation. For a selected length of the VB expansion the characteristic equation [28] is solved. Some selected data dependent on the length of the expansion are compared in Table 4.

TABLE 4

Comparison of the VB method with MO + CI approach for LiH molecule.

VB method		MO method	
Wave function	Energy E/E_h	Wave function	Energy E/E_h
Ψ_1	-7.9434	Φ_0^{MO}	-7.9667
Ψ_5	-7.9809		
Ψ_{10}	-7.9820		
Ψ_{20}	-7.9820	Ψ^{MO+CI}	-7.9820

Certain limitations of the one-determinantal (Hartree-Fock) approximation are overcome by the **Generalized Valence Bond** (GVB) method. One-determinantal functions cannot be used to describe bond dissociation; this is improved by the procedure described below. In the hydrogen molecule the equilibrium geometry and its vicinity can be described by the wave function

$$\Psi \approx \Phi_0^{MO} = \hat{A}\{\phi\alpha, \phi\beta\} = |\psi^+, \psi^-| \qquad [32]$$

Such a function, however, is not capable of describing the separated atoms since it contains the only orbital occupied by an electron pair. In the dissociation limit a couple of separated atoms is described by an RHF wave function for the singlet state

$$\Psi' \approx \Phi'_0 = \hat{A}\{\phi_1\phi_2(\alpha\beta - \beta\alpha)\} \qquad [33]$$

The required orthogonality $<\phi_1|\phi_2> = 0$ prohibits us from using wave function above to describe the chemical bond.

A continuous transition between these limiting cases is covered by the GVB wave function

$$\Psi^{GVB} = \hat{A}\{\phi'_1\phi'_2(\alpha\beta - \beta\alpha)\} = \hat{A}\{\phi'_1\phi'_2 + \phi'_2\phi'_1)\alpha\beta\} \qquad [34]$$

where $S_{12} = <\phi'_1|\phi'_2> \neq 0$. An additional functional freedom associated with such a wave function enables one to balance the optimum ionic and covalent character of the chemical bond. For this reason the binding (dissociation) energy has a larger value than that derived using the one-determinantal functions since the correlation energy is partly included.

The usual treatment of the GVB method is the substitution of a traditional singlet electron pair for the GVB pair, containing a pair of non-orthogonal molecular orbitals coupled into the singlet

$$\phi_a\phi_a\alpha\beta \rightarrow \phi_{1a}\phi_{2a}(\alpha\beta - \beta\alpha) = (\phi_{1a}\phi_{2a} + \phi_{2a}\phi_{1a})\alpha\beta \qquad [35]$$

The general form of the GVB wave function is (21)

$$\begin{aligned}\Psi^{GVB} &= \hat{A}\{[\text{core}][\text{pair}][\text{open}]\} = \\ &= \hat{A}\{[\phi_1\phi_1\alpha\beta\cdots\phi_{p-1}\phi_{p-1}\alpha\beta][\phi_{1p}\phi_{2p}(\alpha\beta - \beta\alpha)\cdots\phi_{1m}\phi_{2m}(\alpha\beta - \beta\alpha)] \\ &\quad [\phi_{m+1}\alpha\cdots\phi_n\alpha]\}\end{aligned} \qquad [36]$$

Usually the additional condition of strong orthogonality is imposed, requiring the orthogonality of all molecular orbitals except those describing the GVB pair. The electronic energy may be written in the form

$$E^{el} = 2\sum_i^n f_i h_{ii} + \sum_{i,j}^n (a_{ij}J_{ij} + b_{ij}K_{ij}) \qquad [37]$$

where

$$J_{ij} = (ii|jj) = <\psi_i|\hat{J}_i|\psi_i> = <\psi_j|\hat{J}_i|\psi_j> \qquad [38]$$

$$K_{ij} = (ij|ij) = <\psi_i|\hat{K}_i|\psi_i> = <\psi_j|\hat{K}_i|\psi_j> \qquad [39]$$

despite the fact that GVB pair contains non-orthogonal orbitals. The last possibility follows from the fact that each GVB pair can be rewritten into the natural orbital form

$$\phi'_{1i}\phi'_{2i}(\alpha\beta - \beta\alpha) \rightarrow (s_{1i}\phi_{1i}\phi_{1i} - s_{2i}\phi_{2i}\phi_{2i})\alpha\beta \qquad [40]$$

where

$$<\phi_{1i}|\phi_{2i}> = 0 \qquad [41]$$

The coefficients f, a and b now become functions of the pair coefficients s_{1i} and s_{2i}. The requirement for the stationary energy leads to a general variational condition

$$\sum_i \langle \delta\phi_i | \hat{F}_i | \phi_i \rangle = 0 \tag{42}$$

where

$$\hat{F}_i = f_i \hat{h} + \sum_j (a_{ij} \hat{J}_j + b_{ij} \hat{K}_j) \tag{43}$$

is the generalized Fock operator. Variation of the orbital ϕ_ν at the unchanged remaining n-1 orbitals yields the condition

$$\langle \delta\phi_\nu | \hat{F}_\nu | \phi_\nu \rangle = 0 \tag{44}$$

or the pseudocharacteristic equation

$$\hat{F}_\nu | \phi_\nu \rangle = \varepsilon_\nu | \phi_\nu \rangle \tag{45}$$

The permitted intermixing of occupied molecular orbitals provides the necessary and sufficient conditions for the stationary energy

$$\langle \phi | (\hat{F}_\nu - \hat{F}_\mu) | \phi_\mu \rangle = 0 \tag{46}$$

for all occupied orbitals ϕ_μ and ϕ_ν.

4.4 MULTICONFIGURATION SCF METHOD

This method is based on the expressing of the multielectron wave function Ψ through the linear combination of several determinantal functions Φ_u

$$\Psi = \sum_u a_u \Phi_u \tag{47}$$

It differs from the CI method in the fact that optimization is performed not only for coefficients of configuration interaction a_u but also for the LCAO coefficients C_{ip}. Hence the name - Multiconfiguration Self-Consistent Field: MC SCF. It differs from the open-shell RHF method in the fact that the number of terms of the CI expansion [47] is not limited to the minimum securing proper symmetry of the electronic wave function. While the coefficients of the linear combination of determinantal functions in the RHF method are known beforehand (from symmetry analysis), they must be calculated in the MC SCF method. In practice, in the series [47] only those configurations which influence the quality of the resulting wave function to the maximum extent are included. Usually 5 to 10 configurations are concerned and, as a rule, no more than 100 configurations.

The variational condition for calculation of the CI coefficients $\{a_u\}$ leads to the characteristic equation

$$(H^{CI} - ES^{CI})\{a\} = 0 \qquad [48]$$

where $H^{CI}_{uv} = \langle\Phi_u|\hat{H}^{el}|\Phi_v\rangle$ are the matrix elements of the electronic Hamiltonian in the determinantal function basis set and $S^{CI}_{uv} = \langle\Phi_u|\Phi_v\rangle$ are the non-orthogonality integrals. The matrix elements H^{CI}_{uv} are calculated according to rules described in Section 4.2.

For calculation of LCAO coefficients the electronic energy will be expressed through the spin-free density functions P_1 and P_2 [189] - [190] of Chapter 1

$$E^{el} = \sum_{i,j}^{n} (P_1)_{ji}\langle i|\hat{h}|j\rangle + (1/2)\sum_{i,j,k,l}^{n} (P_2)_{kl,ij}\langle ij|\hat{g}|kl\rangle \qquad [49]$$

After expressing the LCAO expansion of molecular orbitals $\{\phi\} = C\{\vartheta\}$ for energy variation we shall obtain

$$\delta E^{el} = Tr\{\delta C(hC^{+}P_1 + Z)\} + (\text{complex conjugate term}) \qquad [50]$$

where the electron interaction matrix has the following matrix elements

$$Z_{ip} = \sum_{j,k,l}^{n} \sum_{q,r,s}^{n} C^{*}_{jq} \langle pq|\hat{g}|rs\rangle\, C_{kr}\, C_{ls}\, (P_2)_{kl,ij} \qquad [51]$$

Variation of the orthonormality condition for molecular orbitals $CSC^{+} = I$ yields

$$\sum_{p,q} \delta C^{*}_{ip}\, S_{pq}\, C_{jq} + (\text{complex conjugate term}) = 0 \qquad [52]$$

Then variation of the energy under the orthonormality condition leads to the MC SCF equations in the form

$$hC^{+}P_1 + Z = SC^{+}L \qquad [53]$$

where L is the hermitian matrix of Lagrangian multipliers. The equations above can be solved using special numerical procedures (20,22). One eliminates the non-hermitian part of the matrix L through Jacobi-type rotations. Another possibility is to apply gradient methods for the direct minimization of the total energy, the application of generalized Brillouin theorem, etc. The most frequently used procedures exploit the so called quadratically convergent algorithms. In some specific cases the MC SCF equations can be transformed into a pseudocharacteristic form (23).

Within the framework of the MC SCF methods two fundamentally importance approaches can be distinguished. One - the **pair excited**

MC SCF theory is based on the principle of generating the determinantal functions Φ_u $(u \neq 0)$ by excitation of the electron pair from the occupied orbital ϕ_i (in the ground-state function Φ_0) to the virtual orbitals ϕ_a (in the excited-state function Φ_u). The advantage of this approach rests on the fact that the energy functional assumes multishell form (eq. [73] of Chapter 3) so that procedures of the effective Hamiltonian construction (eq. [85] of Chapter 3) can be applied for the calculation of stationary energy vaues. Another procedure is based on the original Löwdin (13) natural orbital concept which transforms the charge density into a diagonal form. The above concept was later generalized into **geminal MC SCF theory.**

4.5 MANY-BODY PERTURBATION THEORY (MBPT)

When solving the many-body problem, the mathematical formalism of second quantization can be used effectively enabling compact manipulations with relationships among one-particle functions and many-body wave functions. The present formalism is based on introduction of creation and annihilation operators.

The annihilation operator $\hat{X}_j$ initiates omitting a particle from the j-th level of the many-body system

$$\hat{X}_j \; |\Phi_u(1,\ldots,j,\ldots,n)\rangle = (-1)^{n-k} \, \hat{A}_{n-1}\{\prod_{p\neq j}^{n-1} \psi_p\} \qquad [54]$$

while the creation operator $\hat{X}_i^+$ causes completion of the many-body system by adding one more particle at the i-th level

$$\hat{X}_i^+ \; |\Phi_u(1,\ldots,n)\rangle = \hat{A}_{n+1}\{\psi_i \prod_p^n \psi_p\} \qquad [55]$$

Here $\hat{A}$ is the antisymmetrization operator of the type [197] of Chapter 1, k being the order of the annihilated particle in an ordered n-electron configuration Φ_u. The creation and annihilation operator, in general, act upon the state vectors Ψ in the abstract Hilbert space.

An arbitrary n-electron configuration can be expressed in terms of creation operators acting on the vacuum-state vector $|0\rangle$ containing no particle

$$|\Phi_u\rangle = \prod_i^n \hat{X}_i^+ \; |0\rangle \qquad [56]$$

The operator $(\hat{X}_i^+ \hat{X}_i)$ is a diagonal idempotent operator meaning the number of particles at the i-th level. Both, the fermion (electron) creation and annihilation operators satisfy the anti-commutation relationships

$$[\hat{X}_i,\hat{X}_j]_+ = \hat{X}_i\hat{X}_j + \hat{X}_j\hat{X}_i = 0 \qquad [57]$$

$$[\hat{X}_i^+,\hat{X}_j^+]_+ = 0 \qquad [58]$$

$$[\hat{X}_i,\hat{X}_j^+]_+ = \delta_{ij} \qquad [59]$$

Using the above properties the electronic Hamiltonian may be written in the form (24,25)

$$\hat{H}^{el} = \sum_{i,j} <i|\hat{h}|j> \hat{X}_i^+ \hat{X}_j + (1/2) \sum_{i,j,k,l} <ij|\hat{g}|kl> \hat{X}_i^+ \hat{X}_j^+ \hat{X}_l \hat{X}_k \qquad [60]$$

where the matrix elements $<i|\hat{h}|j>$ and $<ij|\hat{g}|kl>$ are expressed in the orthonormal one-electron function (spinorbital) basis set.

In the hole-particle formalism for the 'new vacuum' (the reference state vector) the ground-state electron configuration is taken

$$|\Phi_0> = \prod_i^{occ} \hat{X}_i^+ |0> \qquad [61]$$

($_{occ}$ denotes the occupied spinorbitals). Then excitation of a particle corresponds with the creation of a hole in the new vacuum. In this formalism the electronic Hamiltonian [60] can be transcribed into the so-called **normal form**

$$\hat{H}^{el} = <\Phi_0|\hat{H}^{el}|\Phi_0> + \sum_{i,j}^{m} <i|\hat{F}|j> N[\hat{X}_i^+ \hat{X}_j] +$$

$$+ (1/4) \sum_{i,j,k,l}^{m} <ij||kl> N[\hat{X}_i^+ \hat{X}_j^+ \hat{X}_j \hat{X}_k] \qquad [62]$$

suitable for application in perturbation theory. Here the following notation is introduced: matrix elements

$$<i|\hat{F}|j> = <i|\hat{h}|j> + \sum_k^{occ} <ik||jk> \qquad [63]$$

represent the one-electron effective Fock operator in the spin-orbital basis set, $\epsilon_i = <i|\hat{F}|i>$ are one-electron orbital energies (for canonical MOs), $<ij||kl> = <ij|\hat{g}|kl> - <ij|\hat{g}|lk>$ is the antisymmetrized two-electron integral. The scalar part of the Hamiltonian

$$E^0 = <\Phi_0|\hat{H}^{el}|\Phi_0> = (1/2) \sum_i^{occ} (<i|\hat{h}|i> + \epsilon_i) \qquad [64]$$

means the ground-state reference electronic energy. Normal product

$N[\ldots]$ arranges all the creation operators left from the annihilation ones having the sign $(-1)^p$ with p being the parity of the respective permutation.

In the many-body perturbation theory (MBPT) the electronic Hamiltonian is split into the unperturbed part $\hat{H}^0$ and the perturbation $\hat{H}'$

$$\hat{H}^{el} = \hat{H}^0 + \hat{H}' \qquad [65]$$

Under the so-called **Moller-Plesset partitioning** (26) it is

$$\hat{H}^0 = \langle\Phi_0|\hat{H}^{el}|\Phi_0\rangle + \sum_i^m \epsilon_i \, N[\hat{X}_i^+ \hat{X}_i] \qquad [66]$$

$$\hat{H}' = \sum_{i,j}^m (1 - \delta_{ij})\langle i|\hat{F}|j\rangle \, N[\hat{X}_i^+ \hat{X}_j] +$$

$$+ (1/4) \sum_{i,j,k,l}^m \langle ij||kl\rangle \, N[\hat{X}_i^+ \hat{X}_j^+ \hat{X}_l \hat{X}_k] \qquad [67]$$

where the first part of the perturbation $\hat{H}'$ vanishes for canonical molecular orbitals diagonalizing the Fock operator, $\langle i|\hat{F}|j\rangle = \epsilon_i\delta_{ij}$. The rest of the perturbation represents the pure effect of electron correlation. With the use of the **Rayleigh-Schrödinger perturbation theory** (Section 1.2.1) we obtain

$$|\Psi\rangle = \sum_{n=0}^{\infty} \left\{ \frac{1 - \hat{P}}{E^0 - \hat{H}^0} (\hat{H}' + E^0 - E) \right\}^n |\Phi_0\rangle \qquad [68]$$

and for the correlation energy

$$E_{corr} = E - E^0 = \langle\Phi_0|\hat{H}'|\Psi\rangle \qquad [69]$$

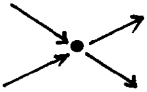
For computation of the correlation energy (without the need of explicit knowledge of the perturbed wave function $|\Psi\rangle$) simple algebraic relationships can be derived (27). For this purpose the diagrammatic representation of individual terms in the Hamiltonian is used. Among various techniques the diagrammatic Goldstone technique (28) and Hugenholtz technique (29) are frequently used; they are derived from the Feynman diagrammatic field theory technique (30).

The following rules are applied below. Oriented lines (specified by arrows) are associated with creation and annihilation operators: a left-pointed arrow will designate an electron, and a right pointed will then denote a hole. A dot (vertex) will be used to designate an interaction; spinor lines emerging from the dot will then correspond to electron creation operators, and spinor lines converging upon the dot will represent electron annihilation operators. Hence

$(1 - \delta_{ij})\langle i|\hat{F}|j\rangle \; \mathcal{N}[\hat{X}_i^+ \hat{X}_j]$

and

$(1/4)\langle ij||kl\rangle \; \mathcal{N}[\hat{X}_i^+ \hat{X}_j^+ \hat{X}_l \hat{X}_k]$



Then we use Wick theorem (31) which states that nonvanishing contributions to the energy come only from fully contracted terms. A contraction between two operators in diagrammatic language means that two lines corresponding to operators being contracted must be tied together. Thus diagrammatic representation of Wick theorem states that in order to have a nonvanishing contribution to the energy all the lines in the diagram must be connected into loops and no diagram with an open line survives.

In evaluating 'linked antisymmetrized diagrams' of the Hugenholtz type the following rules are useful:

1. Label each diagram with general hole (i, j, k, l) and particle (a, b, c, d) indices.

2. The numerator N of the diagram is obtained by the product of one-electron integrals $F_{ij} = (1 - \delta_{ij})\langle i|\hat{F}|j\rangle$ (if any) and of antisymmetrized two-electron integrals $\langle ij||kl\rangle$.

3. The denominator D of the diagram is given by a product of terms $D = \sum_p D_{ia} = \sum_p (\epsilon_i - \epsilon_a)$ where p is a number of pairs of hole (i) and particle (a) lines between each two vercices.

4. Sum the ratio N/D over all hole and particle indices.

5. The sign of the diagram is given by $S = (-1)^{h + l}$ where h is number of hole lines and l is the number of continuous lines forming the closed loops.

6. Multiply the diagram by a weight factor (1/2) for each pair of equivalent lines. An equivalent pair of lines is defined to be two lines beginning at one vertex and ending at another and going in the same direction.

Final expression for the electronic energy can be written in the form of a series

$$E^{el} = \sum_{n=0}^{\infty} E^{(n)} \qquad [70]$$

where the contribution up to the third order of the MPBT, using the diagrams of Fig. 3, are

$$E^{(0)} = \langle\Phi_0|\hat{H}^0|\Phi_0\rangle = E^0 \qquad [71]$$

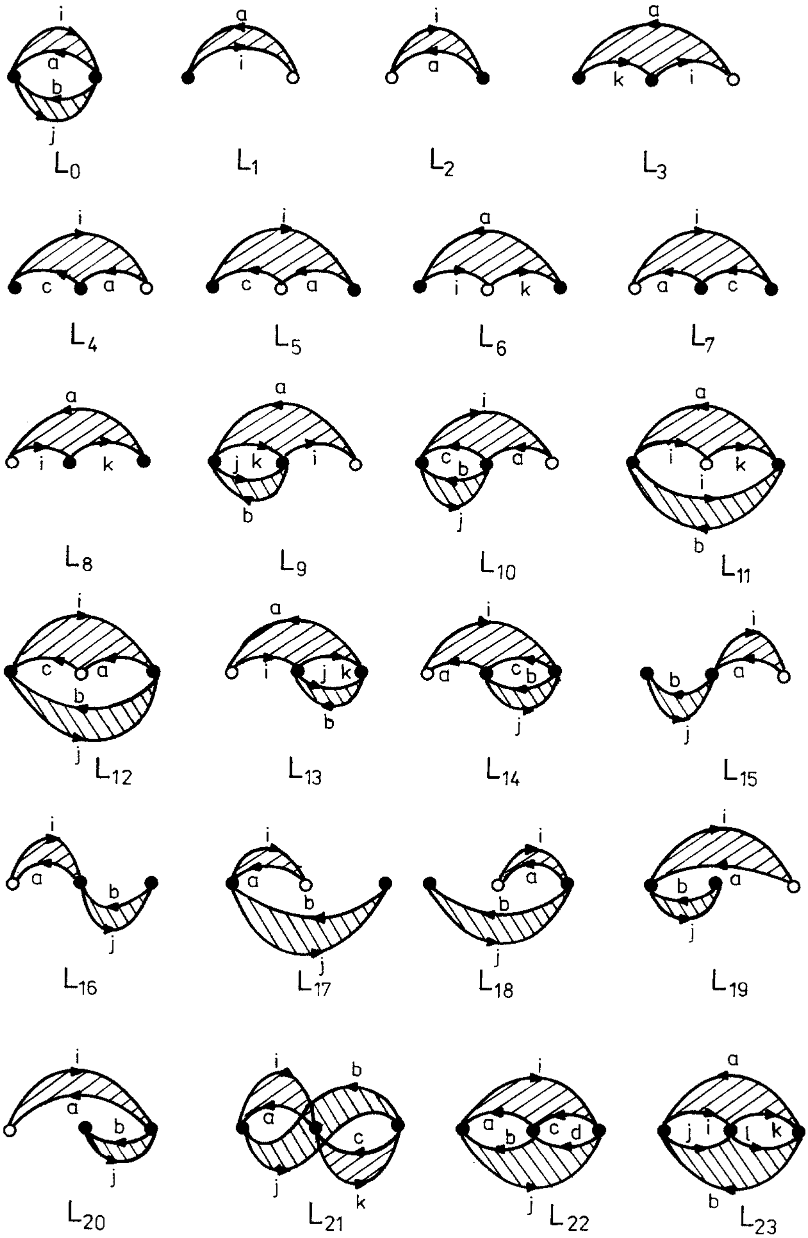


Fig. 3. Hugenholtz diagrams in the third-order MBPT.

$$E^{(1)} = \langle\Phi_0|\hat{H}'|\Phi_0\rangle = 0 \qquad [72]$$

$$E^{(2)} = \langle\Phi_0|\left\{\hat{H}'\frac{1}{E^0 - \hat{H}^0}\hat{H}'\right\}|\Phi_0\rangle = L_0 =$$

$$= \sum_{i,j}^{occ}\sum_{a,b}^{vir} \langle ij||ab\rangle^2/D_{iaj} \qquad [73]$$

$$E^{(3)} = \langle\Phi_0|\left\{\hat{H}'\frac{1}{E^0 - \hat{H}^0}H'\frac{1}{E^0 - \hat{H}^0}H'\right\}|\Phi_0\rangle = L_{21} + L_{22} + L_{23} =$$

$$= \sum_{i,j}^{occ}\sum_{a,b}^{vir} (\langle ij||ab\rangle/D_{iajb}) \left[\sum_{k}^{occ}\sum_{c}^{vir} \langle cb||kj\rangle\langle ka||ci\rangle/D_{kcjb} + \right.$$

$$\left. + (1/8)\sum_{c,d}^{vir}\langle ab||cd\rangle\langle cd||ij\rangle/D_{icjd} + (1/8)\sum_{k,l}^{occ}\langle ab||kl\rangle\langle kl||ij\rangle/D_{kalb}\right] \qquad [74]$$

In the expressions above the denominators consist of orbital energies

$$D_{iajb} = \epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b \qquad [75]$$

The indices i,j,k,l run over the occupied (occ) spinorbitals - hole states, and a,b,c,d over the unoccupied (virtual: vir) spinorbitals - particle states with respect to the reference ground-state configuration $|\Phi_0\rangle$. The above formulae can be further simplified, if transferring from the spinorbital basis set to the orbital basis set (by integrating over spin variables). These formulae are applicable for canonical molecular orbitals of a closed-shell system and for open shell orbitals in the UHF method. In the RHF method for the open-shell system the off-diagonal Lagrangian multipliers $\langle i|\hat{F}|j\rangle$ are non-zero and thus the perturbation $\hat{H}'$ [67] also contains a non-zero first term. The resulting MBPT formulas are then more complex containing also integrals of the type $\langle i|\hat{F}|j\rangle$ arissing from diagrams L_1 - L_{20}. A similar approach applies in the case of localized orbitals.

It is noticeable also that the complete fourth- and fifth-order formulae have been so far derived (32).

A critical aspect of perturbation theory is due to the convergence of the perturbation series [70]. Here satisfaction requires that the correction for all successive PT orders be less than any preceding order correction

$$|E^{(n+1)}| < |E^{(n)}| < |E^{(n-1)}| \qquad [76]$$

The convergence can be either monotonous (all the corrections showing negative signs) or oscillating (with alternating signs of the corrections). The lowest perturbation theory order in which convergence can be judged is the third order. If the energy terms $E^{(0)}$, $E^{(2)}$ and $E^{(3)}$ are taken for terms of a convergent geometric series, then the expression

$$E^{[2,1]} = E^{(0)} + E^{(2)}/(1 - E^{(3)}/E^{(2)}) \qquad [77]$$

stands for its sum (estimate of the convergence limit). This is a special case of the so-called **Padé approximants** $E^{[n,m]}$ of the order (n + m) enabling one to estimate energy to higher orders of the perturbation theory (33). While the second-order MBPT is accessible in a reasonable computational time, the third-order calculations can be as equally tedious as the restricted CI.

For the computation of correlation energy formal perturbation theory can also be used. The electronic Hamiltonian in the configurational function basis set can be represented as the matrix of the configuration interaction H^{CI}. If the diagonal part of the above matrix is taken as the unperturbed Hamiltonian $\hat{H}^0$ and off-diagonal one for perturbation $\hat{H}'$, then for electronic energy terms, according to the Rayleigh-Schrödinger perturbation theory, it is

$$E^{(2)} = \sum_{u\neq 0} H_{0u}\, H_{u0} \,/(E^0 - H_{uu}) \qquad [78]$$

$$E^{(3)} = \sum_{u\neq 0} \sum_{v\neq u\neq 0} H_{0u}\, H_{uv}\, H_{v0} \,/[(E^0 - H_{uu})(E^0 - H_{vv})] \qquad [79]$$

The many-body perturbation theory also can be successfully applied for the direct computation of the ionization energies I_k, alectron affinities A_a and excitation energies $\Delta E_{i\to a}$.

The ionized state $|\Phi_k(n-1)\rangle$ can be described as annihilation of the particle

$$|\Phi_k(n-1)\rangle = \hat{X}_k\; |\Phi_0(n)\rangle \qquad [80]$$

assuming validity of the perturbation theory relationships

$$\hat{H}\; |\Psi_k\rangle = E_k\; |\Psi_k\rangle \qquad [81]$$

$$\hat{H}^0 |\Phi_k\rangle = E_k^0\; |\Phi_k\rangle \qquad [82]$$

so that for the perturbed energy we obtain

$$E_k = E_k^0 + \sum_{m=0}^{\infty} \langle\Phi_k|\hat{H}'\left\{\frac{1 - \hat{P}_k}{E_k^0 - \hat{H}^0}(\hat{H}' + E_k^0 - E_k)\right\}^m|\Phi_k\rangle \qquad [83]$$

Then, for the ionization energy (34)

$$I_k = E_k(n-1) - E_0(n) = [E_k^0(n-1) - E_0^0(n)] +$$

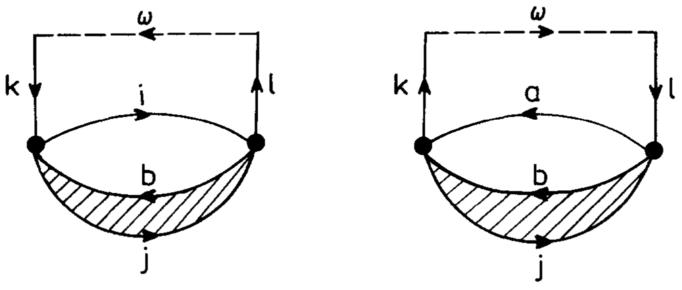
$$+ \sum_{m=0}^{\infty} \left[\langle\Phi_0|\hat{X}_k^+ \hat{H}' \left\{ \frac{1 - \hat{P}_k}{E^0 - \hat{H}^0} (\hat{H}' + E_k - E_k) \right\}^m \hat{X}_k |\Phi_0\rangle - \right.$$

$$\left. - \langle\Phi_0| \hat{H}' \left\{ \frac{1 - \hat{P}_0}{E_k^0 - \hat{H}^0} (\hat{H}' + E_0^0 - E_0) \right\}^m |\Phi_0\rangle \right] \qquad [84]$$

Finally, using the diagrammatic technique the explicit arithmetic formulae for the ionization energy are obtained. For example, in the second-order MBPT (Fig. 4) in the molecular orbital basis set it is

$$I_k = -\varepsilon_k + (1/2) \sum_j^{occ} \sum_b^{vir} \left(\sum_i^{occ} \langle ij||kb\rangle^2/D_{ikjb} - \sum_a^{vir} \langle kj||ab\rangle^2/D_{kajb} \right) \qquad [85]$$

This formula is applicable to closed-shell systems and in the UHF method for open-shell systems. It represents a correction of Koopmans approximation by both the relaxation and correlation terms. This approach has the advantage that the ionization energy is not calculated as a difference between large numbers (total energy of the systems with n-1 and n electrons). Moreover, calculation can be confined only to the SCF procedure for un-ionized systems. A similar procedure can be used to compute electron affinities and excitation energies.



a) b)

Fig. 4. Second-order diagrams for ionization energies: a - relaxation term, b - correlation term; k = l = ω.

The mean value of an arbitrary one-electron operator $\hat{A}$

$$\hat{A} = \sum_{p}^{n} \hat{A}_p = \langle\Phi_0|\hat{A}|\Phi_0\rangle + \sum_{i,j}^{m} \langle i|\hat{A}|j\rangle \, N[\hat{X}_i^{+} \, \hat{X}_j] \qquad [86]$$

can be determined on the basis of the so-called **double perturbation theory**. In the case of the perturbation

$$\hat{H}'(\omega) = \hat{H}' + \omega \, \hat{A} \qquad [87]$$

we arrive at the mean value of $\hat{A}$ in the form

$$\langle\Psi_0|\hat{A}|\Psi_0\rangle = \sum_{i,j}^{m} \langle i|\hat{A}|j\rangle P_{ji} = Tr\{\mathbf{AP}\} \qquad [88]$$

with the one-electron spin-free density matrix given in the form of a series

$$P_{ij} = \sum_{\nu=0}^{\infty} P_{ij}^{(\nu)} \qquad [89]$$

where ν is the perturbation theory order. From the diagrammatic representation of the Rayleigh-Schrödinger MBPT, individual contributions to the density matrix (in the basis set of canonical molecular spinorbitals) can be derived

$$P_{ik}^{(0)} = \delta_{ik} \quad \text{for } i,k \in \text{occ} \qquad [90]$$

$$P_{ai}^{(0)} = P_{ia}^{(0)} = P_{ac}^{(0)} = 0 \quad \text{for } i \in \text{occ, and } a,c \in \text{vir} \qquad [91]$$

$$P_{ik}^{(1)} = P_{ai}^{(1)} = P_{ia}^{(1)} = P_{ac}^{(1)} = 0 \qquad [92]$$

$$P_{ik}^{(2)} = L_{11} =$$

$$= -(1/2) \sum_{j}^{occ} \sum_{a,b}^{vir} (\langle ij||ab\rangle/D_{iajb})(\langle kj||ab\rangle/D_{kajb}) \qquad [93]$$

$$P_{ac}^{(2)} = L_{12} =$$

$$= (1/2) \sum_{i,j}^{occ} \sum_{b}^{vir} (\langle ij||ab\rangle/D_{iajb})(\langle ij||cb\rangle/D_{icjb}) \qquad [94]$$

$$P_{ia}^{(2)} = P_{ai}^{(2)} = L_{13} + L_{14} =$$

$$= (1/2D_{ia}) \sum_{j}^{occ} \sum_{b}^{vir} \Big[\sum_{c}^{vir} \langle aj||cb\rangle(\langle ij||cb\rangle/D_{icjb}) -$$

$$- \sum_{k}^{occ} \langle ib||kj\rangle(\langle ab||kj\rangle/D_{kaij}) \Big] \qquad [95]$$

Here the contributing diagrams are labelled according to Fig. 3.

Conservation of the number of electrons is given by the relationships

$$Tr\{P^{(0)}\} = n \qquad [96]$$

$$Tr\{P^{(\nu)}\} = 0 \text{ for } \nu > 0. \qquad [97]$$

so that the higher-order density matrices are traceless.

The density matrix in the molecular orbital basis set P^{MO} can be transformed to that in the atomic orbital basis set (known as the charge-density bond-order matrix) P^{AO} using the LCAO matrix C

$$P^{AO} = C^{T} P^{MO} C \qquad [98]$$

Then the usual population analysis can be applied to yield orbital and atomic population, atomic charges, etc. according to standard methods (Section 3.7.3).

Note that the zero-order P^{MO} matrix is a diagonal matrix M of occupation numbers of individual molecular spin-orbitals, so that

$$P^{AO} = C^{T} M C \qquad [99]$$

4.6 COUPLED CLUSTER APPROACH

The present method represents an alternative implementation of the Rayleigh-Schrödinger MBPT. Instead of explicit arithmetic expressions for contribution of individual PT orders to the correlation energy $E^{(n)}$, in the Coupled Cluster Approach (CCA) a system of coupled non-linear equations is solved. This approach enables one to compute the correlation energy to high orders of perturbation theory. At the same time the CCA is directly related to the variational CI through formal perturbation theory. Derivation of the CCA, however, is based on neither the variational principle nor perturbation theory (35).

CCA is based on expressing the perturbed state vector through the exponential of the cluster operator $\hat{T}$

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle \qquad [100]$$

This operator $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$ can be decomposed l-fold excitation terms, which are

$$\hat{T}_l = (1/l!) \sum_{\substack{h_1 \ldots h_l \in \Phi_0 \\ p_1 \ldots p_l \notin \Phi_0}} \langle p_1 \ldots p_l || h_1 \ldots h_l \rangle \, N[\hat{X}^{+}_{p_1} \ldots \hat{X}^{+}_{p_l} \; \hat{X}_{h_1} \ldots \hat{X}_{h_l} \qquad [101]$$

Hole indices $h_1,\ldots,h_l$ range over all the occupied spinorbitals and particle indices $p_1,\ldots,p_l$ through unoccupied spinorbitals in the reference configuration wave function $|\Phi_0\rangle$. Matrix elements

$$\langle p_1\ldots p_l||h_1\ldots h_l\rangle = (1/D_{h_1p_1\ldots h_lp_l})\ \mathrm{x}$$

$$\mathrm{x}\left\{\sum_{n=0}\langle\Phi_0|\hat{X}^{+}_{h_1}\hat{X}_{p_1}\ldots\hat{X}^{+}_{h_l}\hat{X}_{p_l}\ \hat{H}'\left(\frac{1}{E^0-\hat{H}^0}\hat{H}'\right)\right\}^{n}|\Phi_0\rangle_{LC} \qquad [102]$$

are determined by the diagrammatic technique (36,37) where only the so-called linked and connected diagrams contribute. Expansion of the wave function $|\Psi\rangle$ then assumes the form

$$|\Psi\rangle = \sum_{n_1n_2\ldots}\frac{(\hat{T}_1)^{n_1}(\hat{T}_2)^{n_2}\ldots}{n_1!\ n_2!\ \ldots}|\Phi_0\rangle = |\Phi_0\rangle + \hat{T}_1|\Phi_0\rangle +$$

$$+ [\hat{T}_2 + (1/2!)\hat{T}_1^2]|\Phi_0\rangle + [\hat{T}_3 + \hat{T}_1\hat{T}_2 + (1/3!)\hat{T}_1^3]|\Phi_0\rangle + \ldots \qquad [103]$$

This expansion is directly connected with CI through the relationship

$$|\Psi\rangle = (\hat{1} + \sum_{l=1}\hat{C}_l)|\Phi_0\rangle \qquad [104]$$

where $\hat{C}_l$ formally form the fixed linear combination of all the l-excited configuration functions. Then

$$\hat{C}_1 = \hat{T}_1 \qquad [105]$$

$$\hat{C}_2 = \hat{T}_2 + (1/2!)\hat{T}_1^2 \qquad [106]$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + (1/3!)\hat{T}_1^3 \qquad [107]$$

and

$$\hat{T}_1 = \hat{C}_1 \qquad [108]$$

$$\hat{T}_2 = \hat{C}_2 - (1/2)\hat{C}_1^2 \qquad [109]$$

$$\hat{T}_3 = \hat{C}_3 - \hat{C}_1\hat{C}_2 - (1/3)\hat{C}_1^3 \qquad [110]$$

etc., represent interrelations between CI and CCA.

Since the perturbation $\hat{H}'$ contains at maximum two-electron terms, then the CCA correlation energy can be derived as

$$E_{corr} = \{\langle\Phi_0|\hat{H}'\ e^{\hat{T}}|\Phi_0\rangle\}_C = \{\langle\Phi_0|\hat{H}'[\hat{T}_1 + \hat{T}_2 + (1/2)\hat{T}_1^2]|\Phi_0\rangle\}_C =$$

$$= (1/2)\sum_{\substack{p_1,p_2\\h_1,h_2}}(\langle h_1h_2|\hat{g}|p_1p_2\rangle - \langle h_1h_2|\hat{g}|p_2p_1\rangle)(\langle p_1p_2||h_1h_2\rangle +$$

$$+ \langle p_1||h_1\rangle\langle p_2||h_2\rangle) + \sum_{p,h} \langle h|\hat{F}|p\rangle\langle p||h\rangle \qquad [111]$$

where the higher order cluster operators contribute to E_{corr} through their coupling with $\hat{T}_1$ and $\hat{T}_2$. The necessary matrix elements of the cluster operator can be calculated as

$$\langle\Phi_u|\hat{T}_1|\Phi_0\rangle = (1/D_{h_1p_1\ldots h_lp_l})\{\langle\Phi_u|\hat{H}'\ e^{\hat{T}}|\Phi_0\rangle\}_C \qquad [112]$$

The computation is performed in iterative an way. According to the use of the cluster operator, different approximate versions of the CCA can be distinguished (LCCA, CPMET, ECPMET) (36).

Many-body computational methods for correlation effects are expected to satisfy the **separability condition.** If the system consists of a definite number of non-interacting subsystems, then its total energy should be additive with a multiplicative wave function. The condition of **size-consistency** is equivalent to this requirement. For example, when studying the number of N non-interacting H_2 molecules the requirement placed upon the total energy is $E[(H_2)_N] = N\ E[H_2]$. Both the CCA and MBPT fulfill this requirement and differ therefore from restricted CI. For example, fo the restricted CI with monoexcited and biexcited configurations the energy for $N \rightarrow \infty$ changes according to the value of $\sqrt{N}$.

4.7 PAIR CORRELATION METHODS

These approximate methods for solving the electron correlation problem were especially developed because the variational CI shows weak convergence with increasing number of expansion terms in the CI series. The motivation for the pair correlation theories rests on the possibility of obtaining a better value for the correlation energy in the biexcited configuration function basis set than allowed by the restricted CI. At the same time there exists a physically accepted reasoning for the pair correlation theories based on the following properties:

1. The electronic Hamiltonian only contains one-particle and two-particle operators.
2. The Pauli exclusion principle prevents the simultaneous occurrence three electrons at the same point in space (Fermi correlation). Then the predominating part of the correlation energy (Coulomb correlation) will be determined by short-range interactions which can be at most two-electron.

The CI expansion of the wave function $|\Psi\rangle$ can be written as

$$|\Psi\rangle = \sum_u a_u \Phi_u = C_0\Phi_0 + \sum_{i,a} C_i^a\,\Phi_i^a + \sum_{i<j}\sum_{a<b} C_{ij}^{ab}\,\Phi_{ij}^{ab} \qquad [113]$$

and the characteristic equation in the form

$$\sum_v \langle\Phi_u|\hat{H}^{el}|\Phi_v\rangle\, a_v = E\, a_u \qquad [114]$$

Then the first row of the characteristic equation (for $\Phi_u = \Phi_0$) yields

$$\langle\Phi_0|\hat{H}^{el}|\Phi_0\rangle C_0 + \sum_{i,a} \langle\Phi_0|\hat{H}^{el}|\Phi_i^a\rangle + \sum_{i<j}\sum_{a<b} \langle\Phi_0|\hat{H}^{el}|\Phi_{ij}^{ab}\rangle C_{ij}^{ab} = E\, C_0 \qquad [115]$$

Then the total energy may be written in the form

$$E = E^0 + \sum_i w_i + \sum_{i<j} w_{ij} \qquad [116]$$

where

$$E^0 = \langle\Phi_0|\hat{H}^{el}|\Phi_0\rangle \qquad [117]$$

$$w_i = (1/C_0) \sum_a \langle\Phi_0|\hat{H}^{el}|\Phi_i^a\rangle\, C_i^a \qquad [118]$$

$$w_{ij} = (1/C_0) \sum_{a<b} \langle\Phi_0|\hat{H}^{el}|\Phi_{ij}^{ab}\rangle\, C_{ij}^{ab} \qquad [119]$$

Since, due to the Brillouin theorem, the w_i terms vanish, then it is sufficient to know the coefficient C_0 and C_i^a to determine the energy. Similar equations can be obtained for further rows of the characteristic equation. By explicitly expanding the row for $\Phi_u = \Phi_i^a$ we discover that the coefficients C_{ij}^{ab} and C_{ijk}^{abc} must be known to determine the coefficients C_i^a. Similarly for the row for $\Phi_u = \Phi_{ij}^{ab}$ the values of C_{ijk}^{abc} and C_{ijkl}^{abcd} should be known to determine C_{ij}^{ab}, etc. Into these relationships certain reasonable approximations are then introduced, based on the cluster expansion of the wave function. Mostly, the decomposition of the C_{ijkl}^{abcd} coefficients include pair excitation coefficients of the type C_{ij}^{ab}, i.e. description of the tetra-excitation through two parallel bi-excitations.

According to the Nesbet hierarchy (38), the variation of the wave function

$$\Psi_i = C_0\Phi_0 + \sum_a C_i^a\,\Phi_i^a \qquad [120]$$

determines the orbital correlation energies w_i

$$E_i = E^0 + w_i \qquad [121]$$

and the variation of the wave function

$$\Psi_{ij} = C_0\Phi_0 + \sum_a C_i^a \Phi_i^a + \sum_b C_j^b \Phi_j^b + \sum_{a<b} C_{ij}^{ab} \Phi_{ij}^{ab} \qquad [122]$$

defines the pair correlation energies w_{ij}

$$E_{ij} = E^0 + w_i + w_j + w_{ij} \qquad [123]$$

In a similar manner, the three-particle corrections w_{ijk} are determined by variation of the wave function Ψ_{ijk}, etc.

The pair correlation methods are derived from the approximate equation (39)

$$<\Phi_{ij}^{ab}|\hat{H}^{el}|\Phi_0> + \sum_{k<l} \sum_{c<d} <\Phi_{ij}^{ab}|\hat{H}^{el}|\Phi_{kl}^{cd}> D_{kl}^{cd} = W_{ij} D_{ij}^{ab} \qquad [124]$$

where $D_{ij}^{ab} = C_{ij}^{ab}/C_0$. This equation represents the approximation of non-linear terms of the cluster expansion of the wave function for tetra-excitation with neglect of tri-excitations. According to further specification the following pair correlation mathods can be distinguished:

1. IEPA (Independent Electron-Pair Approximation) considers the equation

$$<\Phi_{ij}^{ab}|\hat{H}^{el}|\Phi_0> + \sum_{c<d} <\Phi_{ij}^{ab}|\hat{H}^{el}|\Phi_{ij}^{cd}> D_{ij}^{cd} = E_{ij} D_{ij}^{ab} \qquad [125]$$

corresponding to the correlation function

$$\Psi_{ij} = C_0\Phi_0 + \sum_{a<b} C_{ij}^{ab} \Phi_{ij}^{ab} \qquad [126]$$

In this version, moreover, the pair coupling terms are neglected. The method yields 80 - 120 % of correlation energy. Let us note that the second-order Rayleigh-Schrödinger MBPT (with the Moller-Plesset Hamiltonian partitioning) can be used as the first approximation to the IEPA method.

2. CEPA (Coupled Electron-Pair Approximation) considers the electron coupling terms in eq. [124]. When choosing

$$W_{ij} = E^0 + w_{ij} \qquad [127]$$

we arrive at the Mayer version of CEPA-2 (40). With another choice

$$W_{ij} = E^0 + w_{ij} + (1/2) \sum_k (w_{ik} + w_{kj}) \qquad [128]$$

we arrive at the Mayer CEPA-1 version (40). With a different selection

$$W_{ij} = E^0 + w_{ij} + \sum_k w_{kj} + \sum_l w_{il} \qquad [129]$$

we arrive at the Kelly version of CEPA (41). The above CEPA methods, as a rule, yield better results than the variational CI method; this provides a sound reason for their use when solving the electron correlation problem. The third-order Rayleigh-Schrödinger MBPT corresponds to the first approximation of the CEPA method.

3. From eq. [124] when choosing

$$W_{ij} = E^0 + \sum_k w_{ik} \qquad [130]$$

we obtain the Mehler IPPA (Independent-Pair Potential Approximation) method (42).

4. If

$$W_{ij} = E \qquad [131]$$

(E being the variational CI energy restricted to biexcitations) we arrive at the PNO-CI (Pair-Natural Orbitals or Pseudo-Natural Orbitals) method (43).

4.8 GREEN FUNCTION TECHNIQUE

When solving the many-body problem using the perturbation method, the Green function (GF) technique can be successfully applied. For computation of the ionization energies and electron affinity values arising from many-body effects (relaxation and correlation energy) we can use the with one-particle GF defined as an average of the time ordered product of the annihilation and creation operators $\hat{X}_k$ and $\hat{X}_l^+$ of the n-electron system in the ground state (24,25)

$$G_{kl}(t,t') = -i\langle\Psi_0(n)|\hat{T}\{\hat{X}_k(t)\ \hat{X}_l^+(t')\}|\Psi_0(n)\rangle \qquad [132]$$

In this expression $\hat{T}$ stands for the Wick time ordering operator with the sign $(-1)^p$ where p is the parity of the ordering permutation of the creation and annihilation operators. Time evolution is characterized by the relationships

$$\hat{X}_l^+(t') = exp(i\hat{H}t'/\hbar)\ \hat{X}_l^+\ exp(-i\hat{H}t'/\hbar) \qquad [133]$$

$$\hat{X}_k(t) = exp(i\hat{H}t/\hbar)\ \hat{X}_k\ exp(-i\hat{H}t/\hbar) \qquad [134]$$

where

$$\hat{H}^{el} = \hat{H}^0 + \hat{H}' \qquad [135]$$

is the electronic Hamiltonian of the system. If $\hat{H}^{el}$ is not time-dependent, then G_{kl} only depends on (t - t')

$$G_{kl}(t,t') = G_{kl}(t-t',0) = G_{kl}(t-t') \qquad [136]$$

The Fourier transform of GF in the time-less spectroscopic representation is given by (25,44)

$$G_{kl}(\omega) = \int_{-\infty}^{\infty} G_{kl}(t-t')\, e^{i\omega(t-t')}\, d(t-t') =$$

$$= \lim_{\eta\to 0^+} \left\{ \sum_s \frac{\langle\Psi_0(n)|\hat{X}_l^+|\Psi_s(n-1)\rangle\langle\Psi_s(n-1)|\hat{X}_k|\Psi_0(n)\rangle}{\omega + I_s - i\eta} + \right.$$

$$\left. + \sum_r \frac{\langle\Psi_0(n)|\hat{X}_k|\Psi_r(n+1)\rangle\langle\Psi_r(n+1)|\hat{X}_l^+|\Psi_0(n)\rangle}{\omega + A_r + i\eta} \right\} \qquad [137]$$

where η is a small positive number and

$$I_s = E_s(n-1) - E_0(n) \qquad [138]$$

is the ionization energy of the s-th level,

$$A_r = E_0(n) - E_r(n+1) \qquad [139]$$

is the electron affinity of the r-th level.

From the form of the Green function it follows that the ionization energies and electron affinities may be evaluated from the singular points (poles) of GF, when $G(\omega)^{-1} = 0$, so that

$$I_s = -\omega + i\eta \qquad [140]$$

$$A_r = -\omega - i\eta \qquad [141]$$

Green functions also determine the mean value of the one-electron operator $\hat{A}$

$$\hat{A} = \sum_{k,l} \langle k|\hat{A}|l\rangle\, \hat{X}_l^+\, \hat{X}_k \qquad [142]$$

through the relationship

$$\langle\Psi_0|\hat{A}|\Phi_0\rangle = (1/2\pi i) \sum_{k,l} \langle l|\hat{A}|k\rangle \oint G_{kl}(\omega)\, d\omega \qquad [143]$$

Similarly we introduce the Green function G_{kl}^0 for the unperturbed Hamiltonian $\hat{H}^0$ with the eigenfunctions $|\Phi_0(n)\rangle$

$$G_{kl}^0(\omega) = -i\langle\Phi_0(n)|\hat{T}\{\hat{X}_k(t)\, \hat{X}_l^+(0)\}|\Phi_0(n)\rangle \qquad [144]$$

In the case of non-interacting particles the following explicit expression can be written

$$G_{kl}^0(\omega) = \lim_{\eta\to 0^+} \frac{\delta_{kl}}{\omega - \epsilon_k - ai\eta}\ , \text{ for } a \begin{cases} = +1 \text{ for } k \in \text{occ} \\ = -1 \text{ for } k \in \text{vir} \end{cases} \qquad [145]$$

or in the matrix form

$$G^0(\omega)^{-1} = \omega I - E \qquad [146]$$

where I is a unit matrix and E is a diagonal matrix of orbital energies ϵ_k.

The Green function Fourier transform can be calculated by iterative solution of the **Dyson equation**

$$G_{kl}(\omega) = G^0_{kl}(\omega) + \sum_{i,j} G^0_{kl}(\omega)\ M_{ij}(\omega)\ G_{ji}(\omega) \qquad [147]$$

Then in the matrix form

$$G(\omega)^{-1} = G^0(\omega)^{-1} - M(\omega) \qquad [148]$$

Using [146] we obtain a relationship which in a very simple manner links the Green function with the effective Hamiltonian $M(\omega)$

$$G(\omega)^{-1} = \omega I - [E + M(\omega)] \qquad [149]$$

The singularity condition of the Green function $G(\omega)^{-1} = 0$ now yields the pseudocharacteristic equation for determination of the ω (and thus, also of the ionization energy and electron affinity values)

$$\omega I - [E + M(\omega)] = 0 \qquad [150]$$

Since the off-diagonal matrix elements of the effective Hamiltonian are much smaller than the diagonal ones, they do not cause any substantial modification of results (ionization energies are shifted at maximum by 0.05 eV) if they are neglected. In this approximation the equation

$$\omega_k^{(\nu+1)} = \epsilon_k + M_{kk}(\omega)_{|\omega = \omega_k^{(\nu)}} \qquad [151]$$

can be iteratively solved, where $\nu = 1, 2, \ldots$ is the number of the iteration. In graphic representation (Fig. 5) the poles of the Green function are given by the energy values at the intersection points of the line $y = \omega - \epsilon_k$ with the function $M_{kk}(\omega)$. Bands of the photoelectron spectrum (vertical ionization energies) are related to the point of intersection in ascending energy intervals (i.e. M_{-1}, M_{-2}, etc.) which is the first sum in the expression for GF. The electron affinity values are related to the descending energy intervals (M_{+1}, M_{+2}, etc.), i.e. to the second sum in GF. At the same time GF also determines the intensity of a spectroscopic line. For example, the steeper the inclination $M_{kk}(\omega)$ at the point of intersection with $y = \omega - \epsilon_k$, the smaller the intensity of the line in the photoelectron spectrum.

Evaluation of the matrix elements of the effective Hamiltonian is based on the quasi-degenerate many-body perturbation theory (45).

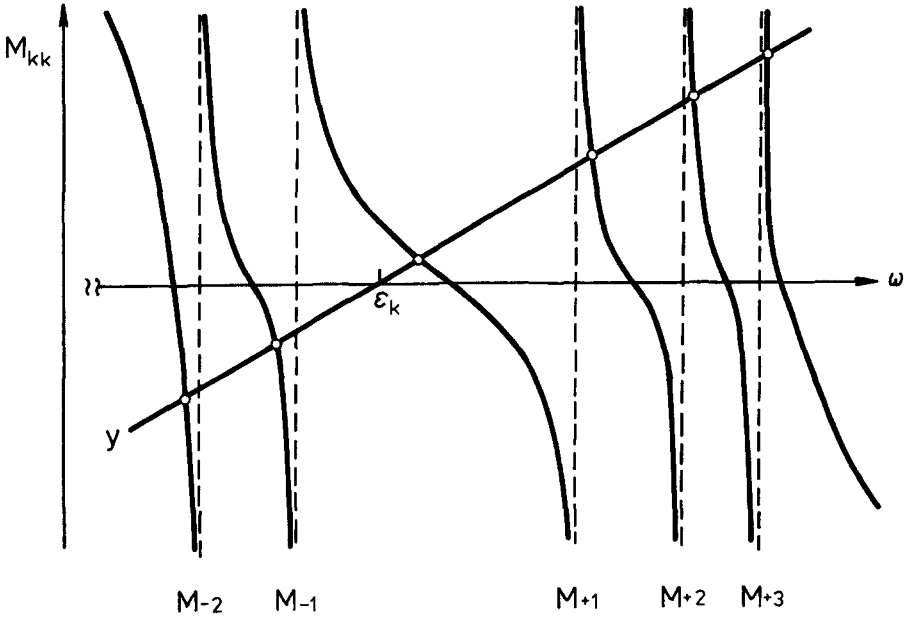


Fig. 5. Dependence of the matrix elements of the effective Hamiltonian M_{kk} upon the spectroscopic parameter ω.

In the simplest second-order perturbation theory (in the molecular spinorbital basis set) the following formula can be derived from diagrams in Fig. 4

$$M_{kl}(\omega) = -(1/2) \sum_{j}^{occ} \sum_{b}^{vir} \left(\sum_{i}^{occ} \frac{<ij||kb><bl||ji>}{\epsilon_i - \omega + \epsilon_j - \epsilon_b} - \sum_{a}^{vir} \frac{<lj||ab><ba||jk>}{\omega - \epsilon_a + \epsilon_j - \epsilon_b} \right) \quad [152]$$

The above formula may be written in several equivalent ways. It is applicable for the closed-shell systems and for the open-shell systems within UHF approach. In the zero-order approximation ($k = 0$, $\nu = 0$, $\omega_k = \epsilon$) we arrive at the expression [85] derived from the non-degenerate MBPT.

The Fermi golden rule of quantum mechanics, defining the probability of a hν transition in a time unit, can be used to calculate intensity of photoelectron processes

$$P(\nu) = \frac{4\pi^2 e^2}{m_e^2 h} \sum_K \left| <\Psi_K | \sum_i A_i \cdot \hat{p}_i | \Psi_0^n > \right|^2 \delta(h\nu - E_e)\, \delta(E_K - E_0 - h\nu_0) \quad [153]$$

E_K and E_0 are the energies of final (ionized) and original state respectively, Ψ_K and Ψ_0 their wave functions, E_e kinetic energy of the released electrons, hν energy of the ionizing radiation, A_i

the released electrons, $h\nu$ energy of the ionizing radiation, A_i vector of the i-th electron affecting electromagnetic field, and finally p_i the electron linear momentum. Applying creation $\hat{X}_k^+$ and annihilation operators $\hat{X}_k$, acting upon the one-electron states $|\varphi>$, we can modify [153] to

$$P(\nu) = \frac{4\pi^2 e^2}{m_e^2 h} \sum_K \left| <\Psi_K| \sum_{k,l} T_{kl}\ \hat{X}_k\ \hat{X}_l^+ |\Psi_0^n> \right|^2 \delta(h\nu - E_e)\ \delta(E_K - E_0 - h\nu_0)$$

$$= - \frac{4\pi e^2}{m_e^2 e^2 h} \sum_{k,l,m,j} T_{mj}^*\ T_{kl}\ Im\left\{ iG_{lkmj}(-h\nu_0 - i\eta) \right\} \delta(h\nu - E_e) \qquad [154]$$

introducing also matrix elements

$$T_{kl} = <\varphi_k|A.\hat{p}|\varphi_l> \qquad [155]$$

where $G_{lkmj}(\nu)$ represents the Fourier transform of the particle-hole component of the **two-particle Green function,** and η a small positive number. Now if we take suitable basis set of one-electron function, e.g. of Hartree-Fock orbitals, calculate the matrix elements T_{kl} and two-particle Green functions G_{lkmj}, we can use expression [154] to completely describe the photoelectron spectrum.

The Green function incorporates all internal molecular properties relevant to the photoelectron spectrum, namely electronic, vibration and rotation interactions, the spin-orbit interactions among others. High precision calculations of Green function however are a complex and time-consuming undertaking. Therefore the transition probability $P(\nu)$ is calculated from a simplified equation, giving exact values of ionization energies and sufficiently adequate description of the shape of the spectrum.

In equation [154] the final ionized state $|\Psi_k>$ can be thought of in terms of an antisymmetrized product of the electronic state $|\Psi_s^{m-1}>$ and that of the released electron $|\Phi_e>$. The contribution of the latter term to ground state wave function is practically zero, so that for sufficiently large values of E_e the operator $\hat{X}_k$ has to annihilate the electron $|\Phi_e>$ in final state $|\Psi_k>$ in order that the probability $P(\nu)$ be non-zero. An approximate expression can be written

$$P(\nu) = \frac{4\pi e^2}{m_e^2 h} \sum_{e,j,l} T_{lj}^*\ T_{el}\ Im\{G_{lj}(h\nu - h\nu_0 - i\eta)\}\ \delta(h\nu - E_e) \qquad [156]$$

where

$$G_{lj}(\omega' - i\eta) = \sum_s \frac{<\Psi_0^m|\hat{X}_j^+|\Psi_s^{m-1}><\Psi_s^{m-1}|\hat{X}_l|\Psi_0^n>}{\omega' + E_s^{n-1} - E_0^n - i\eta} \qquad [157]$$

is the Fourier transform of the corresponding **one-particle Green** function, $\omega' = h\nu$ is a spectral parameter.

In order that we could pass from a two-particle Green function in [154] to a one-particle Green function in [156], we have assumed that $|\Psi_k> = \hat{A}\ \{|\Psi_e>|\Psi_s^{m\ 1}>\}$, that is to say the liberated electron does not correlate with the electrons of the ion. However $|\Phi_e>$ need not necessarily describe a free electron, since generally speaking $|\Phi_e>$ is not a plane wave. The equation [152] enables the construction of optimum one-electron states $|\Phi_e>$, in which the liberated electron feels the remaining electrons; his own effect on the ion is thereby neglected. If energies $h\nu_0 >> I_k$ the liberated electron can be considered unbound and $|\Phi_e>$ can be characterized by a plane wave. If however $h\nu_0 < I_k$, Coulomb-type waves, describing the interaction of a liberated electron with charge distribution of the ion, must be used for the description of $|\Phi_e>$.

The probability of transition $P(\nu)$ is best expressed by eigenvalues $D_i(\nu)$ and eigenvectors $U_{ij}(\nu)$ of the matrix of Green function $G(\nu)$, $G = U^+DU$. This enables another form of [154]

$$P(\nu) = \frac{4\pi e^2}{m_e^2 h}\, Im\Big[\sum_e Tr\{\tilde{D}(h\nu - h\nu_0 - i\eta)\}\ \delta(h\nu - E_e)\Big] \qquad [158]$$

hence we have introduced transformed terms

$$\tilde{D}_{ij}(\nu) = |T_{ei}(\nu)|^2\ D_i(\nu)\ \delta_{ij} \qquad [159]$$

and

$$T_{ei}(\nu) = \sum_j T_{ej}\ U_{ij}(\nu) \qquad [160]$$

In addition we can resort to

$$Im\{D_k(h\nu - i\eta)\} = \pi \sum_s P_k(s)\ \delta(h\nu + E_s^{n-1} - E_0^n) \qquad [161]$$

where $P_k(s)$ represents a physical property called **pole strength**

$$0 \le P_k(s) \le 1 \qquad [162]$$

Since kinetic energy of liberated electrons is

$$E_e = h\nu_0 - I_s \qquad [163]$$

whereby ionization energy $I_s = E_s^{n-1} - E_0^n$, the value of $T_{e,k}\delta(h\nu-E_e)$ would depend on the s evel, hence the term must be rewritten as $T_{e_s k}\delta(h\nu-E_e)$, and for the transition probability we obtain

$$P(\nu) = \frac{4\pi^2 e^2}{m_e^2 h} \sum_{s,k} |T_{e_s k}(h\nu_0 - I_s)|^2\ P_k(s)\ \delta(h\nu + I_s - h\nu_0) \qquad [164]$$

If we disregard the electron correlation, we can substitute the one-electron Green function for the so called **free Green function** G^0, the latter represented by a diagonal matrix. In this approximation

$$P^0(\nu) = \frac{8\pi^2 e^2}{m_e^2 h} \sum_{k \leq n/2} |T_{e_k k}|^2 \, \delta(h\nu - \varepsilon_k - h\nu_0) \qquad [165]$$

where ε_k stands for orbital energy of the k-th MO (for simplicity only closed-shell molecules are considered). This leads to a theoretical prediction of n/2 bands in the ionization spectrum. More bands are actually observed experimentally, due to simultaneous excitation or ionization of the second electron (shake-up or shake-off process). A more adequate description of the ionization process has to take into account also electron correlation, as expressed by [164].

Green function technique is capable of reproducing the ionization energies with high accuracy. An illustrative example is given in Table 5.

TABLE 5
Vertical ionization energies of the N_2 molecule calculated by Green function technique.

Level	Perturbation theory order [a]					
k	$I_k^{(0)}$	$I_k^{\prime(2)}$	$I_k^{(2)}$	$I_k^{(3)}$	$I_k^{(\infty)}$	Exptl.
$3\sigma_g$	17.28	14.87	14.87	15.89	15.45	15.60
$1\pi_u$	16.74	17.01	17.02	16.68	16.76	16.98
$2\sigma_u$	21.17	17.96	18.01	19.66	18.91	18.78

a) $I_k^{(0)}$ - Koopmans approximation, $I_k^{\prime(2)}$ - diagonal approximation of the effective Hamiltonian, $I_k^{(\infty)}$ - final value.

4.9 PCILO AND PCILO/3 METHODS

The present method (Perturbative Configuration Interaction using Localized Orbitals: PCILO) links the classical chemical ideas of localized two-electron bonds with efficient numerical procedures for the computation of electron correlation by perturbative configuration interaction. In the present method the molecule is viewed as being built of localized two-electron fragments (covalent bonds, lone pairs, inner-shell electrons) in mutual interaction.

This interaction is treated by the perturbation theory (46).

In the PCILO method the following procedure is applied:

1. In accordance with chemical intuition the electronic structural formula is postulated for a molecule; in this formula the valence electrons are divided into two-electron covalent bonds and lone electron pairs. Such a bonding model can be described mathematically using bonding topology.

2. Using a unitary transformation, the atomic orbital basis set is transformed into hybrid atomic orbitals (HAO) which possess directional properties. Thereby it is required that a pair of HAOs be oriented in the direction of a covalent bond. In other words, the requirement is that the vector nucleus - centre of gravity of HAO electron density has minimum deviation from the line connecting the nuclei (for the σ-bonding HAOs) in-parallel with orthogonality of HAOs at the same centre. Hybridization can be of the canonical type (sp, sp^2, sp^3, dsp^2, d^2sp^3) or determined by computational procedures, such as the del Re method, EMOA method, etc. (see Section 3.7.2).

3. Over the HAO basis set the strictly localized molecular orbitals (SLMO) are constructed using an external localization criterion. The pair of bonding, ϕ_ν, and antibonding, ϕ_ν^*, SLMOs is searched for each bond in the form of a linear combination of the HAO pairs (h_i^A, h_j^B)

$$\phi_\nu = c_{\nu i}h_i^A + c_{\nu j}h_j^B = N_\nu(h_i^A + d_\nu h_j^B) \qquad [166]$$

$$\phi_\nu^* = c_{\nu i}^*h_i^A + c_{\nu j}^*h_j^B = N_\nu^*(h_i^A - d_\nu h_j^B) \qquad [167]$$

The lone electron pairs occupy the hybrid atomic orbitals $\phi_\nu = h_i^A$. Computation can be performed:

a) by direct minimization of energy

$$E_0 = f(\ldots d_\nu \ldots) \qquad [168]$$

b) using local validity of the Brillouin theorem

$$<\phi_\nu|\hat{F}|\phi_\nu^*> = 0 \qquad [169]$$

c) from modified Roothaan equations of the type

$$F_\nu C_\nu^+ = S_\nu C_\nu^+ E_\nu \qquad [170]$$

The wave function obtained

$$\Phi_0^{SLMO} = \hat{A}_n \{ \prod_\nu^{occ} \phi_\nu \} \qquad [171]$$

represents the reference configuration function yielding the energy

$$E_0^{SLMO} \geq E_0^{SCF} \qquad [172]$$

somewhat higher than the SCF energy; this localization defect is an artifact of the external localization method. Under certain assumptions, the SLMO computation can be omitted and the bond polarity values d_ν can be taken as transferable from one molecule to another for chemically similar bonds.

4. The perturbative configuration interaction is performed over the strictly localized MO basis set. The perturbation $\hat{H}'$ contains integrals of the type $F_{ij} = \langle i|\hat{F}|j\rangle$ for $j \neq i^*$, so that the energy formulae [73] - [74] contain additional terms. In the diagrammatic Rayleigh-Schrödinger MBPT (with Moller-Plesset Hamiltonian partitioning) the following additional energy corrections are obtained (47)

$$E^{(2)}_{m-m} = \sum_i^{occ} \sum_a^{vir} (F_{ia})^2/D_{ia} \qquad [173]$$

$$E^{(3)}_{m-m} = \sum_i^{occ} \sum_a^{vir} (F_{ia}/D_{ia}) \left(\sum_c^{vir} F_{ac}F_{ci}/D_{ic} - \sum_k^{occ} F_{ki}F_{ak}/D_{ka} \right) \qquad [174]$$

$$\begin{aligned} E^{(3)}_{m-b} = \sum_{i,j}^{occ} \sum_{a,b}^{vir} (\langle ij||ab\rangle/D_{iajb}) \Big\{ & F_{ia}F_{ij}(3/D_{jb} + 1/D_{ia}) - \\ & - \sum_k^{occ} [\langle ij||kb\rangle F_{ka}/D_{ka} + (1/2)\langle kj||ab\rangle F_{ik}/D_{kajb}] + \\ & + \sum_c^{vir} [\langle cj||ab\rangle F_{ic}/D_{ic} + (1/2)\langle ij||cb\rangle F_{ac}/D_{icjb}] \Big\} \end{aligned} \qquad [175]$$

The first two terms represent interaction within the framework of the one-electron Fock operator meaning the delocalization energy described by the perturbation theory. The last term represents a coupling of delocalization and correlation effects.

In the original PCILO method (48,49) the Epstein-Nesbet Hamiltonian partitioning was used. The formulae of the perturbative CI have a modified form in which the denominators $D'_{iajb} = E_0^0 - E_I^0 = D_{iajb} + \Delta_{iajb}$ also contain Coulomb and exchange integrals.

5. The one-electron operator $\hat{A}$ mean value can be determined from the one-electron spin-less density matrix P. Additional contributions to the relationships [92] through [95] resulting from the non-zero matrix elements F_{ij} are

$$P_{ia}^{(1)} = P_{ai}^{(1)} = F_{ia}/D_{ia} \qquad [176]$$

$$P_{ik}^{(2)} = -\sum_{a}^{vir} (F_{ia}/D_{ia})(F_{ak}/D_{ka}) \qquad [177]$$

$$P_{ac}^{(2)} = \sum_{i}^{occ} (F_{ai}/D_{ia})(F_{ic}/D_{ic}) \qquad [178]$$

$$\begin{aligned} P_{ia}^{(2)} = P_{ai}^{(2)} &= \sum_{j}^{occ} \sum_{b}^{vir} (\langle ab||ij\rangle/D_{iajb})(F_{jb}/D_{jb}) + \\ &+ (1/D_{ia})\left\{ \sum_{c}^{vir} F_{ac}(F_{ci}/D_{ic}) - \sum_{k}^{occ} F_{ik}(F_{ka}/D_{ka}) + \right. \\ &\left. + \sum_{j}^{occ} \sum_{b}^{vir} [\langle aj||ib\rangle(F_{bj}/D_{jb}) + (\langle ab||ij\rangle/D_{iajb})F_{jb}] \right\} \end{aligned} \qquad [179]$$

These elements directly visualize the electron delocalization and its coupling with electron correlation.

Delocalization treated by perturbation theory, however, is a pure artifact of the localized bonding model used since strict localization is not a physical reality.

The above PCILO method algorithm contains several substantial advantages, from which we list the following.

1. The reference configuration function of the ground electronic state Φ_0^{SLMO} is obtained by a simple and fast procedure since no diagonalization of the m x m dimensional Fock operator matrix (normally an m^3 time-demanding process) occurs.

2. Transformation of the integrals from the HAO basis set into the SLMO basis set is reduced at most to 16 terms

$$\langle ij|\hat{g}|kl\rangle = \sum_{p}^{2} \sum_{q}^{2} \sum_{r}^{2} \sum_{s}^{2} c_{ip}\, c_{jq}\, c_{kr}\, c_{ls} \langle pq|\hat{g}|rs\rangle \qquad [180]$$

which if compared to the case of canonical (delocalized) MOs (which is an m^5 time-consuming process) represents a substantial simplification.

3. Correlation energy contributions derived from chemically equivalent bonds show additive structure. The parturbative CI algorithm can be modified in such a way that only equivalent increments

$$E^{(n)} = \sum_{i}^{occ} \{\ldots\}_i \qquad [181]$$

are added. For example, in the CBr_4 molecule we have 4 equivalent σ C-Br bonds and 12 equivalent lone pairs so that instead of 16 increments it is sufficient to calculate only two

$$E^{(n)} = 4\{\ldots\}_{C-Br} + 12\{\ldots\}_{Br} \qquad [182]$$

4. The energy terms $E^{(0)}$ and $E^{(n)}$ can be interpreted in classical chemical language. It is also useful to specify the interbond correlation energy and the intrabond disperion energy.

The perturbation theory relationships introduces so far are applicable over the basis set of orthogonal spinorbitals, only. However, the SLMOs do not form an orthogonal set, which is the main reason why the PCILO version does not work well on the *ab initio* level. In fact, if the SLMO basis set is orthogonalized, then the advantages descibed above for the PCILO algorithm diminish. The way out of this situation is the introduction of the zero-differential overlap approximation via CNDO, INDO or NDDO methods. In this approximation the non-orthogonality of the SLMOs is not taken into account. Moreover, the CNDO parametrization in the valence s-p basis set enables substantial reduction of the perturbative CI algorithm. The following items can be included among the major advantages for using the CNDO Hamiltonian approximation:

1. the two-electron integrals in the valence s-p basis set are independent of hybridization

$$<p_A q_B | \hat{g} | r_C s_D> = \gamma_{AC}\ \delta_{pr}\ \delta_{qs} \qquad [183]$$

2. The energy terms $E^{(2)}$ and $E^{(3)}$ contain a smaller number of summations. For example, the expression for $E^{(3)}$ contains summations over three indices only. As a consequence of these simplifications, the ground-state energy can be calculated using PCILO procedure with 20 to 100 times less computer time than with the canonical MOs.

The original version of the PCILO method has undergone several modifications and generalizations, with the most significant listed in Table 6. Substantial generalization to include semi-localized bonds is effected by the **extended PCILO method** (PCILO/3 method) (52). Its fundamental principle is represented by the restricted expansion of localized MOs into the HAO basis set as

$$\phi_\mu = \sum_A \sum_i^A c^A_{\mu i}\ \delta_{g(\mu),f(A,i)}\ h^A_i \qquad [184]$$

In this notation, appears the discrete topological function $f(A,i) = b$, which is *a priori* defined over indices of atoms (A) and their hybrid orbitals (i), with b equal to the ordering number of the chemical bond. Lone electron pairs can be taken for

TABLE 6

Various versions of the PCILO method.

Characteristics	Version			
	Original	Improved	Modified	Extended
molecular orbitals	two-center	two-center	two-center	many-center
levels	closed-shell	closed-shell	open-shell	open-shell
Hamiltonian approximation	CNDO	INDO	CNDO, INDO	CNDO, INDO
valence basis set	s-p	s-p	d-s-p	d-s-p
applications to atoms	H-F	H-F	H-Br	H-I
hybridization algorithm	del Re	del Re	EMOA	EMOA
LCAO coefficients	variation of bond polarity		modified Roothaan equations	
Hamiltonian partitioning	Epstein-Nesbet		Moller-Plesset	
perturbation theory	classical 3rd-order		diagrammatic (MBPT) 3rd-order	
references	(48,49)	(50)	(51)	(52)
computer programs [a]	PCILO(220) GSPCILO(272) PCIRAD(327)	PCILINDO (371)	PCILO2(390)	PCILO3(462)

[a] There is a catalogue number of QCPE (Quantum Chemistry Program Exchange) in parentheses.

one-centre bonds (unclosed bonds with the bonding partner at infinity). The consequence of such a bonding topology is that the expansion coefficients matrix C can be arranged into a block-diagonal form. The bond-order matrix is

$$(P^s)^{AB}_{ij} = \sum_{\mu}^{occ(s)} (c^s)^A_{\mu i} \, (c^s)^B_{\mu j} \, \delta_{f(A,i),f(B,j)} \qquad [185]$$

for the spin index $s = \alpha$ or β; this again can be arranged into the block-diagonal form. The matrices P^s modified like this define the matrix elements of the Fock operator $(F^s)^{AB}_{ij}$ so that in the ZDO approximation ($S^{AB}_{ij} = \delta_{ij}$) we obtain the modified Roothaan equations in the form

$$F^s_b \, (C^s_b)^T = (C^s{}_b)^T \, E_b \qquad [186]$$

Since the dimension m_b of individual blocks is much smaller than the total basis set size $m = m_1 + m_2 + \ldots$, then the use of independent diagonalization of each F_b^s block results in a significant reduction of the computational time. Enlarging the number of components in each LMO (i.e. reducing the number of 'bonds') one can approach the SCF level of energy for the given type of Hamiltonian so that the concept of the extended PCILO method represents the intermediate situation between two limiting cases - that of canonical MOs and SLMOs.

The advantage of the extended PCILO method is represented by its ability to describe the many-centre and delocalized bonds (diborane, benzene and other aromatic molecules). The method can also be used with success for the study of hydrogen bonds and weak intermolecular interactions due to dispersion energy. When applied to chemical reactivity problems, the reaction centre (area of splitting of old bonds and formation of new bonds) can be described by semilocalized (semidelocalized) MOs, while bonds not exposed to the changes can be described by strictly localized MOs. Also in coordination compounds the many-centre MOs can be used to describe the chromophore (central atom surrouded donor atoms of ligands) while the ligand residues can be described through SLMOs.

The localization procedure quality can be characterized by two criteria:

1. by the relative localization defect

$$X_{loc} = (E_0^{SCF} - E_0^{LMO})/E_T^{SCF} = \Delta_{loc}/E_T^{SCF} \qquad [187]$$

(the T index means the total molecular energy in the Born-Oppenheimer approximation) which for $X_{loc} < 2\ \%$ yields a good reason to use the given bonding model;

2. by the compensation index

$$X_{com} = E_{m-m}^{(2)}/\Delta_{loc} \qquad [188]$$

which for $X_{com} > 60\%$ defends the use of perturbation theory (compensation of the localization defect by delocalization energy).

4.10 CIPSI METHOD

Since full configuration interaction is not achievable for molecules involving many electrons or large basis sets, approximate schemes were developed. Among them truncations to a certain level of excitation (single + double CI), freezing of some MOs, cluster expansions, etc. are known. An alternative solution consists in perturbing a multiconfigurational wave function resulting from a preliminary variational treatment of the CI matrix reduced to the most important determinants. This CIPSI algorithm (53,54) is based on an iterative selection of a first class determinants {S}, the weight of which in the exact wave function Ψ_m is larger than a certain treshold η: Φ_K belongs to {S} if $|\langle\Psi_m|\Phi_K\rangle| > \eta$. This first class of determinants is treated variationally

$$\hat{P}_S \hat{H} \hat{P}_S |\Psi_m^0\rangle = E_m^{(0)} |\Psi_m^0\rangle \qquad [189]$$

with

$$\hat{P}_S = \sum_{K\in S} |\Phi_K\rangle\langle\Phi_K| \qquad [190]$$

The resulting multiconfigurational wave function

$$\Psi_m^0 = \sum_K C_{mK} \Phi_K \qquad [191]$$

is then perturbed to the second order by the other determinants which do not belong to {S} yielding the energy

$$E_m^{(2)} = \sum_{I\notin\{S\}} \frac{\langle\Psi_m^0|\hat{H}|\Phi_I\rangle^2}{E_m^0 - E_I^0} \qquad [192]$$

In practice the definition of subspace {S} is iterative: starting from an initial guess of {S} one selects the most important determinants of the first-order correction to the wave function. At the k-th iteration, if the first-order coefficient of Φ_I is larger than η^k

$$\left|\frac{\langle\Psi_m^0|\hat{H}|\Phi_I\rangle}{E_m^0 - E_I^0}\right| > \eta^k \qquad [193]$$

the determinantal function Φ_I is added to {S} and the process may be repeated by decreasing the threshold η^k to $\eta^{k+1} < \eta^k$. In such a case there is no *a priori* selection of the multireference space {S}, the quality of which is progressively increased.

The improved CIPSI algorithm (55) defines three classes of determinants for each state:

1. the largest ones S (strong) are generators and define a multiconfigurational zeroth-order wave function, which will be perturbed by allowing all single and double substitutions,
2. the mean ones M (middle), of the order 10^3, are perturbed to all orders, and the normalization defect is corrected through the Davidson-Siegbahn formulae,
3. the most numerous ones *s* (smallest), of the order 10^6, are only included through their second-order correction.

Two threshold parameters η and τ define the borders of these classes, and are progressively decreased for a rational selection of the classes and for a study of the stability of the results.

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APPENDICES

APPENDIX 1. ATOMIC UNITS AND PHYSICAL CONSTANTS

The values of fundamental physical constants (e, m_e, h, ϵ_0, etc.) are determined to a certain precision. The valid figures of these constants determine the threshold of arithmetic expressions such as $\hbar^2/2m_e$ or $e^2/4\pi\epsilon_0$. For this reason the use of the SI system of units brings difficulties in exact quantum-mechanical calculations. For practical reasons the system of atomic units is frequently used in *ab initio* calculations. This system of units has been introduced and used for the reason that different programs would yield exactly the same results so that the compability of programs and transferability od data between them would be retained. It should be noted that the *ab initio* methods operate with an enormous number (10^5 to 10^6) of two-electron integrals the precision of which is 8 or more digits. Therefore the basic physical constants should be determined to the precision of at least 9 digits. The above problem may be avoided by introducing such a system of units which does not require the conversion factors. The atomic unit (a.u.) system fulfils this requirement. The basic units in the a.u. system are represented by bohr (a_0 - unit of length), hartree (E_h - unit of energy), electron rest mass (m_e - unit of mass) and elementary charge (e - unit of electric charge). As a consequence many physical quantities become very simple (e.g., $\hbar = 1$, $\beta = 1/2$, etc.).

Values of fundamental physical constants are collected in Table 1. They are given either in SI units or a.u.

APPENDIX 2. COORDINATE SYSTEMS

In quantum-chemical calculations of various molecular properties we meet with problem of evaluating a number of certain integrals which should be calculetd in a definite coordinate system. The right-handed cartesian coordinate system (0; X, Y, Z) usually serves for the referential coordinate system. Localization of the origin (0) is arbitrary. For several purposes the origin is put into the centre of mass of the molecule and the cartesian axes are identified with maan axes of the inertia moment. In the above procedure the atomic weigths come into effect.

TABLE 1

Values of physical constants and related quantities.

Quantity	Symbol	Value	
		SI units	a.u.
a) Physical constants			
Planck constant	h	6.626176×10^{-34} Js	2π
Elementary charge	e	$1.6021892 \times 10^{-19}$ C	1 (millikan)
Speed of light in vacuum	c	2.99792458×10^{8} ms^{-1}	137.03604
Rest mass of electron	m_e	9.109534×10^{-31} kg	1 (thomson)
Rest mass of proton	m_p	$1.6726485 \times 10^{-27}$ kg	1836.15152
Rest mass of neutron	m_n	$1.6749543 \times 10^{-27}$ kg	1838.68
Avogadro number	N_A	6.022045×10^{23} mol^{-1}	-
Boltzmann constant	k	1.380662×10^{-23} JK^{-1} 8.61735×10^{-5} eV K^{-1}	-
Permittivity of vacuum	ϵ_0	$8.854187818 \times 10^{-12}$ $C^2N^{-1}m^{-2}$	-
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ NA^{-2}	-
Electronic g-factor			
- Zeeman	g	2.00231929	
- spin-orbital	g'	2.00463858	
Reduced Planck constant ($\hbar = h/2\pi$)	$\hbar$	$1.0545887 \times 10^{-34}$ Js	1 (planck)
Fine structure constant ($\alpha = e^2/4\pi\epsilon_0\hbar c$)	α	7.29735×10^{-3}	1/c
Bohr magneton ($\beta = e\hbar/2m_e$)	β	9.274078×10^{-24} JT^{-1}	1/2
Nuclear magneton ($\beta_N = \beta_P = e\hbar/2m_p$)	β_N	5.050824×10^{-27} JT^{-1}	2.723087 x x 10^{-4}
b) Atomic units			
Length (Bohr radius) ($a_0 = 4\pi\epsilon_0\hbar^2/e^2m_e$)	a_0	$5.2917706 \times 10^{-11}$ m	1 (bohr)
Energy ($E_h = e^2/4\pi\epsilon_0a_0$)	E_h	4.359814×10^{-18} J 27.21161 eV	1 (hartree)
Dipole moment ($d_0 = ea_0$)	d_0	8.478418×10^{-30} Cm	1
Quadrupole moment ($Q_0 = ea_0^2$)	Q_0	4.4866×10^{-40} Cm^2	1
Electric field gradient ($\phi_0 = E_h/ea_0^2$)	ϕ_0	9.7174×10^{21} Vm^2	1

For coordination compounds $[ML_n]$ of high symmetry it is useful to put the central atom into the origin. In the crystal field theory, angular overlap method (AOM) and in generating symmetric orbitals for methods of effecive Hamiltonian there is a convention of how to number ligands and their local coordinates axes. These conventions are exemplified in Fig. 1. The corresponding symmetry orbitals in this coordinate system are presented in Table 2.

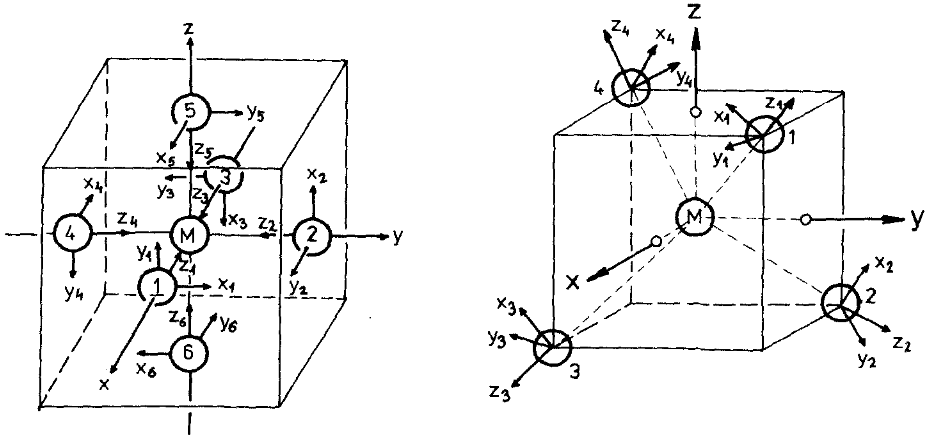

Fig. 1. A coordinate system of octahedral $[ML_6]$ and tetrahedral $[ML_4]$ complexes.

A frequent requirement is represented by transformation of cartesian coordinates (x, y, z) into polar coordinates and *vice versa*. The corresponding transformations are (Fig. 2)

$x = r \cos\varphi \sin\vartheta$

$y = r \sin\varphi \sin\vartheta$

$z = r \cos\vartheta$

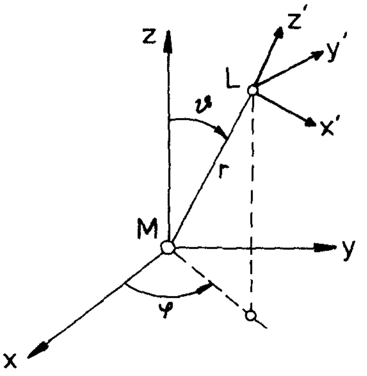

Fig. 2. Cordinates of ligands L with respect to the central atom M.

TABLE 2

Symmetric orbitals of octahedral and tetrahedral complex.

Represen-tation	Central atom	Group orbitals of ligands [a]
A) Octahedral complex		
a_{1g}	s	$(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)/\sqrt{6}$
e_g	$d_{x^2-y^2}$	$(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$
	d_{z^2}	$(2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)/(2\sqrt{3})$
t_{1u}	p_x	$(\sigma_1 - \sigma_3)/\sqrt{2}$
		$(p_{y2} + p_{x5} - p_{x4} - p_{y6})/2$
	p_y	$(\sigma_2 - \sigma_4)/\sqrt{2}$
		$(p_{x1} + p_{y5} - p_{y3} - p_{x6})/2$
	p_z	$(\sigma_5 - \sigma_6)/\sqrt{2}$
		$(p_{y1} + p_{x2} - p_{x3} - p_{y4})/2$
t_{2g}	d_{xz}	$(p_{y1} + p_{x5} + p_{x3} + p_{y6})/2$
	d_{yz}	$(p_{x2} + p_{y5} + p_{y4} + p_{x6})/2$
	d_{xy}	$(p_{x1} + p_{y2} + p_{y3} + p_{x4})/2$
t_{1g}		$(p_{y1} - p_{x5} + p_{x3} - p_{y6})/2$
		$(p_{x2} - p_{y5} + p_{y4} - p_{x6})/2$
		$(p_{x1} - p_{y2} + p_{y3} - p_{x4})/2$
t_{2u}		$(p_{y2} - p_{x5} - p_{x4} + p_{y6})/2$
		$(p_{x1} - p_{y5} - p_{y3} + p_{x6})/2$
		$(p_{y1} - p_{x2} - p_{x3} + p_{y4})/2$
B) Tetrahedral complex		
a_1	s	$(s_1 + s_2 + s_3 + s_4)/2$
		$(p_{z1} + p_{z2} + p_{z3} + p_{z4})/2$
e	d_{z^2}	$(p_{x1} - p_{x2} - p_{x3} + p_{y4})/2$
	$d_{x^2-y^2}$	$(p_{y1} - p_{y2} - p_{y3} + p_{y4})/2$
t_2	p_x, d_{yz}	$(s_1 - s_2 + s_3 - s_4)/2$
		$(p_{z1} - p_{z2} - p_{z3} - p_{z4})/2$
		$[p_{x1} + p_{x2} - p_{x3} - p_{x4} + \sqrt{3}(-p_{y1} - p_{y2} + p_{y3} + p_{y4})]/4$
	p_y, d_{xz}	$(s_1 + s_2 - s_3 - s_4)/2$
		$(p_{z1} + p_{z2} - p_{z3} - p_{z4})/2$
		$[p_{x1} - p_{x2} + p_{x3} - p_{x4} + \sqrt{3}(p_{y1} - p_{y2} + p_{y3} - p_{y4})]/4$
	p_z, d_{xy}	$(s_1 - s_2 - s_3 + s_4)/2$
		$(p_{z1} - p_{z2} - p_{z3} + p_{z4})/2$
		$-(p_{x1} + p_{x2} + p_{x3} + p_{x4})/2$

TABLE 2 (Continued)

Representation	Central atom	Group orbitals of ligands [a]
t_1		$[\sqrt{3}(p_{x1} + p_{x2} - p_{x3} - p_{x4}) + + p_{y1} + p_{y2} - p_{y3} - p_{y4}]/4$ $[\sqrt{3}(p_{x1} - p_{x2} + p_{x3} - p_{x4}) + - p_{y1} + p_{y2} - p_{y3} + p_{y4}]/4$ $-(p_{y1} + p_{y2} + p_{y3} + p_{y4})/2$

[a] For the coordinate system see Fig. 1.

The two-centre, three-centre and four-centre integrals are calculated first at the local coordinate system and then they are transformed, using Euler rotations, to the molecular coordinate system.

APPENDIX 3. A GUIDE THROUGH JUNGLE OF QUANTUM-CHEMICAL METHODS

We compiled rich data on various quantum-chemical methods applicable to coordination compounds; they are strongly bound to recent progress in computer software and hardware. The existing methods form really a jungle the orientation through which is rather problematic. The question, which method is the best one, cannot be answered and one must pass through experience which method is most economical, productive and sufficient enough to study his particular problem. Although the quantum chemistry of organic compounds becomes a routine, this is not the case of the quantum chemistry of coordination compunds. This is not caused only by the increasing number of electrons in metal complexes but also by new phenomena not critical (or rather rare) for organic compounds. Among them the existence of low-lying excited states, relativistic effects and the configurational lability of the Jahn-Teller effect type may be substantial.

In treating molecules we are interested mainly in their equilibrium geometry, possible geometric rearrangements, ground-state characteristics, spectroscopic transitions and ability to undergo certain chemical reactions.

If we speak of a molecule, it is understood that its chemical formula and a rough structural skeleton are known. Thus we can consider atoms in a molecule and, in a modern approach, to use molecular visualization on personal computers (AT-286, as a rule, is enough for this purpose). It is impossible to enumerate all the existing visualization programs but at least ALCHEMY, CHEMCAD and MOLDRAW might be mentioned. They allow one to build up a molecular structure from default structural data - standard bond lengths, bond and dihedral angles, or molecular fragments. Some of these programs have a crystal coordinate input assuming the X-ray data at the disposal.

The molecular visualization programs are often combined with the option for the molecular mechanics. The latter gives a better estimate of the equilibrium geometry, as a result of the total molecular energy minimization. This approach, however, is conditioned by an appropriate parametrization of empirical potentials for molecular mechanics, equivalent to the assumption of a transferability of force constants (harmonic, cubic, bi-quadratic) and standard bonding coordinates (bond lengths, bond and torsion angles) from one molecule to another. Such an assumption is often fulfilled for organic compounds but it may heavily fail for inorganic systems. Moreover, the programs mentioned operate like a 'black-box' system, allowing only to modify the input data but not the basic formulae and parameters. On the other hand, the molecular mechanics may be used as a 'pre-optimizer' of the molecular structure before using a more elaborate quantum-chemical method.

Having a first estimate of the molecular geometry, the molecular-orbital calculations may be performed. The problem which must be clarified first is the selection of a proper method capable of solution the problem under study. Although an *ab initio approach* is superior to any semi-empirical method, we must take into account the time consumption, or cost, of the calculation.

Following the *ab initio* pathway, the basis set selection problem appears. Only the basis sets of good quality (and of the proper balance) are recommended to *ab initio* calculations, but this requirement may lead to enormous difficulties. Note that the number of two-electron integrals to be calculated is proportional to n^4, n being the basis set size. Thus for 100 basis set functions we demand evaluation and storage of 10^8 integrals and their manipulation during the SCF procedure. The coordination compounds, of course, contain heavy transition metal atoms and a lower portion of light hydrogen atoms, so that the basis set dimension is really much higher than for organic compounds of the comparable size. Do not forget that diffuse and polarization functions contribute substantially to the energy calculation and they are definitely necessary for anions. For reasons above the *ab initio* calculations for metal complexes are far from the routine. As some metal complexes have more electronic states close one to another, the SCF procedure may be insufficient even to localize the ground state; the multiconfiruration SCF or limited CI are necessary for these cases and consequently the time and space requirements increase. Therefore the *ab initio* approach, followed by a version of configuration interaction, is presently applied with success to only small (diatomic or triatomic) molecules, or small clusters. Information comparable to presicion of a spectroscopic determination is feasible for these systems.

The pseudopotential method seems to be a good compromisse between the rigorous *ab initio* and non-empirical approximate approach; this permits the MO-LCAO-SCF calculations for coordination compounds of medium size in a real time. On the contrary, definition of a suitable pseudopotential is a 'state of art' and evaluation of pseudopotential integrals is also difficult.

The density functional theories and especially the $X\alpha$ method are also useful to study coordination compounds. Although they yield good results for energy quantities (total molecular energy, ionization and excitation energies), these method suffer for improper definition of the wave function and consequently the calculation of the correlation energy is impossible.

The methods discussed below (Fenske-Hall, CNDO, INDO, NDDO, EHT) exhibit a drawback resting in the fact that the basis sets used for transition metal atoms are not properly balanced. For example, the atomic valence orbitals for the Ni atom consist of 3d, 4s and 4p functions; only 3d and 4s are determined by atomic ground-state calculations for the $3d^8 4s^2$ electron configuration. The remaining 4p functions need determination from excited-state calculations for the $3d^8 4s^1 4p^1$ electron configuration. Thus the orbital exponents for 4p orbitals derived from the later calculations are clearly overestimated; if one handle them in MO calculations, the weight of the $3d^8 4s^1 4p^1$ configuration is implicitly overestimated. This failure can be overcome using the multiconfiguration SCF, but an efficient algorithm for this purpose absents.

The use of node-less orbitals and single-zeta basis sets in all-valence calculations represent another drastic simplification. At least double-zeta orbitals are required for proper radial dependence of d-orbitals in the valence region.

The Fenske-Hall method is popular among the non-empirical methods for coordination compounds. It may be adapted to run on personal computers (AT-386 or AT-486).

Among methods utilizing the zero-differential overlap approximation, the MNDO, AM1 and MNDOC versions belong to the most popular for organic compounds. They were parametrized only for a few sp type elements and thus they are not applicable to coordination compounds so far. Some versions of the INDO method are recommended for inorganic systems: namely the INDO/S or Zerner INDO/1 versions serve as an example. Note that CNDO, INDO and NDDO based methods abstract from the two-centre exchange interaction so that they fail in predicting magnetic properties and a proper separation between the low-spin and high-spin states for binuclear complexes and clusters. This drawback disappears for INDO and NDDO type methods when applied to mononuclear complexes as they both account for all one-centre two-electron integrals.

The EHT model is the most simple all-valence method of the MO type. Despite its rough features it is still applicable to large inorganic systems and frequently used to generate Walsh-type diagrams.

When heavy atoms are concerned, the relativistic contraction of s- and p-orbitals side-by-side with the relativistic expansion of d- and f-orbitals must be considered. Therefore the use of spectroscopic parameters in combination with non-relativistic basis sets loses its reasoning. A quasi-relativistic approach represented by the REX, quasi-relativistic CNDO/1 and INDO/1 methods represents an appropriate approximation. The above three versions are the only methods parametrized universally for all elements ($Z = 1 - 120$).

If desired, the spin-orbit splitting may be included using perturbation theory. When the SOI is too strong (for heavy atoms), variational treatment is necessary and we must pass from the single-component wave function to a four-component molecular spinor.

The orbital energies, LCAO coefficient matrix and the total molecular energy represent a net result of the SCF procedure. These quantities may be further used for a more detailed elaboration.

The LCAO coefficients determine the symmetry of each molecular orbital which spans an irreducible representation of the molecular point group. The symmetry assignment and energies of MOs are used for the first estimate of ionization energies within the Koopmans approximation. Those for the HOMO-LUMO pair may be utilized to discuss possible chemical processes. The HOMO-LUMO separation itself is insufficient in estimating the excitation energies and it must be corrected by the corresponding Coulomb and exchange integrals in the molecular orbital basis set.

It is useful to evaluate contribution of each atomic orbital type (in per-cent) to individual MOs. For example, if the d-orbital component predominates in a given MO, this may be classified as a d-level and, as a rule, it follows the orbital splitting diagrams predicted by the simple crystal field theory. Such a naturally localized metal orbital may exhibit high relaxation under electron ionization and excitation. Owing to high relaxation for a lower in energy level, the HOMO does not necessarily correspond to the first ionization energy (paradoxical violation of the Koopmans theorem). Note that within the UHF approach the energies of α- and β-molecular orbitals may have different values. Therefore the i-th α-MO of a given symmetry may have the j-th β-MO ($j \neq i$) as a corresponding counterpart. Sometimes the open α-MO (not having the corresponding β-MO within the occupied orbitals) may be buried below a set of doubly occupied (as a rule ligand) MOs.

The d-orbital populations may be summed up to yield the total atomic d-population, d^x. This value may be *a posteriori* compared with the reference $d^x s^y p^z$ configuration used *a priori* to define the basis set functions and semiempirical parameters. For example, for the Cu atom both $3d^9 4s^2$ and $3d^{10} 4s^1$ reference configurations are relevant. If one deals with Cu(II) complexes, the former selection is natural, but the resulting d^x value should not be too far from the d^9 value. If, on the contrary, calculated d^x value approaches d^{10}, the later selection is preferred. In an intermediate situation ($9.3 < x < 9.7$) the MC SCF approach is demanded.

The LCAO coefficients themselve are subject to population analysis from which orbital, atomic and eventually overlap populations result. The effective atomic charges indicate nucleophile and/or electrophile centres in the system. However, the definition of atomic charges is rather problematic and may be effected by a diffuse character of valence atomic orbitals. Methods of the CNDO, INDO and NDDO type often show a charge alternation throughout the molecular skeleton - an artifact of the ZDO approximation.

The charge-density (bond-order) matrix **P** is calculated from the LCAO coefficient matrix **C** and this may be useful to evaluate Wiberg (bond-strength) indices. These may correlate with wavenumbers of vibrational spectra.

The total molecular energy can be decomposed to one-centre and two-centre terms. The latter again is an indicatrix of the bond strength.

The density matrix determines the mean value of an arbitrary one-electron operator, for example the dipole and quadrupole moment. The corresponding operator matrix elements in the atomic orbital basis set, however, should be evaluated beforehand. Other important quantities are represented by the molecular electrostatic potential and the difference density function ρ. These differ in different spatial points and thus are presented in the form of contour isovalue diagrams.

The spin density matrix may be calculated for open-shell systems and it may be reduced to orbital and atomic spin densities comparable to data substacted from ESR spectra.

The above semiempirical or non-empirical (except the ETH) methods may be followed by the configuration interaction in order to account for correlation effects.

Methods like PCILO and PCILO/3 are less universal as they need additional information about the bonding topology necessary for selection of hybrid atomic orbitals and two-centre localized or polycentre semi-localized MOs. On the other hand, their algorithm is much faster than a tedious N^3-diagonalization applied to any canonical MO calculation.

Single energy value at the given molecular geometry represents one point of the adiabatic potential surface. Several methods were developed to generate analytical and/or numerical gradients used for the next search of the molecular geometry, in order to localize stationary points of the adiabatic potential surface. Note that the configuration interaction makes the adiabatic potential more flat, thus decreasing the (harmonic) force constants. Having the force constant matrix at the disposal, the complete FG-analysis (in harmonic approximation) may be performed to yield the vibrational frequencies. Then the partition function Q_v may be evaluated and in combination with other partition functions the thermodynamic potentials (H, G, etc.) are admissible.

In studying the elementary chemical reactions the reaction coordinate may be followed and kinetic characteristics are evaluable.

In more complex streochemical situation a detailed map of the adiabatic potential surface around the stationary points is useful.

The numerical values for the adiabatic potential may be used to fit analytical formulae derived from the (pseudo) Jahn-Teller effect theories and finally the set of vibronic coupling constants may be evaluated. Their determination is necessary if one tries pass over the Born-Oppenheimer approximation to study molecular dynamics, stereochemical non-rigidity, fluxionality, etc.

At the end of our presentation we would like to point out that the quantum chemistry of coordination compounds is a well developed discipline with important connections to many orther areas. Unfortunately, we had no space here to introduce and discuss:

a) the linkage of quantum chemistry to molecular spectroscopy, including fotoelectron, electron, vibration, rotation and resonance (ESR, NMR, NQR) spectra;

b) magnetism, electric and optical properties;

c) weak intermolecular interactions and environmental effects covered by the solvent and solid-state effects.

SUBJECT INDEX