Lecture Notes in Physics

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Symmetry of Polycentric Systems

The Polycentric Tensor Algebra for Molecules

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1. Introduction

Philosophers of science have traditionally been fascinated by the regular polyhedra. Pythagoras and Plato assigned them to the primary elements; Kepler speculated about them in "Harmonices Mundi"; and more recently W.Heisenberg, fully aware of this tradition, offers us a modern interpretation of Plato's opinion. Summing up, he says:

"Die letzte Wurzel der Erscheinungen ist also nicht die Materie, sondern das mathematische Gesetz, die Symmetrie, die mathematische Form."[1]

(The ultimate root of the phenomena is not the matter but the mathematical law, the symmetry, the mathematical form.)

Because the intention of this treatise hardly can be explained better, we add another quotation, in which we certainly may read molecule as well as elementary particle:

"Fragt man bei Plato, welches der Inhalt seiner Formen sei, aus welchem Stoff also seine **regulären Körper schließlich** gemacht **seien**, so erhält man die Antwort: aus Mathematik. Denn die Dreiecke, aus denen die regulären Körper gebildet werden sollen, sind ja nicht selbst Materie, da sie als zweidimensionale Gebilde keinen Raum erfüllen. Sie sind gedankliche Konstruktionen, die durch die Art ihrer Zusammenfügung räumliche Gebilde darstellen. In ähnlicher Weise sind in der heutigen Physik die Eigenwerte, die die Elementarteilchen darstellen, eben Eigenwerte einer Gleichung und in sofern rein mathematische Gebilde, denen keine Substanz zugrunde liegt. In gewisser Weise könnte man vielleicht noch die Energie als Substanz bezeichnen, aber auch die Energie und ihre Erhaltung ist eine mathematische Folge einer Invarianz-Eigenschaft der Gleichung, sie ist gewissermaßen in der Gleichung enthalten. Letzten Endes wird also der Materiebegriff in beiden Fällen auf Mathematik zurückgeführt. Der innerste Kern alles Stofflichen ist für uns wie für Plato eine "Form", nicht irgend ein materieller Inhalt."[2]

(If one asks in Plato, what is the essence of his forms, i.e.which material his regular solids are made of, one gets the answer: of mathematics. For the triangles constituting the regular solids are no matter by themselves, because as two-dimensional entities they cover no space. They are constructions of thought, which constitute spatial formations by the mode of their composition. Similarly in modern physics the eigenvalues representing the elementary particles are just eigenvalues of an equation and thus purely mathematical entities based on no substrate. In a sense one might specify the energy as a substrate, but even the energy and its conservation is a mathematical consequence of an invariance of the equation, it is so to speak embodied in the equation. In the end in both cases, the concept of matter is reduced to mathemat-

ics. For us, as for Plato, the very essence of reality is a question of "form", not of material substrate.)

The present treatise is devoted to the elaboration of such principles of form, with particular respect to molecular physics and quantum chemistry. These principles appear on two levels. The classical symmetries of the polyhedra have been replaced in their importance by more fundamental symmetries, which are shared by all elementary particles, and consquently by all molecules. These symmetries, including the homogeneity and the isotropy of space-time and the permutational symmetry according to Pauli's principle, specify the possible forms of Schrödinger equations and of state functions. These symmetries will be presupposed here, and will concern us only in the case of the multi-centre integrals (section 13). For these integrals they prescribe general principles of form not restricted to symmetric molecules.

The main subject of this treatise is the symmetry of the polyhedra realized in "the architecture of molecules". Pauling's book of this title [3] may be regarded as a modern illustration of Plato, and of Kepler's statement, "geometria est archetypus pulchritudinis mundi". The triangles mentioned by Plato as the constituents of the polyhedra are essential to the present analysis, too.

The analysis of symmetry means application of group theory. Except for the theory of transition-metal ions, this application in chemistry has been more or less qualitative: labeling of states and normal vibrations, splitting and selection rules. The construction of symmetry-adapted linear combinations (SALC),going beyond this point, has remained unsystematic, because the linear combination coefficients - in contrast to the Clebsch-Gordan coefficients - have not been considered a basis of an algebra.

Against the "myth of qualitative group theory" [4], the Wigner-Eckart theorem in its several varieties yields qualitative results and makes the quantitative analysis of symmetry a theory of reduced matrix elements or, more generally speaking, a theory of invariants. In atomic spectroscopy, the reduced matrix elements are related to the radial integrals of the atomic orbitals, the Slater integrals for instance, and therefore have a lucid meaning. The same holds for the ligand field theory, which is focussed on the central transition-metal ion. But what is the concrete meaning of the reduced matrix elements in polycentric systems?

As an answer to this question, we shall design a quantitative analysis of symmetry for molecules, which can not be treated as quasi-monoatomic systems. Consequently, this must be a theory of molecular invariants. Since the symmetric coordination polyhedra are a new compo-

nent in comparison to the traditional atomic spectroscopy, to the nuclear shell and to the ligand field theory, this will exercise an influence on the character of molecular invariants as well as on the algebra of coefficients.

With regard to the invariants there are now two different types. At one hand there are still the reduced matrix elements of the Wigner-Eckart theorem. Because these arise from the s.-a. and thus delocalized molecular functions, they gain their significance only indirectly by as second type of invariants localized at the edges, triangles etc. of the polyhedral framework. These invariants involving several atomic centres quite naturally refer to the neighbourhoods within the coordination polyhedra (sections 4, 8, 11) and thus give way to the ideas of coordination chemistry and the theory of chemical binding.

With respect to the theorems mediating the connections of both types of invariants, we need a polyhedral supplement of the tensor algebra. The familiar classes of coefficients in the Wigner-Racah algebra (3jm, 6j, 9j symbols, isoscalars, coefficients of reduction and fractional parentage) are supplemented by classes with reference to the edges, triangles and deformed tetrahedra subtended by the atoms. The most significant, new coefficients represent triangular relations within the polyhedra. In analogy to the familiar isoscalars, they are called polyhedral isoscalars. Principally the new definitons and the somewhat delicate design of the graphic symbols shall be kept as close as possible to the existing Wigner-Racah algebra.

The question for molecular invariants can be formalized quite generally in a basic concept. An arbitrary statement of the ligand field theory may serve as an example, let us say the energy of the state $^1A_{1g}(t_{2g}^2)$ in an octahedral field:

$$E(^1A_{1g}(t_{2g}^2)) = E_o - 8Dq + A + 10B + 5C \tag{1.1}$$

On the left we have a physical quantity $Ph(y)$ depending on a set of quantum numbers y. On the right there are several radial integrals $Int(z)$ likewise depending on quantum numbers z. In (1.1) these are indicated by distinct letters. Seldom is it stressed that the factors -8, 1, 10, and 5 are not more or less occasional numbers but values of functions of y and z and therefore can be enunciated by formulas containing the sets y and z. Factors of this type will be called geometrical factors through out, $GEO(y,z)$ in this case. (1.1) now presents itself as a special case of basic relations:

$$Ph(y) = \sum_z GEO(y,z) \cdot Int(z) \tag{1.2}$$

Another example is the square of a vibrational frequency of a molecule expressed by the force constants with respect to neighbouring atoms. This relation is determined by geometrical factors, too.

Often - especially for symmetrical structures - the geometrical factors are the only accessible, precise data and therefore the most interesting part of the theory. In semi-empirical theories (like Hückel-MO), the integrals $Int(z)$ are treated as parameters. For the fitting of these parameters, the inversion

$$Int(z) = \sum_y GEO(y,z) \cdot Ph(y) \qquad (1.3)$$

is useful.

The task now is to design a systematic theory of the quantities $Int(z)$ at one hand and the geometrical factors at the other, as has been elaborated for atoms and nuclei.

The physical quantities naturally do not depend on the choice of coordinate axes and the numbering of atoms; they are invariants. The generation of a minimum number of invariants $Int(z)$ demands the consideration of symmetry. Since (1.2) is a relation between invariants of different type, there can occur nested relations of this kind. An example is a many-particle matrix element, which, in a first step, is expressed by the one-particle MO-integrals (respectively their invariants). In a second step, the latter are expressed by the multi-centre integrals of the atomic functions (respectively their invariants).

The geometrical factors, being invariants too, have to be reduced to the coefficients of the Wigner-Racah algebra of the relevant point group and its polycentric supplement. The generalization of the Wigner-Racah algebra to point groups has been given by Griffith [5] with restriction to simply reducible groups containing ambivalent classes. Even more recent books in this field cling to this restriction [6, 7, 8]. An exception is the introduction to the energy diagrams published by König and Kremer [9] and preceeding papers by the same authors. Since our results shall equally and immediately apply to systems like $Co(NO_2)_6^{3-}$ (group T_h), Ta_6-clusters with spin-orbit coupling (group $O_h^{\#}$), $Pt(CN)_4^{2-}$ in an magnetic field (group C_{4h}), and $B_{12}H_{12}^{2-}$ (icosahedral group), we include the non-simply-reducible point groups with non-ambivalent classes from the beginning.

Because of the heterogeneous notations in the literature, we recapitulate the Wigner-Racah algebra of non-simply-reducible point groups with non-ambivalent classes in section 2. The price for including these groups is the appearence of several multiplicity indices, which may obscure the esthetic clarity of the theorems. Therefore it is advisable to omit all multiplicity indices and their

related sums from time to time. Mostly these indices take only one
value and are included only as a precaution for the few cases of
multiplicity 2 or 3. After this recapitulation, the principal concepts
refering to point group symmetry only are built up in the sections 3
to 11. In doing so, the preliminary studies [10, 11] are resumed. The
rest of this treatise is new matter. The sections from 12 onwards
contain more detailed results, which depend more on special choices
concerning multiplicities and orbital systems.

Since many-electron matrix elements are reduced to one- or two-
electron matrix elements by geometric relations, we are mainly con-
cerned with the latter. Because of the delocalization of the MOs, the
manyelectron systems in the MO scheme show no polycentric peculiarities
compared to ligand field theory. So they are dealt with only in short
in section 19. On the contrary, the VB scheme, though less usual,
leads to some general ideas in our context (section 20). The main sub-
ject of the further development presumably is the theory of the po-
lycentric coefficients of fractional parentage (the generalization of
the familiar coefficients). For this purpose, one needs the unitary
group or quasi-spin approach adopted by Racah for the many-particle
theory.

Another direction of improvement is sketched in section 21. It is
the application of the present symmetry-analysis on crystals, i.e. the
introduction of space groups into our considerations. This application
offers itself in particular for calculations using atomic or Wannier
functions (for instance tight-binding or OPW methods) and for normal
vibrations of crystals. In the case of symmorphic space-groups this
introduction causes no difficulties, but for the non-symmorphic groups
it is hampered by the deficient elaboration of the Wigner-Racah al-
gebra of these groups.

Another aspect, the application to the molecular normal vibrations,
has been demonstrated in the paper [12] . Since no principal new con-
cepts could be expected to appear, it has not been taken up again
here. The same applies to the more complicated adiabatic and rela-
tivistic effects.

In the foreword of his book [13] , Chesnut has termed group theory
as organized common sense. Organizing in this context also means the
tabulation or the programming of the group-theoretical coefficients,
just as they now are available for the rotation group [14] and by a
recent book [75] for the point groups. Not until the newly defined
coefficients, especially the polyhedral isoscalars, are available nu-
merically, the symmetry-analysis lined out here will take full effect.

2. Summary of the Wigner-Racah algebra of non-simply-reducible point groups with non-ambivalent classes

In the following, we assume as known the results of the monocentric group theory of atoms and molecules presented, let us say, in the books of Edmonds [15] and Griffith [5]. Some parts of the group theory concerning the two-particle interactions and coefficients of fractional parentage (CFP) and missing in Griffith's book have been described in the papers [16, 17] and this concise summary is in part identical with the appendix of [17], where more references are given. A detailed study of the NSR groups has been made by Butler [18], but it is more general than necessary for point groups. We further refer to the lectures given by Butler and Piepho at the NATO Advanced Study Institute on recent advances in group theory [19, 20].

2.1. Representations

We consider a molecule, complex, or cluster with a symmetry group G, optionally a point group, a double point group, or the direct product of a point group and the spin group $SU(2)$. The classes of G are denoted by C and its elements by g, g' etc. The latter are identified with the symmetry operations in the configuration space acting on vectors, triangles and other objects in space, for instance:

$$\vec{r}' = g^{-1}\vec{r} \tag{2.1}$$

The irreducible representations of G are denoted by a, b, c etc. (or $a(G)$, $b(G)$, ... if a distinction is necessary) with the unitary representation matrices $D^a(g)$, and the matrix elements $D^a_{mn}(g)$:

$$D^a(g)D^a(g) = D^a(gg') \text{ or } \sum_n D^a_{mn}(g)D^a_{np}(g') = D^a_{mp}(gg') \tag{2.2}$$

$$D^a(g)^+ = D^a(g)^{-1} = D^a(g^{-1}) \text{ or}$$

$$[D^a(g)^+]_{mn} = [D^a_{nm}(g)]^* = [D^a(g)^{-1}]_{mn} = D^a_{mn}(g^{-1}) \tag{2.3}$$

These obey the orthogonality relation:

$$\sum_{g \in G} D^a_{mn}(g)D^b_{pq}(g)^* = \frac{\text{ordG}}{\text{dima}} \cdot \delta_{ab}\delta_{mp}\delta_{nq} \tag{2.4}$$

The representation contragredient to a is denoted by a^+ and defined by

$$D^{(a^+)}_{mn}(g) = [D^a_{mn}(g)]^* = D^a_{nm}(g^{-1}). \tag{2.5}$$

The reducible finite dimensional representations of G are denoted by σ^A (or $\sigma^A(G)$) with a discriminating index A and the representation by unitary operators, acting on a Hilbert space, by $U(g)$. The operators $U(g)$ are defined in the space representation by

$$\langle g^{-1}\vec{r}|\varphi\rangle = \langle \vec{r}|U(g)|\varphi\rangle. \tag{2.6}$$

2.2. Characters

The characters are defined as usual for irreducible and reducible representations:

$$\chi^a(g) = \sum_m D^a_{mm}(g), \qquad\qquad \sigma^X(g) = \sum_i \sigma^X_{ii}(g) \qquad (2.7)$$

From (2.4) follows the orthogonality relation

$$\text{ord}G^{-1}\sum_{C\subset G}\text{ord}C\cdot\chi^a(C)^*\chi^b(C) = \delta_{ab}, \qquad (2.8)$$

where C are the classes of G and ordC their order, i.e. the number of elements in C. A further orthogonality relation is:

$$\text{ord}G^{-1}\sum_a \chi^a(C)^*\chi^a(C') = \text{ord}C^{-1}\delta_{CC'} \qquad (2.9)$$

The criterion

$$n(X,a) = \text{ord}G^{-1}\sum_C \text{ord}C\cdot\chi^a(C)^*\cdot\sigma^X(C) \qquad (2.10)$$

gives the multiplicity in the decomposition, i.e. the direct sum

$$\sigma^X = \sum_a n(X,a)\cdot a \qquad (2.11)$$

The relation

$$\text{ord}G^{-1}\sum_C \text{ord}C\cdot\chi^a(C)\chi^b(C)\chi^c(C) = n(abc) \qquad (2.12)$$

likewise gives the multiplicity in the decompositions of the direct products:

$$a\times b = \sum_c n(abc)c^+, \quad a\times c = \sum_b n(abc)b^+, \text{ and } b\times c = \sum_a n(abc)a^+ \qquad (2.13)$$

But n(abc) also determines the multiplicity of the identical representation in the triple product $a\times b\times c$. If $n(abc) \geqslant 1$ (abc) is called a triad. In order to discriminate triads from other triples of representations, one defines the symbol:

$$\delta(abc) = \begin{cases} 1 & \text{if } n(abc) \geqslant 1 \\ 0 & \text{if } n(abc) = 0 \end{cases} \qquad (2.14)$$

In the case of $n(abc) \geqslant 2$, we need a multiplicity index in the decompositions (2.13), τ let us say, and shall call (abcτ) a triad too. Because of (2.8) we have for all groups and all irreducible representations a: $n(aa^+1) = 1$.

Concerning the equivalence of a representation a to a^+ or to a real representation a_r, there are three cases:

$$\text{a) } a\sim a^+\sim a_r, \qquad \text{b) } a \not\sim a^+, \qquad \text{c) } a\sim a^+ \not\sim a_r$$

These cases are distinguished by the criterion:

$$\sum_{g\in G}\chi^a(g^2) = \begin{cases} 1 & \text{in case a} \\ 0 & \text{in case b} \\ -1 & \text{in case c} \end{cases} \qquad (2.15)$$

In the cases a) and c), the characters of the representations are real.

In the tables of Koster e.a. [21], the cases are specified for each re-
presentation.

Finally, all point groups are simple phase groups, which satisfy:

$$\sum_{g\epsilon G}\chi^a(g^3) = \sum_{g\epsilon G}\chi^a(g)^3 \qquad (2.16)$$

This means that the identical representation may be contained only in
the totally symmetric or the totally anti-symmetric part of the direct
triple product $a \times a \times a$. The significance of this property will show up
in section 2.4.

2.3. Bases

The bases carrying the representation a are denoted by am (and a dis-
criminating multiplicity index α if necessary). If the basis is realized
by Hilbert space vectors, we use Diracs bra-ket notation through out:

$$U(g)|\ldots am\rangle = \sum_n D^a_{nm}(g)\cdot|\ldots an\rangle \qquad (2.17)$$

In the case of finite-dimensional vector spaces, except the tree-dimen-
sional configuration space, we use $|\ldots am)$ in the same sense.

The basis contragredient to $|am\rangle$ is denoted by $|a^+m\rangle$ having the same
transformation properties as the bras:

$$\langle\vec{r}|am\rangle = \langle am|\vec{r}\rangle^* = \langle a^+m|\vec{r}\rangle \quad \text{or} \quad (F|am) = (am|F)^* = (a^+m|F)$$

Since a and a^+ may be inequivalent, we can not relate am and a^+m in
general. Moreover, such a relation is of marginal interest, because the
final invariant expressions do not contain special bases anymore. But
the basis a^{++}m has the same transformational property as am and there-
fore is proportional to the latter. A detailed consideration leads to

$$a^{++}m = \{a\}\cdot am \qquad (2.18)$$

with a phase factor $\{a\} = 1$ for vector and $\{a\} = -1$ for spinor represen-
tations [22]. The use of braces for this phase factor is justified by
the relations (2.31) and (2.39). The representations of case a) are all
vector representations, those of case c) all spinor representations.
The complex representations of case b) can belong to either type.

We have to take into account (2.18), if we relabel representations:

am $\rightarrow$ b$^+$m   implies   a$^+$m $\rightarrow$ b^{++}m = $\{b\}$ bm

and   a$^+$m $\rightarrow$ bm   implies   am $\rightarrow$ b^{+++}m = $\{b\}$ b$^+$m

For all point groups, the following quasi-ambivalence condition [19]
holds (cf. also eq.(12) of [20]):

$$\{a\}\{b\}\{c\} = 1 \text{ if (abc) is a triad, i.e. } n(abc) \geq 1 \qquad (2.19)$$

Since there is a strict correspondence of co- and contragredient
bases in all sums, we can adopt Einsteins convention: If the same in-

dex occurs twice, as a co- and a contragredient index, the the sum is
to be taken over the range of this index:

$$\sum(\cdots \overset{+}{\underset{m}{a}} \cdots)(\cdots \underset{m}{a} \cdots) = \sum_m(\cdots \overset{+}{\underset{m}{a}} \cdots)(\cdots \underset{m}{a} \cdots) \qquad (2.20)$$

2.4. 3jm symbols

The matrix

$$M^{abc}_{lmn,pqr} = \text{ord}G^{-1}\sum_{g \in G}D^a_{lp}(g)D^b_{mq}(g)D^c_{nr}(g) \qquad (2.21)$$

projects out the identical representation from the direct triple pro-
duct $a \times b \times c$. Because of the relation $M^2 = M$, the eigenvalues of M are
zero and one. The number of the eigenvectors belonging to 1 is given
by n(abc) according to (2.12). The components of these eigenvectors
(numbered by the multiplicity index σ) are the 3jm symbols of the group
G:

$$\text{ord}G^{-1}\sum_g D^a_{lp}(g)D^b_{mq}(g)D^c_{nr}(g)\cdot\binom{abc}{lmn}^\sigma = \binom{abc}{pqr}^\sigma \qquad (2.22)$$

For convenience the eigenvectors are chosen orthogonal:

$$\sum\binom{abc}{lmn}^{\sigma *}\cdot\binom{abc}{lmn}^\tau = \delta(\sigma,\tau) \qquad (2.23)$$

Since a matrix can be represented in terms of its eigenvectors and
-values, another definition of the 3jm symbols is

$$\text{ord}G^{-1}\sum_g D^a_{lp}(g)D^b_{mq}(g)D^c_{nr}(g) = \sum_\sigma\binom{abc}{lmn}^{\sigma *}\cdot\binom{abc}{pqr}^\sigma. \qquad (2.24)$$

The basic transformational property of the 3jm symbols is

$$\sum D^a_{lp}(g)D^b_{mq}(g)D^c_{nr}(g)\binom{abc}{lmn}^\sigma = \binom{abc}{pqr}^\sigma , \qquad (2.25)$$

from which other forms can be derived by (2.2). Because of the choice
(2.23), the orthogonality relations read:

$$\sum\binom{abc}{lmn}^{\sigma *}\binom{abd}{lmp}^\tau = \delta(c,d)\delta(\sigma,\tau)\delta(n,p)/\text{dim}c \qquad (2.26)$$

$$\sum_{\sigma cn}\text{dim}c\binom{abc}{lmn}^{\sigma *}\binom{abc}{pqn}^\sigma = \delta(l,p)\delta(n,q) \qquad (2.27)$$

In [18] Butler shows, that (2.19) allows the choice of the following
simple conjugation property:

$$\binom{abc}{lmn}^{\sigma *} = \binom{a^+b^+c^+}{l \ m \ n}^\sigma \qquad (2.28)$$

Because of the simple phase condition (2.16), all 3jm symbols can be
arranged according to the following symmetry rules. They are symmetric
with respect to cyclic permutations

$$\binom{abc}{lmn}^\sigma = \binom{bca}{mnl}^\sigma = \binom{cab}{nlm}^\sigma \qquad (2.29)$$

and need a phase factor $\{abc\sigma\} = \pm 1$ for odd permutations:

$$\left(\begin{smallmatrix}abc\\lmn\end{smallmatrix}\right)^\sigma = \{abc\sigma\}\left(\begin{smallmatrix}bac\\mln\end{smallmatrix}\right)^\sigma = \{abc\sigma\}\left(\begin{smallmatrix}acb\\lnm\end{smallmatrix}\right)^\sigma = \{abc\sigma\}\left(\begin{smallmatrix}cba\\nml\end{smallmatrix}\right)^\sigma \qquad (2.30)$$

In the case of three different representations a, b, c, the choice of these phase factors is free. The factors $\{aaa\sigma\}$ are fixed, the factos $\{aac\sigma\}$ fixed in part. For SR groups they can be split up into phases associated to the individual representations (cf.eq.(7) of [20]):

$$\{abc\} = (-1)^a \cdot (-1)^b \cdot (-1)^c$$

The phase factors of (2.18) are special cases:

$$\{a\} = \{aa^+1\} \qquad (2.31)$$

From (2.28), (2.18) and (2.19) we get the derived conjugation property:

$$\left(\begin{smallmatrix}abc^+\\lmn\end{smallmatrix}\right)^{\sigma*} = \{c\}\left(\begin{smallmatrix}a^+b^+c\\l\ m\ n\end{smallmatrix}\right)^\sigma = \{c\}\{b\}\left(\begin{smallmatrix}a^+b^+c\\l\ m\ n\end{smallmatrix}\right)^\sigma \qquad (2.32)$$

If the triad contains the identical representation 1, we have the special case:

$$\left(\begin{smallmatrix}a1c\\k1l\end{smallmatrix}\right)^\varepsilon = \delta(\varepsilon,1)\delta(a,c^+)\delta(k,l)/\sqrt{dima} \qquad (2.33)$$

In terms of the 3jm symbols, the coupling of kets is given by

$$|(ab)\sigma cp\rangle = \{c\}\sqrt{dimc}\sum\left(\begin{smallmatrix}a^+b^+c\\m\ n\ p\end{smallmatrix}\right)^\sigma \cdot |am\rangle \cdot |bn\rangle \qquad (2.34)$$

The Clebsch-Gordan coefficients in Butler's "sensible" choice [18] therefore are :

$$\langle am,bn|(ab)\sigma cp\rangle_s = \{c\}\sqrt{dimc}\left(\begin{smallmatrix}a^+b^+c\\m\ n\ p\end{smallmatrix}\right)^\sigma$$

But there may be introduced an arbitrary phase factor K(abcσ):

$$\langle am,bn|(ab)\sigma cp\rangle = K(abc\sigma) \cdot \langle am,bn|(ab)\sigma cp\rangle_s.$$

We therefore shall use only the explicit formula (2.34).

2.5. 6j symbols

The 6j symbols are the invariants defined by:

$$\left\{\begin{smallmatrix}abc\\def\end{smallmatrix}\right\}_{\alpha\beta\gamma\delta} = \sum\left(\begin{smallmatrix}ae^+f\\il\ m\end{smallmatrix}\right)^\alpha \cdot \left(\begin{smallmatrix}dbf^+\\njm\end{smallmatrix}\right)^\beta \cdot \left(\begin{smallmatrix}d^+ec\\n\ lk\end{smallmatrix}\right)^\gamma \cdot \left(\begin{smallmatrix}a^+b^+c^+\\i\ j\ k\end{smallmatrix}\right)^\delta \qquad (2.35)$$

Their symmetries follow from (2.29/30):

$$\left\{\begin{smallmatrix}abc\\def\end{smallmatrix}\right\}_{\alpha\beta\gamma\delta} = \left\{\begin{smallmatrix}cab\\fde\end{smallmatrix}\right\}_{\gamma\alpha\beta\delta} = \left\{\begin{smallmatrix}bca\\efd\end{smallmatrix}\right\}_{\beta\gamma\alpha\delta} , \qquad (2.36)$$

$$\left\{\begin{smallmatrix}abc\\def\end{smallmatrix}\right\}_{\alpha\beta\gamma\delta} = \{d\}\{e\}\{f\}\{afe^+\alpha\}\{df^+b\beta\}\{d^+ce\gamma\}\{abc\delta\}\left\{\begin{smallmatrix}a\ c\ b\\d^+f^+e\end{smallmatrix}\right\}_{\alpha\gamma\beta\delta} \qquad (2.37)$$

and its combinations with (2.36).

$$\left\{\begin{smallmatrix}abc\\def\end{smallmatrix}\right\}_{\alpha\beta\gamma\delta} = \left\{\begin{smallmatrix}a^+e\ f^+\\d^+b\ c^+\end{smallmatrix}\right\}_{\delta\gamma\beta\alpha} = \left\{\begin{smallmatrix}d^+b^+f\\a^+e^+c\end{smallmatrix}\right\}_{\gamma\delta\alpha\beta} = \left\{\begin{smallmatrix}d\ e^+c^+\\a\ b^+f\end{smallmatrix}\right\}_{\beta\alpha\delta\gamma} (2.38)$$

Because of (2.33) the 6j symbol containing the identical representation reduces to:

$$\left\{\begin{smallmatrix}abc\\de1\end{smallmatrix}\right\}_{11\gamma\delta} = \delta(\gamma,\delta)\delta(a,e)\delta(b^+,d)\{abc\delta\}/\sqrt{dima \cdot dimb} \qquad (2.39)$$

This formula justifies the choice of curly brackets for the phase factors in (2.30) and (2.18).

The essential relation of the 6j symbols is:

$$\sum \begin{pmatrix} ae^+f \\ il\ m \end{pmatrix}^\alpha \cdot \begin{pmatrix} dbf^+ \\ njm \end{pmatrix}^\beta \cdot \begin{pmatrix} d^+ec \\ n\ lk \end{pmatrix}^\gamma \cdot \begin{pmatrix} a^+b^+g^+ \\ i\ j\ p \end{pmatrix}^\delta = \delta(c,g)\delta(k,p)\,\text{dimc}^{-1} \cdot \left\{\begin{matrix} abc \\ def \end{matrix}\right\}_{\alpha\beta\gamma\delta} \qquad (2.40)$$

This implies the definition (2.35) as a special case.

From (2.40) further relations can be derived by the help of (2.26/27):

$$\sum \begin{pmatrix} ae^+f \\ il\ m \end{pmatrix}^\alpha \cdot \begin{pmatrix} dbf^+ \\ njm \end{pmatrix}^\beta \cdot \begin{pmatrix} d^+ec \\ n\ lk \end{pmatrix}^\gamma = \sum_\delta \left\{\begin{matrix} abc \\ def \end{matrix}\right\}_{\alpha\beta\gamma\delta} \begin{pmatrix} abc \\ ijk \end{pmatrix}^\delta \qquad (2.41)$$

and the recoupling equation:

$$\sum \begin{pmatrix} ae^+f \\ il\ m \end{pmatrix}^\alpha \cdot \begin{pmatrix} dbf^+ \\ njm \end{pmatrix}^\beta = \sum_{\gamma\delta c}\text{dimc} \left\{\begin{matrix} abc \\ def \end{matrix}\right\}_{\alpha\beta\gamma\delta} \begin{pmatrix} abc \\ ijk \end{pmatrix}^\delta \cdot \begin{pmatrix} d^+ec \\ n\ lk \end{pmatrix}^{\gamma*} \qquad (2.42)$$

For the elimination of the complex conjugation on the right, one has to take into account (2.32).

The relations containing several 6j symbols are as follows:

Orthogonality:

$$\sum_{\alpha\beta f}\text{dimf} \left\{\begin{matrix} abc \\ def \end{matrix}\right\}_{\alpha\beta\gamma\delta}^* \cdot \left\{\begin{matrix} abg \\ def \end{matrix}\right\}_{\alpha\beta\sigma\tau} = \delta(c,g)\delta(\gamma,\sigma)\delta(\delta,\tau)/\text{dimc} \qquad (2.43)$$

Racah s back-coupling rule:

$$\sum_{\varepsilon\eta g}\text{dimg} \{e\}\{dbf^+\beta\}\{abc\delta\}\{adg^+\eta\} \left\{\begin{matrix} bac \\ deg \end{matrix}\right\}_{\varepsilon\eta\gamma\delta} \cdot \left\{\begin{matrix} adg^+ \\ bef \end{matrix}\right\}_{\alpha\beta\varepsilon\eta} = \left\{\begin{matrix} abc \\ def \end{matrix}\right\}_{\alpha\beta\gamma\delta} \qquad (2.44)$$

Biedenharn-Elliott sum rule:

$$\sum_\gamma \{a_1 a_2 a_3 \gamma\} \left\{\begin{matrix} a_1 a_2 a_3 \\ b_1 b_2 b_3 \end{matrix}\right\}_{\alpha_1\alpha_2\alpha_3\gamma} \left\{\begin{matrix} a_3 a_2 a_1 \\ c_3 c_2 c_1 \end{matrix}\right\}_{\beta_3\beta_2\beta_1\gamma} = \sum_{a\alpha\beta\gamma} \{a\} \text{dima}$$

$$\cdot \{ab_1 c_1 \alpha\}\{ab_2 c_2 \beta\}\{ab_3 c_3 \gamma\} \left\{\begin{matrix} c_2 b_2 a \\ b_1 c_1 a_3^+ \end{matrix}\right\}_{\beta_3\alpha_3\alpha\beta} \left\{\begin{matrix} c_1 b_1 a \\ b_3 b_3 a_2^+ \end{matrix}\right\}_{\beta_2\alpha_2\gamma\alpha} \left\{\begin{matrix} c_3 b_3 a \\ b_2 c_2 a_1^+ \end{matrix}\right\}_{\beta_1\alpha_1\beta\gamma} \qquad (2.45)$$

Special cases of these relations are the sum rules over one 6j symbol:

$$\sum_{\gamma c}\text{dimc} \left\{\begin{matrix} abc \\ dbf \end{matrix}\right\}_{\alpha\beta\gamma\gamma} = \delta(\alpha,\beta)\delta(ab^+f\alpha) \qquad (2.46)$$

$$\sum_{\gamma c}\{abc\gamma\}\text{dimc} \left\{\begin{matrix} abc \\ baf \end{matrix}\right\}_{\alpha\beta\gamma\gamma} = \delta(f,1)\delta(\alpha,1)\delta(\beta,1)\sqrt{\text{dima}\cdot\text{dimb}} \qquad (2.47)$$

2.6. The 9j symbols

We now collect the properties of the 9j symbols. They are defined by

$$\left\{\begin{matrix} a & b & c \\ d & e & f \\ g & h & i \end{matrix}\right\}_{\begin{matrix} \alpha \\ \beta \\ \gamma \\ \delta\ \varepsilon\ \eta \end{matrix}} = \sum \begin{pmatrix} a & b & c \\ m_a m_b m_c \end{pmatrix}^{\alpha*} \begin{pmatrix} d & e & f \\ m_d m_e m_f \end{pmatrix}^{\beta*} \begin{pmatrix} g & h & i \\ m_g m_h m_i \end{pmatrix}^{\gamma*} \begin{pmatrix} a & d & g \\ m_a m_d m_g \end{pmatrix}^\delta \begin{pmatrix} b & e & h \\ m_b m_e m_h \end{pmatrix}^\varepsilon \begin{pmatrix} c & f & i \\ m_c m_f m_i \end{pmatrix}^\eta \qquad (2.48)$$

and are invariant to even permutations of rows and columns. The multiplicity indices follow their triads in an obvious way:

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta} = \begin{Bmatrix} b & c & a \\ e & f & d \\ h & i & g \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\epsilon\ \eta\ \delta} = \begin{Bmatrix} d & e & f \\ g & h & i \\ a & b & c \end{Bmatrix}\begin{matrix}\beta\\\gamma\\\alpha\end{matrix}_{\delta\ \epsilon\ \eta} \qquad \text{etc.} \qquad (2.49)$$

In the case of odd permutations of rows or columns, again, the phase factors appear:

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta} = \{abc\alpha\}\{def\beta\}\{ghi\gamma\}\begin{Bmatrix} a & c & b \\ d & f & e \\ g & i & h \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \eta\ \epsilon} = \{adg\delta\}\{beh\epsilon\}\{cfi\eta\}\begin{Bmatrix} a & b & c \\ g & h & i \\ d & e & f \end{Bmatrix}\begin{matrix}\alpha\\\gamma\\\beta\end{matrix}_{\delta\ \epsilon\ \eta} \quad (2.50)$$

The conjugation is related to the reflection about the main diagonal:

$$\begin{Bmatrix} a^+ & b^+ & c^+ \\ d^+ & e^+ & f^+ \\ g^+ & h^+ & i^+ \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta} = \begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta}^{\ *} = \begin{Bmatrix} a & d & g \\ b & e & h \\ c & f & i \end{Bmatrix}\begin{matrix}\delta\\\epsilon\\\eta\end{matrix}_{\alpha\ \beta\ \gamma} \qquad (2.51)$$

As all nj symbols, the 9j symbols containing the identical representation reduce to zero or a simpler symbol:

$$\begin{Bmatrix} a & b & 1 \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta} = \delta(\alpha,1)\delta(\eta,1)\delta(a^+,b)\delta(f^+,i)\begin{Bmatrix} a & a^+1 & 1 \\ d & e & f \\ g & h & f^+ \end{Bmatrix}\begin{matrix}1\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ 1} \qquad (2.52)$$

with the special case:

$$\begin{Bmatrix} a & a^+1 & 1 \\ d & e & f \\ g & h & f^+ \end{Bmatrix}\begin{matrix}1\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ 1} = (1/\sqrt{\text{dima}\cdot\text{dimf}})\{h\}\{a^+hee\}\{hf^+g\gamma\}\begin{Bmatrix} d & e & f \\ h & g^+ & a \end{Bmatrix}_{\delta\epsilon\gamma\beta} \qquad (2.53)$$

There is an analogue of eq.(2.40) for the 9j symbol, from which we can derive the analogues of (2.41 and 42). The latter is the useful rule of de-Shalit:

$$\sum \begin{pmatrix} d & e & f \\ m_d & m_e & m_f \end{pmatrix}^{\beta\ *}\begin{pmatrix} g & h & i \\ m_g & m_h & m_i \end{pmatrix}^{\gamma\ *}\begin{pmatrix} a & d & g \\ m_a & m_d & m_g \end{pmatrix}^{\delta}\begin{pmatrix} b & e & h \\ m_b & m_e & m_h \end{pmatrix}^{\epsilon}$$

$$= \sum_{\alpha\eta c}\text{dimc}\cdot\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta}\cdot\begin{pmatrix} a & b & c \\ m_a & m_b & m_c \end{pmatrix}^{\alpha}\begin{pmatrix} c & f & i \\ m_c & m_f & m_i \end{pmatrix}^{\eta\ *} \qquad (2.54)$$

The orthogonality relation of the 9j symbols reads:

$$\sum_{cf}\sum_{\alpha\beta\eta}\text{dimc}\cdot\text{dimf}\cdot\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta}\cdot\begin{Bmatrix} a & b & c \\ d & e & f \\ g' & h' & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma'\end{matrix}_{\delta'\ \epsilon'\ \eta}^{\ *}$$

$$= \delta(h,h')\delta(g,g')\delta(\delta,\delta')\delta(\epsilon,\epsilon')\delta(\gamma,\gamma')/\text{dimg}\cdot\text{dimh} \qquad (2.55)$$

Instead of (2.48), the 9j symbol can be defined in terms of 6j symbols:

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}_{\delta\ \epsilon\ \eta} = \sum_{\sigma\tau\varphi k}\{k\}\text{dimk}\begin{Bmatrix} a & b & c \\ h & k & e \end{Bmatrix}_{\sigma\epsilon\varphi\alpha}\begin{Bmatrix} d & e & f \\ k & g^+ & a \end{Bmatrix}_{\delta\sigma\tau\beta}\begin{Bmatrix} g & h & i \\ c^+ & f & k \end{Bmatrix}_{\tau\varphi\eta\gamma} \qquad (2.56)$$

Using the orthogonality relation of the 6j symbols, one derives from (2.56) the following sum rule:

$$\sum_{c\alpha\eta}\text{dimc}\cdot\begin{Bmatrix}a & b & c\\d & e & f\\g & h & i\\\delta & \epsilon & \eta\end{Bmatrix}\begin{matrix}\alpha\\\beta\\\gamma\end{matrix}\cdot\begin{Bmatrix}a & b & c\\f^+ i & k\end{Bmatrix}_{\mu\pi\eta\alpha} = \{k\}\sum_{\sigma}\begin{Bmatrix}d & e & f\\b & k & h^+\end{Bmatrix}_{\sigma\epsilon\pi\beta}\cdot\begin{Bmatrix}g & h & i\\k & a^+ d\end{Bmatrix}_{\delta\sigma\mu\gamma} \quad (2.57)$$

2.7. Tensor operators

By definition, a tensor operator is a set of operators having the transformation property:

$$U(g)T_q^a U(g)^+ = \sum_p D_{pq}^a(g)T_p^a \qquad (2.58)$$

The matrix elements of these sets of operators can be factorized according to the Wigner-Eckart theorem (WET):

$$\langle\eta f p|T_q^a|\delta d r\rangle = \sum_\epsilon \langle\eta f\|T^a\|\delta d\rangle_\epsilon\cdot\begin{pmatrix}f^+ & a & d\\p & q & r\end{pmatrix}\epsilon \qquad (2.59)$$

From (2.30 and 32) follows the relation of the reduced matrix elements of T^a and of their adjoint operators $(T^a)^+$:

$$\langle\delta d\|(T^a)^+\|\eta f\rangle_\epsilon = \{f\}\{adf^+\epsilon\}\langle\eta f\|T^a\|\delta d\rangle_\epsilon \qquad (2.60)$$

In consequence of (2.34), the coupling of two operators is given by

$$W_m^{ac}(ab) = \{c\}\sqrt{\text{dimc}}\cdot\sum_{kl}\begin{pmatrix}a^+ & b^+ & c\\k & l & m\end{pmatrix}^\alpha\cdot U_k^a\cdot V_l^b \qquad (2.61)$$

The reduced matrix elements of the set W can be expressed by those of its constituents:

$$\langle\delta d\|W^{ac}(ab)\|\epsilon e\rangle_\beta$$
$$= \{d\}\sqrt{\text{dimc}}\cdot\sum_{\eta f\sigma\tau}\{ad^+f\sigma\}\{ebf^+\tau\}\begin{Bmatrix}a & b & c^+\\e & d & f\end{Bmatrix}_{\sigma\tau\beta\alpha}\langle\delta d\|U^a\|\eta f\rangle_\sigma\langle\eta f\|V^b\|\epsilon e\rangle_\tau \quad (2.62)$$

If the space of the kets is a direct product space, and if the operators U^a and V^b act on either factor space only, the reduced matrix elements of $W^{ac}(ab)$ can be split up into the reduced matrix elements of U^a and V^b with respect to their factor spaces. Because of (2.34), the states of $H_1\otimes H_2$ are

$$|(d_1 d_2)\delta d r\rangle^{1\otimes 2}=\{d\}\sqrt{\text{dimd}}\cdot\sum\begin{pmatrix}d_1 & d_2 & d\\r_1 & r_2 & r\end{pmatrix}^\delta\cdot|d_1 r_1\rangle^1\cdot|d_2 r_2\rangle^2, \qquad (2.63)$$

and the factorization is given by:

$$\langle(d_1 d_2)\delta d\|W^{ac}(ab)\|(e_1 e_2)\epsilon e\rangle_\beta^{1\otimes 2} \qquad (2.64)$$
$$= \sqrt{\text{dimd}\cdot\text{dimc}\cdot\text{dime}}\cdot\sum_{\sigma\tau}\begin{Bmatrix}d_1 & d_2 & d^+\\a^+ & b^+ & c\\e_1^+ & e_2^+ & e\\\sigma & \tau & \beta\end{Bmatrix}\begin{matrix}\delta\\\alpha\\\epsilon\end{matrix}\cdot\langle d_1\|U^a\|e_1\rangle_\sigma^1\cdot\langle d_2\|V^b\|e_2\rangle_\tau^2$$

2.8. Chains of groups

We now collect the interrelations of functions, coefficients, and reduced matrix elements classified according to a group G' and its subgroup G. The most important case is that of the rotation group and a point group.

In general, a representation a' of G' decomposes into a direct sum of representations a of G,

$$a'(G') = \sum_a n(a',a)a(G) \ , \tag{2.65}$$

according to the multiplicity rule:

$$n(a',a) = \sum_{C \subset G} \text{ord}C \cdot \chi^a(C)^* \cdot \chi^{a'}(C) \tag{2.66}$$

The basis functions of $a'(G')$ are adapted to G by the unitary transformation:

$$|a'\alpha a p_a\rangle = \sum \langle a'p'_a | a'\alpha a p_a\rangle \cdot |a'p'_a\rangle \tag{2.67}$$

$$|a'p'_a\rangle = \sum_{\alpha a} \langle a'\alpha a p_a | a'p'_a\rangle \cdot |a'\alpha a p_a\rangle \tag{2.68}$$

A definition of the adaption coefficients, which is independent of the special basis, can be given in analogy to (2.22):

$$\text{ord}G^{-1}\sum_{g \in G} D^{a'}_{mn}(g)D^a_{pq}(g)^* = \text{dima}^{-1}\sum_\alpha \langle a'm | a'\alpha a p\rangle \langle a'\alpha a q | a'n\rangle \tag{2.69}$$

The factor dima^{-1} comes from a different normalization:

$$\sum \langle a'\alpha a p | a'm\rangle \langle a'm | a'\beta b q\rangle = \delta(\alpha,\beta)\delta(a,b)\delta(p,q) \tag{2.70}$$

$$\sum_{\alpha a} \langle a'm | a'\alpha a p\rangle \langle a'\alpha a p | a'n\rangle = \delta(m,n) \tag{2.71}$$

All terms classified according to the representations and bases of G' can be adapted to the subgroup G by this transformation. A case of special interest is that of the 3jm symbols:

$$\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \\ p & q & r \end{pmatrix}\varepsilon = \sum \begin{pmatrix} a' & b' & c' \\ l & m & n \end{pmatrix}^\varepsilon \langle a'l | a'\alpha a p\rangle \langle b'm | b'\beta b q\rangle \langle c'n | c'\gamma c r\rangle \tag{2.72}$$

Applying the WET with respect to G to the left hand side, we get:

$$\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \\ p & q & r \end{pmatrix}\varepsilon = \sum_\eta \text{Is}\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{pmatrix}^\varepsilon_\eta \cdot \begin{pmatrix} a & b & c \\ p & q & r \end{pmatrix}^\eta \tag{2.73}$$

This is nothing but Racah's factorization lemma, which implicitely defines the isoscalar factors (or short isoscalars):

$$\text{Is}\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{pmatrix}^\varepsilon_\eta = \sum \begin{pmatrix} a'b'c' \\ lmn \end{pmatrix}^\varepsilon \langle a'l | a'\alpha a p\rangle \langle b'm | b'\beta b q\rangle \langle c'n | c'\gamma c r\rangle \begin{pmatrix} abc \\ pqr \end{pmatrix}^{\eta*} \tag{2.74}$$

The isoscalars are invariant to even permutations. Odd permutations yield the phase factors:

$$\text{Is}\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{pmatrix}^\varepsilon_\eta = \{a'b'c'\varepsilon\}\{abc\eta\} \cdot \text{Is}\begin{pmatrix} a' & c' & b' \\ \alpha & \gamma & \beta \\ a & c & b \end{pmatrix}^\varepsilon_\eta \tag{2.75}$$

The complex conjugation property is:

$$\text{Is}\begin{pmatrix} a'^+ & b'^+ & c'^+ \\ \alpha^+ & \beta^+ & \gamma^+ \\ a^+ & b^+ & c^+ \end{pmatrix}\varepsilon = \text{Is}\begin{pmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{pmatrix}\varepsilon^* \tag{2.76}$$

The orthogonality relations of the isoscalar factors are:

$$\sum_{\alpha a \beta b \eta} \text{Is} \begin{vmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{vmatrix}_\eta^{\delta^*} \cdot \text{Is} \begin{vmatrix} a' & b' & d' \\ \alpha & \beta & \sigma \\ a & b & c \end{vmatrix}_\eta^{\varepsilon} = \delta(c',d')\delta(\delta,\varepsilon)\delta(\gamma,\sigma)\text{dimc}/\text{dimc}' \qquad (2.77)$$

$$\sum_{\delta\gamma c'} \text{dimc}' \cdot \text{Is} \begin{vmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{vmatrix}_\varepsilon^{\delta^*} \cdot \text{Is} \begin{vmatrix} a' & b' & d' \\ \sigma & \tau & \gamma \\ s & t & c \end{vmatrix}_\eta^{\delta} = \delta(a,s)\delta(b,t)\delta(\alpha,\sigma)\delta(\beta,\tau)\delta(\varepsilon,\eta)\cdot\text{dimc} \qquad (2.78)$$

The isoscalar factor containing the identical representation of G' is very simple:

$$\text{Is} \begin{vmatrix} a' & b' & 1' \\ \alpha & \beta & \\ a & b & 1 \end{vmatrix}_\eta^{\varepsilon} = \delta(a'^+,b')\delta(\alpha,\beta)\delta(a^+,b)\delta(\varepsilon,1)\delta(\eta,1)\sqrt{\text{dima}/\text{dima}'} \qquad (2.79)$$

Further, there is the following sum rule:

$$\sum_{\alpha a}\sqrt{\text{dima}}\cdot\text{Is} \begin{vmatrix} a' & a'^+ & c \\ \alpha & \alpha_+ & \gamma \\ a & a_+ & 1 \end{vmatrix}^{\varepsilon} = \delta(c',1)\delta(\gamma,1)\delta(\varepsilon,1)\sqrt{\text{dima}'} \qquad (2.80)$$

If we invert (2.73) more carefully by using (2.26), we get a more general relation than (2.74):

$$\sum (\begin{smallmatrix} abc \\ lmn \end{smallmatrix})^\varepsilon \langle\acute{a}l|\acute{a}\alpha a\underline{p}\rangle \langle\acute{b}n|\acute{b}\beta b\underline{q}\rangle \langle\acute{c}n|\acute{c}\gamma c\underline{r}\rangle (\begin{smallmatrix} abd \\ pqs \end{smallmatrix})^{\eta^*} \qquad (2.81)$$
$$= \delta(c,d)\delta(r,s)\cdot\text{dimc}^{-1}\cdot\text{Is} \begin{vmatrix} a' & b' & c' \\ \alpha & \beta & \gamma \\ a & b & c \end{vmatrix}_\eta^{\varepsilon}$$

From the WET and (2.73), we get the relation between the reduced matrix elements with respect to G' and those with respect to its subgroup G:

$$\langle\acute{a}\alpha a\|T^{\acute{b}\beta b}\|\acute{c}\gamma c\rangle_\eta = \sum_\varepsilon \text{Is} \begin{vmatrix} a'^+b' & c' \\ \alpha_+\beta & \gamma \\ a^+b & c \end{vmatrix}_\eta^{\varepsilon} \cdot \langle\acute{a}\|T^{\acute{b}}\|\acute{c}\rangle_\varepsilon , \qquad (2.82)$$

where the operators, of course, are adapted by:

$$T_p^{\acute{b}\beta b} = \sum_m \langle\acute{b}m|\acute{b}\beta b\underline{p}\rangle \cdot T_m^{\acute{b}} \qquad (2.83)$$

The combination of the WET and group chains has been discussed in [18, 23]. The idea of the isoscalar factor, stimulating the definition of the polyhedral isoscalar in section 6, first came to the authors knowledge by an earlier paper [24], where the isoscalars are termed V-coefficients of the rotation-point group.

2.9. Product groups and double tensors

In the opening of section 2.1., we allowed the symmetry group to be a product group. Since the irreducible representations of a product group are the direct products of the irreducible representations of the single groups, we have a general doubling of the quantum numbers [5], section 3.2:

$$D_{pp',qq'}^{aa'}(gg') = D_{pq}^a(g)\cdot D_{p'q'}^{a'}(g') \qquad (2.84)$$

with $g\in G$, $g'\in G'$, and $gg'\in G\times G'$. Consequently the same applies to the characters and the 3jm symbols:

$$\chi^{aa'}(gg') = \chi^{a}(g) \cdot \chi^{a'}(g') \quad , \tag{2.85}$$

$$\left(\begin{matrix} aa' & bb' & cc' \\ pp' & qq' & rr' \end{matrix}\right)\epsilon\epsilon' = \left(\begin{matrix} a & b & c \\ p & q & r \end{matrix}\right)\epsilon \cdot \left(\begin{matrix} a' & b' & c' \\ p' & q' & r' \end{matrix}\right)\epsilon' \quad , \tag{2.86}$$

and further to all nj symbols. As concernes the states and operators
the doubling applies, too, but in general not the factorization. The
operators with the transformation property

$$U(gg')T^{aa'}_{qq'}U(gg')^{+} = \sum_{pp'}D^{a}_{pq}(g)D^{a'}_{p'q'}(g')T^{aa'}_{pp'} \tag{2.87}$$

are termed double tensor operators. The WET in this case reads:

$$\langle \eta ffpp|T^{aa}_{qq}|\delta ddrr\rangle = \sum_{\epsilon\epsilon'}\langle \eta ff\|T^{aa'}\|\delta dd\rangle_{\epsilon\epsilon'}\left(\begin{matrix} f^{+} & a & d \\ p & q & r \end{matrix}\right)\epsilon\left(\begin{matrix} f'^{+} & a' & d' \\ p' & q' & r' \end{matrix}\right)\epsilon' \tag{2.88}$$

States and operators allowing a factorization are the (one-par-
ticle) spin orbitals and the summands of the spin-orbit coupling ope-
rator. On the contrary, the many-elecron states of the ΓS-coupling and
the occupation operators of spin orbitals (cf. section 19) can not be
factorized because of the antisymmetrization involved. Consequently
the coefficients of fractional parentage (cf. section 19) allow no
factorization, too.

The possible factorization is also important to the symmorphic
space groups, since they are direct products of the point and trans-
lation groups (cf. section 21).

2.10. The significance of reduced matrix elements

As mentioned in the introduction, the RMEs of one-centre one-parti-
cle matrix elements in essence are radial integrals. The same there-
fore applies to the semi-empirical parameters of the atomic spectro-
scopy and the ligand field theory even being defined without previous
knowlegde of group theory (cf. the introduction of [25]). In other
cases, the meaning of the RMEs is not so obvious and more indirect:

For compound operators we have the relations (2.62 and 64).

For many-particle states, the RMEs are traced back to the RMEs of
one- and two-particle states by the technique of fractional parent-
age [26, 27]. We come back to this subject in section 19 by a diffe-
rent approach.

The RMEs of the symmetry-adapted LCAO-functions have not been ana-
lysed, so far, and are the main issue of this treaty (cf. section 5
and in a more general context section 20).

3. Representations induced by polyhedral edges

This section closely follows [9, 11]. In the theory of molecules, the first step towards quantitative considerations of symmetry is the formation of symmetry-adapted (s.-a. in the following) linear combinations, especially molecular orbitals and symmetric coordinates. This is well known and done heuristically in simple cases or systematically by the projection operator technique. The insertion of such symmetrized molecular orbitals into molecular matrix-elements results in rather complex expressions [28]. We therefore prefer another approach by studying the symmetry-adaption of arbitrary "objects" defined with respect to the vertices and edges of the polyhedra (and later on with respect to the faces, too).

We consider molecules $A_m B_n C_p \ldots$ with a symmetry group G. This may be optionally a point group, a double point group, or the direct product of a point group and the spin group $SU(2)$.

The positions of equivalent atoms A, B etc., which constitute a symmetric polyhedron, are indicated by the vectors $\vec{A_i}$, $\vec{B_k}$ etc, where i and k give the numbering within the equivalent sets. The distance vectors $\vec{S_{ik}} = \vec{A_i} - \vec{A_k}$, $\vec{T_{ik}} = \vec{B_i} - \vec{B_k}$, $\vec{U_{ik}} = \vec{A_i} - \vec{B_k}$ etc. likewise form equivalent sets. In order to simplify the notation and to allow differences of the distance vectors again, we use beside the double indices a simple numbering $\vec{S_{ik}} \rightarrow \vec{S_m}$. The correspondence of $\vec{S_m}$ with $\vec{A_i}$ and $\vec{A_k}$ or of $\vec{U_r}$ with $\vec{A_i}$ and $\vec{B_k}$ can be expressed by a topological matrix $\tau\binom{ABU}{ikr}$, which disapears, if not $\vec{A_i} + \vec{B_k} + \vec{U_r} = 0$. The value in the other case could be chosen equal to one, but, because of the analogy with the 3jm symbols, it is more appropriate to choose $1/\sqrt{Z(ABU)}$, where $Z(ABU)$ is the number of all triangles equivalent to $\vec{A_i} + \vec{B_k} + \vec{U_r} = 0$. The analogy mentioned will be treated in section 6. We sum up the definition:

$$\tau\binom{ABU}{ikr} = \begin{cases} 1/\sqrt{Z(ABU)} & \text{for } \vec{A_i} + \vec{B_k} + \vec{U_r} = 0 \\ 0 & \text{for } \vec{A_i} + \vec{B_k} + \vec{U_r} \neq 0 \end{cases} \tag{3.1}$$

Now the correspondence $\vec{U_{ik}} \rightarrow \vec{U_r}$ can be expressed as follows:

$$\vec{A_i} - \vec{B_k} = \sum_{Um} \sqrt{Z(-ABU)} \cdot \tau\binom{-ABU}{ikm} \cdot \vec{U_m} \tag{3.2}$$

Later on we shall use correspondences of this type also for other numbered objects in the polyhedral framework.

The simple numbering allows to treat the equivalent sets S on an equal footing with the sets A of atomic positions. We thus can write in a unified manner the (in general reducible) representation σ^S of the symmetry group G, induced by the equivalent set S:

$$g\vec{S_i} = \sum_k \sigma^S_{ki}(g) \vec{S_k} \tag{3.3}$$

According to the character formula (2.10) this representation σ^S car

be decomposed into a direct sum (2.11). For finite and compact groups, this decomposition is guaranteed by Maschke's theorem [29]. Moreover, it is proven that the decomposition is achieved by a unitary transformation [30]:

$$\sum_{ik}(S\alpha ar|\vec{S_i})\sigma_{ik}^{S}(g)(\vec{S_k}|S\beta bs) = \delta(a,b)\delta(\alpha,\beta)D_{rs}^{a}(g) \qquad (3.4)$$

or
$$\sum_{k}\sigma_{ik}^{S}(g)(\vec{S_k}|S\alpha as) = \sum_{r}D_{rs}^{a}(g)(\vec{S_i}|S\alpha ar) \qquad (3.5)$$

with
$$\sum_{i}(S\alpha ar|\vec{S_i})(\vec{S_i}|S\beta bs) = \delta(a,b)\delta(\alpha,\beta)\delta(r,s) \qquad (3.6)$$

and
$$\sum_{\alpha ar}(\vec{S_i}|S\alpha ar)(S\alpha ar|\vec{S_k}) = \delta(i,k) , \qquad (3.7)$$

where α and β are the multiplicity indices. On analogy of (2.69), the transformation coefficients also can be defined by:

$$\text{ordG}^{-1}\sum_{g\epsilon G}\sigma_{ik}^{S}(g)D_{rs}^{a}(g)^{*} = \text{dima}^{-1}\sum_{\alpha}(\vec{S_i}|S\alpha ar)(S\alpha as|\vec{S_k}) \qquad (3.8)$$

This relation is derived from (3.5) by (3.7) and (2.4). The notation of the transformation matrix is chosen following Dirac s bra-ket formalism. The analogy is twofold. At first $(\vec{S_i}|S\alpha ap)$ is analogous to $\langle am|a\alpha ap\rangle$. In the same way as we adapt functions to the group G by (2.67), we can adapt s-functions, $s(\vec{r})=\langle\vec{r}|s\rangle$, centered at the atomic positions $\vec{A_i}$ by:

$$\langle\vec{r}|sA\alpha ap\rangle = \sum_{i}\langle\vec{r}-\vec{A_i}|s\rangle(\vec{A_i}|A\alpha ap) \qquad (3.9)$$

This is the formation of s.-a. LCAO-MOs by linear combination. Quoting Cotton [31],we therefore call the coefficients $(\vec{A_i}|A\alpha ap)$ SALC coefficients (i.e. coefficients of symmetry-adapted linear combinations). More details concerning this aspect are elaborated in section 5. We can invert (3.9) by (3.7):

$$\langle\vec{r}-\vec{A_i}|s\rangle = \sum_{\alpha ap}\langle\vec{r}|sA\alpha ap\rangle(A\alpha ap|\vec{A_i}) \qquad (3.10)$$

which, of course, is analogous to (2.68).

But there is another interpretation of (3.10). $\langle\vec{r}-\vec{A_i}|s\rangle = s(\vec{r}-\vec{A_i})$ may be regarded as a function of the discrete variable A_i. (3.10) then gives an expansion of these functions into $(A\alpha ap|\vec{A_i})$ with expansion coefficients $\langle\vec{r}|sA\alpha ap\rangle$ according to (3.9). Thus the SALC coefficients turn out to be s.-a. functions of the positions $\vec{A_i}$. From this point of view they are analogous to s.-a. Hilbbert space functions $r!\varphi ap$. Because this second analogy is very important and fruitful, we work it out in six parallel steps:

1a) Consider the Euclidean space R_3.

1b) Consider the set $A = \{\vec{A_1}, \vec{A_2},...\vec{A_{Z(A)}}\}$, where $Z(A)$ is the number of equivalent positions in A.

2a) Define the functions $\varphi(\vec{r}) = \langle \vec{r} | \varphi \rangle$ on R_3, i.e. $\vec{r} \in R_3$.

2b) Define the functions $G(\vec{A_i}) = (\vec{A_i} | G)$ on A, i.e. $\vec{A_i} \in A$.[+)]

3a) The kets $|\varphi\rangle$ subtend a Hilbert space $H(R_3)$, $\langle \vec{r} | \varphi \rangle$ being the space representation of $|\varphi\rangle$.

3b) The kets $|G\rangle$ subtend a finite, unitary space $U(A)$, $(\vec{A_i} | G)$ being the space representation of $|G\rangle$.

4a) In $H(R_3)$ there are s.-a. functions $\langle \vec{r} | \varphi a p \rangle$ transforming according to (2.17).

4b) In $U(A)$ there are s.-a. functions $(\vec{A_i} | A\alpha a p)$ transforming according to

$$(g^{-1}\vec{A_i} | A\alpha a p) = \sum D^a_{qp}(g)(\vec{A_i} | A\alpha a q) \tag{3.11}$$

Because of (3.3) the transformation property (3.11) is identical with (3.5). This means, that the s.-a. functions in $U(A)$ are just the SALC coefficients, if the appropriate normalization is chosen.

5a) The s.-a. functions $\langle \vec{r} | \varphi a p \rangle$ are orthogonal and complete, if

$$\sum_{\varphi a p} \langle \vec{r} | \varphi a p \rangle \langle \varphi a p | \vec{r}' \rangle = \delta(\vec{r}, \vec{r}') \tag{3.12}$$

$$\int \langle \varphi a p | \vec{r} \rangle \langle \vec{r} | \varphi' a' p' \rangle d^3 r = \delta(a,a')\delta(\varphi,\varphi')\delta(p,p') \tag{3.13}$$

5b) The s.-a. functions $(\vec{A_i} | A\alpha a p)$ are already orthogonal and complete because of (3.6/7).

6a) Because of (3.12/13), we can expand every function $\langle \vec{r} | \eta \rangle \in H(R_3)$ according to

$$\langle \vec{r} | \eta \rangle = \sum_{\varphi a p} \langle \varphi a p | \eta \rangle \langle \vec{r} | \varphi a p \rangle \tag{3.14}$$

with the expansion coefficients:

$$\langle \varphi a p | \eta \rangle = \int \langle \varphi a p | \vec{r} \rangle \langle \vec{r} | \eta \rangle d^3 r \tag{3.15}$$

6b) Because of (3.6/7), we can expand every function $(\vec{A_i} | G) \in U(A)$ according to

$$(\vec{A_i} | G) = \sum_{\alpha a p} (A\alpha a p | G)(\vec{A_i} | A\alpha a p) \tag{3.16}$$

with the expansion coefficients:

$$(A\alpha a p | G) = \sum_i (A\alpha a p | \vec{A_i})(\vec{A_i} | G) . \tag{3.17}$$

This expansion theorem, which is based on (3.6/7) is the main result of our discussion. Eq. (3.10), which was our starting point, is now

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[+)]Here a note on our phraseology may be in order. In a puristic way of speaking, sin(x) is no function, but a value of the function sin. In the same sense $G(\vec{A_i})$ or $(\vec{A_i} | G)$ is no function (or vector in $U(A)$), but a value of the function (or a component of the vector) $|G\rangle$. But to simplify matters, we keep calling $(\vec{A_i} | G)$ a vector, sinx a function, and a_{ik} a matrix.

a special case of (3.16). The symmetry-adaption (3.9) is a special
case of (3.17). Therefore in general $(A\alpha ap|G)$ may be interpreted as
the s.-a. version of $(\vec{A_i}|G)$.

The functions $(\vec{A_i}|G) \in U(A)$ often result from the ordinary function
of $H(R_3)$ by inserting edge vectors, i.e. $\vec{r} = \vec{A_i}$. A case of special in-
terest are the spherical harmonics

$$\langle \vec{r}|lm \rangle = i^l Y_{lm}(\vec{r}/r) , \qquad (3.18)$$

where the phase is chosen in accordance to section 2.3, i.e. $\langle \vec{r}|l^+m \rangle = \langle lm|\vec{r} \rangle$, and the s.-a. spherical harmonics:

$$\langle \vec{r}|l\alpha ap \rangle = \sum \langle lm|l\alpha ap \rangle \langle \vec{r}|lm \rangle \qquad (3.19)$$

If we insert the argument $\vec{A_i}$ into these functions, (3.16/17) yield:

$$\langle \vec{A_i}|l\alpha ap \rangle = 0 \text{ for } n(A,a) = 0, \qquad (3.20)$$

otherwise;

$$\langle \vec{A_i}|l\alpha ap \rangle = \sum_{\beta=1}^{n(A,a)} (\vec{A_i}|A\beta ap) \cdot c(A\beta a, l\alpha) \qquad (3.21)$$

$$c(A\beta a, l\alpha) = \sum_i (A\beta ap|\vec{A_i}) \langle \vec{A_i}|l\alpha ap \rangle \text{ (no } \sum_p \text{ !)} \qquad (3.22)$$

At the first sight, this important result is somewhat surprising. As
functions over R_3 there are infinitely many, linearly independent sphe-
rical harmonics, but as functions over the set A the most of them are
linearly dependent. This results from the special directions enforced
upon the edge vectors by the symmetry. The expansion coefficients
(3.22) do not depend on the numbering of edges and the choice of coor-
dinate axes. They are a property of the polyhedral framework. The ex-
pansion (3.21) has been used in [32] to expand the spherical harmonics
of intergral formulae. A table of the coefficients for a tetrahedral
molecule is also given there (cf. also table 26).

If the representation a is contained only once in σ^A, (3.21) pro-
vides us with a simple tool to calculate the SALC coefficients. We
only have to insert $\vec{A_i}$ into a s.-a. spherical harmonic tabulated in
[21] and get a SALC coefficient up to a normalization factor. This me-
thod has first been used in [10]. If the multiplicity exceeds one, pro-
blems of linear independence and orthogonality arise and the coeffici-
ents are determined only up to a unitary transformation:

$$(\vec{A_i}|A\alpha ap) = \sum_\beta u_{\alpha\beta}^{Aa} \cdot (\vec{A_i}|A\beta ap) \qquad (3.23)$$

For each set A and each irreducible representation a, a new choice has
to be made. These problems are settled systematically in section 12,
where also a uniform choice of SALC coefficients will be proposed for
all edges of all molecules sharing one symmetry group. In the same
section the calculation of the expansion coefficients (3.22) is redu-

ced to a smaller class of coefficients.

Because of the one-to-one correspondence $\vec{A_i}$, $\vec{B_k} \to \vec{U_r}$ according to (3.2), every function $f(\vec{A_i},\vec{B_k})$ can be regarded as well as a function of the related $\vec{U_r}$:

$$f(\vec{A_i},\vec{B_k}) = \sum_{Um} \sqrt{Z(-\overline{ABU})}\tau({}^{-ABU}_{ikm})f(\vec{U_m}) = f(\vec{U_r}) \qquad (3.24)$$

If the funtions considered depend on the difference $\vec{A_i}-\vec{B_k}$ only, the special case $\vec{B_k}=\vec{A_i}$ makes no trouble. The edge vector $\vec{U_r}$ is simply equal to the zero vector. This natural point of view has been adopted in the papers [10, 12, 32]. But if the functions depend on $\vec{A_i}$ and $\vec{B_k}$ separately, we need a more sophisticated treatment of the case $\vec{B_k}=\vec{A_i}$. We have to discriminate the zero edge vectors $\vec{A_i}-\vec{A_i}=\vec{O_i^A}$ according to their position (i.e. with respect to set A and number i), since the functions $f(\vec{O_i^A})$ do depend on A and i.

This new interpretation is consistent with the following correspondence of edge vectors between atoms, i.e. $\vec{S_{ik}}=\vec{A_i}-\vec{B_k}$, and of vectors centred in the origin. These vectors are defined by:

$$\vec{S_{ik}}' = \mu_1\vec{A_i} + \mu_2\vec{B_k} \qquad (3.25)$$

An incommensurable choice of the coefficients μ_i guarantees the a one-to-one mapping, i.e. $\vec{S_{ik}}' \neq \vec{T_{lm}}'$ and $\vec{S_{ik}}' \neq \vec{S_{ki}}'$ especially. Because of this mapping $\vec{S_{ik}} \to \vec{S_{ik}}'$, all functions of $\vec{S_{ik}}$ can be regarded as functions of $\vec{S_{ik}}'$. Especially holds:

$$(\vec{S_{ik}}|S\alpha ap) = (\vec{S_{ik}}'|S'\alpha ap) \qquad (3.26)$$

In the case of zero edge vectors we have $\vec{O_i^A}=\mu_1\vec{A_i}+\mu_2\vec{A_i}=(\mu_1+\mu_2)\vec{A_i}$, which yields the reasonable correspondence $\vec{O_i^A} \to \vec{A_i}$. By (3.18), the symmetry-adaption with respect of arbitrary polyhedral edges is reduced to the symmetry-adaption with respect to vectors in the centre of symmetry. Correspondences of this type will prove to be useful also for objects related to more than two centres.

4. Bicentric matrices

4.1. Molecular integrals

The central theorem of the quantitative group theory is that of Wigner and Eckart. It applies to matrix elements of s.-a. functions and tensor operators refering to the same centre of symmetry. On the contrary, all calculations of molecules starting from localized orbitales at the atomic positions lead to polycentric matrix elements. The following theorem applies to bicentric matrix elements of tensor operators and includes the WET as a special case.

We proceed from an arbitrary set of s.-a. functions of species a:

$$\varphi_p^a(\vec{r}) = \langle \vec{r} | \varphi ap \rangle, \tag{4.1}$$

i.e. with the tranformational property according to (2.6/17):

$$\langle \vec{r} | U(g) | \varphi ap \rangle = \langle g^{-1}\vec{r} | \varphi ap \rangle = \sum D_{qp}^a(g) \langle \vec{r} | \varphi aq \rangle \tag{4.2}$$

By translation to the different atomic positions, we generate the orbitals:

$$\langle \vec{r} | Ai\varphi ap \rangle = \langle \vec{r} - \vec{A_i} | \varphi ap \rangle \tag{4.3}$$

As usual in quantum chemistry [33], the position is not indicated by a vector, but the set A and the number i are treated as additional quantum numbers. The special case of s-orbitals has already been mentioned in (3.9).

The tensor operators are defined by (2.58). In what follows, the operators refer to the centre of symmetry or are invariant under translations, as the operators of momentum and kinetic energy. The general case of shifted operators is treated separately in section 8. The main example of this case are the potential operators. But we stress that s.-a. sums, like $V = \sum_i f(|\vec{r} - \vec{A_i}|)$, are allowed for, because the entire sum refers to the centre of symmetry. The difference between these sums and the invariant operators does not matter in the present discussion, but will give rise to the distinction of proper and improper bicentric matrix elements later on.

After these preliminaries, we state the factorization theorem for the bicentric matrix elements:

$$\langle Ai\varphi_a am | T_n^c | Bk\varphi_b bp \rangle$$
$$= \sum_{d\delta\eta\epsilon\epsilon} \sum (A\varphi_a a \| T^c \| B\varphi_b b)_{S\epsilon e}^{d\delta\eta} \cdot \begin{pmatrix} a^+ b & d \\ m & p & q \end{pmatrix}^\delta \begin{pmatrix} d^+ c & e \\ q & n & r \end{pmatrix}^\eta \cdot (\vec{S}_{ik} | S\epsilon er) \tag{4.4}$$

with $\vec{S}_{ik} = \vec{A_i} - \vec{B_k}$. If we skip all discriminating multiplicity indices, the geometric structure contrasts better:

$$\langle Aiam | T_n^c | Bkbp \rangle = \sum_{de} (Aa \| T^c \| Bb)_{Se}^d \cdot \begin{pmatrix} a^+ b & d \\ m & p & q \end{pmatrix} \begin{pmatrix} d^+ c & e \\ q & n & r \end{pmatrix} \cdot (S_{ik} | Ser) \tag{4.5}$$

The invariants $(A\varphi_a a\| T^c \| B\varphi_b b)_{S\epsilon e}^{d\delta\eta}$ defined by (4.4) are independent of the numbering of atoms and the choice of axes. In general they depend on the lengths A, B, and S.

Taking into account (3.2),(4.4) can be given another form, which at the first sight looks more complicated. But it proves to be useful for the further calculations, because the topological matrix connecting $\vec{A_i}$, $\vec{B_k}$, and $\vec{S_r}$ leads to important, geometric results.

$$\langle Ai\varphi_a am | T_n^c | Bk\varphi_b bp \rangle \tag{4.6}$$
$$= \sum_{d\delta\eta\epsilon e St} (A\varphi_a a\| T^c \| B\varphi_b b)_{S\epsilon e}^{d\delta\eta} \cdot \begin{pmatrix} a^+ b & d \\ m & p & q \end{pmatrix}^\delta \begin{pmatrix} d^+ c & e^+ \\ q & n & r \end{pmatrix}^\eta \cdot \tau\begin{pmatrix} -ABS \\ ikt \end{pmatrix} \sqrt{Z(-ABS)} (\vec{S_t} | S\epsilon er)$$

The sum for S runs over all sets of equivalent edges and the topological matrix selects the right one. This is necessary, since the vertices of the tetrahedron or the octahedron are connected to each other by inequivalent sets of edges.

Proof of (4.4): In the case of a translationally invariant operator, the matrix elements are functions of the distance vectors $\vec{S}_{ik}$ only. In the case of an operator related to the centre of symmetry, they are moreover functions of A and B, because the triangles are specified definitely by A, B, and $\vec{S}_{ik}$. In both cases, they are functions of the edge vectors $\vec{S}_{ik}$ and therefore expandable according to theorem (3.16):

$$\langle Ai\varphi_a am | T_n^c | Bk\varphi_b bp \rangle = \sum_{\epsilon e} (S\epsilon er | X)(\vec{S}_{ik} | S\epsilon er) \tag{4.7}$$

with the collective index $X=(Ai\varphi_a am Tcn Bk\varphi_b bp)$. According to (3.17) the expansion coefficients are

$$(S\epsilon er | X) = \sum_{ik} (S\epsilon er | S_{ik}) \langle Ai\varphi_a am | T_n^c | Bk\varphi_b bp \rangle, \tag{4.8}$$

where the sum for i, k is limited to $\vec{A_i} - \vec{B_k} = \vec{S}_{ik}$ (i.e. the distance must belong to set S). The coefficients (4.8) transform as a direct product $a^+ \times b \times c \times e^+$ and thus can be factorized. For this purpose, we only have to generalize the WET to a fourfold direct product:

$$(S\epsilon er | X) = \sum_{d\delta\eta} (A\varphi_a a\| T^c \| B\varphi_b b)_{S\epsilon e}^{d\delta\eta} \cdot \begin{pmatrix} a^+ b & d \\ m & p & q \end{pmatrix}^\delta \begin{pmatrix} d^+ c & e^+ \\ q & n & r \end{pmatrix}^\eta \tag{4.9}$$

If we insert (4.9) into (4.7), the proof is complete.

From (4.8/9), we can isolate the invariant and express it by all matrix elements:

$$(A\varphi_a a\| T^c \| B\varphi_b b)_{S\epsilon e}^{d\delta\eta}$$
$$= \{b\} dim d \cdot \sum_{ik} \begin{pmatrix} a & b^+ d^+ \\ m & p & q \end{pmatrix}^\delta \begin{pmatrix} d & c^+ e \\ q & n & r \end{pmatrix}^\eta (S\epsilon er | S_{ik}) \langle Ai\varphi_a am | T_n^c | Bk\varphi_b bp \rangle \tag{4.10}$$

with the same limitation of i, k as in (4.8). We have used the phase $\{e\} = 1$, because e must be a tensor representation even for double point groups, i.e. including spin-orbitals in the matrix elements.

If integral formulae are at hand, we can calculate the invariants by
(4.10). Since the wit of (4.4) is to express many matrix elements by
few invariants, this calculation is only efficient, if the 3jm symbols
and SALC coefficients subsequently can be eliminated. In section 15
such a calculation is carried out. The invariants defined by (4.4) or
(4.10) shall be called BRM (bicentric, reduced matrix element).

Because of the relevance of scalar operators, we repeat this spe-
cial case of (4.4/6):

$$\langle Ai\varphi_a am|T|Bk\varphi_b bp\rangle = \sum_{\delta\varepsilon e}(A\varphi_a a\|T\|B\varphi_b b)^\delta_{S\varepsilon e}\cdot\binom{a^+b\ e^+}{m\ p\ r}^\delta \text{dime}^{-1/2}(\vec{S}_{ik}|S\varepsilon er) \tag{4.11}$$

$$= \sum_{\delta\varepsilon e}\sum_{St}\sqrt{Z(-ABS)/\text{dime}}\cdot(A\varphi_a a\|T\|B\varphi_b b)^\delta_{S\varepsilon e}\binom{a^+b\ e^+}{m\ p\ r}^\delta \tau\binom{-ABS}{ikt}(\vec{S}_t|S\varepsilon er)$$

where more precisely $(A\varphi_a a\|T\|B\varphi_b b)^\delta_{S\varepsilon e} = (A\varphi_a a\|T\|B\varphi_b b)^{e^+\delta 1}_{S\varepsilon e}$.

4.2. General bicentric matrices

The relevance of (4.11) goes far beyond the one-particle integrals.
By careful inspection of the proof of (4.4) we observe that the matrix
does not need to be an integral. It only has to transform in the right
way under the symmetry operations. Thus we can reshape (4.11) as a ge-
neral matrix theorem:

In the following $\vec{X}_r$ are arbitrary vectors fixed in a molecular fra-
mework (i.e. not necessarily distance vectors between atoms). If we
can show that a bicentric matrix $M(\vec{X}_r)_{Ai\varphi_a am,Bk\varphi_b bp}$ transforms accor-
ding to

$$M(g^{-1}\vec{X}_r)_{Ai\varphi_a am,Bk\varphi_b bp} \tag{4.12}$$
$$= \sum_{jl}\sum_{nq}D^a_{nm}(g)\overset{*}{\sigma}^A_{ji}(g)D^b_{qp}(g)\sigma^B_{lk}(g)\cdot M(\vec{X}_r)_{Aj\varphi_a an,Bl\varphi_b bp} \ )$$

then the bicentric matrix has the following factorization:

$$M(\vec{X}_r)_{Ai\varphi_a am,Bk\varphi_b bp} = \sum_{\delta\varepsilon e}M(A\varphi_a a\|B\varphi_b b)^\delta_{S\varepsilon e}\binom{a^+b\ e^+}{m\ p\ r}^\delta \text{dime}^{-1/2}(\vec{S}_{ik}|S\varepsilon er) \tag{4.13}$$

The generalized BRM $M(A\varphi_a a\|B\varphi_b b)^\delta_{S\varepsilon e}$ is a scalar function of the vectors
$\vec{X}_r$ with respect to the symmetry group G. In the present context, φ_a and
φ_b mean additional indices not affected by the symmetry operations.

Examples of such bicentric matrices being no integrals are the in-
verse overlap matrix of the atomic orbitals in a molecule, the one-
particle density matrix in the AO basis, and the matrix of the vibra-
tional force constants with respect to the atomic elongations. The
last example has already been dealt with in [12]. The analogous gene-
ralization of (4.4) would be needed, if one considers anharmonic ef-
fects.

The inversion of (4.13) is:

$$M(A\varphi_a a \| B\varphi_b b)^\delta_{S\varepsilon e} = \{b\}\sqrt{\overline{dime}}\cdot\sum_{ik}\binom{a\ b^+e}{m\ p\ r}^\delta (S\varepsilon er|S_{ik})M(\vec{X}_r)_{Ai\varphi_a am, Bk\varphi_b bp} \quad (4.14)$$

As a first, simple example, we now can determine the BRMs of the unit matrix in the AO basis: $E_{Ai\varphi_a am, Bk\varphi_b bp} = \delta(A,B)\delta(i,k)\delta(\varphi_a,\varphi_b)\delta(a,b)\delta(m,p)$
The result is:
$$E(A\varphi_a a \| B\varphi_b b)^\delta_{S\varepsilon e}$$
$$= \delta(A,B)\delta(\varphi_a,\varphi_b)\delta(a,b)\delta(S,0^A)\delta(e,1)\delta(\varepsilon,1)\delta(\delta,1)\sqrt{Z(A)\cdot dime} \quad (4.15)$$

Since the product of two bicentric matrices is a bicentric matric again, the BRMs of the product matrix is determined by those of the factors. But we postpone this calculation, because we need some results of section 6.

The integral and non-integral, bicentric matrices often refer not directly to the irreducible representations of the molecular symmetry group G, but to the angular momentum basis, for the atomic orbitals and elongations are at first given in this basis. We then are confronted with matrices of the type $M(\vec{X}_r)_{Ain_a l_a m_a, Bkn_b l_b m_b}$. Since the angular momentum basis is in general reducible with respect to G, we first have to adapt the basis according to (3.19) and then apply (4.13). This yields the general structure of bicentric matrices in the angular momentum basis:

$$M(\vec{X}_r)_{Ain_a l_a m_a, Bkn_b l_b m_b} = \sum_{\alpha a\beta b\delta\varepsilon e}\sum M(An_a l_a \alpha a \| Bn_b l_b \beta b)^\delta_{S\varepsilon e}\langle 1_a m_a | 1_a \alpha ap_a\rangle \quad (4.16)$$
$$\cdot\langle 1_b \beta bp_b | 1_b m_b\rangle\binom{a^+b\ e^+}{p_a p_b p_e}^\delta \cdot dime^{-1/2}(\vec{S}_{ik}|S\varepsilon ep_e)$$

5. The matrix elements of s.-a. molecular orbitals

The s.-a. MOs can be built up from the AOs $|Ai\varphi_a ap_a\rangle$ defined by (4.1/3). As has been shown in [10, 11], the complete set of symmetrized LCAOs resulting from an equivalent set $|Ai\varphi_a ap_a\rangle$ is given by:

$$|(A\varepsilon e, \varphi_a a)\gamma cp_c\rangle = \sum_{ip_a} K(\gamma cp_c, Ai\varepsilon e, ap_a) \cdot |Ai\varphi_a ap_a\rangle \qquad (5.1)$$

with the compound SALC coefficient:

$$K(\gamma cp_c, Ai\varepsilon e, ap_a) = \{c\}\sqrt{dimc} \cdot \sum \binom{e \ a \ c}{p_e p_a p_c}^\gamma \cdot (\overrightarrow{A_i}|A\varepsilon ep_e) \qquad (5.2)$$

In comparison to [10, 11], the phase factor $\{c\}$ has been included in order to allow for spin-orbitals. The definition is in accordance with (2.34).

The proof of (5.1/2) results from the transformation property of the AOs:

$$U(g)|Ai\varphi_a ap\rangle = \sum_{kq} D^a_{qp}(g)\sigma^A_{ki}(g) \cdot |Ak\varphi_a aq\rangle \qquad (5.3)$$

Since the SALC coefficients reduce the representation σ^A and the 3jm symbols the remaining product representation, the compound SALC coefficients reduce the direct product $a \times \sigma^A$ in (5.3).

In the appendix 1 this method of symmetry-adaption is compared to the conventional technique of the projection operators.

If we now consider the matrix elements of tensor operators, they can be factorized as usual by the WET:

$$\langle(A\varepsilon e, \varphi_a a)\gamma cp_c|T^g_{p_g}|(B\varphi f, \varphi_b b)\delta dp_d\rangle$$
$$= \sum_\alpha \langle(A\varepsilon e, \varphi_a a)\gamma c\|T^g\|(B\varphi f, \varphi_b b)\delta d\rangle_\alpha \binom{c \ g \ d}{p_c p_g p_d}^\alpha \qquad (5.4)$$

Now the ordinary, reduced matrix element of (5.4) is related to the BRM in the following theorem:

$$\langle(A\varepsilon e, \varphi_a a)\gamma c\|T^g\|(B\varphi f, \varphi_b b)\delta d\rangle_\alpha = \{d\}\{c^+dg\alpha\}\sqrt{dimc \cdot dimd} \cdot$$

$$\cdot \sum_{h\eta\theta\beta} \sum_{S\sigma k} \sqrt{Z(-ABS)} \begin{Bmatrix} c^+d \ g \\ e \ f^+k^+ \\ a \ b^+h^+ \\ \gamma \ \delta \ \theta \end{Bmatrix}^\alpha_\eta \cdot PIs \begin{pmatrix} -A \ B \ S \\ \varepsilon \ \varphi \ \sigma \\ e^+f \ k \end{pmatrix}_\beta \cdot (A\varphi_a a\|T^g\|B\varphi_b b)^{h\eta\theta}_{S\sigma k} \qquad (5.5)$$

In this theorem appears a typical, geometric invariant of the polyhedral framework, the "polyhedral isoscalar". It refers to the equivalent triangles (-ABS) and is defined by (6.6). The details are discussed in the following section.

The derivation of the theorem (5.5) is as follows. We first solve (5.4) for the reduced matrix element and then insert (5.1) into the ordinary matrix elements. This yields sums over bicentric matrix elements, which are replaced by (4.6). The five resulting 3jm symbols are

collected in a 9j and one 3jm symbol using the rule of de-Shalit (2.54).
Except for the BRM and the 9j symbol the remainder is equal to the
right side of (6.6) and thus suggests the definition of the polyhe-
dral isoscalar.

The skipping of all additional indices in (5.5) shows again the es-
sential structure, which is given by a triple sum only:

$$\langle\!\langle(Ae,a)c\|T^g\|(Bf,b)d\rangle\!\rangle = \{d\}\{c^+dg\}\sqrt{dimc\cdot dimd'} \tag{5.6}$$
$$\cdot\sum_{hSk}\sqrt{Z(-ABS)}\cdot\begin{Bmatrix}c^+d&g&+\\e&f^+k^+\\a&b^+h^+\end{Bmatrix}\cdot PIs\begin{pmatrix}-A&B&S\\e^+f&k\end{pmatrix}\cdot(Aa\|T^g\|Bb)^h_{Sk}$$

If we regard the reduced matrix elements of the s.-a. MOs as the
physical properties of a molecule, we can say: The theorem (5.5/6) ex-
presses the non-local invariants representing the physical properties
by the BRMs, the local invariants of the coordination. This connection
is mediated by the sums for S and k, i.e. by a sum over the different
coordinations of the atoms and a sum over the representations k con-
tained in σ^S. The sum for h is more technical. As d in the sum (4.5)
it counts the multiplicity of the identical representation in the four-
fold product $a^+\times b\times g\times k^+$ (cf. also eq.(7.15)).

If T^g is the Hamiltonian of the system at hand, the BRMs (with $S\neq0$)
on the right side are the invariant representatives of the resonance
integrals and describe the chemical binding along the polyhedral ed-
ges S. These invariants thus are the appropriate candidates for a
semi-empirical parametrization (Hückel, Wolfsberg-Helmholtz). The au-
thor is of the opinion that relevant parameters must not depend on
the numbering of atoms and the choice of axes (cf. section 13).

From this interpretation we conclude that (5.5) is the first, poly-
hedral example of the structure (1.2). The geometrical factor in this
case is

$$GEO_1(x,y,z) = \{d\}\{c^+dg\alpha\}\sqrt{Z(-ABS)dimc\cdot dimd'}\cdot\sum_{\beta}\begin{Bmatrix}c^+d&g&+\\e&f^+k^+\\a&b^+h^+\end{Bmatrix}\begin{matrix}\alpha\\\beta\\\eta\end{matrix}\cdot PIs\begin{vmatrix}-A&B&S\\\varepsilon&\varphi&\sigma\\e^+f&k\end{vmatrix}\begin{matrix}\\\\ \beta\end{matrix} \tag{5.7}$$
$$\gamma\ \delta\ \theta$$

with x=(AaBbg), y=($\varepsilon e\gamma c,\eta f\delta d,\alpha$), and z=(hη$\theta$S$\sigma$k). (5.5) then reads:

$$\langle\!\langle(A\varepsilon e,\varphi_a a)\gamma c\|T^g\|(B\varphi f,\varphi_b b)\delta d\rangle\!\rangle_\alpha = \sum_z GEO_1(x,y,z)\cdot(A\varphi_a a\|T^g\|B\varphi_b b)^{h\eta\theta}_{S\sigma k} \tag{5.8}$$

In order to invert this relation we need an orthogonality relation
of the geometrical factors for a fixed constellation x=(AaBbg). From
the relations (2.55) and (6.9/10) we derive:

$$\sum_y GEO_1(x,y,z)^*\cdot GEO_1(x,y,z') = \delta(z,z')/dimh \tag{5.9}$$

$$\sum_z dimh\cdot GEO_1(x,y,z)^*\cdot GEO_1(x,y',z) = \delta(y,y') \tag{5.10}$$

and further the inversion of (5.8):

$$(A\varphi_a \| T^g \| B\varphi_b b)^{h\eta\theta}_{S\sigma k} = \sum_y \text{dimh} \cdot \text{GEO}_1(x,y,z) \cdot \langle\!\langle A\varepsilon e, \varphi_a a)\gamma c \| T^g \| (B\varphi f, \varphi_b b)\delta d\rangle\!\rangle_\alpha$$

(5.11)

This relation may be used to adjust semi-empirical parameters.

As in the preceeding section, we write the formulae for the scalar operators again separately, whereby the 9j symbol reduces according to (2.52/53). (5.4) then becomes:

$$\langle\!\langle A\varepsilon e, \varphi_a a)\gamma c p_c | T | (B\varphi f, \varphi_b b)\delta d p_d\rangle\!\rangle$$

(5.12)

$$= \delta(c,d)\delta(p_c,p_d)\sqrt{\text{dimc}}\langle\!\langle A\varepsilon e, \varphi_a a)\gamma c \| T \| (B\varphi f, \varphi_b b)\delta c\rangle\!\rangle$$

and (5.5):

$$\langle\!\langle A\varepsilon e, \varphi_a a)\gamma c \| T \| (B\varphi f, \varphi_b b)\delta d\rangle\!\rangle = \delta(c,d)\begin{Bmatrix} b \end{Bmatrix}\begin{Bmatrix} c^+ f b \delta \end{Bmatrix}\sqrt{\text{dimc}}$$

(5.13)

$$\cdot \sum_{\eta\beta}\sum_{S\sigma k}\begin{Bmatrix} ab^+ k\eta \end{Bmatrix}\sqrt{Z(-ABS)/\text{dimk}} \cdot \begin{Bmatrix} e & f^+ k^+ \\ b^+ a^+ c^+ \end{Bmatrix}_{\gamma\delta\eta\beta}\text{PIs}\begin{pmatrix} -A & B & S \\ \varepsilon & \varphi & \sigma \\ e^+ f & k \end{pmatrix}_\beta \cdot (A\varphi_a \| T \| B\varphi_b b)^\eta_{S\sigma k}$$

6. Polyhedral coefficients referring to edges

In section 3, we have noted the parallelism of the SALC coefficients $(\vec{A}_i | A\alpha ar)$ and the subgroup-adaption coefficients $\langle \acute{a}m | \acute{a}\alpha ar \rangle$, since both types of coefficients decompose reducible representations of the group G. The analogous pairs of equations are (2.69) and (3.8), (2.70) and (3.6), (2.71) and (3.7). We now pursue this parallelism further and show that it also comprises the 3jm symbols of G' and the isoscalar factors of $G' \supset G$.

The representations $\acute{a}(\acute{G})$ etc. are coupled by the 3jm symbols of the group G'_i, which in this section is supposed to be simply reducible. In other words the 3jm symbols of G' couple reducible representations of G. This observation suggests that there might be also a coupling of the reducible representations σ^S of G. Indeed, this is true and the part of the coupling coefficients is now played by the topological matrices $\tau(^{ABC}_{ikl})$. The analogue of eq. (2.25) is:

$$\sum_{ilp} \sigma^A_{ik}(g)\sigma^B_{lm}(g)\sigma^C_{pq}(g)\tau(^{ABC}_{ilp}) = \tau(^{ABC}_{kmq}) \tag{6.1}$$

This equation represents the mapping of the triangle $\vec{A}_i + \vec{B}_l + \vec{C}_p = 0$ onto the equivalent triangle $\vec{A}_k + \vec{B}_m + \vec{C}_q = 0$ by the operation g. The analogue of the orthogonality relation (2.26) is:

$$\sum_{kl} \tau(^{ABC}_{klm})\tau(^{ABD}_{kln}) = \delta(C,D)\delta(m,n)/Z(C) , \tag{6.2}$$

where Z(C) is the number of edge vectors of type C. Note the possible difference of Z(ABC) and Z(C), since one edge vector of type C may be shared by different triangles of type ABC. In this case, C must be invariant to some symmetry operations. Each $\vec{C}_i$ is shared by q=Z(ABC)/Z(C) triangles. Since $\vec{A}_k + \vec{B}_l + \vec{C}_m = 0$ excludes $\vec{A}_k + \vec{B}_l + \vec{D}_n = 0$, the left side of (6.2) is zero unless $\vec{C}_m = \vec{D}_n$. If now $\vec{C}_m = \vec{D}_n$, there are q non-zero summands and, because of the normalization chosen in (3.1), eq.(6.2) is valid.

If the vectors of type A and B point from the centre of symmetry to certain positions, we have Z(ABC)=Z(C) and each $\vec{C}_l$ uniquely determines a pair $(\vec{A}_i, \vec{B}_k)$. Only in this case, we get the second orthogonality condition,

$$\sum_{Cr} Z(C)\tau(^{ABC}_{ikr})\tau(^{ABC}_{lmr}) = \delta(i,l)\delta(k,m) , \tag{6.3}$$

the analogue of (2.27). When using consequences of (6.3), we allways have to make shure that Z(ABC)=Z(C).

We now proceed as with the 3jm symbols of the supergroup G and transform the topological matrix into the s.-a. basis (cf.(2.72)):

$$\tau\begin{pmatrix} A & B & C \\ \alpha & \beta & \gamma \\ a & b & c \\ k & l & m \end{pmatrix} = \sum_{rst} \tau\begin{pmatrix} A & B & C \\ r & s & t \end{pmatrix}(\vec{A}_r | A\alpha ak)(\vec{B}_s | B\beta bl)(\vec{C}_t | C\gamma cm) \tag{6.4}$$

According to the WET, we get the analogue of Racah's factorization lemma (2.73),

$$\tau\begin{pmatrix} A & B & C \\ \alpha & \beta & \gamma \\ a & b & c \\ k & l & m \end{pmatrix} = \sum_{\varepsilon} \text{PIs} \begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\varepsilon} \cdot \begin{pmatrix} abc \\ klm \end{pmatrix}^{\varepsilon} , \tag{6.5}$$

which defines the "polyhedral isoscalar factor" (cf.(2.74)):

$$\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\varepsilon} = \sum_{rst}\tau\begin{pmatrix} ABC \\ rst \end{pmatrix}(\vec{A_r}|A\alpha ak)(\vec{B_s}|B\beta bl)(\vec{C_t}|C\gamma cm)\begin{pmatrix} abc \\ klm \end{pmatrix}^{\varepsilon} \tag{6.6}$$

Since the topological matrices are real and (by choice) invariant to all permutations of columns, we have the following symmetries of the polyhedral isoscalars. They are invariant to even permutations and odd permutations yield a phase factor:

$$\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\varepsilon} = \{abc\varepsilon\}\cdot\text{PIs}\begin{pmatrix} ACB \\ \alpha\gamma\beta \\ acb \end{pmatrix}_{\varepsilon} \tag{6.7}$$

The complex conjugation is simple:

$$\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^{*}_{\varepsilon} = \text{PIs}\begin{pmatrix} A & B & C \\ \alpha_+ & \beta_+ & \gamma_+ \\ a^+ & b^+ & c^+ \end{pmatrix}_{\varepsilon} \tag{6.8}$$

From (6.2) we derive the first orthogonality relation of the polyhedral isoscalars (cf.(2.77)):

$$\sum_{\alpha\alpha\beta b\varepsilon}\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^{*}_{\varepsilon}\text{PIs}\begin{pmatrix} ABD \\ \alpha\beta\sigma \\ abc \end{pmatrix}_{\varepsilon} = \delta(C,D)\delta(\gamma,\sigma)\text{dimc}/Z(C) \tag{6.9}$$

The analogue of (2.78) following from (6.3) is subjected to the restriction $Z(ABC)=Z(C)$:

$$\sum_{C\gamma}Z(C)\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}^{*}_{\varepsilon}\text{PIs}\begin{pmatrix} ABC \\ \sigma\tau\gamma \\ stc \end{pmatrix}_{\eta} = \delta(a,s)\delta(b,t)\delta(\alpha,\sigma)\delta(\beta,\tau)\delta(\varepsilon,\eta)\text{dimc} \tag{6.10}$$

Analogous to (2.79/80), we derive the special case

$$\text{PIs}\begin{pmatrix} ABO \\ \alpha\beta \\ ab1 \end{pmatrix}_{\varepsilon} = \delta(-A,B)\delta(\alpha,\beta)\delta(a^+,b)\delta(\varepsilon,1)\sqrt{\text{dima}}/Z(A), \tag{6.11}$$

and the sum rule:

$$\sum_{\alpha a}\sqrt{\text{dima}}\cdot\text{PIs}\begin{pmatrix} -A & A & C \\ \alpha & \alpha_+ & \gamma \\ a & a^+1 \end{pmatrix} = \delta(C,0^A)\delta(\gamma,1) \tag{6.12}$$

Instead of (6.6), we can derive from (6.5), by the help of (2.26), the more general relation analogous to (2.81):

$$\sum_{rst}\tau\begin{pmatrix} ABC \\ rst \end{pmatrix}(\vec{A_r}|A\alpha ak)(\vec{B_s}|B\beta bl)(\vec{C_t}|C\gamma cm)\begin{pmatrix} abd \\ kln \end{pmatrix}^{\varepsilon}$$
$$= \delta c,d)\delta(m,n)\cdot\text{dimc}^{-1}\cdot\text{PIs}\begin{pmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{pmatrix}_{\varepsilon} \tag{6.13}$$

This relation allows several rearrangements like:

$$\sum_{rs} \tau \binom{ABC}{rst} (\vec{A_r}|A\alpha ak)(\vec{B_s}|B\beta bl) = \sum_{\varepsilon\gamma c} PIs \begin{vmatrix} ABC \\ \alpha\beta\gamma \\ abc \end{vmatrix}_\varepsilon \binom{abc}{klm}^\varepsilon (C\gamma cm|\vec{C_t}) \qquad (6.14)$$

A first application of the polyhedral isoscalars we have already met in (5.5) because we got an expression including the right hand side of (6.6). The polyhedral isoscalars are the group theoretical, i.e. invariant representation of the triangular conditions like $\vec{A_i} + \vec{B_k} + \vec{C_1} = 0$. As we shall see later on, such triple relations of "polyhedral objects" can be generalized.

Another application, already announced in section 4, results from the product of two bicentric matrices:

$$M_{Ai\varphi_a am, Bk\varphi_b bp} = \sum_{Cl\varphi_c cn} \sum P_{Ai\varphi_a am, Cl\varphi_c cn} \cdot Q_{Cl\varphi_c cn, Bk\varphi_b bp} \qquad (6.15)$$

Inserting this into (4.14) yields the BRM of the product matrix in terms of the BRMs of the factors. The derivation resembles that of (5.5) and results in:

$$M(A\varphi_a a \| B\varphi_b b)^\delta_{S\varepsilon e} = \{b\}\{ab^+e\delta\} \sum_{C\varphi_c cT\tau\eta fU\tau\eta f} \sum \sum \sqrt{\frac{Z(STU)dime}{dimf \cdot dimf}} \cdot \begin{Bmatrix} e & f^+f^h \\ c & b & a \end{Bmatrix}_{\delta\tau\tau'\alpha}$$

$$\cdot PIs \begin{vmatrix} S & T & U \\ \varepsilon + \eta & \eta' \\ e^+f & f \end{vmatrix}_\alpha \cdot P(A\varphi_a a \| C\varphi_c c)^\tau_{T\eta f} Q(C\varphi_c c \| B\varphi_b b)^{\tau'}_{U\eta f} \qquad (6.16)$$

7. Triangular coefficients

7.1. Representations induced by triangles

In the same way as the polyhedral edges, the triangles and distorted tetrahedra subtended in the molecular framework form equivalent sets with respect to the symmetry group. These sets again carry reducible representations of the group. This is of interest for the functions depending on the triangles or pseudo-tetrahedra, for instance the molecular three- or four-centre integrals. With regard to this application it is necessary to distinguish the triangles and pseudo-tetrahedra by valued or numbered vertices. This distinction accords to our treatment of the edges as vectors, i.e. as line segments with orientation or valued ends. The numbering becomes essential, if the the vertices of the triangle or pseudo-tetrahedron are equivalent to each other. Thus a triangle or pseudo-tetrahedro is invariant to a symmetry operation only, if all its vertices lie on the reflection plane or the rotation axis. As for the edges we have to take into account degenerate cases, i.e. triangles and pseudo-tetrahedra with coincident vertices. The extreme cases are the null-triangles and null-tetrahedra with three or four coinciding vertices.

In this section we discuss the symmetry-adaption of triangles. If Λ is a set of equivalent triangles Λ_i, then these triangles carry the representation σ^Λ analogous to (3.3):

$$g\Lambda_i = \sum_k \sigma_{ki}^\Lambda (g)\Lambda_k \qquad (7.1)$$

with the characters

$$\sigma^\Lambda(g) = \sum_i \sigma_{ii}^\Lambda (g) \qquad (7.2)$$

They are equal to the number of triangles invariant to the operation g. Again the representation σ^Λ is decomposed according to the branching rule (2.10/11) with a multiplicity $n(\Lambda,a)$. In analogy to (3.4/5), the unitary transformation is given by:

$$\sum_{ik}(\Lambda\alpha ar|\Lambda_i)\sigma_{ik}^\Lambda(g)(\Lambda_k|\Lambda\beta bs) = \delta(a,b)\delta(\alpha,\beta)D_{rs}^a(g) \qquad (7.3)$$

$$\sum_k \sigma_{ik}^\Lambda(g)(\Lambda_k|\Lambda\beta bs) = \sum_r D_{rs}^a(g)(\Lambda_i|\Lambda\alpha ar) \qquad (7.4)$$

The matrix elements $(\Lambda_i|\Lambda\alpha ar)$ are termed triangular SALC (TSALC) coefficients. The unitary relations analogous to (3.6/7) are:

$$\sum_i (\Lambda\alpha ar|\Lambda_i)(\Lambda_i|\Lambda\beta bs) = \delta(a,b)\delta(\alpha,\beta)\delta(r,s) \qquad (7.5)$$

$$\sum_{\alpha ar}(\Lambda_i|\Lambda\alpha ar)(\Lambda\alpha ar|\Lambda_k) = \delta(i,k) \qquad (7.6)$$

Up to now we have used an arbitrary numbering of the triangles

irrespective of the numbers of their vertices. The interrelation of
the vertices and triangles is again expressed by a topological matrix:

$$\tau\left(\begin{matrix}\Delta ACB\\ikml\end{matrix}\right) = \begin{cases} 1/\sqrt{Z(\Delta)} & \text{if the ordered triple } \vec{A_k}, \vec{C_m}, \vec{B_l} \text{ represents the vertices of } \Delta_i \\ 0 & \text{otherwise,} \end{cases} \quad (7.7)$$

where $Z(\Delta)$ is the number of equivalent triangles in the set Δ. The or-
der ACB has been chosen with regard to the molecular three-centre in-
tegrals (cf.(8.1/3)).

The topological matrix is utilized to reduce the triangular SALC
coefficients $(\Delta_i | \Delta\alpha ar)$ to the ordinary SALC coefficients. The technique
is similar to (3.25/26). Each triangle Δ_j is mapped onto a vector $\vec{R_j}$:

$$\vec{R_j} = \sum_{kml} \tau\left(\begin{matrix}\Delta ACB\\jkml\end{matrix}\right)(\mu_1\vec{A_k}+\mu_2\vec{C_m}+\mu_3\vec{B_l}) \quad (7.8)$$

By the choice of the fixed numbers μ_i, we have to take care that $R_j \neq R_k$
if $\Delta_j \neq \Delta_k$. Since this mapping is bijective, we have $\sigma^R = \sigma^\Delta$. Therefore
the triangular SALC coefficients of the set Δ are equal to the ordina-
ry SALC coefficients of the set R:

$$(\Delta_j | \Delta\alpha ar) = (\vec{R_j} | R\alpha ar) \quad (7.9)$$

In principle, this relation would allow the total elimination of the
triangles Δ by the vectors R. Because of (7.8), an integral with the
three centres $\vec{A_k}$, $\vec{C_m}$, and $\vec{B_l}$ can be regarded as a function of one vec-
tor $\vec{R_j}$. Although this interpretation is valid, it might be confusing.
So we keep to the more expressive notation Δ_j and use (7.9) only for
the calculation of $(\Delta_j | \Delta\alpha ar)$.

Using (7.8), we explicitly show that any function of three posi-
tions can be regarded as a function over a set of triangles:

$$F(\Delta_i) = (\Delta_i | F) = \sum_{kml} \tau\left(\begin{matrix}\Delta ACB\\ikml\end{matrix}\right) \cdot F(A_k, C_m, B_l) \quad (7.10)$$

The notation $(\Delta_i | F)$ suggests the same proceeding as in section 3 and
the interpretation of (7.5/6) as the orthogonality and completeness
relations of a set of s.-a. triangle functions. This argument leads
to the conclusion that every triangle function $(\Delta_i | F)$ can be expanded
analogous to (3.16/17):

$$(\Delta_i | F) = \sum_{\alpha a} (\Delta_i | \Delta\alpha ar)(\Delta\alpha ar | F) \quad (7.11)$$

with the expansion coefficients:

$$(\Delta\alpha ar | F) = \sum_i (\Delta\alpha ar | \Delta_i)(\Delta_i | G) \quad (7.12)$$

If such a function depends on the intrinsic parameters of the triangles
only, but not on their orientation in space, then it is invariant on
the set Δ. In this case, we simply write $F(\Delta)$ or F_Δ. An example is the
reduced matrix element in eq.(8.1).

7.2. The coupling of triangular representations

The topological matrices (7.8) are quite analogous to (3.1) and there-
fore have corresponding orthogonality relations:

$$\sum_{kml} \tau(^{\Delta ACB}_{ikml})\tau(^{\theta ACB}_{jkml}) = \delta(\Delta,\theta)\delta(i,j)/Z(\Delta) \qquad (7.13)$$

$$\sum_{\Delta i} Z(\Delta)\tau(^{\Delta ACB}_{ikml})\tau(^{\Delta ACB}_{inpq}) = \delta(k,n)\delta(m,p)\delta(l,q) \qquad (7.14)$$

Since Δ_i uniquely determines the three vertices $\vec{A}_k$, $\vec{B}_l$, and $\vec{C}_m$ (7.14)
is not subjected to a restriction as (6.3).

The topological matrices (7.8) have four columns of indices. A di-
rect treatment in the sense of section 6 would lead to a parallelism
with the group-theoretical 4jm symbols, which couple four irreducible
representations [34]. But the 4jm symbols can be factorized into 3jm
symbols in the following way:

$$(^{abcd}_{ijkl})^{\epsilon\eta e} = \sum(^{abe}_{ijm})^{\epsilon}(^{e^+cd}_{m\ kl})^{\eta}_{dime} \qquad (7.15)$$

The collective index $\epsilon\eta e$ counts the multiplicity of the identical re-
presentation in the direct product $a\times b\times c\times d$. This suggests to try a
corresponding decomposition of the topological matrix (7.8), which is
achieved as follows. Instead by its three vertices, a triangle can be
determined by one of its edges and the opposite vertex. The interrela-
tion of the triangle Δ_j, the edge $\vec{S}_k$, and the vertex $\vec{C}_l$ is expressed
by a further topological matrix. For the purpose of discrimination
from (3.1), we call it a topological matrix of second kind:

$$\tau^2(^{\Delta SC}_{irm}) = \begin{cases} 1/\sqrt{Z(\Delta)} & \text{if } \vec{C}_m \text{ is the 2nd vertex and } \vec{S}_r \text{ points from the} \\ & \qquad\qquad\qquad \text{1st to the 3rd vertex of } \Delta_i \quad (7.16) \\ 0 & \text{otherwise} \end{cases}$$

The original interrelation (7.8) now can be decomposed:

$$\tau(^{\Delta ACB}_{ikml}) = \sum_{Sr} \tau^2(^{\Delta SC}_{irm})\tau(^{-ABS}_{klr})\sqrt{Z(-ABS)} \qquad (7.17)$$

The orthogonality relations follow immediately from the definition:

$$\sum_{rm} \tau^2(^{\Delta SC}_{irm})\tau^2(^{\theta SC}_{jrm}) = \delta(\Delta,\theta)\delta(i,j)/Z(\Delta) \qquad (7.18)$$

$$\sum_{\Delta i} Z(\Delta)\tau^2(^{\Delta SC}_{irm})\tau^2(^{\Delta SC}_{ipq}) = \delta(r,q)\delta(m,p) \qquad (7.19)$$

Of course, (7.18/19) combined with (6.2/3) yield (7.13/14). Again
there is no restriction for (7.19), since Δ_i uniquely determines $\vec{S}_r$
and $\vec{C}_m$.

We now strictly follow the proceeding in section 6 from eq.(6.4)
onwards. The transformation of τ^2 into the s.-a. basis yields:

$$\tau^2 \begin{pmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \\ pqr \end{pmatrix} = \sum_{ikm} \tau^2(^{\Delta SC}_{ikm})(\Delta_i|\Delta\delta dp)(\vec{S}_k|S\sigma sq)(\vec{C}_m|C\gamma cr) \qquad (7.20)$$

and again the factorization by the WET:

$$\tau^2 \begin{pmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \\ pqr \end{pmatrix} = \sum_\varepsilon PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \end{vmatrix}_\varepsilon (\text{dsc}_{pqr})^\varepsilon \tag{7.21}$$

with the "polyhedral isoscalar of the second kind":

$$PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \end{vmatrix}_\varepsilon = \sum_{ikm} \tau^2 (^{\Delta SC}_{ikm})(\Delta_i | \Delta\delta dp)(\vec{S}_k | S\sigma sq)(\vec{C}_m | C\gamma cr)(\text{dsc}_{pqr})^{\varepsilon*} \tag{7.22}$$

The orthogonality relations follow from (7.18/19):

$$\sum_{\sigma s} \sum_{\gamma c \varepsilon} PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \end{vmatrix}^*_\varepsilon PIs^2 \begin{vmatrix} \Theta SC \\ \vartheta\sigma\gamma \\ dsc \end{vmatrix}_\varepsilon = \delta(\Delta,\Theta)\delta(\delta,\vartheta)dimd/Z(\Delta) \tag{7.23}$$

$$\sum_{\Delta\delta} Z(\Delta) PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \end{vmatrix}^*_\varepsilon PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma' \\ dsc' \end{vmatrix}_\eta = \delta(\sigma,\sigma')\delta(s,s')\delta(\gamma,\gamma')\delta(c,c')\delta(\varepsilon,\eta)\cdot dimd \tag{7.24}$$

(7.2) again can be generalized to

$$\sum_{jkm} \tau^2 (^{\Delta SC}_{jkm})(\Delta_j | \Delta\delta dp)(\vec{S}_k | S\sigma sq)(\vec{C}_m | C\gamma cr)(\text{ds'c}_{pq'r})^{\varepsilon*} \tag{7.25}$$
$$= \delta(s,s')\delta(q,q')dims^{-1} PIs^2 \begin{vmatrix} \Delta SC \\ \delta\sigma\gamma \\ dsc \end{vmatrix}_\varepsilon$$

This can be derived from (7.21) by the orthonality relation (2.26).
The relations (2.40), (2.81), (6.14), and (7.25) are all of the same
type, and can be proved by a uniform method. We have a term of the form
$X(^{ss'}_{qq'})$, the left hand side of these equations. Starting now from the
expression $\sum_q D^s_{pq}(g)X(^{ss'}_{qq'})$ we shift the operation g in X from term to term.
In the case of (7.25) for instance, we use the relations

$$\sum_i (\Delta\alpha ar | \Delta_i)\sigma_{ik}(g) = \sum_s D^a_{rs}(g)(\Delta\alpha as | \Delta_k) \tag{7.26}$$

$$\sum_{km} \sigma^S_{lk}(g)\sigma^C_{nm}(g)\tau^2(^{\Delta SC}_{jkm}) = \sum_i \tau^2(^{\Delta SC}_{iln})\sigma_{ij}(g) \tag{7.27}$$

and (2.25). This shifting finally results in:

$$\sum_q D^s_{pq}(g)X(^{ss'}_{qq'}) = \sum_r X(^{ss'}_{pr})D^{s'}_{rq}(g) \tag{7.28}$$

Thus X would achieve a similarity transformation between irreducible
representations. According to Schur's lemma follows:

$$X(^{ss'}_{qq'}) = \delta(s,s')\delta(q,q')\cdot X(^{ss}_{qq}) \quad ,$$

where $X(^{ss}_{qq})$ does not depend on q. By summation for q with (7.22), fi-
nally follows (7.25).

8. Triangular invariants

The most important examples of functions defined on triangles are the molecular three-centre nuclear-attraction integrals. Because of the expansion theorem (7.11) they can be factorized as follows:

$$\langle Ai\varphi_a am | \, |\vec{r}-\vec{C_1}|^{-1} | Bk\varphi_b bq\rangle \tag{8.1}$$

$$= \sum_{\varepsilon\gamma c} \sum_{\Delta j} (A\varphi_a \| Cr^{-1} \| B\varphi_b b)^{\varepsilon}_{\Delta\gamma c} \sqrt{Z(\Delta)} \tau \binom{\Delta ACB}{jikl} \binom{a^+b \; c^+}{m \; q \; n}^{\varepsilon} (\Delta_j | \Delta\gamma cn)$$

By this relation the tricentric, reduced matrix elements $(A.a\|C.\|B.b)^{\varepsilon}_{\Delta\gamma c}$ are defined, the abbreviation of which shall be TRM. Because of the limited, graphical possibilities the symbol of the TRM turns out somewhat similar to that of the BRM. But the third centre of the operator and the index referring to a set of equivalent triangles should suffice for a distinction.

In order to prove (8.1), we consider the expression,

$$I^{\varepsilon c}_n(\vec{A_i},\vec{C_1},\vec{B_k}) = \sum \binom{a^+b \; c^+}{m \; q \; n}\vec{\varepsilon}^* \cdot \text{dimc} \cdot \langle Ai\varphi_a am | \, |\vec{r}-\vec{C_1}|^{-1} | Bk\varphi_b bq\rangle . \tag{8.2}$$

According to (7.10), $I^{\varepsilon c}_n$ is a function of the triangles Δ_j:

$$I^{\varepsilon c}_n(\Delta_j) = \sum_{ilk}\sqrt{Z(\Delta)}\tau\binom{\Delta ACB}{jilk} \cdot I^{\varepsilon c}_n(\vec{A_i},\vec{C_1},\vec{B_k}) \tag{8.3}$$

Noting (7.11), we can readily expand $I^{\varepsilon c}_n$ in triangular SALC coefficients. Since $I^{\varepsilon c}_n$ transforms according to the representation c, the expansion is limited to the coefficients $(\Delta_j|\Delta\gamma cn)$:

$$I^{\varepsilon c}_n(\Delta_j) = \sum_\gamma (A\varphi_a a\|Cr^{-1}\|B\varphi_b b)^{\varepsilon}_{\Delta\gamma c}(\Delta_j|\Delta\gamma cn) \tag{8.4}$$

We now invert the relations (8.2) and (8.3), using (2.27) and (7.14):

$$\langle Ai\varphi_a am | \, |\vec{r}-\vec{C_1}|^{-1} | Bk\varphi_b bq\rangle = \sum_{\varepsilon cn}\binom{a^+b \; c^+}{m \; q \; n}^{\varepsilon} \cdot I^{\varepsilon c}_n(\vec{A_i},\vec{C_1},\vec{B_k}) \tag{8.5}$$

$$I^{\varepsilon c}_n(\vec{A_i},\vec{C_1},\vec{B_k}) = \sum_{\Delta j}\sqrt{Z(\Delta)}\tau\binom{\Delta ACB}{jilk} \cdot I^{\varepsilon c}_n(\Delta_j) \tag{8.6}$$

Inserting now (8.4) and (8.6) into (8.5) we get (8.1).

If we invert (8.4) by (7.5), we get

$$(A\varphi_a a\|Cr^{-1}\|B\varphi_b b)^{\varepsilon}_{\Delta\gamma c} \tag{8.7}$$

$$= \sum_{jilk}(\Delta\gamma cn|\Delta_j)\sqrt{Z(\Delta)}\tau\binom{\Delta ACB}{jilk}\text{dimc}\binom{a^+b \; c^+}{m \; q \; n}\vec{\varepsilon}^*\langle Ai\varphi_a am | \, |\vec{r}-\vec{C_1}|^{-1} | B\varphi_b bq\rangle$$

which is needed in section 15.

Because of the factorization of the topological matrix given in (7.17), eq.(8.1) takes the following form, which is appropriate for further calculations:

$$\langle Ai\varphi_a am | \, |\vec{r}-\vec{C_1}|^{-1} | Bk\varphi_b bq\rangle = \sum_{\varepsilon\gamma c\Delta jSr} \sum (A\varphi_a a\|Cr^{-1}\|B\varphi_b b)^{\varepsilon}_{\Delta\gamma c}\sqrt{Z(\Delta)Z(-ABS)'}$$

$$\cdot\tau\binom{-ABS}{ikr}\tau^2\binom{\Delta SC}{jrl}\binom{a^+b \; c^+}{m \; q \; n}^{\varepsilon}(\Delta_j|\Delta\gamma cn) \tag{8.8}$$

The main application of (8.1 or 8) is the calculation of the matrix elements of the nuclear potential

$$V = \sum_{Cl} Q_C / |\vec{r} - \vec{C_1}| \, ,$$
(8.9)

where Q_C is the charge of the atoms of set C. The potential contains the totally symmetric partial sums

$$V_C = \sum_1 1 / |\vec{r} - \vec{C_1}| \, ,$$
(8.10)

because these sums are just the totally symmetric linear combinations of the operators $1/|\vec{r} - \vec{C_1}|$. We rewrite these sums in the terminology of (5.1/2). The symmetry species occurring in these formulae are all totally symmetric, i.e. a=e=c=1:

$$V_C = \sqrt{Z(C)} \cdot \sum_1 (\vec{C_1}|C11) \cdot |\vec{r} - \vec{C_1}|^{-1}$$
(8.11)

Since the improper two-centre integrals of the entire molecular potential trace back to the three-centre nuclear-attraction integrals, we now can expresses the BRMs of the molecular potential V, or ratherof the partial sums V_C by the TRMs. Because of (8.11), the matrix elements are

$$\langle Ai\varphi_a am | V_C | Bk\varphi_b bq \rangle = \sqrt{Z(C)} \sum_1 (\vec{C_1}|C11) \langle Ai\varphi_a am | |\vec{r} - \vec{C_1}|^{-1} | Bk\varphi_b bq \rangle$$

and further with (8.8):

$$\langle Ai\varphi_a am | V_C | Bk\varphi_b bq \rangle = \sum_{\varepsilon \gamma c} \sum_{\Delta Sr} (A\varphi_a a \| Cr^{-1} \| B\varphi_b b)_{\Delta \gamma c}^{\varepsilon} \sqrt{Z(\Delta)Z(-ABS)Z(C)}$$

$$\cdot \tau \binom{-ABS}{ikr} \binom{a^+ b \ c^+}{m \ q \ n} \varepsilon \sum_{jl} \tau^2 \binom{\Delta SC}{jrl} (\Delta_j | \Delta \gamma cn)(\vec{C_1}|C11)$$
(8.12)

Reshaping (7.25), the sum for j and l is found to be

$$\sum_{jl} \tau^2 \binom{\Delta SC}{jrl} (\Delta_j | \Delta \gamma cn)(\vec{C_1}|C11) = \text{dimc}^{-1} \sum_\sigma PIs^2 \begin{pmatrix} \Delta & S & C \\ \gamma & \sigma_+ \\ c & c_{+1} \end{pmatrix} (\vec{S_r}|S\sigma cn).$$
(8.13)

If we now insert (8.13) into (8.12) and then introduce the result into (4.10), we finally get the intended relationship:

$$(A\varphi_a a \| V_C \| B\varphi_b b)_{S\sigma c}^{\varepsilon} = \sum_{\Delta \gamma} (A\varphi_a a \| Cr^{-1} \| B\varphi_b b)_{\Delta \gamma c}^{\varepsilon} \sqrt{Z(\Delta)Z(C)} \cdot PIs^2 \begin{pmatrix} \Delta & S & C \\ \gamma & \sigma_+ \\ c & c_{+1} \end{pmatrix}$$
(8.14)

This shows that all the TRMs, the orbitals of which adjoin to the edges of type S, contribute to the BRMs belonging to type S. The geometric relationship is mediated by a polyhedral isoscalar of the second kind, which is relatively simple:

$$PIs^2 \begin{pmatrix} \Delta & S & C \\ \gamma & \sigma_+ \\ c & c_{+1} \end{pmatrix} = (1/\sqrt{Z(C)\text{dimc}}) \sum_{jrl} \tau^2 \binom{\Delta SC}{jrl} (\Delta_j | \Delta \gamma cq)(S\sigma cq | \vec{S_r})$$
(8.15)

Introducing (8.14) into (5.13) allows to express all matrix elements of the potential V_C with respect to the s.-a. MOs by the TRMs. Since this relationship is often needed, we integrate it by a geometrical factor:

$$\langle(A\varepsilon e,\varphi_a a)\gamma c\|V_C\|(B\varphi f,\varphi_b b)\delta c\rangle = \sum_z GEO_2(x,y,z)\cdot(A\varphi_a a\|Cr^{-1}\|B\varphi_b b)_{\Delta\alpha k}^{\eta} \qquad (8.16)$$

with the collective indices $x=(Aa,Bb,C)$, $y=(\varepsilon e,\varphi f,\gamma\delta c)$ and $z=(\Delta\alpha k,\eta)$. The geometrical factor is given by:

$$GEO_2(x,y,z) = \sqrt{Z(\Delta)Z(C)dimc}\cdot\sum_{\beta S\sigma k}\sqrt{Z(-ABS)/dimk}\{b\}\{c^+fb\delta\}\{eb^+k\eta\}$$

$$\cdot\begin{Bmatrix}e & f^+k^+\\b^+a^+c^+\end{Bmatrix}_{\gamma\delta\eta\beta}PIs\begin{pmatrix}-A & B & S\\\varepsilon & \varphi & \sigma\\e^+f & k\end{pmatrix}_\beta PIs^2\begin{pmatrix}\Delta & S & C\\\alpha & \sigma\\k & k^+1\end{pmatrix} \qquad (8.17)$$

The double sum for S and σ connecting the two polyhedral isoscalars results from the decomposition (7.17) and represents the higher polyhedral isoscalar related to (7.7):

$$PIs\begin{pmatrix}\Delta & A & C & B\\\alpha & \varepsilon_{+1} & \varphi\\k & e^+1 & f\end{pmatrix}_\beta = \sum_{S\sigma}\sqrt{Z(-ABS)}\cdot PIs\begin{pmatrix}-A & B & S\\\varepsilon & \varphi & \sigma\\e^+f & k\end{pmatrix}_\beta\cdot PIs^2\begin{pmatrix}\Delta & S & C\\\alpha & \sigma\\k & k^+1\end{pmatrix} \qquad (8.18)$$

$$= \sqrt{1/Z(C)}\sum_{jilk}\tau\begin{pmatrix}\Delta ACB\\jilk\end{pmatrix}(A\varepsilon ep|\vec{A}_1)(\vec{B}_k|B\varphi fq)(\Delta_j|\Delta\alpha kr)\begin{pmatrix}e^+f & k\\p & q & r\end{pmatrix}_\beta^*$$

If this isoscalar is introduced, the geometrical factor takes the form:

$$GEO_2(x,y,z) = \sqrt{Z(\Delta)Z(C)}\sum_{\beta k}\sqrt{dimc/dimk}\{b\}\{c^+fb\delta\}\{eb^+k\eta\}$$

$$\cdot\begin{Bmatrix}e & f^+k^+\\b^+a^+c^+\end{Bmatrix}_{\gamma\delta\eta\beta}\cdot PIs\begin{pmatrix}\Delta & A & C & B\\\alpha & \varepsilon_{+1} & \varphi\\k & e^+1 & f\end{pmatrix}_\beta \qquad (8.19)$$

9. Symmetry-adapted geminals and densities

Preparatory to the discussion of the two-particle integrals, we explain the composition of two-particle functions and one-particle densities. The starting point are the atomic orbitals (4.1/3). The usual proceeding is as follows: forming the s.-a. LCAOs according to (5.1/2) and coupling two of these MOs yielding the s.-a. geminals:

$$\left| \left[(A\varepsilon e, \varphi_a a)\gamma c, (B\varphi f, \varphi_b b)\delta d \right]\alpha gr \right\rangle$$
$$= \{g\} \sqrt{\dim g} \cdot \sum \left({}^c_p {}^d_q {}^+g_r \right)^\alpha \left| (A\varepsilon e, \varphi_a a)\gamma cp \right\rangle \cdot \left| (B\varphi f, \varphi_b b)\delta dq \right\rangle \tag{9.1}$$

For sake of clarity, we repeat this equation omitting the multiplicity indices and readily inserting (5.1) into (9.1):

$$\left| \left[(Ae, a)c, (Bf, b)d \right]gr \right\rangle$$
$$= \{g\} \sqrt{\dim g} \cdot \sum_{ijmn} \left({}^c_p {}^d_q {}^+g_r \right) \cdot K(cp, Aie, am) \cdot K(dq, Bjf, bn) \cdot \left| Aiam \right\rangle \cdot \left| Bjbn \right\rangle \tag{9.2}$$

Another possible construction of symmetric geminals in the spirit of valence bond theory is as follows: We directly couple the product of the two AOs and size them according to the distance vectors between their atomic centres:

$$\left| [A, B]Sk, [\varphi_a a, \varphi_b b]\beta ht \right\rangle$$
$$= \{h\} \sqrt{Z(-ABS)\dim h} \cdot \sum_{ij} \tau \left({}^{-ABS}_{ijk} \right) \left({}^a_m {}^b_n {}^+h_t \right)^\beta \cdot \left| Ai\varphi_a am \right\rangle \cdot \left| Bj\varphi_b bn \right\rangle \tag{9.3}$$

One now notices that these two-centre or edge geminals transform according to the direct product representation $\sigma^S \times h$. The final symmetry-adaption then is achieved by

$$\left| ([A, B]S\sigma s, [\varphi_a a, \varphi_b b]\beta h)\mu gr \right\rangle = \sum_{kt} K(\mu gr, Sk\sigma s, ht) \left| [A, B]Sk, [\varphi_a a, \varphi_b b]\beta ht \right\rangle \tag{9.4}$$

This construction was already mentioned in [11], eq.(39). But also in the preceeding sections 4 and 8, (9.3/4) is implicitly contained with the difference that not orbitals of two different particles were coupled yielding a s.-a. geminal but the bra and ket orbitals of one particle yielding a s.-a. density. Hence the derivation of (4.4/6) and (8.1) can be achieved in analogy to (9.3/4) by forming consecutively the one-particle densities:

$$\left[\vec{r} \middle| (Ai\varphi_a a^+, Bj\varphi_b b)\beta ht \right] = \sqrt{\dim h} \cdot \sum \left({}^a_m {}^b_n {}^+h_t \right)^\beta \cdot \left\langle Ai\varphi_a am \middle| \vec{r} \right\rangle \left\langle \vec{r} \middle| Bj\varphi_b bn \right\rangle \tag{9.5}$$

$$\left[\vec{r} \middle| [A, B]Sk, [\varphi_a a^+, \varphi_b b]\beta ht \right] = \sqrt{Z(-ABS)} \sum_{ij} \tau \left({}^{-ABS}_{ijk} \right) \cdot \left[\vec{r} \middle| (Ai\varphi_a a^+, Bj\varphi_b b)\beta ht \right] \tag{9.6}$$

and finally the s.-a. density:

$$\left[\vec{r} \middle| ([A, B]S\sigma s, [\varphi_a a^+, \varphi_b b]\beta h)\mu gr \right] =$$
$$= \sum_{kt} K(\mu gr, Sk\sigma s, ht) \cdot \left[\vec{r} \middle| [A, B]Sk, [\varphi_a a^+, \varphi_b b]\beta ht \right] \tag{9.7}$$

The square brackets on the left-hand side are justified by the relation-

ship to the integrals (11.1 and 7). In the case of (4.4/6), subsequently, the density and the tensor operator have to be coupled. Then follows the integration with respect to $\vec{r}$. The s.-a. density also occurs in the two-particle integrals.

Both types of geminals (9.1 and 2) must be related by a unitary transformation, since only the order of different couplings has been interchanged. The transformation does not depend on the special type of orbitals, i.e. the quantum numbers φ_a and φ_b, and not on the component r. We then have to calculate the coefficients of the expansion

$$|([A,B]S\sigma s,[\varphi_a a,\varphi_b b]\beta h)\mu gr\rangle$$

$$= \sum_{\varepsilon e\gamma c\varphi f\delta d\alpha} \langle[(A\varepsilon e,a)\gamma c,(B\varphi f,b)\delta d]\alpha g|([A,B]S\sigma s,[a,b]\beta h)\mu g\rangle \qquad (9.8)$$

$$\cdot |[(A\varepsilon e,\varphi_a a)\gamma c,(B\varphi f,\varphi_b b)\delta d]\alpha gr\rangle$$

If we use orthonormalized atomic orbitals like δ-functions the coefficients are the overlap integrals of the geminals (9.1 and 4). Because of $\langle Ai\varphi_a am|Bk\varphi_b bn\rangle = \delta(A,B)\delta(i,k)\delta(a,b)\delta(m,n)$, we get:

$$\langle[(A\varepsilon e,a)\gamma c,(B\varphi f,b)\delta d]\alpha g|([A,B]S\sigma s,[a,b]\beta h)\mu g\rangle$$

$$= \sqrt{Z(-ABS)\overline{\dim h \cdot \dim c \cdot \dim d}} \cdot \sum_\pi PIs \begin{pmatrix} -A & B & S \\ \varepsilon & \varphi & \sigma \\ e^+ & f^+ & s \end{pmatrix}_\pi \cdot \begin{Bmatrix} c^+d^+g \\ e \quad f \quad s^+ \\ a \quad b \quad h^+ \end{Bmatrix}_\pi \begin{matrix} \alpha \\ \pi \\ \beta \end{matrix} \quad (9.9)$$
$$\gamma \quad \delta \quad \mu$$

The same transformation applies to the densities, and theorem (5.5) is the result of this recoupling. The geometrical factor (5.7) is equal to (9.9) except for a different normalization and phase.

10. Pseudo-tetrahedral coefficients

We now treat the pseudo-tetrahedra with numbered vertices just as the oriented triangles in section 7. The principles have been lined out there.

If $\mathcal{T}$ is the symbol of a set of equivalent pseudo-tetrahedra $\mathcal{T}_i$, then the eqs.(7.1 to 6) apply with the substitution of $\mathcal{T}$ for Δ (and $\mathcal{U}$ for Θ respectively). We therefore do not repeat them here. We shall term the coefficients of the quadrocentric linear combinations QSALC coefficients, $(\mathcal{T}_i | \alpha\alpha p)$. Quadrocentric linear combinations are s.-a. linear combinations of quadrocentric "objects", especially four-centre integrals. We use the mixtum compositum "quadrocentric" instead of tetracentric, because the letter T has already been used as an abbreviation of tricentric.

The relationship between the tetrahedra and the vertices is again expressed by a topological matrix:

$$\tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\ijklm\end{smallmatrix}\right) = \begin{cases} 1/\sqrt{Z(\mathcal{T})} & \text{if } \vec{A}_j, \vec{B}_k, \vec{C}_1, \vec{D}_m \text{ in this order are the vertices of } \mathcal{T}_i. \\ 0 & \text{otherwise} \end{cases} \tag{10.1}$$

where $Z(\mathcal{T})$ is the number of equivalent tetrahedra in the set $\mathcal{T}$. And again, we associate a vector $\vec{R}_i$ to each pseudo-tetrahedron $\mathcal{T}_i$ by

$$\vec{R}_i = \sqrt{Z(\mathcal{T})} \cdot \sum_{jklm} \tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\ijklm\end{smallmatrix}\right) \cdot (\mu_1\vec{A}_j + \mu_2\vec{B}_k + \mu_3\vec{C}_1 + \mu_4\vec{D}_m), \tag{10.2}$$

and consequently have

$$(\mathcal{T}_i | \mathcal{T}\alpha p) = (\vec{R}_i | R\alpha p), \tag{10.3}$$

which is used to calculate the QSALC coefficients. For details cf. section 7.

Again functions of four centres, $F(\vec{A}_j, \vec{B}_k, \vec{C}_1, \vec{D}_m)$, are regarded as functions of the pseudo-tetrahedra,

$$F(\mathcal{T}_i) = \sqrt{Z(\mathcal{T})} \cdot \sum_{jklm} \tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\ijklm\end{smallmatrix}\right) \cdot F(\vec{A}_j, \vec{B}_k, \vec{C}_1, \vec{D}_m), \tag{10.4}$$

and can be expanded in QSALC coefficients:

$$F(\mathcal{T}_i) = (\mathcal{T}_i | F) = \sum_{\alpha a} (\mathcal{T}_i | \mathcal{T}\alpha p)(\mathcal{T}\alpha p | F) \tag{10.5}$$

with

$$(\mathcal{T}\alpha p | F) = \sum_i (\mathcal{T}\alpha p | \mathcal{T}_i)(\mathcal{T}_i | F). \tag{10.6}$$

The topological matrices (10.1) have the orthogonality relations:

$$\sum_{jklm} \tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\ijklm\end{smallmatrix}\right)\tau\left(\begin{smallmatrix}\mathcal{U}ABCD\\njklm\end{smallmatrix}\right) = \delta(\mathcal{T},\mathcal{U})\delta(i,n)/Z(\mathcal{T}) \tag{10.7}$$

$$\sum_{\mathcal{T}i} Z(\mathcal{T})\tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\ijklm\end{smallmatrix}\right)\tau\left(\begin{smallmatrix}\mathcal{T}ABCD\\irstu\end{smallmatrix}\right) = \delta(j,r)\delta(k,s)\delta(1,t)\delta(m,u) \tag{10.8}$$

Again we can reduce the topological matrix (10.1) by a factorization. For this purpose, we characterize the pseudo-tetrahedra by two opposite

edge vectors, which link the vertices 1 and 3, and 2 and 4 respectively. This relationship is expressed by:

$$\tau^3\begin{pmatrix}\mathcal{F}ST\\ikl\end{pmatrix} = \begin{cases} 1/\sqrt{Z(\mathcal{F})} & \text{if } \vec{S_k} \text{ links the vertices 1 and 2, and } \vec{T_1} \text{ links} \\ & \qquad\qquad \text{the vertices 2 and 4.} \\ 0 & \text{otherwise} \end{cases} \qquad (10.9)$$

The factorization then is given by:

$$\tau\begin{pmatrix}\mathcal{F}ABCD\\ijklm\end{pmatrix} = \sum_{Ss}\sum_{Tt}\tau^3\begin{pmatrix}\mathcal{F}ST\\st\end{pmatrix}\sqrt{Z(-ACS)}\tau\begin{pmatrix}-ACS\\jls\end{pmatrix}\sqrt{Z(-BDT)}\tau\begin{pmatrix}-BDT\\kmt\end{pmatrix} \qquad (10.10)$$

The topological matrix τ^3 now is treated just as τ^2 in section 7. The orthogonality relations are:

$$\sum_{st}\tau^3\begin{pmatrix}\mathcal{F}ST\\ist\end{pmatrix}\tau^3\begin{pmatrix}\mathcal{U}ST\\jst\end{pmatrix} = \delta(\mathcal{F},\mathcal{U})\delta(i,j)/Z(\mathcal{F}) \qquad (10.11)$$

$$\sum_{\mathcal{F}i}Z(\mathcal{F})\tau^3\begin{pmatrix}\mathcal{F}ST\\ist\end{pmatrix}\tau^3\begin{pmatrix}\mathcal{F}ST\\ipq\end{pmatrix} = \delta(s,p)\delta(t,q) \qquad (10.12)$$

The transformation into the s.-a. basis yields:

$$\tau^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\\xyz\end{pmatrix} = \sum_{ist}\tau^3\begin{pmatrix}\mathcal{F}ST\\ist\end{pmatrix}(\mathcal{F}_i|\mathcal{F}\alpha ax)(\vec{S_s}|S\sigma by)(\vec{T_t}|T\tau cz) \qquad (10.13)$$

with the subsequent factorization

$$\tau^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\\xyz\end{pmatrix} = \sum_\varepsilon PIs^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\end{pmatrix}_\varepsilon \cdot\begin{pmatrix}abc\\xyz\end{pmatrix}\varepsilon, \qquad (10.14)$$

where the "polyhedral isoscalar of the third kind" is given by:

$$PIs^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\end{pmatrix}_\varepsilon = \sum_{ist}\tau^3\begin{pmatrix}\mathcal{F}ST\\ist\end{pmatrix}(\mathcal{F}_i|\mathcal{F}\alpha ax)(\vec{S_s}|S\sigma by)(\vec{T_t}|T\tau cz)\begin{pmatrix}abc\\xyz\end{pmatrix}\varepsilon^* \qquad (10.15)$$

From (10.11/12), one derives the orthogonality relations:

$$\sum_{\sigma b}\sum_{\tau c\varepsilon}PIs^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\end{pmatrix}_\varepsilon^* PIs^3\begin{pmatrix}\mathcal{U}ST\\\beta\sigma\tau\\abc\end{pmatrix}_\varepsilon = \delta(\mathcal{F},\mathcal{U})\delta(\alpha,\beta)\text{dima}/Z(\mathcal{F}) \qquad (10.16)$$

$$\sum_{\mathcal{F}\alpha}Z(\mathcal{F})PIs^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\end{pmatrix}_\varepsilon^* PIs^3\begin{pmatrix}\mathcal{F}ST\\\alpha\sigma\tau\\abc\end{pmatrix}_\eta = \delta(\sigma,\sigma)\delta(b,b)\delta(\tau,\tau)\delta(c,c)\delta(\varepsilon,\eta)\cdot\text{dima} \qquad (10.17)$$

Without the factorization (10.10) a rather complex polyhedral isoscalar results from (10.1):

$$PIs\begin{pmatrix}\mathcal{F}ABCD\\\tau\alpha\beta\gamma\delta\\tabcd\end{pmatrix}_{\varepsilon e\varphi f\mu} = \sum_{qi}\sum_{jkl}\tau\begin{pmatrix}\mathcal{F}ABCD\\qijkl\end{pmatrix}(\mathcal{F}_q|\mathcal{F}\tau tp_t)(\vec{A_i}|A\alpha ap_a)(\vec{B_j}|B\beta bp_b)$$

$$\cdot(\vec{C_k}|C\gamma cp_c)(\vec{D_l}|D\delta dp_d)\text{dime}\cdot\text{dimf}\begin{pmatrix}a\ c\ e\\p_a p_c p_e\end{pmatrix}\varepsilon^*\begin{pmatrix}f\ b\ d\\p_f p_b p_d\end{pmatrix}\varphi^*\begin{pmatrix}t\ e\ f\\p_t p_e p_f\end{pmatrix}\mu^* \qquad (10.18)$$

The subsequent application of (10.10) splits up this coefficient as follows:

$$PIs\begin{pmatrix}\mathcal{F}ABCD\\\tau\alpha\beta\gamma\delta\\tabcd\end{pmatrix}_{\varepsilon e\varphi f\mu} = \sum_{S\varepsilon T\varphi}\sqrt{Z(-ACS)Z(-BDT)}\cdot PIs\begin{pmatrix}-ACS\\\alpha\gamma\varepsilon'\\ace\end{pmatrix}_\varepsilon PIs\begin{pmatrix}-BDT\\\beta\delta\varphi'\\bdf\end{pmatrix}_\varphi PIs^3\begin{pmatrix}\mathcal{F}ST\\\tau\varepsilon'\varphi'\\tef\end{pmatrix}_\mu \qquad (10.19)$$

11. Two-particle interaction

11.1. The four-centre integrals

The interaction of the molecular electrons is, except for relativistic effects, represented by the scalar operator $1/r_{12}$, which in general yields four-centre integrals over the atomic orbitals. As now can be foreseen, these integrals can be expanded in QSALC coefficients according to (10.5).

With respect to the four orbitals there are different coupling modes. Either the orbitals in the bra and in the ket are coupled separately yielding two-centre geminals, or the orbitals referring to the same particle are coupled resulting in two s.-a. densities. Whereas the first coupling mode takes into account the separation of the interaction according to electron pairs, the second mode is more capable for the calculation of the integrals. This aspect, being more important in the present context, is accentuated by passing over to the notation usual in quantum chemistry (cf. [35, 36]):

$$\langle Ai\varphi_a am, Bj\varphi_b bn | r_{12}^{-1} | Ck\varphi_c cp, Dl\varphi_d dq \rangle = [Ai\varphi_a a^+ m, Ck\varphi_c cp | r_{12}^{-1} | Bj\varphi_b b^+ n, Dl\varphi_d dq] \tag{11.1}$$

Since the square brackets are defined without complex conjugation, the conjugated representations a^+ and b^+ show up explicitly.

Using the two-centre densities (9.5), the integrals (11.1) are reduced to

$$[Ai\varphi_a a^+ m, Ck\varphi_c cp | r_{12}^{-1} | Bj\varphi_b b^+ n, Dl\varphi_d dq] \tag{11.2}$$

$$= \sum_{\varepsilon e\varphi f} [(Ai\varphi_a a^+, Ck\varphi_c c)\varepsilon er | r_{12}^{-1} | (Bj\varphi_b b^+, Dl\varphi_d d)\varphi fs] \sqrt{\text{dime} \cdot \text{dimf}} \begin{pmatrix} a^+c & e \\ m & p & r \end{pmatrix} \varepsilon \begin{pmatrix} f^+b^+d \\ s & n & q \end{pmatrix} \varphi$$

Note that, in contrast to the one-centre integrals of scalar operators, the representations e and f may be different.

The integrals of the right-hand side now are further reduced by the factorization theorem:

$$[(Ai\varphi_a a^+, Ck\varphi_c c)\varepsilon er | r_{12}^{-1} | (Bj\varphi_b b^+, Dl\varphi_d d)\varphi fs] \tag{11.3}$$

$$= \sum_{\mathcal{F}} \sum_{t \tau \mu g} \tau \begin{pmatrix} \mathcal{F} ABCD \\ t i j k l \end{pmatrix} \sqrt{Z(\mathcal{F})} [(A\varphi_a a^+, B\varphi_b b)\varepsilon e \| r_{12}^{-1} \|(B\varphi_b b^+, D\varphi_d d)\varphi f]^\mu_{\mathcal{F} \tau g} \begin{pmatrix} e^+f & g \\ r & s & u \end{pmatrix} \mu (\mathcal{F}_t | \mathcal{F}_\tau gu)$$

By this relation, the quadrocentric, reduced matrix elements, QRM, are defined. They give the following informations: A QRM belongs to a set $\mathcal{F}$ of tetrahedra, the representation of which is reduced to g (multiplicity τ) by symmetry-adaption; the two-centre densities are coupled yielding the representations e (multiplicity ε) and f (multiplicity φ); finally the coupling of e and f has to yield representation g again (with multiplicity μ).

The proof is as for (4.4/6) or (8.1). Omitting the multiplicities again accentuates the essential structure:

$$[Aia^+m,Ckcp|r_{12}^{-1}|Bjb^+n,Dldq] \tag{11.4}$$

$$= \sum_{ef}[(Aia^+,Ckc)er|r_{12}^{-1}|(Bjb^+,Dld)fs]\sqrt{dime\cdot dimf}\begin{pmatrix}a^+c&e\\m&p&r\end{pmatrix}\begin{pmatrix}f^+b^+d\\s&n&q\end{pmatrix}$$

and

$$[(Aia^+,Ckc)er|r_{12}^{-1}|(Bjb^+,Dld)fs] \tag{11.5}$$

$$= \sum_{\mathfrak{F}tg}\tau\binom{\mathfrak{F}ABCD}{tijkl}\sqrt{Z(\mathfrak{F})}[(Aa^+,Cc)e\|r_{12}^{-1}\|(Bb^+,Dd)f]_{\mathfrak{F}g}\begin{pmatrix}e^+f&g\\r&s&u\end{pmatrix}(\mathfrak{F}_t|\mathfrak{F}gu)$$

The sums for $\mathfrak{F}$ and t contain one non-zero summand only, since they sort out the right pseudo-tetrahedron. Only that for g (and u) is a true sum.

11.2. The matrix elements of the s.-a. molecular orbitals and geminals

The next aim is the calculation of the matrix elements of the operator $1/r_{12}$ with respect to the s.-a. LCAO-MOs (5.1) and the geminals (9.1).

Since now four centres are involved, we need a more economical and compact notation to manage all the quantum numbers. We rewrite (5.1) as follows:

$$|\Lambda\dot{a}p_a\rangle = |(A\dot{a}\dot{a}',\alpha a)\dot{a}\dot{a}p_a\rangle = \sum_{im_a}K(\dot{a}\dot{a}p_a,Ai\dot{a}\dot{a}',am_a)\cdot|Ai\alpha am_a\rangle \tag{11.6}$$

The letters a and α always point to the centres of set A (b and β to B respectively). Λ is a collective index for $(A\dot{a}\dot{a}',\alpha a)\dot{a}$. We further introduce $\Lambda^+=(A\dot{a}\dot{a}'^+,\alpha a^+)\dot{a}$.

As for the integrals (11.1), there are two possible notations of the integrals of the MOs (11.6):

$$\langle\Lambda\dot{a}p_a,\mathcal{B}\dot{b}p_b|r_{12}^{-1}|\mathcal{C}\dot{c}p_c,\mathcal{D}\dot{d}p_d\rangle = [\Lambda^+\dot{a}^+p_a,\mathcal{C}\dot{c}p_c|r_{12}^{-1}|\mathcal{B}^+\dot{b}^+p_b,\mathcal{D}\dot{d}p_d] \tag{11.7}$$

Consequently, there are two types of reduced matrix elements. In the particle-coupling, the application of the WET yields:

$$\langle\Lambda\dot{a}p_a,\mathcal{B}\dot{b}p_b|r_{12}^{-1}|\mathcal{C}\dot{c}p_c,\mathcal{D}\dot{d}p_d\rangle$$
$$= \sum_{\sigma\mu s}\langle(\Lambda\dot{a},\mathcal{B}\dot{b})\sigma s\|r_{12}^{-1}\|(\mathcal{C}\dot{c},\mathcal{D}\dot{d})\mu s\rangle\cdot dims\begin{pmatrix}\dot{a}^+\dot{b}^+s\\p_ap_bp_s\end{pmatrix}\sigma\begin{pmatrix}s^+\dot{c}&\dot{d}\\p_sp_cp_d\end{pmatrix}\mu \tag{11.8}$$

and in the density coupling:

$$\langle\Lambda\dot{a}p_a,\mathcal{B}\dot{b}p_b|r_{12}^{-1}|\mathcal{C}\dot{c}p_c,\mathcal{D}\dot{d}p_d\rangle \tag{11.9}$$
$$= \sum_{\tau\pi t}[(\Lambda^+\dot{a}^+,\mathcal{C}\dot{c})\tau t\|r_{12}^{-1}\|(\mathcal{B}^+\dot{b}^+,\mathcal{D}\dot{d})\pi t]\cdot dimt\begin{pmatrix}\dot{a}^+\dot{c}&t\\p_ap_cp_t\end{pmatrix}\tau\begin{pmatrix}t^+\dot{b}^+\dot{d}\\p_ap_cp_t\end{pmatrix}\pi$$

Both types of reduced matrix elements are interrelated by 6j symbols (cf.[17]):

$$\langle(\Lambda\dot{a},\mathcal{B}\dot{b})\sigma s\|r_{12}^{-1}\|(\mathcal{C}\dot{c},\mathcal{D}\dot{d})\mu s\rangle \tag{11.10}$$
$$= \sum_{\tau\pi t}\begin{Bmatrix}\dot{a}&\dot{b}&s^+\\\dot{d}&\dot{c}&t\end{Bmatrix}_{\tau\pi\mu\sigma}\{\dot{c}\dot{d}s^+\mu\}\{\dot{b}^+\dot{d}t\pi\}dimt\cdot[(\Lambda^+\dot{a}^+,\mathcal{C}\dot{c})\tau t\|r_{12}^{-1}\|(\mathcal{B}^+\dot{b}^+,\mathcal{D}\dot{d})\pi t]$$

The reduced matrix elements in the particle coupling are also immediately related to the integrals of the s.-a. geminals (9.1) now taking

the form:

$$|(\dot{A}\dot{a},\not{B}\dot{b})\sigma sp_s\rangle = \{s\}\sqrt{dims}\cdot\sum\binom{\dot{a}^+\dot{b}^+s}{p_ap_bp_s}^\sigma\cdot|\dot{A}\dot{a}p_a\rangle\cdot|\not{B}\dot{b}p_b\rangle \qquad (11.11)$$

The interaction integrals of these geminals are:

$$\langle(\dot{A}\dot{a},\not{B}\dot{b})\sigma sp_s|r_{12}^{-1}|(\not{C}\dot{c},\not{D}\dot{d})\mu sp_s\rangle$$

$$= \delta(s,s)\delta(p_s,p_s)dims^{-1}\langle(\dot{A}\dot{a},\not{B}\dot{b})\sigma s\|r_{12}^{-1}\|(\not{C}\dot{c},\not{D}\dot{d})\mu s\rangle, \qquad (11.12)$$

where the reduced matrix elements on the right are those of eq.(11.6).

The reduced matrix elements defined in (11.8/9) now must be traced back to the QRMs. Since (11.9) as well as (11.3) are based on the density coupling, their interrelation is more direct:

$$\left[(\dot{A}^+\dot{a}^+,\not{C}\dot{c})\tau t\|r_{12}^{-1}\|(\not{B}^+\dot{b}^+,\not{D}\dot{d})\pi t\right]$$

$$= \sum_{\varepsilon e\varphi f}\sum_{\mu\sigma g\tilde{S}}GEO_3(\varepsilon e\varphi f\mu,\tilde{S}\sigma g)\cdot\left[(A\alpha a^+,C\gamma c)\varepsilon e\|r_{12}^{-1}\|(B\beta b^+,D\delta d)\varphi f\right]_{\tilde{S}\sigma g}^\mu \qquad (11.13)$$

The geometrical factor is derived as follows. We invert (11.9):

$$\left[(\dot{A}^+\dot{a}^+,\not{C}\dot{c})\tau t\|r_{12}^{-1}\|(\not{B}^+\dot{b}^+,\not{D}\dot{d})\pi t\right]$$

$$= \sum\binom{\dot{a}^+\dot{c}\ t}{p_ap_cp_t}^{\tau*}\binom{t^+\dot{b}^+\dot{d}}{p_tp_bp_d}^{\pi*}\langle\dot{A}\dot{a}p_a,\not{B}\dot{b}p_b|r_{12}^{-1}|\not{C}\dot{c}p_c,\not{D}\dot{d}p_d\rangle, \qquad (11.14)$$

where the matrix elements of the right-hand side, because of (11.6), are given by:

$$\langle\dot{A}\dot{a}p_a,\not{B}\dot{b}p_b|r_{12}^{-1}|\not{C}\dot{c}p_c,\not{D}\dot{d}p_d\rangle = \sum_{ijklm}\sum_x K(\dot{\alpha}\dot{a}p_a,Ai\dot{\alpha}\dot{a}',am_a)^*\cdot K(\dot{\beta}\dot{b}p_b,Bj\beta\dot{b}',bm_b)^*$$

$$\cdot K(\dot{\gamma}\dot{c}p_c,Ck\gamma\dot{c}',cm_c)\cdot K(\dot{\delta}\dot{d}p_d,Dl\delta\dot{d}',dm_d)\langle Ai\alpha am_a,Bj\beta bm_b|r_{12}^{-1}|Ck\gamma cm_c,Dl\delta dm_d\rangle \qquad (11.15)$$

We now insert (11.1-3) into (11.15) and the result into (11.14). These substitutions yield the factor:

$$GEO_3(\varepsilon e\varphi f\mu,\tilde{S}\sigma g) = \sum_{ijklm}\sum_{xq}\binom{\dot{a}^+\dot{c}\ t}{p_ap_cp_t}^{\tau*}\cdot\binom{t^+\dot{b}^+\dot{d}}{p_tp_bp_d}^{\pi*}\cdot K(\alpha ap_a,Ai\dot{\alpha}\dot{a}',am_a)^*$$

$$\cdot K(\beta bp_b,Bj\beta\dot{b}',bm_b)^*\cdot K(\gamma cp_c,Ck\gamma\dot{c}',cm_c)\cdot K(\delta dp_d,Dl\delta\dot{d}',dm_d) \qquad (11.16)$$

$$\cdot\sqrt{dime\cdot dimf}\cdot\binom{a^+c\ e}{m_am_cr}^\varepsilon\binom{b^+d\ f}{m_bm_ds}^\varphi\binom{e^+f^+g}{r\ s\ u}^\mu\sqrt{Z(\tilde{S})}\tau\binom{\tilde{S}ABCD}{qijkl}\cdot(\tilde{S}_q|\tilde{S}\sigma gu)$$

This formula contains nine 3jm symbols, which now are rearranged by a two-fold application of the rule of de Shalit (2.54) and the subsequent application of (2.41):

$$GEO_3(\varepsilon e\varphi f\mu,\tilde{S}\sigma g) =$$

$$= (Z(\tilde{S})dim\dot{a}\cdot dim\dot{b}\cdot dim\dot{c}\cdot dim\dot{d}\cdot dime\cdot dimf)^{1/2}\sum_{ijklq}\sum_{\eta\varepsilon'e'\eta'\varphi'f'\mu'}dime'\cdot dimf'$$

$$\left\{\begin{matrix}a' & d'^+e' & e'\\ a & c^+e^+ & \varepsilon\\ \dot{a}^+\dot{c} & t & \tau\end{matrix}\right\}\left\{\begin{matrix}f' & b' & d'^+\\ f^+b & d^+ & \\ t^+\dot{b}^+\dot{d} & & \pi\end{matrix}\right\}^{\varphi'}_{\varphi}\cdot\left\{\begin{matrix}e' & f & g\\ f' & e' & t^+\end{matrix}\right\}_{\eta\eta'\mu\mu'}\cdot\{e'e^+tn\}\binom{a'\ c'^+e'}{r_ar_cr_e}^{\varepsilon'}\binom{f'\ b'\ d'^+}{r_fr_br_d}^{\varphi'}\binom{f'\ e'\ g}{r_fr_eu}^{\mu'*} \qquad (11.17)$$

$$\cdot(\vec{A}_i|A\dot{\alpha}\dot{a}'r_a)\cdot(\vec{B}_j|B\beta\dot{b}'r_b)\cdot(\vec{C}_k|C\gamma\dot{c}'r_c)\cdot(\vec{D}_l|D\delta\dot{d}'r_d)\cdot\tau\binom{\tilde{S}ABCD}{qijkl}\cdot(\tilde{S}_q|\tilde{S}\sigma gu)$$

The last nine factors form a scalar being nearly identical with the po-

lyhedral isoscalar (10.18):

$$GEO_3(\varepsilon e\varphi f\mu,\mathcal{S}\sigma g) = (Z(\mathcal{S})dima\cdot dimb\cdot dimc\cdot dimd\cdot dime\cdot dimf)^{1/2}\sum_{\eta\varepsilon'e'\eta'\varphi'f'\mu'}\sum\{e'e^+t\eta\} \tag{11.18}$$

$$\cdot\{e'f'g\mu'\}\cdot\begin{Bmatrix}a' & c'^+ & e' \\ a & c^+ & e^+ \\ \overset{.}{a}{}^+ & \overset{.}{c} & t \\ \alpha & \gamma & \eta\end{Bmatrix}\begin{matrix}\varepsilon' \\ \varepsilon \\ \tau\end{matrix}\begin{Bmatrix}f' & b' & d'^+ \\ f^+ & b & d^+ \\ t^+ & \overset{.}{b} & \overset{.}{d} \\ \eta' & \beta & \delta\end{Bmatrix}\begin{matrix}\varphi' \\ \varphi \\ \pi\end{matrix}\cdot\begin{Bmatrix}e & f & g \\ f^+ & e' & t^+\end{Bmatrix}_{\eta\eta'\mu\mu'}\cdot PIs\begin{pmatrix}\mathcal{S} & A & B & C & D \\ \sigma & a' & \beta' & \gamma' & \delta' \\ g & a^+ & b^+ & c' & d'\end{pmatrix}_{\varepsilon'e\varphi f\mu'}$$

As a result of the discussion in section 9, we expect that this geometrical factor contains twice a recoupling of the densities according to (9.9) or (5.7). This shows up, if we split up the polyhedral isoscalar by (10.19):

$$GEO_3(\varepsilon e\varphi f\mu,\mathcal{S}\sigma g) = F\cdot\sum_{S\mathcal{A}T\mathcal{V}}\sum_{\eta\varepsilon'e\eta'\varphi'f'\mu'}\sum\{e'e^+t\eta\}\{e'f'g\mu'\}\cdot\begin{Bmatrix}a' & c'^+ & e' \\ a & c^+ & e^+ \\ \overset{.}{a}{}^+ & \overset{.}{c} & t \\ \alpha & \gamma & \eta\end{Bmatrix}\begin{matrix}\varepsilon' \\ \varepsilon \\ \tau\end{matrix}\begin{Bmatrix}f' & b' & d'^+ \\ f^+ & b & d \\ t^+ & \overset{.}{b}{}^+ & \overset{.}{d} \\ \eta & \beta & \delta\end{Bmatrix}\begin{matrix}\varphi' \\ \varphi \\ \pi\end{matrix} \tag{11.19}$$

$$\cdot\begin{Bmatrix}e & f & g \\ f^+ & e' & t^+\end{Bmatrix}_{\eta\eta'\mu\mu'}\cdot PIs\begin{pmatrix}-A & C & S \\ a' & \gamma' & \mathcal{A} \\ a^+ & c' & e^+\end{pmatrix}_{\varepsilon'}\cdot PIs\begin{pmatrix}-B & D & T \\ \beta' & \delta' & \mathcal{V} \\ b' & d' & f^+\end{pmatrix}_{\varphi'}\cdot PIs^3\begin{pmatrix}\mathcal{S} & S & T \\ \sigma & \mathcal{A} & \mathcal{V} \\ g & e' & f'\end{pmatrix}_{\mu'}$$

with the abbreviation $F= \sqrt{Z(\mathcal{S})Z(-ACS)Z(-BDT)dima\cdot dimb\cdot dimc\cdot dimd\cdot dime\cdot dimf}$

The comparison with (5.7) then yields:

$$GEO_3(\varepsilon e\varphi f\mu,\mathcal{S}\sigma g) = \{\overset{.}{c}\}\{\overset{.}{d}\}\sqrt{Z(\mathcal{S})dime\cdot dimf}\cdot\sum_{S\mathcal{A}T\mathcal{V}}\sum_{\eta\varepsilon'e\eta'f'\mu'}\{e'e^+t\eta\}\{e'f'g\mu'\}\{\overset{.}{a}{}^+\overset{.}{c}t\tau\} \tag{11.20}$$

$$\cdot\{\overset{.}{b}{}^+\overset{.}{d}t^+\pi\}\cdot\begin{Bmatrix}e & f & g \\ f^+ & e' & t^+\end{Bmatrix}_{\eta\eta'\mu\mu'}\cdot PIs^3\begin{pmatrix}\mathcal{S} & S & T \\ \sigma & \mathcal{A} & \mathcal{V} \\ g & e' & f'\end{pmatrix}_{\mu}\cdot GEO_1(x_1,y_1,z_1)\cdot GEO_1(x_2,y_2,z_2)$$

with the compound arguments: $x_1=(AaCct)$, $y_1=(\alpha'\overset{.}{a}\overset{.}{a}\overset{.}{a}, \gamma'\overset{.}{c}\gamma\overset{.}{c},\tau)$, $z_1=(e\varepsilon\eta S\mathcal{A}e^+)$, $x_2=(BbDdt^+)$, $y_2=(\beta'\overset{.}{b}\beta\overset{.}{b}, \delta'\overset{.}{d}\delta\overset{.}{d},\pi)$, and $z_2=(f\varphi\eta'T\mathcal{V}f^+)$.

Finally we sum up the results omitting again the multiplicity indices. Because the many-particle matrix elements of the two-particle interaction can be traced back to the matrix elements of the s.-a. geminals using the coefficients of fractional parentage [27, 17], we start with the matrix elements of the geminals. According to (11.12/10/13) we have:

$$\langle(A\overset{.}{a},B\overset{.}{b})s\|r_{12}^{-1}\|(\not{C}\overset{.}{c},\not{D}d)s\rangle \tag{11.21}$$

$$=\sum_{tef\mathcal{S}g}\sum\begin{Bmatrix}\overset{.}{a} & \overset{.}{b} & s^+ \\ \overset{.}{d} & \overset{.}{c} & t\end{Bmatrix}\{\overset{.}{c}ds^+\}\{\overset{.}{b}dt\}dimt\cdot GEO_3(ef,\mathcal{S}g)\cdot[(Aa^+,Cc)e\|r_{12}^{-1}\|(Bb^+,Dd)f]_{\mathcal{S}g}$$

with

$$GEO_3(ef,\mathcal{S}g) =\{\overset{.}{c}\}\{\overset{.}{d}\}\sqrt{Z(\mathcal{S})dime\cdot dimf}\cdot\sum_{ST ef}\{e'e^+t\}\{e'f'g\}\{\overset{.}{a}{}^+\overset{.}{c}t\}\{\overset{.}{b}{}^+\overset{.}{d}t^+\}\begin{Bmatrix}e & f & g \\ f^+ & e' & t^+\end{Bmatrix} \tag{11.22}$$

$$\cdot PIs^3\begin{pmatrix}\mathcal{S} & S & T \\ g & e' & f'\end{pmatrix}\cdot GEO_1((AaCct),(\overset{.}{a}\overset{.}{a},\overset{.}{c}\overset{.}{c}),(eSe^+))\cdot GEO_1((BbDdt^+),(\overset{.}{b}\overset{.}{b},\overset{.}{d}\overset{.}{d}),(fTf^+))$$

Later on from a more general point of view it will turn out, that the factor GEO_3 is even a triple combination of the factors of type GEO_1.

12. Complete bases of irreducible representations

Having delineated the principal structures proper to the symmetric polyhedra, we will implement the theory in the following sections by details concerning the determination of the newly defined coefficients, or of the invariants BRM, TRM, and QRM from specified approximations or ab initio formulae. The starting point is the systematic reconstruction of capable, s.-a. basis sets with respect to the centre of symmetry.

12.1. Generalization of Kopsky's theorem

All s.-a. functions of the translation group can be factorized as $\varphi_{nk}(x) = u_{nk}(x) \cdot \exp(ikx)$ [37] and those of the rotation group as $\varphi_{nlm}(\vec{r}) = R_{nl}(r) \cdot \langle \vec{r} | lm \rangle$, where $u_{nk}(x)$ and $R_{nl}(r)$ are scalar functions of the respective group. This means that there is one function $\exp(ikx)$ or one set of functions $\langle \vec{r} | lm \rangle$, which, combined with an infinite set of scalar functions, constitute the complete set of basis functions.

This suggests the question, wether there is an analogue in the case of point groups. Of course, the s.-a. spherical harmonics (3.12) constitute the complete basis $R_{nl}\langle \vec{r} | l\gamma cp \rangle$, and most books on group theory are content with it. But this basis is not the wanted one; since for each representation c there are several, moreover infinitely many values of l and γ. Thus there are required infinitely many sets of functions instead of one. The perfect analogue would be one set of standard functions $\langle \vec{r} | st.ap \rangle$ so that $R_{na}(\vec{r}) \langle \vec{r} | st.ap \rangle$ constitutes the complete set. It turns out that this perfect analogy exists only for the one-dimensional, irreducible representations, whereas for the many-dimensional, irreducible representations several, standardized sets $\langle \vec{r} | st.\alpha ap \rangle$ are required, the munber of which is equal to dima, i.e. the multiplicity index α runs from 1 to dima.

Whereas the construction of s.-a. spherical harmonics or equivalently of. s.-a. homogeneous polynoms in x, y, z is worked out in long lists of functions [38] and is included in most books on group theory, the present problem has obviously not attracted much attention. Nevertheless it turns out that every arbitrary, s.-a. function $\langle \vec{r} | \varphi ap \rangle$ of species a can be expanded in a finite number of standard functions:

$$\langle \vec{r} | \varphi ap \rangle = \sum_{\alpha=1}^{dima} R_{\alpha a}^{\varphi}(\vec{r}) \cdot \langle \vec{r} | st.\alpha ap \rangle \qquad (12.1)$$

An exception from this indifference is a late paper of Kopsky [39]. We learn from it that the problem previously has been passed casually [40, 41], although - as Kopsky shows - partly in a misleading manner.

Since Kopsky's theorem 1, the only one used here, is equivalent to eq. (12.1), we take this for granted. But Kopsky and his predecessors

confined themselves to the existence of the linearly independent functions and the expansion (12.1). They did not show, how the scalar functions $R_{\alpha a}^{\varphi}(\vec{r})$ are determined by a given, s.-a. function $\langle\vec{r}|\varphi ap\rangle$. On the contrary, we can provide a system of standardized functions with stronger properties allowing the inversion of (12.1) and a systematic calculation of the SALC (including TSALC and QSALC) coefficients.

We can regard (12.1) as a special case of the expansion (3.16). Being unaware about Kopsky's theorem we could prove (12.1) in this way. Every position vector $\vec{r}$ together with its rotated images $g\vec{r}$ makes up an equivalent set $R=\{g\vec{r} \text{ with } g\epsilon G\}$ in the sense of section 3. This means that the standard functions are proportional to the SALC coefficients for general positions (i.e. positions being invariant to no symmetry operation). The normalization is chosen different allowing for continuity if $\vec{r}$ approaches an element of symmetry. In analogy to (3.17), we use the scalar product

$$(F|G) = \sum_{g\epsilon G}\langle F|g\vec{r}\rangle\langle g\vec{r}|G\rangle \tag{12.2}$$

with respect to the discrete set R in order to orthonormalize the standard functions.

We now compile the properties of the standard functions in the following theorem: For each irreducible representation a of a point group G there is a set of standardized functions $\langle\vec{r}|st.\alpha ap\rangle$ having the properties:

1) $\alpha = 1, 2,\ldots,$ dima.

2) $\displaystyle\sum_{g\epsilon G}\langle st.\alpha ap|g\vec{r}\rangle\langle g\vec{r}|st.\beta bq\rangle = \delta(\alpha,\beta)\delta(a,b)\delta(p,q)\cdot\mu(\alpha a,\vec{r})$ (12.3)

  with $\mu(\alpha a,g\vec{r}) = \mu(\alpha a,\vec{r})$ (12.4)

  and $\mu(\alpha a,\vec{r})\geqslant 0$, where $\mu(\alpha a,\vec{r}) \neq 0$ if $\vec{r}$ in general position (12.5)

3) $\displaystyle\sum_{\alpha ap}\langle g\vec{r}|st.\alpha ap\rangle\mu(\alpha a,\vec{r})^{-1}\langle st.\alpha ap|h\vec{r}\rangle = \delta(g,h)$ (12.6)

  for every $\vec{r}$ in general position.

4) Every function $\langle\vec{r}|\varphi ap\rangle$ of species a (component p) is representable by the expansion

$$\langle\vec{r}|\varphi ap\rangle = \sum_{\alpha=1}^{\text{dima}} R_{\alpha a}^{\varphi}(\vec{r})\langle\vec{r}|st.\alpha ap\rangle , \tag{12.7}$$

where the scalar functions $R_{\alpha a}^{\varphi}(\vec{r})$ are defined by:

$$\mu(\alpha a,\vec{r})\cdot R_{\alpha a}^{\varphi}(\vec{r}) = \sum_{g\epsilon G}\langle st.\alpha ap|g\vec{r}\rangle\langle g\vec{r}|\varphi ap\rangle \tag{12.8}$$

5) Among other possibilities, the standard functions can be chosen homogeneous in x, y, z. But in general, the scalar functions are no polynomes.

The proof is based on Kopsky's theorem 1. There are precisely dima linearly independent functions, which we may term $\langle\vec{r}|nap\rangle$ (with $n=1,\ldots,$ dima). With respect to the set $R=\{g\vec{r} \text{ with } g\epsilon G\}$, we can express the linear independence by Gram's determinant [42]:

$$\det \left| (map|nap) \right| > 0, \text{if } \vec{r} \text{ in general position,}$$

with

$$(map|nap) = \sum_{g \in G} \langle map|g\vec{r}\rangle \langle g\vec{r}|nap\rangle. \qquad (12.9)$$

If we admit points of symmetry like $\vec{r} = \vec{S}_i$, the rank of the determinant must decrease because of $n(S,a) < \text{dima}$. Thus in general, we have only

$$\det \left| (map|nap) \right| \geqslant 0. \qquad (12.10)$$

We now define the standard functions by the diagonalization of the matrix $X_{mn}(\vec{r}) = (map|nap)$ by a non-singular transformation:

$$\langle \vec{r}|st.\alpha ap\rangle = \sum_{n=1}^{\text{dima}} u_{\alpha n}(\vec{r}) \langle \vec{r}|nap\rangle \qquad (12.11)$$

This yields our statements (12.3 to 5). The zeroes of $\det |X_{mn}(\vec{r})|$ and of its eigenvalues $\mu(\alpha a, \vec{r})$ prevent us from normalizing the functions without destroying the continuity in the whole range of $\vec{r}$. Because of Kopsky's theorem 1 the functions $\langle \vec{r}|nap\rangle$ and therefore the functions $\langle \vec{r}|st.\alpha ap\rangle$, too, are complete. The completeness relation is (12.6), from which follows (12.7). Inverting this by (12.3) yields (12.8).

It is convenient, but not necessary, to choose the standard functions as homogeneous polynomes. According to Kopsky's theorem 2, the number of independent polynomes is equal to or higher than dima. Hence the number of polynomes is sufficient. We can take them from the lists given in [38]. A general method for the generation of polynomes is described in [43]. Furthermore care has to be taken that the transformation (12.11) preserves the polynomial property. This is possible for instance using Schmidt's orthogonalization without normalization, i.e. without any divisions. Finally the homogeneous polynomes $\langle \vec{r}|st.\alpha ap\rangle$ and the scalar, homogeneous polynomes $\mu(\alpha a, \vec{r})$ are fixed only up to a further transformation of type (12.11).

12.2. Applications

We now come to the applications of the theorem. The relation (12.7), of course, applies to the s.-a. spherical harmonics (3.19):

$$\langle \vec{r}|l\alpha ap\rangle = \sum_{\gamma=1}^{\text{dima}} R_{\gamma a}^{l\alpha}(\vec{r}) \langle \vec{r}|st.\gamma ap\rangle \qquad (12.12)$$

with

$$\mu(\gamma a, \vec{r}) \cdot R_{\gamma a}^{l\alpha}(\vec{r}) = \sum_{g \in G} \langle st.\gamma ap|g\vec{r}\rangle \langle g\vec{r}|l\alpha ap\rangle = \frac{\text{ordG}}{\text{dima}} \cdot \sum_{p} \langle st.\gamma ap|\vec{r}\rangle \langle \vec{r}|l\alpha ap\rangle \qquad (12.13)$$

This simplifies many relations containing spherical harmonics, for instance the determination of the expansion coefficients (3.22). Inserting (12.12) into (3.22) yields, because of $R_{\gamma a}^{l\alpha}(\vec{S}_i) = R_{\gamma a}^{l\alpha}(\vec{S}_k)$:

$$c(S\beta a, l\alpha) = \sum_{\gamma=1}^{\text{dima}} R_{\gamma a}^{l\alpha}(\vec{S}_k) \cdot \bar{c}(S\beta a, st.\gamma) \qquad (12.14)$$

with an arbitrary $\vec{S}_k \in S$ and a limited set of standard coefficients:

$$\bar{c}(S\beta a, st.\gamma) = \sum_i (S\beta ap|\vec{S}_i)\langle\vec{S}_i|st.\gamma ap\rangle \qquad (12.15)$$

This reduces the infinite number of coefficients $c(S\beta a, l\alpha)$ belonging to special sets S to a limited number of coefficients defined by (12.15). The scalar functions $R^{l\alpha}_{\gamma a}(\vec{r})$ have to be determined by (12.13). But this has to be done only once for each symmetry group and not for all the sets S in each molecular framework.

In the determination of the SALC coefficients, an arbitrary, unitary transformation (3.23) has been left in obeyance. This problem is posed anew for each polyhedral structure and each equivalent set of vectors, triangles, or tetrahedra. The choice of a standard basis regulates the multiplicity problem in a uniform way for all structures and all equivalent sets within a given symmetry. All SALC coefficients – and therefore all TSALC and QSALC coefficients, too – can be defined via the standard functions.

The proceeding is as follows: Inserting the edge vectors of an equivalent set S into the standard function yields in dima-n(S,a) cases $\langle\vec{S}_i|S\beta ap\rangle=0$ and in n(S,a) cases $\langle\vec{S}_i|S\alpha ap\rangle\neq0$. The latter are necessary and sufficient to determine the SALC coefficients and to fix especially the index α:

$$(\vec{S}_r|S\alpha ap) = \langle\vec{S}_r|st.\alpha ap\rangle\sqrt{ordG/Z(S)\mu(\alpha a,\vec{S}_r)} \qquad (12.16)$$

Because of the transformation properties of the standard functions, and because of (12.3 to 6), the relations defining the SALC coefficients in section 3 are complied with. By the choice (12.16), the multiplicity indices of all SALC, TSALC, and QSALC coefficients of all molecules sharing one symmetry group are fixed.

By (12.16), the expansion coefficients (12.15) are simplified. Because of (12.3), we get:

$$\bar{c}(S\beta a, st.\gamma) = \delta(\beta,\gamma)\sqrt{\mu(\beta a,\vec{S}_k)Z(S)/ordG} \qquad (12.17)$$

Also the expansion coefficients (3.22) are simplified. Inserting (12.17) into (12.14) yields:

$$c(S\beta a, l\alpha) = R^{l\alpha}_{\beta a}(\vec{S}_k)\sqrt{\mu(\beta a,\vec{S}_k)Z(S)/ordG} \qquad (12.18)$$

In analogy to the parity of the spherical harmonics, $\langle-\vec{r}|jm\rangle$ $=(-1)^j\langle\vec{r}|jm\rangle$, we finally define a parity $\{\alpha a\}=\pm1$ of the standard functions by:

$$\langle-\vec{r}|st.\alpha ap\rangle = \{\alpha a\}\langle\vec{r}|st.\alpha ap\rangle \qquad (12.19)$$

From both relations follows:

$$R^{l\alpha}_{\beta a}(-\vec{r}) = (-1)^l\{\beta a\}\cdot R^{l\alpha}_{\beta a}(\vec{r}) \qquad (12.20)$$

13. Transformation properties and structure of the multi-centre integrals

13.1. General considerations

The theorems (4.4), (8.1), and (11.2/3) demonstrate that the physical informations of the multi-centre integrals are concentrated in the invariants BRM, TRM, and QRM. The theorem are proofs of the existence of these invariants without regard to special atomic orbitals. The theorems (5.5), (8.14), and (11.13) then show, how these informations enter the reduced (and thereby all ordinary) matrix elements of the molecular orbitals and geminals, i.e. the global molecular invariants. This relationship is conditioned exclusively by symmetry and geometry.

The functional type of the atomic orbitals (GTO or STO for instance) affects only the values and functional form of the BRM, TRM, and QRM. By inversion, as for instance given in (4.10) and (8.7), these can be determined in principle from given integral formulae. Since this formal inversion requires all multi-centre integrals, it makes sense only if the integral formulae allow to eliminate the quantum number of the individual atomic orbitals, i.e. the components of the representations. This especially applies to the magnetic quantum numbers.

The general structure of the integrals necessary for this purpose results from their transformation properties in space. This structure is not related to a special molecular symmetry. It requires the integral formulae to be tensorial equations with respect to the angular momentum algebra [15]. Consequently, we have to start with spherical, atomic orbitals

$$\langle \vec{r}|nlm\rangle = R_{nl}(r)\langle \vec{r}|lm\rangle, \tag{13.1}$$

where the spherical harmonics are defined by (3.18). And further we have to express the multi-centre integrals by rotational invariants, 3jm symbols of the rotation group O(3), and spherical harmonics of the atomic distances. Since the rotation group is a supergroup of all point groups, all the integral formulae can be systematically adapted to the special molecular symmetry. Thus without further considerations the polycentric, reduced matrix elements prove to be composed of the following constituents only: 1) the rotational invariants, 2) the isoscalar factors resulting from the group chain $O(3) \supset G$, 3) the expansion coefficients (3.22) or (12.15) resulting from the spherical harmonics of the atomic distances, and 4) the nj symbols of the concerned groups O(3) and G. Using atomic spin orbitals we have to refer to SU(2) and G' instead. The rotational invariants again are the only carriers of the physical information. They are the only factors depending on the special, radial functions $R_{nl}(r)$. The other constituents enter the mediating geometrical factors.

We now derive the universal integral theorems for the atomic orbitals

$$\langle \vec{r} | A n_a l_a m_a \rangle = R_{n_a l_a}(|\vec{r}-\vec{A}|) \cdot \langle \vec{r}-\vec{A} | l_a m_a \rangle \qquad (13.2)$$

defined with respect to the angular momentum basis. These theorems result from the transformation properties.

13.2. Two-centre integrals

The theorem concerning the two-centre integrals states that these integrals over arbitrary, spherical orbitals can be factorized as follows:

$$\langle A n_a l_a m_a | T_M^L | B n_b l_b m_b \rangle \qquad (13.3)$$

$$= \sum_{Jj} \sqrt{4\pi(2J+1)} \cdot \langle n_a l_a \| AB^j, T^L \| n_b l_b \rangle^J \cdot \left(\begin{smallmatrix} j & L & J \\ m & M & M' \end{smallmatrix} \right)^+ \left(\begin{smallmatrix} 1 & J & l_b \\ m_a & M' & m_b \end{smallmatrix} \right)^+ \langle \vec{AB} | sol\ jm \rangle$$

This theorem is the generalization of the Wigner-Eckart theorem. The graphical arrangement of the symbols in the generalized, reduced matrix element shall indicate the coupling of the angular momenta. AB^j stands for the translation operator. The introduction of the solid harmonics

$$\langle \vec{r} | sol\ jm \rangle = r^j \langle \vec{r} | jm \rangle \qquad (13.4)$$

ensures the regular behavior for $\vec{A}=\vec{B}$ [44]. If $\vec{A}=\vec{B}$, all terms vanish except for the ordinary, reduced matrix element of the WET:

$$\langle n_a l_a \| 0^0, T^L \| n_b l_b \rangle^L = \langle n_a l_a \| T^L \| n_b l_b \rangle \qquad (13.5)$$

The angular momenta, of course, can be coupled in an order different from that in (13.3). The invariants of the other couplings are related to those of eq.(13.3) by 6j symbols. But only the symmetric arrangement of (13.3) yields the simple conjugation relation:

$$\langle n_b l_b \| BA^j, T^L \| n_a l_a \rangle^J = \langle n_a l_a \| AB^j, T^L \| n_b l_b \rangle^J \cdot (-1)^{j+J+l_a+l_b} \qquad (13.6)$$

In order to prove (13.3), we form the expression

$$I_m^j(\vec{AB}) = \sum \left(\begin{smallmatrix} j & L & J \\ m & M & M' \end{smallmatrix} \right)^+ \left(\begin{smallmatrix} l_a & J & l_b \\ m_a & M' & m_b \end{smallmatrix} \right)^+ \langle A n_a l_a m_a | T_M^L | B n_b l_b m_b \rangle.$$

It is invariant to translations and therefore a function of the distance vector AB only. We further show the transformation property with respect to rotations:

$$I_m^j(g^{-1}\vec{AB}) = \sum_m D_{mm}^j(g) I_m^j(\vec{AB})$$

Since the spherical harmonics are complete, it follows:

$$I_m^j(\vec{AB}) \sim \langle \vec{AB} | jm \rangle$$

The invariant factor in this proportion, depending on $|\vec{AB}|$ only, is the reduced matrix element. For reasons mentioned above, it is convenient to splitt off the factor $|\vec{AB}|^j$. Converting the result by the orthogonality relations of the 3jm symbols finally yields (13.3).

Examples of (13.3) concerning the identity, the kinetic energy, and the momentum operator (i.e. L=0 and 1) can be found in [45, 46], and further integrals of this type with L=0 in [47, 48], cf. also (A2.13).

13.3. Three-centre nuclear attraction integrals

The description of the three-centre integrals is complicated by the following dilemma: The theorem can be formulated in two different versions, the more effective of which being at the same time the more difficult. Because of the translation invariance, only the internal coordinates of the concerned triangle can appear; but there remain many possibilities of choosing distances and internal angles. Furthermore different choices may be appropriate to different radial functions, GTOs or STOs for instance.

Since symmetry considerations suggest an equivalent treatment of both orbitals, the foolowing reference vectors appear suitable to the integral $\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$:

a) $\vec{AC}$ and $\vec{BC}$

b) $\vec{AB}$ and $\vec{PC}$ with the weighted mean $\vec{P} = (\sigma_A^2\vec{A}+\sigma_B^2\vec{B})/(\sigma_A^2+\sigma_B^2)$

The weight factors σ_X^2 (in the case of GTOs being related to the orbital exponents) may depend on the set X, but not on the individual atomic orbital. Otherwise complications impairing the symmetry considerations arise in section 15. In the case of individual orbital exponents the vectors AC and BC are preferable.

Since now solid harmonics depending on several distances occur, it is convenient to introduce the following combinations of solid harmonics:

$$\langle\vec{r}_1,\vec{r}_2|sol(j_1,j_2)JM\rangle = \sqrt{2J+1}\sum_M(^{J}_{M}\,^{j_1^+j_2^+}_{m_1m_2})\langle\vec{r}_1|sol\ j_1m_1\rangle\langle\vec{r}_2|sol\ j_2m_2\rangle \quad (13.7)$$

At first, we formulate a weak theorem: Every three-centre integral over arbitrary, spherical orbitals has the following structure:

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$$
$$= 4\pi\sum_{LJj}\sqrt{2L+1}\langle An_al_a\|AB^JPC^j\|Bn_bl_b\rangle^L(^{L^+}_{m_a}\,^{1^+}_{m_b}\,^{L^+}_{M})\langle\vec{AB},\vec{PC}|sol(Jj)LM\rangle \quad (13.8)$$

The theorem is weak, because nothing is said about the range of the summations - except for the triangular conditions for the angular momenta - and nothing about the dependence of the rotational invariants. In general these may depend on all the scalar variables $|\vec{AB}|$, $|\vec{PC}|$, and $\vec{AB}\cdot\vec{PC}$. The theorem, of course, applies to any other scalar functions of r_C.

The formulation using the other reference vectors is given by:

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$$
$$= 4\pi\sum_{Lll'}\sqrt{2L+1}\langle An_al_a\|AC^lBC^{l'}\|Bn_bl_b\rangle^L(^{L^+}_{m_a}\,^{1^+}_{m_b}\,^{L^+}_{M})\langle\vec{AC},\vec{BC}|sol(ll')LM\rangle , \quad (13.9)$$

where the rotational invariants now may be functions of $|\overrightarrow{AC}|$, $|\overrightarrow{BC}|$, and $\overrightarrow{AC}\cdot\overrightarrow{BC}$. The theorems (13.8 and 9) can be converted into one another, since the invariants are interrelated by

$$\langle An_al_a\|AC^lBC^{l'}\|Bn_bl_b\rangle^L = (2L+1)^{-1}\sum_{Jjnn'}[nln'l'L\|-\varphi_{AB}\|0J0jL]\cdot\sigma_A^{2n+1}\sigma_B^{2n'+1'}$$
$$\cdot\theta_{AB}^{-j}\cdot\xi_{AB}^{-J}\cdot AB^{2n}PC^{2n'}\langle An_al_a\|AB^JPC^j\|Bn_bl_b\rangle^L \qquad (13.10)$$

with $n' = (J+j-l-l)/2 -n$ and conversely by

$$\langle An_al_a\|AB^JPC^j\|Bn_bl_b\rangle^L = (2L+1)^{-1}\sum_{llNn}[NJnjL\|\varphi_{AB}\|0l0lL]\cdot\sigma_A^{-1}\cdot\sigma_B^{-1'}$$
$$\cdot\xi_{AB}^{2N+J}\cdot\theta_{AB}^{2n+j}\cdot AC^{2N}BC^{2n}\cdot\langle An_al_a\|AC^lBC^{l'}\|Bn_bl_b\rangle^L \qquad (13.11)$$

with $n = (l+l'-J-j)/2 -N$. In these equations we have used the abbreviations $\theta_{AB}=\sqrt{\sigma_A^2+\sigma_B^2}$, $\xi_{AB}=\sigma_A\sigma_B/\theta_{AB}$, and $\varphi_{AB}=\arctan(\sigma_A/\sigma_B)$. The coefficients $[n_3l_3n_4l_4L\|\varphi\|n_1l_1n_2l_2L]$ are, except for a different normalization, equal to the Moshinsky-Smirnov coefficients of the Talmi transformation. We refer to [45], eq.(3.4) and the comprehensive references therein.

In order to prove (13.8), we form again:

$$I_M^L(\overrightarrow{AB},\overrightarrow{PC}) = \sum_{m_am_bM}\binom{l_a\ l_b^+\ L^+}{m_a\ m_b\ M}\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$$

Because of the translational invariance, this is a function of the distances $\overrightarrow{AB}$ and $\overrightarrow{PC}$ only. The rotation property is given by:

$$I_M^L(g^{-1}\overrightarrow{AB},g^{-1}\overrightarrow{PC}) = \sum_M D_{MM}^L(g)\cdot I_M^L(\overrightarrow{AB},\overrightarrow{PC})$$

We therefore can express I_M^L by the spherical harmonics of AB and PC or equivalently by the functions defined in (13.7). The expansion coefficients must be scalar, i.e. functions of $|\overrightarrow{AB}|$, $|\overrightarrow{PC}|$, and $\overrightarrow{AB}\cdot\overrightarrow{PC}$ only:

$$I_M^L(\overrightarrow{AB},\overrightarrow{PC}) = (4\pi\sqrt{2L+1})^{-1}\sum_{Jj}\langle An_al_a\|AB^JPC^j\|Bn_bl_b\rangle^L\langle\overrightarrow{AB},\overrightarrow{PC}|sol(Jj)LM\rangle$$

Converting this equation then yields (13.8). The proof of (13.9) is analogous. The interrelations (13.10/11) result from the following theorem of the solid harmonics defined in (13.7):

$$\langle\vec{r_1},\vec{r_2}|sol(l_1l_2)LM\rangle = \sum_{n_3l_3n_4l_4}[n_3l_3n_4l_4L\|\varphi\|0l_10l_2L](2L+1)^{-1}$$
$$\cdot r_3^{2n_3}\cdot r_4^{2n_4}\cdot\langle\vec{r_3},\vec{r_4}|sol(l_3l_4)LM\rangle$$

with $\vec{r_3}= \vec{r_1}\cos\varphi-\vec{r_2}\sin\varphi$ and $\vec{r_4}= \vec{r_1}\sin\varphi+\vec{r_2}\cos\varphi$. This relation is a special case of the more general theorem (3.3) in [45]. If we put $\vec{r_1} = \xi_{AB}\overrightarrow{AB}$, $\vec{r_2}= \theta_{AB}\overrightarrow{PC}$, $\varphi= -\varphi_{AB}$, it follows $\vec{r_3}= \sigma_A\overrightarrow{AC}$, $\vec{r_4}= \sigma_B\overrightarrow{BC}$ and finally:

$$\langle\overrightarrow{AB},\overrightarrow{PC}|sol(l_1l_2)LM\rangle = \sum_{n_3l_3n_4l_4}[n_3l_3n_4l_4L\|-\varphi_{AB}\|0l_10l_2L](2L+1)^{-1}$$
$$\cdot\sigma_A^{2n_3+l_3}\cdot\sigma_B^{2n_4+l_4}\cdot\xi_{AB}^{-l_1}\cdot\theta_{AB}^{-l_2}\cdot AC^{2n_3}\cdot BC^{2n_4}\cdot\langle\overrightarrow{AC},\overrightarrow{BC}|sol(l_3l_4)LM\rangle$$

Inserting this into (13.8) yields (13.9 and 10). The inverse relation results, if we put $\vec{r_1}= \sigma_A\overrightarrow{AC}$, $\vec{r_2}= \sigma_B\overrightarrow{BC}$, and $\varphi=+\varphi_{AB}$.

The weak theorem now can be strengthened in two conflicting aspects by restricting either the dependence of the invariants or the range of the angular momenta J and j (1 and $1'$ respectively). The strong theorems are:

A) Every three-centre integral of arbitrary, spherical orbitals has the structure (13.8/9), where the rotational invariants depend on AB and PC (AC and BC) only. This in general causes unlimited sums for J and j (1 and $1'$).

B) Every three-centre integral of arbitrary, spherical orbitals has the structure (13.8/9) with the limitation $J+j = l_a+l_b$ ($1+1' = l_a+l_b$). This in general makes the rotational invariants depending on the internal angle, i.e. $\overrightarrow{AB}\cdot\overrightarrow{PC}$ ($\overrightarrow{AC}\cdot\overrightarrow{BC}$).

The structure stated in version B) is preserved by the transformations (13.10/11) in contrast to that of version A).

The integrals of Gauss-type or related orbitals [45-47] occupy a special position. With respect to the reference scheme AB-PC the inequality $J+j \leqslant 2n_a+l_a+2n_b+l_b$ holds for all intergrals. Thus the integrals with $n_a=n_b=0$ are covered by both A) and B).

From the tensor algebraic point of view, the theorem B) has the definite advantage of representing a finite number of integrals by a finite number of invariants, too. Generally in case A), the number is infinite. The limited summation in the case of GTOs is of no much profit, since the group theoretically irrelevant radial quantum numbers interfere in the angular momentum algebra.

On the other hand, explicit formulae of type B) are hard to derive (cf. below), whereas those of type A) result quite naturally from orthogonal expansions. For instance the expansion

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$$
$$= \sum_{n_cn_c'l_cm_c}\sum\langle An_al_am_a|Cn_cl_cm_c\rangle\langle Cn_cl_cm_c|r_C^{-1}|Cn_c'l_cm_c\rangle\langle Cn_c'l_cm_c|Bn_bl_bm_b\rangle$$

in combination with (13.3) yields (13.9) with the invariants

$$\langle An_al_a\|AC^lBC^{l'}\|Bn_bl_b\rangle^L = (-1)^{L+l'+l_a+l_b}\cdot\sum_{n_cn_cl_c}\sum\sqrt{1/(2l_c+1)}\begin{Bmatrix}L & 1 & 1'\\l_c & l_b & l_a\end{Bmatrix}$$
$$\cdot\langle n_al_a\|AC^l\|n_cl_c\rangle^l\langle n_cl_c\|r^{-1}\|n_cl_c\rangle\langle n_cl_c\|CB^{l'}\|n_bl_b\rangle^{l'}$$

A similar proof follows from the addition theorems discussed in [49]:

$$g(|\vec{r}_1+\vec{r}_2|)\langle\vec{r}_1+\vec{r}_2|LM\rangle$$
$$= \sum_{l_1l_2}(-1)^{-l_1+l_2-L}\sqrt{2L+1}\begin{pmatrix}l_1 & l_2 & L\\m & m & M\end{pmatrix}g_{l_1l_2}^L(\vec{r}_1,\vec{r}_2)\langle\vec{r}_1|l_1m_1\rangle\langle\vec{r}_2|l_2m_2\rangle$$

From this relation follows eq.(5.12) of [49] having the same structure as (13.8/9) except for different reference vectors.

The first proof of B) given in [50] is recursive and thus quite complicated. The results of [46] now allow a simpler proof for a special, complete system of orbitals. Since every orbital can be expanded in such a complete system, the theorem B) is valid for all orbital systems in the Hilbert space. Since the properties of a special orbital system do not matter to the present context, we postpone the proof into the appendix 2.

13.4. The four-centre integrals

There is an even larger variety of representing the four-centre interaction integrals. But the principles are the same as for the three-centre integrals and we can be brief. We confine the representation of the distorted tetrahedra ABCD to the vector triple $\vec{AC}$, $\vec{BD}$, and $\vec{PQ}$ with $\vec{P} = (\sigma_A^2 \vec{A} + \sigma_C^2 \vec{C})/(\sigma_A^2 + \sigma_C^2)$ and $\vec{Q} = (\sigma_B^2 \vec{B} + \sigma_D^2 \vec{D})/(\sigma_B^2 + \sigma_D^2)$. Since now three vectors are involved, we extend (13.7) and define:

$$\langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | sol(j_1 j_2) J j_3 LM \rangle$$
$$= \sqrt{2L+1} \cdot \sum \binom{L\ \ J^+ j_3^+}{M\ \ M\ m_3} \langle \vec{r}_1, \vec{r}_2 | sol(j_1 j_2) JM \rangle \langle \vec{r}_3 | sol\ j_3 m_3 \rangle \qquad (13.12)$$

Again we first state, in a weak theorem that, the four-centre integrals over arbitrary spherical orbitals pricipally have the following structure:

$$\langle An_a l_a m_a, Bn_b l_b m_b | r_{12}^{-1} | Cn_c l_c m_c, Dn_d l_d m_d \rangle = \sqrt{4\pi}^3 \sum_{l\overline{l}LJj_i} \sum \sqrt{(2l+1)(2\overline{l}+1)(2L+1)}$$
$$\cdot \left[(An_a l_a^+, Cn_c l_c) 1 \| (AC^{j_4} BD^{j_2})^J PQ^{j_3} \| (Bn_b l_b^+, Dn_d l_d) 1 \right]^L \qquad (13.13)$$
$$\cdot \binom{1^+ 1\ l}{m_a m_c m} \binom{1^+ 1\ l'}{m_b m_d m'} \binom{l\ \ l'^+ L^+}{m\ m'\ M} \langle \vec{AC}, \vec{BD}, \vec{PQ} | sol(j_1 j_2) J j_3 LM \rangle$$

The rotational invariants $[...]^L$ are designed in analogy to the QRMs in (11.2/3) and the reduced matrix elements in (11.9), cf. also [17] eq.(7). In general they are functions of the lengths and the scalar products of the vectors $\vec{AC}$, $\vec{BD}$, and $\vec{PQ}$. Of course, the angular momenta involved can be coupled in a different order. The proof is analogous to that of (13.8/9).

The strong theorems again result from the following restrictions:
A) Every four-centre integral over arbitrary, spherical orbitals has the structure (13.13), where the rotational invariants depend on AC, BD, and PQ only. This in general causes unlimited sums for j_1, j_2, and j_3.
B) Every four-centre integral over arbitrary, spherical orbitals has the structure (13.13) with the limitation $j_1 + j_2 + j_3 \leqslant l_a + l_b + l_c + l_d$. This in general makes the rotational invariants depending on the scalar products $\vec{AC} \cdot \vec{BD}$, $\vec{AC} \cdot \vec{PQ}$, and $\vec{BD} \cdot \vec{PQ}$.
Again the GTOs occupy a special position. In the case of this system,

the formulae of type A) are restricted by $j_1+j_2+j_3 \leqslant 2n_a+l_a+2n_b+l_b+2n_c$ $+l_c+2n_d+l_d$, cf. [45-47]. Thus the integrals with $n_a=n_b=n_c=n_d=0$ are covered by both theorems A) and B).

The proof of A) can be achieved by orthogonal expansions with respect to the centres P and Q or by the addition theorems already mentioned on page 55. The eq.(5.18) of [49] corresponds to (13.13) with other other reference vectors and another coupling of the angular momenta. The proof of theorem B) is sketched in appendix 2.

In the following, we shall regard the rotational invariants as known. Examples are given in the appendix 2 and in section 23.3/4. But it must be said that the theory of the invariants according to the theorem B) is still unsatisfactory and requires further investigation.

14. Multi-centre integrals and molecular symmetry

14.1. Preliminary considerations

If the symmetry is reduced from the rotation group O(3) to a molecular symmetry group G, the WET is valid with respect to both groups and the both reduced matrix elements are interrelated by (2.82). We repeat this relation for O(3):

$$\langle nlm_1|T^L_M|n'jm_j\rangle = \langle nl\|T^L\|n'j\rangle\begin{pmatrix}1^+L & j\\ m_1M & m_j\end{pmatrix} \tag{14.1}$$

With the definition

$$|\varphi dp_d\rangle = |nl\delta dp_d\rangle = \sum\langle lm_1|l\delta dp_d\rangle\cdot|nlm_1\rangle \tag{14.2}$$

the WET reads in G:

$$\langle\varphi dp_d|T^{L\gamma c}_{p_c}|\varphi' ep_e\rangle = \sum_\sigma\langle\varphi d\|T^{L\gamma c}\|\varphi' e\rangle_\sigma\cdot\begin{pmatrix}d^+c & e\\ p_dp_c & p_e\end{pmatrix}^\sigma \tag{14.3}$$

where φ has the meaning $\varphi=(nl\delta)$. (2.82) then reads in this case:

$$\langle\varphi d\|T^{L\gamma c}\|\varphi' e\rangle_\sigma = \langle nl\|T^L\|n'j\rangle\cdot Is\begin{vmatrix}1^+L & j\\ \delta\gamma & \varepsilon\\ d^+c & e\end{vmatrix}_\sigma \tag{14.4}$$

Exactly corresponding relations must exist for the structural formulae of the multi-centre integrals discussed in the preceeding section as generalizations of the WET. These relations are needed, if the universal integral formulae are introduced into the calculations of symmetric molecules.

As a preliminary, we prepare the point group analogues of the spherical harmonics and their combinations (13.7 and 12). As a consequence of section 12, the standard functions $\langle\vec{r}|st.\alpha ap\rangle$ offer themselves. In correspondence to (13.7/12), we define the standard functions of several variables:

$$\langle\vec{r}_1,\vec{r}_2|st.(\alpha_1a_1\alpha_2a_2)\beta bp_b\rangle$$
$$= \sqrt{dimb}\cdot\sum\begin{pmatrix}b & a_1^+a_2^+\\ p_bp_1p_2\end{pmatrix}^\beta\langle\vec{r}_1|st.\alpha_1a_1p_1\rangle\langle\vec{r}_2|st.\alpha_2a_2p_2\rangle \tag{14.5}$$

$$\langle\vec{r}_1,\vec{r}_2,\vec{r}_3|st.(\alpha_1a_1\alpha_2a_2)\beta b\alpha_3a_3\gamma cp_c\rangle \tag{14.6}$$
$$= \sqrt{dimc}\cdot\sum\begin{pmatrix}c & b^+a_3^+\\ p_cp_bp_3\end{pmatrix}^\gamma\langle\vec{r}_1,\vec{r}_2|st.(\alpha_1a_1\alpha_2a_2)\beta bp_b\rangle\langle\vec{r}_3|st.\alpha_3a_3p_3\rangle$$

According to (12.12), the s.-a. solid harmonics can be expanded in standard functions:

$$\langle\vec{r}|sol\ j\sigma ap\rangle = \sum_\alpha S^{j\sigma}_{\alpha a}(\vec{r})\langle\vec{r}|st.\alpha ap\rangle \quad\text{with}\quad S^{j\sigma}_{\alpha a}(\vec{r}) = r^j\cdot R^{j\sigma}_{\alpha a}(\vec{r}) \tag{14.7}$$

The corresponding expansions of the functions (13.7) is:

$$\langle\vec{r}_1,\vec{r}_2|sol(j_1j_2)J\tau bp_b\rangle = \sqrt{(2J+1)/dimb}\cdot\sum_{\alpha_1\sigma_1a_1\beta}\sum Is\begin{vmatrix}J & j_1^+j_2^+\\ \tau & \sigma_1\sigma_2\\ b & a_1^+a_2^+\end{vmatrix}_\beta$$
$$\cdot S^{j_1\sigma_1}_{\alpha_1a_1}(\vec{r}_1)S^{j_2\sigma_2}_{\alpha_2a_2}(\vec{r}_2)\langle\vec{r}_1,\vec{r}_2|st.(\alpha_1a_1\alpha_2a_2)\beta bp_b\rangle \tag{14.8}$$

and that of the functions (13.12):

$$\langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | sol(j_1 j_2) J j_3 L\pi c p_c \rangle$$

$$= \sum_{\alpha_i \sigma_i a_i \tau \beta \gamma b} \sum \sqrt{(2L+1)(2J+1)/dimc\,dimb} \cdot Is \begin{pmatrix} J & j_1^+ j_2^+ \\ \tau & \sigma_1 \sigma_2 \\ b & a_1^+ a_2^+ \end{pmatrix}_\beta \cdot Is \begin{pmatrix} L & J^+ j_3^+ \\ \pi & \tau & \sigma_3 \\ c & b^+ a_3^+ \end{pmatrix}_\gamma \quad (14.9)$$

$$\cdot S^{j_1 \sigma_1}_{\alpha_1 a_1}(\vec{r}_1) S^{j_2 \sigma_2}_{\alpha_2 a_2}(\vec{r}_2) S^{j_3 \sigma_3}_{\alpha_3 a_3}(\vec{r}_3) \langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | st.(\alpha_1 a_1 \alpha_2 a_2)\beta b \alpha_3 a_3 \gamma c p_c \rangle$$

14.2. The particular integral formulae

Now we are prepared to discuss the multi-centre integrals with respect to molecular symmetry. In each case there are three steps: The formulae of section 13 correspond to (14.1) and it is our task to write down the multi-centre analogues of (14.3) and of the interrelation (14.4).

The point group analogue of the two-centre integral (13.3) is:

$$\langle A\varphi_a a p_a | T^{L\gamma c}_{p_c} | B\varphi_b b p_b \rangle$$
$$(14.10)$$
$$= \sum_{\delta d \eta \epsilon e} \sum \sqrt{dimd} \langle \varphi_a \| AB^{\epsilon e}, T^{L\gamma c} \| \varphi_b \rangle^d_{\delta \eta} \cdot \begin{pmatrix} e^+ c & d^+ \\ p_e p_c & p_d \end{pmatrix}_\eta \begin{pmatrix} a^+ d & b \\ p_a p_d & p_b \end{pmatrix}_\delta \cdot \langle \vec{AB} | st. \epsilon e p_e \rangle$$

and the interrelation of the invariants:

$$\langle \varphi_a \| AB^{\epsilon e}, T^{L\gamma c} \| \varphi_b \rangle^d_{\delta \eta}$$
$$(14.11)$$
$$= \sum_{JJ\sigma\tau} \sqrt{4\pi(2J+1)/dimd} \cdot Is \begin{pmatrix} j^+L & J^+ \\ \sigma, \gamma & \tau \\ e^+c & d^+ \end{pmatrix}_\eta Is \begin{pmatrix} 1^+J & 1_b \\ \alpha^+\tau & \beta \\ a^+d & b \end{pmatrix}_\delta S^{j\sigma}_{ee}(\vec{AB}) \langle n_a 1_a \| AB^j, T^L \| n_b 1_b \rangle^J$$

Because of the functions $S^{J\sigma}_{\epsilon e}(\vec{AB})$ the point group invariant is no scalar of the rotation group.

The derivation of these equations is as follows. Because of (14.2), the interrelation of the integrals (14.10) and (13.3) is given by:

$$\langle A\varphi_a a p_a | T^{L\gamma c}_{p_c} | B\varphi_b b p_b \rangle$$
$$= \sum \langle 1_a \alpha a p_a | 1_a m_a \rangle \langle LM | L\gamma c p_c \rangle \langle 1_b m_b | 1_b \beta b m_b \rangle \langle A n_a 1_a m_a | T^L_M | B n_b 1_b m_b \rangle$$

Using now (2.72/73) and (14.7) and comparing the result with (14.10) we get (14.11).

The point group analogue of the three-centre integral (13.8) is:

$$\langle A\varphi_a a p_a | r^{-1}_C | B\varphi_b b p_b \rangle$$
$$= \sum_{\epsilon\gamma c \delta d \eta e} \sum \sqrt{dimc} \langle A\varphi_a a \| AB^{\delta d} PC^{\eta e} \| B\varphi_b b \rangle^c_{\epsilon\gamma} \begin{pmatrix} a^+b & c^+ \\ p_a p_b & p_c \end{pmatrix}_\epsilon \langle \vec{AB}, \vec{PC} | st.(\delta d \eta e)\gamma c p_c \rangle \quad (14.12)$$

and again the interrelation of the invariants:

$$\langle A\varphi_a \| AB^{\delta d} PC^{\eta e} \| B\varphi_b b \rangle^c_{\epsilon\gamma} = 4\pi \sum_{LJ\bar{J}} \sum_{\mu\sigma\tau} \frac{2L+1}{dimc} \cdot Is \begin{pmatrix} 1^+1_b L^+ \\ a^+ \beta b^+ \mu \\ a^+b & c^+ \end{pmatrix}_\epsilon Is \begin{pmatrix} L & J^+ j^+ \\ \mu & \sigma, \tau \\ a & d^+ e^+ \end{pmatrix}_\gamma \quad (14.13)$$
$$\cdot S^{J\sigma}_{\delta d}(\vec{AB}) S^{j\tau}_{\eta e}(\vec{PC}) \langle A n_a 1_a \| AB^J PC^j \| B n_b 1_b \rangle^L$$

These equations again follow from

$$\langle A\varphi_a a p_a | r^{-1}_C | B\varphi_b b p_b \rangle = \sum \langle 1_a \alpha a p_a | 1_a m_a \rangle \langle 1_b m_b | 1_b \beta b p_b \rangle \langle A n_a 1_a m_a | r^{-1}_C | B n_b 1_b m_b \rangle$$

using the expansion (14.8).

With reference to the vectors $\vec{AC}$ and $\vec{BC}$ the corresponding formulae read:

$$\langle A\varphi_a a p_a | r_C^{-1} | B\varphi_b b p_b \rangle$$
$$= \sum_{\epsilon\gamma c\varphi f\varphi'f'} \sum \sqrt{\text{dimc}} \langle A\varphi_a a \| AC^{\varphi f} BC^{\varphi'f'} \| B\varphi_b b \rangle_{\epsilon\gamma}^c \begin{pmatrix} a^+b & c^+\epsilon \\ p_a p_b & p_c \end{pmatrix} \langle \vec{AC}, \vec{BC} | \text{st.}(\varphi f\varphi'f')\gamma c p_c \rangle \qquad (14.14)$$

with

$$\langle A\varphi_a a \| AC^{\varphi f} BC^{\varphi'f'} \| B\varphi_b b \rangle_{\epsilon\gamma}^c = 4\pi \sum_{\text{l1L}} \sum_{\mu\pi\pi'} \frac{2L+1}{\text{dimc}} \cdot \text{Is} \begin{pmatrix} 1^+ & 1^+ & L^+ \\ \alpha^+\beta & \mu \\ a^+b & c^+ \end{pmatrix}_\epsilon \text{Is} \begin{pmatrix} L & 1^+1'^+ \\ \mu & \pi & \pi'_+ \\ c & f^+f'^+ \end{pmatrix}_\gamma \qquad (14.15)$$
$$\cdot S_{\varphi f}^{1\pi}(\vec{AC}) S_{\varphi'f'}^{1'\pi'}(\vec{BC}) \langle An_a a \| AC^1 BC^{1'} \| Bn_b 1_b \rangle^L$$

In section 13, we have criticized that the three-centre integral formulae of type A) can contain infinitely many rotational invariants. This problem does not occur in the case of molecular symmetry, since the sums in (14.12 and 14) are finite because of the limited number of point group representations. But in truth the problem has only been shifted, since according to (14.13 and 14) the finite number of point group invariants is expressed by an infinite number of rotational invariants. For type B), of course, this problem does not exist.

In conclusion, we carry out the corresponding determination of the two-electron integrals. The parallelism of rotation and point group yields the analogue of (13.13):

$$\langle A\varphi_a a p_a, B\varphi_b b p_b | r_{12}^{-1} | C\varphi_c c p_c, D\varphi_d d p_d \rangle = \sum_{\eta_i h_i} \sum_{\sigma\tau g e\epsilon\epsilon'\epsilon'\varphi f} \sqrt{\text{dime} \cdot \text{dime} \cdot \text{dimg}} \qquad (14.16)$$
$$\cdot [(A\varphi_a a^+, C\varphi_c c)\epsilon e \| (AC^{\eta_4 h_4}, BD^{\eta_2 h_2})^{\varphi f}_{PQ}{}^{\eta_3 h_3} \| (B\varphi_b b^+, D\varphi_d d)\epsilon'e']^g_{\sigma\tau}$$
$$\cdot \begin{pmatrix} a^+c & e \\ p_a p_c p_e \end{pmatrix}_\epsilon \begin{pmatrix} b^+d & e' \\ p_b p_d p_e' \end{pmatrix}_\epsilon \begin{pmatrix} e^+e'^+g^+ \\ p_e p_e p_g \end{pmatrix}_\sigma \langle \vec{AC}, \vec{BD}, \vec{PQ} | \text{st.}(\eta_1 h_1 \eta_2 h_2)\varphi f\eta_3 h_3 \tau g p_g \rangle$$

The point group invariants of this theorem are related to the rotational invariants by:

$$[(A\varphi_a a^+, C\varphi_c c)\epsilon e \| (AC^{\eta_4 h_4}, BD^{\eta_2 h_2})^{\varphi f}_{PQ}{}^{\eta_3 h_3} \| (B\varphi_b b^+, D\varphi_d d)\epsilon'e']^g_{\sigma\tau}$$
$$= \sqrt{4\pi^3} \cdot \sum_{j_i \pi_i} \sum_{J\mu L\gamma l} \sum_{\pi_i l'\pi_i} \frac{2L+1}{\text{dimg}} \cdot \sqrt{\frac{(2l+1)(2l'+1)(2J+1)}{\text{dime} \cdot \text{dime} \cdot \text{dimf}}} \cdot \text{Is} \begin{pmatrix} 1^+ & 1 \\ \alpha^+\gamma & c l \\ a^+c & e \end{pmatrix}_\epsilon \text{Is} \begin{pmatrix} 1^+ & 1' \\ \beta^+\delta & l' \\ b^+d & e' \end{pmatrix}_\epsilon$$
$$\cdot \text{Is} \begin{pmatrix} J & j_4^+j^2 \\ \mu & \pi_4 \pi_2 \\ f & h_4 h^2 \end{pmatrix}_\varphi \text{Is} \begin{pmatrix} 1^+1'^+L^+ \\ l \, l' \, \gamma^+ \\ e^+e'^+g^+ \end{pmatrix}_\sigma \text{Is} \begin{pmatrix} L & J^+j^+ \\ \gamma & \mu \pi_3 \\ g & f^+h_3^+ \end{pmatrix}_\tau \cdot S_{\eta_4 h_4}^{j_4 \pi_4}(\vec{AC}) S_{\eta_2 h_2}^{j_2 \pi_2}(\vec{BD}) S_{\eta_3 h_3}^{j_3 \pi_3}(\vec{PQ}) \qquad (14.17)$$
$$\cdot [(An_a 1_a^+, Cn_c 1_c)1 \| (AC^{j_4} BD^{j_2})^J_{PQ}{}^{j_3} \| (Bn_b 1_b^+, Dn_d 1_d)1]^L$$

This results from (13.13) by the adaption to the point group symmetry (14.2). One then uses (2.72/73) and the expansion (14.9).

15. Ab initio determination of the polycentric invariants

Using the integral formulae of section 13 and their adaption to the particular molecular symmetry in section 14, we now can determine the polycentric, reduced matrix elements BRM, TRM, and QRM.

15.1. The proper two-centre integrals

Going to calculate we have to rewrite (14.10) for the centres $\vec{A}_i$ and $\vec{B}_k$. Noting that $\overrightarrow{A_iB_k}=\vec{B}_k-\vec{A}_i=-\vec{S}_{ik}$, we get with (12.19):

$$\langle Ai\varphi_a ap_a|T^c_{p_c}|Bk\varphi_b bp_b\rangle$$
$$= \sum_{\delta d\eta\epsilon\epsilon'}\sum\sqrt{dimd}\langle\varphi_a a\|-S^{\epsilon'e},T^c\|\varphi_b b\rangle^d_{\delta\eta}\cdot\begin{pmatrix}e^+c & d^+ \\ p_e p_c & p_d\end{pmatrix}^\eta\begin{pmatrix}a^+d & b \\ p_a p_d p_b\end{pmatrix}^\delta\{\epsilon'e\}\langle\vec{S}_{ik}|st.\epsilon'ep_e\rangle$$

Inserting this into (4.10) yields the BRMs expressed by the point group invariants:

$$(A\varphi_a a\|T^c\|B\varphi_b b)^{d\delta\eta}_{S\epsilon e}$$
$$= \{c^+den\}\{a^+bd\delta\}\sqrt{dimd}\cdot\sum_{\epsilon'}\bar{c}(S\epsilon e,st.\epsilon')\{\epsilon'e\}\langle\varphi_a a\|-S^{\epsilon'e},T^c\|\varphi_b b\rangle^d_{\delta\eta} \quad (15.1)$$

Using now (14.11) yields the final expression by the rotational invariants of the general two-centre integrals:

$$(A\varphi_a a\|T^{L\gamma c}\|B\varphi_b b)^{d\delta\eta}_{S\epsilon e} = (-1)^{1a+1b+L}\sum_{JJ\sigma\tau\epsilon'}\sum\bar{c}(S\epsilon e,st.\epsilon')\sqrt{4\pi(2J+1)}\cdot S^{j\sigma}_{\epsilon'e}(\vec{S}_r)$$
$$\cdot Is\begin{pmatrix}j^+J^+L \\ \sigma,\tau,\gamma \\ e^+d^+c\end{pmatrix}_\eta Is\begin{pmatrix}1^+1_b^J \\ \alpha_a^a b_\tau^J \\ a^+b & d\end{pmatrix}_\delta\langle n_a1_a\|-S^j,T^L\|n_b1_b\rangle^J \quad (15.2)$$

This completes the ab inition calculation of the two-centre matrix elements. In the next step, the matrix elements of the s.-a. MOs (5.1) or (11.6) can be expressed directly by the rotational invariants. The abbreviation A now includes the main and the angular momentum quantum numbers, i.e. $A = (A\alpha\acute{a},\varphi_a a)\mathring{\alpha} = (A\alpha\acute{a},n_a1_a\alpha a)\mathring{\alpha}$. The s.-a. MOs are:

$$|A\mathring{\alpha}ap_a\rangle = \sum_{iq_a}K(\mathring{\alpha}\mathring{a}p_a,Ai\alpha a,aq_a)\cdot|Ai\varphi_a aq_a\rangle$$

$$= \sum_{iq_a m_a}\sum K(\mathring{\alpha}\mathring{a}p_a,Ai\acute{a}a,aq_a)\langle 1_a m_a|1_a\alpha aq_a\rangle\cdot|Ain_a1_a m_a\rangle \quad (15.3)$$

$$= \sum_{im_a}M(\mathring{\alpha}\mathring{a}p_a,Ai\acute{a}a,(\alpha a)1_a m_a)\cdot|Ain_a1_a m_a\rangle$$

The coefficients $M(\ldots)$ relating the s.-a. MOs directly to the spherical AOs have been defined in [51], eq.(7). From the orthogonality relations (2.26/27), (2.70/71), and (3.6/7) follow those of the composed coefficients M:

$$\sum_{im}M(\mathring{\alpha}\mathring{a}p_a,Ai\acute{a}\acute{a},(\alpha a)1m)\cdot M(\mathring{\beta}\mathring{b}p_b,Ai\acute{b}\acute{b},(\beta b)1m) \quad (15.4)$$
$$= \delta(\mathring{\alpha},\mathring{\beta})\delta(\mathring{a},\mathring{b})\delta(p_a,p_b)\delta(\alpha',\beta')\delta(a',b')\delta(\alpha,\beta)\delta(a,b)$$

$$\sum_{\alpha'\acute{a}\alpha a\mathring{\alpha}\mathring{a}p_a}\sum M(\mathring{\alpha}\mathring{a}p_a,Ai\acute{a}\acute{a},(\alpha a)1m)\cdot M(\mathring{\alpha}\mathring{a}p_a,Aj\acute{a}\acute{a},(\alpha a)1n) = \delta(i,j)\delta(m,n) \quad (15.5)$$

The matrix elements of the MOs (15.3) thus are given by the WET

$$\langle \dot{A}\dot{a}p_a | T^{L\gamma c}_{p_c} | \cancel{B}\dot{b}p_b \rangle = \sum_\mu \langle \dot{A}\dot{a} \| T^{L\gamma c} \| \cancel{B}\dot{b} \rangle_\mu \cdot \begin{pmatrix} \dot{a}^+ c & \dot{b} \\ p_a p_c p_b \end{pmatrix}^\mu \tag{15.6}$$

with the reduced matrix elements

$$\langle \dot{A}\dot{a} \| T^{L\gamma c} \| \cancel{B}\dot{b} \rangle_\mu = \sum_{J\dot{J}S} \langle n_a l_a \| -S^{\dot{J}}, T^{L} \| n_b l_b \rangle^J \cdot \mathrm{GEO}_4(\dot{A}\dot{a}, \cancel{B}\dot{b}, L\gamma c\mu, J\dot{J}S) \tag{15.7}$$

and the geometrical factor:

$$\mathrm{GEO}_4(\dot{A}\dot{a}, \cancel{B}\dot{b}, L\gamma c\mu, J\dot{J}S) = (-1)^{l_a + l_b L} \cdot \sqrt{4\pi(2J+1)} \cdot \sum_{\delta\eta\varepsilon e\sigma\tau\varepsilon'} \bar{c}(S\varepsilon e, \mathrm{st}.\varepsilon')$$

$$\cdot S^{\dot{j}\sigma}_{\varepsilon'e}(\vec{S}_r) \cdot \mathrm{Is} \begin{pmatrix} j^+ J^+ L \\ \sigma, \tau, \gamma \\ e^+ d^+ c \end{pmatrix}_\eta \mathrm{Is} \begin{pmatrix} 1^+_a 1_b J \\ \alpha^+_a \beta^+ \tau \\ a^+ b\ d \end{pmatrix}_\delta \mathrm{GEO}_1(AaBbc, \dot{a}\dot{\alpha}\dot{a}\beta\cancel{B}\dot{b}\dot{b}\mu, d\delta\eta S\varepsilon e) \tag{15.8}$$

The paper [51] dealt with the overlap matrix, i.e. the matrix elements of the identity operator, a special case of (15.6-8).

15.2. The nuclear attraction integrals

For the determination of the TRMs, we have to repeat (14.12 or 14) with respect to the centres $\vec{A}_i$, $\vec{B}_k$, and $\vec{C}_l$. This yields an invariant $\langle A\varphi_a a \| A_i B^{\delta d}_k P_{ik} C^{\eta e}_l \| B\varphi_b b \rangle^c_{\varepsilon\gamma}$ with $\vec{P}_{ik} = (\sigma^2_A \vec{A}_i + \sigma^2_B \vec{B}_k)/(\sigma^2_A + \sigma^2_B)$. Because of the invariance the vectors $\vec{A_i B_k}$ and $\vec{P_{ik} C_l}$ can be replaced by those of an arbitrary, equivalent triangle $\vec{A_x B_y}$ and $\vec{P_{xy} C_z}$. In order to eliminate the misleading indices ikl (or xyz) we replace them by $\vec{AB}_\Delta$ and $\vec{PC}_\Delta$, where the index Δ indicates the set of the triangles under consideration. Inserting now the specified relation (14.12) into (8.7) then yields:

$$(A\varphi_a a \| Cr^{-1} \| B\varphi_b b)^\varepsilon_{\Delta\gamma c} = \sqrt{\mathrm{dim}c} \sum_{\gamma\delta d\eta e} \sum \langle A\varphi_a a \| AB^{\delta d}_\Delta PC^{\eta e}_\Delta \| B\varphi_b b \rangle^c_{\varepsilon\gamma'} \cdot \bar{c}^2_1(\Delta\gamma c, \mathrm{st}.\delta d\eta e\gamma') \tag{15.9}$$

with the expansion coefficients:

$$\bar{c}^2_1(\Delta\gamma c, \mathrm{st}.\delta d\eta e\gamma') = \sum_{ijkl} (\Delta\gamma cn | \Delta_j) \cdot \sqrt{Z(\Delta)} \tau \binom{\Delta ACB}{jilk} \langle \vec{A_i B_k}, \vec{P_{ik} C_l} | \mathrm{st}.(\delta d\eta e)\gamma' cn \rangle \tag{15.10}$$

These coefficients result from the expansion

$$\langle \vec{A_i B_k}, \vec{P_{ik} C_l} | \mathrm{st}.(\delta\eta e)\gamma cn \rangle = \sum_\gamma \bar{c}^2_1(\Delta\gamma c, \mathrm{st}.\delta d\eta e\gamma) \sum_{\Delta j} \sqrt{Z(\Delta)} \tau \binom{\Delta ACB}{jilk} (\Delta_j | \Delta\gamma cn) \tag{15.11}$$

and are the analogues of (12.15).

On the other hand, the insertion of (14.14) into (8.7) yields:

$$(A\varphi_a a \| Cr^{-1} \| B\varphi_b b)^\varepsilon_{\Delta\gamma c} = \sqrt{\mathrm{dim}c} \sum_{\varphi f \varphi' f' \gamma'} \sum \langle A\varphi_a a \| AC^{\varphi f}_\Delta BC^{\varphi' f'}_\Delta \| B\varphi_b b \rangle^c_{\varepsilon\gamma'} \cdot \bar{c}^2_2(\Delta\gamma c, \mathrm{st}.\varphi f\varphi' f'\gamma') \tag{15.12}$$

with a different type of coefficients:

$$\bar{c}^2_2(\Delta\gamma c, \mathrm{st}.\varphi f\varphi' f'\gamma') = \sum_{ijkl} (\Delta\gamma cn | \Delta_j) \sqrt{Z(\Delta)} \tau \binom{\Delta ACB}{jilk} \langle \vec{A_i C_l}, \vec{B_k C_l} | \mathrm{st}.(\varphi f\varphi' f')\gamma' cn \rangle \tag{15.13}$$

The eqs. (15.9 and 12) show that different types of coefficients have to be calculated depending on the reference vectors in the integral formulae. Therefore it is absolutely inexpedient to allow the parameters σ_A and σ_B in the weighted mean $\vec{P}_{ik}$ to depend on the individual

orbitals at a certain centre. Problems also arise, if approximative
formulae require other reference vectors.

Inserting now (14.13) into (15.9) and (14.15) into (15.12) traces
back the TRMs to the rotational invariants. With respect to the refe-
rence vectors $\overrightarrow{AC}$ and $\overrightarrow{BC}$, the result is:

$$(A\varphi_a a \| Cr^{-1} \| B\varphi_b b)^\varepsilon_{\Delta\gamma c}$$

$$= \sum_{1\hat{1}L} GEO_5(Al_a\alpha a, Bl_b\beta b, C\Delta\gamma c\varepsilon, 1\hat{1}L) \cdot \langle An_a l_a \| AC^{1}_{\Delta} BC^{1'}_{\Delta} \| Bn_b l_b \rangle^L \qquad (15.14)$$

with the geometrical factor:

$$GEO_5(Al_a\alpha a, Bl_b\beta b, C\Delta\gamma c\varepsilon, 1\hat{1}L) = 4\pi(2L+1)dimc^{-1/2} \sum_{\varphi f \varphi' f' \tilde{\gamma}} \sum_{\mu\pi\pi'} \bar{c}^2_2(\Delta\gamma c, st.\varphi f \varphi' f' \tilde{\gamma}')$$

$$\cdot Is \begin{pmatrix} 1^+ & 1 & L^+ \\ \alpha^+ & \beta & \mu \\ a^+ & b & c^+ \end{pmatrix}_\varepsilon Is \begin{pmatrix} L & 1^+ & 1'^+ \\ \mu & \pi & \pi' \\ c & f^+ & f'^+ \end{pmatrix}_\varepsilon S^{1\pi}_{\varphi f}(\overrightarrow{AC}_\Delta) S^{1\pi}_{\varphi' f'}(\overrightarrow{BC}_\Delta) \qquad (15.15)$$

Finally the matrix elements of the potential operator (8.10/11) with
respect to the s.-a. MOs can be determined:

$$\langle \acute{A}\grave{a}p_a | V_C | \acute{B}\grave{a}p_a \rangle = \langle \acute{A}\grave{a} \| V_C \| \acute{B}\grave{a} \rangle / \sqrt{dim\grave{a}} \qquad (15.16)$$

$$= \sqrt{1/dim\grave{a}} \cdot \sum_{1\hat{1}L\Delta} GEO_6(\acute{A}\grave{a}\acute{B}\grave{a}C, 1\hat{1}L\Delta) \langle An_a l_a \| AC^{1}_{\Delta} BC^{1'}_{\Delta} \| Bn_b l_b \rangle^L$$

with

$$GEO_6(\acute{A}\grave{a}\acute{B}\grave{a}C, 11L\Delta) = \sum_{\gamma c\varepsilon} GEO_5(Al_a\alpha a, Bl_b\beta b, C\Delta\gamma c\varepsilon, 1\hat{1}L)$$

$$\cdot GEO_2(AaBbC, \acute{a}\grave{a}\beta\grave{b}\grave{a}\beta\grave{a}, \Delta\gamma c\varepsilon) \qquad (15.17)$$

15.3. The interaction integrals

In the same way as before, we restate (14.16) for the centres $\overrightarrow{A}_i$,
$\overrightarrow{B}_j$, $\overrightarrow{C}_k$, and $\overrightarrow{D}_1$. The resulting integral is equal to (11.1-3) and the
isolation of the QRM give the expression in terms of the point group
invariants. Again we introduce the vectors $\overrightarrow{AC}_{\mathfrak{z}}$, $\overrightarrow{BD}_{\mathfrak{z}}$, and $\overrightarrow{PQ}_{\mathfrak{z}}$ (instead
of $\overrightarrow{A_iC_k}$, $\overrightarrow{B_jD_1}$, and $\overrightarrow{P_{ik}Q_{j1}}$) referring to an arbitrary member of the
set $\mathfrak{z}$. The QRMs are:

$$[(A\varphi_a a^+, C\varphi_c c)\varepsilon e \| r^{-1}_{12} \| (B\varphi_b b^+, D\varphi_d d)\varepsilon' e']^\sigma_{\tau g} =$$

$$= \sum_{\eta_1 h_1 \tau \varphi f} \sqrt{dimg} \cdot \bar{c}^3(\mathfrak{z}\tau g, st.(\eta_1 h_1 \eta_2 h_2)\varphi f \eta_3 h_3 \tau') \qquad (15.18)$$

$$\cdot [(A\varphi_a a^+, C\varphi_c c)\varepsilon e \| (AC^{\eta_1 h_1}_{\mathfrak{z}}, BD^{\eta_2 h_2}_{\mathfrak{z}})^{\varphi f} PQ^{\eta_3 h_3}_{\mathfrak{z}} \| (B\varphi_b b^+, D\varphi_d d)\varepsilon' e']^g_{\sigma\tau}$$

where the expansion coefficients are given by:

$$\bar{c}^3(\mathfrak{z}\tau g, st.(\eta_1 h_1 \eta_2 h_2)\varphi f \eta_3 h_3 \tau') \qquad (15.19)$$

$$= \sum_{rijkl} \sum_{r} (\mathfrak{z}\tau g p_g | \mathfrak{z}_r) \sqrt{Z(\mathfrak{z})} \tau \binom{\mathfrak{z}ABCD}{rijkl} \langle \overrightarrow{A_iC_k}, \overrightarrow{B_jD_1}, \overrightarrow{P_{ik}Q_{j1}} | st.(\eta_1 h_1 \eta_2 h_2)\varphi f \eta_3 h_3 \tau' g p_g \rangle$$

These again are obvious generalizations of the coefficients (15.10/13)
and (12.15). They likewise depend on the system of reference vectors
within the pseudo-tetrahedra.

Inserting now (15.18) into (14.17) traces back the QRMs to the ro-

tational invariants:

$$[(A\varphi_a a^+, C\varphi_c c)\varepsilon e \| r_{12}^{-1} \| (B\varphi_b b^+, D\varphi_d d)\varepsilon' e']_{\mathfrak{I}\tau g}^{\sigma} \tag{15.20}$$

$$= \sum_{j_i J} \sum_{\Pi L} GEO_7(A\varphi_a aC\varphi_c c\varepsilon e, B\varphi_b bD\varphi_d d\varepsilon' e', \sigma\mathfrak{I}\tau g; j_i J(11')L)$$

$$\cdot [(An_a 1_a^+, Cn_c 1_c)1 \| (AC_{\mathfrak{I}}^{j_1} BD_{\mathfrak{I}}^{j_2})^J PQ_{\mathfrak{I}}^{j_3} \| (Bn_b 1_b^+, Dn_d 1_d)1]^L$$

with the geometrical factor:

$$GEO_7(\ldots) = (4\pi)^{3/2}((2L+1)/dimg) \sum_{\eta_i h_i \tau \varphi f} \sum \left[\frac{(2l+1)(2l'+1)(2J+1)}{dime \cdot dime' \cdot dimf} \right]^{1/2} \tag{15.21}$$

$$\cdot \sum_{\pi_i \mu} \sum_{\gamma \lambda \lambda'} Is \begin{pmatrix} 1^+ 1 & 1 \\ \alpha^a \gamma & c\lambda \\ a^+ c & e \end{pmatrix}_\varepsilon Is \begin{pmatrix} 1^+ 1 & 1' \\ \beta^b \delta & d\lambda' \\ b^+ d & e' \end{pmatrix}_{\varepsilon'} Is \begin{pmatrix} J & j_1^+ j_2^+ \\ \mu & \pi_4 \pi_1 \\ f & h_1 h_1 \end{pmatrix}_\varphi Is \begin{pmatrix} 1^+ 1'^+ L^+ \\ \lambda^+ \lambda^+ \gamma' \\ e^+ e^+ g \end{pmatrix}_\sigma Is \begin{pmatrix} L & J^+ j_3^+ \\ \gamma' & \mu & \pi_4 \\ g & f^+ h_3 \end{pmatrix}_{\tau'}$$

$$\cdot \bar{c}^3 (\mathfrak{I}\tau g, st. (\eta_1 h_1 \eta_2 h_2) \varphi f \eta_3 h_3 \tau') \cdot S_{\eta_1 h_1}^{j_1 \pi_1} (\overrightarrow{AC_{\mathfrak{I}}}) S_{\eta_2 h_2}^{j_2 \pi_2} (\overrightarrow{BD_{\mathfrak{I}}}) S_{\eta_3 h_3}^{j_3 \pi_3} (\overrightarrow{PQ_{\mathfrak{I}}})$$

And finally, we determine the two-electron matrix elements of the s.-a. LCAO-MOs. From (11.13) and (15.20) results:

$$[(A^+ a^+, \mathcal{C}c)\theta t \| r_{12}^{-1} \| (B^+ b^+, \mathcal{D}d)\theta' t'] = \sum_{j_i J} \sum_{\Pi L \mathfrak{I}} GEO_8(A a \mathcal{C}c\theta e, B b \mathcal{D}d\theta' t'; j_i J(11')L\mathfrak{I})$$

$$\cdot [(An_a 1_a^+, Cn_c 1_c)1 \| (AC_{\mathfrak{I}}^{j_1} BD_{\mathfrak{I}}^{j_2})^J PQ_{\mathfrak{I}}^{j_3} \| (Bn_b 1_b^+, Dn_d 1_d)1]^L \tag{15.22}$$

with the geometrical factor:

$$GEO_8(A a \mathcal{C}c\theta t, B b \mathcal{D}d\theta' t'; j_i J(11')L\mathfrak{I}) \tag{15.23}$$

$$= \sum_{\varepsilon \varepsilon' \theta \tau g} \sum GEO_3(\varepsilon e', d\sigma, \mathfrak{I}\tau g) \cdot GEO_7(A\varphi_a aC\varphi_c c\varepsilon e, B\varphi_b bD\varphi_d d\varepsilon' e', \sigma\mathfrak{I}\tau g; j_i J(11')L)$$

16. Wolfsberg-Helmholtz and Mulliken approximations

Having cleared up the interrelation between the molecular invariants defined in the first sections and the ab initio rotational invariants, we now consider approximations like those of Wolfsberg-Helmholtz and Mulliken. These approximations can be discussed from three different, but connected points of view: namely as approximative formulae for distant centres, as a minimization of the number of semi-empirical parameters, and as an interpretational aid to split up the molecular energy into a quasi-classic part and the "remainder" [52].

At first, it is a trivial requirement, that an approximation or parametrization should not depend on the position and orientation of the molecule in space, i.e. that it should be invariant to translations and rotations. This applies in particular to the symmetry operations of the molecule. But the existence of a relevant literature suggests, that this trivial requirement is by no means a matter of fact [53-55].

The required invariance is self-evident, if the approximations are sujected to the principles of form stated in section 13, if especially both sides of the approximative formulae are tensors of the same species. This condition is not met by the usual form of the Wolfsberg-Helmholtz approximation:

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle$$
$$= k\langle An_al_am_a|Bn_bl_bm_b\rangle[\langle An_al_am_a|r_C^{-1}|Bn_al_am_a\rangle+\langle Bn_bl_bm_b|r_C^{-1}|Bn_bl_bm_b\rangle]$$

The left side and both summands on the right transform according to three different product representations of the rotation group. This demands a meaningful modification, which for instance can be achieved by taking the mean with respect to the magnetic quantum numbers. There are two possibilities:

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle = \frac{k}{2l_b+1}\cdot\sum_{m_b'}\langle An_al_am_a|Bn_bl_bm_b'\rangle\langle Bn_bl_bm_b'|r_C^{-1}|Bn_bl_bm_b\rangle$$
$$+ \frac{k}{2l_a+1}\cdot\sum_{m_a'}\langle An_al_am_a'|Bn_bl_bm_b\rangle\langle An_al_am_a|r_C^{-1}|An_al_am_a'\rangle \tag{16.1}$$

or

$$\langle An_al_am_a|r_C^{-1}|Bn_bl_bm_b\rangle = k\langle An_al_am_a|Bn_bl_bm_b\rangle \tag{16.2}$$
$$\cdot\left[\frac{1}{2l_a+1}\cdot\sum_{m_a}\langle An_al_am_a|r_C^{-1}|An_al_am_a\rangle + \frac{1}{2l_b+1}\cdot\sum_{m_b}\langle Bn_bl_bm_b|r_C^{-1}|Bn_bl_bm_b\rangle\right]$$

The first approximation depends on the angles between the vectors $\overrightarrow{AB}$ and $\overrightarrow{AC}$ or $\overrightarrow{BC}$ respectively. The second one is simpler and leads to a smaller number of parameters. Furthermore it fits with the reference vectors AB-PC and we can use the coefficients (15.10). We therefore prefer (16.2) and determine the corresponding approximation of the rotational invariants. From (13.8) follows:

$$\sum_{m_a} \langle An_a l_a m_a | r_C^{-1} | An_a l_a m_a \rangle = \sqrt{2l_a+1} \langle An_a l_a \| 0^0 AC^0 \| An_a l_a \rangle^0$$

$$= \sqrt{2l_a+1} \cdot \langle n_a l_a \| n_a l_a \rangle$$

with the ordinary, reduced matrix element of (13.5). If we insert this into (16.2) and compare the result with (13.8), we get:

$$\langle An_a l_a \| AB^J PC^J \| Bn_b l_b \rangle^L = \delta(j,0)\delta(J,L)\langle n_a l_a \| AB^L \| n_b l_b \rangle^L (-1)^{L+l_a+l_b}$$
$$\cdot \left[\ 1/\sqrt{2l_a+1} \langle n_a l_a \| n_a l_a \rangle + \ 1/\sqrt{2l_b+1} \langle n_b l_b \| n_b l_b \rangle \right] \tag{16.3}$$

The approximation with respect to the angular momentum basis is the most efficient and selfconsistent. But a similar approximation is possible on the lower level of the point group invariants (section 14) or even on the level of the TRMs. The latter presents itself, if the parametrization shall not require spherical, atomic orbitals. Approximating (8.1) in the sense of (16.2),

$$\langle Ai\varphi_a am | r_{C_1}^{-1} | Bk\varphi_b bq \rangle = k \langle Ai\varphi_a am | Bk\varphi_b bq \rangle$$
$$\cdot \left[\tfrac{1}{\text{dima}} \sum_{m'} \langle Ai\varphi_a am' | r_{C_1}^{-1} | Ai\varphi_a am \rangle + \tfrac{1}{\text{dimb}} \sum_{q'} \langle Bk\varphi_b bq' | r_{C_1}^{-1} | Bk\varphi_b bq \rangle \right], \tag{16.4}$$

yields for the TRMs:

$$(A\varphi_a a \| Cr^{-1} \| Bk\varphi_b b)^\varepsilon_{\Delta\gamma c} = k \frac{\sqrt{Z(\Delta)Z(C)}}{\text{dimc}} \sum_{S\sigma} (A\varphi_a a \| B\varphi_b b)^\varepsilon_{S\sigma c} \cdot PIs^2 \begin{pmatrix} \Delta & S & C \\ \gamma & \varepsilon & 1 \\ c+c & 1 & 1 \end{pmatrix}$$
$$\cdot \sum_{Xx} (1/\sqrt{Z(XCX)\text{dimx}}) \cdot (X\varphi_x x \| Cr^{-1} \| X\varphi_x x)^1_{XCX11}, \tag{16.5}$$

where the sum takes the values $Xx = Aa$ and Bb. ACA and BCB are degenerate triangles.

The Mulliken approximation of the two-electron integrals can be treated in the same way. Again the approximation must be changed into a correct tensor equation. From the several possibilities we take the simplest one:

$$[An_a l_a^+ m_a, Cn_c l_c m_c | r_{12}^{-1} | Bn_b l_b^+ m_b, Dn_d l_d m_d] = \langle An_a l_a m_a | Cn_c l_c m_c \rangle \langle Bn_b l_b m_b | Dn_d l_d m_d \rangle$$
$$\cdot (1/4) \sum_{XxYy} \tfrac{1}{(2l_x+1)(2l_y+1)} \sum_{m_x m_y} [Xn_x l_x^+ m_x, Xn_x l_x m_x | r_{12}^{-1} | Yn_y l_y^+ m_y, Yn_y l_y m_y], \tag{16.6}$$

where the sums take the values: $Xx = Aa, Cc$ and $Yy = Bb, Dd$.
This ansatz together with (13.13) leads to the following approximation of the rotational invariants:

$$[(An_a l_a^+, Cn_c l_c)1 \| (AC^{J_1} BD^{J_2})^J_{PQ}{}^{J_3} \| (Bn_b l_b^+, Dn_d l_d)1]^L = \delta(j_1,1)\delta(j_2,1')$$
$$\cdot \delta(j_3,0)\delta(J,L)(-1)^{l_a+l_b+l_c+l_d+1+1'} \sqrt{1/(2l+1)(2l+1)} \langle n_a l_a \| AC^1 \| n_c l_c \rangle^1$$
$$\cdot \langle n_b l_b \| BD^{1'} \| n_d l_d \rangle^{1'} (1/4) \sum_{XxYy} \sqrt{1/(2l_x+1)(2l_y+1)} \tag{16.7}$$
$$\cdot [(Xn_x l_x^+, Xn_x l_x)0 \| (0^0 0^0)^0 AB^0 \| (Yn_y l_y^+, Yn_y l_y)0]^0$$

As in (16.3), most of the invariants (parameters) are put equal to zero.

Without reference to spherical orbitals, the direct approximation of the QRMs is as follows. In (11.2) we put:

$$[Ai\varphi_a a^+ m, Ck\varphi_c cp | r_{12}^{-1} | B_j\varphi_b b^+ n, Dl\varphi_d dq] = \langle Ai\varphi_a am | Ck\varphi_c cp \rangle \langle Bj\varphi_b bn | Dl\varphi_d dq \rangle \quad (16.8)$$

$$\cdot (1/4) \sum_{Xxi'} \sum_{Yyj'} \frac{1}{dimx \cdot dimy} \cdot \sum_{tu} [Xi'\varphi_x x^+ t, Xi'\varphi_x xt | r_{12}^{-1} | Yj'\varphi_y y^+ u, Yj'\varphi_y yu]$$

and get the approximative TRMs:

$$[(A\varphi_a a^+, C\varphi_c c)\varepsilon e \| r_{12}^{-1} \| (B\varphi_b b^+, D\varphi_d d)\eta f]_{\mathcal{S}\tau g}^{\mu}$$

$$= \frac{\sqrt{Z(-ACS)Z(-BDT)Z(\mathbf{\Delta})}}{dime \cdot dimf} \cdot (A\varphi_a a \| C\varphi_c c)_{See}^{\varepsilon} \cdot (B\varphi_b b \| D\varphi_d d)_{Tnf}^{\eta} \cdot PIs^3 \begin{vmatrix} \mathcal{S} & S & T \\ \tau & \varepsilon & \eta \\ g & e & f \end{vmatrix}_{\mu} \quad (16.9)$$

$$\cdot (1/4) \sum_{XxYy} \sqrt{1/Z(XYXY)dimx \cdot dimy} \cdot [(X\varphi_x x^+, X\varphi_x x)1 \| r_{12}^{-1} \| (Y\varphi_y y^+, Y\varphi_y y)1]_{XYXY11}^1$$

with Xx = Aa, Cc and Yy = Bb, Dd. XYXY are degenerate tetrahedra and thus only two-centre invariants occur.

At this point a comparison with a LCAO-MO parametrization of tetra-hedral transition metal complexes (i.e. a MO extension of the ligand field theory) [56] may be of interest. The authors calculate the two-electron integrals of linear combinations of s.-a. MOs:

$$|\gamma \mathring{a} p_a\rangle = c^{\gamma}(\mathcal{A}) \cdot |\mathcal{A} \mathring{a} p_a\rangle + c^{\gamma}(\mathcal{B}) \cdot |\mathcal{B} \mathring{a} p_a\rangle \quad (16.10)$$

where $|\mathcal{A} \mathring{a} p_a\rangle$ and $|\mathcal{B} \mathring{a} p_a\rangle$ are given by (15.3). Set A means the central ion and set B the ligands. They have to discuss the delocalized integrals

$$\langle \gamma_1 \mathring{a} p_a, \gamma_2 \mathring{b} p_b | r_{12}^{-1} | \gamma_3 \mathring{c} p_c, \gamma_4 \mathring{d} p_d \rangle. \quad (16.11)$$

They do not examine the invariants of these integrals according to (11.8/9), but decompose (16.11) into one-electron integrals using the multipole expansion

$$r_{12}^{-1} = \sum_{lm} (4\pi/2l+1)(r_<^l/r_>^{l+1}) \langle \vec{r_1} | lm \rangle \langle lm | \vec{r_2} \rangle. \quad (16.12)$$

Since the delocalized integrals of such radial functions are not cal-culable, only bilinear combinations of the can be taken into account (tables 11) thus undoing the decomposition.

The bilinear combinations then are parametrized using a manipulated population analysis. Inserting (16.10) and (15.3) into (16.11) yields localized multi-centre integrals, which are subjected to the Mulliken approximation. The result is a long list of separate, numerical coef-ficients (table 11 again). In order to preserve the point group inva-riance ad hoc average of the approximate integrals have to be taken.

On the contrary by inserting (16.9) into (11.13), we get a general construction of such coefficients for arbitrary symmetries. Ad hoc averages are not required, not even for orbitals higher than p (cf. [54]).

17. Floating orbitals

A possibility of avoiding the algebra of higher angular momenta is
the exclusive using of s-orbitals floating in space. The invariants
of the preceeding sections depending on the higher quantum numbers thus
are replaced by a multitude of multicentre s-integrals. The task of
the polycentric algebra then is to collect these s-integrals in such
a way, that each independent integral occurs only once in any molecu-
lar invariant.

There are two ways of proceeding: The s-orbitals can be distributed
freely in space without regard to the atomic positions and then are
combined to s.-a. MOs. In this case we get high and non-structured mul-
tiplicities of the induced symmetry species. On the other hand, the s-
orbitals can be grouped around the atomic positions simulating p-, d-
etc. orbitals. Only from these simulated AOs the s.-a. MOs or VB func-
tions are built up. The attachment of the orbitals to the atomic cen-
tres induces a structure into the multiplicity problem, which is acces-
sible to the polyhedral algebra.

To begin with, we simulate orbitals of the symmetry species a by li-
near combinations of s-orbitals. For this purpose we use one, two or
several equivalent positions $\vec{U}_1$ as required around the centre of sym-
metry. The s-orbitals are localized at these positions:

$$\langle \vec{r}-\vec{U}_1|\sigma s\rangle = \langle \vec{r}|U1\sigma s\rangle \tag{17.1}$$

σ is a discriminating index, for instance an orbital exponent. Accor-
ding to (5.1) the s.-a. orbitals at the centre of symmetry are given
by:

$$\langle \vec{r}|\text{float } \sigma U\alpha ap_a\rangle = \sum_1 \langle \vec{r}|U1\sigma s\rangle(\vec{U}_1|U\alpha ap_a) \tag{17.2}$$

These compound "AOs" now are shifted to the various atomic positions:

$$\langle \vec{r}|Ai\varphi_a ap_a\rangle = \langle \vec{r}-\vec{A}_1|\text{float } \sigma U\alpha ap_a\rangle, \tag{17.3}$$

where now $\varphi_a = (\text{float } \sigma Ua)$.

The invariants of the multi-centre integrals over these shifted or-
bitals result from the invariants of the integrals over the constitu-
ting s-orbitals. As an example, we explicate this for the BRMs. We ex-
press the functions (17.3) directly by the twice shifted s-orbitals:

$$\langle \vec{r}|Ai\varphi_a ap_a\rangle = \sum_1 \langle \vec{r}-\vec{A}_1-\vec{U}_1|\sigma s\rangle(\vec{U}_1|U\alpha ap_a)$$

$$= \sum_{1Ar}\sqrt{Z(-AAU)}\tau(-\genfrac{}{}{0pt}{}{A'AU}{r11})\langle \vec{r}|A'r\sigma s\rangle(\vec{U}_1|U\alpha ap_a) \tag{17.4}$$

$\vec{A'_r}$ are the positions of the s-orbitals and the topological matrix re-
lates them to the atomic positions $\vec{A}_i$.

We now come to the two-centre matrix elements of the orbitals (17.
3/4) where $\varphi_b = (\text{float } \sigma U\beta)$:

$$\langle A i \varphi_a a p_a | T_{p_c}^c | B k \varphi_b b p_b \rangle = \sum_{lm} \sum_{\overline{ArBs}} \sqrt{Z(-\overline{A'AU})Z(-\overline{BBU'})} \cdot \tau\binom{-A'AU}{ril}\tau\binom{-BBU'}{skm}$$
$$\cdot (U\alpha a p_a | \vec{U_l'})(\vec{U_m'} | U\beta b p_b) \langle A'r\sigma s | T_{p_c}^c | B's\sigma's \rangle \tag{17.5}$$

The integrals on the right are a special case of (4.6):

$$\langle A'r\sigma s | T_{p_c}^c | B's\sigma's \rangle = \sum_{\overline{Vt\gamma}} (A'\sigma s \| T^c \| B'\sigma's)_{V\gamma c} \cdot \sqrt{Z(-\overline{A'BV})/dimc} \cdot \tau\binom{-A'BV}{rst}(\vec{V_t} | V\gamma c p_c) \tag{17.6}$$

In order to determine the BRMs, we insert this into (17.5) and the result into (4.10):

$$(A\varphi_a a \| T^c \| B\varphi_b b)_{S\varepsilon e}^{d\delta\eta} = dimd \sum_{\overline{ikulm\overline{ArBs}Vt\gamma}} \sum \sum \sqrt{Z(-ABS)Z(-\overline{A'AU})Z(-\overline{BBU'})Z(-\overline{A'BV})/dimc'}$$
$$\cdot \binom{a~b^+d}{p_a p_b p_d}\delta\binom{d~c^+e}{p_d p_c p_e}\eta \cdot \tau\binom{-ABS}{iku}\tau\binom{-A'AU}{ril}\tau\binom{-BBU'}{skm}\tau\binom{-A'BV}{rst}$$
$$\cdot (S\varepsilon e p_e | \vec{S_u})(U\alpha a p_a | \vec{U_l'})(\vec{U_m'} | U\beta b p_b)(\vec{V_t} | V\gamma c p_c)(A'\sigma s \| T^c \| B'\sigma's)_{V\gamma c} \tag{17.7}$$

We now inspect the sums for i, k, r, and s of the four topological matrices. Because of the triangular relations (3.1), these sums do not vanish only if $\vec{S_u} + \vec{U_l'} = \vec{U_m'} + \vec{V_t}$ or $\vec{U_l'} - \vec{U_m'} = \vec{V_t} - \vec{S_u}$. We decompose this quadrangular relation into two triangular relations by introducing the edge vector $\vec{X_y} = \vec{U_l'} - \vec{U_m'}$. This edge vector is the distance of two s-orbitals before their shift from the centre to the atomic positions. We therefore get the topological relation:

$$\sum_{\overline{ikrs}} \sqrt{Z(-ABS)Z(-\overline{A'AU})Z(-\overline{BBU'})Z(-\overline{A'BV})} \cdot \tau\binom{-ABS}{iku}\tau\binom{-A'AU}{ril}\tau\binom{-BBU'}{skm}\tau\binom{-A'BV}{rst}$$
$$= \delta(-A'AU)\delta(-\overline{BBU'}) \sum_{\overline{Xy}} \sqrt{Z(-\overline{UU'X})Z(-VSX)} \cdot \tau\binom{-UU'X}{lmy}\tau\binom{-VSX}{tuy}, \tag{17.8}$$

where $\delta(-A'AU) = 1$, if there are triangles of the type $-A'AU$, and $\delta(-A'AU) = 0$ otherwise. This relation reminds of the rule of de-Shalit (2.54) with a simple, "topological 9j symbol". We insert (17.8) into (17.7):

$$(A\varphi_a a \| T^c \| B\varphi_b b)_{S\varepsilon e}^{d\delta\eta} = dimd \sum_{\overline{ABUlmXyVt\gamma}} \sum \delta(-A'AU)\delta(-\overline{BBU'}) \sqrt{Z(-\overline{UU'X})Z(-VSX)/dimc'}$$
$$\cdot \binom{a~b^+d}{p_a p_b p_d}\delta\binom{d~c^+e}{p_d p_c p_e}\eta \cdot \tau\binom{-UU'X}{lmy}\tau\binom{-VSX}{tuy}(S\varepsilon e p_e | \vec{S_u})$$
$$\cdot (U\alpha a p_a | \vec{U_l'})(\vec{U_m'} | U\beta b p_b)(\vec{V_t} | V\gamma c p_c)(A'\sigma s \| T^c \| B'\sigma's)_{V\gamma c}$$

To the sums for l and m we apply (6.14) and collect the remainder by (6.6). This yields the intended relationship between the BRMs:

$$(A\varphi_a a \| T^c \| B\varphi_b b)_{S\varepsilon e}^{d\delta\eta} = \sum_{\overline{ABVX}} \sum_{\mu\gamma} \delta(-A'AU)\delta(-\overline{BBU'}) \sqrt{Z(-\overline{UU'X})Z(-VSX)/dimc'}$$
$$\cdot PIs\begin{pmatrix} -U & U & X \\ \alpha_+\beta & \mu \\ a^+b & d \end{pmatrix}\delta~PIs\begin{pmatrix} -V & S & X \\ \gamma & \varepsilon & \mu_+ \\ c & e & d^+ \end{pmatrix}\eta \cdot (A'\sigma s \| T^c \| B'\sigma's)_{V\gamma c} \tag{17.9}$$

The first polyhedral isoscalar characterizes the topology of the unshifted s-orbitals at the centre, the second one the relation of the atomic distances S to the true distances V of the shifted s-orbitals. The BRMs on the right, of course, depend on the distances V, too. According to (4.10), the BRMs of the s-orbitals result from a simple sum

of the integrals:

$$(\acute{A}\sigma s\| T^C \| B\acute{\sigma}s)_{V\gamma c} = \sqrt{1/\text{dimc}} \cdot \sum_{1kp_c} (V\gamma cp_c | \vec{V}_{1k}) \langle \acute{A}i\sigma s | T^c_{p_c} | B k\acute{\sigma}s \rangle$$

$$= \sqrt{1/\text{dimc}} \cdot Z(-\acute{A}\acute{B}V) \sum_{p_c} (V\gamma cp_c | \vec{V}_{1k}) \langle \acute{A}i\sigma s | T^c_{p_c} | B k\acute{\sigma}s \rangle, \tag{17.10}$$

where in the last line the indices of $\vec{V}_{1k} = \vec{A}_1 - \vec{B}_k$ are arbitrary.

In the case of scalar operators, follows from (17.9/10):

$$(A\varphi_a a \| T \| B\varphi_b b)^\delta_{S\varepsilon e} = \sum_{AB'} \sum_{VX} \delta(-\acute{A}AU) \delta(-\acute{B}B\acute{U}) \cdot \sqrt{Z(-\acute{U}\acute{U}X) Z(-VSX) Z(-\acute{A}\acute{B}V)}$$

$$\cdot \text{PIs} \begin{pmatrix} -U & U & X \\ \alpha_+\beta & \mu \\ a_+b & e \end{pmatrix}_\delta \text{PIs} \begin{pmatrix} -V & S & X \\ \varepsilon & \mu_+ \\ 1 & e & e^+ \end{pmatrix} \cdot \langle \acute{A}i\sigma s | T | B k\acute{\sigma}s \rangle, \tag{17.11}$$

where $\vec{A}_i - \vec{B}_k$ must be an edge of the type V.

By (17.9) the fact is emphasized, that the existence of molecular multi-centre invariants is not restricted to the linear combinations of spherical atomic orbitals.

18. Overlap- and structural matrices, orthonormalization

The following two sections concern the connection of our new results with the conventional treatment of symmetric molecules. As far as the MO picture[+] is concerned, we can be brief. Only the VB picture[+] will show again typical multicentre aspects.

The constructing of many-particle functions and their matrix elements is simplified in both pictures by a preceeding orthonormalization of the one-particle basis. Since the original AOs are not orthogonal, we have to turn over to the delocalized, kanonic MOs or to the localized Löwdin AOs [57]. Apart from series expansions with respect to non-diagonal elements, the diagonalization of the overlap matrix of the original AOs is necessary for both methods. By constructing the s.-a. MOs (5.1) the group theoretical preparations for the diagonalization are done [32]. Because of the orthogonality of the MOs belonging to different symmetry species and components, there remains only the diagonalization of the invariant partial matrices according to:

$$\sqrt{1/\dim \dot{a}} \cdot \sum_{\dot{\beta}} \langle \dot{A}\dot{a} \| \dot{B}\dot{a} \rangle \cdot u_{\dot{B}\sigma}^{\dot{a}} = d_{\sigma}^{\dot{a}} \cdot u_{\dot{A}\sigma}^{\dot{a}} \tag{18.1}$$

The meaning of the quantum numbers is given by (11.6) and the sum runs over all sets of equivalent centres, too. $\dot{a}$ represents all occuring symmetry species. $d_{\sigma}^{\dot{a}}$ are the eigenvalues and $u_{\dot{A}\sigma}^{\dot{a}}$ the components of the eigenvectors of the matrices. The reduced matrix elements $\langle \dot{A}\dot{a} \| \dot{B}\dot{a} \rangle$ result from (15.7), if T is the unit operator.

The kanonical MOs then are given by:

$$|\text{kan.}\sigma\dot{a}p_a \rangle = \sum_{\dot{\beta}} (d_{\sigma}^{\dot{a}})^{-1/2} \cdot u_{\dot{B}\sigma}^{\dot{a}} \cdot |\dot{B}\dot{a}p_a \rangle$$

$$= \sum_{\dot{\beta}km_b} (d_{\sigma}^{\dot{a}})^{-1/2} \cdot u_{\dot{B}\sigma}^{\dot{a}} \cdot M(\dot{B}\dot{a}p_a, Bk\beta b', (\beta b)l_b m_b) \cdot |Bkn_b l_b m_b \rangle \tag{18.2}$$

Since the eigenvectors belonging to $d_{\tau}^{\dot{a}}=0$ express the linear dependencies, these cases are omitted in (18.2).

[+] According to the usage of the quantum theory, unitarily equivalent formulations have to be termed representations or pictures. The Russel-Saunders and the jj coupling, or the strong and the weak field picture of the ligand field theory are unitarily equivalent only if including the full configuration and term interaction. In the same sense, "MO picture" means the construction of MOs with the subsequent full CI calculation, and "VB picture" includes all AO configurations. Omissions and approximations, of course, yield different results within the only basic theory, the quantum mechanics.

Because the eigenvalue problem (18.3) contains invariants only, the eigenvalues are invariants, too. The indirect interrelation between the reduced matrix elements $\langle \mathring{A}a \| \mathring{B}a \rangle$ and the eigenvalues $d_\sigma^{\mathring{a}}$ can be made some more explicit by the following sum rules:

$$\sum_\sigma (d_\sigma^{\mathring{a}})^n = \mathrm{tr}((S^{\mathring{a}})^n) \quad \text{with} \quad S_{\mathring{A}\mathring{B}}^{\mathring{a}} = \langle \mathring{A}a \| \mathring{B}a \rangle / \sqrt{\dim \mathring{a}} \quad (18.3)$$

If $S^{\mathring{a}}$ is an m-dimensional matrix, the first m equations of (18.3) fix the eigenvalues. This has been pointed out long ago by Wigner [58]. If we take the sum of (18.3) with respect to $\mathring{a}$, more stringent sum rules result immediately related to the rotational invariants of

$$\langle An_a l_a m_a | Bn_b l_b m_b \rangle = \sum_J \sqrt{4\pi} \langle n_a l_a \| AB^J \| n_b l_b \rangle^J \left(\begin{smallmatrix} 1 & J & 1 \\ m_a & M & m_b \end{smallmatrix} \right) \langle \overrightarrow{AB} | \text{ sol } JM \rangle \quad (18.4)$$

a special case of (13.3). The first sums are:

$$\sum_{\sigma \mathring{a}} d_\sigma^{\mathring{a}} = \sum_{An_a l_a} \langle n_a l_a \| 0^0 \| n_a l_a \rangle^0 \cdot Z(A) / \sqrt{2l_a + 1} \quad (18.5)$$

$$\sum_{\sigma \mathring{a}} (d_\sigma^{\mathring{a}})^2 = \sum_{An_a l_a} \sum_{Bn_b l_b} \sum_{TJ} Z(-ABT) \cdot T^{2J} \cdot |\langle n_a l_a \| T^J \| n_b l_b \rangle^J|^2 \quad (18.6)$$

Similar rules apply to the eigenvalues of all two-centre matrices.

If we assume a more or less "effective" one-particle Hamiltonian for the electrons of a molecule, similar sum rules result for the one-particle energies $\varepsilon_\sigma^{\mathring{a}}$ belonging to the symmetry species $\mathring{a}$:

$$\sum_\sigma (\varepsilon_\sigma^{\mathring{a}})^n = \mathrm{tr}((\widetilde{H}^{\mathring{a}})^n) = \mathrm{tr}((H^{\mathring{a}} S^{\mathring{a}-1})^n) \quad (18.7)$$

The Hamiltonian matrices are given by $\widetilde{H}_{\sigma\tau}^{\mathring{a}} = \langle \text{kan}.\sigma \mathring{a} p_a | H | \text{kan}.\tau \mathring{a} p_a \rangle$ and $H_{\mathring{A}\mathring{B}}^{\mathring{a}} = \langle \mathring{A}a \| H \| \mathring{B}a \rangle / \sqrt{\dim \mathring{a}}$. Because of (18.1) the inverse overlap matrix is:

$$(S^{\mathring{a}-1})_{\mathring{A}\mathring{B}} = \sum_\sigma u_{\mathring{A}\sigma}^{\mathring{a}} \cdot (d_\sigma^{\mathring{a}})^{-1} \cdot u_{\mathring{B}\sigma}^{\mathring{a}} \quad (18.8)$$

For a preliminary, energetic ordering of the molecular orbitals, a Hückel-like approximation of the two-centre matrix elements $\langle Ain_a l_a m_a | H | Bkn_b l_b m_b \rangle$ may be useful. This is an approximation of the type $H = \alpha I + \beta M$, where M is a structural matrix representing the coordinations, cf [52] section 6.2.2 and [59]. The cited references apply only to s/p_π-orbitals and equal atomic distances and we have to generalize the structural matrix by including different distance vectors and anisotropic orbitals. A characteristic of the Hückel approximation for π-electrons is the independence of the matrix elements from the position of the involved atomic centres. This means that the "topological operator" is regarded as being invariant to translations and rotations. This assumption suffices to fix the form of the structural matrix in accord to the principles of section 13. In analogy to (18.4) follows:

$$\langle An_a l_a m_a | \text{Top} | Bn_b l_b m_b \rangle = \sum_J \sqrt{4\pi} \langle n_a l_a \| AB^J, \text{Top} \| n_b l_b \rangle^J \left(\begin{smallmatrix} 1 & J & 1 \\ m_a & M & m_b \end{smallmatrix} \right) \langle \overrightarrow{AB} | \text{sol } JM \rangle \quad (18.9)$$

The rotational two-centre invariants $\langle n_a l_a \| AB^J, \text{Top} \| n_b l_b \rangle^J$ are the ge-

neralization of the Hückel parameter β. Because of the triangular relation $|l_a-l_b| \leqslant J \leqslant l_a+l_b$ and the parity rule $l_a+l_b-J=0$ modulo 2, the number of the invariants in (18.4 and 9) is equal to the σ-, π-, δ- etc. bonds of the orbitals at the centres A and B. This interrelation is made explicit by choosing the distance vector AB parallel to the z-axis. This produces the standard integrals [60] or standard parameters:

$$\text{Top}_m(n_a l_a n_b l_b, AB) = \langle An_a l_a m | \text{Top} | Bn_b l_b m \rangle_{AB/\!/z}$$

$$S_m(n_a l_a n_b l_b, AB) = \langle An_a l_a m | Bn_b l_b m \rangle_{AB/\!/z} \ , \quad (18.10)$$

where in the usual notation $S_0=S_\sigma$, $S_1=S_\pi$, $S_2=S_\delta$ etc. By inverting (18. 4 and 9) the invariants are expressed by the standard integrals:

$$\langle n_a l_a \| AB^J, \text{Top} \| n_b l_b \rangle^J = \sqrt{2J+1} \cdot AB^{-J} \sum_m \binom{l_a \ J \ l_b}{m \ 0 -m}(-1)^{l_b-m} \cdot \text{Top}_m(n_a l_a n_b l_b, AB)$$

$$\langle n_a l_a \| AB^J \| n_b l_b \rangle^J = \sqrt{2J+1} \cdot AB^{-J} \sum_m \binom{l_a \ J \ l_b}{m \ 0 -m}(-1)^{l_b-m} \cdot S_m(n_a l_a n_b l_b, AB) \quad (18.11)$$

The Hückel-like approximation mentioned above now can be written as:

$$\langle Ain_a l_a m_a | H | Bkn_b l_b m_b \rangle = \alpha(n_a l_a)\delta(A,B)\delta(i,k)\delta(n_a,n_b)\delta(l_a,l_b)\delta(m_a,m_b)$$

$$+ \langle Ain_a l_a m_a | \text{Top} | Bkn_b l_b m_b \rangle \quad (18.12)$$

Its eigenvalues belonging to the several symmetry species then for instance follow from (18.7). If the number of parameters is still to large, one might think of the further reduction,

$$\langle n_a l_a \| AB^J, \text{Top} \| n_b l_b \rangle^J = \beta(n_a l_a n_b l_b, AB)\langle n_a l_a \| AB^J \| n_b l_b \rangle^J \ ,$$

where the overlap invariants may be estimated using the Slater orbitals according to the Slater rules.

The heuristical order of the MOs obtained in this way may serve as a preparation for the Hartree-Fock-Roothaan approach [61]. Such a preparation is necessary in the case of symmetric systems. The building up principle requires in this case that we attach a given number of shells with given occupation numbers to each symmetry species. This is so, because the variation of the orbitals does not alter their symmetry species.

For the purpose of the VB picture on the other hand, orthogonalized atomic orbitals are of interest. An appropriate basis is that of the Löwdin orbitals [57]:

$$|\text{Löw.}Ain_a l_a m_a\rangle = \sum_{Bkn_b l_b m_b} (S^{-1/2})_{Bkn_b l_b m_b, Ain_a l_a m_a} \cdot |Bkn_b l_b m_b\rangle \quad (18.13)$$

The problem is the calculation of the root of the inverse overlap matrix. In analogy to (18.8), we first calculate $S^{a-1/2}$, which is the non-group-theoretical part of the calculation. Then inverting (15.3) by (15.5), we go back to the angular momentum basis:

$$(S^{-1/2})_{Ain_a l_a m_a, Bkn_b l_b m_b} = \sum_{\tilde{\alpha}\tilde{a}\alpha\dot{a}} \sum_{\tilde{\beta}\tilde{b}\beta\dot{b}\beta} \sum_{\sigma\dot{a}p_a} M(\ddot{\alpha}\dot{a}p_a, Ai\dot{d}\dot{d}, (\alpha a)1_a m_a)$$

$$\cdot u^{\dot{a}}_{\dot{A}\sigma}(d^{\dot{a}}_{\sigma})^{-1/2} u^{\dot{a}}_{\dot{\beta}\sigma} \cdot M(\ddot{\beta}\dot{a}p_a, Bk\beta\dot{b}, (\beta b)1_b m_b) , \qquad (18.14)$$

where we have to remember $\dot{A} = (A\dot{d}\dot{d}, n_a 1_a \alpha a)\ddot{\alpha}$. On the other hand, the bicentric matrix $S^{-1/2}$ is a special case of (4.16) and allows the following representation by two-centre invariants:

$$(S^{-1/2})_{Ain_a l_a m_a, Bkn_b l_b m_b} = \sum_{\alpha\dot{a}\beta\dot{b}\delta\varepsilon e} S^{-1/2}(An_a 1_a \alpha\dot{a}\| Bn_b 1_b \beta\dot{b})^{\delta}_{S\varepsilon e}$$

$$\cdot \langle 1_a m_a | 1_a \alpha\dot{a} p_a \rangle \langle 1_b \beta\dot{b} p_b | 1_b m_b \rangle \binom{\dot{d}^+ b' \; e^+}{p_a p_b p_e}^{\delta} \sqrt{1/\text{dime}}(\vec{S}_{ik} | S\varepsilon e p_e) , \qquad (18.15)$$

where the BRMs result from the eigenvalues and eigenvectors of (18.1):

$$S^{-1/2}(An_a 1_a \alpha a\| Bn_b 1_b \beta b)^{\delta}_{S\varepsilon e} = \sqrt{Z(-ABS)\text{dime}} \cdot \sum_{\bar{\alpha}\bar{a}\bar{\beta}\bar{b}} \sum_{\eta\bar{\alpha}\bar{a}\sigma} \text{dim}\dot{a} \{bb\dot{a}^+\beta\} \{ab^+ e\delta\}$$

$$\cdot \left\{ \begin{matrix} a'^+ b' \; e \\ b \; a \; \dot{a}^+ \end{matrix} \right\}_{\alpha\beta\delta\eta} \cdot \text{PIs} \begin{pmatrix} -A & B & S \\ \alpha' & \beta' & \varepsilon \\ a' & \dot{b}'+ & e^+ \end{pmatrix}_\eta \cdot u^{\dot{a}}_{\dot{A}\sigma}(d^{\dot{a}}_{\sigma})^{-1/2} u^{\dot{a}}_{\dot{\beta}\sigma} \qquad (18.16)$$

In essence this is an inversion of (5.13).

19. Many-electron systems

19.1. Summary of the occupation operator technique

A concise description of symmetric many-electron systems is achieved by using the occupation operators, as has been shown by Judd in the case of atomic spectroscopy [62]. But the conventional approach to this technique is quite fussy. There is no need of the detour via a special one-particle basis, determinantal functions, the occupation number representation and so on. This applies especially to symmetric systems, the states of which in general are no determinants at all. We therefore define the creation and annihilation operators with respect to an arbitrary orbital $|\varphi\rangle$ directly by their effect on an arbitrary N-particle function $|N\Phi\rangle$. Such a state is only restricted by the fermion property:

$$T(i,k)\langle r_1 \ldots r_N | N\Phi\rangle = (-1) \cdot \langle r_1 \ldots r_N | N\Phi\rangle \, , \tag{19.1}$$

where $T(i,k)$ means the transposition of r_i and r_k:

$$T(i,k)\langle r_1 \ldots r_{i-1} r_i r_{i+1} \cdots r_{k-1} r_k r_{k+1} \cdots r_N | N\Phi\rangle$$
$$= \langle r_1 \ldots r_{i-1} r_k r_{i+1} \cdots r_{k-1} r_i r_{k+1} \cdots r_N | N\Phi\rangle \tag{19.2}$$

The operators $a^+(\varphi)$ and $a(\varphi)$ adding and annihilating an electron in the orbital $|\varphi\rangle$ now are defined by

$$a^+(\varphi)|N\Phi\rangle = |N+1\Phi\varphi\rangle \tag{19.3}$$
$$a(\varphi)|N\Phi\rangle = |N-1\Phi\varphi\rangle \, , \tag{19.4}$$

where the (N+1)- and (N-1)-particle functions are given by

$$\langle r_1 \ldots r_{N+1} | N+1\Phi\varphi\rangle = (1/\sqrt{N+1}) \sum_i (-1)^{N+1-i} T(N+1,i) \langle r_{N+1} | \varphi\rangle \langle r_1 \ldots r_N | N\Phi\rangle \tag{19.5}$$

$$\langle r_1 \ldots r_{N-1} | N-1\Phi\varphi\rangle = \sqrt{N} \int \langle \varphi | r_N \rangle \langle r_1 \ldots r_N | N\Phi\rangle d^3 r_N \tag{19.6}$$

The consistency of these definitions requires the proof, that $a^+(\varphi)$ and $a(\varphi)$ are adjoint operators, i.e.

$$\langle N+1\Psi | a^+(\varphi) | N\Phi\rangle = \langle N\Phi | a(\varphi) | N+1\Psi\rangle^* \tag{19.7}$$

with arbitrary $|N+1\Psi\rangle$ and $|N\Phi\rangle$. (Assuming two determinants differing just by the one orbital $|\varphi\rangle$ makes the proof at least very incomplete.) The proof is as follows:

$$\langle N+1\Psi | a^+(\varphi) | N\Phi\rangle = (1/\sqrt{N+1}) \sum_i \int \ldots \int \langle N+1 | r_1 \ldots r_{N+1}\rangle$$
$$\cdot (-1)^{N+1-i} T(N+1,i) \langle r_{N+1} | \varphi\rangle \langle r_1 \ldots r_N | N\Phi\rangle d^3 r_1 \ldots d^3 r_{N+1}$$

Since the notation of the integration variables is arbitrary, we interchange some of them:

$$= (1/\sqrt{N+1}) \sum_i \int \ldots \int (-1)^{N+1-i} \left[T(N+1,i) \langle N+1\Psi | r_1 \ldots r_{N+1}\rangle \right]$$
$$\cdot \langle r_{N+1} | \varphi\rangle \langle r_1 \ldots r_N | N\Phi\rangle d^3 r_1 \ldots d^3 r_{N+1}$$

Because of (19.1):

$$= \sqrt{N+1} \int \cdots \int \langle N+1 \Psi | r_1 \cdots r_{N+1} \rangle \langle r_{N+1} | \phi \rangle \langle r_1 \cdots r_N | N \Phi \rangle d^3 r_1 \cdots d^3 r_{N+1}$$

and with (19.6):

$$= \int \cdots \int \langle a(\phi)(N+1\Psi) | r_1 \cdots r_N \rangle \langle r_1 \cdots r_N | N\Phi \rangle d^3 r_1 \cdots d^3 r_N = \langle a(\phi)(N+1\Psi) | N\Phi \rangle,$$

which completes the proof.

From (19.1-6) further follow the well-known commutation relations:

$$[a^+(\phi), a^+(\eta)]_+ = 0 \qquad (19.8)$$

$$[a(\phi), a(\eta)]_+ = 0 \qquad (19.9)$$

$$[a^+(\phi), a(\eta)]_+ = \langle \eta | \phi \rangle \qquad (19.10)$$

The last equation indicates the complications arising from the use of non-orthogonal one-particle bases. For this reason, we have set up the kanonical and the Löwdin bases in the preceeding section and pre-suppose an orthogonal basis $\langle i | k \rangle = \delta_{ik}$ in the following. With respect to such a basis, we have the well-known operator representations

$$T = \sum_{ik} \langle i | t | k \rangle a^+(i) a(k) \qquad (19.11)$$

for a one-particle operator and

$$G = (1/2) \sum_{iklm} \langle ik | g | lm \rangle \, a^+(i) a^+(k) a(l) a(m) \qquad (19.12)$$

for a two-particle operator. The essential point in the proof of (19.11) is the expansion

$$T = \sum_{i=1}^{N} t_i = \sum_{ikl} \langle r'_i | k \rangle \langle k | t | l \rangle \langle l | r_i \rangle$$

in combination with (19.6/7). The proof of (19.12) requires the similar expansion of G. The matrix elements of arbitrary N-particle states then are:

$$\langle N\Phi | T | N\Psi \rangle = \sum_{ik} \langle i | t | k \rangle \langle N\Phi | a^+(i) a(k) | N\Psi \rangle \qquad (19.13)$$

and

$$\langle N\Phi | G | N\Psi \rangle = \frac{1}{2} \sum_{iklm} \langle ik | g | lm \rangle \langle N\Phi | a^+(i) a^+(k) a(l) a(m) | N\Psi \rangle, \qquad (19.14)$$

i.e. weighted sums of the one- and two-particle matrix elements. The weight factors are called one- and two-particle density matrices. If the many-particle functions are built up by a systematic, for instance recursive, calculus, the density matrix elements are pure geometric and combinatorial coefficients, cf.eq.(19.23). This scheme now has to be transferred to the symmetrized MO and VB picture.

19.2. Group theory and occupation operators

For the purpose of the MO picture, we use for instance the kanonical orbitals (18.2) as a starting point. These delocalized orbitals have the same transformation properties as the orbitals of one-centre expansions and approximations. We therefore can take over the aufbau principle of the strong field coupling. But in contrast to the atomic spectroscopy, there is no universal energetic order of the orbitals.

This is demonstrated by the example discussed in [52], page 444. The chemical intuition is supported by the topological considerations of the preceeding section.

The following is known from the literature [5, 8, 9, 16, 17]. Combining group theory and occupation operators we follow the cited ref. [62]. A brief indication concerning point groups is given in [6]. The main interest of the following repetition of [16, 17] is to get a model for the VB picture. As in these references, the quantum numbers are optionally single numbers for G' in $\gamma\gamma$-coupling or double indices for $G \times SU(2)$ in ΓS-coupling (cf. section 2.9.). Thus there is no need to mention the spin explicitly. The main point in the sense of this treaty is that (19.13 and 14) again turn into interrelations between reduced many-particle and reduced one- and two-particle matrix elements mediated again by geometric and combinatorial factors.

The occupation operators of a s.-a. canonical (spin) orbital (18.2) $|kan.\sigma \dot{a} p_a\rangle$ are $a^+(kan.\sigma \dot{a} p_a)$ and $a(kan.\sigma \dot{a} p_a)$. In the following, we do not explicitly mention the index kan., because it does not affect the group theory. The operators are (double) tensor operators transforming in accordance with the representations $\dot{a}$ and $\dot{a}^+$ (note the dagger). Since the proof given in [6] does not apply to point groups, we show the transformation property of $a(\sigma \dot{a} p_a)$. In analogy to (2.6), the unitary operator representation of $g \in G$ is defined by

$$\langle r_1 \ldots r_N | U(g) | N \Phi \rangle = \langle g^{-1} r_1 \ldots g^{-1} r_N | N \Phi \rangle \tag{19.15}$$

We thus have:

$$U(g) a(\sigma \dot{a} p_a) | N \Phi \rangle = U(g) | N{-}1 \Phi \sigma \dot{a} p_a \rangle$$
$$= \int \ldots \int |r_1 \ldots r_{N-1}\rangle \langle r_1 \ldots r_{N-1} | U(g) | N{-}1 \Phi \sigma \dot{a} p_a \rangle d^3 r_1 \ldots d^3 r_{N-1}$$

Because of (19.15):

$$= \int \ldots \int |r_1 \ldots r_{N-1}\rangle \langle g^{-1} r_1 \ldots g^{-1} r_{N-1} | N{-}1 \Phi \sigma \dot{a} p_a \rangle d^3 r_1 \ldots d^3 r_{N-1}$$

and with (19.6):

$$= \int \ldots \int |r_1 \ldots r_{N-1}\rangle \langle \sigma \dot{a} p_a | g^{-1} r_N \rangle \langle g^{-1} r_1 \ldots g^{-1} r_N | N \Phi \rangle d^3 r_1 \ldots d^3 r_N \cdot \sqrt{N}$$

With (19.15) again:

$$= \int \ldots \int |r_1 \ldots r_{N-1}\rangle \langle \sigma \dot{a} p_a | g^{-1} r_N \rangle \langle r_1 \ldots r_N | U(g) | N \Phi \rangle d^3 r_1 \ldots d^3 r_N \cdot \sqrt{N}$$

Further with (2.17):

$$= \sum_{q_a} D^{\dot{a}}_{q_a p_a}(g)^* \int \ldots \int |r_1 \ldots r_{N-1}\rangle \langle \sigma \dot{a} q_a | r_N \rangle \langle r_1 \ldots r_N | U(g) | N \Phi \rangle d^3 r_1 \ldots d^3 r_N \cdot \sqrt{N}$$

and (19.6) again:

$$= \sum_{q_a} D^{\dot{a}}_{q_a p_a}(g)^* \cdot a(\sigma \dot{a} p_a) U(g) | N \Phi \rangle$$

Since $|N \Phi \rangle$ is arbitrary, we conclude:

$$U(g)a(\sigma\mathring{a}p_a) = \sum_{q_a} D^{\mathring{a}}_{q_a p_a}(g)^* \cdot a(\sigma\mathring{a}q_a)U(g) \; ,$$

or with (2.5):

$$U(g)a(\sigma\mathring{a}p_a)U(g)^+ = \sum_{q_a} D^{(\mathring{a}^+)}_{q_a p_a}(g)\cdot a(\sigma\mathring{a}q_a) \; , \qquad (19.16)$$

which has to be shown.

The commutators (19.8-10) now appear as:

$$\left[a^+(\sigma\mathring{a}p_a),a^+(\tau\mathring{b}p_b)\right]_+ = \left[a(\sigma\mathring{a}p_a),a(\tau\mathring{b}p_b)\right]_+ = 0$$

$$\left[a^+(\sigma\mathring{a}p_a),a(\tau\mathring{b}p_b)\right]_+ = \delta(\sigma,\tau)\delta(\mathring{a},\mathring{b})\delta(p_a,p_b) \qquad (19.17)$$

The $\delta(\sigma,\tau)$ does not result from group theory, but from the choice of (18.2).

The many-particle functions are built up in priciple recursively:

$$\left|N+1\varepsilon ep_e\right\rangle = \{e\}\sqrt{\mathrm{dime}}\sum\binom{\mathring{a}^+d^+e}{p_a p_d p_e}^{\eta}\cdot a^+(\sigma\mathring{a}p_a)\left|N\delta dp_d\right\rangle \qquad (19.18)$$

with $\varepsilon = (\delta d\sigma\mathring{a}\eta)$. In order to select an orthonormal set from the functions defined in (19.18), the godparent scheme in connection with Löwdins orthogonalization has been proposed in [16]. As an alternative one may think of the seniority or quasi-spin formalism [63]. Further it is advisable to use (19.18) only within each shell and to combine the (open or closed) shells afterwards, cf.[16] section 6. But the details are not relevant in the present context.

If we apply the WET to the creation operators, we get:

$$\left\langle N\varepsilon ep_e\left|a^+(\sigma\mathring{a}p_a)\right|N-1\delta dp_d\right\rangle = \sum_{\eta}\left\langle N\varepsilon e\|a^+(\sigma\mathring{a})\|N-1\delta d\right\rangle_{\eta}\binom{e^+\mathring{a}\;d}{p_e p_a p_d}^{\eta} \qquad (19.19)$$

Except for a factor, the RMEs are the coefficients of fractional parentage (CFP):

$$\left\langle N\varepsilon e\|a^+(\sigma\mathring{a})\|N-1\delta d\right\rangle_{\eta} = (-1)^N\sqrt{N\cdot\mathrm{dime}}\left\langle N\varepsilon e\{|N-1\delta d,\sigma\mathring{a}\right\rangle_{\eta} \qquad (19.20)$$

This relation shows that the concept of fractional parentage is not restricted to certain recursive schemes. It makes sense in much more general circustances. We give an extreme example: $\left|N\varepsilon ep_e\right\rangle$ may be a strong field coupling function, $\left|N-1\delta dp_d\right\rangle$ a weak field coupling function both built up from GTOs, and $a^+(\sigma\mathring{a}p_a)$ the creator of a STO. Because of (19.5), the CFP can be calculated, if the functions are given explicitly. If on the other hand a recursive construction according to (19.18) is used, the CFPs can be calculated recursively without explicit knowledge of the many-particle functions.

The analogue of (19.11) then is:

$$T^c_{p_c} = \sum_{\sigma_i \mathring{a}_i p_i}\sum\left\langle\sigma_1\mathring{a}_1 p_1\left|t^c_{p_c}\right|\sigma_2\mathring{a}_2 p_2\right\rangle a^+(\sigma_1\mathring{a}_1 p_1)a(\sigma_2\mathring{a}_2 p_2)$$

$$= \sum_{\sigma_i\mathring{a}_i p_i\varepsilon}\sum\left\langle\sigma_1\mathring{a}_1\|t^c\|\sigma_2\mathring{a}_2\right\rangle_{\varepsilon}\binom{\mathring{a}^+_1 c\;\mathring{a}_2}{p_1 p_c p_2}^{\varepsilon}a^+(\sigma_1 a_1 p_1)a(\sigma_2 a_2 p_2) \qquad (19.21)$$

From (19.20/21) results the general interrelation between the reduced

many-particle and the reduced one-particle matrix elements:

$$\langle N\delta_1 d_1 \| T^c \| N\delta_2 d_2 \rangle_\eta = \sum_{\sigma_i a_i \epsilon} \langle \sigma_1 \mathring{a}_1 \| t^c \| \sigma_2 \mathring{a}_2 \rangle_\epsilon \cdot g^{N\eta\epsilon}_{\delta_1 d_1, \delta_2 d_2}(\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2, c) \quad (19.22)$$

with the weight factor:

$$g^{N\eta\epsilon}_{\delta_1 d_1, \delta_2 d_2}(\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2, c) = N\sqrt{\dim d_1 \dim d_2} \sum_{\phi f \sigma \tau} \langle N-1\phi f, \sigma_1 \mathring{a}_1 \| N\delta_1 d_1 \rangle_\sigma$$

$$\cdot \langle N-1\phi f, \sigma_2 \mathring{a}_2 \| N\delta_2 d_2 \rangle_\tau \left\{ f\mathring{a}_1 d^+_1 \sigma \right\} \left\{ \mathring{a}^+_1 c\mathring{a}_2 \epsilon \right\} \left\{ \mathring{a}^+_2 \right\} \left\{ \begin{matrix} c & d_2 d^+_1 \\ f^+ \mathring{a}_1 \mathring{a}_2 \end{matrix} \right\}_{\epsilon\tau\sigma\eta} \quad (19.23)$$

This again is a relation of the principal type (1.2) with the geo-metrical factor (19.23). We have termed it g.. keeping to the nota-tion of Griffith [5], section 7.2.

Similar relations result for the two-particle operators. (19.12) reads now:

$$G = (1/2) \sum_{\sigma_i a_i p_i} \langle \sigma_1 \mathring{a}_1 p_1, \sigma_2 \mathring{a}_2 p_2 | g | \sigma_3 \mathring{a}_3 p_3, \sigma_4 \mathring{a}_4 p_4 \rangle$$

$$a^+(\sigma_1 \mathring{a}_1 p_1) a^+(\sigma_2 \mathring{a}_2 p_2) a(\sigma_3 \mathring{a}_3 p_3) a(\sigma_4 \mathring{a}_4 p_4)$$

$$= (1/2) \sum_{\sigma_i a_i p_i \gamma\mu c} \langle (\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c \| g \| (\sigma_3 \mathring{a}_3, \sigma_4 \mathring{a}_4)\mu c \rangle$$

$$\cdot A^+((\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c p_c) A((\sigma_3 \mathring{a}_3, \sigma_4 \mathring{a}_4)\mu c p_c) \quad (19.24)$$

with the pair operators (s.-a. geminal creation operators):

$$A^+((\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c p_c) = \sqrt{\dim c} \sum_{p_1 p_2 p_c} \left(\begin{matrix} \mathring{a}^+_1 \mathring{a}^+_2 c \\ p_1 p_2 p_c \end{matrix} \right)^\gamma \cdot a^+(\sigma_1 \mathring{a}_1 p_1) a^+(\sigma_2 \mathring{a}_2 p_2) \quad (19.25)$$

From these operators follow the two-particle CFP:

$$\langle N\epsilon e \| A^+((\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c) \| N-2\delta d \rangle_\eta$$

$$= \sqrt{N(N-1)\dim e} \langle N\epsilon e \{\| N-2\delta d, (\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c \rangle_\eta \quad (19.26)$$

And the matrix elements of the two-particle operator finally are:

$$\langle N\delta_1 dp | G | N\delta_2 dp \rangle = \frac{N(N-1)}{2} \sum_{\sigma_i a_i \gamma\mu c} \langle (\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c \| g \| (\sigma_3 \mathring{a}_3, \sigma_4 \mathring{a}_4)\mu c \rangle$$

$$\cdot \sum_{\phi f \eta} \langle N-2\phi f, (\sigma_1 \mathring{a}_1, \sigma_2 \mathring{a}_2)\gamma c \| N\delta_1 d \rangle_\eta \langle N-2\phi f, (\sigma_3 \mathring{a}_3, \sigma_4 \mathring{a}_4)\mu c \| N\delta_2 d \rangle_\eta \quad (19.27)$$

again a relation of type (1.2).

As a consequence of the delocalization of the kanonical MOs, the results, shortly summarized here, have no specific polycentric charac-ter. This character again appears, if we calculate the density ma-trix of a molecular state with respect to a localized AO basis, in or-der to read the charge and bond orders with respect to this basis [64]. We only discuss the density matrices of totally symmetric states or the average density of degenerate states. Taking the aver-age is equivalent to picking out the totally symmetric part of the density matrix [65]:

$$\Gamma_{Ai\phi_a a p_a, Bk\phi_b b p_b} = \dim d^{-1} \sum_{p_d} \langle N\alpha d p_d | a^+(Ai\phi_a a p_a) a(Bk\phi_b b p_b) | N\delta d p_d \rangle \quad (19.28)$$

Because of (19.19/20), this is essentially a bilinear sum of CFP in the AO basis. As a typical two-centre matrix,(19.28) falls within the scope of (4.13) and has the following representation:

$$\Gamma_{Ai\varphi_a ap_a, Bk\varphi_b bp_b} = \sum_{\delta\varepsilon e}\Gamma(A\varphi_a a\|B\varphi_b b)^\delta_{S\varepsilon e}\binom{a^+b\ e^+}{p_a p_b p_e}^\delta \sqrt{1/dime}(\overrightarrow{S}_{ik}|S\varepsilon ep_e) \quad (19.29)$$

The BRMs with $S\neq0$ are the symmetry-invariant representation of the bond orders classified according to the bond edges, those with $S=0$ the charge orders. This is the solution of the problem posed in [64], page 60, i.e. the problem to define the bond orders invariantly to symmetry operations in the presence of several bonding electrons.

20. Sketch of the VB picture

In contrast to the MO picture, the VB picture naturally contributes further stimulating aspects to the polycentric algebra. After the initial success by Heitler and London the VB picture [66] has not been popular because of the multitude of configurations. But the calculations, focussed on the atoms and compounds of the first period, have led to a one-sided view. Among the transition-metal and lanthanide compounds treated in the first approximation by the weak field coupling, there are obvious candidates for VB calculations and moreover of its atoms-in-molecules version proposed by Moffitt [67]. In this connection, we again point to the discussion in [52], page 444. In view of the expenditure on CI calculations the VB may become competitive again.

Avoiding orthogonality problems, we start from the Löwdin basis (18.13) and adapt it to the symmetry group:

$$|L\ddot{o}w.Ai\varphi_a ap_a\rangle = \sum |L\ddot{o}w.Ain_a l_a m_a\rangle\langle 1_a m_a|1_a \alpha ap_a\rangle \qquad (20.1)$$

with $\varphi_a=(n_a l_a \alpha)$. The commutation relations of the pertinent occupation operators are:

$$[a^+(L\ddot{o}w.Ai\varphi_a ap_a),a^+(L\ddot{o}w.Bk\varphi_b bp_b)]_+=[a(L\ddot{o}w.Ai\varphi_a ap_a),a(L\ddot{o}w.Bk\varphi_b bp_b)]_+=0$$

$$[a^+(L\ddot{o}w.Ai\varphi_a ap_a),a(L\ddot{o}w.Bk\varphi_b bp_b)]_+=\delta(A,B)\delta(i,k)\delta(\varphi_a,\varphi_b)\delta(a,b)\delta(p_a,p_b)$$

where in detail $\delta(\varphi_a,\varphi_b)=\delta(n_a,n_b)\delta(1_a,1_b)\delta(\alpha,\beta)$. $\qquad (20.2)$

After the model of (19.18), one generates the VB functions by repeated application of the creation operators. Each added (spin) orbital introduces a new centre into the many-particle function, so that every VB function is associated with a more or less asymmetric polyhedron. The vertices, some of which may coincide again, are valued differently by the AOs.

Against the first sight, this building up does not lead to an incalculable multitude of different polyhedra because of two reasons. By (3.25), (7.8), and (10.2) we already have become aquainted with the equivalence of polyhedra and vectors inducing the same representation of the symmetry group. There is only a limited number of such representations, which are determined by the vectors a) in general position, b) on equivalent plains of reflection, and c) on equivalent axes of rotation. Because of this equivalence, the polyhedra fall into classes inducing equivalent representations. Fully identical representations are achieved only, if the numbering of the polyhedra is coordinated.

On the other hand, the number of different polyhedra is limited by the Pauli principle. If all orbitals $|Ai\varphi_a ap_a\rangle$ with fixed A, φ_a, and a are doubly occupied, the result is a full supershell. We use this term with respect to reducible representations. In general a super-

shell contains several ordinary shells belonging to irreducible repre-
sentations. The polyhedron associated with the supershell has 2·dima·
$Z(A)$ vertices, 2·dima of which coincide at each centre. Therefore it
is totally symmetric, and there are no higher polyhedra within a super-
shell.

In the following, P^n represents a set of equivalent polyhedra with
n vertices and P_k^n the k-th polyhedron of this set. The symmetry-adap-
tation of a scalar polyhedral function $(P_k^n|F)$ is analogous to (3.17):

$$(P^n \varepsilon ep_e|F) = \sum_k (P^n \varepsilon ep_e|P_k^n)(P_k^n|F) , \qquad (20.3)$$

where the SALC coefficients $(P^n \varepsilon ep_e|P_k^n)$ are determined via the asso-
ciated vectors $\vec{P_k} = \sum_{A_i} \mu_{Ai} \cdot \vec{A_i}$ with $\vec{A_i} \in P_k^n$.

In parallel to (19.18), we now generate the many-particle VB states:

$$|Q_1^{n+1} \delta dp_d\rangle = \{d\} \sqrt{Z(Q^{n+1}) \text{dima}} \sum_k \binom{a^+c^+d}{p_a p_c p_d}^{\varepsilon} \cdot \hat{\tau}\binom{A \ P^nQ^{n+1}}{i \ k \ 1} \cdot a^+(\text{Löw.}A\varphi_a ap_a)|P_k^n \gamma cp_c\rangle \qquad (20.4)$$

with $\delta = (A\varphi_a a, P^n \gamma c, \varepsilon)$. The quantum numbers δ and γ recursively notify
the antecedents of the state. $\hat{\tau}$ is the generalization of our topolo-
gical matrices and does not vanish only, if Q_1^{n+1} comes from P_k^n by the
addition of the new vertex at A_i:

$$\hat{\tau}\binom{A \ P^nQ^{n+1}}{i \ k \ 1} = \begin{cases} 1/\sqrt{Z(Q^{n+1})}, & \text{if } P_k^n \stackrel{.}{+} \vec{A_i} = Q_1^{n+1} \\ 0 & \text{otherwise} \end{cases} \qquad (20.5)$$

Obviously there are orthogonality relations like:

$$\sum_{ik} \hat{\tau}\binom{A \ P^nQ^{n+1}}{i \ k \ 1} \cdot \hat{\tau}\binom{A \ P^nR^{n+1}}{i \ k \ m} = \delta(Q,R)\delta(1,m)/Z(Q^{n+1}) \qquad (20.6)$$

Apart from the antisymmetrization, the formation of the geminals (9.3)
is a simple example of (20.4). The states generated in this way are
in general non-orthogonal and moreover often linearly dependent. Of
cours, the diagonalization of the overlap matrix of these state may
serve for the orthonormalization again. But because of the high dimen-
sion of the supershells, other methods, like the quasi-spin or seniority
formalism, will be more economic. The functions (20.4) transform in
accord to the reducible product representation $d \times \sigma^{P^n}$.

If T_p^d is a translation invariant or a s.-a. operator at the centre
of symmetry, the matrix elements $\langle Q_k^n \varepsilon ep_e|T_{p_d}^d|R_1^n \acute{e} \acute{e} p_e'\rangle$ are associated
with a polyhedron of 2n vertices composed of the polyhedra Q_k^n and R_1^n.
We express this composition by another topological relation:

$$\hat{\tau}\binom{Q^nR^nP^{2n}}{k \ 1 \ m} = \begin{cases} 1/\sqrt{Z(P^{2n})}, & \text{if } Q_k^n \stackrel{.}{+} R_1^n = P_m^{2n} \\ 0 & \text{otherwise} \end{cases} \qquad (20.7)$$

Having defined this, we can state the following theorem:

$$\langle Q_k^n \varepsilon e p_e | T_{P_d}^d | R_1^n \varepsilon' e' p_e' \rangle = \sum_{f\eta\varphi Pm\pi p}(Q^n \varepsilon e \| T^d \| R^n \varepsilon' e')_{P^{2n}\pi p}^{f\eta\varphi} \cdot \binom{e^+ e'\ f}{P_e P_e' P_f}^\eta \binom{f^+ d\ \ p^+}{P_f P_d P_p}^\varphi$$
$$\cdot \sqrt{Z(P^{2n})} \hat{\tau} \binom{Q^n R^n P^{2n}}{k\ \ l\ \ m} \cdot (P_m^{2n} | P^{2n} \pi p p_p) \tag{20.8}$$

This theorem, including the proof, agrees totally with (4.6). The invariants therefore are termed polyhedral, reduced matrix elements (PRM).

The polyhedral VB functions (20.4) now are combined to SALCs. This is quite analogous to (5.1):

$$|Q^n \varphi f p_f \rangle = \sum_{k p_e} \hat{K}(\eta f p_f, Q^n k \delta d, e p_e) \cdot |Q_k^n \varepsilon e p_e \rangle \tag{20.9}$$

with $\varphi=(\varepsilon e, \delta d, \eta)$, where ε is a compound index corresponding with (20.4). The generalized SALC coefficient is:

$$\hat{K}(\eta f p_f, Q^n k \delta d, e p_e) = \{f\} \sqrt{\dim f} \sum \binom{d^+ e^+ f}{P_d P_e P_f}^\eta \cdot (Q_k^n | Q^n \delta d p_d) \tag{20.10}$$

Apart from (5.1), we already know another example of (20.9), namely the formation of the s.-a. geminals (9.4).

Again we apply the WET to the matrix elements of the states (20.9)

$$\langle Q^n \varphi f p_f | T_{P_c}^c | R^n \gamma g p_g \rangle = \sum_\varepsilon \langle Q^n \varphi f \| T^c \| R^n \gamma g \rangle_\varepsilon \binom{f^+ c\ g}{P_f P_c P_g}^\varepsilon , \tag{20.11}$$

the RMEs of which are related to the PRMs quite in parallel to the relations (5.5 or 8). This relation requires the definition of a polyhedral isoscalar generalizing (6.6):

$$\widehat{PIs}\begin{pmatrix} Q^n R^n P^{2n} \\ \delta\ \ \varrho\ \ \pi \\ d\ \ r\ \ p \end{pmatrix}_\varepsilon = \sum_{klm} \hat{\tau} \binom{Q^n R^n P^{2n}}{k\ \ l\ \ m} (Q_k^n | Q^n \delta d p_d)(R_1^n | R^n or p_r)(P_m^{2n} | P^{2n} \pi p p_p) \binom{d\ r\ p}{P_d P_r P_p}^{\varepsilon^*} \tag{20.12}$$

Then follows the theorem:

$$\langle Q^n \varphi f \| T^c \| R^n \gamma g \rangle_{\varepsilon''} = \sum_z \widehat{GEO}_1(x,y,z) \cdot (Q^n \varepsilon e \| T^c \| R^n \varepsilon' e')_{P^{2n}\pi p}^{h\sigma\tau} \tag{20.13}$$

with the generalized geometrical factor

$$\widehat{GEO}_1(x,y,z) = \{f^+ g c \varepsilon''\} \sqrt{Z(P^{2n})} \dim f \cdot \dim g \cdot \sum_\alpha \widehat{PIs} \begin{pmatrix} Q^n R^n P^{2n} \\ \delta\ \ \delta'\ \ \pi \\ d^+ d'\ \ p \end{pmatrix}_\alpha \cdot \begin{Bmatrix} f^+ g\ \ c \\ d\ \ d'^+ p^+ \\ e\ \ e'^+ h^+ \end{Bmatrix}_\alpha^{\varepsilon''} \begin{matrix} \eta\ \theta\ \tau \\ \alpha \\ \sigma \end{matrix} \tag{20.14}$$

and the compound indices $\varphi=(\varepsilon e, \delta d, \eta)$, $\gamma=(\varepsilon' e', \delta' d, \theta)$, $y=(\delta d \eta f, \delta' d \theta g, \varepsilon')$, $x=(Q^n e, R^n e', c)$, and $z=(h\sigma\tau P^{2n} \pi p)$.

Besides (5.5), another example of (20.13) is hidden in (11.20), since the geometrical factor GEO_3 is composed of three factors of the general type GEO_1. From the general point of view the polyhedral isoscalar of the third kind is nothing but

$$PIs^3 \begin{pmatrix} \mathcal{T}\ S\ T \\ \cdot\ \cdot\ \cdot \\ \cdot\ \cdot\ \cdot \end{pmatrix} = \widehat{PIs} \begin{pmatrix} T^4 S^2 T^2 \\ \cdot\ \cdot\ \cdot \\ \cdot\ \cdot\ \cdot \end{pmatrix} \tag{20.15}$$

The 6j symbol appears in (11.20) instead of a 9j symbol as a result of (2.52/53), because the operator is a scalar.

One-particle operators have the representation

$$T_{P_c}^c = \sum_{AiBk} \sum_{\varphi_x x p_x} \langle L\ddot{o}w.Ai\varphi_a a p_a | t_{P_c}^c | L\ddot{o}w.Bk\varphi_b b p_b \rangle$$
$$\cdot a^+(L\ddot{o}w.Ai\varphi_a a p_a) a(L\ddot{o}w.Bk\varphi_b b p_b) \tag{20.16}$$

and in order to trace back the PRMs to the one-particle matrix elements and their invariants, we must examine the polyhedral matrix elements of the occupation operators, i.e. $\langle Q_1^{n+1}\delta dp_d|a^+(L\ddot{o}w.Ai\varphi_a ap_a)|$ $|P_k^n \varepsilon ep_e\rangle$. These matrix elements are zero, if $P_k^n \colon \vec{A}_i = R_m^{n+1} \neq Q_1^{n+1}$; for the VB functions referring to R_m^{n+1} and Q_1^{n+1} are mutually orthogonal, since they differ by one Löwdin orbital. Hence the matrix elements behave like the topological matrices (20.5) and allow the factorization:

$$\langle Q_1^{n+1}\delta dp_d|a^+(L\ddot{o}w.Ai\varphi_a ap_a)|P_k^n\varepsilon ep_e\rangle = C\cdot\hat{\tau}\begin{pmatrix}Q^{n+1} & A & P^n\\ 1 & i & k\end{pmatrix}$$

The proportionality factor C transforms according to the direct product $d^+\times a\times e$, so that the WET yields a further factorization:

$$\langle Q_1^{n+1}\delta dp_d|a^+(L\ddot{o}w.Ai\varphi_a ap_a)|P_k^n\varepsilon ep_e\rangle \tag{20.17}$$
$$= \sum_\mu \langle Q^{n+1}\delta d\|a^+(A\varphi_a a)\|P^n\varepsilon e\rangle_\mu \begin{pmatrix}d^+ & a & e\\ p_d & p_a & p_e\end{pmatrix}_\mu \cdot \hat{\tau}\begin{pmatrix}Q^{n+1} & A & P^n\\ 1 & i & k\end{pmatrix}$$

At this point, one might argue that the matrix elements transform according to the sixfold product $d^+\times a\times e\times \sigma^{Q^{n+1}}\times \sigma^A\times \sigma^{P^n}$ and should have a more complex coupling structure than (20.17). But since the couplings of the polyhedra and of the orbital representations have been kept strictly apart in (20.4), the matrix behaves like a double tensor of $i^+\times a\times e$ on one hand and of $\sigma^{Q^{n+1}}\times \sigma^A\times \sigma^{P^n}$ on the other.

In analogy to (19.20), the polyhedral CFP are defined as follows:

$$\langle Q^{n+1}\delta d\|a^+(A\varphi_a a)\|P^n\varepsilon e\rangle_\mu = (-1)^{n+1}\sqrt{(n+1)Z(Q^{n+1})\dim d}\,\overline{\langle Q^{n+1}\delta d\,\{|P^n\varepsilon e,A\varphi_a a\rangle}_\mu \tag{20.18}$$

Having defined this, we can determine the PRMs of (20.8) by the BRMs of the Löwdin orbitals, a relation that replaces (19.22) in the VB case. For this purpose, we solve (20.8) for the PRMs:

$$(Q^n\varepsilon e\|T^c\|R^n\varepsilon'\tilde{e})_{P^{2n}\pi p}^{f\eta\varphi} = \sqrt{Z(P^{2n})}\cdot\dim f\cdot\sum_{k l m}(P^{2n}\pi pp_p|P_m^{2n})\cdot\hat{\tau}\begin{pmatrix}Q^n & R^n & P^{2n}\\ k & l & m\end{pmatrix}$$
$$\cdot\begin{pmatrix}f^+ & c & p\\ p_f & p_c & p_p\end{pmatrix}\varphi^* \begin{pmatrix}e^+ & e' & f\\ p_e & p'_e & p_p\end{pmatrix}\eta^* \langle Q^n\varepsilon ep_e|T_{p_c}^c|R^n\varepsilon'ep'_e\rangle \tag{20.19}$$

For the matrix elements on the right side, we substitute (20.16) and (4.6) for the one-particle matrix elements in (20.16). This yields:

$$(Q^n\varepsilon e\|T^c\|R^n\varepsilon'\tilde{e})_{P^{2n}\pi p}^{f\eta\varphi} = \sum_y GEO_9(x,y)\cdot(L\ddot{o}w.A\varphi_a a\|t^c\|L\ddot{o}w.B\varphi_b b)_{S\sigma s}^{g\gamma\alpha} \tag{20.20}$$

with $x=(Q^n\varepsilon e, R^n\varepsilon'\tilde{e}, f\eta\varphi, P^{2n}\pi p)$ and $y=(A\varphi_a a, B\varphi_b b, S\sigma s, g\gamma\alpha)$. For the present, the geometrical factor is given by:

$$EO_9(x,y) = \sqrt{Z(P^{2n})Z(-ABS)}\dim f\cdot\sum_{k l m}\sum_{i j t}(P^{2n}\pi pp_p|P_m^{2n})\hat{\tau}\begin{pmatrix}Q^n & R^n & P^{2n}\\ k & l & m\end{pmatrix}\begin{pmatrix}f^+ & c & p\\ p_f & p_c & p_p\end{pmatrix}\varphi^*$$
$$\cdot\begin{pmatrix}e^+ & e' & f\\ p_e & p'_e & p_f\end{pmatrix}\eta^*\begin{pmatrix}a^+ & b & g\\ p_a & p_b & p_g\end{pmatrix}\gamma\begin{pmatrix}g^+ & c & s\\ p_g & p_c & p_s\end{pmatrix}\alpha\cdot\tau\begin{pmatrix}-ABS\\ i j t\end{pmatrix}(\vec{S}_t|S\sigma sp_s)$$
$$\cdot\langle Q_k^n\varepsilon ep_e|a^+(L\ddot{o}w.Ai\varphi_a ap_a)a(L\ddot{o}w.Bj\varphi_b bp_b)|R_1^n\varepsilon'\tilde{e}p'_e\rangle$$

etween the two occupation operators we insert a comp ete function stem, i.e. $\sum_{Tr}\sum_{\delta dp_d}|T_r^{n-1}\delta dp_d\rangle\langle T_r^{n-1}\delta dp_d|$, expess the resulting ma-

trix elements by (20.17) and collect the 3jm symbols in a 6j symbol:

$$GEO_9(x,y) = \delta(f,g)\delta(s,p)\delta(\alpha,\varphi)dims^{-1}\sqrt{Z(P^{2n})Z(-ABS)}\{ba^+f\gamma\}\sum_{\delta d\mu\mu}\{e'^+bd\mu'\}$$

$$\cdot\begin{Bmatrix}e & a^+d^+\\b & e' & f^+\end{Bmatrix}_{\eta\gamma\mu\mu}\cdot\sum_{klmijtTr}\sum(P^2\pi sp_s|P_m^2)(\vec{S}_t|S\sigma sp_s)\hat{\tau}\begin{pmatrix}Q^nR^nP^{2n}\\k & l & m\end{pmatrix}\tau\begin{pmatrix}-ABS\\ijt\end{pmatrix}$$

$$\cdot\hat{\tau}\begin{pmatrix}Q^nA & T^{n-1}\\k & i & r\end{pmatrix}\hat{\tau}\begin{pmatrix}R^nB & T^{n-1}\\l & j & r\end{pmatrix}\langle Q^n\varepsilon e\|a^+(A\varphi_a a)\|T^{n-1}\delta d\rangle_\mu\langle R^n\varepsilon'e'\|a^+(B\varphi_b b)\|T^{n-1}\delta d\rangle_{\mu'}$$

From this expression, we isolate the following topological invariant, which is remotely similar to a 6j symbol:

$$PW\begin{Bmatrix}Q & R & P^\pi/S^{\sigma s}\\B & A & T\end{Bmatrix} = dims^{-1}\sum_{klmijtr}\sum\hat{\tau}\begin{pmatrix}Q^nR^nP^{2n}\\k & l & m\end{pmatrix}\tau\begin{pmatrix}-ABS\\ijt\end{pmatrix}\hat{\tau}\begin{pmatrix}Q^nA & T^{n-1}\\k & i & r\end{pmatrix}\hat{\tau}\begin{pmatrix}R^nB & T^{n-1}\\l & j & r\end{pmatrix}$$

$$\cdot(\vec{S}_t|S\sigma sp_s)(P^{2n}\pi sp_s|P_m^{2n}) \tag{20.21}$$

It relates the edges S associated with the one-particle BRMs to the polyhedra P^{2n} belonging to the many-particle PRMs. Speaking more precisely, it indicates, which edges S interrelate the centres in Q^n with those in R^n and if the representations σ^S and $\sigma^{P^{2n}}$ have in common the irreducible representation s.

Introducing the polyhedral CFP by (20.18) yields the final expression of the geometrical factor:

$$GEO_9(x,y) = \delta(f,g)\delta(s,p)\delta(\alpha,\varphi)\cdot n\cdot\sqrt{Z(P^{2n})Z(-ABS)Z(Q^n)Z(R^n)}dime\cdot dime'$$

$$\cdot\{ba^+f\gamma\}\sum_{T\delta d\mu\mu'}\sum\{e'^+bd\mu'\}\begin{Bmatrix}e & a^+d^+\\b & e' & f^+\end{Bmatrix}_{\eta\gamma\mu\mu}\cdot PW\begin{Bmatrix}Q & R & P^\pi/S^{\sigma s}\\B & A & T\end{Bmatrix} \tag{20.22}$$

$$\cdot\langle Q^n\varepsilon e\{|T^{n-1}\delta d,A\varphi_a a\rangle_\mu\langle R^n\varepsilon''e\{|T^{n-1}\delta d,B\varphi_b b\rangle_{\mu'}$$

By inserting (20.20) into (20.13), we can directly link the RMEs of the s.-a. VB functions to the one-particle BRMs:

$$\langle Q^n\varphi f\|T^C\|R^n\phi f\rangle_{\varepsilon'} = \sum_{y_2}GEO_{10}(x_1,y_1,y_2)\cdot(L\ddot{o}w.A\varphi_a a\|t^C\|L\ddot{o}w.B\varphi_b b)^{g\gamma\alpha}_{S\sigma s} \tag{20.23}$$

with $\varphi=(\varepsilon e,\delta d,\eta)$, $\phi=(\varepsilon'e',\delta'd',\eta)$, $x_1=(Q^n e,R^n e',c)$, $y_1=(\delta d\eta f,\delta'd'\eta f',\varepsilon')$, and $y_2=(A\varphi_a a,B\varphi_b b,S\sigma s,g\gamma\alpha)$ and the compound factor:

$$GEO_{10}(x_1,y_1,y_2) = \sum_{h\sigma\tau P^{2n}\pi p}\sum\widehat{GEO}_1(x_1,y_1,z_1)\cdot GEO_9(z_2,y_2), \tag{20.24}$$

where $z_1=(h\sigma\tau P^{2n}\pi p)$ and $z_2=(Q^n\varepsilon e,R^n\varepsilon'e',h\sigma\tau,P^{2n}\pi p)$.

Of course, a similar analysis involving the polyhedral two-particle CFP can be made for the two-particle interaction operators.

21. Prospect of crystals

As mentioned in the introduction, the symmetry analysis lined out, so far, can be transferred to crystals, i.e. to space groups. To begin with, we confine the discussion to the formation of SALCs, as far as this can be achieved without using projective representations [68].

21.1. The irreducible representations of space groups

We summarize the concepts needed to set up the irreducible representations of space groups. In general we keep to the book of Streitwolf [37].

The space group is marked by G, the related point group by $G_0 \sim G/T$, where T is the translation group. An element $\{\alpha|\vec{a}\}$ of a space group is the operation defined by a translation $\vec{a} \in T$ and a rotation $\alpha \in G_0$:

$$\{\alpha|\vec{a}\}\vec{r} = \alpha\vec{r} + \vec{a} \qquad (21.1)$$

From this definition follows $\{\beta|\vec{b}\}\{\alpha|\vec{a}\} = \{\beta\alpha|\beta\vec{a}+\vec{b}\}$ and $\{\alpha|\vec{a}\}^{-1} = \{\alpha^{-1}|-\alpha^{-1}\vec{a}\}$. The unitary operator representing $\{\alpha|\vec{a}\} \in G$ in the function space is in accordance with (4.2) defined by:

$$\langle\vec{r}|U(\{\alpha|\vec{a}\})|\varphi\rangle = \langle\{\alpha|\vec{a}\}^{-1}\vec{r}|\varphi\rangle = \langle\alpha^{-1}\vec{r}-\alpha^{-1}\vec{a}|\varphi\rangle = \langle\alpha^{-1}(\vec{r}-\vec{a})|\varphi\rangle \qquad (21.2)$$

The irreducible representations of the space groups are characterized by wave vectors within the first Brillouin zone. To each wave vector $\vec{k}$ belongs a subgroup $G_{o\vec{k}} \subset G_0$, the elements of which leave $\vec{k}$ invariant or transform it into an equivalent wave vector:

$$G_{o\vec{k}} = \{\beta \text{ with } \beta \in G_0 \text{ and } \beta\vec{k} = \vec{k} + \vec{K}\}, \qquad (21.3)$$

where $\vec{K}$ means a lattice vector of the reciprocal lattice. This point group is also termed the little cogroup of $\vec{k}$ [68]. The irreducible, projective representations b of these cogroups enter the ordinary, irreducible representations of the space groups. We designate the irreducible, projective representations of the little cogroups by

$$D^{\vec{k}b}_{p_b q_b}(\beta) \quad \text{with } \beta \in G_{o\vec{k}} , \qquad (21.4)$$

where $\vec{k}$ indicates the pertinent wave vector. Because this concept of projective representations is significant only for some wave vectors at the surface of the Brillouin zone of non-symmorphic space groups, it is entirely avoided by Streitwolf [37]. But it allows the general and concise formulation of all irreducible representations of all space groups (21.10) below, cf. [68].

In order to select the elements of $G_{o\vec{k}}$ from those of G_0, we define the symbol
$$\Delta^{\vec{k}}(\alpha) = \begin{cases} 1 & \text{if } \alpha \quad G_{o\vec{k}}, \text{ i.e. } \alpha\vec{k}=\vec{k}+\vec{K} \\ 0 & \text{if } \alpha \quad G_{o\vec{k}}, \text{ i.e. } \alpha\vec{k}\neq\vec{k}+\vec{K} \end{cases} \qquad (21.5)$$

The coset decomposition of G_0 with respect to $G_{o\vec{k}}$ is:

$$G_o = \sum_i \alpha_i G_{o\vec{k}} \tag{21.6}$$

with the coset representatives α_i.

By applying these representatives to $\vec{k}$, one generates a set of wave vectors $\vec{k}_j$ (within the first Brillouin zone), the so called star of $\vec{k}$, which is designated by ^+k:

$$^+k = \{\vec{k}_j \text{ with } \vec{k}_j = \alpha_j \vec{k} + \vec{K}\} \tag{21.7}$$

We choose $\alpha_1 = \varepsilon$, i.e. $\vec{k}_1 = \vec{k}$. The vectors $\vec{k}_j \in {}^+k$ are termed the prongs of the star.

We now can generalize (21.5) to all $\alpha \in G_o$ by defining

$$\Delta_{ij}^{\vec{k}}(\alpha) = \Delta^{\vec{k}}(\alpha_i^{-1}\alpha\alpha_j), \tag{21.8}$$

or because of (21.5 and 7):

$$\Delta_{ij}^{\vec{k}}(\alpha) = \begin{cases} 1 & \text{if } \alpha\vec{k}_j = \vec{k}_i + \vec{K} \\ 0 & \text{if } \alpha\vec{k}_j \neq \vec{k}_i + \vec{K} \end{cases} \tag{21.9}$$

Now all necessary notations are collected to write down all irreducible representations of the space groups. These are determined by a star ^+k and an irreducible (projective) representation b of $G_{o\vec{k}}$ with $\vec{k} \in {}^+k$. The components of the representations are determined likewise by a double index, i.e. by the prong j ($\vec{k}_j$ respectively) and by the component p_b of $b(G_{o\vec{k}})$. Using (2.4), the representation matrices $D^{(^+kb)}(\{\alpha|\vec{a}\})$ then are given by:

$$D_{ip_b, jr_b}^{(^+kb)}(\{\alpha|\vec{a}\}) = \Delta_{ij}^{\vec{k}}(\alpha) D_{p_b r_b}^{\vec{k}b}(\alpha_i^{-1}\alpha\alpha_j) \cdot \exp(-i\vec{k}_i \cdot \vec{a}) \tag{21.10}$$

The associated bases are denoted $|\beta(^+kb)ip_b\rangle$, where β is a discriminating index.

At this point, we must insert a marginal note concerning the phase in eq. (21.10). This phase is sometimes chosen more complicate as in [69], eq.(4.19) and [70b], eq,(I.4). The difference results from two gauge transformations, A) of the representations of $G_{o\vec{k}}$: $D^{\vec{k}b}(\beta) = \exp(-i\vec{k}\cdot\vec{v}_\beta)\cdot D^{\vec{k}b}(\beta)$ and B) of the bases: $|\beta(^+kb)ip_b\rangle = \exp(-\vec{k}_i\cdot\vec{v}_{\alpha_i})\cdot |\beta(^+kb)ip_b\rangle$, where $\vec{v}_\gamma$ denotes the non-primitive translation belonging to the rotation or reflection γ. We have three reasons for our choice of the phase: A) for internal points of the Brillouin zone our matrices $D^{\vec{k}b}(\beta)$ are genuine vector representations and not only projectively-equivalent to vector representations, cf.eq.(4.25) of [69]. B) In the following relations concerning the bases (21.13 and 14) no phase factors occur. C) Eq. (21.10) is plainly simpler.

The transformation property of the bases with respect to the operation (21.2) is now given by:

$$U(\{\alpha|\vec{a}\})|\beta(^+kb)jr_b\rangle = \sum_{ip_b} D_{ip_b, jr_b}^{(^+kb)}(\{\alpha|\vec{a}\}) \cdot |\beta(^+kb)ip_b\rangle \tag{21.11}$$

The SALCs or tight-binding functions intended have to comply with this
relation. Since we have derived the theory of SALC coefficients for
ordinary vector representations only, we must exclude the few cases
requiring really projective representations.

21.2. Symmetry-adapted functions for symmorphic space groups

We start with a construction, which is restricted to symmorphic
space groups but immediately resumes the molecular symmetry-adaption;
for in the the symmorphic case the Wigner-Seitz unit cell can be trea-
ted like a molecule and the point-group adaption can be simply com-
bined with the well-known Bloch sums [37], eq.(6.14).

The relations (21.10 and 11) suggest that the atomic orbitals must
be adapted to the pertinent little cogroup. The coupling according
to (5.2) then has to be done with respect to the same group. The ad-
aptation thus depends on the point of the Brillouin zone.

In order not to operate with SALC coefficients, 3jm symbols, and
s.-a. atomic orbitals of several point groups simultaneously, we pro-
ceed as follows. All atomic orbitals are classified according to the
irreducible representations of G_0 and in the frame of a universal,
fixed coordinate system. Then the s.-a. Wigner-Seitz-cell orbitals
are formed using the SALC coefficients belonging to G_0. And only in
conclusion, the SALCs are subduced to $G_{0\vec{K}}$ if necessary. If $\vec{A_i}$ are the
position vectors of the equivalent atoms within the Wigner-Seitz cell,
the s.-a. cell orbitals according to (5.1/2) are given by:

$$\langle \vec{r} | (A\varepsilon e, \varphi_a a) \gamma c p_c \rangle = \sum_{ip_a} K^0(\gamma c p_c, A i \varepsilon e, a p_a) \cdot \langle \vec{r} - \vec{A_i} | \varphi_a a p_a \rangle$$

with

$$K^0(\gamma c p_c, A i \varepsilon e, a p_a) = \{c\} \sqrt{\dim c} \sum_{p_e} \binom{e^+ a^+ c}{p_e p_a p_c}^\gamma (\vec{A_i} | A \varepsilon e p_e)$$

For $\vec{k}=0$, G_0 is the little cogroup and the s.-a. tight-binding functions
are simple Bloch sums for the lattice vectors $\vec{R}$:

$$\langle \vec{r} | \delta (^+Oc)Op_c \rangle = \sum_{\vec{R} i p_a} K^0(\gamma c p_c, A i \varepsilon e, a p_a) \langle \vec{r} - \vec{A_i} - \vec{R} | \varphi_a a p_a \rangle \qquad (21.12)$$

with $\delta = (\varphi_a a A \varepsilon e \gamma)$.

In the other cases, the s.-a. Wigner-Seitz-cell orbitals have to
be subduced to the little cogroup $G_{0\vec{K_j}}$ belonging to the relative prong
$\vec{K_j}$. All little cogroups $G_{0\vec{K_j}}$ belonging to the same star are isomorphic
to $G_{0\vec{K}}$:

$$G_{0\vec{K_j}} = \alpha_j^{-1} G_{0\vec{K}} \alpha_j$$

This means for the representation matrices:

$$D_{p_b q_b}^{\vec{k}j b}(\beta_j) = D_{p_b q_b}^{\vec{k}b}(\alpha_j^{-1}\beta\alpha_j) \quad \text{with } \beta_j \epsilon G_{0\vec{K_j}}, \ \beta \epsilon G_{0\vec{K}}$$

The coordinate axes are different for each $\vec{k}_j$ and the bases are related by

$$U(\alpha_j)|\vec{k}bp_b\rangle = |\vec{k}_j bp_b\rangle \tag{21.13}$$

Hence it follows for the adaption coefficients of the group chains $G_o \supset G_{o\vec{k}_j}$ and $G_o \supset G_{o\vec{k}}$:

$$\langle cp_c|\vec{k}_j\beta bp_b\rangle = \sum_{q_c} D^{oc}_{p_c q_c}(\alpha_j)\langle cq_c|\vec{k}\beta bp_b\rangle, \tag{21.14}$$

where c is a representation of G_o with the matrices $D^{oc}(\alpha)$.

We no state that the s.-a. tight-binding functions are given by

$$\langle \vec{r}|\delta(^+kb)jp_b\rangle \tag{21.15}$$
$$= \sum_{R_i} \sum_{p_a p_c}\langle cp_c|\vec{k}_j\beta bp_b\rangle K^o(\gamma cp_c, A i\epsilon\epsilon, ap_a)\cdot\exp(i\vec{k}_j\cdot\vec{R})\cdot\langle \vec{r}-\vec{A}_i-\vec{R}|\varphi_a ap_a\rangle$$

with $\delta=(a\varphi_a A\epsilon\epsilon\gamma c\beta)$.

To prove this, we have to demonstrate the property (21.11/10). With (21.2), we have at first:

$$\langle \vec{r}|U(\{\alpha|\vec{a}\})|\delta(^+kb)jp_b\rangle \tag{21.16}$$
$$=\sum_{R_i}\sum_{p_a p_c}\exp(i\vec{k}_j\cdot\vec{R})\langle cp_c|\vec{k}_j\beta bp_b\rangle K^o(\gamma cp_c, A i\epsilon\epsilon, ap_a)\langle\alpha^{-1}(\vec{r}-\vec{a}-\alpha\vec{A}_i-\alpha\vec{R})|\varphi_a ap_a\rangle$$

Because of (4.2) and (3.3), it follows

$$\langle\alpha^{-1}(\vec{r}-\vec{a}-\alpha\vec{A}_i-\alpha\vec{R})|\varphi_a ap_a\rangle= \sum_{kq_a} D^{oa}_{q_a p_a}(\alpha)\sigma^A_{ki}(\alpha)\langle\vec{r}-\vec{a}-\vec{A}_k-\alpha\vec{R}|\varphi_a aq_a\rangle \tag{21.17}$$

and further with (3.5) and (2.22):

$$\sum_{ip_a} K^o(\gamma cp_c, A i\epsilon\epsilon, ap_a)\cdot D^{oa}_{q_a p_a}(\alpha)\sigma^A_{ki}(\alpha) = \sum_{q_c} K^o(\gamma cq_c, A k\epsilon\epsilon, aq_a)\cdot D^{oc}_{q_c p_c}(\alpha) \tag{21.18}$$

Substituting (21.17/18) into (21.16) yields the intermediate result

$$\langle\vec{r}|U(\{\alpha|\vec{a}\})|\delta(^+kb)jp_b\rangle = \sum_{Rkp_c q_a q_c}\sum \exp(i\vec{k}_j\cdot\vec{R})\langle cp_c|\vec{k}_j\beta bp_b\rangle D^{oc}_{q_c p_c}(\alpha)$$
$$\cdot K^o(\gamma cq_c, A k\epsilon\epsilon, aq_a)\langle\vec{r}-\vec{a}-\vec{A}_k-\alpha\vec{R}|\varphi_a aq_a\rangle. \tag{21.19}$$

This requires the calculation of the sum

$$\sum_{p_c} D^{oc}_{q_c p_c}(\alpha)\langle cp_c|\vec{k}_j\beta bp_b\rangle$$
$$= \sum_{ip_c r_c s_c}\sum D^{oc}_{q_c r_c}(\alpha_i)D^{oc}_{r_c s_c}(\alpha_i^{-1}\alpha\alpha_j)D^{oc}_{s_c p_c}(\alpha_j^{-1})\langle cp_c|\vec{k}_j\beta bp_b\rangle\Delta^{\vec{k}}_{ij}(\alpha),$$

where $\alpha_i^{-1}\alpha\alpha_j\epsilon G_{o\vec{k}}$ because of (21.9). Using (21.14), we get further:

$$= \sum_{ir_c s_c}\sum D^{oc}_{q_c r_c}(\alpha_i)D^{oc}_{r_c s_c}(\alpha_i^{-1}\alpha\alpha_j)\langle cs_c|\vec{k}\beta bp_b\rangle\Delta^k_{ij}(\alpha)$$
$$= \sum_{ir_c q_b}\sum D^{oc}_{q_c r_c}(\alpha_i)\langle cr_c|\vec{k}\beta bq_b\rangle D^{kb}_{q_b p_b}(\alpha_i^{-1}\alpha\alpha_j)\Delta^k_{ij}(\alpha)$$

and finally with (21.14) again:

$$\sum_{p_c} D^{oc}_{q_c p_c}(\alpha)\langle cp_c|\vec{k}_j\beta bp_b\rangle = \sum_{iq_b}\langle cq_c|\vec{k}_i\beta bp_b\rangle D^{kb}_{q_b p_b}(\alpha_i^{-1}\alpha\alpha_j)\Delta^k_{ij}(\alpha) \tag{21.20}$$

We have to insert this result into (21.19). In addition, we substitute $\vec{a}+\alpha\vec{R}=\vec{R}'$ or $\vec{R}=\alpha^{-1}(\vec{R}'-\vec{a})$. Replacing the sum for $\vec{R}$ by a sum for $\vec{R}'$, we get:

$$\langle\vec{r}|U(\{\alpha|\vec{a}\})|\delta(^+kb)jp_b\rangle = \sum_{\overline{Rkiq_x}} \exp(i\alpha\vec{k}_j\cdot(\vec{R'}-\vec{a}))\cdot D^{\overline{k}b}_{q_bp_b}(\alpha_i^{-1}\alpha\alpha_j)\cdot\Delta^{\overline{k}}_{ij}(\alpha)$$

$$\cdot\langle cq_c|\vec{k}_i\beta bq_b\rangle K^0(\gamma cq_c,Ak\varepsilon e,aq_a)\langle\vec{r}-\vec{A}_k-\vec{R}|\varphi_a aq_a\rangle$$

Because of (21.7), $\alpha_i^{-1}\alpha\alpha_j\epsilon G_{o\vec{k}}$, and (21.3), we have:

$$\alpha\vec{k}_j=\alpha_i(\alpha_i^{-1}\alpha\alpha_j)\alpha_j^{-1}\vec{k}_j=\alpha_i(\alpha_i^{-1}\alpha\alpha_j)\vec{k}+\vec{k}_1=\alpha_i\vec{k}+\vec{k}_2+\vec{k}_1=\vec{k}_i+\vec{k}_3+\vec{k}_2+\vec{k}_1=\vec{k}_i+\vec{k}$$

Since $\vec{R'}-\vec{a}$ is a lattice vector in the symmorphic case, this yields:

$$\exp(i\alpha\vec{k}_j\cdot(\vec{R'}-\vec{a})) = \exp(i\vec{k}_i(\vec{R'}-\vec{a}))$$

and we can sum up with (21.15):

$$\langle\vec{r}|U(\{\alpha|\vec{a}\})|\delta(^+kb)jp_b\rangle=\sum_{iq_b}\Delta^{\vec{k}}_{ij}(\alpha)D^{\overline{k}b}_{q_bp_b}(\alpha_i^{-1}\alpha\alpha_j)\exp(-i\vec{k}_i\cdot\vec{a})\langle\vec{r}|\delta(^+kb)iq_b\rangle$$

This proves (21.11/10).

21.3. Construction includung non-symmorphic groups

The Wigner-Seitz cell of non-symmophic groups is not invariant to G_o and in general not to $G_{o\vec{k}}$. Therefore we can no more rely directly upon the SALC coefficients of the point groups in the configuration space as in (21.12).

We propose another method likewise applicable to symmorphic and non-symmorphic groups. To this end we remember section 12. Accoding to (12.16), the SALC coefficients could be determined by substituting the atomic positions into s.-a. functions. If we set aside the ortho-normalization in a first step, every s.-a. may serve for this purpose.

Such s.-a. functions are the symmetrized plain waves according to [37], section 6.2. For internal points of the Brillouin zone, we can set up these symmetrized plain waves again by the help of the SALC coefficients using them now in the reciprocal lattice. We again start with k=0 in order to keep the calculation in G_o descending to G_{ok} in the end.

We choose a set of equivalent lattice vectors in general position. This choice avoids invariance groups $G_{o\vec{k}}$ and their cosets and yields a maximal number of functions. Starting with a lattice vector $\vec{k}$ in general position, we can number the members of the equivalent set by the elements $\beta\,\epsilon\,G_o$: $\vec{k}_\beta=\beta\vec{k}$. We now claim that the following SALC of plain waves belongs to the irreducible representation (^+Oe) of the space group:

$$\langle\vec{r}|W(^+Oe)Op_e\rangle = \sum_{\beta\epsilon G_o} (\vec{k}_\beta|K\varepsilon ep_e)\cdot\exp(-\vec{k}_\beta\cdot\vec{v}_\beta)\cdot\exp(i\vec{k}_\beta\cdot\vec{r}) \qquad (21.21)$$

The proof of (21.21) is contained in that of (21.23).

The symmetrized plain waves of the general case $\vec{k}\neq0$ are:

$$\langle\vec{r}|W\varepsilon\beta(^+kb)jp_b\rangle=\sum_{\beta p_e}(\vec{k}_{\beta'}|K\varepsilon ep_e)\langle ep_e|\vec{k}_j\beta bp_b\rangle\exp(-i\vec{k}_{\beta'}\cdot\vec{v}_{\beta'})\exp[i(\vec{k}_{\beta'}+\vec{k}_j)\cdot\vec{r}]$$
$$(21.22)$$

But in order apply the coupling coefficients of G_o, only we use (21.21) to form the s.-a. tight-binding functions for the special case $\vec{k}=0$:

$$\langle\vec{r}|TB\delta(^+Oc)Op_o\rangle=\sum_{Rt\beta'p_a}K^O(\gamma cp_c,K\beta'\varepsilon e,ap_a)\exp[i\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_t-\vec{v}_{\beta'})]\langle\vec{r}-\vec{R}-\vec{A}_t|\varphi_a ap_a\rangle$$

with $\delta=(\varphi_a aAK\varepsilon e\gamma)$. Descending now to $G_{o\vec{k}_j}$ we generate the s.-a. tight-binding functions for the general case:

$$\langle\vec{r}|TB\eta(^+kb)jp_b\rangle = \sum_{Rt\beta'}\sum_{p_ap_c}K^O(\gamma cp_c,K\beta'\varepsilon e,ap_a)\langle cp_c|\vec{k}_j\beta bp_b\rangle$$
$$\cdot\exp[i\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_t-\vec{v}_\beta)]\exp[i\vec{K}_j\cdot(\vec{R}+\vec{A}_t)]\langle\vec{r}-\vec{R}-\vec{A}_t|\varphi_a ap_a\rangle \qquad (21.23)$$

with $\eta=(\varphi_a aAK\varepsilon e\gamma c\beta)$.

In our final proof, we show that this formula comprises all tight-binding functions of internal points of the first Brillouin zone. At first we have with (21.2):

$$\langle\vec{r}|U(\{\alpha|\vec{a}\})|TB\eta(^+kb)jp_b\rangle = \sum_{Rt\beta'}\sum_{p_ap_c}K^O(\gamma cp_c,K\beta'\varepsilon e,ap_a)\langle cp_c|\vec{k}_j\beta bp_b\rangle$$
$$\cdot\exp[i\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_t-\vec{v}_{\beta'})]\exp[i\vec{K}_j\cdot(\vec{R}+\vec{A}_t)]\langle\alpha^{-1}(\vec{r}-\vec{a}-\alpha\vec{R}-\alpha\vec{A}_t)|\varphi_a ap_a\rangle$$

Substituting $\vec{a}+\alpha\vec{R}+\alpha\vec{A}_t=\vec{R}+\vec{A}_u$ or $\vec{R}+\vec{A}_t=\alpha^{-1}(\vec{R}+\vec{A}_u-\vec{a})$ and using (4.2) yields:

$$= \sum_{Ru\beta'}\sum_{p_ap_cq_a}K^O(\gamma cp_c,K\beta'\varepsilon e,ap_a)\langle cp_c|\vec{k}_j\beta bp_b\rangle\cdot\exp[i\alpha\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_u-\vec{a}-\alpha\vec{v}_{\beta'})]$$
$$\cdot\exp[i\alpha\vec{K}_j\cdot(\vec{R}+\vec{A}_u-\vec{a})]\cdot D^{oa}_{q_ap_a}(\alpha)\langle\vec{r}-\vec{R}-\vec{A}_u|\varphi_a aq_a\rangle$$

Because of $\{\alpha|\vec{a}\}\{\beta|\vec{v}_\beta\} = \{\alpha\beta'|\vec{a}+\alpha\vec{v}_{\beta'}\} = \{\alpha\beta'|\vec{v}_{\alpha\beta'}+\vec{R}'\}$, there is the relation

$$\exp[i\alpha\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_u-\vec{a}-\alpha\vec{v}_{\beta'})] = \exp[i\alpha\vec{K}_{\beta'}\cdot(\vec{R}+\vec{A}_u-\vec{v}_{\alpha\beta'})]$$
$$= \sum_{\gamma'}\sigma^K_{\gamma'\beta'}(\alpha)\cdot\exp[i\vec{K}_{\gamma'}\cdot(\vec{R}+\vec{A}_u-\vec{v}_{\gamma'})].$$

Using this and (21.18), we get:

$$= \sum_{Ru\gamma'}\sum_{p_cq_aq_c}K^O(\gamma cp_c,K\gamma'\varepsilon e,aq_a)D^{oc}_{q_cp_c}(\alpha)\langle cp_c|\vec{k}_j\beta bp_b\rangle\exp[i\vec{K}_{\gamma'}\cdot(\vec{R}+\vec{A}_u-\vec{v}_{\gamma'})]$$
$$\cdot\exp[i\alpha\vec{K}_j\cdot(\vec{R}+\vec{A}_u-\vec{a})]\langle\vec{r}-\vec{R}-\vec{A}_u|\varphi_a aq_a\rangle$$

and further with (21.20):

$$= \sum_{Ru\gamma iq_aq_bq_c}\sum K^O(\gamma cq_c,K\gamma'\varepsilon e,aq_a)\langle cq_c|\vec{k}_i\beta bp_b\rangle\cdot D^{\vec{k}b}_{q_bp_b}(\alpha_i^{-1}\alpha\alpha_j)\Delta^{\vec{k}}_{ij}(\alpha)$$
$$\cdot\exp[i\vec{K}_{\gamma'}\cdot(\vec{R}+\vec{A}_u-\vec{v}_\gamma)]\exp[i\alpha\vec{K}_j\cdot(\vec{R}+\vec{A}_u-\vec{a})]\langle\vec{r}-\vec{R}-\vec{A}_u|\varphi_a aq_a\rangle$$

From $\Delta^{\vec{k}}_{ij}(\alpha)\neq0$ follows again $\alpha\vec{k}_j=\vec{k}_i+\vec{K}'_i$, i.e. for internal points $\alpha\vec{k}_j=\vec{k}_i$. This requirement restricts the method to internal points. We no collect the sums according to (21.10 and 23):

$$= \sum_{iq_b}D^{(^+kb)}_{iq_b,jp_b}(\{\alpha|\vec{a}\})\langle\vec{r}|TB\eta(^+kb)iq_b\rangle$$

and this had to be shown.

We have pointed out, how we principally can determine the s.-a. functions and thereby the SALC coefficients of space groups. A more systematic approach results, if we derive, from the symmetrized plain

waves, the standard functions of the space groups as in section 12. This yields complete orthonormal sets of SALC coefficients.

There still remains the problem of the surface of the Brilluoin zone. In individual cases, one may obtain symmetrized plain waves or tight-binding functions by induction from a symmorphic subgroup as shown in [37].

But the systematic approach requires the projective representations of the little cogroups. As has been shown in [71], also the Clebsch-Gordan coefficients or 3jm symbols of the space groups are related to those of the projective representations of the little cogroups. They are treated systematically in the paper of Dirl [70]. Starting from the references [69-71], one can elaborate the Wigner-Racah algebra, then the polyhedral invariants of the space groups, and apply both in the theorems demonstrated in this treatise.

22. Case study: Tetrahedral structures
22.1. Preliminaries and standard functions

As an example, we consider the polyhedral symmetry properties of some tetrahedral structures like the molecules P_4 and P_4O_6. The basis of this consideration are the classic tables of the characters, the 3jm, the 6j and the 9j symbols of the group T_d. Because of the isomorphism of the point groups T_d and O, we can take over the tables given by Griffith [5] for the octahedral group O. The full matrices of the irreducible representations have been tabulated by McWeeny [30], table 4.19/20. The operation of the group elements of T_d on the position vector $\vec{r}$ is listed in the following table.

Table 1. The elements of T_d and their operation on $\vec{r}$.

g	x y z	g	x y z	g	x y z	g	x y z
E	x y z	$C_3^{xy\bar{z}}$	z-x-y	$\bar{S}_4^z$	y-x-z	S_4^x	-x-z y
C_2^x	x-y-z	$C_3^{\bar{x}y z}$	-z x-y	σ_{xy}	-y-x z	$\sigma_{y\bar{z}}$	x z y
C_2^y	-x y-z	$\bar{C}_3^{xyz}$	y z x	$\sigma_{x\bar{y}}$	y x z	S_4^y	z-y-x
C_2^z	-x-y z	$\bar{C}_3^{x\bar{y}\bar{z}}$	-y z-x	S_4^z	-y x-z	$\sigma_{z\bar{x}}$	z y x
C_3^{xyz}	z x y	$\bar{C}_3^{\bar{x}y\bar{z}}$	-y-z x	σ_{yz}	x-z-y	σ_{zx}	-z y-x
$C_3^{x\bar{y}\bar{z}}$	-z-x y	$\bar{C}_3^{\bar{x}\bar{y}z}$	y-z-x	$\bar{S}_4^x$	-x z-y	$\bar{S}_4^y$	-z-y x

Before considering specified structures, we have to prepare a complete set of standard functions of the group T_d following section 12. From the compilation by Bell [38] we take the following set of non-orthogonal s.-a. functions being complete in the sense of the scalar product (12.2):

1) species A_1:

$$\langle \vec{r}|A_1\rangle = 1 \qquad (22.1)$$

2) species A_2:

$$\langle \vec{r}|A_2\rangle = (x^2-y^2)(y^2-z^2)(z^2-x^2) \qquad (22.2)$$

3) species E (components 1 and 2):

$$\langle \vec{r}|1E1\rangle = 2z^2-x^2-y^2 \qquad \langle \vec{r}|2E1\rangle = 2z^4-x^4-y^4$$
$$\langle \vec{r}|1E2\rangle = \sqrt{3}(x^2-y^2) \qquad \langle \vec{r}|2E2\rangle = \sqrt{3}(x^4-y^4) \qquad (22.3)$$

4) species T_1 (components ξ, η, ζ):

$$\langle \vec{r}|1T_1\xi\rangle = (y^2-z^2)x, \; \langle \vec{r}|2T_1\xi\rangle = (y^2-z^2)yz, \; \langle \vec{r}|3T_1\xi\rangle = (y^2-z^2)x^3$$
$$\langle \vec{r}|1T_1\eta\rangle = (z^2-x^2)y, \; \langle \vec{r}|2T_1\eta\rangle = (z^2-x^2)zx, \; \langle \vec{r}|3T_1\eta\rangle = (z^2-x^2)y^3 \quad (22.4)$$
$$\langle \vec{r}|1T_1\zeta\rangle = (x^2-y^2)z, \; \langle \vec{r}|2T_1\zeta\rangle = (x^2-y^2)xy, \; \langle \vec{r}|3T_1\zeta\rangle = (x^2-y^2)z^3$$

5) species T_2 (components x, y, z):

$$\langle \vec{r}|1T_2 x\rangle = x \qquad \langle \vec{r}|2T_2 x\rangle = yz \qquad \langle \vec{r}|3T_2 x\rangle = x^3$$
$$\langle \vec{r}|1T_2 y\rangle = y \qquad \langle \vec{r}|2T_2 y\rangle = zx \qquad \langle \vec{r}|3T_2 y\rangle = y^3 \qquad (22.5)$$
$$\langle \vec{r}|1T_2 z\rangle = z \qquad \langle \vec{r}|2T_2 z\rangle = xy \qquad \langle \vec{r}|3T_2 z\rangle = z^3$$

Because the elements of the Gram matrix (12.9) are scalar functions of $\vec{r}$, it is advisable to study the scalar functions with respect to T_d in some detail. There are even scalars of order 2n:

$$Sc(2n) = x^{2n} + y^{2n} + z^{2n} \qquad (22.6)$$

and a second type of order 2m+2n:

$$Sc(2m,2n) = y^{2m}z^{2n} + z^{2m}y^{2n} + z^{2m}x^{2n} + x^{2m}z^{2n} + x^{2m}y^{2n} + y^{2m}x^{2n} \qquad (22.7)$$

The latter type includes the special case:

$$Sc(2n,2n) = 2(y^{2n}z^{2n} + z^{2n}x^{2n} + x^{2n}y^{2n})$$

A third type of even scalar functions is:

$$Sc(2m,2n,2p) = \sum_{i \neq j \neq k} x_i^{2m} x_j^{2n} x_k^{2p} \qquad (22.8)$$

including the special case:

$$Sc(2p,2p,2p) = 6x^{2p}y^{2p}z^{2p}$$

The only essential odd scalar is

$$Sc_o = x \cdot y \cdot z, \qquad (22.9)$$

from which all other odd scalars result by multiplication by an even scalar.

Also the even scalars are not independent, but can be reduced to the three basic scalars $Sc(2) = r^2$, Sc_o, and $Sc(2,2) = 2(y^2z^2 + z^2x^2 + x^2y^2)$. We give some examples:

$$Sc(4) = x^4 + y^4 + z^4 = Sc(2)^2 - Sc(2,2)$$
$$Sc(4,2) = 0,5Sc(2) \cdot Sc(2,2) - 3Sc_o^2$$
$$Sc(6) = Sc(2)^3 - 1,5Sc(2) \cdot Sc(2,2) + 3Sc_o^2$$

We now build up the system of standard function beginning with Gram's matrix according to (12.9):

$$S_{mn}^a(\vec{r}) = (map|nap) = \sum_{g \in G} \langle map|g\vec{r}\rangle\langle g\vec{r}|nap\rangle = \text{dima}^{-1}\sum_{g \in G}\sum_p \langle map|g\vec{r}\rangle\langle g\vec{r}|nap\rangle$$
$$= (\text{ordG/dima})\sum_p \langle map|\vec{r}\rangle\langle\vec{r}|nap\rangle \qquad (22.10)$$

The evaluation of the last sum in general requires fewer terms. The first standard function can be taken directly from the sets (22.1-5):

$$\langle\vec{r}|st.1ap\rangle = \langle\vec{r}|1ap\rangle \qquad (22.11)$$

with $\mu(1a,\vec{r}) = S_{11}^a(\vec{r})$ according to (12.3).

In the case of two- and three-dimensional representations, we slightly modify Schmidt's orthogonalization process in order to generate purely polynomial functions:

$$\langle\vec{r}|st.2ap\rangle = S_{11}^a(\vec{r})\langle\vec{r}|2ap\rangle - S_{12}^a(\vec{r})\langle\vec{r}|1ap\rangle \qquad (22.12)$$

with

$$\mu(2a,\vec{r}) = (S_{11}^a)^2 \cdot S_{22}^a - S_{11}^a \cdot (S_{12}^a)^2 = \mu(1a,\vec{r}) \cdot \det\begin{vmatrix} S_{11}^a & S_{12}^a \\ S_{21}^a & S_{22}^a \end{vmatrix} \qquad (22.13)$$

In the case of the three-dimensional representations, the third stand-

ard function is given by:

$$\langle \vec{r}|st.3ap\rangle \tag{22.14}$$
$$= (S^a_{11}S^a_{22}-(S^a_{12})^2)\langle \vec{r}|3ap\rangle -(S^a_{11}S^a_{23}-S^a_{12}S^a_{13})\langle \vec{r}|2ap\rangle -(S^a_{13}S^a_{22}-S^a_{23}S^a_{12})\langle \vec{r}|1ap\rangle$$

with

$$\mu(3a,\vec{r}) = \det\begin{vmatrix} S^a_{11} & S^a_{12} \\ S^a_{21} & S^a_{22} \end{vmatrix}\cdot\det\begin{vmatrix} S^a_{11} & S^a_{12} & S^a_{13} \\ S^a_{21} & S^a_{22} & S^a_{23} \\ S^a_{31} & S^a_{32} & S^a_{33} \end{vmatrix} \tag{22.15}$$

The arrangement is such, that the scalar of the highest order $S^a_{33}(\vec{r})$ does not appear in the third standard function (22.14).

We now compile the standard functions of the separate symmetry species:

1) species A_1:
$$\langle \vec{r}|st.A_1 1\rangle = 1 \quad , \quad \mu(A_1,\vec{r}) = 24 \tag{22.16}$$

2) species A_2:
$$\langle \vec{r}|st.A_2 1\rangle = (x^2-y^2)(y^2-z^2)(z^2-x^2), \ \mu(A_2,\vec{r}) =24(x^2-y^2)^2 (y^2-z^2)^2 (z^2-x^2)^2 \tag{22.17}$$

3) species E: From (22.3) results:
$$S^E_{11}=24(2Sc(4)-Sc(2,2)), \ S^E_{12}=24(2Sc(6)-Sc(4,2)), \ S^E_{22}=24(2Sc(8)-Sc(4,4)) \tag{22.18}$$

and further:
$$\left.\begin{array}{c} \langle \vec{r}|st.1E1\rangle = 2z^2-x^2-y^2, \quad \langle \vec{r}|st.1E2\rangle = \sqrt{3}(x^2-y^2) \\ \mu(1E,\vec{r}) = 24(2Sc(4) - Sc(2,2)) \end{array}\right\} \tag{22.19}$$

$$\left.\begin{array}{c} \langle \vec{r}|st.2E1\rangle = S^E_{11}(\vec{r})\cdot(2z^4-x^4-y^4) - S^E_{12}(\vec{r})\cdot(2z^2-x^2-y^2) \\ \langle \vec{r}|st.2E2\rangle = S^E_{11}(\vec{r})\cdot\sqrt{3}(x^4-y^4) - S^E_{12}(\vec{r})\cdot\sqrt{3}(x^2-y^2) \\ \mu(2E,\vec{r}) = (S^E_{11})^2\cdot S^E_{22} - S^E_{11}\cdot(S^E_{12})^2 \end{array}\right\} \tag{22.20}$$

4) species T_1: From (22.4) results:
$$S^{T_1}_{11}(\vec{r}) = 8(Sc(4,2)-Sc(2,2,2)), \quad S^{T_1}_{12}(\vec{r}) = 8(2Sc(4)-Sc(2,2))Sc_o$$
$$S^{T_1}_{22}(\vec{r}) = 8(Sc(6,2)-Sc(4,4)) \quad , \quad S^{T_1}_{13}(\vec{r}) = 8(Sc(4,4)-Sc(4,2,2)) \tag{22.21}$$
$$S^{T_1}_{33}(\vec{r}) = 8(Sc(6,4)-Sc(6,2,2)), \quad S^{T_1}_{23}(\vec{r}) = 8(Sc(4,2)-Sc(2,2,2))Sc_o$$

and further:
$$\left.\begin{array}{c} \langle \vec{r}|st.1T_1\rangle = (y^2-z^2)x \quad \text{and cyclic permutations} \\ \mu(1T_1,\vec{r}) = 8(Sc(4,2) - Sc(2,2,2)) \end{array}\right\} \tag{22.22}$$

$$\left.\begin{array}{c} \langle \vec{r}|st.2T_1\rangle = S^{T_1}_{11}(\vec{r})\cdot(y^2-z^2)yz - S^{T_1}_{12}(\vec{r})\cdot(y^2-z^2)x \quad \text{cyclic} \\ \mu(2T_1,\vec{r}) = (S^{T_1}_{11})^2\cdot S^{T_1}_{22} - S^{T_1}_{11}\cdot(S^{T_1}_{12})^2 \end{array}\right\} \tag{22.23}$$

$$\left.\begin{array}{c} \langle \vec{r}|st.3T_1\rangle= (S^{T_1}_{11}S^{T_1}_{22}-(S^{T_1}_{12})^2)\cdot(y^2-z^2)x^3 - (S^{T_1}_{11}S^{T_1}_{23}-S^{T_1}_{12}S^{T_1}_{13})\cdot(y^2-z^2)yz \\ -(S^{T_1}_{13}S^{T_1}_{22}-S^{T_1}_{23}S^{T_1}_{12})\cdot(y^2-z^2)x \quad \text{cyclic} \\ \mu(3T_1,\vec{r}) = \text{formula (22.15)} \end{array}\right\} \tag{22.24}$$

5) species T_2: From (22.5) results:

$$S_{11}^{T_2}(\vec{r}) = 8r^2 \qquad S_{22}^{T_2}(\vec{r}) = 4Sc(2,2) \qquad S_{33}^{T_2}(\vec{r}) = 8Sc(6)$$
$$S_{12}^{T_2}(\vec{r}) = 24xyz \qquad S_{13}^{T_2}(\vec{r}) = 8Sc(4) \qquad S_{23}^{T_2}(\vec{r}) = 8r^2xyz \left.\right\} (22.25)$$

and further:

$$\langle\vec{r}|st.1T_2x\rangle = x \quad \text{and cyclic permutations}$$
$$\mu(1T_2,\vec{r}) = 8r^2 \left.\right\}(22.26)$$

$$\langle\vec{r}|st.2T_2x\rangle = 8r^2yz - 24xyz\cdot x \quad \text{cyclic}$$
$$\mu(2T_2,\vec{r}) = (S_{11}^{T_2})^2\cdot S_{22}^{T_2} - S_{11}^{T_2}\cdot(S_{12}^{T_2})^2 \left.\right\}(22.27)$$

$$\langle\vec{r}|st.3T_2x\rangle = (S_{11}^{T_2}S_{22}^{T_2}-(S_{12}^{T_2})^2)x^3 - (S_{11}^{T_2}S_{23}^{T_2}-S_{12}^{T_2}S_{13}^{T_2})yz$$
$$- (S_{13}^{T_2}S_{22}^{T_2}-S_{23}^{T_2}S_{12}^{T_2})x \quad \text{cyclic} \left.\right\}(22.28)$$

$$\mu(3T_2,\vec{r}) = \text{formula (22.15)}$$

22.2. Equivalent sets and their SALC coefficients

After this general preparation, we come to the particular structures having T_d symmetry. There are five different sets of equivalent positions or other equivalent objects. These sets are:

1) The central position invariant to all symmetry operations $\vec{0} = (0,0,0)$
2) Four positions $\vec{A}_r$ on the three-fold rotation axes. These and the following positions are given in table 2.
3) Six positions $\vec{B}_r$ on the two-fold rotation axes.
4) Twelve equivalent positions $\vec{C}_r$ on the reflection planes.
5) 24 general positions $\vec{D}_r$ apart from any element of symmetry.

The position vectors in the latter two cases are not determined uniquely. For instance, $\vec{C}_1=(b,c,c)$ with $b\neq c$ and $2c^2+b^2=1$ would do. For the purpose of numerical calculation, we have arbitrarily chosen the vectors given in table 2.

Table 2. The position vectors of the equivalent sets.

	x	y	z			x	y	z
A_1	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$		C_2	$1/2$	$1/\sqrt{2}$	$1/2$
A_2	$1/\sqrt{3}$	$-1/\sqrt{3}$	$-1/\sqrt{3}$		C_3	$1/2$	$1/2$	$1/\sqrt{2}$
A_3	$-1/\sqrt{3}$	$-1/\sqrt{3}$	$1/\sqrt{3}$		C_4	$1/\sqrt{2}$	$-1/2$	$-1/2$
A_4	$-1/\sqrt{3}$	$1/\sqrt{3}$	$-1/\sqrt{3}$		C_5	$-1/2$	$1/\sqrt{2}$	$-1/2$
B_1	0	0	1		C_6	$-1/2$	$-1/2$	$1/\sqrt{2}$
B_2	0	1	0		C_7	$-1/\sqrt{2}$	$1/2$	$-1/2$
B_3	1	0	0		C_8	$-1/2$	$-1/\sqrt{2}$	$1/2$
B_4	0	0	-1		C_9	$1/2$	$-1/2$	$-1/\sqrt{2}$
B_5	0	-1	0		C_{10}	$-1/\sqrt{2}$	$-1/2$	$1/2$
B_6	-1	0	0		C_{11}	$1/2$	$-1/\sqrt{2}$	$-1/2$
C_1	$1/\sqrt{2}$	$1/2$	$1/2$		C_{12}	$-1/2$	$1/2$	$-1/\sqrt{2}$

Table 2. (continued)

	x	y	z		x	y	z
D_1	1/3	$\sqrt{3}/3$	$\sqrt{5}/3$	D_{13}	$\sqrt{3}/3$	-1/3	$-\sqrt{5}/3$
D_2	1/3	$-\sqrt{3}/3$	$-\sqrt{5}/3$	D_{14}	$-\sqrt{3}/3$	-1/3	$\sqrt{5}/3$
D_3	-1/3	$\sqrt{3}/3$	$-\sqrt{5}/3$	D_{15}	$\sqrt{3}/3$	1/3	$\sqrt{5}/3$
D_4	-1/3	$-\sqrt{3}/3$	$\sqrt{5}/3$	D_{16}	$-\sqrt{3}/3$	1/3	$-\sqrt{5}/3$
D_5	$\sqrt{5}/3$	1/3	$\sqrt{3}/3$	D_{17}	1/3	$-\sqrt{5}/3$	$-\sqrt{3}/3$
D_6	$-\sqrt{5}/3$	-1/3	$\sqrt{3}/3$	D_{18}	-1/3	$\sqrt{5}/3$	$-\sqrt{3}/3$
D_7	$\sqrt{5}/3$	-1/3	$-\sqrt{3}/3$	D_{19}	-1/3	$-\sqrt{5}/3$	$\sqrt{3}/3$
D_8	$-\sqrt{5}/3$	1/3	$-\sqrt{3}/3$	D_{20}	1/3	$\sqrt{5}/3$	$\sqrt{3}/3$
D_9	$\sqrt{3}/3$	$\sqrt{5}/3$	1/3	D_{21}	$\sqrt{5}/3$	$-\sqrt{3}/3$	-1/3
D_{10}	$-\sqrt{3}/3$	$\sqrt{5}/3$	-1/3	D_{22}	$\sqrt{5}/3$	$\sqrt{3}/3$	1/3
D_{11}	$-\sqrt{3}/3$	$-\sqrt{5}/3$	1/3	D_{23}	$-\sqrt{5}/3$	$\sqrt{3}/3$	-1/3
D_{12}	$\sqrt{3}/3$	$-\sqrt{5}/3$	-1/3	D_{24}	$-\sqrt{5}/3$	$-\sqrt{3}/3$	1/3

The enumeration of the vectors of set D corresponds to that of the group elements in table 1.

These five sets of equivalent objects induce the reducible representations $\sigma^0 = A_1$, σ^A, σ^B, σ^C, and σ^D. Using the operations listed in table 1, we can calculate the induced matrices of σ^A etc. according to (3.3). The calculation of the characters is even simpler, since they are equal to the number of positions being invariant to the operation. The characters of the irreducible and the induced representations are listed in table 3.

Table 3. Characters of representations of T_d

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
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
σ^0	1	1	1	1	1
σ^A	4	1	0	0	2
σ^B	6	0	2	0	2
σ^C	12	0	0	0	2
σ^D	24	0	0	0	0

From the character formula (2.10) then follow the branching rules for the induced representations:

$$\sigma^0 = A_1, \quad \sigma^A = A_1 + T_2, \quad \sigma^B = A_1 + E + T_2, \quad \sigma^C = A_1 + E + T_1 + 2T_2$$
$$\sigma^D = A_1 + A_2 + 2E + 3T_1 + 3T_2 \tag{22.29}$$

The decomposition of the representations according to these rules is

achieved by the SALC coefficients. We calculate them by formula (12.16), i.e. by inserting the position vectors of table 2 into the standard functions (22.16-28). The results are listed in the tables 4 to 7.

Table 4.
SALC coefficients $(\vec{A_i}|\text{Aap})$

a p	A_1	A_2	A_3	A_4
$A_1 1$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$T_2 x$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$
$T_2 y$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$
$T_2 z$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$

Table 5.
SALC coefficients $(\vec{B_i}|\text{Bbp})$

b p	B_1	B_2	B_3	B_4	B_5	B_6
$A_1 1$	$\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{6}$
$E\ 1$	$\frac{\sqrt{3}}{3}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{3}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$
$E\ 2$	0	$\frac{-1}{2}$	$\frac{1}{2}$	0	$\frac{-1}{2}$	$\frac{1}{2}$
$T_2 x$	0	0	$\frac{\sqrt{2}}{2}$	0	0	$\frac{-\sqrt{2}}{2}$
$T_2 y$	0	$\frac{\sqrt{2}}{2}$	0	0	$\frac{-\sqrt{2}}{2}$	0
$T_2 z$	$\frac{\sqrt{2}}{2}$	0	0	$\frac{-\sqrt{2}}{2}$	0	0

Table 6. SALC coefficients $(\vec{C_i}|\text{C}\gamma\text{cp})$

γc p	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
$A_1 1$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$
$E\ 1$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$
$E\ 2$	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0
$T_1 \xi$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$
$T_1 \eta$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$
$T_1 \zeta$	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0
$1T_2 x$	$\frac{\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$
$1T_2 y$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{1}{4}$
$1T_2 z$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$	$\frac{-\sqrt{2}}{4}$
$2T_2 x$	$\frac{-\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$
$2T_2 y$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{1}{4}$
$2T_2 z$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-\sqrt{2}}{4}$	$\frac{-1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{2}}{4}$	$\frac{1}{4}$	$\frac{-1}{4}$	$\frac{\sqrt{2}}{4}$

Table 7. SALC coefficients $(\vec{D}_i | D\delta dp)$

$\delta d\ p$	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
$A_1 1$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$
$A_2 1$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$
$1E\ 1$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	0	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$
$1E\ 2$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$
$2E\ 1$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2E\ 2$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	0	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$
$1T_1\xi$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$
$1T_1\eta$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$
$1T_1\zeta$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$
$2T_1\xi$	$\frac{-\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	0	0	0	0
$2T_1\eta$	0	0	0	0	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$
$2T_1\zeta$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	0	0	0	0	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$
$3T_1\xi$	$\frac{-\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$
$3T_1\eta$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$
$3T_1\zeta$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$
$1T_2 x$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$
$1T_2 y$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$
$1T_2 z$	$\frac{\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{-\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{-\sqrt{2}}{12}$
$2T_2 x$	$\frac{\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	0	0	0	0
$2T_2 y$	0	0	0	0	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2T_2 z$	$\frac{-\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{-\sqrt{3}}{12}$	0	0	0	0	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$\frac{-\sqrt{15}}{12}$
$3T_2 x$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$
$3T_2 y$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$
$3T_2 z$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$

Table 7. (continued)

δd p	D_{13}	D_{14}	D_{15}	D_{16}	D_{17}	D_{18}	D_{19}	D_{20}	D_{21}	D_{22}	D_{23}	D_{24}
$A_1 1$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$
$A_2 1$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$	$\frac{-\sqrt{6}}{12}$
$1E\ 1$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	0	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$
$1E\ 2$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2E\ 1$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2E\ 2$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	$\frac{-1}{4}$	0	0	0	0	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
$1T_1\xi$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$
$1T_1\eta$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$
$1T_1\zeta$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{-\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$
$2T_1\xi$	0	0	0	0	$\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2T_1\eta$	$-\sqrt{\frac{15}{12}}$	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	0	0	0	0
$2T_1\zeta$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	0	0	0	0	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$
$3T_1\xi$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$
$3T_1\eta$	$-\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$
$3T_1\zeta$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$
$1T_2 x$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$
$1T_2 y$	$-\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$
$1T_2 z$	$-\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{10}}{12}$	$-\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{2}}{12}$
$2T_2 x$	0	0	0	0	$\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{15}}{12}$	$\frac{\sqrt{15}}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$
$2T_2 y$	$-\sqrt{\frac{15}{12}}$	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	0	0	0	0
$2T_2 z$	$\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{\sqrt{3}}{12}$	$\frac{\sqrt{3}}{12}$	0	0	0	0	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$	$-\sqrt{\frac{15}{12}}$	$\sqrt{\frac{15}{12}}$
$3T_2 x$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$-\frac{\sqrt{5}}{12}$	$-\frac{\sqrt{5}}{12}$
$3T_2 y$	$\frac{-1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{1}{12}$	$-\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$-\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$
$3T_2 z$	$-\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$\frac{\sqrt{5}}{12}$	$-\frac{\sqrt{5}}{12}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{-1}{12}$	$\frac{1}{12}$	$\frac{-1}{12}$	$\frac{1}{12}$

By the help of the preceeding tables, one can determine the s.-a. MOs of every tetrahedral molecule arising from all types of atomic orbitals. Taking the 3jm symbols from Griffith [5], table C2.1., one calculates the coefficients $K(\gamma cp_c, Ai\varepsilon e, ap_a)$ according to formula (5.2). In the paper [10] we already have elaborated the complete set of coefficients with respect to the equivalent set A (i.e. the P atoms of P_4 or P_4O_6, the H atoms of CH_4, and the ligands of many tetrehedral complexes). The most important AOs are those of species s/A_1 and p/T_2. Since the coefficients for the s-orbitals are trivially

$$K(cq, Aia, A_1 1) = \delta(c,a) \cdot (\vec{A_i}|Aaq),$$

we only repeat the coefficients for the p-orbitals in table 8. Because of different phases in the tables of Koster e.a.[21] and Griffith [5] we now get the opposite sign for the triads (ET_2T_2) and $(T_2T_2T_2)$.

Table 8. The coefficients $K(cq, Aia, T_2p)$

a c q \ A_i p	A_1 x	y	z	A_2 x	y	z	A_3 x	y	z	A_4 x	y	z
A_1T_2x	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0
A_1T_2y	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0
A_1T_2z	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$
$T_2A_1 1$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{6}$	$-\frac{\sqrt{3}}{6}$
$T_2E 1$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{6}$	$\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$	$-\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{12}$	$-\frac{\sqrt{6}}{6}$	$-\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{12}$	$\frac{\sqrt{6}}{6}$
$T_2E 2$	$-\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0
$T_2T_1\xi$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$
$T_2T_1\eta$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$
$T_2T_1\zeta$	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0
T_2T_2x	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$
T_2T_2y	$-\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$
T_2T_2z	$-\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$-\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{2}}{4}$	0

As a further example, we calculate the coefficients $K(cq, Bib, T_2p)$, which are needed for the MOs resulting from the p/T_2-orbitals of the oxygen atoms of P_4O_6. These coefficients are listed in table 9. The same coefficients apply to the symmetry coordinates of the molecule:

$$Q_q^{(Bb)c} = \sum_{ip} K(cq, Bib, T_2p) \cdot \Delta B_{ip}, \qquad (22.30)$$

where $\Delta\vec{B_i} = (\Delta B_{ix}, \Delta B_{iy}, \Delta B_{iz})$ is the displacement vector of atom $\vec{B_i}$ [12].

Table **9.** The coefficients $K(cq, Bib, T_2p)$

b c q	B_1 x	y	z	B_2 x	y	z	B_3 x	y	z	B_4 x	y	z	B_5 x	y	z	B_6 x	y	z
A_1T_2x	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0
A_1T_2y	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0
A_1T_2z	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$	0	0	$\frac{\sqrt{6}}{6}$
$E\,T_1\xi$	$\frac{1}{2}$	0	0	$\frac{-1}{2}$	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{-1}{2}$	0	0	0	0	0
$E\,T_1\eta$	0	$\frac{-1}{2}$	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{-1}{2}$	0	0	0	0	0	$\frac{1}{2}$	0
$E\,T_1\zeta$	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{-1}{2}$	0	0	0	0	0	$\frac{1}{2}$	0	0	$\frac{-1}{2}$
$E\,T_2x$	$\frac{\sqrt{3}}{6}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{-\sqrt{3}}{3}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{-\sqrt{3}}{3}$	0	0
$E\,T_2y$	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{-\sqrt{3}}{3}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{-\sqrt{3}}{3}$	0	0	$\frac{\sqrt{3}}{6}$	0
$E\,T_2z$	0	0	$\frac{-\sqrt{3}}{3}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{-\sqrt{3}}{3}$	0	0	$\frac{\sqrt{3}}{6}$	0	0	$\frac{\sqrt{3}}{6}$
$T_2A_1 1$	0	0	$\frac{\sqrt{6}}{6}$	0	$\frac{\sqrt{6}}{6}$	0	$\frac{\sqrt{6}}{6}$	0	0	0	0	$\frac{-\sqrt{6}}{6}$	0	$\frac{-\sqrt{6}}{6}$	0	$\frac{-\sqrt{6}}{6}$	0	0
$T_2E\ 1$	0	0	$\frac{-\sqrt{3}}{3}$	0	$\frac{\sqrt{3}}{6}$	0	$\frac{\sqrt{3}}{6}$	0	0	0	0	$\frac{\sqrt{3}}{3}$	0	$\frac{-\sqrt{3}}{6}$	0	$\frac{-\sqrt{3}}{6}$	0	0
$T_2E\ 2$	0	0	0	0	$\frac{1}{2}$	0	$\frac{-1}{2}$	0	0	0	0	0	0	$\frac{-1}{2}$	0	$\frac{-1}{2}$	0	0
$T_2T_1\xi$	0	$\frac{1}{2}$	0	0	0	$\frac{-1}{2}$	0	0	0	0	$\frac{-1}{2}$	0	0	0	$\frac{1}{2}$	0	0	0
$T_2T_1\eta$	$\frac{-1}{2}$	0	0	0	0	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	$\frac{-1}{2}$
$T_2T_1\zeta$	0	0	0	$\frac{1}{2}$	0	0	0	$\frac{-1}{2}$	0	0	0	0	$\frac{-1}{2}$	0	0	0	$\frac{1}{2}$	0
T_2T_2x	0	$\frac{-1}{2}$	0	0	0	$\frac{-1}{2}$	0	0	0	0	$\frac{1}{2}$	0	0	0	$\frac{1}{2}$	0	0	0
T_2T_2y	$\frac{-1}{2}$	0	0	0	0	0	0	0	$\frac{-1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	$\frac{1}{2}$
T_2T_2z	0	0	0	$\frac{-1}{2}$	0	0	0	$\frac{-1}{2}$	0	0	0	0	$\frac{1}{2}$	0	0	0	$\frac{1}{2}$	0

22.3. Polyhedral isoscalar factors

Whereas the elaboration of the s.-a. linear combinations of orbitals and coordinates is a conventional technique, we now come to the central point of our innovation, the group theoretical description of the topological structures by the various polyhedral isoscalar factors.

The four atoms of P_4 occupy the positions $\vec{A}_i$ given in table 2. The atomic orbitals at these centres define two types of two-centre integrals distinguished by the edge vectors connecting the centres.

1) Both orbitals are located at the same centre, i.e. the edge vector degenerates to $\vec{O}_i^A = \vec{A}_i - \vec{A}_i \sim \vec{A}_i$, cf. page 21. Here and in the following,

the equivalence of sets, i.e. $\vec{M_i} \sim \vec{N_i}$ for instance, implies such a nume-
ration that $\sigma^M_{ik}(g)=\sigma^N_{ik}(g)$ in addition to the ordinary equivalence of
the induced representations, $\sigma^M \sim \sigma^N$. But this does not imply $\vec{M_i}=\vec{N_i}$! As
shown in section 3, this equivalence, $\vec{M_i} \sim \vec{N_i}$, leads to $(\vec{M_i}|M\mu mp) =$
$(\vec{N_i}|N\mu mp)$. This means in the present case: $(\vec{O^A_i}|O^A \alpha ap_a) = (\vec{A_i}|A\alpha ap_a)$.
Since $\vec{O^A_i}$ belongs to position $\vec{A_i}$ only, the topological matrix (3.1) is
given by:

$$\tau(^{-AAO^A}_{\quad ikl}) = \delta(i,k)\delta(k,l)/\sqrt{Z(A)} \qquad (22.31)$$

2) The orbitals are located at different centres. In contrast to set B,
there is only one type of coordination within the set A indicated by
the edge vectors $\vec{S^A_{ik}}=\vec{A_i}-\vec{A_k}$. These twelve vectors lie in the reflection
planes and therefore we have the equivalence $\sigma^{SA} \sim \sigma^C$. An adequate enu-
meration of the edges then allows $\vec{S^A_k} \sim \vec{C_k}$. This correspondence can be
made explicit by an appropriate choice of the coefficients in the rela-
tion (3.25): $\vec{S^{A/}_{ik}}=\mu_1\vec{A_i}+\mu_2\vec{A_k}$. If we take $\mu_1=(1+\sqrt{2})\sqrt{3}/4$ and $\mu_2=(-1+\sqrt{2})\sqrt{3}/4$,
we get $\vec{S^{A/}_{12}}=\vec{C_1}$ etc. We now define the topological matrix of the trian-
gles $-AAS^A$ by:

$$\tau(^{-AAS^A}_{\quad ikl}) = \delta(\mu_1\vec{A_i}+\mu_2\vec{A_k}, \vec{C_1})/\sqrt{Z(C)} , \qquad (22.32)$$

or equivalently

$$\sum_{i\neq k}\tau(^{-AAS^A}_{\quad ikl})\cdot(\mu_1\vec{A_i}+\mu_2\vec{A_k})\sqrt{Z(-AAS^A)} = \vec{C_1} \qquad (22.33)$$

The topological correlations expressed by (22.31 and 32) are listed in
table 10.

Table 10. Non-zero matrix elements of $\tau(^{-AAO^A}_{\quad ikl})$ and $\tau(^{-AAS^A}_{\quad ikl})$

A_i	1	2	3	4	A_i	1	1	1	2	2	2	3	3	3	4	4	4
A_k	1	2	3	4	A_k	2	3	4	1	3	4	1	2	4	1	2	3
$O^A_1 \sim A_1$	1	2	3	4	$S^A_1 \sim C_1$	1	3	2	4	11	9	6	8	10	5	12	7

Basing upon these correlations, we calculate the polyhedral isoscalar
factors of the triangles $-AAO^A$ and $-AAS^A$ according to formula (6.6).
The result is compiled in table 11 on the following page. It differs
from that of [11] because of the different SALC coefficients of table 6
and the different order of the triple product $a \times b \times c$.

In the same way, we treat the equivalent set B. The six centres listed
in table 2 are occupied by the oxygen atoms of P_4O_6. There are now three
types of coordination within this set:
1) The orbitals are located at the same centre again, i.e. the edge vec-
tors are $\vec{O^B_k}=\vec{B_k}-\vec{B_k} \sim \vec{B_k}$. The topological correspondence is quite analo-
gous to (22.31):

$$\tau(^{-BBO^B}_{\quad ikl}) = \delta(i,k)\delta(k,l)/\sqrt{Z(B)} \qquad (22.34)$$

2) The orbitals are located at adjoining centres (for instance $\vec{B_1}$ and

Table 11. Polyhedral isoscalars $PIs\left(\begin{smallmatrix}-AAO^A\\abc\end{smallmatrix}\right)$ and $PIs\left(\begin{smallmatrix}-AAS^A\\ \gamma \\ abc\end{smallmatrix}\right)$

a b γc	$-AAO^A$(alg.)	$-AAO^A$(num.)	$-AAS^A$(alg.)	$-AAS^A$(num.)
$A_1 A_1\ A_1$	$1/4$	0.25000000	$1/4$	0.25000000
$T_2 T_2\ A_1$	$\sqrt{3}/4$	0.43301270	$-\sqrt{3}/12$	-0.14433757
$T_2 T_2\ E$	-	-	$-1/\sqrt{6}$	-0.40824829
$T_2 T_2\ T_1$	-	-	$1/2$	0.50000000
$A_1 T_2 1 T_2$	$\sqrt{3}/4$	0.43301270	$(\sqrt{2}-2)/8$	-0.07322330
$T_2 A_1 1 T_2$	$\sqrt{3}/4$	0.43301270	$(\sqrt{2}+2)/8$	0.42677670
$T_2 T_2 1 T_2$	$-\sqrt{6}/4$	-0.61237244	$1/4$	0.25000000
$A_1 T_2 2 T_2$	-	-	$-(\sqrt{2}+2)/8$	-0.42677670
$T_2 A_1 2 T_2$	-	-	$-(\sqrt{2}-2)/8$	0.07322330
$T_2 T_2 2 T_2$	-	-	$-1/4$	-0.25000000

$\vec{B}_2$). The 24 edge vectors are termed $\vec{S}_1^B$ and are equivalent to the set D: $\vec{S}_1^B \sim \vec{D}_1$. The description of this topological correspondence is complicated by the fact that the vectors $\mu_1 \vec{B}_i + \mu_2 \vec{B}_k$ having one zero component may be equivalent but not equal to a vector of set D. In order to produce an identity, we resort to a certain vector product, which is well defined with respect to the group T_d:

$$[\vec{r} \times \vec{r}']_+ = (yz'+zy')\vec{e}_1 + (zx'+xz')\vec{e}_2 + (xy'+yx')\vec{e}_3 \qquad (22.35)$$

The definition

$$\vec{S}_{ik}^B = (\sqrt{3}/3)\vec{B}_i + (\sqrt{5}/3)\vec{B}_k + (1/3)[\vec{B}_i \times \vec{B}_k]_+ \qquad (22.36)$$

then yields $\vec{S}_{11}^B = \vec{D}_1$ etc. The full list of the correlations is given in table 12, which also indicates the non-zero matrix elements of the topological matrix:

$$\tau\left(\begin{smallmatrix}-BBS^B\\ikl\end{smallmatrix}\right) = \delta(\sqrt{3}\vec{B}_i + \sqrt{5}\vec{B}_k + [\vec{B}_i \times \vec{B}_k]_+, 3\vec{D}_1)/\sqrt{Z(D)} \qquad (22.37)$$

An equivalent expression is:

$$\sum_{ik}\tau\left(\begin{smallmatrix}-BBS^B\\ikl\end{smallmatrix}\right)\sqrt{Z(-BBS^B)}\cdot(\sqrt{\tfrac{3}{3}}\vec{B}_i + \sqrt{\tfrac{5}{3}}\vec{B}_k + \tfrac{1}{3}[\vec{B}_i \times \vec{B}_k]_+) = \vec{D}_1 \qquad (22.38)$$

3) The third possibility is the location of the orbitals at the opposite positions like $\vec{B}_1$ and $\vec{B}_4$. The six edge vectors of this type are termed $\vec{T}_k^B \sim \vec{B}_k$ and the topological matrix is in this case:

$$\tau\left(\begin{smallmatrix}-BBT^B\\ikl\end{smallmatrix}\right) = \delta(\vec{B}_i - \vec{B}_k, 2\vec{B}_l)/\sqrt{Z(B)} \qquad (22.39)$$

The essence of (22.34/37/39) is gathered in table 12. This compilation then allows the calculation of the isoscalar factors of the triangles of the type $-BBO^B$, $-BBS^B$, and $-BBT^B$. These are listed in the tables 13 and 14.

Table 12. Non-zero matrix elements of $\tau\left(^{-BBO}_{ikl}{}^B\right)$, $\tau\left(^{-BBT}_{ikl}{}^B\right)$, and $\tau\left(^{-BBS}_{ikl}{}^B\right)$

B_i	1 2 3 4 5 6	B_i	1 2 3 4 5 6	B_i	1 1 1 1
B_k	1 2 3 4 5 6	B_k	4 5 6 1 2 3	B_k	2 3 5 6
$O_1^B \sim B_1$	1 2 3 4 5 6	$T_1^B \sim B_1$	1 2 3 4 5 6	$S_1^B \sim D_1$	1 15 4 14

B_i	2	2	2	2	3	3	3	3	4	4	4	4	5	5	5	5	6	6	6	6
B_k	1	3	4	6	1	2	4	5	2	3	5	6	1	3	4	6	1	2	4	5
$S_1^B \sim D_1$	20	5	19	6	9	22	11	24	3	16	2	13	18	8	17	7	10	23	12	21

Table 13. Polyhedral isoscalars $PIs\left(^{-BBO}_{abc}{}^B\right)$ and $PIs\left(^{-BBT}_{abc}{}^B\right)$

a b c	$-BBO^B$(alg.)	$-BBO^B$(num.)	$-BBT^B$(alg.)	$-BBT^B$(num.)
$A_1A_1A_1$	1/6	0.16666667	1/6	0.16666667
$E\ E\ A_1$	$\sqrt{2}/6$	0.23570226	$\sqrt{2}/6$	0.23570226
$T_2T_2A_1$	$\sqrt{3}/6$	0.28867513	$-\sqrt{3}/6$	-0.28867513
$A_1E\ E$	$\sqrt{2}/6$	0.23570226	$\sqrt{2}/6$	0.23570226
$E\ A_1E$	$\sqrt{2}/6$	0.23570226	$\sqrt{2}/6$	0.23570226
$E\ E\ E$	$-\sqrt{2}/6$	-0.23570226	$-\sqrt{2}/6$	-0.23570226
T_2T_2E	$-1/\sqrt{6}$	-0.40824829	$1/\sqrt{6}$	0.40824829
$A_1T_2T_2$	$\sqrt{3}/6$	0.28867513	$-\sqrt{3}/6$	-0.28867513
$T_2A_1T_2$	$\sqrt{3}/6$	0.28867513	$\sqrt{3}/6$	0.28867513
$E\ T_2T_2$	$-1/\sqrt{6}$	-0.40824829	$1/\sqrt{6}$	0.40824829
$T_2E\ T_2$	$-1/\sqrt{6}$	-0.40824829	$-1/\sqrt{6}$	-0.40824829
$T_2T_2T_2$	0	0.00000000	0	0.00000000

Table 14. Polyhedral isoscalars $PIs\begin{pmatrix} -BBS^B \\ \gamma \\ abc \end{pmatrix}$

a b γc	algebraic	numerical	a b γc	algebraic	numerical
$A_1A_1\ A_1$	1/6	0.16666667	$E\ T_2 1T_1$	$\sqrt{3}/6$	0.28867513
$E\ E\ A_1$	$-\sqrt{2}/12$	-0.11785113	$T_2E\ 1T_1$	$\sqrt{5}/12$	0.18633900
$T_2T_2\ A_1$	0	0.00000000	$T_2T_2 1T_1$	$-1/12$	-0.08333333
$E\ E\ A_2$	$-\sqrt{6}/12$	-0.20412414	$E\ T_2 2T_1$	0	0.00000000
$A_1E\ 1E$	0	0.00000000	$T_2E\ 2T_1$	$-\sqrt{3}/12$	-0.14433757
$E\ A_1 1E$	$\sqrt{6}/12$	0.20412414	$T_2T_2 2T_1$	$-\sqrt{15}/12$	-0.32274861
$E\ E\ 1E$	$\sqrt{6}/12$	0.20412414	$E\ T_2 3T_1$	$-\sqrt{6}/12$	-0.20412414
$T_2T_2 1E$	0	0.00000000	$T_2E\ 3T_1$	$\sqrt{10}/12$	0.26352314
$A_1E\ 2E$	$-\sqrt{2}/6$	-0.23570226	$T_2T_2 3T_1$	$-\sqrt{2}/12$	-0.11785113
$E\ A_1 2E$	$\sqrt{2}/12$	0.11785113	$A_1T_2 1T_2$	1/6	0.16666667
$E\ E\ 2E$	$-\sqrt{2}/12$	-0.11785113	$T_2A_1 1T_2$	$\sqrt{15}/18$	0.21516574
$T_2T_2 2E$	0	0.00000000	$E\ T_2 1T_2$	$\sqrt{2}/12$	0.11785113

Table 14. (continued)

a b γc	algebraic	numerical	a b γc	algebraic	numerical
$T_2E\ 1T_2$	$\sqrt{30}/36$	0.15214515	$T_2T_22T_2$	$-\sqrt{15}/12$	-0.32274861
$T_2T_21T_2$	$-\sqrt{2}/12$	-0.11785113	$A_1T_23T_2$	$-\sqrt{2}/6$	-0.23570226
$A_1T_22T_2$	0	0.00000000	$T_2A_13T_2$	$\sqrt{30}/36$	0.15214515
$T_2A_12T_2$	$-\sqrt{2}/12$	-0.11785115	$E\ T_23T_2$	$-1/6$	-0.16666667
$E\ T_22T_2$	0	0.00000000	$T_2E\ 3T_2$	$\sqrt{15}/36$	0.10758287
$T_2E\ 2T_2$	$-1/12$	-0.08333333	$T_2T_23T_2$	$-1/12$	-0.08333333

In the molecule P_4O_6, there are further triangles (or two-centre integrals) involving one position of set A and one of set B. The edge vectors between directly adjoining centres are termed $\vec{S}^{AB}_{ik} = \vec{A}_i - \vec{B}_k$ (for instance $\vec{B}_1$ and $\vec{A}_1$), whereas the indirect connection (for instance between $\vec{A}_1$ and $\vec{B}_4$) is expressed by $\vec{T}^{AB}_{ik} = \vec{A}_i - \vec{B}_k$. There are twelve vectors in each set and thus $\vec{S}^{AB}_1 \sim \vec{T}^{AB}_1 \sim \vec{C}_1$. The topological matrices are given by:

$$\tau\left(^{-ABS^{AB}}_{\quad ikl}\right) = \delta(\sqrt{3}\vec{A}_i + (\sqrt{2}-1)\vec{B}_k, 2\vec{C}_1)/\sqrt{Z(C)} \qquad (22.40)$$

$$\tau\left(^{-ABT^{AB}}_{\quad ikl}\right) = \delta(\sqrt{3}\vec{A}_i - (\sqrt{2}-1)\vec{B}_k, 2\vec{C}_1)/\sqrt{Z(C)} \qquad (22.41)$$

The correspondences defined in this way are compiled in table 15.

Table 15. Non-zero matrix elements of $\tau\left(^{-ABS^{AB}}_{\quad ikl}\right)$ and $\tau\left(^{-ABT^{AB}}_{\quad ikl}\right)$

A_i	1	1	1	1	1	1	2	2	2	2	2	2	3	3	3	3	3	3	4	4	4	4	4	4
B_k	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
$S^{AB}_1 \sim C_1$	3	2	1	-	-	-	-	-	4	9	11	-	6	-	-	-	8	10	-	5	-	12	-	7
$T^{AB}_1 \sim C_1$	-	-	-	3	2	1	9	11	-	-	-	4	-	8	10	6	-	-	12	-	7	-	5	-

Finally, the polyhedral isoscalar factors calculated from these correlations are given in table 16.

Table 16. Polyhedral isoscalars $PIs\begin{pmatrix} -ABS^{AB} \\ \gamma \\ abc \end{pmatrix}$ and $PIs\begin{pmatrix} -ABT^{AB} \\ \gamma \\ abc \end{pmatrix}$

a b γc	$-ABS^{AB}$(alg.)	$-ABS^{AB}$(num.)	$-ABT^{AB}$(alg.)	$-ABT^{AB}$(num.)
$A_1A_1\ A_1$	$\sqrt{6}/12$	0.20412414	$\sqrt{6}/12$	0.20412414
$T_2T_2\ A_1$	$\sqrt{6}/12$	0.20412414	$-\sqrt{6}/12$	-0.20412414
$A_1E\ E$	$\sqrt{3}/6$	0.28867513	$\sqrt{3}/6$	0.28867513
$T_2T_2\ E$	$-\sqrt{3}/6$	-0.28867513	$\sqrt{3}/6$	0.28867513
$T_2E\ T_1$	$\sqrt{2}/4$	0.35355339	$\sqrt{2}/4$	0.35355339
$T_2T_2\ T_1$	$\sqrt{2}/4$	0.35355339	$-\sqrt{2}/4$	-0.35355339
$A_1T_21T_2$	1/4	0.25000000	$-1/4$	-0.25000000
$T_2A_11T_2$	$(\sqrt{6}+\sqrt{3})/12$	0.34846171	$(\sqrt{6}+\sqrt{3})/12$	0.34846171
$T_2E\ 1T_2$	$(\sqrt{3}-\sqrt{6})/12$	-0.05978658	$(\sqrt{3}-\sqrt{6})/12$	-0.05978658

Table 16. (continued)

a b γc	$-ABS^{AB}$(alg.)	$-ABS^{AB}$(num.)	$-ABT^{AB}$(alg.)	$-ABT^{AB}$(num.)
$T_2T_2 1T_2$	$-1/4$	-0.25000000	$1/4$	0.25000000
$A_1T_2 2T_2$	$-1/4$	-0.25000000	$1/4$	0.25000000
$T_2A_1 2T_2$	$(\sqrt{6}-\sqrt{3})/12$	0.05978658	$(\sqrt{6}-\sqrt{3})/12$	0.05978658
$T_2E\ 2T_2$	$(\sqrt{3}+\sqrt{6})/12$	0.34846171	$(\sqrt{3}+\sqrt{6})/12$	0.34846171
$T_2T_2 2T_2$	$-1/4$	-0.25000000	$1/4$	0.25000000

In contrast to the edge vectors connecting centres of the same set, S^A for instance, we have to consider S^{AB} and the set of the inverted vectors S^{BA} as sets of inequivalent objects. But both set induce the same representation σ^C and an appropriate numbering yields $\vec{S}_1^{BA} \sim \vec{S}_1^{AB} \sim \vec{C}_1$. The same applies to $\vec{T}_1^{BA} \sim \vec{T}_1^{AB} \sim \vec{C}_1$. We therefore may choose

$$\tau\left(\begin{matrix}-BAS^{BA}\\ikl\end{matrix}\right) = \tau\left(\begin{matrix}-ABS^{AB}\\kil\end{matrix}\right) \text{ and } \tau\left(\begin{matrix}-BAT^{BA}\\ikl\end{matrix}\right) = \tau\left(\begin{matrix}-ABT^{AB}\\kil\end{matrix}\right), \tag{22.42}$$

which yields simple relations of the polyhedral isoscalar factors:

$$PIs\left(\begin{matrix}-BAS^{BA}\\ \gamma \\ bac\end{matrix}\right) = \{abc\}\cdot PIs\left(\begin{matrix}-ABS^{AB}\\ \gamma \\ abc\end{matrix}\right), \quad PIs\left(\begin{matrix}-BAT^{BA}\\ \gamma \\ bac\end{matrix}\right) = \{abc\}\cdot PIs\left(\begin{matrix}-BAT^{BA}\\ \gamma \\ bac\end{matrix}\right) \tag{22.43}$$

At this point one may ask, whether the choice of the topological matrices is unequivocal. Indeed, the matrices are not determined unambiguously, but a different choice of the topological correlations causes only a unitary transformation of the polyhedral isoscalars (a change of phase in the multiplicity free cases). We demonstrate this by an example. If we replace (22.40) by

$$\tau'\left(\begin{matrix}-ABS^{AB}\\ikl\end{matrix}\right) = \delta(-\sqrt{3}\vec{A}_i+(\sqrt{2}+1)\vec{B}_k, 2\vec{C}_1)/\sqrt{Z(C)}, \tag{22.44}$$

the first correlated triple, for instance, is $\vec{A}_1,\vec{B}_1,\vec{C}_6$ instead of $\vec{A}_1$, $\vec{B}_1,\vec{C}_3$ and we must rearrange table 15. The resulting new polyhedral isoscalars are related to those of table 16 by the transformation

$$PIs'\left(\begin{matrix}-ABS^{AB}\\ \gamma \\ abc\end{matrix}\right) = \sum_\sigma u(c)_{\gamma\sigma} PIs\left(\begin{matrix}-ABS^{AB}\\ \sigma \\ abc\end{matrix}\right) \tag{22.45}$$

with $u(A_1)=+1$, $u(E)=+1$, $u(T_1)=-1$, $u(T_2)_{11}=u(T_2)_{22}=0$, $u(T_2)_{12}=u(T_2)_{21}=-1$.

Similar relations, caused by different correlations between the same sets, are found by inspecting the tables 13 and 16:

$$PIs\left(\begin{matrix}-BBO^B\\ abc\end{matrix}\right) = \varphi(b)\cdot PIs\left(\begin{matrix}-BBT^B\\ abc\end{matrix}\right), \quad PIs\left(\begin{matrix}-ABS^{AB}\\ \gamma \\ abc\end{matrix}\right) = \varphi(b)\cdot PIs\left(\begin{matrix}-ABT^{AB}\\ \gamma \\ abc\end{matrix}\right) \tag{22.46}$$

with the phase factors $\varphi(A_1)=+1$, $\varphi(E)=+1$, and $\varphi(T_2)=-1$.

The factors calculated so far also apply to strucures like Be_4Cl_4 and $[Cu(CN)_4]^{2-}$, where the positions of type A occur twice, let us say A and A'. The isoscalars within the set A' are trivially equal to those of set A. There are two types of edge vectors connecting centres of

both sets. If both centres lie on the same axis, we have $\vec{U}_i^{AA'} = \vec{A}_i - \vec{A}_i' \sim \vec{A}_i$. In the other case, the distance vectors $\vec{V}^{AA'}$ induce the representation σ^C and therefore $\vec{V}_1^{AA'} \sim \vec{S}_1^A \sim \vec{C}_1$. From these equivalences follows:

$$PIs\left(\begin{matrix} -AA'U^{AA'} \\ ikl \end{matrix}\right) = PIs\left(\begin{matrix} -AAO^A \\ ikl \end{matrix}\right), \quad PIs\left(\begin{matrix} -AA'V^{AA'} \\ \gamma \\ abc \end{matrix}\right) = PIs\left(\begin{matrix} -AAS^A \\ \gamma \\ abc \end{matrix}\right) \tag{22.47}$$

The molecule $C(CH_3)_4$ requires the additional calculation of the polyhedral isoscalars involving the positions of set C.

22.4. Polyhedral isoscalar factors of the second kind

The next step is the consideration of the triangles subtended by three atomic centres. Within the scope of this principal case study, we calculate the complete set of polyhedral isoscalars of the second kind involving three centres of type A. With regard to the main application of these isoscalars in (8.14), one can confine the calculation to the subclass (8.15). In set A, there are five different types of triangles corresponding to possible three-centre integrals:

1) All three centres coincide. We mark these "null triangles" by Δ_o^A. There are naturally four triangles of this type, i.e. $\Delta_{oi}^A \sim \vec{A}_i$. The topological matrices of the second kind according to (7.16) correlate each triangle with its second vertex $\vec{A}_i$ and with the edge vector connecting the first and third vertex, i.e. with $\vec{O}_i^A$:

$$\tau^2\left(\begin{matrix} \Delta_o^A O^A A \\ i^o k^1 \end{matrix}\right) = \tau\left(\begin{matrix} -AAO^A \\ ikl \end{matrix}\right) = \delta(i,k)\delta(k,l)/\sqrt{Z(A)} \tag{22.48}$$

2) The first and the third centre coincide. These degenerate triangles Σ_o^A correspond to the edge vectors connecting the first and second centre, i.e. $\Sigma_{o1}^A \sim \vec{S}_1^A \sim \vec{C}_1$ and

$$\tau^2\left(\begin{matrix} \Sigma_o^A O^A A \\ i^o k^1 \end{matrix}\right) = \tau\left(\begin{matrix} -AAS^A \\ kli \end{matrix}\right). \tag{22.49}$$

3) The first and the second centre coincide. This set is termed Σ_1^A: $\Sigma_{11}^A \sim \vec{S}_1^A \sim \vec{C}_1$ again. In this case, it is easier to express the correlations in a first step by the topological matrix (7.7) and to calculate τ^2 by the inversion of (7.17):

$$\tau^2\left(\begin{matrix} \Delta SC \\ irm \end{matrix}\right) = \sum_{kl} \tau\left(\begin{matrix} \Delta ACB \\ ikml \end{matrix}\right) \tau\left(\begin{matrix} -ABS \\ klr \end{matrix}\right)\sqrt{Z(-ABS)} \tag{22.50}$$

In the present case we have

$$\tau\left(\begin{matrix} \Sigma_1^A AAA \\ i^1 kml \end{matrix}\right) = \tau\left(\begin{matrix} -AAS^A \\ kli \end{matrix}\right)\delta(k,m) \tag{22.51}$$

and (22.50) yields:

$$\tau^2\left(\begin{matrix} \Sigma_1^A S^A A \\ i^1 r^m \end{matrix}\right) = \sum_l \tau\left(\begin{matrix} -AAS^A \\ mli \end{matrix}\right)\tau\left(\begin{matrix} -AAS^A \\ mlr \end{matrix}\right)\sqrt{Z(-AAS^A)} \tag{22.51}$$

The non-zero matrix elements taken from table 10 are given in table 17.

4) The second and the third centre coincide. This set Σ_2^A is different, but equivalent to Σ_1^A, i.e. $\Sigma_{21}^A \sim \vec{S}_1^A \sim \vec{C}_1$. In this case, the correlations are given by

$$\tau(\sum_{i}^{A}{}_{2}^{AAA}_{kml}) = \delta(m,1)\tau(^{-AAS^A}_{kmi})$$ (22.53)

and via (22.50) by

$$\tau^2(\sum_{i}^{A}{}_{2}^{A}S^{A}_{r\ m}) = \sum_{k}\tau(^{-AAS^A}_{kmi})\tau(^{-AAS^A}_{kmr})\sqrt{Z(-AAS^A)}$$ (22.54)

The result is again compiled in table 17.

5) Finally there is one set of 24 ordinary triangles termed Δ^A with $\Delta^A_m \sim \vec{D}_m$. In the sense of (7.8), the correlation of the triangle (i.e. the number of D) and the vertex numbers is achieved by the linear combination of the position vectors $\mu'_1\vec{A}_k + \mu'_2\vec{A}_m + \mu'_3\vec{A}_1$ with $\mu'_1 = (1+\sqrt{5})/2\sqrt{3}$, $\mu'_2 = (1-\sqrt{3})/2\sqrt{3}$, and $\mu'_3 = (\sqrt{5}-\sqrt{3})/2\sqrt{3}$. We therefore define the topological matrix by

$$\tau(\Delta^{A}_{i}{}^{AAA}_{kml}) = \delta(\mu'_1\vec{A}_k + \mu'_2\vec{A}_m + \mu'_3\vec{A}_1, \vec{D}_i)/\sqrt{Z(D)}$$ (22.55)

With (22.32) eq.(22.50) results in:

$$\tau^2(\Delta^{A}_{i}{}^{A}S^{A}_{r\ m}) = \sum_{kl}\delta(\mu'_1\vec{A}_k + \mu'_2\vec{A}_m + \mu'_3\vec{A}_1, \vec{D}_i)\delta(\mu_1\vec{A}_k + \mu_2\vec{A}_1, \vec{C}_r)/\sqrt{Z(D)}$$ (22.56)

These correlations are listed in table 18.

Table 17. Non-zero matrix elements of $\tau^2(\sum_{i}^{A}{}_{1}^{A}S^{A}_{r\ m})$ and $\tau^2(\sum_{i}^{A}{}_{2}^{A}S^{A}_{r\ m})$

A_m	1	1	1	1	1	1	2	2	2	2	2	2	3	3	3	3	3	3	4	4	4	4	4	4
$S^A_r \sim C_r$	1	2	3	4	5	6	1	4	8	9	11	12	3	6	7	8	10	11	2	5	7	9	10	12
$\sum_{1i}^{A} \sim C_i$	1	2	3	-	-	-	-	4	-	9	11	-	-	6	-	8	10	-	-	5	7	-	-	12
$\sum_{2i}^{A} \sim C_i$	-	-	-	1	2	3	4	-	11	-	-	9	6	-	10	-	-	8	5	-	-	12	7	-

Table 18. Non-zero matrix elements of $\tau^2(\Delta^{A}_{i}{}^{A}S^{A}_{r\ m})$

A_m	1	1	1	1	1	1	2	2	2	2	2	3	3	3	3	3	3	4	4	4	4	4	4
$S^A_r \sim C_r$	8	11	12	9	7	10	3	6	2	5	7	4	1	9	12	2	5	4	1	8	11	6	3
$\Delta^A_i \sim D_i$	11	17	16	2	8	24	1	14	20	10	23	7	22	13	3	9	18	21	5	19	12	4	15

From (7.22) now follow the polyhedral isoscalar factors of the second kind. Because of (22.48 and 49), the factors of the triangles Δ^A_0 and $\sum^A_0$ are very simple:

$$PIs^2(\Delta^{A}_{o}{}^{O^A}_{a\ b\ c}) = PIs(^{-A\ \ A\ \ O^A}_{\ a\ \ b\ \ c})$$ (22.57)

$$PIs^2\begin{pmatrix}\sum^{A}_{o}{}^{O^A} \\ \alpha \\ a\ b\ c\end{pmatrix} = PIs\begin{pmatrix}-A\ \ A\ \ S^A \\ \alpha \\ b\ c\ a\end{pmatrix}$$ (22.58)

There remains the tabulation for the triangles $\sum^A_1$, $\sum^A_2$, and Δ^A. It is given in the tables 19 and 20. Comparing the entries of table 17, we get the following relation, where the unitary matrix is that of (22.45):

$$PIs^2\begin{pmatrix}\sum^{A}_{2}{}^{A}S^{A} \\ \alpha^2\beta \\ a\ b\ c\end{pmatrix} = \sum_{\beta'} u(b)_{\beta\beta'}PIs^2\begin{pmatrix}\sum^{A}_{1}{}^{A}S^{A} \\ \alpha^1\beta \\ a\ b\ c\end{pmatrix}$$ (22.59)

Table 19. Polyhedral isoscalars $\text{PIs}^2\begin{pmatrix}\Sigma_1^A S^A{}_A \\ \alpha^1\beta \\ a\ b\ c\end{pmatrix}$ and $\text{PIs}^2\begin{pmatrix}\Sigma_2^A S^A{}_A \\ \alpha^2\beta \\ a\ b\ c\end{pmatrix}$

$\alpha a\ \beta b\ c$	$\Sigma_1^A S^A{}_A$(alg.)	$\Sigma_1^A S^A{}_A$(num.)	$\Sigma_2^A S^A{}_A$(alg.)	$\Sigma_2^A S^A{}_A$(num.)
$A_1\ A_1 A_1$	$\sqrt{3}/12$	0.14433757	$\sqrt{3}/12$	0.14433757
$A_1 1T_2 T_2$	$(2\sqrt{3}+\sqrt{6})/24$	0.24639964	$(\sqrt{6}-2\sqrt{3})/24$	-0.04227549
$A_1 2T_2 T_2$	$(2\sqrt{3}-\sqrt{6})/24$	0.04227549	$-(\sqrt{6}+2\sqrt{3})/24$	-0.24639964
$E\ E\ A_1$	$\sqrt{6}/12$	0.20412415	$\sqrt{6}/12$	0.20412415
$E\ T_1 T_2$	$1/4$	0.25000000	$-1/4$	-0.25000000
$E\ 1T_2 T_2$	$(\sqrt{6}-2\sqrt{3})/24$	-0.04227549	$-(2\sqrt{3}+\sqrt{6})/24$	-0.24639964
$E\ 2T_2 T_2$	$(\sqrt{6}+2\sqrt{3})/24$	0.24639964	$(2\sqrt{3}-\sqrt{6})/24$	0.04227549
$T_1\ T_1 A_1$	$1/4$	0.25000000	$-1/4$	-0.25000000
$T_1\ E\ T_2$	$-1/4$	-0.25000000	$-1/4$	-0.25000000
$T_1\ T_1 T_2$	$\sqrt{2}/8$	0.17677670	$-\sqrt{2}/8$	-0.17677670
$T_1 1T_2 T_2$	$(1-\sqrt{2})/8$	-0.05177670	$-(1+\sqrt{2})/8$	-0.30177670
$T_1 2T_2 T_2$	$(1+\sqrt{2})/8$	0.30177670	$-(1-\sqrt{2})/8$	0.05177670
$1T_2 1T_2 A_1$	$1/4$	0.25000000	0	0.00000000
$1T_2 2T_2 A_1$	0	0.00000000	$-1/4$	-0.25000000
$1T_2\ A_1 T_2$	$(\sqrt{6}+2\sqrt{3})/24$	0.24639964	$(\sqrt{6}+2\sqrt{3})/24$	0.24639964
$1T_2\ E\ T_2$	$(\sqrt{6}-2\sqrt{3})/24$	-0.04227549	$(\sqrt{6}-2\sqrt{3})/24$	-0.04227549
$1T_2\ T_1 T_2$	$(1-\sqrt{2})/8$	-0.05177670	$-(1-\sqrt{2})/8$	0.05177670
$1T_2 1T_2 T_2$	$-(4+\sqrt{2})/16$	0.33838835	$\sqrt{2}/16$	0.08838835
$1T_2 2T_2 T_2$	$-\sqrt{2}/16$	-0.08838835	$(4+\sqrt{2})/16$	0.33838835
$2T_2 1T_2 A_1$	0	0.00000000	$-1/4$	-0.25000000
$2T_2 2T_2 A_1$	$1/4$	0.25000000	0	0.00000000
$2T_2\ A_1 T_2$	$(2\sqrt{3}-\sqrt{6})/24$	0.04227549	$(2\sqrt{3}-\sqrt{6})/24$	0.04227549
$2T_2\ E\ T_2$	$(2\sqrt{3}+\sqrt{6})/24$	0.24639964	$(2\sqrt{3}+\sqrt{6})/24$	0.24639964
$2T_2\ T_1 T_2$	$(1+\sqrt{2})/8$	0.30177670	$-(1+\sqrt{2})/8$	-0.30177670
$2T_2 1T_2 T_2$	$-\sqrt{2}/16$	-0.08838835	$-(4-\sqrt{2})/16$	-0.16161165
$2T_2 2T_2 T_2$	$(4-\sqrt{2})/16$	0.16161165	$\sqrt{2}/16$	0.08838835

Table 20. Polyhedral isoscalars $\text{PIs}^2\begin{pmatrix}\Delta^A S^A{}_A \\ \alpha\ \beta \\ a\ b\ c\end{pmatrix}$

$\alpha a\ \beta b\ c$	algebraic	numerical	$\alpha a\ \beta b\ c$	algebraic	numerical
$A_1\ A_1 A_1$	$\sqrt{3}/12$	0.14433757	$1E\ 2T_2 T_2$	$-(2-\sqrt{2})/16$	-0.03661165
$A_1 1T_2 T_2$	$-\sqrt{6}/24$	-0.10206207	$1E\ T_1 T_2$	$-\sqrt{3}/24$	-0.07216878
$A_1 2T_2 T_2$	$\sqrt{6}/24$	0.10206207	$2E\ E\ A_1$	$\sqrt{6}/24$	0.10206207
$A_2\ T_1 T_2$	$\sqrt{6}/12$	0.20412415	$2E\ 1T_2 T_2$	$(\sqrt{2}-3)/8\sqrt{6}$	-0.08092433
$1E\ E\ A_1$	$\sqrt{2}/8$	0.17677670	$2E\ 2T_2 T_2$	$-(\sqrt{2}+3)/8\sqrt{6}$	-0.22526189
$1E\ 1T_2 T_2$	$(2+\sqrt{2})/16$	0.21338835	$2E\ T_1 T_2$	$1/8$	0.12500000

Table 20. (continued)

αa βb c	algebraic	numerical
$1T_1$ T_1A_1	$(1+2\sqrt{3})/24$	0.18600423
$1T_1$ E T_2	$(-1+2\sqrt{3})/24$	0.10267090
$1T_1$ T_1T_2	$(2\sqrt{10}-\sqrt{2}-2\sqrt{6})/48$	0.00023671
$1T_1 1T_2T_2$	$(-1-2\sqrt{6}-2\sqrt{5}+\sqrt{2}-2\sqrt{3})/48$	-0.25877091
$1T_1 2T_2T_2$	$(-1+2\sqrt{6}-2\sqrt{5}-\sqrt{2}-2\sqrt{3})/48$	-0.11357233
$2T_1$ T_1A_1	$\sqrt{15}/24$	0.16137431
$2T_1$ E T_2	$-\sqrt{15}/24$	-0.16137431
$2T_1$ T_1T_2	$-(\sqrt{30}+2\sqrt{6})/48$	-0.21617094
$2T_1 1T_2T_2$	$(-\sqrt{15}+2\sqrt{3}+\sqrt{30})/48$	0.10559050
$2T_1 2T_2T_2$	$(-\sqrt{15}+2\sqrt{3}-\sqrt{30})/48$	-0.12262724
$3T_1$ T_1A_1	$(\sqrt{2}-\sqrt{6})/24$	-0.04313651
$3T_1$ E T_2	$-(\sqrt{2}+\sqrt{6})/24$	-0.16098764
$3T_1$ T_1T_2	$(-1+2\sqrt{5}+\sqrt{3})/24$	0.21684112
$3T_1 1T_2T_2$	$(2\sqrt{3}-\sqrt{2}-2\sqrt{10}+2+\sqrt{6})/48$	0.00364213
$3T_1 2T_2T_2$	$(2\sqrt{3}+\sqrt{2}+2\sqrt{10}+2-\sqrt{6})/48$	0.22402877
$1T_2 1T_2A_1$	$(1+\sqrt{3}+\sqrt{10})/24$	0.24559702
$1T_2 2T_2A_1$	$(1+\sqrt{3}-\sqrt{10})/24$	-0.01792612
$1T_2$ A_1T_2	$(\sqrt{3}-3-\sqrt{15})/36$	-0.14280368
$1T_2$ E T_2	$(\sqrt{6}-3\sqrt{2}+2\sqrt{30})/72$	0.12724028
$1T_2$ T_1T_2	$-(1+\sqrt{3})/24$	0.11383545
$1T_2 1T_2T_2$	$(\sqrt{2}+2-2\sqrt{3}+\sqrt{6})/48$	0.04999170
$1T_2 2T_2T_2$	$(\sqrt{2}-2+2\sqrt{3}+\sqrt{6})/48$	0.11099594
$2T_2 1T_2A_1$	$(\sqrt{30}-2\sqrt{3})/48$	0.04194008
$2T_2 2T_2A_1$	$(\sqrt{30}+2\sqrt{3})/48$	0.18627765
$2T_2$ A_1T_2	$(\sqrt{10}+\sqrt{2})/24$	0.19068713
$2T_2$ E T_2	$(\sqrt{5}-2)/24$	0.00983617
$2T_2$ T_1T_2	$\sqrt{30}/48$	0.11410887
$2T_2 1T_2T_2$	$(-\sqrt{15}-\sqrt{30})/48$	-0.19479602
$2T_2 2T_2T_2$	$(-\sqrt{15}+\sqrt{30})/48$	0.03342171
$3T_2 1T_2A_1$	$(\sqrt{2}-2\sqrt{6}+2\sqrt{5})/48$	0.02057021
$3T_2 2T_2A_1$	$(\sqrt{2}-2\sqrt{6}-2\sqrt{5})/48$	0.16576879
$3T_2$ A_1T_2	$(\sqrt{6}+6\sqrt{2}-\sqrt{30})/72$	0.07579924
$3T_2$ E T_2	$(\sqrt{3}+6+2\sqrt{15})/72$	0.21497247
$3T_2$ T_1T_2	$(-\sqrt{2}+2\sqrt{6})/48$	0.07259929
$3T_2 1T_2T_2$	$(1+\sqrt{2}+2\sqrt{6}-2\sqrt{3})/48$	0.08018940
$3T_2 2T_2T_2$	$(1-\sqrt{2}-2\sqrt{6}-2\sqrt{3})/48$	-0.18286031

23. Case study: Matrix elements

In this section, we apply the structural coefficients of the preceding section to the reduction of matrix elements. We begin with relations referring to no special type of AOs and procede step by step from the reduced matrix elements of the s.-a. MOs to the rotational invariants belonging to the integrals of GTOs. Since the representation of one AO by a sum of GTOs having the same angular momentum quantum number only enhances the complexity without further systematic insight, we shall confine each AO to one GTO. Because of clearness, we also take the simple example of the molecule P_4. The MOs of this molecule involve s- and p-orbitals:

$$\langle \vec{r}|\text{Ai000}\rangle = \sqrt{1/4\pi} \cdot \exp(-\alpha^2 |\vec{r}-\vec{A_i}|^2) \tag{23.1}$$

$$\langle \vec{r}|\text{Ai01m}\rangle = -2i \cdot \exp(-\alpha^2 |\vec{r}-\vec{A_i}|^2) \cdot \alpha |\vec{r}-\vec{A_i}| \cdot Y_{1m}((\vec{r}-\vec{A_i})/|\vec{r}-\vec{A_i}|) \tag{23.2}$$

These orbitals transform according to the representations A_1 and T_2 of the group T_d:

$$|\text{Ai00}A_1 i\rangle = |\text{Ai000}\rangle \tag{23.3}$$

$$|\text{Ai01}T_2 p\rangle = \sum_m |\text{Ai01m}\rangle \langle m|1T_2 p\rangle \tag{23.4}$$

From these AOs we build up the s.-a. MOs

$$|(\text{Ae},00A_1)ep_e\rangle = \sum_i (\vec{A_i}|\text{Aep}_e) \cdot |\text{Ai00}A_1 i\rangle \tag{23.5}$$

with $e=A_1$ or T_2 according to (22.29), and

$$|(\text{Ae},01T_2)cp_c\rangle = \sum_{ip} K(cp_c, \text{Aie}, T_2 p) \cdot |\text{Ai01}T_2 p\rangle \tag{23.6}$$

with $e=A_1$ or T_2 again and c from the product $e \times T_2$. This means $c=T_2$ if $e=A_1$ and $c=A_1$, E, T_1, T_2 if $e=T_2$. The coefficients are given in table 8.

23.1. Step one: From the reduced matrix elements to BRMs

We now have to calculate three types of invariants of the molecular Hamiltonian $H=T+Q_A \cdot V_A$. The potential operator is defined in (8.10). The invariants are:

1) $\langle (\text{Ae},00A_1)e\|H\|(\text{Ae},00A_1)e\rangle$
2) $\langle (\text{Ae},01T_2)c\|H\|(\text{Af},01T_2)c\rangle$
3) $\langle (\text{Ae},01T_2)c\|H\|(\text{Ac},00A_1)c\rangle$

Since the Hamiltonian is a scalar operator, (5.13) applies reading now:

$$\langle (\text{Ae},n_a 1_a a)c\|H\|(\text{Af},n_b 1_b b)c\rangle \tag{23.7}$$
$$= \sum_{S\sigma k} \text{GEO}_1(\text{Aa},\text{Ab};ec,fc;S\sigma k)(\text{An}_a 1_a a\|H\|\text{An}_b 1_b b)_{S\sigma k}$$

with the geometrical factors

$$\text{GEO}_1(\text{Aa},\text{Ab};ec,fc;S\sigma k) \tag{23.8}$$
$$= \{c^+fb\}\{ab^+k\}\sqrt{Z(-\text{AAS})\text{dimc}/\text{dimk}} \cdot \begin{Bmatrix} e & f^+k^+ \\ b^+ & a^+c^+ \end{Bmatrix} \cdot \text{PIs}\begin{pmatrix} -A & A & S \\ & \sigma & \\ e^+f & k \end{pmatrix}.$$

Of course, these factors are in dependent of the special AO quantum numbers n_a, l_a, n_b, l_b, and of the exponential parameters.

The involved BRMs are

in case 1): $(AOOA_1 \| H \| AOOA_1)_{Sk}$ with $Sk = O^A A_1$ and $S^A A_1$,

in case 2): $(AO1T_2 \| H \| AO1T_2)_{Sok}$ with $Sok = O^A A_1$, $O^A T_2$, $S^A A_1$, $S^A T_1$, $S^A 1T_2$,

and $S^A 2T_2$,

in case 3): $(AO1T_2 \| H \| AOOA_1)_{Sok}$ with $Sok = O^A T_2$, $S^A 1T_2$, and $S^A 2T_2$.

The geometrical factors of the relation (23.7), calculated by (23.8), are listed in the tables 21-23.

Table 21. The geometrical factors $GEO_1(AA_1, AA_1; ec, fc; Sk)$

e c , f c \ Sk	$O^A A_1$	$S^A A_1$
$A_1 A_1$, $A_1 A_1$	1/2	$\sqrt{3}/2$
$T_2 T_2$, $T_2 T_2$	$\sqrt{3}/2$	-1/2

Table 22. The geometrical factors $GEO_1(AT_2 AT_2; ec, fc; Sok)$

e c , f c \ Sok	$O^A A_1$	$O^A T_2$	$S^A A_1$	$S^A E$	$S^A T_1$	$S^A 1T_2$	$S^A 2T_2$
$T_2 A_1, T_2 A_1$	$\sqrt{3}/6$	$-\sqrt{2}/6$	-1/6	-1/3	1/3	1/6	-1/6
$T_2 E, T_2 E$	$\sqrt{6}/6$	1/6	$-\sqrt{2}/6$	$-\sqrt{2}/3$	$-\sqrt{2}/6$	$-\sqrt{2}/12$	$\sqrt{2}/12$
$T_2 T_1, T_2 T_1$	1/2	$\sqrt{6}/12$	$-\sqrt{3}/6$	$\sqrt{3}/6$	$\sqrt{3}/6$	$-\sqrt{3}/12$	$\sqrt{3}/12$
$T_2 T_2, T_2 T_2$	1/2	$-\sqrt{6}/12$	$-\sqrt{3}/6$	$\sqrt{3}/6$	$-\sqrt{3}/6$	$\sqrt{3}/12$	$-\sqrt{3}/12$
$A_1 T_2, A_1 T_2$	1/2	0	$\sqrt{3}/2$	0	0	0	0
$A_1 T_2, T_2 T_2$	0	$\sqrt{3}/6$	0	0	0	$\dfrac{\sqrt{2}-2}{4 \cdot \sqrt{3}}$	$-\dfrac{\sqrt{2}+2}{4 \cdot \sqrt{3}}$
$T_2 T_2, A_1 T_2$	0	$\sqrt{3}/6$	0	0	0	$\dfrac{\sqrt{2}+2}{4 \cdot \sqrt{3}}$	$-\dfrac{\sqrt{2}-2}{4 \cdot \sqrt{3}}$

Table 23. The geometrical factors $GEO_1(AT_2, AA_1; ec, fc; Sok)$

e c , f c \ Sok	$O^A T_2$	$S^A 1T_2$	$S^A 2T_2$
$T_2 A_1, A_1 A_1$	$\sqrt{3}/6$	$(\sqrt{2}+2)/4\sqrt{3}$	$-(\sqrt{2}-2)/4\sqrt{3}$
$A_1 T_2, T_2 T_2$	$\sqrt{3}/6$	$(\sqrt{2}-2)/4\sqrt{3}$	$-(\sqrt{2}+2)/4\sqrt{3}$
$T_2 T_2, T_2 T_2$	$-\sqrt{6}/6$	$\sqrt{3}/6$	$-\sqrt{3}/6$

Using these factors, an example of the relation (23.7) is given by:

$$
\begin{aligned}
\langle (AT_2, O1T_2)T_1 \| H \| (AT_2, O1T_2)T_1 \rangle = & \ (1/2) \cdot (AO1T_2 \| H \| AO1T_2)_{O^A A_1} \\
& + (\sqrt{6}/12) \cdot (AO1T_2 \| H \| AO1T_2)_{O^A T_2} - (\sqrt{3}/6) \cdot (AO1T_2 \| H \| AO1T_2)_{S^A A_1} \\
& + (\sqrt{3}/6) \cdot (AO1T_2 \| H \| AO1T_2)_{S^A E} + (\sqrt{3}/6) \cdot (AO1T_2 \| H \| AO1T_2)_{S^A T_1} \\
& - (\sqrt{3}/12) \cdot (AO1T_2 \| H \| AO1T_2)_{S^A 1T_2} + (\sqrt{3}/12) \cdot (AO1T_2 \| H \| AO1T_2)_{S^A 2T_2}
\end{aligned}
\tag{23.9}
$$

The same analysis applies to the reduced matrix elements of the overlap matrix. We only have to cancel the Hamiltonian in all relations of this subsection. The energy eigenvalues of the symmetry species E and T_1 then simply are:

$$E(c) = \frac{\langle (AT_2, 01T_2)c \| H \| (AT_2, 01T_2)c \rangle}{\langle (AT_2, 01T_2)c \| (AT_2, 01T_2)c \rangle} \quad \text{with } c=E, T_1 \qquad (23.10)$$

Since the species A_1 and T_2 occur twice and thrice, there remains a two- or a three-dimensional eigenvalue problem in these cases.

23.2. Step two: From BRMs to TRMs

The improper BRMs of the potential operator V_A are further related to the TRMs of the triangles Δ_o^A, Σ_o^A, Σ_1^A, Σ_2^A, and Δ^A by formula (8.14). More precisely we have the following relations (23.11) and (23.12):

$$(An_a1_a a \| V_A \| An_b1_b b)_o{}^A_k$$
$$= \sum_{\Delta\gamma} \sqrt{4 \cdot Z(\Delta)} \cdot PIs^2 \begin{pmatrix} \Delta & o^A & A \\ \gamma & & \\ k & k & A_1 \end{pmatrix} \cdot (An_a1_a a \| Ar^{-1} \| An_b1_b b)_{\Delta\gamma k} , \qquad (23.11)$$

where the summands are determined by the (degenerate) triangles sharing the (degenerate) edge o^A, i.e. $\Delta\gamma = \Delta_o^A$, $\Sigma_o^A 1$, and $\Sigma_o^A 2$. The coefficients of this relation are listed in table 24.

Table 24. The factors $\sqrt{4 \cdot Z(\Delta)} \cdot PIs^2 \begin{pmatrix} \Delta & o^A & A \\ \gamma & & \\ k & k & A_1 \end{pmatrix}$

$\begin{matrix}\Delta\gamma\\k\end{matrix}$	Δ_o^A	$\Sigma_o^A 1$	$\Sigma_o^A 2$
A_1	1	$\sqrt{3}$	–
T_2	$\sqrt{3}$	$(\sqrt{3}+\sqrt{6})/\sqrt{2}$	$(\sqrt{3}-\sqrt{6})/\sqrt{2}$

The corresponding relation referring to the edge S^A is given by:

$$(An_a1_a a \| V_A \| An_b1_b b)_S{}^A_{ok}$$
$$= \sum_{\Delta\gamma} \sqrt{12 \cdot Z(\Delta)} \cdot PIs^2 \begin{pmatrix} \Delta & S^A & A \\ \gamma & \sigma & \\ k & k & A_1 \end{pmatrix} \cdot (An_a1_a a \| Ar^{-1} \| An_b1_b b)_{\Delta\gamma k} , \qquad (23.12)$$

where now $\Delta = \Sigma_1^A$, Σ_2^A, Δ^A and $\gamma=1$, 2, 3. The coefficients of this relation are listed in table 25.

Table 25. The factors $\sqrt{12 \cdot Z(\Delta)} \cdot PIs^2 \begin{pmatrix} \Delta & S^A & A \\ \gamma & \sigma & \\ k & k & A_1 \end{pmatrix}$

$\begin{matrix}\Delta\gamma\\\sigma\gamma k\end{matrix}$	Σ_1^A	Σ_2^A	Δ^A
A_1	1	1	$\sqrt{2}$
1E	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{3}$
2E	–	–	1
$1T_1$	$\sqrt{3}$	$-\sqrt{3}$	$(1+\sqrt{12})/\sqrt{6}$
$2T_1$	–	–	$2\sqrt{15}$

Table 25. (continued)

σγk \ Δγ	Σ_1^A	Σ_2^A	Δ^A
$3T_1$	-	-	$(\sqrt{3}-3)/3$
$11T_2$	$\sqrt{3}$	0	$(1+\sqrt{3}+\sqrt{10})/\sqrt{6}$
$12T_2$	0	$-\sqrt{3}$	$(\sqrt{5}-\sqrt{2})/\sqrt{6}$
$13T_2$	-	-	$(1-\sqrt{12}+\sqrt{10})/\sqrt{12}$
$21T_2$	0	$-\sqrt{3}$	$(1+\sqrt{3}-\sqrt{10})/\sqrt{6}$
$22T_2$	$\sqrt{3}$	0	$(\sqrt{5}+\sqrt{2})/\sqrt{6}$
$23T_2$	-	-	$(1-\sqrt{12}-\sqrt{10})/\sqrt{12}$

Applying these results, we give an example of (23.12):

$$(A01T_2\|V_A\|A01T_2)_{S^A_{T_1}} = \sqrt{3}\cdot(A01T_2\|Ar^{-1}\|A01T_2)_{\Sigma^A_{1}T_1}$$ (23.13)

$$-\sqrt{3}\cdot(A01T_2\|Ar^{-1}\|A01T_2)_{\Sigma^A_{2}T_1} +((1+\sqrt{12})/\sqrt{6})\cdot(A01T_2\|Ar^{-1}\|A01T_2)_{\Delta^A_{1}T_1}$$

$$+2\sqrt{15}\cdot(A01T_2\|Ar^{-1}\|A01T_2)_{\Delta^A_{2}T_1} +((1-\sqrt{3})/\sqrt{3})\cdot(A01T_2\|Ar^{-1}\|A01T_2)_{\Delta^A_{3}T_1}$$

23.3. Step three: Ab initio calculation of BRMs

In the case of proper BRMs, we can relate them to the rotational invariants of the two-centre integrals according to formula (15.2). Because of (12.14), this formula reads for a scalar operator:

$$(An_a l_a a\|T\|An_b l_b b)_{S\varepsilon e} = (-1)^{l_a+l_b}\cdot\sqrt{4\pi\cdot\text{dime}}$$

$$\cdot\sum_j c(S\varepsilon e,j)\cdot S^j\cdot Is\begin{pmatrix}l_a^+ l_b^j \\ a^+ b\ e\end{pmatrix}\cdot\langle n_a l_a\|-S^j,T\|n_b l_b\rangle^j$$ (23.14)

The expansion coefficients $c(S\varepsilon e,j)$ are listed in table 26.

Table 26. The coefficients $c(S\varepsilon e,j)$

$S\ \varepsilon e,j$	$c(S\varepsilon e,j)$	$S\ \varepsilon e,j$	$c(S\varepsilon e,j)$
$0^A A_1,0$	$2/\sqrt{4\pi}$	$S^A 2T_2,1$	$i\sqrt{6/4\pi}$
$0^A e,j>0$	0	$S^A E,2$	$\sqrt{15/8\pi}$
$S^A A_1,0$	$\sqrt{12/4\pi}$	$S^A 1T_2,2$	$-\sqrt{15/8\pi}$
$S^A 1T_2,1$	$i\sqrt{6/4\pi}$	$S^A 2T_2,2$	$\sqrt{15/8\pi}$

The special cases of (23.14) are:

$$\left.\begin{array}{l}(A00A_1\|T\|A00A_1)_{0^A A_1} = 2\cdot\langle 00\|0^\circ,T\|00\rangle^\circ \\[4pt] (A00A_1\|T\|A00A_1)_{S^A A_1} = \sqrt{12}\cdot\langle 00\|-S^{A0},T\|00\rangle^\circ\end{array}\right\}$$ (23.15)

$$\left.\begin{array}{l}(A01T_2\|T\|A00A_1)_{0^A T_2} = 0 \\[4pt] (A01T_2\|T\|A00A_1)_{S^A 1T_2} = -3\sqrt{2}\cdot\langle 01\|-S^{A1},T\|00\rangle^1\cdot S^A \\[4pt] (A01T_2\|T\|A00A_1)_{S^A 2T_2} = 3\sqrt{3}\cdot\langle 01\|-S^{A1},T\|00\rangle^1\cdot S^A\end{array}\right\}$$ (23.16)

$$(AO1T_2\|T\|AO1T_2)_0{}^A{}_{A_1} = 2\cdot\langle 01\|0^\circ,T\|01\rangle^\circ$$

$$(AO1T_2\|T\ AO1T_2)_0{}^A{}_{T_2} = 0$$

$$(AO1T_2\|T\|AO1T_2)_S{}^A{}_{A_1} = \sqrt{12}\cdot\langle 01\|-S^{AO},T\|01\rangle^\circ$$

$$(AO1T_2\|T\|AO1T_2)_S{}^A{}_E = \sqrt{6}\cdot\langle 01\|-S^{A2},T\|01\rangle^2\cdot(S^A)^2$$

$$(AO1T_2\|T\|AO1T_2)_S{}^A{}_{T_1} = 0$$

$$(AO1T_2\|T\|AO1T_2)_S{}^A{}_{1T_2} = -3\sqrt{6}\langle 01\|-S^{A2},T\|01\rangle^2\cdot(S^A)^2$$

$$(AO1T_2\|T\|AO1T_2)_S{}^A{}_{2T_2} = 3\sqrt{6}\langle 01\|-S^{A2},T\|01\rangle^2\cdot(S^A)^2$$

$$\left.\right\} \quad (23.17)$$

Again, the same relations apply to the overlap matrix, if we omit the operator T. In both cases, the matrix elements are reduced to six independent parameters, the rotational invariants.

Up to this point, we have made no reference to a special system of orbitals. In order to calculate the rotational invariants, we do this now and choose the Gauss type orbitals of ref.[46]. By comparing formula (13.3) to formula (4.1) of [46], we conclude:

$$\langle n_a l_a\|AB^j\|n_b l_b\rangle^j = \sqrt{1/4\pi}\cdot(-1)^{l_a+l_b+j}\xi_{\alpha\beta}^j\cdot\varepsilon_{\alpha\beta}^0(n_a n_b, jl_a l_b, AB) , \quad (23.18)$$

where α and β are the orbital exponents of the bra- and ket-orbitals respectively. We use the following abbreviations:

$$\xi_{\alpha\beta} = \alpha\beta/\sqrt{\alpha^2+\beta^2}, \quad \theta_{\alpha\beta} = \sqrt{\alpha^2+\beta^2}, \quad \varphi_{\alpha\beta} = \arctan(\alpha/\beta) \quad (23.19)$$

In the same way, the comparison of (13.3) to formula (4.3) of [46] yields the rotational invariants of the kinetic energy:

$$\langle n_a l_a\|AB^j,T\|n_b l_b\rangle^j \quad (23.20)$$
$$= -(\hbar^2\beta^2/2m)\sqrt{1/4\pi}\cdot(-1)^{l_a+l_b+j}\xi_{\alpha\beta}^j\cdot\varepsilon_{\alpha\beta}^0(n_a n_b+1, jl_a l_b, AB)$$

According to (4.2) of [46], the functions $\varepsilon_{\alpha\beta}^0(\dots)$ are given by:

$$\varepsilon_{\alpha\beta}^0(n_a n_b, jl_a l_b, AB) \quad (23.21)$$
$$= [Nj,00,j\|\varphi_{\alpha\beta}\|n_a l_a, n_b l_b, j]\cdot(\pi/2\theta_{\alpha\beta}^3\sqrt{2j+1})\cdot\varphi^0(\xi_{\alpha\beta}, Nj, AB)$$

with $N = n_a+n_b+(l_a+l_b-j)/2$. Using the coefficients and Gauss-Laguerre type functions listed in appendix 3, we obtain the following six invariants:

$$\langle 00\|0^\circ\|00\rangle^\circ = \sqrt{\pi}/4\theta_{\alpha\beta}^3$$

$$\langle 00\|-S^{AO}\|00\rangle^\circ = (\sqrt{\pi}/4\theta_{\alpha\beta}^3)\cdot\exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01\|-S^{A1}\|00\rangle^1 = -(\sqrt{3\pi}\beta\,\xi_{\alpha\beta}/2\theta_{\alpha\beta}^4)\cdot\exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01\|0^\circ\|01\rangle^\circ = 3\sqrt{3\pi}\xi_{\alpha\beta}/2\theta_{\alpha\beta}^4$$

$$\langle 01\|-S^{AO}\|01\rangle^\circ = (\sqrt{3\pi}\,\xi_{\alpha\beta}/2\theta_{\alpha\beta}^4)\cdot(3-2\xi_{\alpha\beta}^2 S^{A2})\cdot\exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01\|-S^{A2}\|01\rangle^2 = -(\sqrt{6\pi}\xi_{\alpha\beta}^3/\theta_{\alpha\beta}^4)\cdot\exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\left.\right\} \quad (23.22)$$

And with respect to the kinetic energy, we get:

$$\langle 00 \| 0^\circ , T \| 00 \rangle^\circ \quad = 3\sqrt{\pi}\hbar^2 \xi_{\alpha\beta}^2 / 4m\Theta_{\alpha\beta}^3$$

$$\langle 00 \| -S^{A0}, T \| 00 \rangle^\circ \quad = (\sqrt{\pi}\hbar^2 \xi_{\alpha\beta}^2 / 4m\Theta_{\alpha\beta}^3) \cdot (3 - 2\xi_{\alpha\beta}^2 S^{A2}) \cdot \exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01 \| -S^{A1}, T \| 00 \rangle^1 \quad = -(\sqrt{\pi}\hbar^2 \xi_{\alpha\beta}^3 \beta / 2m\Theta_{\alpha\beta}^4) \cdot (5 - 2\xi_{\alpha\beta}^2 S^{A2}) \cdot \exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01 \| 0^\circ , T \| 01 \rangle^\circ \quad = 15\sqrt{3\pi}\hbar^2 \xi_{\alpha\beta}^3 / 2m\Theta_{\alpha\beta}^4 \qquad\qquad (23.23)$$

$$\langle 01 \| -S^{A0}, T \| 01 \rangle^\circ \quad = (\sqrt{3\pi}\hbar^2 \xi_{\alpha\beta}^3 / 2m\Theta_{\alpha\beta}^4) \cdot (15 - 20\xi_{\alpha\beta}^2 S^{A2} + 4\xi_{\alpha\beta}^4 S^{A4}) \cdot \exp(-\xi_{\alpha\beta}^2 S^{A2})$$

$$\langle 01 \| -S^{A2}, T \| 01 \rangle^2 \quad = -(\sqrt{6\pi}\hbar^2 \xi_{\alpha\beta}^5 / m\Theta_{\alpha\beta}^4) \cdot (7 - 2\xi_{\alpha\beta}^2 S^{A2}) \cdot \exp(-\xi_{\alpha\beta}^2 S^{A2})$$

We finally come back to the example (23.9). Inserting (23.17 and 23) into (23.9) yields the reduced matrix element of the kinetic energy with respect·to the s.-a. MO of species T_1:

$$\langle (AT_2, 01T_2)T_1 \| T \| (AT_2, 01T_2)T_1 \rangle$$

$$= \langle 01 \| 0^\circ , T \| 01 \rangle^\circ - \langle 01 \| -S^{A0}, T \| 01 \rangle^\circ + \sqrt{1/2}\langle 01 \| -S^{A2}, T \| 01 \rangle^2 \cdot S^{A2}$$

$$= (\sqrt{3\pi}\hbar^2 \xi_{\alpha\beta}^2 / 2m\Theta_{\alpha\beta}^4) \cdot [15 - (15 - 6\xi_{\alpha\beta}^2 S^{A2}) \cdot \exp(-\xi_{\alpha\beta}^2 S^{A2})] \qquad (23.24)$$

The corresponding element of the overlap matrix is:

$$\langle (AT_2, 01T_2)T_1 \| (AT_2, 01T_2)T_1 \rangle = (3\sqrt{3\pi}\xi_{\alpha\beta}^2 / 2\Theta_{\alpha\beta}^4) \cdot [1 - \exp(-\xi_{\alpha\beta}^2 S^{A2})] \qquad (23.25)$$

23.4. Step four: The ab initio calculation of the TRMs

There finally remains the calculation of the TRMs of the nuclear attraction. Working in the AB–PC scheme, we have the following relation of TRMs and rotational invariants, which is quite analogous to (15.14/15):

$$(A\varphi_a a \| Cr^{-1} \| B\varphi_b b)_{\Delta\gamma c}^\varepsilon$$

$$= \sum_{JjL} GEO_5' (Al_a \alpha a, Bl_b \beta b; C\Delta\gamma c; JjL) \langle An_a l_a \| AB_\Delta^J PC_\Delta^j \| Bn_b l_b \rangle^L , \qquad (23.26)$$

where the geometrical factor is given by:

$$GEO_5' (Al_a \alpha a, Bl_b \beta b; C\Delta\gamma c; JjL) = 4\pi (2L+1)\sqrt{1/dimc} \sum_{\gamma\delta d\eta e\mu\sigma\tau} \sum \bar{c}^2 (\Delta\gamma c, st.\delta d\eta e\gamma')$$

$$\cdot Is \begin{pmatrix} 1^+ l & L^+ \\ \alpha^+_\beta & \mu^+ \\ a^+ b & c^+ \end{pmatrix}_\varepsilon Is \begin{pmatrix} L & J^+ j^+ \\ \mu & \sigma \tau \\ c & d^+ e^+ \end{pmatrix}_{\gamma'} \cdot S_{\delta d}^{J\sigma} (AB_\Delta) S_{\eta e}^{j\tau} (PC_\Delta) \qquad (23.27)$$

With respect to the group T_d and to the low angular momentum quantum numbers, several multiplicity indices become obsolete. Further, all centres involved are of type A:

$$(An_a l_a a \| Ar^{-1} \| An_b l_b b)_{\Delta\gamma c} = \sum_{JjL} GEO_5' (Al_a a, Al_b b; A\Delta\gamma c; JjL)$$

$$\cdot \langle An_a l_a \| AA_\Delta^J PA_\Delta^j \| An_b l_b \rangle^L \qquad (23.28)$$

with

$$GEO_5' (Al_a a, Al_b b; A\Delta\gamma c; JjL) \qquad\qquad (23.29)$$

$$= 4\pi (2L+1)\sqrt{1/dimc} \sum_{\delta d\eta e} Is(\begin{smallmatrix} 1^+ l & L^+ \\ a & b & c^+ \end{smallmatrix}) Is(\begin{smallmatrix} L J^+ j^+ \\ c d^+ e^+ \end{smallmatrix}) \bar{c}^2 (\Delta\gamma c, st.\delta d\eta e) S_{\delta d}^J (AA_\Delta) S_{\eta e}^j (PA_\Delta)$$

In order to save space, it is advisable to compile the·compound coeffi-

cients

$$c^2(\Delta\gamma c,(Jj)Lc)$$
$$= \sqrt{(2L+1)/dimc} \cdot \sum_{\delta d\eta e} Is\binom{L\,J^+\,j^+}{cd^+e^+} c^2(\Delta\gamma c,st.\delta d\eta e) S_{\delta d}^J(AA_\Delta) S_{\eta e}^j(PA_\Delta). \tag{23.30}$$

These coefficients can be calculated directly:

$$c^2(\Delta\gamma c,(Jj)Lc) = \sqrt{(2L+1)Z(\Delta)} dimc^{-1} \sum_{de} Is\binom{L\,J^+\,j^+}{cd^+e^+} \sum_{jrm} \tau\binom{\Delta SA}{jrm}\binom{c\ d^+e^+}{p_c p_d p_e} \tag{23.31}$$
$$\cdot(\Delta\gamma cp_c|\Delta_j)\langle\vec{S_r}|sol\ Jdp_d\rangle\langle\overrightarrow{P_r A_m}|sol\ jep_e\rangle$$

According to section 13.3., the vector $\vec{P_r}$ belonging to $\vec{S_r}$ is determined by the topological correlation

$$\vec{P_r} = \sqrt{Z(S)} \sum_{kl} \tau\binom{-AAS}{klr} \cdot (\alpha^2\vec{A_k}+\beta^2\vec{A_l})/(\alpha^2+\beta^2) \tag{23.32}$$

The isoscalar factors and s.-a. solid harmonics for this calculation are listed in appendix 4. The results can be checked by the sum rule:

$$\sum_{L\gamma c} dimc|c^2(\Delta\gamma c,(Jj)Lc)|^2 = Z(\Delta)(AA_\Delta)^{2J}(PA_\Delta)^{2j}(2J+1)(2j+1)/16\pi^2 \tag{23.33}$$

We arrange the results according to the triangles involved. Since the branching rules of the group chain $R(3) \supset T_d$ depend on the inversion property of the representations, we add the indices g or u to the quantum number L.

1) The triangle is Δ_o^A. This means: $\Delta=\Delta_o^A$, $S=0^A$, $AA_\Delta=0$, $PA_\Delta=0$.

$$c^2(\Delta_o^A A_1,(00)0_g A_1) = 1/2\pi \tag{23.34}$$

2) The triangle is Σ_o^A. This means: $\Delta=\Sigma_o^A$, $S=0^A$, $AA_\Delta=0$, $PA_\Delta=S^A$.

$$c^2(\Sigma_o^A A_1,(00)0_g A_1) = \sqrt{3}/2\pi \qquad c^2(\Sigma_o^A 1T_2,(02)2_g T_2) = -\sqrt{30}S^{A2}/8\pi$$
$$c^2(\Sigma_o^A 1T_2,(01)1_u T_2) = -i\sqrt{6}S^A/4\pi \qquad c^2(\Sigma_o^A 2T_2,(02)2_g T_2) = \sqrt{30}S^{A2}/8\pi$$
$$c^2(\Sigma_o^A 2T_2,(01)1_u T_2) = -i\sqrt{6}S^A/4\pi \qquad c^2(\Sigma_o^A E,(02)2_g E) = \sqrt{30}S^{A2}/8\pi \tag{23.35}$$

3) The triangle is Σ_1^A. This means: $\Delta=\Sigma_1^A$, $S=S^A$, $AA_\Delta=S^A$, $PA_\Delta=\beta^2 S^A/(\alpha^2+\beta^2)$.

Table 27. The coefficients $c^2(\Sigma_1^A\gamma c,(Jj)Lc)$.

J	j	L	γc	c^2	J	j	L	γc	c^2
0	0	0_g	A_1	$\sqrt{3}/2\pi$	1	1	2_g	$2T_2$	$-3\beta^2 S^{A2}/4\pi(\alpha^2+\beta^2)$
1	0	1_u	$1T_2$	$i\sqrt{6}S^A/4\pi$	1	1	2_g	E	$-3\beta^2 S^{A2}/4\pi(\alpha^2+\beta^2)$
1	0	1_u	$2T_2$	$i\sqrt{6}S^A/4\pi$	2	0	2_g	E	$\sqrt{30}S^{A2}/8\pi$
0	1	1_u	$1T_2$	$i\sqrt{6}\beta^2 S^A/4\pi(\alpha^2+\beta^2)$	2	0	2_g	$1T_2$	$-\sqrt{30}S^{A2}/8\pi$
0	1	1_u	$2T_2$	$i\sqrt{6}\beta^2 S^A/4\pi(\alpha^2+\beta^2)$	2	0	2_g	$2T_2$	$\sqrt{30}S^{A2}/8\pi$
1	1	0_g	A_1	$-3\beta^2 S^{A2}/2\pi(\alpha^2+\beta^2)$	0	2	2_g	E	$\sqrt{30}\beta^4 S^{A2}/8\pi(\alpha^2+\beta^2)^2$
1	1	1_g	T_1	0	0	2	2_g	$1T_2$	$-\sqrt{30}\beta^4 S^{A2}/8\pi(\alpha^2+\beta^2)^2$
1	1	2_g	$1T_2$	$3\beta^2 S^{A2}/4\pi(\alpha^2+\beta^2)$	0	2	2_g	$2T_2$	$\sqrt{30}\beta^4 S^{A2}/8\pi(\alpha^2+\beta^2)^2$

4) The triangle is Σ_2^A. This means: $\Delta=\Sigma_2^A$, $S=S^A$, $AA_\Delta=S^A$, $PA_\Delta=\alpha^2 S^A/(\alpha^2+\beta^2)$.

$$c^2(\Sigma_2^A\gamma c,(Jj)Lc) = (-\alpha^2/\beta^2)^j \cdot c^2(\Sigma_1^A\gamma c,(Jj)Lc) \tag{23.36}$$

5) The triangle is Δ^A. This means: $\Delta = \Delta^A$, $S = S^A$, $AA_\Delta = S^A$, and $PA_\Delta = S^A \cdot \sqrt{\alpha^4 + \beta^4 + \alpha^2\beta^2}/(\alpha^2 + \beta^2)$. The distances S^A (between two vertices) and A (between vertex and centre) are related by $A = S^A \cdot \sqrt{3/8}$.

Table 28. The coefficients $c^2(\Delta\gamma c,(Jj)Lc)$.

J	j	L	γc	$c^2(\Delta\gamma c,(Jj)Lc)$
0	0	0_g	A_1	$\sqrt{6}/4\pi$
1	0	1_u	$1T_2$	$i(\sqrt{3}+3)S^A/6\pi$
1	0	1_u	$2T_2$	$i\sqrt{10}S^A/4\pi$
1	0	1_u	$3T_2$	$i(\sqrt{6}-6\sqrt{2})S^A/12\pi$
0	1	1_u	$1T_2$	$iS^A(-\sqrt{15}(\alpha^2+\beta^2)+\sqrt{3}\beta^2-6\alpha^2)/6\pi(\alpha^2+\beta^2)$
0	1	1_u	$2T_2$	$iS^A(\sqrt{2}(\alpha^2+\beta^2)+\sqrt{10}\beta^2)/4\pi(\alpha^2+\beta^2)$
0	1	1_u	$3T_2$	$iS^A(-\sqrt{30}(\alpha^2+\beta^2)+\sqrt{6}\beta^2+6\sqrt{2}\alpha^2)/12\pi(\alpha^2+\beta^2)$
1	1	0_g	A_1	$3\sqrt{2}S^{A2}(\alpha^2-\beta^2)/4\pi(\alpha^2+\beta^2)$
1	1	1_g	$1T_1$	$S^{A2}(\sqrt{10}+\sqrt{2}+2\sqrt{6})/8\pi$
1	1	1_g	$2T_1$	$S^{A2}(\sqrt{30}-\sqrt{6})/8\pi$
1	1	1_g	$3T_1$	$S^{A2}(\sqrt{5}+1-\sqrt{3})/4\pi$
1	1	2_g	$1E$	$3\sqrt{6}\beta^2 S^{A2}/8\pi(\alpha^2+\beta^2)$
1	1	2_g	$2E$	$3\sqrt{2}S^{A2}(2\alpha^2+\beta^2)/8\pi(\alpha^2+\beta^2)$
1	1	2_g	$1T_2$	$-S^{A2}(\sqrt{5}(\alpha^2-\beta^2)+(1+\sqrt{3})(\alpha^2+\beta^2))/4\pi(\alpha^2+\beta^2)$
1	1	2_g	$2T_2$	$S^{A2}(\sqrt{6}(\alpha^2-\beta^2)-\sqrt{30}(\alpha^2+\beta^2))/8\pi(\alpha^2+\beta^2)$
1	1	2_g	$3T_2$	$S^{A2}(-\sqrt{10}(\alpha^2-\beta^2)+(2\sqrt{6}-\sqrt{2})(\alpha^2+\beta^2))/8\pi(\alpha^2+\beta^2)$
2	0	2_g	$1E$	$\sqrt{15}S^{A2}/8\pi$
2	0	2_g	$2E$	$3\sqrt{5}S^{A2}/8\pi$
2	0	2_g	$1T_2$	$-5\sqrt{6}S^{A2}/12\pi$
2	0	2_g	$2T_2$	$\sqrt{5}S^{A2}/4\pi$
2	0	2_g	$3T_2$	$-5\sqrt{3}S^{A2}/12\pi$
0	2	2_g	$1E$	$-\sqrt{30}S^{A2}(\alpha^4+2\alpha^2\beta^2)/4\pi(\alpha^2+\beta^2)^2$
0	2	2_g	$2E$	$\sqrt{10}S^{A2}(\alpha^4-2\alpha^2\beta^2-2\beta^4)/4\pi(\alpha^2+\beta^2)^2$
0	2	2_g	$1T_2$	$S^{A2}(5\alpha^2\beta^2-\sqrt{5}\alpha^2(\alpha^2+\beta^2)+\sqrt{15}\beta^2(\alpha^2+\beta^2))/3\pi(\alpha^2+\beta^2)^2$
0	2	2_g	$2T_2$	$S^{A2}(\sqrt{30}\alpha^2\beta^2+5\sqrt{6}\alpha^2(\alpha^2+\beta^2))/6\pi(\alpha^2+\beta^2)^2$
0	2	2_g	$3T_2$	$S^{A2}(5\sqrt{2}\alpha^2\beta^2-3\sqrt{10}\alpha^2(\alpha^2+\beta^2)-6\sqrt{30}\beta^2(\alpha^2+\beta^2))/6\pi(\alpha^2+\beta^2)^2$

These last coefficients are rather complex. In order to avoid this complexity, one has to transform the three-centre integrals into a scheme of distance vectors, which is independent of the orbital exponents α and β.

With these results, we determine the geometrical factors. From (23. 29 and 30) follows:

$$GEO_5(Al_a a, Al_b b; A\Delta\gamma c; JjL) = 4\pi \cdot \sqrt{2L+1} \cdot Is(^{1\ +1\ L\ +}_{a\ b\ c}) \cdot c^2(\Delta\gamma c,(Jj)Lc) \qquad (23.37)$$

Since the isoscalar factors with $l_a, l_b \leqslant 1$ are very simple, we get the following equation:

$$GEO_5(Al_a a, Al_b b; A\Delta\gamma c; JjL) = 4\pi\sqrt{dimc} \cdot c^2(\Delta\gamma c,(Jj)Lc) \qquad (23.38)$$

We now come back to the example (23.13). Using the tables 27 and 28, we obtain:

$$(AO1T_2\|Ar^{-1}\|AAO1T_2)_{\Sigma_1^A T_1} = 0, \quad (AO1T_2\|Ar^{-1}\|AO1T_2)_{\Sigma_2^A T_1} = 0, \quad (23.39)$$

$$(AO1T_2\|Ar^{-1}\|AO1T_2)_{\Delta^A_{\gamma T_1}} = 4\pi\sqrt{3}\cdot c^2 (\Delta\gamma T_1, (11)1_g T_1) \langle AO1\| AA_\Delta^1 \ PA_\Delta^1 \| AO1 \rangle^1 \quad (23.40)$$

Therefore the BRM of the operator V_A is given by one rotational invariant only:

$$(AO1T_2\| V_A \|AO1T_2)_S{}^A{}_{T_1} = (3S^{A2}/2)(\sqrt{5}+7+10\sqrt{6}-2\sqrt{30}) \langle AO1\|AA_\Delta^1 \ PA_\Delta^1\| AO1\rangle^1 \quad (23.41)$$

As in the preceding subsection, we have not yet made reference to a special system of orbitals. We do this now in order to calculate the rotational invariants of eq.(23.28). For the Gauss-type orbitals of ref. [46] we have the general relation (A2.14). This relation now reads:

$$\langle AO1_a\|AA_\Delta^J \ PA_\Delta^j\|AO1_b\rangle^L = (4\pi/(2L+1))\xi_{\alpha\beta}^J \Theta_{\alpha\beta}^j \cdot \eta_{\alpha\beta}^o (OO,Ll_a1_b,Jj,AA_\Delta,PA_\Delta) \quad (23.42)$$

According to (5.8) of [46] the functions $\eta_{\alpha\beta}^o$ are given by:

$$\eta_{\alpha\beta}^o (OO,Ll_a1_a,Jj,AA_\Delta,PA_\Delta) = -4\pi\Theta_{\alpha\beta}^{-2} \sum_{Nn} [NJ,nj,L\|\varphi_{\alpha\beta}\|O1_a,O1_b,L]$$

$$\cdot \varphi^o(\xi_{\alpha\beta},NJ,AA_\Delta)\cdot\varphi^o(\Theta_{\alpha\beta},n-1j,PA_\Delta) \quad (23.43)$$

The sum is limited by $2N+2n=l_a+1_b-J-j$. Using again the coefficients and functions listed in appendix 3, we get the following rotational invariants:

$$\langle AOO\|AA_\Delta^O PA_\Delta^O\| AOO\rangle^O = (8\pi^2/\Theta_{\alpha\beta}^2)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_O(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^1 PA_\Delta^O\| AOO\rangle^1 = -(16\pi^2\beta\xi_{\alpha\beta}/\Theta_{\alpha\beta}^3)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_O(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^O PA_\Delta^1\| AOO\rangle^1 = -(16\pi^2\beta/\Theta_{\alpha\beta}^2)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_1(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^1 PA_\Delta^1\| AO1\rangle^O = (32\pi^2(\beta^2-\alpha^2)\xi_{\alpha\beta}/\Theta_{\alpha\beta})\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_1(\Theta_{\alpha\beta}^2 PA_\Delta^2) \quad (23.44)$$

$$\langle AO1\|AA_\Delta^1 PA_\Delta^1\| AO1\rangle^1 = (32\pi^2\xi_{\alpha\beta}/\Theta_{\alpha\beta})\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_1(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^1 PA_\Delta^1\| AO1\rangle^2 = (32\pi^2(\beta^2-\alpha^2)\xi_{\alpha\beta}/\Theta_{\alpha\beta}^3)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_1(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^2 PA_\Delta^O\| AO1\rangle^2 = (8\sqrt{30}\pi^2\xi_{\alpha\beta}^3 /5\Theta_{\alpha\beta}^3)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_O(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

$$\langle AO1\|AA_\Delta^O PA_\Delta^2\| AO1\rangle^2 = (32\sqrt{30}\pi^2\alpha\beta/5\Theta_{\alpha\beta}^2)\cdot\exp(-\xi_{\alpha\beta}^2 AA_\Delta^2)\cdot F_2(\Theta_{\alpha\beta}^2 PA_\Delta^2)$$

The fifth invariant is the one needed in the example (23.41).

Appendix 1: Projection operators

In eq. (5.1) we have expressed the s.-a. LCAOs by the general SALC coefficients (5.2). This representation is more expedient than that by projection operators. But, of course, it is possible to interrelate the s.-a. functions generated by both methods.

The projection operators or more generally the shift operators of an irreducible representation c are defined by

$$P_{ik}^c = (\dim c/\mathrm{ord}G)\sum_{g\epsilon G} D_{ik}^c(g)^* \cdot U(g) \qquad (A1.1)$$

If we apply such an operator to the atomic function $|Aj\varphi_a a p_a\rangle$ defined by (4.3), the resultant transforms according to the representation c, component i. The indices k, j, and p_a are redundant; but an unfortunate choice of them can yield zero, although a s.-a. function of species c does exist. Since the orbitals $|Aj\varphi_a a p_a\rangle$ induce the product representation $\sigma^A \times a$ according to (5.3), the decomposition of the representation obeys the character rule resulting from (2.10):

$$n(Aa,c) = (1/\mathrm{ord}G)\sum_C \lambda(C)\chi^c(C)\chi^a(C)^* \sigma^A(C) \qquad (A1.2)$$

If now $n(Aa,c) > 1$, there are several independent sets of species c, which may be found by trying several combinations of the indices k, j, and p_a. On the contrary, the indices ε, e, and γ in (5.1) exactly exhaust the set of species c induced by $|Aj\varphi_a a p_a\rangle$.

We calculate the result of the projection. Because of (5.3) we get

$$P_{1k}^c|Aj\varphi_a a m_a\rangle = (\dim c/\mathrm{ord}G)\sum_{g\epsilon G}\sum_{n_a i} D_{1k}^c(g)^* D_{n_a m_a}^a(g)\sigma_{ij}^A(g)|Ai\varphi_a a n_a\rangle \qquad (A1.3)$$

If we apply P_{1k}^c to the molecular orbitals (5.1), we derive the following interrelation:

$$|(A\varepsilon e,\varphi_a a)\gamma c l\rangle = P_{1k}^c|(A\varepsilon e,\varphi_a a)\gamma c k\rangle = \sum_{j r_a} K(\gamma ck, Aj\varepsilon e, ar_a)P_{1k}^c|Ai\varphi_a ar_a\rangle \qquad (A1.4)$$

This shows that the s.-a. MOs determined by (5.1) may be regarded as linear combinations of the projected orbitals (A1.3), where the sum is taken for the redundant indices j and r_a. The index k is arbitrary, but has to be the same in the SALC coefficient and the projector.

The orthogonality relations of the SALC coefficients resulting from (2.26/27) and (3.6/7) allow the inversion of (A1.4). Starting from $P_{1m}^c|(A\varepsilon e,\varphi_a a)\gamma c k\rangle = \delta(m,k)\cdot|(A\varepsilon e,\varphi_a a)\gamma c l\rangle$ one derives:

$$P_{1m}^c|Aj\varphi_a a s_a\rangle = \sum_{\varepsilon e\gamma} K(\gamma cm, Aj\varepsilon e, as_a)\cdot|(A\varepsilon e,\varphi_a a)\gamma c l\rangle \qquad (A1.5)$$

This completes the wanted interrelations.

Appendix 2: Molecular integrals of Gaussian functions

In favor of the general validity, no reference was made to special orbital systems in section 13. Only the choice of the distance vectors between the atomic centres has regard for the integrals of Gaussian or related orbitals. This appendix has two aims: At first the theorems, i.e. their rotational invariants, are illustrated for a particular system of orbitals; and secondly the proofs of the strong theorems concerning the three- and four-centre integrals are supplemented using this special system of orbitals.

As well known, the GTOs are recommended by their simple integrals. We therefore choose the radial functions in (13.1) from this type. As explained in section 13, only spherical orbitals have the adequate tensorial structure. Such orbital systems have been discussed in [45-47]. The most suitable for our purpose is that of [46], and we routinely refer to this paper. The advantage of this system results from its generation by the gradient operator:

$$\langle \vec{r} | \alpha n l m \rangle = \alpha^{-2n-l} \Delta^n \mathcal{Y}_{lm}(\vec{\nabla}) \exp(-\alpha^2 r^2) \qquad (A2.1)$$

The right transformation property is achieved by inserting the operator into the solid harmonics $\mathcal{Y}_{lm}(\vec{a}) = (ia)^l Y_{lm}(\vec{a}/a)$. As a function of operators we distinguish $\mathcal{Y}_{lm}(\vec{a})$ from $\langle \vec{a} | \text{sol } lm \rangle$ in order to avoid confusion.

Emphasizing the general validity of the theorems, we sketch the relations of this system to other orbital systems. As shown in [46], the definition (A2.1) leads to the following radial functions:

$$N_1(nl) \cdot L_n^{l+1/2}(\alpha^2 r^2) \cdot \exp(-\alpha^2 r^2)$$

Therefore the ordinary spherical GTOs as well as the spherical oscillator functions can be expanded as

$$(\alpha r)^{2n} \exp(-\alpha^2 r^2) \langle \alpha \vec{r} | \text{sol } lm \rangle = N_2(nl) \cdot \sum_{k=0}^{n} \binom{n+l+1/2}{n-k} (-1)^k \langle \vec{r} | \alpha k l m \rangle \quad (A2.2)$$

$$\langle \vec{r} | \text{Osc } \alpha n l m \rangle = N_3(nl) \cdot \sum_{k=0}^{n} \binom{n+l+1/2}{n-k} 2^k \langle \vec{r} | \alpha k l m \rangle , \qquad (A2.3)$$

where $N_i(nl)$ are normalization constants. For other systems of orbitals, $\langle \vec{r} | X n l m \rangle = R_{nl}^X(r) \langle \vec{r} | \text{sol } lm \rangle$, result infinite series expansions with respect to the radial quantum number. The expansion coefficients can be calculated, because the polynoms

$$N_4(nl) \cdot L_n^{l+1/2}(\alpha^2 r^2) \langle \text{sol } lm | \vec{r} \rangle \qquad (A2.4)$$

supplement the system (A2.1) to a biorthonormal system. Thence the coefficients of the expansion

$$\langle \vec{r} | X n l m \rangle = \sum_k c_k^{Xn} \langle \vec{r} | \alpha n l m \rangle \qquad (A2.5)$$

are given by:

$$c_k^{Xn} = N_4(nl)\int_0^\infty L_k^{l+1/2}(\alpha^2 r^2)R_{nl}^X(r)r^{2l+2}dr \qquad (A2.6)$$

The multi-centre integrals contain products of the functions (A2.1) with respect to different centres. These products can be reorganized by a theorem given in [46], eq.(3.3):

$$\alpha_1^{-2n_1-l_1}\Delta_1^{n_1}\mathscr{Y}_{l_1m_1}(\vec{\nabla}_1)\cdot\alpha_2^{-2n_2-l_2}\Delta_2^{n_2}\mathscr{Y}_{l_2m_2}(\vec{\nabla}_2)$$

$$= \sum_{n_3l_3n_4l_4L}\sum[n_3l_3n_4l_4L\|\varphi_{12}\|n_1l_1n_2l_2L]\begin{pmatrix}l_1l_2L\\m_1m_2M\end{pmatrix}^\dagger\cdot\begin{pmatrix}l_3l_4L\\m_3m_4M\end{pmatrix} \qquad (A2.7)$$

$$\cdot\xi_{12}^{-2n_3-l_3}\Delta_3^{n_3}\mathscr{Y}_{l_3m_3}(\vec{\nabla}_3)\cdot\theta_{12}^{-2n_4-l_4}\Delta_4^{n_4}\mathscr{Y}_{l_4m_4}(\vec{\nabla}_4)$$

where $\vec{\nabla}_3=\vec{\nabla}_1-\vec{\nabla}_2$, $\vec{\nabla}_4=(\alpha_1^2\vec{\nabla}_1+\alpha_2^2\vec{\nabla}_2)/\theta_{12}$, $\varphi_{12}=\tan^{-1}(\alpha_1/\alpha_2)$, $\theta_{12}=\sqrt{\alpha_1^2+\alpha_2^2}$, and $\xi_{12}=\alpha_1\alpha_2/\theta_{12}$. The sums in (A2.7) are limited by $2n_3+l_3+2n_4+l_4=2n_1+l_1+2n_2+l_2$. As for the coefficients of this expansion we again refer to [45, 46], and to appendix 3.

The application of the operator $\mathscr{Y}_{lm}(\vec{\nabla})$ to a scalar function $f(r)$ results in

$$\mathscr{Y}_{lm}(\vec{\nabla})f(r) = g^l(r)\langle\vec{r}|sol\ lm\rangle, \qquad (A2.8)$$

where the scalar functions are given by $g^l(r)=\sqrt{1/4\pi}\cdot(\frac{1}{r}\cdot\frac{d}{dr})^l f(r)$. Because of (A2.7), we need the corresponding theorem with respect to the scalar functions of two vector variables $\vec{r}_1$ and $\vec{r}_2$. This is given by

$$\mathscr{Y}_{l_1m_1}(\vec{\nabla}_1)\mathscr{Y}_{l_2m_2}(\vec{\nabla}_2)f(r_1^2,r_2^2,\vec{r}_1\cdot\vec{r}_2)$$

$$= \sum_{L\lambda_1\lambda_2}g_{\lambda_1\lambda_2}^{Ll_1l_2}(r_1^2,r_2^2,\vec{r}_1\cdot\vec{r}_2)\sqrt{2L+1}^{-1}\begin{pmatrix}l_1l_2L\\m_1m_2M\end{pmatrix}^+\langle\vec{r}_1,\vec{r}_2|sol(\lambda_1\lambda_2)LM\rangle, \qquad (A2.9)$$

where the sums are limited by $\lambda_1+\lambda_2\leqslant l_1+l_2$ and $l_1+l_2-\lambda_1-\lambda_2=$ even. An infinite expansion of this type is trivial from the tensorial point of view. The limitation of the sums is the essential statement of (A2.9).

The proof is given by a recursive calculation of the scalar functions $g_{\lambda_1\lambda_2}^{Ll_1l_2}$. (A2.9) is obviously valid, if $l_1=l_2=0$. The first function then is $g_{00}^{000}=f$. If now (A2.9) and the limitation hold for a pair of angular momenta l_1 and l_2, we deduce the same for the pair l_1+1 and l_2. For this purpose, we start from $\mathscr{Y}_{l_1+1m_1}(\vec{\nabla}_1)\mathscr{Y}_{l_2m_2}(\vec{\nabla}_2)f(...)$ and decompose the first spherical harmonic by:

$$\mathscr{Y}_{l_1+1m_1}(\vec{\nabla}_1) = (2l_1+3)\sqrt{4\pi/3(l_1+1)}\sum\begin{pmatrix}l_1\ 1\ l_1+1\\m_1\ \mu\ m_1\end{pmatrix}^+\mathscr{Y}_{l_1m_1}(\vec{\nabla}_1)\mathscr{Y}_{1\mu}(\vec{\nabla}_1)$$

In order to perform the operation $\mathscr{Y}_{1\mu}(\vec{\nabla})=\sqrt{3/4\pi}\nabla_\mu$, we define the following derivatives:

$$g_{\lambda_1\lambda_2k}^{Ll_1l_2}(x_1,x_2,x_3) = \frac{\partial}{\partial x_k}g_{\lambda_1\lambda_2}^{Ll_1l_2}(x_1,x_2,x_3)$$

This yields:

$$\mathscr{Y}_{1\mu}(\vec{\nabla}_1)g_{\lambda_1\lambda_2}^{Ll_1l_2}(r_1^2,r_2^2,\vec{r}_1\cdot\vec{r}_2) =$$

$$= 2g_{\lambda_1\lambda_2 1}^{L l_1 l_2}(r_1^2,r_2^2,\vec{r}_1\cdot\vec{r}_2)\langle\vec{r}_1|\text{sol } 1\mu\rangle + g_{\lambda_1\lambda_2 3}^{L l_1 l_2}(r_1^2,r_2^2,\vec{r}_1\cdot\vec{r}_2)\langle\vec{r}_2|\text{sol } 1\mu\rangle$$

and

$$\mathscr{Y}_{1\mu}(\vec{\triangledown}_1)\langle\vec{r}_1|\text{sol } \lambda_1\mu_1\rangle = (2\lambda_1+1)\sqrt{3\lambda_1/4\pi}\cdot\sum\binom{\lambda_1-1\ 1\ \lambda_1}{\mu_1'\ \ \mu\ \ \mu_1}\langle\vec{r}_1|\text{sol } \lambda_1-1\mu_1'\rangle$$

If we now insert these expressions into $\mathscr{Y}_{l_1+1m_1}(\vec{\triangledown}_1)\mathscr{Y}_{l_2 m_2}(\vec{\triangledown}_2)f(\ldots)$, we
get a new equation of type (A2.9) with l_1+1 instead of l_1. The compar-
ison of the coefficients of the functions $\langle\vec{r}_1,\vec{r}_2|\text{sol}(\lambda_1\lambda_2)LM\rangle$ then
yields the recursive formula of the scalar functions:

$$g_{j_1 j_2}^{J l_1+1 l_2} = -(2l_1+3)\sqrt{4\pi/3(l_1+1)}\sum_L (2L+1)\begin{Bmatrix}l_1 l_2\ L\\ J\ 1\ l_1+1\end{Bmatrix}\cdot\Big[\sum_{\lambda_1}\begin{Bmatrix}J\ j_1 j_2\\ \lambda_1 L\ 1\end{Bmatrix}\langle j_1\|1\|\lambda_1\rangle$$

$$\cdot(2g_{\lambda_1 j_2 1}^{L l_1 l_2}\cdot r_1^{\lambda_1+1-j_1} + g_{\lambda_1 j_2}^{L l_1 l_2}\cdot(2\lambda_1+1)\delta(j_1,\lambda_1-1)) \qquad (A2.10)$$

$$+(-1)^{J+L+1}\sum_{\lambda_2}\begin{Bmatrix}J\ j_1 j_2\\ \lambda_2 1\ L\end{Bmatrix}\langle j_2\|1\|\lambda_2\rangle g_{j_1\lambda_2 3}^{L l_1 l_2}\cdot r_2^{\lambda_2+1-j_2}\Big]$$

Since $g_{\lambda_1 j_2}^{L l_1 l_2}\neq 0$ only, if $\lambda_1+j_2\leq l_1+l_2$, and $\langle j_1\|1\|\lambda_1\rangle\neq 0$ only, if $j_1\leq\lambda_1+1$,
we have the limitation $j_1+j_2\leq\lambda_1+1+j_2\leq l_1+l_2+1$. As for the second sum-
mand, we conclude in the same way $j_1+\lambda_2\leq l_1+l_2$, $j_2\leq\lambda_2+1$ and therefore
$j_1+j_2\leq j_1+\lambda_2+1\leq l_1+l_2+1$. From both limits follows that $g_{j_1 j_2}^{L l_1+1 l_2}\neq 0$
only, if $j_1+j_2\leq l_1+l_2+1$, which had to be shown. The recursion with re-
spect to l_2 is found by a fitting exchange of indices. In the long run
it is, of course, desirable to derive an explicit formula of the func-
tions g.

The analogue of (A2.9) involving three vector variables $\vec{r}_1$, $\vec{r}_2$, and
$\vec{r}_3$ is given by:

$$\mathscr{Y}_{l_1 m_1}(\vec{\triangledown}_1)\mathscr{Y}_{l_2 m_2}(\vec{\triangledown}_2)\mathscr{Y}_{l_3 m_3}(\vec{\triangledown}_3)f(r_1^2,r_2^2,r_3^2,\vec{r}_1\cdot\vec{r}_2,\vec{r}_2\cdot\vec{r}_3,\vec{r}_3\cdot\vec{r}_1)$$

$$= \sum_{j_i JL\lambda}\sum h\binom{l_1 l_2}{j_1 j_2}_{Jj_3}^{L l_3\lambda}(r_1^2,r_2^2,r_3^2,\vec{r}_1\cdot\vec{r}_2,\vec{r}_2\cdot\vec{r}_3,\vec{r}_3\cdot\vec{r}_1) \qquad (A2.11)$$

$$\cdot\binom{l_1 l_2 L}{m_1 m_2 M}\binom{L\ l_3\ \lambda}{M\ m_3\mu}\langle\vec{r}_1,\vec{r}_2,\vec{r}_3|\text{sol}(j_1 j_2)Jj_3\lambda\mu\rangle$$

The essential limitation of the sums is now $j_1+j_2+j_3\leq l_1+l_2+l_3$. The
scalar functions h again can be calculated recursively.

We now are prepared to discuss the particular integrals. As an ex-
ample of the two-centre integrals (13.3), we choose those involving the
momentum operator. For this case, in [46], the integral formula (4.5)
has been derived, which reads:

$$\langle A\alpha n_a l_a m_a|\triangledown_\mu|B\beta n_b l_b m_b\rangle \qquad (A2.12)$$

$$= \sum_{LI}\lambda_{\alpha\beta}^0(n_a n_b,Ll_a l_b,AB)\binom{l\ 1\ l_a}{m_a\ m\ M}\binom{l\ 1\ l_b}{m\ \mu\ m_b}\langle\zeta_{\alpha\beta}\vec{AB}|\text{sol } LM\rangle ,$$

where $\zeta_{\alpha\beta}$ has been defined above and $\lambda_{\alpha\beta}^0(\ldots)$ is given by eq.(4.6) of
[46]. From this follows the generalized reduced matrix element. Be-
cause of the symmetric coupling used in (13.3), a 6j symbol is involved:

$$\langle n_a l_a \| AB_j^j \nabla \| n_b l_b \rangle^J = \sqrt{(2J+1)/4\pi} \cdot \sum_I (-1)^{1+l_a+l_b} \cdot \begin{Bmatrix} 1 & a^J & 1_b \\ 1 & 1 & j \end{Bmatrix} \cdot \xi_{\alpha\beta}^j \eta_{\alpha\beta}^0 (n_a n_b, j l_a l_b, AB)$$
(A2.13)

An example of the weak theorem of the three-centre integrals (13.8) is given by eq.(5.7) of [46]. The rotational invariants now are:

$$\langle An_a l_a \| AB^J PC^j \| Bn_b l_b \rangle^L = (4\pi/(2L+1)) \xi_{\alpha\beta}^J \theta_{\alpha\beta}^j \eta_{\alpha\beta}^0 (n_a n_b, L l_a l_b, Jj, AB.PC) \quad (A2.14)$$

According to [46], eq.(5.8), they depend on the distances AB and PC only. From the same equation follows the limitation of the sums in (13.8) by $J+j \leq 2n_a+l_a+2n_b+l_b$. Therefore $J+j$ may be greater than l_a+l_b.

In order to prove the strong theorem we start from an integral over two ns-orbitals, which is an invariant by itself:

$$\langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle = \sum_J \eta_{\alpha\beta}^0 (n_a n_b, 000, JJ, AB, PC)(\alpha\beta AB.PC)^J P_J \left(\frac{\overrightarrow{AB}.\overrightarrow{PC}}{AB.PC}\right) \quad (A2.15)$$

where P_J is a Legendre polynomial. In accordance to (A2.1), the higher functions are generated by $|\alpha n l m\rangle = \alpha^{-1} \mathcal{Y}_{lm}(\nabla)|\alpha n00\rangle$ and we can represent the shifted orbitals by $|A\alpha n_a l_a m_a\rangle = (-\alpha)^{-l_a} \mathcal{Y}_{l_a m_a}(\nabla_A)|A\alpha n_a 00\rangle$. Since the gradient now operates on the parameters $\overrightarrow{A}$, we can interchange it with the integration and generate the higher integrals from (A2.15) by:

$$\langle A\alpha n_a l_a m_a | r_C^{-1} | B\beta n_b l_b m_b \rangle \quad (A2.16)$$

$$= (-\alpha)^{-l_a}(-\beta)^{-l_b} \mathcal{Y}_{l_a m_a}(\overrightarrow{\nabla}_A) \mathcal{Y}_{l_b m_b}(\overrightarrow{\nabla}_B) \langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle$$

$$= \alpha^{-l_a} \cdot \beta^{-l_b} \cdot \mathcal{Y}_{l_a m_a}(\overrightarrow{\nabla}_{AC}) \mathcal{Y}_{l_b m_b}(\overrightarrow{\nabla}_{BC}) \langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle$$

If we regard the integral $\langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle$ as a function of $\overrightarrow{AC}$ and $\overrightarrow{BC}$ (which is possible), the theorem (A2.9) immediately supplies the intended result (13.9). But because of the more natural interpretation as a function of $\overrightarrow{AB}$ and $\overrightarrow{PC}$, we reshape the derivations by (A2.7). This yields:

$$\langle A\alpha n_a l_a m_a | r_C^{-1} | B\beta n_b l_b m_b \rangle = \sum_{njNJL} \sum [njNJL \| \varphi_{\alpha\beta} \| 0 l_a 0 l_b L] \begin{pmatrix} l_a^+ l_b^+ L \\ m_a m_b M \end{pmatrix} \begin{pmatrix} j^+ J^+ L \\ m M M' \end{pmatrix}$$

$$\cdot \xi_{\alpha\beta}^{-2n-j} \theta_{\alpha\beta}^{-2N-J} \mathcal{Y}_{jm}(\overrightarrow{\nabla}_{AB}) \mathcal{Y}_{JM}(\overrightarrow{\nabla}_{PC}) \Delta_{AB}^n \Delta_{PC}^N \langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle \quad (A2.17)$$

with $l_a+l_b=2n+j+2N+J \geq j+J$. Because the terms $\Delta_{AB}^n \Delta_{PC}^N \langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle$ are scalar functions, the theorem (A2.9) applies now with respect to the vectors $\overrightarrow{AB}$ and $\overrightarrow{PC}$. This yields the following expression of the rotational invariants of the strong theorem:

$$\langle An_a l_a \| AB^{J'} PC^{j'} \| Bn_b l_b \rangle^L \quad (A2.18)$$

$$= (1/4\pi(2L+1)^2) \sum_{njNJ} [njNJL \| \varphi_{\alpha\beta} \| 0 l_a 0 l_b L] \cdot \xi_{\alpha\beta}^{-j} \theta_{\alpha\beta}^{-J} \cdot g_{n_a n_b J'j'}^{nNjJ}(AB^2, PC^2, \overrightarrow{AB}.\overrightarrow{PC})$$

The scalar functions $g_{n_a n_b J'j'}^{nNjJ}$ have to be calculated recursively by (A2. 10) beginning with $g_{n_a n_b 00}^{nNoo} = \xi_{\alpha\beta}^{-2n} \theta_{\alpha\beta}^{-2N} \Delta_{AB}^n \Delta_{PC}^N \langle A\alpha n_a 00 | r_C^{-1} | B\beta n_b 00 \rangle$. From the

limit $j+J \geqslant J'+j'$ according to (A2.9) follows $l_a+l_b \geqslant J'+j'$ as proposed.

Since the expansions (A2.2-4) affect the radial quantum numbers only, the rotational invariants of the integrals of other orbital systems have the same group theoretical structure,

$$\langle AXn_al_a\|AB^JPC^j\|BXn_bl_b\rangle^L = \sum_{n_a'n_b'} c_{n_a}^{n_a}c_{n_b}^{n_b}\langle An_a'l_a\|AB^JPC^j\|Bn_b'l_b\rangle^L,$$

and the strong theorem is valid for any system of atomic orbitals.

We finally come to the four-centre integrals of the electronic interaction. First we discuss the weak version of (13.13). In order to separate the functions (13.12), we have chosen the coupling different from that in eq.(6.4) of [46]. Because of the necessary recoupling, the rotational invariants of (13.13) read:

$$[(An_al_a^+,Cn_cl_c)1\|(AC^{j_1}BD^{j_2})^JPQ^{j_3}\|(Bn_bl_b^+,Dn_dl_d)1]^L = \sqrt{1/(4\pi)^3(2l+1)(2l'+1)}$$

$$\cdot\sum_{pq\ell}\sqrt{2\ell+1}\cdot\sigma^0(n_an_bn_cn_d,ll_al_c,l'l_bl_d,j_3pq,j_1j_2,AC,BD,PQ)\,\xi_{\alpha\gamma}^{j_1}\xi_{\beta\delta}^{j_2}\cdot q^{j_3}\begin{Bmatrix} j_1 & j_2 & \ell \\ p & q & j \\ l & l' & L \end{Bmatrix}$$

with $q=[(\alpha^2+\gamma^2)(\beta^2+\delta^2)/(\alpha^2+\beta^2+\gamma^2+\delta^2)]^{1/2}$. (A2.19)

The invariants are functions of the distances AC, BD, and PQ only and not of the angles between them.

The proof of the strong theorem follows the lines of that given for the three-centre integrals and we can be brief. As in (A2.16), one generates the integrals by the gradient operators with respect to the atomic centres:

$$\langle A\alpha n_al_am_a,B\beta n_bl_bm_b|r_{12}^{-1}|C\gamma n_cl_cm_c,D\delta n_dl_dm_d\rangle = (-\alpha)^{-l_a}(-\beta)^{-l_b}(-\gamma)^{-l_c}(-\delta)^{-l_d}$$

$$\cdot\mathcal{Y}_{l_am_a}(\vec{\nabla}_A)\mathcal{Y}_{l_bm_b}(\vec{\nabla}_B)\mathcal{Y}_{l_cm_c}(\vec{\nabla}_C)\mathcal{Y}_{l_dm_d}(\vec{\nabla}_D)\langle A\alpha n_a00,B\beta n_b00|r_{12}^{-1}|C\gamma n_c00,D\delta n_d00\rangle$$

By repeated application of (A2.7), the differential operators are adapted to the distances $\overrightarrow{AC}$, $\overrightarrow{BD}$, and $\overrightarrow{PQ}$. This leads to the scalar functions

$$f(AC^2,BD^2,PQ^2,\overrightarrow{AC}\cdot\overrightarrow{BD},\overrightarrow{BD}\cdot\overrightarrow{PQ},\overrightarrow{PQ}\cdot\overrightarrow{AC}) = \xi_{\alpha\gamma}^{-2n}\xi_{\beta\delta}^{-2n'}\xi_{\sigma\tau}^{-2N-2N'-J-J'+K}$$

$$\cdot\Delta_{AC}^n\Delta_{BD}^{n'}\Delta_{PQ}^{N+N'+(J+J-K)/2}\langle A\alpha n_a00,B\beta n_b00|r_{12}^{-1}|C\gamma n_c00,D\delta n_d00\rangle$$

with $\sigma=\xi_{\alpha\gamma}$ and $\tau=\xi_{\beta\delta}$. Because of (A2.11) the derivatives of these functions have the structure

$$\mathcal{Y}_{jm}(\vec{\nabla}_{AC})\mathcal{Y}_{j'm'}(\vec{\nabla}_{BD})\mathcal{Y}_{KM}(\vec{\nabla}_{PQ})f$$

$$= \sum_{j_i}\sum_{IkL}h\begin{Bmatrix}(jj')kKL\\(j_1j_2)Ij_3\end{Bmatrix}(AC^2,\ldots,\overrightarrow{PQ}\cdot\overrightarrow{AC})\cdot\begin{pmatrix}jj'k\\mm'\mu\end{pmatrix}^+\begin{pmatrix}kKL\\ \mu MM'\end{pmatrix}^+\langle\overrightarrow{AC},\overrightarrow{BD},\overrightarrow{PQ}|sol(j_1j_2)Ij_3LM\rangle$$

with the limitation $j_1+j_2+j_3 \leqslant j+j'+K$. In analogy to (A2.18), this leads to the rotational invariants of the strong theorem (13.13). Using the abbreviation $F = 1/\sqrt{(4\pi)^3(2l+1)(2l'+1)(2L+1)(2K+1)}$, the result reads:

$$[(An_al_a^+,Cn_cl_c)1\|(AC^{j_1}BD^{j_2})^IPQ^{j_3}\|(Bn_bl_b^+,Dn_dl_d)1]^L =$$ (A2.20)

$$= F \cdot \sum_{n j N J} \sum_{n'j'N'J'} \sum_{kK} [njNJ1 \| \varphi_{\alpha\gamma} \| 01_a 01_c 1] \cdot [n'j'N'J'1 \| \varphi_{\beta\delta} \| 01_b 01_d 1']$$

$$\cdot [N+N'+(J+J'-K)/2, K00K \| \varphi_{\sigma\tau} \| NJN'J'K] \begin{Bmatrix} j & J & 1 \\ j' & J' & 1' \\ k & K & L \end{Bmatrix} \cdot \zeta_{\alpha\gamma}^{-j} \zeta_{\beta\delta}^{-j} \zeta_{\sigma\tau}^{-K} \tag{A2.20}$$

$$\cdot h \begin{pmatrix} jj' \\ j_1 j_2 \end{pmatrix} kKL \atop Ij_3} (AC^2, BD^2, PQ^2, \overrightarrow{AC} \cdot \overrightarrow{BD}, \overrightarrow{BD} \cdot \overrightarrow{PQ}, \overrightarrow{PQ} \cdot \overrightarrow{AC})$$

The balance of the angular momenta follows from $l_a + l_c = 2n + j + 2N + J \geqslant j + J$, $l_b + l_d = 2n' + j' + 2N' + J' \geqslant j' + J'$, and $J + J' \geqslant K$. This results in $l_a + l_b + l_c + l_d \geqslant j + j' + J + J'$ $\geqslant j + j' + K \geqslant j_1 + j_2 + j_3$, which had to be shown.

Appendix 3: Modified Moshinsky-Smirnov coefficients and Gauss-Laguerre type functions

In this appendix, we compile the coefficients involved in the eqs. (13.10/11), (23.21 and 43), (A2.7, 17/18 and 20) as far as they are neeeded in section 23. The coefficients are related to the Moshinsky-Smirnov coefficients by a different normalization:

$$[n_1 l_1, n_2 l_2, L\|\varphi\|n_3 l_3, n_4 l_4, L] \tag{A3.1}$$
$$= (2L+1) \cdot A(n_1 l_1)A(n_2 l_2)A(n_3 l_3)^{-1}A(n_4 l_4)^{-1}\langle n_1 l_1, n_2 l_2 L\|\varphi\|n_3 l_3, n_4 l_4, L\rangle,$$

where

$$A(nl) = \sqrt{4\pi/(2n+2l+1)!!(2n)!!} \tag{A3.2}$$

The Moshinsky-Smirnov coefficients have been calculated by the formulae (11) and (23) in a paper of Trlifaj [72]. In addition to the references given in [45], we mention the papers of Dobeš [73] and Niukkanen [74]. The coefficients are arranged according to the sum $K=2n_1+l_1+2n_2+l_2=2n_3+l_3+2n_4+l_4$ and to the angular momentum quantum number L.

Table 29. The modified Moshinsky-Smirnov coefficients

K L	$n_1 l_1 n_2 l_2$	$n_3 l_3 n_4 l_4$	$[n_1 l_1, n_2 l_2, L\|\varphi\|n_3 l_3, n_4 l_4, L]$
0 0	0 0 0 0	0 0 0 0	1
1 1	0 1 0 0	0 1 0 0	$3\cos\varphi$
	0 1 0 0	0 0 0 1	$-3\sin\varphi$
	0 0 0 1	0 1 0 0	$3\sin\varphi$
	0 0 0 1	0 0 0 1	$3\cos\varphi$
2 0	1 0 0 0	1 0 0 0	$\cos^2\varphi$
	1 0 0 0	0 0 1 0	$\sin^2\varphi$
	1 0 0 0	0 1 0 1	$-\sqrt{3}\sin\varphi\cdot\cos\varphi$
	0 0 1 0	1 0 0 0	$\sin^2\varphi$
	0 0 1 0	0 0 1 0	$\cos^2\varphi$
	0 0 1 0	0 1 0 1	$\sqrt{3}\sin\varphi\cdot\cos\varphi$
	0 1 0 1	1 0 0 0	$\sqrt{3}\sin\varphi\cdot\cos\varphi$
	0 1 0 1	0 0 1 0	$-\sqrt{3}\sin\varphi\cdot\cos\varphi$
	0 1 0 1	0 1 0 1	$\cos^2\varphi-\sin^2\varphi$
2 1	0 1 0 1	0 1 0 1	3
2 2	0 2 0 0	0 2 0 0	$5\cos^2\varphi$
	0 2 0 0	0 0 0 2	$5\sin^2\varphi$
	0 2 0 0	0 1 0 1	$-\sqrt{30}\sin\varphi\cdot\cos\varphi$
	0 0 0 2	0 2 0 0	$5\sin^2\varphi$
	0 0 0 2	0 0 0 2	$5\cos^2\varphi$
	0 0 0 2	0 1 0 1	$\sqrt{30}\sin\varphi\cdot\cos\varphi$
	0 1 0 1	0 2 0 0	$\sqrt{30}\sin\varphi\cdot\cos\varphi$
	0 1 0 1	0 0 0 2	$-\sqrt{30}\sin\varphi\cdot\cos\varphi$

Table 29. (continued)

K L	$n_1 l_1 n_2 l_2$	$n_3 l_3 n_4 l_4$	$[n_1 l_1, n_2 l_2, L \| \varphi \| n_3 l_3, n_4 l_4, L]$
2 2	0 1 0 1	0 1 0 1	$5(\cos^2\varphi - \sin^2\varphi)$
3 1	1 1 0 0	1 1 0 0	$3\cos^3\varphi$
	1 1 0 0	1 0 0 1	$3\sin\varphi \cdot \cos^2\varphi$
	1 1 0 0	0 1 1 0	$3\sin^2\varphi \cdot \cos\varphi$
	1 1 0 0	0 0 1 1	$-3\sin^3\varphi$
	1 1 0 0	0 2 0 1	$-3\sqrt{2}\sin^2\varphi \cdot \cos\varphi$
	1 1 0 0	0 1 0 2	$3\sqrt{2}\sin\varphi \cdot \cos^2\varphi$
	0 0 1 1	1 1 0 0	$3\sin^3\varphi$
	0 0 1 1	1 0 0 1	$3\sin^2\varphi \cdot \cos\varphi$
	0 0 1 1	0 1 1 0	$3\sin\varphi \cdot \cos^2\varphi$
	0 0 1 1	0 0 1 1	$3\cos^3\varphi$
	0 0 1 1	0 2 0 1	$3\sqrt{2}\sin^2\varphi \cdot \cos\varphi$
	0 0 1 1	0 1 0 2	$3\sqrt{2}\sin\varphi \cdot \cos^2\varphi$
4 0	2 0 0 0	2 0 0 0	$\cos^4\varphi$
	2 0 0 0	1 0 1 0	$\sin^2\varphi \cdot \cos^2\varphi$
	2 0 0 0	0 0 2 0	$\sin^4\varphi$
	2 0 0 0	1 1 0 1	$-\sqrt{3}\sin\varphi \cdot \cos^3\varphi$
	2 0 0 0	0 1 1 1	$\sqrt{3}\sin^3\varphi \cdot \cos\varphi$
	2 0 0 0	0 2 0 2	$\sqrt{5}\sin^2\varphi \cdot \cos^2\varphi$
4 2	1 2 0 0	0 1 1 1	$-\sqrt{30}\sin^3\varphi \cdot \cos\varphi$
	0 0 1 2	0 1 1 1	$\sqrt{30}\sin\varphi \cdot \cos^3\varphi$
	0 0 1 2	1 1 0 1	$\sqrt{30}\sin^3\varphi \cdot \cos\varphi$

For the calculations in section 23, we further list the Gauss-Laguerre type functions occurring in the eqs.(23.21 and 43):

$$\varphi^0(\alpha, -11, r) = (-2)^{1-1} F_1(\alpha^2 r^2)$$

$$\varphi^0(\alpha,\ 01, r) = (-2)^1 \cdot \exp(-\alpha^2 r^2)$$

$$\varphi^0(\alpha,\ 11, r) = (-2)^{1+1}(21+3-2\alpha^2 r^2) \cdot \exp(-\alpha^2 r^2)$$

$$\varphi^0(\alpha, 21, r) = (-2)^{1+2}\left[(21+3)(21+5)-4(21+5)\alpha^2 r^2 + 4\alpha^4 r^4\right] \cdot \exp(-\alpha^2 r^2)$$

Appendix 4. Isoscalar factors and s.-a. solid harmonics of the group T_d

In the following, the indices g (gerade) and u (ungerade) mark the even or odd parity of the irreducible representations of the group SO(3).

Table 30. SO(3) compatibility table for the group T_d.

SO(3)	0_g	0_u	1_g	1_u	2_g	2_u
T_d	A_1	A_2	T_1	T_2	$E+T_2$	$E+T_1$

Table 31. The isoscalar factors $Is(^{jkl}_{abc})$ with $j+k+l \leqslant 4$.

j	k	l	a	b	c	Is	j	k	l	a	b	c	Is
0_g	0_g	0_g	A_1	A_1	A_1	1	2_g	2_g	0_g	E	E	A_1	$\sqrt{2/5}$
0_u	0_u	0_g	A_2	A_2	A_1	1	2_g	2_g	0_g	T_2	T_2	A_1	$\sqrt{3/5}$
							2_u	2_u	0_g	E	E	A_1	$\sqrt{2/5}$
1_g	1_g	0_g	T_1	T_1	A_1	1	2_u	2_u	0_g	T_1	T_1	A_1	$\sqrt{3/5}$
1_u	1_u	0_g	T_2	T_2	A_1	1	2_g	2_u	0_u	E	E	A_2	$\sqrt{2/5}$
1_g	1_u	0_u	T_1	T_2	A_2	1	2_g	2_u	0_u	T_2	T_1	A_2	$\sqrt{3/5}$
1_g	1_g	1_g	T_1	T_1	T_1	1							
1_u	1_u	1_g	T_2	T_2	T_1	1							
1_g	1_g	2_g	T_1	T_1	E	$\sqrt{2/5}$							
1_g	1_g	2_g	T_1	T_1	T_2	$\sqrt{3/5}$							
1_u	1_u	2_g	T_2	T_2	E	$\sqrt{2/5}$							
1_u	1_u	2_g	T_2	T_2	T_2	$\sqrt{3/5}$							
1_g	1_u	2_u	T_1	T_2	E	$\sqrt{2/5}$							
1_g	1_u	2_u	T_1	T_2	T_1	$\sqrt{3/5}$							

Table 32. The s.-a. solid harmonics of the group T_d

l	a	p	$\langle \vec{r} | \text{sol lap} \rangle$
0	A_1	1	$1/\sqrt{4\pi}$
1	T_2	x	$i\sqrt{3/4\pi} \cdot x$
1	T_2	y	$i\sqrt{3/4\pi} \cdot y$
1	T_2	z	$i\sqrt{3/4\pi} \cdot z$
2	E	1	$-\sqrt{5/16\pi}(3z^2 - r^2)$
2	E	2	$-\sqrt{15/16\pi}(x^2 - y^2)$
2	T_2	x	$-\sqrt{15/4\pi} \cdot yz$
2	T_2	y	$-\sqrt{15/4\pi} \cdot zx$
2	T_2	z	$-\sqrt{15/4\pi} \cdot xy$

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List of standing abbreviations

AO	atomic orbital
BRM	bicentric reduced matrix element
CFP	coefficient of fractional parentage
CI	configuration interaction
dim...	dimension of ...
GEO	geometrical factor
GTO	Gauss type orbital
Is	isoscalar (factor)
LCAO	linear combination of atomic orbitals
MO	molecular orbital
NSR	non-simply reducible
ord...	order of ...
PIs	polyhedral isoscalar (factor)
PRM	polyhedral reduced matrix element
QRM	quadrocentric reduced matrix element
QSALC	quadrocentric SALC
RME	reduced matrix element
s.-a.	symmetry-adapted
SALC	symmetry-adapted linear combination
SR	simply reducible
STO	Slater type orbital
TRM	tricentric reduced matrix element
TSALC	tricentric SALC
VB	valence bond
WET	Wigner-Eckart theorem
Z(...)	number of ...

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