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Symmetry Adaption

III. On the Diagonalization of the Overlap Matrix

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The overlap matrix of symmetric molecules is diagonalized for arbitrary orbitals as far as this is possible by group theoretical methods. The remaining invariant matrix elements are expressed in coordinate and numeration independent way by "physical" orbital factors and purely geometric factors arising from group algebra only.

Key words: Symmetry adapted orbitals

1. Introduction

In this paper we want to diagonalize the overlap matrix of a molecule or complex $A_mB_nC_p\cdots$ with symmetry group G for an arbitrary set of orbitals $\varphi_{nlm}(r-A_i)$ as far as this is possible by group theoretical methods. We write the orbitals in Dirac's notation:

$$\varphi_{nlm}(r-A_i)=\langle r-A_i \mid nlm\rangle=\langle r \mid Ainlm\rangle \tag{1}$$

The vector A_i indicates the position of the i'th atom of the symmetrically equivalent set A. Symmetrically inequivalent sets consisting of equal atoms will be marked differently.

The treatment of the overlap matrix is not only an end in itself, but also a preparation for the diagonalization of other molecular matrices (energy, vibrational force constants etc.). Thus Sect. 2 will apply to these other matrices too. But Sect. 3 takes into account the special properties of the overlap matrix.

2. Diagonalization

The diagonalization will be performed by the SALC coefficients defined in [1, 2], in the following cited as I and II. The definitions and notations of these papers will

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be taken over. According to Eqs. (20) and (21) of II we have the following formula for the SALC's built up from the atomic orbitals (1):

$$|(A\alpha a, nl\beta\ell)\gamma c p\rangle = \sum_{im} M(\gamma c p, Ai\alpha a, (\beta\ell)lm)\cdot|Ainlm\rangle, \tag{2}$$

where the SALC coefficient is given by:

$$M(\gamma c p, Ai\alpha a, (\beta\ell)lm) = \sum_{qr} \langle aq, \ell r \mid \gamma c p\rangle (A_i \mid A\alpha a q)\langle lm \mid l\beta\ell r\rangle \tag{3}$$

In (3) we have the following coefficients: $\langle aq, \ell r \mid \gamma c p\rangle$ is the Clebsch-Gordan coefficient reducing the product $a\times\ell$ to γc, $\langle lm \mid l\beta\ell r\rangle$ the transformation coefficient from the lm-basis to the s.a. $l\beta\ell r$-basis, and $(A_i \mid A\alpha a q)$ a standard coefficient, according to Eq. (7) of II a suitable linear combination of s.a. spherical harmonics.

We repeat the meaning of (2): $|(A\alpha a, nl\beta\ell)\gamma c p\rangle$ are SALC orbitals of symmetry species c (γ multiplicity index, component p) resulting from atomic orbitals with the quantum numbers n, l, m located at atomic centers of set A. The additional quantum numbers $\beta\ell$ and αa are inserted by the reduction of the reducible representations $\mathscr{D}^1 \to \ell$ and $\sigma^A \to a$ (β and α multiplicity indices). The original overlap matrix $\langle Ainlm \mid Bkn'l'm'\rangle$ is in terms of the SALC orbitals already diagonalized as far as this is possible from symmetry considerations:

$$\langle (A\alpha a, nl\beta\ell)\gamma c p \mid (B\alpha' a', n'l'\beta' b')\gamma' c' p'\rangle = \delta(c, c')\delta(p, p')\langle (A\alpha a, nl\beta b)\gamma c p \mid (B\alpha' a', n'l'\beta'\ell')\gamma' c p\rangle \tag{4}$$

The remaining diagonalization in the indices $A\alpha a$, $nl\beta\ell$, γ will depend on the special atomic orbitals (for instance STO or GTO), on the special distances between the atoms of set A and set B etc. The symmetry invariant matrix elements in (4) are given by:

$$\langle (A\alpha a, nl\beta\ell)\gamma c p \mid (B\alpha' a', n'l'\beta'\ell')\gamma' c p\rangle = \sum_{imjm'} M(\gamma c p, Ai\alpha a, (\beta\ell)lm)^* \cdot M(\gamma' c p, Bj\alpha' a', (\beta'\ell')l'm')\langle Ainlm \mid Bjn'l'm'\rangle \tag{5}$$

This is the starting point of further considerations but not of direct, practical use, when the coefficients M have been calculated; because one needs all original matrix elements to calculate the fewer invariant elements. For this purpose it is more useful to solve (5) with the aid of the orthogonality relation (23) of II:

$$\langle Ainlm \mid Bjn'l'm'\rangle = \sum_{\alpha a\beta} \sum_{\ell\gamma\alpha' a'\beta'} \sum_{\ell'\gamma' c p} M(\gamma c p, Ai\alpha a, (\beta\ell)lm) \cdot M(\gamma' c p, Bj\alpha' a', (\beta'\ell')l'm')^* \langle (A\alpha a, nl\beta\ell)\gamma c p \mid (B\alpha' a', n'l'\beta'\ell')\gamma' c p\rangle \tag{6}$$

In (6) the original overlap matrix is expressed by its symmetry invariants. When there are x invariants, it will be enough to calculate x matrix elements. Taking x relevant equations from (6) one can calculate the invariants and the rest of the matrix elements will follow. This brings out the dependency of matrix elements handled in [3] for the special case of force constants. In order to express the

invariants in coordinate and numeration independent terms one must take into account more specific properties of the matrix under consideration, as will be done in the next section. This will make obsolete the explicit knowledge of the coefficients M and all other coordinate dependent coefficients therein.

Because we shall have to perform Racah algebraic calculations, it is suitable to replace the Clebsch-Gordan coefficients in (3) by the more symmetric vector coupling coefficients Eq. (57) of II:

$$M(\gamma cp, Ai\alpha a, (\beta\ell)lm) = \dim c^{1/2} \sum_{qr} V_\gamma \begin{pmatrix} a^+ & \ell^+ & c \\ q & r & p \end{pmatrix} (\boldsymbol{A}_i \mid A\alpha aq) \langle lm \mid l\beta\ell r \rangle \quad (7)$$

The meaning of a^+ and other Racah algebraic conventions are explained in the appendix of II on nomenclature.

3. Coordinate Independent Expressions

In the case of the overlap matrix the specific properties follow from the two-center integrals. These only depend on the distance vector $\boldsymbol{A}_i - \boldsymbol{B}_k$ between the centers. Because of the completeness of the spherical harmonics and the translation invariance of the integrals we have the form:

$$\langle Ainlm \mid Bkn'l'm' \rangle = \sum_{L=0}^{l+l'} \sum_{M=-L}^{+L} \pi(nn', Lll', |\boldsymbol{A}_i - \boldsymbol{B}_k|) \begin{pmatrix} L^+ & l^+ & l' \\ M & m & m' \end{pmatrix} \langle \boldsymbol{A}_i - \boldsymbol{B}_k \mid LM \rangle \quad (8)$$

Integral formulae with the structure of (8) have been given in [4] and [5] for special orbital types. [6] contains a general proof and a recursive differential equation for the invariants π. From arbitrary formulae the invariants can be calculated, if one solves (8) for π and chooses $\boldsymbol{A}_i = 0$ and $\boldsymbol{B}_k = (0, 0, S) = \boldsymbol{S}$. This yields:

$$\pi(nn', Lll', S) = (4\pi/(2L+1))^{1/2} \sum_m \begin{pmatrix} L & l & l'^+ \\ 0 & m & m \end{pmatrix} \langle 0nlm \mid Sn'l'm \rangle \quad (9)$$

As discussed at some length in II there are discrete sets of symmetry equivalent edge vectors between the centers $\boldsymbol{A}_i$ and $\boldsymbol{B}_k$, which we term $\boldsymbol{S}_i$ etc. Because the triangles $-ABS$ spanned by the vectors $-\boldsymbol{A}_i, \boldsymbol{B}_k, \boldsymbol{S}_n$ are all equivalent, we can use the triangular coefficients Eq. (37) of II to give (8) the following form:

$$\langle Ainlm \mid Bkn'l'm' \rangle = \sum_{LS} \pi(nn', Lll', S) \sum_{Mn} Z(-ABS)^{1/2} \tau \begin{pmatrix} -ABS \\ ikn \end{pmatrix} \begin{pmatrix} L^+ & l^+ & l' \\ M & m & m \end{pmatrix} \langle \boldsymbol{S}_n \mid LM \rangle \quad (10)$$

Inserting this into (5) we can express the invariants by the physical factor π and a geometrical factor G:

$$\langle (A\alpha a, nl\beta\ell)\gamma cp \mid (B\alpha' a', n'l'\beta'\ell')\gamma' cp \rangle = \sum_{LS} \pi(nn', Lll', S) \cdot G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S) \quad (11)$$

with

$$G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma c', L, S) = Z(-ABS)^{1/2} \sum_{imk} \sum_{m'Mn} M(\gamma cp, Ai\alpha a, (\beta\ell)lm)^* \cdot M(\gamma' cp, Bk\alpha' a', (\beta'\ell')l'm')\tau \begin{pmatrix} -ABS \\ ikn \end{pmatrix} \begin{pmatrix} L^+ & l^+ & l \\ M & m & m' \end{pmatrix} \langle \boldsymbol{S}_n \mid LM \rangle \quad (12)$$

(11) is our central equation and the remaining task is to reshape (12) in order to express G by group algebraic invariants. We use (7) and express the $3jm$-symbol in the s.a. basis:

$$\begin{pmatrix} L^+ & l^+ & l' \\ M & m & m' \end{pmatrix} = \sum_{\mu d s} \sum_{\beta\ell r} \sum_{\beta'\ell' r'\varepsilon} \langle LM \mid L\mu d s\rangle \langle lm \mid l\beta\ell r\rangle \langle l'm' \mid l'\beta'\ell' r'\rangle^* \cdot V_\varepsilon \begin{pmatrix} d^+ & \ell^+ & \ell' \\ s & r & r' \end{pmatrix} Is_\varepsilon \begin{pmatrix} L^+ & l^+ & l' \\ \mu d^+ & \beta\ell^+ & \beta'\ell' \end{pmatrix} \quad (13)$$

Inserting this and (7) into (12) yields:

$$G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S) = Z(-ABS)^{1/2} \dim c \sum_{\varepsilon r r' q} \sum_{q' i k n} \sum_{\mu d s} Is_\varepsilon \begin{pmatrix} L^+ & l^+ & l' \\ \mu d^+ & \beta\ell^+ & \beta'\ell' \end{pmatrix} \cdot V_\varepsilon \begin{pmatrix} d^+ & \ell^+ & \ell' \\ s & r & r' \end{pmatrix} V_\gamma^* \begin{pmatrix} a^+ & \ell^+ & c \\ q & r & p \end{pmatrix} V_{\gamma'} \begin{pmatrix} a'^+ & \ell'^+ & c \\ q' & r' & p \end{pmatrix} \cdot (A\alpha a q \mid \boldsymbol{A}_i)(\boldsymbol{B}_k \mid B\alpha' a' q')\langle \boldsymbol{S}_n \mid L\mu d s\rangle \tau \begin{pmatrix} -ABS \\ ikn \end{pmatrix}$$

We sum over p, cancel dim c, and express the three V-coefficients by one V and a Racah coefficient:

$$G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S) = Z(-ABS)^{1/2} \sum_{\varepsilon q q' i k n} \sum_{\mu d s} Is_\varepsilon \begin{pmatrix} L^+ & l^+ & l' \\ \mu d^+ & \beta\ell^+ & \beta'\ell' \end{pmatrix} \Theta_\gamma(a\ell c^+) \cdot W \begin{pmatrix} d^+ & a'^+ & a \\ c & \ell & \ell' \end{pmatrix}_{\varepsilon\gamma'\gamma\eta} V_\eta \begin{pmatrix} d^+ & a'^+ & a \\ s & q' & q \end{pmatrix} \cdot (A\alpha a q \mid \boldsymbol{A}_i)(\boldsymbol{B}_k \mid B\alpha' a' q')\langle \boldsymbol{S}_n \mid L\mu d s\rangle \tau \begin{pmatrix} -ABS \\ ikn \end{pmatrix}$$

Finally we expand $\langle \boldsymbol{S}_n \mid L\mu d s\rangle$ in standard functions, cf. Eq. (12) of II:

$$\langle \boldsymbol{S}_n \mid L\mu d s\rangle = \sum_\delta c(S\delta d, L\mu)(\boldsymbol{S}_n \mid S\delta d s) \quad (14)$$

and now collect the triangular sum of standard functions in a polyhedral isoscalar factor defined in Eq. (42) of II:

$$G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S) = Z(-ABS)^{1/2}$$
$$\cdot \Theta_\gamma(a\ell c^+) \sum_{\mu\delta d} \sum_{\varepsilon\eta} Is_\varepsilon \begin{pmatrix} L^+ & l^+ & l' \\ \mu d^+ & \beta\ell^+ & \beta'\ell' \end{pmatrix} W \begin{pmatrix} d^+ & a'^+ & a \\ c & \ell & \ell' \end{pmatrix}_{\varepsilon\gamma'\gamma\eta} \tag{15}$$
$$\cdot PIs_\eta \begin{pmatrix} -A & S & B \\ \alpha a^+ & \delta d & \alpha' a' \end{pmatrix} c(S\delta d, L\mu)$$

With this equation we have solved our main problem. The invariants of the overlap matrix are expressed by physical factors and the Racah algebraic factors *Is*, *W*, *PIs*, and *c*. Eq. (15) looks rather complicated, because we have taken into account all multiplicities which one can think of. They will seldom occur all together. If the symmetry group is simply reducible (as for instance O_h, T_d, D_{4h}), the indices γ, γ', ε, η are to be skipped. For low coordination number the same is true for α and α' and perhaps δ, for low angular momentum of the orbitals for β and β'. Since $L=2$ is already reached for *p* orbitals, μ will mostly be needed.

4. Special Cases and Sum Rules

In this section we mark the totally symmetric representation $A_{(1g)}$ by o. A simple case of special interest occurs, if one equivalent set *B* contains the central atom only (if there is any). We then have $B=0$, $S=A$, and since $\sigma^0=1$ only, $a'=o$. It further follows $\eta=\alpha'=\gamma'=1$, $\ell'=c$ and $d=a$. Because of

$$W \begin{pmatrix} a^+ & o & a \\ \ell' & \ell & \ell' \end{pmatrix}_{\varepsilon 1 \gamma 1} = (\dim \ell' \cdot \dim a)^{-1/2} \Theta_\gamma(a^+ \ell^+ \ell') \delta(\gamma, \varepsilon)$$

and of Eq. (45) of II the geometrical factor reduces to:

$$G(A\alpha a l\beta\ell, 0o l'\beta'\ell', \gamma\ell', L, A)$$
$$= \sum_\mu Is_\gamma \begin{pmatrix} L^+ & l^+ & l' \\ \mu a^+ & \beta\ell^+ & \beta'\ell' \end{pmatrix} (\dim \ell')^{-1/2} \cdot c(A\alpha a, L\mu) \tag{16}$$

and Eq. (11) becomes:

$$\langle (A\alpha a, nl\beta\ell)\gamma\ell' q \mid (0o, n'l'\beta'\ell')\ell' q \rangle$$
$$= \sum_L \pi(nn', Lll', A) \cdot G(A\alpha a l\beta\ell, 0o l'\beta'\ell', \gamma\ell', L, A) \tag{17}$$

A similar simplification results, if at one atomic set *B* there are *s*-orbitals. It follows: $l'=0$, $\ell'=o$, and further $L=l^+$, $d=\ell^+$, $c=a'$, $\gamma'=\varepsilon=1$, and $\eta=\gamma$. Because of

$$Is \begin{pmatrix} l & l^+ & 0 \\ \mu\ell & \beta\ell^+ & o \end{pmatrix} = [\dim \ell/(2l+1)]^{1/2} \delta(\mu, \beta)$$

the geometrical factor is in this case:

$$G(A\alpha a l\beta\ell, B\alpha' a' 0o, \gamma a, l, S)$$
$$= \left[\frac{Z(-ABS)}{(2l+1)\dim a'}\right]^{1/2} \sum_{\delta d} PIs_\gamma \begin{pmatrix} -A & S & B \\ \alpha a^+ & \delta d & \alpha' a' \end{pmatrix} c(S\delta d, l\beta) \quad (18)$$

For the diagonal elements of (11) exist certain sum rules, which result from sum rules of the geometrical factors. The first one follows from a sum of Racah coefficients,

$$\sum_\gamma \dim c \cdot \Theta_\gamma(a\ell c^+) W \begin{pmatrix} d^+ & a^+ & a \\ c & \ell & \ell \end{pmatrix}_{\varepsilon\gamma\gamma\eta} = (\dim a \cdot \dim \ell)^{1/2} \delta(d, o)\delta(\varepsilon, 1)\delta(\eta, 1) \quad (19)$$

which is a generalization of the rule (2.10) in [7] for the $6j$-symbols. It follows from the orthogonality relation of the Racah coefficients [8], if one puts one representation equal to o. From (19) results:

$$\sum_{\gamma c} \dim c \cdot G(A\alpha a l\beta\ell, A\alpha' a l\beta'\ell, \gamma\gamma c, L, S) =$$
$$(Z(-ABS) \dim a \cdot \dim \ell)^{1/2} \sum_\mu Is \begin{pmatrix} L^+ & l^+ & l \\ \mu o & \beta\ell^+ & \beta'\ell \end{pmatrix} PIs \begin{pmatrix} -A & S & A \\ \alpha a^+ & o & \alpha' a \end{pmatrix} c(So, L\mu) \quad (20)$$

Because of the sum rule

$$\sum_{\beta\ell} (\dim \ell)^{1/2} Is \begin{pmatrix} L^+ & l^+ & l \\ \mu o & \beta\ell^+ & \beta\ell \end{pmatrix} = (2l+1)^{1/2} \delta(L, 0)\delta(\mu, 1)$$

and the analogous one Eq. (48) of II for the polyhedral isoscalars we get subsequently:

$$\sum_{\beta\ell\gamma c} \dim c \cdot G(A\alpha a l\beta\ell, A\alpha' a l\beta\ell, \gamma\gamma c, L, S) =$$
$$\delta(L, 0)[Z(-ASA)Z(S)(2l+1)\dim a/4\pi]^{1/2} PIs \begin{pmatrix} -A & S & A \\ \alpha a^+ & o & \alpha' a \end{pmatrix} \quad (21)$$

and further:

$$\sum_{\alpha a\beta\ell\gamma c} \dim c \cdot G(A\alpha a l\beta\ell, A\alpha a l\beta\ell, \gamma\gamma c, L, S) = \delta(L, 0)\delta(S, 0)Z(A)[(2l+1)/4\pi]^{1/2} \quad (22)$$

The sum rules (20), (21), and (22) yield analogous ones for the invariants (11), the last one being:

$$\sum_{\alpha a\beta\ell\gamma c} \dim c \langle (A\alpha a, nl\beta\ell)\gamma cp \mid (A\alpha a, nl\beta\ell)\gamma cp \rangle = Z(A)\pi(nn, 0ll, 0)[(2l+1)/4\pi]^{1/2} \quad (23)$$

In semiempirical calculations it may be of interest to regard the physical factors π as fitting parameters and to have an inversion of formula (11). This is possible by the following orthogonality relation of the geometrical factors:

$$\sum_{\gamma\gamma' c}\sum_{\beta\ell\beta'\ell'}\sum_{\alpha a\alpha' a'} \dim c \cdot G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S)^* \cdot G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S') = \delta(L, L')\delta(S, S')Z(-ABS)/4\pi \tag{24}$$

Before giving the proof we look for the consequences. We get from (11):

$$\pi(nn', Lll', S) = [4\pi/Z(-ABS)] \cdot \sum_{\gamma\gamma' c}\sum_{\beta\ell\beta'\ell'}\sum_{\alpha a\alpha' a'} \dim c \cdot G(A\alpha a l\beta\ell, B\alpha' a' l'\beta'\ell', \gamma\gamma' c, L, S)^* \langle (A\alpha a, nl\beta\ell)\gamma c p \mid (B\alpha' a', n'l'\beta'\ell')\gamma' c p\rangle \tag{25}$$

Since $\pi(nn', Lll', S)$ represents the typical overlap over a distance S, Eq. (25) brings out the relations enforced upon the invariants, if in a next neighbor approximation some of the π are set equal to zero.

The proof of (24) is as follows. One substitutes (15) into the left side of (24) and then uses successively the orthogonality relations of the Racah coefficients, of the isoscalars [8], and of the polyhedral isoscalars Eq. (49) of II. This yields:

$$(2L+1)^{-1} Z(-ABS) Z(S)^{-1} \delta(L, L)\delta(S, S) \sum_{\mu\delta d} \dim d \,|c(S\delta d, L\mu)|^2 \tag{26}$$

Starting now with the addition theorem of the spherical harmonics [9] we calculate:

$$(2L+1)/4\pi = \sum_m |\langle \boldsymbol{S}_r | Lm\rangle|^2 = \sum_{rm} |\langle \boldsymbol{S}_r | Lm\rangle|^2 / Z(S) = \sum_{r\mu a p} |\langle \boldsymbol{S}_r | L\mu a p\rangle|^2 / Z(S),$$

and further with Eqs. (12) and (10) of II:

$$(2L+1)/4\pi = \sum_{\alpha\mu a} \dim a \cdot |c(S\alpha a, L\mu)|^2 / Z(S) \tag{27}$$

Inserting this into (26) finally yields the right hand side of (24). By the way (27) can serve as a check for the coefficients $c(S\alpha a, L\mu)$ after calculation by Eq. (13) of II.

5. Example

As an example we study the tetrahedron of molecules like P_4 or generally AB_4. Because of the isomorphism between the groups T_d and 0 we can take over the V and W coefficients [10]. Since in the group chain $0_h \supset T_d$ no representation splits up, we also can take over the isoscalars from the chain $0(3) \supset 0_h$:

$$Is \begin{pmatrix} j & k & l \\ a & \ell & c \end{pmatrix}^{0(3)}_{T_d} = Is \begin{pmatrix} j & k & l \\ a' & \ell' & c' \end{pmatrix}^{0(3)}_{0_h} \tag{28}$$

provided that under $0_h \to T_d$: $a' \to a$, $\ell' \to \ell$, $c' \to c$. The isoscalars of 0_h are given in [11].

Thereby the task remains to set up the following lists: The position vectors of the four atoms were already given in I. The edge vectors between the atoms are defined by $\boldsymbol{S}_{ik} = \boldsymbol{R}_i - \boldsymbol{R}_k$. We therefore have:

Table 1. Components of the vectors $\boldsymbol{R}_i$ and $\boldsymbol{S}_{ik}$

	$\boldsymbol{R}_1$	$\boldsymbol{R}_2$	$\boldsymbol{R}_3$	$\boldsymbol{R}_4$	$\boldsymbol{S}_{12}$	$\boldsymbol{S}_{13}$	$\boldsymbol{S}_{14}$	$\boldsymbol{S}_{21}$	$\boldsymbol{S}_{23}$	$\boldsymbol{S}_{24}$	$\boldsymbol{S}_{31}$	$\boldsymbol{S}_{32}$	$\boldsymbol{S}_{34}$	$\boldsymbol{S}_{41}$	$\boldsymbol{S}_{42}$	$\boldsymbol{S}_{43}$
X	1	1	−1	−1	0	2	2	0	2	2	−2	−2	0	−2	−2	0
Y	1	−1	−1	1	2	2	0	−2	0	−2	−2	0	−2	0	2	2
Z	1	−1	1	−1	2	0	2	−2	−2	0	0	2	2	−2	0	−2

The standard functions over $\mathscr{R}$ were likewise given in I. We repeat them for convenience. In order to find out the irreducible representations induced by set $\mathscr{S}$ we have to calculate the characters of σ^S in the manner lined out in I. This yields: $\sigma^S(E)=12$, $\sigma^S(8C_3)=0$, $\sigma^S(3C_2)=0$, $\sigma^S(6S_4)=0$, $\sigma^S(6\sigma_d)=2$. From this follows in the usual way: $\sigma^S=A_1+E+T_1+2T_2$. For the calculations according to Eqs. (7) and (8) of II we need a set of s.a. functions. We choose: $\langle \boldsymbol{r} \mid A_1 0\rangle=1$, $\langle \boldsymbol{r} \mid E1\rangle=3z^2-r^2$, $\langle \boldsymbol{r} \mid E2\rangle=x^2-y^2$, $\langle \boldsymbol{r} \mid T_1 1\rangle=x(y^2-z^2)$, $\langle \boldsymbol{r} \mid T_1 2\rangle=y(z^2-x^2)$, $\langle \boldsymbol{r} \mid T_1 3\rangle=z(x^2-y^2)$, $\langle \boldsymbol{r} \mid \alpha T_2 x\rangle=yz$, $\langle \boldsymbol{r} \mid \alpha T_2 y\rangle=zx$, $\langle \boldsymbol{r} \mid \alpha T_2 z\rangle=xy$, $\langle \boldsymbol{r} \mid \beta T_2 x\rangle=x$, $\langle \boldsymbol{r} \mid \beta T_2 y\rangle=y$, $\langle \boldsymbol{r} \mid \beta T_2 z\rangle=z$. The standard functions are:

Table 2. Standard functions $(\boldsymbol{R}_i \mid R\alpha p)$ over set $\mathscr{R}$

	$\boldsymbol{R}_1$	$\boldsymbol{R}_2$	$\boldsymbol{R}_3$	$\boldsymbol{R}_4$
$(\boldsymbol{R}_i \mid RA_1 0)$	1/2	1/2	1/2	1/2
$(\boldsymbol{R}_i \mid RT_2 x)$	1/2	1/2	−1/2	−1/2
$(\boldsymbol{R}_i \mid RT_2 y)$	1/2	−1/2	−1/2	1/2
$(\boldsymbol{R}_i \mid RT_2 z)$	1/2	−1/2	1/2	−1/2

Table 3. Standard functions $(\boldsymbol{S}_{ik} \mid S\alpha\alpha p)$ over set $\mathscr{S}$
Abbreviations: $s=12^{-1/2}$, $t=24^{-1/2}$, $u=6^{-1/2}$, $v=8^{-1/2}$, $w=2^{-1}$

	$\boldsymbol{S}_{12}$	$\boldsymbol{S}_{13}$	$\boldsymbol{S}_{14}$	$\boldsymbol{S}_{21}$	$\boldsymbol{S}_{23}$	$\boldsymbol{S}_{24}$	$\boldsymbol{S}_{31}$	$\boldsymbol{S}_{32}$	$\boldsymbol{S}_{34}$	$\boldsymbol{S}_{41}$	$\boldsymbol{S}_{42}$	$\boldsymbol{S}_{43}$
$(\boldsymbol{S}_{ik} \mid SA_1 0)$	s	s	s	s	s	s	s	s	s	s	s	s
$(\boldsymbol{S}_{ik} \mid SE1)$	t	$-u$	t	t	t	$-u$	$-u$	t	t	t	$-u$	t
$(\boldsymbol{S}_{ik} \mid SE2)$	$-v$	0	v	$-v$	v	0	0	v	$-v$	v	0	$-v$
$(\boldsymbol{S}_{ik} \mid ST_1 1)$	0	v	$-v$	0	$-v$	v	$-v$	v	0	v	$-v$	0
$(\boldsymbol{S}_{ik} \mid ST_1 2)$	v	$-v$	0	$-v$	0	v	v	0	$-v$	0	$-v$	v
$(\boldsymbol{S}_{ik} \mid ST_1 3)$	$-v$	0	v	v	$-v$	0	0	v	$-v$	$-v$	0	v
$(\boldsymbol{S}_{ik} \mid S\alpha T_2 x)$	w	0	0	w	0	0	0	0	$-w$	0	0	$-w$
$(\boldsymbol{S}_{ik} \mid S\alpha T_2 y)$	0	0	w	0	$-w$	0	0	$-w$	0	w	0	0
$(\boldsymbol{S}_{ik} \mid S\alpha T_2 z)$	0	w	0	0	0	$-w$	w	0	0	0	$-w$	0
$(\boldsymbol{S}_{ik} \mid S\beta T_2 x)$	0	v	v	0	v	v	$-v$	$-v$	0	$-v$	$-v$	0
$(\boldsymbol{S}_{ik} \mid S\beta T_2 y)$	v	v	0	$-v$	0	$-v$	$-v$	0	$-v$	0	v	v
$(\boldsymbol{S}_{ik} \mid S\beta T_2 z)$	v	0	v	$-v$	$-v$	0	0	v	v	$-v$	0	$-v$

Since we have to include the pseudo-triangle $-ROR$, we need the standard function of the zero vector $(\boldsymbol{O} \mid 0A_{10}) = 1$. With the aid of the Tables 2 and 3 we calculate the ten possible polyhedral isoscalars:

$$PIs\begin{pmatrix} -R & 0 & R \\ A_1 & A_1 & A_1 \end{pmatrix} = 1/2, \qquad PIs\begin{pmatrix} -R & 0 & R \\ T_2 & A_1 & T_2 \end{pmatrix} = 3^{+1/2}/2,$$

$$PIs\begin{pmatrix} -R & S & R \\ A_1 & A_1 & A_1 \end{pmatrix} = 1/4 \qquad PIs\begin{pmatrix} -R & S & R \\ T_2 & A_1 & T_2 \end{pmatrix} = -3^{+1/2}/12,$$

$$PIs\begin{pmatrix} -R & SR \\ T_2 & ET_2 \end{pmatrix} = 6^{-1/2}, \qquad PIs\begin{pmatrix} -R & S & R \\ T_2 & T_1 & T_2 \end{pmatrix} = 1/2,$$

$$PIs\begin{pmatrix} -R & S & R \\ T_2 & \alpha T_2 & T_2 \end{pmatrix} = 8^{-1/2}, \qquad PIs\begin{pmatrix} -R & S & R \\ T_2 & \beta T_2 & T_2 \end{pmatrix} = 0,$$

$$PIs\begin{pmatrix} -R & S & R \\ A_1 & \alpha T_2 & T_2 \end{pmatrix} = 1/4, \qquad PIs\begin{pmatrix} -R & S & R \\ T_2 & \alpha T_2 & A_1 \end{pmatrix} = 1/4,$$

$$PIs\begin{pmatrix} -R & S & R \\ T_2 & \beta T_2 & A_1 \end{pmatrix} = 8^{-1/2}, \qquad PIs\begin{pmatrix} -R & S & R \\ A_1 & \beta T_2 & T_2 \end{pmatrix} = -8^{-1/2}$$

Finally we have to calculate the expansion coefficients of spherical harmonics $\langle \boldsymbol{O} \mid L\mu ap \rangle$, $\langle \boldsymbol{R}_i \mid L\mu ap \rangle$, and $\langle \boldsymbol{S}_{ik} \mid L\mu ap \rangle$ according to Eqs. (12) and (13) of II. We use the spherical harmonics $il\, Y_{lm}(\vartheta, \varphi)$ in the convention of [9], Eqs. (2.5.7) and (2.5.8).

Because up to $L=4$ the representations of 0(3) contain those of T_d only once, we can omit the multiplicity index μ in $c(P\alpha a, L\mu)$.

Table 4. Expansion coefficients of spherical harmonics $c(P\alpha a, L)\cdot\sqrt{4\pi}$ for the sets $P=\mathcal{O}$, $\mathcal{R}$, and $\mathcal{S}$

	$P\alpha a=$							
La	$0A_1$	RA_1	RT_2	SA_1	SE	ST_1	$S\alpha T_2$	$S\beta T_2$
$0A_1$	1	2	·	$\sqrt{12}$	·	·	·	·
iT_2	·	·	$2i$	·	·	·	0	$i\sqrt{12}$
$2E$	·	·	·	·	$-\sqrt{30}/2$	·	·	·
$2T_2$	·	·	$-\sqrt{60}/3$	·	·	·	$-\sqrt{15}$	0
$3A_1$	0	$-i\sqrt{140}/3$	·	0	·	·	·	·
$3T_2$	·	·	$i\sqrt{336}/9$	·	·	·	0	$i\sqrt{7}/2$
$3T_1$	·	·	·	·	·	$-i\sqrt{105}/2$	·	·
$4A_1$	0	$-\sqrt{84}/3$	·	$-\sqrt{63}/4$	·	·	·	·
$4E$	·	·	·	·	$\sqrt{2250}/8$	·	·	·
$4T_1$	·	·	·	·	·	0	·	·
$4T_2$	·	·	$\sqrt{80}/3$	·	·	·	$-\sqrt{45}/2$	0

With the aid of these tables we calculate all the geometrical factors $G(Ra\ell\ell, Ra'l'\ell', c, L, P)$ needed for the overlap matrix of the sixteen s- and p-orbitals. The s-orbitals induce A_1 and T_2, the p-orbitals $(A_1+T_2)\times T_2 = A_1+E+T_1+2T_2$.

Because of parity considerations the angular momentum quantum number L in (8) and (11) takes only values which differ from $l+l'$ by an even number.

Table 5. Geometric factors $G(Ral\mathfrak{c}, Ra'l'\mathfrak{c}, c, L, P)\cdot\sqrt{4\pi}$ for s- and p-orbitals at the tetrahedral positions $\boldsymbol{R}_i$

	$(L, P)=$					
$Ral\mathfrak{c}$, $Ra'l'\mathfrak{c}'$, c	(0, 0)	(0, S)	(1, 0)	(1, S)	(2, 0)	(2, S)
RA_10A_1, RA_10A_1, A_1	1	3	·	·	·	·
RT_20A_1, RT_20A_1, T_2	1	-1	·	·	·	·
RT_20A_1, RT_21T_2, A_1	·	·	0	$-i\sqrt{6}$	·	·
RT_20A_1, RT_21T_2, T_2	·	·	0	0	·	·
RT_20A_1, RA_11T_2, T_2	·	·	0	$-i\sqrt{2}$	·	·
RA_11T_2, RA_11T_2, T_2	$1/\sqrt{3}$	$\sqrt{3}$	·	·	0	0
RA_11T_2, RT_21T_2, T_2	0	0	·	·	0	$-\sqrt{3}/2$
RT_21T_2, RT_21T_2, A_1	$1/\sqrt{3}$	$-1/\sqrt{3}$	·	·	0	$-5/\sqrt{6}$
RT_21T_2, RT_21T_2, E	$1/\sqrt{3}$	$-1/\sqrt{3}$	·	·	0	$-1/\sqrt{24}$
RT_21T_2, RT_21T_2, T_1	$1/\sqrt{3}$	$-1/\sqrt{3}$	·	·	0	$5/\sqrt{24}$
RT_21T_2, RT_21T_2, T_2	$1/\sqrt{3}$	$-1/\sqrt{3}$	·	·	0	$-1/\sqrt{24}$

With these geometric factors our program stated by Eq. (11) is fulfilled for the tetrahedron. As an example of (11) and Table 5 we write:

$$\langle(RT_2, n1T_2)T_1p \mid (RT_2, n'1T_2)T_1p\rangle =$$
$$(12\pi)^{-1/2}[\pi(nn, 011, 0)-\pi(nn, 011, S)+5\cdot 8^{-1/2}\pi(nn, 211, S)]$$

This expression is valid for arbitrary types of orbitals. The invariants π for the special case must be taken from the respective integral formula (8) or (9).

Because of (16) and (17) there is no problem to include a central atom. The geometric factors involving the central atom only are:

$$G(0A_10A_1, 0A_10A_1, A_1, 0, 0)=G(0A_11T_2, 0A_11T_2, T_2, 0, 0)=(4\pi)^{-1/2},$$

$$G(0A_11T_2, 0A_11T_2, T_2, 2, 0)=0$$

For the overlap integrals between s.a. orbitals of central atom and ligands one needs the factors:

$$G(0A_10A_1, RA_10A_1, A_1, 0, R)=2/\sqrt{4\pi},$$

$$G(0A_10A_1, RT_21T_2, A_1, 1, R)=2i/\sqrt{4\pi}$$

$$G(0A_11T_2, RT_20A_1, T_2, 1, R)=2i/\sqrt{12\pi}$$

$$G(0A_11T_2, RA_11T_2, T_2, 0, R)=2/\sqrt{12\pi},$$

$$G(0A_11T_2, RA_11T_2, T_2, 2, R)=0$$

$$G(0A_11T_2, RT_21T_2, T_2, 0, R)=0,$$

$$G(0A_11T_2, RT_21T_2, T_2, 2, R)=-2/\sqrt{12\pi}$$

We thus have the overlap integral:

$$\langle (0A_1, n1T_2)T_2 p \mid (RT_2, n'0A_1)T_2 p\rangle = 2i/\sqrt{12\pi}\cdot\pi(nn', 110, R)$$

The extension to d-orbitals is straightforward, since we have extended Table 4 to $L=4$. For an extension to molecules like $C(CH_3)_4$ the sphere of the 12 H atoms has to be handled in the same way as the tetrahedron.

6. Comparison with the Conventional Method

In the book of Ballhausen and Gray [12] the overlap integrals of s.a. orbitals are called group overlaps. We compare the method (GOM) lined out there with ours:

1) The GOM starts at the level of our Eq. (5) and expresses the invariants first by all the integrals $\langle Ainlm \mid Bjn'l'm'\rangle$.
2) Thus GOM needs the numerical values of all the coefficients M, i.e. one has to make an explicit calculation of (2). If there is no general formula for M like (7), one has to make a list for all special cases. Our method does not need anymore the values of M.
3) In each case one then has to investigate by rotational and mirror operations how many and which of the integrals $\langle Ainlm \mid Bjn'l'm'\rangle$ are equal. There is no need to do so in our case. These relations are already taken into account in Eq. (11).
4) The remaining integrals $\langle Ainlm \mid Bjn'l'm'\rangle$ or in the notation of [12] for instance $S(p_{\pi L}, p_{\pi L})$ depend on the orientation of the p-ligand-orbitals with respect to the ligand–ligand direction. There again is no need for such further angular considerations in our case, since the invariants $\pi(nn', Lll', S)$ in (10) and (11) do not depend anymore on angles. The angular, i.e. geometric relations are *all* contained in the factor G.
5) In 0_h symmetry, for instance, it is obvious that for equal radial p-functions: $S(p_{\pi L}, p_{\pi L}, \sqrt{2}R) = S(p_{\sigma L}, p_{\sigma L}, \sqrt{2}R)$, where $\sqrt{2}R$ means the distance of octahedral neighbors. This relation is not induced by symmetry operations of the group 0_h, and may in other cases not be so easily detectable. Our formula (11) includes such relations too. If on the contrary one considers different p-orbitals in our formula, one has to express this by different quantum numbers n and n' in $\pi(nn', Lll', S)$.
6) If one wishes to extend the conventional GOM to higher orbital quantum numbers, one has to go back to (2), whereas in our method the coefficients W and PIs in (15) are the same once and for ever. If there is a sufficient tabulation of the isoscalars, the only additional calculation needed concerns some coefficients $c(S\delta d, L\mu)$ for higher quantum numbers. The ingredients of formula (15) are useful in other molecular calculations too.

7. Prospect

We want to consider some general points of the preceding analysis. First of all the two-center matrix elements of rotationally invariant operators, especially the

kinetic energy operator can be treated in exactly the same manner. Only the invariants π have to be exchanged. For the kinetic energy we refer to [6], where the new invariants are differentially related to π. This raises the question of the potential energy matrix. The matrix elements in this case involve the three-center nuclear attraction integrals, the tensor algebraic form of which is also discussed in [6]. It is justified to announce the preceding analysis as relevant also for this case. In order to give these considerations first a solid, computational foundation, a paper on the invariants of multi-center integrals of a current orbital type is in preparation.

A non-quantum mechanical application in the vibrational analysis of polyhedral skeletons will be published as Paper III of this series.

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