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Symmetry Adaption Reduced to Tabulated Quantities

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The aim of this paper is to give an algebraic formula for symmetry-adapted linear combinations avoiding intuitive or laborious projection operator techniques. By utilization of the tabulated Clebsch-Gordan coefficients and surface harmonics of the point-groups the symmetry-adapted linear combinations are given in formula (4). A five-step algorithm is proposed and the example of a tetrahedron worked out. The relation to methods using site symmetry is discussed.

Key words: Symmetry-adaption formula – LCAO, symmetry adapted – Symmetry coordinates

1. Introduction

For a lengthy period various methods for setting up symmetry-adapted linear combinations of atomic orbitals or atomic displacement vectors have been used. For all such cases Cotton [1] has introduced the general abbreviation SALC. In clearly arranged systems these SALC's may be guessed, or formed, with the aid of some plausible considerations like analogy with the surface harmonics at the molecular centre and the determination of some less obvious linear combinations by orthogonality relations. A systematic approach is possible by the projection operator technique [1, 2]. The drawback of this method is that it requires the knowledge of the complete representation matrices and a summation over the entire symmetry group. Therefore simplifications have been sought by consideration of site symmetries and division of the atomic orbitals in σ- and π-bonding ones. This however requires local, i.e. atom-dependent, coordinate systems and the interrelations between them. Finally group factorization methods were proposed by Melvin [3] and Flurry [4]. We think a satisfactory solution of the problem of SALC's should be a straightforward prescription using tabulated properties of the point groups only. Such a formula is proposed in the following.

2. Induced Representations and SALC's

We first list our notations: $\boldsymbol{r}$ and $\boldsymbol{R}_i$ shall be the position vectors of an electron and of a set of equivalent atoms in a molecule having the symmetry group G. For the functions we use the Dirac notation, because this will save indices: $\varphi_m^{\alpha}(\boldsymbol{r}-\boldsymbol{R}_i) =$

$\langle r | |i\varphi a m\rangle$ are the atomic orbitals classified according to representation a of group G, component m. This classification of functions at position R_i is to be understood in the same sense as the expression "p-orbital at R_i", the relevant group merely being reduced from the full rotation group to G. The function $\varphi_m^a(r)$ at the molecular centre is classified according to a and m and then translated to position R_i. φ may be thought of as an index distinguishing STO or GTO and main quantum numbers etc. Finally $\langle am, bn | cp\rangle$ are the Clebsch-Gordan coefficients and $Y_n^{La}(R) \models \langle R | Lan\rangle$ the symmetry adapted spherical harmonics of group G (related to angular momentum L), termed surface harmonics by Breadley and Cracknell [5], both tabulated, for instance, by Koster *et al.* [6]. The component indices refer to one fixed coordinate system for the entire molecule.

We next have to determine which irreducible representations c will be induced by the atomic orbitals $|i\varphi b m\rangle$. This is done by the character formula

$$n(c) = (1/\mathrm{ord}G) \sum_C \lambda(C)\chi^*(c, C)\chi(b, C)\sigma(C), \tag{1}$$

where the summation index runs over all classes C of group G. $\lambda(C)$ is the number of group elements in class C, $\chi(a, C)$ the character in representation a and $\sigma(C)$ the number of atoms not moved by a symmetry operation of class C. This $\sigma(C)$ is a class function because it is the trace of the matrix $\sigma_{ik}(g)$ defined by the change of atomic positions by the symmetry operation g:

$$gR_i = \sum_k \sigma_{ki}(g) \cdot R_k. \tag{2}$$

This implies $\sigma_{ki}(g) = 1$, if $gR_i = R_k$, and $\sigma_{ki}(g) = 0$ otherwise. Formula (1) is a generalization of the special case of displacement vectors given in Ref. [2], page 155.

Because the representations a induced by the atomic s-orbitals (or, termed otherwise, by the change-of-position matrices $\sigma_{ki}(g)$) will play a certain role in our key theorem, we now specialize (1) to the case of s-orbitals:

$$n(a) = (1/\mathrm{ord}G) \sum_C \lambda(C)\chi^*(a, C)\sigma(C). \tag{3}$$

Here we postpone the less-frequent case $n(a) \geqslant 2$ to a special appendix concerning multiplicities.

We now state the following key theorem:

> The entire set of SALC's induced by the atomic orbitals $|i\varphi b n\rangle$ is given by
>
> $$|(a, b)cp\rangle = N^{-1} \sum_{imn} \langle am, bn | cp\rangle \langle R_i | Lam\rangle \cdot |i\varphi b n\rangle. \tag{4}$$

The SALC's are labelled by the representation c, component p according to which they transform, by representation a (inferred by the change of position) taken from the set determined by formula (3), and of course by b. Since the correct normalization of $|(a, b)cp\rangle$ would depend on the overlap integrals $\langle i\varphi b m | k\varphi b q\rangle$, it will be convenient to have a standard normalization under the assumption of non-overlapping orbitals [7, 8]:

$\langle i\varphi\mathscr{b}m\,|\,k\varphi\mathscr{b}q\rangle = \delta_{ik}\delta_{mq}$. The standard normalization factor is then given by the number M of equivalent atoms:

$$N = \left(\sum_{i} |\langle R_i\,|\,L\mathscr{a}n\rangle|^2 \right)^{1/2}. \tag{5}$$

Because of the appearance of the Clebsch-Gordan coefficients in (4) we have the following relation between the representations $\mathscr{a}$, $\mathscr{b}$, and $\mathscr{c}$: If one representation $\mathscr{a}$ determined by Eq. (3) is selected, the induced representations $\mathscr{c}$ are given by the character formula:

$$m(\mathscr{c},\mathscr{a}) = (1/\mathrm{ord}G) \sum_{C} \lambda(C)\chi^*(\mathscr{c}, C) \cdot \chi(\mathscr{a}, C) \cdot \chi(\mathscr{b}, C). \tag{6}$$

From the consistency of (1) and (6) it follows that:

$$n(\mathscr{c}) = \sum_{a} m(\mathscr{c},\mathscr{a}) \cdot n(\mathscr{a}). \tag{7}$$

For the present, in (4) and (6) the group G is assumed to be simply reducible. For the multiplicity $m(\mathscr{c},\mathscr{a}) \geqslant 2$ we again refer to the pertinent appendix.

3. Proofs

We are now going to prove the propositions of the preceding section. To this end we first have to evaluate the transformation property of the atomic orbital functions $|\,i\varphi\mathscr{b}m\rangle$. In doing so we denote the representation matrices by $D^{\mathscr{a}}_{ik}(g)$ and the operations in the function space by $U(g)$. These operators take effect on the variable r *only* and *not* on the parameters R_i or the function symbol itself: $U(g)f(r) = f(g^{-1}r)$ and $U(g)f(r - R_i) = f(g^{-1}r - R_i)$. Because of the representation property

$$\varphi^{\mathscr{b}}_m(g^{-1}r) = \sum_{n} D^{\mathscr{b}}_{nm}(g)\varphi^{\mathscr{b}}_n(r)$$

we have:

$$U(g)\varphi^{\mathscr{b}}_m(r - R_i) = \varphi^{\mathscr{b}}_m(g^{-1}r - R_i) = \varphi^{\mathscr{b}}_m(g^{-1}(r - gR_i)) = \sum_{k} D^{\mathscr{b}}_{km}(g)\varphi^{\mathscr{b}}_k(r - gR_i)$$

and using Eq. (2) in Dirac notation again:

$$U(g)\,|\,i\varphi\mathscr{b}m\rangle = \sum_{lk} D^{\mathscr{b}}_{km}(g) \cdot \sigma_{li}(g) \cdot |\,l\varphi\mathscr{b}k\rangle. \tag{8}$$

Thus the representation matrix of g is given by the direct product $D^{\mathscr{b}}_{kn}(g) \cdot \sigma_{li}(g)$ and consequently its character is $\chi(\mathscr{b}, C) \cdot \sigma(C)$. The well-known character formula for the reduction of representations [9] then leads to (1). The special equation (3) follows from $\chi(\mathscr{b}, C) = 1$ for $\mathscr{b} = A_{(1g)}$.

To prove our key theorem we need a relation of the Clebsch-Gordan coefficients, which we take from Hamermesh ([10], page 150):

$$\sum_{m} D^{\mathscr{c}}_{mn}(g)\langle\mathscr{a}k, \mathscr{b}l\,|\,\mathscr{c}m\rangle = \sum_{pq} D^{\mathscr{a}}_{kp}(g) \cdot D^{\mathscr{b}}_{lq}(g) \cdot \langle\mathscr{a}p, \mathscr{b}q\,|\,\mathscr{c}n\rangle. \tag{9}$$

We now demonstrate that the functions $|(a, b)cp\rangle$ given in (4) transform according to representation c. Using Eq. (8) we get:

$$U(g)|(a, b)cp\rangle = N^{-1} \sum_{imnkl} \langle am, bn|cp\rangle\langle R_i|Lam\rangle D^{b}_{kn}(g)\sigma_{li}(g) \cdot |l\varphi bk\rangle.$$

Since $\sigma_{li}(g) = \sigma_{il}(g^{-1})$, we have

$$\sum_i \langle R_i|Lam\rangle\,\sigma_{li}(g) = \langle g^{-1}R_l|Lam\rangle = \sum_q D^{a}_{qm}(g)\langle R_l|Laq\rangle$$

and therefore:

$$U(g)|(a, b)cp\rangle = N^{-1} \sum_{mnklq} \langle am, bn|cp\rangle D^{a}_{qm}(g)D^{b}_{kn}(g)\langle R_l|Laq\rangle|\,l\varphi bk\rangle.$$

Now applying (9) we get the desired result:

$$U(g)|(a, b)cp\rangle = \sum_s D^{c}_{sp}(g)|(a, b)cs\rangle.$$

Next we have to show that the standard normalization is correct. With the non-overlap assumption we have:

$$\langle(a, b)cp|(a, b)cp\rangle = N^{-2} \sum_{imnq} \langle am, bn|cp\rangle^*\langle R_i|Lam\rangle^*\langle aq, bn|cp\rangle\langle R_i|Laq\rangle.$$

The sum over the surface harmonics is evaluated by the following method: Because the sum over R_i is the same as over $g^{-1}R_i$ (with $g \in G$), we get:

$$\sum_i \langle R_i|Lam\rangle^*\langle R_i|Laq\rangle = \sum_i \langle g^{-1}R_i|Lam\rangle^*\langle g^{-1}R_i|Laq\rangle$$

$$= \sum_{inp} D^{a*}_{pm}(g) \cdot D^{a}_{nq}(g)\langle R_i|Lap\rangle^*\langle R_i|Lan\rangle.$$

Summing over all elements $g \in G$ and using the orthogonality relations of representation matrices ([10], page 103), we obtain:

$$\sum_i \langle R_i|Lam\rangle^*\langle R_i|Laq\rangle = \delta_{mq}(\dim a)^{-1} \sum_{in} |\langle R_i|Lan\rangle|^2 = \delta_{mq} \sum_i |\langle R_i|Lan\rangle|^2.$$

Now using the orthogonality relations of the Clebsch-Gordan coefficients we obtain:

$$\langle(a, b)cp|(a, b)cp\rangle = N^{-2} \sum_i |\langle R_i|Lan\rangle|^2 = 1$$

therefore Eq. (5) is true.

Since relation (6) is simply the well-known character formula for the reduction of a direct product representation, we have to prove Eq. (7) only. We invert relation (3):

$$\sigma(C) = \sum_a = \chi(a, C) \cdot n(a)$$

and insert this into (1):

$$n(c) = (1/\mathrm{ord}G) \sum_{Ca} \lambda(C)\chi^*(c, C) \cdot \chi(b, C) \cdot \chi(a, C) \cdot n(a).$$

Now using (6) we obtain Eq. (7). The validity of (7) also assures that exhausting the full sets $\mathscr{a}$ and $\mathscr{c}$ according to (3) and (6) will make the SALC system complete. Expressed differently: the transformation given by Eq. (4) is unitary.

4. Application Procedure

To obtain the SALC's from a set of atomic orbitals $|i\varphi\mathscr{b}m\rangle$ one may now carry out the following procedure:

1) Determine in each class of group elements the number $\sigma(C)$ of the atoms not moved by these transformations.
2) Determine the representation $\mathscr{a}$ by formula (3), or in simple cases by inspection utilizing the relation $\sigma(C) = \sum\limits_{\mathscr{a}} \chi(\mathscr{a}, C)$.
3) In the character tables of Refs. [6] and [11] surface harmonics belonging to $\mathscr{a}$ are specified. Of course one will use the lowest possible value of L. A detailed listing is also given in Ref. [5]. One may now tabulate the values $\langle R_i | L\mathscr{a}m\rangle/N$.
4) Choose one $\mathscr{a}$ and determine a representation $\mathscr{c}$ in principle by relation (6), but more conveniently with the help of the tabulations of $\mathscr{a} \times \mathscr{b} = \sum\limits_{\mathscr{c}} n(\mathscr{c}) \cdot \mathscr{c}$.
5) Using the results of step 3) and the tabulation of the Clebsch-Gordan coefficients, we write down the linear combination coefficients:

$$K(\mathscr{c}p, \mathscr{a}, i\mathscr{b}n) = \sum_{m} \langle \mathscr{a}m, \mathscr{b}n | \mathscr{c}p\rangle \langle R_i | L\mathscr{a}m\rangle/N. \tag{10}$$

The SALC's are then

$$|(\mathscr{a}, \mathscr{b})\mathscr{c}p\rangle = \sum_{in} K(\mathscr{c}p, \mathscr{a}, i\mathscr{b}n) \cdot |i\varphi\mathscr{b}n\rangle. \tag{11}$$

For more extensive calculations it may be serviceable to carry out steps 4) and 5) for all representations $\mathscr{b}$ of group G, and to make a full tabulation of all coefficients. When the *s*-, *p*-, *d*- etc. orbitals are then decomposed according to the several representations $\mathscr{b}$, the pertinent coefficients may be picked from these tables.

5. Some Useful Relations

Before going into details we remark that the linear combination coefficients containing the representation $A_{(1g)}$ can, in general, be evaluated

1) $\mathscr{a} = A_{(1g)}$: $\quad K(\mathscr{c}p, A, i\mathscr{b}n) = \delta_{\mathscr{b}\mathscr{c}}\, \delta_{np} \cdot M^{-1/2}$ (12)
2) $\mathscr{b} = A_{(1g)}$: $\quad K(\mathscr{c}p, \mathscr{a}, iAo) = \delta_{\mathscr{a}\mathscr{c}} \langle R_i | L\mathscr{a}p\rangle (4\pi/M)^{1/2}$ (13)
3) $\mathscr{c} = A_{(1g)}$: $\quad K(Ao, \mathscr{a}, i\mathscr{b}n) = \delta_{\mathscr{a}\mathscr{b}^*} \langle R_i | L\mathscr{b}n\rangle^* (4\pi \cdot \dim\mathscr{b}/M)^{1/2}$. (14)

As a precaution we have distinguished the complex conjugate representation $\mathscr{b}^*$ from $\mathscr{b}$, but in most cases $\mathscr{b}^* \sim \mathscr{b}$.

Further abridgement can be achieved by the following multiplication relation. Δ may be any one-dimensional representation and $\mathscr{b}' = \Delta \times \mathscr{b}$; then the relation $\mathscr{a} \times \mathscr{b} = \sum\limits_{\mathscr{c}} n(\mathscr{c}) \cdot \mathscr{c}$

turns over into $\boldsymbol{a} \times \boldsymbol{b}' = \sum_{c'} n(\boldsymbol{c}') \cdot \boldsymbol{c}'$. This implies: When the orbitals of species $\boldsymbol{b}$ induce representation $\boldsymbol{c}$, then the species $\boldsymbol{b}'$ induces $\boldsymbol{c}'$. (In Appendix B of [12], where similar considerations are carried out for the octahedral group, the representations $\boldsymbol{a}'$ are called associated with $\boldsymbol{a}$. In general there will be more than one one-dimensional representation and therefore several different associated representations.) The corresponding relation of the components is slightly more complicated:

$$|\boldsymbol{a}'n\rangle = \sum_{p} \langle \boldsymbol{a}p, \Delta o \,|\boldsymbol{a}'n\rangle \cdot |\boldsymbol{a}p\rangle \cdot |\,\Delta o\rangle .$$

But in nearly all cases all the coefficients $\langle \boldsymbol{a}p, \Delta o\,|\boldsymbol{a}'n\rangle$ are zero except one, for which $|\langle \boldsymbol{a}p, \Delta o\,|\boldsymbol{a}'n\rangle| = 1$.

When we now introduce the unimodular number W (actually a special Racah coefficient of the point group) by

$$W = (1/\dim c) \sum_{sqmpr} \langle \boldsymbol{b}'s\,|\boldsymbol{b}q, \Delta o\rangle \langle \boldsymbol{a}m, \boldsymbol{b}q\,|\boldsymbol{c}p\rangle \langle \boldsymbol{c}p, \Delta o\,|\boldsymbol{c}'r\rangle \langle \boldsymbol{c}'r|\boldsymbol{a}m, \boldsymbol{b}'s\rangle \tag{15}$$

we obtain the relation

$$\langle \boldsymbol{a}m, \boldsymbol{b}'s\,|\boldsymbol{c}'r\rangle = (1/W) \sum_{pq} \langle \boldsymbol{b}'s\,|\boldsymbol{b}q, \Delta o\rangle \langle \boldsymbol{a}m, \boldsymbol{b}q\,|\boldsymbol{c}p\rangle \langle \boldsymbol{c}p, \Delta o\,|\boldsymbol{c}'r\rangle$$

and consequently from (10):

$$K(\boldsymbol{c}'r, \boldsymbol{a}, i\boldsymbol{b}'s) = (1/W) \sum_{pq} \langle \boldsymbol{b}'s\,|\boldsymbol{b}q, \Delta o\rangle K(\boldsymbol{c}p, \boldsymbol{a}, i\boldsymbol{b}q) \langle \boldsymbol{c}p, \Delta o\,|\boldsymbol{c}'r\rangle . \tag{16}$$

This nearly always reduces to a simple proportionality. In the case $\boldsymbol{b}' = \Delta \times \boldsymbol{b} = \boldsymbol{b}$ the components may be reordered and attached with a (complex) sign, for instance in the case $A_2 \times E = E$ of the cubic groups.

When the $\langle \boldsymbol{b}p, \Delta o\,|\boldsymbol{b}'r\rangle$ are not tabulated, one may use

$$\langle \boldsymbol{b}p, \Delta o\,|\boldsymbol{b}'r\rangle = \langle \Delta o, \boldsymbol{b}'^{*}r\,|\boldsymbol{b}^{*}p\rangle . \tag{17}$$

This relation is explicable by the symmetry of the V-coefficients introduced by Griffith [12] analogous to the $3j$-symbols of the rotation group.

6. Example

As an example we study the tetrahedron, which appears in molecules, clusters or complexes of type A_4 or BA_4. In the case of the s- and p-orbitals, and the displacement vectors, respectively, we shall reproduce known results [13]. When considering the tetrahedral clusters Cu_4 [14], Fe_4 [15], or even the molecule P_4, one must also take account of the d-orbitals. Therefore we will work out a full tabulation for orbitals of all symmetry species $\boldsymbol{b}$.

We use the following notation of the components. For E: $1(\sim 3z^2 - r^2)$ and $2(\sim x^2 - y^2)$; for T_1: 1, 2, 3 or, equivalently, yz, zx, xy; and for T_2: 1, 2, 3 equivalent to x, y, z.

Steps 1) and 2)

The symmetry group T_d contains the classes E, $8C_3$, $3C_2$, $6S_4$ and $6\sigma_d$. Because the axes of C_2 and S_4 do not pass through atoms, we have $\sigma(C_2) = \sigma(S_4) = 0$. The axes C_3 and the mirror planes σ_d pass through one and two atoms respectively. Together with the characters of A_1 and T_2 we obtain Table 1. We therefore conclude the induced representations $\mathfrak{a}$ to be A_1 and T_2.

Table 1. Characters $\sigma(C)$, $\chi(A_1, C)$, $\chi(T_2, C)$ of group T_d

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\sigma(C)$	4	1	0	0	2
$\chi(A_1, C)$	1	1	1	1	1
$\chi(T_2, C)$	3	0	-1	-1	1

Step 3)

We first give the positions of atoms: $R_1 = (1, 1, 1)$, $R_2 = (1, -1, -1)$, $R_3 = (-1, -1, 1)$, $R_4 = (-1, 1, -1)$. The relevant surface harmonics are: $\langle R | 0A_1o\rangle = (4\pi)^{-1/2}$ and $\langle R | 1T_2n\rangle = (3/4\pi r)^{1/2} x_n$ with $R = (x_1, x_2, x_3)$.

Table 2. Values of the surface harmonics at the points R_i

	R_1	R_2	R_3	R_4
$\langle R_i | 0A_1o\rangle/N$	1/2	1/2	1/2	1/2
$\langle R_i | 1T_2x\rangle/N$	1/2	1/2	$-1/2$	$-1/2$
$\langle R_i | 1T_2y\rangle/N$	1/2	$-1/2$	$-1/2$	1/2
$\langle R_i | 1T_2z\rangle/N$	1/2	$-1/2$	1/2	$-1/2$

Step 4)

Since we want to consider all representations $\mathfrak{b}$, we set up a table of $\mathfrak{a} \times \mathfrak{b}$:

Table 3. Evaluation of the direct products $\mathfrak{a} \times \mathfrak{b}$

	$\mathfrak{b} = A_1$	A_2	E	T_1	T_2
$\mathfrak{a} = A_1$	A_1	A_2	E	T_1	T_2
$\mathfrak{a} = T_2$	T_2	T_1	$T_1 + T_2$	$A_2 + E + T_1 + T_2$	$A_1 + E + T_1 + T_2$

Step 5)

Because of Eq. (12) the case $\mathfrak{a} = A_1$ is already settled. So we will only tabulate the coefficients with $\mathfrak{a} = T_2$. The one-dimensional representation A_2 enables us to reduce the number of coefficients which must be independently computed. With Eqs. (13) to (17) we obtain the following ($W = 1$ always except for $K(Er, T_2, iT_1s)$: $W = -1$):

$$
\begin{aligned}
K(T_1r, T_2, iA_2o) &= K(T_2r, T_2, iA_1o) &&= \langle R_i | 1T_2r\rangle/N \\
K(A_2o, T_2, iT_1s) &= K(A_1o, T_2, iT_2s) &&= \langle R_i | 1T_2s\rangle/(3^{1/2}N) \\
K(T_1r, T_2, iE2) &= K(T_2r, T_2, iE1) \\
K(T_1r, T_2, iE1) &= -K(T_2r, T_2, iE2) \\
K(E1, T_2, iT_1s) &= K(E2, T_2, iT_2s) \\
K(E2, T_2, iT_1s) &= -K(E1, T_2, iT_2s) \\
K(T_2r, T_2, iT_1s) &= K(T_1r, T_2, iT_2s) \\
K(T_1r, T_2, iT_1s) &= K(T_2r, T_2, iT_2s)
\end{aligned}
$$

To utilize these relations the following table is to be read a) from the head and the left for one coefficient and b) from the bottom and right for the related one.

Table 4. a) The SALC coefficients $K(T_2r, T_2, iA_1o)$, head-line and left; b) the SALC coefficients $K(T_1r, T_2, iA_2o)$, bottom and right

Position $R_i =$		R_1	R_2	R_3	R_4		
Orbital $\ell =$		A_1	A_1	A_1	A_1		
$T_2r =$	T_2x	1/2	1/2	−1/2	−1/2	T_1yz	$= T_1r$
	T_2y	1/2	−1/2	−1/2	1/2	T_1zx	
	T_2z	1/2	−1/2	1/2	−1/2	T_1xy	
		A_2	A_2	A_2	A_2	$= \ell$ Orbital	
		R_1	R_2	R_3	R_4	$= R_i$ Position	

Table 5. a) The SALC coefficients $K(T_2r, T_2, iEs)$, headline and left; b) the SALC coefficients $K(T_1r, T_2, iEs)$, bottom right. Abbreviations: $t = 1/4$, $u = 3^{1/2}/4$, $v = 1/2$

Position $R_i =$		R_1		R_2		R_3		R_4			
Orbital $\ell s =$		$E1$[a]	$E2$	$E1$	$E2$	$E1$	$E2$	$E1$	$E2$		
$T_2r =$	T_2x	$-t$	u	$-t$	u	t	$-u$	t	$-u$	T_1yz	$= T_1r$
	T_2y	$-t$	$-u$	t	u	t	u	$-t$	$-u$	T_1zx	
	T_2x	v	0	$-v$	0	v	0	$-v$	0	T_1xy	
		$E2$	$-E1$	$E2$	$-E1$	$E2$	$-E1$	$E2$	$-E1$	$= \ell s$ Orbital	
		R_1		R_2		R_3		R_4		$= R_i$ Position	

Table 6. a) The SALC coefficients $K(cr, T_2, iT_2s)$, headline and left; b) the SALC coefficients $K(cr, T_2, iT_1s)$, bottom and right. Abbreviations: $t = 12^{-1/2}$, $u = 24^{-1/2}$, $v = 6^{-1/2}$, $w = 8^{-1/2}$

	Position R_i =	R_1			R_2			R_3			R_4				
	Orbital ℓ =	T_2			T_2			T_2			T_2				
	Orbital s =	x	y	z	x	y	z	x	y	z	x	y	z		
cr =	A_1	t	t	t	t	$-t$	$-t$	$-t$	$-t$	t	$-t$	t	$-t$	A_2	= cr
	E_1	$-u$	$-u$	v	$-u$	u	$-v$	u	u	v	u	$-u$	$-v$	$-E_2$	
	E_2	w	$-w$	0	w	w	0	$-w$	w	0	$-w$	$-w$	0	E_1	
	T_1yz	0	$-w$	w	0	w	$-w$	0	$-w$	$-w$	0	w	w	T_2x	
	T_1zx	w	0	$-w$	$-w$	0	$-w$	w	0	w	$-w$	0	w	T_2y	
	T_1xy	$-w$	w	0	w	w	0	w	$-w$	0	$-w$	$-w$	0	T_2z	
	T_2x	0	w	w	0	$-w$	$-w$	0	w	$-w$	0	$-w$	w	T_1yz	
	T_2y	w	0	w	$-w$	0	w	w	0	$-w$	$-w$	0	$-w$	T_1zx	
	T_2z	w	w	0	$-w$	w	0	$-w$	$-w$	0	w	$-w$	0	T_1xy	
		yz	zx	xy	yz	zx	xy	yz	zx	xy	yz	zx	xy	= s Orbital	
		T_1			T_2			T_1			T_1			= ℓ Orbital	
		R_1			R_2			R_3			R_4			= R_i Position	

The SALC's for special cases can now be quoted. We give some examples. The SALC's of species E induced by p-orbitals ($= T_2$) according to Table 6a are:

$$\begin{aligned}|(T_2, T_2)E1\rangle = 24^{-1/2} \cdot [&-p_x(R_1) - p_y(R_1) + 2p_z(R_1) - p_x(R_2) + p_y(R_2)\\ &- 2p_z(R_2) + p_x(R_3) + p_y(R_3) + 2p_z(R_3) + p_x(R_4) - p_y(R_4)\\ &- 2p_z(R_4)]\\ |(T_2, T_2)E2\rangle = 8^{-1/2} \cdot [&p_x(R_1) - p_y(R_1) + p_x(R_2) + p_y(R_2) - p_x(R_3) + p_y(R_3)\\ &- p_x(R_4) - p_y(R_4)]\,.\end{aligned}$$

The d-orbitals yz, zx, xy belong to $T_1, d_1 \sim 3z^2 - r^2, d_2 \sim x^2 - y^2$ to E. We give the species T_1 induced by the d-E-orbitals according to Table 5b:

$$\begin{aligned}|(T_2, E)T_1yz\rangle &= 4^{-1} \cdot [-d_2(R_1) - 3^{1/2}d_1(R_1) - d_2(R_2) - 3^{1/2}d_1(R_2)\\ &\quad + d_2(R_3) + 3^{1/2}d_1(R_3) + d_2(R_4) + 3^{1/2}d_1(R_4)]\\ |(T_2, E)T_1zx\rangle &= 4^{-1} \cdot [-d_2(R_1) + 3^{1/2}d_1(R_1) + d_2(R_2) - 3^{1/2}d_1(R_2)\\ &\quad + d_2(R_3) - 3^{1/2}d_1(R_3) - d_2(R_4) + 3^{1/2}d_1(R_4)]\\ |(T_2, E)T_1xy\rangle &= 2^{-1} \cdot [d_1(R_1) - d_1(R_2) + d_1(R_3) - d_1(R_4)]\,.\end{aligned}$$

7. Relation to the Site Symmetry Method

We have specified the atomic orbitals according to the representations of the symmetry group G of the entire molecule. Other methods already mentioned classify the orbitals according to the representations of the site symmetry groups G_i at position R_i. These are subgroups of g defined by $G_i = \{h \mid hR_i = R_i, h \in G\}$ and are isomorphic to each other by the mapping $g_{ik}G_kg_{ik}^{-1} = G_i$, where g_{ik} is defined by $g_{ik}R_k = R_i$. So they have the same representations $\hat{\mathscr{a}}$, but the orientation of axes is individual for each atom. The orbitals classified according to $\hat{\mathscr{a}}$ at position R_i may be denoted as $\hat{\varphi}_m^{\hat{\mathscr{a}}}(r - R_i) = |\,i\hat{\varphi}\hat{\mathscr{a}}m\rangle$. The SALC's induced by these orbitals are the following linear combinations:

$$|(\hat{\mathscr{a}})\mathscr{c}s\rangle = \sum_{im} K'(\mathscr{c}s, i\hat{\mathscr{a}}m) \cdot |\,i\hat{\varphi}\hat{\mathscr{a}}m\rangle. \tag{18}$$

When the $|\,i\hat{\varphi}\hat{\mathscr{a}}m\rangle$ are atomic orbitals, they are related to the $|\,i\varphi\mathscr{b}r\rangle$ ones by subduction via the (position dependent !) subduction coefficients $\langle\mathscr{b}p\,|\,\mathscr{b}i\hat{\mathscr{a}}n\rangle$, cf. Ref. [16]. The quoted relation is:

$$|\,i\hat{\varphi}\hat{\mathscr{a}}m\rangle = \sum_{p} \langle\mathscr{b}p\,|\,\mathscr{b}i\hat{\mathscr{a}}m\rangle \cdot |\,i\varphi\mathscr{b}p\rangle. \tag{19}$$

If we now insert (19) into Eq. (18), we get

$$|(\hat{\mathscr{a}}, \mathscr{b})\mathscr{c}s\rangle = \sum_{imp} K'(\mathscr{c}s, i\hat{\mathscr{a}}m)\langle\mathscr{b}p\,|\,\mathscr{b}i\hat{\mathscr{a}}m\rangle|\,i\varphi\mathscr{b}p\rangle \tag{20}$$

in concurrence with Eq. (4). Since the $|(\mathscr{a},\mathscr{b})\mathscr{c}s\rangle$ form a complete set and $\langle(\mathscr{a},\mathscr{b})\mathscr{c}s\,|\,(\hat{\mathscr{a}},\mathscr{b})\mathscr{c}s\rangle = A(\hat{\mathscr{a}},\mathscr{a})$ is independent of s, we have in general the relation:

$$|(\hat{\mathscr{a}},\mathscr{b})\mathscr{c}s\rangle = \sum_{\mathscr{a}} A(\hat{\mathscr{a}},\mathscr{a}) \cdot |(\mathscr{a},\mathscr{b})\mathscr{c}s\rangle. \tag{21}$$

This is similar to the recoupling relations of angular momentum and relates the $b \rightarrow a \rightarrow c$ induced basis set to the $b \rightarrow \hat{a} \rightarrow c$ one. Because of $n(c) = 1$ in Eq. (1) with only a few exceptions (21) reduces in most cases to

$$n(c) = 1: \qquad |(\hat{a}, b)cs\rangle = |(a, b)cs\rangle. \tag{22}$$

For the tetrahedron or octahedron, for instance, the only exceptions from (22) occur under the condition that b and c equal T_1 or T_2, in which case sometimes $n(c) = 2$.

The advantage of the orbitals $|i\varphi\hat{a}m\rangle$is the suggestive separation of σ-bonds ($\hat{a} = A_1$) and π-bonds ($\hat{a} = E$ in cases of site symmetry containing a C_3- or C_4-axis). This has its main importance for aggregates of type AX_n, especially when X is an aggregate itself like CN^-. On the contrary, in aggregates of type X_n, like Fe_4, Nb_6, P_4, S_8 etc., this separation is not significant. But even in the case AX_n this separation is not necessarily introduced from the beginning, because according to (22) the $|(a, b)cs\rangle$-SALC'S do not mix σ- and π-orbitals either. For atoms in less symmetric positions, like the H-atoms in $Ni(NH_3)_4^{2+}$, a multiplicity $n(c) \geqslant 2$ occurs of course more frequently, but there will seldom be direct bond to a central atom with such a high coordination number.

When it is in fact necessary to set up the coefficients $K'(cs, i\hat{a}m)$ one can proceed in the following way: for each representation $\hat{a}$ of G_i one takes a parent representation b of G, which does not split under subduction, i.e. $b \rightarrow \hat{a}$. In the example of the tetrahedron, A_1, A_2, E of group T_d go over into A_1, A_2, E of C_{3v}. Then the subduction coefficients merely give a reorientation of the coordinate systems adequate to position R_i, which obviously must be known. Now Eq. (22) yields:

$$K'(cs, i\hat{a}m) = \sum_p \langle b i \hat{a} m | b p\rangle K(cs, a, ibp). \tag{23}$$

Appendix 1: Multiplicities

In the main part we have supposed no multiplicity in two passages. First, concerning (3) and (4), we deferred the case of one representation a occurring more than once, indicated by $n(a) \geqslant 2$. This will be realized when the equivalent atoms are in positions of relatively low site symmetry, the highest possible value being $n(a) = \dim a$, since on condition of lowest site symmetry there are as many equivalent atoms as group elements and the s-orbitals induce the regular representation. To realize the consequences one should consult Eq. (13). Because there must exist two different realizations of a, distinguished by an additional index α as $a\alpha$, we must make use of surface harmonics of different angular momentum L_α : $\langle R | L_\alpha a p\rangle$. The SALC's constructed in this way will not be orthogonal in general for different α. But this is natural, because any orthogonalization like the normalization must depend on the overlap integrals. It is, of course, possible to introduce a standard orthogonalization analogous to (5).

Another well-known multiplicity arises when the group G is not simply reducible [17] and c occurs more than once in the product $a \times b$, i.e. $m(c, a) \geqslant 2$ in Eq. (6). The

Clebsch-Gordan coefficients must then also be labelled by an additional index [16, 18]: $\langle \mathscr{a}m, \mathscr{b}n | \mathscr{c}\gamma p\rangle$. Thus, in general, Eq. (4) must be replaced by:

$$|(\mathscr{a}\alpha, b)\mathscr{c}\gamma p\rangle = N^{-1} \sum_{in} \langle \mathscr{a}m, \mathscr{b}n | \mathscr{c}\gamma p\rangle\langle R_i | L_\alpha \mathscr{a}n\rangle | i\varphi\mathscr{b}n\rangle, \tag{24}$$

where α takes the values from 1 to $n(\mathscr{a})$ and γ from 1 to $m(\mathscr{c}, \mathscr{a})$.

Appendix 2: Hybrid Orbitals

Since the hybrid orbitals located at the molecular centre, suitable to describe σ-bonds with ligand atoms, obviously have the same structure as the s-ligand orbitals, we conclude that the transformation from central surface harmonics to hybrid functions is the inverse one of the transformation from ligand s-orbitals to SALC's. We specify Eq. (4) to the A_1 case:

$$|(\mathscr{a}, A_1)\mathscr{a}p\rangle = N^{-1} \sum_i \langle R_i | L\mathscr{a}p\rangle | i\varphi A_1 o\rangle.$$

We can now give the general formula for σ-hybrid orbitals in coordinations of symmetry group G:

$$|\sigma\text{-hyb}, i\rangle = \sum_{\mathscr{a}m} N^{-1}\langle R_i | Lam\rangle^* | Lam\rangle, \tag{25}$$

the sum running over those $\mathscr{a}$ given by formula (3). To prove Eq. (25) we have to demonstrate that the functions $|\sigma\text{-hyb}, i\rangle$ transform in the same way as the s-orbitals $|i\varphi A_1 o\rangle$:

$$\begin{aligned} U(g)|\sigma\text{-hyb}, i\rangle &= \sum_{anp} N^{-1}\langle R_i | Lam\rangle^* D^{a}_{pm}(g) | Lap\rangle \\ &= \sum_{ap} N^{-1}\langle gR_i | Lap\rangle^* | Lap\rangle \\ &= \sum_{apk} N^{-1} \sigma_{ki}(g)\langle R_k | Lap\rangle^* | Lap\rangle = \sum_k \sigma_{ki}(g) | \sigma\text{-hyb}, k\rangle. \end{aligned}$$

This coincides with transformation (8) for the $\mathscr{b} = A_1$ case.

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