Formulating SALCs with Projection Operators

- ✔ The mathematical form of a SALC for a particular symmetry species cannot always be deduced by inspection (e.g., e_{1g} and e_{2u} pi-MOs of benzene).

- ✔ A *projection operator* is a function that acts on one wave function of the basis set of functions that comprise the SALCs (e.g., one of the six p_z orbitals on the carbon atoms in the ring of benzene) to "project out" the SALC function.

- ✔ A projection operator for each symmetry species must be applied to the reference function to generate all the symmetry-allowed SALCs.

- ✔ The projection operator for a given symmetry species contains terms for each and every operation of the group (not just each class of operations).

Full-Matrix vs. Character Form of the Projection Operator

✔ The full form of the projection operator function for degenerate species, which often directly generates the set of all SALCs belonging to a degenerate symmetry species, requires use of the full operator matrix for each and every operation of the irreducible representation; i.e., the full-matrix form of the irreducible representation.

✔ Because there are no generally available tabulations of the full-matrix forms of the irreducible representations for groups with degenerate species, a simpler form of the projection operator that uses only the characters for each operation is most often used.

☹ The character form of the projection operator for degenerate species generates only one of the degenerate SALCs, requiring other means to deduce the companion functions.

☞ We will only use the character form of the projection operator function.

The Projection Operator in Characters

- ✔ The projection operator in character form, P_i, acting on a reference function of the basis set, φ_t, generates the SALC, S_i, for the ith allowed symmetry species as

$$S_i \propto P_i \varphi_t = \frac{d_i}{h} \sum_R \chi_i^R R_j \varphi_t$$

in which
d_i = dimension of the ith irreducible representation,
h = order of the group,
χ_i^R = each operation's character in the ith irreducible representation,
R_j = the operator for the jth operation of the group.

- ✔ The term $R_j\varphi_t$ gives one of the several basis functions of the set of functions forming the SALCs, in a positive or negative sense.

- ✔ The summation is taken over *all operations* of the group, not all classes of operations.

- ✔ The results $P_i\varphi_t$ are not the final SALCs; they need "cleaning up".

Requirements for a Wave Function

1. The function must be normalized.

$$N^2 \int \Psi\Psi^* d\tau = 1,$$

where N is the normalization constant.

☞ We can routinely ignore the factor d_i / h in the projection operator expression.

2. All wave functions must be orthogonal.

$$\int \Psi_i \Psi_j d\tau = 0 \text{ if } i \neq j$$

Mathematical Simplification
When Taking Products of LCAOs

✔ The $P_i\varphi_t$ products have the general form

$$(a_i\varphi_i \pm a_{i+1}\varphi_{i+1} \;\ldots\; \pm a_n\varphi_n)(b_j\varphi_j \pm b_{j+1}\varphi_{j+1} \;\ldots\; \pm b_m\varphi_m)$$

✔ But in general

$$\int \varphi_i\varphi_j d\tau = \delta_{ij}$$

Thus, all $\varphi_i\varphi_j$ $(i \neq j)$ terms vanish, and all $\varphi_i\varphi_i$ or $\varphi_j\varphi_j$ terms $(i = j)$ are unity.

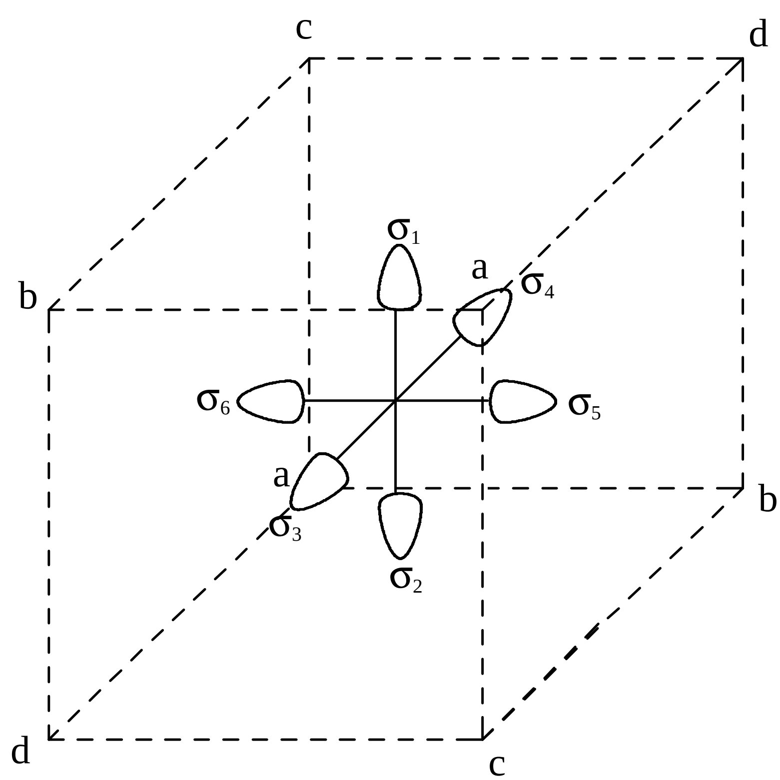
☞ Ignore the cross terms when normalizing or testing for orthogonality!

The σ-SALCs of MX_6 (O_h)

Example: Generate the SALCs for sigma-bonding of six ligands to a central atom in an octahedral MX_6 complex.

✔ From the transformation of six octahedrally arranged vectors pointing toward a central atom, the reducible representation for the six SALCs can be generated and reduced as follows:

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$



Minimizing the Work

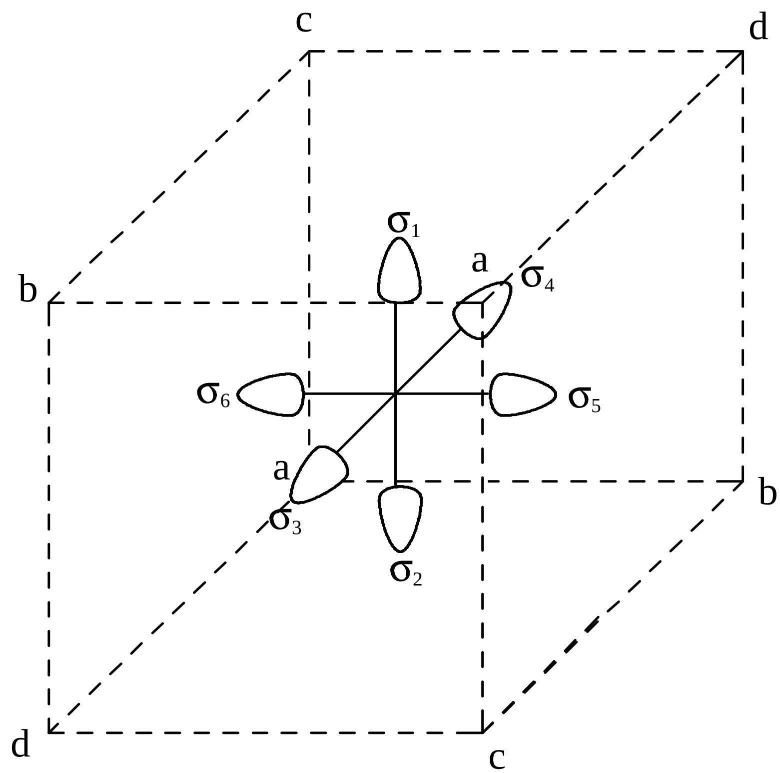
- ✔ O_h has 48 operations, so each projection operator will have 48 terms.

- ✔ The rotational subgroup O has half as many operations (h = 24) but still preserves the essential symmetry.

- ☞ Carry out the work in O and correlate the results to O_h.

- ✔ In O, $\Gamma_\sigma = A_1 + E + T_1$, which has obvious correlations to $\Gamma_\sigma = A_{1g} + E_g + T_{1u}$ in O_h.

Labeling the Symmetry Elements

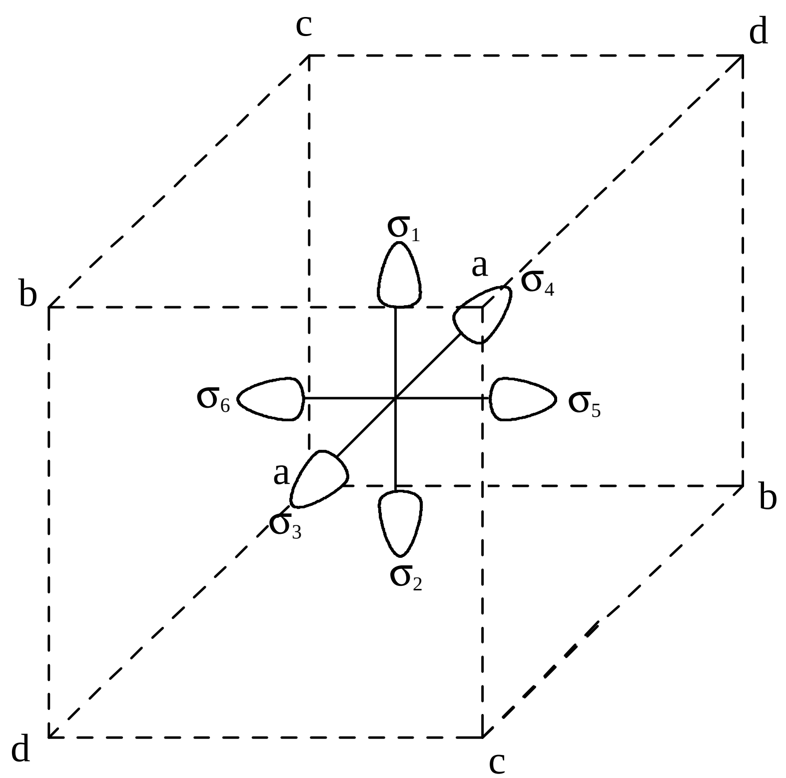


- ✔ $8C_3$ in O refers to $4C_3$ and $4C_3^2$ whose axes run along the cube diagonals.
  - ☞ Label these by the corners through which they pass: e.g., *aa*, *bb*, *cc*, *dd*.
- ✔ $3C_2$, $3C_4$, and $3C_4^3$ have axes that run through *trans*-related pairs of ligands.
  - ☞ Label these by the pairs of ligands through which they pass; e.g., *12*, *34*, *56*.
- ✔ $6C_2'$ have axes that pass through the mid-points of opposite cube edges.
  - ☞ Label these by the two-letter designation of the cube edges through which they pass; e.g., *ac*, *bd*, *ab*, *cd*, *ad*, *bc*.
- ✔ C_3 rotations are clockwise, viewed from the upper cube corner through which the axis passes.
- ✔ C_4 rotations are clockwise, viewed from the lower-numbered ligand.

The Effect of the Operations of O on a Reference Function σ_1

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_1$	σ_1	σ_5	σ_3	σ_6	σ_4	σ_3	σ_6	σ_4	σ_5	σ_1	σ_2	σ_2

C_4	C_4	C_4	C_4^3	C_4^3	C_4^3	C_2'	C_2'	C_2'	C_2'	C_2'	C_2'
12	*34*	*56*	*12*	*34*	*56*	*ac*	*bd*	*ab*	*cd*	*ad*	*bc*
σ_1	σ_5	σ_4	σ_1	σ_6	σ_3	σ_2	σ_2	σ_3	σ_4	σ_5	σ_6



Projection Operator for the A_1 Species in O (A_{1g} in O_h)

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_1$	σ_1	σ_5	σ_3	σ_6	σ_4	σ_3	σ_6	σ_4	σ_5	σ_1	σ_2	σ_2
A_1	1	1	1	1	1	1	1	1	1	1	1	1
$\chi_i^R R_j\sigma_1$	σ_1	σ_5	σ_3	σ_6	σ_4	σ_3	σ_6	σ_4	σ_5	σ_1	σ_2	σ_2

C_4	C_4	C_4	C_4^3	C_4^3	C_4^3	C_2'	C_2'	C_2'	C_2'	C_2'	C_2'
12	*34*	*56*	*12*	*34*	*56*	*ac*	*bd*	*ab*	*cd*	*ad*	*bc*
σ_1	σ_5	σ_4	σ_1	σ_6	σ_3	σ_2	σ_2	σ_3	σ_4	σ_5	σ_6
1	1	1	1	1	1	1	1	1	1	1	1
σ_1	σ_5	σ_4	σ_1	σ_6	σ_3	σ_2	σ_2	σ_3	σ_4	σ_5	σ_6

Summing all the $\chi_i^R R_j\sigma_1$ terms gives

$$P(A_1)\sigma_1 \propto 4\sigma_1 + 4\sigma_2 + 4\sigma_3 + 4\sigma_4 + 4\sigma_5 + 4\sigma_6$$

$$\propto \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$$

SALC for A_{1g}

Normalizing:

$$N^2\int(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)^2 d\tau$$

$$= N^2\int(\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2 + \sigma_6^2) d\tau$$

$$= N^2(1 + 1 + 1 + 1 + 1 + 1) = 6N^2 \equiv 1$$

$$\Rightarrow N = 1/\sqrt{6}$$

Therefore, the normalized A_{1g} SALC is

$$\Sigma_1(A_{1g}) = 1/\sqrt{6}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

Projection Operator for the First of Two E SALCs (E_u in O_h)

✔ In O, $\chi_R = 0$ for $6C_4$ and $6C_2'$. Therefore, ignore the last 12 terms.

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_1$	σ_1	σ_5	σ_3	σ_6	σ_4	σ_3	σ_6	σ_4	σ_5	σ_1	σ_2	σ_2
E	2	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2
$\chi_i^R R_j\sigma_1$	$2\sigma_1$	$-\sigma_5$	$-\sigma_3$	$-\sigma_6$	$-\sigma_4$	$-\sigma_3$	$-\sigma_6$	$-\sigma_4$	$-\sigma_5$	$2\sigma_1$	$2\sigma_2$	$2\sigma_2$

Summing across all $\chi_i^R R_j\sigma_1$ gives

$$P(E)\sigma_1 \propto 4\sigma_1 + 4\sigma_2 - 2\sigma_3 - 2\sigma_4 - 2\sigma_5 - 2\sigma_6$$
$$\propto 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

Normalizing:

$$N^2\int(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)^2 d\tau$$

$$= N^2\int(4\sigma_1^2 + 4\sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2 + \sigma_6^2)d\tau$$

$$= N^2(4 + 4 + 1 + 1 + 1 + 1) = 12N^2 \equiv 1$$

$$\Rightarrow N = 1/\sqrt{12} = 1/(2\sqrt{3})$$

After normalization:

$$\Sigma_2(E) = 1/(2\sqrt{3})(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$$

Test of Orthogonality with $\Sigma_1(A_1)$

$$\int[\Sigma_1(A)][\Sigma_2(E)]d\tau =$$

$$\int(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)d\tau$$

$$= 2 + 2 - 1 - 1 - 1 - 1 = 0$$

☞ But $\Sigma_2(E)$ is only the first of two degenerate functions.

☹ How do we find the partner?

Finding the Partner to $\Sigma_2(E)$ - Method I

Method I: Apply the *E* Projection operator to another reference function, here σ_3.

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_3$	σ_3	σ_1	σ_6	σ_2	σ_6	σ_5	σ_1	σ_5	σ_2	σ_4	σ_3	σ_4
E	2	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2
$\chi_i^R R_j\sigma_3$	$2\sigma_3$	$-\sigma_1$	$-\sigma_6$	$-\sigma_2$	$-\sigma_6$	$-\sigma_5$	$-\sigma_1$	$-\sigma_5$	$-\sigma_2$	$2\sigma_4$	$2\sigma_3$	$2\sigma_4$

This gives

$$P(E)\sigma_3 \propto -2\sigma_1 - 2\sigma_2 + 4\sigma_3 + 4\sigma_4 - 2\sigma_5 - 2\sigma_6$$
$$\propto -\sigma_1 - \sigma_2 + 2\sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6$$

Orthogonal to $\Sigma_1(A)$?

$$\int(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)(-\sigma_1 - \sigma_2 + 2\sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)d\tau$$
$$= -1 - 1 + 2 + 2 - 1 - 1 = 0$$

$\Rightarrow$Yes

Orthogonal to $\Sigma_2(E)$?

$$\int(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)(-\sigma_1 - \sigma_2 + 2\sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)d\tau$$
$$= -2 - 2 - 2 - 2 + 1 + 1 = -6 \neq 0$$

$\Rightarrow$No!

☹ What went wrong?

Notes on Method I for Finding a Degenerate Partner

☞ Changing the reference function after finding the first member of a degenerate set implicitly changes the axis orientation. The resulting function will be one of the following:

- A legitimate partner wave function in either its positive or negative form. [Not this time!]

- The negative of the first member of the degenerate set. [Not a useful result, and not what happened this time.]

- A linear combination of the first member with its partner(s). If this is the case, try various combinations of the two projected functions to find a function that is orthogonal. [Looks like this must be what we got!]

Finding the Partner to $\Sigma_2(E)$ - Method I

By trial and error with various combinations we find that this works:

$$
\begin{array}{rl}
P(E)\sigma_1 = & 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \\
2P(E)\sigma_3 = & -2\sigma_1 - 2\sigma_2 + 4\sigma_3 + 4\sigma_4 - 2\sigma_5 - 2\sigma_6 \\
\hline
 & 3\sigma_3 + 3\sigma_4 - 3\sigma_5 - 3\sigma_6
\end{array}
$$

$$\propto \sigma_3 + \sigma_4 - \sigma_5 - \sigma_6$$

This result is orthogonal to $\Sigma_2(E)$,

$$\int(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)d\tau$$

$$= 0 + 0 - 1 - 1 + 1 + 1 = 0$$

and also to $\Sigma_1(A_1)$,

$$\int(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)d\tau$$

$$= 0 + 0 + 1 + 1 - 1 - 1 = 0$$

The normalized partner wave function, then, is

$$\Sigma_3(E) = \tfrac{1}{2}(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)$$

Finding the Partner to $\Sigma_2(E)$ - Method II

Method II: Apply an operation of the group to the first function found.

Principle: The effect of any group operation on a wave function of a degenerate set is to transform the function into the positive or negative of itself, a partner, or a linear combination of itself and its partner or partners.

☞ Suppose we perform $C_3(aa)$ on our first degenerate function.

✔ Effect of $C_3(aa)$ on the functions of the basis set:

Before	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
After	σ_5	σ_6	σ_1	σ_2	σ_3	σ_4

✔ Effect of $C_3(aa)$ on $\Sigma_2(E)$:

$$(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6) \rightarrow (2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)$$

$$= (-\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 + 2\sigma_6)$$

Is this new function orthogonal to $\Sigma_2(E)$?

$$\int (2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)(-\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 + 2\sigma_6)d\tau$$
$$= -2 - 2 - 1 - 1 - 2 - 2 = -10 \neq 0$$

$\Rightarrow$No!

Finding the Partner to $\Sigma_2(E)$ - Method II

The new function must be a combination of $\Sigma_2(E)$ and the partner function.

By trial-and-error:

$$-\Sigma_2: \quad -2\sigma_1 - 2\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$$

$$-2\{\Sigma_2 \times R[C_3(aa)]\} \quad +2\sigma_1 + 2\sigma_2 + 2\sigma_3 + 2\sigma_4 - 4\sigma_5 - 4\sigma_6$$

$$+3\sigma_3 + 3\sigma_4 - 3\sigma_5 - 3\sigma_6$$

$$\propto \sigma_3 + \sigma_4 - \sigma_5 - \sigma_6$$

This is the same result as found by Method I:

$$\Sigma_3(E) = \tfrac{1}{2}(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)$$

Projection Operator for the First of Three T_{1u} SALCs

Note: In T_1 of the group O, for $8C_3$ $\chi = 0$; therefore, skip the first eight terms in the operator expression.

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_1$	σ_1	σ_5	σ_3	σ_6	σ_4	σ_3	σ_6	σ_4	σ_5	σ_1	σ_2	σ_2
T_1	3	0	0	0	0	0	0	0	0	-1	-1	-1
$\chi_i^R R_j\sigma_1$	$3\sigma_1$									$-\sigma_1$	$-\sigma_2$	$-\sigma_2$

O	C_4	C_4	C_4	C_4^3	C_4^3	C_4^3	C_2'	C_2'	C_2'	C_2'	C_2'	C_2'
label	*12*	*34*	*56*	*12*	*34*	*56*	*ac*	*bd*	*ab*	*cd*	*ad*	*bc*
$R_j\sigma_1$	σ_1	σ_5	σ_4	σ_1	σ_6	σ_3	σ_2	σ_2	σ_3	σ_4	σ_5	σ_6
T_1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$\chi_i^R R_j\sigma_1$	σ_1	σ_5	σ_4	σ_1	σ_6	σ_3	$-\sigma_2$	$-\sigma_2$	$-\sigma_3$	$-\sigma_4$	$-\sigma_5$	$-\sigma_6$

Summing across the $\chi_i^R R_j\sigma_1$:

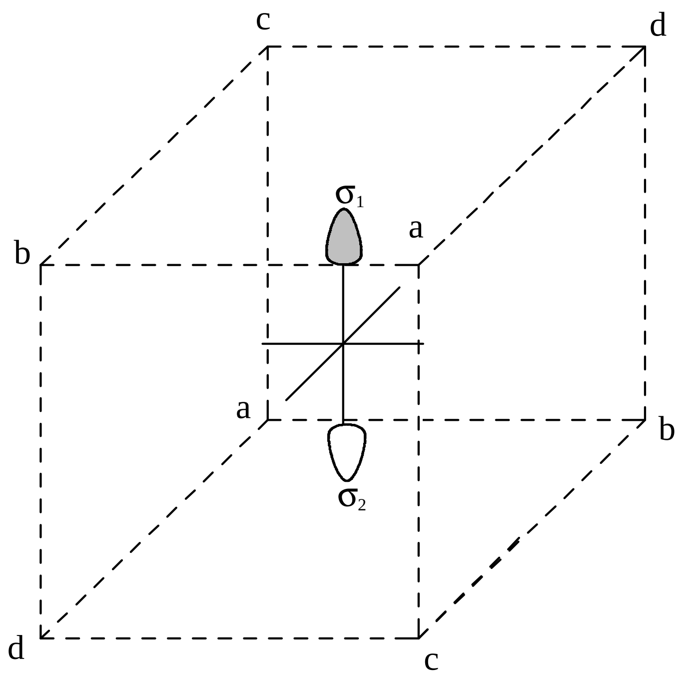
$$P(T_1)\sigma_1 \propto 4\sigma_1 - 4\sigma_2 \propto \sigma_1 - \sigma_2$$

We can readily show that this is orthogonal to the previous three functions for A and E, and on normalization we obtain the SALC

$$\Sigma_4(T_1) = 1/\sqrt{2}\,(\sigma_1 - \sigma_2)$$

Finding the Partner T_{1u} SALCs

The partner functions become apparent from considering the form of $\Sigma_4(T_1)$.



☞ The other two functions must have the same form along the other two orthogonal axes:

$$\Sigma_5(T_1) = 1/\sqrt{2}\ (\sigma_3 - \sigma_4)$$

$$\Sigma_6(T_1) = 1/\sqrt{2}\ (\sigma_5 - \sigma_6)$$

✔ Alternately, note the effects of $C_3(aa)$ and $C_3^2(aa)$ on $(\sigma_1 - \sigma_2)$:

$$R[C_3(aa)] \times (\sigma_1 - \sigma_2) = (\sigma_5 - \sigma_6) \Rightarrow \Sigma_6(T_1)$$

$$R[C_3^2(aa)] \times (\sigma_1 - \sigma_2) = (\sigma_3 - \sigma_4) \Rightarrow \Sigma_5(T_1)$$

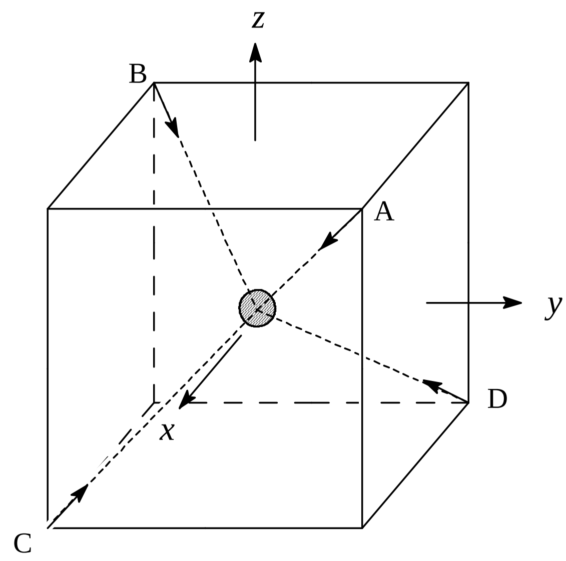
Summary: The Six σ-SALCs of MX_6 (O_h)

$\Sigma_1(A_{1g}) = 1/\sqrt{6}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$

$\Sigma_2(E_u) = 1/(2\sqrt{3})(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$
$\Sigma_3(E_u) = ½(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)$

$\Sigma_4(T_{1g}) = 1/\sqrt{2}\ (\sigma_1 - \sigma_2)$
$\Sigma_5(T_{1g}) = 1/\sqrt{2}\ (\sigma_3 - \sigma_4)$
$\Sigma_6(T_{1g}) = 1/\sqrt{2}\ (\sigma_5 - \sigma_6)$

The σ-SALCs of CH_4 (T_d)



$$\Gamma = A_1 + T_2$$

- ✔ The A_1 SALC is obvious, so only use the projection operator for the T_2 SALCs.

- ✔ The group T_d has h = 24, but its rotational subgroup T has h = 12. Therefore, do the work in T, where the T species corresponds to T_2 of T_d.

- ✔ For the irreducible representation T, the only non-zero characters are E, $C_2(x)$, $C_2(y)$, $C_2(z)$, so the T operator has only four non-vanishing terms:

T	E	...	$C_2(x)$	$C_2(y)$	$C_2(z)$
$R_j s_A$	s_A	...	s_C	s_D	s_B
T	3	...	–1	–1	–1
$\chi_i^R R_j s_A$	$3s_A$	...	$-s_C$	$-s_D$	$-s_B$

The σ-SALCs of CH_4 (T_d)

$$P(T)s_A \propto 3s_A - s_C - s_D - s_B$$

✔ This function is orthogonal to the *A* SALC, $\Phi_1 = \frac{1}{2}(s_A + s_B + s_C + s_D)$, and could be normalized to give the function

$$\Phi(T) = 1/(2\sqrt{3})(3s_A - s_C - s_D - s_B)$$

☹ This SALC is supposed to match with one of the 2*p* AOs on carbon. $\Phi(T)$ makes no sense geometrically for such overlap!

☺ $P(T)s_A$ must be a combination of all three functions:

$$P(T^z)s_A \propto s_A + s_B - s_C - s_D$$

$$P(T^y)s_A \propto s_A - s_B - s_C + s_D$$

$$P(T^x)s_A \propto s_A - s_B + s_C - s_D$$

$$P(T)s_A \propto 3s_A - s_B - s_C - s_d$$

✔ After normalization, the three T_2 SALCs of MX_4 (T_d) are:

$$\Phi_2 = \frac{1}{2}\{s_{\mathrm{A}} + s_{\mathrm{B}} - s_{\mathrm{C}} - s_{\mathrm{D}}\}$$

$$\Phi_3 = \frac{1}{2}\{s_{\mathrm{A}} - s_{\mathrm{B}} - s_{\mathrm{C}} + s_{\mathrm{D}}\}$$

$$\Phi_4 = \frac{1}{2}\{s_{\mathrm{A}} - s_{\mathrm{B}} + s_{\mathrm{C}} - s_{\mathrm{D}}\}$$