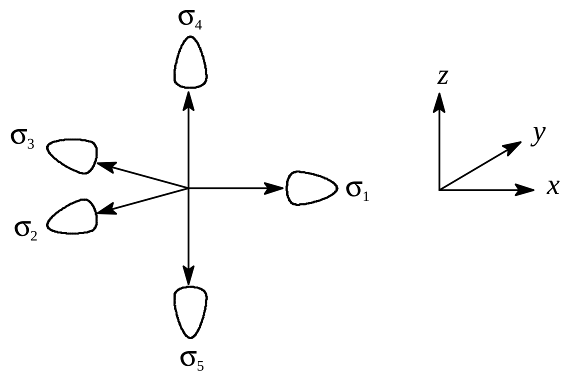
Nonequivalent Positions - Sigma SALCs for *tbp*



$$\Gamma_\sigma = 2A_1' + A_2'' + E'$$

- Not all position functions are accessible by applying the operations of D_{3h} to any single function.

- Equatorial functions (σ_1, σ_2, σ_3) are distinct from axial functions (σ_4, σ_5).

☞ Therefore, a projection operator applied to any reference function can only project a SALC that is a combination of the functions in its own set.

☞ We must break up the problem into two parts.

$$\Gamma_{eq} = A_1' + E' \quad \text{and} \quad \Gamma_{ax} = A_1' + A_2''$$

Nonequivalent Positions - Sigma SALCs for *tbp*
Equatorial SALCs

☞ Do the projections in C_3 to lift the E' degeneracy and give two separate projections.

✔ By inspection:

$$\Phi_{eq}(A_1') = 1/\sqrt{3}(\sigma_1 + \sigma_2 + \sigma_3)$$

✔ From the characters of the two E representations:

$$P(E^a)\sigma_1 \propto \sigma_1 + \epsilon\sigma_2 + \epsilon^*\sigma_3$$
$$P(E^b)\sigma_1 \propto \sigma_1 + \epsilon^*\sigma_2 + \epsilon\sigma_3$$

✔ Add and subtract to form real functions, using

$$\epsilon + \epsilon^* = 2\cos 2\pi/3 = 2(-\tfrac{1}{2}) = -1$$
$$\epsilon - \epsilon^* = 2i \sin 2\pi/3$$
$$\epsilon^* - \epsilon = -2i \sin 2\pi/3$$

$$\{P(E^a)\sigma_1 + P(E^b)\sigma_1\} \propto 2\sigma_1 - \sigma_2 - \sigma_3$$

$$\Rightarrow \Phi_{eq}(E'^a) = 1/\sqrt{6}(2\sigma_1 - \sigma_2 - \sigma_3)$$

$$\{P(E^a)\sigma_1 - P(E^b)\sigma_1\} \propto \sigma_2 - \sigma_3$$

$$\Rightarrow \Phi_{eq}(E'^b) = 1/\sqrt{2}(\sigma_2 - \sigma_3)$$

Axial SALCs

✔ By inspection

$$\Phi_{ax}(A_1') = 1/\sqrt{2}(\sigma_4 + \sigma_5)$$
$$\Phi_{ax}(A_2'') = 1/\sqrt{2}(\sigma_4 - \sigma_5)$$

Nonequivalent Positions - Sigma SALCs for *tbp*
Limiting Case Model

✔ Available AOs on the central atom:

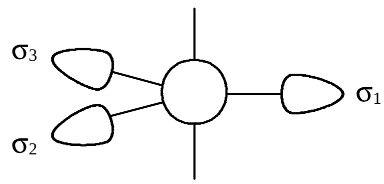
$s = A_1'$ $(p_x, p_y) = E'$ $p_z = A_2''$ $d_{z^2} = A_1'$

✔ By matching AOs with the forms of the SALCs:

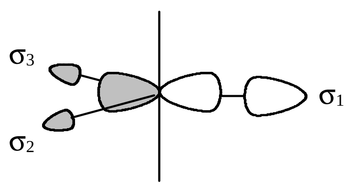
- The equatorial SALCs only interact with $s = A_1'$ and $(p_x, p_y) = E'$
- The axial SALCs only interact with p_z - A_2'' and d_{z^2} - A_1'

☹ This segregation into two separate kinds of interactions is a result of considering the equatorial and axial positions separately.

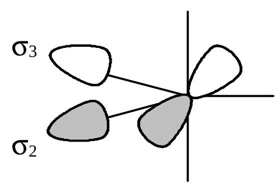
Nonequivalent Positions - Sigma SALCs for *tbp*
Limiting Case Model - LCAOs



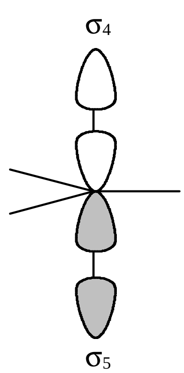
$s + \Phi_1 \ (A_1')$



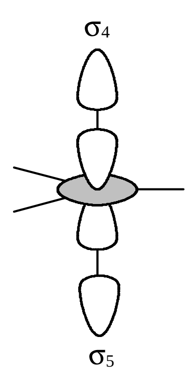
$p_x + \Phi_2 \ (E')$



$p_y + \Phi_3 \ (E')$



$p_z + \Phi_4 \ (A_2'')$



$d_{z^2} + \Phi_5 \ (A_1')$

Nonequivalent Positions - Hybrid Orbitals for *tbp*
Limiting Case Model dsp^3 Hybrids

✔ We can use the forms of our pendant-atom SALC equations to write down equations for the s, p_x, p_y, p_z, and d_{z^2} orbitals as functions of the five dsp^3 hybrids.

$$s = 1/\sqrt{3}\,(\Psi_1 + \Psi_2 + \Psi_3)$$
$$p_x = 1/\sqrt{6}\,(2\Psi_1 - \Psi_2 - \Psi_3)$$
$$p_y = 1/\sqrt{2}\,(\Psi_2 - \Psi_3)$$
$$p_z = 1/\sqrt{2}\,(\Psi_4 - \Psi_5)$$
$$d_{z^2} = 1/\sqrt{2}\,(\Psi_4 + \Psi_5)$$

✔ In matrix form:

$$\begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} & 0 & 0 \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{bmatrix}$$

Nonequivalent Positions - Hybrid Orbitals for *tbp*
Limiting Case Model *dsp*^{3} Hybrids

✔ Use the transposed matrix to write the equation for the hybrids as functions of the AOs:

$$\begin{bmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\\ \Psi_5\end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 & 0 & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} & 0 & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 0 & 0 & -1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \end{bmatrix}$$

From this we get the following individual equations:

$$\Psi_1 = 1/\sqrt{3}s + 2/\sqrt{6}p_x$$
$$\Psi_2 = 1/\sqrt{3}s - 1/\sqrt{6}p_x + 1/\sqrt{2}p_y$$
$$\Psi_3 = 1/\sqrt{3}s - 1/\sqrt{6}p_x - 1/\sqrt{2}p_y$$
$$\Psi_4 = 1/\sqrt{2}(d_{z^2} + p_z)$$
$$\Psi_5 = 1/\sqrt{2}(d_{z^2} - p_z)$$

Nonequivalent Positions - Sigma SALCs for *tbp*
Improving the Model - A Pictorial Approach

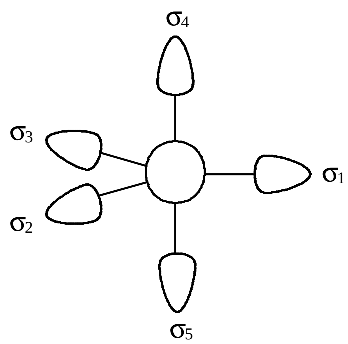
- ✔ Ideally, each equation in the set of σ-SALCs for a *tbp* molecule should have the form

  $$\Phi_i = N(c_{i1}\sigma_1 \pm c_{i2}\sigma_2 \pm c_{i3}\sigma_3 \pm c_{i4}\sigma_4 \pm c_{i5}\sigma_5) \qquad i = 1, 2, 3, 4, 5$$

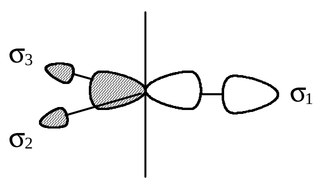
  where the coefficients c_{ij} are nonzero, except as required by symmetry.

- ✔ If we do not exclude any functions from the SALCs *a priori* we can form a nonsegregated set, using a pictorial approach.

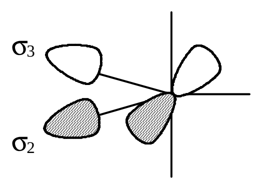
Nonequivalent Positions - Sigma SALCs for *tbp*
Nonsegregated LCAOs



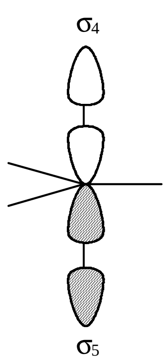
s + Φ_1 (A_1')



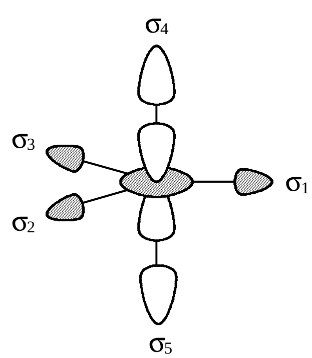
p_x+ Φ_2 (E')



p_y + Φ_3 (E')



p_z + Φ_4 (A_2'')

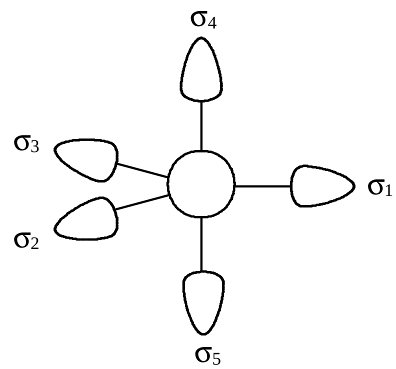


d_{z^2} + Φ_5 (A_1')

Nonequivalent Positions - Sigma SALCs for *tbp*
Restrictions on SALC Equations

$$\Phi_i = N(c_{i1}\sigma_1 \pm c_{i2}\sigma_2 \pm c_{i3}\sigma_3 \pm c_{i4}\sigma_4 \pm c_{i5}\sigma_5) \qquad i = 1, 2, 3, 4, 5$$

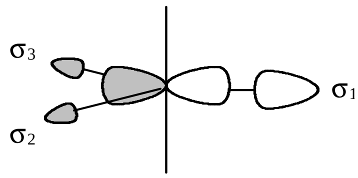
$\Phi_1(A_1')$:



- All five σ functions participate.
- $c_{11} = c_{12} = c_{13} = c_{1\text{eq}}$
- $c_{14} = c_{15} = c_{1\text{ax}}$
- In general, $c_{1\text{eq}} \neq c_{1\text{ax}}$
- Previous expression needs to be modified.

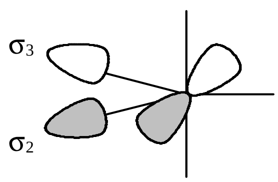
Nonequivalent Positions - Sigma SALCs for *tbp*
Restrictions on SALC Equations

$\Phi_2(E')$:



- σ_4 and σ_5 excluded, so $c_{24} = c_{25} = 0$
- Previous expression is correct.

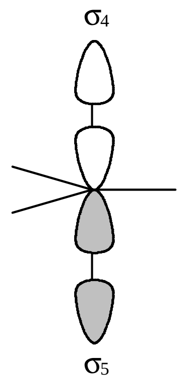
$\Phi_3(E')$:



- σ_4 and σ_5 excluded, so $c_{34} = c_{35} = 0$
- σ_1 also excluded, so $c_{31} = 0$
- Previous expression is correct.

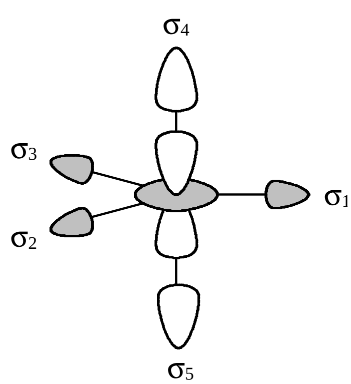
Nonequivalent Positions - Sigma SALCs for *tbp*
Restrictions on SALC Equations

$\Phi_4(A_2'')$:



- σ_1, σ_2, and σ_3 excluded, so $c_{41} = c_{42} = c_{43} = 0$
- Previous expression is correct.

$\Phi_5(A_1')$:



- All five σ functions participate.
- $c_{51} = c_{52} = c_{53} = c_{5eq}$
- $c_{54} = c_{55} = c_{5ax}$
- In general, $c_{5eq} \neq c_{5ax}$
- Previous expression needs to be modified.

Nonequivalent Positions - Sigma SALCs for *tbp*
Equations for the A_1' SALCs

$$\Phi_1 = N_1\{c_{1eq}(\phi_1 + \phi_2 + \phi_3) + c_{1ax}(\phi_4 + \phi_5)\}$$

$$\Phi_5 = N_5\{c_{5ax}(\phi_4 + \phi_5) - c_{5eq}(\phi_1 + \phi_2 + \phi_3)\}$$

☹ Can't hope to write a "one-size-fits-all" equation for these.

☹ Coefficients for the axial positions and equatorial positions will vary on a case by case basis.

☹ For the complete set of equations, $\sum c_{ij}^2 = 1$.

A Special Case - Equal Axial and Equatorial Contributions

$$\Phi_1 = 1/\sqrt{5}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5)$$
$$\Phi_2 = 1/\sqrt{6}(2\sigma_1 - \sigma_2 - \sigma_3)$$
$$\Phi_3 = 1/\sqrt{2}(\sigma_2 - \sigma_3)$$
$$\Phi_4 = 1/\sqrt{2}(\sigma_4 - \sigma_5)$$
$$\Phi_5 = 3/\sqrt{30}\{\sigma_4 + \sigma_5 - 2/3(\sigma_1 + \sigma_2 + \sigma_3)\}$$