How To Construct Ligand Group Orbitals (LGOs)

Deriving Ligand Group Orbitals

1) Start with a complete set of equivalent atomic orbitals (i.e., a complete set of orbitals is one in which any given orbital is taken into another or some combination of other orbitals by a symmetry operation in the point group of interest – the 4 H(1*s*) orbitals in CH_4 constitute a complete set)

2) Determine the characters for reducible representations of all transformations involving the orbitals. For each orbital that is taken into itself by a symmetry operation, count +1. For each that is taken into the negative of itself by a symmetry operation, count –1. For each orbital that is moved into another orbital, count 0. These characters will constitute a reducible representation, $\Gamma_{red.}$

3) Reduce Γ_{red} into a set of irreducible representations. This can be done either by inspection (look and see what set of irreducible reps have characters that add up to those of Γ_{red}) or using our "failsafe formula":

$$a_i = \frac{1}{h}\sum_R \left(\chi^R \cdot \chi_i^R \cdot C^R\right)$$

a_i = # of times the irreducible representation Γ_i appears in Γ_{red}
h = order of the molecular point group
R = an operation in the group
χ^R = character of the operation R in Γ_{red}
χ_i^R = character of the operation R in Γ_i
C^R = # of members in the class to which R belongs

Choose your own adventure:

4) Derive SALCs for the ligand group orbitals by inspection, using atomic orbitals as "generator functions", whose symmetry you match with your LGOs (this is the procedure we used for methane in class.

OR

5) Use the "projection operator", $\hat{P}$, to construct symmetry-adapted linear combinations (SALCs) from the orbitals for *each* irreducible representation – THESE are your LGOs

   The projection operator works on functions, so start by designating each symmetry-equivalent orbital with a function, ϕ_i. Thus, for a set of n orbitals, you should have n functions: ϕ_1–ϕ_n.
   To use the projection operator, you only need to take a single orbital from your complete set and use it to project an irreducible representation:

$$\hat{P}_{\Gamma_{irred}}\phi_i = \sum_R \chi^R_{\Gamma_{irred}} \cdot R(\phi_i)$$

   * For every operation (not just each class), $\chi^R_{\Gamma_{irred}}$ = character of Γ_{irred} under R

   * $R(\phi)$ = function resulting from operating R on ϕ_i

   * For doubly or triply degenerate irreducible representations, this is a bit trickier because you will need to use the projection operator on multiple atoms to generate the correct # of SALCs

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6) Final Optional Step: To normalize your linear combination, use the normalization factor:

for $a\phi_1 + b\phi_2 + c\phi_3 \ldots$ → normalized function is $\frac{1}{\sqrt{a^2 + b^2 + c^2 \ldots}}\left(a\phi_1 + b\phi_2 + c\phi_3 + \ldots\right)$