SALCs for Hybrid Orbitals
Applying Projection Operators to a Set of Hybrid Orbitals

✔ Applying a projection operator to a reference function of the basis set projects a SALC that is an LCAO of all members of the set:

$$P_i\varphi_t \propto S_i \propto c_1\varphi_1 \pm c_2\varphi_2 \pm \ldots \pm c_n\varphi_n$$

✔ When we formulate hybrid orbitals with the aid of group theory, the basis set is the desired hybrids. Therefore, applying a projection operator to a reference hybrid orbital, Ψ_t, would project the SALC for the AO with that symmetry as a function of all the hybrid wave functions, $\Psi_1 \ldots \Psi_n$:

$$P_i\Psi_t \propto S_i(\mathrm{AO}) \propto a_{i1}\Psi_1 \pm a_{i2}\Psi_2 \pm \ldots \pm a_{in}\Psi_n$$

✔ What we want is the hybrids defined as SALCs of the conventional wave functions of all component AOs, $\psi_1 \ldots \psi_n$:

$$\Psi_j \propto b_{1j}\psi_1 \pm b_{2j}\psi_2 \pm b_{nj}\psi_n$$

★ We can use the properties of inverse matrices to convert the expressions for the AOs as SALCs of the hybrids into expressions for the hybrids as SALCs of the AOs.

Inverse Matrices

- Matrices **A** and **B** are inverses of each other if

$$\mathbf{AB} = \mathbf{AA}^{-1} = \mathbf{B}^{-1}\mathbf{B} = \mathbf{E}$$

  where **E** is the identity matrix, a diagonal matrix whose elements are $e_{ij} = \delta_{ij}$ (i.e., all 1's along the trace).

- If $\mathbf{AB} = \mathbf{AA}^{-1} = \mathbf{B}^{-1}\mathbf{B} = \mathbf{E}$, then **A** and **B** are orthogonal to one another, and one is the transpose of the other; i.e., $b_{ij} = a_{ji}$. The row elements of **A** are the column elements of **B** and vice versa.

  Example:

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Inverse Matrices

- If **X** = **AY** and **Y** = **BX**, then **A** and **B** are inverses of each other, and the elements of **B** can be written by taking the transpose of **A**.

  Example:

  Given the equation

$$\begin{bmatrix} -y \\ x \\ z \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

  then

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -y \\ x \\ z \end{bmatrix}$$

Applying Inverse Matrix Relationships

- ✔ We know the symmetry species of the AOs comprising a hybrid set.

- ✔ We can apply projection operators for each species to a reference hybrid to obtain expressions for the AOs as SALCs of the hybrids. (Alternately, we can apply the operators to a reference function of a set of sigma pendant-atom functions with the same geometry.)

- ✔ If we rewrite this set of equations as a matrix equation, we will have an expression of the form

$$[\text{AOs}] = [\mathbf{A}][\text{Hybrids}]$$

- ✔ What we want is an equation of the form

$$[\text{Hybrids}] = [\mathbf{B}][\text{AOs}]$$

- ✔ What we want is the reverse of what we have, so **A** and **B** are inverses of each other. Knowing the coefficients that make up the elements of **A**, we can write the coefficients that make up the elements of **B** by taking the transpose of **A**.

- ✔ Once we know the form of **B**, we can write down a set of equations for all the hybrids as SALCs of the AOs, where the coefficients are the elements of the **B** matrix.

SALCs for Hybrid Orbitals
General Procedure

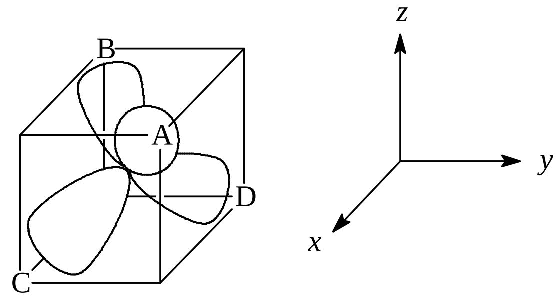
1. Taking the *n* hybrid orbitals as a basis set, construct and decompose a reducible representation Γ_{hyb} to identify the appropriate conventional orbitals to be combined.

2. Using the hybrids themselves or an equivalent set of pendant atom sigma orbitals as the basis set, apply the projection operators for each of the irreducible representations comprising Γ_{hyb} to a representative function of the set to obtain expressions for the conventional orbitals as LCAOs of the hybrids. Normalize all functions.

3. Combine the equations obtained in step 2 into a single matrix equation, using the coefficients to form the $n \times n$ transformation matrix **A**. Take the transpose of **A** to form the transformation matrix **B**.

4. Write a matrix equation for the hybrids by applying the **B** matrix to a column matrix of the conventional orbitals, written in the same order as in the previous matrix equation. Expand the matrix equation to obtain a set of *n* equations, one for each hybrid orbital.

SALCs for Hybrid Orbitals
Equations for *sp*^{3} Hybrids



$$\Gamma_{\mathrm{hyb}} = A_1 + T_2$$

☺ We have previously applied projection operators to a set of four hydrogen atoms to make SALCs for bonding in CH_4. The geometry is the same as a tetrahedral set of *sp*^{3} hybrids. Therefore, our previously obtained equations for the H-SALCs of methane have the same forms as the expressions for the AOs as SALCs of *sp*^{3} hybrids.

$$s = \tfrac{1}{2}(\Psi_A + \Psi_B + \Psi_C + \Psi_D)$$
$$p_x = \tfrac{1}{2}(\Psi_A - \Psi_B + \Psi_C - \Psi_D)$$
$$p_y = \tfrac{1}{2}(\Psi_A - \Psi_B - \Psi_C + \Psi_D)$$
$$p_z = \tfrac{1}{2}(\Psi_A + \Psi_B - \Psi_C - \Psi_D)$$

☞ Written in matrix form, these become the single equation

$$\begin{bmatrix} s \\ p_x \\ p_y \\ p_z \end{bmatrix} = \begin{bmatrix} \tfrac{1}{2} & \tfrac{1}{2} & \tfrac{1}{2} & \tfrac{1}{2} \\ \tfrac{1}{2} & -\tfrac{1}{2} & \tfrac{1}{2} & -\tfrac{1}{2} \\ \tfrac{1}{2} & -\tfrac{1}{2} & -\tfrac{1}{2} & \tfrac{1}{2} \\ \tfrac{1}{2} & \tfrac{1}{2} & -\tfrac{1}{2} & -\tfrac{1}{2} \end{bmatrix} \begin{bmatrix} \Psi_A \\ \Psi_B \\ \Psi_C \\ \Psi_D \end{bmatrix}$$

SALCs for Hybrid Orbitals
Equations for *sp*^{3} Hybrids

✔ Taking the transpose of the operator matrix **A**, we form the matrix **B**:

$$\begin{bmatrix} ½ & ½ & ½ & ½ \\ ½ & -½ & ½ & -½ \\ ½ & -½ & -½ & ½ \\ ½ & ½ & -½ & -½ \end{bmatrix} \Rightarrow \begin{bmatrix} ½ & ½ & ½ & ½ \\ ½ & -½ & -½ & ½ \\ ½ & ½ & -½ & -½ \\ ½ & -½ & ½ & -½ \end{bmatrix}$$

✔ Using this, we obtain

$$\begin{bmatrix} \Psi_A \\ \Psi_B \\ \Psi_C \\ \Psi_D \end{bmatrix} = \begin{bmatrix} ½ & ½ & ½ & ½ \\ ½ & -½ & -½ & ½ \\ ½ & ½ & -½ & -½ \\ ½ & -½ & ½ & -½ \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \\ p_z \end{bmatrix}$$

✔ Using the elements of the **B** matrix as coefficients, we obtain the following individual equations for the hybrids:

$$\Psi_A = ½(s + p_x + p_y + p_z)$$

$$\Psi_B = ½(s - p_x - p_y + p_z)$$

$$\Psi_C = ½(s + p_x - p_y - p_z)$$

$$\Psi_D = ½(s - p_x + p_y - p_z)$$