

Paper 201-Sec A

**Hybridization and its applications,
Hybrid orbitals as Linear Combinations
of Atomic Orbitals**

**SALCs, projection operators, illustrative
examples**

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HYBRID ORBITALS , σ -bonding

The central atom of any molecule with more than 2 atoms can be considered to have undergone hybridisation.

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | | |
|----------|----------|----------|-------------|---------------------|----------------------------|
| A_1 | 1 | 1 | 1 | z | $x^2 + y^2, z^2$ |
| A_2 | 1 | 1 | -1 | R_z | |
| E | 2 | -1 | 0 | $(x, y) (R_x, R_y)$ | $(x^2 - y^2, xy) (xz, yz)$ |
| X_R | 4 | 1 | 2 | | |

C_{3v} NH_3 : 3-bonded and one lone pair of electrons

4 hybrid orbitals

X_R (hybrid orbital) = No of orbitals which do not change the position and direction

- No of orbitals which do not change the position but simply reverse direction when a symmetry operation is performed

Using character table, RR(hybrid orbitals) = $2A_1 + E$

From character table, $A_1 = s, p_z$ and $E = p_x, p_y$

Hence, NH_3 is sp^3 hybridised

| T_d | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | | |
|-------|---|--------|--------|--------|-------------|-------------------|---|
| A_1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2 + z^2$ |
| A_2 | 1 | 1 | 1 | -1 | -1 | | |
| E | 2 | -1 | 2 | 0 | 0 | | $(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$ |
| T_1 | 3 | 0 | -1 | 1 | -1 | (R_x, R_y, R_z) | |
| T_2 | 3 | 0 | -1 | -1 | 1 | (x, y, z) | (xy, xz, yz) |

| | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | |
|------------------|---|--------|--------|--------|-------------|------------------------------|
| Γ_{tetra} | 4 | 1 | 0 | 0 | 2 | $\Gamma_{tetra} = A_1 + T_2$ |

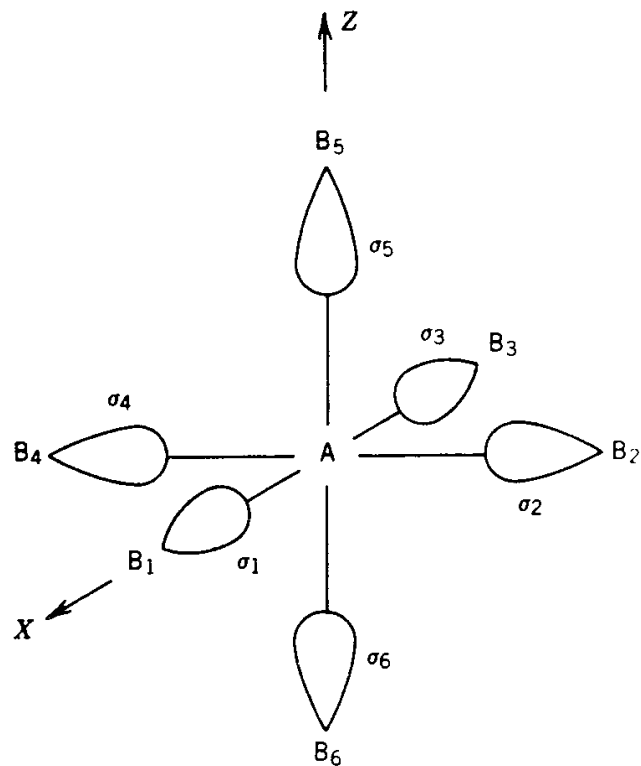
A_1 Orbitals

s

T_2 Orbitals

(p_x, p_y, p_z)
 (d_{xy}, d_{xz}, d_{yz})

AB₆, Octahedral Molecule



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

$$A_{1g}: s$$

$$E_g: (d_{z^2}, d_{x^2-y^2})$$

$$T_{1u}: (p_x, p_y, p_z)$$

| O_h | E | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ | i | $6S_4$ | $8S_6$ | $3\sigma_h$ | $3\sigma_d$ |
|-------------------|-----|--------|--------|--------|--------|-----|--------|--------|-------------|-------------|
| Γ_{σ} | 6 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 4 | 2 |

| O_h | E | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2(=C_4^2)$ | i | $6S_4$ | $8S_6$ | $3\sigma_h$ | $3\sigma_d$ | | |
|----------|---|--------|--------|--------|----------------|----|--------|--------|-------------|-------------|-------------------|---------------------------------|
| A_{1g} | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2 + z^2$ |
| A_{2g} | 1 | 1 | -1 | -1 | 1 | 1 | -1 | 1 | 1 | -1 | | |
| E_g | 2 | -1 | 0 | 0 | 2 | 2 | 0 | -1 | 2 | 0 | | $(2z^2 - x^2 - y^2, x^2 - y^2)$ |
| T_{1g} | 3 | 0 | -1 | 1 | -1 | 3 | 1 | 0 | -1 | -1 | (R_x, R_y, R_z) | |
| T_{2g} | 3 | 0 | 1 | -1 | -1 | 3 | -1 | 0 | -1 | 1 | | (xz, yz, xy) |
| A_{1u} | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | | |
| A_{2u} | 1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | | |
| E_u | 2 | -1 | 0 | 0 | 2 | -2 | 0 | 1 | -2 | 0 | | |
| T_{1u} | 3 | 0 | -1 | 1 | -1 | -3 | -1 | 0 | 1 | 1 | (x, y, z) | |
| T_{2u} | 3 | 0 | 1 | -1 | -1 | -3 | 1 | 0 | 1 | -1 | | |

| D_{3h} | E | $2C_3$ | $3C_2$ | σ_h | $2S_3$ | $3\sigma_v$ | | |
|----------|---|--------|--------|------------|--------|-------------|--------------|-------------------|
| A_1' | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2, z^2$ |
| A_2' | 1 | 1 | -1 | 1 | 1 | -1 | R_z | |
| E' | 2 | -1 | 0 | 2 | -1 | 0 | (x, y) | $(x^2 - y^2, xy)$ |
| A_1'' | 1 | 1 | 1 | -1 | -1 | -1 | | |
| A_2'' | 1 | 1 | -1 | -1 | -1 | 1 | z | |
| E'' | 2 | -1 | 0 | -2 | 1 | 0 | (R_x, R_y) | (xz, yz) |

D_{3h} , two possibilities one is BCl_3 and another PCl_5 ie Trigonal Bipyramidal

| D_{3h} | E | $2C_3$ | $3C_2$ | σ_h | $2S_3$ | $3\sigma_v$ | |
|----------------------------------|-----|--------|--------|------------|--------|-------------|-------------------------|
| $\Gamma_{\sigma}^{\text{total}}$ | 5 | 2 | 1 | 3 | 0 | 3 | $(= 2A'_1 + A'_2 + E')$ |
| $\Gamma_{\sigma}^{\text{ax}}$ | 2 | 2 | 0 | 0 | 0 | 2 | $(= A'_1 + A'_2)$ |
| $\Gamma_{\sigma}^{\text{eq}}$ | 3 | 0 | 1 | 3 | 0 | 1 | $(= A'_1 + E')$ |

A'_1

s

d_{z^2}

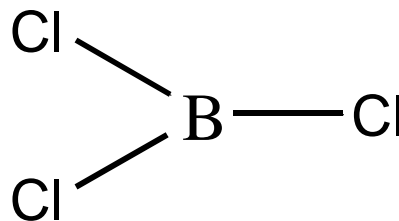
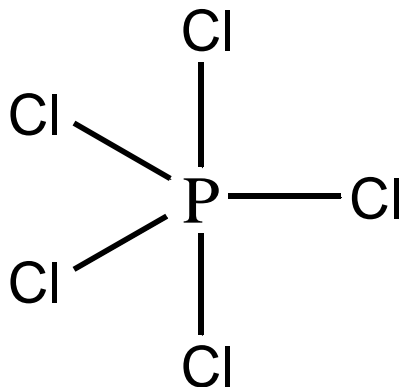
A''_2

p_z

E

(p_x, p_y)

$(d_{xy}, d_{x^2-y^2})$



SALCs, projection operators, illustrative examples

Linear Combination of Atomic Orbitals (LCAO method) :

It is the expression of empirical wave functions as mathematical sums of wave functions on the various atoms of the molecule.

$$AB \rightarrow \text{diatomic molecule} \rightarrow \psi_1 = a\psi + b\psi \quad \psi_2 = a\psi - b\psi$$

a and b are constants called as mixing constants, a and b reflect the relative contribution of each wave function to the LCAO wave function.

The AOs used to construct these MOs :

- Must have similar energies.
- Must overlap appreciably.
- Must have the same symmetry with respect to the internuclear axis.

Ab-anti bonding –less favourable : Ab LCAO - MO has higher energy than bonding LCAO-MO.

SALCs : Set of wave functions that can define molecular properties in a particular symmetry field.

In simple molecules, MX_n : The symmetries of the orbitals on the central M-atom can be matched with those of mathematical combinations of orbitals on the outer X-atoms called **pendant atoms**.

These mathematical constructs of pendant-atom AOs are called **symmetry-adapted linear combinations (SALCs)** :

$$\psi_{MO} = a\psi_{AO}(M) \pm b\psi_{SALC}(nX)$$

$$\psi_{SALC} = c_1\psi_1 \pm c_2\psi_2 \pm c_3\psi_3 \pm \dots \dots \dots c_n\psi_n$$

Projection operator : called a function generating machine as it generates algebraic equations more or less automatically.

The functions to be obtained are linear combinations of atomic wave functions (pendant atom SALCs, π MOs of ring systems) formulated from a collection of specific functions that form a **basis set**.

Each SALC must have the symmetry of an IR within the RR for the problem under consideration.

The projection operator for any symmetry species can be constructed either in terms of the full **operator matrices** of IR or in terms of its **characters**. We will deal with **character** form of the **projection operator**.

- ⇒ Let $\phi_1, \phi_2, \dots, \phi_n \rightarrow$ set of functions that form the basis for a RR of the group. These **basis functions** must be related to each other by operations of the group.
- ⇒ Therefore, each function is interchanged with itself or other functions in the set in either a positive or negative sense through the effect of an operator R, for each of the operations of the group.
- ⇒ To construct SALCs associated with the i^{th} IR, S_i , we may apply the projection operator, P_i , to any one of the several basis functions, ϕ_t , according to the expression :

$$S_i \quad \alpha \quad P_i \phi_t = \frac{d_i}{h} \sum_R \chi_i^R R_j \phi_t \dots \dots \dots \mathbf{1}$$

l_i or d_i = dimension of the i^{th} IR

h = order of the group

χ_i^R = each operation's character in the i^{th} IR

R_j = the operator for the j^{th} operation of the group

- $R_j \phi_t$ = result of this is the basis function, either in the positive or negative sense, obtained when the reference function ϕ_t is subjected to the action of the j^{th} operation.
- Summation is taken over all the individual operations and not over each class of operations – This is because each operation of a given class may transform ϕ_t into a different member of the basis set.
- **Eqn 1** above is not the final wave function we need. One has to normalize the functions generated from the **P_i's** using $N^2 \int \psi \psi^* d\tau = 1$ (N = normalization constant). $\frac{d_i}{h}$ can be ignored as it will be taken into account within N .

In addition, all wave functions generated must meet the quantum mechanical requirement of **orthogonality**. Therefore, for any 2 wave functions of the system, $\int \psi_i \psi_j d\tau = 0$, if $i \neq j$. In carrying out normalization or testing for orthogonality on SALCs, products of wave

- functions that are linear combinations of the basis functions will be taken into account. Therefore, products are of the form –

$$(a_i\phi_i \pm a_{i+1}\phi_{i+1} + \dots \pm a_n\phi_n) (b_j\phi_j \pm b_{j+1}\phi_{j+1} + \dots \pm b_m\phi_m)$$

The basis functions composing these SALCs are assumed to be normalized and orthogonal. Therefore, in the expansion of products, terms - $\phi_i\phi_i$ or $\phi_j\phi_j$ will be unity and $\phi_i\phi_j$ will be zero ($i \neq j$).

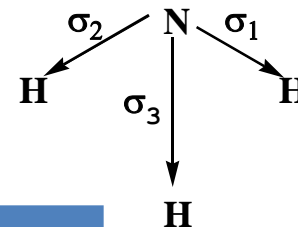
We can write $\int \phi_i\phi_j d\tau = \delta_{ij}$

So we need to think about $\phi_i\phi_i$ terms (non-vanishing) as all cross terms ($\phi_i\phi_j$) will be zero.

- **So to use projection operator one needs the diagonal elements of the matrices.**
- The most important and frequent use of P_i is to find the proper way to combine atomic wave functions on individual atoms in a molecule into MOs that correspond to molecular symmetry.
- The valid MOs should form bases for IRs of the molecular point group.
- There is a problem when symmetry equivalent atoms are present. Eg : C in benzene or F in SF_6 .
- So one needs to know – the IRs to which any given set of equivalent AOs will contribute – the explicit form of the LCAOs that satisfy the symmetry properties of each representation. So we need SALCs constructed from AOs.

Eg : SALCs for C_{3v} system : three-fold symmetry

| C_{3v} | E | C_3 | C_3^2 | $\sigma_v(1)$ | $\sigma_v(2)$ | $\sigma_v(3)$ |
|--------------------------|-------------|-------------|-------------|---------------|---------------|---------------|
| $R_j \sigma_1$ | σ_1 | σ_3 | σ_2 | σ_1 | σ_3 | σ_2 |
| A_1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\chi_i^R(R_j \sigma_1)$ | σ_1 | σ_3 | σ_2 | σ_1 | σ_3 | σ_2 |
| E | 2 | -1 | -1 | 0 | 0 | 0 |
| $\chi_i^R(R_j \sigma_1)$ | $2\sigma_1$ | $-\sigma_3$ | $-\sigma_2$ | 0 | 0 | 0 |



| C_{3v} | E | $2 C_3$ | $3\sigma_v$ |
|----------|---|---------|-------------|
| A_1 | 1 | 1 | 1 |
| E | 2 | -1 | 0 |

2 SALCs have been obtained. But we need one more for the E representation. If we use σ_2 or σ_3 as basis vector,

$$h = 6 \quad \text{classes} = 3$$

$$a_{A_1} = 16[3 \times 1 \times 1 + (2 \times 0 \times 1) + 3 \times 1 \times 1] = 1$$

$$a_E = 16[3 \times 2 \times 1 + (2 \times 0 \times -1) + (3 \times 1 \times 0)] = 1$$

$$P^{A_1}(\sigma_1) = 1(A_1) = 2(\sigma_1 + \sigma_2 + \sigma_3) \approx \sigma_1 + \sigma_2 + \sigma_3$$

$$= 1/\sqrt{3} (\sigma_1 + \sigma_2 + \sigma_3) \quad \text{after normalization}$$

$$P^E(\sigma_1) = 2(E) = 2\sigma_1 - \sigma_3 - \sigma_2 = 1/\sqrt{6} (2\sigma_1 - \sigma_2 - \sigma_3) \quad \text{after normalization}$$

| C_{3v} | E | C_3 | C_3^2 | $\sigma_v(1)$ | $\sigma_v(2)$ | $\sigma_v(3)$ |
|---|---|-------|---------|---------------|---------------|---------------|
| Γ_{SALC} | 3 | 0 | 0 | 1 | 1 | 1 |
| $\Gamma_{\text{SALC}} = A_1 + E$ from character table | | | | | | |

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | | |
|----------|---|--------|-------------|---------------------|-----------------------------|
| A_1 | 1 | 1 | 1 | Z | $x^2 + y^2, z^2$ |
| A_2 | 1 | 1 | -1 | R_z | |
| E | 2 | -1 | 0 | $(x, y) (R_x, R_y)$ | $(x^2 - y^2, 2xy) (xz, yz)$ |

| C_{3v} | E | C_3 | C_3^2 | $\sigma_v(1)$ | $\sigma_v(2)$ | $\sigma_v(3)$ |
|--------------------------|-------------|-------------|-------------|---------------|---------------|---------------|
| $R_j \sigma_2$ | σ_2 | σ_1 | σ_3 | σ_3 | σ_2 | σ_1 |
| $R_j \sigma_3$ | σ_3 | σ_2 | σ_1 | σ_2 | σ_1 | σ_3 |
| E | 2 | -1 | -1 | 0 | 0 | 0 |
| $\chi_i^R(R_j \sigma_2)$ | $2\sigma_2$ | $-\sigma_1$ | $-\sigma_3$ | 0 | 0 | 0 |
| $\chi_i^R(R_j \sigma_3)$ | $2\sigma_3$ | $-\sigma_2$ | $-\sigma_1$ | 0 | 0 | 0 |

$$P^E(\sigma_2) = 2\sigma_2 - \sigma_1 - \sigma_3 \approx -\sigma_1 + 2\sigma_2 - \sigma_3$$

$$P^E(\sigma_3) = 2\sigma_3 - \sigma_2 - \sigma_1 \approx -\sigma_1 - \sigma_2 + 2\sigma_3$$

But these 2 are not orthogonal to the 2 SALCs obtained. And orthogonality has to be strictly satisfied (sum of the products of the corresponding coefficients is zero).

$$(-\sigma_1 + 2\sigma_2 - \sigma_3)(-\sigma_1 - \sigma_2 + 2\sigma_3) = -1 \times -1 + 2 \times -1 + -1 \times 2 = 1 - 2 - 2 = 1 - 4 = -3$$

Therefore, no single vector can give a SALC.

Lets try $\sigma_2 - \sigma_3$:

$$P^E(\sigma_2 - \sigma_3) = 2(\sigma_2 - \sigma_3) - (\sigma_1 - \sigma_2) - (\sigma_3 - \sigma_1) = 2\sigma_2 - 2\sigma_3 - \sigma_1 + \sigma_2 - \sigma_3 + \sigma_1 = 3(\sigma_2 - \sigma_3) \approx \sigma_2 - \sigma_3$$

$$\therefore \text{SALC} = 12(\sigma_2 - \sigma_3)$$

Therefore, one should use $\sigma_2 - \sigma_3$ vector as basis for generating SALC for E representation for a 3-fold symmetry molecule.

| C_{3v} | E | C_3 | C_3^2 | $\sigma_v(1)$ | $\sigma_v(2)$ | $\sigma_v(3)$ |
|--------------------------------------|--------------------------|--------------------------|--------------------------|---------------|---------------|---------------|
| $R_j(\sigma_2 - \sigma_3)$ | $\sigma_2 - \sigma_3$ | $\sigma_1 - \sigma_2$ | $\sigma_3 - \sigma_1$ | - | - | - |
| E | 2 | -1 | -1 | 0 | 0 | 0 |
| $\chi_i^R(R_j(\sigma_2 - \sigma_3))$ | $2(\sigma_2 - \sigma_3)$ | $-(\sigma_1 - \sigma_2)$ | $-(\sigma_3 - \sigma_1)$ | 0 | 0 | 0 |

HYBRID ORBITALS :

The central atom of any molecule with more than 2 atoms can be considered to have undergone hybridization.

χ_R (hybrid orbital) = No. of orbitals which do not change the position and direction – No. of orbitals which do not change the position but simply reverse direction when a symmetry operation is performed

C_{3v} , NH_3 :

3-bonded and one lone pair of electrons. So 4-hybrid orbitals $\phi_1, \phi_2, \phi_3, \phi_4$

$$\chi_E = 4 - 0 = 4$$

$$\chi_{C_3} = 1 - 0 = 1$$

$$\chi_{\sigma_v} = 2 - 0 = 2$$

Using character table : $RR(\text{hybrid orbitals}) = 2A_1 + E$

From character table : $A_1 = s, p_z$

$E = p_x, p_y$

$2A_1$ and E combine to give hybrid orbitals. Therefore, NH_3 is **sp³** in hybridization.

| C_{3v} | E | $2C_3$ | $3\sigma_v$ |
|----------|---|--------|-------------|
| | 4 | 1 | 2 |

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | | |
|----------|---|--------|-------------|-----------------------|----------------------------|
| A_1 | 1 | 1 | 1 | z | $x^2 + y^2, z^2$ |
| A_2 | 1 | 1 | -1 | R_z | |
| E | 2 | -1 | 0 | (x, y) (R_x, R_y) | $(x^2 - y^2, xy)$ (xz, yz) |

$$\chi_E = 3 - 0 = 3$$

$$\chi_{\sigma h} = 3 - 0 = 3$$

$$\chi_{C_3} = 0 - 0 = 0$$

$$\chi_{S_3} = 0 - 0 = 0$$

$$\chi_{C_2} = 1 - 0 = 1$$

$$\chi_{\sigma v} = 1 - 0 = 1$$

$$\Gamma_{RR} (\text{hybrid orbitals}) = A_1' + E'$$

A_1' = s-orbital

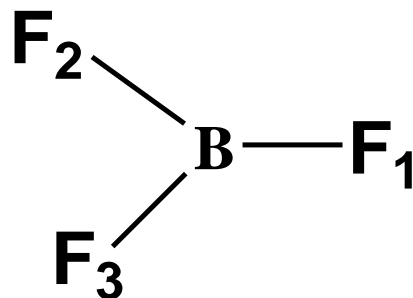
$$E' = (x, y) (x^2 - y^2, xy)$$

\therefore orbitals are $p_x, p_y, d_{xy}, d_{x^2-y^2}$

So, sp^2 or sd^2

But sd^2 is not energetically favourable though it is symmetrically allowed. This is because it requires excitation of electrons from 2p- to 3d-level which involves higher energy.

Example :



| D_{3h} | E | $2C_3$ | $3C_2$ | s_h | $2S_3$ | $3\sigma_v$ | | |
|-----------------|---|--------|--------|-------|--------|-------------|--------------|-------------------|
| A_1' | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2, z^2$ |
| A_2' | 1 | 1 | -1 | 1 | 1 | -1 | R_z | |
| E' | 2 | -1 | 0 | 2 | -1 | 0 | (x, y) | $(x^2 - y^2, xy)$ |
| A_1'' | 1 | 1 | 1 | -1 | -1 | -1 | | |
| A_2'' | 1 | 1 | -1 | -1 | -1 | 1 | z | |
| E'' | 2 | -1 | 0 | -2 | 1 | 0 | (R_x, R_y) | (xz, yz) |
| Γ_σ | 3 | 0 | 1 | 3 | 0 | 1 | See below | |

| D _{3h} | E | C ₃ | C ₃ ² | C ₂ (1) | C ₂ (2) | C ₂ (3) | s _h | S ₃ ¹ | S ₃ ⁵ | σ _v (1) | σ _v (2) | σ _v (3) |
|---|-----------------|-----------------|-----------------------------|--------------------|--------------------|--------------------|-----------------|-----------------------------|-----------------------------|--------------------|--------------------|--------------------|
| R _j σ ₁ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ |
| A ₁ ' | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| χ _i ^R R _j σ ₁ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ | σ ₁ | σ ₃ | σ ₂ |
| For A ₁ ' | | | | | | | | | | | | |
| E' | 2 | -1 | -1 | 0 | 0 | 0 | 2 | -1 | -1 | 0 | 0 | 0 |
| χ _i ^R R _j σ ₁ | 2σ ₁ | -σ ₃ | -σ ₂ | 0 | 0 | 0 | 2σ ₁ | -σ ₃ | -σ ₂ | 0 | 0 | 0 |
| For E' | | | | | | | | | | | | |

$$\therefore \hat{P}^{A_1'}(\sigma_1) = \sigma_1 + \sigma_3 + \sigma_2 + \sigma_1 + \sigma_3 + \sigma_2 + \sigma_1 + \sigma_3 + \sigma_2 + \sigma_1 + \sigma_3 + \sigma_2 = 4\sigma_1 + 4\sigma_2 + 4\sigma_3$$

$$\therefore = 4(\sigma_1 + \sigma_2 + \sigma_3) \approx (\sigma_1 + \sigma_2 + \sigma_3)$$

$$\hat{P}^{A_1'}(\sigma_1) = \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)$$

$$\hat{P}^{E'}(\sigma_1) = 2\sigma_1 - \sigma_3 - \sigma_2 + 2\sigma_1 - \sigma_3 - \sigma_2 = 4\sigma_1 - 2\sigma_2 - 2\sigma_3 = 2(2\sigma_1 - \sigma_2 - \sigma_3) \approx (2\sigma_1 - \sigma_2 - \sigma_3)$$

$$\hat{P}^{E'}(\sigma_1) = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$$

| D_{3h} | E | C_3 | C_3^2 | $C_2(1)$ | $C_2(2)$ | $C_2(3)$ | s_h | S_3^1 | S_3^5 | $\sigma_v(1)$ | $\sigma_v(2)$ | $\sigma_v(3)$ |
|---|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| $R_j(\sigma_2 - \sigma_3)$ | $\sigma_2 - \sigma_3$ | $\sigma_1 - \sigma_2$ | $\sigma_3 - \sigma_1$ | $\sigma_3 - \sigma_2$ | $\sigma_2 - \sigma_1$ | $\sigma_1 - \sigma_3$ | $\sigma_2 - \sigma_3$ | $\sigma_1 - \sigma_2$ | $\sigma_3 - \sigma_1$ | $\sigma_3 - \sigma_2$ | $\sigma_2 - \sigma_1$ | $\sigma_1 - \sigma_3$ |
| E' | 2 | -1 | -1 | 0 | 0 | 0 | 2 | -1 | -1 | 0 | 0 | 0 |
| $\chi_i^{R_j} R_j(\sigma_2 - \sigma_3)$ | $2(\sigma_2 - \sigma_3)$ | $\sigma_2 - \sigma_1$ | $\sigma_1 - \sigma_3$ | 0 | 0 | 0 | $2(\sigma_2 - \sigma_3)$ | $\sigma_2 - \sigma_1$ | $\sigma_1 - \sigma_3$ | 0 | 0 | 0 |
| For E' | | | | | | | | | | | | |

$$\begin{aligned} \hat{P}^{E'}(\sigma_2 - \sigma_3) &= 2(\sigma_2 - \sigma_3) + \sigma_2 - \sigma_1 + \sigma_1 - \sigma_3 + 2(\sigma_2 - \sigma_3) + \sigma_2 - \sigma_1 + \sigma_1 - \sigma_3 \\ &= 2(\sigma_2 - \sigma_3) + 2\sigma_2 - 2\sigma_3 + 2(\sigma_2 - \sigma_3) = 6(\sigma_2 - \sigma_3) \approx \sigma_2 - \sigma_3 \end{aligned}$$

$$\hat{P}^{E'}(\sigma_2 - \sigma_3) = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$$

3 SALCs are :

$$\begin{aligned} &\frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) \\ &\frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \\ &\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3) \end{aligned}$$

In an AB_n molecule, non-equivalent AOs on the central atom are combined into **hybrid orbitals**, which then provide a set of equivalent lobes directed at the set of symmetry equivalent B-atoms. Therefore, A-B bonds to all equivalent B atoms will be equivalent. AB_3 : Trigonal planar : D_{3h}

How to form a set of trigonally directed hybrid orbitals ?

1. Use the 3 σ -bonds as a basis for a representation i.e. find Γ_σ
Reduce Γ_σ to $A_1' + E'$ using character table.
Find the 3 SALCs : shown in previous page

| IR | AOs on A | SALCs on B- atoms |
|----------|-------------------------|--|
| $A_1' =$ | s, d_{z^2} | $\frac{1}{\sqrt{3}} (\sigma_1 + \sigma_2 + \sigma_3)$ |
| $E' =$ | (p_x, p_y) | $\frac{1}{\sqrt{6}} (2\sigma_1 - \sigma_2 - \sigma_3)$ |
| | $(d_{xy}, d_{x^2-y^2})$ | $\frac{1}{\sqrt{2}} (\sigma_2 - \sigma_3)$ |

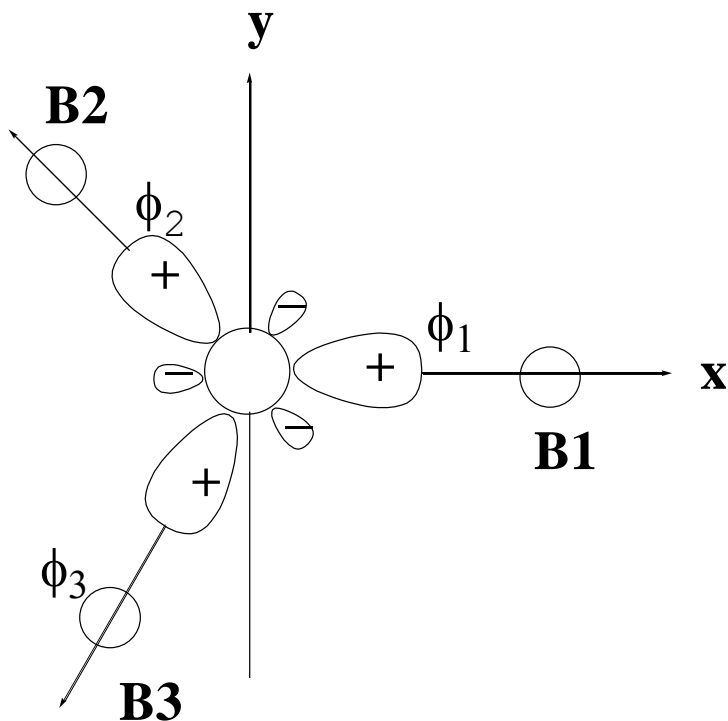
The s-orbital can be combined with 2 p-orbitals to form 3 equivalent lobes projecting from the central atom A towards the B-atoms. We need to find algebraic expression for these combinations.

Let the hybrid orbitals be Φ_1, Φ_2, Φ_3

$$\Phi_1 = c_{11}s + c_{12}p_x + c_{13}p_y$$

$$\Phi_2 = c_{21}s + c_{22}p_x + c_{23}p_y$$

$$\Phi_3 = c_{31}s + c_{32}p_x + c_{33}p_y$$



We can write in matrix form :

$$\begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix}$$

Matrix C

Inverse is :

$$\begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{bmatrix}$$

Matrix D

One can get **C** if one knows how to get **D**.

Matrix D is the transformation of a set of 3 equivalent basis functions into a set of linear combinations having the symmetry of the AOs, which in turn have symmetry corresponding to certain IRs of the molecular symmetry group.

Projection operator generates such SALCs, the coefficients of which are elements of the desired matrix.

Therefore, if we use the \hat{P} technique to transform a set of equivalent σ -orbitals – either the hybrid orbitals on the central atom or the σ -orbitals on the pendant atoms – into SALCs, we obtain a set of coefficients that form matrix D.

1. Form SALCs from the set of equivalent orbitals on the pendant atoms :

$$s = \psi_1(A_1') = \frac{1}{\sqrt{3}} (\sigma_1 + \sigma_2 + \sigma_3)$$

$$p_x = \psi_2(E_a') = \frac{1}{\sqrt{6}} (2\sigma_1 - \sigma_2 - \sigma_3)$$

$$p_y = \psi_3(E_b') = \frac{1}{\sqrt{2}} (\sigma_2 - \sigma_3)$$

2. The matrix of the coefficients is written and its inverse is taken :

$$\text{Matrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ \mathbf{0} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \quad \text{Inverse (transpose)} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & \mathbf{0} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

3. The matrix i.e. inverse obtained is applied to a column vector of the AOs (in the correct order of representations to which they belong) to generate hybrids.

$$\begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & \mathbf{0} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix} = \begin{bmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{bmatrix}$$

$$\Phi_1 = \frac{1}{\sqrt{3}} s + \frac{2}{\sqrt{6}} p_x$$

$$\Phi_2 = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$\Phi_3 = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y$$

These are designated as sp^2 hybrids.

The procedure we have just seen can be extended to obtain the equations for other sets of equivalent hybrid orbitals.

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.

Using the hybrids themselves or an equivalent set of pendant atom σ -orbitals as the basis set, apply the projection operators for each of the IRs 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.

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

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.