

Applications: Hybridization

C734b

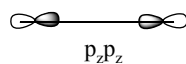
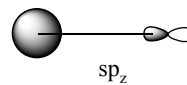
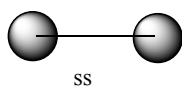
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1

Distinguish bonds by those which have no node of charge density along the bond (\equiv σ -bond) or those with zero charge density in the plane containing the bond axis (π -bond),

Take z-axis \equiv bond axis

σ -bonds would be ss or sp_z or p_zp_z

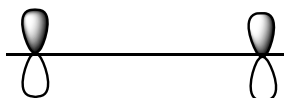


Here s and p_z are atomic orbitals ($l = 0, 1$)

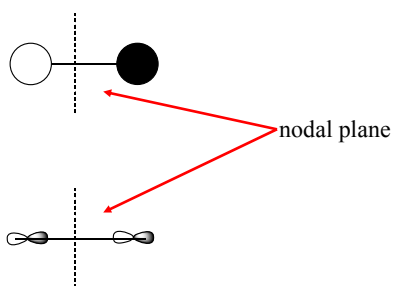
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π -bonds are formed by overlap of p_x or p_y atomic orbitals



If there is a nodal plane perpendicular to the bond axis, this means that the σ - and π -bonds are antibonding.



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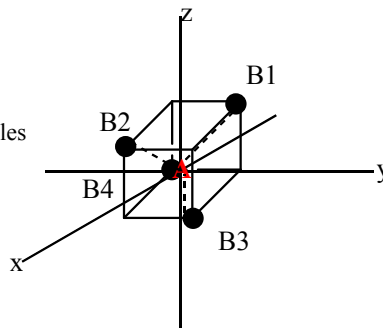
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Example: in CH_4 the 4 C-H bonds are equivalent even though the electron configuration of C = $1s^2 2s^2 2p^2$

\Rightarrow C 2s and 2p orbitals are “mixed: in a linear combination called **hybridization**

Group theory can tell us which orbitals are involved in hybridization (in CH_4 , one s and three p orbitals involved) although sometimes there can > 1 possibility.

Example: σ -bonding in AB_4 molecules



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Let $\sigma_i \equiv$ unit vector oriented from A to B_i and use $\langle \sigma_1, \sigma_2, \sigma_3, \sigma_4 |$ as a basis to determine the characters of the representation Γ_σ .

* Don't need to determine $\Gamma(T)$ since we only need χ_σ

Every σ_i which transforms into itself under symmetry operator T contributes +1 to Character χ_σ . Every σ_i which transforms into $\sigma_j, j \neq i$ makes no contribution to χ_σ .

\Rightarrow non-zero contribution to χ by # of vectors unshifted by the operation

| | | | | | | |
|---------------|---|--------|--------|--------|-------------|--------|
| T_d | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | h = 24 |
| χ_σ | 4 | 1 | 0 | 0 | 2 | |

X_σ is reducible: use $a_j = \frac{1}{h} \sum_k c_k \chi_j(c_k) \chi_\sigma(c_k)$ and T_d character table

Example: $a_1 = \frac{1}{24} [1(1)(4) + (8)(1)(1) + (6)(2)(1)] = 1$

A little work yields: $\Gamma_\sigma = A_1 \oplus T_2$

Now, s orbital forms a basis for A_1 (always) and from character table (x, y, z) and also (xy, yz, zx) form a basis for T_2

\therefore σ -bonds in a tetrahedral AB_4 molecule can be formed by sp^3 and/or sd^3 .

In general orbitals could be $a(sp^3) + b(sd^3)$ although a or b coefficients could be small.

How to choose?

- 1.) The contributing orbitals must be of comparable energy
- 2.) For a bonding MO, the bond should provide a maximum overlap of charge density in the region between the atoms.

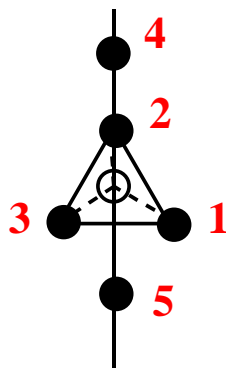
In C $E(3d) > E(2p)$ by ~ 10 eV. Therefore sp^3 predominates.

In Mn and Cr $E(3d) \approx E(4p)$. Therefore, sd^3 probably more important

Example: AB₅ trigonal bipyramid

D_{3h} point group.

For example: PF₅



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| D_{3h} | E | $2C_3$ | $3C_2$ | σ_h | $2S_3$ | $3\sigma_v$ |
|---------------|-----|--------|--------|------------|--------|-------------|
| χ_σ | 5 | 2 | 1 | 3 | 0 | 3 |

Can therefore show: $\Gamma_\sigma = 2A_1' \oplus A_2'' \oplus E'$

From character table: s and $d_{z^2-r^2}$ transform as A_1' ; p_z transforms as A_2''

(p_x, p_y) and $(d_{xy}, d_{x^2-y^2})$ transform as E'

$E[(n+1)s] - E(ns)$ is large as is $E[(n+1)d_{z^2} - E(nd_{z^2})]$

\therefore n quantum number is probably the same for all orbitals

\Rightarrow in PF₅ sd^3 predominates while in molecules with high Z central atom, p- and d-orbitals combine to contribute dsp^3 and d^3sp hybridization.

Same technique can be used for π -bonding (later).

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