Molecular Structures

Molecular Structure

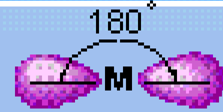
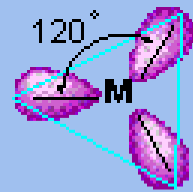
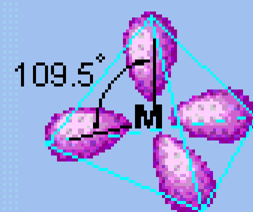
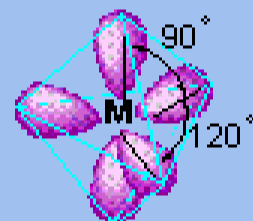
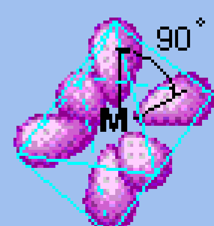
The three-dimensional arrangement of the atoms comprising a molecule

Molecular Structure

- Bond Angle
  - The angle between any two bonds that include a common atom.
- Bond Distance
  - The distance between the nuclei of two bonded atoms.

Valence Shell Electron Pair Repulsion Theory

Predicting Molecular Structures

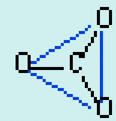
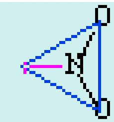
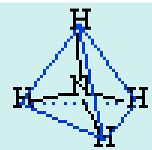
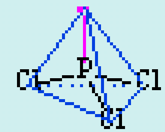
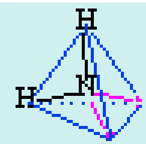
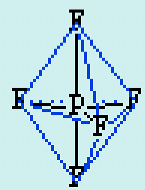
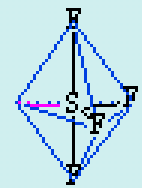
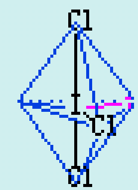
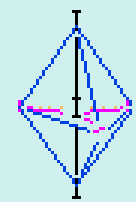
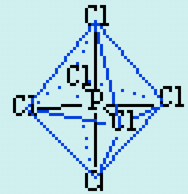
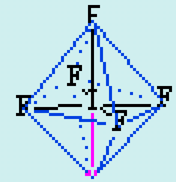
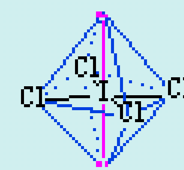
<table>
<tr><th>Number of Regions</th><th>Spatial Arrangement</th><th>Electron-Pair Geometry</th></tr>
<tr><td>Two regions of high electron density (bonds and/or unshared pairs)</td><td>
</td><td>Linear.
180° angle.</td></tr>
<tr><td>Three regions of high electron density (bonds and/or unshared pairs)</td><td>
</td><td>Trigonal planar.
All angles 120°.</td></tr>
<tr><td>Four regions of high electron density (bonds and/or unshared pairs)</td><td>
</td><td>Tetrahedral.
All angles 109.5°.</td></tr>
<tr><td>Five regions of high electron density (bonds and/or unshared pairs)</td><td>
</td><td>Trigonal bipyramidal.
Angles of 90° or 120°. An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).</td></tr>
<tr><td>Six regions of high electron density (bonds and/or unshared pairs)</td><td>
</td><td>Octahedral.
All angles 90° or 180°.</td></tr>
</table>

Bonding & Nonbonding Electron Pairs

- The presence of unshared electron pairs affect molecular structure.
- Electron pair geometry: Geometry which includes all electron pairs.
- Molecular geometry: The structure that includes only the placement of atoms in the molecule.
- Structures are the same if there are no unshared pairs.

Bonding & Nonbonding Electron Pairs

- Structures differ with unshared pairs.
- Both shared (bonding) and unshared (nonbonding) electron-pairs form regions of high electron density.
- Electrostatic repulsion pushes these electron dense regions as far apart as possible.
- Small distortions may occur due to differences in electrostatic strengths.

Regions of High Electron Density (bonds and unshared pairs.)	Molecular Geometries and Examples (chemical bonds are indicated in black, unshared pairs in red)			
Three: trigonal planar arrangement of bonds and/or unshared pairs	 3 Bonds 0 Unshared pairs Trigonal planar CO_3^{2-}, BF_3, NO_3^-	 2 Bonds 1 Unshared pairs Bent (about 120°) NO_2^-, ClNO		
Four: tetrahedral arrangement of bonds and/or unshared pairs	 4 Bonds 0 Unshared pairs Tetrahedral NH_4^+, CH_4	 3 Bonds 1 Unshared pairs Trigonal pyramidal H_3O^+, PCl_3, NH_3	 2 Bonds 2 Unshared pairs Bent (about 109.5°) NH_2^-, H_2O	
Five: trigonal bipyramidal arrangement of bonds and/or unshared pairs	 5 Bonds 0 Unshared pairs Trigonal bipyramidal PF_5, $SnCl_5^-$	 4 Bonds 1 Unshared pairs Seesaw SF_4, ClF_4^-	 3 Bonds 2 Unshared pairs T-shaped ICl_3, ClF_3	 2 Bonds 3 Unshared pairs Linear I_3^-, ClF_2^-
Six: octahedral arrangement of bonds and/or unshared pairs	 6 Bonds 0 Unshared pairs Octahedral PCl_6^-, SF_6, IF_6^+	 5 Bonds 1 Unshared pairs Square pyramidal IF_5, XeF_5^+	 4 Bonds 2 Unshared pairs Square Planar ICl_4^-, XeF_4	

Rules for Predicting Electron-Pair and Molecular Geometry

- *Draw the Lewis Structure*
- *Determine the number of regions of high electron density*
- *Determine the most stable arrangement*
- *Identify the molecular structure*

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Molecular Polarity

- *Polar molecules: Any molecule having one positive and one negative end.*
- *Polar molecules occur due to the formation of polar bonds.*
  - *Positive end: $\sigma+$*
  - *Negative end: $\sigma-$*
- *Dipole moment: A measure of the polarity of a molecule.*

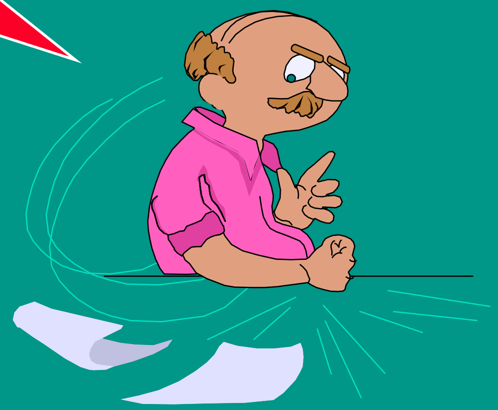
Valence Bond Theory

Hybridization of Atomic Orbitals

Orbital overlap:
A portion of two orbitals overlapping the same region of space

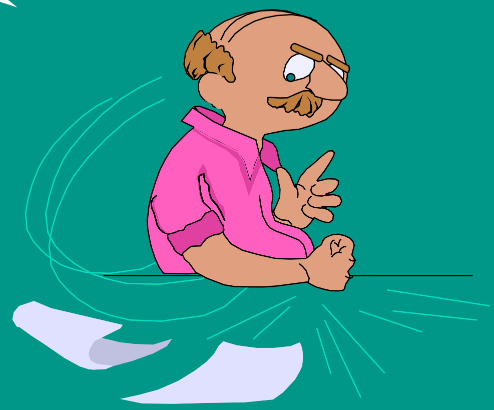
Sigma Bonds
(σ bonds)

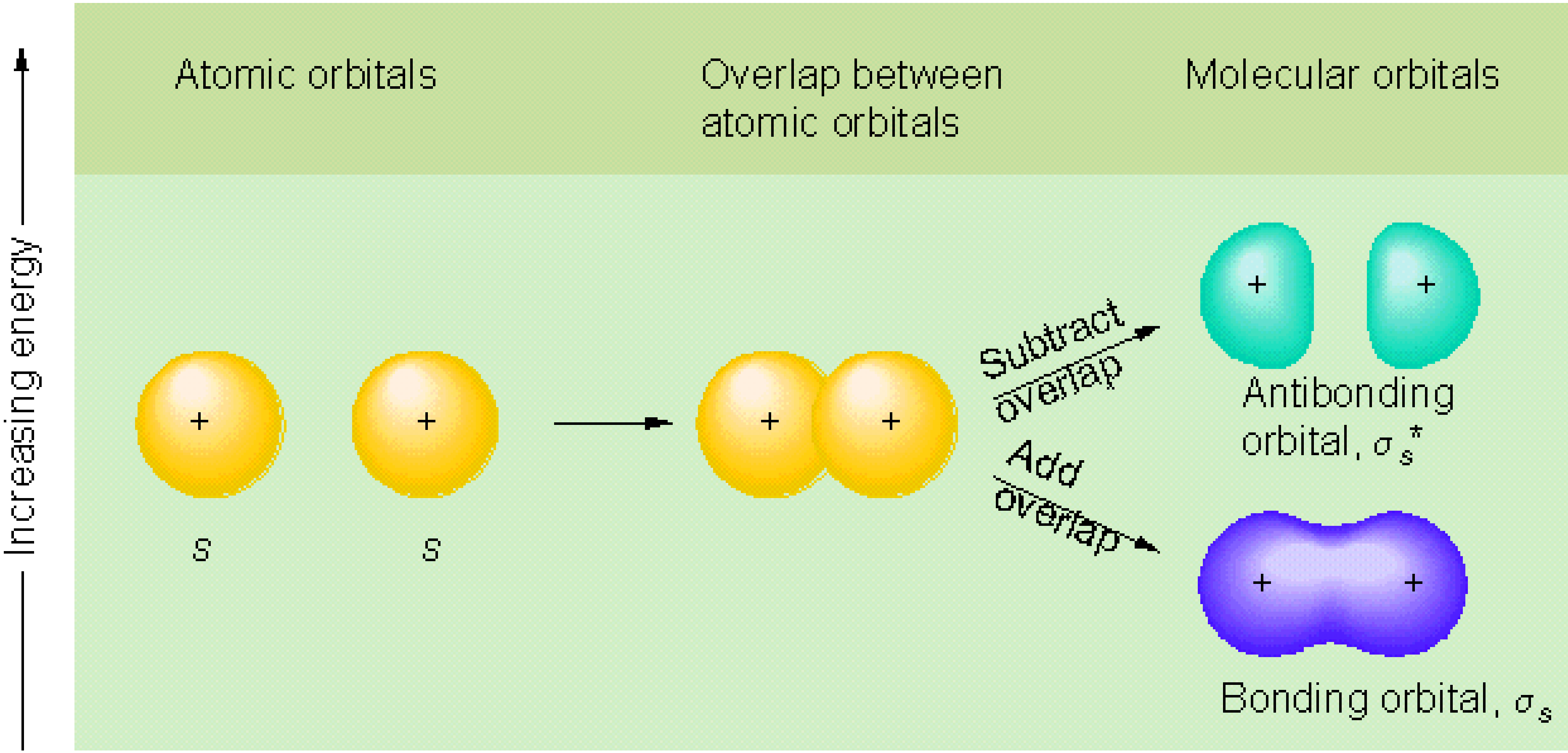
A covalent bond in which the electron density is concentrated in the region between the two nuclei

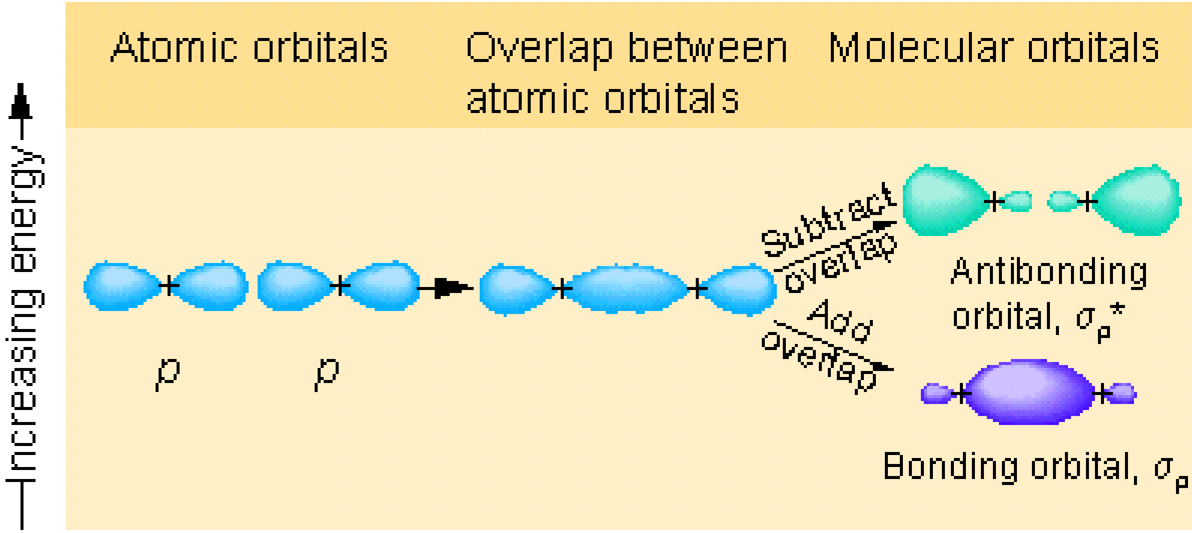


Pi Bonds
(π bonds)

A covalent bond in which the electron dense regions overlap above and below the internuclear axis

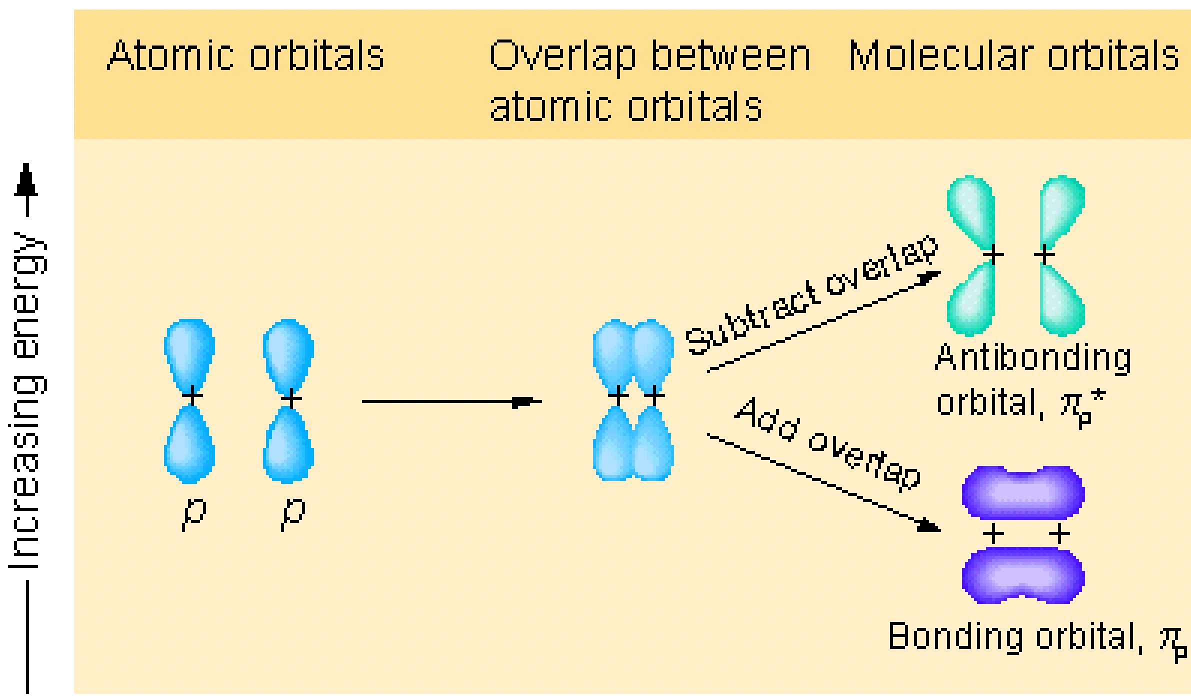



Increasing energy
Atomic orbitals
Overlap between
atomic orbitals
Molecular orbitals
s
s
Subtract
overlap
Add
overlap
Antibonding
orbital, σ_s^*
Bonding orbital, σ_s



Atomic orbitals
Overlap between atomic orbitals
Molecular orbitals
Increasing energy
Subtract overlap
Add overlap
Antibonding orbital, σ_p^*
Bonding orbital, σ_p
p
p

(A)



Atomic orbitals
Overlap between atomic orbitals
Molecular orbitals
Increasing energy
Subtract overlap
Add overlap
Antibonding orbital, π_p^*
Bonding orbital, π_p
p
p

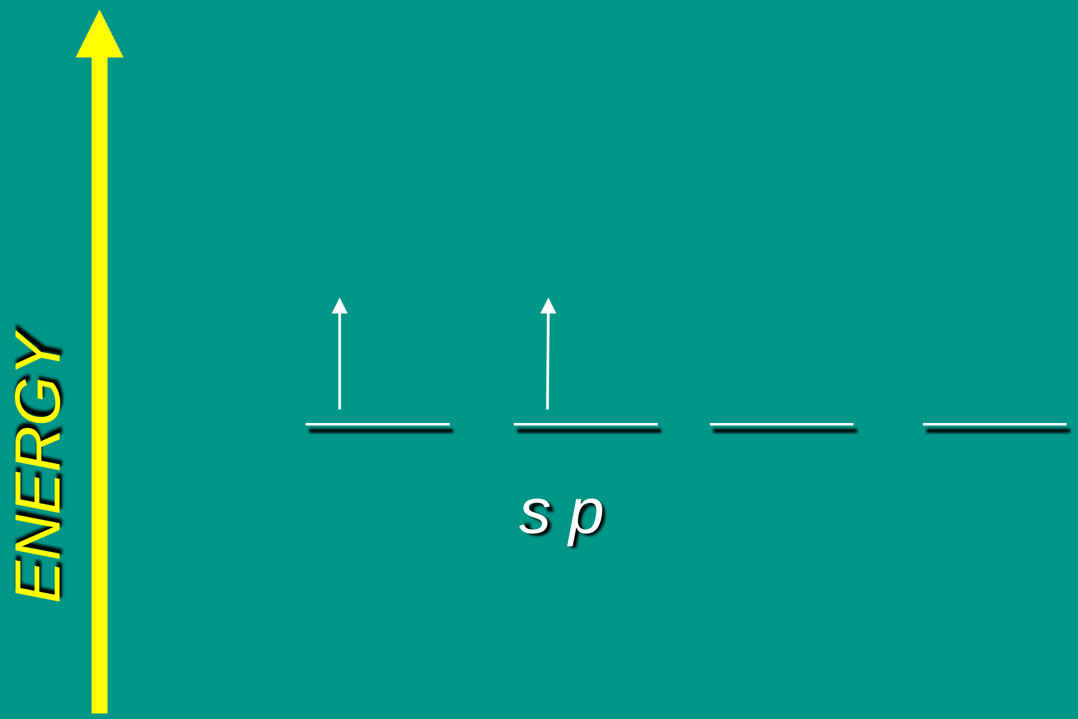
(B)

Hybridization

The mixing of atomic orbitals of an isolated atom to form hybrid orbitals

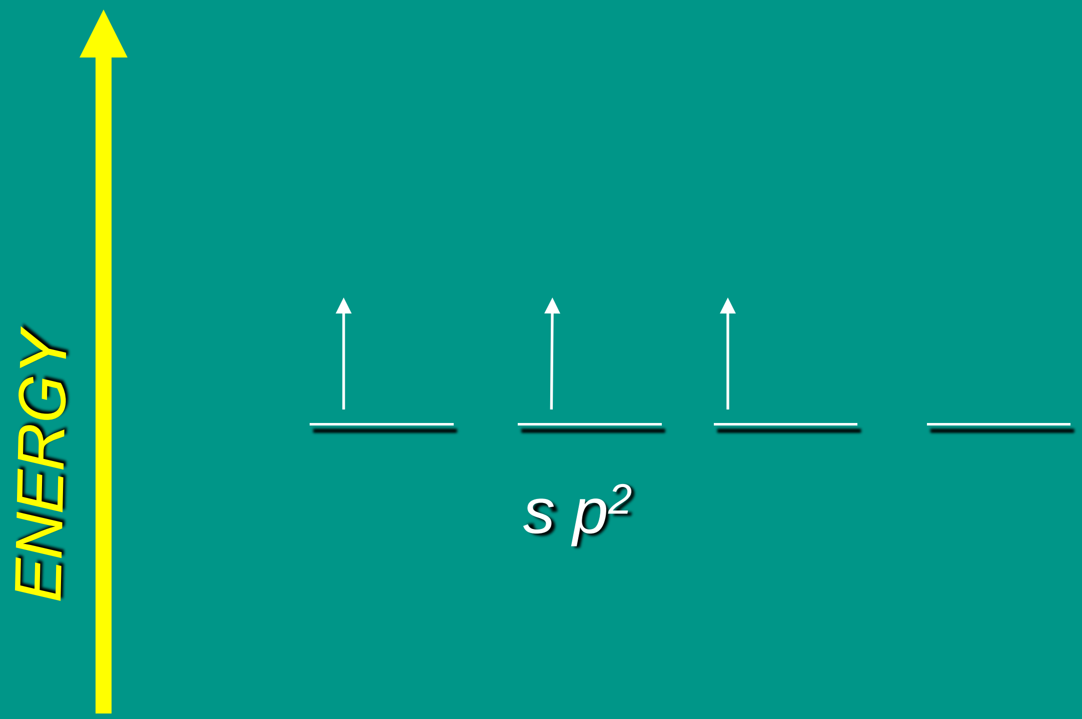
Sp Hybridization

Sp Hybridization

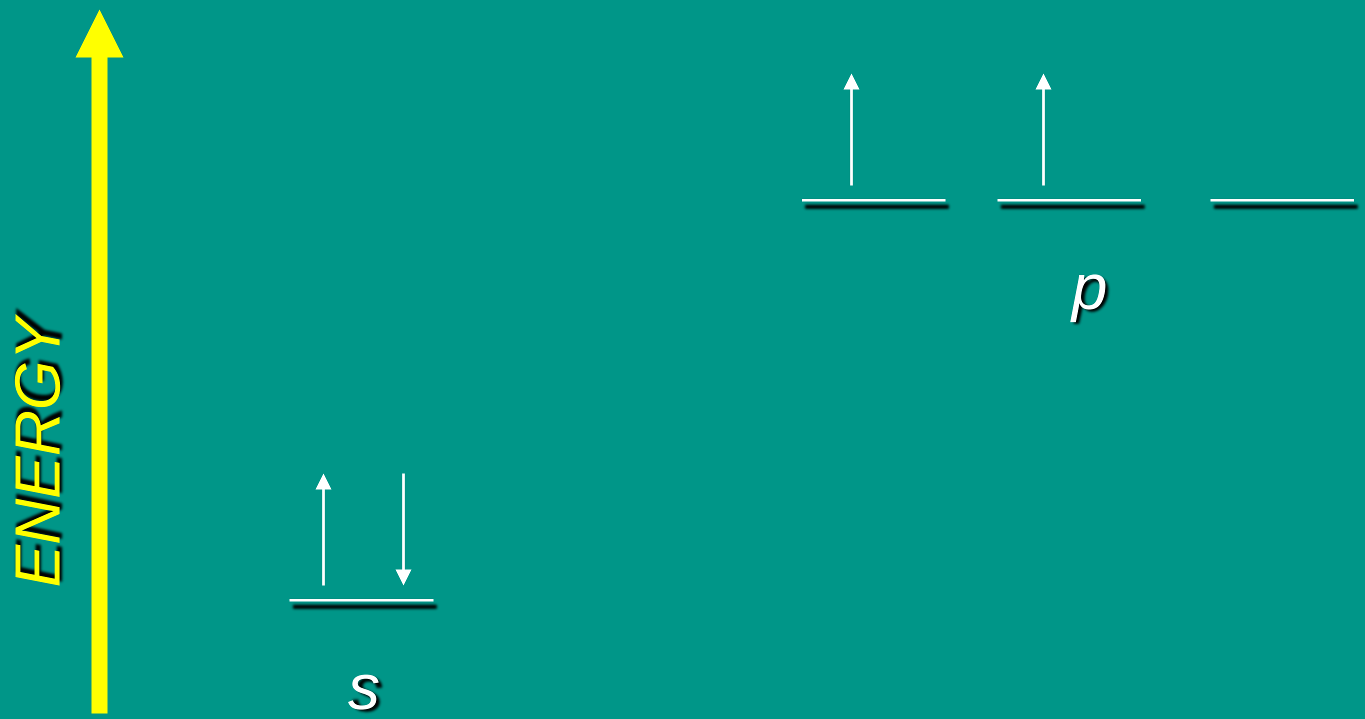


Sp^2 Hybridization

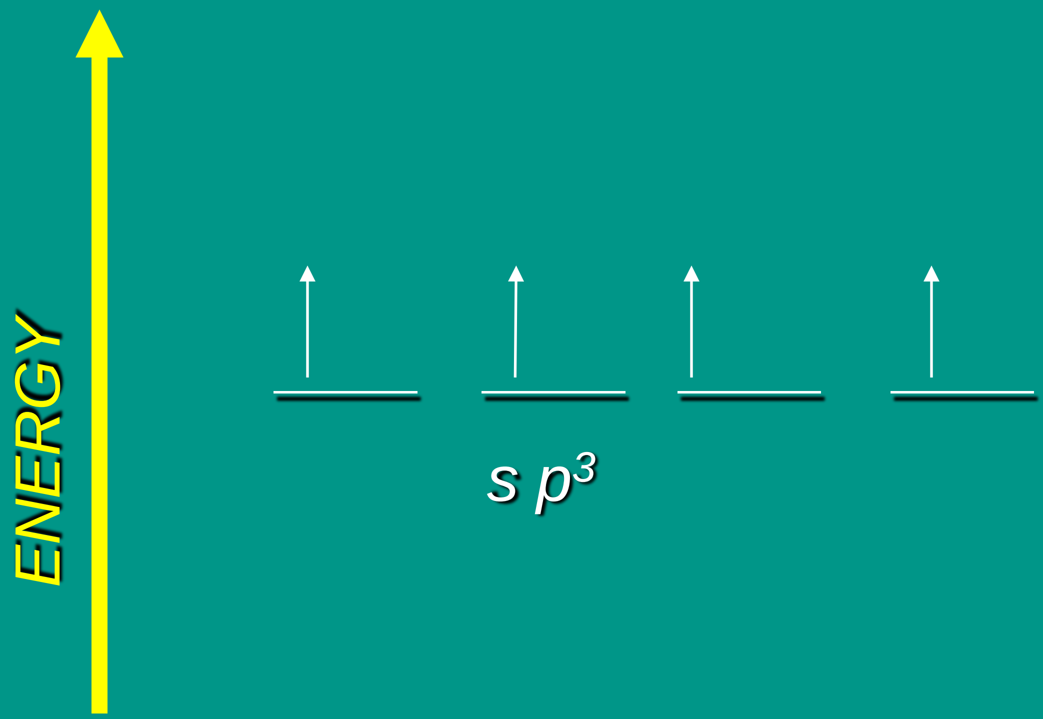
Sp^2 Hybridization



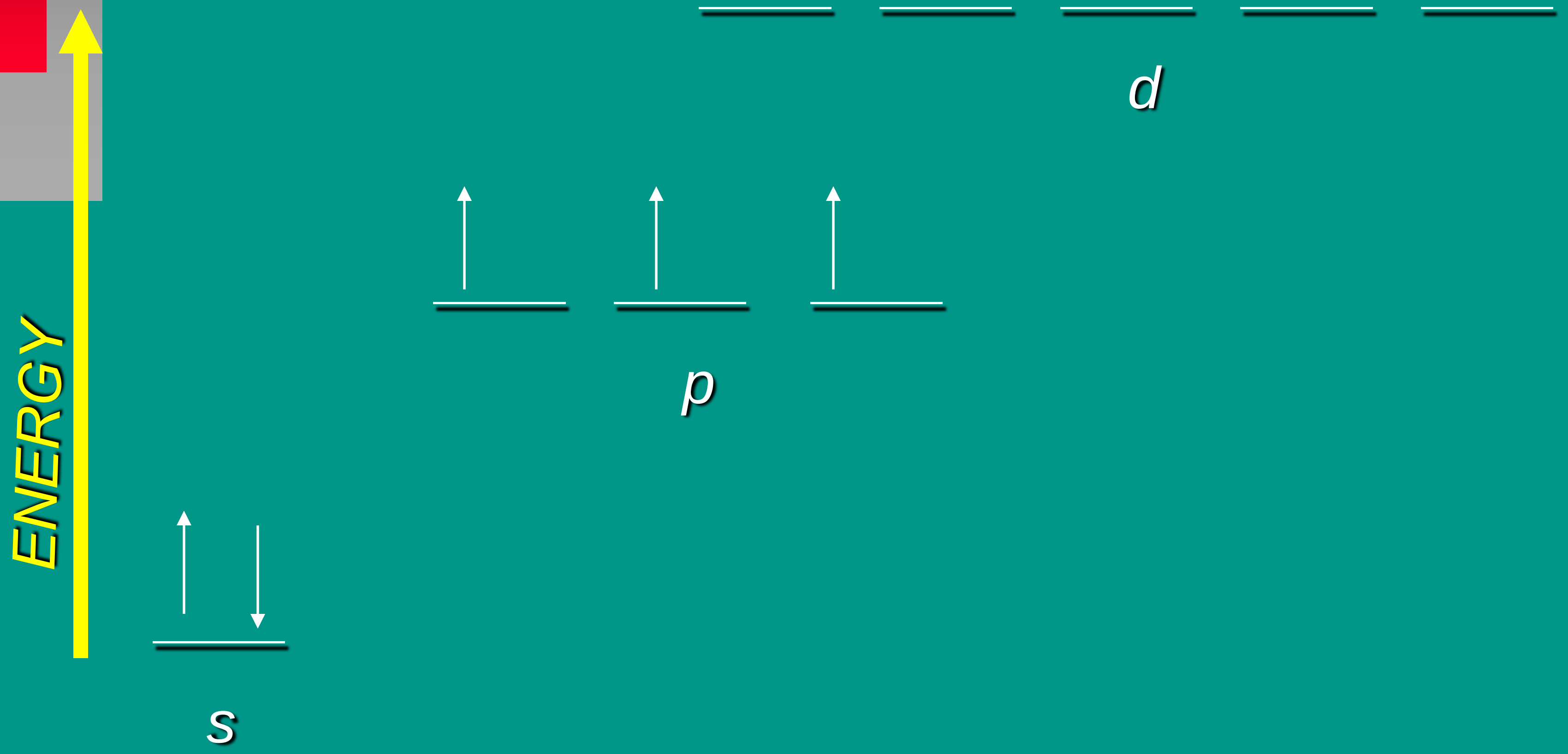
Sp^3 Hybridization



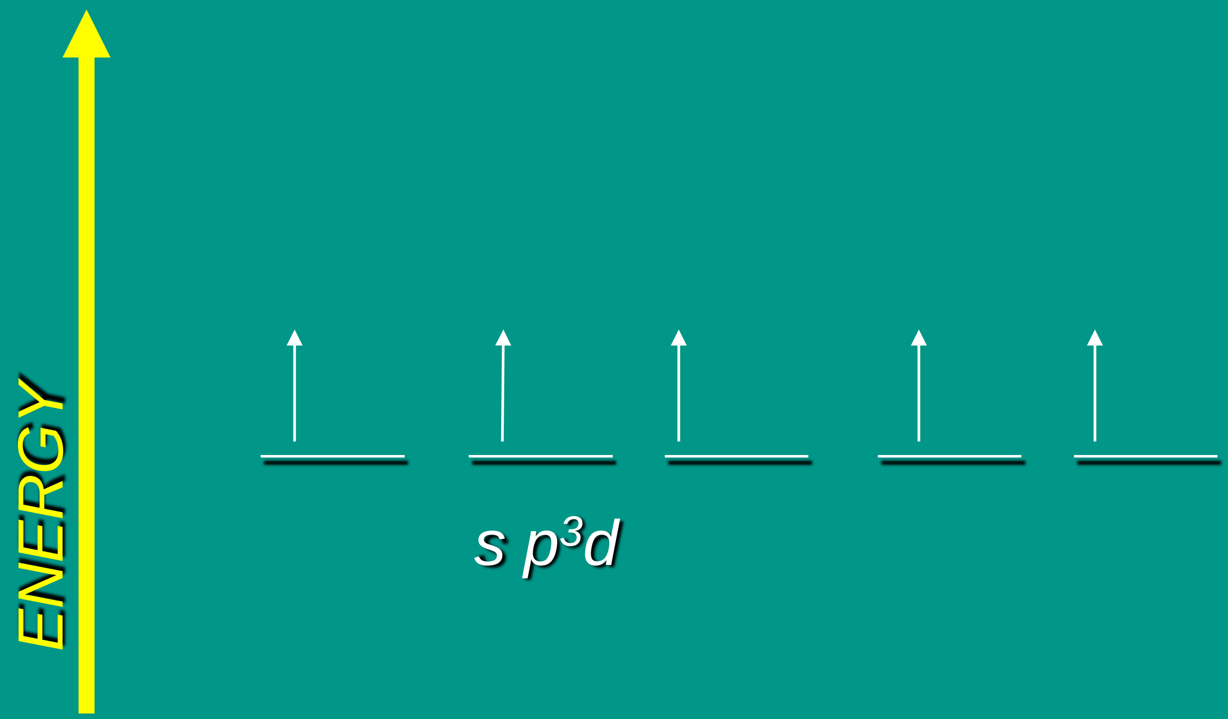
Sp^3 Hybridization



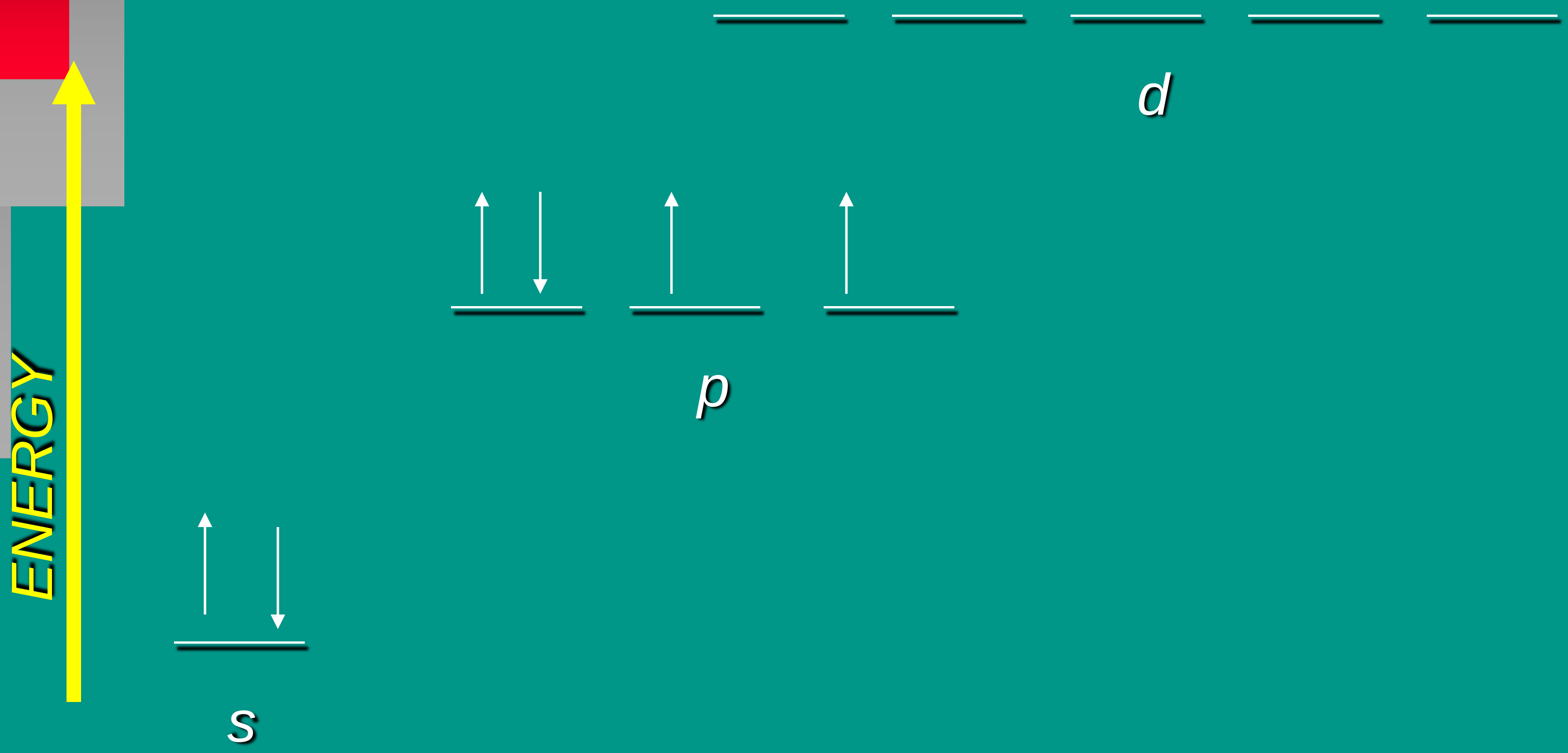
Sp³d Hybridization



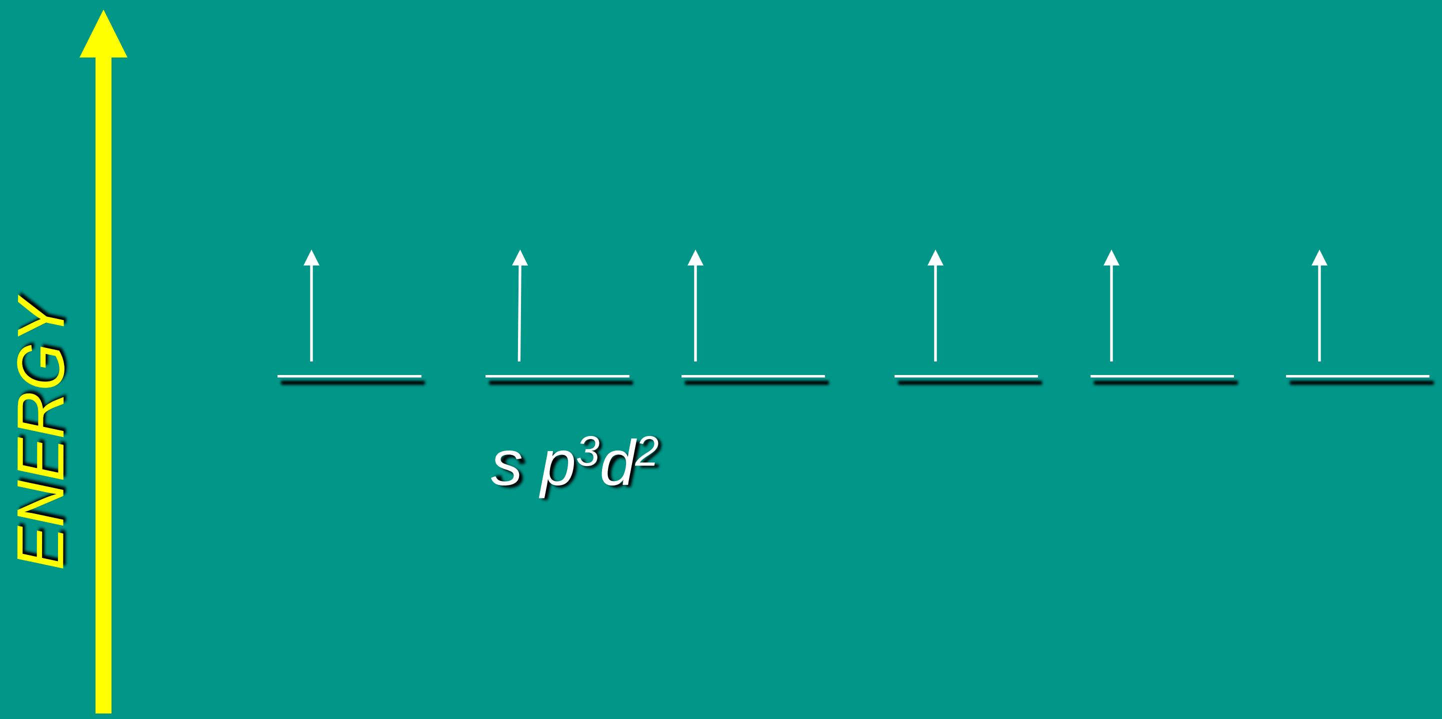
Sp^3d Hybridization



$Sp^3d\,^2$Hybridization



Sp^3d^2 Hybridization



Assigning Hybrid Orbitals

- Determine the Lewis structure
- Determine the electron-pair geometry
- Assign a set of hybridized orbitals

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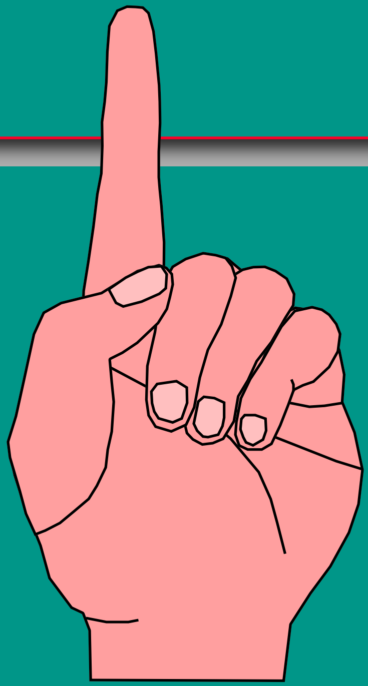
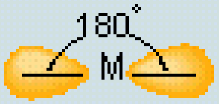
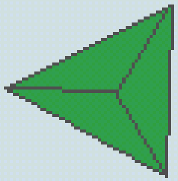
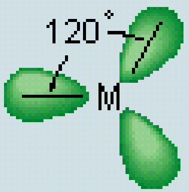
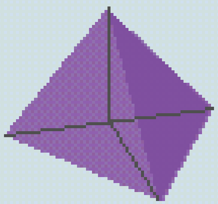
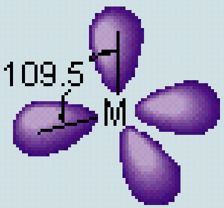
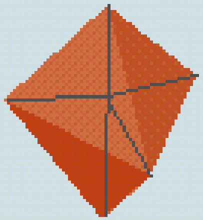
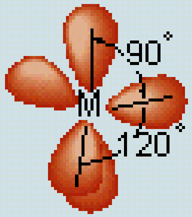
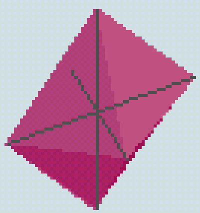
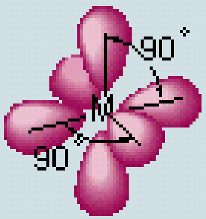
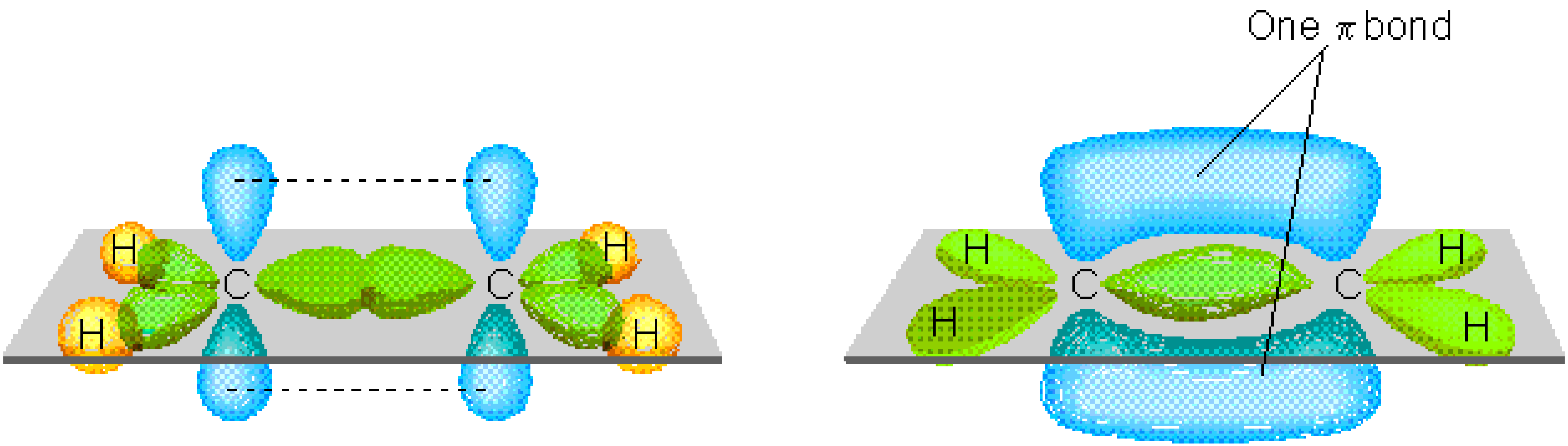


Remember!!!

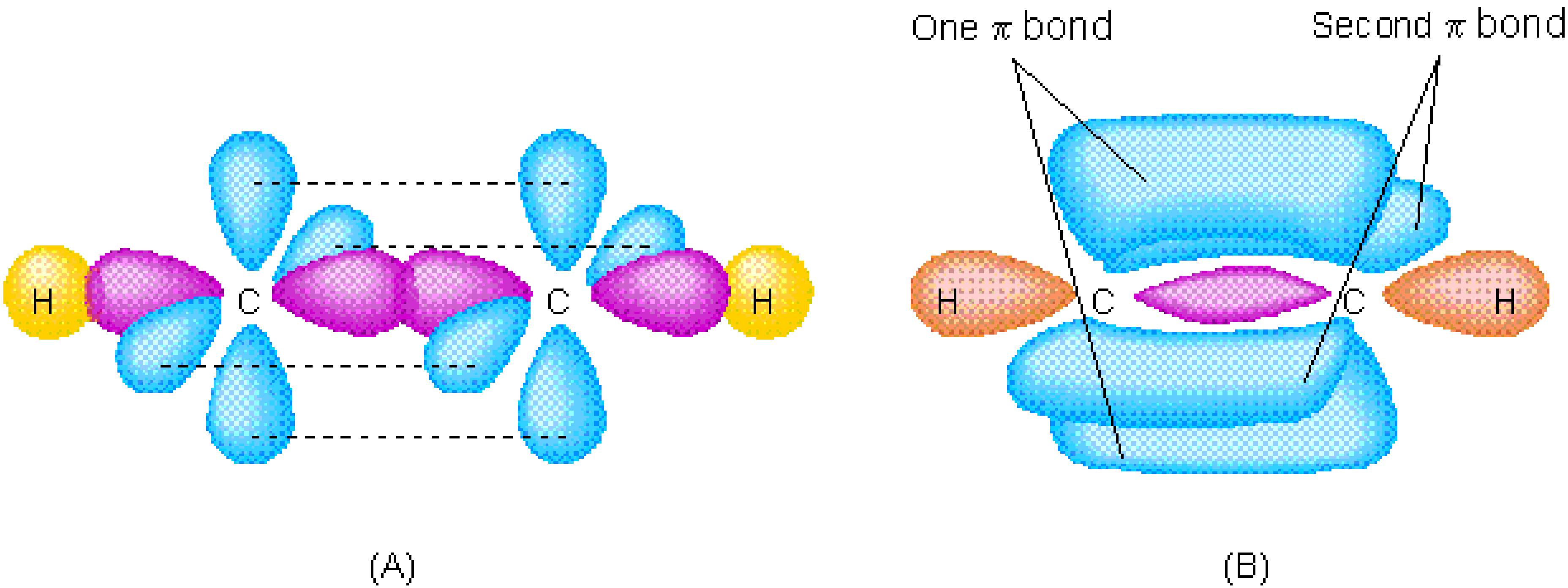
Only sigma bonds form hybrid orbitals

Regions of Electron Density	Arrangement		Hybridization	
2		Linear	*sp*	
3		Trigonal planar	sp^2	
4		Tetrahedral	sp^3	
5		Trigonal bipyramidal	sp^3d	
6		Octahedral	sp^3d^2	

Hybridization Involving Double & Triple Bonds



(A) (B)


H
C
C
H
(A)
One π bond
Second π bond
H
C
C
H
(B)

Let's Close the Door on this one!!