Chapter 10 - Molecular Structure and Bonding Theories

Section 2 – Hybridization and MO Theory

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Bonding Theory

A bond forms when singly occupied orbitals from two atoms overlap. The total number of electrons in both orbitals should be two. As we learned the greater the orbital overlap, the stronger the bond. All orbitals, except s orbitals, because they are spherical in shape, bond in the direction in which they point, to obtain maximum overlap.

This theory works well for H_2 in which both H atoms have the same s^1 electrons – so orbital still has space for one more electron. It also works for F_2 where the orbital overlap will be p overlap as that is the singly occupied orbital.

But it does not work in cases where there are different types of orbitals will overlap to form bonds. For example, in carbon, the electron configuration is $2s^2$ sp^2 orbitals and has four bonds. Technically $2s^2$ should not be able to form overlaps because it is already occupied by two electrons. And then there is orbital shape problem….

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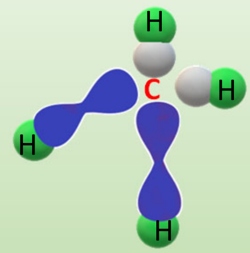
Methane Molecule According to Lewis Theory

Methane, CH_4 where C is central atom: $1s^2\ 2s^2\ 2p^2$

The valence electrons for bonding are in the s (spherical) and p (dumbbell) orbitals.

The orbital overlap for bonding will be two different kinds for the two orbitals. From a glance it seems that two bonds will be longer and two shorter and the bond energy will be different too.

However, in experimentals, all bonds have equal length and strength, therefore, there must be a different theory on how covalent bonds are formed.



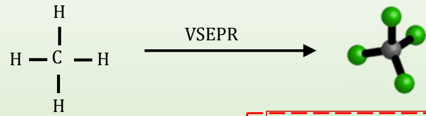
Hybridization

Hybrid orbitals are formed by mixing orbitals, and are named by using the atomic orbitals that combined:

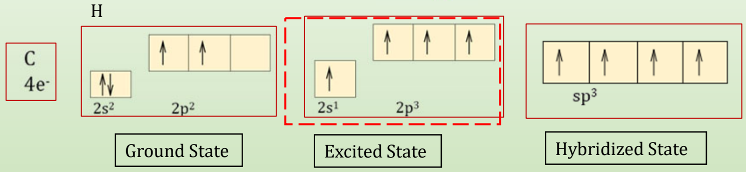
- one *s* orbital + one *p* orbital = two ***sp*** orbitals
- one *s* orbital + two *p* orbitals = three $\boldsymbol{sp^2}$ orbitals
- one *s* orbital + three *p* orbitals = four $\boldsymbol{sp^3}$ orbitals
- one *s* orbital + three *p* orbitals + one *d* orbital = five $\boldsymbol{sp^3d}$ orbitals
- one *s* orbital + three *p* orbitals + two *d* orbitals = six $\boldsymbol{sp^3d^2}$ orbitals

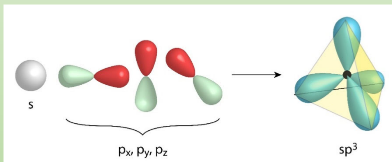
NOTE: All hybridized bonds are called sigma (σ) bonds.

sp^3 — Example: Methane, CH_4

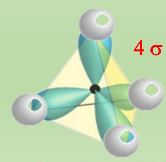


- tetrahedral
- all bonds equivalent





The sp^3 hybrid orbitals point to the corners of a tetrahedron.



Each C $2sp^3$ orbital overlaps a H $1s$ orbital to yield CH_4.

4H [↑] ($1s^1$) **+ C** [↑ ↑ ↑ ↑] (sp^3) ⟶ **CH_4**

All bond angles 109.5°.

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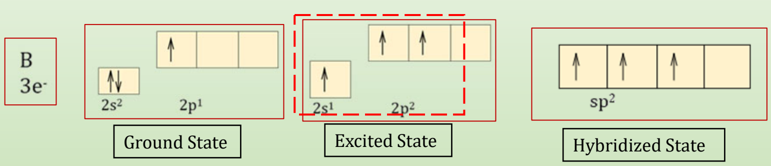
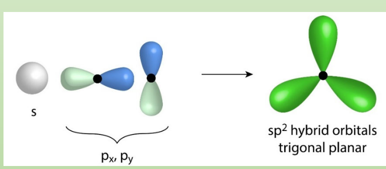
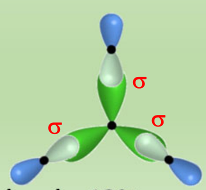
sp^2 — Example: Boron trifluoride, BF_3

- trigonal planar
- all bonds equivalent





The three sp^2 orbitals point to the corners of an equilateral triangle.



Each B sp^2 orbital overlaps with p orbital of F to yield BF_3.

3F [↓↑] ($2s^2$) [↓↑ ↓↑ ↑] ($2p^5$) **+ B** [↑ ↑ ↑] (sp^2) ⟶ **BF_3**

All bond angles 120°.

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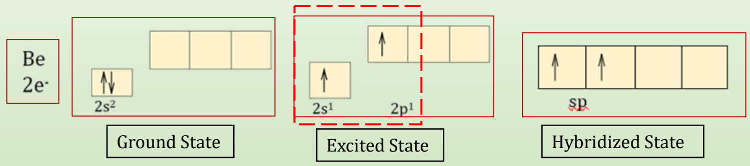
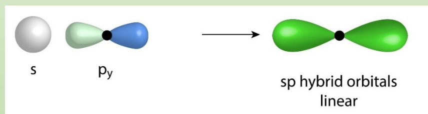
sp **Example: Beryllium Chloride, $BeCl_2$**

Cl— Be —Cl → (VSEPR)

- linear
- both bonds equivalent





The two *sp* orbitals point in opposite directions inline with one another.

Each Be *sp* orbital overlaps with *p* orbital of Cl to yield $BeCl_2$.

$BeCl_2$

Bond angle 180°.

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How to Determine Hybridization

To find the hybridization on the central atom in a molecule:

1. Write the Lewis electron-dot formula.
2. Use AXE to determine the electron geometry about the atom.
3. From the electronic geometry deduce the hybrid orbitals. For example, if AXE formula is AX_2E – there are 3 electron groups therefore 3 orbitals which implies sp^2 (also three orbitals).
4. Assign the valence electrons to the hybrid orbitals one at a time, pairing only when necessary.

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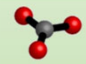
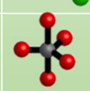
Hybridization Chart

Lewis structure → Number of electron domains → Type of hybridization

AXE formula	Electron groups	Hybrid orbitals	Electronic Geometry	3D shape
AX_2	2	Sp	Linear	
AX_3	3	Sp^2	Trigonal planar	
AX_4	4	Sp^3	Tetrahedral	
AX_5	5	Sp^3d	Trigonal bipyramidal	
AX_6	6	Sp^3d^2	Octahedral	

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Hybridized Orbital Characteristics

Electron Groups	AXE formula	Bond Angle	E.g.	Electronic Geometry	Hybridization	Shape of Molecule
2	AX_2	180°	$BeCl_2$	Linear	sp	Linear
3	AX_3	120 °	BF_3	Trigonal planar	sp^2	Trigonal planar
3	AX_2E	120 °	SO_2	Trigonal planar	sp^2	Bent
4	AX_4	109.5 °	CH_4	Tetrahedral	sp^3	Tetrahedral
4	AX_3E	109.5 °	NH_3	Tetrahedral	sp^3	Trigonal Pyramidal
4	AX_2E_2	109.5 °	H_2O	Tetrahedral	sp^3	Bent
5	AX_5	90 °, 120 °, 180 °	PCl_5	Trigonal bipyramidal	sp^3d	Trigonal Bipyramidal
5	AX_4E	90 °, 120 °, 180 °	SF_4	Trigonal bipyramidal	sp^3d	Seesaw
5	AX_3E_2	90 °, 180 °	CIF_4	Trigonal bipyramidal	sp^3d	T – shape
5	AX_2E_3	180 °	XeF_2	Trigonal bipyramidal	sp^3d	Linear
6	AX_6	90 °, 180 °	SF_6	Octahedral	sp^3d^2	Octahedral
6	AX_5E	90 °	BrF_5	Octahedral	sp^3d^2	Square Pyramidal
6	AX_4E_2	90 °	XeF_4	Octahedral	sp^3d^2	Square Planar
6	AX_3E_3	90 °, 180 °		Octahedral	sp^3d^2	T – Shape
6	AX_2E_4	180 °		Octahedral	sp^3d^2	Linear

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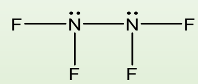
Solved Problem: Determining hybridization type

Use hybridization to give the hybridization and shape of N atom in N_2F_4.



1) The Lewis electron-dot structure shows three bonds and one lone pair around each N atom.
2) This is four electron groups (accurately: AX_3E) for central atom.
3) Therefore, a tetrahedral electron geometry.
4) A tetrahedral arrangement has sp^3 hybrid orbitals.
5) The shape will be trigonal pyramidal for both nitrogen atoms.

Hybridization of Multiple Bonds

Some single bonds are formed by simple orbital overlap e.g., in H-H bond it is a s-s overlap.

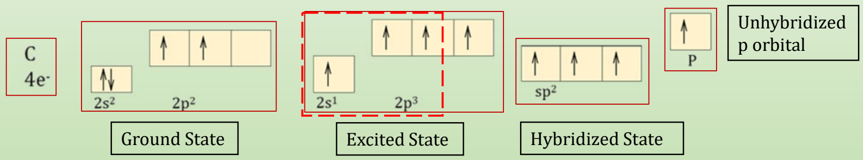
Some single bonds are hybridized (as discussed in previous slides). These are called **sigma bonds**.

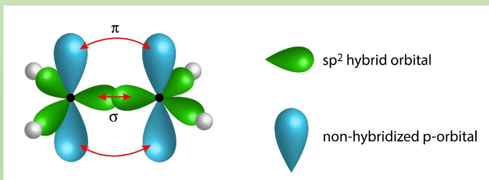
Multiple bonds, double and triple bonds have different kind of orbital overlap.

Ethylene – $CH_2=CH_2$

$$H_2C=CH_2$$

- Number of e- domains = 3
- Hybridization = sp^2 (shape = trigonal planar, bond angle = 120°)
- There are two central atoms; both carbon.
- Each carbon will mix 1 of s and 2 of p orbitals; 1 of p is left over and this forms the pi bond.





Double bond = **1 σ bond** + **1 π bond**

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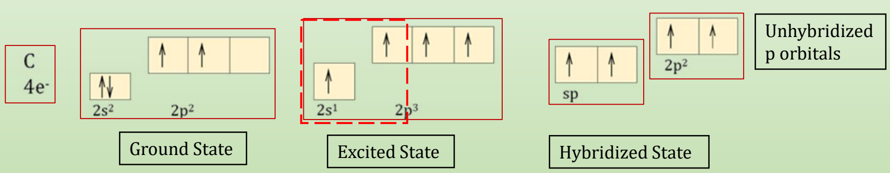
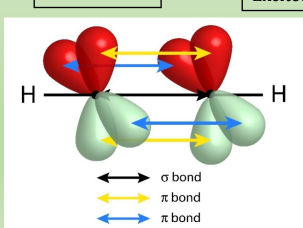
Acetylene C_2H_2

H–C≡C–H

- Number of e- domains = 2
- Hybridization = sp (shape = linear, bond angle = 180°)
- There are two central atoms; both carbon.
- Each carbon will mix 1 of s and 1 of p orbitals; 2 of p orbitals are left over and this form two pi bonds.





Triple bond = **1 σ bond** + **2 π bonds**

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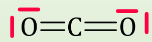
Solved Problem: Predicting hybridization of multiple bonds
What is the hybridization on the central atom in CO_2 and SO_4^{2-}?

CO_2 molecule.

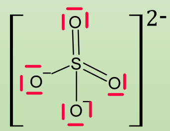
1) First draw the Lewis structure.



2) It has carbon as central atom and two oxygen atoms as terminal atoms.
3) The electronic geometry is AX_2.
4) The hybridization on carbon therefore is sp.

SO_4^{2-} ion.

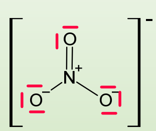
1) The Lewis structure is as follows:



1) Sulfur is the central atom with O terminal atoms.
2) The electronic geometry is AX_4.
3) The hybridization on sulfur is still sp^3.

Solved Problem: Predicting hybridization of multiple bonds
What is the hybridization on the central atom in nitrate ion?

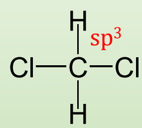
1) Lewis structure is



2) Electronic geometry of N is AX_3
3) Hybridization of a three electron group atom is sp^2.

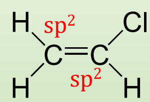
Solved Problem: Counting pi and sigma bonds

How many pi bonds and sigma bonds are in each of the following molecules? Describe the hybridization of each C atom.



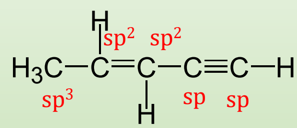
(a)

(a) 4 sigma bonds



(b)

(b) 5 sigma bonds, 1 pi bond



(c)

(c) 10 sigma bonds, 3 pi bonds

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Molecular Orbital Theory

All atoms have atomic orbitals (AO), which when bond and overlap with other atomic orbitals will form molecular orbitals (MO).

The number of AO combining will form the same number of MO. Two atomic orbitals will combine to form two molecular orbitals. (4 AO will give 4 MO etc.)

How the orbitals are combining depends on energy and orientation. (Wavefunctions - + and – regions)

- Half the of MO are bonding with low energy and half will be antibonding at a higher energy level. Electrons usually will be found in the bonding MO.
- Bonding MO are obtained by adding atomic orbitals of similar wavefunction (e.g. ψ+ and ψ+).
- Antibonding MO are obtained by subtracting or opposite wavefunction atomic orbitals (e.g. ψ+ and ψ-).

(read more at: chem.libretexts.org)

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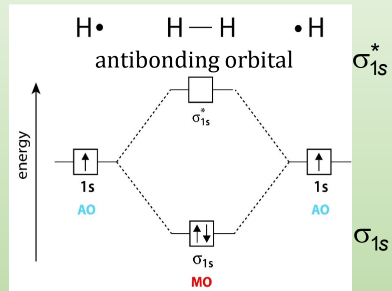
Molecular Orbital Theory

$H + H \rightarrow H_2$

$1s^1 \quad 1s^1 \qquad \sigma_{1s}{}^2$

Two atomic orbitals, both s^1 with one electron each, form 2 MO. These new MO are sigma bonds, one is higher in energy, antibonding, while the other is bonding MO at a lower energy. The two electrons are found in the bonding MO.



bonding orbital

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Key Points

- Valence bond theory
- Hybridization of atomic orbitals
  - *s* and *p*
  - *s*, *p,* and *d*
- Hybridization involving multiple bonds
- Molecular orbital theory
  - Bonding and antibonding orbitals

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