Molecular Geometry and Bonding Theories

What do the molecules look like and why?

Valence Shell Electron Pair Repulsion Theory (VSEPR)

- VSEPR is a model of how molecules arrange themselves and get their shape.
- It is based on the idea that the groups of electrons around the central atom will repel one another to get as far away from each other as possible.

2

VSEPR

- In this class we will explore 5 possibilities for the arrangement of groups of electrons around the central atom
  - 2 groups of electrons
  - 3 groups of electrons
  - 4 groups of electrons
  - 5 groups of electrons
  - 6 groups of electrons

3

2 Groups of electrons

- When a molecule has 2 groups of electrons around the central atom they will arrange themselves in space to be as far from each other as possible.
- The optimum arrangement is for the groups of electrons to be 180° apart.
- This gives a linear molecule.

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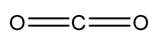

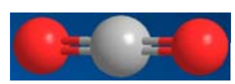

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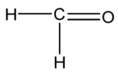
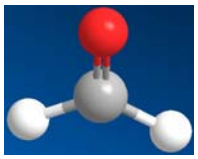
3 Groups of electrons

- When a molecule has 3 groups of electrons around the central atom they will arrange themselves in space to be as far from each other as possible.
- The optimum arrangement is for the groups of electrons to be 120° apart.
- This gives a molecule with a shape called trigonal planar.

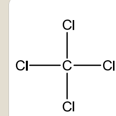
6

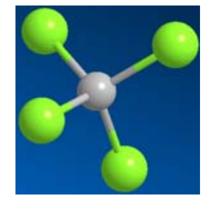




- When a molecule has 4 groups of electrons around the central atom they will arrange themselves in space to be as far from each other as possible.
- The optimum arrangement is for the groups of electrons to be 109.5° apart.
- This gives a tetrahedral molecule.

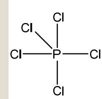
4 Groups of electrons

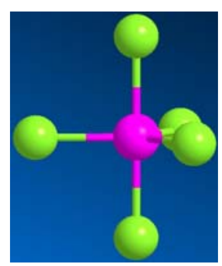




- When a molecule has 5 groups of electrons around the central atom they will arrange themselves in space to be as far from each other as possible.
- The optimum arrangement is for the groups of electrons to be 120° and 90° apart.
- This gives a trigonal bipyramidal molecule.

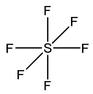
5 Groups of electrons

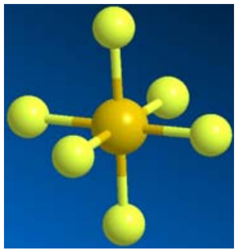




- When a molecule has 6 groups of electrons around the central atom they will arrange themselves in space to be as far from each other as possible.
- The optimum arrangement is for the groups of electrons to be 90° apart.
- This gives a octahedral molecule.

6 Groups of electrons





- These geometries are what I call electron group geometries (EGGs). These are the ONLY possibilities for this.

2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

Electron Group Geometry (EGG)

- Molecular geometries are the shapes of the molecules when we look at the ***bonding groups*** of electrons.
- The ***non-bonding groups*** are the lone pairs and do affect the geometry slightly.
- If there are no lone pairs on the central atom, the molecular and electron group geometries are the same.

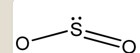
Molecular geometries

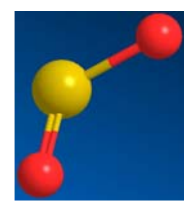
- When we have two groups of electrons, regardless of whether they are bonding or non-bonding, the molecular geometry is always linear. ($BeCl_2$ or CO)

2 groups of electrons

- If there is one lone pair of electrons on the central atom the molecular geometry is called bent. (SO_2)
- Again with no lone pairs the molecular and electron group geometry is the same, trigonal planar.

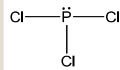
3 groups of electrons





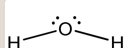
- One lone pair gives rise to a molecular geometry called trigonal pyramidal. (PCl_3)

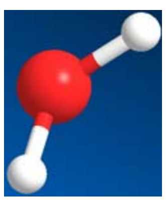
4 groups of electrons



- Two lone pairs gives a molecular geometry called bent (H_2O).
  - This bent is slightly different than that with 3 groups and one lone pair. The bond angle here is smaller.

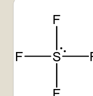
4 groups of electrons

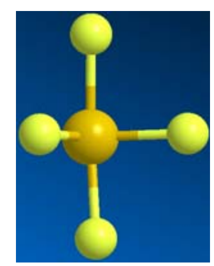




- 1 lone pair give a molecular geometry called see-saw (SF_4)

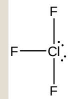
5 groups of electrons

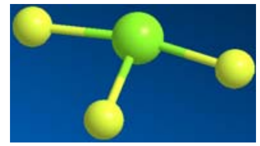




- 2 lone pairs has a shape called T-shaped (ClF_3)

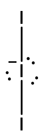
5 groups of electrons





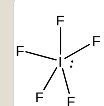
- 3 lone pairs gives a linear molecule (I_3^-)

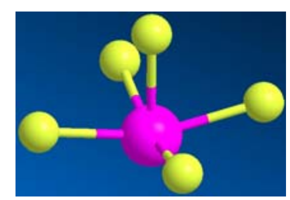
5 groups of electrons



- 1 lone pair gives a shape called square pyramidal (IF_5)

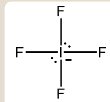
6 groups of electrons

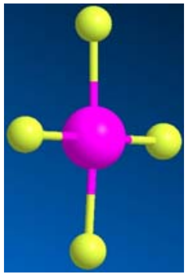




- 2 lone pairs gives a geometry called square planar (IF_4^-)

6 groups of electrons



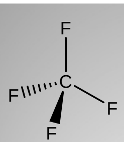


- PO_4^{3-}
- SO_3^{2-}
- $SbCl_5$
- SCl_6

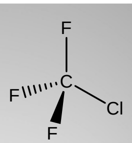
Draw Lewis structures and give geometries

- Just as bonds can be polar, so can molecules.
- If the polar bonds in a molecule are arranged symmetrically, the molecule will be non-polar.
- An asymmetrical arrangement of polar bonds leads to a polar molecule.

Molecular geometry and polarity



The bonds are polar and symmetrically arranged. The molecule is ***non-polar.***



The bonds are polar and asymmetrically arranged. The molecule is ***polar.***

Molecular geometry and polarity

- NO_2
- PH_3
- $CSCl_2$
- SF_4

Draw Lewis Structures, give geometries and polarity

Bonding of covalent molecules

- Model: valence bond theory.
- Covalent bonds form when their orbitals overlap.
- Not the entire picture.

Bonding in carbon

- According to the orbital diagram for carbon, it should only be able to form 2 bonds.

↑↓ ↑ ↑
2s 2p

Only these two orbitals can form bonds.

Something else must be happening.

Bonding in carbon

- When carbon forms bonds it rearranges its valence electrons.

↑↓ ↑ ↑ becomes ↑ ↑ ↑ ↑
2s 2p 2s 2p

- This is still not complete
  - all of the bonds in CH_4 are equivalent
  - the 2p orbitals won't give the correct bond angles.

Bonding in carbon

- Can be resolved.

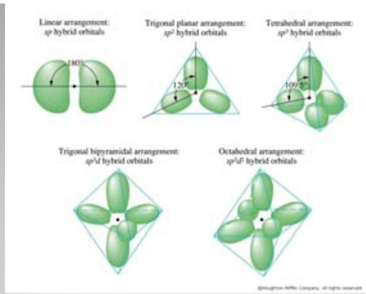
↑ ↑ ↑ ↑ becomes ↑ ↑ ↑ ↑
2s 2p sp^3

- New orbitals formed
  - hybrid orbitals
  - equivalent in energy
  - correct orientation in space

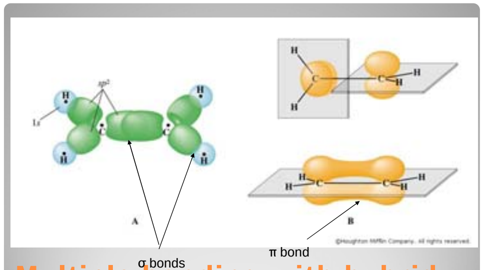
Hybrid orbitals

- Hybrid orbitals are different for each electron geometry

2	linear	sp
3	trigonal planar	sp^2
4	tetrahedral	sp^3
5	trigonal bipyramidal	sp^3d
6	octahedral	sp^3d^2



Hybrid orbitals



Multiple bonding with hybrid orbitals (double bonds)

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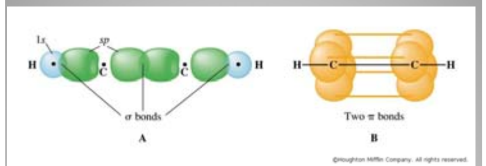

Multiple bonding with hybrid orbitals (triple bonds)

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- SeF_5^+
- SO_4^{2-}
- CH_2Cl_2
- NO_2^-

Draw Lewis structures, give geometries, polarity, hybridization and number of σ and π bonds

45

- Molecular orbital theory
  - still requires atomic orbital overlap
  - does not give the geometry easily
  - does give the magnetism of the molecule
- We'll look at only diatomic molecules for this theory

Another bonding model

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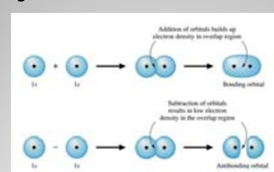
- Orbitals can overlap in two ways
  - energies can add – bonding orbital
  - energies can subtract – anti-bonding orbital



Atomic orbitals overlap

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- Two types of molecular orbitals
  - σ orbitals (can be bonding or anti-bonding)
    - comes from s orbitals
    - p orbitals that overlap end-to-end
  - π orbitals (can be bonding or anti-bonding)
    - comes from p orbitals that overlap side-to-side

Molecular orbitals from atomic orbitals

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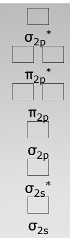


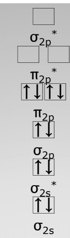
Electrons will fill this following the same rules as before

•Pauli Exclusion Principle

•Hund's Rule

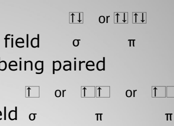
Molecular orbital energy level diagram

10 total valence electrons



Molecular orbital energy level diagram of N_2

- Not referring to ferromagnetism – the usual kind of magnetism
- Diamagnetism
  - No effect from a magnetic field
  - Results from all electrons being paired
- Paramagnetism
  - Attracted to a magnetic field
  - Results from unpaired electrons



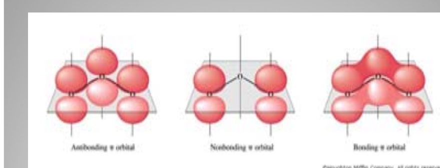
Magnetism of molecules

- O_2^{2-}
- NO

Write MO Energy level diagram and determine magnetism

- Molecular orbital theory gives us a new way of looking at resonance structures
- The molecular orbital stretches across the whole molecule
- This orbital is what we think of as the resonance structures

Molecular Orbital Theory and Resonance



Molecular Orbital Theory and Resonance