Molecular structure: how are the different atoms bonded together (topology) and what is the 3-dimensional configuration (geometry)?

Lewis Theory: Each atom contributes its valence electrons. A covalent bond is formed of 2 e⁻'s and every atom tries to satisfy the octet rule while attaining a formal charge of zero. The 3-dimensional structure is determined by maximizing symmetry and minimizing contacts.

Formal Charge = #valence e⁻ - (#bonds + lone-pair e⁻)

- water
  - $\text{H}_2\text{O}, 8\ e^-$
  - tetrahedral, $\theta \sim 109^\circ$

- formaldehyde
  - $\text{CH}_2\text{O}, 12\ e^-$
  - trigonal planar, $\theta \sim 120^\circ$

- ethylene
  - $\text{C}_2\text{H}_4, 12\ e^-$
  - planar, $\theta \sim 120^\circ$

- nitrate ion
  - $\text{NO}_3^-, 24\ e^-$
Review of Molecular Orbital Theory

Electron (-) charge. NOT a "cloud" of negative charge but a particle w/ wave-like properties. Its location at any point in time is unknown but there is a 99% probability that at any time it can be found within some volume, which is defined as the "orbital".

For any given atom or molecule, there are discrete orbitals defined by energy and shape.

The orbital for a molecule is simply the linear combination of the atomic orbitals for all the atoms involved. For example, to make the \( \text{H}_2 \) molecule:

\[ \text{\ding{183}} + \text{\ding{183}} = ?? \]
Making of Molecular Orbitals: Hydrogen Molecule

\[ \text{[s orbital] is anti-bonding, which means that it has no } e^- \text{ density between the two atoms - i.e., they're not bonded} \]

\[ \text{[p orbital] is defined by the maximum } e^- \text{ density between the atoms above the internuclear axis} \]

Making of Molecular Orbitals: \( \text{[p orbital]} \) Bonds

\[ \text{[p orbital] is anti-bonding, which means that it has no } e^- \text{ density between the two atoms - i.e., they're not bonded} \]

\[ \text{[p orbital] is defined by the maximum } e^- \text{ density between the atoms above the internuclear axis - none along axis} \]
**Orbital Hybridization: Methane**

Methane = CH₄
- Carbon = 6 protons, 6 electrons
- Configuration = 1s²2s²2p² (pₓ, pᵧ, pᶻ)
- 4 Hydrogen atoms = 4 electrons (s)

Have 8 bonding electrons and with 2e⁻ per bond, need 4 bond orbitals

4 valence e⁻ in an s and 3 p orbitals

Hybridize (s + 3 p)

An sp³ hybridized carbon atom
tetrahedral geometry

+ 4 H atoms

4 sp³ orbitals

**Making More Complex Molecules**

Ethylene, C₂H₄
Lewis Formula

Rotational barrier is about 85 kcal/mol

Formamide, HCONH₂
Resonance Forms

Rotational barrier is about 15 kcal/mol
A Momentary Digression ....

Kinetic Considerations.....

\[ R = \text{ideal gas constant} = 2 \text{ cal/mol Kelvin} \]

Rate \( \rate = e^{-Ea/RT} \) where \( Ea \) is the activation energy (barrier)

At room temperature \((T = 300 \text{ K})\), \( RT = 600 \text{ cal/mol} = 0.6 \text{ kcal/mol} \)

The average energy is \( RT \) - many have more, i.e. 5-10\( RT \) or 3-5 \( \text{kcal/mol} \)

Thermodynamic Considerations ....

Consider \( A + B = A-B, K_{eq} = [A-B]/[A][B] \)

And Free energy, \( \Delta G = -RT\ln K_{eq} \)

Let's say that the concentration of product, \([AB]\), is 10-fold higher than reactants at equilibrium (favorable).

Solve for \( \Delta G \) and get \( \Delta G = -1.4 \text{ kcal/mol} \)

That is, each factor of 10 (10-fold) is worth 1.4 \( \text{kcal/mol} \).

At room temp., \(-1\%\) of the molecules have \(-3 \text{ kcal/mol} \) thermal energy

Rotational barrier is about 1.5 \( \text{kcal/mol} \) - spins like a top

Rotational barrier is 85 \( \text{kcal/mol} \)

Does not happen....

Barrier here is about 5 \( \text{kcal/mol} \) - spins like a sputtering top

This conformation or rotamer is about 1 \( \text{kcal/mol} \) higher in energy - ratio \(-1\text{-to-7}\)