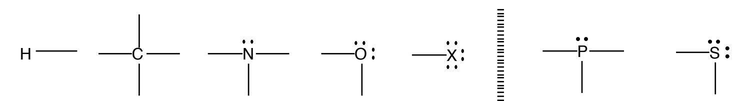
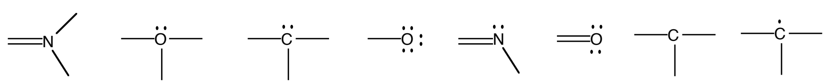
Molecular structure: how are the different atoms bonded together (topology) and what is the 3-dimensional configuration (geometry)?

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.



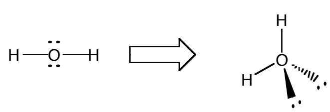
1 e^-	4 e^-	5 e^-	6 e^-	7 e^-	5 e^-	6 e^-
1 bond	4 bonds	3 bonds	2 bonds	1 bond	3-5 bonds	2-4 bonds

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



water

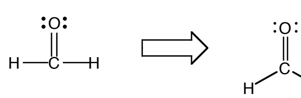
H_2O, 8 e^-



tetrahedral, □ ~ 109°

formaldehyde

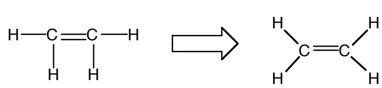
CH_2O, 12 e^-



trigonal planar, □ ~ 120°

ethylene

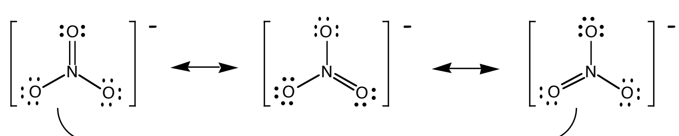
C_2H_4, 12 e^-

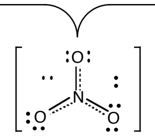


planar, □ ~ 120°

nitrate ion

NO_3^-, 24 e^-

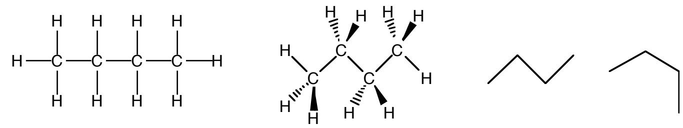




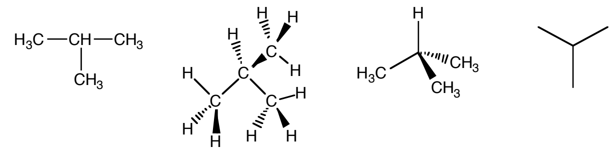
???

n-butane

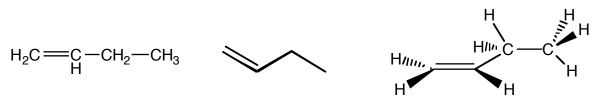
C_4H_{10}, 26 e^-



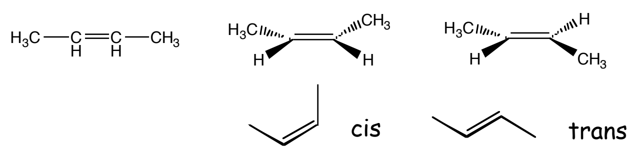
iso-butane, C_4H_{10}



1-butene, C_4H_8

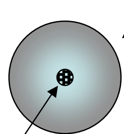


2-butene, C_4H_8



Review of Molecular Orbital Theory

Hydrogen atom

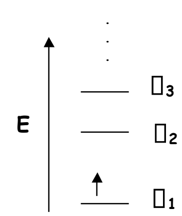


proton (+) charge

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".

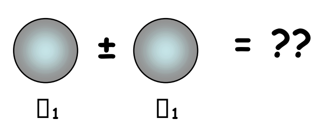
For any given atom or molecule, there are discrete orbitals defined by energy and shape

The lowest energy orbital for hydrogen is an s orbital

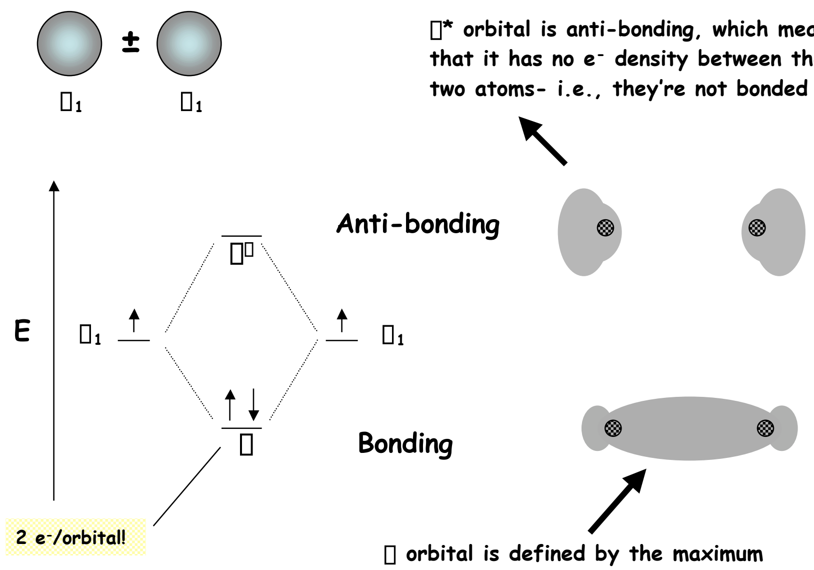


-ground state orbital energy diagram for a neutral hydrogen atom.

The orbital for a molecule is simply the linear combination of the atomic orbitals for all the atoms involved. For example, to make the H_2 molecule:



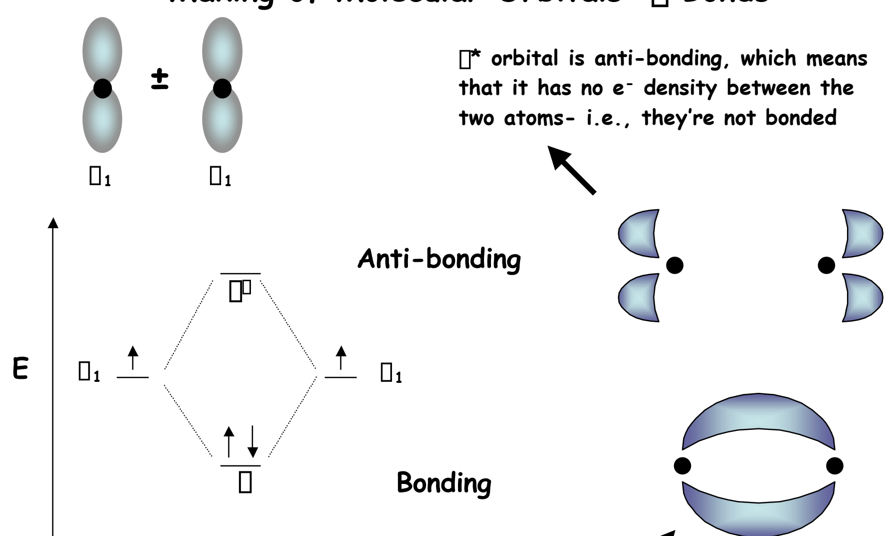
Making of Molecular Orbitals: Hydrogen Molecule



□* orbital is anti-bonding, which means that it has no e⁻ density between the two atoms- i.e., they're not bonded

□ orbital is defined by the maximum e⁻ density between the atoms along the internuclear axis

Making of Molecular Orbitals: □ Bonds



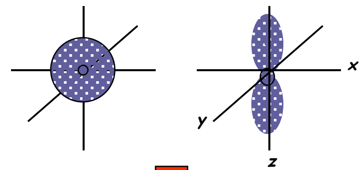
□* orbital is anti-bonding, which means that it has no e⁻ density between the two atoms- i.e., they're not bonded

□ orbital is defined by the maximum e⁻ density between the atoms ABOVE the internuclear axis- none along axis!

Orbital Hybridization: Methane

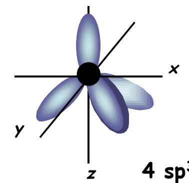
Methane = CH_4
- Carbon = 6 protons, 6 electrons
- Configuration = $1s^2 2s^2 2p^2$ (p_x, p_y, p_z)
- 4 Hydrogen atoms = 4 electrons (s)

4 valence e^- in an s and 3 p orbitals



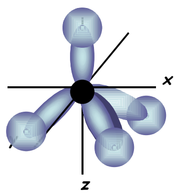
Have 8 bonding electrons and with $2e^-$ per bond, need 4 bond orbitals

Hybridize (s + 3 p)

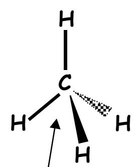


4 sp^3 orbitals

+ 4 H atoms



tetradedral geometry

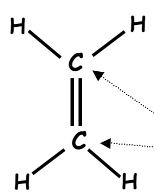


An sp3 hybridized carbon atom

Making More Complex Molecules

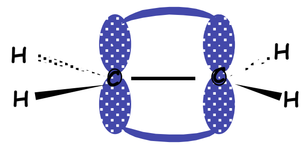
Ethylene, C_2H_4

Lewis Formula

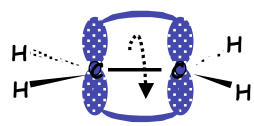


sp^2 carbons

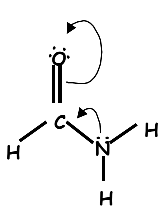
π bond



Rotational barrier is about 85 kcal/mol

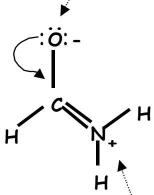


Formamide, $HCONH_2$



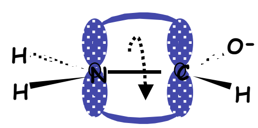
Resonance Forms

One less bond than normal: (-) charge



One more bond than normal: (+) charge

Rotational barrier is about 15 kcal/mol



A Momentary Digression ….

Thermodynamic Considerations …..

Consider A + B = A-B, K_{eq}=[A-B]/[A][B]
And Free energy, ΔG = -RTlnK_{eq}

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

Solve for ΔG and get ΔG = -1.4 kcal/mol

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

Kinetic Considerations……

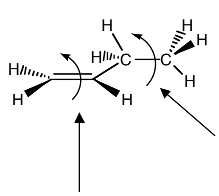
R = ideal gas constant
 = 2 cal/mol Kelvin

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

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

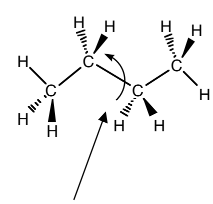
The average energy is RT- many have more, ie 5-10RT or 3-5 kcal/mol

At room temp. ~1% of the molecules have ~3 kcal/mol thermal energy

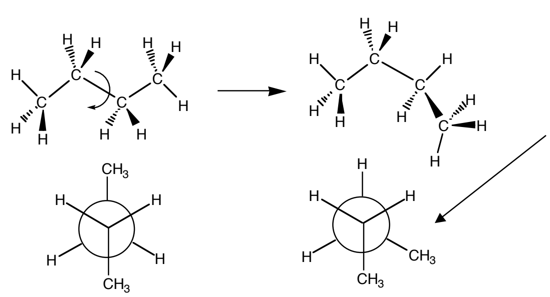


Rotational barrier is about 1.5 kcal/mol- spins like a top

Rotational barrier is 85 kcal/mol
Does not happen….



Barrier here is about 5 kcal/mol- spins like a sputtering top



This conformation or rotamer is about 1 kcal/mol higher in energy- ratio ~ 1-to-7