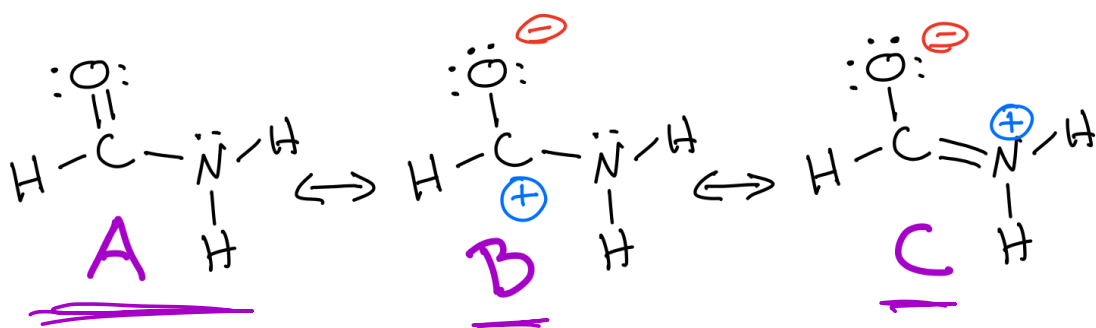


Molecular dipole moments
are the vector sum of
bond dipoles

The curious case of amide contributing structures: All three are important



Why are B and C worth considering?

1) Golden Rules of Chemistry #5 and #7

2) Quantum Mechanics (that explain Golden Rules of Chemistry #5 and #7)

Electrons are so incredibly small that they have some properties of particles and some properties of waves

**** For organic chemistry we focus only on the wave properties of electrons!!!

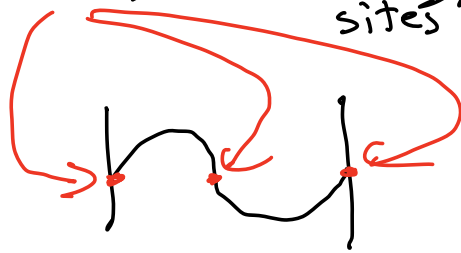
Electrons are three-dimensional waves!!



Properties of waves

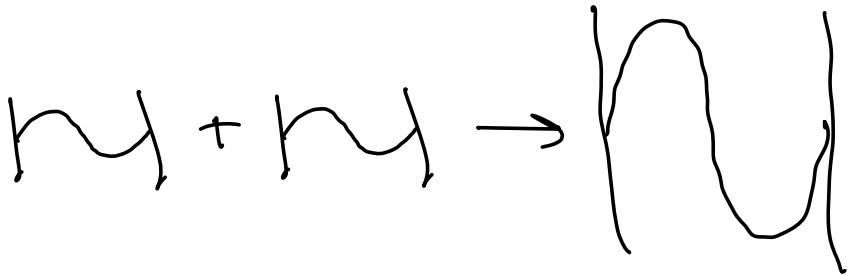
1) Quantized energies \rightarrow think of guitar strings

2) Nodes \rightarrow "no energy" at certain sites in a wave



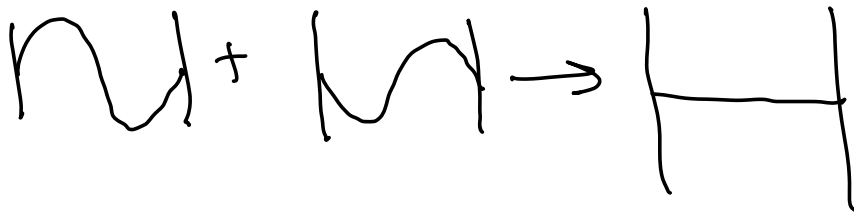
3) Waves add constructively and destructively

Peaks and troughs add



"in phase" \Rightarrow Constructive wave addition

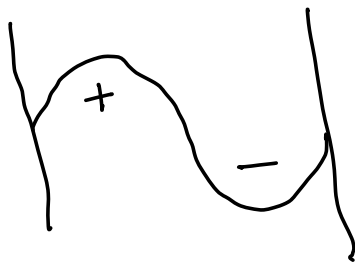
peaks and troughs cancel



"out of phase"

Destructive wave addition

4) There is just as much energy at the top (+) amplitude of a wave as at the bottom (-) amplitude of a wave



5) If you add X wave equations you get X new wave equations as the solution

Basis of molecular orbital theory

6) Around atoms, the location of electron density is described by the Schrödinger equation

A wave equation that describes energy and location

Solutions to the Schrodinger equation – atomic orbitals

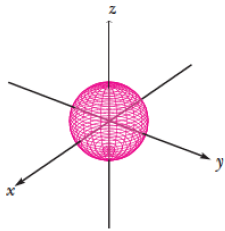
$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^\ell L_{n-l-1}^{2\ell+1}\left(\frac{2r}{na_0}\right) \cdot Y_\ell^m(\theta, \phi)$$

where:

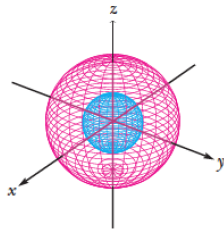
- $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ is the **Bohr radius**,
- $L_{n-l-1}^{2\ell+1}(\dots)$ are the **generalized Laguerre polynomials** of degree $n - \ell - 1$.
- n, ℓ, m are the **principal, azimuthal, and magnetic quantum numbers** respectively: which take the values:
 - $n = 1, 2, 3, \dots$
 - $\ell = 0, 1, 2, \dots, n - 1$
 - $m = -\ell, \dots, \ell$

e density \rightarrow 3d wave!

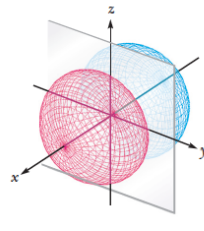
Ψ_{1s}



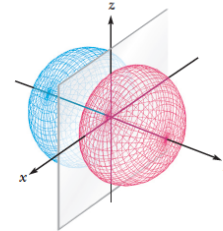
Ψ_{2s}



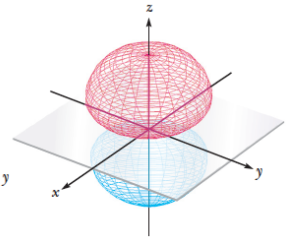
Ψ_{2px}



Ψ_{2py}

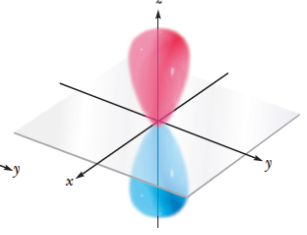
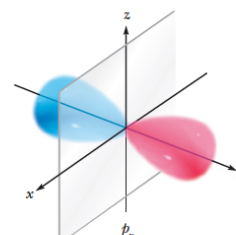
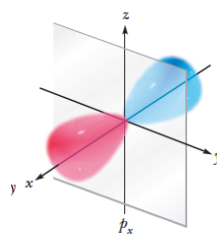
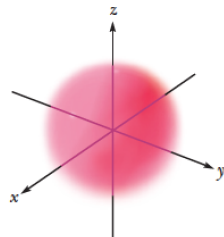
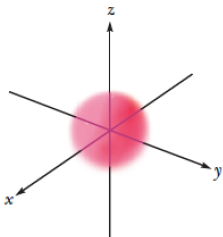


Ψ_{2pz}



(a) 1s and 2s orbitals computed using the Schrödinger equation

(a) 2p Orbitals computed using the Schrödinger equation



(b) Cartoon representations of 1s and 2s orbitals

Different colors represent the sign of the wave function (+ or -)

We plot the square of the wave function (Ψ^2) and refer to this as an "orbital"

Molecular Orbital Theory

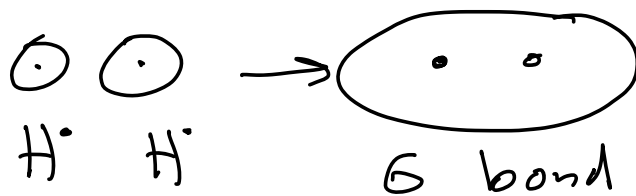
→ To quantify bonding in molecules we simply add all of the atomic orbital wave functions in the molecule

- 1) This creates as many new molecular orbitals as there are component orbitals being added.
- 2) Each molecular orbital extends over the ENTIRE molecule
- 3) Each new molecular orbital contains up to the electron density equal to 2 electrons
⇒ NEVER MORE

All of this can explain π bonds, but it only works for computers to explain σ bonds → humans needed another approach —

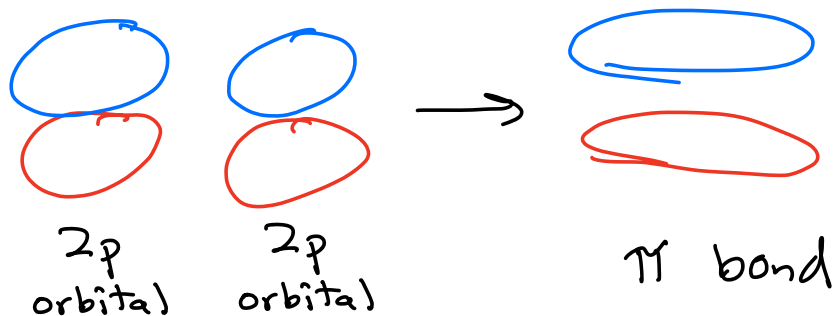
Before we get to Valence Bond Theory, let's review σ bonds and π bonds

σ bonds \rightarrow cylindrical symmetry
 \rightarrow rotate freely



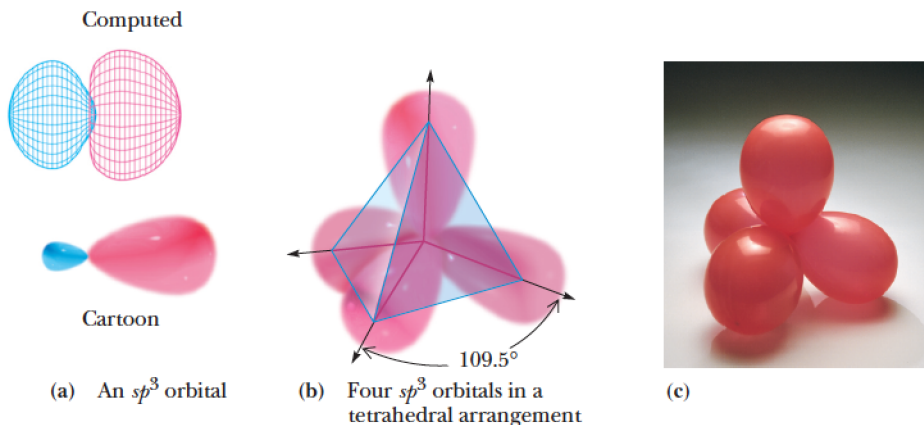
π bond \rightarrow "hot dog bun shape"
 \rightarrow CANNOT rotate freely

\rightarrow Formed from the overlap of 2p orbitals

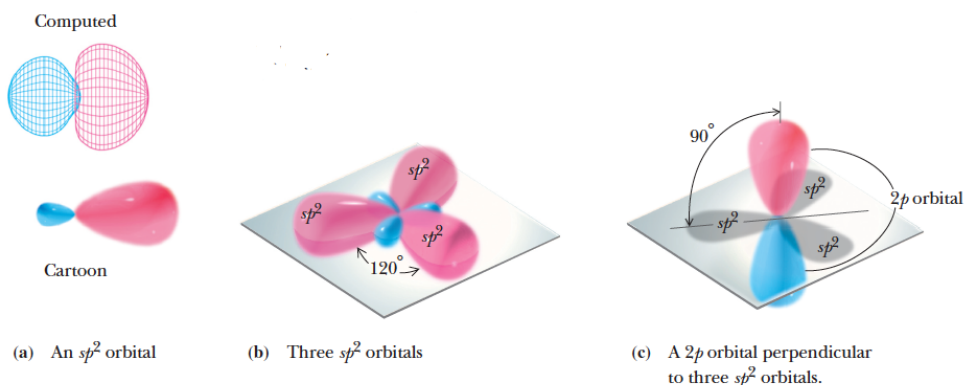


Hybridization – Valence Bond Approach to bonding

$$sp^3 (\Psi_{2s} + \Psi_{2p_x} + \Psi_{2p_y} + \Psi_{2p_z})$$



$$sp^2 (\Psi_{2s} + \Psi_{2p_x} + \Psi_{2p_y}) + \Psi_{2p_z}$$



$$sp (\Psi_{2s} + \Psi_{2p_x}) + \Psi_{2p_y} + \Psi_{2p_z}$$

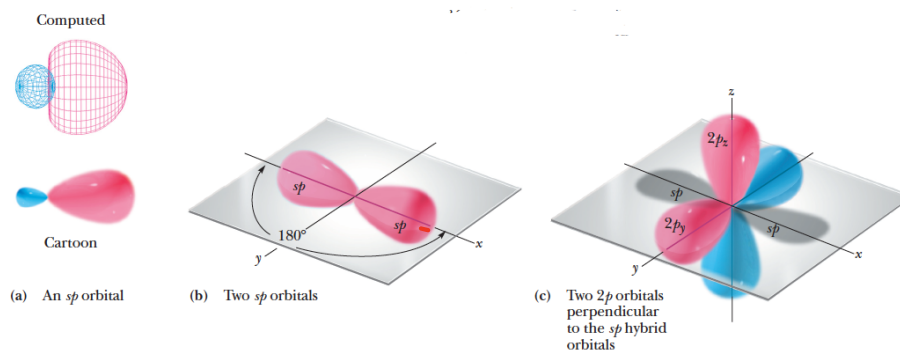


Figure 1.18

Molecular orbital mixing diagram for the creation of any C—C σ bond. (a) In-phase addition of two C hybrid orbitals (albeit sp^3 , sp^2 , or sp orbital) forms a σ orbital that is lower in energy than the two starting orbitals. When the resulting orbital is populated with two electrons, a σ bond results. (b) Addition of the orbitals in an out-of-phase manner (meaning reversing the phasing of one of the starting orbitals) leads to an antibonding σ^* orbital.

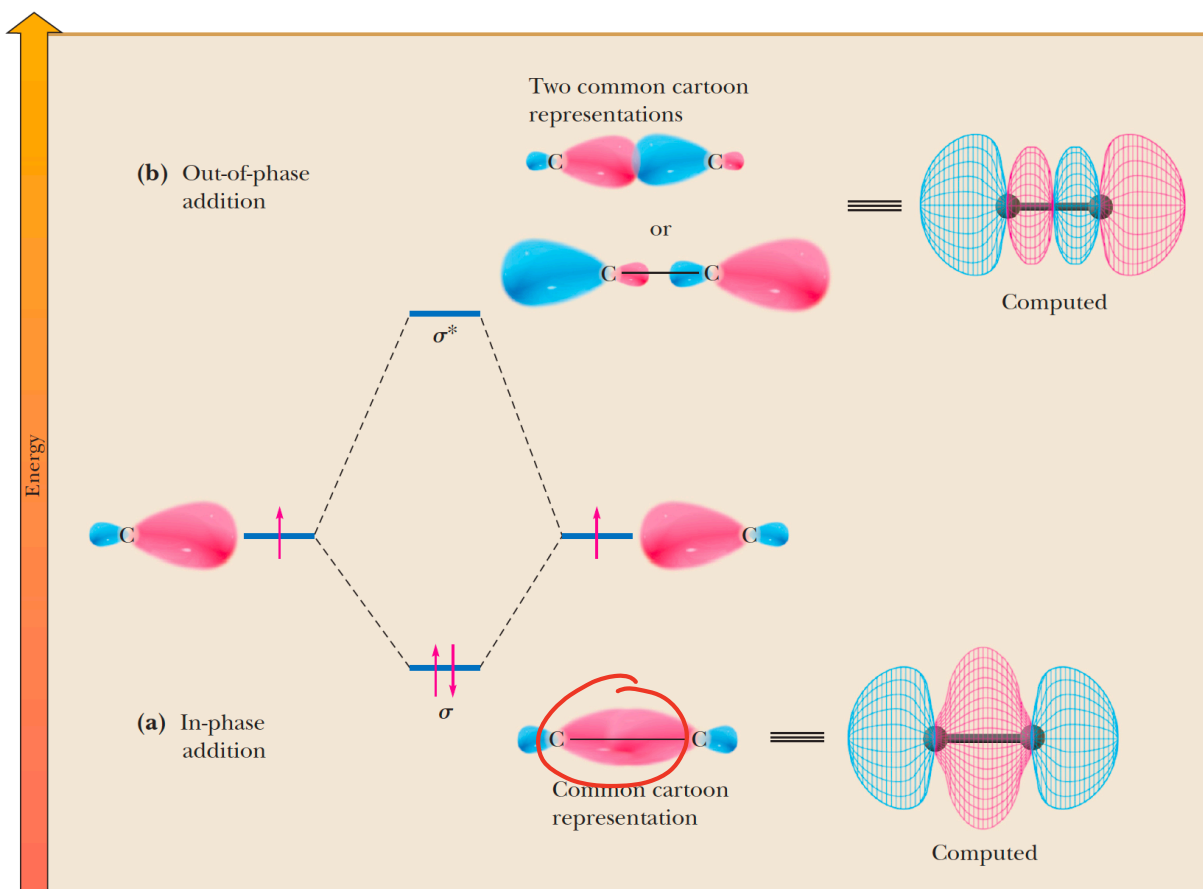
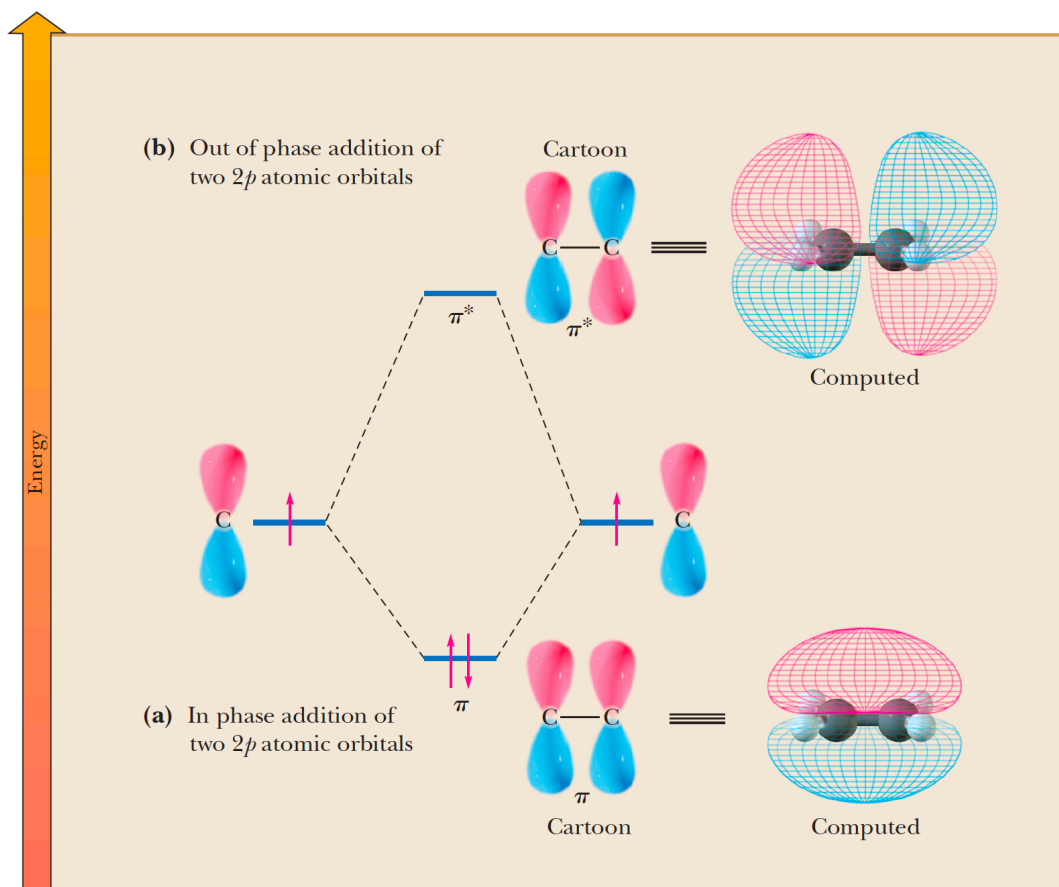
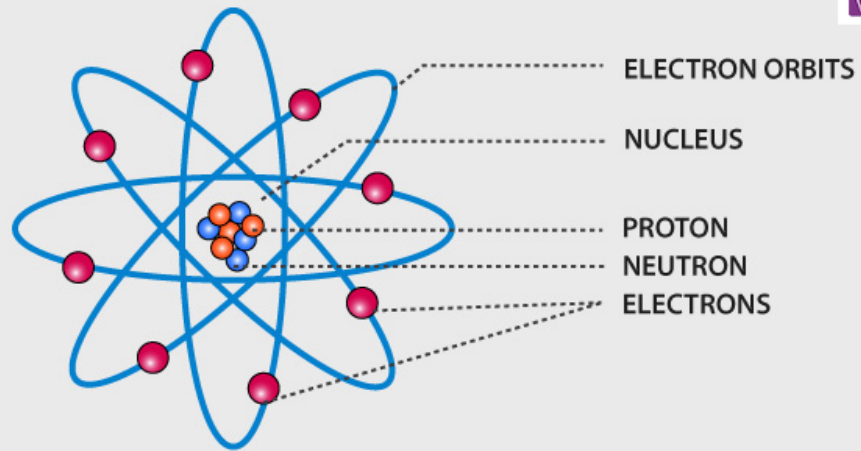


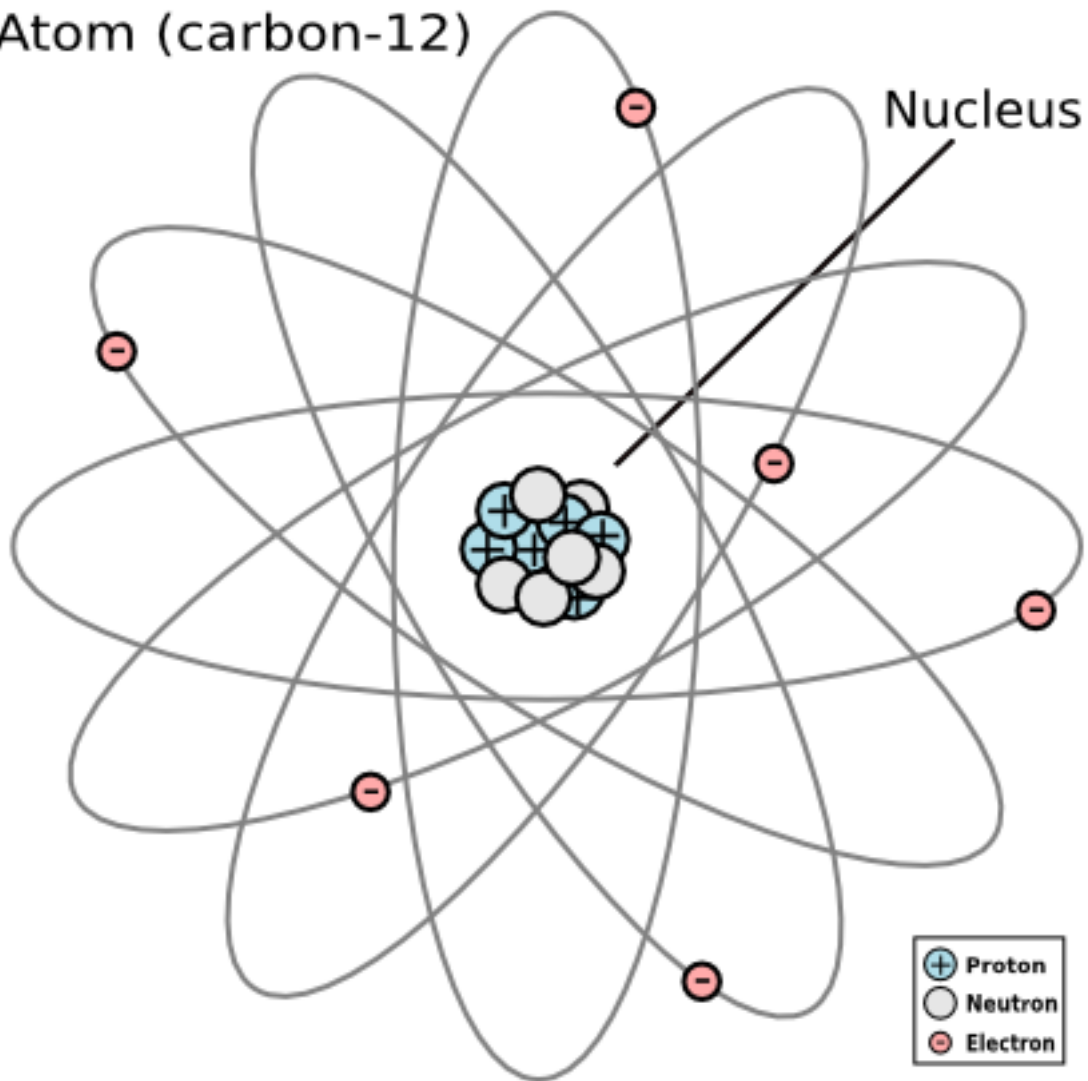
Figure 1.21

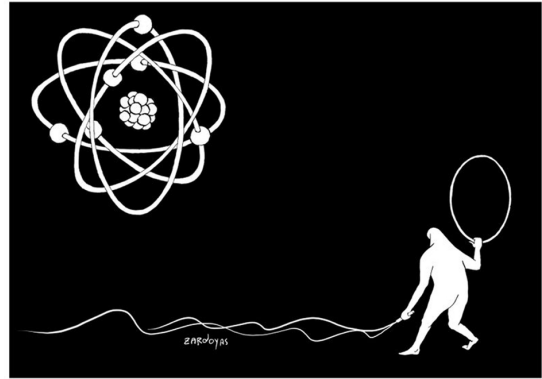
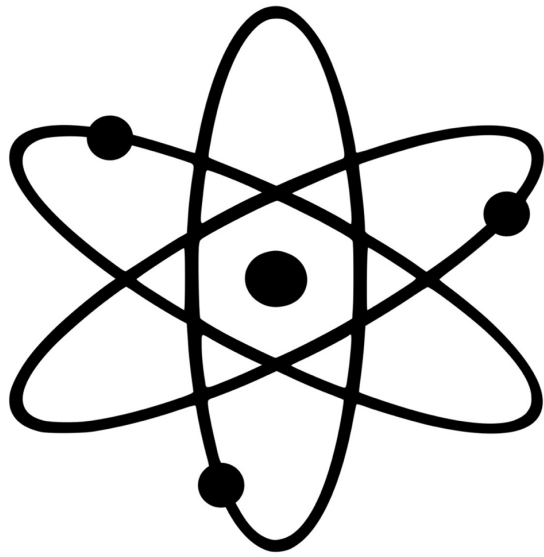
Molecular orbital mixing diagram for the creation of any C—C π bond. (a) Addition of two p atomic orbitals in-phase leads to a π orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons the π orbital gives a π bond. (b) Addition of the p orbitals in an out-of-phase manner (meaning a reversal of phasing in one of the starting orbitals) leads to a π^* orbital. Population of this orbital with one or two electrons leads to weakening or cleavage of the π bond respectively.

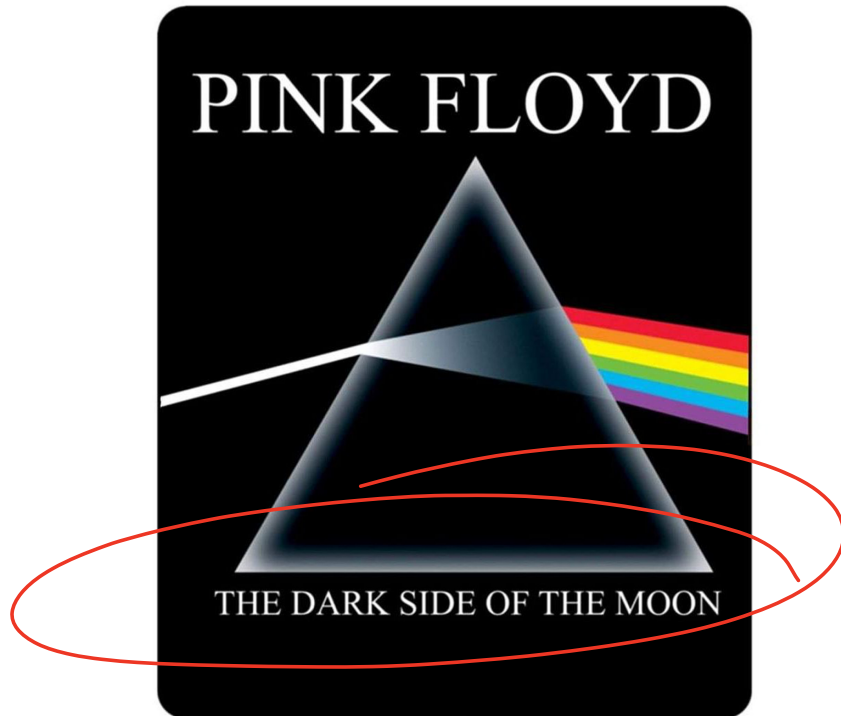


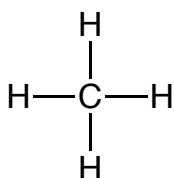


Atom (carbon-12)









Methane

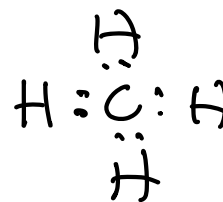
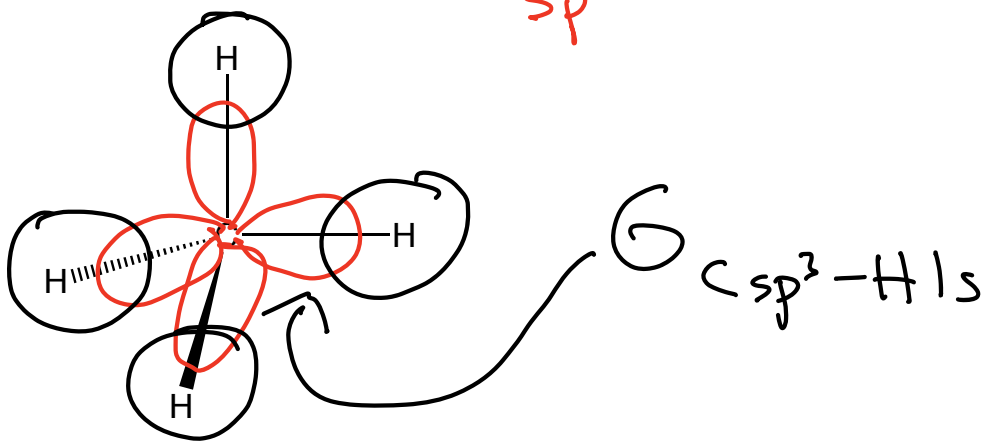
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

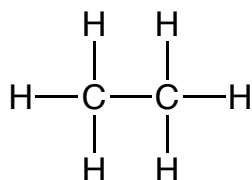
$$\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z})$$

sp³





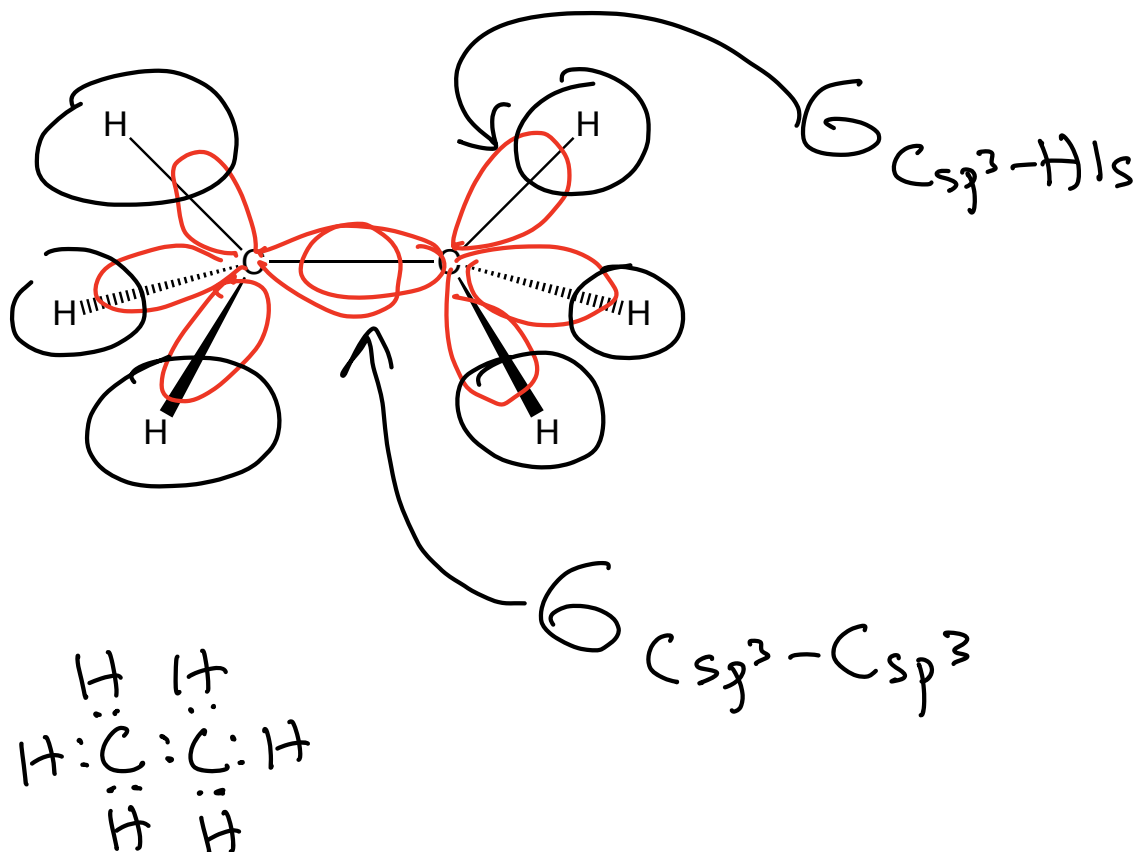
Ethane

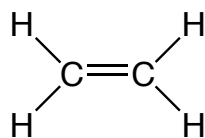
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} \\
 &+ \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}
 \end{aligned}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} \\
 &+ \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}) + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}) \quad \begin{matrix} s^3 \\ s^3 \end{matrix}
 \end{aligned}$$





Ethene
(Ethylene)

Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py} + \Psi_{\text{C}2pz} \\
 &+ \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py} + \Psi_{\text{C}2pz}
 \end{aligned}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\underbrace{\Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py}}_{sp^2}) + \underbrace{\Psi_{\text{C}2pz}} \\
 &+ \Psi_{\text{C}1s} + (\underbrace{\Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py}}_{sp^2}) + \underbrace{\Psi_{\text{C}2pz}}
 \end{aligned}$$

