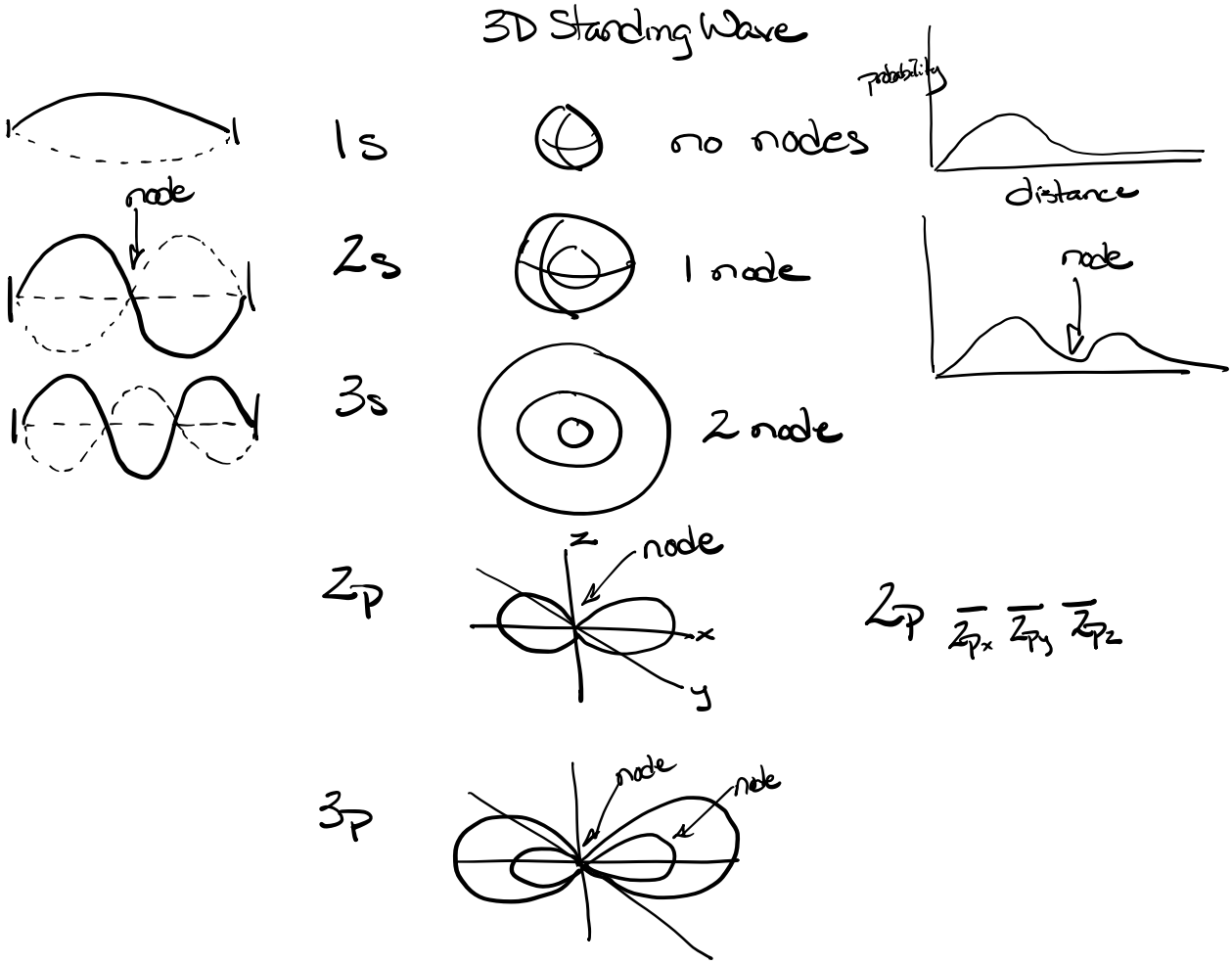
Chapter 2

Atomic Orbitals

Wavefunction - probability density model of where we find an electron

Hydrogen



Hydrogen orbitals are used as rough approximations of the orbitals of other nuclei

- Relative energies & sizes are dependent on nuclear charge & total # e^-

- Aufbau Principle

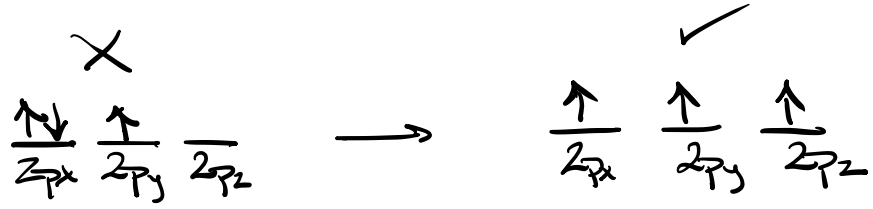
  Orbitals fill bottom to top, lowest E to highest E.

- Pauli Exclusion Principle

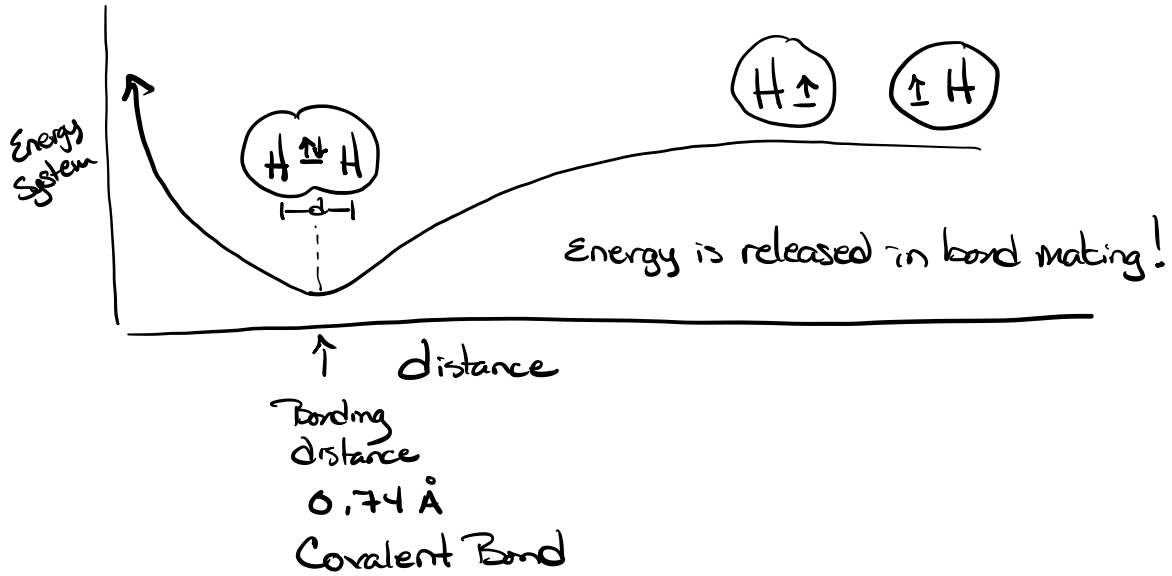
  Two e^- in same orbital must have opposite spin $\underline{\uparrow\downarrow}$

- Hund's Rule

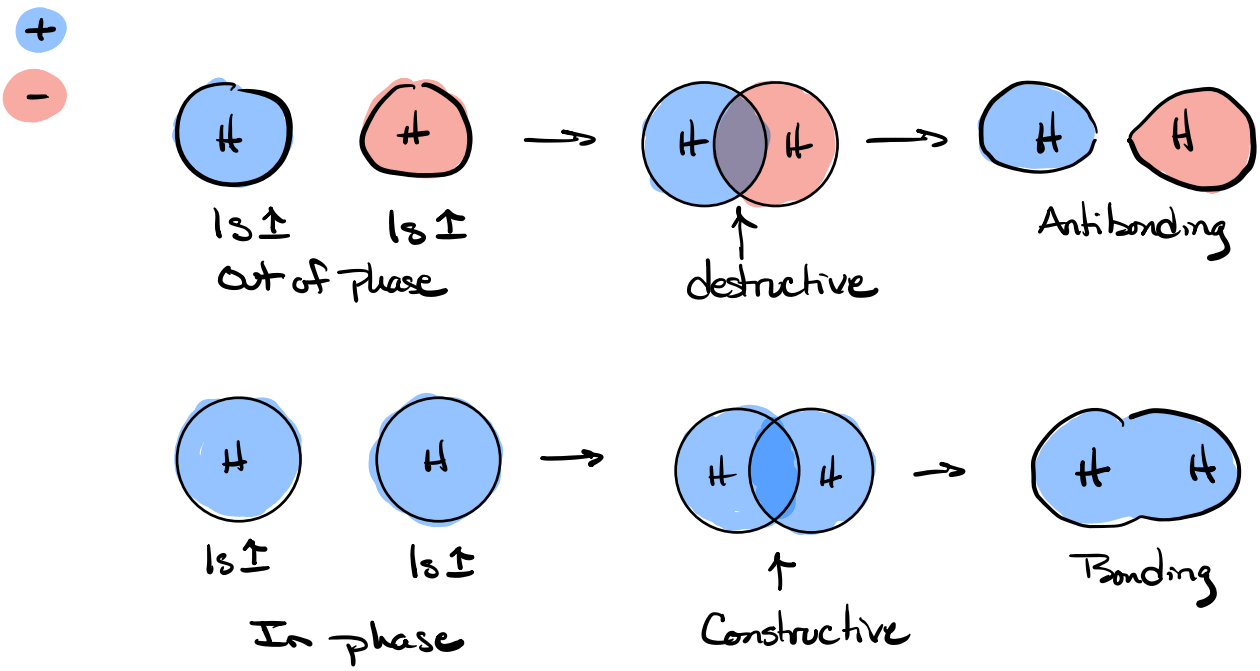
  e^- will distribute before pairing when orbital of equal Energy are available

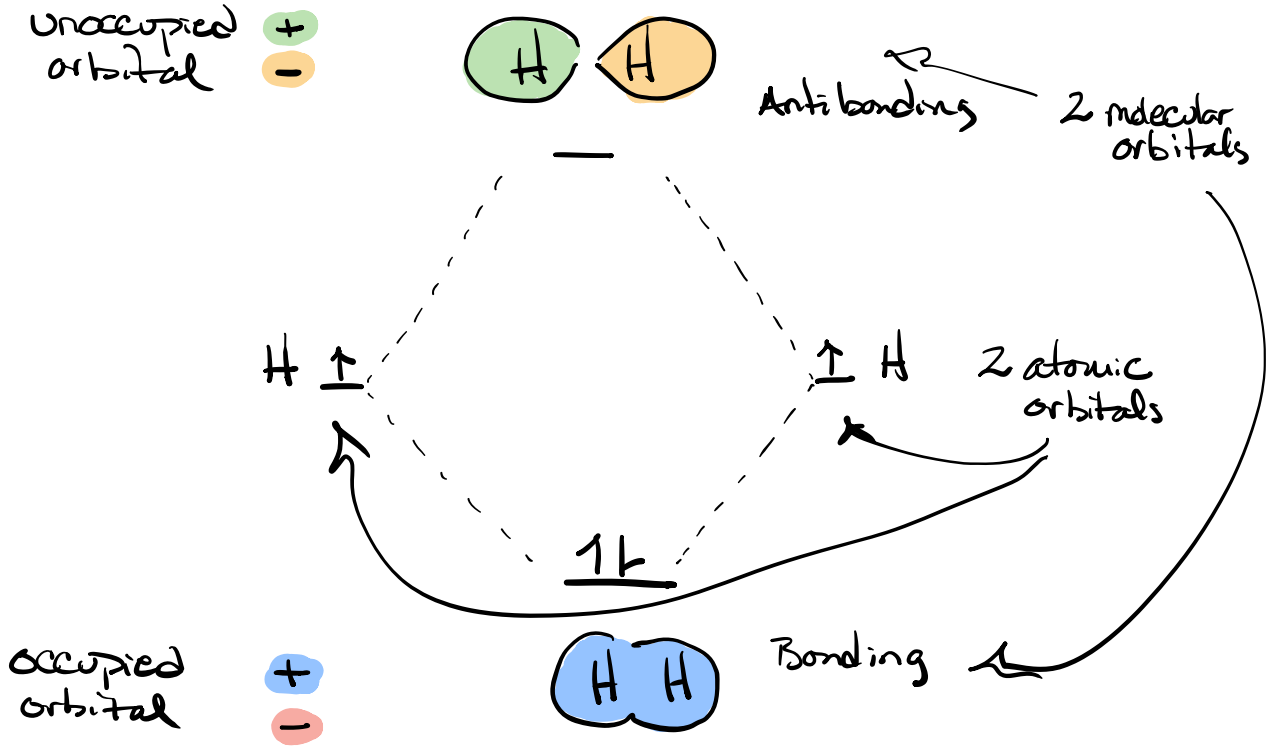


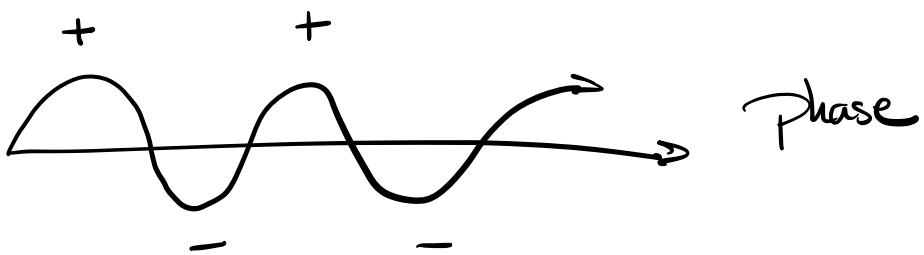
Formation of Molecular Orbitals



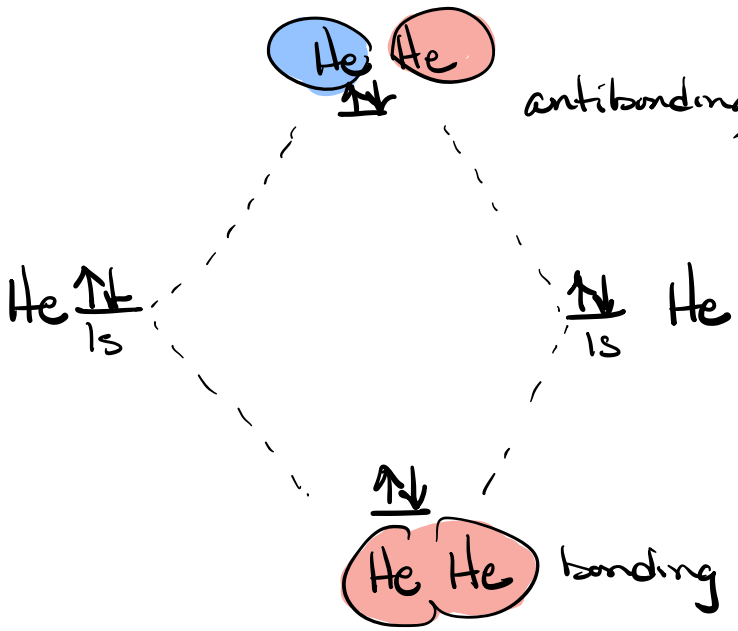
Constructive & Destructive interferrence




Unoccupied orbital
+
−
H H
Antibonding
2 molecular orbitals
H
H
2 atomic orbitals
1s
1s
Occupied orbital
+
−
H H
Bonding

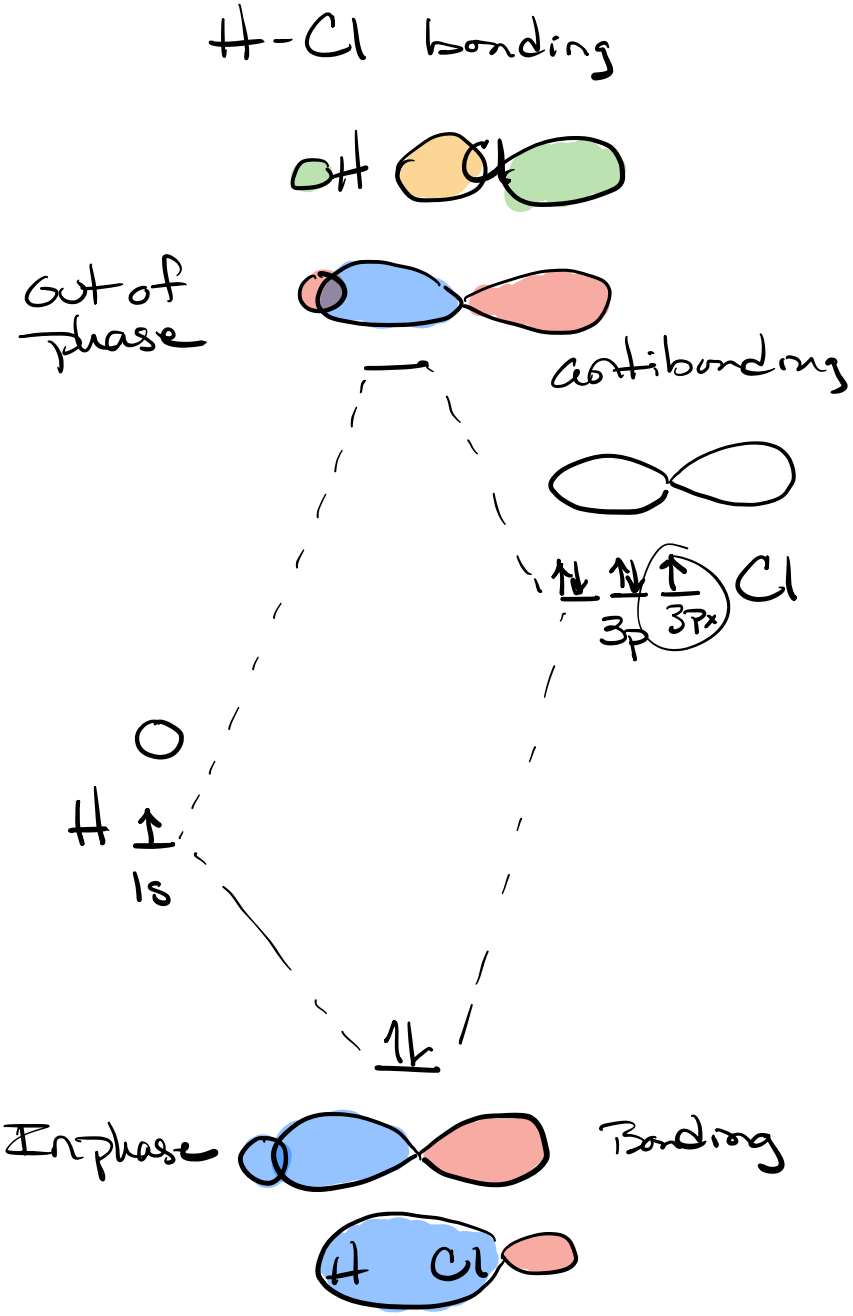

+
+
−
−
Phase

Why is helium not diatomic like hydrogen? H_2 but He



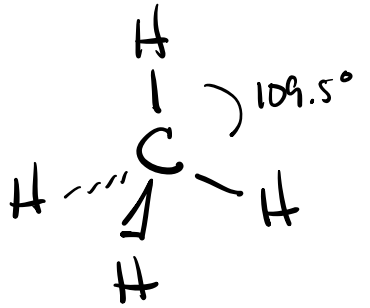
So no net stabilization gain because antibonding is also full.

$\Rightarrow$ Electron density in antibonding orbital disrupts bonding.

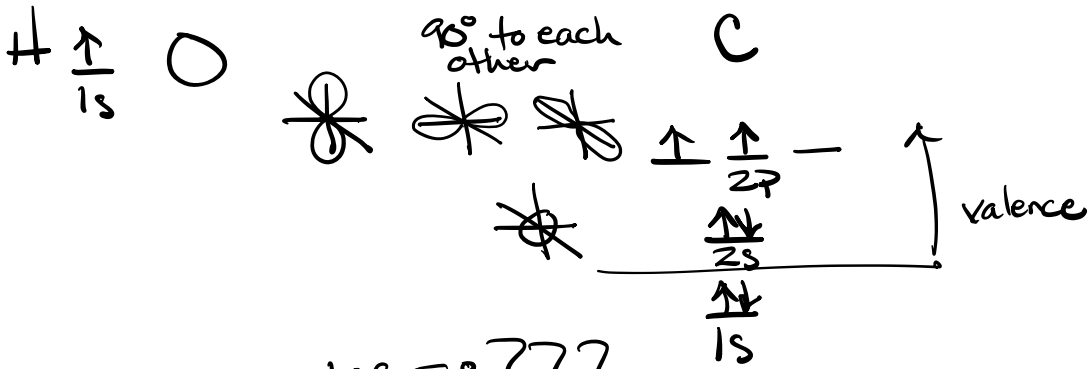

H-Cl bonding
out of phase
antibonding
Cl
3p
3px
H
1s
1k
In phase
Bonding
H Cl

How do we get all the VSEPR Geometries?
Specifically Tetrahedral??

CH_4



AX_4 Tetrahedral
109.5°



109.5°???

Bonding Theorys or Models

Molecular Orbital Theory

- Orbitals are delocalized over whole molecule. Each molecular orbital may contribute bonding interaction to more than just 2 atoms.

- Molecular orbitals are built with linear combinations of atomic orbitals

- Molecular orbitals are wave equations which minimize nuclear-nuclear repulsion, e^- & e^- repulsions & other factors.

- Molecular orbital theory is very good at predicting energy levels and spectroscopy.

Natural Bonding Theory

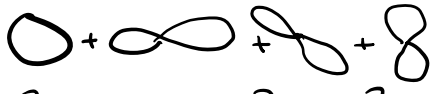
- Stepwise approach where atomic orbitals are used to build hybrid orbitals.

  Linear Combinations of atomic orbitals are used to mathematically construct hybrid orbitals. The hybrid orbitals have better geometry and overlap for making bonding orbitals.

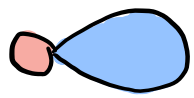
C $1s^2 | 2s^2 2p^2$

Valence e^- atomic orbitals

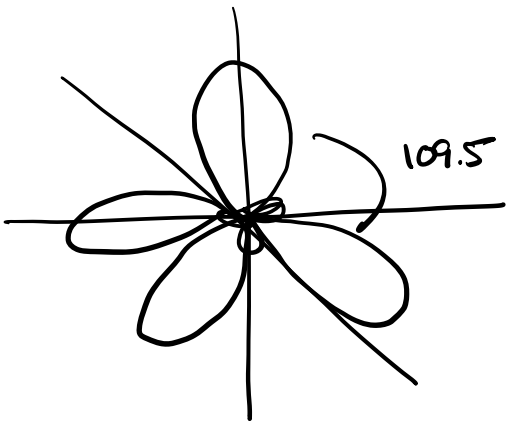
4 atomic Orbitals



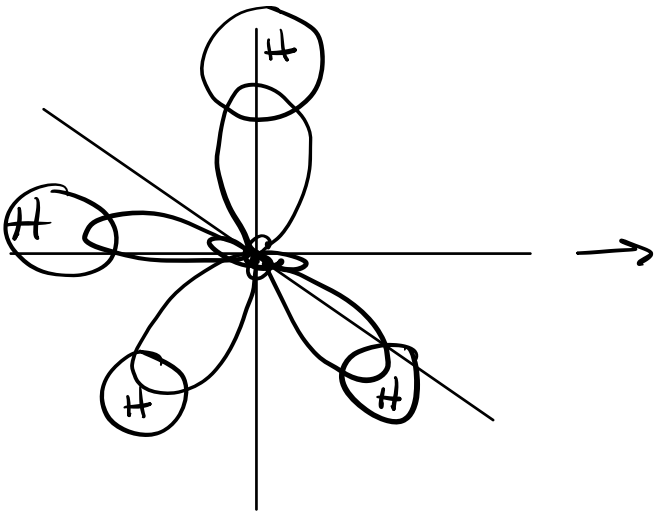
$\frac{1}{4}s + \frac{3}{4}p = sp^3$

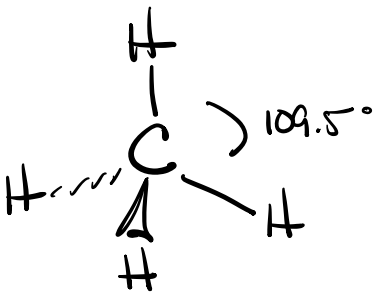


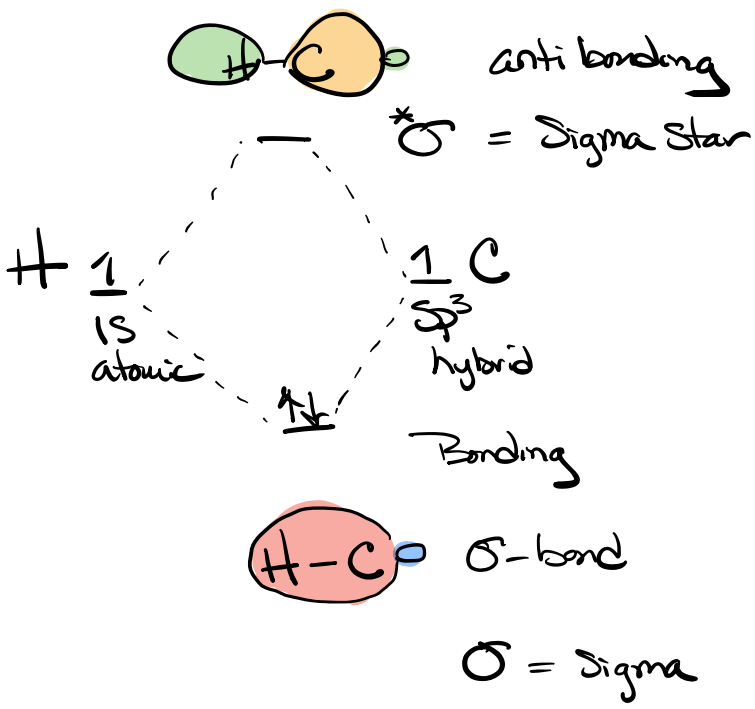
$4 \times sp^3$ Hybrid orbital



4 sp^3 orbitals in tetrahedral Geometry


H
H
H
H


H
C
109.5°
H
H
H


anti bonding
σ^* = Sigma Star
H
1
1s
atomic
1 C
sp^3
hybrid
Bonding
H-C
σ-bond
σ = Sigma

Why two models?

Both useful for different things

Molecular Orbital Theory

- Predicting Spectroscopy
- Aromaticity
- Cycloaddition reactions
- Heats of formation
  Molecular energy

Most of the time → Natural Bonding Theory

Localized Bonding & Hybridization

- Molecular Shape
  VSEPR comes from Natural Bonding Theory
- Bond angles, lengths
- Acid/Base
- Stability of molecule