Molecular Orbital Theory
MOT

Atomic Orbitals

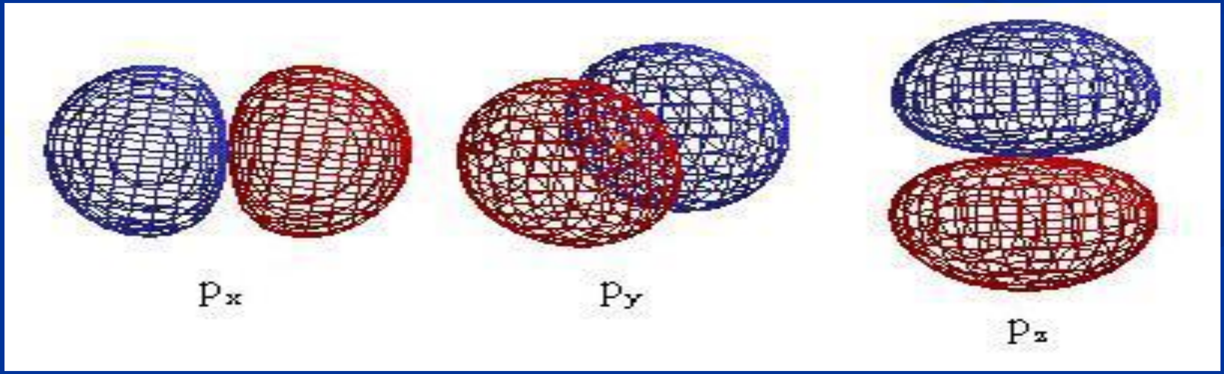
- Heisenberg Uncertainty Principle states that it is impossible to define what time and where an electron is and where is it going next. This makes it impossible to know exactly where an electron is traveling in an atom.
- Since it is impossible to know where an electron is at a certain time, a series of calculations are used to approximate the volume and time in which the electron can be located. These regions are called Atomic Orbitals. These are also known as the quantum states of the electrons.
- Only two electrons can occupy one orbital and they must have different spin states, ½ spin and – ½ spin (easily visualized as opposite spin states).
- Orbitals are grouped into subshells.
- This field of study is called quantum mechanics.

Atomic Subshells

- These are some examples of atomic orbitals:
  - S subshell: (Spherical shape) There is one S orbital in an s subshell. The electrons can be located anywhere within the sphere centered at the atom's nucleus.

http://www.chm.davidson.edu/ronutt/che115/AO.htm

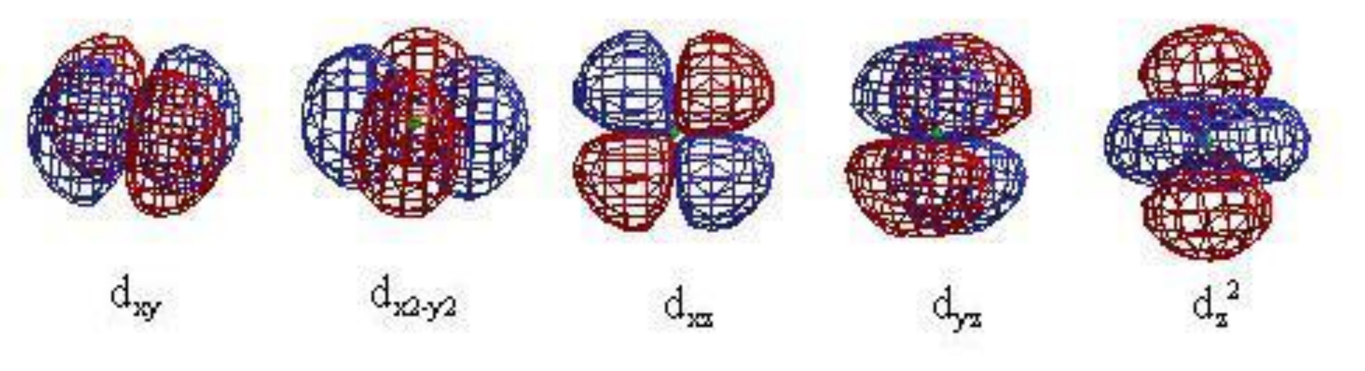
  - P Orbitals: (Shaped like two balloons tied together) There are 3 orbitals in a p subshell that are denoted as p_x, p_y, and p_z orbitals. These are higher in energy than the corresponding s orbitals.



http://www.chm.davidson.edu/ronutt/che115/AO.htm

Atomic Subshells (cont'd)

- D Orbitals: The d subshell is divided into 5 orbitals (d_{xy}, d_{xz}, d_{yz}, d_{z^2} and $d_{x^2-y^2}$). These orbitals have a very complex shape and are higher in energy than the s and p orbitals.



Electronic Configuration

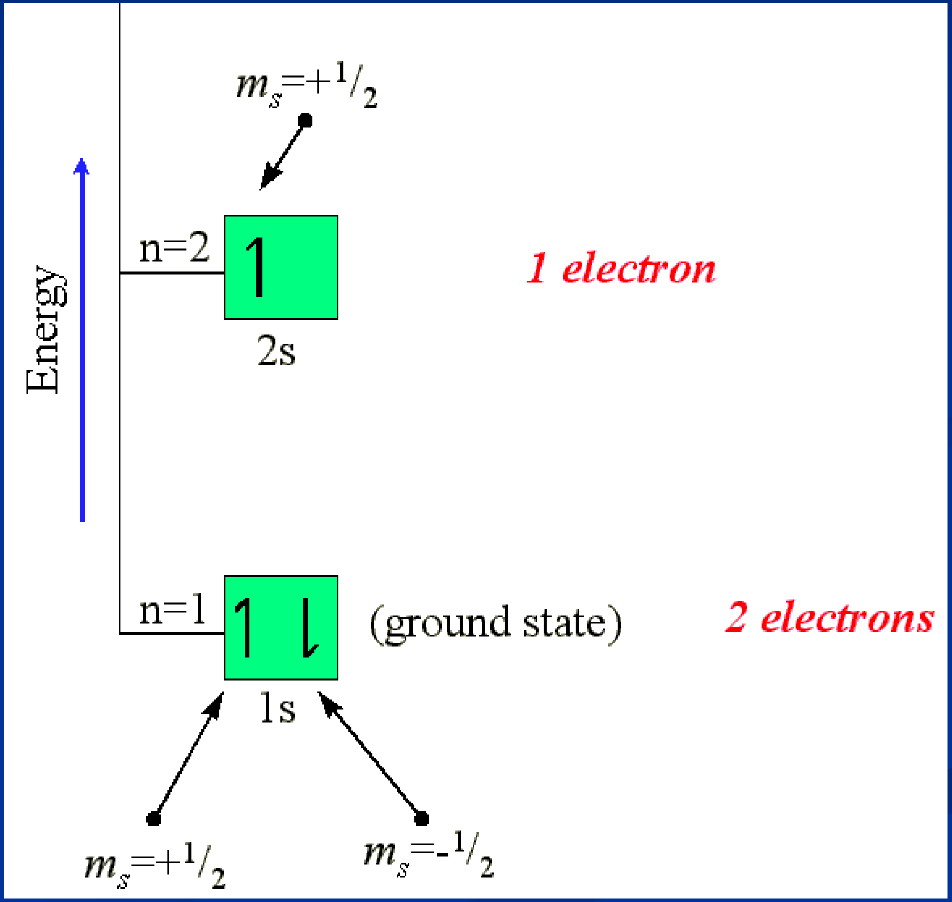
- Every element is different.
  - The number of protons determines the identity of the element.
  - The number of electrons determines the charge.
  - The number of neutrons determines the isotope.
- All chemistry is done at the electronic level (that is why electrons are very important).
- Electronic configuration is the arrangement of electrons in an atom. These electrons fill the atomic orbitals
- Atomic orbitals are arrange by energy level (n), subshells (l), orbital (m_l) and spin (m_s) - in order:

Lithium Electronic Configuration

- The arrows indicate the value of the magnetic spin (m_s) *quantum number (up for +1/2 and down for -1/2)*
- *The occupation of the orbitals would be written in the following way:*

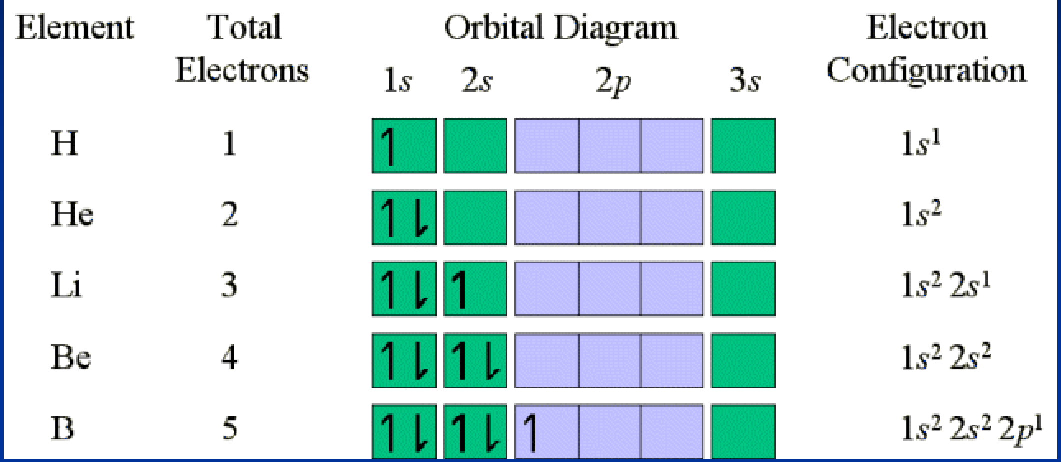
$1s^2 2s^1$

or, "1*s* two, 2*s* one".



http://wine1.sb.fsu.edu/chm1045/notes/Struct/EConfig/Struct08.htm

Electronic Configurations – Box Diagram



Element	Total Electrons	Orbital Diagram						Electron Configuration
		1*s*	2*s*	2*p*			3*s*	
H	1	↑						$1s^1$
He	2	↑↓						$1s^2$
Li	3	↑↓	↑					$1s^2\,2s^1$
Be	4	↑↓	↑↓					$1s^2\,2s^2$
B	5	↑↓	↑↓	↑				$1s^2\,2s^2\,2p^1$

http://wine1.sb.fsu.edu/chm1045/notes/Struct/EConfig/Struct08.htm

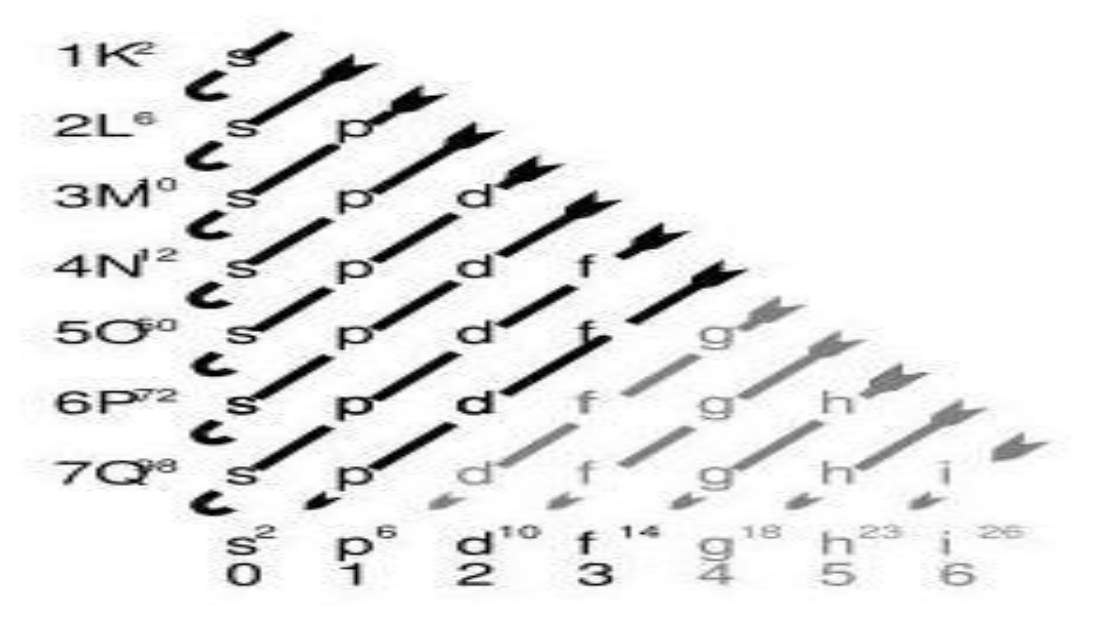
- The two electrons in Helium represent the complete filling of the first electronic shell. Thus, the electrons in He are in a very stable configuration
- For Boron (5 electrons) the 5th electron must be placed in a 2*p* orbital because the 2*s* orbital is filled. Because the 2*p* orbitals are equal energy, it doesn't matter which 2*p* orbital is filled.

Electronic Configuration

- Electronic configurations can also be written in a short hand which references the *last completed orbital shell* (i.e. all orbitals with the same principle quantum number 'n' have been filled)
    - The electronic configuration of Na can be written as [Ne]$3s^1$
    - The electronic configuration of Li can be written as [He]$2s^1$
- The electrons in the stable (Noble gas) configuration are termed *the core electrons*
- The electrons in the outer shell (beyond the stable core) are called *the valence electrons*

Electron Configuration

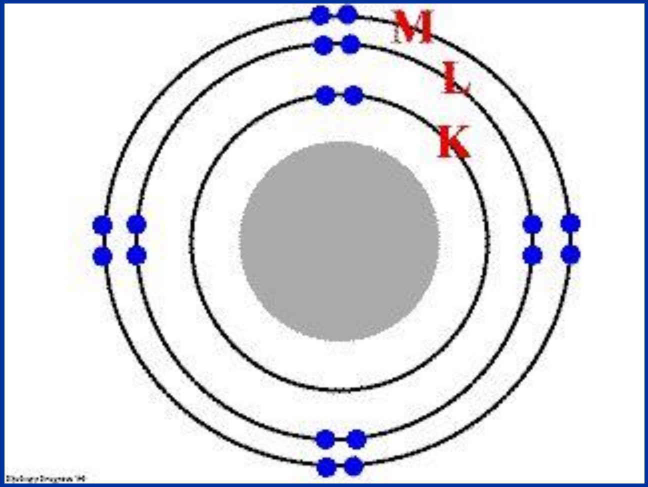
Two ways to remember the order of electrons



$1s^2_2\ 2s^2_4\ 2p^6_{10}\ 3s^2_{12}\ 3p^6_{18}\ 4s^2_{20}\ 3d^{10}_{30}\ 4p^6_{36}\ 5s^2_{38}\ 4d^{10}_{48}\ 5p^6_{54}\ 6s^2_{56}\ 4f^{14}_{70}\ 5d^{10}_{80}\ 6p^6_{86}\ 7s^2_{88}\ 5f^{14}_{102}\ 6d^{10}_{112}\ 7p^6_{118}$

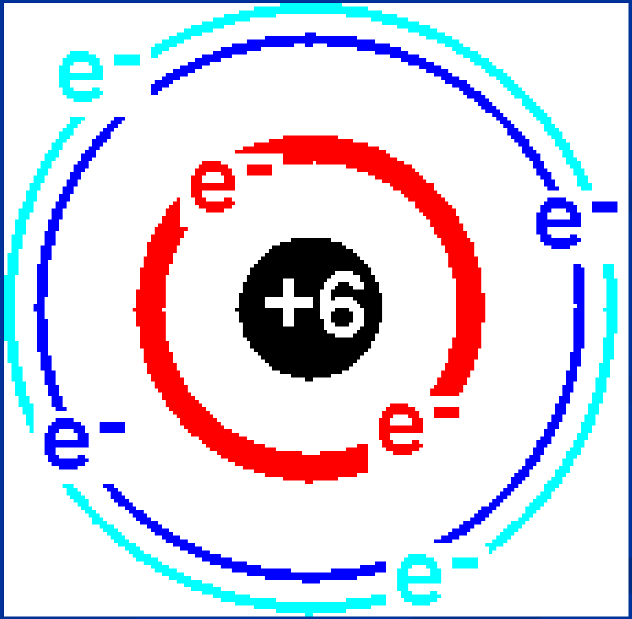
Valence Electrons

- The **valence electrons** are the electrons in the last shell or energy level of an atom.



www.uoregon.edu

The lowest level (K), can contain 2 electrons.
The next level (L) can contain 8 electrons.
The next level (M) can contain 8 electrons.



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Carbon - $1s^2 2s^2 2p^2$ - four valence electrons

Examples of Electronic Configuration

Ne → $1s^2\ 2s^2\ 2p^6$	(10 electrons)
F → $1s^2\ 2s^2\ 2p^5$	(9 electrons)
F^- → $1s^2\ 2s^2\ 2p^6$	(10 electrons)
Mg → $1s^2\ 2s^2\ 2p^6\ 3s^2$	(12 electrons)
Mg^{2+} → $1s^2\ 2s^2\ 2p^6$	(10 electrons)

- Notice – different elements can have the same number of electrons

Molecular Orbital Theory

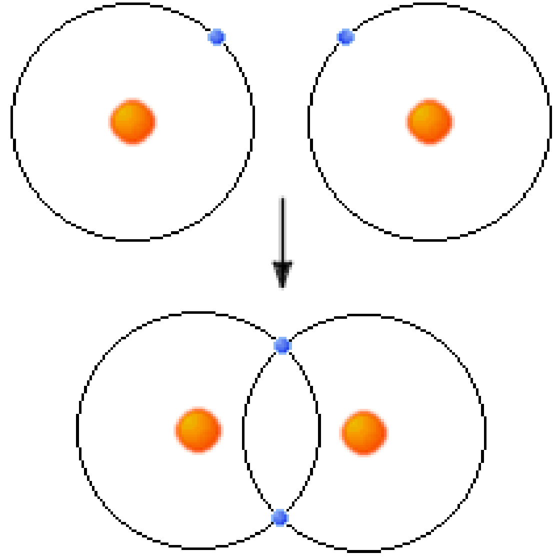
The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations.

Forming a Covalent Bond

- Molecules can form bonds by sharing electron
  - Two shared electrons form a single bond
- Atoms can share one, two or three pairs of electrons
  - forming single, double and triple bonds
- Other types of bonds are formed by charged atoms (ionic) and metal atoms (metallic).

Atomic and Molecular Orbitals (cont'd)

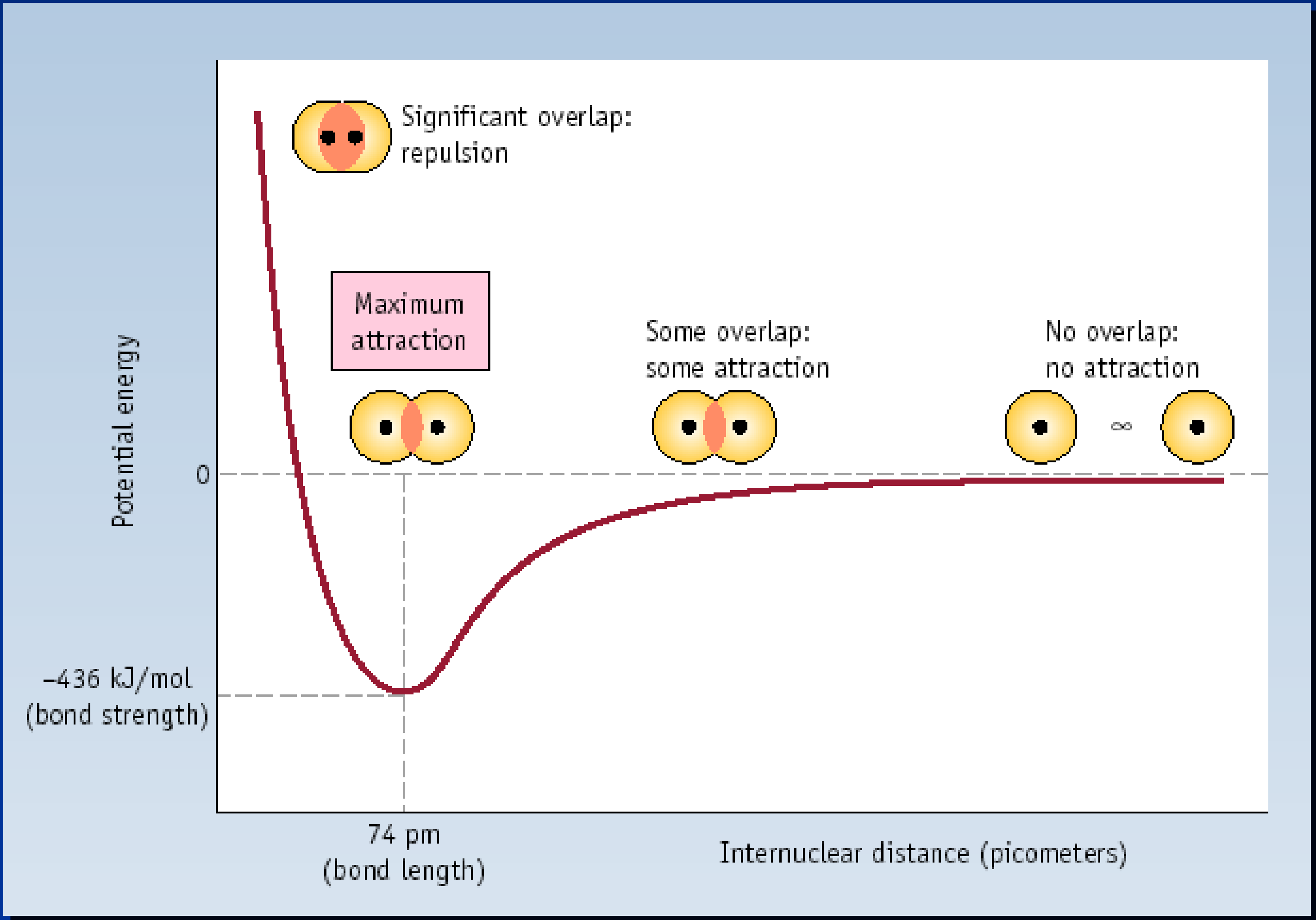
- Orbital Mixing
  - When atoms share electrons to form a bond, their atomic orbitals mix to form molecular bonds. In order for these orbitals to mix they must:
    - Have similar energy levels.
    - Overlap well.
    - Be close together.



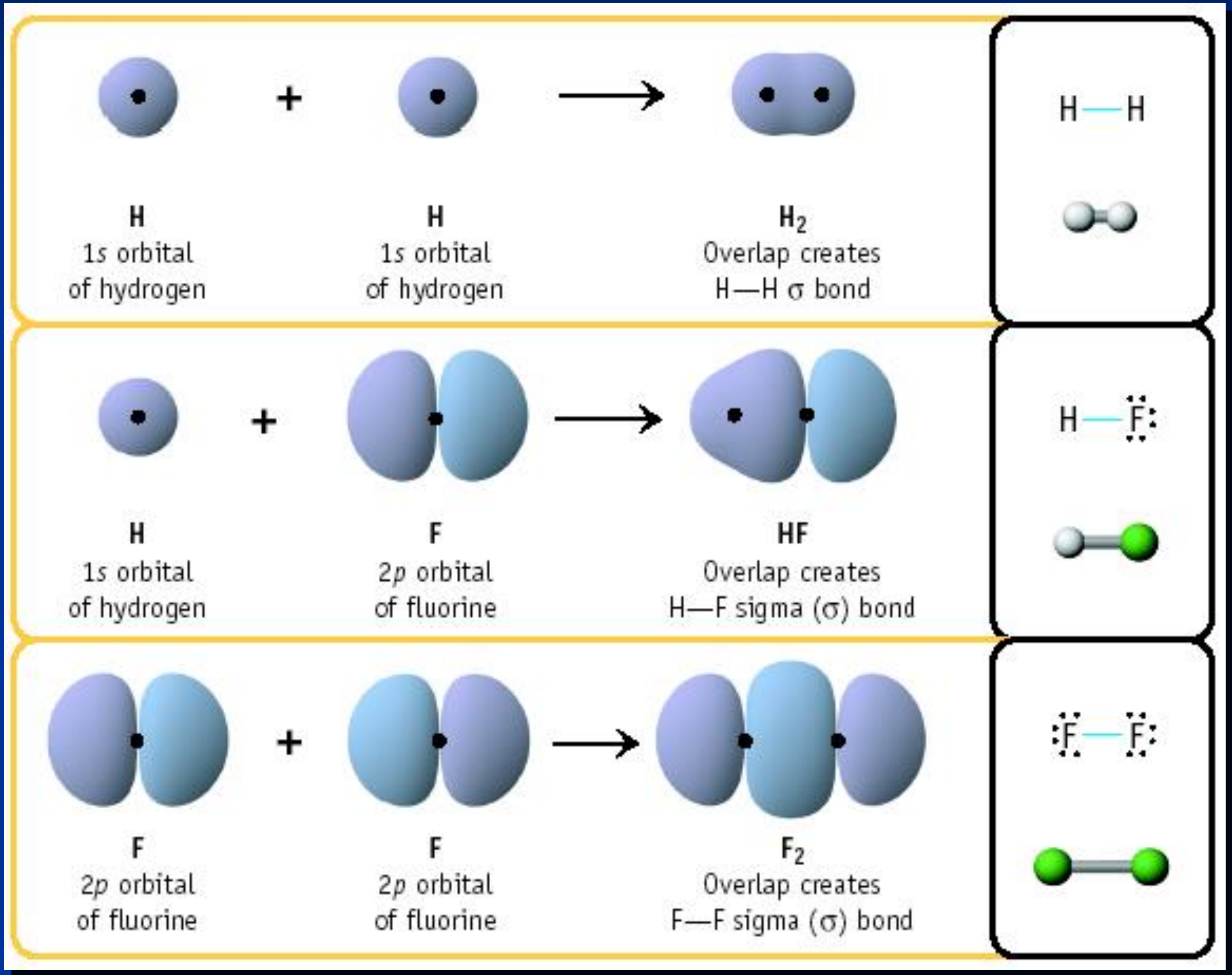
http://library.thinkquest.org/27819/ch2_2.shtml

This is and example of orbital mixing. The two atoms share one electron each from there outer shell. In this case both 1s orbitals overlap and share their valence electrons.

Energy Diagram of Sigma Bond Formation by Orbital Overlap

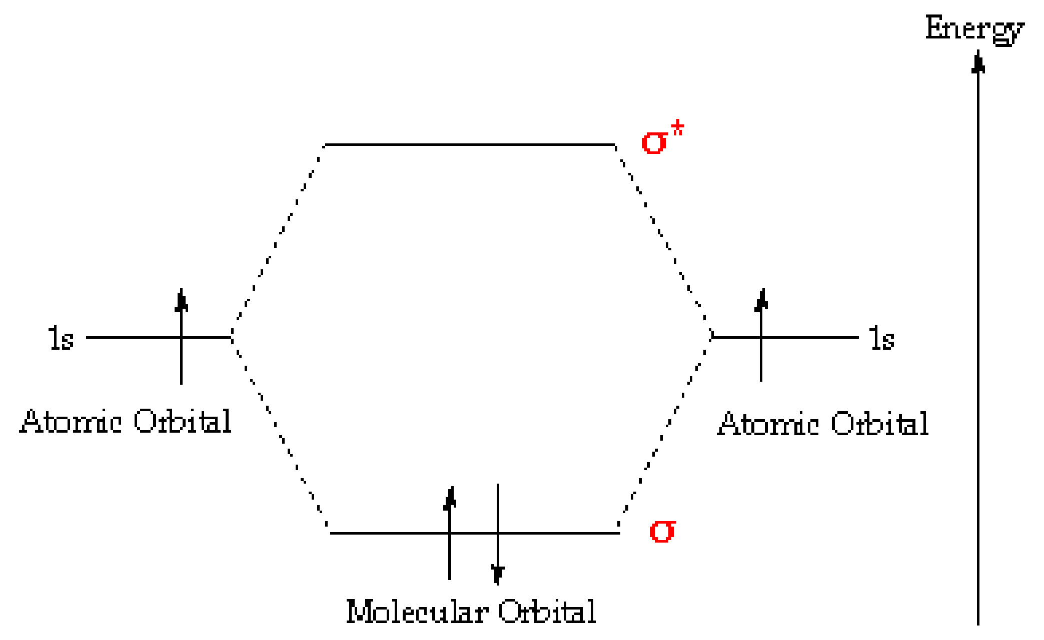


Examples of Sigma Bond Formation



Atomic and Molecular Orbitals

- In atoms, electrons occupy **atomic orbitals**, but in molecules they occupy similar **molecular orbitals** which surround the molecule.
- The two 1s atomic orbitals combine to form two molecular orbitals, one bonding (σ) and one antibonding (σ*).



http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/main.html

- This is an illustration of molecular orbital diagram of H_2.
- Notice that one electron from each atom is being "shared" to form a covalent bond. This is an example of orbital mixing.

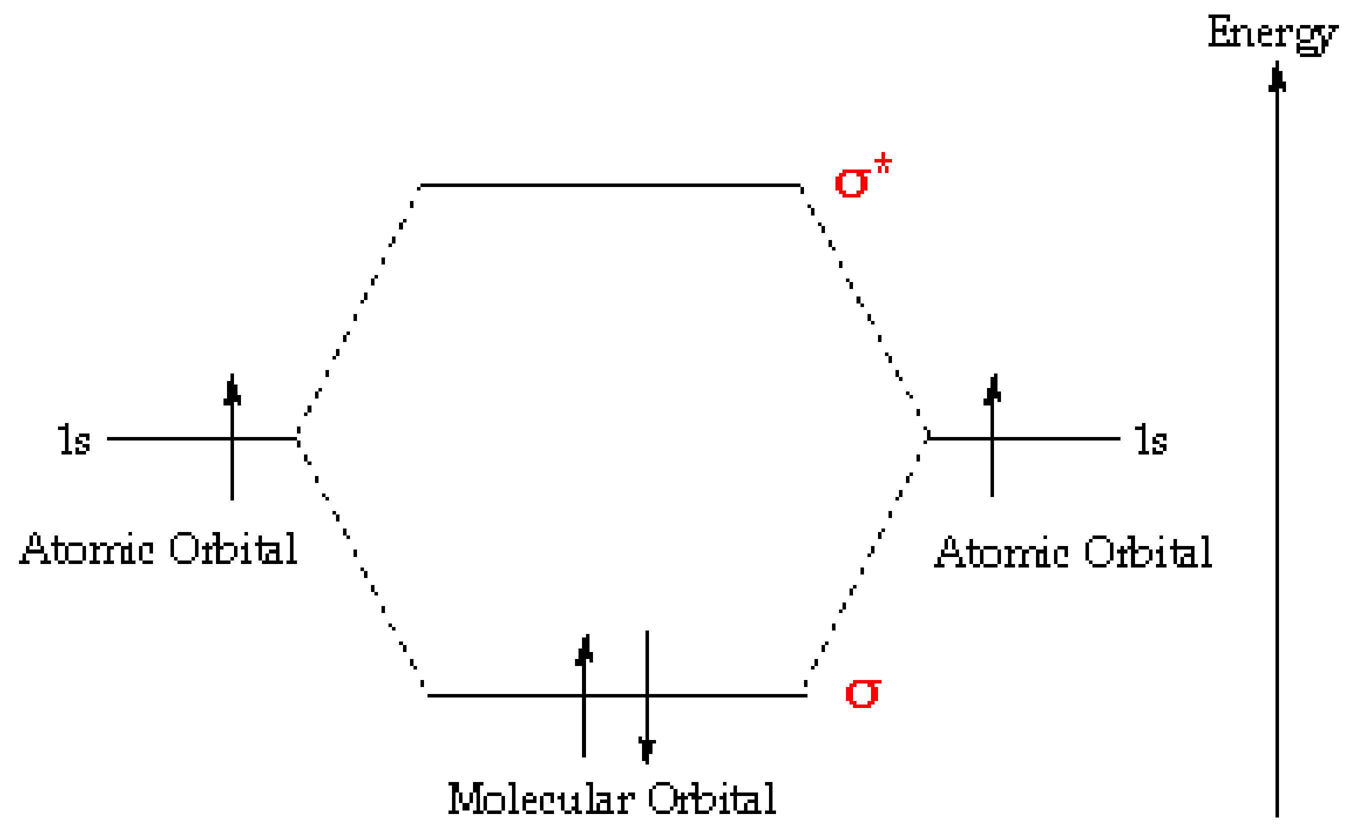
Molecular Orbital Theory

- Each line in the diagram represents an orbital.
- The molecular orbital volume encompasses the whole molecule.
- The electrons fill the molecular orbitals of molecules like electrons fill atomic orbitals in atoms

Molecular Orbital Theory

- Electrons go into the lowest energy orbital available to form lowest potential energy for the molecule.
- The maximum number of electrons in each molecular orbital is two. (Pauli exclusion principle)
- One electron goes into orbitals of equal energy, with parallel spin, before they begin to pair up. (Hund's Rule.)

Molecular Orbital Diagram (H_2)



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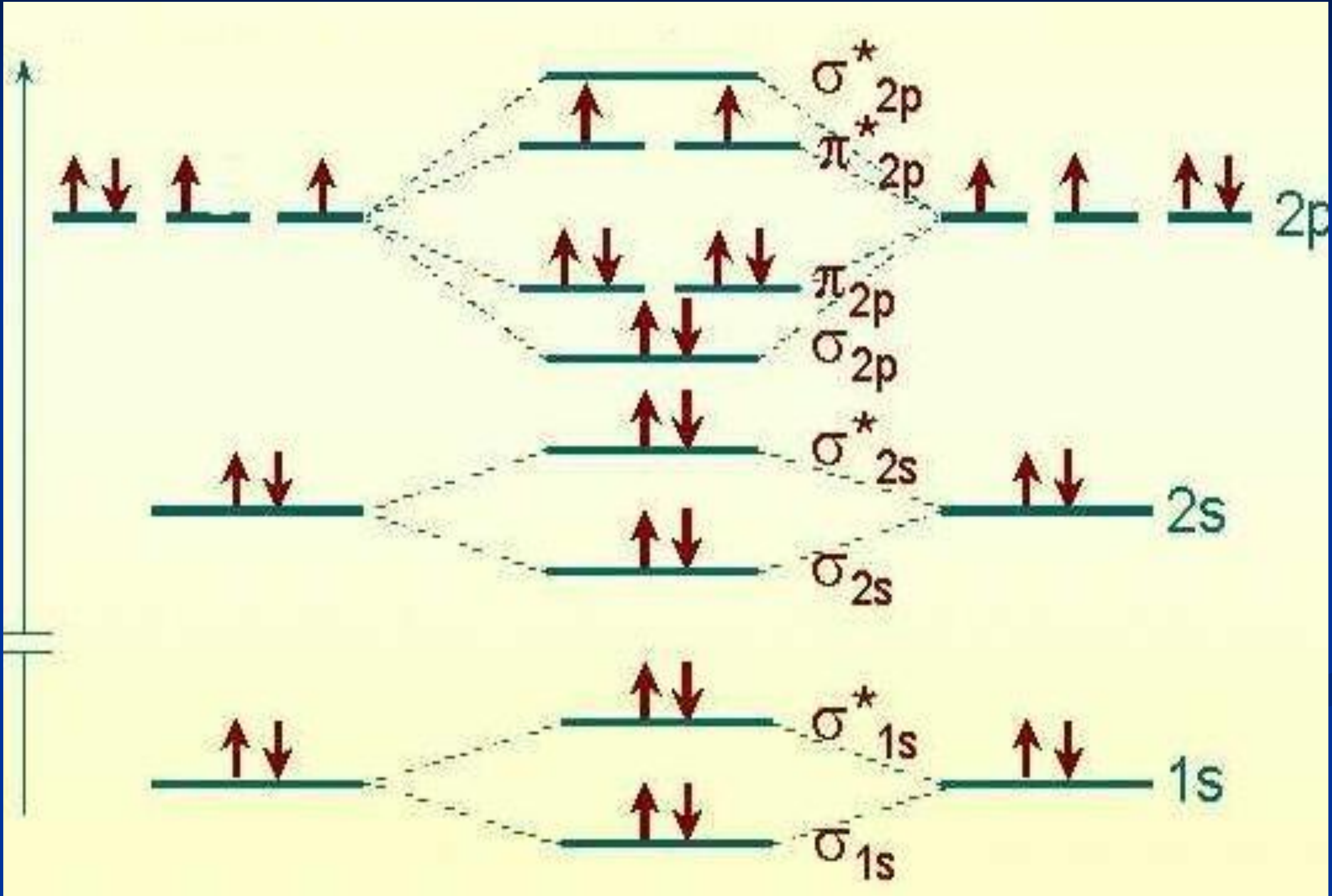
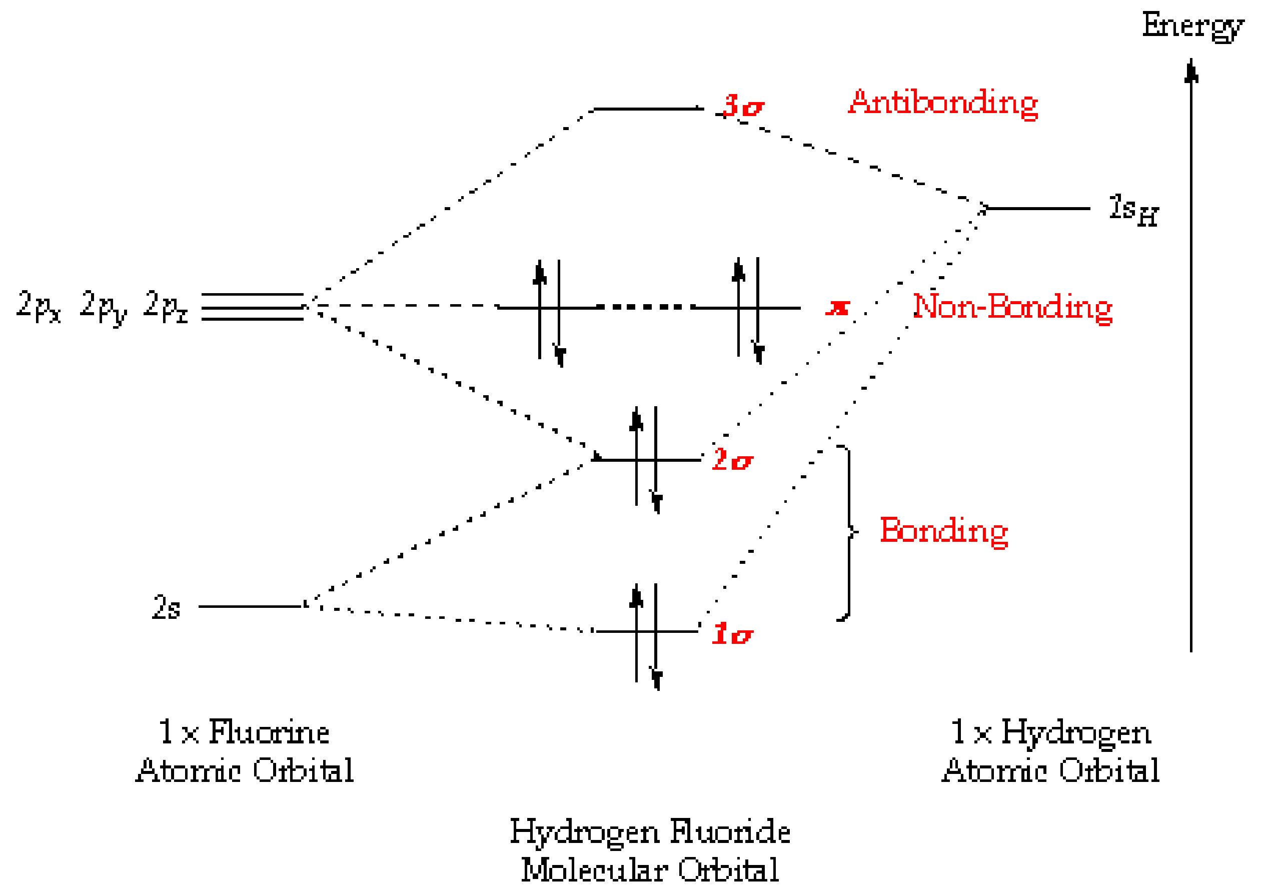
MOT Diagram for O_2



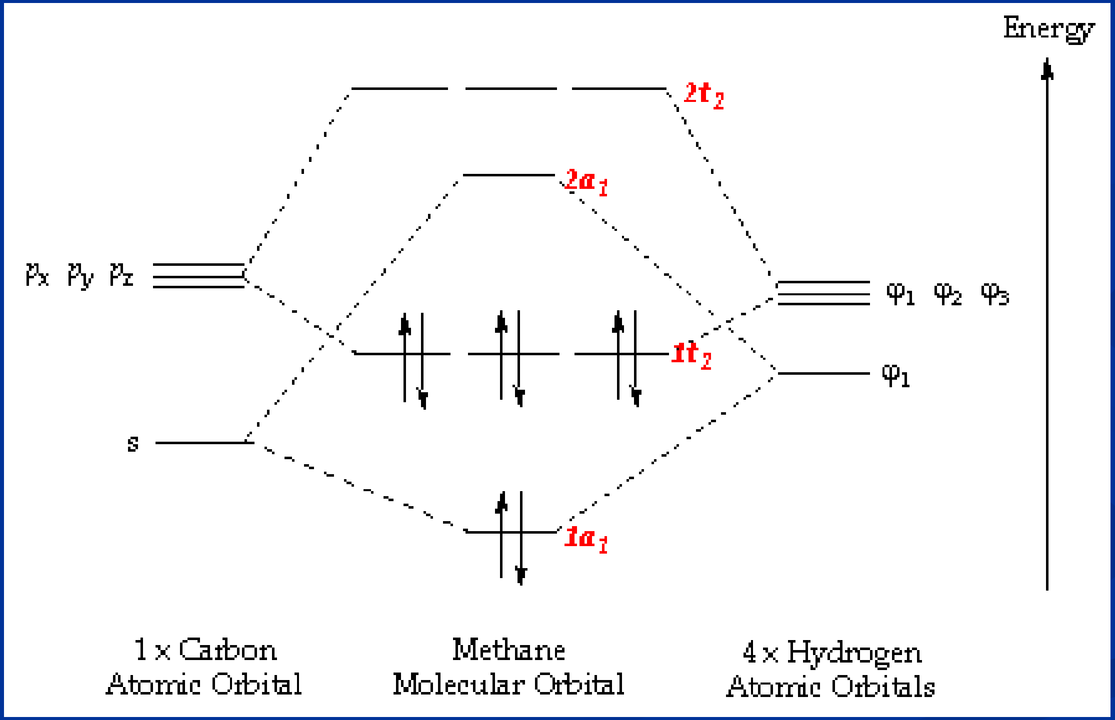
Molecular Orbital Diagram (HF)



http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/main.html

Molecular Orbital Diagram (CH_4)

So far, we have only look at molecules with two atoms. MO diagrams can also be used for larger molecules.



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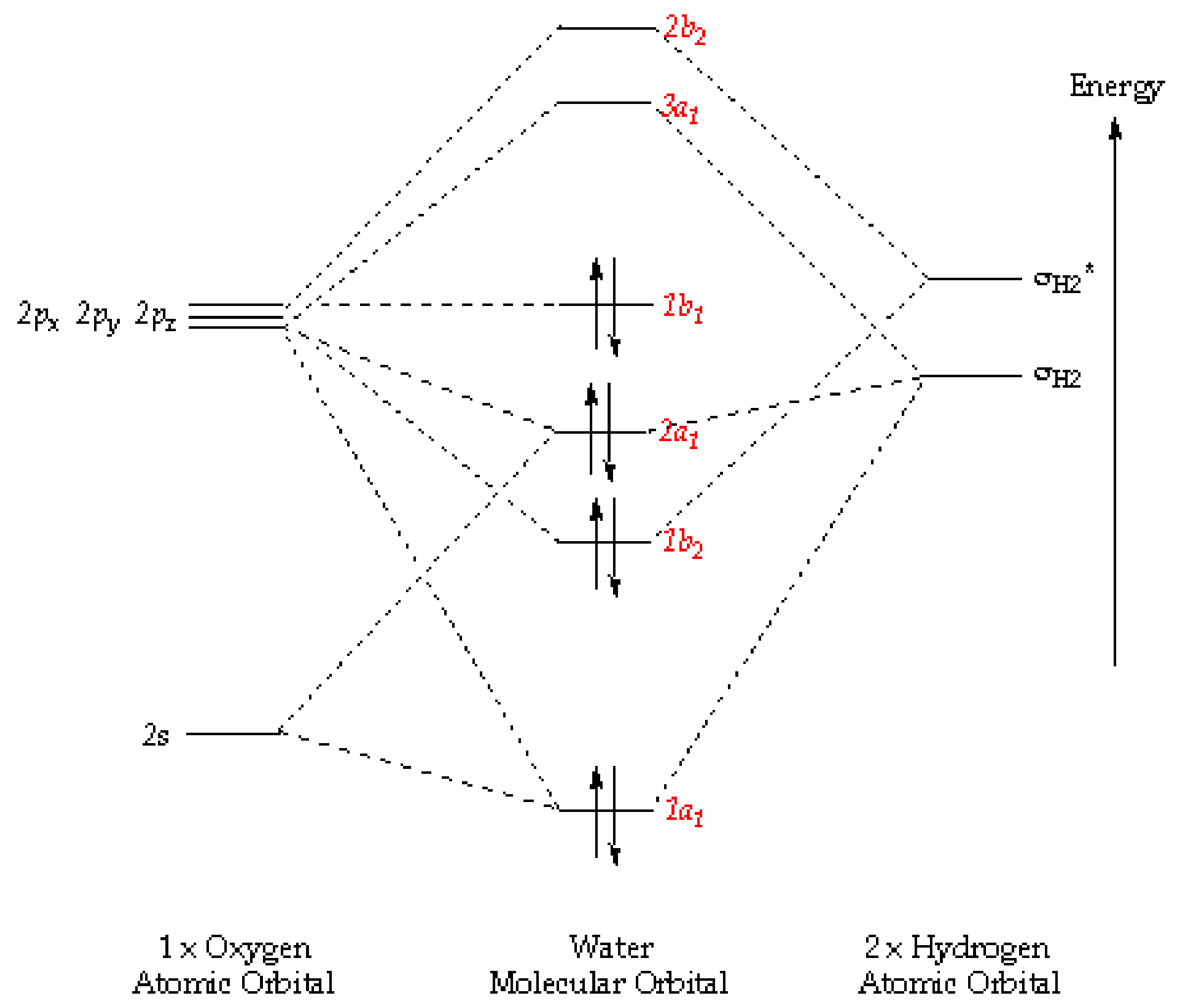
Molecular Orbital Diagram (H_2O)



Conclusions

- Bonding electrons are localized between atoms (or are lone pairs).
- Atomic orbitals overlap to form bonds.
- Two electrons of opposite spin can occupy the overlapping orbitals.
- Bonding increases the probability of finding electrons in between atoms.
- It is also possible for atoms to form ionic and metallic bonds.

Molecular Orbital Theory
Valence Bond Theory

Resonance

MO Theory

- MOs are created by adding and subtracting AOs
- MO Theory can be used by computers to model molecules
- For our purposes, Valence Bond Theory provides enough information
- VBT: Geometry and Sigma Bonding

1.7B Valence Bond Theory

Bonds formed by adjacent AO overlap

Bonds are localized to two atoms not molecule

Theory correlates well with Lewis structures

VBT and Geometry

Second period Elements: 2s and 2p orbitals
S orbital is spherical
P orbitals are 90º to each other

So how do we get 109.5º, 120º, and 180º for sp^3, sp^2, and sp?

Hybrid Orbitals

Pauling: Formation of Hybrid Orbitals
occurs prior to bonding.

Hybrid orbitals lead to observed bond angles

<u>Hybridization:</u>
Combination of AOs
Combine wave functions for each orbital

Hybrid Orbitals

Number of starting Aos must equal number of hybrid orbitals

3 types of hybrid orbitals:
sp, sp^2, sp^3

2nd Period: 1 2s Orbital + 3 2p Orbitals
These form 4 equivalent sp^3 orbitals
Described by 4 new wave functions

Orbital Geometry

Wave function plots show shape of new hybrid orbitals

Axes of four orbitals point to four corners of a regular tetrahedron.

So angle for sp^3 is 109.5º

sp^3 hybrid orbital: 25% s, 75% p

Hybrid Orbitals: sp^3 and sp^2

An atom with four sp^3 hybrid AOs is said to be sp^3 hybridized.

Exs: CH_4, NH_3, H_2O

sp^2 = combo of 2s and two 2p orbitals
Third p orbital not involved in hybridization
Exs: Alkene, Aldehyde, BF_3

Hybrid Orbitals: sp

sp: 1 2s + 1 2p = 2 sp hybrids

Other p orbitals do not participate in hybridization

sp hybrid is 50/50 s/p so most s-like

C -Combo of MO Theory and VBT

VBT: Bonds occur between 2 electrons
VBT: Hybrid Orbitals

MO Theory
CH_4: sp^3 hybrid + 1s of H → MOs
Antibonding and Bonding Orbitals
Sigma bond between C and H
Now consider all C-H bonds to be the same as the C-H bond in methane

C- MO Theory and VBT

All C-C bonds involve the same sp^3-sp^3 orbital overlap.

Treat all C-C single bonds the same: sp^3-sp^3

Treat all C-H bonds the same: sp^3-1s

What about Multiple Bonds?

Double bond consists of sigma and pi bond

Sigma bond: sp2-sp2 overlap
Pi bond: p orbital overlap

Triple bond consists of 1 sigma and 2 pi bonds

Sigma bond: sp-sp overlap

Rules for Drawing Resonance Structures

1. Keep same number of valence electrons
2. Follow covalent bonding rules
3. Can’t change positions of Nucleii
4. Structures must have same number of paired and unpaired electrons

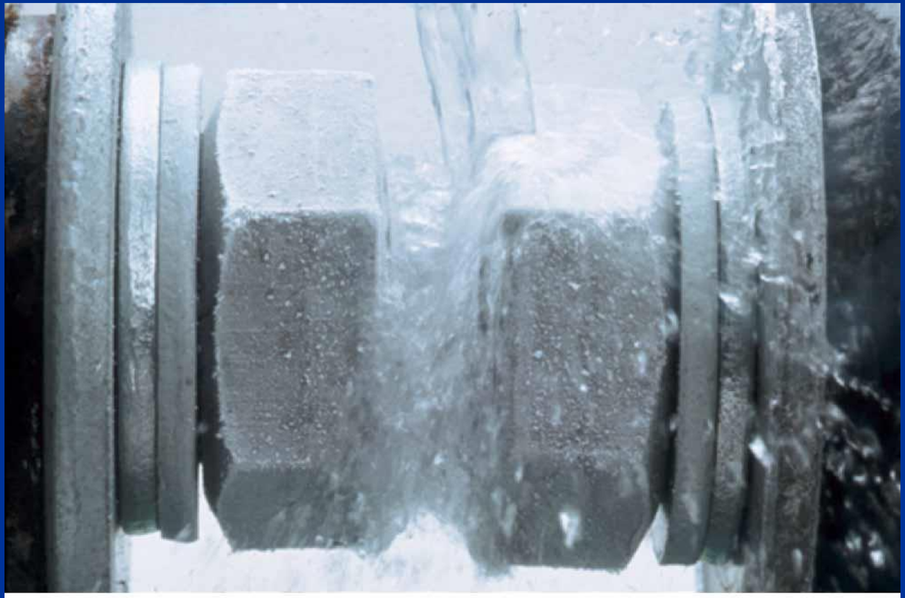
Molecular orbital theory

Paramagnetism

- An atom or molecule is *paramagnetic* if it contains ______________ ______________.
- An atom or molecule is *diamagnetic* if it contains only ____________ ___________ __________ __________.
- Paramagnetic substances are attracted to magnets….
- (Whitten CD video)

Not all models are suitable for all purposes

- Paramagnetic O_2
  - O_2 is paramagnetic (it interacts with a magnetic field). This only happens if O_2 has unpaired electrons
  - Problem: VSEPR predicts O_2 has paired electrons.
- Results of experimental observation require that we adjust our model.



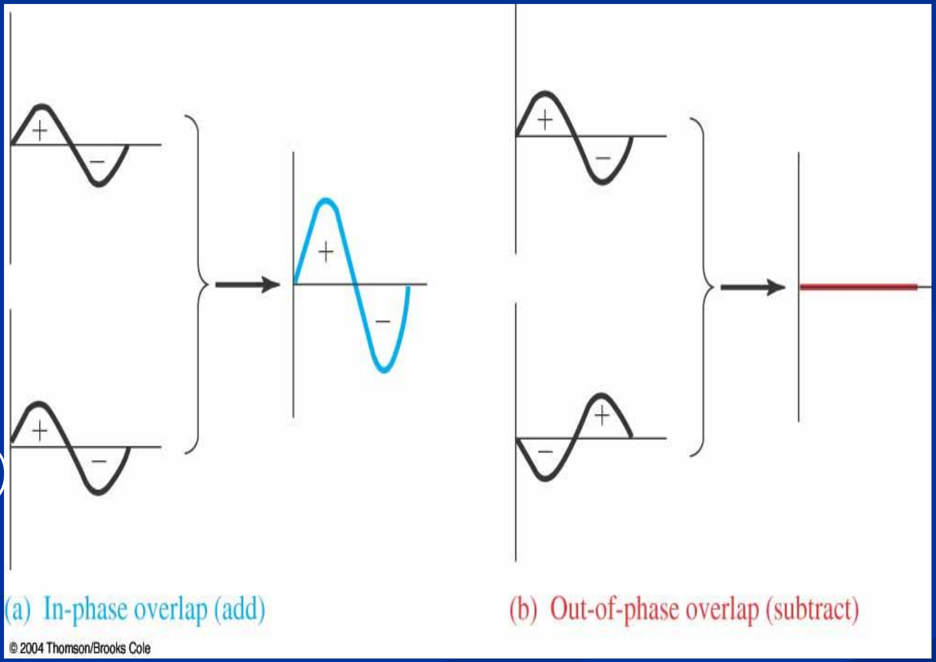
Molecular orbital theory vs VSEPR-valance bond theory

- Two differing explanations of bonding. Each has its strengths and weaknesses.

	VSEPR-VB theory	**MO theory**
Strengths	Explains geometries well, easy to visualize	Atomic orbitals (AOs) combine to form molecular orbitals (MOs); describes several molecular properties (bond energies, magnetic properties)
Weaknesses	Orbitals on atoms remain distinct (this is probably not what happens in reality).	Harder to visualize the results

Molecular orbitals (MO)

- MO formed by combination of AO.
- Two combinations possible:
  - additive (in-phase)
  - subtractive (out of phase)



(a) In-phase overlap (add)

(b) Out-of-phase overlap (subtract)

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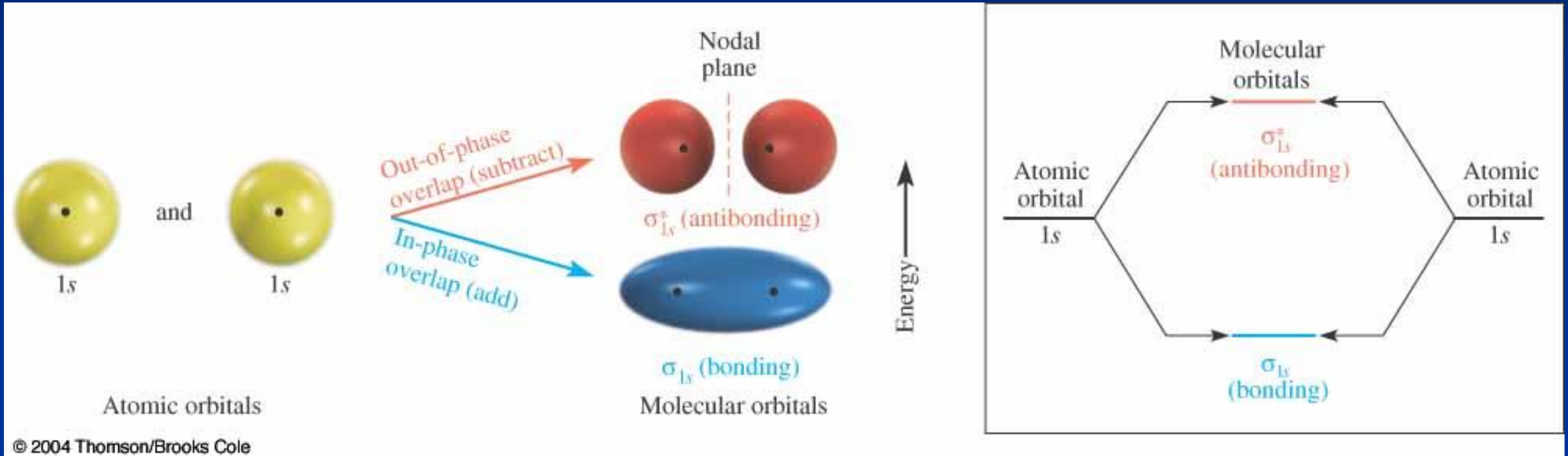
Combining atomic orbitals

- additive combinations of AO are called **bonding orbitals.**
- subtractive combinations of AO are called **anti-bonding orbitals.**

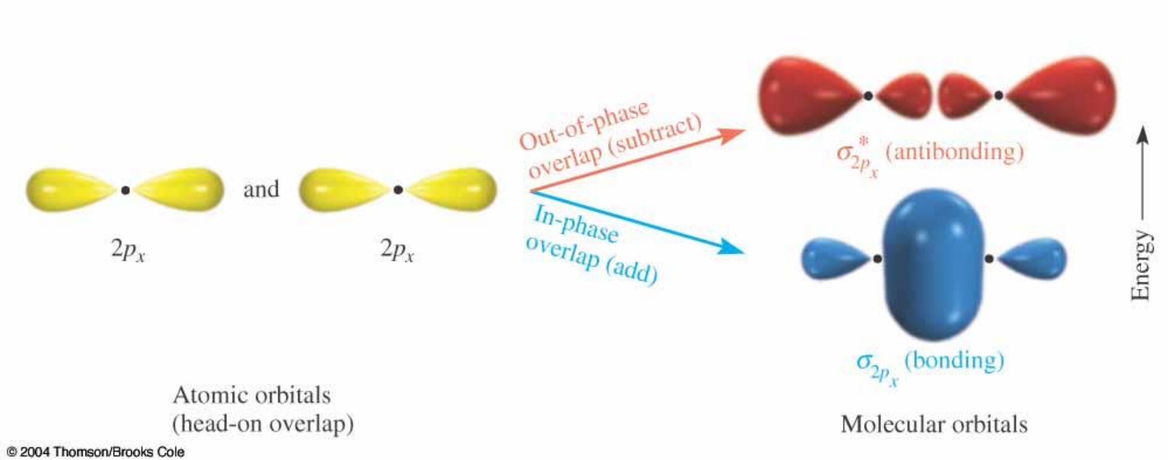
- **The combination of two AO produces TWO MO (one BO, one ABO).**

Creating molecular orbitals from *1s* atomic orbitals



- Combination of two *1s* atomic orbitals forms σ_{1s} and σ^*_{1s} molecular orbitals. The anti-bonding σ^*_{1s} orbital has a *nodal plane*, where the probability of finding the electrons is zero.
- Anti-bonding orbitals are less stable than bonding orbitals. The stability of a molecule or ion is determined by the number of bonding and anti-bonding orbitals filled.
- *2s* orbitals combine like *1s* orbitals.

Creating molecular orbitals from *2p* atomic orbitals

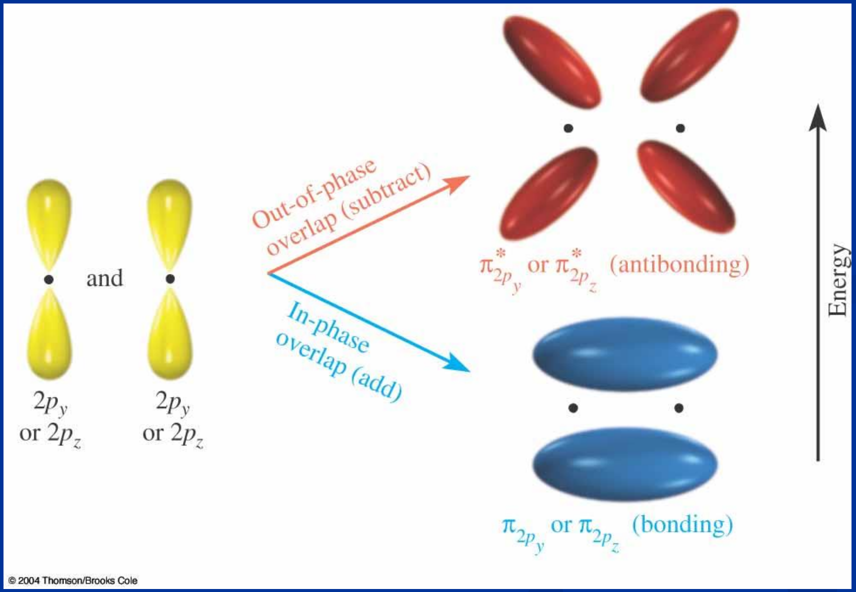


- There are three *p* orbitals for each atom in the *2p* block. One pair of these (p_x) are oriented such that they combine end-to-end to form a $\sigma_{2p}/\sigma^*_{2p}$ pair of MOs.
- Are there any nodal planes?
- what about the other two pair of *2p* AOs?

π MOs from *2p* AOs

- the other two AOs are not lined up end-to-end, but side-by-side.
- These combine to form two pair of π_{2p}/π^*_{2p} MOs

- Are there any nodal planes in the π/π^* orbitals?



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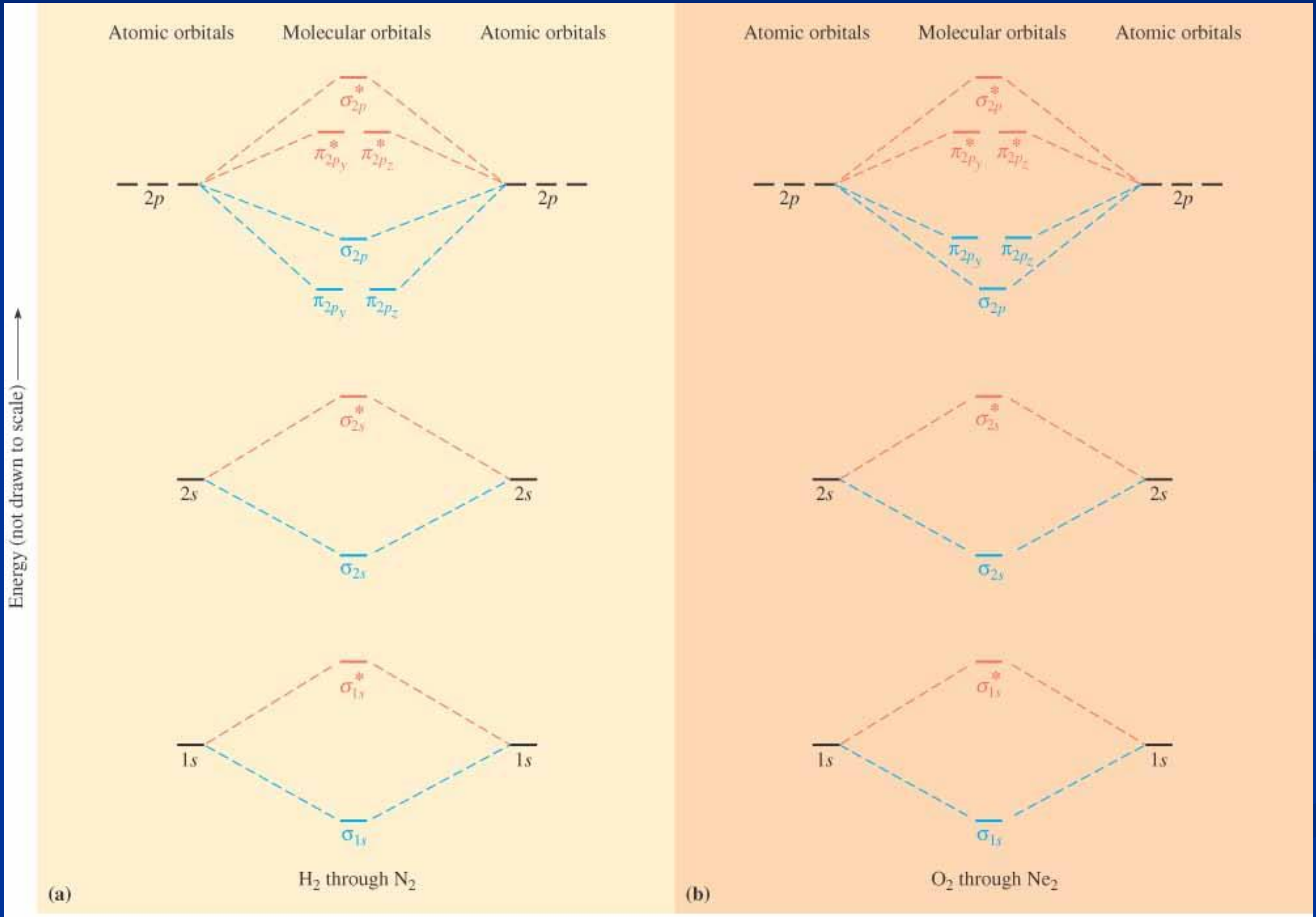
Homonuclear diatomic MO diagrams for H_2 thru Ne_2



(a) H_2 through N_2

(b) O_2 through Ne_2

Using MO diagrams

1. Select and draw the appropriate MO diagram
2. Count up ALL electrons in the molecule (not just valence electrons).
3. Add electrons to the MO diagram starting with the lowest energy level
    1. Must follow Pauli Exclusion Principle
    2. Must follow Hund's Rule

Bond order

$$bond\_order = \frac{bonding\_e^{-} - antibonding\_e^{-}}{2}$$

- the higher the bond order:
  1. the molecule will be ____________ stable.
  2. the bond length will be ___________.
  3. the bond energy will be ____________.

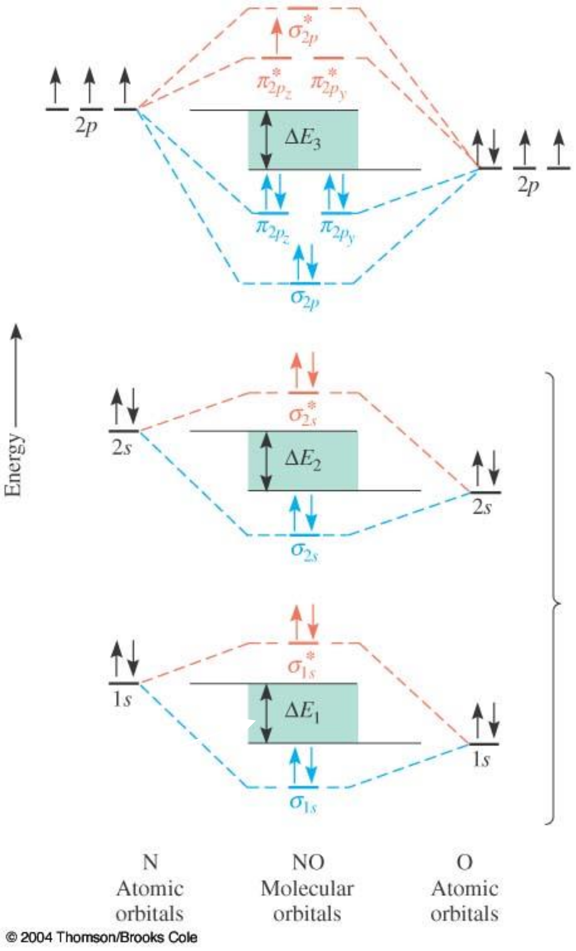
Homonuclear diatomic molecules

- Let’s draw some MO diagrams for the homonuclear diatomic molecules. Determine the bond order for each.

- H_2, He_2, Li_2, B_2, C_2, N_2, O_2, F_2
  - What’s interesting about B_2 and O_2?

- Text, p. 357 provides further data on these molecules.
- Be familiar with calculating bond order and comparing bond orders of different molecules.

Heteronuclear diatomic molecules

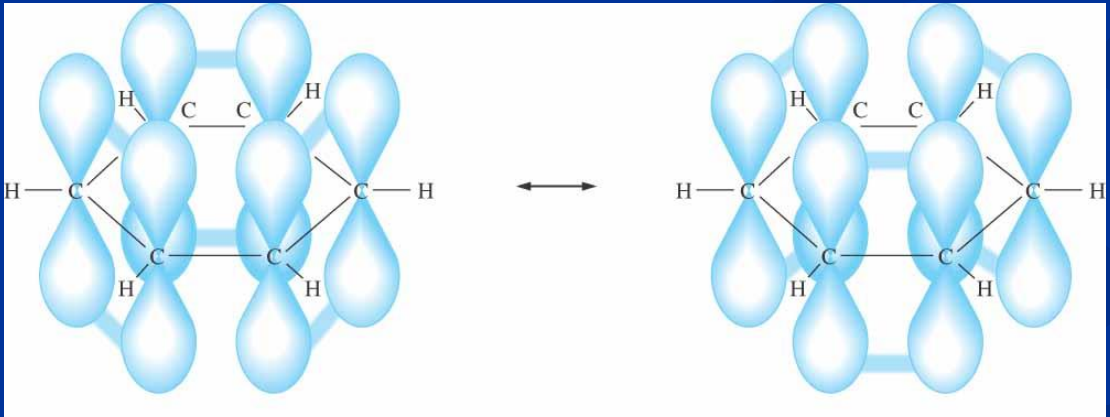


More electronegative elements have lower AO energy

gap between AOs varies from atom to atom. If gap were larger would the molecule be more polar or less polar?

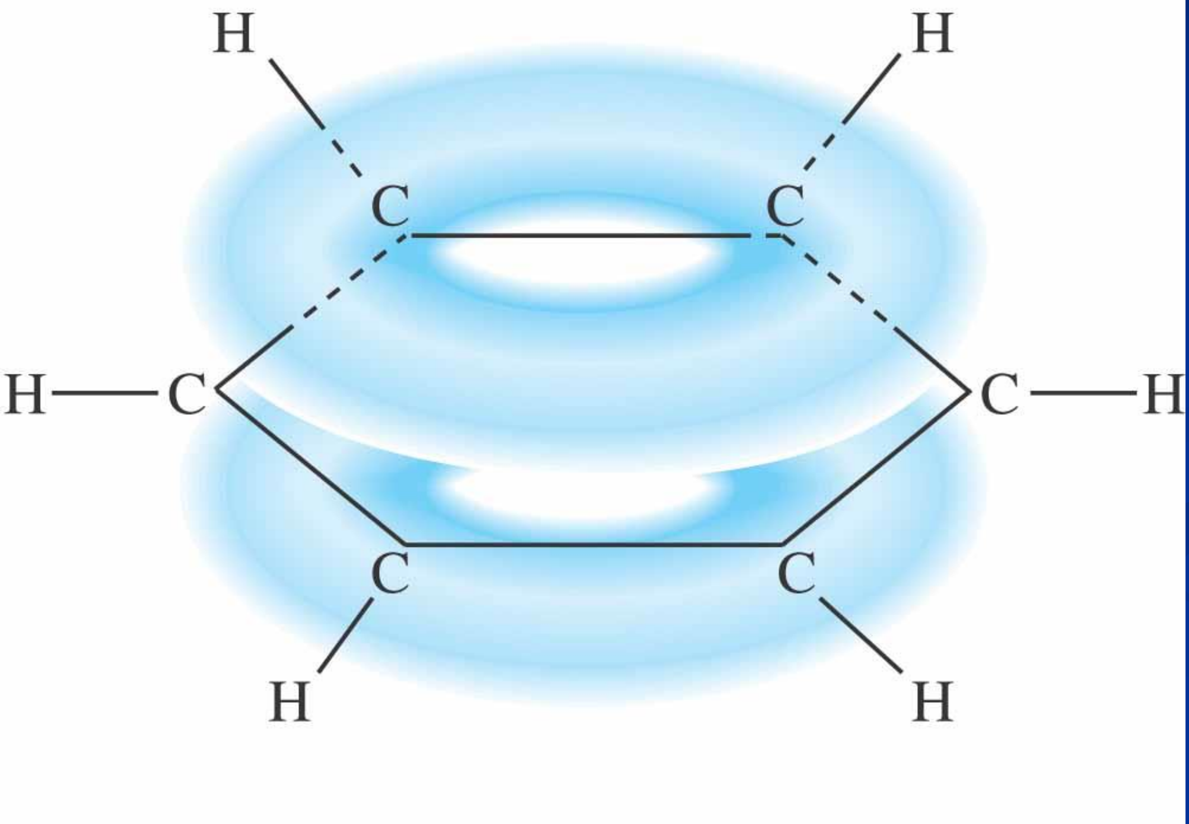
Delocalization: riding the electron superhighway

- *p* AOs can combine in a π bond network, forming a delocalized molecular orbital covering the network length.
- What is the bond order of the carbon bonds?



(b) *p*-Orbital overlap in valence bond resonance structures

Benzene rings



(c) Delocalized MO representation

- Valence Bond Theory
- Bonding theories
- Hybridization

Bonding Theories

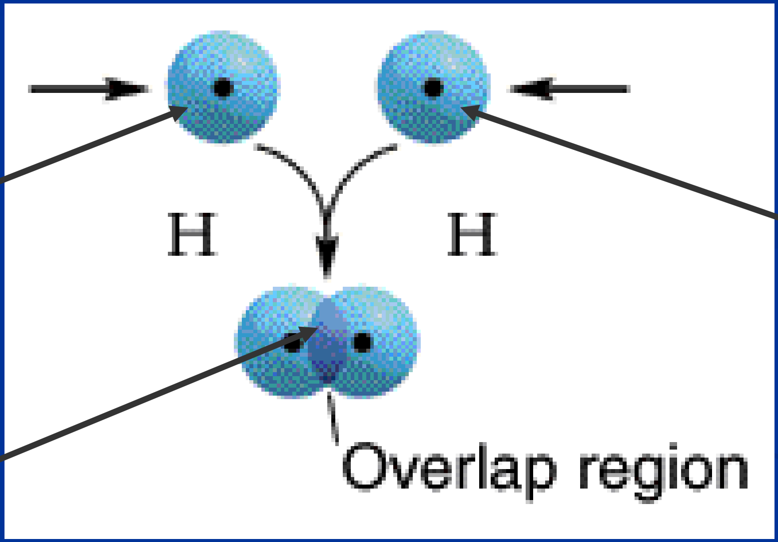
- Lewis structures & VSEPR do not explain:
  - -how a bond forms
  - -what orbitals involved in bonding

- A bonding theory can answer these questions

- Two bonding theories widely used:
  - Valence Bond Theory (VBT)
  - Molecular Orbital Theory (MOT)

Valence bond theory (VBT)

- **Major assumptions of VBT:**
- **Bonds form when orbitals on atoms overlap**



1s orbital of H atom with 1 e$^-$

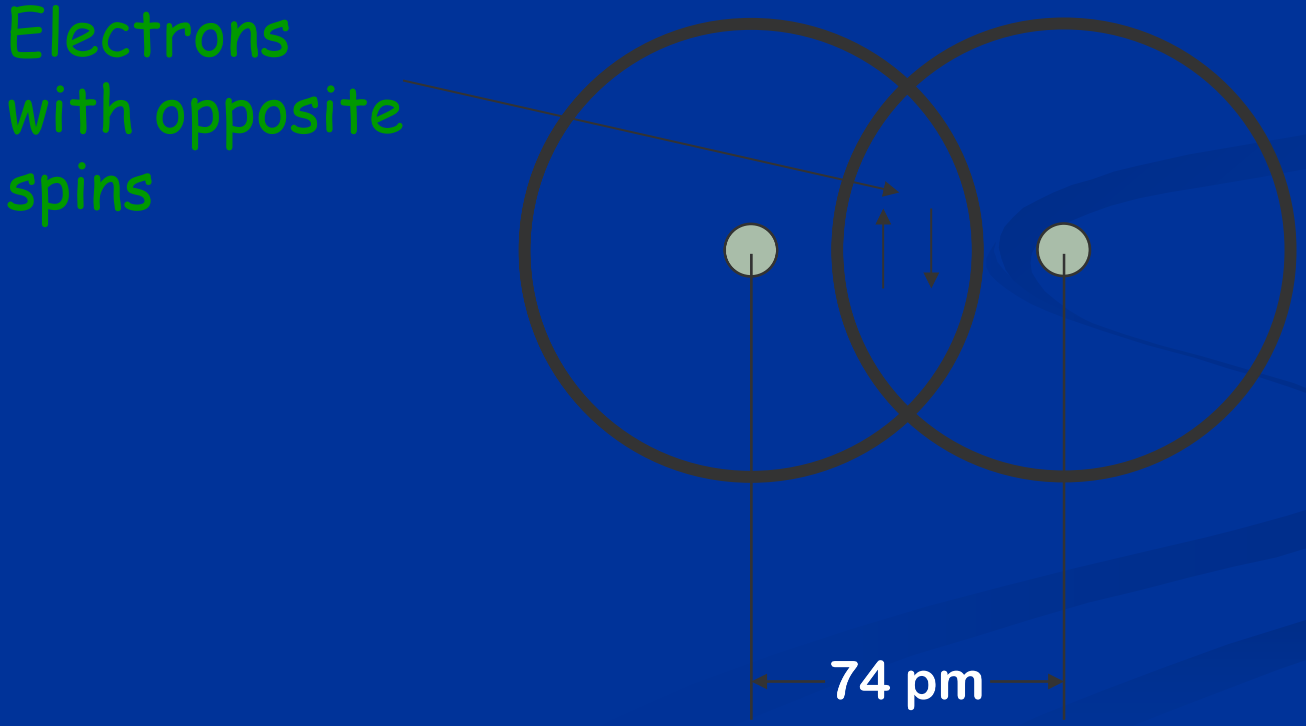
1s orbital of H atom with 1 e$^-$

2 e$^-$s in the overlap region$^-$

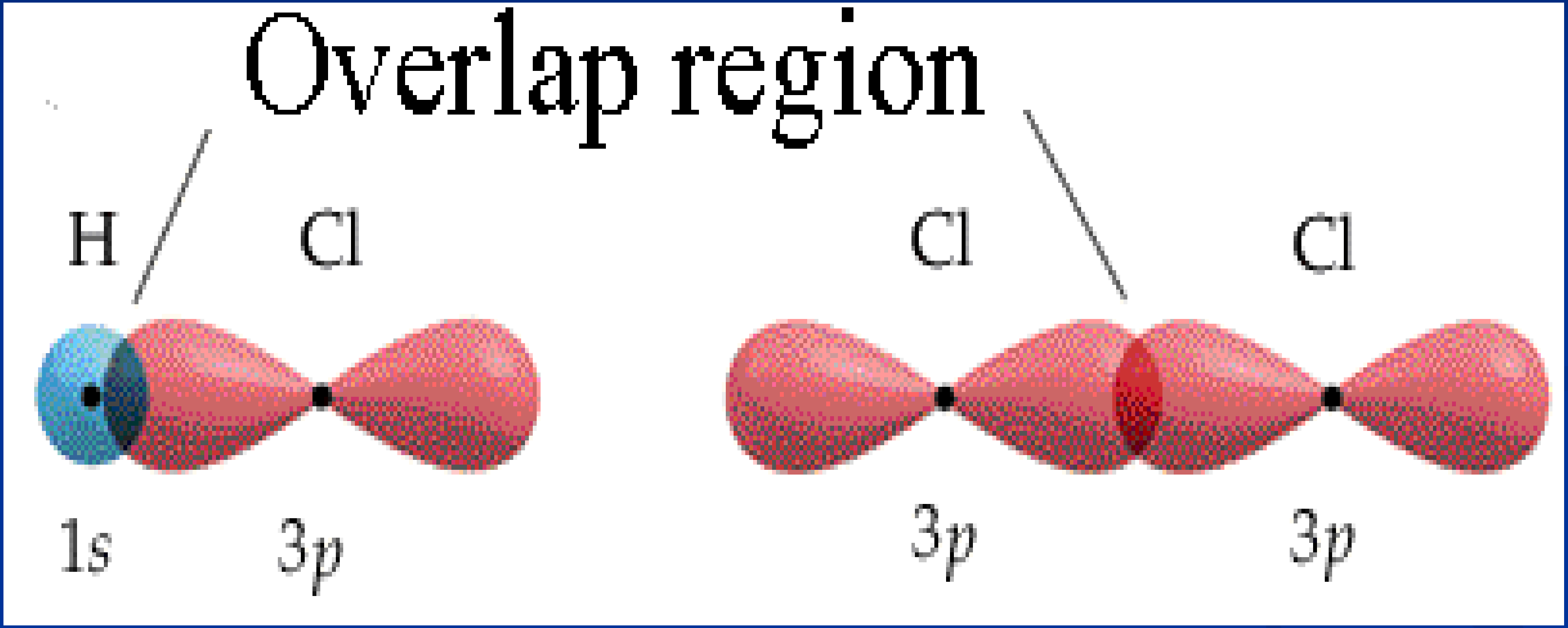
- **Two electrons of opposite spin in the orbital overlap region**

Valence bond theory

- According to this model ⇒ 1*s* orbitals of each atom overlap to form the H-H bond



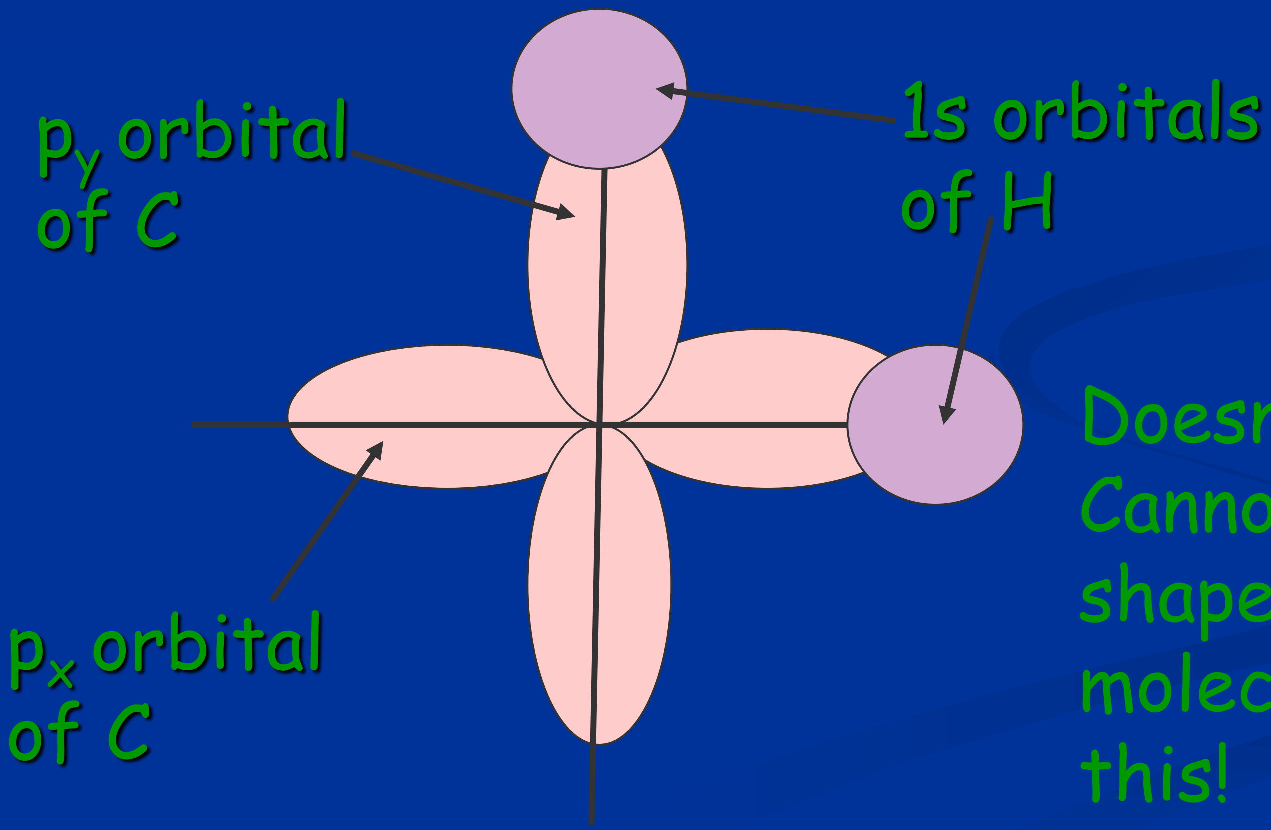
Valence bond theory (VBT)



Problem: Simple overlap of atomic orbitals do not produce the observed shape of molecules

Valence bond theory

- According to the e^- configuration ⇒ C can form 2 bonds



Doesn't work!! Cannot get the shape of CH_4 molecule out of this!

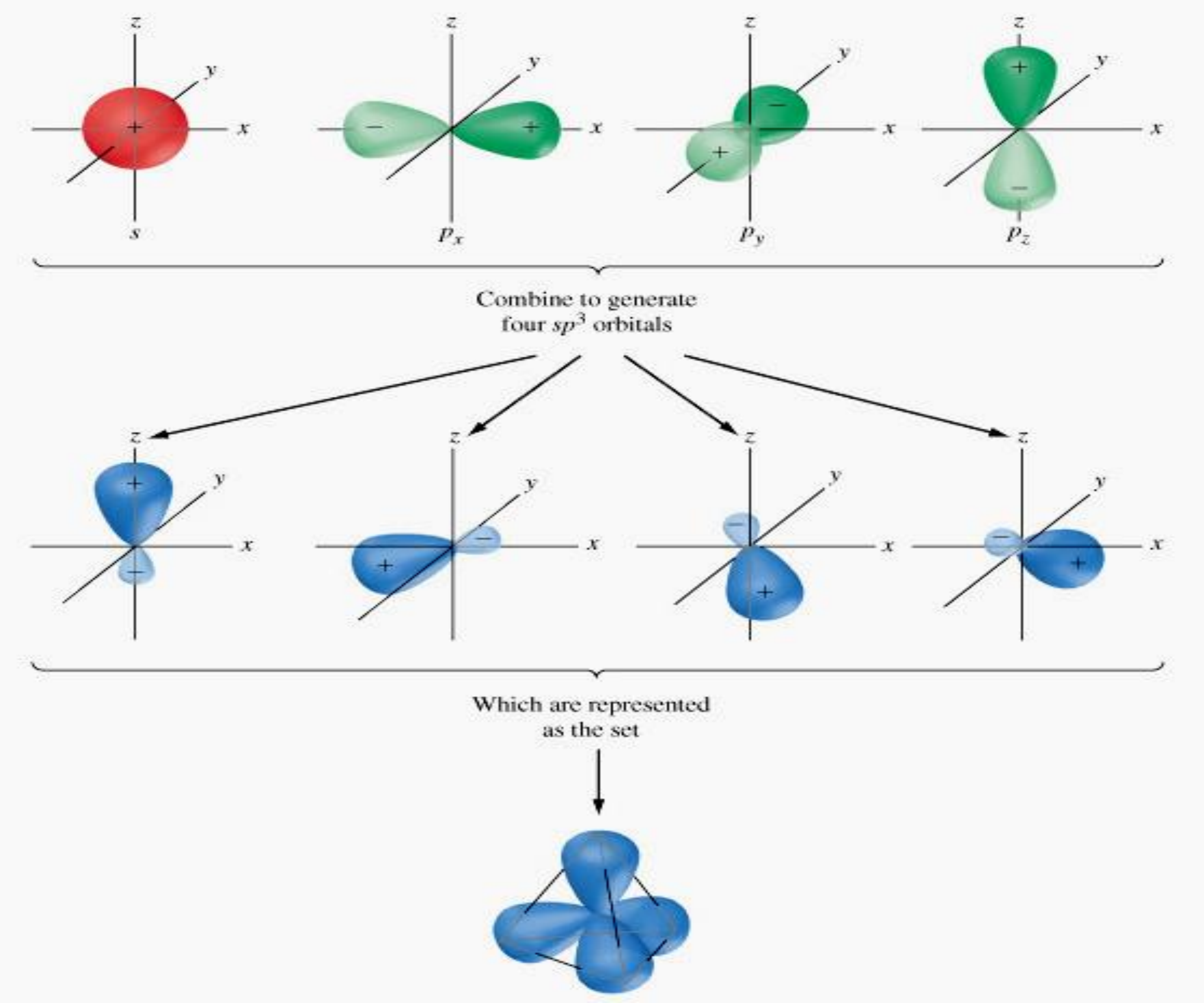
Valence bond theory

- Example – CH_4
- C is the central atom
- Valence e⁻ configuration of C ⇒ $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$ Experiments show 4 equivalent C-H bonds
- How can these 4 bonds be obtained?

Valence bond theory

- How can C get 4 orbitals to overlap with 4 H 1s orbitals & give a tetrahedral shape?
- Answer: Consider hybrid orbitals for C
- What are hybrid orbitals?
- 4 pure atomic orbitals (2s, $2p_x$, $2p_y$, & $2p_z$) of C are mixed $\Rightarrow$ 4 equivalent hybrid atomic orbitals are produced

Valence bond theory



$s + p_x + p_y + p_z$

⇓

4 equivalent hybrid orbitals

⇓

Each is called sp^3 hybrid orbital

Hybridization

$s + p_x + p_y + p_z$

$\Downarrow$

4 equivalent hybrid orbitals

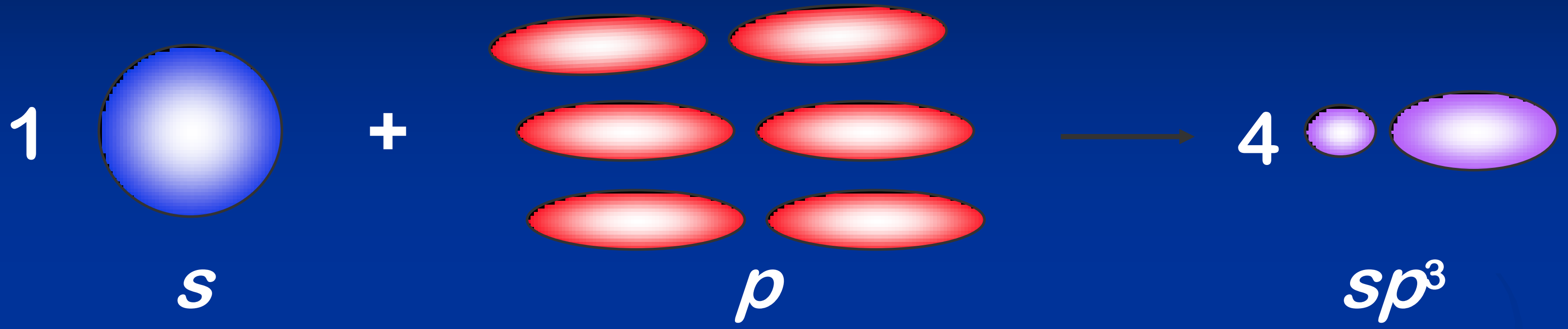
$\Downarrow$

Each is called sp^3 hybrid orbital

$\Downarrow$

VSEPR ⇒ EGG for 4 orbitals ⇒ tetrahedral

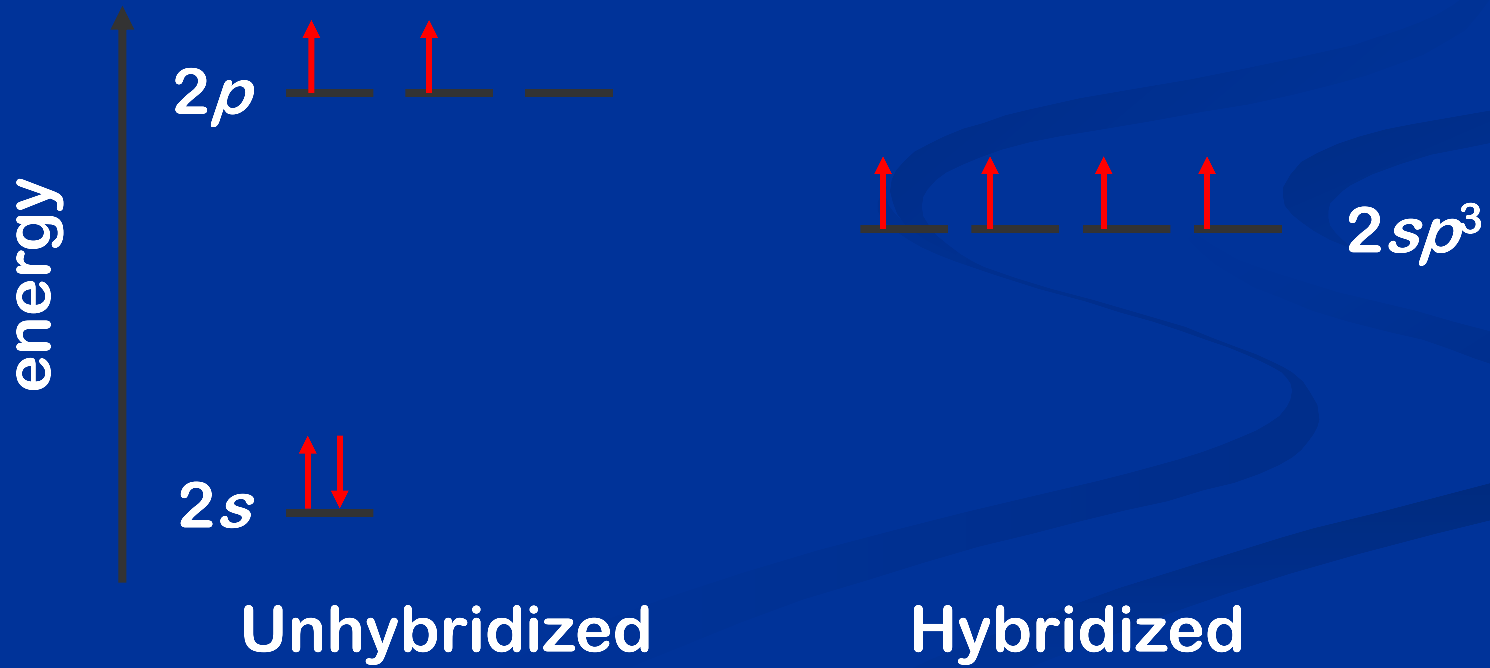
Hybridization



- Each sp^3 hybrid orbital:
- is an atomic orbital
- has mixed s & p character
- has 25% *s* & 75% *p* character

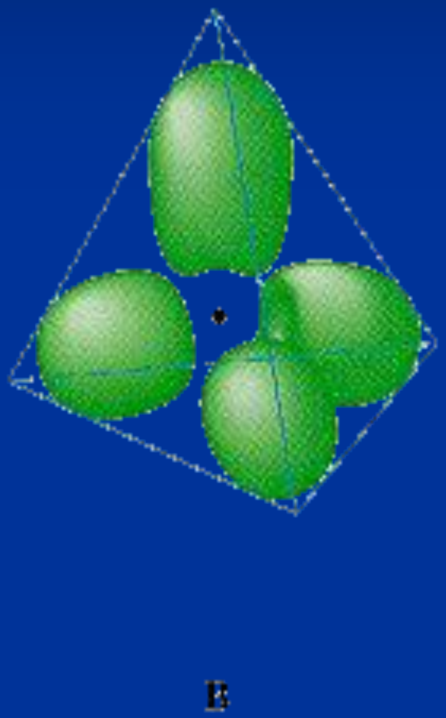
Hybridization

- To explain why carbon forms four identical single bonds ⇒ assume the original orbitals will blend together

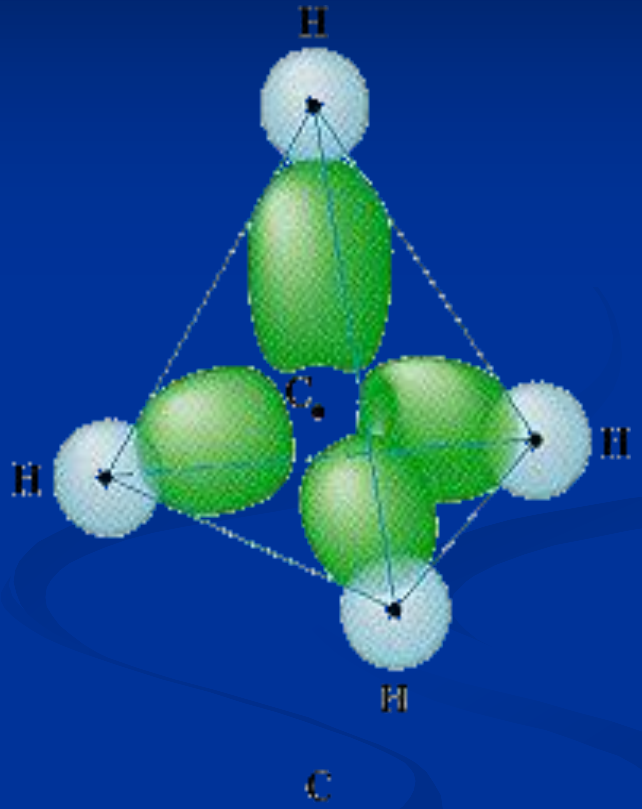


Hybridization

One sp^3
hybrid orbital



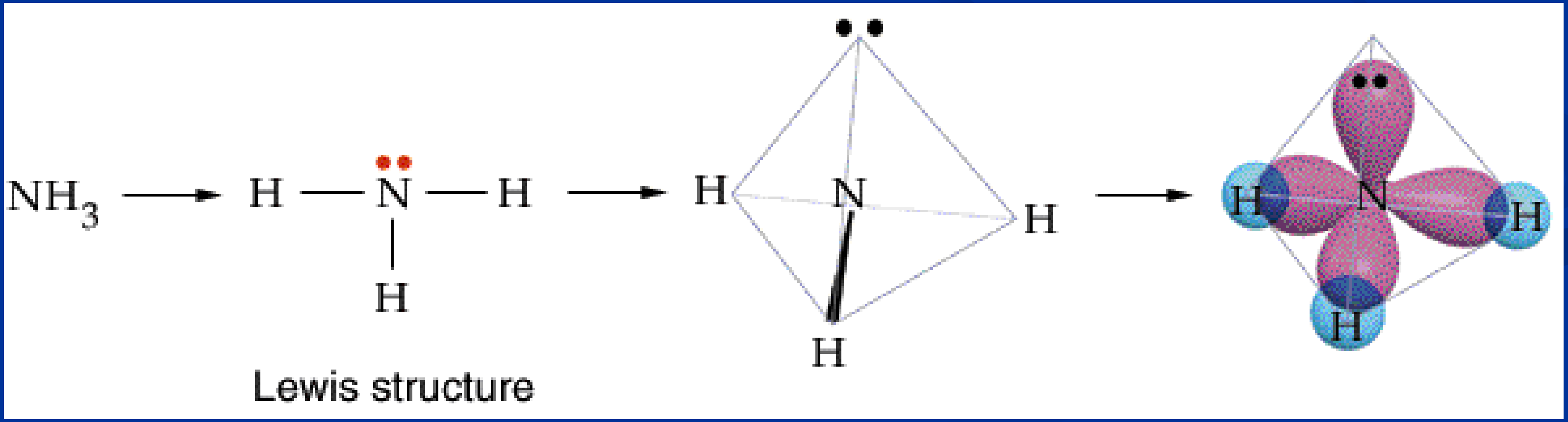
Four sp^3
hybrid orbitals
of carbon



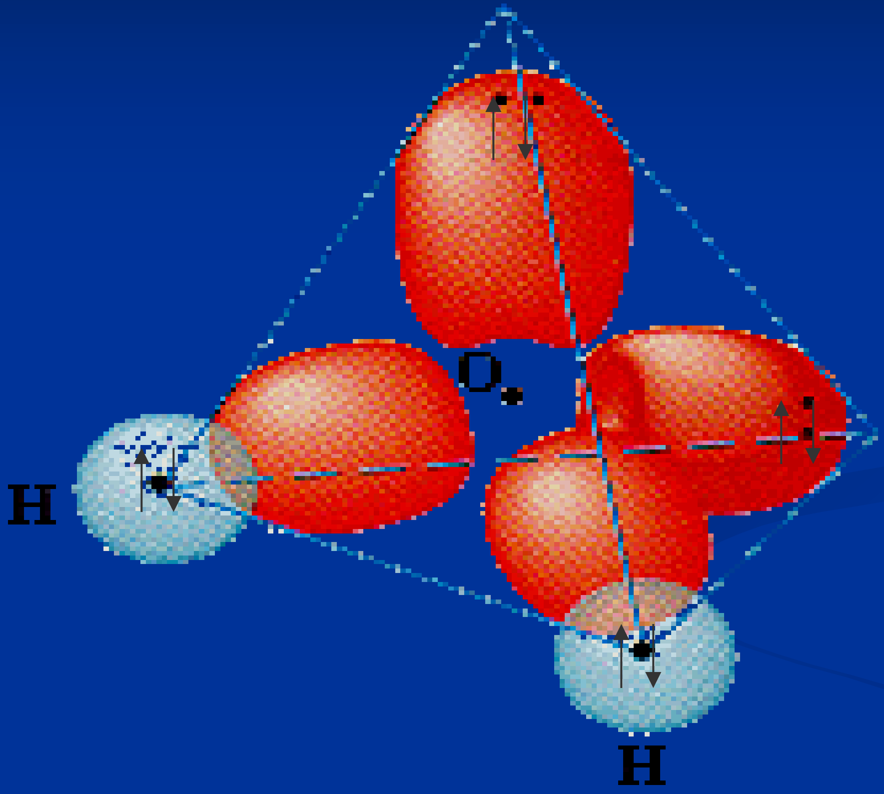
Overlap of sp^3
Orbitals of carbon
With 1s orbitals of H

Hybridization: Ammonia

- Example – Ammonia (NH_3)
- 4 e^- groups ⇒ 4 sp^3 orbitals ⇒ tetrahedral EGG
- 3 bonding & 1 unshared e^- groups
- ∴ trigonal pyramidal geometry



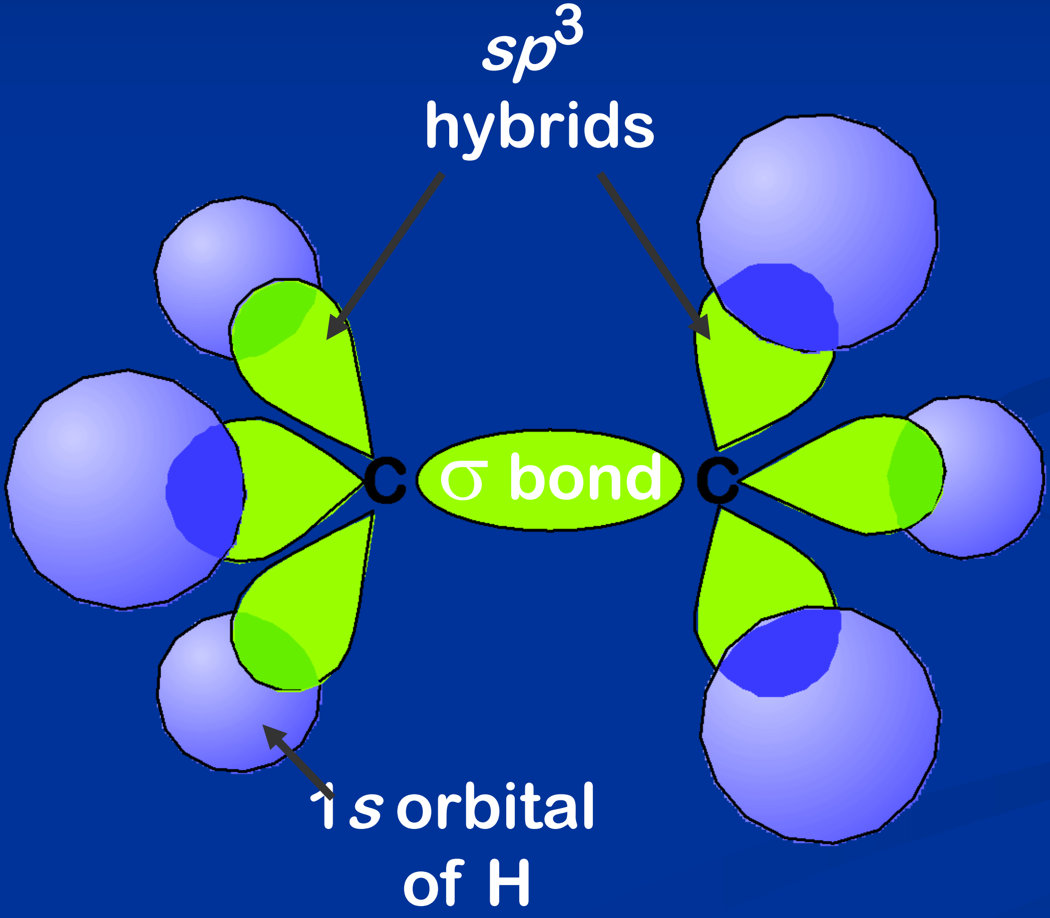
Hybridization: Water



4 e$^-$ groups ⇒ ∴ tetrahedral EGG ⇒ ∴ 4 sp^3 orbitals
Two lone pairs & two bond pairs

C-C single bonds

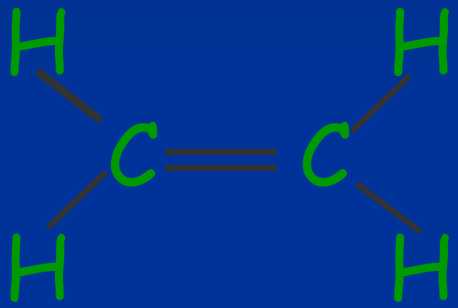
Example: Ethane (CH_3CH_3)



σ bond - formed by an endwise (head-on) overlap

Double Bond (Bond order of 2)

- **Example:** Ethene (CH_2CH_2)



-
- Each C has 3 e^- groups ⇒ ∴ trigonal planar EGG ⇒ ∴ Need 3 equivalent orbitals

Double bond

- To get 3 equivalent hybrid orbitals:

$$s + p_x + p_z$$

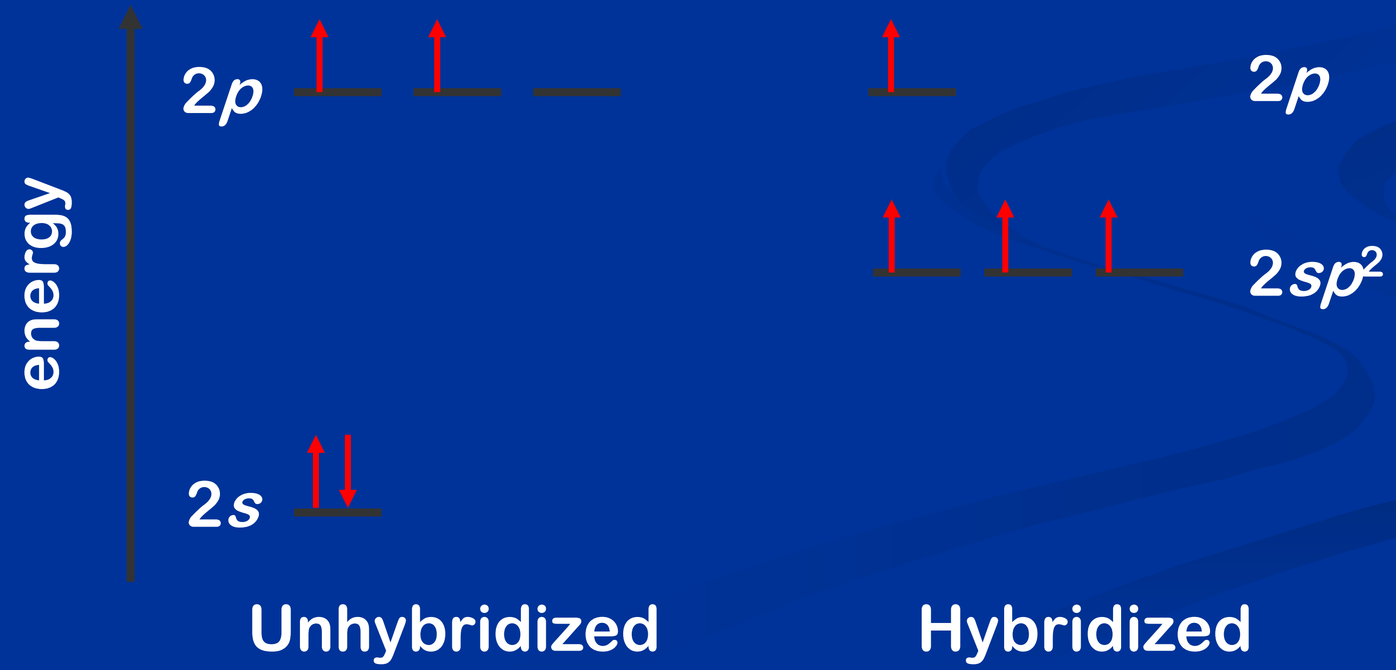
$$\Downarrow$$

$$sp^2 + sp^2 + sp^2$$

-
- Best EGG for three orbitals ⇒ trigonal planar
- Each sp^2 hybrid orbital overlaps with one H 1s orbital

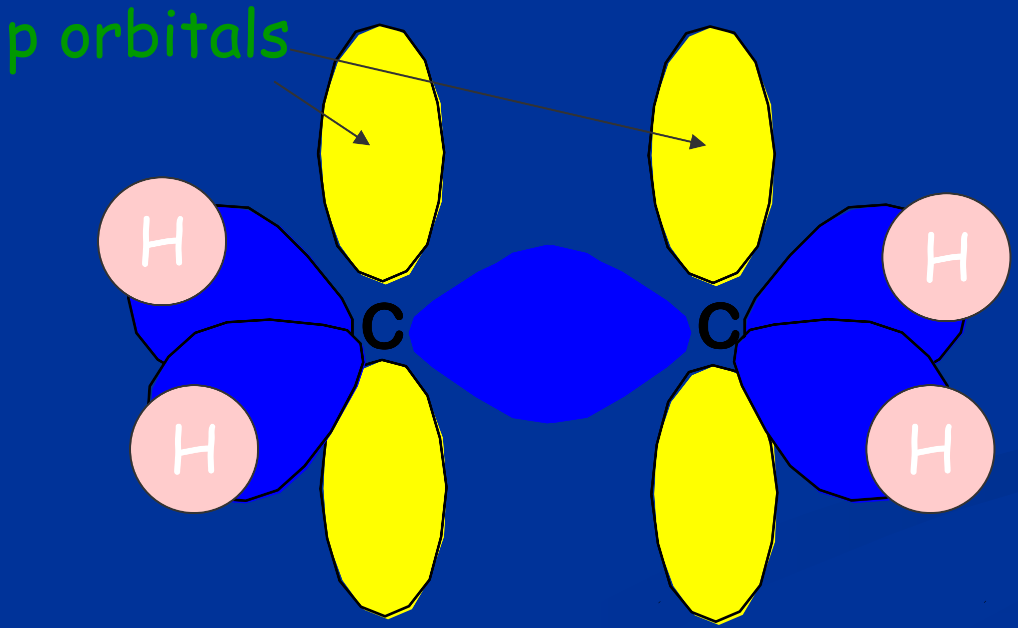
Double bond

- For trigonal planar EGG ⇒ three *sp^2* hybrids
- One *p* orbital remains



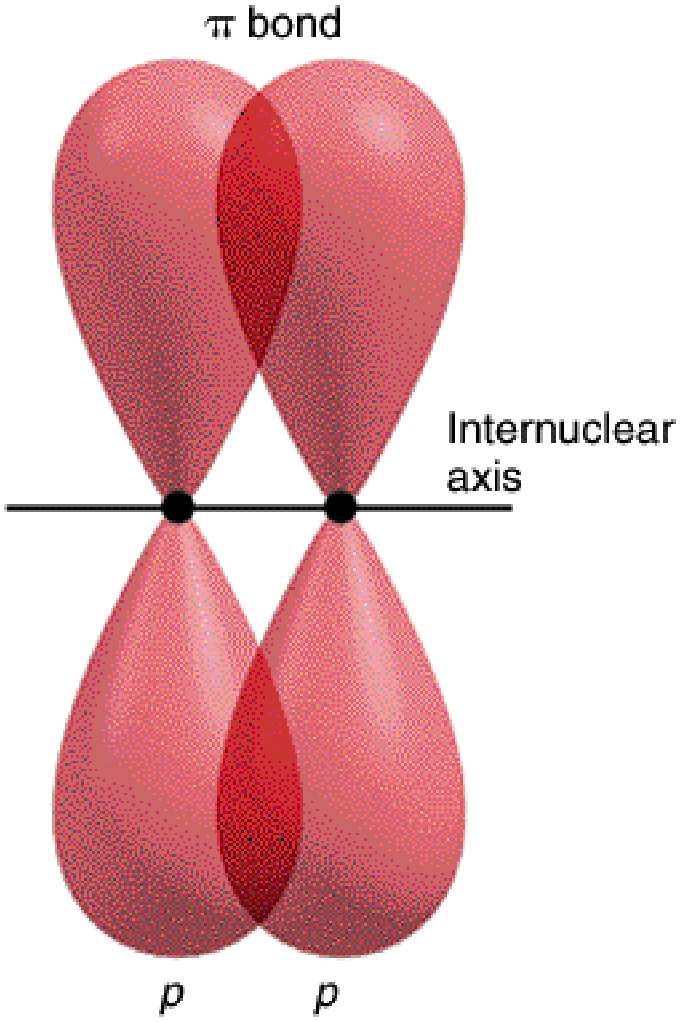
Double bond

- What happens to the remaining unhybridized *p* orbitals on each C?
- The two p orbitals overlap side-to- side
- Result ⇒ formation of a second bond ⇒ π (pi) bond

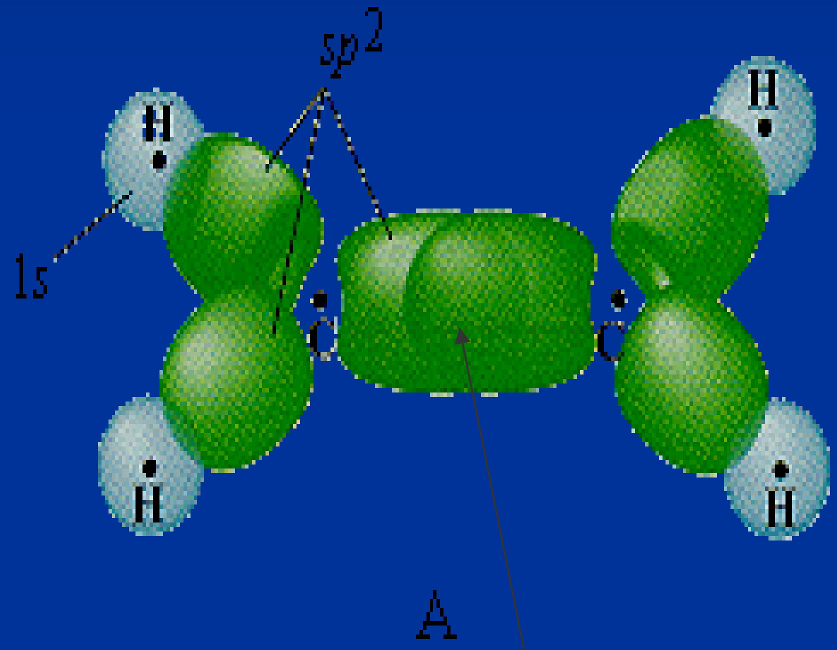


A π bond is a sideways overlap that occurs both above and below the plane of the molecule

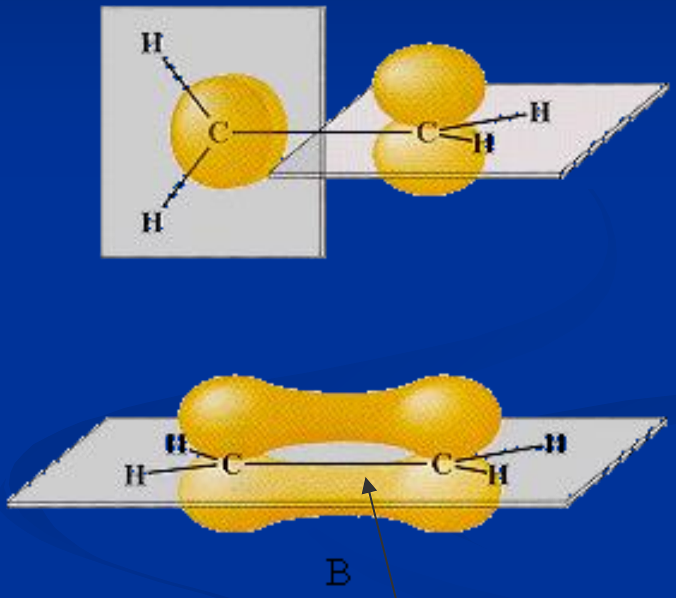
π bond formation



σ & π bonds

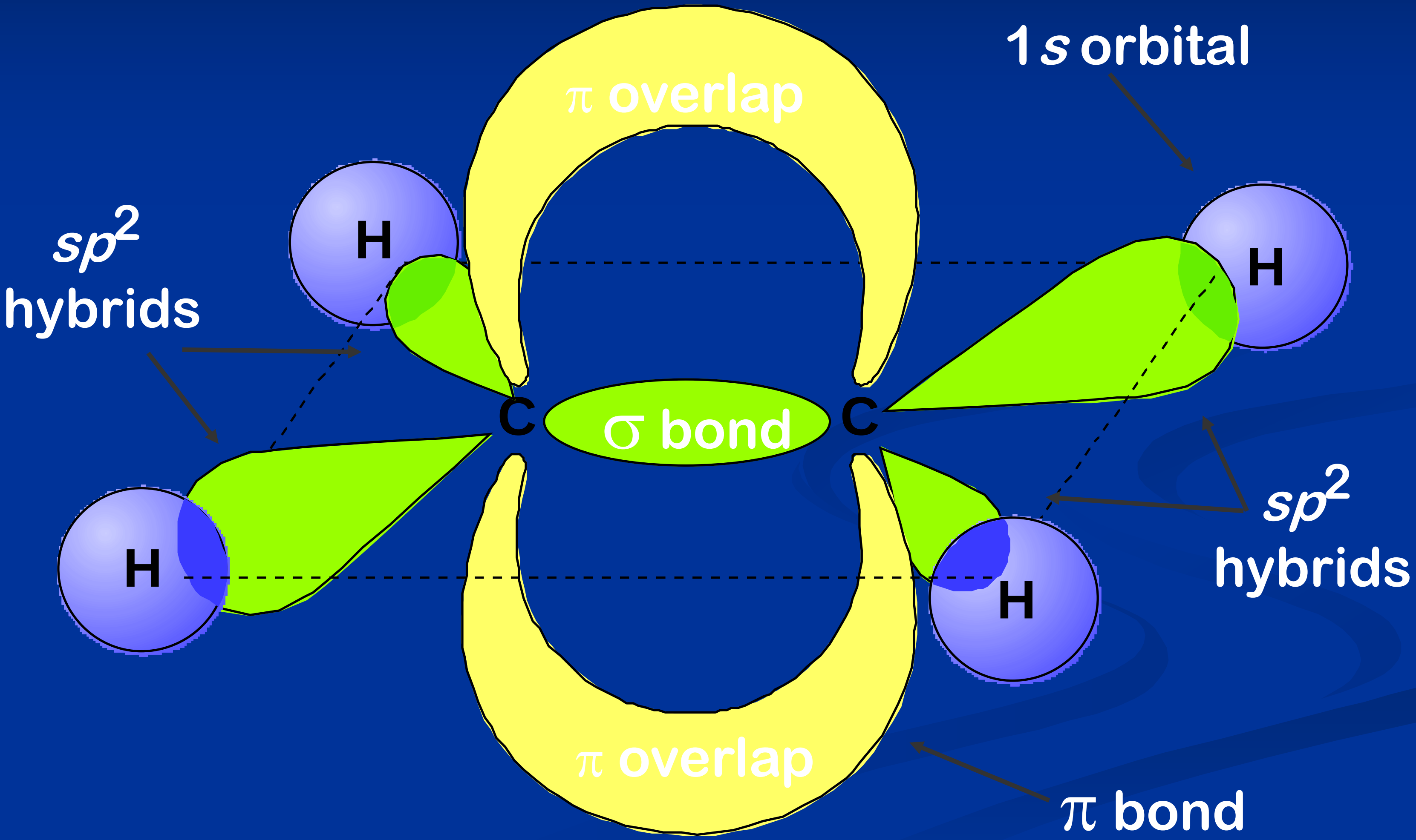


σ-bond



π-bond

Bonding in ethene



Triple bond (bond order of 3)

- **Example:** Ethyne (CHCH)

$$H—C\equiv C—H$$

- Each C has 2 e^- groups ⇒∴ linear EGG ⇒∴ Need 2 equivalent orbitals

Triple bond

- To get 3 equivalent hybrid orbitals:

$$s + p_x$$

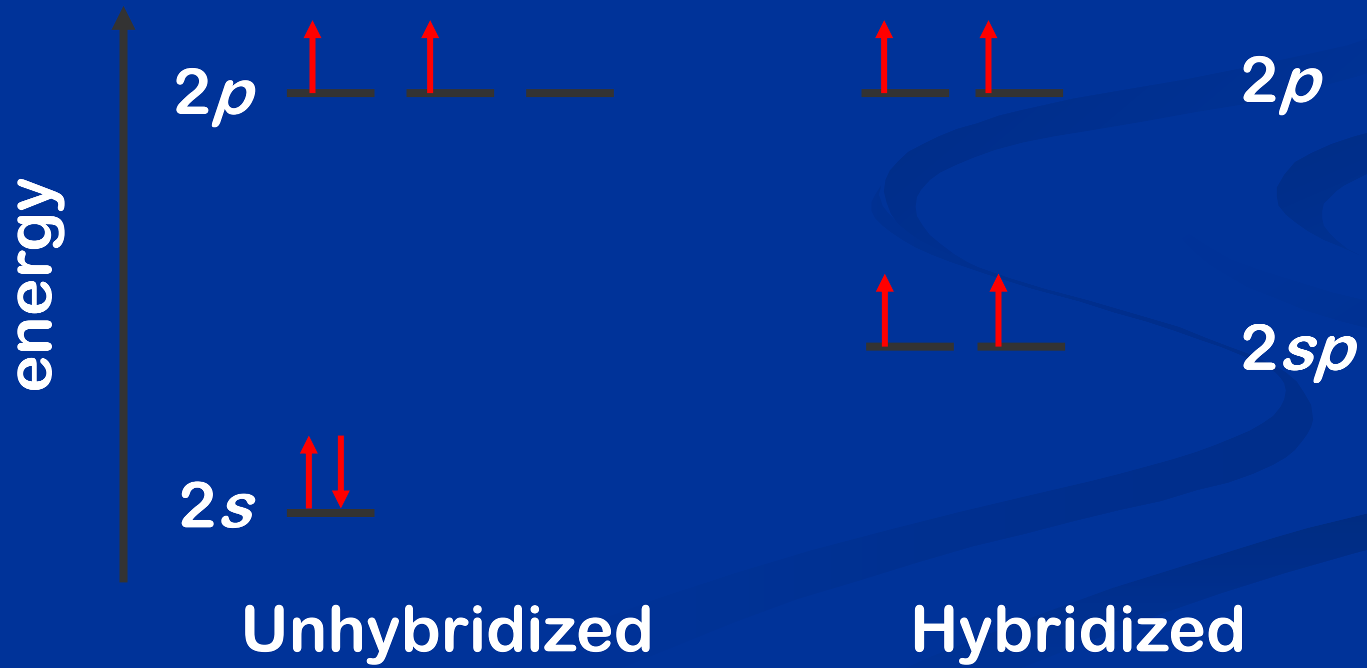
$$\Downarrow$$

$$sp + sp$$

-
- Best EGG for two orbitals ⇒ linear
- Each sp hybrid orbital overlaps with one H 1s orbital

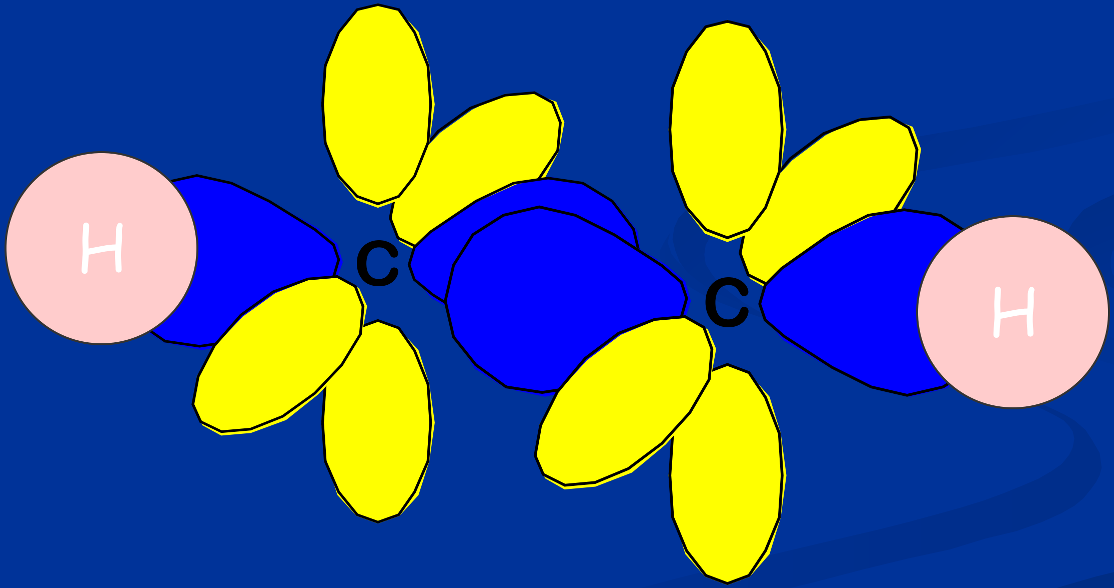
sp hybrid orbital

- For linear EGG ⇒ need two sp hybrids
- Two *p* orbitals remain unhybridized

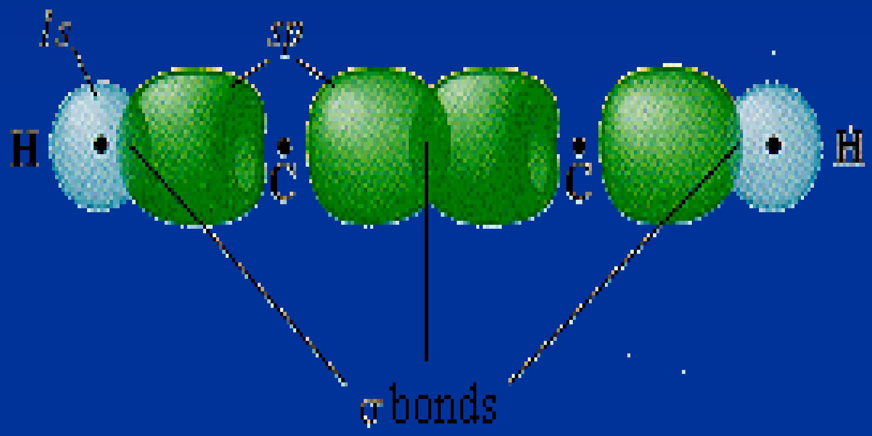


sp hybrid orbital

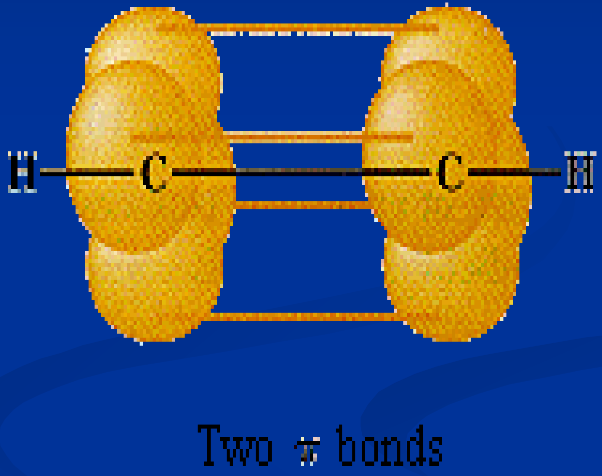
Now two *p* orbitals are available to form π bonds.



Triple bonds (bond order of 3)

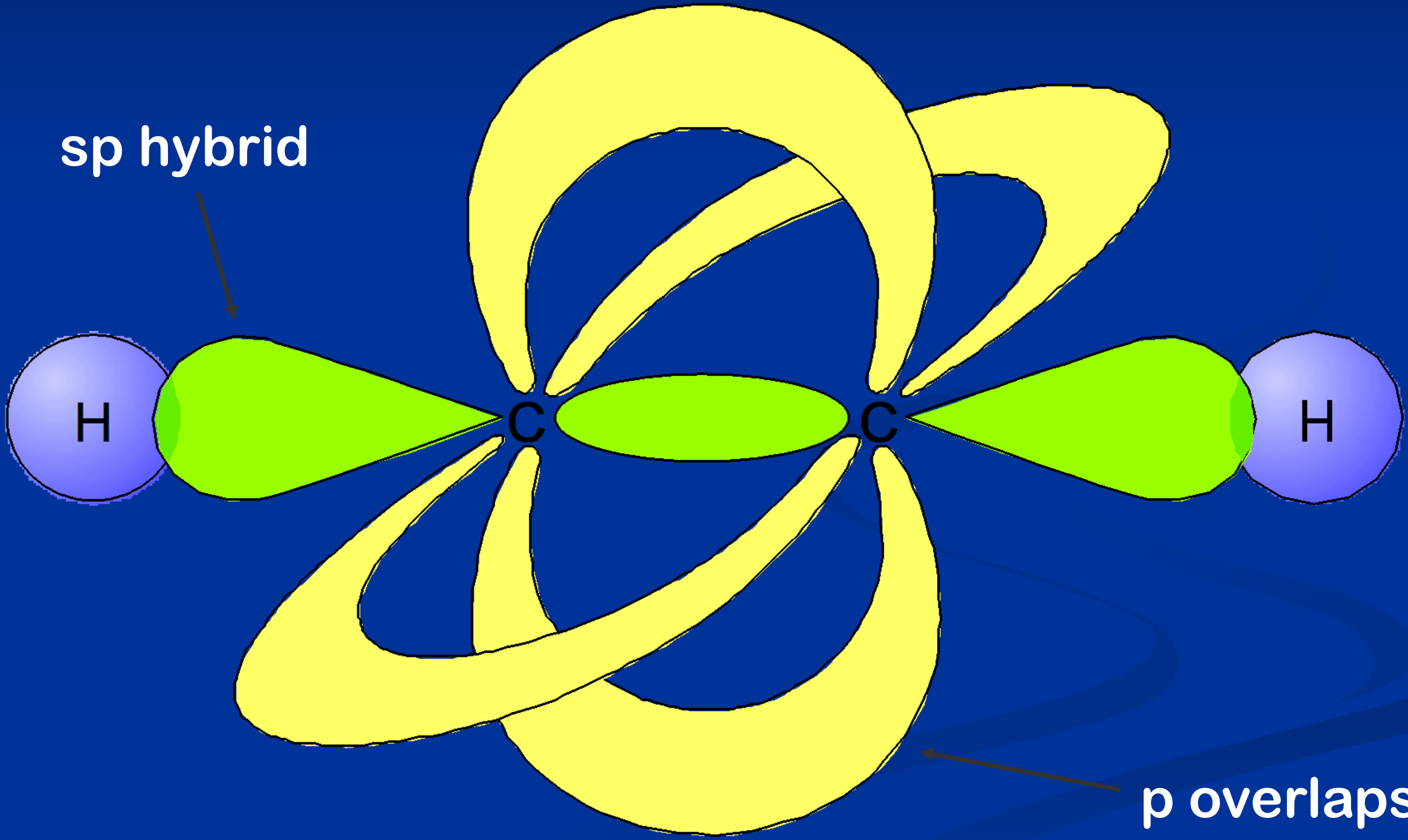


A



B

Bonding in ethyne



sp hybrid

p overlaps