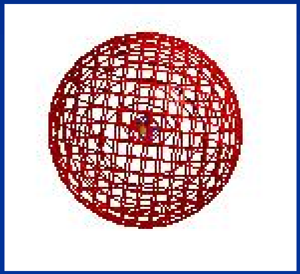
Molecular Orbital Theory

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.

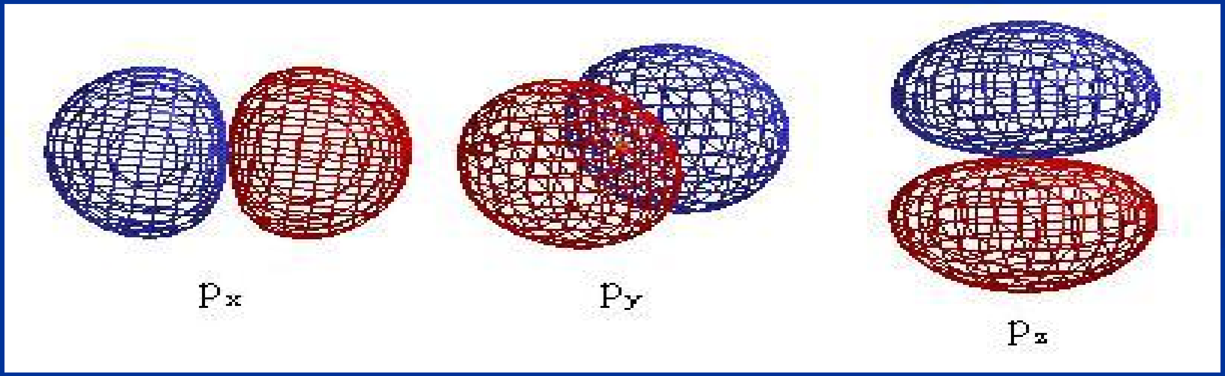
Atomic Subshells

- 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

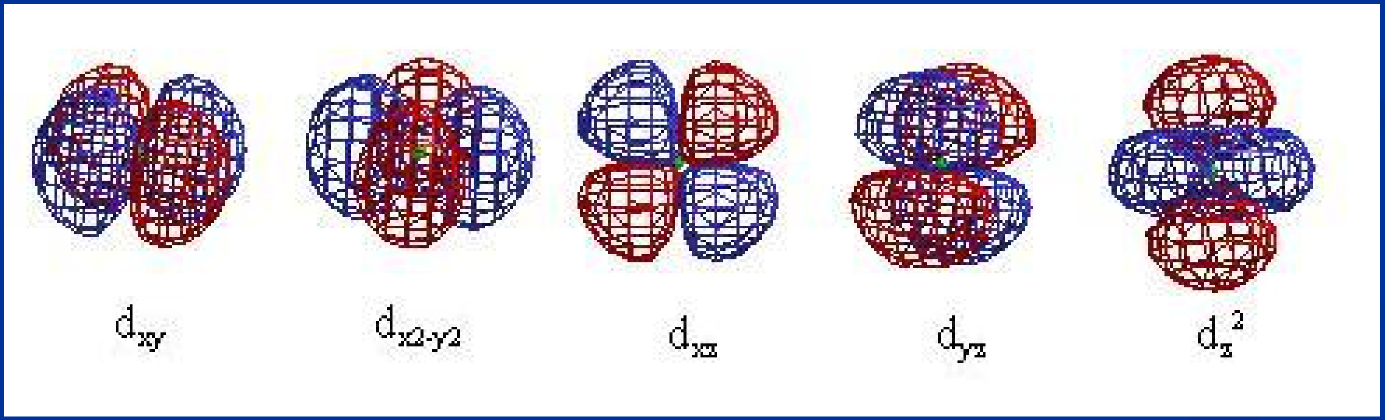
  - P Orbitals: (Shaped like two balloons tied together) There are 3 orbitals in a p subshell that are denoted as p_x, p_y, and p_z orbitals. These are higher in energy than the corresponding s orbitals.



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

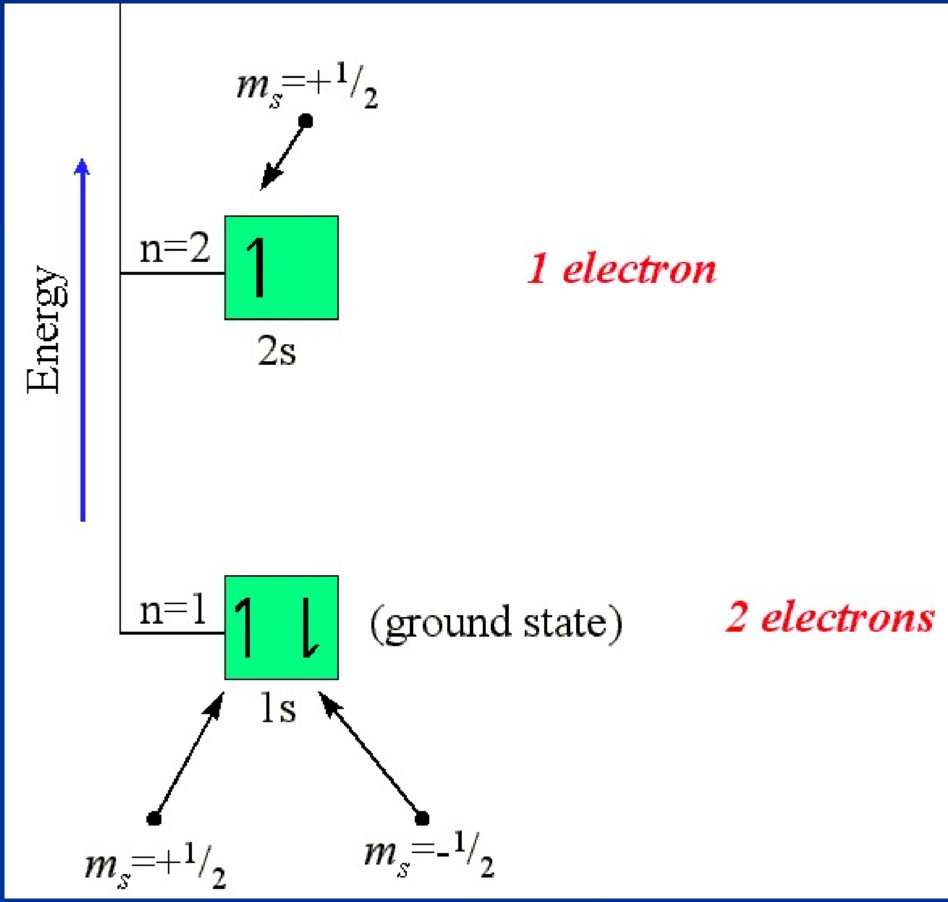
- Every element is different.
  - The number of protons determines the identity of the element.
  - The number of electrons determines the charge.
  - The number of neutrons determines the isotope.
- All chemistry is done at the electronic level (that is why electrons are very important).
- Electronic 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, <u>"1s two, 2s one".</u>



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

Electronic Configurations – Box Diagram

Element	Total Electrons	Orbital Diagram						Electron Configuration
		$1s$	$2s$	$2p$			$3s$	
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 $2p$ orbital because the $2s$ orbital is filled. Because the $2p$ orbitals are equal energy, it doesn't matter which $2p$ orbital is filled.

Electronic Configuration

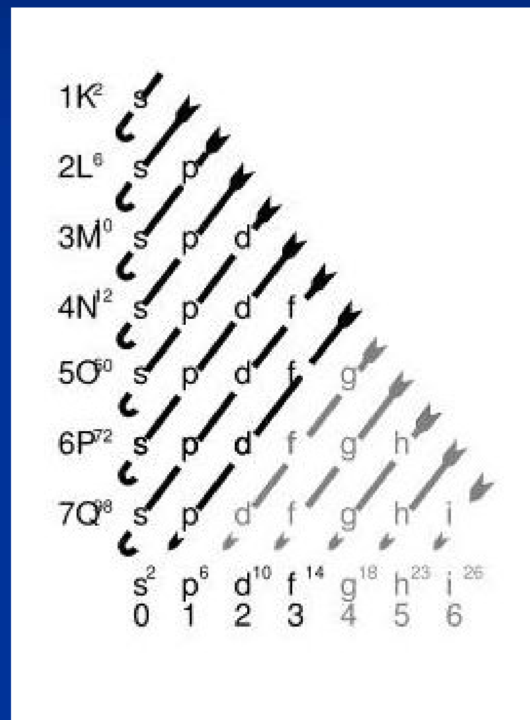
- Electronic configurations can also be written in a short hand which references the *last completed orbital shell* (i.e. all orbitals with the same principle quantum number 'n' have been filled)

  - 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

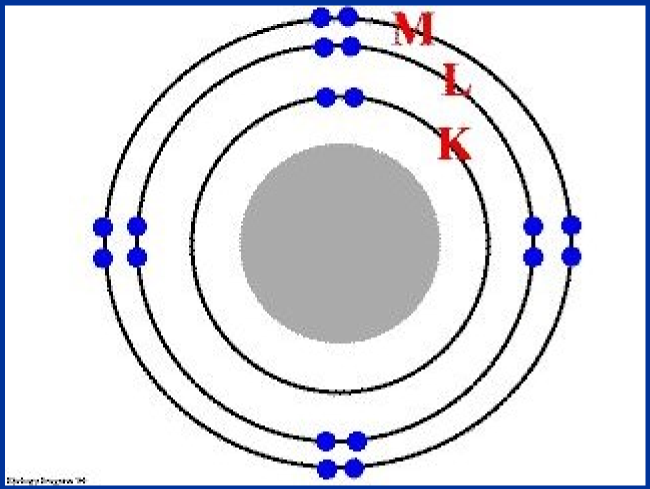


$1s^2_2\ 2s^2_4\ 2p^6_{10}\ 3s^2_{12}\ 3p^6_{18}\ 4s^2_{20}\ 3d^{10}_{30}\ 4p^6_{36}\ 5s^2_{38}\ 4d^{10}_{48}\ 5p^6_{54}\ 6s^2_{56}\ 4f^{14}_{70}\ 5d^{10}_{80}\ 6p^6_{86}\ 7s^2_{88}\ 5f^{14}_{102}\ 6d^{10}_{112}\ 7p^6_{118}$

http://en.wikipedia.org/wiki/Image:Electron_orbitals.svg

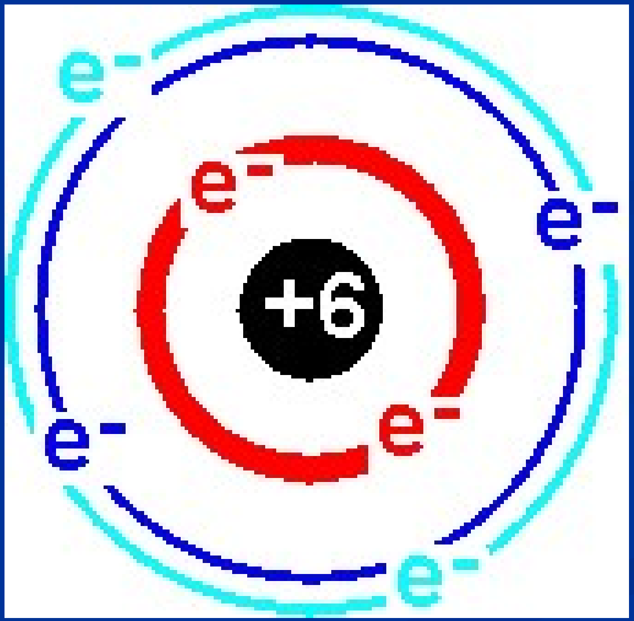
Valence Electrons

- 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

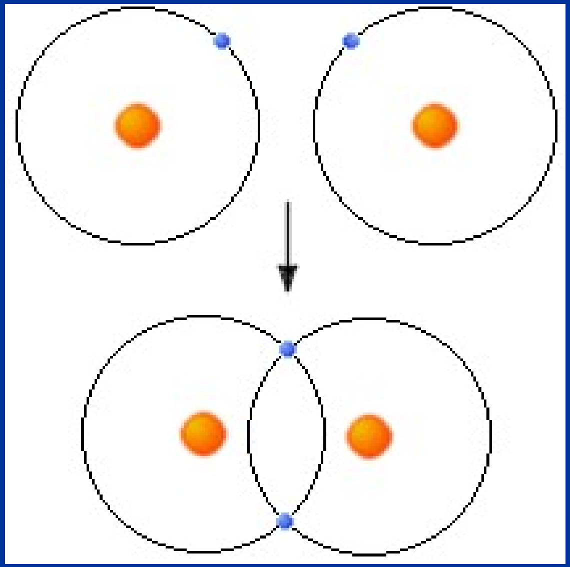
The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations.

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)

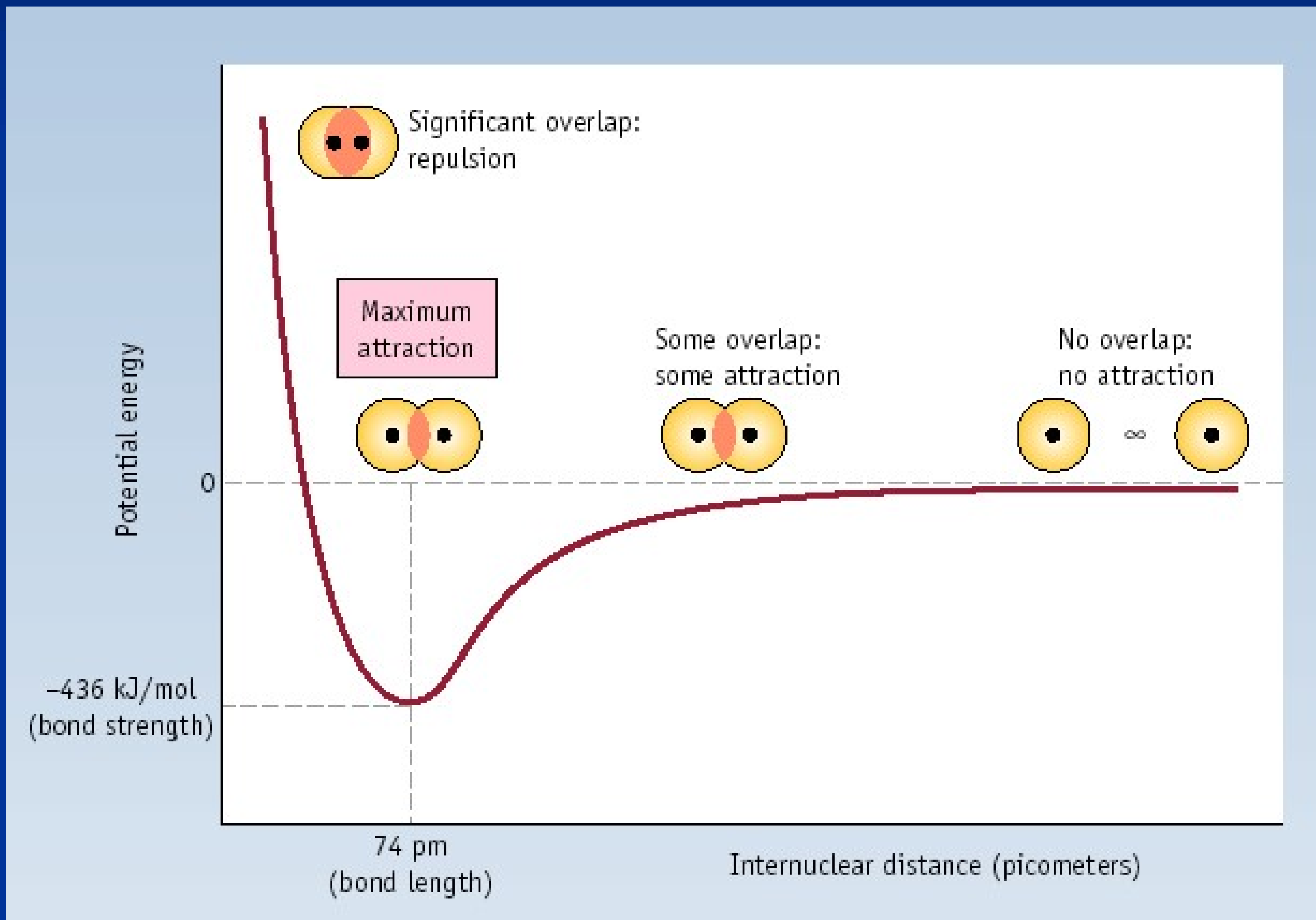
- Orbital Mixing
  - When atoms share electrons to form a bond, their atomic orbitals mix to form molecular bonds. In order for these orbitals to mix they must:
    - Have similar energy levels.
    - Overlap well.
    - Be close together.



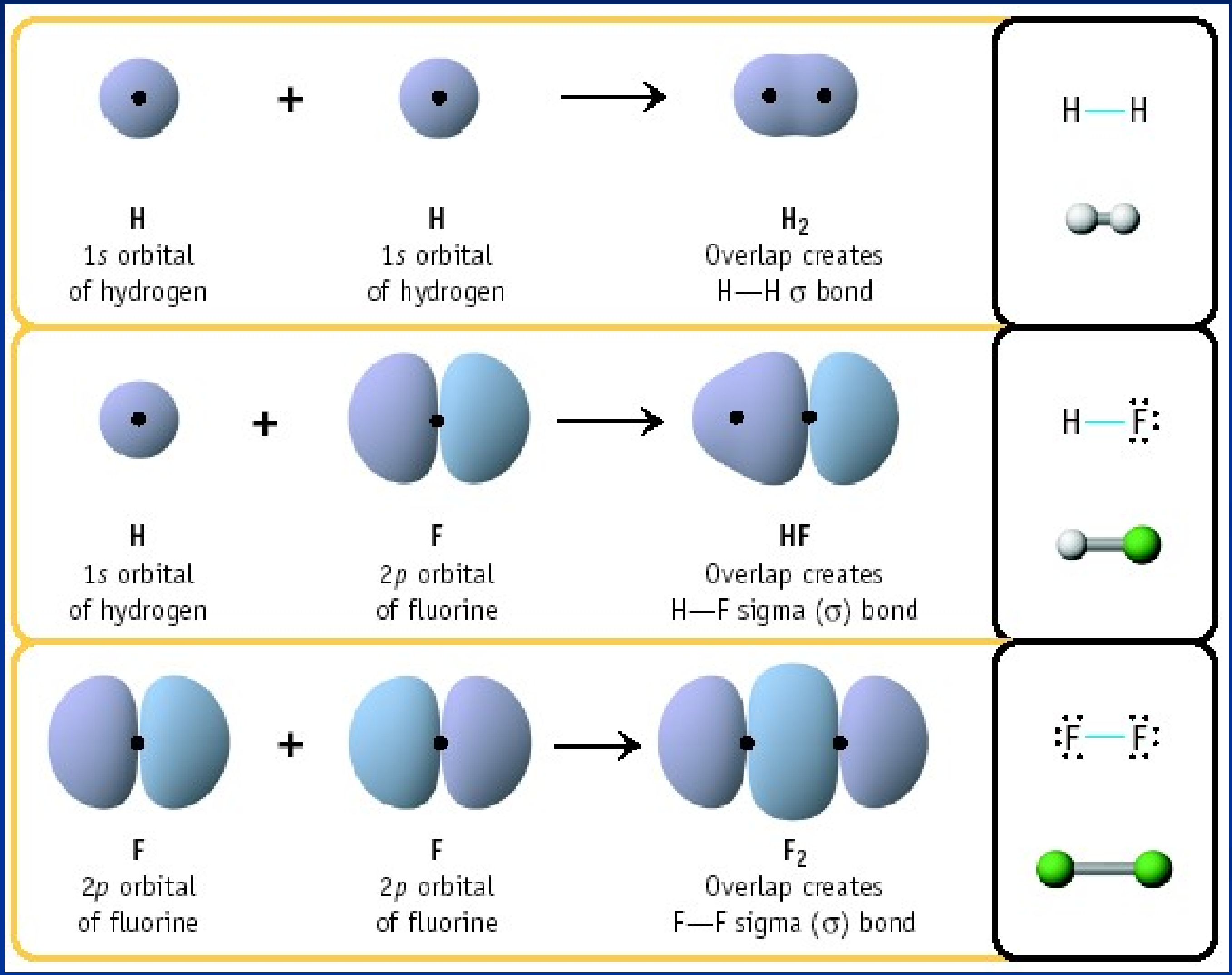
http://library.thinkquest.org/27819/ch2_2.shtml

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

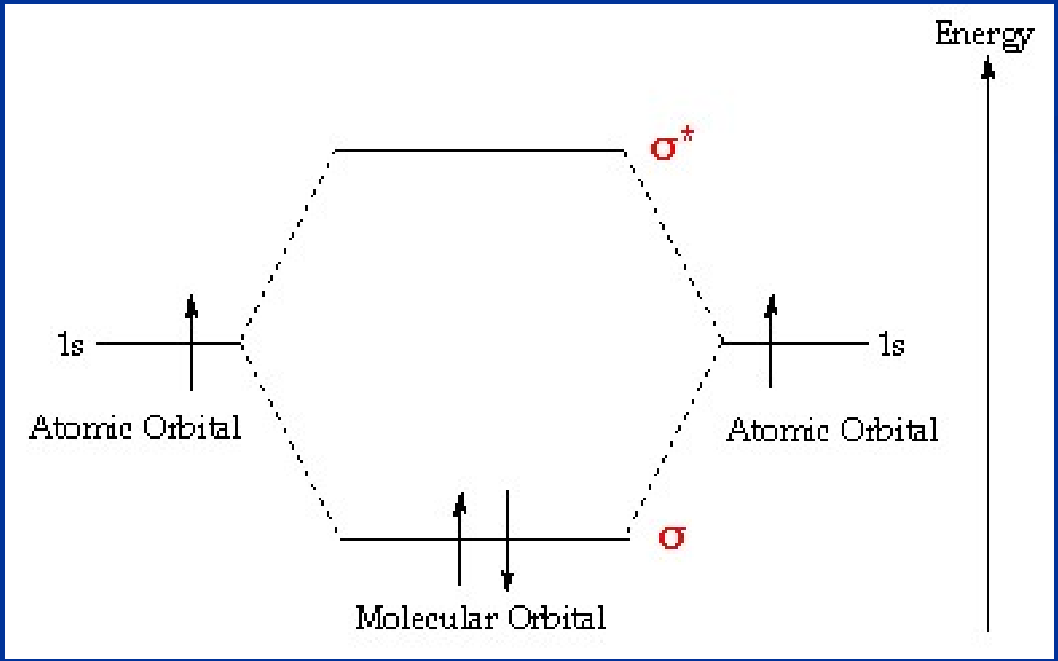


Examples of Sigma Bond Formation



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.

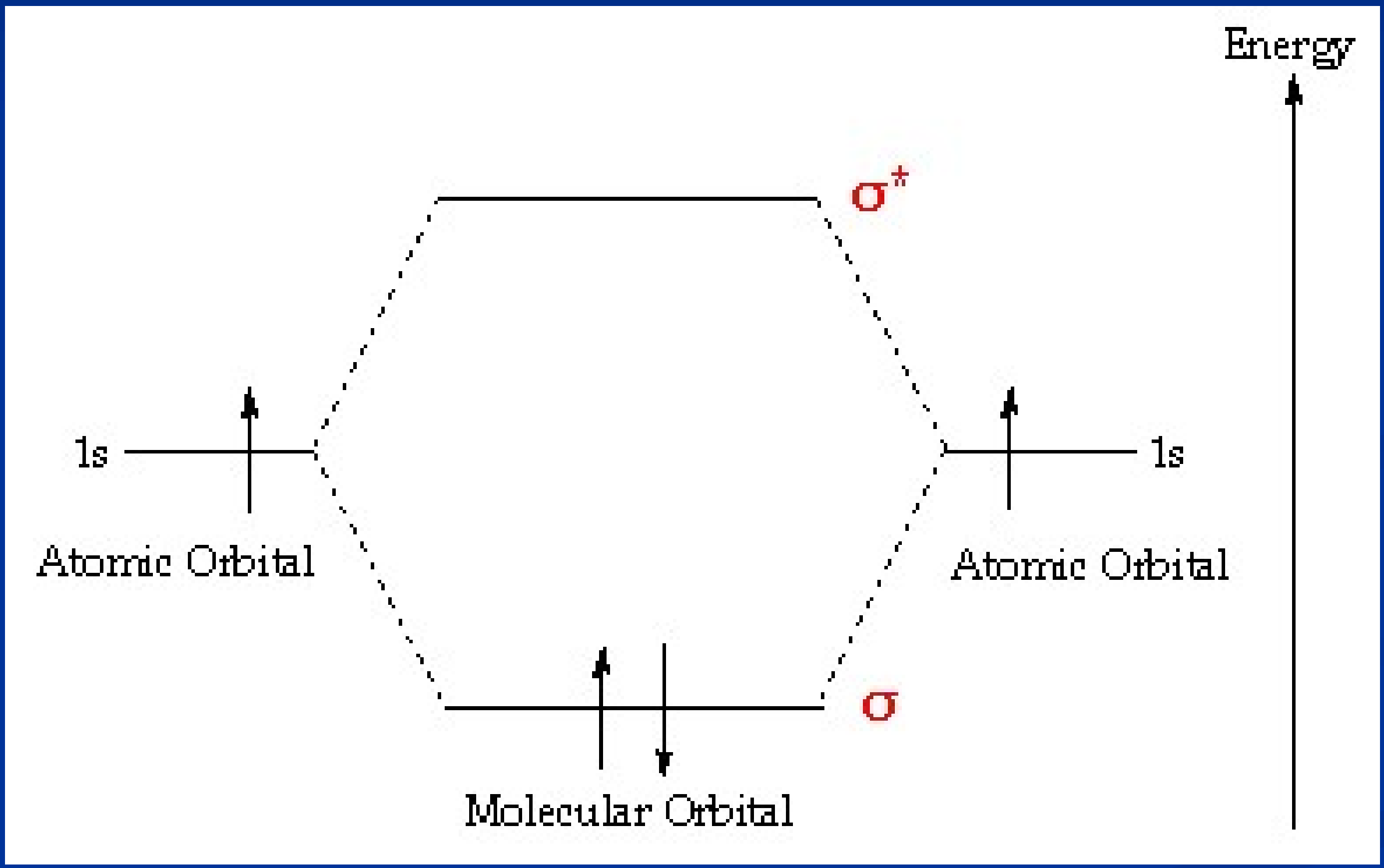
Molecular Orbital Theory

- 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

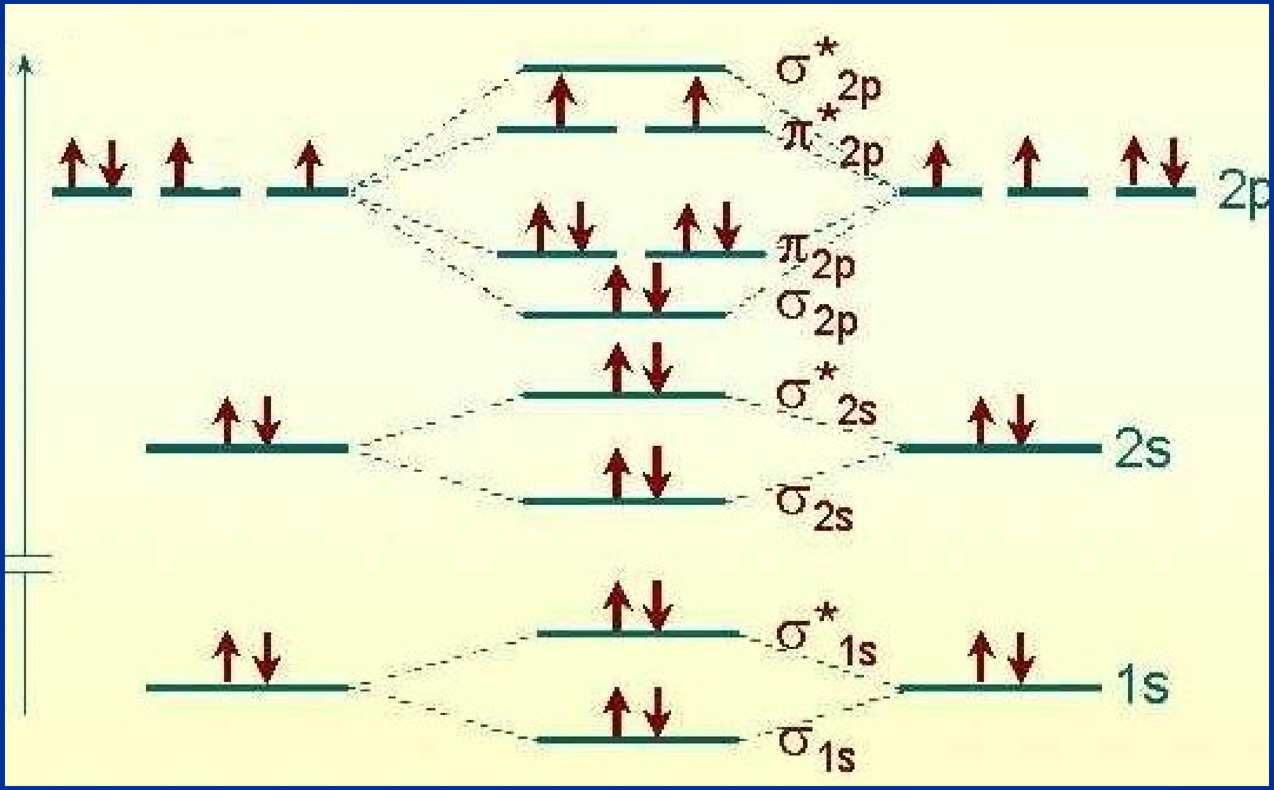
- Electrons go into the lowest energy orbital available to form lowest potential energy for the molecule.
- The maximum number of electrons in each molecular orbital is two. (Pauli exclusion principle)
- One electron goes into orbitals of equal energy, with parallel spin, before they begin to pair up.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

Molecular Orbital Diagram (H_2)



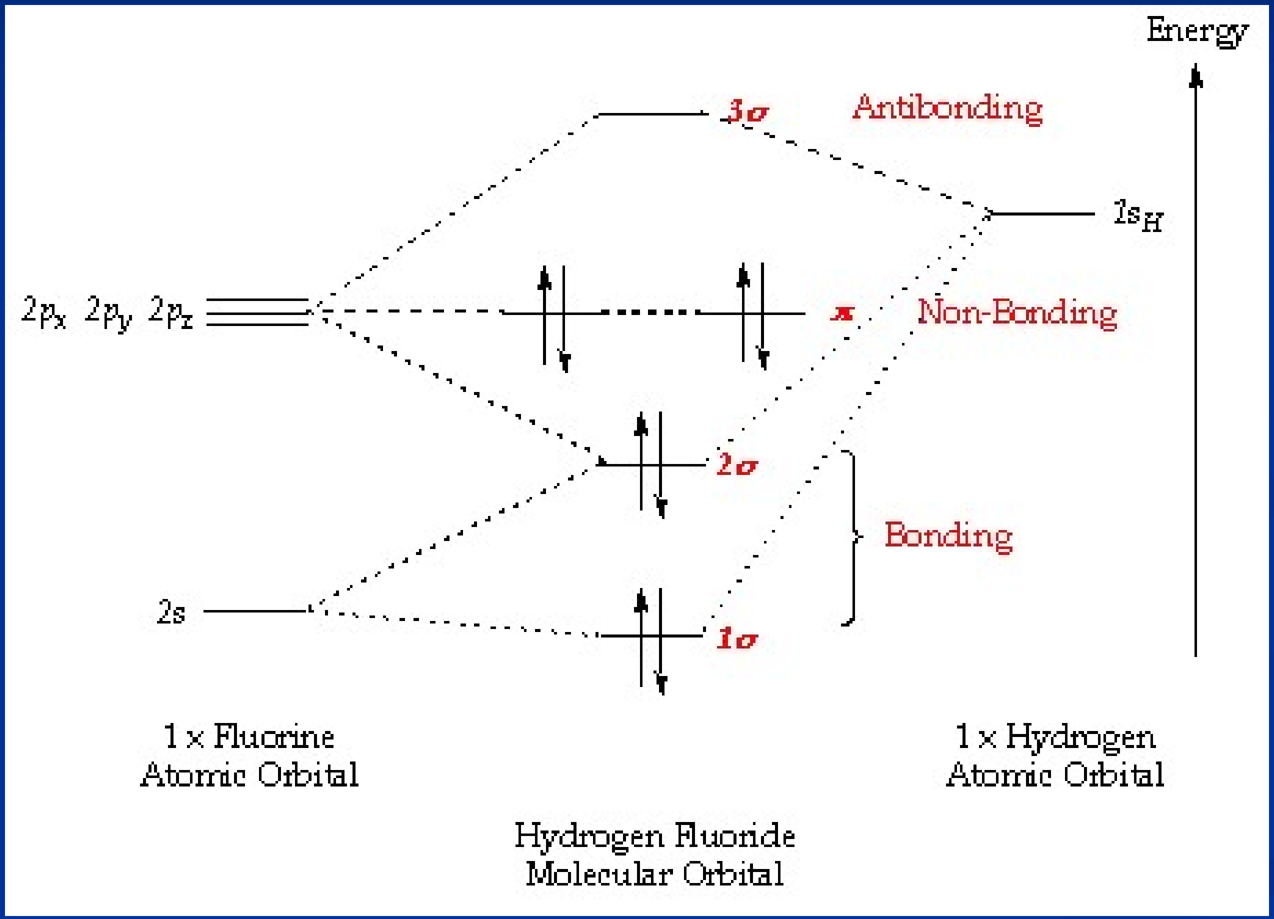
http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/main.html

MO Diagram for O_2



http://www.chem.uncc.edu/faculty/murphy/1251/slides/C19b/sld027.htm

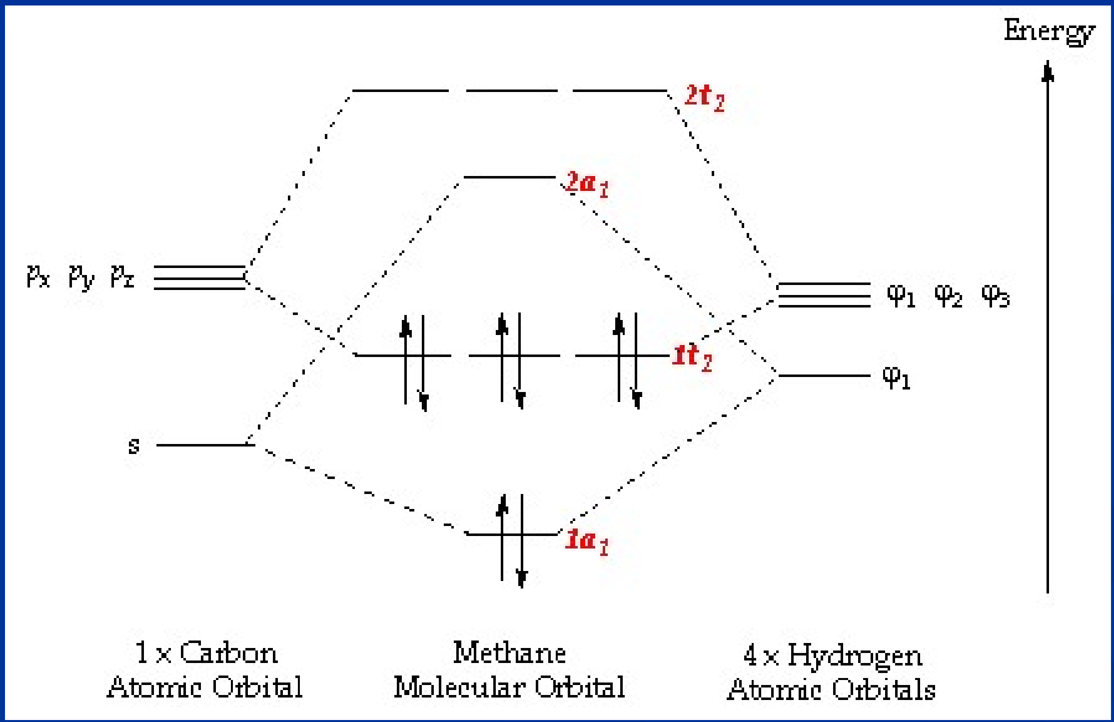
Molecular Orbital Diagram (HF)



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

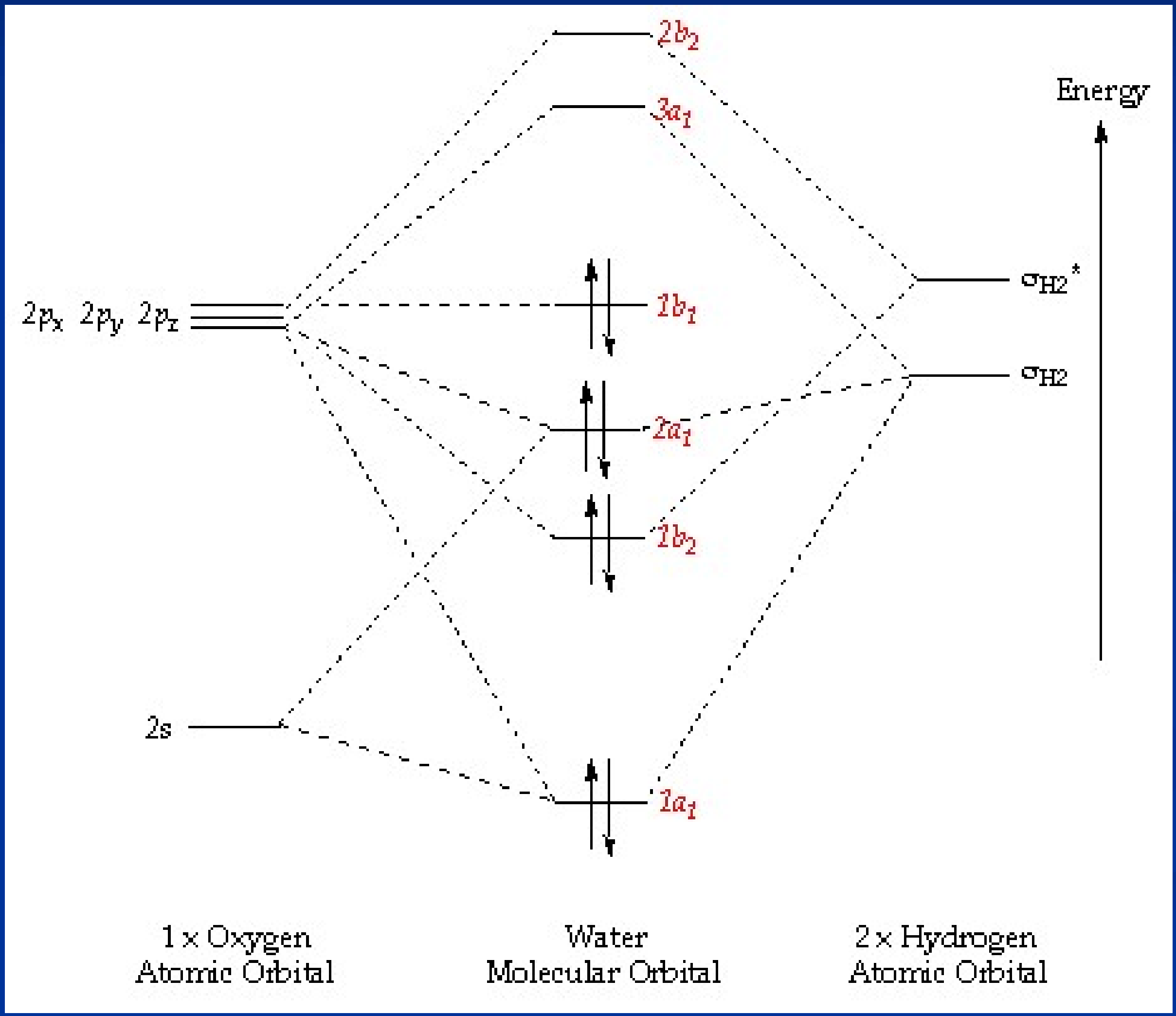
Molecular Orbital Diagram (CH_4)

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



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

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.

References

- http://www.chemguide.co.uk/atoms/properties/atomorbs.html
- http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/main.html
- http://en.wikipedia.org/wiki/Molecular_orbital_theory
- http://library.thinkquest.org/27819/ch2_2.shtml