# Chemical Bond in Diatomic Molecules
## Chapter 23

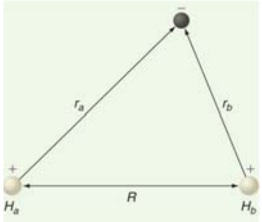
This chapter presents a qualitative treatment of molecular orbitals for chemical bonding (covalent bonds) using the simplest molecule, $H_2^+$.

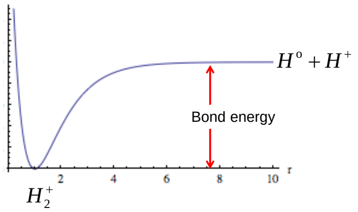
$$H + H^+ \longrightarrow H_2^+$$

$H_2^+$ is more stable than widely separated H atom and an $H^+$ ion because of the delocalization of the electron over the molecule and localization of the electron in the region between the two nuclei.

As the participant atomic species come together to form a bond the energy of the molecule move through a minimum energy position (equilibrium bond distance = bond length).

$H_2^+$

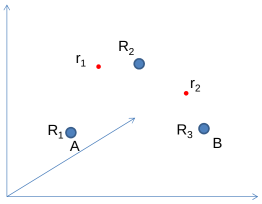




Covalent bond resembles the superposition of charge distribution (valence electrons) among individual atoms - delocalization. Core electrons remain localized on individual atoms.

Molecular wave function;

$$\psi_i^{molecule} = \psi(\mathbf{r}_1,\mathbf{r}_2,.....,\mathbf{r}_n,\mathbf{R}_1,\mathbf{R}_2,.....,\mathbf{R}_m)$$



Molecular wave function

$$\psi_i^{molecule} = \psi(\underbrace{\mathbf{r}_1,\mathbf{r}_2,.....,\mathbf{r}_n}_{\text{electron}},\overbrace{\mathbf{R}_1,\mathbf{R}_2,.....,\mathbf{R}_m}^{\text{nuclear}})$$

The Born-Oppenheimer approximation

The nuclei have much larger masses in comparison to electron mass and will have a negligibly small velocity. Born-Oppenheimer takes advantage of this fact and makes the assumption that since the nuclei are much heavier in mass compared to the electron, their motion can be ignored while solving the electronic Schrödinger equation.

That is, the nuclei are assumed to be stationary while electrons move around it.

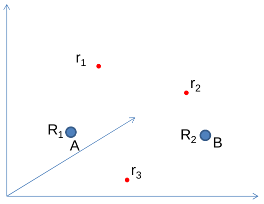
Therefore the motion of the nuclei and the electrons can be separated. The nuclear-nuclear motion/repulsion issues can be treated independently.

The Born-Oppenheimer approximation simplifies the handling of the Schrödinger equation for a molecule.

$$\psi_i^{molecule} \approx \underbrace{\psi_{BO}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)}\psi_{nuclear}(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_m)$$

Solve electron motion for a given set of $\mathbf{R_i}$ s.

http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Chemical_Bonding/General_Principles/Born_Oppenheimer_Approximation



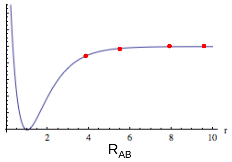
$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\left(\frac{Z_Ae^2}{4\pi\varepsilon_0 r_{iA}} + \frac{Z_Be^2}{4\pi\varepsilon_0 r_{iB}}\right) + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\text{Electronic energy (Kinetic + Potential), } E_{el}} + \underbrace{\frac{Z_AZ_Be^2}{4\pi\varepsilon_0 R_{AB}}}_{\text{'constant' } E_{nuc}}$$

$$\hat{H}_{el} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\left(\frac{Z_Ae^2}{4\pi\varepsilon_0 r_{iA}} + \frac{Z_Be^2}{4\pi\varepsilon_0 r_{iB}}\right) + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}$$

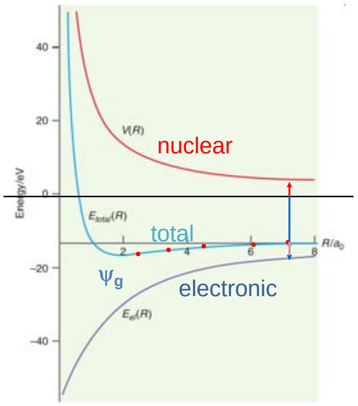
## Molecular Orbitals

Once electronic energy $E_{el}$ and wave functions (molecular orbitals) are solved with SE for a given nuclear configuration $R_{AB}$, the nuclear repulsion energy is then added for a given nuclear configuration $R_{AB}$ on top of $E_{el}$ to obtain the total energy at $R_{AB}$.

Change $R_{AB}$ and repeat the process.



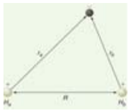
$$E_{total} = E_{el}$$



## LCAO-MO Model – $H_2$

The spaces in which electrons can reside in a molecule (MO) extends over the molecule. Molecular orbital description of chemical bond is based on the principle that; $\psi_{el} = \psi$ can be written as a linear combination of atomic orbitals on individual atoms LCAO in the molecule.

For the simplest molecule, the simplest MO is constructed by the LC of the AOs $\phi_a$ and $\phi_b$ (basis functions) coming from atoms $H_a$ and $H_b$.



$$\psi_1 = c_a\phi_a + c_b\phi_b$$

an approximation

$$\psi_1 = c_a\phi_a + c_b\phi_b$$

The next step is to solve for coefficients $c_i$ by the variation method, minimize <ε> value.

Expression for <ε>;

$$\langle\varepsilon\rangle = \frac{\int \psi_1^* \hat{H}_{el}\psi_1\, d\tau}{\int \psi_1^*\psi_1\, d\tau}$$

$$\langle\varepsilon\rangle = \frac{(c_a)^2\int\phi_a^*\hat{H}_{el}\phi_a\,d\tau + (c_b)^2\int\phi_b^*\hat{H}_{el}\phi_b\,d\tau + 2c_ac_b\int\phi_a^*\hat{H}_{el}\phi_b\,d\tau}{(c_a)^2\int\phi_a^*\phi_a\,d\tau + (c_b)^2\int\phi_b^*\phi_b\,d\tau + 2c_ac_b\int\phi_a^*\phi_b\,d\tau}$$

Assumptions:

$$\int\phi_a^*\widehat{H}\phi_b d\tau = \int\phi_b^*\widehat{H}\phi_a d\tau \quad \text{and} \quad \int\phi_a^*\phi_b d\tau = \int\phi_b^*\phi_a d\tau$$

*Bra – ket notation*

$$\left\langle\phi_a^* \mid \widehat{H} \mid \phi_b\right\rangle = \left\langle\phi_b^* \mid \widehat{H} \mid \phi_a\right\rangle \quad \text{and} \quad \left\langle\phi_a^* \mid \phi_b\right\rangle = \left\langle\phi_b^* \mid \phi_a\right\rangle$$

Assumption valid for homonuclear di-atomics.

$$\langle\varepsilon\rangle = \frac{(c_a)^2\int\phi_a^*\hat{H}_{el}\phi_a\,d\tau + (c_b)^2\int\phi_b^*\hat{H}_{el}\phi_b\,d\tau + 2c_ac_b\int\phi_a^*\hat{H}_{el}\phi_b\,d\tau}{(c_a)^2\int\underline{\phi_a^*\phi_a}\,d\tau + (c_b)^2\int\underline{\phi_b^*\phi_b}\,d\tau + 2c_ac_b\int\underline{\phi_a^*\phi_b\,d\tau}}$$

Defining:

$$\left.\begin{aligned}\int\phi_a^*\widehat{H}\phi_a d\tau &= H_{aa} < 0\\ \int\phi_a^*\widehat{H}\phi_b d\tau &= H_{ab} < 0\end{aligned}\right\}$$

$$\left.\begin{aligned}\int\phi_a^*\phi_a d\tau &= S_{aa} = 1\\ \int\phi_a^*\phi_b d\tau &= S_{ab}; \quad 0 < S_{ab} < 1\end{aligned}\right\}$$

Rewriting: $$\langle\varepsilon\rangle = \frac{(c_a)^2 H_{aa} + (c_b)^2 H_{bb} + 2c_ac_b H_{ab}}{(c_a)^2 + (c_b)^2 + 2c_ac_bS_{ab}}$$

$\int\phi_a^*\widehat{H}\phi_a d\tau = \boldsymbol{H_{aa}}$ interaction energy electron ***a*** to nucleus ***a***

$\int\phi_a^*\widehat{H}\phi_b d\tau = \boldsymbol{H_{ab}}$ interaction energy nucleus ***a*** to nucleus ***b***

$\int\phi_a^*\phi_a d\tau = \boldsymbol{S_{aa}} = 1$ overlap of a. o. of atom A

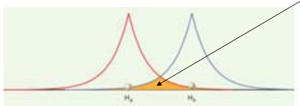
$\int\phi_a^*\phi_b d\tau = \boldsymbol{S_{ab}}$ overlap of a. o. of A and a. o. of B

Exchange integral; $H_{ab} < 0$

$$H_{ab} = \int\phi_a^*\widehat{H}\phi_b d\tau \leq 0$$

Overlap integral; $0 < S_{ab} < 1$

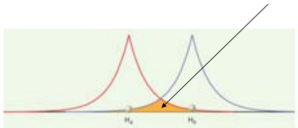
$$S_{ab} = \int\phi_a^*\phi_b d\tau > 0$$



↑ not in individual atoms!!

$$\langle\varepsilon\rangle = \frac{(c_a)^2 H_{aa} + (c_b)^2 H_{bb} + 2c_ac_b H_{ab}}{(c_a)^2 + (c_b)^2 + 2c_ac_bS_{ab}} = \frac{\textit{negative}}{\textit{positive}} < 0$$

*Overlap* integral



The larger the overlap (wavefunctions in phase) lower the energy of the system <ε>, more stable is the covalent bond.

Determining the lowest energy use the variation method.

Differentiation of <ε> expression w.r.t the $c_i$ parameters and equating to zero (to find coefficients);

$$(2c_a + 2c_bS_{ab})\varepsilon = 2c_aH_{aa} + 2c_bH_{ab}$$

$$(2c_b + 2c_aS_{ab})\varepsilon = 2c_bH_{bb} + 2c_aH_{ab}$$

$$\left.\begin{aligned}c_a(H_{aa} - \varepsilon) + c_b(H_{ab} - \varepsilon S_{ab}) &= 0\\ c_a(H_{ab} - \varepsilon S_{ab}) + c_b(H_{bb} - \varepsilon) &= 0\end{aligned}\right\}$$ Secular equations

For non-trivial solution the determinant;

$$\begin{vmatrix} H_{aa} - \varepsilon & H_{ab} - \varepsilon S_{ab}\\ H_{ab} - \varepsilon S_{ab} & H_{bb} - \varepsilon\end{vmatrix} = 0$$ Secular determinant

The order of the determinant depends on (equal to) the # AO s of the basis set used.

Expand the determinant:

Yields a polynomial in ε, solution of which will give the energies of the system.

$$\varepsilon = \frac{1}{2-2S_{ab}^2}[H_{aa}+H_{bb}-2S_{ab}H_{ab}] \pm \frac{1}{2-2S_{ab}^2} \times \left[\sqrt{(H_{aa}^2+4H_{ab}^2+H_{bb}^2-4S_{ab}H_{ab}H_{bb}-2H_{aa}(H_{bb}+2S_{ab}H_{ab}-2S_{ab}^2H_{bb}))}\right]$$

For the homonuclear diatomic,

$$\varepsilon_1 = \frac{H_{aa}+H_{ab}}{1+S_{ab}} \quad \text{and} \quad \varepsilon_2 = \frac{H_{aa}-H_{ab}}{1-S_{ab}}$$

Secular determinant: $\begin{vmatrix} H_{aa}-\varepsilon & H_{ab}-S_{ab}\varepsilon \\ H_{ba}-S_{ba}\varepsilon & H_{bb}-\varepsilon \end{vmatrix} = 0$

homonuclear diatomic $\begin{vmatrix} H_{aa}-\varepsilon & H_{ab}-S_{ab}\varepsilon \\ H_{ab}-S_{ab}\varepsilon & H_{aa}-\varepsilon \end{vmatrix} = 0$

expanding $(H_{aa}-\varepsilon)^2-(H_{ab}-S_{ab}\varepsilon)^2=0$

Taking the root: $(H_{aa}-\varepsilon)=\pm(H_{ab}-S_{ab}\varepsilon)$

Yields $\varepsilon_1 = \dfrac{H_{aa}+H_{ab}}{1+S}$ and $\varepsilon_2 = \dfrac{H_{aa}-H_{ab}}{1-S}$

For homonuclear diatomic,

$H_{aa} = H_{bb} < 0$

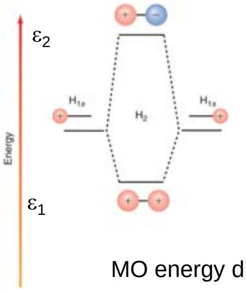
$H_{ab} < 0$

Makes $\varepsilon_2 > \varepsilon_1$.

Substituting ε in secular equations we get information about the coefficients.

and $c_a = c_b$ for $\varepsilon_1$

$c_a = -c_b$ for $\varepsilon_2$



MO energy diagram

|equal coefficients|.

Substituting the energy values in;

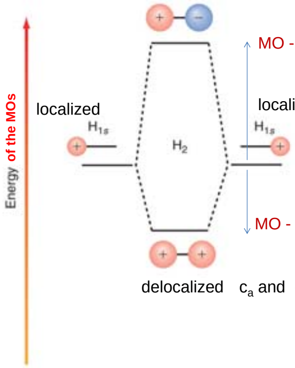
$$c_a(H_{aa}-\varepsilon)+c_b(H_{ab}-\varepsilon S_{ab})=0$$
$$c_a(H_{ab}-\varepsilon S_{ab})+c_b(H_{bb}-\varepsilon)=0$$

Gives the coefficients after normalization

$$c_a = c_b = \frac{1}{\sqrt{2+2S}} \quad for\ \varepsilon_1$$
$$c_a = \frac{1}{\sqrt{2-2S}} \quad for\ \varepsilon_2\ and\ c_b = -c_a$$

and the wavefunctions

$$\psi_1 = c_a\phi_a + c_b\phi_b = \frac{1}{\sqrt{2+2S}}(\phi_a+\phi_b) \quad for \quad \varepsilon_1$$
$$\psi_2 = c_a\phi_1 - c_b\phi_2 = \frac{1}{\sqrt{2-2S}}(\phi_a-\phi_b) \quad for \quad \varepsilon_2$$



delocalized $c_a$ and $c_b$ *opposite* sign - antisymmetric

localized

localized

MO - raised E

Determined by $H_{ab}$ and $S_{ab}$.

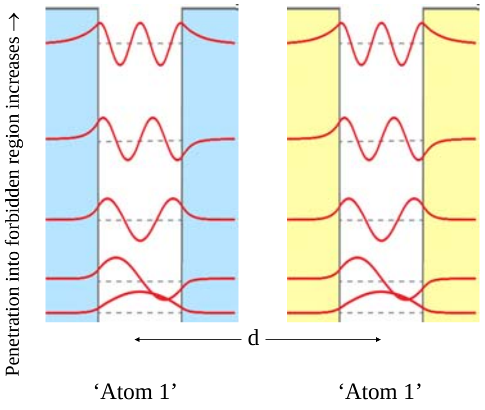
$\varepsilon_2 = \dfrac{H_{aa}-H_{ab}}{1-S}$

$\varepsilon_1 = \dfrac{H_{aa}+H_{ab}}{1+S}$

MO - lowered E

Determined by $H_{ab}$ and $S_{ab}$.

delocalized $c_a$ and $c_b$ *same* sign - symmetric

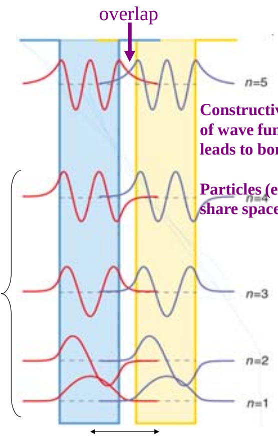


High energy states

‘Valence orbitals’
weakly bound
States (atom)

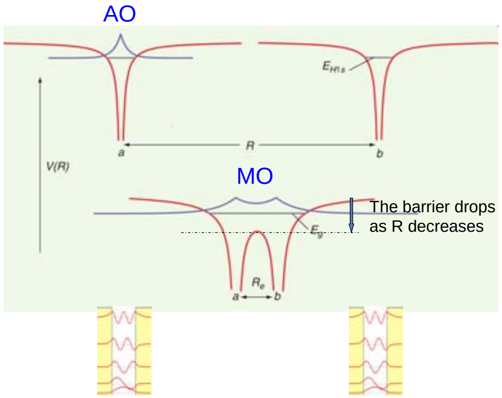
Low energy states

‘core orbitals’
strongly bound
states

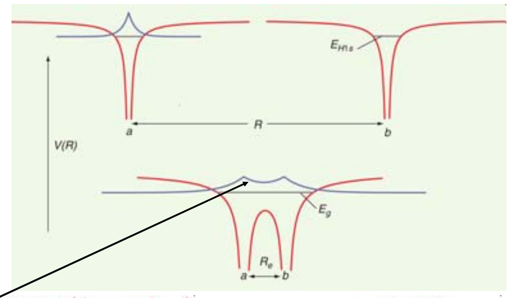


**Constructive interference of wave functions leads to bonding.**

**Particles (electrons) would share space on both atoms.**



The barrier drops
as R decreases

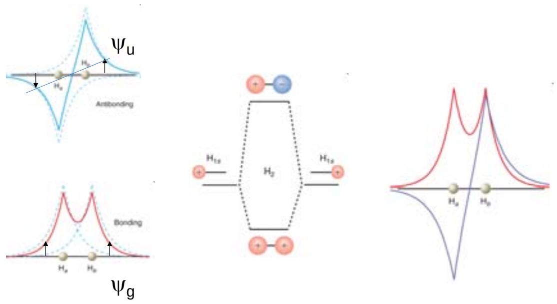


$$\psi_g = c_g(\phi_{H1s_a} + \phi_{H1s_b})$$

$$\psi_u = c_u(\phi_{H1s_a} - \phi_{H1s_b})$$

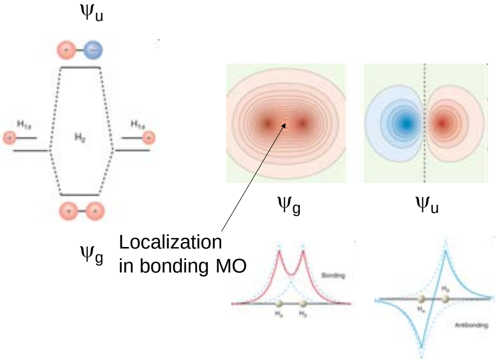
$$\phi_{H1s} = \frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{3/2} e^{-\zeta r/a_0}$$

equal coefficients.

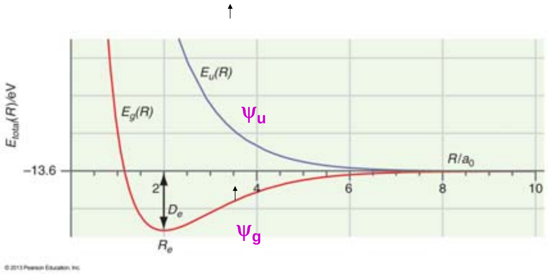


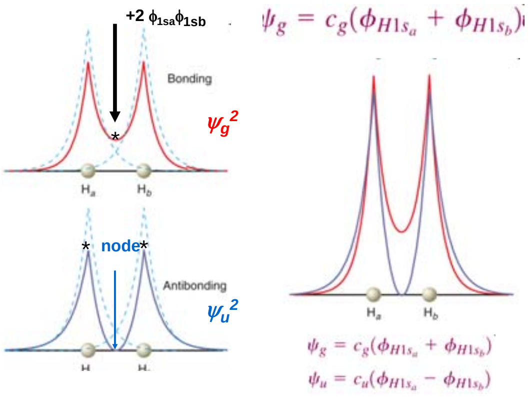
Symmetry classification of MOs:
g symmetric (about center of molecule)
u antisymmetric

In MOs electron is delocalized.



Localization
in bonding MO

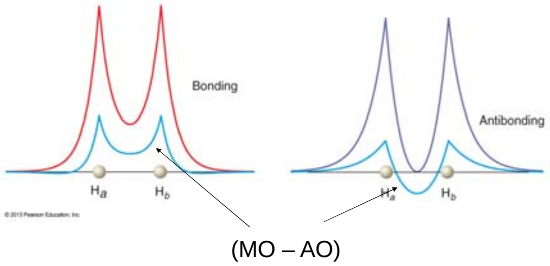




$$\psi_g = c_g(\phi_{H1s_a} + \phi_{H1s_b})$$

$$\psi_g = c_g(\phi_{H1s_a} + \phi_{H1s_b})$$

$$\psi_u = c_u(\phi_{H1s_a} - \phi_{H1s_b})$$



## Molecular Orbitals: Homonuclear Diatomic Molecules

Molecular orbitals are spaces in a molecule electrons could reside.

The wave function for MOs are constructed as linear combinations of atomic orbitals of the atoms involved LCAO-MO.

The extent to which each orbital from an atom contribute to the MO is related to the square of the respective coefficient.

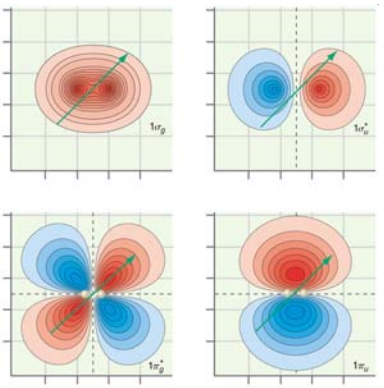
$$\psi_j = \sum_{i=1}^{N} c_{ij}\phi_i$$

The MOs have shapes and spatial extents.

The MOs of homonuclear diatomics are divided into two groups with regard to two symmetry operations. (g or u symmetry, w.r.t. center of molecule indicated)

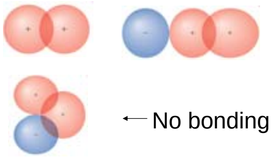
1. Rotation about nuclear (z) axis - rotation do not change MO - σ symmetry.

2. MO has a nodal plane in the molecular axis – π symmetry.



Note the * antibonding orbital; high energy counterpart of bonding orbital.

Only AOs of the same symmetry can form MOs.



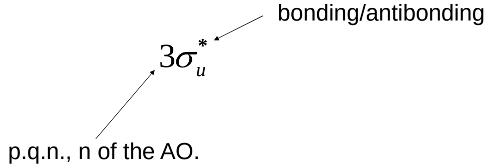
Bonding – in phase (same sign)
Anti-bonding – out of phase

← No bonding of any sort.

Further, the AOs involved should have comparable energies as well to form bonds. (to get a significant coefficient) in the LCAO-MO;

$$\psi_j = \sum_{i=1}^{N} c_{ij}\phi_i$$

Notation: MO homonuclear diatomic molecules



bonding/antibonding

$3\sigma_u^*$

p.q.n., n of the AO.

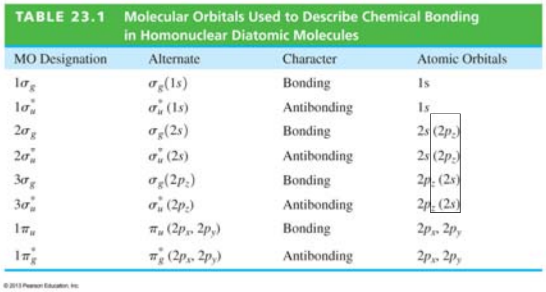


**TABLE 23.1 Molecular Orbitals Used to Describe Chemical Bonding in Homonuclear Diatomic Molecules**

| MO Designation | Alternate | Character | Atomic Orbitals |
|---|---|---|---|
| $1\sigma_g$ | $\sigma_g(1s)$ | Bonding | 1s |
| $1\sigma_u^*$ | $\sigma_u^*(1s)$ | Antibonding | 1$s$ |
| $2\sigma_g$ | $\sigma_g(2s)$ | Bonding | $2s\ (2p_z)$ |
| $2\sigma_u^*$ | $\sigma_u^*(2s)$ | Antibonding | $2s\ (2p_z)$ |
| $3\sigma_g$ | $\sigma_g(2p_z)$ | Bonding | $2p_z\ (2s)$ |
| $3\sigma_u^*$ | $\sigma_u^*(2p_z)$ | Antibonding | $2p_z\ (2s)$ |
| $1\pi_u$ | $\pi_u(2p_x, 2p_y)$ | Bonding | $2p_x, 2p_y$ |
| $1\pi_g^*$ | $\pi_g^*(2p_x, 2p_y)$ | Antibonding | $2p_x, 2p_y$ |

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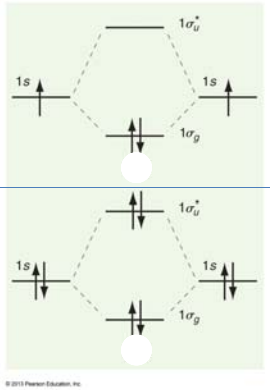
$H_2$

$(1\sigma_g)^2$

$He_2$

$(1\sigma_g)^2(1\sigma_u^*)^2$



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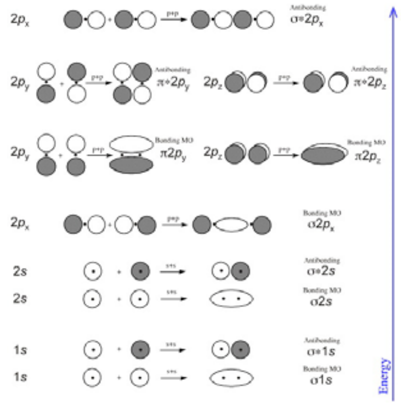
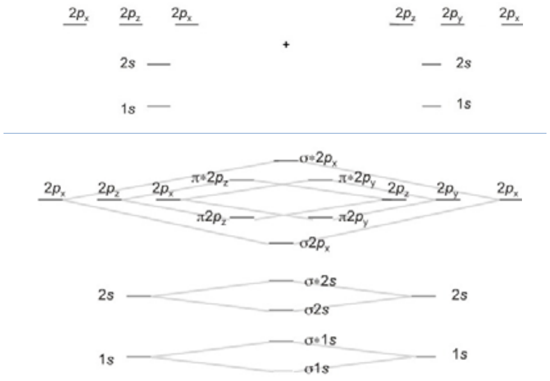
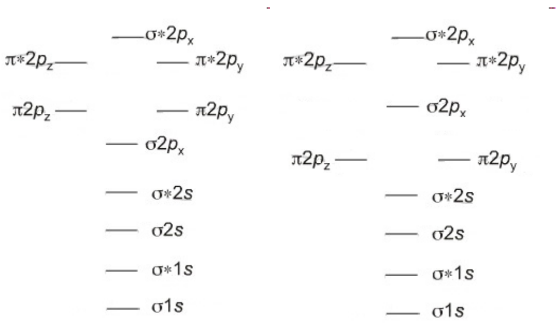


Minimal basis set sufficient for diatomics.





$\sigma*2p_x$

$\pi*2p_z$ $\pi*2p_y$

$\pi2p_z$ $\pi2p_y$

$\sigma2p_x$

$\sigma*2s$

$\sigma2s$

$\sigma*1s$

$\sigma1s$

$\sigma*2p_x$

$\pi*2p_z$ $\pi*2p_y$

$\sigma2p_x$

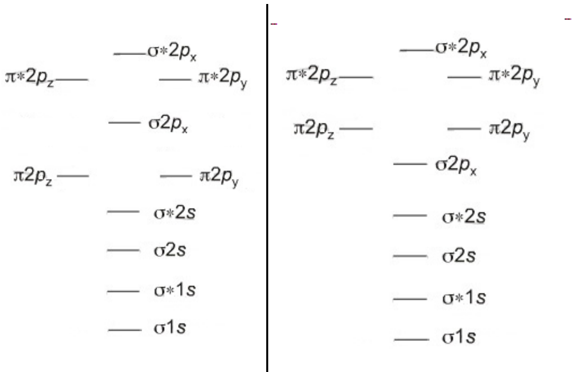
$\pi2p_z$ $\pi2p_y$

$\sigma*2s$

$\sigma2s$

$\sigma*1s$

$\sigma1s$

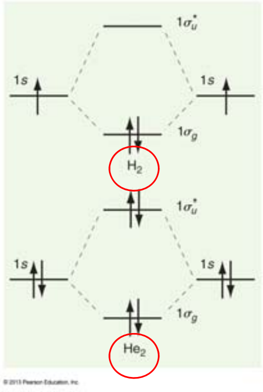


$B_2$, $C_2$, $N_2$

$O_2$, $F_2$

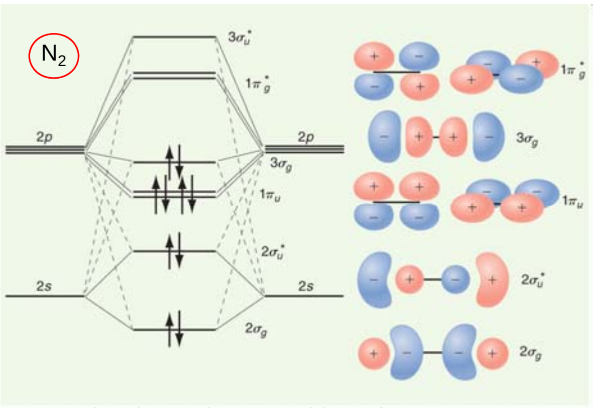
$$(1\sigma_g)^2$$

$$(1\sigma_g)^2(1\sigma_u^*)^2$$



Closed-Shell Molecular Orbital Coefficients - $H_2$

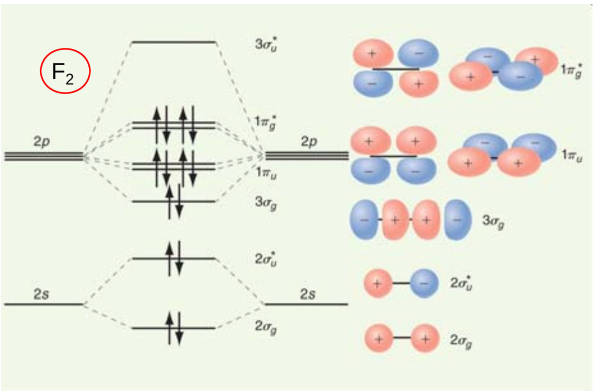
| | | 1 | 2 |
|---|---|---|---|
| MO: | | 1 | 2 |
| Eigenvalues: | | -0.59018 | 0.70055 |
| (ev) | | -16.05961 | 19.06286 |
| | | Sg+ | Su+ |
| 1 H1 | S | 0.54587 | 1.24613 |
| 2 H2 | S | 0.54587 | -1.24613 |

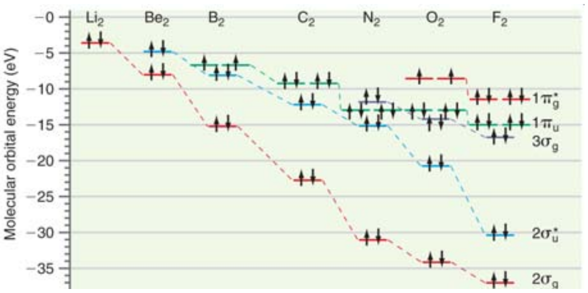


Note the change in energy hierarchy.

```
Closed-Shell Molecular Orbital Coefficients

MO:            1          2           3          4           5

Energy   -15.50632  -15.50495  -1.40847 -0.72753    -0.54859
  (eV) -421.94859 -421.91138 -38.32647 -19.79720 -14.92781

              Sg+       Su+          Sg+       Su+         Piu

1 N1 S1     0.70318  -0.70282    -0.17370    -0.17256  0.00000
2 N1 S      0.01286  -0.02571     0.50000     0.74662  0.00000
3 N1 PX     0.00000   0.00000     0.00000     0.00000  0.62965
4 N1 PY     0.00000   0.00000     0.00000     0.00000  0.00000
5 N1 PZ    -0.00171   0.00924    -0.23027     0.25277  0.00000
6 N2 S1     0.70318   0.70282    -0.17370     0.17256  0.00000
7 N2 S      0.01286   0.02571     0.50000    -0.74662  0.00000
8 N2 PX     0.00000   0.00000     0.00000     0.00000  0.62965
9 N2 PY     0.00000   0.00000     0.00000     0.00000  0.00000
10 N2 PZ    0.00171   0.00924     0.23027     0.25277  0.00000
```

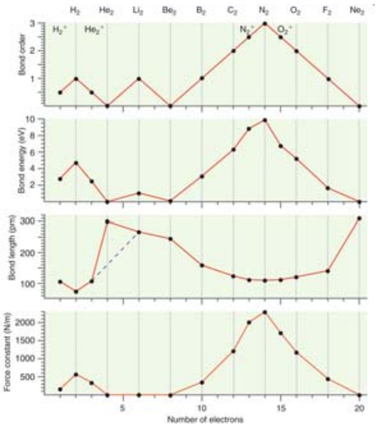
```
MO:                 6        7         8          9       10

Eigenvalues: -0.54859  -0.53025  0.26531  0.26531  1.04079
       (ev) -14.92781 -14.42883  7.21946  7.21946 28.32122

                  Piu       Sg+      Pig       Pig      Su+

1 N1 S1        0.00000   0.06956  0.00000  0.00000  0.12483
2 N1 S         0.00000  -0.39958  0.00000  0.00000 -1.09460
3 N1 PX        0.00000   0.00000 -0.82265  0.00000  0.00000
4 N1 PY        0.62965   0.00000  0.00000 -0.82265  0.00000
5 N1 PZ        0.00000  -0.60424  0.00000  0.00000  1.16295
6 N2 S1        0.00000   0.06956  0.00000  0.00000 -0.12483
7 N2 S         0.00000  -0.39958  0.00000  0.00000  1.09460
8 N2 PX        0.00000   0.00000  0.82265  0.00000  0.00000
9 N2 PY        0.62965   0.00000  0.00000  0.82265  0.00000
10 N2 PZ       0.00000   0.60424  0.00000  0.00000  1.16295
```



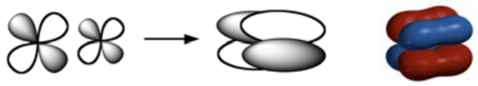


Electronic configuration, <u>bond length</u> (pm), <u>bond order</u> and <u>bond energy</u> (kJ mol$^{-1}$ of $Li_2$ to $F_2$ [$\sigma_{1s}^2\sigma^*_{1s}^2$]….

| | <u>Electronic configuration</u> | <u>Bond length</u> | <u>Bond energy</u> |
|---|---|---|---|
| Li-Li | $\sigma_{2s}^2$ | 267 | 110 |
| Be..Be | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2$ | exist? | exist? |
| B-B | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^2$ | 159 | 290 |
| C=C | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^4$ | 124 | 602 |
| N≡N | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^4\ \sigma_{2p}^2$ | 110 | 942 |
| O=O | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \sigma_{2p}^2\ \pi_{2p}^4\ \pi^*_{2p}{}^2$ | 121 | 494 |
| F-F | $\sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \sigma_{2p}^2\ \pi_{2p}^4\ \pi^*_{2p}{}^4$ | 142 | 155 |



Delta bond:



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By Ben Mills - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=6834588

Delta bonds (δ bonds) are covalent chemical bonds, where four lobes of one atom is involved with four lobes of the another atom.

This overlap leads to the formation of a bonding molecular orbital with two nodal planes which contains the internuclear axis and go through both atoms.

https://en.wikipedia.org/wiki/Delta_bond

<u>Molecular Orbitals: Hetero-nuclear Diatomic Molecules</u>

e.g. HF - Energies of AOs unequal.

(mimimal) basis functions - $\phi_{H1s}$ and $\phi_{F2pz}$

$$\psi_1 = \underset{\uparrow}{c_{1H}}\phi_{H1s} + \underset{\uparrow}{c_{1F}}\phi_{F2p_z} \quad \text{and} \quad \psi_2 = \underset{\uparrow}{c_{2H}}\phi_{H1s} + \underset{\uparrow}{c_{2F}}\phi_{F2p_z}$$

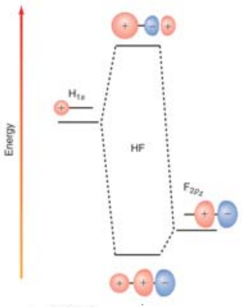
$$\Downarrow$$

$$\varepsilon_1 = -19.6\ \text{eV} \qquad \psi_1 = 0.34\phi_{H1s} + 0.84\phi_{F2p_z}$$

$$\varepsilon_2 = -10.3\ \text{eV} \qquad \psi_2 = 0.99\phi_{H1s} - 0.63\phi_{F2p_z}$$

## Hetero-nuclear Diatomic Molecules

The AO energies of basis functions are unequal.



$$\varepsilon_1 = -19.6\ \text{eV} \qquad \psi_1 = 0.34\phi_{H1s} + 0.84\phi_{F2p_z}$$

$$\varepsilon_2 = -10.3\ \text{eV} \qquad \psi_2 = 0.99\phi_{H1s} - 0.63\phi_{F2p_z}$$

Unequal coefficients.

Reminder: square of the coefficient is the contribution to electron probability distribution in the bond.

$$\psi_1 = c_{1H}\phi_{H1s} + c_{1F}\phi_{F2p_z} \quad \text{and} \quad \psi_2 = c_{2H}\phi_{H1s} + c_{2F}\phi_{F2p_z}$$

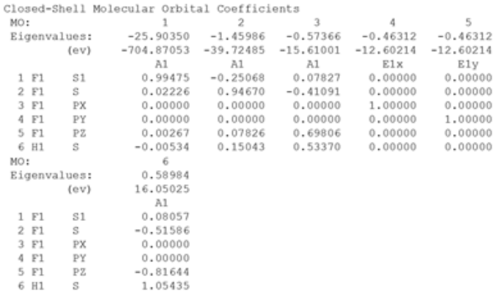
$$\psi_1 = c_{1H}\phi_{H1s} + c_{1F}\phi_{F2pz}$$

$$\int \psi_1{}^*\psi_1 d\tau = c_{1H}{}^2 + c_{1F}{}^2 + 2c_{1H}c_{1F}S_{HF}$$

$c_{1H}{}^2 = 0.34^2 = 0.12$ Around H

$c_{1F}{}^2 = 0.84^2 = 0.71$ Around F

$2c_{1H}c_{1F}S_{HF} = 0.17$ Shared H and F



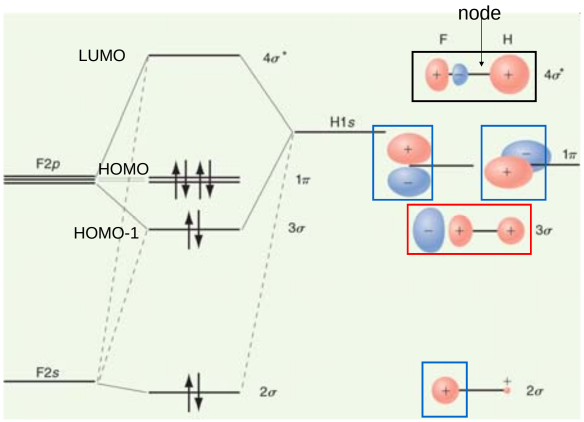
```
Closed-Shell Molecular Orbital Coefficients
 MO:                    1          2          3          4          5
 Eigenvalues:     -25.90350   -1.45986   -0.57366   -0.46312   -0.46312
          (ev)   -704.87053  -39.72485  -15.61001  -12.60214  -12.60214
                       A1         A1         A1        E1x        E1y
  1 F1     S1       0.99475   -0.25068    0.07827    0.00000    0.00000
  2 F1     S        0.02226    0.94670   -0.41091    0.00000    0.00000
  3 F1     PX       0.00000    0.00000    0.00000    1.00000    0.00000
  4 F1     PY       0.00000    0.00000    0.00000    0.00000    1.00000
  5 F1     PZ       0.00267    0.07826    0.69806    0.00000    0.00000
  6 H1     S       -0.00534    0.15043    0.53370    0.00000    0.00000
 MO:                    6
 Eigenvalues:       0.58984
          (ev)     16.05025
                       A1
  1 F1     S1       0.08057
  2 F1     S       -0.51586
  3 F1     PX       0.00000
  4 F1     PY       0.00000
  5 F1     PZ      -0.81644
  6 H1     S        1.05435
```

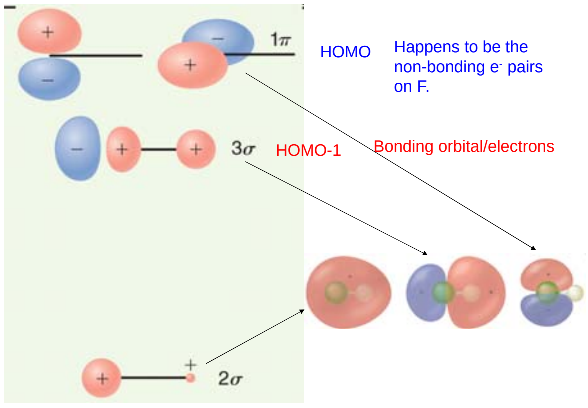
```
Closed-Shell Molecular Orbital Coefficients
MO:              1         2         3         4         5
Eigenvalues: -25.90350 -1.45986  -0.57366  -0.46312  -0.46312
       (ev) -704.87053 -39.72485 -15.61000 -12.60214 -12.60214


               A1      A1       A1       E1x   E1y


1 F1 S1       0.99475 -0.25068  0.07827 0.00000 0.00000
2 F1 S        0.02226  0.94670 -0.41091 0.00000 0.00000
3 F1 PX       0.00000  0.00000  0.00000 1.00000 0.00000
4 F1 PY       0.00000  0.00000  0.00000 0.00000 1.00000
5 F1 PZ       0.00267  0.07826  0.69806 0.00000 0.00000
6 H1 S       -0.00534  0.15043  0.53370 0.00000 0.00000
```

in phase

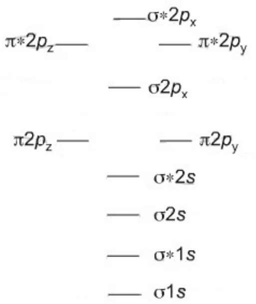




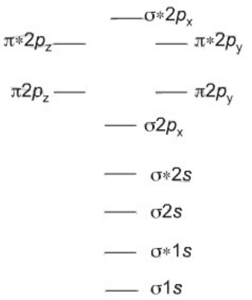
HOMO Happens to be the non-bonding $e^-$ pairs on F.

HOMO-1

Bonding orbital/electrons



CO, $CN^-$



NO, $O_2^+$, $O_2^-$

## Molecular Electrostatic Potential (MEP)

The potential felt by a test charge (unit positive) at various points in the molecule.

MEP is calculated by considering the positively charged nuclear framework and the negatively charged electron cloud of the molecule.

A negative MEP signifies attraction of a unit positive charge, therefore a negatively charged point in the molecule.

A positive MEP signifies repulsion of a unit positive charge, therefore a positively charged point in the molecule.

$$\phi(r) = \frac{q}{4\pi\varepsilon_0 r}$$

$$\phi_{nuclei}(x_1, y_1, z_1) = \sum_i \frac{q_i}{4\pi\varepsilon_0 r_i}$$

$$\rho(x, y, z) = -e\int \dots \int (\psi(x, y, z; x_1, y_1, z_1; \dots; x_n, y_n, z_n))^2 \times dx_1\, dy_1\, dz_1 \dots dx_n\, dy_n\, dz_n$$

$$\phi(x_1, y_1, z_1) = \sum_i \frac{q_i}{4\pi\varepsilon_0 r_i} - e\iiint \frac{\rho(x, y, z)}{4\pi\varepsilon_0 r_e}\, dx\, dy\, dz$$

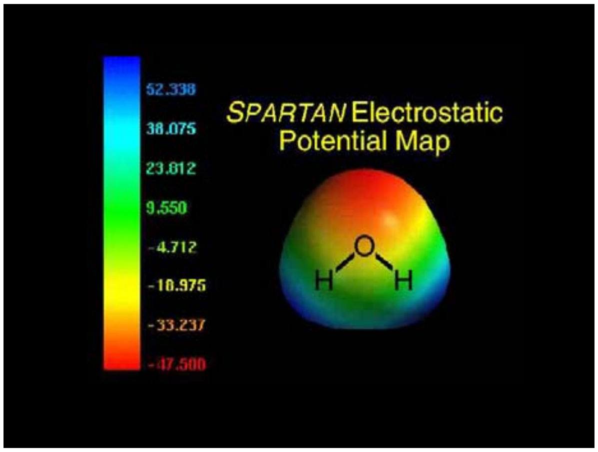
## Electrostatic Potential Surfaces

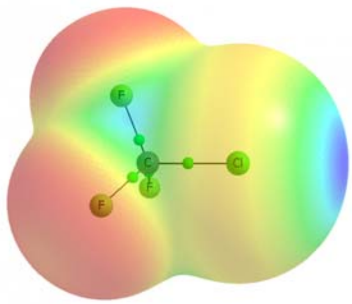
Molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally.

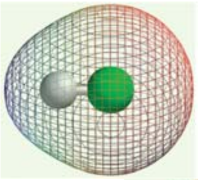
The surface is a constant electron density surface.

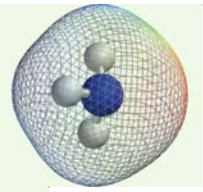
The potential at the surface is mapped on to the surface. The surface (solid/transparent or mesh) is color coded according to the electrical potential.

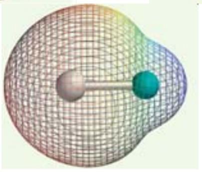
Knowledge of the charge distributions can be used to determine how molecules interact with one another.

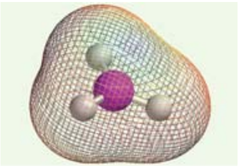


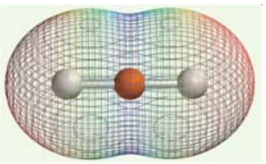


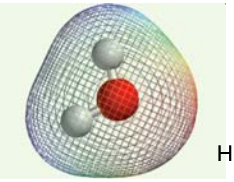

HF


$NH_3$


LiH


$BH_3$


$BeH_2$


$H_2O$