The overlap term is non-zero. Let overlap term go to zero.

Overlap term is non-zero

Sigma bond order is one

Three Orbitals!

now let us look at a more complicated system.

Ethylene

\[ \Psi_2 = c_1 \Phi_1 - c_1 \Phi_2 \]

\[ E_2 = - \frac{1}{1 - S_{12}} \beta \]

\[ \Psi_1 = c_1 \Phi_1 + c_1 \Phi_2 \]

\[ E_1 = \frac{1}{1 + S_{12}} \beta \]

\( \Phi_1 \) \quad \( \Phi_2 \)

\( \pi \) system of ethylene

\( \pi \) bonding 
fill with 2 e-

\( \pi^* \) antibonding
empty orbital

C2H4

H2

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4

H2 C2H4
How do we calculate the energies and coefficients of the MO's?

We are going to use the LCAO approximation to make three MO's.

Use Symmetry!

The ends are the same so they must contribute equally to any MO. So we can make linear combinations where atoms one and three contribute equally.

$$\Phi_1 = p_{z1} + p_{z3}$$
$$\Phi_2 = p_{z1} - p_{z3}$$
$$\Phi_3 = p_{z2}$$

The second carbon is unique.

Coulomb integral

$$\int p_{za} \phi_{za} = E = \alpha = 0$$

Interaction integral

$$\int p_{za} \hat{H} p_{za} = E_{int} = \beta$$

Huckel Approximation

Only if the two p orbitals are adjacent otherwise Interaction is 0.

We need to normalize our LCAOs

$$\int \Phi_1^2 = 1$$

$$\int N^2 (p_{z1} + p_{z3}) (p_{z1} + p_{z3}) = 1$$

$$N^2 (p_{z1}^2 + 2p_{z3}p_{z1} + p_{z3}^2) = 1$$

$$N^2 \times 2 = 1$$

So $N = \frac{1}{\sqrt{2}}$

We are going to use the LCAO approximation to make three MO's.

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$$\Phi_1 = \frac{1}{\sqrt{2}} (p_{z1} + p_{z3})$$
$$\Phi_2 = \frac{1}{\sqrt{2}} (p_{z1} - p_{z3})$$
$$\Phi_3 = p_{z2}$$

The second carbon is unique.

Same Symmetry
$\Phi_1 = \frac{1}{\sqrt{2}} (p_{z1} + p_{z3})$

$\Phi_3 = p_{z2}$

Bonding MO

$\Phi_1 = \frac{1}{\sqrt{2}} (p_{z1} + p_{z3})$

$\Phi_3 = p_{z2}$

$\frac{1}{\sqrt{2}} \int (p_{z1} + p_{z3}) \hat{H} p_{z2} = \frac{1}{\sqrt{2}} 2\beta = \sqrt{2} \beta$

Antibonding MO

$\frac{1}{\sqrt{2}} \int (p_{z1} + p_{z3}) \hat{H} (-p_{z2}) = -\frac{1}{\sqrt{2}} 2\beta = -\sqrt{2} \beta$

Energy = $\sqrt{2} \beta$

Energy = $-\sqrt{2} \beta$

$\frac{1}{\sqrt{2}} \int (p_{z1} + p_{z3}) \hat{H} (-p_{z2}) = -\frac{1}{\sqrt{2}} 2\beta = -\sqrt{2} \beta$

Energy = $-\sqrt{2} \beta$

Antibonding

$\frac{1}{\sqrt{2}} \int (p_{z1} + p_{z3}) \hat{H} (-p_{z2}) = -\frac{1}{\sqrt{2}} 2\beta = -\sqrt{2} \beta$

Energy = $-\sqrt{2} \beta$

Antibonding

What about $\Phi_2$?

There is no overlap between ends so

$E = 0$
This is painful!

It makes the brain hurt.

So use a computer instead.

Simple Huckel Molecular Orbital Theory Calculator

http://www.ic.sunysb.edu/Class/orgchem/shmo/

What is the \( \pi \) bond order in the allyl anion?
What is the \( \pi \) bond order in the allyl cation?
What is the \( \pi \) bond order in the allyl radical?

A 0     B .5     C 1     D 1.5    E 2

This is painful!

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Simple Huckel Molecular Orbital Theory Calculator

http://www.ic.sunysb.edu/Class/orgchem/shmo/

The 2 electron cation \( \pi \) system is more stable as a ring. It is an aromatic system

Is a ring more stable(A) or less (B)

The 4 electron anion \( \pi \) system is less stable as a ring. It is an antiaromatic system

Is a ring more stable(A) or less (B)