

L3 Constructing MO Diagrams

Building your own MOs

- now we will consider some of the components of a MO diagram to obtain a greater depth of understanding
- our purpose is not to be able to reproduce a memorised diagram, but to understand the processes in forming a diagram so that given any (relatively simple!) molecule you can build the MO diagram
- this requires we bring together material from a range of your other courses on MOs, mathematics and physical chemistry
- in this section we will look at:
 - why combine AOs to form MOs?
 - positioning of the fragment orbital energy levels
 - combining fragment orbitals to form MOs, ie what the MOs look like
 - why some AO components larger than others
 - the mathematics behind these general "rules"

Linear Combination of Atomic Orbitals

- qualitatively MOs are formed by combining or "adding" **fragment orbitals** (FOs) once "as is" and once with the phase of all components reversed, this is equivalent to "subtracting" the FO, and produces a bonding/antibonding pair, **Figure 1**

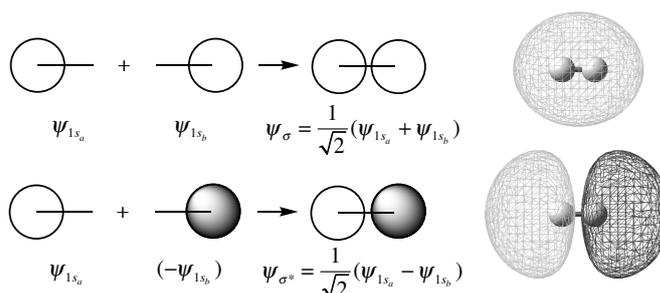


Figure 1 "cartoon" and "real" MOs of H₂

- the MOs we draw are representations of the "real" orbitals (far right of **Figure 1**) which are obtained from solving the Schrödinger equation
- you have already met this process in your chemical bonding (quantum mechanics) course, **Figure 2**

Covered in detail in
your Quantum
Mechanics courses

removed due to
copyright

Figure 2 Slide from the quantum mechanics chemical bonding course

- mathematically a MO is a **linear combination** of **atomic orbitals** or LCAO
- The general formula is:

$$\psi_{\Gamma} = N(c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n) = N\sum c_i\psi_i$$

- Γ = symmetry label of the MO and N = normalisation criteria
- the coefficients c's (are numbers) that determine the magnitude of the contribution of each atomic orbital relative to the others
- i is an index that runs over all the contributing atomic orbitals, we say that the AOs of a molecule form a **basis set** for the molecule
- when a calculation is carried out the computer is optimising these c's for the molecular system, an output of the calculation is the LCAOs or MOs, another output is the energy of each MO
 - however we can estimate the c's and the energy qualitatively!
 - this allows us to avoid the complex mathematics involved in quantitatively solving the Schrödinger equation
 - *very often we work backwards, from the final MOs and energies to understand the overlap and interaction of fragment orbitals and thus obtain insight into the bonding within a molecule*
- in this course we don't combine the AOs on different centres when drawing diagrams, we want to show the individual AO components, **Figure 3**

IMPORTANT

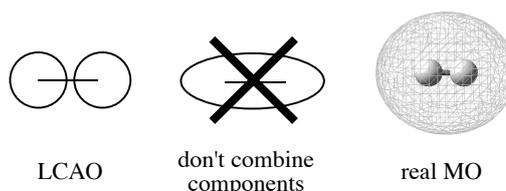


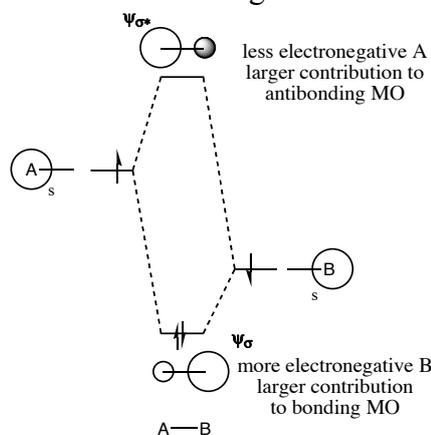
Figure 3 leave AO components separate

Orbital Size in a MO diagram

- the size of the AO reflects the magnitude of the c's in the LCAO equation,
 - we can qualitatively predict the relative size of the c's
 - the more stable (lower energy) FO makes a larger contribution to the bonding MO, the less stable (higher energy) FO makes a larger contribution to the antibonding MO, **Figure 4a**
 - you have seen this before in Prof. Ramon Vilar's course, **Figure 4b**
 - if the orbitals are degenerate both contribute the same amount to the MO

IMPORTANT

From your 1st year
Molecular
Structure course



removed due to
copyright

Figure 4 (a) AO contribution to MOs and (b) slide from lecture course by Prof. Ramon Vilar

Fragment Orbitals Energy Positioning

- molecular orbital diagrams take the orbitals from two chemical **fragments** and combine them (allow them to interact) to form the MOs
- these fragments can be quite complex however, they can also be simple atoms as in the H atom fragments of H₂.
- how do you know where to put fragment orbital (FO) energy levels?
- for atomic orbitals the *orbital energy depends roughly on the electronegativity* of the atoms, the more electronegative the atom the lower (more negative) the orbital energies
 - you should know the rough ordering of electronegativity for atoms in the first row of the periodic table, **Table 1**
 - main group metals, elements and transition metals all tend to have quite low electronegativity, ie they are electropositive. Their AOs all lie quite high in energy relative to H, **Table 2**

IMPORTANT

H	Li	Be	B	C	N	O	F
2.20	0.98	1.57	2.04	2.55	3.04	3.44	3.98
	Na	Mg	Al	Si	P	S	Cl
	0.93	1.31	1.61	1.90	2.19	2.58	3.16

Table 1 Pauling electronegativity of the first row elements

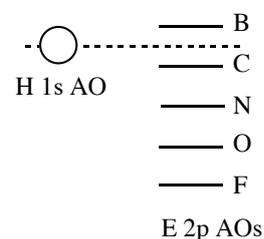


Figure 5 Relative electronegativity

Ca	Mn	Co	Ni	Cu	Al	Si	P
1.00	1.55	1.88	1.91	1.90	1.61	1.90	2.19

Table 2 Pauling electronegativity of selected transition metals and main group elements

- a rough estimate of the energy levels for the 2p AOs of the first row elements is made in **Figure 5** based on their relative electronegativity with respect to H.
 - the energy of the H 1sAO is taken as a "zero".
 - the **top valence** AOs are evaluated relative to the H 1sAO reference, the top valence AOs of the first row are the 2p AOs (NOT the 2s AOs)
- other properties such as the ionization energy can be used to predict the relative position of AOs, these will be given to you if you need them.
- for second row elements, the 2s AOs lie significantly below the 2p AOs and *the s-p energy gap increases substantially along the row*, **Figure 6**
 - this tends to mean that the 2s AOs will interact only if the atoms are directly adjacent to each other in the periodic table
 - for example the 2s AOs will form a bonding/antibonding pair in CN⁻ but not in CO, **Figure 7**
 - the best way to check is to carry out a calculation
 - when MO mixing is strong the ordering can change!

IMPORTANT

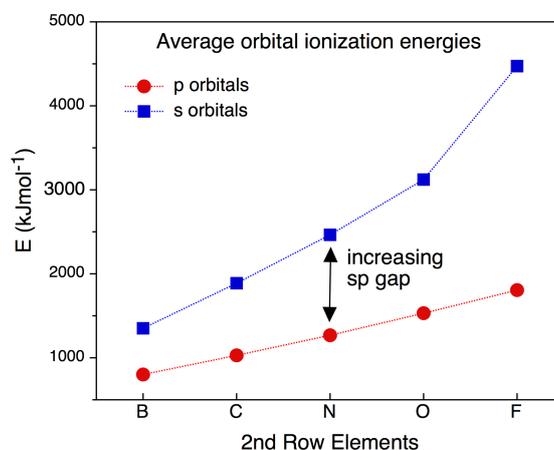


Figure 6 Increasing sp gap

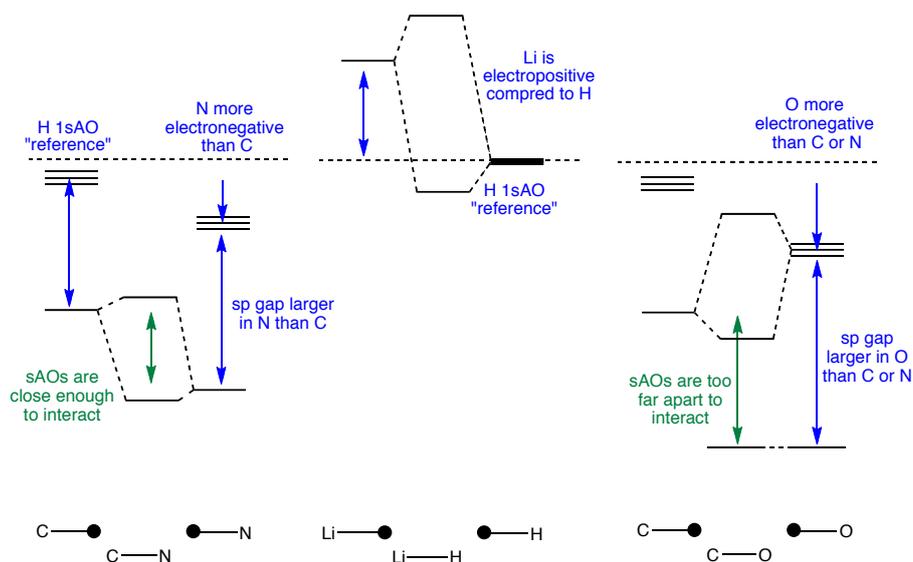


Figure 7 Effects of relative electronegativity and increasing sp gap

resources available
on-line:
http://www.huntresearchgroup.org.uk/teaching/year2_mos.html

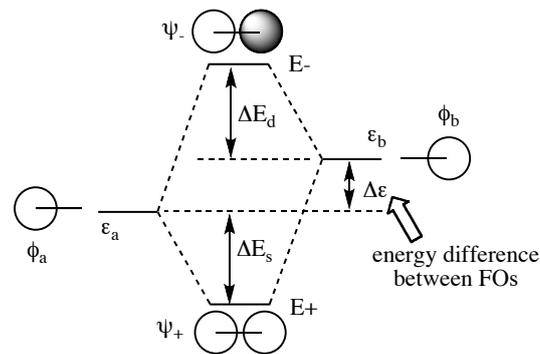
- some practice via self-study! A document, molecular orbitals for heteronuclear diatomic molecules is available online, you are **expected** to have read and attempted these examples
 - links to revision from last year
 - and more complex details we have introduced this year
 - emphasises the interpretation as well as construction of MO diagrams
 - in a relatively simple package!

In-Class Activity

- where would you put the FOs for a MO diagram of MgCl_2 ?
 - use the fragments " Cl_2 " $\text{Cl}-\bullet-\text{Cl}$ and $\bullet-\text{Mg}-\bullet$ for $\text{Cl}-\text{Mg}-\text{Cl}$
- first take the **socratic quiz** to give you some hints
 - What are the valence orbitals of Mg?
 - What relative energy will the valence orbitals of Mg have (and why)?
 - What relative energy will the valence orbitals of Cl have (and why)?
 - When we form the $\text{Cl}-\bullet-\text{Cl}$ fragment how large will the interaction energy of the MOs be?
- then draw the fragments and fragment orbitals below

The Stabilisation/Destabilisation Energy

- we have determined the "cartoon" form of the MOs, but how far apart do we put the bonding and antibonding MO energy levels?
- the **splitting energy** (E) is the energy of stabilisation (ΔE_s) plus the energy of destabilisation (ΔE_d), overall it is the amount of energy by which the MO energy is shifted from the FO energy, **Figure 8**
 - ϵ_a and ϵ_b are the energy of fragment orbitals ϕ_a and ϕ_b
 - the energy difference between the FOs is $\Delta\epsilon$
 - E_+ and E_- are the energy of the MOs ψ_+ and ψ_- .



$$\text{splitting energy } E = \Delta E_s + \Delta E_d$$

Figure 8 Splitting energy

- The splitting energy is dependent on three things:

IMPORTANT

- the energy difference between orbitals: $\Delta\epsilon = \epsilon_a - \epsilon_b$
 $\epsilon_a = \langle \phi_a | H | \phi_a \rangle$ $\epsilon_b = \langle \phi_b | H | \phi_b \rangle$
- the orbital coupling, $H_{ab} = \langle \phi_a | H | \phi_b \rangle$
- and the extent of orbital overlap: $S_{ab} = \langle \phi_a | \phi_b \rangle$
- some comments
 - the "triangular" brackets are Dirac notation for an integral over all spatial and spin coordinates: $\langle \psi_i | H | \psi_j \rangle = \int \psi_i H \psi_j d\tau$
 - you have seen this notation previously in your quantum mechanics course
 - S_{ab} recovers the direct spatial overlap of orbitals, **Figure 9**
 - H includes all the nuclear-electronic and electron-electron interactions within a molecule, thus you can think of H_{ab} as an orbital interaction modified by the local environment within the molecule, **Figure 9**

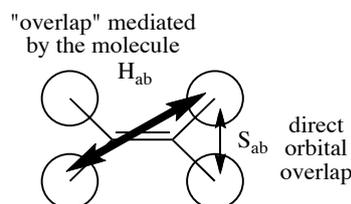


Figure 9 H_{ab} and S_{ab}

FO Energy Difference and Orbital Coupling

- qualitatively there is a sliding scale of **splitting energies** ($\Delta\epsilon$), degenerate orbitals have a large splitting energy and then as the fragment orbitals shift apart in energy the splitting energy decreases, a point will be reached when $\Delta\epsilon$ is sufficiently large that the fragment orbitals do not interact at all (the system is now ionic and not covalent!) **Figure 10**

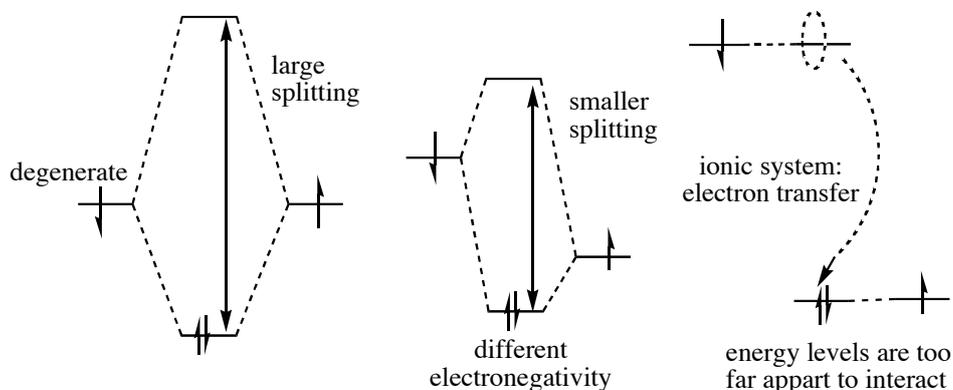


Figure 10 Increasing energy difference between the fragment orbitals

- the orbital coefficients are linked closely with the interaction energy:
 - if the FOs are far apart in energy then there is minimal stabilisation and destabilisation and there is minimal covalent interaction, one FO will dominate or have a much larger contribution (large c in the LCAOs)
 - as the energy of the FOs gets closer then the stabilisation/destabilisation energy increases and the covalent mixing increases, the c 's become similar
 - the most covalent orbitals have equal contributions from both FOs in the final MO, the c 's are identical

The orbital overlap

- the larger the **orbital overlap** the greater the energy splitting
 - for clarity we don't always draw the orbitals actually overlapping
 - orbitals that are close together interact with each other through electron-electron interactions and also interactions with the "other" positive nuclei, thus orbitals which are close have a large H_{ab} as well as a large S_{ab}

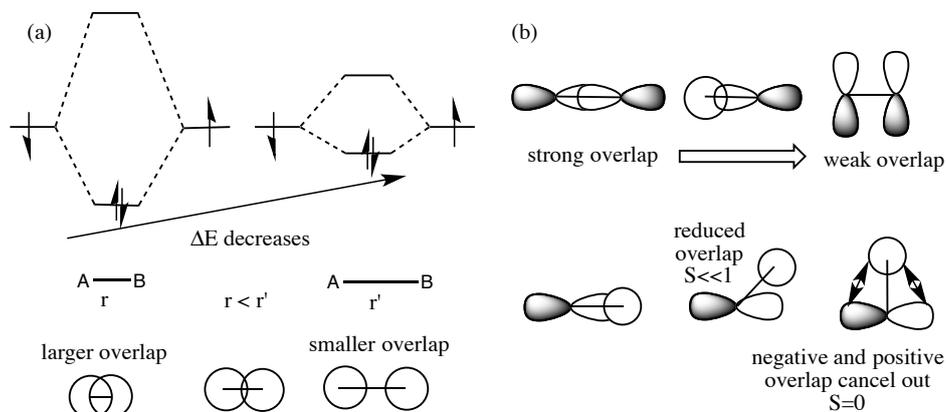


Figure 11 overlap (a) distance and (b) orientation dependence

- the magnitude of the orbital overlap depends on an interplay between the relative location, orientation and diffusivity of the orbitals involved.
 - the closer orbitals are, the larger S_{ab} and H_{ab} , **Figure 11a**

- the more dense an orbital the stronger the overlap and larger S_{ab} and H_{ab}
- the more diffuse an orbital the weaker it's interactions with other orbitals
- within a shell interactions decrease $s > p > d$.
- the more directed an interaction the better the overlap (and impact on S_{ab} and H_{ab}), for example, p_σ orbitals have lobes directed toward each other and have better overlap than p_π orbitals, interactions decrease $s_\sigma > sp_\sigma > p_\sigma > p_\pi$, and the orientation of p orbitals in p-s interactions is important, **Figure 11b**

Making Connections: Quantum Mechanics

- we can link these qualitative arguments (inorganic chemistry) to some equations (physical chemistry)
 - The Schrödinger equation is $E\psi = H\psi$
 - has components one of which is the Hamiltonian, **Figure 12a**

$$H = T_n + T_e + V_{ee} + V_{en} + V_{nn} \quad H_e = T_e + V_{ee} + V_{en}$$
 - the other component is the wavefunction, which we represent via the LCAO theory, which means we expand the MO (ψ) in terms of the atomic orbitals (ϕ) where the coefficients c_n represent the size of each FO, **Figure 12b**

**removed due to
copyright**

Figure 12: Relevant slides from your QM chemical bonding course

- let us assume we have two AOs which will combine to form a bonding and antibonding MO and that each contribution is identical:

$$\psi = \sum c_n \phi_n$$

$$\psi = c_a \phi_a \pm c_b \phi_b$$

$$\psi = c(\phi_a \pm \phi_b)$$

- we know the electron must reside within the MO. That is, when we integrate over the MO the integral must be 1. Requiring this equality to hold gives us an expression for c .

Reminder from your QM course!

- you are expected to be able to carry out the following derivations, as these come from your QM course I won't cover them again in Lectures but this is to make very clear what I expect you to know.
- determine the expression for the coefficient c

$$\text{require } \int \psi^* \psi d\tau = \langle \psi | \psi \rangle = 1 \quad \text{given } \psi = c(\phi_a \pm \phi_b)$$

$$\langle \psi | \psi \rangle = \langle c(\phi_a \pm \phi_b) | c(\phi_a \pm \phi_b) \rangle$$

$$\langle \psi | \psi \rangle = c^2 (\underbrace{\langle \phi_a | \phi_a \rangle}_{=1} + \underbrace{\langle \phi_b | \phi_b \rangle}_{=1} \pm 2 \underbrace{\langle \phi_a | \phi_b \rangle}_{=S_{ab}})$$

$$1 = \langle \psi | \psi \rangle = c^2 2(1 \pm S_{ab})$$

$$c^2 = \frac{1}{2(1 \pm S_{ab})} \quad \therefore c = \frac{1}{\sqrt{2(1 \pm S_{ab})}}$$

$$\psi = \frac{1}{\sqrt{2(1 \pm S_{ab})}} (\phi_a \pm \phi_b)$$

- we can also simplify the expression for the energy

$$H\psi = E\psi$$

$$\text{premultiply both sides by } \psi^* \quad \psi^* H\psi = \psi^* E\psi$$

$$\text{integrate } \int \psi^* H\psi d\tau = E \int \psi^* \psi d\tau$$

$$\text{require } \int \psi^* \psi d\tau = \langle \psi | \psi \rangle = 1$$

$$\int \psi^* H\psi d\tau = E \quad \text{Dirac notation } E = \langle \psi | H | \psi \rangle$$

- now we can obtain expressions for the energy of the bonding and antibonding MOs

$$E = \langle \psi | H | \psi \rangle \quad \text{and} \quad \psi_+ = c_+ (\phi_a + \phi_b)$$

$$\langle \psi | H | \psi \rangle = c_+^2 \langle \phi_a + \phi_b | H | \phi_a + \phi_b \rangle$$

$$\langle \psi | H | \psi \rangle = c_+^2 [\langle \phi_a | H | \phi_a \rangle + \langle \phi_a | H | \phi_b \rangle + \langle \phi_b | H | \phi_a \rangle + \langle \phi_b | H | \phi_b \rangle]$$

$$\langle \phi_a | H | \phi_a \rangle = H_{aa} = \epsilon_a \quad H_{bb} = \epsilon_b \quad \text{assume } H_{ab} = H_{ba}$$

$$\langle \psi | H | \psi \rangle = c_+^2 [H_{aa} + 2H_{ab} + H_{bb}] = c_+^2 [\epsilon_a + \epsilon_b + 2H_{ab}]$$

$$E_+ = \langle \psi | H | \psi \rangle \quad \text{and} \quad c = \frac{1}{\sqrt{2(1 \pm S_{ab})}}$$

$$E_+ = \frac{\epsilon_a + \epsilon_b + 2H_{ab}}{2(1 + S_{ab})} \quad \text{and} \quad E_- = \frac{\epsilon_a + \epsilon_b - 2H_{ab}}{2(1 - S_{ab})}$$

IMPORTANT

- the important equations for us are:

$$E_+ = \frac{\epsilon_a + \epsilon_b + 2H_{ab}}{2(1 + S_{ab})} \quad \text{and} \quad E_- = \frac{\epsilon_a + \epsilon_b - 2H_{ab}}{2(1 - S_{ab})}$$

Making Connections: Basic Example

- however, let's simplify the equations before we explore them in more detail.
 - start with

$$E_+ = \frac{\epsilon_a + \epsilon_b + 2H_{ab}}{2(1+S_{ab})} \quad \text{and} \quad E_- = \frac{\epsilon_a + \epsilon_b - 2H_{ab}}{2(1-S_{ab})}$$

- assume that the interacting AOs (ϕ_a, ϕ_b) have energies (ϵ_a, ϵ_b) that are degenerate i.e the same energy. To simplify even further we assume there is zero direct overlap ($S_{ab}=0$)

$$\text{assume } \epsilon_a = \epsilon_b = \epsilon \text{ and } S_{ab} = 0$$

$$E_+ = \frac{\epsilon + \epsilon + 2H_{ab}}{2(1+0)} \quad E_- = \frac{\epsilon + \epsilon - 2H_{ab}}{2(1-0)}$$

$$E_+ = \frac{2\epsilon + 2H_{ab}}{2} = (\epsilon + H_{ab}) \quad E_- = \frac{2\epsilon - 2H_{ab}}{2} = (\epsilon - H_{ab})$$

- the "pictorial" representation of this result is shown in **Figure 13** below,

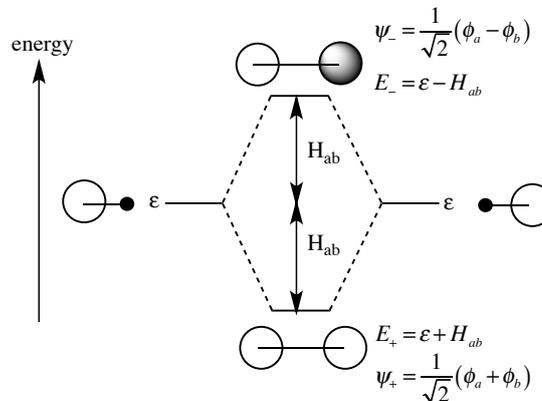


Figure 13 Splitting energy for degenerate FOs

- by convention H_{ab} is negative, ϵ is also negative, so adding two negative numbers means the energy goes down for E_+ and up for E_- .
- the important point is that the splitting energy is dependent on the orbital coupling H_{ab}

Making Connections: Including Orbital Overlap

- now consider solutions to the Schrödinger equation where we allow the orbitals to overlap $S_{ij} \neq 0$, we will leave $\epsilon = \epsilon_a = \epsilon_b$ (otherwise the equations are too complex!)

$$E_{\pm} = \frac{H_{aa} + H_{bb} \pm 2H_{ab}}{2(1 \pm S_{ab})} \quad \epsilon = H_{aa} = H_{bb} \quad E_{+} = \frac{\epsilon + H_{ab}}{1 + S_{ab}} \quad E_{-} = \frac{\epsilon - H_{ab}}{1 - S_{ab}}$$

- the splitting energies are shown in **Figure 14**
 - including the effects of S_{ab} shifts the energy of both MOs up
 - we are already familiar with this effect in the "rule" that antibonding MOs are always destabilised more than bonding MOs are stabilised

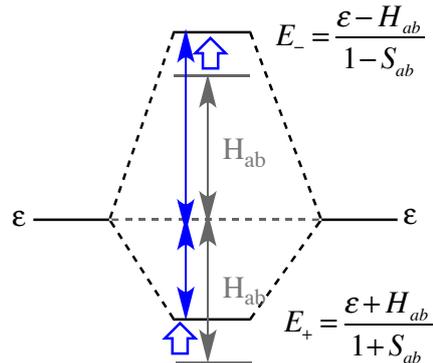


Figure 14 Splitting energy including overlap effects

- *think* about the equation by putting some numbers in, lets say $S_{ab}=0.2$ (overlap can vary between 0 and 1 but it is normally much smaller than 1).
 - the antibonding MO has an energy $(\epsilon - H_{ab})$ multiplied by $1/0.8=1.25$, the magnitude of the energy of destabilisation is increased.
 - the bonding MO has an energy of $(\epsilon + H_{ab})$ multiplied by $1/1.2=0.83$, the magnitude of the energy of stabilisation is decreased.
- you have seen these approximations before but in a slightly different context!

removed due to
copyright

Figure 15: Relevant slides from your QM chemical bonding course

Making Connections: Non-degenerate Fragment Orbitals

- now we release the degeneracy constraint, and allow the energy of the fragment orbitals to differ, $\epsilon_a \neq \epsilon_b$ but we assume $S_{ab}=0$ for simplicity
 - this was covered in your Quantum Mechanics course when you solved for the secular determinant of H_2 . See **Figure 17** for the derivation, the result:

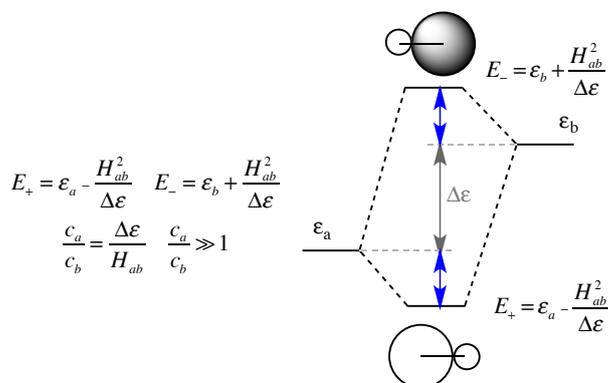


Figure 16 Splitting energy for non-degenerate FOs

- the new splitting energies are shown in **Figure 16**.
 - the energy of each MO is now dependent on the square of H_{ab}
 - and the energy is inversely proportional to the energy gap ($\Delta\epsilon$) between the FOs, the larger the energy gap the smaller the shift in the MO energies.
 - the orbital coefficients also differ, the larger the energy gap (and smaller H_{ab}) the greater the difference between the c_a and c_b contributions.
- thus we have now provided a more quantitative argument based on quantum mechanics for the initial qualitative assertion about MO splitting energies: "degenerate orbitals have a large splitting energy. As the fragment orbitals shift apart in energy the splitting energy decreases"

Covered in detail in
your Quantum
Mechanics courses

removed due to
copyright

Figure 17: Relevant slides from your QM chemical bonding course

Key Points

- be able to explain the acronym LCAO, give the general equation, describe each of the components and illustrate the process on a diagram
- be able to explain and predict the relative size of AO contributions to MOs
- be able to rationalise the relative position of fragment orbital energy levels
- be able to define and illustrate the splitting energy on a diagram
- be able to discuss employing equations, diagrams and examples each of the key quantities ($\Delta\varepsilon$, S_{ab} and H_{ab}) that influence the splitting energy
- be able to make a connection to your quantum mechanics including deriving the relevant equations
- be able to explain, compare and contrast the equations for E_+ and E_- for different levels of approximation, employing diagrams and examples
- be able to employ this knowledge to form general MO diagrams

Self Study Problems / Exam Preparation

- compute the orbitals for (linear) FHF-, draw and annotate a MO diagram consistent with the MOs you observe
- assuming $\varepsilon_a \neq \varepsilon_b$ and $S_{ab}=0$, what happens to the MO energy levels as $\Delta\varepsilon$ gets larger?
- when is S_{ab} likely to be small?
- show that $c=1/\sqrt{2}$ when $S_{ab}=0$
- (advanced for experts) First, solve the secular determinant for 3 overlapping p_z orbitals on a 3-atom chain (energies and wavefunctions). Draw the relevant MOs based on your mathematical equations. Then, draw a MO diagram (using the processes described in this course) using two p_z AOs as one fragment and a single p_z AO as the other fragment. Finally, check your answers by computing the MOs of the allene anion ($C_3H_5^-$). Compare the maths, MO theory and computational results.

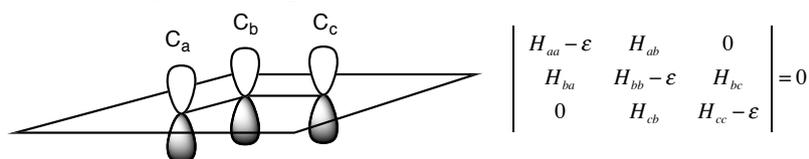


Figure 18: Three atom conjugated chain Hückel problem