Molecular Orbital Approach to Bonding

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The following slides were modified from a gift from Professor Martyn Poliakoff Of the Department of Chemistry in Nottingham, England. Tom Poliakoff also used these slides and prepared them, to my knowledge. You might also check The MIT open courseware lecture to refresh your memory of molecular orbitals.

MIT Open Courseware lecture
- https://www.youtube.com/watch?v=llaa-iEYDLI
- HF https://www.youtube.com/watch?v=estiedAIxII
- B₂H₆ https://www.youtube.com/watch?v=GD5CrjyAKx4
- CO http://www.chemtube3d.com/orbitalsCO.htm
# Bond Dissociation Energies

Can you account for these trends? Yes, you can.

## Average Bond Dissociation Energies, $D$ (kJ/mol)$^a$

<table>
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<tr>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
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<td>366$^a$</td>
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<tr>
<td>I—I</td>
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## Multiple covalent bonds

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<tr>
<td>N≡N</td>
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</table>

$^a$ Exact value
Ideal hydrogen-oxygen fuel cell operation

Fuel energy input
$\Delta H = 285.83 \text{ kJ/mol}$

Electric energy output
$\Delta G = 237.13 \text{ kJ/mol}$

$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- + O \rightarrow H_2O$

$T\Delta S = 48.7 \text{ kJ/mol}$

$\text{H}^+ \text{ ions migrate across electrolyte}$

Water
More Bond Dissociation Energies

<table>
<thead>
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<td>Si—C</td>
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<td>Si—Cl</td>
<td>456(42)</td>
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<td>Si—F</td>
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<td>(CH$_3$)$_3$Si—Si(CH$_3$)$_3$</td>
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<tr>
<td>(Aryl)$_3$Si—Si(aryl)$_3$</td>
<td>368(31)</td>
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<tr>
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Video: Oxygen

http://www.periodicvideos.com/videos/008.htm
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Valence Bond Approach: Localized Bonds, just like Lewis Structures and VSEPR

Basis of VB approach: overlap orbitals in each bond separately. Each bond is LOCALISED between two atoms.

Molecular Orbital Approach: De-Localized Orbitals and Electrons in them ➔ Energy Levels, Magnetism

In molecular orbital (MO) approach - overlap orbitals for the whole molecule - bonding is therefore DELOCALISED. We will look first at DIATOMIC MOLECULES and only later move on to POLYATOMIC MOLECULES.

MOLECULAR ORBITAL THEORY FOR DIATOMIC MOLECULES

In principle, set up Schrödinger wave equation for molecule and solve it.
Solution will involve **molecular orbitals** - similar to atomic orbitals - but centred around all of the nuclei in molecule. Each defined by sets of quantum numbers, with electron probability density determined by $\psi^2$, where $\psi = $ molecular wave function.

**Approximate method:**
At any moment, electron near one nucleus - approximate behaviour like electron in atomic orbital for that atom. Over time - electron associated with other nuclei in molecule. Therefore construct molecular orbitals (m.o.'s) by forming:

**Linear Combination of Atomic Orbitals**
It is this, **LCAO**, method which we will use to construct m.o.'s.

Simplest example - $H_2$: two H atoms $H_A$ and $H_B$

Only two a.o.'s ($1s_A$, $1s_B$) to form linear combinations.

**General rule:**

<table>
<thead>
<tr>
<th>n a.o.'s</th>
<th>n m.o.'s</th>
</tr>
</thead>
</table>

So we can only construct 2 m.o.'s for $H_2$ - and these are:

$$\psi_b = 1s_A + 1s_B \quad \text{and} \quad \psi_a = 1s_A - 1s_B$$

i.e. the sum ($\psi_b$) and the difference ($\psi_a$) of the constituent a.o.'s.

Consider the electron distribution in each of these:
\( s/s \quad + \quad + \quad \rightarrow \quad \bullet \quad + \quad \bullet \quad \sigma_2s \)

\( s + s \) overlap everywhere positive \(\rightarrow\) **BONDING M.O.**

\( + \quad - \quad \rightarrow \quad + \quad - \quad \sigma^{*}2s \)

\( s - s \) overlap everywhere negative \(\rightarrow\) **ANTI-BONDING M.O.**

**Bonding Interaction**  
**Anti-Bonding Interaction**

\[ \psi_b = 1s_A + 1s_B \]

\[ \psi_a = 1s_A - 1s_B \]
Consider in each case the **INTERNUCLEAR REGION**

Probability of finding electron there is:

\[ \psi_b > 1s_A, 1s_B > \psi_a \]

Electron in this region attracted to BOTH nuclei, therefore most favourable position. Hence, electron in \( \psi_b \) will be at lower energy than in non-interacting a.o.'s, and electron in \( \psi_a \) will be at higher energy still.

Thus an electron in \( \psi_b \) will hold the nuclei together, one in \( \psi_a \) will push them apart.

\( \psi_b \) is a BONDING m.o.,
\( \psi_a \) is an ANTI-BONDING m.o.
Thus we can draw **ENERGY LEVEL DIAGRAM** for m.o.'s of \( H_2 \) :

By aufbau & Pauli principles - the 2 electrons go into \( \psi_b \) - with paired spins.
MO’s for $\text{H}_2$ molecule

http://www.chemtube3d.com/orbitalsCO.htm
M.O.'s for homonuclear diatomics ($A_2$) for elements of first row of the Periodic Table

For Li$_2$, Be$_2$, B$_2$ etc., more complex than for H$_2$, HHe - more available a.o.'s - 1s, 2s, 2p. Are there restrictions on overlap?

(1) **VALENCE** electrons only - core electrons too close to nucleus, too tightly bound

(2) Most efficient overlap between orbitals of same energy, i.e. for homonuclear diatomics this means 2s/2s, 2p/2p (for heteronuclear diatomics - see later)

(3) **SYMMETRY RESTRICTIONS**

These are best shown pictorially

Let us see how this works for 2s and 2p orbitals.
**BOND ORDER**

By Lewis/V.B. theory - one pair of electrons = one bond.
To be consistent, in M.O. theory, define BOND ORDER as follows:

Bond order = \[
\frac{\text{(No. of electrons in bonding m.o.'s)} - \text{(No. of electrons in antibonding m.o.'s)}}{2}\]

Thus, for H\(_2\), bond order = \(\frac{2 - 0}{2} = 1\)  (i.e. a single bond - as expected)

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**Magnetic Properties of Molecules**

All electrons paired - repelled by magnetic field - **DIAMAGNETIC**

One or more unpaired electrons - attracted into magnetic field - **PARAMAGNETIC**

H\(_2\) is diamagnetic.
M.O. Energy Level Diagram for $A_2$ ($A = \text{Li, Be}$)

Remember: $1s$ orbitals effectively non-bonding.

Use Aufbau, Pauli, Hund - just as in filling atomic orbitals

**Li$_2$**

Only two valence electrons, i.e. $\sigma_s^2 \sigma_s^* 0$. Bond order = 1. Diamagnetic

Li$_2$ exists in gas phase over metallic lithium.

"Be$_2"$\n
$\sigma_s^2 \sigma_s^* 2$

Bond order = 0 - no net bonding energy, so molecule does not exist.

Beryllium in gas phase is monatomic.
For p orbitals - three per atom. Define z-axis as molecular axis. Hence $p_z$ orbitals can overlap in same way as s orbitals.

$p_z/p_z$ overlap everywhere positive $\rightarrow$ BONDING M.O.

$\Psi_b = p_z + p_z$
End-to-end overlap forms $\sigma 2p_z$ MO

$\Psi_a = p_z - p_z$
End-to-end overlap forms $\sigma^* 2p_z$ MO

$p_z - p_z$ overlap everywhere negative $\rightarrow$ ANTI-BONDING M.O.
$p_x$, $p_y$ orbitals are perpendicular to axis, but can still interact

$p_x/p_x$ or $p_y/p_y$

$p_x + p_x$ overlap everywhere positive $\rightarrow$ BONDING M.O.

**Bonding Interaction**

$\psi_b = p_x + p_x \text{ or } \psi_b = p_y + p_y$

Side-to-side overlap forms $\Pi 2p_x \text{ or } 2p_y$ MO
\[ \psi_a = p_x - p_x \quad \text{or} \quad \psi_b = p_y - p_y \]

Side-to-side overlap forms \( \Pi^*2p_x \) or \( y \) MO.

Need to consider all possibilities (could be needed for heteronuclear diatomics)

**Anti-Bonding Interaction**
\[ \rho_x / \rho_x \text{ or } \rho_y / \rho_y \]

**Bonding Interaction**

\[ \psi_b = \rho_x + \rho_x \text{ or } \psi_b = \rho_y + \rho_y \]

Side-to-side overlap forms \( \Pi 2 \rho_x \text{ or } \Pi y \text{ MO} \)

**Anti-Bonding Interaction**

\[ \psi_a = \rho_x - \rho_x \text{ or } \psi_b = \rho_y - \rho_y \]

Side-to-side overlap forms \( \Pi^* 2 \rho_x \text{ or } \Pi^* y \text{ MO} \)
m.o.'s derived from 2p a.o.'s:

1. \( \rho_x, \rho_y \) alike in all respects except orientation, so m.o.'s derived from them must be degenerate.

2. Sideways (\( \pi \)) overlap is less efficient than end-on (\( \sigma \)), so \( \pi \) m.o.'s less bonding than \( \sigma \)
Electronic configuration: \( \sigma_s^2 \sigma^*_s^2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi^*_x^1 \pi^*_y^1 \)

Note Hund's rule again! Bond order = \( \frac{8 - 4}{2} = 2 \) (double bond) and PARAMAGNETIC.

V.B. theory could not explain paramagnetism.

M.O. Energy Level Diagram for \( A_2 \) (\( A = O \))

"No mixing of 2s and 2p"
Homonuclear Diatomics

No mixing vs. mixing of sigma orbitals
Derived from 2s and 2p$_z$
HETERONUCLEAR DIATOMIC MOLECULES

Simplest would be HHe. Differs from H₂ in two ways:
(1) A.O. energies for H, He different. He - greater nuclear charge, electrons more tightly bound.
(2) Now three electrons to feed into m.o.'s.

Energy level diagram is now:

For heteronuclear diatomics, m.o.'s formed symmetrically above and below AVERAGE energy of constituent a.o.'s
For HHe, bond order = (2 - 1)/2 = 1/2 i.e. v. wk. "1/2" bond - not formed under normal conditions - v. unstable.

Unpaired electron, PARAMAGNETIC.

Note for "He₂" - extra electron in antibonding m.o. - therefore bond order = 0. Molecule does not exist - no force to hold atoms together. He is monatomic gas.
s/pz gives bonding and anti-bonding pair.

\[ \sigma_{sp_z} \]

\[ \sigma^*_{sp_z} \]

s/pₓ or pᵧ and pₓ/pₓ or pᵧ all non-bonding (positive and negative overlaps cancel. No overlap at all for pₓ/pᵧ.

Before moving on to show the energy level diagram for A₂ molecules - we need to be clear about the labels for m.o.’s
Two types of m.o. - in terms of symmetry to rotation about molecular axis.

s/s, p_z/p_z, s/p_z - completely symmetrical to such rotation.
All such given Greek symbol : $\sigma$ ("sigma")

p_x/p_x, p_y/p_y - change sign every 180° rotation - these are
given symbol : $\pi$ ("pi")

Note - same symbols as for valence bonds (above)

Bonding and antibonding orbitals of each type -
differentiated by asterisk ("star") on the antibonding ones.

What is the m.o. energy level for these A_2 molecules?
Remember: 1s orbitals effectively non-bonding,

Use Aufbau, Pauli, Hund - just as in filling atomic orbitals

\[ \text{Li}_2 \]

Only two valence electrons, i.e. \( \sigma_s^2 \sigma_s^* \). Bond order = 1. Diamagnetic

\[ \text{Li}_2 \text{ exists in gas phase over metallic lithium.} \]

\[ \text{"Be}_2" \]

\( \sigma_s^2 \sigma_s^* \)  

Bond order = 0 - no net bonding energy, so molecule does not exist.

Beryllium in gas phase is monatomic.
Homonuclear Diatomics
No mixing vs. mixing of sigma orbitals
Derived from 2s and 2p_z

(a) No mixing
(b) Mixing of \( \sigma_g \) orbitals

\[
\begin{align*}
\sigma_u^* & \quad \pi_g^* \quad \pi_g^* \\
\pi_u & \quad \pi_u \\
\sigma_g & \\
\end{align*}
\]
$O_2$ is paramagnetic
O₂ is only one of a series of diatomic oxygen species:

- \( \text{O}_2^+ \) - "oxidation of oxygen" in \( \text{O}_2^+\text{PtF}_6^- \);
- \( \text{O}_2 \) - normal form of oxygen
- \( \text{O}_2^- \) - superoxide ion, e.g. \( \text{K}^+\text{O}_2^- \);
- \( \text{O}_2^{2-} \) - peroxide ion, e.g. \( \text{Na}_2^{2+}\text{O}_2^{2-} \)

Electron configurations:

\[
\text{O}_2^+ \quad \sigma^2 \sigma^*^2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi^*_{px}^1 \pi^*_{py}^0
\]

- electron lost from anti-bonding m.o. - stronger bond than O₂. Bond order = 2.5
- Paramagnetic - but less so than O₂ - only one unpaired electron.

\[
\text{O}_2^- \quad \sigma^2 \sigma^*^2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi^*_{px}^2 \pi^*_{py}^1
\]

- electron gained in anti-bonding m.o. - weaker bond than O₂. Bond order = 1.5
- Paramagnetic (one unpaired electron).
Superoxide Dismutase (SOD)

\[ \text{O}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \]
\( \text{O}_2^{2-} \quad \sigma_s^2 \sigma_s^* 2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi_{px}^* \pi_{py}^* \)

Bond order = 1.  Diamagnetic

Note bond lengths

\( \text{O}_2^{+} - 112 \text{ pm} \)
\( \text{O}_2 - 120 \text{ pm} \)
\( \text{O}_2^- - 126 \text{ pm} \)
\( \text{O}_2^{2-} - 149 \text{ pm} \)

Weaker bonds, therefore longer bonds

Electronic configuration:

\[ \sigma_s^2 \sigma_s^* 2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi_{px}^* \pi_{py}^* \]

F₂

Isoelectronic with \( \text{O}_2^{2-} \)

Bond order = 1.  Diamagnetic

"Ne₂"

\[ \sigma_s^2 \sigma_s^* 2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi_{px}^* \pi_{py}^* \sigma_{pz}^* \]

Bond order = 0

Therefore does not exist.  Neon is a monatomic gas
## TABLE 9.5  Bond Energies (in kJ/mol)*

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>432</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>411</td>
<td>346</td>
<td></td>
<td>167</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>386</td>
<td>305</td>
<td>167</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>459</td>
<td>358</td>
<td>201</td>
<td>142</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>363</td>
<td>272</td>
<td>—</td>
<td>—</td>
<td>226</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>565</td>
<td>485</td>
<td>283</td>
<td>190</td>
<td>284</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>428</td>
<td>327</td>
<td>313</td>
<td>218</td>
<td>255</td>
<td>249</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>362</td>
<td>285</td>
<td>—</td>
<td>201</td>
<td>217</td>
<td>249</td>
<td>216</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>295</td>
<td>213</td>
<td>—</td>
<td>201</td>
<td>—</td>
<td>278</td>
<td>208</td>
<td>175</td>
<td>149</td>
</tr>
</tbody>
</table>

### Single Bonds

### Multiple Bonds

<table>
<thead>
<tr>
<th></th>
<th>C≡C</th>
<th>C≡N</th>
<th>C≡O</th>
<th>C≡C</th>
<th>C≡N</th>
<th>C≡O</th>
<th>S≡O (in SO₂)</th>
<th>S≡O (in SO₃)</th>
<th>O≡O</th>
<th>H₂O (in H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>602</td>
<td>615</td>
<td>745</td>
<td>799</td>
<td>835</td>
<td>887</td>
<td>1072</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>835</td>
<td>887</td>
<td>1072</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S≡O (in SO₂)</td>
<td>532</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S≡O (in SO₃)</td>
<td>469</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O≡O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O (in H₂O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Bond Dissociation Energies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>498.36</td>
</tr>
<tr>
<td>Cl -O</td>
<td>267.47</td>
</tr>
<tr>
<td>N-O</td>
<td>631.32</td>
</tr>
<tr>
<td>Br -O</td>
<td>235.4</td>
</tr>
<tr>
<td>C-O</td>
<td>1076.38</td>
</tr>
<tr>
<td>I -O</td>
<td>240</td>
</tr>
<tr>
<td>S-O</td>
<td>517.90</td>
</tr>
<tr>
<td>P-O</td>
<td>598</td>
</tr>
<tr>
<td>Si-O</td>
<td>799.6</td>
</tr>
</tbody>
</table>

Source: [CRC Handbook of Chemistry and Physics](https://www.crcpress.com/product/isbn/9781420036393)  
What about B, C and N??

Energy difference between s and p orbitals is not so great as in O and F. Therefore there is significant interaction of sigma molecular orbitals Derived from 2s and 2p.

<table>
<thead>
<tr>
<th></th>
<th>Valence State Ionization Energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2s</td>
</tr>
<tr>
<td>B</td>
<td>14.0</td>
</tr>
<tr>
<td>C</td>
<td>19.4</td>
</tr>
<tr>
<td>N</td>
<td>25.6</td>
</tr>
<tr>
<td>O</td>
<td>32.3</td>
</tr>
<tr>
<td>F</td>
<td>40.2</td>
</tr>
</tbody>
</table>

This leads to a different ordering of the mo ‘s. The so-called “s-p mixing”. It’s not difficult – look it up in an advanced book, if you are interested
What about B, C and N??

This is of major importance:

\[ \sigma_s^2 \sigma_s^* \pi_{px}^2 \pi_{py}^2 \sigma_{pz}^2 \]

Bond order = \((8 - 2)/2 = 3\)
i.e. triple bond, very strong, stable molecule.
Diamagnetic.
(Note the different order of s/p orbitals)

N₂

B₂ and C₂

C₂ is important in flames and comets, interstellar space
Light Emission from Comets

- Light from the Sun is absorbed by cometary molecules
- The absorbed energy is re-emitted at specific wavelengths (colours)
- The light is detected with a spectrometer on a large telescope
Heteronuclear Diatomic Molecules (AB) Involving First Row Elements

Remember two basic principles:

(1) A.o. energies decrease as nuclear charge increases.

(2) Bonding/antibonding m.o.'s formed symmetrically below/above average of a.o. energies, respectively.

M.o. energy level diagram based on that for $A_2$: 
Molecular Orbital Energy Level Diagram for a Heteronuclear Diatomic

e.g. for CO - similar to N₂
- but with different a.o. energies for C and O, i.e. O > C.

Electronic configuration:
\[ \sigma_s^2 \sigma^*_s^2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \]

Bond order = \((8 - 2)/2 = 3\)

Just like N₂ : ISOELECTRONIC (i.e. same no. of electrons).
DIAMAGNETIC.
A different type of heteronuclear diatomic:

\[
\begin{align*}
\text{HF} & : \quad \text{H} 1s^1 \quad \text{F} 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1 \\
\end{align*}
\]

Overlap between H1s and F2p_z giving:

- \( \sigma_{sp_z} \) (bonding)
- \( \sigma^*_{sp_z} \) (anti-bonding)

H 1s \quad \text{node} \quad \text{F} 2s \quad \text{non-bonding electrons on F}
Electronic configuration:
\[ \text{[F}_2\text{s}^2\text{p}^4]\sigma_{\text{sp}}^2\sigma^*_{\text{sp}}^0 \]

Diamagnetic. Bond order = 1

F2s non-bonding - too low in energy

F2p_x,2p_y non-bonding because of wrong symmetry
In the vast majority of cases, bonds can be described as **LOCALISED** between pairs of nuclei - therefore can use VB approach.

At this stage we only need to use molecular orbitals (m.o’s) when **DELOCALISATION** of electrons occurs - i.e. when several Lewis structures have to be drawn.

Even in these cases we can use the **VB approach for the σ-framework**, and construct m.o.’s only for the **π-bonds**.

Just look at **TWO examples** - one inorganic (CO$_3^{2-}$), one organic (benzene, C$_6$H$_6$).
**Carbonate ion, CO$_{3}^{2-}$**

Regular trigonal planar, equal bonds, all angles $120^0$.

**$\sigma$-framework:** use sp$^2$ hybrids on both C and O's.

2 electrons in each bond + lone pairs in remaining sp$^2$
hybrids on O's = 18 electrons

Total number of valence electrons = 4 (C) + 18 (3 O's) + 2 (negative charges) = 24

Therefore have 6 electrons to put into $\pi$-type orbitals

Which orbitals are available for $\pi$-bonding?

On each atom, sp$^2$ hybrid formation uses $p_x$ and $p_y$
orbitals. Therefore one $p_z$ orbital on each atom is
available for $\pi$-bonding - 4 orbitals in total.
Remember general rule: n a.o.'s \rightarrow n m.o.'s

Therefore we will form 4 m.o.'s

Details of how to calculate what these look like left until later.
By analogy with diatomic m.o.'s - most strongly bonding m.o. will be the one which increases electron density in all of the bonds:

The most antibonding m.o. will have NODES on all of the bonds:
The remaining two turn out to be non-bonding, giving the energy level for the $\pi$-bonding in $\text{CO}_3^{2-}$ as follows:

![Diagram of molecular orbitals for CO3^2-]

- The 6 electrons just fill the bonding and non-bonding m.o.'s.
- One $\pi$-bond shared out equally in a delocalised m.o.
- Each bond therefore $1\sigma + 1/3\pi$
- All electrons paired - therefore DIAMAGNETIC
Benzene, $\text{C}_6\text{H}_6$

Remember that there are two equivalent Lewis structures for benzene:

Simplified drawing - CH at each corner.

Benzene is in fact a regular hexagon - all C-C bonds equal, and with a length intermediate between C-C and C=C.

$\sigma$-framework - sp$^2$ hybridisation at each C, forming a $\sigma$-bond to H and two adjacent C atoms

$\pi$-bonding - a $p_z$ orbital on each C, i.e. 6 a.o.’s, therefore 6 m.o.’s will be formed.

A.o.’s for $\pi$-bonding:
sigma bonds in Benzene
Pi-bonds $C_6H_6$
By analogy with carbonate - most strongly bonding m.o. formed by adding all of these a.o.’s together (incr. electron density in each bond).

Also by analogy with carbonate - most strongly antibonding m.o. formed by combining all of these a.o.’s together to give NODES between each pair of C atoms.

In addition, the remaining 4 m.o.’s will comprise two **WEAKLY BONDING** and two **WEAKLY ANTIBONDING** combinations.

Thus we have a \( \pi \)-bonding m.o. energy level for benzene:

```
  strongly antibonding
     \_\_
   \_\_
     \_\_

6 p\text{z} a.o.'s

strongly bonding
     \_\_
   \_\_
     \_\_

weakly antibonding

weakly bonding
     \_\_
   \_\_
     \_\_

strongly bonding
```
Pi-bonds C$_6$H$_6$
There are 6 electrons (one per C atom) - and these fill the strongly and weakly antibonding m.o.’s. These orbitals are DELOCALISED, and explain the observed properties of benzene. Note stability as all bonding m.o.’s are full, and all electrons paired.

Note - there is a simple pictorial method for obtaining the relative energies of the $\pi$-m.o.’s of benzene and any other cyclic $C_nH_n$ compound. Draw a circle round the shape of the molecule with one corner at the lowest part of the circle - and the corners just touching the circle. This gives the m.o. energies!
Any molecule where $\pi$-electrons are *delocalised* is said to show **CONJUGATION** - and the properties of such molecules are different from those with localised multiple bonds - lots of examples in Organic Chemistry.

In particular, cyclic compounds like benzene (with a **FULL SHELL** of $\pi$-m.o’s) are described as being **AROMATIC**. Aromaticity confers specific properties on such compounds. In particular they are more stable (**lower energy**) than would have been predicted on the basis of localised double bond formation.
**Carbon Monoxide**

VSIE

\[ O_{2s} = 32.3 \text{ eV} \]
\[ O_{2p} = 15.8 \text{ eV} \]

\[ C_{2s} = 19.4 \text{ eV} \]
\[ C_{2pz} = 10.6 \text{ eV} \]
Carbon Monoxide

**Consequence:**

CO binds to metals, such as iron, through its Carbon rather than O. Can produce dative bond by donating Electron density from 3 s to empty orbital On metal, and will accept electron density From the metal via π-backbonding.