Anderson Serangoon Junior College
H3 Chemistry
Basic Principles Of Spectroscopy Tutorial

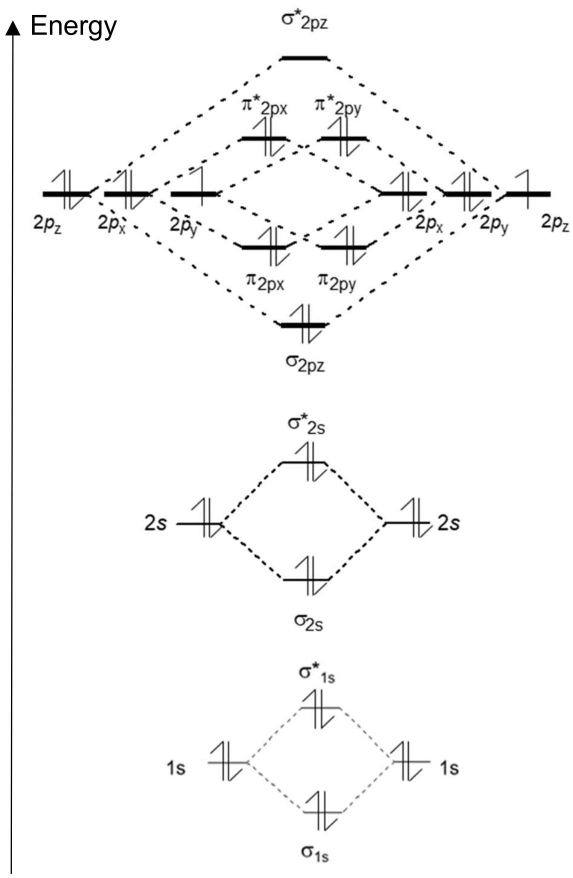
1 When electrons are being removed from or gained by molecular oxygen, the following species could form: peroxide O_2^{2-}, superoxide O_2^{-} and dioxygenyl ion O_2^{+}.

Draw an MO diagram for each and rank them in order of increasing bond length, and find the number of unpaired electrons in each.

MO diagram for O_2^{2-}

O: $1s^2 2s^2 2p^4$
O_2 has 16 electrons

Therefore, O_2^{2-} has 18 electrons (9 electrons for each atomic orbital)

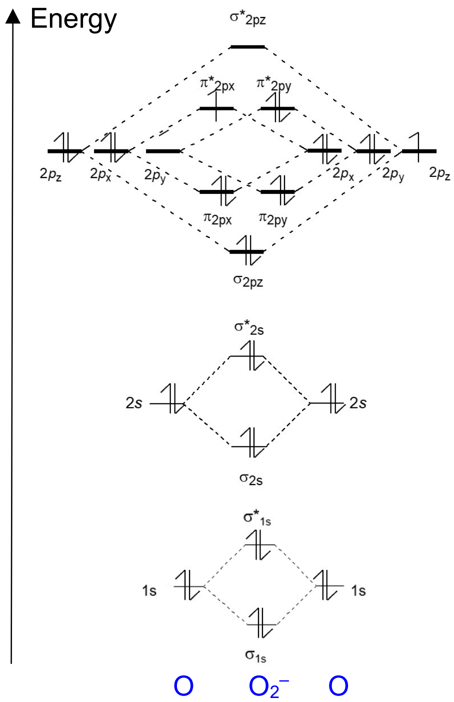


O O_2^{2-} O

With reference to the O_2^{2-} MO diagram,
Bond order of O_2^{2-} = ½(10 – 8)
= 1 (*lowest bond order*), <u>0 unpaired electrons</u>

Note: the electrons in the MO diagram can also be written just above the line.

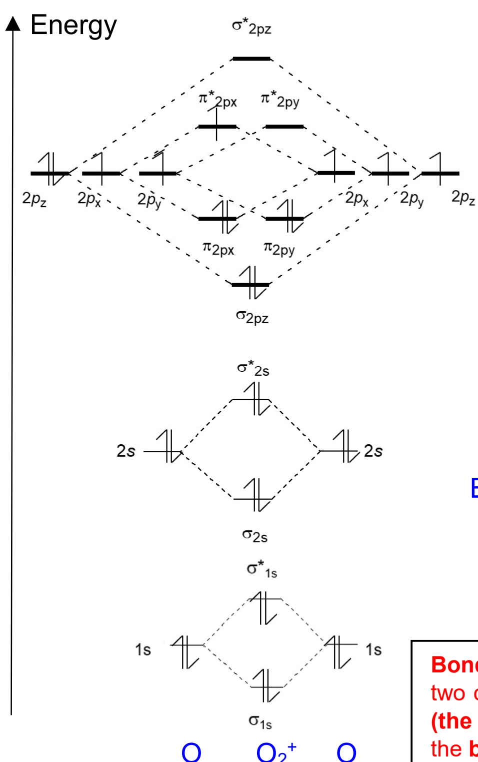
MO diagram for O_2^- O_2^- has 17 electrons (one O AO has 8 electrons, the other has 9)



Bond order of O_2^- = ½ (10 – 7)

= 1.5, 1 unpaired electron

MO diagram for O_2^+ O_2^+ has 15 electrons (one O AO has 8 electrons, the other has 7)



Bond order of O_2^+ = ½ (10 – 5)

= 2.5 (*highest bond order*),
1 unpaired electron

Bond length is defined as the **distance** between the centers of two covalently bonded atoms. The **number of bonded electrons (the bond order) determines the length of the bond**. The higher the **bond order**, the stronger the pull between the two atoms and the shorter the **bond length**

∴ rank in increasing bond length would be $O_2^+ < O_2^- < O_2^{2-}$.

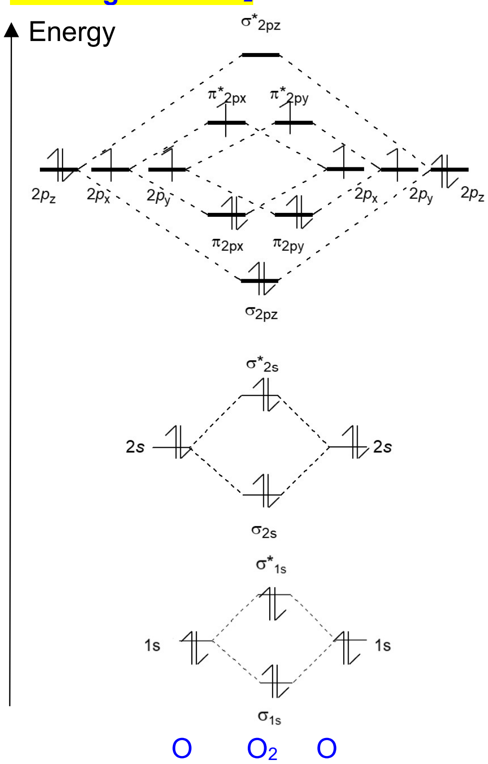
2 The bond strength in the oxygen molecule, 496 kJ mol^{-1}, is similar to that of the N=N in diazo compounds, 410 kJ mol^{-1}. Its bonding is therefore often represented by structure **I**.

However, the oxygen molecule is paramagnetic, showing that it contains unpaired electrons. This can be represented by the alternative structure **II**. This would predict that it contains a O–O single bond, similar in strength to the O–O bond in hydrogen peroxide, H_2O_2, 150 kJ mol^{-1}.

O=O	·O–O·
I	**II**

Draw a molecular orbital diagram for the O_2 molecule and use it to explain why it contains unpaired electrons but has a bond order of 2.

MO diagram for O_2

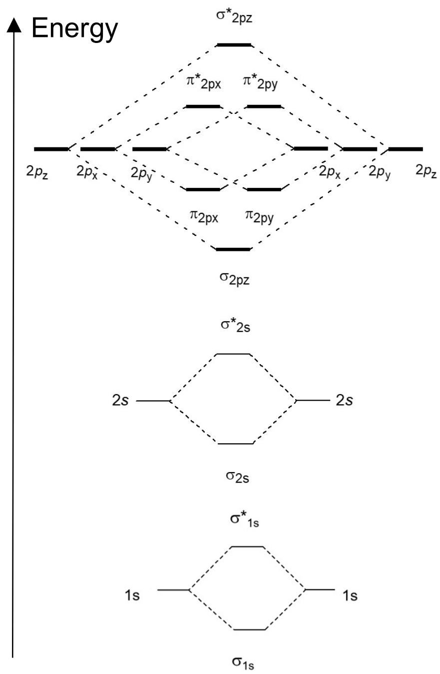


As the two π^*_{2p} orbitals are degenerate, the <u>last two electrons occupy them singly</u>, resulting in <u>2 unpaired electrons</u>.

Bond order = ½ (10 – 6)
= <u>2</u>

3 Molecular Orbital (MO) Theory was introduced by Mulliken in the 1940's and 1950's for which he won the 1964 Nobel Prize in Chemistry. It allows for the prediction of bond orders and paramagnetism of simple molecules.

(a) Give a relative energy diagram for the MO's of diatomic molecules which possess only 1s, 2s and 2p electrons.



(b) Give the MO configurations and bond orders of H_2, H_2^-, He_2 and He_2^-.

Species	MO configuration	(or) MO configuration	bond order
H_2	σ_{1s}^2	$1\sigma^2$	1
H_2^-	$(\sigma_{1s})^2\,(\sigma^*_{1s})^1$	$1\sigma^2\,1\sigma^{*1}$	0.5
He_2	$(\sigma_{1s})^2\,(\sigma^*_{1s})^2$	$1\sigma^2\,1\sigma^{*2}$	0
He_2^-	$(\sigma_{1s})^2\,(\sigma^*_{1s})^2\,(\sigma_{2s})^1$	$1\sigma^2\,1\sigma^{*2}\,2\sigma^1$	0.5

Note: the MO configurations can be written either way.

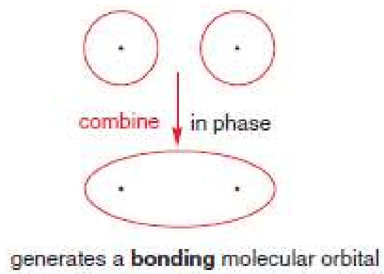
(c) Which species in **(b)** are expected to have the same stability?

H_2^- and He_2^- are expected to have the same stability.

4 Consider a homonuclear diatomic molecule in which the 2s and $2p_z$ atomic orbitals combine to give a set of four sigma–symmetric molecular orbitals.

(a) Draw the lowest energy combination of atomic orbitals (the combination that gives the fewest nodes) and the resulting molecular orbital. State the number of nodes.

When two 2s orbitals combine constructively head–on,



There is no nodal plane.

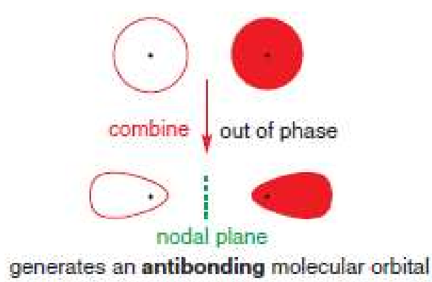
(b) Draw the highest energy combination of atomic orbitals (the combination that gives the most nodes) and the resulting molecular orbital. State the number of nodes.

When two $2p_z$ orbitals combine destructively head–on,

There is 1 nodal plane.

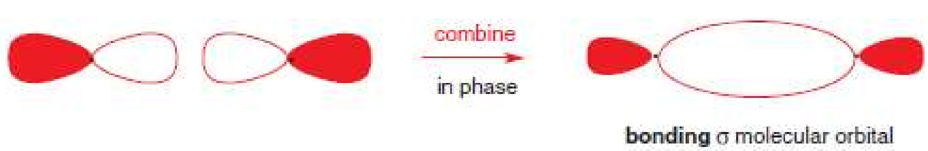
(c) Draw the remaining two molecular orbitals and state the number of nodes each molecular orbital has.

When two 2s orbitals combine destructively head–on,



There is 1 nodal plane.

When two $2p_z$ orbitals combine constructively head–on,



There is no nodal plane.

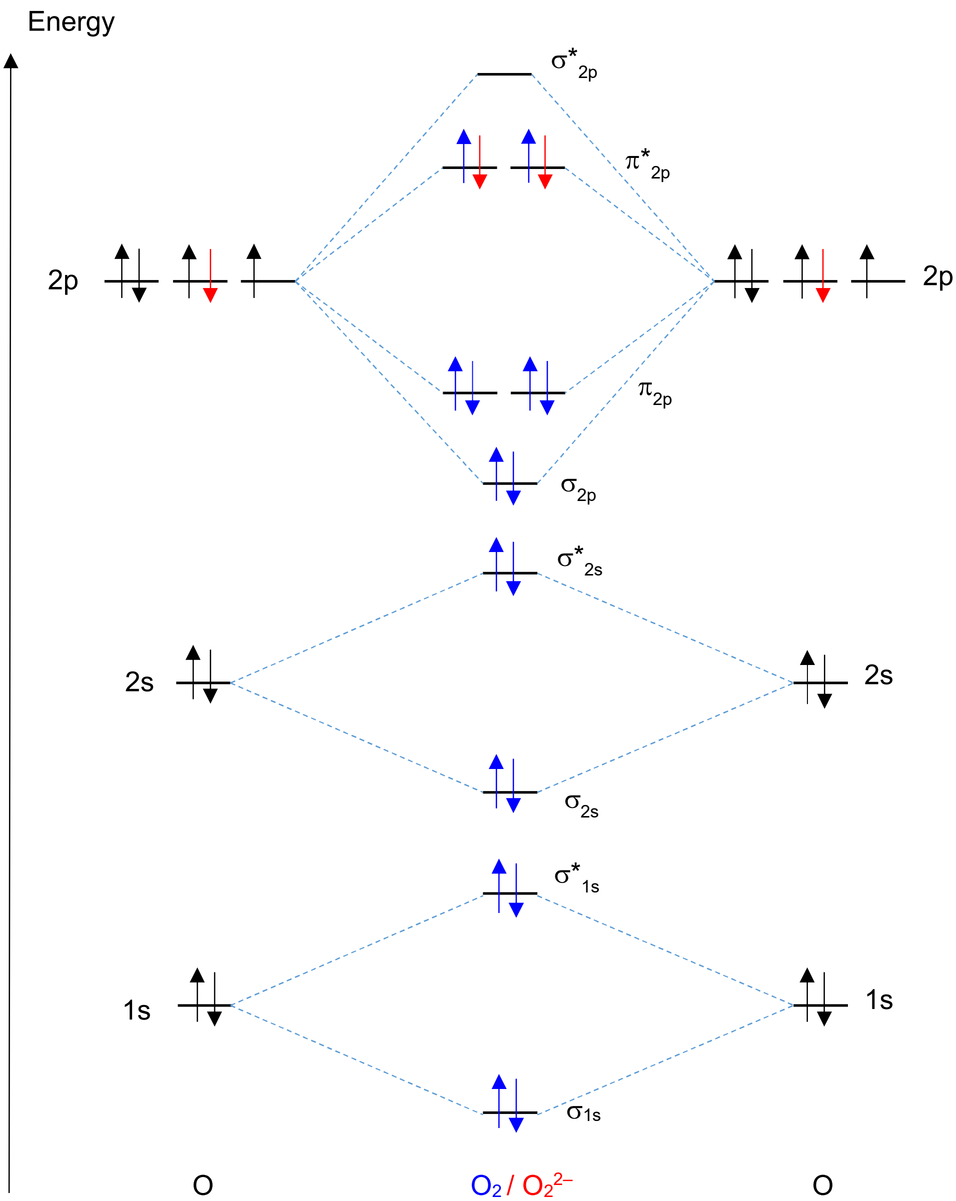
5 **(a)** **(i)** Draw and use molecular orbital diagrams to predict how the bond order will change during each of the following two processes. Hence in each case explain whether the neutral molecule **or** the anion will have the stronger bond.

$$O_2 + 2e^- \longrightarrow O_2^{2-}$$

$$C_2 + 2e^- \longrightarrow C_2^{2-}$$

[4]

MO diagram for O_2 and O_2^{2-} (suggest to draw both side-by-side)



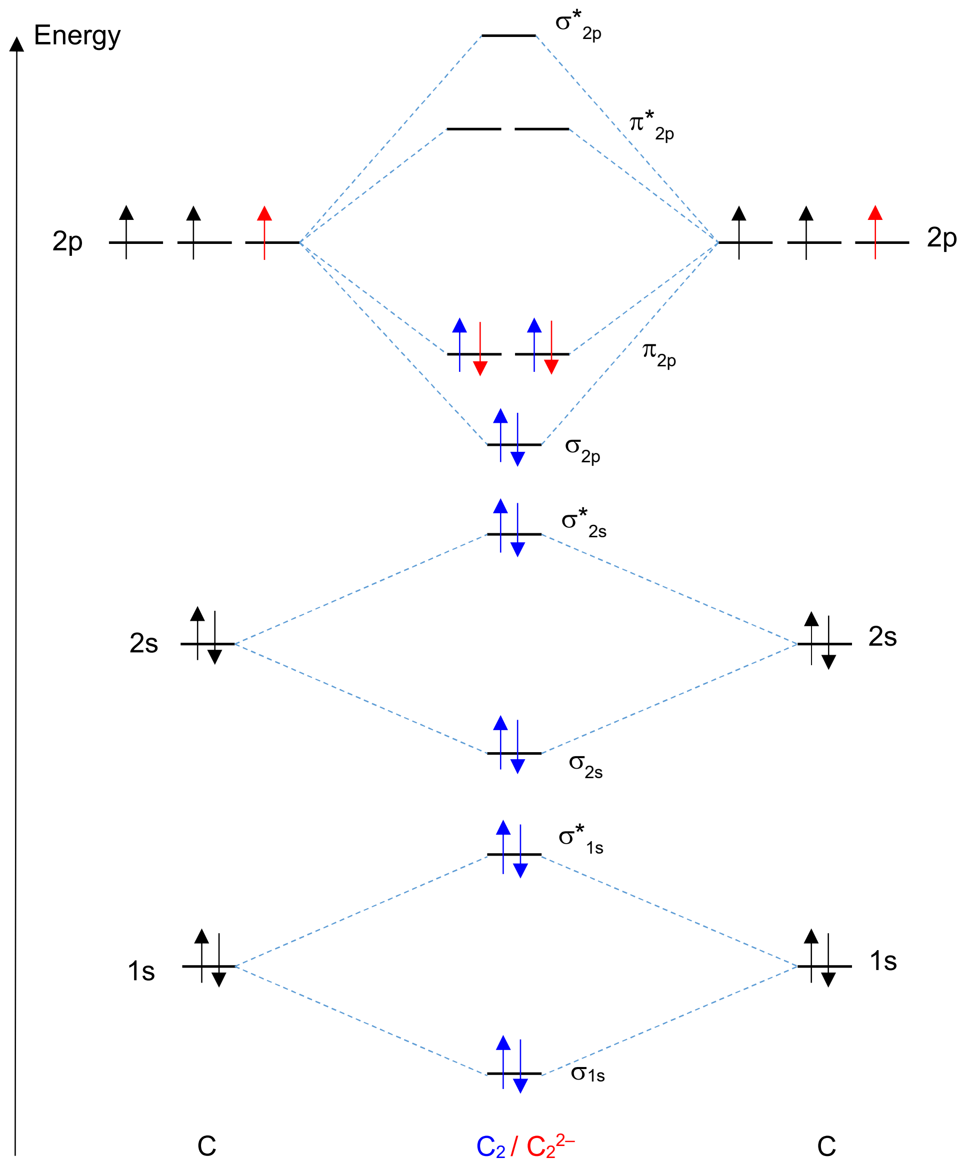
Bond order of O_2 = ½(10 – 6)
= 2

Bond order of O_2^{2-} = ½(10 – 8)
= 1

Bond order decreased from 2 to 1 when O_2 is reduced to O_2^{2-}.

Hence the neutral O_2 has stronger bond.

MO diagram for C_2 and C_2^{2-}



Bond order of C_2 = ½(8 – 4)
= 2

Bond order of C_2^{2-} = ½(10 – 4)
= 3

Bond order increased from 2 to 3 when C_2 is reduced to C_2^{2-}. Hence the anionic C_2^{2-} has stronger bond.

(ii) For each of these four species identify the HOMO by giving its symbol (σ, σ^*, π, π^*, *n*). [2]

Species	**HOMO**
O_2	π^*
O_2^{2-}	π^*
C_2	π
C_2^{2-}	π (σ if s–p mixing)

[N2019H3/3(a)]