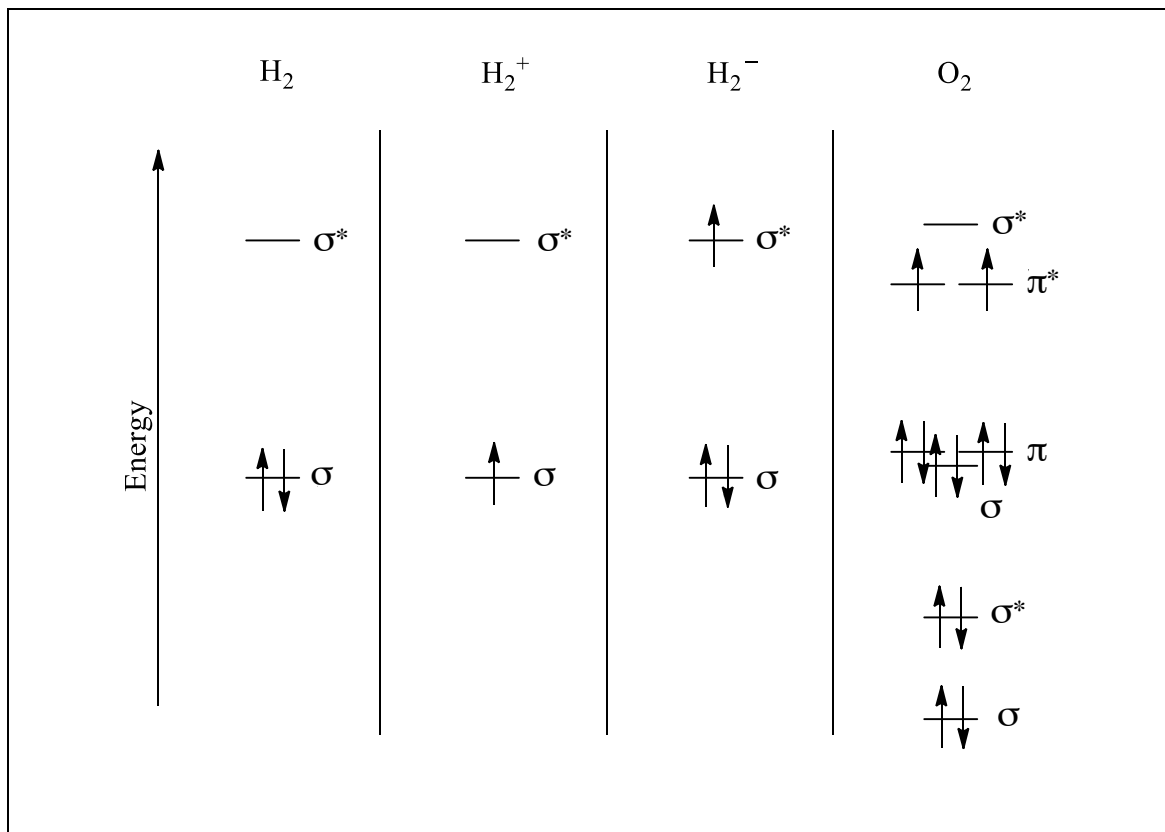- The molecular orbital energy level diagrams for $H_2$, $H_2^+$, $H_2^-$ and $O_2$ are shown below. Fill in the valence electrons for each species in its ground state and label the types of orbitals ($\sigma$, $\sigma^*$, $\pi$, $\pi^*$).



Give the bond order of each species.

| $H_2$: ½ (2 - 0) = 1 | $H_2^+$: ½ (1 - 0) = ½ | $H_2^-$: ½ (2 - 1) = ½ | $O_2$: ½ (8 - 4) = 2 |
|---|---|---|---|

Which of the four species are paramagnetic?

**$H_2^+$,  $H_2^-$ and  $O_2$**

The bond lengths of $H_2^+$ and $H_2^-$ are different. Which do you expect to be longer? Explain your answer.

**$H_2^-$ will be longer.  Both have bond order of 0.5, but $H_2^-$ is a multi-electron system so is destabilised by electron-electron repulsion.  $H_2^+$ is single electron system so has no electron-electron repulsion.**

**Marks
3**

- The molecular orbital energy level diagrams for $F_2$ and $B_2$ are shown below. Fill in the valence electrons for each species in its ground state. Hence calculate the bond order for $F_2$ and $B_2$ and indicate whether these molecules are paramagnetic or diamagnetic.



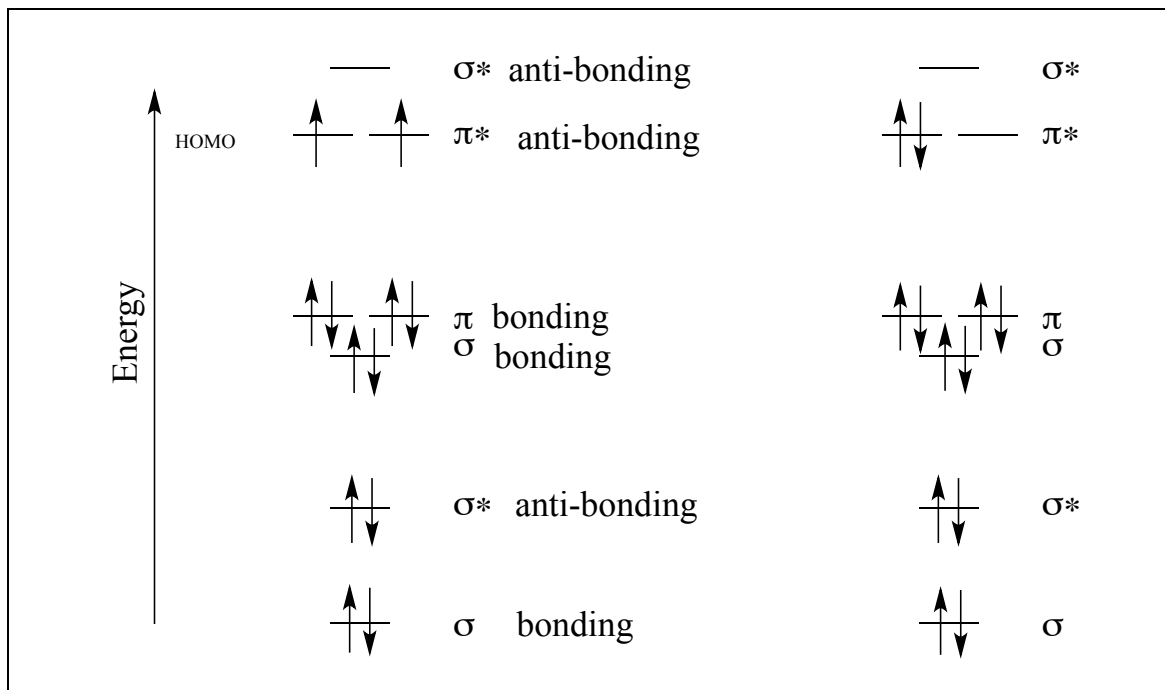| | $F_2$ | $B_2$ |
|---|---|---|
| Bond order | **½ (8 − 6) = 1** | **½ (4 − 2) = 1** |
| Paramagnetic or diamagnetic | **diamagnetic** | **paramagnetic** |

**Marks
8**

- Oxygen exists in the troposphere as a diatomic molecule.

  How many valence electrons in the $O_2$ molecule?    | **12** |

  The molecular orbital energy levels for $O_2$ are shown below. On the left-hand diagram, fill in the **valence** electrons for oxygen, $O_2$, in the ground state.

(a) What is the bond order for $O_2$?    | **½ (8 – 4) = 2** |

(b) Clearly label a bonding orbital and an anti-bonding orbital on the left-hand diagram.

(c) Clearly label the HOMO of $O_2$ on the left-hand diagram.

(d) On the right-hand diagram, indicate the lowest energy electronic configuration for $O_2$ which has no unpaired electrons.

The blue colour of liquid $O_2$ arises from an electronic transition whereby one 635 nm photon excites two molecules to the state indicated by the configuration in (d) *at the same time*. What wavelength photon would be emitted by one molecule returning from this state to the ground state?

**If one 635 nm photon excites two molecules, then half as much energy is will be emitted when one molecule returns to the ground state.**

**As $E = hc / \lambda$, if the energy is *halved*, the wavelength *doubles*: $\lambda$ = 1270 nm.**

Answer: **1270 nm**

Suggest a heteronuclear diatomic species, isoelectronic with $O_2$, that might be expected to have similar spectroscopic behaviour.    | **$NO^-$, NF** |

**Marks**
**8**

- The OH radical is the most important species in the atmosphere for removing pollutants. A molecular orbital diagram of this species is shown below. Core orbitals are omitted.
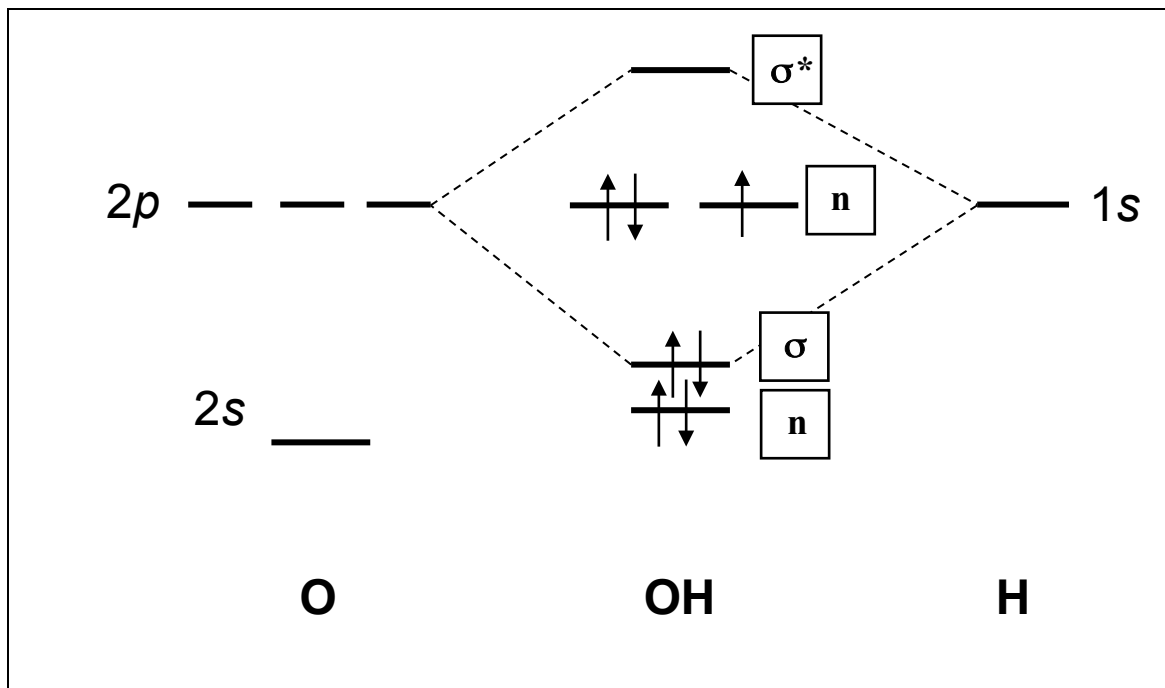


Using arrows to indicate electrons with their appropriate spin, indicate on the above diagram the ground state occupancy of the atomic orbitals of O and H, and of the molecular orbitals of OH.

In the provided boxes on the above diagram, label the molecular orbitals as *n, σ, σ*, π, π*,* etc.

What is the bond order of the O–H bond?

**There are 2 bonding and no anti-bonding electrons. The bond order is 1.**

Why do we call OH a "radical"? How does the MO diagram support this?

**It has an unpaired electron in a non-bonding orbital. This electron is found in the higher energy n orbital on the above MO diagram**

| | **Marks** |
|---|---|
| • The following diagram shows the molecular orbital energy level diagrams for the valence electrons in the homonuclear diatomic molecules $C_2$, $N_2$ and $O_2$. | **6** |

Complete the diagram by filling in the remaining *valence* electrons for each molecule and determining its bond order.
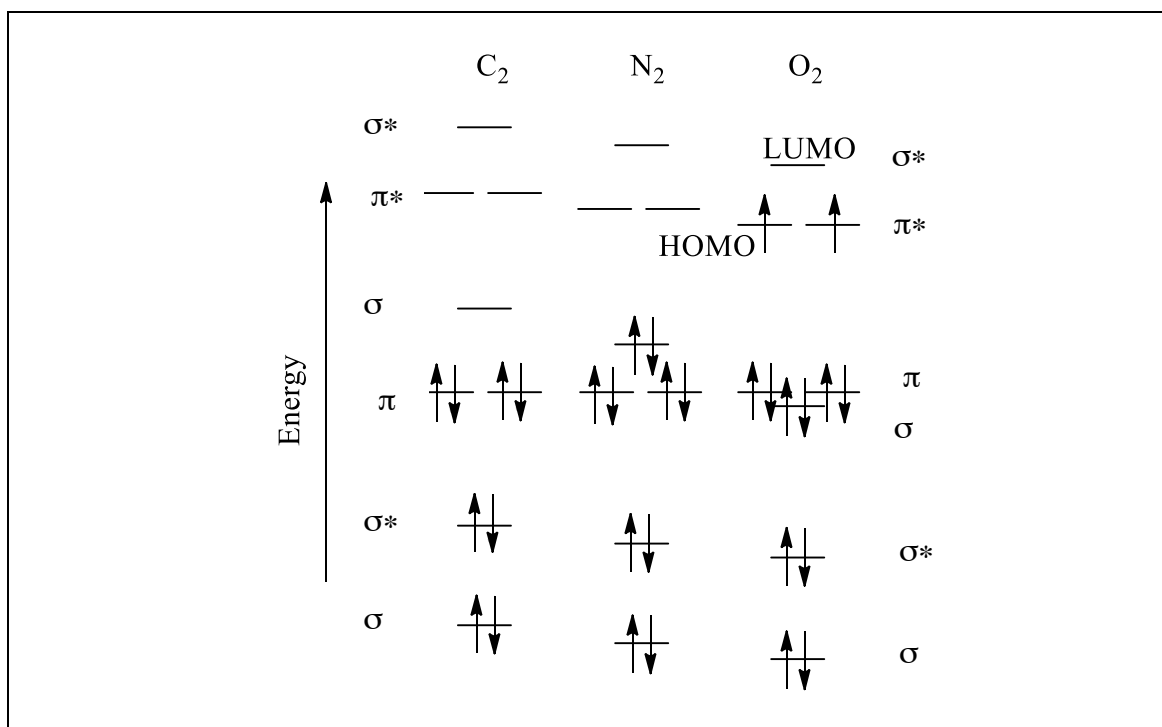


| Bond order: | 2 | 3 | 2 |
|---|---|---|---|

Explain why the energy of the lowest energy σ orbital shown above gets lower from left to right across the periodic table.
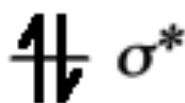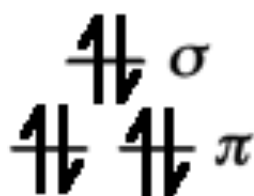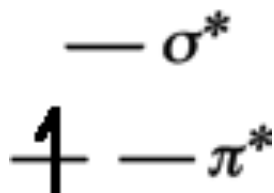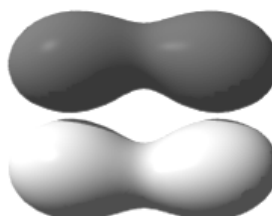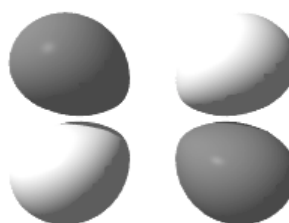
**The atomic number of the elements increase moving across a period, reflecting an increase in the number of protons. This results in an increasing effective nuclear charge which pulls the electrons closer to the nucleus and lowers the energy of their orbitals.**

Clearly label the HOMO and LUMO of $O_2$ on the diagram above.

| | **Marks** |
|---|---|
| f) The NO molecule formed in the reaction in part d) is also formed in its ground electronic state. Complete the molecular orbital diagram for NO by filling in the valence electrons in the occupied orbitals. Sketch the shape of the $\pi$ and $\pi^*$ orbitals, clearly showing all nodes. Determine the bond order of NO and whether it is paramagnetic or diamagnetic. | **6** |

| MO orbital energy level diagram for NO | Sketch of the $\pi$ MO |
|---|---|
| $— \sigma^*$ <br><br> $\stackrel{\uparrow}{} — \pi^*$ <br><br><br> $\stackrel{\uparrow\downarrow}{} \sigma$ <br> $\stackrel{\uparrow\downarrow}{} \stackrel{\uparrow\downarrow}{} \pi$ <br> $\stackrel{\uparrow\downarrow}{} \sigma^*$ <br><br> $\stackrel{\uparrow\downarrow}{} \sigma$ |  |
| | Sketch of the $\pi^*$ MO |
| |  |

| Bond order of NO: ½ **(8 – 3) = 2.5** |
|---|
| Paramagnetic or diamagnetic? **Paramagnetic (as it has 1 unpaired electron)** |

**Marks
6**

- In order to predict if it is possible to form the $He_2^+$ cation, complete the following steps.

  In the boxes below, draw an energy level diagram showing labelled electron orbitals and their occupancies for the two reacting species, He and $He^+$.

  In the other box below, draw an energy level diagram showing labelled electron orbitals and their occupancies in a postulated $He_2^+$ molecule. Use the same energy scale.
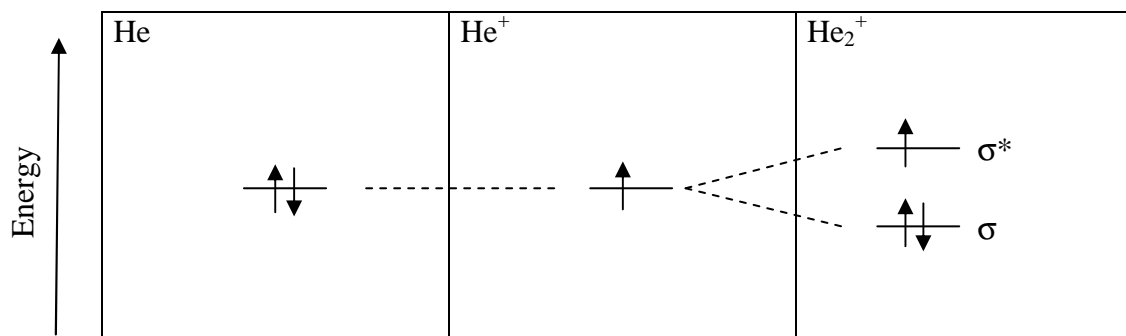


Draw the lobe representation of the two occupied molecular orbitals in this molecule. Show all nuclei and nodal surfaces.
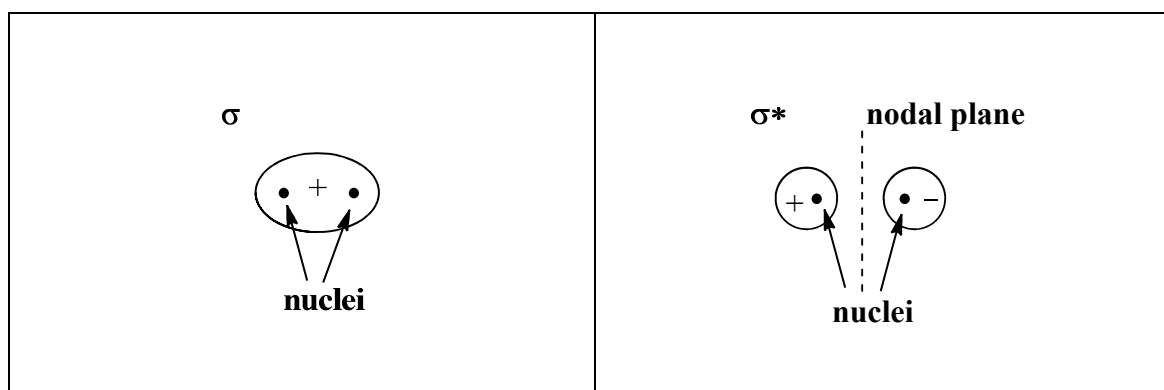


What is the bond order of this molecular ion?

**It has 2 bonding (σ) and 1 antibonding (σ\*) electron. Hence:**

> **bond order = ½ (number of bonding – number of antibonding electrons)
> = ½ (2 – 1) = ½**

Make a prediction about the stability of $He_2^+$ in comparison to the $H_2$ molecule.

**$H_2$ has a bond order of 1 and $He_2^+$ has a bond order of ½ so the bond in $H_2$ is probably stronger.**

**As the nuclear charge in He is larger than H, the bonding orbital is more stable in $He_2^+$ than the bonding orbital in $H_2$ so the ½ bond in $He_2^+$ is likely to be more than half as strong as the single bond in $H_2$.**

- The following diagram shows the energy level diagram for the molecular orbitals in the HF molecule (centre), in comparison to the atomic energy levels of hydrogen (left) and fluorine (right).
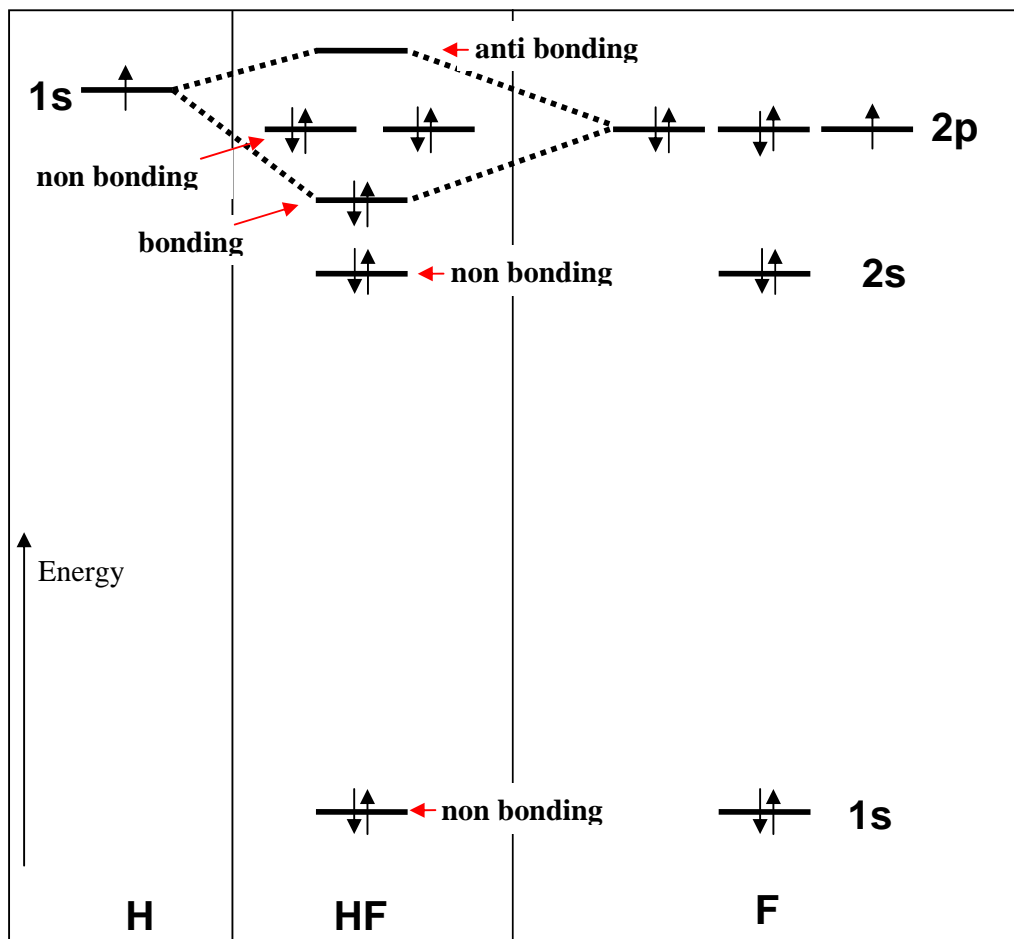


Add the ground state electron configuration to the diagrams for all three species using the arrow notation for electron spin.

Label the orbitals of HF according to whether they are bonding, non-bonding, or anti-bonding.

Sketch the σ-bonding orbital showing the position of the atomic nuclei.
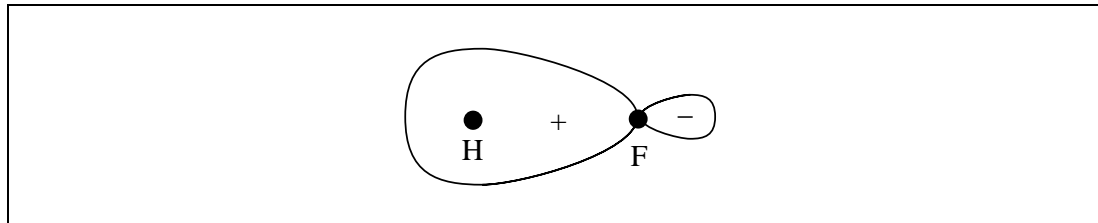
| | **Marks** |
|---|---|
| | **6** |

- Carbon forms a homonuclear diatomic molecule which is observed in comets, flames and interstellar clouds.

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the $C_2$ molecule. Indicate on this diagram the ground state electronic configuration of $C_2$ using the arrow notation for electron spins.
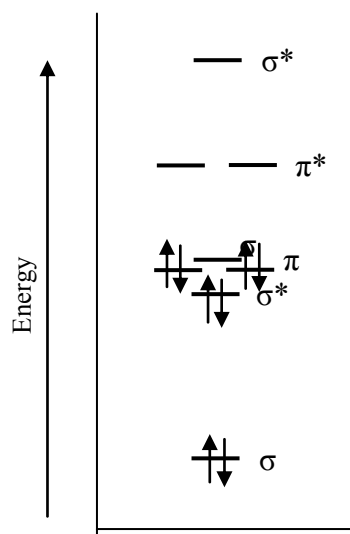


In its ground state, is $C_2$ paramagnetic or diamagnetic?

> **all electrons are paired: diamagnetic**

The lowest energy excited state of $C_2$ possesses two electrons with parallel, unpaired spins. What is the bond order of $C_2$ in this excited state?

**The lowest energy excited state corresponds to an electron being excited from $\pi$ to $\sigma$, leading to the configuration $\sigma^2 \sigma^{*2} \pi^3 \sigma^1$.**

**There are 6 bonding electrons ($1 \times \sigma + 3 \times \pi + 1 \times \sigma$) and 2 antibonding electrons ($2 \times \sigma^*$). The bond order is thus:**

**bond order = ½ (number of bonding e⁻ – number of antibonding e⁻)**
**= ½ (6 – 2) = 2**

> Answer: **2**

Starting in this excited state, further exciting an electron from the lowest $\sigma^*$ orbital to the next lowest $\sigma$ orbital brings about the doubly excited state responsible for green emission in flames. What is the bond order of this doubly excited state?

**This excitation leads to the configuration $\sigma^2 \sigma^{*1} \pi^3 \sigma^2$.**

**There are now 7 bonding electrons ($1 \times \sigma + 3 \times \pi + 2 \times \sigma$) and 1 antibonding electrons ($2 \times \sigma^*$). The bond order is thus:**

**bond order = ½ (7 – 1) = 2**

> Answer: **3**

**Marks
6**

- Carbon and nitrogen can combine to form a cyanide ion or a neutral free radical.

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the free radical CN. Indicate on this diagram the ground state electronic configuration of CN using the arrow notation for electron spins.

**\* C has 4 valence electrons and N has 5 valence electrons, giving a total of 9 electrons to place on the diagram. These occupy orbitals from the bottom upwards, with a maximum of 2 in each. The overall configuration is shown and corresponds to $(\sigma)^2(\sigma^*)^2(\pi)^4(\sigma)^1$**
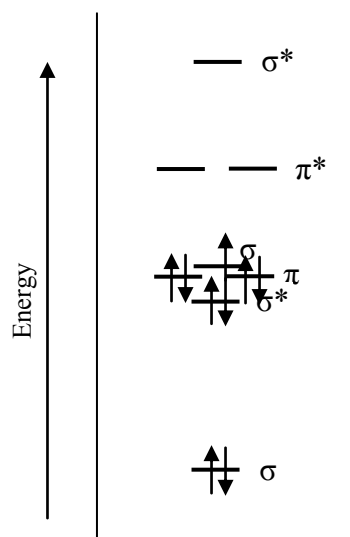


How would you expect the magnetic properties of CN to differ from that of CN⁻?

**CN has an unpaired electron. This makes it *paramagnetic* (it is attracted into a magnetic field).**

**CN⁻ has an extra electron. This pairs up with the electron in the highest occupied σ-orbital. As all the electrons are now paired, CN⁻ is *diamagnetic* (it is weakly repelled by a magnetic field).**

**CN is paramagnetic whereas CN⁻ is diamagnetic.**

How would adding an electron to CN to form CN⁻ affect the strength of the bond between the two atoms? Explain your answer.

**The extra electron in CN⁻ occupies a σ-orbital. This is a bonding orbital and so CN⁻ has more bonding electrons than CN and would be expected to have a stronger bond as a result.**

**Equivalently, bond order can be used to rationalize the bond strength:**

**bond order = ½ (number of bonding– number of antibonding electrons)**

**CN has 7 bonding and 2 antibonding electrons. CN⁻ has 8 bonding and 2 antibonding electrons. Hence,**

**bond order of CN = ½ (7 – 2) = 2.5**
**bond order of CN⁻ = ½ (8 – 2) = 3**

**CN⁻ has a higher bond order than CN and would therefore be expected to have a stronger bond.**

**ANSWER CONTINUES ON THE NEXT PAGE**

Why do we only need to consider the valence electrons when discussing the bonding of CN?

**The core electrons are tightly held onto by the atoms. There is little overlap between the core orbitals on the two atoms.**

**Even if the 1$s$ core electrons on each atom are considered, they would occupy *both* the bonding σ and antibonding σ* orbitals formed from their overlap. This would not change the bond order. Their contribution to the bonding is minimal.**

**Marks
6**

- Carbon and oxygen can combine to form carbon monoxide, the second most abundant molecule in the universe.

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in CO. Indicate on this diagram the ground state electronic configuration of CO using the arrow notation for electron spins.
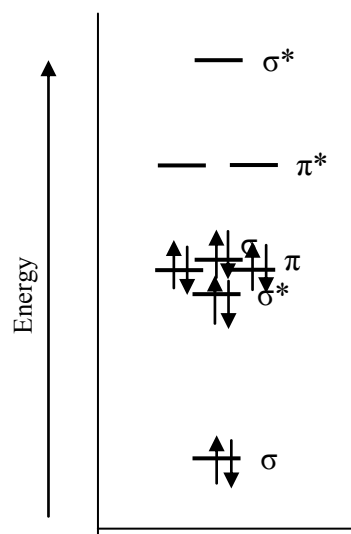


What homonuclear diatomic molecule has the same electronic structure as CO? Comment on the bond orders of these two species.

**$N_2$. This is has the same number of valence electrons – it is *isoelectronic*. N has 5 valence electrons so $N_2$ has $2 \times 5 = 10$ valence electrons. C has 4 and O has 6 valence electrons so CO has $4 + 6 = 10$ valence electrons. They both have a triple bond: i.e. they both a bond order of 3:**

**bond order = ½ (no. of bonding electrons – no. of antibonding electrons)
= ½ (8 - 2) = 3**

How would adding an electron to CO to form $CO^-$ affect the strength of the bond between the two atoms? Explain your answer.

**The extra electron would go into the $\pi^*$ antibonding orbital. The bond order would consequently drop from 3 to 2.5: bond order = ½ (8 - 3) = 2.5**

**Hence the bond would be weaker.**

Are the atomic orbital energies of oxygen lower or higher than carbon? Explain your answer and comment on how this may affect the electron density in bonding orbitals of the CO molecule.

**Oxygen is more electronegative: the energies of its orbitals are lower than those of carbon. This is because oxygen is the smaller atom with a higher nuclear charge. The bond would therefore be polarised with a greater amount of the shared electron density on the oxygen end of the bond.**

| | **Marks** |
|---|---|
| | **5** |

- The following relate to the electronic structure of the $N_2^-$ molecular ion.

How many valence electrons are in $N_2^-$?

$$5 \times 2 \ (\text{N}) + 1 \ (\text{charge}) = 11$$

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in $N_2^-$. Indicate on this diagram the ground state electronic configuration of $N_2^-$ using the arrow notation for electron spins.
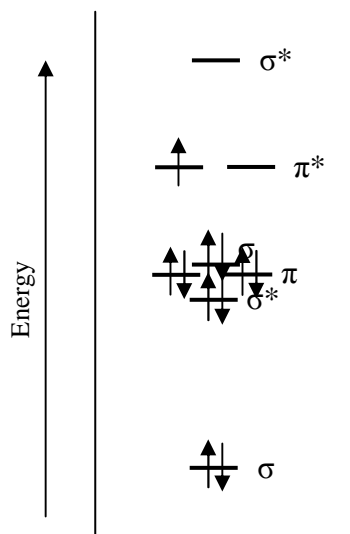


Calculate the bond order of $N_2^-$.

$$\text{½ (bond electrons – antibonding electons)} = \text{½ (8 – 3)} = 2.5$$

Is the bond strength in $N_2^-$ stronger or weaker than the bond strength in $N_2$? Why?

**The triple bond in $N_2$ is reduced to a bond order of 2.5 in $N_2^-$ so the bond in $N_2$ is stronger.**

**(Equivalently, the extra electron in $N_2^-$ has to occupy an antibonding $\pi^*$ orbital. This weakens the bond.)**

Do you expect $N_2^-$ to be paramagnetic? Explain your answer.

**$N_2^-$ has an unpaired electron in the $\pi^*$ orbital. It is thus expected to be paramagnetic.**

- The $N_2^+$ ion plays a role in the colourful display of the Northern Lights (the *Aurora Borealis*).

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the $N_2^+$ ion. Indicate on this diagram the ground state electronic configuration of $N_2^+$ using the arrow notation for electron spins.
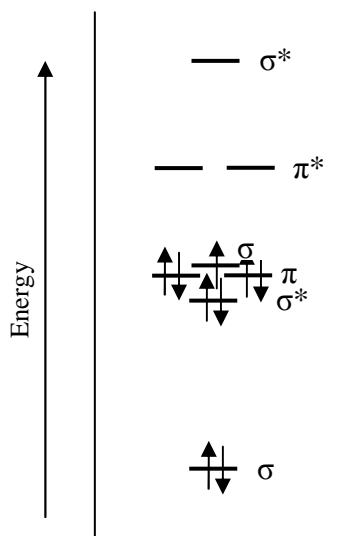


Calculate the bond order of $N_2^+$.

**Bond order = ½ (7 – 2) = 2.5**

Indicate the lowest energy electron excitation in this ion by identifying the initial and final states of the electron undergoing the excitation.

**The lowest energy excitation corresponds to the electron moving from $\pi \rightarrow \sigma$**

The line at 3914 Å (391.4 nm) in the emission spectrum of the *Aurora Borealis* is due to $N_2^+$ returning to its ground state. Calculate the energy gap (in eV) between the molecular orbitals involved in this transition.

**As $E = \dfrac{hc}{\lambda}$, the line corresponds to an energy of:**

$$E = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{(391.4 \times 10^{-9})} = 5.075 \times 10^{-19} \text{ J}$$

**As 1 eV = $1.602 \times 10^{-19}$ J, this corresponds to:**

$$E = 5.075 \times 10^{-18} =, \frac{5.075 \times 10^{-19}}{1.602 \times 10^{-19}} = 3.172 \text{ eV}$$

Answer: **3.172 eV**

**Marks**
**5**

- The NO molecule plays an important signalling role in the human body.

How many valence electrons are in the molecule NO? | **11 (5 from 5, 6 from O)**

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the NO molecule. Indicate on this diagram the ground state electronic configuration of NO using the arrow notation for electron spins.
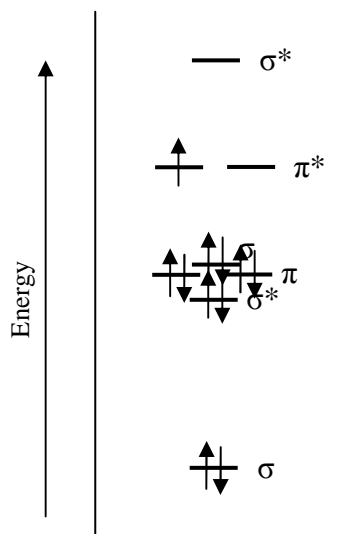


Calculate the bond order of NO. | **Bond order = ½ (8 – 3) = 2.5**

Is the NO molecule diamagnetic or paramagnetic? Explain your answer.

**NO contains an unpaired electron so it is paramagnetic.**

Would removing an electron from NO to form $NO^+$ strengthen or weaken the bond between the two atoms? Explain your answer.

**The highest energy electron in NO is in the $\pi^*$ (antibonding) level. Removal of this electron to form $NO^+$ increases the bond order to:**

**bond order = ½ (8 – 2) = 3**

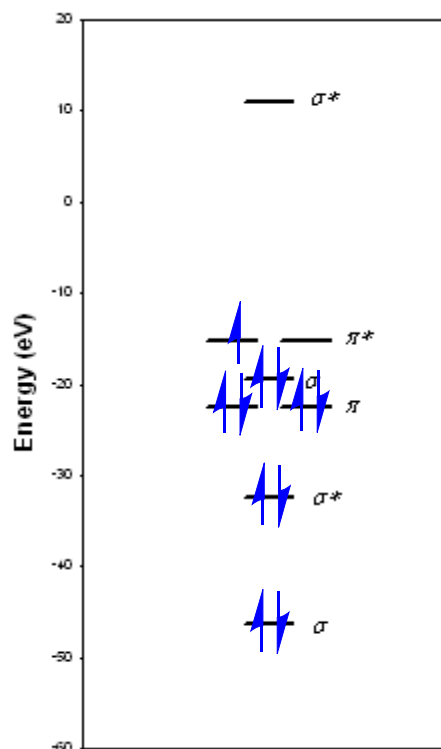**The higher bond order signifies a stronger bond.**

**Marks
4**

- The following relate to the electronic structure of the $O_2^+$ molecular ion.

How many valence electrons are there in $O_2^+$?

> **6 e⁻ on each O, minus 1 for the
> +ve charge: 11 e⁻**

Complete the MO diagram for the ground state electronic configuration of $O_2^+$ by inserting an arrow to represent each valence electron.



What is the bond order of $O_2^+$?

> **There are 8 electrons in bonding orbitals (two in σ and four in π) and 3 electrons in anti-bonding orbitals (two in σ* and one in π*):
> bond order = ½ (8-3) = 5/2**

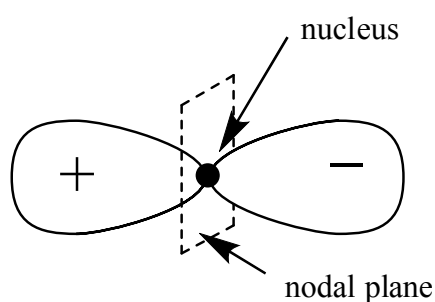Do you expect $O_2^+$ to be paramagnetic? Explain your answer.

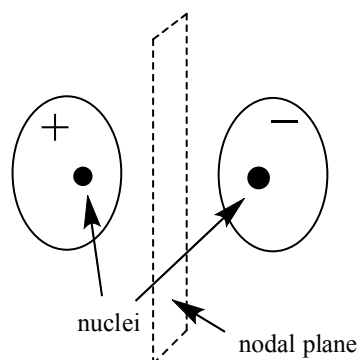> **It has an unpaired electron (in the π* level) so will be paramagnetic**

**2**

- Sketch the following wave functions as lobe representations.

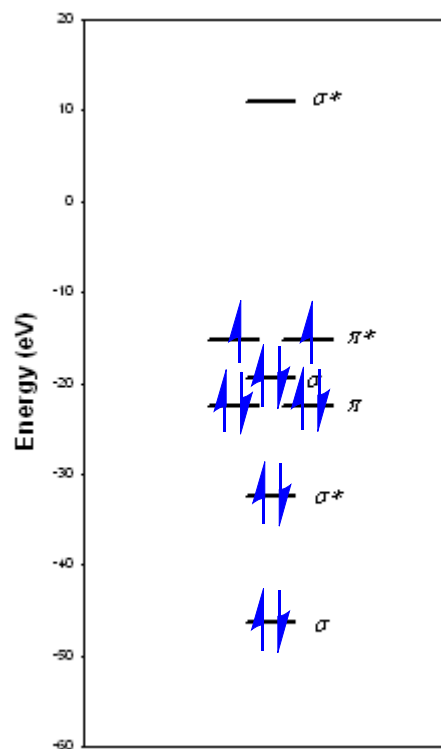(a) a 2*p* atomic orbital



(b) a σ* molecular orbital

**Marks
4**

- Oxygen gas, $O_2$, constitutes about 21% of the Earth's atmosphere.

How many valence electrons are there in $O_2$?

**$2 \times 6 = 12$**

Complete the MO diagram for the ground state electronic configuration of $O_2$ by inserting an arrow to represent each valence electron.
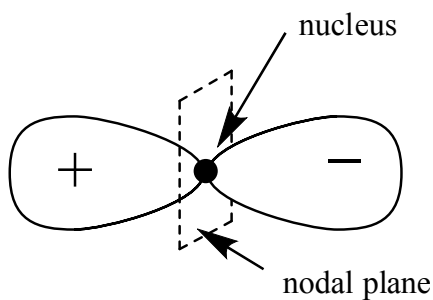


What is the bond order of $O_2$?

**½ (8-4) = 2**

Do you expect $O_2$ to be paramagnetic? Explain your answer.

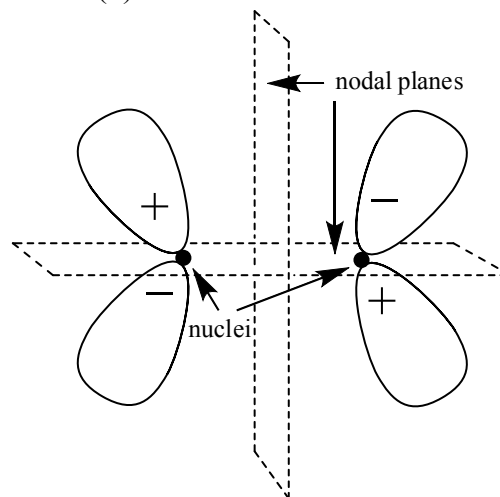**$O_2$ is paramagnetic as it possesses two unpaired electrons (in $\pi^*$)**

**2**

- Sketch the following wave functions as lobe representations.

(a) a 2p atomic orbital



nucleus

nodal plane

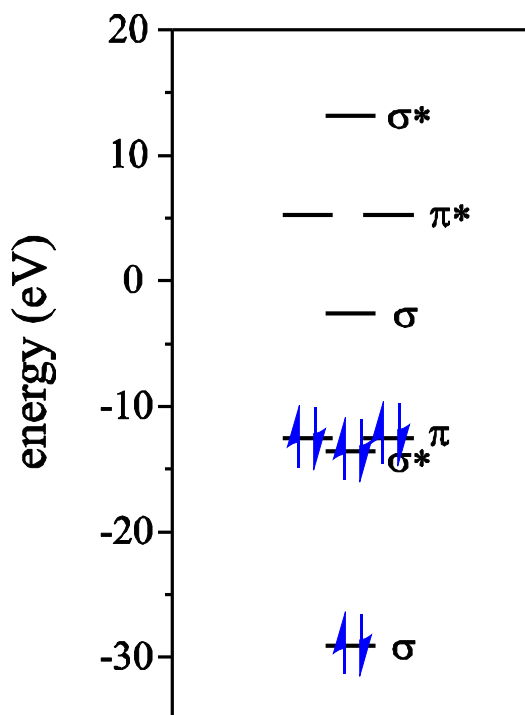(b) a $\pi^*$ molecular orbital



nodal planes

nuclei

**Marks
5**

- $C_2$ is a reaction intermediate observed in flames, comets and circumstellar shells.

How many valence electrons are there in $C_2$?

**4 from each C hence 8 overall**

Complete the calculated MO diagram for the ground state of $C_2$ by inserting the appropriate number of valence electrons into the appropriate orbitals.



What is the bond order of $C_2$?

**There are 6 bonding electrons (in σ and π) and 2 antibonding electrons (in σ*). Hence the bond order = ½ (6 - 2) = 2**

What is the longest wavelength of light that the ground state $C_2^+$ ion will absorb? Show working.

**The *longest* wavelength corresponds to the *lowest* energy transition that is possible. This is from the highest occupied orbital (π) to the lowest unoccupied (σ). From the diagram, the energies of these orbitals are *approximately* -12.5 eV and -2.5 eV respectively. The transition energy is therefore ~10 eV.**

**10 eV corresponds to $10 \times (1.602 \times 10^{-19} \text{ J}) = 1.602 \times 10^{-18}$ J.**

**From Planck's equation, the energy is related to the wavelength:**

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

**so**

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{(1.602 \times 10^{-18} \text{ J})} = 1.2 \times 10^{-7} \text{ m or } 120 \text{ nm}$$

Answer: **$1.2 \times 10^{-7}$ m or 120 nm**