Anderson Serangoon Junior College
H3 Chemistry
Basic Principles of Spectroscopy

Lesson Outline

Note: You should follow the sequence of content below. Skipping any pages will affect your understanding of later parts.
All videos can be found in MS Teams Channel "Basic Principles of Spectroscopy".

	Content	Page	Instructions for SDL lesson Relevant videos
1	Introduction	3	Self-read
2	Electromagnetic spectrum 2.1 What is electromagnetic radiation? 2.2 Generation of light from atoms 2.3 Line emission spectra (quantisation of energy & energy level transitions)	3 - 5	Self-read
3	Molecular Orbital (MO) Theory 3.1 Atomic Orbital	6	Self-read
	3.2 Molecular Orbital 3.3 Linear Combination of Atomic Orbitals 3.4 HOMO and LUMO 3.5 Bond order	7 7 - 8 9 9	- Self-read - Watch Video 1 for elaboration
	3.6 Homonuclear diatomic molecules	9– 14	- Watch Video 2a_A Brief Introduction to Molecular Orbital Theory - Watch Video 2b_Summary
	3.7 Conjugated and aromatic molecules	15 – 16	- Watch Video 3_Molecular Orbitals of Conjugated Alkenes
4	Self-check exercises	17 - 19	- Attempt all Self-check exercises. - Watch Video 4_Self-check Exercise 1 and 2
5	Additional readings	20	Self-read

H3 Chemistry
Basic Principles Of Spectroscopy

Learning outcomes
Students should be able to:

(a) understand basic Molecular Orbital (MO) theory, involving

  (i) atomic and molecular orbitals

  (ii) bonding, anti–bonding and non–bonding orbitals

  (iii) molecular orbitals with σ and π symmetry

(b) understand that molecular orbitals represent discrete electronic energy levels in molecules [see also (e)(ii)]

(c) apply Linear Combination of Atomic Orbitals (LCAO) principles to obtain the shape and relative energies of molecular orbitals in the following:

  (i) simple homonuclear diatomic molecules such as H_2, O_2, and F_2

  (ii) benzene and linear polyenes (molecular orbitals of π symmetry only)

  [quantitative treatment of LCAO is **not** required]

(d) construct and interpret molecular orbital diagrams, and identify the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) for the following:

  (i) simple homonuclear diatomic molecules such as H_2, O_2, and F_2

  (ii) benzene and linear polyenes (molecular orbitals of π symmetry only)

  [knowledge of orbital mixing between orbitals of the same symmetry is **not** required]

(e) understand the following in relation to the fundamental principles of spectroscopy:

  (i) properties of electromagnetic radiation
  - the electromagnetic spectrum (with range of wavelengths for different types of radiation used in spectroscopy)
  - the photon as a discrete packet (quantum) of electromagnetic energy
  - the relationship between wavelength, frequency and speed of light, including the use of equation, $E = h f$

  (ii) the quantisation of energy in relation to
  - electronic, vibrational and rotational energy levels
  - nuclear energy levels in applied magnetic field

  (iii) energy level transitions associated with the absorption and emission of photos with energy matching the energy gap

References
1. *Organic Chemistry (7th Edition)*, John McMurry, Brooks/Cole
2. *Organic Chemistry (Sixth Edition)*, Francis A. Carey, McGraw–Hill
3. *Understanding Advanced Organic Chemistry and Analytical Chemistry,* Chan & Tan, World Scientific
4 *Teaching the Revised H3 Chemistry,* Yan Yaw Kai, NIE

Questions to ponder…

Other than chemical tests, have you ever wondered if chemists have other ways to confirm structures of unknown compounds? How do they work? What are the limitations?

Have you ever wondered what happens to the atomic orbitals in atoms after molecules are formed?

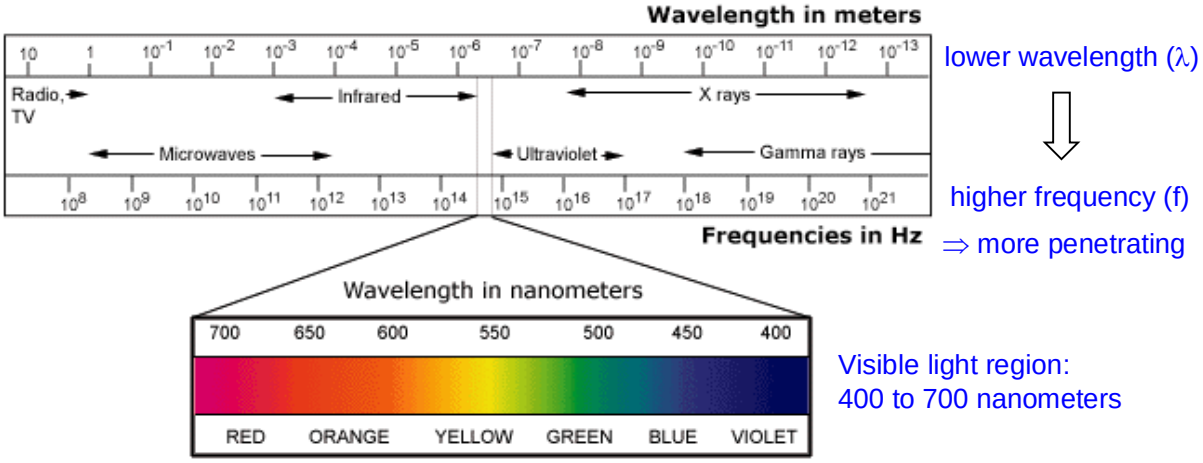
1. Introduction

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. While we are unable to "see" the matter at the atomic level, spectroscopy provides a method for the structural identification of organic and inorganic compounds. There are various spectroscopic techniques involving electromagnetic radiation of different frequencies.

As the substance interacts with electromagnetic radiation, it provides information on the structure and properties of the substance. Thus, spectroscopy is a valuable tool to study the structure and properties of matter. Spectroscopy is widely used in modern research and its applications span across all fields of science and society.

2. Electromagnetic spectrum

The electromagnetic spectrum is the range of frequencies (the spectrum) of electromagnetic radiation and their respective wavelengths and photon energies.



2.1 What is electromagnetic radiation?

An electromagnetic (EM) radiation has the following properties:

- Travels in a straight line
- Can propagate through a vacuum
- Behave as waves, with frequency (*f*) and wavelength (λ)
- Velocity, c = 2.998 x 10^8 m s^{-1} [*Data Booklet*: 3.00 x 10^8 m s^{-1}]
- c = *f* λ [Since c is a constant, there is an inverse relationship between f and λ!]

The diagrams below illustrates the relationship between frequency and wavelength.

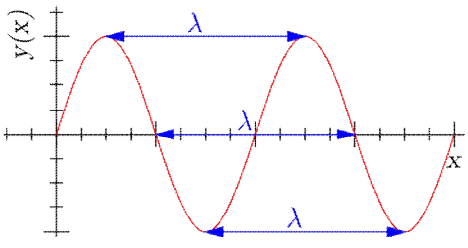


Fig. 1: Wavelength (λ) is the distance between successive crests of a wave.

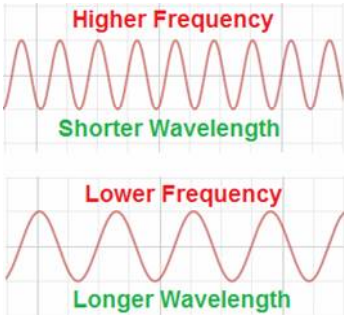


Fig. 2: Frequency (f) is the number of waves per unit time. EM radiations of shorter wavelength has higher frequency.

Max Planck, a German theoretical physicist, proposed the theory of quantisation of energy of electromagnetic radiation. The theory states that electromagnetic radiation, e.g. visible light and ultraviolet radiation, exists as packets or units of energy called quanta or photons that have neither mass nor charge. It exhibits both the properties of waves and particles, but here in spectroscopy, we shall focus on its wave–like nature.

The energy of each photon (E) is related to the frequency (f) of the radiation by the equation

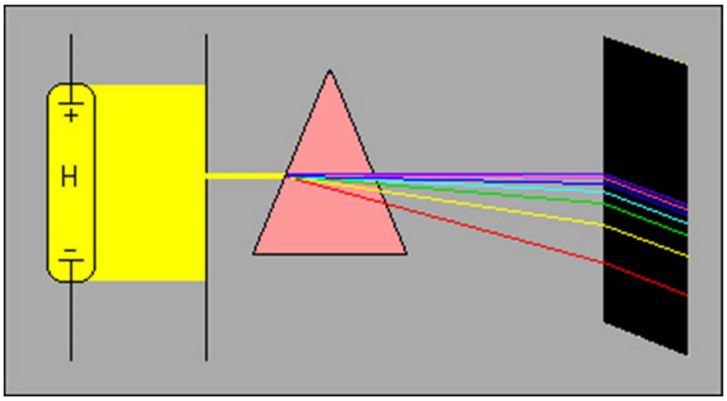
$E = h f$, where h is the Planck constant, 6.63×10^{-34} J s

Since $f = \frac{c}{\lambda}$, Planck's equation can also be written as $E = h\frac{c}{\lambda}$

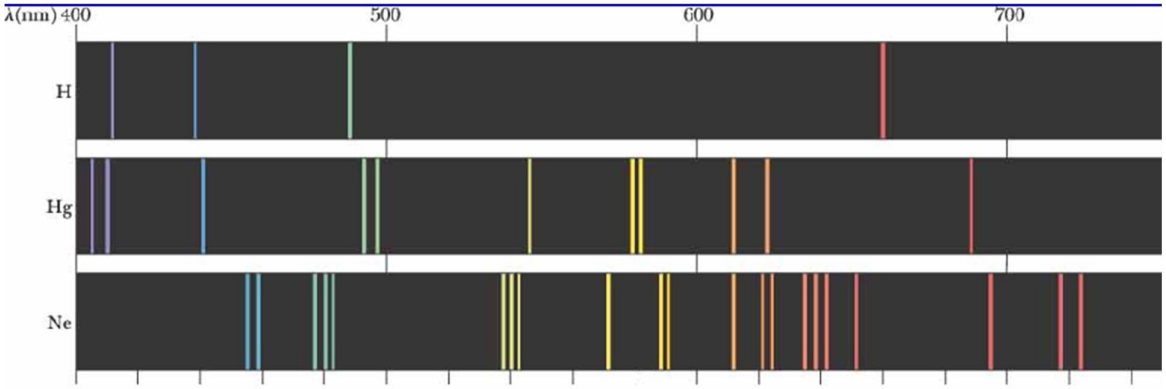
2.2 Generation of light from atoms

One of the earliest spectroscopic studies involved the investigation of electromagnetic (EM) radiation emitted by energetically excited atoms. An element, such as hydrogen, can be excited by an electrical potential until it gives off light. The emitted EM radiation is then passed through a prism, which separates it into its constituent wavelengths.

Each element gives a unique line spectrum (discrete), unlike the continuous spectrum of all wavelengths given by white light.



The following image shows examples of line emission spectra of different elements, where each element gives EM radiation of a few specific wavelengths (shown by the thin lines) unique to itself.



How does emission spectrum come about and why is it different for each element?

2.3 Significance of line emission spectra

The emission spectrum of an element is the spectrum of electromagnetic radiation emitted due to electrons making a transition from a high energy state to a lower energy state. The energy of the emitted photons is equal to the energy difference between the two states.

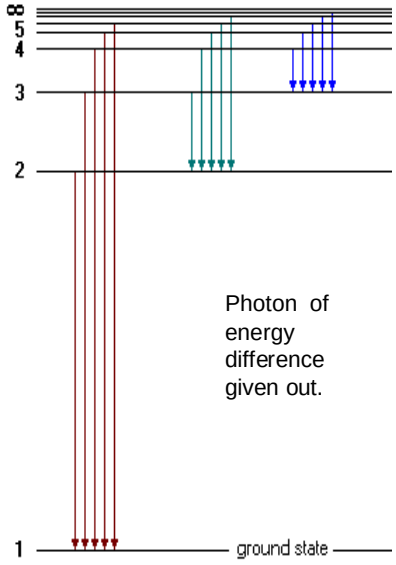


Fig. 3 on the left shows the possible transitions from higher to lower energy state for an element.

When electron moves to lower energy state, energy corresponding to the difference between the energy states (or energy levels) are given out in the form of photons of electromagnetic radiations.

Notice the energy levels of the different energy states are different, giving rise to photons of different energies (E) emitted when different possible transitions are made (represented by the downward arrows).

Since $E = h\frac{c}{\lambda}$, we see wavelengths of different EM radiations in the line spectrum.

As shown by the line emission spectra of atoms, energetically excited atoms can only emit light of certain specific wavelengths (not the whole spectrum), and we can conclude that only photons of certain specific energies are emitted from atoms of each element.

This shows that there are specific energy gaps within atoms, which reveals the specific shells with specific energy level for electrons. Thus, the energy of electrons in atoms is said to be quantised, i.e. electrons can have only certain allowed energies.

Why do different elements produce different emission spectra?

Due to differences in the number of electrons and the nuclear charges between elements, the energy levels of the electronic shells of two different elements are **different**. For instance, the energy level of the 2s orbital of carbon atom is lower than that of boron because of the higher nuclear charge (more protons).

Apart from atoms, energies of molecules are also quantised. Molecules may possess electronic, vibrational and rotational energies. Therefore, molecules are also expected to absorb or emit electromagnetic radiation of specific frequencies / wavelengths. These give rise to different spectroscopy which we will study in later topics.

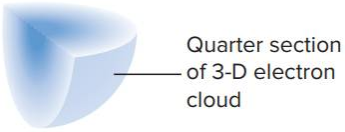
Excitation	Radiation absorbed	Spectroscopy
electronic	UV–visible	UV–vis spectroscopy
vibrational	infra–red	infra–red spectroscopy
rotational	microwave	microwave spectroscopy
nuclear	radio waves	NMR spectroscopy

3. Molecular Orbital (MO) Theory

3.1 Revisiting the Atomic Orbitals

> Recall in H2: An orbital represents a three–dimensional volume of space around the nucleus in which there is a **high probability (> 95%) of finding an electron**.

In a hydrogen atom, the only orbital of concern is the 1s orbital, which is spherical.



The probability of finding an electron decreases rapidly as the distance from the nucleus increases, although it *never goes all the way to zero*, even at large distances. As a result, there is no definite boundary to the atom, and the atom has no definite size.

For practical purposes, we represent the 1s orbital as a sphere within which there is 95% probability of finding the electron.

Other orbitals such as p orbitals and d orbitals are also described by other wavefunctions.

In p orbitals, there are two lobes of high probability, one on either side of the nucleus. The nucleus lies at the **nodal plane** of this dumbbell–shaped orbital (See diagram below). The probability of finding an electron on the nodal plane is zero. The wavefunction has different signs on opposite sides of the nodal plane, e.g., + on top and – below (this is arbitrary).

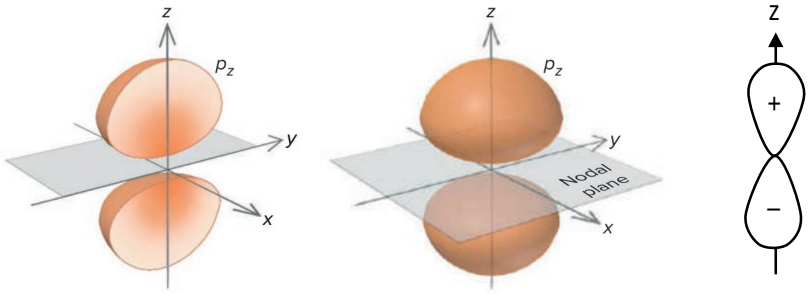
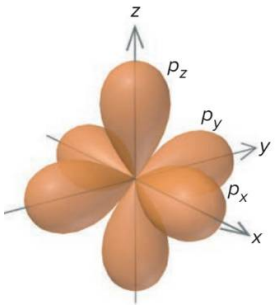
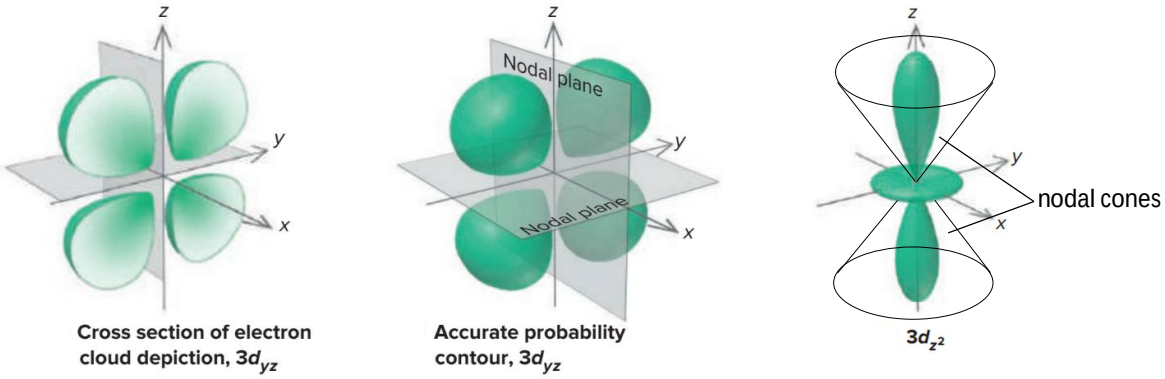


Fig. 4 shows a p orbital with nodal plane between the lobes and signs on each of the lobe.

The three p orbitals in the same subshell have different spatial orientations but are degenerate.



For d orbitals, there are two nodal planes for each of the d orbitals with four lobes, and two nodal cones for the d_{z^2} orbital. An electron in a d orbital spends equal time in all its lobes (the same is true of an electron in a p orbital too), and the five d orbitals in the same subshell are degenerate.



Cross section of electron cloud depiction, $3d_{yz}$

Accurate probability contour, $3d_{yz}$

$3d_{z^2}$

3.2 Molecular Orbitals

In Valence Bond (VB) theory, the molecule is pictured as a group of atoms bonded through the overlapping of valence–shell atomic and/or hybrid orbitals occupied by *localised* electrons.

However, in Molecular Orbital (MO) theory, the molecule is pictured as a collection of nuclei with (molecular) orbitals, that extend over the whole molecule and where the bonding electrons are distributed (i.e. *delocalised*).

Like an atomic orbital, each molecular orbital can only contain two electrons with the opposite spins, i.e. +½ or –½. A molecular orbital that "houses" the two electrons spreads throughout the molecule, but with concentration of electron density within the inter–nuclei region, i.e. the probability of finding an electron within the inter–nuclei region is ~95%. It is derived from the mathematical combination of the wavefunctions of atomic orbitals.

Like an atomic orbital, each molecular orbital represents a discrete energy level (and energy state) for an electron within the molecule. It also has a characteristic shape. A molecular orbital can, in principle, extend over the whole molecule, since each of the electrons (whether valence or inner–shell) in a molecule is attracted by all of the nuclei in the molecule.

3.3 Linear Combination of Atomic Orbitals (LCAO)

LCAO is essentially a mathematical method that employ wave mechanics to describe the molecular orbitals. It provides only an approximation to the exact electronic structure of molecules. We can perceive a *molecular orbital* as a mathematical wave function describing the *wave–like behaviour of an electron* in a molecule, whereas an *atomic orbital* describes that of an *electron* in an atom.

In considering the wave nature of electrons, there are both constructive and destructive interference when these waves combine. In the former case, the intensities of the waves are added, while in the latter, the intensities are subtracted or cancelled.

Source: https://www.fizzics.org/interference–of–waves/

For atomic orbitals to interact to form MOs, they must have

- same symmetry
- similar energy
- spatial overlap

Molecular orbitals (MO) are constructed by taking *linear combinations* of the valence orbitals of atoms within the molecule. MOs can be bonding, anti–bonding or non–bonding.

Bonding MOs

When two atomic orbitals overlap, one molecular orbital is formed from the constructive interference (in–phase) of the electron waves and it is called the bonding MO.

The build–up of electron density within the inter–nuclei region draws the two atoms closer together. Thus, electrons found in a bonding MO stabilise the molecule, resulting in a lower energy level for the MO that is formed from the atomic orbitals.

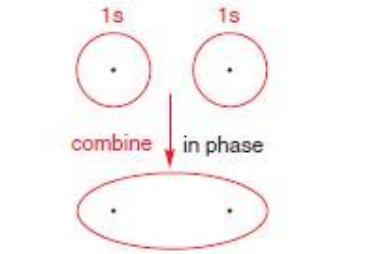
The bonding MO is denoted by the symbol σ. Subscript is usually added to represent the atomic orbitals from which the MO is generated. e.g. σ_{1s} or σ_{2s}.

Anti–bonding MOs

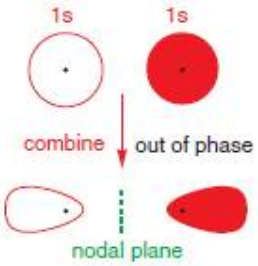
The destructive interference (out–of–phase) of the electron waves reduces the electron density between the two nuclei. This is shown by the lack of electron density between the two nuclei at the nodal plane. The MO formed in this way is termed the anti–bonding MO.

It is denoted by the symbol σ^*. Similarly, subscript is added to represent the atomic orbitals from which the MO is generated. e.g. σ^*_{1s} or σ^*_{2s}.

Since there is a lower probability of finding electrons in the inter–nuclei region, there is greater repulsion between the positively charged nuclei, which causes them to be further apart. This weakens the bond, and thus electrons found in anti–bonding MO tend to destabilise the molecule. As a result of the increased inter–nuclei repulsion, the energy level of an anti–bonding MO is higher than the atomic orbitals that formed the anti–bonding MO.



generates a **bonding** molecular orbital



generates an **antibonding** molecular orbital

Non–bonding MOs

Non–bonding MOs will have the same energy as the atomic orbitals of one of the atoms in the molecule. The pair of electrons in this non–bonding MO is equivalent to the lone pair of electrons in the Lewis structure. It arises from atomic orbitals that have no other atomic orbital to combine with it.

As a result, the electrons in the non–bonding MO mostly reside on the atom which provides the atomic orbitals. Thus, electrons in the non–bonding MO do not affect the strength of covalent bond that forms. The non–bonding MO is denoted by the symbol *n* (occupied) or *n** (unoccupied).

3.4 What are HOMO and LUMO?

The **highest occupied molecular orbital** (HOMO) is the molecular orbital that, according to the Aufbau principle, is occupied last. The **lowest unoccupied molecular orbital** (LUMO) is the next higher molecular orbital.

3.5 Bond order

Bond order assesses the net number of bonds between two atoms in a molecule. The greater the bond order between a given pair of atoms, the greater the bond strength.

The bond order identifies a *shared electron pair* in *bonding* MO as counting as a 'bond' and an *electron pair* in an *anti–bonding* MO as an 'anti–bond' between two atoms. More precisely, the bond order is defined as

$$\text{bond order} = \frac{(\text{no. of electrons in bonding MOs}) - (\text{no. of electrons in anti–bonding MOs})}{2}$$

Non–bonding electrons are ignored when calculating bond order.
We will look at examples on how to calculate bond order

3.6 Homonuclear diatomic molecules

Similar to the atomic orbitals in an atom, the energy level of the MOs are also quantised, and these are filled with electrons in the same way following:

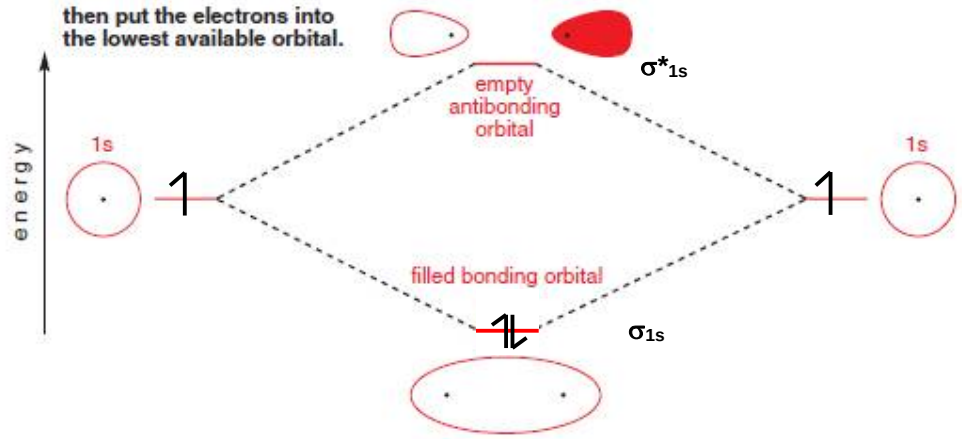
- **Aufbau Principle** – Molecular orbital which has the lowest energy is filled first.
- **Pauli's Exclusion Principle** – Each molecular orbital can accommodate a maximum of two electrons having opposite spins.
- **Hund's rule of multiplicity** – When filling a set of degenerate orbitals, an electron goes to an empty orbital first, before completely filling up any of these similar energy orbitals.

Example 1: Hydrogen (H_2)

The bonding orbitals formed from 1s–1s interactions of the H atoms have another important feature in common: they are all cylindrically symmetrical. Bonding orbitals with cylindrical symmetry like this are known as σ orbitals, and the bonds which result from *putting two electrons into these orbitals* are known as σ bonds.

The single bond in the H_2 molecule is therefore a σ bond. The anti–bonding orbitals which result from combining these atomic orbitals are also cylindrically symmetrical and are called σ* orbitals, with the * denoting their anti–bonding character.

Each hydrogen atom has one electron and so the resulting hydrogen molecule contains two electrons. Always fill up orbitals from the lowest energy first, putting a maximum of two electrons into each orbital, so both of these electrons go into the bonding MO. The anti–bonding MO remains empty (as shown in the diagram on the next page).



Why hydrogen is diatomic but helium is not?

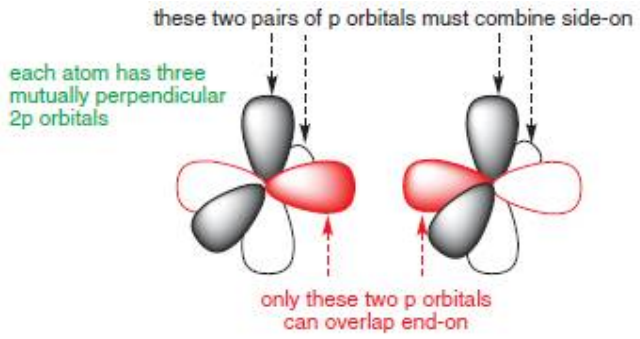
Like H atoms, He atoms have their electrons in 1s orbitals, so we can construct an energy level diagram for He_2 in a similar way.

But each helium atom has two electrons so now both the bonding MO and the anti–bonding MO are full. Any bonding due to the electrons in the bonding orbital is cancelled out by the electrons in the anti–bonding orbital, and the He_2 molecule falls apart. He_2 does not exist.

Example 2: Oxygen (O_2)

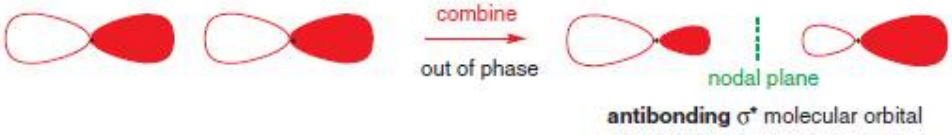
Combining 2s orbitals is essentially just the same; they form bonding and anti–bonding orbitals just as 1s orbitals do and with similar shapes too, but higher energies, because the 2s orbitals are higher in energy that the 1s orbitals.

In O_2, the 2p orbitals must combine in two different ways – one p orbital from each atom can overlap head–on, but the other two p orbitals on each atom must overlap side–on.

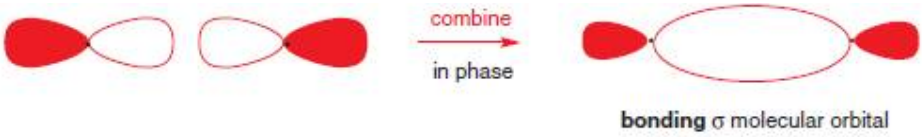


Why?
The p orbitals are perpendicular to one another. After the 1st p orbital has overlapped head–on with another p orbital from another atom, the two remaining p orbitals can only overlap side–on with their corresponding p orbitals.

For the head–on overlap, if the two 2p orbitals combine out–of–phase, there will be a node between the atoms, and any electron in this MO would spend most of its time not between the nuclei. This is an anti–bonding orbital.

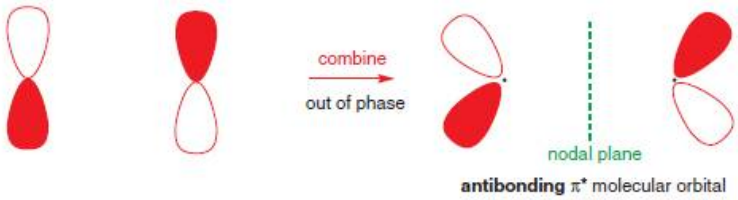


If the orbitals combine in–phase, there will be a build–up area of electron density between the nuclei, and somewhat less outside, so overall filling this orbital with electrons would lead to an attraction between the atoms and a bond would result.

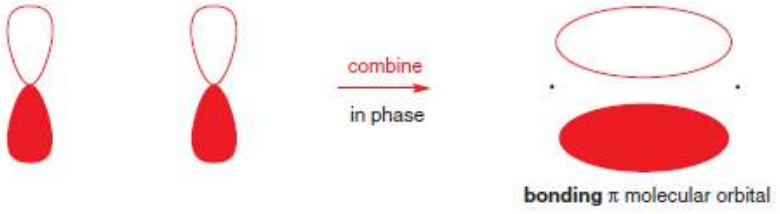


Both of these MOs have cylindrical symmetry and are therefore designated σ and σ* orbitals.

Each atom presents its other two 2p orbitals for side–on overlap. This is what the anti–bonding MO formed by out–of–phase combination of two side–on p orbitals looks like.



And this is the bonding, in–phase combination.

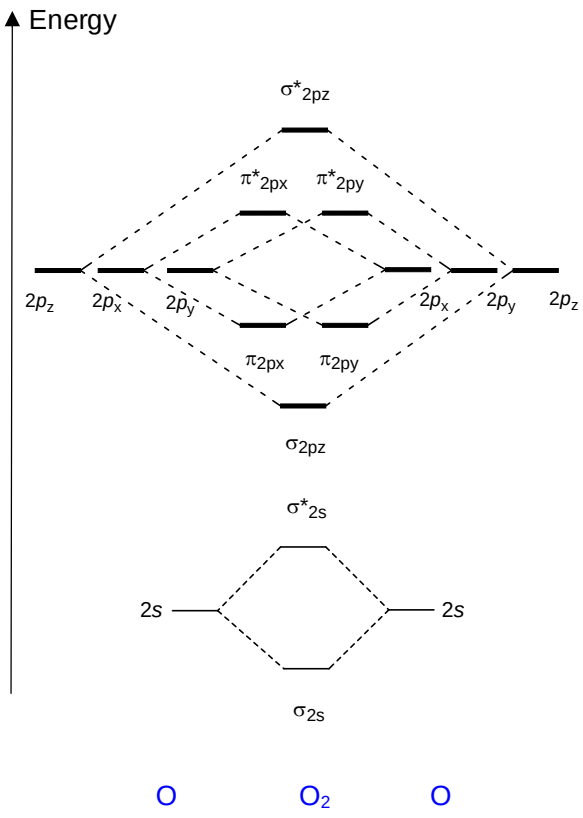


The bonding orbital is a π orbital and the antibonding orbital is a π* orbital. Since an atom has three mutually perpendicular 2p orbitals, two of which can interact side–on in this way, there will exist a pair of degenerate mutually perpendicular π orbitals and likewise a pair of degenerate mutually perpendicular π* orbitals.

The two types of MOs arising from the combinations of the p orbitals are, however, not degenerate. A more effective overlap arises when the atomic orbitals overlap head–on than when they overlap side–on. As a result, the 2p–2p σ orbital is lower in energy than the 2p–2p π orbitals.

The interaction of four valence atomic orbitals on one atom (2*s*, 2p_x, 2p_y and 2p_z) with a set of *four atomic orbitals* on another atom leads to the formation of a total of *eight molecular orbitals*: σ_{2s}, σ^*_{2s}, σ_{2pz}, σ^*_{2pz}, π_{2px}, π_{2py}, π^*_{2px} and π^*_{2py}.

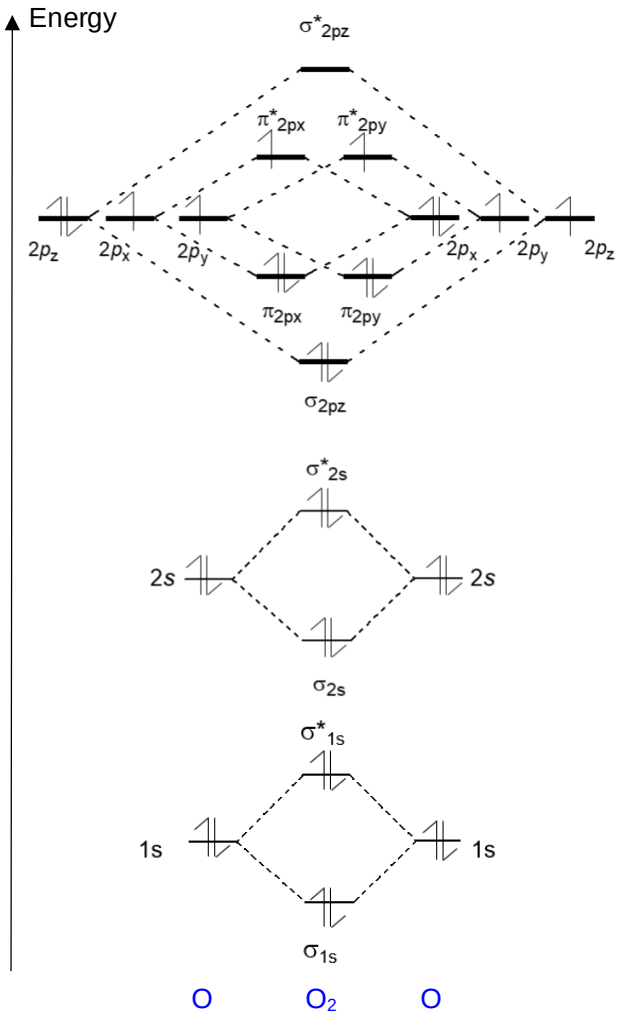
[The atomic orbitals that overlap head–on is assigned arbitrarily, can be along any axis.]



Note: The axis notation (x,y or z) is not important. However, for consistent reference, we shall use $2p_z$ orbitals for head-on overlap and $2p_x$ and $2p_y$ orbitals for side-on overlap throughout the notes and tutorial.

The interaction of the two 1s atomic orbitals from both oxygen atoms is similar to that seen for the 2s atomic orbitals.

Filling in the 16 electrons of oxygen molecule, the molecular orbitals of O_2 is:



Bond order = $\frac{(10-6)}{2} = \underline{2}$

What to include when drawing the molecular orbitals:

Tick	Features to include
	Vertical axis for Energy
	Atomic orbitals for the two atoms on 2 sides of the diagram, drawn in increasing energy level with clear labels of the specific orbital or subshell
	Energy levels for the molecular orbitals drawn in the middle of the diagram, both bonding and anti-bonding from the overlap of atomic orbitals of the 2 atoms. Use dotted lines (----) to show molecular orbitals formed from related atomic orbitals. Label the resulting molecular orbitals, to show if it is σ or π MO. The anti-bonding orbital is always higher than the bonding orbitals and labelled with *.
	Label at the bottom of the drawing to indicate which element or species the atomic/molecular orbital belongs to.

FYI: Two special properties of molecular oxygen

The two unpaired electrons in molecular oxygen result in the following special properties:

- **Paramagnetism**
  Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments.

  Unlike most other substances, liquid O_2 is attracted into a magnetic field. In the following video, liquid O_2 remains suspended between the poles of a magnet until the liquid boils away. In contrast, liquid N_2 poured between the poles of a magnet remains unattracted and instead, flows straight down.

  https://www.youtube.com/watch?v=yJs5ENtilIo&gl=SG&hl=en–GB

  This phenomenon is called paramagnetism and arises due to the presence of unpaired electrons in molecular oxygen.

  According to our usual Valence Bond (VB) Theory model of chemical bonding, bonds are formed from head–on or side–on overlap of atomic orbitals. The two unpaired electrons in the $2p_y$ and $2p_z$ orbitals of the oxygen atom pair up with that of the other oxygen atom to form a σ bond and a π bond. Thus, according to VB theory, all electrons in molecular oxygen should be paired up. But the paramagnetism of molecular oxygen contradicts this.

  Fortunately, the Molecular Orbital (MO) Theory model of chemical bonding in molecules is able to explain this phenomenon, by showing how molecular oxygen does indeed have two unpaired electrons!

  Thus, according to MO theory, the electronic configuration of the oxygen molecule is $(\sigma_{2s})^2(\sigma_{*2s})^2(\sigma_{2pz})^2(\pi 2_{px},\pi_{2py})^4(\pi_{*2px},\pi_{*2py})^2$.

- **Stability towards spontaneous combustion**
  Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Moreover, these reactions would result in an increase in entropy. In other words, we humans should spontaneously combust!

  But we have only considered the thermodynamic aspect of this reaction, and yet to consider the kinetic aspect. The reaction may be spontaneous, but it is very, very slow, because the energy barrier towards spontaneous human combustion (and that of other organic matter) is very, very high!

  This is because virtually all organic compounds, as well as H_2O, CO_2 and N_2, have only paired electrons, whereas molecular oxygen has two unpaired electrons (of the same spin). In order for the combustion reaction to proceed, at least one of the unpaired electrons in O_2 will need to change its spin. This requires a large amount of energy to bring about, i.e., E_a is very large.

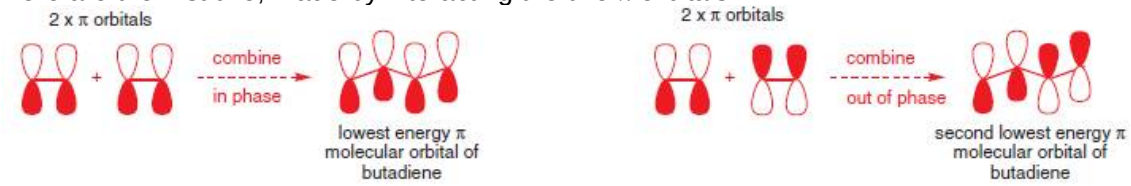
3.7 Conjugated and aromatic molecules

In butadiene and benzene, every carbon atom is **sp^2 hybridised** with **one p orbital available** to overlap with its neighbouring carbon atom. The uninterrupted chain of p orbitals gives rise to having alternate double and single bonds. When two double bonds are separated by just one single bond, the two double bonds are said to be conjugated.

Polyalkene – Butadiene

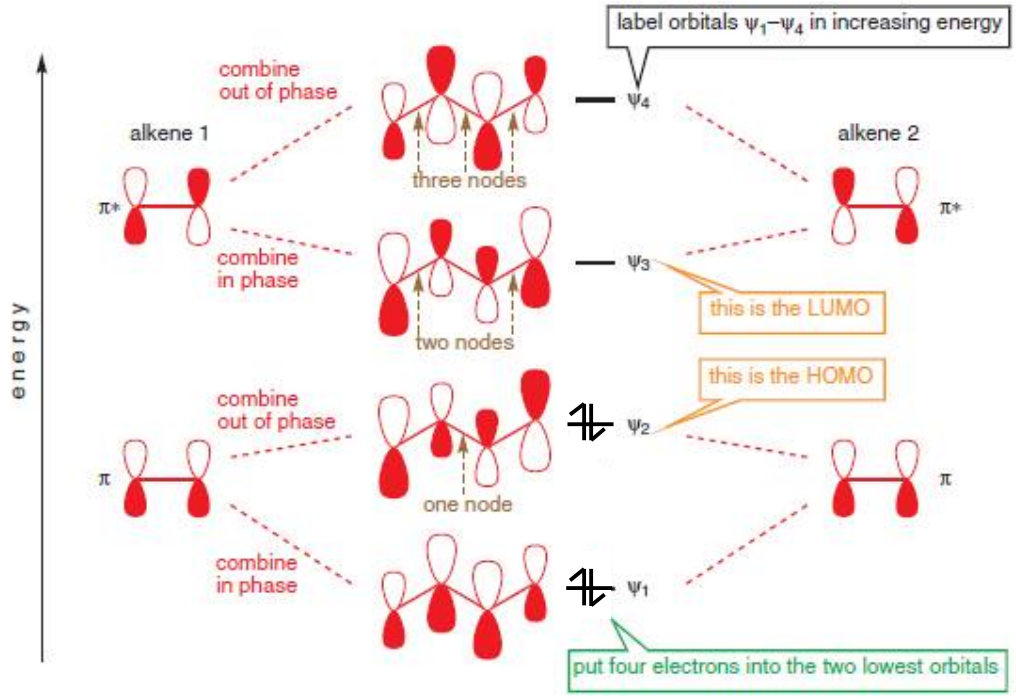
Butadiene has two π bonds, each made up of two p orbitals: a total of four atomic orbitals. We would therefore expect four molecular orbitals, housing four electrons. These orbitals extend over the whole molecule. There are two π orbitals and two π* orbitals, and they can interact in–phase or out–of–phase.

Here are the first two, made by interacting the two π orbitals:



and the next two, made from two π* orbitals:

We can represent all four molecular orbitals like this, stacked up in order of their energy in a molecular orbital energy level diagram. With four orbitals, we cannot just use '*' to represent anti–bonding orbitals, so conventionally they are numbered ψ1–ψ4 (ψ is the Greek letter psi).

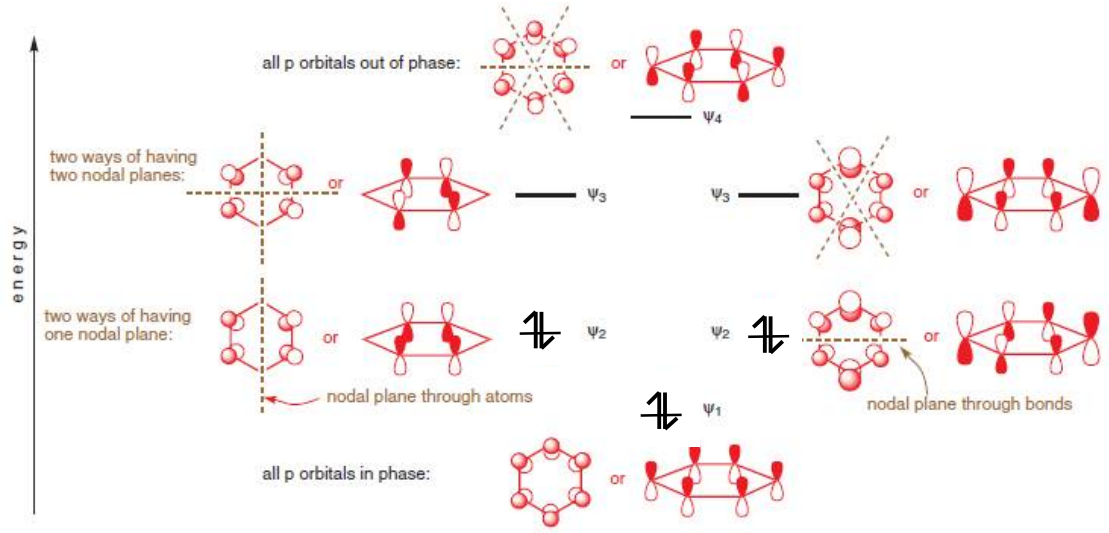


The number of nodes (changes in phase as you move from one orbital to the next) increases from zero in ψ_1 to three in ψ_4. One of the consequences of conjugation is to reduce the gaps between filled and empty orbitals, and so allow absorption of light of a longer wavelength.

Benzene

In benzene, all six p orbitals can combine to form six new molecular orbitals, and the electrons in these orbitals form a ring of electron density above and below the plane of the molecule. The electrons are in molecular orbitals spread equally over all the carbon atoms.

We can think of the π molecular orbitals of benzene as resulting from the combination of the six p orbitals in a ring and, as with butadiene, each successively higher energy orbital contains one more node. This is what we get for benzene:



- The molecular orbital lowest in energy, ψ_1, has no nodes, with all the orbitals combining in-phase.

- The next lowest molecular orbital will have one nodal plane, which can be arranged in two ways depending on whether or not the nodal plane passes through a bond or an atom. It turns out that these two different molecular orbitals both have exactly the same energy, that is, they are degenerate, and we call them both ψ_2.

- There are likewise two ways of arranging two nodal planes and again there are two degenerate molecular orbitals ψ_3.

- The final molecular orbital ψ_4 will have three nodal planes, which must mean all the p orbitals combining out-of-phase. Six electrons slot neatly into the three lowest energy bonding orbitals.

4. Self–check exercises

Exercise 1
Though the helium molecule He_2 does not exist, the cation He_2^+ does exist.

Use molecular orbital diagrams and calculate the bond order to explain your answer.

Exercise 2

Which of the three species is the least stable due to bond order: O_2, O_2^+, O_2^{2-}?

Exercise 3

(a) Construct a molecular orbital energy level diagram for F_2.

(b) How does the diagram change if two electrons are added? What does this tell you about what happens when two electrons are added to F_2?

5. Additional reading

Quantum Mechanical Model of the Atom

The Wave Nature of Electrons

Light particles have been known to possess wave–like properties, from the way they interact with each other (interference) and the slight bending that occurs when light encounters the edge of an object (diffraction).

In 1924, Louis de Broglie argued that electrons and other particles should also possess wave–like properties. This phenomenon is referred to as *wave–particle duality*, and was proven by electron diffraction experiments, and put to use in the electron microscope.

Thus, a particle with a certain mass m and moving at velocity v (i.e., with a certain momentum mv) possesses an associated wave of wavelength λ.

$$\lambda = \frac{h}{mv}$$, where h is the Planck constant
(found in the first page of your *Data Booklet*)

The Uncertainty Principle

The consequence of electrons having wave–like properties is that it becomes impossible to know exactly both the momentum (i.e., mass x velocity) and position of the electron at the same instant in time. This a statement of **Heisenberg's Uncertainty Principle**.

The Quantum Mechanical Model

Instead of trying to define the exact position and momentum of an electron, we focus on the probability of finding the electron in a given volume of space. The probability of finding an electron in a given point in space is determined from the square of a function called ψ ("psi"), i.e., ψ^2. ψ is a mathematical function which describes the behaviour of an electron particle–wave and it is called the **wavefunction**.

These wavefunctions are equations obtained from calculations based on the **quantum mechanical model** of the atom, proposed in 1926 by Erwin Schrödinger. Each wavefunction describes an orbital that an electron may be associated with in an atom, i.e., the orbital is the region of space in which there is a high (95%) probability of finding the electron.

Because wavefunctions are mathematically obtained, each orbital has a specific energy associated with it. Therefore, electrons in atoms can exist only at certain "allowed" energy levels determined by the orbitals they are associated with.