**Anglo-Chinese Junior College**
**Department of Chemistry**

# Molecular Orbital Theory and Basic Principles of Spectroscopy

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in collaboration with H3 Chemistry NLC

**Contents** **Page**

## Molecular Orbital Theory



## Basic Principles of Spectroscopy



## Learning Outcomes

**Candidates 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 the equation, $E = hf$
  (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 photons with energy matching the energy gap

## Recommended readings and resources

1 Inorganic Chemistry third edition, Catherine Housecroft and Alan Sharpe

2 Organic Chemistry second edition, Jonathan Clayden, Nick Greeves and Stuart Warren

3 The Molecular Nature of Matter and Change with Advanced Topics eighth edition, Martin Silberberg and Patricia Amateis

4 http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/mo.html

5 https://www.masterorganicchemistry.com/2017/05/05/the-pi-molecular-orbitals-of-benzene/

6 http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/

7 http://www.chem.kyushu-.ac.jp/~robertson/General_Chemistry/Files/Molecular_orbital_theory.pdf

8 https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Map%3A_Physical_Chemistry_(McQuarrie_and_Simon)/09%3A_The_Chemical_Bond%3A_Diatomic_Molecules/9.10%3A_Molecular_Orbital_Theory_Predicts_that_Molecular_Oxygen_is_Paramagnetic

# 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 $\lambda$.

$$\lambda = \frac{h}{mv}$$ , where $h$ is the Planck's 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 is 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 at a given point in space is determined from the square of a function called ψ ("psi"), i.e., $\psi^2$. ψ is a mathematical function which describes the behaviour of an electron particle-wave, and is called the **wavefunction**.

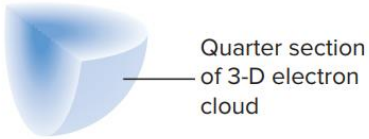
These wavefunctions are equations obtained from calculations based on the **quantum mechanical model** of the atom, proposed in 1926 by Erwin Schrödinger. Schrödinger's equation can only be solved for one electron system; for multi-electrons systems, appropriate approximations are required to solve it. Solving the equation gives rise to 3 quantum numbers describing a three dimensional space called an atomic orbital.

- Principal quantum number, *n*, defines the orbital size
- Angular momentum quantum number, *l*, defines the shape
- Magnetic quantum number, $m_l$, defines the orientation of the orbital.

As 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.

## Revisiting the Atomic Orbitals

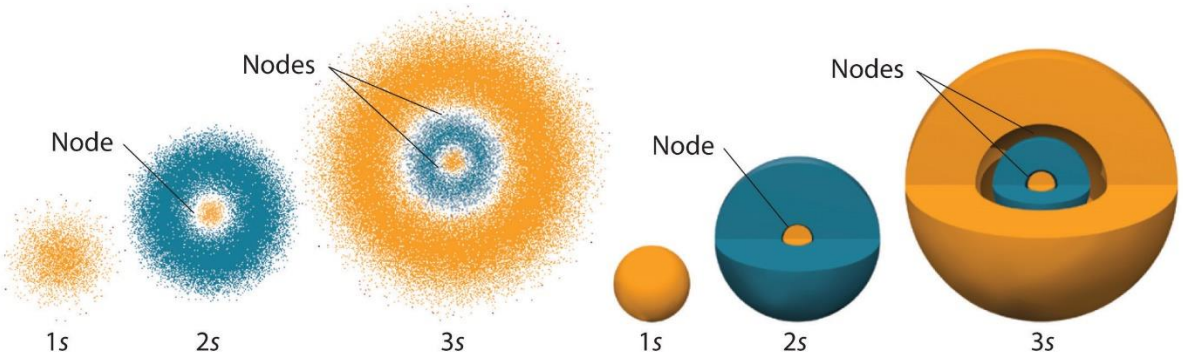
In a hydrogen atom, the only orbital of concern is the 1s orbital, which is spherical.



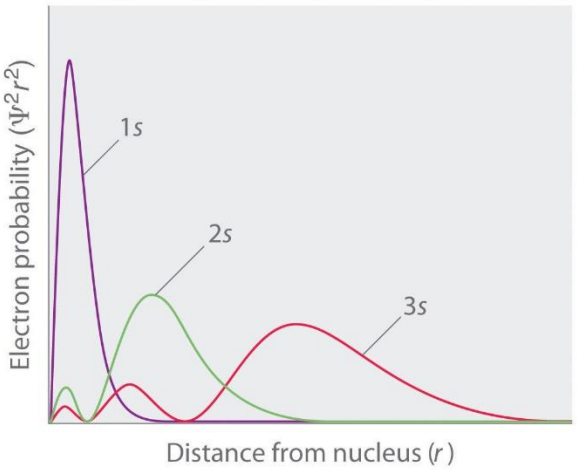

The probability of finding an electron decreases rapidly as the distance from the nucleus increases, although it never goes all the way to zero, even at large distances. As a result, there is no definite boundary to the atom, and the atom has no definite size.

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

The figure below shows the electron probability, contour probability and radial probability of 1s, 2s and 3s orbitals respectively. The shape of the graph of electron probability vs. distance from nucleus (r) can be understood from the fact that as r increases, surface area ($4\pi r^2$) increases more rapidly than the decrease in electron probability.



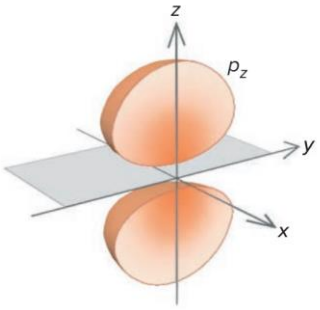

**(a) Electron probability** **(b) Contour probability**



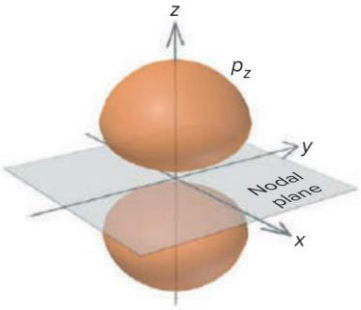

**(c) Radial probability**

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

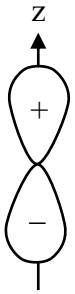
In 2p orbitals, there are two lobes of high probability, one on either side of the nucleus. The nucleus lies at the **nodal plane** of this dumbbell-shaped orbital. The probability of finding an electron on the nodal plane is zero. The wavefunction has different signs on opposite sides of the nodal plane plane – this is denoted either by different colours or arbitrary assigned with plus (+) and minus (–). (Note that the + and – assigned do not corresponds to electronic charge!).



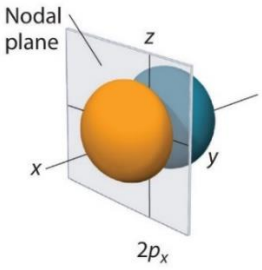

Cross section of electron cloud depiction, $2p_z$



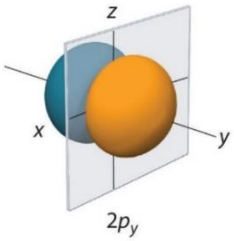

Accurate probability contour, $2p_z$



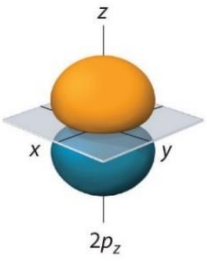

The three p orbitals in the same subshell have different spatial orientations but are degenerate.



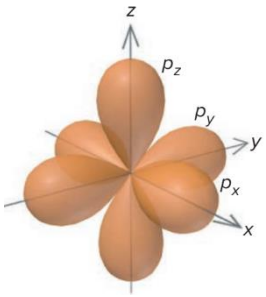

$2p_x$



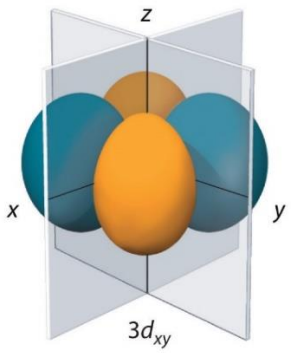

$2p_y$



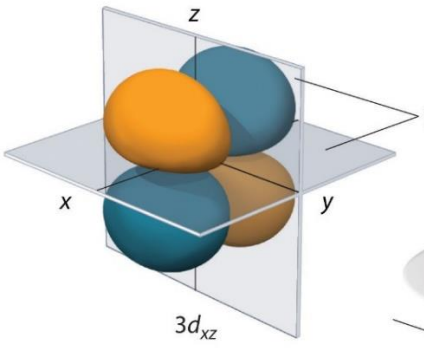

$2p_z$



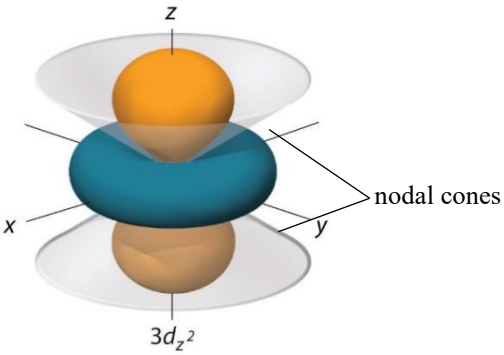

For 3d orbitals, there are two nodal planes for each of the d orbitals with four lobes, and two nodal cones for the $d_{z^2}$ orbital. An electron in a d orbital spends equal time in all its lobes (the same is true of an electron in a p orbital too), and the five d orbitals in the same subshell are degenerate.



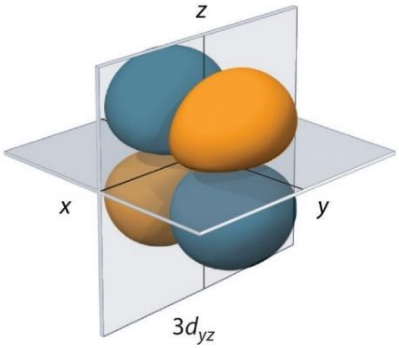

$3d_{xy}$



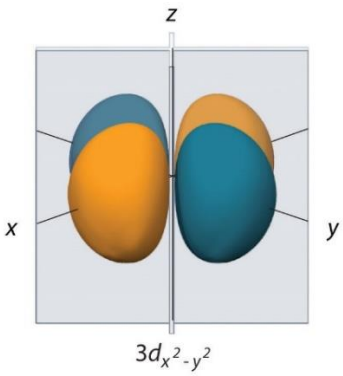

$3d_{xz}$




$3d_{z^2}$




$3d_{yz}$




$3d_{x^2-y^2}$

# The Molecular Orbital (MO) Theory Model of Chemical Bonding

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. Together with the use of Lewis structures, it provides us a straightforward way of rationalising the observed geometries of molecules. An example would be how the carbon and hydrogen atomic orbitals in methane overlap to form bonding electron pairs and how the arrangement of 4 H around C give rise to tetrahedral geometry.

Valence bond theory, however, does not explain all aspects of bonding. For example, it is not successful in describing the magnetic properties and the excited states of molecules. Molecular orbital theory, where the molecule is pictured as a collection of nuclei with (molecular) orbitals that extend over the whole molecule provide a more accurate picture.

A molecular orbital represents the probability of finding the electron within a given region of space in a molecule, and is derived from the mathematical combination of the wavefunctions of atomic orbitals. Like an atomic orbital, each molecular orbital represents a particular 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.

## Linear Combination of Atomic Orbitals (LCAO)

Molecular orbitals are constructed by taking linear combinations of the valence orbitals of atoms within the molecule.

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

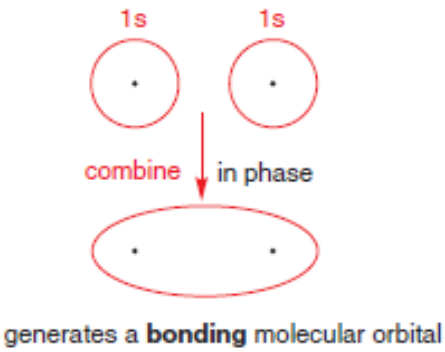
- Same symmetry
- Similar energy
- Spatial overlap

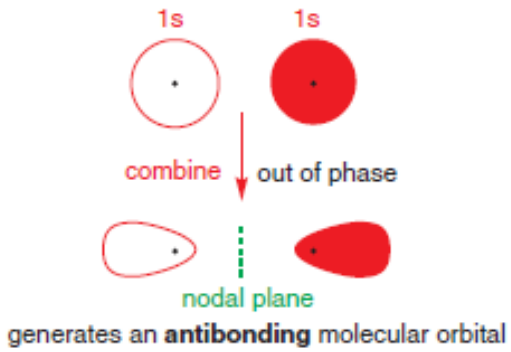
LCAO MO theory provides only an approximation to the exact electronic structure of molecules.

## Homonuclear Diatomic Molecules

As atomic orbitals are wavefunctions, they can be combined in the same way that waves combine - either constructively (in phase) or destructively (out of phase). Using two 1s orbitals drawn as circles (representing spheres) with dots to mark the nuclei and shading to represent phase, we can combine them in phase, resulting in an orbital spread over both atoms. This leads to formation of bonding molecular orbital. An electron in a bonding MO lowers the molecule's energy.

When atomic orbitals combine out of phase, it gives rise to a molecular orbital with a nodal plane down the centre between the two nuclei, where the wavefunctions of the two atomic orbitals exactly cancel one another out and with two regions of opposite phase. This leads to formation of anti-bonding molecular orbital. An electron in an antibonding orbital raises the molecule's energy.



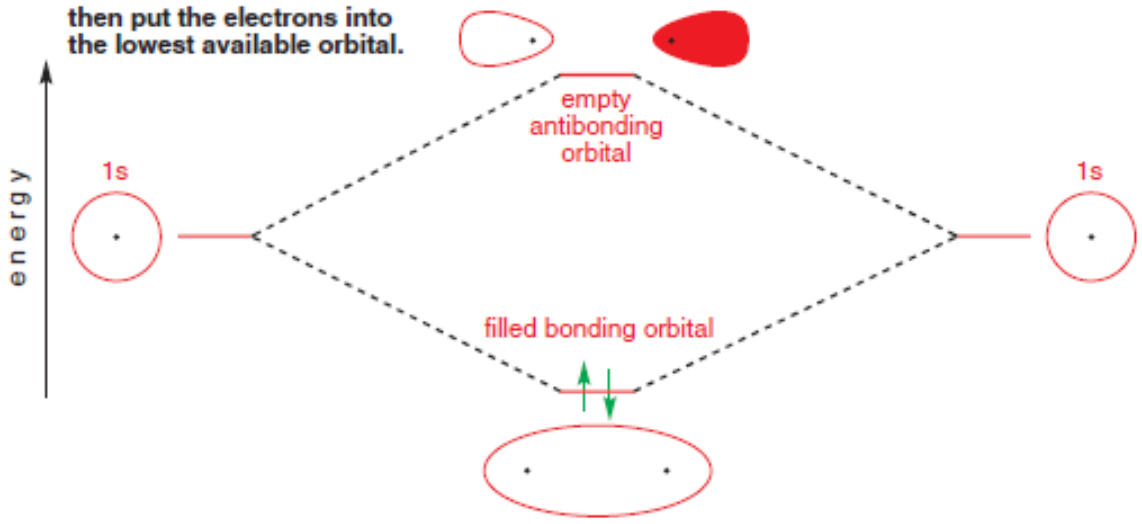

Filling of molecular orbitals

- Aufbau Principle – This principle states that those molecular orbitals which have the lowest energy are filled first.

- Pauli's Exclusion Principle – According to this principle, each molecular orbital can accommodate a maximum of two electrons having opposite spins.

**Example 1: Molecular Orbital Diagram of Hydrogen**

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 orbital. The antibonding orbital remains empty.




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

**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 antibonding MO are full. Any bonding due to the electrons in the bonding orbital is cancelled out by the electrons in the antibonding orbital, and the $He_2$ molecule falls apart. $He_2$ does not exist.

**Bond order:** The bond order assesses the net number of bonds between two atoms in the molecular orbital formalism; the greater the bond order between a given pair of atoms, the greater the bond strength.

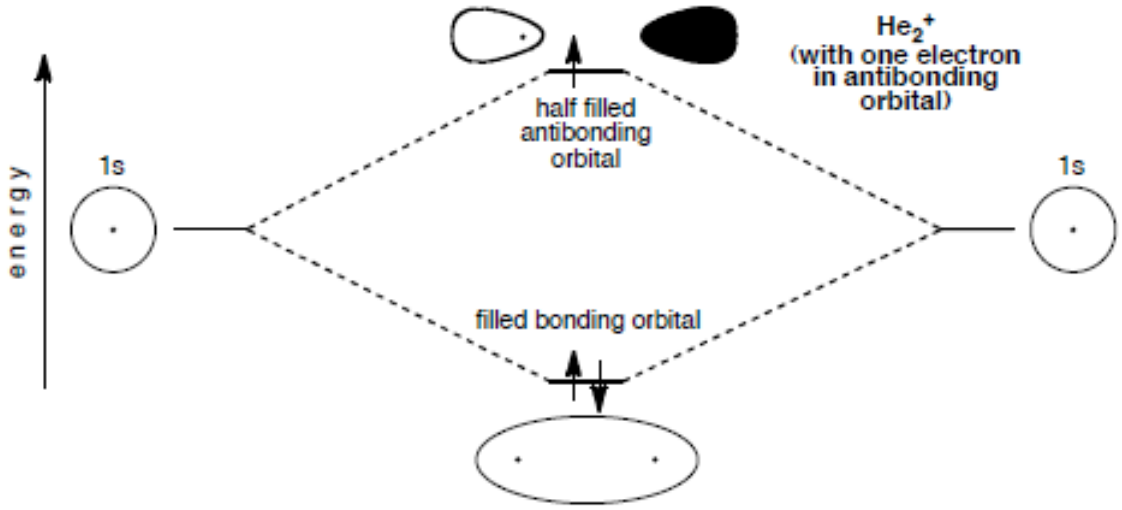
The bond order identifies a shared electron pair as counting as a 'bond' and an electron pair in an antibonding orbital as an 'antibond' between two atoms. More precisely, the bond order is defined as

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

Non-bonding electrons are ignored when calculating bond order.

**Question 1:** The helium molecule $He_2$ does not exist but the cation $He_2^+$ does exist. Why?

Answer: $He_2$ does not exist because the number of anti-bonding electrons is the same as the number of bonding electrons. The bond order is zero. $He_2^+$ has two bonding electrons and only one anti-bonding electron. The bond order is one half. $He_2^+$ does exist.

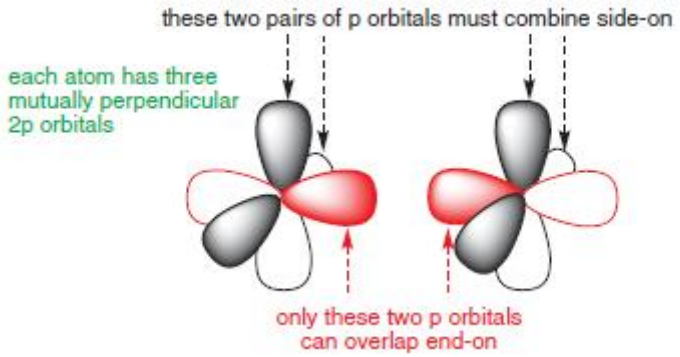



## Example 2: Molecular Orbital Diagram of Oxygen

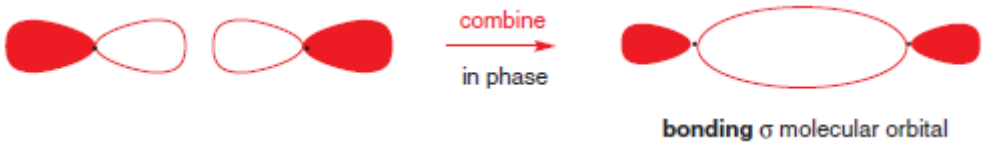
Combining 2s orbitals is essentially just the same; they form bonding and antibonding orbitals just as 1s orbitals do and with similar shapes too, but higher energies, because the 2s orbitals are higher in energy that the 1s orbitals.

The bonding orbitals formed from 1s–1s and 2s–2s interactions 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 antibonding orbitals which result from combining these AOs are also cylindrically symmetrical and are called σ* orbitals, with the * denoting their antibonding character.

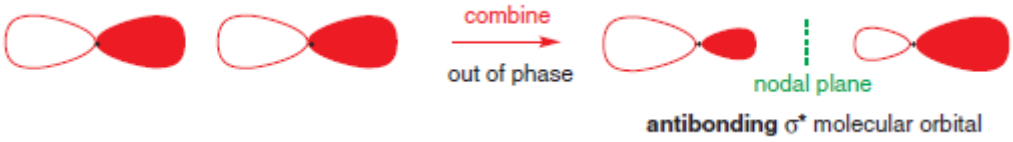
In $O_2$, the 2p orbitals must combine in two different ways—one p orbital from each atom can overlap head-on, but the other two p orbitals on each atom must combine side-on.



If the orbitals combine in phase, there will be a rich 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.

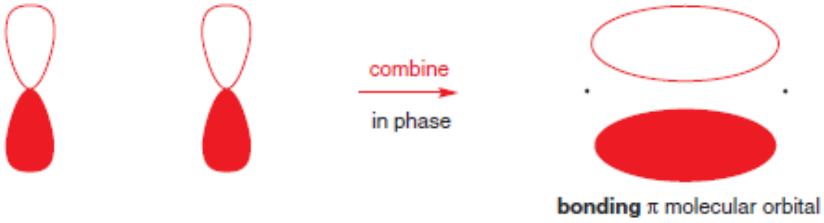



For the head-on overlap, if the two 2p orbitals combine out of phase, there will be a node between the atoms, and any electron in this MO would spend most of its time not between the nuclei. This is an antibonding orbital.

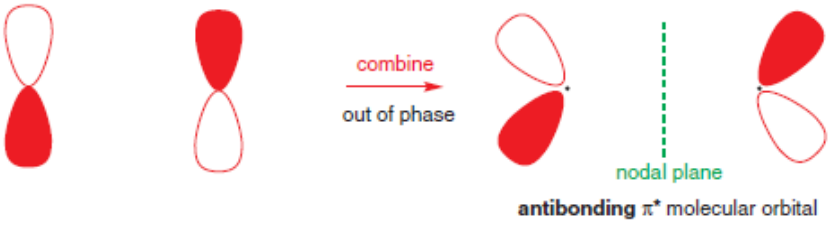



Both of these MOs have cylindrical symmetry and are therefore designated σ and σ* orbitals.

Each atom presents its other two 2p orbitals for side-on overlap. And this is the bonding, in-phase combination:



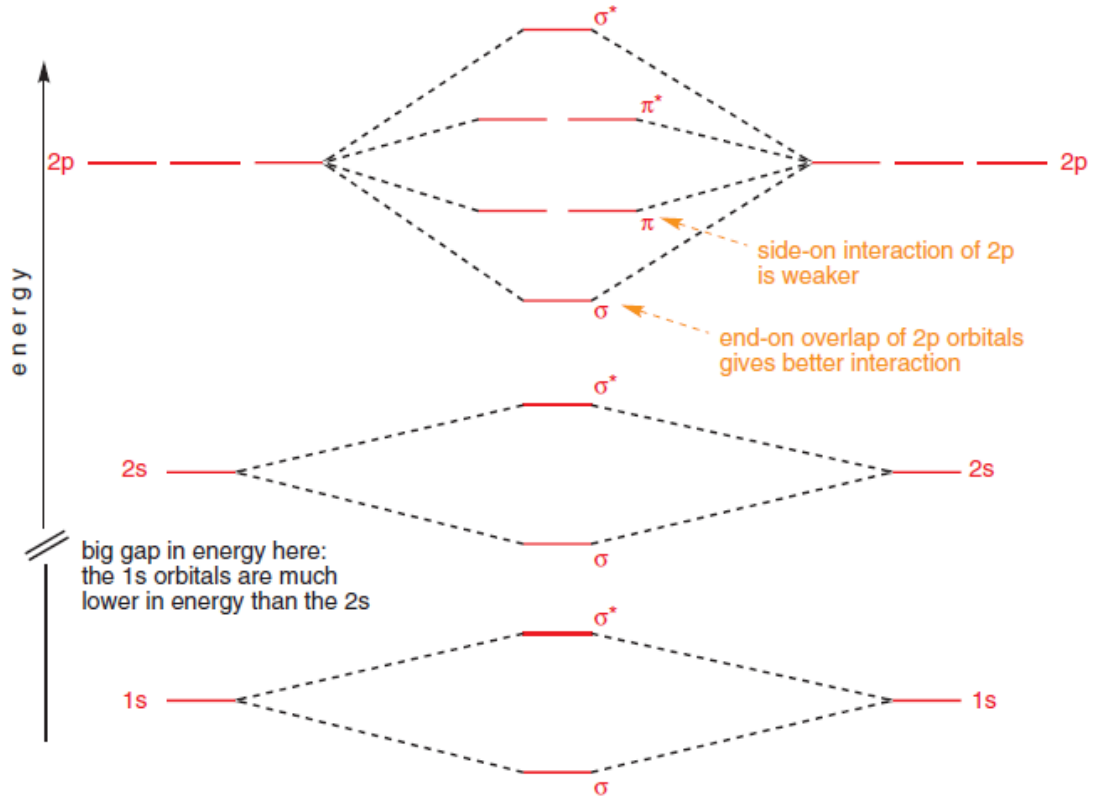

And this is what the antibonding MO formed by out-of-phase combination of two side-on p orbitals looks like:



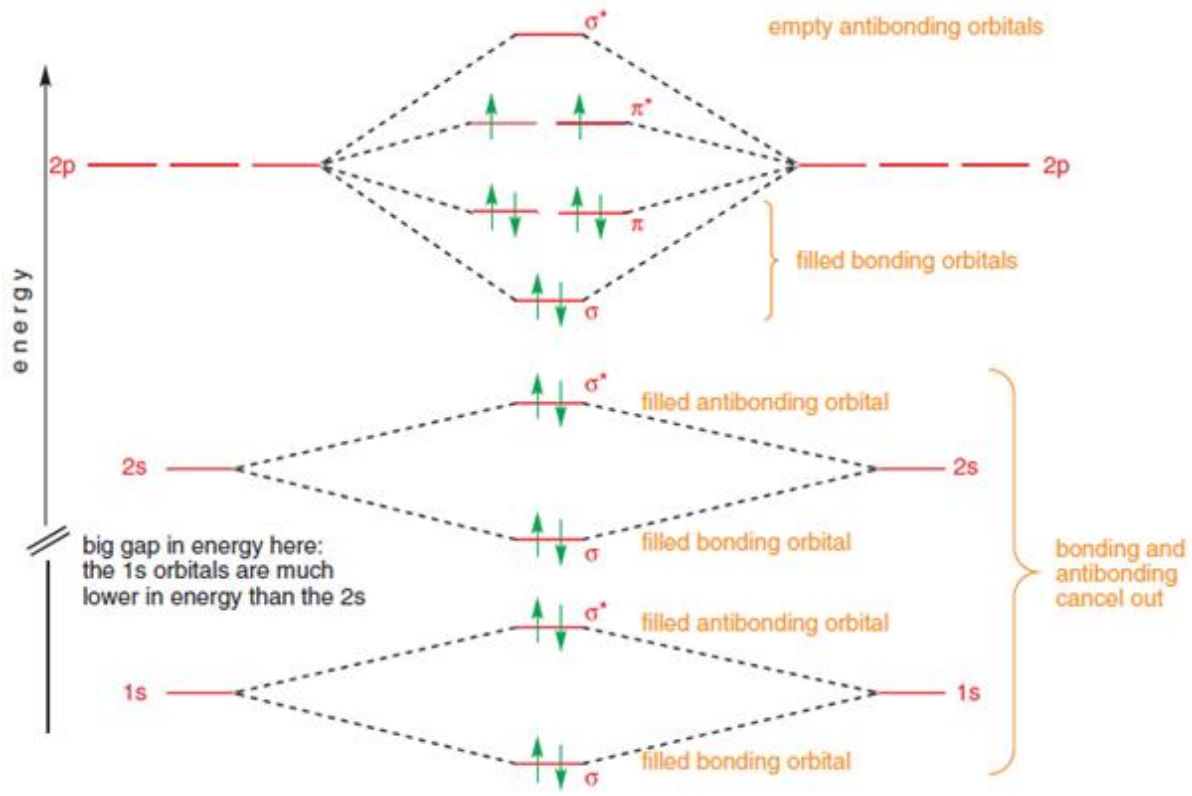

The bonding orbital is a π orbital and the antibonding orbital is a π* orbital. Since an atom has three mutually perpendicular 2p orbitals, two of which can interact side-on in this way, there will exist a pair of degenerate mutually perpendicular π orbitals and likewise a pair of degenerate mutually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

The two sorts of MOs arising from the combinations of the p orbitals are, however, not degenerate — more overlap is possible when the AOs 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*, 2$p_x$, 2$p_y$ and 2$p_z$) with a set of four atomic orbitals on another atom leads to the formation of a total of eight molecular orbitals: $\sigma_{2s}$, $\sigma_{2s}^*$, $\sigma_{2p}$, $\sigma_{2p}^*$, $\pi_x$, $\pi_y$, $\pi_x^*$ and $\pi_y^*$.




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




Bond order = ½ (10 – 6) = 2

**Two special properties of molecular oxygen**

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

- **Paramagnetism**

  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.

  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 electronic configuration of the oxygen atom is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$.

  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 $\sigma$ bond and a $\pi$ 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!

- **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 extremely 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.

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

- For $O_2$: there are 12 valence electrons, bond order =(10−6)/2 = 2
- For $O_2^+$: there are 11 valence electrons, bond order = (10−5)/2 = 5/2
- For $O_2^{2-}$: there are 14 valence electrons, bond order = (10−8)/2 = 1

From the bond orders, $O_2^{2-}$ is the least stable.

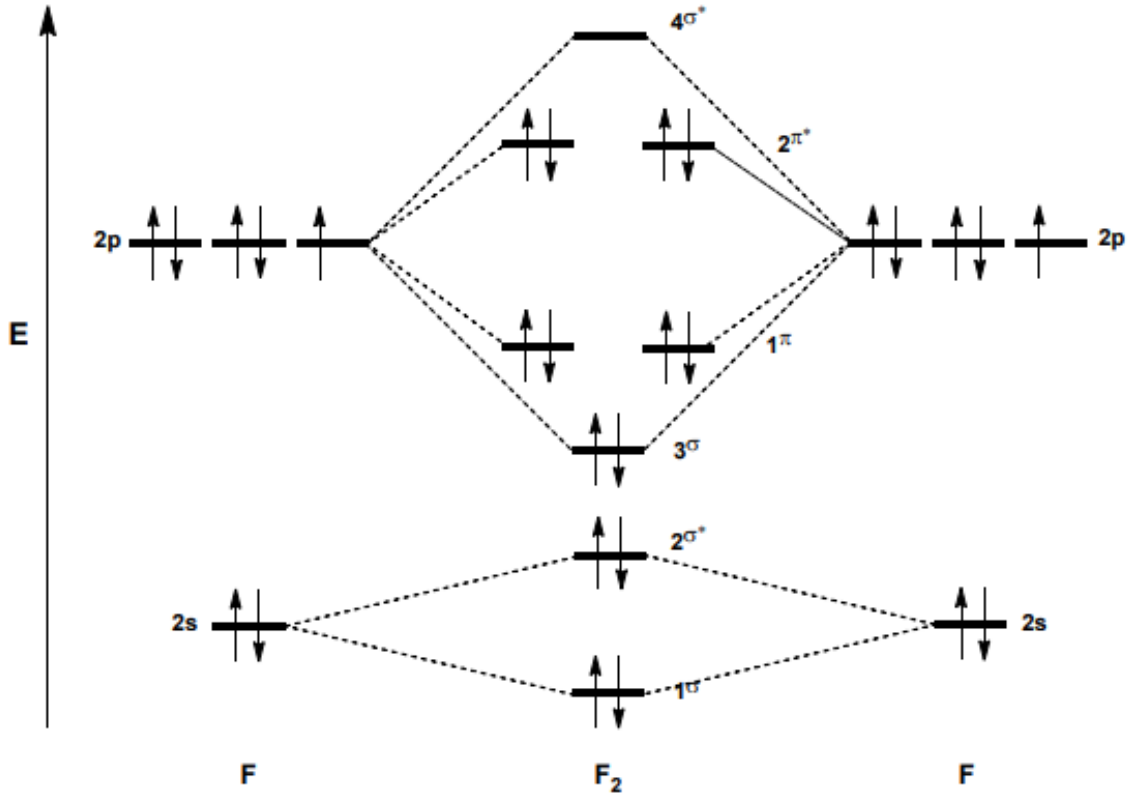
## Question 3: Molecular Orbital Diagram of Fluorine

(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 $F_2$?

Answer:

(a) The electron configuration for F is $1s^2 2s^2 2p^5$. Each F has 7 valence electrons and $F_2$ has 14 valence electrons.




(b) If two electrons are added, they go into the antibonding orbital. This decreases the F-F bond order from 1 to 0. As such, when two electrons are added to $F_2$, the F-F bond breaks and two $F^-$ anions are formed.

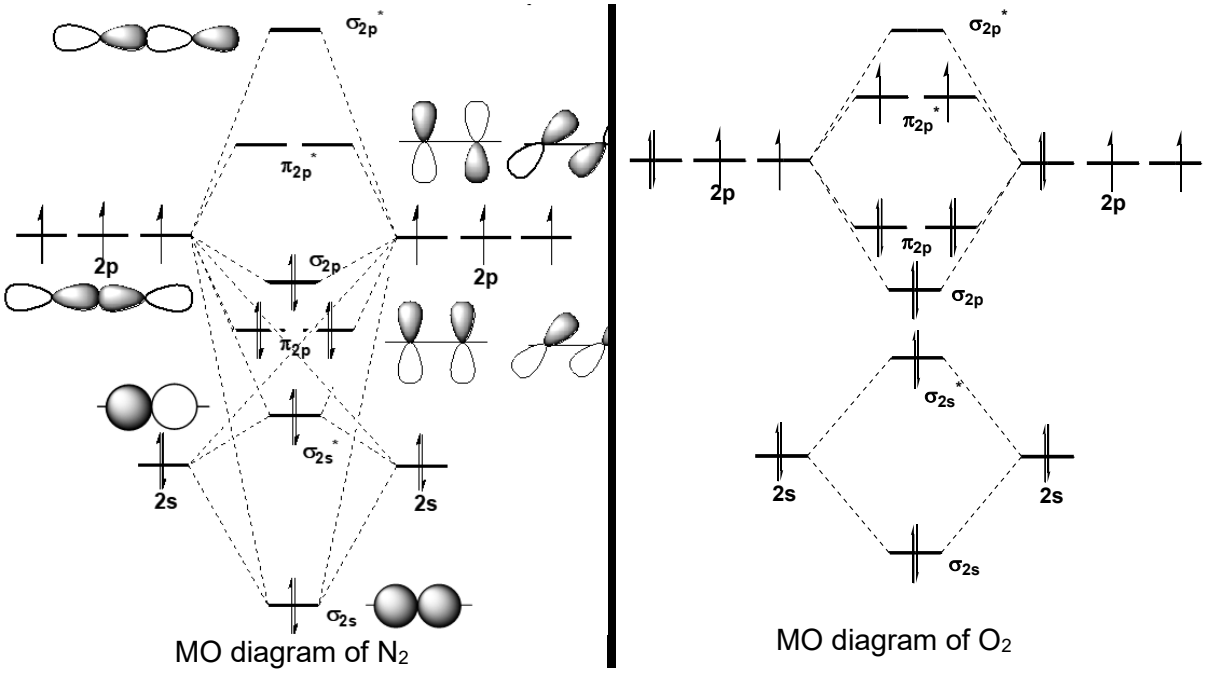
## Question 4: Molecular orbitals within $F_2^{\pm}$

The MOs depicted below are derived from 2p atomic orbitals in $F_2^+$. Provide their orbital designations. State which is occupied by at least one electron in $F_2^+$ and which is occupied by only one electron in $F_2^+$.

π*, σ, π and σ* respectively. π*, σ and π are occupied by at least one electron in $F_2^+$. π* is occupied by only one electron in $F_2^+$.

## Molecular Orbital Diagram of Nitrogen – Extra Reading

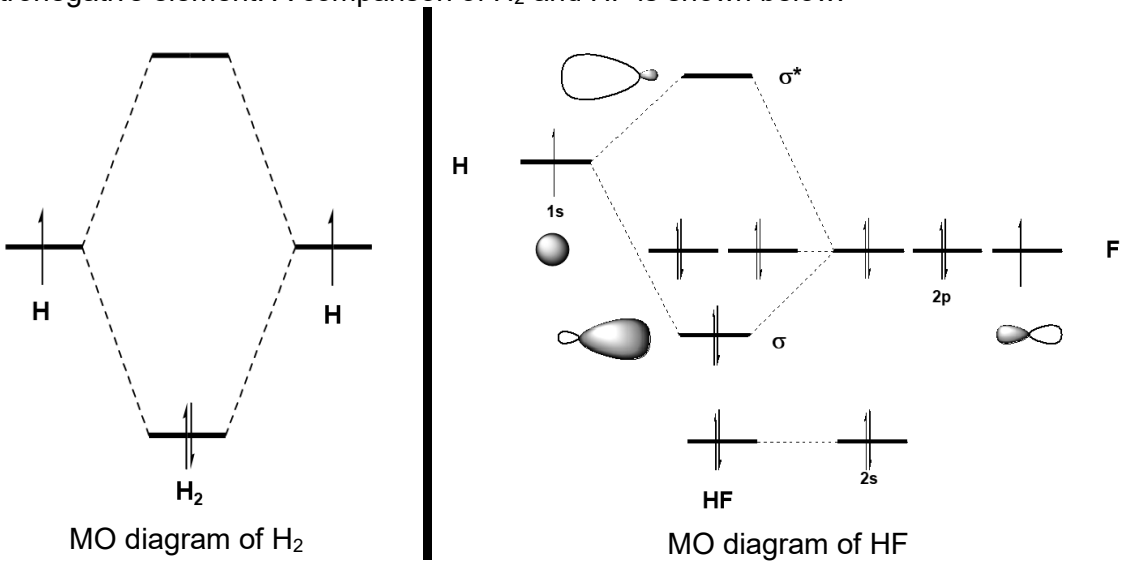
The molecular orbitals within $N_2$ are arranged slightly differently from that of $O_2$ because for $N_2$, the 2s and 2p orbitals are relatively similar in energy levels which results in significant interaction between them (i.e. 2s and 2p orbitals mix with one another).




Due to significant interaction between 2s and 2p orbitals, $\sigma_{2s}$ is stabilised more and $\sigma_{2p}$ is stabilised less. Hence the $\sigma_{2s}$ MO energy is lowered and the $\sigma_{2p}$ MO energy is increased to a level where it is above that of $\pi_{2p}$.

## Molecular orbital diagram for diatomic species with different electronegativity – Extra

The construction of MO for diatomic species with different electronegativity is similar to that for those with the same electronegativity, except that the atomic orbitals of the more electronegative element will be lower in energy than that of less electronegative element and consequently, the few MOs with the lower energies will resembles more of the more electronegative element. A comparison of $H_2$ and HF is shown below.



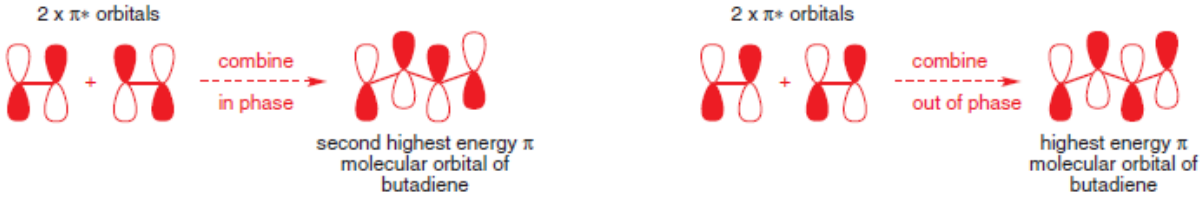
# Conjugated and Aromatic Molecules

In butadiene and benzene, every carbon atom is $sp^2$ hybridised with one p orbital available to overlap with its neighbours. The uninterrupted chain of p orbitals is a consequence of 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.

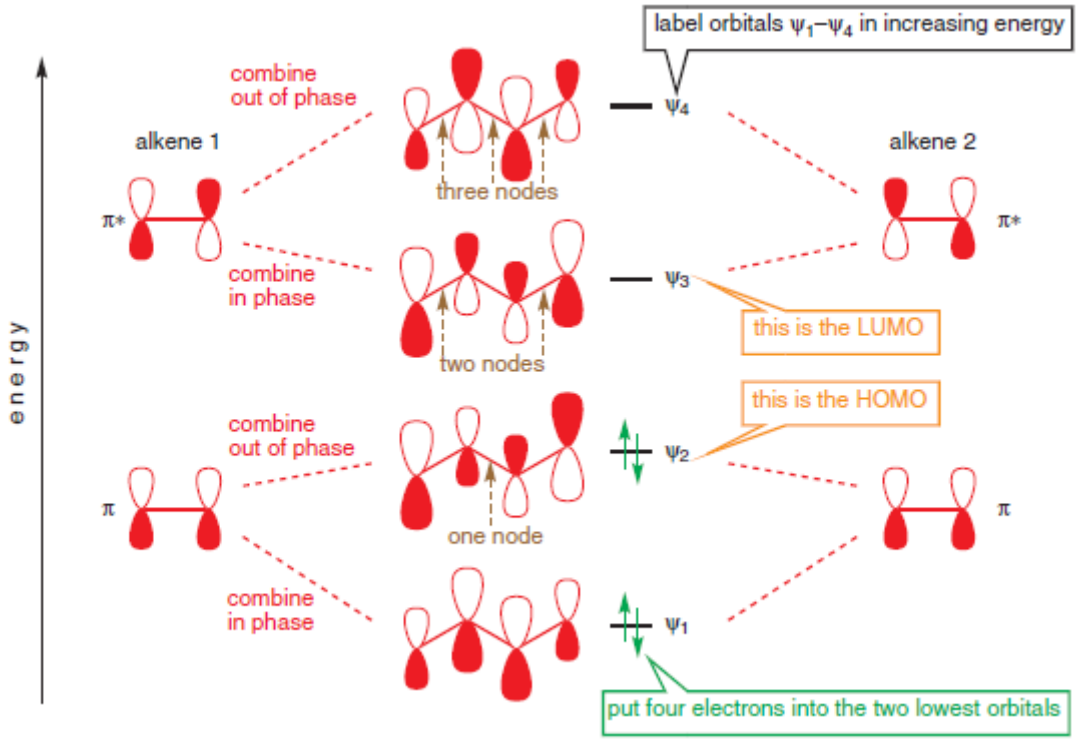
## Polyalkene – Butadiene

Butadiene has two π bonds, each made up of two p orbitals: a total of four atomic orbitals. We'd 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:

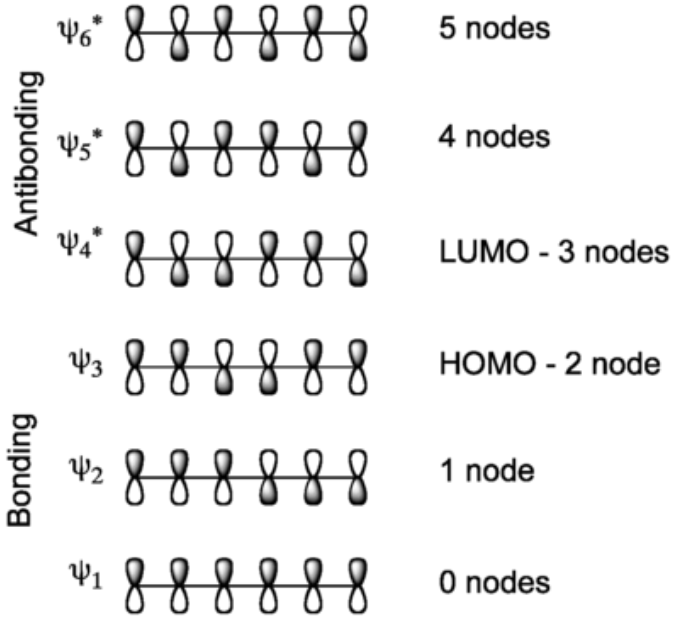



We can represent all four molecular orbitals like this, stacked up in order of their energy in a molecular orbital energy level diagram. With four orbitals, we can't just use '*' to represent antibonding orbitals, so conventionally they are numbered ψ1–ψ4 (ψ is the Greek letter psi).

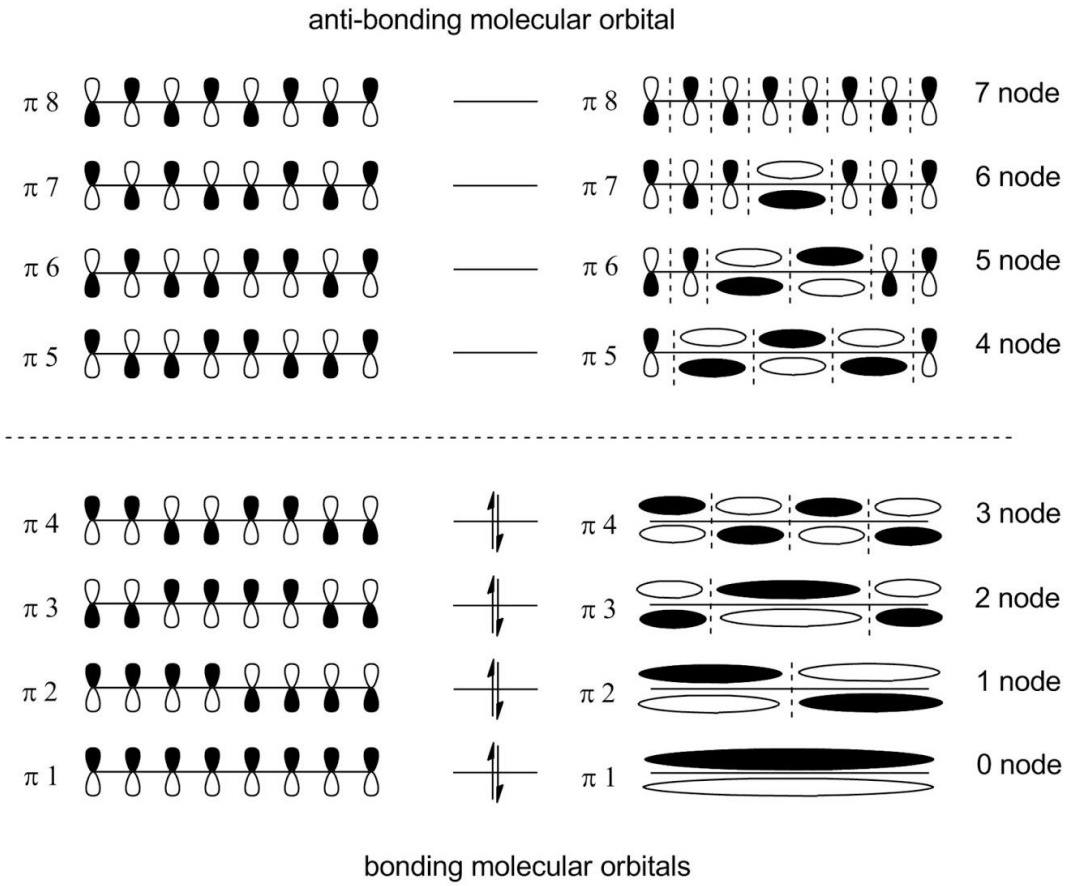


The number of nodes (changes in phase as you move from one orbital to the next) increases from zero in $\psi_1$ to three in $\psi_4$. One of the consequences of conjugation is to lessen the gaps between filled and empty orbitals, and so allow absorption of light of a longer wavelength.

**1,3,5-hexatriene**



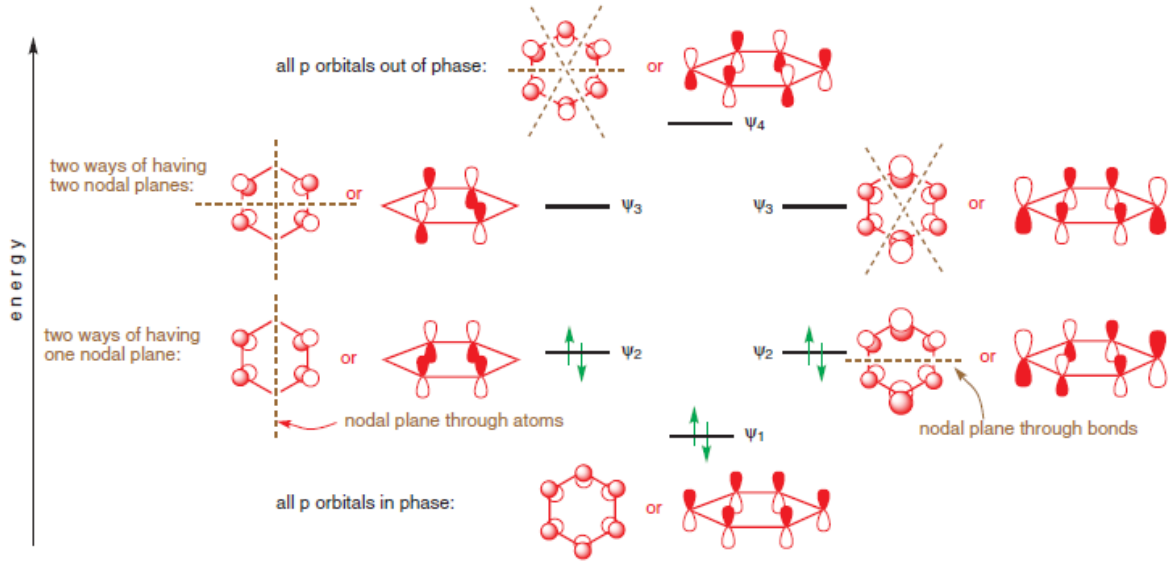

**1,3,5,7-octatetraene**



## Benzene

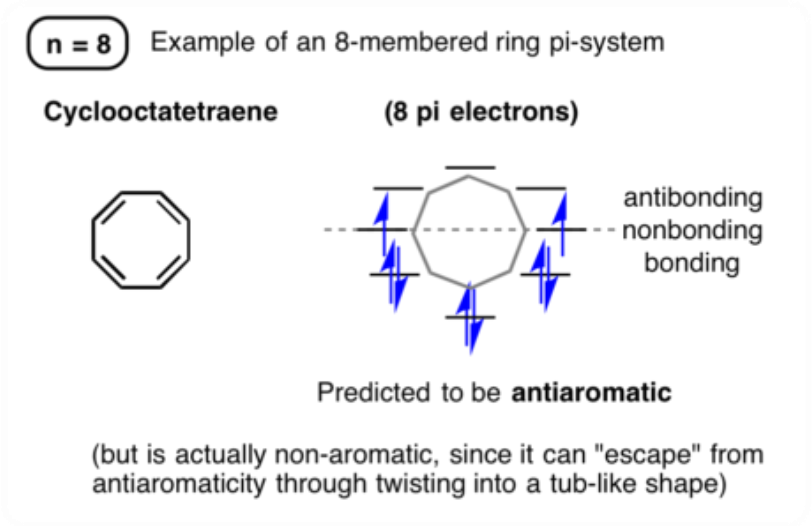
In benzene, all six p orbitals can combine to form six new molecular orbitals, and the electrons in these orbitals form a ring of electron density above and below the plane of the molecule. The electrons are in molecular orbitals spread equally over all the carbon atoms.

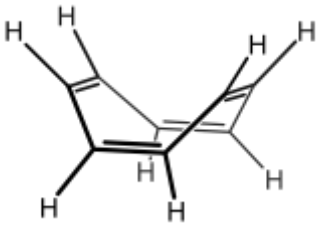
We can think of the π molecular orbitals of benzene as resulting from the combination of the six p orbitals in a ring and, as with butadiene, each successively higher energy orbital contains one more node. This is what we get for benzene:




The molecular orbital lowest in energy, $\psi_1$, 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 $\psi_2$. There are likewise two ways of arranging two nodal planes and again there are two degenerate molecular orbitals $\psi_3$. The final molecular orbital $\psi_4$ 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.

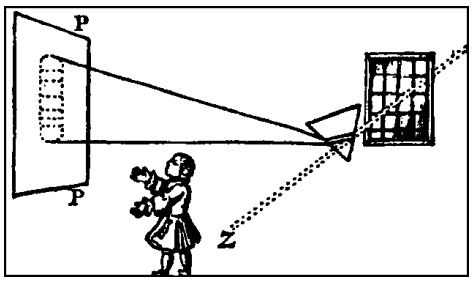
## What about 1,3,5,7-cyclooctatetraene? – Extra Reading



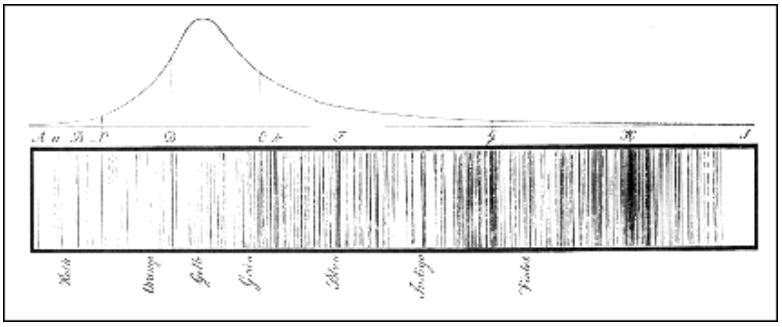
## A Brief History of Spectroscopy

In 1666, Sir Isaac Newton allowed sunlight from a small, circular hole to fall on a prism, producing a rainbow of colour, thus proving that **light was not homogeneous**. He called this array of colours “a spectrum”.



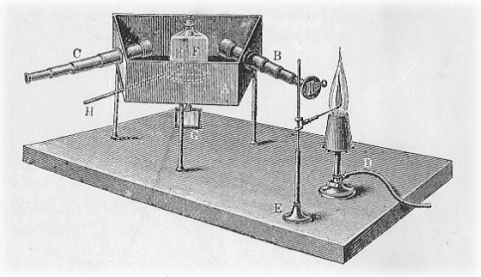

Newton's experimental arrangement (Voltaire's Eléments de la Philosophie de Newton, 1738).

In 1814, Joseph von Fraunhofer while measuring the dispersive powers of various kinds of glass for light of different colours, noticed that a bright 'orange' line (due to sodium) in the **emission spectrum** of the flame he was using was in the same position as the dark D-line in the **absorption spectrum** of sunlight. This same line had been observed in flames from alcohol and sulfur as well as from candles.



The thin black lines Fraunhofer observed in the sun’s spectrum.

In 1859, Gustav Robert Kirchhoff (a physicist) and Robert Wilhelm Bunsen (a chemist; inventor of Bunsen burner) made a prism-based device that separated the visible light emitted when substances were vaporised in the flame of Bunsen's specially-designed burner (it had a high-temperature, non-luminous flame). They determined that each gas had its own signature spectrum. Kirchhoff also realised that when emitted light passed through a cooler gas of the same substance, the bright spectral lines were replaced by dark ones - in the same position. Kirchhoff had discovered the secret to the Sun's Fraunhofer lines - the dark lines in the solar spectrum (the light from the Sun) were the same as the emission lines observed by various heated chemical substances.




Spectroscope of Kirchhoff and Bunsen.

## Principles of Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic (EM) radiation with matter. The results of how these physical quantities vary are reflected in a **spectrum** of the sample.

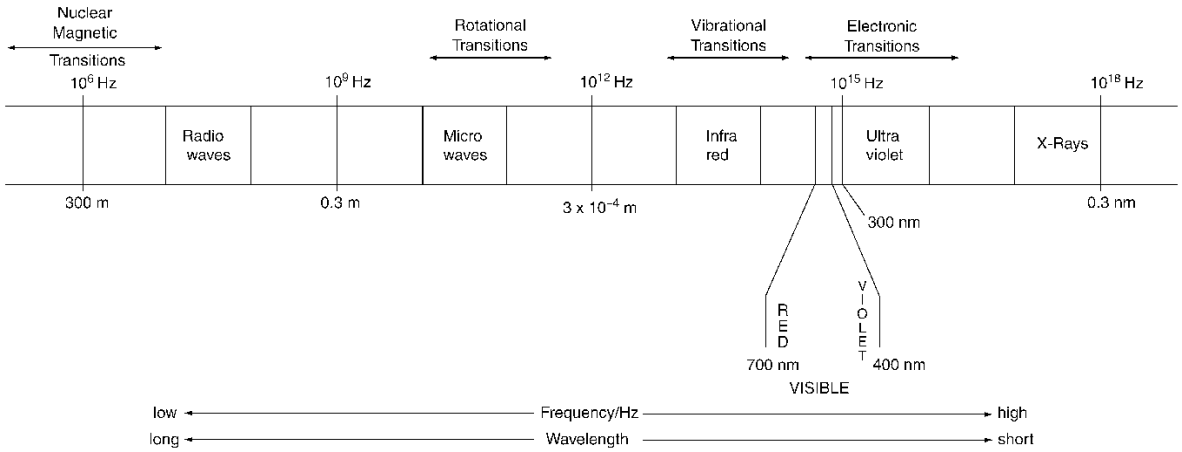
A **spectrum** is a diagram that shows the amount of EM radiation emitted or absorbed as a function of wavelength or frequency. It can take the form of a graph of intensity vs. wavelength or frequency. Depending on the frequency of light used, it can give us different information about the chemical being studied, *e.g.* functional groups or spatial arrangements of atoms.

The EM spectrum covers a wide range of wavelengths and frequencies, from the ultra-short 1 nm ($1 \times 10^{-9}$ m) wavelengths of X-rays through to the very long 3000 km ($3 \times 10^{6}$ m) wavelengths of the ELF (extra-low frequency) systems used to communicate with nuclear submarines. Of particular interest in the study of H3 Pharmaceutical Chemistry will be the ultraviolet/visible (UV/Vis), infra-red (IR) and radio-wave regions.

**UV/Vis spectroscopy:** the excitation of a particle at an electronic ground state to an electronic excited state. This electronic transition will only take place in the ultraviolet/visible region of the EM spectrum.

**IR spectroscopy:** arises due to different modes of vibration of bonds, giving rise to a periodic change in the dipole moment of the molecules. This vibrational transition takes place in the infra-red region.

**NMR spectroscopy:** arises due to the nature of immediate chemical or electronic environment of nuclei, giving rise to a flip in the spin state of the nucleus. This "flipping" of the spin state of nucleus takes place in the radio-wave region.




The electromagnetic spectrum with f and λ scales.

EM radiation can be thought to behave as both particles and waves due to the **Wave Particle Duality** and travels at constant speed, the speed of light ($3.00 \times 10^{8}$ ms$^{-1}$), in the form of photons. **Photons** are particles with considerable wave-like properties, that have no mass, but are associated with a quantity of energy. They can be considered packets of energy, and the amount of **energy is proportional to its frequency**.

The relationship, put forward by Max Planck:

$$\boldsymbol{E = hf}$$

where ***E*** = energy in J, ***h***, Planck's constant = $6.63 \times 10^{-34}$ Js, ***f*** = frequency in Hz.

## Types of Energy in Spectroscopy

The relationship, put forward by Max Planck:

$$E = hf \qquad [1]$$

The frequency and wavelength of EM radiation are related by the speed of light, c.

$$c = f\lambda \qquad [2]$$

Combining these two equations give us: $E = \frac{hc}{\lambda}$ **[3]**

We can see that the higher the frequency or shorter the wavelength, more energy is associated with that photon, and vice versa.

**Example 1**
Calculate the energy of a photon of yellow light with a wavelength of 600 nm.

$$E = \frac{(6.63 \times 10^{-34})(3.00 \times 10^{8})}{600 \times 10^{-9}}$$

$\therefore E =$ **$3.31 \times 10^{-19}$ J**

Convert this energy per photon into an energy *per mole* of photons.

To do so, we multiply the above value by the Avogadro constant.

$E = 3.31 \times 10^{-19} \times 6.02 \times 10^{23} =$ **200 kJ mol$^{-1}$**

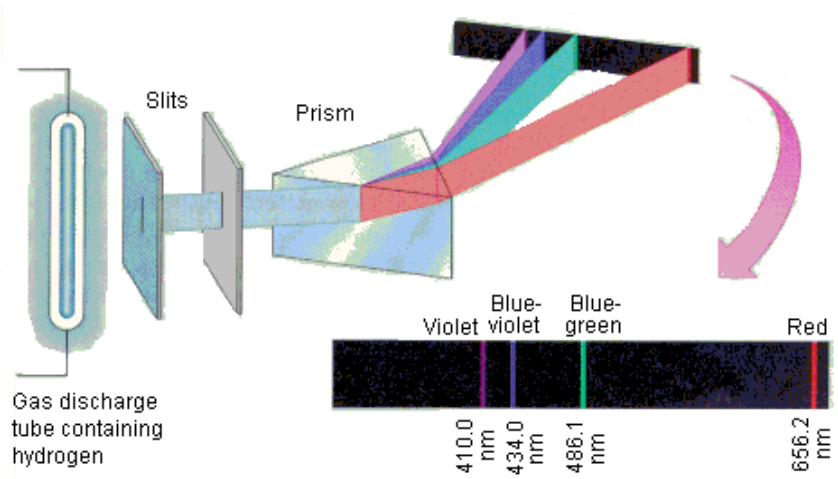
The following table shows the energy-per-mole-of-photons for some important areas of the EM spectrum.

| region of spectrum | energy transition | average frequency, f/Hz | average wavelength, λ/m | average energy per mole |
|---|---|---|---|---|
| X-ray | Bond breaking | $1 \times 10^{17}$ | $3 \times 10^{-9}$ | 20,000 kJ mol$^{-1}$ |
| UV/Vis | Electronic | $1 \times 10^{15}$ | $3 \times 10^{-7}$ | 200 kJ mol$^{-1}$ |
| IR | Vibrational | $1 \times 10^{13}$ | $3 \times 10^{-5}$ | 2 kJ mol$^{-1}$ |
| Microwave | Rotational | $1 \times 10^{10}$ | $3 \times 10^{-2}$ | 2 J mol$^{-1}$ |
| Radio waves | Nuclear spin (NMR)<br>Electron spin (ESR) | $1 \times 10^{18}$ | 3 | 0.02 J mol$^{-1}$ |

*Electronic energy:* movement of electrons between electronic energy levels (or orbitals)
*Vibrational energy:* regular periodic stretching and relaxing and the bending of bonds
*Rotational energy:* speed of rotation of the molecule around various axes
*Translational energy:* how fast the molecule is moving through space
*Nuclear magnetic energy:* interaction of magnetic field with nuclei that have magnetic moments

## Quantisation of Energy Levels

Consider the following set up to determine the emission spectrum of hydrogen. An electric current is used to excite the sample of hydrogen gas.



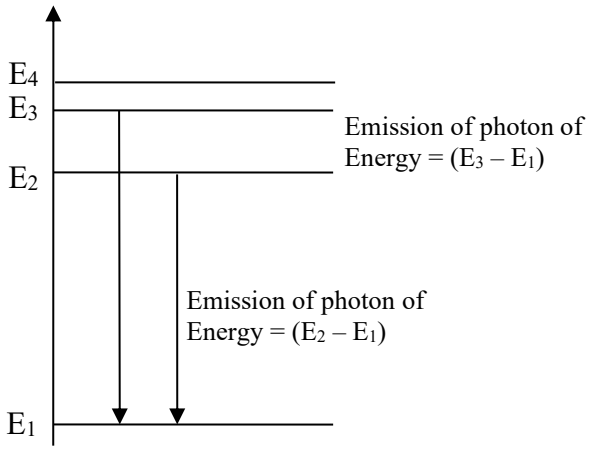

The 4 narrow bands that appear have the following characteristics:

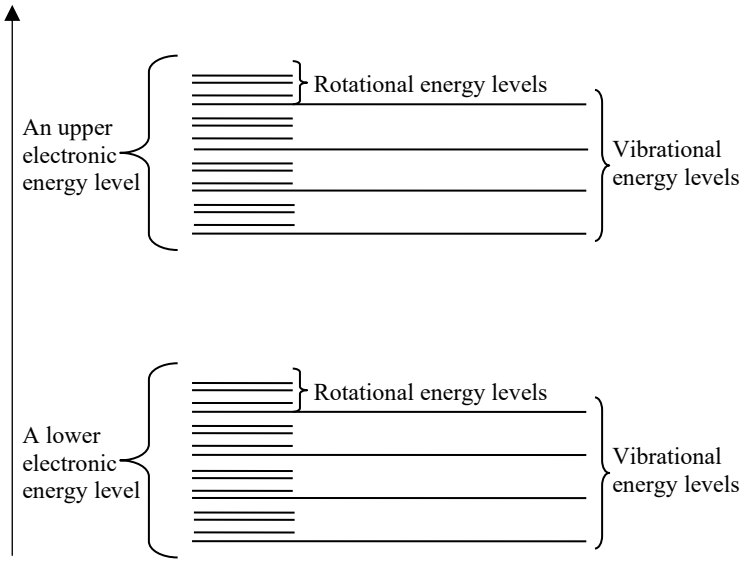
| Wavelength / nm | Colour |
|---|---|
| 656.2 | Red |
| 486.1 | Blue-green |
| 434.0 | Blue-violet |
| 410.0 | Violet |

From the data, we can conclude that these hydrogen atoms emitted radiation at **certain wavelengths** (or frequencies) and hence only photons of certain energies were emitted.

These photons were emitted as a result of electrons moving from a higher energy level to a lower energy level. The energy of the photons emitted would then be equal to the energy difference of the quantised energy levels.

This implies that there are only a limited number of energy levels within the hydrogen atom for electrons to be excited to. Since these energy levels are finite in number, they are "countable" (discrete) and we say that they are **quantised**.






Energy levels in a molecule.

The large energy differences between electronic energy levels coincide with the **ultraviolet/ visible radiation** region.

Vibrational energy levels are ten times closer and their energy difference corresponds to the **infra-red** region.

Rotational energy levels are even smaller and correspond to the **microwave** region. They will not be discussed in H3 Chemistry.

## Types of Spectroscopy

### Absorption Spectroscopy

The sample is irradiated with electromagnetic radiation and the energies at which the sample absorbs are recorded. Examples: UV/Vis spectroscopy, IR spectroscopy. This form of spectroscopy is most important in the identification of organic compounds.

Since energy levels are quantised, only photons of energy equal to that of the energy gap will be absorbed.

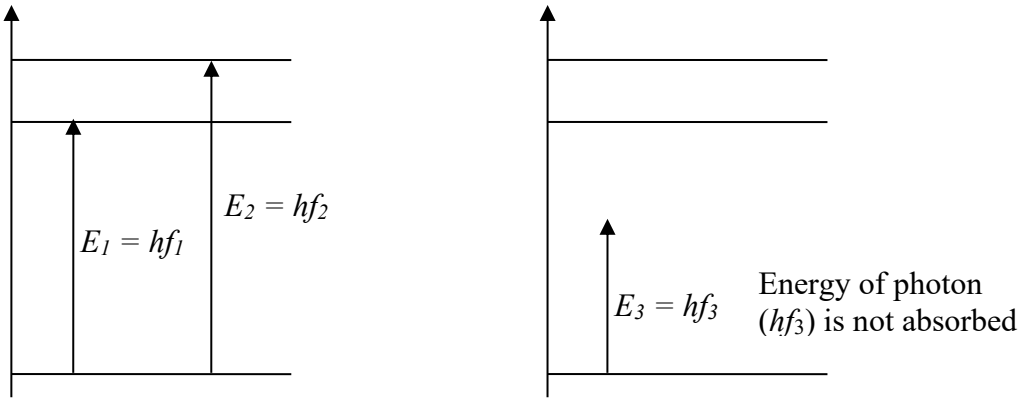



Illustration of certain packets of energy allowing transitions, but not others.

Since the energy levels of molecules are quantised, they will be expected to absorb EM radiation of specific frequencies / energies (*e.g.* the differences in vibrational energy levels are of the magnitude such that infrared radiation is absorbed).

### Emission Spectroscopy (Not in Syllabus)

The sample is first allowed to absorb energy (*e.g.* by using high temperatures) and then radiates this energy as light. This radiation of energy is recorded in a spectrum.
Examples: Atomic Emission Spectroscopy (useful for identifying metals).

### Scattering Spectroscopy (Not in Syllabus)

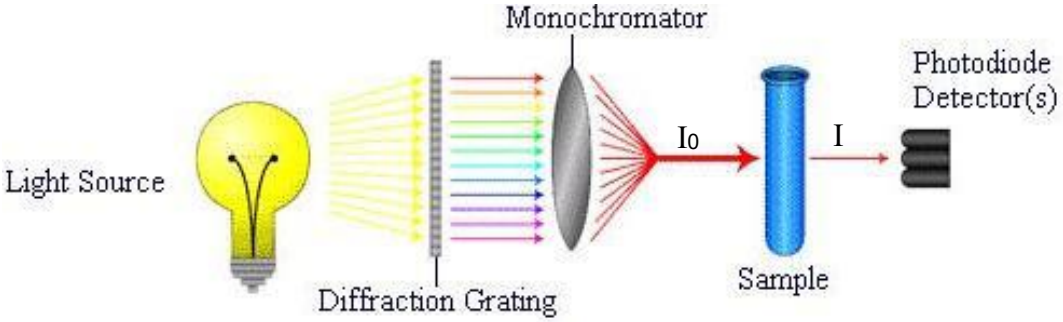
The sample is irradiated with electromagnetic radiation and the way in which the radiation is scattered will be measured. Examples: Raman spectroscopy, X-Ray crystallography.

## Spectroscopic Measurements

The structural information of an unknown compound can be studied using absorption spectroscopy which measures the amount of radiation absorbed at each frequency. Generally, as a beam of radiation with intensity $I_0$ is absorbed in its passage through an unknown sample, its intensity decreases.

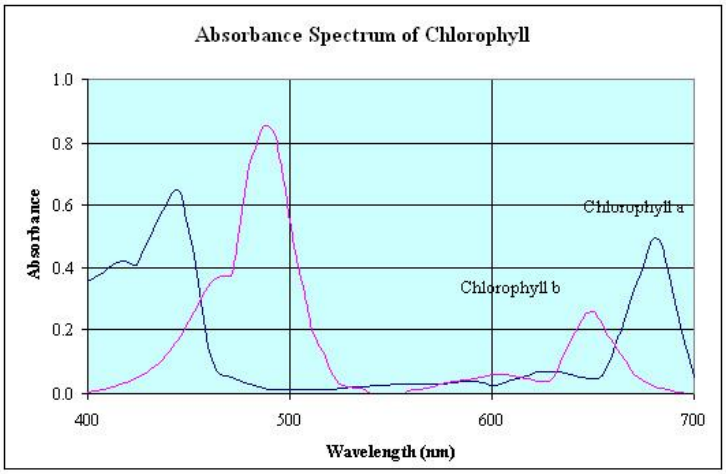
The measurement of amount of radiation absorbed can be determined by comparing the intensities of the emerging beam (I) with the incident beam ($I_0$). These measurements are expressed graphically by a spectrum, which plots the radiation as a function of wavelength or frequency. Two quantities can be used to measure the intensity of the radiation: **percent transmittance** (*%T*) and **absorbance** (*A*).

$$T = \frac{I}{I_0} \times 100\% \qquad A = log_{10}\left(\frac{I_0}{I}\right)$$




Simple illustration of a spectrometer used in UV/Vis and IR spectrometry.

**UV/Vis spectra** are presented as a graph of ***absorbance*** against ***wavelength (λ)***.

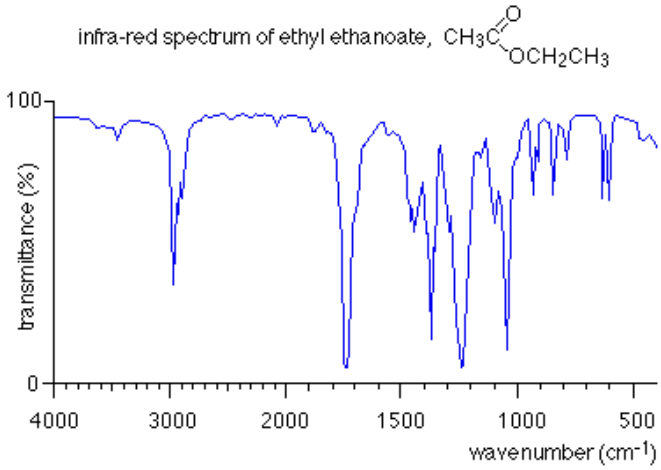


**IR spectra** are presented as a graph of ***transmittance*** against ***frequency***. The units for frequency are however not in Hz but $cm^{-1}$, known as ***wavenumbers***. It is the reciprocal of wavelength in cm, or the number of wavelengths per cm. It is related to Hz as follows:

$$f = c \times \frac{1}{\lambda} \qquad [c = 3.00 \times 10^{8} \text{ m s}^{-1} \Longrightarrow c = 3.00 \times 10^{10} \text{ cm s}^{-1}]$$

**Example 2**
Calculate the frequency in Hz for an IR frequency of wavenumber 2000 $cm^{-1}$.

$f = 3.00 \times 10^{10} \times 2000 =$ **$\underline{6.00 \times 10^{13}\ \text{Hz}}$**




**NMR spectra** are presented as a graph of ***absorbance*** against ***change of frequency*** in parts per million (symbol δ). This frequency scale is chosen because the **actual** frequency of absorption of a peak depends on the irradiating frequency, which in turn depends on strength of the magnetic field around the sample. There is no absolute frequency at which a particular absorption occurs.