CHEMISTRY (ALLIED)

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For, B.Sc Forensic Science students

WHAT IS SCIENCE ?

Science (from the Latin word *scientia*, meaning "knowledge") is a systematic enterprise that builds and organizes knowledge in the form of testable explanations and predictions about the universe.

SCIENCE			
	Empirical Science		Formal Science
Basic	Physics, Chemistry, Biology, Earth science, and space science	Anthropology, Economics, Political science, Sociology, Human geography, and psychology	Logic, mathematics and statistics
Applied	Engineering, Agricultural science, Medicine, and materials science	Business administration, public policy, marketing, law, pedagogy, and international development	Computer science

CHEMISTRY

Chemistry is the scientific discipline involved with the elements and compounds composed of atoms, molecules and ions.
Study of their composition, structure, properties, behaviour and the changes they undergo during a reaction with other substances.

Chemistry: central science because it provides a foundation for understanding both basic and applied scientific disciplines at a fundamental level.

Branches of Chemistry:

- **Organic Chemistry**
- **Inorganic Chemistry**
- **Physical Chemistry**

Branches In Chemistry

Organic Chemistry: The word organic refers to the compounds which contain the carbon atoms in it, the study of carbon-hydrogen and its compounds.

Ex. Hydrocarbons, polymers, etc.

Inorganic Chemistry: The study of compounds, which does not consist of carbon-hydrogen atoms in it. In simple words, it is opposite to that of Organic Chemistry. The substances which do not have carbon-hydrogen bonding are the metals, salts, chemical substances, etc.

Ex. Metals, non-metals, noble gases, etc.
Many of the elements are technologically important: titanium, iron, nickel and copper, for example, are used structurally and electrically.

Physical chemistry: Branch of chemistry concerned with interactions and transformations of materials. Unlike other branches, it deals with the principles of physics underlying all chemical interactions seeking to measure, correlate, and explain the quantitative aspects of reactions.
Ex. gas laws, concepts and principles for instruments

Introduction to Inorganic Chemistry

Todays Topic: Atomic structure -de Broglie matter wave, Heisenberg uncertainty Principle.

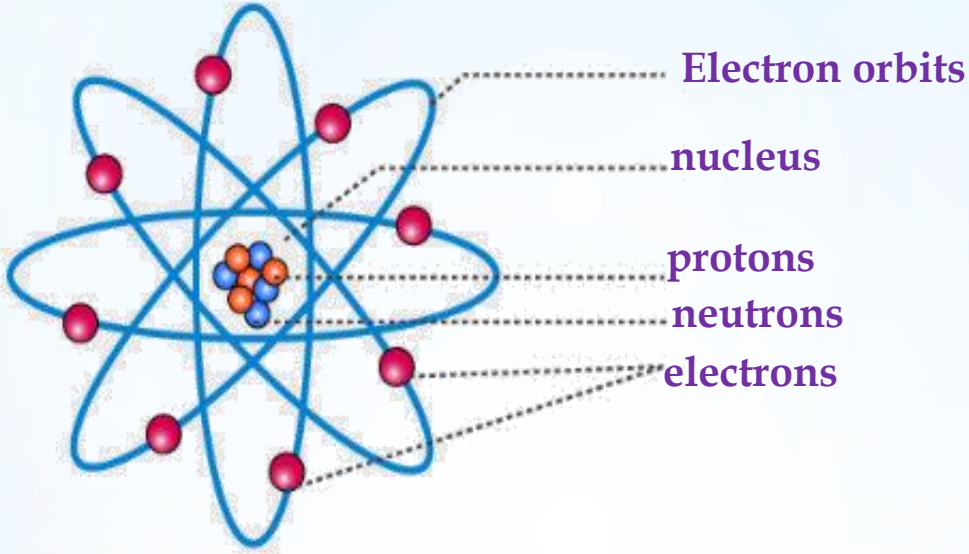
Atom: It is the smallest unit of ordinary matter that forms a chemical element. Every solid, liquid, gas, and plasma is composed of neutral or ionized atoms. Atoms are extremely small, typically around 100 picometers (1X 10^{-12}m).

Matter is any substance that has mass and takes up space by having volume.

Atomic structure: It refers to the structure of atom comprising a nucleus (center) in which the protons (positively charged) and neutrons (neutral) are present.
The negatively charged particles called electrons revolve around the center of the nucleus.
The study about the structure of atom gives a great insight into the entire class of chemical reactions, bonds and their physical properties to produce new chemicals.

Structure of the atom

The first scientific theory of atomic structure was proposed by John Dalton in 1800s.



The atomic structure of an element refers to the constitution of its nucleus and the arrangement of the electrons around it. Primarily, the atomic structure of matter is made up of protons, electrons and neutrons.

To study or understand about the elements, structure of the atom is must.

What is Element

- A substance that cannot be broken down into simpler substances by chemical means.
- An element is composed of atoms that have the same atomic number, that is, each atom has the same number of protons in its nucleus as all other atoms of that element.
- Today 117 elements are known, of which 92 are known to occur in nature, while the remainder have only been made with particle accelerators.
- Eighty-one of the elements have isotopes that are stable.

- The others, including technetium, promethium, and those with atomic numbers higher than 83, are radioactive.

The most notable contributions to the structure of the atom were by the following scientists.,
John Dalton, J.J. Thomson, Ernest Rutherford and Niels Bohr.
Their ideas and the contributions on the structure of the atom were remarkable.

Dalton's Atomic Theory

According to Dalton's atomic theory, involve a rearrangement of atoms to form products.

The following are the postulates of his theory:

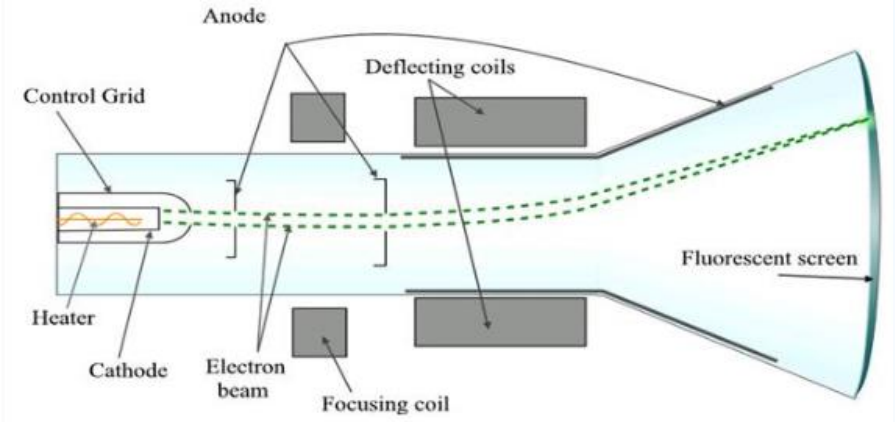
- Every matter is made up of atoms.
- Atoms are indivisible.
- Specific elements have only one type of atoms in them.
- Each atom has its own constant mass that varies from element to element.
- Atoms undergo rearrangement during a chemical reaction.
- Atoms can neither be created nor be destroyed but can be transformed from one form to another

Demerits of Dalton's Atomic Theory

- *The theory was unable to explain the existence of isotopes*
- *Nothing about the structure of atom was appropriately explained*
- *Later, the scientists discovered particles inside the atom that proved, the atoms are divisible*
- *Didn't explained the subatomic particles.*

JJ Thomson's atomic model

The concept of the electrons around the nucleus. He was later awarded the Nobel prize for the **discovery of "electrons"**. His work is based on an experiment called cathode ray experiment.



- *Based on conclusions from his cathode ray experiment, Thomson described the atomic structure as a positively charged sphere into which negatively charged electrons were embedded.*
- *Thomson's atomic structure described atoms as electrically neutral, i·e· the positive and the negative charges were of equal magnitude.*

Limitations of Thomson's Atomic Structure:

Thomson's atomic model does not clearly explain the stability of an atom. Also, further discoveries of other subatomic particles, couldn't be placed inside his atomic model·

Rutherford's Structure of Atom

Modified the atomic structure with the discovery of another **subatomic particle called "Nucleus"**. His atomic model is based on the Alpha ray scattering experiment.

- The nucleus is at the centre of an atom, where most of the charge and mass are concentrated.
- Atomic structure is spherical.
- Electrons revolve around the nucleus in a circular orbit, similar to the way planets orbit the sun.

Limitations of Rutherford Atomic Model:

- If electrons have to revolve around the nucleus, they will spend energy and that too against the strong force of attraction from the nucleus, they will lose all their energy and will fall into the nucleus so the stability of atom is not explained.

- If electrons continuously revolve around the 'nucleus, the type of spectrum expected is a continuous spectrum. But in reality, what we see is a line spectrum.

Subatomic Particles

Protons

Protons are positively charged subatomic particles. The charge of a proton is 1e, which corresponds to approximately 1.602×10^{-19}

The mass of a proton is approximately 1.672×10^{-24}

Protons are over 1800 times heavier than electrons.

The total number of protons in the atoms of an element is always equal to the atomic number of the element.

Neutrons

The mass of a neutron is almost the same as that of a proton i.e. 1.674×10^{-24}

Neutrons are electrically neutral particles and carry no charge.

Different isotopes of an element have the same number of protons but vary in the number of neutrons present in their respective nuclei.

Electrons

The charge of an electron is -1e, which approximates to -1.602×10^{-19}

The mass of an electron is approximately 9.1×10^{-31}.

Due to the relatively negligible mass of electrons, they are ignored when calculating the mass of an atom.

*Bohr's Atomic Theory

Neils Bohr put forth his model of the atom in the year 1915. This is the most widely used atomic model to describe the atomic structure of an element which is based on Planck's theory of quantization.

Postulates:

- ✓ The electrons inside atoms are placed in discrete orbits called "stationery orbits".
- ✓ The energy levels of these shells can be represented via quantum numbers.
- ✓ Electrons can jump to higher levels by absorbing energy and move to lower energy levels by losing or emitting its energy.
- ✓ As longs as, an electron stays in its own stationery, there will be no absorption or emission of energy.
- ✓ Electrons revolve around the nucleus in these stationery orbits only.
- ✓ The energy of the stationary orbits is quantized.

Limitations of Bohr's Atomic Theory:

- ➢ Bohr's atomic structure works only for single electron species such as H, He^{+}, Li^{2+}, Be^{3+}, ….
- ➢ When the emission spectrum of hydrogen was observed under a more accurate spectrometer, each line spectrum was seen to be a combination of no of smaller discrete lines.
- ➢ Both Stark and Zeeman effects couldn't be explain using Bohr's theory.

Dual Nature of Matter

The electrons which were treated to be particles, the evidence of photoelectric effect shows they also have wave nature. This was proved by "Thomas young" with the help of his double slit experiment.

De-Broglie concluded that since nature is symmetrical, so should be light or any other matter wave.

Matter has both particle and wave nature, which was clearly explained by the De-Broglie experiments, for the measurement of the wavelength of the particles.

De Broglie's hypothesis stated that there is symmetry in nature and that if light and radiation behave as both particles and waves, matter too will have both the particle and wave nature.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The 'Lambda' here represents the wavelength of the particle and 'p' represents the momentum of the particle.

The significance of the de Broglie relationship is that it proves mathematically that matter can behave as a wave. In layman terms, de Broglie equation says that every moving particle – microscopic or macroscopic –has its own wavelength.
For macroscopic objects, the wave nature of matter is observable.

Heisenberg's Uncertainty principle

Quantum mechanics is the discipline of measurements on the minuscule scale. That measurements are in macro and microphysics can lead to very diverse consequences.

Heisenberg uncertainty principle or basically uncertainty principle is a vital concept in Quantum mechanics.

The uncertainty principle says that both the position and momentum of a particle cannot be determined at the same time and accurately.

The result of position and momentum is at all times greater than h/4π. The formula for Heisenberg Uncertainty principle is articulated as,

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Where

h is the Planck's constant ($6.62607004 \times 10^{-34}$ m^2 kg/s)

Δ_p is the uncertainty in momentum

Δ_x is the uncertainty in position

We'll go through the questions of the Heisenberg Uncertainty principle.

Problem - 1

Problem 1: The uncertainty in the momentum Δp of a ball travelling at 20m/s is 1×10^{-6} of its momentum. Calculate the uncertainty in position Δx? Mass of the ball is given as 0.5kg.

Known numerics are,

v = 20m/s,

m = 0.5kg,

h = $6.62607004 \times 10^{-34}$ m^2 kg / s

$\Delta p = p\times1\times10^{-6}$

As we know that,

P = m×v = 0.5×20 = 10kgm/s

$\Delta p = 10\times1\times10-6$

$\Delta p = 10^{-5}$

Heisenberg Uncertainty principle formula is given as,

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\Delta \times \geq \frac{h}{4\pi\Delta p}$$

$$\Delta \times \geq \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}} = 0.527 \times 10^{-29} m$$

Atomic Orbitals

- It is a mathematical tool derived from quantum mechanics, to locate the position of the electrons in an atom.
- It is a representation of the three-dimensional volume in which an electron is most likely to be found.
- It cannot be observed experimentally (*electron density* can, however, be observed experimentally).

In atomic theory and quantum mechanics:

An **atomic orbital** is a mathematical function describing the location and wave-like behaviour of an electron in an atom.

Each orbital in an atom is characterized by a unique set of values of the three quantum numbers n, ℓ, and m, which respectively correspond to the electron's energy, angular momentum, and an angular momentum vector component (the magnetic quantum number).

Quantum numbers

- Atomic orbitals can be uniquely defined by a set of integers known as quantum numbers.
- These quantum numbers only occur in certain combinations of values, and their physical interpretation changes depending on whether real or complex versions of the atomic orbitals are employed.

The quantum numbers can be defined as "the sets of numerical values which give acceptable solutions to the Schrödinger wave equation for the hydrogen atom".

Four quantum numbers can describe an electron in an atom completely:

1. Principal quantum number (n)
2. Azimuthal quantum number (ℓ)
3. Magnetic quantum number (m_ℓ)
4. Spin quantum number (s)

The spin-orbital interaction, however, relates these numbers.

Quantum numbers

Principal quantum number:

This describes the electron shell, or energy level, of an electron. The value of 'n' ranges from 1 to the shell containing the outermost electron of that atom, that is

$$n = 1, 2, \ldots$$

For example, in caesium (Cs), the outermost valence electron is in the shell with energy level 6, so an electron in caesium can have an n value from 1 to 6.

Azimuthal quantum number:

Also known as the (angular quantum number or orbital quantum number), this describes the subshell, and gives the magnitude of the orbital angular momentum through the relation.

$$L^2 = \hbar^2 \ \ell \ (\ell + 1)$$

In chemistry and spectroscopy, $\ell = 0$ is called an s orbital, $\ell = 1$ a p orbital, $\ell = 2$ a d orbital, and $\ell = 3$ an f orbital.

The value of ℓ ranges from 0 to $n - 1$, so the first p orbital ($\ell = 1$) appears in the second electron shell ($n = 2$), the first d orbital ($\ell = 2$) appears in the third shell ($n = 3$), and so on: $\ell = 0, 1, 2, \ldots, n - 1$

Uses of Azimuthal quantum number

- A quantum number beginning in n = 3, ℓ = 0, describes an electron in the s orbital of the third electron shell of an atom.
- In chemistry, this quantum number is very important, since it specifies the shape of an atomic orbital and strongly influences chemical bonds and bond angles.
- The azimuthal quantum number can also denote the number of angular nodes present in an orbital.
- For example, for p orbitals, ℓ = 1 and thus the amount of angular nodes in a p orbital is 1.
- Shape of orbital is also given by azimuthal quantum number.

Magnetic quantum number

This describes the specific orbital (or "cloud") within that subshell, and yields the *projection* of the orbital angular momentum *along a specified axis*:

$$L_z = m_\ell \hbar$$

The values of mℓ range from −ℓ to ℓ, with integer intervals,
The s subshell (ℓ = 0) contains only one orbital, and therefore the mℓ of an electron in an s orbital will always be 0.

The p subshell (ℓ = 1) contains three orbitals (in some systems, depicted as three "dumbbell-shaped" clouds), so the mℓ of an electron in a p orbital will be −1, 0, or 1. The d subshell (ℓ = 2) contains five orbitals, with mℓ values of −2, −1, 0, 1, and 2.

Spin quantum number

This describes the spin (intrinsic angular momentum) of the electron within that orbital, and gives the projection of the spin angular momentum *S* along the specified axis:

$$Sz = ms\ \hbar.$$

In general, the values of m_s range from −s to s, where s is the spin quantum number, an intrinsic property of particles:

$$m_s = -s, -s+1, -s+2, ..., s-2, s-1, s.$$

An electron has spin number $s = 1/2$, consequently m_s will be ±1/2, referring to "spin up" and "spin down" states. Each electron in any individual orbital must have different quantum numbers because of the Pauli exclusion principle, therefore an orbital never contains more than two electrons.

Overview of quantum numbers

Name	Symbol	Orbital meaning	Range of values	Value examples
Principal quantum number	n	shell	$1 \leq n$	$n = 1, 2, 3, \ldots$
Azimuthal quantum number (angular momentum)	ℓ	subshell (s orbital is listed as 0, p orbital as 1 etc.)	$0 \leq \ell \leq n - 1$	for $n = 3$: $\ell = 0, 1, 2$ (s, p, d)
Magnetic quantum number (projection of angular momentum)	m_ℓ	energy shift (orientation of the subshell's shape)	$-\ell \leq m_\ell \leq \ell$	for $\ell = 2$: $m_\ell = -2, -1, 0, 1, 2$
Spin quantum number	m_s	spin of the electron ($-1/2$ = "spin down", $1/2$ = "spin up")	$-s \leq m_s \leq s$	for an electron $s = 1/2$, so $m_s = -1/2, +1/2$

Example: The quantum numbers used to refer to the outermost valence electrons of a carbon (C) atom, which are located in the 2p atomic orbital, are; $n = 2$ (2nd electron shell), $\ell = 1$ (p orbital subshell), $m_\ell = 1, 0, -1$, $m_s = 1/2$ (parallel spins).

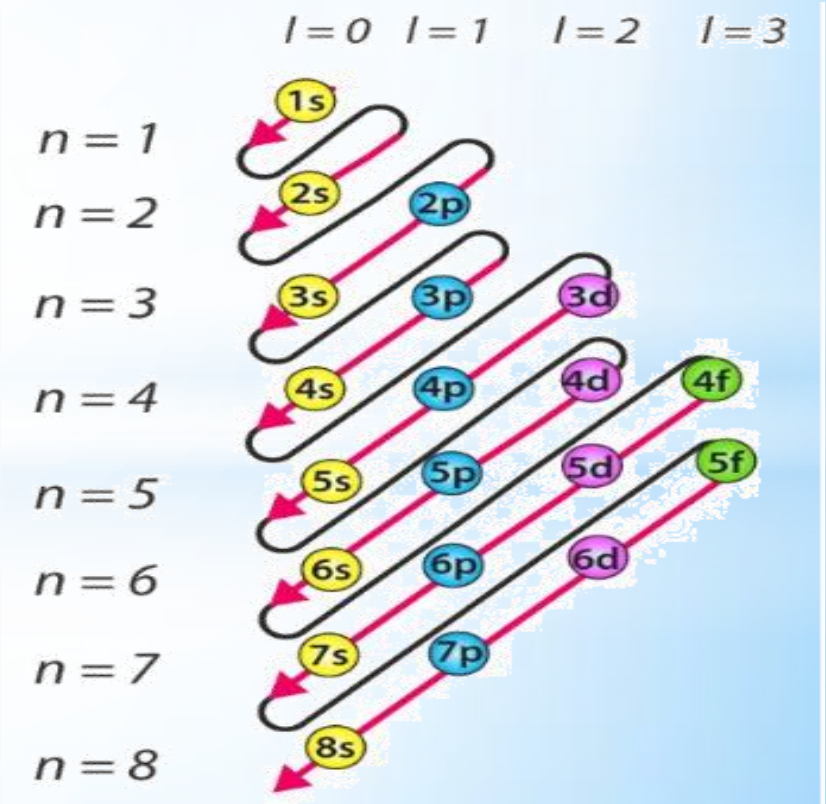
Aufbau Principle

The word 'Aufbau' has German roots with the meaning of 'construct' or 'build up'.
A diagram illustrating the order in which atomic orbitals are filled is provided below.
The Aufbau principle states in which electrons are filled in the atomic orbitals of an atom in its ground state.
It states that electrons are filled into atomic orbitals in the increasing order of orbital energy level.
The available atomic orbitals with the lowest energy levels are occupied before those with higher energy levels.

Here,
'n' refers to the principal quantum number and 'l' is the azimuthal quantum number.

The Aufbau principle can be used to understand the location of electrons in an atom and their corresponding energy levels.

For example, carbon has 6 electrons and its electronic configuration is $1s^2 2s^2 2p^2$.



Salient features of Aufbau Principle

- Electrons first occupy those orbitals whose energy is the lowest. This implies that the electrons enter the orbitals having higher energies only when orbitals with lower energies have been completely filled.
- The order in which the energy of orbitals increases can be determined with the help of the (n+l) rule, where the sum of the principal and azimuthal quantum numbers determines the energy level of the orbital.
- Lower (n+l) values correspond to lower orbital energies. If two orbitals share equal (n+l) values, the orbital with the lower n value is said to have lower energy associated with it.
- The order in which the orbitals are filled with electrons is: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, and so on.

Exception:
The electron configuration of chromium (at. No:24) is $[Ar]3d^5 4s^1$ or $[Ar]3d^4 4s^2$ (as suggested by the Aufbau principle). [Ar] is 18 = $1s^2 2s^2 2p^6 3s^2 3p^6$

Answer: $[Ar]3d^5 4s^1$
[Ar] is 18 = $1s^2 2s^2 2p^6 3s^2 3p^6$

This exception is attributed to several factors such as the increased stability provided by half-filled subshells and the relatively low energy gap between the 3d and the 4s subshells.

Pauli exclusion Principle

An Austrian physicist named Wolfgang Pauli formulated the principle in the year 1925. With this principle, he basically described the behaviour of the electrons.

Each electron should have or be in its own unique state (singlet state).

There are two salient rules that the Pauli Exclusion Principle follows:

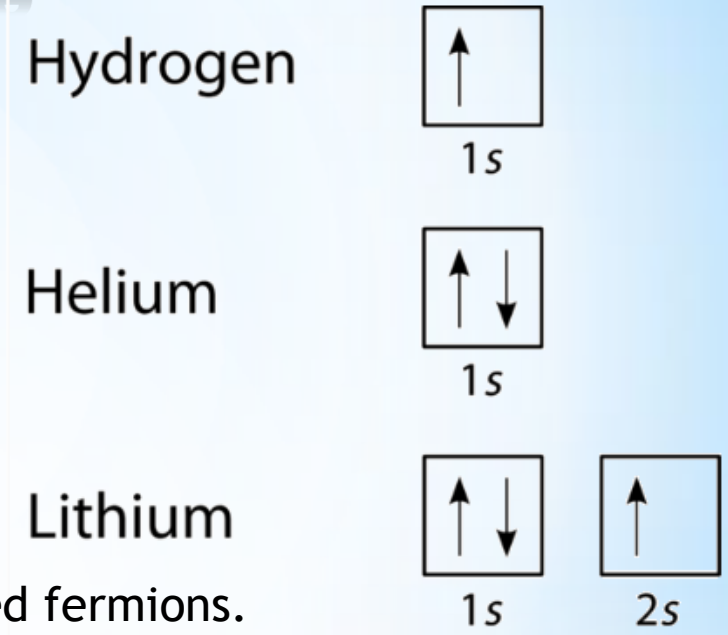
- Only two electrons can occupy the same orbital.
- The two electrons that are present in the same orbital must have opposite spins or it should be antiparallel.

Wolfgang Pauli was also awarded the Nobel prize in the year 1945 for the discovery of the 'Pauli exclusion principle' and his overall contribution in the field of quantum mechanics.

We can take a neutral helium atom as a common example.
The atom has 2 bound electrons and they occupy the outermost shell with opposite spins.
Here, we will find that the two electrons are in the 1s subshell where n = 1, l = 0, and $m_l = 0$. Their spin moments will also be different. One will be $m_s = -1/2$ and the other will be +1/2.
If we draw a diagram then the subshell of the helium atom will be represented with 1 "up" electron and 1 "down" electron.

Formulation of the pauli exclusion principle

- The number of electrons in the outermost shell is also directly related to the different chemical properties that elements possess.
- Elements with the same number of electrons in the outermost shell will have similar properties.



Key Points

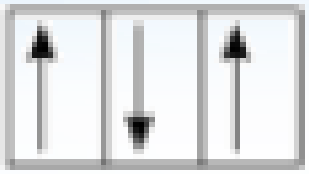
1. Electrons are part of subatomic particles called fermions.
2. Fermions are particles with half-integer spin.
3. All fermions including neutrons and protons (derived particles) obey the Pauli exclusion principle.
4. Pauli exclusion principle states that no two identical electrons (fermions) can have the same quantum state.
5. Bosons, which have integer values of spin do not obey the Pauli exclusion principle. Photons, gravitons, gluons are an example of bosons.

Hunds Rule

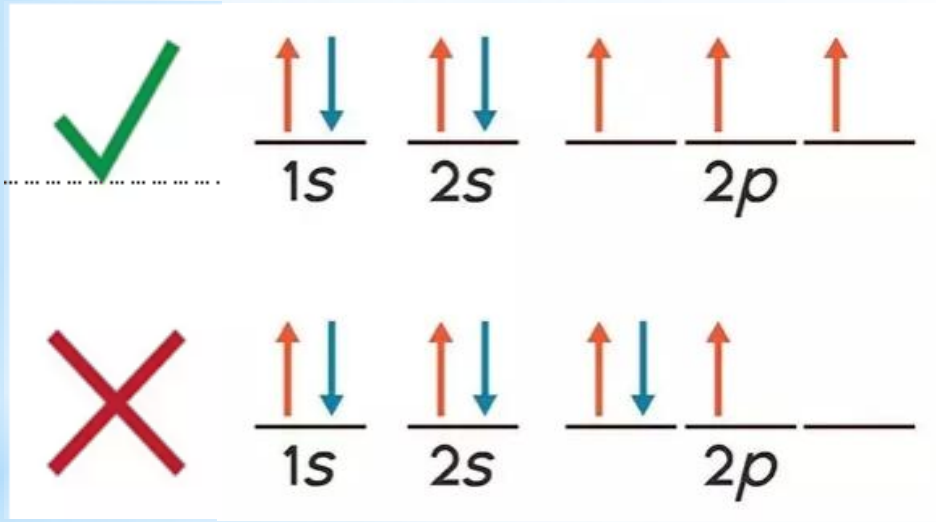
The problem with pauli's rule is that it does not tell about the three 2p orbitals and the order that they will be filled/pair in.

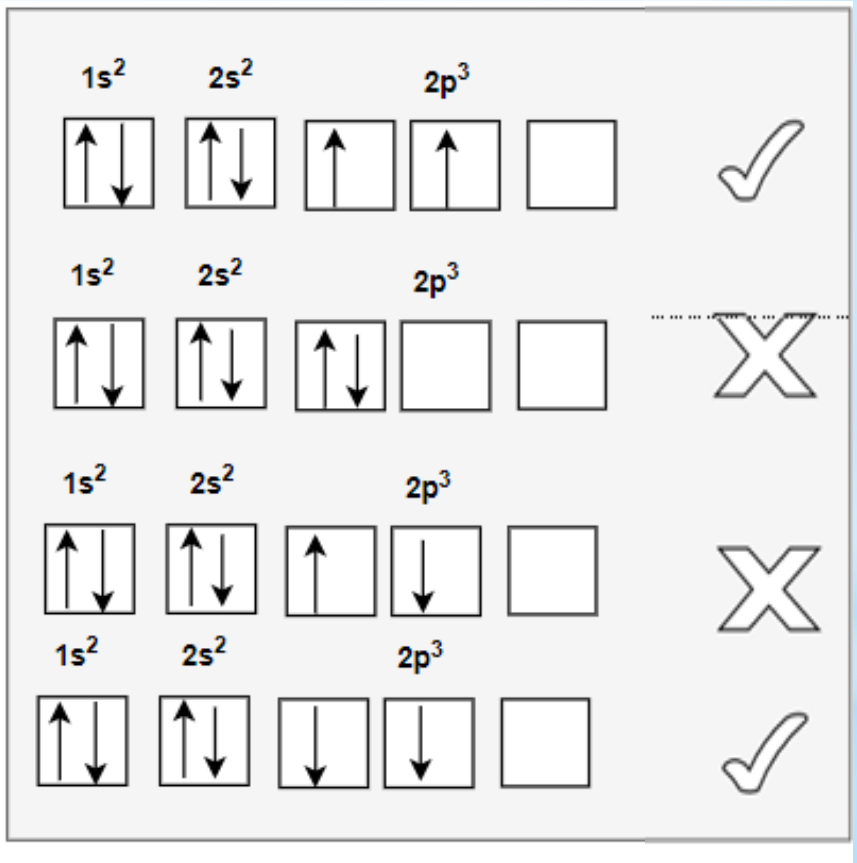
German physicist Friedrich Hund formulated around 1927, rule of arrangement of electrons in subshell and its spin values.
It states that:
1. In a sublevel, each orbital is singly occupied before it is doubly occupied.
2. The electrons present in singly occupied orbitals possess identical spin.

- The electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied.
- It says if two or more than two orbitals having the same amount of energy are unoccupied then the electrons will start occupying them individually before they fill them in pairs.
- When all the orbitals of an atom are full it is most stable. The orbitals that have full energy level are the most stable, for example, noble gases. These type of elements do not react with other elements.



Examples





Study of Periodic table

What Is the Periodic Table?

- It is a table that was created to study the properties and understanding of the elements.
- Dmitri Mendeleev was the first scientist to create a periodic table of the elements in 1869.
- This table showed that when the elements were ordered by increasing atomic weight, a pattern appeared where properties of the elements repeated periodically.
- This periodic table is a chart that groups the elements according to their similar properties.

Why was the Periodic Table Created?

Why Mendeleev made a periodic table?
Many elements remained to be discovered in Mendeleev's time.
The periodic table helped predict the properties of new elements.