Chapter 4: The Atom in Wave Mechanics

The theory of quantum mechanics is the theory of the submicroscopic world and differs from classical mechanics in that in classical mechanics, quantities have single values, whereas in quantum mechanics, we assign probabilities to values within a certain range.

1-The Wave Model of the Atom (Modern Atomic Theory)

Modern atomic theory was founded on fundamental modifications to Bohr's model, with some of the most important changes being:

- The dual nature of electrons.
- Heisenberg's Uncertainty Principle.
- Finding the appropriate equation to describe the wave-like motion of electrons, determining their shapes and energies. The concept of circular orbits was replaced with the concept of probability of existence within a specific region of space. The term 'orbit' was replaced with 'orbital,' and we define an orbital as the region in space where the probability of finding the electron is certain.

2- The Dual Nature of Electron

Every moving body, such as an electron, is accompanied by wave-like motion. This type of wave is called matter waves and is distinct from electromagnetic waves in that its velocity does not equal the speed of light, and it does not separate from the moving body.

$$\lambda = \frac{h}{m.\vartheta}$$

The accompanying wave for a microscopic body is so small that it cannot be measured, felt, or detected. Therefore, the wave associated with these microscopic bodies does not manifest and has no physical meaning. Hence, the particle nature of these microscopic bodies always appears under all conditions. To observe the wave property of matter particles, both the mass and velocity of the body must be small. This implies that the wave property of matter particles can only be observed in atomic particles such as electrons, protons, and neutrons (microscopic).

Example: Calculate the de Broglie wavelength associated with an electron having a velocity of 5.10^6 m/s.

$$\lambda = \frac{h}{m.\vartheta} = \frac{6.626.10^{-34}}{9.1.10^{-31}x5.10^6} = 1.45x10^{-10}m = 1.45\text{Å}$$

The wavelength here is close to atomic dimensions

Example: Calculate the de Broglie wavelength associated with a body of mass 60 kg and a speed of 20 m/s.

$$\lambda = \frac{h}{m.\vartheta} = \frac{6.626.10^{-34}}{60x20} = 5.52x10^{-37}m$$

It is evident that it is impossible for us to detect such a wave due to our devices' limitations. This does not mean that this wave does not exist.

Heisenberg's Uncertainty Principle (The Uncertainty Principle)

This principle states that it is impossible to simultaneously determine two complementary properties of a particle with absolute precision. In other words, it's impossible to determine both the exact position and exact velocity of a particle at the same time. Instead, we can only know the probable location of the electron around the nucleus and the most probable velocity it can have. The Heisenberg principle is mathematically represented by the relationship :

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

Where Δx uncertainty is position of the particle, Δp uncertainty in the momentum of the particle.

Finding the appropriate equation that describes the wave-like motion of electrons and determines their shapes and energies

In 1926, using the ideas of Planck and Einstein, the physicist Schrödinger was able to formulate a wave equation that describes the motion of electrons in an atom. He showed that the energy of an electron in an atom is related to a wave function, whose partial variables can be either Cartesian coordinates Ψ(x, y, z) or spherical cylindrical coordinates Ψ(r, θ, ϕ). The wave function itself does not have any physical meaning, but the probability of finding electrons in a specific region of space is proportional to the square of the wave function, denoted as Ψ^2.

The Schrödinger equation for the hydrogen atom is written in its general form as follows:

$$\Delta\Psi(r,\theta,\varphi) + \frac{8\pi^2 m}{h^2}\left(E + k\frac{e^2}{r}\right)\Psi(r,\theta,\varphi) = 0$$

Where:

- Ψ is the wave function.
- m is the mass of the electron.
- h is the reduced Planck constant.
- E is the total energy of the electron.

The mathematical solution of the Schrödinger equation allowed the inference of three quantum numbers: n , ℓ and m. Subsequently, physicist Dirac proposed a more complex wave equation in which Ψ depends on coordinates (x, y, z) and time coordinates, leading to the deduction of a new quantum number, m_s.

2- Quantum Numbers

- Principal Quantum Number (n):

This is the quantum number used by Bohr in explaining the hydrogen atom's spectrum, and it takes all positive integer values n = 1, 2, 3, ... ∞. The principal quantum number is used to determine:

- The energy level or main electron shell in atoms.
- The number of electrons that can be accommodated in a specific energy level can be calculated using the relationship:

$$2n^2 = \text{The number of electrons that can be accommodated in a specific energy level}$$

Where n: is the principal quantum number (or energy level).

The following table illustrates the maximum capacity for the first four principal energy levels:

The maximum capacity of electrons is $2n^2$	**The principal energy level (n)**
Two electrons	The first
8 electrons	The second
18 electrons	The third
32 electrons	The fourth

The above law does not apply to energy levels higher than the fourth level. The fifth level theoretically accommodates 50 electrons, and the sixth level accommodates 72 electrons. However, the atom becomes unstable if the number of electrons exceeds 32 electrons.

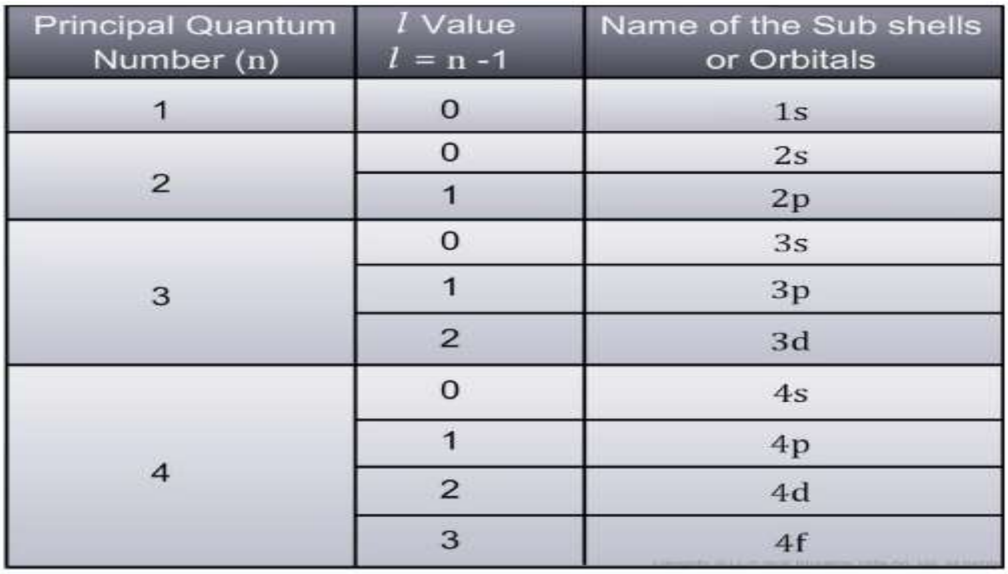
- Secondary Quantum Number ℓ

It is used to determine the sublevels of energy that exist within the principal energy levels. The secondary quantum number takes integer values :

$$0 \leq \ell \leq n-1$$

ℓ	0	1	2	3
The symbol for the sublevel or subshell	s	P	d	f

The number of sublevels in each principal energy level is equal to the value of n for the principal level.



Principal Quantum Number (n)	l Value l = n -1	Name of the Sub shells or Orbitals
1	0	1s
2	0	2s
	1	2p
3	0	3s
	1	3p
	2	3d
4	0	4s
	1	4p
	2	4d
	3	4f

- Magnetic quantum number m_ℓ or m

The magnetic quantum number m_ℓ takes on values within the range of $-\ell \leq m_l \leq +\ell$ and its maximum value is $2\ell + 1$. It is used to determine:

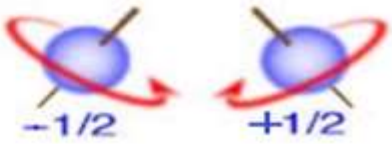
The number of orbitals (subshells) within a given subshell. It also indicates the orientation of the orbital in space.

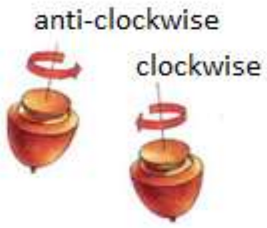
Quantum state representation	Number of orbitales	The values of m m_ℓ	The values of ℓ	Subshell notation
□	1	0	0	S
□□□	3	-1,0,1	1	P
□□□□□	5	-2,-1,0,1,2	2	d
□□□□□□□	7	-3,-2,-1,0,1,2,3	3	f

- Spin quantum number m_s or s

The spin quantum number refers to the direction of the axial rotation of the electron around itself (i.e., its spin direction) in the atom. It can have only two values(+½ and -½). The clockwise spin is indicated by +½ or upwards arrow(↑) and anti-clockwise spin by -½ or downwards arrow(↓).

If there are electrons in the same orbital, each of them will spin in the opposite direction to the other electron's spin. The value of the spin quantum number (m_s) for one will be +1/2, and for the other, it will be -1/2.





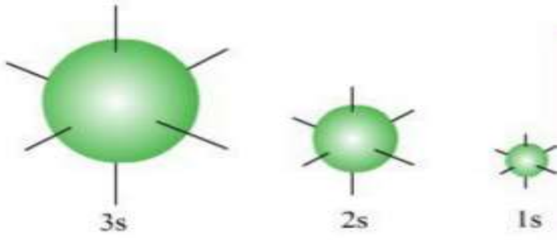
As a result of the electrons' spins in opposite directions while orbiting around their respective axes in the same orbital, this leads to the creation of two opposing magnetic fields in space. These magnetic fields attract each other, reducing the electrostatic repulsion between the electrons. This phenomenon facilitates the presence of two electrons in the same orbital.

3- Orbitals shapes and properties

Subshell s

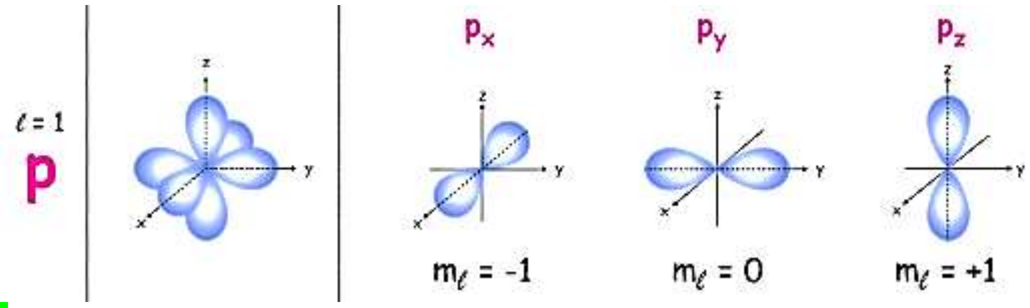
1. It contains one orbital.
2. It begins to appear from the first principal energy level.
3. Its maximum capacity is two electrons.
4. It has a spherical shape.

5. Its size and energy increase with an increase in the principal quantum number.



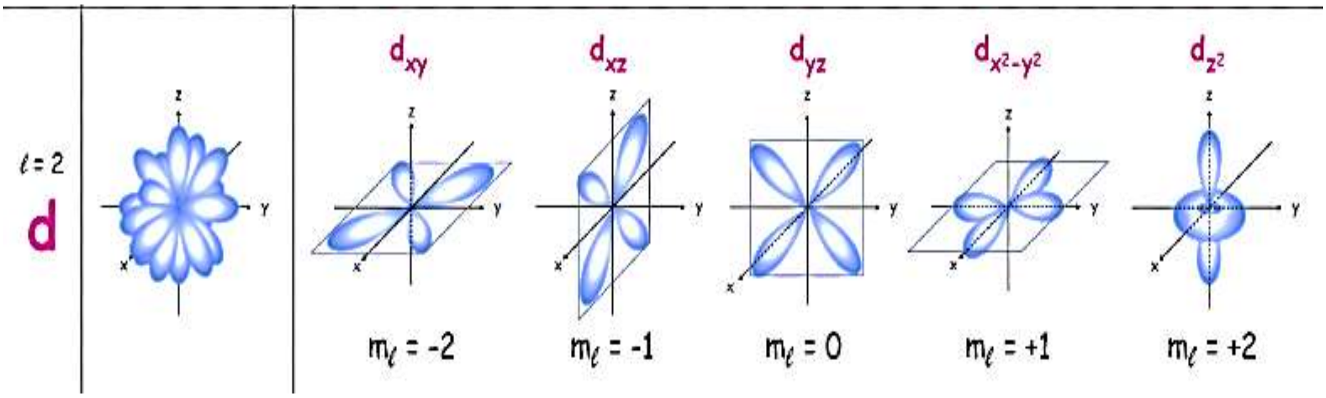
Subshell P

1- It contains three orbitals in each Subshell, and each orbital is oriented along one of the axes.
2- It starts appearing from the second principal energy level (or shell).
3- Its maximum capacity is (6) electrons.
4- Its size and energy increase with an increase in the principal quantum number.



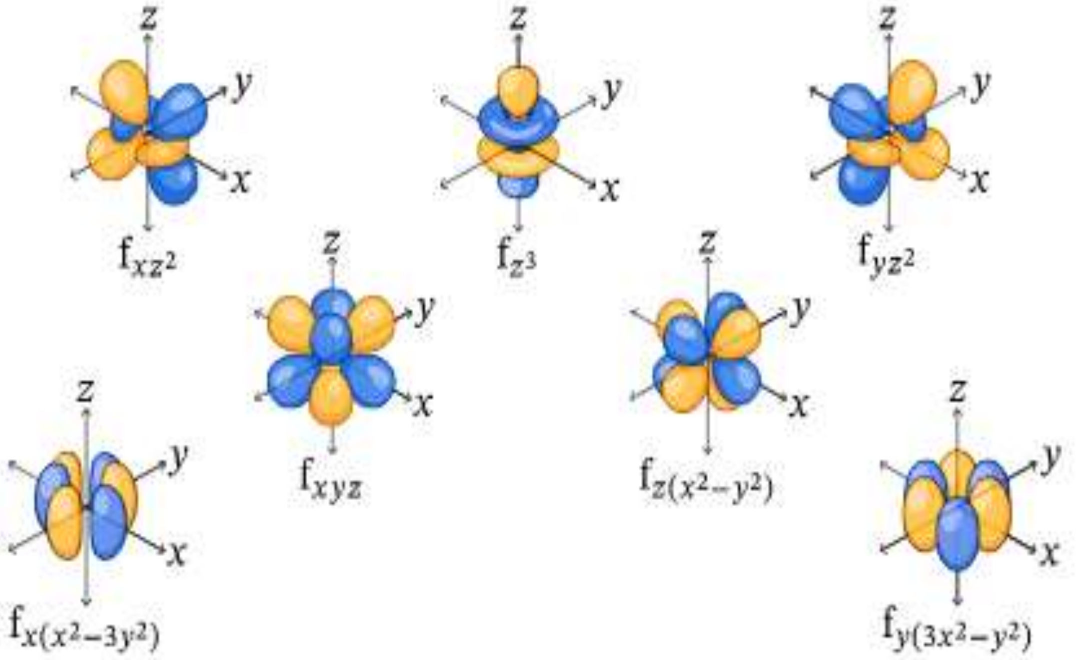
Subshell d

1- It contains five orbitals in each Subshell.
2- It starts appearing from the third principal energy level.
3- Its maximum capacity is (10) electrons.
4- Its size and energy increase with an increase in the principal quantum number.



Subshell f

1- It contains seven orbitals in each Subshell.
2- It starts appearing from the fourth principal energy level.
3- Its maximum capacity is (14) electrons.
4- Its size and energy increase with an increase in the principal quantum number.



4-The electronic structure of an atom

The electronic structure of an atom refers to the arrangement that electrons take within atomic orbitals. This distribution relies on principles and rules:

The Pauli Exclusion Principle (1925)

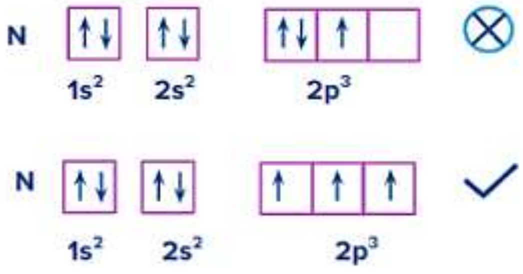
Within the same atom, electrons cannot have the same set of four quantum numbers: n, ℓ, m_ℓ and m_s. If two electrons share the same values for n, ℓ, m_ℓ they must differ in their spin quantum number, m_s.

Example

$$_{2}He: 1S^2 \ \boxed{\uparrow\downarrow}$$

Hund's rule

Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied and all electrons in singly occupied orbitals have the same spin.



Klechkovski's Rule (Aufbau Principle- building-up principle)

This rule states that electrons in the ground state of an atom are distributed first into the sublevels with the lowest energy, followed by sublevels with the sum of the n+ℓ being as small as possible. When n+ℓ is equal in multiple sublevels, the sublevel with the smaller principal quantum number (n) is filled first.

Example:

3d and 4d

$$3d:\left.\begin{matrix} n=3\\ \ell=2\end{matrix}\right\} n+l=5$$

$$4S:\left.\begin{matrix} n=4\\ \ell=0\end{matrix}\right\} n+l=4$$

$$\Rightarrow E_{3d} > E_{4S}$$

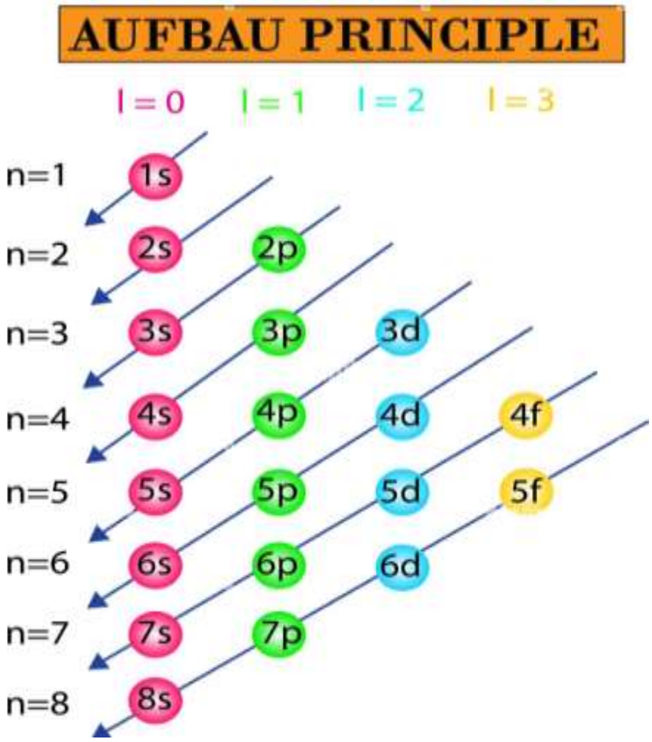
5d and 4f

$$5d:\left.\begin{matrix} n=5\\ \ell=2\end{matrix}\right\} n+l=7$$

$$4f:\left.\begin{matrix} n=4\\ \ell=3\end{matrix}\right\} n+l=7$$

$$\Rightarrow E_{5d} > E_{4f}$$

The following figure provides a simplified illustration of the filling order of sublevels, following the arrow's direction.



The order in which the atomic orbitals are filled by electrons is like:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f,6d, 7p, and more.

Its general form is:

$$n^{1\to 2}(n-2)f^{1-14}(n{-}1)d^{1\to 10}np^{1\to 6}$$

Electrons occupying sublevels are written in exponent form.

There are some special cases in electron filling. The d-subshell becomes more stable when it is either fully filled with 10 electrons or half-filled with 5 electrons. Therefore, the presence of two electrons in the s-subshell along with four or nine electrons in the d-subshell leads to the transfer of one electron from the s-subshell to the d-subshell.

$$nS^2(n-1)d^4 \to nS^2(n-1)d^5$$

$$nS^2(n-1)d^9 \to nS^2(n-1)d^{10}$$

Exceptional configurations:
Chromium expected configuration

$_{24}\mathrm{Cr}$:$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Actual Cr Configuration: $_{24}\mathrm{Cr}$:$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ ← HALF FULL

Copper expected configuration: $_{29}\mathrm{Cu}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

Actual Cu Configuration: $_{29}\mathrm{Cu}$:$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ ← FULL

5-The representation of electronic structure

Electron configuration: It is the arrangement of electrons in an atom's quantum orbitals according to the Klechkowski rule or in ascending order of the sum of $n + \ell$. To simplify Electron configuration, we replace the sum of fully occupied subshells with the symbol of the corresponding noble gas that precedes the element in the periodic table.

Example:

$_{26}\mathrm{Fe}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

$_{26}\mathrm{Fe}$: $[\mathrm{Ar}]_{18}\ 4S^2\ 3d^6$

Important definitions

Valence Electrons: These are the electrons that occupy the outermost electron shells, which come after the noble gases in the electron distribution.

Example:

$$_{26}\mathrm{Fe} : [\mathrm{Ar}]_{18}\ \overbrace{4S^2\ 3d^6}^{\text{8 Valence Electrons}}$$

Note: The subshell electrons of f and d, when filled, are not counted as valence electrons. The subshells that contain valence electrons are referred to as the outer electron structure, while the filled subshells that correspond to the noble gas electron configuration are called core electrons.

$$Fe_{26} : \overbrace{[Ar]}^{\text{core electrons}} \underbrace{4S^2\ 3d^6}_{\text{outer electron structure}}$$

$$Zn_{30} : \overbrace{[Ar]_{18}\ 3d^{10}}^{\text{core electrons}} \underbrace{4S^2}_{\text{outer electron structure}}$$

Outer and Inner Subshells

1. **Outer Subshells:** These are the secondary subshells nS and np with the highest possible principal quantum number n in the electronic distribution.
2. **Inner Subshells:** These are the secondary subshells nf and nd with the highest possible quantum number n in the electronic distribution.

Note: To determine the electronic structure of multi-electron ions, we first write the electronic distribution for the atom following the increasing order of the principal quantum number n. Then, we remove electrons from the outer then inner subshells.

Example:

$$_{26}Fe : [Ar]_{18}\ 4S^2\ 3d^6$$
$$_{26}Fe : [Ar]_{18}\ 3d^6\ 4S^2$$
$$_{26}Fe^{+2} : [Ar]_{18}\ 3d^6\ 4S^0$$
$$_{26}Fe^{+3} : [Ar]_{18}\ 3d^5\ 4S^{0^{2}9}$$