QUANTUM NUMBERS

The quantum numbers, a set of four values essential for determining the potential position of an electron within an atom, are derived from the Schrödinger wave equation, with the first three being particularly obtained from it.

Quantum Model

Bohr's atomic model solely considered the particle nature of electrons, but the quantum model of the atom, which evolved later, relies on fundamental principles and equations to provide a more comprehensive understanding of atomic behavior.

de Broglie Equation

Louis de Broglie proposed that particles, including electrons, exhibit both wave and particle characteristics. His equation relates the wavelength (λ) of a particle to its momentum (p): $\lambda = h/p$, where h is Planck's constant. This wave-particle duality concept was instrumental in shaping the quantum model.

Erwin Schrödinger further contributed to the quantum model by formulating an equation that describes the behavior of electrons as standing waves. The Schrödinger equation is given by:

$$\frac{\delta^2\Psi}{dx^2} + \frac{\delta^2\Psi}{dy^2} + \frac{\delta^2\Psi}{dz^2} + \frac{8\pi^2\Psi}{dh^2}(\mathrm{E} - \mathrm{v})\,\Psi = 0$$

Here:

Here, the symbols represent the following variables:

Ψ: a function representing the wave function.

x, y, z: directional coordinates.

m: mass of the electron.

h: Planck's constant.

E: total electric energy.

V: total potential energy.

This mathematical formulation provides a sophisticated description of electron behavior, treating the electron as a standing wave within the three-dimensional space defined by the coordinates x, y, z. The equation captures the interplay between kinetic and potential energies, offering a comprehensive understanding of the quantum mechanical aspects of atomic systems. The quantum model, incorporating these principles, has proven to be more comprehensive in explaining the intricate behaviors of subatomic particles within the realm of quantum mechanics.

Wave Function

The wave function, a critical concept in quantum mechanics, serves as a solution to the Schrödinger equation, a fundamental equation governing the behavior of subatomic particles. However, not all solutions are considered valid; certain criteria must be met for acceptance.

Continuity of the Wave Function

Valid wave functions must exhibit continuity, ensuring a seamless and uninterrupted mathematical representation.

Finiteness of the Wave Function

The wave function must be finite, implying that its values remain bounded within a defined range, avoiding divergence to infinity.

Single-Validness of the Wave Function

A crucial requirement is that the wave function must be single-valued, meaning that for each set of coordinates, there is only one corresponding value of the wave function.

Continuity of the First Derivative

The first derivative of the wave function must also be continuous, contributing to the overall smoothness and well-defined nature of the wave function.

The wave function provides essential information about the probability amplitude of an electron wave, offering insights into the likelihood of finding an electron at a particular location within a given space. Due to its connection with probability, the wave function is also referred to as the amplitude wave function. This terminology underscores its role in describing the amplitude or likelihood of an electron's presence in specific regions, contributing to a more profound understanding of the probabilistic nature inherent in the behavior of subatomic particles.

(i) Principal Quantum Number (n)

(Proposed by Bohr)

It characterizes the magnitude of the electron wave and the overall energy of the electron. Expressed as integral values such as 1, 2, 3, 4, and so on, it is represented by letters like K, L, M, N, and so forth.

- Number of subshells present in n^{th} shell = n

n	subshell
1	s
2	s, p
3	s, p, d
4	s, p, d, f

- Number of orbitals present in n^{th} shell = n^2.
- The maximum number of electrons which can be present in a principal energy shell is equal to $2n^2$.

  No energy shell in the atoms of known elements possesses more than 32 electrons.
- Angular momentum of any orbit = $\frac{nh}{2\pi}$

(ii) Azimuthal Quantum Number (λ)

(Proposed by Sommerfield)

It defines the configuration of the electron cloud and indicates the quantity of subshells within a shell. Its values range from 0 to (n – 1), where each specific value of λ corresponds to a distinct subshell.

value of λ	subshell
0	s
1	p
2	d
3	f

Number of orbitals in a subshell = $2\lambda + 1$

Maximum number of electrons in particular subshell = $2 \times (2\lambda + 1)$

Orbital angular momentum $L = \frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \eta\sqrt{\ell(\ell+1)}[h = \frac{h}{2\pi}]$

i.e. Orbital angular momentum of s orbital = 0, Orbital angular momentum of p orbital

$$= \sqrt{2}\frac{h}{2\pi},$$

Orbital angular momentum of d orbital $= \sqrt{3}\frac{h}{2\pi}$

(iii) Magnetic Quantum Number (m)

(Proposed by Linde)

It delineates the orientations of subshells, with values ranging from $-\lambda$ to $+\lambda$, encompassing zero, thus totaling $(2\lambda + 1)$ values. Each value is associated with an orbital.

For instance, the s-subshell features one orbital, the p-subshell consists of three orbitals (p_x, p_y, and p_z), the d-subshell encompasses five orbitals (d_{xy}, d_{yz}, d_{zx}, $d(x^2\text{-}y^2)$, $d(z^2)$), and the f-subshell comprises seven orbitals. The overall count of orbitals within a principal energy level is 'n^2'.

(iv) Spin Quantum Number (s)

(Proposed by Samuel Goudsmit & Uhlenbeck)

It signifies the spin of the electron, with values of $+\frac{1}{2}$ and $-\frac{1}{2}$ denoting clockwise and anticlockwise spinning, respectively.

(i) Spin magnetic moment $\mu_S = \frac{eh}{2\pi mc}\sqrt{s(s+1)}$ or $\mu = \sqrt{n(n+2)}$ B.M.

(n = no. of unpaired electrons)

(ii) It represents the value of spin angular momentum which is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$

(iii) Maximum spin of atom $= \frac{1}{2}$ x No. of unpaired electron.

Rules for Filling of Orbitals

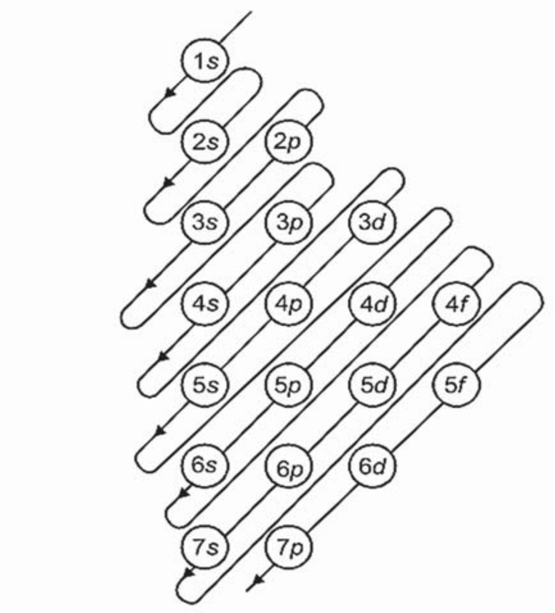
1. Aufbau Principle

Aufbau is a German word and its meaning 'Building up'

The Aufbau principle provides a sequence for filling up different subshells based on the relative order of energies among them.

- **Principle:** The subshell with the lowest energy is filled first, and once it reaches its maximum electron capacity, the subsequent subshell with higher energy begins to be populated.

  The sequence in which various subshell are filled is the following.



$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^6$

2. $(n + \lambda)$ Rule

In accordance with it, the order in which different subshells are filled can also be determined by considering the $(n + \lambda)$ value for a specific subshell.

Principle Of $(n + \lambda)$ Rule

The subshell with the lowest $(n + \lambda)$ value is filled first. In the case where two or more subshells share the same $(n + \lambda)$ value, the one with the lowest n value is filled first.

Sub Shell	n	λ	$n + \lambda$	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)
4d	4	2	6	(1)
5p	5	1	6	(2)
6s	6	0	6	(3)

For H atom the energy of orbital depends only on the value of n.

i.e., $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$..................

3. Pauli's Exclusion Principle

In 1925, Pauli postulated that no two electrons within an atom can possess identical values for all four quantum numbers.

- An orbital can accomodates maximum 2 electrons with opposite spin.

4. Hund's Maximum Multiplicity Rule

(Multiplicity: Many of the same kind)

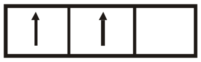
Hund's rule dictates that electrons are allocated among the orbitals of a subshell to maximize the number of unpaired electrons with parallel spin. In other words, within a subshell, electron pairing does not occur until each orbital in that subshell has received one electron, all with the same spin.

Spin Multiplicity

It is given by $2S + 1$ where S is the total spin.

(a)

(b)



For (a), $S = +\frac{1}{2} - \frac{1}{2} = 0$

Spin multiplicity $= 2S + 1 = 0 + 1 = 1$ (singlet)

For (b), $S = +\frac{1}{2} + \frac{1}{2} = 1$

Spin multiplicity $= 2S + 1 = 2 \times 1 + 1 = 3$ (triplet)

Ex. Find out the angular momentum of an electron in

(a) 4s orbital (b) 3p orbital (c) 4th orbital

Sol. Angular momentum in an orbital $= \frac{h}{2\pi}\sqrt{\ell(\ell+1)}$

(a) $\lambda = 0$ for 4s orbital, hence orbital angular momentum = 0

(b) $\lambda = 1$ for 3p orbital

$$\therefore \quad \text{Angular momentum} = \frac{h}{2\pi}\sqrt{(1+1)\times 1} = \frac{h}{\sqrt{2}\pi}$$

(c) Angular momentum in 4th orbit

$$= \frac{nh}{2\pi} = \frac{4\ h}{2\pi} = \frac{2\ h}{\pi}$$

Ex. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(i) $n = 4, \lambda = 2, m = 0$ (ii) $n = 3, \lambda = 1, m = \pm 1$

(iii) $n = 4, \lambda = 0, m = 0$ (iv) $n = 3, \lambda = 2, m = \pm 2$

Sol. (i) $4dz^2$ (ii) $3p_x$ or $3p_y$

(iii) 4s (iv) or $3d_{xy}$