# The structure of Atom

## Lecture-6. (Note-No-01)

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(1) Describe Rutherford's atomic model and give its limitations.

Rutherford proposed a model of the atom which is named after him. This is also called the Nuclear atomic model. According to it:

1. Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom, leaving the rest of the atom almost empty.

2. The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it.

(3) The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.

Limitations of Rutherford atomic model:- The assumption that electrons were orbiting around the nucleus was unfortunate. According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen actually as then

the atom would be unstable which it is not. This is the chief weakness of Rutherford's atomic model

(2) Describe Bohr's atomic model and give its limitations.
CE

Bohr's atomic model was based on planck's quantum theory and was built on the following postulates

① Electrons travel around the nucleus in specific permitted circular orbits and in no others. — Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus. The orbits are given the letter designation n and each is numbered 1, 2, 3 etc (or, K, L, M, etc) as the distance from the nucleus increases.

② While in these specific orbits, an electron does not radiate or lose energy. Therefore in each of these orbits, the energy of an electron remains the same. Hence the specific orbits available to the electron in an atom are referred to as stationary energy levels or simply energy levels.

③ An electron can move from one energy level to another by quantum or photon jumps only. When an electron resides in the orbit which is lowest in energy, the electron is said to be in the ground state when an electron is supplied energy, it

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absorbs one quantum or photon of energy and jumps to a higher energy level. The electron then has — potential energy and is said to be in an excited state. The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom.

$$\Delta E = E_{high} - E_{low} = h\nu$$

where $h$ is planck's constant and $\nu$ is the frequency of a photon.

④ The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of planck's constant divided by $2\pi$

$$\text{angular momentum} = mvr = n\frac{h}{2\pi}$$

where, $m$ = mass of electron, $v$ = velocity of the electron $r$ = radius of the orbit, $n = 1, 2, 3 \cdots$ etc. and $h$ = planck's constant

Shortcomings of the Bohr atomic model:

① The great success of the Bohr theory was in its ability to predict lines in the hydrogen atom spectrum. But it was spectacularly unsuccessful for every other atom containing more than one electron.

② We no longer believe in well-defined electron orbits

as was assumed by Bohr. In fact, in view of modern advances, like dual nature of matter, uncertainty principle, any mechanical model of the atom stands rejected.

③ Bohr's model of electronic structure could not account for the ability of atoms to form molecules through chemical bonds.

④ Bohr's theory could not explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of atoms.

(3) What are quantum numbers? Why four quantum numbers are necessary to describe an electron in an atom.

Quantum numbers:- The term quantum number is used to identify the various energy levels available with the atom in which the electron of the atom can reside. An electron in an atom is completely described by its four quantum numbers. The four quantum numbers are

- ① principal quantum number
- ② Subsidiary quantum number
- ③ Magnetic quantum number
- ④ [illegible] quantum number

state when an electron is supplied [illegible]

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The necessity of four quantum numbers is described below.

① The principal quantum number, n:- This quantum number denotes the principal shell in which the electron belongs. This is also referred to as major energy level. It represents the average size of the electron cloud, i.e., the average distance of the electron from the nucleus. The principal quantum number is denoted by n and $n = 1, 2, 3, \ldots$ In a polyelectron atom, the electron that has a higher principal quantum number is at a higher energy level. An electron with $n = 1$ has the lowest energy and is bound most firmly to the nucleus. There is a limited number of electrons in an atom which can have the same principal quantum number and is given by $2n^2$, where n is the principal quantum number.

② Subsidiary quantum number, l :- The subsidiary quantum number, l defines the shape of the orbital occupied by the electron and the angular momentum of the electron. For any given value of the principal quantum number n, the subsidiary quantum number, l may have all integral values from 0 to n-1, each of which refers to an energy sublevel or subshell. The total number of

such possible sublevels in each principal level is numerically equal to the principal quantum number of the level under consideration. These sublevels are also symbolised by letters s, p, d, f etc.

③ Magnetic quantum number, m :— This quantum number has been proposed to account for the splitting up of spectral lines. An application of a strong magnetic field to an atom reveals that electrons with the same values of principal quantum number, n and of subsidiary quantum number, l may still differ in their behaviour. They must, therefore, be differentiated by introducing a new quantum number, the magnetic quantum number m. For each value of the subsidiary quantum number 'l', the magnetic quantum number m, may assume all the integral values between +l to −l through zero. Therefore for each value of l there will be (2l+1) values of m.

④ Spin quantum number, s :— This quantum number has been introduced to account for the spin of electrons about their own axis. Since an electron can spin clockwise or anticlockwise, there are two possible values of s that are equal and opposite. As quantum numbers can differ only by unity from each other

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there are two values given to S ; $+\frac{1}{2}$ and $-\frac{1}{2}$ depending upon whether the electron spins in one direction or the other. Two electrons with the same sign of the spin quantum numbers are said to have parallel spins while those having opposite signs of the spin quantum numbers are said to have antiparallel spin.

4. Show the differences between orbit and orbital.

The points of difference between an orbit and orbital are given below in a tabular form

| Orbit | Orbital |
|---|---|
| ① An orbit is a definite circular path at a definite distance from the nucleus in which the electron revolves round the nucleus. | ① An atomic orbital represents the space round the nucleus in an atom where there is maximum probability of finding an electron having a certain energy. |
| ② An orbit indicates an exact position or location of an electron in an atom. | ② An orbital does not specify the definite or exact position of an electron in an atom. |
| ③ There is a certainty about the movement of an electron in an orbit. | ③ Due to uncertainty principle, there is no certainty about the movement of an electron in an orbital. |

| Orbit | Orbital |
|---|---|
| ④ orbits are circulate shape | ④ orbitals have different shapes. e.g., s-orbital is spherical. p orbitals are dumb-bell shaped etc |



5. State and Explain Pauli's Exclusion principal.

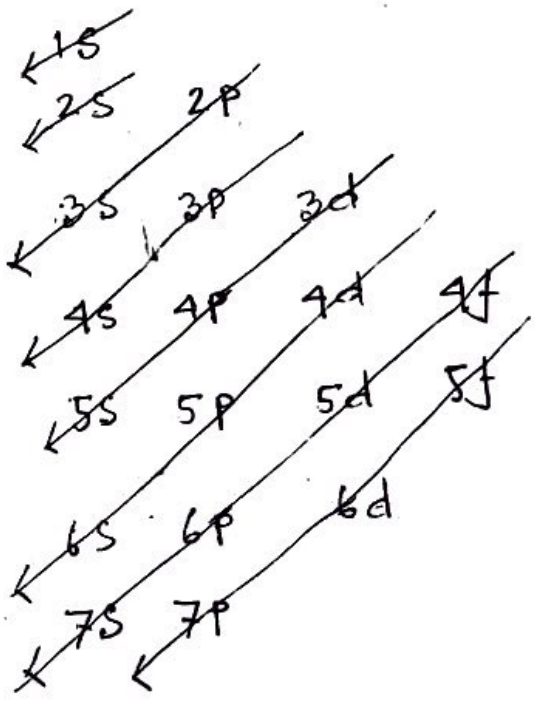
Pauli's Exclusion principal: No two electrons in an atom can have the same set of four identical quantum numbers.

Explanation: Even if two electrons have the same values for n, l and m, they must have different values of s. Thus every electron in an atom differs from every other electron in total energy and, therefore, there can be as many electrons in a shell as there are possible arrangements of different quantum numbers

6. State and explain Aufbau principal.

Aufbau principal: In the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first.

Explanation: Lower energy orbitals are, therefore, better seats for electrons and better seats are occupied first. Aufbau order of orbitals for feeding in electrons are given below.




The increasing order of energy of various orbitals is as follows.

1S < 2S < 2P < 3S < 3P < 4S < 3d < 4P < 5S < 4d < 5P < 6S .....

7. State and Explain "Hund's" rule.

Hund's rule: Electrons are distributed among the degenerate orbitals of a subshell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.

Explanation:- This rule is based on the fact that electrons, being of the same charge, repel each other and hence try to keep farthere aparet from each other as much as possible. This they do by entering the degenerate orbitals as fare as possible. Their entering the orbitals in this mannere minimises the inter-electronic repulsion energy of the system and hence we get a stable system.

8. What do you mean by Heisenberg uncertainty principle?

Heisenberg uncertainty principle:— It is impossible to measure simultaneously the exact position and momentum of an electron.

Mathematical expression for the principle:-
If $\Delta x$ represents the uncertainty in the measurement of the position and $\Delta P$ represents the uncertainty in the measurement of the momentum of an electron.

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then according to this principle, these two quantities are related as

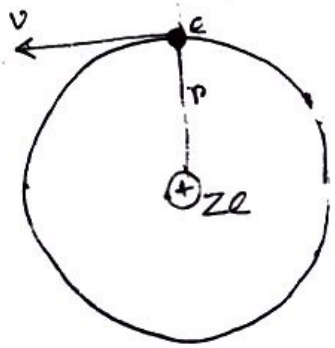
$$\Delta x \cdot \Delta P \geq \frac{h}{2\pi}$$ (Uncertainty relation)

Where h is the plank's constant.

(9.) Derive an expression for the radius of any orbit in the hydrogen atom.

OR.

Derive an expression for the radius of any orbit in the atom.




Consider an electron of charge e revolving around a nucleus of charge Ze, where Z is the atomic number and e the charge on a proton. Let m be the mass of the electron, r the radius of the orbit and v the tangential velocity of the revolving electron.

According to the Coulomb's Law, the electrostatic force of attraction between the nucleus and the electron

$$= \frac{Ze \times e}{r^2}$$

$$= \frac{Ze^2}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

or, $\frac{Ze^2}{r} = mv^2$ [multiplying both sides by r] ..... ①

According to one of the postulates of Bohr's theory, angular momentum of the revolving electron is given by the expression

$$mvr = \frac{nh}{2\pi}$$

or, $v = \frac{nh}{2\pi mr}$ ——— ②

Substituting the value of v in the equation ② we get

$$\frac{Ze^2}{r} = \frac{m\, n^2h^2}{4\pi^2m^2r^2}$$

or $r = \frac{n^2h^2}{4\pi^2mZe^2}$ ——— ⑤

since the value of h, m and e had been determined experimentally, substituting these values and substituting

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(7)

the value of Z, we get the radii of various orbits. As $n = 1, 2, 3 \ldots\ldots$

(10.) Derive an expression for the energy of any orbit of the atom.

The energy associated with a revolving electron at any instant is equal to the sum of its kinetic energy (K.E) and potential energy (P.E). Kinetic energy of a moving electron is due to its motion in the circular orbit while the potential energy arises because the electron lies in the electric field of the positive nucleus. Again we know that $K.E = \frac{1}{2}mv^2$ and $P.E = -\frac{Ze^2}{r}$.

Total energy of the electron is given by

$$E = K.E + P.E$$

or, $$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} \quad \text{——— (1)}$$

As $$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \text{or, } mv^2 = \frac{Ze^2}{r}$$

From equation (1) we get

$$E = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r}$$

$$E = -\frac{Ze^2}{2r} \quad \text{——— (2)}$$

We know the radius of an orbit is

$$r = \frac{n^2h^2}{4\pi^2 m Ze^2} \quad \text{where } n = 1, 2, 3 \cdots$$

Substituting the value of $r$ in the equation (2) we get

$$E = -\frac{Ze^2}{2} \cdot \frac{4\pi^2 m Ze^2}{n^2h^2}$$

or, $$E = -\frac{2\pi^2 m Z^2 e^4}{n^2h^2} \quad \text{——— (3)}$$

Substituting the values of $\pi$, $m$, $Z$, $e$, $h$ and $n$ we get the Energy of various orbits.

11. Which of the orbitals namely 1p, 2s, 2p, 3f are not possible? Give reason for your answer.

The orbitals which are not possible are 1p and 3f. The reason for their non-existence is given below

We know, when $n=1$, $l=0$.
$l=0$ value means that 1st shell has only one subshell namely 1s for which $l=0$. Thus 1st shell does not contain 1p orbital.

Again, when $n=3$, $l=0, 1, 2$. Three values of $l$ mean that 3rd shell has only three subshells

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namely 3s (for which $l=0$), 3p (for which $l=1$) and 3d (for which $l=2$). Thus 3rd shell does not contain 3f orbital.

12. An electron is in 4f orbital. What possible values for the quantum number of n, l, m and s it can be.

We know, for 4f orbital,

$n = 4, \quad l = 3$

for $l = 3$, $\quad m = -3, -2, -1, 0, +1, +2, +3$

Hence, seven values of m imply that 4f orbital is divided into seven degenerate orbits. Thus this electron may reside one of these seven degenerate orbitals.

For this electron. $s = +\frac{1}{2}$ or $-\frac{1}{2}$.

13. What is the maximum number of electrons in 4d orbital.

We know, the maximum number of electron in an orbital $= 2(2l+1)$

for 4d orbital, $l = 2$

Thus for 4d orbital maximum number of electron is $= 2(2 \cdot 2+1) = 10$.

14. write the name of the orbital for which the quantum numbers are $n=2$, $l=1$.

We know, When

$n = 2$

$l = 0, 1$

Again, $l = 1$ indicates p subshell. or p-orbital

Thus, for quantum numbers $n=2$ and $l=1$, the orbital is 2P.

15. Give the symbols for orbital types when the values of $l$ are 0, 2, and 3.

$l = 0$, the symbols of the orbital = S

$l = 2$, the symbols of the orbital = d

$l = 3$, the symbols of the orbital = f.

16. In which orbital between 3d and 4P, electrons will go first give the reason.

The orbital having the lowest value of $(n+l)$ has the lowest energy and hence is filled up first with electrons according to Aufbau principle when two or more orbitals have the same value of $(n+l)$, the orbital with lowere value of n is lowere in energy and hence is filled up first with

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electrons.

NOW for 3d orbital, the value of $n+l = 3+2=5$

for 4p orbital, the value of $n+l = 4+1 = 5$.

$(n+l)$ value of these two orbitals are same. But between these two orbitals, 3d has the lowere value of n (3). Therefore electrons will go 3d orbital first.

17. Give the actual configuration of cr(24) and cu(29). and explain why these configuration are stable.

Expected configuration of cr(24) and cu(29) are.

cr(24) $\longrightarrow$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

cu(29) $\longrightarrow$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

Actual configuration of cr(24) and cu(29) are.

cr(24) $\longrightarrow$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

cu(29) $\longrightarrow$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$.

According to Hund's rule, half filled and full filled orbitals are morce stable. For that reason one electron from 4s orbital gets shifted to 3d orbital to make 3d orbital

half filled and full-filled which is more stable than $3d^4$ and $3d^9$.

18. Write down the electric configuration of Cr (24), $Zn^{2+}$ (30), Sc (21), Ag (47), $Cu^{2+}$, $Cr^{3+}$, $Fe^{2+}$, $Fe^{3+}$ and determine their position in periodic table

Electronic configuration

group of periodic table

① $Cr(24) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ ⟶ 6

② $Sc(21) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ ⟶ 3

③ $Ag(47) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^{10}$ ⟶ 11

④ $Cu^{2+} \rightleftharpoons Cu_{29} - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10} - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ ⟶ 11

⑤ $Fe^{2+} = Fe_{26} - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ⟶ 8

⑥ $Zn^{2+} = Zn_{30} - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} - 2e^-$

$= 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ⟶ 12

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19. , give the values of $n$, $l$, $m$ and $s$ for $n = 1, 2, 3, 4$.

| n | l | m | s | Number of electrons in sub shell | No of electrons in orbit |
|---|---|---|---|---|---|
| 1 | 0 | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | 2 |
| 2 | 0 | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | 8 |
| | 1 | $+1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $-1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| 3 | 0 | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | 18 |
| | 1 | $-1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $+1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | 2 | $+2$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $-2$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $-1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $+1$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |
| | | $+2$ | $+\frac{1}{2}, -\frac{1}{2}$ | 2 | |

$n = 1, 2, 3, 4 \ldots$

$l = n-1$

$m = \pm l$

$s = \pm \frac{1}{2}$

$= +\frac{1}{2}, -\frac{1}{2}$

| n | l | m | s | No of electron in orbital |
|---|---|---|---|---|
| 4 | 0 | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | 2 |
| | 1 | -1 | $+\frac{1}{2}, -\frac{1}{2}$ | 6 |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +1 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | 2 | -2 | $+\frac{1}{2}, -\frac{1}{2}$ | 10 |
| | | -1 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +1 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +2 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | 3 | -3 | $+\frac{1}{2}, -\frac{1}{2}$ | 14 |
| | | -2 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | -1 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | 0 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +1 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +2 | $+\frac{1}{2}, -\frac{1}{2}$ | |
| | | +3 | $+\frac{1}{2}, -\frac{1}{2}$ | |

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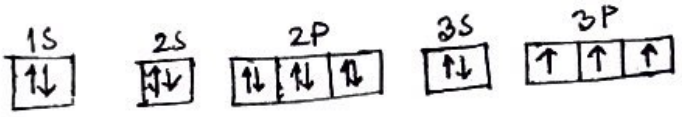
(20.) Why does $PCl_5$ exist but $NCl_5$ not exist.

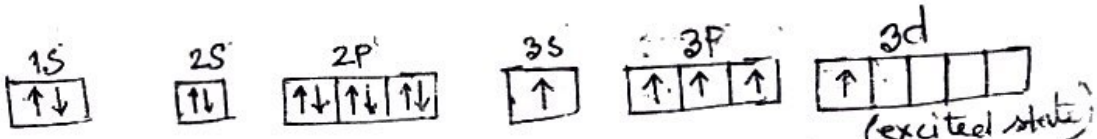
The electronic configuration of P

$P(15) = 1s^2\ 2s^2 2p^6\ 3s^2 3p^3$ (ground state)

= 

(ground state)

In the case of P, the last energy level or orbit is third orbit. Third orbit has 3S, 3P and 3d orbital. At excited state, one electron goes from 3S orbital to adjacent 3d orbital and make five half-filled orbitals.

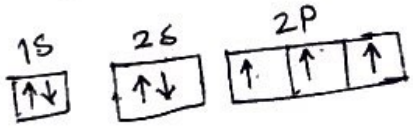



These five half-filled orbitals react with five half-filled chlorine atom and forms $PCl_5$.

But in the case of N.

The electronic configuration of N

$N(7) = 1s^2 2s^2 2p^3$

= 

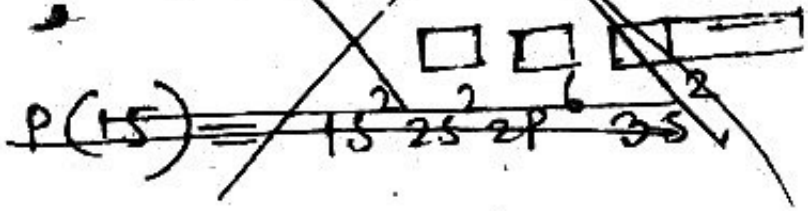
(ground state)

In the case of N, the last orbit is 2nd orbit. 2nd orbit has two orbitals namely 2S and 2P. NO 2d orbital exists. Hence, at excited state, five half-filled orbitals formation is not possible.

20. Why does $PCl_5$ exist but $NCl_5$ not form.

The electronic configuration of P

$P(15) = 1s^2 2s^2 2p^6 3s^2 3p^3$ (ground state)




For that reason $PCl_5$ exist but $NCl_5$ does not exist.