

Modern Instrumental Methods of Analysis

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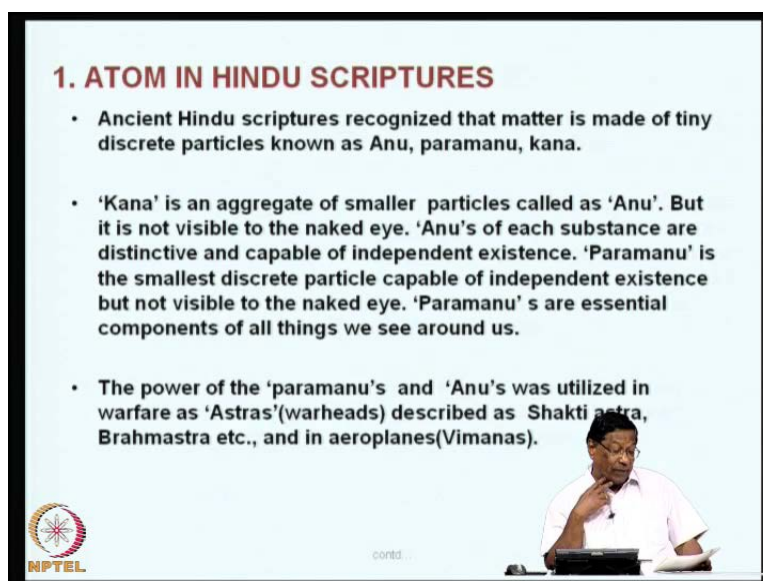
Indian Institute of Science, Bangalore

Lecture No. # 02

Atomic Structure



Greetings and welcome to the second lecture of this course on modern instrumental methods of analysis. In the last class, we had seen what an analytical chemist does and what an analytical scientist does. And, most of the... We have also seen that most of the modern instrumental methods of analysis are based on the atomic structure and transitions occurring during the atomic excitations and nuclear excitations. So, let us take a look at the atomic structure and molecular structure also to some extent.

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1. ATOM IN HINDU SCRIPTURES

- Ancient Hindu scriptures recognized that matter is made of tiny discrete particles known as Anu, paramanu, kana.
- 'Kana' is an aggregate of smaller particles called as 'Anu'. But it is not visible to the naked eye. 'Anu's of each substance are distinctive and capable of independent existence. 'Paramanu' is the smallest discrete particle capable of independent existence but not visible to the naked eye. 'Paramanu' s are essential components of all things we see around us.
- The power of the 'paramanu's and 'Anu's was utilized in warfare as 'Astras'(warheads) described as Shakti astra, Brahmastra etc., and in aeroplanes(Vimanas).

  contd.

The concept that the matter is built up of tiny discrete particles traces its origin to the ancient Hindu scriptures, such as Vedas. The descriptions of molecules and atoms and electrons have been given as kana, paramanu and Anu. Basically, a kana is an aggregate of smaller particles called as Anu. It is not visible to the naked eye, but it is capable of independent existence. Paramanu is the smallest discrete particle capable of independent

existence, but not visible to the naked eye. Paramanus are the essential components of all the atoms, all the things we see around us. The power of paramanus and Anus was utilized in warfare as Astras: Shakthi astras – you would have heard when you listened to Mahabharatha; you would have heard Shakthi astra, Bramastra during atomic warheads being used. And, all these Astras or weapons utilized the power of the atoms. Therefore, we have to conclude that the universal nature of the atoms and electrons and protons, nucleus, etcetera – they were all well-recognized even during the Indian social milieu since 2000 B. C.

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2. DALTON'S THEORY (1802)

- Matter is composed of tiny real particles called atoms which are indivisible and cannot be created or destroyed.
- Atoms of all substances are identical in nature, weight, size and other properties. Atoms of pure substance differ in weight & other characteristics from other substances.
- Atoms combine in definite proportions to form chemical compounds.

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However, it was John Dalton, who proposed the modern theory of atoms. And, he is considered recognized as the father of modern atomic theory, who provided the first scientific hypothesis of the structure of the atom somewhere in 1802 or so. He suggested that the matter is composed of tiny real particles called as atoms, which are indivisible; they cannot be created nor destroyed. And, atoms of each pure substance are identical in nature, weight and size and other properties also. Atoms of one pure substance differ in weight and other characteristics from those of other substances. Further, he suggested that the union of atoms in definite numerical proportions results in chemical combinations of compounds, etcetera. Subsequent developments in science led to the expansion of atomic theory and experimental data generated by a number of scientists, such as Michael Faraday, Rutherford, J. J. Thomson and other peers with the discovery of electrons, X-rays, radioactivity, nuclear reactions and other subatomic particles.


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3.FUNDAMENTAL COMPONENTS OF ELEMENTARY PARTICLES

Particle	Notation	Mass* (AMU)	Charge* esu $\times 10^{10}$	Relative charge
Electron	e	0.0005486	-4.8029	-e
Proton	P, ${}^1_1\text{H}$	1.00757	+4.8029	+e
Neutron	n, ${}^1_0\text{n}$	1.00893	0	0
Positron	e^+ , B^+	0.0005486	+4.8029	+e
Neutrino	ν	0	0
Antineutrino	0	0
Meson	π	0.156	± 4.8029	$\pm e$
	μ	0.118	± 4.8029	$\pm e$
Deuteron	d, ${}^2_1\text{D}$	2.01416	+4.8029	+e
Alpha	α , ${}^4_2\text{He}$	4.00279	+9.6058	+2e

*AMU - Atomic mass unit, equivalent to 1.6603×10^{-24} g
+esu is the fundamental unit of electrical charges

contd. ...



It is now widely recognized that the atoms are divisible. They do contain smaller particles, which may or may not be having independent existence. And, some of them are capable of independent **existence**; that is what we mean outside the atom. And, some of them may be capable of staying inside the atom independently. Some others are capable of existing momentarily outside the atom or inside. Among **the stable** particles, only electrons, protons and neutrons are recognized as having independent existence.

The electrons are made up of small energetic particles, whose existence was proved by Sir J. J. Thomson. Electrons are fundamental particles of all substances. And, **particle** – protons are also fundamental particles. And, the other particles that we are looking at are electrons, protons, neutrons, positrons, neutrinos, antineutrinos, mesons, deuteron and alpha particles. And, you would see that most of these particles are not capable of independent existence, but many of them have been proved only theoretically.

However, it was Sir William Crookes in 1879 showed that in highly evacuated discharged tubes, when high potentials were applied, cathode rays streamed from the negative poles. And, these cathode rays were negatively charged. They travel in straight lines, cast shadows on the targets placed in their path; and, produce mechanical motion in pin wheels, produce fluorescence in glasses; and, heat thin **metals** to incandescence just like the tungsten bulbs, and impart negative charges to objects in their path and get deflected in the applied electrostatic and magnetic fields. Further, it was shown that they

cause ionization in the gases; that means suppose you are passing cathode ray tubes in a container full of gases, they also cause ionization of the gases; that means more electrons will be released from the given system. Also, known to expose photographic plates, yield X-rays against stable targets, etcetera. These particles were named as electrons.

And, in 1897, Sir J. J. Thomson evaluated the ratio of the charge to mass ratio for the electrons from different sources and showed them to be identical; that means the electrons are the essential part of almost all atoms that we know of. And, they are having a charge of about 4.8029×10^{-10} esu. What is esu? An esu is the fundamental unit of an electrical charge. And, we also have here mass charges, mass unit that is known as AMU, that is, atomic mass unit – equivalent to 1.6603×10^{-24} gram. And, De Broglie in 1925 advanced the theory that electrons also possess wave properties; that means the electrons would be moving like waves. And, what are the properties of waves? They cause reflection; they cause diffraction. This formed the basis of the theoretical explanation of the extra nuclear structure of the atoms.

Now, let us discuss about proton. In 1911, Rutherford showed that the beams of positive particles, positive rays are also called as canal rays, could be obtained in discharged tubes of cathode rays, whose charge and masses depend upon the residual gases in the atoms in the tubes. So, when the residual gas was hydrogen, maximum ratio of charge to mass ratio was obtained; and, these particles are called protons; and, found to be identical with hydrogen atoms from which single electron had been removed. And, just like electrons, protons are also considered a fundamental particle, whose mass is 1.00757 atomic mass units. In general, we take it as 1 atomic mass. But, actual mass is 1.00757 AMU and its charge is 4.8029×10^{-10} es units. And, in a sense, what we are telling is an electron will have one negative charge and a proton will have one positive charge. So, if an atom has to be neutral, it must have equal number of protons and electrons.


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+esu is the fundamental unit of electrical charges

contd. ...



Now, if the atom is only made up of protons and electrons, the weight of the atom should be exactly same as the number of protons and number of electrons; and, the charge and weight should be matching. In number of cases, we see that the atoms are heavier than the number of protons that are already there, expected to be there. Now, this give rise to the conclusion that another particle, which is as heavy as a proton is also part of an element, which contributes to the weight of the atom. This is known as neutron. And, even though the independent existence of a neutron particle was predicted around 1920, it was Chadwick in 1932, who definitely proved that bombardment of light elements, such as lithium, beryllium, etcetera with alpha particles, that is, helium atoms give rise to a penetrating radiation, which consisted of neutral particles of approximately unit mass corresponding to the reaction; beryllium reacting with helium – that goes to carbon and gives rise to a particle of no charge.

While it is difficult to generate neutrons from heavier elements, a variety of nuclear reactions are known to occur in nuclear reactors, which unequivocally prove the existence of neutrons. The atomic mass of a neutron is also almost approximately same, that is, 1.00893 and the charge is 0 of course. Over the years, a number of other unstable particles were discovered, which were **capable of independent, incapable of independent existence**. And, these particles are known as positron, neutrino, antineutrino, mesons and other particles like deuteron; and, alpha particles have come to be recognized as the fundamental components of an atom. So, we have protons; charge is 1 and denoted as P;

mass is this much (Refer Slide Time: 14:22). And then, we have neutrons; and then, positrons, neutrinos, antineutrinos – all these things carry specific charges. And, mesons are there; deuterons are there; their mass is approximately 2.01416. And, alpha particles are essentially helium atoms with basically with a mass of 4.00279 and charge is 9.6058 and **electronic** relative charge is 2.

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4. MODERN ATOMIC THEORY

- An atom consists of a positively charged nucleus of about (10^{-12} cm) and comparatively heavy.
- An extra nuclear arrangement of electrons which is comparatively large $(\cong 10^{-8} \text{ cm})$ and diffuse in character.
- Nucleus consists of a number of protons and neutrons. They are formally related as:



Neutron $\xrightleftharpoons[e^-]{e^+}$ Proton

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What does modern atomic theory tell us about the atomic structure? Basically, it tells us that an atom consists of a positively charged nucleus of about to 10 raised to minus 12 centimeter dia and which is comparatively heavy. An extra nuclear arrangement of electrons, which is comparatively large in size, that is, approximately 10 raised to minus 8 centimeter; that means compared to the nucleus, the electronic charge is approximately 10,000 times larger; that means the electrons are there moving around the nucleus in a space of about 10 to the power of 4 times – 10,000 times space; and, the electronic structure is approximately diffused in character. Nucleus consists of a number of protons and neutrons. They are formally related as neutron collecting a charge becomes a proton; and, a proton losing a charge becomes a neutron, other way around.

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▪ Nuclear forces arise from the creation and annihilation of π mesons by nuclear particles (nucleons). During radio active decay processes, changes in nuclear charges occur according to the following mechanisms.

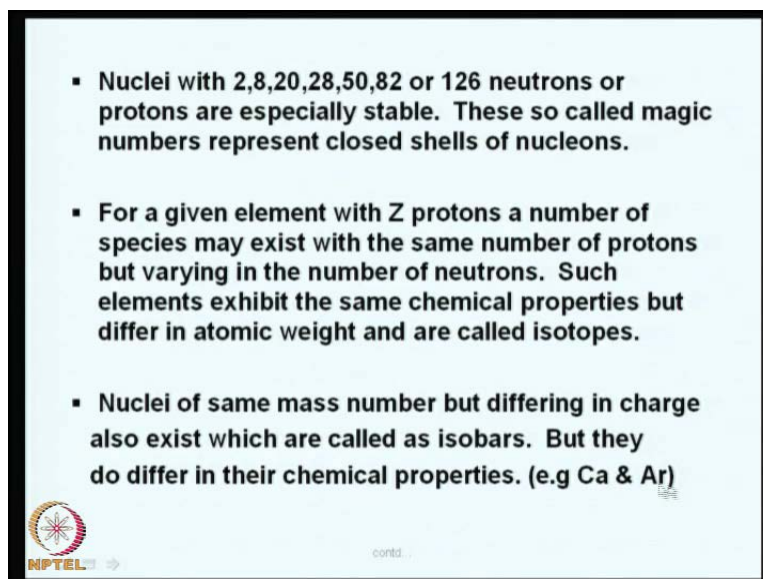
$$P \rightleftharpoons n + \pi^+$$
$$\pi^\pm \rightleftharpoons \mu^\pm + \nu$$
$$\nu^\pm \longrightarrow e^\pm + z \nu$$
$$\mu^- + P \longrightarrow n + \nu$$


contd. ...



And, nuclear forces – first, let us consider only the nucleus; nuclear forces arise also from the creation and annihilation of pi mesons, which are also fundamental nuclear particles. They are known as nucleons. During radioactive decay processes, changes in the nuclear charges occur according to the following equation; that is, first reaction if you see, proton goes to neutron plus pi plus and pi plus or minus will change to **meson** – mu plus or minus plus some radiation and we will have electronics charge. And, the **musons** will react with protons to produce a neutron; that means the change from a proton to a neutron is not exactly a single step reaction. This we will have to appreciate.



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▪ Nuclei with 2,8,20,28,50,82 or 126 neutrons or protons are especially stable. These so called magic numbers represent closed shells of nucleons.

▪ For a given element with Z protons a number of species may exist with the same number of protons but varying in the number of neutrons. Such elements exhibit the same chemical properties but differ in atomic weight and are called isotopes.

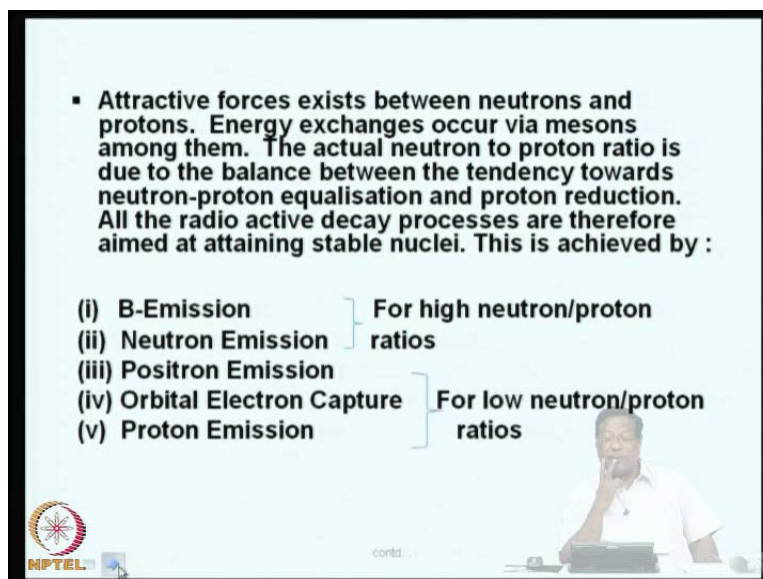
▪ Nuclei of same mass number but differing in charge also exist which are called as isobars. But they do differ in their chemical properties. (e.g Ca & Ar)

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Now, let us take a look at what type of nucleus are stable. See any nucleus would not be stable on its own and it will decay. So, we have certain considerations, which will tell us whether a nucleus is stable or not. Now, nuclei with 2, 8, 20, 28, 50, 82 and 126 neutrons or protons together are especially stable. These so-called magic numbers represent closed shells of the nucleons also. For a given element with Z protons, a number of species may exist with the same number of protons, but varying in the number of neutrons. These are known as isotopes. Such elements exhibit the same chemical properties, but differ in the atomic weight and are called isotopes. Another point we will have to consider is nuclei of the same mass number, but differing in charge also exist, which are called as isobars; that is, they have the same mass number, but differ in the charges. They are different elements actually, but they do differ in their characteristic properties or chemical properties, etcetera, which is expected. So, for example, you can consider that calcium and argon – both of them have the same mass number; that is, total of protons and neutrons in their nucleus.

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▪ Attractive forces exist between neutrons and protons. Energy exchanges occur via mesons among them. The actual neutron to proton ratio is due to the balance between the tendency towards neutron-proton equalisation and proton reduction. All the radio active decay processes are therefore aimed at attaining stable nuclei. This is achieved by :

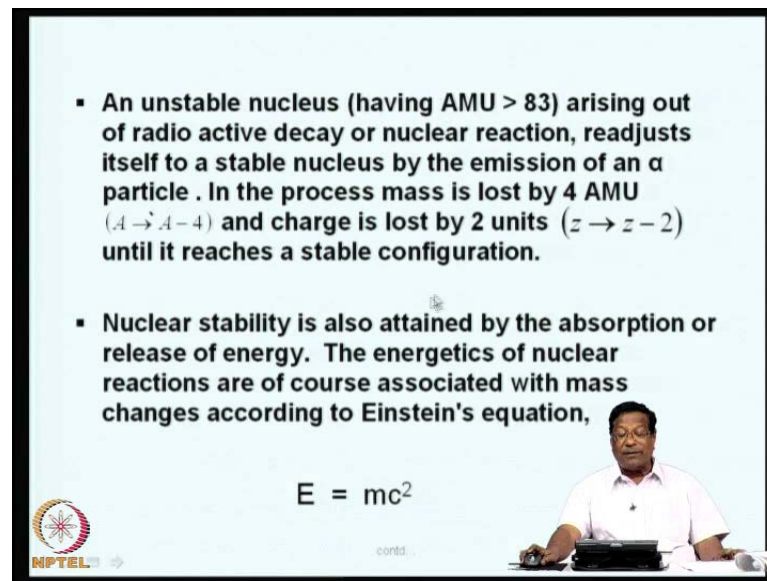
(i) B-Emission	}	For high neutron/proton ratios
(ii) Neutron Emission		
(iii) Positron Emission	}	For low neutron/proton ratios
(iv) Orbital Electron Capture		
(v) Proton Emission		

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Now, if the neutrons and protons are present in the nucleus, how do they coexist together? Because protons have positive charge and neutrons have no charge, there has to be some sort of binding property to hold the neutrons also together. We conclude that there must be some sort of attractive forces between neutrons and protons. Energy exchanges must also be occurring via mesons among them. The actual neutron to proton ratio in a given compound is due to the balance between the tendency towards neutron-proton equalization to reach the magic numbers as well as proton reduction; minimum number of protons for a given compound, so that isotopes are less.

And, all the radioactive decay processes what we see are attempts by an active element aimed at attaining stable nuclei, that is, the magic number 2, 8, 18 and those things what we had referred earlier. This can be achieved by either beta emission, that is, electrons; and then, neutron emission – heavier neutrons can be thrown away from the nucleus. And, this (Refer Slide Time: 20:36) mechanism, that is, loss of neutrons by beta emission and neutron emission occurs for high atomic weight substances with high neutron and proton ratios. And, other way is to lose the electrons. And, they could be in the form of positrons, orbital electron capture and proton emission. This is predominant among substances with low atomic weight.

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▪ An unstable nucleus (having AMU > 83) arising out of radio active decay or nuclear reaction, readjusts itself to a stable nucleus by the emission of an α particle . In the process mass is lost by 4 AMU ($A \rightarrow A - 4$) and charge is lost by 2 units ($z \rightarrow z - 2$) until it reaches a stable configuration.

▪ Nuclear stability is also attained by the absorption or release of energy. The energetics of nuclear reactions are of course associated with mass changes according to Einstein's equation,

$$E = mc^2$$

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An unstable atomic nucleus – what kind of atomic nucleus should be unstable? You see we see so many elements with atomic weight of 2, 3, 4 and etcetera; and, we say that atoms attain their nucleus stable state by emitting the positrons and other things, what we have seen in the last slide. And, an unstable nucleus is one having an atomic mass unit of more than 83. So, this arising out of radioactive decay or nuclear reaction; what does a radioactive decay or nuclear reaction do? It readjusts itself to a stable nucleus by the emission of a particle. In the process, mass is lost by 4 atomic units and the charge is lost by 2 units – z goes to z minus 2. And, atomic weight reduces by 4 units until it reaches a stable configuration.


Nuclear stability is also attained by the absorption or release of energy. Excess energy if it is there, it is simply lost and the atom reaches the stable state. The energetics of nuclear reaction are therefore associated with the mass changes, which is according to the Einstein's equation – E is equal to m c square; where, e is the energy; m is the mass; and, c is the velocity of light, a very famous equation, which won in the nobel prize including the contribution to the theory of relativity.

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▪ The release of energy takes place either in the form of heat or as radiations. The mass change corresponding to the conversion of hydrogen into helium,

$$2\ {}^1_1\text{H} + 2\ {}^1_0\text{n} \rightarrow\ {}^4_2\text{He} + Q$$

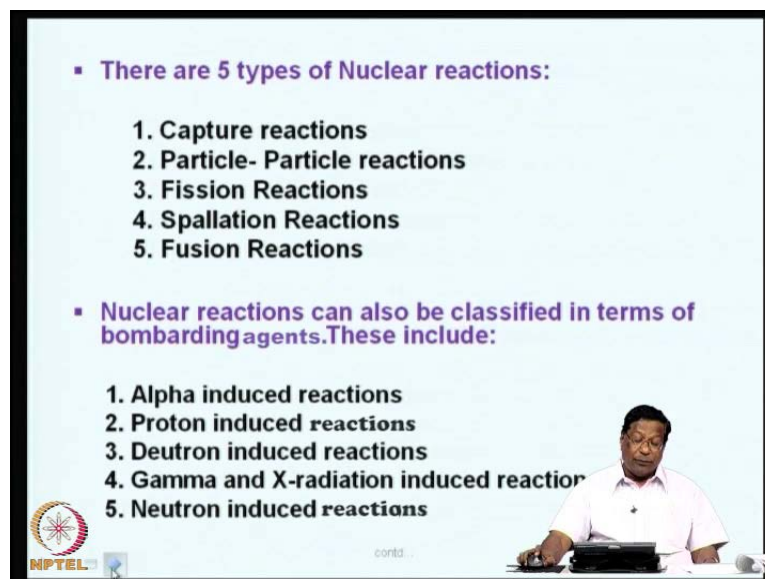
is 0.0302 AMU. This is equivalent to 28.12 Mev of energy per helium atom or 6.45×10^8 k cal per gram atom of helium. This is equivalent to the temperatures prevailing on sun. Hence nuclear reactions are of interest as a source of energy.



contd.

The release of energy from a nucleus takes place either in the form of heat or as radiation. The mass change corresponding to the conversion of hydrogen into helium is represented like this – we have 2 hydrogens with 1 proton and 1 neutron; and then, 2 neutrons with 1 atomic mass unit and 0 charge. Both of them combined to give you an atomic mass of 4 units and charge of 2 units plus there is a small quantity, that is, Q, that is, energy; that means when 2 protons and 2 neutrons combine, there is formation of helium, but some amount of energy is released. And, this energy using that Einstein's equation corresponds to about 0.0302 atomic mass units; very small quantity. But, this is equivalent to 28.12 million electronic volts of energy per helium atom or approximately 6.45×10^8 kilo calories per gram of the helium. This is equivalent to the temperatures prevailing on the sun. Therefore, nuclear reactions are of interest to us as a source of energy.

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▪ There are 5 types of Nuclear reactions:

1. Capture reactions
2. Particle- Particle reactions
3. Fission Reactions
4. Spallation Reactions
5. Fusion Reactions

▪ Nuclear reactions can also be classified in terms of bombarding agents. These include:

1. Alpha induced reactions
2. Proton induced reactions
3. Deuteron induced reactions
4. Gamma and X-radiation induced reaction
5. Neutron induced reactions

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We have so many nuclear reactors nowadays; and, they produce lot of energy to sustain the society. What types of nuclear reactions are there? If you consider, nuclear reactions can occur by capturing the capture reactions, particle-particle reaction – they come and hit each other and then energy could be released; fission reactions – the fission reactions means a [Repeated Audio-Video] (Refer Slide Time: 25:16) substance getting decomposed to produce protons, neutrons and other things, radiations, etcetera. Spallation reactions and fusion reaction – nuclear fusion – all of you must have heard, which is also a source of nuclear energy, that is, electrical energy in the ultimate use.

Nuclear reactions can also be classified in terms of bombarding agents. These bombarding agents include alpha induced reactions, that is, helium, atoms; and then, proton induced reactions – bombardment with hydrogen; deuteron induced reactions – bombardment with deuterons; gamma and X-radiation induced reactions, and neutron induced reactions. We will not go into details of these reactions, because as and when the need arises, I will come back to this and explain to you more in detail.

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5. THE ELECTRONIC STRUCTURE OF THE ATOMS

- ✓ In 1904 Sir J.J. Thomson proposed the corpuscular theory of matter. He pictured the positive charge of an atom distributed uniformly throughout a sphere of protons and neutrons of about 10^{-8} cm. Negative charge was surrounding it in a jelly-like fashion.
- ✓ Rutherford modified this theory that electrons revolve around the nucleus in such a way that the centrifugal force exactly balances the inward attractive forces much like our planets do around the sun. This view was also not tenable because within the atom, particles having opposite charges are present. Hence regardless of their speed, they enter the nucleus. Moreover the electron losing energy would emit continuous radiation without any sharp breaks.

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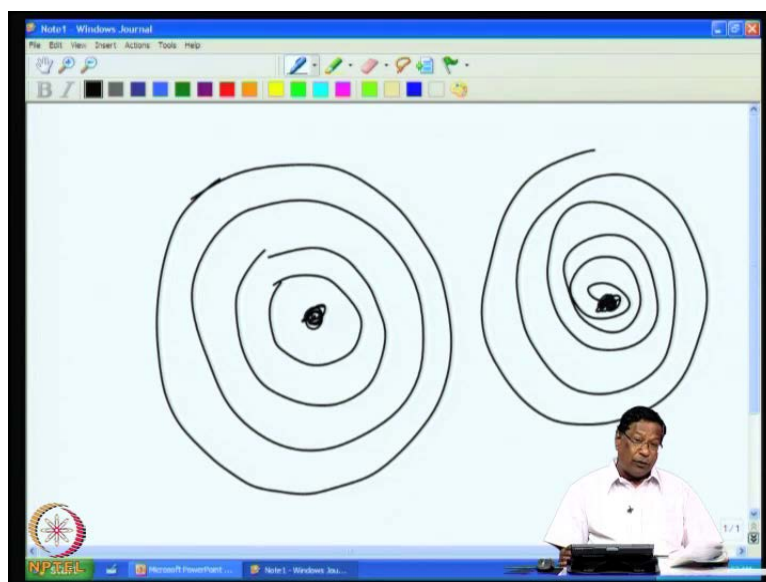
Now let us take a look at the electronic structure of the atoms. Now, the (Refer Slide Time: 27:48) electronic structure as I have already told you, is around the nucleus in a space of about 10,000 times the size of the nucleus; and, in which, there must be electrons having same charge as a proton, but having about 1 by 1640th of a mass; that means the charge must be very high; charge to mass ratio is very high in electrons. And, these electrons were first proposed – found out and discovered you can say – in 1904 when Sir J. J. Thomson proposed the corpuscular theory of matter. He pictured the positive charge of an atom distributed uniformly throughout a sphere of protons and neutrons in which of about 10^{-8} centimeter around which negative charge was surrounding it in a jelly-like fashion, that is, like an amoeba.

The charge is here; the positive charge is here; electrons are around it; the electronic mass is moving around like this; and then, it does not have a specific shape. And, this view was somehow not liked by all, because it was not confirmed by the experiments. And therefore, Rutherford modified this theory that electrons revolve around the nucleus in such a way that the centrifugal force exerted by the electrons exactly balances the nuclear charge. So, the nucleus being a positive charge will attract the electrons. But, if the electron is going round and round in such a way that the force of attraction is exactly equal to the force of repulsion, then they will not combine; that was the logic. So, what did he do? He suggested that forces are there, are exactly balanced, so that an atom can be stable. And, this you can imagine like our arrangement of the solar system – sun is

there; mercury is there; after that, we have Venus, then we have earth, then mars, etcetera.

Now, all these planets are going around the sun, but they do not end up falling into the sun. Even though sun is quite bigger and having larger mass, larger attractive forces, but still the orbital motion of the planets makes them stay in their orbits and do not fall into the solar system into the sun. So, this view was also exactly not **tenable**. Of course, it provided a beautiful way of imagining how an atom can be stable. Unfortunately, this view was also **not stable, tenable**, because within the atom, particles having opposite charges will always keep on losing some of the energy, so that it will describe a path that finally ends up landing in the path.

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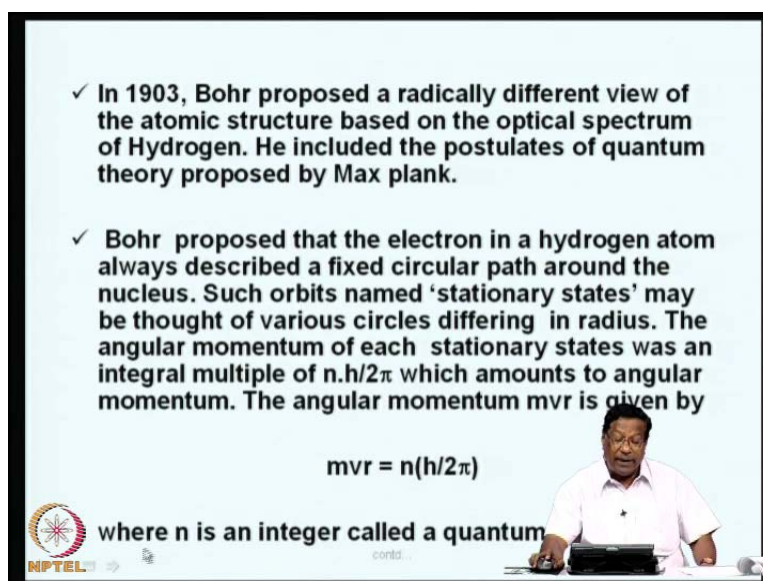
Suppose here is the nucleus and then electrons are there going round and round, where the forces are matching. Unfortunately, this system is not tenable. Actually, what happens, here is the nucleus; and then, electron going round and round will **precess** around it until finally, it lands into the nucleus. This is not very nice, because it does not give us a stable electronic structure, but which is against our experience that elements are essentially very stable. This kind of arrangement what we see here are not conducive to confidence that the electrons are very stable; that means the element is not stable; that means everything is in a state of **unstability**, which is not correct; that is, how do we

know that? It is our experience. So, what do we do? We have to modify this theory somewhat.

And, the Rutherford's theory (Refer Slide Time: 33:17) – what was the problem? The view was not tenable, because within the atom, particles having opposite charges are always present inside the atom also. And, how do you explain that? Inside the nucleus, we have positive charged nucleus and then mesons, **mesons** and other things. Hence, regardless of their speed, even if the electrons are around it, going round and round, however stable it is, they enter the nucleus and finally annihilate themselves. Moreover, the electron losing energy would emit continuous radiation. This is another part, which I want to talk to you.

See an element is characterized by a spectrum. And, this spectrum as it gets excited, lose its energy, etcetera, electromagnetic radiations are coming out. And, the electromagnetic radiation if it is coming out continuously, it means there is loss of energy continuously. This is again not possible, because our experience shows that the electron losing energy would emit continuous radiation without any sharp break. But, what actually we see in a spectrum is a series of **lines**, which represent specific amount of energy; it is not continuous. First, one line; then, another line; there is a gap; and then, another line. Like that when it works like this, we know that the spectrum is not continuous and the theory has to be modified.

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- ✓ In 1903, Bohr proposed a radically different view of the atomic structure based on the optical spectrum of Hydrogen. He included the postulates of quantum theory proposed by Max plank.
- ✓ Bohr proposed that the electron in a hydrogen atom always described a fixed circular path around the nucleus. Such orbits named 'stationary states' may be thought of various circles differing in radius. The angular momentum of each stationary states was an integral multiple of $n \cdot h/2\pi$ which amounts to angular momentum. The angular momentum mvr is given by

$$mvr = n(h/2\pi)$$

where n is an integer called a quantum number

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In 1903, Niels Bohr, a great physicist of our times – he proposed a radically different view of the atomic structure based on the optical spectrum of hydrogen. He took the spectrum of hydrogen and he included the postulates of quantum theory proposed by Max Planck. So, what exactly did he do? He proposed that an electron in a hydrogen atom always describes a fixed circular path called as stationary states – orbits. He thought of that the electrons are moving around at different energy levels compared to the nucleus. The one which is very near the nucleus will have very high energy; the one which is farther away will have lower energy, like that, which are quantized. And, the quantification comes from an integral multiple of $n h$ upon 2π ; where, n is an integral number; h is Planck's constant; π is 3.142, etcetera, which amounts to angular momentum. Therefore, the angular momentum of a particle, $m v r$ is given by $n h$ upon 2π ; where, n is an integer called as a quantum number.

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✓ He also postulated that as long as the electron remained in a given orbit it neither radiates nor absorbs energy. When the electron moves from one orbit to another it was considered to involve the absorption or emission of definite quantity of energy depending upon whether the electron moved from lower state to higher one or vice versa. This energy manifests as radiation and the frequency of such radiation is manifested as a spectral line which could be related to the energies of electron in the two states E_1 & E_2 as:

$$E_2 - E_1 = h \nu$$

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contd.

He also postulated that as long as the electron remained in a given orbit, it neither radiates energy nor absorbs energy. So, it is stable. When the electron... But, it will absorb or emit radiation when it falls down to a lower stationary orbit. And then, it has to be different. The energy corresponding to the change of the electron from one level to another is fixed. So, it has to give a spectrum, which corresponds to an exact frequency or energy in terms of it corresponding to that. So, it was considered.

When the electron moves from one orbit to another, it was considered to involve either the absorption or emission of definite quantity of energy depending upon whether the electron moved from lower state to highest one or higher state to lower one. This energy manifests as radiation and the frequency of such radiation manifests as a spectral line, which could be related to the energies of the electrons in the two states. For example, we write E_2 , that is, the first energy level; and, E_1 – second energy level; the transition is taking place. The energy corresponding to that would be $h\nu$. From any level, E_3 to E_1 for example, it will be only a multiple of again $h\nu$, but corresponding to the change in the energy level; n could be 1, 2, 3 etcetera. So, we have number of lines corresponding to electrons falling in different energy levels.

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✓ **Line spectra of hydrogen atom**

Lyman series	$n = 2, 3, 4, \dots$ to $n = 1$
Balmer series	$n = 3, 4, 5, \dots$ to $n = 2$
Paschen series	$n = 4, 5, 6, \dots$ to $n = 3$
Brackett series	$n = 5, 6, 7, \dots$ to $n = 4$
Pfund series	$n = 6, 7, \dots$ to $n = 5$

✓ **Origin of hydrogen spectrum**

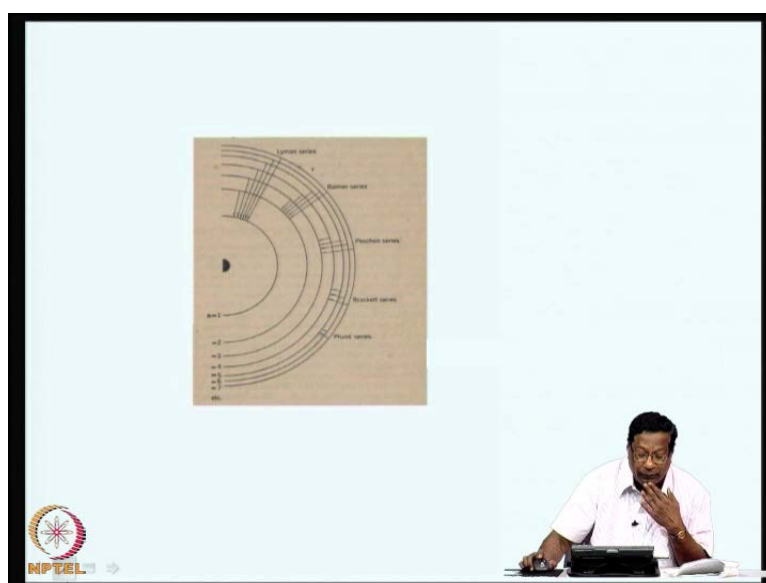
✓ **Bohr's theory could explain the spectra of hydrogen and He^+ , Li^{2+} & Be^{3+} etc. But it failed completely when applied to multiple electron systems. It could not account for splitting of optical lines (fine structure) when spectroscopes of high resolution power were employed.**

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Now if you take a look at hydrogen atom, you would see that five different kinds of lines you will get – spectrum. One is known as Lyman series. Here what happens, if you consider that bottom level is n is equal to 1, an electron can fall from n is equal to 2 to 1, 3 to 1, 4 to 1, 5 to 1 and infinity to 1. So, you will see a number of lines ending up where the electron ends up at energy level n is equal to 1. Now, you can imagine other situations, where they do not fall to the lowest energy level, but one level above the previous one. So, what happens, let us call it n is equal to 2; the level 2 is at a slightly lower energy than the level 1; that is, very near the nucleus n is equal to 1. It will be having very high energy.

Now, when the electron falls to state 2, it cannot fall from 1 to 2, but it can fall from 3 to 2, 4 to 2, 5 to 2; like that it can fall. And, all the changes that occur are corresponding to the changes in the electron falling to energy level 2 from their higher levels. Similarly, you can imagine, when n is equal to 3, corresponding **electronic** changes can occur from 4, 5, 6, etcetera. Similarly, n is equal to 4, n is equal to 5. And, when you look at the spectrum, you will see a Lyman... They are called as Lyman series, Balmer series, Paschen series, Brackett series and Pfund series.

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Now, let me take you back to this figure. You can see that here Lyman series is where the electrons are falling to energy level 1; and, Balmer series corresponds to level 2; Paschen series corresponds to level 3; Brackett is 4; Pfund series is 5. You would see that the energy corresponding to these Lyman, Paschen series, etcetera, would be having different energy level. Therefore, you will see that the Lyman series involves changes at very high level. So, in the electronic spectrum, they should be occurring at very high end of the electromagnetic spectrum. After that, the Balmer series, where n is equal to 2, would be having lines, which are slightly lower than the Lyman series. So, this Balmer series of lines is what you will see in the visible region. The Lyman series (Refer Slide Time: 41:42) corresponds to ultraviolet region. Similarly, Paschen series comes in IR range, etcetera. So, this accounted for the number of lines that you see in the electronic spectrum of hydrogen.

The origin – Bohr's theory could explain (Refer Slide Time: 42:06) the spectra of hydrogen and simple elements like helium plus, lithium 2 plus, beryllium 3 plus; that means essentially one electron system. Hydrogen is having one proton and one electron, no neutron. Helium plus is having one electron, because normal charge of helium is 2; helium plus 1 is **one electron – one charge** less than that. So, it is essentially like hydrogen atom. Similarly, lithium plus 2 will be having only one electron in the lithium atom; beryllium 3 – same case.

But, this theory while it explained the origin of spectrum corresponding to different energy levels, etcetera, it failed completely when applied to multiple electron systems. Where there are more than one or two electrons, how do you really explain that this corresponds to Lyman series, this change corresponds to Balmer series, etcetera? Too many lines, too complicated and it was not possible to explain. Further, it could not account for splitting of optical lines. That is known as fine structure when spectroscopes of high resolving powers were employed. What happens now, single peak – single line – spectral line – it splits into two in high resolving powers or under magnetic field. Suppose you take the same spectrum in a magnetic field. Then, instead of one line, you will see two lines like twins – double images. Bohr's theory could not explain this.

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6. SOMMERFELD THEORY

➤ In 1916 Sommerfeld modified Bohr's theory to include elliptical orbits which includes circular orbits only as a special case. The velocity of an electron moving in an orbit will be greatest when it approaches closest to the nucleus and least when it is farthest.

This introduces variability in the orbit also which as a whole will precess around the nucleus. This precessional movement will result in small energy changes and will be responsible for fine structure in the spectrum.

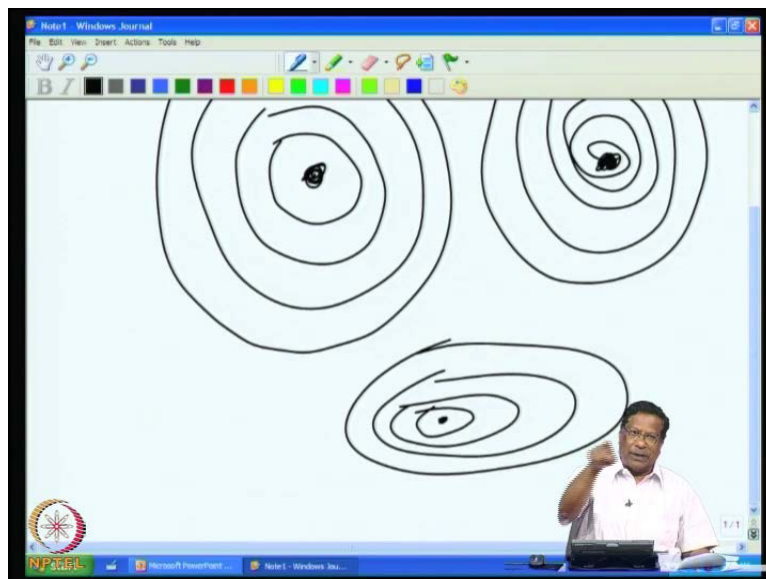
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The slide features a small inset image of a man in a white shirt sitting at a desk with a laptop, likely the presenter.

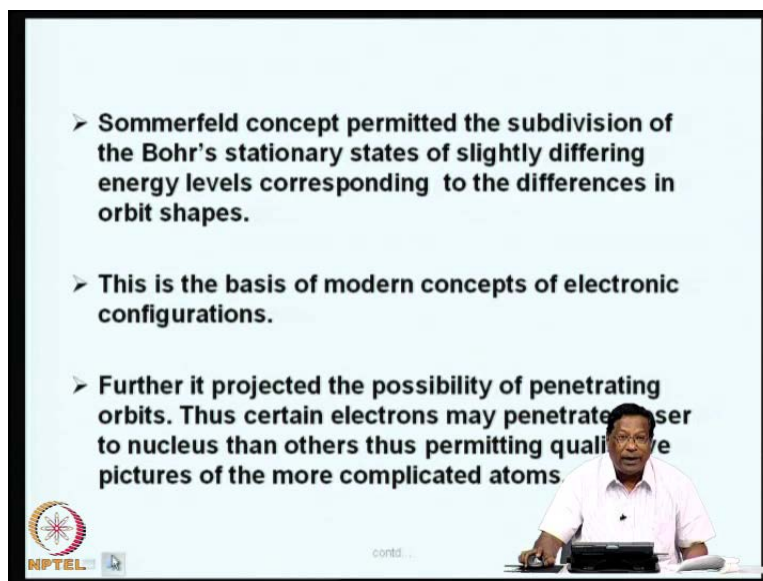
Somewhere around in 1916, Sommerfeld modified Bohr's theory to include elliptical orbits, which includes circular orbit as a special case. Now, you know what an ellipse is.

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Here is the nucleus; and, here is first orbit, then second orbit, third orbit, fourth orbit, like that. These figures are ellipses. He suggested that the electron moves around not in circular orbit, but when it approaches the nucleus, it will resist faster and then go slowly. Again, it comes nearer and goes slowly; like that in the first orbit, second orbit, third orbit. This is how he imagined a nuclear structure. A circular orbit is only a special case of elliptical orbit, because the axes of both are same in circular orbits. So, the velocity of an electron moving in (Refer Slide Time: 45:26) an orbit will be greatest when it approaches closest to the nucleus and least when it is farthest. This introduces variability in the orbit also, which as a whole will precess around the nucleus. This precessional movement will result in small energy changes, which will be reflected as a fine structure or double spectrum lines, split lines and all those things. So, this was a sort of improvement in the electronic structure.

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The slide features a light blue background with a black border. On the right side, a lecturer in a white shirt is seated at a desk with a laptop. On the left side, there is a list of three bullet points. At the bottom left is the NPTEL logo, and at the bottom center is the text 'contd. ...'.

- Sommerfeld concept permitted the subdivision of the Bohr's stationary states of slightly differing energy levels corresponding to the differences in orbit shapes.
- This is the basis of modern concepts of electronic configurations.
- Further it projected the possibility of penetrating orbits. Thus certain electrons may penetrate closer to nucleus than others thus permitting qualitative pictures of the more complicated atoms.

The Sommerfeld concept permitted the subdivision of the Bohr's theory of stationary states of slightly differing energy levels corresponding to the differences in orbit shapes. This is the basis of modern concepts of electronic configurations. Further, it projected the possibility of penetrating **objects**. See penetrating **object** means the orbits need not stay independent of each other, but the electron could move into the orbit of another level also; that means the electrons could move back and forth in different orbits. So, this was a very important concept, which it projected the possibility. Thus, certain electrons may penetrate closer to the nucleus than what is expected; and thus, permitting qualitative pictures of more complicated atoms.

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7. ELECTRONIC DISTRIBUTIONS IN ATOMS

- # The rule of 8: Inert gas atoms with the exception of Helium contain eight electrons in their outermost arrangement .
- # Helium, Neon, argon, krypton, xenon and radon contain 2,10,18,36,54 and 86 electrons and represent the end of various horizontal series of periodic classification.
- # C.R.Bury postulated that maximum number of electrons in the various shells are 2,8,18 and 32. He also stated that no shell can contain more than 8 electrons unless another shell further removed from the nucleus is being formed. This concept permitted logical explanation for the configurations of transition and inner transition elements i.e filling up of inner electronic levels while the outer most ones remained constant.

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Electronic distributions of atoms – if we continue our discussion, there are about another three concepts, which are very important for us to understand. One is the rule of 8 – that means inert gas atoms with the exception of Helium contain eight electrons in their outermost **orbit**. This is one of the rule of 8. And, what are such elements? Helium, neon, argon, krypton, xenon and radon – these are known as inert gases, which you see in the periodic table, which we will also see at this end of this class. And, they contain 2, 10, 18, 36, 54 and 86 electrons. They represent the end of various horizontal series of periodic classification of the elements.

Professor C. R. Bury postulated that maximum number of electrons in various shells are 2, 8, 18 and 32. He also stated that no shell can contain more than 8 electrons unless another shell further removed from the nucleus is being formed. This concept permitted logical explanations for the configuration of transition and inner transitional elements in the periodic table, that is, filling up of electronic levels while the outermost ones remain constant; inner levels are being filled.


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Electronic configurations of inert gas atoms

Symbol	At.No	K	L	M	N	O	P
He	2	2					
Ne	10	2	8				
Ar	18	2	8	8			
Kr	36	2	8	18	8		
Xe	54	2	8	18	18	8	
Rn	86	2	8	18	32	18	8



contd. ...




You can see these are the atomic numbers: helium, neon, etcetera – 2, 8, 8, 18, 18 and 8. All the last elements are 8; last shell contains eight electrons.

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8. QUANTUM DESIGNATIONS FOR ELECTRONS

- The Bohr-Sommerfeld concept of electrons revolving around the atomic nuclei is limited to well defined shapes is essentially a rough pictorial presentation.
- Modern concepts based on wave mechanics depict comparative density of the electronic charges at any given point within the atom based on the theory of probability.
- Essentially this means electrons will tend to group themselves in a series of positions relative to the nucleus which may be considered as energy levels w.r.t the nucleus. Transitions are permitted only between these energy levels giving rise to spectrum.



contd. ...

And, quantum designations... Bohr-Sommerfeld concept also gave the concept of electrons revolving around the nucleus, is limited to well-defined shapes is essentially a rough pictorial presentation only. Even with all the improvements that we have seen so far, it is only a rough pictorial presentation, rather than the exact situation. Modern concepts are based on wave mechanics. Imagine that electrons are moving around; even

if it is revolving around it, it would be moving in a circular fashion, but in a wave motion and the comparative density of the electronic charges at any given point within the atom based on the theory of probability. So, this is how the actual electronic structure as we understand keeps on changing.

And essentially, what does it mean? This means electrons will tend to group themselves in a series of positions relative to the nucleus, which may be considered as energy levels with respect to the nucleus. Electrons are there. They keep on moving around in the wave motion, but they maintain a certain distance. And, this distance gives you the approximate energy levels with respect to the nucleus. The nearer the nucleus, higher is the energy level; farther the nucleus, lower is the energy level. So, transitions are permitted in between these energy levels giving rise to a spectrum – electronic spectrum.

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• Electrons are best described in terms of four quantum numbers: Principal Quantum number(n) , Orbital quantum number(l), magnetic quantum number(m) and Spin quantum number(s).
The energy levels corresponding to n are given by

$$w = \frac{-2\pi^2 z^2 e^4 \mu}{h^2} \left(\frac{1}{n^2} \right)$$

where w - energy of the electron
z - Total number of electrons atomic number)
e - Electronic charge
 μ - Electronic mass and
h - Planks constant

Crudely this amounts to the mean distance of the electron from the nucleus. Principle quantum number may have value from n=1 to infinity where ∞ refers to the complete removal of the electron & production of a positive ion. They may be designated as K shell, L shell, M shell etc.


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Now, electrons are best described in terms of four quantum numbers. That is a principle quantum number n and orbital quantum number l, magnetic quantum number m and spin quantum number denoted as s. Now, the exact equation is something like this. w is equal to minus 2 pi square z square e raised to 4. And, this is mu divided by Planck's constant square into 1 over n square; where, w is the energy of the electron and z is the total number of electrons, e is the electronic charge, mu is the electronic mass and h is Planck's constant.

Crudely, what does it mean? It means this amounts to the mean distance. The electron can be found from the nucleus. Principle quantum number may have values from n is equal to 1 to infinity; of course, infinity means where an electron cannot be found, that is, an ion. But, it is not actually so. In actual practice, it can vary from 1, 2, 3, 4, 5, etcetera. And, infinity refers to complete removal of the electron from the system and production of a positive ion like hydrogen ion and helium ion, etcetera. They may be designated as K shell, L shell, M shell, etcetera.

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✓ Orbital Quantum number l is a measure of the orbital angular momentum of the electron which is a vector quantity

$$\frac{h\sqrt{l(l+1)}}{2\pi}$$

The values of l vary from zero to $(n-1)$. Hence for

$n = 1$,	l value is 0
$n = 2$	l value is 0,1
$n = 3$,	l value is 0,1,2
$n = 4$,	l value is 0,1,2,3

contd




The orbital quantum number is another **one** associated with orbital angular momentum of the electron, which is a vector quantity given by h into square root of l into l plus 1 upon 2π . The values of l vary from 0 to n minus 1; and, n is equal to 1 corresponds to l is equal to 0; and, n is equal to 2 corresponds to 0 and 1, etcetera. So, we have each shell...

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Customarily these levels are named after the spectral terms namely $s(l=0)$, $p(l=1)$, $d(l=3)$ and $f(l=4)$ etc and the electrons present in these orbitals are referred as s, p, d and f electrons.

A wave function associated with the orbital motion of an electron is called an orbital. Thus we have s, p, d, f orbitals also.

✓ Magnetic Quantum number (m_l)
some spectral lines split if the source is kept in a magnetic field. This is known as Zeeman Effect. The orbital angular momentum vector undergoes a precessional movement and describes a cone about an axis in the direction of the field the magnitude of which is given by $ml(h/2\pi)$.



Customarily, these levels are named after the spectral terms, s means l is equal to 0; p is l is equal to 1; d shell is l is equal to 3; and, f shell is l is equal to 4, etcetera. And, the electrons present in these orbitals are referred s, p, d, f electrons. A wave function associated with the orbital motion of an electron is called an orbital. Thus, we have s, p, d, f orbitals also. Basically what we mean to say is there are s, p, d, f electrons as well as s, p, d, f orbitals. The s, p, d, f electrons means an electron present in s, p, d, f orbitals.

Then, we have a magnetic quantum number m_l . And, the origin is when the atoms are split in magnetic fields, you will get **double split** lines. This is known as Zeeman effect. And, the orbital angular momentum vector undergoes a precessional movement and describes a cone about an axis in the direction of the field of the magnitude, which is given by m_l into h upon 2π .

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The magnetic quantum number is an integral value and varies from $-l$ to $+l$. Thus for s electron

s electron $l = 0$ and $m_l = 0$

p electron $l = 1$ and $m_l = -1, 0, +1$

d electron $l = 2$ and $m_l = -2, -1, 0, +1, +2$

f electron $l = 3$ and $m_l = -3, -2, -1, 0, +1, +2, +3$



contd

So, these values vary from minus l to plus l . So, s electron can have l is equal to 0; and, p electron can have l is equal to minus 1, 0, plus 1, etcetera. So, we have a number of magnetic quantum number also.

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- Spin Quantum Number (s)

An electron also rotates on its own axis. Hence it has its own angular momentum amounting to:

$$\frac{h \sqrt{s(s+1)}}{2\pi}$$

where $s = 1/2$ or $-1/2$ depending upon whether it is precessing along the applied magnetic field or opposing it. For each value of m_l there are two electrons differing in spin.

- No two electrons within any atom can have same 4 Quantum numbers. This is known as Pauli exclusion Principle. Each electron differs from every other electron in a given atom in its total energy.



contd

And, spin quantum number corresponds to a similar situation, where an electron rotates on its own axis given by h into square root of s into s plus upon 2π ; where, s is plus half or minus half.

We will continue our class in the next class, how to look at the electronic structure of the atoms in different situations for corresponding different elements.

Thank you.