Advanced Measurement Techniques in Fluid Mechanics and Heat Transfer

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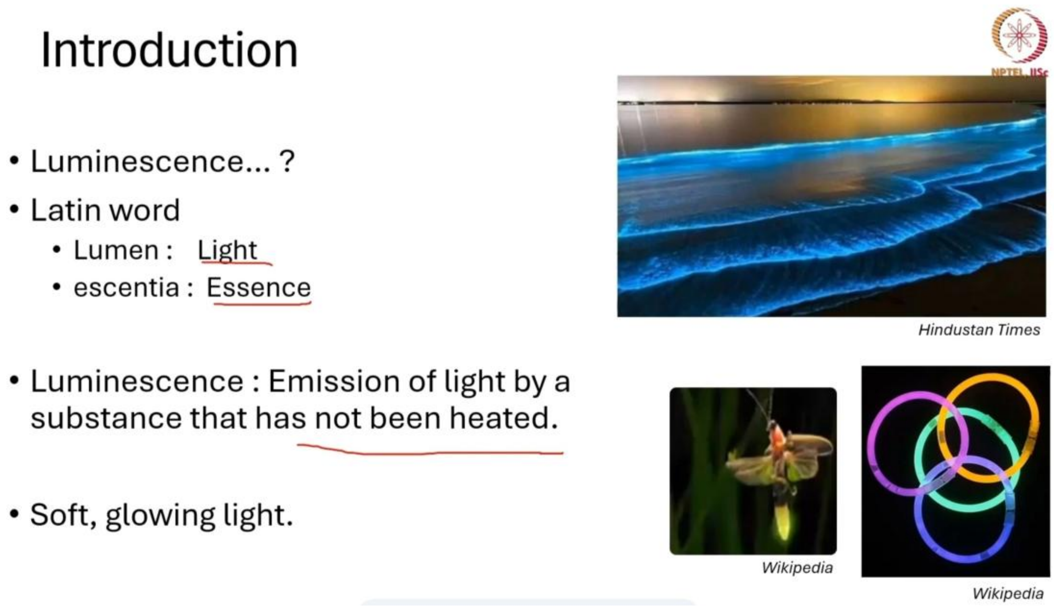
Week – 10
Lecture - 49

Emission Spectroscopy – 1

In this session, we are going to discuss the topics of luminescence and emission spectroscopy. In the first part of the lecture, we will first discuss what luminescence is, why it occurs, and what the different physical concepts involved in it are. Later, we will go through the details of what electromagnetic radiation is, what the electromagnetic spectrum is, and then finally we will go into emission spectroscopy. Later, we'll be discussing the applications of luminescence and emission spectroscopy at the end of the lecture, so firstly, let's see what luminescence is. The word luminescence comes from a pair of Latin words, lumen and essentia. Lumen means light, and essentia means essence.

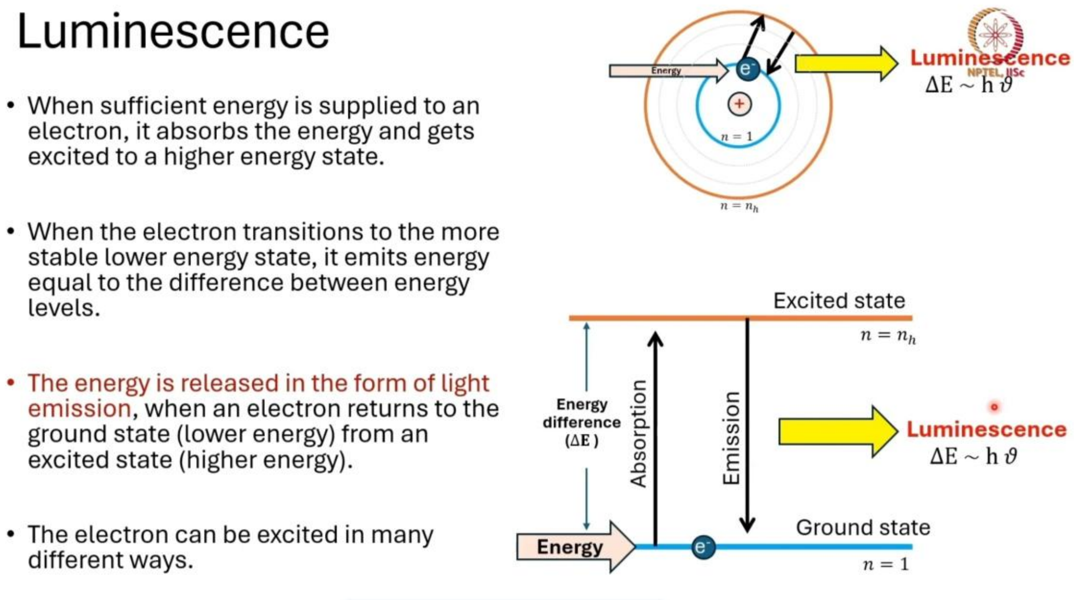
Coming to the definition of luminescence, the emission of light by a substance that has not been heated is luminescence. Here we have to focus on not being heated; this has been specifically included in the definition because luminescence is categorically different from another phenomenon that we observe, which is blackbody radiation, where light radiation is emitted by virtue of the temperature of the object. Luminescence is different from blackbody radiation; thus, not being heated is added in the definition. In general, luminescence is soft glowing light.



On the right side, three different examples of luminescence have been provided that we see in real life. The first image corresponds to a bioluminescent beach in Karnataka. In the seawater, there are bioluminescent plankton that undergo biochemical reactions, releasing light, and at night, the waters glow due to this bioluminescence. Another example is fireflies, which also emit light due to bioluminescence. The third example is the glow sticks that we generally see during concerts.

In these sticks, there are chemicals that react and emit light when they are activated. All three of these are examples of luminescence. However, the sources of luminescence may differ. All of them emit a soft glowing light. So, let's see.

How does luminescence occur? We all know that electrons orbit around the nucleus in an atom. So let us consider a simple atom where an electron is revolving around the nucleus. From the Morse model, we know that there are different energy levels in an atom where the electron can revolve around the nucleus. Here, n is the principal quantum number, which signifies these different energy levels, and the higher the energy level, the farther the electron is from the nucleus. From quantum physics, it is known that the energy levels that electrons occupy are discrete and not continuous, which are signified by these principal quantum numbers: n=1, n= 2, n= 3, and so on, as we move away from the nucleus, which has been represented here as two different energy levels where $n = n_h$ is some higher energy state.

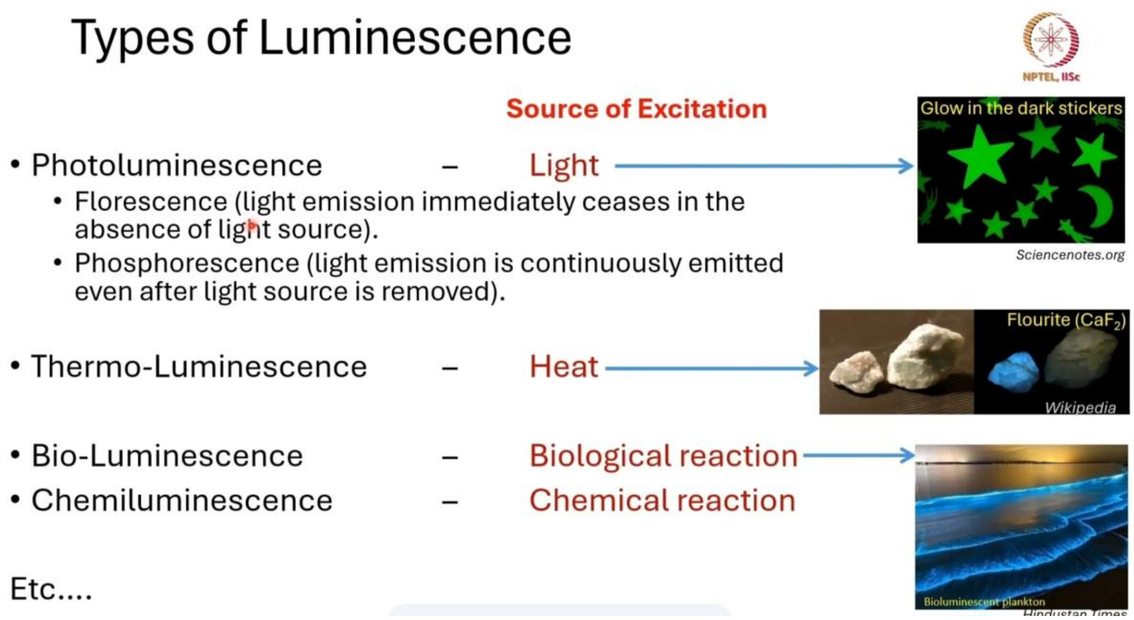


and n= 1 is the ground state where the electron is initially present. Now, when sufficient energy is provided to the electron, the electron absorbs this energy and transitions to a higher energy state. The higher energy state to which the electron excites can be determined by the energy difference between the excited state and the ground state, and it should match the energy provided initially. Since this excited state, which is the higher energy state, is unstable, the electron relaxes to the ground state, and this same energy difference is emitted by the electron in the form of electromagnetic radiation, which is light. The frequency of the electromagnetic radiation can be obtained using the relation

$$E = h\nu \quad .$$

where nu is the frequency, h is Planck's constant, and ΔE is the energy difference between the two energy states between which the electron has transitioned. Here, the initial energy provided to the electron can be of different types. However, as the electron relaxes from the excited state to the ground state, it emits light, which is why it is called luminescence. So, depending on the type of energy provided to the electron initially, there are different types of luminescence. The first kind is photoluminescence, where the source of excitation is light itself.

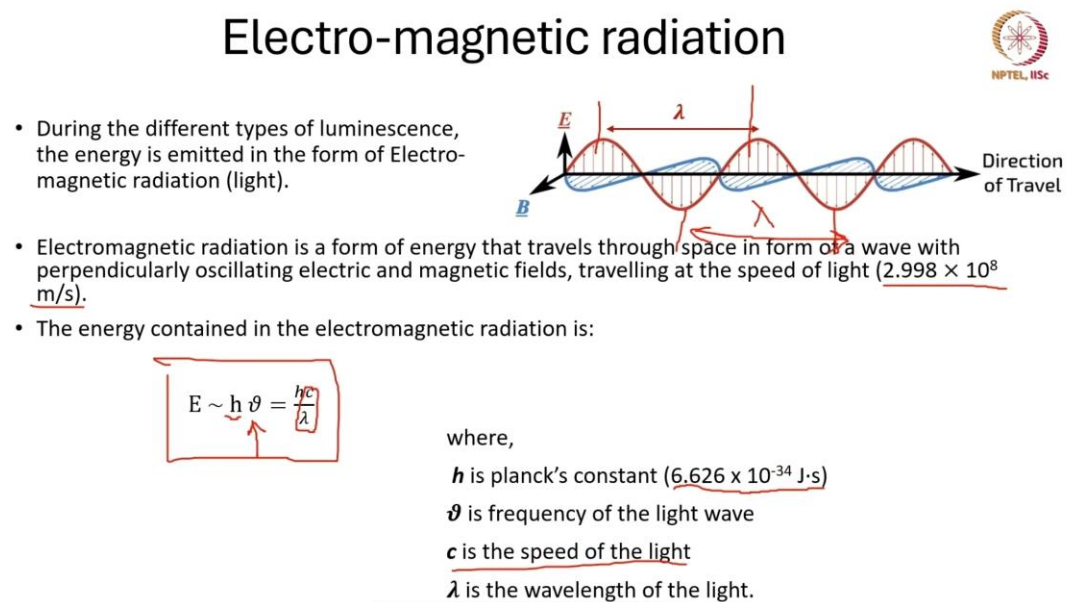
Some common examples of this are glow-in-the-dark stickers. During the daytime, these stickers are exposed to ambient light, and they absorb this light; during the night, they glow when the lights are switched off. These glow-in-the-dark stickers are an example of phosphorescence, which is where the light emission is continuously emitted even after the light source is removed. whereas other types of photoluminescence are fluorescence, where the light emission immediately ceases in the absence of a light source. The fluorescent tube lights that we use in our houses are a good example of the phenomenon of fluorescence.



In these fluorescent tubes, when the electrical current passes through the mercury vapor inside the tube, it produces ultraviolet light, and when this ultraviolet light incidents on the phosphor coating on the inner surface of the tube, that phosphor glows, emitting visible light. This is an example of fluorescence. Other types of luminescence include thermoluminescence, where heat is a source of excitation. The example for thermal luminescence is a mineral called fluoride; when a small amount of this mineral is heated using a candle in a dark room, it emits light. Another kind of luminescence is bioluminescence, which we have already discussed before, where the bioluminescent plankton undergo biochemical reactions, releasing light; here, the source of excitation is a biological reaction.

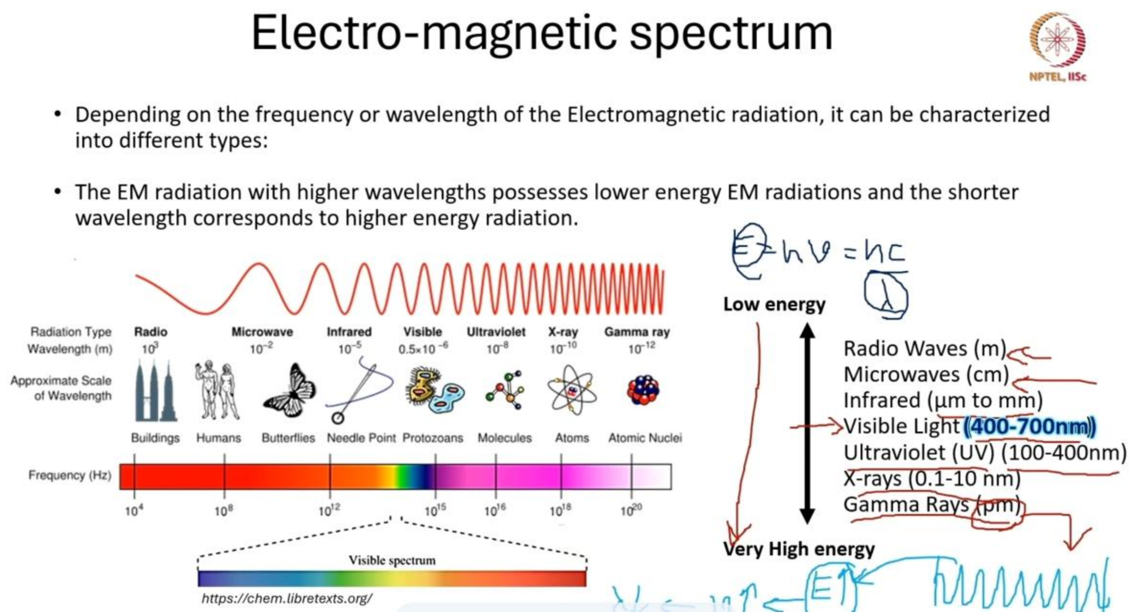
Chemiluminescence is another type of luminescence in which the source of excitation is the energy released during the chemical reaction. Apart from this, there are other types of luminescence, as well. Now that we have discussed luminescence, let us see what information the emitted radiation possesses. In order to understand and interpret the light radiation that is emitted due to luminescence, we first have to go back to the basics of electromagnetic radiation. The light radiation is nothing but electromagnetic radiation, which is a form of energy that travels through space in the form of a wave.

The wave consists of mutually perpendicular oscillating electric and magnetic fields, and this wave travels at the speed of light, which is 2.998×10^8 meters per second. The energy contained in the electromagnetic radiation is given by the relation E equals h nu, where h is Planck's constant, whose value is 6.626×10^{-34} joule seconds. Nu is the frequency of the light wave.



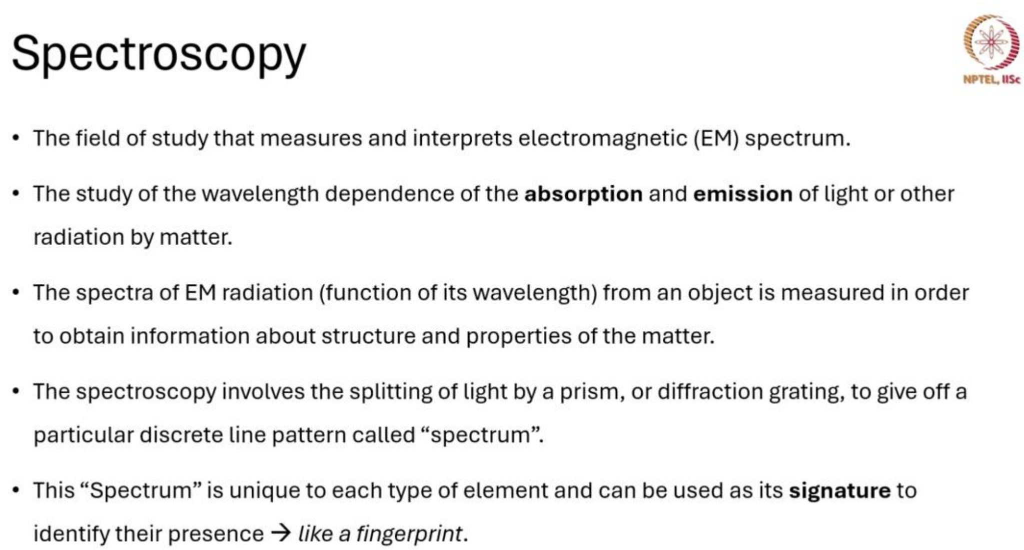
The frequency can be rewritten as c divided by λ, where c is the speed of light and λ is the wavelength of the light, which is the distance between any two crests or troughs of the wave. Thus, depending on the frequency or wavelength of the electromagnetic radiation, it can be characterized into different types. The different types of electromagnetic radiation are listed from lower energy to higher energy, where the electromagnetic radiation with the longest wavelengths, which are the radio waves whose wavelengths are all in the order of meters and kilometers, has the lowest energy; and as the wavelength decreases, the energy of the electromagnetic radiation increases. Next come the microwaves, whose wavelength is in the order of centimeters, and infrared radiation comes next. The visible light that allows us to see the world has a wavelength range of nanometers.

Next comes the ultraviolet radiation whose energy is higher than that of the visible range and has a wavelength between 100 and 400 nanometers. Beyond this, the x-rays are more energetic, with a wavelength in the order of 0.1 to 10 nanometers, and gamma rays, which have a very short wavelength in the order of picometers. Here, the smaller wavelength corresponds to a smaller distance between the successive waves. The smaller the wavelength, the more waves will pass through a point in a given second, which means higher energy is transmitted, resulting in higher frequency and shorter wavelength.



This figure shows the scale of different wavelengths of electromagnetic radiation in comparison to real-life objects. As explained before, the radio waves have the longest wavelength, which is in the order of meters and kilometers, almost as much as the size of the buildings. The microwaves are a little shorter, and infrared has a wavelength almost in the range of the size of the tip of a needle, while visible light has an even smaller wavelength, which is almost similar in size to protozoa, which are around one micron; as we go toward even shorter wavelengths, the wavelength of ultraviolet radiation is almost on the order of the size of molecules, the wavelength of X-rays is almost the size of atoms, and the wavelength of gamma rays. The order of the atomic nucleus is here; we can see the whole visible spectrum, which allows us to see the world, is only present in this small band between 400 and 700 nanometers, in which we have different colors corresponding to different wavelengths of light, where the shorter wavelengths are towards the violet and blue colors. whereas the longer wavelength in visible light has a red color.

Now that we have covered the topics of electromagnetic radiation, the electromagnetic spectrum, wavelength, and frequency, let's go to spectroscopy. Spectroscopy is a field of study that measures and interprets the electromagnetic spectrum. The study of the wavelength dependence of the absorption and emission of light by matter is spectroscopy. The spectra of electromagnetic radiation from an object are measured in order to obtain information about the structure and properties of the matter. The spectroscopy involves the splitting of a light beam by a prism or diffraction grating to give off a particular discrete line pattern called a spectrum.

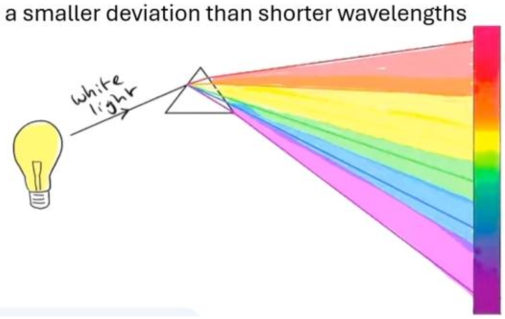


This spectrum is unique to each element and can be used as a signature to identify its presence. It's like a fingerprint for different elements. This spectrum will be discussed in detail in subsequent slides. White light is nothing but colorless daylight. It is an electromagnetic radiation that contains all the wavelengths of the visible spectrum at equal intensity.

Thus, when white light is passed through a dispersive prism, it splits into a continuous spectrum of different wavelengths, as you can see here. The different wavelengths of light in white light are refracted and deflected at different angles. This is because the refractive index of the material varies with the wavelength of the light. Generally, the longer wavelengths, such as red, undergo smaller deviation than shorter wavelengths. This can be seen here where the white light enters the prism; the red in the white light deviates at shallow angles, whereas the shorter wavelengths deviate at steeper angles.

Dispersion of Electromagnetic radiation

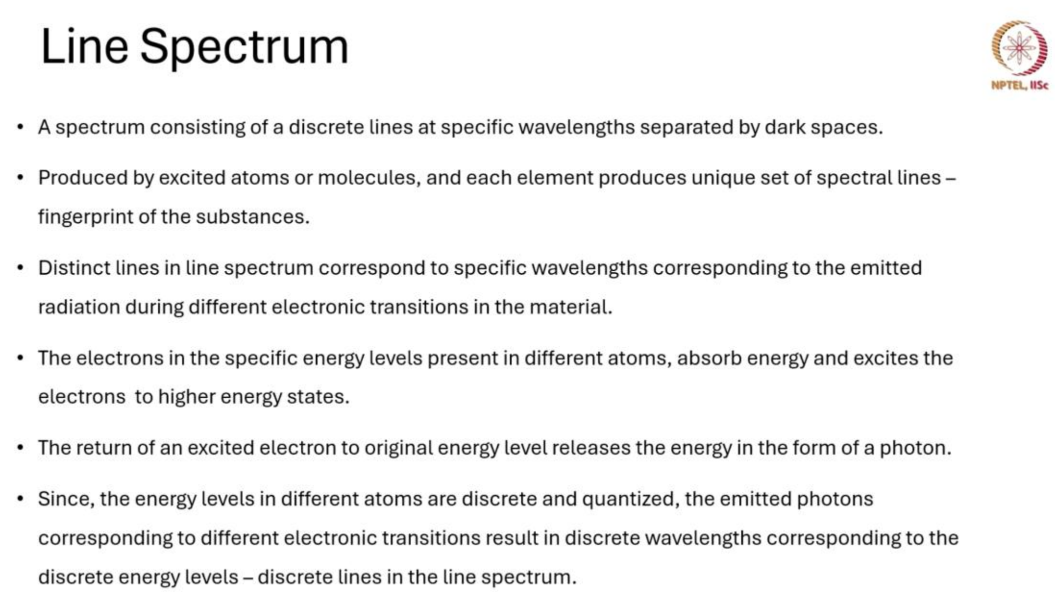
- When white light is passed through a dispersive prism, it splits into a **continuous spectrum** of different wavelengths.
  - The different wavelengths of light inside the white light are refracted, deflected at different angles.
  - The refractive index of prism material varies with wavelength of light.
  - Generally, longer wavelengths (red) undergo a smaller deviation than shorter wavelengths (blue).
- The **continuous spectrum** in the visible range is shown.
  - All the frequencies or wavelengths are shown in the band.



Thus, the white light gets split into different colors corresponding to different wavelengths, giving this continuous spectrum in the visible range where all the different frequencies or wavelengths are shown in the band. In the visible range, where red is at 700 nanometers and violet is at 400 nanometers, we have so far discussed the continuous spectrum, which is formed due to the splitting of white light using a prism, resulting in a continuous band of different wavelengths corresponding to different colors. However, there is another type of spectrum called a line spectrum, which consists of discrete lines at specific wavelengths separated by dark bands, as shown here. Each of these different lines in the line spectrum corresponds to different energies and different wavelengths. The earlier discussions regarding luminescence indicate that the electron present in the ground state, when provided with sufficient energy, transitions to a higher energy state, and since the electron is unstable in the higher energy state, it relaxes to the ground state, resulting in the emission of radiation, the energy of which corresponds to the difference between the two states.

It is equal to the energy gap between the different energy levels involved in the electronic transition. Thus, $\Delta E = h\nu = hc/\lambda$. We know that in different atoms and molecules, the electronic configurations are different. Thus, when energy is provided to different molecules, the electronic transitions involved in these molecules will be different; because of this, the energy levels and the energy differences between those levels involved in those electronic transitions are also different. Thus, the energy released when the electrons return to their original state is also different.

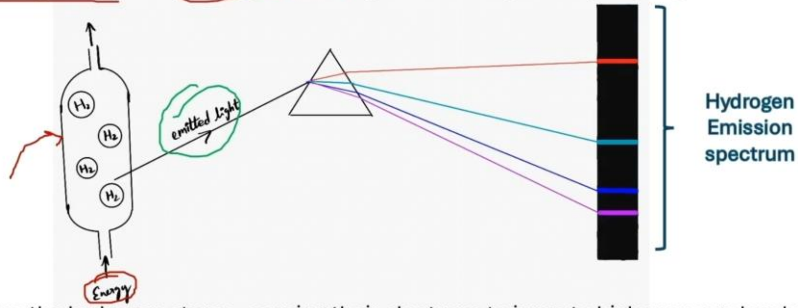
Therefore, each element produces a unique set of spectral lines, which is like a fingerprint of that substance. The distinct lines in the spectrum correspond to specific wavelengths of emitted radiation during different electronic transitions in the material. In complex molecules, multiple electronic transitions may occur between different energy levels, which result in the emission of multiple photons at different energies and different wavelengths. Thus, when the electrons are in different energy levels, they release energy in the form of photons at different energy levels, such as E1, E2, and so on, corresponding to different λ, λ1, λ2, and so on, when they return to their original energy state. Thus, these different photon emissions, corresponding to different electronic transitions, result in multiple specific bands seen in the line spectrum.



Since the emission is happening only in these specific wavelengths, the rest of the wavelengths in which the emissions are not occurring appear black in the spectrum. Thus, it is known as a line spectrum. Also, the energy levels in different atoms are discrete and quantized, and the emitted photons correspond to different electronic transitions, resulting in discrete wavelengths corresponding to discrete energy levels and thus discrete lines in the line spectrum. As explained before, to understand the line emission spectrum better, let's take an example of the hydrogen emission spectrum. The hydrogen emission spectrum can be obtained using a hydrogen gas lamp, as shown here, where hydrogen gas is filled inside a lamp and electrical energy is provided to this hydrogen gas lamp in the form of electrical current.

Example: Hydrogen Emission Spectrum

- In Hydrogen gas lamp an electrical current is passed through the hydrogen gas within the lamp.



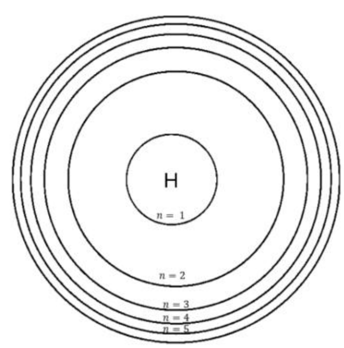
- This excites the hydrogen atoms, causing their electrons to jump to higher energy levels.
- As the electrons return to ground state, they release energy in the form of photons, which are emitted as light.
- The emitted light from a hydrogen gas lamp produces a **specific line spectrum**, consisting of distinct wavelengths corresponding to the energy transitions of the hydrogen atom.

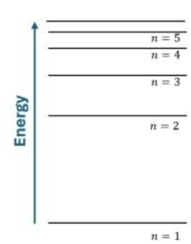
Example: Hydrogen Emission Spectrum

- Based on quantum mechanics principles, the electrons in the atoms can only occupy specific, discrete and quantized energy levels.
- The different energy levels in an atom can be obtained using Bohr model

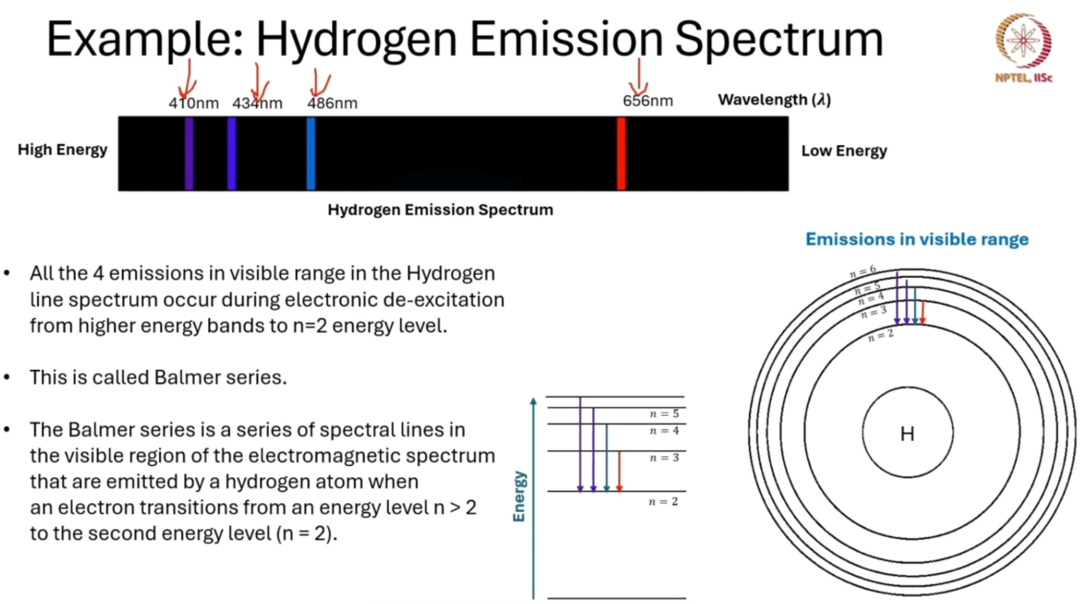
$$E_n = -\frac{2\pi^2 me^4}{n^2h^2}; \qquad \Delta E = E_2 - E_1 = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ eV$$

- Here, *m* and *e* are mass and charge of electron. *n* is the principal quantum number (integer) which refers to different quantized energy levels.
- Different energy levels denoted by the principal quantum number 'n' are present around the nucleus, with higher energy bands away from the nucleus.
- That means the electrons transitions to higher energy levels when they absorb energy.



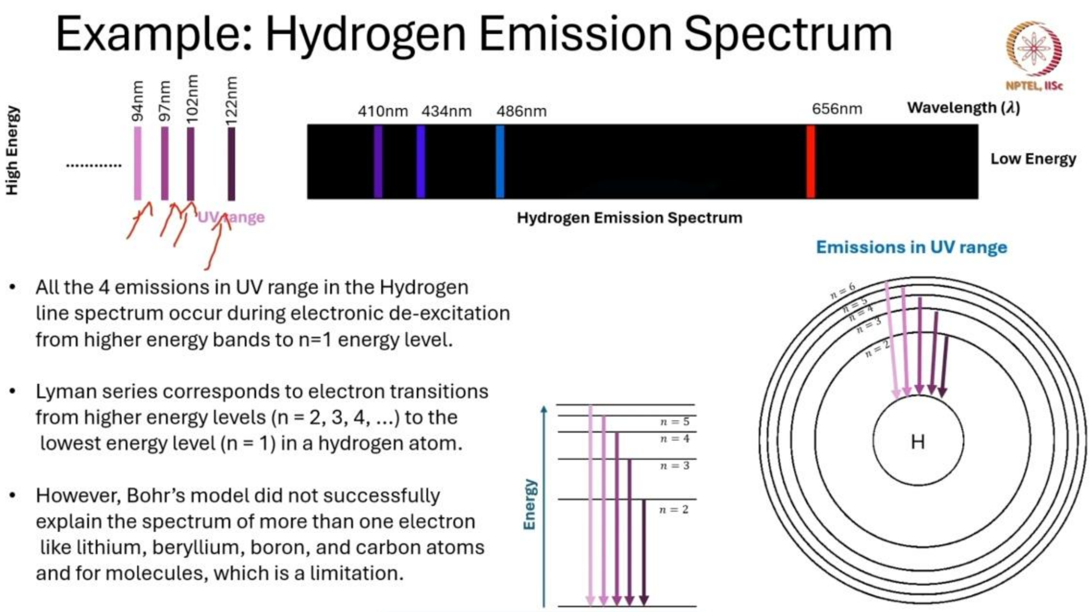


When this electrical current is passed through the hydrogen gas, the hydrogen atoms absorb this energy and get excited, thus causing the electrons inside the hydrogen atoms to jump into higher energy levels. Now, since the higher energy levels are stable, the electrons tend to return to lower energy levels, and they release energy in the form of photons as they transition to lower energy levels. Thus, the light emitted from the hydrogen gas lamp contains different wavelengths corresponding to different electronic transitions during the excitation and relaxation of electrons. Now, using a prism, we can split different wavelengths inside this emitted light, and similar to the process that we have already seen while obtaining the continuous spectrum, the longer wavelengths deflect at shallower angles, whereas the shorter wavelengths deflect at steeper angles, and these discrete individual wavelengths contained in the emitted light of the hydrogen gas lamp form discrete lines. On the hydrogen emission spectrum, since the emitted light from the hydrogen lamp doesn't contain the wavelengths in between these discrete lines, the line spectrum of the hydrogen shows dark bands or dark spaces in between these specific lines.



Thus, the emitted light from the hydrogen gas lamp produces a specific line spectrum consisting of distinct wavelengths corresponding to the energy transitions of the hydrogen atom. Now let us see how the different energy levels are present in a hydrogen atom. Based on quantum mechanics principles, the electrons in an atom can only occupy specific energy levels that are discrete and quantized. That means the electrons are not allowed to possess continuous energies; they can only possess discrete energies, and these discrete energy levels can be obtained using the Bose model. And here in this relation, m is the mass of the electron, e is the charge of the electron, and n is the principal quantum number, which refers to the different quantized energies.

Here, as we can see the different energy levels in a hydrogen atom, as the principal quantum number value increases, they move away from the center. Now let's see. The different electronic transitions that occur in a hydrogen atom when energy is supplied to it. As we can see here, the hydrogen atom contains only one electron, and that one electron occupies the ground state, which is the n equal to 1 energy level when it is not excited. However, when the energy is supplied to it, this electron can get excited to higher energy levels, which are equal to 2, 3, or 4, or so on, depending on the energy supplied to it.



Once the electron gets excited to higher energy levels, it loses energy in the form of light and transitions back to lower energy levels. Here, the hydrogen emission spectrum shows four wavelengths corresponding to hydrogen emission in the visible range. From these four wavelength values, we'll try to estimate what the different energy levels are corresponding to these four line spectra. Using this equation, the energy difference between two energy levels involved in an electronic transition is equal to the energy of the emitted light, which is equal to hc/λ. First, we will try to see what the energy corresponding to the wavelength of 656 nanometers is, using this 656 nanometer here.

We can obtain the combination of n1 and n2 corresponding to the two energy levels involved in the electronic transition related to this specific wavelength emission. Thus, when energy is supplied to the electron, when the electron transitions to n equal to 3, and then when it relaxes to n equal to 2, that corresponds to this specific wavelength of 656 nanometers. Similarly, if we calculate the different combinations of energy levels corresponding to the other wavelengths for 486 nanometers, the electron has to transition to n equal to 4 and then relax to n equal to 2, and this energy difference between n equal to 4 and n equal to 2 corresponds to hc/λ. Where λ is 486 nanometers for 434 nanometers, we follow the same process, and for this, the electron has to transition from n equal to 5 to n equal to 2. When we follow the same process for 410 nanometers, which is the lowest wavelength, then we obtain that the electron has to get excited to n equal to 6 and then relax to n equal to 2.

Just to summarize, in the visible range, the four wavelengths in the line spectrum correspond to these four transitions, and this type of transition, where the electrons relax or de-excite from higher levels to the n equal to 2 level, is called the Balmer series. As explained before, these four spectral lines in the hydrogen emission spectrum are only present in the visible range, and if electron transitions occur between the energy levels with higher energy, then we obtain spectral lines in the UV range. So, if we go further into the UV range, more spectral lines are observed at 102 nanometers, 97 nanometers, and 94 nanometers, which are very low wavelengths corresponding to high energy, and this corresponds to the transition of electrons from n equal to 2, n equal to 3, n equal to 4, n equal to 5, and n equal to 6 to n equal to 1. Thus, the electronic transitions from different energy levels to the lowest energy level, which is n equal to 1, are called the Lyman series. Even though Bohr's model could explain different electronic transitions for the hydrogen atom and allowed us to calculate the combination of different energy levels between which the electronic transition occurred, corresponding to different wavelengths that we have observed in the line spectra of hydrogen emission in the UV range as well as in the visible range, it is only possible because hydrogen has only one electron and it is a simple system.

Bohr's model couldn't successfully explain the spectrum in substances with more than one electron, such as lithium, beryllium, boron, or carbon, or even for molecules, which is a limitation. Nevertheless, this gives us a basic understanding of how different electronic transitions between energy levels correspond to different spectral lines in the line spectrum obtained from the emission spectrum of the given substance. We will discuss the further topics of how the spectrum varies when the molecules are excited and the use of spectroscopy in different applications in the next lecture. Thank you.