

Modern Instrumental Methods of Analysis

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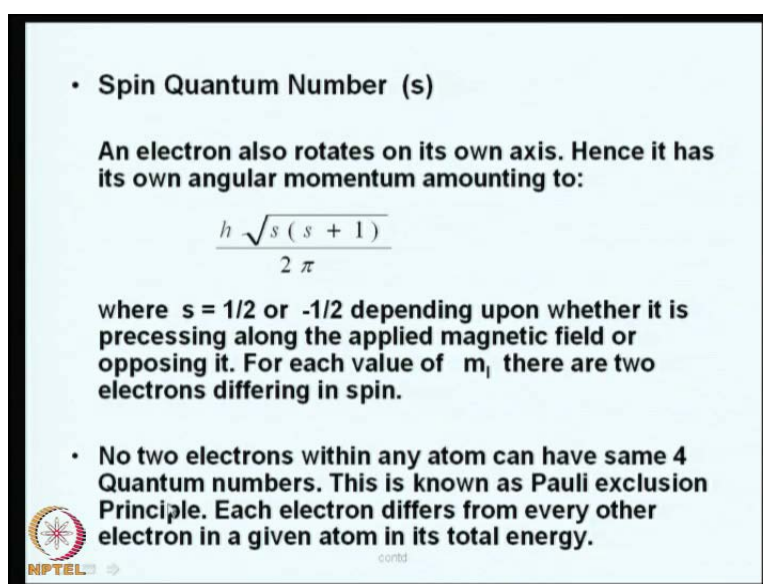
Indian Institute of Science, Bangalore

Lecture No. # 03

Physical Properties of Electromagnetic Radiation

The electron has got its own spin quantum number; that means it can recess on its own axis, so that the angular momentum is defined by Planck's constant multiplied by spin quantum number into spin quantum number plus 1 divided by 2 pi.

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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.

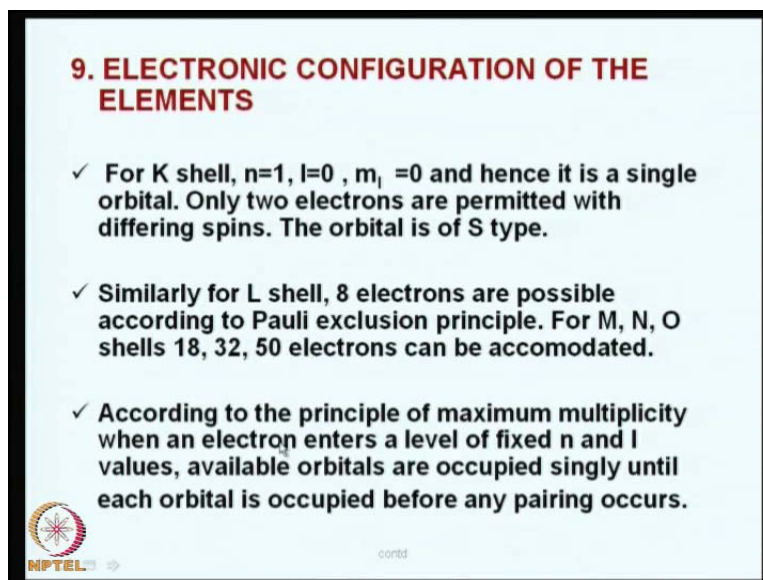
• No two electrons within any atom can have same 4 Quantum numbers. This is known as Pauli exclusion Principle. Each electron differs from every other electron in a given atom in its total energy.

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The value of s is given **1 half** or minus half depending upon whether it is precessing along the applied magnetic field or opposing the magnetic field. For each value of m_l , there are two electrons differing in spin. Therefore, what we can summarize is no two electrons within any atom can have the 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; that means either principle quantum number or **orbital moment** quantum number or magnetic quantum number or spin quantum number – all the four cannot be


the same. At least in one of them, the electron should differ in every atom. So, this gives rise to a plan, where we can keep on filling the electrons and build up the elements.

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9. ELECTRONIC CONFIGURATION OF THE ELEMENTS

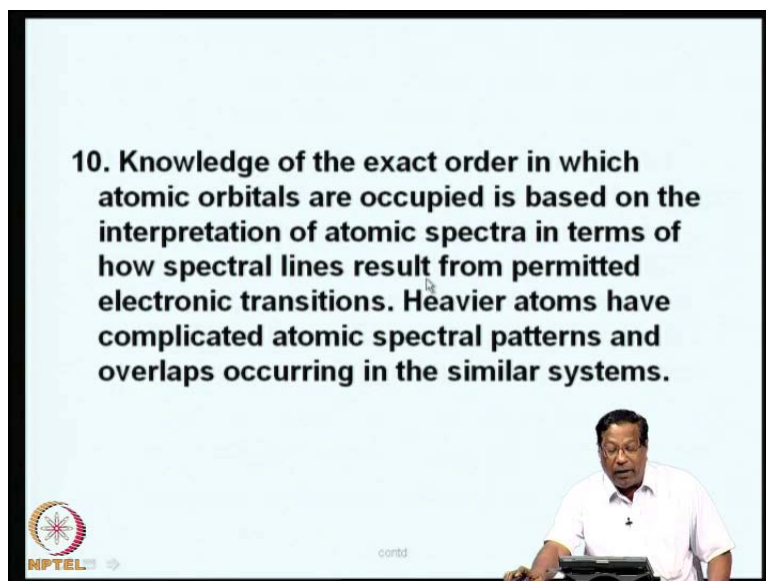
- ✓ For K shell, $n=1$, $l=0$, $m_l=0$ and hence it is a single orbital. Only two electrons are permitted with differing spins. The orbital is of S type.
- ✓ Similarly for L shell, 8 electrons are possible according to Pauli exclusion principle. For M, N, O shells 18, 32, 50 electrons can be accommodated.
- ✓ According to the principle of maximum multiplicity when an electron enters a level of fixed n and l values, available orbitals are occupied singly until each orbital is occupied before any pairing occurs.

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For example, for K shell, we have principle quantum number n would be 1; and, l should be $n - 1$, that is, 0; and, m_l should have $2l + 1$; that corresponds to m_l should be 0. And hence, it is a single orbital. Only two electrons are permitted in this orbital with differing spins: one could be plus half and another could be minus half. The orbital is of S type; that means it is symmetrical around the nucleus. Similarly, for L shell, we have eight electrons according to Pauli exclusive principle. For M, N, O shells, we have 18, 32 and 50 electrons can be accommodated.

According to the principle of maximum multiplicity, when an electron enters a level of fixed principle quantum number n and l values, available orbitals are occupied singly until each orbital is occupied before any pairing occurs. This is important for us, because among the 5 orbitals, we have 3 orbitals in the p_x , p_y and p_z in three different directions. Even then, one electron should go to p_x , one electron should go to p_y , and another electron should go to p_z . Then only, another – fourth electron can enter the p_x . Like that this gives us a plan to fill the electrons and build up the atoms.

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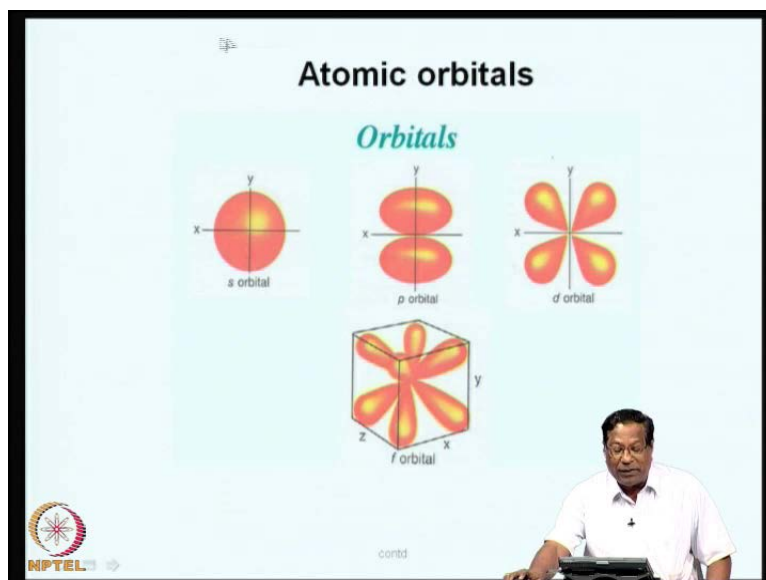


10. Knowledge of the exact order in which atomic orbitals are occupied is based on the interpretation of atomic spectra in terms of how spectral lines result from permitted electronic transitions. Heavier atoms have complicated atomic spectral patterns and overlaps occurring in the similar systems.

The slide features a light blue background with a black border. In the bottom right corner, there is a small inset image of a man in a white shirt sitting at a desk. The NPTEL logo is in the bottom left, and the word 'contd' is centered at the bottom.

The knowledge of the exact order in which atomic orbitals are occupied is based on the interpretation of atomic spectra in terms of how spectral lines result from permitted electronic transitions. Heavier atoms have complicated atomic spectral patterns and overlaps occurring in the similar systems.

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Atomic orbitals

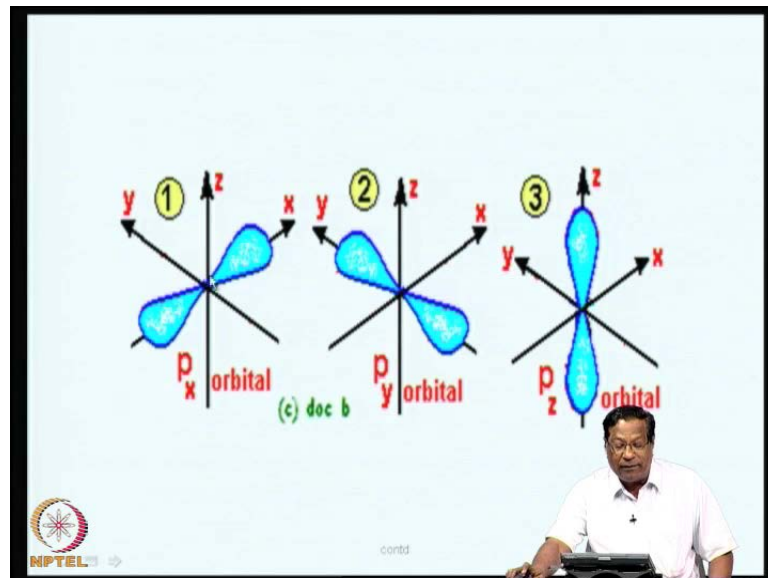
Orbitals

The slide displays four diagrams of atomic orbitals on a light blue background. Each diagram includes x, y, and z axes. The s orbital is a red sphere. The p orbital consists of two red lobes along the x-axis. The d orbital has four red lobes in a cloverleaf pattern. The f orbital is a complex shape with six red lobes. A man in a white shirt is visible in the bottom right corner. The NPTEL logo is in the bottom left, and the word 'contd' is centered at the bottom.

You can take a look at this. This is the s orbital that is round, spherical; p orbital – there could be three p orbitals: one along p x; one along p y; and, one along p z. And then, d orbital shapes are like this, where the probability of electron being found around the

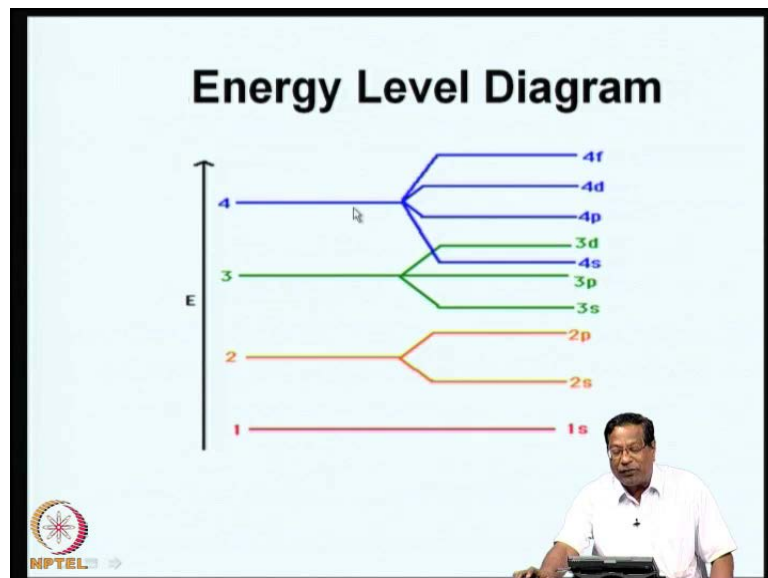
nucleus in this region of space is maximum. And then, s orbitals – we have shapes something similar to this.

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So, this is p x, p y and p z orbital.

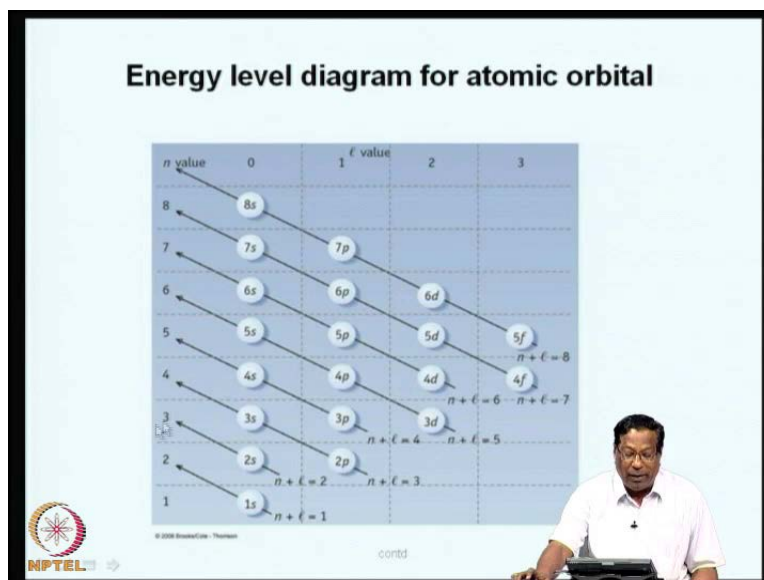
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Now, the energy level diagram also will tell us that first the 1s orbital is filled in which two electrons are permitted; and then, the next electron will go to 2s; and then, 2p; then,

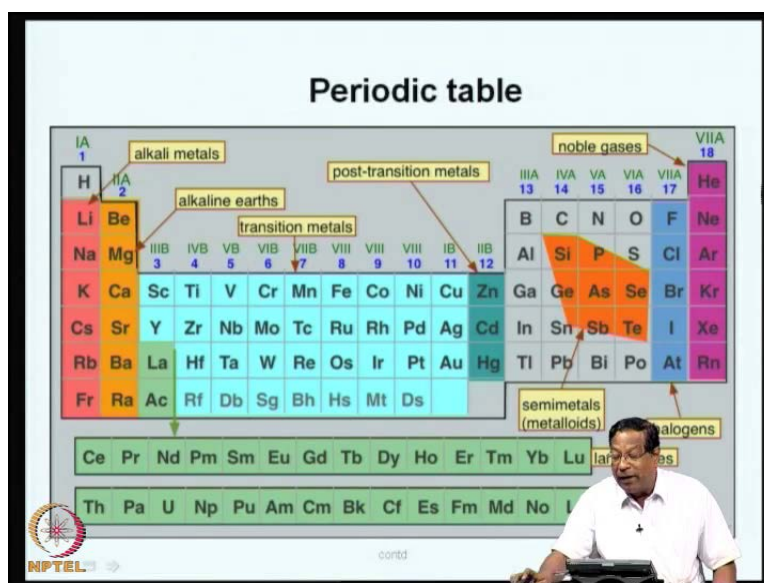
3s, 3p; and then finally, as the electrons keep on increasing in number, the orbital energy levels can get mixed up and the electronic structure becomes complicated.

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So, this gives rise to a filling order. We can imagine like this – first is 1s, and then 2s, and then 3s, 2p, then 4s, 3p, 5s, 4p, 3d. Like that we can have electrons filled for each element, where atomic number increases by one unit and the electrons also increase by one number.

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So, if you go around looking at it and then try to fit the electrons in different orbitals, we will have hydrogen with one electron and then helium with two electrons, then lithium, beryllium, boron carbon, nitrogen, oxygen and fluorine that go on adding one electron each; and, one atomic number also keeps on increasing if you are arrange all these in a proper order. As described by Professor Mandeleev, we have a periodic table and this periodic table is a summation of all the elements that we know on the earth. And, this is the best way of representation.

For example, here (Refer Slide Time: 06:49) you can see all these are basically nonreactive elements, where electrons like helium, neon, argon, krypton, xenon, radon – they are all called as noble gases. And then, here is hydrogen, lithium, sodium, potassium, cesium, rubidium, francium, where one electron is there in the outer most orbital, that is, s orbital. And then, beryllium, magnesium, etcetera – these are all basically divalent metals. And then, we have transition metals in which the electrons get filled up in the inner orbital – d orbitals. And, zinc, cadmium and mercury are known as post transition metals. And then, we have nonmetals in this region **IIIA, IVA, VA, VIA and VIIA** groups.

And, here (Refer Slide Time: 07:44) you can lanthanides as well as actinides. And, here also inner filling of the d and f orbitals take place – f orbitals in lanthanides and actinides and d orbitals in the transition metals. And, you can see the portion marked in the red corresponds to silicon, phosphorous, sulphur, selenium, arsenic, tellurium, germanium, a little bit of tin, etcetera. These are called as semimetals or metalloids. And, fluorine, chlorine, bromine, iodine, etcetera are all called as halogens, which are nothing but basically gases. But, they are all found in the environment as salts when combined with the metals represented in this area (Refer Slide Time: 08:37). Here we stop for the atomic structure.

What I want to tell you at this stage is that the elements found in this periodic table are all in the nature available to us. And, these elements are used in different combinations in different substances. And, they enter into the atmosphere, etcetera and then we have the problem of determination of these elements in trace and ultratrace elements. So, with this structure in our mind, let us go and take a look at how the electromagnetic radiation interacts with these metals.

All the analytical methods available to us for the characterization and determination of the analyte can be broadly classified into **spectrophotometry** – spectrometric and non spectrometric methods. This classification is not exactly based on scientific principles, but it emphasizes the importance of spectroscopic techniques compared to other forms of chemical analysis. In general, spectroscopy refers to the interaction of various types of electromagnetic radiation with matter, but can be logically extended to include acoustic waves, ion beams and electrons, etcetera. In one form or another, all these techniques measure the change in the intensity of the radiation or energy changes when the matter is exposed to electromagnetic radiation including X-rays, gamma rays, ultraviolet, infrared, microwaves, and radio waves, etcetera. So, let us look at the nature of the electromagnetic radiation.

What is electromagnetic radiation? The characteristics of electromagnetic radiations are best described by a classical sinusoidal wave model. This model fails to account for the absorption and emission of the radiant energy. Phenomenon associated with such processes can be explained by considering the electromagnetic radiation as a continuous stream of discrete particles of energy called as photons. The wave particle duality of the electromagnetic radiation is basically complimentary to each other and rationalized by wave mechanics. So, a plane-polarized electromagnetic radiation of a particular frequency follows a sinusoidal oscillation along the direction in which the wave is propagating. So, if the wave is going like this, the wave will be going like this and it has got an electronic component as well as a magnetic component. That is why it is called electromagnetic radiation.

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- Mathematically an electromagnetic wave can be described as a sine wave

$$A = A_0 \sin \theta$$

where **A** is the amplitude at any point
A₀ is the peak amplitude
θ is the continuous variable

Such a plane-polarized wave is represented mathematically. So, mathematically, an electromagnetic wave can be described as a sine wave something like this – A is equal to A₀ into sine theta; where, A is the amplitude at any point; A₀ is the peak amplitude; and, theta is the continuous variable.

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- Alternately

$$A = A_0 \sin \omega t$$

Where $\omega t = \theta$, ω is the angular velocity radians/unit time.

A complete cycle occurs when ωt changes from 0-360°.
This is called one complete oscillation or one period.
Hence the time over which one complete occurs is given by

$$t_{\text{cycle}} = \omega / 2\pi$$

or $\nu = \text{frequency} = \frac{1}{t_{\text{cycle}}} = \frac{2\pi}{\omega}$

Now, it can also be represented as A₀ into sine omega t; where, omega t is equal to theta and omega is the angular velocity in radians per unit time. A complete cycle occurs when **w t** changes from 0 to 360 degrees. This is called one complete oscillation or one period.

Hence, the time over which one complete oscillation occurs is given by t cycle is equal to 2π divided by ω ; or, ν – frequency is equal to $1/t$; that is, 2π by ω .

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• For any wave moving at a constant velocity v , we can write

$$v = \nu \lambda$$

where ν is the frequency in ms^{-1}
 ν is in Hertz (cycles per second or s^{-1}) and
 λ in meters

• The frequency ν is proportional to the energy E of the photon given by

$$E = h \nu$$

where $h = 6.62 \times 10^{-27}$ ergs when E is expressed in ergs and
 $= 6.63 \times 10^{-34}$ joules. E is expressed as joules.

• Sometimes it is convenient to use "wave number" denoted by $(\bar{\nu})$ to describe the radiation for example in infra red spectrometry. Then the photon energy is expressed as,

$$E = hc \bar{\nu}$$

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Now, for any wave moving at a constant velocity, we can write v as a velocity is the multiple of frequency and wavelength; where, ν is the frequency in milli seconds; ν is in hertz, that is, cycles per second; and, λ is in meters. The frequency ν is the proportional to the energy of the photon given by E is equal to $h \nu$; that is, Planck's constant h defined as 6.62×10^{-27} ergs when E is expressed in ergs. And, if you express it in joules, its value would be 6.63×10^{-34} joules. And sometimes, it is convenient to use wave number denoted by $\bar{\nu}$ to describe the radiation, for example, in infrared spectrometry. Then, the photon energy is expressed as E is equal to $h c \bar{\nu}$; where, c is the velocity of light.


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PROPERTIES OF E.M. RADIATION			
Name of the unit	Symbol	Unit for	Used in
Nanometer	Nm	λ	UV, visible, near-infrared
Angstrom*	\AA	λ	X-ray, UV-visible (in older work)
Milimicron*	m μ	λ	Visible (in older work)
Micron, Micrometer	μm	λ	Infrared (common in physics literature)
wavenumber (reciprocal cm)	cm^{-1}	ν/c	Infrared, UV- visible (less common)
Electron volt*	eV	E	X-ray, γ -ray
Hertz	Hz	ν	Radiofrequency, microwave
Cycles per s	Cps	ν	Radiofrequency (less common in current literature)

Now, we have talked of so many properties of electromagnetic radiation. Let us take a look at the units, because these are the units we will be talking about frequently. Now, you know here it is nanometer; its symbol is Nm and unit is unit for wavelength; and, this symbol nanometer is used in ultraviolet visible and near-infrared regions. And, you can also use angstroms and symbol is like **A zero**; and, it is used in X-ray, UV-visible spectrophotometry in older work. You can also describe the same thing as milli microns; and, this is used in visible range, that is, in older work. Nowadays, most of these units are used as nanometers.

And, wave number – as I told you, the unit is in centimeters inverse and frequency divided by velocity of light; it is used in infrared as well as in UV-visible. But, it is very less common in UV-visible. You can also use electronic volts (eV); and, unit for energy used in X-ray and gamma ray. And, hertz is of course, the unit for frequency and it is used in radio frequency and microwave applications. Cycles per second is also is the unit for frequency and it is used in radio frequency, but nowadays it is used very less in current literature.

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- It may be noted that regardless of the units of expression any electromagnetic radiation of frequency ν will have unique wavelength and energy.
The longer the wavelength, the lower is the energy and frequency.
- Energy is closely related to temperature of any object, it can be expressed as

$$E \propto K_B T$$

where K_B = Boltzmann's constant
= 1.380×10^{-16} ergs $K^{-1} \text{ atom}^{-1}$ or 1.380×10^{-23} joule $K^{-1} \text{ atom}^{-1}$

If we consider energy per mole of the material

$$E \propto R T$$

where R = the gas constant
= 8.3145×10^7 erg $K^{-1} \text{ mol}^{-1}$ or 8.3145 joule $K^{-1} \text{ mol}^{-1}$

And, the same thing I can tell you that it may be noted that regardless of the time of the units of expression, any electromagnetic radiation of frequency ν will have unique wavelength and energy. The longer the wavelength, lower is it is energy and frequency. Energy is closely related to the temperature of any object also. It can be expressed as E is proportional to $K_B T$; where, K_B is the Boltzmann's constant and its value is 1.380×10^{-16} ergs and units are $K^{-1} \text{ atom}^{-1}$ or 1.380×10^{-23} joules $K^{-1} \text{ atom}^{-1}$. If we consider energy per mole of the material, then E can be defined as being proportional to RT ; where, R is the gas constant and its value is 8.3145×10^7 ergs $K^{-1} \text{ mole}^{-1}$ or 8.3145 joules $K^{-1} \text{ mole}^{-1}$.



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- The energy of the photons should not be confused with brightness or intensity of the source. But it relates to the colour of the light.
- The power of a light source is given by

$$P = \text{number of photons} \times \text{photon energy}$$

It is the energy of a beam of radiation that reaches a given area per second.

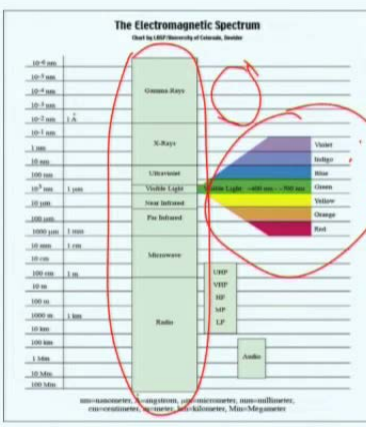
- Intensity (I) of a source of radiation is the power emanating per unit solid angle.



Now, the energy of the photons should not be confused with the brightness or intensity of the source. But, it relates to the colour of the light. The power of a light source is given by P is equal to number of photons light it emits multiplied by the energy of the photon. It is the energy of a beam of radiation that reaches a given area per second. Intensity of a source of radiation is the power emanating per unit solid angle. This is a very important concept that we will be talking about later.

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ELECTROMAGNETIC SPECTRUM



✓

✓

Soft x rays
Hard x rays
Vacuum uv
uv
v-



Now, you can see the electromagnetic spectrum as consisting of a range of radiations. You can define it in terms of frequency, that is, here. You can define it in terms of angstroms, micrometers and then millimeters, centimeters, and meters, etcetera. And, you can define them in terms of specific radiation, such as gamma rays, X-rays, ultraviolet, visible light, near-infrared, far-infrared. Then, we have microwaves and then we have radio waves. You can see that the visible light is only a very small portion of the whole electromagnetic range and it is composed of seven colors, that is, violet, indigo, blue, green, yellow, orange and red.

If you take a look at this electromagnetic radiation, you can see that the range starts from 10^6 meters up to 10^{-10} meters (Refer Slide Time: 20:04) up to 100 megameters, that is, kilometers. And, the lowest would be gamma rays and the range is from 10^{-10} up to 1 angstrom unit. All the radiations corresponding to this are called as gamma rays. And, these rays can be used for the determination of elements in techniques, such as γ etcetera. And then, X-rays – you know that there are different kinds of X-rays: soft X-rays and hard X-rays (Refer Slide Time: 20:55). Soft X-rays are used in medical science for the image in the bones and tissues, etcetera; and, hard X-rays are used for the determination of metals.


And after the X-rays, comes the ultraviolet rays. In the ultraviolet rays, we have (Refer Slide Time: 21:25) far ultraviolet, then ultraviolet, and then visible region – vacuum ultraviolet. These are the three parts/regions of ultraviolet: one is vacuum ultraviolet, another is far ultraviolet, then we have normal ultraviolet. Up to 165 nanometers we have vacuum ultraviolet; and then, between 165 to 180, it is all far ultraviolet; and, 180 to 350 nanometers, we have ultraviolet; from 350 to 800 nanometers, we have visible range and that visible range is represented by these areas – different colours (Refer Slide Time: 22:26). And then, after that, we have near-infrared followed by infrared; and then, far infrared and then followed by microwave and radio waves.

You can see that all these ranges (Refer Slide Time: 22:47) of the electromagnetic radiations are used in one form or the other of a spectroscopic determination. So, it is very important for us to know electromagnetic radiations – they are all used for the determination of several metals and then organic substances etcetera. And, all these things are used for the UV-visible, infrared, vacuum ultraviolet; and then, we have infrared, far-infrared, microwave, ESR, such techniques – they are all useful.

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TRANSMISSION OF RADIATION

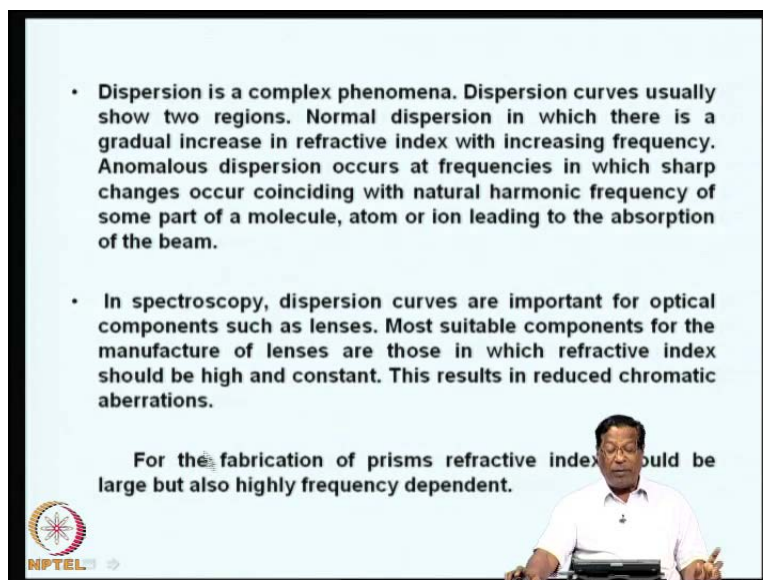
- The rate of propagation of electromagnetic radiation through a transparent material (such as atoms, ions, molecules, particles) is less than that of vacuum. However frequency change will not be observed which means that permanent energy transfer to the medium does not occur.
- Therefore the interaction involved must be only temporary deformation of the electronic clouds associated with the atoms and molecules (10^{-14} to 10^{-15} s). Since the velocity of radiation in the media is wavelength dependent the refractive index of the media also must change. The variation of R.I with wavelength is called 'dispersion'.



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Now, we would like to know how the radiation is transmitted, because whenever we use electromagnetic radiations in our instruments, there are two types of interactions will occur: one is regarding the interaction of matter with the instrument components; and, another is interaction of the electromagnetic radiation with the sample. Now, this is how the transmission of radiation takes place. Before that, let us understand that the rate of propagation of electromagnetic radiation through a transparent material, such as atoms, ions, molecules and particles, is less than that of vacuum. However, frequency change will not be observed in the vacuum or elsewhere, which means that permanent energy transferred to the medium does not occur. Therefore, the interaction involved must be only temporary deformation of the electronic clouds associated with the atoms and molecules of the order of let us say about 10 raised to minus 14 to minus 15 seconds. Since the velocity of radiation in the media is wavelength dependent, the refractive index of the media also must change. The variation of refractive index with wavelength is called dispersion. So, essentially, what we are talking about is interaction of electromagnetic radiation with materials, not the samples or analyte what we call it. Variation of refractive index is called dispersion.

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- Dispersion is a complex phenomena. Dispersion curves usually show two regions. Normal dispersion in which there is a gradual increase in refractive index with increasing frequency. Anomalous dispersion occurs at frequencies in which sharp changes occur coinciding with natural harmonic frequency of some part of a molecule, atom or ion leading to the absorption of the beam.
- In spectroscopy, dispersion curves are important for optical components such as lenses. Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant. This results in reduced chromatic aberrations.

For the fabrication of prisms refractive index should be large but also highly frequency dependent.


And, what is this dispersion? Dispersion is basically a very complex phenomena. Dispersion curves usually show two regions. One is normal dispersion in which there is a gradual increase in the refractive index with increasing frequency. Sometimes anomalous dispersion occurs at frequencies in which sharp changes occur coinciding with the natural harmonic frequency of some part of the molecule or a group of a molecule or a functional group of a molecule or of that of ion leading to the absorption of the beam. So, in general, there are two types of dispersions: one is normal, which shows the increase in refractive index with increasing frequency; another is sharp changes occur.

In spectroscopy, dispersion curves are important for optical components such as lenses. So, here the most suitable components for the manufacture of lenses are those in which refractive index should be very high and it should be constant, it should not show anomalous dispersion of the electromagnetic radiation. Now, why? If it does not show all these things, this results in reduced chromatic aberrations. For the fabrication of prisms for example, you have to pass the radiation through a prism and it should not show any other aberrations except changes in the frequency or changes in the wavelength. So, for the fabrication of prisms, refractive index should be as large as possible, but also highly frequency dependent. Similarly, diffraction.

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DIFFRACTION OF RADIATION


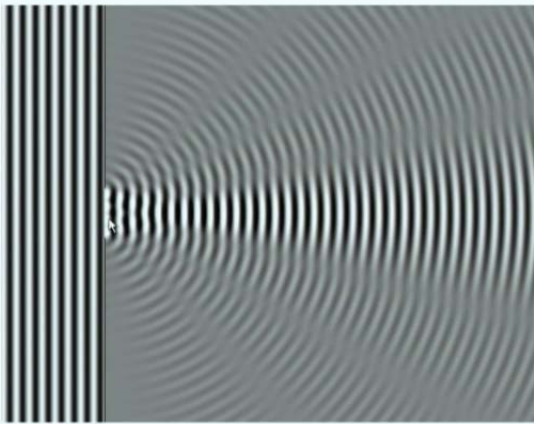
- Diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference which can be easily demonstrated in the laboratory.
- When a parallel beam of light is allowed to pass through a pin hole, two closely spaced pin holes are seen on a screen placed across it.
- If the radiation is monochromatic a series of dark and light image appear perpendicular to the plane of the radiation.



Diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference, which can be easily demonstrated in the laboratory. When a parallel beam of light is allowed to pass through a pinhole, two closely spaced pinholes are seen on a screen placed across it.

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PIN HOLE DIFFRACTION



If the radiation is monochromatic, what you would see is a series of dark and light images appearing perpendicular to the plane of radiation like this. So, here we have a

radiation going along and we have a small this thing – a pinhole; and, the radiation that are coming out on this side, where we place a screen on this side, you would see a sharp image of **black and white, black and white, black and white**. So, this phenomenon is diffraction.

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REFLECTION OF RADIATION

- Mirrors reflect the radiation falling on them. Without any loss of the incident radiant power. Hence they are used as optical components of a spectrum. Concave mirrors reflect the radiation as well as concentrate the reflected radiation at its focal point.
- When radiation crosses an interface between media differing in refractive index reflection always occurs. For a beam entering an interface at rt.angles the fraction reflected is given by

$$\frac{I_r}{I_o} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

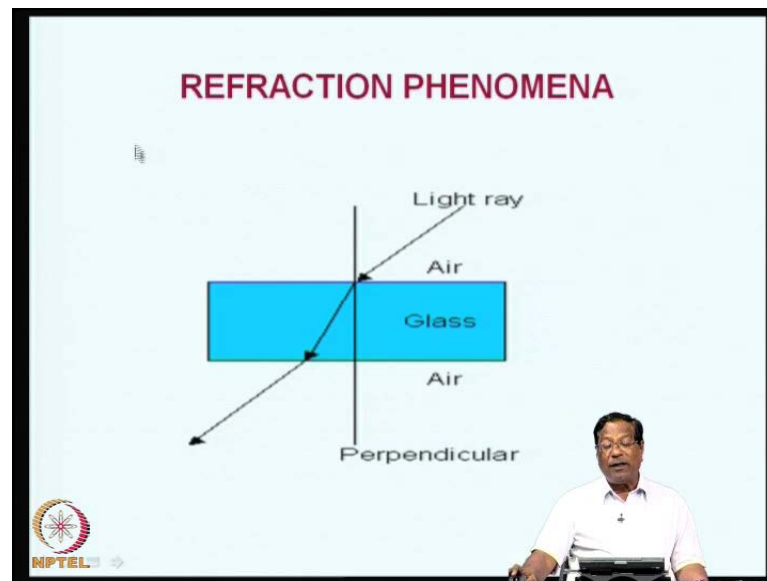
where I_o intensity of the incident beam and
 I_r is the reflected intensity,
 n_1 & n_2 are the refractive indexes of the

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Now, let us take a look at another phenomenon, that is, reflection of radiation. So, what is reflection of radiation? Mirrors – you would have seen the objects in the mirror and mirrors basically reflect the radiation falling on them without any loss of the incident radiant power. Hence, they are used as optical components of a spectrum. Concave mirrors – you would have seen in your cars and scooters and motorcycles, etcetera; they reflect the radiation as well as they concentrate the reflected radiation at its focal point.

When radiation crosses an interface between media differing in refractive index, reflection always occurs, some amount of **reflection**. For a beam entering an interface at right angles, the fraction reflected is given by I_r upon I_o ; that is, the reflection ratio is n_2 minus n_1 whole square divided by n_2 plus n_1 whole square; where, we can define I_o as the intensity of the incident beam; and, I_r is the intensity of the reflected beam; and, n_1 and n_2 are the refractive indexes of the two media. So, this is a very simple phenomenon. No matter what you do, reflection always occurs and reflection is not good in spectrophotometry or in any other instruments unless the aim is to concentrate the reflected light, such as a concave mirror or something like that.

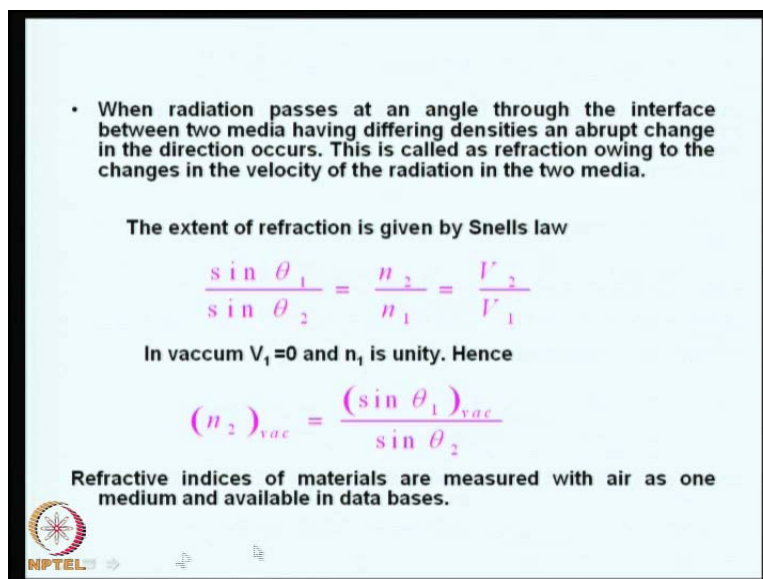
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And then, what is refraction? Here I am showing you the figure of refraction. There is a light ray coming from one media entering another media, such as glass and going out of the glass again. Now, you can see that the light ray even though it is parallel, even though it is a single beam, it does not proceed along the same way; instead, it bends and then proceeds in another direction. So, you can see that there are two interfaces: one is this area, where it is air or vacuum; another area is this glass or quartz or water or any other medium in which light passes through; and, from the medium, again it enters into another medium. So, there are two interfaces: vacuum or air.

Usually, vacuum – we do not come across in our day to day life, where light passes through the vacuum. So, it is in general changed to air. So, you can use a vacuum also, but there is no problem. But, the normal situations where we see are light rays entering from air into one medium and then passing out through again into the air medium after the medium ends. So, we have a light ray that bends like this (Refer Slide Time: 31:52) and then goes out; and, this is perpendicular.

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• When radiation passes at an angle through the interface between two media having differing densities an abrupt change in the direction occurs. This is called as refraction owing to the changes in the velocity of the radiation in the two media.


The extent of refraction is given by Snells law

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{V_2}{V_1}$$

In vaccum $V_1=0$ and n_1 is unity. Hence

$$(n_2)_{vac} = \frac{(\sin \theta_1)_{vac}}{\sin \theta_2}$$

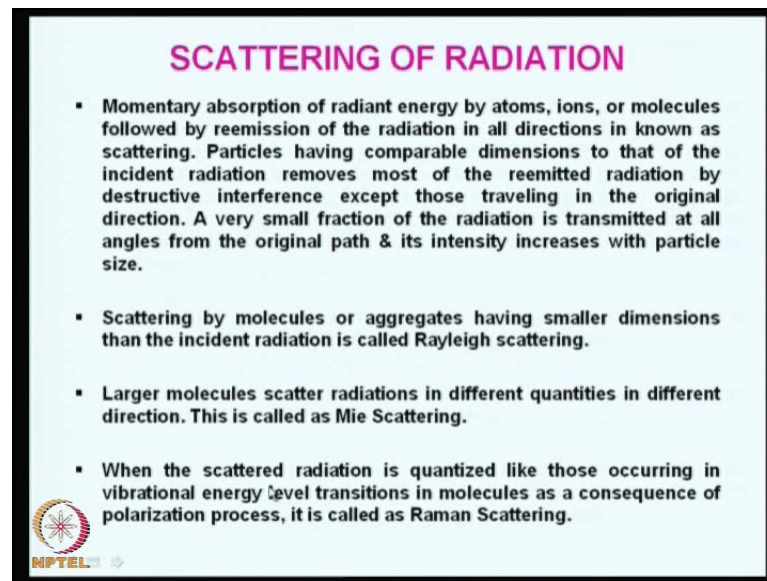
Refractive indices of materials are measured with air as one medium and available in data bases.



When the radiation passes at an angle through the interface between two media having different densities, an abrupt change in the direction occurs; here (Refer Slide Time: 32:13) abrupt change. This is called as refraction owing to the changes in the velocity of the radiation in the two media. So, the velocity of the radiation changes in the media. The extent of refraction is given by Snells law; that is, sine theta 1 divided by sine theta 2 is equal to n 2 by n 1. That is also the ratio of the velocity of the radiation in the two medium; that is, V 2 by V 1.


Now, all these things are college physics and chemistry. So, I am not going into details of all these things, but you can look at the college physics text books, which will explain these phenomenon in more detail. For example, in vacuum, V 1 given is equal to 0 and n 1 is unity. So, you can write n 2 is equal to sine theta 1 divided by sine theta 2. So, refractive indices of materials can be measured with air as one medium and available in databases. Lot of substances, which are capable of refracting a radiation falling on them are known and these are available in the databases.

(Refer Slide Time: 33:53)



SCATTERING OF RADIATION

- Momentary absorption of radiant energy by atoms, ions, or molecules followed by reemission of the radiation in all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation removes most of the reemitted radiation by destructive interference except those traveling in the original direction. A very small fraction of the radiation is transmitted at all angles from the original path & its intensity increases with particle size.
- Scattering by molecules or aggregates having smaller dimensions than the incident radiation is called Rayleigh scattering.
- Larger molecules scatter radiations in different quantities in different direction. This is called as Mie Scattering.
- When the scattered radiation is quantized like those occurring in vibrational energy level transitions in molecules as a consequence of polarization process, it is called as Raman Scattering.

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Now, let us take a look at another phenomena, that is, scattering of radiation. Momentary absorption of radiant energy by atoms, molecules or ions followed by reemission of the radiation in all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation removes most the reemitted radiation by destructive interference except those travelling in the original direction; that is, **along the after passing through the substance**. A very small radiation... **Particles having comparable dimensions to that of the incident radiation removes most of the reemitted radiation by destructive interference except those travelling in the original direction**. A very small fraction of the radiation is transmitted at all angles from the original path and its intensity increases with the particle size. This is one phenomena.

Another phenomena is scattering by molecules or aggregates having smaller dimensions than the incident radiation is known as Rayleigh scattering. Larger molecules – what do they do? They scatter the radiations in different quantities in different directions. This is called as Mie scattering. When the scattered radiation is quantized like those occurring in vibrational energy level transitions in molecules as a consequence of polarization process, then it is known as Raman scattering. This is another type of scattering, which is quantized and used in the Raman's spectra.

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POLARIZATION OF RADIATION


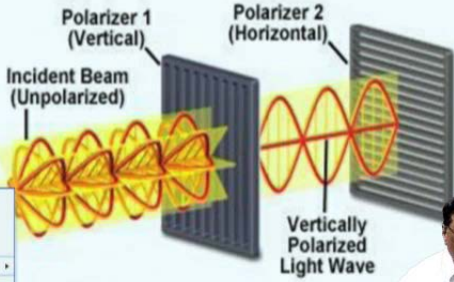
- Ordinary radiation consists of a bundle of electro magnetic waves in which vibrations are equally distributed among a huge number of planes centered along the path of the beam.
- Viewed end on it looks like an infinite set of electric vectors fluctuating from zero to a maximum amplitude A .
- The vector in any one plane say XY can be resolved into two mutually perpendicular components. Removal of one of the two resolved planes of vibration produces a plane polarized beam. It occupies a single plane. Radio waves emanating from an antenna and micro waves produced by a Klystron tube are plane polarized.
- Polarized ultraviolet and visible radiation is produced by passing the e.m beam through a media that selectively absorbs, reflects or refracts that vibrates in only one plane.



What is polarization? This is another phenomenon that is important for us to know what is polarization.

(Refer Slide Time: 35:44)

POLARIZATION OF LIGHT WAVES



Basically, what you see when a light beam is passing around, you would see that the electronic vectors are there, magnetic vectors are there. A beam of light passing through a media – if you view it from the receivers end, that is, if the light is coming towards the observer, you would see a number of beams, a number of parts that is electrical and magnetic part bundled together in not so systematic manner. But, it is a big bundle

coming towards you in which the electronic and the magnetic vectors are mixed up in a big bundle without any sense of direction or something. Of course, there is a sense of direction, but you would see that they are not properly organized. So, if you put a vertical polarizer in a vertical plane, what you would see is all other things are eliminated, except a vertically polarized light wave; you would see like this. This is known as polarization.

Ordinary radiation (Refer Slide Time: 37:06) consists of a bundle of electromagnetic waves in which vibrations are equally distributed among huge number of planes centered along the light path of the beam. Viewed end on it looks like an infinite set of electric vectors fluctuating from 0 to a maximum amplitude A . The vector in any one plane say XY can be resolved into two mutually perpendicular components; that we have already seen when we started studying the electromagnetic radiation. Removal of the one of the two resolved planes of vibration produces a plane polarized beam. It occupies a single plane. And, radio waves emanating from antennas and microwaves produced by Klystron tube are plane polarized. These are the day to day experiences. You would have heard lot of radio, FM radio and other things; and, you must be having a microwave oven also in your house. And, the radio waves and microwaves are plane polarized in our day to day life. A polarized ultraviolet and visible radiation is also required. It is produced by passing the electromagnetic beam through a media that selectively absorbs or reflects or refracts that vibrates in only one plane. So, electromagnetic radiations we need which are plane polarized.


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DIFFRACTION OF RADIATION

- **Diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference which can be easily demonstrated in the laboratory.**

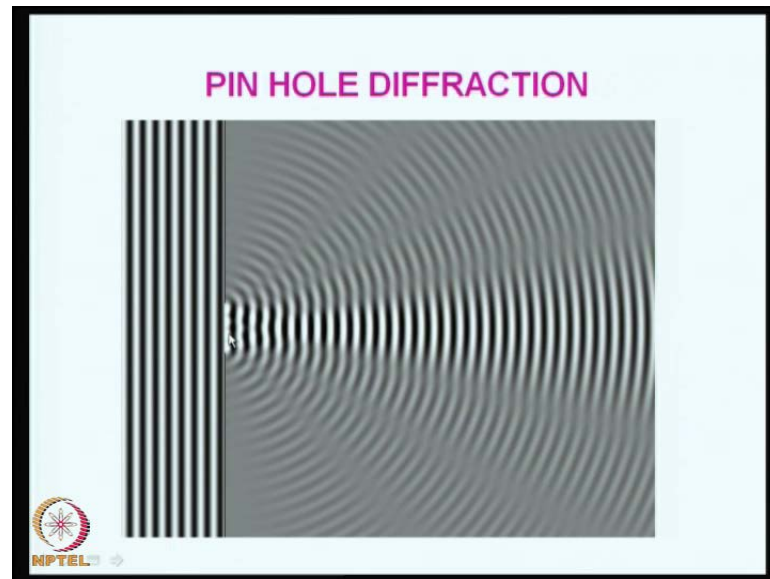
- **When a parallel beam of light is allowed to pass through a pin hole, two closely spaced pin holes are seen on a screen placed across it.**

- **If the radiation is monochromatic a series of dark and light image appear perpendicular to the plane of the radiation.**



Let us look at another phenomenon that is diffraction of radiation. What is diffraction? Basically, diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference, which can be easily demonstrated in the laboratory. You also would have experienced the diffraction in your day to day life.

(Refer Slide Time: 39:19)



For example, if there is a source of light that is passing through and a small opening is made, you would see interference fringes with **light and dark, light and dark, light and dark** patches that are visible here. Even in day to day life, such systems are very readily if you have the patience to look at them around you. For example, when a (Refer Slide Time: 39:46) parallel beam of light is allowed to pass through a small pinhole, two closely spaced pinholes are seen on a screen placed across it. Now, if the radiation is monochromatic, a series of dark and light images appear perpendicular to the plane of radiation. This is the one what I had showed you.

(Refer Slide Time: 40:08)

➤ In the above figure it can be shown that

$$\overline{CF} = \overline{BC} \sin \theta$$



For two beams to be in phase at D, it is necessary that \overline{CF} should correspond to the wavelength of the radiation. Hence

$$\lambda = \overline{CF} = \overline{BC} \sin \theta$$

Since reinforcement also occur at $2\lambda, 3\lambda$ etc. Hence,

$$n\lambda = \overline{BC} \sin \theta$$

where n is an integer called the order of the interference.



In the above figure, it can be shown that **vector** CF is equal to **vector** BC into sine theta. For two beams to be in phase at D, it is necessary that **vector** CF should correspond to the wavelength of the radiation. Therefore, lambda is equal to **vector** CF; that should be equal to BC into sine theta, where BC is the vector. Since reinforcement can also occur at 2 lambda, 3 lambda, etcetera, n lambda should be a function of the vector BC multiplied by sine theta; where, n is an integer called as the order of the interference.

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➤ When the phase differences remain entirely constant with time the system is said to be coherent. Then only a regular diffraction pattern is observed.

The spacing of the bands depends on the distance between the slits 'd' and the following relation holds:

$$n\lambda = d \sin \theta$$

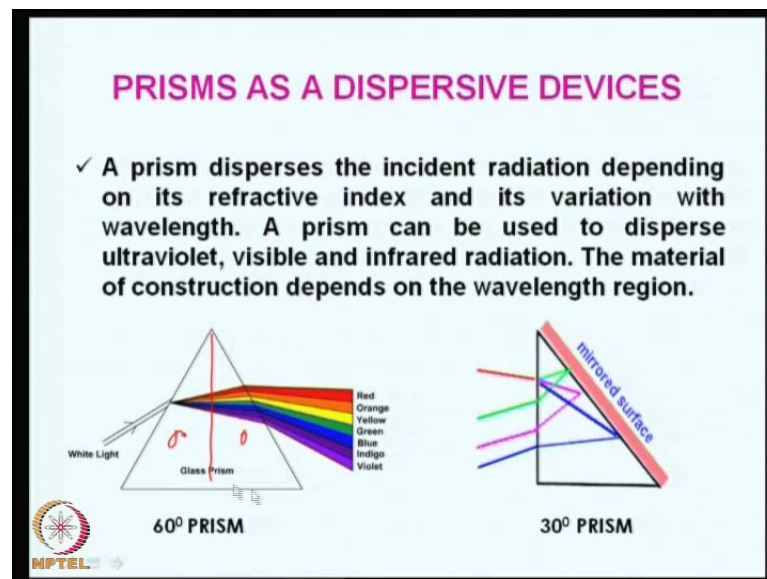
➤ If two different wavelengths of red & blue are used, the two colors will be separated on the screen. If white light is used a number of small rainbows containing all the colors will appear.

➤ By placing a moving slit across the screen any color or wavelength can be selected. This principle is used in gratings. We will study more about gratings and their uses in spectrophotometry.



Now, this diffraction... When the phase differences remain entirely constant with time, the system is said to be coherent. Then only a regular diffraction pattern is observed. The spacing of the bands depends upon the distance between the slits d and the following relation holds good: $n\lambda$ is equal to $d \sin \theta$. This is a very famous equation and you should not be forgetting in your entire career if you are undergoing this course. If two different wavelengths of red and blue are used, the two colors will be separated on the screen. If white light is used, a number of small rainbows containing all the colours will appear. By placing a moving slit across the screen, any colour or wavelength can be selected. This principle is used in gratings. We will study more about gratings and their uses in spectrophotometry, which is very common nowadays in more detail when we are studying the spectrophotometry and UV visible, ultraviolet. and then in atomic absorption, etcetera.

(Refer Slide Time: 42:25)



Now, prisms are the poor cousins of diffraction units. For example, basically, what is a prism? All of you would have seen prism. A prism basically disperses the incident radiation depending on its refractive index and its variation with wavelength. A prism can be used to disperse ultraviolet, visible and infrared radiation. The material of construction depends upon the wavelength region. For example, for ultraviolet, what you would need is a prism made of silica or quartz. For glass, ordinary... For visible region, glass will do. For infrared region, you need salts, for example sodium chloride,

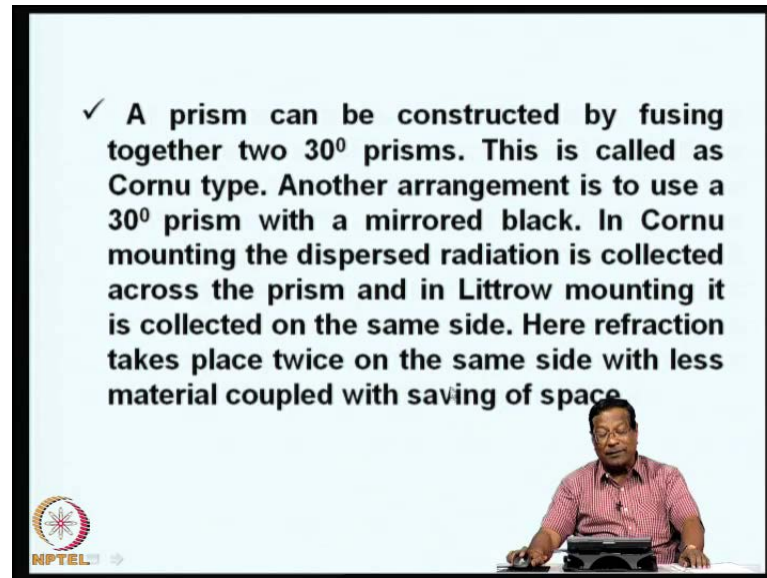
potassium chloride, potassium bromide; like that salts, which can be crystallized into these kinds of prisms, which will disperse the infrared radiation.

Here in this (Refer Slide Time: 43:29) figure, you would see that when we are passing the white light through the prism, it separates into its components starting from red, orange, yellow, green, blue, indigo and violet. These are the rainbow colours what you see normally in rainbows. Now, the same thing essentially happens here and in the nature also, where the rain drops acts as the prisms when the sunlight passes through the rain drops and they get reflected at a particular angle; and, you would see the rainbow colours into the sky, which is a beautiful sight to behold.


Now, the same principle is used in these things in spectrophotometry as well as in a atomic absorption, infrared, etcetera. And, you can see that I have shown you two prisms (Refer Slide Time: 44:34) here. One is 60 degree prism that is this angle – this is 60 degrees; and, they can be made by the fusion. Suppose you draw a line here. If you draw a line (Refer Slide Time: 44:59) here, they are made by the fusion of the right-handed and left-handed prisms: one here and one here – the right-handed and left-handed prisms. And, by fusing together, you can make a 60 degree prism. And, the other one what I have shown (Refer Slide Time: 45:33) here is a 30 degree prism; and, this prism is made by – on one side it is coated with a mirror surface.


Here (Refer Slide Time: 45:48) the light of the desired wavelength comes through like this and then passes through and then goes out of the prism on the opposite direction. Now, here what is happening? The light is coming inside and then changing, going and hitting the mirrored surface, gets reflected and comes back on the other side. This type is known as Cornu mounting and the 30 degree prism is known as Littrow mounting.

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✓ A prism can be constructed by fusing together two 30° prisms. This is called as Cornu type. Another arrangement is to use a 30° prism with a mirrored black. In Cornu mounting the dispersed radiation is collected across the prism and in Littrow mounting it is collected on the same side. Here refraction takes place twice on the same side with less material coupled with saving of space.

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A prism this is called Cornu. And, mirrored black, etcetera – this I have already referred to you. Here the refraction takes place twice on the same side with less material coupled with the saving of space.