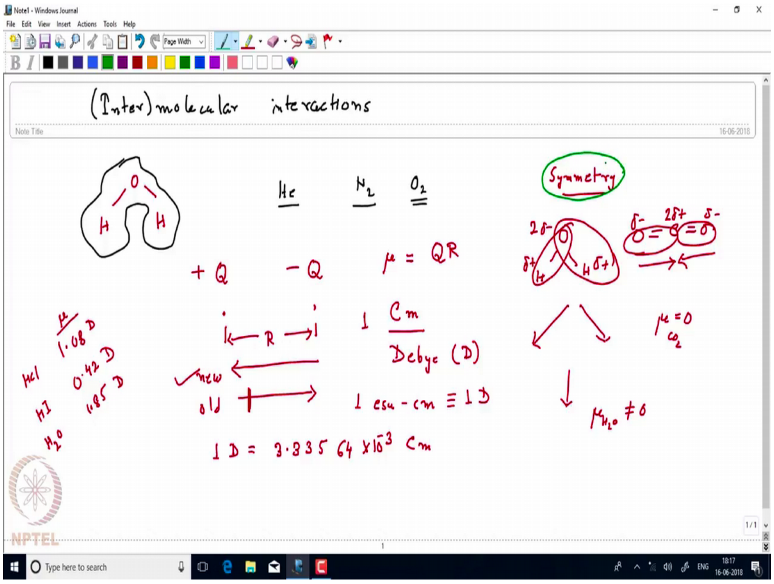
Advanced Chemical Thermodynamics & Kinetics
Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 06
Molecular Interactions 0I

Hello everyone. So, in today's lecture, we will start a new topic which is on intermolecular interactions.

(Refer Slide Time: 00:22)



We will be talking about Molecular Interactions or interactions between molecules. So, this is inter-molecular interactions. Now what do we mean by intermolecular interactions and why it is important to understand them or to study them? You remember that matter exists in three different forms like gaseous form, liquid form, and solid form where liquid and solid are known as a furnace phases of matter.

Now, the existence of condensed phase, if you remember the very beginning discussion at the very beginning on exist on real gases what are their experiments of real gas that the existence of a liquids liquid phase actually tells that there is an attractive interactions or overall there are interactions of various types between the molecules and that basically leads to a cohesive force which actually depends of course, on temperature and then you can have a very particular state of matter going from gas to liquid and liquid to solid.

Now, in this chapter we will be discussing on this nature of these forces or nature of the potential on the molecules which basically acts inter between the molecules. Now of course, you also probably studied quantum mechanics or we talk about the very like structure of molecules why molecules are formed and what are the forces acting between the constituents between of the molecules like what are the forces acting between two atoms.

And there probably you have studied the electronic structure of diatomic molecules in detail or you studied that formation of a chemical bond is very much quantum mechanical in nature because when you bring two hydrogen atoms together and form an H 2 or H 2 plus which is a more simpler system one electron system. So, there you studied that there are 2 kinds of forces, one is a Caulomic force which is a every forces electrostatic, but the electrostatic forces one is a Caulomic force, which is basically the attractive force between the electron and the two nuclei and also the repulsion between the 2 nuclei and, but that force does not stabilize the molecule, which is H 2 plus there are also other forces.

So, the other force is basically known as exchange force and the exchange force is, basically you can visualize that the electron is basically shuttling between the 2 atoms and although its not a very like rigorous way of saying that it is shuttling between the 2 atoms, because it is very much quantum mechanical in nature you cannot visualize it very properly, but the existence of chemical one is due to the exchange force.

Now, moving on one can now think about what happens between the molecules, in a similar way you can actually think about the interactions between different H 2 molecules or say different H2O molecule that will be a more specific molecule to discuss and thereby you can actually understand what are the specific interactions between the water molecules that give rise to the condensation of H2O molecules, which actually leads to formation of liquid water from water vapor.

Now, those kinds of forces will be understanding or trying to understand in this lecture. Now let us begin our discussion what are basically these forces. Now all of you know that most of these forces are which are intermolecular forces are of columbic in nature in the sense that there will be some electron cloud around each atom or overall in the molecule, there will some electron distribution and due to this electron distribution there will be some dipole created in the molecule and that dipole basically attracts with another molecular dipole and thereby there will be an attraction between the water molecules.

But what we are talking right now is basically about permanent dipole movements now a molecule may not actually possess a permanent dipole moment for example, helium atoms they do not possess any permanent dipole moment because helium there is its basically monatomic let us say nitrogen molecules these are also do not have a permanent dipole moment or any homonuclear diatomic molecule they do not have a permanent dipole moment.

So, there we have actually induce dipole moment and then we have interactions between the different induced dipole moment which can lead to some attractive interaction overall. So, we will be talking about that. So, let us first define what is a dipole and already you know in from your high school physics that what is a definition of a dipole. So, if you have a charge distribution where I have say a charge which is of magnitude plus Q and another charge which has a magnitude of minus Q and suppose these are the locations of the 2 charges and suppose they separated by a distance R.

So, then the dipole moment is defined as or the magnitude of the dipole moment is defined as Q times R I am using small R. So, maybe we can write it replace it as capital R. So, this is the magnitude of the dipole moment, now dipole moment is a vector quantity which means it has X, Y and Z components and actually if we want to write the or want to know the direction of the dipole moment the convention is basically it is acting from the negative end of the dipole to the positive end of the dipole.

Now, the older convention was basically going from positive end to the negative end and writing a plus sign here just to indicate that this is the positive end, but will straight to the new convention. Now dipole moment also has some unit and as you can see the unit will be like unit of charge times unit of displacement. So, you can think that the SI unit of charge is coulomb and the distance is meter. So, the natural unit is a coulomb meter, but there is a useful unit which is basically I have been used to measure the dipole moment of molecules and atoms, atoms do not have permanent dipole moment, molecules and ions and many other species.

So, that unit is known as Debye unit, which you write as D and this is the after the name of Peter Debye we did lot of pioneering work on measurement and formulation of molecular dipole moments. And there is a relationship between Debye and the by definition; so, this coulomb meter definition will be something like if I have 1 coulomb positive charge and 1 coulomb negative charge which has separated by 1 meter then the dipole moment will be 1 coulomb meter.

Similarly, we can define a Debye which actually tells us that if I have 2 charges which are one electrostatic unit these are the CGS unit of electrostatics charges, which you have studied probably in a high school physics and if there separated by 1 centimeter. So, then this 1 esu centimeter is equivalent to one Debye. So, there is a relationship between 1 esu centimeter and coulomb meter and usually we write that 1 Debye is 3.33564 into 10 to the power minus 30 coulomb meter.

Now, as I said earlier that this unit Debye is very useful for polarizabilities of the molecular dipole moments. We come to polarizability later, now talking about just permanent electric dipole moment. So, then we can say that this I mean the reason behind this choice of Debye is that usually at molecular dipole moment are on the order few Debye's for example, I have I can write some of the examples here for example, Hcl which has a permanent electric dipole moment hydrogen chloride molecule that has mu equal to 1.08 Debye and for HI hydrogen iodide it is 0.42 Debye.

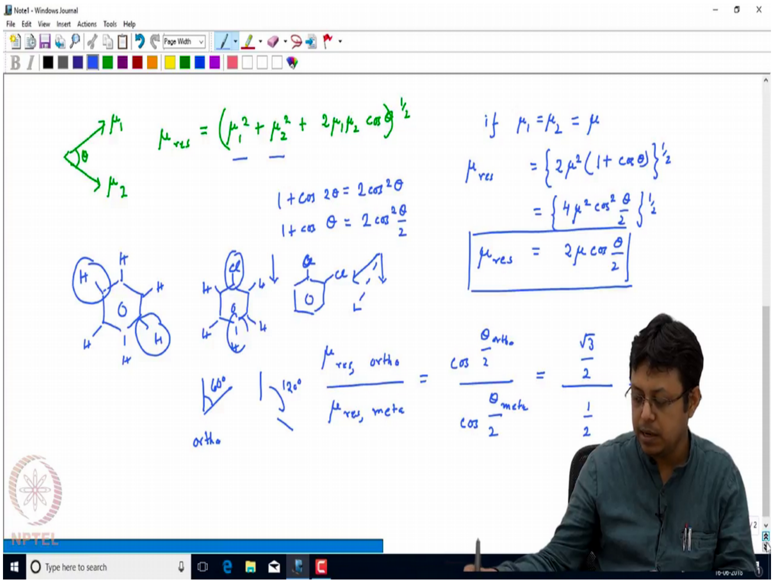
So, as you see that the molecular dipole moments are on the order of Debye. So, it is still in very useful way and the first example which we started with H2O has dipole moment of 1.85 Debye. Now the question is I will know that molecule possess a permanent dipole moment or not that is very much connected to the symmetry of the molecule which is actually more fundamental property which we are not going to discuss here. So, you probably studied the symmetry of molecules in a quantum mechanics course or any other specialized course on the symmetry of molecules.

Now, you know for example, as you just said in water molecule. So, the oxygen atom will be always partial will possess a partially negative charge which is due to the fact that the hydrogen is less electronegative than the oxygen. So, you can actually write it as delta plus and delta minus why. So, because there is a bond moment of the OH and similarly for the other bond will also have a moment. And so, we can actually write that the partial negative charge on the oxygen atom will be 2 delta minus something like that and due to this. So, there is a charge separation and you can now think due to this one. I will have a dipole moment which actually acts in this direction and due to the other bond. I will also have another dipole moment which actually acts in this direction and since dipole moment is a vectorial quantity they do not actually cancel out will have net dipole moment which acts as a in this direction.

However you can think that if I have a linear molecule something like carbon dioxide. So, for carbon dioxide which is a linear molecule there also you have the partial negative charge on oxygen and partial positive charge on the carbon atoms, but here the interesting thing is. So, there is a dipole moment due to the this co bond and there is also a dipole moment for this co bond and because of the geometry these two and the orientation of these two dipole moments or two bond moments to be more specifically the net dipole moment is 0, but for water since it is a bent structure the net dipole moment is non zero. So, dipole moment actually depends on the existence of dipole moment depends very much on the symmetry of the molecule, but again we are not going to go into the details of the symmetry properties of the molecule.

So, let us now focus more on the dipole moment if we have say addition of many dipoles like we have done here what will be the resultant dipole, and since it is vector. So, the general addition subtraction rule of vectors is also applied here. So, for example, if I have two dipoles inside a molecule which are permanent dipoles which are you can think as bond moments.

(Refer Slide Time: 12:26)



$$\mu_{res} = \left(\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta\right)^{1/2}$$

$$1 + \cos 2\theta = 2\cos^2\theta$$

$$1 + \cos\theta = 2\cos^2\frac{\theta}{2}$$

if $\mu_1 = \mu_2 = \mu$

$$\mu_{res} = \left\{2\mu^2(1+\cos\theta)\right\}^{1/2}$$

$$= \left\{4\mu^2\cos^2\frac{\theta}{2}\right\}^{1/2}$$

$$\boxed{\mu_{res} = 2\mu\cos\frac{\theta}{2}}$$

$$\frac{\mu_{res,\ ortho}}{\mu_{res,\ meta}} = \frac{\cos\frac{\theta_{ortho}}{2}}{\cos\frac{\theta_{meta}}{2}} = \frac{\frac{\sqrt{3}}{2}}{\frac{1}{2}}$$

So, then the resultant dipole moment will be nothing, but if this is suppose mu 1 and this I call it as mu 2 and then the resultant dipole moment will be mu 1 square or the magnitude of the resultant dipole moment will be mu 2 square plus 2 mu 1 mu 2 cosine theta where theta is the angle between the 2 dipole moments and we are talking about only the magnitude. So, for example, if I have 2 mu's are similar. So, let us say if mu 1 is equal to mu 2 something like we have seen for water where these OH bond moments should be equal because it is just identical atoms O and H. So, if that is the case, so we will have for water the resultant dipole moment for water. Now you notice here carefully. So, I will just adjust the mus same. So, it will be let us say mu 1 one equal to mu 1 equal to mu. So, these first two terms will be twice mu square and the second term will also be twice mu square.

So, I will have totally I can take twice mu square as common and then I will have one plus cos theta and square root of that. So, and then we can actually apply the cosine rule like cosine 2 theta is nothing, but 1 minus 2 cos square theta. So, we can write it is as 1 plus cos 2 theta is basically 2 cos square theta or here actually I can write the theta as 2 times theta by 2. So, I am writing it as 1 plus cos theta is nothing, but 2 times cosine square theta by 2. So, ultimately I will have 4 four mu square cosine square theta by 2 square root of that. So, ultimately the resultant dipole moment comes as twice mu cosine theta by 2.

So, that will be for there is a general principle now we have to find out the angle for water molecule what are the angle I mean if it is water molecule we can actually just calculate it very easily, but this is the expression which we just derived this is for any general molecule where actually we have 2 dipoles which are of equal in nature and there is a angle between them which is theta since we can actually add the dipole moments the interesting thing is that suppose for benzene we have all hydrogen atoms here as you already know and as you can think that all the bond moments will basically cancel with the opposite bond moments like the see this H bond moment will be canceled by this H bond moment and so, on.

So, if we actually have a substituted page in something like let us say a Chlorobenzene like this. So, you can actually readily predict that there is a CCL bond moment and there is a CH bond moment and they do not of course, cancel with each other. So, we will have some resultant dipole moment for Chlorobenzene, but similarly if we have say dichlorobenzene like say ortho substituted dichlorobenzene something like that. So, you can think that it will be as if the dipole moment of 2 Chlorobenzene molecules. So, for Chlorobenzene the dipole moment direction will be like this because chlorine is more electronegative and our choice is from negative to the positive end and for Chlorobenzene we can actually get the resultant dipole moment along this direction.

So, how do you find it. So, this is also very easy to understand because the as you can see the angle between them will be nothing, but 60 degree. So, this angle will be the right two mu cosine 60 degree by 2 or 2 mu cos 30 degree. So, we can actually get a ratio of the dipole moment between 2 subsidized substituted benzene for example, if we ask this question what will be the resultant dipole moment for the ortho die substituted Chlorobenzene and what will be the resultant dipole moment for the meta dye substituted Chlorobenzene and remember that for ortho actually the angle is 60 degree.

But for meta as you can very easily figure out that this angle will be 120 degree and here the bond moments of the individual dipole moments are basically same because its just Chlorobenzene. So, its a CCL and opposite to it in the trans position not transposition in the just opposite carbon position. So, you have the an opposite to it in the para position you have a CH dipole moment. So, the resultant will be same and you can think that as if for this dye substituted benzenes it is basically a resultant of the 2 dipole moments, but oriented in a particular angle.

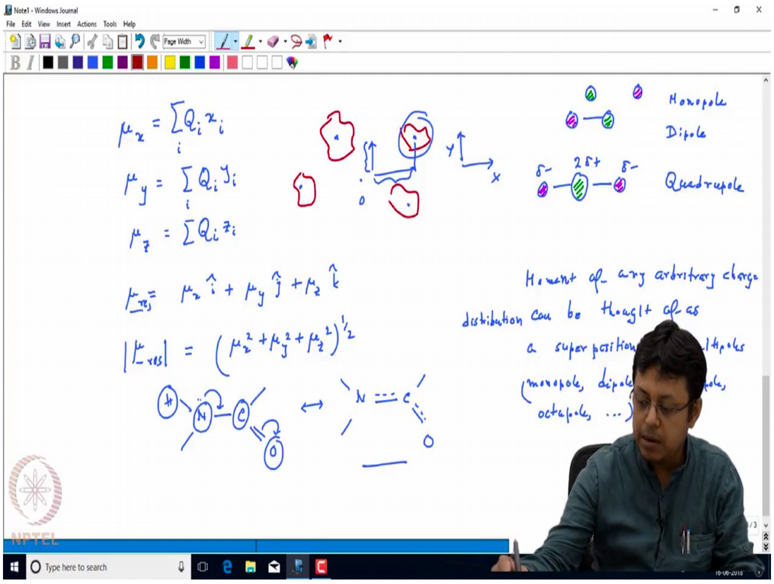
So, for ortho this angle will be this ratio will be nothing, but cosine theta by 2 for ortho divided by cosine theta by 2 where this theta is four meta. So, what will have is it is the top one for ortho actually it is 60 degree and 60 divided by 2 is 30 degree. So, cosine 30 degree is root 3 by 2 divided by I will have cosine 120 degree by 2 which is cosine 60 degree which is 1 by 2. So, overall will have are the ratio as root 3 what which is nothing, but 1.7 and this again follows from the vectorial addition of dipole moments because the dipole moments are basically vectorial in nature.

Now, the next thing is that here we have given you a very nice example in the sense that I have 2 bonds and there are some bond moments which are individually dipole moments and these 2 dipole moments are permanent dipole moments which are oriented in space in a particular angle and due to this angle which is dependent again on the molecular geometry. So, we will have basically vectorial addition of the dipole moments and we can get the resultant dipole and for that actually you can calculate the dipole moment of the dye substituted benzene from the mono substituted 1 or you can actually calculate the ratio of the dye substituted benzene, now in the way we have shown here.

Now, here look at it carefully that this resultant dipole moment is higher for ortho than their meta which is which makes sense because if your angle is small. Suppose this if your angle would have been 0. So, then the cosine 0 will be 1. So, the resultant dipole will be just twice mu and if the angle is 60 degree it will be something like that if it is 120 degree it will be something less than that and if it is 180 degree, then the dipoles will cancel with each other something like we have seen for carbon dioxide. And then we they will have a perfect cancellation of the dipole moments and the resultant dipole will moment will be 0.

So, it all depends on the angle between them, but for a polyatomic molecule where actually do not have such a clear separation of very nice dipole moments and from a particular origin then we can actually still work out and find a dipole moment from a particular point in space or the origin. So, in that case what we do is that you basically calculate the partial charge or electron density is more specifically in on each atom and then you basically do a vectorial sum; so, to be more specific mathematically.

(Refer Slide Time: 21:16)


$$\mu_x = \sum_i Q_i x_i$$

$$\mu_y = \sum_i Q_i y_i$$

$$\mu_z = \sum Q_i z_i$$

$$\underline{\mu}_{res} = \mu_x \hat{i} + \mu_y \hat{j} + \mu_z \hat{k}$$

$$|\underline{\mu}_{res}| = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

Moment of any arbitrary charge distribution can be thought of as a superposition ltipoles (monopole, dipole pole, octapole, ...)

So, what I am saying here is that the resultant mu suppose I have a total mu like this and then what I am writing is that suppose I have many atoms in this. Suppose this is an arbitrary molecule and these are basically atoms and each atom has some electron density around it and for that we have some charge and then we can actually ask this question what is the x component of the dipole moment.

And then what we have to do is that we have to find the position of each atom suppose each atom I am writing the ith atom as x i and then we can actually associate the partial charge for this ith atom and this position is with respect to some origin let us say this is the origin and then we will find that for example, for this atom what is the coordinate along say X axis if this is our X coordinate and what is the coordinate along say Y axis. So, suppose this was the Y coordinate and then we can actually write down the X component dipole moments as the sum of the all the X component dipole moments for individual atoms and then we sum over all the i similarly for Y direction also we can get a similar way.

So, the charges partial charges times basically the position of that atom. So, since we are talking about now the y component it will be something like y i and similarly we can also talk about the z component of the dipole moment and then we can get something like this for individual atoms and then we can actually talk about that total overall dipole moment which will be nothing, but mu x and if we want to have the addition of vectors. So, we have to also multiply the by the unit vector mu y into j plus mu z into k where i j k are basically the unit vectors along X Y and Z direction or we can get the direction or magnitude of the overall dipole moment as square root of mu x square plus mu y square plus mu z square.

So, will give you an example where we will actually tell you a particular bond which is the amide bond and we will be talking about the amide bond is very important in peptide chemistry because when 2 amino acids basically form a peptide bond it is basically the amide bond which we talk about and the more or less the geometry of the amide bond is planar. So, the amide bonds is something like this and you can now think about the partial charges on hydrogen on nitrogen on carbon and oxygen and why they are might bond is planar the reason is because of this lone pair on the nitrogen it act this amide bond the NC bond actually has a partial double bond character.

So, this is known as a resonance structure which probably you already know. So, this NCO unit actually basically relies on a plane. So, that that gives the planarity of the amide bond. So, these are basically resonance structures and this is basically a resonance hybrid structure of the amide moiety you can actually calculate if you know the partial charges along a particular and the position of each atom from a particular origin then you can actually calculate the overall dipole moment of the amide bond and in this way you can actually find out what is the overall dipole moment of a particular group in a molecule you can also find out the overall dipole moment of the molecule itself.

Now, the question is dipole moment is not the only thing that the molecule possesses because here we are talking about the distribution of charges in the molecule and we talked about only dipole. Now dipole is not the only thing that we have and we also have something like quadrupole. What is a quadrupole? We already gave you an example which is a carbon dioxide. Now this is basically higher order moments and this comes from detailed tensor algebra which we will not consider here. So, for example, CO2 which does not have a permanent dipole moment can actually have quadrupolar moment and let me actually show you the negative as with a in a different colour and the positive also in a different colour.

But for a dipole for a similar drawing we have already shown how the dipole is represented. So, dipole is represented as the separation of the 2 charges like this. And similarly you can also think about a monopole which is either a positive charge or negative charge something like this. So, we have actually many different poles or these are actually in general called multipoles. So, like monopole then we have dipole and then we have quadrupole you can also get quadrupole from a very different arrangements, but we are not going to the details you can actually find it in the recommended text which you were supposed to have a look at and then also you have octupole and many other distribution of the charges.

But those are very particular distribution in the sense that the way we have described it like we can have a dipole like it is a its basically two distinct distribution of 2 distinct charges. Then we have quadrupole which is has a very particular arrangement like it is a linear arrangement of a negative charge, then twice their positive charge which has basically charge of twice the negative charge then again another negative charge something like that now in reality a molecule will have a moment which is not like this because you will have arbitrary charge distribution, but you can always write these arbitrary charge distribution are the total moment due to this arbitrary charge distribution as a linear combination of monopole plus dipole plus quadrupole plus octupole and so on.

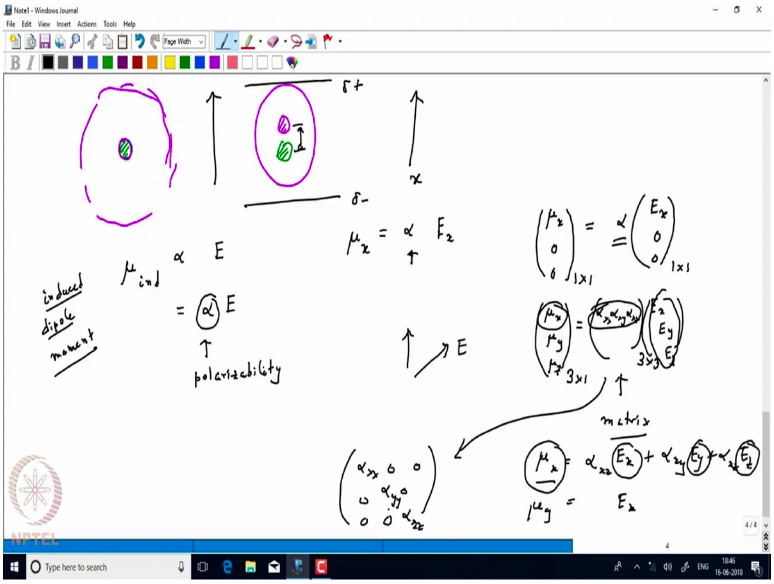
So, basically these are geometrically having basically symmetric moment structures and any multipole or moment or basically what you call as any moment of a multipole can be thought of as superposition of monopoles of many multipoles basically. So, what I am saying the moment of any arbitrary charge distribution moment of any arbitrary charge distribution that can be thought of as a superposition of many multipoles and the multipoles are basically monopole then we have dipole then we have quadrupole then we have octupole and so on.

So, again this in this discussion you always remember that when you go for an higher order mono higher order multipole for example, if I were going from the monopole to the dipole then the monopole actually contains a net unit charge the dipole does not have a net unit charge, but it has a dipole moment then the quadrupole doesnt have a net unit charge because as you can see it is a minus delta minus 2 delta plus delta minus. So, there is no net unit charge and also there is no dipole moment, but it has a quadrupolar moment and then similarly for an octupole if we talk about it does not have any permanent charge. So, its not a it does not have any monopole it does not have any dipole moment it does not have any octupolar quadrupolar moment.

But what it has is basically an octupolar moment. So, these are all basically fundamental charge distribution and with that we can actually constitute the higher order moments and any arbitrary charge distribution you can actually write in terms of that, but will not extend our discussion on this multipole or moments right now rather will be now focusing more on the dipole moment and what happens for basically if we actually have an external electric field if it is applied to a molecule. So, let us try to understand that first, now the way we have talked about it is basically I have a permanent electric dipole moment now this permanent electric dipole moment at sometimes a molecule may not have actually a permanent electric dipole moment; however, due to the presence of an electric field the dipole moment can be created.

Now, how one can visualize this phenomena, now as you know that the simplest charge distribution or the simplest entity you know simplest atom you can think of is the hydrogen atom and in the hydrogen atom what you can think that there is a positive charge we are actually writing the positive charge as green center something like this.

(Refer Slide Time: 31:38)



And there is a diffused electron cloud around it, but which is basically a electron cloud, but the center of the electron cloud actually perfectly coincides with the center of the positive charge.

So, as such there is no separation between these charge centers. So, which means the r in the dipole moment expression or the distance between the positive and the negative charges is 0 for which the permanent dipole moment of any atom is basically 0. Now there can be instantaneously electron cloud fluctuation which can actually give to partial separation over very short period of time of this electron center of the electron charge distribution and the nuclei and that can actually give rise to a momentarily dipole, but that we are not considering at this moment and this dipole is basically arises out of own because it is just a time dependent dipole, but if you think that on average this electron cloud will basically orient itself in many possible directions.

So, the orientation of this dipole will be very random. So, on average you can think that the average position of the negative cloud with respect to the positive cloud is basically there already there always superimposed on the time average position. So, there will be no permanent electric dipole. Now suppose we are applying an external electric field along say this direction and electric field as you know basically will push the electrons and the nuclei in the opposite direction and as a matter of fact what you will see is I will have positive end here and the center of the electric charge will be slightly shifted something like that.

Now, this you can realize suppose if I put the hydrogen atom inside a capacitor where this is basically the negative end of the capacitor, this is the positive end a capacitor. So, the capacitor will try to distort the electron cloud it will try to pull the electron cloud and also pull the nuclei and then I will get a small separation and I will create a dipole. Now this dipole is a static dipole at this moment because we are just applying a static electric field which you can visualize as applying or placing the molecule or the atom in this case its a hydrogen atom inside a capacitor. Now that dipole is not a permanent dipole that dipole is an induced dipole moment because it appeared due to the presence of the external electric field.

Now, there are two things here atoms and molecules since they actually have electrons and nuclei whenever we apply say for example, an electric field we are usually considering the electric dipole moment here, but similarly we can also talk about the magnetic dipole moment where actually we apply an external magnetic field to it, but we are not talking about magnetic dipole moment right now I will be only focusing on the electric dipole moment at this moment.

Now, if we create an electric dipole moment like this and that dipole moment we write it as mu suffix ind. So, ind means actually this is induced dipole moment as opposed to the permanent dipole moment which we have just discussed. So, then you can think that the strength of this induced dipole moment to some approximation will be proportional to the strength of the act like electric field meaning. If the electric field is too strong, I will actually distort the electron cloud and the move the nuclei in the other direction more and more efficiently. So, on basically increasing the distance between them which means the magnitude of the dipole which is created or which is induced will be more and more which means actually the in a strength of the or the magnitude of the induced dipole moment is proportional to the electric field or we can actually write the proportionality constant as something like alpha.

Now, this alpha is known as the polarizability of the molecule or will come back to the other higher order. Let us just it can be actually proportional to the non-linear way on the electric field also, but let us not discuss it at this moment. Let us not focus on the polarizability or the alpha term now what is alpha now you can think that mu is a vector quantity as we already know. So, mu will have basically mu x mu y and mu z and suppose this direction is let us say it is X direction.

So, I have an x component of the dipole moment and then I also apply the electric field along X direction. So, in this case this alpha is nothing, but a scalar because you have only one vector which is mu x and the if the other 2 components are 0 which is which means actually the mu is only along X direction we can write it something like this like we have X component Y component and Z component is 0 and as you know that we are writing it as a column vector. So, basically this alpha in that case is just a number because the electric field is also applied along X axis; however, this may not be. So, simple like this because you can have you can still apply an electric field along X direction, but you can have create a dipole in the X and Y direction also.

Meaning what I am trying to say here I can actually apply an electric field in E x, but then I can actually create a dipole which has components along mu x mu y and mu z all these components and in this case as you can see that this is basically one row one column kind of matrix and. So, that is why the alpha is just a number, but if we have components like this 3 by 1 and then this alpha is nothing, but it has to be 3 by 3 matrix because you can have in more in more general that you will apply the electric field along X can actually induce the dipole moment along x y z all the direction.

In this case alpha is basically in this case a matrix I mean it is basically 3 by 3 matrix and in more general alpha is basically of the hyper polarizabilities. So, we will come back to what is hyper polarizability alpha in this case is a matrix, but will not go into the details we will just consider alpha here as a number in the sense that or a or a scalar. So, that if we are assuming that if we apply the electric field around x will always have dipole moment along created along x. So, you can think that from matrix multiplication that I will have terms like alpha xx, alpha xy, alpha xz something like that.

So, if I want to know what are the magnitude of mu x. So, mu x as you can see will be alpha xx time E x alpha xx times E x plus alpha xy times E y plus alpha xz time E z. So, what I am trying to say here when we apply the electric field along E x we created a dipole moment along mu x we also created a dipole moment along mu y something like that and also it has a dipole moment along E z or we can actually view or you can ask the different question what is mu x and mu x is actually contributed by both E x and E y as well as E z if it is a three dimensional problem and thus we see that applied field and on a particular direction may create actually dipole in all of the direction.

Now, you can actually think about a crystal where actually the electrons are a very unique distribution and if the crystal axis does not match with the applied electric field axes then actually you can create dipole in all other direction, but you can think that I can always rotate the crystal in such a way that I will get you get rid of this meaning I will always if I apply the electric field along E x i always get the component along E x and. So, on if I apply it along E y i will get always along E y. So, mathematically you can say that in that case we are basically diagonalizing these matrix meaning all other components of this matrix is 0.