Bio-Physical Chemistry
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Lecture - 09
Intermolecular Interactions

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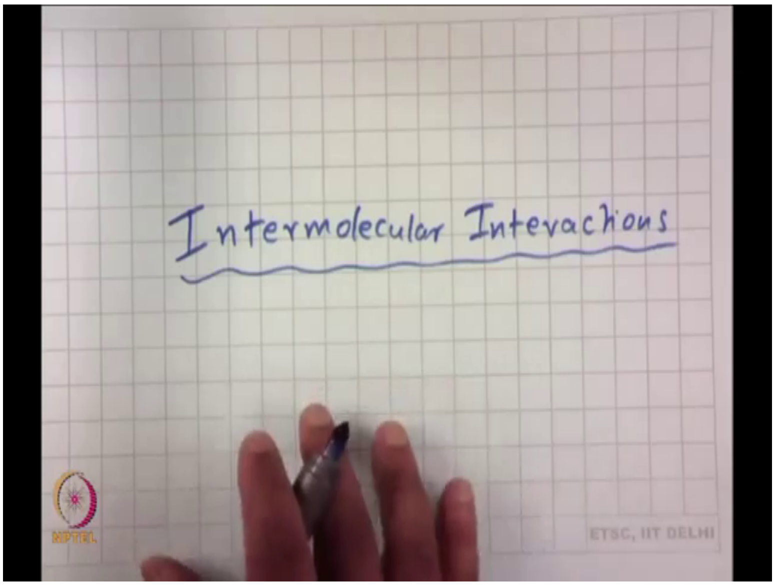

Ok So, we will start with today's class just. So, the topic of today's class would be Intermolecular Interactions right and you know what I am going to stress on this. Up till this point, we have looked at you know essentially Coulombic force right between charges and how the intervening salt solution would be screening. The effect of the charge or the ions from the effect of the electrostatic potential given out by the charge right.

But you know there are many interactions also which are not necessarily between charged systems. You know systems can also be neutral, but still show interactions. Those are essentially your Van der Waals forces or London dispersion forces right. But you know before going there actually, I do not think we will be able to make it that far today. What we are going to look up is you know some specific aspects. For example, we have looked at Coulombic potential right.

Now, what happens if in between the two charges: one is a point charge and the other one becomes a dipole right. How does the interaction potential change? And then what happens if you have instead of one dipole, two interacting dipoles right. What will happen in that case? How will the interaction potential change? Because that is typically, you know degradation of interactions we should look at, before we understand what dispersion forces are all about, you know.

So, just to recap what we had from last day.

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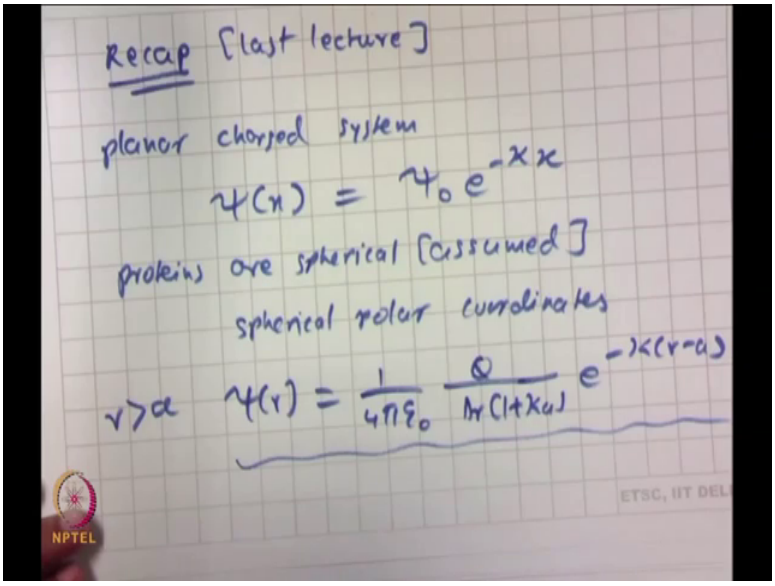

Recap [last lecture]

planar charged system

$$\psi(x) = \psi_0 e^{-\kappa x}$$

proteins are spherical [assumed]

spherical polar coordinates

$$r > a \quad \psi(r) = \frac{1}{4\pi\varepsilon_0} \frac{Q}{r(1+\kappa a)} e^{-\kappa(r-a)}$$

So, this is what we said, it is a recap of the last lecture. So, if you have a planar charged system then we saw that psi of x which is a electrostatic potential at a distance x from this charged plane is equal to remember, what it was.

Student: Psi.

Psi 0 e to the power minus kappa x. So, there was a exponential gradient right or an exponential decay of your charge or electrostatic potential right. Coupled to psi 0, where psi 0 is the potential at the surface of the plane that is x is equal to 0.

That is what we defined psi 0 to be. Then we said that, proteins are spherical or assumed to be spherical. So, then our system will change to spherical polar coordinates right.

Student: hm.

So, that is what we used. So, then the final expression we got from there is, it is psi of r is equal to 1 by 4 pi epsilon 0 Q by.

Student: D.

D of r 1 plus kappa a times e to the power minus kappa r minus a. So, this is the final thing we reached at and here; obviously, the assumption was r would be.

Student: Greater than a.

Greater than a ok, because this protein is not a point charge, it has a certain dimension and we are saying the dimension or the radius of the protein is.

Student: a.

a. So, whatever charges you are looking at is beyond a, because at the surface you have this psi of a, which we also derived. Now, think about this if, because now the protein has this you know radius a if it is a point charge. For example, if the charge is a point charge then what will happen? If it is a point charge then a would be what? 0, right.

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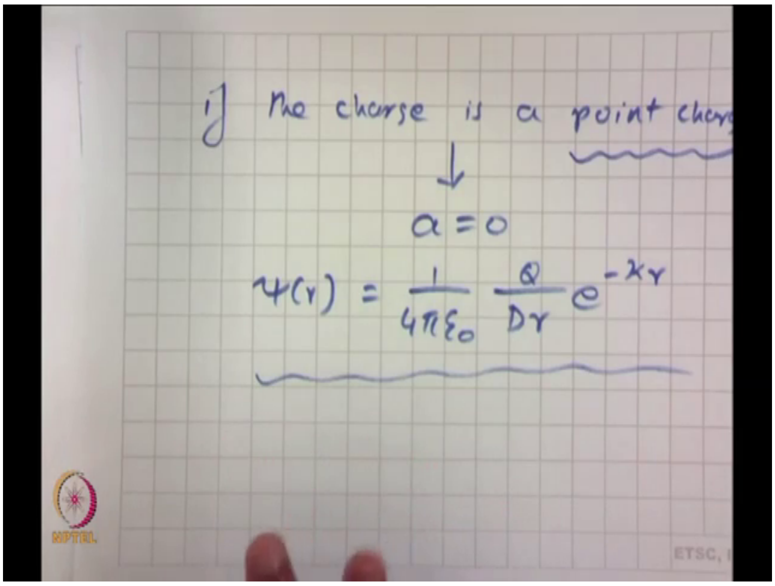

if the charge is a point char

$$\downarrow$$

$$a = 0$$

$$\psi(r) = \frac{1}{4\pi\varepsilon_0}\frac{Q}{Dr}e^{-\kappa r}$$

Student: 0.

It is now radius so; that means, a is equal to 0 and then psi of r is equal to 1 by 4 pi epsilon 0 Q by D times r e to the power minus kappa r right, because a is 0 now. So, this is for a point charge right. So, this is for a point charge and this is what we get. So, the one we saw before that the one we wrote down before was a very general solution right and now you are doing specific, that is you are saying that a essentially tends to 0.

But you see the concept in this case is still captured, why? Because you look at this psi of r still has a dependence upon kappa right and if you only look at, if you do not consider e to the power minus kappa r what is this? This is essentially like a Coulombic potential is not it.

Student: Yes.

Essentially like Coulombic potential. So, along with the Coulombic potential what you are adding is an exponential variation of the charge in the radius, in the radial direction depending upon kappa right.

So, this is what you really need to remember right. I mean definite the derivations and the concepts behind these derivations or what you get from the final equation ok. So, moving on what we will do is, we will start with Intermolecular Interactions right, but before that let me make a couple of points.

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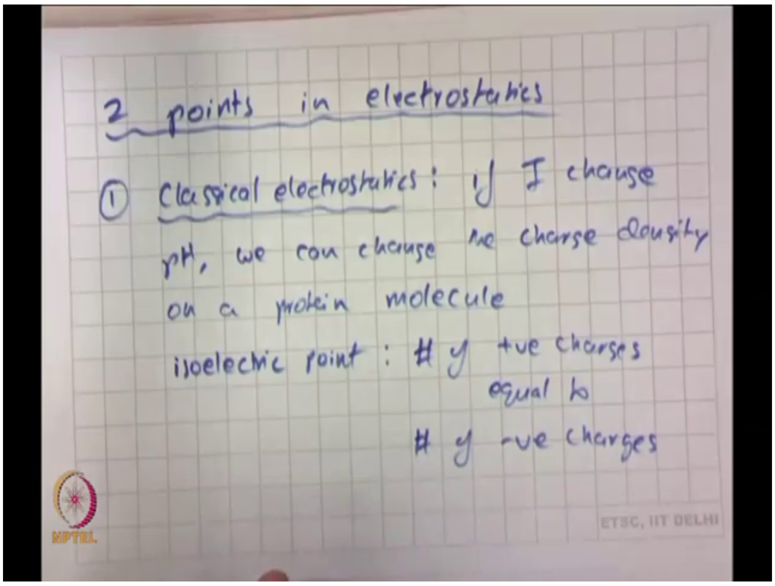

2 points in electrostatics

① Classical electrostatics: if I change pH, we can change the charge density on a protein molecule

isoelectric point : # of +ve charges equal to # of -ve charges

So, let us talk about two points in electrostatics and I will tell you what two points I am talking about. So, how can electrostatics come into picture? There are two ways essentially specially for proteins. We are already always thinking of proteins, because that is what we are talking about our bio molecule the one is classical electrostatics; The one is classical electrostatics.

Now, what does this have to deal with? So, in classical electrostatics remember, classical electrostatics deals with charges, attractions, repulsions and all these things that is what classical electrostatics is all about. So, you can understand if I change or if we change pH if we change pH we can change the charge density on a protein molecule.

So, what do we mean by that? Have you guys heard about this term called the isoelectric point?

Student: Yes.

Right. So, an isoelectric point what happens?

Student: Neutral.

Neutral means number of positive charges equal to.

Student: Negative (Refer Time: 08:17).

Number of negative charges right. So, number of positive charges equal to number of negative charges. Now, why is this isoelectric points so important? Ok the reason is this.

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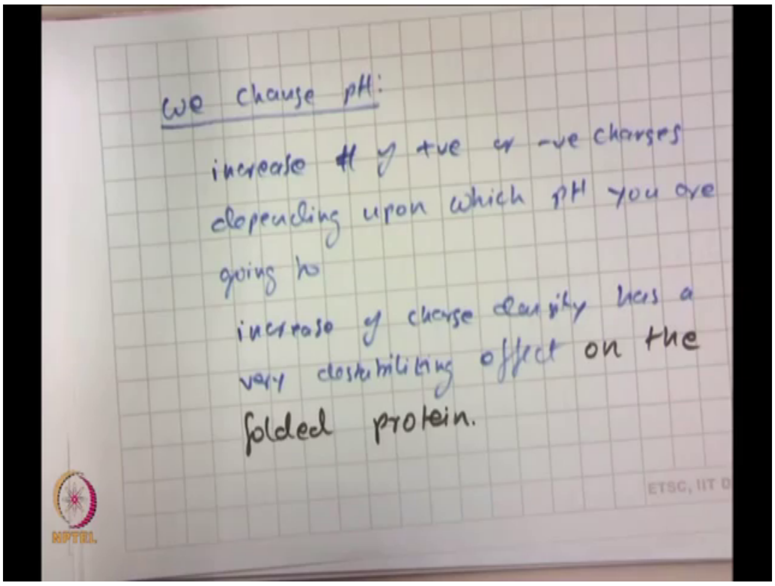

We change pH:

increase # of +ve or -ve charges depending upon which pH you are going to

increase of charge density has a very destabilizing effect on the folded protein.

Suppose, we change pH, suppose we change pH; that means, either we go to the acidic side or to the basic side; that means, either we moving to the left of the iso electric point or right of the isoelectric point isoelectric point being in the middle, because it is neutral all right.

So, what will happen based on this you will increase number of positive or negative charges right, depending upon which pH you are going to; that means, if you are lowering the pH you are essentially protonating you increasing positive charges.

If you are going to the basic pH what are you doing? You are deprotonating; that means, you are essentially increasing the negative charges, but either way what you are doing is when you are moving away from the isoelectric point, you are increasing charge density. Now, increase of charge density increase of charge density has a very destabilizing effect has a very destabilizing effect on the folded protein, has a very destabilizing effect on the folded protein.

Now, what I mean by that? What I mean is remember, a folded protein is a compact protein right. So, volume is small, when you increase the charge density; that means, you either acidified increase a positive charge or you go to the alkaline side; that means, increase a negative charge is what will happen? If you consider that the protein is not getting effected for the time being then it will start increasing the amount of either negative or positive charges on the protein.

But the volume of the protein is small right and you are increasing the negative and positive charges. Now, because you are moving away from the isoelectric point so, what will you give rise to? Gives rise to repulsive interactions between like charges right.

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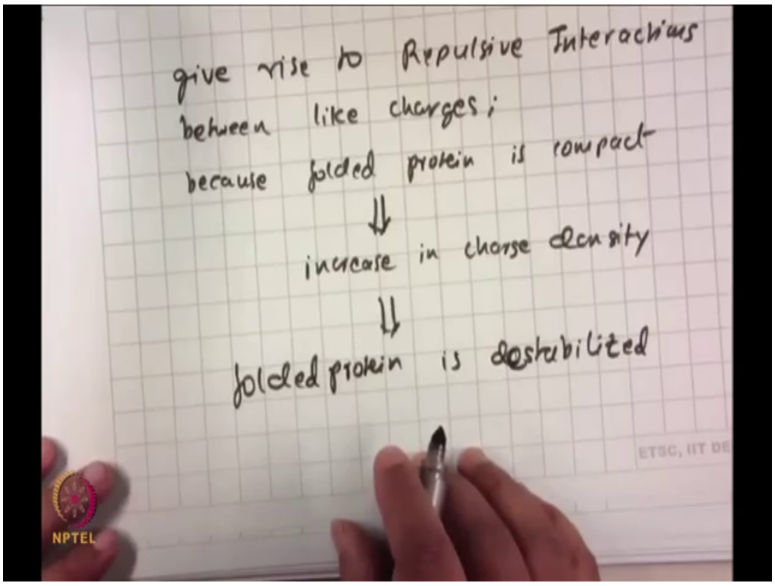

give rise to Repulsive Interactions
between like charges;
because folded protein is compact

$\Downarrow$

increase in charge density

$\Downarrow$

folded protein is destabilized

So; that means, because of this; because of this you give rise to; you give rise to repulsive interactions between like charges. Now, because folded protein is compact is compact. It is a folded protein, it is compact, this increase or decrease of charges leads to a huge increase in charge density right.

So, what you mean by this, charge density is what? Charge density is essentially the number of charges per unit volume. Now, your volume of the protein is not changing; that means, I am saying that the protein is remaining in the folded form, but you increasing what the number of like charges. So, how will the protein respond? The protein will try to respond by getting rid or trying to get rid of the repulsions between the like charges.

Student: Hm.

So, how can the protein get rid of the repulsions of the like charges?

Student: Increase (Refer Time: 12:35).

It starts opening up; that means, it starts increasing it is volume so; that means, it has to get rid of the excess repulsive charges. So, that is why the moment you unfold a protein the volume increases hence, the charge density immediately what?

Student: Decreases.

Decreases right and hence, the protein opens up. So, then because of increase in charge density protein or folded protein is destabilized your folded protein is destabilized right.

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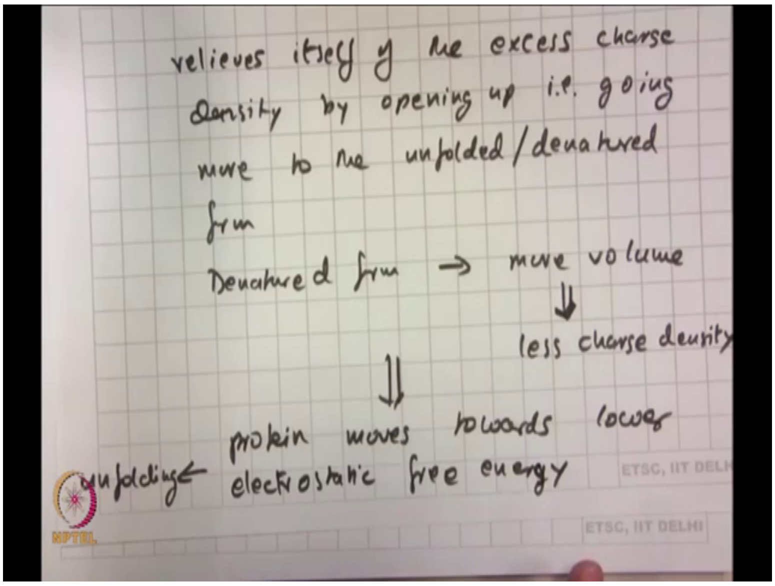

relieves itself of the excess charge density by opening up i.e. going more to the unfolded / denatured form

Denatured form → more volume

⇓

less charge density

⇓

unfolding ← protein moves towards lower electrostatic free energy

So, what does it do in return? In return it what it does is, relieves itself of the excess charge density by opening up that is going more to the unfolded form, unfolded or denatured form and denatured form denatured form has more volume hence, it leads to less charge density.

So, in effect if someone is going to ask you tell me in one sentence what does a pH induced denaturation mean or how does it happen? It simply happens or why does it happen? It simply happens, because the protein, where does it go? It goes to a lower electrostatic free energy, because if it is in the compact form its free energy is increased right, because there is so much of repulsive interactions.

So, because of this increase in pH, it tries to go to the that point or that system or that state where the electrostatic free energy is lower. So, that is; that means, protein moves towards lower electrostatic free energy and this is essentially your unfolding of the protein. Is everybody clear about this, right.

So, this is another way of trying to you know think about pH induced denaturation of protein. So, it is it essentially based on charges right and this is why it happens, because the protein has to respond to whatever charge density it has and try to lower the free energy, because that is free energy is you know what all about.

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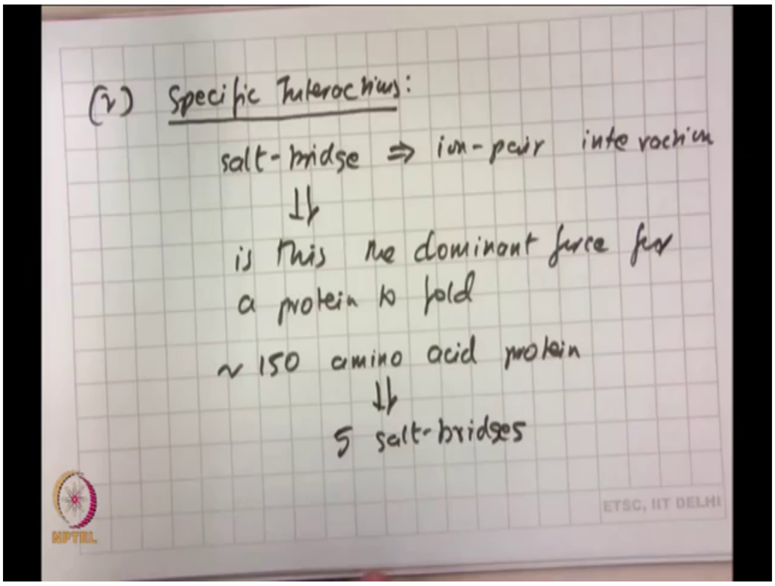

(2) Specific Interactions:

salt-bridge ⇒ ion-pair interaction

⇅

is this the dominant force for a protein to fold

~ 150 amino acid protein

⇅

5 salt-bridges

Now, that is one, then there is one more. I said two right now second one is specific interactions. Second one is specific interactions. So, what do we mean by specific interactions? I am sure you heard, you have heard of this term, salt bridge have you heard of? Salt bridge are also known as ion pair interaction. Now, if I ask you this, do you think this salt bridge or ion pair interaction is the most dominant force in protein folding? What do you think? Yes or no?

Do you think it is? Someone is saying no.

Student: No.

How would you prove that it is no? See there was a time there was a time where people thought that these ion pair or salt bridge interactions are the ones which are the most dominant feature. You know before this hydrophobic effect, you know was not that well known, but the problem is this the thing is the question we are asking is this. The dominant force is this the dominant force for a protein to fold. How can we think about this? Let us try to argue this fact.

Let us consider a 150 amino acid protein, let us consider 150 amino acid protein. When people looked at the structure of the protein, what they saw was they had only 5 salt bridges in the 150 amino acid protein. They had 5 salt bridges, 5 salt bridges means out of 150 amino acids only 10 amino acids are actually involved in forming the salt bridges or ion pair interaction the rest 140 are not.

Hence, in terms of the number of amino acids involved in these interactions, do not you think it is too small to become the most dominant force? So, this is how people argued against the fact that it should not be the dominant force, because see people were trying to rationalize right by proteins fold and what are the forces behind it and then this is one of the ways.

So, they look at the number of interacting pairs present and they saw there are 5 pairs 10 amino acids, which is too small for 150 amino acid protein to fold, only based on that ion pair interaction right.

So, there must be some other issues going on, but anyway. So, the idea was these are two types of interactions one is a classical charge interaction and the other one is specific between the respective ion pairs which are forming the salt bridges right. So, this is what about you know classical electrostatics screen Coulombic potential all those things.

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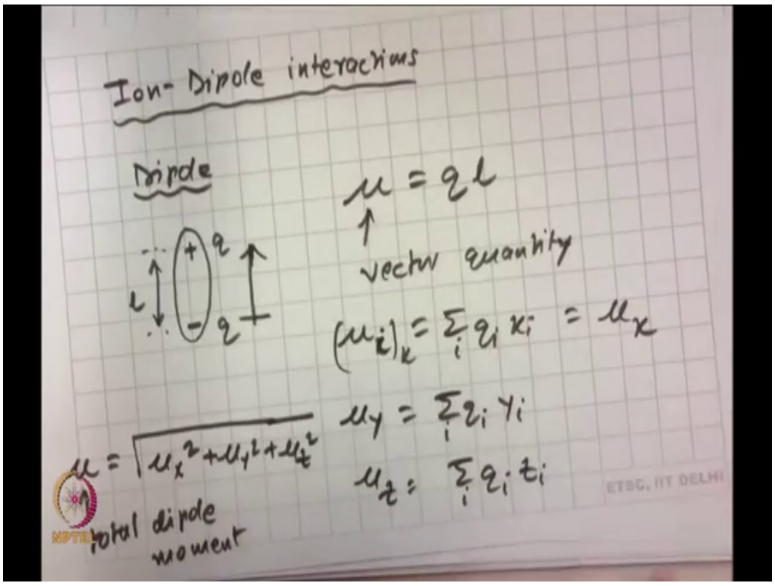

Ion- Dipole interactions

Dipole

$\mu = ql$

$\uparrow$ vector quantity

$(\mu_i)_x = \sum_i q_i x_i = \mu_x$

$\mu_y = \sum_i q_i y_i$

$\mu_z = \sum_i q_i z_i$

$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$

total dipole moment

Let us look try looking at something else, what we are now going to look at is ion dipole interactions.

So, as I said at the start of the class, we are essentially talking about charges. Now, we are talking about a charge under dipole, but before we actually try deriving expressions for these let us look at what a dipole means. So, suppose I have something like this, there is a positive charge, there is a negative charge right.

So, this is plus q this is minus q and say the length is l. So, this is a typical dipole right. So, dipole means as the two ends of the dipole, I have similar charges q minus q right similar, but separated by a distance what

Student: l

l right and then, because we have a dipole like this we are going to have something known as what?

Student: Dipole moment.

A dipole moment, very good. So, the dipole moment mu is equal to.

Student: q.

q times.

Student: l.

l right, its q times l, where q obvious is a charge and l is the length in between. Where do you consider the length from? It is between the central mass of the negative charge and the central mass of the positive charge.

So, that is essentially what your dipole is. See, I am not taking it to the extreme ends, I am taking it from the centre of mass right, the centre here and the centre here essentially, but remember dipole moment is a vector quantity right dipole moment is a vector quantity, always remember that, because it has direction. And where does the direction grow? How is the direction like?

Student: (Refer Time: 20:58).

Right, this is the direction nature of your dipole [FL] that is why it is a vector quantity. Vector is all about directions, it is not a scalar quantity. But think about this when you are talking about a protein or you are talking about any molecule as such a simpler molecule. You will not be having only one dipole, you will be having series of dipoles right, because we having series of bonds where there are atoms connected which have different electronegative negativities rather.

So, hence they would be giving rise to dipoles each and every bond. So, what I can write is say suppose; if I am writing the dipole moment in the x direction, I can write it is say, I can write say mu i in the x direction is sigma i q i xi ok. So, this is in the x direction. So, this is essentially equal to mu of x. What does it mean? So; that means, the total dipole moment the total dipole moment.

So, look at this mu of x in the x direction is equal to a summation of what? All the charges, i means the respective charges right or the respective you know these things, having the charge qi; having the charge qi and x is the what x coordinate of that and you are summing over what you are summing over all the possible interactions it can have; that means, you have one charge and you can interact with many other charges, it can have many other dipoles.

Say summing over all dipoles in the x direction, but when we are talking about a three dimensional system. We are not going to have only x right, we are going to have what y and z right. So, then what I can write is; what I can write is, I can write your total that is.

.

mu y would be equal to sigma i q i yi right and similarly, mu z would be sigma i q i zi. So, again x y and z are the coordinates respectively and that is those of the directions are looking at for your dipole moments so this is mu x mu y and mu z. If I have these; if I have these, what is your total dipole moment now?

The magnitude; so, I can write; so, I can write based on this mu is equal to root over mu x squared plus mu y squared plus mu z squared. This is your total dipole moment. This essentially it is square root of the sums of the squares of a dipole moments in the respective coordinates ok.

So, this is your total dipole moment clear. Now, having looked at the dipole now, think what will happen now.

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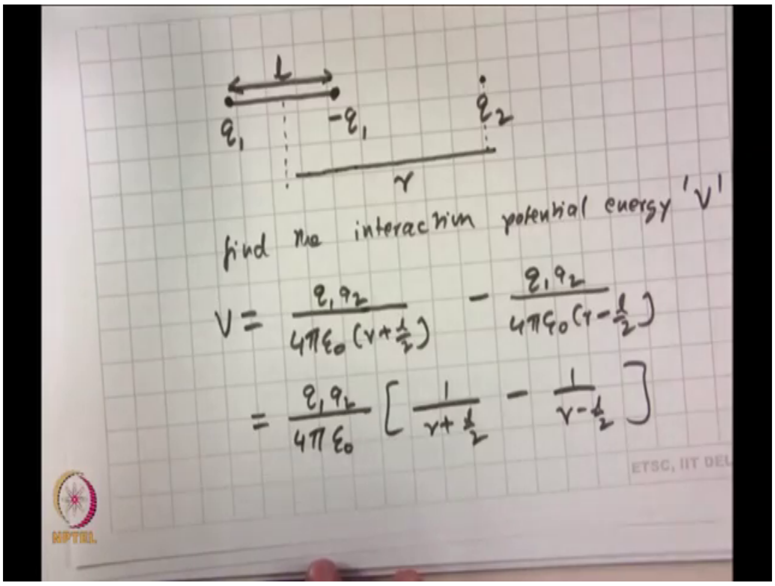

find the interaction potential energy 'V'

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 (r+\frac{l}{2})} - \frac{q_1 q_2}{4\pi\varepsilon_0 (r-\frac{l}{2})}$$

$$= \frac{q_1 q_2}{4\pi\varepsilon_0}\left[\frac{1}{r+\frac{l}{2}} - \frac{1}{r-\frac{l}{2}}\right]$$

Suppose, I have a system like this, I have a dipole which is like this right. So, this is my dipole this is my dipole, this is say minus charge q 1 and this is a positive side q 1 ok. The length of the dipole is l; that means, the distance of separation between the positively charge and the negative charge is l right.

Now, remember what are we talking about, we started with what the ion dipole interaction right. So, already have a dipole now, I need to have an ion or a charge. So, what I do is I put a charge, here this is a charge and see this charge is q 2.

Now, see they are on the same line right it is a collinear geometry. It is a essentially on the same line and then what it tell is, I give you this information this is the distance this is the distance between the center of the dipole and this charge which is a point charge is given by r ok.

Now, our idea is; our idea is find the interaction potential energy V. It is the same as u of r it is the interaction potential energy V. I am just changing it to V, because you know the dipole moment has that mu symbol and I just want to avoid you know symbolisms your confusion between the symbols, because V was very close to mu.

So, this is what I have to find ok. Now, how would we do that? You look at the system, your V is equal to right, this is the dipole now right. So, it has two charge dense this is a monopole essentially; that means, only one charge. How many Coulombic, how many Coulombic interactions would be having here? You would be having two Coulombic interactions right: one is essentially repulsive which is between this guy and this guy and the other one is what.

Student: Attractive.

Attractive which is this and this [FL]. So, let us look at that. So, I can write the first one is what based on Coulombs law. So, between q 1 and q 2 is say q 1 q 2 by 4 pi epsilon 0. I am not putting any other dielectric here. I am just taking the primitive in vacuum let us do that, because we are going to put in another dielectric system in a solvent then another d would come at the bottom right.

That is only difference we know. So, let us do it like this. Now, what is the distance between q 1 and q 2?

Student: r plus l by 2.

r plus l by 2, excellent. So, what I have is r plus l by 2. Now, whatever the next one?

Student: Minus.

So, this is you can see this is a positive one right, because it is a.

Student: Repulsive.

Repulsive potential, this one would be minus q 1 q 2 4 pi epsilon 0 then r.

Student: Minus l by 2.

Minus l by 2 clear. So, now, what I can write is, I can make a make a little more simple, I can write q 1 q 2 4 pi epsilon 0 then I can write this as 1 by r plus l by 2 minus 1 by r minus l by 2.

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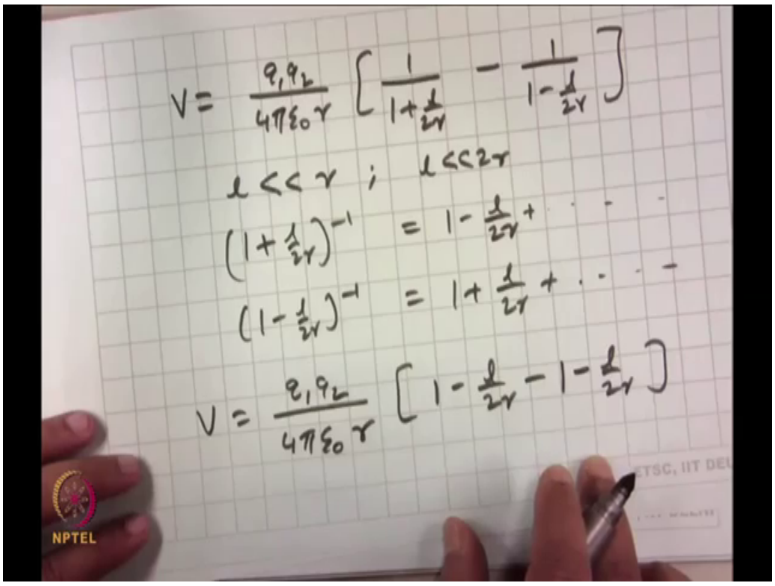

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}\left[\frac{1}{1+\frac{l}{2r}} - \frac{1}{1-\frac{l}{2r}}\right]$$

$$l << r \;;\quad l << 2r$$

$$\left(1+\frac{l}{2r}\right)^{-1} = 1 - \frac{l}{2r} + \cdots$$

$$\left(1-\frac{l}{2r}\right)^{-1} = 1 + \frac{l}{2r} + \cdots$$

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}\left[1 - \frac{l}{2r} - 1 - \frac{l}{2r}\right]$$

Now, once I have this, I will make another approximation now. What I will do is like this. So, I will say that then V is equal to q 1 q 2 by 4 pi epsilon 0 r, I will take an r common out of the brackets then I will write it as 1 by 1 plus l by 2 r minus 1 by 1 minus l by 2 r. Is everybody with this? Right, I just took an r common from the denominator that is what I did and. So, I realize why I did that?

If this was not present what is this? This essentially Coulombic potential between two charges right, but immediately you can see now, you have an extra term out here. So, you know that your interaction potential energy will not be a Coulombic potential energy, because your Coulombic potential energy is already out here and then you have this term.

So, it has it is bound to be different, but how different is it. Now, let us try to simplify this, based on the assumption; that means, I say that l, l which is the length of the dipole right, is or the separation of the dipolar ends of the is much less than r,

Student: r

which is the separation of the charge from the dipole which is the center of the dipole. And if I do that what will happen; if I do that what will happen? Then I can write. So, this 1 plus; that means, based on this I can write l is much less than 2 r.

So, 1 plus l by 2 r to the power minus 1 can be approximate as what?

Student: 1 plus 1 minus l.

1 minus

Student: l by 2.

l by 2 r plus the higher terms.

Student: (Refer Time: 29:39).

Plus the higher terms, but you know my l is much less than r. So, I neglect the higher terms. The same thing happens for 1 minus l by 2 r minus 1, what should this give me?

Student: 1 plus l.

1 plus l by 2 r plus you neglect the higher terms ok, you with me under that point?

So, now see how it simplifies. So, I have V is equal to q 1 q 2 by 4 pi epsilon 0 r, then what is the first term coming to be 1 minus

Student: l by.

l by 2 r. What is the next term to be?

Student: Minus l by 2r.

1, then I can also again write l by 2 r right [FL]. Is everybody following that? So, it is essentially 1 plus l by 2 r, but I have just remove the brackets and I have just done it 1 minus l by 2 r and what should this give me?

Student: (Refer Time: 30:34).

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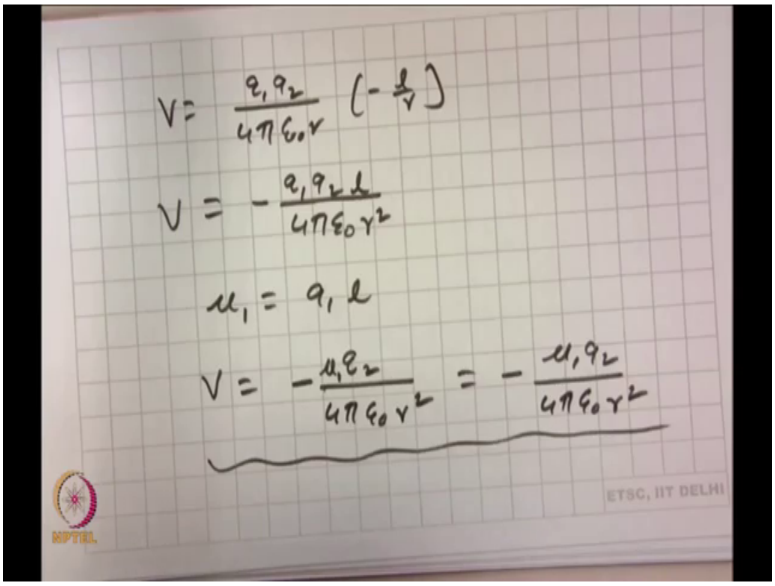

$$V = \frac{q_1 q_2}{4\pi \varepsilon_0 r}\left(-\frac{l}{r}\right)$$

$$V = -\frac{q_1 q_2 l}{4\pi \varepsilon_0 r^2}$$

$$\mu_1 = q_1 l$$

$$V = -\frac{\mu_1 q_2}{4\pi \varepsilon_0 r^2} = -\frac{\mu_1 q_2}{4\pi \varepsilon_0 r^2}$$

So, what should give me exactly so; that means, V is equal to q 1 q 2 by 4 pi epsilon 0 r the 1 cancels right.

Student: (Refer Time: 30:46).

The 1cancels and we are left with minus 2 1 over 2 r. So, essentially.

Student: Minus (Refer Time: 30:51).

l by r alright minus l by r. So, I have out here is minus l by r which now comes to be q 1 q 2 l over 4 pi epsilon 0 r squared with a negative sign with a negative sign.

Now, one thing you have seen, which is very evident, it is no longer 1 by r

Student: Yes.

It is how; it is 1 by r squared. So, this one the interaction potential dies off more rapidly than 1 by r. So, 1 by r remember, we talked about shortrange long range interactions r to the power minus rho right. So, 1 by r is essentially a long range interaction. When you go to 1 by r squared it dies off more rapidly; that means, you are going to

Student: Shorter range.

Shorter range.

So, think how short the ranges are for your London dispersion forces r to the power 6 and r to the power 12. Now, that is one. Can you tell me how you know how we can simplify it further? There is one substitution we can make, tell me quick? You have this right, what is mu 1 equal to?

Student: q 1 into l.

q 1 into l right, that is what the definition of dipole moment was. So, then V becomes equal to what minus.

Student: q 1 .

q 2 right, then mu 1 over 4 pi epsilon 0 r squared. So, let me write in a better form minus q 1 q 2 over 4 pi epsilon 0 r squared. So, these are the difference, 1 was the r squared. Now, before when we are talking about the Coulombic interaction, we talked about only q 1 and q 2 respective charges. You never talked about dipole moment right, because it was a monopole. It was just a single charge, but now you have a dipole moment coming in, because if a dipole moment coming in, we cannot just talk about one charge. A dipole has what, how many?

Student: 2 charges.

2 charges. So, you are having interactions from both. So, we in that case replace it by what the dipole moment of the respective dipole and that is how your interaction energy changes, clear. So, if you now go back to the original you know lineage collinear geometry we said. Now, think about this q 2 right is positive, q 1 is negative.

So, q 2 is here, if q 2 had been negative where would have would it have gone? It would have gone to the other side

Student: No sir.

Or if q 1 had been here or if q 2 had been negative then this V would have actually been.

Student: Positive.

Positive.

Student: Positive.

So, that is you know you have to keep in mind, good. Now, let us take a very general case, the general case is see, I am not always going to have a linear geometry; that means, I am not going to always going to have a dipole and then a charge sitting on the same line.

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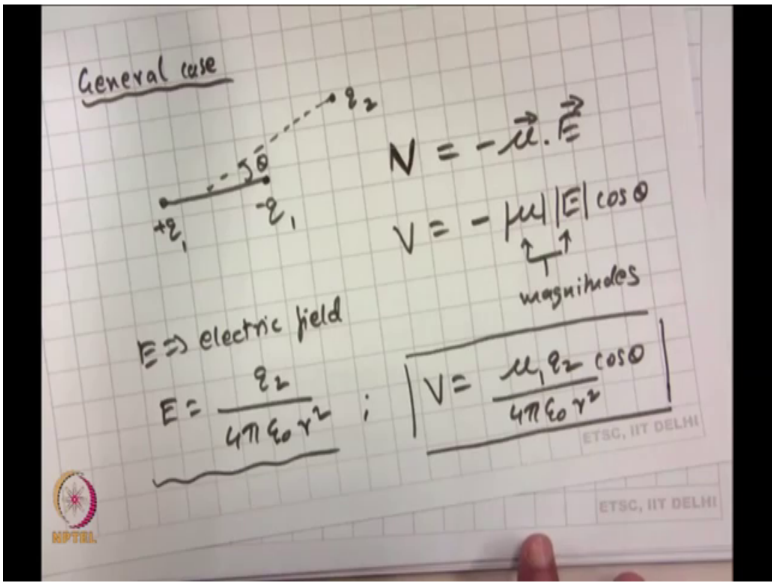

General case

$V = -\vec{\mu}\cdot\vec{E}$

$V = -|\mu||E|\cos\theta$

magnitudes

$E \Rightarrow$ electric field

$E = \dfrac{q_2}{4\pi\varepsilon_0 r^2}$; $\boxed{V = \dfrac{\mu_1 q_2 \cos\theta}{4\pi\varepsilon_0 r^2}}$

Instead, what I am going to have is a more general case let us look at a more general case. What I am going to have is a dipole like this, a dipole like this.

Say this is plus q minus q and I can have a charge out here. So, this is q 1 q 1 and I can have a charge out here which is q 2 which is actually at a certain angle theta with a dipole. So, this is the most general case why? Because if there is if this q 2 comes here; that means, collinear then theta is equal to what 0 right, because it is a special case of this one, there is no angle between these two ok.

If this is the case then what you know people have shown or what is known is, the electric field the electric field or the electric you know the interaction potential energy, I can write as say ok. I can write as V V is equal to minus mu dot E, it is minus mu dot E.

Remember, these are vector quantities, if you look at your books what you would see is these are in bold letters, because it is a vector quantities. These are not scalar quantities. Now, this is sorry this is V actually just keep that in mind. Now, if it is the dot product if it is the dot product then I can write V to be equal to what minus.

Student: Minus mu E. (Refer Time: 35:50).

Ok Mu E cosine of theta. See if the angular dependence coming in now, but remember when we go from this dot product to the scalar product essentially. What are these quantities? Do you know what these quantities are they are? they are referred to like these. These are referred to as these are scalar products. These are referred to as absolute magnitudes of the respective vectoral forms ok.

So, these are your magnitudes these are magnitudes right. So, essentially the magnitude of a dipole is ql that is what it is, what you know. What you do not know is this E is the electric field E is the electric field and this electric field and this electric field which is given out by q 2 essentially the charge and this electric field can be written as q 2 by 4 pi epsilon 0 r squared ok.

Now, this can be derived, we will not derive this. So, the electric field can be written as from the charge as q 2 by 4 pi epsilon 0 r square. Guys, this is not a potential, you are looking at a field. Now, it is a electric field the potential is defined as mu dot E this is the electric field. So, if you have this is what E is now look at the most general form, then your V should be equal to mu right and now I am talking about the magnitudes. I am taking out this absolute for you know symbolism mu dot E cosine of theta.

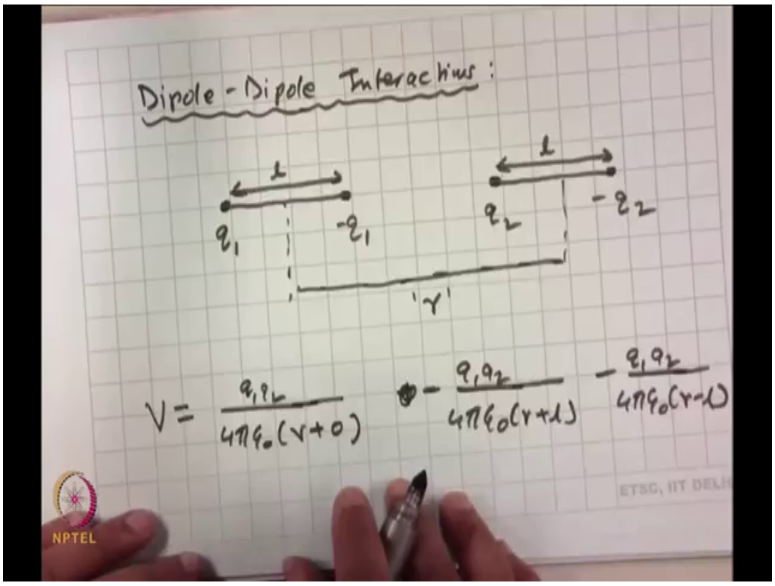
So; that means, mu q 2 by 4 pi epsilon 0 r squared cosine of theta and I am putting in mu 1 out here. So, this expression please remember, this expression is the most general form of the expression, when you have your charge at any given angle with the dipole right and you can easily realize the similarity between this one and that one ok. I can also put a negative sign out here. I forgot actually the negative sign, because that is how it was defined anyway the charge will take care of that essentially.

So, now if you look at these two; if you look at these two so, this is what we derived for a collinear geometry right and this is what we are now deriving for any general angle, theta can be anything. So, under what conditions will this one reduce to this if theta is equal to 0 cosine of theta would be?

Student: 1.

Cosine of 0 would be 1 and hence, this would go to this and that is what we actually had started with, good. Now let me see how much time we have ok. I will just start this, then we will you know go on with this in the next class.

(Refer Slide Time: 38:59)



Dipole - Dipole Interactions :

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 (r+0)} - \frac{q_1 q_2}{4\pi\epsilon_0 (r+l)} - \frac{q_1 q_2}{4\pi\epsilon_0 (r-l)}$$

What I will do now is, I will change from ion dipole and I will go to Dipole Dipole Interactions. See, if you know if you understand what you are trying to do, we you know trying to slowly go up step by step; that means, the first step was the Coulombic point charges the next is a point charge and a dipole, but now we have done that we go to a.

Student:(Refer Time: 39:31).

Dipole dipole now right and later we will come to molecules where essentially you do not have any well developed dipoles. You give rise to instantaneous dipoles and that is what your Van der Waals interaction is all about, but these are all about where molecules already have a dipole built in [FL].

So, now again let us take a very general case so; that means, I have two dipoles like this. So, this is keep this on the same line. Let us make the geometry to be collinear ok. Let this be no q 1 minus q 1 q 2 minus q 2, well let this length be l, let the length of this dipole also be l keeping things simple and let the distance, let the distance between the dipoles from the middle of the two dipoles be r.

Just like we described before, the difference being in the previous case we had only q 2; that means, q 2 this minus q 2 plus q that merged on the same point, because it was charge.

Now, we have separated them giving rise to dipole ok. Now, this you have to tell me, if I am going to write V, if I am going to write V which is the interaction energy or the interaction potential, how many terms I am going to get?

Student: 4.

We are going to get 4 terms, is everybody clear about that? Why? You look at one charge is q 1 q 2, this positive end q 1 minus q 2 2 right then minus q 1 q 2 then minus q 1 minus q 2 2; that means, total of 4.

So, you can see what has happened? When you are in a Coulombic interaction you had only one potential one. Hence, here 1 by r when you are going to ion dipole yet to. So, actually you went to 1 by r square you see how it is slowly falling in place right and the reason is now physically can you reason out why it is decaying so rapidly from a Coulombic to ion dipole interaction where it was 1 by r and 1 by r square. It is simple, it was only out charge out there right, but here when you going to ion dipole one charge is experiencing actually what two charges now.

Student: Two charges.

So, they are scrambling it much more rapidly now when you go to 4 like this 4 interactions you will be having a essentially much higher you know interactions in terms of Coulombic interactions with each and everything; that means, try to think about this if I look at this charge q 2 essentially, how many interactions would I be having with? Minus q 2 1 minus q 1 and then 1 3. So, I might expect that would be 1 by r cubed.

Let us see we look at that. So, then I can write what I can write is I can write V is equal to say, if I take this 1 and this 1, I can write q 1 by q 2 4 pi epsilon 0. Now, what should I write the distance in q 1 and q 2?

Student: (Refer Time: 43:03).

Ha.

Student: (Refer Time: 43:06) r plus l by 2; r plus.

R plus l by 2 are you sure.

Student: r,r(Refer Time: 43:10).

It should not be r plus l?

Student: Yes. r plus l by 2 .

Are you sure? Check, I will I am keeping it for you ok. Tell me, I will come back, tell me what about between minus q 1 ok, what about between say let us take this minus what about between q 1 and minus q 2? I can write q 1 q 2 by 4 pi epsilon 0. What is q 1 and q 2?

Student: r plus l.

r plus l, thank you. So, this essentially is?

Student: 0.

r plus 0, this essentially r right. So, this is r plus l [FL] ok. Now, what about this one and this one? Minus q 1 q 2 you have another 1 right. So, I did q 1 minus q 2 this is attractive right now, I am doing minus q 1 q 2 minus q 1 q 2 over 4 right 4 pi epsilon 0 r minus l, because we get this right.

Now, we are looking at minus q 1 q 2, this halves are l by 2 right. You take that out, you get essentially r minus l. We still have one more term, what is that?

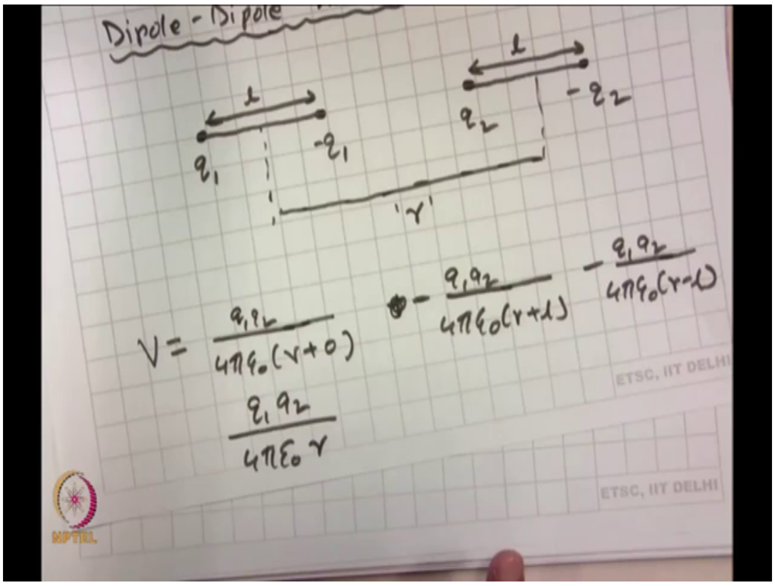
Student: (Refer Time: 44:16).

Ha.

Student: Plus (Refer Time: 44:19).

Plus, because see we did q 1 q 2, but we have not done minus q 1 minus q 2 right.

(Refer Slide Time: 44:27)



$$V = \frac{q_1 q_2}{4\pi\epsilon_0 (r+0)} - \frac{q_1 q_2}{4\pi\epsilon_0 (r+l)} - \frac{q_1 q_2}{4\pi\epsilon_0 (r-l)}$$

$$\frac{q_1 q_2}{4\pi\epsilon_0 r}$$

so, that that will again give q 1 q 2 by 4 pi epsilon 0 then.

Student: r.

r. Is everybody with how it was built? So, you can see it is a potential which has 4 terms.

Student: So, I think two terms more can be added I think (Refer Time: 44:45). q 2 will be interacting with q 2.

Between.

Student: q 2 q 2 interaction to and q 1 interactions are (Refer Time: 44:52) repulsive interactions (Refer Time: 44:54).

It is the dipole.

Student: Dipole (Refer Time: 44:57).

Which one are you talking about?

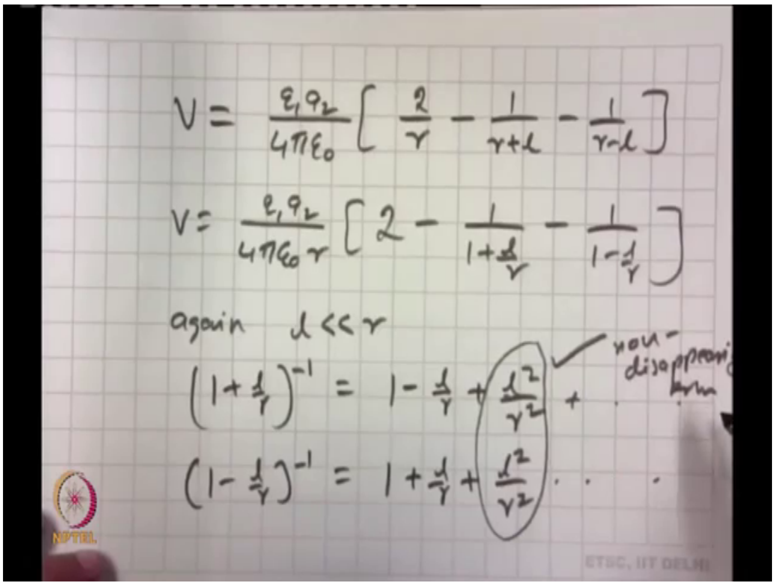
Student: v 1 has the charges are they are q 1 and q 1 2 charges, are there they are (Refer Time: 45:02) attracting with each other.

No, your dipole moment is taking care of that right that is mu is equal to q times l that charge interaction always be there, but if you are; if you are talking about that interaction then your dipole will never separate right. It will always be there and that is what a dipole moment is taking care of right. It is mu is equal to q times l that is what a dipole moment is coming in, that is what will coming in.

Student: (Refer Time: 45:26).

So, that interaction is already taken care of by the dipole moment that is what I am trying to tell you that is why you have this one. Let me go to the final derivation, if I can and then you will see how it comes through.

(Refer Slide Time: 45:43)



$$V = \frac{q_1 q_2}{4\pi\varepsilon_0}\left[\frac{2}{r} - \frac{1}{r+l} - \frac{1}{r-l}\right]$$

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}\left[2 - \frac{1}{1+\frac{l}{r}} - \frac{1}{1-\frac{l}{r}}\right]$$

again $l << r$

$$\left(1+\frac{l}{r}\right)^{-1} = 1 - \frac{l}{r} + \boxed{\frac{l^2}{r^2}} + \ldots$$

$$\left(1-\frac{l}{r}\right)^{-1} = 1 + \frac{l}{r} + \boxed{\frac{l^2}{r^2}} \ldots$$

non- disappeari term

So, then I can simplify it by writing V is equal to q 1 q 2 by 4 pi epsilon 0. I can take that as common, then I can write essentially what will I be having? I will be having something which is I will be having 2 by r right. I will be having 2 by r then I will be having minus 1 by

Student: r plus.

r plus l and then we are having minus.

Student: 1 minus.

1 minus 1 by r minus?

Student: l.

l, right. I do not think I am missing anything right, ok. So, then I do one more simplification. I say 4 pi epsilon 0, I take r out again and what I do is I get 2 then minus 1 by 1 plus l by r right minus 1 by 1 minus l by r right.

Now, again we take the assumption, l is much less than r, but guys here is one small problem. The problem is if I am going to do 1 plus l by r minus 1, what am I going to get? I am going to get 1 minus l by r plus l square by r square and so on right, negative positive alternating.

If I do 1 minus l by r minus 1, what am I going to get? I am going to get 1 plus l by r plus l square by r square dot dot dot tell me why am I keeping the third term too.

Student: (Refer Time: 47:22) r terms will be cancel out.

The l by r terms actually will cancel out. If my l by r terms cancel out, we have to keep those terms until that term which is a non disappearing, because if my l by r term cancels out then we have nothing. We essentially boiled down to a Coulombic interaction which is not true. So, this term is the first non disappearing term.

So, as we are seeing out here that a 1 plus l by r minus 1 right. It gives you 1 minus l by r plus l square by r square and as we were discussing you know last time when we did it between a charge and a dipole we did not go to this third term right. We just stopped at the second term which is l by r.

But here as you will see as we just wrote, it is a non disappearing term of the respective expansion. We need it right, because you will see that l by r and l by r these would actually cancel out right and hence, we will need this term. So, writing you know this one again.

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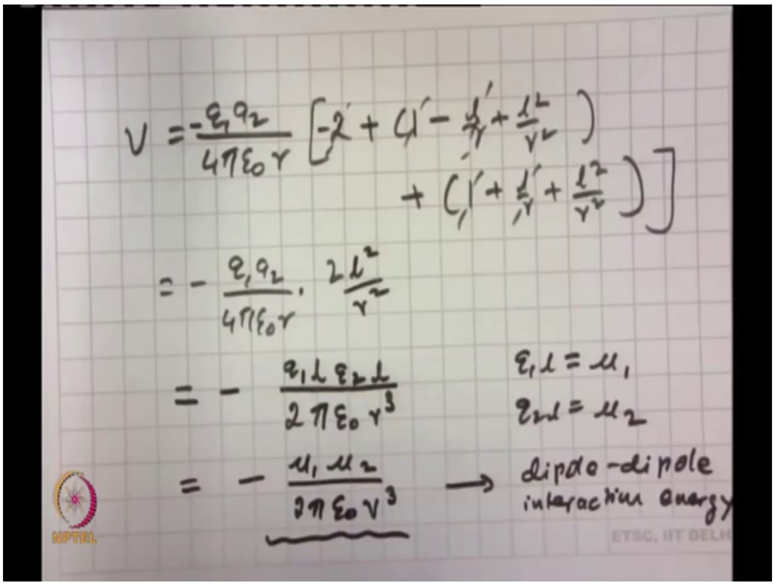

$$V = -\frac{q_1 q_2}{4\pi\varepsilon_0 r}\Big[-\cancel{2} + \big(\cancel{1} - \cancel{\tfrac{l}{r}} + \tfrac{l^2}{r^2}\big) + \big(\cancel{1} + \cancel{\tfrac{l}{r}} + \tfrac{l^2}{r^2}\big)\Big]$$

$$= -\frac{q_1 q_2}{4\pi\varepsilon_0 r} \cdot \frac{2l^2}{r^2}$$

$$= -\frac{q_1 l\, q_2 l}{2\pi\varepsilon_0 r^3}$$

$q_1 l = \mu_1$

$q_2 l = \mu_2$

$$= \underline{-\frac{\mu_1 \mu_2}{2\pi\varepsilon_0 r^3}} \longrightarrow$$ dipole-dipole interaction energy

What I can do is I can do V is equal to minus q 1 q 2 4 pi epsilon 0 r. I have taken a negative sign out right and hence, accordingly sign conventions or signs would change inside the brackets. This 2 becomes minus 2. It was positive before and term becomes negative and everything else is taken care of.

So, here you can see if I have 1 minus l by r plus l square over r square and 1 plus l by r plus l squared over r square. I do that respective thing what happens is l by r l by r, they cancel out right and we are left with l square by r square l square by r square, because 2 also cancels out with 1 and 1. So, what you are left with is V is equal to minus q 1 q 2 by 4 pi epsilon 0 r right times. What is the other term we should be having here.

Student: (Refer Time: 49:25).

2.

Student: l squared.

l squared over.

Student: r square.

r squared right. Now, if I am having 2 l square over r square just think about this, how can I simplify it further?

Student: (Refer Time: 49:42).

Alright, I can simplify it further by taking this. I can say it is minus q 1 right, then I can take l out here. I can also write q 2 l out here, because we started with l, the length of the dipoles were the same right. Then this r squared right I have pi epsilon 0 r cubed. This 2 what will happen, it will cancel out with 4 right and we left with a term here.

So, essentially what I can write is. So, essentially what I can write is minus. So, q 1 l can be written as.

Student: Mu 1.

Mu 1 q 2 l can be written as.

Student: Mu 2.

Mu 2 and hence, we have mu 1 mu 2 by.

Student: 2 Pi epsilon 0.

Pi epsilon 0 r cubed ok. So, this is the final form of interaction between here. What interaction we looking at? Two dipoles. So, you think about the corresponding expression for a charge and a dipole. So, here you can see you have two dipoles mu 1 and mu 2 that is two dipole moments, when you had a charge and a dipole 1, what did you have you had mu 1 times q and then there was a cosine theta term which came from the angular orientation.

But see, it is very you know easy to understand you start going from a Coulombs law q one q 2 2 charges you go to an ion and dipole. So, dipole will be having a dipole moment mu 1, you have an ion charge q and then you go to two dipoles where you have the two dipole moments mu 1 mu 2, what is happening though is, you can see here it becomes now r cubed for ion and dipole it was.

Student: r .

r squared and for Coulomb there is two charges or two ions it was.

R right.

Student: r (Refer Time: 51:38).

So, that is how your interaction is changing. I mean that is essentially how your interaction is dying down. So, this is your short range decay; that means, you start short range force. You started from a longer range force which was Coulomb 1 by r then you moved to 1 by r square then you moved to 1 by r cubed ok. So, this is again your dipole dipole interaction energy so, dipole dipole interaction energy right.

Now, one thing you have to keep in mind is, in the same way we did for an ion dipole we brought in a cosine of theta term, why? Because; obviously, we never know that the ion can be at a specific angle with respect to the dipole right. So, in this case too we will be having a theta term which we will look at in the next class ok.

Thank you.