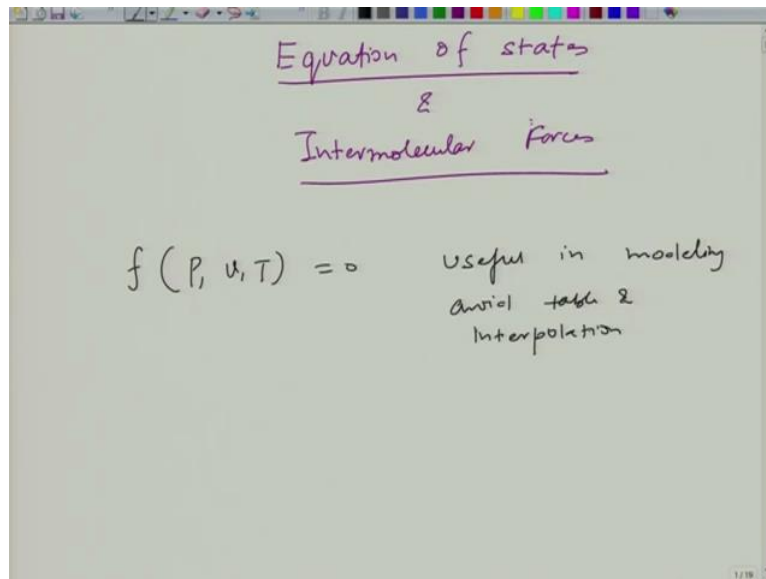


**Chemical Engineering Thermodynamics**  
**Professor Jayant K. Singh**  
**Department of Chemical Engineering**  
**Indian Institute of Technology Kanpur**  
**Lecture 30**  
**Equation of State**

Welcome back, in today's lecture we are going to start a new topic, it's on equation of state or in general intermolecular forces and the type of models we often use in expanding the thermodynamic behavior.

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So, when it comes to equation of state, it simply means relating the pressure, volume and temperature in some empirical fashion. So, we can write something like this, so essentially a function which relates these variables is nothing but equation of state. It is useful in modeling, okay. So useful in modeling let us say vapor liquid equilibria, liquid-liquid equilibria, so this becomes a very valuable set of equations sometimes.

The other thing which it can do is, it can also avoid writing properties and tables, okay. And interpolations we often use in case we are using tables, so it can avoid that. So, thus equation of state becomes very useful.

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$f(P, u, T) = 0$  useful in modeling  
and table 2  
interpolation

$P = f(T, V)$

IG:  $P = \frac{RT}{v}$

- derived from kinetic theory of gas

- no intermolecular forces except when they collide with the wall of container

$$f(P, V, T) = 0; P = f(T, V) \text{ Ideal gas: } P = \frac{RT}{V}$$

And one of the important assumptions of ideal gas is that it does not occupy any volume, it does not have any specific volume and that means the particles can pass through each other, okay without filling each other. So, it has no intermolecular forces, okay. Except when they collide with the container of the wall. So, walls of the container.

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- molecules no vol. trans, rot, vib

$u = K.E + \frac{P}{v} = f(T)$

velocity

-> directly to T via Maxwell-Boltzmann Statistics

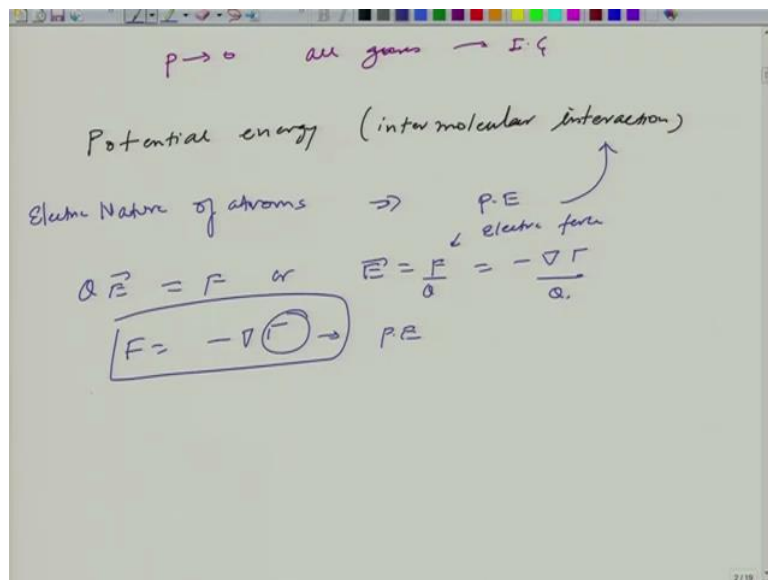
$p \rightarrow 0$  all gases -> I.G.

So in another word it has velocity, so essentially in the case of the ideal gas the molecules have 0 volume or no volume, okay. And it has no intermolecular forces and the energy, the internal energy is nothing but the kinetic energy, okay. Typically, internal energy will be kinetic energy plus potential energy. Since potential energy is 0, so is kinetic energy and thus you have only function of temperature. So this kinetic energy velocity is directly related to temperature from using this one Maxwell's Boltzmann statistic one can show that, so they are directly related to temperature via Maxwell Boltzmann statistic, okay.

So from this definition it is very clear that there is no intermolecular forces, so essentially the pressure is directly related to the overall volume of the container and hence one can also show that when pressure goes to 0, okay all gases tends towards ideal gas, okay. One can derive this expression using statistical mechanism as well but we will not go into those directions, okay.

So kinetic energy in this case gets contributions from the translation, rotational vibration of the molecules, okay. Whereas potential energy is nothing but relative position of the atom in the space but in the case of ideal gas of course there is no meaning because it doesn't have any attractions but now let us look at the potential energy.

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So potential energy or the intermolecular forces or interaction how does it arise? So most of the atoms in general have this nature where you have this positive nucleus and essentially the electrons are negatively charged around it, so the nature of atoms is electrical, there is an electrical measure of atoms and this results to potential energy or in general this results to the intermolecular interactions.

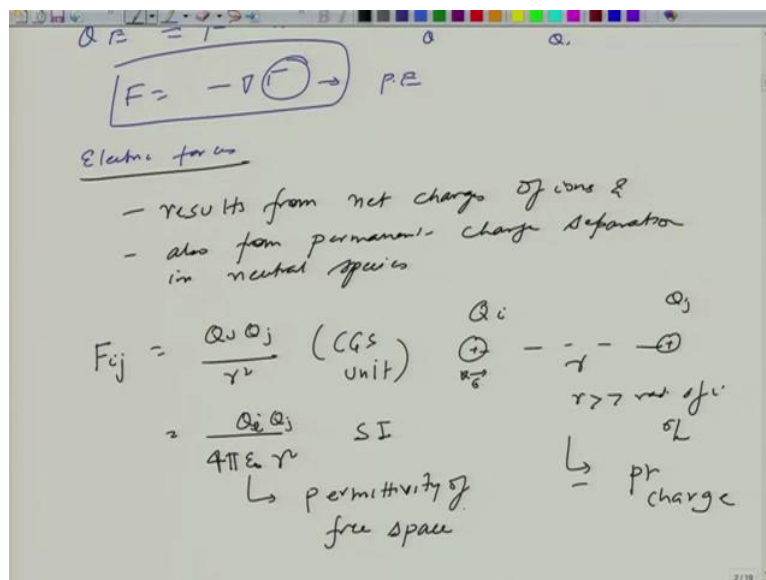
So, when they are close by it adds to those kind of interactions. So often you can apply for such electrical nature the concept of electric field.

$$Q\vec{E} = F \text{ or } \vec{E} = \frac{F}{Q} = -\frac{\nabla\Gamma}{Q}$$

$$F = -\nabla\Gamma$$

So essentially F is minus gradient of gamma, gamma is our potential energy, okay. So this is the kind of force which we can now try to derive it. This kind of expression or this kind of electrical force this results from the net charge of the ions and permanent charge separation in a neutral species. So you can consider net charges, there are very few examples of specific point charges systems but we will take that in order to illustrate this intermolecular forces.

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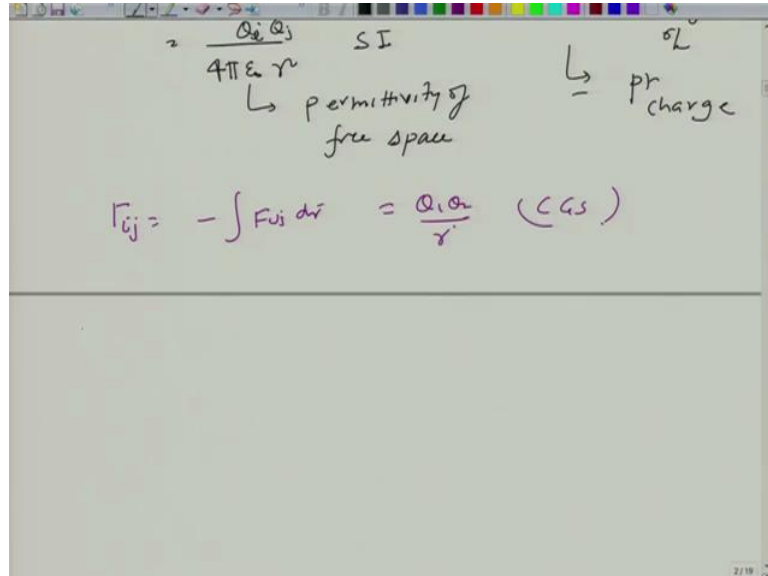


So, as I was saying that electrical forces results from net charges of ions. And also from permanent charge separation in neutral spaces, okay. So let us consider an example here. So let us consider this as positive charge ion with  $Q$  of  $i$  and this is again let's say a positive charge ion with  $Q$  and  $j$ , okay. And here this distance between the ions are, if the size of this let us say  $\sigma$  if  $r$  is much-much greater than the radius of the ion, radius of  $i$  which is in this case could be  $\sigma$  by 2, let us say then we can say that this is point charge, okay.

$$F_{ij} = \frac{Q_i Q_j}{r^2} \text{ (CGS unit)} = \frac{Q_i Q_j}{4\pi\epsilon_0 r^2} \text{ (SI unit)}$$

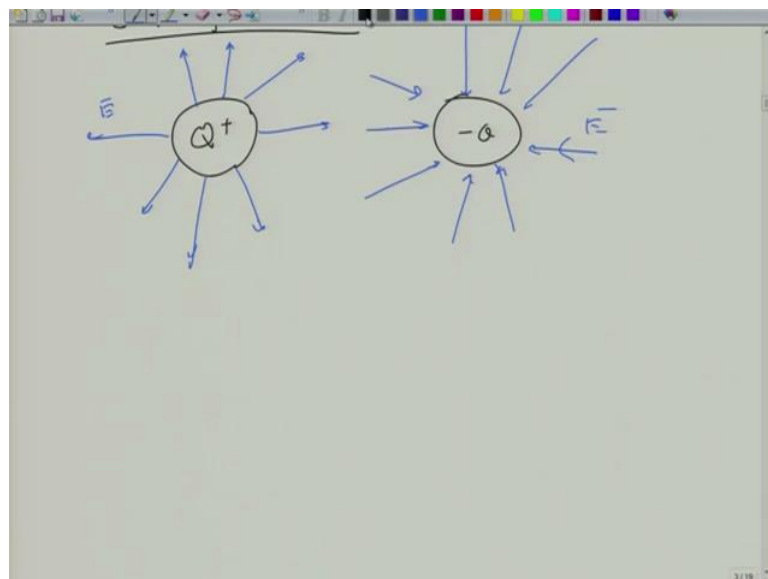
$$\Gamma_{ij} = - \int F_{ij} d\vec{r} = \frac{Q_1 Q_2}{r} (CGS)$$

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Now one can find out the potential energy by taking the minus integral of  $j dr$  this is  $Q_1 Q_2$  by  $r$  again in a CGS unit, okay. So this is by simple for the case of this point charges. Now as I said the effect here is due to the kind of electrical nature because of that you have this kind of forces and a potential energy, so that means that these charges would emanate or would have an electrical field around themselves.

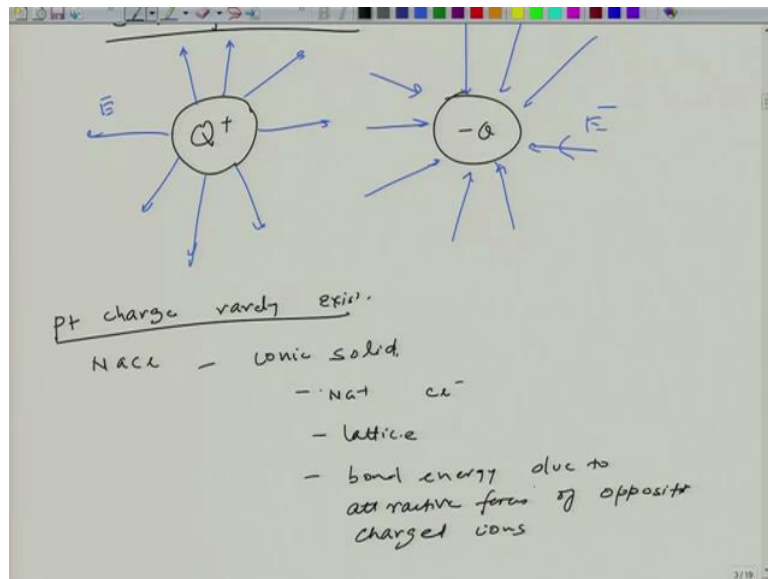
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One can also draw schematically the kind of electrical field lines for such kind of point charges, so this is your positive  $Q$  and for the case of the positive charge the electric lines will originate from this, okay. So this is your  $E$  for the case of a negative charge minus  $Q$  the electric line will be towards itself, so this is how the electric line would be, okay.

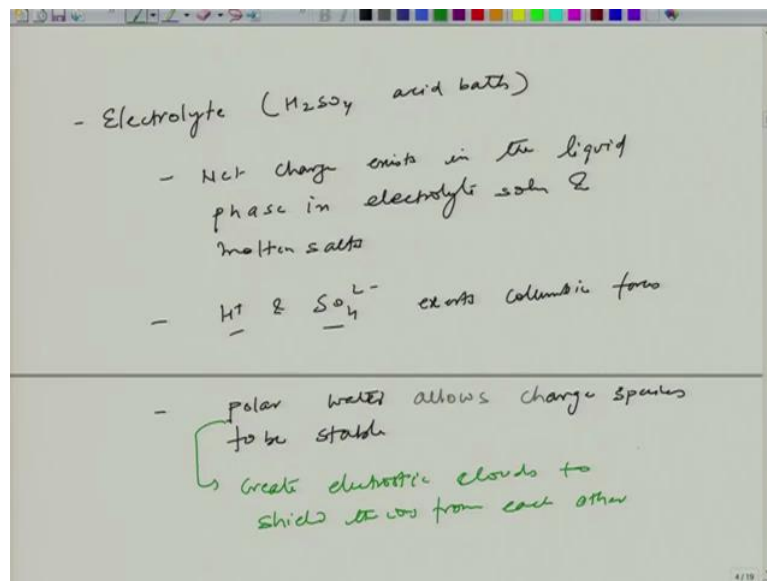
Now as I said the point charges are rare but there are of course examples.

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So molecule example would be your NaCl, okay. So NaCl is nothing but ionic solid and it is made up of positive and negative charge ions within a crystal lattice. So it's made of Na plus and Cl minus they are on the lattice, okay and thus creating a solid structure where these ions are placed. Overall the system is neutral but this consists of Na plus and Cl minus and because of this positive and negative charge there is a strong bond energy due to attractive forces of oppositely charged particles or charged ions in this case, okay.

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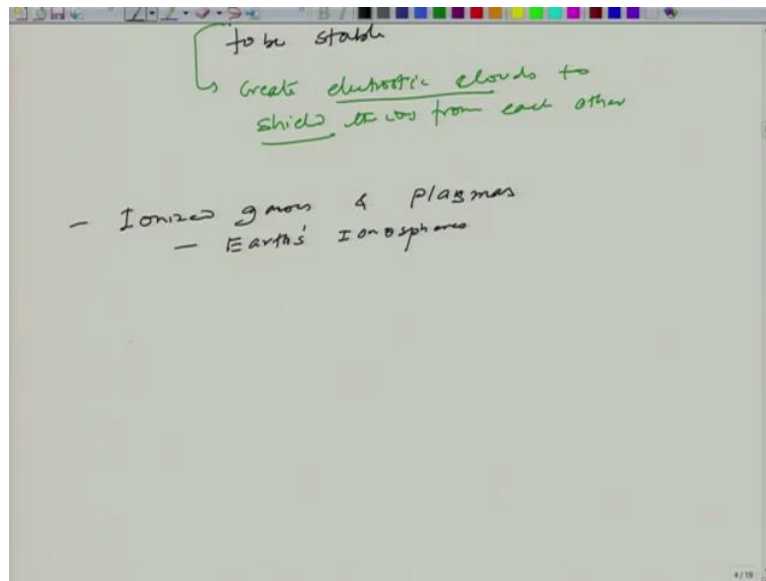


So in addition to this you will have ions floating around in kind of a liquid solution that is called sometimes electrolyte, okay. So here the example could be let us say  $H_2SO_4$  acid bath, okay. So here is a net charge exist in the liquid phase in electrolyte solution and molten salt. So in particular case of  $H_2SO_4$  you will have H plus and  $SO_4^{2-}$  will exert coulombic forces, okay.

Now it is in the water and hence the polar water will try to screen, will try to screen the electrostatic cloud or let me first write down here, the polar water will allow this ions to be stable, okay. So because of the nature of the polar, the polar structure the water, okay. So the nature of the water is that it will try to form an electrostatic cloud that shields the ions from one another.

So what it does, it creates electrostatic cloud to shield the ions from each other and thus creates stability of this ions in the solution phase, okay. So this is a typical electrolyte solution where the screening effect is dominant and that is why even though it is a strong ion but since the solution itself contains solvent which is a polar in nature which helps the system to become stabilized by this mechanism of electrostatic cloud screening effects or shielding effect, okay.

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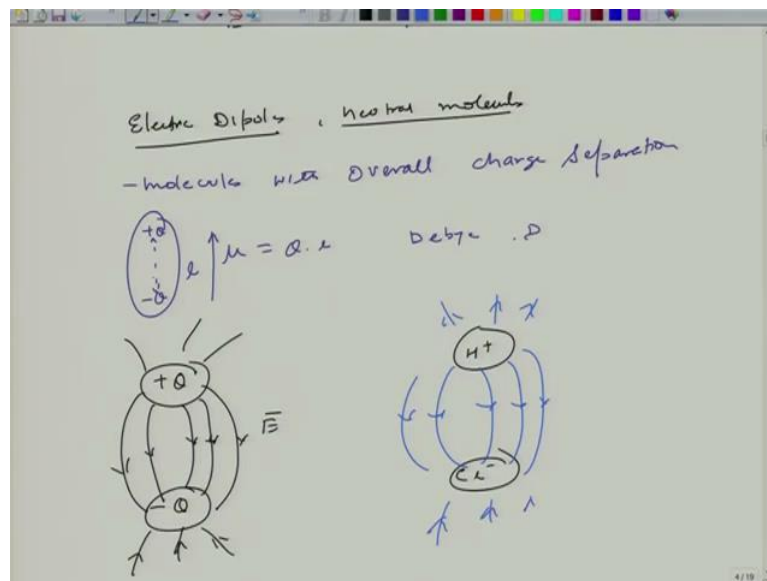


In addition to this electrolyte you will have other kind of system such as Ionized gas and plasma, okay. So this you might find it in Earth's ionosphere but in addition plasmas are also used in the etching and as well as deposition of thin films in integrated circuit manufacturing, okay. So this is a typical ionised form the system but most of the cases when we are going to deal with molecules they will be neutral in nature.

And even though they are neutral in nature they will impart electrostatic interactions, they will have dipoles may not be a permanent dipole could be an instantaneous dipole and something which will lead to this intermolecular interactions and this is something which now we are going to discuss a bit to provide little bit of clarity of different types of interactions which we have in such kind of molecules.



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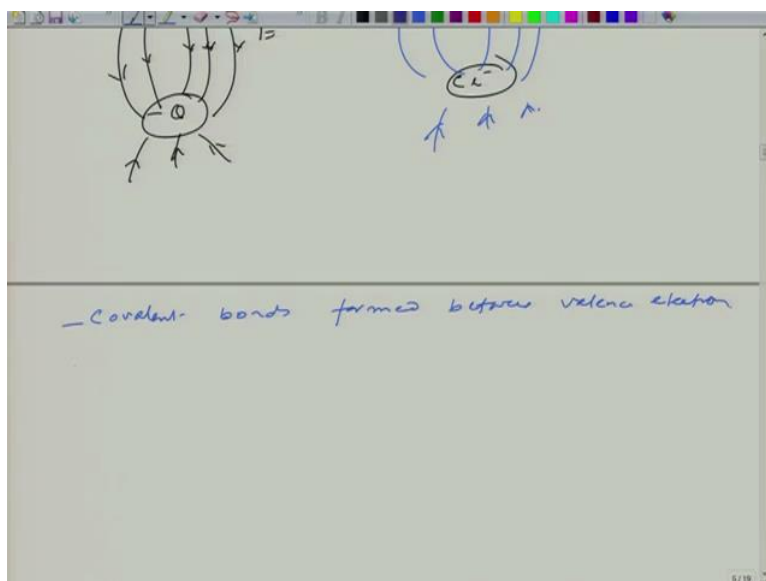
So there could be an electrical dipole, okay. Even though for neutral molecules, okay. For example water even there is neutral it does have a dipole moment. So how do you define that? Essentially you have molecules with overall charge separation, okay. So it's neutral but it is charge separation, so let us say if this is molecule here, so this is minus Q and this is plus Q, so it is neutral but the charges are separated over its volume and the distance here could be l, okay.

$$\mu = Q \cdot l$$

The unit of this is Debye, okay. So if you look at the electric field this will also have electric field but now it can be shown that I can draw this as, something like this. Let's say I can draw it here plus Q separate minus Q separated here and this will have something like this electric field around itself, okay.

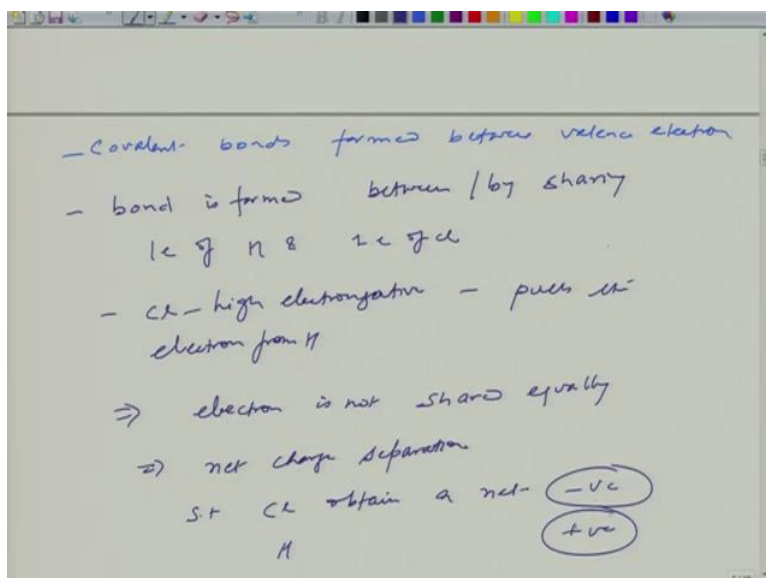
So this will be the electric field, okay. For such neutral molecule where the charges are separated, let us take an example of HCl which is strong electro-negatively charge which is like acid and in this case you have the cl which is electronegative, okay. So in this case I can write something like this H plus and cl minus, right? So you will have in the similar sense this kind of electrical field, okay.

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Now for the case of HCl there would be covalent bond which are formed between the valence electron, okay. And this is because of the fact that chlorine gains electron density at the expense of H because chlorine is more electronegative, okay. So it pulls the electron from the hydrogen, okay.

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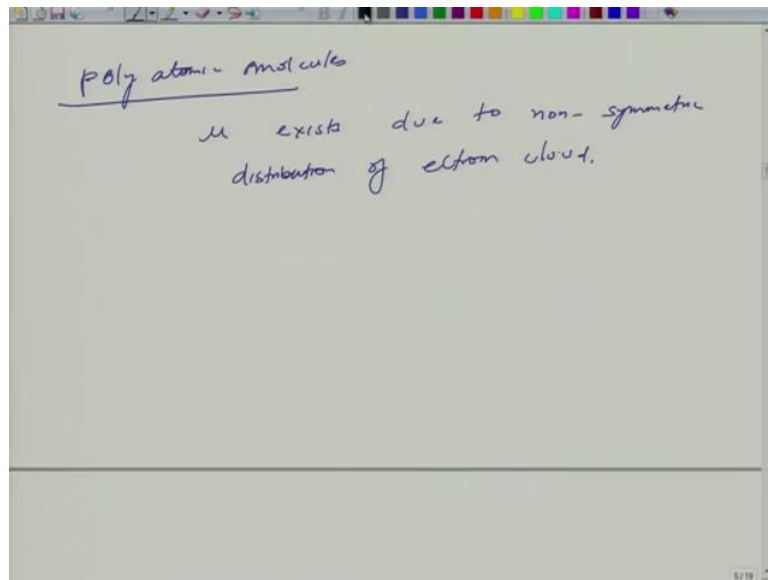


So covalent bond is formed between the valence electron and this happens because of the bond formation between one electron of hydrogen and one electron of chlorine. So that means the bond is formed by sharing, so it is not just between by sharing, okay. One electron of H and one electron of chlorine, okay. So as I said the chlorine is high electronegative, okay. So it pulls the electron from H, okay. So which clearly means that even if it pulls, okay which means that

essentially what happens that electron is not shared equally which means electron is not shared equally and thus it can create a kind of net charge separation, okay.

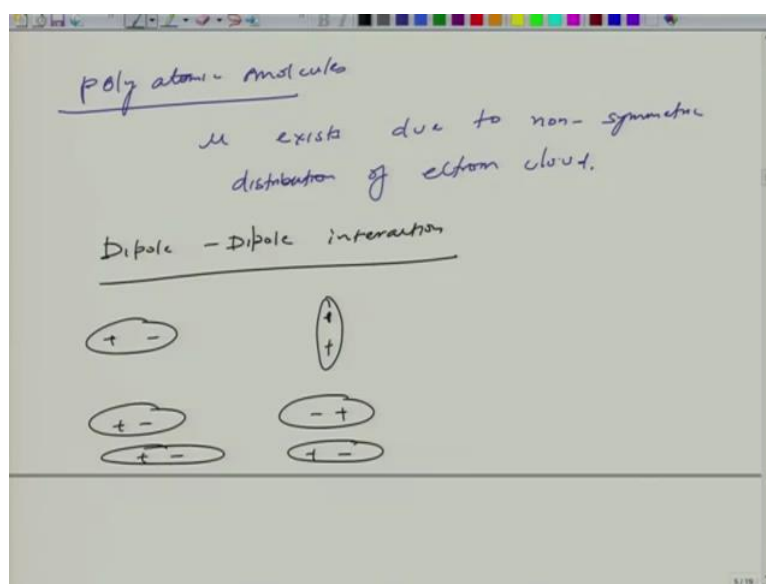
Such that Cl obtain a net negative charge and H obtains a net positive charge, okay. So this is you are going to see that for the case of HCL.

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Now if you can extend this exercise for Poly atomic molecules, so one can generalize this behavior by saying that there will be dipole moment if there is a non-symmetric distribution of the charges that means  $\mu$  exist due to non-symmetric distribution of electron cloud, okay. So let us consider now 2 molecules with dipole moments and hence there would be not just a charge interactions but it will be between dipole- dipole interactions.

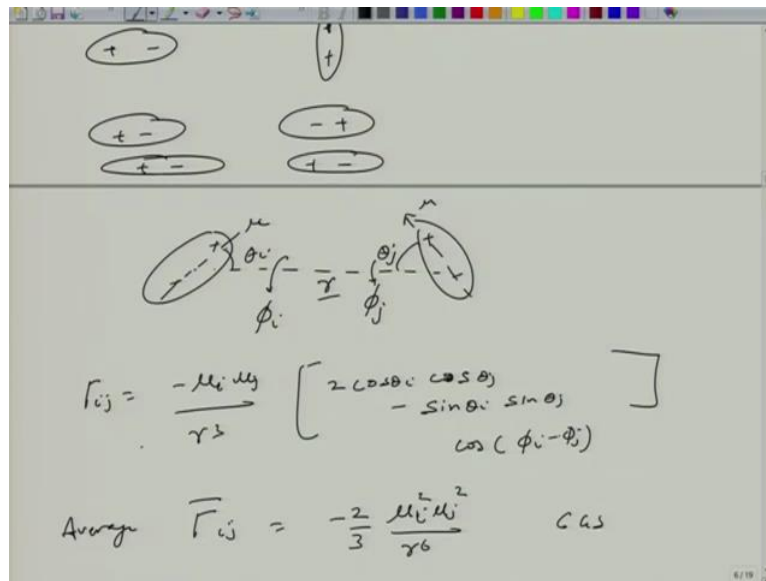
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So dipole-dipole interactions. So earlier we looked into charged-charged interactions for the point charges now we are looking at dipole-dipole interactions. For this there could be many orientations of the molecules which will play a role. So let us just draw one. So I'm just saying if this is charge separation with positive and negative and hence there is a dipole moment here and other molecule could be something like this, okay.

Or you could have something like this, okay. This would of course be repulsive in nature, okay. And this would be attractive in nature, right? So there could be many configurations as you can see and all these configurations of the molecules would lead to the kind of a different energies and thus this configuration effectively... this energy effectively would need to be average over in the various different possible confirmations, okay.

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So for example in the case of simple or generalized kind of arrangement where let us say you have this molecules the center of mass is here and another one is like this, okay. And I can draw a kind of axis were the dipole moment, the angle with respect to dipole moment here is something or this axis something like theta i. Similarly, for this again dipole moment here is negative to positive is again theta j and in addition they may not be on the plane, okay.

They may be in a different plane, so essentially you have to look at also the angle kind of phi i and phi j is a similar notion as in a dihedral angle, so you have to see whether they are kind of a rotated by theta phi out of plane and in that case this would be let say phi i and the other one is phi j and given this kind of information you should be able to find out effectively the energy between I and j, you can show that this can be written as simply like this, okay.

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{r^3} [2 \cos \theta_i \cos \theta_j - \sin \theta_i \sin \theta_j] \cos(\phi_i - \phi_j)$$

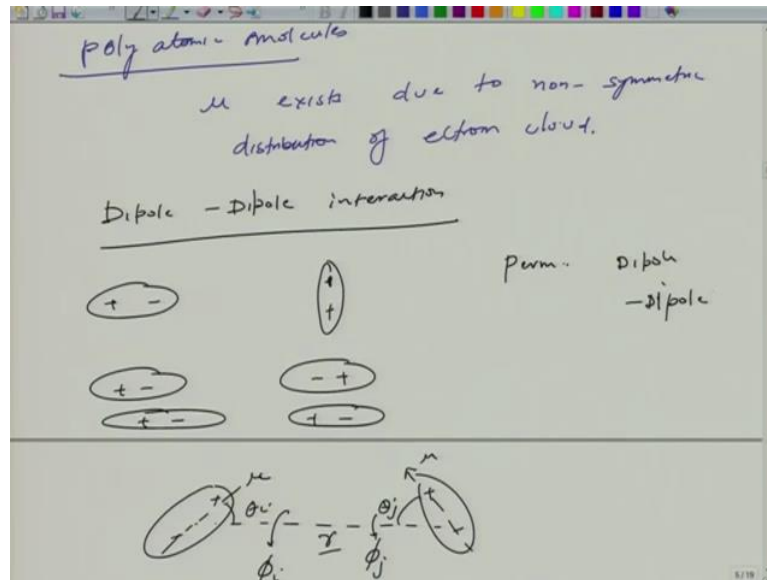
Now this is something which we can derive it, I am not expecting that to you to derive here but just to tell you that if you have this kind of configuration you can consider this to be a point charge of course Q. There is a specific length of this from negative to positive and you know this distance r, okay from this point to this point, so you can find out the point charges here consecutive point charges, interactions with this and as well as this and similarly for others.

And one can do this rearrangement in mathematically and you can show this kind of expression, okay. And this is for just one expression there will be for others, so essentially one can average this kind of interaction.

$$\text{Average, } \overline{\Gamma_{ij}} = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{r^6} \text{ (CGS)}$$

So, this kind of interaction between the dipole-dipole, okay is one of the very prominent contribution towards the London interaction, okay.

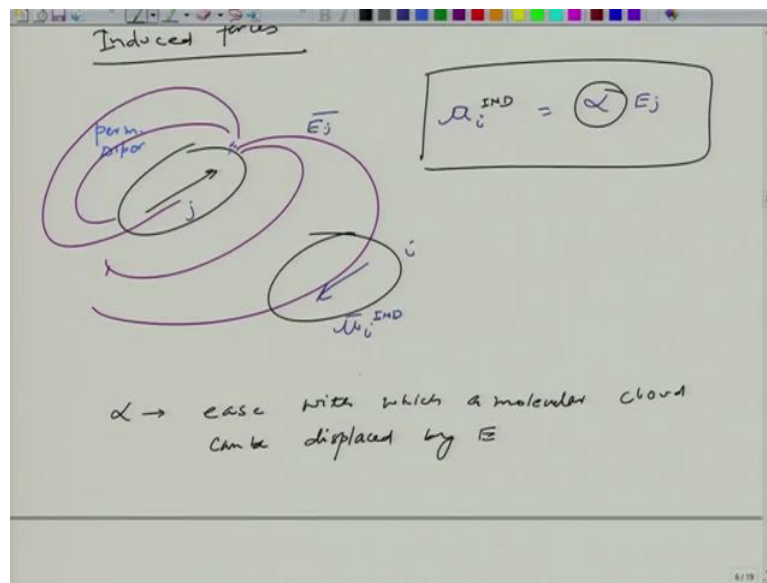
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Now this had a permanent dipole, remember. This is nothing but a permanent dipole, so it is like a permanent dipole-dipole interaction.

But there could be other cases where you can have one molecule permanent dipole and other molecule which doesn't have any specific dipole, okay. But because of polarizability that means it can change the electronic cloud, okay. So, it can have some kind of displacement and leading to the charge redistribution creating dipole moment, so that is feasible. So, in that case you can have an induced dipole.

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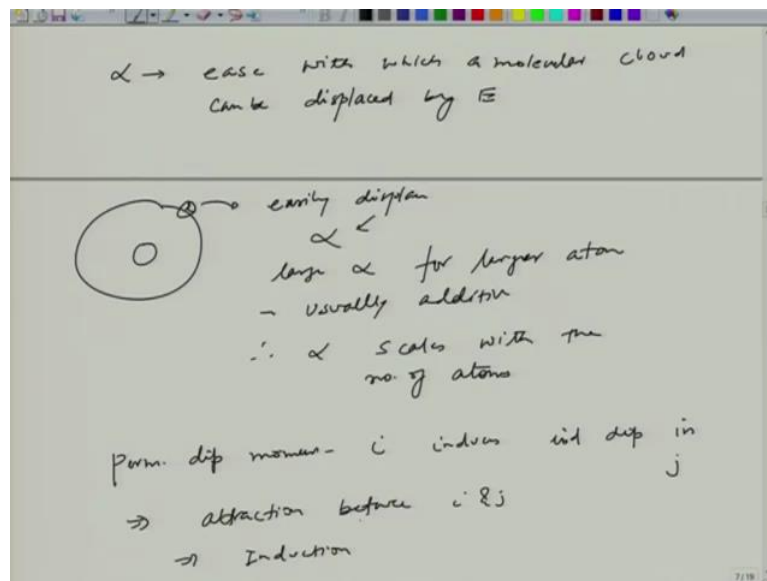


So this is another important contribution and this comes from the fact that permanent dipole. Let us say this is a permanent dipole, okay. So this is a permanent dipole, okay. And there will be of course electric field, okay. And around itself, okay. And then if another molecule comes, okay. Such that this permanent dipole induces the effect distributed the electronic cloud in such a way that due to the charge distribution now it has net effective charge separation creating an induced dipole, okay.

And this is electric field let us say  $E$  of  $j$ , so  $\mu_i$  induced, okay so this is  $I$  and this is  $j$  is nothing but  $\alpha$  times  $E$  of  $j$ , so the induced dipole is nothing but the proportional to the electric field provided by the permanent dipole, okay. Now with this you have now kind of again dipole dipole interactions, okay. Now the  $\mu_i$  or the strength of the  $\mu_i$  depends on of course  $\alpha$ , okay.

So  $\alpha$  something called polarizability which is nothing but ease with which molecular cloud can be displaced by an electric field, okay.

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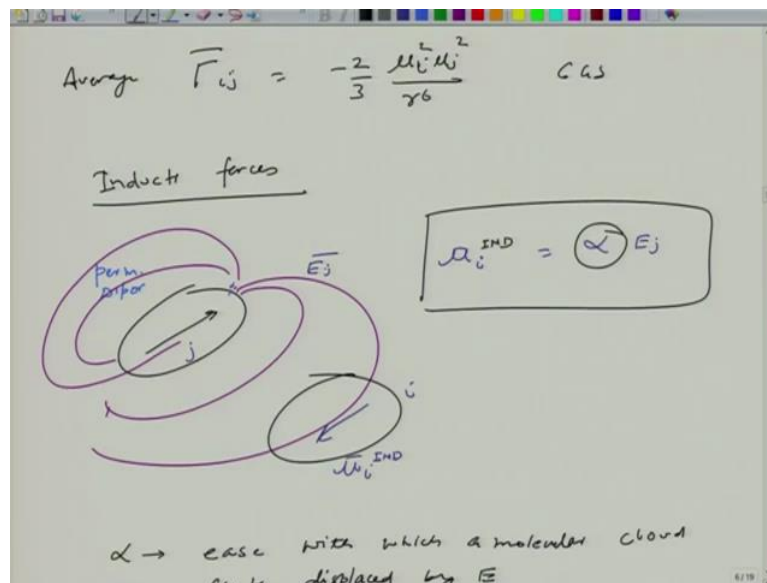
So if you think from this point of view that nucleus is electron, how easily this can be displaced depends on lambda. So larger the alpha value, so how easily we can displace the electron depends on this alpha value. The larger alpha means easy to displace or remove okay. So usually for larger items we have alpha is large, okay. So usually large alpha for larger items, okay.

And usually alpha is additive which means that for the case of molecules if the number of atom increases and hence alpha should also increase, okay. Therefore alpha scales with the number of atoms and larger molecules will have larger value of alpha and hence they have this tendency to have this induced dipole moment in the presence of electric field creating this induction phenomena which we call.

So this phenomena which we just described, okay where a permanent dipole moment molecules or atom  $i$  induces induced dipole in  $j$ , okay leading to attraction between  $i$  and  $j$  this is called induction, okay. Basically this is nothing but induction force.



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The force which is coming up is induction force. So this will be induction forces.

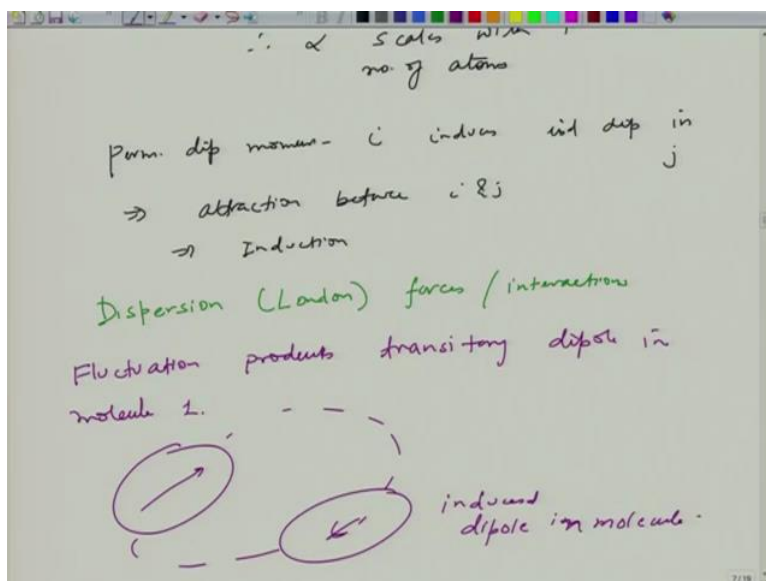
$$\mu_i^{IND} = \alpha E_j$$

So as far as this potential energy form is concerned, it is going to be same as this, okay. Instead of  $\mu_i$ , it is going to be  $\mu_i$  induced, okay.

So we just talked about point charges, dipole-dipole charges and then as well as induction. The last part is the one where we do not have a permanent dipole, okay. But the fluctuation in the electronic motions, okay. The electronic clouds can have fluctuations and that fluctuations in the electronic nature of the cloud creates momentarily kind of dipole moment. So over the time of course the dipole moment is going to be 0 but for momentarily it can have a dipole moment and that itself can have electric field creating an induced dipole in the other words.

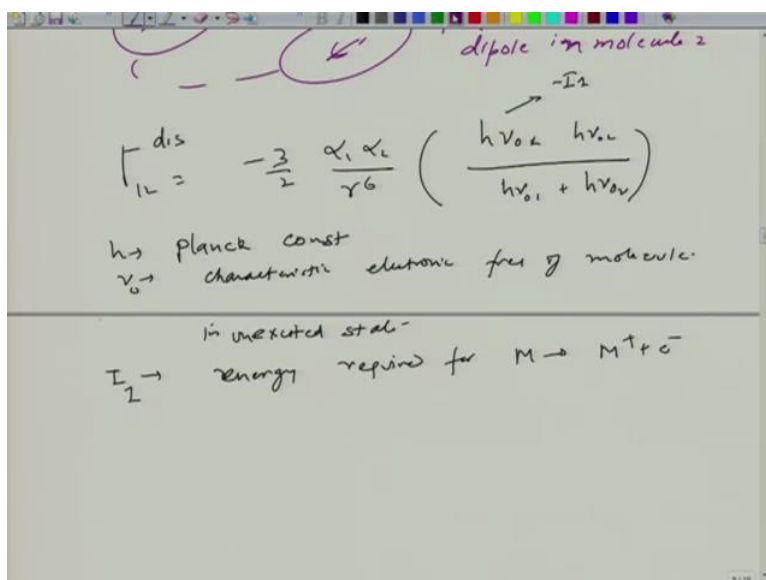
So it is common in many-many molecules where the particles may not have a permanent dipole but you still have this kind of interactions which are called dispersion forces or dispersion interactions.

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And this is something which was first found by London and this is why we call also London forces or interactions. So as I was saying that the fluctuation produces transitory dipole, okay. So it is like this again if you have a transitory dipole because of fluctuation you have a dipole moment and then you have this electric field creating induced dipole in molecule 2, okay. Now this fluctuations something which depends on ionisation potential.

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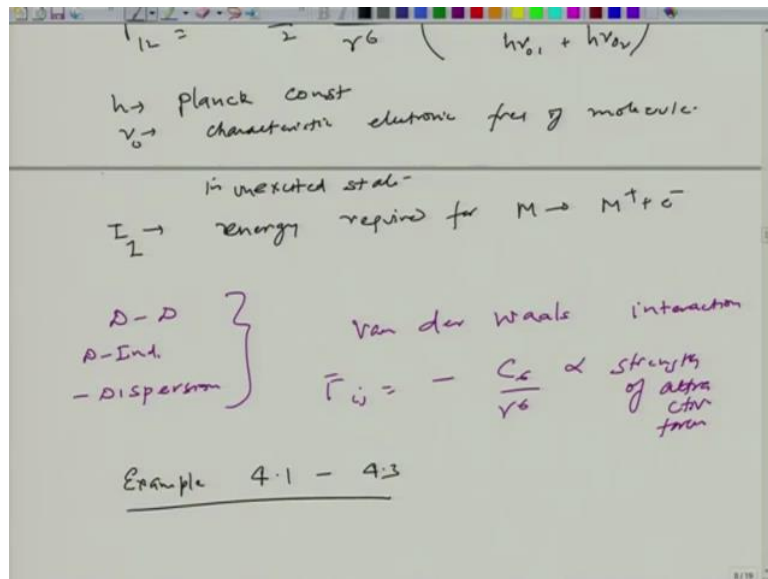


So the corresponding energy for such dispersion interactions can be written as follows is minus  $\frac{3}{2} \alpha_1 \alpha_2$  again,  $\alpha$  is nothing but polarisability, okay. And this is square  $h \nu_0$  for 1,  $h \nu_0$  for 2,  $h \nu_0$  1 plus  $h \nu_0$  2, okay. So this is basically nothing but for 1 and 2, okay. Now this is proportional or approximated to this ionisation potential, okay. Now  $h$  here is Planck constant,  $\nu$  is  $\nu_0$  here, okay is the characteristic frequency, electronic frequency of molecule in unexcited state.

$$\Gamma_{12}^{dis} = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{r^6} \left( \frac{h\nu_{01} h\nu_{02}}{h\nu_{01} + h\nu_{02}} \right)$$

And I of course is this, it is nothing but the energy required is called ionisation, okay. It is a first ionization potential  $I_1$ , it is energy required for something like this  $M$  goes to  $M^+$  plus electron minus, okay. So this is the 3 interactions we have observed beside the point charges is the following.

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So, you have dipole-dipole then you have induced, permanent dipole and induced, okay. Then you have this dispersion. Now these 3 terms or 3 contributions are a part of London wall interactions, okay and if you carefully see all the 3 on an average can be written as  $C_6 / r^6$ , so that means this interactions London wall interactions whether it is a dipole-dipole, dipole induced or dispersion interactions are proportional to  $1 / r^6$  is also negative and this is of course proportional to the strength of attractive forces, okay.

$$\bar{\Gamma}_{ij} = -\frac{C_6}{r^6} \propto \text{strength of attractive forces}$$

Now before I close what you can do is, you can also look at the textbook, the book in this course and try to solve some examples, okay which is 4.1 to 4.3 this will further add to the understanding of what I discovered, okay. So with this I will stop today's class and I will continue this exercise particularly relate to the models which often we use and the corresponding state principle in the next class.