Advanced Chemical Thermodynamics & Kinetics
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Lecture - 07
Molecular Interactions 02

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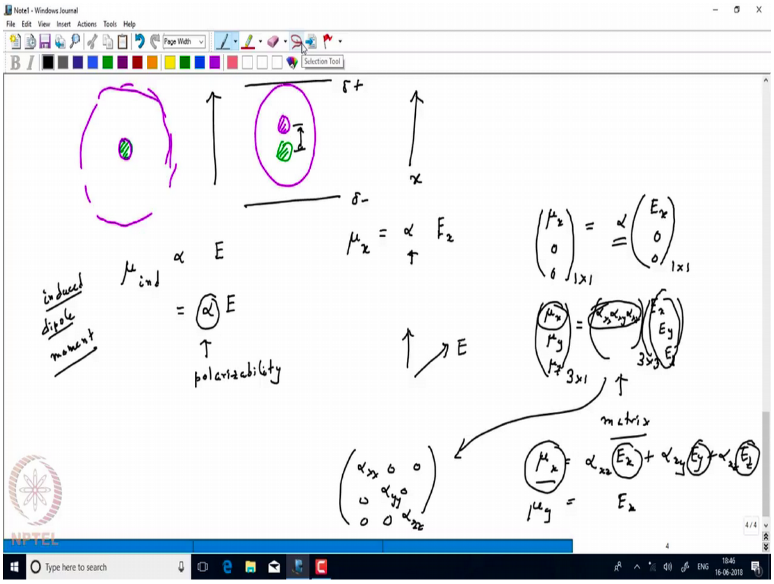

So, we are not going into much more details polarizability. Now as I said that we this is an actually an approximation in the sense that if the field strengths are low enough, then we can think that these polar induced dipole moment. Actually depends linearly on the electric field, but more generally the induced dipole moment can also have non-linear dependence.

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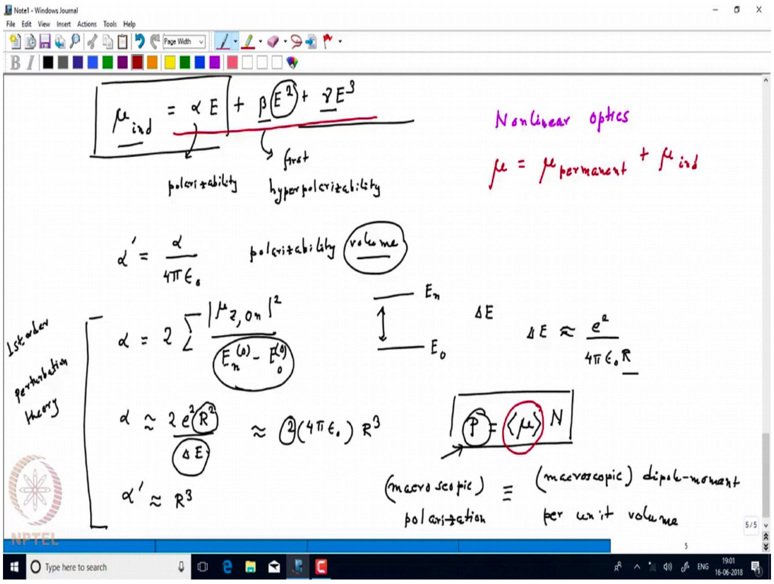

$$\boxed{\mu_{ind} = \alpha E} + \beta E^2 + \gamma E^3$$

polarizability

first hyperpolarizability

Nonlinear optics

$\mu = \mu_{permanent} + \mu_{ind}$

$\alpha' = \frac{\alpha}{4\pi\epsilon_0}$ polarizability volume

1st order perturbation theory

$\alpha = 2\sum \frac{|\mu_{z,0n}|^2}{E_n^{(0)} - E_0^{(0)}}$

E_n

E_0

ΔE

$\Delta E \approx \frac{e^2}{4\pi\epsilon_0 R}$

$\alpha \approx \frac{2e^2R^2}{\Delta E} \approx 2(4\pi\epsilon_0)R^3$

$\boxed{P = \langle\mu\rangle N}$

$\alpha' \approx R^3$

(macroscopic) polarization $\equiv$ (macroscopic) dipole-moment per unit volume

And, we can actually write the induced dipole moment as sum of terms where actually the first term is the linear term which is basically known as polarizability and the second term and the third term and so on we write those constants as hyper polarizabilities.

So, for example, this beta is known as the first hyper polarizability the name is basically self explanatory because alpha was the polarizability. So, beta is a first hyper polarizability and similarly gamma will be termed as the second hyper polarizability and so on. Now, you can see that mu induced is a vector. So, if you have always three components mu x, mu y, and mu z now if I have E square here. So, is then actually I will have E x, E y, E z and I will have basically twice of that and then you can think that the dimension of beta will not be just 3 by 3 matrix. So, it will be a higher order matrix and in general we call those as tensors.

So, we cannot actually go through all these details of the tensor algebra how basically the dimension of the beta or the gamma or the higher order hyper polarizabilities basically has the dimension. But will more or less restrict our discussion on the induced dipole moment which actually depends only up to the first term and where actually we are ignoring all the higher order dependence on the electric field.

Now, this higher order dependence will of course, depend when will of course, become important when the electric field strength is very high for example, here. So, far we have been discussing about the application of the electric field as a static electric field. So, far we have discussed this application of the electric field external electric field as a static electric field, but we could also do it by applying light because light has a electric field as well as a magnetic field of course, which are oscillating in time and in space because light is a propagating wave.

But, when light is applied on light is basically shed on atoms and molecules the physics that happens is very much the same that the electron and are basically a slashed around the nuclei from their equilibrium position and then you create a dipole. But this dipole also oscillates, because the electric field of light also oscillates and there actually make an approximation which is known as the induced dipole approximation, because we only consider the electric field of the light to affect the dipole moment. And there we talk about the creation of the dipole moment or the induced dipole moment as electric dipole moment.

We do not consider the magnetic field of the light in general and there we can actually have a very intense light source for example, if you use a lasers and focus it very tightly then actually the electric field in the focus at the focus will be very very high and then all these higher order terms which are dependent on E square and E cube will be non negligible. And then we have to consider those term and that gives rise to our entirely fascinating new field which is the extremely fascinating which is known as non-linear optics, basically where actually you can see very fascinating example like we send a red light to a crystal and then we get a blue light at the output and how basically the energies of the 2 photons gets added up and the new photon is thrown to the output and those kind of experiments are routinely done with a lasers.

Now, coming back to the polarizability or the linear polarizability often we write the polarizability in terms of the polarizability volume which is basically a reduced way of writing it we defined at the inter polarizability by 4 pi epsilon 0 where epsilon 0 is basically the permittivity of vacuum. So, I hope that you have already learnt all these basics of electrostatics in your high school physics and you know that in that case we can we which can just tell this alpha prime as the polarizability volume, why volume because actually it has a dimension of volume.

Now, why it will take a dimension of volume is also like we can understand it from a very different perspective. So, if we want to write the quantum mechanical way of what is the polarizability expression using perturbation theory second order perturbation theory I am just writing the expression for you and then we have basically, we have something like mu let us say we are talking about the Z component of the dipole moment and then we have mu Z and we have say some 0 state I will come back to it what are the about the notation here.

So, here what I am saying here I had 2 energy levels which I have noted here and. So, these energy levels are basically the unperturbed energy levels and of 2 this corresponds to the energies of 2 unperturbed energy levels E 0 and E n and you can think that these 2 an approximation represents the homo lumo energy levels in a polyatomic molecule now you can make a approximation. So, like in the sense that this thing you can think about roughly as the energy difference of the homo lumo in the molecule. So, I am just replacing it as a delta E and the mu you can think about some charge distribution times the distance. So, overall this alpha you can approximate to be something like. So, this charge distribution if you think that each atom has some charge of which is fundamental electronic charge which I am writing as E. So, it is e square R square divided by delta E.

Now, as you can see that if I reduce the delta E I or if I actually have the less separation between homo and lumo then actually I will have more polarizability as well as if we have more R square which means actually if we have more of the R or the distance between the dipoles which actually it directly connects to their volume I will have more and more polarizability. But to get to know how basically it is why we are calling it as a polarizability volume let us let us do 1 more step now how do you calculate the delta E.

Now, the delta E as you can think we can actually say that this delta E is basically as if there is a positive charge and I am moving the positive charge over a distance say R and then we can think that basically connects to the excitation energy from say homo to lumo and we can think that again this is a very crude description, but the delta E you can actually approximate as e square divided by 4 pi epsilon 0 R. So, this is this basically tells that if I have a unit positive charge at a location R from some origin and then I am removing that unit positive charge from that location to infinity. So, this will be the energy required to do that.

So, this is by definition of the electrical potential energy that is stored if I keep the positive charge or if I that is basically spent if I want to move that positive charge to infinity. Now, we can actually replace this value of delta E in this equation and what we found here is that I will have alpha is will be something like 2 two times 4 pi epsilon 0 into I have one R here and one R here, so I will have R cube.

So, if I by definition alpha prime is nothing but alpha divided by 4 pi epsilon 0 and if we ignore the factor of 2 here. So, we see that alpha prime is roughly equal to R cube which is basically roughly the volume. So, that is why you call it as a polarizability for them, but again this description all of you may not be very familiar with you can actually look at the quantum mechanics textbook. And, if you know little bit about perturbation theory or basically the second order perturbation theory this is actually first order because here actually the denominator as you can see is basically N minus E 0. So, they are basically the first order perturbation theory tells you how the energy level shifts when an external field is applied.

The second order perturbation theory tells you when what happens when I couple the 2 energy levels. So, this actually directly comes from the first order perturbation theory, now the next thing is that this polarization which we talked about it actually depends on the frequency of the external field because here we are applying an external electric field and we are creating polarization or basically dipole moment we have not actually defined the term polarization the term polarization or is basically it tells you what a it is called a macroscopic polarization or simply as polarization.

So, suppose when you do this experiment on say gas or a liquid where actually we have some molecules which has a very high alpha which means actually if I apply an external electric field which can be static or which can be a time varying electric field as we see with the light then actually I create a static dipole or a time varying dipole which is an electric dipole in this case and it depends the strength of the dipole depends on the magnitude of the alpha or the polarizability. So, basically this polarizability tells you how with what is we can actually distort the electron cloud so that we can actually create dipole moment momentarily as long as the electric field is present.

If we actually remove the electric field or if we can turn off the light then actually there is no polarizability because it just stays as long as the light is there. So, that is why it is an induced dipole moment and then we can actually add up all these dipole moments or very small molecules and then we can think about creating a macroscopic polarization.

Now, on average you can think that if I am applying a electric field in a particular direction more or less there will be some preferential orientation of this molecular of the tiny electric dipoles along this direction which can actually give you net polarizability and a macroscopic polarizability along a particular direction and that we talk about as some mu times the number density and this mu now is an average mu which you can think of and times the number density. So, this is basically known as the macroscopic polarization.

So, macroscopic polarization is directly connected to the mu induced usually the mu induced is described in a molecular context and when you talk about in the in the atomic or molecular context and when you talk about a macroscopic system then actually we have to take the average mu and then multiply it by the number density of the molecules then basically this P or the definition of P is something like that it is basically the macroscopic O dipole moment per unit volume because number density is nothing, but the number of atoms or molecules per unit volume.

So, P is nothing, but at a dipole moment per unit volume. So, we can write it as it is nothing, but the macroscopic or the measurable dipole moment that you can measure per unit volume. So, we will now try to understand what is the value of this mu average because when you applying an external electric field you have to understand that what is the mu average. Now, you can think that in case the way we have written this equation of mu induced that it depends on the electric field the total mu will be something like the mu permanent which we talked at the very beginning, the molecules may have a permanent dipole moment and then the induced dipole moment.

Now, you can think if I have water molecules now water molecules already have permanent dipole moments and if I do not apply any electric field then it will have the each molecule will possess only the permanent dipole moment, but in a macroscopic system all these dipole moments in the absence of any external field will be randomly oriented. So, what will have is that will have a net 0 dipole moment or net 0 polarization in the system, but when we apply an external electric field then all these permanent dipoles will try to orient themselves along the field as well as the field will also induce some induced dipole moment. So, the total dipole moment which is basically contributed as a permanent dipole moment past the induced dipole moment in the presence of the field that dipole will try to orient itself along the field.

So, you have a distribution of dipole moment along the field and that will give rise to a macroscopic polarization in the system that we are now going to discuss. So, before you go to the derivation of the average value of this induced dipole moment basically it is a orientational average of the induced dipole moment. Let us also discuss some other aspects of the induced dipole moment when it is created as I mean as an application of the external electric field now what we are going to ask is basically what is the energy which is required to what is the potential energy of a dipole which is at an angle let us say theta with respect to the applied electric field. So, what we have to do here is basically suppose I have a dipole.

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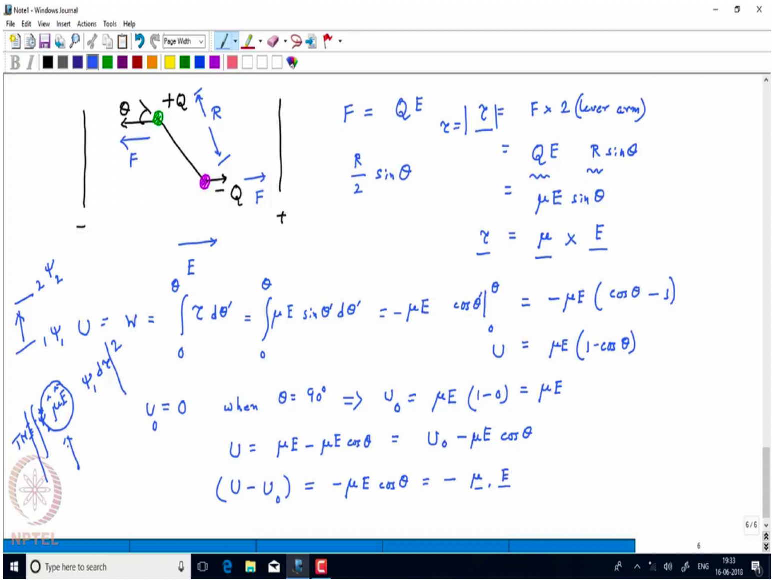

$F = QE$

$\frac{R}{2}\sin\theta$

$\tau = |\underline{\tau}| = F \times 2 \text{ (lever arm)}$

$= \underset{\sim}{QE} \; \underset{\sim}{R} \sin\theta$

$= \mu E \sin\theta$

$\underline{\tau} = \underline{\mu} \times \underline{E}$

$U = W = \int_0^\theta \tau \, d\theta' = \int_0^\theta \mu E \sin\theta' \, d\theta' = -\mu E \cos\theta' \Big|_0^\theta = -\mu E(\cos\theta - 1)$

$U = \mu E(1 - \cos\theta)$

$U_0 = 0$ when $\theta = 90^\circ \Rightarrow U_0 = \mu E(1 - 0) = \mu E$

$U = \mu E - \mu E\cos\theta = U_0 - \mu E\cos\theta$

$(U - U_0) = -\mu E\cos\theta = -\underline{\mu} \cdot \underline{E}$

And again let us take the charges as plus Q and minus Q and suppose we are applying an external electric field which can be time dependent also then the sign of the dipole will change with time because it will follow the electric field and suppose you have a positive end or a negative end here and a positive end here something like that. So, then what you can think that the dipole is now tilted like this it is it at an arbitrary angle and we can think that this angle is basically theta and then what we are having here is that we are actually having force on the dipole on the 2 ends.

So, basically we are creating a torque on the dipole and as before I was using green for the positive side and pink for the negative side. So, you have been created a force along each charges on each charges of the dipole now, what is this magnitude of this force now again as before let us think that the distance between the charges that create this dipole is R and the electric field is now applied the from the positive side is this and negative side is this. So, the electric field is applied something like this and the question we are asking what is the force that is acting on the dipole on the charges first.

Now, the force acting on this charge for example, the plus charge which will be in this direction and the force which is acting on the negative charge of the dipole negative end of the dipole we should say which is acting in this direction. Now, this magnitude of the force will be basically the charge times the field which is basically if I write the charge as Q and electric field as E which is a strength of the field the question is what is the torque acting on this particular dipole. So, then we talk about the lever arm of the dipole and remember that the lever arm is basically we have to take a projection of this distance between the dipole half of that towards the direction. So, in this case it will be R by 2 sin theta.

So, the overall torque which will be acting on the dipole which will be basically addition of these 2 forces and then it will be force times 2 times the dimension of this of this lever arm basically two times the length of the lever arm. So, then the force is nothing, but Q into E and this lever arm into two times is basically R sin theta. So, this is not I should not write it as a cross because I am just writing it as a simple multiplication. So, it is basically Q E R sin theta and Q R already we know that this is a mu. So, it is basically mu E into sin theta which is nothing, but in the vector notation mu is a vector which is a dipole moment and E is also an vector which is the applied electric field.

So, the torque is nothing but actually the vector product between mu and E. So, mu is sin theta is the magnitude of the torque. So, the torque itself is mu cross E now the question is what will be the energy of the dipole, now you can think that I am basically rotating the dipole from a angle which is which was initially at 0 degree with respect to the electric field which means actually which was like at some angle 0 degree and then I am actually rotating it to an angle theta. So, that the dipole is has now a particular orientation and due to this rotation I am doing some work and that work done you will be basically stored as the potential energy of the system which is basically the potential energy of the dipole itself.

So, this work done in order to calculate we have to basically talk about like work done in if I have a linear motion it will be forced into displacement and now if we have if you are applying a torque it will be nothing, but the force equivalent of rotational motion which is a torque times the instead of displacement it will be the rotational angle. So, it will be tau d theta and going from say 0 to will have to a particular angle let us say theta and then we can actually use d theta prime because theta prime is variable.

Now, what is tau already we talked about the magnitude of tau ok. So, tau is basically the magnitude of the torque applied. So, that is mu E sin theta D theta. So, you are using theta prime here from 0 to theta now derivation of cos theta is basically minus sin theta. So, integration of minus sin theta is cos theta. So, the integrand is nothing, but mu E again the e is independent of theta mu and E. So, we will have the integrand as minus cos theta and which is evaluated between the limits 0 and theta.

So, it will be minus mu E cos theta and cos theta evaluated between 0 and theta. So, it is minus mu E. So, when theta the upper limit is theta I will have cos theta I we can write it as theta prime and then when the lower limit is 0 cos theta is 1. So, this value of the integrand the work done is nothing, but mu E into one minus cos theta. So, that is the work done and this work done will be stored as a potential energy of the system now we have to define a 0 of potential energy. Now, the 0 potential energy you can think that when the angle between this dipole which is created and the external field is 90 degree then you can think that that is basically an position quite a basically this dipole and the field are not interacting because it is basically the force acting on the dipole due to the field will be 0 because cosine 90 is 0.

So, then we can think that in that from that perspective we can choose U equal to 0 or the 0 of potential when theta is 90 degree or basically pi by 2 and that will give us that U 0 or basically the 0 of the energy will actually corresponds to basically again U will be a constant and that constant we are taking it to be 0. So, we better actually write it as U 0. So, the U 0 will be nothing, but mu E 1 minus cos theta when theta is 90 degree. So, it is one minus 0. So, it is nothing, but mu E.

So, we are talking we are taking that to be U. So, what we said is that this work done will be stored as basically the potential energy of the system. So, this is nothing but the total potential energy U and we just saw that mu E is nothing, but the potential energy or the 0 of potential which you can choose. So, then we just define that U is nothing, but as you can see here mu E minus mu E cos theta. So, which is basically U 0 minus mu E cos theta. So, if we just always plot the potential energy with respect to a 0 of potential which we chose to be the potential U 0 to be 0. So, that fellow will be minus mu E cos theta.

So, which is nothing, but minus in a vectorial notation which is nothing, but minus mu dot E. So, it is basically the dot product of the electric field with the dipole moment again that dipole moment can be permanent or the dipole moment can be induced even the dipole moment is permanent when the electric field is applied there can be a induced part also in addition to the permanent and for those atoms or molecules which do not have a permanent dipole moment it is all induced.

So, will get a definition of the energy stored with respect to a 0 of potential again the 0 of potential was chosen as the configuration where the dipole is basically oriented a perpendicular to the applied electric field as minus mu dot U. Now, this expression probably you have seen when we talk about basically transition between one energy level to another energy level whatever is a transition it can be an electronic energy level then we apply and electromagnetic energy at visible frequencies or ultraviolet frequencies.

So, something like we have already seen and then we talk about a mu which is also an induced dipole moment because when we applied light as we said that light actually has an electric field which is oscillating in time. So, you have an oscillating induced dipole moment, but you can actually think all these spectroscopic transition or you can actually explain all this spectroscopic transition which we initially study in our quantum mechanics or spectroscopic class from a very much quantum mechanical point of view has a classical picture where basically we are I mean again in quantum mechanics using second order perturbation theory you learn that we are coupling the two states.

But here what we are saying here is that it has a classical thing as if a indue created a induced dipole in the system and this induced dipole which is known more specifically as the transition dipole and this transition dipole moment is trying to align with the field. And that alignment is basically stored as the energy as we said and this is basically the energy for the transition and this is known as a at a transition moment integral and when you write the transition moment integral spectroscopically and we write are basically an operator which acts between the 2 states suppose I have the 2 states something like that 1 and 2 and the wave functions I will say psi 2 and psi 1.

So, I am coupling it. So, that I will have a transition from state 1 to state 2 and then we write in the wave function wave that I have a psi 1 1 wave function then I have an operator which is the transition moment operator which is coupling the psi 1 with psi 2 and that operator we write as minus basically mu E the minus sign we can drop it for the time being because we take always the magnitude. So, here we wrote actually the operator rotation mu operator and E operator and then you write psi 2 here and psi 2 star here and then you integrate over the entire volume.

So, this is basically the transition moment integral, now original transition moment integral also have a square because actually it is the intensity that matters. So, you have to think about this interaction the electric field interaction twice because electric field when it acts twice basically it acts like first I field interacts and then its complex conjugate interacts which is equivalent to interaction of a photon let us not go into a details of that and then the point here I wanted to make is that the operator form is the same as the classical form.

So, it is a mu dot E only. So, we have a exact analog analogy with quantum mechanics actually quantum mechanical this transition moment integral operator are actually borrowed from classical physics where we see that the we are creating a dipole and it is a electric dipole which is basically created and the electric field of light is causing this transition. So, by logic we will have the operator of the form of mu dot e which we just explained.