Ultrafast Optics and Spectroscopy
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Lecture - 12

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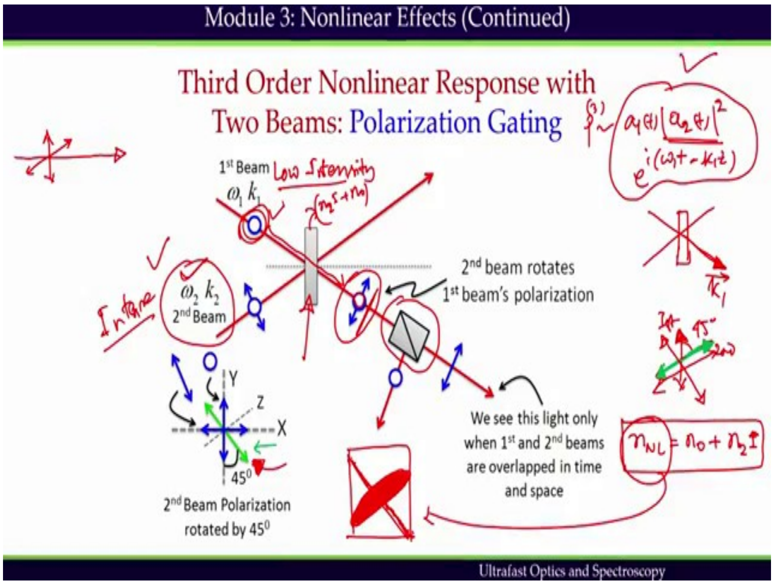

So far, we have used two beams and they are coupling. In non-collinear configuration, one can also use three beams.

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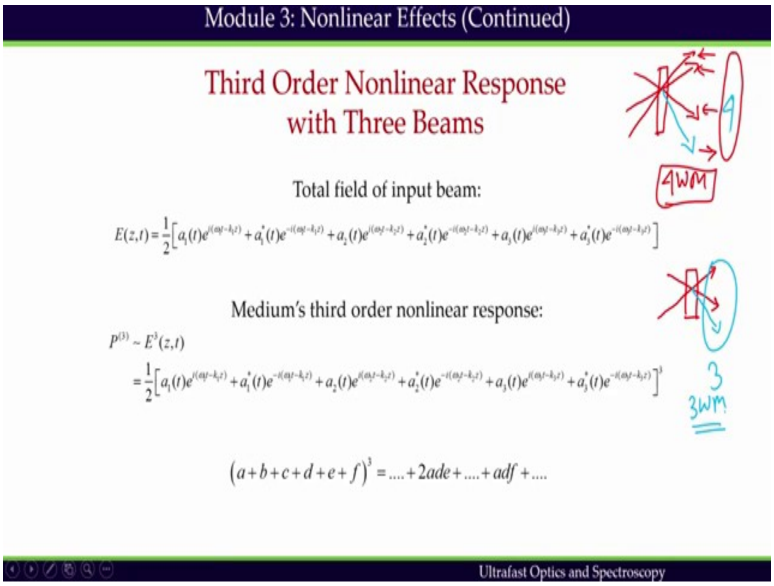

So, I can have I have a medium; I have this three beams propagating like this way they are interacting in the medium and if we have three beams then an additional beam will be created. And, if the additional beam is created I will change the color let us say again, I will get a blue and I will say that I have created an additional beam along this way.

So, effectively what we do here is that in non-linear process we have three input beams interacting and giving another in output beam. Total four beams are in the interaction region and that is why we call it; we call this kind of process is added as four-wave mixing. There are four different waves which are getting mixed together that is why four-wave mixing. Similarly, if we go back to our previous work; sorry previous slide we have discussed two beam coupling and two beams has created a new beam.

So, I have total three beams which are getting coupled. So, this is my third beam. So, there are three beams which are getting coupled, here four beams are getting coupled and so, here three beams are getting coupled, we can call this process has three-wave mixing. So, this is the way is that there is another way of naming these this processes. So, we will go back to this four-wave mixing.

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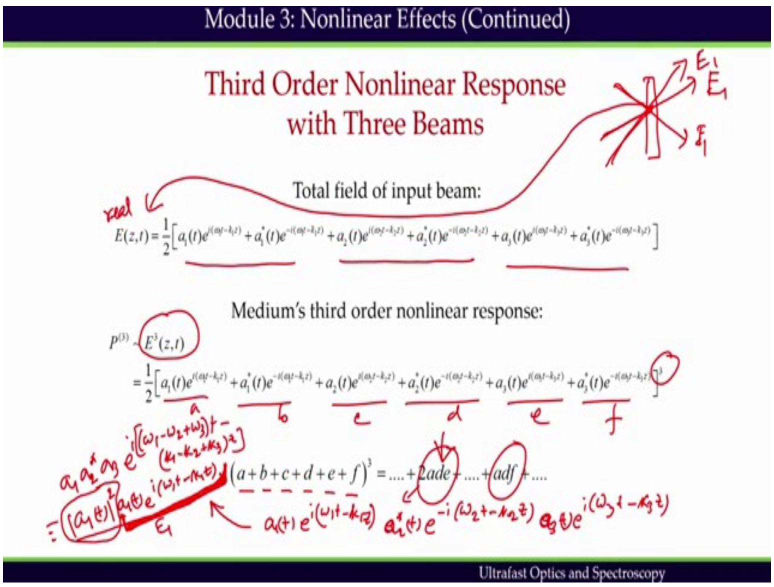

In four-wave mixing we have three beams coupled and one more beam is created that is why it is four-wave mixing. The real resultant field due to three input beams can now be represented by. So, I have a medium I will change the color. I have a medium and then there are three beams which are getting coupled in the interaction regime in the medium in at this point.

So, if I have three beams E 1, E 2 and E 3 then we know that fields would be additive. At this point electric field real field is going to be nothing, but this. The first beam complex notation and it is conjugate, complex notation by the second beam and the third beam. So, if I consider third order response then I have this cube term and finally, this whole equation is reduced down to the simplified tenth standard equation which is a plus b plus c plus d plus e plus f cube which will have many many terms.

Among them we will select only very important two terms one is ade, another one is adf. For ade if we look at ade term, then I can write down this term can be written down as a is a 1 t from here it is a, this is b, this is c, this is d, this is e and this is f. So, ade term is going to be a 1 t e to the power i omega 1 t minus k minus k 1 z multiplied by d which is a 2 star t e to the power minus i omega 2 t minus k 2 z multiplied by e which is a 3 t a 3 t e to the power i omega 3 t minus k 3 z.

So, this is my ade term which can be reduced to this can be reduced to this equation a 1 a 2 star a 3 e to the power i omega 1 minus omega 2 plus omega 3 t minus k 1 minus k 2 plus k 3 z, this can be simplified. A very interesting variant of this term is obtained when we take identical three input beams. Let us say these three input beams are coming from the same the same input beam. So, we can split an input beam and we can idea; we can use identical three beams.

If they are identical then what we get this equation will be reduced down to this equation: a 1 t modular square, then a 1 t e to the power i omega 1 t minus k 1 z, if we use identical three beams. What does it mean? It means that I have this beam which is the input beam E 1, they are identical. So, all are E 1 now. All are E 1, E 1 and E 1 their propagation directions are different, but they are they are their propagation narrations are different, but they are still E 1 beam. So, that can be expressed by this.

So, this beam what we are seeing is that if we have identical three beams due to this third order non-linear process associated with this ade term, we can get a get back a beam new beam the new polarization is created which is again getting affected by its own intensity a 1 or square modulus is nothing, but its own intensity. So, intensity of the beam affects itself we have already seen that two such important self affecting processes – self phase modulation and self focusing. This is the two self affecting process we have already seen.

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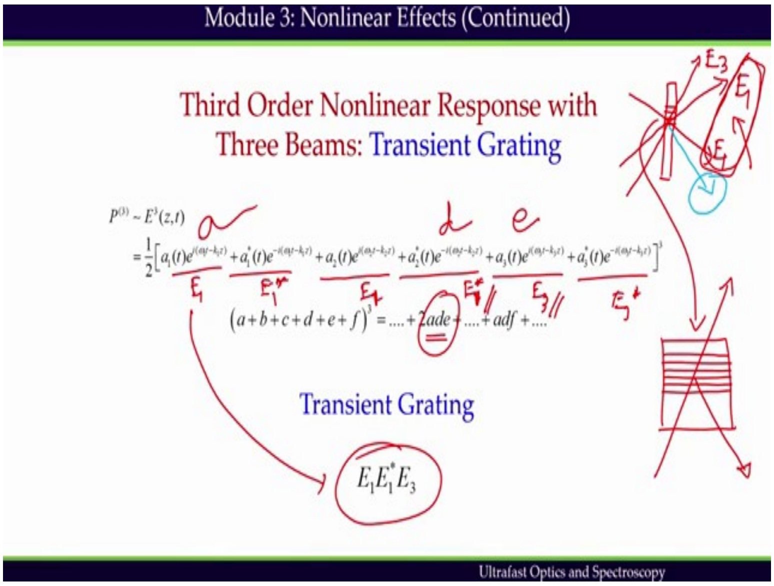

But, instead of now instead of taking all identical beams; we can also consider two identical beams and a second beam. So, instead of taking when you take a three identical beams we call degenerate four-wave mixing and there are two consequences of degenerate four-wave mixing. One consequence is self phase modulation, another one is self focusing. But, if we do not consider three identical beams instead of three identical beams we can consider two identical beams interfering like this way. These are two identical beams and this one is the third beam is a different beam.

So, let us say this is E 1 and I call this one is E 3; one can say E 2 also does not matter. The way we are representing we are representing by ade term that is why we are calling it E 3; it is just a matter of convention.

So, now if we use E 3 term then what will happen they this due to this non-linear process where two beams are identical and one beam is big different then what will happen? Part of this E 3 beam will be diffracted back along this wave and we create the diffracted back along this wave. And, this is called transient grating and this diffraction occurs due to the transient grating. So, what happens I will show the math's which is responsible for this phenomenon, but I will give you the idea immediately coupling of these two identical beams creates transient grating in the medium.

In the medium: if we magnify this region, we will see that in the medium transiently we create a grating like this and due to this grating now I have E 3 is coming and this E 3 is getting Bragg diffracted like this way part of this beam will be Bragg diffracted. So, this diffraction occurs due to the transient grating created by the two identical laser beams. So, the again this ade term, the transient grating which is responsible for this is going to be E 1 E 1 star E 3.

So, the this is this is your E 1 this is E 1 star E 1 star and this is E 2, this is E 2 star and this is E 3 and this is E 3 star. So, basically we are saying that E 1 this is this two are identical. So, they are identical. So, we have made it 1; E 2 there is no E 2 here and so, it is a still an ade term. This is a this is a, then we see this is d, and then this is this is e term. So, this is ade term and we are seeing that ade term here is E 1, then E 1 star yes E 1 start this one and then E 3; this E 3 term.

So, the transient grating would be will be created when two identical pulses are interacting with another third beam. So, these two identical beams E 1 identical beams will create the transient grating and the third beam will be Bragg diffracted due to this due to this grating.

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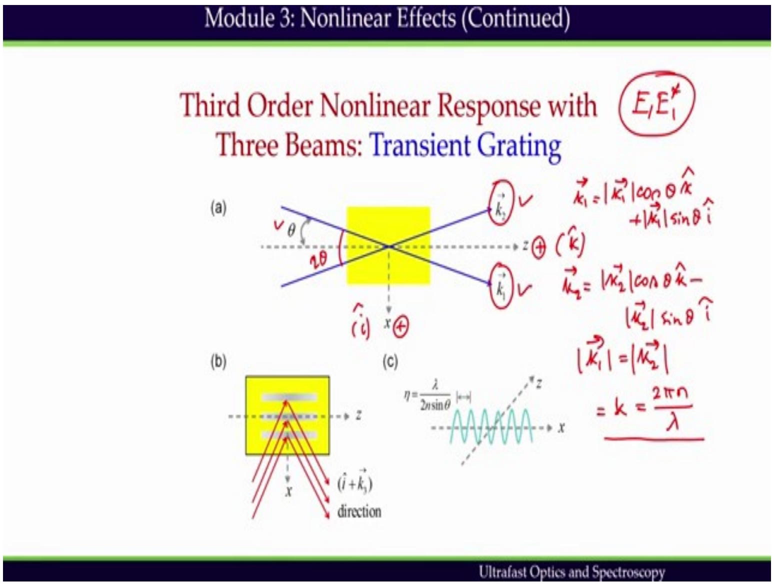

So, let us understand what does it mean by this transient grating and how we create that. Let us consider that k 1 and k 2. This is the k 1 and k 2 are wave vectors of the excitation pair pulse, the pump pulse let us say. These are the identical pulses, we are talking about.

So, we are now looking at the E 1 E star 1 term first. So, in order to look at this they are interacting at, but they are interacting at an angle 2 theta angle. So, basically with the with the z axis, they are forming theta angle and they are interacting like this wave.

If these wave vectors are decomposed into the components along the z-direction this is the positive z-direction and this is the positive x-direction. We are going to decompose this two wave vectors along these two direction then one can write down that k 1, this wave vector equals k 1 magnitude cos theta this k vector it is a unit vector along the z-direction plus k 1 magnitude sin theta i; i is again unit vector along the x axis. So, i is unit vector along x axis is and k cap is the unit vector along the z axis.

So, I can decompose this k 1 along the z and x axis. On the other hand k 2, similarly we can write down this k 2 vector can be written down as k 2 magnitude of cos theta along z direction minus; minus is because I am now decomposing along this direction. So, this is minus x direction. On the other hand, for k 1 we have decomposed along this and this direction that is why that is why this minus sign we are getting minus sign for the k 2. We can write down this minus k 2 magnitude sin theta i.

So, this is an expression which we get immediately if we decompose these two vectors k 1 and k 2 along that z and x axis. Once we have decompose it, then as these two excitation pair pulses are taken to be identical we can write down that this k 1 magnitude their directions can be different, but the magnitudes are the same because they are identical. We have said that we are looking at identical two beams and that can be written as k which is nothing, but 2 pi n by lambda; n is the refractive index of the medium. This expression is already obvious to us because in mathematical formulation or representation of ultra mass pulses we have seen that how the magnitude of the wave vector is related to the wavelength.

And so, two pulses interfering at an angle 2 theta exhibits the same magnitude of k vectors, but their propagation directions are different. So, we have to remember that although the propagation this k 1 and k 2 we are representing because their directions are different, but their wave vector magnitudes are the same.

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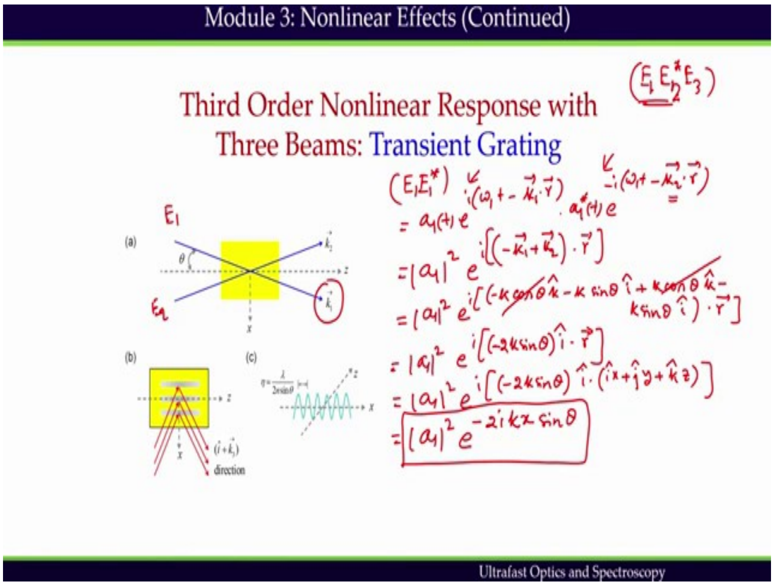

So, if we have these two a relationship then we can take a look at the first two terms. We will we are going to look at this E 1 E 1 star. We are actually interested in finally, we are interested in E 1 E 1 star E 3. This is the term we are interested in.

But, first we will look at this first two term and what is the effect of these consequences of these two products. So, we will write down these consequences a 1 it is nothing, but a 1 t e to the power i omega 1 t minus k 1 dot r multiplied by a 1 star t e to the power minus I omega 1 t minus k 2 dot r. We are saying that E 1 multiplied E 1 star, but this is actually E 2 star which is equivalent; E 1 and E 2 are the same thing. So, this these two terms we have to get the product of it and if we get the product of it. So, basically here E 1 star or E 2 star they are equivalent ok.

So, we can we should remember this one. Although we are presenting as e one, but if they are there that is why it is it is actually it can be that is why we are taking this k 2 that is a two directions are different. So, this is E 1, this is E 2, but we are representing their only difference is the k 2 that is the that are the direction. So now, if we if we simplify this one we get a 1 square modulus multiplied by e to the power i this omega 1 is cancelling out.

So, I get only minus k 1 plus k 2 dot r. This omega 1 will cancel out because there is a negative sign here and there is a positive sign here. So, they will cancel out. So, if I further now plug that in the previous expression we have decomposed k 1 and k 2 vectors along the x and y's direction. So, that decomposed expression if we write down here is going to be square e to the power i.

Now, I can write down this one as minus k that is the magnitude cos theta then direction this is the unit vector along the z direction minus k sin theta then i, that is the unit vector along the x axis plus k cos theta, then k is the unit vector along the z axis minus k sin theta i unit vector under x axis dot r. This is what we ge. We can further simplify by a 1 square modulus square e to the power i then minus 2k sin theta i dot r. This is what we get because this cos theta is cancelling out. So, I get only sin theta term.

And, r can be now decomposed into its characteristic x, y, z directions. So, I can write down e to the power i minus 2k sin theta then i dot r can be written as i x plus j y plus k z. This is the we can write down and we know that i dot i will exist other will cancel out; it will become 0 that is why we can write down as e to the power minus 2 i k x sin theta. So, this is the term which we get finally, as the product of these two identical beams.

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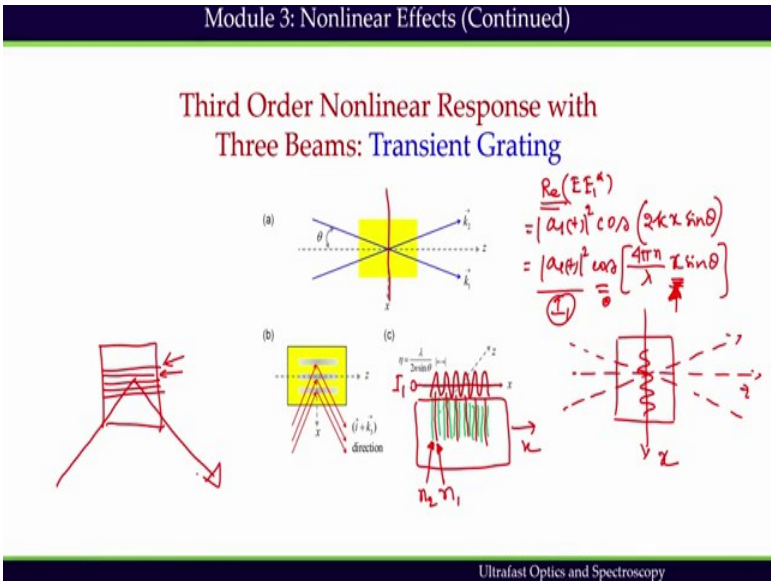

And, taking only the real part of this what we get? We get is that this real part of this E 1 E 1 star that we get as a 1 t square modulus then real part is going to be cos of that function. So, 2kx sin theta cos of that function and k we know that it is going to be previously we have already written that cos k is going to be cos then 4 pi n by lambda x sine theta. This is 2 pi for k and this multiplied by 2 that is why we get 4 pi.

So, this is the expression what we get for the real field and what does it mean? It means that the joint effect of first two identical pulses or beams results in sinusoidal variation of intensity in the sample which causes which causes spatially varying population of ground and excited state species along the transverse direction as shown here. So, what does it mean? It means that this real field is showing a variation of the intensity. So, this is variation of the intensity along the x axis. What is x axis? It is the transverse direction along this direction.

So, if the if the medium is like this and if two beams are interacting along this direction, they are propagating along this direction. This is my z direction. Then what I am getting is that a variation of the intensity will occur along this direction along the z direction. Along this z direction I will have a variation and what does it mean by variation sorry x direction. Variation of intensity along the x direction it means that let us say this is intensity.

So, this intensity will be modulated by x direction, x axis ok. Now, cos value for a certain x I will get cos value 0 which means intensity will be 0 or for a certain value of x. I will get cos value maximum which will get maximum intensity which means that, along this x axis direction, I will have intensity of this beam to be going up and down with respect to 0. So, this is your 0 value with respect to 0 value is going up and down and when a medium I have also what does it mean? It means that along this x axis because this is the regimes where we are getting intensity right.

And, there are regimes where we do not get intensity; the intensity becomes 0 which is shown here with the help of this color this green color. So, in this green color positions are zero intensity. So, we are getting zero intensity here. So, what will happen because in order to excite a molecule few molecules; let us say I have in this medium, I have excited I have different molecules in this medium and what we see along this x axis? Along this x axis we see a spatial variation of the excited state species and ground state species.

This green color positions will have no intensity; it means that molecules will not be excited to the excited state. On the other hand, this red color positions having high intensity which means maximum number of molecules will be excited to the excited state. So, effectively this variation of the intensity along the x axis will create a variation of the excited state population in the medium and that excited state population is creating a different refractive index. So, what does it mean? It means that the medium refractive index here and medium refractive index here are different.

So, I have a medium now where I have transiently created this grating and this points having different refractive index compared to this empty space and if you have a variation of the refractive index; that means, if I have third beam coming along this direction it will be diffracted back due to this grating and that is exactly what we have shown. The wavelength of that variation can be calculated with the help of this eta. This eta is representing the spacing between the spatial variation of the refractive indices or spatial variation of the intensity along the x axis which definitely depends on this lambda, the excitation wavelength.

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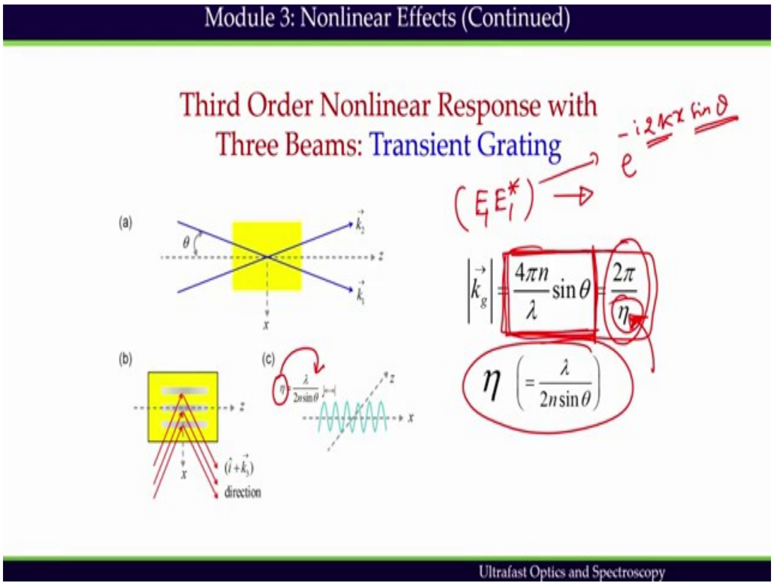

So, what we are seeing here is that the magnitude of the wave vector for the resultant field, if I have now the third beam coming then the magnitude of the resultant field the grating wave originated by. So, so basically this E; E 1 E 1 star. This identical beams is creating a creating this spatial variation of the of the refractive index and also spatial variation of the excited state species and the ground state species of the intensity. And, its wave vector can be represented by this equation and any wave can be represented by 2 pi by eta. The eta is the wavelength of that reputation.

So, if this oscillation is represented by this eta wavelength that is connected to the excitation wavelength following this equation. So, this wave vector we get from the previous calculation. The calculation shows that final expression for this field is going to be depending on minus i 2k x sin theta, right?. So, from here we can say that the we can say that the wave vector is going to be this one 2k sin theta this is going to be the wave vector and that is exactly what we have written here wave vector. But, for that wave vector I have wavelength to be eta; eta is the variation of the intensity.

So, eta can be written as lambda by 2n sin theta. This is the spacing of the periodic variation of the spatially varying field and that is exactly the spacing between the excited species and then and the so, the ground state species or the grating spacing in the transient grating created by the interaction of two identical beams.

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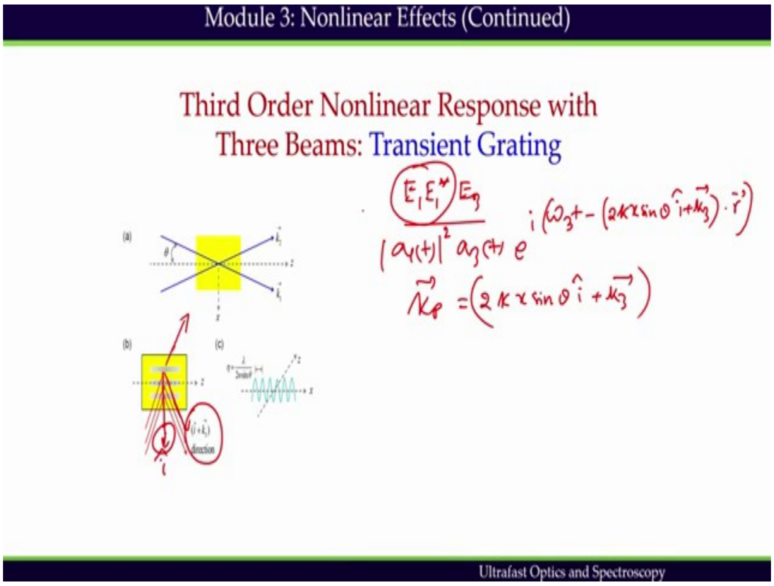

Finally, the third order polarization due to this E 1 E 1 star and E 3 term can be given by this a 1 t magnitude square a 3 t. Now e to the power i omega 3 t minus 2 k x sin theta i plus k 3 dot r. This is the way the total polarization would behave and this polarization k_p that polarization wave vector can be then written as 2k x sin theta i plus k 3.

So, along this direction we have this new beam created and what is that direction i plus k 3 i is along this direction which is the unit vector along the x direction. So, x plus k 3; k 3 direction is going to be along. So, k 3 direction is going to be along this direction. So, this is the k 3 direction new beam direction, this is the i direction. So, finally, I get the beam to be like this. So, this i plus k 3 direction is shown here.

This indicates that the emitted beam generated due to E 1 E 1 star E 3 third order nonlinearity features frequency is same as of the third beam, but it exhibits different direction the direction is going to be i plus k 3 direction. This is nothing, but the Bragg diffraction of the third beam that is the way we get the diffraction of the third wave. Part of the beam will be diffracted back to along this I plus k 3 direction and the diffraction is created by the two identical interaction of these two identical beams.

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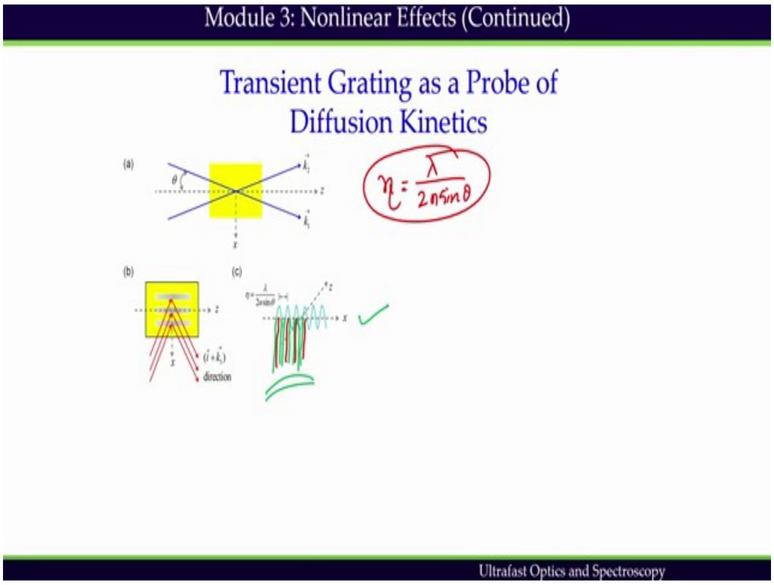

Now, spatial pattern of excited and ground state molecules will be created as I have told you that if I have along this x-axis if I have this intensity maximum here, here, here, here and then intensity is zero at this positions. This positions here, then here, then here, then here, these are the positions where intensities are 0 which means that I will have a spatially varying excited state species and ground state species. Whenever I have intensity zero, it means that molecules are not excited. So, that regime region will contain only ground state species and the region where I have intensity the region will be excited, the molecules would be excited to the excited state.

So, this spatial variation of the intensity created by two identical pulses will also create spatially varying excited and ground state species in the in the medium and the spacing will be controlled by the equation which we have shown already. That is going to be eta it is going to be lambda by 2n sin theta. This is the wave special the spacing will be controlled.

Now, the time delayed third beam which is the probe beam can then be deflected off this grating. In other words their excitation with the pair pulse leads to periodic spatial variation of the complex index of refraction of the medium. Some space in the sample possesses excited state molecules and some in the medium possesses ground state molecules. These spaces are periodic which behaves like a diffraction grating. Now, the third beam is diffracted of the transient grating and in the experiment the diffracted pulse energy is monitored as a function of time delay between pump and probe. The energy of the diffracted beam depends on diffraction efficiency of the transient grating.

The transient grating signal depends on any process which acts to destroy the grating pattern. For example, excited state population relaxation can destroy the grating pattern which reduces the diffraction efficiency. Thermal or mass diffusion along the x-axis can also destroy the grating pattern. Thus by recording diffracted beam energy as a function of time delay between pump that is the pair pulse and probe one can estimate diffusion kinetics of the molecules in the solution. So, when you when you consider diffusion kinetics we can actually write down few equations.

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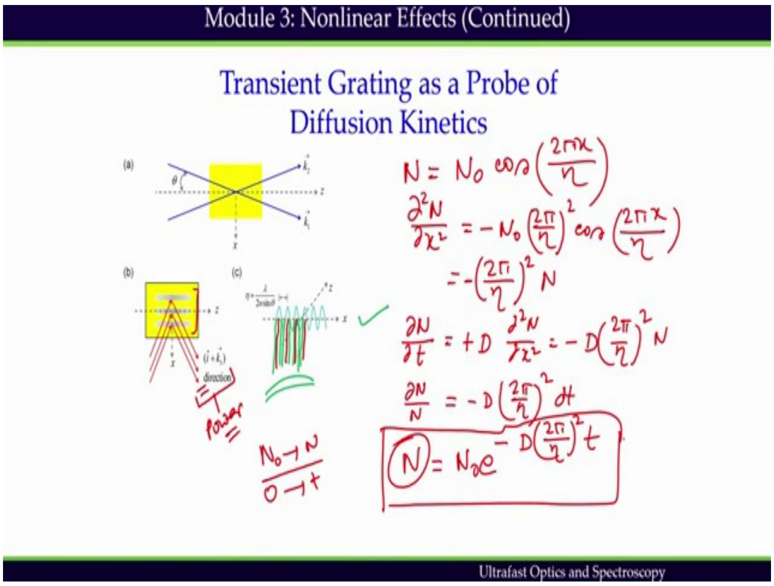

N is the population which will vary along this x axis like this way cos 2 pi x by eta(χ). So, this is the way the population excited state species will vary and if we take the second derivative with respect to x d 2 N dx 2 equals this is going to be minus N naught 2 pi by eta whole square cos 2 pi x by eta which is nothing, but 2 pi by eta whole square multiplied by n with a negative sign. Now, we know that Einstein diffusion equation that is that is going to be dN/dt equals partial derivative diffusion constant d 2 N dx 2 which is which we can write as this can be this is this is positive.

Now, this can be written as minus D 2 pi by eta whole square N, and we can then write down we can integrate this equation we can write down this way d N by N equals minus D 2 pi by eta whole square dt. This is the way we can write down and finally, what we get if we integrate it and then we can within the limit of N naught to N naught to N then within this limit where 0 to t limit, we get final expression as N equals N naught e to the power minus D 2 pi by eta whole square t.

So, as a function of time we see that the change in population due to diffusion and that we can monitor with the help of diffracted energy. If we use a power meter here and if we keep looking at the energy how the energy is changing as a function of time delay between p r pulse identical pulse and the probe then we see that it is changing the diffraction. So, in order to diffract this beam, I need to have this grating sustained and this grating can be washed off due to diffusion and that can be plotted with respect to time following this equation. So, one can find out the diffusion kinetics.

We will stop here and we will continue this module in the next lecture.