Rate Processes

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Module No. # 01

Lecture No. # 34

Reaction Dynamics: Scattering

Hello good morning everybody. So, we were discussing reaction dynamics. Now, last lecture we started to discuss this cross beam experiment, and in that case, we also talked about this angular distribution of products. In that case, two cross beams are used like this and your detector is placed somewhere over here; may be this way, so that it can detect the flux of particles that is coming out of the reaction, that is coming out of collision.

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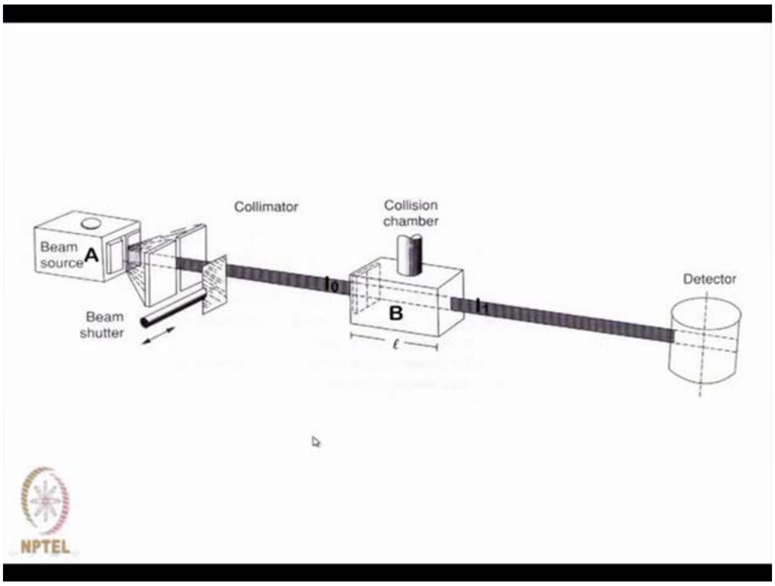

So, now this is a typical schematic of a beam experiment that where you see that this is a beam source. It is basically a single beam, so maybe you can put another beam this way maybe at an angle of 90 degree, this way and you can introduce the second beam second molecule in the collision chamber. So, that will make the crossed beam arrangement.

Now, this is a beam source where you generate gases molecules, and that maybe, like something like, supersonic nozzle or may be just the molecule is coming out due to diffusion. In that case, pressure difference is less, but for supersonic the pressure difference is very high, and in that case you need to introduce carrier gas, but for the other gas, you may select by using a chopper. Here this beam source, then it is a collimator if it is a charged material, I mean charged entities or charged gases molecules, and then, you may put some electric field that will collimate it. You can select your area through which it is passing, you can make it narrower it you can make it bigger. Then there is a beam shutter that sometime it allows the beam to pass through or sometime it does not allow. So, that is why you have to have a shutter.

You have got a collision chamber for the collision process to take place; you need to have a collision chamber and then this is the outgoing side that is the molecules or the mixture of products and reactants unconverted reactant that will go this way. You have got a detector which detects the flux of particles. So, it is a collision chamber, it is typically a gas phase reaction and now the question is we started to have our discussion based on collision theory. Now, why it is so means why collision processes is taken into account in order to understand this chemical reaction dynamics that is molecular reaction dynamics.

Now, collision theory is the is elementary theory, I mean the basic theory which deals with chemical reaction rates and it is thought to be the reason that is collision is thought to be the reason for chemical transformation to take place. So, if there is no collision, then there is no chance of this exchange of atom from one centre to another centre. So, that is why collision is very important and collision is basically a scattering event. That is why scattering theory has been introduced over here to understand the dynamics, to understand the chemical reactivity and how to control chemical reactivity. So, these are the involved associated questions. Therefore, we tend to treat the chemical reaction in the frame work of scattering theory.

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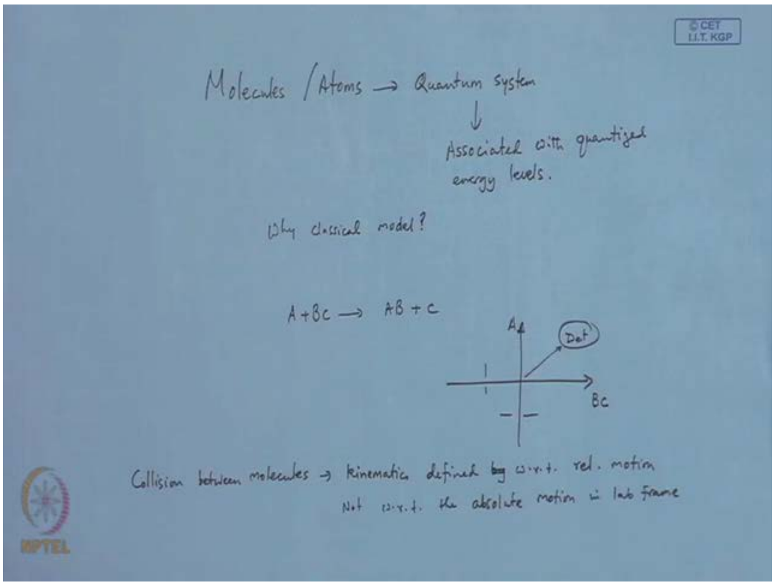

Now, next question is Molecules/ Atoms. These are all quantum systems that are associated with quantized energy levels. Next question, why? Then if these molecules that are the interacting entities are quantum system, then why should we use classical theory. Why not directly quantum theory applied to such cases?

Why classical model, then question is why classical model? Now, the essential physical concepts are much easier to understand in classical picture and classical scattering models are still used even for moderately sized molecules or smaller molecule having atoms may be greater than 2-3. In that case, quantum chemical calculations, quantum chemical simulations are very much expensive, it is time consuming and it is very much expensive. Classical model can explain many things nicely, so that is why classical model is introduced and you already have talked about these types of scattering event. One is elastic scattering, another is inelastic scattering and third one is reactive scattering.

Now, for elastic scattering, total kinetic energy of the initial state of collision partners are conserved. I mean before and after collision dis-conserved inelastic scattering. So, the kinetic energy is transferred to the internal states of the reaction partners but in that case, chemical structure is conserved. May be if the kinetic energy is converted to some vibrational degrees of freedom, may be you will generate vibrationally excited molecules. So, that is why it is not although it is inelastic scattering but it does not relate to any restructuring of atoms within the molecule.

The third one is reactive scattering. In that case, kinetic energy, internal energy states and chemical structure all are changed. So, I mean in that case redistribution of atom may be A plus BC giving rise to AB plus C. So, you see that it is restructure chemical structure is modified, so that is called this reactive scattering.

Now, when it is the question of crossed beam experiment that is to find out the flux and that is angular distribution, so in that case you have two beams this way, another one this way and another this way. So, this is your say BC and this is your A and your detector is placed, detector is here and it will change its orientation. The data which is obtained from the detector is basically your obtained in laboratory frame.

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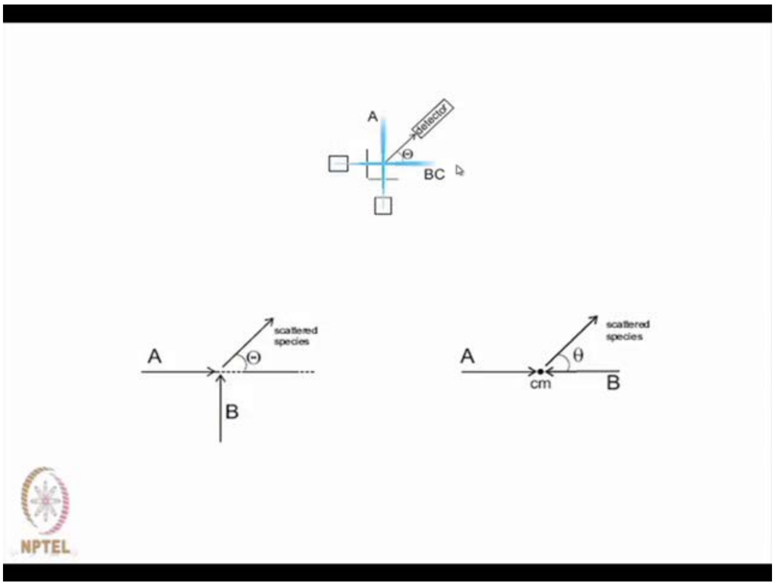

So, laboratory frame means like this, this is your A, this your BC and this is the theta, the angle of the detector that is the angle with respect to may be BC or may be with respect to A. Let us say, it is the angle with respect to BC and scattered species is detected over here. So, you see this is A, this is B like A plus BC, this is a scattered species and these are in laboratory frame of reference. So, you have to convert to the centre of mass system because in this case, it is more important to talk in terms of the relative motions rather than with reference to a laboratory frame. That is why in order and the data is plotted that is the scattered species, the signal for this scattered species is plotted, I mean the flux of this scattered species is plotted in reference to your centre of mass system.

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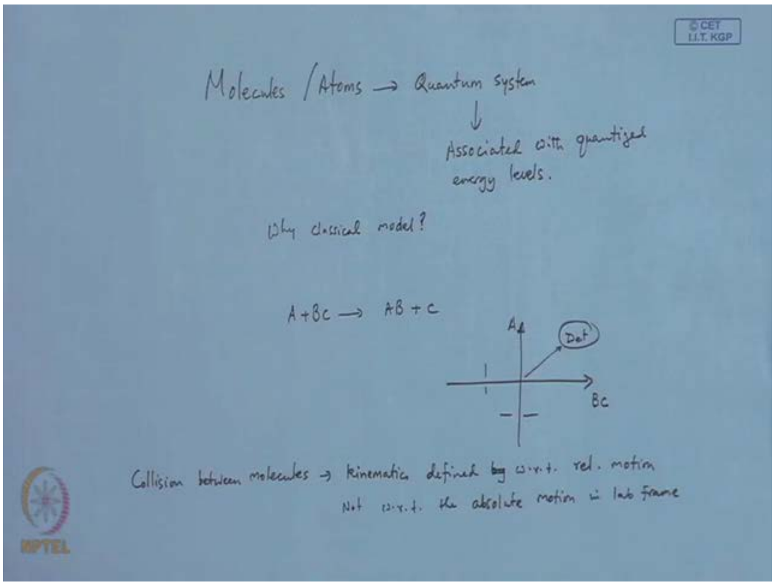

Now, for collision between molecules, the relevant kinematics are defined by their motion relative to one another. So, collision between molecules, the relevant kinematics defined by with respect to relative motion, relative with respect to one, with respect to another and not with respect to the absolute motion in laboratory frame. So, that is most important.

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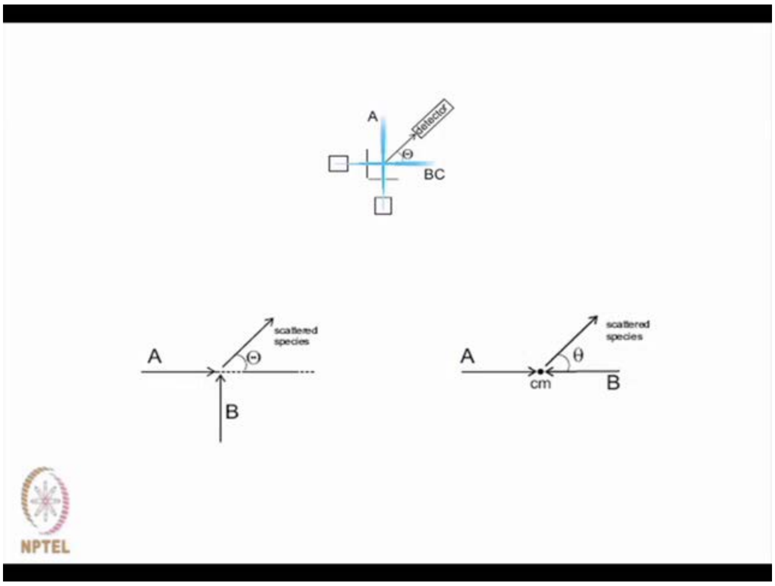

Therefore, we need to have a transformation of the laboratory access system to the centre of mass code in it like this. This is laboratory system; this is centre of mass system. So, in that case, transformation as I told in my last lectures that we never you do I mean for a cross beam experiment, you get the detected signal and then you have to convert it into the centre of mass system. So, how to do that?

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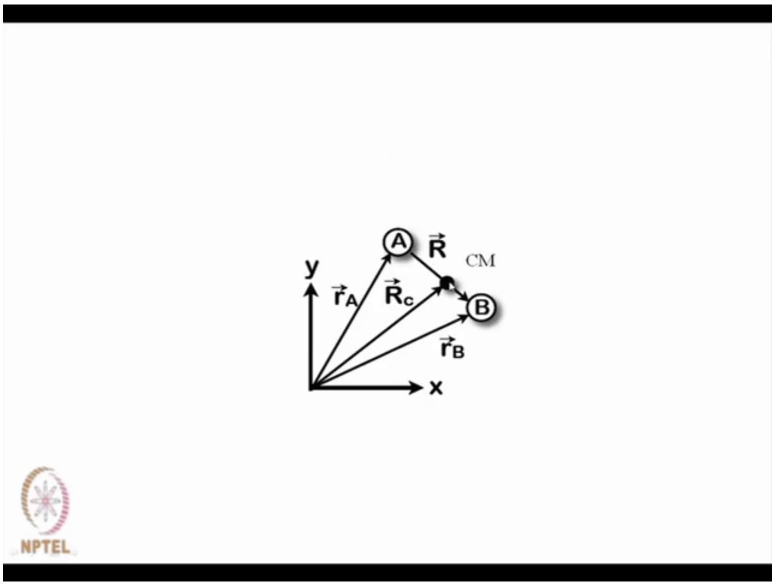

So, this is your centre of mass, this is A, this is B. So, this is rA vector, this radius vector of A, radius vector of B, this is the origin and this is the radius vector corresponding to the centre of mass.

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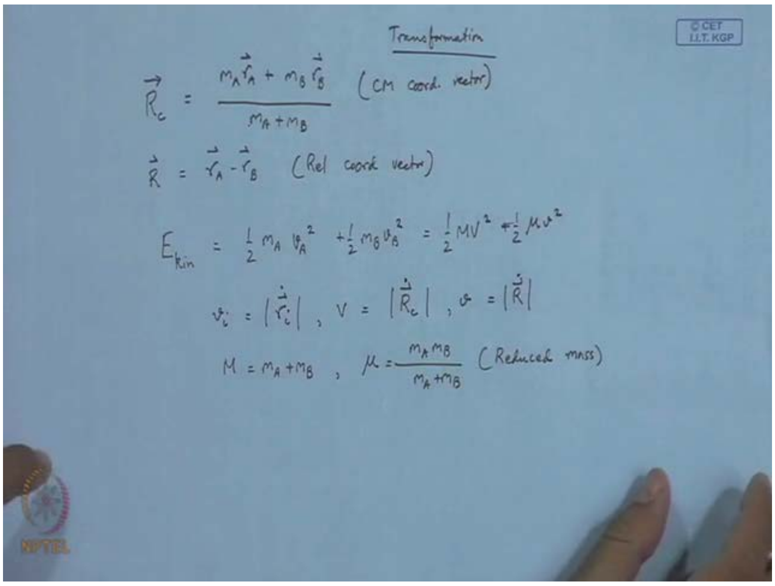

Now, Rc this vector is equal to mA rA plus mB rB divided by mA plus mB. So, this is with respect to I mean this is Rc that is coordinate vector of the centre of mass. This corresponds to the coordinate vector and the relative coordinate vector R is the relative coordinate vector is rA minus rB. It is the relative coordinate vector and this is the centre of mass coordinate vector CM coordinate vector and from vector principle it can be easily shown that the kinetic energy E kinetic energy for this system E kinetic that is the kinetic energy of the system can be written like this half mA vA square plus half mB vB square. This equal to half MV square plus half mu v square where vi is equal to ri. This vector dot v is equal to Rc vector dot and v is equal to R vector dot. This way you can write and caps M is equal to mA plus mB and this reduced mass mu is equal to mA mB divided by mA plus mB. So, this is the reduced mass.

So, this way you can transform. So, this transformation is very important, you have to transform into the new coordinate I mean this is your centre of mass coordinate. Therefore, you need to transform, this means using this concept you have to transform data from the laboratory frame to the centre of mass frame. So, this is the transformation that is transformation, so you have to transform using this concept.

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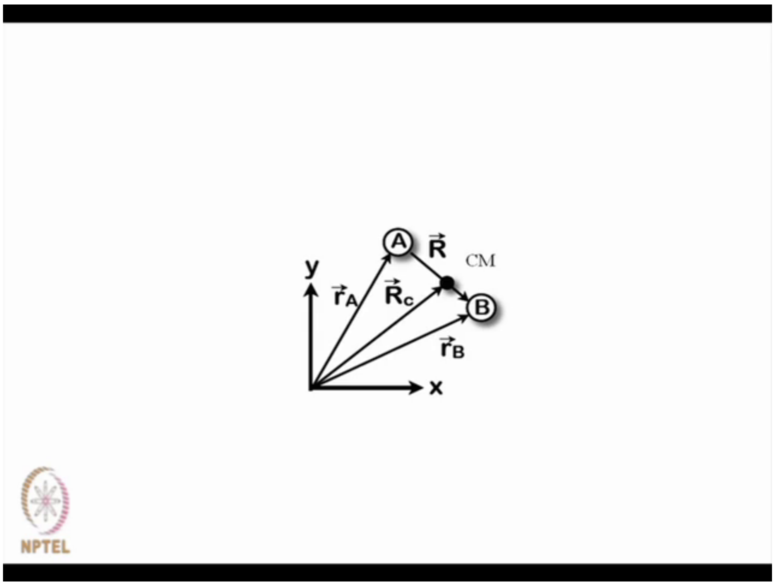

We talked about this differential cross section. Differential cross section means it is your d sigma, d omega is the differential cross section and that you can and I already have told the expression for sigma. If these reactants are not oriented, then it should not depend on the phi angle only; it will depend on theta angle.

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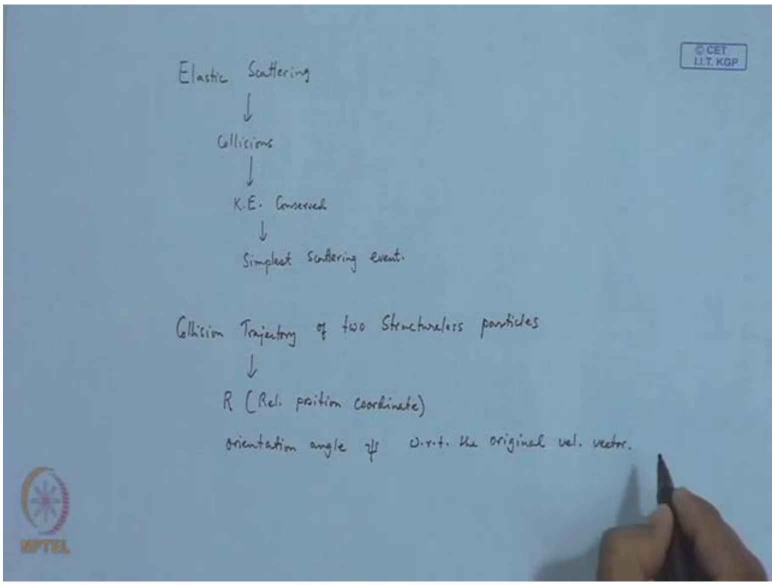

Now, next for elastic scattering as there are three types of scattering of which one is elastic scattering. In that case, collisions happen and kinetic energy is conserved and it is the simplest collisions, then kinetic energy conserved and is the simplest scattering event.

Let us see, we would like to look into the collision trajectory of two structure less particles that is they undergo collision and total angular momentum is also comes up. Two coordinates are there, I mean two coordinates of phi is to describe the relative motion of the collision partners and in that case, one is the relative position vector. In that case, we need two coordinates, one is relative position coordinate and orientation angle that is psi and that is with respect to the original velocity vector.

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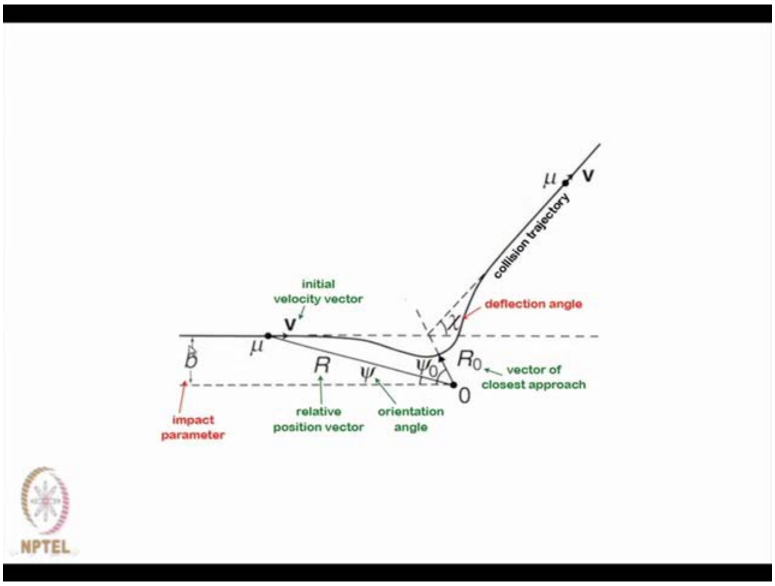

So, let us see what is that? So, you see here, this is the impact parameter and this is the trajectory. You see, just look into the mouse and this is the collision trajectory initial velocity vector and it is there is a depth over here. This is the relative position vector with respect to the origin and this R0 is the vector for the closest approach, psi 0 is the angle at the midpoint with respect to this initial velocity vector, psi is orientation angle that is this vector the angle that this R vector is making with respect to the initial velocity vector, b is the impact parameter and this is the deflection angle. That is the angle that is made by the initial vector and the final vector, this final vector this is the angle, so this is the amount of deflection that has happened. So, if there is no collision or something, then the particle should have adopted this dotted line along this. Now what does this mean? Let us try to see.

So, this means that it is the collision trajectory of the centre of mass system and this solid curve represents a trajectory with initial velocity V and the impact parameter b. This is the relative separation R which is a function of t uniquely defined in terms of distance R and it also depends on the orientation angle psi.

The trajectory is you see, this trajectory symmetric about this symmetric at this point, symmetric about that I mean at this point here and this is the distance of closest approach R0. The final deflection angle is this. Now, in this case if there is no potential, no potential means there is no attractive potential, I mean no potential is acting between the interacting particles, then it should have followed this dotted line that is dash line if there is no interaction potential.

The trajectory is identical to that crest by particle of mass mu that is a reduced mass deflected by a potential VR. It is a potential which is at the origin. If you put a potential at the origin and this if it is like V or VR, if you put VR potential as a function of R about the origin, then this particle of mass mu should have experienced some force and as a result of it, there is a change in path with respect to your dotted line. In this case, we can imagine the trajectory as the trajectory of a projectile of mass mu and which is seen by the observer who is placed on who is who is located on b. So, this is a representation of the collision trajectory.

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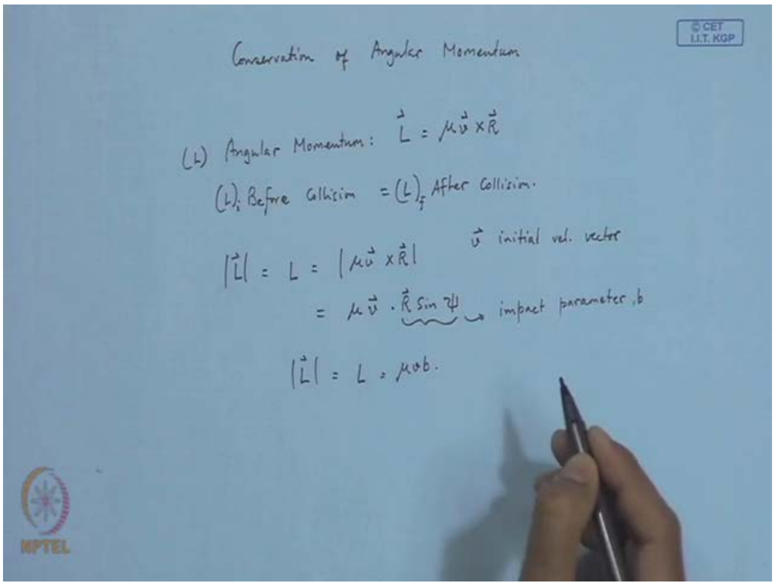

Let us look into the conservation of the physical quantities. As I told that conservation is there, so let us look into that conservation of physical quantities, conservation of angular momentum. So, please refer to this figure here. Now, angular momentum is represented by angular momentum which is L is equal to mu v cross R. So, angular momentum L before collision is equal to L after collision.

So, mod L is equal to L which is which is equal to mu v cross R and in this case, v is the initial velocity vector which is mu v dot R sin psi. Now, this is one expression you can write in this way and what is b, b is basically R sin psi R sin psi means you can replace this R sin psi with impact parameter. So, you can relate this with impact parameter b, so ultimately L equal to L which is equal to mu v into b.

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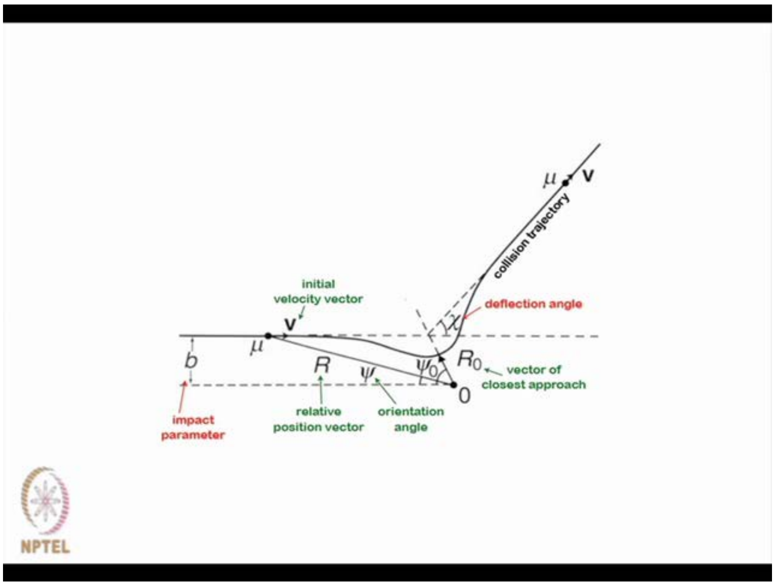

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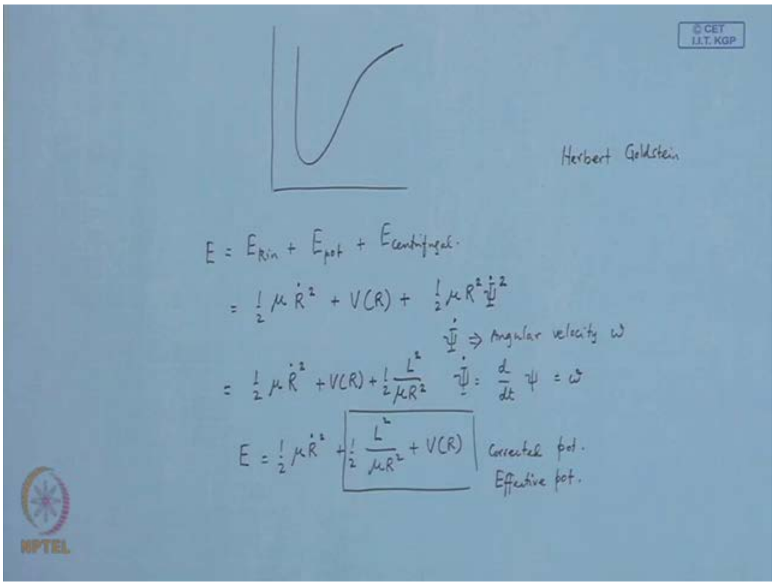

Now, what about total energy of the system? The same way for the physical quantities what about the total energy of the system? Total energy is the means if you recall such type of system where there is like potential energy is having this type of form. So, if you consult a standard classical mechanics text book, then you will be finding that E will have three components- E kinetic plus E potential plus E centrifugal. That is why the term centrifugal barrier has been introduced because a barrier is phased and which looks like as if centrifugal force is operative.

So, for a two particle case if you plot the potential energy I mean total energy of the system, then it will have these parts and you can write each component in this way that half mr square like mu R dot square plus V R plus half mu R square psi dot square. Now, psi is the angular velocity omega. So, psi dot is basically d dt psi dot is angular velocity d dt of psi which is called the angular velocity, so that means this how this orientation is changing this angular velocity as a result of that this is changing. So, you have got this one, so this R is changing, therefore the psi is also changing. So, this is your psi, this is changing, this angle is changing with respect to this, therefore with time psi is changing. That is why this psi d dt is used which is equal to omega, the angular velocity.

So, basically you can write from this half mu R dot square half mR square plus VR plus half L square by mu R square. So, that means your total energy is equal to half mu R dot square plus half L square mu R square plus VR. This part is the corrected potential; it is called the effective potential. It is the normal potential plus the as a result of this centrifugal force, so it is called the centrifugally corrected effective potential.

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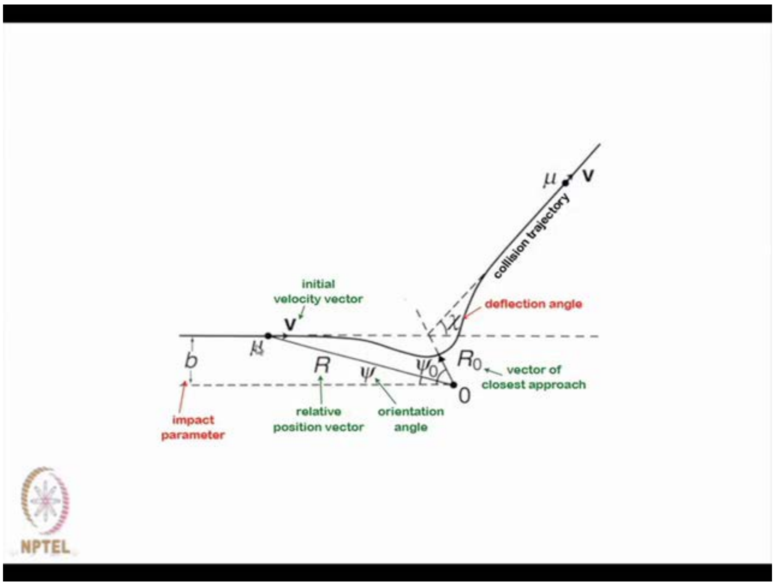

So, this is the centrifugally corrected potential. Now, centrifugally corrected potential is like it is the centrifugal energy that is energetic enough in the rotation of the position vector. So, that is why a centrifugal force is coming into action, therefore this vector is changing. So, when it is here, your angle was different, when it is coming, this vector position vector is changing its angle.

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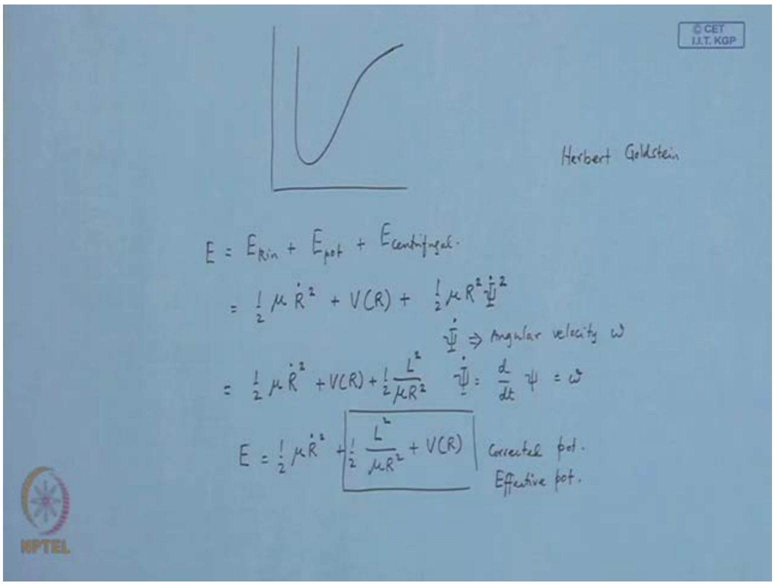

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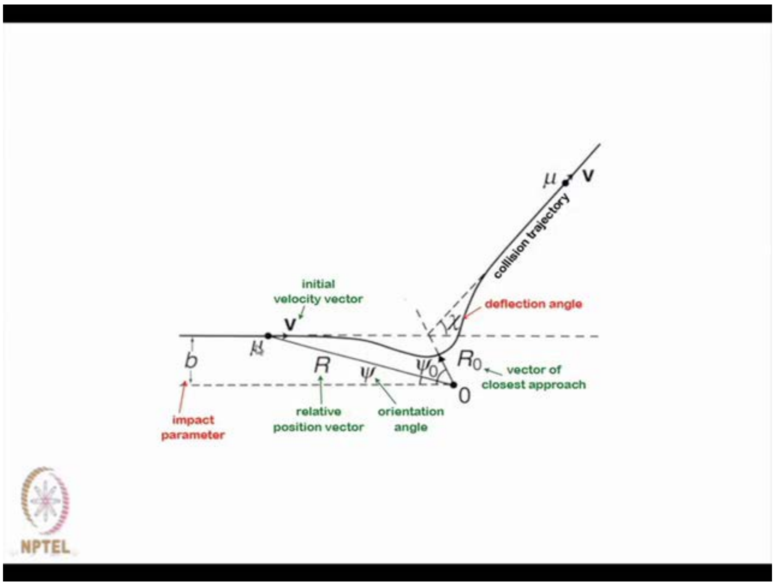

So, this collisional angular momentum L is equal to angular momentum associated with the rotation of R about the psi. The effective potential of the collision contents both that is the interaction potential as I told that is the interaction potential and this centrifugal energy that is because of this movement it is changing. So, that is why effective potential term has been introduced over here because you see again if you see like this that this is changing, this length is changing because as it is coming this way. So, your this vector you see what is happening that this is your starting vector, it is changing its position. This angle is changing this way think of this tip when the particle is here that is mu particle. This particle of mass m when it is moving this way, this vector this relative position vector, the tip will do like this. Therefore, your this vector will move this way, so additional rotation.

So, angular momentum associate with the rotation of R. Therefore, if you add up this energy contribution to the total energy of the system, then your potential is now become normal potential plus interaction. I mean normal potential means it is the interaction potential. Interaction potential means may be attracting may be repulsive.

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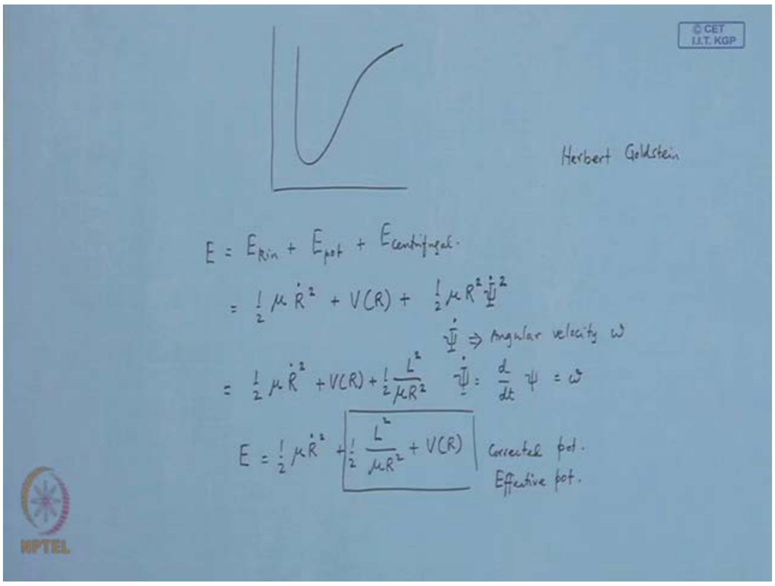

So, interaction potential plus this centrifugal potential, I mean centrifugal this energy contains this centrifugal energy because of this rotation of the R vector and of course, the interaction energy. So, that is why it is called the corrected or effective potential. So, you are advised to go through any standard classical mechanics text book like Herbert Goldstein where you will be finding a detailed account of this process. How this I mean this centrifugal energy is coming? Centrifugal potential that adds up to your interaction potential giving rise to corrected or the effective potential or centrifugally corrected potential.

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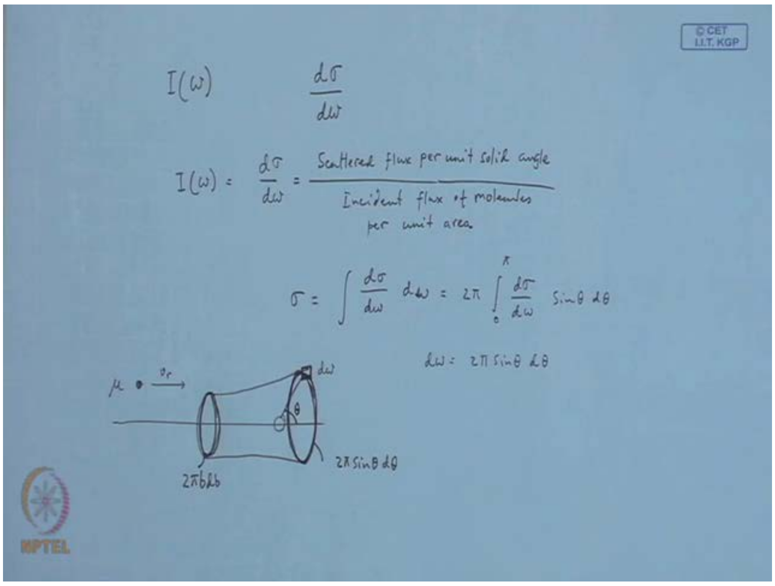

So, next as I already told that like intensity of the scattered molecule at a solid angle omega that is the how to calculate that intensity of the scattered molecule or the flux of the scattered molecules at an angle I omega. The flux of molecule associated I mean flux of molecule scattered into the solid angle omega.

So, in that case this is related to your differential cross section in relation to differential cross section d sigma d omega. Now, what is this I omega? Which is d sigma d omega which is equal to scattered flux per unit solid angle divided by incident flux of molecules per unit area. This cross section as already told you that cross section sigma can be written as integral because it is an you have to average it out for different, you have to total integral cross section; you have to find it in terms of the total angle.

So, that is why total cross section can be calculated by d sigma, d omega and this is your twice pi integral 0 to pi d sigma d omega sin theta d theta where d omega is nothing but 2 pi sin theta d theta. This way you can find out. That is about this experimentally, how to observe because this way and what is the experimental arranged in that. This is your mu mass, this way it is vr and this is your d omega and this area I am making it a strip like thing, this is also a strip. So, this is your 2 pi sin theta d theta and this is your 2 pi b db and this is your angle theta, maybe in laboratory frame. So, you have to have your detector over here, I mean you have to detect in solid angle d omega.

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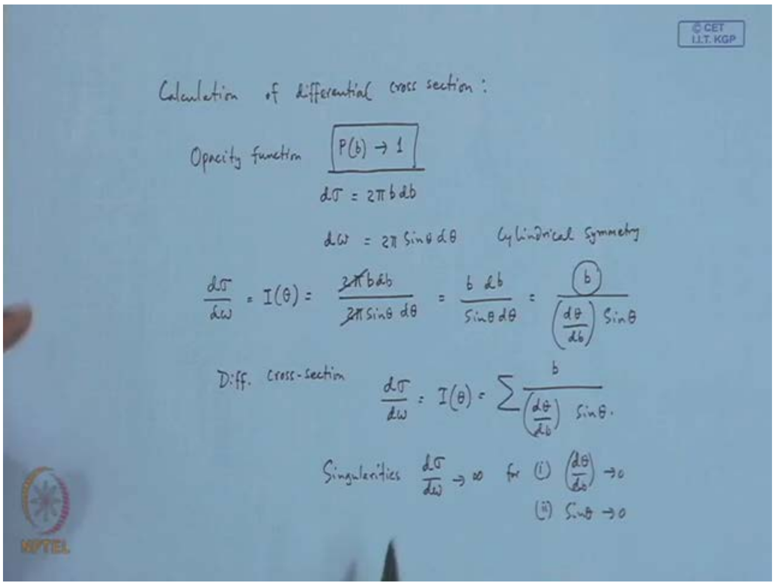

Next, calculating the differential cross section. How to calculate the differential cross section? In this case for simplicity, so calculations of differential cross section. So, in that case the reaction probability functions or may be the opacity function, let us take this opacity function Pb to the unity. In this case, if this is one the differential cross section can be written as if this is one d sigma is equal to 2 pi b db. You can check it, it can be written in this way and again because of scattering problem. Since, the scattering problem is of cylindrical symmetry, the solid angle element d omega can be written as twice pi sin theta d theta. Therefore, this is because of solid angle and a cylindrical symmetry.

So, assuming scattering to be cylindrical symmetry and the solid angle element will be that is d omega will be written as this. Therefore, differential cross section d sigma, d omega which is equal to I theta can be written as twice pi b db divided by twice pi sin theta d theta. So, just recall this previous diagram, you should be able to do with this diagram, look into this diagram; you should be able to get some idea.

So, I theta that is differential cross section which is this, therefore 2 pi 2 pi gets cancelled. So, b db divided by sin theta d theta. Therefore, it is your b by d theta db sin theta, so therefore differential cross section has got relation with b. Of course, your in this case for simplicity your opacity function has been taken to the closed unit or it is unity. Therefore, it depends on b and impact parameter b of course, sin theta and d theta db that is variation of theta with b that is this factor.

Now, the next question is the value of b may not be unique value, may be more than 1 value of b may contribute into the same, I mean more than 1 value of b may be relevant for the same scattering angle. So, in that case what you have to do? What you have to do that in that case, you need to take this summation, so summation to get the overall contribution. Overall contribution means contribution from different impact parameters means same scattering angle but may be that same scattering angle could be due to different b values.

So, in that case we have to take that into account as well, therefore we need to sum over those things. Therefore, the dependence that is differential cross section finally comes out to be, so differential cross section can be written as d sigma d omega which is equal to I theta which is equal to sum over b, then by d theta db into sin theta. So, d theta db into sin theta.

So, several interesting aspects may be obtained from here, more than 1 that is in one case suppose you have got two things that is differential cross section. You see that it depends on b but in the denominator you have d theta db and sin theta. So, what is happening that this differential cross section will have singularities? So, singularities that is d sigma, d omega will tend to infinity as in one case, either this or that becomes 0 that is tends to infinity for number 1 d theta db tends to 0 or number 2 sin theta tends to 0. Sin theta tends to 0 means one situation and d theta db tends to 0 means another situation.

So, these are the two possibilities, I mean two extreme situations that one might be looked means we might look into. So, singularities therefore we have got two situations. So, we will take this up in the next lecture and I am going to elaborate into that. Before that, we have a quick look.

We have started with crossed beam, I mean started with crossed beam experiment and then we told that this classical scattering is important because quantum mechanical calculations, although they are accurate because these are quantum systems but for 3 or more than 3 atomic system. I mean it is very difficult, it is very time consuming and it is costly; it becomes costly in that sense.

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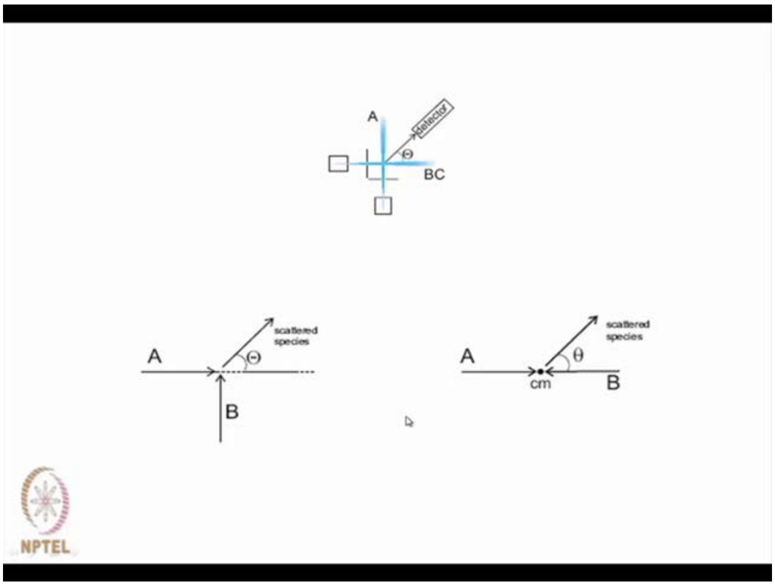

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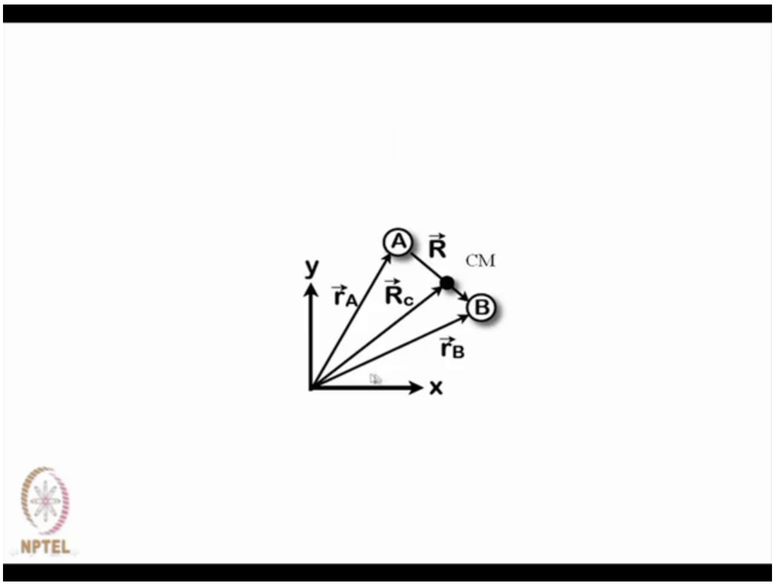

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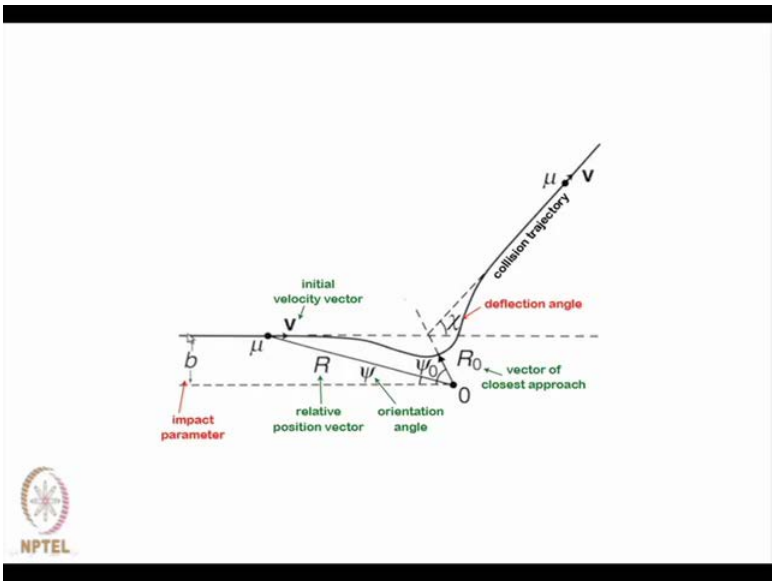

So, that is why we take up this classical thing and for your two beam experiment, you have to convert from the laboratory frame to centre of mass system and that we have discussed how to do that. Then we talked about this kinematics, I mean how to do this transformation. Then we talked about elastic scattering and given this, we discussed this figure also that is the scattering diagram, I mean collision trajectory how means the path that it is following.

Then we talked about this conservation of various physical quantities, then how this idea of centrifugally corrected potential. Finally, we talked about this calculation of the differential cross section and how two situations can be obtained. So, when d theta db is 0 or may be sin theta equal to 0, then two singularities may be obtained. So, these will be taken up in the next piece of lecture. So, till then thank you.