

Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'
Prof. P.C. Deshmukh
Department of Physics
Indian Institute of Technology-Madras

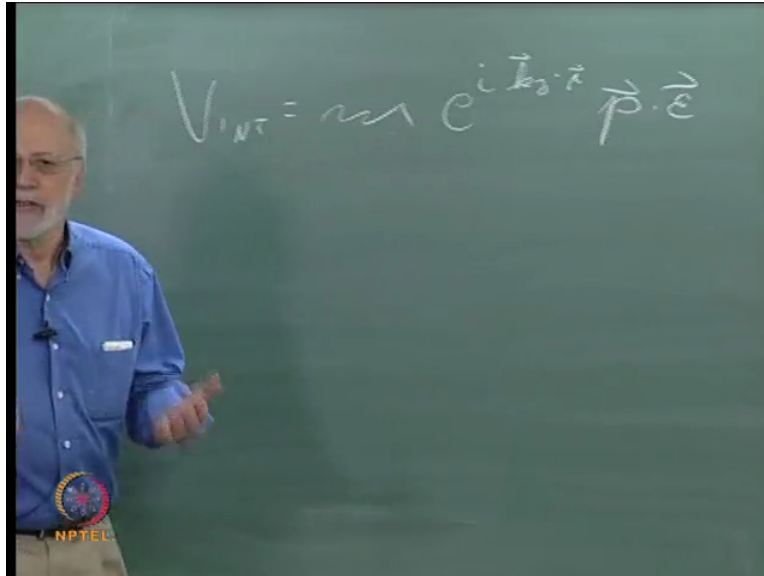
Lecture 44
Photoionization and Photoelectron Angular Distributions

Greetings, we are very privileged to have today Professor S. T. Manson will give two guest lectures in this course and today is the first one. So, today we will review the topic of Photoionization in which he has expertise for a very long time and anybody reading literature in Atomic physics would have come across his papers for well over four decades now.

So, what you see, thank you? And whether it is a privilege or not you will decide after the lecture and you may not agree. Well, today what I am going to do is enlarged on what you have already learned about photoionization starting perhaps with some things that you already know. It is a matter of fact the first invited talk I ever gave never mind, how long ago it was. The gentleman who invited me gave me some very useful advice.

What he told me was your audience is always grateful for anything that you tell them that they already know and that is extremely good advice, because it connects with the audience. If you start off too high you have lost them to begin with. Now, I am hoping that some of the things that I say in the beginning you have already had in this course and know something about. So, let us start.

This is very you know from my point of view it is very low tech. There is piece of chalk a blackboard and some notes scribbled to keep myself more or less in order, okay. Photoionization that is the interaction of ionizing radiation, light ionizing electromagnetic radiation with matter and we are going to talk specifically about photoionization and atoms because that is what I know about.
(Refer Slide Time: 2:37)



And to begin with light and matter the coupling goes something like this the interaction Hamiltonian is a bunch of constants here and then e to the $i\mathbf{k}\cdot\mathbf{r}$ $\mathbf{p}\cdot\mathbf{e}$ and what these things are this is the wave number of the light this is the momentum of the electron that is the polarization of the light. This is hard. And so we simplify things.

And if the wave number of the light is small enough that is if the photo of photon energy is low enough then for the typical size of an atom this is a small number. Now, what do we have when we have e to a very small exponent you can make a Taylor series expansion, you know. Like e to the x is $1 + x + x$ squared over 2 etc and okay. How far shall we go to truncate it, you know.

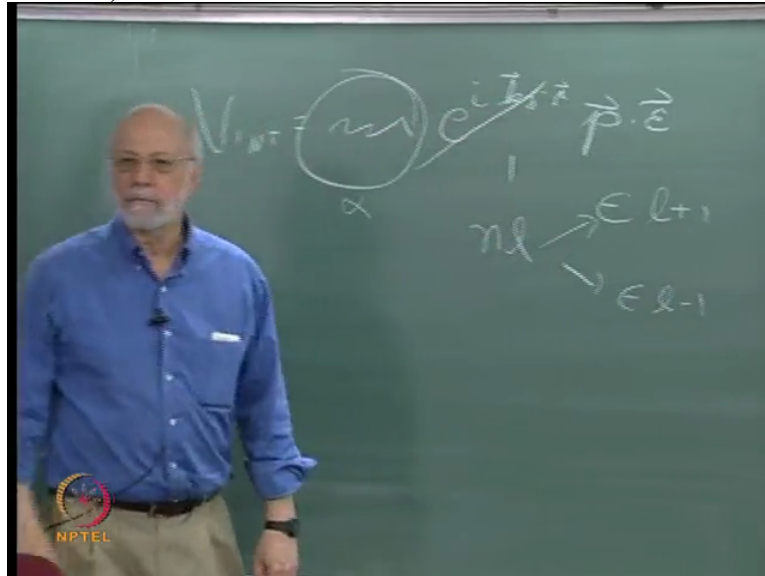
So, you know, you do not want to go to infinity; How about one? That makes it a lot easier. This for historical reasons is known as the dipole approximation. Now, is another, there are several important things about this interaction: Hamiltonian aside from, this dipole approximation. Number one is that, it interacts with a single electron; does not interact with two electrons; it does not interact with three electrons; it is a single particle interaction.

That is very important. Secondly, this is small. A matter of fact it is of the order of alpha, the fine structure constant. Now, the fine structure constant is what it is? It is roughly 1 over 137 or taken roughly it is one percent point 01. And so, when you get, remember, when you get a probability or a cross-section, which is the absolute square of a matrix element, you get alpha square in there.

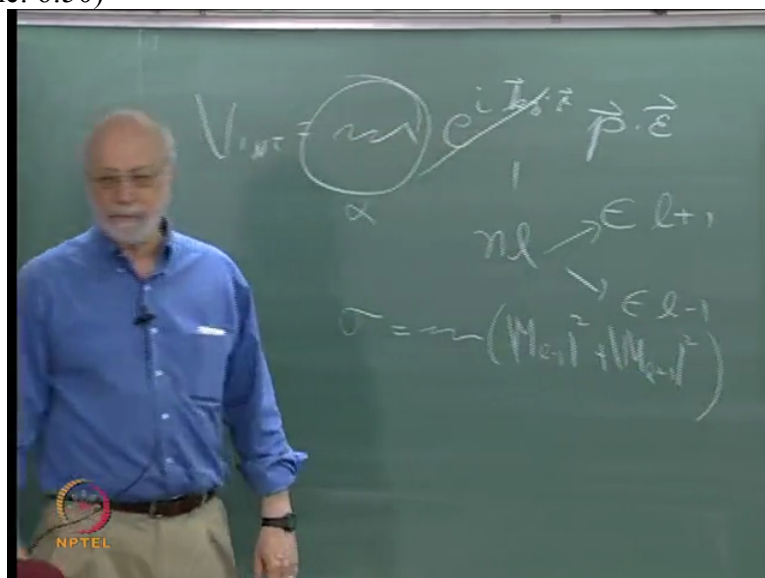
So, light really does not perturb the system very much. So, it is an excellent probe of the proper of the properties of the target system. You see, When can use other probes electron or proton? There in the coupling instead of being of the order of alpha, there is the order one.

So, when you use those as a probe you get a kind of a concatenation of the properties of the target and the properties of the interaction.

Here you can get rid of the properties of the interaction because they are really small. That is a, that is another very important thing about photoionization okay. Then, using angular momentum rules, you get selection rules in photo ionizing transitions. (Refer Slide Time: 05:53)



In other words if you started if you are photo ionizing an nl electron of an atom or molecule or anything actually you have certain selection rules namely that this can go to a final state. I write epsilon meaning it is ionizes some energy in the continuum epsilon $l + 1$ and epsilon $l - 1$. In other words, you can have that is the selection rules l to $l + 1$ or -1 . And the cross section or the probability is made up of the sum of the absolute squares. (Refer Slide Time: 6:50)



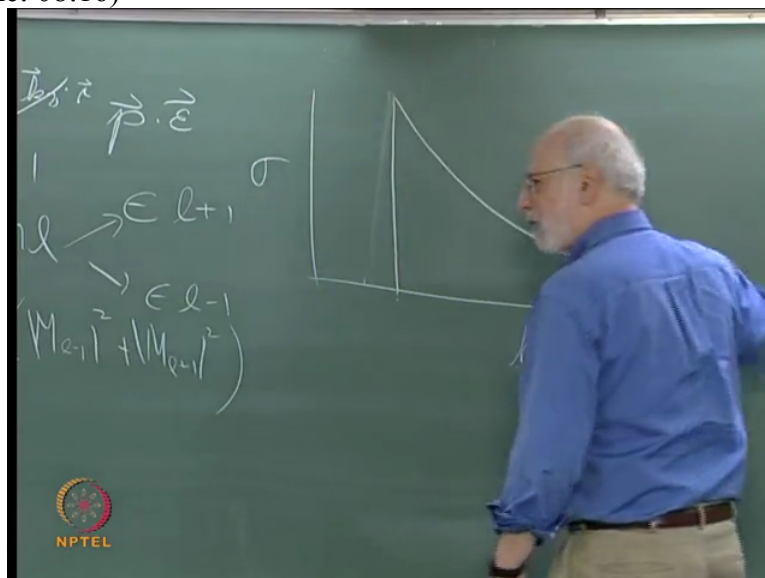
So, in a general sense, the cross section for photoionization is again a bunch of constants. We do not worry about the constants from now. And M_{l-1} absolute squared plus M_{l+1}

absolute square. And if you doing a calculation, this is what you have to do, Oh, in many electron atoms it gets Messier and if you put in relativity it gets Messier. But this is the fundamental idea.

It is the sum of the absolute squares of the various matrix elements we sometimes call them amplitudes. Now, at this level of approximation I want you to understand the approximations that we have made. This is first order perturbation theory. However with this alpha here, first order is really very, very good because the next order is down by a factor another factor of alpha and alpha is smaller than 1%.

So, first order perturbation theory is good. And if you are at low energy, this is very good. So, while it is not absolutely exact it is pretty close to exact. And so, using this, for the hydrogen atom, you can do the calculation. We say exactly. However, exactly it is kind of exactly ish and what ish means is uh..

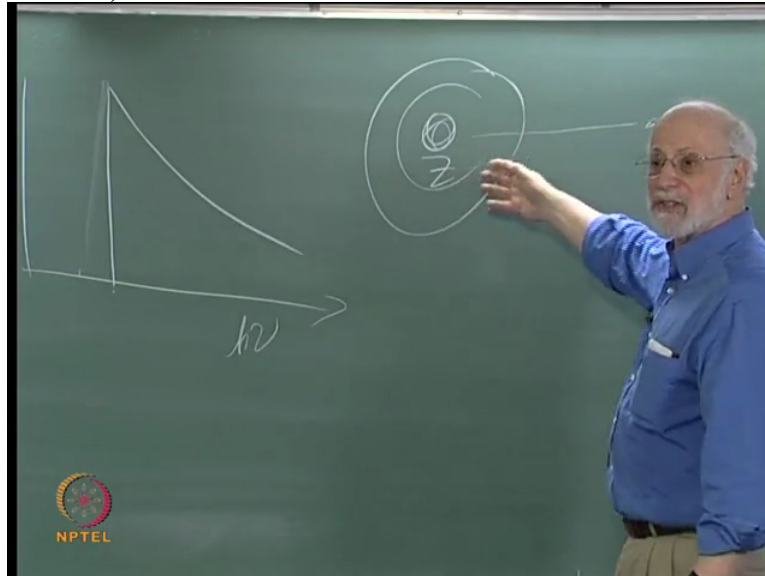
(Refer Slide Time: 08:16)



But anyway, at this level we can do hydrogen exactly, the hydrogen atom exactly. And we find a cross-section or probability with enter. This is the photon energy, this is the cross section and it looks something like this: whoops, is supposed to be a much straighter line. It has some threshold energy and falls off monotonically. It was originally thought that for all atoms, things behave this way. Not true.

ah. If you do a hydrogenic model of an atom that is assuming ineffective z and do the calculation, well, it is this thing scales would see. But everything looks like this. However, with real atoms things are different experiment tells us that. You see, to do even approximate, what happens in a real atom? You have to take the electron or the electrons of the atom, in some realistic potential.

(Refer Slide Time: 09:46)



Now, a realistic potential, let us say, you have some many electron atom charge z . You kick out an electron, that electron when it is out here, sees a singly ionized system. So, it sees as z of 1 when it is all the way in here right next to nucleus it sees as e of capital Z . So, you need a potential V of R which goes as capital Z over r , r goes to 0 and goes as 1 over r actually-attractive, for r goes to infinity.

This, this too is really important. If you use a potential, which does not have those properties, you can get complete nonsense. And if you look back in the literature, before people use this and just use the effective Z 's in the calculations, that is what they got and okay. So, in order to calculate this, you have to calculate amplitude, a matrix element, as a word of this thing.

I am not going to go into the tale about how you do it, but look the matrix element from some state. I and some final state is just initial state the interaction, final state. Now, as I mentioned, this is nearly exact. So, if you get an initial state wave function and a final state wave function, that are close to exact, you get a very good answer.

However, for real systems for multi electron systems getting initial state wave functions and final state wave functions which are nearly exact is really difficult. So, one has to make some approximations. You see the Schrodinger equation I am going to do essentially everything non- relativistic. All we are going to talk about the Schrodinger equation rather than the Dirac equation.

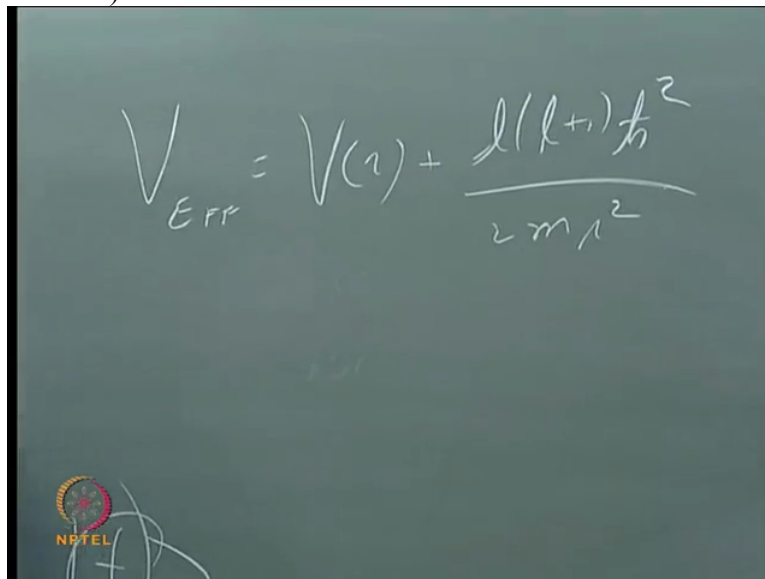
Meanwhile, the Schrodinger equation is a partial differential equation. Fundamentally we know two ways of solving partial differential equations, exactly. One of them is separation of

variables; the other one is guessing if you cannot do either of those two you have to use approximations.

Now, sometimes we can get very good approximations. And but, let me mention that for more than one electron. We know no way of separating of separation of variables. Maybe there is some coordinate system that we have not figured out yet, where you can. But nobody's figured that out. So, one has to use various kinds of approximations. Anyway, we will come to that. Now, so, the electron moves in some potential like this.

However, if you remember, if you make this approximation of a single particle potential, that is just a function of scalar r very important. Scalar r the Schrodinger equation is then separable okay. However, you get kind of a funny equivalent one dimensional equation. Why is it funny? Because you have an extra term in there you have a house oh I call it an effective potential which is the actual potential plus the centrifugal potential.

Any that is just like in classical physics, if you have a rotating coordinate system, this is the i and you are just looking in the radial direction, they used to call them fictional forces. I do not think they do anymore. I am very old and that is that's what they used to call them. (Refer Slide Time: 14:28)

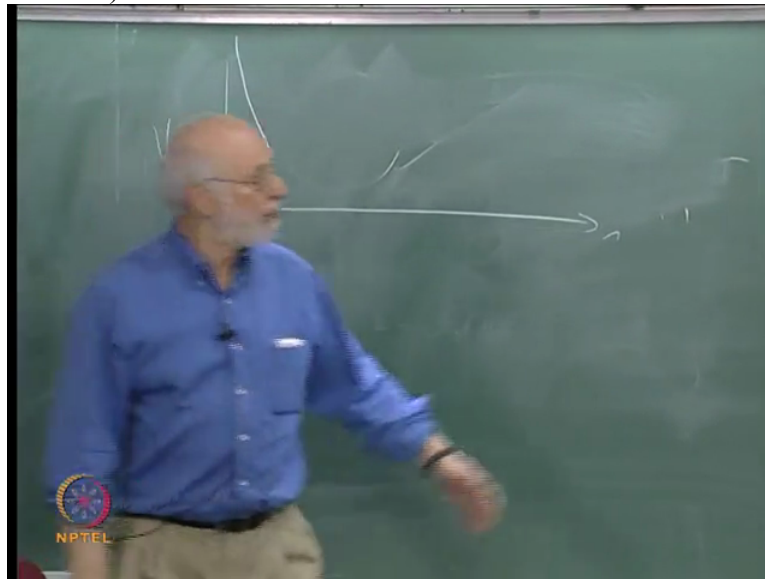

$$V_{\text{eff}} = V(r) + \frac{l(l+1)\hbar^2}{2m r^2}$$

And anyway, so, you have this V effective which is the V of $r + l$ of $l + 1$ h bar squared over $2m r$ squared. No. this is just like in classical physics, where the kinetic energy due to rotation is the square of the angular momentum, over the yeah, with a one-half the square of the angular meant one-half l squared over the moment of inertia.

What is the moment of inertia of a single particle one have? you know, $m r$ it is just $m r$ squared; that is what this is, that is all. However, just considering this, you know, without

doing any detailed calculations. Just considering this, have some consequences, because this V of r is attractive. This is repulsive anybody who has ever swung something around knows that that force is repulsive because it tends to know.

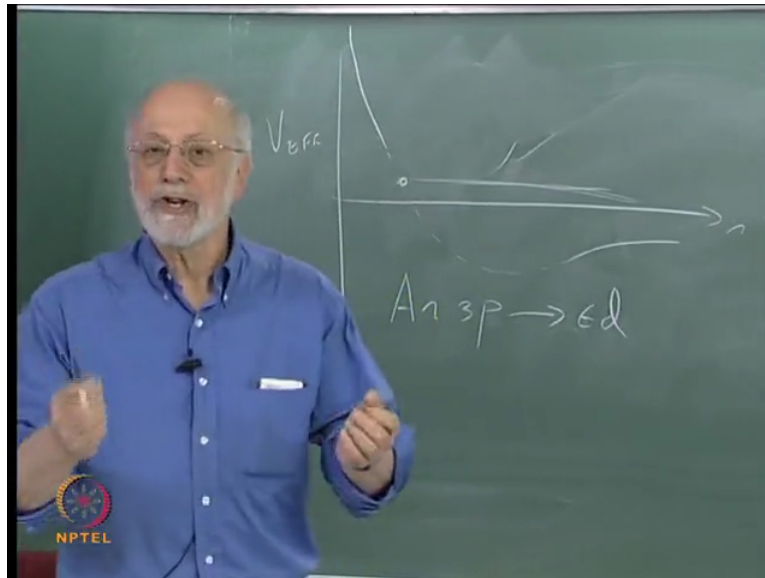
If you have ever seen in the Olympics the Hammer throw, would they go like this, we are just using this okay. Clearly at small distances, since V goes as 1 over r and this goes is 1 of r squared, that dominates. At large values of r 1 of r , 1 of r squared, this dominates. (Refer Slide Time: 16:08)



So, what do we know? If I draw the V effective versus r we just show at least four nonzero l , talk about that for a moment, you get something at small r which goes like this, because it is just this behaviour. Something a large r . On the other hand, this behaviour dominates and you notice that minus sign a . I wrote it small but it is really minus it is attractive. So, it looks like this. And how they meet in the middle, is of importance.

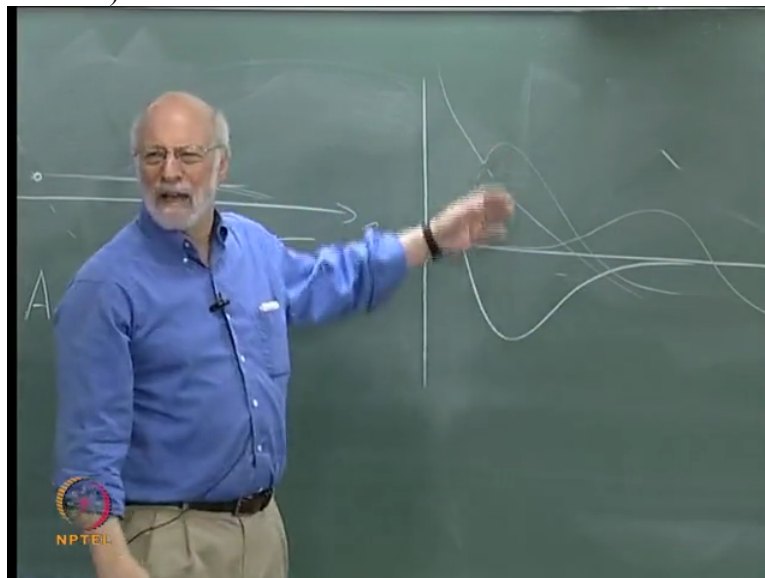
So, you know it might be it might be something like this. Say just to give an idea. So, the electron moves in the field and makes a potential, effective potential, something like this. As l gets larger and larger, this gets bigger and bigger. And so, what this means is, that it is some given energy. It is like this, the wave function.

Let us talk about the final state to the moment wave function, of the final state; this is the classical turning point. It does not mean that there is no wave function inside it. Of course, however, what it does mean is that in the classically forbidden region, the amplitude of the wave function is small. In other words, this angular momentum barrier pushes the wave function amplitude out. What is the consequence of that? (Refer Slide Time: 18:34)



Let us consider a particular transition one that I happen to know about and we are going to talk about Argon 3p. Now an Argon 3p the major transition is going to be 2 epsilon d. It turns out that, in almost all cases, the major transition is l to $l + 1$ as opposed to l to $l - 1$. Both are allowed, you need to have both. But that is the major transition. Now, what happens on a graph?

(Refer Slide Time: 18:59)



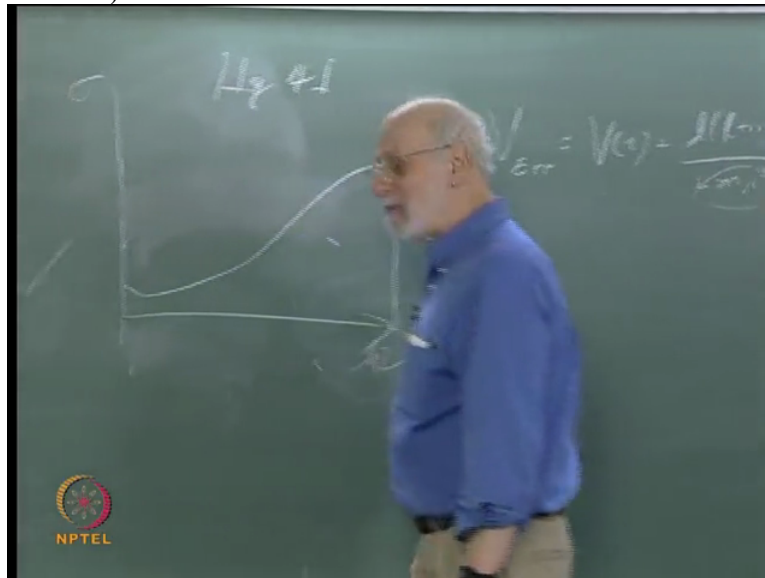
Something like this: This is the following 3p wave function looks. Maybe something like this: However, the d potential and so at say right at threshold the d epsilon V might look like this. And what you see here is a very, very little overlap here. Remember, this is what we got. If the initial and final state have no region of overlap, the matrix element is going to be zero. If they have a small region of overlap it will be small. And what happens as the energy goes up, well, if the energy goes up like, if it is up here, it will look more like this. Ooh! A big overlap here, what does that mean? It means this matrix

element is going to increase with energy. Remember well I have erased it but the cross section, the sum of the absolute squares.

So, what that means, as far as across the cross sectional probability is concerned, it is going to be smaller at this. This is as a function of e let's say this is the threshold energy this is $h\nu$ it is going to look something like this and then eventually as it moves is energy gets higher moves in further it starts to oscillate in this region it is kind of oscillates itself to death.

So, rather than this kind of behaviour we get this, this thing is known as a delayed maximum. It was first discovered, Oh about 45 years ago. I am old enough to remember when it was discovered. And and explained and you can have much more dramatic cases, a really dramatic case is the 4f state of mercury, because the main transition is 4Hfg and in that case the cross section looks something like this:

(Refer Slide Time: 21:30)



This is then Hg 4f it actually drops off a little from threshold but that is due to the f 2d the l to l -1. But you see the h that is l equal four, that is really large. And it pushes the wave all the way out. And it looks something like this: And this maximum rather than being at threshold is. I think it is about 140 eV above threshold. That is a lot. I remember when people first saw this.

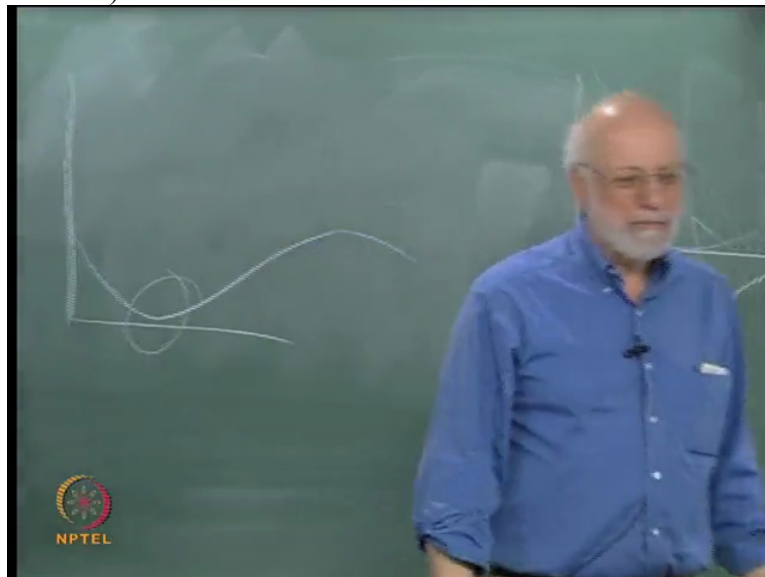
You know, they did the cross section was so small here that when they looked around here at this energy, they could not see anything. But when they got up here they saw the 4f photoelectrons. Their explanation was these were experimentalists you understand. Their explanation was that the threshold energy, was photon energy dependent. That is obvious nonsense. It does not.

Oh, they were very well known people who have that in their papers. It was obvious nonsense. And it did not fit with quantum mechanics. As I say these were just people who measured it and they said, you know, how can you because you know for measuring around here, remember, the Einstein relation. If you know the photon energy and you measure the photoelectron energy then you know the binding energy.

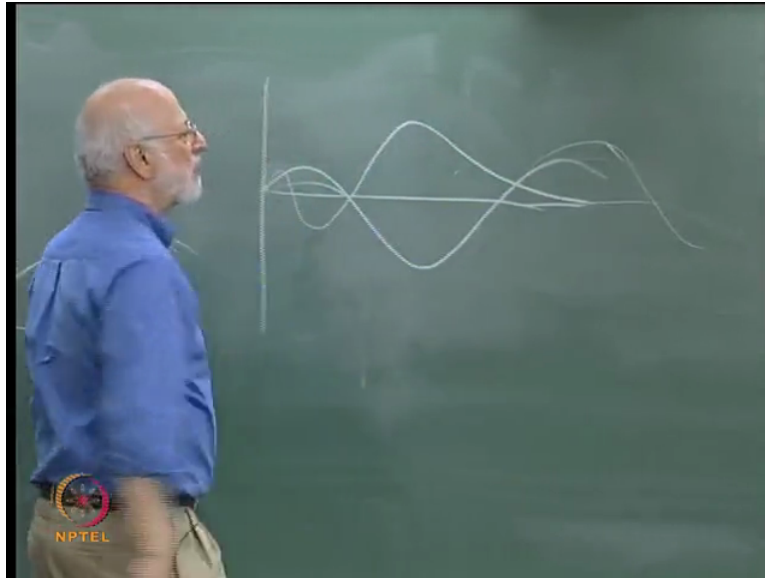
But they measured it above the binding energy here and I could not see anything. Is yeah the binding energy must have changed. What a slap, I mean, it was just elementary quantum mechanics shows that that could not possibly be. Anyway, so, this business of a delayed maximum is ubiquitous. It is all over the periodic table. I am, the only case you do not see it, is for a wave that like a s transition because $s\ l = 0$ you do not have this.

And so what is interesting here is that with a very, very simple model, you can explain this phenomenology, some phenomenology. There is another interesting thing that we find. It is actually first found experimentally. I think it was in 1928. Now, that I do not actually remember, I was not around in 1928. And and that is, some cross sections were found to behave like this.

So, as a matter of fact was, it was the outer shell of the, of the alkalis sodium etc. And the cross section is behave something like this:
(Refer Slide Time: 25:02)



It was a minimum. A very, it was not quite 0, but awfully close. It was first discovered by a British experimentalist by the name of Ditch Burn, 1928. He went back to it in the 40's and it was explained in the later 40's, by very well known British atomic theorists, by the name of David Bates. The explanation was the following.
(Refer Slide Time: 25:45)



And in me, this was the outer shell of sodium the sodium 3s which looks something like this. Remember 3s has two nodes and that is kind of thing. They at threshold board zero energy. The continuum wave function it is kept out a little bit because you have centrifugal repulsion. But it is only $l=1$, so it is not tremendous; but it looks something like this.

So, and what happens out here does not matter, because but the important thing is: the major overlap is this region, right. You have a positive initial state; a negative final state wave fun in that region, the product is negative. If you go to higher and higher energy this moves in and eventually you get something like this, where the main overlap is positive.

You go from negative to positive somewhere if it is continuous, somewhere in the middle, it goes through a zero. And this was the explanation. And this remains an isolated curiosity for a number of years. I mean, we were in the late 40's, when Bates explained it, there were other developments about why it did not actually go to zero and that is because they were relativistic split.

Splitting, that was explained by a man by the way Mike Seaton in 1952. But then in the early 60's, some calculations by a man by the name of John Cooper, found that this was not an isolated curiosity. It happened for almost every valence level in atom as long as the valence wave function had a node. So, it did not happen for 1s2 p3d 4d but it happened for all the higher ones. When they were avail as when they were out of shells.

And since and then it became to be called a Cooper minimum. Sort of an interesting story because John Cooper did not have a PhD in physics. He had a master's degree in music and an undergraduate degree in physics. He was hired as a programmer to work with a very well-

known scientist at the National Bureau standards in the United States. By name Ugo Fano and when Fano found out he do a little physics he gave him real physics to do.

And he was the one who found all these minima and it got named after him. Anyway, so, this is a something which is found all over the periodic table and simply an overlap effect. There was no classical analogue of this it is not a resonance effect, it is just an overlap between wave functions and this shows that they really are wave functions. They are not a figment of our imagination and not just a mathematical construct.

They really exist. I agree and their phases and overlaps really do have consequences okay. All of this can be learned from a model like that. I mean you can do better and get things more exactly but qualitatively you got it. However real wave functions are not simply some single particle wave functions, they are more complicated than that. And this too is important in the following sense.

That when you know that one of the postulates of quantum mechanics actually says that you can always expand the wave functions in any complete set. And sometimes we should be pick a set and we try to do that. We right away function as a sum of terms. There is a name for this. This is called Configuration interaction for historical reasons.

But it merely is expanding a wave function in a complete set, of course, complete sets are generally infinite. We can never do an infinite set C to a finite one, you truncate it. And this can be done for the initial state. And it can also be done for the final stage. For the final state it is a little bit messy, because remember, in the final stage you are dealing with an unbound electron, a continuum electron.

As opposed the initial state, when you are dealing with a bound electron or discrete electron, now, discrete wave functions are normalized to unity. Continuum wave functions are not they are normalized to the delta. You know delta function normalization, delta functions in turn in. So, it mathematically is a lot messier. The ideas are exactly the same. But mathematically it is a lot Messier and we call that Inter Channel Coupling. Nice, fancy phrase.

But it really is the same thing as we have in the discrete but it is in the continuum and again the mathematical methods are different. The fact that you can write wave functions like that and need to, is important; because remember, the interaction of a photon with an electron, it is just a single particle interaction; However, experimentally it is found that you can get ionization plus excitation.

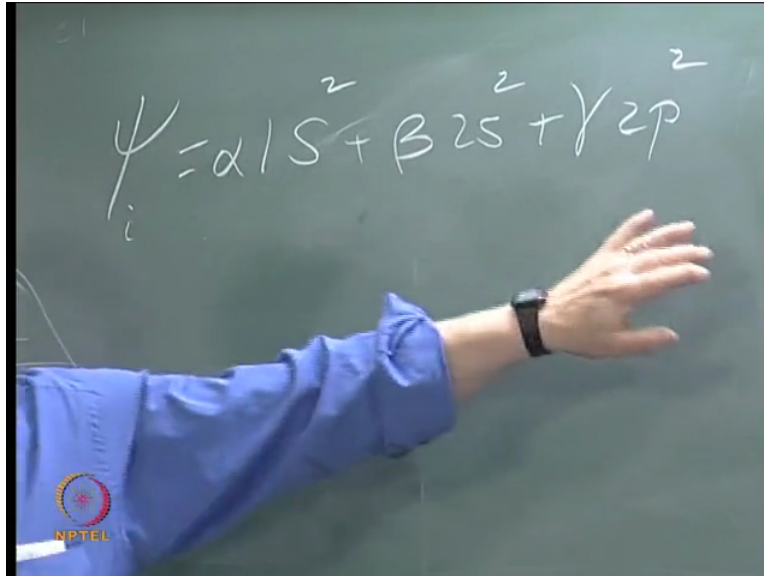
In other words, one electron ionized and the other excited with a single photon. Or you can get two electrons out with a single photon. A matter of fact a about a decade or two decades ago, there was a big flurry of activity in the double photoionization of Helium. Since it only has two electrons that is a and b trying to calculate that and do things about that. However, how can that happen?

If the photon only interacts with a single electron, well. Obviously then, if it really does happen and it does we measure that experimentally, remember, ultimately the only arbiter of whether or not we are doing a good job, whether or not we are right is experiment. What we do has to agree with the experiment at least qualitatively. If we are if it is to have any validity at all, okay.

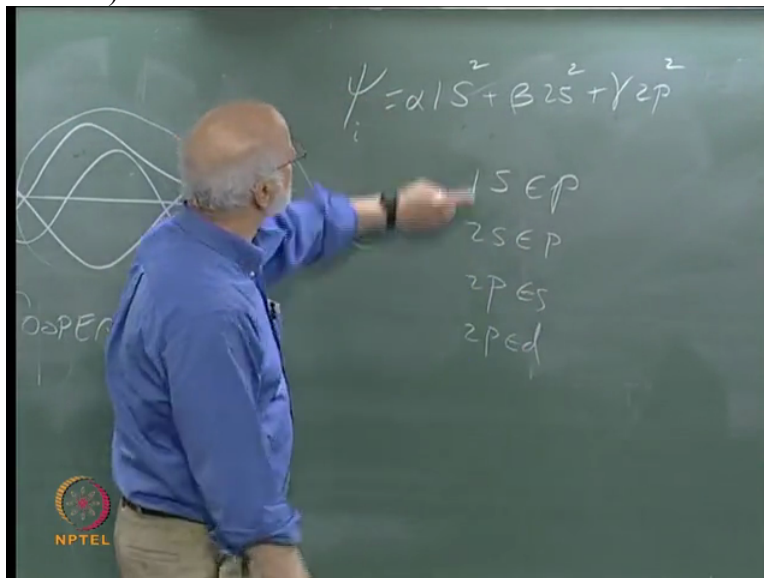
So, we say it is a double ionization and we know, the photon interacts with only a single electron. There is only one conclusion that the electrons have to talk to each other in some general sense. Or the motion has to be correlated. We call this correlation, there is lots of other names, for it multi particle interactions electron-electron correlation; it is called in number of different things.

But that is what it is think of it as electrons talking to one another. In electronease whatever that happens to be. So, what we try to do is, understand this electron, these understand the language of electrons. ah, again one of the ways to put this into the calculation, not the only way is, by expanding in a complete set. Or again you can never expand in a complete set so a truncated complete set.

And that is the way you can get ionization plus excitation; because then let us say, here sure a simple case, How can you get ionization plus excitation in Helium? Well, helium as you know ground state can be written $1s^2$. However, it is not exactly that. If you just take two $1s$ type wave functions, however, however you pick them, and take the product, you can get reasonable results of many things but not for everything.
(Refer Slide Time: 35:37)



And if you try to expand that in a complete set, you might have something a wave function, which is at the initial state alpha 1s squared plus beta 2s squared plus gamma 2p squared. So, say alpha beta and gamma are some coefficients and you see these are different configurations. And that is why this expansion is sometimes called configuration interaction. And typically for the helium atom, this is close to 1 and these two are small. (Refer Slide Time: 36:23)



Now, let me show you why you need to do this, if you are going to consider ionization plus excitation, because ordinarily what you get is just from this. You get a final state 1s epsilon P in other words the photon comes in it is one of like but you can also get to s epsilon P and 2p epsilon s and 2p epsilon d. How do you do that? Well. From here to here, it is a one electron matrix element from 1s to 2p;

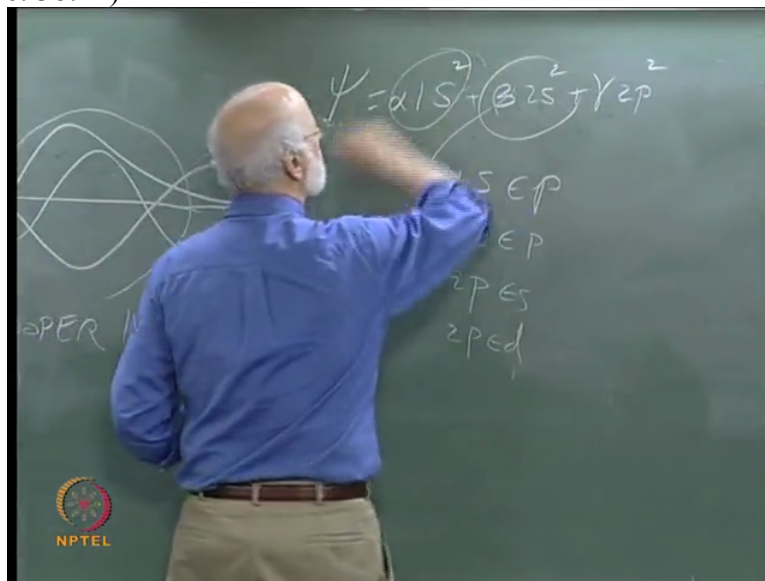
From here to here either those two one electron matrix element, so, expansion of the wave function like this to be a more exact wave function, gives you the possibility of multi particle.

And so, these beta and gamma are small alpha is close to 1; but this beta and gamma somehow result, from the electrons talking to each other. And exactly how you get this wave these wave functions is a whole lecture in itself.

We are not going to do that today. So, this and also you can put the continuum in here, so, you can get double ionization. So, electron correlation is part and parcel of multi electron transitions without electrons talking to each other; without electron correlation it is not possible and so, looking at experimentally, at multi particle transitions in with a single photon in.

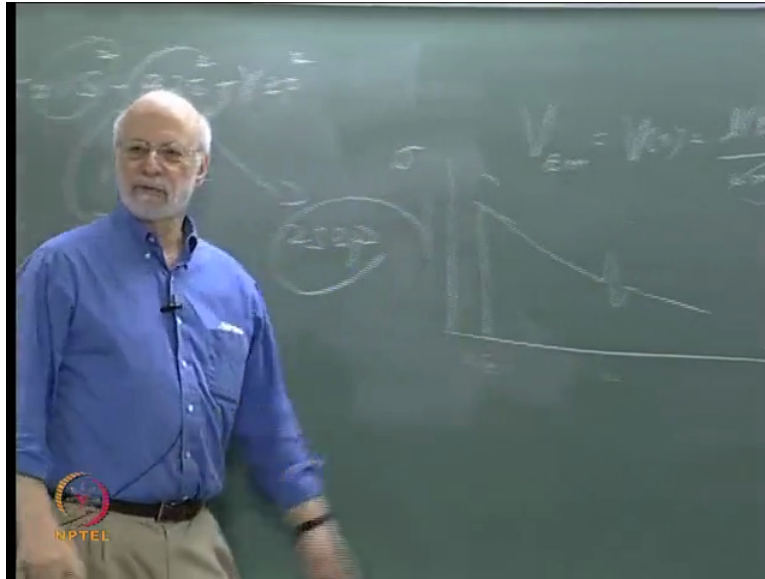
Is in effect measuring this correlation; or giving a measure of this correlation. Parenthetically there is another process which can give you multi electron ionization having to do with the inner shell. And it is called now getting the outer shell there is another process which we call autoionization. This is what it is not exactly the same thing but it is related. In other words, let us say we start off with this.

(Refer Slide Time: 38:44)



This can not only be depending on the photon energy knocked into the continuum, but could also be just excited. So, instead of like this, you can go to a state say 2s 2p. You can get there from here with the right energy. But the 2s remains the same and then and the two p2s the other two s goes to 2p. It is a perfectly valid dipole transition and this actually happens as one as the first was one of the first ones discovered.

(Refer Slide Time: 39:45)

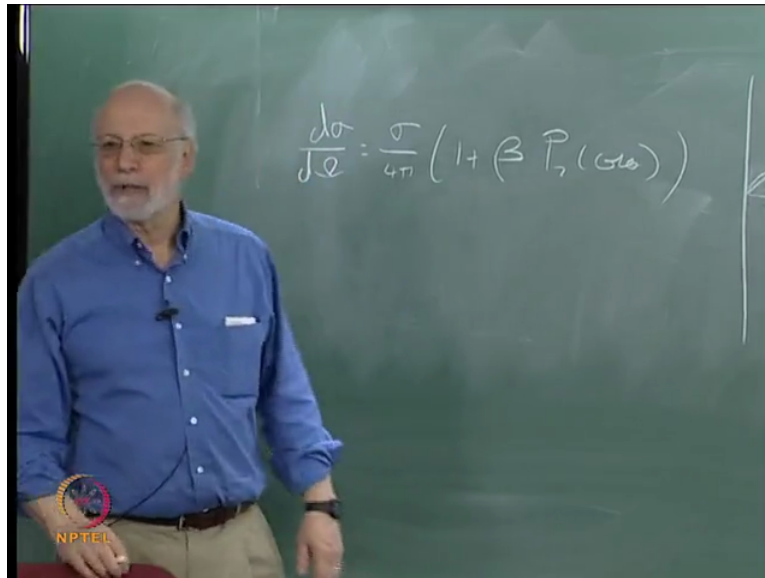


But what happens when you have this. You see, show you here, the, this is a photon energy scale and here is the cross section, what you get is Helium. Its binding energy is of the order of 25 eV and it goes dropping down and all of a sudden let at about 60 eV you find something like this, a resonant. And what that is, is that, discrete like state, which lies well above the Ionization threshold.

Well this lies were well above the threshold of 1s epsilon P. So what happens is, at the same energy, get a transition between them the 2s goes down to the 1s and the two P takes it the energy of that and goes we radiate it without any radiation and goes out. That is called Autoionization. And again and this is only possible if you have, if you allow the possibility of a more complicated wave function, more complicated than a single than a single particle.

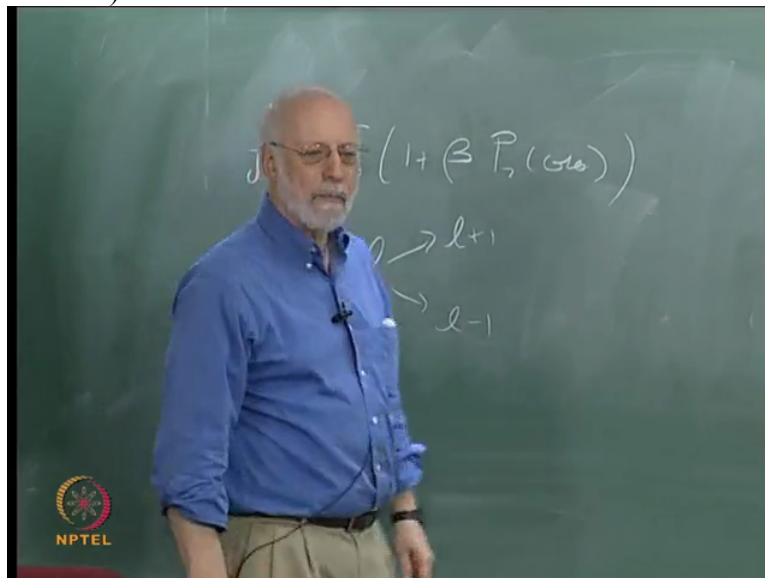
All right. Well, moving right along, there are a couple of other things I would have liked to, have talked about but I do not have that much time. So let us talk a little bit about Photoelectron Angular Distributions, because when you do a photoionization you can measure the probability or the cross section. But you can also measure the angles at which the electrons come out and it turns out.

(Refer Slide Time: 41:50)



That you probably know this formula that the differential cross section $\frac{d\sigma}{d\Omega}$ is $\frac{\sigma}{4\pi} (1 + \beta P_2(\cos\theta))$ where P_2 is just the second order Legendre polynomial $\frac{3}{2} \cos^2\theta - 1$, I believe, and β is the so-called asymmetry parameter. And you can work out an expression for this β which tells you something about the angular distribution.

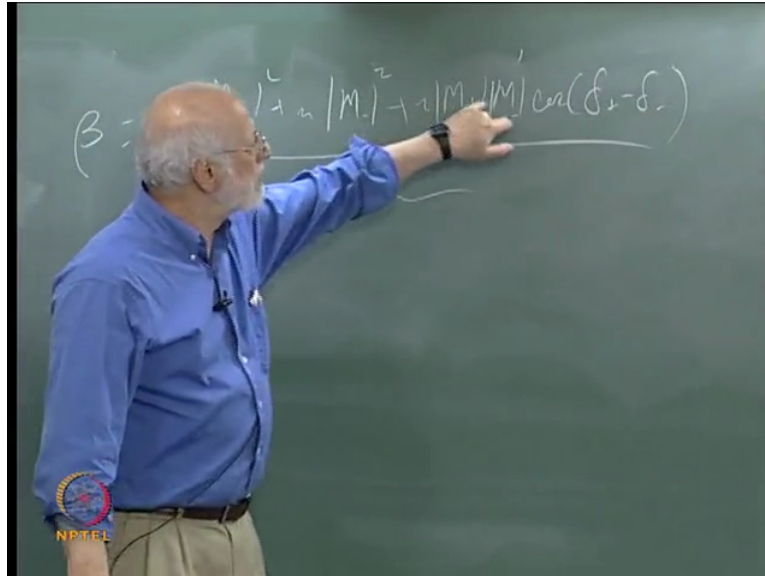
(Refer Slide Time: 42:34)



Now the interesting thing about this β is that remembering, that you get l to $l+1$ and l to $l-1$ transition, you get interference between these two amplitudes. And so if I call the amplitude for this m plus and the amplitude for this and minus you get an expression for β that looks something like this. Again this just means some coefficients over something of mine, okay.

This part we already know about is like the cross section.

(Refer Slide Time: 43:40)



But look at this is the magnitude of matrix elements, times the cosine of the difference in the phases of these matrix elements, basis. We did not learn anything about them from the actual cross sections. But they appear in the angular distribution. In other words, there is interference between these two amplitudes. Now wait a second, though time out, for a second we have an l to $l+1$ transition, l to $l-1$ transition.

This angular momentum, angular momentums are good quantum numbers. So, how can you mix them? And you have to think about what you are measuring? To measure the angular distribution, what do you do? You look at the angle and the energy of the photoelectron. By the way the angle the way I have written it here this is assuming linearly polarized electrons and photons, I mean.

And this is the angle with the, that it makes with the polarization vector. So, the symmetry is not around the photon direction, but the photon polarization vector. And so what do you do you measure the energy and the angle effectively, what that means? The angle is the direction, you are measuring the momentum, okay. What are the Eigen and now you'll recall from elementary quantum mechanics.

The Eigen function of a system if you measure a particular quantity, at the moment you make the measurement, you force it into an Eigen function of that quantity, particular one, all right. I mean you change the wave function, yeah, exactly what it means. What is the Eigen function of momentum? You know that. It is a plane wave.

This plane wave look like let us say one of the z direction because it is easiest it is not a special case I just take my coordinate system and put it so whatever direction of the electron is moving. I call that the Z direction and what is that equal to you may have seen this in

scattering theory it is 1 to the l to $l + 1$ of $k r$, $p l$ of cosine theta, a very well known expansion.

If you have not learned about this, you will. In any case notice when it is assumed. So if you measure momentum, no longer are in a fix angular momentum state. Why momentum and angular momentum do not commute? I mean, quantum mechanics does work and so by measuring this you are measuring a mixture. You are forcing the wave function into a mixture of different l states.

And that is how this interference arises. Now the study of beta is very useful from the following point of view. From the cross section itself, you learn only about the magnitude of matrix elements or amplitudes. And fundamentally the most fundamental information you can get about a process is the matrix element. And a matrix element has two attributes its magnitude and its phase.

The angular distribution allows you to get information about the phase. There are very few processes which gives you information about this. This is one of them and so this is a really interesting one to study. And a great deal of work has really gone into over the years studying angular distributions.

And unfortunately my time is limited to a last minute and so, what happens is this beta, since the matrix elements are energy dependent and the phases are energy-dependent. These betas are energy dependent and they can by measuring them you learn particularly if you measure them and the cross-sections you know something about some of these and about the phases.

And so, this can give you ultimately, as a matter of fact, there are some experiments, that are called complete experiments. Where they measure all of the magnitudes of the matrix elements and all of the relative phases, you only get phase shift differences here. So, you get the relative phases and this is known as a complete experiment.

And I guess since my time is pretty much up I will stop here and well I feel it has been a privilege to talk to you, whether you feel it is a privilege, I have no idea. Thank you.