Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'
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Lecture 46
Photo-absorption by Free and Confined Atoms and Ions- Recent Developments

Greetings, anybody who is doing atomic physics is well aware of the vast research contributions Steve Manson, made to this field. Today, we have the opportunity to discuss the result with them and even be making presentation on photoionization of Free and Confined Adams the recent time. See, Thank you.

I have to give a disclaimer to begin with. I found this presentation and put it together about seven o'clock this morning. So it may be a little bit rough. I have not had time to go through it as much as I would have liked to, before making a presentation.

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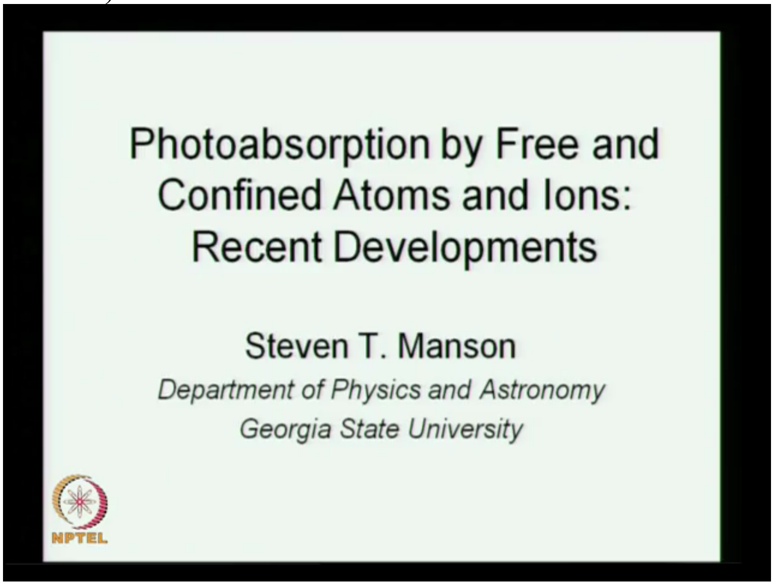

Photoabsorption by Free and Confined Atoms and Ions: Recent Developments

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In any case, what I am going to talk about today as the title suggests some relatively recent results in the area of photo absorption by a number of different kinds of targets. And you know, it will not be an exhaustive study but I all tried to be representative, if you representative results in various areas.

Now, to begin with, up until oh, probably the 1960's it was thought that photo absorption photo ionization of atoms was pretty much a one electron process in their work. There may have been correlations that did a little but they were not terribly, terribly important, this turned out not to be true.

And over the years, we have found all sorts of interesting things which occur owing to the fact that the world is not a single particle world. Wave functions are not single particle wave function. What really, really do include many body correlations? Correlation is just a general term we use to say that the electrons of an atom or molecule or solid or anything do not move independently, but they are correlated with each other; thus, the term correlation, okay.

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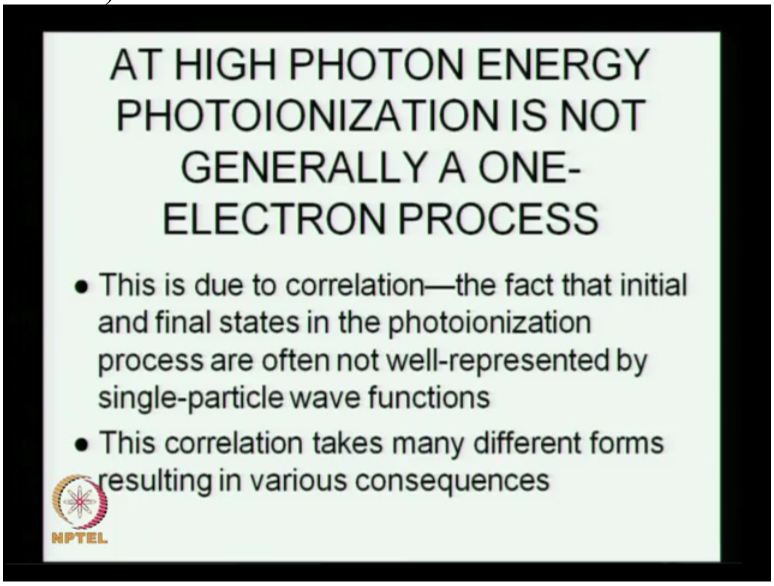

AT HIGH PHOTON ENERGY PHOTOIONIZATION IS NOT GENERALLY A ONE-ELECTRON PROCESS

- This is due to correlation—the fact that initial and final states in the photoionization process are often not well-represented by single-particle wave functions
- This correlation takes many different forms resulting in various consequences

To begin with, that's what this says: I said it in other words. It is not a one electron process. And this correlation could take many different forms; it can be in the end. Remember, in the calculate photoionization, you have an initial state wave function and a final state wave function and you will take an integral with something in the middle.

But something in the middle is general. The initial state wave function, final state wave function has to do with the particular case, you are dealing with, all right.

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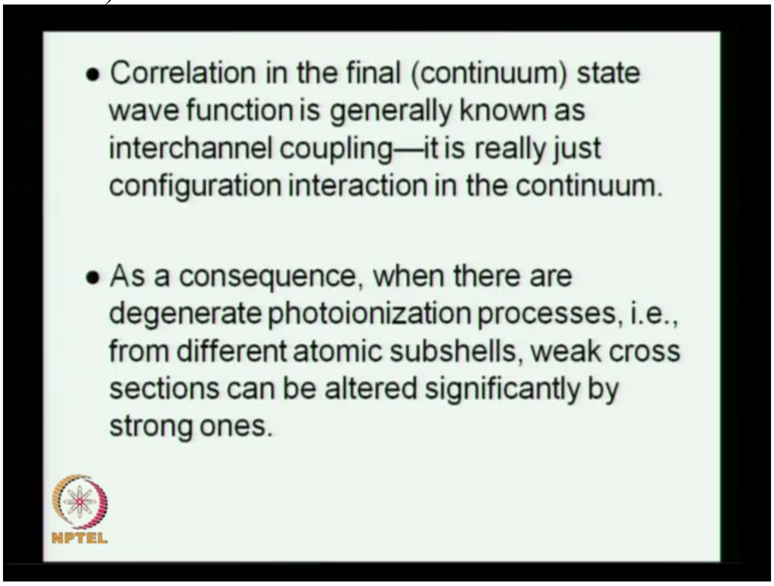

- Correlation in the final (continuum) state wave function is generally known as interchannel coupling—it is really just configuration interaction in the continuum.
- As a consequence, when there are degenerate photoionization processes, i.e., from different atomic subshells, weak cross sections can be altered significantly by strong ones.

Now, take a look at this. In the final continuum state wave function, correlation or configuration interaction is generally goes under the rubric of Inter channel coupling. One of the reasons we use that term it is really sexy; it sounds like, it sounds like something very, very special.

And it confuses experimentalist which is always good. The essence of this is that, when you have generic channels. What I, but I mean by generic channel is, when you could have photo ionization from more than one sub shell at a given energy, you know what high energy. You can get all the different sub shells.

Well, it turns out that due to this, what is called Inter channel coupling, if you have a channel with a large cross-section and a little of it is mixed in with another channel, with a weak channel it can make a big change. The other way does not do anything. You mix a little of a weak channel with something is strong.

You know, it is like, if you have something weighing a thousand pounds of something, weighing one pound and you get a tenth of a percent mixing. Well, a tenth of a percent a thousand pounds is one pounds, it will double the one pound weight; tenth of a percent of the one-pound added to the thousand are not going to do nothing.

So this is kind of the idea of this and what has been found, for example, in at high energies it this can actually change the asymptotic form of the wave function, of the not the wave function, of the cross section. It turns out in a single particle model, you get one asymptotic form; and when you put in into channel coupling, it just changes in many of the channels. Then the tails I do not want to go into right now.

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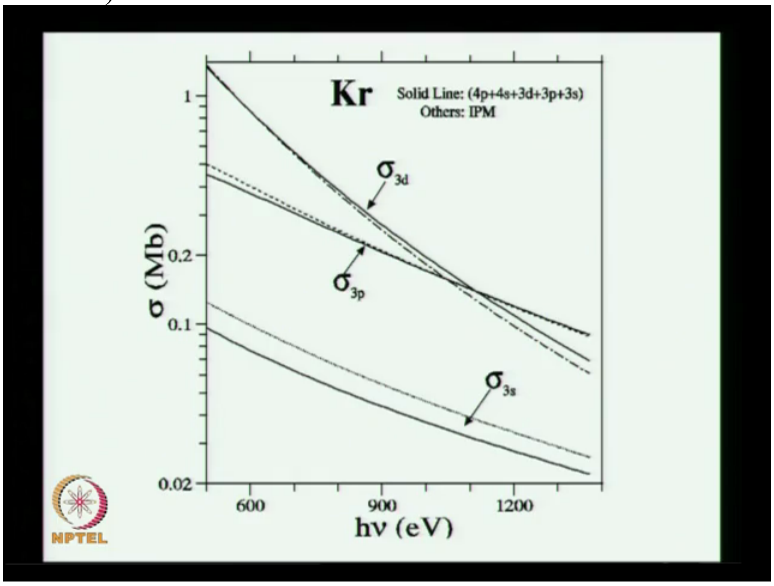

Another thing that happens and this is interesting. This is a calculation for the photo ionization of Krypton in the range you can see about 600 to 1,200 eV, the thresholds of these 3s, 3p and 3d are several hundred eV. So, this is really well, well above threshold. By the way, up until, this work was done it was thought that where there are correlation effects, but they're mostly around threshold.

This is not around threshold; this is very high above threshold. And look at what happens. We have another round six hundred. We have these dashed lines. These dashed lines are essentially a single particle model. But when we put in this inter channel coupling, look what happens, with the biggest one nothing. With the one, that is the middle sized one, something; and the smallest one, a lot; this just continues on and look what happens here.

When you go up to high energy, highish energy, this one is the biggest one and it does not change. These to change; this is a consequence of what we call the other Channel coupling. And I guess I do not have it in this slide, but there is also experiment and while the experiment is not perfect, it does a pretty good job. In every case, the solid line is closer to experiment than the dashed line, showing that. We have some idea what we are doing.

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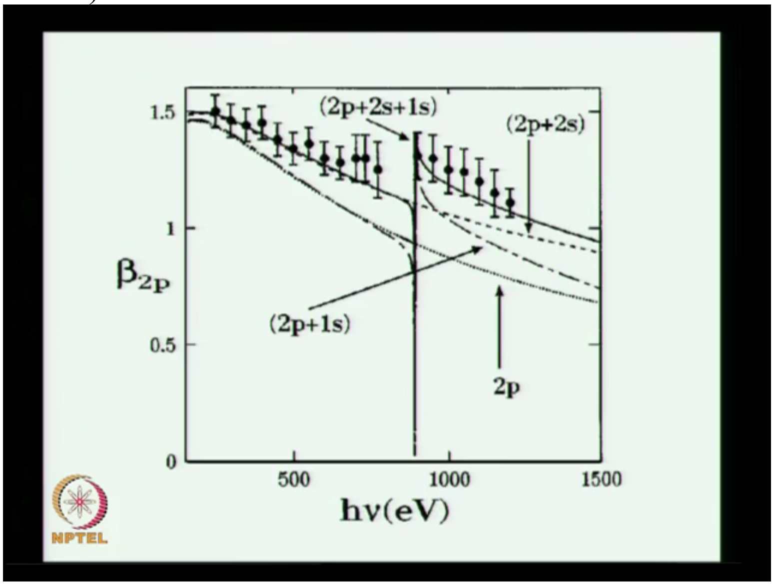

Now, this is a nice one. This is instead of the cross section. It is the so-called Angular distribution parameter beta. This was kind of cool because independent particle model gives this. The coupled model gives this. Do not worry about all the variations there and this is experiment. As you can see, with when you put in the inter channel coupling every point is within error bars of the experiment and this is not.

This led to some consternation when we submitted this as a paper. And we had a big fight we were right, but we lost anyway, because there had been some earlier experiments that basically had been misinterpreted because they thought that things were single particle. However, we also looked at the measurement of the cross sections of the, see, at this energy, you can have the 2s and 2p of neon.

By the way, this is neon I should have mentioned that. And we are well above threshold. Threshold, the neon for the 2p is about 020 ReV and for the 2s by 40 eV. And here, we are talking about a kilovolt 1000 eV, we near threshold. So, what we looked at, then, was the ratio of the two cross sections the 2p in the 2s cross sections.
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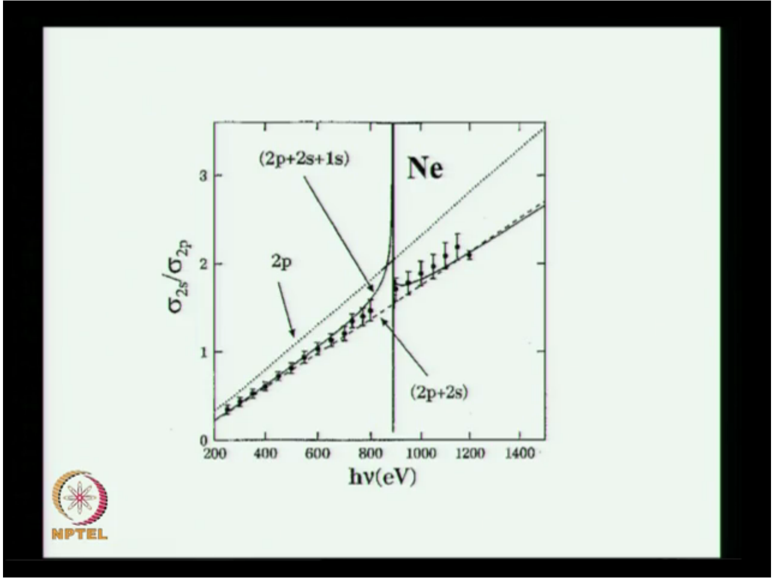

Now, from an experimental point to you there is a very good thing to do because many of the experimental errors are cancelled out that way when you taste take a ratio of two cross sections. And here is what we got is the ratio, a solid line is our calculation. And these are the experimental points. And the all of these experimental points were done before the experiment, before the calculation.

And the experiment said okay. If you think, you are so smart, we are going to measure a point and going to do a really, really good job of it; you get tiny error bars. That is, that one right here, that was done after the calculation. It is a really, really good calculation. In other words, all these equations that we write on the board and things, they really work; if you do a right, okay.
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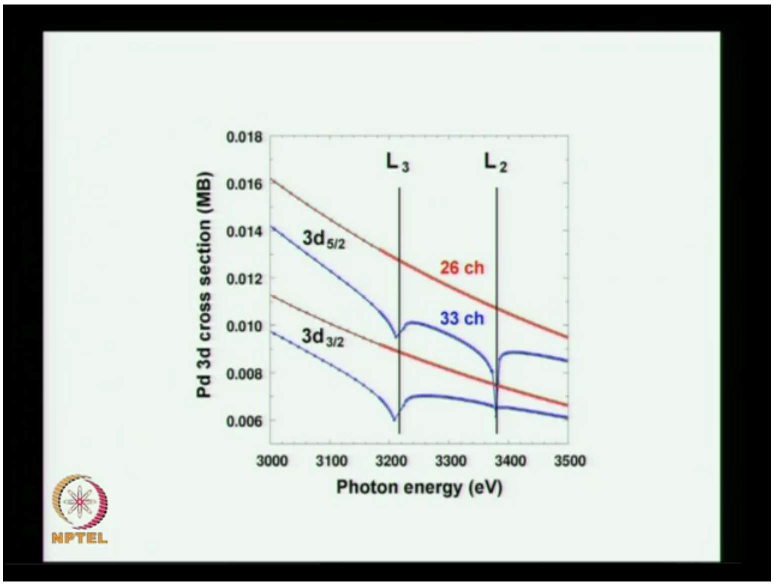

However, now, we have found something new. This is in palladium, says so right here Pd, one of the things, you learn in this business a long enough, you learn where all the chemical symbols mean. It is something. Look and here is what we found. In this case, this is the 22p threshold where the 22p thresholds are. That is just, that is a different kind of notation, it is called x-ray notation. And we have two of them because now these are deep.

Look 3.2, 3.3 kilovolts and relativity is important here. So, the spin-orbit effect is really, really large and you get rather than a single 2p level, you get the 2p1 half and the 2p3 halves; that is what three halves and one half of these are and the difference is almost 200 eV. That is a big spin orbit splitting. You have to remember that the spin-orbit splitting goes as z to the fourth. Do you remember?

There is a z in it from the nuclear charge and then there's another z cubed that comes from the one over r cubed in it; so z to the fourth, so the effect of z for a 2p and palladium is really large. And to the fourth that makes it really big. So, but, look at, what we find, we find that in the 3d cross section due to this inter channel coupling, we get actual structure, significant structure.

And when we leave out the 2p we do not put it in coupling with it, we get this. So, not only do we get a change in magnitude. By the way I did not show the 2p cross sections here, but they are much bigger there well above the ceiling here. So, not only do we get a change of magnitude like we saw in an earlier slide, but we also get structure.

Yes, I am sorry (Question time: 12:20 not audible) because there was an experiment done in, in silver which is the next element. Show that in a moment. This is the experiment along with the theory. This is the actual experimental results we figured that move changing z by one for such an inner shell would not matter much.

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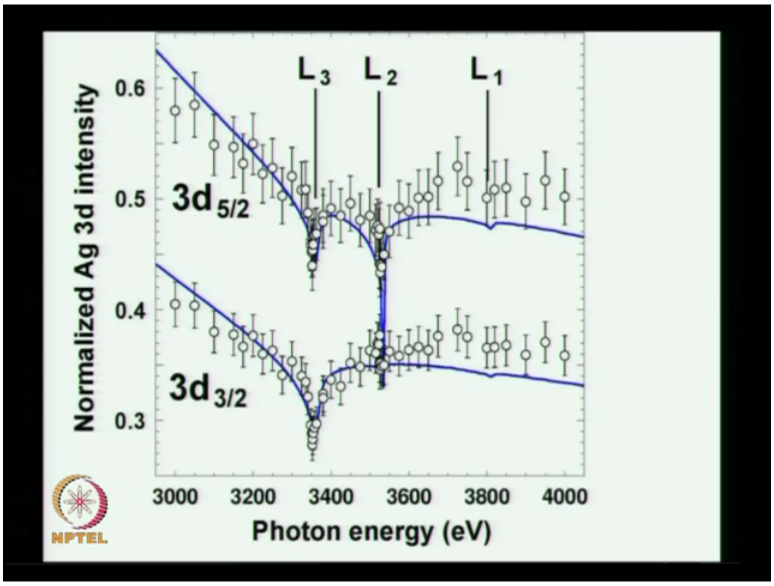

And the experiment was only, was only relative. So, it had to be normalized at one point. But as you see, the agreement is really awfully good. But to do better again, we take the ratio of the two channels.

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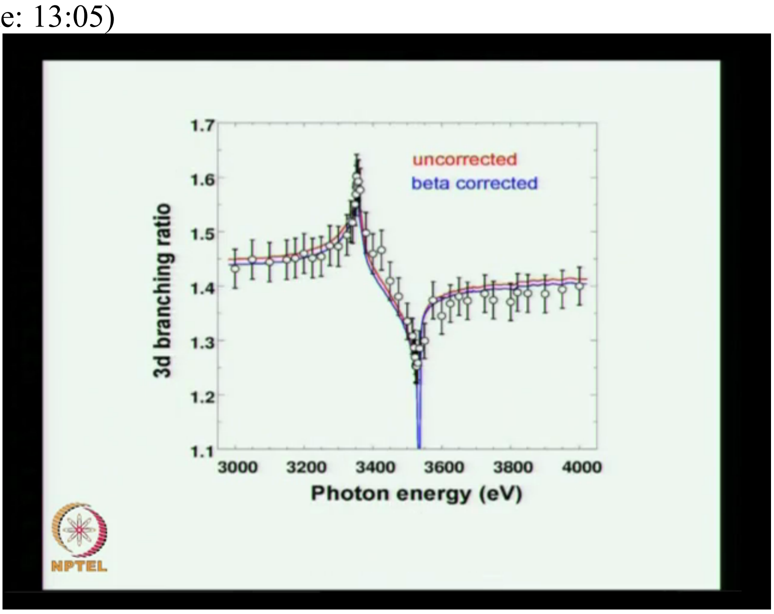

And this is it, is the ratio. So, here nothing is normalized to anything else; that is pretty remarkable agreement. In other words, we were pretty sure we understand what's going on. Because again, there is nothing normalized anything else here. Actually how we got to this was a funny story.

I was at a conference and I gave a talk that included something about inter channel coupling and after the talk one of the people in the conference talked to me he said he had some experimental results to show me and asked me if I understood him. And he showed me the result and I said yes I understand them.

And we can do that and then we did it. Actually the calculations were done here, I mean not in this room. But I mean here at IIT and okay, enough about that. What about Ions? No free atoms.

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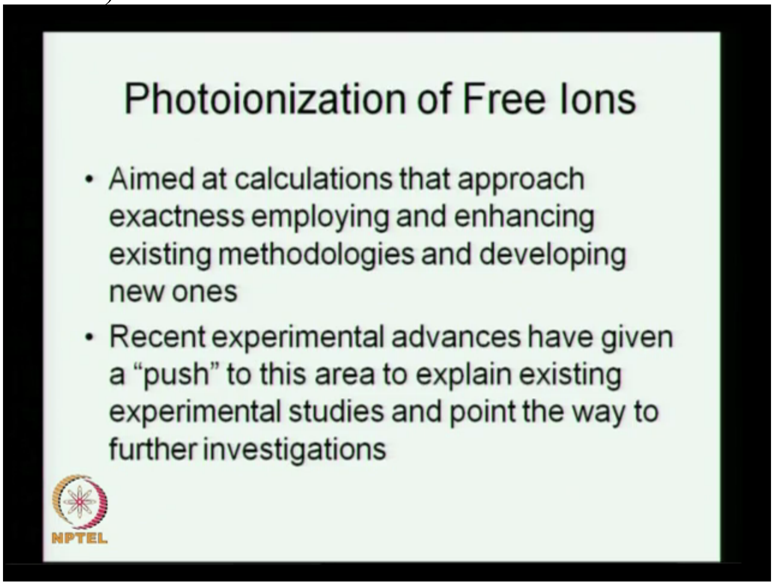

Photoionization of Free Ions

- Aimed at calculations that approach exactness employing and enhancing existing methodologies and developing new ones
- Recent experimental advances have given a "push" to this area to explain existing experimental studies and point the way to further investigations

And here we are aimed at calculations that approach exactly and owing to the fact that there are really good possibilities for doing experiment. Now, there has been a big push to do really good calculations on ions; on the photo ionization of ions. See, ordinarily it is hard to get positive ions here, because they do not remain around very long. Let us see what we get here. This is scandium, actually scandium double plus.

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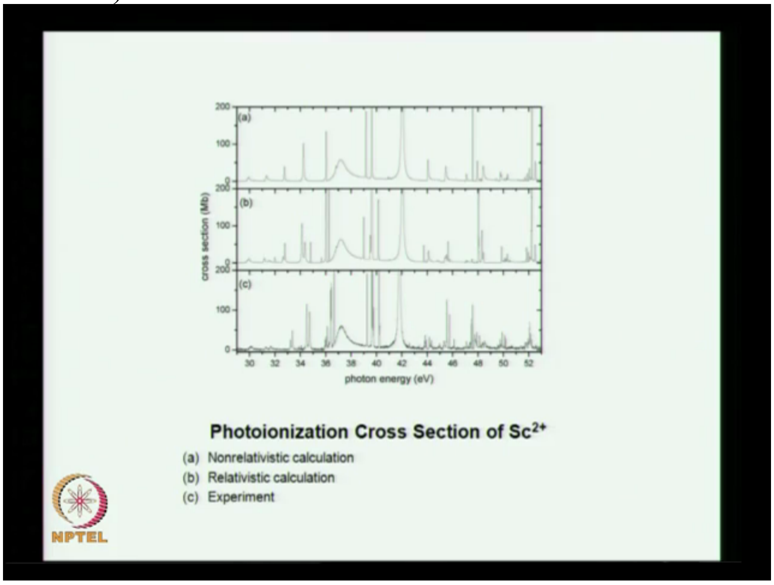

Photoionization Cross Section of Sc^{2+}

(a) Nonrelativistic calculation
(b) Relativistic calculation
(c) Experiment

Why are we interested in scandium double plus, how on earth did we pick something like this? Well, it is the simplest ionic system that has an opened in d shelves. This, the structure of this is argon plus a 3d electron. What turns out that once you get d electrons there in open shelves, it becomes a far more difficult calculation? Having been involved in the calculation, I can tell you it is really difficult.

Anyway, here is our result: This is non-relativistic, this is relativistic and this is experiment. And as you can see the agreement is not bad. You see, what relativity does here, you have a single resonance that it breaks into two and you really do have to. The agreement is not perfect that is pretty good we think we have a pretty good handle on how things work here.

I am not going to go into detail about the calculation but this was a relativistic or matrix calculation and you know we did some.

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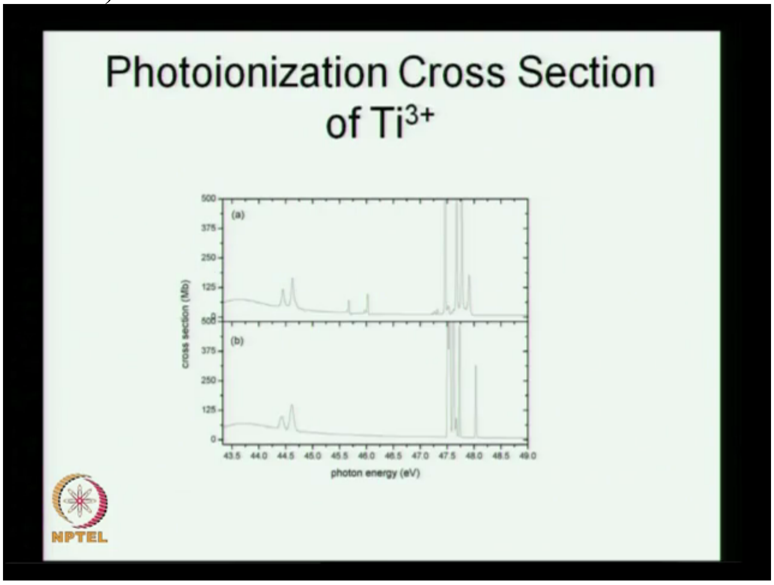

Photoionization Cross Section of Ti^{3+}

This is the next one; in the iso-electronic sequence again, argon plus a single electron. And let us see now this which is, which trying to remember, which is experiment, which is theory. I believe this is this is theory, this experiment and what's this. That was contaminants. That is why we did not see it in the theory.

Anyway, so, you get the idea then we went on to a whole bunch of different ones and they just get very messy. I am gonna oh really oops go back here, okay.

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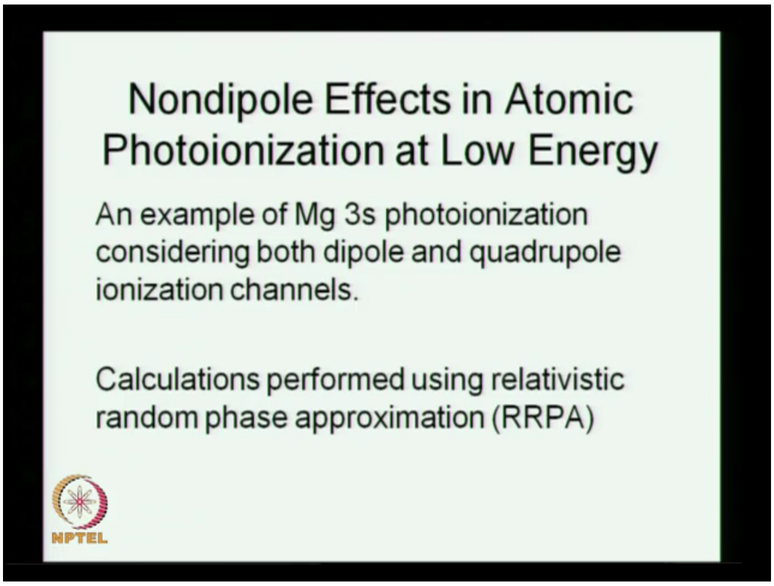

Nondipole Effects in Atomic Photoionization at Low Energy

An example of Mg 3s photoionization considering both dipole and quadrupole ionization channels.

Calculations performed using relativistic random phase approximation (RRPA)

That is enough of that, all right. Another thing up until relatively recently it has been taken as gospel. That, for relatively low energies, the dipole approximation was essentially perfect. You did not have to worry about anything else; turns out that it is not true. There are many examples of non dipole effects being important at low energy. However, it is not in the total cross section, but in the angular distributions.

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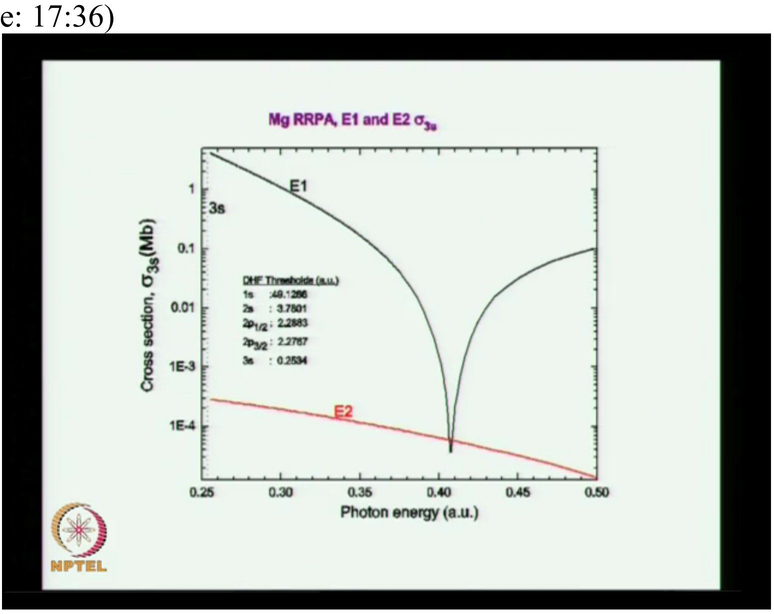

And here is an example, for magnesium 3s and the example is interesting because the in a dipole channel which is called E1, you have what is called the Cooper minimum. It goes down to a very low cross section. And in that region, you see, the e to the quadrupole cross section which is really, very small right around here, it gets larger. That has really interesting consequences.

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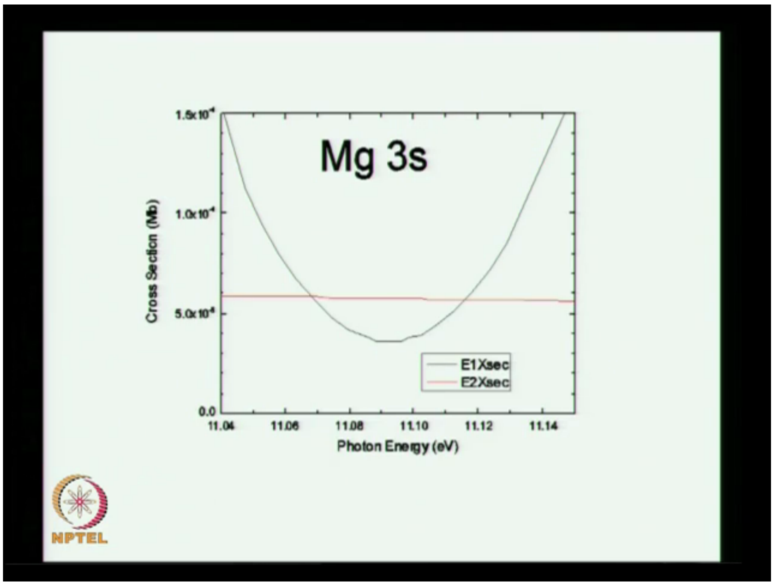

That is a close-up.
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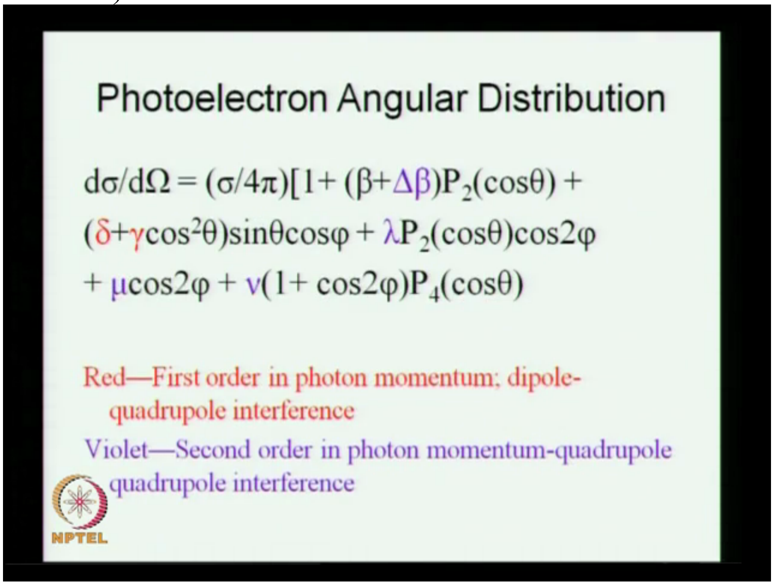

Photoelectron Angular Distribution

$$d\sigma/d\Omega = (\sigma/4\pi)[1+ (\beta+\Delta\beta)P_2(\cos\theta) + (\delta+\gamma\cos^2\theta)\sin\theta\cos\varphi + \lambda P_2(\cos\theta)\cos2\varphi + \mu\cos2\varphi + \nu(1+ \cos2\varphi)P_4(\cos\theta)$$

Red—First order in photon momentum; dipole-quadrupole interference

Violet—Second order in photon momentum-quadrupole quadrupole interference

See, the photoelectron angular distribution when you include the next order look something like this. The red and the violet are the non dipole part. So, if you do not have dipole, if you do not have just dipole, you just have beta 1 plus beta times p2. That is the second Legendre polynomial. And the rest of this drops out. So, and as you can see you would only get a dependence on theta.

Theta being the angle that the photoelectron direction makes with the polarization but here, you get that and Phi the angle that it makes with the, with the photon direction as well and what we find then, it is just to give you an idea.
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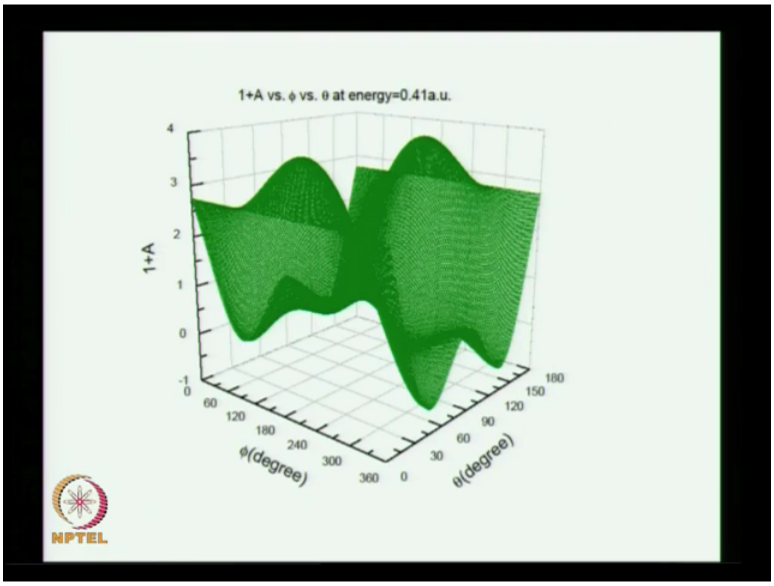

Don't worry about that. Instead of a simple of sine squared a, sine square theta plus B cosine squared theta distribution, you get something very, very complicated as a function of theta, as a function. I mean, clearly it is not constant as a function of Phi function of theta get a really really complicated angular distribution.

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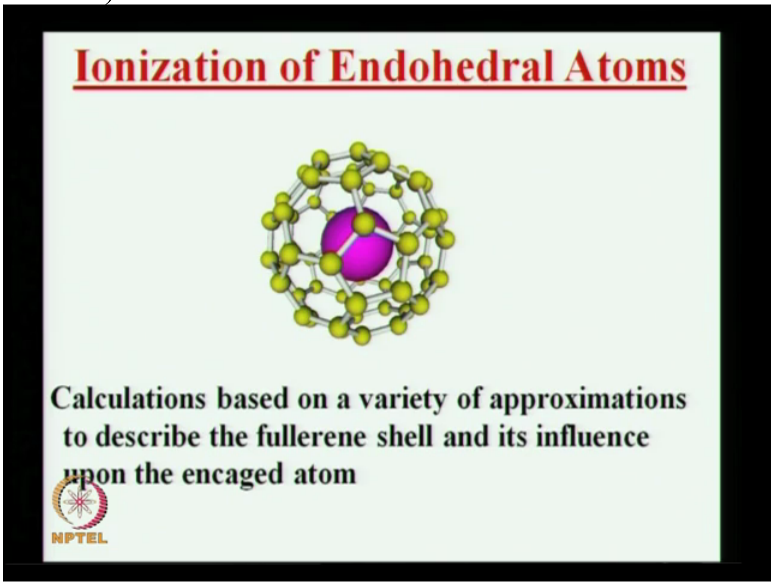

Ionization of Endohedral Atoms

Calculations based on a variety of approximations to describe the fullerene shell and its influence upon the encaged atom

Another thing that has been of interest lately, about 20 years ago, Buckminster Fullerene was discovered. The c60 that was shaped like a Soccer ball was also shaped like a Geodesic. Geodesic is a kind of structure and it got its name from an architect whose name was Buckminster Fuller who built, who designed buildings like that. And so they are not exactly but close to being circular.

They are called Fullerenes Bucky balls and some other things as well. But the actual full name is Buck Mr, Buck Minster Fullerene, okay. Not only can you create these structures, but you can put things inside of them. You can confine atoms inside and this has been done experimentally. And okay, you can ask yourself, how does this affect the property of the atoms? Or another way to think about this is.

If we put the atoms in there and we have changed plan, it changes the properties. Are these, or this, this system it is actually a molecule? I guess is, it useful for anything the answer is maybe. For example, people have talked about using a structure like this for drug delivery to a specific location. By putting it inside the Bucky ball and having something at the location that will dissolve the Bucky ball.

So, the Michelle keeps the drug from interacting anywhere else other than the location we want. And you can imagine how this would be useful for something like chemotherapy. I do not know if you know exactly, how chemotherapy works? But chemotherapy is basically a poison. And the idea of it is and is supposed to be used to kill the Tumor before it kills the patient.

But it is close very often, if you can get it directed to the Tumor, and not to the rest of the patient that would be really good, for the patient. Not so good for the Tumor, but good for the patient. But really chemotherapy is just poison and we hope that it is more toxic to the Tumor than to the person; because there is no way to at present, to really make sure that it works there.

The human system being what it is I mean think of it, you can in your head, you take an aspirin, it goes to your stomach and how does that work? You know it works everywhere you would like to get something directly to your head. But there, there were no good outlets. Anyway, so, that is one possible application. So, what we are interested in now is how the existence of a cage, around an atom, changes its properties.

And as you can see this is a relatively complicated system. I mean, if we take the ordinary one, the one that is most common is c60. So, to do this calculation we have 61 atoms that seem really hard. So, you make some approximations. First of all, we work with systems where the atom is located in the center. So, we maintain spherical symmetry, although the c60 is not exactly symmetric. It is very close, not exactly spherical, but it is pretty close.
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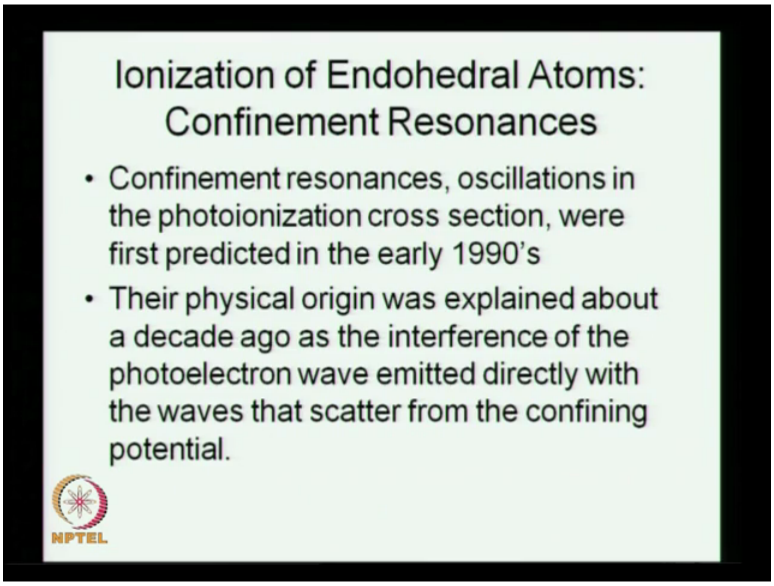

Ionization of Endohedral Atoms: Confinement Resonances

- Confinement resonances, oscillations in the photoionization cross section, were first predicted in the early 1990's
- Their physical origin was explained about a decade ago as the interference of the photoelectron wave emitted directly with the waves that scatter from the confining potential.

Now, the first thing that we found was confinement resonances in the photo ionization cross-section when you put something in there and the physical explanation is real simple. You can have the photoelectron going right out, when it is ionized by radiation. Or it can go backwards hit the wall, then go out. So, you have two different waves going out. Actually, you get lots of them.

And they interfere and the interference is based on the actual geometry of the situation. So, actually from these, from the interferences, you can learn something about the geometry. And we have done numerous calculations of this sort of thing and here is an example.

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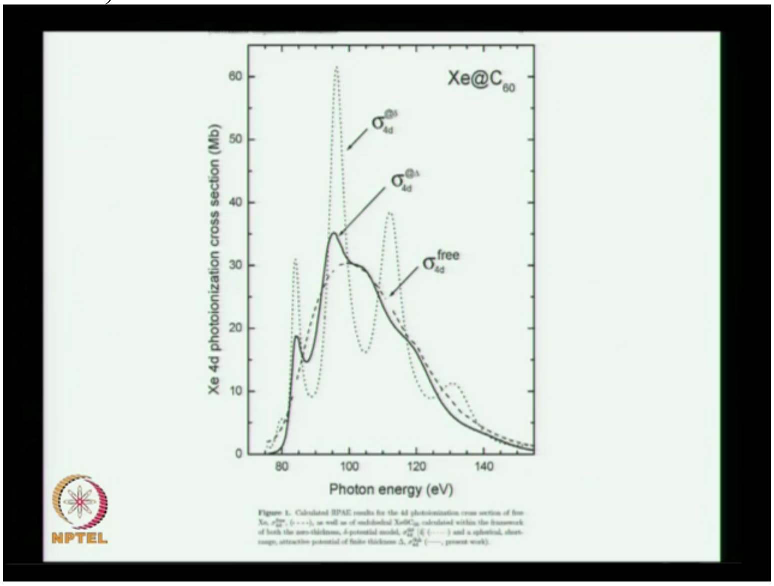

This is in Zenon 4d and the dashed line is the free atom. And the solid line is what we think it actually is, inside a fullerene making a model of the c60. And the dotted line is a very simple model which we think is wrong. Anyway, there just to give you an idea this is what these confinement oscillations look like. And they are ubiquitous. We find them everywhere.

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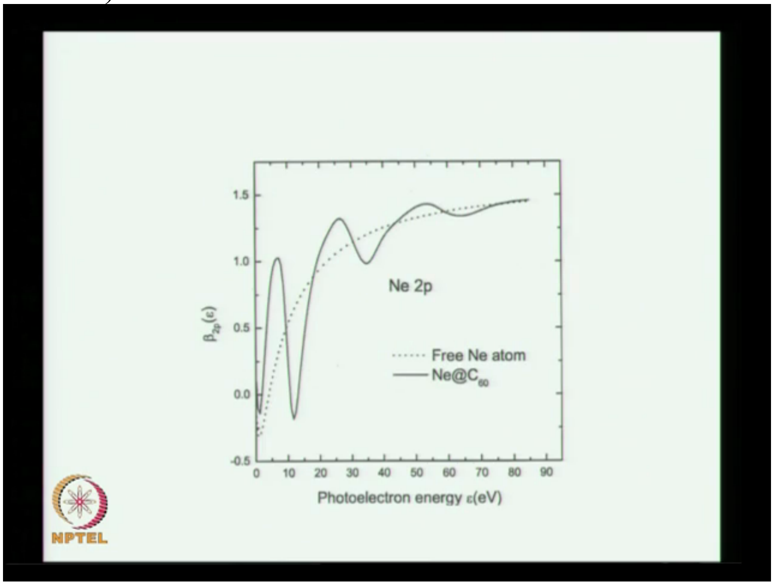

We find them in data in the angular distribution parameter. Here this is for neon to p and the dashed line or it is actually a dotted line, I guess is, for the free atom. And you see, the, our calculation for Neon at C60 it bounces around it. It oscillates for resonates wherever you had like.

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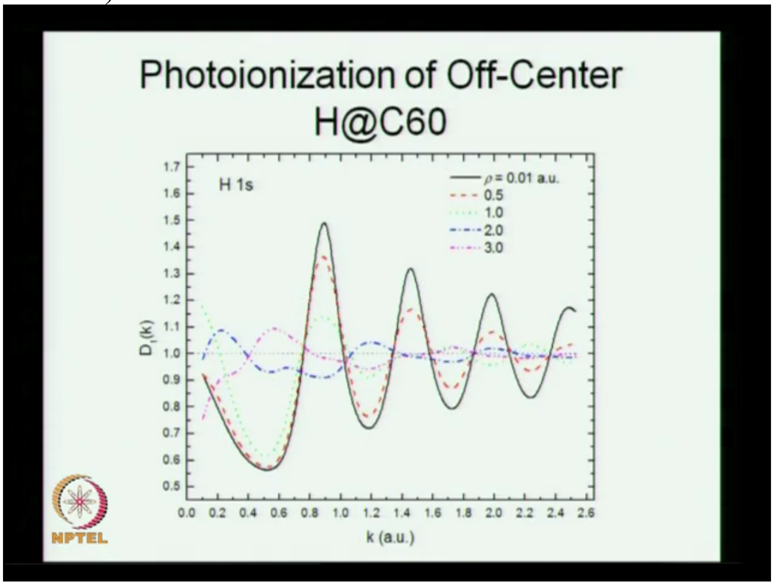
Photoionization of Off-Center H@C60

Now, this, one can ask what happens if you move off center? Well, here, without going into detail calculations, you can guess, because as long as you are on the center and the phase difference is the same, no matter which way you go. But if you are off center you get one phase here but if you are going further here get a different phase. So, probably this, a confinement oscillation business, we get much less.

And in fact it does you have a look at this carefully. Here, the solid line it is basically at the center and this I do not know, what colour is, the violet. It is well off the center and you see it is almost gone. Just, it is just, basically the geometry of the situation. So, we have some idea what happens if it is off center. So, if you do an experiment and you see these oscillations, you know it is pretty much close to the center, okay.

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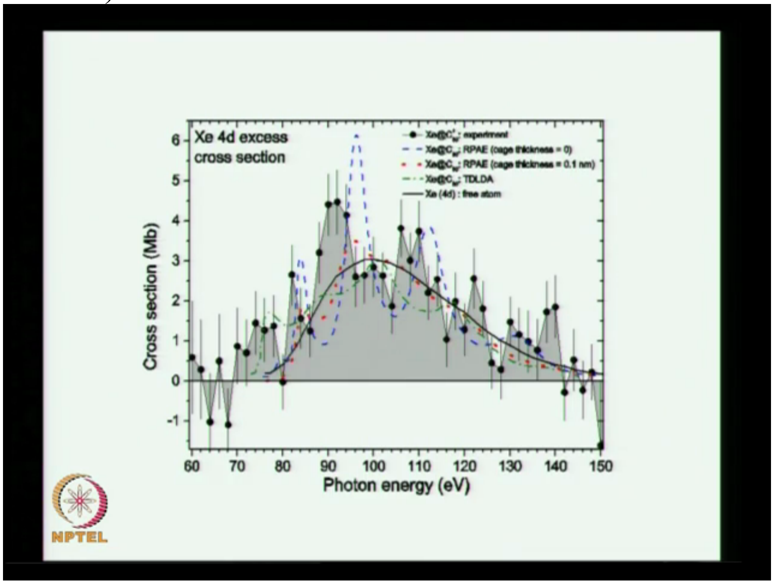

So, here is an experiment that was done. And this is in Zenon 4d. And as you can see, they really do see these oscillations, they are actually larger than the error bars, is a new experiment that has small error bars that also sees this. So, it really does exist and this is one of the phenomena that were, that was predicted well before, it was measured, all right.

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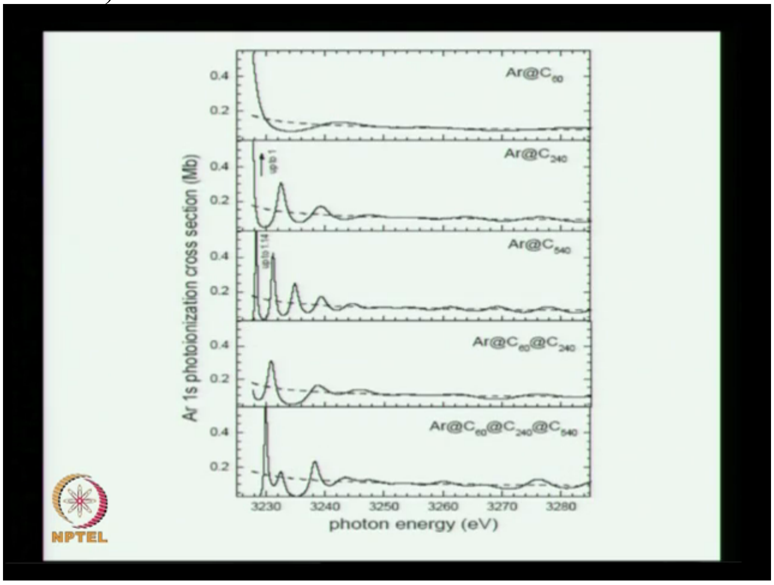

Moving right along, C60 is not the only flowing, as you can see here we show a series of calculations of Argon in C60 and Argon in C240. You see the, the oscillations differ. By the way, this is the 1s of Argon. We, the reason we took the one s is, one s is a Argon is really, really tiny it does not know about the, who are all around it. So, everything you are seeing here is due to the final state; nothing because, the initial state does not change.

And that is, that is why we picked this calculation to do. So, we could focus on just as what is happening in the final state. And you see with the 240, you get more with 540, you get still more in the way of these oscillations. And if you get a really big fullerene, you can not only put an atom inside, you can put another fullerene inside. And that is where the bottom two curves are.

You have argon in C60 in C240 and the bottom we have Argon in C60 and two in C240, in C540. All of these are possible at least in principle. And this is the kind of things are relatively simple calculations show, okay.

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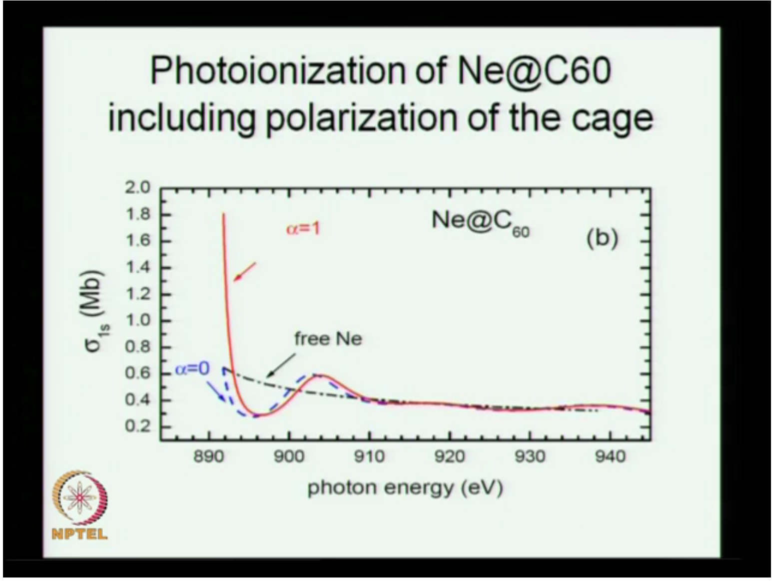

Photoionization of Ne@C60 including polarization of the cage

However, oh! Let us not talk about that.

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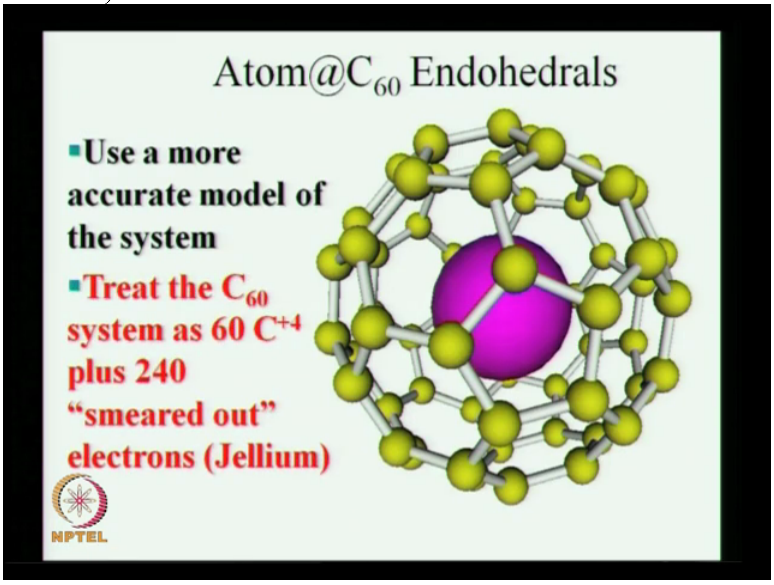

Atom@C_{60} Endohedrals

- **Use a more accurate model of the system**
- **Treat the C_{60} system as 60 C^{+4} plus 240 "smeared out" electrons (Jellium)**

In the calculations that I have just shown you, the electrons of the fullerene itself are considered innert they are just sitting there. And it is just the atomic electrons that see a different potential. What about, is it possible to have interactions between the atomic electrons and the shell electrons? The answer is, yes. But, in order to do that, we have to consider all of them and so we have a use a more accurate model of the system.

And we treat the system in the following way: We smear out the, but we, you see, the carbon atoms they have 2s and 2p electrons that are relatively weakly bound. And then they have 1s electrons that are bound by about 300 eV. So, they are very different. So, what we do? We consider the carbon fullerene as a bunch of carbon plus fours, that is carbon nuclei with the 1s is still there so, the net charge is just plus 4.

And we take all of the other electrons and assume that delocalized. That is 240 electrons there. And then we take the positive charge and rather than having 60 points. We smear it out. It is called Jellium, that is from the solid state physics and it is an approximation to be sure. But it is easier to solve. So, this is a Jellium approximation.

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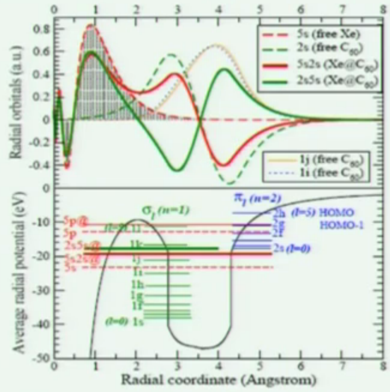

FIG. 1: (Color online) Bottom: The average radial LDA potential of Xe@C_{60}. $\pi(n=2)$ and $\sigma(n=1)$ levels of free C_{60}, and valence $5p$ and $5s$ levels of free Xe are shown. Also, $5p$@, corresponding to the confined Xe, and $5s2s$@ and $2s5s$@, two hybrid states, are displayed. Top: Radial wavefunctions of some relevant free-system states and two hybrid states.

And all sorts of things happen now. First, let me tell you, supposing, I were doing Zenon inside of a C60. Well, then, I would be doing a calculation of for the 240 electrons, of the C60 plus, the 54 electrons of Zenon which is 294 electrons. ah. That is a big messy calculation. And so, I have to do some approximation. And the approximation that I do is called the Time-dependent Local Density Approximation.

And you know I have to; so, what I have here, then is the Atomic potential plus a well representing the shell potential. And that is here, atomic potential and a shell potential. And then I do the calculation for those 294 electrons, in this potential, gets messy. Now, one of the things we see, supposing you have an atomic level that is bound by some energy here; suppose, you have a well level that is also bound by some energy here.

And they nearly degenerate. What happens? Well, the general perturbation theory tells me what happens? I am going to get a wave function that is a linear combination of the two. And that is exactly what we see. This is the 5s free Zenon. However, in here, it is mixed and I get two wave functions: one that looks like this, the other that looks like this; in other words, positive and negative mixing of this wave function, and this one.

This is an Atomic wave function there is a shell wave function. And they mix. This is called Hybridization, the molecular physicist knew about it for years not in this particular case. I did not know about it though. Now, remember, when doing photo ionization this would be my initial state. If I have a very different initial state, I am going to get a very different cross section. That is the importance of Hybridization. It changes things very greatly.

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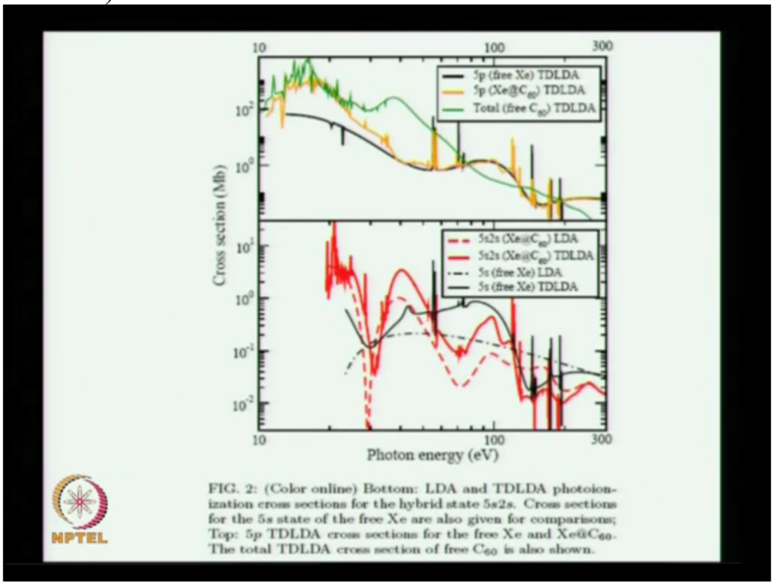

FIG. 2: (Color online) Bottom: LDA and TDLDA photoionization cross sections for the hybrid state 5s2s. Cross sections for the 5s state of the free Xe are also given for comparisons; Top: 5p TDLDA cross sections for the free Xe and Xe@C_{60}. The total TDLDA cross section of free C_{60} is also shown.

For example, this, see this black line, solid black line; I want you to focus on that, that is the 5s of Zenon, free atom. This is one of the combined levels and it looks like this. Now, you now, you say, well it is not terribly different. Yes, it is. This is a logarithmic scale just as much as a factor of 10, it completely changes the cross-section.

There is no relation at all. So, Hybridization, which the simple model does not take into account, is very, very important. That is what we find. Another thing that should be noticed; it is also interesting. The 5p of Zenon is not hybridized; but look at what we find, this is the 5p a free Zenon. This is the cross section of free C60.

Again, this is a factor of 100, so, about 100 times larger. Remember, what we talked about in the first example, I showed. Not in this business, with free atoms. If you have a cross section which is generic with a much larger cross section, you can get very strong Inter Channel coupling.

That is what happens here. Look at this, this yellow. Actually, kind of a nice yellow, it is kind of mustard, I think, not just yellow. What happens to the 5p only to the center channel coupling, the cross section goes from about 50 to about what 800 or so. It increases by about an order of magnitude because it mixed with something that is really very large; little piece of that. So, what we find is very significant Inter Channel coupling.

Here, there is something called a Sum Rule which says that the integral over the cross section suitably scaled should be the number of electrons in that state. So, 5p should be about 6 and this comes out, if I integrate this over this, particular range actually you need to integrate out to infinity; but just over that range you get about 5.5 in, in the neon and or and Zenon. Here in this case with the inter channel coupling, you get something like 50.

In other words, strength from the Shell is transferred for some reason to the atom. And furthermore, when the cross section for the Shell goes down and it is no longer much larger you see, you get pretty much the same cross-section except for these Confinement Oscillations. So, this makes a consistent picture here. And however, these are non-trivial calculations. These require a lot. What comes next?

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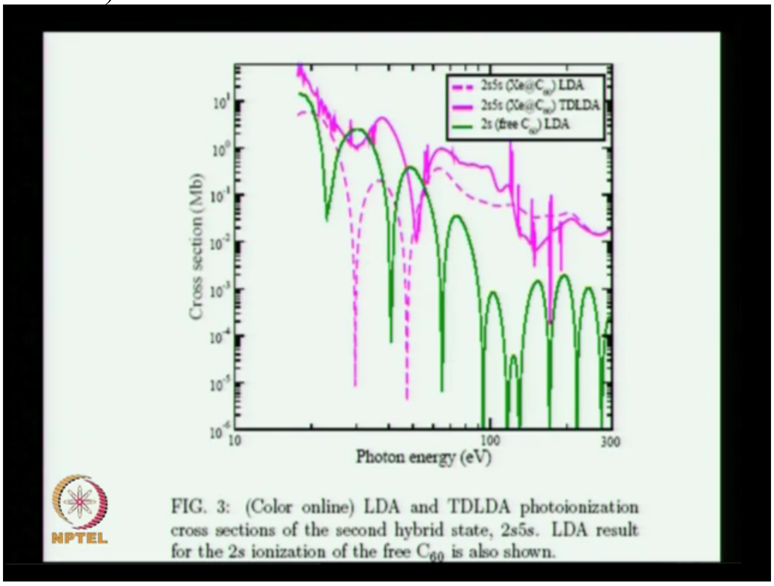

FIG. 3: (Color online) LDA and TDLDA photoionization cross sections of the second hybrid state, 2s5s. LDA result for the 2s ionization of the free C_{60} is also shown.

Do I remember? Oh, you see, you remember, they were two different, you know, when you had the, the Atomic level and the Shell level, it mixed into two different cross sections into 200 states. So, two different cross sections was too messy, to show all of them on previous slides. This one is the other one looks like this. By the way, this is the cross section for the free C60. But you get all sorts of interesting phenomenology here.

And that is about it. That gives you sort of a flavour of the kinds of things that we have been doing; and the kinds of things that we are capable of doing. Now I glossed over the details of the calculations, a lot of them took a long time and are very messy. But they can be done and they can give you all sorts of information.

And not only explain experiment, but give a guide to how experiment might be done. You know what? Experiments to do what might be interesting; because usually experiment comes first, but not always. Sometimes we predict things first. And I will stop here and thank you for as that says. Thank you for your attention.