

Select/Special Topics in ‘Theory of Atomic Collisions and Spectroscopy’
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Lecture 40
Fano Parameterization of Breit-Wigner formula

Greetings, this is the last unit of this course. And there are just a few classes in this. We already got the expression for the Breit Wigner formula. And today we will introduce the Fano parameters which describe the complete expression for the scattering cross section inclusive of the background and the resonance.

(Refer Slide Time: 00:42)

Various contributions to the scattering x-sec

$$\sigma_{tot} = \frac{4\pi}{k^2} \left[\sum_{l=0}^{\infty} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \operatorname{Re} \sin \xi_l(k) \operatorname{Re} \left(\frac{\frac{1}{2}\Gamma}{E_r - E - \frac{1}{2}i\Gamma} \right) \right] \right]$$

Sum of contributions from all partial waves

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\underbrace{\sin^2 \xi_l(k)}_{\text{'pure' background part}} + \underbrace{\frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2}}_{\text{'pure' resonance part}} + \underbrace{2 \sin \xi_l(k) \operatorname{Re} \left(\frac{\frac{1}{2}\Gamma}{E_r - E - \frac{1}{2}i\Gamma} \right)}_{\text{'interference' part}} \right]$$


Joachain, Quantum Collisions Theory, Eq 4.223, page 98
 Arno Bohm, Quantum Mechanics, Eq 9.1, page 439
 Bransden & Joachain, Physics of Atoms & Molecules, Eq 12.137, page 596

PCD STITACS Unit 7 Quantum Theory of Collisions - Part 4 2

So, let me quickly recapitulate the result we obtained in the previous class. So, this is the total cross section. And we found that it had three terms, one coming from the background alone, one coming from the resonance part and the third part which came from the interference between the background and the resonance part right.

So, these are the three terms. And then we have such terms for each partial wave l going from 0 through infinity. And the expression for the l th partial wave cross-section is now written in terms of these three parts right.

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$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2\sin \xi_l(k) \left(\frac{1}{2}\Gamma \right) \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

complex number: z

$$z = \frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} = \frac{\cos \xi_l + i \sin \xi_l}{a - ib} \times \frac{a + ib}{a + ib} \text{ where } a = E_r - E \text{ \& } b = \frac{1}{2}\Gamma$$

$$z = \frac{\cos \xi_l + i \sin \xi_l}{a - ib} \times \frac{a + ib}{a + ib} \quad \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) = \frac{(E_r - E) \cos \xi_l - \frac{1}{2}\Gamma \sin \xi_l}{(E_r - E)^2 + \left(\frac{1}{2}\Gamma\right)^2}$$

$$z = \frac{a \cos \xi_l - b \sin \xi_l + i(b \cos \xi_l + a \sin \xi_l)}{a^2 + b^2}$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2\sin \xi_l(k) \left(\frac{1}{2}\Gamma \right) \frac{(E_r - E) \cos \xi_l - \frac{1}{2}\Gamma \sin \xi_l}{(E_r - E)^2 + \left(\frac{1}{2}\Gamma\right)^2} \right]$$

PCD 511TACS Unit 7 Quantum Theory of Collisions - Part 4 3

So, let us look at this expression now. So you have got a real part of this complex number. So, I look at this complex number and rewrite it in a slightly different way okay. So, I take this complex number and I write it in terms of a and b okay. So, you have got in the complex number a real part here and an imaginary part here. But then you also have got a real part here and a imaginary part in the numerator which is cosine Psi and sine Psi.

So, you multiply and divide by the complex conjugate of the denominator. And then reconstruct this complex number, so that you will have an effective real part and an effective imaginary part. So, having done that you write this complex number in terms of this real parts which is now a cosine Psi - b sine Psi divided by a square + b square and the imaginary part will be b cosine Psi plus a sine Psi divided by a square + b square okay.

So, we need the real part of this complex number the real part of z. So, or zee as the young people call it, my generation always called it as z but now it is or zee I think. So, this is the real part of this complex number zee and what do we have here. So, this term will now go over here okay.

So, let us rewrite this scattering cross section for the lth partial wave in terms of this real part of the complex number z and that is in this blue box okay, right. So, this is a fairly straight forward substitution. Most of this is really very simple. There is no involved mathematics. It is just a matter of rearrangement of terms but done very cleverly by Fano. And that is what we are going to appreciate today.
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Eq 223, p. 98, Joachain, Quantum Collision Theory

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \sin \xi_l(k) \left(\frac{1}{2}\Gamma \right) \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

↕ equivalent ↕

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \sin \xi_l(k) \left(\frac{1}{2}\Gamma \right) \frac{(E_r - E) \cos \xi_l - \frac{1}{2}\Gamma \sin \xi_l}{(E_r - E)^2 + \left(\frac{1}{2}\Gamma\right)^2} \right]$$

We now **re-write** the above expressions in another equivalent form, using the **parameters q and ϵ** , introduced by **Fano** in the context of photoionization.

PCD STITACS Unit 7 Quantum Theory of Collisions - Part 4

So, we essentially find that these two forms of writing the l th wave partial, l th partial wave cross section in these two forms these are necessarily equivalent forms. What we will do now is to introduce the parameters which were defined by Fano in that famous paper. And we rewrite this expression in terms of q and ϵ .

So, that we express the effective cross section σ_l of the l th partial wave in terms of q and ϵ rather than the terms that you see over here okay. So, this is just an effective rewriting of the same expression. So, there is no new result okay. But the same expression when it is written in terms of these new parameters it gives us a very convenient and a very powerful tool to analyse the spectra, the collision spectra.

(Refer Slide Time: 04:40)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \sin \xi_l(k) \left(\frac{1}{2}\Gamma \right) \frac{(E_r - E) \cos \xi_l - \frac{1}{2}\Gamma \sin \xi_l}{(E_r - E)^2 + \left(\frac{1}{2}\Gamma\right)^2} \right]$$

Let: $a = E_r - E$; $b = \frac{1}{2}\Gamma$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{b^2}{a^2 + b^2} + 2 \sin \xi_l(k) b \frac{a \cos \xi_l - b \sin \xi_l}{a^2 + b^2} \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l + \frac{b^2}{a^2 + b^2} + \frac{2ab \sin \xi_l \cos \xi_l}{a^2 + b^2} - \frac{2b^2 \sin^2 \xi_l}{a^2 + b^2} \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l \left\{ \frac{a^2 - b^2}{a^2 + b^2} \right\} + \frac{b^2}{a^2 + b^2} + \frac{2ab \sin \xi_l \cos \xi_l}{a^2 + b^2} \right]$$

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So, here is a result now. So, let us rewrite it. And we rewrite it by introducing two auxiliary numbers a and b . And in terms of a and b , we rewrite this cross section in terms of a and b .

So, the middle terms become b^2 over $a^2 + b^2$ + b^2 over $a^2 + b^2$ b is half gamma. So, you are here you see you have got a quarter of a gamma square right.

And then you have got a square + b^2 right. So, the middle term is here. So, the only thing that is done is to rewrite it in terms of a and b over here. And then you rearrange the terms because you have two terms coming from here one coming from the multiplication of twice sine Ψ b with a cosine Ψ , and the other when you multiply this factor with b sine Ψ . So, you get these one two three four terms.

And then you combine the terms in sine square Ψ because you have got sine square Ψ over here and a sine square Ψ also in the fourth term. So, you combine the two terms and rearrange these terms a little bit so that you get $a^2 + b^2$ in the denominator in each of the three terms. So, that is the idea.

(Refer Slide Time: 06:01)

$$a = E_r - E \quad ; \quad b = \frac{1}{2}\Gamma$$

$$\sigma_l = \frac{4\pi}{k^2}(2l+1) \left[\sin^2 \xi \left\{ \frac{a^2 - b^2}{a^2 + b^2} \right\} + \frac{b^2}{a^2 + b^2} + \frac{2ab \sin \xi \cos \xi}{a^2 + b^2} \right]$$

$$\sigma_l = \frac{4\pi}{k^2}(2l+1) \left[\frac{b^2(1 - \sin^2 \xi) + \sin^2 \xi a^2}{a^2 + b^2} + \frac{2ab \sin \xi \cos \xi}{a^2 + b^2} \right]$$

$$\sigma_l = \frac{4\pi}{k^2}(2l+1) \left[\frac{b^2(\cos^2 \xi) + \sin^2 \xi a^2}{a^2 + b^2} + \frac{2ab \sin \xi \cos \xi}{a^2 + b^2} \right]$$

$$\sigma_l = \frac{4\pi}{k^2}(2l+1) \sin^2 \xi \left[\frac{b^2(\cot^2 \xi) + a^2}{a^2 + b^2} + \frac{2ab \cot \xi}{a^2 + b^2} \right]$$

Now having done this, you rearrange these terms one more time okay. And I will not comment so much on these rearrangements they are quite straightforward but a very effective. They are extremely effective. So, you rearrange these terms and I am going to use a form.

So, this expression for the l th partial wave cross-section is very much the same as we got in the previous class except that it has been rewritten in terms of these auxiliary parameters a and b which are respectively just the energy difference from the resonance energy and the half width of the resonance okay. So, they are rewritten in terms of a and b . So, these are like intermediate auxiliary parameters.

(Refer Slide Time: 06:57)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \left[\frac{b^2 (\cot^2 \xi) + a^2}{a^2 + b^2} + \frac{2ab \cot \xi}{a^2 + b^2} \right]$$

$$a = E_r - E \quad \& \quad b = \frac{\Gamma}{2}$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \left[\frac{b^2 q^2 + a^2}{a^2 + b^2} - \frac{2abq}{a^2 + b^2} \right]$$

$$\tan \delta_l^r = \frac{\Gamma(E)/2}{(E_r - E)}$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \left[\frac{b^2 q^2 + a^2 - 2abq}{a^2 + b^2} \right]$$

$$\text{define (FANO)}$$

$$\epsilon = -\cot \delta_l^r = -\frac{a}{b}$$

$$q = -\cot \delta_l^b$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \left[q^2 + \frac{a^2}{b^2} - 2\frac{a}{b}q \right] \frac{b^2}{a^2 + b^2}$$

$$\tan \delta_l^r = -\frac{1}{\epsilon} = -\frac{b}{a}$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \frac{\left(q - \frac{a}{b} \right)^2}{1 + \left(\frac{a}{b} \right)^2}$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$

So, here we are. We have a and b. Then we do know that the tangent of the phase shift at resonance is given by gamma over twice the difference of this energy and this is in fact how we had defined the resonance with. This was the definition of gamma as you will remember. So, now we have this expression and what we do is to define these two parameters epsilon and q following Fano.

So, this is how Fano defined the two parameters epsilon and q. So, epsilon is nothing but the negative of the cotangent of the resonant phase shift. And q is nothing but the negative of the cotangent of the background phase shift okay. So, these are two parameters and notice that this epsilon is nothing but a ratio of a over b with a negative sign okay.

So, epsilon is just minus a over b and q is this q come comes from the background phase shift comes from the cotangent of the background phase shift or the negative of the cotangent of the background phase shift. So, we will rewrite these terms. So, instead of a and b we will now rewrite it in terms of the Fano parameters epsilon and q. Now how do we do that.

So, we notice that if you take the reciprocal of q, reciprocal of E you get b over a okay. And then you have the partial wave cross-section which is $2l + 1$ sine square is Psi. So, you combine these two terms using just the usual properties of the cotangent functions okay. And notice that you already get the q parameter appearing over here. But the epsilon is yet to arrive in our expression.

So, we again reorganize these terms okay. So, this is a straightforward rearrangement of the terms. So, you have you rewrite this term with a square + b square as common. You have got three terms and these are the three terms. So, now you have b square you factor out from this.

So, you get only q square in this term and then a square over b square and then since b square has been factored out you get 1 over b .

So, this becomes $\text{minus twice } a \text{ over } b q$ and what is this, this is nothing but the square of q minus a over b but a over b is nothing but the negative of ϵ okay. So, now we can write the l th partial wave cross section which contains all the three contributions one from the background then, from the resonance part and then, from the interference part.

So, all the three together because that is what an experiment is going to see the experiment does not distinguish you know when it when you have a detector it is not going to sense which part is coming from which term. So, you will get a net effect and that net effect is now written in terms of these two parameters.

So, the a over b is here, the q is here. And that allows us to write the scattering cross section for the l th partial wave in terms of the Fano parameters q and ϵ . So, the numerator here is just the square of $q + \epsilon$ and the denominator is just $1 + \epsilon$ square okay. So, this is effectively just the same expression.

There is nothing new in this that we have found today except that we have rewritten the scattering cross section for the l th partial wave in terms of two parameters, one related to the phase shift from the background and the other coming from the phase shift at resonance okay. Thus, net scattering phase shift we had written as the sum of two parts in our previous classes in the last unit.

But we did was to express the total scattering phase shift as the sum of two parts so we have separated out the dynamics resulting from the background and the dynamics which was coming from the resonance structure.

(Refer Slide Time: 11:57)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\underbrace{\sin^2 \xi_l(k)}_b + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \sin \xi_l(k) \frac{1}{2} \Gamma \operatorname{Re} \left(\frac{e^{i\delta_l^{(i)}}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

FANO parameters $\epsilon = -\cot \delta_\ell^r(k)$ $\tan \delta_\ell^r = \frac{\Gamma(E)/2}{(E_r - E)}$
 $q = -\cot \xi_l(k)$ $= -\frac{1}{\epsilon} = \frac{b}{a}$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l \frac{\left(\frac{q - \frac{a}{b}}{1 + \left(\frac{a}{b}\right)^2} \right)^2}{1 + \epsilon^2} = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$

PCD STTACS Unit 7 Quantum Theory of Collisions - Part 4 8

So, these are the three terms that we begin with okay. The background part, the resonance part and the interference part okay. Labelled by b, r and i respectively and now we have these Fano parameters q and epsilon. And in terms of this we have the same cross-section, the same scattering cross section which contains information about all of these three together but written in this single term but in terms of two parameters which are q and epsilon. (Refer Slide Time: 12:35)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\underbrace{\sin^2 \xi_l(k)}_b + \frac{\frac{1}{4}\Gamma^2}{(E_r - E)^2 + \frac{1}{4}\Gamma^2} + 2 \sin \xi_l(k) \frac{1}{2} \Gamma \operatorname{Re} \left(\frac{e^{i\delta_l^{(i)}}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$

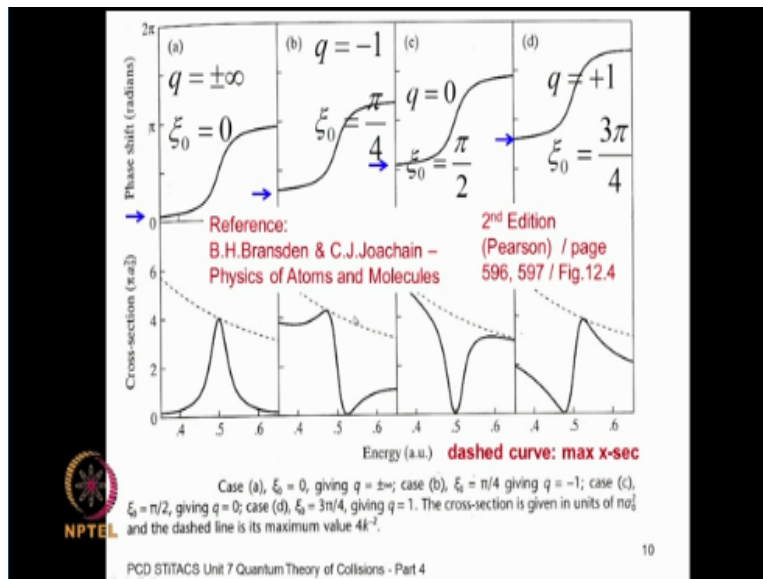
$$\epsilon = -\cot \delta_\ell^r(k); q = -\cot \xi_l(k) \quad \tan \delta_\ell^r = \frac{\Gamma(E)/2}{(E_r - E)} = -\frac{1}{\epsilon} = \frac{b}{a}$$

when ξ_l :small, $\sigma_l \rightarrow \sigma_l^{(r)}$

NOTE: when $q = -\epsilon$, $\sigma_l = 0$

PCD STTACS Unit 7 Quantum Theory of Collisions - Part 4 9

So, this is our effective expression for the scattering cross section in terms of the Fano parameters. Notice that when the background phase shift is small, when sigma goes to 0 then you have only the resonant part of the scattering cross section right. And when q is minus epsilon the cross section can actually vanish okay. So, there is nothing. No stopping from the scattering cross section to disappear and it is not always that when you have resonance effects the scattering cross section must only increase because it can also decrease, it can even vanish, it can even go to zero. (Refer Slide Time: 13:23)



So, here is a figure from Bransden Joachain's book which I would like to discuss. And this is figure 12.4 in Bransden and Joachain's book and it has got four panels a, b, c and d. And they represent different cases which are described in the caption for the figure. So, here you notice that the background cross-section this is for S waves so which is why the quantum number l is equal to zero which is the subscript of Ψ .

So, this is for l equal to 0 S wave scattering. So, that is the example which is discussed over here. And for this case, here the background cross background phase shift which is Ψ is 0. So, Ψ_0 is 0 and this would correspond to q being either plus infinity or minus infinity. So, you will see how it is related it is very straightforward.

Then here the background cross section phase shift is higher than over here. So, it is about halfway between 0 and π by 2. So, this background phase shift is about π by 2. And then, in panel c the background phase shift is about π by 2, this is π by 4 in panel b. In panel c the background phase shift is π by 2 and in panel d it is 3π by 4.

So, this is π by 2, this is π , this is about three fourth. So, this background phase shift is about three fourth of π . And these are the corresponding cross sections and they come in all kinds of shapes. And that is the reason it becomes very fruitful to analyse them in terms of what we call as a shape parameter which is the q because they all have different q values. So, let us look at these figures carefully panel by panel.

So, I will discuss each panel separately. So, in each of these you have got a dashed curve which is just what the maximum cross-section at that energy which would be possible but then because of resonances the cross-section changes sometimes widely, sometimes it also

goes to zero. So the dash curve only represents the maximum cross-section which can occur at that particular energy or momentum.
(Refer Slide Time: 16:03)

Case (a), $\xi_0 = 0$, giving $q = \pm\infty$; case (b), $\xi_0 = \pi/4$ giving $q = -1$; case (c), $\xi_0 = \pi/2$, giving $q = 0$; case (d), $\xi_0 = 3\pi/4$, giving $q = +1$. The cross-section is given in units of πa_0^2 and the dashed line is its maximum value $4k^{-2}$.

(a) $\xi_0 = 0 \rightarrow q = \pm\infty$	$\varepsilon = -\cot \delta_\ell^r(k)$ $q = -\cot \xi_\ell(k)$
(b) $\xi_0 = \frac{\pi}{4} \rightarrow q = -1$	
(c) $\xi_0 = \frac{\pi}{2} \rightarrow q = 0$	
(d) $\xi_0 = \frac{3\pi}{4} \rightarrow q = +1$	

$\ell = 0$
s-wave scattering

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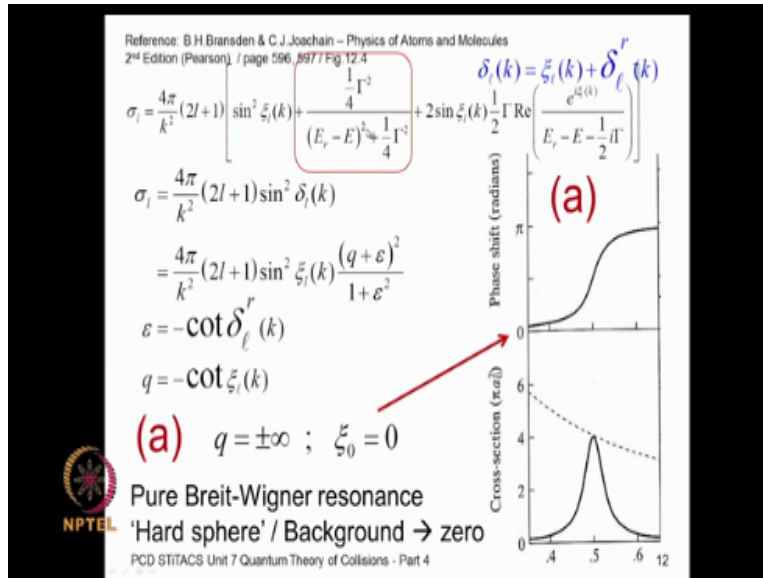
11

So, let us look at these parameters carefully. So, we are discussing $l = 0$ the s wave scattering in terms of the Fano shape parameters. And notice that when this background cross phase shift is 0 look at this when would when Ψ_0 is 0, what do you get for cotangent of Ψ , it will be either plus infinity or minus infinity right.

So, that is how the parameters are related okay. So, when about the background phase shift is 0, the Fano q parameter would be plus or minus infinity. So, the value of q is essentially determined by the phase shift of the background scattering okay. When the background phase shift is π by 4 which is what we see saw in the second panel right. When the background phase shift is π by 4 what is the negative cotangent of π by 4, it is -1 okay.

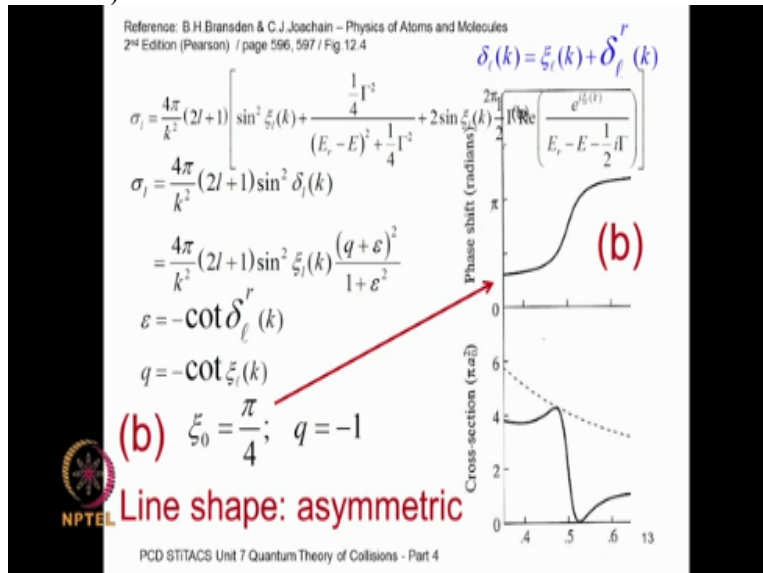
What when the background phase shift is π by 2, when the background phase shift is π by 2 the cotangent would go to 0 and $q = 0$. And in the fourth panel the background phase shift was 3π by 4 and the Fano q parameter would be plus 1. So, these are simply coming from the values of the background phase shift okay.

But they give you a range of q values which can be anything from plus infinity to minus infinity at the background phase shift can be anything from 0 to π or modular π right. So, the background phase shift can be anything which means that the q parameter can be just about anything and as you see from these figures they determine the shape of the resonance.
(Refer Slide Time: 18:02)



So, here is the case which was in panel a. And in this case the background phase shift is 0, q is plus infinity or minus infinity and what do you get, you get a cross-section. If you put these values q equal to plus infinity or minus infinity in the expression for the scattering cross section.

You get essentially the pure Breit-Wigner resonance which we have discussed at length in our previous unit in our previous classes. So, you get the pure Breit-Wigner resonance in this case when q is either plus infinity or minus infinity. So, that can always be a special case that you have just a pure resonance.
(Refer Slide Time: 18:51)



But then you may have as in case b, a background phase shift which is $\pi/4$ and in this case q is minus 1. And notice that this would give you a net cross-section which is given by this formula here and what does it turns out to have an asymmetric line shape. So, typically the resonance profiles have asymmetric line shapes but not necessarily.

They may also be symmetric like in the Breit-Wigner pure resonance. It does have a symmetric line shape. In this case it is asymmetric.

(Refer Slide Time: 19:34)

Reference: B.H Bransden & C.J. Joachain - Physics of Atoms and Molecules
2nd Edition (Pearson) / page 596, 597 / Fig.12.4

$$\delta_l(k) = \xi_l(k) + \delta_l^r(k)$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{1}{4} \frac{\Gamma^2}{(E_r - E)^2 + \frac{1}{4} \Gamma^2} + 2 \sin \xi_l(k) \frac{\Gamma}{2} \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \delta_l(k)$$

$$= \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$

$$\varepsilon = -\cot \delta_l^r(k) \quad (c) \quad \xi_0 = \frac{\pi}{2}$$

$$q = -\cot \xi_l(k) \quad q = 0$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} = 0$$

$$\delta_l^r(k) = \frac{n\pi}{2}; \quad n: \text{odd integer}$$

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In case c the background phase shift is pi by 2 which begins over here and q is 0. And when q is 0, you have got only the square of epsilon in the numerator here in this formula okay. But what is epsilon. It is related to the resonance phase shift. And the resonance phase shift is pi by 2 okay. We have seen that in our previous discussion. So, what does it mean you get a scattering cross section which actually goes to 0. And this resonance is often called as a window resonance okay. Because as you can see you get a window like behaviour, a window like shape in the red in the scattering cross section. So, this is often referred to as a window resonance.

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Reference: B.H Bransden & C.J. Joachain - Physics of Atoms and Molecules
2nd Edition (Pearson) / page 596, 597 / Fig.12.4

$$\delta_l(k) = \xi_l(k) + \delta_l^r(k)$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{1}{4} \frac{\Gamma^2}{(E_r - E)^2 + \frac{1}{4} \Gamma^2} + 2 \sin \xi_l(k) \frac{\Gamma}{2} \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \delta_l(k)$$

$$= \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$

$$\varepsilon = -\cot \delta_l^r(k)$$

$$q = -\cot \xi_l(k)$$

$$(d) \quad \xi_0 = \frac{3\pi}{4}; \quad q = +1$$

Line shape: asymmetric

PCD STITACS Unit 7 Quantum Theory of Collisions - Part 4

And then we also had the other case which is the ah background phase shift being three-fourth of pi. And then you have got q =+1. And as was the case for q =-1, you have an

asymmetric line profile. So, most of the profiles for various different values of q will be asymmetric okay.

In certain cases you may get some kind of symmetry that depends and the actual shape, the information about the shape of the profile is then contained in the q parameter. So, this is the famous Fano's q parameter. And you can see that how specially if you are an experimentalist you would like to look at the shape and analyse it in some simple terms.

So, Fano parameters let you analyse the shape of the resonances in a very neat form. (Refer Slide Time: 21:34)

The slide displays two equivalent mathematical expressions for the scattering cross section σ_l of the l th partial wave. The first formula is a complex expression involving phase shifts $\xi_l(k)$, a parameter Γ , and a real part of a complex fraction. The second formula is a simplified Fano-like form:
$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$
 The parameters b , r , and i in the first formula are circled in blue. Below the formulas, a reference is provided: "Reference: We shall begin by discussing the method developed particularly by Fano† that is aimed especially at a description of auto-ionization. After" followed by a list of references: "† FANO, U., Nuovo Cim. 12 (1955) 166; Phys. Rev. 124 (1961) 1806; work of RICK, O. K., J. chem. Phys. 1 (1933) 375." To the right is the cover of the book "ELECTRONIC AND IONIC IMPACT PHENOMENA" by H. A. MASSEY and R. S. BURHOP, Volume 1, published by the Clarendon Press. The NPTEL logo is visible in the bottom left corner.

So, here is our expression for the scattering cross section of the l th partial wave. So, this formula is no different from this one. There is nothing in this formula which is not there in the first formula. The two are completely equivalent but the second one is in terms of parameters which have got rather simple interpretation when you are looking at a scattering spectrum.

When you look at the scattering cross section and study it as a function of energy or momentum then, you can analyse the shapes of the resonances very neatly using the Fano shape parameters. And ah here I have given some reference but plural references because there are so many of them okay.

And I am borrowing some discussion from the book by Massey and Burhop on electronic and ionic impact phenomena. This is a very classic book on scattering theory and then of course there are a large number of papers by Fano and other reviews and so on. So, I am not going to attempt to review the entire literature extensively except point out some of the key references. (Refer Slide Time: 22:50)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\underbrace{\sin^2 \xi_l(k)}_{\mathbf{b}} + \underbrace{\frac{\Gamma^2}{4}}_{\mathbf{r}} + \frac{1}{(E_r - E)^2 + \frac{\Gamma^2}{4}} + 2 \sin \xi_l(k) \underbrace{\frac{1}{2}}_{\mathbf{i}} \Gamma \operatorname{Re} \left(\frac{e^{i\xi_l(k)}}{E_r - E - \frac{1}{2}i\Gamma} \right) \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$

Ugo Fano
Physical Review
Vol. 124 Number 6
December 15,
1961
p. 1866 to 1878

Configuration interaction in a many-electron system
• bound-bound
• bound-continuum

NPTEL
PCD SITACS Unit 7 Quantum Theory of Collisions - Part 4
17

So, this is these are the three terms which are of importance to us the background term, the resonance term and the interference term. And these play this formula in terms of the Fano parameters becomes extremely useful when you study the configuration interaction between bound to bound and bound to continuum transitions.

So, that that's what you get in a phenomenon like auto ionization okay. In auto ionization you have got alternate channels which are open for the photo absorption process. The photo absorption can result in either a bound to bound transition from an inner electron of the atom or from a bound to continuum transition from an outer electron.

Because both the processes can be degenerate and it will be a resonant process because the bound to bound transition is always between discrete levels which are quantized okay. So, this will be a resonant process. And essentially you have these two possibilities. So, you can have an electron in the bound state or in a two electron system you can have one electron in a bound state and the other also in an excited bound state.

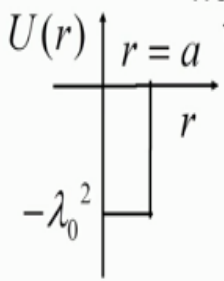
So, this will be a bound to bound transition from discrete bound to discrete bound okay. And this channel is degenerate with an outer bound into the continuum and these two represent two different configurations or occupation numbers of the single electron states are obviously different in these two.

So, you essentially have a configuration interaction between the continuum and the discrete. And that is what Fano parameters help us analyse. So, this is the classic paper which I mentioned earlier also most atomic physicists have got this reference by heart they know volume 124, number 6 everything. They almost know it by heart. It is a classic paper. (Refer Slide Time: 24:54)

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \left[\sin^2 \xi_l(k) + \frac{1}{4} \frac{\Gamma^2}{(E_r - E)^2 + \frac{1}{4} \Gamma^2} + 2 \sin \xi_l(k) \frac{1}{2} \Gamma \operatorname{Re} \left(\frac{e^{i\delta_l(E)}}{E_r - E - \frac{1}{2} i\Gamma} \right) \right]$$

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \xi_l(k) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$

We developed our formalism for a square well potential



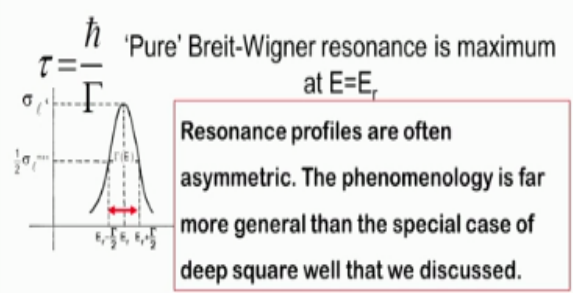
How would the interpretation of above terms proceed for more *realistic potentials*?

PCD SITACS Unit 7 Quantum Theory of Collisions - Part 4 18

So, we analysed this in terms of the square well potential right. The expressions we got were in terms of the scattering by a square well. That was our prototype of a potential. But then our interest is in realistic potentials. And the realistic potentials would be somewhat different from square well potential. The square well potential is just an attractive model potential.

And we will therefore now like to ask how will this analysis go if you worked with a more realistic potential then, some of the parameters may end up having either a different interpretation or they if you are to use the same kind of expression then you must find out what would be the meanings of these parameters and how to interpret them. So, let us discuss that.

(Refer Slide Time: 26:00)



$\tau = \frac{\hbar}{\Gamma}$

'Pure' Breit-Wigner resonance is maximum at $E = E_r$

Resonance profiles are often asymmetric. The phenomenology is far more general than the special case of deep square well that we discussed.

Maximum cross section is not at E_r

← hard sphere part

Resonance profiles: asymmetric

Joachim QCT Fig. 4.9. A typical behaviour of the cross section σ_l when $\ell_1 = \frac{1}{2} \pi$ at $E = E_r$. The quantity $\frac{1}{2} \Gamma$ corresponds to "hard sphere" scattering and $\sigma_l^{\text{max}} = 4\pi(2l+1)/k^2$.

So, let us consider a pure Breit Wigner resonance which has its maximum at $E = E_r$. This is a symmetric. You know classic Lorentzian shape okay. But most of the resonance profiles are

often asymmetric. And then we can deal with potentials which are much different than the square well potential.

And the typical resonance profile as you see in this figure. You have got the background cross-section which goes almost flat over this small energy region, over a wider energy region background cross section of course would change but over a narrow region it would be relatively flat.

And over this the actual cross section has got a completely different symmetry okay. It is an asymmetric cross section and obviously has some value of q which is somewhere between minus infinity and plus infinity and we can specify exactly what is the value of q for this particular shape resonance okay.

So, the maximum of the cross section as you see is not necessarily at the value of E_r . It can be somewhere else. So, the criterion of the resonance energy is that it is the energy at which the resonant part of the phase shift goes through π by 2 okay. That is the criterion and not the value of the cross section itself.

The cross section can hit the roof. And it can be a maximum, it can also disappear in a window resonance, it can even go to 0 or it can have any other value in the intermediate range anywhere between zero and whatever is the maximum value that it can get. So, you have got the background part which is relatively flat over this narrow energy region. (Refer Slide Time: 27:52)

$U(r)$ vs r graph showing a square well of depth $-\lambda_0^2$ and radius a .
 $k^2 = \lambda_0^2 + k^2$
 $r < a: y_{el}(r) = C_1 r j_l(\kappa r)$
 $R_{el}(r) = \frac{y_{el}(r)}{r}$
 Joachan 'Quantum Theory of Collisions: Eq 4.151 page 87'
 Recapitulate the terms for the square well potential so that we can examine the modifications necessary for other forms of the potential.
 $\gamma_l = -\tan^{-1} \left(\frac{\kappa j_l'(\kappa a)}{j_l(\kappa a)} \right)$
 de w. evaluated at $r = a$
 $\frac{\kappa j_l'(\kappa a)}{j_l(\kappa a)}$ Logarithmic derivative of the radial wave function at $r = a$
 NPTEL
 PCD 5T1FACS Unit 7 Quantum Theory of Collisions - Part 4 Joachan 'Quantum Theory of Collisions: Eq 4.153 page 87' 20

And to understand these terms we will very quickly recapitulate some of the terms that we have discussed at length for the square well ah potential which we have discussed at length in

our previous classes. So, I will only summarize the essential results just to relate so that we can relate to those terms.
(Refer Slide Time: 28:12)

$U(r)$ vs r diagram showing a potential well of depth $-\lambda_0^2$ for $r < a$ and zero for $r > a$.

$\kappa^2 = \lambda_0^2 + k^2$

$r < a: y_{el}(r) = C_1 r j_l(\kappa r)$

$R_{el}(r) = \frac{y_{el}(r)}{r}$

$r > a: y_{el}(r) = j_l(kr) - \tan \delta_l(kr) n_l(kr)$

$\gamma_l = \left. \frac{\left(\frac{dR_l(r)}{dr} \right)}{R_l(r)} \right|_{r=a} = \left. \frac{\left(\frac{d}{dr} j_l(\kappa r) \right)}{j_l(\kappa r)} \right|_{r=a}^{\text{interior}} = \left. \frac{\kappa j_l'(\kappa r)}{j_l(\kappa r)} \right|_{r=a}$

Prime: derivative w.r.t. κr evaluated at $r = a$

$\gamma_l = \frac{\kappa j_l'(\kappa a)}{j_l(\kappa a)}$ **Logarithmic derivative of the radial wave function at $r = a$**

PCD STITACS Unit 7 Quantum Theory of Collisions - Part 4 Joachain 'Quantum Theory of Collisions', Eq. 4.151 page 87 21

And we you will remember that we had solutions for the inner region, we had solutions for the outer region, we had the wave functions, the exact radial functions okay. For the outer region and for the inner region we have the expression for the continuity of the logarithmic derivative coming from the continuous nature of the radial function and also its derivative.
(Refer Slide Time: 28:42)

$r > a: y_{el}(r) = j_l(kr) - \tan \delta_l(kr) n_l(kr)$

Normalize the radial wave function outside the well to unit amplitude:

$R_l(kr) = \frac{y_l(kr)}{r}$

$r \geq a: y_l(k, r) = \sin\left(kr - \delta_l(kr) - \frac{l\pi}{2}\right)$

$\gamma_l = \left. \frac{\left(\frac{dR_l(r)}{dr} \right)}{R_l(r)} \right|_{r=a} = \left. \frac{\left(\frac{d}{dr} j_l(\kappa r) \right)}{j_l(\kappa r)} \right|_{r=a}^{\text{interior}} = \left. \frac{\kappa j_l'(\kappa r)}{j_l(\kappa r)} \right|_{r=a}$

$\kappa^2 = k_0^2 + \lambda_0^2$

near: $E = E_r$

$r < a: y_l^{\text{internal}}(k, r) = \frac{(2l+1)!!}{(ka)^l} \left[\frac{\frac{1}{4} \Gamma^2}{(E_r - E)^2 + \frac{1}{4} \Gamma^2} \right] \kappa r j_l(\kappa r)$

\rightarrow internal amplitude peaks at the resonance energy $E = E_r$.

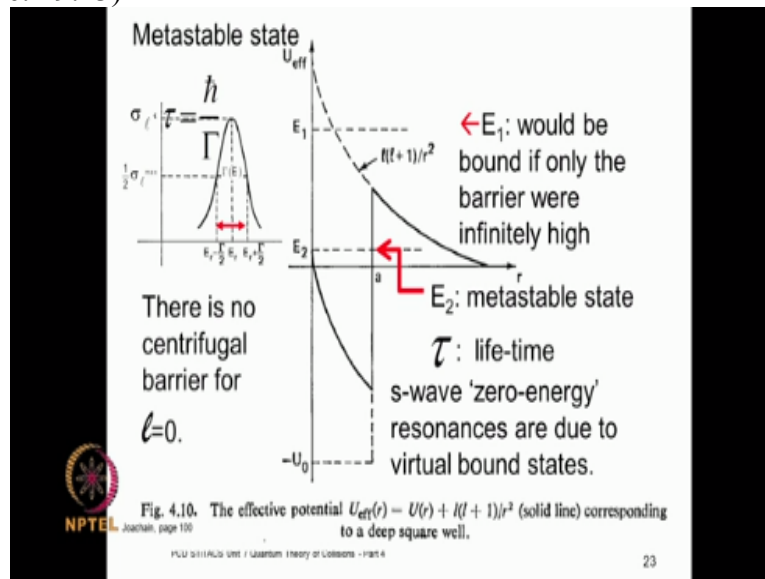
The particle gets nearly bound in the well.

PCD STITACS Unit 7 Quantum Theory of Collisions - Part 4 22

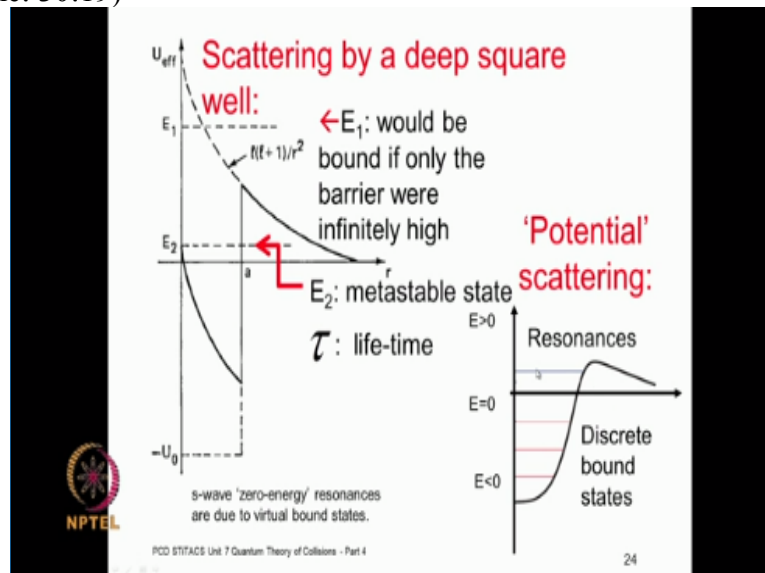
And what happens as a result of this is that when you exploit the continuity of the radial function and it is derivative okay. You have the corresponding expression for the outer region; outside you have got the total phase shift which is the sum of the background part and the resonance part.

And near the resonance if you rewrite this expression what it gives you for the internal wave function, is a function of an amplitude which is the most amplitude. So, what this whole

analysis is resulting in is that the particle tends to get bound in the well for this particular case. So, that is what happens at a resonance. So, there is a bound state which and the particle tends to get mind. It tends to get bound in that in the well.
 (Refer Slide Time: 29:43)



So, you can have for l not equal to 0. You can have the centrifugal barrier; you can have metastable states in this. And then for $l = 0$, we know that there is no centrifugal barrier because it is l into $l + 1$ by r square whereas. So, s wave resonances are coming because of the virtual bound states which we have discussed at some length especially in the context of the Levinson's theorem we have discussed this feature to us in considerable detail.
 (Refer Slide Time: 30:19)



So, now you have this potential scattering. So, this is no longer just a square well okay. It can have some other shape. And this figure we here in the lower right corner over here represents an alternative potential shape. It can be anything else. In general it is quite complex. It will

not even have an analytical form okay. And in most situations you end up getting numerical forms.

So, you cannot really sketch them so easily like this but by and large the only thing that is conveyed in this figure is that this is how you will deal with potential scattering from those potentials which are different from the square well potential and this is a prototype of all of them okay. So, you can have discrete bound states over here, you can have metastable resonances over here which will give you shape resonances. (Refer Slide Time: 31:24)

Scattering by a deep square well:

$$e^{2i\delta_\ell(k)} = e^{2i\delta_\ell^r(k)} \left[\frac{\gamma_\ell(ka) - r_\ell + is_\ell}{\gamma_\ell(ka) - r_\ell - is_\ell} \right] = e^{2i[\xi_\ell(k) + \rho_\ell(k)]}$$

$$\delta_\ell(k) = \xi_\ell(k) + \rho_\ell(k) = \xi_\ell^r(k) + \delta_\ell^r(k) \quad \tan \rho_\ell(k) = \frac{s_\ell(k)}{\gamma_\ell(k) - r_\ell(k)}$$

$$\tan \delta_\ell^r(E) = \left[\frac{\Gamma(E)/2}{(E_r - E)} \right] \quad e^{2i\delta_\ell(k)} = e^{2i\delta_\ell^r(k)} \left[\frac{E - E_r - i\frac{1}{2}\Gamma}{E - E_r + i\frac{1}{2}\Gamma} \right]$$

'Potential' (some other shape) scattering:

How would the above relations get modified? we expand, for other potentials:

$$\gamma_\ell(E) = \gamma_\ell(E_r) + (E - E_r) \left[\frac{d\gamma_\ell(E)}{dE} \right]_{E=E_r}$$

NPTEL Joachain/QCT/Eq 4.236p102 PCD SITACS Unit 7 Quantum Theory of Collisions - Part 4 25

And then you can analyse this in terms of the phase shifts at resonance and the phase shift in the background region which is Psi. And our question that we are addressing is how would the above relations all of these relations how will they get modified if we deal not with an ideal square well potential but with some other potential the prototype of which is what our figure suggested.

So, our first conclusion is that if our potential is no longer the square well potential what we had for gamma and gamma plays a big role over here. Notice that all the rapid fluctuations are coming because of gamma. r and s and Psi, they change relatively smoothly across the resonance region. It is the gamma which changes widely and that is of importance.

And because gamma is changing widely for a potential which is other than the square well potential, you will not be able to use the same expression for gamma as you did for the square well potential for which we had the exact solutions for the inner region and the outer region. For some arbitrary potential we can hope to expand gamma about the resonance energy and we carry out a power series expansion and consider only the first term.

We already know that compared to the energy differences between adjacent resonances, the width of a resonance is rather small which is why they appear as spikes. So, it is sufficient to take the first order term in the power series expansion for gamma. So, you have a power series expansion for gamma, this is the first order term. And this is what we will use for gamma.

(Refer Slide Time: 33:34)

Scattering by a deep square well:

$$\tan \delta_l^r(E) = \frac{\Gamma(E)/2}{(E_r - E)}$$

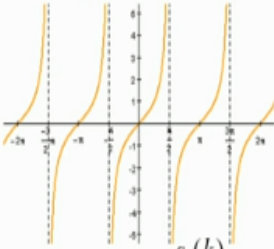
Tangent function

at $E = E_r$

$$\gamma_l(k) = r_l(k)$$

$$\rho_l = \delta_l^r = \frac{n\pi}{2}$$

n : odd integer



$$\tan \rho_l(k) = \frac{s_l(k)}{\gamma_l(k) - r_l(k)}$$

At resonance:

$$\gamma_l(k) \approx r_l(k)$$

PCO 511TACS Unit 7 Quantum Theory of Collisions - Part 4 26

So, now let us look at the expression for the resonant phase shift. And this is just simply determined by the properties of the tangent functions which we have discussed earlier also. And notice that at resonance when $E = E_r$ this denominator goes to zero. So, the tangent shoots up right. And phase shift is $n\pi$ by 2 okay. So, that is the criterion mind you for a resonance.

It is not in terms of what is the value of the cross-section, it is in terms of what is the value of the scattering phase shift of the resonance part of the scattering okay. The net phase shift being separated in the background part Ψ and the resonance part δ . So, this phase shift ρ which is the part of the phase shift other than the background, when it is specifically at the resonance we use a specific symbol for it which is δ with a superscript r .

So, this is nothing but ρ at resonance and this will be $n\pi$ by 2 and essentially if you look at this alternative expression for the tangent of the phase shift. When this tangent blows up as one would expect at resonance effectively you have γ becoming nearly equal to r , so that this denominator would go to 0.

So, γ being equal to r is the same condition as the resonance condition $E = E_r$ and the resonance phase shift going to π by 2 or $n\pi$ by 2 where n is an odd number. So, $\gamma = r$

is now an equivalent criterion to recognize the resonance condition for square well scattering potential. So, at resonance gamma is nearly equal to r. So, that is our conclusion. (Refer Slide Time: 35:42)

If $[\gamma_l]^{potential\ scattering} \iff [r_l]^{square\ well\ scattering}$,

what would $[s_l]^{potential\ scattering}$ correspond to, so that

we may write $\tan \delta_l^r(E) = \left[\frac{\Gamma(E)/2}{(E_r - E)} \right] ?$

$potential\ scattering \rightarrow$ 'some other' / realistic potential, **other than the** deep square well potential we have considered.

? interpretation of $[s_l]^{potential\ scattering} ?$ & $[\Gamma_l]^{potential\ scattering} ?$

NPTEL
PCO STTACS Unit 7 Quantum Theory of Collisions - Part 4
27

What we will do now is that if we now carry forward the same interpretation that if gamma being associated or being set equal to r works for scattering potential. And if we were to extend this correspondence to other cases also, when you have a potential which is different from a square well potential then, if we were to write the tangent of the phase shift using a similar expression.

What would be the meaning of gamma it could be different okay. Because you are re-interpreting this in terms of the square well parameters but for a potential case presuming that gamma being equal to r works even for other cases. So, this will give us an effective interpretation of the width of the resonance width. So, let us look at other cases of potential scattering.

When I use the term potential scattering, I am specifically looking at those potentials which are other than the square well potential. What I have for a square well potential is what I indicate explicitly by writing a square well scattering as a superscript over here. So, anything which is a potential scattering this is of course also a potential but it is a specific potential that we have worked with and for which we have got the exact solutions.

Whereas this is in general some other potential which is a more realistic potential prototype of which we have the figure for. And in general it would be some other potential other than the square well deep square well potential okay. And then we will ask the question that if this correspondence holds good even for potential scattering.

Then what would be the interpretation of s and what would be the interpretation of gamma. Over here the interpretation of r is what we pin down as a reference level okay. So, r would be the same as gamma but gamma for the potential scattering is not the same as gamma for a square wave scattering.

We have seen that you can expand it about the energy and you then include at least the first order correction term okay. So, we will now ask what would be the interpretation of the parameters s and gamma in this case for potential scattering. (Refer Slide Time: 38:25)

'Potential scattering':

In the region of the resonance, $\xi_l, r_l, s_l \rightarrow$ nearly invariant with energy.

$\gamma_l(k) \rightarrow$ changes with energy.

At resonance $\rho_l(k) \leftrightarrow \delta_l^r$

$$\gamma_l(E) = \gamma_l(E_r) + (E - E_r) \left[\frac{d\gamma_l(E)}{dE} \right]_{E=E_r}$$

$$\tan \rho_l(k) = \frac{s_l(k)}{\gamma_l(k) - r_l(k)} \quad \tan \delta_l^r(E) = \frac{\Gamma(E)}{(E_r - E)}$$

As in the case of resonances in scattering by deep square well, if $\gamma_l = r_l$ we get:

$$\tan \delta_l^{(r)}(k) = \frac{s_l(k)}{(E - E_r) \left[\frac{d\gamma_l(E)}{dE} \right]_{E=E_r}}$$

Labels in the slide: 'spherical square well', 'potential scattering', 'NPTEL', 'POD STITACS Unit 7 Quantum Theory of Collisions - Part 4', '28'.

So, this is the expansion of gamma. So, you have got this is the first order change in gamma that you will need to consider when you deal with potentials other than the square well potential. And you do know that the representation of the remaining part of the phase shift which is other than the background phase shift which is Rho has got a specific notation in our analysis which is delta superscript r.

And we know that this expression holds good for the square well potential. And we know that for the square well potential the tangent of this phase shift you can write in terms of s, r and gamma and equivalently in terms of this gamma over the energy difference. This is how we defined gamma, so that this becomes equal to this at resonance right.

So, this is how this width gamma was defined. And now to write it in terms of s and r, we write this gamma in terms of this expansion on the right hand side. So, you have got this expansion here and then you have got s and r over here. But these may have a different interpretation than what we had for the square well case.

So, now our criterion to identify the interpretation of s and r and then also the resonance width gamma is that we presume that just as in the case of the deep square well potential this is our reference for comparison that we interpret r to be the same as gamma. So, this terms becomes equal to this right.

So, these two terms would be equal and they will cancel each other and you get an effective expression for the tangent of phase shift in which we do not have s and gamma anymore, you do have the derivative of gamma with respect to energy coming from this term. And this is valid for the potential scattering which is for the case when the scattering potential is something different from the square well potential.

(Refer Slide Time: 40:51)

If $\gamma_l = r_l$, $\tan \delta_l^{(r)}(k) = \frac{s_l(k)}{(E - E_r) \left[\frac{d\gamma_l(E)}{dE} \right]_{E=E_r}}$ (potential scattering)

$\tan \delta_l^{(r)}(k) = \frac{-s_l(k)}{(E_r - E) \left[\frac{d\gamma_l(E)}{dE} \right]_{E=E_r}}$ (potential scattering)

what would $\frac{\Gamma(E)}{2}$ be?

We expect to be able to write, in the neighborhood of 'resonance': $\tan \delta_l^{(r)}(E) = \frac{\left[\frac{\Gamma(E)}{2} \right]}{(E_r - E)}$ (potential scattering)

$\frac{\Gamma(E)}{2} \overset{\text{correspondence}}{\leftrightarrow} \frac{-s_l(k)}{\left[\frac{d\gamma_l(E)}{dE} \right]_{E=E_r}}$

NPTEL
PCD 5T1TACS Unit 7 Quantum Theory of Collisions - Part 4
29

So, this is the expression that we have, presuming that gamma and r are the same. But this is no longer the gamma ah of the ah square well potential, it is the one corresponding to the actual potential. And this is the leading term and then you have got a correction which is the first derivative of gamma with respect to energy. So, here I have rewritten this. I have got E minus Er in the denominator which I now write in terms of Er - E.

So, I have a minus sign over here. So, these two terms are essentially the same except that I have absorbed the negative sign in the denominator and attach it to the numerator okay. And what this allows me to do is to determine what would be how to interpret the resonance width okay. The resonance width has now got a new meaning for the potential scattering.

Because if the resonance width is to be, so defined that half of that divided by the energy difference will still be related to the tangent of the phase shifted resonance. Then, if we now have a correspondence which means between this part which is in this blue box and this part

which is in this blue box. So, these two parts must correspond to each other and that gives us an interpretation of the resonance width gamma for the potential scattering right.

Because these two must correspond to each other so that you can write gamma or you can interpret gamma once again in the same fashion that half of that divided by the energy difference will be the tangent of the phase shift at resonance. So, this is the correspondence which is emerging from this comparison okay.

(Refer Slide Time: 42:58)

$\frac{\Gamma(E)}{2} \quad \text{correspondence} \quad \leftrightarrow \quad \left. \frac{d\gamma_\ell(E)}{dE} \right|_{E=E_r} = \frac{-s_\ell(k)}{2}$

enables us to write, in the neighborhood of 'resonance':

$$\tan \delta_\ell^r(E) = \frac{\Gamma(E)/2}{(E_r - E)}$$

However, now, **for the present case of potential scattering**, it cannot be guaranteed that $\Gamma(E)$ is a positive quantity.

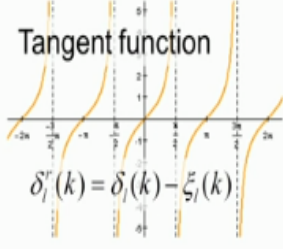
30

So, here this particular correspondence, it allows us to write the expression for the tangent of the resonance phase shift in the same form as we did for the square well scattering. And now because gamma has been interpreted in this particular form, we cannot presume any longer that this gamma will always be a positive quantity.

Because you know that the dynamics is governed by all these cotangent curves and they can take all kinds of value. So, you cannot guarantee their gamma is a positive quantity. So, it does not have to be a positive quantity.

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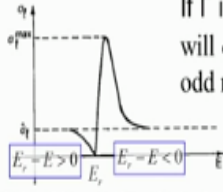
$$\tan \delta_{\ell}^r(E) = \left[\frac{\Gamma(E)/2}{(E_r - E)} \right]$$
potential scattering

Tangent function


If Γ is positive, δ_{ℓ}^r will increase through an odd multiple of $\pi/2$.

$$\delta_{\ell}^r(k) = \delta_{\ell}^i(k) - \xi_{\ell}(k)$$

If Γ is negative, δ_{ℓ}^r will decrease through an odd multiple of $\pi/2$.



Joachain
 OCT


Fig. 4.8. A typical behaviour of the cross section σ_l when $\xi_l = \frac{1}{2}\pi$ at $E = E_r$. The quantity ξ_l corresponds to "hard sphere" scattering and $\sigma_l^{\max} = 4\pi(2l+1)k^2$.

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And then if you look at the properties of the tangent function then if gamma is positive then, what happens to the resonance phase shift that it increases through an odd multiple of pi by 2 but if it is negative it actually decreases through an odd multiple of pi by 2. So, that is an upshot of this particular analysis. So, this is for a typical resonance coming from some other potential.

(Refer Slide Time: 44:15)

Ugo Fano
 Physical Review
 Vol. 124 Number 6
 December 15,
 1961
 p. 1866 to 1878



Configuration interaction in a many-electron system

- bound-bound
- bound-continuum

One of the MOST frequently cited paper!
Thousands of citations!

PHYSICAL REVIEW VOLUME 124, NUMBER 6 DECEMBER 15, 1961

Effects of Configuration Interaction on Intensities and Phase Shifts*

Ugo Fano
 1912-2001

U. Fano
 National Bureau of Standards, Washington, D. C.
 (Received July 14, 1961)

The interference of a discrete autoionized state with a continuum gives rise to characteristically asymmetric peaks in excitation spectra. The earlier qualitative interpretation of this phenomenon is extended and revised. A theoretical formula is fitted to the shape of the $2d^3\ ^1P$ resonance of He observed in the inelastic scattering of electrons. The fitting determines the parameters of the $2d^3\ ^1P$ resonance as follows: $E = 90.1$ eV, $F = 0.04$ eV, $f = 2$ to 4×10^4 . The theory is extended to the interaction of one discrete level with two or more continua and of a set of discrete levels with one continuum. The theory can also give the position and intensity shifts produced in a Rydberg series of discrete levels with interaction with a level of another configuration. The connection with the nuclear theory of resonance scattering is indicated.

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So, this is something which is of great importance in the ah ah analysis of auto ionization resonances and in particular the configuration interactions between the bound to bound and bound to continuum states. And a classic example of this is two electron systems, which I will discuss in some details.

(Refer Slide Time: 44:39)

Autoionization

Two-electron systems: He atom, H^- negative ion


Two-electron systems: part of many-electron atomic system

Description in terms of zero-order approximation

→ Interaction V_{12} between the two electrons is switched off

→ one-particle hydrogen-like states which define a set of 'configurations'

→ Actual state: configuration interaction



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And a two electron system, like the helium atom okay or it could be the hydrogen negative ion. So, these are the simplest examples of two electron systems. But then a two electron system can be a subset of any many electron systems. And you can analyse the atomic properties of many electron atoms in terms of the analysis for the two electron systems. So, we will describe this in terms of zero order approximation.

And in the zero order approximation, you pretend that the interaction between the two electrons is switched off which means that you can continue to use the hydrogenic quantum numbers. Well you will remember that the hydrogenic quantum numbers like n , l , m and so on. They essentially come from symmetry properties. They come from those Eigen values of those operators which commute with the Hamiltonian okay.

But once you break the symmetry of the Hamiltonian because once you have me you do have the spherical symmetry for the hydrogen atom. So, n , l , m are good quantum numbers for the hydrogen atom but there would not be really good quantum numbers for any other atom, any atom other than the hydrogen atom right. So, those quantum numbers will not be the so-called good quantum numbers.

But we will continue to use the hydrogenic quantum numbers. But then you will now have configuration interactions okay, between these different hydrogenic states. So, we will have one particle hydrogen-like states which will define different configurations. So, I will give examples of some of these.

And the actual state action really will be a configuration interaction, which means that if you have a superposition if you have the atomic system described by a superposition of two

configurations. One in which you have got one set of hydrogenic quantum numbers, other in which you have a different set of quantum numbers, hydrogenic quantum numbers.

But obviously you are conceding that the hydrogenic quantum numbers are not good quantum numbers because the state is described by a superposition of these two okay. (Refer Slide Time: 47:03)

Possible configurations of 2-e systems: He atom, H⁻ -ve ion

I $1s^2, 1s2s, 1s3s, \dots, 1sE_c s$
 $1s^2, 1s2p, 1s3p, \dots, 1sE_c p$ E_c : continuum
bound-bound

II $2s^2, 2s3s, 2s4s, \dots, 2sE_c s$
 $2s^2, 2s2p, 2s3p, \dots, 2sE_c p$ **bound-continuum**

III $2p^2, 2p3p, 2p4p, \dots, 2pE_c p$
 $2p^2, 2p3s, 2p4s, \dots, 2pE_c s$ Etc.,

N=2
n=3

NPTEL

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So, you have the two electron system like the helium atom or the negative hydrogen ion. And let us consider some configurations. You can have $1s^2$ that is what would come to your mind. You may also have $1s 2s$ for the two electrons right. You may also have $1s3s$. And you may also have one $1sE_c s$, E_c is a continuum energy so it can go into the continuum. And then you may have infinite number of different possibilities.

You may also have $1s^2$ and then $1s2p$ why not. You may have $1s3p$. So, you have got very many different possibilities. So, you have a large number of actually infinite numbers of possibilities, different configurations in which the two electron system can reside. And in general the two electron system if you want to describe it in a complete set of basis it will then have a superposition of all of these basis states.

But then this is not the only one. You may also have $2s^2$. So, you may have another series which is built on $2s^2$ configuration. So, $2s^2, 2s3s, 2s4s, 2s$ continuum s . You may also have $2s^2, 2s2p, 2s3p$ and $2s$ continuum p and so on right. And both the possibilities are considered over here you may have liked each of these you know stipulates a bound to bound excitation from a discrete bound state to another discrete bound state.

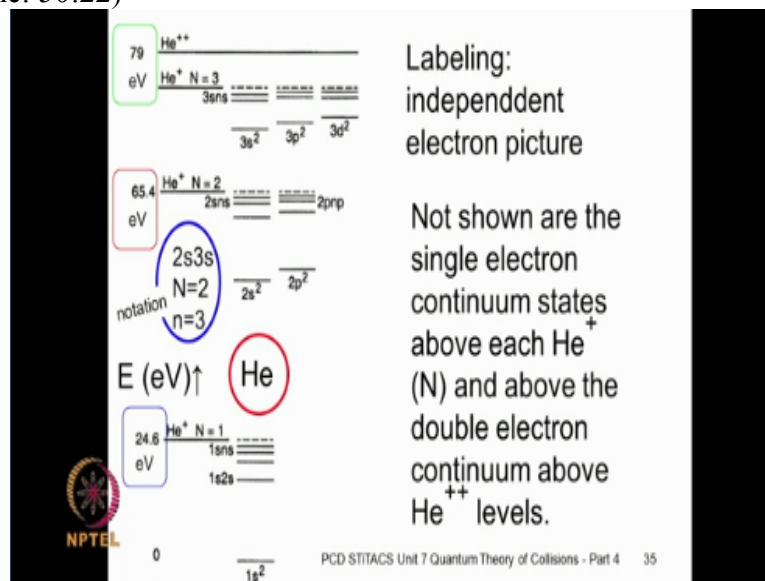
But it also accommodates a transition from a bound state to a continuum state. And it includes the configuration interactions between bound to bound and bound to continuum

states. You may have other possibilities. And here notice that there are two principal quantum numbers which are involved. So, you write one of them with an uppercase N and the other with a lowercase n.

So, which one is written with an upper case and which one with a lower case so there is you know means sometimes annotations differ but you just have to be careful that one of them represents both our principal quantum number: one for one of the electrons and the other for the other electron. In any case the electrons are indistinguishable you are not putting a tag on any one of them but it only represents the configuration of that particular state.

So, you may have other possibilities. This is built on $2s^2$. This is built on $2p^2$. So, you can have a $2p^2$ then $2p^3p$, $2p^4p$ then $2p^2$, $2p^3s$, $2p^4s$ and so on. And how many can you think of. So, let us pack them all in etcetera okay. It is one of the very nice words in the English language okay. It includes everything especially your ignorance right. So, everything is included in that.

(Refer Slide Time: 50:22)



So here you are. So, if you look at the helium atom the two electron system. You have got the $1s^2$ configuration. Then you can have a $1s2s$, then you can have a $1s3s$, $1s4s$ or $1sns$ in general till you can knock out $1s$ into the continuum s okay. And that would be the series limit. And this series limit is at 24.6 electron volts for the helium atom.

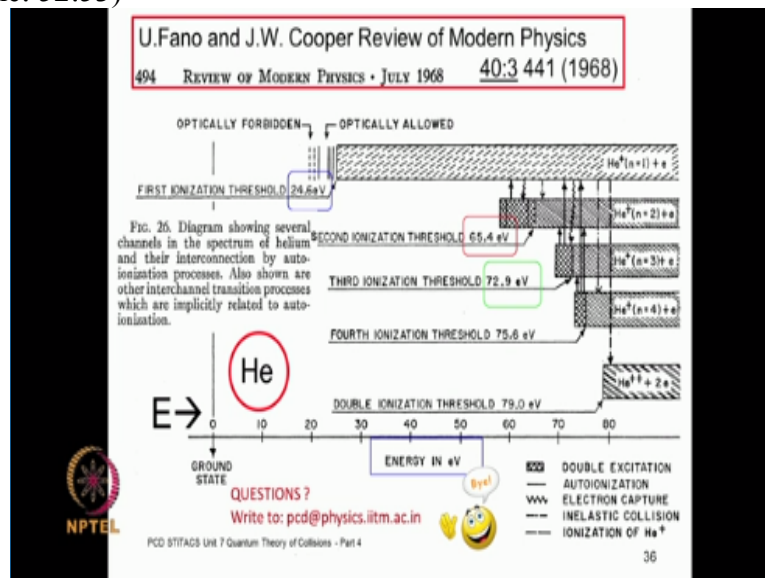
Then, you can have another one which is built on this $2s^2$ which is what I mentioned in the previous slide okay. And then, you can have the notation is this that $2s3s$ corresponds to one electron having a principal quantum number 2 and the other having 3. It does not matter which one is which.

Then, you can have another one and you can actually have an infinite series. And notice that the discrete bound to bound of one series can be embedded in the continuum of another. So, those are degenerate and you can expect you know resonances coming from this possibility that whenever you have two alternative channels like an a young's double slit experiment.

The amplitudes of the wave functions would superpose not the intensities okay. So, here the labelling is in terms of the independent electron picture which we know is not correct. But what we are doing is correct because we are using configuration interaction which is a superposition of the one electronic state. So, we have not shown in this figure the single electron continuum states above each ion ion limit for the different quantum numbers n .

And we have also not shown in this figure the double electron continuum. But then there are other figures in literature and I will show you this classic figure from ah Fano and ah Cooper's paper. So, here you have the series limits over here which is 24.6 over here then, 65.4 for this then, 79 for this and so on. And there will be so many which go through the roof of this picture okay.

(Refer Slide Time: 52:53)



So, you have this classic figure from Fano in Cooper's review in modern physics in 1968. Many of you would have seen this is one of the most famous figures in literature on resonances. Notice that you have the only difference between this figure and the previous figure is that energy is increasing from left to right where as in the previous figure the energy was increasing from bottom to the top.

So, it is the same as a previous figure but it is tilted through rotated to 90 degrees and what is also shown are the continuum over here. So, you have got the first ionization threshold at 24.6 which we have seen, the second ionization threshold at 65.4 then, you have at 72.9. And

then you have many more okay. So, all these other ones I had not shown in the previous one but then you do know that there are infinite numbers of them.

And notice that the bound to bound transitions some of these discrete lines they are embedded in this continuum and that is true for a large number of different cases. So, what you will then have is a resonance between a bound to bound transition and a bound to continuum transition. You will get a resonance and you can analyse in terms of the Fano shape parameter. So, I will proceed from this point in the next class.

If there is any question for today, I will be happy to take otherwise we conclude the class at this point.