Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'
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Lecture 41
Configuration Interaction between Discrete and Continuum

Greetings, we began discussion on Fano Resonances and we have already come a significant way in this discussion. We have discussed the Fano parameters related them to the general formula coming from Collision Physics. And we began to discuss the Helium Atom Spectrum as a prototype of a many Electron system. So, this is two electrons system; two electrons is the smallest many electron system. So, it is best to develop the formalism in terms of a two electrons system.
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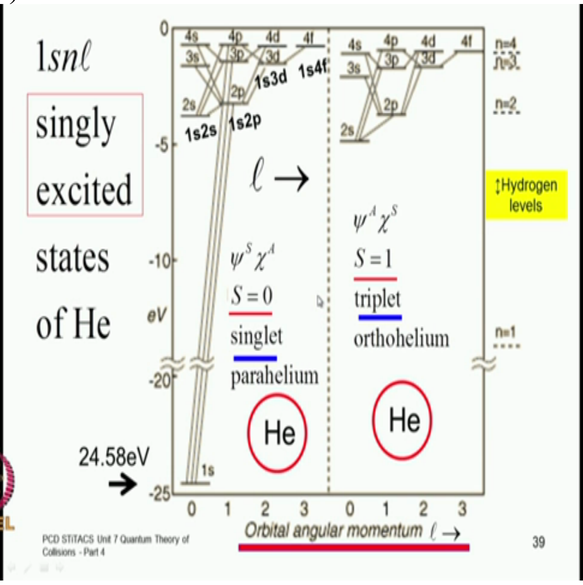

And I will spend some time at the beginning of today's class, to discuss the Helium Atom Spectrum. So, here you have two electrons and these are the singly excited states of the Helium Atom. So, you have got one electron in the 1s and then, the second can go into the 2s or the 3s or the 4s or it can also go into the 2p, 3p, 4p or 3d, 4 d, 4 f and so on.

So, as you go from left to right in this diagram you are going to higher orbital angular momentum states so l = 0; l = 1, 2, 3 and so on okay. Now, this is part of the story because, here you have in the two electrons; one electron in the 1s and the second in the 2s. But then, there is, there are two possibilities; because the two electrons can pair into a singlet or triplet. So, this is the singlet panel. And there is a likewise a triplet panel, okay.

So, you can have singlet as well as triplets. So, you can have you know these two combinations of the of any two electron system. So, I am going to look at some of these diagrams a little closely, magnify some parts. So that, you know, we can focus attention on details.

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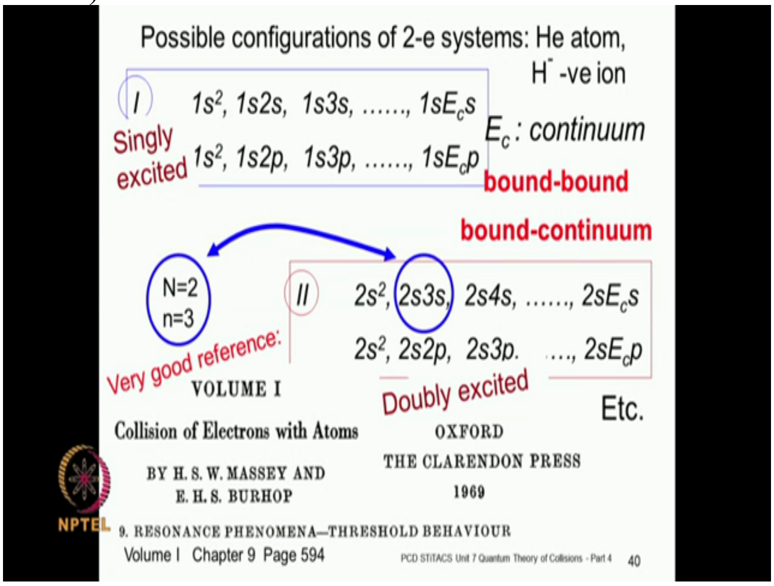

Possible configurations of 2-e systems: He atom, H^--ve ion

I $1s^2$, $1s2s$, $1s3s$, ……, $1sE_cs$

Singly excited $1s^2$, $1s2p$, $1s3p$, ……, $1sE_cp$

E_c: continuum

bound-bound

bound-continuum

N=2
n=3

II $2s^2$, $2s3s$, $2s4s$, ……, $2sE_cs$

$2s^2$, $2s2p$, $2s3p$. …, $2sE_cp$

Doubly excited

Etc.

Very good reference:

VOLUME I

Collision of Electrons with Atoms

BY H. S. W. MASSEY AND
E. H. S. BURHOP

OXFORD
THE CLARENDON PRESS
1969

9. RESONANCE PHENOMENA—THRESHOLD BEHAVIOUR

Volume I Chapter 9 Page 594

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So, here are the possible configurations of the two electrons system. You can have the 1s to 2 s electrons in the 1s, then, you can have 1 in the 1s, the other in the 2s; 1 in the 1s, the second in the 3s and then in the 4s and so on. And then, finally into the continuum which is indicated by Ec. But then, it can go to l = 1 state so you have the 1s2p, 1s3p and so on. These are the things that I showed in the previous diagram.

And I will strongly recommend this book by Massey and Burhop, Volume I, which is a very good reference for these details. So, these are the different configurations based on the 1 s state, but then, you can have, you know, these are the singly excited states. So, there is a bound to bound transition and over here, there is a bound to continuum transition, okay.

So, these are the singly excited states: one of the two electrons is excited to the other electrons. But then, you can have excitations of both the electrons. And then, you have W excited states. So, these W excited states, you can have both of them into 2s2; then, 1 in the 2s, the other in the 3s, 1 in the 2s, the other in the 4s; and then 1 in the 2s, the other in the continuum s.

But then, you can also have one in the 2s and the other in the 2 in the 3p this should be 3p and not 2p. No, it can be 2p. And then you can have the 2s3p. That, and then, finally continuum p as well, right. And then you can have 3s2s and so on. So, all of those I have not shown. So, there are these several singly excited state configurations. And several doubly excited state configurations.

And here, are two quantum numbers are involved, two principal quantum numbers are involved; both are bound states. So, they have the principal quantum number. And one is indicated by an uppercase N and the other by a lowercase n so is another.

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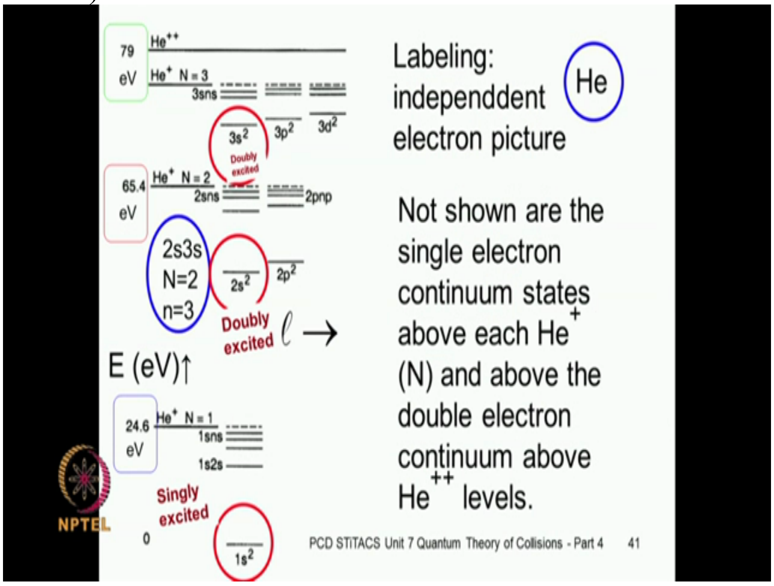

Labeling: independdent electron picture

Not shown are the single electron continuum states above each He^{+} (N) and above the double electron continuum above He^{++} levels.

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So here is a look at the same diagram. And here you have got the 1s2 and these are the singly excited states of the Helium, okay. So, this has got an ionization threshold of 24.6 electron volts. Then, you have the doubly excited states and these are based on the 2s2 2p2 and so on possibilities right. And then, you have some more of these like the W excited states based on the 3s2 and so on.

So, they have different Ionization threshold. So, this is 24.6, this one is 64.6 65.4, this is 79, okay. So, these are the different thresholds for these limits. Then again, as I showed in the previous diagram, you can have the Orbital Angular Quantum number, moving from left to right, okay. So, you have the s states over here, the p states over here and then d over here and so on.

So, as you move to the right you can go to higher Angular Momentum Quantum states. The labelling as you notice is done in terms of independent electron picture okay. So, the quantum numbers are the hydrogenic quantum numbers. Although this is the many electron system and the hydrogenic quantum numbers, are not really good quantum numbers.

So, what gives you a good quantum number is a configuration interaction between these states, ok. So, the real wave function will be a superposition of these different states and some of these could also include the continuum states. And it is this configuration interaction which is of great interest to our discussion today. So, now, in these diagrams which I showed until now, today, I have not shown the continuum.

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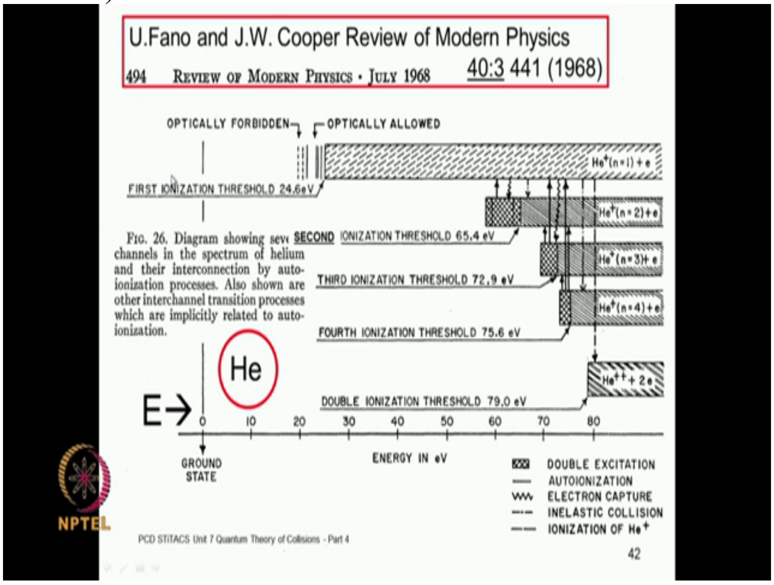

U.Fano and J.W. Cooper Review of Modern Physics

494 Review of Modern Physics • July 1968 40:3 441 (1968)

OPTICALLY FORBIDDEN
OPTICALLY ALLOWED
$He^+(n=1)+e$
FIRST IONIZATION THRESHOLD 24.6eV
$He^+(n=2)+e$
SECOND IONIZATION THRESHOLD 65.4 eV
$He^+(n=3)+e$
THIRD IONIZATION THRESHOLD 72.9 eV
$He^+(n=4)+e$
FOURTH IONIZATION THRESHOLD 75.6 eV
He
$He^{++}+2e$
DOUBLE IONIZATION THRESHOLD 79.0 eV
E→
0 10 20 30 40 50 60 70 80
GROUND STATE
ENERGY IN eV

▩ DOUBLE EXCITATION
— AUTOIONIZATION
ʍʍ ELECTRON CAPTURE
--- INELASTIC COLLISION
—— IONIZATION OF He^+

Fig. 26. Diagram showing sev channels in the spectrum of helium and their interconnection by autoionization processes. Also shown are other interchannel transition processes which are implicitly related to autoionization.

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But I will show it in the next slide which we had a glance at toward the end of the previous class. And this is from far no in Cooper's Review of Modern Physics which is very awfully cited literature in this. And here, this is the same spectrum except that energy is moving from, energy increases from left to right in the previous diagrams. It was from bottom to the top, okay.

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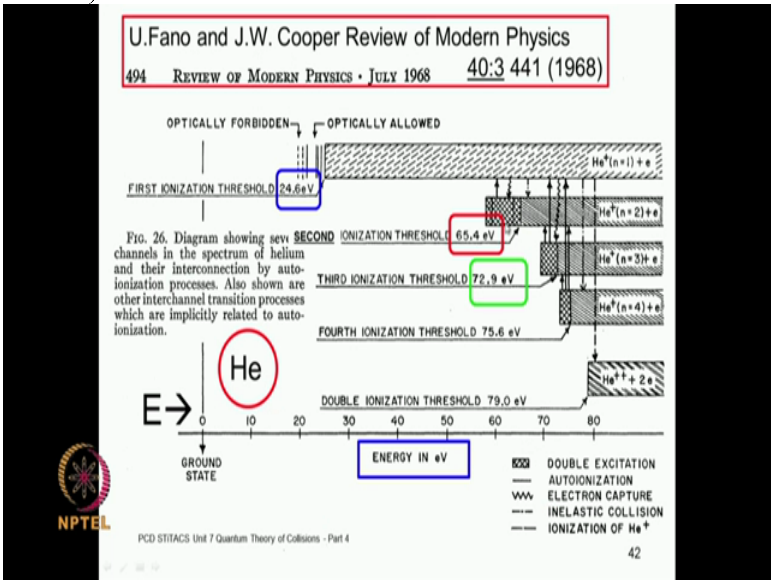

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GROUND STATE
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Fig. 26. Diagram showing sev channels in the spectrum of helium and their interconnection by autoionization processes. Also shown are other interchannel transition processes which are implicitly related to autoionization.

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So, I have rotated this diagram through 90 degrees and here energy is going from left to right. So, this is the first ionization threshold which I showed you in the previous figure which is 24.6 electron volts and then you have the second one at 65.4 and so on right. So, these are the Ionization thresholds, which move from left to right as you go to higher ionization thresholds.

Furthermore, you have we have shown also in this, these discrete bound to bound states and you will notice that they have an overlap with the ionization continuum of the single excited states. So, there will be configuration interaction between the doubly excited states and the singly excited continuum.

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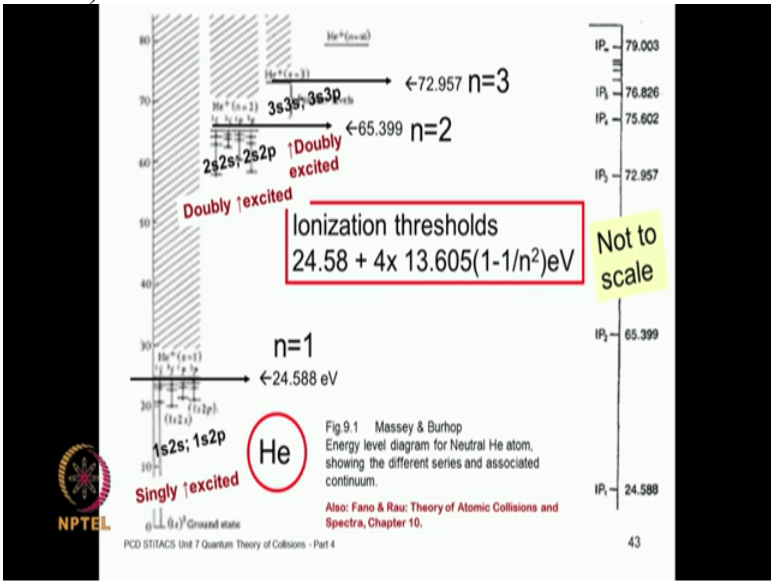

Ionization thresholds
$24.58 + 4x\ 13.605(1-1/n^2)eV$

Fig.9.1 Massey & Burhop
Energy level diagram for Neutral He atom, showing the different series and associated continuum.

Also: Fano & Rau: Theory of Atomic Collisions and Spectra, Chapter 10.

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So, let us have some further look at this. Now, there are some more details coming up in this diagram and that is the reason I am showing this diagram in pieces, you know; part by part because if you put everything in the same figure, all at once, there is so much information over there that we tend to miss out, some of the details.

So, here we have in this diagram, we have shown the 1s to ground state of the Helium Atom. So, these are the singly excited states as we have seen. So, this is the single excited state continuum. This is the doubly excited n = 2 continuum, right. So, the 2s, 2p states and so on are over here okay.

And then you have got the continuum for this. And then, likewise further n equal to 3 states. So, these are the Ionization thresholds and you can have the, the Ionization threshold is of course given by the usual Rydberg Bommer formula. So, you can just put it over here and you will get the corresponding ionization thresholds.

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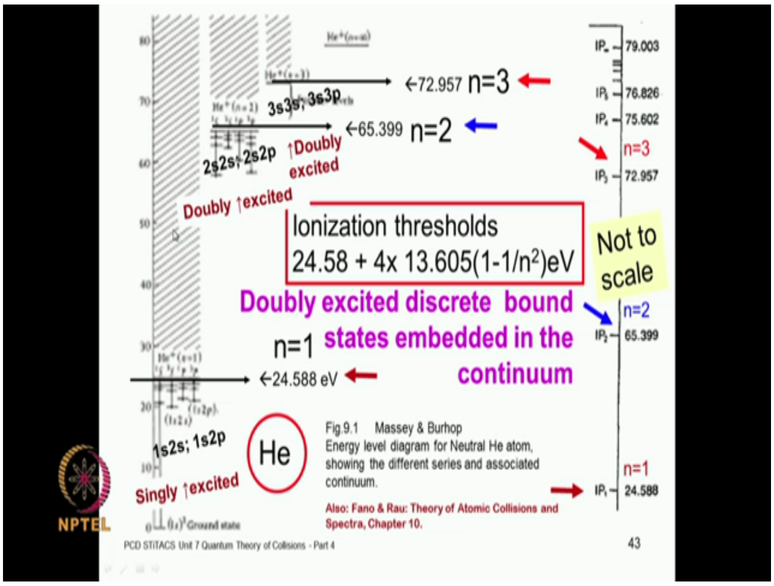

Ionization thresholds
24.58 + 4x 13.605(1-1/n²)eV

Doubly excited discrete bound states embedded in the continuum

Not to scale

Fig 9.1 Massey & Burhop
Energy level diagram for Neutral He atom, showing the different series and associated continuum.

Also: Fano & Rau: Theory of Atomic Collisions and Spectra, Chapter 10.

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Now for Helium, of course, that is equal to 2 so you get 4 over z square. And that is, what it is. So, here is the Energy scale and this is not 2. So, these scales are different. So, you have got 24.56 over here which comes here, okay. Then, you have the n = 2 limit which is here shown on the scale of a ok.

And then you have got the n = 3 and you have the W excited discreet bound states. All of these are embedded in the continuum on the left side okay. So, all the W excited states on the right are embedded in the continuum of what is on the left.

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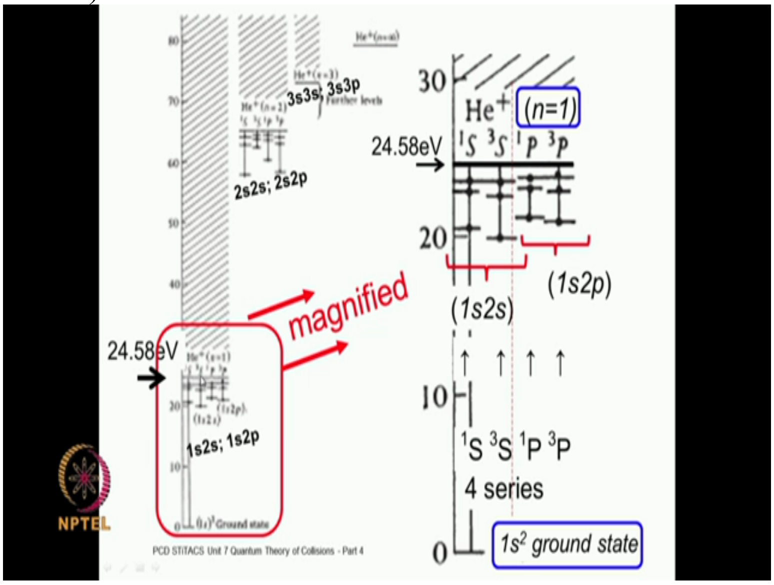

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And that is the configuration interaction in which, you will have a bound to bound configuration, having a configuration mixing with a bound to continue. So, here is a magnification of this part alone. So, this is the singly excited state configuration, right converging to the series limit at 24.58, okay.

And it is this part which is magnified over here but now I show not only the 1s 2s and 1s2p separately but I also show the singlet and the triplet. So, there are actually if you notice over here, there are 4 red box series. But they are so tiny that one could miss out on that. And that is the reason I have magnified this diagram.

So, you have got the 1s, 2s, singlet and the triplet and then you have got the 1 s, 2 p again, singlet and triplet combinations as I mentioned earlier, okay. So, you have a number of possibilities. So, all of these are built on the 1s to ground state, okay. So, this is the magnification of this part which is the singly excited configuration.

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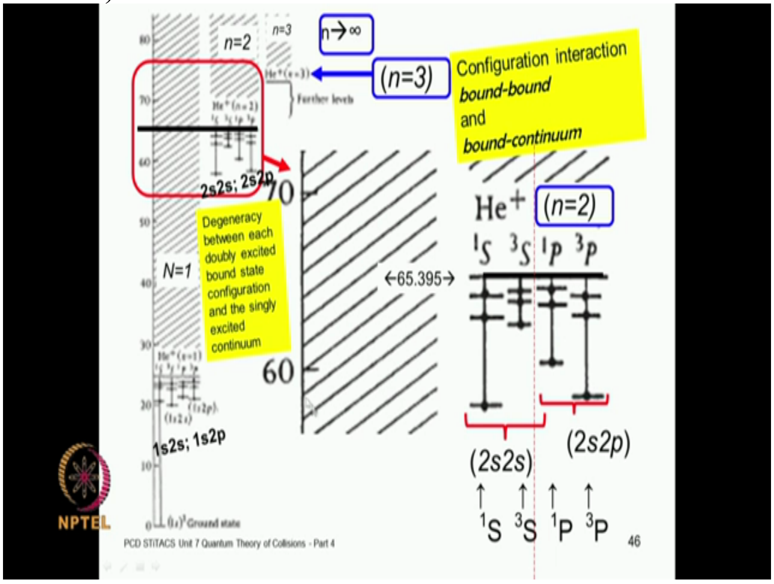

Now, if you look at the w excited configuration. So, here is a magnification of this part of the W excited configuration based on 2s, 2s, 2s, 2p, etc. But, then again, the 2s, 2s, you have a singlet and triplet, okay. And likewise for the 2s, 2p also, you will have a singlet and triplet p, okay. So, you will have a number of Rydberg series coming out of this.

So, here is a, so, this is again, a magnification. So, there are actually 4 Rydberg series in the double excitations. So, this is what leads to the configuration interaction between the bound to bound and bound to continuum because all of these discrete states, doubly excited discreet states, they are embedded in the continuum.

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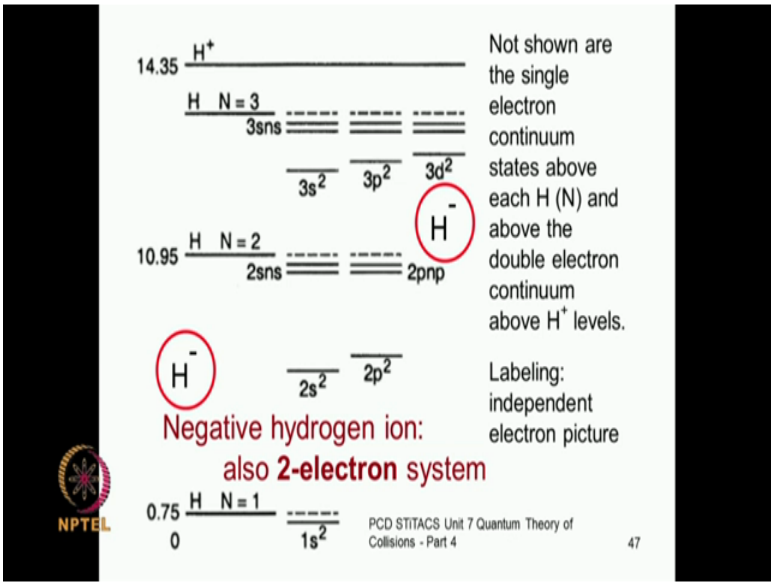

Not shown are the single electron continuum states above each H (N) and above the double electron continuum above H^+ levels.

Labeling: independent electron picture

Negative hydrogen ion: also **2-electron** system

So, here you will have a similar spectrum also for the negative hydrogen atom which is again a two electron system so I am not going to discuss this in great length. But just to point out that the hydrogen minus will also have similar, very similar Rydberg series. So, when you work with photo detachment and so on, you will be using a spectrum of this kind, okay.

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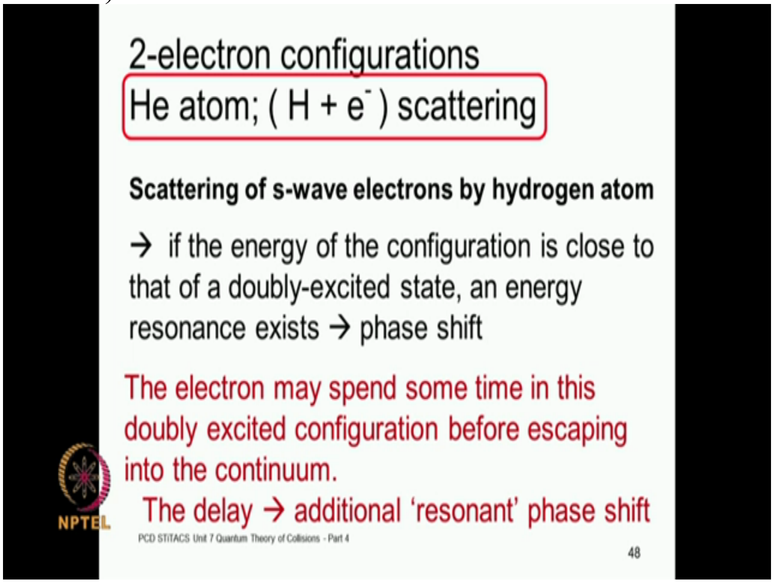

2-electron configurations

He atom; (H + e^-) scattering

Scattering of s-wave electrons by hydrogen atom

→ if the energy of the configuration is close to that of a doubly-excited state, an energy resonance exists → phase shift

The electron may spend some time in this doubly excited configuration before escaping into the continuum.

The delay → additional 'resonant' phase shift

So, now, this is the main question of interest that you have these two electron configurations and a many electron system, you can, you can discuss important correlations in terms of these two electron configurations. So, when you have the energy of a doubly excited state in two possible configurations.

One of which is a bound and the other is bound continuum, then you will have resonances and what is going to happen is that the electron may spend some time in the excited state configuration before escaping into the continuum. So the electron can, of course, escape into the continuum because energetically that is possible. So, it would happen.

But before it does so, there would be a little bit of time that it spends in the doubly excited state and what this time delay will do is, to cause an additional phase shift, which will be a resonant phase shift; because the double excitations belong to the discrete bound states. And they are therefore at very sharp, not, not really sharp they have their lifetimes.

But, they are at specific energies at the resonance energies. So, there will be a resonant phase shift coming from this.

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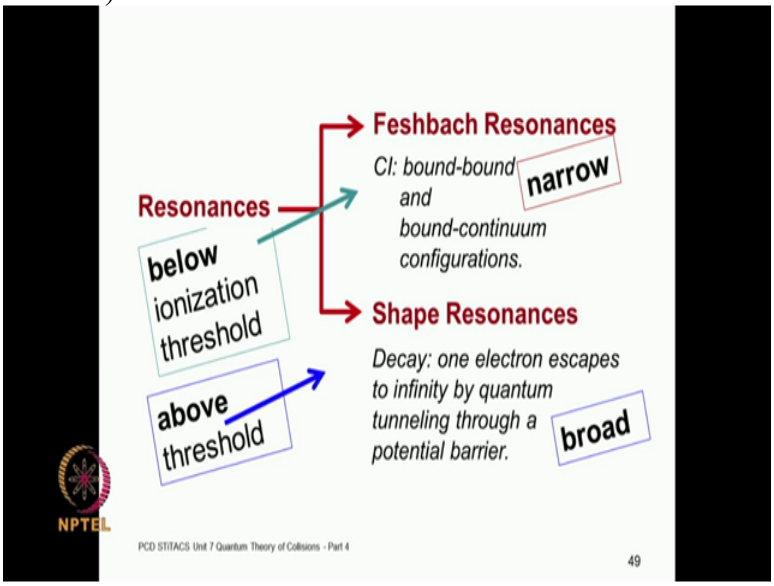

Resonances

below ionization threshold

above threshold

Feshbach Resonances

CI: bound-bound and bound-continuum configurations.

narrow

Shape Resonances

Decay: one electron escapes to infinity by quantum tunneling through a potential barrier.

broad

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And it is this that we are going to learn from Fano how to analyze this. So, we mentioned in some of the earlier classes that there are these two kinds of resonances: the Feshbach resonance or the Fano Feshbach resonance as I normally refer to it and the other is the Shape resonance.

So, the Feshbach resonances are because of configuration interaction between the bound to Bound and bound to continuum configurations. The shape resonances are due to the form of the potential, okay. So, this is when the electron can tunnel through a potential barrier and then it finds itself to be exposed to two different alternative states: One which is trapped in the inner well and the other after tunnelling through the barrier.

So, these are the two possibilities and Feshbach resonances will therefore occur below the Ionization thresholds, okay; where a shape resonance will be above the thresholds okay. So, these in, in both cases, you do undergo a phase shift through pi, as you go through the resonance. So, the final Feshbach resonances are relatively narrow and this is just a gross feature one has to get into the details.

Because within the family of far no Feshbach resonances, there are very many different kinds of shapes and widths that we have already talked about in our previous class, so, what happens is that our interest now is in studying the electron correlations, the configuration interactions, which lead to the Fano Feshbach resonances.

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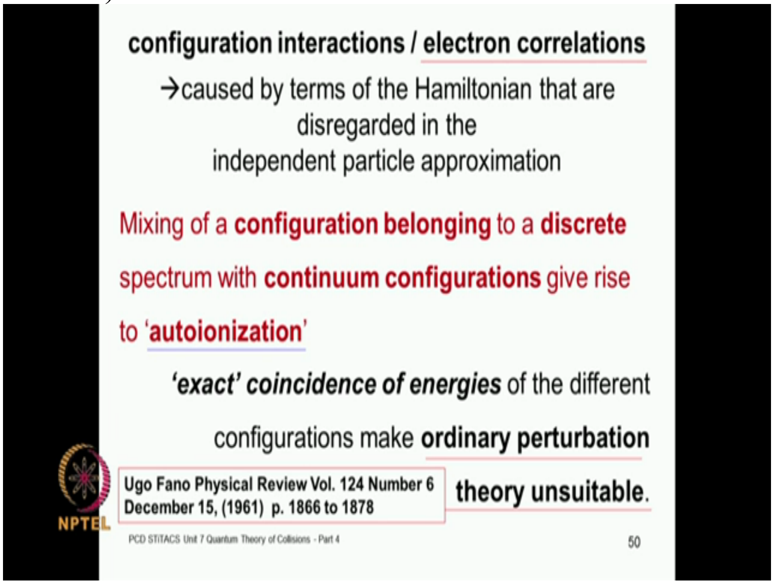

configuration interactions / electron correlations

→caused by terms of the Hamiltonian that are disregarded in the independent particle approximation

Mixing of a **configuration belonging** to a **discrete** spectrum with **continuum configurations** give rise to '**autoionization**'

'exact' coincidence of energies of the different configurations make **ordinary perturbation theory unsuitable.**

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

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And they lead to authorization these resonances that we are talking about are more specifically called as autoionization resonances and what happens is because the discrete bound state is embedded in the continuum at some energy, the energy difference between the two states becomes exact. And then it becomes impossible to use ordinary perturbation theory.

Because in perturbation theory, you often have the energy difference in the denominator and then things blow up. So, you need special techniques and that is what Fano introduced in this marvellous paper.

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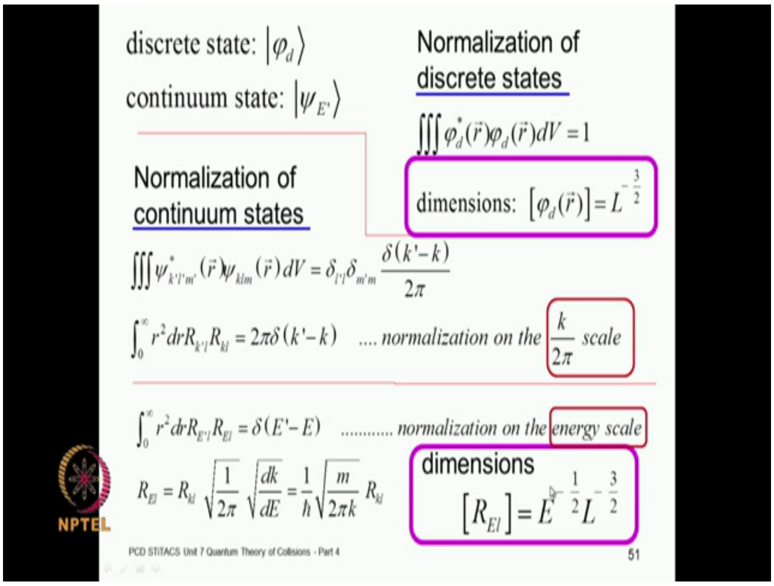

discrete state: $|\varphi_d\rangle$

continuum state: $|\psi_{E'}\rangle$

Normalization of discrete states

$$\iiint \varphi_d^*(\vec{r})\varphi_d(\vec{r})dV = 1$$

dimensions: $[\varphi_d(\vec{r})] = L^{-\frac{3}{2}}$

Normalization of continuum states

$$\iiint \psi_{k'l'm'}^*(\vec{r})\psi_{klm}(\vec{r})dV = \delta_{l'l}\delta_{m'm}\frac{\delta(k'-k)}{2\pi}$$

$\int_0^\infty r^2 dr R_{k'l} R_{kl} = 2\pi\delta(k'-k)$ .... *normalization on the* $\frac{k}{2\pi}$ *scale*

$\int_0^\infty r^2 dr R_{E'l} R_{El} = \delta(E'-E)$ .... *normalization on the energy scale*

$$R_{El} = R_{kl}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{dk}{dE}} = \frac{1}{\hbar}\sqrt{\frac{m}{2\pi k}}R_{kl}$$

dimensions

$$[R_{El}] = E^{-\frac{1}{2}}L^{-\frac{3}{2}}$$

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So, let us refer to this configuration interaction between discrete and discrete and continuum. So, the discrete state, I will indicate by Phi d so get familiar with the notation. I am using the continuum state by Psi E, okay, the discrete states r square integrable. So, I normalize them using the using the usual integral normalization integral.

And the dimension of the discrete states are of course L to the -3 by 2 okay the continuum states however, are not square integrable and these are then normalized on the delta function like a delta function scale. You can normalize them on a k over 2 phi scale in which this is how the normalization would go. Or we have discussed this normalization earlier as well, in scattering theory.

And you can also normalize them on the energy scale. And if you normalize them on the energy scale then, the dimension of the ray of the functions would be e to the - half L to the -3 by 2. So, mind you, the dimensions of the discrete states at the dimension of the continuum states are different because of how we have chosen the normalization okay. So, these dimensions are different and that is something that you must keep in mind.

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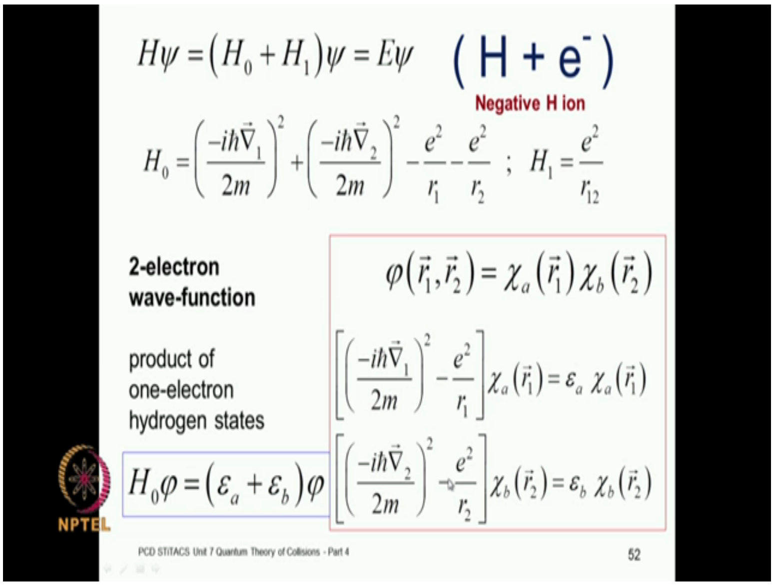

$$H\psi = (H_0 + H_1)\psi = E\psi$$

(H + e⁻)

Negative H ion

$$H_0 = \left(\frac{-i\hbar\vec{\nabla}_1}{2m}\right)^2 + \left(\frac{-i\hbar\vec{\nabla}_2}{2m}\right)^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} \; ; \; H_1 = \frac{e^2}{r_{12}}$$

2-electron wave-function

$$\varphi(\vec{r}_1, \vec{r}_2) = \chi_a(\vec{r}_1)\chi_b(\vec{r}_2)$$

product of one-electron hydrogen states

$$\left[\left(\frac{-i\hbar\vec{\nabla}_1}{2m}\right)^2 - \frac{e^2}{r_1}\right]\chi_a(\vec{r}_1) = \varepsilon_a\,\chi_a(\vec{r}_1)$$

$$\left[\left(\frac{-i\hbar\vec{\nabla}_2}{2m}\right)^2 - \frac{e^2}{r_2}\right]\chi_b(\vec{r}_2) = \varepsilon_b\,\chi_b(\vec{r}_2)$$

$$H_0\varphi = (\varepsilon_a + \varepsilon_b)\varphi$$

So, this will also be a similar case for the negative hydrogen ion. And you can think of this two electron system whether it is a negative hydrogen ion or a helium atom okay, as a two electron system. And if you ignore the interaction between these two electrons then, it is as if you are having a Hamiltonian for one hydrogen atom and another hydrogen atom okay, right. It is almost like that.

So, the two energies would add up if you ignore the interaction between the two electrons, okay. So, you have got the kinetic energy operator for one electron and the kinetic energy operator for the second electron and the potential energy of each of the electron in the field of the nucleus. But you have ignored in H0. This is the unperturbed Hamiltonian, the interaction between the two electrons. So, this is your unperturbed Schrodinger Equation.

And it gives you an energy which is just the sum of the two energies. Now, you can write the two electron wave function as a product of these hydrogenic states and your product, then becomes your, two electron wave function becomes a product of these two. And these are obtained as solutions of these two independent Schrodinger equations.

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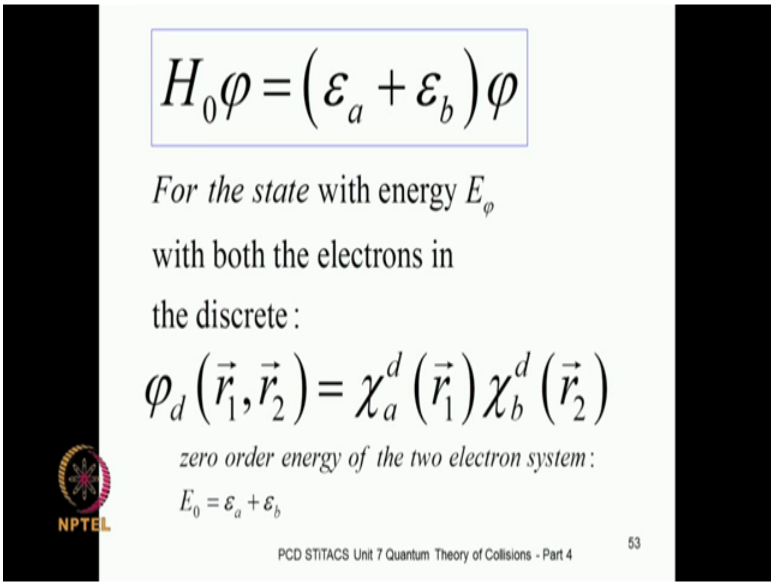

$$\boxed{H_0\varphi=\left(\varepsilon_a+\varepsilon_b\right)\varphi}$$

For the state with energy E_φ

with both the electrons in

the discrete:

$$\varphi_d\left(\vec{r}_1,\vec{r}_2\right)=\chi_a^d\left(\vec{r}_1\right)\chi_b^d\left(\vec{r}_2\right)$$

zero order energy of the two electron system:

$E_0=\varepsilon_a+\varepsilon_b$

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Now, this is the case when both the electrons are in the discrete, ok. But, we considered various possibilities you can have 1s, 2s, 1s, 3s and so on. But, both are in the discrete; but, what if 1 is in the continuum? And this is the zero order energy for the two electron system when, both are in the discrete.

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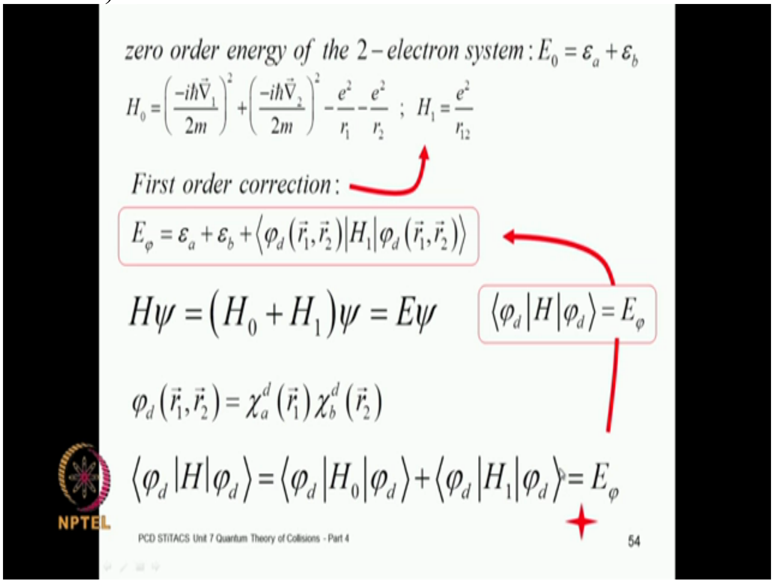

zero order energy of the 2-electron system: $E_0=\varepsilon_a+\varepsilon_b$

$$H_0=\left(\frac{-i\hbar\vec{\nabla}_1}{2m}\right)^2+\left(\frac{-i\hbar\vec{\nabla}_2}{2m}\right)^2-\frac{e^2}{r_1}-\frac{e^2}{r_2}\ ;\ H_1=\frac{e^2}{r_{12}}$$

First order correction:

$$\boxed{E_\varphi=\varepsilon_a+\varepsilon_b+\left\langle\varphi_d\left(\vec{r}_1,\vec{r}_2\right)\middle|H_1\middle|\varphi_d\left(\vec{r}_1,\vec{r}_2\right)\right\rangle}$$

$$H\psi=\left(H_0+H_1\right)\psi=E\psi \qquad \boxed{\left\langle\varphi_d\middle|H\middle|\varphi_d\right\rangle=E_\varphi}$$

$$\varphi_d\left(\vec{r}_1,\vec{r}_2\right)=\chi_a^d\left(\vec{r}_1\right)\chi_b^d\left(\vec{r}_2\right)$$

$$\left\langle\varphi_d\middle|H\middle|\varphi_d\right\rangle=\left\langle\varphi_d\middle|H_0\middle|\varphi_d\right\rangle+\left\langle\varphi_d\middle|H_1\middle|\varphi_d\right\rangle=E_\varphi$$

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But then you can also have 1 in the continuum. And the first order correction, when you do include the interaction if both the electrons were in the discrete would then be given by the matrix element or the perturbation Hamiltonian in the unperturbed states which is Phi d which is just a product of those two one electron hydrogenic states.

So, this would give you the first order correction. So, this goes into the energy matrix E Phi, okay. So, we are going to construct the energy matrix for various possibilities. So, you have now the perturbation H1 and E Phi will give you the energy correction due to the electron-electron interaction, if both the electrons are in the discrete.

So, this is the possibility we have considered over here. So, E Phi is the correction, okay. And of this, H0 is nothing but the sum of the two energies that we got earlier. And H1 comes from this correction over here. So, this is what gives you the E Phi which goes into the correction right okay.

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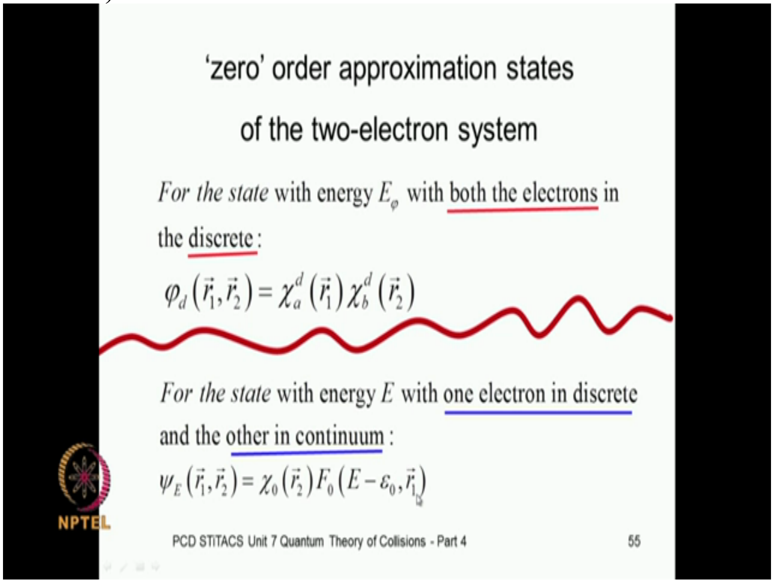

'zero' order approximation states of the two-electron system

For the state with energy E_φ with both the electrons in the discrete:

$$\varphi_d(\vec{r}_1,\vec{r}_2)=\chi_a^d(\vec{r}_1)\chi_b^d(\vec{r}_2)$$

For the state with energy E with one electron in discrete and the other in continuum:

$$\psi_E(\vec{r}_1,\vec{r}_2)=\chi_0(\vec{r}_2)F_0(E-\varepsilon_0,\vec{r}_1)$$

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So, this is when both the electrons are in the discrete. Now, what if one of the electrons is in the continuum? Now if one of the electrons is in the continuum then one electron state is represented by the bound state which is Chi and the other will have energy, which is E - epsilon 0 with a position coordinate r1, okay.

So, the product, so you still express the two electron wave function is a product of the two wave functions; one for the discrete state and the other for the continuum.

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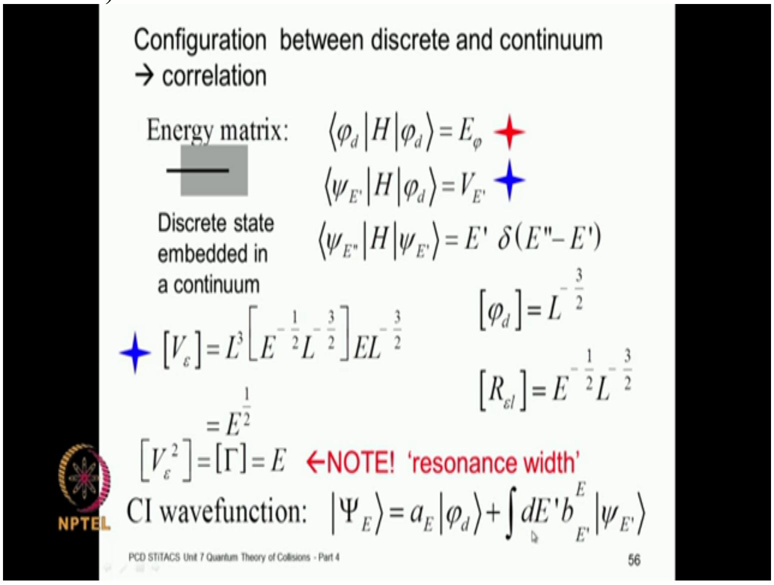

Configuration between discrete and continuum → correlation

Energy matrix: $\langle\varphi_d|H|\varphi_d\rangle=E_\varphi$ ✦

$\langle\psi_{E'}|H|\varphi_d\rangle=V_{E'}$ ✦

Discrete state embedded in a continuum

$\langle\psi_{E''}|H|\psi_{E'}\rangle=E'\,\delta(E''-E')$

$[\varphi_d]=L^{-\frac{3}{2}}$

✦ $[V_\varepsilon]=L^3\left[E^{-\frac{1}{2}}L^{-\frac{3}{2}}\right]EL^{-\frac{3}{2}}$

$=E^{\frac{1}{2}}$

$[R_{\varepsilon l}]=E^{-\frac{1}{2}}L^{-\frac{3}{2}}$

$[V_\varepsilon^2]=[\Gamma]=E$ ←NOTE! 'resonance width'

CI wavefunction: $|\Psi_E\rangle=a_E|\varphi_d\rangle+\int dE'b_{E'}^{E}|\psi_{E'}\rangle$

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So, now you have this continuum and the discrete state is embedded in this continuum. So, this is now your energy matrix. So, you have got the energy contribution when both the electrons are in the discrete, that is Phi d which is what we indicated earlier when you have one in the discrete and the other in the continuum, right? Then, you have VE and then here this is just a matrix element of the Hamiltonian in the continuum states.

So, this will have a delta function popping on, right, because both of these energies are in the continuum. So, this is now the framework of the energy matrix. Now, the thing to remember as I mentioned earlier is that, this has got a dimensions of L to the -3 by 2 and this will have a dimension of E to the minus half and L to the -3 by 2.

So, what is the dimension of VE dimension of V will be e to the half okay. So, this V has got a dimension of root energy and this is to be remembered because when we take it square, you get the energy width which has got the dimensions of energy okay. So that comes out as V square in our analysis.

So, just remember these dimensions. Now, the configuration interaction wave function will be a superposition of the discrete state and the continuum state and the continuum you will have integration over a range of energies right dE prime, right. So, this is your configuration interaction wave function and now our task is to determine these coefficients a and b to go from there okay.

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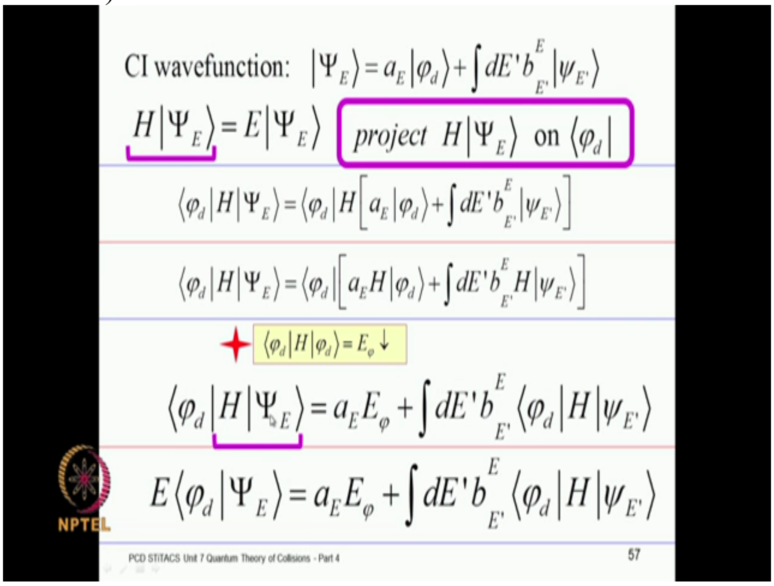

CI wavefunction: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \int dE' b^E_{E'}|\psi_{E'}\rangle$

$\underbrace{H|\Psi_E\rangle} = E|\Psi_E\rangle$ $\boxed{project\ H|\Psi_E\rangle \text{ on } \langle\varphi_d|}$

$\langle\varphi_d|H|\Psi_E\rangle = \langle\varphi_d|H\left[a_E|\varphi_d\rangle + \int dE' b^E_{E'}|\psi_{E'}\rangle\right]$

$\langle\varphi_d|H|\Psi_E\rangle = \langle\varphi_d|\left[a_E H|\varphi_d\rangle + \int dE' b^E_{E'} H|\psi_{E'}\rangle\right]$

$\langle\varphi_d|H|\varphi_d\rangle = E_\varphi \downarrow$

$\langle\varphi_d\underbrace{|H|\Psi_E\rangle} = a_E E_\varphi + \int dE' b^E_{E'}\langle\varphi_d|H|\psi_{E'}\rangle$

$E\langle\varphi_d|\Psi_E\rangle = a_E E_\varphi + \int dE' b^E_{E'}\langle\varphi_d|H|\psi_{E'}\rangle$

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So, here we are. So, this is our Schrodinger equation. Now, let us project this on a discrete state because this is the Schrodinger equation for the two electron system and it will have components on the two electron bound states, or one in the bound state and the other in the continuum. So, in this case, we project it on the discrete state possibility.

So, let us take the projection of this Schrodinger equation on the state Phi d. So, we have got two terms: one coming from the discrete and the other coming from the continuum, right? So, these are the two states. Now, we already know this what is it this? We have already determined, because this is the E Phi, right? This is our E Phi which would go into the energy matrix. So, this is E Phi so we put this over here.

And now you have got the matrix element of H in this continuum and Phi d. So, this H over here is nothing but, E Psi right. So, I pull E common and now you have got a projection of Psi on Phi D.

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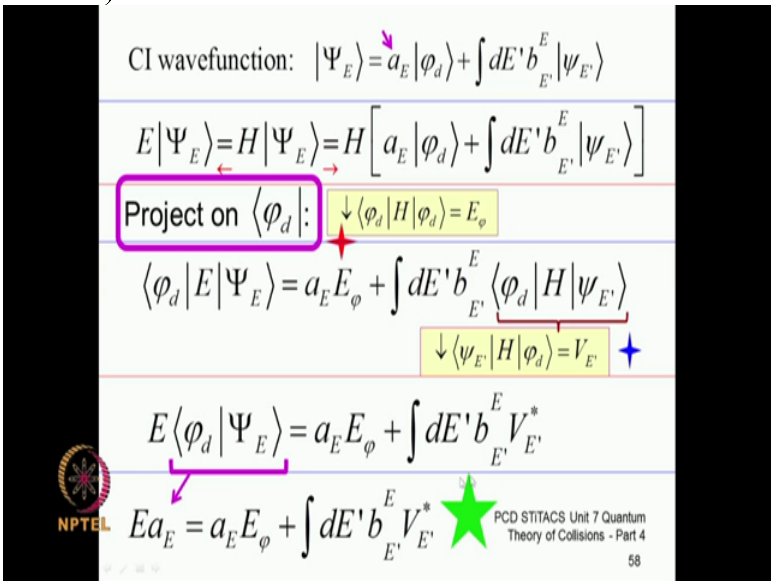

CI wavefunction: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \int dE' b^E_{E'} |\psi_{E'}\rangle$

$$E|\Psi_E\rangle = H|\Psi_E\rangle = H\left[a_E|\varphi_d\rangle + \int dE' b^E_{E'} |\psi_{E'}\rangle\right]$$

Project on $\langle\varphi_d|$: $\downarrow \langle\varphi_d|H|\varphi_d\rangle = E_\varphi$ ✦

$$\langle\varphi_d|E|\Psi_E\rangle = a_E E_\varphi + \int dE' b^E_{E'} \underbrace{\langle\varphi_d|H|\psi_{E'}\rangle}$$

$\downarrow \langle\psi_{E'}|H|\varphi_d\rangle = V_{E'}$ ✦

$$E\underbrace{\langle\varphi_d|\Psi_E\rangle} = a_E E_\varphi + \int dE' b^E_{E'} V^*_{E'}$$

$$E a_E = a_E E_\varphi + \int dE' b^E_{E'} V^*_{E'} \quad ★$$

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Which you get from, from, from here which will give you aE. So, now just I have written this Schrodinger equation, so that on the left you have got E Psi, on the right you have got H, operating on the superposition of the discrete and the bound states. So, this is the projection that we are considering right on Phi d. So, here you get the E Phi which is here. So, if E Phi comes here.

This coefficient is aE coming from here and then, this factor is nothing but V which we have written earlier, right. So, you get V over here. And this is the projection of Psi on Phi d. So, the projection of Psi on Phi d is this coefficient aE which comes here right. So, you have got E aE equal to aE E Phi + this integral, okay.

Now, I will refer to this equation with this green star because I am going to need it in subsequent analysis okay. So, whenever we need to refer to this I will pull it up with a reference to this green star. It is like giving it an equation number.

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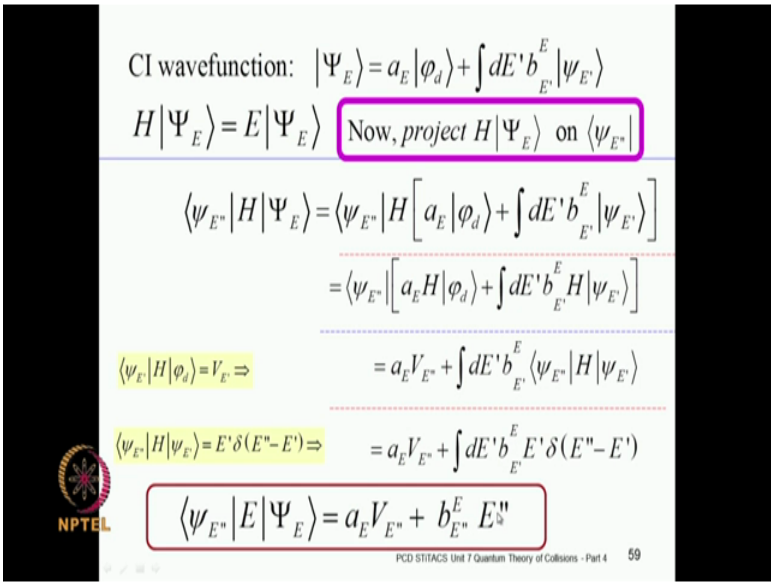

CI wavefunction: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \int dE' b_{E'}^{E} |\psi_{E'}\rangle$

$H|\Psi_E\rangle = E|\Psi_E\rangle$ $\boxed{\text{Now, } \textit{project } H|\Psi_E\rangle \text{ on } \langle\psi_{E''}|}$

$$\langle\psi_{E''}|H|\Psi_E\rangle = \langle\psi_{E''}|H\left[a_E|\varphi_d\rangle + \int dE' b_{E'}^{E} |\psi_{E'}\rangle\right]$$

$$= \langle\psi_{E''}|\left[a_E H|\varphi_d\rangle + \int dE' b_{E'}^{E} H|\psi_{E'}\rangle\right]$$

$\langle\psi_{E'}|H|\varphi_d\rangle = V_{E'} \Rightarrow$

$$= a_E V_{E''} + \int dE' b_{E'}^{E} \langle\psi_{E''}|H|\psi_{E'}\rangle$$

$\langle\psi_{E''}|H|\psi_{E'}\rangle = E'\delta(E''-E') \Rightarrow$

$$= a_E V_{E''} + \int dE' b_{E'}^{E} E'\delta(E''-E')$$

$$\boxed{\langle\psi_{E''}|E|\Psi_E\rangle = a_E V_{E''} + b_{E''}^{E} E''}$$

So, here you have got this configuration interaction. Now, we will this time project it on the continuum, okay. Now, this continuum state is a mix of, this is the configuration interaction state okay. It is a mix of, a discrete and a continuum right. So, it has got both the components and we now project this Schrodinger equation on such a state which is a mix of discrete and continuum.

So, this is our projection now. Look at it term by term. So, this is the projection on the discrete part and here is a projection on the continuum okay. So, now what do we get? We look at each term separately aE, we can pull out as we can, as a factor, we can factor it out. And then, you have got the matrix element of H , Psi and Phi d which is nothing but V okay.

So, from this term, we get aE VE and likewise from this term we will get a Dirac delta okay, because these two states are in the continuum. So, you get a Dirac delta there. So, now you have this relation and now we have the left hand side which is e and these two will of course give you a Dirac delta.

You can see it coming. And then, on the right hand side, you have this Delta function integration over E prime. So, only the term in E prime = E double prime will survive. So, you get a coefficient b with E E double Prime and this E becomes double prime, that is because of the Dirac delta integration, okay.
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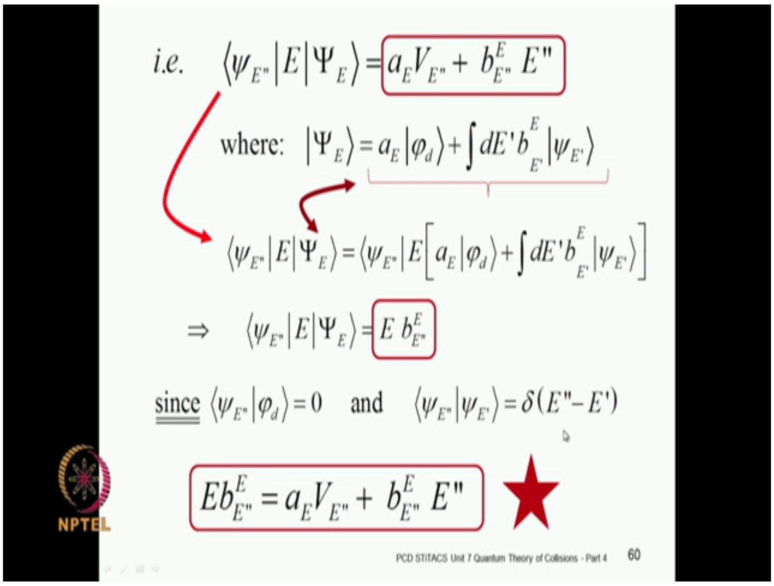

$$i.e.\quad \langle\psi_{E''}|E|\Psi_E\rangle = \boxed{a_E V_{E''} + b^E_{E''}\,E''}$$

where: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \underbrace{\int dE' b^{E}_{E'}|\psi_{E'}\rangle}$

$$\langle\psi_{E''}|E|\Psi_E\rangle = \langle\psi_{E''}|E\left[a_E|\varphi_d\rangle + \int dE' b^{E}_{E'}|\psi_{E'}\rangle\right]$$

$$\Rightarrow\quad \langle\psi_{E''}|E|\Psi_E\rangle = \boxed{E\,b^E_{E''}}$$

since $\langle\psi_{E''}|\varphi_d\rangle = 0$ and $\langle\psi_{E''}|\psi_{E'}\rangle = \delta(E''-E')$

$$\boxed{Eb^E_{E''} = a_E V_{E''} + b^E_{E''}\,E''}\ ★$$

So, here are the relations we have. Now, this is the result that we got on the previous slide and in this, I now put this superposition on the right side. So, now I get 2 terms, okay. And from the first term E and aE are scalars, they will come out. And you will get a projection of the continuum state on the discrete. But though they are orthogonal, so, that will vanish, right.

And then from here you will get the note, of the scalar product of these two which will give you a Dirac delta okay. So, let us put both of these over here. And now, you get from the first term you get 0, from the second you get a delta function. You carry out the integration, you get the term in E prime = E double prime.

So, you get this equation here. And this is the one which I will refer to as a red star. So, now you have got two equations that I am going to be referring to; one with the grease green star and the other with the red star.
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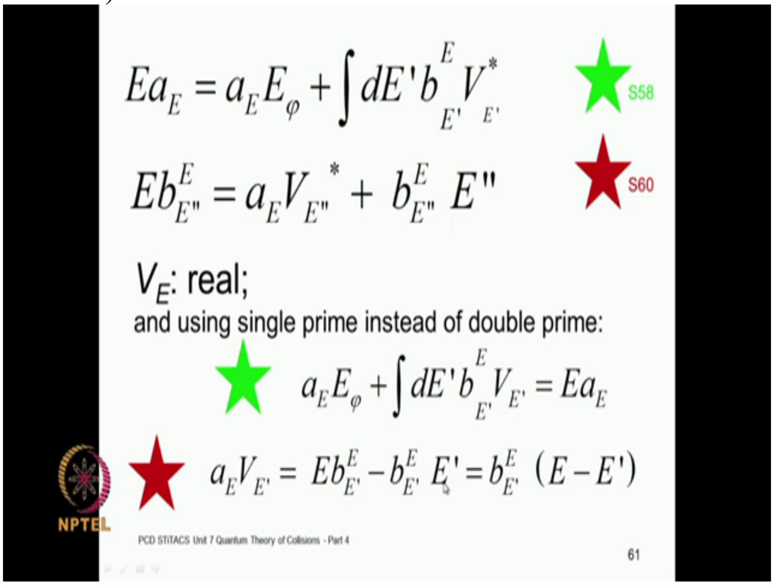

$$Ea_E = a_E E_\varphi + \int dE' b^{E}_{E'} V^*_{E'} \quad ★ \text{ S58}$$

$$Eb^E_{E''} = a_E V_{E''}^{\,*} + b^E_{E''}\,E'' \quad ★ \text{ S60}$$

V_E: real;
and using single prime instead of double prime:

$$★\quad a_E E_\varphi + \int dE' b^{E}_{E'} V_{E'} = Ea_E$$

$$★\quad a_E V_{E'} = Eb^E_{E'} - b^E_{E'}\,E' = b^E_{E'}\,(E-E')$$

So, these are the two relations; one with the green, one with the red. So, these are the two relations that we are now going to analyze, okay. Now, VE is real and here we have used two primes so there is no need to use two primes we will use only one prime. So, I will rewrite them without the double prime and writing them as real numbers okay.

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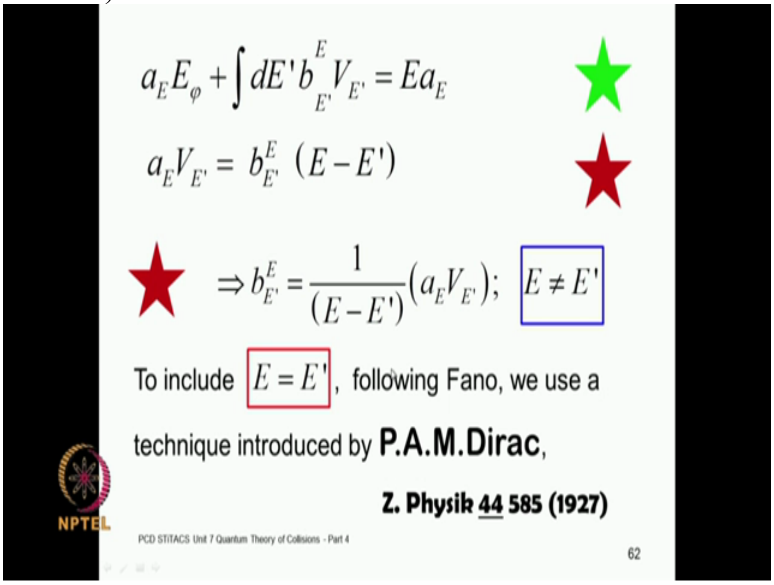

$$a_E E_\varphi + \int dE' b^E_{E'} V_{E'} = E a_E$$ ★

$$a_E V_{E'} = b^E_{E'} \, (E - E')$$ ★

★ $$\Rightarrow b^E_{E'} = \frac{1}{(E-E')}(a_E V_{E'}); \quad \boxed{E \neq E'}$$

To include $\boxed{E = E'}$, following Fano, we use a technique introduced by **P.A.M.Dirac**,

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So, what do we get from this relation red star. From here, V = aE VE divided by E - E prime, which is fine as long as E is not equal to E prime okay. So, all this will work as long as E is not exactly equal to E prime. But that is just the case we really want to handle, okay. That is precisely what we want to handle.

So, to be able to include the E equal to E prime Fano used a very beautiful technique which was devised originally by Dirac and this is the Fano Dirac technique okay. So, they make use of principle value integration to address this situation, so I will show you how it is done. So, the purpose is to address this particular case of E = E prime.

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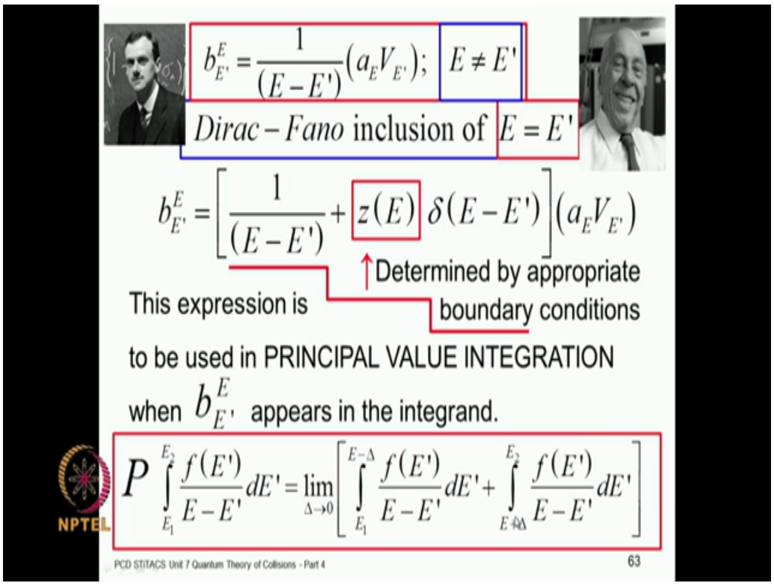

$b_{E'}^{E} = \frac{1}{(E-E')}(a_E V_{E'})$; $\boxed{E \neq E'}$

Dirac – Fano inclusion of $\boxed{E = E'}$

$$b_{E'}^{E} = \left[\frac{1}{(E-E')} + \boxed{z(E)}\,\delta(E-E')\right](a_E V_{E'})$$

↑Determined by appropriate boundary conditions

This expression is to be used in PRINCIPAL VALUE INTEGRATION when $b_{E'}^{E}$ appears in the integrand.

$$P\int_{E_1}^{E_2} \frac{f(E')}{E-E'}dE' = \lim_{\Delta\to 0}\left[\int_{E_1}^{E-\Delta}\frac{f(E')}{E-E'}dE' + \int_{E+\Delta}^{E_2}\frac{f(E')}{E-E'}dE'\right]$$

And this is the Dirac Fano technique and what this technique does is following Dirac. And this is really beautiful device to handle such situations. That instead of writing b like this, you write it as 1 over E - E prime. So, the aE VE prime is here, which is here. So, this is the aE VE prime, okay. That factor is here and then over here, you add a function Z multiplied by the Dirac delta.

Because you are going to use it in some integral so that will leave a value only when E prime = E, which is just what you want, okay. So, that is the trick, okay. So, this is to be used in Principal Value Integration. So, this is the Dirac Fano trick and you will see that, it really does wonders for us. And the function z is so chosen that it meets the appropriate boundary conditions; because the boundary conditions are known to us, okay.

So, by putting appropriate boundary conditions, you can determine the function z. And now, whenever you have bE in the integrand, then, you can use this Dirac Fano, substitute. So, this is the brilliant mathematical device which Fano used in this context. So, this is to be done using the principal value integration, whenever b appears in the integrand and the principal value of integral which I am sure all of you would have worked with.

In your mathematical physics courses or some other courses and Collision theory and so on. So, whenever you evaluate an integral from E1 to E2, and then, you have a problem over here, when E prime goes to E, then you go close enough and then, hop over that point and then do the rest of the integration, okay. So, that is the Principal value integral. That is how it is defined.

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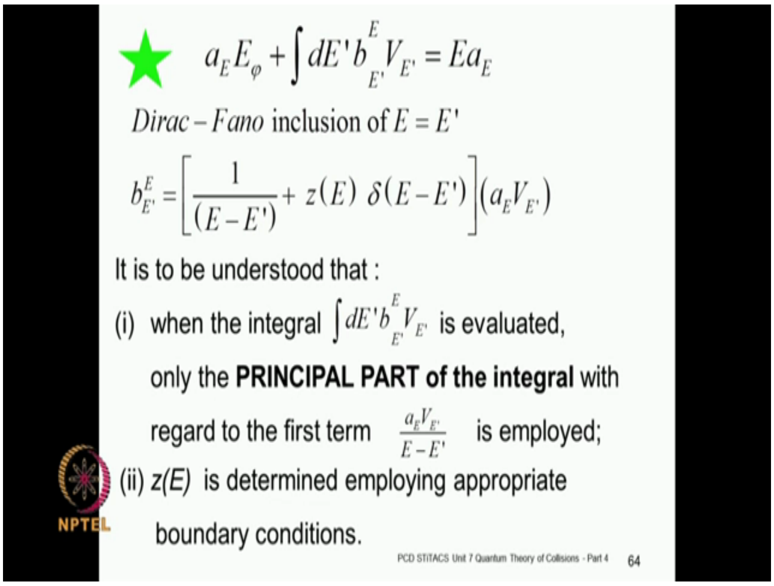

★ $a_E E_\varphi + \int dE' \, b^E_{E'} V_{E'} = E a_E$

$Dirac - Fano$ inclusion of $E = E'$

$$b^E_{E'} = \left[\frac{1}{(E-E')} + z(E)\ \delta(E-E') \right] (a_E V_{E'})$$

It is to be understood that :

(i) when the integral $\int dE' \, b^E_{E'} V_{E'}$ is evaluated, only the **PRINCIPAL PART of the integral** with regard to the first term $\frac{a_E V_{E'}}{E-E'}$ is employed;

(ii) *z(E)* is determined employing appropriate boundary conditions.

So, this is our Dirac, Dirac Fano proposal and what is understood is that, whenever you have this type of an integral to be determined, then, you should carry out a principal value of this integration and use z appropriate to boundary condition. So, these are the two things which go into this technique. So, it is the idea is very simple; but extremely beautiful and very powerful, okay.

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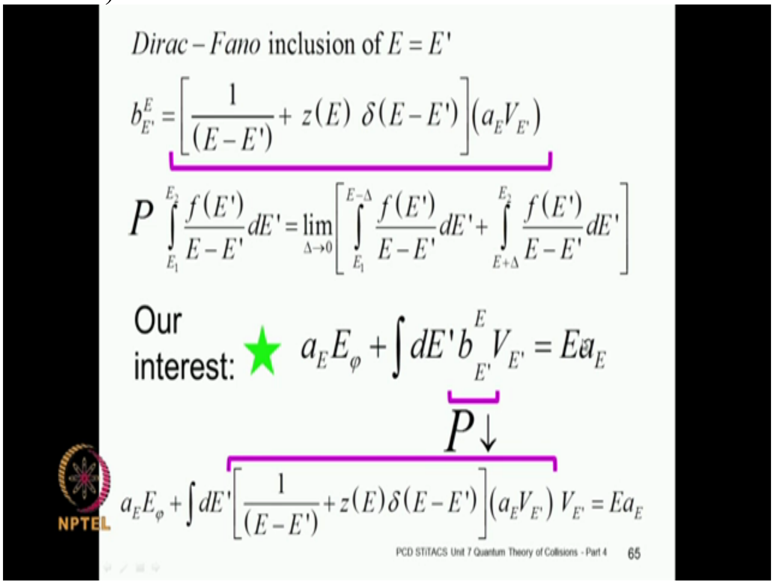

$Dirac - Fano$ inclusion of $E = E'$

$$b^E_{E'} = \underbrace{\left[\frac{1}{(E-E')} + z(E)\ \delta(E-E') \right] (a_E V_{E'})}$$

$$P \int_{E_1}^{E_2} \frac{f(E')}{E-E'} dE' = \lim_{\Delta \to 0} \left[\int_{E_1}^{E-\Delta} \frac{f(E')}{E-E'} dE' + \int_{E+\Delta}^{E_2} \frac{f(E')}{E-E'} dE' \right]$$

Our interest: ★ $a_E E_\varphi + \int dE' \, \underbrace{b^E_{E'}}_{P\downarrow} V_{E'} = E a_E$

$$a_E E_\varphi + \int dE' \overbrace{\left[\frac{1}{(E-E')} + z(E)\delta(E-E') \right] (a_E V_{E'})} V_{E'} = E a_E$$

So, let us see what it does for us in this particular case. So, here, we have the principal value integral defined. And our interest is in this relation here, which we have identified as a green star, and over here, this integral will be replaced by the principal value integral. So, this integral this bE is to be replaced by this factor here coming from the principal value integration trick of Dirac Fano. And we will work with this relation instead of this, okay.

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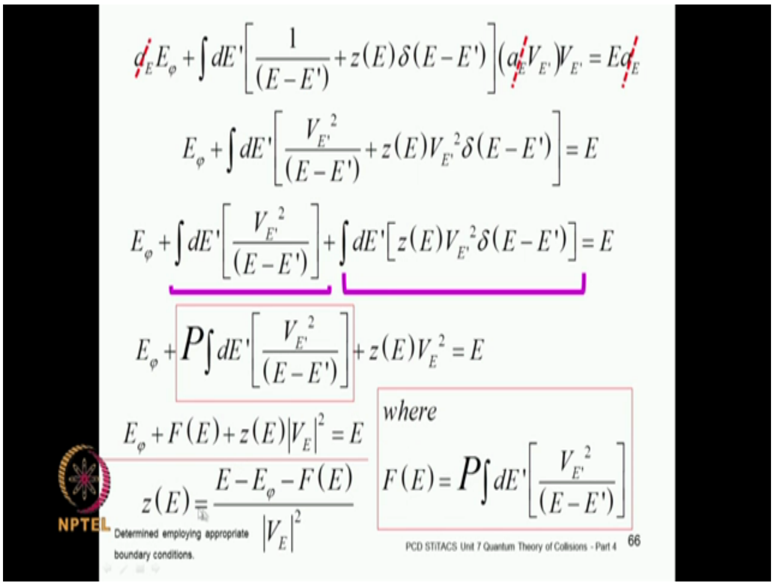

$$\cancel{a_E}E_\varphi + \int dE'\left[\frac{1}{(E-E')} + z(E)\delta(E-E')\right](\cancel{a_E}V_{E'})V_{E'} = E\cancel{a_E}$$

$$E_\varphi + \int dE'\left[\frac{V_{E'}^{2}}{(E-E')} + z(E)V_{E'}^{2}\delta(E-E')\right] = E$$

$$E_\varphi + \underbrace{\int dE'\left[\frac{V_{E'}^{2}}{(E-E')}\right]} + \underbrace{\int dE'\left[z(E)V_{E'}^{2}\delta(E-E')\right]} = E$$

$$E_\varphi + \boxed{P\int dE'\left[\frac{V_{E'}^{2}}{(E-E')}\right]} + z(E)V_{E}^{2} = E$$

$$E_\varphi + F(E) + z(E)|V_E|^2 = E$$

where

$$F(E) = P\int dE'\left[\frac{V_{E'}^{2}}{(E-E')}\right]$$

$$z(E) = \frac{E - E_\varphi - F(E)}{|V_E|^2}$$

Determined employing appropriate boundary conditions.

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So, here we are. So, now, this is the relation that we have agreed to work with this in this. We have already employed the Dirac Fano trick. Now, first we cancel out aE which is common in all the terms, okay. So, aE is cancelled out. We need not carry it any further. The rest of the equation is here after cancelling aE. Now, in this we have got three terms, one is EPhi which is here, then you have this term which is here.

And then you have got the third term, which is integration over E prime z VE square and the Dirac delta okay. So, there are these three terms in this expression, okay are we all together, okay. So, now, here what do we get? We make use of the principal value integration. From this term you have got a Dirac delta integral okay. So, this is the Dirac delta integrator and this will give you a value which is appropriate only for E prime = E.

Because the integration is over E prime, so you get a value which is appropriate only for E prime = E. So, you get zVE square from this term. And here, you will now carry out a principal value integration, because the value for E = E prime is already taken care of over here, okay. That is already taken care of. So, your problem is done actually. It is really brilliant idea.

So, now, it also tells us what z should be because z is now a solution of this. So, this principal value integral, you represent for compactness by a function E. This is a function, some function of E. There is no difficulty in evaluating it. There is no singularity in that, right. So, you evaluate this integral and you represent it by some function of E. And that tells us what z should be it is given by this okay.

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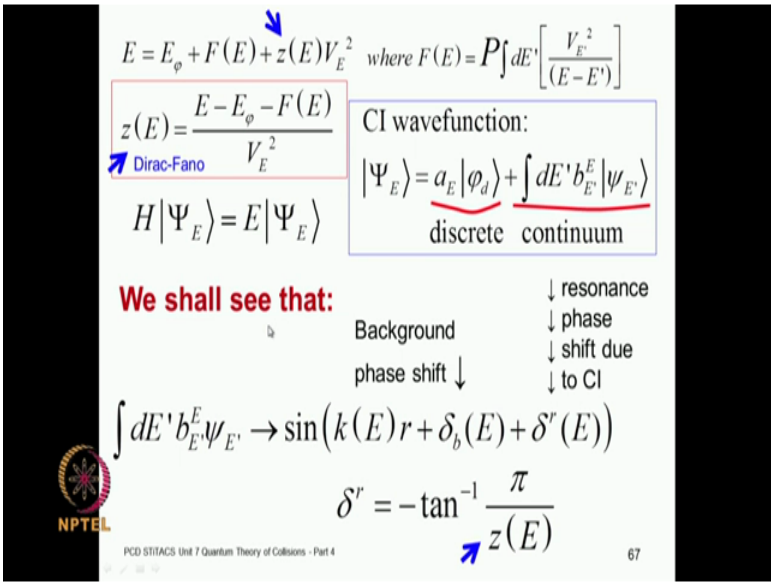

$E = E_\varphi + F(E) + z(E) V_E^2$ where $F(E) = P\int dE' \left[\frac{V_{E'}^2}{(E-E')}\right]$

$z(E) = \frac{E - E_\varphi - F(E)}{V_E^2}$

Dirac-Fano

$H|\Psi_E\rangle = E|\Psi_E\rangle$

CI wavefunction:

$|\Psi_E\rangle = \underbrace{a_E|\varphi_d\rangle}_{\text{discrete}} + \underbrace{\int dE' b_{E'}^E |\psi_{E'}\rangle}_{\text{continuum}}$

We shall see that:

Background phase shift ↓

↓ resonance ↓ phase ↓ shift due ↓ to CI

$\int dE' b_{E'}^E \psi_{E'} \to \sin\left(k(E)r + \delta_b(E) + \delta^r(E)\right)$

$\delta^r = -\tan^{-1}\frac{\pi}{z(E)}$

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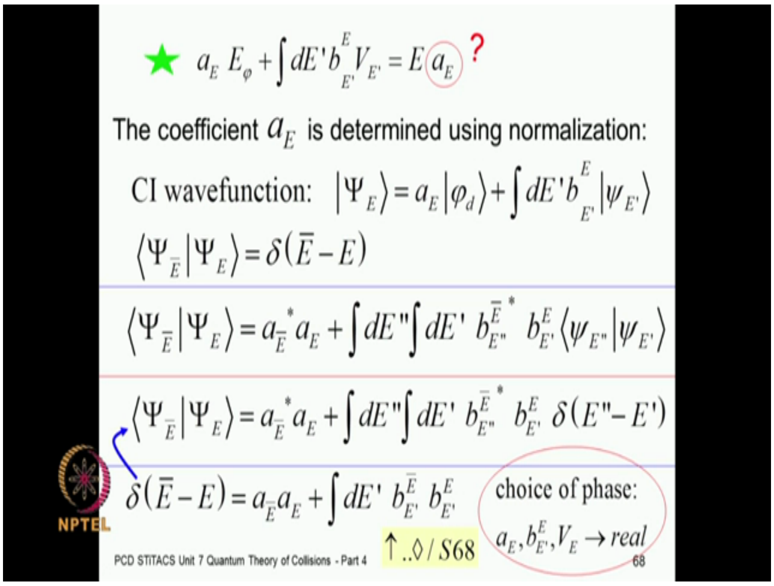
So, now we have almost all the pieces that we need. And now, it is just a matter of rearrangement of these terms to extract our final state configuration interaction wave function. So, here, the z is given by the Dirac Fano trick. The configuration interaction is this, as we know. So, what we are going to see, is that this, this particular state which is in the continuum.

This will look very similar to a continuum state solution that we have worked with in scattering theory all along. You will remember that this goes a sine kr + delta, right. So, you have got the sine kr, k depends on energy. So, it is sine kr + delta which is the background phase shift. But then, there is an additional phase shift which is coming from the configuration interaction. This is the resonant part, okay.

So, there is this additional phase shift which is coming because of the time delay that the electron may get bound into the doubly excited bound state for some time before it escapes into the continuum. So, you have got a background phase shift and then a resonant phase shift due to the configuration interaction.

The resonant phase shift it will turn out and you will see this coming in the next, you know, as we go further, in this class. That this resonant part of the phase shift will turn out to be given by negative tran inverse Phi over z, okay. That is what it will turn out to be but that is a result which you will see coming.

(Refer Slide Time: 38:28)



★ $a_E E_\varphi + \int dE' b_{E'}^{E} V_{E'} = E \boxed{a_E}$?

The coefficient a_E is determined using normalization:

CI wavefunction: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \int dE' b_{E'}^{E} |\psi_{E'}\rangle$

$\langle\Psi_{\bar{E}}|\Psi_E\rangle = \delta(\bar{E} - E)$

$\langle\Psi_{\bar{E}}|\Psi_E\rangle = a_{\bar{E}}^{*} a_E + \int dE'' \int dE' \, b_{E''}^{\bar{E}*} \, b_{E'}^{E} \langle\psi_{E''}|\psi_{E'}\rangle$

$\langle\Psi_{\bar{E}}|\Psi_E\rangle = a_{\bar{E}}^{*} a_E + \int dE'' \int dE' \, b_{E''}^{\bar{E}*} \, b_{E'}^{E} \, \delta(E'' - E')$

$\delta(\bar{E} - E) = a_{\bar{E}} a_E + \int dE' \, b_{E'}^{\bar{E}} \, b_{E'}^{E}$

choice of phase: $a_E, b_{E'}^{E}, V_E \rightarrow real$

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↑..◊/S68

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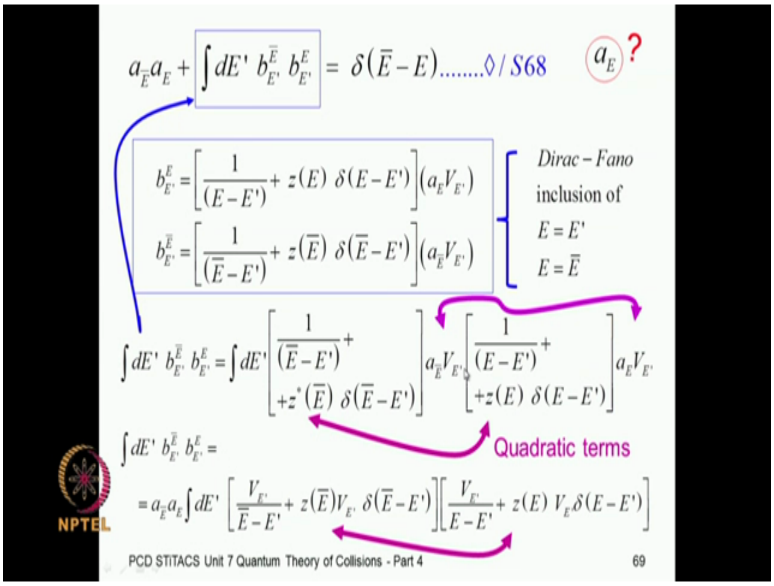
So, now we have to determine this coefficient a according to normalization. And this is our normalization here, okay. Your Configuration Interaction state is you have a combination of the discrete state and the continuum state. The discrete state is weighted by this coefficient a, okay. This is what we want to determine.

These states are, of course, Dirac delta normalized. So, if you take this Dirac delta on the left, ok then, on the right side, you have got a projection of this on itself, right. So, you will get a E star aE from the first term, right. Phi and Psi are orthogonal. And then, you will get the bE star bE times this, right okay. So, we have used these orthogonality is earlier as well.

So, this is the left-hand side is nothing but the Dirac delta and then, the right hand side, you have got the aE bar aE. There are two different energies I am considering, mind you, both are in the continuum E and E bar, ok. So, you have got two coefficients aE and a E bar and over here, because you carry out this delta function integration over E double prime.

So, that the only term that survives is the one for which a double prime is equal to E single prime. So, you have got the E bar, E single prime. And then, the bE and the subscript here is again E single prime, okay. That is the Dirac delta integration, okay.

(Refer Slide Time: 40:27)



$$a_{\bar E}a_E + \boxed{\int dE'\, b^{\bar E}_{E'}\, b^{E}_{E'}} = \delta(\bar E - E) \text{........} \lozenge / S68$$

a_E ?

$$b^{E}_{E'} = \left[\frac{1}{(E-E')} + z(E)\,\delta(E-E')\right](a_E V_{E'})$$

$$b^{\bar E}_{E'} = \left[\frac{1}{(\bar E-E')} + z(\bar E)\,\delta(\bar E-E')\right](a_{\bar E} V_{E'})$$

Dirac – Fano inclusion of
$E = E'$
$E = \bar E$

$$\int dE'\, b^{\bar E}_{E'}\, b^{E}_{E'} = \int dE' \left[\frac{1}{(\bar E-E')} + z^*(\bar E)\,\delta(\bar E-E')\right] a_{\bar E} V_{E'} \left[\frac{1}{(E-E')} + z(E)\,\delta(E-E')\right] a_E V_{E'}$$

Quadratic terms

$$\int dE'\, b^{\bar E}_{E'}\, b^{E}_{E'} =$$

$$= a_{\bar E} a_E \int dE' \left[\frac{V_{E'}}{\bar E-E'} + z(\bar E) V_{E'}\,\delta(\bar E-E')\right]\left[\frac{V_{E'}}{E-E'} + z(E)\, V_E \delta(E-E')\right]$$

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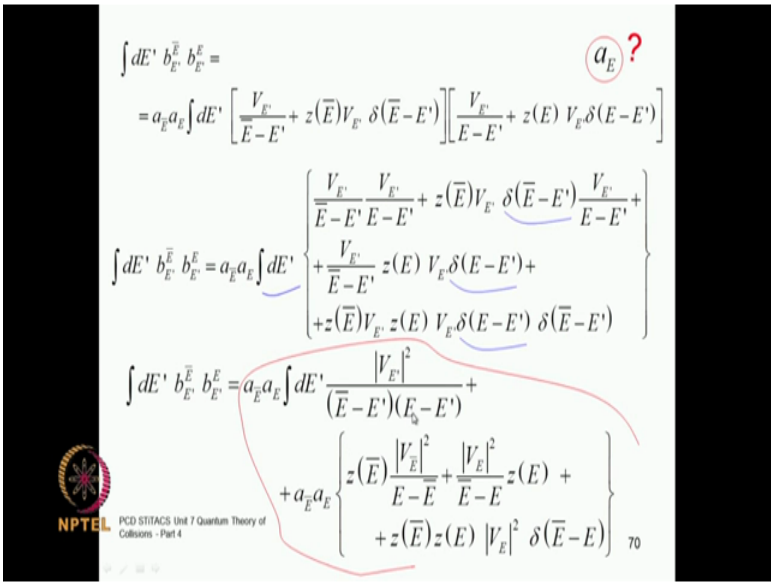
Now, here is a relation which we have obtained earlier which is from the previous slide which I indicate by this diamond here the only thing I have done in moving this to the next slide is I take this aE bar on one side. So, I have delta E bar minus E over here, okay. So, this is the relation I get from the previous slide. This is the Dirac Fano trick. So, we have putting all our pieces together.

Now in this relation, which is indicated by this diamond relation, here, this over here, I use the Dirac Fano inclusion of, E equal to for E equal to E prime because both are here. You have got E prime over here. So, you have one for E bar and the other one for E, right. So, you have two substitutions over here; one coming from this relation and the other coming from the corresponding relation for E bar. So, this is our E and this is for E bar.

So, these two go into these two pieces, okay. So, I substitute this and now I have got an equation which looks slightly large. But we can handle it on the screen. So, remember that you will get quadratic terms when you multiply you will get z over here and another zover here. You have V over here and another V over here, so, you will get quadratic terms z and V. So, let us write all of these terms.

So, you have the aE VE and aE VE prime over here. So, there is an aE bar and aE, So aE bar comes here; the aE comes here, the VE bar, the VE prime is inside, okay. The VE prime is inside because it is under integration. So, it does not come out, ok. And then, you have two terms over here. So, the VE prime remains under the integrand.
So, you get VE prime over E bar - E prime here. Then, you have got the second function. There is a Dirac delta here. And then, you have got a VE prime sitting on top of this E -E prime and then, this function z and then this Dirac delta which is young, okay.
(Refer Slide Time: 43:29)



$$\int dE'\, b^{\bar{E}}_{E'}\, b^{E}_{E'} =$$

$$\boxed{a_E}\,?$$

$$= a_{\bar{E}} a_E \int dE' \left[\frac{V_{E'}}{\bar{E}-E'} + z(\bar{E}) V_{E'}\, \delta(\bar{E}-E')\right]\left[\frac{V_{E'}}{E-E'} + z(E)\, V_{E'} \delta(E-E')\right]$$

$$\int dE'\, b^{\bar{E}}_{E'}\, b^{E}_{E'} = a_{\bar{E}} a_E \underbrace{\int dE'} \left\{ \begin{array}{l} \frac{V_{E'}}{\bar{E}-E'} \frac{V_{E'}}{E-E'} + z(\bar{E}) V_{E'}\, \underbrace{\delta(\bar{E}-E')} \frac{V_{E'}}{E-E'} + \\ + \frac{V_{E'}}{\bar{E}-E'}\, z(E)\, V_{E'} \underbrace{\delta(E-E')} + \\ + z(\bar{E}) V_{E'}\, z(E)\, V_{E'} \underbrace{\delta(E-E')}\, \delta(\bar{E}-E') \end{array} \right\}$$

$$\int dE'\, b^{\bar{E}}_{E'}\, b^{E}_{E'} = a_{\bar{E}} a_E \int dE' \frac{|V_{E'}|^2}{(\bar{E}-E')(E-E')} + $$

$$+ a_{\bar{E}} a_E \left\{ \begin{array}{l} z(\bar{E}) \frac{|V_{\bar{E}}|^2}{E-\bar{E}} + \frac{|V_E|^2}{\bar{E}-E} z(E) + \\ + z(\bar{E}) z(E)\, |V_E|^2\, \delta(\bar{E}-E) \end{array} \right\}$$

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So, now you have got 1, 2, 3, 4, 4 terms 2. So, 2 terms of multiplying 2 terms over here. So you will get 4 terms. So, they are here. 1, 2, 3 and 4, we have just multiplied them out. And I think, this is when I was preparing these slides, I realized that it is really nice to be able to use in this Technology Enhanced Learning Program that we have the provision to flash these slides at the click of a mouse.

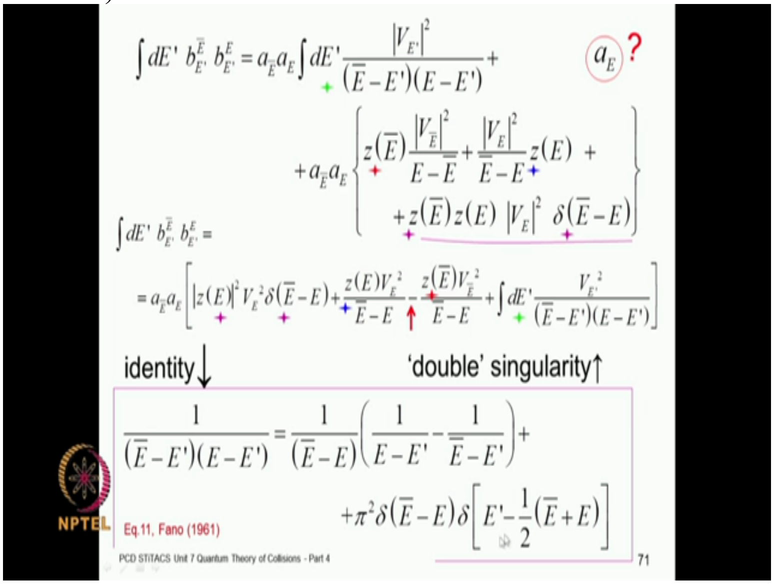
So, that we can concentrate focus of a discussion on the physics and not get lost in carrying out mere substitutions that itself takes such a long time on a blackboard if you were to write it using a chalk. So, this comes at the click of a mouse and we can actually concentrate on the physics on how the analysis is done. So, here we have these 4 terms, right.

And you can of course, look at the PDF at leisure and make sure that everything is done, right. So, here you have 4 terms: 1, 2, 3 and 4. Out of these 4 terms, these 3 have got Dirac delta. And you are carrying out integration over E primes, so, they will give you terms in which only E prime = E will survive, right. And then, there will be a 4th integral which will be left coming from this quadratic term in V, right.

So, those are the 4 terms. So, here is the result of those 4 terms. So, here you have got the first one. You have got this integral over E prime or this is quadratic in V. So, here it is, okay. And from the remaining 3 terms, you carry out the Dirac delta integration. And you are left with only those terms corresponding to which E prime is equal to E bar in this time, over here. E prime must be equal to E and over here E prime must be equal to E bar, okay.

So, those are the three terms which are left with. But remember that in the last integral you have carried out integration over E prime, so E prime must be equal to E bar. So, when you write this Dirac delta E prime has been written as E bar, okay. So, that is something that you have to keep track off.

(Refer Slide Time: 46:03)



$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} = a_{\bar{E}} a_E \int dE' \frac{|V_{E'}|^2}{(\bar{E}-E')(E-E')} +$$

a_E ?

$$+ a_{\bar{E}} a_E \left\{ z(\bar{E}) \frac{|V_{\bar{E}}|^2}{E-\bar{E}} + \frac{|V_E|^2}{\bar{E}-E} z(E) + + z(\bar{E}) z(E) |V_E|^2\, \delta(\bar{E}-E) \right\}$$

$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} =$$

$$= a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' \frac{V_{E'}^2}{(\bar{E}-E')(E-E')} \right]$$

identity↓

'double' singularity↑

$$\frac{1}{(\bar{E}-E')(E-E')} = \frac{1}{(\bar{E}-E)} \left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'} \right) + + \pi^2 \delta(\bar{E}-E)\, \delta\left[E' - \frac{1}{2}(\bar{E}+E) \right]$$

Eq.11, Fano (1961)

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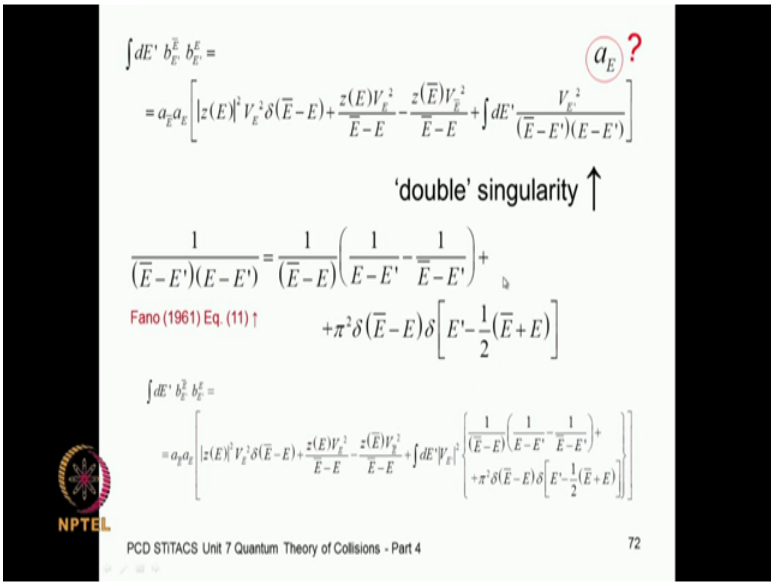
So, now we have got all the terms and I have now, I have got these 4 terms. But I rewrite them. So, this first term which is indicated by this four point green star which comes here. So, it is just a rearrangement of terms. But the colour code will show you which term is where. Then I have this term coming over here with the difference that here I had E - E bar. But now, I have E bar - E. So, I have plugged in a minus sign to compensate for that, okay.

And then, I have this term which comes here as it is. And then, I have this term with the Dirac delta E bar - E coming here, which is a quadratic term z and V, okay. Good. So, now we have a double singularity here okay. So, what do we do? We use a identity which is well known in mathematics. So, when you have a double singularity of this kind you use this identity that which lets you take advantage of the Dirac delta integrations.

So, I will not prove this identity I will use it. So, this is the identity that we will use and this was used by Fano in this work. So, instead of this 1 over E bar - E prime multiplied by E - E prime, you use the right hand side of this and this will give you the Dirac delta or product of Dirac delta in the numerator and then the rest of the terms.

(Refer Slide Time: 48:00)



$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} =$$

$$= a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' \frac{V_{E'}^2}{(\bar{E}-E')(E-E')} \right]$$

$\boxed{a_E}$?

'double' singularity ↑

$$\frac{1}{(\bar{E}-E')(E-E')} = \frac{1}{(\bar{E}-E)}\left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'}\right) +$$

Fano (1961) Eq. (11) ↑

$$+\pi^2 \delta(\bar{E}-E)\, \delta\left[E' - \frac{1}{2}(\bar{E}+E)\right]$$

$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} =$$

$$= a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' |V_E|^2 \left\{ \begin{array}{l} \frac{1}{(\bar{E}-E)}\left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'}\right) + \\ +\pi^2 \delta(\bar{E}-E)\, \delta\left[E' - \frac{1}{2}(\bar{E}+E)\right] \end{array} \right\} \right]$$

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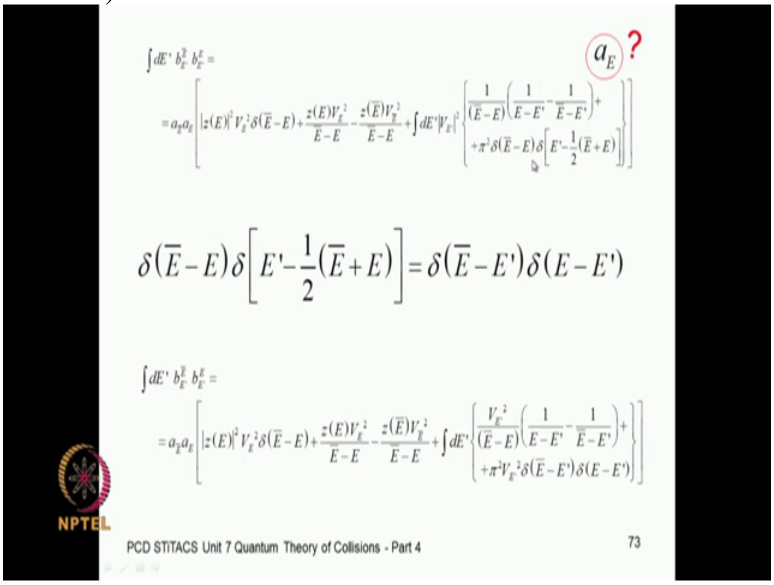
So, we will use this identity over here and using this identity this integral now takes this form. So, instead of this integral you have the dE prime VE prime square coming here; the dE prime, VE prime square. And here this one over double singularity is now written in this beautiful bracket which is this entire right hand side of this identity okay. So, this is the relation that we now have to work with okay.

(Refer Slide Time: 48:46)



$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} =$$

$$= a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' |V_E|^2 \left\{ \begin{array}{l} \frac{1}{(\bar{E}-E)}\left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'}\right) + \\ +\pi^2 \delta(\bar{E}-E)\, \delta\left[E' - \frac{1}{2}(\bar{E}+E)\right] \end{array} \right\} \right]$$

$\boxed{a_E}$?

$$\delta(\bar{E}-E)\, \delta\left[E' - \frac{1}{2}(\bar{E}+E)\right] = \delta(\bar{E}-E')\, \delta(E-E')$$

$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} =$$

$$= a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' \left\{ \begin{array}{l} \frac{V_{E'}^2}{(\bar{E}-E)}\left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'}\right) + \\ +\pi^2 V_{E'}^2 \delta(\bar{E}-E')\, \delta(E-E') \end{array} \right\} \right]$$

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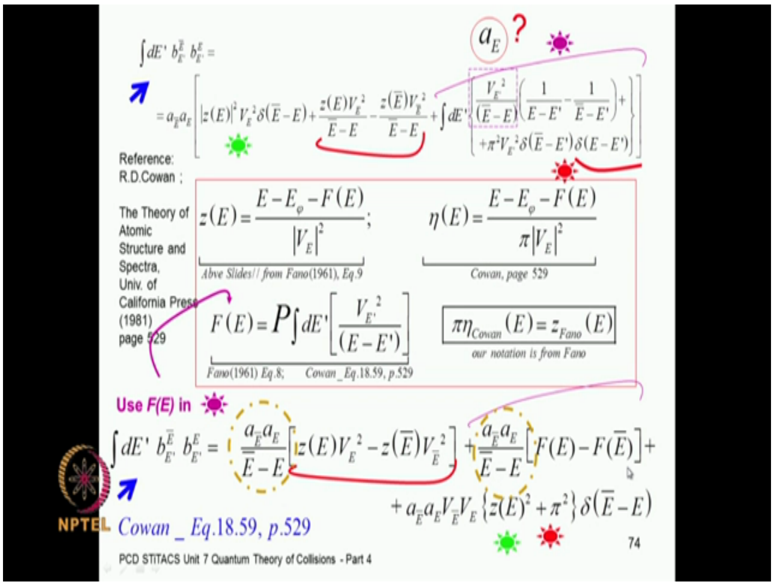
So, I brought it to the top of this slide now. Now, here again, if you play with the Dirac delta's is you can show that the product of these 2 direct delta's is completely equivalent to this. So, we will use that. And using this combination instead of this, we simplify this further, okay. And let us now analyze this relation.

(Refer Slide Time: 49:22)



a_E ?

$$\int dE' \, b_{E'}^{\bar{E}} \, b_{E'}^{E} = a_{\bar{E}} a_E \left[|z(E)|^2 V_E^2 \delta(\bar{E}-E) + \frac{z(E) V_E^2}{\bar{E}-E} - \frac{z(\bar{E}) V_{\bar{E}}^2}{\bar{E}-E} + \int dE' \left\{ \boxed{\frac{V_{E'}^2}{(\bar{E}-E)}} \left(\frac{1}{E-E'} - \frac{1}{\bar{E}-E'} \right) + \pi^2 V_{E'}^2 \delta(\bar{E}-E') \delta(E-E') \right\} \right]$$

Reference:
R.D.Cowan ;
The Theory of Atomic Structure and Spectra, Univ. of California Press (1981) page 529

$$\underbrace{z(E) = \frac{E - E_\varphi - F(E)}{|V_E|^2}}_{\text{Abve Slides// from Fano(1961), Eq.9}}; \qquad \underbrace{\eta(E) = \frac{E - E_\varphi - F(E)}{\pi |V_E|^2}}_{\text{Cowan, page 529}}$$

$$\underbrace{F(E) = P \int dE' \left[\frac{V_{E'}^2}{(E-E')} \right]}_{\text{Fano(1961) Eq.8; Cowan\_Eq.18.59, p.529}} \qquad \boxed{\pi \eta_{Cowan}(E) = z_{Fano}(E)}$$

our notation is from Fano

Use *F(E)* in

$$\int dE' \, b_{E'}^{\bar{E}} \, b_{E'}^{E} = \frac{a_{\bar{E}} a_E}{\bar{E}-E} \left[z(E) V_E^2 - z(\bar{E}) V_{\bar{E}}^2 \right] + \frac{a_{\bar{E}} a_E}{\bar{E}-E} \left[F(E) - F(\bar{E}) \right] + a_{\bar{E}} a_E V_{\bar{E}} V_E \left\{ z(E)^2 + \pi^2 \right\} \delta(\bar{E}-E)$$

Cowan _ Eq.18.59, p.529

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So, this is the relation that we are going to analyze and I will, I have used most of the discussion is from Fano's paper. There is some from Cowan's paper and some from some other sources. So, I will cite all the references and it is good to use them in combination. So, in addition to Fano's paper, I recommend Cowan's Book, Theory of Atomic Structure and Spectra.

And the notation is slightly different which is why I am alerting you to that, that the principal value function this integral has is, has the same notation in both Fano and Cowan. But the difference is Xia that what Fano calls as z instead of that, Cowan uses Eeta. But his function differs from Fano's by a factor of Phi, okay. So that is the only difference and if you are using a combination of these two sources.

Then you have to be careful with the literature okay. So, here what we will do is, we have this relation here, in which, you have an integral over E prime of a quadratic term in VE bar - E. And this is where you can use the principal value integral which is represented by the function f, okay. So we will use F of E instead of this term over here, okay; because the E = E prime or E = E bar we have already taken care of using the Fano Dirac trick.

So, now by using this F instead of this, we now get all of these terms are now, over here. So, first I write these 2 terms which come here, okay. So these 2 terms come here. Then you have this term, these terms in which you have got V square over E bar- E. So these are replaced by the Principal value integration FE - FE bar, right. These are the two which are coming here okay, right.

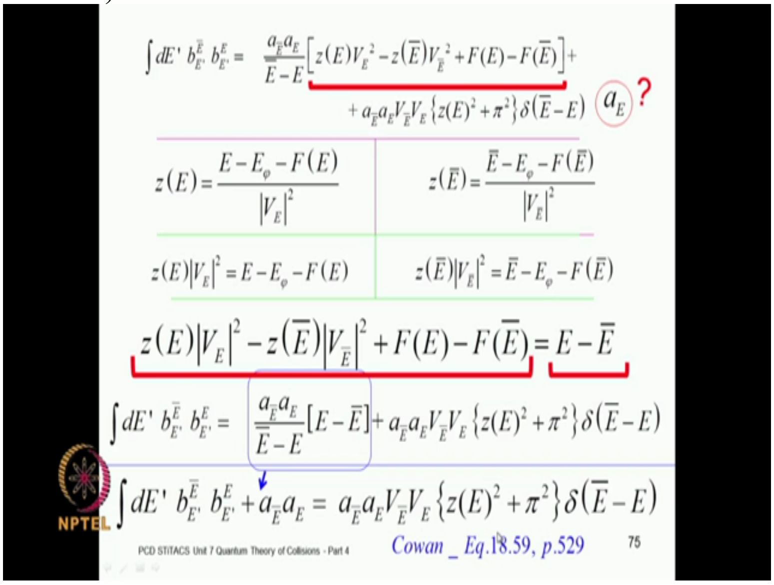
And then you have this term which comes here under and what you are left with? You left with one term of here which has got the pi square V square. So, the V square is here, aE bar a

E is here and the pi square is here. And then you have got the E prime = E. So, instead of E bar - E prime, you have got E bar - E; because E Prime has to be equal to E. So, that is what you get here, okay.

So, now, I think we are getting it in a mathematical form which is becoming compact and we can address it, in a tractable form. So, notice that these terms, both have got this factor common. This is aE bar aE or E bar - E. This is aE bar aE over E bar - E. So, you can combine these two terms. You can factor this out and write it, write the remaining terms separately, okay, right.

Yes (Question time 53:04 not audible) yeah. Oh E prime is here. It goes into the z that is taken care of already, okay. So, when you take the principal value integration, you are hopping over the singularity, okay. You go as far as the singularity and then pick up the integration from the point next to it.

And the point of singularity is taken care of by the functions z, okay. So, here, here you are. And now, you have got this term as common in this factor. So, we can factor it out.
(Refer Slide Time: 54:01)



$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} = \frac{a_{\bar{E}}a_E}{\bar{E}-E}\underbrace{\left[z(E)V_E^{\,2}-z(\bar{E})V_{\bar{E}}^{\,2}+F(E)-F(\bar{E})\right]}+$$

$$+\,a_{\bar{E}}a_E V_{\bar{E}}V_E\left\{z(E)^2+\pi^2\right\}\delta(\bar{E}-E) \quad \textcircled{a_E}\,?$$

$z(E)=\dfrac{E-E_\varphi-F(E)}{\lvert V_E\rvert^2}$	$z(\bar{E})=\dfrac{\bar{E}-E_\varphi-F(\bar{E})}{\lvert V_{\bar{E}}\rvert^2}$
$z(E)\lvert V_E\rvert^2=E-E_\varphi-F(E)$	$z(\bar{E})\lvert V_{\bar{E}}\rvert^2=\bar{E}-E_\varphi-F(\bar{E})$

$$\underbrace{z(E)\lvert V_E\rvert^2-z(\bar{E})\lvert V_{\bar{E}}\rvert^2+F(E)-F(\bar{E})}=\underbrace{E-\bar{E}}$$

$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E} = \boxed{\frac{a_{\bar{E}}a_E}{\bar{E}-E}}[E-\bar{E}]+a_{\bar{E}}a_E V_{\bar{E}}V_E\left\{z(E)^2+\pi^2\right\}\delta(\bar{E}-E)$$

$$\int dE'\, b_{E'}^{\bar{E}}\, b_{E'}^{E}+a_{\bar{E}}a_E = a_{\bar{E}}a_E V_{\bar{E}}V_E\left\{z(E)^2+\pi^2\right\}\delta(\bar{E}-E)$$

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Cowan _ Eq.18.59, p.529

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And I have factored it out and written the remaining 4 terms. So, they are now in terms of F and FE bar. So, here I have, here I have F and FE bar. And here I have zEV square and here I have ZE bar VE bar square, right. So, these are the 4 terms which will be in the remaining factor. So, those are the 4 terms in the remaining fold. In the second factor this has been factored out and this is the residual part which we had written here.

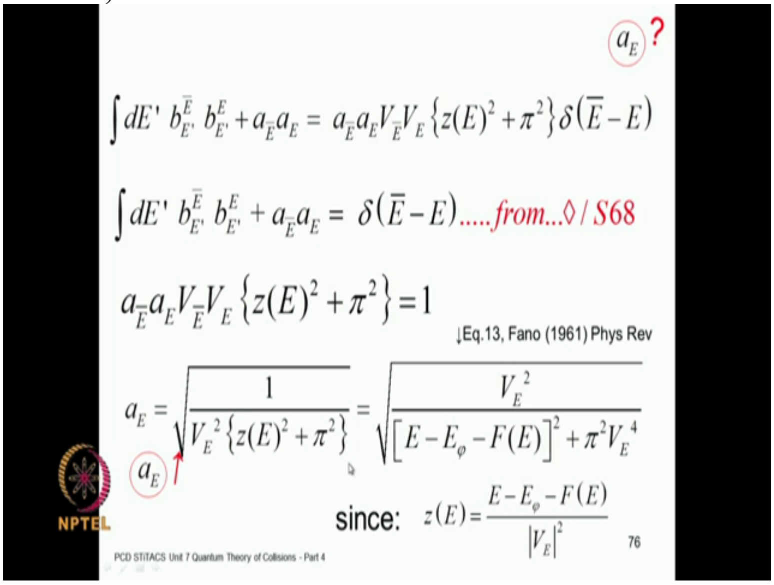
Which had this z square + Phi square and the Dirac delta, so here it is. So, you have the aE bar aE VE bar VE z square, plus Phi square, the Dirac delta, right. So, you got all the terms, z if we know, we already have seen that z is given by this relation and we are now able to anticipate a very important, very nice result.

So, this is the value of the function z at E but we have 2 energy indices, one is without the bar and the other is with the bar. So, this is Eddie bar and you put both of them. So, you have got two expressions because you have got z VE square and then z E bar VE bar square. So, you have to use the one with appropriate notation and the difference between these 4 is then nothing but E - E bar, because of this cancellation.

Because when you cancel this, ok the E Phi drops out, right. And then you have only the E-, E bar, okay. So, now we have got a simpler relation. So, this is the left hand side which comes here the right hand side. You have got aE bar aE or E bar - E which is here. What is under this red underlining is now just the difference between E and E bar which is here.

And then you have got these 2 terms over here, which is z square + Phi square, Dirac delta multiplied by a E bar aE and VE bar VE. So here we are. Now I rewrite this by moving this term to the left, so I have got on the left hand side this term minus this; but I have it with a plus sign because I have E - E bar in the numerator and it is negative in the denominator.

So, I have got aE bar aE with a plus sign on the left. So this is the relation that I will bring to the top of the next slide.
(Refer Slide Time: 57:12)



a_E ?

$$\int dE'\, b^{\bar{E}}_{E'}\, b^{E}_{E'} + a_{\bar{E}} a_E = a_{\bar{E}} a_E V_{\bar{E}} V_E \left\{ z(E)^2 + \pi^2 \right\} \delta(\bar{E} - E)$$

$$\int dE'\, b^{\bar{E}}_{E'}\, b^{E}_{E'} + a_{\bar{E}} a_E = \delta(\bar{E} - E) \text{.....from...◊ / S68}$$

$$a_{\bar{E}} a_E V_{\bar{E}} V_E \left\{ z(E)^2 + \pi^2 \right\} = 1$$

↓Eq.13, Fano (1961) Phys Rev

$$a_E = \sqrt{\frac{1}{V_E^{\,2}\left\{ z(E)^2 + \pi^2 \right\}}} = \sqrt{\frac{V_E^{\,2}}{\left[E - E_\varphi - F(E) \right]^2 + \pi^2 V_E^{\,4}}}$$

a_E ↑

since: $z(E) = \dfrac{E - E_\varphi - F(E)}{|V_E|^2}$

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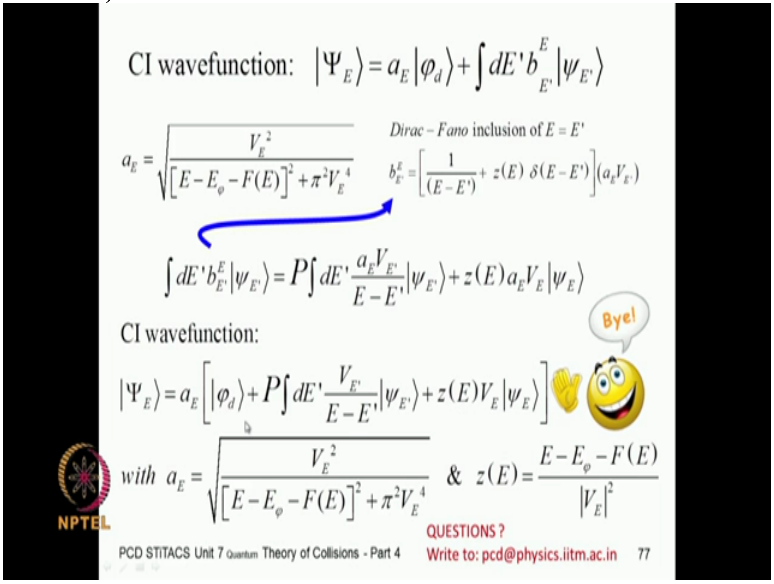
So, here we are. So, we have got these 2 terms on the left. Now, this is the relation that we have referred to earlier from slide 68, okay which I had indexed by a diamond okay. And now if you look at these two relations it is obvious that this factor over here must be equal to unity okay.

The left-hand sides of both the equations are the same; the right-hand sides are very nearly the same except for this factor which must be equal to1. And that tells you what the coefficient aE must be. This is what we were looking for, okay. We wanted to know, what is the weight factor in the Configuration Interaction mixing?

So, this is the weight factor. And this now comes out as a square root of 1 over V square z square + pi square okay. So, here you can write z because we know what z is. That is E - E Phi - F over VE square. So, you can rewrite in terms of this function of E instead of z. So, this is your weight factor a.

(Refer Slide Time: 59:40)



CI wavefunction: $|\Psi_E\rangle = a_E|\varphi_d\rangle + \int dE' b^E_{E'}|\psi_{E'}\rangle$

$$a_E = \sqrt{\frac{V_E^2}{[E-E_\varphi-F(E)]^2+\pi^2 V_E^4}}$$

Dirac – Fano inclusion of $E = E'$

$$b^E_{E'} = \left[\frac{1}{(E-E')} + z(E)\,\delta(E-E')\right](a_E V_{E'})$$

$$\int dE' b^E_{E'}|\psi_{E'}\rangle = P\int dE' \frac{a_E V_{E'}}{E-E'}|\psi_{E'}\rangle + z(E)a_E V_E|\psi_E\rangle$$

CI wavefunction:

$$|\Psi_E\rangle = a_E\left[|\varphi_d\rangle + P\int dE' \frac{V_{E'}}{E-E'}|\psi_{E'}\rangle + z(E)V_E|\psi_E\rangle\right]$$

$$\text{with } a_E = \sqrt{\frac{V_E^2}{[E-E_\varphi-F(E)]^2+\pi^2 V_E^4}} \quad \& \quad z(E) = \frac{E-E_\varphi-F(E)}{|V_E|^2}$$

QUESTIONS ?
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So, we now have this. And now we have taken care of the E = E prime and now we get the Configuration interaction. We have got all the terms. We have the b, this mixing we got this coefficient. So, we now get the complete wave function and in this we make use of the principal value integration as we have done, right.

So, you have the complete configuration interaction wave function in which you have the aE, Phi d which is here. And then, you have this piece over here. But because of this Dirac delta integration, you have got only the term corresponding to E prime = E which is why you get this zE, VE, Psi okay.

So, this is the configuration interaction wave function that we have now reduced and we will use this in our next class when I will discuss the resonance phase shift, okay. Because I mentioned that what happens as a result of the configuration interaction that the electron which has the possibility of escaping into the continuum, because one of the two configurations belongs to the continuum.

It has a possibility of spending some time in the doubly excited bound state. So, this is the bound to bound and bound to continuum configuration interaction. And because it spends some time over here, that time delay manifests as an additional phase shift that is the resident phase shift which I had anticipated a little bit toward the beginning of this class. But we will see it more explicitly in the next class. Any question?