Select/Special Topics in Atomic Physics
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Lecture - 33
Atomic Photoionization Cross-Sections, Angular Distribution of Photoelectrons

Greetings, so with today's class and the next one we will be concluding the unit 7, basically on Photoionization Cross-Section. And we will also get expression for the Angular Distribution of Photoelectrons.

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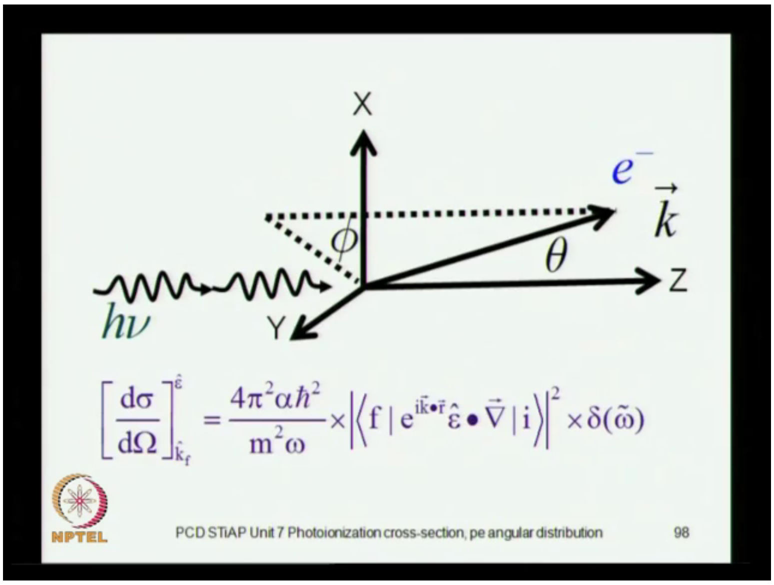

$$\left[\frac{d\sigma}{d\Omega}\right]^{\hat{\varepsilon}}_{\hat{k}_f} = \frac{4\pi^2\alpha\hbar^2}{m^2\omega}\times\left|\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle\right|^2\times\delta(\tilde{\omega})$$

And we found that the differential cross-section, which is the cross-section per unit solid angle, for a given direction of incidents with respect to which you describe this geometry. And if you have the incident electromagnetic radiation having electric vector polarize along, the unit vector epsilon and you set it up along this X axis, for our consideration k f is the unit vector along the photoelectron momentum as it escapes the atom. Then you express it in terms of this matrix element modulus squared and essentially this is coming from the time dependent perturbation theory, and an application of Fermi's golden rule as we discussed in our previous class.

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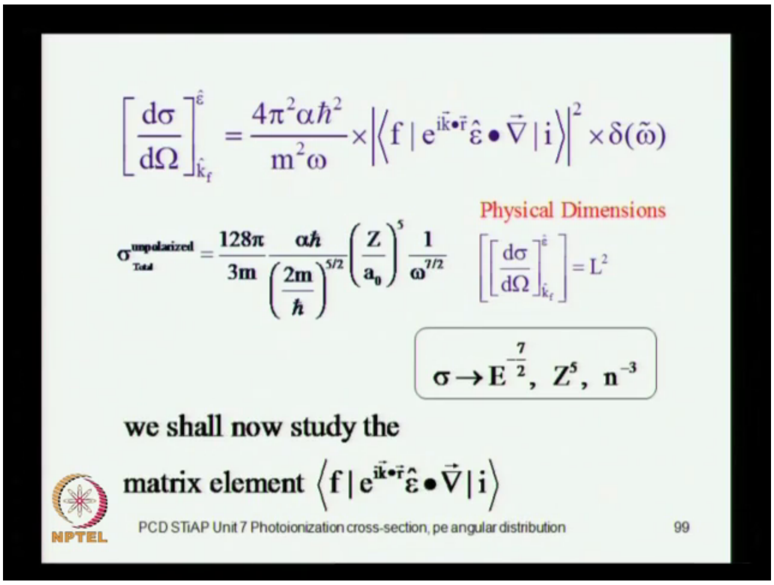

$$\left[\frac{d\sigma}{d\Omega}\right]^{\hat{\varepsilon}}_{\hat{k}_f} = \frac{4\pi^2\alpha\hbar^2}{m^2\omega}\times\left|\left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle\right|^2\times\delta(\tilde{\omega})$$

Physical Dimensions

$$\left[\left[\frac{d\sigma}{d\Omega}\right]^{\hat{\varepsilon}}_{\hat{k}_f}\right] = L^2$$

$$\sigma^{\text{unpolarized}}_{\text{Total}} = \frac{128\pi}{3m}\frac{\alpha\hbar}{\left(\frac{2m}{\hbar}\right)^{5/2}}\left(\frac{Z}{a_0}\right)^5\frac{1}{\omega^{7/2}}$$

$$\boxed{\sigma \rightarrow E^{-\frac{7}{2}},\ Z^5,\ n^{-3}}$$

we shall now study the

matrix element $\left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle$

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We also found that the differential cross-section has got the dimensions of l square, it is usually measured in units of mega bond, which is 10 to the minus 18 centimeter. And then if you integrate it over various directions of polarizations and all the polar angles, then we find that the cross-section certainly drops as the energy increases. So, the rate at which it drops with energy is e to the minus 7 by 2, so obviously, the photoionization cross-section is maximum at the photoionization threshold, that is when the photoelectron energy will be roughly 0.

So, right at the threshold you expect the photoionization cross-section to be maximum and then it would fall monotonically, according to this power law which is e to the minus 7 by 2. Now, of course, a number of approximations gone into this, the bond approximation and there are several other considerations, as a result of which there is a departure from this e to the minus 7 by 2. Also the fact that the cross-section is not always decreasing monotonically, it can go down and go up and there are these additional considerations that one really has to talk about. It also goes as the 5th power of Z and has n to the minus 3, where n is the principle quantum number. So, we will have a closer look and this matrix element, which goes into the photoionization cross-section.

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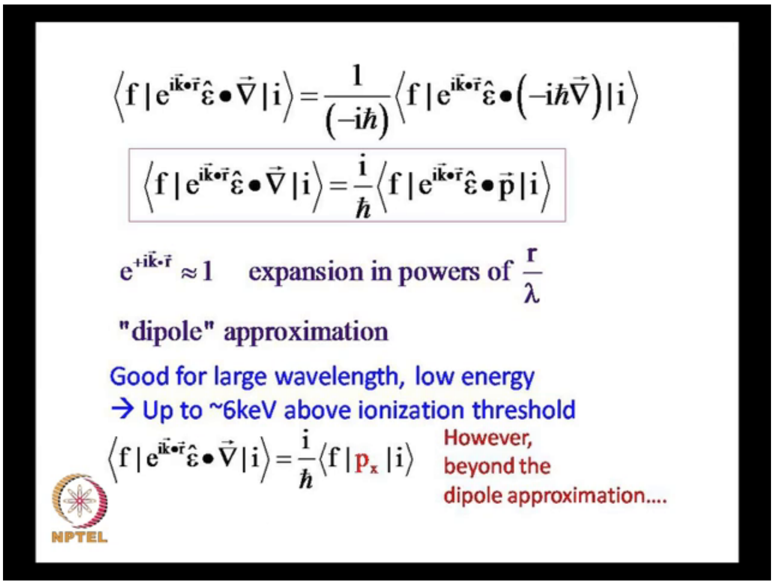

$$\langle f | e^{i\vec{k}\bullet\vec{r}} \hat{\varepsilon}\bullet\vec{\nabla}|i\rangle = \frac{1}{(-i\hbar)}\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\left(-i\hbar\vec{\nabla}\right)|i\rangle$$

$$\boxed{\langle f | e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle = \frac{i}{\hbar}\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{p}|i\rangle}$$

$e^{+i\vec{k}\cdot\vec{r}} \approx 1$ expansion in powers of $\frac{r}{\lambda}$

"dipole" approximation

Good for large wavelength, low energy

→ Up to ~6keV above ionization threshold

$$\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle = \frac{i}{\hbar}\langle f|p_x|i\rangle$$

However,
beyond the
dipole approximation....

And this matrix element is the matrix element of the gradient operator, so you write it in terms of momentum operator, so you get a factor of i over h cross outside and you have got the momentum operator inside the matrix element. And here you have got e to the i k dot r which you can expand as a power series in r over lambda, k dot r is k r cos theta, k is 2 phi over lambda. So, e to the i k dot r is actually a power series, if you take the leading term you have e to the i k dot r nearly equal to 1, which is called a dipole approximations.

And I will explain why it is called as a dipole approximations, so tentatively we will use the term dipole approximation, and very quickly we will recognize why it is called dipole approximation. And this is will work for low energies for large wave lengths, and this will work for low energies, which are not all that low, they can this works all the way up to about 5 or 6000 electron volts above the ionization threshold. Although there are exceptions and one has to make corrections for them.

And if you now set this e to the i k dot r equal to 1, then you have an equality in this approximation in which you no longer have to write, the e to the i k dot r explicitly, because it has main approximated to unity that is set equal to 1. So, the last expression that you see over here is appropriate within the dipole approximation, although one has to go beyond the dipole approximation, but that is the matter of detail.

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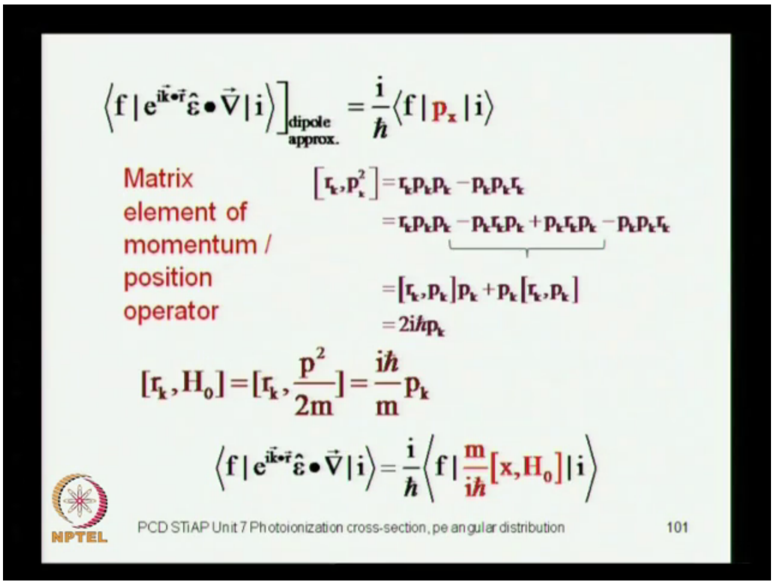

$$\left\langle f \middle| e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \middle| i \right\rangle\Big]_{\substack{\text{dipole}\\\text{approx.}}} = \frac{i}{\hbar}\langle f | p_x | i \rangle$$

Matrix element of momentum / position operator

$$[r_k, p_k^2] = r_k p_k p_k - p_k p_k r_k$$

$$= r_k p_k p_k \underbrace{- p_k r_k p_k + p_k r_k p_k}_{} - p_k p_k r_k$$

$$= [r_k, p_k] p_k + p_k [r_k, p_k]$$

$$= 2i\hbar p_k$$

$$[r_k, H_0] = [r_k, \frac{p^2}{2m}] = \frac{i\hbar}{m} p_k$$

$$\left\langle f \middle| e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \middle| i \right\rangle = \frac{i}{\hbar}\left\langle f \middle| \frac{m}{i\hbar}[x, H_0] \middle| i \right\rangle$$

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So, now, we have an expressions of the dipole approximation for this matrix element, which enters our expression for the differential cross-section. And although we find that this is the matrix element of the momentum operator, and momentum in proportional to velocity this formal the matrix element sometimes called as the momentum form or also as the velocity form. But, you can also write it in another form, which is known as the position form or the length form and the reason you can do it, is because a position operator and the momentum operator, these two operators have got well-known commutation relations.

So, you can convert from one to the other, and this is the commutation between r and P square, the reason I am considering the commutation between r and P square is because in the Hamiltonian you have got the potential energy operator, which depends on r. And you have got the kinetic energy operator, which depends on P square. So, if you consider the commutation between r and P square, you find using basic commutation relation that this is equal to twice i h cross P for each component k, k going from 1, 2, 3 for X, Y, Z.

And that tells us that the Hamiltonian would have a commutation relation with the position operator, which is given by the commutation of r with the kinetic energy operator it will of course, commute to the position with the potential energy operator, which depends on r alone. So, it would commute with the potential energy operator, and the commutation with P square would give us i h cross over m P k for the kth component, so this matrix element, which is the matrix element of P k, so this is the matrix element of the kth component of the momentum operator. So, this can be written in terms of the matrix element of the commutator of the position operator and the Hamiltonian, scaled by this m over i h cross which is coming from here.

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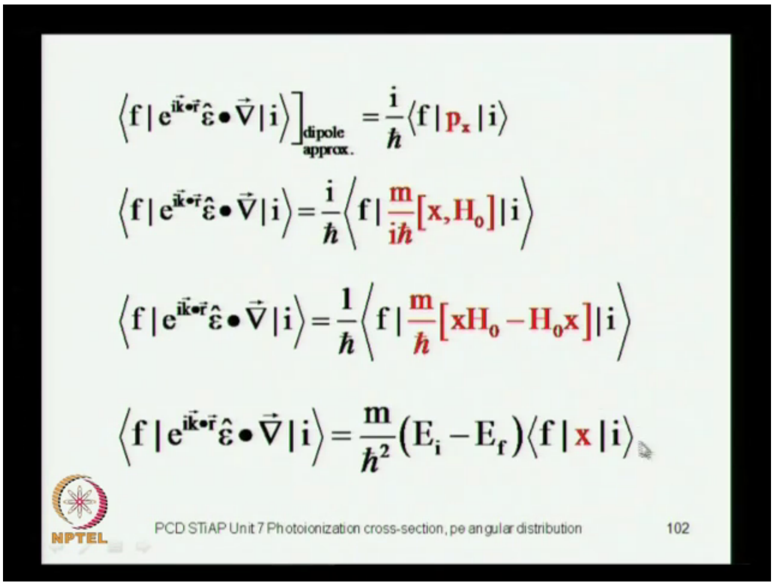

$$\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i\right\rangle\Big]_{\substack{\text{dipole}\\ \text{approx.}}} = \frac{i}{\hbar}\langle f \,|\, p_x \,|\, i\rangle$$

$$\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i\right\rangle = \frac{i}{\hbar}\left\langle f \,|\, \frac{m}{i\hbar}[x,H_0] \,|\, i\right\rangle$$

$$\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i\right\rangle = \frac{1}{\hbar}\left\langle f \,|\, \frac{m}{\hbar}[xH_0 - H_0x] \,|\, i\right\rangle$$

$$\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i\right\rangle = \frac{m}{\hbar^2}(E_i - E_f)\langle f \,|\, x \,|\, i\rangle$$

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So, you can write the matrix element, in terms of the matrix element of the momentum operator, or effectively in terms of commutator x with H 0. And now you take the x H 0 commutator explicitly, which is x as 0 minus H 0 x, so you will get two terms in the right hand side, but then i and f are both Eigen states of the unperturbed Hamiltonian H 0. So, when H 0 operates on f, you will get E f times f, and when H 0 operates on i, and it would operate on either sides it is imation operator.

So, you will get E i times the state vector i and using this you find that this matrix element is equal to that this m over h cross square, and you get E i minus E f and you have this ((Refer Time: 08:24)) matrix element. So, the matrix element of the momentum operator this is the quantity which we want to evaluate, but equivalently we can also evaluate this matrix element, which is the matrix element of the position operator rather than the momentum operator.

The differences that when you have the momentum operator you will have to take the derivative of the function on which it is operating, and then carry out then integration, whereas for the position operator you will only multiplied out, because both of this are space integrals. But, when getting the space integral in one case, you will have to take the derivative of the function on which it is operating, so which is what you will have to do in the momentum operator.

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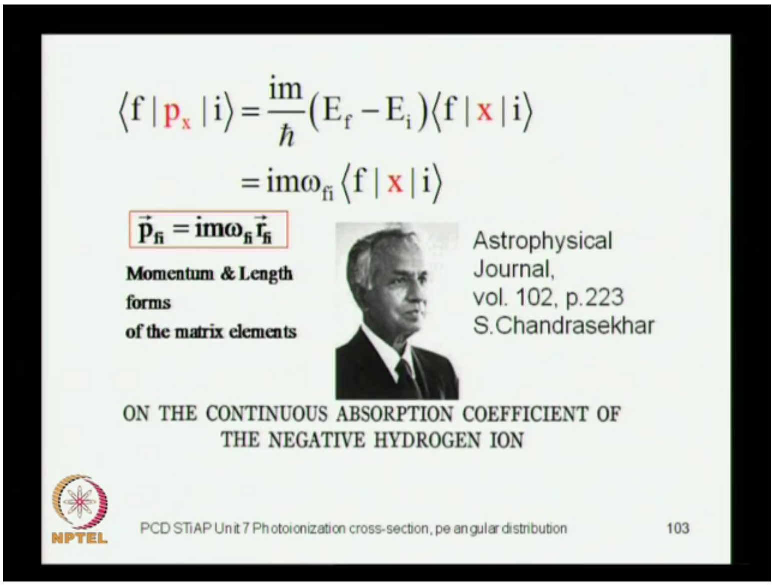

$$\langle f|p_x|i\rangle = \frac{im}{\hbar}(E_f - E_i)\langle f|x|i\rangle$$

$$= im\omega_{fi}\langle f|x|i\rangle$$

$$\boxed{\vec{p}_{fi} = im\omega_{fi}\vec{r}_{fi}}$$

Momentum & Length
forms
of the matrix elements

Astrophysical
Journal,
vol. 102, p.223
S.Chandrasekhar

ON THE CONTINUOUS ABSORPTION COEFFICIENT OF
THE NEGATIVE HYDROGEN ION

And in either case you must get the same result, because there is the complete equivalence between the matrix element of the momentum operator, with the matrix element of the position operator. All you have to do is to multiply by this i m times the frequency of transition, this is the circular frequency, because you get the energy over h cross. Now, these two forms of the matrix elements are called as the momentum form in the length form of the matrix element.

And it is a matter of rate pride with which I like to report this particular thing, because the different form of the matrix element, the length form the momentum form and in fact, there is a third form also, which is known as the acceleration form. And this analysis was done by Chandrasekhar, and this is reported in the astrophysical journal, volume 102. And this is a very beautiful paper by S. Chandrasekhar he is of course known, very well known for a lot of excellent work in astrophysics. But, this is also at this goes back to Chandrasekhar and his contribution spectroscopy.

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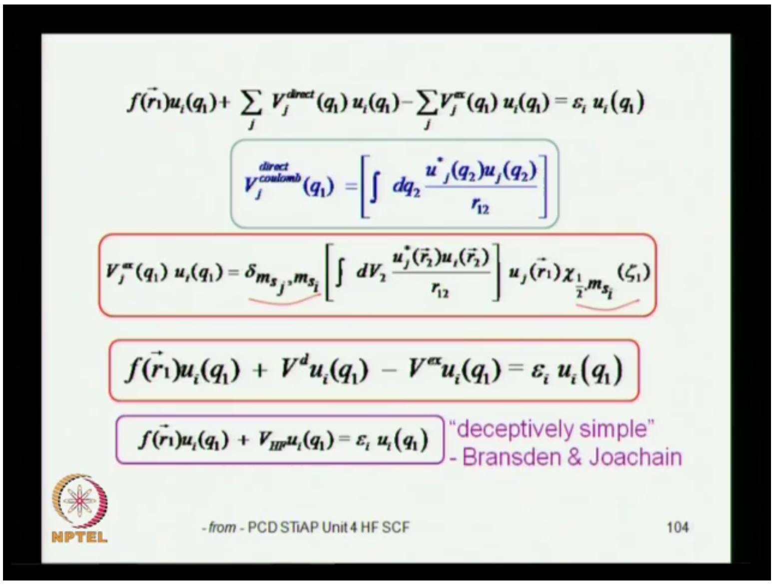

$$f(\vec{r}_1)u_i(q_1) + \sum_j V_j^{direct}(q_1)\, u_i(q_1) - \sum_j V_j^{ex}(q_1)\, u_i(q_1) = \varepsilon_i\, u_i(q_1)$$

$$\boxed{V_j^{\substack{direct \\ coulomb}}(q_1) = \left[\int dq_2 \frac{u^*_j(q_2)u_j(q_2)}{r_{12}}\right]}$$

$$\boxed{V_j^{ex}(q_1)\, u_i(q_1) = \delta_{m_{s_j}, m_{s_i}} \left[\int dV_2 \frac{u_j^*(\vec{r}_2)u_i(\vec{r}_2)}{r_{12}}\right] u_j(\vec{r}_1)\chi_{\frac{1}{2}, m_{s_i}}(\zeta_1)}$$

$$\boxed{f(\vec{r}_1)u_i(q_1) + V^d u_i(q_1) - V^{ex} u_i(q_1) = \varepsilon_i\, u_i(q_1)}$$

$$\boxed{f(\vec{r}_1)u_i(q_1) + V_{HF} u_i(q_1) = \varepsilon_i\, u_i(q_1)}$$

"deceptively simple"
- Bransden & Joachain

- *from* - PCD STiAP Unit 4 HF SCF

So, you will nevertheless need to recall a discussion from unit 4 on Hartree-Fock, because whereas in the for the hydrogen atom, the length form in the momentum form will give you the exact identity, it does not matter which form you are using. For a real atom when you extend this analysis for many electron systems, and you carry forward the formulation from single electron atom to many electron atoms, and use the same kind of formulation. You have to take account of the fact that, in a real atom there are large number of electrons, and column interaction between them is what needs to be handled correctly.

And when you take into the account the column interaction and also the anti symmetrical the wave function, your lead to the Hearty-Fork equation, and this is the Hearty-Fork equation that we discussed in the unit 4. And let me remind you that there are two potentials over here, one is the direct potential in which q gets integrated out. So, this the direct potential is then it depends only on the coordinate q 1, but the exchange potential is a global potential, because here if you integrate 2, you have to keep track of the fact that this is u i and use this u j.

So, you really need to solve this equation for all the electrons, so this is the potential which is the global potential, it is not a local potential. And since this is not a local potential you have the Hearty-Fork potential which is some of these two terms, the direct potential and exchange potential. But, the exchange potential makes the Hearty-Fork equation looks very similar to an Eigen value equation, but as we discussed in unit 4 it is a deceptively simple form, it is not an Eigen value equation. And the reason it is not an Eigen value equation, is because of the nonlocal potential. Now, what is the consequences of the non local potential in the present context.

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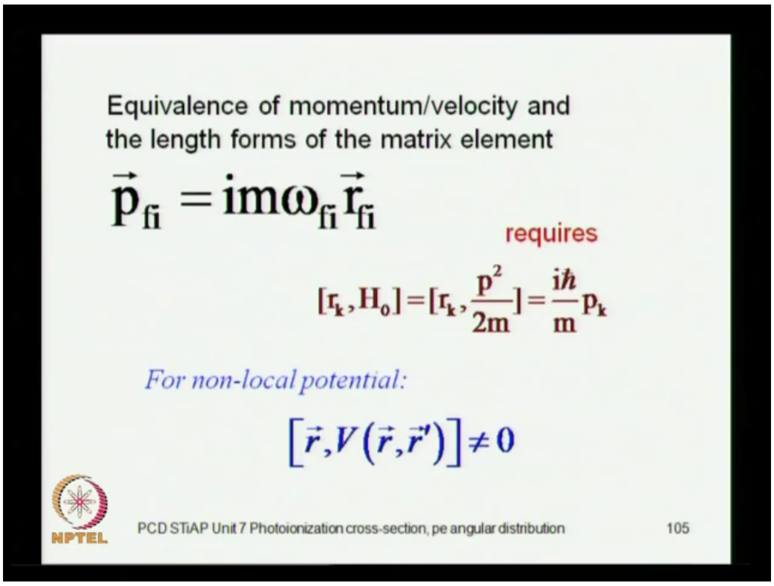

Equivalence of momentum/velocity and the length forms of the matrix element

$$\vec{p}_{fi} = im\omega_{fi}\vec{r}_{fi}$$

requires

$$[r_k, H_0] = [r_k, \frac{p^2}{2m}] = \frac{i\hbar}{m} p_k$$

For non-local potential:

$$[\vec{r}, V(\vec{r}, \vec{r}')] \neq 0$$

The non local potential will cause a breakdown of the equivalence between the momentum form, and the length form of matrix element. Because, the equivalence between these two forms that you just have a multiplier i m omega, and this is the only thing which connects. If you just multiply the length form by this factor i m omega, you should get the momentum form this thing assumes that, the position operator commutes with the potential energy operator.

And the potential energy operator, if it is nonlocal it does not depend just on the argument r, but it also depends on r times. So, the position operator will not then commute, with the nonlocal potential and you will not then get an equivalence between the length form and the momentum form of the matrix element. So, when you do the calculation, you will get one result if you use the length form, you will get another result if you use the velocity form, so this are certain details.

The other thing that I mention is that, if you just look at this e to the minus 7 by 2 law, you get the feeling as if you know the cross-section, the photoionization cross-section will have a certain maximum value of the threshold. And from there on it will only fall monotonically, according to e to the minus 7 by 2, so there may be you will expect that, there will be some corrections it may not be strictly e to the minus 7 by 2, but at least qualitatively it will always decrease with the energy.

Now, even qualitatively this does not happen necessarily in all cases, even in the single particle approximation, and the reason it does not happen is because the cross-section it falls goes through a local minimum raises again and then falls.

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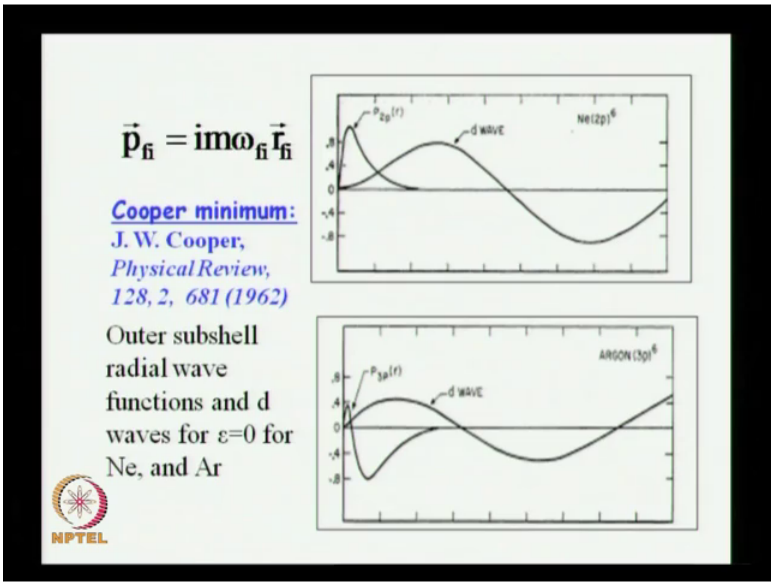

$$\vec{p}_{fi} = im\omega_{fi}\vec{r}_{fi}$$

Cooper minimum:
J. W. Cooper,
Physical Review,
128, 2, 681 (1962)

Outer subshell radial wave functions and d waves for $\varepsilon=0$ for Ne, and Ar

So, this local minimum is what is called as Cooper minimum, and the reason it happens is because of a very simple reason which I will mention in brief that, if you look at photoionization of neon atom. Now, neon as got tan electrons, so you have 1 is to 2 is to 2 P 6, so 2 P is the outer shell of neon, and you consider the photo ionization of the 2 P electrons from the neon atom, which are being knocked out into the continuum by absorption of the electromagnetic energy.

So, now, let us have a look at the 2 P wave function, the 2 P wave function, if you look at the matrix element of the position operator all you have done is to sandwich the position operator between the initial state, which is 2 P and the final state which is the continuum what it is continuum P to d transition. So, let us consider dipole transitions from 2 P to d that can also be a transition from 2 P to s, but the dominant contribution comes from 2 P to d, so we will consider the 2 P to d transition.

And this is the d continuum wave and to get the none zero matrix element over here, this is the matrix element which is contributing to the photoionization cross-section. This matrix element is coming from the overlap of the 2 P wave function with the continuum d. Now, if you consider instead of neon just the next atom in the periodic table just below neon, which is argon which is a very similar atom, it is chemical property is very similar both are inert gas atoms. But, then there is a significant difference in the nature of the wave function of the outer 2 P wave function for neon, and the outer 3 P wave function for argon.

What is the difference 3 P as got one node, the number of nodes are radial function has as we studied earlier is n minus l minus 1, so for n equal to 2, 2 P is node less, but n equal to 3, 3 P has got one node. So, here you see that 3 P goes through a node, and now if you look at the overlap between the continuum d state, and the initial state, for neon it is positive whereas, for argon this overlap is negative. And then as the energy increases the continuum d state will go more and more into the core, and then all there will be more oscillations of the continuum d state in a region.

And at a certain point, the positive contributions of the overlap and the negative contributions of the overlap will actually cancel, and from this negative later on you can also get a positive sign of the matrix element. So, the sign of the matrix element of position operator will actually change as a function of energies in the case of argon, but that is not going to happen in the case of neon. So, what does it do to the matrix element, matrix element actually undergoes a change in sign, and when it undergoes a change in sign it will go through a 0; and when it goes through a 0, the matrix element is 0 there will be no photoionization.

So, the cross-section will actually go to a 0, but then as energy increases again the oscillator strength build up, now this is what is called as a Cooper minimum it is not always l this strength 0, but that is again a matter of detail. Because, you can have a transition into various channels not just between 2 P to d, but you also has transition P to s. Then again 2 P is not a single state, you have 2 P 3 half and 2 P 1 half and then from 2 P 3 half you do not have transitions to a single d state, you have transitions to two different d states.

So, you will have a transition from 2 P 3 half to d 5 half 2 P 3 half to d 3 half and this are the channels in which photoionization will take place. And the cooper minimum in each channel will not be necessarily at the same energy, so the cross-section itself will not be necessarily 0, but it will certainly be a minimum and this is what is called as cooper minimum.

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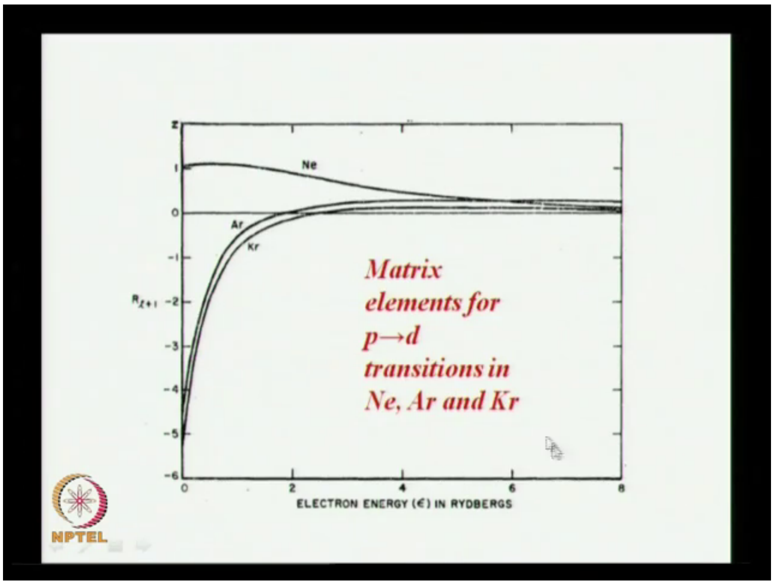

Matrix elements for $p \rightarrow d$ transitions in Ne, Ar and Kr

So, this is a picture of matrix element for neon it is positive and then eventually it goes to 0, as electron energy photo electron energy increases, in the case of argon and krypton also, certainly the matrix element eventually goes to 0 at high energies. But, then it starts out as negative goes through a 0, cuts the 0 line over here turns positive and then goes to 0, so argon and krypton will have a cooper minimum, but not neon.

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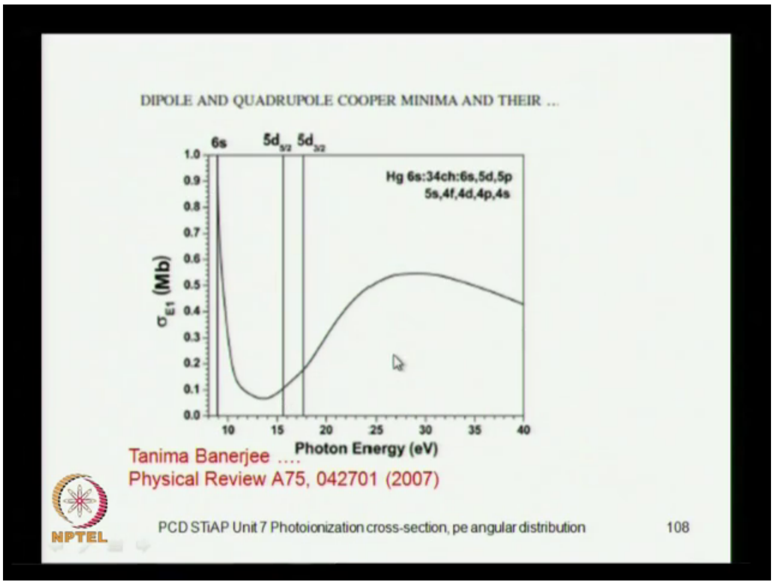
DIPOLE AND QUADRUPOLE COOPER MINIMA AND THEIR ...

Tanima Banerjee ....
Physical Review A75, 042701 (2007)

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So, here is an example of copper minimum, in which you see that the photoionization cross-section, this is a calculation of the mercury 6 s, you see that the photoionization cross-section has dropped, it goes through a minimum and then it raises gain. So, it is not always a monotonically decreasing function of energy.

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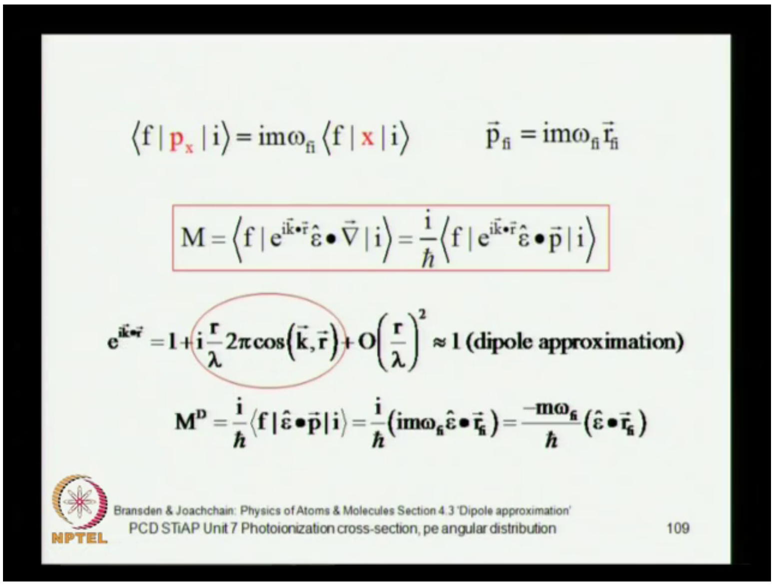

$$\langle f | p_x | i \rangle = im\omega_{fi} \langle f | x | i \rangle \qquad \vec{p}_{fi} = im\omega_{fi}\vec{r}_{fi}$$

$$\boxed{M = \left\langle f | e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla} | i \right\rangle = \frac{i}{\hbar}\left\langle f | e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{p} | i \right\rangle}$$

$$e^{i\vec{k}\bullet\vec{r}} = 1 + i\frac{r}{\lambda}2\pi\cos\left(\vec{k},\vec{r}\right) + O\left(\frac{r}{\lambda}\right)^2 \approx 1 \text{ (dipole approximation)}$$

$$M^D = \frac{i}{\hbar}\langle f | \hat{\varepsilon}\bullet\vec{p} | i \rangle = \frac{i}{\hbar}\left(im\omega_{fi}\hat{\varepsilon}\bullet\vec{r}_{fi}\right) = \frac{-m\omega_{fi}}{\hbar}\left(\hat{\varepsilon}\bullet\vec{r}_{fi}\right)$$

Bransden & Joachchain: Physics of Atoms & Molecules Section 4.3 'Dipole approximation'

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So, this is what we have found so far, and it is coming because we are looking at the matrix element in the dipole approximation, in which we consider the length and velocity or length and momentum forms of the matrix element. So, this is the expression for the matrix element and I written superscript d for the dipole approximation, which is what we have got. But, if you take the next term over here, so e to the i k dot r, if you take the next term you will then get corrections to the dipole approximations. And then you will get higher multi poles and from dipole you will go to quarter poles and so on. So, you have Cooper minimum also in the quarter pole approximations, so this is the quarter pole cross section of the same atom which is mercury.

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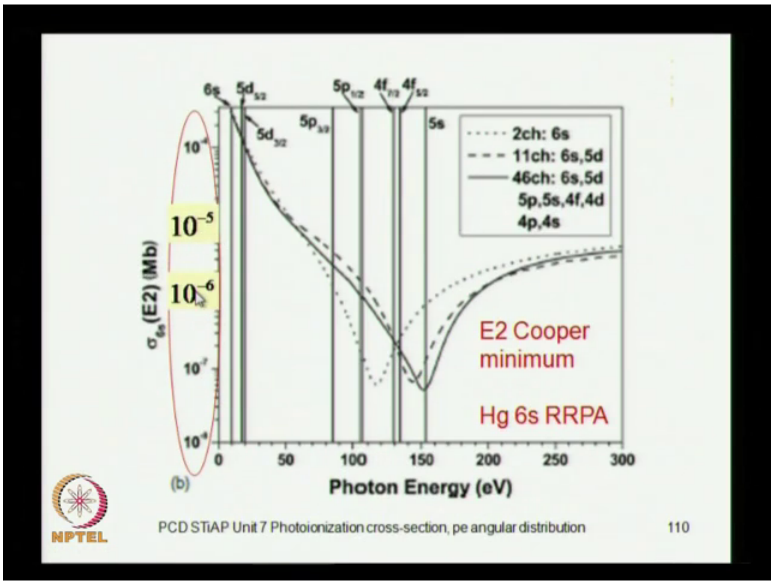

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And you have got similar phenomenology governing the dynamics of photoionization in higher multi pole approximation as well, here the cross-sections are extremely small, so this is like 10 to the minus 5, this is on logarithmic scale. So, this is 10 to the minus 5 mega bonds, this is 10 to the minus 6 and these are extremely week cross-section. So, usually they cannot be detected, but there effects can be seen through other measurements like angular distribution of the photoelectrons, so it is nevertheless an important property to investigate. So, now let me show you the result for mercury 4 f and in this case you have a local minimum over here.

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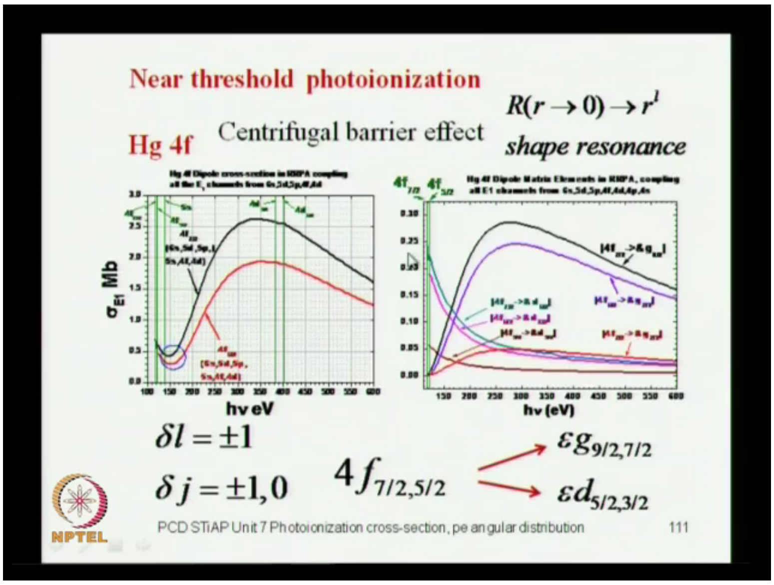
Near threshold photoionization

Hg 4f Centrifugal barrier effect

$R(r \to 0) \to r^l$

shape resonance

$\delta l = \pm 1$

$\delta j = \pm 1, 0$

$$4f_{7/2,5/2} \begin{matrix} \nearrow \varepsilon g_{9/2,7/2} \\ \searrow \varepsilon d_{5/2,3/2} \end{matrix}$$

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And it would be tempting to suspect that this is a Cooper minimum, but then it is not, the reason it is not a Cooper minimum is because your initial state is 4 f and from 4 f you can have dipole in the dipole approximations. Transitions where delta l is either plus or minus 1 and delta j is plus or minus 1 or z, so these are the dipole selection rule that we get from Wigner's. And using these selection rules, that the initial state which is 4 f spin orbit double it, so you got 4 f 7 half and 4 f 5 half, there are two levels.

And then you can have transitions with under these selection rules either to g states or to d states, but then again to continuum g states, which will also be spin orbit split. So, now, you consider all channels from the initial spin orbit double it to all possible final states, which also realistically split and consider all transitions, which are possible within the dipole approximations. So, it is not just a single channel any more, but you have a number of channels, so you have three channels which go from f to g, and another three from f to d.

Now, what happens is that the centrifugal barrier the g waves is much larger, you know what centrifugal barrier is, in the hydrogen atom radial equation we had this term l into l plus one by r square. So, that is the one which is refer to as the centrifugal barrier potential it is the shudder potential, it comes because of the reduction of three dimensional problem to this one dimensional radial equation. But, then it will have real effects and this means that as a result of this centrifugal barrier, which is repulsive potential.

The continuum final states, which will have larger l that will not be able to penetrate into the core and I had discussed this also in the context of scattering, that the continuum states, if they have larger of angle of momentum, they will not be able to penetrate into the core. But, then the penetration will increase if the photoelectron energy or the photonenergy will increase. So, the cross-section will be minimum at the threshold, but as you increase the energy at which photoionization is taking place, then the cross-section in those channels will actually go up.

So, in the case of mercury 4 f photo ionization, you have the 4 f to g photoionization it increases from the threshold, whereas the photoionization from 4 f to d waves that decreases monotonically. And the sum of the cross-section is what you see from integrating the cross-section and all of this x channels, so it starts dropping down from the cross-section goes to a minimum; and then raises again, because oscillator strain picks up in the other channel.

So, this is not the Cooper minimum, but then it has a similar behavior, so notice over here that the photoionization cross-section is not monotonically decreasing, it monotonically decreases only beyond this, but there is a delayed maximum. This is because of the centrifugal barrier effect, and there is a local minimum which is coming because there is competition between oscillator strengthen f to d channel and f to g channels. So, these are some very interesting details, which one as to be concerned with, and we cannot apply these are all without additional considerations. So, let me now remind you the definition of the oscillator strength that we had in the classical model.

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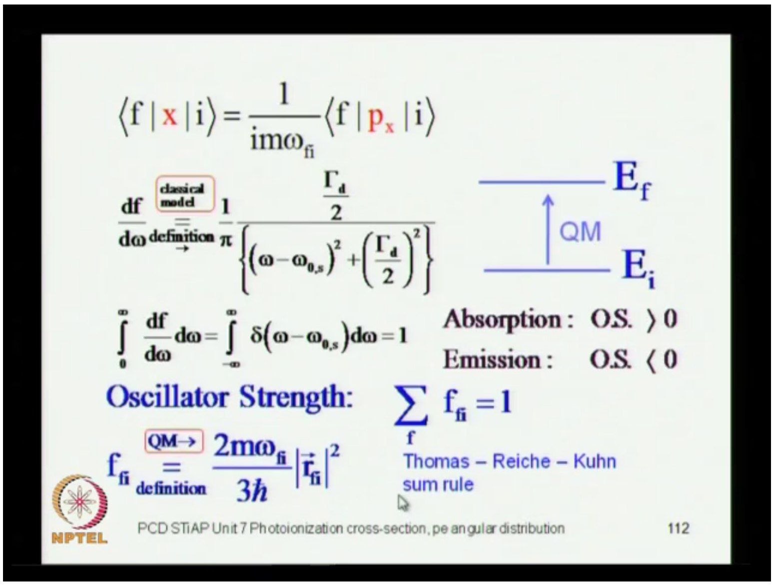

$$\langle f|x|i\rangle = \frac{1}{im\omega_{fi}}\langle f|p_x|i\rangle$$

$$\frac{df}{d\omega} \underset{\text{definition}\rightarrow}{\overset{\boxed{\text{classical model}}}{=}} \frac{1}{\pi}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega-\omega_{0,s})^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

$$\int_0^\infty \frac{df}{d\omega}d\omega = \int_{-\infty}^{\infty}\delta(\omega-\omega_{0,s})d\omega = 1$$

Absorption : O.S. $\rangle 0$

Emission : O.S. $\langle 0$

Oscillator Strength:

$$f_{fi} \underset{\text{definition}}{\overset{\boxed{\text{QM}\rightarrow}}{=}} \frac{2m\omega_{fi}}{3\hbar}\left|\vec{r}_{fi}\right|^2$$

$$\sum_f f_{fi} = 1$$

Thomas – Reiche – Kuhn sum rule

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And now we are using the quantum model, in which we are considering explicit transitions from quantum state E i to a quantum state E f. So, in this case the quantum mechanical definition of the oscillator strength is now revised, and it is given in terms of this dipole matrix element. So, this is the definition of the quanta mechanical oscillator strength, and in is much as this classical oscillator strength definition, give you an integral of the oscillator strength over all the frequencies to be equal to 1. In the quantum mechanical definition, you have this omega which is the difference between E f and E i.

So, this can be either positive or negative depending on whether you talking about absorption or emission. So, the oscillator strength can be either greater than 0 or less than 0, which allows for whether you talking about absorption or emission. And similar to a sum rule over here, this is the sum rule that all of the oscillator strength when you integrate over all frequencies adds up to 1. So, the quantum mechanical oscillator strength also adds up to 1, this is known as the Thomas-Ritchie-Kuhn sum rule and we will derive this rule now.

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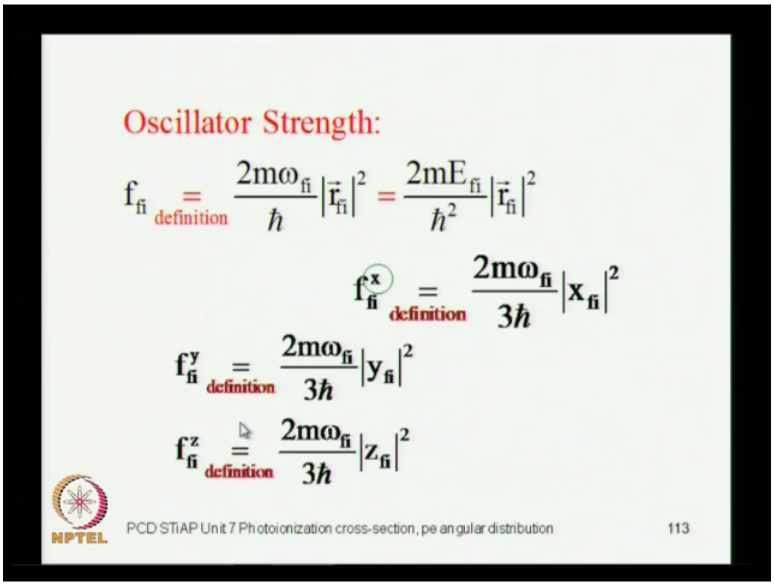

Oscillator Strength:

$$f_{fi} \underset{\text{definition}}{=} \frac{2m\omega_{fi}}{\hbar}|\vec{r}_{fi}|^2 = \frac{2mE_{fi}}{\hbar^2}|\vec{r}_{fi}|^2$$

$$f_{fi}^{x} \underset{\text{definition}}{=} \frac{2m\omega_{fi}}{3\hbar}|x_{fi}|^2$$

$$f_{fi}^{y} \underset{\text{definition}}{=} \frac{2m\omega_{fi}}{3\hbar}|y_{fi}|^2$$

$$f_{fi}^{z} \underset{\text{definition}}{=} \frac{2m\omega_{fi}}{3\hbar}|z_{fi}|^2$$

So, this is by definition of oscillator strength and this is for position vector, let me write the corresponding expression for a single component, one of the three components of the position vector like x. So, this is what this definition Boyze on to for the X component, and similarly there are corresponding expressions for the Y component and the Z component.

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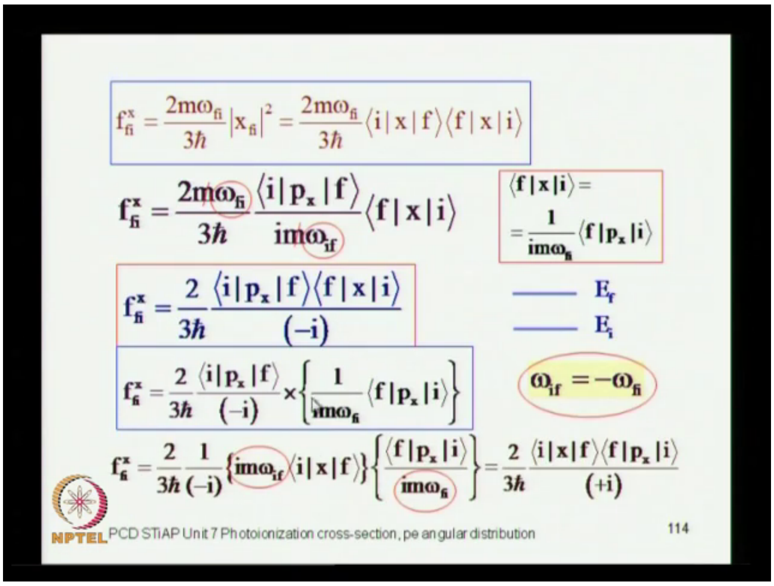

$$f_{fi}^{x} = \frac{2m\omega_{fi}}{3\hbar}|x_{fi}|^2 = \frac{2m\omega_{fi}}{3\hbar}\langle i|x|f\rangle\langle f|x|i\rangle$$

$$f_{fi}^{x} = \frac{2m\omega_{fi}}{3\hbar}\frac{\langle i|p_x|f\rangle}{im\omega_{if}}\langle f|x|i\rangle$$

$$\langle f|x|i\rangle = \frac{1}{im\omega_{fi}}\langle f|p_x|i\rangle$$

$$f_{fi}^{x} = \frac{2}{3\hbar}\frac{\langle i|p_x|f\rangle\langle f|x|i\rangle}{(-i)}$$

$$f_{fi}^{x} = \frac{2}{3\hbar}\frac{\langle i|p_x|f\rangle}{(-i)}\times\left\{\frac{1}{im\omega_{fi}}\langle f|p_x|i\rangle\right\}$$

$$\omega_{if} = -\omega_{fi}$$

$$f_{fi}^{x} = \frac{2}{3\hbar}\frac{1}{(-i)}\{im\omega_{if}\langle i|x|f\rangle\}\left\{\frac{\langle f|p_x|i\rangle}{im\omega_{fi}}\right\} = \frac{2}{3\hbar}\frac{\langle i|x|f\rangle\langle f|p_x|i\rangle}{(+i)}$$

Now, let me take the expression for the X component, this is the modulus squared for this matrix element, so I write this modulus square in this form, which is i X f times it is complex conjugate. Now, we already have equivalence between position form and the moment form, so using this form we can write these elements in momentum form. So, I have written the first of these elements in terms of the momentum operator, so one is in terms of the momentum operator, the other is still if the terms of the position operator.

And this is the process that we are talking about that you have got two quantum state c i and e f and u talk about the energy difference, but of course the omega i f is equal to minus omega f i, because one energy is above the other. So, the two frequency which are coming here omega f i and omega i f, so this have got opposite sign. So, they do the numbers cancel each other, but they leave a minus sign that you must track of, and the m of course, in the denominator cancel this m and this is what you get for the oscillator strength.

So, now you have this expression, the matrix element for this can also be written in terms of the momentum operator. And if you take into account this same relationship and the equivalence between position, and position form and the momentum form of the matrix element, you have this again omega i f and omega f i over here. So, you will get again a minus 1 psi and then the common factor like m cancel out and then you are left with a rather simple expression.

So, this is got a very similar form, but it is important to keep track of these details, because you will see that it leads as to a very important result. So, this is the form that I will like you to keep track off, I am going to use it on the next line and then also I am going to use this form which is completely equivalent to this.

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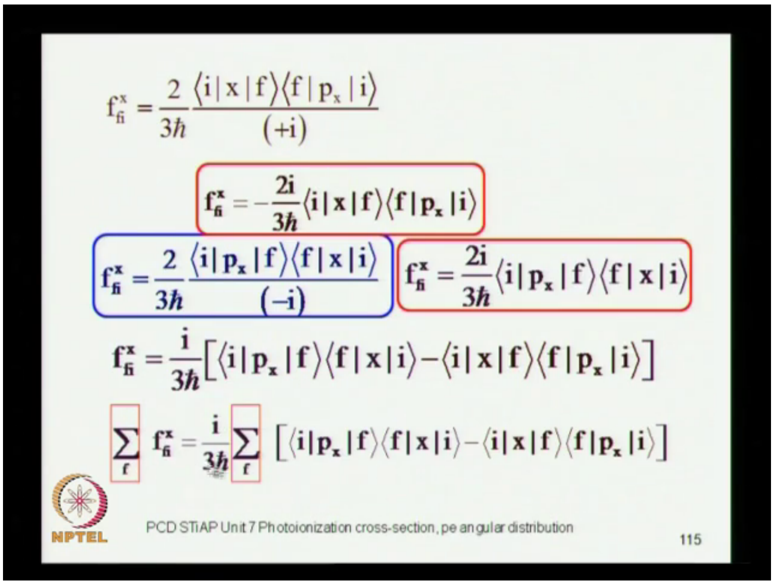

$$f_{fi}^x = \frac{2}{3\hbar}\frac{\langle i|x|f\rangle\langle f|p_x|i\rangle}{(+i)}$$

$$\boxed{f_{fi}^x = -\frac{2i}{3\hbar}\langle i|x|f\rangle\langle f|p_x|i\rangle}$$

$$\boxed{f_{fi}^x = \frac{2}{3\hbar}\frac{\langle i|p_x|f\rangle\langle f|x|i\rangle}{(-i)}} \quad \boxed{f_{fi}^x = \frac{2i}{3\hbar}\langle i|p_x|f\rangle\langle f|x|i\rangle}$$

$$f_{fi}^x = \frac{i}{3\hbar}\left[\langle i|p_x|f\rangle\langle f|x|i\rangle - \langle i|x|f\rangle\langle f|p_x|i\rangle\right]$$

$$\boxed{\sum_f} f_{fi}^x = \frac{i}{3\hbar}\boxed{\sum_f}\left[\langle i|p_x|f\rangle\langle f|x|i\rangle - \langle i|x|f\rangle\langle f|p_x|i\rangle\right]$$

So, this is the last from that we got, and all I have done is to write this i in the numerator, so now it because minus 2 i over 3 h cross, now this is the form which I had on the previous slide, and both of these forms are completely equivalent. So, I can write the oscillator strength, as half of what is over here plus half of what is over here, because both are exactly the same. So, before I do that let me take bring this minus i also to the top and then I change the sign, so this is 2 i over 3 h cross. And now I can write the oscillator strength as half of this expression in this red loop, and half of this expression in the red loop.

So, if I add these two pieces add half of each of this pieces, I should get the oscillator strength, now when you take half the 2 3rd will become 1 3rd in both, so you get this 1 3rd and this is the some of these two terms. And this allows us to this is the matrix element corresponding to the transition of from i to f, but now I can sum over all the final states. So, carry out a summation over all the final states and this is a summation of over all the final states of the left-hand side, also on the right-hand side.

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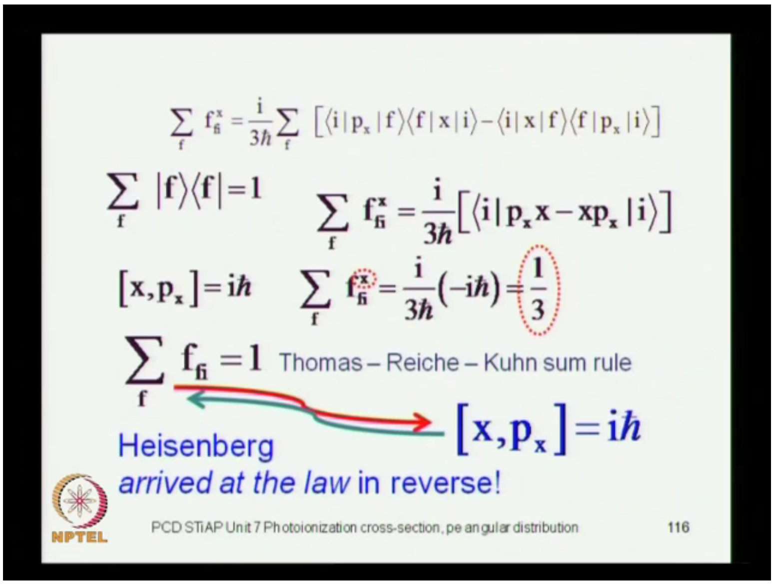

$$\sum_f f_{fi}^x = \frac{i}{3\hbar}\sum_f \left[\langle i|p_x|f\rangle\langle f|x|i\rangle - \langle i|x|f\rangle\langle f|p_x|i\rangle\right]$$

$$\sum_f |f\rangle\langle f| = 1 \qquad \sum_f f_{fi}^x = \frac{i}{3\hbar}\left[\langle i|p_x x - x p_x|i\rangle\right]$$

$$[x, p_x] = i\hbar \qquad \sum_f f_{fi}^x = \frac{i}{3\hbar}(-i\hbar) = \frac{1}{3}$$

$$\sum_f f_{fi} = 1$$ Thomas – Reiche – Kuhn sum rule

$$[x, p_x] = i\hbar$$

Heisenberg
arrived at the law in reverse!

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And what you have on the right side, when you can carry out a summation over all the final states you get the unit operator over here, that is the resolution of unity. So, the resolution of the unity, when you consider all the final states allows you to recognize that here you taking the difference between these two terms. And the operator whose matrix element is under consideration is nothing but, the commutator between position and momentum, it is P x X minus X P x and that is something that you know from the Heisenberg principle of uncertainty, which is i h cross.

So, plug it in and when you put this term over here, you find that all of these oscillator strains when you sum over all the final states gives you 1 3rd, but that is only for the X component, you get a similar result for the Y component and similar for the Z component. So, when you add the three pieces for the X, Y and Z, you find that there is a some rule very similar what you had seen in the classical case and this is the Thomas-Ritchie-Kuhn sum rule as it is called. Now, it is rather exciting to observe that we arrived at the Thomas-Ritchie-Kuhn rule, using the uncertain defensible.

So, if you know the uncertain defensible, suppose you can get the Thomas-Ritchie-Kuhn rule on the other hand, if you have reasons to believe that the sum rule should be correct, but did not know the uncertain defensible. And ask a question, what is it that will make the sum rule valid, the answer would be that position and momentum operate is do not commute, and they are commutator is actually equal to minus h cross. This is in fact, exactly how Heisenberg got it, Heisenberg was working with a large number of problems in involving, and so on.

He was working with spectroscopic some rules, and this was one of the inputs which lead him into discovering the non-commutation, between the position and momentum operator, so you will find a reference to this formal invoiced book, so this is really very nice.

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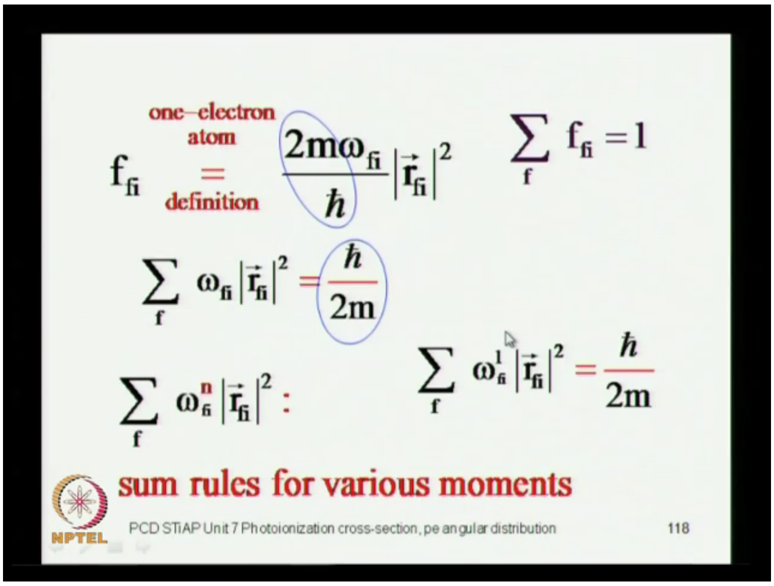

$$f_{fi} \overset{\text{one-electron atom}}{\underset{\text{definition}}{=}} \frac{2m\omega_{fi}}{\hbar}\left|\vec{r}_{fi}\right|^2 \qquad \sum_f f_{fi} = 1$$

$$\sum_f \omega_{fi}\left|\vec{r}_{fi}\right|^2 = \frac{\hbar}{2m}$$

$$\sum_f \omega_{fi}^{n}\left|\vec{r}_{fi}\right|^2 : \qquad \sum_f \omega_{fi}^{1}\left|\vec{r}_{fi}\right|^2 = \frac{\hbar}{2m}$$

sum rules for various moments

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And now let me go back to this definition of oscillator strength in quantum mechanics, this is for one electron atom, for N electron atoms, you can sum over j going from 1 through N for all the electrons. Because, they will be a similar oscillator strength for each electron, and when you sum over these terms for all the N electrons, then you find that this summation will be equal to N, not equal to 1. So, if N is equal to 1 you get the Thomas-Ritchie-Kuhn sum rule as we derived, but then for N electrons it will give you N, which is the number of electrons.

So, these are the sum rules and notice that, there is a 2 m over h cross over here, so I can rewrite this sum rule, which is this, which is the summation of all of these terms. But, if I write this sum rule without this 2 m over h cross factor, so sum over f omega times the modulus square, this will obviously be equal to h cross over 2 m. So, you can write this as a sum over f of omega to the power 1 of the modulus square, this same thing except that and making all of us conscious of the fact, that this is the first power of omega.

And you can construct such summations for other powers of omega as well, like omega square, omega cube, omega to the power N, and there are many several other some rule which I will not go into details for this course. But, there are large number of some rules, so we have got only the first one which is Thomas-Ritchie-Kuhn sum rule, but there are other sum rule for other moments. So, these are called as moments of the frequencies of omega to the power 1 is what we are considered, but there are higher powers also that can be considered.

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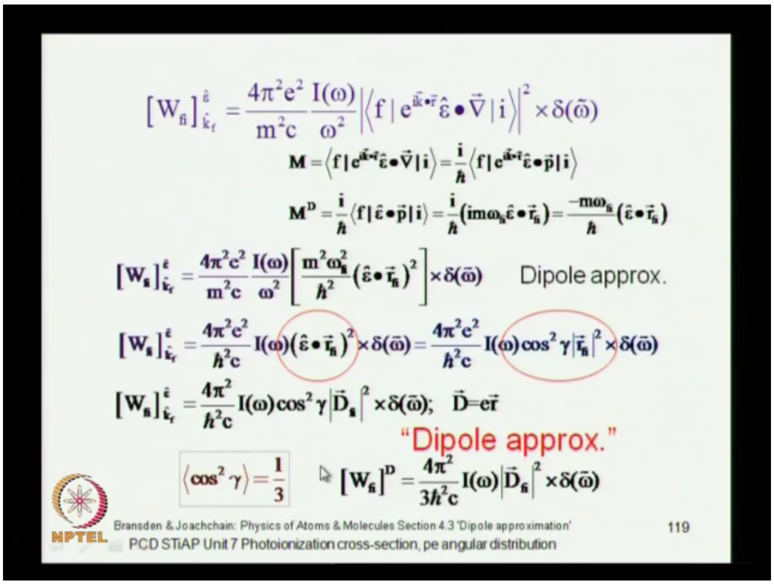

$$[W_{fi}]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{4\pi^2 e^2}{m^2 c}\frac{I(\omega)}{\omega^2}\left|\left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle\right|^2 \times\delta(\tilde{\omega})$$

$$M = \left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle = \frac{i}{\hbar}\left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{p}\,|\,i\right\rangle$$

$$M^D = \frac{i}{\hbar}\langle f\,|\,\hat{\varepsilon}\bullet\vec{p}\,|\,i\rangle = \frac{i}{\hbar}(im\omega_{fi}\hat{\varepsilon}\bullet\vec{r}_{fi}) = \frac{-m\omega_{fi}}{\hbar}(\hat{\varepsilon}\bullet\vec{r}_{fi})$$

$$[W_{fi}]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{4\pi^2 e^2}{m^2 c}\frac{I(\omega)}{\omega^2}\left[\frac{m^2\omega_{fi}^2}{\hbar^2}(\hat{\varepsilon}\bullet\vec{r}_{fi})^2\right]\times\delta(\tilde{\omega})$$ Dipole approx.

$$[W_{fi}]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{4\pi^2 e^2}{\hbar^2 c}I(\omega)(\hat{\varepsilon}\bullet\vec{r}_{fi})^2\times\delta(\tilde{\omega}) = \frac{4\pi^2 e^2}{\hbar^2 c}I(\omega)\cos^2\gamma\,|\vec{r}_{fi}|^2\times\delta(\tilde{\omega})$$

$$[W_{fi}]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{4\pi^2}{\hbar^2 c}I(\omega)\cos^2\gamma\,|\vec{D}_{fi}|^2\times\delta(\tilde{\omega});\quad \vec{D}=e\vec{r}$$

"Dipole approx."

$$\boxed{\langle\cos^2\gamma\rangle = \frac{1}{3}}\qquad [W_{fi}]^D = \frac{4\pi^2}{3\hbar^2 c}I(\omega)|\vec{D}_{fi}|^2\times\delta(\tilde{\omega})$$

Bransden & Joachchain: Physics of Atoms & Molecules Section 4.3 'Dipole approximation'

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So, this is what we have got that, this is the expression for the transition rate in the dipole approximation, we arrived at some simple expressions, this is the dipole approximation. And in which e to the i k dot r is set equal to 1 you have got epsilon dot r, so that is cosine term, which is cos square omega. And now you have got e square in the numerator and the square of the matrix element of a position operator, that is the dipole, do you see that, because you have got e square and d.

So, you can write this in terms of the square of the dipole operator and this is possible because you approximated that e to the i k dot r equal to unity, so whenever you set e to the i k dot r equal to unity, when you going to do it, you will do it for large wave lengths. When r over lambda, e to the i k dot r which is a power series r over lambda can be truncated at the leading term, which is equal to unity, so that is a low energy approximation, it is called a dipole approximation for the reason that is now obvious to you, so this is why it is called a dipole approximation. And you can certainly integrate this out over various angle, if you take the average of cos square gamma over all the different angles, then you get an expression. So, you get 1 over 3 for the dipole approximation for this transition rate.

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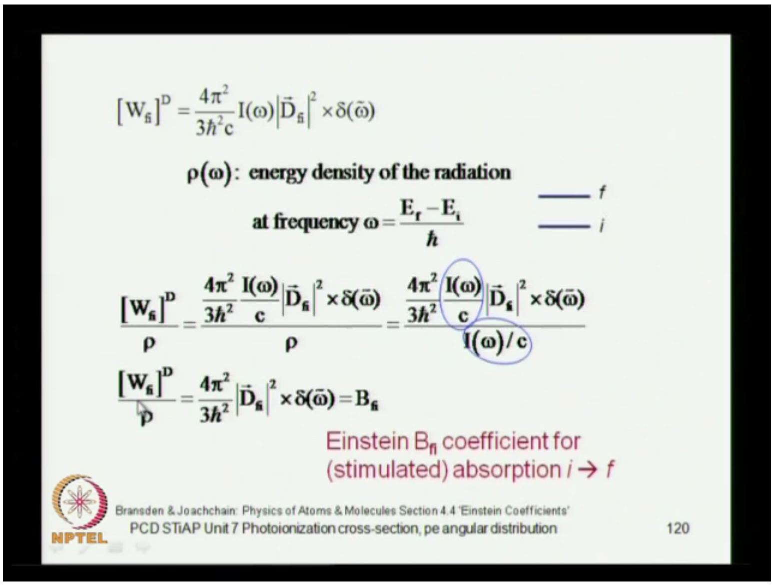

$$[W_{fi}]^D = \frac{4\pi^2}{3\hbar^2 c} I(\omega) \left|\vec{D}_{fi}\right|^2 \times \delta(\bar{\omega})$$

$\rho(\omega)$: **energy density of the radiation**

at frequency $\omega = \frac{E_f - E_i}{\hbar}$

$$\frac{[W_{fi}]^D}{\rho} = \frac{\frac{4\pi^2}{3\hbar^2}\frac{I(\omega)}{c}\left|\vec{D}_{fi}\right|^2 \times \delta(\bar{\omega})}{\rho} = \frac{\frac{4\pi^2}{3\hbar^2}\frac{I(\omega)}{c}\left|\vec{D}_{fi}\right|^2 \times \delta(\bar{\omega})}{I(\omega)/c}$$

$$\frac{[W_{fi}]^D}{\rho} = \frac{4\pi^2}{3\hbar^2}\left|\vec{D}_{fi}\right|^2 \times \delta(\bar{\omega}) = B_{fi}$$

Einstein B_{fi} coefficient for (stimulated) absorption $i \rightarrow f$

Bransden & Joachchain: Physics of Atoms & Molecules Section 4.4 'Einstein Coefficients'

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And this just for the sake of completeness, I will show that these expression correspond to what you might have learned as Einstein coefficients A and D. So, those are directly related to this, because you would expect them to be related to the absorption and emission process. So, you have got in the dipole approximations this transition rate per unit energy density, if low is the energy density at frequency omega, then you have 2 divided by rho, but the energy density is intensity over the speed of light.

So, you got this i over c in numerator as well as in the denominator, so these terms will cancel each other and you are left with this transition rate per unit energy density, and this is what corresponds which is defined as Einstein's B coefficients. So, this is the Einstein B coefficients for stimulated absorption from i to f.

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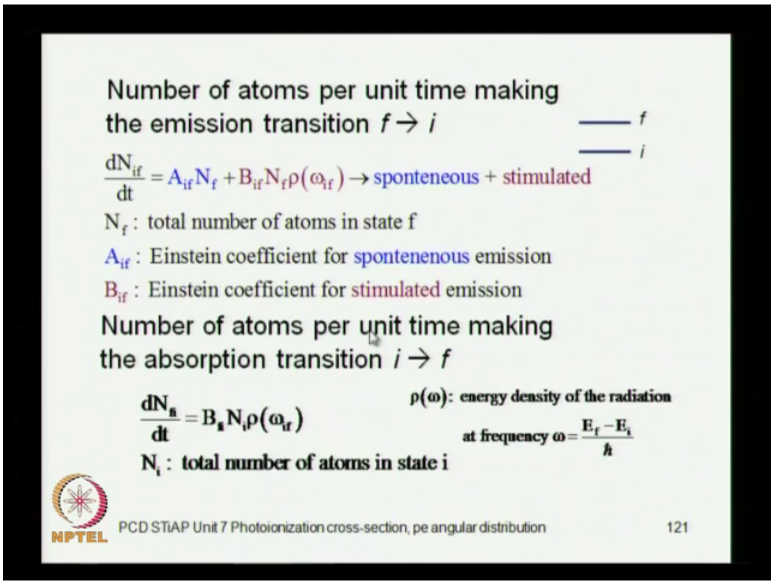

Number of atoms per unit time making the emission transition $f \rightarrow i$

$$\frac{dN_{if}}{dt} = A_{if} N_f + B_{if} N_f \rho(\omega_{if}) \rightarrow \text{sponteneous} + \text{stimulated}$$

N_f : total number of atoms in state f

A_{if} : Einstein coefficient for spontenenous emission

B_{if} : Einstein coefficient for stimulated emission

Number of atoms per unit time making the absorption transition $i \rightarrow f$

$$\frac{dN_{fi}}{dt} = B_{fi} N_i \rho(\omega_{if})$$

N_i : total number of atoms in state i

$\rho(\omega)$: energy density of the radiation at frequency $\omega = \frac{E_f - E_i}{\hbar}$

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Then you have a similar term for the emission also, but then emission can be because of two processes, either spontaneous or simulator. So, for spontaneous emission you have got a rate which depends on the number of atoms in the final state multiplied by rate coefficient, which is the Einstein's a coefficients. And then for the simulator process, you will have the rate determined not just by this number, but also by the density of radiation field at that frequency; and another coefficient which is the third Einstein's coefficient which is B i f.

So, there are three Einstein coefficients to talk about, and these are the three coefficients and then the rate at which the population will change is determined by number of atom’s per unit time making the absorption transmission i to f, which will be given by this rate expression with the absorption.

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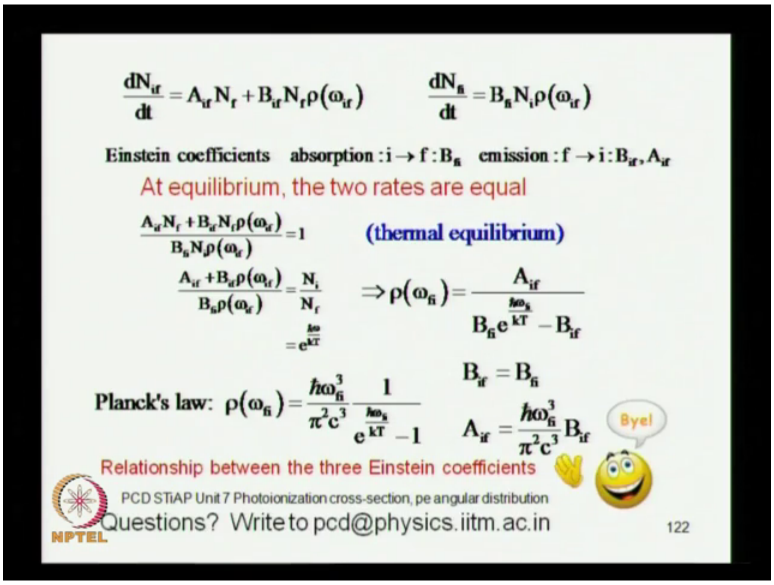

$$\frac{dN_{if}}{dt} = A_{if}N_f + B_{if}N_f\rho(\omega_{if}) \qquad \frac{dN_{fi}}{dt} = B_{fi}N_i\rho(\omega_{if})$$

Einstein coefficients absorption : $i \rightarrow f : B_{fi}$ emission : $f \rightarrow i : B_{if}, A_{if}$

At equilibrium, the two rates are equal

$$\frac{A_{if}N_f + B_{if}N_f\rho(\omega_{if})}{B_{fi}N_i\rho(\omega_{if})} = 1$$

(thermal equilibrium)

$$\frac{A_{if} + B_{if}\rho(\omega_{if})}{B_{fi}\rho(\omega_{if})} = \frac{N_i}{N_f} = e^{\frac{\hbar\omega}{kT}} \qquad \Rightarrow \rho(\omega_{fi}) = \frac{A_{if}}{B_{fi}e^{\frac{\hbar\omega_{fi}}{kT}} - B_{if}}$$

$$B_{if} = B_{fi}$$

Planck's law: $\rho(\omega_{fi}) = \frac{\hbar\omega_{fi}^3}{\pi^2c^3}\frac{1}{e^{\frac{\hbar\omega_{fi}}{kT}} - 1}$ $\qquad A_{if} = \frac{\hbar\omega_{fi}^3}{\pi^2c^3}B_{if}$

Relationship between the three Einstein coefficients

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Questions? Write to pcd@physics.iitm.ac.in

And now you have these expressions now both for absorption as well as emission, and if have equilibrium then these two rates will be necessarily equal. So, you just set them equal to each other, and you are find that this ratio is given by the ratio of the population, which is given by an exponential factor depending on the absolute temperature of the system.

So, this gives you an expression for the ratio of two populations and you can swap this equation play with this, and get the expression for the energy density and this frequency. What must this correspond to, it must correspond to Planck's law, it must be the Planck's law, and this is the Planck's law. So, now, if you required if you demand equivalence between this expression and this expression, it is obvious that it will hold good if B i f is equal to B f i and A i f is equal to h cross omega cube over this factor times the B coefficients. So, this the relationship between the three Einstein coefficients.

So, with this I will conclude today’s class, if there are any questions I will be happy to take otherwise, we take it from here, we need one more class in which I will get the expression for the angular distribution of the four electrons.

Student: (( ))

Well as long as you can make an approximation that, the potential is a local potential, so if you a have nonlocal potential, so in the Hearty-Fork you will not get the equivalence between the length form and velocity form. However, if you make a local density approximation to the

Hearty-Fork, like the slater exchange approximation or any local density potential, so if you make a local density approximation to the Hearty-Fork exchange potential, then that effective potential will again become local and that is required for the equivalence between the length form and velocity form.

So, typically the equivalence holds good for local density potentials, or other potentials to which you make a density approximation, but then there are some other situations also, like when you do many body theory. If you do a complete many body theory using the random Farris approximation for example, you do get equivalence between the length form and velocity form, but that is different reason. It is not because the potential is local, but it is for different reason, so there are some other situations also, any other question.

So thank you.