Select/Special Topics in Atomic physics

Prof. P.C Deshmukh
Department of Physics
Indian Institute of Technology, Madras

Lecture - 31
Atomic Photoionization Cross-Sections, Angular Distribution of Photoelectrons

Greetings, we will continue with the unit 7, and our task at this is to get acquainted with atomic photoionization process and how to get the, if not all the measurable parameters at least some of the important ones. Like I said that when you perform a photoionization experiment, when always likes to do a complete experiment and then you can certainly measure the cross section, which is related to the transition probability.

You can also measure the angular distributions of the photoelectrons and then you can also measure the spin polarization parameters of the photo electrons. And only of when you make a measurement of all of these you really do, what is called as a complete experiment, because all of these measurements are compatible with each other. So, we will set up the theoretical frame work at least to the extent of discussing, the photo ionization cross section, and also the angular distributions of the photo electrons.

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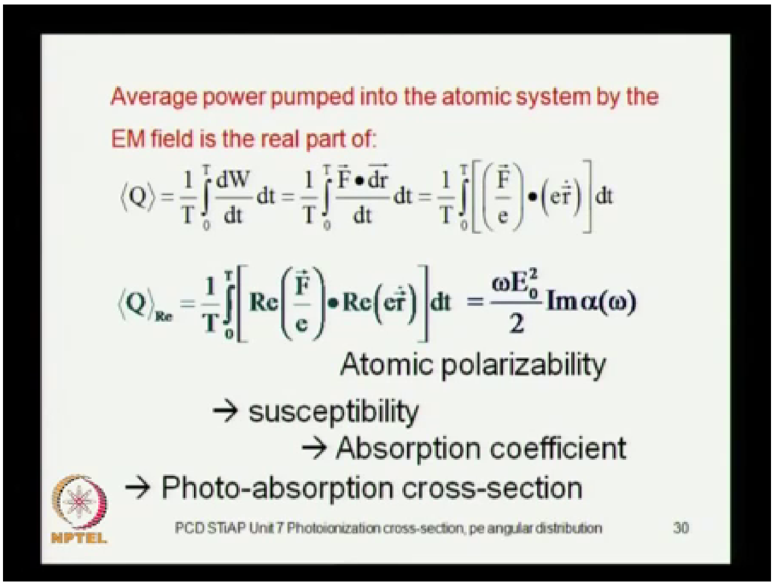

Average power pumped into the atomic system by the EM field is the real part of:

$$\langle Q\rangle = \frac{1}{T}\int_0^T \frac{dW}{dt}dt = \frac{1}{T}\int_0^T \frac{\vec{F}\bullet\overrightarrow{dr}}{dt}dt = \frac{1}{T}\int_0^T\left[\left(\frac{\vec{F}}{e}\right)\bullet\left(e\dot{\vec{r}}\right)\right]dt$$

$$\langle Q\rangle_{Re} = \frac{1}{T}\int_0^T\left[\mathrm{Re}\left(\frac{\vec{F}}{e}\right)\bullet\mathrm{Re}\left(e\dot{\vec{r}}\right)\right]dt = \frac{\omega E_0^2}{2}\mathrm{Im}\,\alpha(\omega)$$

Atomic polarizability

→ susceptibility

→ Absorption coefficient

→ Photo-absorption cross-section

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And in our previous class, we discussed that photoionization of course, is because electromagnetic energy is absorbed by the atomic system, by the quantum atomic system. And therefore, the photoionization cross section will be related to how much of power is pumped into the atomic system, by the electromagnetic field, so that is a parameter of interest from the point of view of the classical description of this process. And we will conclude our discussion on the classical description of this process and then today we will also get into the quantum mechanical description of the photoionization process.

So, we know that photoionization cross section has to do with the photoionization probability, and this will naturally be related to how much of power is pumped into the quantum atomic system, by the electromagnetic field. So, we obtain this expression in our previous class, which is to evaluate the average power which is pumped into the system a by the electromagnetic field.

And we found that it is related to the imaginary part of the atomic polarizability, so this is the connection that we got in our previous class. And it is an important one, because a lot of literature on photoionization process will refer to atomic polarizability, will refer to oscillator strengths and so on. So, I am preparing the background, so that you can become familiar with the literature in this field; and the polarizability off force is then related to some macroscopic properties like susceptibility. And then of course, there is the quantum mechanical expression for the photo absorption cross section, which I have also we will begin to discuss today itself.

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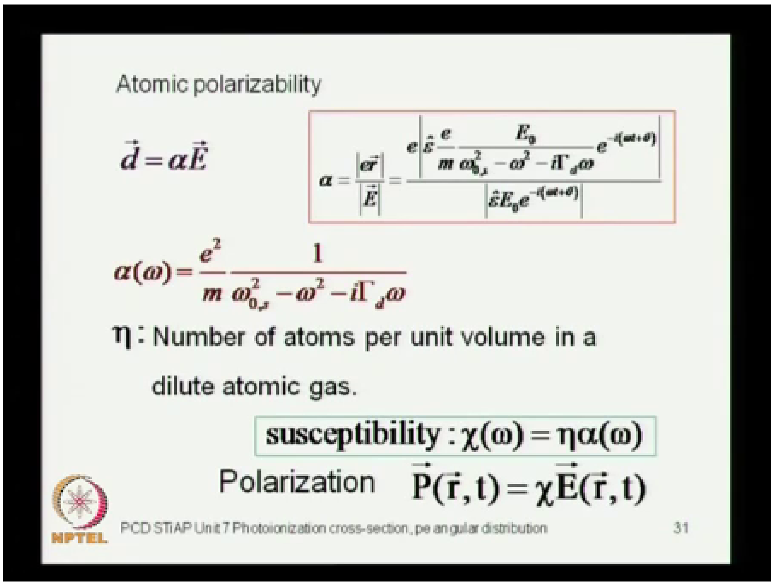

Atomic polarizability

$$\vec{d} = \alpha \vec{E}$$

$$\boxed{\alpha = \frac{|e\vec{r}|}{|\vec{E}|} = \frac{e\left|\hat{\varepsilon}\frac{e}{m}\frac{E_0}{\omega_{0,s}^2 - \omega^2 - i\Gamma_d\omega}e^{-i(\omega t+\theta)}\right|}{\left|\hat{\varepsilon}E_0 e^{-i(\omega t+\theta)}\right|}}$$

$$\alpha(\omega) = \frac{e^2}{m}\frac{1}{\omega_{0,s}^2 - \omega^2 - i\Gamma_d\omega}$$

η : Number of atoms per unit volume in a dilute atomic gas.

$$\boxed{\text{susceptibility} : \chi(\omega) = \eta\alpha(\omega)}$$

Polarization $\vec{P}(\vec{r},t) = \chi\vec{E}(\vec{r},t)$

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So, this is the expression for the atomic polarizability, alpha is the a polarizability, d is the dipole moment and we found that, if you have you divide the modulus of the dipole moment by the modulus of the electric intensity, to get this atomic polarizability. And if you have asset of number of atoms per unit volume in a dilute atomic gas, then you will have the susceptibility, which is scaled from the atomic polarizability by the number of atoms per unit volume. So, these are usual macroscopic expressions and then the susceptibilities also related to the polarization properties of the medium.

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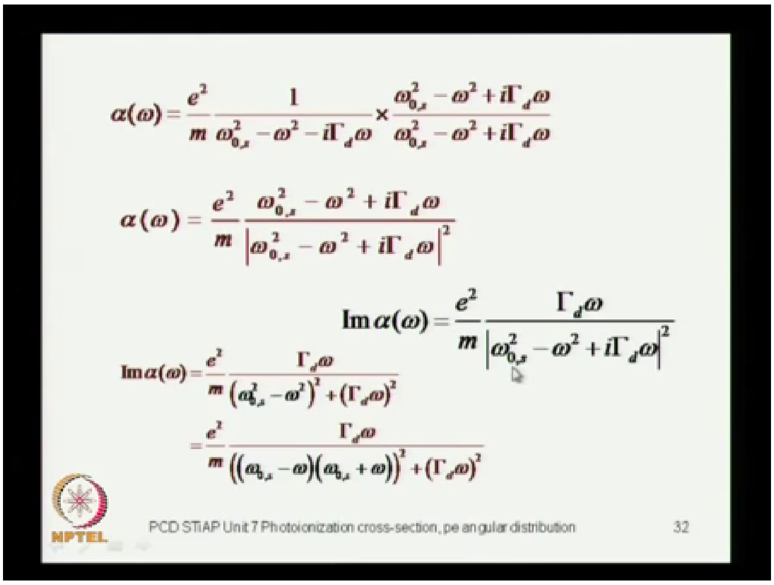

$$\alpha(\omega) = \frac{e^2}{m}\frac{1}{\omega_{0,s}^2 - \omega^2 - i\Gamma_d\omega} \times \frac{\omega_{0,s}^2 - \omega^2 + i\Gamma_d\omega}{\omega_{0,s}^2 - \omega^2 + i\Gamma_d\omega}$$

$$\alpha(\omega) = \frac{e^2}{m}\frac{\omega_{0,s}^2 - \omega^2 + i\Gamma_d\omega}{\left|\omega_{0,s}^2 - \omega^2 + i\Gamma_d\omega\right|^2}$$

$$\mathrm{Im}\,\alpha(\omega) = \frac{e^2}{m}\frac{\Gamma_d\omega}{\left|\omega_{0,s}^2 - \omega^2 + i\Gamma_d\omega\right|^2}$$

$$\mathrm{Im}\,\alpha(\omega) = \frac{e^2}{m}\frac{\Gamma_d\omega}{\left(\omega_{0,s}^2 - \omega^2\right)^2 + \left(\Gamma_d\omega\right)^2}$$

$$= \frac{e^2}{m}\frac{\Gamma_d\omega}{\left(\left(\omega_{0,s} - \omega\right)\left(\omega_{0,s} + \omega\right)\right)^2 + \left(\Gamma_d\omega\right)^2}$$

So, now what I have done is to multiply and divide by the complex conjugate of the denominators, so that I can extract the imaginary part of the atomic polarizability. So, that is the quantity of interest as we have already recognized, so I have just multiplied and divided by the complex conjugate of the denominator. And then I can extract the imaginary part of this quantity, which is now this is the real part, so the imaginary part of the numerator is this gamma omega, gamma is connected to the damping coefficient in our oscillatory equation.

And you can play with these terms a little bit, recognized that this is just the difference of two squares, so you can write this as a plus b into a minus b and there is a whole square here.

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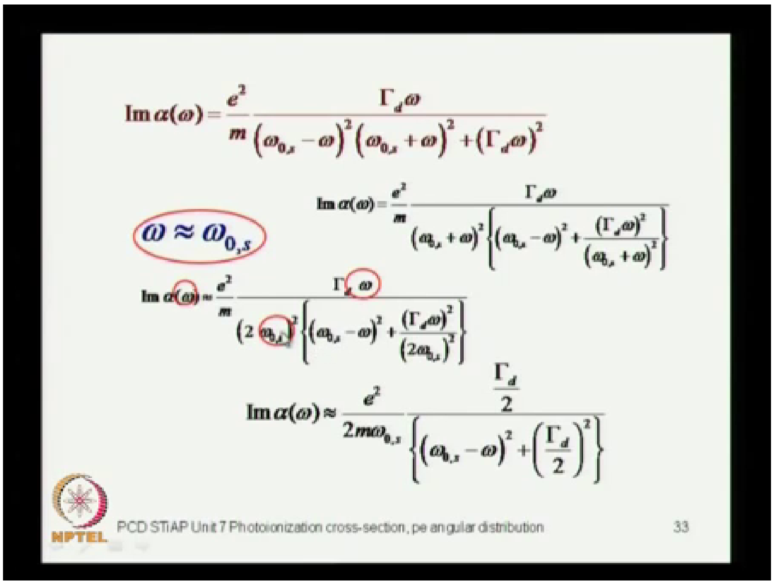

$$\operatorname{Im}\alpha(\omega)=\frac{e^2}{m}\frac{\Gamma_d\omega}{(\omega_{0,s}-\omega)^2(\omega_{0,s}+\omega)^2+(\Gamma_d\omega)^2}$$

$$\operatorname{Im}\alpha(\omega)=\frac{e^2}{m}\frac{\Gamma_d\omega}{(\omega_{0,s}+\omega)^2\left\{(\omega_{0,s}-\omega)^2+\frac{(\Gamma_d\omega)^2}{(\omega_{0,s}+\omega)^2}\right\}}$$

$$\boxed{\omega\approx\omega_{0,s}}$$

$$\operatorname{Im}\alpha(\boxed{\omega})\approx\frac{e^2}{m}\frac{\Gamma_d\boxed{\omega}}{(2\boxed{\omega_{0,s}})^2\left\{(\omega_{0,s}-\omega)^2+\frac{(\Gamma_d\omega)^2}{(2\omega_{0,s})^2}\right\}}$$

$$\operatorname{Im}\alpha(\omega)\approx\frac{e^2}{2m\omega_{0,s}}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega_{0,s}-\omega)^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

So, you can rewrite these terms in somewhat simple form and what we do is to extract the omega 0 plus omega has a common factor, from these two terms. So, the second term in the denominator as to be divided by this omega 0 plus omega whole square, because that is the term which is taken as a common factor between these two terms. So, outside over here, the sum of these two is not very different from twice a natural frequency, inside over here the difference matters and we have to keep track of that.

This is the usual approximation scheme that one employs, that you can always ignore small numbers, but only when they come together as additive terms to large numbers, so that is all they raise to it. So, now near the natural frequency, you have these frequency terms omega, omega 0 is to be nearly equal and then you have got an omega 0 square here, there is an omega here, so you get 1 over omega as a common factor, and then the rest of the factor which appears in the expression for the imaginary part of the atomic polarizability.

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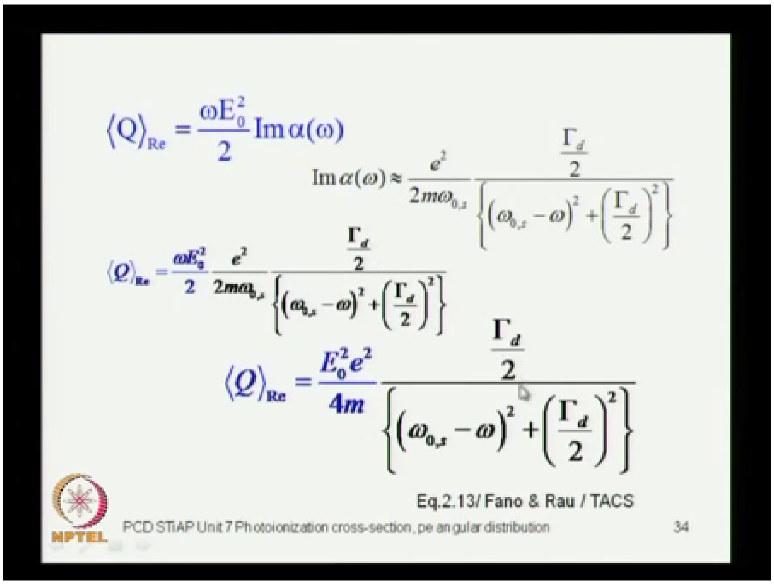

$$\langle Q\rangle_{Re} = \frac{\omega E_0^2}{2}\mathrm{Im}\,\alpha(\omega)$$

$$\mathrm{Im}\,\alpha(\omega) \approx \frac{e^2}{2m\omega_{0,s}}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega_{0,s}-\omega)^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

$$\langle Q\rangle_{Re} = \frac{\omega E_0^2}{2}\frac{e^2}{2m\omega_{0,s}}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega_{0,s}-\omega)^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

$$\langle Q\rangle_{Re} = \frac{E_0^2 e^2}{4m}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega_{0,s}-\omega)^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

Eq.2.13/ Fano & Rau / TACS

Now, notice that this is related to the actual power, which have been pumped into the quantum atomic system by the electromagnetic field. And you have a very simple expression which is coming from the imaginary part of the atomic polarizability, so you plug in this imaginary part of that atomic polarizability expression, and get this power which is pumped in, in terms of this. Now, some of you might already recognize the form of this function, so I will just draw your attention to that, but you will quickly see what exactly it is.

I have also referred to the relationship that you will find in Fano and Rau's book, which comes from chapter 2 of this book. Because, one of my objectives is to help you gain aquatints with what is the most common literature in this field, and Fano and Rau book is a classic one in this particular context.

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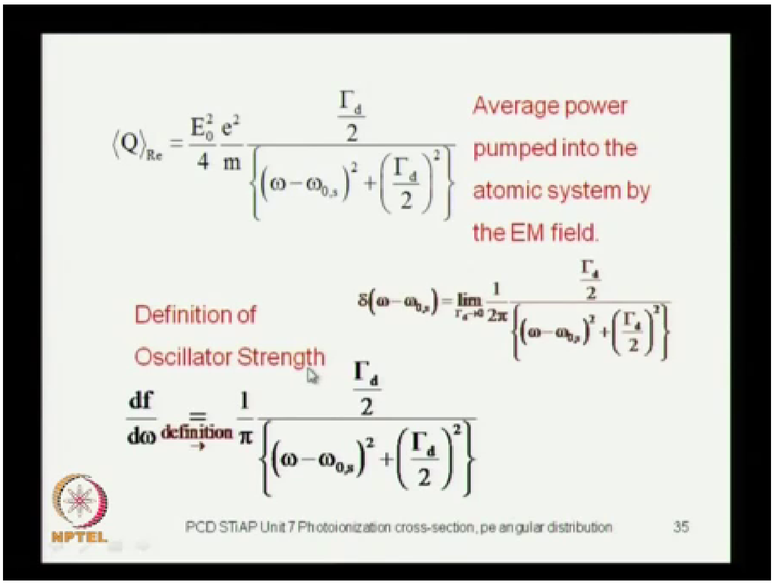

$$\langle Q\rangle_{Re} = \frac{E_0^2}{4}\frac{e^2}{m}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega-\omega_{0,s})^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

Average power pumped into the atomic system by the EM field.

$$\delta(\omega-\omega_{0,s}) = \lim_{\Gamma_d\to 0}\frac{1}{2\pi}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega-\omega_{0,s})^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

Definition of Oscillator Strength

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

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So, if you look at this form, you probably already recognize that this is a delta function, now the Dirac delta function has got very many manifestations, there are many representations of the Dirac delta function. Not just this square block, you have got sinusoidal expressions, then various there are several shades number of functions which confirm to the functional definition of a Dirac delta function, and you will find most of them in ((Refer Time: 07:55)).

So, this has a form which is similar to a Dirac delta function not surprising, because you know that the maximum power absorption is going to take place at the natural frequency of the oscillators. So, what we do is to introduce a definition of what is called as an oscillator strength, and this is the term which gets used in, which is borrowed from classical oscillator model into quantum mechanics as well. So, the classical oscillator a model it is defined, in this particular form this is the definition of what is called as the oscillator strength distribution, notice that it is d f by d omega. So, it gives you some sort of a spectral distribution over various frequencies, so this is the definition of what is called as an oscillator strength.

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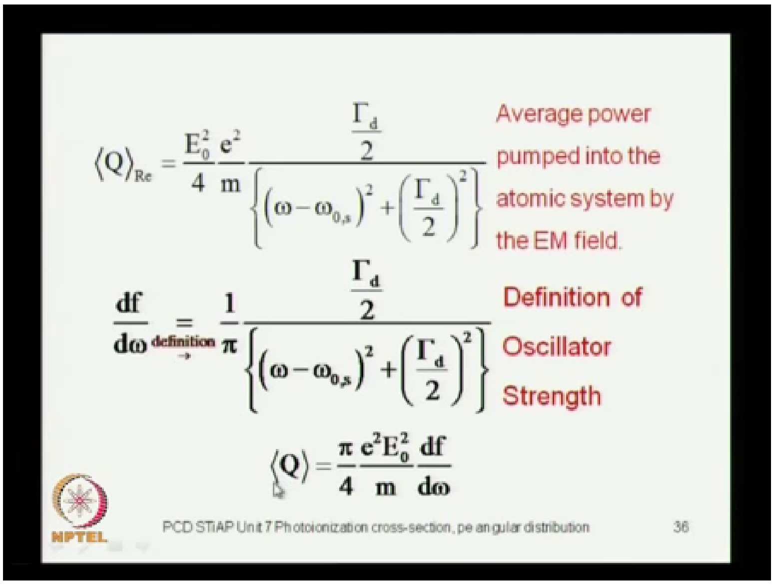

$$\langle Q\rangle_{Re} = \frac{E_0^2}{4}\frac{e^2}{m}\frac{\frac{\Gamma_d}{2}}{\left\{(\omega-\omega_{0,s})^2+\left(\frac{\Gamma_d}{2}\right)^2\right\}}$$

Average power pumped into the atomic system by the EM field.

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

Definition of Oscillator Strength

$$\langle Q\rangle = \frac{\pi}{4}\frac{e^2E_0^2}{m}\frac{df}{d\omega}$$

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And using this definition, you can write the expression for the average power, which is pumped into the atomic system by the electromagnetic field, in terms of what we have now defined as the oscillator strength. So, the oscillator strength appears explicitly in this, and eventually it will get related also to the photo absorption cross section. So, this is the definition of the oscillator strength, and it is been defined in a very peculiar manner.

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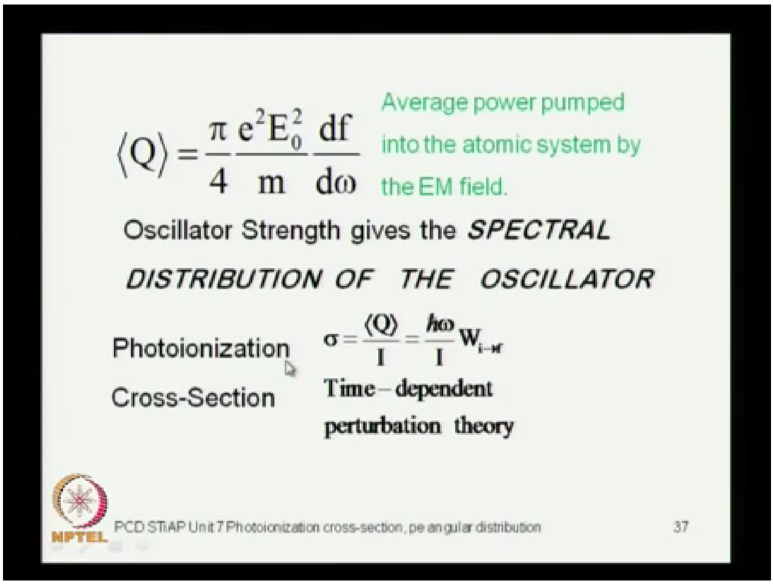

$$\langle Q\rangle = \frac{\pi}{4}\frac{e^2E_0^2}{m}\frac{df}{d\omega}$$

Average power pumped into the atomic system by the EM field.

Oscillator Strength gives the *SPECTRAL DISTRIBUTION OF THE OSCILLATOR*

Photoionization Cross-Section

$$\sigma = \frac{\langle Q\rangle}{I} = \frac{\hbar\omega}{I}W_{i\to f}$$

Time − dependent perturbation theory

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And that is a god reason for it which will become transparent very soon, that as you notice that this gives you the spectral distribution of the oscillator. And the photo ionization cross section, which we will get from the quantum mechanical expression, we will get into discussing that very soon, it will be related to this average power, which is pumped into the system per unit intensity of the electromagnetic field. Because, you need to normalize it in a certain way, so this is the relation that we will extract from our quantum mechanical description.

In the mean time I will let you find the dimensions of the power, and the intensity and find out what are the physical dimensions of sigma that you expect. And you must get them from both the quantum mechanical formulation, as well as the classical formulation.

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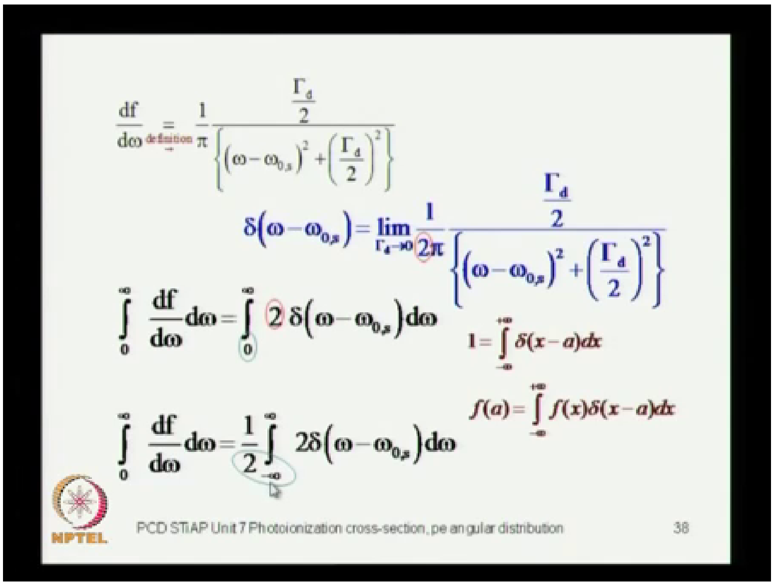

$$\frac{df}{d\omega} \underset{\text{definition}}{=} \frac{1}{\pi} \frac{\frac{\Gamma_d}{2}}{\left\{ \left(\omega - \omega_{0,s}\right)^2 + \left(\frac{\Gamma_d}{2}\right)^2 \right\}}$$

$$\delta\left(\omega - \omega_{0,s}\right) = \lim_{\Gamma_d \to 0} \frac{1}{2\pi} \frac{\frac{\Gamma_d}{2}}{\left\{ \left(\omega - \omega_{0,s}\right)^2 + \left(\frac{\Gamma_d}{2}\right)^2 \right\}}$$

$$\int_0^\infty \frac{df}{d\omega} d\omega = \int_0^\infty 2\,\delta\left(\omega - \omega_{0,s}\right) d\omega$$

$$1 = \int_{-\infty}^{+\infty} \delta(x-a)\,dx$$

$$f(a) = \int_{-\infty}^{+\infty} f(x)\,\delta(x-a)\,dx$$

$$\int_0^\infty \frac{df}{d\omega} d\omega = \frac{1}{2} \int_{-\infty}^\infty 2\delta\left(\omega - \omega_{0,s}\right) d\omega$$

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So, this is your oscillator strength and it is very similar to a Dirac delta function, this is the exact expression for the Dirac delta function, which satisfies the usual defining criterion of a Dirac delta. So, you see the connection between the Dirac delta and the oscillator strength, notice that there is a factor of 2 over here. So, now if you want to integrate the oscillator strength over all the frequencies, you will obviously, integrate from frequency 0 through infinity.

So, that you have an integral over the entire frequency range, but you have got a factor of 1 over 2, which is included in the Dirac delta. But then you can extend this integration range from 0 to infinity to a minus infinity to plus infinity, and you can do it without any assail, because that the electric intensity of the radiation field was 0 at time less than 0. And similarly in this context, if you extend this range of integration from 0 to infinity to minus infinity to plus infinity, all you have to do is to take half of that integral.

So, this is a straight forward extension of the range of integration by doubling the range of integration and then taking a factor of half. So, you take 1 half of this range of integration, but now you have got a factor of 2 here and another factor of 2 over here, which will cancel each other.

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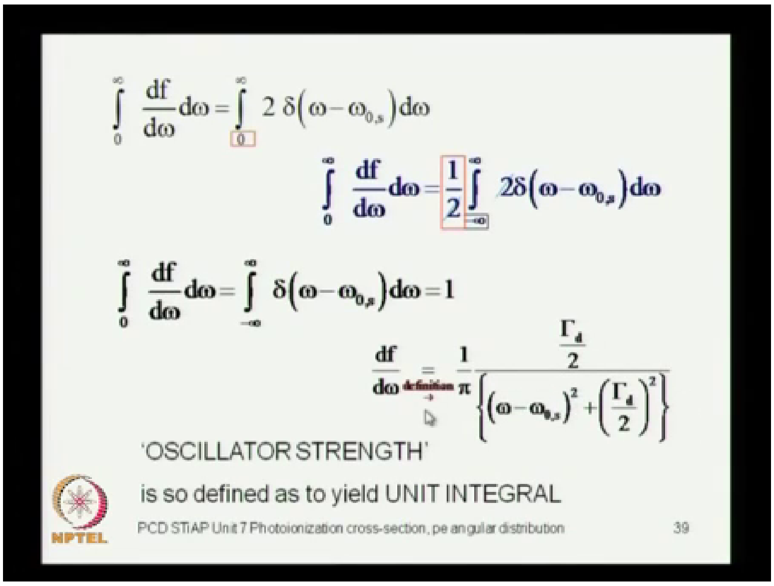

$$\int_0^\infty \frac{df}{d\omega}d\omega = \int_{\boxed{0}}^\infty 2\,\delta(\omega-\omega_{0,s})d\omega$$

$$\int_0^\infty \frac{df}{d\omega}d\omega = \boxed{\frac{1}{2}}\int_{\boxed{-\infty}}^\infty 2\delta(\omega-\omega_{0,s})d\omega$$

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

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

'OSCILLATOR STRENGTH'

is so defined as to yield UNIT INTEGRAL

And what you get is the integration of the delta function over the entire range minus infinity to plus infinity, so you get normalized value which is plus 1, essentially what you discover is that the oscillator strength has been defined very appropriately. Because, by choosing this definition as 1 over pi times this factor, we find that the oscillator strength is so defined, this is the choice that we are made. And it is a very appropriate choice, because when you integrate it you get unity, so that is how it has actually been introduced.

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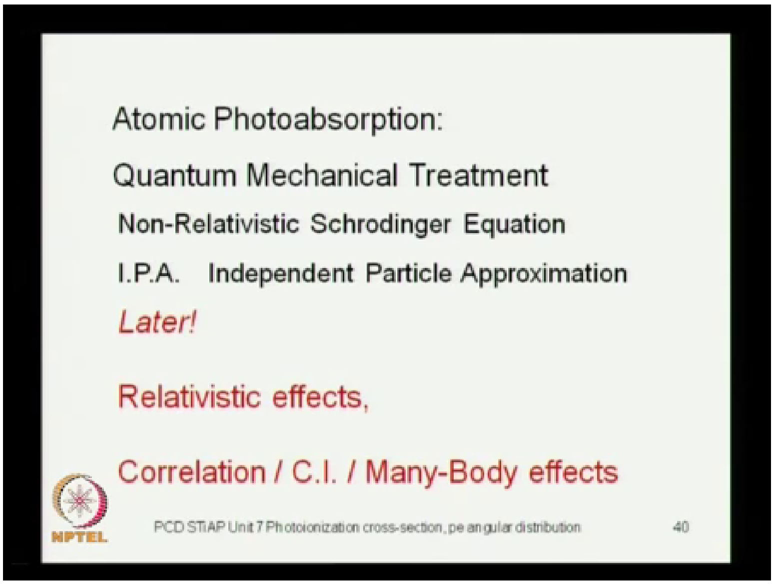

Atomic Photoabsorption:

Quantum Mechanical Treatment

Non-Relativistic Schrodinger Equation

I.P.A. Independent Particle Approximation

Later!

Relativistic effects,

Correlation / C.I. / Many-Body effects

So, now we get into the quantum mechanical treatment, because now we have the terminology from the classical model of a electrons, which are treated like oscillators in the atomic system, which are bound to some equilibrium positions by spring constant. There is a dissipation and we used essentially, the model of a classical damped driven oscillator to get these expressions. So, now, we get into the quantum mechanical treatment, and you would have done part of this in your quantum mechanics course, in the context of the time dependent perturbation theory.

Because, that is the tool which we are going to use, but I will go through it very quickly, so essentially we will have a simple treatment, in which we will make use of the non-relativistic Schrodinger equation, we will work within the approximation of independent particle models. So, that all the many body effects and correlation, and all these other details that we know are important, they will have to be added on, but we will first develop the basic formalism, for the simple one electron model using the non-relativistic Schrodinger equation.

And then we can always plug in additional a details like, relativistic effects, correlating effects and so on. So, all these many body effects, correlation effects, configuration interactions and so on, will then after we added on later to our consideration, but this is just the starting point.

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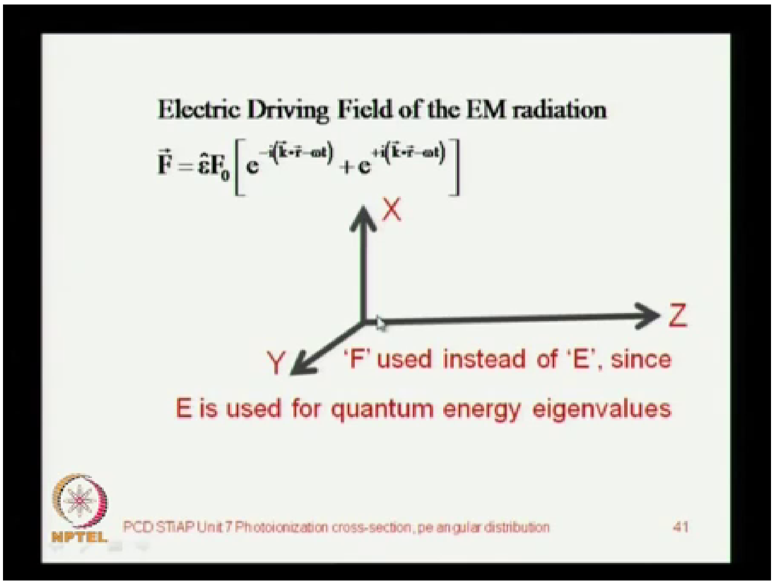

Electric Driving Field of the EM radiation

$$\vec{F} = \hat{\varepsilon}F_0\left[e^{-i(\vec{k}\cdot\vec{r}-\omega t)} + e^{+i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

'F' used instead of 'E', since E is used for quantum energy eigenvalues

So, our quantum mechanical problem here is this, that you have got an atomic system at there is a certain coordinate system, which I will make use of, and this is in the presence of an electric driving field, which is represented by this force F, which is a time dependent. This is the space and time dependence of the force, essentially you have got the real part which is the cosine term, and the electromagnetic energy is incident in a certain direction, and I choose this direction of incidence to be the z axis.

And as a result of photo absorption, one electron let us say is not out of the atomic system, and it shoots off in what we call as a unique exit channel, in terms of our in going way boundary conditions. So, it shoots off in a particular direction, there is a certain unique direction in which it takes off.

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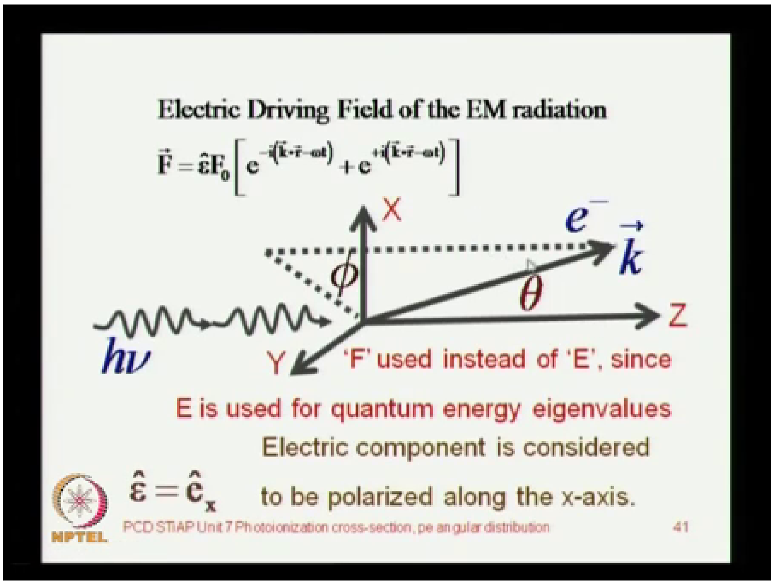

Electric Driving Field of the EM radiation

$$\vec{F} = \hat{\varepsilon}F_0\left[e^{-i(\vec{k}\cdot\vec{r}-\omega t)} + e^{+i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

'F' used instead of 'E', since E is used for quantum energy eigenvalues

$\hat{\varepsilon} = \hat{e}_x$ Electric component is considered to be polarized along the x-axis.

And let us say it takes off along a polar angle theta, and an iso methyl angle 5 with respect to the z x plain, so we will use the cylindrical symmetry in this particular geometry. So, this is the physical process that we are going to we talking about, it takes off with momentum h cross k, so this is the photoelectron momentum. And this is the photo electron which is not out of the atomic system, as a result of absorption of one quantum of electromagnetic energy one photon.

So, we consider again for the sake of our initial consideration, that the electric component of the electromagnetic field is polarized along the x axis, so this unit vector e is the same as the unit vector along the x axis which is e x. So, this is our geometry with reference to which we will develop the basic formulation, subsequently we can extend this treatment to un polarized light, or any other state of polarization.

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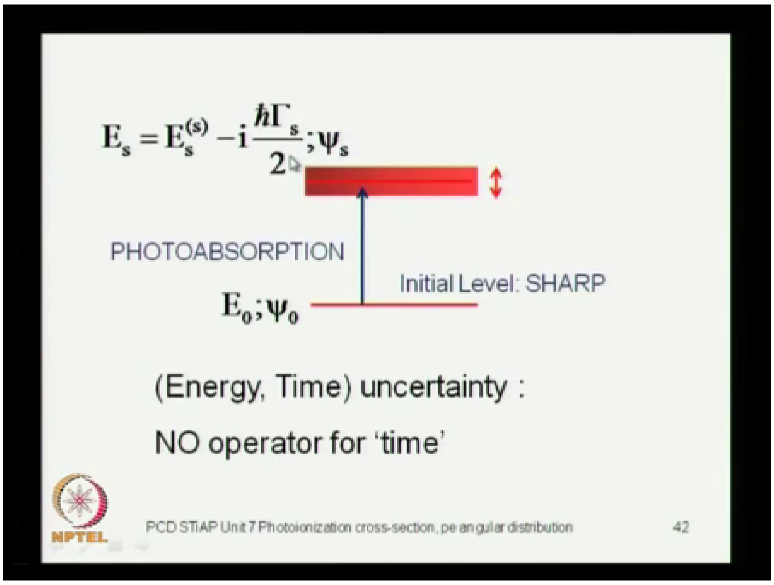

$$E_s = E_s^{(s)} - i\frac{\hbar\Gamma_s}{2}; \psi_s$$

PHOTOABSORPTION

Initial Level: SHARP

$E_0; \psi_0$

(Energy, Time) uncertainty :

NO operator for 'time'

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So, this is what is happening in photo absorption, you have got a certain initial state energy E 0, and eigen state represented by psi 0 and the photo absorption raises it to a certain exited state. Now, the initial level is sharp and the final state will have a certain width, now this is characteristic of the un certainty principle. But, uncertainty principle you have to remember, this is the energy time uncertainty and I did mention this in one of our earlier discussions as well, that the energy time un certainty really appears on a very different footing than the uncertainty for position and momentum.

Because, there is no operator for time in quantum mechanics, when you consider q and p as position and momentum, linear position and liner momentum or angular momentum and angles, any canonically conjugate pairs can be taken as q and p. But, these are dynamical variables, which are quantized for which you have operators and then q and p in quantum mechanics come out as eigen values of the position operator or eigen values of the momentum operator and so on. You do not get time as an eigen value of an operator for time, it is a certain parameter.

But, it still has the same sort of energy time and certainty between the canonically conjugate variables, and because of this excited state has got a certain width, which is represented by this. So, the energy actually is a complex number, rather than a real number, energies are typically real, these are real eigen values of a Hermitian operator, so one should ask as to why does the excited decay at all. If you have an atomic system, and if it is excited form the ground state to an excited state, if the excited state is also a stationary eigen state, it could actually have infinite life time, if its energy is sharp like the energy of 2 s, 3 s.

It is the same as the energy the energy of the 1 s divided by n square, you divide it by 2 square, 3 square, 4 square whatever it is and you get a single number as a result of dividing 13.6 by 4 or 9 or 16 or whatever you get a single number. And it is a sharp energy, and if it is a sharp energy level it would have a infinite life, so there is something which is missing in this consideration, and I hope that what the answer is, if it well and good. If not give it a taught and you should certainly, we can talk about this some other context, but over here I just want to draw your attention to the fact, that in real atomic systems you do have these excited states, which have got a certain width.

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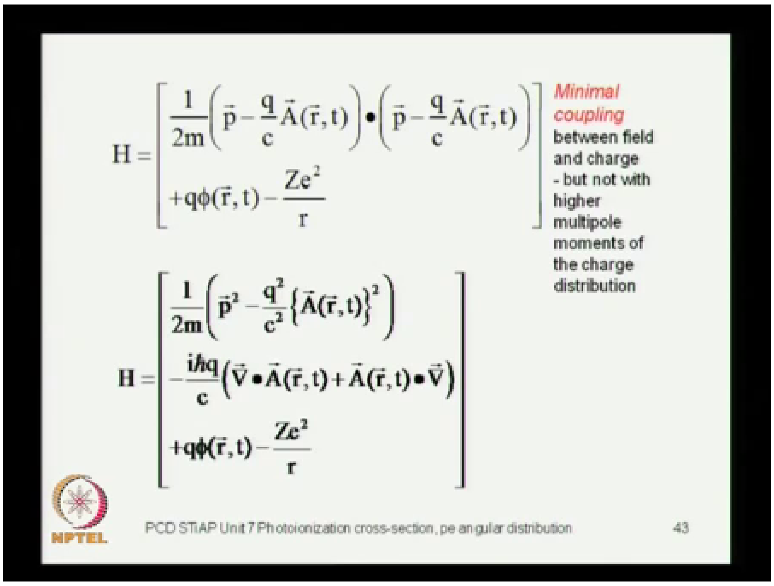

$$H = \begin{bmatrix} \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}(\vec{r},t)\right) \bullet \left(\vec{p} - \frac{q}{c}\vec{A}(\vec{r},t)\right) \\ + q\phi(\vec{r},t) - \frac{Ze^2}{r} \end{bmatrix}$$

Minimal coupling between field and charge - but not with higher multipole moments of the charge distribution

$$H = \begin{bmatrix} \frac{1}{2m}\left(\vec{p}^2 - \frac{q^2}{c^2}\left\{\vec{A}(\vec{r},t)\right\}^2\right) \\ - \frac{i\hbar q}{c}\left(\vec{\nabla} \bullet \vec{A}(\vec{r},t) + \vec{A}(\vec{r},t) \bullet \vec{\nabla}\right) \\ + q\phi(\vec{r},t) - \frac{Ze^2}{r} \end{bmatrix}$$

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And now you can set up the Hamiltonian, for the quantum system together with the electromagnetic field, so that the generalized momentum is now p minus q a over c. And then what I have made you this is the, what is called as a minimal coupling, essentially what it means that you are not taking into account the interaction between the field and higher multiples of the charge distribution, so you have just the leading term. So, this is the minimal coupling Hamiltonian for the interaction of a quantum atomic system with an electromagnetic field.

And you can expand this term remember that p and A do not really compute, p is a gradient operator, so it will not commute with the vector potential operator A, so p dot A and A dot p will not be the same. So, you have to take into consideration the del dot A and the A dot A term very carefully, there is also a term in e square coming from the scalar product of this operator A with this operator A. So, these are some of the terms, and one would hope to use perturbation theory, and the whole contention of perturbation theory is that the perturbation is weak compared to the original Hamiltonian, so that is the most important thing.

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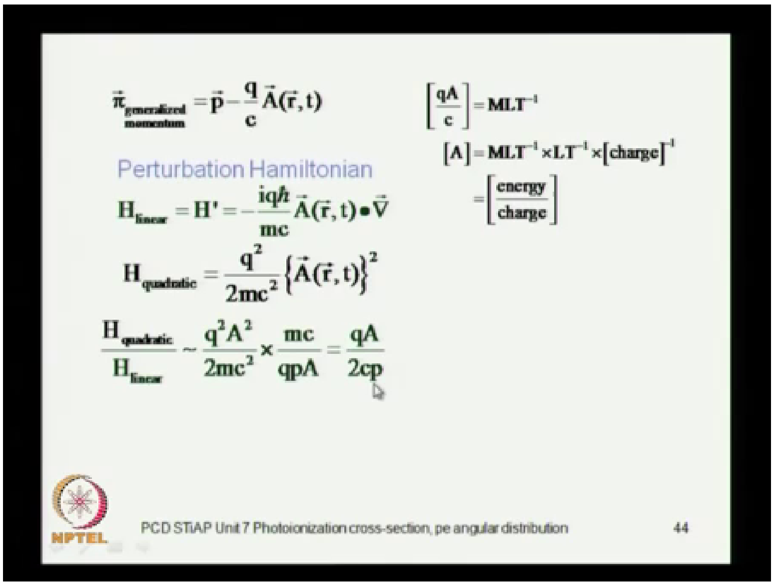

$$\vec{\pi}_{\substack{\text{generalized}\\\text{momentum}}} = \vec{p} - \frac{q}{c}\vec{A}(\vec{r},t)$$

$$\left[\frac{qA}{c}\right] = MLT^{-1}$$

$$[A] = MLT^{-1} \times LT^{-1} \times [\text{charge}]^{-1} = \left[\frac{\text{energy}}{\text{charge}}\right]$$

Perturbation Hamiltonian

$$H_{\text{linear}} = H' = -\frac{iq\hbar}{mc}\vec{A}(\vec{r},t)\bullet\vec{\nabla}$$

$$H_{\text{quadratic}} = \frac{q^2}{2mc^2}\left\{\vec{A}(\vec{r},t)\right\}^2$$

$$\frac{H_{\text{quadratic}}}{H_{\text{linear}}} \sim \frac{q^2A^2}{2mc^2} \times \frac{mc}{qpA} = \frac{qA}{2cp}$$

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And this is our generalized momentum, notice that the vector potential has got the dimensions of energy over charge, and the perturbation Hamiltonian, there are two terms at the perturbation Hamiltonian. There is a linear term in A, and there is also a quadratic term in e square which we have seen in the previous expression for the Hamiltonian. The Hamiltonian inclusive of perturbation it had both the linear term, as well as the quadratic term. So, now, if you take the ratio of the quadratic term to the linear term just order of magnitude estimate, it is q A over 2 of twice c p, so that is the rough estimate of the importance of the quadratic term, compared to the linear term.

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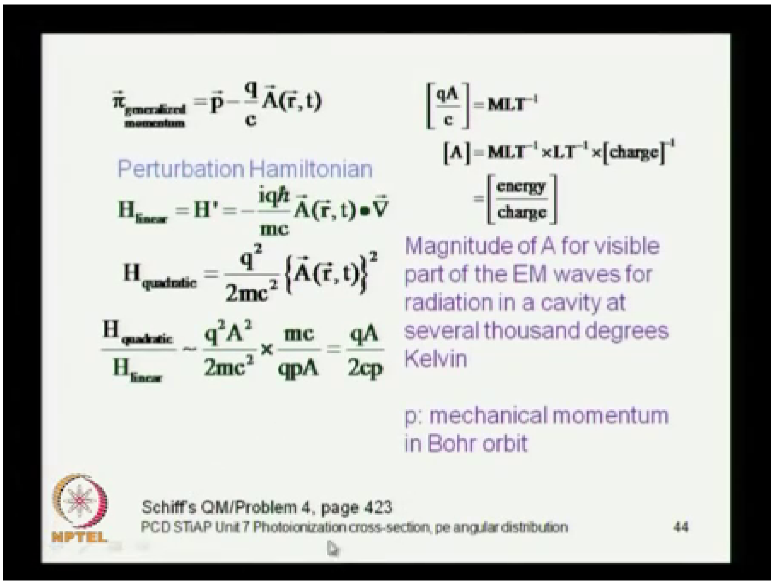

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$$\left[\frac{qA}{c}\right] = MLT^{-1}$$

$$[A] = MLT^{-1}\times LT^{-1}\times[\text{charge}]^{-1}$$

$$= \left[\frac{\text{energy}}{\text{charge}}\right]$$

Magnitude of A for visible part of the EM waves for radiation in a cavity at several thousand degrees Kelvin

p: mechanical momentum in Bohr orbit

Schiff's QM/Problem 4, page 423

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And this is a very nice problem in shifts quantum mechanics, that if you take the magnitude of A and just for the sack of exercise, take it for the visible part of the electromagnetic spectrum. Because, if you have radiation in a cavity you can estimate how much energy density is there, you can measure what would be the magnitude of A, for such a cavity at a certain frequency, because you have got the frequency distribution formula from which of the planks formula.

So, you can get an expression for the magnitude of A, for visible part of the spectral range, and you can take it for a cavity at several 1000's of Kelvin's just to be at safe side, because you want to consider what will happen if you have really strong, high temperatures. And then for p so that will give an estimate of a number for A, q and c are of course, constants, this is the electron change and the speed of light, and for p you can take the mechanical momentum of an electron in the Bohr orbit, just to get some sort of and art of magnitude estimate.

And if you find this ratio, you will find that the quadratic term is much weaker compared to the linear term, and that is a reason you can related through it. So, you certainly can through it, but then this approximation has to be justified, and this is the way you discover that the quadratic term is ignorable. And in fact, in weak fields you can ignore it, when the fields are very small your are left to photon processes and then you can use the, when you deal with lasers and so on, very high intensity radiation.

Then, you cannot do this approximation, but we will work within the domain of the weak fields, and in this approximation the quadratic term can be ignorable. And using the same analysis, the same line of thinking you will also find that, the linear term is a small fraction of the original unperturbed Hamiltonian. So, that now you convince yourself that perturbation theory can actually be used.

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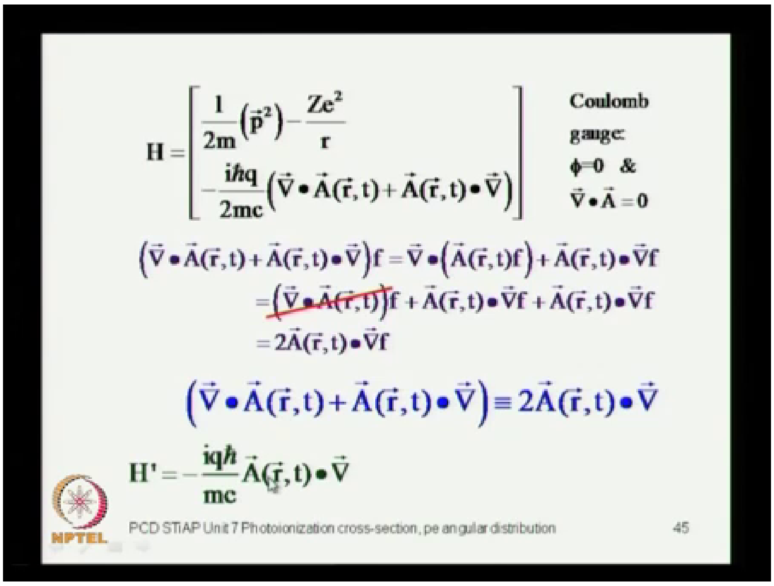

$$H = \left[\frac{1}{2m}\left(\vec{p}^2\right) - \frac{Ze^2}{r} - \frac{i\hbar q}{2mc}\left(\vec{\nabla}\bullet\vec{A}(\vec{r},t) + \vec{A}(\vec{r},t)\bullet\vec{\nabla}\right) \right]$$

Coulomb gauge: $\phi = 0$ & $\vec{\nabla}\bullet\vec{A} = 0$

$$\left(\vec{\nabla}\bullet\vec{A}(\vec{r},t) + \vec{A}(\vec{r},t)\bullet\vec{\nabla}\right)f = \vec{\nabla}\bullet\left(\vec{A}(\vec{r},t)f\right) + \vec{A}(\vec{r},t)\bullet\vec{\nabla}f$$
$$= \cancel{\left(\vec{\nabla}\bullet\vec{A}(\vec{r},t)\right)}f + \vec{A}(\vec{r},t)\bullet\vec{\nabla}f + \vec{A}(\vec{r},t)\bullet\vec{\nabla}f$$
$$= 2\vec{A}(\vec{r},t)\bullet\vec{\nabla}f$$

$$\left(\vec{\nabla}\bullet\vec{A}(\vec{r},t) + \vec{A}(\vec{r},t)\bullet\vec{\nabla}\right) \equiv 2\vec{A}(\vec{r},t)\bullet\vec{\nabla}$$

$$H' = -\frac{iq\hbar}{mc}\vec{A}(\vec{r},t)\bullet\vec{\nabla}$$

So, we will trough off the term phi use the coulomb gauge, and this is the del dot A operator, so let us not through it yet, although in the coulomb gauge the divergence of A, which is the scalar which vanishes. But, here this is the operator this del dot A would operator on an obituary function of f and then you will get the divergence of a product of two functions, a vector function A and scalar function f. So, you have to take the product of these two functions, and take the divergence and that will give you two terms.

One of which will have the scalar divergence of A, which certainly can be thrown in coulomb gauge, so this term would vanish. But, there remaining two terms would add up, and now you have got the approximations for these two terms, in the coulomb gauge this is exact, that in the coulomb gauge these two terms add up to twice A dot del. And that is the equivalent operator that you can put in your interaction Hamiltonian, which is the perturbation Hamiltonian.

So, this is now your perturbation Hamiltonian, and we will make use of perturbation theory the perturbation is time dependent. So, we will make use of the time dependent perturbation theory, and you will expect to meet forms golden rule in this context.

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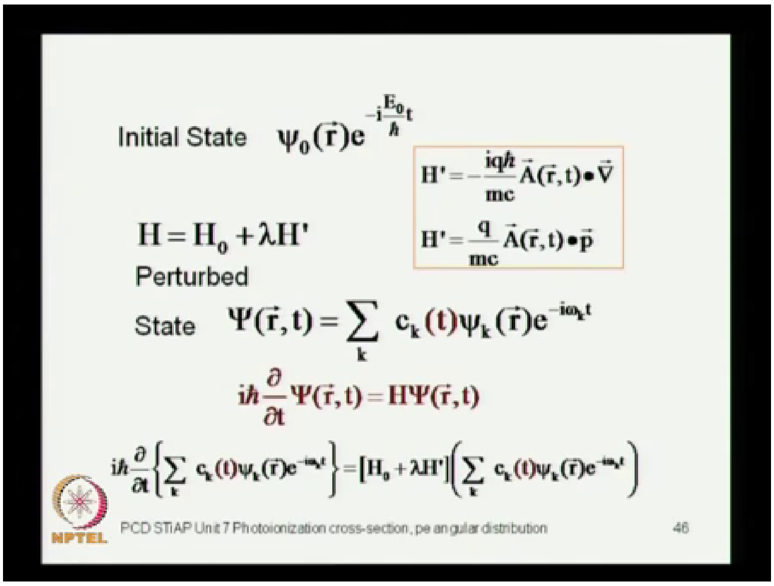

Initial State $\psi_0(\vec{r})e^{-i\frac{E_0}{\hbar}t}$

$$H' = -\frac{iq\hbar}{mc}\vec{A}(\vec{r},t)\bullet\vec{\nabla}$$

$$H' = \frac{q}{mc}\vec{A}(\vec{r},t)\bullet\vec{p}$$

$$H = H_0 + \lambda H'$$

Perturbed State $\Psi(\vec{r},t) = \sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}$

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = H\Psi(\vec{r},t)$$

$$i\hbar\frac{\partial}{\partial t}\left\{\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right\} = [H_0 + \lambda H']\left(\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right)$$

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So, this is our initial state, this is your perturbation and we introduce an order parameter lambda, the only values of significance are lambda e equal to 1 and lambda equal to 0. So, lambda is just a mathematical construct to develop the perturbation approximation and you expect that the system way function, is now a linear superposition of the unperturbed states.

But, then you allow the expansion coefficients to be time dependent, in other words you allow for transitions between various states, because what the transitions will do is to change the occupation number of different states. So, the probability of occupancy of a particular state becomes times dependent, so that is the idea over here. So, this is your system way function, your still working within the domain of perturbation theory, so that you do believe that your system way function can be represented, as a linear superposition of the unperturbed wave function, that is the premise of un perturbation theory.

That the perturbation is not violent that it throws the system out of the Hilbert spaces, that it originally belong to, so now all we do is to substitute this summation over here, this summation symbol k is generic, it includes summation over discrete state. And it will also include an integration over the continuum states, because eigen spectrum consists of both the discreet part, which convergences to the series limit, but above the series limit there is a continuum, so do not forget that. And in fact, in photoionization you do have transitions to the continuum, so that is really important for us. So, you have got this expansion of the system way function, which is plucked into the Schrodinger equation with the full Hamiltonian, which is H 0 plus lambda times H prime.

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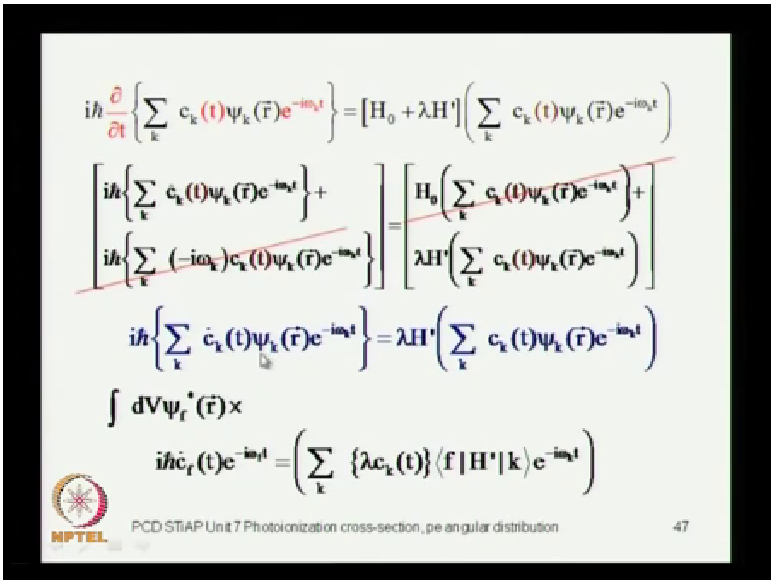

$$i\hbar\frac{\partial}{\partial t}\left\{\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right\}=[H_0+\lambda H']\left(\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right)$$

$$\begin{bmatrix} i\hbar\left\{\sum_k \dot{c}_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right\}+ \\ \cancel{i\hbar\left\{\sum_k (-i\omega_k)c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right\}} \end{bmatrix}=\begin{bmatrix} \cancel{H_0\left(\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right)}+ \\ \lambda H'\left(\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right) \end{bmatrix}$$

$$i\hbar\left\{\sum_k \dot{c}_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right\}=\lambda H'\left(\sum_k c_k(t)\psi_k(\vec{r})e^{-i\omega_k t}\right)$$

$$\int dV\psi_f^*(\vec{r})\times$$

$$i\hbar\dot{c}_f(t)e^{-i\omega_f t}=\left(\sum_k \{\lambda c_k(t)\}\langle f|H'|k\rangle e^{-i\omega_k t}\right)$$

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And the expansion coefficients are now time dependent, so here you take the time derivative of a product of two functions of time, one is the coefficient c which is dependent, the other is this e to the minus psi omega t. So, you can do these derivatives very easily, and from the two size of the equation you find that, there are these common terms. Because, this H 0 operating on psi k will give you the eigen value equation, for the unperturbed Hamiltonian, so you can cancel these terms with what you have on the left hand side.

And essentially you get a rate equation for these coefficients c k, now let us extract the term for a particular final state, so the way to do is to take the projection of this whole equation on a states psi f. So, you just multiply it by psi f complex conjugate, integrate over the whole space, because that will give you the orthonormality condition between f and k, which will give you the chronicle delta s delta f k. In case of the continuum functions you will have the corresponding Dirac delta, when you do the integration, but this whole treatment is generic.

So, you multiply by psi f star complex conjugate and integrate over the whole space, so you get only one term corresponding to k equal to f, so here you have got the coefficient c f dot, which is written over here. ((Refer Time: 29:49)) This is i h cross, this psi k with psi f has given you the delta f k and summation over k has given you a single term, you got the e to the minus i omega k equal to f, so this is a minus i omega f t over here. And then you have got the corresponding terms over the right hand side, but when you project this right hand side on psi f, you get the matrix element of the Hamiltonian, which is the perturbation Hamiltonian in the states f and k

So, that is the matrix element, which will be a measure of the probability amplitude that the interaction h prime will induce a transition from the state k to the state f. So, the probability of the process is going to come from this particular term, as you can began to see, so this is actively a space integral, it is integration over r theta phi.

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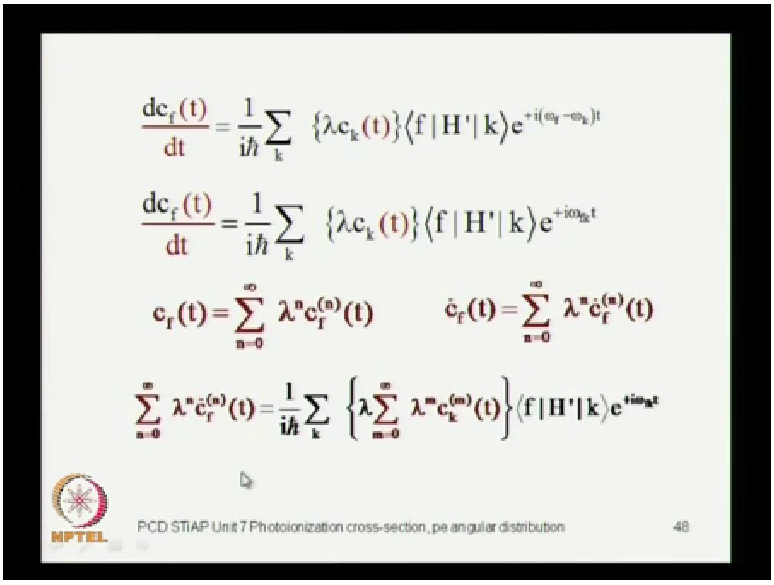

$$\frac{dc_f(t)}{dt} = \frac{1}{i\hbar}\sum_k \{\lambda c_k(t)\}\langle f|H'|k\rangle e^{+i(\omega_f-\omega_k)t}$$

$$\frac{dc_f(t)}{dt} = \frac{1}{i\hbar}\sum_k \{\lambda c_k(t)\}\langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

$$c_f(t) = \sum_{n=0}^{\infty} \lambda^n c_f^{(n)}(t) \qquad \dot{c}_f(t) = \sum_{n=0}^{\infty} \lambda^n \dot{c}_f^{(n)}(t)$$

$$\sum_{n=0}^{\infty} \lambda^n \dot{c}_f^{(n)}(t) = \frac{1}{i\hbar}\sum_k \left\{\lambda \sum_{m=0}^{\infty} \lambda^m c_k^{(m)}(t)\right\}\langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

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And this is the matrix element which is of importance, so you get the expression for the rate coefficient, this is the coefficient and this is the rate at which it is changing with time. Now, we again do a perturbation expansion of this coefficient, because in the perturbation theory you expect that, this coefficient is expressible in a power series of the order of parameter lambda. Lambda is the perturbation order parameter, so you will have certain zero th order approximation to that, and first order approximation and so on.

And depending on how much detail you want to put into your perturbation theory analysis, you can do either first order perturbation theory, a second order perturbation theory and so on. So, you have an expansion in this order parameter, so here I have expanded this, this coefficients c in terms of this perturbation order parameter, which is just a mathematical construct in our moral. Eventually we will be interested in only limiting conditions lambda equal to 0, is no perturbation lambda equal to 1 is a full perturbation, so those are the only two conditions of physical importance.

So, we find what is a the rate at which this coefficient changes with times, so you get lambda is an order parameter which is time independent, and you get the time dependent. So, the doted represents differentiation with respect to time, and now you can plug in these expansions, in this expression that we got from first order perturbations. So, you got lambda on both sides of this equation, and certainly your analysis must be independent of lambda, it cannot depend on lambda, because lambda is just a mathematical order parameter that you constructed.

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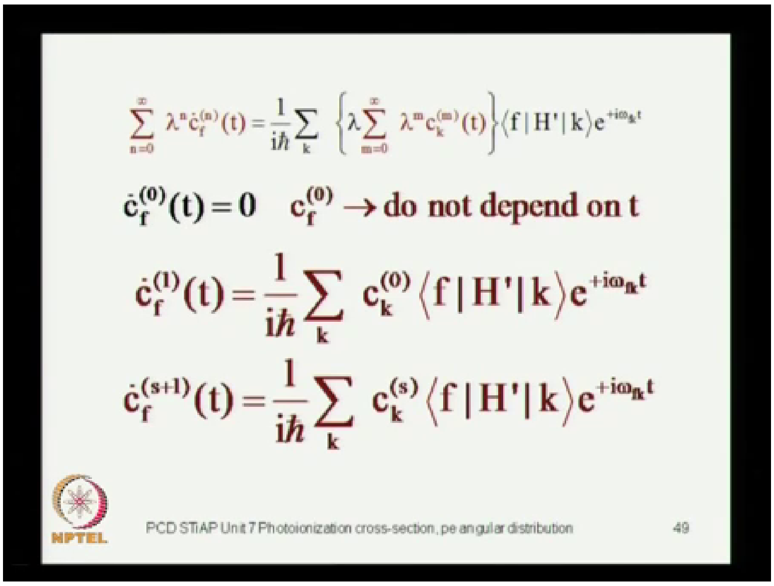

$$\sum_{n=0}^{\infty} \lambda^n \dot{c}_f^{(n)}(t) = \frac{1}{i\hbar}\sum_k \left\{\lambda \sum_{m=0}^{\infty} \lambda^m c_k^{(m)}(t)\right\}\langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

$$\dot{c}_f^{(0)}(t) = 0 \quad c_f^{(0)} \rightarrow \text{do not depend on t}$$

$$\dot{c}_f^{(1)}(t) = \frac{1}{i\hbar}\sum_k c_k^{(0)}\langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

$$\dot{c}_f^{(s+1)}(t) = \frac{1}{i\hbar}\sum_k c_k^{(s)}\langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

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So, you expect that terms corresponding to the same powers of lambda on the right hand side and the left hand side are equal, so that is the necessary condition, which you can apply very comfortably, and by setting in the powers the terms which come as coefficients of corresponding powers of lambda. When you take the 0th power of lambda, you get the 0th order coefficient to be independent of time, it is time derivative vanishes d c by d t of these 0th order coefficient vanishes not surprisingly.

Because, these will certainly not depend on time, but then when you will do the same for a first order terms you get an expression for the rate at which this coefficient changes with time, in terms of this matrix element. And now it is in terms of all the other coefficients, which belong to the unperturbed problem, so you can really go ahead and use perturbation theory and get this particular factor.

So, you can continue this and by induction in get the expression for the time derivative of this coefficient for the s plus 1 th term, in terms of the previous one, and you can get all of these terms in this perturbation theory. Of course, one assumes in this that the perturbation actually converges, perturbation theory can be used whenever you cannot solve the problem exactly. But, there are a number, so conditions which have to be satisfied, first of all the perturbation has to be really small compared to the unperturbed Hamiltonian. But, then it is also taken for granted when you apply perturbation theory, that the perturbation series will actually converge, which is not always really the case. So, you do run into complex situations in real systems, when you cannot use perturbative methods and you have to use some other methods.

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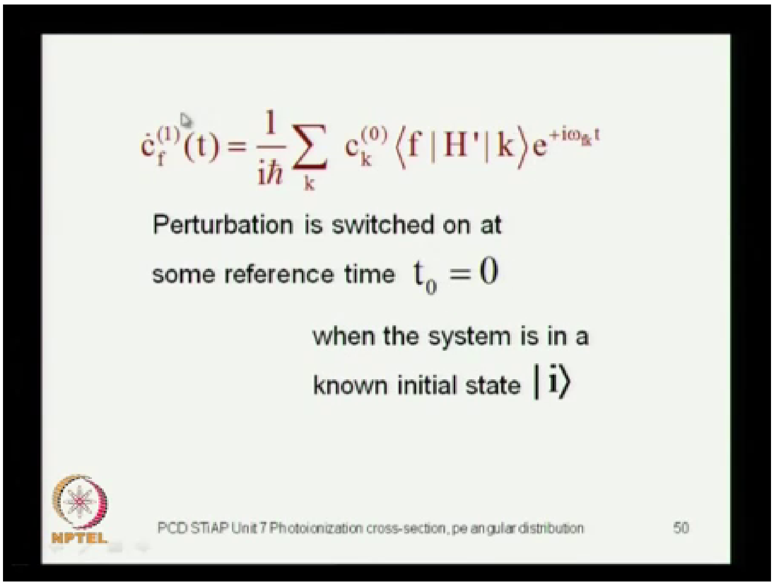

$$\dot{c}_f^{(1)}(t) = \frac{1}{i\hbar}\sum_k c_k^{(0)} \langle f|H'|k\rangle e^{+i\omega_{fk}t}$$

Perturbation is switched on at

some reference time $t_0 = 0$

when the system is in a

known initial state $|i\rangle$

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But here, we work with in the domain of first order perturbation theory, and we presume that the perturbation is switched on at a certain instant of time which is take as 0, so t 0 is equal to 0 at this particular instant of time. And at that this instant of time, we presume that the system is particular known initial eigen state, what it means is that out of all of these infinite coefficient c k 0, there is only one coefficient which is equal to 1, and all the other coefficients are 0.

Because, that is the initial state which we presume as a known state, when that this system at the, when you turn on the potential the system is in a given quantum state, then you know that the expansion coefficient for that particular state is exactly equal to 1, because the entire probability is contained in that particular state. So, you presume that the system is in an known initial state i, which means that this coefficient is equal to 1, if k is equal to i and it is equal to 0, if k is not equal to 1, that is what it means. And you can plug in this chronicle delta in this expansion, and then you get a single term and the right hand side.

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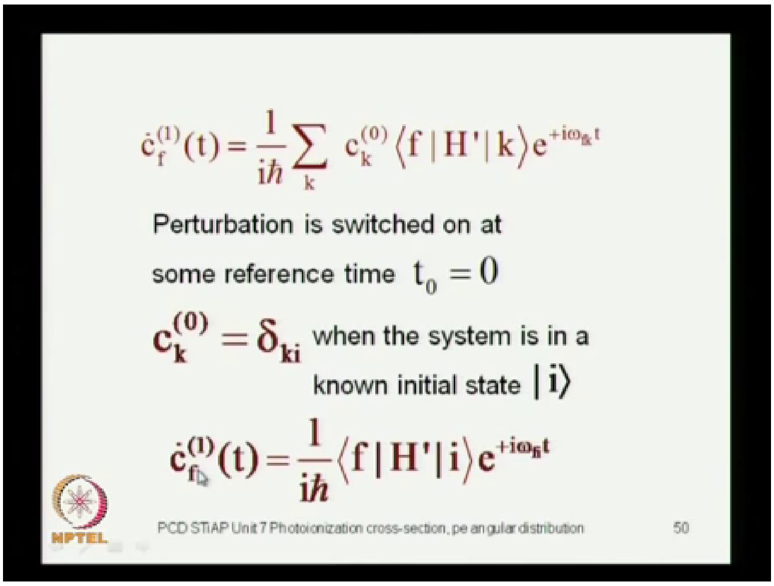

$$\dot{c}_f^{(1)}(t) = \frac{1}{i\hbar}\sum_k c_k^{(0)} \langle f \,|\, H' \,|\, k \rangle e^{+i\omega_{fk} t}$$

Perturbation is switched on at some reference time $t_0 = 0$

$c_k^{(0)} = \delta_{ki}$ when the system is in a known initial state $|\, i \rangle$

$$\dot{c}_f^{(1)}(t) = \frac{1}{i\hbar} \langle f \,|\, H' \,|\, i \rangle e^{+i\omega_{fi} t}$$

So, inside of this summation over k you get only one term corresponding to the initial state k equal to i, so this the expression that you get for the rate at which this coefficient will change with time. And that will change tell you the probability of occupancy of that level, because the probability amplitude is the measure, this coefficient is a measure of how the state is occupied at a given instant of time t.

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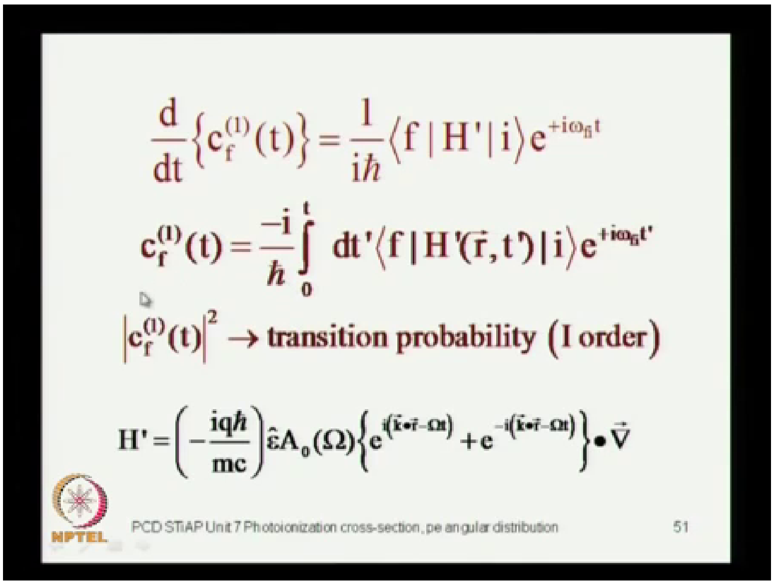

$$\frac{d}{dt}\left\{c_f^{(1)}(t)\right\} = \frac{1}{i\hbar}\langle f \,|\, H' \,|\, i\rangle e^{+i\omega_{fi}t}$$

$$c_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt'\langle f \,|\, H'(\vec{r},t') \,|\, i\rangle e^{+i\omega_{fi}t'}$$

$$\left|c_f^{(1)}(t)\right|^2 \rightarrow \text{transition probability (I order)}$$

$$H' = \left(-\frac{iq\hbar}{mc}\right)\hat{\varepsilon}A_0(\Omega)\left\{e^{i(\vec{k}\bullet\vec{r}-\Omega t)} + e^{-i(\vec{k}\bullet\vec{r}-\Omega t)}\right\}\bullet\vec{\nabla}$$

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So, you take the derivative of this coefficient and this is the equation that we have got, so you integrate this, you integrate it overtime time t. And you get a measure of the probability itself, which is just the modulus square of the probability amplitude, which will give you a measure of the transition probability to the state f from the state i. And this transition probability is the first order transition probability, it is effected by a certain perturbation, which we have already introduced earlier.

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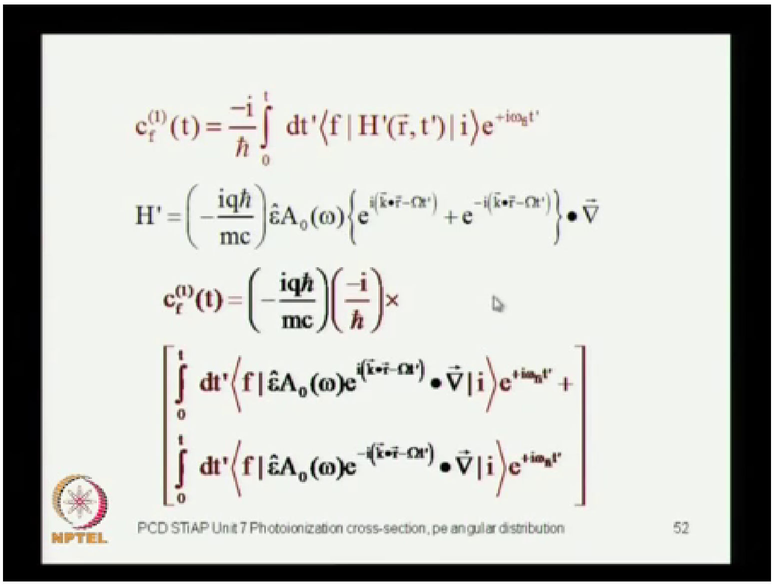

$$c_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt'\langle f \,|\, H'(\vec{r},t') \,|\, i\rangle e^{+i\omega_{fi}t'}$$

$$H' = \left(-\frac{iq\hbar}{mc}\right)\hat{\varepsilon}A_0(\omega)\left\{e^{i(\vec{k}\bullet\vec{r}-\Omega t')} + e^{-i(\vec{k}\bullet\vec{r}-\Omega t')}\right\}\bullet\vec{\nabla}$$

$$c_f^{(1)}(t) = \left(-\frac{iq\hbar}{mc}\right)\left(\frac{-i}{\hbar}\right)\times$$

$$\left[\begin{array}{l}\int_0^t dt'\left\langle f \,|\, \hat{\varepsilon}A_0(\omega)e^{i(\vec{k}\bullet\vec{r}-\Omega t')}\bullet\vec{\nabla} \,|\, i\right\rangle e^{+i\omega_{fi}t'} + \\ \int_0^t dt'\left\langle f \,|\, \hat{\varepsilon}A_0(\omega)e^{-i(\vec{k}\bullet\vec{r}-\Omega t')}\bullet\vec{\nabla} \,|\, i\right\rangle e^{+i\omega_{fi}t'}\end{array}\right]$$

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So, this is now our expression for the probability amplitude, and what you have in this are these integrals, there are these time dependent integrals, there is this integration from 0 to t the time is dummy label. So, I have used t prime instead of t, that you have integrated integration it from 0 to a certain time t, so the time label is now t prime. And the time dependent functions to be integrated out are contained over here, in this frequency dependent term; and there is also in this interaction Hamiltonian you have got a time dependent term here. So, these are the terms which are time dependent, and you will have to focus the time integration over those particular terms, the rest of it is a space integral. So, there are two integrations over here, integration over space, as well as integration over time.

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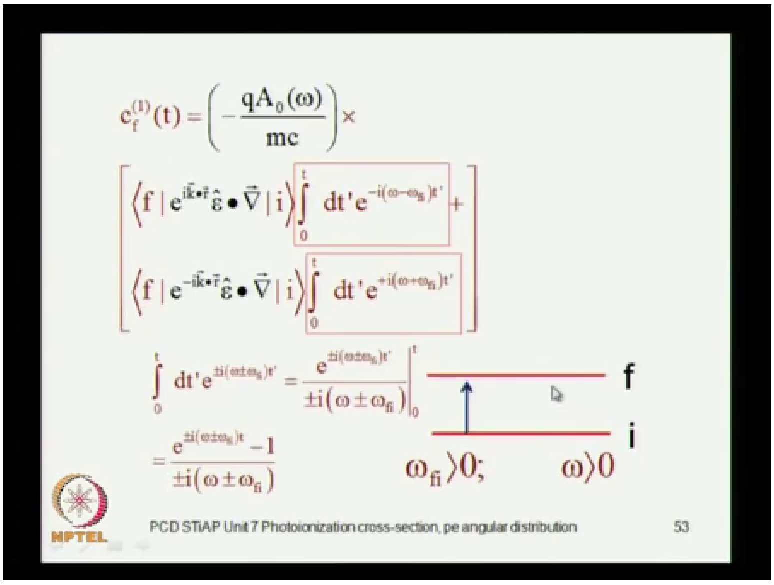

$$c_f^{(1)}(t) = \left(-\frac{qA_0(\omega)}{mc}\right)\times$$

$$\left[\left\langle f\,|\,e^{i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle \boxed{\int_0^t dt' e^{-i(\omega-\omega_{fi})t'}} + \left\langle f\,|\,e^{-i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla}\,|\,i\right\rangle \boxed{\int_0^t dt' e^{+i(\omega+\omega_{fi})t'}}\right]$$

$$\int_0^t dt' e^{\pm i(\omega\pm\omega_{fi})t'} = \left.\frac{e^{\pm i(\omega\pm\omega_{fi})t'}}{\pm i(\omega\pm\omega_{fi})}\right|_0^t$$

$$= \frac{e^{\pm i(\omega\pm\omega_{fi})t} - 1}{\pm i(\omega\pm\omega_{fi})}$$

$\omega_{fi} \rangle 0; \quad \omega \rangle 0$

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So, let us look at the time integrals now, and the time integrals are essentially these functions as you can see very easily from the previous term, I pointed out that there is a term here, there is a frequency omega t prime over here, and there is a omega t prime over here. This omega as got a subscript f i which comes from the energy difference between the final state and the initial states, so it is a natural frequency between those two states.

So, here this omega is a frequency of the radiation field, you have to subtract from it the frequency corresponding to the energy difference between the initial state and the final state, and these are the two time integrals to be evaluated. So, one is with a minus sign and the other with a plus sign, so here we handle both of them together, the one is with the plus sign and there is one with minus sign. And ((Refer Time: 39:58)) these are the results of the time integrals, so it is a very simple exponential function, so you can integrate it quite easily.

So, this is your integration with respect to time, now mind you omega is a certain frequency of the radiation field, which is a positive number. And omega f i will either be positive or negative depending on whether your looking, at the difference of energy between e f and e i, but are you subtracting the energy of e i from e f all the other way round, the sign of this will change. So, at a given frequency only one of the two things is going to take place, so at a given frequency you cannot have omega equal to omega f i, and also equal to omega mi equal to minus omega f i. So, we will focus our attention on absorption process, so out of these two integrals these two only one that we will you need to consider, corresponding to the absorption process.

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Google page, on 7th October 2012

Commemoration of Niels Bohr's 127th birthday

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And this while I was preparing these slides this was few days ago, the 7th of October some of you use the Google you might have seen this picture. And in this picture Google showed this transition, for an election jumping from here to here and this is not how quantum transitions take place. So, I thought that it was an interesting picture, which Google posted and I was very delighted to see, that was in commemoration of Niels Bohr 127th birthday, on 7th of October. But, that is not how the transitions takes place, and here we are talking about quantum transitions.

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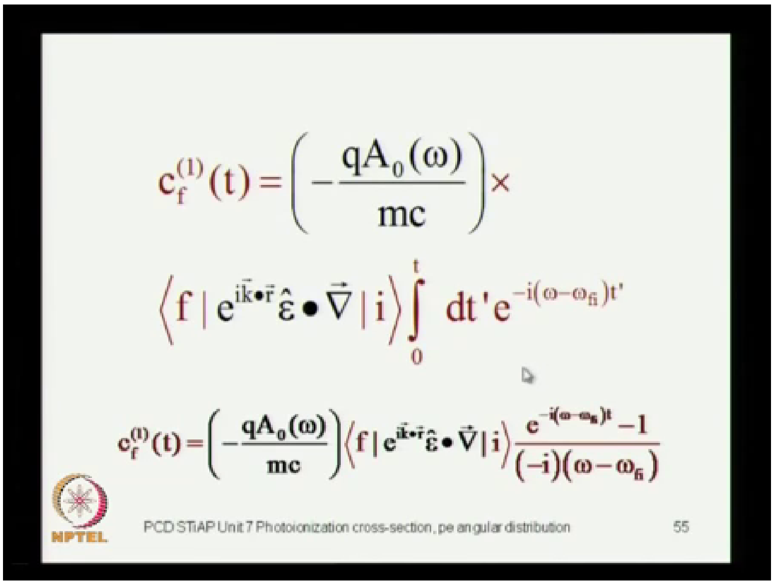

$$c_f^{(1)}(t) = \left(-\frac{qA_0(\omega)}{mc}\right) \times$$

$$\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i \right\rangle \int_0^t dt' e^{-i(\omega-\omega_{fi})t'}$$

$$c_f^{(1)}(t) = \left(-\frac{qA_0(\omega)}{mc}\right)\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i \right\rangle \frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}$$

So, the transition probability is given by this particular matrix element and a time integral and now, there is only one of the two time integrals that we have to consider. So, we evaluate this time integral and put the limits, which are over t prime, t prime equal to t prime equal to 0, and you get rather simple extractions that you are quite familiar with these integrals. So, this is the expression for the first order coefficient that you get from time independent perturbation theory.

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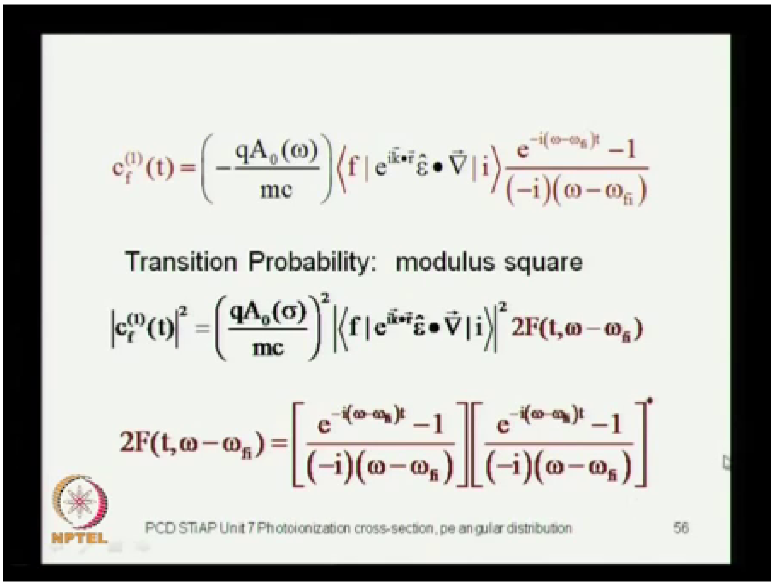

$$c_f^{(1)}(t) = \left(-\frac{qA_0(\omega)}{mc}\right)\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i \right\rangle \frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}$$

Transition Probability: modulus square

$$\left|c_f^{(1)}(t)\right|^2 = \left(\frac{qA_0(\sigma)}{mc}\right)^2 \left|\left\langle f \,|\, e^{i\vec{k}\bullet\vec{r}}\,\hat{\varepsilon}\bullet\vec{\nabla} \,|\, i \right\rangle\right|^2 2F(t,\omega-\omega_{fi})$$

$$2F(t,\omega-\omega_{fi}) = \left[\frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}\right]\left[\frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}\right]^*$$

Now, the transition probability itself is the square of the modulus, so let us do that, so this is the modules square and then you have this quantity multiplied by it is complex conjugate, which will go into the modulus square. So, that quantity is here multiplied by it is complex conjugate, and together this product is what I have written as twice F, this is just a simple notation you will recognize, why this twice a function F has been used. Because, once again you will find that the Dirac delta comes out of this particular form.

So, that is a reason this factor has been isolated, because it makes our treatment very easy, so in anticipation of that i have introduced this function F. And this is therefore, the definition of F, F is defined by this relation, so that twice F is equal to this quantity multiplied by it is complex conjugate, ((Refer Time: 43:32)). So, this is your expression for the modulus square of this first order coefficient.

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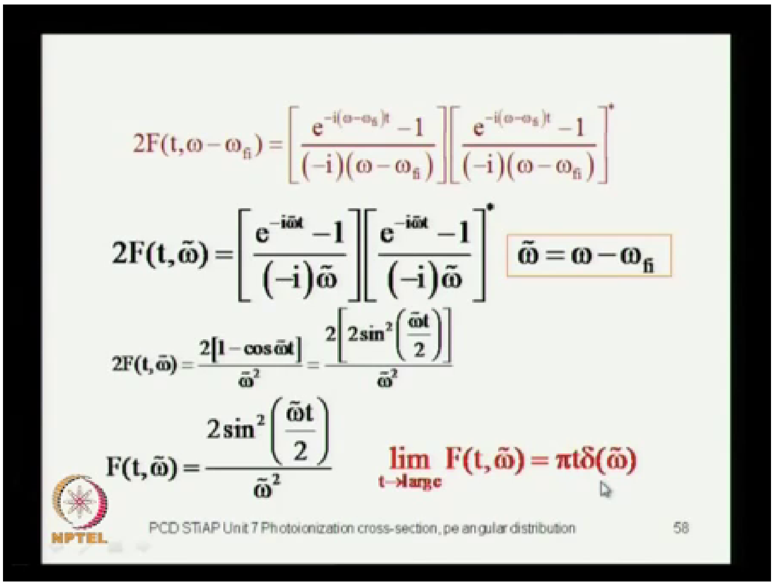

$$2F(t,\omega-\omega_{fi}) = \left[\frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}\right]\left[\frac{e^{-i(\omega-\omega_{fi})t}-1}{(-i)(\omega-\omega_{fi})}\right]^*$$

$$2F(t,\tilde{\omega}) = \left[\frac{e^{-i\tilde{\omega}t}-1}{(-i)\tilde{\omega}}\right]\left[\frac{e^{-i\tilde{\omega}t}-1}{(-i)\tilde{\omega}}\right]^* \qquad \boxed{\tilde{\omega}=\omega-\omega_{fi}}$$

$$2F(t,\tilde{\omega}) = \frac{2[1-\cos\tilde{\omega}t]}{\tilde{\omega}^2} = \frac{2\left[2\sin^2\left(\frac{\tilde{\omega}t}{2}\right)\right]}{\tilde{\omega}^2}$$

$$F(t,\tilde{\omega}) = \frac{2\sin^2\left(\frac{\tilde{\omega}t}{2}\right)}{\tilde{\omega}^2} \qquad \lim_{t\to large} F(t,\tilde{\omega}) = \pi t\delta(\tilde{\omega})$$

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This is our definition of twice F, and mean we will be interested in transitions near the resonant frequency, which is the frequency difference between the initial state and the final state. So, e f minus e i is the energy difference divided by h cross will give you the resonant frequency. And this difference between omega and this resonant frequency, whatever little difference there may be there, is what I have write as omega tilde.

So, it is this difference which comes in both of these terms, and this function if you just work out this product of the complex conjugates, you find that it is given by this sign square theta over omega delta square term, which some of you perhaps recognize it as a delta function already. So, this has got the form of the delta function and that is the advantage of introduction it, so this is pi t times delta omega. This is the omega tilde which is actually the between the frequency of the radiation field, and the energy difference divided by h cross between the two levels.

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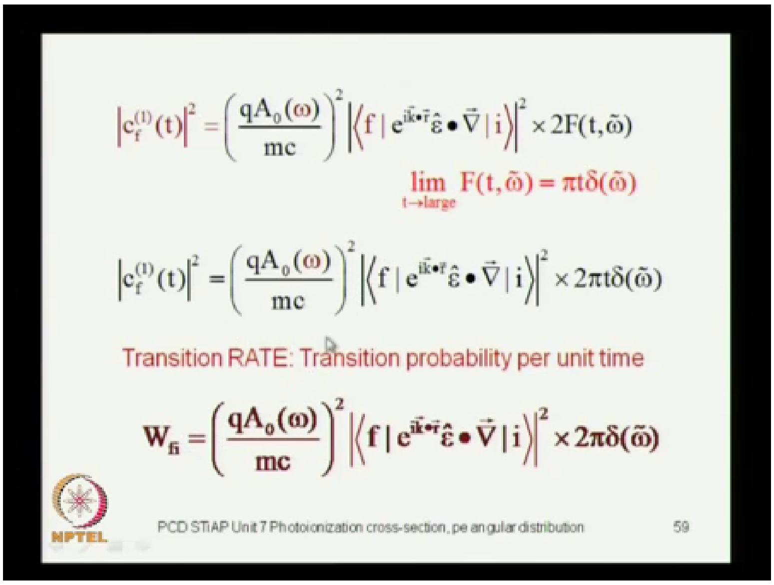

$$|c_f^{(1)}(t)|^2 = \left(\frac{qA_0(\omega)}{mc}\right)^2 \left|\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle\right|^2 \times 2F(t,\tilde{\omega})$$

$$\lim_{t\to \text{large}} F(t,\tilde{\omega}) = \pi t\delta(\tilde{\omega})$$

$$|c_f^{(1)}(t)|^2 = \left(\frac{qA_0(\omega)}{mc}\right)^2 \left|\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle\right|^2 \times 2\pi t\delta(\tilde{\omega})$$

Transition RATE: Transition probability per unit time

$$W_{fi} = \left(\frac{qA_0(\omega)}{mc}\right)^2 \left|\langle f|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\bullet\vec{\nabla}|i\rangle\right|^2 \times 2\pi\delta(\tilde{\omega})$$

So, this is now the modulus square of the coefficient, notice that there is a time dependent over here. So, if you take the transition rate which is the transition probability per unit time, you will differentiate this with respect to time, and that twice pi t when you differentiate with respect to time t will go away and you will get the transition rate which has been written as W, this is the transition rate it has got this square factor q a over m c square.

Then, it has got the square of this modulus of the transition matrix element, this is the matrix element for transition that this interaction induces a transition from the state i to the state f. And then there is this trice at times Dirac delta function, you will expect this to be related to the absorption coefficient. And earlier in our class day, I had asked you to look at the dimensions for sigma, I had asked you to look at the dimensions for q over i and ultimately the expression that you get from this must agree, with even you should get the exact correspondence, the exact dimensional equivalence.

So, it is a good exercise to find, what exactly is the dimension of W and good idea to get it from first principles plug it the dimension of q, plug in the dimension of A, plug in the dimension of m, plug in the dimension of c, get it first principles and make sure that you do not mess out any term.

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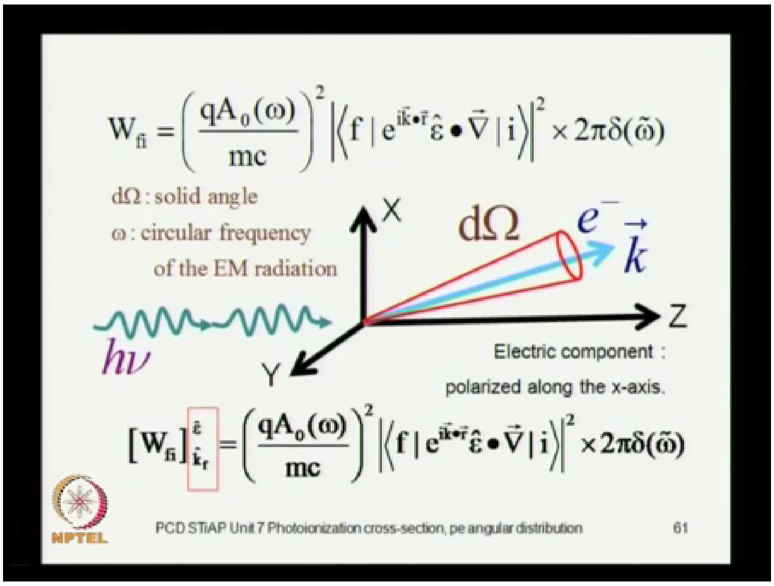

$$W_{fi} = \left(\frac{qA_0(\omega)}{mc}\right)^2 \left|\langle f | e^{i\vec{k}\bullet\vec{r}} \hat{\varepsilon} \bullet \vec{\nabla} | i \rangle\right|^2 \times 2\pi\delta(\tilde{\omega})$$

dΩ : solid angle

ω : circular frequency of the EM radiation

Electric component : polarized along the x-axis.

$$[W_{fi}]^{\hat{\varepsilon}}_{\hat{k}_f} = \left(\frac{qA_0(\omega)}{mc}\right)^2 \left|\langle f | e^{i\vec{k}\bullet\vec{r}} \hat{\varepsilon} \bullet \vec{\nabla} | i \rangle\right|^2 \times 2\pi\delta(\tilde{\omega})$$

So, this is the physical process that we are talking about, and we have found an expression for the transition rate, which is given by this expression. Now, the process we have considered is the following, we have considered the electric field to be polarized along the x axis. So, this is for a given direction of polarization, which is the unit vector epsilon, epsilon carrot and then we also considered a particular photoelectron ejection in which an exit channel was identified to be along the direction, of the photoelectron way vector k.

So, I carry this information as superscript and subscript on this transition rate, because this transition rate has been arrived at for a particular process, that we have considered. When we consider un polarized light or when we consider possible photoelectron ejection and some of the other directions also you need to integrate over these angels. So, this is some information that you have to keep track of, that we have considered the electric component to be polarized along the x axis, and the photo electron ejection to have taken place along the momentum direction k.

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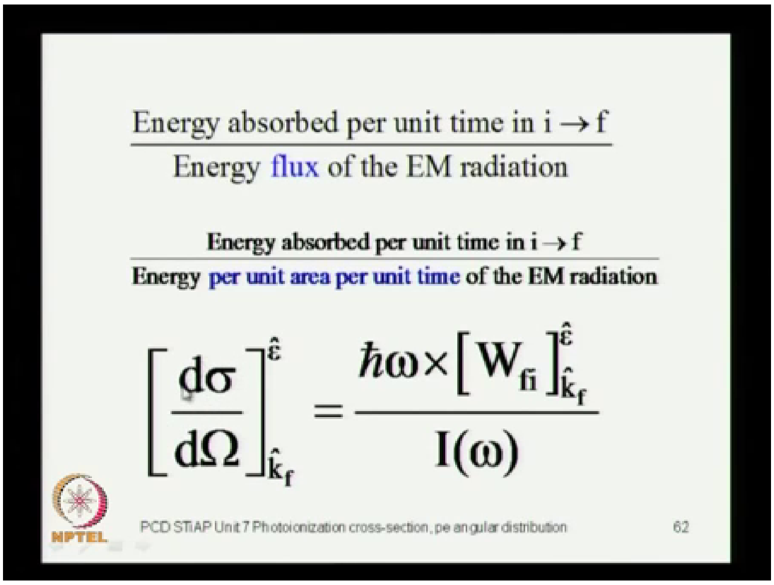

$$\frac{\text{Energy absorbed per unit time in } i \to f}{\text{Energy flux of the EM radiation}}$$

$$\frac{\textbf{Energy absorbed per unit time in } i \to f}{\textbf{Energy per unit area per unit time of the EM radiation}}$$

$$\left[\frac{d\sigma}{d\Omega}\right]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{\hbar\omega \times \left[W_{fi}\right]_{\hat{k}_f}^{\hat{\varepsilon}}}{I(\omega)}$$

Now, our interest will be in getting an expression for the energy absorbed per unit time in this process, but we need to normalize it with respect to the energy flux in the electromagnetic radiation. So, we need to find what is the energy absorb per unit time, and we have to get the energy flux, which is the energy per unit area per unit time of the electrometric radiation. So, this is what gives us the differential cross section, it is differential cross section, because it is with reference to photoelectron ejection in a particular angle.

So, there is certain solid angle which will contain the direction of photo ejection, and this d omega is a solid angle, this is with reference to this polarization vector of the electromagnetic field, and the direction of ejection of the photoelectron. And the energy absorbed will be just this rate that we got in our previous slide, so this rate must be multiplied by the energy itself, which is h cross omega. And you have divide it by the intensity of the field which is energy per unit area per unit time.

So, this will give you the expression for the cross section for the photoionization process, now once the dimensions of this quantity, these dimensions multiplied by energy dimensions divided by the dimensions of energy, must again give you the correct dimensions for the cross section. So, that is a small exercise for you now you need to find what is this intensity, intensity at a frequency omega.

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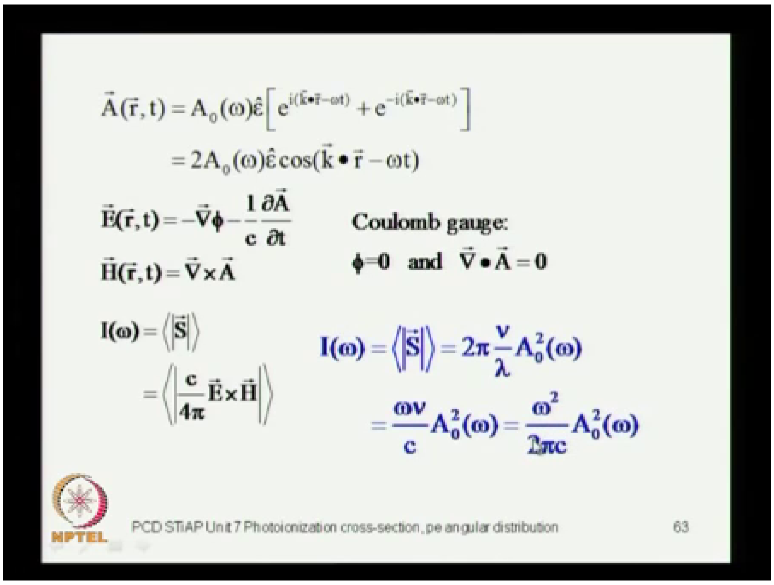

$$\vec{A}(\vec{r},t) = A_0(\omega)\hat{\varepsilon}\left[e^{i(\vec{k}\bullet\vec{r}-\omega t)} + e^{-i(\vec{k}\bullet\vec{r}-\omega t)}\right]$$

$$= 2A_0(\omega)\hat{\varepsilon}\cos(\vec{k}\bullet\vec{r}-\omega t)$$

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}$$

$$\vec{H}(\vec{r},t) = \vec{\nabla}\times\vec{A}$$

Coulomb gauge:

$\phi=0$ **and** $\vec{\nabla}\bullet\vec{A}=0$

$$I(\omega) = \left\langle\left|\vec{S}\right|\right\rangle = \left\langle\left|\frac{c}{4\pi}\vec{E}\times\vec{H}\right|\right\rangle$$

$$I(\omega) = \left\langle\left|\vec{S}\right|\right\rangle = 2\pi\frac{v}{\lambda}A_0^2(\omega) = \frac{\omega v}{c}A_0^2(\omega) = \frac{\omega^2}{2\pi c}A_0^2(\omega)$$

So, how do you get the intensity, so you go the vector field which is given by this expression here, this is the cosine function. And in terms of the vector field you can get the intensity, because the electric intensity is given by del A by del t in the coulomb gauge phi is equal to 0. So, the electric intensity is just the rate of change of the magnetic vector potential divided by c, that is the Gaussian's unit that the using and then the magnetic field is the curl of A.

So, this is the Gaussian, I am not using the psi, so that is the most common system of units and atomic physics. So, the intensity is given, then by the average value of the pointing vector and you have got E which you can get from A, you get H from the curl of A, so all you have to do is to evaluate this cross product get the pointing vector, and get it is average value over one time period. And that will give you the electric intensity, which turns out to be omega square over twice pi c A 0 square, that is how it comes out to be related to the square of the amplitude of the wave, but there are the other factors, and you cannot ignore them.

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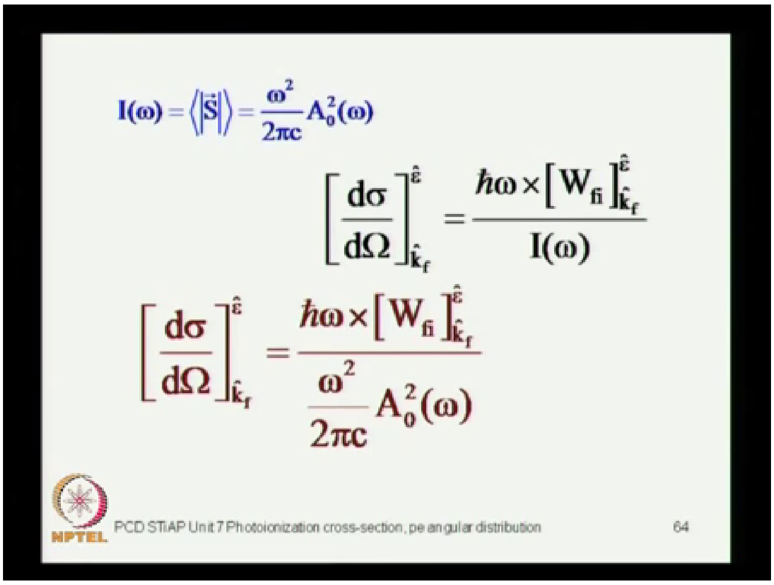

$$I(\omega) = \left\langle |\vec{S}| \right\rangle = \frac{\omega^2}{2\pi c} A_0^2(\omega)$$

$$\left[\frac{d\sigma}{d\Omega}\right]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{\hbar\omega \times \left[W_{fi}\right]_{\hat{k}_f}^{\hat{\varepsilon}}}{I(\omega)}$$

$$\left[\frac{d\sigma}{d\Omega}\right]_{\hat{k}_f}^{\hat{\varepsilon}} = \frac{\hbar\omega \times \left[W_{fi}\right]_{\hat{k}_f}^{\hat{\varepsilon}}}{\frac{\omega^2}{2\pi c} A_0^2(\omega)}$$

So, the intensity is given by this expression and you can, then plug in this expression for the intensity, in the expression for the photoionization cross section. And this is what gives you the complete expression for the photoionization differential cross section, for photoionization in particular direction k f, when the incident light is polarized along the unit vector epsilon. So, I will conclude the discussion over here today, we will continue from here in the next class.

And we will then extend this to the expression for the total cross section for photoionization, and we will also integrate over all possible direction, and different polarization states, there is any question I will be happy to take.

Student: Omega square minus omega not square, that you I mean that when gamma tends to 0, that you said Dirac delta function, but when you applied in that particular integration, we never use the fact that gamma is

No, the gamma which was used in that expression, refer to see it is coming from damping and remind yourself of damping is, because whenever you say that energy is lost, because fiction less. Fiction is of course, not an elementary force, elementary force is only electromagnetic gravity and so on, and they are all conservative. So, strictly speaking there can be no energy dissipation, which is good that energy, that is why energy is really conserved. Now, the reason damping comes in is because there is dissipation taking place, only because you have not set up the problem comprehensively, you do not have the atom to be completely an isolated system.

See you have solved the problem, your done the quantum mechanics of the hydrogen, it really takes me back to the question, which I raised in the class, and I asked you to think it over. That if you have an atomic system in an exited state, it as no business to decay at all, it should stay there forever, it should have infinite life. Why does it decay at all, why does an exited state of an atom decay, the exited state is also an eigen state, it is a stationary eigen state. Or at least if it is a stationary eigen state, this stationary means, that del rho by del t vanishes.

The probability density is not a function of time and therefore, the system will have infinite life, I am sure some of you will going to have this question in the viva exam, that why does an exited state of an atom decay at all. It is not meant to decay at all, if it is an eigen state of a stationary problem, the reason it decays is because you have really not solved the problem for the entire universe; you have separated the hydrogen atom, as if the hydrogen atom exists by itself, and that is the thing in the universe and that is the only thing in the universe, is nothing else.

But, then there is a rest of the universe, and there is this coupling between the rest of the universe at this, and that coupling is something that you missed out in formulating your original problem. Your original problem was set up for Hamiltonian, which is p square over 2 m plus a certain potential, that never made any reference to the interaction of this atomic system with the rest of the universe. This is the unspecified degree of freedom, which is what appears in your classical problems, when you have heat laws.

When there is an energy dissipation it is taking place, because you have not taken into account these other degrees of freedom, which are also interacting with the system. So, when you set up an equation of motion, what you call as the free body diagram in classical mechanics, you do not have these additional degrees of freedom. Likewise when you solve the Schrodinger equation for the hydrogen atom, there are these un specified degrees of freedom. And those unspecified degrees of freedom are responsible for the fact, that your exited state is strictly speaking not a stationary eigen state.

So, it has got a certain life time, and that life time is connected with the width that is uncertainty principal between energy and time. So, it is coming from a completely different considerations, not because you have two non commuting operators for energy and time, you do not an operator for time. Actually there have been some attempts in the early days of quantum mechanics to introduce of an operate of time there are some papers in that direction, but to the best of my knowledge it has not let to anything very concrete, and nothing very tangible has come out of it.

So, in quantum mechanics time is not treated as an operator it is a parameter, but there is an energy time and certainty, and as a result of this you have this states, which are coupled to the rest of the universe. Those are the unspecified degrees of freedom, and they manifest as damping, they cost of decay of excited state, so they correspond to the gamma d of the classical model. So, I introduce the classical model, only because the terminology of oscillator strengths is carried over into quantum mechanics.

And the oscillator strength terminology comes from this very classical, old fashion idea that an electron is bound in an atomic system with certain spring constants k, we certainly know that that is not the case, that is not really quantum mechanics, that does not fit into our model. But, it is precisely this idea which gives rights to the expression for the oscillator strength, in fact oscillator strength is defined in terms of this, if you recall the expression for oscillator strength.

So, the oscillator strength requires you to make use of this model, and unless one is really familiar with this, it is difficult to appreciate literature in this field papers by Fano and so on. So, that is the reason I spent some time discussion some time on classical model, and the idea of damping is related to the width of an exited state, because it decays any another question.

So thank you very much.