Quantum Mechanics and Molecular Spectroscopy
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Lecture – 13
Interaction Hamiltonian – Part 3

Hello, welcome to lecture number 13 of the quantum mechanics and molecular spectroscopy course. We will quickly go through the contents of lecture number 12 before we proceed with lecture number 13.

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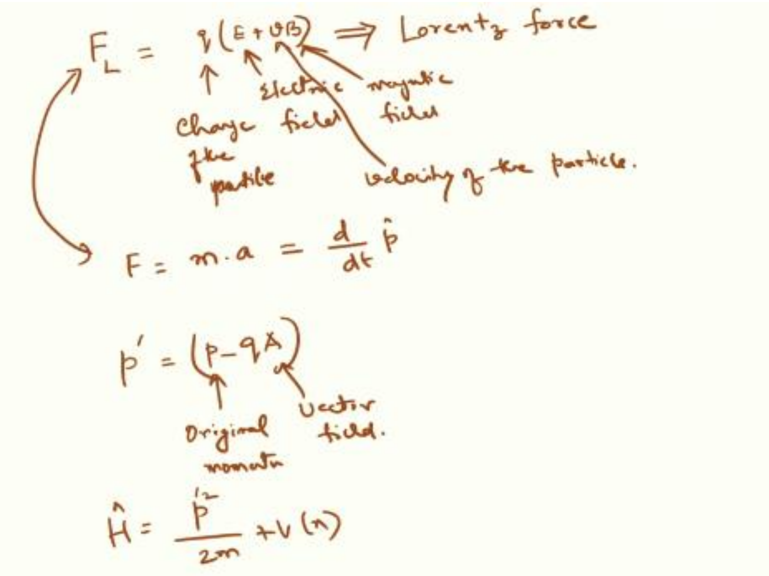

In the last class, I told that a charge particle when placed in electromagnetic radiation or the light will experience what is known as Lorentz force okay and Lorentz force FL = q times E + vB okay, where q is the charge of the particle, so this is the Lorentz force okay where q is the charge of the particle and E is the electric field, B is the magnetic field and v is the velocity.

And this in terms of classical mechanics force is given as mass into acceleration which could be written as d by dt of momentum okay. So, we use the analogy of this and converted the momentum P or P prime = P – qA where P is the original momentum and A is the vector field okay. Having done this, then we cast the total Hamilton H as P prime square by two 2m + V of x, we consider only in the Vx direction.

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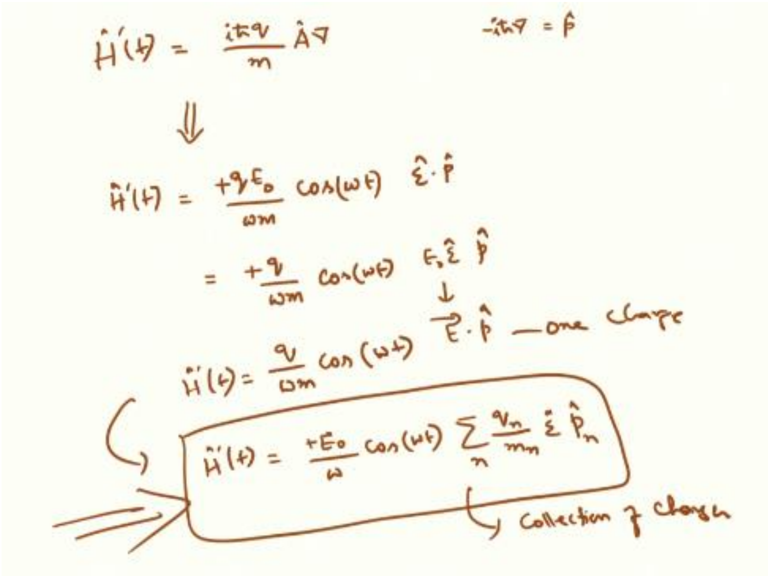

After doing the necessary math, we came across the equation in which H prime of t is given by ih bar q by m A del okay that is your but –ih bar del is nothing but operator P okay. Then we could condense this equation to finally H prime of t = –q E0 by omega m Cos omega t E dot P okay. So, this could be written as –q by, sorry plus, there was a + omega m Cos omega t and you know E0 into E P and this E0 into E can be written as E.

So q by omega m Cos omega0 E dot P. So, this is H prime of t okay, but in the case of particles which are atom or a molecule which has large number of particles, so which all of the charge particles will interact with the light. So this H prime t, this is for one charge, and when for collection of charges will turn out to be minus, sorry + E0 by omega m Cos omega t sigma over n okay qn mn.

Sorry this is not needed because m is changing, going to be different for different particles mn P okay because p is going to be momentum of the associated particle. So this is for collection of charges okay. So, we will start this lecture with this equation.

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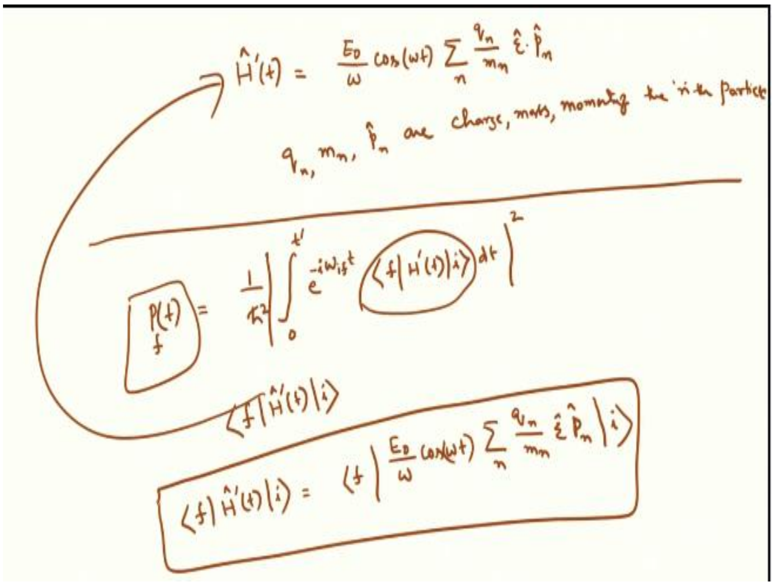

So what we have? At the end of the last class we had just H prime of t = E0 by omega Cos omega t sigma over n qn mn epsilon P okay where qn, mn, Pn are charge, mass, momentum of the nth particle okay. So this is what we have. Now if you go back to the coefficient or the probability, your P of t that is the probability of f = 1 over h bar square integral or modulus of integral 0 to t prime e to the power of –i omega if t integral f H prime of t i dt modulus square okay.

That means we still have to evaluate this integral f H prime of t i. So unless this integral is evaluated, of course you cannot evaluate this P of t okay. Now to evaluate this integral, now we know the Hamiltonian, so we need to plug in this value of H prime of t okay. So your integral f H prime of t i is given by f E0 by omega Cos omega t sigma over n qn mn epsilon Pn i. So this is the integral that I need to evaluate okay.

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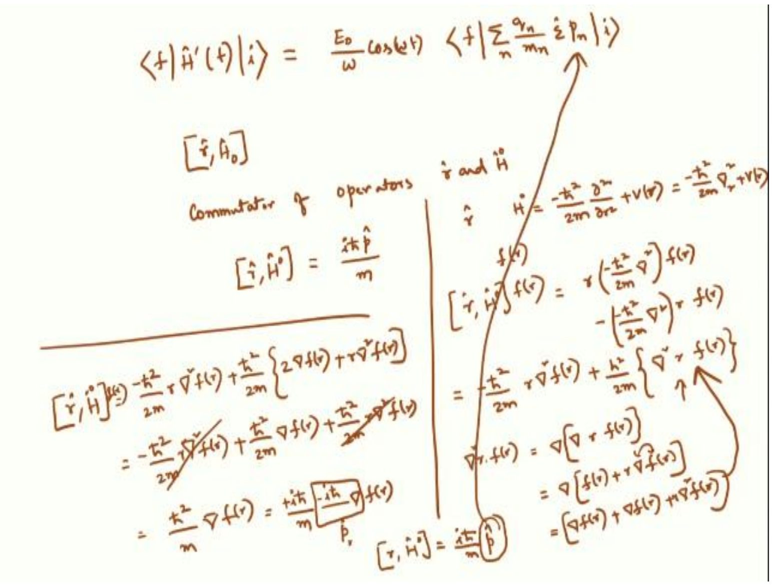

Now, I am going to slightly rewrite this equation or this integral f H prime of t i = now E0 by omega Cos omega t I will take it outside integral f because E0 is a constant, omega is a constant, Cos omega t is a constant as far as this integral is concerned f because f and i are the eigen function of the time-independent Hamiltonian okay f times sigma over n qn by mn epsilon Pn i okay.

Now to begin with we will start with slightly some other equation. So if I take a quantity called r, H0 commutator, that is the commutator of operators r and H0 okay, right. Now this can be evaluated at this commutator r, H0 can be evaluated to be ih bar P by m okay. Now, I am going to take a small detour and try to evaluate this commutator, but always remember the commutators are evaluated with respect to some function.

So if there is an r operator and there is H0 operator okay, H0 is along the direction of r, so this will be equal to –h bar square by 2m d square by dr square with some potential V of r okay that is your H0 okay. Now, then all of this will act on a function f of r. So let us evaluate the commutator. By the way this is also called –h bar square by 2m del r square + V of r okay. So now what you have to evaluate?

You have to evaluate r, H0 commutator with respect to f of r function okay. So this will be equal to r times –h bar square by 2m del square f of r – -h bar square by 2m del square r f r okay. Now take the first term, so that this is going to be –h bar square by 2m because that is constant r time del square f of r okay. Now the second one is this is minus of this minus, this will be plus, h bar square by 2m del square r f of r okay.

Now if you take this, I am just going to evaluate this, so del square r f of r this is equal to, but del is nothing but del-del, del square, so that is nothing but del of del r f of r. So one can first evaluate this, so this is nothing but del times, now this is a differential, del is nothing but d by dr, so the differential function, so first acts on r so it will give you 1, so we will get f of r okay.

Now second this will act on del f of r okay, so what you will get is + r times del f of r. Now again the second del acts on it or the second differential acts on, so you will get del f of r plus, now you have again a function, so this is one function and this is another function del of r is 1 okay. So we will get del f of r because that is 1 + del acting on del f of r giving me r into del square f of r okay.

So, now I am going to plug this in here, what you will get is, so what I am evaluating? I am evaluating r H0 commutator. So this is equal to –h bar square by 2m r del square f of r + h bar square by 2m, what do you have, del f r del f r, 2 del f r + this is r del square f of. Now if i expand this, this will be –h bar square by 2m r del square f of r + this 2 and this 2 will get canceled, we will get h bar square by 2m del f r + h bar square by 2m r del square f r.

I will see that this term and this term will get canceled. So this will be equal to h bar square by 2m del f r. So, this is nothing but this is = -ih bar, so there is no 2 here just m, by m multiplied by ih, so this is +i – ih bar by, so minus i square, minus into minus, plus ih bar del f of r, sorry finally you do not have f of r because it is evaluated with respect to f of r. So then you have to put f of r here as well.

So then your r, but this is nothing but P of r okay. So what you get r, H commutator will be equal to ih bar by m P okay. So, because now I want to use this P operator here okay.

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\begin{aligned}
\langle f|\hat{H}'(t)|i\rangle &= \frac{E_0}{\omega}\cos(\omega t)\,\langle f|\sum_n \frac{q_n}{m_n}\hat{\varepsilon}P_n|i\rangle \\
[r,\hat{H}^0] &= \frac{i\hbar p}{m} \\
&= \frac{E_0}{\omega}\cos(\omega t)\,\langle f|\sum_n q_n\hat{\varepsilon}\cdot\frac{\hat{p}_n}{m_n}|i\rangle \\
&= -\frac{iE_0}{\hbar\omega}\cos(\omega t)\,\langle f|\sum_n q_n\hat{\varepsilon}\,[r_n,\hat{H}^0]|i\rangle \\
&= \frac{-iE_0}{\hbar\omega}\cos\omega t\,\langle f|\sum_n (q_n\hat{\varepsilon}r_n\hat{H}^0 - q_n\hat{\varepsilon}\hat{H}^0 r_n)|i\rangle \\
&= \frac{-iE_0}{\hbar\omega}\cos\omega t\left\{\langle f|\sum_n q_n r_n\hat{\varepsilon}\hat{H}^0|i\rangle - \langle f|\sum_n q_n\hat{H}^0\hat{\varepsilon}r_n|i\rangle\right\} \\
&= \frac{iE_0}{\hbar\omega}\cos\omega t\left\{E_i\underbrace{\langle f|\sum_n q_n r_n\hat{\varepsilon}|i\rangle} - E_f\underbrace{\langle f|\sum_n q_n r_n\hat{\varepsilon}|i\rangle}\right\}
\end{aligned}
$$

So let us continue. So what was the equation that we had, this one okay. So f H prime of t i = E0 by omega Cos omega t acting on f sigma over n qn by mn Pn i and we found that r, H0 commutator is equal to ih bar P by m okay. Now what I am going to do this? So I am going to plug in it here. So this now will be equal to E0 by omega Cos omega t f sigma over n qn into Pn by mn okay. So Pn by mn is i.

So this is nothing but E0 by omega Cos omega t, so ih go on the other side that will i will become –ih. So you have h bar –i that is what you get okay. Sigma over f epsilon sigma, sorry f sigma over n qn epsilon n rn H0 i okay. So that is the new Hamiltonian when you have plugged in this value. So this will be equal to –i E0 by h bar omega Cos omega t into f ok. Now let us expand this commutator.

So this will be sigma over n qn rn H0 – qn H0 rn i okay, I have just expanded this commutator rn, H0 because that it will be rn H0 – H0 rn. So this will be equal to –i E0 by h bar omega Cos omega t okay. I will write it as two. Because there are 2 terms here, we can write it as 2 separate integrals. So f of sigma over n qn rn okay because r is just, now epsilon H0 acting on i – f sigma over n qn H0 epsilon rn i okay.

So now this H0 will act on i and give me Ei i. So this will now be equal to i E0 by h bar omega Cos omega t this H0 acting on i give me Ei i, so Ei f because Ei is a number f sigma over n qn rn epsilon i. Now this H0 will act on the other side because you know H0 is a Hermitian operator and we know the turnover rule. So if I use turnover, this H0 can act on f and give me Ef okay, complex conjugate of it.

But energies are always real, so complex conjugate of Ef star will be only Ef. So this will be – Ef integral f sigma over n qn rn i. Now you will see the integral in both cases is the same.

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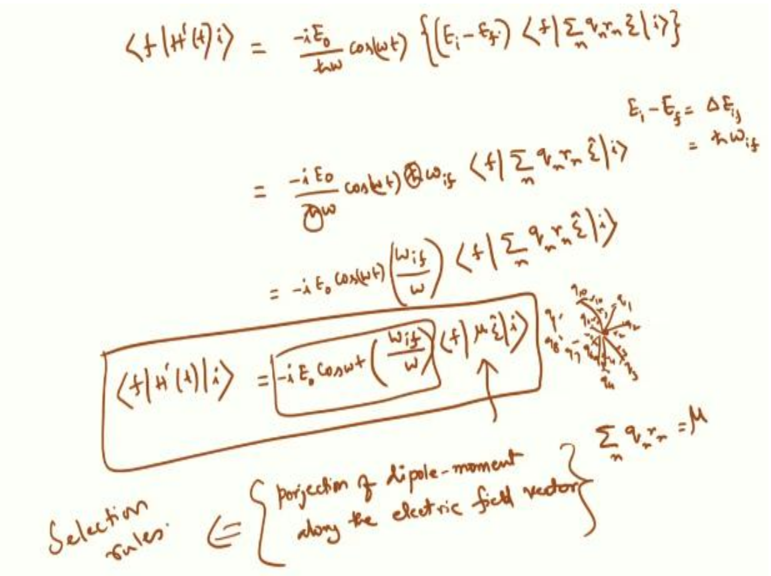

So essentially your f H prime of t i can be written as –E0 i by h bar omega Cos omega t into Ei – Ef into integral f sigma over n qn rn epsilon divided by i okay. Now what is Ei – Fi, Ef sorry, Ei – Ef = delta Eif, so this is nothing but h cross omega if. So this is nothing but this is equal to –i E0 h cross omega Cos omega t, this will be h bar omega if integral f sigma over n qn rn epsilon i okay.

Now this h bar omega and this h bars will get canceled, so what you will get is this –i E0 Cos omega t omega if by omega, so this is very important term okay remember, and f sigma over n qn rn i. Now for if there are charges like this distributed over some this one okay, so this is charge q1, this is charge q2, this is charge q3, q4, q5, q6, q7, q8, q9, q10, this is my center q11 and then you have radiuses r1, r2, r3, r4, r6, r11, r10, etc.

So what is this if I take, so this is a product of q and rn sum over okay. If you have charges distributed like that that will give you the dipole moment. So for n charges sigma over n qn rn should be equal to mu that is the dipole moment of the molecule okay. So that is nothing but is equal to –i E0 Cos omega t omega if by omega f mu epsilon i okay. Now, what is mu dot eps or mu epsilon?

Mu epsilon simply means that the mu has to have a dot product with along to the epsilon that is the electric field vector okay. So that is given by this equation. Now, one could understand okay if you forget these pre factors, this integral depends on the dipole moment of the atom or the molecule okay. By the way, dipole moment of atom I do not know because its permanent dipole moment is 0.

But dipole moment is not permanent dipole moment. You must understand mu is not equal to mu0, we will come to that it later sometime, but essentially the initial and final states will couple okay with respect to the projection of the dipole moment along the electric field vector. So this is nothing but the projection of dipole moment along the electric field vector okay.

And the projection of the dipole moment along the electric field vector determines the selection rules and this will lead to selection rules okay. We will stop it here for this class and continue in the next lecture.