Quantum Mechanics and Molecular Spectroscopy
Prof. G. Naresh Patwari
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 11
Interaction Hamiltonian – Part 1

Hello, welcome to lecture number 11 of the course quantum mechanics and molecular spectroscopy. As usual, we will start with a quick recap of the previous lecture and then proceed with the lecture number 11. In the previous lecture, we talked about the electric field and magnetic fields of the propagating light.

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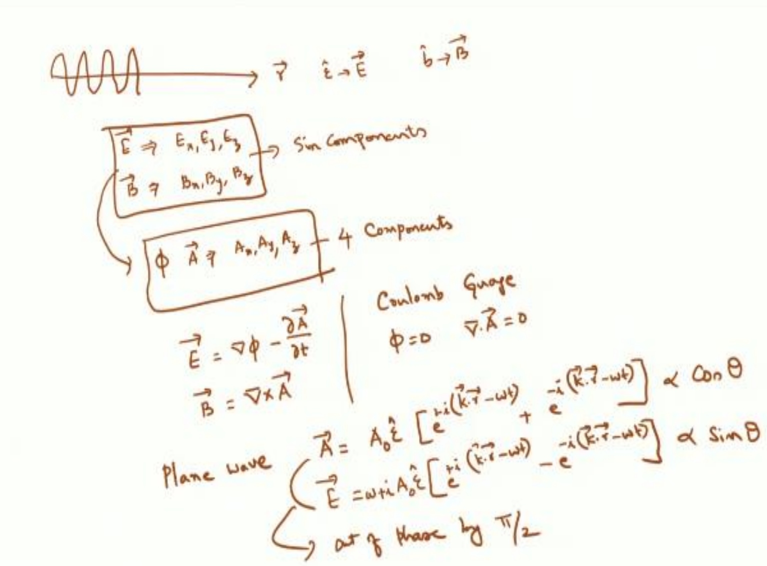

So, if a light is propagating along a direction r or let us say its vector is represented by r, then there is an electric field which has a direction e and the corresponding electric field is E and there is a magnetic field b with the corresponding direction okay. Now, there are 3 components of both electric fields and magnetic field. So, E will consists of Ex, Ey and Ez similarly the magnetic field will have 3 components that is b Bx, By and Bz okay.

But in Hamiltonian, we have potential and not the field, so we need to convert this into potentials. So, there is a transformation that takes the electric and magnetic field to scalar and vector potentials, phi is the scalar potential and there is a vector potential A, which will have 3 components Ax, Ay and Az. So, totally we have 4 components, 1 scalar potential and 3 vector potential, so 4 components.

And these 4 components must be reduced from the electric and magnetic fields which have 6 components and the relationship between the magnetic field or electric field with the vector and scalar potentials are E = del phi – dA by dt and B = del cross A okay. Now, what we will do is since we have to go from 6 components to 4 components, of course there is some redundancy. So, there are infinite ways one can have this transformation.

One of the transformations that we will call it as coulomb gauge in which we say phi = 0 and del dot A = 0. So, there are 6 components. So, we are reducing to 4 components with two criteria that are fixed okay. So therefore, now the transformation becomes easier okay. Now, in a plane wave notation, A is given as A = A0 and it will move in the same direction as electric field, this one into e to the power of –i k dot r – omega t, sorry it should be plus, + e to the power of –i k dot r – omega t okay.

Now this is exponential i theta + exponential –i theta, so this is proportional to Cos theta okay and you can see the electric field is a time derivative with respect to vector potential. So, E will be equal to –i A0, sorry or +i rather, e to the power of minus –i k into omega k dot r – omega t –e to the power of –i, so this should be plus k dot r – omega t. So, this should be proportional to Sin theta.

So, which means the vector potential A and the electric field E are out of phase with respect to each other by pi by 2. So they are out of phase by pi by 2 okay.

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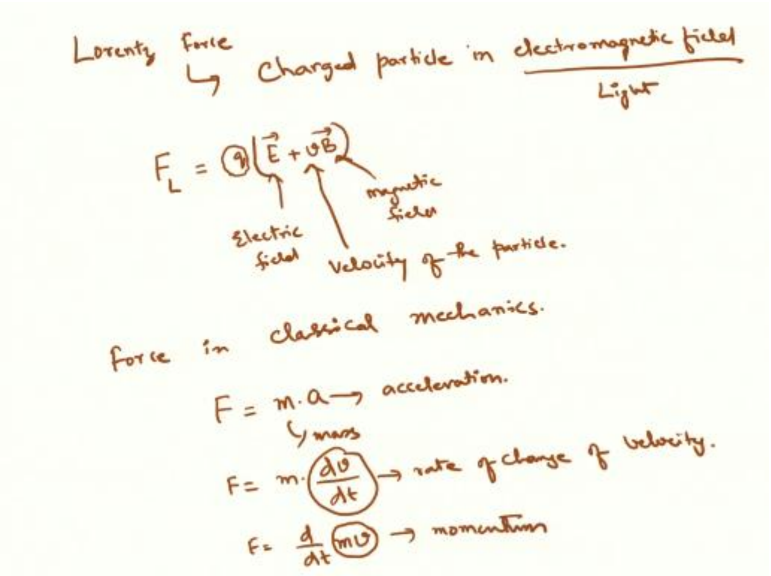

Now, let us get on to the contents of this lecture. For example, if you take a charged particle and you put it in the electric field or electromagnetic radiation that is light, then the charged particle experiences what is known as a Lorentz force okay. This Lorentz force is experienced by charged particle in electromagnetic field or just electromagnetic field is nothing but light. So, if I expose a charged particle to the light, then it feels a Lorentz force.

So, I will write Lorentz force as FL, this is equal to q times electric field + phi into B okay, where you know this is electric field and B is magnetic field, phi is the velocity of the particle okay. So, of course that will depend on which, that will depend on the charge q okay, so more the charge more will be the force. For atomic systems of course, atomic and molecular system the charge is fixed because the electrons have fixed charge okay.

Of course, nuclei could have a different charge which could be multiples of the electronic charge. Now, this is the force that is called Lorentz force, but let us take a small detour and think what is forts in terms of classical mechanics. What is force correspond? Force F = mass into acceleration okay. So, this is mass and this is acceleration okay. Now, acceleration is nothing but rate of change of velocity.

So this is nothing but F = m times dv by dt, this thing what, rate of change of velocity okay. Now mass is a fixed quantity, it is a number for a given particle. So one can write F = d by dt of mv okay. Now what is mv? Momentum? This is nothing but momentum okay.

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$$F = \frac{d}{dt}(mv) = \frac{d}{dt}p \Rightarrow \text{rate of change of momentum.}$$

$$F_L = q(E + vB)$$

$$F_L = qE \Rightarrow \text{Electric dipole approximation.}$$

$$\vec{E} = \underset{\substack{\uparrow \\ 0}}{\nabla\phi} - \frac{\partial\vec{A}}{\partial t}$$

$$= q\left(-\frac{\partial}{\partial t}\vec{A}\right)$$

$$\vec{E} = -\frac{\partial\vec{A}}{\partial t}$$

$$F_L = -\frac{d}{\partial t}(q\vec{A})$$

$$F = \frac{d}{dt}(p) \Rightarrow \text{rate of change of momentum}$$

$$p = -q\vec{A}$$

So, now force can be written as d by dt of mv that is nothing but d by dt of P. So force can also be reconsidered as rate of change of momentum. So this is nothing but the rate of change of momentum okay. Now let us get to the Lorentz force okay, FL = q times E + v times B. Now in general the magnetic field its magnitude is going to be is much smaller okay. So one can neglect okay and if you neglect that we get FL = qE okay.

This is called electric dipole approximation wherein we are only looking at the electric field of the electromagnetic radiation okay. So we are neglecting the magnetic field. Of course, if you are going to do spectroscopy like NMR or EPR, it is not going to be valid, but for a general spectroscopy terms like you know rotational, vibrational and electronic, this is valid okay. Now FL = q dot E okay.

Now, I can write this as q times –d by dt of A okay because E = del phi –dA by dt that is what we said you know and in the coulomb gauge you have d phi = 0. So which means E will turn out to be –dA by dt. Now if I write this your FL is equal to, of course q is a charge of a system, so that can be taken out, it is a constant with respect to time okay. So this can be written as –d by dt of qA okay.

Now this is force okay, Lorentz force is given by d by dt of –qA okay. Now, force as I said is equal to d by dt of P that is nothing but rate of change of momentum okay. Now if you compare these 2 forces, of course force is a force you know, whether it is of some mechanical origin or of electromagnetic origin, it is a force satisfy. Now, you can clearly see, by comparing these 2 equations you can see momentum P = –qA okay. This is the momentum that a charged particle will gain in a vector potential okay.

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$$\hat{H} = \frac{p^2}{2m} + \hat{V}(x)$$

$$p' = p + p(\text{electric field})$$

$$p' = (p - q\vec{A})$$

$$\hat{H} = \frac{p'^2}{2m} + \hat{V}(x)$$

$$\hat{H} = \frac{(p - q\vec{A})^2}{2m} + \hat{V}(x)$$

$$\hat{H} = \frac{\left(-i\hbar\frac{\partial}{\partial x} - qA\right)^2}{2m} + \hat{V}(x)$$

So, in your Hamiltonian H what do you have? We have P square by 2m + your potential V of x okay. Now, but P in this case is the velocity or the momentum that a particle has on its own, but the moment you put the charge particle in the electric field, then its momentum is going to get modified. So, your P prime will be equal to P + the newly attained momentum because of the electric field P and that is the perturbation that you have.

So, your P prime will now be equal to P – qA. So, your Hamiltonian H will be nothing but actually it should be P prime square by 2m + V x okay. Now let us write in terms of, this is not really the, so you have Hamiltonian, so you write the corresponding operator. So, this will be equal to P – qA square by 2m + V of x, why V of x because I told you that for this course the potential is generally independent of time okay.

So, this is equal to H into, now this will be nothing but what is your P, this is nothing but –ih bar d by dx that is the P – qA whole square by 2m + V of x, that is my Hamiltonian.

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$$\hat{H} = \frac{\left(-i\hbar\frac{\partial}{\partial x} - qA\right)^2}{2m} + \hat{V}(x)$$

$$= \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{q^2A^2}{2m} + \frac{i\hbar}{2m}\frac{\partial}{\partial x}qA + qA\frac{i\hbar}{2m}\frac{\partial}{\partial x}\right) + \hat{V}(x)$$

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{i\hbar}{2m}\frac{\partial}{\partial x}qA + \frac{i\hbar}{2m}qA\frac{\partial}{\partial x} + \frac{q^2A^2}{2m} + \hat{V}(x)$$

$$\hat{H} = \underbrace{\boxed{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x)}}_{\hat{H}^0} + \frac{i\hbar}{2m}\frac{\partial}{\partial x}qA + \frac{i\hbar}{2m}qA\frac{\partial}{\partial x} + \frac{q^2A^2}{2m}$$

$$\hat{H} = \hat{H}^0 + \frac{i\hbar}{2m}\frac{\partial}{\partial x}qA + \frac{i\hbar}{2m}qA\frac{\partial}{\partial x} + \frac{q^2A^2}{2m}$$

So when I write that, so Hamiltonian H = –ih bar d by dx, I am only looking in the one dimension case okay, one can generalize to 3 dimensions okay, – qA whole square p square by 2m + V of x. So this is nothing but A square + B square + 2AB. So A square will be –h bar square by 2m d square by dx square, A square, that is B square will be q square A square by 2m okay and 2AB okay or it cannot be 2AB because they are operator AB – PA okay.

In fact I can take a negative sign outside. So, this is equal to AB, this is minus and this is minus, so just AB. So, h bar + h bar, h bar by 2m, sorry ih bar by 2m okay d by dx of qA +

okay and if I multiply this, this will be qA times ih bar by 2m qA times d by dx okay, this whole times potential V of x okay. So your H will now be equal to –h bar square by 2m d square by dx square okay, –h square d square.

So this is q square by A square, so this will be + ih bar by 2m let us say d by dx of qA + ih bar by 2m qA d by dx + q square A square by 2m + V of x. Now, you will see this equation if you take the first term and the last term, this is nothing your normal Hamiltonian. So, H = –h bar square by 2m d square by dx square + V of x + ih bar by 2m d by dx of qA + ih bar by 2m qA d by dx + q square A square by 2m.

Now, this is nothing but your H0, the Hamiltonian of the original molecule. So, your H will now be equal to H0 + ih bar by 2m d by dx qA + ih bar by 2m qA d by dx + q square A square by 2 m okay.

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$$\hat{H} = \hat{H}^0 + \frac{i\hbar q}{2m}\frac{\partial}{\partial x}A + \frac{i\hbar q}{2m}A\frac{\partial}{\partial x} + \frac{q^2}{2m}A^2$$

$$\frac{\partial}{\partial x}A|\psi(x)\rangle = \frac{\partial A}{\partial x}\cdot\psi(x) + A\cdot\frac{\partial}{\partial x}\psi(x)$$

$$= \nabla\cdot\vec{A} + A\nabla$$

$\hookrightarrow$ Coulomb Gauge $\nabla\cdot\vec{A} = 0$

$$= A\nabla = A\frac{\partial}{\partial x}.$$

$$\hat{H} = \hat{H}^0 + \frac{i\hbar q}{2m}A\frac{\partial}{\partial x} + \frac{i\hbar q}{2m}A\frac{\partial}{\partial x} + \frac{q^2}{2m}A^2$$

$$= \hat{H}^0 + \frac{i\hbar q}{m}A\frac{\partial}{\partial x} + \frac{q^2}{2m}A^2$$

$$\hat{H} = H^0 + \frac{i\hbar q}{m}A\nabla + \frac{q^2}{2m}A^2$$

Now, let us evaluate the term. So, let me write down again the Hamiltonian H = H0 + ih bar by 2m d by dx of, q is a constant so we can take it out, A + h bar by 2m q A d by dx + q square by 2m A square okay. Now let us evaluate the term d by dx of A, but this is Hamiltonian, it has to be always evaluated with respect to some function okay, some functions psi of x.

So this is equal to, now there are product of, so that you will get dA by dx into psi of x + A times d by dx of psi of x okay. Now this is nothing but del dot A okay + A this is nothing but del. Now according to coulomb gauge del dot A = 0. So, this is nothing but A delta or this is nothing but A d by dx. So, your H = H0 + ih bar q by 2m d by dx of A that is nothing but A d by dx.

And there is another term which is similar to that is equal to ih bar q by 2m A d by dx + q square by 2m A square. So, this is nothing but H0 plus these two terms are equal, so two times. So, this will be ihq A d by dx + q square by 2m A square. So, this is nothing but H0 + ih bar q by m, sorry by m A del + q square by 2m A square okay.

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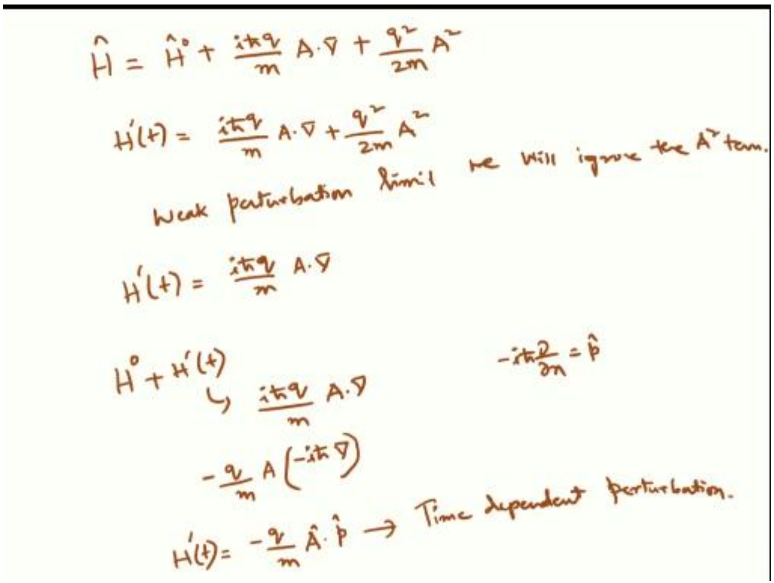

So, your Hamiltonian now comes out to be H = H0 + ih bar q by a dot del + q square by 2m A square okay. So that is the Hamiltonian that you are going to get. So which means your H prime of t should be equal to ih bar q by m A dot del + q square by 2m A square okay. Now in spectroscopy, the amount of light is very feeble, so that is called weak perturbation. In the weak perturbation limit, we will ignore the A square term.

Therefore, H prime of t will be equal to ih bar q by m A dot del that is your Hamiltonian or the perturbation Hamiltonian. So your total Hamiltonian is nothing but H0 + H prime t. So H0 is something that is the molecular Hamiltonian and your perturbation Hamiltonian time-dependent perturbation is just given by ih bar q by m A dot del okay. Now, I can slightly modify this, now we know the perturbation Hamiltonian.

So this is nothing but A q by m times –ih bar del okay. What is –ih bar del, –ih bar del is nothing but P okay, remember, –ih bar d by dx = operator P. So, this is nothing but –q by m A that is your H prime of t okay. So this is my time-dependent perturbation okay. Now we know what is the time-dependent perturbation okay. Let us stop it here and continue in the next class.