Quantum Mechanics and Molecular Spectroscopy

Prof. G. Naresh Patwari
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 10
Properties of Light (Classical Treatment)

Hello, welcome to lecture number 10 of quantum mechanics and molecular spectroscopy course. As usual, we will begin with a short recap of the previous lecture and carry on with the present lecture. In the previous lecture we talked about the perturbation theory of the many states.

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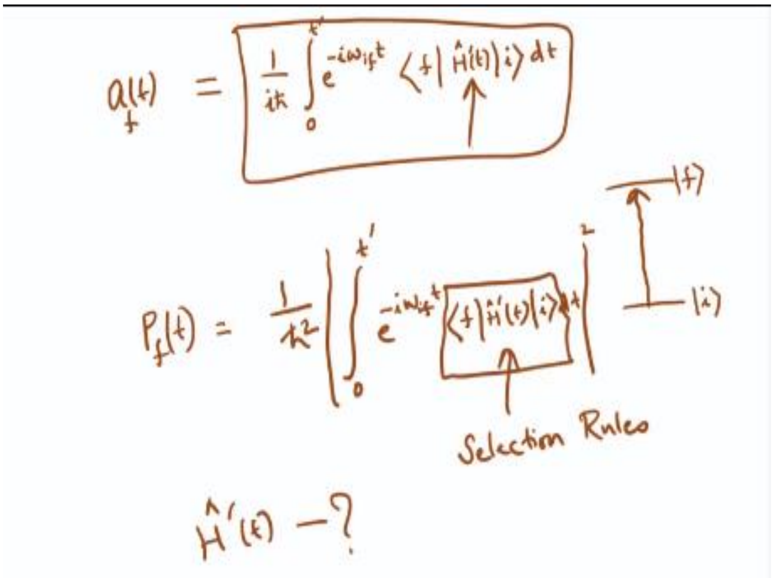

Finally, using the first-order approximation, we came up with the equation a of t of a state f which could be a final state, its coefficient will be equal to 1 over ih bar integral e to the power of –i omega if t integral f H prime t i dt with some limits 0 to t prime. Now, what does this indicate? It indicates if there are 2 states, the initial state i and the final state f okay, the transition from the initial state to final state and that coefficient is given by this equation okay.

And you will also see that this transition from the initial state i to f will be brought about by this time-dependent perturbation okay. Now, that is only the coefficient, but the probability is the square of the coefficient. Therefore, probability of transition to a state f will be equal to, now 1 over ih will be –1, but then probability always has to be positive. So, this will be 1 by h bar square e to the power of –i omega i ft integral f H prime of t i dt modulus squared.

So it has to be a real number or a real positive number is what is the P of t would be. So, this is the final equation, so this is the probability and that depends on this integral and it turns out that this integral also governs so called selection rules. That means under what condition you can start from initial state i and end up with the final state f. However, what we do not know as of now is this H prime t okay.

Now, it is not very difficult to realize that H prime t or the perturbation Hamiltonian or the time-dependent perturbation should come from the light. So, which means we need to look at light and that is the content of lecture number 10.

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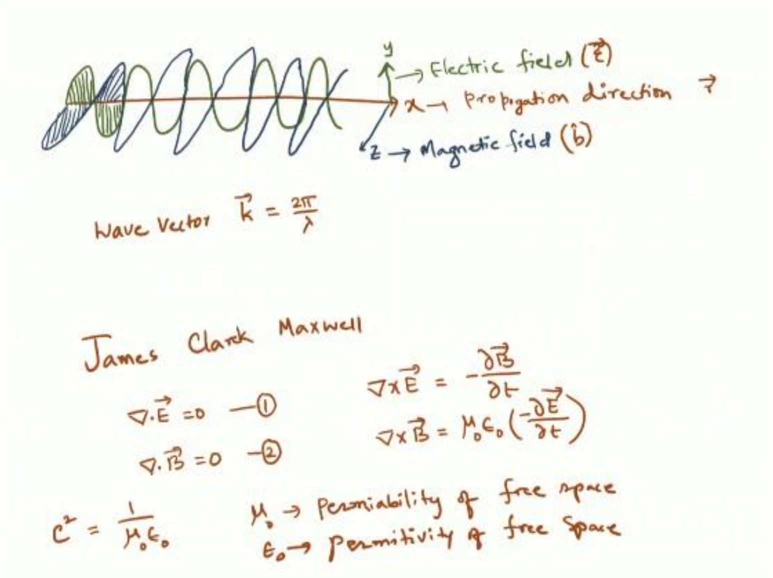

Now light you know can propagate, let us assume that it propagate along the x axis okay and then there is a vector or electric field that goes up and down like that, so along y axis okay. So your electric field vector is going along x and y axis and you know that electric field vector will go up and down, something like that. Now there is also a corresponding magnetic field which goes in the z axis, something like that okay. So, this is my z axis.

So, along z you have this magnetic field, y axis you have electric field, and this your x axis will be propagation direction. So, the propagation direction, the magnetic field and the electric field are mutually perpendicular to each other okay, right. Let us assume that there are 3 vectors that represent these quantities okay. Now for propagation direction, there is a vector called r okay, which is nothing but the radial vector that means you are going away from some point okay.

And there is an electric field vector, which I will call it as epsilon okay or epsilon like that and there is a magnetic field vector called b and these are unit vectors along that direction and you will see the electric field vector will keep changing the direction okay. Once it goes up, then comes down and changes at sign and goes the other direction, similarly your magnetic field, but the propagation direction is along the x axis in one direction okay, that is not going to change its sign.

The other thing that is important is something called wave vector. Now, wave vector is nothing but how many units of wavelength does the wave travel okay. Now this is given by, wave vector is also called as k and is given by 2 pi by lambda. Maxwell gave 4 equations, okay. Those 4 equations are very well known called Maxwell's equations and this says del E or del dot E = 0, so let us call equation number 1.

Then you have del dot B = 0, this is second equation. Third equation is del cross E = –dB by dt and del cross B = mu0 epsilon0 –dE by dt okay where mu0 is permeability of free space and epsilon0 is permittivity of free space such that okay. C square that is speed of light = 1 over mu0 times epsilon0 okay. Now that is the general description of the light in terms of Maxwell's equation.

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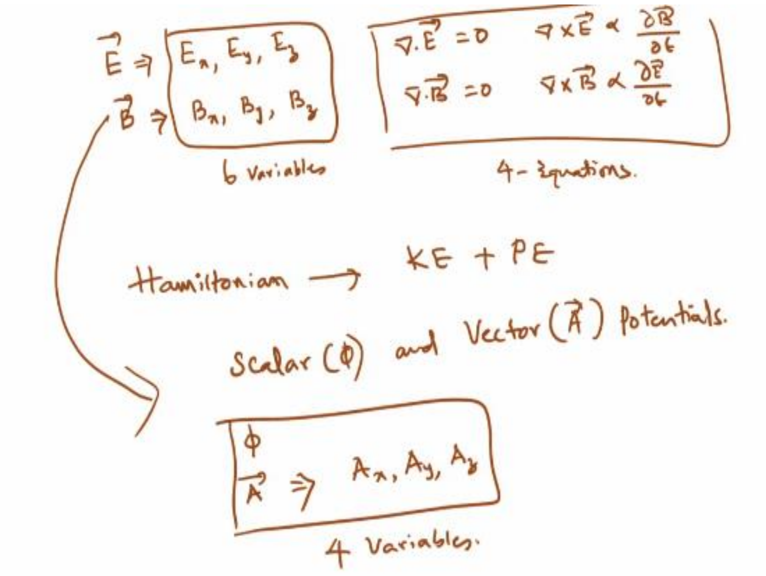

Now the Maxwell's equations are associated with electric field and magnetic field, okay. Now the electric field, let us say E okay, will have 3 components, Ex, Ey and Ez. This is in general you know light propagating in arbitrary directions. Similarly, one of or more than one of them could be zeros. Say for example if it is traveling along x direction, it will either have y or z or yz, it will be in yz, so Ex will be 0 okay, something like that.

So, you have B will also have Bx, By, Bz, but you see Maxwell's equations are only 4 equations involving E and B okay. So, we know Maxwell's equation was del dot E = 0 and del dot B = 0 and del cross E is proportional to db by dt and del cross B is proportional to dE by dt okay, I have just omitted the constants, but you see there are 6 variables and there are 4 equations.

So there is somewhat of redundancy in the number of variables okay, but that is not really the point that I would like to capture. The most important point that I want to say is that when we will treat Hamiltonian okay, the Hamiltonian has kinetic and potential energy terms okay. So Hamiltonian, it has kinetic energy plus potential energy. It has no concept of field and what the classical light is saying, it has electric field and magnetic field, but what we want is kinetic energy and potential energy.

So, we need to convert these electric fields and magnetic field into appropriate potentials, that is what we need okay. So, now we make a transformation okay. So in the transformation, we would start describing the electric field and magnetic field or the classical wave light in 2 other quantities called vector and scalar potentials because we need potentials and not fields, okay. So we make an alternate description of this and we get to what is known as scalar and vector potentials okay.

Now this will turn out to be phi, this one, it is a scalar potential, scalar potential just means that it is a number okay and there is a vector potential A and this will have 3 components Ax, Ay, Az okay. Totally, we have 4 variables and now what we are going to do? To move from electric and magnetic fields to scalar and vector potentials, you are going from 6 variables to 4 variables. That means once again you have redundancy.

So, there will be infinite number of possible combination in which you can read your 6 variables to 4 variables okay.

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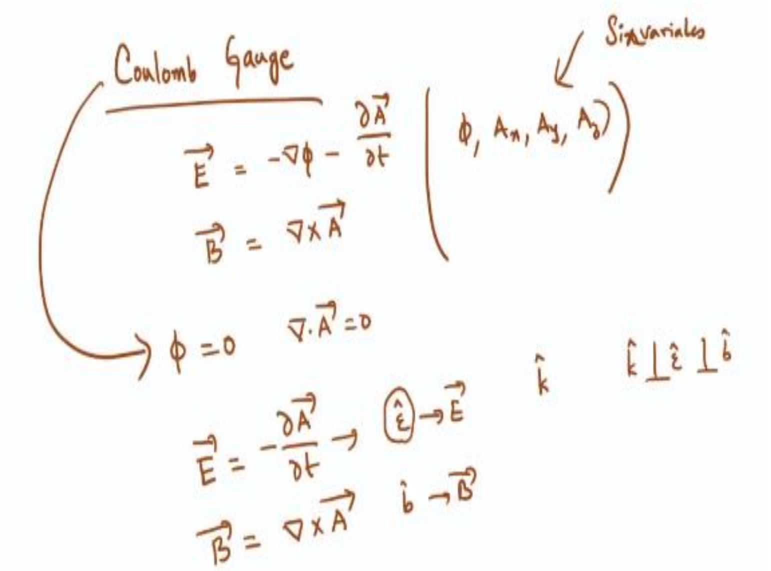

Now, you can take some physically important fixations. So, I say I want to fix this quantity, I want to fix that quantity and then you can reduce the number of possibilities okay and in electrodynamics this is called gauge fixation okay, and for this course we employ what is known as Coulomb gauge okay. Now, before that, we also need a relationship. Before we do the gauge fixation, we also need a relationship between the electric field, magnetic field and the scalar and vector potential.

So, your electric field E is given us –del phi – dA by dt and your magnetic field B is given by del cross A okay. Now, then we have as I told you there are 4 variables; phi, Ax, Ay, Az and these have to be fixed from 6 variables of okay. Now then we use something called Coulomb gauge in which okay, it is a constraint okay. Coulomb gauge is a constraint in which we say phi = 0 and del dot A = 0. So this is the column gauge.

Coulomb gauge fixes these two quantities okay. Now when I fix these quantities, then your E becomes –dA by dt, just A is just time derivative okay and B will be equal to delta cross A okay. Now you can see very simply the following, okay. Now the vector potential is time derivative of A and B which is the magnetic field is nothing but the curl of A okay. That means that B will be in perpendicular direction with respect to B okay.

Now we have 3 vectors. By the way, E let us say we had unit vector epsilon for E and you had unit vector b for magnetic field okay. It turns out that A will also be along the unit vector epsilon because it is just a time derivative, so the direction is not going to change, but del cross A is the curl, so it is going to change okay. So, A will be perpendicular to B. That means vector field A will be perpendicular to the magnetic field B.

So, what is perpendicular to the magnetic field B, the electric field. So the direction of the electric field and the vector potential will be the same. However, even the direction is same, they are not going to be the same because A that is the vector potential is a time derivative of E okay. Then you have the wave vector k which tells you the propagation direction. So, which means totally what you have is that your k vector is perpendicular to E vector which is perpendicular to b vector.

So, all the 3, the additional propagation or the wave vector, the epsilon that is the electric field vector and b that is the magnetic field vector all 3 will be perpendicular to each other okay.

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

Phase factor.

$$\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right) = \frac{2\pi \cdot x}{\lambda} - 2\pi\nu t = (\vec{k}\cdot\vec{r} - \omega t)$$

$$\vec{A} = A_0 \hat{\varepsilon}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] = 2A_0\hat{\varepsilon}\cos\left[\vec{k}\cdot\vec{r}-\omega t\right]$$

$\omega \rightarrow$ angular frequency

$\vec{r} \rightarrow$ propagation direction

$\vec{k} \Rightarrow$ wave vector.

Now, very generally let us take vector A should be equal to A0 some maximum into epsilon that is going to be the unit vector okay, e to the power of i k dot r – omega t + e to the power of –i k dot r – omega t okay. Now k dot r is nothing but the dot product of the wave vector and the propagation direction, which simply means that the propagation vector and wave vector are on the same direction, so which simply means that this term is now called phase factor.

Now, if you remember the classical wave equation, this is nothing but your alpha, remember alpha was 2 pi by x by lambda – nu t. Now, if I convert this 2 pi into x by lambda – 2 pi nu into t. So, this is nothing but 2 pi by lambda is k, k vector, let us say the direction of propagation is x but it could be r, so r in general can be – 2 pi nu is omega into t. So, that is exactly what you have here okay.

Now, if I want to write A, let me write once more A0 epsilon e to power of i k dot r –omega t + e to the power of –i k dot r – omega t okay, but this is nothing but e to the power of i theta + e to the power of –i theta, that is Cos theta. So, this can be called to 2 A0 epsilon Cos of k dot r – omega t okay, where you know, I already told omega is angular frequency, r is propagation direction and k is wave vector okay.

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

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

↳ Plane-wave representation.

$$\vec{E} = -A_0 \omega \hat{\varepsilon}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} - e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] \propto \sin\theta.$$

$$= -2A_0\omega\hat{\varepsilon}\,\sin\left[\vec{k}\cdot\vec{r}-\omega t\right] \qquad E_0 = -2A_0\omega$$

$$= E_0\hat{\varepsilon}\,\sin\left[\vec{k}\cdot\vec{r}-\omega t\right]$$

$\vec{A}$ and $\vec{E}$ are out-of-plane w.r.t by $\pi/2$

Now in the coulomb gauge or in general E was equal to del phi – dA by dt okay and my A = A0 into e to the power of –i k dot r – omega t + e to the power of –i k dot r – omega t. By the way, this is also called plane-wave representation okay. Now, this is nothing but if I take E, the E will be the first derivative of this with respect to time okay. Now, we will see k dot r will be constant and minus omega t will be just be this.

So, this will be A0 omega into epsilon divided by e to the power of i k dot r – omega t –e to the power of –i k dot r – omega t okay. Now, this is nothing but if you see this is Cos theta, so this will be equal to Sin theta proportional okay. So, this will be 2 A0 omega epsilon Sin of k dot r – omega t okay. There is a negative sign, I am sorry for it, because when you take a derivative this minus omega it will have negative sign, so there is a negative sign.

So, this I can write it as E0 epsilon Sin k dot r – omega t where E0 = –2 A0 omega. I have now started looking at the thing as electric field and vector potential okay. So, the vector potential and the electric field are time derivative with respect to each other. So, you can see that the vector potential is Cos theta function and the electric field is Sin theta function and you know Sin theta and the Cos theta are a phase shift of pi by 2.

So, therefore the vector potential A and the electric field E are out of phase with respect to each other by pi by 2 that is 90 degrees. So, whenever the electric field goes up, the vector potential comes down and whenever the electric field goes down, the vector potential comes up and the other way around okay. So, the electric field and vector potential are time derivatives with respect to each other.

One can give a classical analogy of you know harmonic oscillator or pendulum okay. Now, when you take the pendulum and go to the top, so let us suppose there is a pendulum and it will move like this in a harmonic path, okay let me redraw it.

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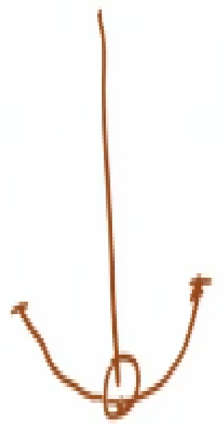

Think of a pendulum which has a moment like that, this is the maximum okay. So, when you go to the top, we have maximum potential energy because of potential energy is, okay you are moving it away, so the potential energy will be maximum. However, when you reach here, its momentum is 0 because it is going to, it went up but it has to come down okay.

Similarly at the bottom it will have maximum momentum because it has to go through this, but it has the minimum potential okay. So, the momentum and the potential, they are out of sync with respect to each other in the case of harmonic oscillator or a pendulum. This is the same in the case of the electric field and the vector potential. When one is maximum, other is minimum okay. We will stop here and continue in the next lecture.