

Quantum Mechanics and Molecular Spectroscopy
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Lecture – 12
Interaction Hamiltonian – Part 2

Hello, welcome to lecture number 12 of the course quantum mechanics and molecular spectroscopy. We will have a quick recap of the previous lecture before we start with this lecture. In the previous lecture, we talked about the time-dependent perturbation okay.

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$$\hat{H} = \hat{H}^0 + \hat{H}'(t)$$

$$\hat{H}'(t) = \frac{i\hbar q}{m} A \cdot \nabla$$

$$\hat{H}(t) = -\frac{q}{m} A \hat{P}$$

$$P_f(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{-i\omega_f t'} \langle f | \hat{H}'(t') | i \rangle dt' \right|^2$$

$\langle f | \hat{H}'(t) | i \rangle \Rightarrow$ Selection Rules

So, when the total Hamiltonian is $H = H_0 + H'$ of t , we evaluated H_0 prime of t by putting the charged particle in the electromagnetic radiation and evaluating the Lorentz force from that. From the Lorentz force, we got the corresponding momentum and that momentum was used in the kinetic energy operator and from there we did some mathematics or simple algebra and we got the final momentum or kinetic energy operator in terms of H' of t okay.

So, the H' of t that came out in the last class was $i\hbar q/m q A \text{ into del}$ which could be written as $-q/m A \text{ into } P$ okay. So, this is the H' of t . Now, we know the total probability or the probability of a transition P of f time t is nothing but $1/\hbar^2$ square modulus square of integral 0 to t some t' prime e to the power of $-i\omega_f t'$ integral f H' prime of t' i dt' whole square.

And we told this integral that is nothing but $\langle f | \hat{H}'(t) | i \rangle$ will give you selection rules okay. However, to evaluate this integral, one needed $\hat{H}'(t)$ okay and now by doing this we got the $\hat{H}'(t)$ which we can plug it in this integral okay.

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The image shows a handwritten derivation of the perturbation Hamiltonian $\hat{H}'(t)$ in plane wave notation. The steps are as follows:

$$\langle f | \hat{H}'(t) | i \rangle$$

$$= \langle f | -\frac{q}{m} \hat{A} \cdot \hat{p} | i \rangle$$

Plane wave notation.

$$\hat{H}'(t) = -\frac{q}{m} \hat{A} \cdot \hat{p}$$

$$= -\frac{q}{m} \left[A_0 \hat{\epsilon} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \right] \cdot \hat{p}$$

$$\hat{H}'(t) = -\frac{q A_0}{m} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \hat{\epsilon} \cdot \hat{p}$$

H atom Bohr radius = $0.529 \text{ \AA} = 0.0529 \text{ nm}$

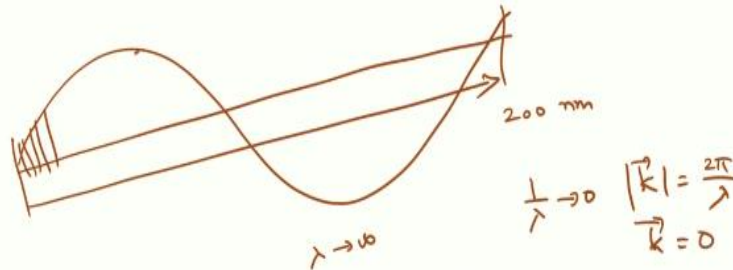
So, your integral $\langle f | \hat{H}'(t) | i \rangle$ will be nothing but integral of $f -q$ by $m A$ into $P I$ okay. So, this is what we need to evaluate. So, let us go back to $\hat{H}'(t)$ and look at it in a more detailed way. So, this is nothing but $-q$ by $m A$ okay, but A in plane wave notation, I can always write in plane wave notation. So, that is nothing but $-q$ by m , plane wave notation of A will be $A_0 \epsilon$ okay, e to the power of $i k \cdot r - \omega t$ okay + e to the power of $-i k \cdot r - \omega t$ into P okay.

So, this is nothing but is equal to $-q A_0$ not by m into e to the power of $i k \cdot r - \omega t$ + e to the power of $-i k \cdot r - \omega t$, this is $-i$, $-\omega t \epsilon$ dot P okay. So this is the equation that we are looking at okay. Now I am going to make one approximation okay. What is the approximation? Approximation is let us suppose you have a molecule or an atom okay. What is the size of atom?

Size of the atom is typically let us say a one nanometer or a molecule is one nanometer, atoms are much smaller okay because of radius of hydrogen atom or the Bohr radius of hydrogen atom is 0.529 angstroms okay. H atom Bohr radius = 0.529 angstroms, this is equal to 0.0529 nanometers okay.

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~100nm in Vacuum Ultraviolet.
 200-800 nm → UV-Vis
 Electronic absorption.



Now, there is one problem is that let us say even if you take, let us look at the electronic absorption or the infrared absorption or the microwave absorption in the rotation, so what is the wavelength of the light even if you have go to you know vacuum ultraviolet, it will be about 100 nanometers of the order of 100 nanometers in vacuum ultraviolet, but in general UV spectroscopy starts from 200 to 800 nanometers.

This is UV or electronic absorption okay. So, this is about this much. Let suppose which means by just let us suppose this is one full wavelength, is not it? So, there does it say this is about 200 nanometers, okay this distance, let us say you know one wavelength of light. Now, if I put 1 nanometer particle in it, so I have to make 200 divisions of this, is not it, 1, 2 like that I have to make 200 divisions of 1 nanometer.

If the size of the molecule it says 1 nanometer, so this will be very small, something like that okay. So, the size of the molecule is so small in comparison to the wavelength. That means effectively you do not see the wave going up and down because for a small portion of the light the wave is not changing at all okay. So, that means $1/\lambda$ that means λ tends to infinity okay that is because it is very long because at least 200 or it could have even more okay, at least 200.

So, you get you know the change in the profile of the electric field on magnetic field can hardly be felt okay. So as λ tends to be infinity, $1/\lambda$ tends to 0 and your k modulus of k is given by $2\pi/\lambda$, that means k will tend to 0.

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$$\hat{H}(t) = -\frac{qA_0}{m} \left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right] \hat{\epsilon} \cdot \hat{p}$$

$\rightarrow 0 \quad \vec{k}\cdot\vec{r} \Rightarrow 0$
 neglect $\vec{k}\cdot\vec{r}$ term

$$\hat{H}'(t) = \frac{-qA_0}{m} \left[e^{-i\omega t} + e^{i\omega t} \right] \hat{\epsilon} \cdot \hat{p}$$

$$= -\frac{qA_0}{m} \cos(\omega t) \cdot 2 \hat{\epsilon} \cdot \hat{p}$$

$$\hat{H}'(t) = \frac{-2A_0q}{m} \cos(\omega t) \hat{\epsilon} \cdot \hat{p}$$

$$= \frac{-2A_0\omega q}{m\omega} \cos(\omega t) \hat{\epsilon} \cdot \hat{p}$$

$$\hat{H}'(t) = \frac{E_0 q}{m\omega} \cos(\omega t) \hat{\epsilon} \cdot \hat{p}$$

$E_0 = -2A_0\omega$

So, in your interaction Hamiltonian H prime of $t = -q$ by $m A_0$ e to the power of $i k \cdot r - \omega t + e$ to the power of $-i k \cdot r - \omega t$ dot P . This k is tending to 0, that means $k \cdot r$ term can be approximated to 0 okay or we neglect $k \cdot r$ term okay. So, this is something called limit of the wavelength in the size of the molecule which you know it can be neglected. That means your H prime t will now become $-q$ by A_0 by m e to power of $-i \omega t + e$ to the power of $i \omega t$ into $\epsilon \cdot P$ okay.

Now, that means this is, what is this, this is nothing but $-q A_0$ by m this is $\cos \omega t$ into 2 into P . So, this is equal to $-2 A_0 q$ by $m \cos \omega t$ into P okay that is the equation that you have. So your H prime t is this much. Now, if you go back and look at the plane wave description okay, then you had $E_0 = -2 A_0 \omega$ okay. So, I am going to make substitutions in this. So $-2 A_0 \omega = E_0$.

Then if you go back and look at the plane wave notation about couple of classes before, so this will come out to be minus okay, this is $-2 A_0 \omega$, so this is minus, so what I will do is I will multiply the numerator and denominator with ω . So, you will get $2 A_0 \omega q$ by $m \omega \cos \omega t$ $\epsilon \cdot P$, but this value $-2 A_0 \omega$ is not it what E_0 . So, your H prime of $t = E_0 q$ by $m \omega \cos \omega t$ to $\epsilon \cdot P$. So, let me rewrite this equation in the next slide okay.

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$$\hat{H}'(t) = \frac{E_0 q}{m\omega} \cos(\omega t) \hat{\epsilon} \cdot \hat{p}$$

$\hat{\epsilon}$ unit vector of electric field
 E_0 maximum amplitude of the electric field.

Electric dipole Hamiltonian.

$$\hat{H}'(t) = \frac{E_0 q}{2m\omega} \left[e^{i\omega t} + e^{-i\omega t} \right] \hat{\epsilon} \cdot \hat{p}$$

$$\langle f | \hat{H}'(t) | i \rangle$$

for multiple charge particles.

$$\hat{H}'(t) = E_0 \cos(\omega t) \sum_n \frac{q_n}{m_n} \hat{\epsilon} \cdot \hat{p}$$

So, what you have is H' of $t = E_0 q$ by $m \omega \cos \omega t \cdot P$. What is this epsilon? This epsilon is nothing but unit vector of the electric field and what is E_0 not? E_0 is the maximum amplitude of the electric field okay. Now there is something very interesting that has come. We converted electric field into scalar potential and vector potentials okay and eventually by doing enough mathematical transformation, we are back with electric fields.

Because E_0 is the electric field that is a maximum limit of the electric field, it represents electric field and epsilon is the unit vector electric field, but we had to do this because we wanted the potent H' of t that is your time-dependent perturbation okay. Now, the time-dependent perturbation that you have is this H' of t okay $E_0 q m \omega \cos \omega t$ epsilon dot P .

That means your H' of t that I would like to write is equal to $E_0 q$ by $m \omega \cos$ is nothing but e to the power of $i \omega t + e$ to the power of $-i \omega t$, of course divided by 2, so let 2 here epsilon P . So, that is my electric dipole Hamiltonian. Why do we need this electric dipole Hamiltonian? Because if you look at the selection rule, $\langle f | H'$ of $t | i \rangle$ you need to plug in this okay.

Now, there is some small modification I want to do to H' of t before we finish this lecture okay. Now what is happening, you are taking only q , that means only one charge particle okay, one charge particle of charged q , but in general atoms and molecules have multiple charge particles. So, your H' of t , so for multiple charge particles you have H' of $t = E_0 \cos \omega t \sum_n \frac{q_n}{m_n} \hat{\epsilon} \cdot \hat{p}$ okay. So q_n is the charge particle.

So, what are you doing? You are looking at the collection of charge particles, not just not one, because atoms and molecules are charge particles collection okay. So, you have to run this over all charge particles and this Hamiltonian is the electric dipole Hamiltonian for many charge particles okay. So, we will stop here in this lecture and continue in the next class.