Fundamentals of Spectroscopy

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Lecture - 6

Intensity of a Transition Depends on the Transition Dipole Moment - I

One of the most important ideas in spectroscopy is that the intensity of absorption or emission of light by an atom or a molecule depends on the transition dipole moment of the atom or molecule. So, let us look at what this transition dipole moment is first and then in this lecture we will derive that the intensity depends on this quantity.

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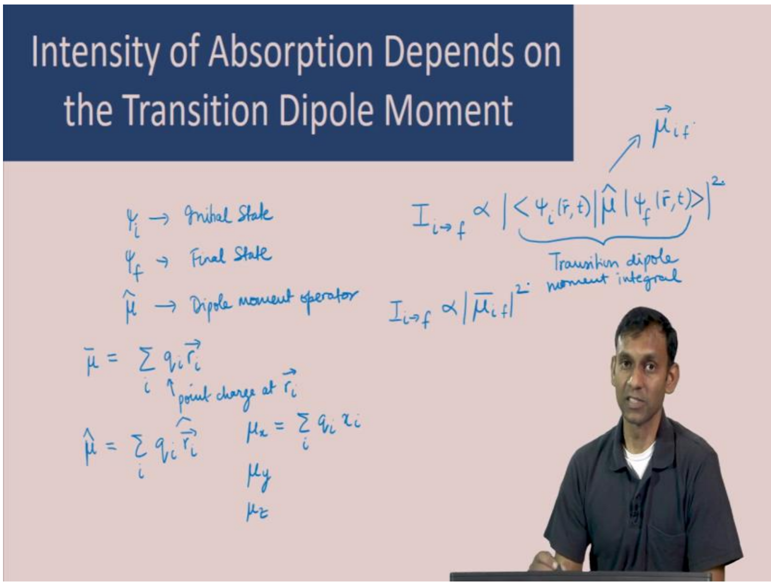

Intensity of Absorption Depends on the Transition Dipole Moment

$\psi_i \rightarrow$ Initial State

$\psi_f \rightarrow$ Final State

$\hat{\mu} \rightarrow$ Dipole moment operator

$$\bar{\mu} = \sum_i \underset{\uparrow \text{point charge at } \vec{r}_i}{q_i} \vec{r}_i$$

$$\hat{\mu} = \sum_i q_i \hat{\vec{r}}_i \qquad \mu_x = \sum_i q_i x_i$$

μ_y

μ_z

$$I_{i\to f} \propto \Big| \overset{\nearrow \vec{\mu}_{if}}{\underbrace{\langle \psi_i(\bar{r},t) | \hat{\mu} | \psi_f(\bar{r},t) \rangle}_{\text{Transition dipole moment integral}}} \Big|^2$$

$$I_{i\to f} \propto |\bar{\mu}_{if}|^2$$

So, assume that the molecule is in a state Psi i, let us say this is the initial state of the molecule and let us say Psi f is the final state of molecule the transition dipole moment is defined in terms of these initial and final state and one more quantity which is the dipole moment operator. So, let us look at what this dipole moment operator is? To define the dipole moment operator we start with the dipole moment property which is this vector quantity which is the sum over i qi ri where qi is the point charge at the position ri.

So, using this property we can define the dipole moment operator mu hat as the corresponding position vector replaced by the position operator. So, this dipole moment operator has three components the x component would be sum over qi times x I and similarly you can write the expressions for the y and z component. Now the intensity of a transition from the state i to the state f is proportional to the square of the following integral Psi i r, t mu operator Psi f r, t the magnitude whole squared.

This integral is called the transition dipole moment integral and this integral is usually denoted by mu of i f. So, in other words the intensity of the transition from i to f is proportional to mu i f magnitude squared.

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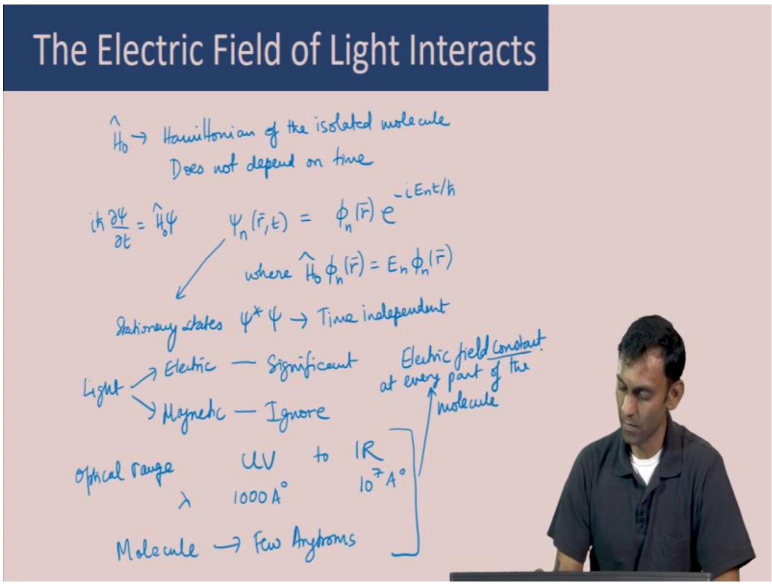

The Electric Field of Light Interacts

$\hat{H}_0 \rightarrow$ Hamiltonian of the isolated molecule

Does not depend on time

$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_0 \psi \qquad \psi_n(\bar{r}, t) = \phi_n(\bar{r}) e^{-iE_nt/\hbar}$

where $\hat{H}_0 \phi_n(\bar{r}) = E_n \phi_n(\bar{r})$

Stationary states $\psi^* \psi \rightarrow$ Time independent

Light $\rightarrow$ Electric — Significant

Light $\rightarrow$ Magnetic — Ignore

Electric field constant at every part of the molecule

Optical range UV to IR

λ 1000 A° 10^7 A°

Molecule $\rightarrow$ Few Angstroms

We will now derive this result let us start by assuming that the molecule is isolated and in the dark and the Hamiltonian of this molecule is H 0 so this is the Hamiltonian of the isolated molecule. We assume that this Hamiltonian does not depend on time, so the solutions of the Schrodinger equation of this Hamiltonian the Schrodinger equation is I H bar del Psi by Del t is equal to H 0 Psi and the solutions are Psi n r, t is equal to Phi n of r multiplied by e to the power of i E n t by h bar where H 0 Phi n of r is equal to E n Phi n of r we have already seen this result in our study of the basics of quantum mechanics.

The solutions of the Schrodinger equation are stationary states because Psi star Psi is time independent. Consider this molecule interacting with light, so light has an electric field and a magnetic field associated with it. The interaction of the molecule with the electric field is most significant and we will only consider this interaction and ignore the interaction with the magnetic field because that is relatively less significant as compared to the interaction with the electric field.

Let us now quantify the interaction of the electric field with the molecule for this we assume that the light is in the optical range by which I mean that it is between the UV to the IR range and the corresponding wavelength of UV is about 1000 angstroms and the IR is about 10 to the power of 7 angstroms. Now the size of the molecule itself is few angstroms this implies that the electric field is constant at every part of the molecule.

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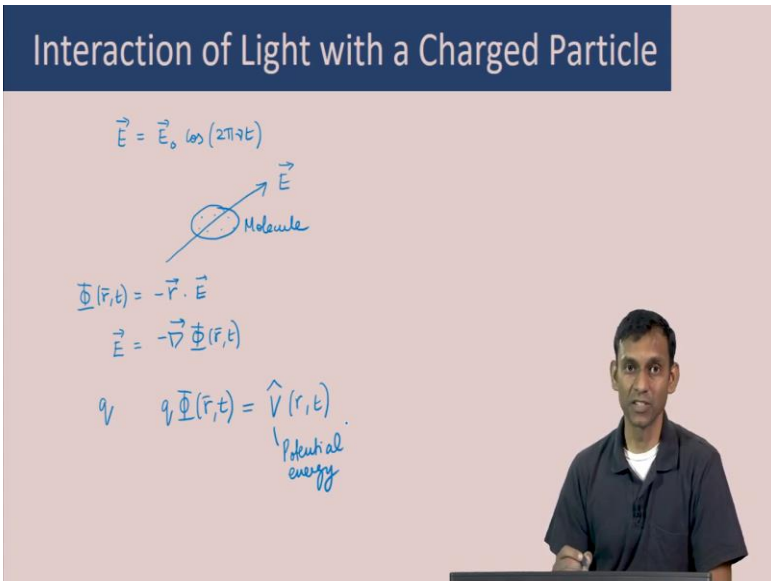

Interaction of Light with a Charged Particle

$$\vec{E} = \vec{E}_0 \cos(2\pi\nu t)$$

$$\Phi(\vec{r},t) = -\vec{r}\cdot\vec{E}$$

$$\vec{E} = -\vec{\nabla}\Phi(\vec{r},t)$$

$$q \qquad q\Phi(\vec{r},t) = \hat{V}(r,t)$$

The functional form of the electric field of frequency nu is the vector E is equal to E 0 cosine 2 pi nu t. So, let us assume that here is the molecule and it has point charges in it and this is the direction of the electric field interacting with the molecule. The scalar potential corresponding to the interaction of the field with the molecule can be written as Phi capital Phi r, t is equal to minus the vector r dotted with the field E.

So, this is the potential of the field at the point having the position vector r note that this form of the potential gives back the electric field as the negative gradient of the potential. The potential energy of a point charge q in this field is q multiplied by the potential and this we denote as V of r, t this is the potential energy. Let us look at the potential energy of the interaction of the molecule which is made up of several point charges with the electric field.

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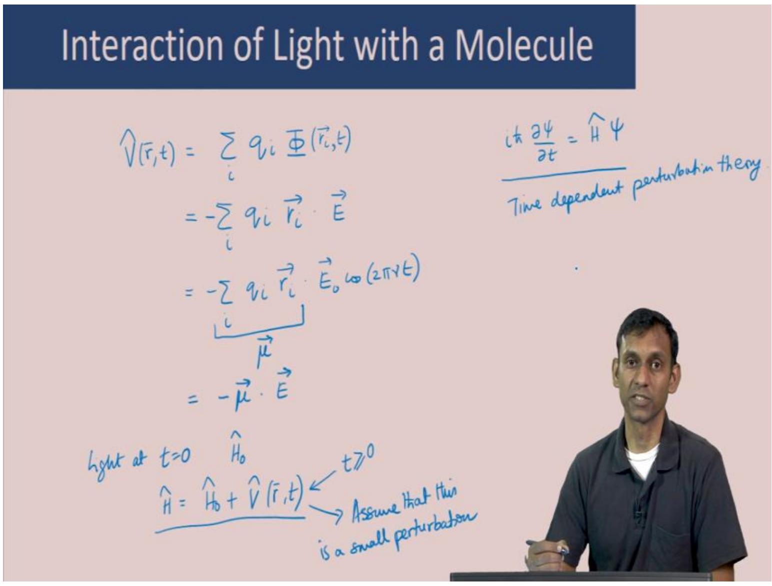

Interaction of Light with a Molecule

$$\hat{V}(\vec{r},t) = \sum_i q_i \, \Phi(\vec{r}_i,t)$$

$$= -\sum_i q_i \, \vec{r}_i \cdot \vec{E}$$

$$= -\underbrace{\sum_i q_i \, \vec{r}_i}_{\vec{\mu}} \cdot \vec{E}_0 \cos(2\pi\nu t)$$

$$= -\vec{\mu} \cdot \vec{E}$$

light at $t=0$ $\hat{H}_0$

$$\hat{H} = \hat{H}_0 + \hat{V}(\vec{r},t) \leftarrow t \geq 0$$

→ Assume that this is a small perturbation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

Time dependent perturbation theory

The form of the total interaction of the electric field with the molecule is V of r, t is equal to sum over i all the point charges of the molecule multiplied by the potential of the field. If we write the expression of the potential this becomes sum over I qi - ri dot E. And if we write this explicitly the form of the electric field then this becomes qi ri dot E 0 cosine of 2 pi nu t. We notice here that this summation is nothing but the dipole moment mu and so we can write the potential energy as minus the dot product of the dipole moment and the electric field.

Suppose that the molecule is initially isolated and the light is turned on at T is equal to 0 light at T is equal to 0 then the initial Hamiltonian of the molecule is H 0 and the Hamiltonian with the light on becomes H 0 plus V of r, t where this potential energy which is the interaction of the molecule with the light starts at t is equal to 0. So, this is only at t greater than or equal to 0. The problem now boils down to solving the Schrodinger equation for this Hamiltonian that is i h-bar Del Psi by Del t is equal to h Psi where the Hamiltonian is given here and furthermore we assume that this is a small perturbation.

The procedure that we'll use to solve the Schrodinger equation for small perturbation is time-dependent perturbation theory. You and this will use the basic quantum mechanics ideas that we have talked about in the previous lectures.

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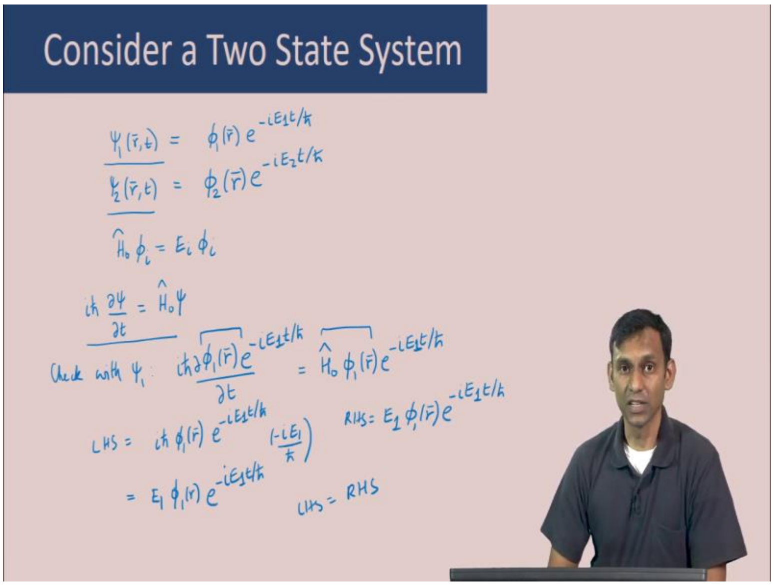

Consider a Two State System

$$\underline{\psi_1(\bar{r},t)} = \phi_1(\bar{r})\, e^{-iE_1t/\hbar}$$

$$\underline{\psi_2(\bar{r},t)} = \phi_2(\bar{r})\, e^{-iE_2t/\hbar}$$

$$\hat{H}_0 \phi_i = E_i \phi_i$$

$$\underline{i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_0 \psi}$$

Check with ψ_1: $i\hbar \dfrac{\partial\, \overbrace{\phi_1(\bar{r})}\, e^{-iE_1t/\hbar}}{\partial t} = \overbrace{\hat{H}_0\, \phi_1(\bar{r})}\, e^{-iE_1t/\hbar}$

$$\text{LHS} = i\hbar\, \phi_1(\bar{r})\, e^{-iE_1t/\hbar} \left(\frac{-iE_1}{\hbar}\right) \qquad \text{RHS} = E_1\, \phi_1(\bar{r})\, e^{-iE_1t/\hbar}$$

$$= E_1\, \phi_1(r)\, e^{-iE_1t/\hbar}$$

LHS = RHS

A molecule usually has an infinite number of stationary states but for simplicity of the derivation and for notation we will consider that there are only two states. So, we say that the two states are Psi 1 of r, t these are stationary states and we write them in the form Phi 1 r e to the power of -i E 1 t by h bar and another state Psi 2 r, t is equal to Phi 2 r e to the power of –i e 2 t by h bar here Phi 1 and Phi 2 are eigen functions of the Hamiltonian H 0.

Now it is easy to verify that these stationary states Phi 1 and Phi 2 are solutions of the Schrodinger equation. So, let us just confirm that with one of these functions let us say Psi 1 so i h-bar Del Psi by Del t is equal to H 0 Psi if we substitute check with Psi 1. So, we substitute into the Schrodinger equation i h-bar Phi 1 r e to the power of - e1 t by H bar del of this del t is equal to H 0 of Phi 1 r e to the power of -i E 1 t by h bar.

Now since this part does not depend on time we can take it out and this becomes i h-bar Phi 1 r and differential is e to the power of - i E 1 t by h bar multiplied by -i E 1 by h bar that is the LHS and we can simplify this a little bit more and the H 0 can be cancelled out i times i is -1, so this becomes E 1 Phi 1 of r e to the power of -i E 1 t by h bar and the RHS is H 0 times Phi 1 we know is E 1 times Phi 1 because Phi 1 is an eigen function and the rest we can just write like this and so the LHS is equal to the RHS confirming that this Phi 1 here or for that matter Phi 2 are solutions of the Schrodinger equation.

In this two-state system we will further consider that the system is initially in the state Psi 1 and we will proceed with the derivation based on that.

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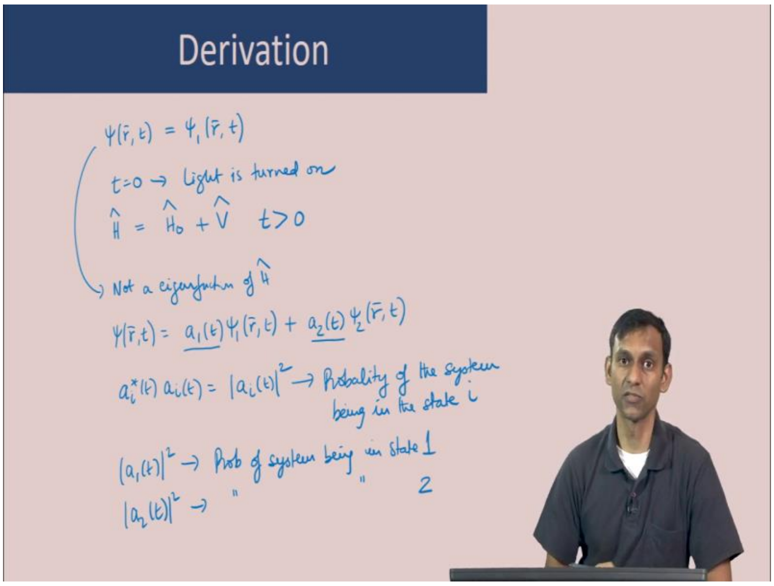

Derivation

$\psi(\bar{r},t) = \psi_1(\bar{r},t)$

$t=0 \rightarrow$ Light is turned on

$\hat{H} = \hat{H}_0 + \hat{V} \quad t>0$

$\rightarrow$ Not a eigenfuction of $\hat{H}$

$\psi(\bar{r},t) = \underline{a_1(t)}\psi_1(\bar{r},t) + \underline{a_2(t)}\psi_2(\bar{r},t)$

$a_i^*(t)\,a_i(t) = |a_i(t)|^2 \rightarrow$ Probality of the system being in the state i

$|a_1(t)|^2 \rightarrow$ Prob of system being in state 1

$|a_2(t)|^2 \rightarrow$ " " 2

Since the system is in the states i 1 we can write its wave function sigh r, t as Psi 1 of r, t now we consider that the light is turned on at t is equal to 0 so the Hamiltonian for time t greater than 0 becomes H 0 plus the interaction of the molecule with the light this is for t greater than 0 the wave function Psi now is not a eigan function of this Hamiltonian H. So, let us say that the wave function now has this form Psi of r, t is a linear combination of Psi 1 and Psi 2 where these coefficients a1 and a2 are time dependent.

Our job will be to determine these coefficients a1 and a2. Now it is important to note that when the wave function is a linear combination like this the term a i star t a i t which is the magnitude of a i t square is the probability of finding the system in the state i. So a 1 t magnitude squared is the probability of system being in state 1 and similarly a 2 t magnitude square is the probability of the system being in state 2.

This is an important thing we have to keep in mind and with this we will now go ahead and calculate a 1 and a 2 and then use this to find the probability of the system being in the state 2 and therefore undergoing a transition from the state 1 to state 2.