Quantum Mechanics and Molecular Spectroscopy
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Lecture – 24
Selection Rules

Hello, welcome to the lecture number 24 of the course quantum mechanics and molecular Spectroscopy okay. Now in the several classes, we were looking at the transition moment integral and its relation to other quantities such as Einstein's A coefficient, B coefficient and the absorption spectrum through Beer-Lambert law, but from now onwards I am going to take a slightly different turn okay and try to get the selection rules okay.

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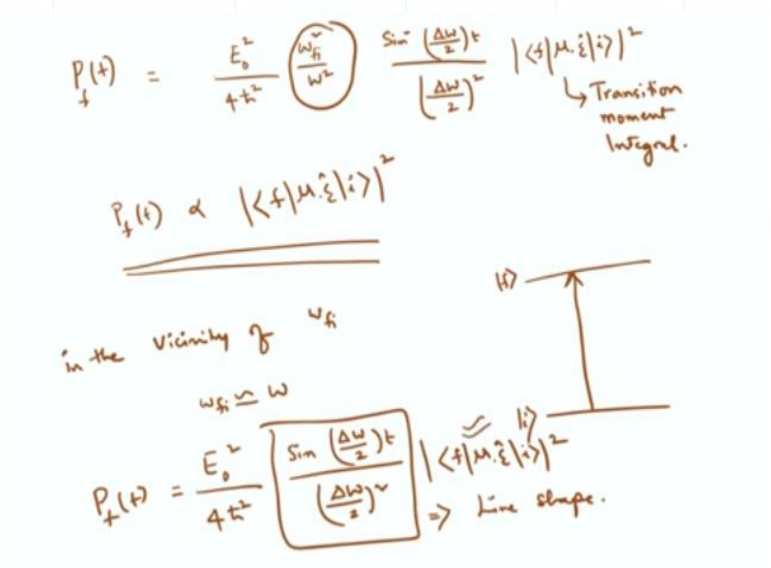

$$P_f(t) = \frac{E_0^2}{4\hbar^2} \boxed{\frac{\omega_{fi}^2}{\omega^2}} \frac{\sin^2\left(\frac{\Delta\omega}{2}\right)t}{\left(\frac{\Delta\omega}{2}\right)^2} |\langle f|\mu.\hat{\varepsilon}|i\rangle|^2$$

↳ Transition moment Integral.

$$P_f(t) \propto |\langle f|\mu.\hat{\varepsilon}|i\rangle|^2$$

in the vicinity of ω_{fi}

$$\omega_{fi} \simeq \omega$$

$$P_f(t) = \frac{E_0^2}{4\hbar^2} \boxed{\frac{\sin^2\left(\frac{\Delta\omega}{2}\right)t}{\left(\frac{\Delta\omega}{2}\right)^2}} |\langle f|\mu.\hat{\varepsilon}|i\rangle|^2$$

⇒ Line shape.

Now if you go back quite a few classes, then we came across this equation which I will write it down as probability of transition P of t to state f is given by E 0 square divided by 4 h bar square omega fi by omega square sin square delta omega by 2 into t divided by delta omega by 2 square modulus of f mu dot e i square and we remember we called it as transition moment integral okay.

Now it turns out that Pf of t is proportional to your transition moment integral square. So what are you doing here? You are going from a state i to state f okay and we also related all this to Einstein's A coefficient, Einstein B coefficient and the extinction coefficient through Beer-Lambert law. We also looked at the line shapes okay. All these experimental quantities could be related to this.

Now it turns out that if I slightly rewrite, so in the vicinity of omega fi okay that means what I am doing is omega fi is approximately equal to omega that means you will have a transient only when there is a resonance okay. So in that scenario, one can rewrite this equation Pf of t, so when you have omega fi is equal to omega, I can ignore this term, so I will get this will be equal to E 0 square by 4 h bar square sin of delta omega by 2 into t divided by delta omega by 2 square into f mu dot epsilon i square okay.

Now we know this function is the line shape okay, it determines the line shape okay. Now what we have? Of course, all these are non zeros, so the selection will be allowed or not is given by this integral okay.

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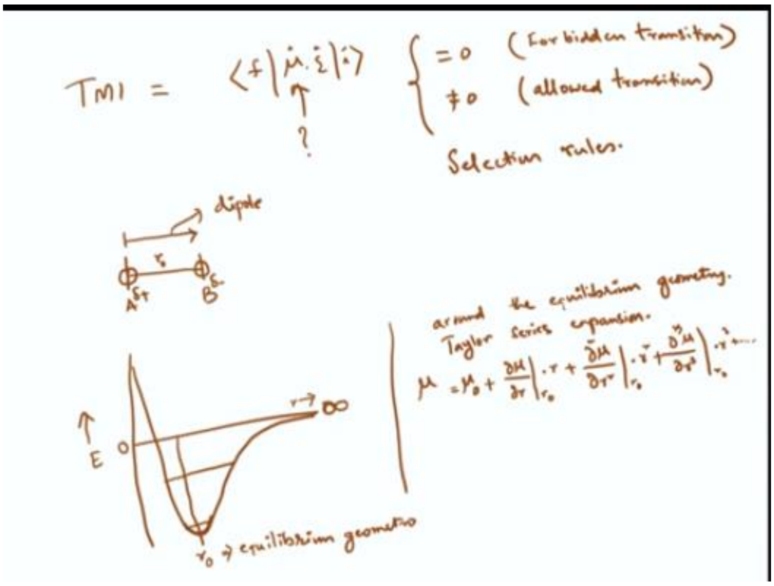

$$TMI = \langle f|\hat{\mu}\cdot\hat{\varepsilon}|i\rangle \begin{cases} = 0 & \text{(Forbidden transition)} \\ \neq 0 & \text{(allowed transition)} \end{cases}$$

Selection rules.

around the equilibrium geometry.
Taylor series expansion.

$$\mu = \mu_0 + \frac{\partial\mu}{\partial r}\Big|_{r_0}\cdot r + \frac{\partial^2\mu}{\partial r^2}\Big|_{r_0}\cdot r^2 + \frac{\partial^3\mu}{\partial r^3}\Big|_{r_0}\cdot r^3 + \dots$$

So one can write transition moment integral TMI = f mu dot epsilon i okay. This is my transition moment integral and whether the transition from 1 to 2 or f to i will be allowed or not will depend on this integral. If this integral is 0, the transition is forbidden. If this is 0 then it is forbidden, this is not equal to 0, then you are allowed and 0 not equal to 0 they combine what is known as selection rules okay.

Now what we will do in this lecture is to look at this operator mu okay. Now let us think of a molecule AB okay. So two atoms A and B are combined and A and B because they are not the same, so there will be say let us say delta plus and delta minus, so you have a dipole and if the equilibrium distance is r0, so for example if you have AB molecule, one can draw a potential energy surface like this that is the zero of energy.

The distance goes to infinity asymptotically okay. Now what I am trying to do is that, of course if you go from here to say here there is a huge change in the geometry or the bond distance that it spans. So one can always think that the movements are not, so one is looking at around the equilibrium position if you look at around the equilibrium geometry, one can write mu as a Taylor series expansion okay.

So, what I will write mu = mu 0 + d mu by dr evaluated r0 into r + d square mu by dr square evaluated r0 into r square + d cube mu by dr cube evaluate at r0 into r cube + etc., etc. okay, one can write a Taylor series. Now let us look at it in a slightly more useful way.

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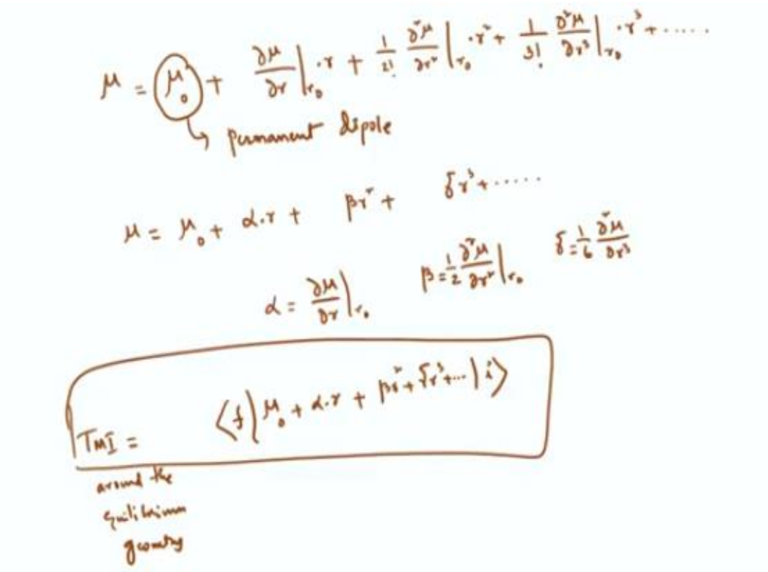

$$\mu = \boxed{\mu_0} + \left.\frac{\partial \mu}{\partial r}\right|_{r_0} \cdot r + \frac{1}{2!}\left.\frac{\partial^2 \mu}{\partial r^2}\right|_{r_0} \cdot r^2 + \frac{1}{3!}\left.\frac{\partial^3 \mu}{\partial r^3}\right|_{r_0} \cdot r^3 + \cdots$$

$$\mu = \mu_0 + \alpha \cdot r + \beta r^2 + \delta r^3 + \cdots$$

$$\alpha = \left.\frac{\partial \mu}{\partial r}\right|_{r_0} \quad \beta = \frac{1}{2}\left.\frac{\partial^2 \mu}{\partial r^2}\right|_{r_0} \quad \delta = \frac{1}{6}\frac{\partial^3 \mu}{\partial r^3}$$

$$\boxed{TMI = \langle f | \mu_0 + \alpha \cdot r + \beta r^2 + \delta r^3 + \cdots | i \rangle}$$

So the dipole moment mu is a Taylor series expansion some fixed + d mu by dr at r0 multiplied by r + 1 over 2 factorial d square mu by dr square r0 into r square + 1 over 3 factorial d square mu by dr cube evaluated r0 r cube + etc. So this is how I can write my mu as a Taylor series expansion around the equilibrium geometry and this mu 0 is the permanent dipole and what is d mu by dr, how the dipole moment changes with respect to r okay.

This is the first derivative and you have second derivative. So one can write it as mu = mu0 + alpha dot r + 1 over 2 beta r square + 1 over 6 gamma r cube, etc., etc. where alpha equals to d mu by dr evaluated r0, beta is nothing but d square mu by dr square evaluated r0 and gamma equals to d square, actually one could take even the constants into, so if I write this as half then I can delete this and if I delete this then one can write 1 over 6 d square mu by dr cube okay.

So one can write such equation. So this is your permanent dipole, this is a first derivative of mu, this is second derivative coefficient and the third derivative coefficients okay. So, this is how one can write in terms of Taylor series expansion. So therefore, your TMI around the equilibrium geometry is given by f times mu0 + alpha dot r + beta r square + gamma r cube + etc., etc. So this is the transition moment that we need to evaluate okay.

When I say dipole moment, its basically linear combination of permanent dipole moment and its derivative at various levels of various degrees with respect to r okay. So, this is the transient moment integral that I need to consider.

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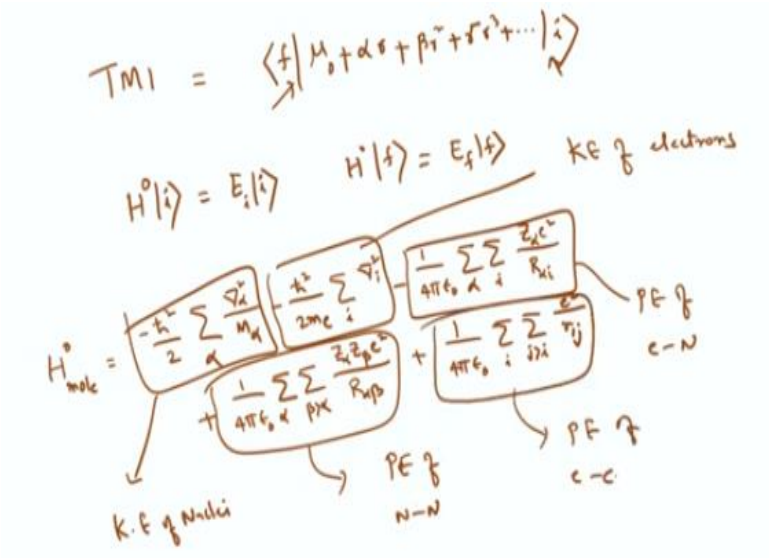

So therefore, one can write TMI = f mu 0 + alpha r + beta r square + gamma r cube + so that is the transition moment integral I am interested in okay. Now let us look at this equation phi okay, so what are my solutions. So what are my solutions I said H0 into i = Ei i and H0 into f = Ef okay, what are my H0, H0 is the Hamiltonian for which I know the solutions. So, E and Ef are the eigenvalues of the functions eigenfunctions i and f okay.

Now what is H0 that is the thing that we have to figure out okay. In this course from up till now we have never bothered what is H0, H0 we just assume is some Hamiltonian for which we know the solutions and once we know the solution we can evaluate the transient moment integral and that transient moment integral can relate to various experimentally measurable quantities, but right now we have not even thought about what the H0 could be?

Now if you write the entire molecular Hamiltonian which I am going to write so H molecule okay, so H0 molecule is nothing but –h bar square by 2 sum over alpha del square alpha by m alpha that is the kinetic energy of the nuclei where alpha is its index minus h bar square by 2 me sigma over i del square i so i is the index on the electron so the kinetic energy of all the electrons minus attraction between the nucleus and all the electrons.

So, this will be 1 by 4 pi epsilon 0 sum over alpha sum over i z alpha e square by R alpha i so there is a distance between the electron and the nucleus, then you have a nuclear-nuclear repulsion so that is equal to 1 over 4 pi epsilon 0 sum over alpha sum over beta greater than alpha z alpha z beta e square by R alpha beta that is the nuclear repulsion because alpha and beta are 2 nucleus.

And you do not want to count the repulsion between the same nucleus that is why alpha is not equal to beta and then you have to have only one, if nucleus 1 is repelling nucleus 2 so it is same as nucleus 2 repelling nucleus 1, so to make sure that you do not repeat the terms use this kind of notation plus similarly with electron 4 pi epsilon 0 sum over i sum over j greater than i e square by r ij. So, we have five terms, so this is KE of nuclei, this is KE of electrons.

This is nothing but PE of electrons and nucleus that is attraction, this is what PE of nucleus to nucleus that is repulsion and this is nothing but your PE of e that is nothing but electron-electron repulsion.

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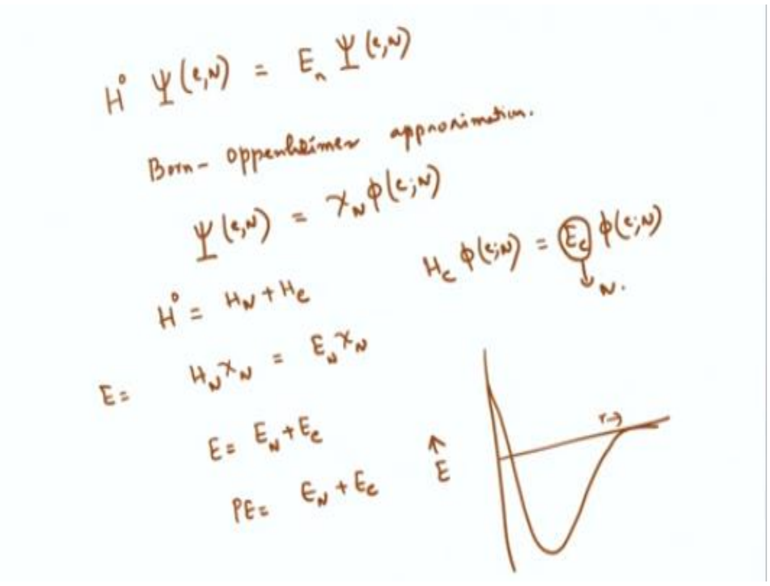

$H^{\circ}\ \Psi(e,N) = E_n \Psi(e,N)$

Born- oppenheimer approximation.

$\Psi(e,N) = \chi_N \phi(e;N)$

$H_e \phi(e;N) = \boxed{E_e} \phi(e;N)$

$\downarrow$ N.

$H^{\circ} = H_N + H_e$

$H_N \chi_N = E_N \chi_N$

$E =$

$E = E_N + E_e$

$PE = E_N + E_e$

H0 of molecule multiplied by psi now which is a function of electrons and nucleus should be equal to En psi which is function of electrons and nucleus okay. Now it turns out that this is not a possible solution, so what we do is what we use something called Born Oppenheimer approximation okay.

This approximation says that the total wave function psi of electrons and nucleus can be separated as Chi of nucleus and phi of electrons parametrically dependent on nuclei and the total Hamiltonian H0 can be written as H nuclei + H electrons okay. Now it turns out that when I look at H nucleus, the H nucleus even though is this H nucleus the total energy is equal to H nucleus Chi nucleus okay will give you E nucleus Chi nucleus.

But the total energy E is nothing but EN + E electron, but you see the phi, so now if you have H electron acting on phi electron and that is parametrically depends on nucleus. What does parametrically depend on nucleus means, for every different nuclear position the Hamiltonian of the electrons will be different give a different solution. So, that will be nothing but Ee + phi, so this Ee also depends on nucleus because the wave function itself.

So if you take the total energy or the nuclear energy, nuclear energy is just not the repulsion but it also kind of has the electronic component into it and that is called potential energy okay. So when you have PE that is nothing but you have EN nucleus + E electron okay. So what you do is you can make a potential surface okay that is E so that depends on how the electrons and the nuclei are arranged as a function of distance okay.

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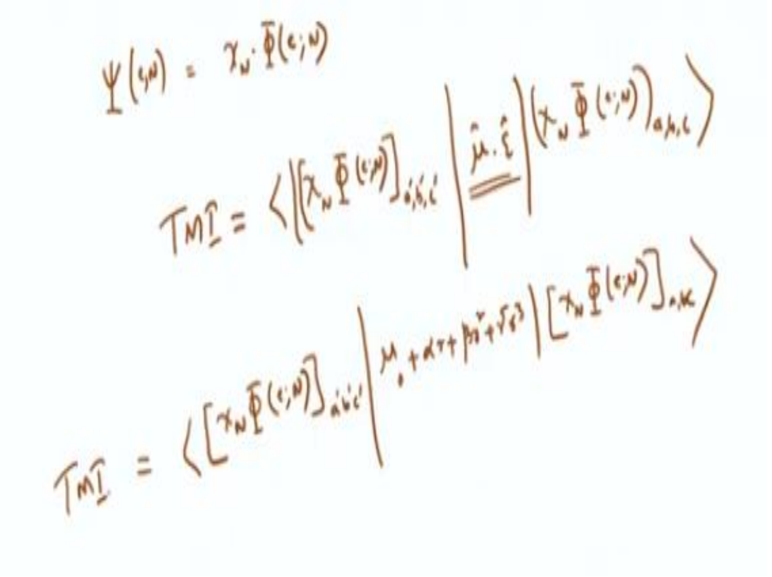

Now one of the issues that we have is the following. So when you have total wave function which is when the total wave function psi of e, n is nothing but Chi of N into phi of e and parametrically depend on N okay, now this is my total solution okay, and of course it will have its own quantum numbers. So, what I am looking at is the following okay. I am starting from a final function f, now this f function could be written as the following.

Chi nucleus phi electron nucleus, all of this having some quantum number let us say a, b, c or I will call it as a prime, b prime, c prime, I will come to what these are okay and this multiplied by your mu dot E multiplied by function i which I will call it as Chi N phi e dot N having quantum numbers a, b, c okay. So, what I am trying to do here I am going from initial wave function which will have quantum number a, b, c.

And this quantum number could involve the nuclear quantum numbers or quantum numbers related to the nuclear motion and the quantum numbers related to the electronic motion and with some values a, b, c and I am going from there and changing my quantum numbers to a prime, b prime, c prime okay. Now what I am trying to do is the following. I am going from one set of electronic and nuclear coordinates to a different set of electronic and nuclear coordinates.

And this transition is brought about by this operator. So, now we can think of it this way, so this operator is really complicated in some sense is that Chi N phi e, N whole thing of a prime, b prime, c prime mu 0 + r + beta r square + gamma r cube whole Chi N to phi e, N whole thing of a, b, c. So, I am looking at such a transition moment integral okay, so when I take the total wave function okay.

So this is how we are going to look at this transition moment integral, but of course the way it is written it is almost impossible to solve, so we have to make right approximations to be able to solve this transition moment integral, evaluate the transition moment integral and look at the selection rules which we will continue in the next lecture. Thank you.