Spectroscopic Technique for Pharmaceutical and Biopharmaceutical Industries
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Lecture 17
Atomic and Molecular Spectroscopy

Hello friends, welcome back to the lecture. In the last lecture I have discussed about how to get the electronic states of a molecule, I will continue from the last lecture and then I will move to molecular spectroscopy where I will see how the electronic orbitals of or electronic states of molecules is determined and how does spectra of this molecule look like. So in the last lecture what we did is, we not only discussed how to get the spectra of atoms, we also started looking at the applications.

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So two different kind of applications we have already looked at. One is application of atomic spectroscopy in environment and the second was the use in forensic science, so continuing with the last lecture now I am going to discuss what are the other applications of the atomic spectroscopy. Atomic spectroscopy is quite often used in agriculture application, as we know that soil provides essential nutrients to the plants and hence soil analysis provides a measure of soil potential to supply the necessary nutrients to the plants.

It is also well known that different kind of plants require different kinds of essential nutrients and so if you analyze soil you will be able to tell which kind of crop is suitable to the kind of soil which our place has. Plants can also be sampled to monitor nutrient optic efficiency and also to check the toxic metal accumulation for health reasons. So what happens is that if toxic elements are present in the soil that is taken up by the plant and when you eat the plants food or you use any products from the plants for eating purpose that can have health problems, that can create problems in health.

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So it is very important to analyze the soil to look at what are the contents available in the soil, soils may become contaminated by the accumulation of heavy metals and metalloids. Through emission from the rapidly expanding industrial areas, mine tailings, disposals of high metal waste, leaded gasoline and paints so soil is always flown to decontaminated by the accumulation of toxic metals which is mostly coming from the different industries.

The heavy metals such as lead, chromium, zinc, cadmium, copper iron and nickel are generally found at contaminated sites. So these are the toxic metals or some heavy metals such as copper, iron, nickel and zinc are required in small quantity by organism. So it is not true that metals are toxic only, some metals are required as unessential metal by organism, however large concentration of this metals which are useful metals are also harmful to us, are also harmful for us and so elemental analysis of soils is required.

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Now next application is clinical applications, the majority of sample analyzed in the clinical sample are taken from the main group of biological fluids such as whole blood, plasma, serum and urine sometime we also analyze hard and soft tissues such as bone, finger, nails and hair. Flame based analysis for the major and minor essential elements graphite furnace analysis for the trace elements and vapor analysis is done for the group of toxic metals. So the different kind of flame based analysis is done for different kinds of metals.

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The tests are done for checking the quantity of several metals presents in the blood sample, for example some of the metals are essential, for example calcium, magnesium, sodium and potassium. There are some minor elements which are also essential for example zinc, copper and iron and there are essential trace elements like chromium, manganese, molybdenum, cobalt, vanadium, selenium and nickel where as there are some toxic elements such as lead, mercury, arsenic, cadmium, aluminum and antimony.

So the essential elements are required and if the concentration of this metals are lower in our body that can create problem, for example if there is no iron then a person is in anemic condition and a person is suffering from the anemia, so low concentrations of iron is not good. Similarly the high concentration of iron is also not useful, so you need to have a balance of iron in our body and if I want to know, what is the amount of the iron in our blood sample or in our body? Then we need to analyze these metal ions.

So here is list of some metals ions and their reference range in our body and you can see this in the red you have the toxic metals, for example lead, its value should be less than 0.9 microgram per gram of blood, so this is very important. If it is higher than that then they are not good for us, mercury should be less than 0.1 micro gram per gram, so this are the prescribed level and our body should not have higher concentration of the particular toxic metal than the reference range.

So the other toxic metals are arsenic, cobalt and you can see for the iron which is essential element the concentration range is from 745 to 1050 microgram per gram, what does that mean is, you should not have iron less than 745 and you should not have iron greater than 1050 microgram per gram. If iron is less then the person is suffering from anemia and similarly higher iron content is also not good for our body and since these are very essential elements of our body and so it is always required that you need to check the concentration of these metals ions in our body from time to time. And in that context your atomic absorption spectroscopy or spectroscopy based on, spectroscopy based on your atomic spectroscopy is needed.

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5. Pharmaceutical Applications

- **Analysis of diclofenac sodium sample :** Diclofenac sodium, [sodium (o-f(2, 6-dichloro-phenyl) aminog phenyl) acetate] is a synthetic Non Steroidal Anti-Inflammatory Drug (NSAID). As diclofenac sodium stands among the NSAID more prescribed drug, the amount of metals and other contaminants present in the formulations should be followed so as to minimize undesirable effects, and should assure that bioavailability is not affected.

Samples of diclofenac sodium samples are analyzed for Na, K, Ca and Al analysis

Atomic spectroscopy has pharmaceutical applications, it can be used for analysis of diclofenac sodium sample, diclofenac sodium is a synthetic non-steroidal anti-inflammatory drug this is well known most prescribed drug or highly prescribed drug but there is chances of this getting contaminated with the metal ion. Now amount of metal and other contaminant present in the formulation of this drug should be followed as to minimize undesirable effect and should assure that bioavailability is not affected.

So sample of diclofenac sodium samples are analyzed for sodium, potassium, calcium and aluminum analysis. So most of the formulation for drug are analyzed for your metal contain because the contaminants can have undesirable effects.

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Similarly, magnesium stearate sample is also analyzed for cadmium, nickel and lead. Apart from this metal monitoring can be used as a finger print, either to control raw material quality use in the different pharmaceutical forms or to control the production process and the final product. So not only (so) this metals are not only analyzed for having undesirable but also to check the quality if different pharmaceutical products.

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Product	Therapeutic Area	Manufacturer	Metal/Metalloid
Tagitol®	Imaging agent	Bracco Diagnostics, Inc.	Ba
Lithobid®	Treatment of Schizophrenia	Noven Therapeutics, LLC	Li
Gastrogafin®	Imaging Agent	Bracco Diagnostics	Na
Platinol®	Chemotherapy	Bristol-Myers Squibb Co.	Pt
Paraplatin®	Chemotherapy	Bristol-Myers Squibb Co.	Pt
Silvadene®	Antimicrobial	Monarch Pharmaceutical	Ag
Ferroquine	Antimalarial		Fe

Here I am giving example of metals which is used in pharmaceutical, there is a long list of products where the analysis of metals is done for a particular biopharmaceutical or

pharmaceutical product, for example Pro-Hance R which is used as an imaging agent and this is from Bracco diagnostics Inc the gadolinium is your analyzed. Multi-Hance R which is imaging agent this is also a Bracco diagnostics Inc and here what we analyze is again gadolinium.

Ferinject R is used as imaging agent and this is from Syner Med Limited. Here your analysis of iron is done. Venofer is an imaging agent again it is from Syner Med Limited and here again iron analysis is done. Dexferrun R it is from Vifor Pharma and again here iron is involved and so analysis of iron is being done. Lumen-Hance R it is an imaging agent from ImaRx pharma Corporation and here analysis of magnesium is done.
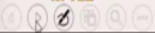
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Product	Therapeutic Area	Manufacturer	Metal/Metalloid
Tagitol®	Imaging agent	Bracco Diagnostics, Inc.	Ba
Lithobid®	Treatment of Schizophrenia	Noven Therapeutics, LLC	Li
Gastrogafin®	Imaging Agent	Bracco Diagnostics	Na
Platinol®	Chemotherapy	Bristol-Myers Squibb Co.	Pt
Paraplatin®	Chemotherapy	Bristol-Myers Squibb Co.	Pt
Silvadene®	Antimicrobial	Monarch Pharmaceutical	Ag
Ferroquine	Antimalarial		Fe

Tagitol R it is a imaging agent it is from Bracco diagnostics Inc barium analysis is done and Lithobid which is used for schizophrenia it is from Noven Therapeutics, LLC and here analysis of lithium is done. Gastrogafin R it is an imaging agent from Bracco diagnostics and here analysis of sodium is done. Platinol it is used in chemotherapy it is from Bristol-Myers Squibb company and here analysis of platinum is done. The Paraplatin it is used in chemotherapy it is from Bristol-Myers Squibb company here analysis of platinum is done. Silvadene it is antimicrobial property and it is from Monarch Pharmaceutical here analysis of silver is done. Ferroquine it is antimalarial property and here analysis of iron is done. So there are lot of pharmaceutical products where analysis of different metals are done.

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So, now we will go to another application, metal analysis is quite often done in petrochemical industries. Here what is done is our atomic absorption spectroscopy or atomic spectroscopy techniques are used to measure refinery contaminant element such as sodium, vanadium, iron and nickel. Also atomic spectroscopy used to measure fuel elements lead, Mn etc it can also be used to measure the lube oil element.

For example in the fresh lube oil a content of calcium, barium, magnesium, zinc, molybdenum and sodium is done to look at the quality of the lube oil. And in the used lube oil the analysis of silver, aluminum, chromium, iron, manganese, nickel, lead, Sn, platinum, zinc are being done, that tells you about the quality or the degradation of the lube oil.

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Some Other Applications

- Determination of traces of potassium in NaCl and sodium in KCl.
- Determination of alkaline and earth-alkaline metals in electrolytes for infusion.
- Trace elements in multivitamin formulations.
- Aluminium assay in biological samples such as rat-fodder or antacids
- Zinc in insulin and cobalt in vitamin B12
- Determination of lithium in antidepressives.

There are some other applications, for example determination of traces of potassium in sodium chloride and sodium in potassium chloride, determination alkaline and earth alkaline metals in electrolytes for infusion. Trace elements in multivitamins formulations, so multivitamins formulations have lot of trace elements and it is important to analyze those trace elements. Similarly, atomic spectroscopy is used in aluminum assay in biological sample such as rat-fodder or antacids, it is also used to look at zinc in insulin and cobalt in vitamin B12. Atomic spectroscopy is also used in the determination of lithium in antidepressives.

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Some Other Applications

- Determination of silicon in dimethylpolysiloxane.
- Copper determination in herbs such as lupuli strobuli
- Gold content of an organic gold compound used for the cure of chronic polyarthritis.
- Determination of iron in diverse iron-containing medicaments.
- Determination of traces of lead in zinc oxide and zinc oxide formulations.

Other application includes determination of silicon in dimethylpolysiloxane, copper determination in herbs such as lupuli strobuli, gold content of an organic gold compound used for the cure of chronic polyarthritis. Determination of iron in diverse iron containing medicaments, determination of traces of lead in zinc oxide and zinc oxide formulations. So there are several applications and what I am listing is only few of them.

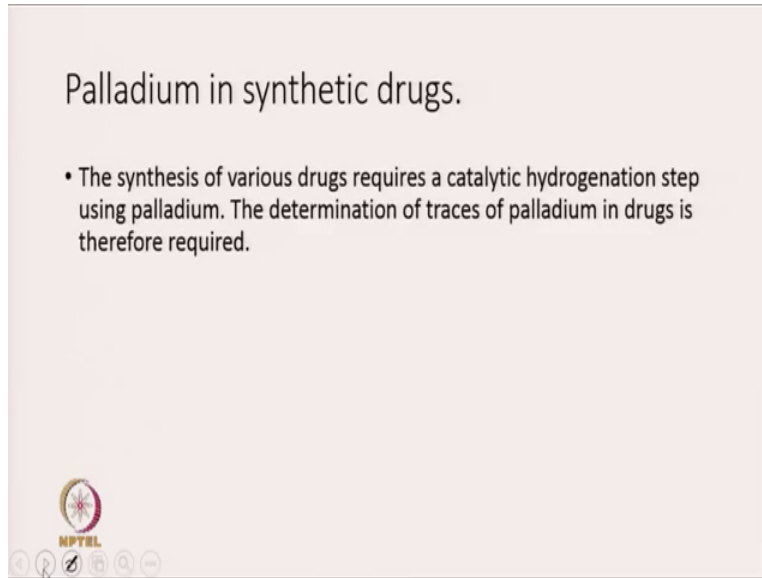(Refer Slide Time: 19:14)

Some Other Applications

- Zirconium determination in material used in dental medicine
- Mercury in pharmaceuticals, plant materials and herbs
- Thallium, cadmium and lead in herbs

For example atomic spectroscopy is also used in Zirconium determination in material used in dental medicine. Similarly, atomic spectroscopy is used to look at amount of mercury in

pharmaceutical, plants material and herbs. It can also be used to look at the amount of the thallium, cadmium, and lead in herbs.

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Palladium is quite often used to synthesize drugs, so the determination traces of palladium in drugs is very important. Palladium is basically used as a catalyst for hydrogenation step during the manufacturing of drug. But when you purify your drug then small amount of palladium may be left and therefore it is required to look at the traces of palladium in drugs.

Potassium determination in urine and this is basically done to look at bioavailability study of sustain release of potassium tablets. So if you want to look at bioavailability of any drug which has a metal ion you can look at the amount of that metal in the urine sample, so potassium can be determined in urine either after sufficient dilution at 766.5 nanometer or little or no dilution directly at 404.7 nanometer. So just by looking at the absorption at the different wavelength you can know what is the concentration of potassium in urine sample.

So, during the last lecture I only discussed your the spectra of alkali metals and alkaline metals, what I left was spectra of other poly-electron atoms. Since I did not have time that day I could not talk about the spectra of other poly-electron atoms. So here what I am going to do is I will talk about selection rule for the atoms which have poly-electron in outer most orbital. The selection rule is delta L is equal to 0 plus minus 1 except L is equal to 0 to L is equal to 0 is not allowed.

For the promotion of only one electron, delta L is plus minus 1 that is what we know but the general rule given here involves the total orbital angular momentum, so we are talking here about total orbital angular momentum, quantum number L and applies to the promotion of any number of electrons, so it will be more than, it can be more than one electron.

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Now one of the very important information about the selection rule for multi-electron atom is even to even, odd to odd is not allowed, even to odd is allowed or odd to even is allowed but not even to even not odd to odd. So what I mean by even and odd? So even and odd refers to arithmetic sum of sigma i li over all the electrons and this selection rule is called the Laporte rule. So what we need to do is we need to calculate sigma li and if it comes out to be odd then you tell that this is odd system and if it comes out to be even then you are dealing with even.

So what is the result of this, the transition of forbidden between states arising from the same configuration, so same configuration for example suppose S2 we are talking about or P2 we are talking about, then from P2 there can be different terms but the transition between the different terms of the same configuration is not allowed. For example of the terms arising from 1s2, 2s2, 2p1, 3d1 configuration of carbon atom 1P to 1D transition would be allowed if we consider only delta S and delta L selections rules, but Laporte rule forbids it.

Laporte rules forbids the transition between states arising from the same configuration. Similarly any transition between states arising from 1s2, 2s2, 2p1, 3d1 configuration where sigma will be equal to 1 plus 2, 3 and those arising from 1s2, 2s2, 3d1, 4f1 where sigma li will be your 2 plus 3, 5 are also forbidden. So these are two important example to understand what we mean by even to even is not allowed, odd to odd is not allowed or even to odd is allowed or odd to even is allowed.

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Rule 3 is delta J should be 0 or plus minus 1 except that J is equal to 0 to J is equal to 0 is not allowed and that I have discussed several times, so I am not going to discuss in detail. And rule 4 is delta S is equal to 0, so now we have looked at the transition between electronic states of different metal ions. We have discussed about 3 different cases, one is hydrogen like atoms, then we looked at alkali and alkaline metals and now we have looked at the metals where more than one electron in outer most orbital. So now we are done with atoms spectra of atoms.

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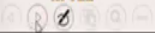
Now we will move to electronic spectroscopy of diatomic molecules.

So to get the energy states in the homo-nuclear diatomic molecule we need to understand the molecular orbital theory. So molecular orbital approach gives a fair qualitative description of electronic structure of diatomic and polyatomic molecule. So here we will discuss only about qualitative part, in this approach what we consider? We consider that two nuclei without their electron are distance apart equal to the equilibrium (nuclear) inter-nuclear distance and what we will do is to construct molecular orbitals around them.

So since it is diatomic molecule so there will be 2 nucleus and what we are going to do is we are going to assign atomic orbital to one and atomic and atomic orbital to second nucleus and then we will construct molecular orbital around them. After molecular orbital construction then we will fill electrons in the pairs, in order of increasing energy of orbitals to give ground configuration of the molecules. This the basis of constructing the molecular orbital is known as linear combination of atomic orbitals (LCAO).

So here molecular orbital wave function is expressed as linear combination of atomic orbital wave function which is Xi i on both nuclei, so wave function for the molecular orbital is given by sigma ci this is the coefficient of wave function Xi and Xi is wave function of atomic orbitals, so if there are diatomic molecules then there will be two terms here, two terms.

There is a very important restriction for linear combination, for effective linear combination three condition should be satisfied, the energies of atomic orbitals must be comparable, the atomic orbital should overlap as much as possible and atomic the orbital must have same symmetry property with respect to certain symmetry elements of the molecule this is very important and so you cannot go and take any atomic orbital and you make a molecular orbital, energies of the atomic orbital must be comparable so that is very important.

For a homonuclear diatomic molecule with nuclei labelled 1 and 2 the LCAO method gives the MO wave function

$$\psi = c_1\chi_1 + c_2\chi_2 \qquad \dots\dots(2)$$

Energy of MO and coefficients can be obtained from Schrödinger equation

$$H\psi = E\psi \qquad \dots.(3)$$

Multiplying both sides by ψ^* and integrating over all space gives

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \dots\dots(4)$$

Combining equation (2) and (4) we will get avg energy....

$$\bar{E} = \frac{\int (c_1^2\chi_1 H\chi_1 + c_1 c_2\chi_1 H\chi_2 + c_1 c_2\chi_2 H\chi_1 + c_2^2\chi_2 H\chi_2)d\tau}{\int (c_1^2\chi_1^2 + 2c_1 c_2\chi_1\chi_2 + c_2^2\chi_2^2)d\tau} \qquad \dots(5)$$

So, suppose I have a homo-nuclear diatomic molecule, this is one atom, this is second atom then if I level this 1 and the second atom with 2 then LCAO method gives the molecular orbital wave function as Psi is equal to c1 CHI 1 plus c2 CHI 2 where CHI 1 is associated with the nucleus 1 and CHI 2 is associated with nucleus 2, so CHI 1 is wave function associated with nucleus 1 and CHI 2 is wave function associated with nucleus 2. Now we can go ahead and calculate energy of molecular orbital. So energy will be given as H Psi is equal to E Psi and if you multiply this by Psi star and then you integrate it and divide this by Psi star Psi d tau you are going to get energy and this is well known variation theorem.

So combining the equation 2 and equation 4, so let us put Psi at this place and you plug in the value of Psi what you are going to get is this whole term. So basically you are checking this star Hamiltonian multiplied by the Psi d tau and you are integrating and here you are integrating Psi star Psi d tau. So what you are going to get is C1 square CHI 1 H CHI 1 plus C1C2 CHI 1 H CHI 2 plus C1C2 CHI 2 H CHI 1 plus C2 square CHI 2 H CHI 2 and d tau. And when you solve this what you are going to get is C1 square CHI 1 square plus 2 C1C2 CHI 1 CHI 2 plus C2 square CHI 2 square d tau.

- If the atomic orbital wave functions are normalized

$$\int \chi_1^2 \, d\tau = \int \chi_2^2 \, d\tau = 1 \quad \text{...(6)}$$

And,

$$\int \chi_1 H \chi_2 \, d\tau = \int \chi_2 H \chi_1 \, d\tau = H_{12} \quad \text{.....(7)}$$

$$\int \chi_1 \chi_2 \, d\tau = S \quad \text{.....(8)}$$

S is called the overlap integral as it is a measure of the degree to which χ_1 and χ_2 overlap each other.

After simplification equation (5) becomes

$$\bar{E} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1 c_2 S + c_2^2} \quad \text{....(9)}$$

Using the variational principle to optimize c_1 and c_2, putting $\frac{d\bar{E}}{dc_1}$ and $\frac{d\bar{E}}{dc_2}$ equal to zero.

If the atomic orbitals wave function are normalized then CHI 1 square d tau when it is integrated will be equal to CHI 2 square d tau and that will be equal to 1 and let us give short notation for this H12, H12 is integral of CHI 1, Hamiltonian CHI 2 d tau and then give a notation for this integral as S, if we do that which is very simple to write this energy term, where energy will be c1 square H11 where H11 will be CHI 1 Hamiltonian CHI 1 d tau with integral.

For a homonuclear diatomic molecule with nuclei labelled 1 and 2 the LCAO method gives the MO wave function

$$\psi = c_1 \chi_1 + c_2 \chi_2 \quad \text{.....(2)}$$

Energy of MO and coefficients can be obtained from Schrödinger equation

$$H\psi = E\psi \quad \text{....(3)}$$

Multiplying both sides by ψ^* and integrating over all space gives

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$$\bar{E} = \frac{\int (c_1^2 \chi_1 H \chi_1 + c_1 c_2 \chi_1 H \chi_2 + c_1 c_2 \chi_2 H \chi_1 + c_2^2 \chi_2 H \chi_2) \, d\tau}{\int (c_1^2 \chi_1^2 + 2c_1 c_2 \chi_1 \chi_2 + c_2^2 \chi_2^2) \, d\tau} \quad \text{...(5)}$$

So if you remember here, you see here this is CHI 1 H CHI 1.

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- If the atomic orbital wave functions are normalized

$$\int \chi_1^2 \, d\tau = \int \chi_2^2 \, d\tau = 1 \quad ...(6)$$

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Using the variational principle to optimize c_1 and c_2, putting $\frac{d\bar{E}}{dc_1}$ and $\frac{d\bar{E}}{dc_2}$ equal to zero.

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And that is what we are writing as H11, so E will be C1 square H11 plus 2C1C2 H12 since this two are equal so there will be twice of C1 C2 H12 and then C2 square H22 divided by C1 square plus 2 C1 C2 S plus C2 square. Now we can use variation principle to optimize C1 and C2 by putting the dE by dC1 and dE by dC2 equal to 0, that is what we did when we were discussing the two electron system, two electron system in an atom.

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Equation (9) becomes

$$c_1(H_{11} - E) + c_2(H_{12} - ES) = 0$$
$$c_1(H_{12} - E) + c_2(H_{22} - ES) = 0 \qquad \qquad ......(10)$$

Equations (10) are the secular equations and the two values of E which satisfy them are obtained by solution of the two simultaneous equations or from secular determinant

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{12} - ES & H_{22} - E \end{vmatrix} = 0 \quad ...(11)$$

H_{12}= Resonance integral = β
H_{11}= H_{22}= Coulomb integral = α
Secular determinant becomes,

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \qquad ...(12)$$

So if we do that, what we are going to get is this equation C1 H11 minus E plus C2 H12 minus ES is equal to 0 and the second equation will be C1 H12 minus E plus C2 H22 minus ES is equal to 0.

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- If the atomic orbital wave functions are normalized

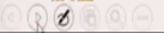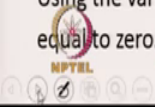$$\int \chi_1^2 \, d\tau = \int \chi_2^2 \, d\tau = 1 \quad ...(6)$$

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S is called the overlap integral as it is a measure of the degree to which χ_1 and χ_2 overlap each other.

After simplification equation (5) becomes

$$\bar{E} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1 c_2 S + c_2^2} \qquad ....(9)$$

Using the variational principle to optimize $c_1 \; and \; c_2$, putting $\frac{d\bar{E}}{dc_1}$ and $\frac{d\bar{E}}{dc_2}$ equal to zero.

So these two equations we will get if we differentiate E with respect to C1 and E with respect to C2.

Equation (9) becomes

$$c_1(H_{11} - E) + c_2(H_{12} - ES) = 0$$
$$c_1(H_{12} - E) + c_2(H_{22} - ES) = 0$$

......(10)

Equations (10) are the secular equations and the two values of E which satisfy them are obtained by solution of the two simultaneous equations or from secular determinant

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{12} - ES & H_{22} - E \end{vmatrix} = 0 \quad ...(11)$$

H_{12} = Resonance integral = β
H_{11} = H_{22} = Coulomb integral = α
Secular determinant becomes,

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad ...(12)$$

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And when we make it zeroes then we have two equations, this equation are called secular equations and two values of E will be obtained if can solve this and the way we solve it is by writing a matrix where the matrix is 2 into 2 matrix. The first element is H11 minus E, H12 minus ES, H12 minus ES and H22 minus ES.

Now if you remember H12 it involves wave function of both nuclei and that is why H12 is called resonance integral. Now let us put it as beta and H11, H22 is coulomb integral and they involve the individual nuclei, and put it as alpha. So then secular determinants become alpha minus E, beta minus ES, beta minus ES alpha minus E is equal to 0.

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Equation (12) becomes

$$(\alpha - E)^2 - (\beta - ES)^2 = 0 \quad .....(13)$$

From equation (13) we obtain two values of E, namely E_+ and E_-

$$E_\pm = \frac{\alpha \pm \beta}{1 \pm S} \quad ....(14)$$

For very approximate MO wave functions and energies we can assume that S=0 and H is the same as in the atom, giving $\alpha = E_A$, the AO energy.

Hence, $\quad E_\pm \approx E_A \pm \beta \quad ....(15)$

And when you solve that what you get is alpha minus E square minus beta minus ES square is equal to 0 and if we solve this we can get two values of E which is known as E plus-minus and that will be equal to alpha plus minus beta divided by 1 plus-minus S. If we assume that S is equal to 0 then we have E plus minus is equal to EA plus minus beta.

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With this approximation that S=0, secular equations become

$$c_1(\alpha - E) + c_2\beta = 0$$
$$c_1\beta + c_2(\alpha - E) = 0 \quad \Big\} \quad ... \quad (16)$$

Putting $E = E_+$ or E_- we get $c_1/c_2 = 1$ or -1, respectively. Wave functions:

$$\psi_+ = N_+(\chi_1 + \chi_2)$$
$$\psi_- = N_-(\chi_1 - \chi_2) \quad \Big\} \quad .....(17)$$

N_+ and N_- are normalization constants obtained from conditions

$$\int \psi_+^2 d\tau = \int \psi_-^2 d\tau = 1 \quad .....(18)$$

Neglecting $\int \chi_1\chi_2 d\tau$, the overlap integral gives $N_+ = N_- = 2^{-1/2}$

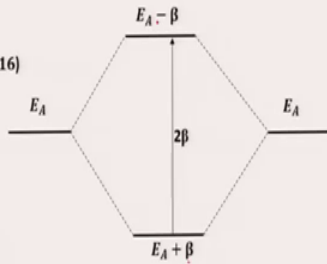$$\psi_\pm = 2^{-1/2}(\chi_1 \pm \chi_2) \quad .....(19)$$

Fig: Formation of two molecular orbitals from two identical atomic orbitals

So same approximation we can write, here we have taken S is equal to 0, so ES term vanishes and so what we get is these two equations, if we put the value of E plus and E minus then we can get C1 by C2 is equal to either 1 or minus 1 and now we can write the two wave function

corresponding to two molecular orbital. N plus, N minus are normalization factor which can be obtained from the condition this and when you do that what you will get is N plus is equal to N minus is equal to 2 minus half. So these is your wave function, E we have already calculated, E is EA plus beta and EA minus beta and difference between this two is 2 beta. So two atomic orbitals on linear combination give you two molecular orbitals with energy EA plus beta and EA minus beta.

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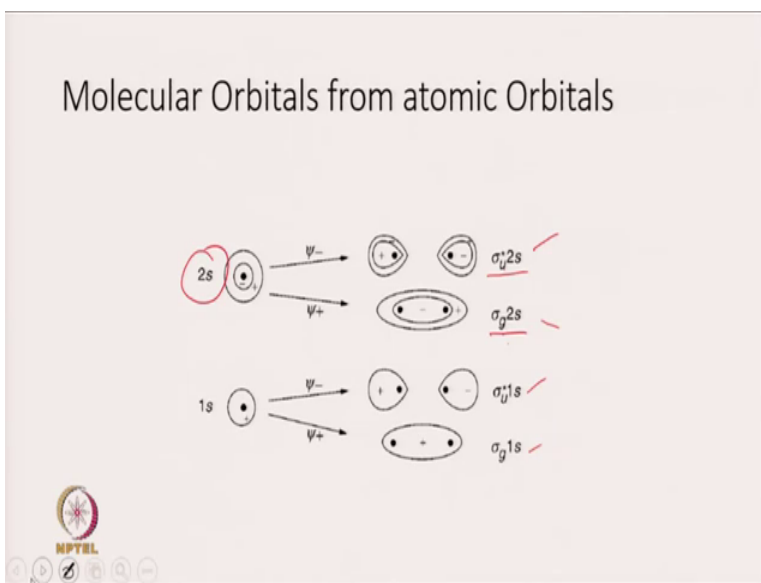
So now we know that two atomic orbitals combine to get two molecular orbitals. Let us see and take orbitals one by one and see which kind of molecular orbitals we can get from different atomic orbitals.

For example we take 2s orbital then if they will combine to give you two molecular orbitals, two molecular orbital and one is your sigma g and this sigma u star, this is bonding orbital, this is anti-bonding orbital so this is an u for ungerard and g is for gerard, so 1s will combine to give you sigma u star 1s and sigma g 1s.

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Molecular Orbitals from atomic orbitals
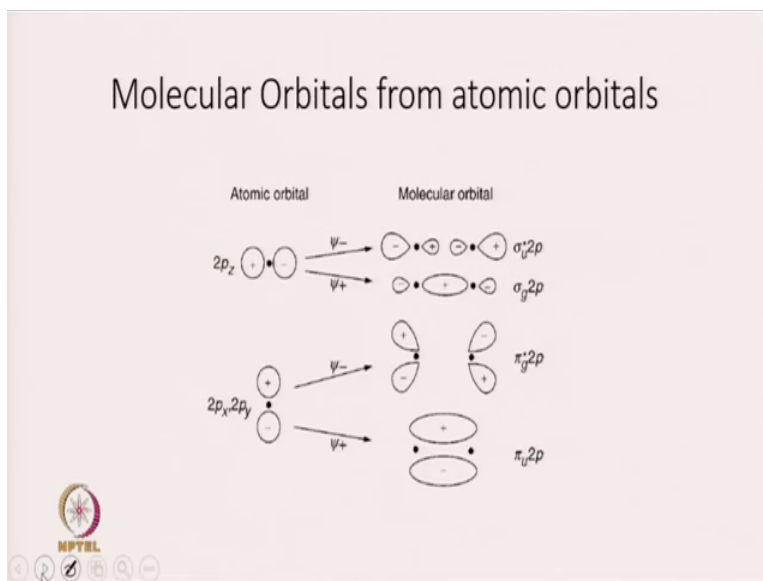
Two atomic orbital or 2pz will combine to give sigma g 2p and sigma u star 2p and 2px and 2py will combine to give Pi 2p and Pi g star 2p. Now we can see that sigma will result from side to side overlap, side to side overlap whereas this Pi will result from this kind of overlapping, Pi will result from this kind of overlapping.

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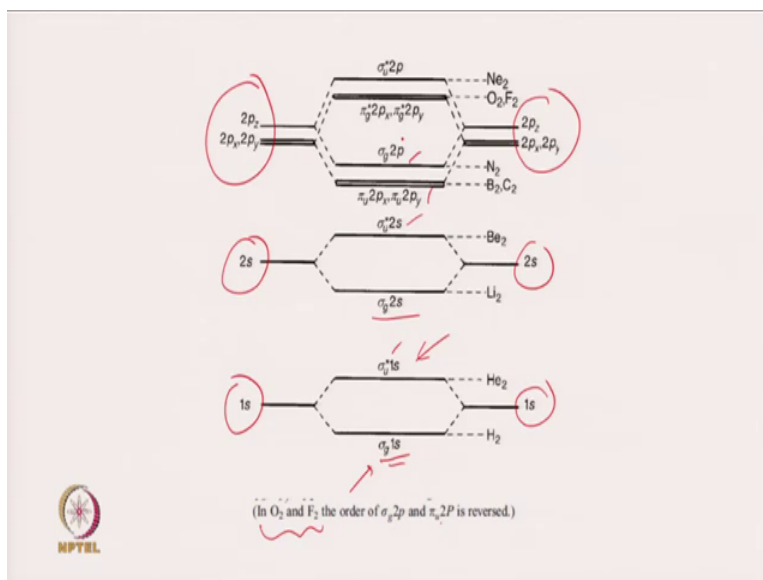
Now we can write the molecular orbitals, so in any atom you have 1s orbital, 2s orbital and this 2px, 2py, 2pz orbital. For the second one you have 1s, 2s, the 2px, 2py, 2pz orbital and 1s is going to overlap with 1s and giving you sigma g1s and sigma u star 1s, 2s orbital of one atom is

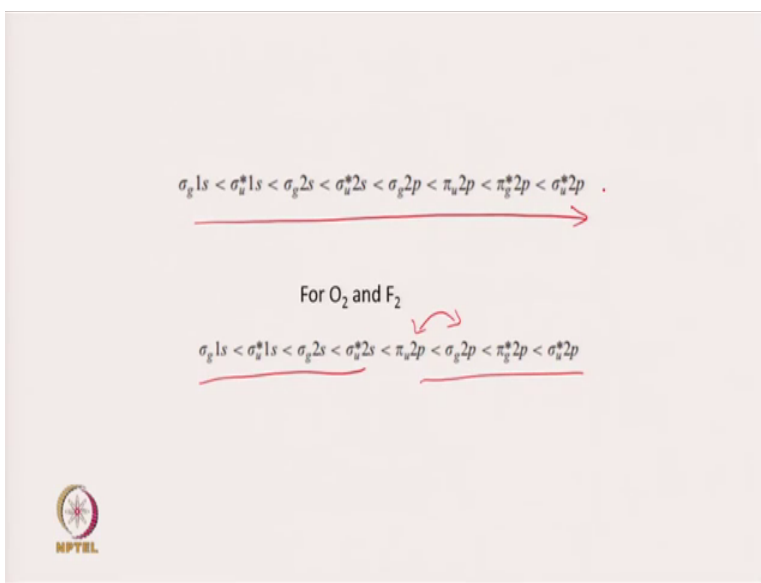going to combine with 2s orbital of another atom giving sigma g 2s and sigma u star 2s and this is the way your energy increases.

So lowest is sigma g 1s and sigma u star 1s these are the different electronic steps, different molecular orbital and their energies. Only difference comes in oxygen and fluorine where sigma g 2p this is sigma g 2p and Pi u 2p this one is reversed, it means that this will come down and this will come up. Otherwise your this molecular orbital picture is valid for your any homo-diatomic molecule.

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$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \sigma_g 2p < \pi_u 2p < \pi_g^* 2p < \sigma_u^* 2p \quad .$$

For O_2 and F_2

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p < \sigma_g 2p < \pi_g^* 2p < \sigma_u^* 2p$$

So this is your different molecular orbitals and their energies, so lowest is sigma g 1s and then sigma u star 1s, sigma g 2s, sigma u star 2s and this is the way energy is increasing. For oxygen and f2 there is a difference it the last, so you see here that till this point it is same after that sigma your g 2p and Pi u 2p there is exchange and again last two is same, so this is the way your molecular orbital picture describes you the energy of the different molecular orbitals.

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Now let us think about (your) electronic states for diatomic molecules. Till now we have looked at what is the different molecular orbitals, how they different their energies? Now we are going to look at electronic states. Vector L is strongly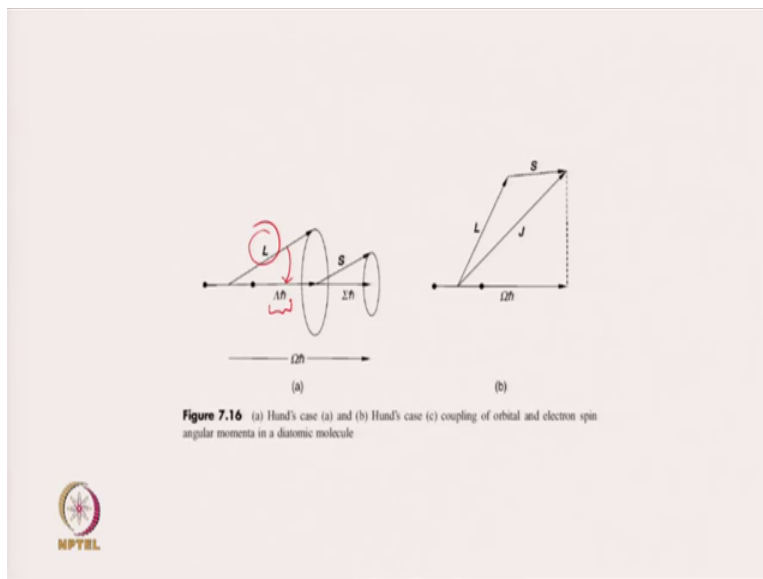 coupled to the electrostatic field, so in the diatomic molecule it is very important to remember vector L is strongly coupled to the electrostatic field and the consequently frequency of precession about the inter-nuclear axis is so high that the magnitude of L is not defined in other words L is not a good quantum number for diatomic molecule, what we are going to look at is your orbital angular momentum along the inter-nuclear axis which is defined and which is equal to lamtha h cross, this is lamtha and h cross where the quantum number lamtha can take values 0, 1, 2, 3.

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Figure 7.16 (a) Hund's case (a) and (b) Hund's case (c) coupling of orbital and electron spin angular momenta in a diatomic molecule

So look at this picture here we are not concerned about L, what we are concerned about is its component along the inter-nuclear axis and that is your lamtha h cross, lamtha h cross.

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Electronic states in diatomic molecule

• All the electronic states with Λ (lamtha) > 0 are doubly degenerate.

• Classically, this degeneracy can be thought of as being due to the electrons orbiting clockwise or anticlockwise around the internuclear axis, the energy being the same in both cases.

• If Λ = 0 there is no orbiting motion and no degeneracy.

• The value of Λ, like that of L in an atom, indicated by the main part of the symbol for an electronic state which is degenerated $\Sigma, \Pi, \Delta, \Phi, \Gamma, ...$ corresponding to Λ = 0, 1, 2, 3, ...

Now all the electronic states with lamtha greater than 0 are doubly degenerated, classically this degeneracy can be thought of as being due to the electrons orbiting clockwise or anticlockwise around the inter nuclear axis. The energy being the same in both cases. Lamtha is equal to 0 there is no orbiting motion and no degeneracy, so lamtha is equal to 0 does not have any degeneracy but lamtha is greater than 0 are doubly degenerate. Value of lamtha like that of L in an atom

indicated by main part of the symbol for an electronic state, so if lamtha is 0 it means you have wasted sigma, if lamtha is 1 corresponds to Pi, lamtha is 2 corresponds to phi, lamtha is 3 corresponds to tau.

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Table 8.1 Symbols for many-electron states in linear molecules.

Λ	0	1	2	3	4
Letter	Σ	Π	Δ	Φ	Γ

Table 8.2 Symbols for MO types in a linear molecule.

$\lambda\ (\pm\mathrm{m})$	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

$(1\sigma_g)^2 \longrightarrow \Sigma_g$ $\qquad\qquad 1\sigma_g 1\sigma_u^{*1} \longrightarrow \Sigma_u$

So that is what it is written here that lamtha 0 corresponds to sigma, 1 corresponds to Pi, 2 corresponds to delta, 3 corresponds to phi, 4 corresponds to tau. Now symbol for molecular orbital in linear molecule, right now we have looked at the molecular orbital and what will be the lambda value which is basically plus minus m is for sigma this lambda is equal to 0, for Pi this lambda is equal to 1, delta it is 2, phi 3 and this gamma 4.

So for example if we are dealing with 1 sigma g2, which is basically ground state of s2 atom. Now you see there are two electrons in sigma and so sigma lambda or sigma m will be equal to 0.

Electronic states in diatomic molecule

- All the electronic states with Λ (lamtha) > 0 are doubly degenerate.

- Classically, this degeneracy can be thought of as being due to the electrons orbiting clockwise or anticlockwise around the internuclear axis, the energy being the same in both cases.

- If Λ = 0 there is no orbiting motion and no degeneracy.

- The value of Λ, like that of L in an atom, indicated by the main part of the symbol for an electronic state which is degenerated Σ, Π, Δ, Φ, Γ, ... corresponding to Λ = 0, 1, 2, 3, ...

And 0 corresponds to if you look at if lamtha is equal to 0 it corresponds to sigma state.

Table 8.1 Symbols for many-electron states in linear molecules.

Λ	0	1	2	3	4
Letter	Σ	Π	Δ	Φ	Γ

Table 8.2 Symbols for MO types in a linear molecule.

λ	0	1	2	3	4
letter	σ	π	δ	φ	γ

$(1\sigma_g)^2 \rightarrow \Sigma_g$

$1\sigma_g 1\sigma_u^* \rightarrow \Sigma_u$

And that's what we are writing sigma and g multiply by g gives you g and so it will have Gerard symmetry. Now look at the first excited state of hydrogen molecule, 1 sigma g, 1 sigma u star that is the molecular orbital. Again if you look at the value of sigma it is 0, so the value of lambda it is 0 for sigma, so this is 0, this is 0, 0 plus 0 and this is summation u, only thing changes is the symmetry and so these are the different electronic s states associated with the

particular configuration. So sigma g is basically associated with or 1 sigma g 2 and this sigma u is associated with this excited state of hydrogen molecule, so this is about L part.
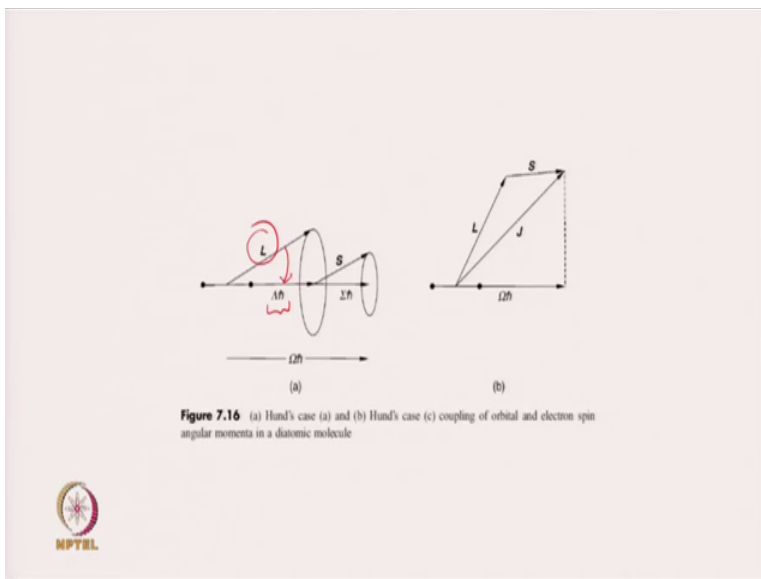
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S-coupling in diatomic Molecule

- The coupling of S to the internuclear axis is caused not by the electrostatic field, which has no effect on it, but by the magnetic field along the axis due to the orbital motion of the electrons.

- The component of S along the internuclear axis is $\Sigma\hbar$.

- The quantum number Σ is analogous to M_s in an atom and can take the values : $\Sigma = S, S-1, ..., -S$.

Now what about S Coupling of S to inter nuclear axis is caused not by the electrostatic field, so S is just a positive here which has no effect on it. So electrostatic field does not have effect on S but by the magnetic field along the axis due to orbital motion of the electron.

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Figure 7.16 (a) Hund's case (a) and (b) Hund's case (c) coupling of orbital and electron spin angular momenta in a diatomic molecule

Although the electrostatic field does not have effect on S, we still have to look at the component along this because your S or LS coupling will be in this direction only because L is in this direction.

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S-coupling in diatomic Molecule

- The coupling of S to the internuclear axis is caused not by the electrostatic field, which has no effect on it, but by the magnetic field along the axis due to the orbital motion of the electrons.

- The component of S along the internuclear axis is $\Sigma\hbar$.

- The quantum number Σ is analogous to M_s in an atom and can take the values : $\Sigma = S, S-1, ..., -S$.

And so component of S along inter nuclear axis sigma h cross and quantum number sigma is analogous to Ms in an atom and can take value from S to minus S.

What does that mean is S remains a good quantum number and for the state with lamtha is greater than 0, there are two S plus 1 component corresponding to number of values that sigma can take and that is we have already discussed in the atomic orbital that if it can take 2s plus 1 component. So the multiplicity of the state is the value of 2s plus 1 as we have seen in atomic spectra and is indicated as in atoms in by a pre super script as for example in 3 Pi if s is 1 then divide 2 plus 1 3.

Now again go to hydrogen atom ground state, it is 1 sigma g2 and since you have a sigma g2 this can be like this, so s is going to be 0 and so multiplicity will be going to be 1, (so) since both can be occupied like this so s is equal to 0 and multiplicity will be equal to 1. Now take this case, so in this case you have one electron here and one electron here and now multiplicity can be due to this or can be due to 1 up and another down, when both are up then your multiplicity is going to be 3 and when both are down 1 is down and 1 is up then your S is equal to 0 and multiplicity is going to be 1. So due to S you have two different energy states, whereas electronics states where for 1 sigma g2 there will be 1 electronic state.

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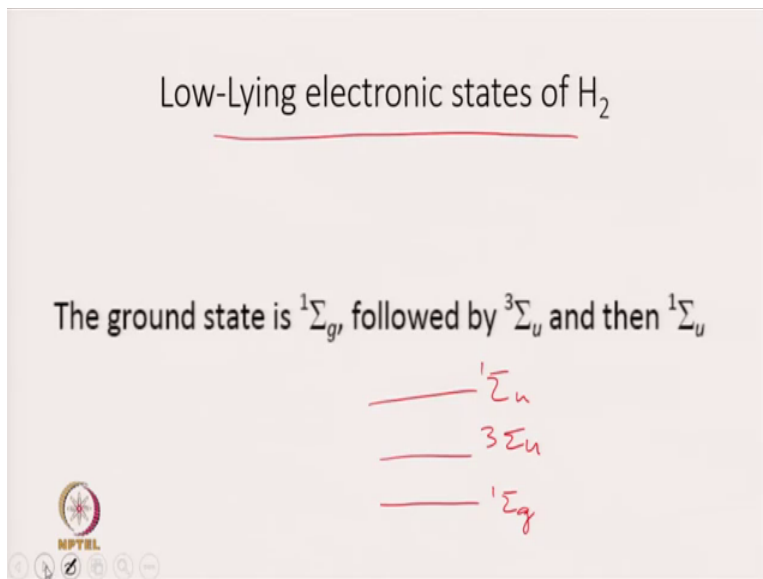
So if you look at low lying electronic states of H2 here we considered only your the first molecular orbital or lowest energy molecular orbital and the first excited state. So here you are going to have three different energy states, the ground state is 1 sigma g and then you have a 3 sigma u and 1 sigma u, so this is the electronic states of hydrogen atom.

Other diatomic molecules electronic configuration are written by assigning electrons to a selected set of shells. Closed shells do not contribute to either the total spin quantum number S or lamtha of the molecular term, the electronic configuration in which all shells are closed gives only a single term this is 1 sigma g, high spin multiplicity is possible only if there are open shells.

Now I will discuss only one case and then I will stop, for example lithium 2, the ground state is equal to in ground state there are 2 electron in sigma g, 2 electron in sigma u and 2 electron in 2

sigma g, so all shells are closed, so term symbol of ground state of lithium 2 is 1 sigma g. Now let us look at one excited state of lithium 2, so there are 2 electron in 1 sigma g, 2 electron in 1 sigma u star, 1 electron in 2 sigma g and 1 electron in 2 sigma u star, so 2 electron from 2 sigma goes to 2 sigma u star, since both electron in open shell has m is equal to 0, this is electron is in sigma so m is equal to 0, so your lamtha will be 0 and both S is equal to 0 and S is 1 is possible because these are in two different states.

So it can be like this, it can be like this also and so S is equal to 1 here, in this case S is equal to 1, in this case S is equal to 0 and so both S is equal to 0 and S is equal to 1 is possible and overall parity will be g cross u is equal to u and so you have two different term 1 sigma u and 3 sigma u. So this is the way you can get electronic states of different states of lithium 2 plus or lithium 2. So we looked at in this lecture, we looked at how to get the different electronic states of your diatomic molecule and once we know that and using selection rule we can know what kind of spectra we can expect for a diatomic molecule.

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So i will stop here and thank you for listening, most of this material has been taken from modern spectroscopy book by Hollas, so I will recommend this book to you. So please go through it and try to understand, thank you very much.