Chemistry Atomic Structure and Chemical Bonding
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Lecture – 35
Coupling of Two Angular Momenta

Welcome back to the lectures on Chemistry, on the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am in the Department of Chemistry Indian Institute of Technology, Madras. We will continue with the lecture on the Interaction between two spin half systems, Quantum Chemistry. A little bit on my personal on a personal note. Actually, I want to thank one of the great teachers I have ever had in my life who taught me Angular Momentum, and who taught many things about the Coupling between Angular Momenta, and the whole of the theory of NMR spectroscopy. And it is extremely important sometime during these lectures I mentioned that I learned from some of these very people.

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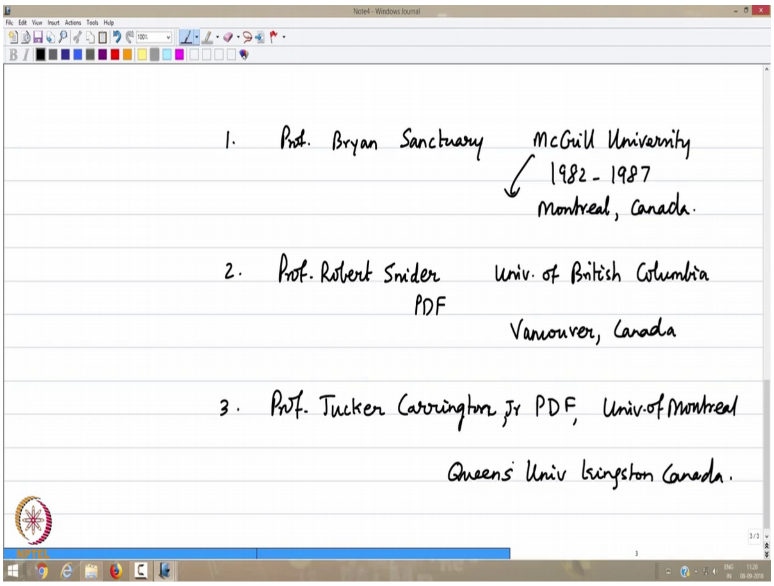

And, the first and foremost among them is Professor Bryan Sanctuary McGill University because he was my PhD mentor, during the period 1982 to 1987. This is one of the most famous Universities in Canada and all over the world; it is in Montreal Canada. And another extremely important and one of the most influential professors in the academic value system that I have learned is also Professor Robert Snider with whom I spent the first postdoctoral period in the university of British Columbia. This is on the other side of Canada namely in Vancouver, one of the most beautiful cities in the world.

And thirdly in these areas; particularly in the areas of Angular Momentum the third and an equally important learning that has happened to me is through my association with Professor Tucker Carrington junior. His father is also Tucker Carrington and he was a professor, he yes he was earlier a Professor of Physical Chemistry in the University of Yark Yark, but Professor Tucker Carrington when I was associated with him as a postdoctoral fellow pdf. So, I should write junior he was in the University of Montreal; currently he is now a Chair Professor in the Queen's University Kingston Canada; I mean many many years ago back.

These are three professors from whom, I should say I have learnt the most of angular momentum; both from the point of view of magnetic resonance where we used the convention that the angular momentum commutation relations have a plus ih bar on the right hand side namely the ix iy commutator is plus ih bar iz. That is what we do in all of magnetic resonance and all of the electron spectroscopy electronic spectroscopy: and then the moment you go to molecular spectroscopy and you look at rotational angular momentum and the coupling of angular momentum with vibrational motion and all the others. The sign changes due to the anomalous computation relations and due to fact that we use a molecule fixed coordinate system.

So, angular momentum from both of the body fixed axis as well as the space fixed axis. I mean I learnt a lot of these things from all the three professors. So, it is important for me to remember at least. At some point of time that there were great people who taught me of course, whatever the mistakes I make are mine ok, that is also known.

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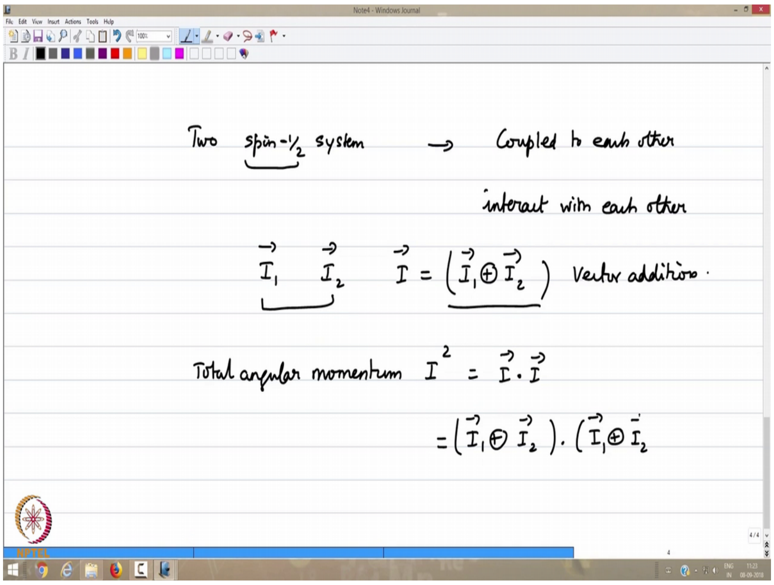

Let us start with two spin half systems, not two independent spin half systems. So, I would write two spin one half system, the spin one halves are coupled to each other or interact with each other. An angular momentum being a vector, if we assume that the spin 1 has an angular momentum I 1 we are removing the h bar out of the picture, because this is a dimensionless angular momentum, at any point of time we can always bring it back to the measured quantities by putting in the right dimensions.

One spin with I 1 and another with I 2 in the total angular momentum associated with the two spin system is I 1 plus I 2 it is a vector addition. Therefore, the total angular momentum square which we will call as I the total angular momentum squared I squared is I dotted with I. And the equation is I 1 plus I 2 dotted with I 1 plus I 2 which when you expand gives you I 1 squared plus I 2 squared plus 2 I 1 dotted I 2.

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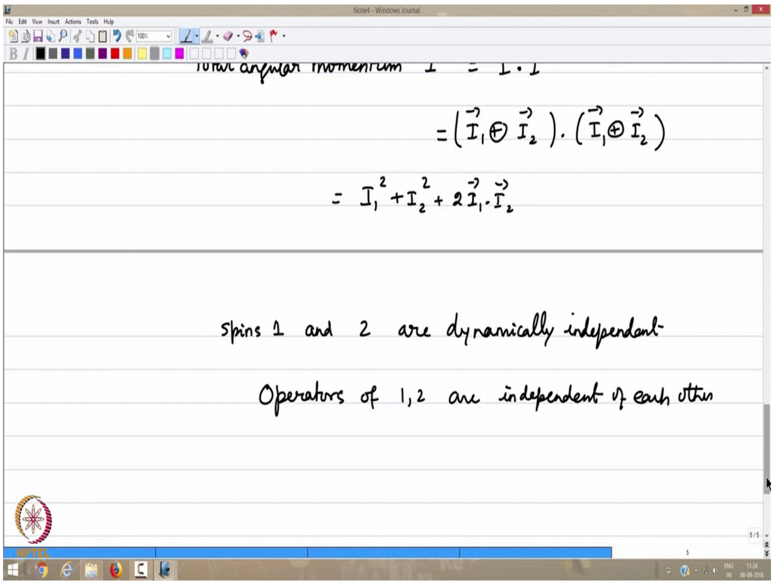

Remember: spins 1 and 2 are dynamically independent. Independent in the sense the operators associated with these two spins. This is what it is operators associated with two spins are independent of each other.

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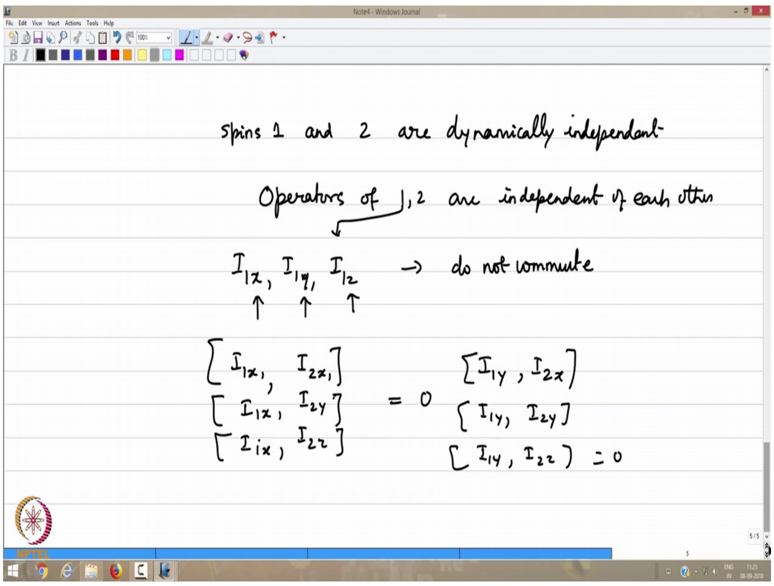

Therefore, the first thing we have to know is that the operator for spin one which contains I 1 x, I 1 y, I 1 z; these are the x component of spin 1, y component of spin 1 and z component of spin 1. They are related to each other they do not commute among themselves. However, I 1 x commutes independently with I 2 x, I 2 y, I 2 z ok. The commutator if you take this the commutator of I 1 x with I 2 x, or I 2 y or I 2 z they are all 0. And likewise, for if you replace x by I 1, y I 1, y.

And with the corresponding these are the three quantities that you have corresponding quantities with I 2 x, I 2 y, I 2 z, all these commutators are 0. And similarly, for I 1 z with I 2 x. However, the commutator of I 1 x and I 1 y they have the same relationship that we have studied till now in the last two lectures two or three lectures you have seen. So, this is what is called the Dynamical Independence of the operators associated with independent particles we will keep this in mind.

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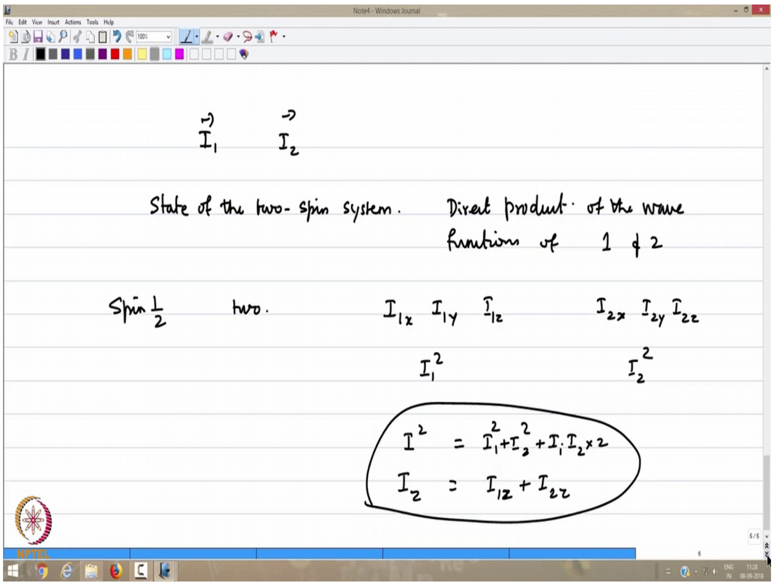

The moment we have two spin one halves I 1 and I 2 interact with each other, then what is the state of the two spin system? You had already some indication of a joint probability or a joint wavefunction and now you have to go back to the first exercise in the model problems of quantum mechanics that we did. Namely the particle in a one dimensional box and the particle in a two dimensional box. If you recall the particle in a two dimensional box we considered the motion in a plane, but the x and y coordinates were independent of each other. And, since there was no potential of interaction between the two particles in that system, except that they both were confined to infinite boundaries potential boundaries.

You recall that we wrote the overall wave function of the two particle systems as the x component the overall wave function for the two dimensional the particle in a box system x and y; as the product of the two one dimensional systems the x component only and the y component only. In a similar way if we talk about two independent particles the joint probability or the joint wave function associated with this is the direct product it is called Direct Product. I will explain that in a minute ok, of the wave functions of the two wave functions of the two independent particles of particles 1 and 2.

So, let us start with the spin half system to begin with because that is easy the rest is I mean algebraically more complicated, but not the principles. So, let us take spin half two spin half systems. So, we have what is called the I 1 x, I 1 y, I 1 z and I 2 x, I 2 y, and I 2 z. Then we have I 1 square, I 2 square. And then, we also have I squared which is I 1 square plus I 2 square plus I dot, 1dot I 2 times 2 ok. Then we can also write the I z as the sum of the two z components of the two individuals means I 2 z. So, we will need to look at the effect of some of these things in our analysis of two spin a half system.

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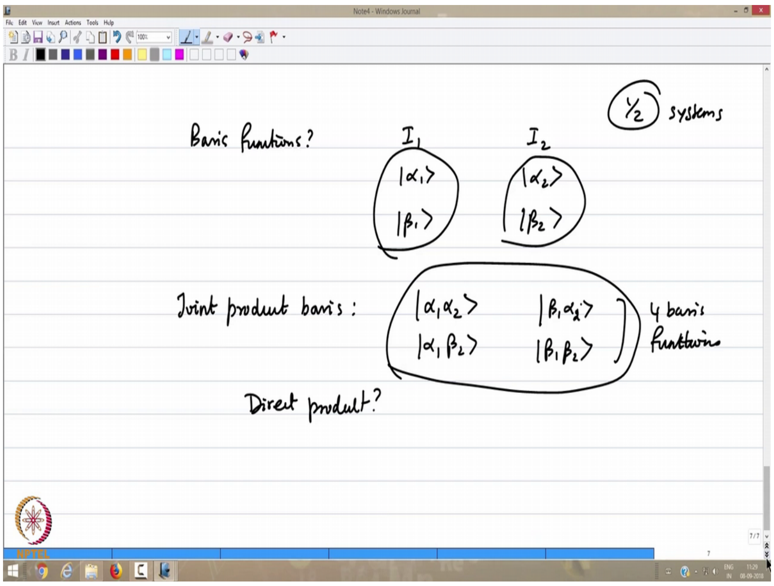

What are the basis functions? For spin 1, I 1 we wrote down alpha 1 and beta 1 per spin I 2 in the half system both I 1 and I 2. We have alpha 2 and beta 2, the 2 corresponds to or denotes the spin 2 state and the 1 substitute corresponds to spin 1 state. The joint product basis, now contains alpha 1 and any one of these alpha 2, alpha1, beta 2 and likewise beta 1 alpha 2 and beta 1, beta 2 therefore, we have 4 basis functions. Why it is called direct product? The total number of basis functions we have is 4, compared to the total number of basis functions that we have for a spin 1 which is 2 and spin 2 which is also 2.

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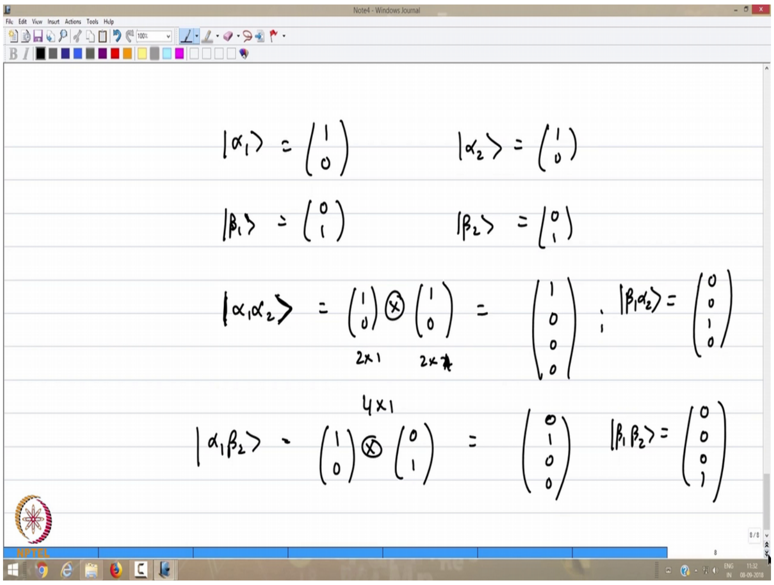

And if you write the matrix representation, please remember alpha 1 corresponded to the matrix 1 by column vector 1 by 1 comma 0. And beta 1 corresponded to the column matrix or column vector 0 1, alpha 2 is also represented as 1 0 into dimension as a single spin system and beta 2 is 0 1. However the joint state of the two spin system alpha 1, alpha 2 is the direct product of the two column vectors. And the direct product will now give you this is a 2 by 1, this is a 2 by 1 the direct product gives you 4 by 1, it is a column vector 1 0 0. And likewise the state alpha 1 beta 2 is the direct product in matrix representation of the 1 0 0 1 which is 0 1 0 0. And you can see immediately the state beta 1, alpha 2 is going to be 0 0 1 0 and beta 1, beta 2 is the matrix 0 0 0 1.

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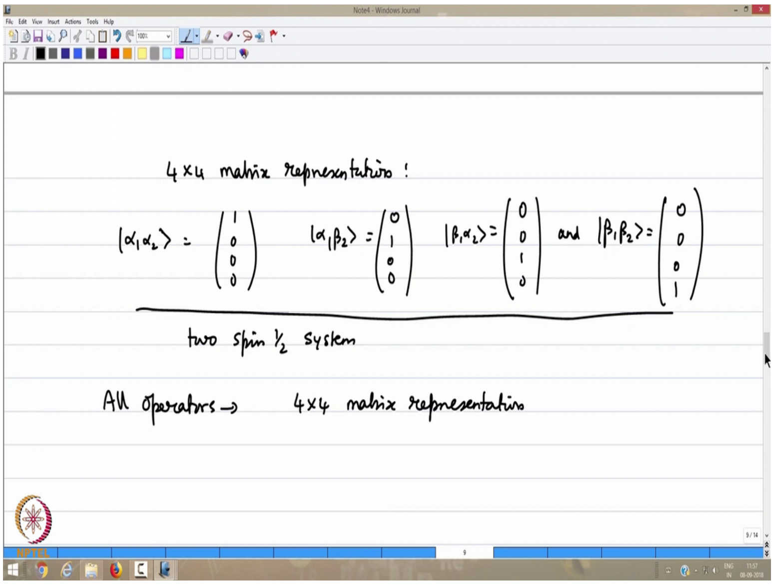

So, the 4 by 4 matrix representation for 4 by 4 matrix representation for the two spin operators they follow. So, you have 4 states alpha 1, alpha 2 given by the column 1 0 0 alpha 1, beta 2 given by the column 0 1 0 0, beta 1 alpha 2 given by this 0 0 1 0 and beta 1, beta 2 even by 0 0 0 1 ok. These are the 4 states for a two spin half system. Therefore, all operators for the two spin half systems will have 4 by 4 matrix representation.

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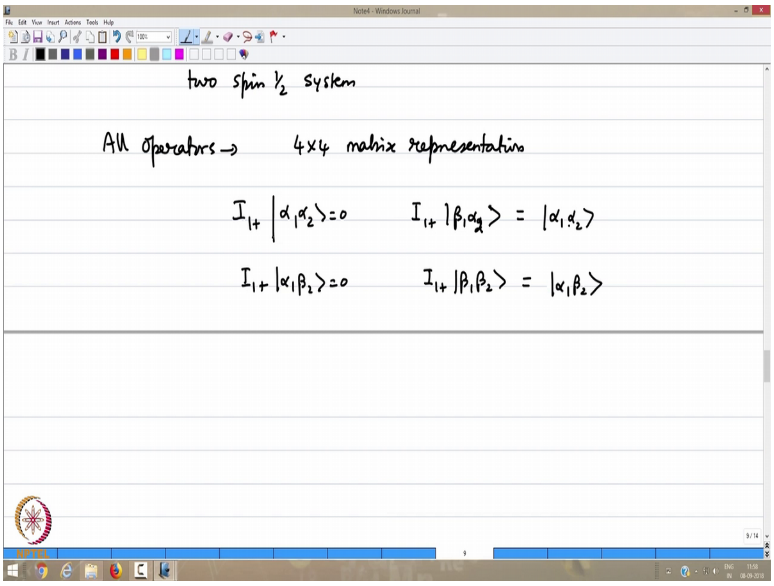

Very quickly we can see this I 1 plus. Now if you think about I 1 plus on alpha 1 with alpha 2. It is 0 I 1 plus on beta 1 alpha 1 alpha 2 is going to give you alpha 1, alpha 2, I 1 plus on alpha 1, beta 2 is also 0 and I 1 plus on beta 1, beta 2 will give you alpha 1, beta 2 ok.

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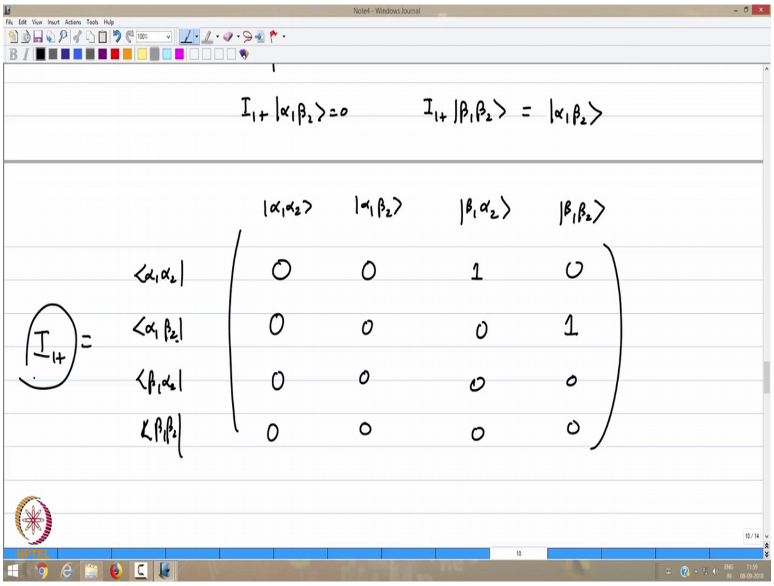

Therefore, what you see here is that the representation for I 1 plus in a matrix form will be now four states; alpha 1, alpha 2, alpha 1, beta 2, beta 1, alpha 2 and beta 1, beta 2. And the same thing here on the side alpha 1, alpha 2, alpha 1, beta 2, beta 1, alpha 2 and beta 1, beta 2. This is I 1 plus is 0, I 1 plus on alpha 1 is also 0, I 1 plus on beta 1 will give you alpha 1, alpha 2 before this is one. I 1 plus on beta 1 beta 2 will give you alpha 1 beta 2 and that is not the same thing; that means, this is 0. And, likewise all these things I 1 plus on all the these are alpha 1, alpha 2 states. So all four of them are 0's. We have to only look at this one this is alpha 1, beta 2. Therefore, here you have alpha 2 therefore, it is 0 because I 1 plus will not change the second spin half state it will beta 2 beta 2 therefore, this will be 1.

And the rest of it also 0 because this is a beta state the betas will be changed to alpha it is always 0 ok. So, this is a way of writing down the matrix element representations matrix representations for operators. Of course, you have got three operators 1 x, 1 y, 1 z or 1 plus1 minus and 1 z whichever it is; so you have three operators on the for the spin 1. And three operators for a spin 2 and therefore, you have essentially 9 such product operators, but if you calculate for a spin half; including the identity which is the fourth operator there are sixteen operators and sixteen operators will be represented by these 4 by 4 matrix representation in some way. This is the idea of what is known as a direct product.

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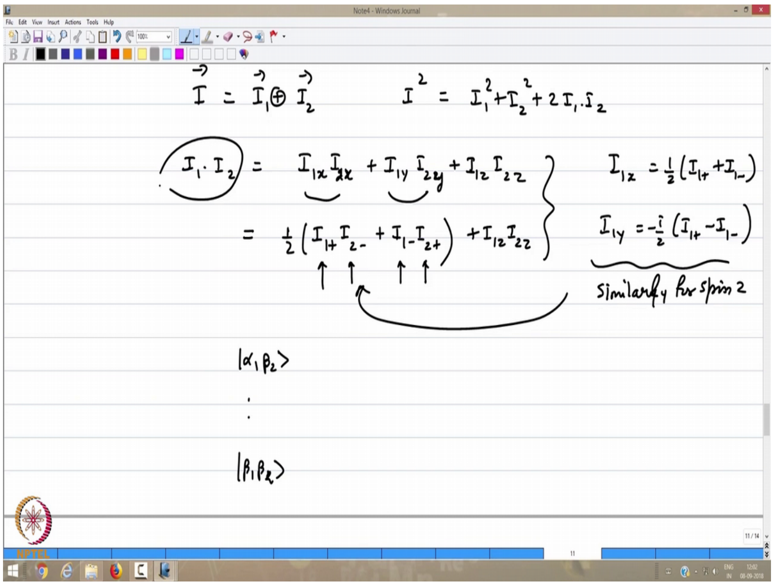

But let us get to the simple interaction between the two spin half systems, namely the total angular momentum I, given as the sum of the two angular momenta I 2. Therefore let us first to look at I squared, which is I 1 squared plus I 2 square plus 2 I 1 dot I 2. Now I 1 dot I 2 can be represented by the corresponding plus minus operators. So, you can write this as: I 1 x, I 1, I 2 x plus I 1 y, I 2 y plus I 1 z, I 2 z. and this can be changed to plus minus operator so it is a very elementary algebra for you to verify that. This gives you 1 by 2, I 1 plus I 2 minus plus I 1 minus I 2 plus I 1 z I 2 z quick hint I 1 x is 1 by 2, I 1 plus plus I 1 minus and I 1 y is minus I by 2 I 1 plus minus I 1 minus. And similarly for spin 2 use that substitution to get this form.

Therefore, the operator I 1 dot I 2 now contains the raising operator for spin 1 and the lowering operator for spin2 as well as the lowering operator for spin 1 and raising operator for spin 2. I 1 z and I 2 z of course, act on the Eigen functions and they do not change the Eigen functions, but the raising and lowering operators will change the Eigen functions of alpha 1, alpha 2 or alpha 1 and beta 2 something else. And therefore, you have to watch that the operator I 1 dot I 2 the base these are not probably the suitable basis functions these 4 basis functions that we have; they are not Eigen functions of this operator.

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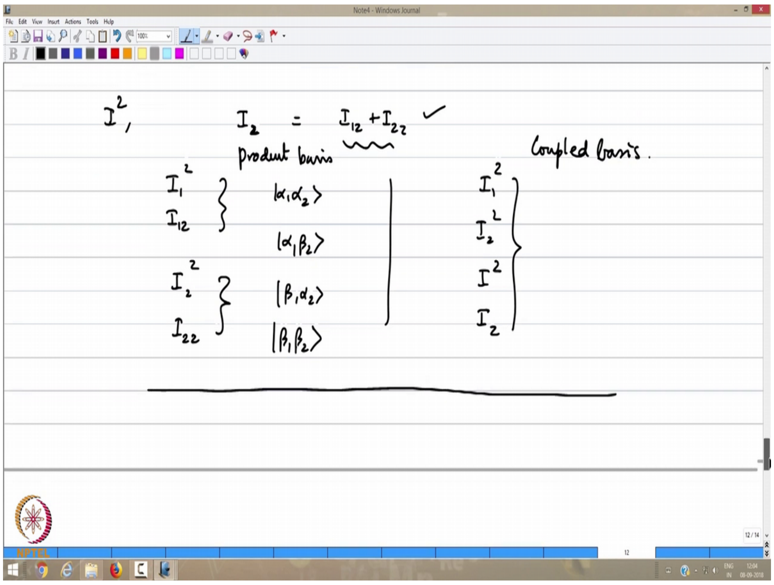

Also if you look at it the I z which is the z component of the total angular momentum, I square the, z component is I 1 z plus I 2 z. and this needs to be calculated for the alpha 1 alpha 2 all the four states and you can calculate that. So, we have two sets of operators namely I 1 square I 1 z which were used to define the states alpha and beta. And I 2 square I 2 z which were used to define the alpha beta states of spin two. This is one set of operators and the corresponding Eigen functions alpha 1, alpha 2, alpha 1, beta 2, beta 1, alpha 2, and beta 1, beta 2.

On the other hand the coupling between the two gives you again the spin 1, I 1 squared and spin 2 I 2 square, but now it gives you I square and it gives you I z. So, these are the four operators for which we may need to find Eigen functions using the properties of the operation of these operators on these functions. So, this is called coupled basis and this is called the product basis ok. So, I will indicate the first couple of steps and then the rest of it can be derived in the same way.

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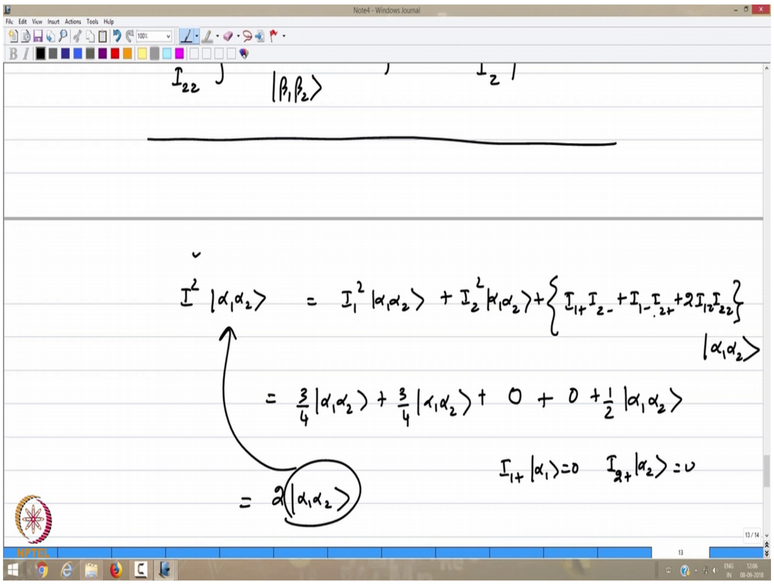

Let us look at the I square on alpha 1 alpha 2 I square on alpha 1 alpha 2 is I 1 square on alpha 1 alpha 2 plus I 2 squared on alpha 1 alpha 2 plus two times I 1 dot I 2. So, that is already a 1 by 2. So what you will have is: I 1 plus I 2 minus plus I 1 minus I 2 plus plus two times I 1 z, I 2 z acting on the state alpha 1 alpha 2 I 1 square will give you 3 by 4 or alpha 1 and alpha 2, I 2 square and alpha 2 also gives you 3 by 4. And the state back alpha 1, alpha 2 and you can easily see that I 1 plus acting on alpha 1 is 0.

Therefore, it gives you the first term is 0 and I 1, I 2 plus acting on alpha 2 that is also 0. Therefore, the second term acting on the state gives you 0, but the third term acting on the state alpha 1, alpha 2 is the product of I 1 z acting on alpha 1 and I 2 z acting on alpha 2 and each one gives you a half. Therefore, is 1 by 4 when the sum is 1 by 2 because there is a 2 here. And it also gives you alpha 1 alpha 2 so, the answer here is 2 times alpha 1 alpha 2. Therefore, the state alpha 1, alpha 2 is an Eigen function of I square no problem.

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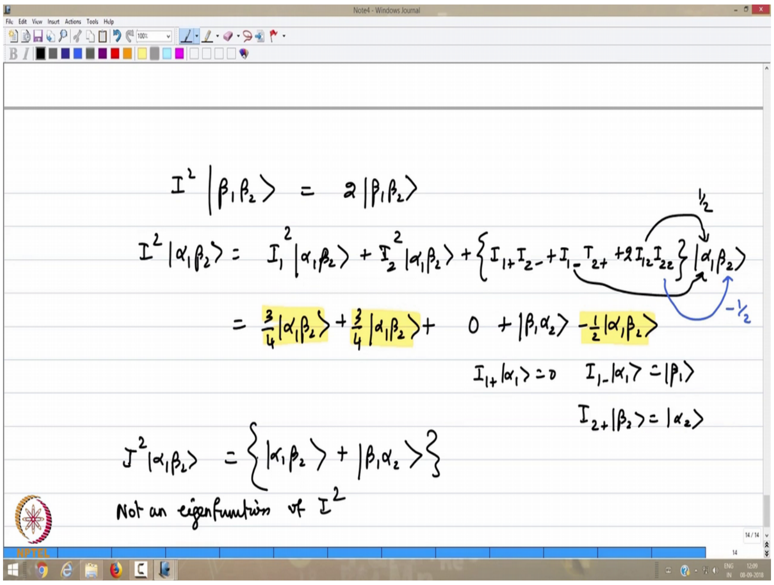

What about beta 1 beta 2? Is easy to verify this on I square you will get exactly the same thing 2 times beta 1 beta 2. I leave it to you as an exercise to do the same way that you have done the other one. However, I square on alpha 1 beta 2 is quite interesting and you will see it right away that it is not alpha 1 beta 2 is not an Eigen function of I square. So, it is I 1 square acting on alpha 1, beta 2, plus I 2 square acting on alpha 1, beta 2, plus I 1, plus I 2, minus plus I 1, minus I 2, plus plus 2 I 1 z I 2 z acting on alpha 1, beta 2.

This is of course, I 1 square on alpha 1 gives you the same things therefore, you have 3 by 4alpha 1 beta 2. And you have also a 3 by 4 acting on alpha 1 beta 2. But now, the first term I 1 plus acting on alpha 1 is going to be 0 therefore, this is 0. However, the second term which is I 1 minus I 2 plus you can see that I 1 minus acting on alpha 1 gives you beta 1, it brings the state down and I 2 plus acting on beta 2 gives you alpha 2. And therefore, you can say that the product of this is going to give you beta 1 alpha 2. And, then you have the two I 1 z, I 2 z acting on alpha 1.

Remember I 1 z on alpha 1 gives you half and I 2 z on beta 2 gives you minus half. Therefore, the product is minus 1 by 4 times 2 is minus half so what you will have is minus 1 by 2, alpha 1, beta 2 ok. So, you can see what you get, you get the state alpha 1 beta 2, 3 by 4 plus 3 by 4 minus 1 by 2. These three states you can put them together 3 by 4 alpha 1, beta 2, 3 by 4alpha 1, beta 2 minus 1 by 2 alpha 1 beta 2 that gives you simply alpha 1 beta 2 ok. But the other state is beta 1 alpha 2 therefore, you see I squared on alpha 1, beta 2 gives you that. So, if this is obviously, not an Eigen function of I square it gives you a product of two states.

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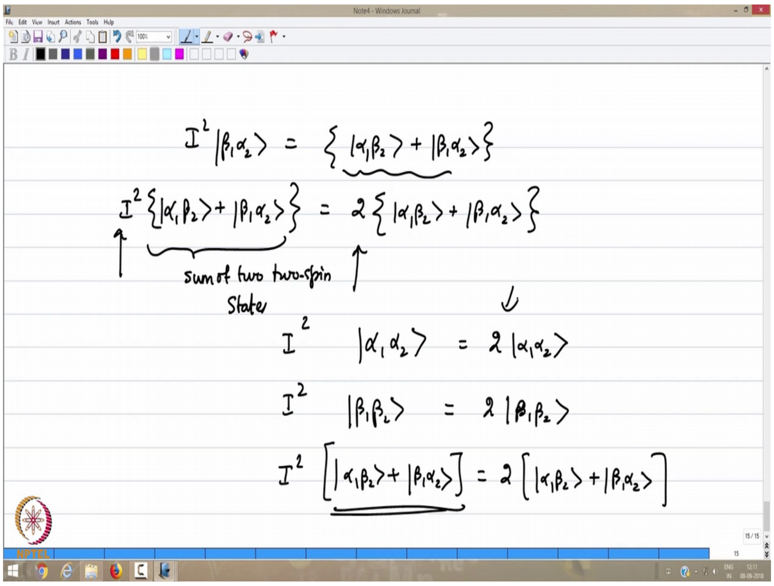

And likewise do exactly the same thing I squared on beta 1, alpha 2 will give you the same thing namely alpha 1, beta 2 plus beta 1, alpha 2 ok. So, it is quite clear that I square on alpha 1, beta 2 plus beta 1, alpha 2 gives you twice, because it gives you once for this and the same thing for the other. Therefore, it gives you twice alpha 1 beta 2 plus beta 1 alpha 2. So, the state alpha 1, beta 2 plus beta 1, alpha 2 which is the sum of two spin states, that is an Eigen function of the total angular momentum I squared the square of the angular momentum I square with the Eigen value two.

So, you have got three functions namely alpha 1, alpha 2, that is if an Eigen function of I square giving you two alpha 1 alpha 2. I square on beta 1 beta 2 is also an Eigen function with the Eigen value same Eigen value beta 1 beta 2 and the third one I square on alpha 1 beta 2 plus beta 1 alpha 2 is also an Eigen function of the I square operator alpha 1 beta 2 plus beta 1 alpha 2. So, you have got three functions out of the four one being a linear combination of two of them all giving you an Eigen value 2.

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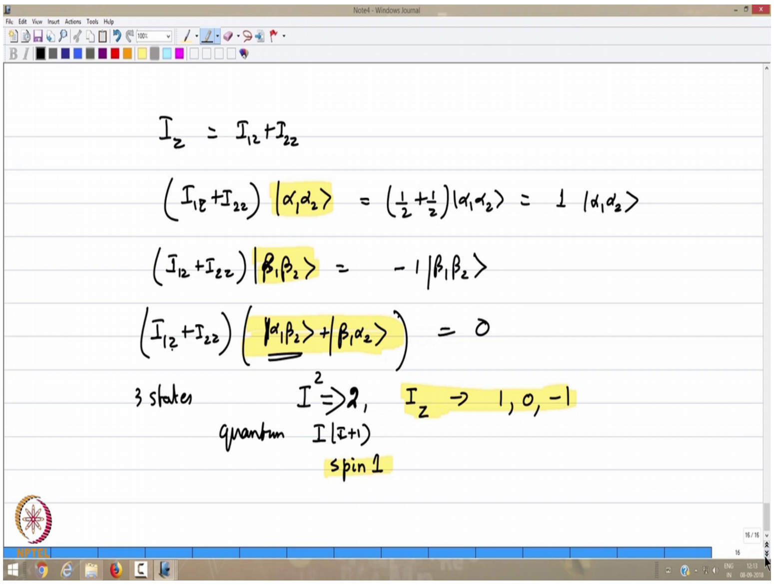

What about I z on these three functions? I z is I 1 z plus I 2 z. I 1 z plus I 2 z acting on alpha 1 alpha 2 will give you I 1 z on alpha 1 is the half and I 2 z on alpha 2 is a half in the state will be the same. So, it is half plus half on alpha 1 alpha 2 therefore, this is one times alpha 1 alpha 2 ok. And likewise I 1 z plus I 2 z on alpha 1 sorry on beta 1 beta 2 will give you this will give you minus half this will also give you minus half so you will get minus 1 times beta 1, beta 2. And it is easy for you to verify that I 1 z plus I 2 z on this combination states of alpha 1 beta 2 plus beta 1 alpha 2, if you do that you can see that.

Let us take the first one I 1 z on alpha 1 will give you plus the half I 2 z 1 beta 2 will give you a minus half it is a sum. Therefore, the product the sum is 0 and likewise I 1 z on beta 1 gives you minus half times the same states and this gives you a plus half times the same states. Therefore, this gives you 0.So, what you have is there are three states, three states which have your total angular momentum value I is equal to I square is equal to 2. And the total angular momentum z component having one 0 and minus one this corresponds to of course, the quantum number I is 1.

I square gives you an Eigen value2, but the quantum number is I into I plus 1 and therefore, this is a spin 1 ok. There are three states the alpha 1, alpha 2, beta 1, beta 2, and this combination. These three states form a spin one system in which the total angular momentum is given by the square namely I into I plus 1 and the component of the z angular momentum operator total angular momentum operator z component has three values 1 0 1 minus 1 therefore, this is called a Spin one state.

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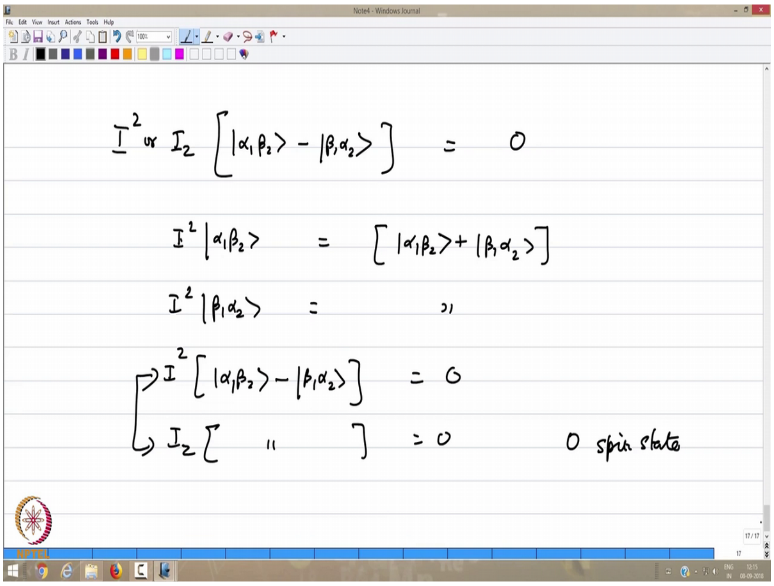

You will also find out that there is only one more state namely alpha 1, beta 2, minus beta 1, alpha 2. If you take this state and you calculate the effect of I square or I z on this you will see that the answer you get is 0. You will just to see this for I square on the state you know that I square on alpha 1 beta 2 gives you 2 times alpha 1 sorry; it gives you not 2 times it gives you this combination alpha 1, beta 2, plus beta 1, alpha 2. And you also know that I square on beta 1, alpha 2, gives you the same thing.

Therefore, if you take the difference between the two states beta 1 alpha 2 of course, these two will cancel each other and you will get 0. And the same thing like this I z on these, you can see that I z is I 1 z plus I 2 z on alpha 1 beta 2 anyway gives you 0 and it also gives you 0 therefore, I z acting on the state is 0. Therefore, you have a state which has which is an Eigen function of the I square operator with I equal to 0 and I z operator with also the m equal to 0. Therefore, this is called the 0 spin state ok.

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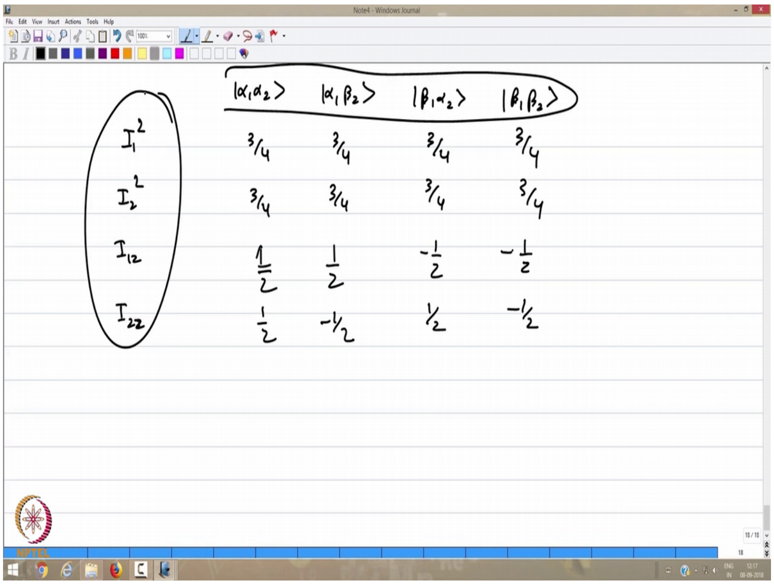

So, let me summarize that if you have I 1 square, I 2 square, I 1 z, I 2 z then the four operators that you have the product operators they are all Eigen functions. So, let me write them in a tabular form for you let me write alpha 1, alpha 2, I 1 square will give you 3 by 4, alpha 1 beta 2, I 1 square will also give you 3 by 4. And then you have beta 1, alpha 2, and beta 1, beta 2, so all of these will be 3 by 4 and this is 3 by 4, 3 by 4, 3by 4 and 3 by 4. And the I 1 z on the state gives you 1, I 1 z on this state gives you again 1 half sorry, 1 half and I 1 z on the beta state gives you minus 1 half and I 1 z on the beta 1 beta 2 state gives you minus 1 half.

And this will be I 2 z acting on alpha 2 gives you a plus 1 half I 2 z acting on beta 2 gives you minus 1 half I 2 z acting on alpha 2 gives you plus 1 half and I 2 z acting on beta 2 gives you minus 1 half. Therefore, all these are Eigen functions of these four operators.

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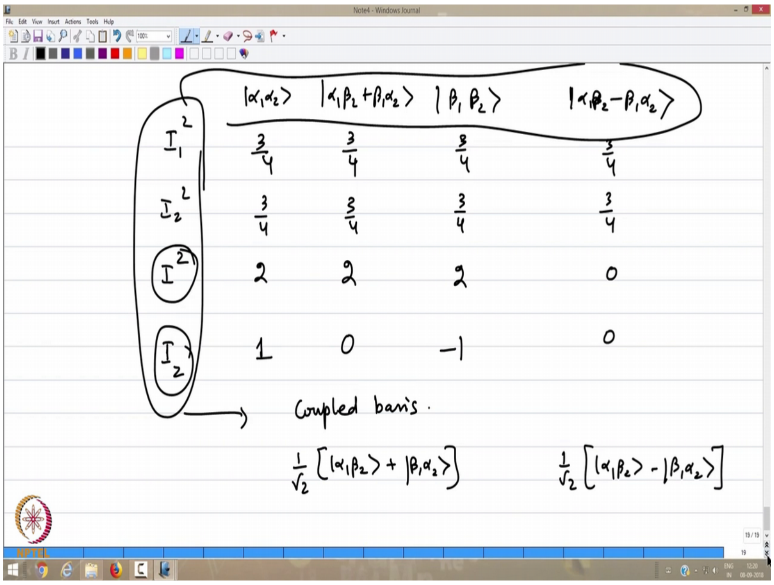

The Eigen functions for the four operators, that we have I 1 square I 2 square I square and I z if we do this you will see that alpha 1 alpha 2 alpha 1 beta 2 plus beta 1 alpha 2 then beta 1 beta 2 and the state alpha 1 beta 2 minus beta 1 alpha 2. If you take these I 1 square gives you 3 by 4 I. one square on this gives you can see that 3 by 4 plus 3 by 4, but the this is sum so this will also be 3 by 4. I 1 square on this gives you 3 by 4 and I 1 square it gives 3 by 4; I 2 square 3 by 4, 3 by 4, 3 by 4 and 3 by 4.

I square on the state gives you twice the state, I square on this gives you twice the state, and I square on this gives you twice,and I square on the state gives you 0. And the I z on alpha 1 gives you one the state (Refer Time: 36:59) on the state gives you 0 then under state gives you minus one times the state and I z on the state gives you 0. Therefore, you see that these four are Eigen functions of these four operators and this contains the sum of the angular momenta both of the components as well as the total angular momenta and therefore, this is called Coupled basis.

One last statement the states have to be normalized. And since the states are orthogonal to each other the normalization simply means that the state is now 1 by root 2, alpha 1, beta 2, plus beta 1, alpha 2, that is a normalized state. And the state 1 by root 2, alpha 1, beta 2, minus beta 1, alpha 2, is also a normalized state therefore, we have the labels now.

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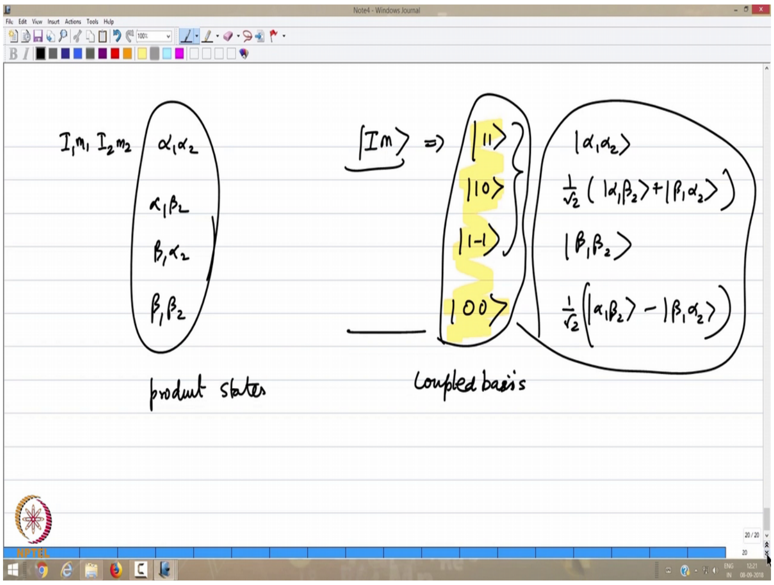

We have the labels namely I m labels corresponding to 1 1 1 0, 1 minus 1. if we do that these states are alpha 1, alpha 2, 1 by root 2 alpha 1 beta 2 plus beta 1 alpha 2 and the other state is beta 1 beta 2 and I m 0 0 state is 1 by root2, alpha 1, beta 2, minus beta 1, alpha 2. (Refer Time: 38:36). So, these are the im states and here you have I 1 m one I 2 m two. So, these are the product states the four of them alpha 1, alpha 2, alpha 1, beta 2, beta 1, alpha 2, beta 1, beta 2.

So, these four states are; obviously, taken as a linear combination here to give you what is called the couple states these are the product states. And the coupled states are labeled by this quantum number let me write that highlight this, the these are the coupled part basis states. Now, if we write this as a matrix element or as a matrix relation you have the following namely.

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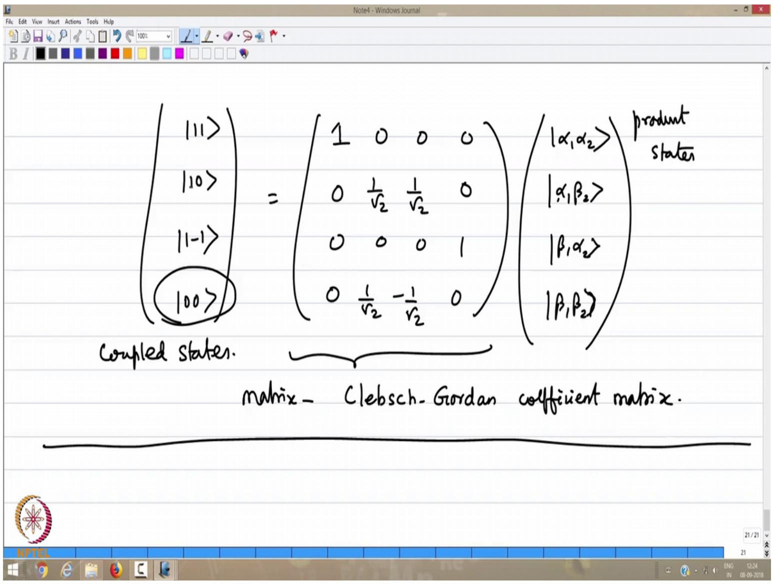

1 1 1 0, 1 minus 1 and 0 0 if you write this as a column and you write the matrix of coefficients with the states alpha 1, alpha 2, which is the product alpha 1, beta 2, beta 1, alpha 2, and beta 1, beta 2. If you write that then you can see immediately that the state 1 1 is the same as that state. Therefore, the coefficient here is 1 0 0 0 because 1 1 is not connected to any other the state 1 0 is a linear combination of these two states. And therefore, it is 1 by root 2: 1 by root 2 and 0 the state 1 minus 1 you can see that from this relation 1 by root 2, 1 by 2 is the state 1 0 and 1 minus 1 is connected only to that. Therefore, that is this then 0 0 is a linear combination with a negative sign between them so this is 1 by root 2, 1 minus 1 by root 2 0.

What is this matrix? This matrix is known as Clebsch–Gordan coefficient matrix Clebsch–Gordan coefficient matrix which connects product states to coupled states, to coupled states. We will see what it is impact is in the electron coupling between the two electrons and the fundamental principle that was first stated by Wolfgang Pauli as the principle of anti symmetry. And, the anti symmetric Paulli's anti symmetric principle for anti symmetry or when the two electrons are exchanged we will have this whatever we have done will have a strong implications on that.

In the next lecture we will connect this to the actual electron states and also what is called a singlet and the triplet states that you are familiar with in quantum chemistry from elementary spectroscopy. These are essentially what are called the singlet and the triplet states a 0 0 state, this is called in a singlet state and is the most famous one in quantum mechanics. And, first it was used by Wolfgang Pauli it was predicted to have a 0 spin and it is called the anti symmetric state. When the two electron spins are interchanged and the other three states are called the triplet states. We will see more of that in the next lecture until then.

Thank you very much.