

Select/Special Topics in Atomic Physics  
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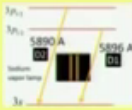
Lecture - 4  
Degeneracy of the Hydrogen Atom: SO(4)

Greetings, we will continue our discussion on the Degeneracy of the Hydrogen Atom.

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Select/Special Topics in Atomic Physics

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Unit 1(iv) Lecture 4

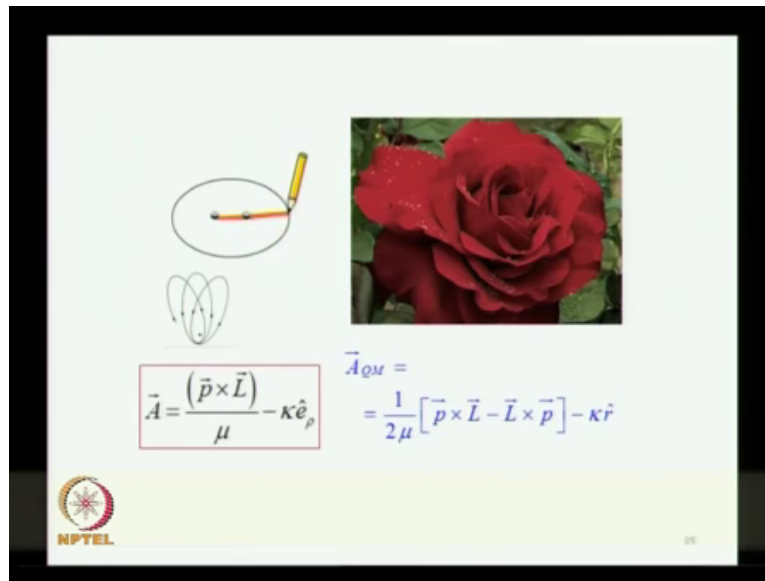
Degeneracy of the Hydrogen Atom : SO(4)

$E_{3p}^{\text{Na atom}} \neq E_{3s}^{\text{Na atom}}$  but  $E_{3p}^{\text{H atom}} = E_{3s}^{\text{H atom}}$



And essentially the question that we have raised is, why is it that the 3 p energy of sodium is different from the 3 s, where as in the hydrogen atoms, there is a degeneracy both of this 3 p and 3 s belongs to same Eigen value, so this is the main question that we have been addressing.

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We have set the context of our solution to this problem, which is going to be quantum testament of the Laplace runge vector, which I discussed briefly, and which your studied in your classical mechanics course. This is an additional quantity, which is conserved for 1 over r potential, it is conserved strictly for the 1 over r potential, and the potential must be 1 over r for the entire domain of space from r going from 0 through infinity that is a requirement.

In the sodium atom, the potential is 1 over r for the outer most electron only in the accent asymptotic s as r tense to infinity. But, this r tense to 0 the potential goes as minus z over r, where z is a number of photons in the nuclear, so it is minus 1 over r as r tense to infinity, but minus 11 over r as r tense to 0. So, it is not on top of 1 over r in the entire domain of space, so that is the difficulty with the potential for the hydrogen atom that it is 1 over r over entire reason of space.

And for this 1 over r potential there are some very peculiar you know consequences, like an classical mechanics the Laplace vector is conserved, you have this ellipse motion for the classical 1 over r potential kepler problem. And the ellipse does not presses there is no loss at motion, something like what would look like the petals of a rose from a distance, if this ellipse were to presses it would look like the petals of a rose, and this is what does not happen for the hydrogen atom or for the classical two body kepler problem.

However, the hydrogen atom is a quantum system, in fact, all systems in nature are essentially quantum systems, including the astronomical huge object including the planetary system, the

galaxy and everything, but that is the separate issue. Now, over here, you must quantize the Laplace ring vector, and this is how you quantize it you have to symmetries operator. Because p and L do not commute, they correspond to measurement, which are not compatible with each other.

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**H atom**

$$\vec{A}_{\text{Classical}} = \frac{(\vec{p} \times \vec{L})}{\mu} - \kappa \hat{e}_r$$

$$\vec{F} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2} \hat{e}_r, \dots \text{SI units}$$

$$\vec{F} = \frac{q_1 q_2}{r^2} \hat{e}_r, \dots \text{Gaussian units}$$


$$\vec{F} = \frac{q_1 q_2}{r^2} \hat{e}_r = \frac{\kappa}{r^2} \hat{e}_r$$

$$\kappa = e^2$$

$$\vec{p} \times \vec{L} \rightarrow \frac{1}{2} [(\vec{p} \times \vec{L}) + (\vec{p} \times \vec{L})^\dagger] = \frac{1}{2} [\vec{p} \times \vec{L} - \vec{L} \times \vec{p}]$$

$$\vec{A}_{\text{QM}} = \frac{1}{2\mu} [\vec{p} \times \vec{L} - \vec{L} \times \vec{p}] - \kappa \hat{r} \quad \text{Pauli-Lenz Quantization}$$

**Dimensions:**  $\left[ \frac{\text{CM}}{\text{QM}} \vec{A}_{\text{LRL}} \right] = \frac{\text{ML}^3 \text{T}^{-2}}{\text{ML}^2 \text{T}^{-1} \times \text{LT}^{-1}} = [\kappa] = [\hbar] \times [\vec{v}]$



And therefore, you have to symmetries this operated, so this is the quantum Pauli Lenz vector, as we call it and this is the classical two body problem. And remember that you can use SI units, now we are not dealing with the gravitation 1 over r potential, but the electrometric 1 over r square, but in SI system of units you have got this 1 over 4 phi epsilon 0 where is in Gaussian you do not have it, and when has to keep track of these details depending on which system of units your using.

So, we will use the Gaussian system of units, in which the proportionality will be e square for the electromagnetic 1 over r potential. So, we are going to use kappa equal to e square at a later point in our analysis, so remember that, now we have done the symmetrization of this operator. So, we have a quantum Pauli Lenz operator now, and you must always keep track of what they mentions are appropriate for kappa r or for the vector Pauli Lenz vector itself.

And you will immediately notice that these dimensions are M L 3 M L to the 3 T to the minus 2 which are in facts this is coming from the product of the dimensional of the angular of momentum, multiplied by the dimension of the linear momentum for unit mass. That is

because we introduced this specific angular of momentum right which was the angular momentum per unit mass, so  $M$  into  $v$  would be the linear momentum, but you can also define the Laplace only a vector in some book defined, as what we have on the screen multiplied by the mass and the whole thing just gets scaled by that factor.

But, the dimensions also go up by a factor of  $M$  to the 1, so you are must keep track of that because you will see different things in different box. So, it is basically the product of the angular of momentum multiplied by linear momentum or linear momentum of per unit mass depending on you know which, you know text your following.

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Closed Algebra ?

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$


$$[A_i, L_j] = i\hbar \epsilon_{ijk} A_k$$

$$[A_i, A_j] = -2i \frac{\hbar}{\mu} H \epsilon_{ijk} L_k$$

*We restrict ourselves to a subspace  $\mathcal{R}(\mathcal{E})$  for a particular  $\mathcal{E}(\mathcal{O})$*

$SO(4)$ ,  $n = 4$ ;  $\frac{n(n-1)}{2} = 6$  : Lie Group of Dimension 6

Generators:  $L_x, L_y, L_z, A_1, A_2, A_3$

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We ask the question, if the components of the angular of momentum and the components of the Pauli Lenz operator do they constitute the closed algebra. So, if you take the commutator of components of the angular of momentum, then the commutator of any two is return in terms of the third component. So, the algebra is closed within the components of the angular momentum, if you take the commutator of component of angular of momentum  $L$ , and construct the commutator with components of the Pauli Lenz vector operator, then the answer is in terms of the component of the Pauli Lenz operators.

So, once again there is a suggestion that you get a closed algebra between these two sets of operators. However, if you construct the commutator of these two, two components of the Pauli Lenz vector operator, the answer is in terms of the angular momentum, which is fine with us as far as the closure of the algebra is concerned. But, that is not the only operator which you

get on the right hand side, you also get the Hamiltonian and this is an extra creature, which hops up on the right hand side, which means that the algebra is really not closed.

However, what you can do is to work in a subspace of the halberd space, belonging to particular energy value. You takes one of the bound straight energies, and work within this sub space, bound state energies have energies less than 0 that is the e less than 0 what refer what is being refer to over here. And within this sub space than H operating on any vector in this subspace will give you the corresponding energy, which will just be an number, it will be just a number with in, so many electrons are more joules you know and whatever energy unit your using, it will just be a number.

And within this subspace you have a closed algebra, which is generated by this 6 components, which then constitute the lie group of dimension 6. So, if this is the SO 4 group the number of components SO n in any n is given by n in to n minus 1 by 2, so for n equal to 4 you have 4 in to 3 by 2 which is 6. And the 6 generators of this group SO 4 are the 3 components of the angular of momentum, and the 3 components of the Pauli Lenz vector operator.

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Within the subspace  $\mathcal{R}(E)$   
for a particular  $E < 0$ ,  
 $\forall \mathbf{a}_{op} = \mathbf{a}_{op}(\vec{l}, \vec{A}), [\vec{A}, H] = 0 \quad \dots \text{operators!}$   
and  
 $\forall f \in \mathcal{R}(E) \quad \vec{A}^2 = \frac{2H}{\mu}(L^2 + \hbar^2) + \kappa^2$   
 $\mathbf{a}_{op} f = g \in \mathcal{R}(E)$

NPTEL

And these 6 generate the SO 4 group, what it means is that in this subspace if you have any operator a this script a, any operator which is the combination of angular of momentum and Pauli Lenz operator. Then if this operator operates on any function in this sub space, the result g will also belong to the same subspace that is what essentially it means, when we say

that we are working within the certain subspace of the Hilbert spaces, you confirm yourself to that limited portion of the Hilbert space, which is the finite extract you scoop out that part of the Hilbert space, in which all the energy belongs to a particular bound state energy  $E$  less than 0. And within the subspace you have got a closed algebra generated by these 6 generators of the SO 4 group, and within the subspace you can then work out, these details and these are left as home work exercise in your problem set number 1, you will find that these two operators are orthogonal to each other.

You will also find that if you take the scalar product  $\vec{A} \cdot \vec{A}$ , the result will turn out to be this  $2H$  over  $\mu L$  square plus  $\hbar$  cross square plus  $\kappa$  square. I had referred to this result earlier that this is something that will be anticipated, this is the there is a extra term  $\hbar$  cross square which is coming, which you did not see for the classical Laplace vector this comes from the fact that the quantum operators do not commute. So, if you just make use of the commutation rules and you will get this quit easily.

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*On the space  $\mathcal{R}(E)$ ,*

$\sqrt{-2\mathcal{H}} = \sqrt{-2E},$

*just a number.*

$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$

$[A_i, L_j] = i\hbar \epsilon_{ijk} A_k$

$[A_i, A_j] = -2i \frac{\hbar}{\mu} H \epsilon_{ijk} L_k$

$\vec{A}' = \sqrt{\frac{-\mu}{2E}} \vec{A}$

$E < 0$  : Bound States

Restrict ourselves to subspace of the Hilbert space for a particular value of  $E$


*natural indexing*

$\vec{L} = \{L_{23}, L_{31}, L_{12}\}$

$\vec{A}' = \{L_{14}, L_{24}, L_{34}\}$

6 generators  $\{L_{ij}\}$ :  $SO(4)$

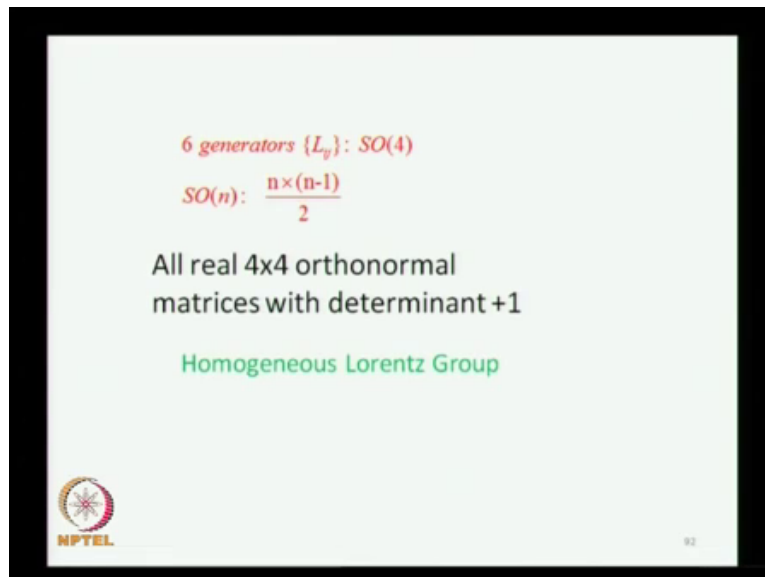
$SO(n): \frac{n \times (n-1)}{2}$



So, this is what we have now, and we are working within this subspace of the Hilbert space. It is also useful to define another operator  $\vec{A}'$  instead of  $\vec{A}$  and this no big new physics, which is being introduced over here, this is just a multiplier you know for introduced for scaling you are find that this makes our you know relationship somewhat easy to write and also easy to interpret. So, you will find, so we will also be using this operator  $\vec{A}'$ , but there is no new dynamic which is being introduce over here.


We will also make use of you know natural indexing, so instead of calling the components as  $L_x, L_y, L_z$  and  $A_x, A_y, A_z$  or  $A_{\text{prime } x}, A_{\text{prime } y}, A_{\text{prime } z}$  we will index them by this subscript that is just a matter of book keeping and convenient, and we will work with this 6 components are generated of  $SO(4)$ .

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Now, it turns out that all of these you know operator which are 4 by 4 orthonormal matrices they all have determinants plus 1, and they constitute a group which is known as the homogeneous Lorentz group. So, this is the name of the group in this context of the hydrogen atom symmetry, you will remember that the rank of  $SO(3)$  group,  $SO(3)$  is a group that we assign to the symmetry of hydrogen atom, based on our simplicity analysis in which all we made use of was the rotational symmetry of the potential  $1/r$  right. So, you had angular momentum generator of rotations, and from the three components you add the  $SO(3)$  symmetry.

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**Recall:** Rank of  $SO(3) = 1$

- Max number of mutually commuting generators.
- For  $SO(3)$ , RANK= 1; no two generators commute.

Number of Casimir Operators = Rank of the Group  
**Racah's theorem**

Casimir operator for  $SO(3)$ :  $J^2$

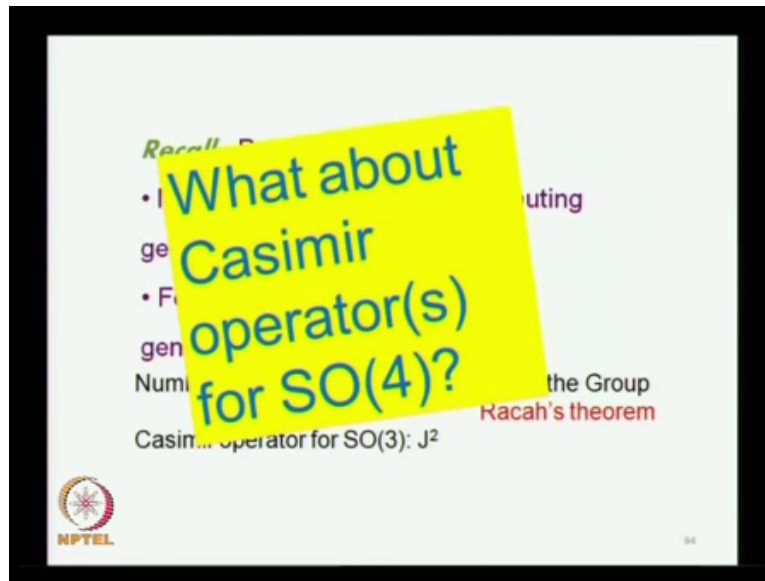
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None of these two components commutes with each other because  $J_x$  does not commute with  $J_y$ , and no two components commute. So, the maximum number of mutually commuting generator for  $SO(3)$  is 1 and that, in fact, is the Casimir rank that is the largest number of commuting, you know generators and the rank of  $SO(3)$  is 1. So, the Casimir operators for  $SO(3)$  is  $J^2$ , there is only one Casimir,  $J^2$  is the only operator which commutes with all the three generators, which is the definition of Casimir operator by Racah theorem it is equal to the rank of the group, the rank of this group is 1.

So, there is only one Casimir, and this Casimir for  $SO(3)$  is  $J^2$ , and the question now we going to ask is what are the Casimir operator for  $SO(4)$ . Now, that we know that the symmetry of the hydrogen atom, we expect to be completely define in terms of  $SO(4)$ , rather than  $SO(3)$ , we are going to now look for the Casimir operator for the  $SO(4)$ .

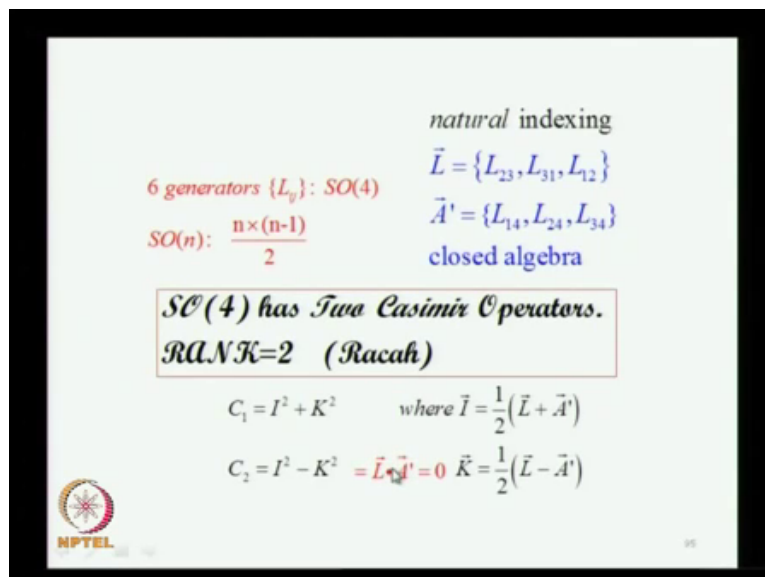


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So, let us ask this question what about Casimir operator for  $SO(4)$ , so we will construct them now.

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What we will do, we will is to discover that SO 4 has got a rank 2 and there are two Casimir operator you will see what these are. And to get these two Casimir operators I define two auxiliary operators I and K, these are just some and the different of the angular momentum, and the Pauli Lenz vectors  $L \pm A$  prime by 2. So, these just half the


some and the different, these are not the Casimir operator, but the Casimir operator are define in terms of  $I$  and  $K$ .

So, to define  $I$  and  $K$  I have introduce these two operators  $I$  and  $K$  as intermediate auxiliary operators. And the Casimir operators are defined as  $I$  square plus  $K$  square gives you 1 Casimir operator, and  $I$  square minus  $K$  square gives you the other Casimir operator, now how do we know this Casimir operators. Let us check it out, it also turns out that  $I$  square minus  $K$  square, and all you have to do is to literally do this term by term, there is fairly lengthy algebra.

In which most of us makes careless mistakes, which makes that already lengthy algebra lengthier, it can get to be very festering. But, please spend all these hours because you have to work out these commutation relation yourself, you are going to be tested for that and they are all based you can all do that, because they are all based on very simple commutation between position and momentum, which all of you have been using this basic commentator for quite some now.

So, there is nothing new in it, so all you have to do is to use the basic commutation relation very carefully, and these result will power of that very easily. So,  $I$  square minus  $K$  square you will find is exactly equal to the scale of product of  $L$  with  $A$  prime, which you know vanishes. And this is a very important result because then you know that  $I$  square Eigen values and  $K$  square Eigen values will be equal because  $L$  square minus  $A$  square has to identically vanish. So, it has to identically vanish then the corresponding Eigen value of  $I$  square and  $K$  square must be necessarily to equal, we are going use that.

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$$C_1 = I^2 + K^2 \quad \text{where } \vec{I} = \frac{1}{2}(\vec{L} + \vec{A}')$$

$$C_2 = I^2 - K^2 \quad \vec{K} = \frac{1}{2}(\vec{L} - \vec{A}')$$


$$\forall i, \quad \forall i,$$

$$[C_1, I_i] = 0 \quad [C_2, I_i] = 0$$

$$[C_1, A_i] = 0 \quad [C_2, A_i] = 0$$

How do we know these are Casimir operators well check out, what is a criteria of Casimir it must component with every generator that is the definition of Casimir operator. Casimir operator is 1, which commutes with every generators of that group, so find the commutations of the first Casimir operator, which is C 1 with each component of the angular momentum, do the same with each component of the Pauli Lenz vector operator, and you will discover that it does actually commute. So, you convince yourself thereby that C 1 is the Casimir operator, do the same with C 2 for every I you will find that C 2 also commutes with all the 6 components. And that pretty must settle the issue that C 1 and C 2 are Casimir operators.

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$$C_1 = I^2 + K^2 \quad \text{where } \vec{I} = \frac{1}{2}(\vec{L} + \vec{A}')$$

$$C_2 = I^2 - K^2 \quad \vec{K} = \frac{1}{2}(\vec{L} - \vec{A}')$$

One can show that:

$$[I_x, I_y]_- = i\hbar I_z \quad \text{etc.} \quad [K_x, K_y]_- = i\hbar K_z \quad \text{etc.}$$

$$[I, K]_- = 0 \quad \text{etc.} \quad [I, H]_- = 0 = [K, H]_-$$

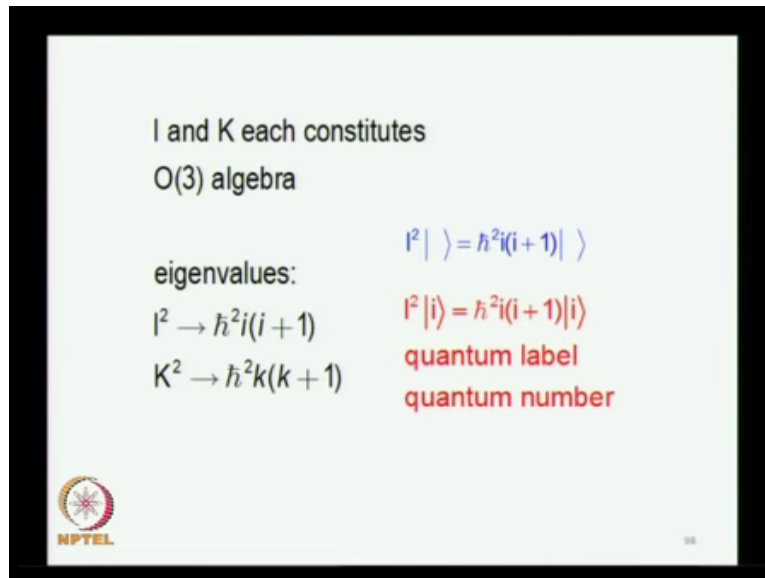
Now, further more if you work out the commutation between two components of  $I$ , take the commutation of  $I_x$  with  $I_y$ . How will you do that, when you take the commutation of  $I_x$  with  $I_y$ , you will take the  $x$  component of this commuted with the  $y$  component. And then you will need the commutation between  $L$  and  $A$ , you know what those commutation relations are, we have introduced them already use them carefully step by step tire some algebra that is not something that we want to spend our time in the class because it twins like the algebra, but it good works for you do it at home.

So, work out this any physics related problem we can discuss over here that there is no need to spell out all the details step, and spend hours doing this algebra, which you can each do simply based on the basic commutation rules. So, when you take the commutation of  $I_x$  with  $I_y$ , the result is  $I_z$  and have you not see this result earlier, what does it suggest you. It reads like angular momentum does it not right it reads angular momentum.

So, you are going to begin to suspect that the auxiliary of operator that you introduced  $I$  is an angular momentum operator, same think with  $K$ ,  $K$  is also angular momentum operator. So, in other words auxiliary operator  $I$  and  $K$  that we have introduced  $r$  angular momentum operators, they will generate the  $O(3)$  as any angular momentum does, you will also find that the operator  $I$  and  $K$  commute which means completely independent.

So, there are two different operators  $I$  and  $K$  they are completely independent both are like angular momentum. You will also find that they commute with the Hamiltonian, which is I think to do because we have to be sure that we are working with operators which will operate on any function belonging to the subspace of Hilbert space belonging to a particular bound state energy, and you want to stay within the subspace because that is what we have decided to work, so that we have closer.

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I and K each constitutes  
O(3) algebra

eigenvalues:

$$I^2 \rightarrow \hbar^2 i(i+1)$$
$$K^2 \rightarrow \hbar^2 k(k+1)$$
$$I^2 | \rangle = \hbar^2 i(i+1) | \rangle$$
$$I^2 | i \rangle = \hbar^2 i(i+1) | i \rangle$$


quantum label  
quantum number



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So, each of the operators I and K they constitute the O 3 algebra, which means that they have Eigen value equations like angular momentum. So, I square operating on a vector will give you an Eigen value, which we know from angular momentum algebra is  $\hbar^2 i(i+1)$  we already know that from our angular momentum quantum mechanics right. This is not a new result for us, having established that I and K are angular momentum, these result automatically comes because this come along with the definition or the defining criterion of angular momentum. So, all of these are natural you know ingredients of the properties of angular momentum, so you can put a label, we know how to put a label in a state vector. So, we use the label i to designate state this vector, we do the same with K square.

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$$C_1 = I^2 + K^2 \quad \text{where } \vec{I} = \frac{1}{2}(\vec{L} + \vec{A}')$$

$$C_2 = I^2 - K^2 = \vec{L} \cdot \vec{A}' = 0 \quad \vec{K} = \frac{1}{2}(\vec{L} - \vec{A}')$$

$$[I_x, I_y]_- = i\hbar I_z \text{ etc.} \quad [K_x, K_y]_- = i\hbar K_z \text{ etc.}$$

$$[I, K]_- = 0 \text{ etc.} \quad [I, H]_- = 0 = [K, H]_-$$

$\vec{I}, \vec{K}$ : pseudo-angular momentum operators  
 $\vec{L}$ : axial vector,  $\vec{A}$ : polar vector  
 "True" angular momentum  $\vec{L} = \vec{I} + \vec{K}$  (pseudovector)  
 axial vector

And this is the summary of the whole picture that we have got, so we began with the classical Laplace vector. We reminded our self what consequences it has on the classical two body problem, we found that strictly for 1 over r potential, it gives you an additional constant of motion. So, there is an additional conservation principle for which you looks for an associated symmetry, and this symmetry for the classical problem is called as dynamical symmetry.

Because, it comes from the nature of the force which must be 1 over r square that is the necessary, and sufficient condition for the conservation of the constants of the ellipse. So, that this ellipse does not exists for the bold problem for the hydrogen atom quantum problem, you again have 1 over r potential, so we have exactly the same form of the potential, we got the same kind of dynamic.

But, when you quantize this system and we agreed the quantization does not necessary mean that you have discreet energy or anything that it is one of the consequences. But, the signature of quantum mechanics is that you must replace the classical dynamical variables with quantum operators. So, you quantize the classical Laplace vector operator, but you cannot do it by simply replacing p and l by corresponding operator, the reason is you do not get a hermition operator form that.

And the reason it does not happen is because p and l do not commute they are not compatible observable. So, you symmetries it and this is the prescription for quantization that you must


symmetries a operator, you get the corresponding operator which is known as the Pauli Lenz operator. You find that you can define a closed algebra between angular momentum, and Pauli Lenz operator, but only if you restrict yourself to a subspace that you must scoop out of the entire Hilbert space.

A subspace which belongs to a certain bound state energy, and within that bound state energy you got closed algebra. You introduce the Casimir operators  $C_1$  and  $C_2$  in terms of  $I$  and  $K$  which are intermediate auxiliary operator, which we now recognize as angular momentum of operators. But, not quite these are called as pseudo angular momentum operator rather than angular momentum operators, why pseudo angular momentum, they are not exactly angular momentum.

They all angular momentum operator, because they have the same algebra, but they are not exactly the same, because there still certain difference what is the difference that difference is the following that  $I$  and  $K$  are made up of mix of this two operators  $L$  and  $A$  right. You must super posed  $L$  on  $A$ ,  $L$  plus  $A$  prime and  $L$  minus  $A$  prime,  $A$  prime or  $A$  you know what the relationship is that is just a multiplied, so do not worry about that. But, you are doing in addition of angular momentum with the Lenz vector or the Laplace Lenz vector.

Now, the Laplace Lenz vector is a polar vector, angular momentum is ancient vector, one is a vector the other is pseudo vector. So, when you take a some the two the result is neither a polar vector nor an ancient vector, so it has got some attributes similar to angular momentum. But, it not exactly the same and to highlight the fact that this is not a pseudo vector, like the usual angular momentum vector is you call it as a pseudo angular momentum operator. So, we have now introduce  $I$  and  $K$  which are pseudo angular momentum operator, but they do satisfy the entire algebra of the angular momentum, they are generates of  $O(3)$ .

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$$\text{since } C_1 = I^2 + K^2,$$

$$2\hbar^2 k(k+1) = c_1 = 2\hbar^2 i(i+1); i = k$$

ALSO:

$$C_1 = I^2 + K^2$$

$$\vec{I} = \frac{1}{2}(\vec{L} + \vec{A}')$$

$$\vec{K} = \frac{1}{2}(\vec{L} - \vec{A}')$$

$$C_1 = \frac{1}{4}(\vec{L}^2 + \vec{L} \cdot \vec{A}' + \vec{A}' \cdot \vec{L} + \vec{A}'^2) + \frac{1}{4}(\vec{L}^2 - \vec{L} \cdot \vec{A}' - \vec{A}' \cdot \vec{L} + \vec{A}'^2)$$

$$C_1 = \frac{1}{4}(\vec{L}^2 + \vec{A}'^2) + \frac{1}{4}(\vec{L}^2 + \vec{A}'^2)$$

To get  $c_1$ ,  
we need  
e.v. of  $\vec{A} \cdot \vec{A}$

$$\vec{A}'^2 = \left( \sqrt{\frac{-\mu}{2E}} \vec{A} \right) \cdot \left( \sqrt{\frac{-\mu}{2E}} \vec{A} \right) = \frac{\mu}{2E} \vec{A} \cdot \vec{A}$$

$$2\hbar^2 k(k+1) = c_1 = 2\hbar^2 i(i+1); i = k$$

And now, we will do a little bit of you know mathematical you know very simple straight forward jukling with these operators. And we will find something very fascinating answers about our fundamental question of the hydrogen atom degeneracy come out of it is very simple it is stunningly simple. We have also found that since I square and K square must be equal because I square minus K square goes to 0 right.

The Eigen value of C 1 will be twice the Eigen value of K square or twice the Eigen value of C 1 right. So, the Eigen value which I have written lower case C 1 of the operator which is written as upper case C 1, the Eigen value is twice the Eigen value of I square or twice a Eigen value of K square they are both equal. So, it does not matter whether you use I or K because I must be equal to K and this is the Eigen value of the Casimir C 1.

You can also get this Eigen value by working out this square of I and the square of K and then getting the Eigen value of whatever turns out to be from the right hand side. So, you can do it explicitly term by term, so what is I square since I is half of L plus A prime, you take the square of it you have to be careful because L does not commute with A prime. So, you have to write L dot A prime in and A dot L separately it is not twice 1 of the two terms, you have to write them separately.

Same thing with I square minus K square, so you have L dot A prime and A prime dot L over here, with negative sign over here. So, you take I square plus K square work it outN now this L dot A prime term with the plus sign will cancel this L dot A prime term with minus sign




likewise this  $\vec{A} \cdot \vec{L}$  will cancel this  $\vec{A} \cdot \vec{L}$ . And then you get half of  $L^2$  plus  $\vec{A}^2$  because you get two identical terms.

And  $\vec{A}^2$  is in terms of  $\vec{A} \cdot \vec{A}$  this is how  $\vec{A}^2$  must be defined in terms of  $\vec{A} \cdot \vec{A}$  by an appropriate scaling. The square root of minus sign, let not worry you because the energy in the denominators is intensively negative, we are working in the bound state part of the hydrogen atom spectrum. So, these bound state energy are intensively negative right you are going to have square root of a positive number, you are not going to have the imaginary square root of minus 1 anywhere.

And what you find is that to get the Eigen value of this operator Casimir  $C_1$ , you must find the Eigen value of  $\vec{A} \cdot \vec{A}$ , which defines through this scaling  $\mu$  over  $2E$  what this  $\vec{A}^2$  is and this  $\vec{A}^2$  appears expressively in  $C_1$ . So, let us get Eigen value of  $\vec{A} \cdot \vec{A}$ , so one expression for  $C_1$  we already obtained earlier, which was twice of  $\hbar^2 k^2$  into  $i$  plus 1 or  $k$  into  $k$  plus 1.

And then we get another expression for  $C_1$  by constructing the Eigen value of this right hand side over here. But, for that we should also get the Eigen value of  $\vec{A} \cdot \vec{A}$ , once we do that we will get two equivalent expression for Eigen values of  $C_1$  which you can then equate to each other, and that where almost be the solution to our problem. So, we going to use this result very soon.

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$$\vec{A} = \frac{1}{\mu} [\vec{p} \times \vec{L} - i\hbar \vec{p}] - \kappa \frac{\vec{r}}{r}$$

Equivalent form of the Pauli-Lenz Operator

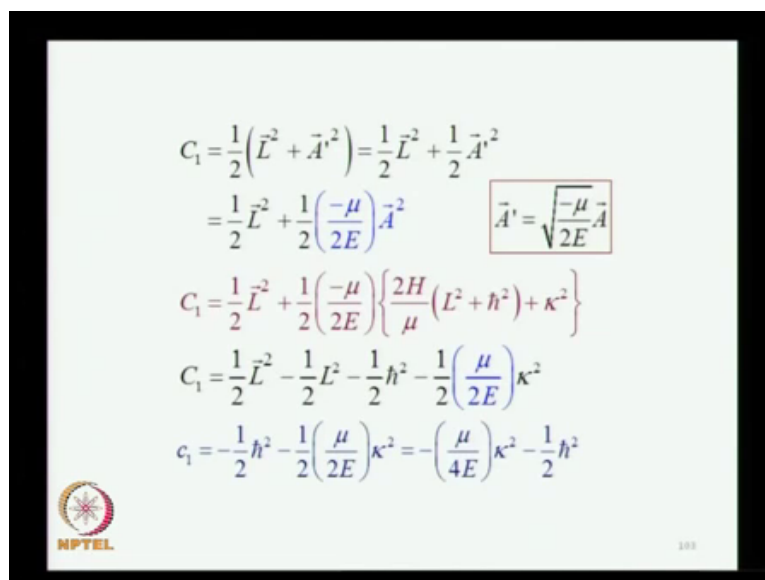
$$\vec{A} \cdot \vec{A} = \frac{1}{\mu^2} [\vec{p} \times \vec{L} - i\hbar \vec{p}]^2 - \frac{1}{\mu} [\vec{p} \times \vec{L} - i\hbar \vec{p}] \cdot \kappa \frac{\vec{r}}{r} - \frac{\kappa}{\mu} \frac{\vec{r}}{r} \cdot [\vec{p} \times \vec{L} - i\hbar \vec{p}] + \kappa^2 \frac{r^2}{r^2}$$

$$\vec{A} \cdot \vec{A} = \frac{2}{\mu} H (\vec{L}^2 + \hbar^2) + \kappa^2$$

Now, again a little bit of work and patients is required to show this equivalent form, which is left as home work exercise. You have already defined the Pauli Lenz vector operator, you can write it equivalently in another form which I have now written at the top of this slide. And using this form, you can get A dot A term by term, again take the dot product of this term with itself, then the dot product of this with the second term, and then the reverse dot product.

So, you just have to work out these terms step by step, what you find that as a result of this, you will have an another form of A dot A, which has a term in h cross square which distinguishes with from the classical A dot A, in the classical A dot A you do not have this h cross square. But, now you in this is coming simply because now we are working with quantum operators we do not commute.

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$$\begin{aligned}
 C_1 &= \frac{1}{2}(\vec{L}^2 + \vec{A}'^2) = \frac{1}{2}\vec{L}^2 + \frac{1}{2}\vec{A}'^2 \\
 &= \frac{1}{2}\vec{L}^2 + \frac{1}{2}\left(\frac{-\mu}{2E}\right)\vec{A}^2 \quad \boxed{\vec{A}' = \sqrt{\frac{-\mu}{2E}}\vec{A}} \\
 C_1 &= \frac{1}{2}\vec{L}^2 + \frac{1}{2}\left(\frac{-\mu}{2E}\right)\left\{\frac{2H}{\mu}(L^2 + \hbar^2) + \kappa^2\right\} \\
 C_1 &= \frac{1}{2}\vec{L}^2 - \frac{1}{2}L^2 - \frac{1}{2}\hbar^2 - \frac{1}{2}\left(\frac{\mu}{2E}\right)\kappa^2 \\
 c_1 &= -\frac{1}{2}\hbar^2 - \frac{1}{2}\left(\frac{\mu}{2E}\right)\kappa^2 = -\left(\frac{\mu}{4E}\right)\kappa^2 - \frac{1}{2}\hbar^2
 \end{aligned}$$

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So, you have the Casimir operator C 1 and for A dot A which is the A square we have now written this explicit expression, which you find in the beautiful bracket right, which means that the Eigen value of C 1 can be extracted from the Eigen value of L square, you know what the Eigen value of L square is it is h cross square into l in to l plus 1 right, it can be obtained from the Eigen value of these operators over here, kappa square is just kappa square times of unit operator.

So, you know that the value is just a kappa square you know kappa square is equal to E square in our analysis I mentioned that at the beginning of this class. So, you know that h cross square is known mu over 2 E is going to multiply this 2 H over mu, so the mu will

cancel  $H$  in the subspace is just a number, which is equal to  $E$ . So, whenever you have  $h$  in the numerator and  $E$  in the denominator they cancel each other, there exactly equal.

Because  $h$  is no longer an operator, so far as subspace of the Hilbert space that you have working well, it going to operate on any vector in that space, and give you the corresponding Eigen value, which is one of the bound state energy which is  $E$ . So, it will cancel and now you can simplify this algebra, and you have a very simple result, you have got half  $L$  square. Then you have got minus half  $L$  square there is this half over here this minus  $\mu$  over  $2 E$  cancels  $2 H$  over  $\mu$  and then you have the  $L$  square taking in.

So, you have half  $L$  square minus half  $L$  square and from the remaining two terms, you have minus half  $h$  cross square in minus half  $\mu$  over  $2 E$  kappa square right, very simple and this is really amazing. Because, now the half  $L$  square cancel you have got the Eigen value of  $C_1$ , but you also had an expression for  $C_1$  earlier right, and now you can equate these two, they must be equal, they must be exactly equal. So, I am just re written the two terms with the second term first term second, some time I do this thing just to confuse you way is the same right.

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$$2i(i+1)h^2 = \longrightarrow -\frac{\mu\kappa^2}{4E} - \frac{1}{2}h^2$$

$$\left\{2i(i+1) + \frac{1}{2}\right\}h^2 = -\frac{\mu\kappa^2}{4E} \quad \boxed{\kappa = e^2}$$

$$\left\{\frac{4i(i+1)+1}{2}\right\}h^2 = -\frac{\mu\kappa^2}{4E}$$

$$E = -\frac{\mu\kappa^2}{2h^2 \{4i(i+1)+1\}}$$

$$4i(i+1)+1 = 4i^2 + 4i + 1 = (2i+1)^2 = n^2$$

$$\text{with } n = (2i+1), \quad E = -\frac{\mu\kappa^2}{2h^2 n^2}$$

So, do not worry too much about it, so you have got  $C_1$  this is the Eigen value, which we got earlier to be twice  $i$  into  $i$  plus  $1$  times  $h$  cross square right. And now we get another result, which is in terms of this  $\mu$  kappa square over  $4 E$  minus half  $h$  cross square. Now, if you

forget this middle thing, you got what is on the extreme left to be equal to what is on the extreme right. What is the value, it is giving you the energy of the hydrogen atom.

It is giving you the energy of the hydrogen atom, in terms of  $l$  here is the relation between  $l$ , which you know is an angular momentum Eigen value. You know it is either 0 or half 1 or 3 half or 2 right, this is coming from the Eigen value of the operator  $l$  which is an angular momentum operator, it can have Eigen value which are either 0 half 1 3 half 2 etcetera.

So, you got this relationship and you write it for the energy, and you get energy to be equal to  $1/n^2$ , where  $n$  is  $2l + 1$ . Now, this is incredible result, we saw this result  $1/n^2$  in the Bohr formula, it was first obtained empirically by Bohr, and then by Bohr this was same an empirical formula. Then we got it from the Bohr model of the hydrogen atom, which was introduced by 1913 based on the certain set of postulates of quantization of angular momentum of this Kepler like orbits.

But, we wanted to dispense with the model, because there are no orbits in quantum mechanics. So, the Bohr formula is something that we know call as a whole quantum theory, we dispense with that at all though it gives the correct  $1/n^2$  result, the model itself is not quite correct is like getting good answer, correct answer using an wrong reasoning. Like you can divide 64 by 16 and cancel 6 in the numerator in the denominator, and get the answer 4 answer is correct, but the reasoning is stupid right.

So, there is no orbits in quantum mechanics, so you cannot really be using the Bohr model of the hydrogen atom. Because, you cannot really have an orbit, the idea of an orbit is not compatible with the fact that position and momentum are not simultaneously measurable. So, then you introduced a Schrodinger equation or the Eigen equation, you know uncertain principle, and you know that Eigen equation form of quantum mechanics is completely equivalent to the Schrodinger form of quantum mechanics.

And using one or the other, you can solve the problem of the hydrogen atom, let us take the hydrogen atom of the Schrodinger equation for the hydrogen atom if you like. Separate the radial part, the angular part get this harmonically from the angular part, put the boundary condition of the radial part, and the answer is  $1/n^2$ . Now, we have got  $1/n^2$ , but we did not use any same empirical relationship, we did not use the Bohr model, and we did not use the Schrodinger equation either did we within solve  $\psi = e^{i(kx - Et)}$  anywhere.

What did we do, we began with the Pauli Lenz vector, we fiddle with the properties of the Pauli Lenz quantum vector operator, recognize it is property, introduced the Casimir operator, did a little bit of algebra, found the what are the Eigen value of Casimir operator  $C_1$  and  $C_2$ . And by simply doing this algebra, we get the  $1/n^2$  formula of the hydrogen atom, and I will like you to ponder over this question, and ask yourself without using the Schrodinger equation, without using the Bohr model.

How is it that you get the correct quantum answer that the energy level of the hydrogen atom are given by  $1/n^2$ . We already discuss the answer, but I want it to come out to the top of your mind very clearly because when you do that you will understand precisely what is mean by quantization. So, just give it thought but we are of course, going to discuss that, so this is the  $1/n^2$  formula, there is something motivate.

Because,  $n$  in this case is an integer I can take value 0, half etcetera you know that from property of angular momentum algebra. So, if you define now an integer  $i$  is either half of integer or integer, so  $2i + 1$  always being integer for  $i$  equal to 0 half and so on corresponding values of  $n$  will be 1, 2, 3, 4 and so on. So, these are the natural integers that you will get right, these are what you call as principle quantum number for the hydrogen atom.


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$i, k_z$ : each can take  
(2k+1) values  $n = (2i+1)$   
Degeneracy: (2k+1) × (2k+1)

$i$	$2i$	$n = 2i+1$	$n^2 = (2i+1)^2$
0	0	1	1
$\frac{1}{2}$	1	2	4
1	2	3	9
$\frac{3}{2}$	3	4	16
2	4	5	25

$E = -\mu\kappa^2 \frac{1}{2\hbar^2 (2i+1)^2}$ ;  
 $i = k = 0, \frac{1}{2}, 1, \dots$

Rydberg  
Balmer  
Bohr  
 $n^2$   
degeneracy  
explained



But, what is more is the fact that since  $i$  and  $k$  or angular momentum operators, they have degeneracy which is  $2k + 1$  4 right. So, there is a  $2i + 1$  4 degeneracy for  $i$ , and the two

$k + 1$  degeneracy for  $k$ , but  $i$  is equal to  $k$ , so the degeneracy is actually  $2k + 1$  times  $2k + 1$ . And  $2k + 1$  is now an integer which is  $n$ , so you have  $n^2$  for degeneracy, this was our question, why is that the hydrogen atom Eigen function are degenerate.

Why is the energy of  $3p$  equal to the energy of  $3s$  for the hydrogen atom whereas, for the sodium atom it is not the case. Now, for the sodium atom we know it is not the case because the potential is not  $1/r$  over the entire space  $0$  through infinity, it is  $1/r$  only at  $r \rightarrow \infty$ , but not  $r \rightarrow 0$ . As  $r \rightarrow 0$  the sodium atom potential or for any other atom, it will go through  $-Z/r$  whereas,  $r \rightarrow \infty$  the potential will go as  $-1/r$ .

So, it has it is hydrogen like, but still different and for the sodium atom you do have rotational symmetry. And then you get the radial function for the sodium atom if you set up, then you already know that for bound state energies for the discrete part of spectrum, note energy value is degenerate in one dimensional form. So, that result is quite consistent happily satisfied by the sodium atom, but it is not satisfied by the hydrogen atom.

And it for this reason that the symmetry of the hydrogen atom is something that you would have called as accidental symmetry, but only as long as you did not understand what is a deeper cause that accident, now we do not have to call it as an accidental symmetry anymore, we know precisely what it is the symmetry is  $SO(4)$  and not  $SO(3)$ . Because, the symmetry is  $SO(4)$  there is an additional symmetry coming in, this additional symmetry is a special feature of the  $1/r$  potential.

The situation is quite similar to the classical problem there is an analog in classical mechanics. Because, by studying the property of Laplace-Runge-Lenz vector, you can get the equation of the orbit without actually solving any question of motion that is the analog over here. So, now let us look at this reason degeneracy, so I can take the value  $0, 1/2, 3/2, 5/2$  etcetera, correspondingly  $2l + 1$  will be twice this, and  $n$  which is  $2l + 1$  will be these integers  $1, 2, 3, 4, 5$ , etcetera.

And the degeneracy will be  $n^2$ , and this is precisely the degeneracy you find for the hydrogen atom. You do know that this degeneracy then gets multiplied by another factor of  $2$  because of spin, so that will come from relativistic hydrogen atom when we do that that is topic for our unit 3. And we will see how spin it is quantum mechanics, so you get the

rydberg balmer bohr relationship, you are able to explain the degeneracy of the hydrogen atom, now in terms of the SO 4 symmetry.

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We explained:

$$E_{3p}^{\text{Na atom}} \neq E_{3s}^{\text{Na atom}} \quad (\text{potential is NOT } 1/r)$$

$$\text{but } E_{3p}^{\text{H atom}} = E_{3s}^{\text{H atom}} \quad (\text{potential IS } 1/r)$$

Next class: U1L5:  
H atom wavefunctions

... any questions ?  
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And that is where I will conclude today's class I will happy to take some questions, but now we fully understand that to get the yellow lines d 1, d 2 lines of sodium atom there has to be a transition from 3 p to 3 s. This would not happen, if the same energy, if this takes for degeneracy right, so the d 1, d 2 lines comes from the fact that 3 p energy is different from 3 s, which is what we expected from the radial equation that you get by separating the angular part from the radial part right.

You get a one dimensional problem, and you have got a fundamental theorem in quantum mechanics that for the discrete part of the spectrum, you do not have any degeneracy. And that result is completely satisfied by the spectrum of the sodium atom, but the hydrogen atom which is of course, the simplest atom that one can think of it would leave us with a problem, which would make look like an accident of nature. And it is only, because we had not fully recognized the symmetry of the hydrogen atom it is SO 4, we get the Casimir operator and from the properties of the Casimir operators.

We get the spectrum which is  $1/n^2$ , but it also explain the degeneracy of the hydrogen atom. In our next class which will be tomorrow, I will discuss the wave function of the hydrogen atom, and this is again interesting, because we got the Eigen values of the hydrogen atom without solving the Schrödinger equation, right we did not actually solve the

definitional equation anywhere. We will now get if the wave function of the hydrogen atom, without using the Schrodinger equation.

Nothing wrong with the Schrodinger equation, great it is an heart quantum mechanics, but there is something to quantum mechanics which is more than the Schrodinger equation. And that is we are trying to you know develop some comfort with this Questions.

Student: Vivek initial start the same there are three generator  $L_x$  and  $L_y$  and  $L_z$  from the you wrote casimir rank. So, after knowing this six how one directly goes to I mean is there any wave we can see this might be as perhaps to figure out.

Well the way to do it is to figure out what would be the proximate Casimir operator for the particular group. Essentially the number of Casimir operator you can get is equal to the rank of the group, and this is the very famous theorem which was establish by Rogers, this is known as Rogers theorem. At the rank of this group for  $SO(3)$  is 1 because more two generators commute with each other, angle of momentum in quantum mechanics we define thorough the commutation relation.

And none of this two generators commute with the each other,  $L_x$  is not commute to the  $L_y$  and  $L_y$  does not commute with the  $L_z$ , and  $L_z$  is not commute to the  $L_x$ . So, there is only one Casimir, and Casimir also showed that you can always construct a bilinear combination of the generators, what is this bilinear combination for the Casimir for  $SO(3)$  it is  $J^2$ . Because,  $J^2$  is a bilinear combination it is equal to  $J_x^2 + J_y^2 + J_z^2$  square right.

So, this  $J^2$  is Casimir for  $SO(3)$  for  $SO(4)$  you have 6 generators, the rank of this group is 2, and you have to find what will be the Casimir operators. So, there are various ways that people do to construct the Casimir operators, essential you can get this only from what you have. In fact, I gave an example when we introduce the original Laplace vector, I said that you often learn about the equation motion. And then you also learn about the conservation principle, but can you get one from the other, the answer is yes that you if you begin the equation motion  $f$  equal to  $m \ddot{r}$  right.

And then you construct the cross product with the angel momentum or the specific angular momentum, what came out was a constancy which was the Laplace vector. So, by plane with the term that you have, you get new physics develop new in science so the operators that we



have to begin with our  $L$  and  $A$  and there is only, so much algebra that you can do this to operate. And if you start juggling with this term, it does not take too long to find that  $i^2$  plus  $k^2$  minus  $i^2$  will give you the Casimir. You can very easily verify well very easily, so for the physics is concerned, when you actually sit down to do it, it does take a little while it is laborious, but not difficult, any other question, if not.

Thank you all very much.