

Select/Special Topics in Atomic Physics
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Lecture - 37
Stark - Zeeman Spectroscopy

Well, let us continue our discussion on the Zeeman effect, and the Zeeman effect is actually Zeeman spectroscopy is a whole family of experimental situations. And then there are you know specific names that acts to various special features of the spectroscopic conditions, which are different in different situations. So, then it is called as a normal Zeeman effect or anomalous Zeeman effect and the paschen back effect.

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$$\vec{\mu} = -\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \quad i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \vec{\mu} \cdot \vec{B} + \xi(r) \vec{s} \cdot \vec{\ell} \right] \psi(\vec{r}, t)$$

Three cases Zeeman effect perturbation but $|\vec{B}|^2$ not imp

(1) $|\vec{\mu} \cdot \vec{B}| > |\xi(r) \vec{s} \cdot \vec{\ell}|$
normal Zeeman effect

(2) $|\vec{\mu} \cdot \vec{B}| \sim |\xi(r) \vec{s} \cdot \vec{\ell}|$
Paschen - Back ZE

(3) $|\vec{\mu} \cdot \vec{B}| < |\xi(r) \vec{s} \cdot \vec{\ell}|$
anomalous Zeeman effect

(1) "Normal ZE" \rightarrow strong $\vec{B}_{\text{external field}}$
 \rightarrow spin-orbit: relatively weak
Unperturbed eigenfunctions are eigenfunctions of $L^2, (S^2), L_z, S_z$
Good quantum numbers: n, ℓ, m_ℓ, m_s
(1) $\{\psi^{(0)}\} = \{|n, \ell, m_\ell, m_s\rangle\}$

$\Delta E = \langle n, \ell, m_\ell, m_s | (-\vec{\mu} \cdot \vec{B}) | n, \ell, m_\ell, m_s \rangle = \langle n, \ell, m_\ell, m_s | \left[-\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \cdot \vec{B} \right] | n, \ell, m_\ell, m_s \rangle$

$\Delta E = \langle n, \ell, m_\ell, m_s | \left(\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \cdot \vec{B} \right) | n, \ell, m_\ell, m_s \rangle$

$\vec{\mu} = -\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar}$

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So, essentially we reconciled with the idea that you have got the unperturbed Hamiltonian, which is the kinetic energy Hamiltonian and the potential energy in the field of the nucleus. And this is to be treated as the unperturbed Hamiltonian, the perturbation comes from an internal interaction, which is ignored in the non relativistic Hamiltonian. The internal interaction being the spin orbit interactions because spin is a intrinsic angular momentum, which the electron has and this is then to be included as a perturbation.

And then there is an external field, an external magnetic field to which the atom would respond as if it had a net magnetic moment. And this magnetic moment would come from two sources, one is the orbital angular momentum, and the other is the spin angular

momentum. So, depending on the relative strengths of these two perturbations, there is a perturbation source $\mu \cdot B$ and the other is the spin orbit interaction.

So, if the magnetic field is strong then; obviously, the $\mu \cdot B$ would be stronger than the $s \cdot l$ the spin orbit interaction. And this is what is regarded as a or it is called as a normal Zeeman effect, and this is just like a proper noun, so it is like anybody's name is to why he has that name is you know, it is for historical reasons then for nothing else. Not because it is normal and other phenomena are unusual in some sense, then you may have a situation in which the magnetic field is of the same order, in the sense that it generally an interaction, which is of the same order as the spin orbit interaction.

And then you need to consider both of these together, and then you may have a situation in which the spin orbit interaction is really significant, this is what will happen. If the applied external magnetic field is really extremely weak, and this is what is called as the weak field effect, and this is sometimes called as the anomalous Zeeman effect. And you will, you know as the discussion progresses you will see why one is called the first case is called the normal and the last case as anomalous.

So, that will become quite clear, so let this begin with the strong field consideration, in which the interaction due to the magnetic dipole moment of the atom. Generates an interaction $\mu \cdot B$, which is much larger than those spin orbit interaction, so this requires; obviously, a strong magnetic field. But, then remember that the magnetic field is not considered to be, so strong that b^2 terms become important, so we retain our consideration within the linear phenomena, phenomena which are linear in the magnetic field.

So, it is strong, but not, so strong as to consider the b^2 terms, now the unperturbed Eigen functions in which you must take the matrix element of the perturbation Hamiltonian, this is the cardinal rule that are talks about which we have referred to right. So, these unperturbed functions in this situation can be considered to be n, l, m_l and m_s because if the magnetic field who was weak and the spin orbit interaction was strong, then j would be a good quantum number j and m_j would be good quantum numbers right and not m_l and m_s .

So, the strength of the field determines what are the right quantum numbers to be used, so in this case you will use the m_l, m_s quantum numbers as generating the Eigen basis of the unperturbed Hamiltonian. This is not something you will be able to do if you are really dealing with very weak fields, in which the spin orbit interaction is strong. So, your good

quantum numbers in this case are n , l , m_l and m_s and the perturbation to be determined is then due to this magnetic field, the first thing you have to do is to get the interaction Hamiltonian, which is the $\mu \cdot B$ interaction.

And you determine the correction which is the first order perturbation correction in this unperturbed states, and you typically you could in this certain sense ignore the spin. But, you do not really have to ignore the spin because most of the situations that you come across the common phenomena that you meet, do not require that consideration explicitly as will become very clear now. So, this is the interaction now and this μ has got two sources, one is the orbital angular momentum this other is the spin remember that the g for the orbital angular momentum is 1 and that for the electron spin is 2.

So, you have got the bore magnet on keep track of the signs there are two minus signs over here because μ is minus μ_B . And this the first minus sign is coming from here, which is the interaction Hamiltonian which is minus $\mu \cdot B$, so there are two minus signs over there and they cancel each other, and this is the correction that you have really have to determine. So, this would be the consideration for the normal Zeeman effect, and this is what you choose to do because you work in the domain of strong magnetic fields not, so strong as to require the B^2 consideration, but strong enough to ignore the spin orbit interaction.

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$$\vec{\mu} = -\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \quad i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \vec{\mu} \cdot \vec{B} + \xi(r) \vec{s} \cdot \vec{\ell} \right] \psi(\vec{r}, t)$$

Zeeman effect perturbation

(1) $|\vec{B} \cdot \vec{\mu}| > |\xi(r) \vec{s} \cdot \vec{\ell}|$ "Normal ZE" \rightarrow strong $\vec{B}_{\text{external field}}$
normal Zeeman effect \rightarrow spin-orbit: relatively weak

Good quantum numbers: n, ℓ, m_ℓ, m_s $\{\psi^{(0)}\} = \{|n, \ell, m_\ell, m_s\rangle\}$

$$\Delta E = \langle n, \ell, m_\ell, m_s | \left(\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \cdot \vec{B} \right) | n, \ell, m_\ell, m_s \rangle \quad m_s = \pm \frac{1}{2}$$

$$= \mu_B (m_\ell + 2m_s) B$$

The correction to energy is determined by $(m_\ell + 2m_s)$
 so it is the same for a given sum $(m_\ell + 2m_s)$
 regardless of the individual values of m_ℓ & m_s .

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So, this is what we have got now if you consider B to be along the z axis, then $l \cdot s$ and $B \cdot s$ will give you l_z and s_z operators right and m_l and m_s are their Eigen values. Because,

m_l and m_s are simultaneous Eigen states of L_z and S_z , these two sources of angular momentum are completely independent of each other, and the Eigen value of this $\vec{B} \cdot \vec{L} + 2\vec{B} \cdot \vec{S}$ will be m_l plus twice m_s because of this consideration I take \vec{B} to \vec{B} along the z axis.

So, this is your energy correction and m_s of course, can take two values which is either plus 1 or minus 1. Now, this is the correction now and this correction depends on the sum of m_l plus twice m_s , and it does not depend individually on the value of m_l and m_s . So, various combinations of m_l and m_s which will give you the same value of m_l plus twice m_s , because you can get to the same sum for different values of the individual components which go into the sum. So, you really have to consider the sum m_l plus twice m_s rather than the individual values m_l and m_s .

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$$\Delta E = \langle n, \ell, m_\ell, m_s | \left(\mu_B \frac{\vec{L} + 2\vec{S}}{\hbar} \cdot \vec{B} \right) | n, \ell, m_\ell, m_s \rangle \quad m_s = \pm \frac{1}{2}$$

$$= \mu_B (m_\ell + 2m_s) B \quad \text{for } 2p \ell = 1: m_\ell = -1, 0, +1$$

$m_\ell = 1 \& m_s = -\frac{1}{2}$ gives $m_\ell + 2m_s = 0$
 $m_\ell = -1 \& m_s = +\frac{1}{2}$ also gives $m_\ell + 2m_s = 0$

$\Delta E = \mu_B (m_\ell + 2m_s) B = 0$
 for these two 'pairs' of m_ℓ, m_s .

1st we construct a table: m_ℓ m_s $m_\ell + 2m_s$

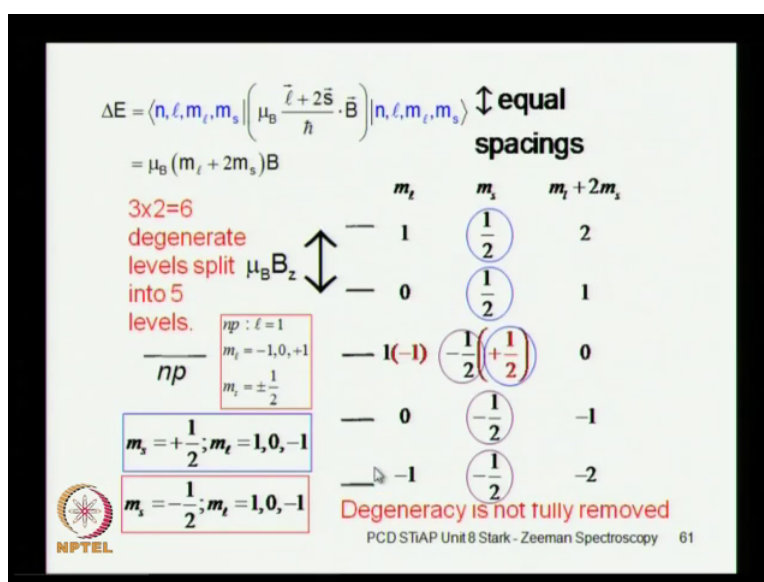
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Now, let us take an example that if you consider the 2 p the Zeeman effect with the for the 2 p electrons, then for the 2 p ℓ is equal to 1, m_l can take 3 values minus 1 0 and 1 spin of course, is half. So, m_s can take two values plus half and minus half, and m_l equal to 1 and m_s equal to minus half will give you m_l plus twice m_s equal to 0, so it will not lead to any change in the energy. Because, the energy depends on this sum and this sum vanishes right.

Likewise, if you have m_l equal to minus 1 and m_s equal to plus half and both the possibilities are contained over here. So, if you have this possibility then again you will have m_l plus twice m_s equal to 0, so in these two cases you do not have any correction for both of these combinations. So, in this case the magnetic field will not change the energy, and the

degeneracy with respect to this quantum numbers will not be removed. So, what we are going to do is to first construct a table of various possible values of m_l and possible values of m_s , this should be m_s . And then we will construct the sum m_l plus twice m_s , and then see what energy corrections come out of this consideration.

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So, this is our table which is m_l , m_s and m_l plus twice m_s , so m_l can take values 1 0 minus 1 0 and so on and m_s can take values either plus half. So, the first 3 levels correspond to m_s equal to plus half, and the lower 3 levels correspond to m_s equal to minus half, but these 2 levels are degenerate. So, although you see 5 levels over here, you are looking at 6 states the 3 values of m_l and the 2 values of m_s will give you 3 into 2 6 possible states, out of which two remain degenerate right.

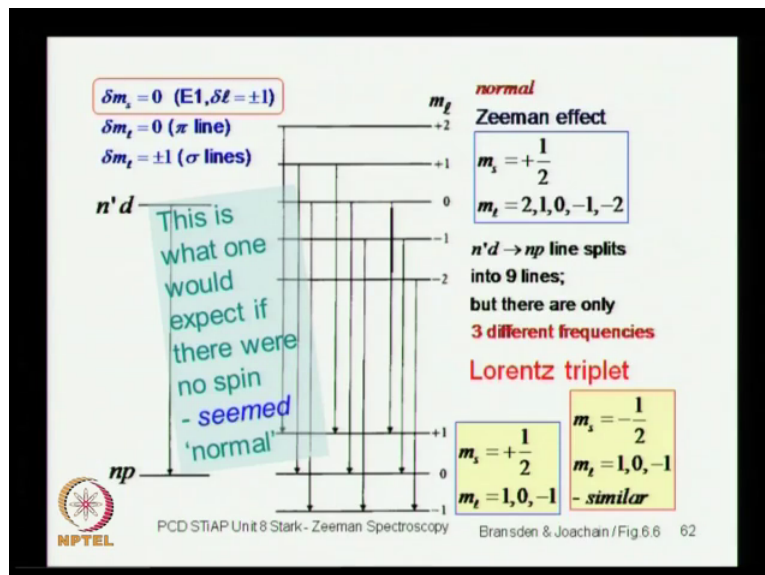
The correspond to this combination m_l equal 1 and m_s equal to minus half and m_l equal to minus 1 and m_s equal to plus half. So, these two combinations they remain degenerate, and their energy is not changed because the delta e for that is 0 m_l plus twice m_s is 0. And the remaining one you do have an energy, which is different from what you had for the original unperturbed Eigen state, which is np and you see that the spacing is proportional to the spacing between these numbers, and this spacing difference between these numbers is just unity, so all of there will be equally space levels.

So, you have equal spacing's because of this reason and the 6 degenerate levels split into 5 levels, these two remain degenerate and their energy also does not change at all. So, now, let

us consider only those levels for m_s equal to plus half, this is just for our discussion it is not that we are going to ignore m_s equal to minus half. But, we will find that when we consider m_s equal to minus half we get the same result.

So, to begin with let us take a subset of these levels corresponding to m_s equal to plus half. So, these are these 3 levels you could also consider the other set corresponding to m_s equal to minus half, which at these three levels. So, you take either the top 3 or the lower 3 levels, and then we will see what kind of you know splitting of the spectra takes place as a result of this.

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So, let us consider these states for l equal to 2 you have this energy, and for l equal to 1 for principal quantum number n you have this. So, typically you would have a d to p transition, a d to p dipole transition in the hydrogenic atom, if you keep this in a magnetic field the $\mu \cdot b$ interaction will split the $n d$ levels into 5 levels. These are the ones corresponding to m_l equal to plus 2 plus 1 0 minus 1 and minus 2, likewise the $n p$ state will split into 3 levels 1 0 and minus 1 for three different values of m_l .

And then you can have transitions from the d levels to the p level right, but now the single line that would have resulted in the unperturbed hydrogen atom splits into many. And you can see that there are a total of 9 transitions subject to these selection rules because the dipole interaction is not going to change the spin, so δm_s is 0. And we have considered only the m_s equal to plus half states in this right.

Because, for the dipole transition the spin is not going to be changed, there is nothing in the dipole interaction which will influence the spin. And then you have transitions corresponding to Δm equal to either 0 or plus or minus 1, so if it is equal to 0 these are called as pi lines, and if Δm is equal to either plus 1 or minus 1 these are called as sigma lines. So, the single line subject to these transitions selection rules, splits into these 9 transitions.

However, out of these 9 transitions there are only 3 frequencies which result because if you look at the differences, the difference between this and this remains the same. If because they are all shifting by an equal amount, which is what we just discussed in when we were discussing the previous slide. So, there are only 3 different frequencies which result from these 9 lines, and these three frequencies are called as the Lorentz triplet, these were observed in the Zeeman effect and you have these Lorentz triplet.

And you could now consider the m_s equal to minus half and do exactly the same analysis, once again you will find that the d to p for m_s equal to minus half to m_s equal to minus half, with Δm_s equal to 0 that single transition will again split into 9 levels. But, again corresponding to this 3 different frequencies, which will be exactly the same as these frequencies. So, it really does not give you any new frequency, you get a net sum of a triplet, even after the consideration of m_s equal to plus half and m_s equal to minus half.

So, it is not that you have really ignored the spin, so even if you do consider the spin, you get the same set of levels and this is just what you would get, if you were to ignore the spin. This is precisely what you would get, if you were not even aware of spin and in the early days of quantum mechanics when spin was not known, this is what was seen in the d to p spectrum and this was expected to be what should have been seen, so it was called as a normal Zeeman effect. And it results not because spin has no role to play at all, but because it does not have any consequence on the appearance of the spectrum, which appears as a triplet. Now, this is the case for d to p does not matter whether it is d to p or also p to s.

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$\delta m_s = 0$ (E1, $\delta \ell = \pm 1$)

$\delta m_\ell = 0$ (π line)

$\delta m_\ell = \pm 1$ (σ lines)

$n'd \leftrightarrow np$

$n'p \leftrightarrow ns$

Lorentz triplet


(I) $|\vec{B} \cdot \vec{\mu}| > |\zeta(r)\vec{s} \cdot \vec{\ell}|$

normal Zeeman effect

normal Zeeman effect

$n'd \rightarrow np$ line splits into 9 lines; but there are only **3 different frequencies**

$n'p \rightarrow ns$ line splits into 6 lines, but also having only **3 different frequencies**



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So, let us consider the other case, so you have seen the Lorentz triplet in the d to p transitions, but if you consider the p to s transitions. If you consider the p to s transitions, then again you would have 6 lines resulting from this, but these 6 lines again correspond only to 3 different frequencies. So, you can do exactly the same analysis and you will find that only 3 frequencies appear, and it is for this reason that this high field or strong field Zeeman effect is called as the normal Zeeman effect, because most of the atomic transitions in the early days of spectroscopy were studied between the d and p states or p and s states. And in both cases you saw a triplet mainly the Lorentz triplet, in both cases it is not that the electron spin was hidden, but it did not have any major consequence on these sets of transitions, which was studied in the early days of spectroscopy. So, this is called as a normal Zeeman effect.

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$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \vec{\mu} \cdot \vec{B} + \zeta(r) \vec{s} \cdot \vec{l} \right] \psi(\vec{r}, t)$$

Three cases

(1) $|\vec{B} \cdot \vec{\mu}| > |\zeta(r) \vec{s} \cdot \vec{l}|$
normal Zeeman effect

(2) $|\vec{B} \cdot \vec{\mu}| \sim |\zeta(r) \vec{s} \cdot \vec{l}|$
Paschen-Back ZE

(3) $|\vec{B} \cdot \vec{\mu}| < |\zeta(r) \vec{s} \cdot \vec{l}|$
anomalous Zeeman effect

Zeeman effect perturbation

(2) "Paschen-Back ZE"
 $|\vec{B}|$ is somewhat strong,
but H_{s-o} also needs to be considered.

(2) $\{\psi^{(0)}\} = \{|n, \ell, m_\ell, m_s\rangle\}$
since s-o: weak

The good quantum numbers are: n, ℓ, m_ℓ, m_s .

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So, now we consider slightly stronger fields, so that $\vec{v} \cdot \vec{\mu}$ term is more important than the spin orbit interaction. But, it is not, so overwhelmingly strong that the spin orbit interaction is to be completely ignored at all, so this is what is called as the paschen back effect. And in this case again m_l, m_s are good quantum numbers, and the reason these are considered as m_l these are considered as good quantum numbers because if the $\vec{s} \cdot \vec{l}$ interaction was strong if this right hand side of this inequality was stronger than the left.

Then j, m_j would be good quantum numbers and not m_l, m_s , so because the right side of this inequality is still the weaker one. So, if this is still the less important term, so we can continue to use m_l and m_s as the good quantum numbers, and in this basis we can find what the corrections are.


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$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \boxed{\vec{\mu} \cdot \vec{B} + \xi(r) \vec{s} \cdot \vec{\ell}} \right] \psi(\vec{r}, t)$$

$$\{\psi^{(0)}\} = \{|n, \ell, m_\ell, m_s\rangle\}$$

$$\Delta E_{\text{M}}^{\text{PB-ZE}} = \Delta E_{\text{M}}^{\text{PB-ZE}} + \Delta E_{\text{s-o}}^{\text{PB-ZE}}$$

$$\Delta E_{\text{M}}^{\text{PB-ZE}} = \langle n, \ell, m_\ell, s, m_s | (-\vec{\mu} \cdot \vec{B}) | n, \ell, m_\ell, s, m_s \rangle$$

$$\Delta E_{\text{s-o}, \ell \neq 0}^{\text{PB-ZE}} = \langle n, \ell, m_\ell, m_s | \xi(r) \vec{\ell} \cdot \vec{s} | n, \ell, m_\ell, m_s \rangle$$


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So, what are the corrections to be studied, now the correction is due to the 2 perturbations, now we are not going to ignore $s \cdot l$ interaction altogether. It is not, so strong as to make m_l and m_s ineffective making you require make to use j, m_j . So, you can continue to use m_l, m_s quantum numbers, but you must take corrections due to both of these terms in this basis, and there are two contributors to the paschen back effect. And this is the superscript here stands for the paschen back Zeeman effect because it belongs to the family of Zeeman effect.


But, this is a special consideration in which the two perturbations are more or less equally important, never the less the magnetic dipole term is more important than the spin orbit interaction. So, the situation which is under consideration for the paschen back effect, and this is the correction due to the magnetic dipole terms, and this is the correction for the due to the spin orbit interaction. Wherever l is not equal to 0 for l equal to 0 of course, the spin orbit interaction vanishes. So, l is not 0 in this case and these are the two corrections that we must now estimate and get the correction to the unperturbed energy.

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$$\Delta E_M^{\text{PB-ZE}} = \langle n, \ell, m_\ell, s, m_s | (-\vec{\mu} \cdot \vec{B}) | n, \ell, m_\ell, s, m_s \rangle$$

$$\vec{\mu} = -\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar}$$

$$\Delta E_M^{\text{PB-ZE}} = \langle n, \ell, m_\ell, s, m_s | \left(\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \cdot \vec{B} \right) | n, \ell, m_\ell, s, m_s \rangle$$


$$\Delta E_M^{\text{PB-ZE}} = \frac{\mu_B}{\hbar} B \hbar (m_\ell + 2m_s) = \mu_B B (m_\ell + 2m_s)$$


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So, let us proceed to get these let us first get the $\mu \cdot B$ correction this is due to the magnetic dipole moment. And the magnetic dipole moment is because of the angular momentum coming from orbital angular momentum, as well as the spin angular momentum. So, the two sources and the correction therefore, has this l plus twice s over \hbar cross dot B , and if you consider again B to B along the z axis as we discussed earlier you will get m_l plus twice m_s this 2 is coming from the g factor for the electron which is 2. And this is m_l plus twice m_s correction, so you of course, get an m_l times \hbar cross, so there is an \hbar cross which will cancel this \hbar cross in the denominator, and this is the correction due to the magnetic dipole term to the paschen back effect.

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$$\begin{aligned}
 \Delta E_{s-o, \ell \neq 0}^{PB-ZE} &= \langle n, \ell, m_\ell, m_s | \xi(r) \vec{\ell} \cdot \vec{s} | n, \ell, m_\ell, m_s \rangle \\
 &= \langle n, \ell | \xi(r) | n, \ell \rangle \langle \ell, m_\ell, s, m_s | \vec{\ell} \cdot \vec{s} | \ell, m_\ell, s, m_s \rangle \\
 &= \langle n, \ell | \xi(r) | n, \ell \rangle \langle \ell, m_\ell, s, m_s | \ell_x s_x + \ell_y s_y + \ell_z s_z | \ell, m_\ell, s, m_s \rangle \\
 &= \langle n, \ell | \xi(r) | n, \ell \rangle \langle \ell, m_\ell, s, m_s | \ell_z s_z | \ell, m_\ell, s, m_s \rangle
 \end{aligned}$$


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Now, what about the spin orbit interaction, now this is the correction that we have to obtain. So, the spin orbit interaction we know from the wholly with hyson transformation of the direct Hamiltonian, it is got this explicit form which is $\xi(r)$ times $\vec{l} \cdot \vec{s}$, and $\vec{l} \cdot \vec{s}$ is $l_x s_x + l_y s_y + l_z s_z$. And since, you are taking the matrix element in $m_l m_s$ states l_x and l_y or s_x and s_y can be written in terms of the ladder operators.

And if you did that you will find that from orthogonality of the m_l, m_s states they will not contribute anything to the energy correction. The only term that will contribute is the z component which is l_z and s_z , so it is only the z component which needs to be considered, these two components will not contribute anything to the energy corrections and now you have to get this $l_z s_z$.

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$$\begin{aligned}
 \Delta E_{s-o, \ell \neq 0}^{PB-ZE} &= \langle n, \ell, m_\ell, m_s | \xi(r) \vec{\ell} \cdot \vec{s} | n, \ell, m_\ell, m_s \rangle \\
 &= \langle n, \ell | \xi(r) | n, \ell \rangle \langle \ell, m_\ell, s, m_s | \ell_z s_z | \ell, m_\ell, s, m_s \rangle \\
 &= \langle n, \ell | \xi(r) | n, \ell \rangle (m_\ell \hbar) (m_s \hbar) \\
 &= \langle n, \ell | \left(\frac{e}{2m^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \right) | n, \ell \rangle (m_\ell \hbar) (m_s \hbar) \\
 &= \frac{e}{2m^2 c^2} \int_0^\infty r^2 dr [R_{n\ell}(r)]^2 \left(\frac{Ze}{r^3} \right) \times (\hbar^2 m_\ell m_s)
 \end{aligned}$$


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So, let us proceed to do that, so $\ell_z s_z$ these two this is a product of this is a direct product of kits right. So, it is a direct product of ℓ, m_ℓ, s, m_s , so you will get $m_\ell \hbar$ cross coming from the operation of ℓ_z , and $m_s \hbar$ cross coming from this, so now, you have got this correction for the spin orbit interaction. You now have to evaluate these space integrals because $\xi(r)$ has got this explicit form, and this space integral has to be evaluated to get the correction.

Now, this can be easily done because you know the radial functions and you also know that the potential goes as Ze/r or minus Ze/r . So, you have to take its derivative with respect to r , so you get $1/r^2$ coming from this derivative, and there is a $1/r$ over here. So, you need the radial integral of $1/r^3$ in hydrogenic unperturbed wave functions radial functions, so these are the radial integrals which can be easily determined, since all of these radial functions are known.

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$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \langle n, \ell, m_\ell, s, m_s | \hat{z}(r) \vec{\ell} \cdot \vec{s} | n, \ell, m_\ell, s, m_s \rangle = \frac{e}{2m^2 c^2} \left\{ \int_0^\infty r^2 dr [R_{nl}(r)]^2 \left(\frac{Ze}{r^3} \right) \right\} \times (\hbar^2 m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{Ze^2 \hbar^2}{2m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \times (m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{Ze^2 \hbar^2}{2m^2 c^2} \times \frac{Z^3}{a_0^3 n^3 \ell \left(\ell + \frac{1}{2} \right) (\ell + 1)} \times (m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{Ze^2 \hbar^2}{2m^2 c^2} \times \frac{Z^3}{\left(\frac{\hbar^2}{me^2} \right)^3 n^3 \ell \left(\ell + \frac{1}{2} \right) (\ell + 1)} \times (m_\ell m_s)$$

$a_0 = \frac{\hbar^2}{me^2}$



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And, if you evaluate these radial integrals this is like getting the average value of 1 over r cube, and then you have got this m_ℓ and m_s coming from here. So, if you take the average value of 1 over r cube you get this term over here, which goes as 1 over n cube one over the bohr radius cube. And then we have seen these terms earlier in our consideration of radial functions of the hydrogen atom, so this is the correction to the paschen back effect, coming from the spin orbit interaction.

So, let us rewrite this because it is nice to extract the fine structure constant out of this, so put in the explicit value of a_0 which is \hbar^2 cross square over m_e square. And this substitution gives you this \hbar^2 cross square over m_e square to the power 3 over here. So, we are just rewriting this expression with explicit expression for the bohr radius.

(Refer Slide Time: 25:35)

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{-Ze^2\hbar^2}{2m^2c^2} \times \frac{m^3e^6 \times Z^3}{\hbar^4n^3\ell\left(\ell + \frac{1}{2}\right)(\ell+1)} \times (m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{Z^2\left(\frac{e^2}{\hbar c}\right)^2}{2} \times \frac{me^4 \times Z^2}{\hbar^4n^3\ell\left(\ell + \frac{1}{2}\right)(\ell+1)} \times (m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \frac{(Z\alpha)^2}{n} \times E_n \times \frac{1}{\ell\left(\ell + \frac{1}{2}\right)(\ell+1)} \times (m_\ell m_s)$$

$$\Delta E_{s-o, \ell \neq 0}^{PB-ZE} = \lambda_{n\ell} (m_\ell m_s)$$

Perturbation energy correction depends on ℓ , and the degeneracy with respect to the ℓ quantum number is removed.

Bransden & Joachain / Page 295
Eq. 6.103 & 6.106

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And then we extract the fine structure constant because you have got e^2 over $\hbar c$ you have got e to the power 6 here, e^2 over $\hbar c$ here. So, you have got a total of 8 powers of e , so there are 4 powers of e here and 4 over here, but by rewriting these terms in this fashion you can write this as $Z\alpha^2$. So, that is the advantage in you know grouping these terms in this form.

So, again you can get the bohr energy expression out of it, and then you find that the paschen back correction goes as $Z\alpha^2$, then it is proportional to the energy do not forget the minus sign over here because E_n is minus of this right. So, you have got an E_n over here, and then you have got the ℓ dependence here, you also have the m_ℓ and m_s . And essentially this term together depends on both n as well as ℓ .

So, in a simple way it is in a compact manner written as $\lambda_{n\ell}$, with a subscript n and ℓ because it will depend specifically on different values of n and ℓ . And then it will be proportional to do the product not to individual values, but to the product of m_ℓ and m_s ; obviously, it will be 0 if either m_ℓ or m_s is 0 right m_s of course, is either half or minus half. So, this is a perturbation energy correction, and notice that this depends on ℓ and the degeneracy with respect to the ℓ quantum number is removed in the paschen back effect.

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$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \boxed{\vec{\mu} \cdot \vec{B} + \zeta(r) \vec{s} \cdot \vec{\ell}} \right] \psi(\vec{r}, t)$$

$$\{\psi^{(0)}\} = \{|n, \ell, m_\ell, m_s\rangle\}$$

$$\Delta E^{\text{PB-ZE}} = \Delta E_{\text{M}}^{\text{PB-ZE}} + \Delta E_{\text{s-o}}^{\text{PB-ZE}}$$

$$\Delta E_{\text{M}}^{\text{PB-ZE}} = \mu_B B (m_\ell + 2m_s)$$

$$\Delta E_{\text{s-o}, \ell \neq 0}^{\text{PB-ZE}} = \lambda_{n\ell} (m_\ell m_s)$$

$$\Delta E^{\text{PB-ZE}} = \mu_B B (m_\ell + 2m_s) + \lambda_{n\ell} m_\ell m_s$$


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So, this is our consideration of both the terms, so now, you combine the two you have got two contributions, one is this contribution the magnetic dipole contribution, the other is the spin orbit contribution. The magnetic dipole contribution goes as m_ℓ plus twice m_s , and the spin orbit contribution goes as λ times m_ℓ into m_s . So, now, you must add the two to get the correction, and this is where the fun begins because it is not trivial. So, you have to look at these two terms this is m_ℓ plus twice m_s this goes as λ times m_ℓ and m_s .

(Refer Slide Time: 28:21)

$$\Delta E^{\text{PB-ZE}} = \mu_B B (m_\ell + 2m_s) + \lambda_{n\ell} m_\ell m_s$$

$$E_{n'} = E_n^{(0)} + \mu_B B (m_\ell' + 2m_s') + \lambda_{n'\ell'} m_\ell' m_s'$$


$$E_n = E_n^{(0)} + \mu_B B (m_\ell + 2m_s) + \lambda_{n\ell} m_\ell m_s$$

$$\boxed{\delta m_s = 0 \quad \text{and} \quad \delta m_\ell = 0, \pm 1}$$

$$\delta E = E_{n'}^{(0)} - E_n^{(0)} + \mu_B B (m_\ell' - m_\ell) + (\lambda_{n'\ell'} m_\ell' - \lambda_{n\ell} m_\ell) m_s$$

$$\frac{\delta E}{\hbar} = \delta \nu \text{ frequency shifted spectral lines}$$

observed in the Paschen-Back ZE.



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So, if you look at these two energies if you have an excited state n prime, and a lower state n . Then you can have different transitions from n prime to n , coming from these different combinations, so you will have an excited state corresponding to n prime, and a lower state corresponding to n . And you can have all kinds of different transitions because one term depends on the sum of m_l and m_s , the other term depends on the product of m_l and m_s right.

And it is the same over here for the lower state as well, so you can have many, many different kinds of frequencies coming out of this. And if you look at transitions corresponding to the dipole selection rules that Δm equal to 0, and Δm equal to either 0 or plus or minus 1. Then these are the possible transitions that you can see, and they will result in a corresponding frequency shift, which is ΔE over h cross and all of these are observed in the paschen back effect.

(Refer Slide Time: 29:34)

The slide displays the following content:

Equation:
$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \vec{\mu} \cdot \vec{B} + \xi(r) \vec{s} \cdot \vec{l} \right] \psi(\vec{r}, t)$$

Three cases

- (1) $|\vec{B} \cdot \vec{\mu}| > |\xi(r) \vec{s} \cdot \vec{l}|$ "normal" Zeeman effect
- (2) $|\vec{B} \cdot \vec{\mu}| \sim |\xi(r) \vec{s} \cdot \vec{l}|$ Paschen-Back ZE
- (3) $|\vec{B} \cdot \vec{\mu}| < |\xi(r) \vec{s} \cdot \vec{l}|$ anomalous Zeeman effect

Zeeman effect perturbation

(3) "Anomalous ZE" \rightarrow weak $\vec{B}_{\text{external field}}$

Unperturbed eigenfunctions are eigenfunctions of $L^2, (S^2), J^2, J_z$ but not of L_z nor of S_z

(3) $\{\psi^m\} = \{(\psi)jm\}$

$(\psi)jm = \sum_{m_l} \sum_{m_s} |m_l m_s\rangle \langle m_l m_s | jm\rangle$

is the most common one ... hence most important – in some sense!

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Now, comes an interesting situation that you have a weak field, then once you have a weak field this term the spin orbit interaction is going to dominate. So, because the spin orbit interaction dominates the unperturbed Eigen functions must be considered to be Eigen states of j square and j_z and not of l_z and s_z . So, now, the quantum numbers you must use for the unperturbed states are l, s, j, m_j and not l, s, m_l, m_s it is because now the spin orbit interaction is the dominant interaction, the magnetic field is weak.

And therefore, the dominant interaction is the spin orbit interaction the good quantum numbers will be Eigen states of j^2 and j_z , and not l^2 and l_z and s_z . So, this is what is called as anomalous Zeeman effect it is, in fact a rather common one and in some sense more important. But, only for extrardical reason it is called as anomalous because when it was seen in the earlier times it could not be interpreted when spin was not known.

So, it was only after uhlenbeck and goudsmit inserted spin in their discussion, and they got lucky because they had inserted it not on the basis of any physical understanding of the phenomenon. But, out of what turned out to be a good guess and later on it was rationalized in the Dirac theory because it is essentially a relativistic phenomnal.

(Refer Slide Time: 31:28)

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} - \vec{\mu} \cdot \vec{B} + \xi(r) \vec{s} \cdot \vec{\ell} \right] \psi(\vec{r}, t)$$

(3) "Anomalous ZE" \rightarrow weak $\vec{B}_{\text{external field}}$ $\{ \psi^{(0)} \} = \{ |(\ell s) jm\rangle \}$

$$H_0 = -\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{r} + \xi(r) \vec{s} \cdot \vec{\ell}$$

$|(\ell s) jm\rangle = \sum_{m_\ell} \sum_{m_s} |m_\ell m_s\rangle \langle m_\ell m_s | jm \rangle$
eigenfunctions of L^2, S^2, J^2, J_z

$$H' = -\vec{\mu} \cdot \vec{B}$$

$$H' = -\vec{\mu} \cdot \vec{B} = -\left(-\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \right) \cdot \vec{B}$$

not of L_z, S_z
 $\vec{\mu} = -\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar}$

$$H' = \left(\mu_B \frac{\vec{\ell} + 2\vec{s}}{\hbar} \right) \cdot \vec{B}$$

$$H' = \frac{\mu_B}{\hbar} (\ell_z + 2s_z) B$$

$\vec{B} = |\vec{B}| \hat{e}_z$

Remember!
 m_ℓ, m_s are not good quantum numbers

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So, now, your good quantum numbers are j and m_j , and these you can express in terms of the m_l , m_s spaces by expanding j and m_j in the uncoupled basis of l and s , and these are the corresponding Clebsch-Gordan coefficients. So, these are the Eigen functions of l^2 , s^2 , j^2 and j_z , and this is the interaction Hamiltonian whose matrix element must be determined. The Bohr magneton has got both of these components. So, with the 2 minus signs you have to keep track of the term of both the minus signs.

And now you consider B to be along the z axis, so out of the $\vec{l} \cdot \vec{B}$ term and $\vec{s} \cdot \vec{B}$ term you need to consider only the l_z and s_z right. But, if you put in s_z and l_z , you are not able to operate on an Eigen state of l_z and s_z right, so m_l and m_s are not good quantum

numbers. So, this is really the tricky part because m_l and m_s are not good quantum numbers in this case.

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$$H' = -\vec{\mu} \cdot \vec{B} = -\left(-\mu_B \frac{\vec{L} + 2\vec{S}}{\hbar} \right) \cdot \vec{B} = \left(\mu_B \frac{\vec{L} + 2\vec{S}}{\hbar} \right) \cdot \vec{B}$$

$$\vec{L} + 2\vec{S} = \vec{J} + \vec{S} \quad (\vec{B} = B\hat{e}_z)$$

$$\Delta E_{AZE}^{Weak-Field} = \left\langle \ell s j m_j \left| \frac{\mu_B}{\hbar} (\vec{J} + \vec{S}) \cdot \vec{B} \right| \ell s j m_j \right\rangle$$

$$= \mu_B B m_j + \frac{\mu_B}{\hbar} B \left\langle \ell s j m_j \left| S_z \right| \ell s j m_j \right\rangle$$

$$\Delta E_{AZE}^{Weak-Field} = \overset{j}{\Delta E_{AZE}^{Weak-Field}} + \overset{s}{\Delta E_{AZE}^{Weak-Field}}$$

$\overset{s}{\Delta E_{AZE}^{Weak-Field}} = \left\langle \alpha j m_j \left| V_z \right| \alpha j m_j \right\rangle = ?$

\vec{V} : vector operator

Two ways:

- 1) Vector operator identities
- 2) Wigner-Eckart Theorem

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So, this is really the tricky part, but it can be handled using special techniques including the Wigner Eckart theorem and some other, you know aspects of the angular momentum algebra which we will discuss now. So, this is what we have got, we have to determine this correction due to the term $\vec{L} + 2\vec{S}$. $\vec{L} + 2\vec{S}$ is the same as $\vec{J} + \vec{S}$ because $\vec{L} + \vec{S}$ is \vec{J} . So, one of the \vec{S} can be observed in \vec{J} , so this interaction $\vec{L} + 2\vec{S}$ is effectively $\vec{J} + \vec{S}$ and you therefore, have to consider the matrix elements of this operator, which is the z component of $\vec{J} + \vec{S}$.

But, in Eigen states and these j and m_j is an Eigen state of J_z no problem there, but this is not an Eigen state of S_z . So, for the first term J_z you can operate by J_z on this, and you will get m_j times \hbar cross, but you do not get an Eigen value equation with S_z because this is not an Eigen state of S_z . So, from the first one from J_z you get $m_j \hbar$ cross together with this \hbar cross in the denominator that \hbar cross is cancelled, and the first term corresponding to this contributes this correction to the energy, this second term we have to figure out how to handle that.

So, this is coming from the j term and the net correction is now due to two contributors, one which is based on j , and the other which is based on s and now our question is how do we find this matrix element. So, that is the question that we must address, and it is by no means a straightforward one, so there are two alternative ways to get this one uses certain vector

identities, and the other method uses the Wigner Eckart theorem. And we will discuss both of these, because it is good to learn these techniques.

And you remember here that you need the matrix element in j, m_j state of a certain component of a vector operator, we do know that the angular momentum is a vector operator. So, our question onto how do I get matrix element in j, m_j state of an arbitrary vector operator, if you can get it for an arbitrary vector operator we can use that for the angular momentum s , which is also a vector operator.

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Equivalent criterion for a vector \vec{A} to be \vec{A}_{op} .

$$U_R^\dagger A_i U_R = \sum_{j=1}^3 R_{ij} A_j \quad [A_i, J_i]_- = 0 \quad \forall i=1,2,3$$

$$[A_x, J_y]_- = A_x J_y - J_y A_x = i\hbar A_z$$

$$[A_x, J_z]_- = A_x J_z - J_z A_x = -i\hbar A_y$$

$$[A_y, J_z]_- = A_y J_z - J_z A_y = i\hbar A_x$$

$$[A_y, J_x]_- = A_y J_x - J_x A_y = -i\hbar A_z$$

$$[A_z, J_x]_- = A_z J_x - J_x A_z = i\hbar A_y$$

$$\Rightarrow \text{identities:} \quad [A_z, J_y]_- = A_z J_y - J_y A_z = -i\hbar A_x$$

$$(1) \quad \vec{J} \times \vec{V} + \vec{V} \times \vec{J} = 2i\hbar \vec{V}$$

$$(2) \quad [J^2, [\vec{J}^2, \vec{V}]] = 2\hbar^2 (J^2 \vec{V} + \vec{V} J^2) - 4\hbar^2 (\vec{V} \cdot \vec{J}) \vec{J}$$

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And now, you will remember that in an earlier unit and believe in unit 2, we defined what is the criterion that must be employed for an operator to be for a vector to be a vector operator. And the criteria that we discussed were in terms of the commutation relations of the components of this vector with the angular momentum components, so these commutation rules are equivalently how they transform under rotations, how the components transform under the rotations.

And whether you study this response to rotation or study the commutation algebra, the both give you essentially the same results they are completely equivalent as we have discussed in unit 2. So, this is the criterion that must be employed to recognize a vector to be a vector operator in quantum mechanics, and since we are dealing with a vector operator, we know that these identities are satisfied. And these lead to two additional identities, which come directly as a consequence of these commutation rules.

So, this is a matter of detail you have to work out a little bit of algebra, but if you construct the cross product $\mathbf{J} \times \mathbf{V}$ and add to it $\mathbf{V} \times \mathbf{J}$. And uses these commutation rules nothing else, you will get that the right hand side is twice $i\hbar \mathbf{V} \times \mathbf{J}$ you already can see that a $\mathbf{V} \times \mathbf{J}$ that is what you get right. So, you have this identity you have likewise another identity which comes from the same consideration, which is the second identity over here.

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(2)
$$[J^2, [J^2, \vec{V}]] = 2\hbar^2 (J^2 \vec{V} + \vec{V} J^2) - 4\hbar^2 (\vec{V} \cdot \vec{J}) \vec{J}$$

$$\Rightarrow \langle \ell s j m_j | [J^2, [J^2, \vec{V}]] | \ell s j m_j \rangle =$$

LHS matrix element vanishes

$$\langle \ell s j m_j | [2\hbar^2 (J^2 \vec{V} + \vec{V} J^2) - 4\hbar^2 (\vec{V} \cdot \vec{J}) \vec{J}] | \ell s j m_j \rangle$$

$$\Rightarrow 0 = \langle \ell s j m_j | [2\hbar^2 (J^2 \vec{V} + \vec{V} J^2) - 4\hbar^2 (\vec{V} \cdot \vec{J}) \vec{J}] | \ell s j m_j \rangle$$

$$\langle \ell s j m_j | [J^2 \vec{V} + \vec{V} J^2] | \ell s j m_j \rangle = 2 \langle \ell s j m_j | (\vec{V} \cdot \vec{J}) \vec{J} | \ell s j m_j \rangle$$

$$\hbar^2 j(j+1) \langle \ell s j m_j | (\vec{V} + \vec{V}) | \ell s j m_j \rangle = 2 \langle \ell s j m_j | (\vec{V} \cdot \vec{J}) \vec{J} | \ell s j m_j \rangle$$

$$\hbar^2 j(j+1) \langle \ell s j m_j | \vec{V} | \ell s j m_j \rangle = \langle \ell s j m_j | (\vec{V} \cdot \vec{J}) \vec{J} | \ell s j m_j \rangle$$

This result: also from WET
Bransden & Joachain
Physics of Atoms & Molecules
Eq 6.113 and A4.58

ΔE_{Zeeman} requires $\langle \alpha j m_j | S_z | \alpha j m_j \rangle$

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And one of the techniques that we are going to use is based on the second identity, which is that this commutator is equal to what is on the right hand side. And this is an identity it holds good for any vector operator \mathbf{V} it does not matter what it is, the only requirement is that it must be a vector operator. So, you checkout if it is a vector operator and in our consideration, we are certainly interested in the matrix elements of the components of the spin angular momentum, which we do know is a vector operator, so we will be able to use this identity.

So, you now take the matrix element of both sides the left side as well as the right hand side, in angular momentum states corresponding to the coupled basis which is $|\ell s j m_j\rangle$ right. So, because this is an identity the matrix element of the left hand side is equal to the matrix element of the right hand side, and now this matrix element of the left hand side, you can evaluate explicitly using angular momentum algebra. So, using angular momentum algebra if you evaluate the matrix element of the left hand side explicitly that is again a matter of doing little bit of algebra.

But, you find that the matrix element of left hand side vanishes, it does not mean that the left hand side of this identity is 0 it is not. It is only the matrix element in this particular case, which vanishes, which also means that the matrix element of the operator on the right side also vanishes. So, you can now use that, so that the matrix element of this part minus the matrix element of this part vanishes, which means that the matrix element of the first term is equal to the matrix element of the second term, there is a factor 2 here and a factor 4 here.

So, if you divide both sides you get this matrix element equal to twice of this, and essentially what you have is using these identities from the left hand side you have a J^2 operating on this right. So, what happens when J^2 operates on this, $|j, m\rangle$ is an Eigen state of J^2 , the Eigen value is $\hbar^2 j(j+1)$. So, that will come out and you will be left with the matrix element of V alone, likewise over here this J^2 can operate on the left and again you get $\hbar^2 j(j+1)$.

So, you get $\hbar^2 j(j+1)$ is the common factor and you have to obtain the matrix element of this V and this V . So, twice of V and then there is a factor of 2 on the right hand side, so those will cancel each other, and on the left side you get the matrix element of V on the right side you get the matrix element of this scalar operator $V \cdot J$ and J . And now you have J operating on $|m\rangle$ that is good because we know how the $|m\rangle$ Eigen states respond to the J operator.

So, this is a useful thing and this is what we need with V identified as s you are actually interested in only the z 'th component. So, you can extract that corresponding component which is of interest, you can also get this result from the Wigner eckart theorem, and this is the result that we will use in our next class. But, this result can be obtained also from the Wigner eckart theorem, and I will like to discuss that technique as well because these are powerful techniques.

And they have applications in various other spectroscopy's, not just Zeeman spectroscopy, but in several other branches of atomic spectroscopy, molecular spectroscopy or spectroscopy in condensed matter and so on. So, these are nice techniques to learn.

(Refer Slide Time: 42:16)

Wigner – Eckart Theorem

$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' || T^{(k)} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((jk) j' m' | (jk) m q)$$

$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' || T^{(k)} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((jk) j' m' | j m k q)$$

Matrix element of
the spherical
component of I.T.O.


=

Physical
part

×

Geometrical
part

CGC from: $\vec{j} + \vec{k} = \vec{j}'$



from STIAP Unit 2

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So, this is the Wigner Eckart theorem this is the matrix element of an q'th component of an irreducible tensor operator. And this is given by the product of a physical part which is contained in the reduced matrix element, and the geometrical part which involves the clebsch gordan coefficient right. So, this is a wigner eckart theorem and the clebsch gordan coefficient under consideration, comes from the coupling of j and k and what is this j, j is the angular momentum coming from this right side, and k is the angular momentum like term which comes from the rank of the irreducible tensor operator. So, this is the clebsch gordan coefficient that you would get, if you were to couple j with k to get j prime which is the angular momentum on the left side, so keep that in mind.

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$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' || T^{(k)} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((jk) j' m' | (jk) m q \rangle$$

$k=1$: vector operator \mapsto consider $T \rightarrow \vec{J}$

$$\langle \alpha' j' m' | \vec{J}_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' || \vec{J} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m q \rangle$$

for $q=0$

$$\langle \alpha' j' m' | \vec{J}_{q=0}^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' || \vec{J} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m 0 \rangle$$

$$\langle \alpha' j' m' | J_z | \alpha j m \rangle = \frac{\langle \alpha' j' || \vec{J} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m 0 \rangle$$

$$m \hbar \delta_{\alpha' \alpha} \delta_{j' j} \delta_{m' m} = \frac{\langle \alpha' j' || \vec{J} || \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m 0) ?$$

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So, this is the Wigner Eckart theorem, now k being you are dealing with the vector operator, so the rank is equal to 1. And we will consider the angular momentum itself, so we will consider we will apply the Wigner Eckart theorem to the angular momentum, so $T_k q$ is $J_k q$. So, we have written the Wigner Eckart theorem for the angular momentum operator, we have identified k equal to 1 here now, now we have q equal to 0, we will consider a particular case q can be either minus 1 or 0 or plus 1.

So, we will consider one of these which is q equal to 0, so let us take q equal to 0, so I put q equal to 0 in this Clebsch Gordon coefficient. And now I put q equal to 0 here as well, the corresponding component is the J_z , so you get the component j_z which is the one of interest. So, this is the matrix element of J_z and on the right side, you need this reduced matrix element and the Clebsch Gordon coefficient with k equal to 1 and q equal to 0.

So, this is what you want on the left side $j m$ is an Eigen state of J_z belonging to the Eigen value $m \hbar$ cross, and then from the orthogonalities of α and α' and J and j prime and m and m prime you get this form of a delta. So, the left side can be solved readily, and the right hand side you have got the product of reduced matrix element and the Clebsch Gordon coefficients. The question is how do you get this Clebsch Gordon coefficient now.

(Refer Slide Time: 44:58)

$$m\hbar\delta_{\alpha'\alpha}\delta_{j'j}\delta_{m'm} = \frac{\langle\alpha'j'|\hat{J}|\alpha j\rangle}{\sqrt{2j'+1}} \times ((j1)j'm'|j1m0\rangle)$$

We have to determine the CGC $((j1)j'm'|j1m0\rangle)$

$\vec{j} + \vec{k} = \vec{j}'$ like $\vec{i} + \vec{k} = \vec{j}$ with $k = j_2 = 1$

$k = j_2 = 1 \rightarrow$ Refer CGC Table 2³, $q = m_2 = 0$
 page 76, Condon & Shortley, TAS \therefore see column 2

$\delta_{j'j} \rightarrow (j' = j)$ i.e. $(j = j_1) \rightarrow$ see row 2

$((j_1 j_2)jm|(j_1 j_2)m_1 m_2)$ TABLE 2³. $(j_1 1 m_1 m_2 | j_1 1 j m)^*$

$j =$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\sqrt{\frac{(j_1 + m)(j_1 + m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$	$\sqrt{\frac{(j_1 - m + 1)(j_1 + m + 1)}{(2j_1 + 1)(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$
j_1	$-\sqrt{\frac{(j_1 + m)(j_1 - m + 1)}{2j_1(j_1 + 1)}}$	$\frac{m}{\sqrt{j_1(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 + m + 1)}{2j_1(j_1 + 1)}}$
$j_1 - 1$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{2j_1(2j_1 + 1)}}$	$-\sqrt{\frac{(j_1 - m)(j_1 + m)}{j_1(2j_1 + 1)}}$	$\sqrt{\frac{(j_1 + m + 1)(j_1 + m)}{2j_1(2j_1 + 1)}}$

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So, this is the clebsch gordan coefficient that you have to determine, and how would you determine that, you have to get the clebsch gordan coefficient corresponding to k equal to 1 right. So, I have sent you the tables of clebsch gordan coefficients, then we have also uploaded this at our course webpage, and from that table the tables for different values of j 2, the 1 which is relevant in our case for the present case is the one for which j 2 is equal to 1 because k is equal to 1.

So, we will take what is labeled a stable 2 in the set of tables that I have given you, so this is the table that you will find in what has been sent to you, and this is also uploaded is the course webpage. So, from this you have to find there are 3 into 3, 9 elements and one of these is what you want to use which one, so the first thing to do is to notice that q is our m 2, and this is equal to 0. So, m 2 equal to 0, so we must look at the middle column right.

The other thing you notice is that you have a delta j j prime here right, which means that j prime is equal to j and in the other case j is equal to j 1. So, we must use the middle row right, so we must use the matrix element which appears at the intersection of the middle row and the middle column. So, this is the matrix element to be determined, so all we have to do is to plug in the values of m and j 1 over here and we will get this clebsch gordan coefficient which can be inserted here, and then you can use this expression along with the reduced matrix element.

(Refer Slide Time: 47:07)

$$m\hbar\delta_{\alpha'\alpha}\delta_{j'j}\delta_{m'm} = \frac{\langle\alpha'j'|\hat{J}|\alpha j\rangle}{\sqrt{2j'+1}} \times ((j1)j'm'|j1m0\rangle)$$

We have to determine the CGC $((j1)j'm'|j1m0\rangle)$

$\vec{j} + \vec{k} = \vec{j}'$ like $\vec{i} + \vec{j} = \vec{j}$ with $k = j_2 = 1$
 $((j_1j_2)jm|(j_1j_2)m_1m_2)$

TABLE 2*. $(j_1 1 m_1 m_2 | j_1 1 j m)^*$

$j =$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\sqrt{\frac{(j_1 + m)(j_1 + m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$	$\sqrt{\frac{(j_1 - m + 1)(j_1 + m + 1)}{(2j_1 + 1)(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$
j_1	$-\sqrt{\frac{(j_1 + m)(j_1 - m + 1)}{2j_1(j_1 + 1)}}$	$\frac{m}{\sqrt{j_1(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 + m + 1)}{2j_1(j_1 + 1)}}$
$j_1 - 1$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{2j_1(2j_1 + 1)}}$	$-\sqrt{\frac{(j_1 - m)(j_1 + m)}{j_1(2j_1 + 1)}}$	$\sqrt{\frac{(j_1 + m + 1)(j_1 + m)}{2j_1(2j_1 + 1)}}$

$((j_1j_2)jm|(j_1j_2)m_1m_2) = \frac{m}{\sqrt{j_1(j_1 + 1)}} \quad ((j1)j'm'|j1m0) = \frac{m'}{\sqrt{j(j + 1)}}$

$$m\hbar\delta_{\alpha'\alpha}\delta_{j'j}\delta_{m'm} = \frac{\langle\alpha'j'|\hat{J}|\alpha j\rangle}{\sqrt{2j'+1}} \times \frac{m'}{\sqrt{j(j + 1)}}$$

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So, this is what you have to determine this is the intersection of the middle column and the middle row, and you have to determine m over j 1 root of j 1 into j 1 plus 1. But, in our case we have instead of j m we have j prime m prime, so this is just bookkeeping and the Condon and shortly notation has to be translated into our notation, for the present case. So, our clebsch gordan coefficient is m prime over root of j into j plus 1, so this is the coefficient that must be plugged in.

So, this is what you get alright, so this is the left hand side which is m h cross into these chronicle deltas, then you have got the reduced matrix element and the clebsch gordan coefficient which is now evaluated explicitly using the Condon and shortly table, and then this is m prime over root j into j plus 1.

(Refer Slide Time: 48:09)

$$m\hbar\delta_{\alpha'\alpha}\delta_{jj'}\delta_{m'm} = \frac{\langle\alpha'j'|\vec{J}|\alpha j\rangle}{\sqrt{2j'+1}} \times \frac{m'}{\sqrt{j(j+1)}}$$

$$\langle\alpha'j'|\vec{J}|\alpha j\rangle = \sqrt{j(j+1)}\hbar\delta_{\alpha'\alpha}\delta_{jj'} \times \sqrt{2j+1}$$


Eq.11.20/p673/ The theory of Atomic Structure & Spectra
 R.D.Cowan

$$\langle\alpha'j'|\vec{J}|\alpha j\rangle = \sqrt{j(j+1)}\hbar\delta_{\alpha'\alpha}\delta_{jj'} \rightarrow \text{see Eq.A4.53 in}$$

Physics of Atoms & Molecules by Bransden & Joachain

difference: $\sqrt{2j+1}$
 → this can be absorbed in the 'definition' of the reduced matrix element.

See the remark at the top of page 1008 of Appendix 4 in Bransden & Joachain's book.



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So, this allows us to write the reduced matrix element, so you take this term and this term on the left side, now this m and this m' has to be equal there is a $\delta_{m'm}$ over here. So, this reduced matrix element must be equal to root of j into j plus 1 coming from here, \hbar cross into these two Kronecker deltas coming from here, and the root $2j$ plus 1 coming from here, when you do the cross multiplication right. So, this is what you must get, and if you see Cowan's book the theory of atomic structure and spectra, this is precisely the result that you will find.

However, if you see Bransden and Joachain equation 453 you find this result which is; obviously, different what is a difference, the root $2j$ plus 1 is different. Because, it can always be observed in the reduced matrix element, if you remember when we discussed the Wigner-Eckart theorem, we had mentioned that the Wigner-Eckart theorem is both a theorem and the definition, it is the definition of the reduced matrix element. And it is possible to incorporate the root $2j$ plus 1 in the definition of the reduced matrix element. So, you can include this and then the two results are completely in conformity with each other there is no contradiction between them.

(Refer Slide Time: 49:44)

$$\begin{aligned}
 \langle \alpha' j' m' | \vec{J}_q^{(k-1)} | \alpha j m \rangle &= \frac{\langle \alpha' j' | \vec{J}^{(k-1)} | \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m q) \\
 \langle \alpha' j' m' | \vec{V}_q^{(k-1)} | \alpha j m \rangle &= \frac{\langle \alpha' j' | \vec{V}^{(k-1)} | \alpha j \rangle}{\sqrt{2j'+1}} \times ((j1) j' m' | j1 m q) \\
 \text{Ratio: } \frac{\langle \alpha' j' m' | \vec{V}_q^{(k-1)} | \alpha j m \rangle}{\langle \alpha' j' m' | \vec{J}_q^{(k-1)} | \alpha j m \rangle} &= \frac{\langle \alpha' j' | \vec{V}^{(k-1)} | \alpha j \rangle}{\langle \alpha' j' | \vec{J}^{(k-1)} | \alpha j \rangle} \\
 \langle \alpha' j' m' | \vec{V}_q^{(k-1)} | \alpha j m \rangle &= \frac{\langle \alpha' j' | \vec{V}^{(k-1)} | \alpha j \rangle}{\langle \alpha' j' | \vec{J}^{(k-1)} | \alpha j \rangle} \langle \alpha' j' m' | \vec{J}_q^{(k-1)} | \alpha j m \rangle \\
 &= C \langle \alpha' j' m' | \vec{J}_q^{(k-1)} | \alpha j m \rangle
 \end{aligned}$$

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So, we will use this result and this is a matrix element that we were interested in determining, which is the product of the reduced matrix element, and the clebsch-gordan coefficient, corresponding to k equal to 1. Now, this is what we did for the angular momentum, what we want is for an arbitrary vector this we get from the Wigner eckart theorem, applied to the vector operator v. And now, if you take the ratio of these two that the ratio is an completely equal to the ratio of these two reduced matrix element.

And notice that any further consideration of this result will be independent of the definition of the reduced matrix element because in this ratio the root 2 j plus 1 would go off, so there is no ambiguity coming because of that. So, now, you have got this ratio which you have found, so now, the matrix element of the q'th component of this vector operator is given by this factor here right, this is the ratio which is some constant. And then there is the remaining matrix element to be determined, but this is the matrix element of the angular momentum operator.

(Refer Slide Time: 51:14)

$$\begin{aligned}
 \langle \alpha' j' m' | \vec{V}_q^{(k=1)} | \alpha j m \rangle &= \frac{\langle \alpha' j' | \vec{V}_q^{(k=1)} | \alpha j \rangle}{\langle \alpha' j' | \vec{J}_q^{(k=1)} | \alpha j \rangle} \langle \alpha' j' m' | \vec{J}_q^{(k=1)} | \alpha j m \rangle \\
 &= C \langle \alpha' j' m' | \vec{J}_q^{(k=1)} | \alpha j m \rangle \\
 \langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle &= \sum_{m'=-j}^j \langle \alpha j m | \vec{V} | \alpha j m' \rangle \cdot \langle \alpha j m' | \vec{J} | \alpha j m \rangle \\
 \langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle &= \sum_{m'=-j}^j C \langle \alpha j m | \vec{J} | \alpha j m' \rangle \cdot \langle \alpha j m' | \vec{J} | \alpha j m \rangle \\
 \langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle &= C \langle \alpha j m | J^2 | \alpha j m \rangle = C \hbar^2 j(j+1) \\
 \text{C is independent of the m quantum numbers} &\Rightarrow C = \frac{\langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle}{\hbar^2 j(j+1)} \\
 \langle \alpha j m' | \vec{V}_q^{(k=1)} | \alpha j m \rangle &= C \langle \alpha j m' | \vec{J}_q^{(k=1)} | \alpha j m \rangle \\
 \langle \alpha j m' | \vec{V}_q^{(k=1)} | \alpha j m \rangle &= \frac{\langle \alpha j m' | \vec{V} \cdot \vec{J} | \alpha j m \rangle}{\hbar^2 j(j+1)} \langle \alpha j m' | \vec{J}_q^{(k=1)} | \alpha j m \rangle
 \end{aligned}$$

"PROJECTION THEOREM" → Sakurai / Modern Quantum Mechanics / Eq.3.10.40
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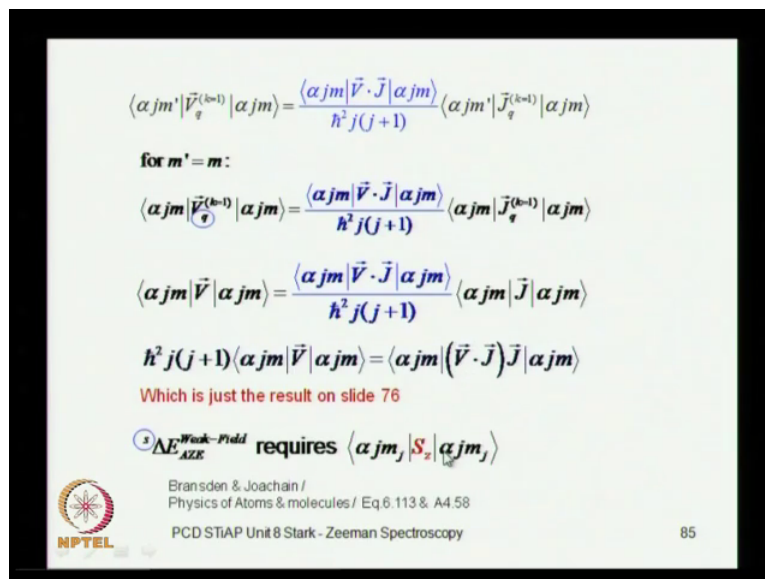
So, this is the constant C which we have used, and now if you look at $\vec{V} \cdot \vec{J}$ because you had the matrix element of $\vec{V} \cdot \vec{J}$ right that is operator which we had to consider. So, now, you have the $\vec{V} \cdot \vec{J}$ operator whose matrix element, and you can sandwich the unit operator in between, so sum over m prime going from minus j to plus j $\langle \alpha j m' | \alpha j m \rangle$ gives you the unit operator. So, I have sandwiched the resolution of the unity in between, and then take the dot product of these two.

So, this is the matrix element of the dot product of two vectors, and this comes exploiting this resolution of unity in terms of the dot product on the matrix element of the corresponding operators. So, using this, this is the matrix element of \vec{V} which we know is a matrix element of \vec{J} scaled by this factor C, and now this $\alpha \cdot J$ this is the term that you want to determine, which we know over here is $C \alpha \cdot J$. So, we take particular values we drop the primes here.

So, when α' is equal to α and j' is equal to j you take $\alpha j m | \vec{V} \cdot \vec{J} | \alpha j m$ in this case, so you can always take a special case of that to get C. Because, the value of C does not depend on the geometry, it does not depend on the azimuthal quantum numbers m. So, you take a particular case and for this case, you have the same relation which holds good, now J^2 operates on $j m$ giving you an Eigen value $\hbar^2 j(j+1)$.

So, this give us a value of C explicitly in terms of this matrix element divided by h cross square j into j plus 1. So, now, C being independent of the m quantum numbers we can exploit this, and we can use this value of C over here because we are looking at the matrix element of the q'th component of V. And now you have got the C, but the C is now determined explicitly in terms of this V dot J. So, this result is called as projection theorem in quantum mechanics, and you will find it in sakurai's book or in many other books, so this is the projection theorem.

(Refer Slide Time: 54:00)



$$\langle \alpha j m' | \vec{V}_q^{(k=1)} | \alpha j m \rangle = \frac{\langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle}{\hbar^2 j(j+1)} \langle \alpha j m' | \vec{J}_q^{(k=1)} | \alpha j m \rangle$$

for $m' = m$:

$$\langle \alpha j m | \vec{V}_q^{(k=1)} | \alpha j m \rangle = \frac{\langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle}{\hbar^2 j(j+1)} \langle \alpha j m | \vec{J}_q^{(k=1)} | \alpha j m \rangle$$

$$\langle \alpha j m | \vec{V} | \alpha j m \rangle = \frac{\langle \alpha j m | \vec{V} \cdot \vec{J} | \alpha j m \rangle}{\hbar^2 j(j+1)} \langle \alpha j m | \vec{J} | \alpha j m \rangle$$

$$\hbar^2 j(j+1) \langle \alpha j m | \vec{V} | \alpha j m \rangle = \langle \alpha j m | (\vec{V} \cdot \vec{J}) \vec{J} | \alpha j m \rangle$$

Which is just the result on slide 76

$\Delta E_{\text{Zeeman}}^{\text{Weak-Field}}$ requires $\langle \alpha j m_j | S_z | \alpha j m_j \rangle$

Bransden & Joachain /
Physics of Atoms & molecules / Eq.6.113 & A4.58
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And using the projection theorem, if you now consider m prime equal to m this is just a special case of the projection theorem for m prime equal to m. Now, this is a relation which holds good for every component q, so if add the three components and multiply by the corresponding unit vectors e x e y e z that relation will hold good for vector as well right. So, you have got this matrix element of the q'th component this relationship can be generalized, write the matrix element of the vector operator itself.

And this is just the result that we had got in earlier using the identities for the vector operators, but now we got the same result using the Wigner eckart theorem. So, this is a result that we have got, and now we are interested in this because we need the matrix element of the z component of S and our body was that since the operate the opponent over here, which is this ket is not an Eigen state of S z we had to figure out how to proceed.

So, we have found a result which is going to be useful in getting this particular matrix element, and we got this matrix element using two alternative procedures, one using vector identities, and the second using the Wigner eckart theorem. So, this is what we will do in the next class which is to use this result, which comes out of the theorem that I just mentioned, the projection theorem. And using this result, we will figure out how to get the weak field Zeeman effect, because we need the matrix element of S_z over here. Questions.

Student: The will contain s_z again will contain S_z will be acting on the $j m_j$.

We will handle it, but this is may able to result which is going to be useful. So, in the next class we will get the complete expansion, any question?

Thank you.