# Notes for Quantum Mechanics

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{2004, 11, 23, 11, 31, 28.3195952}
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# Lecture 30
# The Zeeman effect as a review of perturbation theory and CG coefs

If one puts an atom in a magnetic field it will change the energy levels. This is called the Zeeman effect. The change or perturbation in the hamiltonian is $-\bar{\mu}\cdot\vec{B}$. Now since we have both orbital angular momentum and spin - both will contribute to the magnetic moment so

$\hat{H}' = -(\bar{\mu}_L + \bar{\mu}_S)\cdot\vec{B}.$

We will assume it is small and calculation the change in energy using perturbation theory, i.e. $E_n' = \langle\hat{H}'\rangle_{nn} = \langle | \hat{H}' | \rangle$. Now one of the questions that comes about is what eigenfunctions (*e.g.* $|j, m_j\rangle$ or $|m_l\, m_s\rangle$) should be used. The answer is that we should use the set that are the "best" ones. We will see what this means in a moment.

Now if you remember $\bar{\mu}_S = \frac{-e}{mc}\hat{S}$ and $\bar{\mu}_L = \frac{-e}{2\,mc}\hat{L}$. The spin magnetic moment is different in form by a factor of two because of the anomalous magnetic moment (a "g factor" of 2) . Lets let the B field be in the z direction so that

$\hat{H}' = \frac{e}{mc}(\hat{L}_z + 2\hat{S}_z)B_z = \frac{eB_z}{mc}(\hat{J}_z + \hat{S}_z)$

Now since our "original Hamiltonian" in this case was $\hat{H}_0 + \hat{H}_{SO}$ we will use the $|n, l, s, j, m_j\rangle$ as the relevant "best kets" to use. Later we will see a case where the $|m_l\, m_s\rangle$ states are better

Perturbation theory tells us to figure out $\langle \text{nlsjm} | \hat{H}' | \text{nlsjm}_j\rangle = \frac{eB_z}{mc}\langle \text{nlsjm}_j | \hat{J}_z + \hat{S}_z | \text{nlsjm}_j\rangle =$

$= \frac{eB_z}{mc}\langle \text{nlsjm}_j | \hat{J}_z + \hat{S}_z | \text{nlsjm}_j\rangle = \frac{eB_z}{mc}[\hbar m_j + \langle \text{nlsjm}_j | \hat{S}_z | \text{nlsjm}_j\rangle]$ where I have been careful to label the $m_j$

But now how do we figure out $\langle \text{nlsjm}_j | \hat{S}_z | \text{nlsjm}_j\rangle$ since $|\text{nlsjm}_j\rangle$ is not an eigenket of $\hat{S}_z$ ???

We know how to do this. We can expand $|\text{nlsjm}_j\rangle$ in terms of $|\text{nls}\, m_l\, m_s\rangle$ using the C-G coefficients.

Lets use a notation where CG(ls; j $m_j$, $m_l$ $m_s$) stands for the CG coefficient crisping l⊗s e.g. $1 \otimes \frac{1}{2}$ (note that in regular notation CG(ls; j $m_j$, $m_l$ $m_s$)=$\langle \text{nlsm}_l\, m_s | \text{nlsjm}_j\rangle = \langle \text{nlsjm}_j | \text{nlsm}_l\, m_s\rangle$ )

$$|\text{nlsjm}_j\rangle = \sum_{m_l}\sum_{m_s} |\text{nls}\, m_l\, m_s\rangle\langle \text{nlsm}_l\, m_s | \text{nlsjm}_j\rangle = \sum_{m_l}\sum_{m_s\, m_{j=m_l+m_s}} \text{CG(ls; j}\, m_j, m_l\ m_s)\ |\text{nls}\, m_l\, m_s\rangle$$

remember $m_j = m_l + m_s$

$$\langle \text{nlsjm}_j | \hat{S}_z | \text{nlsjm}_j\rangle = \sum_{m_l}\sum_{m_s\, m_{j=m_l+m_s}}\sum_{m_l'}\sum_{m_s'\, m_{j'=m_l'+m_s'}} \text{CG(ls; j}\, m_j, m_l'\ m_s')\ \text{CG(ls; j}\, m_j, m_l\ m_s)\langle \text{nls}\, m_l'\ m_s' | \hat{S}_z | \text{nls}\, m_l\ m_s\rangle =$$

$$\sum_{m_l}\sum_{m_s\, m_{j=m_l+m_s}}\sum_{m_l'}\sum_{m_s'\, m_{j'=m_l'+m_s'}} \hbar m_s \text{CG(ls; j}\, m_j, m_l\ m_s)\ \text{CG(ls; j}\, m_j, m_l'\ m_s')\langle \text{nls}\, m_l'\ m_s' | \text{nls}\, m_l\ m_s\rangle =$$

$$\sum_{m_l}\sum_{m_s\, m_{j=m_l+m_s}}\sum_{m_l'}\sum_{m_s'\, m_{j'=m_l'+m_s'}} \hbar m_s \text{CG(ls; j}\, m_j, m_l\ m_s)\ \text{CG(ls; j}\, m_j, m_l'\ m_s')\delta_{m_l' m_l}\delta_{m_s' m_s} =$$

$$\sum_{m_l}\sum_{m_s\, m_{j=m_l+m_s}} \hbar m_s \text{CG(ls; j}\, m_j, m_l\ m_s)^2$$

[Aside for graduate school: Using something which we don't know called the Wigner-Eckart theorem we will find that for $s = \frac{1}{2}$, i.e. $j = l \pm \frac{1}{2}$ we get $\langle \text{nlsjm}_j | \hat{S}_z | \text{nlsjm}_j\rangle = \pm\frac{m_j\hbar}{2l+1}$ we can use this to check the answer we get]


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Now let a choose a particular case. For example lets let l=2, then $j = \frac{5}{2}$ or $\frac{3}{2}$. Lets choose $j = \frac{3}{2}$ Now also choose $m_j = \frac{1}{2}$.

[Aside: The correct answer from the Wigner -Eckart theorem is $-\frac{1}{2}\hbar/(2\cdot 2+1) = -\frac{1}{10}\hbar$. The minus sign comes in because $j = l - \frac{1}{2}$.]

Now from our work we know that

$\langle \text{nlsjm}_j \mid \hat{S}_z \mid \text{nlsjm}_j\rangle = \sum_{m_l}\sum_{\substack{m_s \\ m_j = m_l + m_s}} \hbar \text{m}_s \text{CG}(\text{ls; j } m_j, m_l\ m_s)^2$. We have chosen $j = \frac{3}{2}$ $m_j = \frac{1}{2}$. Lets see what values of $m_l$ and $m_s$ can be used. We have two possibilities. Either $m_l$=1 and $m_s = \frac{-1}{2}$ or $m_l$=0 and $m_s = \frac{1}{2}$

It may be easier to expand the ket first

$\mid n,\ l = 2,\ s = \frac{1}{2},\ j = \frac{3}{2},\ m_j = \frac{1}{2}\rangle = \sqrt{\frac{3}{5}} \mid n, l = 2,\ s = \frac{1}{2}, m_l = 1, m_s = \frac{-1}{2}\rangle - \sqrt{\frac{2}{5}} \mid n, l = 2, s = \frac{1}{2},\ m_l = 0, m_s = \frac{1}{2}\rangle$

So we can write this expansion out

$\langle n\, 2\, \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2} \mid \hat{S}_z \mid n\, 2\, \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\rangle = \hbar\, \frac{1}{2}\left(-\sqrt{\frac{2}{5}}\right)^2 - \frac{1}{2}\left(\sqrt{\frac{3}{5}}\right)^2 = \frac{1}{2}\ \frac{2}{5} - \frac{1}{2}\ \frac{3}{5} = \frac{-1}{10}\hbar$ and the answer checks!

So finally

$\langle \text{nlsjm} \mid \hat{H}' \mid \text{nlsjm}_j\rangle = \frac{e\hbar B_z}{mc}[m_j + \sum_{m_l}\sum_{\substack{m_s \\ m_j = m_l + m_s}} m_s \text{CG}(\text{ls; j } m_j, m_l\ m_s)^2$

So the answer for l=2 $s = \frac{1}{2}$ $j = \frac{3}{2}$ $m_j = \frac{1}{2}$ is

$\langle \hat{H}' \rangle = \frac{-1}{10}\ \frac{e\hbar B_z}{mc}$ Now this number is not exact since the eigenkets $\mid \text{nlsjm}_j\rangle$ are not eigenkets of $\hat{S}_z$ but it is the first order correction to the energy. (In fact, its may be better to think of it as a pseudo-second order correction since we already made an approx in the case of S-O coupling) One hopes that the next order is much smaller.

**The Strong field zeeman effect**

So far we have assumed that the Zeeman effect is smaller than the spin-orbit coupling. Suppose we have a very strong field where the Zeeman effect becomes much larger than the S-O coupling. Then its better to treat the eigenkets we use as the eigenkets best suited for .

$\hat{H}_0 + \hat{H}_{\text{Zeeman}}$ and then treat $\hat{H}_{\text{SO}}$ as the perturbation $\hat{H}'$

Now since the eigenkets $\mid \text{nlsjm}_j\rangle$ or $\mid \text{nlsm}_l\, m_s\rangle$ are eigenkets for $\hat{H}_0$ but only the $\mid \text{nlsm}_l\, m_s\rangle$ are eigenkets of $\hat{H}_{\text{Zeeman}}$ we will choose $\mid \text{nlsm}_l\, m_s\rangle$. (In this case, we have not made an approx. $\hat{H}_{\text{Zeeman}}$ has no $\frac{1}{r^3}$ term to mess us up so writing out the Hamiltonian

$[\hat{H}_0 + \frac{eB_z}{mc}(\hat{L}_z + 2\hat{S}_z)] \mid \text{nlsm}_l\, m_s\rangle = \text{E} \mid \text{nlsm}_l\, m_s\rangle$

$E_{n\, m_l\, m_s} = -\frac{Z^2 \mathcal{R}}{n^2} + \frac{e\hbar B_z}{mc}(m_l + 2\, m_s)$

The Correction from the perturbation $\hat{H}_{\text{SO}} = \frac{e^2}{4\, m^2\, c^2\, r^3}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$ | is now

$\langle \text{nlsm}_l\, m_s \mid \hat{H}' \mid \text{nlsm}_l\, m_s\rangle = \frac{e^2}{4\, m^2\, c^2}\langle \text{nlsm}_l\, m_s \mid \frac{e^2}{4\, m^2\, c^2\, r^3}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \mid \text{nlsm}_l\, m_s\rangle =$

$\frac{e^2}{4\, m^2\, c^2}\langle \text{nlsm}_l\, m_s \mid \frac{1}{r^3}\left(\hat{J}^2 - l(l+1)\hbar^2 - \frac{3}{4}\hbar^2\right) \mid \text{nlsm}_l\, m_s\rangle$


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and if we split up the radial and angular parts we get

$$\frac{e^2}{4m^2c^2}\left\langle \text{nlsm}_l\, m_s \,\middle|\, \frac{1}{r^3} \,\middle|\, \text{nlsm}_l\, m_s\right\rangle\left[\left\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\right\rangle - l(l+1)\hbar^2 - \frac{3}{4}\hbar^2\right]=$$

We recall from QM28 that

$$\left\langle \text{nlsjm} \,\middle|\, \frac{1}{r^3} \,\middle|\, \text{nlsjm}\right\rangle = \int_0^\infty R^*{}_{\text{nl}}(r)\, \frac{1}{r^3}\, R_{\text{nl}}(r)\, r^2\, dr = \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)\, n^3\, a_0{}^3}$$ so we have

$$\left\langle \text{nlsm}_l\, m_s \mid \hat{H}' \mid \text{nlsm}_l\, m_s\right\rangle = \frac{e^2\hbar^2}{4m^2c^2}\, \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)\, n^3\, a_0{}^3}\left[\frac{1}{\hbar^2}\left\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\right\rangle - l(l+1) - \frac{3}{4}\right]=$$

$$\frac{E_n\,\alpha^2}{2n}\, \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)}\left[\frac{1}{\hbar^2}\left\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\right\rangle - l(l+1) - \frac{3}{4}\right]$$

note that : $\frac{e^2\hbar^2}{4m^2c^2n^3a_0{}^3} = \frac{\mathcal{R}\alpha^2}{2n^3} = \frac{E_n\,\alpha^2}{2n}$

Now $\mid \text{nlsm}_l\, m_s\rangle$ is not an eigenket of $\hat{J}^2$ so once again, we had better expand

$$\mid \text{nlsm}_l\, m_s\rangle = \sum_j \sum_{m_j} \mid \text{nlsjm}_j\rangle\langle \text{nlsjm}_j \mid \text{nlsm}_l\, m_s\rangle = \sum_j \sum_{m_j} \text{CG(ls; j}\, m_j, m_l\ m_s) \mid \text{nlsjm}_j\rangle$$
$$m_j = m_l + m_s$$

now there is no sum of $m_j$ because $m_{j=m_l+m_s}$ and $m_l$ and $m_s$ are given

$$\frac{1}{\hbar^2}\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\rangle = \frac{1}{\hbar^2}\sum_{j'}\ \sum_{j}\ \text{CG(ls; j'}\, m_j', m_l\ m_s)\text{CG(ls; j}\, m_j, m_l\ m_s)\left\langle \text{nlsjm}_j \,\middle|\, \hat{J}^2 \,\middle|\, \text{nlsjm}_j\right\rangle$$
$$m_{j'=m_l'+m_{s'}} \qquad m_{j=m_l+m_s}$$

$$= \sum_j \text{CG(ls; j}\, m_j, m_l\ m_s)^2 \text{j(j+1)}$$
$$m_{j=m_l+m_s}$$

Once again lets pick l=2 so we know that l=2, $s = \frac{1}{2}$ we now need to pick in this case $m_l$ and $m_s$

Lets pick $m_l$= -1 $m_s = \frac{1}{2}$ Now this means that $m_j = -1 + \frac{1}{2} = \frac{-1}{2}$ j can be either $\frac{5}{2}$ or $\frac{3}{2}$

It might be easier to just think of expanding the ket first

$$\mid n\ l = 2\ s = \frac{1}{2}\ m_l = -1\ m_s = \frac{1}{2}\rangle = \sqrt{\frac{2}{5}}\ \mid n\, l = 2\, s = \frac{1}{2}\ j = \frac{5}{2}\ m_j = \frac{-1}{2}\rangle - \sqrt{\frac{3}{5}}\ \mid n\, l = 2\, s = \frac{1}{2}\ j = \frac{3}{2}\ m_j = \frac{-1}{2}\rangle$$

$$\frac{1}{\hbar^2}\left\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\right\rangle = \left(\sqrt{\frac{2}{5}}\right)^2 \frac{5}{2}\left(\frac{5}{2}+1\right) + \left(-\sqrt{\frac{3}{5}}\right)^2 \frac{3}{2}\left(\frac{3}{2}+1\right) = \frac{2}{5}\,\frac{35}{4} + \frac{3}{5}\,\frac{15}{4} = \frac{115}{20} = \frac{23}{4}$$

so finally

$$\left\langle \text{nlsm}_l\, m_s \mid \hat{H}' \mid \text{nlsm}_l\, m_s\right\rangle = \frac{E_n\,\alpha^2}{2n}\, \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)}\left[\frac{1}{\hbar^2}\left\langle \text{nlsm}_l\, m_s \mid \hat{J}^2 \mid \text{nlsm}_l\, m_s\right\rangle - l(l+1) - \frac{3}{4}\right]$$

$$= \frac{E_n\,\alpha^2}{2n}\, \frac{1}{2\left(2+\frac{1}{2}\right)(2+1)}\left[\frac{23}{4} - 2\,(2+1) - \frac{3}{4}\right] = \frac{E_n\,\alpha^2}{2n}\, \frac{1}{15}\,[5-6] = -\frac{E_n\,\alpha^2}{2n}\, \frac{1}{15}$$


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