Notes for Quantum Mechanics

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Lecture 28
Corrections to the Hydrogen atom energy levels
Spin-Orbit coupling and Relativistic Effects

In the early days people thought the sun went around the earth. In essence they were correct. In fact from the point of view of the center of mass, they both go around each other like two dancers - Since the sun is so much heavier of course it makes more sense to think that the sun is at the center with the earth moving around it; but from the point of view of the earth, the sun goes around the earth. In the same way we can think of a hydrogen atom as a proton going around an electron. A moving charge is a current and creates a magnetic field in the vicinity of the electron. This wouldn't do anything however we found that electrons have spin and therefore a magnetic moment. So there must be an *additional term* in the hamiltonian which must look something like $-\vec{\mu}\cdot\vec{B}$

We had figured out before that the magnetic moment of the electron was $\frac{-e}{\mathrm{mc}}\hat{S}$ (after the factor of 2 which if you remember was the anomalous magnetic moment)

Now the magnetic field in the middle of a current loop from the Biot-Savart law is
$\mathrm{B}=\frac{2\pi}{\mathrm{cr}}\,I$ where I is the currect due to the proton. Now $\mathrm{I}=\mathrm{e}/\tau$ where tau is the period of the orbit.

Now $L = \mathrm{mvr} = \mathrm{mr}\,\frac{2\pi\mathrm{r}}{\tau}$ So $\mathrm{I} = \frac{\mathrm{eL}}{2\pi\mathrm{mr}^2}$ and $B = \frac{e}{\mathrm{cmr}^3}\mathrm{L}$

and we set the new part of the hamiltonian which we will call $H_{\mathrm{SO}} = \frac{e^2}{m^2 c^2 r^3}\hat{L}\cdot\hat{S}$

The SO refers to spin-orbit. Now this is not completely correct since we worked in the rest frame of the electron, which is an accelerating reference frame. Correcting for this (Thomas precession) gives

$$\hat{H}_{\mathrm{SO}} = \frac{e^2}{2\,m^2 c^2 r^3}\hat{L}\cdot\hat{S}$$

We are working with they hydrogen atom. The hamiltonian is

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2\,m} - \frac{\mathrm{Ze}^2}{r} = \frac{1}{2\,m}\left(\hat{p}_r{}^2 + \frac{\hat{\boldsymbol{L}}^2}{r^2}\right) - \frac{\mathrm{Ze}^2}{r} \qquad \text{where} \qquad (\hat{p}_r{}^2) = -\hbar^2\left[\frac{1}{r}\,\frac{d}{\mathrm{dr}}\,r\right]^2 = -\hbar^2\,\frac{1}{r}\,\frac{d^2}{\mathrm{dr}^2}\mathrm{r}$$

The energy levels are $E_n = -\,|\,E_n\,| = -\frac{Z^2\,\mathcal{R}}{n^2}$

and the eigenstates are $\langle\vec{r}|\mathrm{nlm}\rangle = \langle \mathrm{r},\theta,\phi|\mathrm{nlm}\rangle = R_{\mathrm{nl}}(r)Y_l{}^m(\theta,\ \phi)$ (we will just leave things in terms of R_{nl} instead of writing out the Laguerre polynomials)

We would now like to calculate the corrections to the energy due to $\hat{H}_{\mathrm{SO}}$.We will use perturbation theory!

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$E_n^{(1)}=\hat{H}_{nn}'==\langle nlm|\hat{H}_{SO}|nlm\rangle$

The beauty of this was for the hamiltonian $\hat{H}_0$, was that all the angular dependence was in the $\hat{\boldsymbol{L}}^2$ term. Won't the $\hat{H}_{SO}$ term mess things up? Yes it will. In addition we will have to bring in spin. How do we do all this?

First we had better define a new angular momentum which is the sum of the spin and orbital angular momentum $\hat{J} = \hat{L} + \hat{S}$. Perhaps this is a new operator which commutes with the new Hamiltonian $(\hat{H}_0+\hat{H}_{SO})$ and we can find eigenfunction of $\hat{J}^2$ and $\hat{J}_z$ which must give us the angular *and* spin dependent eigenfunctions. We will return to this in a moment.

Lets now go ahead on use perturbation theory.

$E_n^{(1)}=\hat{H}_{nn}' = \int_0^\infty r^2 dr \int d\Omega\, R_{nl}(r) Y_l^m(\theta,\ \phi) \frac{e^2}{2 m^2 c^2 r^3} \hat{L}\cdot\hat{S}\, R_{nl}(r) Y_l^m(\theta,\ \phi)$

Now L has derivatives of θ and ϕ so we can write

$E_n^{(1)}=\frac{e^2}{2 m^2 c^2}[\int_0^\infty R_{nl}(r) \frac{1}{r^3}\ R_{nl}(r)\, r^2 dr][\int Y_l^m(\theta,\ \phi)\hat{L}\cdot\hat{S} Y_l^m(\theta,\ \phi) d\Omega]$

First lets do the r term

$\langle\, nlsjm \,|\, \frac{1}{r^3}\, |nlsjm\rangle = \int_0^\infty R^*{}_{nl}(r)\, \frac{1}{r^3}\, R_{nl}(r)\, r^2\, dr\ = \frac{1}{l(l+\frac{1}{2})(l+1)\, n^3\, a_0{}^3}$ and I simply set $f(r) = f\ = \frac{1}{l(l+\frac{1}{2})(l+1)\, n^3\, a_0{}^3}$

Now let me just tell you that in the position representation we can calculate the following - the third of which I used above.

$\langle nlsjm \,|\, \frac{1}{r}\, |nlsjm\rangle = \int_0^\infty R^*{}_{nl}(r)\, \frac{1}{r}\, R_{nl}(r)\, r^2\, dr = \frac{1}{n^2\, a_0}$

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

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

Aside:

As an example in our particular case for n=2 and l=1 and picking $j = \frac{3}{2}$ $m_j = \frac{3}{2}$ and getting from lecture 26

$|\frac{3}{2}\ \frac{1}{2}\rangle \doteq \sqrt{\frac{1}{3}}\, Y_1{}^1\, |-\rangle\ + \sqrt{\frac{2}{3}}\, Y_1{}^0\, |+\rangle$

Now lets write down the R_{21} piece: $\varphi_{21\,m}\ = R_{21}\, Y_1{}^m = \frac{1}{\sqrt{3}\ (2\, a_0)^{3/2}}\ \frac{r}{a_0}\ e^{-r/a_0}\ Y_1{}^m$

The full wave function becomes

$|\frac{3}{2}\ \frac{1}{2}\rangle \doteq\ \frac{1}{\sqrt{3}\ (2\, a_0)^{3/2}}\ \frac{r}{a_0}\ e^{-r/a_0}[\ \sqrt{\frac{1}{3}}\, Y_1{}^1\, |-\rangle\ + \sqrt{\frac{2}{3}}\, Y_1{}^0\, |+\rangle\ ]$

$\langle n = 2\, l = 1\ s = \frac{1}{2}\ j\ = \frac{3}{2}\ m = \frac{1}{2}\ |\ \frac{1}{r^k}\ |nlsjm\rangle =$

$\int d^3 r\ \frac{1}{\sqrt{3}\ (2\, a_0)^{3/2}}\ \frac{r}{a_0}\ e^{-r/a_0}\left(\sqrt{\frac{1}{3}}\, Y_1{}^1\, \langle -\ |\ + \sqrt{\frac{2}{3}}\ Y_1{}^0\, \langle +\ |\rangle\right) \frac{1}{r^k}\ \frac{1}{\sqrt{3}\ (2\, a_0)^{3/2}}\ \frac{r}{a_0}\ e^{-r/a_0}\ \left(\sqrt{\frac{1}{3}}\, Y_1{}^1\, |-\rangle\ + \sqrt{\frac{2}{3}}\ Y_1{}^0\, |+\rangle\right)$

$= \frac{1}{3\,(2\, a_0)^3}\ \frac{1}{a_0{}^2} \int d^3 r\, r^2\ \frac{1}{r^k}\ e^{-2\, r/a_0}\ \left(\frac{1}{3}\ |\ (Y_1{}^1\ |)^2\ + \frac{2}{3}\ |\ Y_1{}^0\ |^2\right) = \ = \frac{1}{24\, a_0{}^5} \int d r\, r^4\ \frac{1}{r^k}\ e^{-2\, r/a_0}$

for k=1

$\frac{1}{24\, a_0{}^5} \int_0^\infty d r\, r^3\, e^{-2\, r/a_0} = \frac{1}{24\, a_0{}^5}\ \frac{3\, a_0{}^4}{8} = \frac{1}{64\, a_0}$ (constant off by 16??)

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Integrate[$r^3 E^{-2 r/a}$, r]

$$-\frac{1}{8} a e^{-\frac{2r}{a}} (3 a^3 + 6 r a^2 + 6 r^2 a + 4 r^3)$$

remember $\langle \vec{r} | \mathrm{nlm} \rangle = \langle r, \theta, \phi | \mathrm{nlm} \rangle = R_{\mathrm{nl}}(r)\, Y_l^m(\theta, \phi)$

we have taken care of the $R_{\mathrm{nl}}(r)$ so we just have to worry about $\langle\theta,\phi|\mathrm{lm}\rangle = Y_l^m(\theta, \phi)$

- OK -Lets attack the $\hat{L}\cdot\hat{S}$ term.

Now $\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\cdot\hat{S}$ so $\hat{L}\cdot\hat{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$

$\langle\mathrm{nlm}|\hat{H}_{\mathrm{SO}}|\mathrm{nlm}\rangle = \langle\mathrm{nlm}|\frac{e^2}{2 m^2 c^2 r^3}\hat{L}\cdot\hat{S}|\mathrm{nlm}\rangle = \frac{e^2 f}{4 m^2 c^2}\langle\mathrm{lm}|(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)|\mathrm{lm}\rangle$

We recall if $\hat{J} = \hat{J}_1 + \hat{J}_2$ then $[\hat{J}^2, \hat{J}_1^2] = 0$ so in our case

$[\hat{J}^2, \hat{L}^2] = 0$ $[\hat{J}^2, \hat{S}^2] = 0$ So $[\hat{H}_0 + \hat{H}_{\mathrm{SO}}, \hat{J}^2] = [\hat{L}\cdot\hat{S}, \hat{J}^2] = [\hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{J}^2] = 0$ were I have been careless with the constants out in front (1)

We also know anything with $\hat{L}$ commutes with any $\hat{S}$ since they are different spaces

so $[\hat{H}_{\mathrm{SO}}, \hat{J}_i] = [\hat{H}_{\mathrm{SO}}, \hat{L}_i] + [\hat{H}_{\mathrm{SO}}, \hat{S}_i] = \frac{e^2 f}{4 m^2 c^2}\{[\hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{L}_i] + [\hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{S}_i]\} = \frac{e^2 f}{4 m^2 c^2}\{[\hat{J}^2, \hat{L}_i] + [\hat{J}^2, \hat{S}_i]\}$
$= \frac{e^2 f}{4 m^2 c^2}[\hat{J}^2, \hat{J}_i] = 0$ So $[\hat{H}_0 + \hat{H}_{\mathrm{SO}}, \hat{J}_z] = 0$ (2)

Which means that $[\hat{H}_0 + \hat{H}_{\mathrm{SO}}, \hat{J}_z] = 0$ $[\hat{H}_0 + \hat{H}_{\mathrm{SO}}, \hat{J}^2] = 0$

But note that $\hat{H}_{\mathrm{SO}}$ does not commute with $\hat{L}_z$ and $\hat{S}_z$ since the terms individually above in (2) do not go to zero (they dont commute with $\hat{J}^2$).

Proof : *e.g* $\frac{1}{2}[\hat{J}^2, \hat{L}_z] = [\frac{1}{2}\hat{L}^2 + \frac{1}{2}\hat{S}^2 + \sum_i \hat{L}_i\hat{S}_i, \hat{L}_z] = \sum_i [\hat{L}_i\hat{S}_i, \hat{L}_z] = \sum_i \hat{L}_i[\hat{S}_i, \hat{L}_z] + [\hat{L}_i, \hat{L}_z]\hat{S}_i = \sum_i [\hat{L}_i, \hat{L}_z]\hat{S}_i =$

$[\hat{L}_x, \hat{L}_z]\hat{S}_x + [\hat{L}_y, \hat{L}_z]\hat{S}_y + [\hat{L}_z, \hat{L}_z]\hat{S}_z = -i\hbar\hat{L}_y\hat{S}_x + i\hbar\hat{L}_x\hat{S}_y \neq 0$ remember $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{\mathrm{ijk}}\hat{L}_k$

Incidentally checking $[\hat{J}^2, \hat{L}_z + \hat{S}_z] - i\hbar\hat{L}_y\hat{S}_x + i\hbar\hat{L}_x\hat{S}_y - i\hbar\hat{S}_y\hat{L}_x + i\hbar\hat{S}_x\hat{L}_y = 0$ as should be

We should also check $[\hat{H}_{\mathrm{SO}}, \hat{L}^2] = \frac{e^2 f}{4 m^2 c^2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{L}^2] = 0$ using (1) and similarly

$[\hat{H}_{\mathrm{SO}}, \hat{S}^2] = \frac{e^2 f}{4 m^2 c^2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{S}^2] = 0$

Remember in QM26 that I said when adding angular momentum. i.e. $\hat{J} = \hat{L} + \hat{S}$ we can specify either :

1) the eigenvalues of $\hat{J}^2$ $\hat{J}_z$ $\hat{L}^2$ and $\hat{S}^2$ OR

2) the eigenvalues of $\hat{L}_z$, $\hat{S}_z$ $\hat{L}^2$ and $\hat{S}^2$

But since the Hamiltonian does not commute with $\hat{L}_z$, $\hat{S}_z$ so it is best if we use the first of these possibilities

So let the eigenfuctiuons (now adding S) be called

$|\mathrm{nlsjm}\rangle$ where the eigenvalues will be E_n $l(l+1)\hbar^2$ $s(s+1)\hbar^2$ $j(j+1)\hbar^2$ m_j

(Remember in Qm26 we used $|\mathrm{nlm}\rangle$)

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Lets also use the CG coefficients to write out |nlsjm⟩ for the particular case where l=1. We know $s = \frac{1}{2}$ Lets also assume n=2 which is the lowest n for which we can have l=1

Lets count the states

for l=1, m=1,0,-1 so there are 3, but for each of these $s = \frac{+1}{2}$ or $\frac{-1}{2}$ for a total of 6. Writing these out in a notation of $|m_l\, m_s\rangle$ (since l=1 and $s = \frac{1}{2}$ is true for everything)

$$\left|1\ \tfrac{1}{2}\right\rangle \left|1\ \tfrac{-1}{2}\right\rangle \left|0\ \tfrac{1}{2}\right\rangle \left|0\ \tfrac{-1}{2}\right\rangle \left|-1\ \tfrac{1}{2}\right\rangle \left|-1\ \tfrac{-1}{2}\right\rangle$$

Now using the CG coefficients lets write out the j m_j representation

My notation will be $|\mathrm{jm}_j\rangle = |m_l\, m_s\rangle$ $j = \frac{3}{2}$ and $\frac{1}{2}$

$$\left|\tfrac{3}{2}\ \tfrac{3}{2}\right\rangle = \left|1\ \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{3}{2}\ \tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|1\ \tfrac{-1}{2}\right\rangle + \sqrt{\tfrac{2}{3}}\left|0\ \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|1\ \tfrac{-1}{2}\right\rangle - \sqrt{\tfrac{1}{3}}\left|0\ \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{3}{2}\ \tfrac{-1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|0\ \tfrac{-1}{2}\right\rangle + \sqrt{\tfrac{1}{3}}\left|-1\ \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2}\ \tfrac{-1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|0\ \tfrac{-1}{2}\right\rangle - \sqrt{\tfrac{2}{3}}\left|-1\ \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{3}{2}\ \tfrac{-3}{2}\right\rangle = \left|-1\ \tfrac{-1}{2}\right\rangle$$

Good, we have 6

Now for good measure lets write this out in position representation for the spacial part and matrix representation for the spin part so we can see what they look like - this is somewhat schematic hence the use of ≐ Again for notation:

$$|\mathrm{jm}_j\rangle = |m_l\, m_s\rangle \doteq Y_l^m\,|+\rangle \doteq \begin{pmatrix}\square\\ \square\end{pmatrix}$$

$$\left|\tfrac{3}{2}\ \tfrac{3}{2}\right\rangle = \left|1\ \tfrac{1}{2}\right\rangle \doteq Y_l^1\,|+\rangle \doteq \begin{pmatrix}Y_1^1\\ 0\end{pmatrix}$$

$$\left|\tfrac{3}{2}\ \tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|1\ \tfrac{-1}{2}\right\rangle + \sqrt{\tfrac{2}{3}}\left|0\ \tfrac{1}{2}\right\rangle \doteq \sqrt{\tfrac{1}{3}}\,Y_1^1\,|-\rangle + \sqrt{\tfrac{2}{3}}\,Y_1^0\,|+\rangle \doteq \begin{pmatrix}\sqrt{\tfrac{2}{3}}\ Y_1^0\\ \sqrt{\tfrac{1}{3}}\ Y_1^1\end{pmatrix}$$

$$\left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|1\ \tfrac{-1}{2}\right\rangle - \sqrt{\tfrac{1}{3}}\left|0\ \tfrac{1}{2}\right\rangle \doteq \sqrt{\tfrac{2}{3}}\,Y_1^1\,|-\rangle - \sqrt{\tfrac{1}{3}}\,Y_1^0\,|+\rangle \doteq \begin{pmatrix}-\sqrt{\tfrac{1}{3}}\ Y_1^0\\ \sqrt{\tfrac{2}{3}}\ Y_1^1\end{pmatrix}$$

$$\left|\tfrac{3}{2}\ \tfrac{-1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|0\ \tfrac{-1}{2}\right\rangle + \sqrt{\tfrac{1}{3}}\left|-1\ \tfrac{1}{2}\right\rangle \doteq \sqrt{\tfrac{2}{3}}\,Y_1^0\,|-\rangle + \sqrt{\tfrac{1}{3}}\,Y_1^{-1}\,|+\rangle \doteq \begin{pmatrix}\sqrt{\tfrac{1}{3}}\ Y_1^{-1}\\ \sqrt{\tfrac{2}{3}}\ Y_1^0\end{pmatrix}$$

$$\left|\tfrac{1}{2}\ \tfrac{-1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|0\ \tfrac{-1}{2}\right\rangle - \sqrt{\tfrac{2}{3}}\left|-1\ \tfrac{1}{2}\right\rangle \doteq \sqrt{\tfrac{1}{3}}\,Y_1^0\,|-\rangle - \sqrt{\tfrac{2}{3}}\,Y_1^{-1}\,|+\rangle \doteq \begin{pmatrix}-\sqrt{\tfrac{2}{3}}\ Y_1^{-1}\\ \sqrt{\tfrac{1}{3}}\ Y_1^0\end{pmatrix}$$

$$\left|\tfrac{3}{2}\ \tfrac{-3}{2}\right\rangle = \left|-1\ \tfrac{-1}{2}\right\rangle \doteq Y_1^{-1}\,|-\rangle \doteq \begin{pmatrix}0\\ Y_1^{-1}\end{pmatrix}$$

Now *all* of these states have the same n. In our example n=2 so before adding the SO coupling $E_2 = -\frac{\mathcal{R}}{4}$ = -3.4 eV so we have a 6-fold degeneracy. Now lets find the first order corrections to the energy $\langle \mathrm{nlsjm}|\hat{H}_{\mathrm{SO}}|\mathrm{nlsjm}\rangle$

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Now we know $\langle \text{nlsjm} \,|\, \hat{H}_0 \,|\text{nlsjm}\rangle = E_n = -\frac{Z^2 \mathcal{R}}{n^2}$ $\quad \mathcal{R} = \frac{\text{me}^4}{2\hbar^2} = 13.6\,\text{eV}$ $\quad a_0 = \frac{\hbar^2}{\text{me}^2}$

Let's also define the fine structure constant $\alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137}$

$\langle \text{nlsjm}|\hat{H}_{\text{SO}}|\text{nlsjm}\rangle = \langle \text{nlsjm}|\frac{e^2 f(r)}{4 m^2 c^2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)|\text{nlsjm}\rangle =$

$\langle \text{nlsjm}|\frac{e^2 \hbar^2 f}{4 m^2 c^2}(j(j+1) - l(l+1) - s(s+1))|\text{nlsjm}\rangle =$

$\frac{e^2 \hbar^2}{4 m^2 c^2}(j(j+1) - l(l+1) - s(s+1))\, f$

Now plugging in for f

$\langle \text{nlsjm} \,|\, \hat{H}_{\text{SO}} \,|\text{nlsjm}\rangle = \frac{e^2 \hbar^2}{4 m^2 c^2}(j(j+1) - l(l+1) - s(s+1)) \frac{1}{l(l+\frac{1}{2})(l+1)\, n^3 a_0{}^3} = \frac{\mathcal{R}\alpha^2}{2 n^3} \frac{(j(j+1) - l(l+1) - \frac{3}{4})}{l(l+\frac{1}{2})(l+1)} =$

$\frac{\mathcal{R}\alpha^2}{2 n^3 l(l+\frac{1}{2})(l+1)} \begin{cases} l & j = l + \frac{1}{2} \\ -(l+1) & j = l - \frac{1}{2} \end{cases}$

Now just before we figure out how big this is. I have to tell you that there is another correction of the same order. Its the relativistic correction and I will do some quick guess to this.

The relativstic Correction

Lets first start classically. T=$\frac{p^2}{2m}$ is the non-relativistic kinetic energy. If the particle is moving fast we better add a correction. We have to use

$(T = E - \text{mc}^2 = \sqrt{p^2 c^2 + m^2 c^4} - \text{mc}^2 = \text{mc}^2\left[1 + \left(\frac{p}{\text{mc}}\right)^2\right]^{1/2} - \text{mc}^2 = \text{mc}^2\left[1 + \frac{1}{2}\left(\frac{p}{\text{mc}}\right)^2 - \frac{1}{8}\left(\frac{p}{\text{mc}}\right)^4 \ldots\right) - \text{mc}^2$

$= \frac{p^2}{2m} - \frac{1}{8 m^3 c^2} p^4$

Now we will just turn this into QM $\frac{\hat{p}^2}{2m} - \frac{1}{8 m^3 c^2} \hat{p}^4$. We will call $\hat{H}_{\text{rel}} = -\frac{1}{8 m^3 c^2} \hat{p}^4$

Lets use perturbation theory again and find $E_{\text{rel}}{}^1 = \langle \text{nlsjm} \,|\, \hat{H}_{\text{rel}} \,|\, \text{nlsjm}\rangle = -\frac{1}{8 m^3 c^2} \langle \text{nlsjm} \,|\, \hat{p}^4 \,|\, \text{nlsjm}\rangle$

There is a trick to this since $\hat{p}$ is hermitian.

$\langle \,|\, \hat{p}^4 \,|\rangle = \langle \,|\, \hat{p}^{2\dagger} \hat{p}^2 \,|\rangle$ where the $|\text{nlsjm}\rangle$ are eigenkets. Now adding this term into the Hamiltonian may change the eigenkets. (We were lucky above, since we found that the new terms commuted with the hamiltonian. These will not. $[\hat{p}^4$, V(r)]≠0

Here is where I "cheat" again. Actually I am using 1st order perturbation theory. What I want to do is that it does not change the eigenkets much, so we will stick with the original ones i,e, $|\text{nlsjm}\rangle$

The Schrodinger eqn is $\left[\frac{\hat{p}^2}{2m} + \text{V(r)}\right]|\rangle = \text{E}|\rangle$ so

we know $\hat{p}^2|\rangle = 2\text{m(E-V(r))}|\rangle$ Taking the hermitian conjugate of this gives $\langle|\hat{p}^{2\dagger} = \langle|2\text{m(E-V(r))}$

So $\langle \,|\, \hat{p}^4 \,|\rangle = \langle \,|\, \hat{p}^{2\dagger} \hat{p}^2 \,|\rangle = \langle|[2 m(E - V(r)][2 m(E - V(r)]\,|\rangle = 4 m^2[E^2 - 2 E \langle V\rangle + \langle V^2\rangle]$

and the correction is

$\langle \hat{H}_{\text{rel}}\rangle = -\frac{1}{8 m^3 c^2}\langle \,|\, \hat{p}^4 \,|\rangle = -\frac{1}{8 m^3 c^2} 4 m^2[E^2 - 2 E \langle V\rangle + \langle V^2\rangle] = \frac{-1}{2\,\text{mc}^2}[E^2 - 2 E \langle V\rangle + \langle V^2\rangle] =$

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But $V(r) = -\frac{Ze^2}{r}$

so the correction is (Setting Z=1, and remembering $\mathcal{R} = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0}$ $a_0 = \frac{\hbar^2}{me^2}$)

$$\langle \hat{H}_{rel} \rangle = \frac{-1}{2mc^2}\left[E^2 + 2\,EZe^2\left\langle\frac{1}{r}\right\rangle - Z^2 e^4\left\langle\frac{1}{r^2}\right\rangle\right] = \frac{-1}{2mc^2}\left[E^2 + 2\,EZe^2\frac{1}{n^2 a_0} + Z^2 e^4\frac{1}{(l+\frac{1}{2})n^3 a_0{}^2}\right] = \frac{-1}{2mc^2}\left[E^2 - 4E^2 + \frac{4n}{(l+\frac{1}{2})}\right] =$$

$$\frac{-E_n{}^2}{2mc^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right] = -\frac{\mathcal{R}\alpha^2}{4n^4}\left[\frac{4n}{l+\frac{1}{2}} - 3\right]$$

Now we can add this to the SO correction and we have $\left(s(s+1) = \frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}\right)$ and when we put in $l = j \pm \frac{1}{2}$ it doesn't change the answer

$$\langle \hat{H}_{SO} + \hat{H}_{rel} \rangle = \frac{\mathcal{R}\alpha^2}{2n^3}\frac{\left(j(j+1) - l(l+1) - \frac{3}{4}\right)}{l(l+\frac{1}{2})(l+1)} - \frac{\mathcal{R}\alpha^2}{4n^4}\left[\frac{4n}{l+\frac{1}{2}} - 3\right] = \frac{\mathcal{R}}{n^2}\frac{\alpha^2}{n^2}\left[\frac{n\left(j(j+1) - l(l+1) - \frac{3}{4}\right)}{2l(l+\frac{1}{2})(l+1)} - \frac{n}{l+\frac{1}{2}} + \frac{3}{4}\right] = \frac{\mathcal{R}}{n^2}\left[\frac{\alpha^2}{n^2}\left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right)\right]$$

We can the full formula for the energy levels of hydrogen including the relativistic and SO contributions, which are together called the fine-structure (actually there is more called the hyperfine structure but thats for grad school since our time is up)

$$E_{nj} = -\frac{\mathcal{R}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

for our case where $n = 2$ $\quad \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) = \begin{cases} \frac{\alpha^2}{16} \text{ for } j = \frac{3}{2} \\ \frac{5}{16}\alpha^2 \text{ for } j = \frac{1}{2} \end{cases}$

Now we can see several things here

1) the 6-fold degeneracy for l=1, has now been broken up into the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ states so its still degenerate since there are 2 $j = \frac{1}{2}$ states and 4 $j = \frac{3}{2}$ states.

2) the size of the correction by a factor α^2~1/10000 and larger for the $j = \frac{1}{2}$ state than the $\frac{3}{2}$ state

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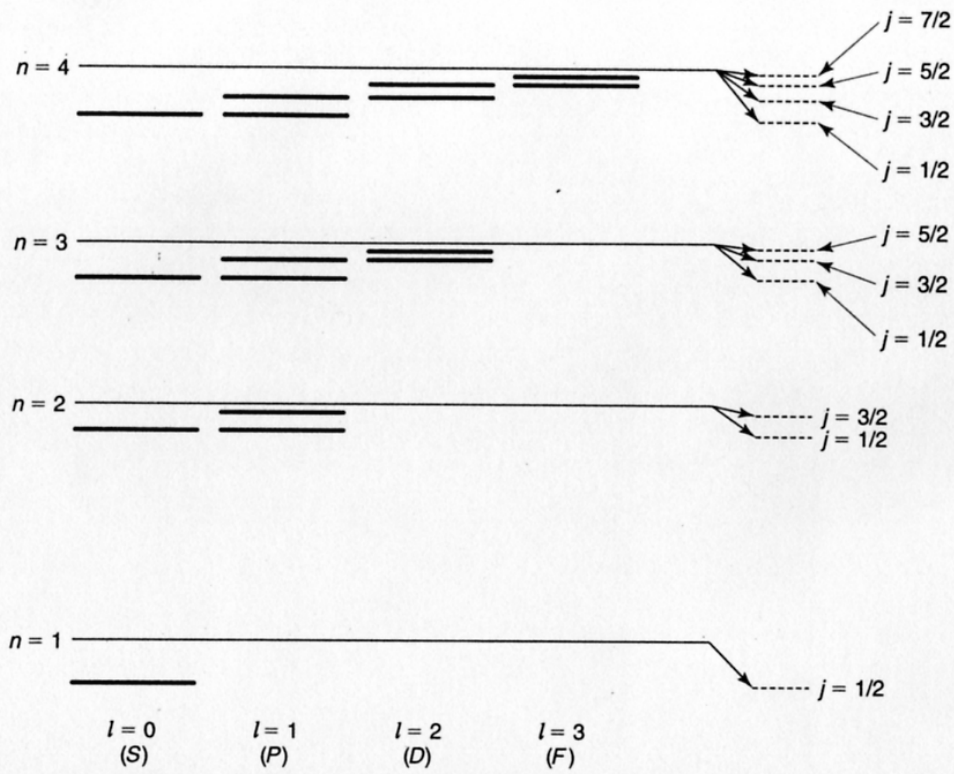

Figure 6.9: Energy levels of hydrogen, including fine structure (not to scale).

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