return to the Dirac theory to see the effect of spin at the relativistic level which we call "higher order" correction.

We will consider electron in Coulomb field of a nucleus.: $A = 0;\ q\phi = -e\phi = V(r) = \frac{-Ze^2}{(4\pi\varepsilon_0)r}$

Recall,

$$\textcircled{B1} \rightarrow (E'+2mc^2)\underline{\underline{\eta}}(r) = c(-i\hbar\nabla - qA)\cdot\vec{\underline{\underline{\sigma}}}\cdot\underline{\underline{\psi}}(r) + q\phi\underline{\underline{\eta}}(r)$$

$$(E'+2mc^2)\underline{\underline{\eta}}(r) = c(-i\hbar\nabla\cdot\vec{\underline{\underline{\sigma}}})\underline{\underline{\psi}} + V(r)\underline{\underline{\eta}}(r)$$

$$\Rightarrow \underline{\underline{\eta}}(r) = (E'+2mc^2-V(r))^{-1}c(-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla)\underline{\underline{\psi}}(r)$$

Substituting the $\underline{\underline{\eta}}(r)$ above in $\textcircled{A1}$ will [illegible]

A and ϕ

Recall $\textcircled{A1}$; $E'\underline{\underline{\psi}} = c(-i\hbar\nabla - qA)\cdot\vec{\underline{\underline{\sigma}}}\,\underline{\underline{\eta}} + q\phi\underline{\underline{\psi}}$

$$\rightarrow E'\underline{\underline{\psi}} = c^2(-i\hbar\nabla\cdot\vec{\underline{\underline{\sigma}}})\frac{(-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla)\underline{\underline{\psi}}}{(E'+2mc^2-V(r))} + V(r)\underline{\underline{\psi}}.$$

Now, $\frac{1}{E'+2mc^2-V(r)} = \frac{1}{2mc^2\left(1+\frac{E'-V(r)}{2mc^2}\right)} = \frac{1}{2mc^2}\left[1-\frac{E'-V(r)}{2mc^2}\right]$

$\frac{p^2}{m^2c^2} \simeq \frac{v^2}{c^2}$

$$\therefore E'\underline{\underline{\psi}} = c^2(-i\hbar\nabla\cdot\vec{\underline{\underline{\sigma}}})\frac{1}{2mc^2}\left[1-\frac{E'-V(r)}{2mc^2}\right](-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla)\underline{\underline{\psi}} + V(r)\underline{\underline{\psi}}$$

$$= \frac{1}{2m}\left[1-\frac{E'-V(r)}{2mc^2}\right](-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla)^2\underline{\underline{\psi}} - \frac{1}{2m}\frac{(-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla V(r))(-i\hbar\vec{\underline{\underline{\sigma}}}\cdot\nabla\psi)}{2mc^2} + V(r)\underline{\underline{\psi}}$$

$$= \frac{-\hbar^2}{2m}\left[1-\frac{(E'-V(r))}{2mc^2}\right](\vec{\underline{\underline{\sigma}}}\cdot\nabla)^2\underline{\underline{\psi}} - \frac{\hbar^2}{4m^2c^2}[\vec{\underline{\underline{\sigma}}}\cdot\nabla V(r)][\vec{\underline{\underline{\sigma}}}\cdot\nabla\underline{\underline{\psi}}] + V(r)\underline{\underline{\psi}}$$

Now make use of few 'σ' based identities. →

We make use of: $(\underline{\underline{\vec{\sigma}}}\cdot\nabla)^2 = \nabla^2$

$$(\underline{\underline{\vec{\sigma}}}\cdot\nabla V)(\underline{\underline{\vec{\sigma}}}\cdot\nabla\underline{\underline{\Psi}}) = (\nabla V)\cdot(\nabla\underline{\underline{\Psi}}) + i\underline{\underline{\vec{\sigma}}}\cdot\left[(\nabla V)\times(\nabla\underline{\underline{\Psi}})\right]$$

Also, $\nabla V(r) = \frac{dV}{dr}\hat{r}$ ∵ sph symm of $V(\vec{r})$

$$\therefore (\nabla V)\cdot(\nabla\underline{\underline{\Psi}}) = \frac{dV}{dr}\frac{\partial\underline{\underline{\Psi}}}{\partial r}$$

$$\therefore i\underline{\underline{\vec{\sigma}}}\cdot\left[(\nabla V)\times(\nabla\underline{\underline{\Psi}})\right] = i\underline{\underline{\vec{\sigma}}}\cdot\left(\frac{dV}{dr}\right)\hat{r}\times\nabla\underline{\underline{\Psi}} = -\underline{\underline{\vec{\sigma}}}\cdot\left(\frac{dV}{dr}\right)\frac{1}{r\hbar}\vec{r}\times\hat{p}\underline{\underline{\Psi}}$$

$$= -\frac{1}{r\hbar}\left(\frac{dV}{dr}\right)\underline{\underline{\vec{\sigma}}}\cdot\hat{L}\underline{\underline{\Psi}}$$

∴ We have,

$$E'\underline{\underline{\Psi}} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + \frac{\hbar^2}{2m}\frac{(E'-V(r))}{2mc^2}\nabla^2 - \frac{\hbar^2}{4m^2c^2}\left\{\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r} - \frac{1}{r\hbar}\left(\frac{dV}{dr}\right)\underline{\underline{\vec{\sigma}}}\cdot\hat{L}\right\}\right]\underline{\underline{\Psi}}$$

$$E'\underline{\underline{\Psi}} = \Bigg[\underbrace{-\frac{\hbar^2\nabla^2}{2m} + V(r)}_{H_0} + \frac{\hbar^2}{4m^2c^2}\underset{\underset{\frac{\hat{p}^2}{2m}}{\approx}}{(E'-V(r))}\nabla^2 + \frac{\hbar}{4m^2c^2}\frac{1}{r}\left(\frac{dV}{dr}\right)\underline{\underline{\vec{\sigma}}}\cdot\hat{L} - \frac{\hbar^2}{4m^2c^2}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}\Bigg]\underline{\underline{\Psi}}$$

$$= \left[H_0 + \left(\frac{-1}{4m^2c^2}\frac{\hat{p}^4}{2m}\right) + \frac{1}{2m^2c^2}\frac{1}{r}\left(\frac{dV}{dr}\right)\vec{S}\cdot\hat{\underline{\underline{L}}} - \frac{\hbar}{4m^2c^2}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}\right]\underline{\underline{\Psi}}$$

↓ KE correction

↓ Spin-orbit correction

↓ PE correction ↓ Darwin term.

$\vec{S} = \frac{\hbar\underline{\underline{\vec{\sigma}}}}{2} \Rightarrow (\vec{S}\cdot\vec{S})\underline{\underline{\Psi}} = s(s+1)\hbar^2\underline{\underline{\Psi}}$

$s = \frac{1}{2}$

↓ Spin angular momentum operator

$\underline{\underline{\vec{S}}}^i\underline{\underline{\Psi}} = \pm\frac{\hbar}{2}\underline{\underline{\Psi}}$ $i=1,2,3$

Recall Pauli Eq^n ⒶⒷ and use $\vec{S}$;

$$E'\underline{\underline{\Psi}} = \left[\frac{1}{2m}(-i\hbar\nabla)\cdot(-i\hbar\nabla) + 2\frac{e\hbar}{2m}\vec{S}\cdot\vec{B} + V(r)\right]\underline{\underline{\Psi}}$$

↓ g_s the gyromagnetic ratio

∴ Intrinsic magnetic moment: $\vec{\mu} = -\mu_B\underline{\underline{\vec{\sigma}}} = -g_s\frac{\mu_B}{\hbar}\vec{S} = -g_s\frac{e}{2m}\vec{S}$

Angular momentum and magnetic moment

$\vec{\mu} = \oint i\, d\vec{s}$

$d\vec{s} = \frac{1}{2}\vec{r}\times d\vec{u}$; $\mu = \frac{1}{2}\oint \frac{dq}{dt}\vec{r}\times d\vec{u}$

$= \frac{1}{2}\oint dq\, \vec{r}\times\frac{d\vec{u}}{dt}$

$= \frac{1}{2}\oint dq\, \vec{r}\times\vec{v}$

$= \frac{1}{2m}\oint dq\, \vec{r}\times\vec{p}$

$= \frac{1}{2m}\oint dq\, \vec{L}$

$= \frac{1}{2m}\vec{L}\oint dq$ since $\vec{L}$ is a constant of motion in the central field

$= \frac{-e\vec{L}}{2m}$

$|\mu| = \frac{e}{2m}\hbar\sqrt{l(l+1)}$

$= \mu_B\sqrt{l(l+1)}$

$\hookrightarrow 9.27\times10^{-24}\,JT^{-1}$

$\mu_z = -\frac{e}{2m}\hbar m_l$

$= -\mu_B m_l$

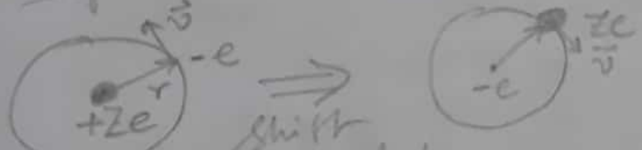
Similarly for spin the Dirac theory gave

$\mu_z = -2\mu_B m_s$

$\downarrow$

$g_s \to 2.0023192\ldots$ for more accurate QED estimates when light is treated quantum mechanically

Magnetic field due to relative motion of nucleus



Shift origin to electron

$\vec{B} = \frac{\mu_0}{4\pi}\oint \frac{i\, d\vec{u}\times\vec{r}}{r^3}$

Consider a circular loop with constant r

$\therefore \oint i\, d\vec{u} = \oint \frac{dq}{dt}d\vec{u} = Ze\frac{d\vec{u}}{dt}$
$= Ze(-\vec{v})$.

$\therefore$ for circular loop: $\vec{B} = \frac{\mu_0}{4\pi}\frac{Ze}{r^3}(-\vec{v})\times\vec{r} = \frac{\mu_0}{4\pi}\frac{Ze}{r^3}\vec{r}\times\vec{v}$

Now $\vec{E} = \frac{Ze}{4\pi\epsilon_0 r^2}\hat{r} = \frac{Ze}{4\pi\epsilon_0 r^3}\vec{r} \Rightarrow \vec{B} = \frac{\mu_0 Ze}{4\pi r^3}\times\frac{4\pi\epsilon_0 r^3}{Ze}\vec{E}\times\vec{v}$

$= \mu_0\epsilon_0\vec{E}\times\vec{v} = \frac{\vec{E}\times\vec{v}}{c^2}$

$\therefore$ Correction to energy of electron due to coupling of its intrinsic magnetic moment due to spin with the effective magnetic field due to relative motion of nucleus around it : $-\mu_{spin}\cdot B_{field}$

$= \left(-g_s\frac{\mu_B}{\hbar}\vec{S}\right)\cdot\left(\frac{\vec{E}\times\vec{v}}{c^2}\right) = \frac{1}{c^2}\left(-g_s\frac{\mu_B}{\hbar}\vec{S}\right)\cdot\left\{\left(\frac{1}{e}\frac{\vec{r}}{r}\frac{dV}{dr}\right)\times\vec{v}\right\}$

$= \frac{g_s\mu_B}{\hbar c^2 em}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{S}\cdot(\vec{r}\times\vec{p})$

Almost a trick done only! ✓ $\uparrow$ $\vec{E}$, easy to check the $V = -Ze^2/4\pi\epsilon_0 r$

$$= \frac{g_s}{2c^2 m^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{L}\cdot\vec{S}$$

Note that this is identical to What we got from Dirac theory except for the g_s which is 2. So a compensating 2 in the denominator must be there to be at par with Dirac theory and indeed such a factor exists. The imperfection in the above analysis is that the shift of origin is not an inertial translation but a non-inertial one since the rotating frame is non-inertial. As a result, an additional component of motion would arise which known as the Thomas Precession leading to the desired will take away half of the energy, 2 in the denominator.

Now let us revert back to our correction.

Recall, $E'\underline{\Psi} = \Big[H_0 + \underbrace{\left(\frac{-1}{4m^2c^2}\frac{\hat{p}^4}{2m}\right)}_{\substack{\downarrow \\ \text{KE} \\ \text{correction}}} + \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\left(\frac{dV}{dr}\right)\vec{S}\cdot\vec{L}}_{\substack{\downarrow \\ L\cdot S \\ \text{interaction}}} - \underbrace{\frac{\hbar^2}{4m^2c^2}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}}_{\substack{\downarrow \\ \text{PE} \\ \text{correction}}}\Big]\underline{\Psi}$

There is a basic problem: four component $\underline{\Psi}$ were normalised as $\int(\psi^\dagger\psi + \eta^\dagger\eta)\,dr = 1$

$\therefore$ 2 component $\underline{\Psi}$ is not normalised.

$\therefore$ H with the correction terms derived must not be Hermitian; Indeed $\left[\frac{\partial}{\partial r}\right]$ is not Hermitian.

$\therefore$ So the problem of normalisation of $\underline{\Psi}$ can be fixed by making the H Hermitian by adding the Hermitian counterpart of $\frac{\partial}{\partial r}$ to H. → Proposed by Darwin.

So the PE correction is renamed as the Darwin term:

$$\frac{1}{2}\left[\left(-\frac{\hbar^2}{4m^2c^2}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}\right) + \left(-\frac{\hbar^2}{4m^2c^2}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}\right)^\dagger\right]$$

$$\Rightarrow D_{ab} = \left(-\frac{\hbar^2}{8m^2c^2}\right)\left[\left[\left(\frac{dV}{dr}\frac{\partial}{\partial r}\right)\right]_{ab} + \left[\left(\frac{dV}{dr}\frac{\partial}{\partial r}\right)^*_{ba}\right]\right]$$

$$\therefore D_{ab} = \left(-\frac{\hbar^2}{8m^2c^2}\right)\left[\langle a|\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}|b\rangle + \left(\langle b|\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r}|a\rangle\right)^*\right]$$

$$= \left(\frac{-\hbar^2}{8m^2c^2}\right)\left[\int \psi_a^* \left(\frac{dV}{dr}\right)\nabla \psi_b \cdot dV + \int \psi_b \left(\frac{dV}{dr}\right)\nabla \psi_a^* \, dV\right]\cdot\hat{r}$$

$$= \left(\frac{-\hbar^2}{8m^2c^2}\right)\left[\;'' + '' + \int \psi_a^* \left(\nabla\left(\frac{dV}{dr}\right)\right)\psi_b \, dV - \text{same}\right]\cdot\hat{r}$$

$$= \left(-\frac{\hbar^2}{8m^2c^2}\right)\left[\int \nabla\left[\psi_a^* \frac{dV}{dr}\psi_b\right] dV - \int \psi_a^* \left(\nabla\left(\frac{dV}{dr}\right)\right)\psi_b \, dV\right]\cdot\hat{r}$$

$$= \left(\frac{-\hbar^2}{8m^2c^2}\right)\left[\underbrace{\left[\psi_a^* \frac{dV}{dr} \psi_b\right]_{-\infty}^{+\infty}}_{=0} - \int \psi_a^* (\nabla^2 V)\psi_b \, dV\right]\cdot\hat{r}$$

$$= \frac{\hbar^2}{8m^2c^2}\left[\int \psi_a^* (\nabla^2 V)\psi_b \cdot dV\right]\cdot\hat{r}$$

$$\text{with } V(r) = \frac{Ze^2}{4\pi\varepsilon_0 r} \;;\; \left[\int \psi_a^* (\nabla^2 V)\psi_b \, dV\right]\cdot\hat{r} =$$

$$= \left[\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\int \psi_a^* \nabla^2\left(\frac{1}{r}\right)\psi_b \, dV\right]\cdot\hat{r}$$

$$= (\;)\left[\int \nabla\left(\psi_a^* \frac{\partial}{\partial r}\left(\frac{1}{r}\right)\psi_b\right) dV - \int \frac{\partial}{\partial r}\left(\frac{1}{r}\right)\nabla(\psi_a^*\psi_b)\, r^2 \sin\theta \, d\theta \, d\phi \, dr\right]\cdot\hat{r}$$

$$= (\;)\left[\;'' \; + 4\pi\int_0^\infty \frac{\partial}{\partial r}(\psi_a^*\psi_b)\, dr\right] = 4\pi(\;)\,\psi_a^*(r=0)\,\psi_b(r=0)$$

$$\therefore D_{ab} = \left(\frac{\hbar^2 4\pi}{8m^2c^2}\right)\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\langle a|\delta(r)|b\rangle$$

$$\therefore \text{P.E correction : Darwin term} = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\underset{\downarrow}{\delta r}$$

only contribute for l=0
since there is a node
at r=0 for l>0

$$H = H_0 + H_1' + H_2' + H_3'$$

H_1' ↓ Relativistic Correction to KE

H_2' ↓ Spin orbit interaction

H_3' → Darwin term.

→ two component spinor

$$\underline{\Psi}_{nlm_lm_s} = \psi_{nlm_l}\left[\chi_{\frac{1}{2},m_s}\right]_{1\times 2} \qquad \chi_{\frac{1}{2},+\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix} \qquad \chi_{\frac{1}{2},-\frac{1}{2}} = \begin{pmatrix}0\\1\end{pmatrix}.$$

(spin orbitals or Pauli wavefunctions)

$$H_0 \underline{\Psi}_{nlm_lm_s} = E_n \underline{\Psi}_{nlm_lm_s} \rightarrow \underset{m_s = \pm\frac{1}{2}}{\overset{\uparrow}{2}}n^2 \text{ degenerate}$$

We calculate 1st order correction due to H_1', H_2', H_3' with the spinorbitals as the zeroth order wavefn

$$H_1' = -\frac{p^4}{8m^3c^2} = -\hbar^4\frac{\nabla^2\nabla^2}{8m^3c^2}$$

→ H_1' operate on ψ_{nlm_l} not the spinor part

It also turns out that H_1' commutes with L_x, L_y, L_z

∴ H_1' is not going to mix states with specific l, m_l and m_s

Note that otherwise degenerate perturbation theory should have been required. → Diagonalise H_1' in degenerate basis

But H_1' is already diagonal in $\underline{\Psi}_{nlm_lm_s}$

$$\therefore \Delta E_1 = \left\langle \underline{\Psi}_{nlm_lm_s} \right| -\frac{p^2p^2}{8m^3c^2} \left| \underline{\Psi}_{nlm_lm_s} \right\rangle$$

$$= \frac{1}{2mc^2}\left\langle \middle| \frac{p^2}{2m}\frac{p^2}{2m} \middle| \right\rangle = \frac{1}{2mc^2}\left\langle \middle| \left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2 \middle| \right\rangle$$

$$= \frac{1}{2mc^2}\left[\langle | H_0 H_0 \rangle + \frac{Ze^2}{4\pi\varepsilon_0}\left\langle \middle| \frac{1}{r}H_0 \right\rangle + \left\langle \middle| H_0 \frac{Ze^2}{4\pi\varepsilon_0 r} \middle| \right\rangle + \frac{Z^2e^4}{(4\pi\varepsilon_0)^2}\left\langle \middle| \frac{1}{r^2} \middle| \right\rangle\right]$$

$$= \frac{1}{2mc^2}\left[E_n^2 + 2\frac{Ze^2}{4\pi\varepsilon_0}E_n\left\langle\frac{1}{r}\right\rangle_{nlm_l} + \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle_{nlm_l}\right]$$

$$= -E_n\frac{(Z\alpha)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right]$$

$$\frac{1}{\alpha} = 137.035\,999\,1\ldots \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$$

one interpretation of $1/\alpha$ is that it is the max. no. charge Z which can support a stable electron orbital around it: $\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}$; $mvr = \hbar$ [illegible]

Spin-orbit term

$$H_2' = \frac{1}{2m^2c^2}\,\frac{1}{r}\left(\frac{dV}{dr}\right)\hat{\vec{L}}\cdot\hat{\vec{S}} = \xi(r)\,\hat{\vec{L}}\cdot\hat{\vec{S}} = \xi(r)\left(\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y+\hat{L}_z\hat{S}_z\right)$$

Note $\hat{L}_i$, $i=1,2,3$ commutes with $\hat{L}^2$. Also, L^2 trivially commutes with S_i since it does not operate on spin.

Also, L^2 does not operate on the radial part.

The three above considerations imply that L^2 commutes with $\xi(r)\,\hat{L}\cdot\hat{S}$.

$\Rightarrow$ H_2' will not mix states with specific l.

However $\hat{\vec{L}}\cdot\hat{\vec{S}}$ does not commute with L_z

$\Rightarrow$ H_2' will mix states with different m_l for a given l

∴ H_2' needs to be diagonalized within the $(2l+1)$ member subspace of $\{\underline{\underline{\Psi}}_{nlm_lm_s}\}$ $m_l = -l$ to l $\Rightarrow (2l+1)\times(2l+1)$ matrix.

∴ Linear combinations of $\underline{\underline{\Psi}}_{nlm_lm_s}$ are to be found such that $\hat{\vec{L}}\cdot\hat{\vec{S}}$ is diagonal.

Let us define $\hat{\vec{J}} = \hat{\vec{L}}+\hat{\vec{S}} \Rightarrow \hat{\vec{J}}\cdot\hat{\vec{J}} = \hat{\vec{L}}\cdot\hat{\vec{L}} + \hat{\vec{S}}\cdot\hat{\vec{S}} + 2\,\hat{\vec{L}}\cdot\hat{\vec{S}}$

$$\Rightarrow \hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{1}{2}\left(\hat{J}^2 - L^2 - \hat{S}^2\right)$$

Note that $\{\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\}$ all commutes with each other and so with $\hat{\vec{L}}\cdot\hat{\vec{S}}$. $\hat{L}_z$ and $\hat{S}_z$ commute with $\hat{L}^2$ and $\hat{S}^2$.
Note also that although they do not commutes with $\hat{\vec{L}}\cdot\hat{\vec{S}}$ and thereby $\hat{J}^2$. *

∴ The eigen spectrum of $\vec{L}\cdot\vec{S}$ that we are looking for will be described by quantum numbers $n\,l\,s\,j\,m_j$

where $\hat{J}^2\,\underline{\underline{\Psi}}_{nlsjm_j} = j(j+1)\hbar^2\,\underline{\underline{\Psi}}_{nlsjm_j}$

$\hat{J}_z\,\underline{\underline{\Psi}}_{nlsjm_j} = m_j\hbar\,\underline{\underline{\Psi}}_{nlsjm_j}$

with $-j \le m_j \le j$ and $j = l+s,\ l-s,\ s=\frac{1}{2}$

Note $\underline{\underline{\Psi}}_{nlsjm_j} = R_{nl}(r)\left[\chi_{sjm_j}\right]$

---

* Set of states that are common between $\hat{L}^2$ and $\hat{L}_z$ are $|n l m_l m_s\rangle$
" " " " $\hat{L}^2$ and $\hat{J}^2$ are $|n l j m_j\rangle$
"Preservation of # of quantum numbers is essential".

Scanned by CamScanner

$$\therefore \Delta E_2 = \left\langle n\,l\,s\,j\,m_j \left| \xi(r)\,\hat{\vec{L}}\cdot\hat{\vec{S}} \right| n\,l\,s\,j\,m_j \right\rangle$$

$$= \int R_{nl}^{*}(r)\,\left[s\,j\,m_j\right]^{\dagger} \xi(r)\,\hat{L}\cdot\hat{S}\,R_{nl}(r) \times \left[s\,j\,m_j\right] r^2 \sin\theta\, d\theta\, d\phi\, dr$$

$$= \int |R_{nl}(r)|^2 \xi(r)\, r^2 dr \left\langle l\,s\,j\,m_j \left| \vec{L}\cdot\vec{S} \right| l\,s\,j\,m_j \right\rangle$$

$$\langle \xi(r) \rangle_{nl} = \left(\frac{Ze^2}{4\pi\epsilon_0}\right)\frac{1}{2m^2c^2}\,\frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)}$$ for $l \neq 0$

diverges at $l=0$

since $V \to \infty$ at $r \to 0$

and $\psi(r \to 0) \neq 0$

for $l=0$

$$\langle l\; s\,j\,m_j | \hat{\vec{L}}\cdot\hat{\vec{S}} | l\; s\,j\,m_j \rangle$$

$$= \frac{\hbar^2}{2} \langle |\hat{J}^2 - \hat{L}^2 - \hat{S}^2| \rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$s = \frac{1}{2}$

$$j = l + \tfrac{1}{2} \Rightarrow \langle |\hat{L}\cdot\hat{S}| \rangle = \frac{\hbar^2}{2}\left[(l+\tfrac{1}{2})(l+\tfrac{3}{2}) - l(l+1) - \tfrac{3}{4}\right]$$

$$= \frac{\hbar^2 l}{2} \Longrightarrow \boxed{0 \text{ for } l=0} \rightarrow \text{vanishes for } l=0$$

$$j = l - \tfrac{1}{2} \Rightarrow \langle |\hat{L}\cdot\hat{S}| \rangle = \frac{\hbar^2}{2}\left[(l-\tfrac{1}{2})(l+\tfrac{1}{2}) - l(l+1) - \tfrac{3}{4}\right]$$

$$= \frac{\hbar^2}{2}(-l-1)$$

$$\therefore \Delta E_2 \doteq \left(\frac{Ze^2}{4\pi\epsilon_0}\right)\frac{1}{2m^2c^2}\,\frac{Z^3\hbar^2}{a_0^3 n^3 2}\left[\frac{1}{l(l+\frac{1}{2})(l+1)}\right] \times \begin{cases} l & \text{for } j = l+\frac{1}{2} \\ -l-1 & j = l-\frac{1}{2} \end{cases}$$

$$= \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{2m^2c^2}\,\frac{Z^4\,\hbar^2}{\left(\frac{e^2}{4\pi\epsilon_0}\right)^{-3}\left(\frac{\hbar^2}{m}\right)^3 n^3}\left[\;\;''\;\;\right]$$

$$= \frac{1}{4}\left(\frac{e^2}{4\pi\epsilon_0}\right)^4 \frac{Z^4}{\hbar^4 c^4}\,\frac{mc^2}{n^3}\left[\quad\right]$$

$$= \frac{1}{4}\, Z^4 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^4 \frac{mc^2}{n^3}\left[\quad\right]$$

$$= \frac{1}{4}\, Z^4 \alpha^4 \frac{mc^2}{n^3}\left[\;\right]$$

$$= -\frac{1}{2}\left[-\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}\right] Z^2\alpha^2 \frac{1}{n}\left[\quad\right]$$

Bohr radius a_0

$$\frac{mv^2}{a_0} = \frac{e^2}{4\pi\epsilon_0 a_0^2}$$

$$v = \frac{\hbar k}{m} = \frac{\hbar}{m}\frac{2\pi}{\lambda} = \frac{\hbar}{m}\frac{2\pi}{2\pi a_0}$$

$$= \frac{\hbar}{m a_0}$$

$$\therefore \frac{m}{a_0}\left(\frac{\hbar}{m a_0}\right)^2 = \frac{e^2}{4\pi\epsilon_0 a_0^2}$$

$$\Rightarrow a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

Recall $\alpha = \dfrac{e^2}{4\pi\epsilon_0 \hbar c}$

$$a_0^2 c^2 = \frac{e^2 \hbar^2}{4\pi\epsilon_0 m \alpha^2}$$

$$\Delta E_2 \underset{\cancel{\alpha}}{=} -\frac{1}{2} E_n (Z\alpha)^2 \frac{1}{n} \frac{1}{l(l+\frac{1}{2})(l+1)} \times \begin{cases} l & \text{for } j=l+\frac{1}{2} \\ -l-1 & \text{for } j=l-\frac{1}{2} \end{cases}$$

E_n : Recall our interpretation of $\frac{1}{\alpha}$ as the highest Z value which can sustain stable electron orbits with electron moving (at most) as fast as c

$\therefore \frac{1}{\alpha} \longrightarrow c$

$\Rightarrow Z \longrightarrow \alpha c Z$

$\therefore -\frac{1}{2}mv^2 = -\frac{1}{2}mc^2(\alpha Z)^2$ or more correctly as per Bohr quantization

$$E_n = -\frac{1}{2}mc^2\left(\frac{\alpha Z}{n}\right)^2$$

Remember that $\langle \vec{L}\cdot\vec{S}\rangle = 0$ for $l=0$

$\Rightarrow \underline{\Delta E_2 = 0 \text{ for } l=0}$ (although it appears from [illegible] alone that it may contribute for $\langle L\cdot S\rangle$ via the factor)

$\underline{\text{Darwin term:}}$ $\Delta E_3 = \left\langle \psi_{n00} \middle| \frac{\pi\hbar^2}{2m^2c^2}\frac{Ze^2}{4\pi\varepsilon_0}\delta(r) \middle| \psi_{n00} \right\rangle$ omitting the spinor part.

(already argued that it is valid for $l=0$ only)

$$= \frac{\pi\hbar^2}{2m^2c^2}\frac{Ze^2}{4\pi\varepsilon_0}\left|\psi_{n00}(r=0)\right|^2$$

$$= \frac{\pi\hbar^2}{2m^2c^2}\frac{Ze^2}{4\pi\varepsilon_0}\,4\frac{Z^3}{n^3a_0^3}\frac{1}{4\pi}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar^2}{2m^2c^2}\frac{Z^4}{\left(\frac{e^2}{4\pi\varepsilon_0}\right)^{-3}\left(\frac{\hbar^2}{m}\right)^3}\frac{1}{n^3}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0}\right)^4\frac{Z^4}{\hbar^4c^4}\frac{mc^2}{2}\frac{1}{n^3}$$

$$= (\alpha Z)^4\frac{mc^2}{2}\frac{1}{n^3}$$

$$= \frac{1}{2}mc^2\left(\frac{Z\alpha}{n}\right)^2(\alpha Z)^2\frac{1}{n}$$

$$= -E_n(\alpha Z)^2\frac{1}{n}$$ only for $l=0$

Recall $R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2}e^{-\frac{Zr}{a_0}}$

$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}}$

$\frac{1}{\sqrt{4\pi}}$ will come for Y_{00}

Net correction $\Delta E_{tot} = \Delta E_1 + \Delta E_2 + \Delta E_3$

$\underline{l=0}$; $\Delta E_2 = 0$

$$\therefore \Delta E_{tot} = -\frac{E_n(\alpha Z)^2}{n^2}\left[\left(\frac{3}{4}-\frac{n}{\frac{1}{2}}\right)+0+n\right] = -\frac{E_n(\alpha Z)^2}{n^2}\left[\frac{3}{4}-n\right]$$

$$= \frac{E_n(\alpha Z)^2}{n^2}\left[\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right]$$

for $l \geq 1$, $j = l + \frac{1}{2}$

$$\Delta E_{for} = \Delta E_1 + \Delta E_2 + \underset{0}{\underset{\parallel}{\Delta E_3}}$$

→ since Darwin term contributes only for $l = 0$

$$= -\frac{E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}} + \frac{n l}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= -\frac{E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{2nl(l+1) - nl}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= -\frac{E_n (\alpha Z)}{n^2}\left[\frac{3}{4} - \frac{2nl(l+\frac{1}{2})}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= \frac{E_n (\alpha Z)^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]$$

for $l \geq 1$, $j = l - \frac{1}{2}$

$$\Delta E_{for} = -\frac{E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}} - \frac{n(l+1)}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= -\frac{E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{2nl(l+1) + n(l+1)}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= -\frac{E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{2n(l+1)(l+\frac{1}{2})}{2l(l+1)(l+\frac{1}{2})}\right]$$

$$= \frac{-E_n (\alpha Z)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l}\right]$$

$$= \frac{E_n (\alpha Z)^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]$$

$$\therefore \Delta E_{for} = \frac{E_n (\alpha Z)^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]$$ for all values of l.

$$\therefore E_{nl} \xrightarrow[\text{after fine structure correction}]{} E_{nj} = \underset{-ve}{\underset{\downarrow}{E_n}}\left[1 + \frac{(\alpha Z)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

$E_{nj} < E_{nl}$ as $Z \uparrow$ binding of electron increases – think of length contraction $L = L_0\sqrt{1-\frac{v^2}{c^2}}$

Note for $n=1$, $l=0$, $j=\frac{1}{2} \Rightarrow \frac{n}{j+\frac{1}{2}} = 1$

$n=2 \Rightarrow l_{max} = 1 \Rightarrow j_{max} = \frac{3}{2} \Rightarrow \left(\frac{n}{j+\frac{1}{2}}\right)_{min} = 1$; $\left(\frac{n}{j+\frac{1}{2}}\right)_{max} = 2$

$j_{min} = \frac{1}{2}$