

Finestructure Intervals in Hydrogenlike Atoms

no specific reference
in Dawydov & Sakurai

1) We now consider the H-atom problem where the electron has spin \vec{S} , and therefore a magnetic moment...

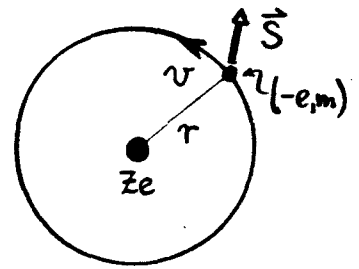
$$\rightarrow \vec{\mu}_s = -g_s \mu_0 \vec{S}. \quad (1)$$

Here \vec{S} is dimensionless (i.e. it is measured in units of \hbar), and $\vec{S}^2 = s(s+1) = 3/4$, $S_z = \pm s = \pm \frac{1}{2}$ for an electron.

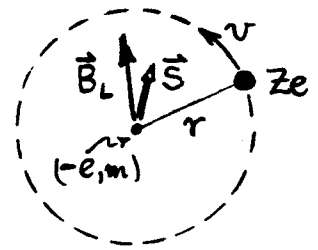
Also, in Eq. (1): $\mu_0 = e\hbar/2mc$ is the Bohr magneton, and $g_s = 2$ (Dirac value). For now, the proton (Ze) will remain spinless... what we will look at is how the e-moment $\vec{\mu}_s$ couples to the magnetic field \vec{B}_L generated

by the apparent motion of the proton about the electron. This coupling (the so-called "spin-orbit coupling") generates the fine structure levels of the atom.

motion in proton restframe



motion in electron restframe



2) Per above sketch, in the rest frame of the electron, the orbiting proton Ze generates a magnetic field of size...

$$\rightarrow \vec{B}_L = \vec{E} \times \frac{\vec{v}}{c} = (Ze \frac{\vec{r}}{r^3}) \times \frac{\vec{v}}{c} = \frac{Ze}{mc} \frac{1}{r^3} (\vec{r} \times m\vec{v})$$

↖ orbital & momentum

$$\text{or } \underline{\underline{\vec{B}_L = 2Z(\mu_0/r^3) \vec{L}}} \quad \int^{\infty} \mu_0 = e\hbar/2mc, \quad \vec{L} \text{ is dimensionless (units of } \hbar). \quad (2)$$

This is the apparent field at the site of the electron. Then, apparently, the e-moment $\vec{\mu}_s$ will exhibit the magnetic energy...

$$\rightarrow \boxed{E_{fs} = (-)\vec{\mu}_s \cdot \vec{B}_L = 2(Zg_s\mu_0^2/r^3) \vec{S} \cdot \vec{L}} \quad (3)$$

REMARKS

1. We see why the finestructure energy E_{fs} is said to be due to "spin-orbit coupling"... we have $E_{fs} \propto \vec{S} \cdot \vec{L}$, a coupling of the electron spin & momentum to its orbital & momentum. $\vec{S} \cdot \vec{L}$ coupling affects all electrons in all atoms.

2. In Eq. (3), the electron-proton separation is $r \sim a_0 = \hbar^2/mc^2$ (Bohr radius), and $\vec{S} \cdot \vec{L}$ is just a number ~ 1 . Then, to within numerical factors, the size is

$$\rightarrow E_{fs} \sim \mu_0/a_0^3 \sim \left(\frac{e\hbar}{mc} / \frac{\hbar^2}{mc^2} \right)^2 \frac{1}{a_0} = \alpha^2 \frac{e^2}{a_0} \sim \alpha^2 \times \text{electronic binding.} \quad (4)$$

Where $\alpha = e^2/\hbar c \approx 1/137$ is the finestructure constant (again!). So we are considering energy corrections of $O(\alpha^2)$ relative, and $O(\alpha^4)$ absolute (on the energy scale mc^2). In this sense, the E_{fs} which follows from Eq. (3) is a perturbation on $E^{(\text{electronic})}$; we expect $E(\text{fine}) = mc^2 [O(\alpha^2) + O(\alpha^4) + O(\alpha^6) + \dots]$.

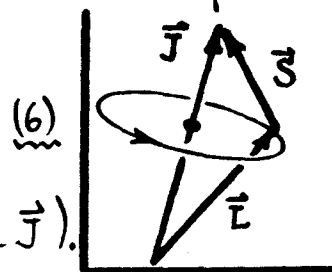
3. While E_{fs} in Eq. (3) is the apparent spin-orbit energy, it is not quite right; in fact it is too big by a factor of 2. The actual fs interaction energy is:

$$E_{fs} = \zeta \vec{S} \cdot \vec{L}, \quad \text{w/ } \zeta = Z g_s \mu_0^2 / r^3. \quad \text{Corrected for Thomas precession.} \quad (5)$$

The factor 2 is taken out by a relativistic correction known as the Thomas precession effect[†], which is basically a time-dilation correction that occurs in transforming between the electron and proton rest frames. We will discuss the Thomas precession below... for now, we just accept that ζ has lost a factor 2 in going from Eq. (3) to Eq. (5).

3) Since the electron's orbital & spin momenta $\vec{L} \nparallel \vec{S}$ are coupled [per Eq. (5)] by the magnetic interaction just described, then--by the Vector Model (see p. 4 [12] above)--they add together to form a resultant, viz.

$$\rightarrow \vec{J} = \vec{L} + \vec{S},$$



and they precess rapidly about \vec{J} (so as to average out comp^{ts} $\perp \vec{J}$).

It is appropriate to move from a state wavefn $|n; l, m_l; s, m_s\rangle$, characterized by principal quantum # n , where $\vec{L}^2 \nparallel L_z$ and $\vec{S}^2 \nparallel S_z$, are diagonal, to a

[†] Jackson "Classical Electrodynamics" (2nd ed., 1975), Sec. 11.8.

new wavefun $|n; l, s; j, m_j\rangle$, where \vec{L}^2 , \vec{S}^2 , \vec{J}^2 & J_z are diagonal. We "lose" m_l & m_s here [their directions must now be referred to the precession axis... in fact $m_l + m_s = m_j$], but we gain j & m_j . Thus, do a Clebsch-Gordan transform:

$$|nlm_l s m_s\rangle \rightarrow |nl s j m_j\rangle = \sum_{m_l, m_s} C(m_l m_s j m_j) |nl m_l\rangle \otimes |s m_s\rangle \Big|_{m_l + m_s = m_j}, \quad (7)$$

(see pp. 4 [3]-[6] above). The C 's are the (numerical) Clebsch-Gordan coefficients, the $|nl m_l\rangle = \frac{1}{r} R_{nl}(r) Y_{lm_l}(\theta, \varphi)$ are the spinless H-atom wavefuns, and the $|s m_s\rangle$ are the spin $1/2$ spinors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ & $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ for spin \uparrow & \downarrow [Sakurai, Sec (3.2)]. The symbol \otimes indicates a direct product state (the $|nl m_l\rangle$ & $|s m_s\rangle$ are disjoint).

We don't need details of the CG transform in Eq. (7) just yet, but we can use

$$\rightarrow \vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}, \quad \text{so} \quad \vec{L} \cdot \vec{S} = \frac{1}{2} [\vec{J}^2 - \vec{L}^2 - \vec{S}^2]; \quad (8)$$

... so, w.r.t. eigenfuns $|nl s j m_j\rangle$...

$$\langle \vec{L} \cdot \vec{S} \rangle = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)]. \quad (9)$$

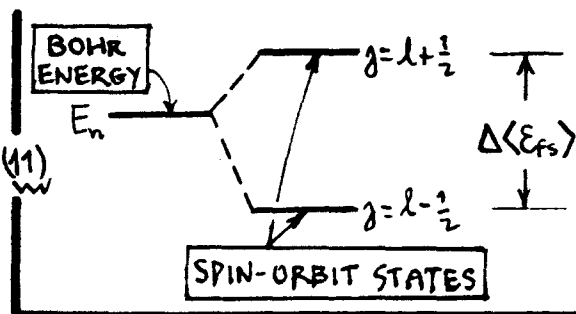
This is a major utility of the CG transform in Eq. (7)... in the "coupled repⁿ" (i.e. the $|nl s j m_j\rangle$, where \vec{L} & \vec{S} have coupled to form \vec{J}), the coupling $\vec{L} \cdot \vec{S}$ is precisely diagonal. In fact we can calculate all values of $\langle \vec{L} \cdot \vec{S} \rangle$ here...

$$\left[\begin{array}{l} s = \frac{1}{2} \text{ for electron} \Rightarrow j = l \pm \frac{1}{2} \quad (l \neq 0), \text{ or } j = \frac{1}{2} \quad (l=0, \text{ S-states}) \\ \text{so } \langle E_{fs} \rangle = \zeta_{AV} \langle \vec{L} \cdot \vec{S} \rangle, \quad \text{w} // \quad \zeta_{AV} = Z g_s \mu_0^2 \langle 1/r^3 \rangle; \end{array} \right] \quad (10)$$

$$\Rightarrow \langle E_{fs} \rangle \equiv 0, \text{ in S-states } (l=0);$$

$$\text{and} // \rightarrow \langle E_{fs} \rangle = \begin{cases} +\frac{1}{2} l \zeta_{AV}, & \text{for } j = l + \frac{1}{2}, \\ -\frac{1}{2} (l+1) \zeta_{AV}, & \text{for } j = l - \frac{1}{2}. \end{cases} \quad (11)$$

$$\text{so} // \Delta \langle E_{fs} \rangle = (l + \frac{1}{2}) \zeta_{AV}, \text{ fs splitting}. \quad (12)$$



ASIDE Spectroscopic Notation Revisited

Before, we denoted Bohr states E_n by $n[l]$, e.g. $\begin{cases} 2P \Rightarrow n=2, l=1; \\ 3D \Rightarrow n=3, l=2; \text{ etc.} \end{cases}$

Now, states with energy $E_n + \langle E_{fs} \rangle$ must have g -values indicated. The g -value is attached as a subscript, i.e. $n[l]_g$. Thus we have new states...

$$\left[n[l] \xrightarrow[\text{coupling}]{\vec{L} \cdot \vec{S}} \begin{cases} n[l]_{g=l+\frac{1}{2}} \\ n[l]_{g=l-\frac{1}{2}} \end{cases}, \text{ e.g. } \begin{array}{l} 2P \rightarrow 2P_{3/2} \text{ \& } 2P_{1/2}; \\ 3D \rightarrow 3D_{5/2} \text{ \& } 3D_{3/2}. \end{array} \right] \text{ fs doublets. } \quad (13)$$

4) Now we evaluate the fs "Coupling constant" $\zeta_{Av} = Z g_s \mu_0^2 \langle 1/r^3 \rangle$ of Eq. (10). The $\langle \rangle \Rightarrow$ a QM expectation value in the state $|nl s m_s\rangle$. But since $1/r^3$ is independent of spin & orbital & momentum (a fact already used in Eq. (10)), then only the $|nl m_l\rangle$ are involved, and we can use the well-known result...

$$\langle nl m_l | \frac{1}{r^3} | nl m_l \rangle = \left(\frac{Z}{a_0} \right)^3 / l(l+1)(l+\frac{1}{2}), \quad \text{for } l \neq 0, \text{ as quoted e.g. in Davydov Eq. (38.17e)} \quad (14)$$

$$\xrightarrow{\text{sof}} \zeta_{Av}(nl) = g_s (Z^4/n^3) \left[\frac{\mu_0^2}{a_0^3} \right] / l(l+1)(l+\frac{1}{2}). \quad (15)$$

The combination of atomic cnsts in [] in Eq. (15) can be written as...

$$\mu_0^2/a_0^3 = \left(\frac{e\hbar}{2mc} \right)^2 / \left(\frac{\hbar^2}{me^2} \right)^3 = \frac{1}{4} \alpha^4 mc^2, \quad \text{w/ } \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137};$$

$$\xrightarrow{\text{sof}} \zeta_{Av}(nl) = \frac{1}{4} g_s (Z\alpha)^4 mc^2 / n^3 l(l+1)(l+\frac{1}{2}). \quad (16)$$

Put $g_s = 2(1+a)$, $a \approx 0.001$ the electron g -factor anomaly. The fs energies are:

$$\langle E_{fs} \rangle = (1+a) \frac{(Z\alpha)^2 |E_n|}{n(2l+1)} \times \begin{cases} +1/(l+1), & \text{for } g=l+\frac{1}{2} \\ -1/l, & \text{for } g=l-\frac{1}{2} \end{cases}; \quad |E_n| = \frac{(Z\alpha)^2 mc^2}{2n^2} \quad \text{BOHR ENERGIES}$$

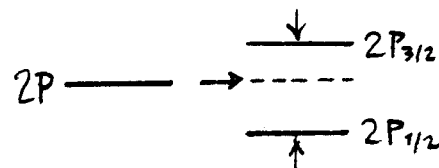
$$\text{And/} \quad \boxed{\Delta \langle E_{fs} \rangle = (1+a) \frac{(Z\alpha)^2 |E_n|}{n l(l+1)}} \quad (17)$$

$$\xrightarrow{\text{sof}} \begin{array}{c} \text{---} n[l]_{g=l+\frac{1}{2}} \\ \uparrow \\ \text{---} n[l] \text{---} \xrightarrow{\Delta E_{fs}} \text{---} \\ \downarrow \\ \text{---} n[l]_{g=l-\frac{1}{2}} \end{array}$$

EXAMPLE Use Eq. (17) to calculate the fs splitting in the 2P state of atom H.

Have $Z=1$, and $n=2$, $l=1$. Eq. (17) yields...

$$\rightarrow \Delta \langle E_{fs} \rangle = \frac{1}{32} (1+a) \alpha^4 m c^2.$$



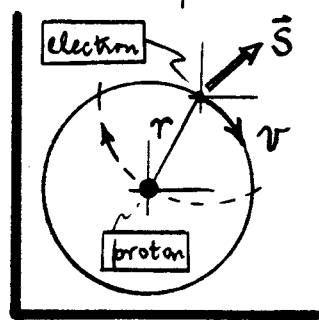
Use the combination $\frac{1}{2} \alpha^2 m c^2 = h c R_{\infty}$ (hydrogen ionization energy, ²⁴ R_{∞} = Rydberg const for ∞ nuclear mass), since this combⁿ has been measured more accurately. Then

$$\rightarrow \Delta \langle E_{fs} \rangle / h = \frac{1}{16} (1+a) \alpha^2 c R_{\infty} = \underline{10,961.98 \text{ MHz}}. \quad (18)$$

The measured value is $10,969.15 (\pm 10 \text{ ppm}) \text{ MHz}$ [Shyn, Rebane, Robiscoe, and Williams, Phys. Rev. A 3, 116 (1971)], so our simple theory is pretty close -- we are low by only 0.07% for $\Delta \langle E_{fs} \rangle$ in the 2P state. Still, the difference between expt. & theory is $\sim 70 \times$ the measurement error, so a more refined theory is needed.

5) Now we discuss the Thomas precession factor of 2, mentioned below Eq. (5). It results from a time-dilation effect. Following is a heuristic derivation of the factor 2, which contains the basic physics. ⁹

1. Assume a circular electron orbit for simplicity. If -- in the electron "rest" frame -- the time required for the proton to complete one (apparent) revolution is T' , then in the proton rest frame the revolution time is $\underline{T = \gamma T'}$, ²⁵ $\gamma = [1 - (v/c)^2]^{-1/2}$ and v is the electron orbital velocity [this is the standard relation of a proper time T' for the electron to the corresponding T in a moving frame; it need not be modified for $v = \text{const}$ in a cir-



⁹ More complete treatments can be found in Duncoff & Inglis, Phys. Rev. 50, 784 (1936); Aharoni "Special Theory of Relativity" (Oxford, 1959), pp. 52-53; Jackson, op.cit. p. fs 6.

cular orbit]. The orbital ω velocities will then be: $\omega' = 2\pi/T'$ (in e rest frame), and $\omega = 2\pi/T = \omega'/\gamma < \omega'$ (in p rest frame).

2. Since the electron spin \vec{S} maintains a fixed direction in space in the e rest-frame, then in the p rest-frame, \vec{S} appears to precess at the difference freq^y

$$\rightarrow \Omega_T = \omega' - \omega = (\gamma - 1)\omega \approx \frac{1}{2}(v/c)^2 \omega. \quad (19)$$

Ω_T is called the Thomas precession frequency. We can find a more relevant form for it by noting that for a circular orbit...

$$\left\{ \begin{array}{l} m r^2 \omega = \hbar L \\ m v^2 / r = Z e^2 / r^2 \end{array} \right\} \Omega_T \approx \frac{1}{2}(v/c)^2 \omega = 2(\mu_0 / \hbar) Z \mu_0 L / r^3. \quad (20)$$

Where L is the dimensionless electron orbital \hbar momentum (units of \hbar).

3. The precession of \vec{S} at Ω_T (in p-frame) can be attributed to the presence of a (fictitious) magnetic field H_T which produces a Larmor precession at frequency Ω_T , i.e. we define this "Thomas field" by

$$\gamma H_T = 2(\mu_0 / \hbar) H_T = \Omega_T \Rightarrow \boxed{H_T \approx Z \mu_0 L / r^3}. \quad (21)$$

Since the actual proton revolution freq. ω is less than the apparent freq. ω' in the electron frame, the sense of H_T must be to reduce the magnetic field due to the proton's motion as seen by the electron. Previously -- in the e-frame -- we calculated that field to be $H_L = 2Z\mu_0 L / r^3$ [see Eq. (2) above]. Now, we must take the effective field as...

$$\boxed{H_L(\text{eff.}) = H_L - H_T = \frac{1}{2} H_L.} \quad (22)$$

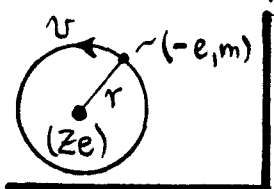
So, here's the Thomas factor-of-two, as discussed below Eq. (5). This calculation is correct to $\mathcal{O}(v/c)^2$ [per Eq. (19)]. Higher-order corrections remain.

6) The spin-orbit energies E_{fs} of Eq. (17) [here drop the clumsy $\langle \rangle$] are of order α^2 relative to the Bohr energies, as we may emphasize by writing ($g_s = 2$):

$$\left\{ \begin{array}{l} \text{UNPERTURBED BOHR ENERGIES: } E_n = -\frac{1}{2} (Z\alpha/n)^2 mc^2, \\ \text{SPIN-ORBIT ENERGIES } \left\{ \begin{array}{l} E_{fs}^{(\pm)} = \mp E_n \left(\frac{Z\alpha}{n} \right)^2 n / (2l+1) (j + \frac{1}{2}), \text{ for } j = l \pm \frac{1}{2} (l \neq 0) \end{array} \right. \\ \xrightarrow{S_{op}} E_{nl}^{(\pm)} = E_n + E_{fs}^{(\pm)} = E_n \left\{ 1 \mp \left[\frac{n}{(2l+1)(j + \frac{1}{2})} \right] \left(\frac{Z\alpha}{n} \right)^2 \right\}. \end{array} \right. \quad (23)$$

\uparrow fs correction

But $(Z\alpha/n) = \frac{v}{c}$, where v is the nominal electron velocity in the n^{th} orbit. From the simple Bohr model (for circular orbit of radius r)...



$$\left. \begin{array}{l} mv^2/r = Ze^2/r^2 \\ mvr = n\hbar \end{array} \right\} \beta = \frac{v}{c} = \frac{Z\alpha}{n}. \quad (24)$$

So the spin-orbit energies $E_{fs}^{(\pm)}$ are corrections of $O(\beta^2)$ relative to the Bohr energies E_n , and $O(\beta^4)$ relative to the electron intrinsic energy mc^2 .

This is the language of relativistic corrections (of which the Thomas correction is just the most prominent).

We will now show that there are other "natural" relativistic corrections of $O(\beta^4)$. These must be accounted for in order to get the H-atom energy levels correct to $O(\alpha^4)$... which was our goal per remarks below Eq. (4).

7) Go back to the unperturbed (spinless) H-atom problem, viz.

$$\mathcal{H}_0 |nlm\rangle = E_n |nlm\rangle, \text{ where (nonrelativistically):}$$

$$\mathcal{H}_0 = K + V \quad \left\{ \begin{array}{l} K = \vec{p}^2 / 2m, \text{ Newtonian K.E.} \\ V = -Ze^2/r, \text{ Coulomb pot.} \end{array} \right. \quad (25)$$

Relativistically, the K.E. is found from...

$$\rightarrow mc^2 + K = \sqrt{(mc^2)^2 + (\vec{p}c)^2} = mc^2 \left[1 + \frac{1}{2}(\vec{p}/mc)^2 - \frac{1}{8}(\vec{p}/mc)^4 + \dots \right]$$

$$\text{So // } \boxed{K = \underbrace{\frac{1}{2m} \vec{p}^2}_{\textcircled{1}} - \underbrace{\frac{1}{8m^3c^2} \vec{p}^4}_{\textcircled{2}} + \dots} \quad \begin{array}{l} \textcircled{1} \text{ is } \mathcal{O}(\beta^2) [\mathcal{O}(\alpha^2)] \leftrightarrow \text{for Bohr energies;} \\ \textcircled{2} \text{ is } \mathcal{O}(\beta^4) [\mathcal{O}(\alpha^4)] \leftrightarrow \text{Comparable to } E_{fs}. \end{array}$$

So we get a "natural" $\mathcal{O}(\alpha^4)$ correction out of the unperturbed atom. We incorporate it in the Hamiltonian as... (26)

$$\left[\mathcal{H}_0 \rightarrow \mathcal{H} = \mathcal{H}_0 + \mathcal{V}(\text{rel.}), \quad \text{w// } \underline{\underline{\mathcal{V}(\text{rel.}) = -\vec{p}^4/8m^3c^2}}, \text{ then } \mathcal{O}(\alpha^4). \right] \quad (27)$$

To see how $\mathcal{V}(\text{rel.})$ corrects the Bohr energies E_n , we could go back to Eq. (25), put $\vec{p} = -i\hbar \nabla$ as usual, and solve the 4th order PDE. This is tedious.

Instead we use a clever trick, first noted by Pauli. It is that the operator $\mathcal{V}(\text{rel.})$, representing our new relativistic correction, commutes with \mathcal{H}_0 [¶]

$$\rightarrow [\mathcal{H}_0, \mathcal{V}(\text{rel.})] \equiv 0 \Rightarrow \langle \mathcal{V}(\text{rel.}) \rangle \text{ is } \underline{\text{diagonal}} \text{ w.r.t. the } |nlm\rangle. \quad (28)$$

So we need not even go to the coupled repⁿ to get $\langle \mathcal{V}(\text{rel.}) \rangle$... we just need expectation values w.r.t. the unperturbed states $|nlm\rangle$. It becomes semi-trivial if we note...

$$\left[\begin{array}{l} \frac{1}{2m} \vec{p}^2 = E_n - V, \text{ w.r.t. } |nlm\rangle, \text{ and } : [\vec{p}^2, V] = 0, \text{ imply :} \\ \underline{\underline{\mathcal{V}(\text{rel.}) = -(E_n - V)^2/2mc^2}}, \text{ w.r.t. } |nlm\rangle. \end{array} \right] \quad (29)$$

The eigenenergies of $\mathcal{H}_0 \rightarrow \mathcal{H}_0 + \mathcal{V}(\text{rel.})$ in Eq. (27) are then...

$$\rightarrow \langle \mathcal{H} \rangle = \langle \mathcal{H}_0 \rangle + \langle \mathcal{V}(\text{rel.}) \rangle = E_n - \frac{1}{2mc^2} \left\langle \left[E_n + \frac{Ze^2}{r} \right]^2 \right\rangle \quad (30)$$

(next page)

¶ Proof that $[\mathcal{H}_0, \mathcal{V}(\text{rel.})] = 0$ is straight forward. Key is to show $[\vec{p}^2, V(r)] = 0$.

The $V(\text{rel.})$ correction energy is now easily worked out...

$$\left[\begin{aligned} \langle [E_n + \frac{Ze^2}{r}]^2 \rangle &= E_n^2 + 2E_n Ze^2 \langle \frac{1}{r} \rangle + (Ze^2)^2 \langle \frac{1}{r^2} \rangle; \\ \text{use: } \langle \frac{1}{r} \rangle &= \frac{1}{n^2} \left(\frac{Z}{a_0} \right), \quad \langle \frac{1}{r^2} \rangle = \frac{1}{n^3(l+\frac{1}{2})} \left(\frac{Z}{a_0} \right)^2 \quad \checkmark \text{ [Davydov Eqs. (38.17)]}. \end{aligned} \right. \quad (31)$$

$\checkmark a_0 = \hbar^2 / me^2$

... plus some algebra, to get energies...

$$\langle \mathcal{H} \rangle = E_n \left[1 + \underbrace{\left(\frac{Z\alpha}{n} \right)^2}_{\text{Bohr term}} \underbrace{\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4} \right)}_{V(\text{rel.}) \text{ term}} \right] \quad \checkmark \text{ for S-states } (l=0), \text{ replace } l \text{ by } j = \frac{1}{2} \text{ in this equation.} \quad (32)$$

These are the eigenenergies of the spinless H-atom, correct to $\mathcal{O}(\beta^4)$ [$\mathcal{O}(\alpha^4)$].
Notice that S-states are actually shifted (unlike zero shift for fs calcⁿ).

8) Now we gather the $\mathcal{O}(\beta^4)$ corrections, $E_{fs}^{(\pm)}$ and the $V(\text{rel.})$ term in Eq. (32), together to form the overall H-atom energies correct to $\mathcal{O}(\alpha^4)$...

$$E_{nj}^{(\pm)} = E_n + \langle V(\text{rel.}) \rangle + E_{fs}^{(\pm)} = E_n \left[1 + \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4} \right) + \left(\frac{Z\alpha}{n} \right)^2 \frac{n}{(2l+1)(j+\frac{1}{2})} \right] \quad \checkmark \text{ } j = l \pm \frac{1}{2}$$

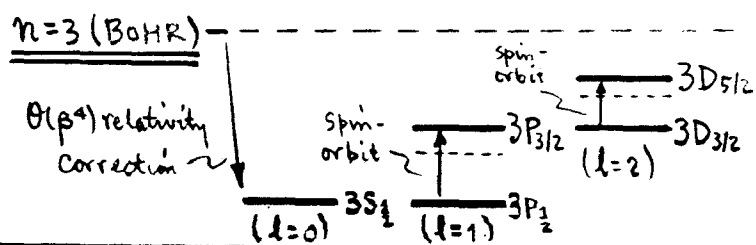
... combining terms, find...

$$E_{nj} = E_n \left\{ 1 + \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right] \right\} \quad \checkmark \text{ good for all } j \text{ (incl. } j = \frac{1}{2} \text{ } \checkmark l=0) \quad (33)$$

REMARKS

see Davydov Eq. (67.14).

1. E_{nj} of Eq. (33) agrees with the result from Dirac's fully relativistic eqn to $\mathcal{O}(\alpha^4)$.
2. The l -degeneracy in E_n has been removed, but now states with the same j are degenerate. In particular, the hydrogenic $2S_{1/2}$ & $2P_{1/2}$ states are degenerate.
3. An energy level in the atom has now been corrected as follows...



The ordering of levels is radically changed by $V(\text{rel.})$. But the splitting of Eq. (17) is not changed, since $\langle V(\text{rel.}) \rangle$ depends on l , but not j .