6.4. Fine Structure of the Hydrogen Atom Spectrum

One of the most important examples of the utility of R-S perturbation theory is in the study of atomic spectra. The dominant force in atomic systems is that given by the Coulomb potential,

$$V(R) = -\frac{q^2}{4\pi\epsilon_0}\frac{1}{R} = -\frac{e^2}{4\pi\epsilon_0 R}$$, for the

electron in the field of a proton. As we have seen in the multi-electron system of Helium-like atoms, the inter-electron Coulomb potential alters the nuclear-electron Coulomb spectrum. Even in single electron systems like Hydrogen, there are corrections to the Coulomb spectrum due to additional forces on the electron. The dominant corrections in Hydrogen come from the relativistic corrections to the electrons motion. The complete special relativistic quantum mechanical laws of motion for an electron in a Coulomb field of a (infinitely heavy) proton was discovered by Dirac.

The Dirac equation however can be approximated in terms of a power series expansion in the electron's velocity over the speed of light v/c. We will confine our selves to the study of the Dirac Hamiltonian for the first order $\frac{v}{c}$ corrections to the electron Coulomb motion. What is Dirac found that in first order his complete description of the relativistic electron motion was described by the Schrödinger Hamiltonian

$$H = mc^2 + \underbrace{\frac{1}{2m}\vec{P}^2 + V(R)}_{\equiv H_0} + H_{fs}$$

- mc^2: Constant rest energy of e^- (just adds a constant to all energies)
- H_0: Central potential Coulomb Hamiltonian
- H_{fs}: fine structure Hamiltonian

where the corrections to the simple Hydrogen Coulomb potential Hamiltonian "H atom" given by the "fine structure" Hamiltonian H_{fs}

$$H_{fs} = H_{Kin} + H_{so} + H_D$$

with H_{Kin} the special relativistic correction to the kinetic energy

$$T = E - mc^2$$

$$= \sqrt{\vec{p}^2c^2 + m^2c^4} - mc^2$$

$$= mc^2\left(1 + \frac{\vec{p}^2}{m^2c^2}\right)^{1/2} - mc^2$$

$$= mc^2\left(1 + \frac{1}{2}\frac{\vec{p}^2}{m^2c^2} - \left(\frac{1}{2}\right)^3\left(\frac{\vec{p}^2}{m^2c^2}\right)^2 + \cdots\right) - mc^2$$

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

Thus $\boxed{H_{Kin} = -\frac{1}{8m^3c^2}\vec{p}^4}$.

The electron, as we know, has spin and the "spin-orbit" Hamiltonian, H_{so}, describes the corrections to the Coulomb Hamiltonian due to it.

Physically these arise due to the motion of the electron in the nuclear electrostatic field. In the electron's frame, according to special relativity, there is a magnetic field $\vec{B}'$ as well as electric field $\vec{E}'$. To lowest order the $\vec{B}'$ field is given by $\vec{B}' = -\frac{1}{c^2}\vec{v}\times\vec{E}$ (Griffiths eq. 10.120)

where $\vec{v} = \frac{1}{m}\vec{p}$ is the velocity of the electron in the nucleus' frame. Since the electron has a magnetic moment due to its spin

$$\vec{\mu} = \vec{M} = \frac{\pm q}{m}\vec{S} = g\frac{q}{2e}\mu_B\frac{1}{\hbar}\vec{S}$$

$\vec{M} = \gamma\vec{S}$

anomalous magnetic moment $g \approx 2$ for e^- (by Dirac theory)

Bohr Magneton $\mu_B = \frac{e\hbar}{2m}$

it interacts with the nuclear magnetic field

$$H_{mag} = -\vec{M}\cdot\vec{B}'$$

$\vec{M} = \gamma\vec{S}$

Now $\vec{B}' = -\frac{1}{c^2}\frac{1}{m}\vec{p}\times\vec{E}$ but the Coulomb field is $\vec{E} = -\frac{1}{q}\frac{dV(R)}{dR}\frac{\vec{R}}{R}$,

Thus $\vec{B}' = \frac{1}{qc^2}\frac{1}{R}\frac{dV(R)}{dR}\frac{1}{m}\vec{p}\times\vec{R}$

but $\vec{p}\times\vec{R} = -\vec{R}\times\vec{p} = -\vec{L}$; hence

$$H_{mag} = +\frac{1}{m^2c^2}\frac{1}{R}\frac{dV(R)}{dR}\vec{L}\cdot\vec{S}$$

This result is actually a factor of 2 too large, we must include the precession of the electron spin wrt the nucleus' frame this Thomas precession results in an additional interaction energy

$$H_{Thomas} = -\frac{1}{2}H_{mag}$$

Thus we finally obtain

$$H_{so} = H_{mag} + H_{Thomas}$$

$$\boxed{H_{so} = \frac{1}{2m^2c^2}\frac{1}{R}\frac{dV(R)}{dR}\vec{L}\cdot\vec{S}}$$

$$\frac{e}{}$$

This is a "spin-orbit coupling" due to the interaction of the electron's spin magnetic moment and the magnetic field in the electron's frame due to its motion in the nuclear electric field.

Finally, the last correction to the electron's Hamiltonian that I've found in lowest order is the "Darwin" term H_D. In the Dirac equation the interaction of the electron with the nuclear Coulomb field is local, it depends only on the instantaneous position $\vec{R}$ of the electron. When approximating this interaction as a $1/c$ power series, the corrections from interactions with the field the order of a Compton wavelength $\frac{\hbar}{mc}$ away arise. Thus we effectively Taylor expand the Coulomb field about the electron's position and smear it out over a volume the order of a Compton wavelength cubed, $\left(\frac{\hbar}{mc}\right)^3$. Heuristically

$$V(\vec{R}) \longrightarrow \int d^3\epsilon\, f(\vec{\epsilon})\, V(\vec{R}+\vec{\epsilon})$$

where $f(\vec{\epsilon})$ vanishes outside a Compton wavelength in all directions i.e. it is spherically symmetric and has a volume integral equal to 1.

So

$$\int d^3\epsilon\, f(\vec{\epsilon})\, V(\vec{R}+\vec{\epsilon}) = \int d^3\epsilon\, f(\vec{\epsilon}) \Big[V(\vec{R}) + \vec{\epsilon}\cdot\vec{\nabla} V(\vec{R}) + \tfrac{1}{2}\epsilon^i\epsilon^j \nabla_i\nabla_j V + \cdots \Big]$$

$$\approx V(R) + \frac{2\pi}{3}\int_0^{\hbar/mc} d\epsilon\, \epsilon^4 f(\epsilon)\left(\nabla^2 V(R)\right)$$

where $\int d^3\epsilon f(\epsilon)\,\vec{\epsilon} = 0$ due to the spherical symmetry of $f(\vec{\epsilon})$.

$$\approx V(R) + a\left(\frac{\hbar}{mc}\right)^2 \nabla^2 V(R)$$

where a is a constant depending upon the explicit form of $f(\vec{\epsilon})$ that is derived from the Dirac equation. We can only quote Dirac's result

$$a = \frac{1}{8}.$$

Thus $$H_D = \frac{\hbar^2}{8m^2c^2}\nabla^2 V(R)$$

Substituting the Coulomb potential $V(R) = \frac{-e^2}{R 4\pi\epsilon_0}$ we find

$$H_D = -\frac{\hbar^2 e^2}{4\pi\epsilon_0 8m^2c^2}\nabla^2\left(\frac{1}{R}\right)$$

$$= -4\pi\delta^3(\vec{R})$$

So $$\boxed{H_D = \frac{\pi e^2\hbar^2}{2m^2c^2}\delta^3(\vec{R})}$$

Since we are using C-M coordinates here $\delta^3(\vec{R})$ implies the electron is in contact with the nucleus, which is at the origin. Thus such a term $\delta^3(\vec{R})$ in the Hamiltonian is called a "Contact term".

Thus we find (from Dirac theory) the lowest order special relativistic corrections to the simple Hydrogen Coulomb Hamiltonian (dropping the inconsequential constant rest mass energy)

$$H = H_0 + H_{fs} \quad ; \quad H_0 = \frac{1}{2m}\vec{P}^2 + V(R)$$

$$H_{fs} = H_{kin} + H_{so} + H_D$$

with $V(R) = -\frac{e^2}{R 4\pi\epsilon_0}$

$$H_{kin} = -\frac{1}{8m^3c^2}\vec{P}^4$$

$$H_{so} = \frac{1}{2m^2c^2}\frac{1}{R}\frac{dV(R)}{dR}\vec{L}\cdot\vec{S} = \frac{1}{m^2c^2}\frac{1}{R^3}$$

$$H_D = \frac{\pi e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2}\delta^3(\vec{R}) \; .$$

This result has the rigorous derivation from the non-relativistic reduction of the Dirac equation. Above we physically motivated the results.

As the notation implies we will apply R-S perturbation theory to calculate the energy levels of H. Hence the energy shifts determined by H_{fs} should be small compared to the energy levels of the unperturbed Hamiltonian, H_0. To see this recall that the unperturbed energy levels of H_0 where given by

$$E_n^0 = \frac{-me^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{e^2}{4\pi\epsilon_0 2a_0}\frac{1}{n^2}$$

$$= \frac{-mc^2\alpha^2}{2n^2} \quad \text{with } n = 1, 2, \ldots$$

where $a_0 = \frac{\hbar}{mc\alpha} = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ = Bohr radius and

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c}\left(= \frac{e^2}{4\pi\epsilon_0 \hbar c}\right) = \frac{1}{137.0360}$$ is known as the fine structure constant.

Using these parameters the unperturbed Hamiltonian can be written as

$$H_0 = mc^2\alpha^2\left(\frac{a_0^2}{2\hbar^2}\vec{p}^2 - \frac{a_0}{R}\right).$$

$\hbar c\alpha = e^2/4\pi\epsilon_0$ ✓

Thus we see that the scale of H_0 (i.e. E_n^0) is determined by $mc^2\alpha^2$, the operator in brackets being a number the order of 1.

The perturbing Hamiltonia in these variables become

$$H_{kin} = mc^2\alpha^4\left(-\frac{a_0^4}{8\hbar^4}\vec{P}^4\right)$$

$$H_{so} = mc^2\alpha^4\left(\frac{a_0^3}{2\hbar^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}\right)$$

$$H_D = mc^2\alpha^4\left(\frac{\pi}{2}a_0^3\delta^3(\vec{R})\right)$$

where the Coulomb potential is

$$V(R) = -\frac{e^2}{R} = -mc^2\alpha^2\frac{a_0}{R}, \text{ hence}$$

$$\frac{dV(R)}{dR} = mc^2\alpha^2\frac{a_0}{R^2}.$$

Thus we see that the scale of H_{fs} is given by $(mc^2\alpha^2)\alpha^2$; it is α^2 times

smaller than the scale of H_0. So indeed our perturbation parameter $\lambda = \alpha^2 \approx \left(\frac{1}{137}\right)^2$ is quite small. We expect perturbation theory to give accurate results for the energy shifts. They should be the order of $\alpha^2 10\,eV \approx 10^{-3}\,eV$.

In order to apply the R-S perturbation scheme, we must begin by solving the unperturbed problem. The unperturbed Hamiltonian $H_0 = \frac{1}{2m}\vec{p}^2 - \frac{e^2}{R}$ as we said has eigenvalues

$$E_n^0 = -\frac{mc^2\alpha^2}{2}\frac{1}{n^2} \quad ; n = 1, 2, \ldots .$$

Since $V(R)$ is a central potential it is Rotationally invariant. As well H_0 is independent of the electron's spin, we ignored it completely when considering the Coulomb problem earlier. Hence H_0 commutes with $\vec{L}$ & $\vec{S}$. Thus we can choose as we did earlier, the set $\{H_0, \vec{L}^2, \vec{S}^2, L_z, S_z\}$ as our CSCO with eigenstates labelled by

$$|n, l, s; m, m_s\rangle = |n, l, m\rangle \otimes |s, m_s\rangle$$

with $n=1,2\ldots$ the energy eigenvalues, the principal quantum number. The Orbital angular momentum quantum number is l with

$$l = 0, 1, 2, \ldots, n-1$$

and $m = -l, -l+1, \ldots, l-1, +l$ the z-component of the orbital angular momentum. Of course the electron has spin $S = \frac{1}{2}$ and so the z-component of spin is $m_s = \pm \frac{1}{2}$. Thus

$$H_0 |n, l, s=\tfrac{1}{2}; m, m_s\rangle = E_n^0 |n, l, s=\tfrac{1}{2}; m, m_s\rangle$$

$$\vec{L}^2 | \quad \rangle = l(l+1)\hbar^2 | \quad \rangle$$

$$\vec{S}^2 | \quad \rangle = \tfrac{3}{4}\hbar^2 | \quad \rangle$$

$$L_z | \quad \rangle = m\hbar | \quad \rangle$$

$$S_z | \quad \rangle = m_s\hbar | \quad \rangle .$$

Thus we see that E_n^0 is degenerate for each n there are

2 Spin $= \pm\frac{1}{2}$ states

$$(2s+1)\sum_{l=0}^{n-1}(2l+1) = 2\left(\frac{2(n-1)n}{2}+n\right)$$

$$= 2n^2 \text{ eigenstates}$$

with the same E_n^0. Thus E_n^0 is $2n^2$-fold degenerate.

As we stated H_0 commutes with $\vec{S}$ and $\vec{L}$ hence it commutes with the total angular momentum $\vec{J} = \vec{L}+\vec{S}$. We could use as a CSCO the set of operators $\{H_0, \vec{L}^2, \vec{S}^2, \vec{J}^2, J_z\}$. The eigenstates for this set are given by

$|n, l, s; J, M\rangle$ where (recall pages -777- to -789-) $n = 1, 2, \ldots$ and $l = 0, 1, \ldots, n-1$, $s = \frac{1}{2}$ as before, and now $J = \begin{cases} \frac{1}{2} & \text{if } l = 0 \\ l+\frac{1}{2}, l-\frac{1}{2} & \text{if } l > 0, \end{cases}$ and of course $M = -J, -J+1, \ldots, J-1, +J$.

As pointed out earlier, this basis is much more useful when considering

spin-orbit couplings since

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

in this basis, i.e.

$$\vec{L}\cdot\vec{S}\,|n,l,s;J,M\rangle = \frac{\hbar^2}{2}\left[J(J+1) - l(l+1) - \frac{3}{4}\right] \times |n,l,s;J,M\rangle .$$

And so we have

$$\vec{J}^2\,|n,l,s;J,M\rangle = J(J+1)\hbar^2\,|n,l,s;J,M\rangle$$

$$J_z\,|\ \ \ \rangle = M\hbar\,|\ \ \ \rangle .$$

Hence we find the degeneracy of E_n^0 to be

$$\sum_{l=0}^{n-1}\ \sum_{J=l-\frac{1}{2}}^{l+\frac{1}{2}} (2J+1) = \sum_{l=0}^{n-1} 2(2l+1) = 2n^2 ,$$

as required. Further knowing the Clebsch-Gordon coefficients, we have no difficulty in transforming from one basis to another!

Recalling that $H_{fs} = H_{kin} + H_{so} + H_D$ with

$$H_{kin} = -\frac{1}{8m^3c^2}\vec{P}^4$$

$$H_{so} = \frac{e^2}{4\pi\epsilon_0 2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}$$

$$H_D = \frac{\pi e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2}\delta^3(\vec{R}),$$

we have that $[\vec{L}^2, H_{fs}] = 0 = [\vec{S}^2, H_{fs}]$

as well we also have $[\vec{J}^2, H_{fs}] = 0$

and $[J_z, H_{fs}] = 0$. These follow from $R, \vec{P}^2, \vec{L}\cdot\vec{S}, \delta^3(\vec{R})$ being rotationally invariant, so they commute with $\vec{J}^2$ and J_z. Further $R, \vec{P}^2$ and $\delta^3(\vec{R})$ are independent of spin so they commute with $\vec{S}$ and so rotational invariance implies they also commute with $\vec{L}^2$. Likewise $\vec{L}^2$ and $\vec{S}^2$ are scalars so they commute with $\vec{L}$ & $\vec{S}$ and so $\vec{L}\cdot\vec{S}$ (they are the Casimir operators for the L & S $SU(2)$ groups respectively). Note that $[\vec{L}\cdot\vec{S}, L_z] \neq 0$, and so $[H_{fs}, L_z] \neq 0$. Thus H_{fs} is

diagonal in the $|n,l,s;J,M\rangle$ basis but not the $|n,l,s;m,m_s\rangle$ basis for a fixed n.

Hence we will use the $|n,l,s;JM\rangle$ basis in which H_0, H_0, H_{fs} are all diagonal for a fixed n.
In detail, we have

$$[\vec{L}^2, H_{fs}] = 0$$

$$\Rightarrow$$

$$0 = \langle n,l',s=\tfrac{1}{2};J',M'|[\vec{L}^2, H_{fs}]|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= [l'(l'+1)\hbar^2 - l(l+1)\hbar^2]\langle n,l',s=\tfrac{1}{2};J',M'|H_{fs}|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$\Rightarrow$$

$$\langle n,l',s=\tfrac{1}{2};J',M'|H_{fs}|n,l,s=\tfrac{1}{2};J,M\rangle \propto \delta_{ll'}$$

Likewise $[\vec{J}^2, H_{fs}] = 0$

$$\Rightarrow$$

$$\langle n,l',s=\tfrac{1}{2};J',M'|H_{fs}|n,l,s=\tfrac{1}{2};J,M\rangle \propto \delta_{JJ'}$$

and $[J_z, H_{fs}] = 0$

$$\Rightarrow \langle n,l',s=\tfrac{1}{2};J',M'|H_{fs}|n,l,s=\tfrac{1}{2};JM\rangle \propto \delta_{MM'}.$$

Hence we find

$$\langle n, l', s=\tfrac{1}{2}; J', M' | H_{fs} | n, l, s=\tfrac{1}{2}; J, M \rangle$$

$$= \delta_{ll'} \delta_{JJ'} \delta_{MM'} \langle n, l, s=\tfrac{1}{2}; J, M | H_{fs} | n, l, s=\tfrac{1}{2}; J, M \rangle$$

The matrix elements of H_{fs} in the $|n, l, s; J, M\rangle$ basis are already diagonal. This is particularly useful since first order degenerate R-S perturbation theory requires us to diagonalize exactly this matrix. The eigenvalues are the diagonal elements themselves and they are the energy level shifts.

So let's find expressions for these diagonal matrix elements in general and then explicitly discuss the $n=1, 2$ cases.

First we consider the diagonal matrix elements of

$$H_{Kin} = -\frac{1}{8m^3c^2} \vec{p}^4 = mc^2 \alpha^4 \left[\frac{-a_0^4}{8\hbar^4} \vec{p}^4 \right]$$

Since $H_0 = mc^2\alpha^2\left[\frac{a_0^2}{2\hbar^2}\vec{p}^2 - \frac{a_0}{R}\right]$

$= \frac{1}{2m}\vec{p}^2 - \frac{e^2}{R_{atc.}}$ we can

write $\vec{p}^2 = 2m\left(H_0 + \frac{e^2}{R_{atc.}}\right)$ and so

$\vec{p}^4 = 4m^2\left[H_0^2 + \frac{e^4}{(4\pi\epsilon_0)^2R^2} + H_0\frac{e^2}{R_{atc.}} + \frac{e^2}{R_{atc.}}H_0\right]$.

Hence $H_{kin} = -\frac{1}{2mc^2}\left[H_0^2 + \frac{e^4}{R^2_{(4\pi\epsilon_0)^2}} + H_0\frac{e^2}{R_{atc.}} + \frac{e^2}{R_{atc.}}H_0\right]$

and

$$\langle n,l,s=\tfrac{1}{2};JM|H_{kin}|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= -\frac{1}{2mc^2}\left\{(E_n^0)^2 + \frac{e^4}{(4\pi\epsilon_0)^2}\langle n,l,s=\tfrac{1}{2};J,M|\frac{1}{R^2}|n,l,s=\tfrac{1}{2},J,M\rangle\right.$$

$$\left. + 2E_n^0\frac{e^2}{4\pi\epsilon_0}\langle n,l,s=\tfrac{1}{2};J,M|\frac{1}{R}|n,l,s=\tfrac{1}{2};J,M\rangle\right\}$$

Thus we must evaluate matrix elements of powers of R.

Since R is independent of spin and is Rotationally invariant it commutes with $\vec{S}$ & $\vec{L}$ (i.e. R is independent of angular coordinates in the $|\vec{r}\rangle$ basis in spherical polar coordinates $\langle\vec{r}|R = r\langle\vec{r}|$). Thus we find in the $|n,l,s;m,m_s\rangle$ basis that

$$\langle n,l',s';m',m_s'|R^q|n,l,s;m,m_s\rangle$$
$$= \delta_{ll'}\delta_{ss'}\delta_{mm'}\delta_{m_s m_s'}\langle n,l,s;m,m_s|R^q|n,l,s;m,m_s\rangle$$

since $[\vec{L}^2,R]=0=[\vec{S}^2,R]=[L_z,R]=[S_z,R]$.

Since $|n,l,s;m,m_s\rangle = |n,l,m\rangle\otimes|s,m_s\rangle$

and R only acts on the spatial variables, not the spin and since $\langle s,m_s|s,m_s\rangle = 1$ we have

$$\langle n,l,s;m,m_s|R^q|n,l,s;m,m_s\rangle$$
$$= \langle n,l,m|R^q|n,l,m\rangle .$$

Further, $[\vec{L}, R] = 0 \Rightarrow [L_\pm, R] = 0$,

thus we have for instance

$$0 = \langle n,l,m | [R^q, L_+] | n,l,m-1 \rangle$$

$$= \langle n,l,m | L_-^\dagger R^q - R^q L_+ | n,l,m-1 \rangle$$

$$\propto \left[\langle n,l,m-1 | R^q | n,l,m-1 \rangle - \langle n,l,m | R^q | n,l,m \rangle \right]$$

$\Rightarrow$

$$\langle n,l,m | R^q | n,l,m \rangle = \langle n,l,m-1 | R^q | n,l,m-1 \rangle$$

The diagonal matrix elements of R^q are independent of m_l. This can be seen explicitly by recalling the $|n,l,m\rangle$ wavefunctions

$$\langle \vec{r} | n,l,m \rangle = \psi_{nlm}(\vec{r})$$

$$= R_{nl}(r) Y_l^m(\theta,\varphi)$$

Thus

$$\langle n,l,m|R^q|n,l,m\rangle$$

$$= \int d^3r\, \psi^*_{nlm}(\vec{r})\, r^q\, \psi_{nlm}(\vec{r})$$

$$= \underbrace{\int d\Omega\, Y_l^{m*}(\theta,\varphi) Y_l^m(\theta,\varphi)}_{=1} \int_0^\infty dr\, r^2 r^q |R_{nl}(r)|^2$$

$$= \int_0^\infty dr\, r^2 r^q |R_{nl}(r)|^2$$ which is independent of m.

Now applying these results to the $|n,l,s;J,M\rangle$ matrix elements we find

$$\langle n,l,s=\tfrac{1}{2};J,M|R^q|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= \sum_{m'=-l}^{+l} \sum_{m_s'=-1/2}^{+1/2} \sum_{m=-l}^{+l} \sum_{m_s=-1/2}^{+1/2}$$

$$\langle n,l,s=\tfrac{1}{2};J,M|n,l,s=\tfrac{1}{2};m',m_s'\rangle^*$$

$$\langle n,l,s=\tfrac{1}{2};m',m_s'|R^q|n,l,s=\tfrac{1}{2};m,m_s\rangle^*$$

$$\times \langle n,l,s=\tfrac{1}{2};m,m_s|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= \sum_{m=-\ell}^{+\ell} \sum_{m_s=-1/2}^{+1/2} \langle n,\ell,s=\tfrac{1}{2};J,M|n,\ell,s=\tfrac{1}{2};m,m_s\rangle$$
$$\langle n,\ell,s=\tfrac{1}{2};m,m_s|R^q|n,\ell,s=\tfrac{1}{2};m,m_s\rangle$$
$$\langle n,\ell,s=\tfrac{1}{2};m,m_s|n,\ell,s=\tfrac{1}{2};J,M\rangle$$

$$= \langle n,\ell|R^q|n,\ell\rangle \times \sum_{m=-\ell}^{+\ell} \sum_{m_s=-1/2}^{+1/2}$$

$$\langle n,\ell,s=\tfrac{1}{2};J,M|n,\ell,s=\tfrac{1}{2};m,m_s\rangle\langle n,\ell,s=\tfrac{1}{2};m,m_s|$$
$$|n,\ell,s=\tfrac{1}{2};J,M\rangle$$

(using completeness)

$$= \langle n,\ell|R^q|n,\ell\rangle \underbrace{\langle n,\ell,s=\tfrac{1}{2};J,M|n,\ell,s=\tfrac{1}{2};J,M\rangle}_{=1}$$

$$= \langle n,\ell|R^q|n,\ell\rangle$$
$$= \int_0^\infty dr\, r^{q+2} |R_{n\ell}(r)|^2$$
$$= \langle n,\ell,s=\tfrac{1}{2};J,M|R^q|n,\ell,s=\tfrac{1}{2};J,M\rangle$$

Putting this together we obtain

$$\langle n,l,s=\tfrac{1}{2};J,M|H_{Kin}|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= -\frac{1}{2mc^2}\left\{(E_n^0)^2 + \frac{e^4}{(4\pi\epsilon_0)^2}\langle n,l|R^{-2}|n,l\rangle + 2E_n^0\frac{e^2}{4\pi\epsilon_0}\langle n,l|R^{-1}|n,l\rangle\right\}$$

Now recall $E_n^0 = -\frac{mc^2}{2}\alpha^2\frac{1}{n^2}$

and $\frac{e^2}{4\pi\epsilon_0} = \alpha\hbar c = mc^2\alpha^2 a_0$; thus

$$\langle n,l,s=\tfrac{1}{2};J,M|H_{Kin}|n,l,s=\tfrac{1}{2};J,M\rangle = -mc^2\alpha^4\left[\frac{1}{8n^4} + \frac{a_0^2}{2}\langle n,l|\frac{1}{R^2}|n,l\rangle - \frac{a_0}{2n^2}\langle n,l|\frac{1}{R}|n,l\rangle\right]$$

Of course we could have obtained this result directly by using the $|n,l,s=\frac{1}{2};J,M\rangle$ wavefunctions given on page -788-.

Next we consider the energy shifts due to the Darwin term

$$H_D = \frac{\pi e^2 \hbar^2}{4\pi\epsilon_0 2m^2c^2}\delta^3(\vec{R})$$

$$= mc^2\alpha^4\left(\frac{\pi}{2}a_0^3\delta^3(\vec{R})\right)$$

Again $\delta^3(\vec{R})$ is rotationally invariant and independent of the spin. Thus in the $|n,l,s;m,m_s\rangle$ basis depends only on n and l and is diagonal.

$$\langle n,l',s=\tfrac{1}{2};m',m_s'|\delta^3(\vec{R})|n,l,s=\tfrac{1}{2};m,m_s\rangle$$

$$= \langle n,l',m'|\delta^3(\vec{R})|n,l,m\rangle\langle s=\tfrac{1}{2},m_s'|s=\tfrac{1}{2},m_s\rangle$$

$$= \int d^3r\, \psi^*_{n,l'm'}(\vec{r})\delta^3(\vec{r})\psi_{nlm}(\vec{r})\delta_{m_s m_s'}$$

$$= \delta_{m_s m_s'}\psi^*_{nl'm'}(0)\psi_{nlm}(0)$$

$$= \delta_{m_s m_s'}R^*_{nl'}(0)R_{nl}(0)Y^{m'*}_{l'}(0,0)Y^m_l(0,0)$$

Now recall that $R_{nl}(r)$ is given by the associated Laguerre polynomials

(Griffiths 4.89) & 4.59 4.55

times r^l. Thus as $r \to 0$ $R_{nl} \sim r^l$ which vanishes unless $l=0$. Thus

$$\boxed{\langle n, l', s=\tfrac{1}{2}; m', m_s' | \delta^3(\vec{R}) | n, l, s=\tfrac{1}{2}; m, m_s \rangle = \delta_{m_s m_s'} \delta_{ll'} \delta_{l0} \delta_{mm'} \delta_{m0} |R_{n0}(0)|^2 \frac{1}{4\pi}},$$

hence only s-states have non-vanishing H_D matrix elements.

Hence

$$\langle n, l, s=\tfrac{1}{2}; J, M | H_D | n, l, s=\tfrac{1}{2}; J, M \rangle$$

$$= \sum_{m'=-l}^{+l} \sum_{m_s'=-\frac{1}{2}}^{+\frac{1}{2}} \sum_{m=-l}^{+l} \sum_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} \langle n, l, s=\tfrac{1}{2}; J, M | n, l, s=\tfrac{1}{2}; m', m_s' \rangle$$

$$\langle n, l, s=\tfrac{1}{2}; m', m_s' | H_D | n, l, s=\tfrac{1}{2}; m, m_s \rangle$$

$$\langle n, l, s=\tfrac{1}{2}; m, m_s | n, l, s=\tfrac{1}{2}; J, M \rangle$$

$$= \sum_{m=-l}^{+l} \sum_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} mc^2 \alpha^4 \frac{\pi}{2} a_0^3 \left| \langle n, l, s=\tfrac{1}{2}; J, M | n, l, s=\tfrac{1}{2}; m, m_s \rangle \right|^2 \times$$

$$\times \delta_{l0} \delta_{m0} |R_{n0}(0)|^2 \frac{1}{4\pi}$$

So

$$= \sum_{m_s=-1/2}^{+1/2} \delta_{l0} \frac{mc^2\alpha^4}{8} a_0^3 |R_{n0}(0)|^2 \langle n, l=0, s=\tfrac{1}{2}; J, M |$$

$$| n, l=0, s=\tfrac{1}{2}; m=0, m_s \rangle$$

but for $l=0$ $J=\frac{1}{2}$ and $m_s = M$; thus for fixed M only $m_s = M$ contributes $\Rightarrow$

$$= \delta_{l0} \frac{mc^2\alpha^4}{8} a_0^3 |R_{n0}(0)|^2$$

So we obtain the diagonal matrix elements of H_D

$$\langle n, l, s=\tfrac{1}{2}; J, M | H_D | n, l, s=\tfrac{1}{2}; J, M \rangle$$

$$= \frac{mc^2\alpha^4}{8} a_0^3 |R_{n0}(0)|^2 \delta_{l0}$$

Finally we must determine the diagonal matrix elements of H_{SO}

$$H_{so} = mc^2\alpha^4\left(\frac{a_0^3}{2\hbar^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}\right)$$

$$= \frac{e^2}{2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}$$

Recalling that $\vec{L}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$ this becomes

$$H_{so} = \frac{mc^2\alpha^4 a_0^3}{4}\frac{1}{R^3}\frac{1}{\hbar^2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right).$$

The unperturbed eigenstates of H_0 in the $|n,l,s=\frac{1}{2};J,M\rangle$ basis are eigenstates of $\vec{L}\cdot\vec{S}$ also

$$H_{so}|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= \frac{mc^2\alpha^4 a_0^3}{4}\left[J(J+1) - l(l+1) - \frac{3}{4}\right]\frac{1}{R^3}|n,l,s=\tfrac{1}{2};J,M\rangle$$

So the diagonal matrix elements are

$$\boxed{\begin{aligned}&\langle n,l,s=\tfrac{1}{2};J,M|\,H_{so}\,|n,l,s=\tfrac{1}{2};J,M\rangle \\ &= \frac{mc^2\alpha^4 a_0^3}{4}\left[J(J+1) - l(l+1) - \frac{3}{4}\right]\left\langle n,l\left|\frac{1}{R^3}\right|n,l\right\rangle\end{aligned}}$$

Using the results of page -936- for matrix

elements of R^6.

Hence to summarize we found that the unperturbed matrix elements of H_{fs} are diagonal in the $|n,l,s=\frac{1}{2};J,M\rangle$-basis

$$\langle n,l',s=\tfrac{1}{2};J',M'|H_{fs}|n,l,s=\tfrac{1}{2};J,M\rangle$$
$$=\delta_{ll'}\delta_{JJ'}\delta_{MM'}\langle n,l,s=\tfrac{1}{2};J,M|H_{fs}|n,l,s=\tfrac{1}{2};J,M\rangle$$

with $H_{fs}=H_{kin}+H_{so}+H_D$. The individual diagonal matrix elements are given by

$$\langle n,l,s=\tfrac{1}{2};J,M|H_{kin}|n,l,s=\tfrac{1}{2};J,M\rangle$$
$$=-mc^2\alpha^4\left(\frac{1}{8n^4}-\frac{a_0}{2n^2}\left\langle n,l\left|\frac{1}{R}\right|n,l\right\rangle+\frac{a_0^2}{2}\left\langle n,l\left|\frac{1}{R^2}\right|n,l\right\rangle\right)$$

$$\langle n,l,s=\tfrac{1}{2};J,M|H_{so}|n,l,s=\tfrac{1}{2};J,M\rangle$$
$$=mc^2\alpha^4\left(J(J+1)-l(l+1)-\frac{3}{4}\right)\frac{a_0^3}{4}\left\langle n,l\left|\frac{1}{R^3}\right|n,l\right\rangle$$

(all H_{fs} diagonal matrix elements are independent of M!)
(So there will remain a $(2J+1)$ degeneracy)

$$\langle n,l,s=\tfrac{1}{2};J,M|H_D|n,l,s=\tfrac{1}{2};J,M\rangle = mc^2\alpha^4 \frac{a_0^3}{8}|R_{n0}(0)|^2 \delta_{l0}$$

Where the radial expectation values are given by

$$\langle n,l|R^q|n,l\rangle = \int_0^\infty dr\, r^{q+2}|R_{nl}(r)|^2$$

with the unperturbed hydrogenic wavefunctions given by

$$\langle \vec{r}|n,l,m\rangle = R_{nl}(r)Y_l^m(\theta,\varphi).$$

Recall that the hydrogen radial wavefunction $R_{nl}(r)$ is given by powers of r times an exponential damping factor (page -233-)

$$R_{nl}(r) = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \times \left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) e^{-\frac{r}{na_0}}$$

with the associated Laguerre polynomials

$$L_q^p(z) \equiv (q!)^2 \sum_{N=0}^{q-p} \frac{(-1)^{p+N} z^N}{(q-p-N)!\,(p+N)!\,N!}$$

(i.e. $R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$

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

$$R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{r}{\sqrt{3}\,a_0} e^{-r/2a_0}.)$$

Hence we will need, when evaluating $\langle n,\ell | R^q | n,\ell \rangle$, integrals of powers of r times e^{-pr/a_0}

$$I(k,p) \equiv \int_0^\infty dr\, r^k e^{-pr/a_0}$$

re-scaling r according to $t = \frac{p}{a_0} r$

$$dr = \frac{a_0}{p} dt$$

The integral becomes

$$I(k,p) = \left(\frac{a_0}{p}\right)^{k+1} \underbrace{\int_0^\infty dt\, t^k e^{-t}}_{=\Gamma(k+1)}$$

where the gamma function $\Gamma(n+1) = n!$ for n an integer. Thus

$$\boxed{I(k,p) = \Gamma(k+1)\left(\frac{a_0}{p}\right)^{k+1}}$$

So for example

$$\langle n=1, l=0 | R^q | n=1, l=0\rangle = \int_0^\infty dr\, r^{q+2} |R_{10}(r)|^2$$

$$= \frac{4}{a_0^3}\int_0^\infty dr\, r^{q+2} e^{-2r/a_0} = \frac{4}{a_0^3} I(q+2, 2)$$

$$= \frac{4}{a_0^3}\Gamma(q+3)\left(\frac{a_0}{2}\right)^{q+3}$$

$$= \frac{a_0^q}{2^{q+1}}\Gamma(q+3)$$

while for $n=2$ we have

$$\langle n=2, l=0 | R^q | n=2, l=0\rangle = \int_0^\infty dr\, r^{q+2} |R_{20}(r)|^2$$

$$\langle n=2, l=0 | R^q | n=2, l=0 \rangle = \int_0^\infty dr\, r^{q+2} \frac{1}{(2a_0)^3} e^{-r/a_0} \times \left(4 + \frac{r^2}{a_0^2} - \frac{4r}{a_0}\right)$$

$$= \frac{1}{(2a_0)^3}\left[4I(q+2,1) + \frac{1}{a_0^2} I(q+4,1) - \frac{4}{a_0} I(q+3,1)\right]$$

$$= \frac{1}{2} a_0^q \Gamma(q+3) + \frac{1}{8} a_0^q \Gamma(q+5) - \frac{2}{4} a_0^q \Gamma(q+4)$$

$$= \frac{1}{2} a_0^q \left(\Gamma(q+3) + \frac{1}{4}\Gamma(q+5) - \Gamma(q+4)\right)$$

and

$$\langle n=2, l=1 | R^q | n=2, l=1 \rangle = \int_0^\infty dr\, r^{q+2} |R_{21}|^2$$

$$= \int_0^\infty dr\, r^{q+2} \frac{1}{(2a_0)^3} \frac{r^2}{3a_0^2} e^{-r/a_0}$$

$$= \frac{1}{24 a_0^5} I(q+4,1)$$

$$= \frac{a_0^q}{24} \Gamma(q+5)$$

It is now straightforward to apply these results to the $n=1$, $n=2$ energy levels of hydrogen.

$\underline{n=1}$ The degeneracy of the $E^0_{n=1}$ eigenvalue is 2 due to the electron spin

The eigenstates of $\{H_0, \vec{L}^2, \vec{S}^2; \vec{J}^2, J_z\}$ for this degenerate energy subspace are

$$|n=1, l=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M=\pm\tfrac{1}{2}\rangle .$$

According to conventional spectroscopic notation this energy level is denoted $|S_{1/2}$. In general the E^0_n levels are denoted by their nl_J quantum numbers with $l=0,1,2,3,\ldots$ assigned the letters $s,p,d,f,\ldots$

So $|S_{1/2}$ is 2-fold degenerate.

According to R-S degenerate perturbation theory the first order energy shifts are given by the eigenvalues of the perturbing Hamiltonian H_{fs} in the unperturbed E_n^0-basis (page - 871). Using $|n,l,s;J,M\rangle$ as the basis H_{fs} is diagonal, and so we can read off the energy shifts from the diagonal matrix elements of H_{fs}.

So we have for the $1S_{1/2}$ states

1) $$\langle n=1,l=0,s=\tfrac{1}{2};J=\tfrac{1}{2},M|H_{Kin}|n=1,l=0,s=\tfrac{1}{2};J=\tfrac{1}{2},M\rangle$$
$$= -mc^2\alpha^4\left(\frac{1}{8}-\frac{a_0}{2}\langle 1,0|\frac{1}{R}|1,0\rangle+\frac{a_0^2}{2}\langle 1,0|\frac{1}{R^2}|1,0\rangle\right)$$
$$= -mc^2\alpha^4\left(\frac{1}{8}-\frac{1}{2}+\frac{a_0^2}{2}\frac{2}{a_0^2}\right) = -mc^2\alpha^4\left(1-\frac{1}{2}+\frac{1}{8}\right)$$
$$= -\frac{5}{8}mc^2\alpha^4$$

2) $$\langle n=1,l=0,s=\tfrac{1}{2};J=\tfrac{1}{2},M|H_{so}|n=1,l=0,s=\tfrac{1}{2};J=\tfrac{1}{2},M\rangle$$
$$= mc^2\alpha^4\underbrace{\left(\tfrac{1}{2}(\tfrac{1}{2}+1)-0(0+1)-\tfrac{3}{4}\right)}_{=0}\frac{a_0^3}{4}\langle 1,0|\frac{1}{R^3}|1,0\rangle$$
$$=0.$$

3) $\langle n=1, \ell=0, s=\frac{1}{2}; J=\frac{1}{2}, M | H_D | n=1, \ell=0, s=\frac{1}{2}; J=\frac{1}{2}, M \rangle$

$$= mc^2\alpha^4 \frac{a_0^3}{8} |R_{10}(0)|^2$$

$$= \frac{1}{2} mc^2\alpha^4$$

As observed earlier, all diagonal matrix elements of H_{fs} are independent of M and so the $2J+1 = 2$-fold degeneracy of $|S_{1/2}\rangle$ remains. This is due to the fact that for $|S_{1/2}\rangle$ the degeneracy is due to the electron spin. Since the H_{SO} matrix element is zero and it only involves the electron's spin, the degeneracy remains. So putting these together we have

$$\langle n=1, \ell=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M' | H_{fs} | n=1, \ell=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M \rangle$$

$$= \delta_{MM'} \Big(\underbrace{-\tfrac{5}{8} mc^2\alpha^4}_{H_{kin}} + \underbrace{0}_{H_{SO}} + \underbrace{\tfrac{1}{2} mc^2\alpha^4}_{H_D} \Big)$$

$$= \delta_{MM'} \left(-\tfrac{1}{8} mc^2\alpha^4 \right)$$

Thus we see that the effect of H_{fs} on the 2-$1S_{1/2}$ degenerate energy levels is merely to shift both of them down in energy by the same amount

$$E_{1S_{1/2}} = E^0_{n=1} + \langle n=1, l=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M | H_{fs} | n=1, l=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M \rangle$$

$$= -\frac{mc^2\alpha^2}{2(1)^2} - \frac{1}{8}mc^2\alpha^4$$

$$\boxed{E_{1S_{1/2}} = -\frac{mc^2\alpha^2}{2}\left(1+\frac{\alpha^2}{4}\right)}$$

$E_{1S_{1/2}}$ remains 2-fold degenerate.

$$\left(= -13.6058036\,(1+0.0000133)\ \text{eV} \right)$$

using $mc^2 = 0.5110034(14)$ MeV

$\frac{1}{\alpha} = 137.03604(11)$

$\underline{n=2}$ The $E^0_{n=2}$ level is $2n^2 = 8$-fold degenerate. It contains the

$2S_{1/2}$ states $|n=2, l=0, s=\tfrac{1}{2}, J=\tfrac{1}{2}, M=\pm\tfrac{1}{2}\rangle$
there are 2 of them

Recall for given n; $l=0,1,\ldots,n-1$; $J=$ ~~$l+s, l-s$~~ $= l+\frac{1}{2}, l-\frac{1}{2}$

and $M=-J,\ldots,+J$.

and the $2P_{1/2}$ states

$$|n=2, l=1; s=\tfrac{1}{2}; J=\tfrac{1}{2}, M=\pm\tfrac{1}{2}\rangle,$$

there are 2 of these and finally the $2P_{3/2}$ states

$$|n=2, l=1, s=\tfrac{1}{2}; J=\tfrac{3}{2}, M=-\tfrac{3}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{3}{2}\rangle$$

There are 4 of these for a total of 8 degenerate states.

Since H_{fs} (matrix elements) are independent of M;

$2S_{1/2}$ will remain 2-fold degenerate
$2P_{1/2}$ will remain 2-fold degenerate
$2P_{3/2}$ will remain 4-fold degenerate.

Consider first the $2S_{1/2}$ states

$\underline{2S_{1/2}}$ 1) $\langle 2S_{1/2}|H_{kin}|2S_{1/2}\rangle$

$$\left(=\langle n=2, l=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M|H_{kin}|n=2, l=0, s=\tfrac{1}{2}; J=\tfrac{1}{2}, M\rangle\right)$$

$$=-mc^2\alpha^4\left(\frac{1}{8(2)^4}-\frac{a_0}{2(2)^2}\langle 2,0|\frac{1}{R}|2,0\rangle+\frac{a_0^2}{2}\langle 2,0|\frac{1}{R^2}|2,0\rangle\right)$$

1) $\langle 2S_{1/2}|H_{Kin}|2S_{1/2}\rangle$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{a_0}{8}\langle 2,0|\frac{1}{R}|2,0\rangle + \frac{a_0^2}{2}\langle 2,0|\frac{1}{R^2}|2,0\rangle\right)$$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{a_0}{8}\left(\frac{1}{2}\frac{1}{a_0}\right)\left(\Gamma(2)+\frac{1}{4}\Gamma(4)-\Gamma(3)\right) + \frac{a_0^2}{2}\left(\frac{1}{2a_0^2}\right)\left(\Gamma(1)+\frac{1}{4}\Gamma(3)-\Gamma(2)\right)\right)$$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{1}{16}\left(1+\frac{1}{4}6-2\right) + \frac{1}{4}\left(1+\frac{2}{4}-1\right)\right)$$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{1}{32} + \frac{1}{8}\right)$$

$$= -\frac{13}{128}mc^2\alpha^4$$

---

2) $\langle 2S_{1/2}|H_{SO}|2S_{1/2}\rangle$

$$= mc^2\alpha^4\underbrace{\left(\frac{1}{2}\left(\frac{1}{2}+1\right)-0(0+1)-\frac{3}{4}\right)}_{=0}\frac{a_0^3}{4}\langle 2,0|H_{SO}|2,0\rangle$$

$$= 0$$

---

3) $\langle 2S_{1/2} | H_\delta | 2S_{1/2} \rangle$

$$= mc^2 \alpha^4 \frac{a_0^3}{8} |R_{20}(0)|^2$$

$$= mc^2 \alpha^4 \frac{a_0^3}{8} \frac{4}{8a_0^3}$$

$$= \frac{1}{16} mc^2 \alpha^4 .$$

Combining these results we find

$$\langle 2S_{1/2} | H_{fs} | 2S_{1/2} \rangle = -\frac{5}{128} mc^2 \alpha^4$$

Thus the $2S_{1/2}$ levels remain 2-fold degenerate with their energies shift down by the same amount

$$E_{2S_{1/2}} = E^0_{n=2} + \langle 2S_{1/2} | H_{fs} | 2S_{1/2} \rangle$$

$$= -\frac{mc^2\alpha^2}{2(2)^2} - \frac{5}{128} mc^2 \alpha^4$$

$$E_{2S_{1/2}} = -\frac{mc^2\alpha^2}{8}\left(1 + \frac{5}{16}\alpha^2\right)$$

Finally we consider

$2p_{1/2}$ 1) $\langle 2p_{1/2}|H_{kin}|2p_{1/2}\rangle$

$$= -mc^2\alpha^4\left(\frac{1}{8(2)^4} - \frac{a_0}{2(2)^2}\langle 2,1|\frac{1}{R}|2,1\rangle + \frac{a_0^2}{2}\langle 2,1|\frac{1}{R^2}|2,1\rangle\right)$$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{a_0}{8}\left(\frac{1}{24a_0}\right)\Gamma(4) + \frac{a_0^2}{2}\left(\frac{1}{24a_0^3}\right)\Gamma(3)\right)$$

$$= -mc^2\alpha^4\left(\frac{1}{128} - \frac{1}{32} + \frac{1}{24}\right)$$

$$= -mc^2\alpha^4\left(\frac{3-12+16}{384}\right)$$

$$= -\frac{7}{384}mc^2\alpha^4$$

---

2) $\langle 2p_{1/2}|H_{so}|2p_{1/2}\rangle$

$$= mc^2\alpha^4\left(\tfrac{1}{2}(\tfrac{1}{2}+1) - 1(1+1) - \tfrac{3}{4}\right)\frac{a_0^3}{4}\langle 2,1|\frac{1}{R^3}|2,1\rangle$$

$$= -mc^2\alpha^4\,\frac{a_0^3}{2}\langle 2,1|\frac{1}{R^3}|2,1\rangle$$

$$= -\frac{1}{48}mc^2\alpha^4$$

---

and of course

3) $\langle 2p_{1/2} | H_D | 2p_{1/2} \rangle$

$$= mc^2 \alpha^4 \frac{a_0^3}{8} |R_{20}(0)|^2 \delta_{\ell=1,0}$$

$$= 0$$

Combining these results we find

$$\langle 2p_{1/2} | H_{fs} | 2p_{1/2} \rangle = -\left(\frac{7}{384} + \frac{1}{48}\right) mc^2 \alpha^4$$

$$= -\frac{5}{128} mc^2 \alpha^4$$

As expected the $2p_{1/2}$ levels remain 2-fold degenerate with their energy levels shifted down by the same amount

$$E_{2p_{1/2}} = E^0_{n=2} + \langle 2p_{1/2} | H_{fs} | 2p_{1/2} \rangle$$

$$= -\frac{mc^2\alpha^2}{2(2)^2} - \frac{5}{128} mc^2 \alpha^4$$

$$\boxed{E_{2p_{1/2}} = -\frac{mc^2\alpha^2}{8}\left(1 + \frac{5}{16}\alpha^2\right)}$$

And for the 4-fold degenerate states

$2p_{3/2}$ 1) $\langle 2p_{3/2}|H_{kin}|2p_{3/2}\rangle$

$$= -mc^2\alpha^4\left(\frac{1}{8(2)^4} - \frac{a_0}{2(2)^2}\langle 2,1|\frac{1}{R}|2,1\rangle + \frac{a_0^2}{2}\langle 2,1|\frac{1}{R^2}|2,1\rangle\right)$$

$$= -\frac{7}{384}mc^2\alpha^4 \quad \left(=\langle 2p_{1/2}|H_{kin}|2p_{1/2}\rangle\right)$$

---

2) $\langle 2p_{3/2}|H_{so}|2p_{3/2}\rangle$

$$= mc^2\alpha^4\left(\overbrace{\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) - \frac{3}{4}}^{=1}\right)\frac{a_0^3}{4}\langle 2,1|\frac{1}{R^3}|2,1\rangle$$

$$= mc^2\alpha^4\frac{a_0^3}{4}\langle 2,1|\frac{1}{R^3}|2,1\rangle$$

$$= +\frac{1}{96}mc^2\alpha^4$$

---

3) $\langle 2p_{3/2}|H_D|2p_{3/2}\rangle$

$$= mc^2\alpha^4\frac{a_0^3}{8}|R_{20}(0)|^2\delta_{l=1,0}$$

$$= 0$$

Combining these results we find

$$\langle 2p_{3/2} | H_{fs} | 2p_{3/2} \rangle = -\left(\frac{7}{384} - \frac{1}{96}\right) mc^2 \alpha^4$$

$$= -\frac{1}{128} mc^2 \alpha^4$$

As expected, the $2p_{3/2}$ levels are 4-fold degenerate with their common energies shifted down by the same value

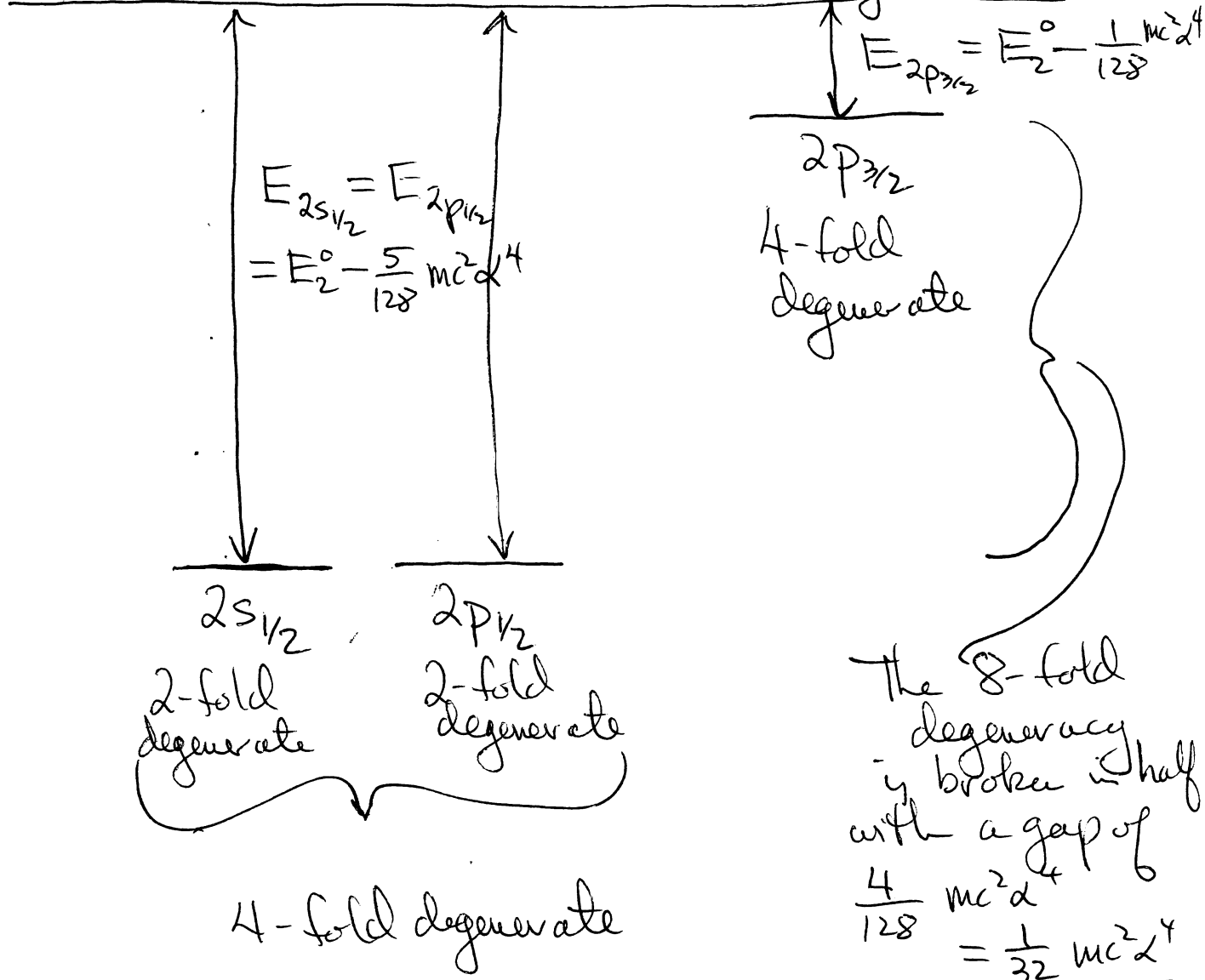
$$E_{2p_{3/2}} = E^0_{n=2} + \langle 2p_{3/2} | H_{fs} | 2p_{3/2} \rangle$$

$$= -\frac{mc^2\alpha^2}{2(2)^2} - \frac{1}{128} mc^2 \alpha^4$$

$$\boxed{E_{2p_{3/2}} = -\frac{mc^2\alpha^2}{8}\left(1 + \frac{1}{16}\alpha^2\right)}$$

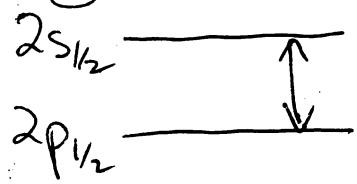
We can depict the results of our first order perturbation calculation graphically as:

$\left(-3.4\,eV \approx\right) E_2^0 = -\frac{mc^2\alpha^2}{8}$ unperturbed $n=2$ energy level is 8-fold degenerate



Note the $2s_{1/2}$, $2p_{1/2}$ degeneracy is removed by quantum fluctuations in the electromagnetic field (photon). These will be calculated in a full quantum mechanical treatment of

electrodynamics (QED). One finds that the $2s_{1/2}$ level is raised w.r.t the $2p_{1/2}$ level by the "Lamb shift"



6.5. The Hydrogen Atom In Electric and Magnetic Fields

In addition to the fine structure relativistic corrections to the Coulomb Hydrogen spectrum, we can also consider the effects of external, constant uniform electric and magnetic fields on the spectrum. The electric field $\vec{E}$ and magnetic field $\vec{B}$ are given in terms of the scalar ϕ and vector $\vec{A}$ potentials:

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial}{\partial t}\vec{A}$$

Recall that the physical values of the electric & magnetic fields $\vec{B}, \vec{E}$ are