6.4. Fine Structure of the Hydrogen Atom Spectrum

One of the most important examples of the utility of R-S perturbation theory in the study of atomic spectra is the dominant force in atomic systems not given by the Coulomb potential,

\[ V(R) = -\frac{e^2}{4\pi \varepsilon_0} \frac{1}{R} = -\frac{e^2}{\pi \varepsilon_0 R}, \]

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 were 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 \( c \). We will confine our selves to the study of the Dirac Hamiltonian for the first order \( 1^\text{st} \) corrections to the electronic Compton motion. That is, Dirac Fermi's split in lowest order this complete description of the relativistic electron motion was described by the Schrödinger Hamiltonian

\[
H = mc^2 + \frac{\hbar^2}{2m} \mathbf{\hat{P}}^2 + V(R) + H_{\text{fs}}
\]

where the corrections to the simple Hydrogen Coulomb potential Hamiltonian are given by the "fine structure" Hamiltonian \( H_{\text{fs}} \).
\[ H_{fs} = H_{\text{kin}} + H_{so} + H_D \]

with \( H_{\text{kin}} \) the special relativistic correction to the kinetic energy:

\[ T = E - mc^2 \]

\[ = \sqrt{\frac{\hat{p}^2}{\hat{p}^2 c^2} + m^2 c^4} - mc^2 \]

\[ = mc^2 \left( 1 + \frac{\hat{p}^2}{m^2 c^4} \right)^{\frac{1}{2}} - mc^2 \]

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

\[ - mc^2 \]

\[ \approx \frac{1}{2m} \hat{p}^2 - \frac{1}{8m^3 c^2} \hat{p}^4 \]

Thus:

\[ H_{\text{kin}} = - \frac{1}{8m^3 c^2} \hat{p}^4 \]

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 electric static field. In the electron's frame, according to special relativity, there is a magnetic field $\vec{B}'$ as well as an electric field $\vec{E}'$. To lowest order, the $\vec{B}'$ field is given by

$$\vec{B}' = -\frac{1}{c^2} \vec{\gamma} \times \vec{E}$$

(Griffiths, eq. 10.120)

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

$$\vec{\mu} = \vec{M} = \frac{g}{m} \vec{S} = g \frac{e}{2} \hbar \vec{S}$$

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

anomalous magnetic moment $g \approx 2.5$ (by Dirac theory)

it interacts with the nuclear magnetic field

$$H_{\text{mag}} = -\mu_B \vec{B}'$$
Now $\vec{B}' = -\frac{1}{c^2} \frac{1}{m} \vec{p} \times \vec{E}$ but the
Coulomb field is $\vec{E} = -\frac{1}{\epsilon_0} \frac{dV(R)}{dR} \frac{\vec{R}}{R}$,
Thus $\vec{B}' = \frac{1}{q} c^2 \frac{1}{R} \frac{dV(R)}{dR} \frac{1}{m} \vec{p} \times \vec{R}$
but $\vec{p} \times \vec{R} = -\vec{R} \times \vec{p} = -\vec{L}$; hence

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

This result is actually a factor of 2 too large, we must include the
precession of the electron spin w.r.t.
the nuclear frame. This Thomas precession
results in an additional interaction
energy $H_{thomas} = -\frac{1}{2} H_{mag}$

Thus we finally obtain

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

$$H_{so} = \frac{1}{2 m^2 c^2} \frac{1}{R} \frac{dV(R)}{dR} L \cdot \vec{S}$$
This is a "spin-orbit coupling" due to the interaction of the electron's spin magnetic moment with 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 is second order 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 $\mathbf{R}$ of the electron. When approximating this interaction as a power series, the corrections from interactions with the field of the order of a Compton wavelength to away arise. Thus, we effectively Taylor expand the Coulomb's field about the electron's position and smear it out over a volume the order of a Compton wavelength cubed, $(\hbar c)^3$. Heuristically,

$$V(\mathbf{R}) \to \int d^3 \mathbf{r} f(\mathbf{r}) V(\mathbf{R} + \mathbf{r})$$
where \( f(\vec{r}) \) vanishes outside a Compton wavelength in all directions, i.e. it is spherically symmetric and has a volume integral equal to 1.

\[
\int d^3 \vec{r} f(\vec{r}) = \int d\Omega f(\hat{r}) \int_0^\infty r^2 V(r) dr
\]

\[
+ \frac{2 \pi^3}{3} \int \hat{r} \cdot \nabla V(r)
\]

\[
+ \frac{1}{2} \sum_{i,j} \nabla_i \nabla_j V
\]

\[
\approx V(R) + \frac{2 \pi^3}{3} \int d\Omega f(\hat{r}) (\nabla^2 V(R))
\]

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

where \( a \) is a constant depending upon the explicit form of \( f(r) \) 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 \[ V(R) = -\frac{e^2}{R} \]

we find

\[ H_D = -\frac{\hbar^2e^2}{4\pi\varepsilon_08m^2c^2} \nabla^2 \left( \frac{1}{R} \right) \]

\[ = -\frac{\pi}{12} S^3(R) \]

\[ H_D = \frac{\pi e^2\hbar^2}{12m^2c^2} S^3(R) \]

Since we are using C-M coordinates here \( S^3(R) \) implies the electron is in contact with the nucleus, which is at the origin. Such a term \( S^3(R) \) 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).

\[ H = H_0 + H_{fs} \quad ; \quad H_0 = \frac{\hbar^2}{2m} \hat{P}^2 + V(R) \]

\[ H_{fs} = H_{\text{kin}} + H_{so} + H_D \]

with \( V(R) = -\frac{e^2}{R} \)

\[ H_{\text{kin}} = -\frac{1}{8m^3c^2} \hat{P}^4 \]

\[ H_{so} = \frac{1}{2m^2c^2} \frac{1}{R} \frac{dV(R)}{dR} \]

\[ H_D = \frac{\pi e^2 \hbar^2}{4\pi^2} \frac{\hat{S}^2(R)}{2m^2c^2} \]

This result has the rigorous derivation
from the non-relativistic reduction
of the Dirac equation. Above we
physically motivated the result.
As the notation implies, we will apply R-S perturbation theory to calculate the energy levels of $H_0$. Hence the energy shifts determined by $H_{1S}$ should be small compared to the energy levels of the unperturbed Hamiltonian $H_0$. To see this recall that the unperturbed energy levels of $H_0$ are given by

$$E_n = -\frac{m e^4}{(4\pi \epsilon_0)^2 \hbar^2 n^2} = -\frac{e^2}{\hbar^2} \frac{1}{2\alpha_0} \frac{1}{n^2}$$

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

where $\alpha = \frac{e}{mc} = \text{Bohr radius}$ and

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

Using these parameters the unperturbed Hamiltonian can be written as

$$H_0 = mc^2 \alpha^2 \left(\frac{a_0^2}{2\hbar^2} \frac{p^2}{R} - \frac{a_0}{R}\right)$$
Thus we see that the scale of \( H_0 \) (i.e. \( E_0 \)) is determined by \( \frac{m c^2}{\hbar^2} \) the operator in brackets being of the number the order of 1. The perturbation Hamiltonian in these variables become

\[
H_{\text{Kin}} = mc^2 \alpha^4 \left( -\frac{a_0^4}{8\hbar^4} \phi^4 \right)
\]

\[
H_{\text{So}} = mc^2 \alpha^4 \left( \frac{a_0^3}{2\hbar^2} \frac{1}{R^3} \phi^5 \right)
\]

\[
H_0 = mc^2 \alpha^4 \left( \frac{\hbar}{2} \frac{a_0^3}{S^3(\overline{R})} \right)
\]

where the Coulomb potential is

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

\[
\frac{dV(R)}{dR} = mc^2 \alpha^2 \frac{a_0}{R^2}
\]

Thus we see that the scale of \( H_0 \) is given by \( (mc^2\alpha^2) \alpha^2 \); it is \( \alpha^2 \) times
smaller than the scale of \( \lambda_0 \). So indeed our perturbation parameter \( \lambda = \frac{\alpha^2}{\pi} \left( \frac{137}{2} \right)^2 \) is quite small. We expect perturbation theory to give accurate results for the energy shifts; they should be of the order of \( \alpha^2 \lambda_0 \approx 10^{-3} \text{eV}. \)

In order to apply the R-S perturbation scheme, we must begin by solving the unperturbed problem. The unperturbed Hamiltonian \( H^0 = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{R} \) as we said has eigenvalues

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

Since \( V(R) \) is a central potential it is rotationally invariant. As well \( H^0 \) is independent of the electron’s spin and we ignored it completely when considering the Coulomb problem earlier. Hence \( H^0 \) commutes with \( \mathbf{I} \& \mathbf{S} \). Thus we can choose as we did earlier, the set \( \{ E, H^0, \mathbf{I}^2, \mathbf{S}^2, \mathbf{L}^2, \mathbf{S} \cdot \mathbf{L} \} \) as our CSNO with eigenstates labelled by

\[
| n, l, s; m_s, m_s > = | n, l, m > \otimes | s, m_s >
\]
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, \( S_z \) of course the electron has spin \( S = \frac{1}{2} \) and so the \( z \)-component of spin is \( m_s = \pm \frac{1}{2} \). Then

\[
\hat{H}_n l, l, s = \frac{1}{2}, m, m_s \rangle = E_n^0 \ l n, l, s = \frac{1}{2}, m, m_s \rangle
\]

\[
\hat{L}^2 \ | \ \psi \rangle = l(l+1)\hbar^2 | \ \psi \rangle
\]

\[
\hat{S}^2 \ | \ \psi \rangle = \frac{3}{4} \hbar^2 | \ \psi \rangle
\]

\[
\hat{L}_z \ | \ \psi \rangle = m \hbar | \ \psi \rangle
\]

\[
\hat{S}_z \ | \ \psi \rangle = m_s \hbar | \ \psi \rangle
\]

Thus we see that \( E_n^0 \) is degenerate for each \( n \) there are
\[ 2^{\text{spin}} = \frac{1}{2} \]

\[
(2s+1) \sum_{l=0}^{n-1} (2l+1) = 2 \left( \frac{2(n-1)n + n}{2} \right) = 2n^2 \text{ eigenstates}
\]

with the same \( E_n \). Thus \( E_n \) is 2

\[ 2n^2 \text{-fold degenerate.} \]

As we selected \( H_0 \) commutes with \( \hat{S} \) and \( \hat{J} \) hence it commutes with the total angular momentum \( \hat{J} = \hat{L} + \hat{S} \).

We could use as a CSKO the set of operators \( \{ H_0, \hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z \} \). The eigenstates for this set are given by:

\[ | n, l, s; J, M \rangle \]

where (recall pages -777- to -789-)

\[ n = 1, 2, \ldots \]

\[ l = 0, 1, \ldots, n-1 \]

\[ s = \frac{1}{2} \]

as before, and

\[ J = \begin{cases} \frac{1}{2} & \text{if } l = 0 \\ \sqrt{l + 1}, l = \frac{1}{2} & \text{if } l > 0 \end{cases} \]

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
\[ \hat{\mathcal{L}} \cdot \hat{\mathbf{s}} = \frac{1}{2} (\hat{\mathcal{L}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{s}}^2) \] is diagonal
in this basis, i.e.,
\[ \hat{\mathcal{L}} \cdot \hat{\mathbf{s}} \left| n, l, s; J, M \right> = \frac{\hbar^2}{2} \left[ J(J+1) - l(l+1) \right. \\
\left. - \frac{3}{4} \right] \hat{J}_z \\
\left| n, l, s; J, M \right>. \]

And so we have
\[ \hat{J}^2 \left| n, l, s; J, M \right> = J(J+1) \hbar^2 \left| n, l, s; J, M \right> \]
\[ J \geq 1 \quad \left| n, \hbar \right> = M \hbar \left| 1 \right>. \]

Hence we find the degeneracy of \( E_0 \)
to be
\[ \sum_l \sum_{J=|l-\frac{1}{2}|}^{2J} (2J+1) = \sum_l \sum_{J=|l-\frac{1}{2}|}^{2J} 2(2l+1) = 2n^2, \]
\[ n = 0, 1, 2, \ldots \]

as required. Further knowing the
Clebsch-Gordan coefficients, we have no difficulty in transforming from one
basis to another.
Recalling that \( H_{fs} = H_{kin} + H_{so} + H_{D} \) with

\[
H_{kin} = -\frac{1}{8m^2c^2} \vec{p}^4
\]

\[
H_{so} = \frac{\hbar e^2}{4\pi \varepsilon_0 \omega_0^2 c^2} \vec{L} \cdot \vec{S}
\]

\[
H_{D} = \frac{\hbar e^2}{4\pi \varepsilon_0 \omega_0^2 c^2} S^2(\vec{r})
\]

we have that \([\vec{L}, H_{fs}] = 0 = [\vec{S}, H_{fs}]\)

as well as we also have \([\vec{J}^2, H_{fs}] = 0\) and \([\vec{J}_z, H_{fs}] = 0\). These follow from \(\vec{R}, \vec{P}^2, \vec{L} \cdot \vec{S}, S^2(\vec{r})\) being rotationally invariant, so they commute with \(\vec{J}^2\) and \(\vec{J}_z\).

Further \(\vec{R}, \vec{P}^2\) and \(S^2(\vec{r})\) are independent of spin so they commute with \(\vec{S}\) and so rotational invariance implies they also commute with \(\vec{L}\). Likewise \(\vec{J}^2\) and \(\vec{S}\) are scalars so they commute with \(\vec{L}\) and \(\vec{S}\) and so \(\vec{L} \cdot \vec{S}\) (they are the Casimir operators for the \(SU(2)\) groups respectively). Note that \([\vec{L} \cdot \vec{S}, \vec{L}_z] \neq 0\) and so \([\vec{S}, \vec{L}_z] \neq 0\). Thus \(H_{fs}\) is
diagonal in the \( \{|n,l,s;J,M\rangle\} \) basis but not the \( \{|n,l,s;\pm n,\pm m\rangle\} \) basis for a fixed \( n \).

Hence we will use the \( \{|n,l,s;J,M\rangle\} \) basis in which \( H, H'_0, H_{fs} \) are all diagonal for a fixed \( n \).

In detail, we have

\[
\left[ J_z, H_{fs} \right] = 0
\]

\[

\begin{align*}
\Rightarrow \quad D &= \langle n, \ell', s = \frac{1}{2}; J', M' | J_z \cdot (\hat{L}^2 - \ell(\ell + 1)\hat{t}^2) | n, \ell, s = \frac{1}{2}; J, M \rangle \\
&= \langle n, \ell', s = \frac{1}{2}; J', M' | H_{fs} | n, \ell, s = \frac{1}{2}; J, M \rangle \times \delta_{\ell\ell'} \delta_{s\frac{1}{2}} \\
\Rightarrow \quad \langle n, \ell', s = \frac{1}{2}; J', M' | H_{fs} | n, \ell, s = \frac{1}{2}; J, M \rangle &\propto \delta_{JJ'} \\
\Rightarrow \quad \langle n, \ell', s = \frac{1}{2}; J', M' | H_{fs} | n, \ell, s = \frac{1}{2}; J, M \rangle &\propto \delta_{JJ'} \delta_{MM'} \delta_{\ell\ell'} \delta_{s\frac{1}{2}}.
\end{align*}

\]
Hence we find

\[ \langle n, l', s = \frac{1}{2}; J', M | H_{F5} | n, l, s = \frac{1}{2}; J, M \rangle \]

\[ = \delta_{ll'} \delta_{JJ'} \delta_{MM'} \langle n, l, s = \frac{1}{2}; J, M | H_{F5} | n, l, s = \frac{1}{2}; J, M \rangle \]

The matrix elements of \( H_{F5} \) in the \( n, l, s; J, M \) basis are already diagonal. This is particularly useful since first-order degenerate RIS perturbation theory requires \( \langle \psi | H_{F5} | \psi \rangle \) to diagonalize the matrix. The eigenvalues are the diagonal elements, 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

\[ H_{\text{kin}} = -\frac{1}{8m^3c^2} \overrightarrow{p}^4 = mc^2 x^4 \left[ -\frac{a_0^4}{8\hbar^4} \overrightarrow{p}^4 \right] \]
Since \( H_0 = mc^2 \Delta^2 \left[ \frac{a_0^2}{2m^2} \vec{P}^2 - \frac{a_0}{R} \right] \)
\[ = \frac{1}{2m} \vec{P}^2 - \frac{e^2}{R} \]
we can write \( \vec{P}^2 = 2m (H_0 + \frac{e^2}{R^2}) \) and so
\[ \vec{P}^4 = 4m^2 \left[ H_0^2 + \frac{e^4}{R^2} + H_0 \frac{e^2}{R^2} + \frac{e^2}{R^2} H_0 \right]. \]
Hence
\[ H_{\text{kin}} = -\frac{1}{2mc^2} \left[ H_0^2 + \frac{e^4}{R^2} + H_0 \frac{e^2}{R^2} + \frac{e^2}{R^2} H_0 \right] \]
and
\[
\langle n, l, s = \frac{1}{2}; J, M \mid H_{\text{kin}} \mid n, l, s = \frac{1}{2}; J, M \rangle
\]
\[ = -\frac{1}{2mc^2} \left\{ (E_n^0)^2 + \frac{e^4}{R^2} \langle n, l, s = \frac{1}{2}; J, M \mid \frac{1}{R^2} \mid n, l, s = \frac{1}{2}; J, M \rangle \right\}
\[ + 2 E_n^0 \frac{e^2}{R} \langle n, l, s = \frac{1}{2}; J, M \mid \frac{1}{R} \mid n, l, s = \frac{1}{2}; J, M \rangle \]

Thus we must evaluate matrix elements of powers of \( R \).
Since $R$ is independent of spin and is rotationally invariant, it commutes with $\hat{S}$ Since $R$ is independent of angular coordinates in the $|\vec{r}\rangle$ basis in spherical polar coordinates, $<\vec{r}|R = r|\vec{r}\rangle$. Thus we find in the $|n, l, s; m, m_s\rangle$ basis that

$$<n, l', s'; m', m_s|R^{\dagger}|n, l, s; m, m_s>$$

$$= \delta_{ll'}\delta_{ss'}\delta_{m'm}\delta_{m_sm_s}<n, l, s; m, m_s|R^{\dagger}|n, l, s; m, m_s>$$

Since $[L^2, R]=0 = [S^2, R] = [L_z, R] = [S_z, R]$. Since $|n, l, s; m, m_s\rangle = |n, l, m > \otimes |s, m_s\rangle$ and $R$ only acts on the spatial variables, not the spin and since $<s|m_s|s, m_s> = 1$ we have

$$<n, l, s; m, m_s|R^{\dagger}|n, l, s; m, m_s>$$

$$= <n, l, m |R^{\dagger}|n, l, m >.$$
Further, \( [L, R^\dagger] = 0 \Rightarrow [L_\pm, R] = 0 \).

Thus we have for instance
\[
0 = \langle n, l, m | [R^\dagger L_+] | n, l, m-1 \rangle \\
= \langle n, l, m | \begin{bmatrix} L_+ R^\dagger - R^\dagger L_+ \end{bmatrix} | n, l, m-1 \rangle
\]
\[
\propto \begin{bmatrix} \langle n, l, m-1 | R^\dagger | n, l, m-1 \rangle \\
- \langle n, l, m | R^\dagger | n, l, m \rangle \end{bmatrix}
\]}
\[
= \langle n, l, m-1 | R^\dagger | n, l, m \rangle
\]

The diagonal matrix elements of \( R^\dagger \) are independent of \( m \). This can be seen explicitly by redefining the \( | n, l, m \rangle \) as Legendre polynomials:
\[
\langle \tilde{r} | n, l, m \rangle = 2^{-1} \tilde{r}^m \frac{d^m}{dr^m} (r^2 - 1)^{l+1/2}
\]
\[
= R_{nl}(\tilde{r}) Y^m_l(\theta, \phi)
\]

Thus
\[ \langle n, l, m | R^2 | n, l, m \rangle \]
\[ = \int d^3r \ 2^l \ 4^m_n(\mathbf{r}) \ r^2 \ 4^m_n(\mathbf{r}) \]
\[ = \int d\Omega \ y^m_2(\theta, \phi) \ y^m_n(\theta, \phi) \int_0^\infty dr \ r^2 \ r^2 |R_{nl}(r)|^2 \]
\[ = 1 \]
\[ = \int_0^\infty dr \ r^2 \ r^2 |R_{nl}(r)|^2 \quad \text{which is independent of } m. \]

Now applying these results to the \( l, s, J, M \) matrix elements we find
\[ \langle n, l, s = \frac{1}{2}; J, M | R^2 | n, l, s = \frac{1}{2}; J, M \rangle \]
\[ = \sum_{m} \sum_{m'} \sum_{m''} \sum_{m'''} \frac{(-1)^l}{2} \frac{(-1)^l}{2} \frac{(-1)^l}{2} \]
\[ \frac{(-1)^l}{2} \frac{(-1)^l}{2} \frac{(-1)^l}{2} \]
\[ m = -l \quad m' = -\frac{l}{2} \quad m'' = -l \quad m''' = -\frac{l}{2} \]
\[ \langle n, l, s = \frac{1}{2}; J, M | n, l, s = \frac{1}{2}; m', m'' \rangle \times \]
\[ \langle n, l, s = \frac{1}{2}; m', m'' | R^2 | n, l, s = \frac{1}{2}; m, m' \rangle \times \]
\[ \times \langle n, l, s = \frac{1}{2}; m, m' | n, l, s = \frac{1}{2}; J, M \rangle \]
\[ -936 - \]

\[ \sum_{m=\pm \ell} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} \langle n,l,s=\frac{1}{2}; J,M | n,l,s=\frac{1}{2}; m,m_s \rangle \]

\[ \langle n,l,s=\frac{1}{2}; m,m_s | R_R | n,l,s=\frac{1}{2}; m,m_s \rangle \]

\[ \langle n,l,s=\frac{1}{2}; m,m_s | n,l,s=\frac{1}{2}; J,M \rangle \]

\[ = \langle n,l,R_R | n,l \rangle \times \sum_{m=\pm \ell} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} \langle n,l,s=\frac{1}{2}; J,M | n,l,s=\frac{1}{2}; m,m_s \rangle \]

\[ \langle n,l,s=\frac{1}{2}; J,M | n,l,s=\frac{1}{2}; m,m_s \rangle \]

\[ \langle n,l,s=\frac{1}{2}; J,M | n,l,s=\frac{1}{2}; J,M \rangle = 1 \]

\[ = \langle n,l|R_R | n,l \rangle \]

\[ = \int_0^\infty dr r^{q+2} |R_{n,e}(r)|^2 \]

\[ = \langle n,l,s=\frac{1}{2}; J,M | R_R | n,l,s=\frac{1}{2}; J,M \rangle \]
Putting them together we obtain

\[ \langle n, l, s = \frac{1}{2}; j, M | H_{\text{Kin}} | n, l, s = \frac{1}{2}; j, M \rangle \]

\[ = -\frac{1}{2mc^2} \left\{ (E_n^0)^2 + \frac{e^4}{4\hbar c} \langle n, l | R^{-2} | n, l \rangle \right\} 
\]

\[ + 2E_n^0 \frac{e^2}{\hbar c} \langle n, l | R^{-1} | n, l \rangle \right\}^3 \]

Now recall \( E_n^0 = -\frac{mc^2}{2} \frac{1}{n^2} \frac{1}{\hbar^2} \)

and \( e^2 = \frac{1}{\hbar c} = mc^2 \frac{1}{\hbar^2} a_0 \); thus

\[ \langle n, l, s = \frac{1}{2}; j, M | H_{\text{Kin}} | n, l, s = \frac{1}{2}; j, M \rangle \]

\[ = -mc^2 \alpha^4 \left[ \frac{1}{8n^4} + \frac{a_0^2}{2 \hbar^2} \langle n, l | \frac{1}{R^2} | n, l \rangle \right] \]

\[ - \frac{a_0}{2n^2} \langle n, l | \frac{1}{R} | n, l \rangle \right\}^3 \]

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

$$
H_D = \frac{\pi e^2 \hbar^2}{8 \pi^3 \cdot 2m^2 c^2} \mathcal{S}^3 (\mathbb{R})
$$

$$
= mc^2 \chi^4 \left( \frac{\pi}{2} a_0^3 \mathcal{S}^3 (\mathbb{R}) \right)
$$

Again $\mathcal{S}^3 (\mathbb{R})$ is rotationally invariant and independent of the spin, $\mathbf{m}$ is fixed, $m, ms \neq 0$ basis depends only on $\mathbf{m}$ and is diagonal.

$$
\langle n, l', s=\frac{1}{2}; m', ms' | \mathcal{S}^3 (\mathbb{R}) | n, l, s=\frac{1}{2}; m, ms \rangle
$$

$$
= \langle n, l', m' | \mathcal{S}^3 (\mathbb{R}) | n, l, m \rangle \langle s=\frac{1}{2}; ms | s=\frac{1}{2}; ms \rangle
$$

$$
= \int d^3r \mathbf{4} \chi^* (\mathbb{R}) \mathcal{S}^3 (\mathbb{R}) \chi (\mathbb{R}) \delta_{ms' ms}
$$

$$
= \delta_{ms' ms} \mathbf{4} \chi (0) \chi (0)
$$

$$
= \delta_{ms' ms} \mathbf{R}^* (0) \mathbf{R} (0) \chi (0, 0) \chi (0, 0)
$$

Now recall that $\mathbf{R}(\mathbb{R})$ is given by the associated Laguerre polynomials.
times $r^2$. Thus as $r \to 0$ 
$$R_{n,0} \sim r^2$$
which vanishes unless $l = 0$. Thus
\[
\langle n', l', s = \frac{1}{2}; m', m' \sigma | 8 \sigma (\mathbf{R}) | n, l, s = \frac{1}{2}; m, m \sigma \rangle = \delta_{m' m} \delta_{l' l} \delta_{s' s} S_{n,0} S_{m,0} \left| R_{n,0} (0) \right|^2 \frac{1}{4 \pi},
\]
hence only $s$-states have non-vanishing HD matrix elements.

Hence
\[
\langle n, l, s = \frac{1}{2}; J, M | H_D | n, l, s = \frac{1}{2}; J', M' \rangle
= \sum_{l'} \sum_{l} \sum_{s} \sum_{s'} \sum_{M} \sum_{M'} \left| \langle n, l, s = \frac{1}{2}; J, M | n, l, s = \frac{1}{2}; M', M' \rangle \right|^2
\]
\[
\langle n, l, s = \frac{1}{2}; m, m \sigma | H_D | n, l, s = \frac{1}{2}; m, m \sigma \rangle
\langle n, l, s = \frac{1}{2}; m, m \sigma | H_D | n, l, s = \frac{1}{2}; J, M \rangle
= \sum_{l} \sum_{s} \sum_{M} \left| m c^2 a^4 \frac{\pi a^3}{2 a_0} \langle n, l, s = \frac{1}{2}; J, M | n, l, s = \frac{1}{2}; m, m \sigma \rangle \right|^2
\]
\[
\times 8 \delta_{l 0} \delta_{l 0} \left| R_{n,0} (0) \right|^2 \frac{1}{4 \pi}.
\]
\[
S_0 = \sum_{l=0}^{\infty} \frac{\alpha^3}{8} \frac{M^2 \alpha^4}{\xi_0} \left| R_{n_01} \right|^2 \delta_{n_0, l=0, s=\frac{1}{2}, J, M} \left| n, l=0, s=\frac{1}{2}, m=0, m_s \right>.
\]

But for \( l=0 \) \( J=\frac{1}{2} \) and \( m_s=M \); Thus

for fixed \( m \) only \( m_s=M \) contribute \( \Rightarrow \)

\[
= \delta_{l=0} \frac{M^2 \alpha^4}{8} \alpha^3 \left| R_{n_01} \right|^2.
\]

So we obtain the diagonal matrix elements of \( H_0 \):

\[
\langle n, l, s=\frac{1}{2}; J, M | H_0 | n, l, s=\frac{1}{2}; J, M \rangle
\]

\[
= \frac{M^2 \alpha^4}{8} \alpha^3 \left| R_{n_01} \right|^2 \delta_{l=0}.
\]

Finally, we must determine the diagonal matrix elements of \( H_{so} \).
\[ H_{so} = m c^2 \alpha^4 \left( \frac{a_0^3}{2 \hbar^2} \frac{1}{R^3} \, \hat{L} \cdot \hat{S} \right) \]
\[ = \frac{e^2}{4 \pi \hbar^2 \alpha^2 m c^2} \frac{1}{R^3} \, \hat{L} \cdot \hat{S} \]

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

\[ H_{so} = \frac{m c^2 \alpha^4 a_0^3}{4} \frac{1}{R^3} \frac{1}{\hbar^2} \left( \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right). \]

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

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

So the diagonal matrix elements are

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

Using the results of page 9336, 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

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

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

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

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

$$= -mc^2 \alpha^4 \left( \frac{1}{8n^4} - \frac{a_o}{2n^2} \langle n, l | \frac{1}{R} | n, l \rangle \right.$$

$$\left. + \frac{a_o^2}{2} \langle n, l | \frac{1}{R^2} | n, l \rangle \right)$$

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

$$= mc^2 \alpha^4 \left( J(J+1) - l(l+1) - \frac{3}{4} \right) \frac{a_o^3}{4} \langle n, l | \frac{1}{R^3} | n, l \rangle$$
(All Hfs diagonal matrix elements are independent of M.)
So there will remain a (2J+1) degeneracy.

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

Where the radial expectation values are given by
\[ \langle n,l \mid R^2 \mid n,l \rangle = \int_0^\infty dr r^8 \langle n,l \mid R_{n0}^2 \mid n,l \rangle \]
with the unperturbed hydrogenic wave functions given by
\[ \langle n,l \mid n,l,m \rangle = R_{n0}(r) Y_{l}^{m}(\theta, \phi) \]

Recall that the hydrogen radial wavefunction \( R_{n0}(r) \) is given by powers of \( r \) times an exponential damping factor (page 233-)

\[ R_{n0}(r) = -\left[ \frac{(2)}{na_0} \frac{(n-l-1)!}{2n! (n+l)!} \right]^{1/2} \times \]
\[ \times \left( \frac{2r}{na_0} \right)^l \frac{2l+1}{2l+1} \left( \frac{2r}{na_0} \right) e^{-\frac{r}{na_0}} \]
with the associated Laguerre polynomials

\[ L_p^q(z) = (q!)^{-1} \sum_{n=0}^\infty \frac{(-1)^{p+n} z^n}{(q-p-n)! (p+n)! n!} \]

(i.e.,

\[ R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \]

\[ R_{20}(r) = \frac{1}{(2a_0)^{3/2}} (2 - \frac{r}{a_0}) e^{-r/2a_0} \]

\[ R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{r}{\sqrt{3} a_0} e^{-r/2a_0} \]

Hence we will need, when evaluating \( \langle n, e | R_{R_8} | n, e \rangle \), integrals of powers of \( r \) times \( e^{-pr/a_0} \)

\[ I(k, p) = \int_0^\infty dr \ r^k \ e^{-pr/a_0} \]

Re-scaling \( r \) according to \( t = \frac{2}{a_0} r \)

\[ dr = \frac{a_0}{2} \ dt \]

The integral becomes
\[ I(k,p) = \left( \frac{a_0}{P} \right)^{k+1} \int_0^\infty dt \, t^k \, e^{-t} = \Gamma(k+1) \]

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

\[ I(k,p) = \Gamma(k+1) \left( \frac{a_0}{P} \right)^{k+1} \]

So for example

\[ \langle n=1, l=0 \mid R^6 \mid n=1, l=0 \rangle = \int_0^\infty dr \, r^6 \, e^{-2r/a_0} \left| R_{10}(r) \right|^2 \]

\[ = \frac{4}{a_0^3} \int_0^\infty dr \, r^6 \, e^{-2r/a_0} = \frac{4}{a_0^3} I(q+2, 2) \]

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

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

while for \( n=2 \) we have

\[ \langle n=2, l=0 \mid R^6 \mid n=2, l=0 \rangle = \int_0^\infty dr \, r^6 \, e^{-2r/a_0} \left| R_{20}(r) \right|^2 \]
\[ \langle n=2, l=0 | R_2^0 | n=3, l=0 \rangle = \int_0^\infty dr \, r^{g+2} \frac{1}{(2a_0)^3} \, e^{-r/a_0} \times (4 + \frac{r^2}{a_0^2} - 4 \frac{r}{a_0}) \]

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

\[ = \frac{1}{2} a_0^6 \, \Gamma \left( q+3 \right) + \frac{1}{8} a_0^6 \, \Gamma \left( q+5 \right) - \frac{2}{4} a_0^6 \, \Gamma \left( q+4 \right) \]

\[ = \frac{1}{2} a_0^6 \left( \Gamma \left( q+3 \right) + \frac{1}{4} \, \Gamma \left( q+5 \right) - \Gamma \left( q+4 \right) \right) \]

and

\[ \langle n=2, l=1 | R_2^1 | n=3, l=1 \rangle = \int_0^\infty dr \, r^{g+2} | R_2 \left( 1 + \frac{1}{2} \right) |^2 \]

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

\[ = \frac{1}{24 a_0^5} \, I \left( q+4, 1 \right) \]

\[ = \frac{a_0^5 \, \Gamma \left( q+5 \right)}{24} \]
It is now straightforward to apply these results to the \( n=1 \), \( n=2 \) energy levels of hydrogen.

\[ \text{N=1} \]

The degeneracy of the \( E^0_{n=1} \) eigenvalues is 2 due to the electron spin.

The eigenstates of \( E^0_{n=0}, L_z, \frac{\hbar}{2}, J_z, J_\uparrow, J_\downarrow \) for this degenerate energy subspace are

\[ |n=1, l=0, s=\frac{1}{2}, J=\frac{1}{2}, M=\pm \frac{1}{2} \rangle. \]

According to conventional spectroscopic notation, this energy level is

\[ 1S_{1/2} \].

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 \( 1S_{1/2} \) 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 $E_0$-basis (page 871). Using $|n,s;J,M\rangle$ 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) $\langle n=1, l=0, s=\frac{1}{2}; J=\frac{1}{2}, M \mid H_{kin} \mid n=1, l=0, s=\frac{1}{2}; J=\frac{1}{2}, M \rangle$

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

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

$= -\frac{5}{8} mc^2 \alpha^4$

2) $\langle n=1, l=0, s=\frac{1}{2}; J=\frac{1}{2}, M \mid H_{so} \mid n=1, l=0, s=\frac{1}{2}; J=\frac{1}{2}, M \rangle$

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

$= 0$
3) \[ \langle n=1, l=0, s=\frac{1}{2}, J=\frac{1}{2}, M_c | H_{so} | n=1, l=0, s=\frac{1}{2}, J=\frac{1}{2}, M_c \rangle \]

\[ = \frac{1}{2} MC^2 \alpha^4 \frac{A_0}{8} |R_{10}(0)|^2 \]

As observed earlier, all diagonal matrix elements of \( H_{so} \) are independent of \( M_c \) and so the \( 2J+1 = 2 \) -fold degeneracy of \( |S\rangle \) remains. This is due to the fact that for \( 1S_{1/2} \), 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

\[ \langle n=1, l=0, s=\frac{1}{2}, J=\frac{1}{2}, M_c ' | H_{so} | n=1, l=0, s=\frac{1}{2}, J=\frac{1}{2}, M_c \rangle \]

\[ = \delta_{M_c M_c '} \left( \frac{-5}{8} MC^2 \alpha^4 + 0 + \frac{1}{2} MC^2 \alpha^4 \right) \]

\[ = \delta_{M_c M_c '} \left( -\frac{1}{8} MC^2 \alpha^4 \right) \]
Thus we see that the effect of $H_{ls}$ in the 2-$ls_{1/2}$ degenerate energy levels is merely to shift both of these down in energy by the same amount.

$$E_{ls_{1/2}} = E_{n=1}^0 + \langle n=1, l=0, s=\frac{1}{2}; J=\frac{3}{2}, M \mid H_{ls} \mid n=1, l=0, s=\frac{1}{2}; J=\frac{3}{2}, M \rangle$$

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

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

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

$$E_{ls_{1/2}} = -13.6058036 \left( 1 + 0.00000133 \right) \text{ eV}$$

$$= -13.6058036 \left( 1 + 0.00000133 \right) \text{ eV}$$

using $mc^2 = 0.511034 \text{ (14)} \text{ MeV}$

$$\alpha = 137.03604 \text{ (11)}$$

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

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

$n=2$ The $E_{n=2}^0$ level is $2n^2 = 8$-fold degenerate. It contains the 2-$ls_{1/2}$ states $| n=2, l=0, s=\frac{1}{2}; J=\frac{3}{2}, M=\pm \frac{3}{2} \rangle$

There are 2 of these.
Recall for given \( n; l = 0, 1, \ldots, n-1; \, J = \frac{n+1}{2}, \frac{n-1}{2} \) and \( M = -J, \ldots, +J \).

and the 2 \( P_{\frac{1}{2}} \) states

\[ |n=2, l=1; s=\frac{1}{2}; J=\frac{1}{2}, M=\pm\frac{1}{2} \rangle, \]

There are 2 of these and finally

the 2 \( P_{\frac{3}{2}} \) states

\[ |n=2, l=1; s=\frac{1}{2}; J=\frac{3}{2}, M=\pm\frac{3}{2}, \pm\frac{1}{2}, \pm\frac{1}{2} \rangle \]

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

Since \( H_{\text{kin}} \) is independent of \( M \); 2 \( S_{\frac{1}{2}} \) will remain 2-fold degenerate

2 \( P_{\frac{1}{2}} \) will remain 2-fold degenerate

2 \( P_{\frac{3}{2}} \) will remain 4-fold degenerate

Consider first the 2 \( S_{\frac{1}{2}} \) states

\[ 2 \langle \frac{1}{2} | H_{\text{kin}} | 2 \rangle \]

\[ \langle n=2, l=0, s=\frac{1}{2}; J=\frac{1}{2}, M=\pm\frac{1}{2}, \pm\frac{1}{2} \rangle \]

\[ = -mc^2\frac{1}{8(2)!} \left( \frac{1}{20} \right)^2 \langle 20 | \langle l^2 | 20 \rangle \right. \]

\[ + \frac{a_0^2}{2} \langle 20 | \frac{1}{R^2} | 20 \rangle \]
1) $\langle 2s_{1/2} | H_{\text{kin}} | 2s_{1/2} \rangle$

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

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

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

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

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

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

$$= mc^2 \chi^4 \left( \frac{1}{2} (\frac{1}{2} + 1) - \frac{1}{2} (0 + 1) - \frac{3}{4} \right) \frac{a_0^3}{4} \left\langle 2,0 \left| H_{\text{so}} \right| 2,0 \right\rangle$$

$$= 0$$
3) \[ \langle 2s_{1/2} \mid H_{\text{HF}} \mid 2s_{1/2} \rangle \]
\[ = mc^2 \chi^4 \frac{a_0^3}{8} |R_{20}(0)|^2 \]
\[ = mc^2 \chi^4 \frac{a_0^3}{8} \frac{4}{8a_0^3} \]
\[ = \frac{1}{16} mc^2 \chi^4. \]

Combining these results we find
\[ \langle 2s_{1/2} \mid H_{\text{HF}} \mid 2s_{1/2} \rangle = -\frac{5}{128} mc^2 \chi^4 \]

Thus the 2s\(_{1/2}\) levels remain 2-fold degenerate with their energies shift down by the same amount

\[ E_{2s_{1/2}} = E_0^{\text{n=2}} + \langle 2s_{1/2} \mid H_{\text{HF}} \mid 2s_{1/2} \rangle \]
\[ = -\frac{mc^2 \chi^2}{2 (2)^2} - \frac{5}{128} mc^2 \chi^4 \]

Thus \[ E_{2s_{1/2}} = -\frac{mc^2 \chi^2}{8} \left( 1 + \frac{5}{16} \chi^2 \right) \]
Finally we consider

\[ 2p_{1/2} \]

\[ \langle 2p_{1/2} | H_{\text{kin}} | 2p_{1/2} \rangle \]

\[ = -mc^2 \lambda^4 \left( \frac{1}{8(2)^4} - \frac{a_0^2}{2(2)^2} \langle 2,1 | \frac{1}{R^3} | 2,1 \rangle \right) \]

\[ + \frac{a_0^2}{2} \langle 2,1 | \frac{1}{R^2} | 2,1 \rangle \right) \]

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

\[ = -mc^2 \lambda^4 \left( \frac{1}{128} - \frac{1}{32} + \frac{1}{24} \right) \]

\[ = -mc^2 \lambda^4 \left( \frac{3 - 12 + 16}{384} \right) \]

\[ = -\frac{7}{384} mc^2 \lambda^4 \]

---

2)

\[ \langle 2p_{1/2} | H_{\text{so}} | 2p_{1/2} \rangle \]

\[ = mc^2 \lambda^4 \left( \frac{1}{2} (\frac{1}{2} + 1) - 1(1+1) - \frac{3}{4} \right) \frac{a_0^3}{4} \langle 2,1 | \frac{1}{R^3} | 2,1 \rangle \]

\[ = -mc^2 \lambda^4 \frac{a_0^3}{2} \langle 2,1 | \frac{1}{R^3} | 2,1 \rangle \]

\[ = -\frac{1}{48} mc^2 \lambda^4 \]
and of course

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

$$= mc^2 a^4 \frac{a_0^3}{8} |R_{2010}|^2 \sum_{l=1,0}$$

$$= 0$$

Combining these results we find

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

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

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

$$E_{2p_{1/2}} = E_0^{n=2} + \langle 2p_{1/2} | H_{fs} | 2p_{1/2} \rangle$$

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

$$E_{2p_{1/2}} = -\frac{mc^2 a^2}{8} \left(1 + \frac{5}{16} a^2\right)$$
And for the 4-fold degenerate states 

\( 2P_{3/2} \):

\[
\langle 2P_{3/2} | H_{\text{kin}} | 2p_{3/2} \rangle = - mc^2 \lambda^4 \left( \frac{1}{8(2)^4} - \frac{a_0}{2(2)^2} \langle 2,1 \mid \frac{1}{R} \mid 2,1 \rangle + \frac{a_0^2}{2} \langle 2,1 \mid \frac{1}{R^2} \mid 2,1 \rangle \right) = - \frac{7}{384} mc^2 \lambda^4 \hspace{1cm} (\langle 2p_{3/2} | H_{\text{kin}} | 2p_{3/2} \rangle)
\]

\( 2) \langle 2p_{3/2} | H_{\text{so}} | 2p_{3/2} \rangle = 1 \)

\[
= mc^2 \lambda^4 \left( \frac{3}{2} \left( \frac{3}{2} + 1 \right) - \frac{1(1+1) - \frac{3}{4}}{4} \right) a_0^3 \langle 2,1 \mid \frac{1}{R^3} \mid 2,1 \rangle = mc^2 \lambda^4 \frac{a_0^3}{4} \langle 2,1 \mid \frac{1}{R^3} \mid 2,1 \rangle
\]

\[
= \frac{1}{96} mc^2 \lambda^4
\]

\( 3) \langle 2p_{3/2} | H_{\text{D}} | 2p_{3/2} \rangle
\]

\[
= mc^2 \lambda^4 \frac{a_0^3}{8} |R_{20}(0)|^2 \sum_{l=0}^{l=0} 0
\]

\[
= 0
\]
Combining these results we find
\[
\langle 2p_{3/2} | H_{ts} | 2p_{3/2} \rangle = -\left( \frac{7}{384} - \frac{1}{96} \right) mc^2 x^4
\]

\[
= -\frac{1}{128} mc^2 x^4
\]

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

\[
E_{2p_{3/2}} = E_{n=2}^0 + \langle 2p_{3/2} | H_{ts} | 2p_{3/2} \rangle
\]

\[
= - \frac{mc^2 x^2}{2(2)^2} - \frac{1}{128} mc^2 x^4
\]

\[
E_{2p_{3/2}} = - \frac{mc^2 x^2}{8} \left( 1 + \frac{1}{16} x^2 \right)
\]

We can depict the results of our first order perturbation calculation graphically as:
\[ E_2^0 = -\frac{mc^2\alpha^2}{8} \]

Unperturbed \( n=2 \) energy level is 8-fold degenerate.

\[ E_{2p_{\frac{3}{2}}} = E_2^0 - \frac{1}{128} mc^2 \alpha^4 \]

2\( p_{\frac{3}{2}} \)

4-fold degenerate

2\( s_{\frac{1}{2}} \)

2-fold degenerate

4-fold degenerate

The 8-fold degeneracy is broken with a gap of

\[ \frac{4}{128} mc^2 \alpha^4 = \frac{1}{32} mc^2 \alpha^4 \approx 4.5 \times 10^{-5} \text{ eV} \]

Note: The 2\( s_{\frac{1}{2}} \), 2\( p_{\frac{1}{2}} \) degeneracy is removed by quantum fluctuations of the electromagnetic field (photon). These will be calculated in a full quantum mechanical treatment.
electrodynamics (QED). One finds that the $2s_{1/2}$ level is raised with the $2p_{1/2}$ level by the "Lamb shift"
\[
\begin{array}{c}
2s_{1/2} \\
\uparrow \\
2p_{1/2}
\end{array}
\quad \text{by } 4.4 \times 10^{-6} \text{ eV (or } 1057 \text{ MHz)}
\]

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 $\mathbf{E}$ and magnetic field $\mathbf{B}$ are given in terms of the scalar $\phi$ and vector potentials $\mathbf{A}$

\[
\mathbf{B} = \nabla \times \mathbf{A}
\]

\[
\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}
\]

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