The Hydrogen atom, beyond leading order

So far, we've used $H_0 = \frac{P^2}{2M} - \frac{e^2}{R}$. This is not exact.

Neglects: * spin of electron
* spin (and internal structure) of proton
* relativistic effects

$$H = H_0 + H_{SO} + H_r + H_D + H_{HF} + \ldots$$

H_{SO} = spin-orbit of electron, electron has magnetic moment

$H_r = \frac{-(P^2)^2}{8m^3c^2}$ = relativistic correction (HW 1, #3)

H_D = Darwin term = contact interaction (HW1, #4)

all of same order $\Rightarrow$ fine structure

H_{HF} = smaller by $\frac{m_e}{m_p}$

Spin-orbit coupling

$$H_{SO} = \frac{-e}{4m^2c^2} \vec{S} \cdot (\vec{\nabla} V \times \vec{P}) = \xi(R)\, \vec{L} \cdot \vec{S}, \quad \text{where}$$

$$\xi(R) = \frac{e^2}{2m^2c^2R^3}. \qquad \text{Note: } H_{SO} = 0 \text{ for } l = 0.$$

Trick: $\vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$ $\vec{J} = \vec{L} + \vec{S}$.

So, consider states labelled by $|n, l, s, j, m_j\rangle$.

Use: $\langle n, l| \left(\frac{1}{R^3}\right) |n, l\rangle = \frac{1}{a_0^3} \frac{1}{n^3\, l(l+1)(l+\frac{1}{2})}$ (for $l \neq 0$).

(Can be proved using $R_{nl}(r)$ formulas.)

$$\langle n, l, s, j, m_j | \vec{L} \cdot \vec{S} | n, l, s, j, m_j\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

So, from 1st order perturbation theory:

$$\Delta E_{SO} = \langle n, l, s, j, m_j | H_{SO} | n, l, s, j, m_j\rangle = \begin{cases} \dfrac{e^2\hbar^2}{4m^2c^2a_0^3} \cdot \dfrac{[j(j+1) - l(l+1) - s(s+1)]}{n^3\, l(l+1)(l+\frac{1}{2})} & (l \neq 0) \\ 0 & (l = 0) \end{cases}$$

[Note: we must use *degenerate* perturbation theory, since there are states with same $E_{0,n} = \frac{-e^2}{2a_0 n^2}$, different ℓ, s. But, H_{so} is already diagonalized in the j, m_j basis.]

Rewrite:

$$\Delta E_{so} = \begin{cases} \dfrac{\alpha^2}{n^3}\left[\dfrac{j(j+1) - \ell(\ell+1) - s(s+1)}{\ell(\ell+1)(2\ell+1)}\right] \underbrace{\left(\dfrac{e^2}{2a_0}\right)}_{1 \text{ Rydberg} = 13.6057 \text{ eV}} & \ell \neq 0 \\ 0 & \ell = 0 \end{cases}$$

where $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137.036\ldots}$

Now $j = \ell \pm \frac{1}{2}$, so:

$$\Delta E_{so} = \begin{cases} \dfrac{\alpha^2}{n^3}\left(\dfrac{e^2}{2a_0}\right)\left[\dfrac{\pm 1}{(j+\frac{1}{2} \mp \frac{1}{2})(2j+1)}\right] & \ell \neq 0 \\ 0 & \ell = 0 \end{cases}$$

For homework:

$$\Delta E_r + \Delta E_D = \frac{\alpha^2}{n^3}\left(\frac{e^2}{2a_0}\right)\left[\frac{3}{4n} - \frac{1}{j+\frac{1}{2}\mp\frac{1}{2}} + \delta_{\ell,0}\right]$$

Combining these:

$$\Delta E_{so} + \Delta E_r + \Delta E_D = \boxed{\frac{\alpha^2}{n^3}\left(\frac{e^2}{2a_0}\right)\left(\frac{3}{4n} - \frac{1}{j+\frac{1}{2}}\right) \equiv \Delta E_{fine}}$$ (for *any* ℓ, $j = \ell \pm \frac{1}{2}$).

(Can also be found by solving Dirac equation directly.)

For lowest few levels, in terms of $\alpha^2\left(\frac{e^2}{2a_0}\right) = 7.24522 \times 10^{-4}$ eV.

$n=1,\ \ell=0,\ j=\frac{1}{2}$:	$\Delta E_{fine} = \alpha^2\left(\frac{e^2}{2a_0}\right)\left(-\frac{1}{4}\right)$	$1S_{1/2}$
$n=2,\ \ell=0,\ j=\frac{1}{2}$	$\Delta E_{fine} = \alpha^2\left(\frac{e^2}{2a_0}\right)\left(-\frac{5}{64}\right)$	$2S_{1/2}$ } remain degenerate!
$n=2,\ \ell=1,\ j=\frac{1}{2}$	$\Delta E_{fine} = \alpha^2\left(\frac{e^2}{2a_0}\right)\left(-\frac{5}{64}\right)$	$2P_{1/2}$ }
$n=2,\ \ell=1,\ j=\frac{3}{2}$	$\Delta E_{fine} = \alpha^2\left(\frac{e^2}{2a_0}\right)\left(-\frac{1}{64}\right)$	$2P_{3/2}$

$n=3,\ l=0,\ j=\frac{1}{2}$ $\quad \Delta E_{fine} = \alpha^2\left(\frac{e^2}{2a_0}\right)\left(-\frac{1}{36}\right)$ } remain degenerate

$n=3,\ l=1,\ j=\frac{1}{2}$ $\quad$ " $\left(-\frac{1}{36}\right)$

$n=3,\ l=1,\ j=\frac{3}{2}$ $\quad$ " $\left(-\frac{1}{108}\right)$ } remain degenerate

$n=3,\ l=2,\ j=\frac{3}{2}$ $\quad$ " $\left(-\frac{1}{108}\right)$

$n=3,\ l=2,\ j=\frac{5}{2}$ $\quad$ " $\left(-\frac{1}{324}\right)$

Counting electron spin, each level n has $2n^2$ states.
Fine structure splits each level n into n distinct levels, depending on $j=\frac{1}{2}, \frac{3}{2}, \ldots, \frac{2n-1}{2}$.

<u>Hyperfine structure</u> takes into account that <u>protons</u> have spin also.

$\Rightarrow$ proton has magnetic moment $\vec{\mu}_p = \dfrac{-e}{2m_pc}\, g_p\, \vec{I}$ ← proton spin operator (spin $=\frac{1}{2}$).

g_p = g-factor of proton $= 5.585694701 \pm 0.000000056$ (dimensionless)

Compare to electron's magnetic moment:

$$\vec{\mu}_e = \frac{e}{2m_ec}\, g_e \vec{S}$$

$g_e = 2.0023193043622 \pm 0.0000000000015$ ← predicted by Quantum Electro Dynamics
≈ 2

Note: e = charge on electron (<u>negative</u>).

Recall the fine-structure SO Hamiltonian can be written as:

$$H_{so} = \frac{e^2}{2m_e^2c^2}\frac{1}{R^3}\vec{S}\cdot\vec{L} = \frac{e}{2m_ec}\frac{1}{R^3}\vec{\mu}_e\cdot\vec{L}$$

In the same way, there should be a proton-spin-orbit coupling:

$$H_{so,\,proton} = \frac{-e}{2m_ec}\frac{1}{R^3}\vec{\mu}_p\cdot\vec{L} = \frac{e^2 g_p}{4m_em_pc^2}\frac{1}{R^3}\vec{I}\cdot\vec{L}$$

But there is more:

$$H_{dipole\text{-}dipole} = \frac{1}{R^3}\left[\vec{\mu}_e\cdot\vec{\mu}_p - \frac{3\,\vec{\mu}_e\cdot\vec{R}\;\vec{\mu}_p\cdot\vec{R}}{R^2}\right]$$

$$H_{contact} = -\vec{\mu}_e\cdot\vec{\mu}_p\,\frac{8\pi}{3}\,\delta^{(3)}(\vec{R})$$

The hyperfine Hamiltonian is $H_{HF} = H_{so,\,proton} + H_{dipole\text{-}dipole} + H_{contact}$

So $$H_{HF} = \frac{e}{2m_e c}\left[\frac{1}{R^3}(\vec{S}-\vec{L}) - \frac{3}{R^5}(\vec{R}\cdot\vec{S})\vec{R} - \frac{8\pi}{3}\delta^{(3)}(\vec{R})\,\vec{S}\right]\cdot\vec{\mu}_p$$

$$= \frac{e^2 g_p}{2m_e m_p c^2}\left[\frac{1}{R^3}(\vec{L}-\vec{S})\cdot\vec{I} + \frac{3}{R^5}(\vec{R}\cdot\vec{S})(\vec{R}\cdot\vec{I}) + \frac{8\pi}{3}\delta^{(3)}(\vec{R})\,\vec{S}\cdot\vec{I}\right]$$

This is smaller than the fine-structure corrections, because $m_p \approx 1836\, m_e$ is large.

So treat it as a perturbation, using the $|n,\ell,s,j,m_j\rangle$ eigenstates of $H_0 + H_{fine}$. But add new labels I, m_I for proton spin.

Need to evaluate matrix elements of H_{HF} in this basis.

Important tool: <u>the Landé formula.</u>

For any vector operator $\vec{A}$,

$$\boxed{\langle j,m_j|\vec{A}|j,m_j'\rangle = \frac{\langle j m_j|\vec{A}\cdot\vec{J}|j,m_j\rangle}{\hbar^2 j(j+1)}\langle j,m_j|\vec{J}|j,m_j'\rangle}$$

This is a special case of the Wigner-Eckart Theorem (covered later).

Apply to $\vec{A} = \frac{1}{R^3}(\vec{L}-\vec{S}) + \frac{3}{R^5}(\vec{S}\cdot\vec{R})\vec{R}$.

Then need $\frac{1}{R^3}\langle(\vec{L}-\vec{S})\cdot\vec{J}\rangle$ and $\frac{1}{R^5}\langle(\vec{R}\cdot\vec{S})(\vec{R}\cdot\vec{J})\rangle$ in the state $|j,m_j\rangle$

First: $(\vec{L}-\vec{S})\cdot\vec{J} = (\vec{L}-\vec{S})\cdot(\vec{L}+\vec{S}) = L^2 - S^2 = \hbar^2(\ell(\ell+1) - \tfrac{3}{4})$

Second: Note $\vec{R}\cdot\vec{J} = \vec{R}\cdot(\vec{L}+\vec{S}) = \underbrace{\vec{R}\cdot(\vec{R}\times\vec{P})}_{=0} + \vec{R}\cdot\vec{S} = \vec{R}\cdot\vec{S}$

$$\text{So } \langle(\vec{R}\cdot\vec{S})(\vec{R}\cdot\vec{S})\rangle = \frac{\hbar^2}{4}\langle\vec{R}\cdot\vec{\sigma}\,\vec{R}\cdot\vec{\sigma}\rangle = \frac{\hbar^2}{4}R^2$$

So $$\langle j,m_j|\vec{A}\cdot\vec{J}|j,m_j\rangle = \frac{\hbar^2\,\ell(\ell+1)}{R^3}$$

So, in matrix elements with common n, ℓ, s, j, we have:

$$H_{HF} = \frac{e^2 g_p}{2m_e m_p c^2}\left[\frac{1}{R^3}\frac{\ell(\ell+1)}{j(j+1)}\vec{J}\cdot\vec{I} + \frac{8\pi}{3}\delta^{(3)}(\vec{R})\,\vec{S}\cdot\vec{I}\right]$$

only non-zero if $\ell \neq 0$.

only non-zero if $\ell = 0$. (because $|\Psi(0)|^2 = 0$ for $\ell \neq 0$.)

Look at the $l=0$ case first (includes $n=1$ ground state)

Then $\vec{L}=0$, so $\vec{S}\cdot\vec{I} = \vec{J}\cdot\vec{I} = \frac{1}{2}\left[F^2 - J^2 - I^2\right]$, where

$\vec{F} = \vec{J}+\vec{I} = \vec{L}+\vec{S}+\vec{I}$ = total angular momentum.

$$\left.\begin{array}{lll} F^2 \text{ has eigenvalues} & \hbar^2 f(f+1) \\ F_z \text{ has} \quad \text{''} & \hbar f \end{array}\right\} f = \text{integer in general; } 0 \text{ or } 1 \text{ for } l=0.$$

Use basis kets $|n, l, s, j, f, m_f\rangle$, so that H_{HF} is diagonal among degenerate states.

$$\text{Then: } \langle H_{HF}\rangle = \frac{e^2 g_P}{2m_e m_p c^2}\left[\frac{8\pi}{3}\underbrace{\langle n,l|\delta^{(3)}(\vec{R})|n,l\rangle}_{|\psi(0)|^2 = \frac{1}{\pi n^3 a_0^3}}\frac{\hbar^2}{2}\underbrace{\left[f(f+1)-s(s+1)-I(I+1)\right]}_{\substack{0-3/4-\frac{3}{4} \text{ for } f=0 \\ 2-3/4-3/4 \text{ for } f=1}}\right]$$

So, for $l=0$ states:

$$\Delta E_{HF} = \underbrace{\frac{4e^2\hbar^2 g_P}{3m_e m_p c^2 a_0^3}}_{\frac{8}{3}\frac{m_e}{m_p} g_P \alpha^2\left(\frac{e^2}{2a_0}\right) = 5.878\times 10^{-6}\,\text{eV.}}\left(\frac{1}{n^3}\right)\begin{cases} +1/4 & \text{for } f=1 \\ -3/4 & \text{for } f=0\end{cases} \qquad (l=0)$$

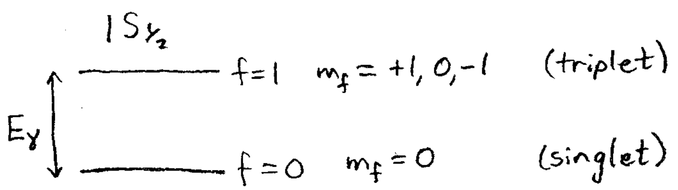
So, the $1S_{1/2}$ ground state of H splits.

When the $f=1$ state decays to the $f=0$ state, a photon is emitted with energy $E_\gamma = 5.878\times 10^{-6}$ eV.

Since $E_\gamma = h\nu$, the light will have frequency $\nu = 1.4204\times 10^9$ Hz.

Wavelength $\lambda = \frac{c}{\nu} = 21.12$ cm.

This is the "21 cm line" used in radio astronomy.



Now for the $l\neq 0$ case.

Again use basis kets $|n, l, s, j, f, m_f\rangle$, and

$$\vec{J}\cdot\vec{I} = \frac{1}{2}\left[F^2 - J^2 - I^2\right] \rightarrow \frac{\hbar^2}{2}\left[f(f+1) - j(j+1) - I(I+1)\right].$$

So $$\langle H_{HF}\rangle = \frac{e^2 g_p}{2 m_e m_p c^2}\underbrace{\left\langle \frac{1}{R^3}\right\rangle}_{\frac{1}{a_0^3 n^3 \ell(\ell+1)(\ell+\frac{1}{2})}} \frac{\ell(\ell+1)}{j(j+1)}\,\frac{\hbar^2}{2}\left[f(f+1)-j(j+1)-I(I+1)\right]$$

Therefore,

$$\Delta E_{HF} = \underbrace{\frac{e^2\hbar^2 g_p}{2 m_e m_p c^2 a_0^3}}_{\frac{m_e}{m_p} g_p \alpha^2 \left(\frac{e^2}{2a_0}\right)} \left(\frac{1}{n^3}\right) \underbrace{\left[\frac{f(f+1)-j(j+1)-I(I+1)}{(2\ell+1)\,j(j+1)}\right]}_{=\frac{\pm 1}{(2\ell+1)(f+\frac{1}{2})}} \qquad (\ell \neq 0)$$

for $f = j \pm \frac{1}{2}$.

So $$\boxed{\Delta E_{HF} = \frac{\alpha^2}{n^3}\left(\frac{e^2}{2a_0}\right)\frac{m_e}{m_p} g_p \left[\frac{\pm 1}{(2\ell+1)(f+\frac{1}{2})}\right]}$$

(Actually, agrees with $\ell=0$ formula, too!)

where $f = j \pm \frac{1}{2}$, for <u>any</u> ℓ.

This splits each $|n,\ell,s,j\rangle$ level into two.

In terms of $E_\gamma = \frac{8}{3}\frac{m_e}{m_p} g_p \alpha^2\left(\frac{e^2}{2a_0}\right)$, for $n=2$ (1st excited level)

$2S_{1/2}$ $(\ell=0, j=\frac{1}{2})$ → $f=1$: $\Delta E_{HF} = \frac{1}{32}E_\gamma$; → $f=0$: $\Delta E_{HF} = \frac{-3}{32}E_\gamma$ } splitting $= \frac{1}{8}E_\gamma$

$2P_{1/2}$ $(\ell=1, j=\frac{1}{2})$ → $f=1$: $\Delta E_{HF} = \frac{1}{96}E_\gamma$; → $f=0$: $\Delta E_{HF} = -\frac{1}{32}E_\gamma$ } splitting $= \frac{1}{24}E_\gamma$

$2P_{3/2}$ $(\ell=1, j=\frac{3}{2})$ → $f=2$: $\Delta E_{HF} = \frac{1}{160}E_\gamma$; → $f=1$: $\Delta E_{HF} = -\frac{1}{96}E_\gamma$ } splitting $= \frac{1}{60}E_\gamma$

Note that the state labelled by each f remains $(2f+1)$ degenerate.
Since $\Delta E_{HF} \propto \frac{1}{2f+1}$, the "center of mass" of each HF splitting is unchanged.

So far, we have worked to 1st order in perturbation theory for both fine and hyperfine Hamiltonians.

However, there is a <u>2nd-order</u> effect that is larger than the hyperfine splitting...

<u>The Lamb shift</u> comes from electron emitting, absorbing virtual photons:

$$\Delta E_{Lamb} = \sum_{n',l',j'} \; \sum_{\omega,\hat{k},\hat{\varepsilon}} \frac{|\langle n', l', j'; \omega, \hat{k}, \hat{\varepsilon} |\, H_{int} \,| n, l, j \rangle|^2}{E_n^{(0)} - E_{n'}^{(0)} - \hbar\omega}$$

$$H_{int} = -\frac{e}{c}\int d^3\vec{r}\; \vec{J}(\vec{r}) \cdot \vec{A}(\vec{r},t)$$ due to photon

$|n', l', j'; \omega \hat{k}, \hat{\varepsilon}\rangle$ = state with a photon with frequency ω, wavevector direction $\hat{k}$, polarization $\hat{\varepsilon}$.

$|n, l, j\rangle$ = state with no photons

This is very hard. $\sum_{\omega}$ is actually an integral $\int_0^\infty d\omega$, diverges!

Need a cutoff $\int_0^{\omega_{max}} d\omega$, renormalize electron mass to remove contribution $\propto \omega_{max}$.

Final result:

For $l=0$ states, $\Delta E_{Lamb} \approx \frac{\alpha^3}{n^3}\left(\frac{e^2}{2a_0}\right) \underbrace{k_{Lamb}(n)}_{\approx 6.5 \text{ (depends a little on } n)}$.

For $l \neq 0$ states, $\Delta E_{Lamb} \approx \frac{\alpha^3}{n^3}\left(\frac{e^2}{2a_0}\right)$ [non-zero but very small]

Summary for n=2 level
(1st excited state)