Hyperfine Structure in hydrogen

So far we have completely ignored the nuclear spin and nuclear electric field distribution. The most important of these contributions are the nuclear spin $I$, with its associated magnetic moment $M_N$, and the nuclear electric quadrupole moment $Q$ (it's zero for the proton, but not for the deuteron, for example.)

Note that parity conservation forbids an electric dipole moment for an elementary particle (or any nondegenerate system):

If $\vec{D} = \alpha \vec{I}$ for some $\alpha \neq 0$,

Consider the effect of reversing all coordinates about an origin centered on the nucleus.

Like all angular momenta, $\vec{I}$ is an axial vector, with $\vec{I} = \vec{I'}$. However, $\vec{D}$ is a polar vector (charge x position), so $\vec{D'} = -\vec{D}$, and

$\vec{D'} = -\alpha \vec{I'}$ (different physics!)

Thus $\alpha = 0$ so long as parity isn't violated. This fails to hold only for the weak interaction, which could cause a very small nuclear dipole moment.

The search for a neutron dipole moment continues, and indirect searches for proton or electron dipole moments have been conducted as well (by Hinds, Sandars, and others). For example, experimentally,

$|d_{\text{neutron}}| < 8.7 \times 10^{-28}$ e·cm (Fortson group, PRA 52, 3521 (1995))

$|d_e| < 1.8 \times 10^{-27}$ e·cm (Coombs group, PRA 50, 2960 (1994))

<By 1995 with $^{205}$Tl, Demille trying for $10^{-28}$!>

Anyhow, for ordinary $H$ we need worry only about the magnetic dipole hyperfine structure.

Now $<1.5 \times 10^{-27}$: same group, PRL 88, 071805 (2002).
Magnetic dipole hyperfine Hamiltonian: \( \mathbf{\Delta} = \frac{\mathbf{\hat{M}} \times \mathbf{r}}{r^3} \left( \frac{M_N}{4\pi} \right) \)  

where \( \mathbf{\hat{M}} = gN M_N \left( \frac{\mathbf{S}}{\hbar} \right) \)  

\( M_N \) is the nuclear Bohr magneton, \( M_N = \frac{e\hbar}{2m_p} \) (smaller than \( M_B \) by \( \frac{m_e}{m_p} \) \( 5.051 \times 10^{-29} \text{ J/T} \)).  

\( g_N \) = nuclear \( g \)-factor  
\( = 5.59 \) for proton, \( I = \frac{1}{2} \)  
\( = 0.857 \) for deuteron, \( I = 1 \)  

Also commonly used is the gyromagnetic ratio \( \gamma_N \),  
\( \mathbf{\hat{M}} = \gamma_N \mathbf{I} \), \( \gamma_N = \frac{gN M_N}{\hbar} \)

For the one-electron case:  

Since \( \mathbf{\hat{M}}, \mathbf{I} \) and \( \mathbf{S} \) are all nonzero, several terms arise in the interaction. Things get very tricky, particularly for \( S \)-states because there is a finite electron amplitude at the nucleus. A very careful derivation is given by Weissbluth, who shows that in H-like systems,  

\[ H_{\text{hfs}} = \frac{M_N}{4\pi} \frac{2m_p gN}{\hbar} \left( \frac{\mathbf{I} \cdot (\mathbf{I} - \mathbf{S})}{r^3} + 3 \left( \frac{\mathbf{S} \cdot \mathbf{r}}{r^3} \right)^2 \right) + \frac{8\pi}{3} I \cdot S \cdot C^{(2)} \]  

**Fermi contact interaction** for \( S \) states  

Compare with \( H_{\text{fs}} = \frac{KE^3}{2m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \) (for \( Z = 1 \), from 38)  

Writing \( g_N = gN \frac{e}{2m_p} \), \( M_B = \frac{e\hbar}{2m_e} \), the prefactor in 39 becomes \( \frac{M_N}{4\pi} \frac{2m_p}{2m_e m_p} \), \( g_N \Rightarrow \) smaller than fine structure by \( \frac{m_e}{m_p} \)  

(note that \( M_0 E_0 = \frac{1}{c^2} \))
For many-electron atoms (85) is generalized by simply adding the contributions of the \( n \) electrons.

**Evaluation of hfs for \( \Pi \):**

Since \( H_{\text{hfs}} = (\text{stuff}) \cdot \left( \frac{\vec{r} - \vec{s}}{r^3} + \frac{3}{r^5} \vec{r} \cdot (\vec{s} \cdot \vec{r}) + \frac{8\pi}{3} \vec{s} \cdot \vec{d} \right) \cdot \vec{A}'(\vec{L}, \vec{s}, \vec{r}) \)

If we define a new angular momentum vector

\[ \vec{F} = \vec{J} + \vec{I} \quad (\vec{F} = \vec{L} + \vec{s}) \]

the interaction will be diagonal in \( F \) and the off-diagonal terms in \( J \) and \( I \) will be small, since the fine structure levels \( J \) are split by the much larger \( F \) interaction, and the nuclear levels \( I \) by immense amounts.

Evaluate the dipole-dipole part first, ignoring the Fermi contact term for now. Define, following Weissbluth,

\[ \vec{b'} = \left( \frac{\vec{r} - \vec{s}}{r^3} + \frac{3}{r^5} \vec{r} \cdot (\vec{s} \cdot \vec{r}) \right) \]

We need the Landé formula, a consequence of the Wigner-Eckart theorem that will be proved next week. For now, we assert that "it can be shown that"

\[ \langle J m | \vec{b'} \cdot \vec{F} | J m' \rangle = \frac{\langle J m | \vec{b'} \cdot \vec{F} | J m' \rangle}{\frac{1}{2} (J + 1)} \langle J m | \vec{F} | J m' \rangle \]

The matrix element of \( \vec{b'} \cdot \vec{F} \) is easy:

\[ \langle J m | \vec{b'} \cdot \vec{F} | J m \rangle = \langle J m | \left( \frac{\vec{r} - \vec{s}}{r^3} + \frac{3}{r^5} (\vec{r} \cdot \vec{F}) (\vec{s} \cdot \vec{r}) \right) | J m \rangle \]

\( \odot \) \( \odot \)
For term (a),

\[
\langle Jm \mid (\vec{L} - \vec{S}) \cdot \vec{J} \mid Jm \rangle = \langle Jm \mid \vec{L}^2 - \vec{S}^2 \mid Jm \rangle = (L(L+1) - S(S+1)) \frac{1}{2} \frac{\hbar^2}{\alpha}
\]

For term (b), note that

\[
\vec{r} \cdot \vec{J} = \vec{r} \cdot (\vec{L} + \vec{S}) = \vec{r} \cdot (\vec{r} \times \vec{p}) + \vec{r} \cdot \vec{S}
\]

\[
= \vec{r} \cdot \vec{S}
\]

So \( (\vec{r} \cdot \vec{J}) \cdot (\vec{S} \cdot \vec{r}) = (\vec{r} \cdot \vec{S})^2 \)

\[
= \frac{\hbar^2}{4} (\vec{S} \cdot \vec{J}) (\vec{S} \cdot \vec{r})
\]

\[
= \frac{\hbar^2}{4} \vec{r}^2, \text{ using the theorem on p. DE-7.}
\]

Thus,

\[
\langle Jm \mid \vec{B} \mid Jm' \rangle = \frac{(L(L+1) - S(S+1)) \left< \frac{1}{r^3} \right> + \frac{3}{2} \left< \frac{r^2}{r^5} \right>}{J(J+1)} \langle Jm \mid \vec{J} \mid Jm' \rangle
\]

And for \( S = \frac{1}{2} \)

\[
\frac{L(L+1)}{J(J+1)} \left< \frac{1}{r^3} \right> \langle Jm \mid \vec{J} \mid Jm' \rangle
\]

This means that we can replace \( B \) in equation (39) with the quantity,

\[
\frac{L(L+1)}{J(J+1)} \left< \frac{1}{r^3} \right> \vec{J}, \text{ giving}
\]

\[
H_{\text{eff}}^{\text{eff}} = \frac{4 \hbar^2}{\alpha \pi \gamma_N} \left( \frac{L(L+1)}{J(J+1)} \left< \frac{1}{r^3} \right> \vec{J} \cdot \vec{J} \right. + \frac{8 \pi}{3} \left| \gamma(0) \right|^2 \left[ \vec{J} \right] \left[ \vec{J} \right]
\]

\[ (40) \]

Now find actual value for some \( H \) levels:
Only the $I\cdot S$ contact term contributes. It is the perturbation due to the interaction of the nuclear spin dipole $\vec{I}_N$ with the B field of the electron.

For $H(1S)$, $|\psi_{1S}|^2 = \frac{4}{\alpha_0^3} \text{ (radial)} \times \frac{1}{\eta \mu} \text{ (angular)}$

With $F = \frac{3}{2}$ and $J = \frac{3}{2}$ for $L = 0$

$I \cdot S = \frac{1}{2} (F^2 - S^2 - I^2)$

and we have $S = \frac{1}{2}$

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

$F = 0, 1$ (2 sublevels)

$\langle \alpha F m_F / I \cdot S / \alpha F m_F \rangle = \frac{\hbar^2}{2} (F(F+1) - \frac{3}{2})$

"$nL S J I$" irrelevant, symbolize by $\alpha$

$E_{F=0} = -\frac{3}{4} \left( \frac{16}{3} \frac{\mu_0 \gamma_{\mu N} \eta}{\alpha_0^3} \right) \left( \frac{\mu_0}{4\hbar} \right)$

$E_{F=1} = +\frac{1}{4} \text{ (same)}$

$\Rightarrow \Delta E = 0.047 \text{ cm}^{-1} = 1420 \text{ MHz}$

In higher $nS$ states, scales as $\frac{1}{n^3}$ due to scaling of $|\psi_{1S}|^2$. 
This is the famous "21 cm line" of astrophysics; it is forbidden for electric dipole radiation but can occur for magnetic dipole transitions. Note: \( \Delta E \) implies \( R_{nu} \) at nucleus.

\[ hfs \text{ of } ^2P \text{ for } F = 0 \]

Now only \( \vec{I} \cdot \vec{J} \) contributes; writing \( \vec{F} = \vec{I} + \vec{J} \) again,

\[ \langle \frac{1}{r^3} \rangle = \frac{\pi^2}{a_0^3} \frac{1}{n^3 (l+1)(l+1/2)} \]

\[ \langle F n_F | \vec{I} \cdot \vec{J} | F n_F \rangle = \frac{1}{2} \langle F n_F | F^2 - I^2 - J^2 | F n_F \rangle = \frac{\hbar^2}{2} \left( F (F+1) - \frac{3}{4} - J (J+1) \right) \]

\[ 2 \; ^2P_{1/2} \]: here \( F = 0, \; 1 \) and \( J = 1/2 \)

\[
\begin{cases}
E_{F=0} = \frac{2 L (L+1)}{J (J+1)} \frac{1}{24 a_0^3} \left( \frac{-3}{2} \right) \mu_B N k \hbar \frac{m_e}{4\pi} = \frac{-1}{6} \frac{\mu_B \mu_N}{a_0^3} \\
E_{F=1} = \frac{1}{18} \left( \frac{1}{2} \right) \frac{\mu_B \mu_N}{a_0^3} = \frac{+1}{18} \frac{\mu_B \mu_N}{a_0^3} \\
\end{cases}
\]

(24 \times \text{ smaller than for } 1 \; ^2S_{1/2} \text{)}

(3 \times \text{ smaller than for } 2 \; ^2S_{1/2} \text{)}

\[ 2 \; ^2P_{3/2} \]: \( J = 3/2 \) and \( F = 1, \; 2 \)

\[
\begin{cases}
E_{F=1} = -\frac{1}{18} \frac{\mu_B \mu_N}{a_0^3} \\
E_{F=2} = +\frac{1}{30} \frac{\mu_B \mu_N}{a_0^3} \\
\end{cases}
\]

(2 \; \text{times smaller than for } 2 \; ^2P_{3/2} \text{)}
So we have, for \( H, n=2 \),

\[
\begin{align*}
2^2 P_{3/2} &\quad F=2  \\
F=1 &\quad \text{fs splitting } = 10700 \text{ MHz}  \\
F=0 &
\end{align*}
\]

\[
\begin{align*}
2^2 S_{1/2} &\quad \bar{v} = 178 \text{ MHz}  \\
F=0 &
\end{align*}
\]

\[
\begin{align*}
2^2 P_{1/2} &\quad F=1  \\
F=0 &\quad \text{Lamb shift } = 1058 \text{ MHz}  \\
F=0 &
\end{align*}
\]

(Remember \( 1 \text{ cm}^{-1} \equiv 29979 \text{ MHz} \); binding energy \( \cong 27420 \text{ cm}^{-1} \))

**Off-diagonal terms** -- \( \Delta J = \pm 1 \) terms change the HFS by about 300 Hz. Numerous other corrections are needed to compare with the best radio frequency measurements,

\[\Delta E \left( H, \frac{1}{2}, \pm \frac{1}{2} \right) = 1420.405751800 \text{ (28 MHz)} \]

(by Crampton, Kleppner, & Ramsey, Phys. Rev. Lett. 11, 358 (1963))

**HFS in Other Atoms**

The magnetic dipole HFS works similarly except that the radial matrix elements must be approximated. The best-studied case is that of the alkali atoms, with a single electron outside a closed shell. The qualitative structure is the same as for \( H \), but \( |y_0|^2 \) and \( \langle \frac{r}{e} \rangle \) must be estimated.

The ground \( 2S_{1/2} \) state of \( \text{Cs}^{133} \), with \( I = \frac{7}{2} \), is a special case. The \( F=4 \leftrightarrow F=3 \) transition is the current standard for frequency,

\[\Delta v \left( \text{Cs} \right) = 9192631770.000 \ldots \text{ Hz}\]