Hyperfine structure (+ general "nuclear effect")

So far, we've examined:

1) gross structure -
   \[ \text{electrostatic interactions} \] (Hydrogen-like) \[ \text{just } e^- \text{ charge + charge of nucleus} \]
   \[ \text{more generally } \text{e}^-\text{e}^- \text{ interactions also plays a big role} \]
   (shielding)

2) fine structure -
   \[ \text{relativistic corrections} \]
   \[ \text{spin-orbit interactions} \]
   \[ \text{related to magnetic moment of electron} \]
   \[ \text{spin of electron} \]
   \[ |\vec{\mu}| \sim \mu_B \approx \frac{e\hbar}{2m_e} \]
   for single unpaired electron \[ \mathbf{H}_S = -\vec{\mu} \cdot \mathbf{B} \]

   recall \[ \mathbf{J} = \mathbf{L} + \mathbf{S} \]
   For \( s = \frac{1}{2} \), have \( J = l - \frac{1}{2} \) and \( J = l + \frac{1}{2} \)
   if \( l \neq 0 \)

3) hyperfine - shifts + energy splitting
   due to nuclear effects
   (smaller than fine structure)

   \[ \text{nucleus is not a point-like charge, but has structure and spin} \]
   \[ \text{we'll treat energy corrections due to finite size, mass of nucleus shortly} \]
the hyperfine structure, in terms of hyperfine energy levels, comes about due to the fact that the nucleus can have a spin angular momentum, and thus a magnetic moment.

We're going to try to give a rough sketch for how the nuclear spin gives rise to hyperfine structure. For a rigorous treatment based on a relativistic, quantum treatment, see lecture notes of N. Johnson. (https://www3.nd.edu/~johnson/Publications/book.pdf Ch. #5)

Let's start with the semi-classical picture as presented in Foot, which works well for hydrogen and will set the stage for a more general result.

The nucleus has a magnetic moment that can be related to the nuclear spin \( I \) as

\[
\vec{M}_N = g_I \mu_N \vec{I}
\]

where \( \mu_N = \frac{h}{4\pi m_e} \), i.e.

The nuclear magneton is lower than the Bohr magneton by the electron-to-proton mass ratio.

\[
I, (m_I = -I, I-1, \ldots, I)
\]
Given this nuclear magnetic moment $\mu$, there is an energy correction in the presence of a magnetic field (from generic contribution) $\vec{B}$

$$\Delta E_{\text{fs}} = -\mu \cdot \vec{B} = -g_I \mu_N \frac{\mathbf{I} \cdot \mathbf{B}}{2}$$

In the absence of an external field, it is the effective field due to the presence of electrons that shifts the energy. There are three basic contributions to this field $\vec{B}_e$:

a) "Field" produced by fact that electron has spin, and thus a magnetic moment. This can also be thought of in terms of the dipole-dipole interaction between $\mu_e$ and $\mu_n$ (when they're spatially separated), i.e.

$$\vec{B}_{e,s} = \frac{M_0}{4\pi} \left[ \frac{\mu_e - 3 (\mu_e \cdot \vec{r}) \vec{r}}{r^3} \right]$$

This can also be recast as

$$\vec{B}_{e,s} = \frac{2M_0 M_n}{4\pi r^3} \left[ \frac{s}{2} - 3 (s \cdot \vec{r}) \frac{\vec{r}}{r} \right]$$

Note: This is just the classical expression for point-like dipoles, and we'll use an alternative approach for s-orbitals that overlap with the nucleus.

b) the effective field that the nuclear spin feels due to the orbit of the electron. For states with $l \neq 0$, the "current" of the electron orbiting the nucleus leads to an effective field

$$\vec{B}_{e,l} = \frac{2M_0 M_n}{4\pi r^3} \frac{L}{r^3}$$

c) For the s-states, the contribution due to "dipole-dipole" averages to zero [anisotropic], but a Fermi contact interaction remains, which can be described in terms of the effective field

$$\vec{B}_{e,\text{Fermi}} = -\frac{2}{3} M_0 g_s \mu_N \frac{3}{8} S(S+1) \left| \psi(0) \right|^2 \vec{s}$$
So, summing up,

\[ H_{\text{HFS}} = -\mu_B \cdot B \quad \text{and} \quad \mu_B = g_I m_N \mu_N \]

\[ B_e = -\frac{2 \mu_0 \mu_B}{4\pi} \left[ \frac{I}{r^3} - \frac{(\mathbf{S} - (3\mathbf{I} \cdot \mathbf{F}) \mathbf{F})}{r^3} + \frac{4\pi}{3} g_S |\Psi(0)|^2 \mathbf{S} \right] \]

- orbit term
- dipole-dipole term
- Fermi contact term

For an s-orbital, the first two contributions are both zero, and we have for the \( l=0 \) state

\[ H_{\text{HFS}} = \frac{2 \mu_0 \mu_B g_I m_N}{4\pi} \frac{g_S |\Psi(0)|^2}{3} \mathbf{I} \cdot \mathbf{S} \]

For hydrogenic atoms \( |\psi_n(0)|^2 = \frac{1}{n^3} \left( \frac{Z}{n a_0} \right)^3 \)

\[ \Rightarrow H_{\text{HFS}} = \frac{2}{3\pi} \mu_0 g_I g_S \mu_B m_N \frac{Z^3}{h^3 a_0^3} \mathbf{I} \cdot \mathbf{S} \]

For this \( l=0 \) s-state, \( \mathbf{J} = \mathbf{S} \) and the electron spin and nuclear spin add together as \( \mathbf{F} = \mathbf{I} + \mathbf{S} \) with F-values of \( I-J \) to \( I+J \) (in steps of 1) for \( I \geq J \)

\[ \Rightarrow F^2 = I^2 + S^2 + 2I \cdot S \]

\[ \Rightarrow I \cdot S = \frac{1}{2} [F^2 - I^2 - S^2] \Rightarrow [F(F+1) - I(I+1) - S(S+1)] \]

Note: np values from \(-F,F,-F+1,\ldots\)
this gives us an energy correction to hydrogenic s-state levels if

\[ \Delta E = \frac{2}{3\pi} \mu_0 g_{e} g_{f} M_{B} M_{N} \frac{Z^3}{n^3 a_0^3} \left[ \frac{F(F+1)-I(I+1)-S(S+1)}{2} \right] \]

we expect that this should work fairly well for hydrogen + hydrogenic atoms, so let's check:

\[ Z = 1 \]

for the hydrogen nucleus (i.e. a proton), \( g_f = 5.5883 \)

and \( I = \frac{1}{2} \)

for the electron we have \( S = \frac{1}{2} \) and \( g_s \approx 2 \) (we'll look at \( n=1 \))

The allowed \( F \)-values are \( F = 0, 1 \).

\[ \Delta E_{F=0} = -\frac{3}{2} \left[ \frac{2}{3\pi} (5.5883) \mu_0 M_B M_N \frac{1}{a_0^3} \right] \]

\[ \Delta E_{F=0} \] \( \frac{\Delta E_{F=0}}{\Delta E_{F=1}} \) \( = 3 \)

\[ \Delta E_{F=1} = +\frac{1}{2} \left[ \frac{2}{3\pi} \right] \]

\[ \Delta E_{F=1} - \Delta E_{F=0} = \frac{4}{3\pi} g_f \mu_0 M_B M_N \frac{1}{a_0^3} \approx \hbar \times 1.42 \text{ GHz} \]

This corresponds to \( \lambda = 21 \text{ cm} \), used extensively in radio astronomy

gross | fine | hyperfine

\( -13.6 \text{ eV} \) | \( 44 \text{ GHz, } 180 \text{ meV} \) | \( \Delta E_{F=1} \approx 8 \text{ GHz, } 40 \text{ meV} \) | \( \Delta E_{F=0} \approx 1.42 \text{ GHz, } 6 \text{ meV} \)

\( \Delta E \) spins digitized

\( \Delta E \) spins anti-aligned
This result fails for the more general case (multi-electron atom) \( l \neq 0 \) but a result having similar form follows from a proper treatment using relativistic quantum mechanics.

\[
\hat{H} = \hat{H}_{\text{dip}} + \hat{H}_{\text{quad}}
\]

- electric dipole moment of nucleus
- magnetic quadrupole moment of nucleus

(relevant for \( I > \frac{1}{2} \) and \( l \neq 0 \), interaction of quadrupole moment \( \hat{Q} \) with \( \hat{E} \))

\[
\hat{H}_{\text{dip}} = A \frac{\hat{I} \cdot \hat{J}}{r^3}
\]

same form as before

\[
\hat{H}_{\text{quad}} = B \frac{3 (\hat{I} \cdot \hat{J})^2 + \frac{3}{2} (\hat{I} \cdot \hat{J}) - \hat{I}(\hat{I}+1) \hat{J}(\hat{J}+1)}{2IJ(2I-1)(2J-1)}
\]

(only for \( I = \frac{1}{2}, l \neq 0 \))

we calculated \( A \) for hydrogen-like atoms, but in general these values come from experiment.

\[
F \text{ is a good quantum number here, as is its } z \text{-projection, } m_F.
\]

\( F = I + J \)

will be good also in B-fields

these \( |I, J, F, m_F> \) states (\( m_F \) for short) can be expressed in terms of the quantum number \( \tilde{I} \) of the nuclear spin \( \tilde{J} \) of the electron spin \( J \), as

\[
|F, m_F> = \sum_{m_I, m_J} <F, m_F | I, m_I, J, m_J> |I, m_I, J, m_J>
\]

\[
\text{Clebsch-Gordan coefficients}
\]

\[
<F, m_F | I, m_I, J, m_J> = \sqrt{2F+1} (-1)^{I-J+m_F} (I \, J \, F)
\]

Wigner 3j
The first-order energy shift is given by

$$\Delta E_{\text{th}} = \frac{1}{2} A_{\text{hf}} K + B_{\text{hf}} \frac{3}{2} K (K+1) - 2J (I+1) J (J+1)$$

$$2 I (2I-1) 2J (2J-1)$$

where

$$K = F (F+1) - I (I+1) - J (J+1) = 2 \langle s \cdot s \rangle$$

for some details on measurement of $A_{\text{hf}}$ & $B_{\text{hf}}$ constants, see RMP, 49, 31 (1977)
by Arimondo & Ingwerson

see slides for some experimental values.

Some notes: $A_{\text{hf}} > 0$ is referred to as "regular",

whereas $A_{\text{hf}} < 0$, as in $^{40}$K, $J$ is called "inverted"

For the alkalis, $S = \frac{1}{2}$, the ground state ($L=0$) Zeeman levels, i.e., the states $|F, m_F, m_J, m_S, m_L\rangle$ are constructed by superposition of only two states in the $|I, m_I, J, m_J\rangle$ basis.

For $L=0$, we have $J=0$ such that we use $|I, m_I, S, m_S\rangle$, and call these states $|m_S, m_I\rangle$ for short.

Recall that $m_F = m_S + m_I$, and $m_S = \pm \frac{1}{2}$, such that the allowed $m_I$ values are $m_I = m_F - m_S = m_F + \frac{1}{2}$ for $m_S = \pm \frac{1}{2}$

In general, $|F, m_F\rangle = \alpha |m_S = \frac{1}{2}, m_I = m_F - \frac{1}{2}\rangle + \beta |m_S = -\frac{1}{2}, m_F = m_F + \frac{1}{2}\rangle$

$\alpha, \beta$ are Clebsch-Gordan coefficients.

This form will help us understand how we have states with vanishing magnetic moment ($m_F = 0$) at low fields.
Other "nuclear" effects

We also get corrections to the energy levels due to details of the nucleus' mass, variations in its spin, and the non-zero size of the nucleus (not a point-like charge).

Size effects → volume shift. In HW1, you calculated the energy corrections that one would expect due to the non-uniformity of the nuclear charge distribution from that of a point charge, which led to a potential that was not proportional to $1/r$ for small $r$ values.

→ This effect is sometimes considered a hyperfine effect (comes from nuclear property) and sometimes absorbed as part of other effects (as in the discussion of proton size puzzle with Lamb shift measurements).

Simple toy model (as in HW1) for hydrogen-like atom

Consider a sphere with uniform charge density, having total charge $Q_N = Z e$ and radius $R = A^{1/3} R_0$ where $A ≈ 2Z$ is the atomic mass number (# of nucleons) and $R_0 ≈ 1.2$ fm (radius close to proton radius $r_p$).

The potential energy experienced by the electron

$$V(r) = \begin{cases} 
\frac{Z e^2}{4\pi \varepsilon_0 R} \frac{1}{2} (\frac{r^2}{R^2} - 3) & \text{for } r \leq R \\
\frac{Z e^2}{4\pi \varepsilon_0 r} & \text{for } r > R 
\end{cases}$$
This volume effect leads to an energy correction:

\[ \Delta E = \langle H' \rangle \text{ where } H' = V(r) - V_{\text{point charge}} \]

\[ = \begin{cases} \frac{Z e^2}{4 \pi \varepsilon_0} \frac{1}{2} \left( \frac{r^2}{R^2} + \frac{2R}{r} - 3 \right) & \text{for } r \leq R \\ 0 & \text{for } r > R \end{cases} \]

\[ \Delta E = \langle H' \rangle = \langle \psi_{\text{new}} | H' | \psi_{\text{new}} \rangle \]
because \( R \) is so small, this effect is only important (non-zero) for \( l = 0 \) states.

\[ \Delta E = \frac{Z e^2}{4 \pi \varepsilon_0} 2R \int_0^R \frac{1}{R_{\text{new}}(r)} \left( \frac{r^2}{R^2} + \frac{2R}{r} - 3 \right) r^2 dr \]

\[ \Delta E = \frac{Z e^2}{4 \pi \varepsilon_0} 2R \left[ \frac{R^3}{5} \right] \]

\[ = \frac{Z e^2}{10 \varepsilon_0} R^2 \left| R_{\text{new}}(0) \right|^2 
\Rightarrow \frac{4Z^3 \hbar^3}{n^3 a_0^3} \]

\[ = \frac{Z^4}{a_0^3} \frac{e^2 R^2}{10 \varepsilon_0} \quad \Rightarrow \quad \text{Footnote Eq. (6.26)} \]

result applied to alkalis, etc.

based on central field approximation,
2. mass effects → we'll only discuss the reduced mass effect, which requires a correction due to our assuming that $\frac{M_{\text{nucleus}}}{m_e} = \infty$.

\[ E_n = -\frac{e^2}{4\pi \varepsilon_0} \frac{Z^2}{\alpha^2} = -\frac{e^2}{4\pi \varepsilon_0} \frac{Z^2}{\frac{m_e + M_N}{m_e} + 1} = \frac{E_n^\infty}{M_N} = E_n^\infty \left(1 + \frac{m_e}{M_N}\right)^{-1} \]

\[ \approx E_n^\infty \left(1 - \frac{m_e}{M_N}\right) \]

So, the correction for a finite nuclear mass

\[ \Delta E_n = -E_n^\infty \frac{m_e}{M_N} \]

this correction always

\[ \propto E_n^\infty \], such that it shifts energies up, but correction term gets smaller as $m_N$ increases.