Hyperfine structure (+ general "nuclear effects")

so far, we've examined:

electrostatic interactions

1) **gross structure** – { Hydrogen-like → just e^- charge + charge of nucleus
more generally → $e^- - e^-$ interactions (shielding) also plays a big role

2) **fine structure** – relativistic corrections
– spin-orbit interactions $\propto \vec{S} \cdot \vec{L}$

spin of electron

relates to magnetic moment

$|\vec{\mu}| \sim \mu_B = \frac{e\hbar}{2m_e}$

for single unpaired electron $H_{LS} = -\vec{\mu} \cdot \vec{B}$

orbital ang. mome[ntum]

for $l \neq 0$, effective B-field due to motion in $V(r)$ elect[rostatic] potential

recall $\vec{J} = \vec{L} + \vec{S}$

for $s = \frac{1}{2}$, have $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$ if $l \neq 0$

general

$l-s$ to $l+s$ for $l > s$;

$s-l$ to $s+l$ for $s > l$

$E(P_{3/2}) - E(P_{1/2}) = \Delta E_{S-O}$

3) **hyper fine** – shifts + energy splitting due to nuclear effects

(smaller than fine structure)

nucleus is not a point-like charge, but has structure and spin

we'll treat energy corrections due to finite size, variations in the mass of nucleus shortly

② 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 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 W. Johnson

@ https://www3.nd.edu/~johnson/Publications/book.pdf

Ch. #5

Let's start w/ 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

$$\vec{\mu}_I = g_I \mu_N \vec{I}$$

$\rightarrow$ Note: $\boxed{\text{Different conventions}}$ you'll see several different formulations depending on the source. Some have positive g_I, some have negative. Some absorb μ_N/μ_B factor into g_I, and express as

$$\vec{\mu}_I = g_I \mu_B \vec{I}$$

where $\mu_N = \mu_B \frac{m_e}{m_p}$, i.e.

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

$I, (m_I = -I, -I+1, \ldots, I)$

(3) Given this nuclear magnetic moment $\vec{\mu}_I$, there is an energy correction ~~due~~ in the presence of a magnetic field (from generic contributions) $\vec{B}$

$$H_{HFS} = -\vec{\mu}_I \cdot \vec{B} = -g_I \mu_N \vec{I} \cdot \vec{B}$$

while $g_s \approx 2$ for the electron sp[in]

g_I value will depend [on] nucle[ar] struc[ture]

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 ~~two~~ 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 $\vec{\mu}_I$ and $\vec{\mu}_e$ (when they're spatially separated), i.e. $\frac{\mu_0}{4\pi r^3}\left[\vec{\mu}_I \cdot \vec{\mu}_e - 3(\vec{\mu}_I \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r})\right]$

where $\vec{r} = \vec{r}_e - \vec{r}_N \approx \vec{r}_e$

this can also be recast as the field due to $\vec{\mu}_e$,

$$\vec{B}_{e,s} = \frac{\mu_0}{4\pi}\left[\frac{\vec{\mu}_e - 3(\vec{\mu}_e \cdot \hat{r})\hat{r}}{r^3}\right]$$

$$\approx \frac{2\mu_0 \mu_B}{4\pi r^3}\left[\vec{S} - 3(\vec{S} \cdot \hat{r})\hat{r}\right]$$

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 nucleus spin feels due to the orbit of the electron. For states w/ $l \neq 0$, the "current" of the electron orbiting the nucleus leads to an effective field contribution

$$\vec{B}_{e,L} \approx -\frac{2\mu_0 \mu_B}{4\pi r^3}\vec{L}$$

(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 $\vec{B}_{e,Fermi} = -\frac{2}{3}\mu_0 g_s \mu_B \vec{S}\, \delta^3(\vec{r}) \approx -\frac{2}{3}\mu_0 g_s \mu_B |\psi(0)|^2 \vec{S}$

④ So, summing up,

$$H_{HFS} = -\vec{\mu}_I \cdot \vec{B} \quad \text{and} \quad \text{w/ } \vec{\mu}_I = g_I \mu_N \vec{I}$$

$$\vec{B}_e \approx -\frac{2\mu_0 \mu_B}{4\pi}\left[\underbrace{\frac{\vec{L}}{r^3}}_{\text{orbit term}} - \underbrace{\frac{\left(\vec{S} - (3\vec{S}\cdot\hat{r})\hat{r}\right)}{r^3}}_{\text{dipole-dipole}} + \underbrace{\frac{4\pi}{3} g_s |\Psi(0)|^2 \vec{S}}_{\text{Fermi contact}}\right]$$

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

$$H_{HFS} = \frac{2\mu_0 \mu_B g_I \mu_N \cancel{4\pi}}{\cancel{4\pi}\, 3} g_s |\Psi(0)|^2 \vec{I}\cdot\vec{S}$$

for hydrogenic atoms w/ s-orbital $\quad |\Psi_{n0}(0)|^2 = \frac{1}{\pi}\left(\frac{Z}{n a_0}\right)^3$

$$\Rightarrow \quad H_{HFS} = \frac{2}{3\pi}\mu_0 g_I g_s \mu_B \mu_N \frac{Z^3}{n^3 a_0^3} \vec{I}\cdot\vec{S}$$

for this $l=0$ s-state, $\vec{J} = \vec{S}$ and the electron spin and nuclear spin add together as $\underline{\vec{F} = \vec{I} + \vec{J}}$ w/ $\underline{\text{F-values of}}$ $I-J$ to $I+J$ (in steps of 1) for $\underline{I>J}$

so $\vec{F} = \vec{I} + \vec{S}$

and $J-I$ to $J+I$ for $\underline{J>I}$

recall our treatment of $\underline{\vec{L}\cdot\vec{S} \text{ w/ } \vec{J} = \vec{L} + \vec{S}}$

note: m_F values from $-F, -F+1, \ldots, F-1, F$

$$\Rightarrow \hat{F}^2 = \hat{I}^2 + \hat{S}^2 + 2\vec{I}\cdot\vec{S}$$

expectation values

$$\hookrightarrow \vec{I}\cdot\vec{S} = \frac{1}{2}\left[\hat{F}^2 - \hat{I}^2 - \hat{S}^2\right] \rightarrow \left[F(F+1) - I(I+1) - S(S+1)\right]$$

this gives us an energy correction to hydrogenic s-state levels of

$$\Delta E = \overbrace{\frac{2}{3\pi}\mu_0 g_I g_s \mu_B \mu_N \frac{Z^3}{n^3 a_0^3}}^{A} \left[\frac{F(F+1) - I(I+1) - S(S+1)}{2}\right]$$

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

for the hydrogen nucleus (i.e. a proton), $Z=1$, $g_I = 5.5883$

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

for the electron we have $S = \frac{1}{2}$ and $g_S \simeq 2$ (we'll look @ $n=1$)

The allowed F-values are $F = 0, 1$.

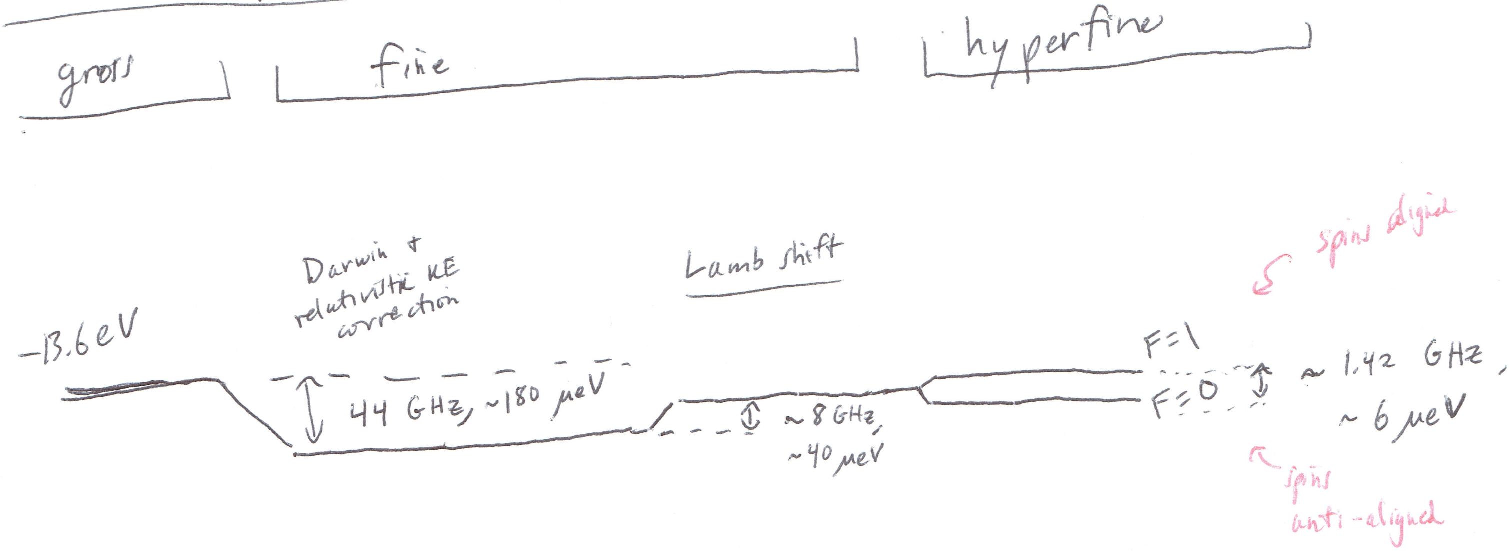
$$\Delta E_{F=0} = -\frac{3}{2}\left[\frac{2}{3\pi}(5.5883)\mu_0 \mu_B \mu_N \frac{1}{a_0^3}\right]$$

$$\left|\frac{\Delta E_{F=0}}{\Delta E_{F=1}}\right| = 3$$

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

$$\Delta E_{F=1} - \Delta E_{F=0} = \frac{4}{3\pi} g_I \mu_0 \mu_B \mu_N \frac{1}{a_0^3} \simeq h \times 1.42 \text{ GHz}$$

this corresponds to $\lambda = 21$ cm, used extensively in radio astronomy



⑥ This result fails for the more general case (multi-electron atoms, $\ell \neq 0$)

but a result having similar form follows from a proper treatment using relativistic quantum mechanics.

$$H_{HFS} = \underset{\substack{\uparrow \\ \text{magnetic} \\ \text{dipole moment} \\ \text{of nucleus}}}{H_{dip}} + \underset{\substack{\uparrow \\ \text{electric} \\ \text{quadrupole} \\ \text{moment of} \\ \text{nucleus}}}{H_{quad}}$$

(relevant for $I > \frac{1}{2}$ and $\ell \neq 0$, interaction of quadrupole moment w/ $\vec{\nabla} E$)

$$H_{dip} = \underbrace{A_{hfs} \vec{I} \cdot \vec{J}}_{\text{same form as before}}$$

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

$$H_{quad} = B_{hfs} \frac{3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1)}{2IJ(2I-1)(2J-1)}$$

{only for $I > \frac{1}{2}$, $\ell \neq 0$}

$\underline{F}$ is a good quantum number here, as is its z-projection, $\underline{m_F}$.

$(\vec{F} = \vec{I} + \vec{J})$ ↳ will be ~~a~~ good @ low B-fields

these $|I, J, F, m_F\rangle$ states ($|F, m_F\rangle$ for short) can be expressed in terms of the quantum #s of the nuclear spin & electron spin as.

$$|F, m_F\rangle = \sum_{\substack{m_I, m_J \\ \text{satisfying} \\ m_F = m_I + m_J}} \boxed{\langle F, m_F | I, m_I, J, m_J \rangle} |I, m_I, J, m_J\rangle$$

~~$\langle I, J, F, m_F | I, J, m_I, m_J \rangle |I, J, m_I, m_J\rangle$~~

↳ Clebsch-Gordon coefficient

$$\langle I, m_I, J, m_J | F, m_F \rangle = \sqrt{2F+1}\,(-1)^{I-J+m_F} \underbrace{\begin{pmatrix} I & J & F \\ m_I & m_J & -m_F \end{pmatrix}}_{\text{Wigner 3j}}$$

7 The first-order energy shift is given by

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

where $K = F(F+1) - I(I+1) - J(J+1) = 2\langle \vec{I}\cdot\vec{J}\rangle$

for some details on measurement of A_{hfs} + B_{hfs} constants, see RMP 49 31 (1997) by Arimondo + Inguscio

see slides for some experimental values.

Some notes: $A_{hfs} > 0$ is referred to as "regular", whereas $A_{hfs} < 0$, as in ^{40}K, is called "inverted"

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

For $\ell = 0$, we have $J = S$ 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 $m_I = m_F - m_S = m_F \mp \frac{1}{2}$ for $m_S = \pm\frac{1}{2}$

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

α, β are Clebsch-Gordon coefficients.

This form will help us understand how we have states w/ 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).

① Size effects → Volume shifts – in HW1, you calculated the energy corrections that one would expect due to the ~~modification~~ deviation of the nuclear charge distribution from that of a point charge, which led to a potential that was not proportional to $\frac{1}{r}$ 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 w.r. Lamb shift measurement)

Simple toy model (~ same as HW#1) for hydrogen-like atom

Consider a sphere w/ uniform charge density, having total charge $Q_N = Ze$ and radius $R \approx A^{1/3} r_0$

where $A \approx 2Z$ is the atomic mass number (# of nucleons)

and $r_0 \simeq 1.2$ fm (radius close to proton radius $r_p \sim .9$

the potential energy experienced the electron

$$V(r) = \begin{cases} \dfrac{Ze^2}{4\pi\varepsilon_0 R}\dfrac{1}{2}\left(\dfrac{r^2}{R^2} - 3\right) & \text{for } r \le R \\[2ex] = \dfrac{Ze^2}{4\pi\varepsilon_0 r} & \text{for } r > R \end{cases}$$

(4) this volume effect lead to an energy correction:

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

$$= \begin{cases} \dfrac{Ze^2}{4\pi\varepsilon_0 R}\dfrac{1}{2}\left(\dfrac{r^2}{R^2} + \dfrac{2R}{r} - 3\right) & \text{for } r \le R \\ 0 & \text{for } r > R \end{cases}$$

$$\Delta E = \langle H' \rangle = \langle \psi_{n\ell m} | H' | \psi_{n\ell m} \rangle$$

because R is so small, this effect is only important (non-zero) for $\ell = 0$ states

$$\Delta E = \frac{Ze^2}{4\pi\varepsilon_0 2R} 4\pi \int_0^R |R_{n\ell}(r)|^2 \left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr$$

$$\Delta E \approx \frac{Ze^2}{\cancel{4\pi}\varepsilon_0 2R} \cancel{4\pi} |R_{n0}(0)|^2 \underbrace{\int_0^R \left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr}_{\frac{R^3}{5}}$$

$$= \frac{Ze^2}{10\varepsilon_0} R^2 |R_n(0)|^2$$

$\hookrightarrow \dfrac{4Z^3}{n^3 a_0^3}$

$$= \frac{Z^4}{a_0^3 n^3} \frac{e^2 R^2}{10\varepsilon_0} \Longrightarrow \text{Foot Eq (6.26)}$$

$\hookrightarrow$ result applied to alkalis, etc. based on central field approximation

$\propto R^2 Z$

2 mass effects → we'll only discuss the reduced mass effect, ~~due to~~

which requires a correction due to our assuming that $\frac{M_{nucleus}}{m_e} = \infty$

$$E_n = -\frac{e^2}{4\pi\varepsilon_0 a_\mu}\frac{Z^2}{2n^2} = \underbrace{\frac{-e^2}{4\pi\varepsilon_0 a_0}\frac{Z^2}{2n^2}}_{E_n^\infty}\frac{M_N}{m_e + M_N} = \frac{E_n^\infty}{\frac{m_e}{M_N}+1} = E_n^\infty\left(1+\frac{m_e}{M_N}\right)^{-1}$$

$$\simeq E_n^\infty\left(1-\frac{m_e}{M_N}\right)$$

So, the correction for a finite nuclear mass

is $\boxed{\Delta E_n = -E_n^\infty \frac{m_e}{M_N}}$

this correction always $\propto -E_n^\infty$, such that it shifts energies up, and correction term gets smaller as M_N increases.