Hyperfine structure

Note Title 12/28/2004

Hyperfine structure comes from the interaction between the electron and the real nucleus

Two types of effects – structure
– isotope shifts

Hyperfine structure:

electric and magnetic effects

- electric: interaction of even charge moments of the nucleus with the electric field of the electron
- magnetic: one interpretation – interaction of odd magnetic moments and magnetic field generated by the electron

You will find various theoretical treatments, which are mostly wrong. Rigorous, QM relativistic theories:

- Walter Johnson's lecture notes
- Armstrong, Theory of the Hyperfine Structure of Free Atoms

We do know the Hamiltonian, but exactly calculating hyperfine structure for many electron atoms is not possible right now — so, we try to understand the general atomic structure, and then fit the theory to measurements

Start with a semi-classical argument:

Classical derivation of magnetic dipole part of interaction is instructive (can basically get hyperfine splitting of hydrogen ground state this way)

* in cgs:

$$\vec{B}_L = \frac{e}{mr^3}\vec{L} = \frac{2\mu_0}{r^3}\frac{\vec{L}}{\hbar}$$ magnetic field at nucleus from electron orbital motion

$$\vec{B}_S = \frac{3\hat{r}(\hat{r}\cdot\vec{\mu}) - \vec{\mu}}{r^3} + \frac{8\pi}{3}\vec{\mu}\,\delta^3(\vec{r})$$ magnetic field from spin (dipole) - see Jackson

General case is tricky, but we can do s-states:

$$H_{hyp} = -\vec{\mu}_I \cdot \vec{B} = -g_I \frac{\mu_N}{\hbar} \vec{I} \cdot \vec{B}$$

$$\vec{B} = -\frac{2\mu_0}{r^3}\frac{\vec{L}}{\hbar} - \frac{3\hat{r}(\hat{r}\cdot\vec{\mu}) - \vec{\mu}}{r^3} - \frac{8\pi}{3}\vec{\mu}\,\delta^3(\vec{r})$$

zero for an s-state

averages to zero for an s-state

only this term contributes

$$H_{hyp} = g_I \frac{\mu_N}{\hbar} 2 \frac{\mu_0}{\hbar} \frac{8\pi}{3} \vec{I}\cdot\vec{S}\,\delta^3(\vec{r})$$

1st order energy shift: $\langle njF | H_{hyp} | njF \rangle = \Delta E$

$$\Delta E = 2 g_I \frac{\mu_N \mu_0}{\hbar^2} \frac{8\pi}{3} \langle njF | \vec{I}\cdot\vec{S}\,\delta^3(\vec{r}) | njF \rangle$$

$\vec{F} = \vec{J} + \vec{I} = \vec{S} + \vec{I}$ for an s-state

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

$$\Delta E = \frac{8\pi}{3} g_I \mu_N \mu_0 \left[F(F+1) - S(S+1) - I(I+1) \right] \cdot$$

$$\langle n | \delta^3(\vec{r}) | n \rangle$$

$$\langle \delta(\vec{r}) \rangle = \int |\psi_{n00}(\vec{r})|^2 \delta(\vec{r})\, d^3\vec{r} = |\psi_{n00}(0)|^2 = \frac{Z^3}{\pi a_\mu^3 n^3}$$

So, $$\Delta E = \frac{8}{3} g_I \mu_N \mu_0 \frac{Z^3}{a_\mu^3 n^3} \left[F(F+1) - S(S+1) - I(I+1) \right]$$

Let's try ground state of Hydrogen!

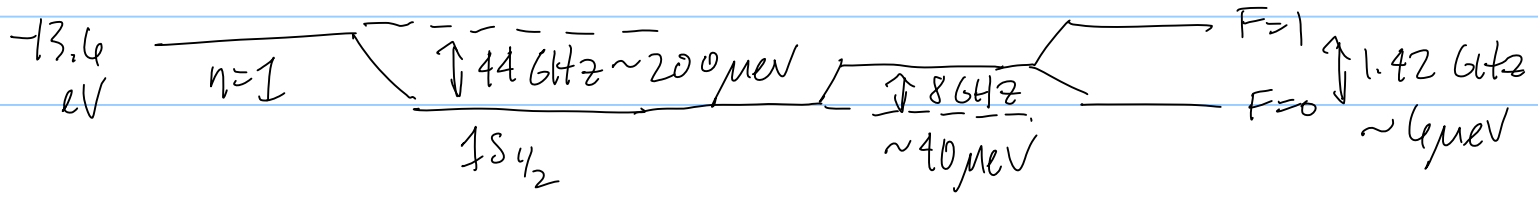
$g_I = 5.5883$ (proton) $S = 1/2,\ I = 1/2,\ F = 1, 0$

$$\Delta E_{F=1} - \Delta E_{F=0} = \frac{8}{3} g_I \mu_N \mu_0 \frac{1}{a_\mu^3} \cdot 2$$

$\Delta E \sim 1422$ MHz $\rightarrow \lambda = 21$ cm – used in radio astronomy!

real value = 1,420,405,751.7667 (9) Hz

(comparison between Hydrogen maser and Cs clock)



In general:

Using relativistic QM, can show for magnetic dipole interaction:

$$H_{dip} = A\,\vec{I}\cdot\vec{J}$$

this is reasonable — look at argument for Hydrogen

And electric quadrupole: vanishes for s-states or $I = 0, 1/2$

$$H_Q = B\,\frac{3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1)}{2IJ(2I-1)(2J-1)}$$

Note that both are diagonal in $\vec{F} = \vec{I} + \vec{J}$, so we use states:

$$|F, m_F\rangle = \sum_{\substack{m_I, m_J \\ (m_F = m_I + m_J)}} \langle jI; F m_F \,|\, jI; m_J m_I\rangle \; |jI; m_J m_I\rangle$$

$\langle jI; F m_F \,|\, jI; m_J m_I\rangle$: CG for adding $\vec{J}$ and $\vec{I}$ to make $\vec{F}$

And, the first order energy shift is:

$$\Delta E = W = \frac{A}{2}k + \frac{B}{8I(2I-1)J(2J-1)}\left\{3k(k+1) - 4I(I+1)J(J+1)\right\}$$

where $k = F(F+1) - I(I+1) - J(J+1)$

A and B are not calculated, but measured — see the nice summary in Metcalf's book, or the classic paper by Ennio and Massimo (Rev. Mod. Phys, 49 31 (1977))

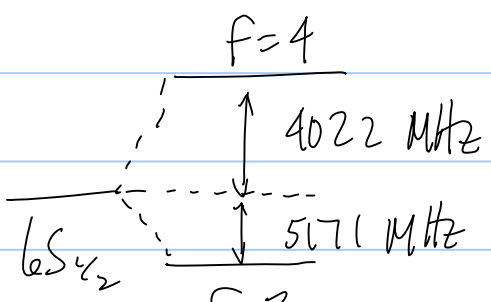
There are many, many digits known for A for the alkalis. In fact, A for Cs is our primary frequency standard!

Element	Abundance	I	F_g ($J_g=1/2$)	A (MHz)	ΔE_{fs} (GHz)	F_e ($J_e=1/2$)	A (MHz)	F_e ($J_e=3/2$)	A (MHz)	B (MHz)
^{1}H	99.985	1/2	0,1	1420.405	10.968	0,1	59.18	1,2	23.67	–
^{6}Li	7.5	1	1/2,3/2	152.137		1/2,3/2	17.375	1/2,3/2,5/2	−1.155	−0.10
^{7}Li	92.5	3/2	1,2	401.752	10.091	1,2	45.914	0,1,2,3	−3.055	−0.221
^{23}Na	100	3/2	1,2	885.813	515.53	1,2	94.3	0,1,2,3	18.69	2.90
^{39}K	93.26	3/2	1,2	230.859	1730.4	1,2	28.85	0,1,2,3	6.06	2.83
^{40}K	0.0117	4	7/2,9/2	−285.731		7/2,9/2	–	5/2,7/2,9/2,11/2	−7.59	−3.5
^{41}K	6.73	3/2	1,2	127.007		1,2	–	0,1,2,3	3.40	3.34
^{85}Rb	72.17	5/2	2,3	1011.910	7123.0	2,3	120.72	1,2,3,4	25.009	25.88
^{87}Rb	27.83	3/2	1,2	3417.341		1,2	406.2	0,1,2,3	84.845	12.52
^{133}Cs	100	7/2	3,4	2298.157	16611.8	3,4	291.90	2,3,4,5	50.34	−0.38

TABLE C.4. Fine- and hyperfine structure constants for the various alkali-metal atoms. The parameters A and B can be used in Eqs. 4.2 and 4.3 to calculate the shift and the splitting from the hyperfine interaction. The values for A and B are from Ref. 28.

Let's do alkali ground states as an example:

^{133}Cs : $I = 7/2$, $F = 4, 3$



$$k_4 = 4(5) - 7/2(9/2) - 1/2(3/2)$$

$$W_4 = A \cdot 14/8 = 4022 \text{ MHz}$$

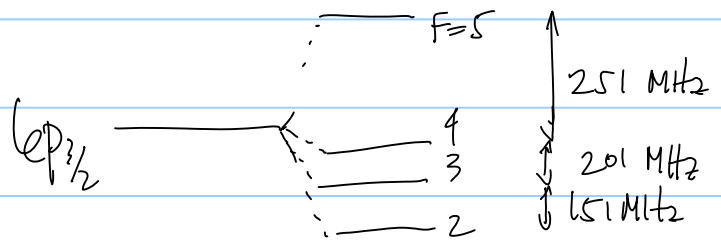
$$k_3 = 3(4) - 7/2(9/2) - 1/2(3/2)$$

$$W_3 = -A\,18/8 = -5171$$

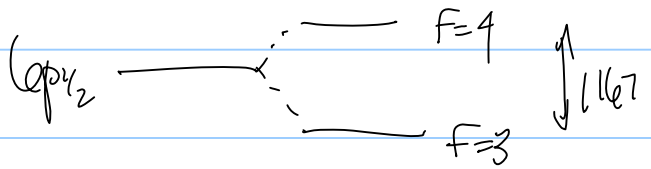
$$W_4 - W_3 = 1/2\,A\,(2I+1)$$

ground state hyperfine splitting

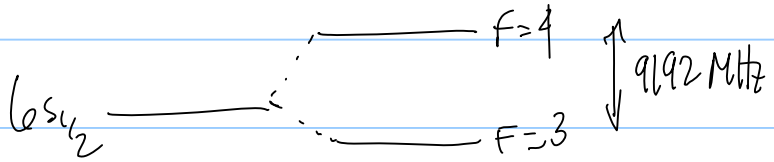
Including excited states



we get states $F = I + 3/2, \ldots, I - 3/2$



states $F = I + 1/2$, $F = I - 1/2$



get states $F = I + 1/2, I - 1/2$

Jargon: $A>0$ "regular"
$A<0$ "inverted"

* Special note: for the alkalis, the ground state Zeeman levels each are made up of 2 states in the $|jI; m_j m_I\rangle$ basis

Since $l=0$, $j=s$ and we use basis states $|SI; m_I m_s\rangle$, often abbreviated as $|m_s m_I\rangle$

Now, $m_s = \pm 1/2$, and we must have $m_F = m_s + m_I$, which means that $m_I = m_F - m_s = m_F \mp 1/2$

For ground states, then $|F, m_F\rangle = \alpha\,|m_s = 1/2, m_I = m_F - 1/2\rangle +$
$\beta\,|m_s = -1/2, m_I = m_F + 1/2\rangle$

where α and β are the appropriate CG coefficients

Brian's Appendix:

Flavor of the relativistic QM treatment for a many-electron atom:

(from Armstrong)

electrostatic potential at the electron:

$$V(r_e) = \sum_n \int \frac{\rho(\vec{r}_n)}{|\vec{r}_e - \vec{r}_n|} d\tau_n$$

$\rho(\vec{r}_n)$ is the nuclear charge distribution, r_e is the location of an electron

magnetic vector potential at the electron:

$$\vec{A}(r_e) = \frac{1}{c} \sum_n \int \frac{\vec{j}(\vec{r}_n)}{|\vec{r}_e - \vec{r}_n|} d\tau_N$$

cgs units again

two currents: convective: $\vec{j}_c = \frac{e}{2}\left[\psi_N^* \sum_n g_{en} \vec{v}_n \psi_N - \psi_N \sum_n g_{en} \vec{v}_n \psi_N^*\right]$

spin: $\vec{j}_s = \vec{\nabla} \times \psi_N^* \sum_n g_{sn} \frac{e\hbar}{2m_p} \vec{s}_n \psi_N$

ψ_N is the nuclear wavefunction — $\rho = \psi_N^* \left(\sum g_{en} e\right) \psi_N$ $g_{en} = 1$ proton, $g_e = 0$ neutron

$g_{sn} = -3.8263$ neutron, $g_{sn} = 5.5856$ proton

using $\vec{j} = \vec{j}_c + \vec{j}_s$, we can get a closed form for $\vec{A}$

Then:

$$H_{hyp} = \sum_i \left(\frac{Ze^2}{r_i} - eV(r_i) + \vec{\alpha}_i \cdot e\vec{A}(r_i) \right)$$

recall $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$

assuming a non-relativistic nucleus and $\psi = \psi_N \psi_e$ (separable in electrons and nucleons)

$$H_{hyp} = \sum_i \sum_{k>0} \left[\frac{-e}{r_i^{k+1}} \vec{C}_i^{(k)} \cdot \vec{F}^{(k)} + \frac{ie}{r_i^{k+1}} \sqrt{\frac{k+1}{k}} \left(\vec{\alpha}_i \vec{C}_i^{(k)} \right)^{(k)} \cdot \vec{N}^{(k)} \right]$$

electric

magnetic

here $C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}$

$F_q^{(k)} = e \sum_n g_{en} r_n^k C_{nq}^{(k)}$ nuclear electrostatic operator - just expansion of charge moments of the nucleus

$$N_q^{(k)} = \beta_N \sum_n \sqrt{k(2k-1)}\, r_n^{k-1} \left[\frac{2 g_{en}}{k+1} \left(\vec{C}_n^{(k-1)} \vec{L}_n \right)_q^{(k)} + g_{sn} \left(C_n^{(k-1)} S_n \right)_q^{(k)} \right]$$

nuclear magnetic moments

orbital

spin

$$\begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & -1 \end{pmatrix} \quad \begin{matrix} & & -1 \end{matrix}$$

Charge interaction:

$\left(\frac{-e}{r_i^{k+1}} \vec{C}_i^{(k)}\right) \cdot \vec{F}^{(k)}$ looks a lot like

$W = \int \rho(x) \Phi(x) d^3x$ — see Jackson, interaction between electric field from electron

$\Phi \propto \sum_{lm} q_{lm} \frac{1}{r^{l+1}} Y_{lm}$ and charge moments of the nucleus

Magnetic interaction:

harder to see in relativistic form

ex: $N_q^{(1)} = \beta_N \sum_n \left[g_{ln} \left(\vec{L}_n\right)_q^{(1)} + g_{sn} \left(\vec{S}_n\right)_q^{(1)} \right]$ dipole moment!

remember — $C^{(0)} = \text{const.}$

we call this $\vec{I}$ — nuclear spin

$\frac{1}{r_i^{k+1}} \left(\vec{\alpha}_i C_i^{(k)}\right)^{(k)}$ is kind of like $\vec{J}$, which is like the magnetic field produced by the electron at the nucleus (think electron currents)

$\vec{\alpha}_i$ mixes in the effect of spin

In the end, rewritten as:

$$H_{hyp} = \sum_{k>0} \left(\vec{Q}^{(k)} \cdot \vec{F}^{(k)} + \vec{M}^{(k)} \cdot \vec{N}^{(k)} \right)$$

$\vec{Q}^{(k)}$ and $\vec{M}^{(k)}$ are tensor operators in the vector space of the electrons – have $\vec{l}_i$ and $\vec{s}_i$ in them

1st order P.T. – only interested in the diagonal parts of these operators, which break up into dipole, quadrupole, etc terms

H_{hyp} is diagonal in $\vec{F} = \vec{I} + \vec{J}$ ← electron angular momentum
↑ nuclear spin

Neither I nor J are really good quantum numbers:

I: pretty damn good

J: OK if fine structure splittings are large

turns out that $\vec{M}^{(1)} \propto \vec{J}$ and $\vec{N}^{(1)} \propto \vec{I}$, so magnetic dipole energy in 1st order is:

$$\langle \psi_N \psi_E | \vec{N}^{(1)} \cdot \vec{M}^{(1)} | \psi_N \psi_E \rangle = A \langle \psi_N \psi_E | \vec{I} \cdot \vec{J} | \psi_N \psi_E \rangle$$

$$H_D = A \vec{I} \cdot \vec{J}$$

electric quadrupole: this gets hard

$$H_Q = B \frac{3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1)}{2IJ(2I-1)(2J-1)}$$

vanishes for s states or $I = 0, \frac{1}{2}$

total energy shifts in 1st order PT:

$$W = \frac{A}{2}k + \frac{B}{8I(2I-1)J(2J-1)}\left\{3k(k+1) - 4I(I+1)J(J+1)\right\}$$

And since H_{hyp} is diagonal in $\vec{F}$, we construct states as:

$$|IJFm_F\rangle = \sum_{\substack{m_I \\ m_J}} \sqrt{2F+1}\,(-1)^{J-I+m_F} \begin{pmatrix} I & J & F \\ m_I & m_J & -m_F \end{pmatrix} |Im_I\rangle |Jm_J\rangle$$

3-j symbol

same as Clebsch-Gordon coefficient