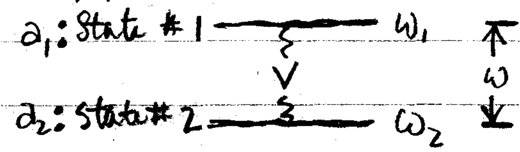
5/2/71 (13) This is essentially the Two-State Quantum Oscillation problem worked out in WKBK #21, p.33. We assume the superposition...

$$\psi(x,t) = \sum_{k=1}^{2} a_k(t)\,\phi_k(x)\,e^{-i\omega_k t}$$



$$i\hbar\frac{\partial}{\partial t}\psi = (H+\mathcal{V})\psi \implies$$

$$\sum_k (i\hbar\dot{a}_k + \hbar\omega_k a_k)\,\phi_k\,e^{-i\omega_k t} = \sum_k (\hbar\omega_k + \mathcal{V})\,a_k\,\phi_k\,e^{-i\omega_k t}$$

Operate with $\langle\phi_j|\ \rangle$ and use orthonormality of the ϕ_k, etc to give

cancel

$$(i\hbar\dot{a}_j + \hbar\omega_j a_j)\,e^{-i\omega_j t} = \hbar\omega_j a_j e^{-i\omega_j t} + \sum_k \mathcal{V}_{jk}\,a_k\,e^{-i\omega_k t}$$

where: $\mathcal{V}_{jk} = \langle\phi_j|\mathcal{V}|\phi_k\rangle$. But $\begin{cases} \mathcal{V}_{11} = \mathcal{V}_{22} = 0 \text{ given} \\ \text{let: } \mathcal{V}_{12} = V = \mathcal{V}_{21}^* \end{cases}$

Then get two coupled eqtns...

$$i\hbar\dot{a}_1 = V e^{+i\omega t} a_2, \quad i\hbar\dot{a}_2 = V^* e^{-i\omega t} a_1$$

where: $\omega = \omega_1 - \omega_2$ is unperturbed energy separation

Decoupling the eqtns, we find...

$$\ddot{a}_1 - \left(i\omega + \frac{\dot{V}}{V}\right)\dot{a}_1 + (|V|^2/\hbar^2)\,a_1 = 0$$

$$\ddot{a}_2 + \left(i\omega - \frac{\dot{V}^*}{V^*}\right)\dot{a}_2 + (|V|^2/\hbar^2)\,a_2 = 0$$

Assume $\dot{V} = 0$ (i.e. $\mathcal{V}_{12}$ is time-indpt), and define

$$\Omega = V/\hbar \quad \leftarrow \text{may be complex in general}$$

See binder on "Problems with WWTheory" Mar. 1968, p.1 of "Effect of Non-Monochromatic V, Part II (17 June 1968).

Then we have

$$\ddot{a}_1 - i\omega\dot{a}_1 + |\Omega|^2 a_1 = 0 \,, \quad \ddot{a}_2 + i\omega\dot{a}_2 + |\Omega|^2 = 0$$

Assuming a solution of the form

$$a_1(t) = A e^{-\mu t}$$

and plugging in, we get a secular eqtn for μ

$$\mu^2 + i\omega\mu + |\Omega|^2 = 0 \Rightarrow \mu_{1,2} = -\frac{i\omega}{2}(1 \pm Q)$$

where: $\underline{\underline{Q}} = \left[1 + (2|\Omega|/\omega)^2\right]^{\frac{1}{2}} = \left[1 + |2V_{12}/\hbar\omega|^2\right]^{\frac{1}{2}}$ {same Q as in prob. 68

The general solution for $a_1(t)$ is thus

$$a_1(t) = A_1 e^{-\mu_1 t} + A_2 e^{-\mu_2 t}$$

$a_2(t)$ can be generated from this via the first coupled eqtn...

$$a_2 = i\hbar\dot{a}_1 / V e^{+i\omega t} \,, \text{ or}$$

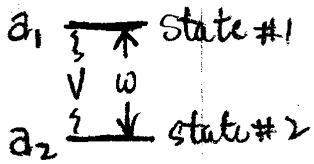
$$a_2(t) = \frac{e^{-i\omega t}}{i\Omega}\left(\mu_1 A_1 e^{-\mu_1 t} + \mu_2 A_2 e^{-\mu_2 t}\right)$$

The boundary conditions: $a_1(0) = 1$, $a_2(0) = 0$ give...

$$\left.\begin{array}{l} A_1 + A_2 = 1 \\ \mu_1 A_1 + \mu_2 A_2 = 0 \end{array}\right\} \Rightarrow A_1 = \frac{\mu_2}{\mu_2 - \mu_1} \,, \quad A_2 = \frac{\mu_1}{\mu_1 - \mu_2}$$

or

$$A_1 = \frac{Q-1}{2Q} \,, \quad A_2 = \frac{Q+1}{2Q}$$



The full solutions are therefore

$$a_1(t) = \left(\frac{Q-1}{2Q}\right) e^{+\frac{i}{2}(Q+1)\omega t} + \left(\frac{Q+1}{2Q}\right) e^{-\frac{i}{2}(Q-1)\omega t}$$

$$a_2(t) = \underbrace{\left\{\frac{\omega}{2\Omega}\left(\frac{Q^2-1}{2Q}\right)\right\}}_{= \left(\frac{V}{Q\hbar\omega}\right)^*}\left[e^{-\frac{i}{2}(Q+1)\omega t} - e^{+\frac{i}{2}(Q-1)\omega t}\right]$$

or, equivalently...

$$a_1(t) = e^{+\frac{i}{2}\omega t}\left[\cos\left(\tfrac{1}{2}Q\omega t\right) - \frac{i}{Q}\sin\left(\tfrac{1}{2}Q\omega t\right)\right]$$

$$a_2(t) = e^{-\frac{i}{2}\omega t}\left(\frac{(2\Omega/\omega)^*}{iQ}\right)\sin\left(\tfrac{1}{2}Q\omega t\right)$$

These forms essentially agree with the results of eq.(9), p.35, WKBK #21. The transition probability $1\to 2$ for $t>0$ is

$$P_{1\to 2}(t) = |a_2(t)|^2 = \frac{|2\Omega/\omega|^2}{Q^2}\sin^2\left(\tfrac{1}{2}Q\omega t\right)$$

or

$$P_{1\to 2}(t) = \frac{Q^2-1}{2Q^2}\left[1-\cos(Q\omega t)\right]$$ $\Rightarrow$ quantum oscillation between states 1 & 2 at freq. $Q\omega$

For weak V, $|V| \ll \hbar\omega$, and $Q \simeq 1 + 2|V/\hbar\omega|^2$, and

$$P_{1\to 2}(t) \simeq 2\left|\frac{V}{\hbar\omega}\right|^2\left[1-\cos(Q\omega t)\right]$$

$$P_{1\to 2}(t) = \frac{4|V|^2}{(\hbar\omega)^2+4|V|^2}\sin^2\left(\frac{1}{2}\left[1+\left(\frac{2|V|}{\hbar\omega}\right)^2\right]^{\frac{1}{2}}\omega t\right)$$

4/27/71 (2) a) The expression given for the Dirac energies agrees with Schiff Eq. (53.26), p. 486, Davydov eq. (71.20), p. 274, Sakurai eq (3.311), p. 127 and PHYS 532 lecture (56), 3/9/70, p. 99. From any one of these sources, we get the expansion

$$\mathcal{E}_{nj} \simeq \mathcal{E}_n\left[1+\left(\frac{Z\alpha}{n}\right)^2\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right], \text{ to } \theta(Z\alpha)^4$$

where: $\mathcal{E}_n = -\frac{1}{2}(Z\alpha)^2 mc^2/n^2$ are the Bohr energies

These are precisely the Schrodinger energies calculated in PHYS 507 lecture (66), 4/28/71, p. 272 -- including the spin-orbit interaction and the relativistic correction, to $\theta(Z\alpha)^4$

b) The $2P_{3/2} - 2P_{1/2}$ separation as calculated in PHYS 507 lecture (65), 4/26/71, p. 268 is -- for hydrogen ($Z=1$)

$$\Delta\epsilon_{21} = \frac{1}{16}\alpha^2 I, \quad I = \text{ionization energy } (n=1 \to n=\infty \text{ transition})$$

Now can write $I = Rhc$, where R = Rydberg cnst. The freq. separation is thus

$$\Delta\nu_{21} = \Delta\epsilon_{21}/h = \frac{1}{16}\alpha^2 Rc, \quad \text{where } R = R_\infty$$

Use latest TPL cnsts...

$$\left.\begin{aligned} \alpha &= 1/137.03602 \pm 1.5\text{ ppm} \\ R_\infty &= 109{,}737.312 \text{ cm}^{-1} \pm 0.1\text{ ppm} \\ c &= 2.9979250\times10^{10}\text{ cm/sec} \pm 0.3\text{ ppm} \end{aligned}\right\} \Delta\nu_{21} = 10{,}949.28 \text{ MHz} \pm .03\ (3\text{ppm})$$

Value quoted by Lamb (for D) is $\Delta\nu_{21} = 10{,}971.59 \pm 0.20$ MHz.

Of course we should take into account correction for $g_s \neq 2$, reduced mass and isotope effect, Breit correction, etc.

See PHYS 531 lecture (29), 12/11/69, p. 22, and Schiff, pp. 466-471

4/27/71 Letting $E = i\hbar\frac{\partial}{\partial t}$ and $\vec{p} = -i\hbar\vec{\nabla}$, the KG eqtn is

$$\left(i\hbar\frac{\partial}{\partial t} - V\right)^2\psi = \left(-\hbar^2c^2\vec{\nabla}^2 + (mc^2)^2\right)\psi$$

If we assume a stationary state, $\psi(\vec{r},t) = \psi(\vec{r})\,e^{-\frac{i}{\hbar}Et}$, then this is

$$\vec{\nabla}^2\psi + \left[\left(\frac{E-V}{\hbar c}\right)^2 - \left(\frac{mc}{\hbar}\right)^2\right]\psi = 0$$

a) Now let $V(r) = -Ze^2/r$ and $\psi(\vec{r}) = \frac{1}{r}u(r)\,Y_{lm}(\vartheta,\varphi)$. Using

$$\vec{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{r^2}, \quad \vec{L} \text{ in units of } \hbar$$

(from Merz. p. 176, or PHYS 506 lecture (41), 2/5/71, p. 182), and noting

$$\vec{L}^2\,Y_{lm}(\vartheta,\varphi) = l(l+1)\,Y_{lm}(\vartheta,\varphi)$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\frac{1}{r}u(r) = \frac{1}{r}\frac{\partial^2}{\partial r^2}u(r)$$

we have (after cancelling $\frac{1}{r}Y_{lm}(\vartheta,\varphi)$)

$$\left\{\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + \left[\left(\frac{E+Ze^2/r}{\hbar c}\right)^2 - \left(\frac{mc}{\hbar}\right)^2\right]\right\}u(r) = 0$$

or $$\left\{\frac{\partial^2}{\partial r^2} + \left[\frac{E^2-(mc^2)^2}{(\hbar c)^2} + \left(\frac{2EZ\alpha}{\hbar c}\right)\frac{1}{r} - \frac{l(l+1)-(Z\alpha)^2}{r^2}\right]\right\}u(r) = 0$$

which is the desired radial eqtn. Now let $E = mc^2 + \mathcal{E}$, so that

$$\frac{E^2-(mc^2)^2}{(\hbar c)^2} = \frac{2m\mathcal{E}}{\hbar^2}\left(1+\frac{\mathcal{E}}{2mc^2}\right), \quad \left(\frac{2EZ\alpha}{\hbar c}\right)\frac{1}{r} = \frac{2m}{\hbar^2}\left(1+\frac{\mathcal{E}}{mc^2}\right)\frac{Ze^2}{r}$$

$$\therefore \left\{\frac{\partial^2}{\partial r^2} + \left[\frac{2m}{\hbar^2}\left(1+\frac{\mathcal{E}}{2mc^2}\right)\mathcal{E} + \frac{2m}{\hbar^2}\left(1+\frac{\mathcal{E}}{mc^2}\right)\frac{Ze^2}{r} - \frac{l(l+1)-(Z\alpha)^2}{r^2}\right]\right\}u(r) = 0$$

In the non-relativistic limit, $c\to\infty$, we have $\alpha\to 0$, and ...

$$\left\{ \frac{\partial^2}{\partial r^2} + \left[\frac{2m}{\hbar^2}\left(\mathcal{E} - V(r)\right) - \frac{\ell(\ell+1)}{r^2} \right] \right\} u(r) = 0, \quad V(r) = -Ze^2/r$$

But this is just the S. radial eqtn -- see PHYS 506 lecture (41), 2/5/71, p. 183, or lecture (46), 2/22/71, p. 203.

b) We can convert eq ~~(13)~~ above into a counterpart of the S. eqtn solved in PHYS 506 lecture (46), 2/22/71, pp. 203-207, if we define

$$\lambda(\lambda+1) = \ell(\ell+1) - (Z\alpha)^2 \Rightarrow \lambda = -\tfrac{1}{2} \pm \sqrt{(\ell+\tfrac{1}{2})^2 - (Z\alpha)^2}$$

choose (+) only, so $\lambda = \ell$ for $c \to \infty$.

Unit of length: $a = \hbar c / E\alpha \underset{\mathcal{E} \ll mc^2}{\simeq} \hbar c / mc^2 \frac{e^2}{\hbar c} = \hbar^2/me^2$ { Bohr radius

Dimensionless radial variable: $\rho = r/a$

Energy parameter: $\kappa^2 = \dfrac{(mc^2)^2 - E^2}{\alpha^2 E^2} > 0$ for bound states
($E = mc^2 - |\mathcal{E}| < mc^2$)

The radial eqtn then becomes

$$\left\{ \frac{\partial^2}{\partial \rho^2} + \left[-\kappa^2 + \frac{2Z}{\rho} - \frac{\lambda(\lambda+1)}{\rho^2} \right] \right\} u(\rho) = 0$$

The solution which is well-behaved at $\rho = 0$ & $\rho = \infty$ is

$$u(\rho) \propto \rho^{\lambda+1} e^{-\kappa\rho} \, {}_1F_1\left(\lambda + 1 - \frac{Z}{\kappa}, 2\lambda + 2; 2\kappa\rho\right)$$

with: $\boxed{\lambda + 1 - \frac{Z}{\kappa} = -N,}$ $N = 0, 1, 2, \ldots$ ← radial q. #

This gives the quantum condition ... → $\frac{1}{2} + \delta - \frac{Z}{\kappa} = -N$

$$\kappa^2 = \frac{(mc^2)^2 - E^2}{\alpha^2 E^2} = Z^2 / (N+1+\lambda)^2$$

Define: $n = N + \ell + 1$, principal q. #

Define: $\lambda = -\frac{1}{2} + \delta$, $\delta = \sqrt{(\ell+\frac{1}{2})^2 - (Z\alpha)^2}$

$$\therefore \frac{(mc^2)^2 - E^2}{E^2} = \frac{(Z\alpha)^2}{(N+\frac{1}{2}+\delta)^2} \Rightarrow E = mc^2 \Big/ \left[1+\left(\frac{Z\alpha}{N+\frac{1}{2}+\delta}\right)^2\right]^{\frac{1}{2}}$$

← agrees with Schiff eq (51.16) p. 470; also PHYS 531 lecture (29), 12/11/69, p. 24.

The quantized energies are $\mathcal{E} = E - mc^2$, or

$$\mathcal{E}_{n\ell} = mc^2\left(\left[1+\left(\frac{Z\alpha}{N+\frac{1}{2}+\delta}\right)^2\right]^{-\frac{1}{2}} - 1\right) \qquad \underline{\underline{QED}}$$

c) An expansion of $\mathcal{E}_{n\ell}$ to $\mathcal{O}(Z\alpha)^4$ proceeds as...

$$\delta = (\ell+\tfrac{1}{2})\left[1-\left(\frac{Z\alpha}{\ell+\frac{1}{2}}\right)^2\right]^{\frac{1}{2}} \simeq (\ell+\tfrac{1}{2}) - \frac{(Z\alpha)^2}{2\ell+1}$$

$$\therefore \left[1+\left(\frac{Z\alpha}{N+\frac{1}{2}+\delta}\right)^2\right]^{-\frac{1}{2}} \simeq \left[1+\left(\frac{Z\alpha}{n-\frac{(Z\alpha)^2}{2\ell+1}}\right)^2\right]^{-\frac{1}{2}} \simeq \left[1+\left(\frac{Z\alpha}{n}\right)^2\left(1+\frac{(Z\alpha)^2/n}{\ell+\frac{1}{2}}\right)\right]^{-\frac{1}{2}}$$

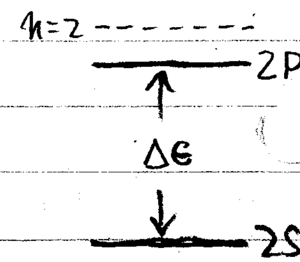
$$\hookrightarrow \simeq \left[1+bx+cx^2\right]^{-\frac{1}{2}} \begin{cases} x = (Z\alpha)^2 \ll 1 \\ b = \frac{1}{n^2}, \; c = 1/n^3(\ell+\frac{1}{2}) \end{cases}$$

$$\simeq 1 - \tfrac{1}{2}bx - \tfrac{1}{2}\left(c - \tfrac{3}{4}b^2\right)x^2 \leftarrow \text{see Dwight, p. 12}$$

$$\text{w/} \left[1+\left(\frac{Z\alpha}{N+\frac{1}{2}+\delta}\right)^2\right]^{-\frac{1}{2}} \simeq 1 - \frac{1}{2}\left(\frac{Z\alpha}{n}\right)^2 - \frac{1}{2}\left(\frac{Z\alpha}{n}\right)^4\left(\frac{n}{\ell+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\therefore \mathcal{E}_{n\ell} \simeq -\frac{1}{2}\left(\frac{Z\alpha}{n}\right)^2 mc^2\left[1+\left(\frac{Z\alpha}{n}\right)^2\left(\frac{n}{\ell+\frac{1}{2}} - \frac{3}{4}\right)\right], \text{ to } \mathcal{O}(Z\alpha)^4$$

This has the same structure as the Dirac result, but with ℓ replacing j in the fs term. The $n=2$ level splits into a single 2P state and 2S state as shown, with a total splitting



$$\Delta\epsilon = \mathcal{E}_{21} - \mathcal{E}_{20} = \frac{1}{16}\alpha^2 I\left(4-\frac{4}{3}\right) = \frac{8}{3}\Delta\epsilon(\text{Dirac})$$

$I = \frac{1}{2}\alpha^2 mc^2 = 13.6\,\text{eV} = \text{H atom ionization}$

5/11/71 76 $\Sigma_{12} = \vec{S}_1\cdot\vec{S}_2 - 3(\vec{S}_1\cdot\hat{r}_{12})(\vec{S}_2\cdot\hat{r}_{12}) \overset{?}{=} \frac{1}{2}\left[\vec{S}^2 - 3(\vec{S}\cdot\hat{r}_{12})^2\right]$

Where $\vec{S} = \vec{S}_1 + \vec{S}_2$ is total spin (in units of $\hbar$). Denote $\hat{r}_{12}$ simply by $\hat{r}$. The identity we must prove is

$$2(\cancel{\vec{S}_1\cdot\vec{S}_2}) - 6\cancel{(\vec{S}_1\cdot\hat{r})(\vec{S}_2\cdot\hat{r})} \overset{?}{=} (\vec{S}_1+\vec{S}_2)^2 - 3\left((\vec{S}_1+\vec{S}_2)\cdot\hat{r}\right)^2$$

$$\overset{?}{=} \left(\vec{S}_1^2 + \vec{S}_2^2 + 2\cancel{(\vec{S}_1\cdot\vec{S}_2)}\right) - 3\left((\vec{S}_1\cdot\hat{r})^2 + (\vec{S}_2\cdot\hat{r})^2 + 2\cancel{(\vec{S}_1\cdot\hat{r})(\vec{S}_2\cdot\hat{r})}\right)$$

or,, $\vec{S}_1^2 + \vec{S}_2^2 - 3\left((\vec{S}_1\cdot\hat{r})^2 + (S_2\cdot\hat{r})^2\right) \overset{?}{=} 0$

The easiest way to deal with this is to use the Dirac identity for $\vec{\sigma}$ = Pauli matrices ($\vec{\sigma} = 2\vec{S}$), which is * FF

$$(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\vec{\sigma}\cdot(\vec{A}\times\vec{B})$$

which hold for any two vectors $\vec{A}$ & $\vec{B}$ which commute with $\vec{\sigma}$. $\hat{r}$ is a Choice prospect, so we get

$$(\vec{\sigma}\cdot\hat{r})^2 = \underbrace{\hat{r}\cdot\hat{r}}_{=1} + i\vec{\sigma}\cdot\underbrace{(\hat{r}\times\hat{r})}_{0} = 1 \Rightarrow (\vec{S}_{1,2}\cdot\hat{r})^2 = \frac{1}{4}$$

For S_1 & $S_2 = \frac{1}{2}$, the above identity becomes

$$\underbrace{\vec{S}_1^2}_{3/4} + \underbrace{\vec{S}_2^2}_{3/4} - 3\left(\frac{1}{4}+\frac{1}{4}\right) \overset{?}{=} 0 \quad \text{Yass!} \quad \text{QED.}$$

Now we want to average the following quantity over angles...

$$(\vec{S}\cdot\hat{r})^2 = (S_x x + S_y y + S_z z)^2/r^2$$

* See PHYS 531 problem # 5

Expanding the RHS, we note that cross-terms such as (56)
$\overline{xy}, \overline{yz}$ etc. will average to zero. Thus

$$\overline{(\vec{S}\cdot\hat{r})^2} = \frac{1}{r^2}\left(S_x^2\,\overline{x^2} + S_y^2\,\overline{y^2} + S_z^2\,\overline{z^2}\right)$$

But $\overline{x^2} = \overline{y^2} = \overline{z^2} = \frac{1}{3}r^2$. So we get

$$\overline{(\vec{S}\cdot\hat{r})^2} = \frac{1}{3}\left(S_x^2 + S_y^2 + S_z^2\right) = \frac{1}{3}\vec{S}^2$$

or// $3\overline{(\vec{S}\cdot\hat{r})^2} = \vec{S}^2$ and $\overline{\Sigma}_{12} = \frac{1}{2}\left[\vec{S}^2 - 3\overline{(\vec{S}\cdot\hat{r})^2}\right] \equiv 0$

So $\overline{\Sigma}_{12}$ is $\equiv 0$ for both singlet & triplet states.

5/11/71 (77) The interaction of interest is

$\varepsilon_{hfs} = -\vec{\mu}_n\cdot(\vec{H}_e)_{AV}$, where AV $\Rightarrow$ average in direction of $\vec{J}$

i.e. $(\vec{H}_e)_{AV} = (\vec{H}_e\cdot\vec{J})\vec{J}/\vec{J}^2$. So we have

$$\left.\begin{aligned}\varepsilon_{hfs} &= +g_n\mu_0\,\vec{I}\cdot\frac{(\vec{H}_e\cdot\vec{J})\vec{J}}{\vec{J}^2} = A_{hfs}(\vec{I}\cdot\vec{J})\\ \text{where: } A_{hfs} &= g_n\mu_0(\vec{H}_e\cdot\vec{J})/J(J+1)\end{aligned}\right\}\ \underline{\underline{QED}}$$

In a state which is an eigenfcn of $\vec{F} = \vec{I} + \vec{J}$, can write

$\vec{F}^2 = \vec{I}^2 + \vec{J}^2 + 2(\vec{I}\cdot\vec{J})$ or// $(\vec{I}\cdot\vec{J}) = \frac{1}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$

$$\therefore\ \varepsilon_{hfs}(F) = \frac{1}{2}A_{hfs}\left[F(F+1) - I(I+1) - J(J+1)\right]$$

where F ranges over $I+J$ to $|I-J|$ in integral steps.

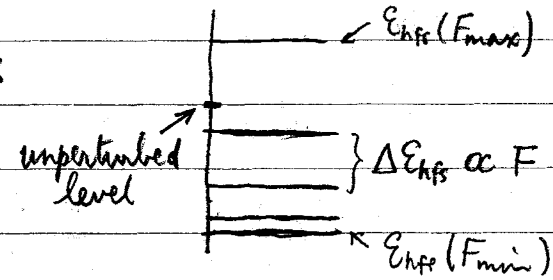
Suppose $J \geq I$ for convenience. Then there are $2I+1$ values of F, ranging from $F_{max} = J+I$ to $F_{min} = J-I$. There are just this many energy levels, ranging from...

$$\mathcal{E}_{hfs}(F_{max}) = +A_{hfs} J I \quad \text{to} \quad \mathcal{E}_{hfs}(F_{min}) = -A_{hfs}(J+1) I$$

Spacing between adjacent levels is

$$\Delta\mathcal{E}_{hfs}(F) = \mathcal{E}_{hfs}(F) - \mathcal{E}_{hfs}(F-1) = A_{hfs} F$$

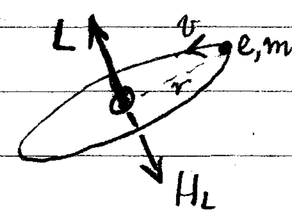
So the energy spectrum is as indicated at right...



For the calculation of A_{hfs}, we follow the treatment in PHYS 531 Lecture # 11, 10/23/69, pp. 6-9. Write

$$\vec{H}_e = \vec{H}_L + \vec{H}_S \quad \begin{cases} \vec{H}_L = \text{fld by } e \text{ at nucleus due to orbital motion.} \\ \vec{H}_S = \text{" " " " " due to } e\text{-spin.} \end{cases}$$

$$\vec{H}_L = \vec{E} \times \frac{\vec{v}}{c} = -\frac{e^2}{r^3}\vec{r} \times \frac{m\vec{v}}{mc} = -(2\mu_0/r^3)\vec{L}$$



No Thomas precession factor, because we are in the rest frame of the nucleus. For the spin fld, take dipole fld

$$\vec{H}_S = \frac{1}{r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right], \quad \vec{\mu} = -g_s \mu_0 \vec{S}$$

Approx g_s by 2, so that

$$\vec{H}_S = (2\mu_0/r^3)\left[\vec{S} - 3(\vec{S}\cdot\hat{r})\hat{r}\right]$$

$\mu_0^2/a_0^3 = \frac{1}{4}\alpha^4 mc^2 \leftarrow$ PHYS 507, # 65, 4/26/71, p.268.

$$\therefore\ \vec{H}_e = -\frac{2\mu_0}{r^3}\left[(\vec{L}-\vec{S}) + 3(\vec{S}\cdot\hat{r})\hat{r}\right]$$

Now we can calculate, with $\vec{J} = \vec{L}+\vec{S}$ ...

$$\vec{H}_e\cdot\vec{J} = -\frac{2\mu_0}{r^3}\left[\vec{L}^2 - \vec{S}^2 + 3(\vec{S}\cdot\hat{r})^2\right]$$

But $\vec{S}^2 = 3/4$ & $(\vec{S}\cdot\hat{r})^2 = 1/4$ for a spin ½ particle (from prob. 76), so the last two terms cancel. All we have left when we take the exp. value is $\langle\vec{L}^2\rangle = l(l+1)$. So we get

$$\langle\vec{H}_e\cdot\vec{J}\rangle = -2\mu_0\left\langle\frac{1}{r^3}\right\rangle l(l+1)$$

But $\left\langle\frac{1}{r^3}\right\rangle = \left(\frac{Z}{na_0}\right)^3 / l(l+1)(l+\frac{1}{2})$ { prob 4 on PHYS 506 final. on PHYS 506 # 48, 2/26/71, p.210

Calc. N.G. for S-states

$$\therefore\ \langle\vec{H}_e\cdot\vec{J}\rangle = -2\mu_0\left(\frac{Z}{na_0}\right)^3 / (l+\tfrac{1}{2})$$

Now the desired coupling coefficient is

$$A_{hfs} = g_n\mu_0\langle\vec{H}_e\cdot\vec{J}\rangle / j(j+1)$$

$$= -2g_n\mu_0^2\left(\frac{Z}{na_0}\right)^3 / j(j+1)(l+\tfrac{1}{2})$$

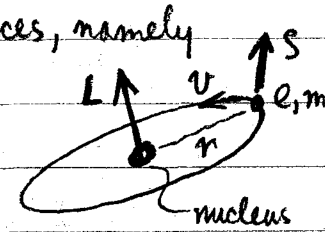
But $g_n = -|g_n|$ is (usually) (−)ve for nuclei (e.g. protons), and we can use $\mu_0^2/a_0^3 = \frac{1}{4}\alpha^4 mc^2$. Then ...

$$A_{hfs} = +|g_n|\alpha^4 mc^2\left(\frac{Z}{n}\right)^3 / j(j+1)(2l+1)$$ QED

This is for a single-e atom, for a state with $l \neq 0$.

Solution to QM Problem (77) 5/22/72

1) It is instructive to do the problem for a one-electron atom; generalization to the many-electron case is stfwd. The magnetic field generated by the electron at the nucleus is due to two sources, namely



$$\vec{H}_e = \vec{H}_L \left(\substack{\text{due to } e's \\ \text{orbital motion}}\right) + \vec{H}_S \left(\substack{\text{due to } e's \\ \text{spin mag. mom.}}\right). \quad (1)$$

The orbital field is stfwdly calculable as

$$\vec{H}_L = \vec{E} \times \frac{\vec{v}}{c} = -\frac{e}{r^3}\,\vec{r} \times \frac{m\vec{v}}{mc} = -(2\mu_0/r^3)\vec{L}, \quad (2)$$

where $\mu_0 = e\hbar/2mc$ is the Bohr magneton (and $\vec{L}$ is a dimensionless orbital ∡ momentum). There is no Thomas precession factor because the rest frame of the nucleus is a proper frame. For the field due to the spin, we take the dipole expression

$$\vec{H}_S = \frac{1}{r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right], \text{ with } \vec{\mu} = -g_s\mu_0\vec{S}. \quad (3)$$

Approximate $g_s = 2$, so that this field is

$$\vec{H}_S = (2\mu_0/r^3)\left[\vec{S} - 3(\vec{S}\cdot\hat{r})\hat{r}\right]. \quad (4)$$

Combining (2) & (4), the net electron field is

$$\vec{H}_e = -(2\mu_0/r^3)\left[(\vec{L}-\vec{S}) + 3(\vec{S}\cdot\hat{r})\hat{r}\right]. \quad (5)$$

We shall need this explicit expression when later we calculate the coupling constant in detail.

2) Whatever $\vec{H}_e$ is, the prescription of the vector model is to take its projection on $\vec{J}$, which is

$$(\vec{H}_e)_{\vec{J}} = (\vec{H}_e \cdot \vec{J})\,\vec{J}/\vec{J}^2. \tag{6}$$

It is this field which interacts with the nuclear moment $\vec{\mu}_n = -g_n \mu_0 \vec{I}$ to produce the hfs Ham$^{\underline{n}}$, which is

$$\left.\begin{aligned} \mathcal{H}_{hfs} &= -\vec{\mu}_n \cdot (\vec{H}_e)_{\vec{J}} = A_{hfs}\,(\vec{I}\cdot\vec{J}), \\ \text{where}: A_{hfs} &= g_n \mu_0\,(\vec{H}_e \cdot \vec{J})/\vec{J}^2. \end{aligned}\right\} \tag{7}$$

The $\vec{I}\cdot\vec{J}$ coupling here is conveniently discussed in terms of a coupled rep$^{\underline{n}}$, where the states are eigenfcns of the total system ∡ momentum $\vec{F} = \vec{I} + \vec{J}$ (more precisely, eigenfcns of $\vec{F}^2$ and F_z). This is the same trick that was used to discuss $\vec{L}\cdot\vec{S}$ coupling -- we constructed eigenfcns of $\vec{J} = \vec{L} + \vec{S}$. W.r.t. these eigenfcns...

$$\vec{I}\cdot\vec{J} = \tfrac{1}{2}\left[\vec{F}^2 - \vec{I}^2 - \vec{J}^2\right];$$

$$\langle \vec{I}\cdot\vec{J} \rangle = \tfrac{1}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]. \tag{8}$$

where F, I, J are the q.#s associated with $\vec{F}, \vec{I}, \vec{J}$. Then the hfs energies w.r.t. these eigenfcns are

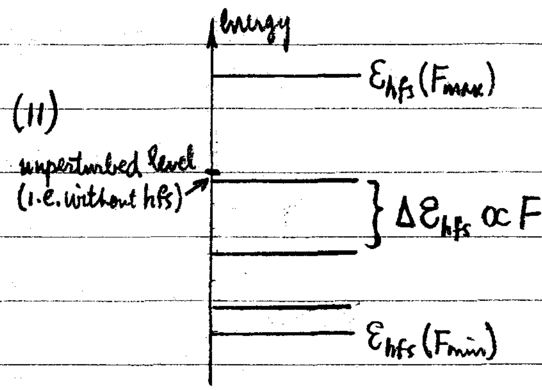
$$\left.\begin{aligned} \mathcal{E}_{hfs}(F) &= \langle \mathcal{H}_{hfs} \rangle = \tfrac{1}{2} A\left[F(F+1) - I(I+1) - J(J+1)\right], \\ \text{where}: A &= \langle A_{hfs} \rangle = g_n \mu_0 \langle \vec{H}_e \cdot \vec{J} \rangle / J(J+1). \end{aligned}\right\} \tag{9}$$

3) Normally (as we shall see) A turns out to be positive; we shall assume this in discussing the energy spectrum of eq.(9). For fixed I & J, there are just $2I+1$ or $2J+1$ values of F (whichever is smaller), and hence just this number of $\mathcal{E}_{hfs}(F)$ levels. For convenience, assume $J \geqslant I$. Then F ranges from $F_{max} = J+I$ to $F_{min} = J-I$, so that there are $2I+1$ levels $\mathcal{E}_{hfs}(F)$, which range over

$$\mathcal{E}_{hfs}(F_{max}) = +AJI \quad \text{to} \quad \mathcal{E}_{hfs}(F_{min}) = -A(J+1)I. \tag{10}$$

The spacing between adjacent levels is

$$\Delta\mathcal{E}_{hfs}(F) = \mathcal{E}_{hfs}(F) - \mathcal{E}_{hfs}(F-1) = AF, \tag{11}$$



a result which is known as the Lande interval rule. The energy spectrum is as indicated at right. In an external magnetic field, each level F splits into 2F+1 sublevels (i.e. the m_F states), which go linearly with the field -- this is known as the hfs Zeeman effect.

4) To calculate the coupling cnst $A = \langle A_{hfs} \rangle$, we must evaluate $\langle \vec{H}_e \cdot \vec{J} \rangle$ from eq. (9). To this end, we note that with $\vec{J} = \vec{L} + \vec{S}$

$$\vec{H}_e \cdot \vec{J} = -(2\mu_0/r^3)\left[(\vec{L}^2 - \vec{S}^2) + 3(\vec{S}\cdot\hat{r})^2\right]. \tag{12}$$

Here we have taken advantage of the fact that since $\vec{L}$ & $\vec{r}$ are $\perp$, $\vec{L}\cdot\hat{r} \equiv 0$ (this can also be shewn rigourously in a QM exp. value sense). Now in the coupled repⁿ we are using, the $\vec{J}$ eigenfcns which appear are in fact eigenfcns of $\vec{L}^2$ & $\vec{S}^2$ (they are $|L,S,J,m_J\rangle$ eigenfcns), hence $\langle \vec{L}^2 \rangle = L(L+1)$ and $\langle \vec{S}^2 \rangle = S(S+1)$ in eq. (12). Also, it may be shewn (e.g. problem 76) that $\langle (\vec{S}\cdot\hat{r})^2 \rangle = 1/4$*, for spin $S = 1/2$.

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* This may be shewn most easily by use of the "Dirac Identity", i.e.

$$(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\vec{\sigma}\cdot(\vec{A}\times\vec{B})$$

which may be proved stfwdly. Here $\vec{A}$ & $\vec{B}$ are any two QM vectors which commute with $\vec{\sigma}$, the Pauli matrices for spin 1/2. With $\vec{\sigma} = 2\vec{S}$, and the choice $\vec{A} = \vec{B} = \hat{r}$, this immediately gives $(\vec{S}\cdot\hat{r})^2 = 1/4$.

Then $-\vec{S}^2 + 3(\vec{S}\cdot\hat{r})^2 = 0$ for spin 1/2, so eq (12) gives

$$\langle \vec{H}_e \cdot \vec{J} \rangle = -2\mu_0 \left\langle \frac{1}{r^3} \right\rangle L(L+1). \tag{13}$$

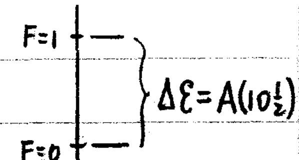
But $\langle 1/r^3 \rangle = (Z/na_0)^3 / L(L+1)(L+\frac{1}{2})$ for $L \neq 0$ states of a one-electron atom. Using this in eq. (13), and the resulting expression for A of eq. (9), we find

$$A = \langle A_{hfs} \rangle = -2 g_n \mu_0^2 \left(\frac{Z}{na_0}\right)^3 / J(J+1)(L+\tfrac{1}{2}). \tag{14}$$

Note that the $L(L+1)$ factor has fortuitously cancelled, and that A is finite for S-states (i.e. for $L=0$). In fact it turns out that a rigorous calculation for S-states produces just the value of A in eq. (14) (with $L=0$ and $J=\frac{1}{2}$ of course), so that this expression may be used for <u>all</u> states of a one-electron atom†. Now the nuclear g-value is usually (−) ve, so write $g_n = -|g_n|$, and note that $\mu_0^2/a_0^3 = \frac{1}{4}\alpha^4 mc^2$. Then eqtn (14) becomes

$$A(nLJ) = +|g_n|\,\alpha^4 mc^2 (Z/n)^3 / (2L+1)J(J+1), \tag{15}$$

which is the final desired form of the hfs coupling cnst for a single-electron atom.



As an application of eqtn (15), we note that for the $1S_{1/2}$ gnd state of atomic hydrogen ($Z=1$, $n=1$, $L=0$ and $J=\frac{1}{2}$), $A(10\frac{1}{2}) = \frac{4}{3}|g_p|\alpha^4 mc^2$, where g_p is the proton g-value. With proton spin $I=\frac{1}{2}$, the state splits as shown, with a predicted hfs of $\Delta\mathcal{E} = A(10\frac{1}{2})$. In frequency units, $\Delta\nu = \Delta\mathcal{E}/h = 1420$ Mc, which is the famous 21 cm line of radio-astronomy.

† This point is discussed by N.F. Ramsey in "Molecular Beams" (Oxford, 1963), pp. 72-76. Also see Ramsey's "Nuclear Moments" (Wiley, 1953), pp. 9-16.