5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
5.80 Small-Molecule Spectroscopy and Dynamics
Fall, 2008

Problem Set #2 ANSWERS

Reading Assignment: Bernath, Chapter 5

The following handouts also contain useful information:

C & S, page 117, radial expectation values of r^k for 1-e^- atoms
$LS \rightarrow (j,j')_J$ Coupling Patterns
Herzberg pp. 177-181, The Interval Rule: Analysis of Multiplets

Problems 1-4 deal with material from my 2/11/94 lecture (Lecture 7). A lot of background material is provided. These problems illustrate non-text material dealing with 2×2 secular equations, perturbation theory, transition probabilities, quantum mechanical interference effects, and atomic **L**-**S**-**J** vs. $j_1 - j_2 - \mathbf{J}$ limiting cases. C & S references are to Condon and Shortley "The Theory of Atomic Spectra.' Problems 5-9 are standard textbook problems, more basic, and much easier than 1-4 and 10.

BACKGROUND MATERIAL FOR PROBLEMS 1-4

(i) Transition Amplitudes for $np^2 \leftarrow np\ n's$ Transitions in the **L**-**S**-**J** Limit

$$\mu \equiv -e3^{-1/2}\int_0^\infty R_{np}\quad r\quad R_{n's}dr \qquad \text{C\&S, p. 245.}$$

C&S, p. 247 gives all nonzero transition amplitudes:

$$\left\langle p^2\,{}^1S|\mu|sp\ {}^1P_1\right\rangle = -(20)^{1/2}\mu$$
$$\left\langle p^2\,{}^1D|\mu|sp\ {}^1P_1\right\rangle = +10\mu$$
$$\left\langle p^2\,{}^3P_0|\mu|sp\ {}^3P_1\right\rangle = -(20)^{1/2}\mu$$
$$\left\langle p^2\,{}^3P_1|\mu|sp\ {}^3P_0\right\rangle = -(20)^{1/2}\mu$$
$$\left\langle p^2\,{}^3P_1|\mu|sp\ {}^3P_1\right\rangle = +(15)^{1/2}\mu$$
$$\left\langle p^2\,{}^3P_1|\mu|sp\ {}^3P_2\right\rangle = -5\mu$$
$$\left\langle p^2\,{}^3P_2|\mu|sp\ {}^3P_1\right\rangle = -5\mu$$
$$\left\langle p^2\,{}^3P_2|\mu|sp\ {}^3P_2\right\rangle = +(75)^{1/2}\mu.$$

All other transition amplitudes are zero, most notably:

$$\left\langle p^2\,{}^3P_0|\mu|sp\ {}^3P_0\right\rangle = 0$$

because there is no way to add one unit of photon angular momentum to an initial state with J = 0 to make a final state with J = 0.

(ii) Energy levels for np^2 and np n′s in the L–S–J Basis Set

In the L–S–J limit, for p^2 (see C&S, pp. 198, 268):

$$\mathbf{H}^{ee} = \begin{array}{c|ccccc} & {}^1S_0 & {}^3P_0 & {}^3P_1 & {}^3P_2 & {}^1D_2 \\ \hline {}^1S_0 & F_0+10F_2 & & & & \\ {}^3P_0 & & F_0-5F_2 & & & \\ {}^3P_1 & & & F_0-5F_2 & & \\ {}^3P_2 & & & & F_0-5F_2 & \\ {}^1D_2 & & & & & F_0+F_2 \end{array}$$

$$\mathbf{H}^{SO} = \begin{array}{c|ccccc} & {}^1S_0 & {}^3P_0 & {}^3P_1 & {}^3P_2 & {}^1D_2 \\ \hline {}^1S_0 & 0 & -2^{1/2}\zeta & & & \\ {}^3P_0 & -2^{1/2}\zeta & -\zeta & & & \\ {}^3P_1 & & & -\tfrac{1}{2}\zeta & & \\ {}^3P_2 & & & & \tfrac{1}{2}\zeta & 2^{-1/2}\zeta \\ {}^1D_2 & & & & 2^{1/2}\zeta & 0 \end{array}$$

So we have three effective Hamiltonians for $(np)^2$

$$\mathbf{H}(0) = \begin{vmatrix} F_0+10F_2 & -2^{+1/2}\zeta \\ -2^{+1/2}\zeta & F_0-5F_2-\zeta \end{vmatrix} = F_0 + \frac{5}{2}F_2 - \frac{1}{2}\zeta + \begin{vmatrix} \Delta_0 & V_0 \\ V_0 & -\Delta_0 \end{vmatrix}$$

$$\Delta_0 = \frac{15}{2}F_2 + \frac{1}{2}\zeta \qquad V_0 = -2^{+1/2}\zeta$$

$$\mathbf{H}(1) = F_0 - 5F_2 - \frac{1}{2}\zeta$$

$$\mathbf{H}(2) = \begin{vmatrix} F_0-5F_2+\zeta/2 & 2^{-1/2}\zeta \\ 2^{-1/2}\zeta & F_0+F_2 \end{vmatrix} = F_0 - 2F_2 + \frac{1}{4}\zeta + \begin{vmatrix} -\Delta_2 & V_2 \\ V_2 & +\Delta_2 \end{vmatrix}$$

$$\Delta_2 = 3F_2 - \frac{1}{4}\zeta \qquad V_0 = -2^{-1/2}\zeta$$

Similarly, for the sp configuration:

$$\mathbf{H} = \begin{array}{c|ccc} & {}^3P_2 & {}^3P_1 & {}^1P_0 \\ \hline {}^3P_2 & F_0-G_1+\frac{1}{2}\zeta & & \\ {}^3P_1 & & F_0-G_1-\frac{1}{2}\zeta & 2^{-1/2}\zeta \\ {}^1P_0 & & 2^{-1/2}\zeta & F_0+G_1 \\ {}^3P_0 & & & \end{array} \qquad \begin{array}{c} \\ \\ \\ F_0-G_1-\zeta \end{array}$$

and there are three effective Hamiltonians for (n′s)(np)

$$\mathbf{H}(0) = F_0 - G_1 - \zeta$$

$$\mathbf{H}(1) = F_0 - \frac{1}{4}\zeta + \begin{vmatrix} -\Delta_1 & V_1 \\ V_1 & \Delta_1 \end{vmatrix} \qquad \Delta_1 = G_1 + \frac{1}{4}\zeta \qquad V_1 = 2^{-1/2}\zeta$$

$$\mathbf{H}(2) = F_0 - G_1 + \frac{1}{2}\zeta$$

(iii) Now we are ready to discuss the energy level diagram and relative intensities of all spectral lines for transitions between $(np)^2 \leftarrow (n's)(np)$ configurations. The relevant parameters are:

$F_0(np,np) - F_0(n's,np) \equiv \Delta F_0$	(difference in repulsion energy for np by np vs. np by n′s; $\Delta F_0 > 0$ if n′ = n)
$\zeta(np)$	(spin-orbit parameter for np; same for both configurations), $\zeta > 0$ by definition
$F_2(np, np)$	(quadrupolar repulsion between two np electrons) $F_2 > 0$.
$G^1(n's, np)$	(exchange integral) $G_1 > 0$.
μ	(np ← n′s transition moment integral)

All spectral line frequencies and intensities may be derived from these 5 fundamental electronic constants. Note that there are 5 L–S–J terms in np^2 and 4 L–S–J terms in np n′s, in principle giving rise to a "transition array" consisting of 5×4 transitions. The 5 parameters determine 20 frequencies and 20 intensities! We are not limited to the L–S–J or the $j_1 - j_2 - J$ limit.

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1. Construct level diagrams for the p^2 and sp configurations at the L–S–J limit ($\zeta = 0$), the j–j limit ($F_2 = 0$ for p^2, $G_1 = 0$ for sp), and at several intermediate values of ζ/F_2 or ζ/G_1. This sort of diagram is called a "correlation diagram". For graphical purposes it is convenient to keep constant the quantity, which determines the splitting between highest and lowest levels of p^2,

$$\frac{225}{4}F_2^2 + \frac{15}{2}F_2\zeta + \frac{9}{4}\zeta^2 \equiv \Delta E\left(p^2\right),$$

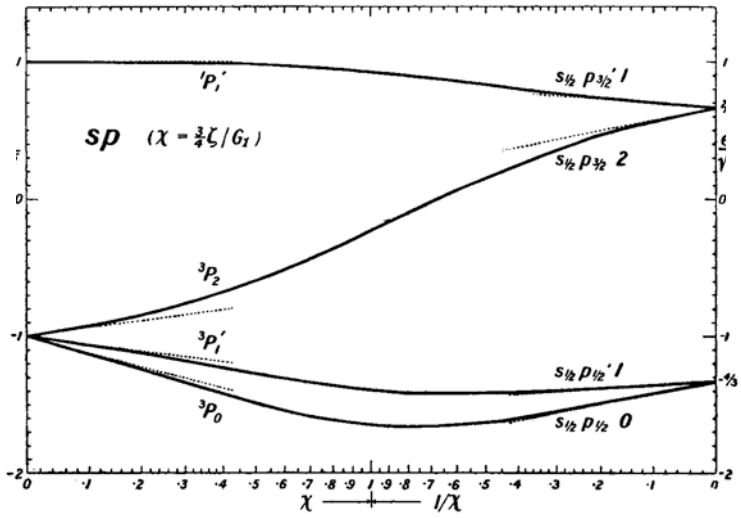
and a similar quantity for sp,

$$G_1^2 + \frac{9}{16}\zeta^2 + \frac{1}{2}G_1\zeta \equiv \Delta E(sp).$$

Correlation diagrams for sp and p^2 configurations can be found on pages 272 and 275 of Condon and Shortley.

For sp, $\chi = \dfrac{3\zeta}{4G_1}$

$\dfrac{\varepsilon / G_1}{\left[1+\chi^2\right]^{1/2}}$

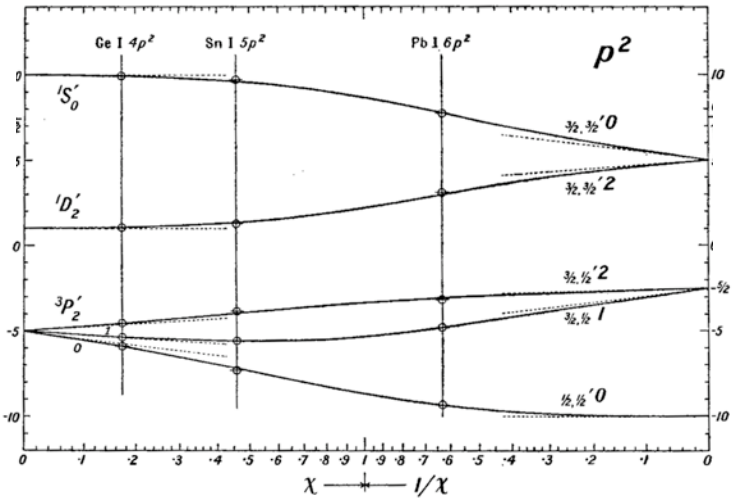


$\dfrac{\varepsilon \Big/ \left(\dfrac{3\zeta}{4}\right)}{\left[1+(1/\chi)^2\right]^{1/2}}$

Fig. 1[11]. The configuration $s\,p$ in intermediate coupling.

For p^2, $\chi = \dfrac{\zeta}{5F_2}$

$\dfrac{\varepsilon / F_2}{\left[1+\chi^2\right]^{1/2}}$



$\dfrac{\varepsilon \Big/ \left(\dfrac{\zeta}{3}\right)}{\left[1+(1/\chi)^2\right]^{1/2}}$

Fig. 4[11]. The configuration p^2 in intermediate coupling. ($\chi = \frac{1}{5}\zeta/F_2$.)

2. Use the first order non-degenerate perturbation theory correction to the *wavefunctions* to compute the intensities for $p^2 \leftarrow sp$ transitions near the L–S–J limit ($\zeta \ll F_2$ for p^2, $\zeta \ll G_1$ for sp). For example, the "nominal" sp $^1P_1$ level becomes

$$\left|\text{`sp }^1P_1\text{'}\right\rangle = \left|\text{sp }^1P_1\right\rangle + \frac{\mathbf{H}_{^1P_1\,^3P_1}}{E^0_{^1P_1} - E^0_{^3P_1}}\left|\text{sp }^3P_1\right\rangle = \left|\text{sp }^1P_1\right\rangle + \frac{2^{-1/2}\zeta}{2G_1 + \frac{1}{2}\zeta}\left|\text{sp }^3P_1\right\rangle.$$

The transition probability is the square of the transition amplitude, so the "nominally forbidden" transition $p^2\ ^3P_1 \leftarrow sp\ ^1P_1$ has a transition probability

$$P\left({}^3P_1 \leftarrow {}^1P_1\right) = \left|\left\langle \text{`sp } {}^1P_1\text{'} \middle| \mu \middle| \text{`p}^2 \ {}^3P_1\text{'} \right\rangle\right|^2 = \frac{2\zeta^2}{\left(2G_1 + \frac{1}{2}\zeta\right)^2}\mu^2(15).$$

Note that, for the transitions between either of the two sp J = 1 levels and either of the two p^2 J = 2 or J = 0 levels, the transition probability includes two amplitudes which must be summed before squaring. This gives rise to quantum mechanical interference effects. In fact, it is because of these interference effects that the j–j limit $(3/2, 3/2)_2 \leftarrow (1/2, 1/2)_1$ and $(1/2, 1/2)_0 \leftarrow (1/2, 1/2)_1$ transitions become rigorously forbidden.

ψ's corrected to 1st order

p^2:

$$\left|\text{`}{}^1D_2\text{'}\right\rangle = \left|{}^1D_2\right\rangle + \frac{2^{-1/2}\zeta}{6F_2 - \frac{1}{2}\zeta}\left|{}^3P_2\right\rangle$$

$$\left|\text{`}{}^3P_2\text{'}\right\rangle = \left|{}^3P_2\right\rangle - \frac{2^{-1/2}\zeta}{6F_2 - \frac{1}{2}\zeta}\left|{}^1D_2\right\rangle$$

$$\left|\text{`}{}^3P_1\text{'}\right\rangle = \left|{}^3P_1\right\rangle$$

$$\left|\text{`}{}^3P_0\text{'}\right\rangle = \left|{}^3P_0\right\rangle + \frac{\sqrt{2}\zeta}{15F_2 + \zeta}\left|{}^1S_0\right\rangle$$

$$\left|\text{`}{}^1S_0\text{'}\right\rangle = \left|{}^1S_0\right\rangle - \frac{\sqrt{2}\zeta}{15F_2 + \zeta}\left|{}^3P_0\right\rangle$$

sp:

$$\left|\text{`}{}^3P_2\text{'}\right\rangle = \left|{}^3P_2\right\rangle$$

$$\left|\text{`}{}^3P_1\text{'}\right\rangle = \left|{}^3P_1\right\rangle - \frac{2^{-1/2}\zeta}{2G_1 + \frac{1}{2}\zeta}\left|{}^1P_1\right\rangle$$

$$\left|\text{`}{}^1P_1\text{'}\right\rangle = \left|{}^1P_1\right\rangle + \frac{2^{-1/2}\zeta}{2G_1 + \frac{1}{2}\zeta}\left|{}^3P_1\right\rangle$$

$$\left|\text{`}{}^3P_0\text{'}\right\rangle = \left|{}^3P_0\right\rangle$$

Calculate intensities of selected 'forbidden' transitions:

0

$$\left\langle {}^{1}\mathrm{D}_2 \right| \mu \left| {}^{3}\mathrm{P}_1 \right\rangle = \cancel{\left\langle {}^{1}\mathrm{D}_2 \right| \mu \left| {}^{3}\mathrm{P}_1 \right\rangle} - \frac{2^{-1/2}\zeta}{2\mathrm{G}_1 + \frac{1}{2}\zeta} \left\langle {}^{1}\mathrm{D}_2 \right| \mu \left| {}^{3}\mathrm{P}_1 \right\rangle$$

$$- \frac{2^{-1/2}\zeta}{\frac{1}{2}\zeta - 6\mathrm{F}_2} \cancel{\left\langle {}^{3}\mathrm{P}_2 \right| \mu \left| {}^{3}\mathrm{P}_1 \right\rangle}^{0} + \frac{\zeta^2 \cancel{\left\langle {}^{3}\mathrm{P}_2 \right| \mu \left| {}^{1}\mathrm{P}_1 \right\rangle}^{0}}{\left(4\mathrm{G}_1 + \zeta\right)\left(\frac{1}{2}\zeta - 6\mathrm{F}_2\right)}$$

$$= -2^{-1/2}\zeta \left[\frac{10\mu}{2\mathrm{G}_1 + \frac{1}{2}\zeta} + \frac{-5\mu}{-6\mathrm{F}_2 + \frac{1}{2}\zeta} \right]$$

3. Condon and Shortley (p. 294) give the transformations from the L–S–J to the $j_1 - j_2 - J$ basis set. These transformed functions correspond to the functions that diagonalize $\mathbf{H}^{SO}$.

p^2

$$\left(\frac{3}{2}\,\frac{3}{2}\right)_2 = \left(\frac{2}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_2 \right\rangle + \left(\frac{1}{3}\right)^{1/2} \left| {}^{1}\mathrm{D}_2 \right\rangle$$

$$\left(\frac{3}{2}\,\frac{1}{2}\right)_2 = \left(\frac{1}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_2 \right\rangle - \left(\frac{2}{3}\right)^{1/2} \left| {}^{1}\mathrm{D}_2 \right\rangle$$

$$\left(\frac{3}{2}\,\frac{1}{2}\right)_2 = \left| {}^{3}\mathrm{P}_1 \right\rangle$$

$$\left(\frac{3}{2}\,\frac{3}{2}\right)_0 = \left(\frac{2}{3}\right)^{1/2} \left| {}^{1}\mathrm{S}_0 \right\rangle - \left(\frac{1}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_0 \right\rangle$$

$$\left(\frac{1}{2}\,\frac{1}{2}\right)_0 = \left(\frac{1}{3}\right)^{1/2} \left| {}^{1}\mathrm{S}_0 \right\rangle + \left(\frac{2}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_0 \right\rangle$$

sp

$$\left(\frac{1}{2}\,\frac{3}{2}\right)_2 = \left| {}^{3}\mathrm{P}_2 \right\rangle$$

$$\left(\frac{1}{2}\,\frac{3}{2}\right)_1 = \left(\frac{2}{3}\right)^{1/2} \left| {}^{1}\mathrm{P}_1 \right\rangle + \left(\frac{1}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_1 \right\rangle$$

$$\left(\frac{1}{2}\,\frac{1}{2}\right)_1 = \left(\frac{1}{3}\right)^{1/2} \left| {}^{1}\mathrm{P}_1 \right\rangle - \left(\frac{2}{3}\right)^{1/2} \left| {}^{3}\mathrm{P}_1 \right\rangle$$

$$\left(\frac{1}{2}\,\frac{1}{2}\right)_0 = \left| {}^{3}\mathrm{P}_0 \right\rangle$$

Construct the new p^2 **H**(0), **H**(1), **H**(2) and sp **H**(0), **H**(1), **H**(2) matrices in the j–j basis using the above transformations.

The p^2 and sp **H**(J) matrices are easily found in the $\mathbf{j}_1 - \mathbf{j}_2 - \mathbf{J}$ basis by determining the unitary transforms which transform the $\mathbf{j}_1 - \mathbf{j}_2 - \mathbf{J}$ basis functions into $\mathbf{L} - \mathbf{S} - \mathbf{J}$ basis functions and using the fact that:

$$\widetilde{\mathbf{H}} = \mathrm{U}^{\dagger}\mathbf{H}\mathrm{U}$$

p^2, J = 0 : $\mathbf{U}\vec{x} = \vec{x}'$

$$\begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \rightarrow \begin{matrix} \left| {}^1S_0 \right\rangle \\ \left| {}^3P_0 \right\rangle \end{matrix} \qquad \mathbf{U}^\dagger = \left(\mathbf{U}^*\right)^T$$

$$\uparrow \mathbf{U} \qquad \uparrow \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \end{pmatrix}_0 \quad \begin{pmatrix} \frac{3}{2} & \frac{3}{2} \end{pmatrix}_0$$

$$\mathbf{U}^\dagger = \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{bmatrix}$$

$$\mathbf{U}^\dagger\mathbf{H}\mathbf{U} = \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{bmatrix} \begin{bmatrix} \mathbf{H}_{11} & \mathbf{H}_{12} \\ \mathbf{H}_{12} & \mathbf{H}_{22} \end{bmatrix} \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{bmatrix}$$

$$= \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{bmatrix} \begin{bmatrix} \sqrt{\frac{1}{3}}\mathbf{H}_{11} + \sqrt{\frac{2}{3}}\mathbf{H}_{12}, & \sqrt{\frac{2}{3}}\mathbf{H}_{11} - \sqrt{\frac{1}{3}}\mathbf{H}_{12} \\ \sqrt{\frac{1}{3}}\mathbf{H}_{12} + \sqrt{\frac{2}{3}}\mathbf{H}_{22}, & \sqrt{\frac{2}{3}}\mathbf{H}_{12} - \sqrt{\frac{2}{3}}\mathbf{H}_{12} \end{bmatrix}$$

$$= \begin{bmatrix} \frac{1}{3}\mathbf{H}_{11} + \frac{2}{3}\mathbf{H}_{22} + \frac{2\sqrt{2}}{3}\mathbf{H}_{12} & \frac{\sqrt{2}}{3}\left(\mathbf{H}_{11} - \mathbf{H}_{22}\right) + \frac{1}{3}\mathbf{H}_{12} \\ \frac{\sqrt{2}}{3}\left(\mathbf{H}_{11} - \mathbf{H}_{22}\right) - \frac{1}{3}\mathbf{H}_{12} & \frac{2}{3}\mathbf{H}_{11} + \frac{1}{3}\mathbf{H}_{22} - \frac{2\sqrt{2}}{3}\mathbf{H}_{12} \end{bmatrix}$$

$\mathrm{Tr}\left(\widetilde{\mathbf{H}}\right) = \mathrm{Tr}\left(\mathbf{H}\right) = \mathbf{H}_{11} + \mathbf{H}_{22}$ checks ✔

$$\left|\left\langle p^2\,{}^1D_2' \middle| \mu \middle| sp\,{}^3P_1' \right\rangle\right|^2 = \frac{\zeta^2}{2}\left[\frac{10}{2G_1 + \frac{1}{2}\zeta} + \frac{5}{6F_2 - \frac{1}{2}\zeta}\right]^2 \mu^2$$

$G_1, F_2 \gg \zeta$ in $\mathbf{L-S-J}$ limit

$$\left\langle \text{`}p^2\text{' `}{}^1S_0\text{'} \middle| \mu \middle| sp\text{`}{}^3P_1\text{'} \right\rangle = \cancelto{0}{\left\langle {}^1S_0 \middle| \mu \middle| {}^3P_1 \right\rangle} - \frac{\sqrt{2}\zeta}{15F_2 - \zeta} \cancelto{0}{\left\langle {}^3P_0 \middle| \mu \middle| {}^3P_1 \right\rangle}$$

$$- \frac{2^{-1/2}\zeta}{2G_1 + \frac{1}{2}\zeta} \left\langle {}^1S_0 \middle| \mu \middle| {}^1P_1 \right\rangle + 0\left(\frac{\zeta^2}{F_2 G_1}\right) \left\langle {}^3P_0 \middle| \mu \middle| {}^3P_1 \right\rangle$$

$$= -\frac{\sqrt{2}\zeta}{15F_2 - \zeta}\left(-\sqrt{20}\mu\right) - \frac{2^{-1/2}\zeta}{2G_1 + \frac{1}{2}\zeta}\left(-\sqrt{20}\mu\right)$$

$$\left| \left\langle p^2\text{`}{}^1S_0\text{'} \middle| \mu \middle| sp\text{`}{}^3P_1\text{'} \right\rangle \right|^2 = 40\mu^2\zeta^2 \left[\frac{1}{15F_2 - \zeta} + \frac{1}{4G_1 + \zeta}\right]^2$$

$\mathbf{L-S-J}$ coupling $\quad F_2, G_1 \gg \zeta$

ζ can be neglected in the denominator

$$\widetilde{\mathbf{H}}(1) = \frac{1}{3}\begin{bmatrix} \mathbf{H}_{11} + 2\mathbf{H}_{22} + 2\sqrt{2}\mathbf{H}_{12} & -\mathbf{H}_{12} + \sqrt{2}\left(\mathbf{H}_{22} - \mathbf{H}_{11}\right) \\ -\mathbf{H}_{12} + \sqrt{2}\left(\mathbf{H}_{22} - \mathbf{H}_{11}\right) & 2\mathbf{H}_{11} + \mathbf{H}_{22} - 2\sqrt{2}\mathbf{H}_{12} \end{bmatrix}$$

$$\mathbf{H}'_{11} = \frac{1}{3}\left[F_0 - G_1 - \frac{1}{2}\zeta + 2\left(F_0 + G_1\right) + 2\sqrt{2}\left(\frac{1}{\sqrt{2}}\zeta\right)\right]$$

$$= F_0 + \frac{1}{3}G_1 + \frac{1}{2}\zeta \qquad \leftarrow \left(\frac{3}{2}\,\frac{3}{2}\right)_1$$

$$\mathbf{H}'_{12} = -\frac{1}{\sqrt{2}}\zeta + \sqrt{2}\left[F_0 + G_1 - \left(F_0 - G_1 - \frac{1}{2}\zeta\right)\right]$$

$$= 2\sqrt{2}G_1$$

$$\mathbf{H}'_{22} = \frac{1}{3}\left[2\left(F_0 - G_1 - \frac{1}{2}\zeta\right) + \left(F_0 + G_1\right) - 2\sqrt{2}\left(\frac{1}{\sqrt{2}}\zeta\right)\right]$$

$$= F_0 - \frac{1}{3}G_1 - \zeta \qquad \leftarrow \left(\frac{1}{2}\,\frac{1}{2}\right)_1$$

$$\widetilde{\mathbf{H}}(1) = \begin{bmatrix} F_0 + \frac{1}{3}G_1 + \frac{1}{2}\zeta & 2\sqrt{2}G_1 \\ 2\sqrt{2}G_1 & F_0 - \frac{1}{3}G_1 - \zeta \end{bmatrix}$$

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J = 2, sp

U = 1

$$\widetilde{\mathbf{H}}(2) = F_0 - G_1 + \frac{1}{2}\zeta \qquad \leftarrow \left(\frac{3}{2}\frac{1}{2}\right)_2$$

Most of the work done on the last four pages can also be found in the notes for Lecture #7.

$$\mathbf{H}_{11} = F_0 + 10F_2$$

$$\mathbf{H}_{12} = -\sqrt{2}\zeta$$

$$\mathbf{H}_{22} = F_0 - 5F_2 - \zeta$$

$$\mathbf{H}'_{11} = \frac{1}{3}\left(F_0 + 10F_2\right) + \frac{2}{3}\left(F_0 - 5F_2 - \zeta\right) + \frac{2}{3}\sqrt{2}\left(-\sqrt{2}\zeta\right)$$

$$= F_0 - 2\zeta \qquad \leftarrow \left(\frac{1}{2}\frac{1}{2}\right)_0$$

$$\mathbf{H}'_{12} = \frac{\sqrt{2}}{3}\left(15F_2 + \zeta\right) + \frac{1}{3}\left(-\sqrt{2}\zeta\right) = 5\sqrt{2}F_2$$

$$\mathbf{H}'_{22} = \frac{2}{3}\left(F_0 + 10F_2\right) + \frac{1}{3}\left(F_0 - 5F_2 - \zeta\right) - \frac{2}{3}\sqrt{2}\left(-\sqrt{2}\zeta\right)$$

$$= F_0 + 5F_2 + \zeta \qquad \leftarrow \left(\frac{3}{2}\frac{3}{2}\right)_0$$

$$\widetilde{\mathbf{H}}(0) = \begin{bmatrix} F_0 - 2\zeta & 5\sqrt{2}F_2 \\ 5\sqrt{2}F_2 & F_0 + 5F_2 + \zeta \end{bmatrix}$$

p^2, J = 1
U = 1

$$\widetilde{\mathbf{H}}(1) = F_0 - 5F_2 - \frac{1}{2}\zeta \qquad \leftarrow \left(\frac{3}{2}\frac{1}{2}\right)_1$$

p^2, J = 2

$$\begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ -\sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} \end{bmatrix} \begin{bmatrix} a\left(\frac{3}{2}\frac{1}{2}\right)_2 \\ b\left(\frac{3}{2}\frac{3}{2}\right)_2 \end{bmatrix} = \begin{bmatrix} \alpha \left| {}^3P_2 \right\rangle \\ \beta \left| {}^1D_2 \right\rangle \end{bmatrix}$$

$\uparrow \mathbf{U} \qquad \vec{x} \qquad \vec{x}\,'$

$$\mathbf{U}^{\dagger} = \begin{bmatrix} \sqrt{\frac{1}{3}} & -\sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} \end{bmatrix} = \frac{1}{3}\begin{bmatrix} 1 & -\sqrt{2} \\ \sqrt{2} & 1 \end{bmatrix}$$

$$\widetilde{\mathbf{H}} = \frac{1}{3}\begin{bmatrix} 1 & -\sqrt{2} \\ \sqrt{2} & 1 \end{bmatrix}\begin{bmatrix} \mathbf{H}_{11} & \mathbf{H}_{12} \\ \mathbf{H}_{12} & \mathbf{H}_{22} \end{bmatrix}\begin{bmatrix} 1 & \sqrt{2} \\ -\sqrt{2} & 1 \end{bmatrix} = \frac{1}{3}\begin{bmatrix} 1 & -\sqrt{2} \\ \sqrt{2} & 1 \end{bmatrix}\begin{bmatrix} \mathbf{H}_{11} - \sqrt{2}\mathbf{H}_{12} & \sqrt{2}\mathbf{H}_{11} + \mathbf{H}_{12} \\ \mathbf{H}_{12} - \sqrt{2}\mathbf{H}_{22} & \sqrt{2}\mathbf{H}_{12} + \mathbf{H}_{22} \end{bmatrix}$$

$$= \frac{1}{3}\begin{bmatrix} \mathbf{H}_{11} + 2\mathbf{H}_{22} - 2\sqrt{2}\mathbf{H}_{12} & \sqrt{2}\left(\mathbf{H}_{11} - \mathbf{H}_{22}\right) - \mathbf{H}_{12} \\ \sqrt{2}\left(\mathbf{H}_{11} - \mathbf{H}_{22}\right) - \mathbf{H}_{12} & 2\mathbf{H}_{11} + \mathbf{H}_{22} + 2\sqrt{2}\mathbf{H}_{12} \end{bmatrix}$$

$$\mathbf{H}'_{11} = \frac{1}{3}\left[\mathrm{F}_0 - 5\mathrm{F}_2 + \frac{1}{2}\zeta + 2\left(\mathrm{F}_0 + \mathrm{F}_2\right) - 2\sqrt{2}\left(\frac{\zeta}{\sqrt{2}}\right)\right]$$

$$= \mathrm{F}_0 - \mathrm{F}_2 - \frac{1}{2}\zeta \qquad \leftarrow \left(\frac{3}{2}\frac{1}{2}\right)_2$$

$$\mathbf{H}'_{12} = \frac{1}{3}\left[\sqrt{2}\left(-6\mathrm{F}_2 + \frac{1}{2}\zeta\right) - \frac{1}{\sqrt{2}}\zeta\right] = -2\sqrt{2}\mathrm{F}_2$$

$$\mathbf{H}'_{22} = \frac{1}{3}\left[2\left(\mathrm{F}_0 - 5\mathrm{F}_2 + \frac{1}{2}\zeta\right) + \left(\mathrm{F}_0 + \mathrm{F}_2\right) + 2\sqrt{2}\left(\frac{1}{\sqrt{2}}\zeta\right)\right]$$

$$= \mathrm{F}_0 - 3\mathrm{F}_2 + \zeta \qquad \leftarrow \left(\frac{3}{2}\frac{3}{2}\right)_2$$

$$\widetilde{\mathbf{H}}\left(\mathrm{J}=2\right) = \begin{bmatrix} \mathrm{F}_0 - \mathrm{F}_2 - \frac{1}{2}\zeta & -2\sqrt{2}\mathrm{F}_2 \\ -2\sqrt{2}\mathrm{F}_2 & \mathrm{F}_0 - 3\mathrm{F}_2 + \zeta \end{bmatrix}$$

sp configuration

J = 0 , U = 1

$$\widetilde{\mathbf{H}}(0) = \mathrm{F}_0 - \mathrm{G}_1 - \zeta$$

J = 1, $\mathbf{U} = \begin{bmatrix} \sqrt{\frac{1}{3}} & -\sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} \end{bmatrix}$ $\left(\frac{3}{2}\frac{1}{2}\right)_1$ $\left(\frac{1}{2}\frac{1}{2}\right)_1$

$\left|{}^3\mathrm{P}_1\right\rangle$

$\left|{}^1\mathrm{P}_1\right\rangle$

$$\widetilde{\mathbf{H}}(1)=\frac{1}{3}\begin{bmatrix}1 & \sqrt{2}\\ -\sqrt{2} & 1\end{bmatrix}\begin{bmatrix}\mathbf{H}_{11} & \mathbf{H}_{12}\\ \mathbf{H}_{12} & \mathbf{H}_{22}\end{bmatrix}\begin{bmatrix}1 & -\sqrt{2}\\ \sqrt{2} & 1\end{bmatrix}$$

4. Use perturbation theory as in Problem 2 to compute the transition intensities near the j–j limit ($F_2 \ll \zeta$ or $G_1 \ll \zeta$). You should discover that destructive interference starts to turn off the transitions that will become the forbidden $^3P_2 \leftarrow {}^1P_1$ and $^3P_0 \leftarrow {}^1P_1$ transitions in the L–S–J limit.

Transition amplitudes in the j – j basis [units of μ].
See also C + S, p. 265

sp \ p^2	$\left(\frac{1}{2}\frac{1}{2}\right)_0$	$\left(\frac{3}{2}\frac{3}{2}\right)_0$	$\left(\frac{3}{2}\frac{1}{2}\right)_1$	$\left(\frac{3}{2}\frac{1}{2}\right)_2$	$\left(\frac{3}{2}\frac{3}{2}\right)_2$
$\left(\frac{3}{2}\frac{1}{2}\right)_2$	0	0	-5	5	$\sqrt{50}$
$\left(\frac{3}{2}\frac{1}{2}\right)_1$	0	$-\sqrt{20}$	$-\sqrt{5}$	-5	$\sqrt{50}$
$\left(\frac{1}{2}\frac{1}{2}\right)_1$	$-\sqrt{20}$	0	$\sqrt{10}$	$-\sqrt{50}$	0
$\left(\frac{1}{2}\frac{1}{2}\right)_0$	0	0	$\sqrt{20}$	0	0

Perturbed j – j basis functions (use result of Problem Set 2, #3).

p^2

$$\left(\frac{1}{2}\frac{1}{2}\right)_0' = \left(\frac{1}{2}\frac{1}{2}\right)_0 - \frac{5\sqrt{2}F_2}{5F_2-3\zeta}\left(\frac{3}{2}\frac{3}{2}\right)_0$$

$$\left(\frac{3}{2}\frac{3}{2}\right)_0' = \left(\frac{3}{2}\frac{3}{2}\right)_0 + \frac{5\sqrt{2}F_2}{5F_2-3\zeta}\left(\frac{1}{2}\frac{1}{2}\right)_0$$

$$\left(\frac{3}{2}\frac{1}{2}\right)_1' = \left(\frac{3}{2}\frac{1}{2}\right)_1$$

$$\left(\frac{3}{2}\frac{1}{2}\right)_2' = \left(\frac{3}{2}\frac{1}{2}\right)_2 + \frac{2\sqrt{2}F_2}{4F_2-\frac{3}{2}\zeta}\left(\frac{3}{2}\frac{3}{2}\right)_2$$

$$\left(\frac{3}{2}\frac{3}{2}\right)_2' = \left(\frac{3}{2}\frac{3}{2}\right)_2 - \frac{2\sqrt{2}F_2}{\underbrace{4F_2-\frac{3}{2}\zeta}_{-\alpha}}\left(\frac{3}{2}\frac{1}{2}\right)_2$$

sp

$$\left|\left(\frac{3}{2}\frac{1}{2}\right)_2'\right\rangle = \left(\frac{3}{2}\frac{1}{2}\right)_2$$

$$\left|\left(\frac{3}{2}\frac{1}{2}\right)_1'\right\rangle = \left(\frac{3}{2}\frac{1}{2}\right)_1 + \frac{2\sqrt{2}G_1}{\frac{2}{3}G_1 + \frac{3}{2}\zeta}\left(\frac{1}{2}\frac{1}{2}\right)_1$$

$$\left|\left(\frac{1}{2}\frac{1}{2}\right)_1'\right\rangle = \left(\frac{1}{2}\frac{1}{2}\right)_1 - \underbrace{\frac{2\sqrt{2}G_1}{\frac{2}{3}G_1 + \frac{3}{2}\zeta}}_{-\beta}\left(\frac{3}{2}\frac{1}{2}\right)_1$$

$$\left|\left(\frac{1}{2}\frac{1}{2}\right)_0'\right\rangle = \left(\frac{1}{2}\frac{1}{2}\right)_0$$

p^2:

$$\left|\left(\frac{3}{2}\frac{3}{2}\right)_2'\right\rangle \rightarrow \left|{}^3P_2\right\rangle$$

$$\left|\left(\frac{1}{2}\frac{1}{2}\right)_0'\right\rangle \rightarrow \left|{}^3P_0\right\rangle$$

sp:

$$\left|\left(\frac{3}{2}\frac{1}{2}\right)_1'\right\rangle \rightarrow \left|{}^1P_1\right\rangle$$

$$\left\langle \left|\left(\frac{3}{2}\frac{3}{2}\right)_2'\right| \hat{\mu} \left|\left(\frac{3}{2}\frac{1}{2}\right)_1'\right| \right\rangle = \left\langle \left(\frac{3}{2}\frac{3}{2}\right)_2 \left|\hat{\mu}\right| \left(\frac{3}{2}\frac{1}{2}\right)_1 \right\rangle$$

$$+\alpha\left\langle \left(\frac{3}{2}\frac{1}{2}\right)_2 \left|\hat{\mu}\right| \left(\frac{3}{2}\frac{1}{2}\right)_1 \right\rangle + \beta\underbrace{\left\langle \left(\frac{3}{2}\frac{3}{2}\right)_2 \left|\hat{\mu}\right| \left(\frac{1}{2}\frac{1}{2}\right)_1 \right\rangle}_{0}$$

$$+0(\alpha\beta)$$

$$\left\langle \left|\left(\frac{3}{2}\frac{3}{2}\right)_2'\right| \hat{\mu} \left|\left(\frac{3}{2}\frac{1}{2}\right)_1'\right| \right\rangle = \sqrt{50} - 5\alpha \quad ; \quad \alpha = \frac{-2\sqrt{2}F_2}{4F_2 - \frac{3}{2}\zeta} > 0 \qquad \left(\begin{array}{c}\text{because } \zeta \gg F_2 \\ \text{near j-j limit}\end{array}\right)$$

Correlates to ${}^3P_2 \leftarrow {}^1P_1$ transition and approaches zero intensity in **L–S–J** limit.

$$\left\langle \text{`}\left(\frac{1}{2}\frac{1}{2}\right)_0\text{'}\,|\hat{\mu}|\,\text{`}\left(\frac{3}{2}\frac{1}{2}\right)_1\text{'}\right\rangle = \left\langle \left(\frac{1}{2}\frac{1}{2}\right)_0 |\hat{\mu}| \left(\frac{3}{2}\frac{1}{2}\right)_1\right\rangle$$

$$+\alpha\left\langle \left(\frac{3}{2}\frac{3}{2}\right)_0 |\hat{\mu}| \left(\frac{3}{2}\frac{1}{2}\right)_1\right\rangle + \beta\left\langle \left(\frac{1}{2}\frac{1}{2}\right)_0 |\hat{\mu}| \left(\frac{1}{2}\frac{1}{2}\right)_1\right\rangle + 0(\alpha\beta)$$

$$= +\sqrt{20}\alpha - \sqrt{20}\beta = \sqrt{20}\,(\alpha-\beta); \qquad \beta = -\frac{2\sqrt{2}G_1}{\frac{2}{3}G_1 + \frac{3}{2}\zeta}$$

5. Positronium is an atom-like system formed from an electron and a positron. Predict the energy-level pattern and the wavelengths of some of the electronic transitions of positronium.

Predict the wavelengths of some electronic transitions in positronium: The energy level pattern will be hydrogenic.

$$E(\mu, n) \propto \frac{1}{\mu n^2} \qquad ; \qquad \mu = \text{reduced mass.}$$

For $\mu \gg m_e$, $\mu = \dfrac{Mm_e}{M+m_e} \approx m_e$

For $M = m_e$, $\mu = \dfrac{m_e^2}{2m_e} = \dfrac{1}{2}m_e$

We can calculate the positronium energy levels by scaling the Rydberg Formula:

$$\tilde{\nu}_{pos} = \frac{1}{2}R_\infty\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = 54839\left(\frac{1}{n^2} - \frac{1}{m^2}\right)\text{cm}^{-1}$$

$$\frac{1}{\lambda} = 54839\left(\frac{1}{n^2} - \frac{1}{m^2}\right); \quad n = \text{principal quantum number of terminus state, } m > n.$$

"Lyman" series: $\dfrac{1}{\lambda} = 54839\left(1 - \dfrac{1}{m^2}\right)\text{cm}^{-1}; \qquad \lambda = 1823.5\left(\dfrac{m^2}{m^2-1}\right)\text{Å}$

"Balmer" series; $\dfrac{1}{\lambda} = 54839\left(\dfrac{1}{4} - \dfrac{1}{m^2}\right)\text{cm}^{-1}; \qquad \lambda = 7294.1\left(\dfrac{m^2}{m^2-4}\right)\text{Å}$

m		Lyman	Balmer	
2		2431.4Å	– – – – –	
3	near	2051.4Å	13129.3Å	near
4	UV	1945.1Å	9725.5Å	IR
5		⋮	8683.4Å	
6		⋮	8205.9Å	
Series Limit		1823.5Å	7294.1Å	red

6. Without using microstates, derive the ground-state terms and energy levels for the transition elements of the third row (Sc through Zn) of the periodic table. (Remember Cr and Cu are exceptions to the regular Aufbau filling of electrons into orbitals.)

1) Hund's first rule: states with the highest spin multiplicity are lowest in energy.
2) Hund's second rule: for states with identical S, highest L is lowest in energy.

Element	Config.	Ground state	
Sc	s^2d	^2D	
Ti	s^2d^2	^3F	(L = 2 + 1)
V	s^2d^3	^4F	(L = 2 + 1 + 0)
Cr	sd^5	^7S	1/2 filled shell is particularly stable
Mn	s^2d^5	^6S	(L = 2 + 1 + 0 – 1 – 2 = 0)
Fe	s^2d^6	^5D	(L = 2 – 1 + 0 + 1)
Co	s^2d^7	^4F	(like V)
Ni	s^2d^8	^3F	(like Ti)
Cu	sd^{10}	^2S	full d shell is particularly stable

See Bernath, Chapter 5, pages 31 and 32.

7. (a) What are $\langle r \rangle$ and $\langle 1/r \rangle$ for the 1s orbital of hydrogen?

$\langle r \rangle_{n\ell}$ and $\left\langle \frac{1}{r} \right\rangle_{n\ell}$ for Hydrogen. You can do the integrals yourself or look them up. See, for instance, Condon and Shortley, page 117.

$$\langle r \rangle = \frac{a_0}{2}\left[3n^2 - \ell(\ell+1)\right]$$

$$\langle r \rangle_{1s} = \frac{3}{2}a_0$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}\frac{1}{n^2}$$

$$\left\langle \frac{1}{r} \right\rangle_{1s} = \frac{1}{a_0}$$

(b) What is the transition dipole moment in debye for the $2p_z \leftarrow 1s$ transition of hydrogen?

Calculate $\mu(2p \leftarrow 1s)$

$P = -er\cos\theta$

$$\mu = \langle 2p | P(r,\theta) | 1s \rangle$$

Using the equations and tables on page 132 and 133 of C & S

$$\mu = \frac{-1}{\sqrt{3}}\left[2^8 2^7 3^{-11}\right]^{1/2}$$

8. In the atomic spectrum of neutral Ca there is a normal multiplet of six lines at 0, 14, 36, 106, 120, and 158 cm^{-1} above the lowest frequency line of the multiplet. What are the quantum numbers of the states involved in the transition?

Bernath, Chapter 5, #15

I first tried the problem very late at night and I found it completely intractable even though I knew it was easy. It seems much more straightforward at 11:00 AM. Check Lecture 8 notes, page 3 for insight.

A six line pattern is characteristic of a $^3D \leftarrow {}^3P$ transition. This is plausible for Ca, because Ca has two e^- outside of a closed 3p shell, [Ar].

Step 1: Numerology…

One can make some educated guesses based on the separations between observed lines.

$$\left.\begin{aligned} 36-14&=22\\ 14-0&=14 \end{aligned}\right\} \frac{22}{14} = 1.6 \simeq \frac{3}{2}$$

This could be the signature of J = 3, 2, and 1 of a ^3D state.

$$\left.\begin{aligned} 158-106&=52\\ 106-0&=106 \end{aligned}\right\} \frac{106}{52} = 2.0_4 \simeq \frac{2}{1}$$

This could be the signature of J = 2, 1, 0 of a ^3P state.

Assuming this is correct, are the ζ's calculated plausible?

For the '^3D', $3\zeta = 22\ cm^{-1}$, $2\zeta = 14\ cm^{-1}$ ∴ $\zeta_d \simeq 7.0\ cm^{-1}$.

For the '^3P', $2\zeta = 106\ cm^{-1}$, $\zeta = 52\ cm^{-1}$ ∴ $\zeta_p \simeq 53\ cm^{-1}$.

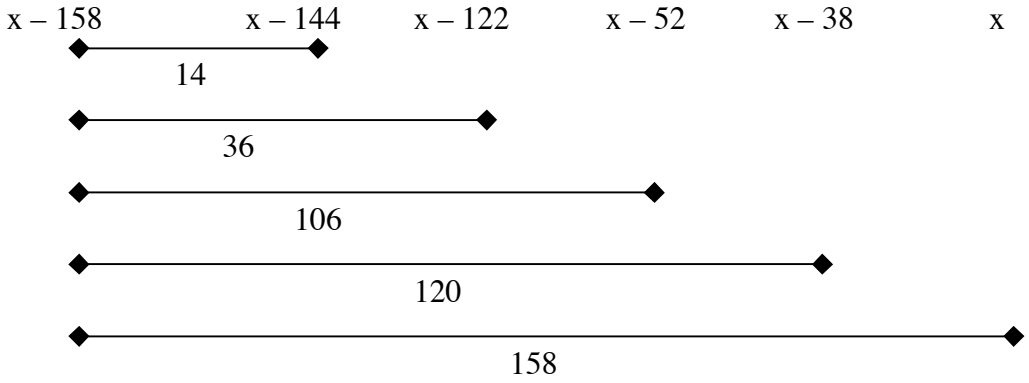
This is reasonable, as ζ decreases with increasing ℓ. Also, ζ decreases with increasing n, so if the ^3D state is on top, then this is even better.

Assume:

	J	E/cm^{-1}
^3D	3	x + 36
	2	x + 14
	1	x
^3P	2	158
	1	52
	0	0

Transition	Line position/cm^{-1}
$^3D_1 - {}^3P_0$	x
$^3D_2 - {}^3P_1$	x + 14 – 52 = x – 38
$^3D_3 - {}^3P_2$	x + 36 – 158 = x – 122
$^3D_1 - {}^3P_1$	x – 52
$^3D_2 - {}^3P_2$	x + 14 – 158 = x – 144
$^3D_1 - {}^3P_2$	x – 158

listing transitions red → blue:



This assignment appears to be correct.

9. The following wavenumbers are listed in Moore's tables for the $n^2P° - 3^2S$ transitions of Na:

n	J	Wavenumber (cm^{-1})
5	0.5	35,040.27
5	1.5	35,042.79
6	0.5	37,296.51
6	1.5	37,297.76
7	0.5	38,540.40
7	1.5	38,541.14
8	0.5	39,298.54
8	1.5	39,299.01
9	0.5	39,794.53
9	1.5	39,795.00
10	0.5 and 1.5	40,137.23

(a) Correct the line positions for the effect of spin-orbit coupling and determine ζ for each of the excited n^2P terms of Na.

Bernath, Eq. (5.97)

$$\langle \mathbf{H}^{SO} \rangle = \zeta \langle \mathbf{L}\cdot\mathbf{S} \rangle$$

$$= \frac{1}{2}\zeta\left[J(J+1) - L(L+1) - S(S+1)\right]$$

This is the np Rydberg series, so L = 1, S = $\frac{1}{2}$

$$\langle \mathbf{H}^{SO} \rangle = \frac{1}{2}\zeta\left[J(J+1) - \frac{11}{4} \right]$$

$E_{J+1} - E_J = \zeta(J+1)$; $\zeta = \frac{2}{3}\Delta E_{(J+1)-J}$

$\bar{E}_{np}$ is the degeneracy weighted average of $J = \frac{3}{2}$ and $J = \frac{1}{2}$:

$\Omega_{\frac{3}{2}} = 4$, $\Omega_{\frac{1}{2}} = 2$ (Ω_J are degeneracies)

$$\bar{E}_{np} = \frac{4E_{\frac{3}{2}} + 2E_{\frac{1}{2}}}{6}$$

n	$\bar{E}_{np}/cm^{-1}$	ζ_{np}/cm^{-1}
5	35041.95	1.12
6	37297.34	0.55
7	38540.89	0.33
8	39298.85	0.21
9	39794.84	0.21
10	40137.23	0.00

[Note: I've defined $E(3^2S_{1/2}) = 0$]

(b) Devise an extrapolation procedure to determine the ionization potential and the quantum defect for this Rydberg series.

Extrapolation of np Rydberg series to determine ionization potential.

The energies of the np orbitals can be fit to the following formula:

$$\bar{E}_{np} = IP - \frac{R}{(n - \mu_p)^2}$$

IP = Na Ionization Potential

R = Rydberg constant [109734.72 cm^{-1} for Na]

μ_p = Quantum defect for the np series

I tried several different fits using the Field group's non-linear least squares fitting program. I first tried a fit giving each $\bar{E}$ equal statistical weight. The resultant fit had systematic residuals. This comes as no surprise, as the Rydberg formula is more accurate at high n. A second fit was done with the 5p, 6p, and 7p levels de-weighted. The uncertainty in the fitted value of the IP decreased considerably.

Fit #1

$\delta(\bar{E}_{np}) = 0.1\ cm^{-1}$

Fit #2

$\delta(\bar{E}_{np}) =$ large for low n

IP = 41452.7(9) cm^{-1} IP = 41450.3(1) cm^{-1}

μ_p = 0.8623(6) μ_p = 0.8583(2)

A better fit could be obtained by systematically de-weighting the lower np levels and by observing and including higher np levels.

The IP listed in Charlotte Moore's tables is 41449.65 cm^{-1}, over six standard deviations off from the value determined by fit #2.

Results of the two fits follow…

NUMBER OF DATA POINTS: 6 FIT #1
Na np quantum defect determination

INITIAL PARAMETERS

1	IP	0.41451500D+05	cm^{-1}
2	Ryd	0.10973472D+06	cm^{-1}
3	mu	0.86070000D+00	

OUTPUT FROM LAST LSQ PASS

NUMBER	NAME	FINAL VALUE	STANDARD DEVIATION	
1	IP	0.41452684D+05	0.9303D+00	cm^{-1}
	Ryd	0.10973472D+06		cm^{-1}
2	mu	0.86231148D+00	0.6148D–03	

OBSERVED AND CALCULATED TRANSITION FREQUENCIES

Line	J′	RK	BK	J″	RK	BK	EXPT	CALC	EXPT-CALC	SD	units
5p	0.0	1	2	0.0	1	1	35041.950	35043.121	–1.171	0.100	cm^{-1}
6p	1.0	1	2	0.0	1	1	37297.340	37295.412	1.928	0.100	cm^{-1}
7p	2.0	1	2	0.0	1	1	38540.890	38539.725	1.165	0.100	cm^{-1}
8p	3.0	1	2	0.0	1	1	39298.850	39298.768	0.082	0.100	cm^{-1}
9p	4.0	1	2	0.0	1	1	39794.840	39795.610	–0.770	0.100	cm^{-1}
10p	5.0	1	2	0.0	1	1	40137.230	40138.454	–1.224	0.100	cm^{-1}

fit residual uncertainty in $\bar{E}$

NUMBER OF DATA POINTS: 6 FIT #2
Na np quantum defect determination

INITIAL PARAMETERS

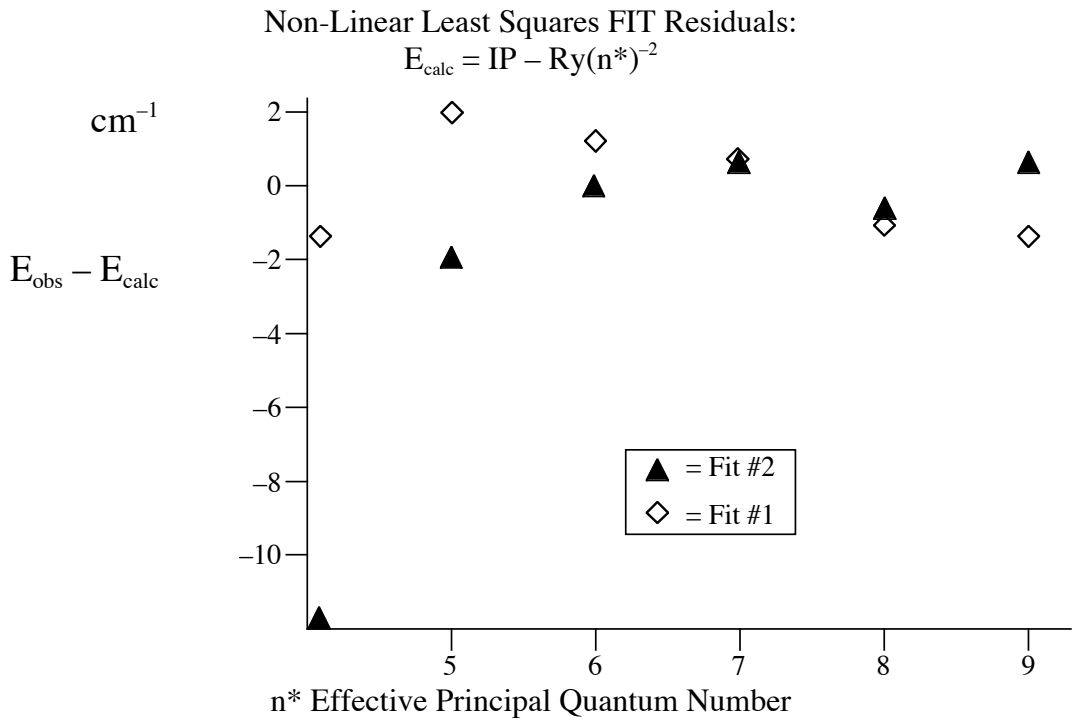
1	IP	0.41451500D+05	cm^{-1}
2	Ryd	0.10973472D+06	cm^{-1}
3	mu	0.86070000D+00	

OUTPUT FROM LAST LSQ PASS

NUMBER	NAME	FINAL VALUE	STANDARD DEVIATION	
1	IP	0.41450306D+05	0.9915D–01	cm^{-1}
	Ryd	0.10973472D+06		cm^{-1}
2	mu	0.85828733D+00	0.2182D–03	

OBSERVED AND CALCULATED TRANSITION FREQUENCIES

Line	J′	RK	BK	J″	RK	BK	EXPT	CALC	EXPT-CALC	SD	units
5p	0.0	1	2	0.0	1	1	35041.950	35053.191	–11.241	15.000	cm^{-1}
6p	1.0	1	2	0.0	1	1	37297.340	37299.538	–2.198	5.000	cm^{-1}
7p	2.0	1	2	0.0	1	1	38540.890	38541.163	–0.273	1.000	cm^{-1}
8p	3.0	1	2	0.0	1	1	39298.850	39298.816	0.034	0.100	cm^{-1}
9p	4.0	1	2	0.0	1	1	39794.840	39794.869	–0.029	0.100	cm^{-1}
10p	5.0	1	2	0.0	1	1	40137.230	40137.233	–0.003	0.100	cm^{-1}



The spin-orbit operator for the hydrogen atom is

$$\hat{\mathbf{H}}_{SO} = \xi(r)\hat{\ell}\cdot\hat{s}$$

$$\xi(r) = \frac{1}{2\mu^2 c^2}\frac{1}{r}\frac{\partial V}{\partial r} \qquad \text{Bernath (5.46)}$$

$$= \frac{1}{2\mu^2 c^2}\frac{Ze^2}{4\pi z_0 r^3}$$

For np orbitals of **H**,

$$\zeta_{np} = \langle np|\xi(r)|np\rangle \propto n^{-3}$$

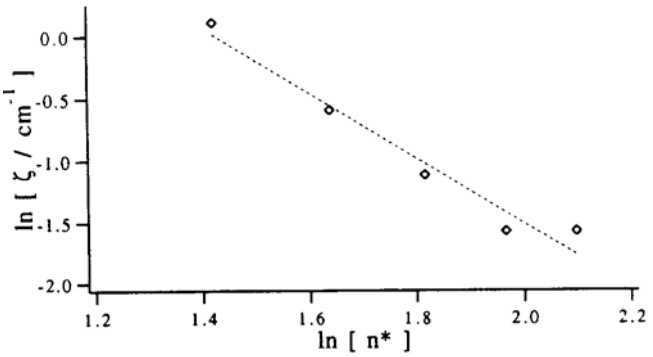
Alkalis, like Na, are nearly one-electron atoms like H, so we might expect ζ_{np} to scale similarly in Na; possibly as $n^{\star -3}$. The $n^\star$ dependence of ζ_{np} can be determined by doing a log-log plot of ζ_{np} vs. $n^\star$.

Assume $\quad \zeta_{np} = A_p\left(n^\star\right)^{-k}$

$$\ln\zeta_{np} = \ln A_p - k\ln n^\star$$

The 10p orbital cannot be included because the spin-orbit splitting is not resolved. I did one fit including the 9p and the other without it.

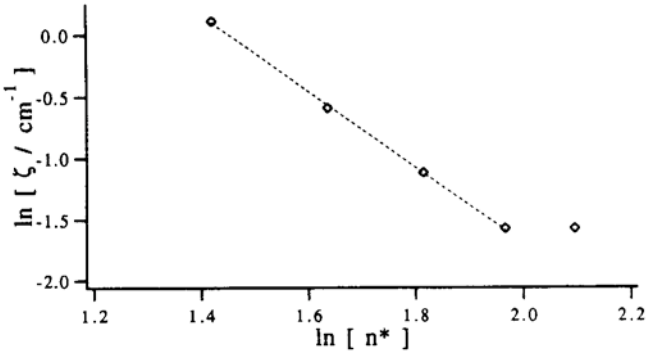
n* Dependence of Spin-Orbit Constant



$\zeta_{np} = A_p(n^*)^{-k}$

$k_{fit} = 2.6$

n* Dependence of Spin-Orbit Constant



$\zeta_{np} = A_p(n^*)^{-k}$

$k_{fit} = 3.1$

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10. On the basis of first-order perturbation theory, the hyperfine structure of the ground electronic state of the H atom involves the interaction of the spins of the electron and proton with one another, and with any applied magnetic fields. It is possible to integrate out the spatial coordinates and to consider the system as two spins S = I = 1/2 governed by the spin Hamiltonian

$$\hat{H}_{spin} = \frac{b_F}{\hbar^2}\hat{I}\cdot\hat{S} + \frac{k_S}{\hbar}\hat{S}_z + \frac{k_I}{\hbar}\hat{I}_z \equiv \hat{H}_{hfs} + \hat{H}_{Zeeman},$$

in which b_F, k_S, and k_I are given by

$$b_F = \frac{2\mu_0}{3} g_e \mu_B g_I \mu_I \left|\psi_{1s}(0)\right|^2$$
$$k_S = g_e \mu_B B_0$$
$$k_I = -g_I \mu_N B_0$$

and g_e, g_I, μ_B, μ_N are the g-factors and magnetons for the electron and the proton. The spin Hamiltonian can be split into two parts, $b_F \hat{I}\cdot\hat{S}/\hbar^2$ [referred to as the hyperfine structure (hfs) Hamiltonian], and

$\left(k_S \hat{S}_z + k_I \hat{I}_z\right)/\hbar$ (referred to as the Zeeman Hamiltonian). SI units are used and $\mu_0 = 4\pi \times 10^{-7}$ **N A**$^{-2}$ is the permeability of vacuum.

(a) Calculate the values of b_F, k_S, and k_I (the latter two as multiples of the field strength, B_0) for the hydrogen 1s state.

Calculate the values of b_F, k_s, and k_I

$$b_F = \frac{2}{3}\mu_0 g_e \mu_B g_I \mu_I \left|\psi_{1s}(0)\right|^2$$

$$\mu_0 = 4\pi\cdot 10^{-7}\,\mathrm{NA^{-2}}$$

$$\mu_B = 9.274\cdot 10^{-24}\,\mathrm{JT^{-1}}$$

$$\mu_N = 5.051\cdot 10^{-27}\,\mathrm{JT^{-1}}$$

$$g_e = 2.0023$$

$$g_I = 5.5856$$

$$\psi_{1s}(r) = \frac{1}{\pi^{1/2}}\frac{1}{a_0^{3/2}} e^{-r/a_0} \qquad ; \qquad \left|\psi_{1s}(0)\right|^2 = \frac{1}{\pi a_0^3}$$

Unit check:

$$\left(\mathrm{NA^{-2}}\right)\left(\mathrm{Nm}\right)^2\left(\mathrm{NA^{-1}m^{-1}}\right)^{-2}\mathrm{m^{-3}} = \mathrm{Nm} = \mathrm{J}$$

$1.60210 \cdot 10^{-19}\mathrm{J} = 8065.7\ \mathrm{cm^{-1}} \cdot 29979\ \mathrm{MHz/cm^{-1}}$

$6.6257 \cdot 10^{-28}\ \mathrm{J} = 1\ \mathrm{MHz}$

$$b_F = \frac{\frac{8}{3}\cdot 10^{-7}\cdot 2.0023\cdot 9.274\cdot 10^{-24}\cdot 5.5856\cdot 5.051\cdot 10^{-27}\left(0.529177\cdot 10^{-10}\right)^{-3}}{6.6257\cdot 10^{-28}}\,\mathrm{MHz}$$

$b_F = 1422.9$ MHz

$$k_I = -g_I \mu_N B_0$$

$$= \frac{-5.5856\cdot 5.051\cdot 10^{-27}}{6.6257\cdot 10^{-28}}\left(B_0 / \mathrm{Tesla}\right)\mathrm{MHz}$$

$$= -42.6\left(B_0 / \mathrm{Tesla}\right)\mathrm{MHz}$$

$$k_S = g_e \mu_B B_0$$

$$= \frac{2.0023\cdot 9.274\cdot 10^{-24}}{6.6257\cdot 10^{-28}}\left(B_0 / \mathrm{Tesla}\right)\mathrm{MHz}$$

$$= 28026\left(B_0 / \mathrm{Tesla}\right)\mathrm{MHz}$$

(b) Now consider an isolated H atom (with no applied magnetic field). Show that the matrix of $\widehat{H}_{hfs}$ with respect to the $|m_S m_I\rangle$ basis is

$$\mathbf{H}_{hfs} = \frac{b_F}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Find the energies and eigenstates in this basis and construct the matrix **X** that diagonalizes $\mathbf{H}_{hfs}$. What will be the eigenstates $|FM_F\rangle$ of $\widehat{H}_{hfs}$ expressed in terms of the $|m_S m_I\rangle$ states? Give a discussion of this in terms of vector coupling.

The eigenvectors of $\widehat{\mathbf{H}}_{hfs}$ are listed on the next page.

$$\underset{\approx}{X} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2^{-1/2} & 2^{-1/2} & 0 \\ 0 & 2^{-1/2} & -2^{1/2} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

The eigenvalues of $\widehat{\mathbf{H}}_{hfs}$ are $-\frac{3}{4}b_F$ and $\frac{1}{4}b_F$. The triplet, F = 1, lies at higher energy. The splitting between the F = 0 and F = 1 levels is b_F = 1422.9 MHz.

```
program matgen
integer r
double precision a(4,4), bf, ks, ki, h
write(5,*) 'Magnetic field?  [Units of Tesla]'
read(5,*) h
bf = 1422.9
ki = –42.6*h
ks = 28026*h
***     | mI, mS >

***     | 1/2, 1/2 >, | 1/2, –1/2 >, | –1/2, 1/2 >, | –1/2, –1/2>

        a(1,1) = 0.25*bf + 0.50*ki + 0.50*ks
        a(1,2) = 0.00d0
        a(1,3) = 0.00d0
        a(1,4) = 0.00d0
***
        a(2,1) = a(1,2)
        a(2,2) = –0.25*bf + 0.50*ki – 0.50*ks
        a(2,3) = 0.50*bf
        a(2,4) = 0.00d0
***
        a(3,1) = a(1,3)
```

```
        a(3,2) = a(2,3)
        a(3,3) = –0.25*bf – 0.50*ki + 0.50*ks
        a(3,4) = 0.00d0
***
        a(4,1) = a(1,4)
        a(4,2) = a(2,4)
        a(4,3) = a(3,4)
        a(4,4) = 0.25*bf – 0.50*ki – 0.50*ks

        write(5,110) 'Magnetic Field / Tesla = ',h
        open(file='matrix.dat', unit=2, status='unknown')
        do r = 1,4
                write(2,100) a(r,1), a(r,2), a(r,3), a(r,4)
                write(5,100) a(r,1), a(r,2), a(r,3), a(r,4)
        enddo
        close(2)

100     format(4f10.2)
110     format(a30,f6.3)

        end
```

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .000

	|1⟩	|2⟩	|3⟩	|4⟩
⟨1|	355.73000	.00000	.00000	.00000
⟨2|	.00000	–355.73000	711.45000	.00000
⟨3|	.00000	711.45000	–355.73000	.00000
⟨4|	.00000	.00000	.00000	355.73000

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–1067.1800	355.7200	355.7300	355.7300
Vector:				
⟨1|	.00000	.00000	1.00000	.00000
⟨2|	.70711	.70711	.00000	.00000
⟨3|	–.70711	.70711	.00000	.00000
⟨4|	.00000	.00000	.00000	1.00000

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .001

	|1⟩	|2⟩	|3⟩	|4⟩
⟨1|	369.72000	.00000	.00000	.00000
⟨2|	.00000	–369.76000	711.45000	.00000
⟨3|	.00000	711.45000	–341.69000	.00000
⟨4|	.00000	.00000	.00000	341.7300

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–1067.3134	341.7300	355.8634	369.7200
Vector:				
⟨1|	.00000	.00000	.00000	1.00000
⟨2|	–.71405	.00000	.70010	.00000
⟨3|	.70010	.00000	.71405	.00000
⟨4|	.00000	1.00000	.00000	.00000

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .005

	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$
$\langle 1\|$	425.68000	.00000	.00000	.00000
$\langle 2\|$	.00000	–425.90000	711.45000	.00000
$\langle 3\|$	.00000	711.45000	–285.55000	.00000
$\langle 4\|$	.00000	.00000	.00000	285.77000

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–1070.6275	285.7700	359.1775	425.6800
Vector:				
$\langle 1\|$	.00000	.00000	.00000	1.00000
$\langle 2\|$	–.74100	.00000	.67151	.00000
$\langle 3\|$	.67151	.00000	.74100	.00000
$\langle 4\|$	.00000	1.00000	.00000	.00000

In the absence of an external field, the spin of the proton and the electron spin are strongly coupled when anti-parallel.

(c) Determine (in terms of b_F, k_S, k_I) the matrices with elements $\left\langle m_S' m_I' \middle| \hat{H}_{spin} \middle| m_S'' m_I'' \right\rangle$ and $\left\langle F' M_F' \middle| \hat{H}_{spin} \middle| F'' M_F'' \right\rangle$ in the general case when an applied field, B_0, is present.

$$\mathbf{H} = \begin{array}{c} \left|m_I, m_s\right\rangle \\ \\ \\ \\ \\ \end{array} \begin{array}{c} \left|\frac{1}{2}\frac{1}{2}\right\rangle \\ \\ \\ \\ \end{array} \begin{array}{c} \left|\frac{1}{2}-\frac{1}{2}\right\rangle \\ \\ \\ \\ \end{array} \begin{array}{c} \left|-\frac{1}{2}\frac{1}{2}\right\rangle \\ \\ \\ \\ \end{array} \begin{array}{c} \left|-\frac{1}{2}-\frac{1}{2}\right\rangle \\ \\ \\ \\ \end{array} \begin{bmatrix} \frac{1}{4}b_F + \frac{1}{2}k_I + \frac{1}{2}k_s & 0 & 0 & 0 \\ 0 & \frac{1}{4}b_F + \frac{1}{2}k_I - \frac{1}{2}k_s & \frac{1}{2}b_F & 0 \\ 0 & \frac{1}{2}b_F & -\frac{1}{4}b_F - \frac{1}{2}k_I + \frac{1}{2}k_s & 0 \\ 0 & 0 & 0 & \frac{1}{4}b_F - \frac{1}{2}k_I - \frac{1}{2}k_s \end{bmatrix}$$

(d) From the results of part (c) show how the zero field $|FM_F\rangle$ levels split in a weak magnetic field. In this case it is necessary to treat the magnetic field as a perturbation, namely

$$\hat{H}^{(0)} = \frac{b_F}{\hbar^2}\hat{I}\cdot\hat{S}, \qquad \hat{H}^{(1)} = \frac{k_S}{\hbar}\hat{S}_z + \frac{k_I}{\hbar}\hat{I}.$$

Give a plot of the splitting of these levels as calculated earlier for fields, B_0, from 0 to 0.2 T (put your energy scale in MHz).

See printouts of Fortran program on Athena and graph created, using program output, with 'Igor' on a Mac.

Notice that at 0.2 Tesla (2000 Gauss) $\vec{I}$ and $\vec{s}$ are almost entirely decoupled.

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .100

	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$
$\langle 1\|$	1754.90000	.00000	.00000	.00000
$\langle 2\|$	.00000	–1759.16000	711.45000	.00000
$\langle 3\|$	.00000	711.45000	1047.70000	.00000
$\langle 4\|$	.00000	.00000	.00000	–1043.44000

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–1929.1902	–1043.4400	1217.7302	1754.9000
Vector:				
$\langle 1\|$	.00000	.00000	.00000	1.00000
$\langle 2\|$	–.97261	.00000	.23244	.00000
$\langle 3\|$	.23244	.00000	.97261	.00000
$\langle 4\|$	.00000	1.00000	.00000	.00000

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .010

	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$
$\langle 1\|$	495.64000	.00000	.00000	.00000
$\langle 2\|$	.00000	–496.07000	711.45000	.00000
$\langle 3\|$	.00000	711.45000	–215.38000	.00000
$\langle 4\|$	.00000	.00000	.00000	215.81000

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–1080.8855	215.8100	369.4355	495.6400
Vector:				
$\langle 1\|$	.00000	.00000	.00000	1.00000
$\langle 2\|$	–.77251	.00000	.63501	.00000
$\langle 3\|$	.63501	.00000	.77251	.00000
$\langle 4\|$	.00000	1.00000	.00000	.00000

MATRIX BEFORE DIAGONALIZATION:

Magnetic Field / Tesla = .200

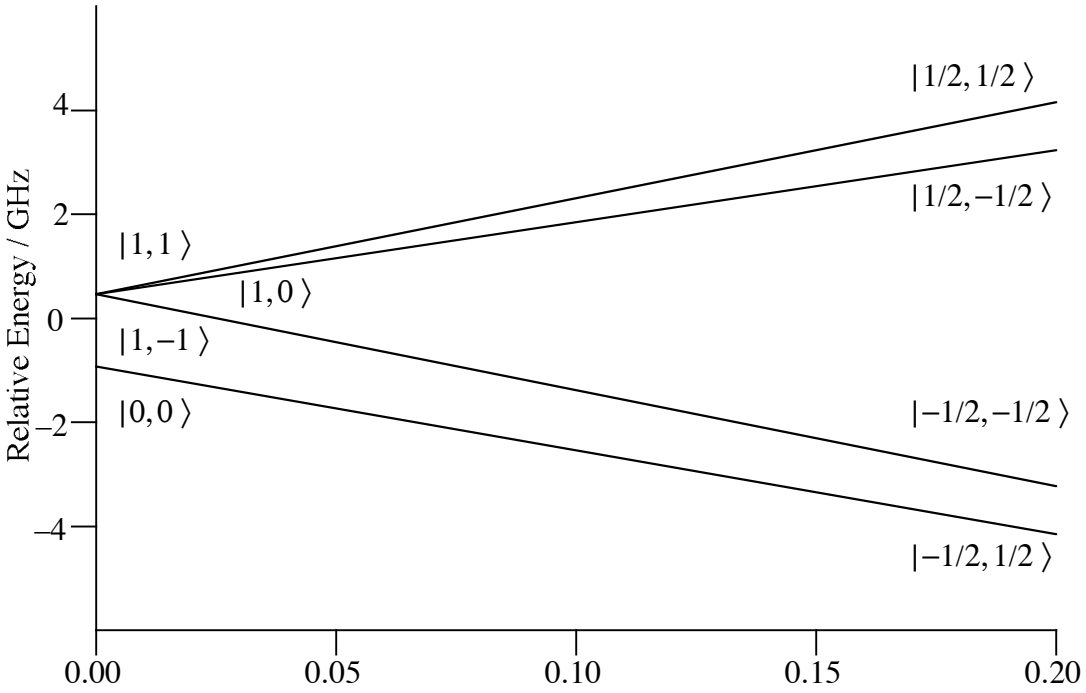
	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$
$\langle 1\|$	3154.07000	.00000	.00000	.00000
$\langle 2\|$	.00000	–3162.59000	711.45000	.00000
$\langle 3\|$	.00000	711.45000	2451.13000	.00000
$\langle 4\|$	.00000	.00000	.00000	–2442.61000

EIGENVALUES & EIGENVECTORS:

	# 1	# 2	# 3	# 4
Value:	–3251.3516	–2442.6100	2539.8916	3154.0700
Vector:				
$\langle 1\|$	.00000	.00000	.00000	1.00000
$\langle 2\|$	–.99231	.00000	.12380	.00000
$\langle 3\|$	.12380	.00000	.99231	.00000
$\langle 4\|$	.00000	1.00000	.00000	.00000

Hydrogen 1s Levels in a Magnetic Field

$\left|F, m_F\right\rangle$ …… $\left|m_s, m_I\right\rangle$



Magnetic Field / Tesla

(e) Determine the energy levels in a strong magnetic field of 1 T, regarding the hyperfine interaction as a small perturbation, that is,

$$\hat{H}^{(0)} = \frac{k_S}{\hbar}\hat{S}_z + \frac{k_I}{\hbar}\hat{I}_z, \qquad \hat{H}^{(1)} = \frac{b_F}{\hbar^2}\hat{I}\cdot\hat{S}.$$

In this case show explicitly that the first-order perturbation spin functions are

$$\psi_1^{(1)} = \phi_1^{(0)}, \qquad \psi_4^{(1)} = \phi_4^{(0)},$$
$$\psi_2^{(1)} = \phi_2^{(0)} + \frac{b_F}{2\left(g_e\mu_B B_0 + g_I\mu_N B_0\right)}\phi_3^{(0)},$$
$$\psi_3^{(1)} = \phi_3^{(0)} - \frac{b_F}{2\left(g_e\mu_B B_0 + g_I\mu_N B_0\right)}\phi_2^{(0)},$$

while the second-order energies corresponding to these four functions are

$$E_1 = \frac{1}{2}g_e\mu_B B_0 - \frac{1}{2}g_I\mu_N B_0 + \frac{1}{4}b_F,$$
$$E_2 = \frac{1}{2}g_e\mu_B B_0 + \frac{1}{2}g_I\mu_N B_0 - \frac{1}{4}b_F + \frac{b_F^2}{4\left(g_e\mu_B B_0 + g_I\mu_N B_0\right)},$$
$$E_3 = -\frac{1}{2}g_e\mu_B B_0 - \frac{1}{2}g_I\mu_N B_0 - \frac{1}{4}b_F - \frac{b_F^2}{4\left(g_e\mu_B B_0 + g_I\mu_N B_0\right)},$$
$$E_4 = -\frac{1}{2}g_e\mu_B B_0 + \frac{1}{2}g_I\mu_N B_0 + \frac{1}{4}b_F.$$

The electron spin resonance (ESR) spectrum for the hydrogen atoms has only *two* equally intense lines, because the magnetic moment of the proton is too small to contribute to the intensity, and because the mixing of the $|m_S m_I\rangle$ states in the strong field is small. Show explicitly with numerical results that this is indeed the case for the problem that you are considering. Calculate the splitting of the two ESR lines in MHz, and compare your result with the experimentally observed value of 1420.4 MHz. What is the corresponding wavelength? How could you use this calculation to substantiate the existence of interstellar clouds of atomic hydrogen?

$|m_s, m_I\rangle$

$$|1\rangle = \left|\frac{1}{2}\,\frac{1}{2}\right\rangle$$

$$E_1^0 = \frac{1}{2}\left(k_s + k_I\right) = \frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right)$$

$$|2\rangle = \left|\frac{1}{2} -\frac{1}{2}\right\rangle$$

$$E_2^0 = \frac{1}{2}\left(k_s - k_I\right) = \frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right)$$

$$|3\rangle = \left|-\frac{1}{2}\,\frac{1}{2}\right\rangle$$

$$E_3^0 = -\frac{1}{2}\left(k_s - k_I\right) = -\frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right)$$

$$|4\rangle = \left|-\frac{1}{2} -\frac{1}{2}\right\rangle$$

$$E_4^0 = -\frac{1}{2}\left(k_s + k_I\right) = -\frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right)$$

$$E_2^0 - E_3^0 = B_0\left(g_e\mu_B + g_I\mu_N\right)$$

$$H_{23}^{(1)} = \frac{1}{2}b_F \qquad \text{all other } H_{ij}^{(1)} = 0$$

$$= H_{32}^{(1)}$$

$$|\psi_i\rangle = |\psi_i\rangle^\circ + \sum_{j\neq i}\frac{H_{ij}}{E_i^\circ - E_j^\circ}|\psi_j\rangle^\circ$$

$$|1\rangle = |1\rangle^\circ$$

$$|2\rangle = |2\rangle^\circ + \frac{b_F}{2B_0\left(g_e\mu_B + g_I\mu_N\right)}|3\rangle^\circ$$

$$|3\rangle = |3\rangle^\circ - \frac{b_F}{2B_0\left(g_e\mu_B + g_I\mu_N\right)}|2\rangle^\circ$$

$$|4\rangle = |4\rangle^\circ$$

$$E_1 = E_1^{(0)} + H_{11}^{(1)} \qquad ; \qquad H_{ij}^{(1)} \text{ are the elements of } \widehat{\mathbf{H}}_{hfs} \text{ given in part b)}$$

$$= \frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right) + \frac{1}{4}b_F$$

$$E_2 = E_2^{(0)} + H_{22}^{(1)} + \frac{\left[H_{23}^{(1)}\right]^2}{E_2^\circ - E_3^\circ}$$

$$= \frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right) - \frac{1}{4}b_F + \frac{b_F^2}{4B_0\left(g_e\mu_B + g_I\mu_N\right)}$$

$$E_3 = E_3^{(0)} + H_{33}^{(1)} + \frac{\left[H_{32}^{(1)}\right]^2}{E_3^o - E_2^o}$$

$$= -\frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right) - \frac{1}{4}b_F - \frac{b_F^2}{4B_0\left(g_e\mu_B + g_I\mu_N\right)}$$

$$E_4 = E_4^{(0)} + H_{44}^{(1)}$$

$$= -\frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right) + \frac{1}{4}b_F$$

The calculated position of the F = 0 $\rightarrow$ F = 1 transition is b_F = 1422.9 MHz.

The transitions are from $|3\rangle \rightarrow |1\rangle$ and $|4\rangle \rightarrow |2\rangle$.

$$\tilde{\nu}_1 = E_1 - E_3 = \frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right) + \frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right) + \frac{1}{2}b_F + \frac{b_F^2}{4B_0\left(g_e\mu_B + g_I\mu_N\right)}$$

$$\tilde{\nu}_2 = E_2 - E_4 = \frac{1}{2}B_0\left(g_e\mu_B + g_I\mu_N\right) - \frac{1}{4}b_F + \frac{b_F^2}{4B_0\left(g_e\mu_B + g_I\mu_N\right)}$$

$$+\frac{1}{2}B_0\left(g_e\mu_B - g_I\mu_N\right) - \frac{1}{4}b_F$$

Splitting = $\Delta\tilde{\nu} = \left(E_1 - E_3\right) - \left(E_2 - E_4\right) = \frac{1}{2}b_F - \left(-\frac{1}{2}b_F\right) = b_F = 1422.9\ \text{MHz}$.

$$\nu = 1422.9\ \text{MHz} = 1.4229\ \text{GHz} = 1.4229{\cdot}10^9\ \text{s}^{-1}$$

$$\lambda = \left[1.4229{\cdot}10^9\ \text{s}^{-1} / 2.9979{\cdot}10^{10}\ \text{cm s}^{-1}\right]^{-1} = 21.07\ \text{cm}.$$

At zero field, one observes a single line, F = 0 $\rightarrow$ F = 1. In the presence of a modest B field, the line will split and the doublet will shift to the blue (doublet will be seen in a range of a few to a few tens of GHz). The observed splitting of the doublet will change depending upon whether the interstellar cloud is moving towards or away from us, and this is due to the Doppler shift.