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5.80 Small-Molecule Spectroscopy and Dynamics
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
5.76 Modern Topics in Physical Chemistry
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Problem Set #2

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. $j_1 - j_2 - J$ 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

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

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

$$\langle p^2\ ^1S | \mu | sp\ ^1P_1 \rangle = -(20)^{1/2} \mu$$

$$\langle p^2\ ^1D | \mu | sp\ ^1P_1 \rangle = +10 \mu$$

$$\langle p^2\ ^3P_0 | \mu | sp\ ^3P_1 \rangle = -(20)^{1/2} \mu$$

$$\langle p^2\ ^3P_1 | \mu | sp\ ^3P_0 \rangle = -(20)^{1/2} \mu$$

$$\langle p^2\ ^3P_1 | \mu | sp\ ^3P_1 \rangle = +(15)^{1/2} \mu$$

$$\langle p^2\ ^3P_1 | \mu | sp\ ^3P_2 \rangle = -5 \mu$$

$$\langle p^2\ ^3P_2 | \mu | sp\ ^3P_1 \rangle = -5 \mu$$

$$\langle p^2\ ^3P_2 | \mu | sp\ ^3P_2 \rangle = +(75)^{1/2} \mu.$$

All other transition amplitudes are zero, most notably:

$$\langle p^2\ ^3P_0 | \mu | sp\ ^3P_0 \rangle = 0$$

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):

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

$$\mathbf{H}^{SO} = \begin{array}{c} {}^1S_0 \\ {}^3P_0 \\ {}^3P_1 \\ {}^3P_2 \\ {}^1D_2 \end{array} \left| \begin{array}{cc} 0 & -2^{1/2}\zeta \\ -2^{1/2}\zeta & -\zeta \\ & & -\frac{1}{2}\zeta \\ & & & \frac{1}{2}\zeta & 2^{-1/2}\zeta \\ & & & 2^{1/2}\zeta & 0 \end{array} \right|$$

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

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

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

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

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

$$\Delta_2 = 3F_2 - \frac{1}{4}\zeta \quad V_2 = -2^{-1/2}\zeta$$

Similarly, for the sp configuration:

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

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

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

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

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

(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	($np \leftarrow n's$ 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.

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 ,

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

and a similar quantity for sp ,

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

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

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

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

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

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.

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} .

$$\begin{array}{l} p^2 \\ \text{sp} \end{array} \quad \begin{array}{l} \left(\frac{3}{2} \frac{3}{2}\right)_2 = \left(\frac{2}{3}\right)^{1/2} |^3P_2\rangle + \left(\frac{1}{3}\right)^{1/2} |^1D_2\rangle \\ \left(\frac{3}{2} \frac{1}{2}\right)_2 = \left(\frac{1}{3}\right)^{1/2} |^3P_2\rangle - \left(\frac{2}{3}\right)^{1/2} |^1D_2\rangle \\ \left(\frac{3}{2} \frac{1}{2}\right)_2 = |^3P_1\rangle \\ \left(\frac{3}{2} \frac{3}{2}\right)_0 = \left(\frac{2}{3}\right)^{1/2} |^1S_0\rangle - \left(\frac{1}{3}\right)^{1/2} |^3P_0\rangle \\ \left(\frac{1}{2} \frac{1}{2}\right)_0 = \left(\frac{1}{3}\right)^{1/2} |^1S_0\rangle + \left(\frac{2}{3}\right)^{1/2} |^3P_0\rangle \\ \left(\frac{1}{2} \frac{3}{2}\right)_2 = |^3P_2\rangle \\ \left(\frac{1}{2} \frac{3}{2}\right)_1 = \left(\frac{2}{3}\right)^{1/2} |^1P_1\rangle + \left(\frac{1}{3}\right)^{1/2} |^3P_1\rangle \\ \left(\frac{1}{2} \frac{1}{2}\right)_1 = \left(\frac{1}{3}\right)^{1/2} |^1P_1\rangle - \left(\frac{2}{3}\right)^{1/2} |^3P_1\rangle \\ \left(\frac{1}{2} \frac{1}{2}\right)_0 = |^3P_0\rangle \end{array}$$

Construct the new $p^2\ \mathbf{H}(0), \mathbf{H}(1), \mathbf{H}(2)$ and $\text{sp } \mathbf{H}(0), \mathbf{H}(1), \mathbf{H}(2)$ matrices in the $j-j$ basis using the above transformations.

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.
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.
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.)
7. (a) What are $\langle r \rangle$ and $\langle 1/r \rangle$ for the 1s orbital of hydrogen?
(b) What is the transition dipole moment in debye for the $2p_z \leftarrow 1s$ transition of hydrogen?
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?
9. The following wavenumbers are listed in Moore's tables for the $n^2P^\circ - 3^2S$ 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.
 - (b) Devise an extrapolation procedure to determine the ionization potential and the quantum defect for this Rydberg series.
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

$$\hat{H}_{\text{spin}} = \frac{b_{\text{F}}}{\hbar^2} \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} + \frac{k_{\text{S}}}{\hbar} \hat{S}_z + \frac{k_{\text{I}}}{\hbar} \hat{I}_z \equiv \hat{H}_{\text{hfs}} + \hat{H}_{\text{Zeeman}},$$

in which b_F , k_S , and k_I are given by

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

$$k_S = g_e \mu_B B_0$$

$$k_I = -g_I \mu_N B_0$$

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 $(k_S \hat{S}_z + k_I \hat{I}_z) / \hbar$ (referred to as the Zeeman Hamiltonian). SI units are used and $\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2}$ 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.
- (b) Now consider an isolated H atom (with no applied magnetic field). Show that the matrix of \hat{H}_{hfs} with respect to the $|m_S m_I\rangle$ basis is

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

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

- (c) Determine (in terms of b_F , k_S , k_I) the matrices with elements $\langle m'_S m'_I | \hat{H}_{\text{spin}} | m''_S m''_I \rangle$ and $\langle F'M'_F | \hat{H}_{\text{spin}} | F''M''_F \rangle$ in the general case when an applied field, B_0 , is present.
- (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

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

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).

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

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

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

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

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

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

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?