5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Problem Set #1
Due February 23, 1987

Problems 1-4 deal with material from the February 11, 1987 Lecture. 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. $j_i - j_2 - J$ limiting cases. Problems 5-8 are standard textbook problems, more basic, and much easier than 1-4.

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5. J. I. Steinfeld (2nd Ed.), p. 36, #2

   (a) Given the matrix elements of the coordinate x for a harmonic oscillator

   $$\langle v|\boldsymbol{x}|v'\rangle = \int \psi_v^\star x\psi_v' dx = 0 \qquad \text{unless } v' = v \pm 1$$

   and

   $$\langle v + 1|\boldsymbol{x}|v\rangle = (2\beta)^{-1/2}(v + 1)^{1/2},$$
   $$\langle v - 1|\boldsymbol{x}|v\rangle = (2\beta)^{-1/2}(v)^{1/2},$$

   where $\beta = 4\pi^2 mv/h$ where $v = \frac{1}{2\pi}(k/m)^{1/2}$ and v is the vibrational quantum number. Evaluate the nonzero matrix elements of $\boldsymbol{x}^2$, $\boldsymbol{x}^3$, and $\boldsymbol{x}^4$; that is, evaluate the integrals

   $$\langle v|\boldsymbol{x}^r|v'\rangle = \int \psi_v x^r \psi_{v'} dx$$

   for $r = 2, 3,$ and 4 (without actually doing the explicit integrals, of course!).

   (b) From the results of (a), evaluate the average values of x, x^2, x^3, and x^4 in the vth vibrational state. Is it true that $\overline{x^2} = (\overline{x})^2$, or that $\overline{x^4} = \left(\overline{x^2}\right)^2$? What conclusions can you draw about the results of a measurement of x in the vth vibrational state?

6. J. I. Steinfeld (2nd Ed.), p. 74, #1

   In the spectrum of rubidium, an alkali metal, the short-wavelength limit of the diffuse series is 4,775 Å. The lines of the first doublet in the principal series ($5^2P_{3/2} \rightarrow 5^2S_{1/2}$ and $5^2P_{1/2} \rightarrow 5^2S_{1/2}$) have wavelengths of 7,800 Å and 7,947 Å, respectively.

   (a) By means of term symbols, write a general expression for the doublets of the sharp series, giving explicitly the possible values for n, the principal quantum number.

   (b) What is the spacing in cm^{-1} of the first doublet in the sharp series?

(c) Compute the first ionization potential of rubidium in cm^{-1} and electron volts (eV).

7. J. I. Steinfeld (2nd Ed.), p. 74, #2

In the first transition row of the periodic table there is a regular trend in ground state multiplicities from calcium (singlet) to manganese (sextet) to zinc (singlet), with one exception.

(a) Why does the multiplicity rise to a maximum and then fall?

(b) Explain the discontinuity shown by chromium (atomic number 24).

(c) Niobium, the element under vanadium in the second transition row, also shows a discontinuity in multiplicity, though vanadium does not. Explain.

8. J. I. Steinfeld (2nd Ed.), p. 75, #7

Evaluate the transition dipole moment matrix element between the ($n = 1, \ell = 0, m = 0[1\ ^2\text{S}]$) and the ($n = 2, \ell = 1, m = 1[2\ ^2\text{P}]$) states of atomic hydrogen. The wave functions are

$$\psi_{100} = \frac{1}{\pi^{1/2}a_0^{3/2}}e^{-r/a_0}Y_{00}(\theta, \phi),$$

$$\psi_{211} = \frac{1}{4(2\pi)^{1/2}a_0^{5/2}}re^{-r/2a_0}Y_{11}(\theta, \phi),$$

neglecting electron and nuclear spin. Remember that the dipole operator is a 3–vector,

$$\boldsymbol{\mu} = e_0\mathbf{r} = e_0(\hat{\boldsymbol{i}}\sin\theta\cos\phi + \hat{\boldsymbol{j}}\sin\theta\sin\phi + \hat{\boldsymbol{k}}\cos\theta).$$

Transition Amplitudes for $np^2 \leftarrow np\ n$'s Transitions in the L–S–J Limit

$$\mu \equiv -e\ 3^{-1/2}\int_0^\infty R_{np}rR_{n's}dr \qquad \text{Condon \& Shortley, p. 245.}$$

Condon & Shortley, p. 247 give all non–zero transition amplitudes:

$$\left\langle p^2\ ^1\text{S}|\boldsymbol{\mu}|sp\ ^1\text{P}_1\right\rangle = -(20)^{1/2}\mu$$

$$\left\langle p^2\ ^1\text{D}|\boldsymbol{\mu}|sp\ ^1\text{P}_1\right\rangle = +10\mu$$

$$\left\langle p^2\ ^3\text{P}_0|\boldsymbol{\mu}|sp\ ^3\text{P}_1\right\rangle = -(20)^{1/2}\mu$$

$$\left\langle p^2\ ^3\text{P}_1|\boldsymbol{\mu}|sp\ ^3\text{P}_0\right\rangle = -(20)^{1/2}\mu$$

$$\left\langle p^2\ ^3\text{P}_1|\boldsymbol{\mu}|sp\ ^3\text{P}_1\right\rangle = +(15)^{1/2}\mu$$

$$\left\langle p^2\ ^3\text{P}_1|\boldsymbol{\mu}|sp\ ^3\text{P}_2\right\rangle = -5\mu$$

$$\left\langle p^2\ ^3\text{P}_2|\boldsymbol{\mu}|sp\ ^3\text{P}_1\right\rangle = -5\mu$$

$$\left\langle p^2\ ^3\text{P}_2|\boldsymbol{\mu}|sp\ ^3\text{P}_2\right\rangle = +(75)^{1/2}\mu.$$

All other transition amplitudes are zero, most notably:

$$\left\langle p^2\ {}^3\mathrm{P}_0|\boldsymbol{\mu}|sp\ {}^3\mathrm{P}_0\right\rangle = 0$$

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

Energy Levels for np^2 and npn's in the L–S–J Basis Set

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

$$\mathbf{H}^{ee} = \begin{array}{c} {}^1\mathrm{S}_0 \\ {}^3\mathrm{P}_0 \\ {}^3\mathrm{P}_1 \\ {}^3\mathrm{P}_2 \\ {}^1\mathrm{D}_2 \end{array} \left|\begin{array}{ccccc} F_0 + 10F_2 & & & & \\ & F_0 - 5F_2 & & & \\ & & F_0 - 5F_2 & & \\ & & & F_0 - 5F_2 & \\ & & & & F_0 + F_2 \end{array}\right|$$

$$\mathbf{H}^{SO} = \begin{array}{c} {}^1\mathrm{S}_0 \\ {}^3\mathrm{P}_0 \\ {}^3\mathrm{P}_1 \\ {}^3\mathrm{P}_2 \\ {}^1\mathrm{D}_2 \end{array} \left|\begin{array}{ccccc} 0 & -2^{1/2}\zeta & & & \\ -2^{1/2}\zeta & -\zeta & & & \\ & & -\frac{1}{2}\zeta & & \\ & & & \frac{1}{2}\zeta & 2^{-1/2}\zeta \\ & & & 2^{-1/2}\zeta & 0 \end{array}\right|$$

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

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

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

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

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

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

Similarly, for the sp configuration

$$\mathbf{H} = \begin{array}{c} {}^3\mathrm{P}_2 \\ {}^3\mathrm{P}_1 \\ {}^1\mathrm{P}_1 \\ {}^3\mathrm{P}_0 \end{array} \left|\begin{array}{cccc} F_0 - G_1 + \frac{1}{2}\zeta & & & \\ & F_0 - G_1 - \frac{1}{2}\zeta & 2^{-1/2}\zeta & \\ & 2^{-1/2}\zeta & F_0 + G_1 & \\ & & & F_0 - G_1 - \zeta \end{array}\right|$$

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

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

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

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

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.

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1. Construct level diagrams for p^2 and sp 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

$$\left|{}^{\prime}sp\ {}^1P_1{}^{\prime}\right\rangle = \left|sp\ {}^1P_1\right\rangle + \frac{H_{{}^1P_1{}^3P_1}}{E^0_{{}^1P_1} - E^0_{{}^3P_1}}\left|sp\ {}^3P_1\right\rangle$$

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

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

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

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, in 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 $\mathbf{H}^{SO}$.

$$\underline{p^2} \quad \left(\frac{3}{2}\frac{3}{2}\right)_2 = \left(\frac{2}{3}\right)^{1/2}\left|{}^3P_2\right\rangle - \left(\frac{1}{3}\right)^{1/2}\left|{}^1D_2\right\rangle$$

$$\left(\frac{3}{2}\frac{1}{2}\right)_2 = \left(\frac{1}{3}\right)^{1/2}\left|{}^3P_2\right\rangle + \left(\frac{2}{3}\right)^{1/2}\left|{}^1D_2\right\rangle$$

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

$$\left(\frac{3}{2}\frac{3}{2}\right)_0 = \left(\frac{2}{3}\right)^{1/2}\left|{}^1S_0\right\rangle - \left(\frac{1}{3}\right)^{1/2}\left|{}^3P_0\right\rangle$$

$$\left(\frac{1}{2}\frac{1}{2}\right)_0 = \left(\frac{1}{3}\right)^{1/2}\left|{}^1S_0\right\rangle + \left(\frac{2}{3}\right)^{1/2}\left|{}^3P_0\right\rangle$$

$$\underline{sp} \quad \left(\frac{1}{2}\frac{3}{2}\right)_2 = \left|{}^3P_2\right\rangle$$

$$\left(\frac{1}{2}\frac{3}{2}\right)_1 = \left(\frac{2}{3}\right)^{1/2}\left|{}^1P_1\right\rangle - \left(\frac{1}{3}\right)^{1/2}\left|{}^3P_1\right\rangle$$

$$\left(\frac{1}{2}\frac{1}{2}\right)_1 = \left(\frac{1}{3}\right)^{1/2}\left|{}^3P_1\right\rangle + \left(\frac{2}{3}\right)^{1/2}\left|{}^3P_1\right\rangle$$

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

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.

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.