5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1985

Problem Set #3

1 Hund's Coupling Cases.

(a) Write the case (a) e and f–symmetry 3×3 effective Hamiltonian matrices for the $^2\Pi$, $^2\Sigma^+$ problem we have considered in Lecture. Include only the zeroth and first order matrix elements of $\mathbf{H}^{\text{ROT}}$ and $\mathbf{H}^{\text{SO}}$. Show that the effective rotational constants for $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are $B \pm B^2/A$ near the case (a) limit.

(b) Consider the case (b) limit where $A \ll BJ$. Form the approximate case (b) eigenfunctions for $^2\Pi$ as

$$\psi_\pm = 2^{-1/2}\left[\left|^2\Pi_{1/2}\right\rangle \pm \left|^2\Pi_{3/2}\right\rangle\right]$$

and re-express the full 3×3 matrix in this basis.

(i) You will find that both of the $^2\Pi$ eigenstates follow a $BN(N+1)$ rotational energy level expression. Which group of states E_+, ψ_+ or E_-, ψ_- corresponds to $N = J + 1/2$ and which to $N = J - 1/2$?

(ii) What is the ΔN selection rule for spin-orbit $^2\Pi \sim ^2\Sigma^+$ perturbations?

(iii) What is the ΔN selection rule for B$\mathbf{J}\cdot\mathbf{L}$ $^2\Pi \sim ^2\Sigma^+$ perturbations?

(c) Consider the case (c) limit for a "p–complex". This means that the $^2\Pi$ and $^2\Sigma^+$ states correspond to the $\lambda = 1$ and $\lambda = 0$ projections of an isolated $\ell = 1$ atomic orbital. In this case $\left\langle ^2\Pi|B\mathbf{L}_+|^2\Sigma^+\right\rangle = B[1 \cdot 2 - 0 \cdot 1]^{1/2} = 2^{1/2}B$. $B_\Pi = B_\Sigma = B$, $\left\langle ^2\Pi|A\mathbf{L}_+|^2\Sigma^+\right\rangle = 2^{1/2}A$, $A_\Pi = A$. Write the case (c) matrix and find the eigenvalues for $E_\Pi = E_\Sigma = E$. What is the pattern forming rotational quantum number when $A \gg BJ$? For each J–value you should find two near degenerate pairs of e, f levels above one e, f pair. What is the splitting of these two groups of molecular levels? How does this compare to the level pattern (degeneracies and splitting) for a ^2P atomic state?

(d) Consider the case (d) limit for a "p–complex". Use the same definitions of E_Π, E_Σ, B_Π, B_Σ, A_Π, α, β as for case (c) but set $A = 0$. Your transformed case (b) matrix will be helpful here. Show that R is the pattern forming quantum number by finding the relation between R and J for each of the six same-J, e/f eigenvalues.

2. Effective Hamiltonian Matrices.

(a) Set up the Hamiltonian,

$$\mathbf{H} = \mathbf{H}^{\text{ROT}} + \mathbf{H}^{\text{SPIN-ORBIT}}$$

for the 9 basis functions:

	Λ	S	Σ	Ω	
$^3\Pi$	1	1	1	2	$\left\|^3\Pi_2\right\rangle \|v_\Pi\rangle$
	−1	1	−1	−2	$\left\|^3\Pi_{-2}\right\rangle \|v_\Pi\rangle$
	1	1	0	1	$\left\|^3\Pi_1\right\rangle \|v_\Pi\rangle$
	−1	1	0	−1	$\left\|^3\Pi_{-1}\right\rangle \|v_\Pi\rangle$
	1	1	−1	+0	$\left\|^3\Pi_0\right\rangle \|v_\Pi\rangle$
	−1	1	1	−0	$\left\|^3\Pi_{-0}\right\rangle \|v_\Pi\rangle$
$^3\Sigma^+$	0	1	1	1	$\left\|^3\Sigma_1^+\right\rangle \|v_\Sigma\rangle$
	0	1	0	0	$\left\|^3\Sigma_0^+\right\rangle \|v_\Sigma\rangle$
	0	1	−1	−1	$\left\|^3\Sigma_{-1}^+\right\rangle \|v_\Sigma\rangle$.

Let

$$\alpha \equiv \langle \Lambda = 1 \| A\mathbf{L}_+ \| \Lambda = 0 \rangle$$

$$\beta \equiv \langle \Lambda = 1 \| \mathbf{L}_+ \| \Lambda = 0 \rangle$$

and use

$$\langle 1|\mathbf{H}|2\rangle = (-1)^{2J+S_1+S_2+\sigma_1+\sigma_2} \langle -1|\mathbf{H}| - 2\rangle$$

where $\sigma = 1$ for Σ^- states and 0 for all other states, to ensure phase consistency for

$$\langle \Lambda = 1|\mathbf{H}|\Lambda = 0\rangle \text{ and } \langle \Lambda = -1|\mathbf{H}|\Lambda = 0\rangle$$

matrix elements.

(b) Construct the e/f parity basis using the following phase definitions

$\boldsymbol{\sigma}_v \, |v, n\Lambda^\sigma S\Sigma, \Omega JM\rangle = (-1)^{J-2\Sigma+S+\sigma} \, |v, n - \Lambda^\sigma S - \Sigma, -\Omega JM\rangle$

e-levels $\quad \boldsymbol{\sigma}_v \psi = +(-1)^J \psi$

f-levels $\quad \boldsymbol{\sigma}_v \psi = -(-1)^J \psi$.

(c) Factor the 9×9 Hamiltonian into a 5×5 and a 4×4 matrix using the e/f basis functions.

(d) Obtain the centrifugal distortion correction terms for the $\left\langle ^3\Pi_0|\mathbf{H}|^3\Pi_0\right\rangle_e$, $\left\langle ^3\Pi_1|\mathbf{H}|^3\Pi_1\right\rangle_e$, and $\left\langle ^3\Pi_1|\mathbf{H}|^3\Pi_0\right\rangle_e$ matrix elements.

$$D_\Pi \equiv -\sum_{v_{\Pi'}} \frac{\left\langle v_\Pi|B|v'_\Pi\right\rangle^2}{E^0_{\Pi_v} - E^0_{\Pi_{v'}}}.$$

(e) Obtain the correction terms for the effect of remote $^3\Sigma^+$ levels on $^3\Pi$ for the $\left\langle ^3\Pi_0|\mathbf{H}|^3\Pi_0\right\rangle_{e \text{ and } f}$ and $\left\langle ^3\Pi_1|\mathbf{H}|^3\Pi_1\right\rangle_{e \text{ and } f}$ matrix elements.

$$o \equiv \sum_{v'_\Sigma} \frac{\left[\frac{1}{2}\alpha\left\langle v_\Pi|v'_\Sigma\right\rangle\right]^2}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

$$p \equiv 4\sum_{v'_\Sigma} \frac{\left[\frac{1}{2}\alpha\beta\left\langle v_\Pi|v'_\Sigma\right\rangle\left\langle v_\Pi|B|v'_\Sigma\right\rangle\right]}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

$$q \equiv 2\sum_{v'_\Sigma} \frac{\left[\beta\left\langle v_\Pi|B|v'_\Sigma\right\rangle\right]^2}{E^0_{\Pi v} - E^0_{\Sigma v'}}$$

Express diagonal contributions to the Λ–doubling of the $\Omega = 0$ and 1 $^3\Pi$ substates in terms of o, p, and q.