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5.80 Small-Molecule Spectroscopy and Dynamics  
Fall 2008

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# Lecture #17 Supplement

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## A. Energy Level Structure of ${}^2\Pi$ and ${}^2\Sigma$ States: Case (a) and Case (b) Limits

The  ${}^2\Pi$  Hamiltonian matrix was shown to be

$$\begin{array}{ccc} {}^2\Pi_{3/2}^{\pm} & 1/2A + B(x^2 - 2) & B(x^2 - 1)^{1/2} \\ {}^2\Pi_{1/2}^{\pm} & B(x^2 - 1)^{1/2} & -1/2A + Bx^2 \\ & x \equiv J + \frac{1}{2} & \end{array}$$

Case (a) limit  $|A - 2B| \gg Bx$

Use second-order perturbation theory to express the effect of the off-diagonal matrix element on the energy. The second order correction is valid when  $|A - 2B| \gg Bx$ . ( $\Delta E \gg V$ ).

$$\begin{aligned} E_{3/2} &= \frac{1}{2}A + B(x^2 - 2) + \frac{B^2}{A}(x^2 - 1) \\ E_{1/2} &= -\frac{1}{2}A + Bx^2 - \frac{B^2}{A}(x^2 - 1) \end{aligned}$$

Notice that if we define three new effective parameters the energy level expressions take on particularly

simple forms.

$$A_{\text{eff}} = A - 2B$$

$$B_{3/2 \text{ eff}} = B + \frac{B^2}{A}$$

$$B_{1/2 \text{ eff}} = B - \frac{B^2}{A}$$

Thus

$$E_{3/2} = \frac{1}{2}A_{\text{eff}} + B_{3/2 \text{ eff}}(x^2 - 1)$$

$$E_{1/2} = -\frac{1}{2}A_{\text{eff}} + B_{1/2 \text{ eff}}(x^2 - 1)$$

Thus we have two stacks of energy levels for which the extrapolated  $x = 1$  levels are symmetrically split on either side of  $E_{\Pi}$  and whose effective rotational constants (just like for  $^1\Sigma$  molecule) can be averaged to give the true  $B_{\Pi}$  rotational constant.

A second limiting case is obtained when  $A = 0$ . This is the case (b) limit. If  $A = 0$ , we must diagonalize the  $^2\Pi$  Hamiltonian matrix. We solved the problem for two levels separated by  $2d$ , with an off-diagonal matrix element  $V$  connecting them, and for an average energy  $E_o$ . In the present problem

$$E_o = E_{\Pi} - B + Bx^2$$

$$d = -B$$

$$V = B(x^2 - 1)^{1/2}$$

$$E^{\pm} = E_o \pm d \left( 1 + \left( \frac{V}{d} \right)^2 \right)^{1/2}$$

$$E^{\pm} = E_{\Pi} + B(x^2 - 1) \mp \left[ 1 - \left( \frac{B(x^2 - 1)^{1/2}}{-B} \right)^2 \right]^{1/2}$$

$$= E_{\Pi} + B(x^2 - 1) \mp Bx$$

Observe the difference in energy between an  $E^+$  level for  $x \rightarrow x + 1$  and  $E^-$  level for  $x \rightarrow x$ . (Note the  $\pm$  does not refer to parity in this problem.)

$$E^+(x + 1) - E^-(x) = B(x^2 + 2x + 1 - x - 1 - 1 - x^2 - x + 1) = 0$$

Thus pairs of levels corresponding to “ $\Omega = 3/2$ ”,  $J + 1$  and “ $\Omega = 1/2$ ”,  $J$  are exactly degenerate. If  $A$  is not quite zero, then these pairs will be slightly split and the splitting is called the spin-splitting. At high

enough  $J$ , a  ${}^2\Pi$  molecule will always develop this case (b) energy level pattern. The spacing between these degenerate pairs of levels is

$$E^+(J+1) - E^+(J) = B(x^2 + 2x + 1 - 1 - x - 1 - x^2 + 1 + x) = 2Bx$$

Note that the spacing between successive rotational levels of a  ${}^1\Sigma^+$  state is  $2BJ$ . Thus we see another striking similarity between  ${}^2\Pi$  in the case (b) limit and the familiar  ${}^1\Sigma$  molecule. We have not considered  $\Lambda$  doubling yet; in actuality  ${}^2\Pi$  levels in the case (b) limit fall in near degenerate groups of four, two of each parity.

Consider the  ${}^2\Sigma^+$  state. No diagonalization is necessary so we do not have to talk about limiting cases.

$$\begin{aligned} E({}^2\Sigma^{+\pm}) &= B[x^2 \pm (-1)^{J+S}x] \\ E({}^2\Sigma^{++}(x+1)) - E({}^2\Sigma^{++}(x)) &= B[x^2 + 2x + 1 + (-1)^{J+1+S}(x+1)] - B[x^2 + (-1)^{J+S}x] \\ &= B[2x + 1 - (-1)^{J+S}(x+1) - (-1)^{J+S}x] \\ &= B(2x+1)[1 - (-1)^{J+S}] \end{aligned}$$

Thus  ${}^2\Sigma^{++}(J+1)$  and  ${}^2\Sigma^{++}(J)$  are either degenerate or they are separated by

$$(4x+2)B$$

Note that for  ${}^1\Sigma$  levels

$$E({}^1\Sigma(J+1)) - E({}^1\Sigma(J-1)) = (4J+2)B.$$

The  ${}^2\Sigma^+$  levels therefore occur in degenerate pairs, both members of each pair of the same total parity, the parity of successive pairs alternating, and the spacing between adjacent pairs is  $2Bx$ . Again we see an exact analog with  ${}^1\Sigma$  energy level structure where a new quantum number  $N$

$$N = J \pm \frac{1}{2}$$

is suggested for which the rotational energy levels of both  ${}^2\Sigma$  and  ${}^2\Pi$  states look like the rotational energy levels of a  ${}^1\Sigma$  state, but with  $J$  replaced by  $N$ .

## B. Matrix Elements for ${}^2\Pi$ and ${}^2\Sigma$ States Including $\Pi \sim \Sigma$ Perturbation

The Hamiltonian is

$$\mathbf{H} = \mathbf{H}_{ev} + B(r)\mathbf{R}^2 + AL \cdot \mathbf{S} \quad (1)$$

$\mathbf{H}_{ev}$  is the electronic and vibrational (vibronic) Hamiltonian. It only has diagonal matrix elements. We will neglect the spin-rotation term because it is small and the spin-spin term because it is rigorously zero (there is only one spin!).

The Hamiltonian was put into a convenient form in the previous handout.

$$\begin{aligned} \mathbf{H} = \mathbf{H}_{ev} + B(r) \left[ (\mathbf{J}^2 - \mathbf{J}_z^2) + (\mathbf{S}^2 - \mathbf{S}_z^2) + \mathbf{L}_\perp^2 - (\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+) - (\mathbf{J}_+\mathbf{S}_- + \mathbf{J}_-\mathbf{S}_+) \right] \\ + AL_z\mathbf{S}_z + \left( B(r) + \frac{1}{2}A \right) (\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+) \end{aligned} \quad (2)$$

If we choose the  $|v\rangle |n\Lambda S \Sigma\rangle |\Omega JM\rangle$  basis we know all the matrix elements necessary to construct the  ${}^2\Pi$ ,  ${}^2\Sigma$  Hamiltonian matrix. Some simplifications:

1. The diagonal matrix elements of  $\mathbf{H}_{ev} + B(r)\mathbf{L}_\perp^2$  are by definition  $T_e + G(v)$ , where  $T_e$  is the electronic energy and  $G(v)$  is the vibrational energy.
2.  $\langle v|B(r)|v\rangle \equiv B(v)$ .
3. Diagonal matrix elements of  $(\mathbf{S}^2 - \mathbf{S}_z^2) = \frac{1}{2} \left( \frac{1}{2} + 1 \right) - (\pm \frac{1}{2})^2 = \frac{1}{2}$  for all doublet states (i.e.,  $S = \frac{1}{2}, \Sigma = \pm \frac{1}{2}$ ).
4.  $J(J+1) = \left( J + \frac{1}{2} \right)^2 - \frac{1}{4}$ .

$$\begin{aligned} \langle v | \langle n\Lambda' S' \Sigma' | \langle \Omega' J' M' | \mathbf{H} | \Omega JM \rangle | n\Lambda S \Sigma \rangle | v \rangle = \\ \left\{ T_e + G(v) + B(v) \left[ J(J+1) - \Omega^2 + \frac{1}{2} \right] + A\Lambda\Sigma \right\} \delta_{J'J} \delta_{\Omega'\Omega} \delta_{M'M} \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Sigma'\Sigma} \\ - \{ \text{matrix elements of } B(r)(\mathbf{J}_+\mathbf{S}_- + \mathbf{J}_-\mathbf{S}_+) \} \delta_{J'J} \delta_{M'M} \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Omega'\Omega \pm 1} \delta_{\Sigma'\Sigma \pm 1} \\ - \{ \text{matrix elements of } B(r)(\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+) \} \delta_{J'J} \delta_{M'M} \delta_{S'S} \delta_{\Sigma'\Sigma} \delta_{\Lambda'\Lambda \pm 1} \delta_{\Omega'\Omega \pm 1} \\ + \left\{ \text{matrix elements of } \left( B(r) + \frac{1}{2}A \right) (\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+) \right\} \\ \delta_{J'J} \delta_{M'M} \delta_{\Omega'\Omega} \delta_{\Lambda'\Lambda \pm 1} \delta_{\Sigma'\Sigma \mp 1} (\delta_{S'S} + \delta_{S'S \mp 1}) \end{aligned} \quad (3)$$

The first { } contains the diagonal part of  $\mathbf{H}$ , the second { } contains the part off-diagonal by one in  $\Omega$  and  $\Sigma$ , the third { } contains the part off-diagonal by one in  $\Omega$  and  $\Lambda$ , and the fourth { } contains the part off-diagonal by one in  $\Sigma$ ,  $\Lambda$ , and  $S$ . Only the

$$\frac{1}{2}A(\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+)$$

part of the fourth { } can have matrix elements off-diagonal in  $S$ . The first term of (3) allows us to immediately write the diagonal matrix elements. The states we are considering are:

$$\begin{aligned} |^2\Pi_{3/2}\rangle &= |JM, \Omega = 3/2\rangle |\Lambda = 1, \Sigma = 1/2, S = 1/2\rangle \\ |^2\Pi_{1/2}\rangle &= |JM, \Omega = 1/2\rangle |\Lambda = 1, \Sigma = -1/2, S = 1/2\rangle \\ |^2\Pi_{-1/2}\rangle &= |JM, \Omega = -1/2\rangle |\Lambda = -1, \Sigma = 1/2, S = 1/2\rangle \\ |^2\Pi_{-3/2}\rangle &= |JM, \Omega = -3/2\rangle |\Lambda = -1, \Sigma = -1/2, S = 1/2\rangle \\ |^2\Sigma_{1/2}\rangle &= |JM, \Omega = 1/2\rangle |\Lambda = 0, \Sigma = 1/2, S = 1/2\rangle \\ |^2\Sigma_{-1/2}\rangle &= |JM, \Omega = -1/2\rangle |\Lambda = 0, \Sigma = -1/2, S = 1/2\rangle \end{aligned} \quad (4)$$

$$\langle ^2\Pi_{3/2}|\mathbf{H}^2|^2\Pi_{3/2}\rangle = \langle ^2\Pi_{-3/2}|\mathbf{H}^2|^2\Pi_{-3/2}\rangle = T_\Pi + G_\Pi(v) + \frac{1}{2}A_\Pi + B_\Pi(v) \left[ \left( J + \frac{1}{2} \right)^2 - 2 \right]$$

$$\langle ^2\Pi_{1/2}|\mathbf{H}^2|^2\Pi_{1/2}\rangle = \langle ^2\Pi_{-1/2}|\mathbf{H}^2|^2\Pi_{-1/2}\rangle = T_\Pi + G_\Pi(v) - \frac{1}{2}A_\Pi + B_\Pi(v) \left( J + \frac{1}{2} \right)^2 \quad (5)$$

$$\langle ^2\Sigma_{1/2}|\mathbf{H}^2|^2\Sigma_{1/2}\rangle = \langle ^2\Sigma_{-1/2}|\mathbf{H}^2|^2\Sigma_{-1/2}\rangle = T_\Sigma + G_\Sigma(v) + B_\Sigma(v) \left( J + \frac{1}{2} \right)^2. \quad (6)$$

The second term of (3) allows us to construct off-diagonal matrix elements among the  $^2\Pi$  functions and among the  $^2\Sigma$  functions, but not between  $^2\Pi$  and  $^2\Sigma$  functions.

$$\begin{aligned} -\langle v(\Omega \pm 1)JM, n\Lambda S(\Sigma \pm 1) | B(r)(\mathbf{J}_+\mathbf{S}_- + \mathbf{J}_-\mathbf{S}_+) | v, \Omega JM, n\Lambda S \Sigma \rangle = \\ -B(v)[(S \mp \Sigma)(S \pm \Sigma + 1)(J \pm \Omega + 1)(J \mp \Omega)]^{1/2} \end{aligned} \quad (7)$$

Note that  $B(r) \rightarrow B(v)$  since we took matrix elements diagonal in  $v$  and within an electronic state. The matrix elements are

$$\langle ^2\Pi_{3/2}|\mathbf{H}^2|^2\Pi_{1/2}\rangle = \langle ^2\Pi_{-3/2}|\mathbf{H}^2|^2\Pi_{-1/2}\rangle = -B_\Pi(v) \left[ \left( J + \frac{1}{2} \right)^2 - 1 \right]^{1/2} \quad (8)$$

$$\langle ^2\Pi_{3/2}|\mathbf{H}^2|^2\Pi_{-1/2}\rangle = \langle ^2\Pi_{-3/2}|\mathbf{H}^2|^2\Pi_{1/2}\rangle = 0 \quad (9)$$

$$\langle ^2\Pi_{3/2}|\mathbf{H}^2|^2\Pi_{-3/2}\rangle = 0 \quad (10)$$

$$\langle ^2\Pi_{1/2}|\mathbf{H}^2|^2\Pi_{-1/2}\rangle = 0 \quad (11)$$

All of the  ${}^2\Pi$  matrix elements between values of  $\Omega$  with opposite signs would require  $\Lambda = 1 \rightarrow -1$  or a change in  $\Lambda$  by 2. No operator in our Hamiltonian can do that.

$$\langle {}^2\Sigma_{1/2} | \mathbf{H} | {}^2\Sigma_{-1/2} \rangle = -B_{\Sigma}(v) \left( J + \frac{1}{2} \right) \quad (12)$$

The third and fourth terms of equation (3) allow us to write the matrix elements between  ${}^2\Pi$  and  ${}^2\Sigma$  states.

$$\begin{aligned} & - \langle v', n'(\Lambda \pm 1) S \Sigma, (\Omega \pm 1) J M | B(r) (\mathbf{J}_+ \mathbf{L}_- + \mathbf{J}_- \mathbf{L}_+) | v, n \Lambda S \Sigma, \Omega J M \rangle = \\ & - \langle v', n'(\Lambda \pm 1) S \Sigma | B(r) L_{\pm} | v, n \Lambda S \Sigma \rangle \langle (\Omega \pm 1) J M | \mathbf{J}_{\mp} | \Omega J M \rangle \end{aligned} \quad (13)$$

The first factor of (13) cannot be simplified further and is treated as an unknown constant. This is a matrix element between two electronic states, each with its own set of vibrational eigenfunctions.

The  ${}^2\Pi$ ,  ${}^2\Sigma$  matrix elements from this term are

$$\langle {}^2\Pi_{3/2} | \mathbf{H} | {}^2\Sigma_{1/2} \rangle = \langle {}^2\Pi_{-3/2} | \mathbf{H} | {}^2\Sigma_{-1/2} \rangle = - \langle v', \Pi | B_{\Pi\Sigma} \mathbf{L}_+ | v, \Sigma \rangle \left[ \left( J + \frac{1}{2} \right)^2 - 1 \right]^{1/2} \quad (14)$$

$$\langle {}^2\Pi_{1/2} | \mathbf{H} | {}^2\Sigma_{-1/2} \rangle = \langle {}^2\Pi_{-1/2} | \mathbf{H} | {}^2\Sigma_{1/2} \rangle = - \langle v', \Pi | B_{\Pi\Sigma} \mathbf{L}_+ | v, \Sigma \rangle \left( J + \frac{1}{2} \right) \quad (15)$$

If the vibrational wave functions are known for the  $v'$ ,  ${}^2\Pi$  and  $v$ ,  ${}^2\Sigma$  states, then  $B_{\Pi\Sigma}$  can be calculated

$$B_{\Pi\Sigma} = \left\langle v', \Pi \left| \frac{\hbar^2}{2\mu r^2} \right| v, \Sigma \right\rangle. \quad (16)$$

Normally  $B_{\Pi\Sigma}$  is left as an unknown constant. Finally, the fourth term of equation (3) gives us the last matrix element between the  ${}^2\Pi$  and  ${}^2\Sigma$  functions.

$$\begin{aligned} & \left\langle v', n'(\Lambda \pm 1) S (\Sigma \mp 1), \Omega J M \left| \left( B(r) + \frac{1}{2} A \right) (\mathbf{L}_+ \mathbf{S}_- + \mathbf{L}_- \mathbf{S}_+) \right| v, n \Lambda S \Sigma, \Omega J M \right\rangle \\ & = \left\langle v', n'(\Lambda \pm 1) \left| \left( B(r) + \frac{1}{2} A \right) \mathbf{L}_{\pm} \right| v, n \Lambda \right\rangle \langle S (\Sigma \mp 1) | \mathbf{S}_{\mp} | S \Sigma \rangle \end{aligned} \quad (17)$$

The first factor of (17) cannot be simplified. The second factor is one of our known matrix elements of  $\mathbf{S}_{\pm}$ . Thus the final necessary matrix element of the Hamiltonian is

$$\langle {}^2\Pi_{1/2} | \mathbf{H} | {}^2\Sigma_{1/2} \rangle = \langle {}^2\Pi_{-1/2} | \mathbf{H} | {}^2\Sigma_{-1/2} \rangle = \langle v', \Pi | B_{\Pi\Sigma} \mathbf{L}_+ | v, \Sigma \rangle + \frac{1}{2} \langle v, \Pi | A_{\Pi\Sigma} \mathbf{L}_+ | v, \Sigma \rangle \quad (18)$$

The matrix elements for the  ${}^2\Pi$ ,  ${}^2\Sigma$  Hamiltonian are in equations (4), (5), (6), (8), (9), (10), (11), (12), (14), (15), and (18). The matrix is a  $6 \times 6$  matrix which contains only 10 zeroes. The matrix could be factored into two  $3 \times 3$  blocks if suitable linear combinations of the functions with the same value of  $|\Lambda|$  and  $|\Omega|$  are taken. Such linear combinations correspond to the choice of “parity” basis functions. Like  $J$  and  $M$ , the eigenvalue of the parity operator is a rigorously good quantum number (in the absence of electric and magnetic fields).

## C. Parity

1. What is the parity operator?
2. What effect does it have on our basis functions?
3. How do we construct parity eigenfunctions?
4. What are the eigenvalues of the parity operator operating on parity eigenfunctions?

Parity is a difficult concept and impossible to explain without recourse to a detailed examination of the form of the actual  $|\Omega JM\rangle$  and  $|n\Lambda S\Sigma\rangle$  functions.

The parity operator can be regarded as a reflection in a plane containing the diatomic molecule ( $\sigma_v$ ). The effect of this operation is

$$\sigma_v |n\Lambda S\Sigma\rangle = (-1)^{S-\Sigma+\Lambda} |n - \Lambda S - \Sigma\rangle. \quad (19)$$

If  $\Lambda = 0$ , then it is possible to have two different types of  $\Sigma$  states:  $\Sigma^+$  and  $\Sigma^-$ . This extra label, used only for  $\Sigma$  (i.e.,  $\Lambda = 0$ ) states, represents an intrinsic property of  $\Sigma$  states.

$$\sigma_v |n\Lambda = 0S\Sigma\rangle = \pm(-1)^{S-\Sigma} |n\Lambda = 0S - \Sigma\rangle \quad (20)$$

The  $\pm$  on the RHS of (20) is the same  $\pm$  that appears as a right superscript for  $\Sigma$  states. Generalizing equation (19) by letting  $\sigma = 0$  for  $\Sigma^+$  states and  $\sigma = 1$  for  $\Sigma^-$  states and  $\sigma = 0$  for all  $\Lambda > 0$  states we have

$$\sigma_v |n\Lambda S\Sigma\rangle = (-1)^{S-\Sigma+\Lambda+\sigma} |n - \Lambda S - \Sigma\rangle \quad (21)$$

also

$$\sigma_v |\Omega JM\rangle = (-1)^{J-\Omega} |-\Omega JM\rangle \quad (22)$$

and

$$\sigma_v |v\rangle = |v\rangle. \quad (23)$$

Combining (21), (22), (23) and using  $\Omega = \Lambda + \Sigma$ :

$$\sigma_v |v, n\Lambda S\Sigma, \Omega JM\rangle = (-1)^{J-2\Sigma+S+\sigma} |v, n - \Lambda S - \Sigma, -\Omega JM\rangle. \quad (24)$$

We have now shown the effect of the parity operator on our basis functions. Parity eigenfunctions are constructed by forming linear combinations of  $|\Omega JM\rangle |n\Lambda S\Sigma\rangle$  functions such that  $\sigma_v$  operating on the linear combination gives back the same linear combination, multiplied either by +1 or -1.

The  $\pm 1$  coefficient is the eigenvalue of the parity operator and is a good quantum number (there are no matrix elements off-diagonal in parity). The parity functions for our  ${}^2\Pi$ ,  ${}^2\Sigma$  problem are

$${}^2\Pi_{3/2}^{\pm} = \frac{1}{\sqrt{2}} \left[ |{}^2\Pi_{3/2}\rangle \mp (-1)^{J+S} |{}^2\Pi_{-3/2}\rangle \right] \quad (25a)$$

$${}^2\Pi_{1/2}^{\pm} = \frac{1}{\sqrt{2}} \left[ |{}^2\Pi_{1/2}\rangle \mp (-1)^{J+S} |{}^2\Pi_{-1/2}\rangle \right] \quad (25b)$$

$${}^2\Sigma^{+\pm} = \frac{1}{\sqrt{2}} \left[ |{}^2\Sigma_{1/2}^+\rangle \mp (-1)^{J+S} |{}^2\Sigma_{-1/2}^+\rangle \right] \quad (25c)$$

$${}^2\Sigma^{-\pm} = \frac{1}{\sqrt{2}} \left[ |{}^2\Sigma_{1/2}^-\rangle \pm (-1)^{J+S} |{}^2\Sigma_{-1/2}^-\rangle \right]. \quad (25d)$$

It is now possible to construct matrix elements using parity basis functions. I will list the matrix elements:

$$\langle {}^2\Pi_{3/2}^{\pm} | \mathbf{H} | {}^2\Pi_{3/2}^{\pm} \rangle = T_{\Pi} + G_{\Pi}(v) + \frac{1}{2}A_{\Pi} + B_{\Pi}(v) \left[ \left( J + \frac{1}{2} \right)^2 - 2 \right] \quad (26)$$

$$\langle {}^2\Pi_{1/2}^{\pm} | \mathbf{H} | {}^2\Pi_{1/2}^{\pm} \rangle = T_{\Pi} + G_{\Pi}(v) - \frac{1}{2}A_{\Pi} + B_{\Pi}(v) \left( J + \frac{1}{2} \right)^2 \quad (27)$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \mathbf{H} | {}^2\Pi_{1/2}^{\pm} \rangle = -B_{\Pi}(v) \left[ \left( J + \frac{1}{2} \right)^2 - 1 \right]^{1/2} \quad (28)$$

$$\langle {}^2\Sigma^{+\pm} | \mathbf{H} | {}^2\Sigma^{+\pm} \rangle = T_{\Sigma^+} + G_{\Sigma^+}(v) + B_{\Sigma^+}(v) \left[ \left( J + \frac{1}{2} \right)^2 \pm (-1)^{J+S} \left( J + \frac{1}{2} \right) \right] \quad (29)$$

$$\langle {}^2\Sigma^{-\pm} | \mathbf{H} | {}^2\Sigma^{-\pm} \rangle = T_{\Sigma^-} + G_{\Sigma^-}(v) + B_{\Sigma^-}(v) \left[ \left( J + \frac{1}{2} \right)^2 \mp (-1)^{J+S} \left( J + \frac{1}{2} \right) \right] \quad (29a)$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \mathbf{H} | {}^2\Sigma^{+\pm} \rangle = -\langle v' | \Pi | B_{\Pi\Sigma^+} \mathbf{L}_+ | v, \Sigma \rangle \left[ \left( J + \frac{1}{2} \right)^2 - 1 \right]^{1/2} \quad (30)$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \mathbf{H} | {}^2\Sigma^{-\pm} \rangle = -\langle v', \Pi | B_{\Pi\Sigma^-} \mathbf{L}_+ | v, \Sigma \rangle \left[ \left( J + \frac{1}{2} \right)^2 - 1 \right]^{1/2} \quad (30a)$$

$$\langle {}^2\Pi_{1/2}^{\pm} | \mathbf{H} | {}^2\Sigma^{+\pm} \rangle = \frac{1}{2} \langle v', \Pi | A_{\Pi\Sigma^+} \mathbf{L}_+ | v, \Sigma \rangle + \langle v', \Pi | B_{\Pi\Sigma^+} \mathbf{L}_+ | v, \Sigma \rangle \left[ 1 \pm (-1)^{J+S} \left( J + \frac{1}{2} \right) \right] \quad (31)$$

$$\langle {}^2\Pi_{1/2}^{\pm} | \mathbf{H} | {}^2\Sigma^{-\pm} \rangle = \frac{1}{2} \langle v', \Pi | A_{\Pi\Sigma^-} \mathbf{L}_+ | v, \Sigma \rangle + \langle v', \Pi | B_{\Pi\Sigma^-} \mathbf{L}_+ | v, \Sigma \rangle \left[ 1 \mp (-1)^{J+S} \left( J + \frac{1}{2} \right) \right] \quad (31a)$$

This is all you will need until we start to worry about second-order effects such as centrifugal distortion and lambda doubling.