5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture # 19 Supplement

Second-Order Effects: Centrifugal Distortion and Λ–Doubling

Centrifugal distortion originates from vibration-rotation interactions. In other words, it results from the fact that the rotational constant B isn't a constant at all but rather a function of r and as a result can have matrix elements off-diagonal in v. Since differences between vibrational energy levels are much larger than differences between rotational energy levels, it is appropriate to introduce corrections to the rotational Hamiltonian matrix elements by second-order perturbation theory involving summations over vibrational levels of the form:

$$D \equiv \sum_{v' \neq v} \frac{\langle v|B(r)|v'\rangle \langle v'|B(r)|v\rangle}{E_v - E_{v'}}. \tag{1}$$

We must now examine our rotational Hamiltonian matrix to obtain the precise centrifugal distortion corrections appropriate to each of the matrix elements. The simple minded prescription: "Replace $B(r)$ by $B(v) - D(v)J(J+1)$ wherever $B(r)$ occurs" will be shown to be incorrect. We will use the $^2\Pi$, $^2\Sigma$ Hamiltonian again as an example.

First consider corrections to the $\left\langle {}^2\Pi_{1/2}|\mathbf{H}|{}^2\Pi_{1/2}\right\rangle$ matrix element. The relevant matrix elements off-diagonal in v (but diagonal in $|\Lambda|$ and S) are

$$\begin{gathered}\left\langle v, {}^2\Pi^{\pm}_{1/2}|B(r)\mathbf{R}^2|v', {}^2\Pi^{\pm}_{1/2}\right\rangle \\ \left\langle v, {}^2\Pi^{\pm}_{1/2}|B(r)\mathbf{R}^2|v', {}^2\Pi^{\pm}_{3/2}\right\rangle.\end{gathered} \tag{2}$$

Since our basis functions are actually product functions, and since $B(r)$ only operates on $|v\rangle$ and $\mathbf{R}^2$ only operates on $\left|\Pi^{\pm}_{\Omega}\right\rangle$, we can factor these matrix elements.

$$\begin{gathered}\langle v|B(r)|v'\rangle \left\langle {}^2\Pi^{\pm}_{1/2}|\mathbf{R}^2|{}^2\Pi^{\pm}_{1/2}\right\rangle \\ \langle v|B(r)|v'\rangle \left\langle {}^2\Pi^{\pm}_{1/2}|\mathbf{R}^2|{}^2\Pi^{\pm}_{3/2}\right\rangle.\end{gathered} \tag{3}$$

The second order correction to $\left\langle {}^2\Pi_{1/2}, v | B(r)\mathbf{R}^2 | {}^2\Pi_{1/2}, v \right\rangle$ is therefore

$$E^{(2)}_{1/2,1/2} = \sum_{v'} \frac{\langle v|B(r)|v'\rangle^2 \left[\left\langle {}^2\Pi^{\pm}_{1/2} | \mathbf{R}^2 | {}^2\Pi^{\pm}_{1/2} \right\rangle^2 + \left\langle {}^2\Pi^{\pm}_{1/2} | \mathbf{R}^2 | {}^2\Pi^{\pm}_{3/2} \right\rangle^2 \right]}{G(v) - G(v')}. \tag{4}$$

Rewrite (4) using the definition of D,

$$E^{(2)}_{1/2,1/2} = -D \left[\left\langle {}^2\Pi^{\pm}_{1/2} | \mathbf{R}^2 | {}^2\Pi^{\pm}_{1/2} \right\rangle^2 + \left\langle {}^2\Pi_{1/2} | \mathbf{R}^2 | {}^2\Pi_{3/2} \right\rangle^2 \right]. \tag{5}$$

The first matrix element is the coefficient of $B(v)$ in equation (27) of the previous handout and the second matrix element is the coefficient in (28), thus

$$E^{(2)}_{1/2,1/2} = -D \left[\left(J + \frac{1}{2} \right)^4 + \left[\left(J + \frac{1}{2} \right)^2 - 1 \right] \right]. \tag{6}$$

Similar arguments give the centrifugal distortion corrections to the other diagonal matrix elements. For $\left\langle {}^2\Pi_{3/2} | \mathbf{H} | {}^2\Pi_{3/2} \right\rangle$ we get

$$E^{(2)}_{3/2,3/2} = -D \left\{ \left[\left(J + \frac{1}{2} \right)^2 - 2 \right]^2 + \left[\left(J + \frac{1}{2} \right)^2 - 1 \right] \right\}. \tag{7}$$

For $\left\langle {}^2\Sigma^{+\pm} | \mathbf{H} | {}^2\Sigma^{+\pm} \right\rangle$ we get

$$E^{(2)}_{\Sigma\Sigma^{+}} = -D \left\{ \left(J + \frac{1}{2} \right)^2 \mp (-1)^{J+S} \left(J + \frac{1}{2} \right) \right\}^2. \tag{8}$$

Similarly

$$E^{(2)}_{\Sigma\Sigma^{-}} = -D \left\{ \left(J + \frac{1}{2} \right)^2 \pm (-1)^{J+S} \left(J + \frac{1}{2} \right) \right\}^2. \tag{8a}$$

All that is left now is corrections to off-diagonal matrix elements. The only off-diagonal matrix element for which a centrifugal distortion correction is necessary is $\left\langle {}^2\Pi_{1/2} | \mathbf{H} | {}^2\Pi_{3/2} \right\rangle$. The second order correction is

$$E^{(2)}_{1/2,3/2} = \sum_{v'} \frac{\langle v|B(r)|v'\rangle^2}{\frac{1}{2}[G_{1/2}(v) + G_{3/2}(v)] - \frac{1}{2}[G_{1/2}(v') + G_{3/2}(v')]} \times \\ \left[\left\langle {}^2\Pi_{1/2} | \mathbf{R}^2 | {}^2\Pi_{3/2} \right\rangle \left\langle {}^2\Pi_{3/2} | \mathbf{R}^2 | {}^2\Pi_{3/2} \right\rangle + \left\langle {}^2\Pi_{1/2} | \mathbf{R}^2 | {}^2\Pi_{1/2} \right\rangle \left\langle {}^2\Pi_{1/2} | \mathbf{R}^2 | {}^2\Pi_{3/2} \right\rangle \right]. \tag{9}$$

Note that the energy denominator of (9) is more complicated than in equation (4), but if the spin-orbit constant A_{Π} is independent of v, then the energy denominator reduces to $G(v) - G(v')$. It is possible to choose this symmetric form for the energy denominator because $G_{3/2}(v) - G_{1/2}(v) \equiv A(v)$ and typically $|A(v)| \ll G(v) - G(v-1) \equiv \Delta G\left(v - \frac{1}{2}\right)$. Notice that a truncated power series explanation gives

$$\frac{1}{\Delta G(v) + A} \approx \frac{1}{\Delta G(v)}\left(1 - \frac{A}{\Delta G(v)}\right).$$

$$E^{(2)}_{1/2,3/2} = +D\left[\left(J + \frac{1}{2}\right)^2 - 1\right]^{1/2}\left[2\left(J + \frac{1}{2}\right)^2 - 2\right] \tag{10}$$

A diagrammatic approach to these second-order corrections makes their derivation mechanical and easily understood.

1. Write down two basis functions on opposite sides of a piece of paper. The second-order corrections to their matrix element of **H** is to be obtained.

2. Inspect the matrix elements of **H** of the left-hand function with all other basis functions and list in the middle of the page those other basis functions which have non-zero matrix elements with the left-hand function.

3. Draw lines connecting these middle basis functions with the left-hand functions and write above each line the actual matrix element.

4. Examine the Hamiltonian matrix elements of the right-hand function with the middle basis functions. For each non-zero element draw a connecting line and write the matrix element over it.

5. Inspect the completed diagram for all continuous paths from left to right. The second-order corrections are simply products of the matrix elements above the connecting lines divided by an energy denominator of the form

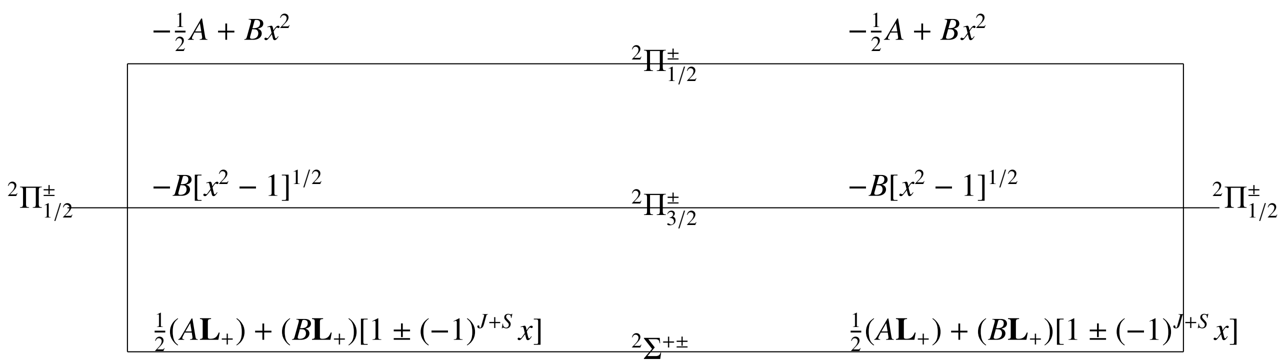
$$\frac{1}{2}(E_{\text{left}} + E_{\text{right}}) - E_{\text{middle}}(v'). \tag{11}$$

   I will now use this diagrammatic method to obtain the second-order matrix elements responsible for the lambda doubling in $^2\Pi$ states.

All electronic states with $|\Lambda| > 0$ have pairs of levels, one for each sign of Λ. These pairs of levels would be degenerate (exactly the same energy) if we did not consider second-order corrections to the Hamiltonian matrix. The energy separation between these pairs of levels which is introduced by second-order effects is called the lambda doubling. A typical size for a lambda doubling is 10^{-4} cm^{-1} although lambda doublings 10^4 times *larger* or *smaller* than this are not uncommon. When one chooses a parity basis set, it turns out that the two components of a Λ doublet have opposite parity. It also turns out that the existence of a non-zero lambda doubling is due [with one exception: $^3\Pi_0$ which is substantially due to spin-spin matrix elements of $\alpha\left(\mathbf{S}_+^2 + \mathbf{S}_-^2\right)$] to second-order interactions of Π states with Σ states. The physical reason for this is simple. Σ states have $\Lambda = 0$, thus second order matrix elements exist which connect basis functions (non-parity basis) with $\Lambda > 0$ to functions with $\Lambda < 0$. There is a second reason: Σ levels, unlike Π or Δ levels, do not come in nearly degenerate pairs with one member of each parity. Thus, since only levels of the same parity can interact (repel each other), only for Σ states can an imbalance exist in the repulsion of $|\Lambda| > 0$ opposite parity levels.

We now construct the diagram for second order effects of $^2\Sigma^+$ states on $^2\Pi$ states.

Let $x \equiv J + \frac{1}{2}$



(12)

We are only concerned with $^2\Sigma$ states in the middle. The two upper paths gave us the centrifugal distortion corrections. The thorough student will notice that there are some second-order terms of the form A^2 and AB that we have not considered (and will not).

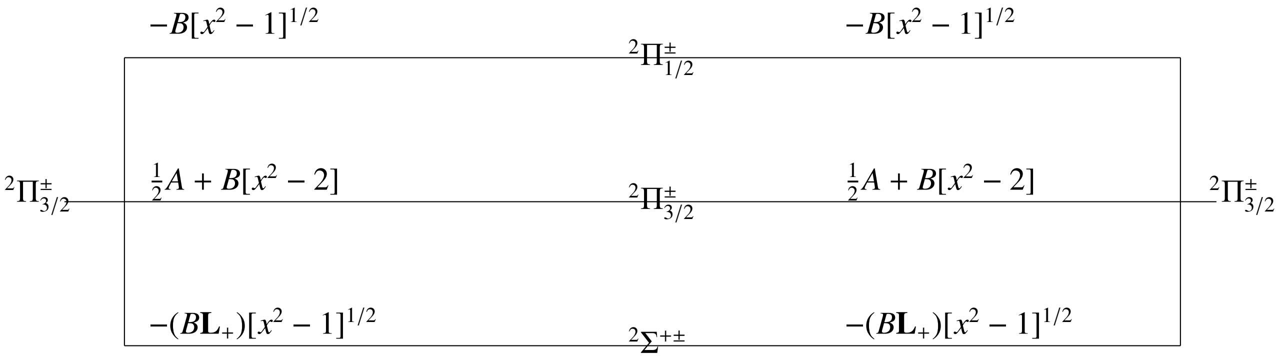
Thus

$$E^{(2)}_{1/2,1/2} = \sum_{v'} \frac{\frac{1}{4}(A\mathbf{L}_+)^2 + (B\mathbf{L}_+)^2\left[1 \pm 2(-1)^{J+S}x + x^2\right] + (A\mathbf{L}_+)(B\mathbf{L}_+)\left[1 \pm (-1)^{J+S}x\right]}{E_\Pi - E_\Sigma(v')}. \tag{13}$$

Since we are only interested in terms contributing to Λ–doubling, let us throw away all non-parity-dependent terms.

$$E^{(2)\pm}_{1/2,1/2} = \sum_{v'} \frac{\pm(-1)^{J+S}x[2(B\mathbf{L}_+)^2 + (A\mathbf{L}_+)(B\mathbf{L}_+)]}{E_\Pi - E_\Sigma(v')} \tag{14}$$

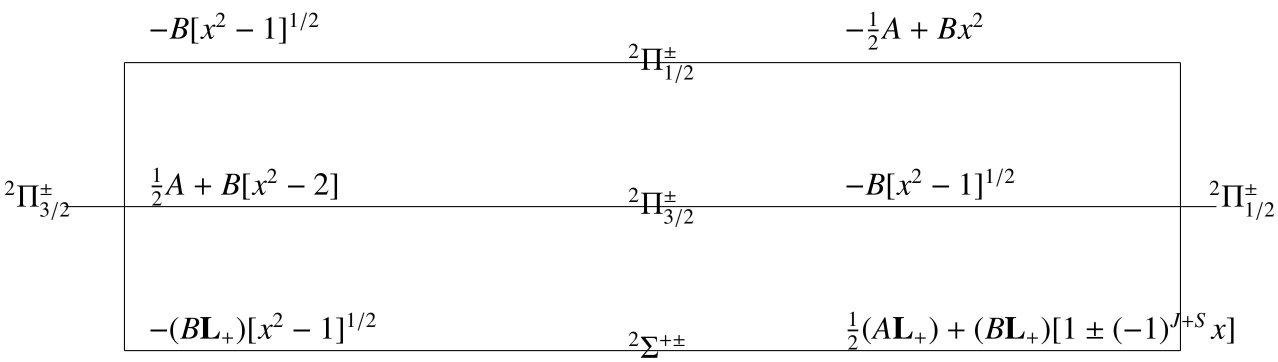
The purist will notice that $E_\Sigma(v')$ has a parity dependence also but we will neglect this.



(15)

$$E^{(2)}_{3/2,3/2} = \sum_{v'} \frac{(B\mathbf{L}_+)^2(x^2-1)}{E_\Pi - E_\Sigma(v')} \tag{16}$$

$$\text{thus} \qquad E^{(2)\pm}_{3/2,3/2} = 0 \tag{16a}$$



(17)

$$E^{(2)}_{3/2,1/2} = \sum_{v'} \frac{-[x^2-1]^{1/2}\left[\frac{1}{2}(A\mathbf{L}_+)(B\mathbf{L}_+)+(B\mathbf{L}_+)^2\right] \mp (B\mathbf{L}_+)^2(-1)^{J+S}x[x^2-1]^{1/2}}{E_\Pi - E_\Sigma(v')} \tag{18}$$

$$E^{(2)\pm}_{3/2,1/2} = \sum_{v'} \frac{\mp(-1)^{J+S}(B\mathbf{L}_+)^2 x[x^2-1]^{1/2}}{E_\Pi - E_\Sigma(v')} \tag{19}$$

Equations (14), (16a) and (19) contain all you need to reproduce the finest details of $^2\Pi$ lambda doubling in terms of two unknown parameters.

$$\beta(\Pi\Sigma) \equiv \sum_{v'} \frac{(B\mathbf{L}_+)^2}{E_\Pi - E_\Sigma(v')} \tag{20a}$$

$$\alpha\beta(\Pi\Sigma) \equiv \sum_{v'} \frac{(A\mathbf{L}_+)(B\mathbf{L}_+)}{E_\Pi - E_\Sigma(v')} \tag{20b}$$

$$E^{(2)\pm}_{1/2,1/2} = \pm(-1)^{J+S}x[2\beta(\Pi\Sigma) + \alpha(\Pi\Sigma)] \tag{21a}$$

$$E^{(2)\pm}_{3/2,3/2} = 0 \tag{21b}$$

$$E^{(2)\pm}_{3/2,1/2} = E^{(2)\pm}_{1/2,3/2} = \mp(-1)^{J+S}x[x^2-1]^{1/2}\beta(\Pi\Sigma) \tag{21c}$$

It's really easy!