5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #2: Coupled Harmonic Oscillators: Truncation of an Infinite Matrix

For next time, start Bernath, Chapter 5.

1. Approximate separation into subsystems
   * $\widehat{\mathbf{H}}(1,2) = \underbrace{\hat{h}(1)+\hat{h}(2)}_{\mathbf{H}^\circ} + \widehat{\mathbf{H}'}(1,2)$

     $\psi^\circ(1,2) = \phi(1)\phi(2) \qquad E^\circ = \varepsilon_1 + \varepsilon_2$
   * Matrix elements of $\widehat{\mathbf{H}}^\circ$ diagonal, $\widehat{\mathbf{H}'}$ non-diagonal

2. Harmonic Oscillator Matrix Elements
   Simple formulas

3. Organize infinite **H** matrix in order of E° along diagonal

4. Factor ("BLOCK DIAGONALIZE") **H** according to
   * selection rules for **H′**
   * permutation symmetry

5. Perturbation Theory * non-degenerate
   * degenerate
   * quasi-degenerate (Van Vleck transformation)

6. Correct each block of **H** for effects of out-of-block terms

7. Secular determinant for each quasi-degenerate block of **H**. Energy level diagram and fitting formulas.

2 coupled identical harmonic oscillators (like bending vibration of a linear molecule, e.g. CO_2)

$$\widehat{\mathbf{H}}_1 = \frac{1}{2}\hat{P}_1^2/\mu + \frac{1}{2}kQ_1^2$$

$$\widehat{\mathbf{H}}_1\phi_{v_1}(Q_1) = \hbar\omega_1(v_1 + 1/2)$$

same for $\widehat{\mathbf{H}}_2(Q_2, \hat{P}_2)$

$\omega_1 = (k/\mu)^{1/2}$ (reduced mass)

$v_1 = 0, 1, \ldots$

$\omega_2 = \omega_1 \equiv \omega$

same for $\widehat{\mathbf{H}}_2\phi_{v_2}(Q_2) = \hbar\omega_2(v_2 + 1/2)$

$$\widehat{\mathbf{H}} = \underbrace{\widehat{\mathbf{H}}_1(Q_1, \hat{P}_1) + \widehat{\mathbf{H}}_2(Q_2, \hat{P}_2)}_{\mathbf{H}^\circ} + \underbrace{aQ_1Q_2}_{\mathbf{H}'}$$

define basis set $\psi^o_{v_1v_2}(Q_1, Q_2) = \phi_{v_1}(Q_1)\phi_{v_2}(Q_2)$ complete, orthonormal, and convenient

$$\widehat{\mathbf{H}}^\circ\psi^o_{v_1v_2} = \hbar\omega[v_1 + 1/2 + v_2 + 1/2] = E^o_{v_1v_2} = \hbar\omega(v_1 + v_2 + 1)$$

Matrix of $\widehat{\mathbf{H}}^\circ$ is diagonal

$$\mathbf{H}_{v_1 v_1' ; v_2 v_2'} = \hbar\omega\left(v_1 + v_2 + 1\right)\delta_{v_1 v_1'}\delta_{v_2 v_2'}$$

We also know all matrix elements of Q_i (Q = x in H–O Handout) in H–O basis set

$$Q_{v, v\pm1} = \int \psi_v^* Q \psi_{v\pm1} dQ = \left[\frac{\hbar}{4\mu\omega}\right]^{1/2} \left(\underbrace{2v+1\pm1}_{2v_>}\right)^{1/2}$$

All of the non-zero matrix elements of Q follow the "selection rule" $\Delta v = \pm1$

So it is an easy matter to write down *all* matrix elements of $\widehat{\mathbf{H}}' = aQ_1Q_2$ in $\psi^o_{v_1 v_2}$ basis set.

$$\mathbf{H}'_{v_1 v_2 ; v_1' v_2'} = \hbar\omega 2b\left[v_{1>} v_{2>}\right]^{1/2} \delta_{v_1' v_1 \pm1}\delta_{v_2' v_2 \pm1}$$

$b \equiv \frac{a}{4k}$ a and k have same units, so b is unitless [$aQ_1Q_2 + kQ^2{}_1/2$ are both energies].

So we have all formulas needed to write **H** but we need to think about how to organize the matrix according to the FOUR indices $v_1\ v_2\ v_1'\ v_2'$.

Arrange matrix so that $E^o_{v_1 v_2}$ along diagonal increases monotonically

* we usually look at E levels from bottom up

* $\frac{\mathbf{H}'_{ij}}{E^o_i - E^o_j}$ perturbation theory - near degeneracies require special treatment

$E^\circ = \hbar\omega(v_1 + v_2 + 1)$

	v_1v_2			dimension of block
$E^\circ = \hbar\omega(1)$	00			1×1
(2)	10, 01			2×2
(3)		20, 11, 02		3×3
(4)			30, 21, 12, 03	4×4
…				
(n)		n0, ……0n		n x n

block index ↑

So we are done with $\mathbf{H}^\circ$.

$n \leftarrow$ block index

What do we know about $\mathbf{H}'$? $\Delta v_1 = \pm1$, $\Delta v_2 = \pm1$, $\Delta\overbrace{(v_1 + v_2)}^{\Updownarrow} = 0, \pm2$

* fill in blocks along diagonal $\Delta n = 0$ for $\mathbf{H}'$

* off--diagonal $\Delta n = 2$ elements between blocks (see top of handout, page 1)

In $\mathbf{H}'$, blocks are connected only by $\Delta n = \pm 2$.

$\therefore$ rigorous factorization of $\mathbf{H}$ into even n and odd n blocks (consequence of operator form of $\mathbf{H}'$)

There is also another symmetry. Oscillators 1 and 2 are identical. Construct new basis functions that are eigenfunctions (consequence of symmetry) of pertmutation operator, P(1,2)

Since $\left[\hat{\mathbf{H}}, \hat{\mathrm{P}}(1,2)\right] = 0$ permutation symmetry (+1 or –1) is a rigorous (GOOD) QN

$$\left|\mathrm{v}_1\mathrm{v}_2, \pm\right\rangle = 2^{-1/2}\left[\left|\mathrm{v}_1 = \mathrm{v}\right\rangle\left|\mathrm{v}_2 = \mathrm{v}'\right\rangle \pm \left|\mathrm{v}'\right\rangle\left|\mathrm{v}\right\rangle\right]$$

also $\mathrm{P}(1,2)|\mathrm{v}\rangle|\mathrm{v}\rangle = +|\mathrm{v}\rangle|\mathrm{v}\rangle$

0,0
1,1
2,2 all even
3,3
etc.

\+ and – symmetry blocks
all $\mathbf{H}_{+,-} = 0$
even n, odd n
all $\mathbf{H}_{\text{even n,odd n}} = 0$

doubly factored $\mathbf{H}$ — see bottom of handout on page 1.

FOUR RIGOROUSLY SEPARATE BLOCKS
even n, +
even n, –
odd n, +
odd n, –

Each of these four blocks is partly block-diagonalized.

* off-diagonal elements within sub-blocks
* off-diagonal elements between adjacent ($\Delta n = 2$) sub-blocks.

Look at (odd n, +) block in more detail.

v_1		v_2	n
0		0	1
$2^{-1/2}(20$	+	$02)$	3
1		1	3
$2^{-1/2}(40$	+	$04)$	5
$2^{-1/2}(31$	+	$13)$	5
2		2	5

$\hbar\omega$

$$\begin{pmatrix} \boxed{1} & 0 & 2\mathrm{b} & 0 & 0 & 0 \\ 0 & \boxed{3} & \boxed{4\mathrm{b}} & 0 & \sqrt{12}\mathrm{b} & 0 \\ 2\mathrm{b} & \boxed{4\mathrm{b}} & \boxed{3} & 0 & 0 & 4\mathrm{b} \\ 0 & 0 & 0 & \boxed{5} & \boxed{4\mathrm{b}} & \boxed{0} \\ 0 & \sqrt{12}\mathrm{b} & 0 & \boxed{4\mathrm{b}} & \boxed{5} & \boxed{4\sqrt{3}\mathrm{b}} \\ 0 & 0 & 4\mathrm{b} & \boxed{0} & \boxed{4\sqrt{3}\mathrm{b}} & \boxed{5} \end{pmatrix}$$

degenerate blocks

note: even-n blocks are only quasi-degenerate

Now we have simplified as much as is possible rigorously. Each of the four blocks is still infinite and can't be solved exactly. Perturbation Theory is needed to get rid of high-n part of matrix.

Perturbation Theory!