

■ Ammonia molecule,  $H = H_L + H_R + V$ ,  $V$  treated as perturbation

symmetry arguments ( $\langle L_2 | V | R_1 \rangle = \langle L_1 | V | R_2 \rangle = f$ ,  $\langle L_2 | V | L_1 \rangle = \langle R_1 | V | R_2 \rangle = c$ ) require the Hamiltonian to have the following structure in the basis  $\{|R_1\rangle, |L_1\rangle, |R_2\rangle, |L_2\rangle\}$

$$H = \begin{pmatrix} E1 & -A1 & c & f \\ -A1 & E1 & f & c \\ c & f & E2 & -A2 \\ f & c & -A2 & E2 \end{pmatrix};$$

First separate this out into unperturbed and perturbed parts, keeping the degenerate subspaces as part of  $H_0$

$$H_0 = \begin{pmatrix} E1 & -A1 & 0 & 0 \\ -A1 & E1 & 0 & 0 \\ 0 & 0 & E2 & -A2 \\ 0 & 0 & -A2 & E2 \end{pmatrix};$$

**(V = H - H0) // MatrixForm**

$$\begin{pmatrix} 0 & 0 & c & f \\ 0 & 0 & f & c \\ c & f & 0 & 0 \\ f & c & 0 & 0 \end{pmatrix}$$

Find the eigenvalues and vectors for  $H_0$  (note much simpler than full  $H$ ):

**{e0s, kets} = Eigensystem[H0] // Simplify**  
 $\{-A1 + E1, A1 + E1, -A2 + E2, A2 + E2\},$   
 $\{1, 1, 0, 0\}, \{-1, 1, 0, 0\}, \{0, 0, 1, 1\}, \{0, 0, -1, 1\}\}$

Note that the eigenstates are even and odd combinations of the  $R$ s and  $L$ s. The first and 3rd states are even, the 2nd and 4th odd.

**bras = Inverse[kets<sup>T</sup>]**

$$\left\{ \left\{ \frac{1}{2}, \frac{1}{2}, 0, 0 \right\}, \left\{ -\frac{1}{2}, \frac{1}{2}, 0, 0 \right\}, \left\{ 0, 0, \frac{1}{2}, \frac{1}{2} \right\}, \left\{ 0, 0, -\frac{1}{2}, \frac{1}{2} \right\} \right\}$$

key step: now need to express  $V$  in the eigenbasis of  $H_0$

**(Vp = bras.V.kets<sup>T</sup>) // MatrixForm**

$$\begin{pmatrix} 0 & 0 & c + f & 0 \\ 0 & 0 & 0 & c - f \\ c + f & 0 & 0 & 0 \\ 0 & c - f & 0 & 0 \end{pmatrix}$$

note that  $V_p$  has no diagonal elements, so it has no effect to first order. Note also that  $V_p$  only has matrix elements between the two even and the two odd eigenstates.

We must therefore use second order perturbation theory. For the symmetric ground state, we get

$$e0s[[1]] + \frac{(c + f)^2}{e0s[[1]] - e0s[[3]]}$$

$$-A1 + E1 + \frac{(c + f)^2}{-A1 + A2 + E1 - E2}$$

For the antisymmetric ground state, we get

$$\mathbf{e0s}[\mathbf{2}] + \frac{(\mathbf{c} - \mathbf{f})^2}{\mathbf{e0s}[\mathbf{2}] - \mathbf{e0s}[\mathbf{4}]}$$

$$\mathbf{A1} + \mathbf{E1} + \frac{(\mathbf{c} - \mathbf{f})^2}{\mathbf{A1} - \mathbf{A2} + \mathbf{E1} - \mathbf{E2}}$$