Vibronisches Eigenwert - Problem

$$\underbrace{\left(T_K \underline{\underline{1}} + \underline{\underline{W}}\right)}_{\underline{\underline{H}}} \begin{pmatrix} \tilde{\chi}_n^{(1)} \\ \tilde{\chi}_n^{(2)} \end{pmatrix} = E_n \begin{pmatrix} \tilde{\chi}_n^{(1)} \\ \tilde{\chi}_n^{(2)} \end{pmatrix}$$

$$\tilde{\chi}_n^{(1)} = \sum_\ell a_\ell^n \chi_\ell \ ; \ \tilde{\chi}_n^{(2)} = \sum_\ell b_\ell^n \chi_\ell$$

$$\Rightarrow \quad \sum_\ell \underline{\underline{H}} \begin{pmatrix} a_\ell^n \\ b_\ell^n \end{pmatrix} \chi_\ell = \sum_\ell E_n \begin{pmatrix} a_\ell^n \\ b_\ell^n \end{pmatrix} \chi_\ell$$

$$\int \chi_m^* \, dQ \ : \quad \boxed{\sum_\ell \underline{\underline{H}}_{m\ell} \begin{pmatrix} a_\ell^n \\ b_\ell^n \end{pmatrix} = E_n \begin{pmatrix} a_m^n \\ b_m^n \end{pmatrix}}$$

Vibronische "Supermatrix" mit Elementen $H_{ij;m\ell}$

elektron. vibrator. QZ

Benutze

$$\langle \chi_\ell | Q | \chi_m \rangle = \sqrt{\frac{m+1}{2}} \, \delta_{\ell, m+1} + \sqrt{\frac{m}{2}} \, \delta_{\ell, m-1}$$

Auswertung für

$$\underline{\underline{H}} = \frac{\omega_u}{2} \left(- \frac{\partial^2}{\partial Q_u^2} + Q_u^2 \right) \underline{\underline{1}} + \begin{pmatrix} E_g & \lambda Q_u \\ \lambda Q_u & E_u \end{pmatrix}$$

"Säkular- Supermatrix"

g-u-Zustände: Vibronische Säkularmatrix mit Symmetrie

$$
\begin{array}{cc}
 & \begin{array}{cccccccccc} |g;0\rangle & |\check{u};0\rangle & |g;1\rangle & |\check{u};1\rangle & |g;2\rangle & |\check{u};2\rangle & |g;3\rangle & |\check{u};3\rangle & \dots \end{array} \\
\underline{\underline{H}} = & \left(\begin{array}{c|c|c|c} \quad & \quad & \quad & \quad \\ \hline \quad & \quad & \quad & \quad \\ \hline \quad & \quad & \quad & \quad \\ \hline \quad & \quad & \quad & \quad \end{array} \right) \begin{array}{c} |g;0\rangle \\ |\check{u};0\rangle \\ |g;1\rangle \\ |\check{u};1\rangle \\ |g;2\rangle \\ |\check{u};2\rangle \\ |g;3\rangle \\ |\check{u};3\rangle \\ |g;4\rangle \\ |\check{u};4\rangle \\ \vdots \end{array}
\end{array}
$$

Symmetrieadaptierte Untermatrizen ($\lambda' = \frac{\lambda}{\sqrt{2}}$)

$$\underline{\underline{H}}_g = \begin{pmatrix} E_g & \lambda'\sqrt{1} & & & & \\ \lambda'\sqrt{1} & E_u + \omega_u & \lambda'\sqrt{2} & & & \mathbf{0} \\ & \lambda'\sqrt{2} & E_g + 2\omega_u & \lambda'\sqrt{3} & & \\ & & \lambda'\sqrt{3} & E_u + 3\omega_u & \lambda'\sqrt{4} & \\ & \mathbf{0} & & \lambda'\sqrt{4} & \ddots & \end{pmatrix}$$

$$\underline{\underline{H}}_u = \begin{pmatrix} E_u & \lambda'\sqrt{1} & & & & \\ \lambda'\sqrt{1} & E_g + \omega_u & \lambda'\sqrt{2} & & & \mathbf{0} \\ & \lambda'\sqrt{2} & E_u + 2\omega_u & \lambda'\sqrt{3} & & \\ & & \lambda'\sqrt{3} & E_g + 3\omega_u & \lambda'\sqrt{4} & \\ & \mathbf{0} & & \lambda'\sqrt{4} & \ddots & \end{pmatrix}$$