

Total classical vibrational (harmonic) energy for general, non-linear molecule

$$E_{\text{vib}} = T_{\text{vib}} + V = \frac{1}{2} \dot{\mathbf{S}}^T \mathbf{G}^{-1} \dot{\mathbf{S}} + \frac{1}{2} \mathbf{S}^T \mathbf{F} \mathbf{S}$$

The different vibrational motions are **coupled**

For example:

$$\mathbf{F} = \left\{ \begin{array}{ccc} f_{rr} & f_{rr'} & f_{r\theta} \\ f_{rr'} & f_{rr} & f_{r\theta} \\ f_{r\theta} & f_{r\theta} & f_{\theta\theta} \end{array} \right\}$$

We try to redefine the coordinates to get uncoupled motions

Answer: *Normal coordinates* (classical mechanics, 18th century)

$$E_{\text{vib}} = T_{\text{vib}} + V = \frac{1}{2} \dot{\mathbf{S}}^T \mathbf{G}^{-1} \dot{\mathbf{S}} + \frac{1}{2} \mathbf{S}^T \mathbf{F} \mathbf{S}$$

$$\mathbf{Q} = \left\{ \begin{array}{c} Q_1 \\ Q_2 \\ Q_3 \\ Q_4 \\ \vdots \\ Q_{3N-6} \end{array} \right\}$$

$$\mathbf{S} = \mathbf{L} \mathbf{Q}$$

?

Determine matrix L so, that

$$T_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \dot{Q}_r^2 = \frac{1}{2} \dot{\mathbf{Q}}^T \dot{\mathbf{Q}},$$

$$V = \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

Independent motions

Now some derivation

$$\mathbf{S} = \mathbf{LQ} \quad T_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \dot{Q}_r^2 = \frac{1}{2} \dot{\mathbf{Q}}^T \dot{\mathbf{Q}}, \quad V = \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

$$\mathbf{E}_{\text{vib}} = T_{\text{vib}} + V = \frac{1}{2} \dot{\mathbf{S}}^T \mathbf{G}^{-1} \dot{\mathbf{S}} + \frac{1}{2} \mathbf{S}^T \mathbf{F} \mathbf{S}$$

$$T_{\text{vib}} = \frac{1}{2} (\mathbf{L}\dot{\mathbf{Q}})^T \mathbf{G}^{-1} (\mathbf{L}\dot{\mathbf{Q}}) = \frac{1}{2} \dot{\mathbf{Q}}^T (\mathbf{L}^T \mathbf{G}^{-1} \mathbf{L}) \dot{\mathbf{Q}}.$$

$$\mathbf{L}^T \mathbf{G}^{-1} \mathbf{L} = \mathbf{E}, \quad \text{in order that} \quad T_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \dot{Q}_r^2 = \frac{1}{2} \dot{\mathbf{Q}}^T \dot{\mathbf{Q}},$$

$$\mathbf{L}^T \mathbf{F} \mathbf{L} = \mathbf{\Lambda} \quad \text{in order that} \quad V = \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

E is unit matrix; Λ is diagonal matrix with diagonal elements $\Lambda_{rr} = \lambda_r$

Now some more derivation

Combine

$$\mathbf{L}^T \mathbf{G}^{-1} \mathbf{L} = \mathbf{E}, \quad \text{and} \quad \mathbf{L}^T \mathbf{F} \mathbf{L} = \mathbf{\Lambda}$$

to get

$$\mathbf{L}^T = \mathbf{L}^{-1} \mathbf{G}$$

$$\mathbf{L}^{-1} \mathbf{G} \mathbf{F} \mathbf{L} = \mathbf{\Lambda}$$

$$\mathbf{G} \mathbf{F} \mathbf{L} = \mathbf{L} \mathbf{\Lambda}.$$

Eigenvalue problem!

Why that?

Because the r 'th column of the \mathbf{L} matrix

$$\mathbf{L}_r = \begin{pmatrix} L_{1r} \\ L_{2r} \\ L_{3r} \\ L_{4r} \\ \vdots \\ L_{3N-6r} \end{pmatrix}.$$

fulfills the (eigenvalue) equation

$$\mathbf{G} \mathbf{F} \mathbf{L}_r = \lambda_r \mathbf{L}_r$$

λ_r is the r 'th eigenvalue of **GF**

$$(\mathbf{G} \mathbf{F} - \lambda_r \mathbf{E}) \mathbf{L}_r = \mathbf{O},$$

\mathbf{L}_r is the r 'th eigenvector of **GF**

We can determine the λ_r and the \mathbf{L} matrix by diagonalizing \mathbf{GF} with a computer.

With the normalization condition

$$\mathbf{L}\mathbf{L}^T = \mathbf{G}$$

and

$$\mathbf{Q} = \mathbf{L}^{-1}\mathbf{S}$$

we have

$$E_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \dot{Q}_r^2 + \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

Motions are uncoupled; classical normal vibrations

Now to quantum mechanics

$$E_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \dot{Q}_r^2 + \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

$$P_r = \frac{\partial T_{\text{vib}}}{\partial \dot{Q}_r} = \dot{Q}_r. \quad \text{Introduce conjugate momenta}$$

Classical

$$E_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} P_r^2 + \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2.$$

QM

$$P_r \rightarrow \hat{P}_r = -i\hbar \frac{\partial}{\partial Q_r}.$$

$$\hat{H}_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \left(-\hbar^2 \frac{\partial^2}{\partial Q_r^2} + \lambda_r Q_r^2 \right).$$

Vibrational Hamiltonian

$$\widehat{H}_{\text{vib}} = \frac{1}{2} \sum_{r=1}^{3N-6} \left(-\hbar^2 \frac{\partial^2}{\partial Q_r^2} + \lambda_r Q_r^2 \right).$$

$$\widehat{H}_{\text{vib}} = \sum_{r=1}^{3N-6} \widehat{H}_r,$$

$$\widehat{H}_r = \frac{1}{2} \left(-\hbar^2 \frac{\partial^2}{\partial Q_r^2} + \lambda_r Q_r^2 \right).$$

The Hamiltonian is the sum of 3N-6 independent contributions, so we can separate into 3N-6 independent Schrödinger equations

Vibrational Schrödinger equation

$$\widehat{H}_{\text{vib}}\psi_{\text{vib}}(Q_1, Q_2, \dots, Q_{3N-6}) = E_{\text{vib}}\psi_{\text{vib}}(Q_1, Q_2, \dots, Q_{3N-6}).$$

separates into 3N-6 partial Schrödinger equations

$$\widehat{H}_r\psi_r(Q_r) = \frac{1}{2} \left(-\hbar^2 \frac{\partial^2}{\partial Q_r^2} + \lambda_r Q_r^2 \right) \psi_r(Q_r) = E_r\psi_r(Q_r)$$

with

$$E_{\text{vib}} = \sum_{r=1}^{3N-6} E_r$$

$$\psi_{\text{vib}}(Q_1, Q_2, \dots, Q_{3N-6}) = \psi_1(Q_1)\psi_2(Q_2)\psi_3(Q_3) \dots \psi_{3N-6}(Q_{3N-6}) = \prod_{r=1}^{3N-6} \psi_r(Q_r).$$

The 3N-6 partial Schrödinger equations

$$\widehat{H}_r \psi_r(Q_r) = \frac{1}{2} \left(-\hbar^2 \frac{\partial^2}{\partial Q_r^2} + \lambda_r Q_r^2 \right) \psi_r(Q_r) = E_r \psi_r(Q_r)$$

are eigenvalue equations for the one-dimensional harmonic oscillator, and so

$$E_r = E_{v_r} = \hbar \sqrt{\lambda_r} \left(v_r + \frac{1}{2} \right), \quad v_r = 0, 1, 2, 3, \dots$$

$$\phi_r(Q_r) = \phi_{v_r}(Q_r) = N_{v_r} \mathcal{H}_{v_r} \left(\frac{Q_r}{\alpha_r} \right) \exp \left(-\frac{Q_r^2}{2\alpha_r^2} \right)$$

$$N_{v_r} = \frac{\alpha_r}{\sqrt{2^{v_r} v_r! \sqrt{\pi}}} \quad \alpha_r^4 = \frac{\hbar^2}{\lambda_r}.$$

Total quantum-mechanical vibrational (harmonic) energy for general, non-linear molecule

$$E_{\text{vib}}(v_1, \dots, v_{3N-6}) = \sum_{r=1}^{3N-6} \hbar \sqrt{\lambda_r} \left(v_r + \frac{1}{2} \right)$$

$$\psi_{\text{vib}}(Q_1, Q_2, \dots, Q_{3N-6}) = \prod_{r=1}^{3N-6} \phi_{v_r}(Q_r).$$

Vibrational (harmonic) term value for general, non-linear molecule

$$\begin{aligned} G_v(v_1, \dots, v_{3N-6}) &= \frac{1}{hc} E_{\text{vib}}(v_1, \dots, v_{3N-6}) \\ &= \frac{1}{2\pi c} \sum_{r=1}^{3N-6} \sqrt{\lambda_r} \left(v_r + \frac{1}{2} \right) = \sum_{r=1}^{3N-6} \omega_r \left(v_r + \frac{1}{2} \right). \end{aligned}$$

where

$$\omega_r = \frac{1}{2\pi c} \sqrt{\lambda_r} \quad \text{Unit: cm}^{-1}$$

is the *harmonic vibrational wavenumber*, called *normal frequency* in older literature

We make normal coordinate analysis in a minimum for V

$$V_{\text{harm}} = \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

All $Q_r = 0$ corresponds to a minimum, energy increases for $Q_r \neq 0$, and so all $\lambda_r > 0$

So the *harmonic vibrational wavenumbers* are all *real*:

$$\omega_r = \frac{1}{2\pi c} \sqrt{\lambda_r}$$

**Calculated by
MOLPRO, for
example, unit: cm^{-1}**

We could make normal coordinate analysis in a *saddle point* for V

$$V_{\text{harm}} = \frac{1}{2} \sum_{r=1}^{3N-6} \lambda_r Q_r^2$$

There is (at least) one r , where $Q_r = 0$ corresponds to a **maximum**, energy **decreases** for $Q_r \neq 0$, and so $\lambda_r < 0$

So the corresponding **harmonic vibrational wavenumber** is **imaginary**:

$$\omega_r = \frac{1}{2\pi c} \sqrt{|\lambda_r|} \times i$$

Calculated by
MOLPRO, for
example, unit: cm^{-1}

There is no normal vibration associated with an imaginary harmonic vibrational wavenumber!

The imaginary harmonic vibrational wavenumber just indicates that MOLPRO (e.g.) has found a saddle point (and no minimum) of V as stationary point.

Harmonic vibrational term values for $^{12}\text{C}^{16}\text{O}$

$$G_{\text{vib}} = \omega_e \left(v + \frac{1}{2} \right) = 2169.8 \left(v + \frac{1}{2} \right),$$

Unit: cm^{-1}

$$v = 0, 1, 2, 3, \dots$$

Harmonic vibrational term values for H_2^{16}O

$$G_{\text{vib}} = 3832.0 (v_1 + 1/2) + 1648.9 (v_2 + 1/2) + 3942.5 (v_3 + 1/2),$$

Unit: cm^{-1}

$$v_r = 0, 1, 2, 3, \dots$$

Harmonic vibrational term values for $^{12}\text{CH}_3\text{D}$

$$G_{\text{vib}} = 3064.1 (v_1 + 1/2) + 2282.1 (v_2 + 1/2) \\ + 1362.0 (v_3 + 1/2) + 3156.5 (v_4 + \underline{1}) \\ + 1521.7 (v_5 + \underline{1}) + 1206.2 (v_6 + \underline{1}),$$

Unit: cm^{-1}

$v_r = 0, 1, 2, 3, \dots$

Two-dimensional normal modes?

Harmonic vibrational term values for $^{12}\text{CH}_4$

$$G_{\text{vib}} = 3025.5 (v_1 + 1/2) + 1582.7 (v_2 + 1) \\ + 3156.8 (v_3 + \underline{3/2}) + 1367.4 (v_4 + \underline{3/2})$$

Unit: cm^{-1}

$v_r = 0, 1, 2, 3, \dots$

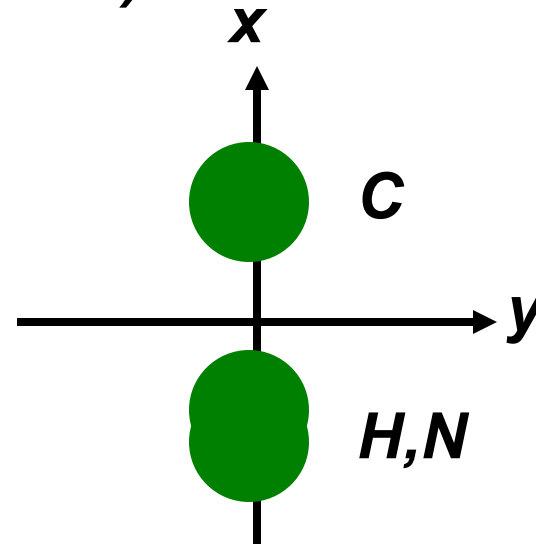
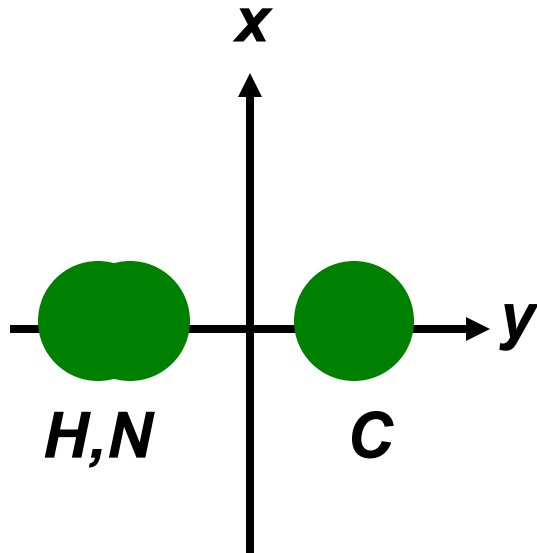
Three-dimensional normal modes?

Two- (and three-) dimensional harmonic oscillators??

Consider linear triatomic molecule, i.e. HCN

In the molecule-axis system, HCN can bend in the xz - and the yz -planes.

Molecule seen from end (along z axis):

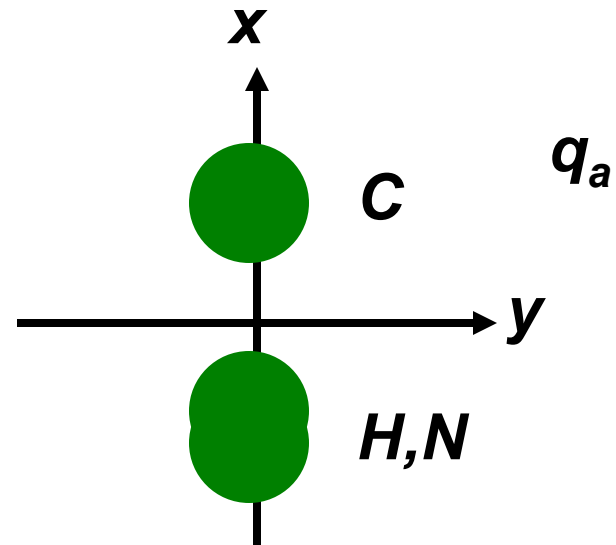
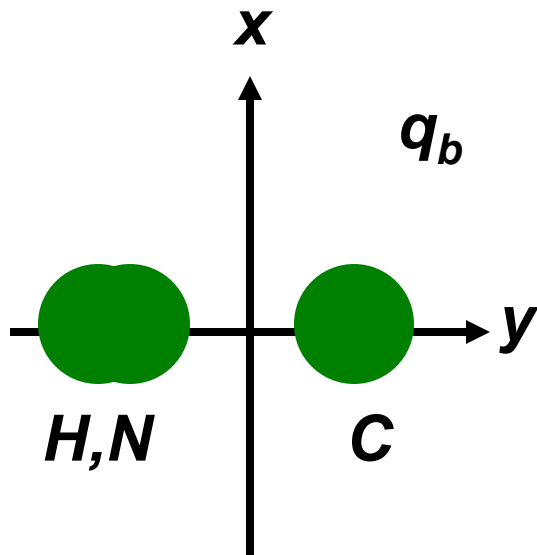


Two- (and three-) dimensional harmonic oscillators??

These two vibrations are associated with the same potential energy, obviously, and the same reduced mass

$$\widehat{H}_{2D} = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial q_a^2} + \frac{\partial^2}{\partial q_b^2} \right] + \frac{1}{2}k \left[q_a^2 + q_b^2 \right].$$

x **y** **x** **y**



The Hamiltonian for both vibrations

$$\widehat{H}_{2D} = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial q_a^2} + \frac{\partial^2}{\partial q_b^2} \right] + \frac{1}{2}k [q_a^2 + q_b^2].$$

is the sum of two independent contributions

$$\widehat{H}_{2D} = \widehat{H}_a + \widehat{H}_b,$$

$$\widehat{H}_\sigma = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial q_\sigma^2} + \frac{1}{2}kq_\sigma^2,$$

So we can **separate** the 2D Schrödinger equation

$$\widehat{H}_{2D}\phi_{2D}(q_a, q_b) = E\phi_{2D}(q_a, q_b)$$

into two one-dimensional equations

$$\widehat{H}_\sigma\phi_\sigma(q_\sigma) = E_\sigma\phi_\sigma(q_\sigma),$$

Then

$$E = E_a + E_b$$

$$\phi_{2D}(q_a, q_b) = \phi_a(q_a)\phi_b(q_b)$$

But we know the 1D harmonic-oscillator solutions of

$$\widehat{H}_{2D}\phi_{2D}(q_a, q_b) = E\phi_{2D}(q_a, q_b)$$

Solutions

$$E_a = \hbar\sqrt{\frac{k}{\mu}}\left(v_a + \frac{1}{2}\right) \quad E_b = \hbar\sqrt{\frac{k}{\mu}}\left(v_b + \frac{1}{2}\right),$$

$$\phi_a(q_a) = \phi_{v_a}(q_a) = N_{v_a}\mathcal{H}_{v_a}\left(\frac{q_a}{\alpha}\right)\exp\left(-\frac{q_a^2}{2\alpha^2}\right)$$

$$\phi_b(q_b) = \phi_{v_b}(q_b) = N_{v_b}\mathcal{H}_{v_b}\left(\frac{q_b}{\alpha}\right)\exp\left(-\frac{q_b^2}{2\alpha^2}\right),$$

$$\mathbf{v}_a, \mathbf{v}_b = \mathbf{0}, \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}, \dots$$

Total energy

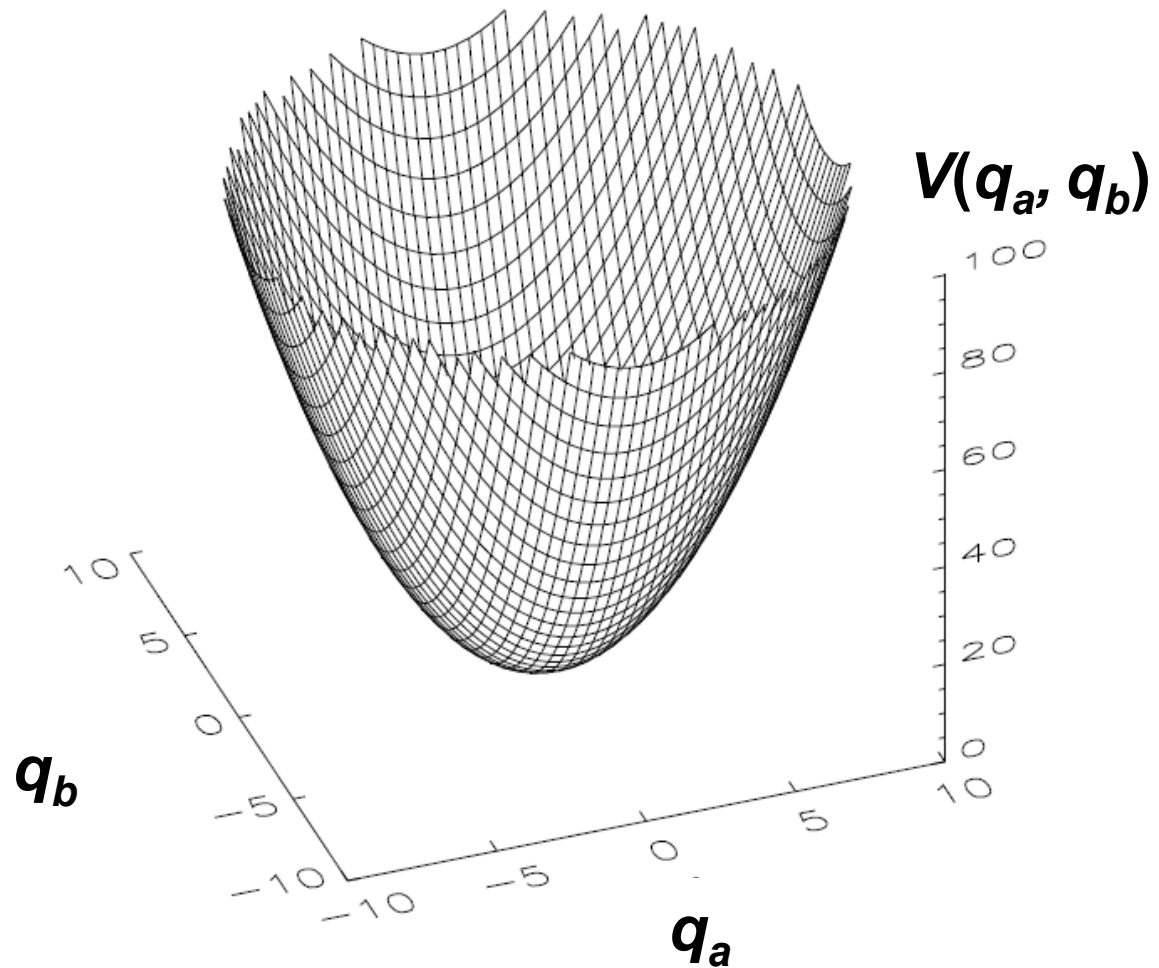
$$E_{2D} = \hbar \sqrt{\frac{k}{\mu}} (v_a + v_b + 1) = \hbar \sqrt{\frac{k}{\mu}} (v + 1) .$$

$$\mathbf{v = v_a + v_b = 0, 1, 2, 3, 4, \dots}$$

$$\mathbf{v = v_a + v_b = 0+v, 1+(v-1), 2+(v-2), \dots, v+0}$$

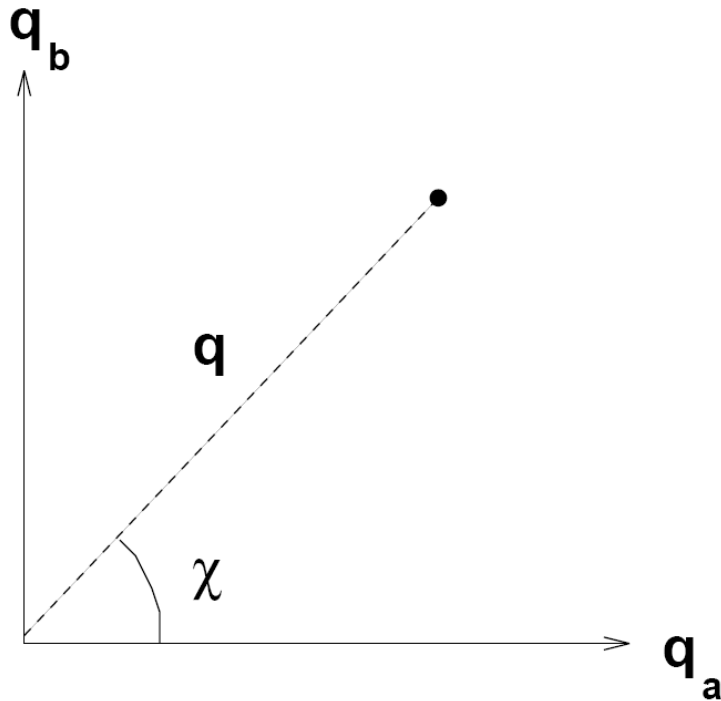
There are $v+1$ possibilities for (v_a, v_b) with the same energy – the energy is $(v+1)$ -fold degenerate [($v+1$)-fach entartet].

Potential energy function for 2D isotropic harmonic oscillator



Alternative description of 2D isotropic harmonic oscillator

New coordinates



$$q_a = q \cos \chi$$

$$q_b = q \sin \chi$$

Hamiltonian in the new coordinates

$$\widehat{H}_{2D} = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial q^2} + \frac{1}{q} \frac{\partial}{\partial q} + \frac{1}{q^2} \frac{\partial^2}{\partial \chi^2} \right] + \frac{1}{2} k q^2.$$

Eigenfunctions

$$\phi_{v,\ell}(q, \chi) = N_{v,\ell} \left(\frac{q}{\alpha} \right)^{|\ell|} L_{(v+|\ell|)/2}^{|\ell|} \left(\frac{q}{\alpha} \right) \exp \left(-\frac{q^2}{2\alpha^2} \right) \exp (i\ell\chi),$$

$$v = 0, 1, 2, 3, \dots$$

$$\ell = \underbrace{-v, -v+2, -v+4, \dots, v-2, v}_{v+1 \text{ values}}$$

v+1 values - (v+1)-fold degeneracy

Eigenfunctions

$$\phi_{v,\ell}(q, \chi) = N_{v,\ell} \left(\frac{q}{\alpha}\right)^{|\ell|} L_{(v+|\ell|)/2}^{|\ell|} \left(\frac{q}{\alpha}\right) \exp\left(-\frac{q^2}{2\alpha^2}\right) \exp(i\ell\chi),$$

$$N_{v,\ell} = \sqrt{\frac{(v - |\ell|)!}{\{[(v + |\ell|)/2]!\}^3}}.$$

$$\alpha^4 = \frac{\hbar^2}{k\mu}$$

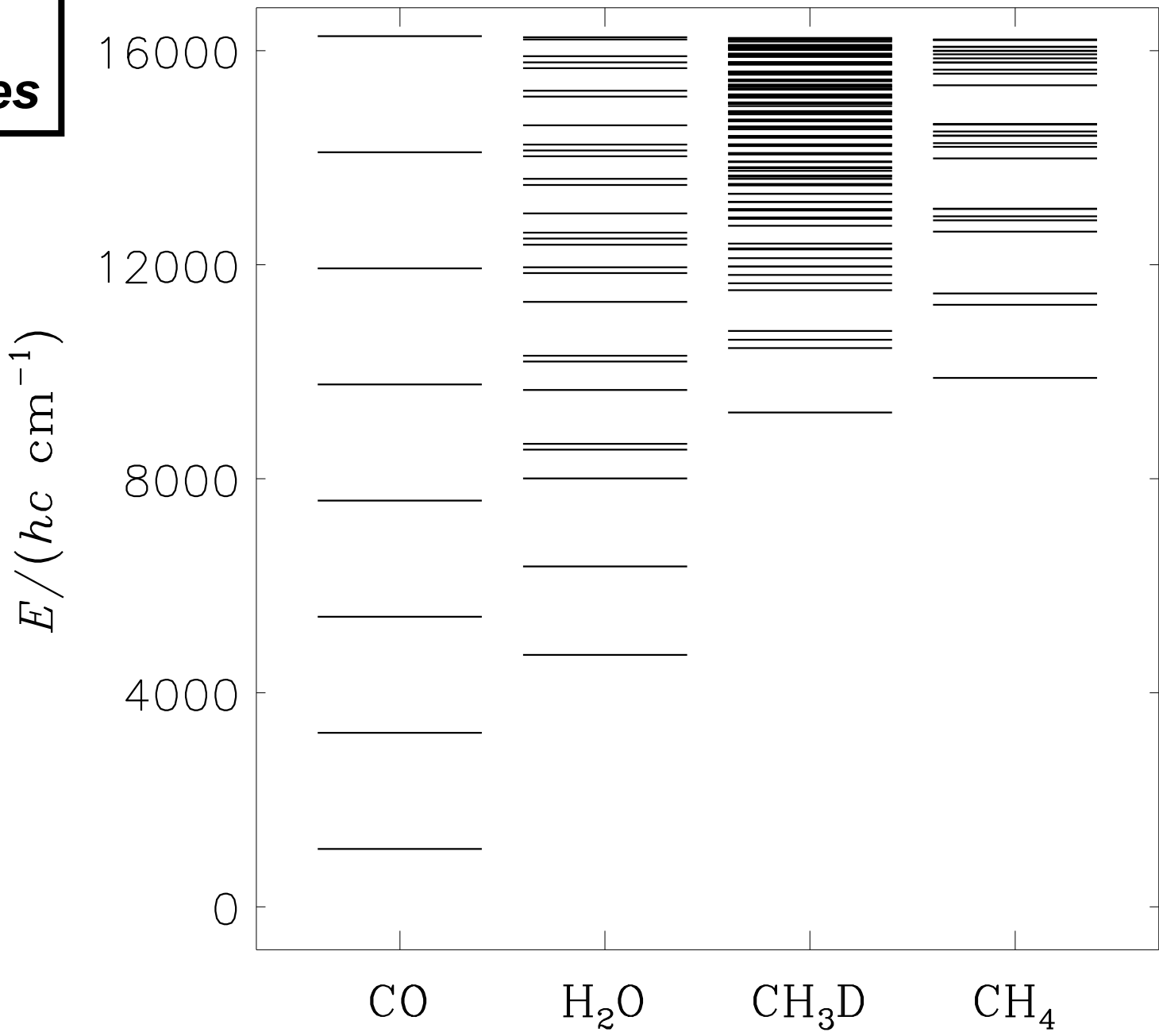
Associate Laguerre polynomial

The energy must be the same as before

$$E_{2D} = \hbar \sqrt{\frac{k}{\mu}} (v + 1).$$

v+1 ℓ -values - (v+1)-fold degeneracy

***Harmonic
term values***



Normal modes of H_2O

