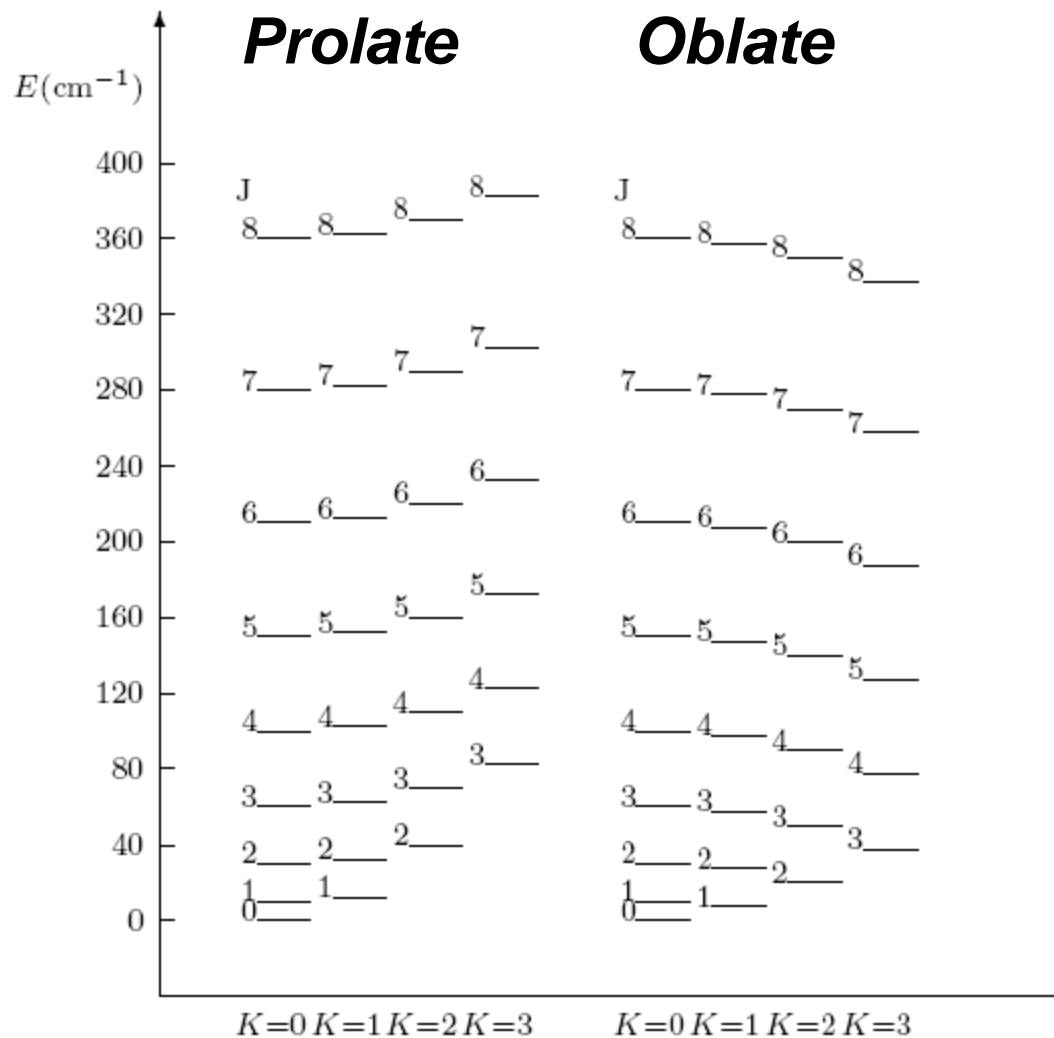


Klausurtermin
„Molekültheorie und Spektroskopie“

Datum: **Mittwoch, 05.03.2014**
Zeit: **10:00 (s.t.)**
Raum: **G.10.02 Hörsaal 9**

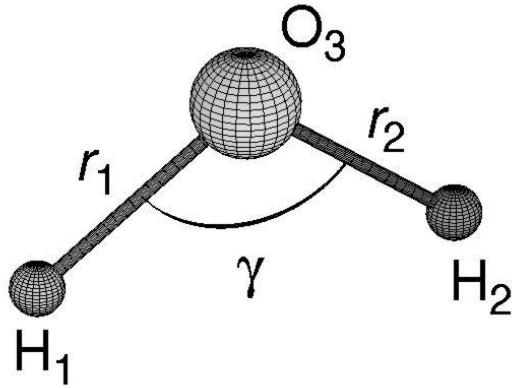
Schriftliche Hilfsmittel sind ohne Einschränkung erlaubt.
Bitte einen Taschenrechner mitbringen.

Term values / Symmetric tops



$$F_{\text{rot}} = B_e J(J + 1) + (A_e - B_e) K^2, \quad F_{\text{rot}} = B_e J(J + 1) - (B_e - C_e) K^2,$$

Rotation / Asymmetric top



$$I_{aa}^e < I_{bb}^e < I_{cc}^e$$

$$A_e > B_e > C_e$$

General Hamiltonian

$$\hat{H}_{\text{rot}}^0 = \hbar^{-2}(A_e \hat{J}_a^2 + B_e \hat{J}_b^2 + C_e \hat{J}_c^2)$$

No simplification possible

- So what now ?

Asymmetric top

Matrix diagonalization – Diagonalize asymmetric rotor

Hamiltonian in basis of $|J, k, m\rangle$ functions

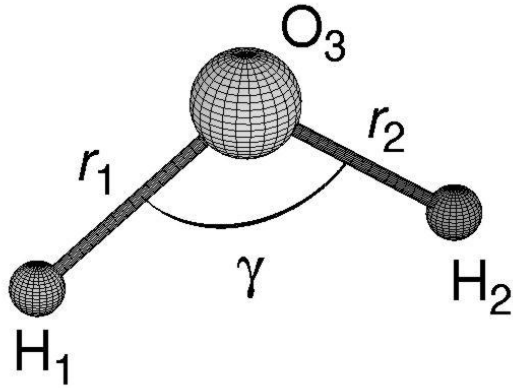
$$\psi_{\text{rot}} = \sum_k c_k |J, k, m\rangle$$

Matrix elements:

$$\begin{aligned} H_{(J,k,m),(J,k,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{asymm}} | \psi_{J,k,m} \rangle = \langle J, k, m | \widehat{H}_{\text{asymm}} | J, k, m \rangle \\ &= \frac{\hbar^2}{4} \left\{ \left(\frac{1}{I_{xx}} + \frac{1}{I_{yy}} \right) [J(J+1) - k^2] + \frac{2k^2}{I_{zz}} \right\}, \end{aligned}$$

$$\begin{aligned} H_{(J,k,m),(J,k\pm 2,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{asymm}} | \psi_{J,k\pm 2,m} \rangle \\ &= \langle J, k, m | \widehat{H}_{\text{asymm}} | J, k \pm 2, m \rangle \\ &= \frac{\hbar^2}{8} \left(\frac{1}{I_{xx}} - \frac{1}{I_{yy}} \right) \sqrt{J(J+1) - k(k \pm 1)} \\ &\quad \times \sqrt{J(J+1) - (k \pm 1)(k \pm 2)}. \end{aligned}$$

Rotation / Asymmetric top



$$I_{aa}^e < I_{bb}^e < I_{cc}^e$$

$$A_e > B_e > C_e$$

K = K_a is angular momentum projection on a axis

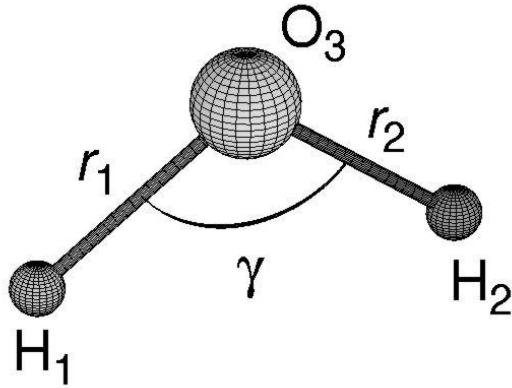
Prolate limit:

Hypothetical symmetric top with same A_e, C_e as asymmetric top in question, but B_e = C_e

This symmetric top has

$$F_{\text{rot}} = B_e J(J + 1) + (A_e - B_e) K_a^2,$$

Rotation / Asymmetric top



$$I_{aa}^e < I_{bb}^e < I_{cc}^e$$

$$A_e > B_e > C_e$$

K = K_c is angular momentum projection on c axis

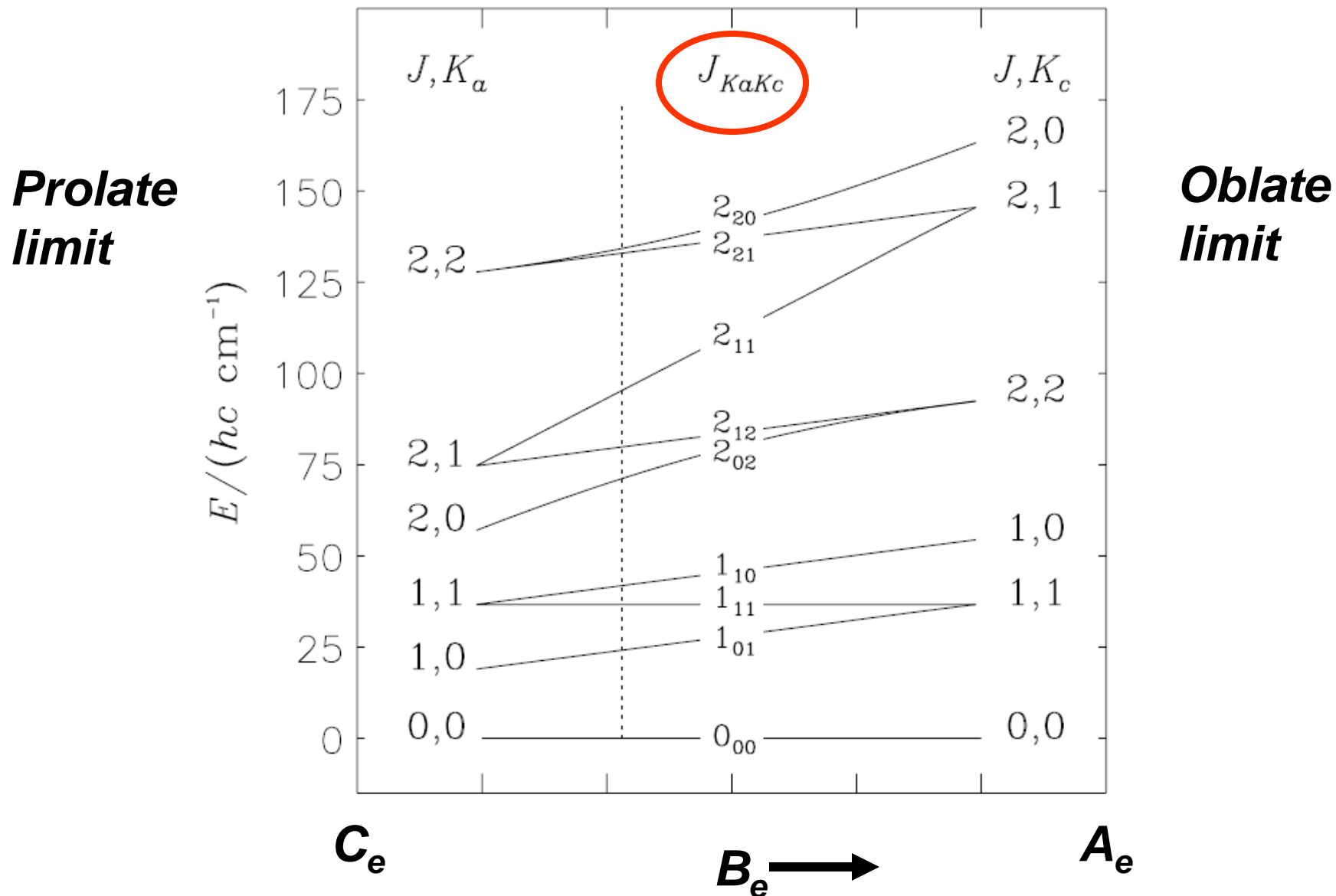
Oblate limit:

Hypothetical symmetric top with same A_e, C_e as asymmetric top in question, but B_e = A_e

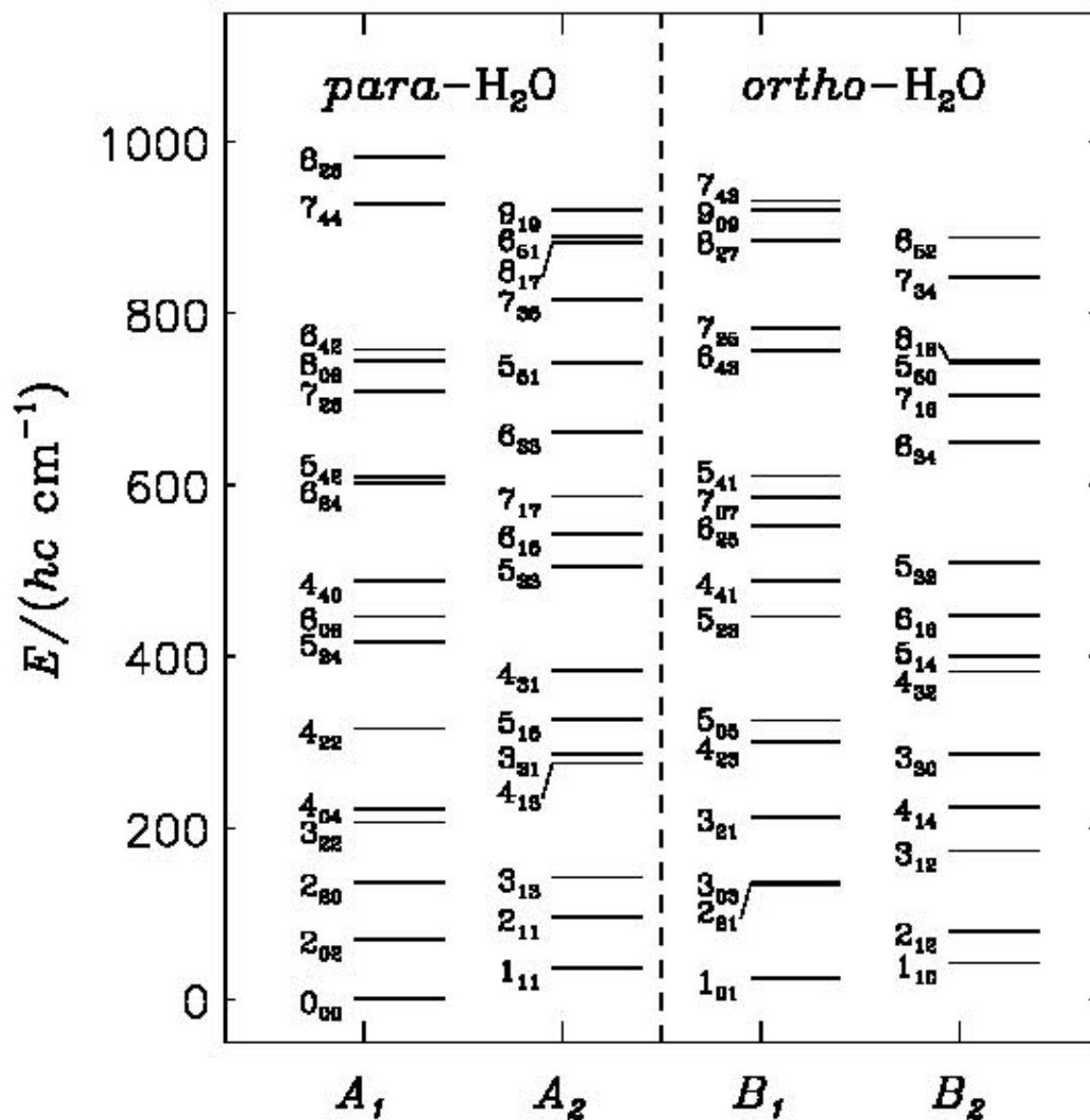
This symmetric top has

$$F_{\text{rot}} = B_e J(J + 1) - (B_e - C_e) K_c^2,$$

Asymmetric top / Correlation diagram



Example: H₂O rot. energy levels



Asymmetry parameter

$$\kappa = \frac{2B_e - A_e - C_e}{A_e - C_e}.$$

= -1 in prolate limit

= +1 in oblate limit

quantifies asymmetry

Rigid rotor types / Energies

(i.a) Prolate symmetric top

$$F_{\text{rot}} = B_e J(J + 1) + (A_e - B_e)K^2,$$

(i.b) Oblate symmetric top

$$F_{\text{rot}} = B_e J(J + 1) - (B_e - C_e)K^2,$$

(ii) Linear molecule

$$E_{\text{lin}} = E_J = \frac{\hbar^2}{2I_{bb}} J(J + 1),$$

(iii) Spherical top molecule

$$F_{\text{rot}} = B_e J(J + 1),$$

$$J = 0, 1, 2, \dots, K = |k|, \text{ and } k = 0, \pm 1, \pm 2, \dots \pm J$$

Rigid rotor types / Wavefunctions

(i.a) Prolate symmetric top

(i.b) Oblate symmetric top

(iii) Spherical top molecule

$$\psi_{\text{rot}} = |J, k, m\rangle$$

(ii) Linear molecule

$$\psi_{\text{rot}} = Y_{Jm}(\theta, \phi)$$

$$J = 0, 1, 2, \dots, K = |k|, \text{ and } k = 0, \pm 1, \pm 2, \dots, \pm J$$
$$m = -J, -J+1, -J+2, \dots, J$$

Rigid rotor types / Wavefunctions

Simplest approximation for symmetric tops and spherical tops

$$\psi_{\text{rot}} = |J, k, m\rangle$$

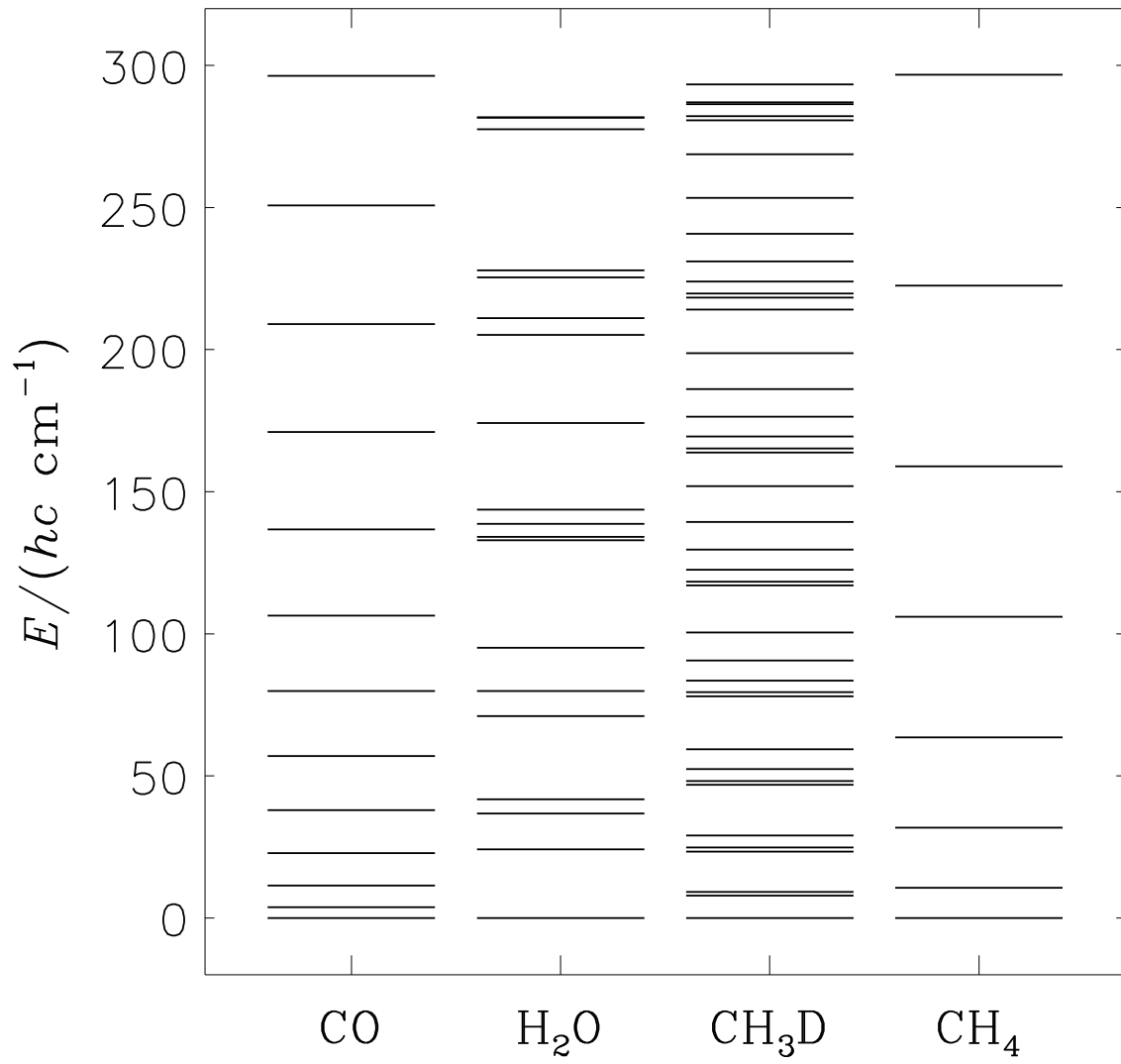
Simplest approximation for linear rotors

$$\psi_{\text{rot}} = Y_{Jm}(\theta, \phi)$$

Simplest approximation for asymmetric top molecules

$$\psi_{\text{rot}} = \sum_k c_k |J, k, m\rangle$$

***Rigid rotor
term values***



Nuclear-motion wavefunction

describes vibrational and rotational motion.

Simplest approximation

$$\Psi_n = \Psi_{\text{vib}} \Psi_{\text{rot}}$$

Better approximation

$$\Psi_n = \sum_p c_p \Psi_{\text{vib}}^{(p)} \Psi_{\text{rot}}^{(p)}$$

„Rotation-vibration“ interaction

Matrix diagonalization

Problem I: What is Ψ_{rot} ?

We know the rotational wavefunctions for one rigid rotor, probably:

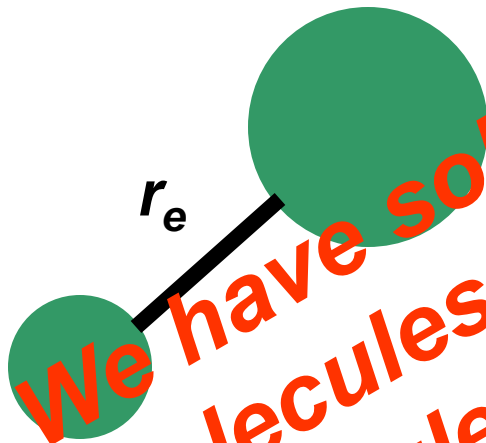
$$E_{\text{rot}} = \frac{h^2}{2I_e} J(J+1) \quad J=0,1,2,3,\dots$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\Psi_{\text{rot}} = Y_{Jm}(\theta, \phi)$$

? ?

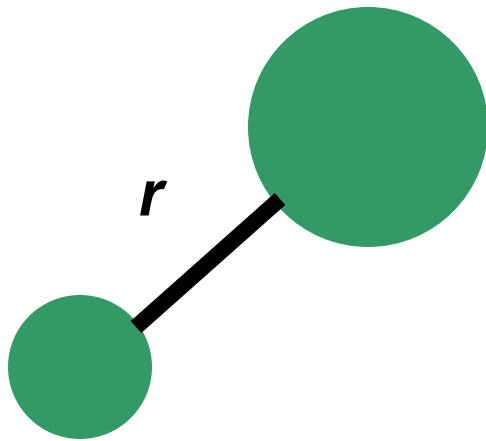
Spherical harmonic function (Kugelfkt.)



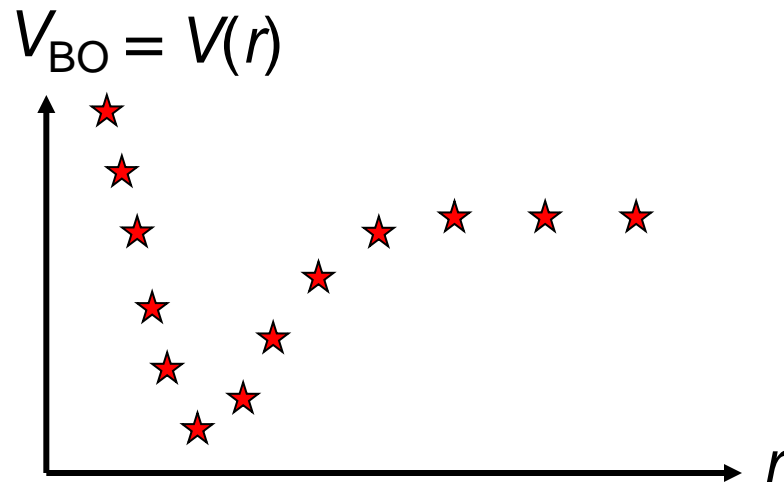
We have solved Problem I: Linear molecules, symmetric top, asymmetric tops, spherical tops

Problem II: What is ψ_{vib} ?

Probably, we know approximate vibrational wavefunctions for a diatomic molecule:

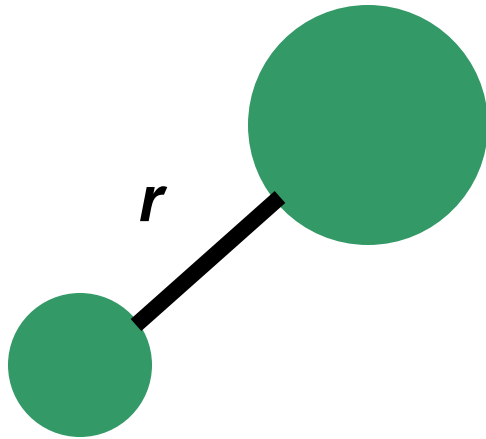


The vibration is governed by Born-Oppenheimer potential energy function (from ab initio, for example)



Problem II: What is ψ_{vib} ?

Approximations for $V(r)$



Morse potential

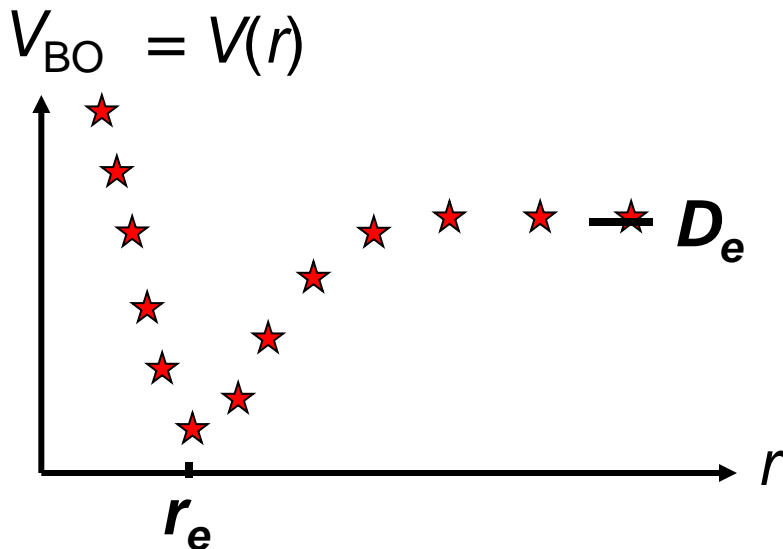
$$V(r) = D_e [1 - \exp(-a(r - r_e))]^2$$

Simons-Parr-Finlan potential

$$V(r) = D_e \left[1 - \frac{r_e}{r} \right]^2 .$$

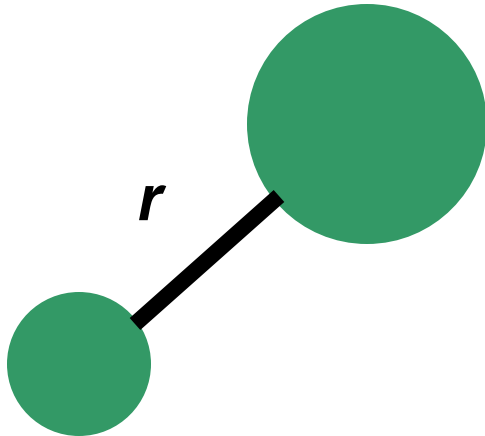
Harmonic potential

$$V_{\text{harm}}(r) = \frac{1}{2} k (r - r_e)^2 ,$$



Problem II: What is ψ_{vib} ?

In order to get a model that can be (easily?) extended to larger molecules, we consider the harmonic potential



$$V_{\text{harm}}(r) = \frac{1}{2}k (r - r_e)^2,$$

Force constant

$$k = \left(\frac{d^2V}{dr^2} \right)_{r=r_e}$$

Problem: No dissociation possible!

Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \phi_{\text{vib}}}{\partial r^2} + \frac{1}{2} k (r - r_e)^2 \phi_{\text{vib}}(r) = E_{\text{vib}} \phi_{\text{vib}}(r).$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Set $x = r - r_e$

$$-\frac{\hbar^2}{2\mu} \frac{d\phi_{\text{vib}}}{dx^2} + \frac{1}{2} k x^2 \phi_{\text{vib}}(x) = E_{\text{vib}} \phi_{\text{vib}}(x)$$

This is the Schrödinger equation for the harmonic oscillator – we (should) know the solutions

Harmonic oscillator

$$E_{\text{vib}} = E_v = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) = \hbar \omega \left(v + \frac{1}{2} \right).$$

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

$$\phi_v(x) = N_v \mathcal{H}_v \left(\frac{x}{\alpha} \right) \exp \left(-\frac{x^2}{2\alpha^2} \right).$$

Hermite polynomial

$$N_v = \frac{\alpha}{\sqrt{2^v v! \sqrt{\pi}}},$$

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

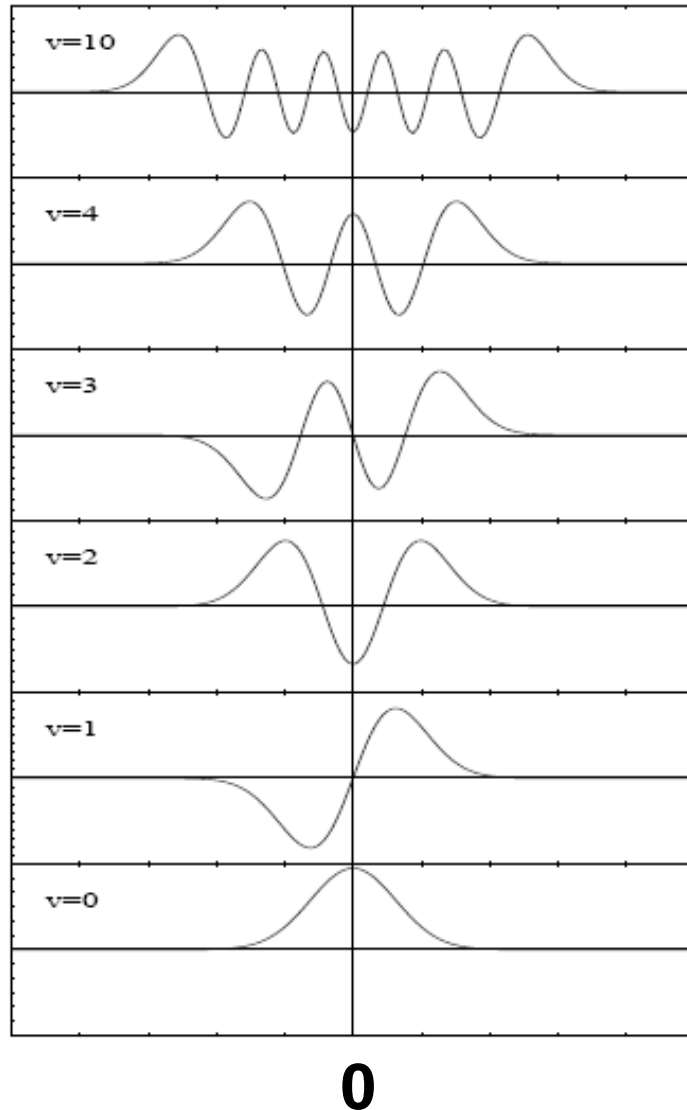
Hermite polynomials

v	$\mathcal{H}_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$
7	$128y^7 - 1344y^5 + 3360y^3 - 1680y$
8	$256y^8 - 3584y^6 + 13440y^4 - 13440y^2 + 1680$

***Order of
polynomial = v***

Harmonic oscillator wavefunctions

$\phi_v(x)$

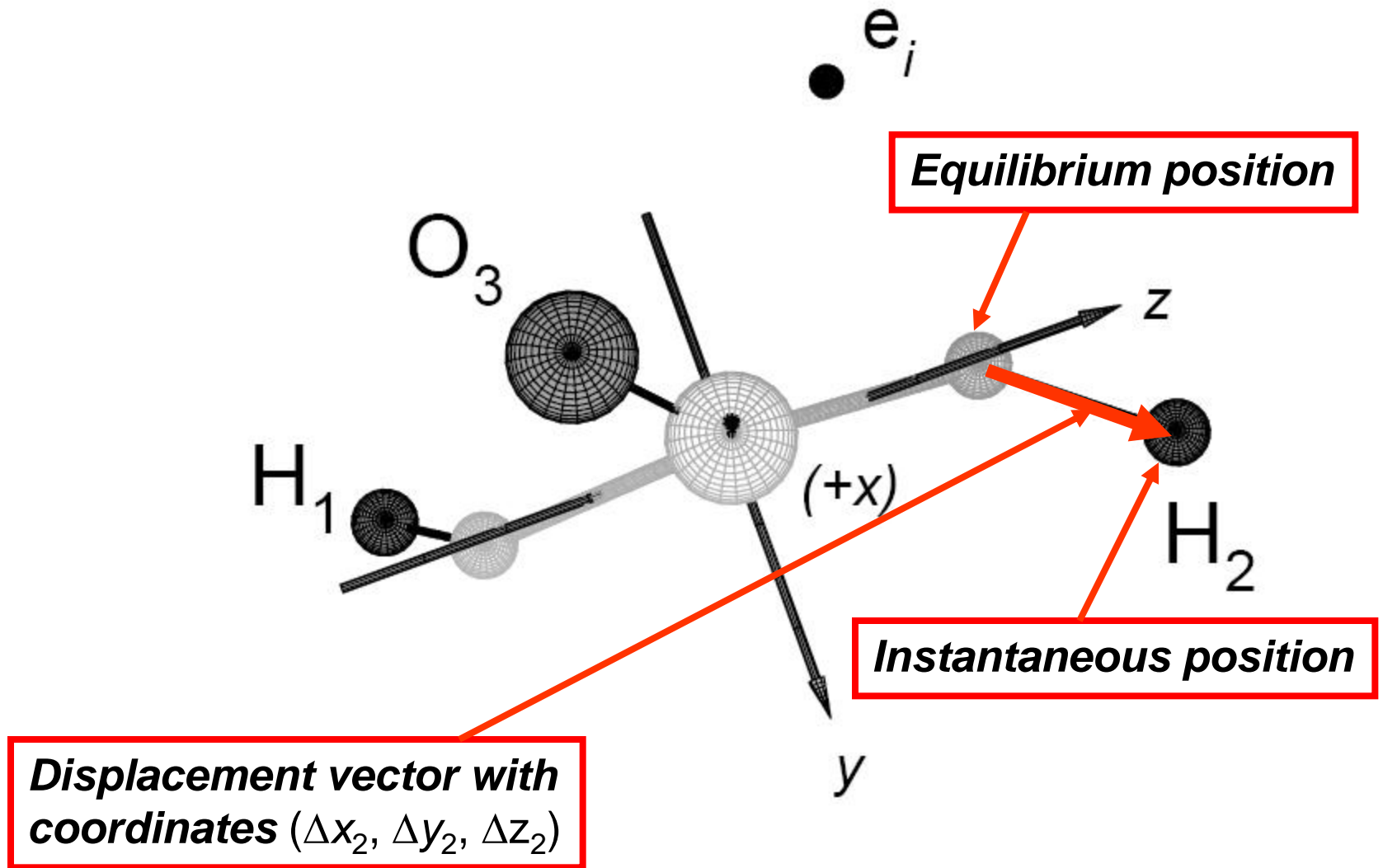


$$\phi_v(-x) = \begin{cases} \phi_v(x) & \text{for } v \text{ even} \\ -\phi_v(x) & \text{for } v \text{ odd} \end{cases}$$

**Number of nodes
(Nullstellen) = v**

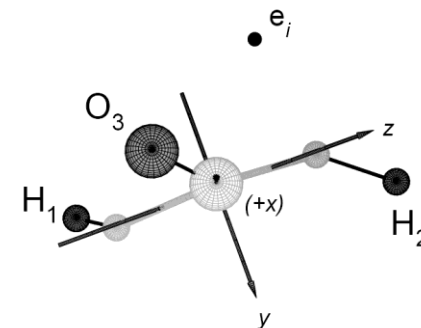
Vibrational energies of larger molecules?

Example: H₂O molecule in *xyz* system



Example: H₂O molecule

For water, there are nine displacement coordinates
($\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3$)



Total classical energy in terms of these coordinates
(for general molecule with N nuclei), $u_1 = \Delta x_1, u_2 = \Delta y_1$ etc.

$$E_{\text{vib}} = \frac{1}{2} \sum_{i=1}^{3N} m_i \dot{u}_i^2 + V_N(u_i),$$

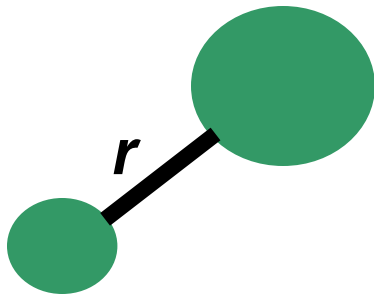
$$\dot{u} = du/dt$$

We expand the potential energy function about equilibrium

$$V_N = \frac{1}{2} \sum_{i,j=1}^{3N} k_{ij} u_i u_j + \frac{1}{6} \sum_{i,j,k=1}^{3N} k_{ijk} u_i u_j u_k + \frac{1}{24} \sum_{i,j,k,l=1}^{3N} k_{ijkl} u_i u_j u_k u_l + \dots,$$

Problem II: What is Ψ_{vib} ?

In order to get a model that can be (easily?) extended to larger molecules, we consider the harmonic potential



$$V_{\text{harm}}(r) = \frac{1}{2}k (r - r_e)^2,$$

We make the analogous (harmonic) approximation for polyatomic molecules

$$E_{\text{vib}}^0 = \frac{1}{2} \sum_{i=1}^{3N} m_i \dot{u}_i^2 + \frac{1}{2} \sum_{i,j=1}^{3N} k_{ij} u_i u_j,$$

Harmonic force constant

Potential energy surface V

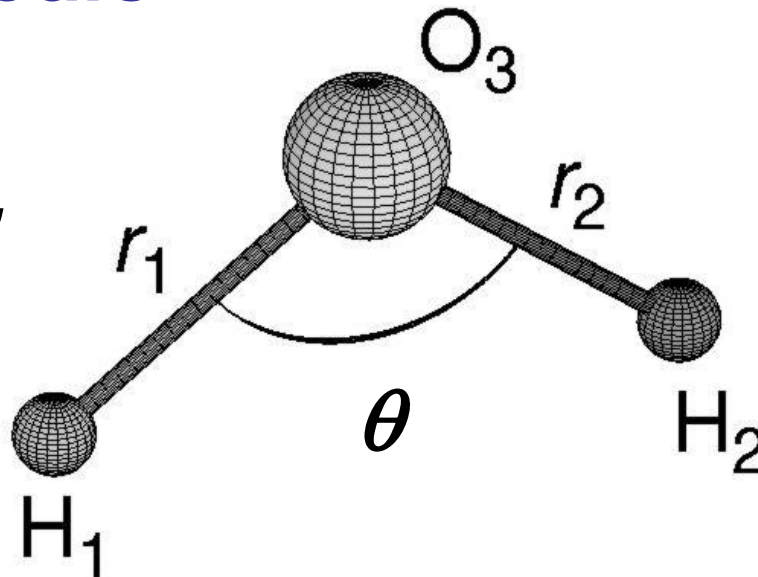
The displacement coordinates ($\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3, \dots$) are not so useful for expressing V .

Geometrically defined coordinates are better.

Geometrically defined coordinates?

Example: H_2O molecule

Bond lengths, bond angles, dihedral angles ...



Harmonic potential surface for H₂O

$$\mathbf{S} = \begin{Bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta \theta \end{Bmatrix} = \begin{Bmatrix} r_1 - r_e \\ r_2 - r_e \\ \theta - \theta_e \end{Bmatrix}$$

$$\begin{aligned} V(\Delta r_1, \Delta r_2, \Delta \theta) &= \frac{1}{2} f_{rr} (\Delta r_1^2 + \Delta r_2^2) + \frac{1}{2} f_{\theta\theta} \Delta \theta^2 + f_{rr'} \Delta r_1 \Delta r_2 \\ &+ f_{r\theta} (\Delta r_1 + \Delta r_2) \Delta \theta + \frac{1}{6} f_{rrr} (\Delta r_1^3 + \Delta r_2^3) \\ &+ \frac{1}{6} f_{\theta\theta\theta} \Delta \theta^3 + \frac{1}{2} f_{rr\theta} (\Delta r_1^2 + \Delta r_2^2) \Delta \theta \\ &+ \frac{1}{2} f_{r\theta\theta} (\Delta r_1 + \Delta r_2) \Delta \theta^2 + \frac{1}{2} f_{rrr'} (\Delta r_1^2 \Delta r_2 + \Delta r_1 \Delta r_2^2) \\ &+ f_{rr'\theta} \Delta r_1 \Delta r_2 \Delta \theta + \dots \end{aligned}$$

Isotopologues (isotopically substituted molecules) have same V – force constants are *isotope independent*

Harmonic V for H_2O

$$\begin{aligned} V(\Delta r_1, \Delta r_2, \Delta\theta) &= \frac{1}{2} f_{rr} (\Delta r_1^2 + \Delta r_2^2) + \frac{1}{2} f_{\theta\theta} \Delta\theta^2 + f_{rr'} \Delta r_1 \Delta r_2 \\ &+ f_{r\theta} (\Delta r_1 + \Delta r_2) \Delta\theta \\ &= \frac{1}{2} \mathbf{S}^T \mathbf{F} \mathbf{S} \end{aligned}$$

$$\mathbf{S} = \begin{Bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta\theta \end{Bmatrix} = \begin{Bmatrix} r_1 - r_e \\ r_2 - r_e \\ \theta - \theta_e \end{Bmatrix} \quad \mathbf{F} = \begin{Bmatrix} f_{rr} & f_{rr'} & f_{r\theta} \\ f_{rr'} & f_{rr} & f_{r\theta} \\ f_{r\theta} & f_{r\theta} & f_{\theta\theta} \end{Bmatrix}$$

Quadratic form; superscript T = transposition

Harmonic V for general, non-linear molecule

$$V = \frac{1}{2} \mathbf{S}^T \mathbf{F} \mathbf{S}$$

\mathbf{S} is column vector with $3N-6$ rows containing the geometrically defined coordinates

\mathbf{F} is $(3N-6) \times (3N-6)$ isotope-independent matrix

Classical vibrational kinetic energy for general, non-linear molecule

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

\mathbf{S} is column vector with $3N-6$ rows containing the geometrically defined coordinates

$$\dot{\mathbf{S}} = d\mathbf{S}/dt$$

\mathbf{G} is $(3N-6) \times (3N-6)$ isotope-**dependent** matrix, depends on nuclear masses and equilibrium structure

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