

# Computing ro-vibrational spectra with an Eckart frame

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Spectroscopists often use a zeroth-order harmonic model and perturbation theory to analyse ro-vibrational spectra.

However, for

- high-lying states
- molecules with
  - large amplitude motions
  - important anharmonicity, Coriolis, or centrifugal coupling

one, instead, needs numerically accurate solutions to the Schroedinger equation

$$\hat{H}\psi_n = E_n\psi_n$$

What is  $\hat{H}$ ?

How does one solve the Schroedinger equation?

$$\hat{H} = \hat{K} + \hat{V}$$

To compute a spectrum one must choose coordinates that describe the shape and orientation of the molecule and find the associated kinetic energy operator (KEO).

- the chain rule

To obtain the potential

- solve the electronic Schroedinger equation for many different shapes
- fit a function to these points

## How does one solve the Schroedinger equation ?

- represent wavefunctions with basis functions

$$\psi_n(\mathbf{r}, \boldsymbol{\theta}) = \sum_k c_k^n f_k(\mathbf{r}, \boldsymbol{\theta})$$

- compute eigenvalues and eigenvectors of the Hamiltonian matrix

# Fundamental Recipe

$$\hat{K} + \hat{V} \rightarrow \hat{H} \xrightarrow{\text{basis}} \mathbf{H} \rightarrow \begin{array}{l} \text{eigenvalues,} \\ \text{eigenvectors} \end{array} \rightarrow \begin{array}{l} \text{energies,} \\ \text{wavefunctions} \end{array}$$

→ Spectrum

NB : I am not fitting with an effective Hamiltonian ;  
I am not using perturbation theory

## Compute a ro-vibrational spectrum

- without approximating the potential
  - the potential is not re-represented as a sum-of-products
  - the potential is not re-represented as a sum of terms with one, two, etc coordinates
- without approximating the kinetic energy operator (KEO)
  - terms in the KEO are not neglected
  - coordinate-dependent functions in the KEO are not expanded
- We wish to compute many levels (not just fundamental bands)

# We want to be able to deal with large amplitude motion

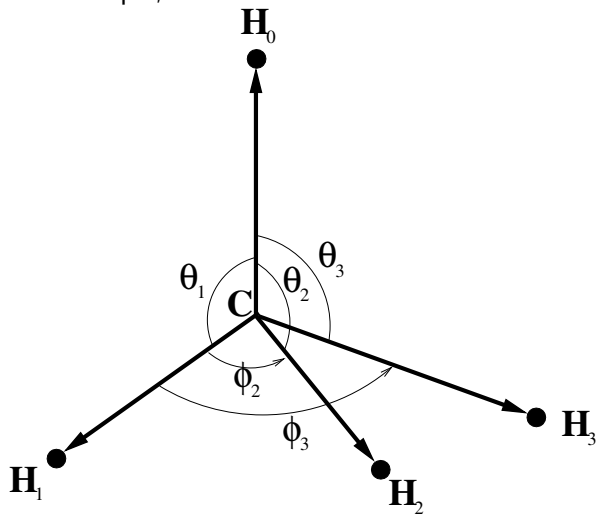
Normal coordinates are not appropriate for molecules with large amplitude motion

For large amplitude motion it is best to :

- choose  $N - 1$  vectors to describe the shape and orientation
- use the lengths of the vectors and the associated spherical polar angles as vibrational coordinates



For example,



## Consider first the $J = 0$ problem

The general KEO is

$$T = T_s + T_b$$

with

$$T_s = - \sum_{k=0}^{N-2} \frac{1}{2\mu_k} \frac{\partial^2}{\partial r_k^2}$$

and

$$T_b = T_{b,\text{diag}} + T_{b,\text{off}} .$$

$$\begin{aligned}
T_{\text{b,diag}} &= [B_0(r_0) + B_1(r_1)] \left[ -\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \theta_1 \frac{\partial}{\partial \theta_1} + \frac{1}{\sin^2 \theta_1} L_z^2 \right] \\
&\quad + \sum_{k=2}^{N-2} [B_0(r_0) + B_k(r_k)] l_k^2 \\
&\quad + B_0(r_0) \left[ 2L_z^2 + 2 \sum_{k \neq k'=2}^{N-2} l_{kz} l_{k'z} \right] \\
T_{\text{b,off}} &= B_0(r_0) \left[ (L_+) a_1^- + (L_-) a_1^+ + \sum_{k \neq k'=2}^{N-2} (l_{k+} l_{k'-} + l_{k-} l_{k'+}) \right]
\end{aligned}$$

## A convenient basis is

$$f_{k_1, l_1, k_2, l_2, m_2 \dots} = \chi_{k_1}(r_1) \Theta_{l_1}^{m_1}(\theta_1) \chi_{k_2}(r_2) \Theta_{l_2}^{m_2}(\theta_2) \Phi_{m_2}(\phi_2) \dots$$

with  $m_1 = -m_2 - m_3 - \dots$

In this basis

- there are simple equations for all KEO matrix elements
- singularities in the KEO cause no trouble.

Between 10 and 100 1-d functions required for each coordinate.

$\Rightarrow > 10^{3N-6}$  multi-d basis functions required.

The Hamiltonian matrix is

- too large to calculate
- too large to store in memory
- too large to diagonalise

# Diagonalization can be avoided by using iterative methods

- A spectrum can be computed from time-independent methods that require only evaluating matrix-vector products
- Matrix-vector products can be done without storing the matrix
- Only a few vectors are stored

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \rightarrow \begin{pmatrix} \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot \end{pmatrix} = \mathbf{T}$$

- Among the eigenvalues of  $\mathbf{T}$  are eigenvalues of  $\mathbf{H}$
- Eigenvectors of  $\mathbf{H}$  are obtained from those of  $\mathbf{T}$

# Key advantages of an iterative approach

- Obviates the need to store a matrix representation of the Hamiltonian
- Even better, Hamiltonian matrix elements are never calculated
- Using such methods one does not need to approximate the potential because multi-dimensional quadrature does not significantly increase the cost



Even for  $J = 0$  methane, a product basis calculation is large

$$|\alpha_0 \alpha_1 \alpha_2 \alpha_3\rangle |l_1 l_2 m_2 l_3 m_3\rangle$$

It would be necessary to use  $\sim 20^9$  basis functions (4000 GB for one vector)!

# Contracted basis functions

It is better to use products of eigenfunctions of reduced-dimension Hamiltonians.

E.g.,

$$H = H_{bend} + H_{stretch} + \Delta_{coupling}$$

$$H_{bend} b(\boldsymbol{\theta}) = E_b b(\boldsymbol{\theta})$$

$$H_{stretch} s(\mathbf{r}) = E_s s(\mathbf{r})$$

$s(\mathbf{r})b(\boldsymbol{\theta})$  is a contracted basis function.

A small number of the  $s(\mathbf{r})b(\boldsymbol{\theta})$  are retained.

# How do we incorporate coupling between bends and stretches?

To evaluate matrix-vector products for the matrix

$$\langle s'(\mathbf{r})b'(\boldsymbol{\theta}) | \Delta_{\text{coupling}} | b(\boldsymbol{\theta})s(\mathbf{r}) \rangle$$

we exploit the fact that  $\Delta V$  is diagonal in the DVR used to solve the stretch problem :

$$\langle s'(\mathbf{r})b'(\boldsymbol{\theta}) | \Delta V | b(\boldsymbol{\theta})s(\mathbf{r}) \rangle = \sum_{\alpha} D_{s'\alpha}^t F_{b'b}^{\alpha} D_{\alpha s}$$

$\langle s'(\mathbf{r})b'(\boldsymbol{\theta})|\Delta V|b(\boldsymbol{\theta})s(\mathbf{r})\rangle$  is too big to store

	$s$	$s'$	$s''$	$\dots$
$s$	$V_{b'b}^{ss}$	$V_{b'b}^{ss'}$	$V_{b'b}^{ss''}$	$\dots$
$s'$	$V_{b'b}^{s's}$	$V_{b'b}^{s's'}$	$V_{b'b}^{s's''}$	$\dots$
$s''$	$V_{b'b}^{s''s}$	$V_{b'b}^{s''s'}$	$V_{b'b}^{s''s''}$	$\dots$
$\dots$	$\dots$	$\dots$	$\dots$	$\dots$

$= \langle b's'|\Delta V|bs\rangle$

# $F_{b'b}^\alpha$ is not too big to store

	$\alpha$	$\alpha'$	$\alpha''$	$\dots$
$\alpha$	$F_{b'b}^\alpha$	0	0	0
$\alpha'$	0	$F_{b'b}^{\alpha'}$	0	0
$\alpha''$	0	0	$F_{b'b}^{\alpha''}$	0
$\dots$	0	0	0	$\dots$

$= \langle b'\alpha' | \Delta V | b\alpha \rangle$

Basis	$l_{max} = m_{max}$	$n_{bend}$	$E_b^{cut}$	$n_b$	$n_i$	$n_{stretch}$	$E_s^{cut}$	$n_s$
Basis I	25	3.26M	8090	280	10	5049	20000	260

$$33 \times 10^9 \rightarrow 72 \times 10^3$$

reduction of six orders of magnitude

If the molecule-fixed axes are attached to two vectors the KEO is still compact :

$$T = T_s + T_{\text{br}} + T_{\text{cor}}$$

with

$$T_{\text{br}} = T_{\text{br,diag}} + T_{\text{br,off}} .$$

$$\begin{aligned}
T_{\text{br,diag}} &= [B_0(r_0) + B_1(r_1)] \left[ -\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \theta_1 \frac{\partial}{\partial \theta_1} + \frac{1}{\sin^2 \theta_1} (J_z - L_z)^2 \right] \\
&\quad + \sum_{k=2}^{N-2} [B_0(r_0) + B_k(r_k)] l_k^2 \\
&\quad + B_0(r_0) \left[ J^2 - 2(J_z - L_z)^2 - 2J_z(L_z) + 2 \sum_{k \neq k'=2}^{N-2} l_{kz} l_{k'z} \right] \\
T_{\text{br,off}} &= B_0(r_0) \left[ (L_+) a_1^- + (L_-) a_1^+ + \sum_{k \neq k'=2}^{N-2} (l_{k+} l_{k'-} + l_{k-} l_{k'+}) \right] \\
T_{\text{cor}} &= -B_0(r_0) [J_-(a_1^+ + L_+) + J_+(a_1^- + L_-)]
\end{aligned}$$



$$f_{k_1, l_1, k_2, l_2, m_2 \dots, J, K, M} = \chi_{k_1}(r_1) \Theta_{l_1}^{m_1}(\theta_1) \chi_{k_2}(r_2) \Theta_{l_2}^{m_2}(\theta_2) \Phi_{m_2}(\phi_2) \dots \\ \times D_{MK}^{J*}(\alpha, \beta, \gamma)$$

with  $m_1 = K - m_2 - m_3 - \dots$

A factor of  $2J + 1$  larger than the already huge product vibrational basis!

With  $m_1 = K - m_2 - m_3 - \dots$

- all matrix elements of the KEO are known in closed form
- singularities in the KEO cause no trouble

# An obvious strategy is to use a basis of products of $D_{MK}^{J*}$ and vibrational eigenfunctions

The Hamiltonian may be written

$$H = H_{vib} + H_{rv} .$$

Eigenfunctions of  $H_{vib}$ ,  $|v\rangle$ , are, in turn, computed in a  $s(\mathbf{r})b(\boldsymbol{\theta})$  basis.

The  $b(\boldsymbol{\theta})$  are computed in a basis of products of angular functions.

# Two problems

- In the basis in which there are simple equations for the matrix elements and singularities are sure not to cause trouble, the *vibrational* basis functions depend on  $K$  and hence  $b(\theta)$  must be computed for each  $K$
- In the two-vector embedded KEO, coupling between rotation and vibration can be so large that the  $D_{MK}^{J*} |v\rangle$  basis is too big

Neither of these problems exists if one uses the Watson KEO  
in normal coordinates (Eckart frame),  
but we wish to be able to deal with large amplitude motion.

## A $K$ -independent bend basis

We use  $m_1 = -m_2 - m_3 - \dots$

rather than  $m_1 = K - m_2 - m_3 - \dots$

Some of the matrix elements required to compute  $|v\rangle$  in this basis are infinite

They involve the factor

$$\langle \Theta_{l_1}^{m_2} | \frac{1}{\sin^2 \theta_1} | \Theta_{l_1'}^{m_2} \rangle ,$$

which is infinite if  $m_2 = 0$ ,

$\theta_1$  is the angle between  $\vec{r}_0$  and  $\vec{r}_1$ .

As long as all wavefunctions are tiny near  $\theta_1 = 0, \pi$   
the infinite integrals cause no trouble

# Test the new basis

First, test to see if it can be used to compute, without contraction, ro-vibrational states.



# Ro-vibrational levels of $\text{H}_2\text{O}_2$

TABLE I: Selected rotational levels of  $\text{H}_2\text{O}_2$  (in  $\text{cm}^{-1}$ ).

Basis :  $l_x = m_x = 27$ ,  $n_{r0} = 8$ ,  $n_{r1} = 4$ ,  $n_{r2} = 4$ .

	old basis	new basis
J=1,even		
A+	10.92037	10.92037
B+	12.74179	12.74179
B+	21.90777	21.90777
J=10,even		
A+	93.98948	93.98948
A+	102.22920	102.22920
A+	130.82938	130.82938
A+	176.70749	176.70749
B+	115.14294	115.14294
B+	141.80373	141.80373
B+	187.67813	187.67813

TABLE I: Basis size and spectral range (in  $\text{cm}^{-1}$ ).

	old basis	new basis
J=1,even		
$N_{basis}$	2.757 M	2.761 M
$\Delta E$	81 K	86 K
J=10,even		
$N_{basis}$	18.54 M	19.73 M
$\Delta E$	82 K	489 K

- The basis size only increases slightly
- The spectral range is larger, increases with increasing  $J$

- Results with the two bases agree to  $0.00001 \text{ cm}^{-1}$ .
- The new basis works well because wavefunctions are tiny when H-O-O is nearly linear.

Fix the stretch coordinates and solve a bend-rotation problem for  $\text{CH}_4$ .

TABLE I:  $J = 5$  bend-rotation levels of the ground state of methane computed with the shared-K basis and the non-shared-K basis (in  $\text{cm}^{-1}$ ).

$T_d$	shared-K		non-shared-K	
	$L = 25$	$L = 29$	$L = 25$	$L = 29$
$F_1$	160.56526 ( $A_2$ )	160.56516 ( $A_2$ )	160.56541 ( $A$ )	160.56516 ( $A$ )
	160.56527 ( $E$ )	160.56516 ( $E$ )	160.56532 ( $B$ )	160.56516 ( $B$ )
			160.56547 ( $B$ )	160.56516 ( $B$ )
$F_2$	160.57101 ( $A_1$ )	160.57090 ( $A_1$ )	160.57110 ( $A$ )	160.57090 ( $A$ )
	160.57101 ( $E$ )	160.57090 ( $E$ )	160.57120 ( $A$ )	160.57090 ( $A$ )
			160.57114 ( $B$ )	160.57090 ( $B$ )
$E$	160.58580 ( $E$ )	160.58569 ( $E$ )	160.58589 ( $A$ )	160.58569 ( $A$ )
			160.58601 ( $B$ )	160.58569 ( $B$ )
			160.58885 ( $A$ )	160.58844 ( $A$ )
$F_1$	160.58854 ( $A_2$ )	160.58844 ( $A_2$ )	160.58857 ( $B$ )	160.58844 ( $B$ )
	160.58857 ( $E$ )	160.58844 ( $E$ )	160.58876 ( $B$ )	160.58844 ( $B$ )

Results with the two bases agree to  $0.00001 \text{ cm}^{-1}$ .

TABLE I: Selected  $J = 5$  bend-rotation levels (lowest  $F_2$  level of the Tetradecad) of methane computed with the shared-K basis and non-shared-K basis (in  $\text{cm}^{-1}$ ).

shared-K			non-shared-K		
$L = 25$	$L = 29$	$L = 31$	$L = 25$	$L = 29$	$L = 31$
5409.99210 ( $A_1$ )	5409.81211 ( $A_1$ )	5409.81114 ( $A_1$ )	5410.02992 ( $A$ )	5409.81246 ( $A$ )	5409.81117 ( $A$ )
5409.98310 ( $E$ )	5409.81200 ( $E$ )	5409.81114 ( $E$ )	5410.27410 ( $A$ )	5409.81577 ( $A$ )	5409.81143 ( $A$ )
			5409.96826 ( $B$ )	5409.81190 ( $B$ )	5409.81114 ( $B$ )

Results with the two bases agree to  $0.004 \text{ cm}^{-1}$  for  $L=29$

Results with the two bases agree to  $0.0003 \text{ cm}^{-1}$  for  $L=31$

# The contracted basis built from the non-shared $K$ basis works well

TABLE I: Errors ( $\text{cm}^{-1}$ ) of  $J = 1$  bend-rotation levels in the contracted basis with respect to levels computed with the full primitive  $L = 29$  non-shared  $K$  basis

$N_{\text{poly}}$		1	2	3	4	< 5	> 6	> 6	
$n_b$		6	21	56	126	231	280	437	
$E_{\text{cut}}$		1580	3150	4730	6310	7440	8090	9020	
$(v_1 v_2 v_3 v_4 \Gamma_v) \Gamma_{vr} C_s$									non-shared- $K$
$(0000A_1)F_1$	$A$	0.2353	0.0044	0.0002	0.0000	0.0000	0.0000	0.0000	10.7083
	$A$	0.6343	0.0298	0.0024	0.0003	0.0000	0.0000	0.0000	10.7083
	$B$	0.7070	0.0317	0.0025	0.0003	0.0000	0.0000	0.0000	10.7083
$(0100E)F_2$	$A$	17.8425	0.3453	0.0166	0.0013	0.0003	0.0002	0.0000	1583.8499
	$B$	19.4902	0.4063	0.0292	0.0024	0.0004	0.0003	0.0001	1583.8499
	$B$	20.2336	0.7049	0.0396	0.0041	0.0009	0.0005	0.0001	1583.8499
$(0100E)F_1$	$A$	27.0161	0.7630	0.0249	0.0016	0.0002	0.0001	0.0000	1583.9879
	$B$	29.4793	0.9008	0.0519	0.0051	0.0010	0.0006	0.0001	1583.9879
	$B$	28.5257	0.9534	0.0229	0.0016	0.0003	0.0001	0.0000	1583.9879

# The contracted basis is orders of magnitude smaller

Vibrational basis size comparison :

- $6.7 \times 10^6 \gg n_b$

## Ro-vibrational coupling is too strong

Although the contracted basis is much smaller,  
the size of the contracted bend-stretch basis  
required for  $J > 5$  is too big.



For many molecules, ro-vibrational coupling is smaller in an Eckart frame.

It is straightforward to use an Eckart frame with normal coordinates.

How does one use an Eckart frame with polyspherical coordinates?

The best of both worlds : vibrational coordinates that enable one to deal with large-amplitude motion AND an Eckart frame that minimizes ro-vibrational coupling

# For a 3-atom molecule it is possible to derive the Eckart frame - Radau coordinate KEO

H. Wei and T. Carrington, Chem. Phys. Lett. **287**, 289-300 (1998)

$$T = T^{\text{vib}} + T^{\text{rot}} + T^{\text{cor}},$$

where

$$T^{\text{vib}} = -\frac{1}{2m_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial R_2^2} - \left( \frac{1}{2m_1 R_1^2} + \frac{1}{2m_2 R_2^2} \right) \frac{\partial}{\partial c} (1 - c^2) \frac{\partial}{\partial c},$$

$$T^{\text{rot}} = \frac{1}{2} [G_{xx} J_x^2 + G_{yy} J_y^2 + G_{zz} J_z^2 + G_{xy} (J_x J_y + J_y J_x)],$$

$$T^{\text{cor}} = -\frac{i}{2} \sum_{v=R_1, R_2, c} \left[ G_{vz} \frac{\partial}{\partial v} + \frac{\partial}{\partial v} G_{vz} \right] J_z,$$

$$\begin{aligned}
G_{R_1 z} &= -\Lambda \epsilon \rho R_2 \sin(\theta - \theta_e), \\
G_{R_2 z} &= \Lambda \rho R_1 \sin(\theta - \theta_e), \\
G_{cz} &= \Lambda \sin \theta [1 - \epsilon \rho^2 - \rho(R_1/R_2 - \epsilon R_2/R_1) \cos(\theta - \theta_e)], \\
G_{xx} &= \Lambda(1 - c^2)^{-1} [S_1^2 + S_2^2/\epsilon], \\
G_{yy} &= \Lambda(1 - c^2)^{-1} [C_1^2 + C_2^2/\epsilon], \\
G_{xy} &= \Lambda(1 - c^2)^{-1} [-S_1 C_1 + S_2 C_2/\epsilon], \\
G_{zz} &= \Lambda[1 + \epsilon \rho^2],
\end{aligned}$$

where

$$\begin{aligned}
S_1 &= \sin(\theta - \eta_e) + \epsilon \rho (R_2/R_1) \sin(\theta_e - \eta_e), \\
C_1 &= \cos(\theta - \eta_e) + \epsilon \rho (R_2/R_1) \cos(\theta_e - \eta_e), \\
S_2 &= \epsilon \rho \sin(\theta - \theta_e + \eta_e) + (R_1/R_2) \sin \eta_e, \\
C_2 &= \epsilon \rho \cos(\theta - \theta_e + \eta_e) + (R_1/R_2) \cos \eta_e, \\
1/\Lambda &= m_1 [R_1^2 + (\epsilon \rho R_2)^2 + 2\epsilon \rho R_1 R_2 \cos(\theta - \theta_e)],
\end{aligned}$$

- difficult to use
- almost impossible to derive for a larger molecule

For any molecule-fixed axis system, the classical kinetic energy is,

$$K_{class} = \frac{1}{2} (J \quad p) \begin{pmatrix} G_{rr} & G_{rv} \\ G_{rv}^t & G_{vv} \end{pmatrix} \begin{pmatrix} J \\ p \end{pmatrix}$$

We want to use

- a vibrational KEO in polyspherical coordinates
- the volume element  $\sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \cdots d\phi_2 \cdots dr_1 \cdots$
- a standard  $\Theta_{l_1}^{m_1}(\theta_1)\Theta_{l_2}^{m_2}(\theta_2)\Phi_{m_2}(\phi_2) \cdots$  bend basis.

This enables us to deal with large amplitude vibrational motion

The proper KEO is

$$K_{QM} = K_{vib}^{Radau} + \frac{1}{2} \mathbf{J}^t \mathbf{G}_{rr} \mathbf{J} + K_{vr} + K_{vr}^\dagger$$

with

$$K_{vr} = \frac{1}{2} \sum_{k\alpha} p_k (G_{rv})_{k\alpha} J_\alpha$$

where

$$p_k = \frac{1}{i} \frac{\partial}{\partial r} \quad \text{when } k = r$$

$$p_k = \frac{1}{i} \frac{\partial}{\partial d\phi} \quad \text{when } k = \phi$$

$$p_k = \frac{1}{i} \left( \frac{\partial}{\partial \theta} + \frac{1}{2} \cot \theta \right) \quad \text{when } k = \theta$$

# How does one compute $G_{rv}$ and $G_{rr}$ in an Eckart frame?

- We do not have expressions for the elements.
- We can calculate the value of  $G_{rv}$  and  $G_{rr}$  at each polyspherical point.
- For  $\mathbf{I}^{-1}$  this is done by finding the orientation of the Eckart frame and using the Cartesian coordinates of the nuclei.
- The orientation of the Eckart frame is found from a singular value decomposition (SVD)

For  $G_{rv}$  we use ideas of (Rolf) Meyer, Pickett, McCoy and Sibert, Lauvergnat, etc

$$\mathbf{G}_{rv} = \mathbf{C}\mathbf{G}_{vv}$$

$$\mathbf{C} = \mu\mathbf{X}$$

$$X_{\alpha,k} = \sum_{i=1}^N m_i \epsilon_{\alpha\beta\gamma} x_{\beta i} \frac{\partial x_{\gamma i}}{\partial Q_k}$$

$X$  is calculated from elements of the inverse of  $B$   
where

$$B_{k,\alpha i} = \frac{\partial Q_k}{\partial x_{\alpha i}}$$

whose elements are computed from finite difference derivatives



# For H<sub>2</sub>O numerical and analytic $G$ matrix elements agree well

At  $r_1 = 1.7$  bohr,  $r_2 = 1.5$  bohr,  $\theta = 100^\circ$

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gv(1,1)	$4 \times 10^{-14}$
gv(1,2)	$< 10^{-14}$
gv(1,3)	$< 10^{-14}$
gv(3,3)	$2 \times 10^{-13}$

grv(2,1)	$< 10^{-14}$
grv(2,2)	$1 \times 10^{-14}$
grv(2,3)	$< 10^{-14}$

grr(1,1)	$< 10^{-14}$
grr(3,3)	$1 \times 10^{-14}$
grr(1,3)	$< 10^{-14}$
grr(2,2)	$< 10^{-14}$

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# One expects better convergence when using an Eckart frame

With the  $z$  axis along a Radau vector the Coriolis coupling is proportional to  $B_0(r_0)$  (for  $\text{H}_2\text{O}$   $19 \text{ cm}^{-1}$ )

$$T_{cor} = B_0(r_0) \left[ -2p_{\theta_1} J_y \right]$$

In an Eckart frame the Coriolis coupling is zero at equilibrium.

# $J = 20$ results for $\text{H}_2\text{O}$ demonstrate advantage of Eckart

Assign	$K_a$ $K_c$	Large basis		Small basis		PS1997
		SKF	DVR	SKF	DVR	
		Bond-z	Eckart	Bond-z	Eckart	
G.S.	$l_x = 31$	$n_\theta = 32$	$l_x = 20$	$n_\theta = 21$		
0	20	4048.353	0.001	2.590	0.001	0.00
1	20	4048.353	0.001	7.571	0.001	0.00
2	18	4738.706	0.000	3.651	0.000	-0.01
3	18	4738.718	0.000	8.283	0.000	-0.01
4	16	5292.163	0.000	6.389	0.001	0.00
5	16	5294.099	0.000	9.865	0.000	-0.01
		5611.387	0.001	25.048	0.001	
		5611.388	0.000	58.993	0.001	
6	14	5680.816	0.000	4.634	0.000	-0.01
7	14	5739.274	0.001	14.933	0.001	0.00
8	12	5966.857	0.000	9.839	0.000	0.00
9	12	6167.755	0.000	15.985	0.000	-0.01
		6379.385	0.001	31.418	0.001	
		6379.432	0.000	55.576	0.000	
10	10	6407.484	0.000	36.524	0.000	0.01
11	10	6664.180	0.001	38.896	0.001	0.00
12	8	6935.460	0.000	33.623	0.000	0.00

# When used with a contracted basis the Eckart frame is much better

$K_a$	$K_c$	Converged	Eckart	Bond-z	Eckart	Bond-z
G.S.		$l_x = 31$	$n_{vib} = 23$	$n_{vib} = 23$	$n_{vib} = 134$	$n_{vib} = 134$
			$E_{cut}=10K \text{ cm}^{-1}$	$E_{cut}=10K \text{ cm}^{-1}$	$E_{cut}=20K \text{ cm}^{-1}$	$E_{cut}=20K \text{ cm}^{-1}$
0	20	4048.353	0.04	94.8	0.000	0.84
1	20	4048.353	0.04	94.8	0.000	0.84
2	18	4738.706	0.04	52.8	0.000	0.28
3	18	4738.718	0.04	52.8	0.000	0.28
4	16	5292.163	0.05	33.0	0.000	-0.12
5	16	5294.099	0.05	33.7	0.000	-0.08
		5611.387	0.45	85.3	0.001	4.60
		5611.388	0.45	152.0	0.000	4.61
6	14	5680.816	0.05	305.6	0.000	-0.88
7	14	5739.274	0.04	374.1	0.000	-0.25
8	12	5966.857	0.04	146.6	-0.001	-0.36
9	12	6167.755	0.04	23.1	0.000	0.19
		6379.385	0.46	50.7	0.000	2.22
		6379.432	0.46	305.3	0.000	2.22
10	10	6407.484	0.04	279.7	0.000	0.49
11	10	6664.180	0.04	23.4	0.000	0.79
12	8	6935.460	0.05	19.7	0.000	1.05

Two problems impede the calculation of a ro-vibrational spectrum using a KEO in polyspherical coordinates and a contracted basis.

- In the standard basis vibrational eigenfunctions must be computed for each  $K$ . For molecules for which vectors can be defined so that  $\theta_1 = 0, \pi$  is inaccessible, this problem is solved by taking  $m_1 = -m_2 - m_3 - \dots$
- With the standard choice of molecule-fixed axes the ro-vibrational coupling is large. This problem can be solved by using Eckart axes and computing G matrix elements numerically.
- Results for methane soon !

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Because the basis is huge it would be far too costly to form the potential matrix and explicitly multiply the matrix with vectors.

To illustrate the computation of a matrix-vector product consider

$$w_{l'm'} = \sum_{lm} V_{l'm',lm} x_{lm}$$

replace

$$\begin{aligned} V_{l'm',lm} &= \int d\theta \int d\phi Y_{l'm'}(\theta, \phi) V(\theta, \phi) Y_{lm}(\theta, \phi) \\ &\approx \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m \end{aligned}$$

$$w_{l'm'} = \sum_{lm} \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m x_{lm}$$

$$w_{l'm'} = \sum_{\beta} T_{l'\beta}^{m'} \sum_{\gamma} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) \sum_m Q_{m\gamma} \sum_l T_{l\beta}^m x_{lm}$$

The largest vector is labelled by the grid indices.