Polyspherical coordinates and kinetic energy operators with TANA (and TNUM)

Coordinates

KEO
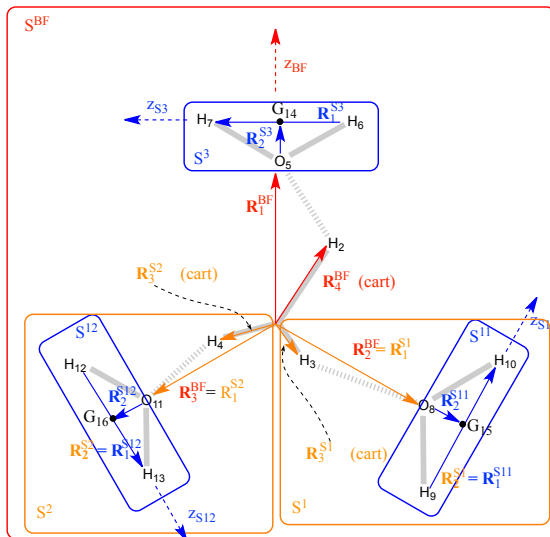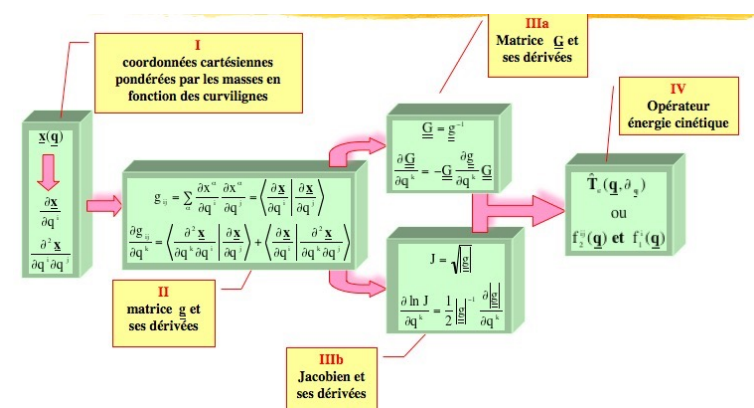
A. Nauts	D. Lauvergnat
F. Gatti	M. Ndong

Outline

- KEO, Tana/Tnum ...

- Simple examples:

  – Water molecule

  – Hydrogen peroxide

- Subsystems

  – Two examples

- Overview

*T*NUM / *T*ANA *programs*

Historic:

2001   First **T**NUM version in F77

          No dynamic memory allocation

2004   last F77 version

2004   First F90 version

          Coupled with E*L*V*IB*R*OT* (too strongly)

2010-   New structure of the coordinate transformations

=> highly flexible. It is very easy to add a new transformation.

2012-   First **T**ANA version

=>Analytical KEO for polyspheric coordinates.

=> Export the KEO in MCTDH .op file

> Not new. Other similar programs : 1969, 1982 ...

> Bad idea!!

> Originality of TNUM

> Both codes share the same input data file.
> => It enables to check the exactness of Tana KEO with respect to Tnum one.

TNUM / TANA installation

1) Download the latest release:
   curl -LJ https://github.com/lauvergn/Tnum-Tana/archive/refs/tags/v0.9.zip --output Tnum-Tana-0.9.zip
   unzip Tnum-Tana-0.9.zip

2) Compile the code:
   make OPT=0

3) Run some tests (optional)
   make OPT=0 ut

   The procedure should run 22 tests without error.

4) More details about the installation are on GitHub:
   https://github.com/lauvergn/Tnum-Tana/wiki#installation

5) New tests files
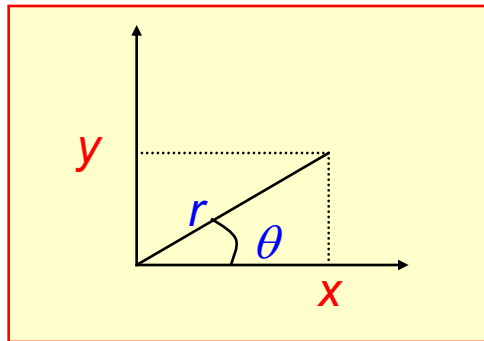   In the Tnum-Tana directory
   curl -LJ https://github.com/lauvergn/KEO_Tana_school/archive/refs/heads/main.zip --output tests.zip
   unzip tests.zip

Choice of coordinates: difficulties

The kinetic energy operator (KEO), **T**, is a Laplacian.

Example : Polar coordinates

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} \qquad d\tau = rdrd\theta$$

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{4r^2} \qquad d\tilde{\tau} = drd\theta$$
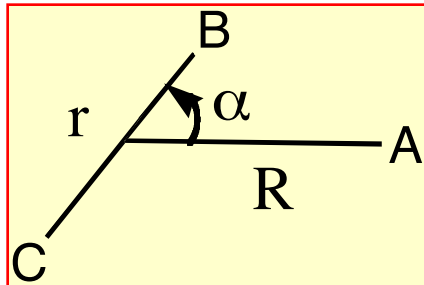
$$\tilde{\Psi} = \sqrt{r} \cdot \Psi$$

When curvilinear coordinates, **q**, are used, the analytical expression of **T** can be extremely intricate (number of terms, complexity of the expression).

   It can be obtained analytically (Jacobi, polysherical, TANA ...)

   It can be expressed numerically (TNUM)

Example : Jacobi coordinates (ABC)

$$M = \frac{m_A m_{BC}}{m_{ABC}} \qquad et \qquad m = \frac{m_B m_C}{m_{BC}}$$

Deformation *part*

$$\hat{T}_{def} = \frac{-\hbar^2}{2}\left\{\frac{1}{M}\left[\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right] + \frac{1}{m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + \left(\frac{1}{M}\frac{1}{R^2} + \frac{1}{m}\frac{1}{r^2}\right)\left[\frac{\partial^2}{\partial\alpha^2} + \frac{\cos(\alpha)}{\sin(\alpha)}\frac{\partial}{\partial\alpha}\right]\right\}$$

$$d\tau_{def} = R^2 r^2 .\sin(\alpha)dRdrd\alpha$$

+ **Coriolis** *part (coupling between the rotation and the deformation)*

+**Rotation** *part*

+**Center of mass** *part*

Several routes to obtain a Kinetic Energy Operator $\hat{T}$:

- *Using the Jacobian matrices to get the metric tensors[1,2]:*

$$\hat{T}_{\mathbf{q}}(\mathbf{q}, \partial_{\mathbf{q}}) = -\frac{\hbar^2}{2} \sum_{ij} \rho(\mathbf{q})^{-1} \frac{\partial}{\partial q^i} \rho(\mathbf{q}) G^{ij}(\mathbf{q}) \frac{\partial}{\partial q^j} + v(\mathbf{q})$$

$$d\tau = \rho(\mathbf{q}) dq^1 \cdots dq^n$$

Contravariant components of metric tensor

Used for the numerical implementation[3] (TNUM[4]).

non-Euclidean volume element

- Using the conjugate momenta, $\vec{\hat{P}}_i$, associated with the vectors, $\vec{R}_i$ [5,6]:

$$\hat{T} = \frac{1}{2} \sum_{i,i'} M_{i,i'} \vec{\hat{P}}_i^{\dagger} \cdot \vec{\hat{P}}_{i'}$$

Used for the analytical expression / implementation (TANA[7]).

M is diagonal for Jacobi vectors:

$$M_{i,i'} = \frac{1}{\mu_i} \delta_{i,i'}$$

[1] B. Podolsky, Phys. Rev. ... t, C. Iung, Phys. Rev. A 45, 6217–6235 (1992).
[2] A. Nauts and X. Chapu... ung Phys. Rep. 484 1–69 (2009).
[3] J. Laane et al.,JMS 198... . Ndong, L. Joubert-Doriol, H.-D. Meyer, A.
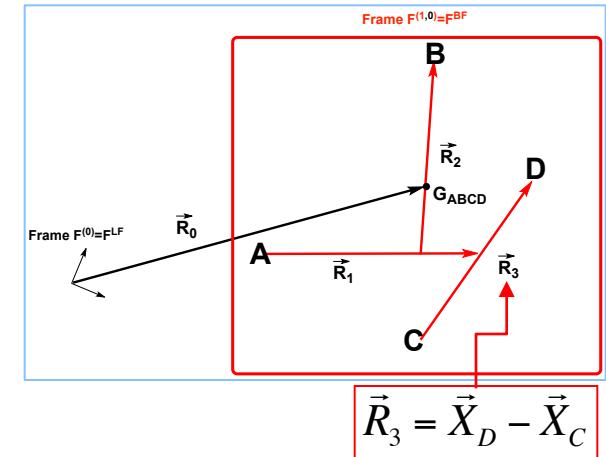[4] D. Lauvergnat et A. Nauts, ... D. Lauvergnat, JCP 136, p034107, (2012).

KEO and polyspherical coordinates: Tana

1. **The molecular system is described with a bunch of vectors**

   Relation between the atomic positions and the vectors:

   $$\vec{R}_i = \sum_k \mathbf{A}_{i,k} \cdot \vec{X}_k$$

   $$\vec{R}_3 = \vec{X}_D - \vec{X}_C$$

   $$M = A \cdot \left[\frac{1}{m_k} \right] \cdot A^t$$

2. **Spherical coordinates of $\vec{R}_i$**
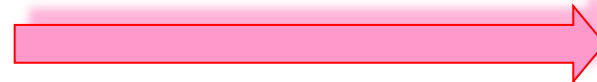
3. **KEO:**

   $$\hat{\mathbf{T}} = \frac{1}{2} \sum_{i,i'} M_{i,i'} \vec{\hat{P}}_i^\dagger \cdot \vec{\hat{P}}_{i'}$$

   The analytical expression is well known

   $$\vec{\hat{P}}_i = \hat{P}_{R_i} \vec{e}_i + \frac{\vec{e}_i \times \vec{\hat{L}}_i}{R_i}$$
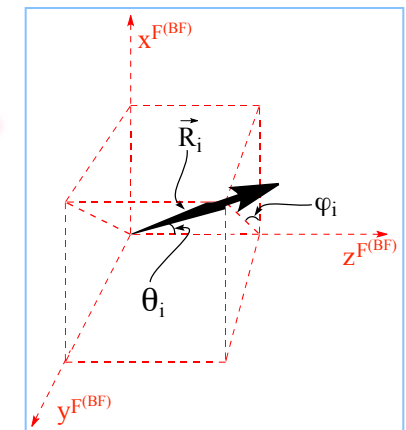
[1] F. Gatti, C. Iung Phys. Rep. 484 1–69 (2009).   [2] F. Gatti, C. Munoz, C. Iung, JCP, 114 8275 (2001).

Outline

- KEO, TANA/TNUM ...

- Simple examples:

  – Water molecule

  – Hydrogen peroxide

- Subsystems

  – Two examples

- Overview

OH$_2$ in valence coordinates: data

1) **Atom list:**

```
&Coord_transfo name_transfo='bunch_poly'
          nat=3 inTOout=f /
```

O H H

Get the right atomic masses
m_H=1837.15...
m_O=29156.94...

2) **Vector definitions:**

use of u_2 ($\cos(\theta_2)$) instead of θ_2.

Add 1 vector in the Frame

```
&Coord_transfo name_transfo='poly' cos_th=t /
```

Along the z-axis frame

```
    &vector nb_vect=1  iAtA=1   iAtB=2  Frame=t /
      &vector            iAtA=1   iAtB=3 /
```

Vector between atoms 1 and 3
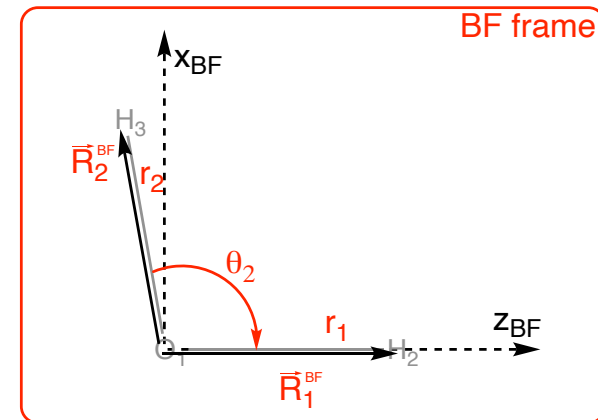
BF frame

x_{BF}

H_3

$\vec{R}_2^{BF}$ r_2

θ_2

r_1 z_{BF}

H_2

O

$\vec{R}_1^{BF}$

OH$_2$ in valence coordinates: output

M matrix:

```
        M_Tana (without the center-of-mass contribution)
  1       0.0005786177        0.0000342971
  2       0.0000342971        0.0005786177
```

KEO (MCTDH format)

```
-1.7148572603041540d-005 |1   q^-1 |2    q^-1*dq*q |3    dq
1.7148572603041540d-005 |1    q^-1 |2    q^-1*dq*q |3    q^2*dq
3.4297145206083079d-005 |1    q^-1 |2    q^-1 |3    dq*q*dq
-3.4297145206083079d-005 |1    q^-1 |2    q^-1 |3    dq*q^3*dq
-1.7148572603041540d-005 |1    q*dq*q^-1 |2    q^-1*dq*q |3    q
-1.7148572603041540d-005 |1    q*dq*q^-1 |2    q^-1 |3    dq
1.7148572603041540d-005 |1    q*dq*q^-1 |2    q^-1 |3    dq*q^2
-1.7148572603041540d-005 |1    q^-1 |2    q*dq*q^-1 |3    dq
1.7148572603041540d-005 |1    q^-1 |2    q*dq*q^-1 |3    dq*q^2
-1.7148572603041540d-005 |1    q^-1*dq*q |2    q*dq*q^-1 |3    q
-1.7148572603041540d-005 |1    q^-1*dq*q |2    q^-1 |3    dq
1.7148572603041540d-005 |1    q^-1*dq*q |2    q^-1 |3    q^2*dq
-2.8930886422588747d-004 |1    q^-2 |3    dq^2
2.8930886422588747d-004 |1    q^-2 |3    dq*q^2*dq
-2.8930886422588747d-004 |1    dq^2
-2.8930886422588747d-004 |2    q^-2 |3    dq^2
2.8930886422588747d-004 |2    q^-2 |3    dq*q^2*dq
-2.8930886422588747d-004 |2    dq^2
```

Term in:

$$-\frac{1}{2\mu_{OH}}\frac{\partial^2}{\partial r_1^2}$$

OH$_2$ in valence coordinates: the full input file

```
&variables
     Old_Qtransfo=f nb_Qtransfo=3
     Tana=t Write_QMotions=t/

&Coord_transfo name_transfo='bunch_poly' inTOout=f
     nat=3 nb_X=0  /
O H H

&Coord_transfo name_transfo='poly' cos_th=t /
     &vector nb_vect=1 Frame=t iAtA=1 iAtB=2 /
      &vector                 iAtA=1 iAtB=3 /


&Coord_transfo name_transfo='active' /
1 1 1

&minimum  /
r1 1. angs
r2 1. angs
u2 0.5
```

Tana: To get the analytical KEO (t)
Old_Qtransfo: To switch to the new input format (f)
nb_Qtransfo: number of coordinate transformations (always 3 for Tana)

Defines the active/inactive coordinates. You should give as many integers as curvilinear coordinates (3nat-6).
- Coordinates associated with 1 are actives.
- Coordinates associated with 100 are inactives
Here, all coordinates are actives

Defines the reference geometry from the curvilinear coordinates (here, r1, r2, u2)

To run "TANA" from the KEO_Tana_school-main directory:

./dat_polyOH2_RRu

Output files:
res: log file
freq.xyz: check the geometry and the coordinates
keo.op: KEO for MCTDH

OH$_2$ in valence coordinates: output, bis

T<small>ANA</small> and T<small>NUM</small> comparison:

```
================================================
--- First comparison with internal analytical KEO
================================================
 BEGINNING comparison_G_FROM_Tnum_Tana
    end calc G with Tana
    end calc G with Tnum
        max diff G:    1.0842021724855044E-019
Relative max diff G:   1.8737797325818844E-016

    end calc f2, f1 with Tnum
    end calc f2, f1 with Tana
        max diff f2:    5.4210108624275222E-020
Relative max diff f2:   1.8737797325818844E-016
        max diff f1:    5.4210108624275222E-020
Relative max diff f1:   3.2968400306584266E-016
        max diff vep:   2.7952087259391911E-020
     vep from Tana:    -4.8020893691158784E-006
     vep from Tnum:    -4.8020893691159063E-006

        max error:   0.33E-15
```

After the analytical derivation of the KEO, two calculations at the reference geometry are performed to get the metric tensor, G, the extra-potential term ... :

- With T<small>NUM</small>
- With T<small>ANA</small>

=> The relative error (max error) MUST be almost zero (< 10^{-10}).

If it is not the case:
- there is a bug
- your input file is wrong (wrong vectors, valence angle close to 0 or π ...)

```
&variables
    Old_Qtransfo=f nb_Qtransfo=3
    Tana=t Write_QMotions=t /

&Coord_transfo name_transfo='bunch_poly' inTOout=f
    nat=3 nb_X=0  /
O H H

&Coord_transfo name_transfo='poly' cos_th=t /
    &vector nb_vect=1 Frame=t iAtA=1 iAtB=2 /
      &vector              iAtA=1 iAtB=3 /


&Coord_transfo name_transfo='active' /
1 1 1

  &minimum read_xyz0=t read_xyz0_with_dummy=f unit='angs' /
      8     0.000000     0.000000     0.127160
      1     0.000000    0.758081    -0.508642
      1     0.000000   -0.758081    -0.508642
```

Defines the reference geometry from the Cartesian coordinates (here in Ångström)

To run "TANA" from the KEO_Tana_school-main directory:

./dat_polyOH2_RRu-cart0

OH$_2$ in Jacobi coordinates: data

One *dummy atom (here center of mass, COM) will be set.*

```
&Coord_transfo name_transfo='bunch_poly'
               nat=3 nb_X=1 inTOout=f /
O H H

&dummyX tab_At_TO_X=1,2 type_dummyX='COM' /
```

List of atoms to define the COM

⚠ Atom and center ordering:
```
centers:  O H H GOH
order:    1 2 3 4
```

```
&Coord_transfo name_transfo='poly' cos_th=t /

   &vector nb_vect=1 iAtA=1  iAtB=2 Frame=t /
     &vector          iAtA=4  iAtB=3 /
```

Vector between G$_{OH}$ (#4) and H (#3)

OH$_2$ in Jacobi coordinates: output

M matrix:

```
        M_Tana (without the center-of-mass contribution)
  1       0.0005786177        -0.0000000000
  2      -0.0000000000         0.0005765848
```

The M matrix is diagonal

KEO (MCTDH format)

```
-2.8930886422588747d-004 |1   q^-2 |3   dq^2
2.8930886422588747d-004 |1   q^-2 |3   dq*q^2*dq
-2.8930886422588747d-004 |1   dq^2
-2.8829239505164130d-004 |2   q^-2 |3   dq^2
2.8829239505164130d-004 |2   q^-2 |3   dq*q^2*dq
-2.8829239505164130d-004 |2   dq^2
```

Less terms than the KEO in valence coordinates.

OH$_2$ in Radau coordinates: data
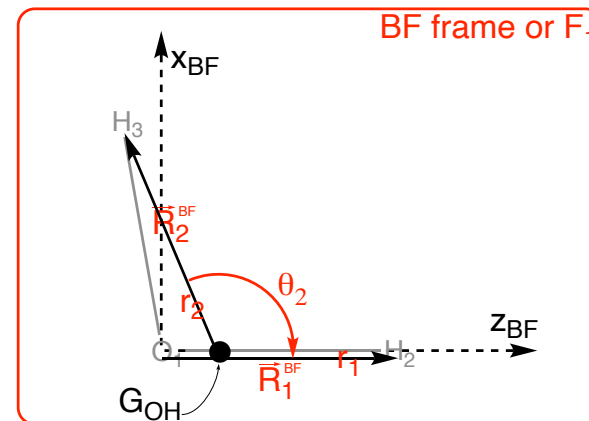
One dummy atom (here center of mass, Radau center) will be set.

```
&Coord_transfo name_transfo='bunch_poly'
            nat=3 nb_X=1 inTOout=f /
O H H

&dummyX tab_At_TO_X=1,  2,3 type_dummyX='Radau' /
```
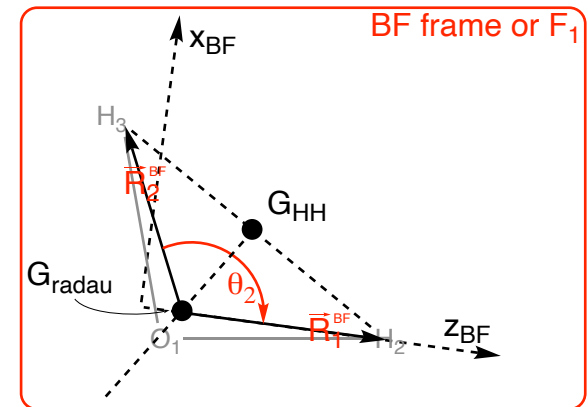
List of atoms to define the center
⚠ The first atom (here #1) is particular

```
&Coord_transfo name_transfo='poly' cos_th=t /

    &vector nb_vect=1 iAtA=4  iAtB=2 Frame=t /
      &vector        iAtA=4  iAtB=3 /
```

All vectors are defines from the Radau center (#4) to the H (#2 and #3)

⚠ Atom and center ordering:
```
centers:  O H H XRadau
order:    1 2 3 4
```

OH$_2$ in Radau coordinates: output

M matrix:

```
         M_Tana (without the center-of-mass contribution)
  1          0.0005443206        -0.0000000000
  2         -0.0000000000         0.0005443206
```

> The M matrix is diagonal
> The values are 1/M$_H$

KEO (MCTDH format)

```
-2.7216029162284596d-004 |1   q^-2 |3   dq^2
2.7216029162284596d-004 |1   q^-2 |3   dq*q^2*dq
-2.7216029162284596d-004 |1   dq^2
-2.7216029162284596d-004 |2   q^-2 |3   dq^2
2.7216029162284596d-004 |2   q^-2 |3   dq*q^2*dq
-2.7216029162284596d-004 |2   dq^2
```

> Almost the same expression as for Jacobi KEO, but the constant are different.

1) Atom list:

```
&Coord_transfo name_transfo='bunch_poly'
                nat=4 inTOout=f /
O O H H
```

2) Vector definitions:


```
&Coord_transfo name_transfo='poly' cos_th=t /
```

Add the vector definitions

Use the following Cartesian coordinates (Å):

8	0.000000	0.698113	-0.050539
8	0.000000	-0.698113	-0.050539
1	0.870648	0.891269	0.404314
1	-0.870648	-0.891269	0.404314

HOOH in valence coordinates
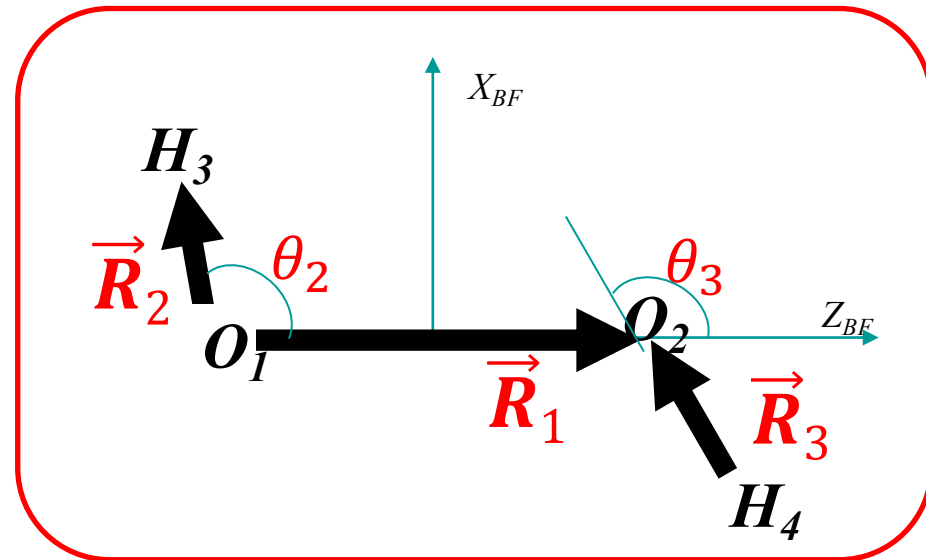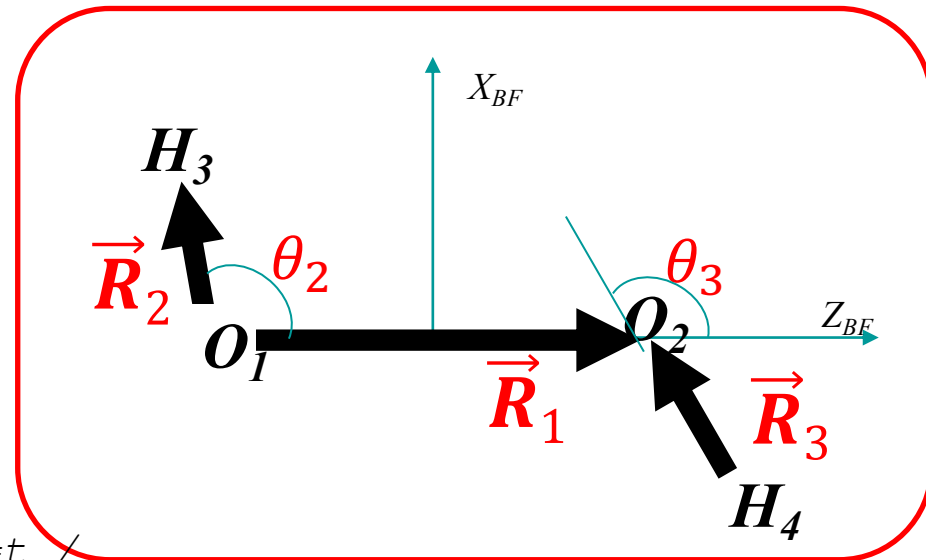
1) Atom list:

```
&Coord_transfo name_transfo='bunch_poly'
               nat=4 inTOout=f /
O O H H
```

2) Vector definitions:

```
&Coord_transfo name_transfo='poly' cos_th=t /

    &vector nb_vect=2 iAtA=1  iAtB=2 Frame=t /
       &vector          iAtA=1  iAtB=3 /
       &vector          iAtA=4  iAtB=2 /
```

HOOH in valence coordinates

M matrix:

M_Tana (without the center-of-mass contribution)
```
 1        0.0000685943        0.0000342971        0.0000342971
 2        0.0000342971        0.0005786177        0.0000000000
 3        0.0000342971        0.0000000000        0.0005786177
```

KEO (some terms):

```
-1.7148572603041540d-005 |1   q^-1 |3   qs*dq |4   q^-1*dq*q |5   qs |6   cos
1.7148572603041540d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   dq*q*qs |6   cos
1.7148572603041540d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   q^2*qs^-1 |6   dq*sin
1.7148572603041540d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   qs |6   dq*sin
3.4297145206083079d-005 |1   q^-1 |4   q^-1 |5   q^3*qs^-2 |6   dq^2
3.4297145206083079d-005 |1   q^-1 |4   q^-1 |5   q |6   dq^2
```

Outline

- KEO, T~ANA~/T~NUM~ ...

- Simple examples:

  – Water molecule

  – Hydrogen peroxide

- **Subsystems**

  – **Two examples**

- Overview

KEO and polyspherical coordinates

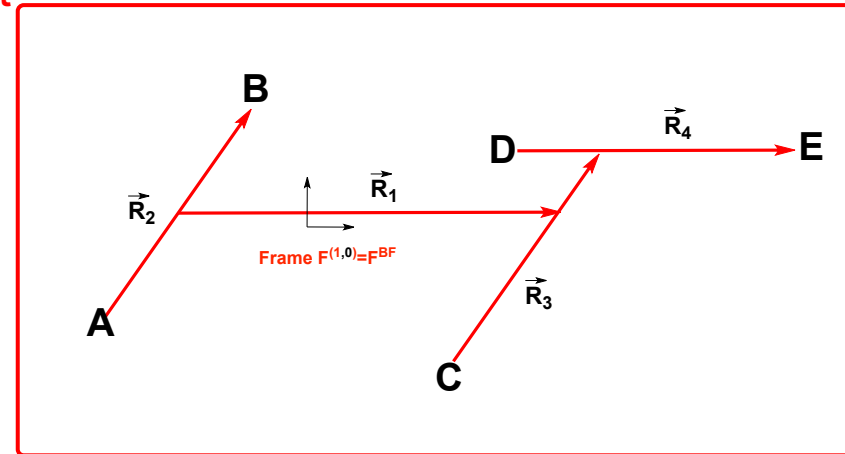The analytical expression of each term is simple, but ....

Ex: Problems with trans parametrization:

θ_4 is angle the between the vectors $\vec{R}_4$ and $\vec{R}_1$.
$=> \theta_4 \sim 0$
"Singularity" or pole

You end up with strong and artificial couplings (θ_4 and φ_4).

More flexibility is required :
z-matrix .... or subsystems

Polyspherical coordinates and subsystems

The molecular system is split into subsystems (subset of the vectors) and each subsystem is attached to a new frame (oriented with respect to a previous frame).

Ex: The new frame, $F^{(1,1,0)}$, is oriented with respect to previous one, $F^{(1,0)}$, with 3 Euler angles (α, β, γ).

- *In $F^{(1,1,0)}$, $\theta_4 \gg 0$*
- *and $\beta \gg 0$*

Remark: α is the previous φ_3 and β is the previous θ_3.
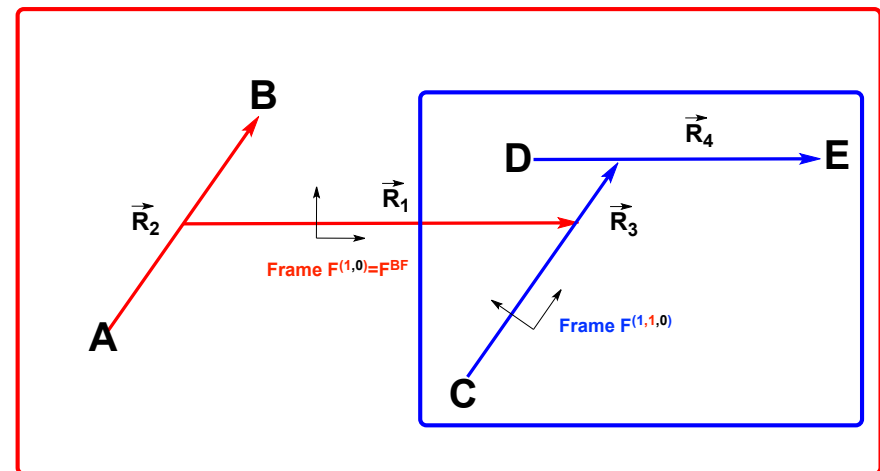
With the subsystems, the singularities can be avoided

=> nested subsystems

```
&Coord_transfo name_transfo='bunch_poly'
              nat=8 inTOout=f /
O C C C H H H

&Coord_transfo name_transfo='poly' cos_th=t /
    &vector nb_vect=?? iAtA=4  iAtB=3 Frame=t /
      &vector          iAtA=3  iAtB=2 /
      ....
```
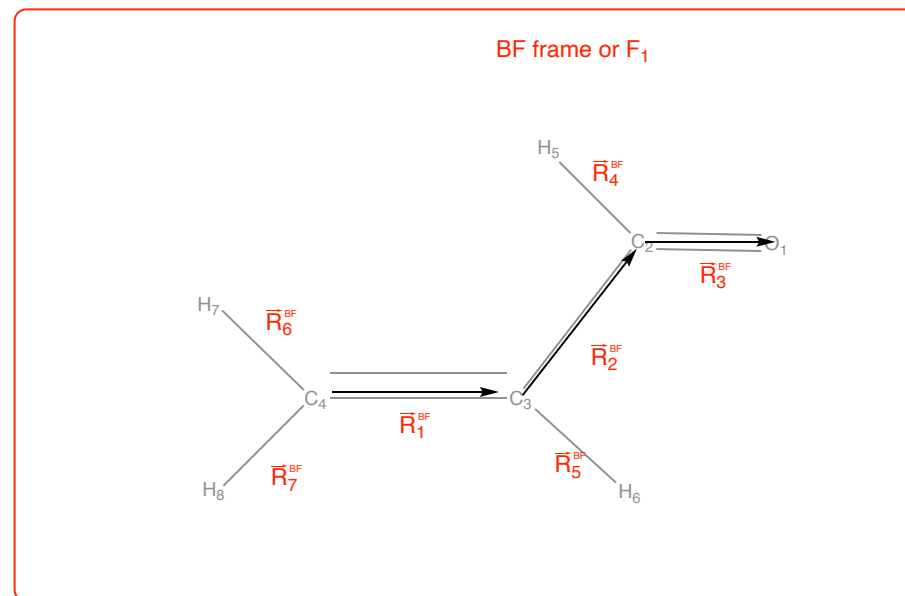

BF frame or F_1

To run "TANA" from the KEO_Tana_school-main directory:

./dat_C3H4O

> **The code stops!**
> **Why?**

Use the following Cartesian coordinates (Å):

8	-1.185723	-1.372699	0.000000
6	-0.122201	-0.774130	0.000000
6	0.000000	0.731002	0.000000
6	1.160929	1.341975	0.000000
1	0.844212	-1.307114	0.000000
1	-0.932833	1.282731	0.000000
1	2.094148	0.792171	0.000000
1	1.247882	2.420718	0.000000

```
Qdyn0 coordinates (not transformed):
R1_F(BF) 2.479105
R2_F(BF) 2.853646
u2_F(BF) 0.535805
R3_F(BF) 2.306212
u3_F(BF) 0.999603
phi3_F(BF) 0.000000
R4_F(BF) 2.085581
u4_F(BF) −0.549986
phi4_F(BF) 0.000000
R5_F(BF) 2.048050
u5_F(BF) 0.524590
phi5_F(BF) 3.141593
R6_F(BF) 2.046829
u6_F(BF) −0.526046
phi6_F(BF) 0.000000
R7_F(BF) 2.045141
u7_F(BF) −0.535316
phi7_F(BF) 3.141593
```

$u_3 = \cos(\theta_3)$ is almost 1.
You are at a pole.

BF frame or F_1

To run "TANA" from the KEO_Tana_school-main directory:

./dat_C3H4O

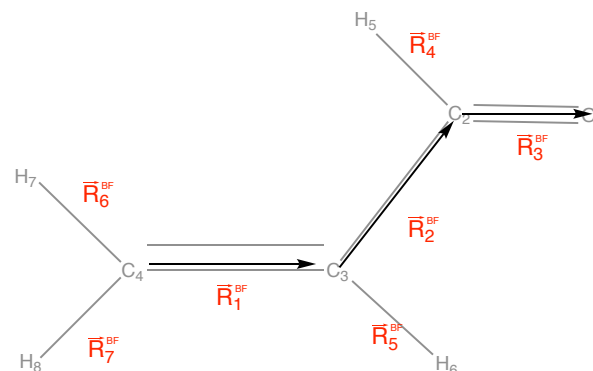The code stops!
Why?

Use the following Cartesian coordinates (Å):

8	−1.185723	−1.372699	0.000000
6	−0.122201	−0.774130	0.000000
6	0.000000	0.731002	0.000000
6	1.160929	1.341975	0.000000
1	0.844212	−1.307114	0.000000
1	−0.932833	1.282731	0.000000
1	2.094148	0.792171	0.000000
1	1.247882	2.420718	0.000000

Subsystem: example

```
&Coord_transfo name_transfo='bunch_poly'
               nat=8 inTOout=f /
O C C C H H H H

&Coord_transfo name_transfo='poly' cos_th=t /
    &vector nb_vect=??  iAtA=4  iAtB=3 Frame=t
      &vector nb_vect=2 iAtA=3  iAtB=2 Frame=t /
        &vector          iAtA=2  iAtB=1 /
        &vector          iAtA=2  iAtB=5 /
      &vector            iAtA=3  iAtB=6 /
      &vector            iAtA=4  iAtB=7 /
      &vector            iAtA=4  iAtB=8 /
```


BF frame or F_1
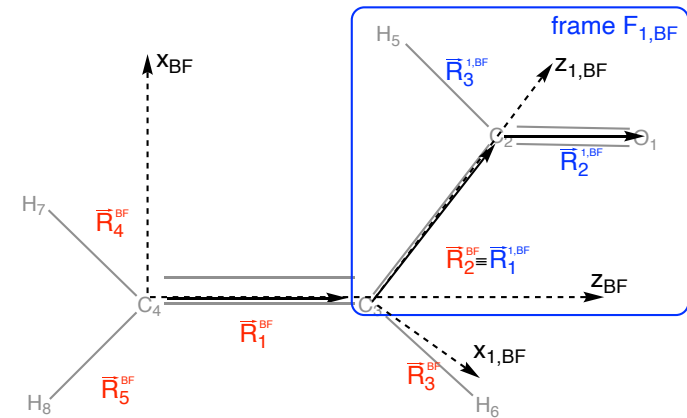
Qdyn0 coordinates (not transformed):

|	
R1_F(BF)	2.479105
R1_F(1,BF)	2.853646
ubeta_F(1,BF)	0.535805
R2_F(1,BF)	2.306212
u2_F(1,BF)	0.559384
gamma_F(1,BF)	3.141593
R3_F(1,BF)	2.085581
u3_F(1,BF)	0.410487
phi3_F(1,BF)	3.141593
R3_F(BF)	2.048050
u3_F(BF)	0.524590
phi3_F(BF)	3.141593
R4_F(BF)	2.046829
u4_F(BF)	-0.526046
phi4_F(BF)	0.000000
R5_F(BF)	2.045141
u5_F(BF)	-0.535316
phi5_F(BF)	3.141593

Example: Furan


```
&Coord_transfo name_transfo='bunch_poly'
              nat=9 nb_X=3 inTOout=f /
O C C C C H H H H

&dummyX tab_At_TO_X=2,4 type_dummyX='COM' /
&dummyX tab_At_TO_X=3,5 type_dummyX='COM' /
&dummyX tab_At_TO_X=2,3,3,5 type_dummyX='COM' /


&Coord_transfo name_transfo='poly' cos_th=t /
     &vector nb_vect=7  iAtA=10  iAtB=11 Frame=t /
        &vector          iAtA=12  iAtB=1 /
        &vector          iAtA=4   iAtB=2 /
        &vector          iAtA=5   iAtB=3 /
        &vector          iAtA=4   iAtB=8 /
        &vector          iAtA=5   iAtB=9 /
        &vector          iAtA=2   iAtB=6 /
        &vector          iAtA=3   iAtB=7 /
```

Do you need a subsystem ?
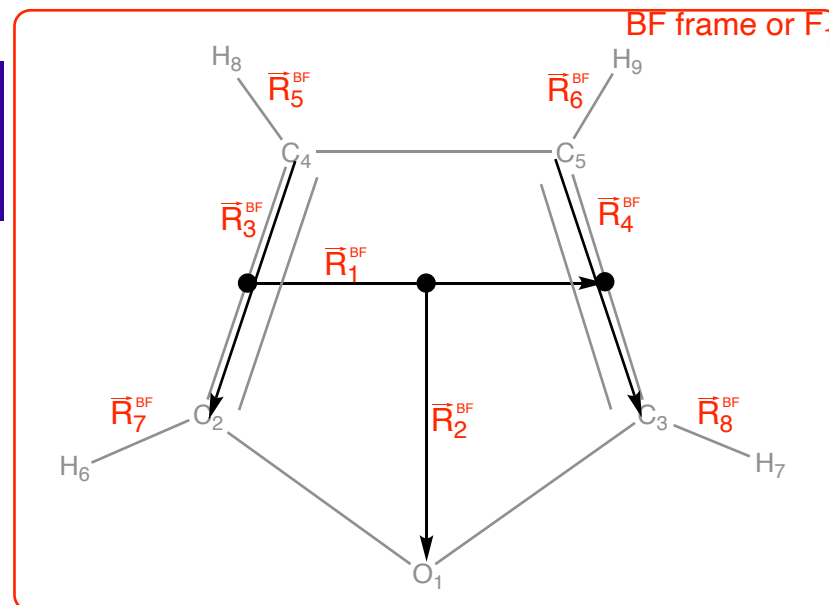
Use the following Cartesian coordinates (Å):

8	0.000000	0.000000	1.169994
6	0.000000	1.094421	0.336796
6	0.000000	-1.094421	0.336796
6	0.000000	0.722289	-0.950050
6	0.000000	-0.722289	-0.950050
1	0.000000	2.065649	0.813863
1	0.000000	-2.065649	0.813863
1	0.000000	1.365721	-1.814317
1	0.000000	-1.365721	-1.814317

Outline

- KEO, TANA/TNUM ...

- Simple examples:

  – Water molecule

  – Hydrogen peroxide

- Subsystems

  – Two examples

- **Overview**

TANA: tips and tricks

1. Vectors:
    - The first vector defines the z-axis of the BF frame (z_{BF}).
    => In the namelist, &vector, you must set frame=t and nb_vect.
    - All the valence angles of the vectors in this frame are defined from the z_{BF} (or the first vector).
    - These are also true when other frames are defined (sub-system).

2. Internal coordinate transformation
    You CANNOT add transformations on top of the polyspherical coordinates (e.g. symmetrization, linear combinations). This is not implemented in TANA, because the sum of products will be lost.
    Remark: this is possible with TNUM, but you don't have the analytical KEO.

3. Reference geometry:
    By default, the geometry is read from the internal coordinates (distances, angles ...), but it is not always easy to determine the corresponding values.
    It is easy to read the Cartesian geometry, and then TNUM computes the internal coordinates.

4. Check the reference geometry and coordinates
    The file *freq.xyz* contains the reference geometry, as well as the displacements of all the internal coordinates.
    => Use the jmol code to visualize the displacements.

5. KEO and the reference geometry
    - Always check the TANA vs TNUM error.
    - When all the 3nat-6 internal coordinates are active (full dimensionality), the analytical KEO is independent of the reference geometry.
    - When a reduced dimensionality model is used, the KEO usually depends on the reference geometry.

Conclusions and perspectives

KEO and polyspherical coordinates:

      + *Analytical expression of T*
      + *Large systems (no built-in limitation)*

      -   *Need more coordinate transformations (1D)*
      -   *Need simplifications ...*

      -   *Need a graphical interface*

Some references

KEO general:

Gatti, F., Lasorne, B., Meyer, H.-D., & Nauts, A. (2017). Applications of Quantum Dynamics in Chemistry (Vol. 98). Springer International Publishing. https://doi.org/10.1007/978-3-319-53923-2

Tana:

Ndong, M., Joubert-Doriol, L., Meyer, H.-D., Nauts, A., Gatti, F., & Lauvergnat, D. (2012). The Journal of Chemical Physics, 136(3), 034107. https://doi.org/10.1063/1.3675163

Ndong, M., Nauts, A., Joubert-Doriol, L., Meyer, H., Gatti, F., & Lauvergnat, D. (2013). The Journal of Chemical Physics, 139(20), 204107. https://doi.org/10.1063/1.4828729

Tnum:

Lauvergnat, D., & Nauts, A. (2002). The Journal of Chemical Physics, 116(19), 8560–8570. https://doi.org/10.1063/1.1469019

Marsili, E., Agostini, F., Nauts, A., & Lauvergnat, D. (2022). Philosophical Transactions of the Royal Society A..., 380(2223). https://doi.org/10.1098/rsta.2020.0388
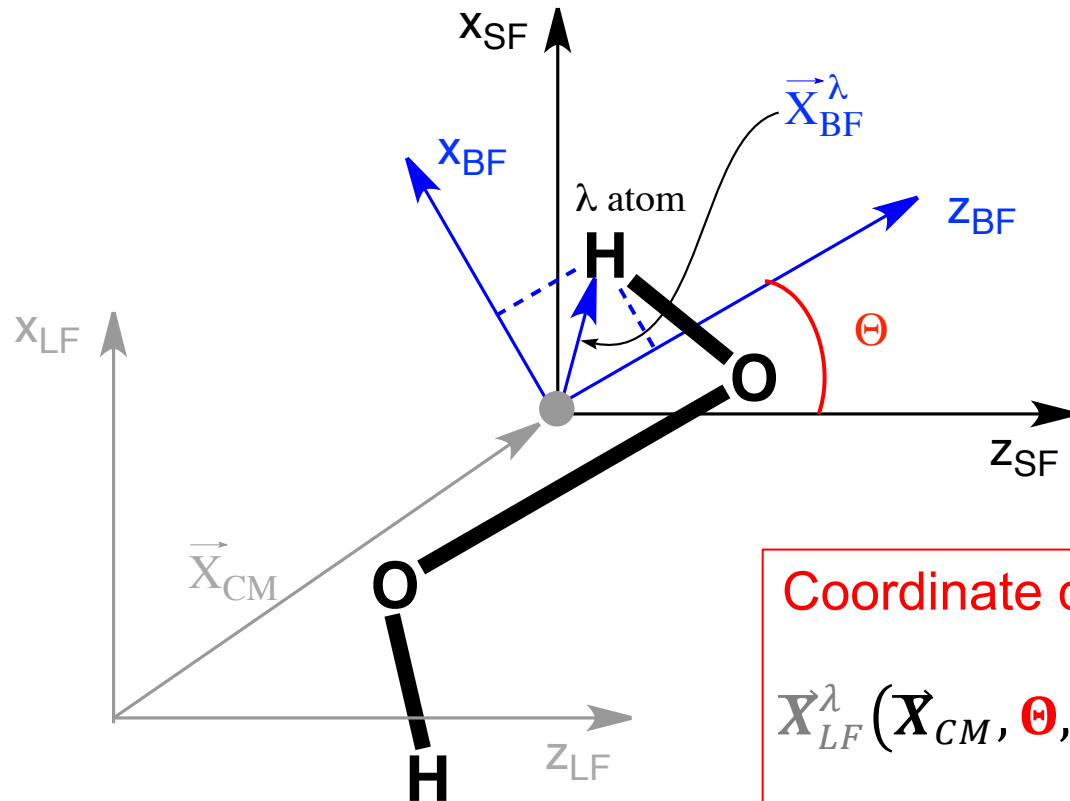
Internal coordinates:

$$Q = \{r_1, r_2, \alpha_2, r_3, \alpha_3, \varphi_3\}$$

Euler Angles

$$\Theta = \{\varphi, \theta, \chi\} \text{ or } \{\alpha, \beta, \gamma\}$$

Coordinate changes: LF→BF→{Q,Θ}

$$\vec{X}^\lambda_{LF}(\vec{X}_{CM}, \Theta, Q) = \vec{X}_{CM} + \mathbf{R}_{Euler}(\Theta) \cdot \vec{X}^\lambda_{BF}(Q)$$

$$X^\lambda_{SF}$$

Dictates the way the BF frame
is attached to the molecules

Example with subsystems: water dimer

1) Atom list:

```
&Coord_transfo name_transfo='bunch_poly'
              nat=6 nb_X=2 inTOout=f /
O H H   O H H   GA  GB


&dummyX tab_At_TO_X=2,3  type_dummyX='COM' /  GA
&dummyX tab_At_TO_X=5,6  type_dummyX='COM' /  GB
```


2) Vector definitions:

```
&Coord_transfo name_transfo='poly' /
  &vector nb_vect=2 Frame=t   iAtA=1  iAtB=4 zmat_order=t /   R1_BF: O1->O4   zBF
    &vector nb_vect=1 Frame=t iAtA=3  iAtB=2 /                R1_S2: H3->H2   zBFA
      &vector               iAtA=7  iAtB=1 /                  R2_S2: G7A->O1
    &vector nb_vect=1 Frame=t iAtA=5  iAtB=6 /                R1_S3: H5->H6   zBFB
      &vector               iAtA=8  iAtB=4 /                  R2_S3: G8B->O4
```
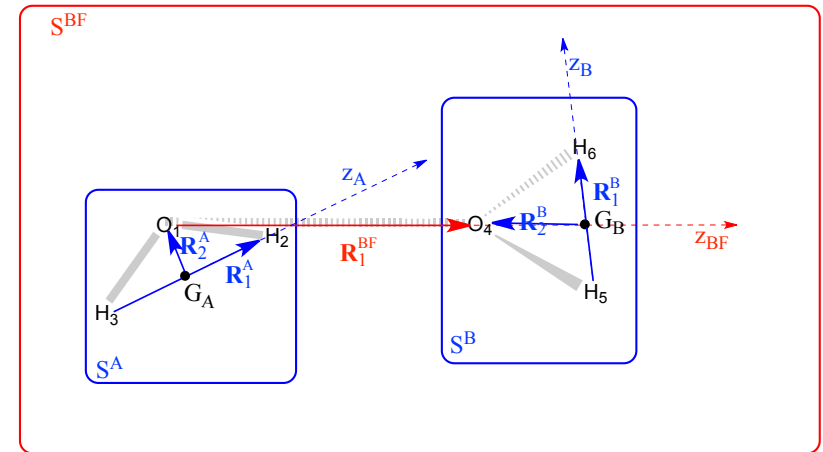
$$\int b_k(q)^* b_\ell(q) d\tau_q = \delta_{k,\ell}$$

Primitive basis functions

1) Primitive Basis set : $\int b_k^*(Q^i) b_\ell(Q^i) d\tau_i = \delta_{k\ell}$

Basis set has to be adapted to the coordinates.

> *By choosing the right volume element, $d\tau_i = \rho_i(Q^i) dQ^i$, these bases are orthonormal.*

– Periodic coordinates (dihedral angle) : Fourier basis
– Coordinate associated to a localized motion (distance, angles...) : sine basis (particle-in-a-box), Harmonic Oscillator basis (Hermite polynomials)
– Coordinate associated to a dissociation (distance) : plane wave basis
– Overall rotation : Spherical Harmonics (linear conformation), Wigner

Remarks:

The primitive basis set are defined with a specific volume element, $d\tau_i$. Therefore, the full volume element, $d\tau$, must be expressed as the product of the individual ones.

=> $\rho(\boldsymbol{Q}) = \prod \rho_i(Q^i)$ MUST be imposed ($d\tau = \rho(\boldsymbol{Q}) dQ^1 \dots Q^n$)

$$\hat{\boldsymbol{T}}_e(q, \partial_q) = \sum_{ij} -\frac{\hbar^2}{2} G^{ij} \frac{\partial^2}{\partial q^i \partial q^j} + \sum_i \left(-\frac{\hbar^2}{2} \sum_j G^{ij} \frac{\partial \ln \rho}{\partial q^j} + \frac{\partial G^{ij}}{\partial q^j} \right) \frac{\partial}{\partial q^i} + V_{extra}(\boldsymbol{q})$$

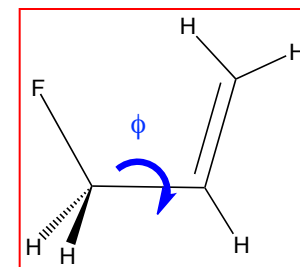## *Quantum approach: coordinates, KEO ...*

- Overview and quantum mechanics

- Coordinates and KEO

- Models

Models (curvilinear coordinates)

All coordinates are treated at the same level

Exact model:

$3N-6$ *coordinates* (Q)

The constraints are set up in T.

Constrained models (rigid, flexible):

1 active coordinate: ϕ

11 inactive coordinate: Q_{inact} *(distances, angles…)*

Related to Born-Oppenheimer

Adiabatic Approximation (ADA, HADA):

$\Psi^{ADA}(\phi, Q_{inact}) = \varphi_U(\phi) \, \Phi_U(Q_{inact}; \phi)$

Exact when the channel number is large.

Coupled Adiabatic Channels (cHAC):

$\Psi(\phi, Q_{inact}) = \Sigma_U \, \varphi_U(\phi) \, \Phi_U(Q_{inact}; \phi)$

Adiabatic: Light, Bačić JCP 87 (1987) 4008.

SRBM: Bunker et al. JMS 1977

RPH : Miller, Handy, Adams, JCP 72 (1980) 99

MBM : Bowman, Gazdy JCP 93 (1990) 1774

Hougen JMS 181 (1997) 287

Fehrensen, Luckhaus, Quack, CPL 300 (1999) 312

Lauvergnat, Nauts, Chem. Phys. 305, 105 (2004)

Reduced (constrained) models: T_{RD}

What you are NOT ALLOWED to do

Remove terms of T_{exact}

T_{RD} may be non-Hermitian!!

What you MUST to do

Get a contravariant metric tensor: $\mathbf{G}_{RD}(\mathbf{Q})$

Then use the "usual" expression:

$$\hat{\mathbf{T}}_{RD}(\mathbf{Q}, \partial_{\mathbf{Q}}) = -\frac{\hbar^2}{2} \sum_{ij} \rho_{RD}(\mathbf{Q})^{-1} \frac{\partial}{\partial Q^i} \rho_{RD}(\mathbf{Q}) G_{RD}^{ij}(\mathbf{Q}) \frac{\partial}{\partial Q^j} + v(\mathbf{Q})$$

Sum, from 1 to n

$$d\tau = \rho_{RD}(\mathbf{Q}) dQ^1 \cdots dQ^n$$

How to choose m?

1- "Ad hoc" operator:

    Example: 2D-polar operator

$$\mathbf{G}_{RD} = \frac{1}{m}\begin{bmatrix} 1 & 0 \\ 0 & 1/R^2 \end{bmatrix} \; ; \; d\tau = \sin(\theta)d\theta dR$$

2- Remove lines and columns from $\mathbf{G}_{exact}$

3- Remove lines and columns from $\mathbf{g}_{exact}$

and invert of the matrix to get $\mathbf{G}_{RD}$

metrix tensor of "really/physically" constrained molecular system

Example : 1D (Rigid contraints)
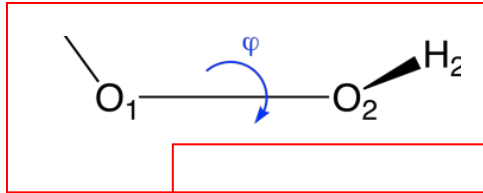
$$\hat{T}_{def} = f_2(\varphi) \frac{\partial^2}{\partial \varphi^2} + f_1(\varphi) \frac{\partial}{\partial \varphi} + \upsilon(\varphi)$$

$$d\tau_{def} = d\varphi$$

Numerical KEO
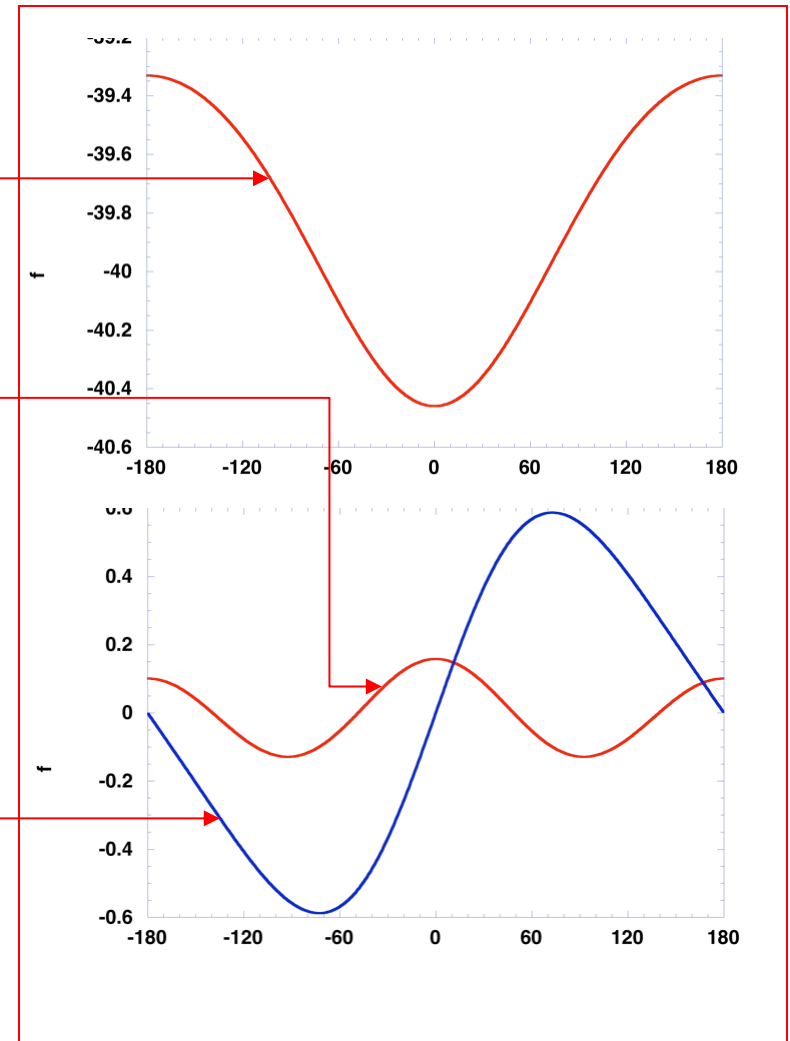
Reduced models: *summary*

1. The energy transfer between the active and inactive coordinates (Q_{act} <=> Q_{inact}) has to be small during the process time scale (weak IVR).

2. For an isolated molecule, the nuclear center of mass motion can be separated rigorously from the other motions.

3. For the so-called vibrational calculations at J=0 (null total angular momentum), the wave function can be separated into a vibrational and a rotation (Ψ_{rot}=constant) parts.

not really reduced dimensionality approaches

Quantum approach: coordinates, KEO ...

- Overview and quantum mechanics

- Coordinates and KEO: Tɴᴜᴍ

- Models

$$\hat{T}_e(q,\partial_q) = \sum_{ij} -\frac{\hbar^2}{2} G^{ij} \frac{\partial^2}{\partial q^i \partial q^j} + \sum_i \left(-\frac{\hbar^2}{2} \sum_j G^{ij} \frac{\partial \ln \rho}{\partial q^j} + \frac{\partial G^{ij}}{\partial q^j} \right) \frac{\partial}{\partial q^i} + V_{extra}(\boldsymbol{q})$$

KEO, numerical approach: T[NUM][1]

Calculate

-*numerically and exactly*

-**for molecular systems of any size**

the metric tensor for a given value of the curvilinear coordinates *q*.

Similar numerical procedures:

1-2 active **coordinate(s) (inversion of ammonia[2], ring puckering[3-5], torsion[6])**

6-9 active **coordinates (inversion of ammonia, CH_4...)[6,7]**

B-matrix used to calculate the gradient and hessian in internal coordinates

[1] D. Lauvergnat et al., JCP 2002, 116, p8560
[2] D. J. Rush et al., JPC A 1997, 101, p3143
[3] J. R. Durig et al.,JPC 1994, 98, p9202
[4] S. Sakurai et al.,JCP 1998, 108, p3537
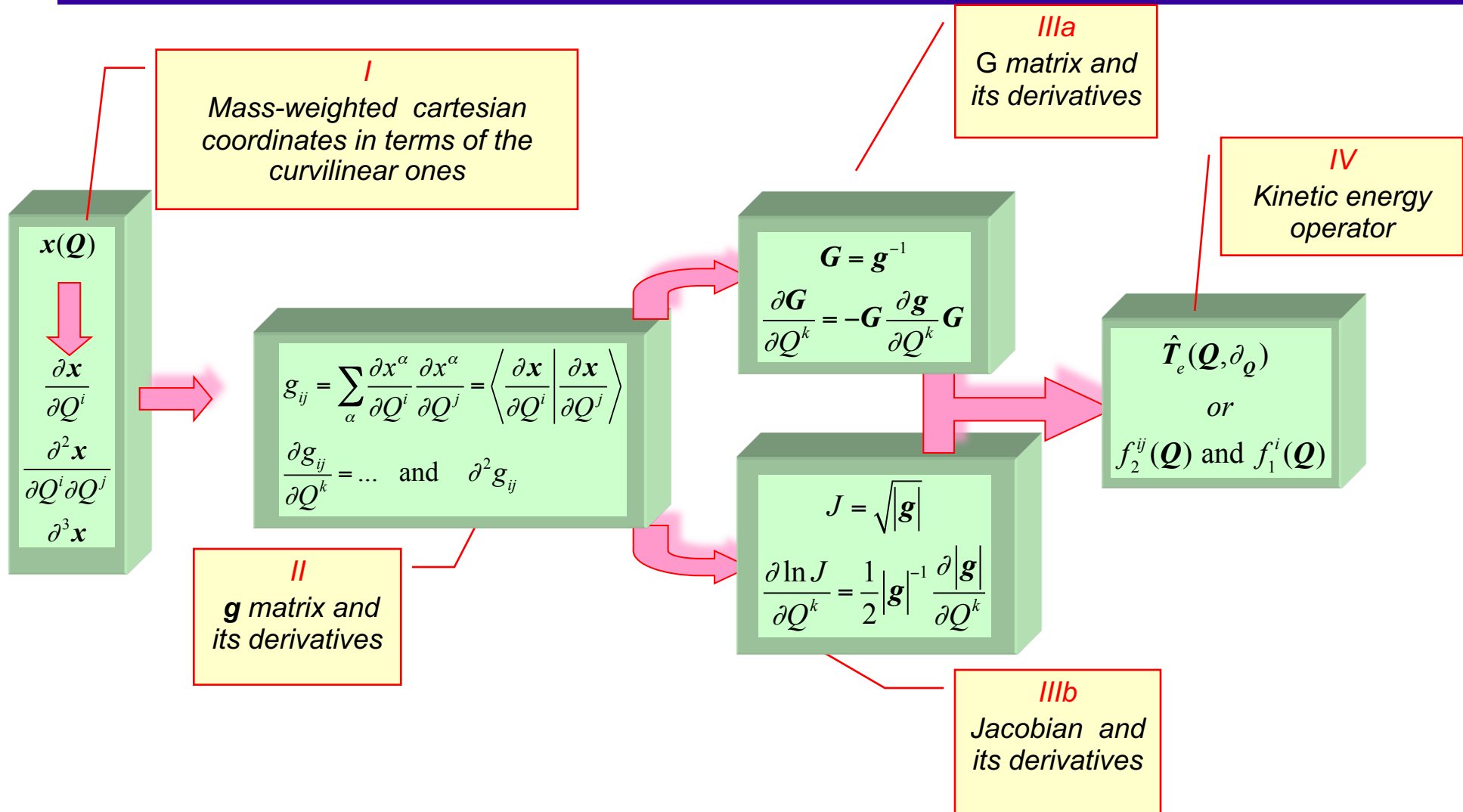[5] J. Laane et al.,JMS 1982, 91, p286

[6] M. L. Senent, CPL 1998, 296, p299
[7] D. Luckhaus, JCP 2000, 113, p1329
[8] E. Mátyus et al.,JCP 2009, 130, p134112

$$\hat{T}_e(q,\partial_q) = \sum_{ij} -\frac{\hbar^2}{2} G^{ij} \frac{\partial^2}{\partial q^i \partial q^j} + \sum_i \left(-\frac{\hbar^2}{2} \sum_j G^{ij} \frac{\partial \ln \rho}{\partial q^j} + \frac{\partial G^{ij}}{\partial q^j} \right) \frac{\partial}{\partial q^i} + V_{extra}(q)$$

(Numerical) Calculation of *T*

I
Mass-weighted cartesian coordinates in terms of the curvilinear ones

$x(Q)$

$\dfrac{\partial x}{\partial Q^i}$

$\dfrac{\partial^2 x}{\partial Q^i \partial Q^j}$

$\partial^3 x$

II
g matrix and its derivatives

$$g_{ij} = \sum_\alpha \frac{\partial x^\alpha}{\partial Q^i} \frac{\partial x^\alpha}{\partial Q^j} = \left\langle \frac{\partial x}{\partial Q^i} \middle| \frac{\partial x}{\partial Q^j} \right\rangle$$

$$\frac{\partial g_{ij}}{\partial Q^k} = \dots \quad \text{and} \quad \partial^2 g_{ij}$$

IIIa
G *matrix and its derivatives*

$$G = g^{-1}$$

$$\frac{\partial G}{\partial Q^k} = -G \frac{\partial g}{\partial Q^k} G$$

IIIb
Jacobian and its derivatives

$$J = \sqrt{|g|}$$

$$\frac{\partial \ln J}{\partial Q^k} = \frac{1}{2} |g|^{-1} \frac{\partial |g|}{\partial Q^k}$$

IV
Kinetic energy operator

$$\hat{T}_e(Q, \partial_Q)$$

or

$$f_2^{ij}(Q) \text{ and } f_1^i(Q)$$

Coordinates: $x(q)$ (T_{NUM})

q_{t_i} ──linear flexible ordre *n*ormal modes RPH ...──→ $q_{t_{i+1}}$

q_{prim} ──*zmatrix*──→ X_{F_1}

q_{prim} ──*zmatrix*──→ $X_{vectors}$
q_{prim} ──*polyspherical*──→ $X_{vectors}$ } ──*Bunch*──→ X_{F_1}

q_{prim} ──*analytical*──→ X_{F_1}

q_{dyn} ⟹ q_t ⟹ q_{prim} ⟹ X_{F_1}

Coordinates used in the dynamics

Intermediate coordinates

Primitive coordinates (z-matrix ...)

Cartesian coordinates in F_1

Primitive
(z-matrix)

Symmetrization
(linear)

Reaction Path
Coord.

active Coord.
(constraints)

$\mathbf{q}_{cart}$

$\mathbf{q}_{prim} \equiv \mathbf{q}_{zmat}$

$\mathbf{q}_{sym}$

$\mathbf{q}_{RPH} = \mathbf{q}_{dyn}$

$\mathbf{q}_{act}$

$$\begin{cases} R_+ = \frac{1}{2}(R_2 + R_3) \\ R_- = \frac{1}{2}(R_2 - R_3) \end{cases}$$

$$\begin{cases} \alpha_+ = \frac{1}{2}(\alpha_2 + \alpha_3) \\ \alpha_- = \frac{1}{2}(\alpha_2 - \alpha_3) \end{cases}$$

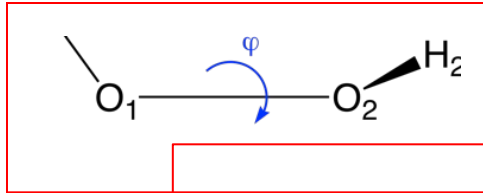Normal coordinates (5) with
all coordinates except ϕ_3.

Example : 1D (Rigid contraints)

$$\hat{T}_{def} = f_2(\varphi)\frac{\partial^2}{\partial\varphi^2} + f_1(\varphi)\frac{\partial}{\partial\varphi} + \upsilon(\varphi)$$

$$d\tau_{def} = d\varphi$$

Numerical KEO