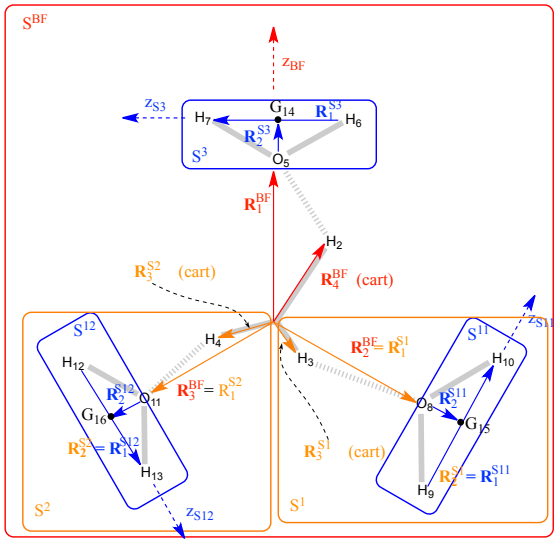
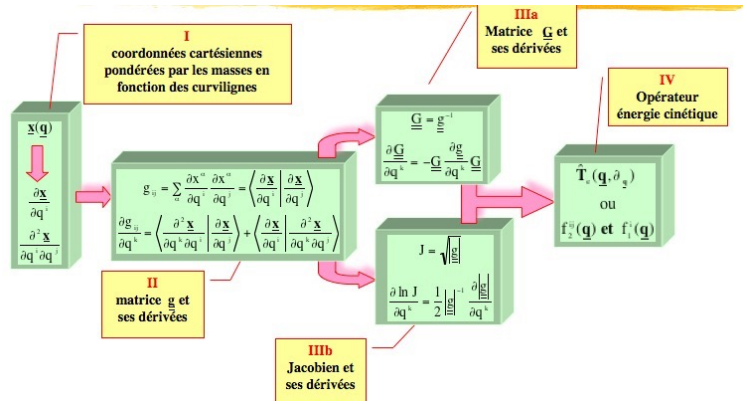
# *Polyspherical coordinates and kinetic energy operators with TANA (and TNUM)*

## *Coordinates*




## *KEO*





***A. Nauts*** ***D. Lauvergnat***

***F. Gatti*** *M. Ndong*

## *Outline*

- KEO, TANA/TNUM ...
- Simple examples:
  - Water molecule
  - Hydrogen peroxide
- Subsystems
  - Two examples
- Overview

# *TNUM / TANA programs*

**Historic:**

2001 First **TNUM** version in F77

No dynamic memory allocation

2004 last F77 version

2004 First F90 version

Coupled with ELVIBROT (too strongly)

2010- New structure of the coordinate transformations

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

2012- First **TANA** 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*

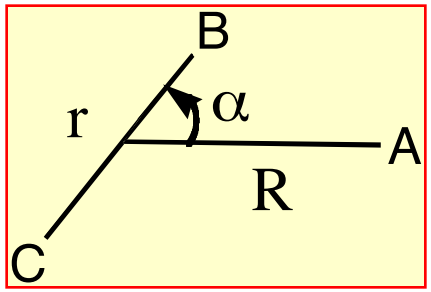
*3) Run some tests (optional)*
*make OPT=0 ut*

*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*

# Example : Jacobi coordinates (ABC)




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

***Deformation*** *part*

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

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

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

+***Rotation*** *part*

+***Center of mass*** *part*

# How to get the analytical expressions of T?

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

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

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

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

*Contravariant components of metric tensor*

*non-Euclidean volume element*

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

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

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

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

*M is diagonal for Jacobi vectors:*

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

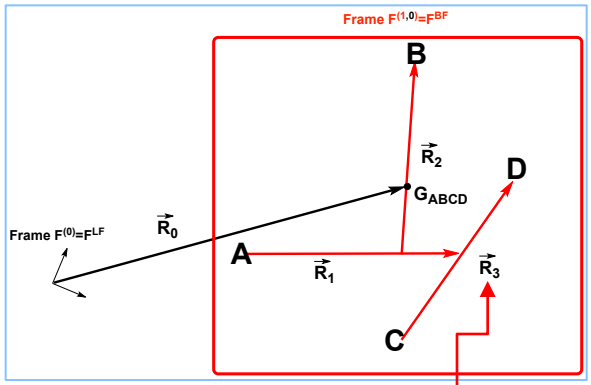

[1] B. Podolsky, Phys. Rev. t, C. Iung, Phys. Rev. A 45, 6217–6235 (1992).
[2] A. Nauts and X. Chapu ung Phys. Rep. 484 1–69 (2009).
[3] J. Laane et al.,JMS 19 . Ndong, L. Joubert-Doriol, H.-D. Meyer, A. D. Lauvergnat, JCP 136, p034107, (2012).
[4] D. Lauvergnat et A. Nau

# KEO and polyspherical coordinates: Tana

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

***Relation between the atomic positions and the vectors:***

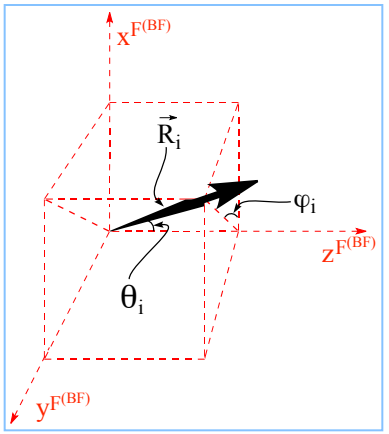
$$\vec{R}_i = \sum_k \mathbf{A}_{i,k} \cdot \vec{X}_k$$




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

$$M = A \cdot \left[ 1/m_k \right] \cdot A^t$$

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




3. ***KEO:***

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

*The analytical expression is well known*

$$\hat{\vec{P}}_i = \hat{P}_{R_i} \vec{e}_i + \frac{\vec{e}_i \times \hat{\vec{L}}_i}{R_i}$$

*[1] F. Gatti, C. Iung Phys. Rep. 484 1–69 (2009).* *[2] F. Gatti, C. Munoz, C. Iung, JCP, 114 8275 (2001).*

## *Outline*

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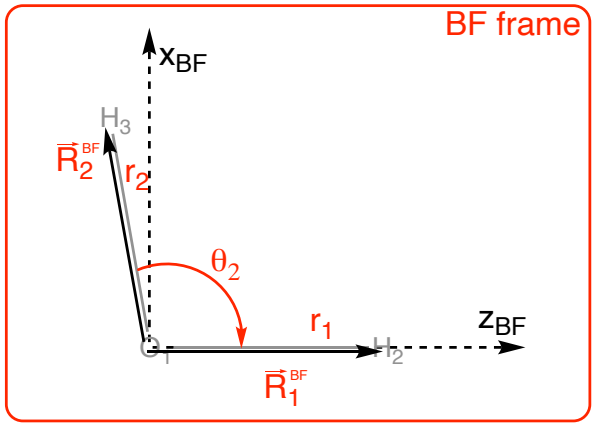
# $OH_2$ in valence coordinates: data




**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:**

Add 1 vector in the Frame

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

Along the z-axis frame

Vector between atoms 1 and 3

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

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

# $OH_2$ 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

**TANA and TNUM 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 TNUM
- With TANA

=> 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 $\pi$ ...)

# $OH_2$ in valence coordinates: the full input file, bis

```
 &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:

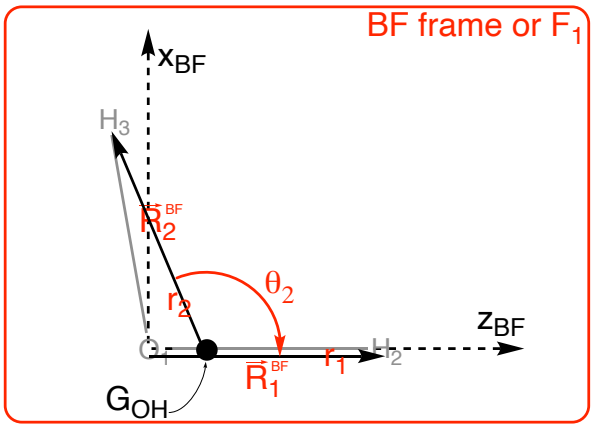
./dat_polyOH2_RRu-cart0

# $OH_2$ 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

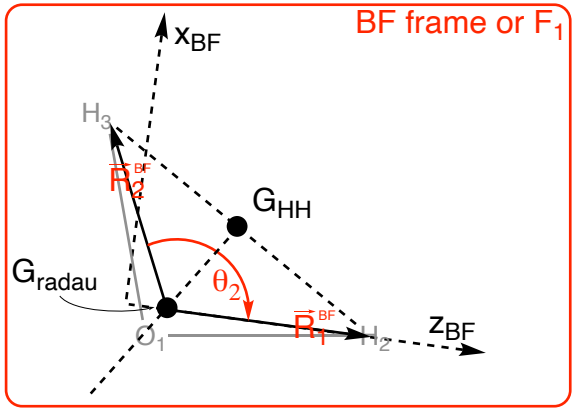
One dummy atom (here center of mass, Radau center) will be set.

```
 &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)




The two vectors are uncoupled.
=> The M matrix is diagonal

Radau/Heliocentric Coordinates:
It can be generalized with an atom (the sun) and other atoms (the planets).

⚠ Atom and center ordering:

```
centers:  O H H XRadau
order:    1 2 3 4
```

*Smith, F. PRL, 45, 1157–1160, 1980.*

# $OH_2$ 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)**

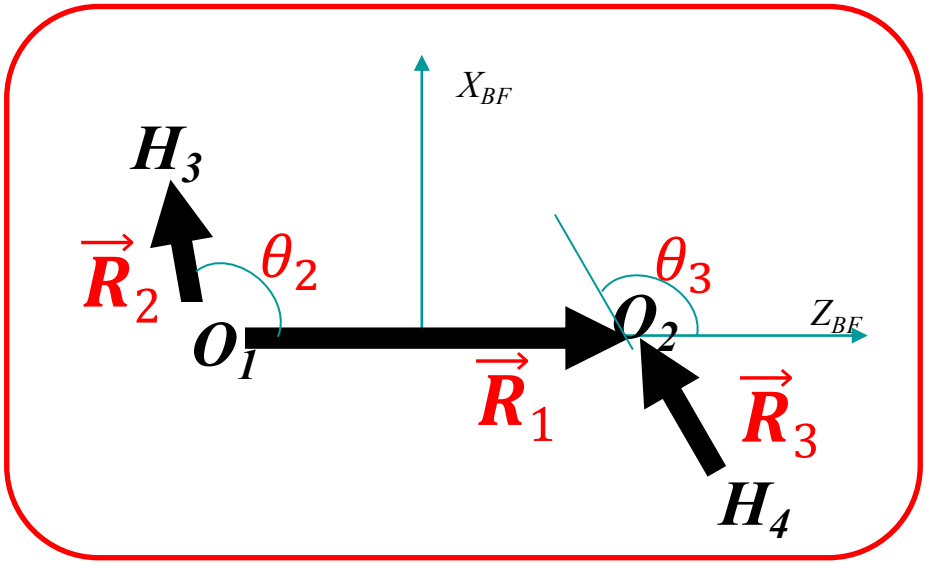
```
-2.7216029162284596d-004 |1   q^-2 |3   dq^2
2.7216029162284596d-004 |1   q^-2 |3   dq*q^2*dq
-2.7216029162284596d-004 |1   dq^2
-2.7216029162284596d-004 |2   q^-2 |3   dq^2
2.7216029162284596d-004 |2   q^-2 |3   dq*q^2*dq
-2.7216029162284596d-004 |2   dq^2
```

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

# 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 /
```

*Add the vector definitions*

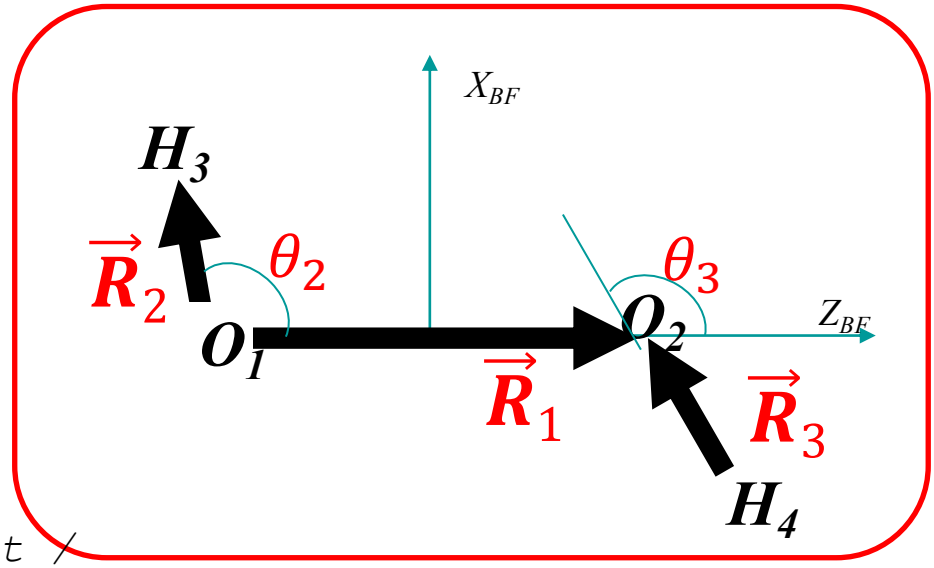
Use the following Cartesian coordinates (Å):

| | | | |
|---|---|---|---|
| 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):**

```
-1.71485726030415400d-005 |1   q^-1 |3   qs*dq |4   q^-1*dq*q |5   qs |6   cos
1.71485726030415400d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   dq*q*qs |6   cos
1.71485726030415400d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   q^2*qs^-1 |6   dq*sin
1.71485726030415400d-005 |1   q^-1 |3   qs*dq |4   q^-1 |5   qs |6   dq*sin
3.42971452060830790d-005 |1   q^-1 |4   q^-1 |5   q^3*qs^-2 |6   dq^2
3.42971452060830790d-005 |1   q^-1 |4   q^-1 |5   q |6   dq^2
```

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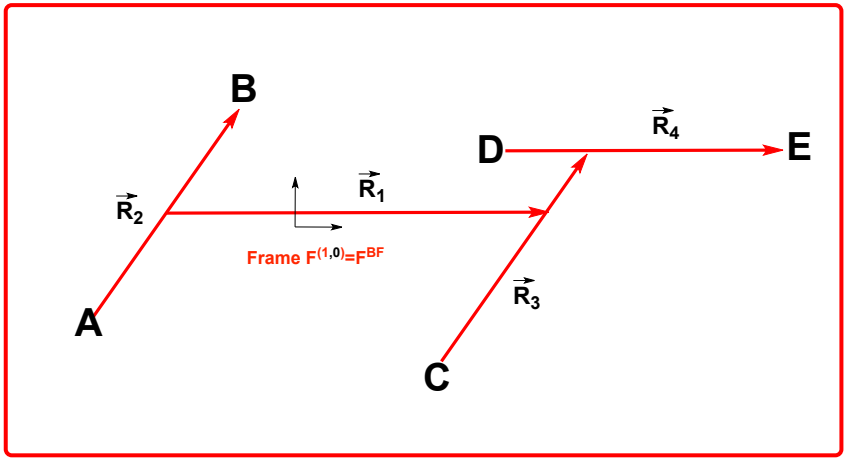
- KEO, TANA/TNUM ...
- Simple examples:
  - Water molecule
  - Hydrogen peroxide
- Subsystems
  - Two examples
- Overview

# KEO and polyspherical coordinates

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




Ex: Problems with trans parametrization:

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

You end up with strong and artificial couplings ($\theta_4$ and $\varphi_4$).

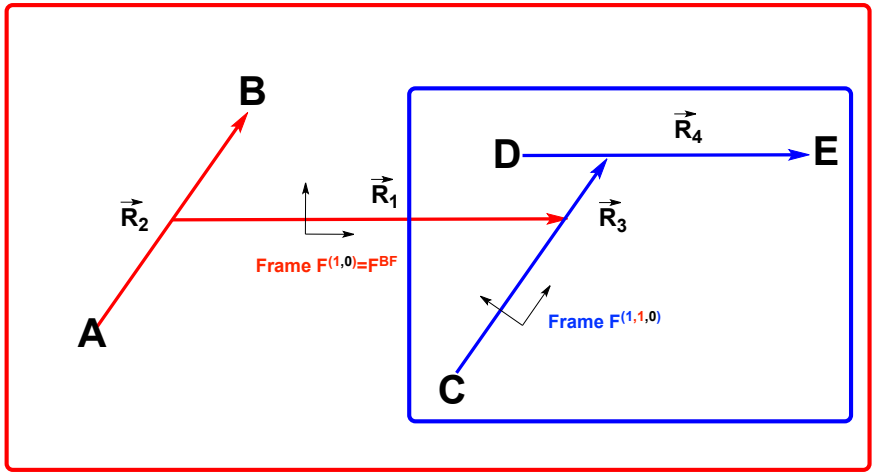
More flexibility is required :
z-matrix .... or subsystems

# 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 $(\alpha,\beta,\gamma)$.*

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




*Remark: $\alpha$ is the previous $\varphi_3$ and $\beta$ is the previous $\theta_3$.*

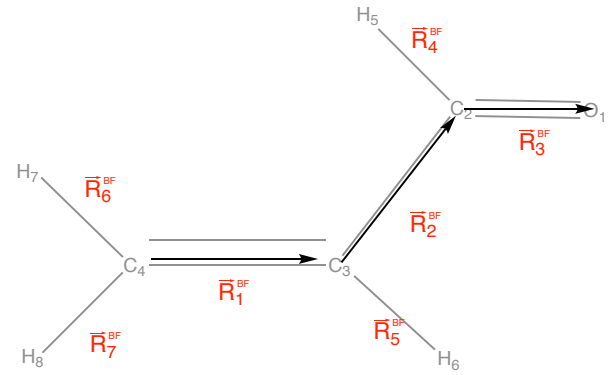
*With the subsystems, the singularities can be avoided*

*=> nested subsystems*

# 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          iAtA=3  iAtB=2 /
       ....
```




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

./dat_C3H4O

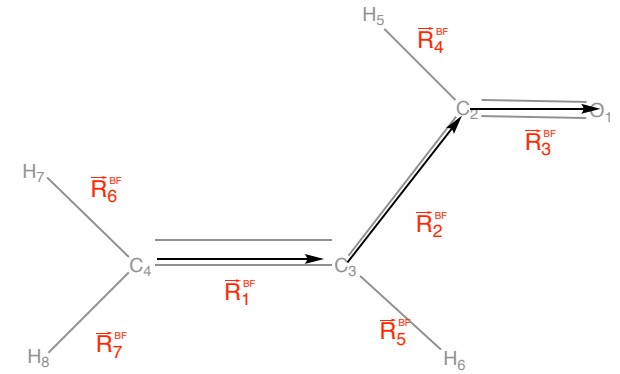
The code stops!
Why?

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
O 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.




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

./dat_C3H4O

The code stops!
Why?

Use the following Cartesian coordinates (Å):

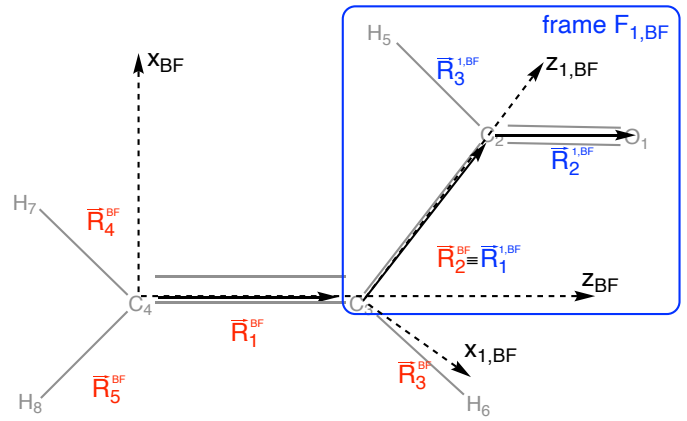
| | | | |
|---|---|---|---|
| 8 | -1.185723 | -1.372699 | 0.000000 |
| 6 | -0.122201 | -0.774130 | 0.000000 |
| 6 | 0.000000 | 0.731002 | 0.000000 |
| 6 | 1.160929 | 1.341975 | 0.000000 |
| 1 | 0.844212 | -1.307114 | 0.000000 |
| 1 | -0.932833 | 1.282731 | 0.000000 |
| 1 | 2.094148 | 0.792171 | 0.000000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

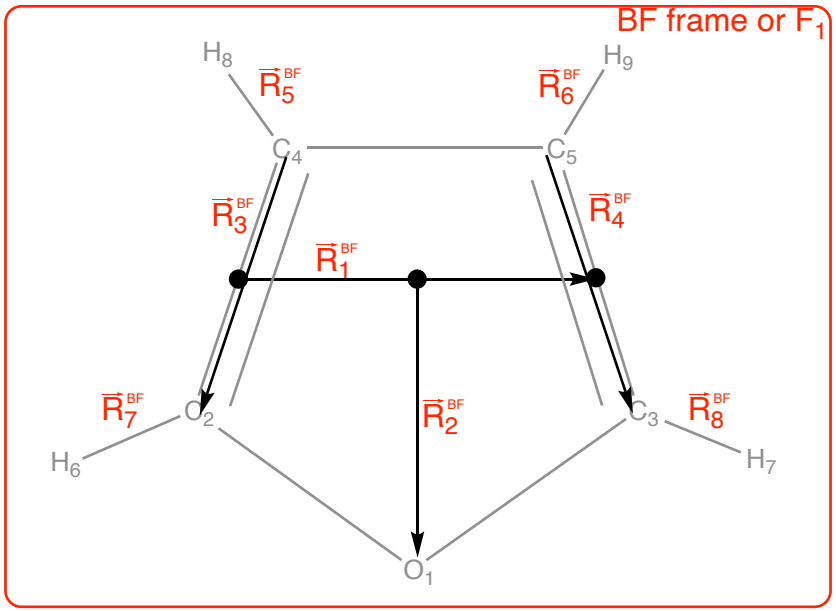
# Example: Furan

```
 &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:

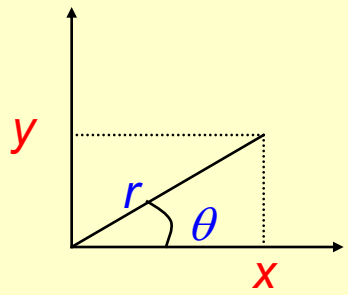
Lauvergnat, D., & Nauts, A. (2002). The Journal of Chemical Physics, 116(19), 8560–8570. https://doi.org/10.1063/1.1469019

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


ThankYou!

# *Choice of coordinates: difficulties*

The kinetic energy operator (KEO), ***T***, is a Laplacian.
Example : Polar coordinates




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

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{4r^2} \qquad d\tilde{\tau} = dr d\theta$$

$$\tilde{\Psi} = \sqrt{r} \cdot \Psi$$

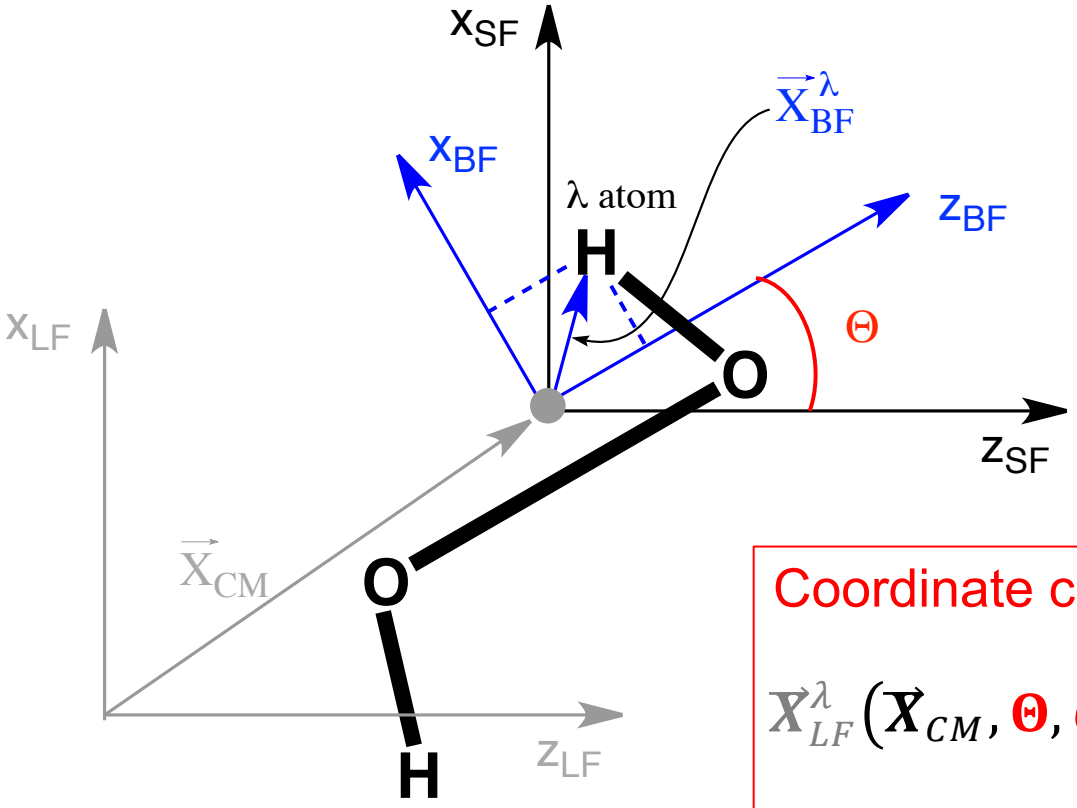
When curvilinear coordinates, ***q***, are used, the analytical expression of ***T*** can be extremely intricate (number of terms, complexity of the expression).

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

It can be expressed numerically (TNUM)

# Overview of the molecular rotation-vibration dynamics

## Body-Fixed and Internal coordinates




Internal coordinates:

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

Euler Angles

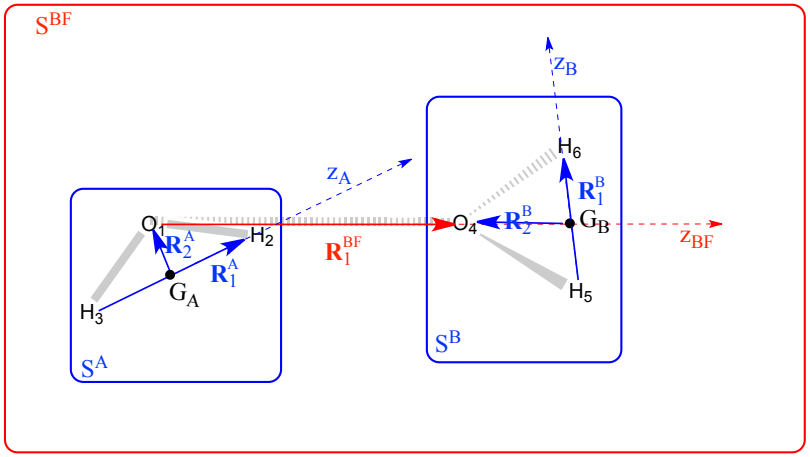
$$\boldsymbol{\Theta} = \{\varphi, \theta, \chi\} \text{ or } \{\alpha, \beta, \gamma\}$$

Coordinate changes: LF→BF→{$\boldsymbol{Q}$,$\boldsymbol{\Theta}$}

$$\vec{\boldsymbol{X}}^{\lambda}_{LF}\left(\vec{\boldsymbol{X}}_{CM}, \boldsymbol{\Theta}, \boldsymbol{Q}\right) = \vec{\boldsymbol{X}}_{CM} + \underbrace{\mathbf{R}_{Euler}(\boldsymbol{\Theta}) \cdot \vec{\boldsymbol{X}}^{\lambda}_{BF}(\boldsymbol{Q})}_{\vec{\boldsymbol{X}}^{\lambda}_{SF}}$$

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 ($d\tau = \rho(\boldsymbol{Q}) dQ^1 \ldots Q^n$)

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

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

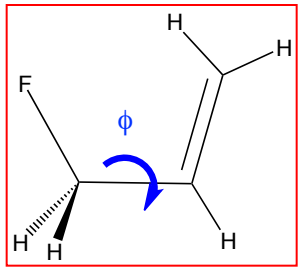
- Overview and quantum mechanics
- Coordinates and KEO
- Models

# 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: $\phi$*

*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:*

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

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

*Sum, from 1 to n*

# Reduced models: $\mathbf{G}_{RD}$

*How to choose m?*

*1- "Ad hoc" operator:*

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

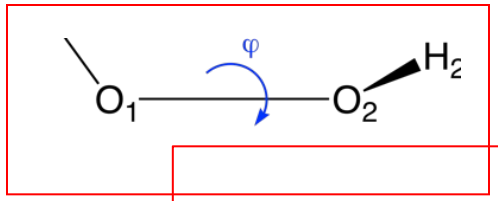
*2- Remove lines and columns from* $\mathbf{G}_{exact}$

*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*

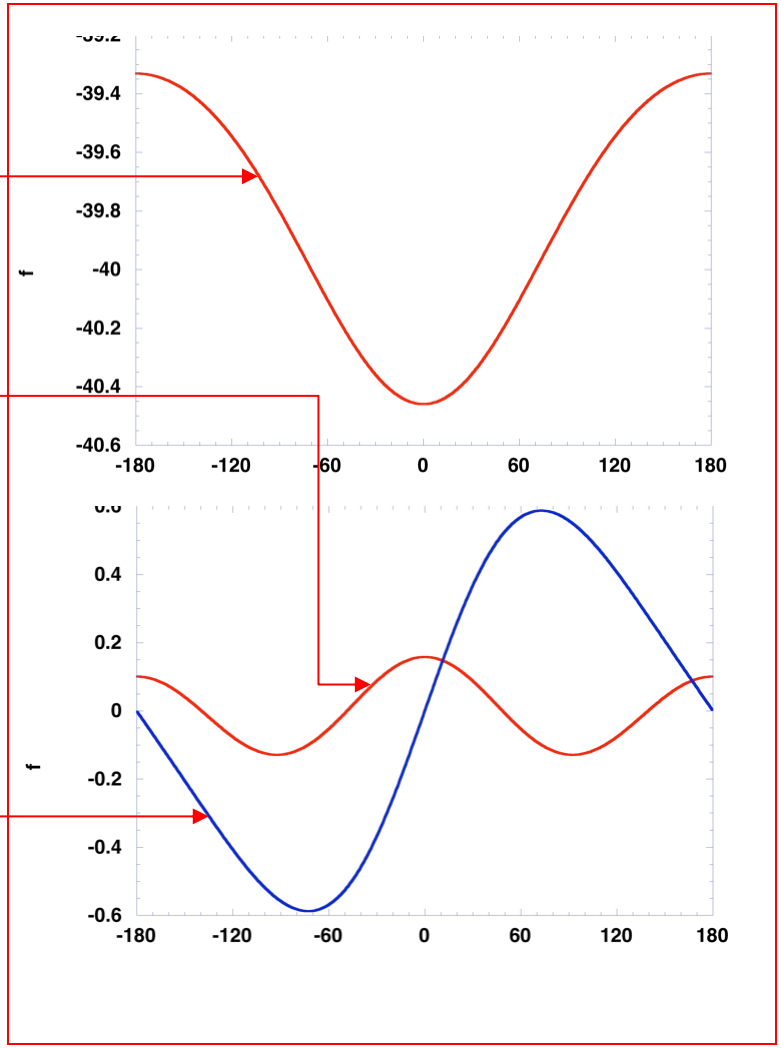
# Example : 1D (Rigid contraints)




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

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

***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 ($\Psi_{rot}$=constant) parts.

*not really reduced dimensionality approaches*

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

- Overview and quantum mechanics
- Coordinates and KEO: TNUM
- Models

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

# KEO, numerical approach: TNUM[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])**

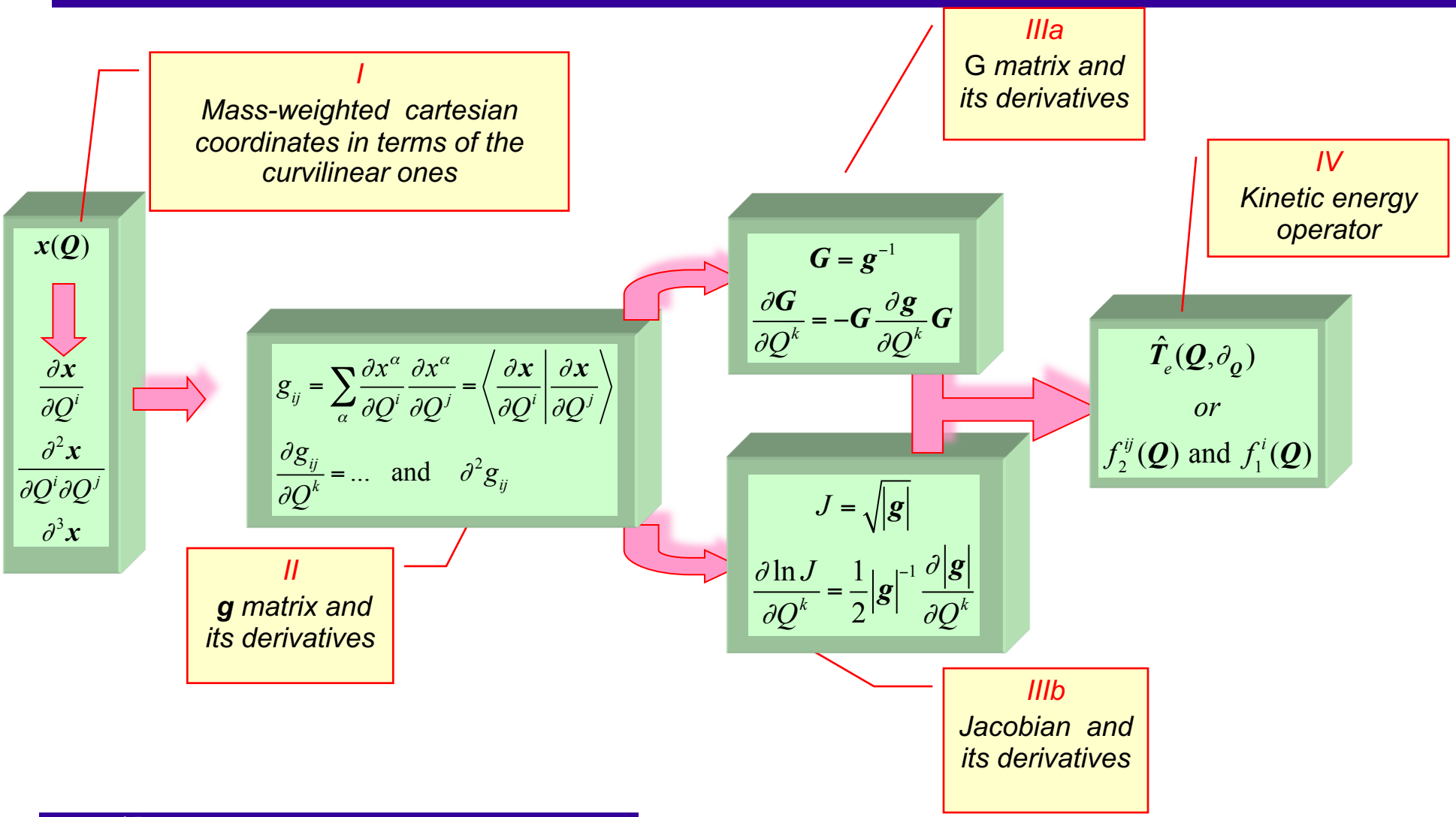
***6-9 active* coordinates (inversion of ammonia, $CH_4$…)[6,7]**

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

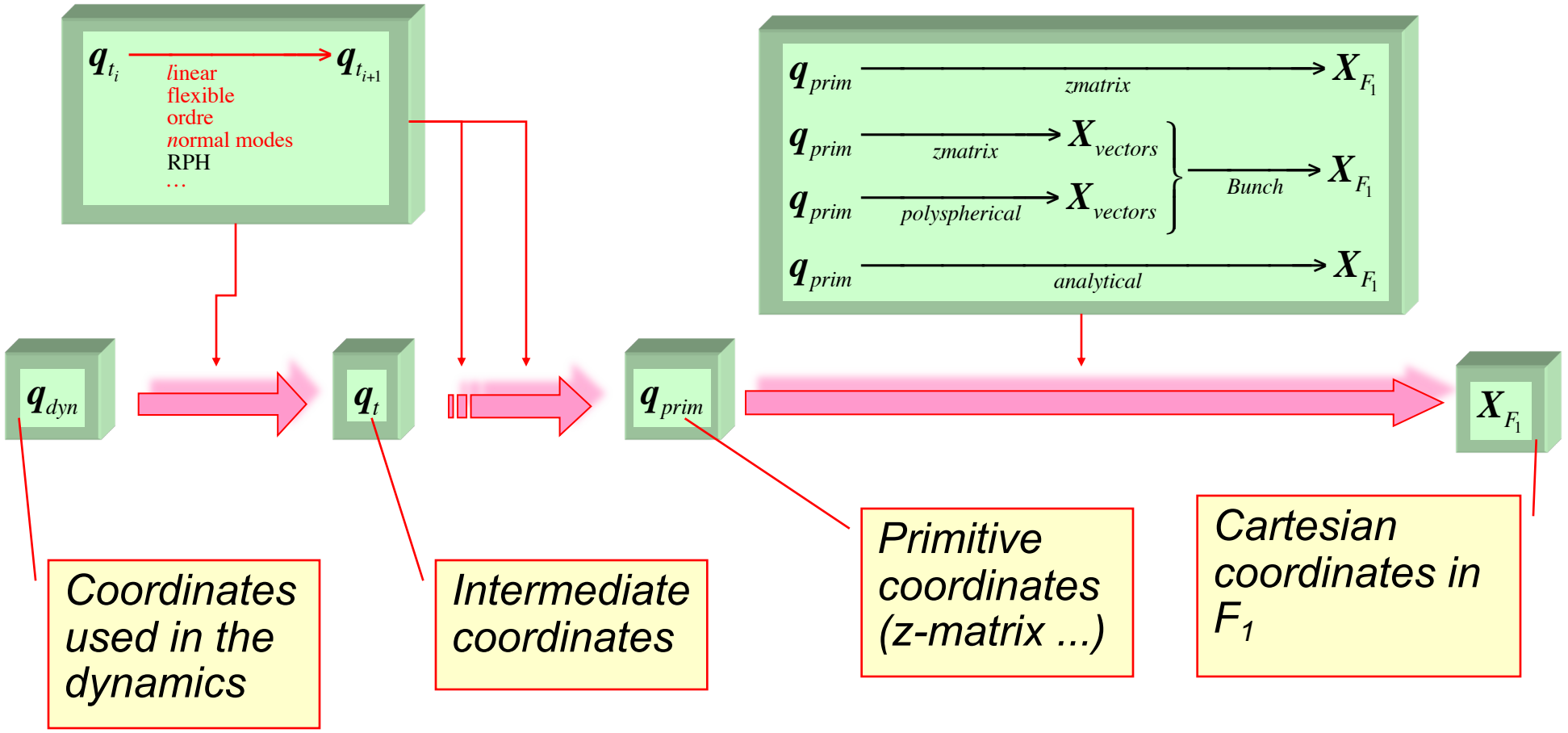

*[1] D. Lauvergnat et al., JCP 2002, 116, p8560*
*[2] D. J. Rush et al., JPC A 1997, 101, p3143*
*[3] J. R. Durig et al.,JPC 1994, 98, p9202*
*[4] S. Sakurai et al.,JCP 1998, 108, p3537*
*[5] J. Laane et al.,JMS 1982, 91, p286*
*[6] M. L. Senent, CPL 1998, 296, p299*
*[7] D. Luckhaus, JCP 2000, 113, 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*



# Coordinates: $x(q)$ (TNUM)



# Coordinates, example: HOOH

TNUM

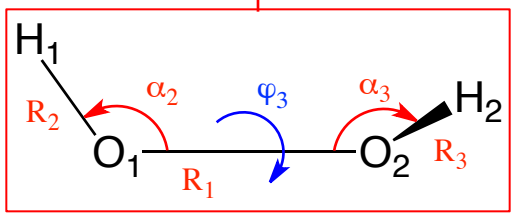
*Primitive (z-matrix)*

*Symmetrization (linear)*

*Reaction Path Coord.*

*active Coord. (constraints)*

$\mathbf{q}_{cart}$ → $\mathbf{q}_{prim} \equiv \mathbf{q}_{zmat}$ → $\mathbf{q}_{sym}$ → $\mathbf{q}_{RPH}=\mathbf{q}_{dyn}$ → $\mathbf{q}_{act}$

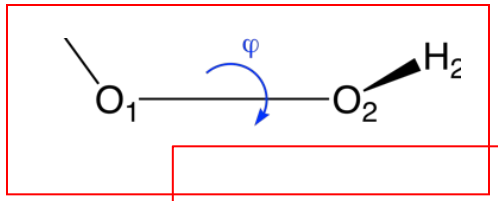



$$\begin{cases} R_+ = \frac{1}{2}(R_2 + R_3) \\ R_- = \frac{1}{2}(R_2 - R_3) \end{cases}$$

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

*Normal coordinates (5) with all coordinates except $\phi_3$.*

# Example : 1D (Rigid contraints)




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

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

***Numerical KEO***