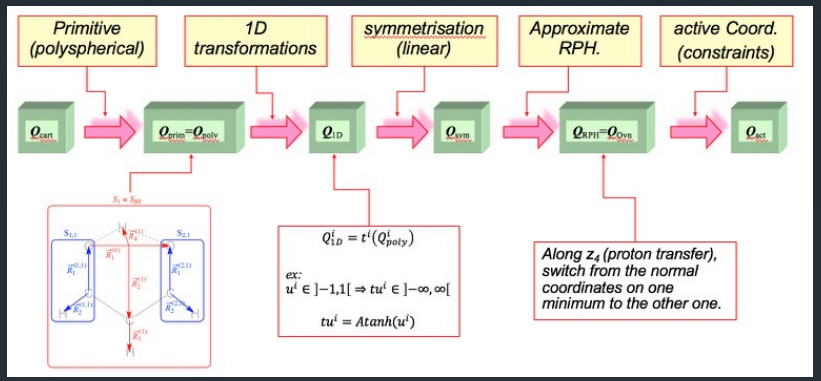
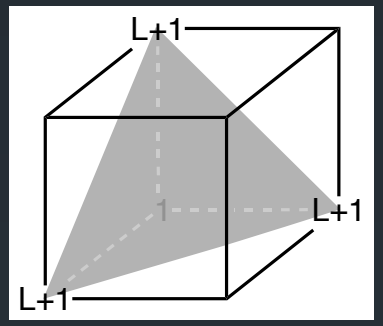
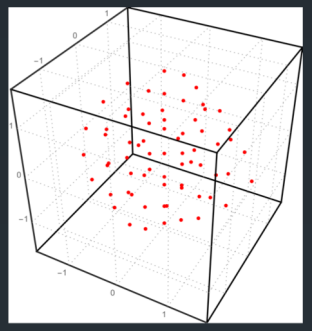
Quantum Dynamics: curvilinear coordinates and Smolyak sparse scheme.



Coordinates





$$NB = \frac{(n+L)!}{n! \cdot L!} \qquad NQ \ll (L+1)^n$$

Smolyak Scheme

Thanks to Daniel Borgis

A. Nauts UCLouvain

Y. Scribano D. Benoit

Z. Bacic P. Felker

R. Vuilleumier

A. Chen (post-doc)

Schrödinger Equation for N-particles

N particles => 3N coordinates, $\boldsymbol{Q}$

Schrödinger Equations

- Time-independent:

$$\hat{\boldsymbol{H}}(\boldsymbol{Q})\psi(\boldsymbol{Q}) = E\,\psi(\boldsymbol{Q})$$

with $\hat{\boldsymbol{H}}(\boldsymbol{Q})=\hat{\boldsymbol{T}}(\boldsymbol{Q})+\hat{\boldsymbol{V}}(\boldsymbol{Q})$

- Time-dependent:

$$i\hbar\frac{\partial\psi(\boldsymbol{Q},t)}{\partial t} = \hat{\boldsymbol{H}}(\boldsymbol{Q})\psi(\boldsymbol{Q},t)$$

The Hamiltonian can be time-dependent

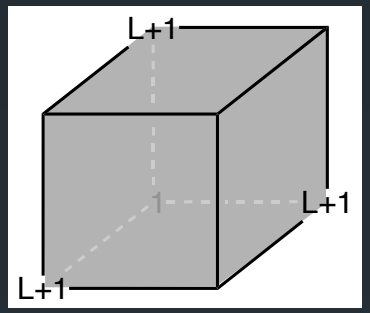
The wave function:

- We need to know, the $\psi(\boldsymbol{Q})$ or $\psi(\boldsymbol{Q},t)$ over the whole of space !!
- How to represent ψ?

It is important to represent Ψ in a compact form.

Direct-product basis and grid

- Expansion on a basis in nD:



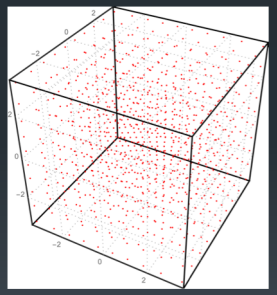
$$B_{DP}^{nD} = b_{\ell_1}^1 \otimes b_{\ell_2}^2 \cdots \otimes b_{\ell_n}^n$$

Number of basis functions

$$NB = nb_1 \times nb_2 \ldots nb_n$$

$$\Psi(Q_1, Q_2) = \sum_{i_2=1}^{nb_2} \sum_{i_1=1}^{nb_1} \Psi_{i_1 i_2}^{bb} \, \mathrm{b}_{i_2}(Q_2) \, \mathrm{b}_{i_1}(Q_1)$$

- Expansion on a grid in nD:



$$G_{DP}^{nD} = G_{\ell_1}^1 \otimes G_{\ell_2}^2 \cdots \otimes G_{\ell_n}^n$$

Number of grid points:

$$NQ = nq_1 \times nq_2 \times \cdots nq_n$$

For the basis, one needs some contraction schemes.

For the grid, one needs another approach than the usual direct-product grid....

in 6D : NB~NQ ~ 10^6
in 9D : NB~NQ ~ 10^9
The “curse” of dimensionality

How can we reduce NB and NQ?

Two steps:
1. Electronic motions ⇒ PES
2. Atomic motions

1. Chose a good model / approximation :
   - The Born-Oppenheimer separation of the electrons and nuclei
   - Adiabatic separation between fast and slow motions
   - Eckart conditions: good vibration/rotation separation
   - Do we need all degrees of freedom?

2. Chose a good set of nuclear (atomic) coordinates:
   - Choose coordinates well adapted to the process (rotation, dissociation ...)
   - Kinetic energy operator, $\hat{T}$

3. Chose a compact basis set (grid):
   - Basis set well adapted to the process
   - With direct-products, the basis or the grid sizes grow exponentially!

The "curse" of dimensionality

Overview:

1. Chose a good model / approximation :
   - The Born-Oppenheimer separation of the electrons and nuclei
   - Adiabatic separation between fast and slow motions
   - Eckart conditions: good vibration/rotation separation
   - Do we need all degrees of freedom?

2. Chose a good set of nuclear (atomic) coordinates :
   - Choose coordinates well adapted to the process (rotation, dissociation ...)
   - Kinetic energy operator, $\hat{T}$

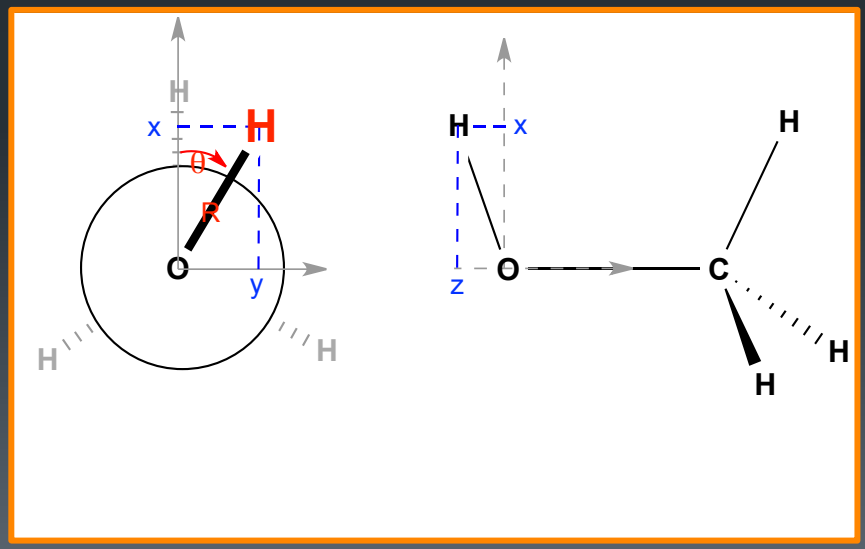
3. Chose a compact basis set (grid) :
   - Basis set well adapted to the process
   - With direct-products, the basis or the grid sizes grow exponentially!

Chose a good set of coordinates
example: Methanol in 2D

Comparison between two sets of coordinates to describe the OH torsion:

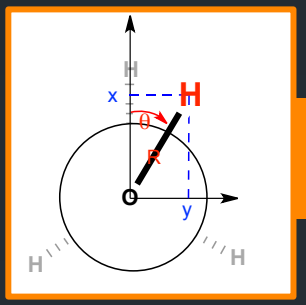
1. Cartesian coordinates (x,y) of H (z is fixed)
2. Polar coordinates (R, θ) of H

Using a simple but realistic 2D-model

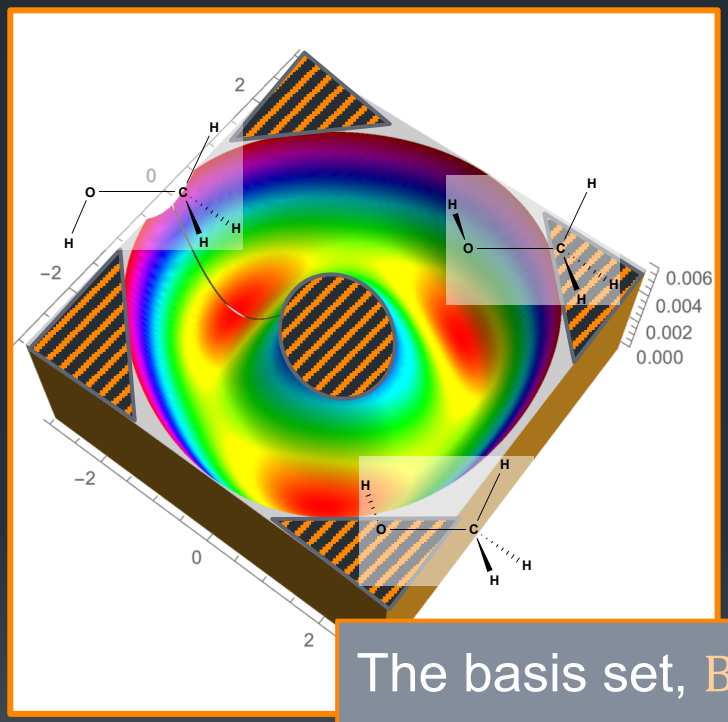


Chose a good set of coordinates

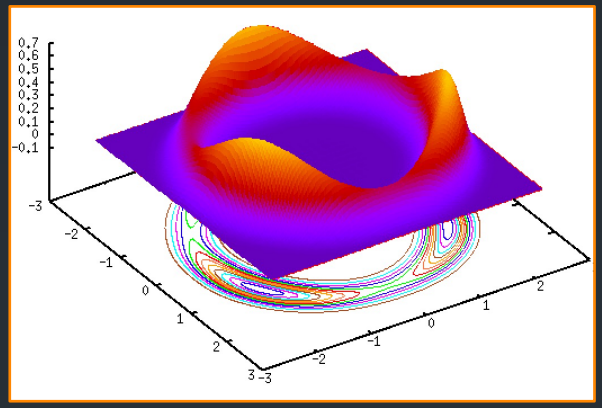
example: Methanol in 2D (x,y)

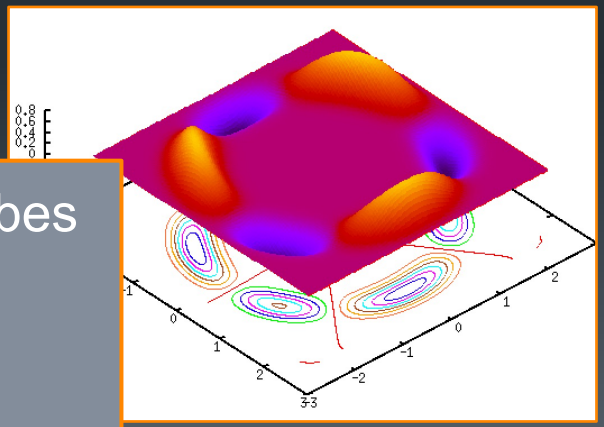


2D potential



Wave functions



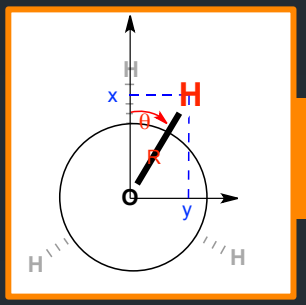


The basis set, $\mathrm{B}_x \otimes \mathrm{B}_y$, describes "non-accessible" regions.

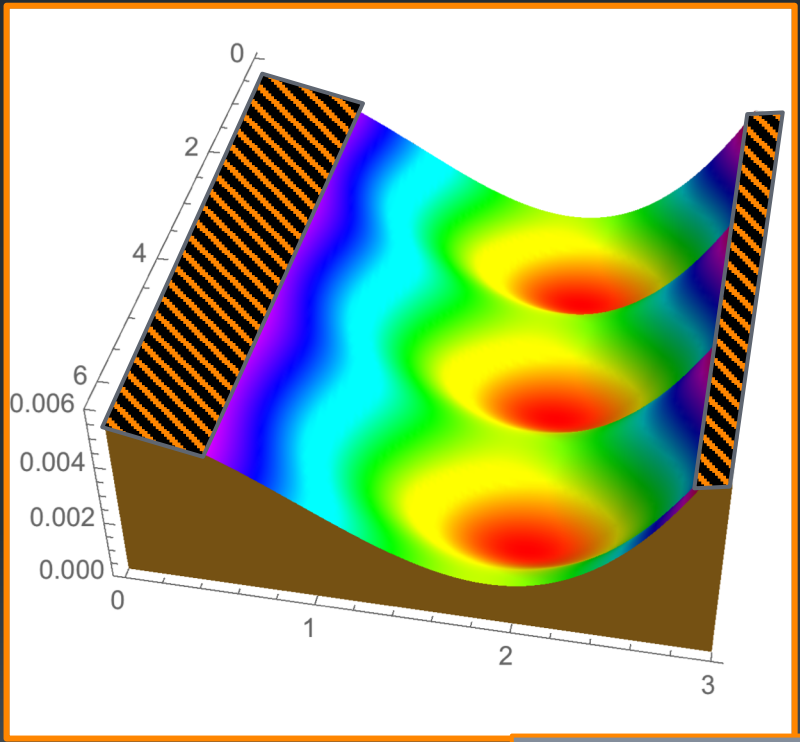
Can we avoid that?

Chose a good set of coordinates

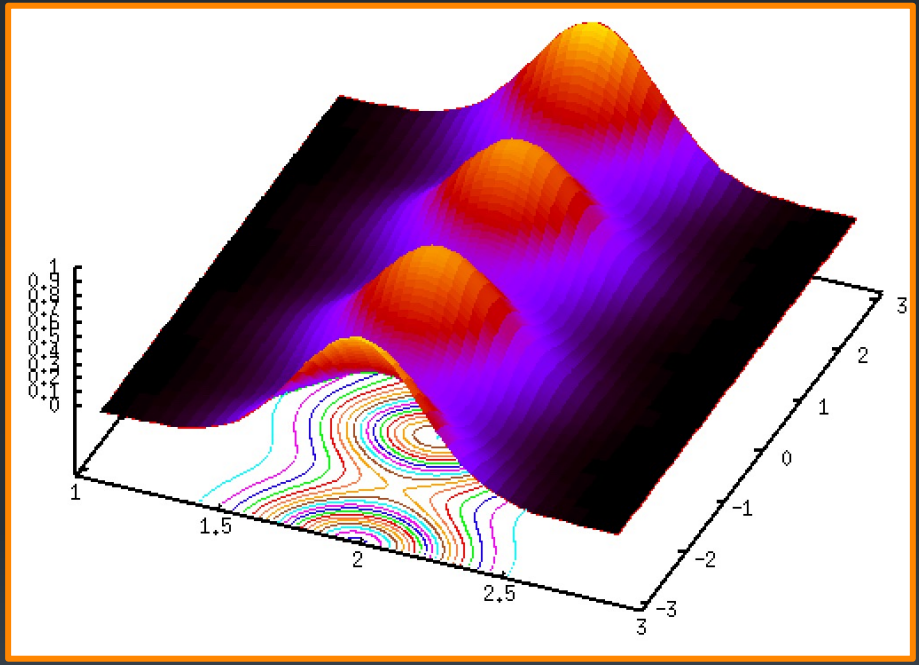
example: Methanol in 2D (R, θ)



2D potential



Wave functions



With those coordinates we can avoid more easily the physically "non-accessible" regions.

Choice of coordinates

Optimal coordinates must give an almost separable Hamiltonian:

$$\hat{H}(Q_1, Q_2 \cdots) = \hat{H}_1(Q_1) + \hat{H}_2(Q_2) + \cdots$$

They have to be adapted to the process, the energy ...:

- Collisions:

  Jacobi, polyspherical

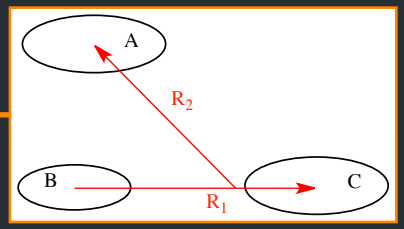
- Reactive scattering:

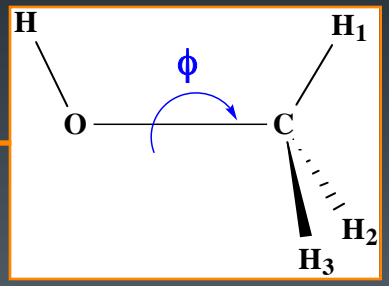
  Hyperspherical

- Spectroscopy:

  Normal modes, polyspherical,

  Valence, z-matrix





Choice of coordinates

Optimal coordinates must give an almost separable Hamiltonian:

$$\hat{H}(Q_1, Q_2 \cdots) = \hat{H}_1(Q_1) + \hat{H}_2(Q_2) + \cdots$$

They have to be adapted to the process, the energy ...:

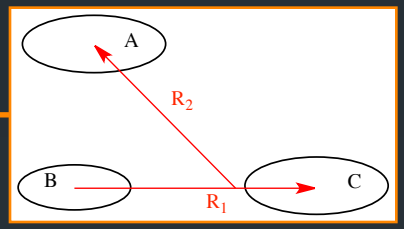
- Collisions:

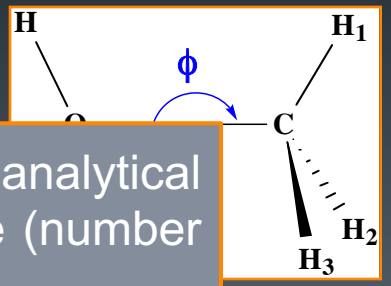
  Jacobi, polyspherical

- Reactive scattering:

  Hyperspherical

- Spectroscopy:

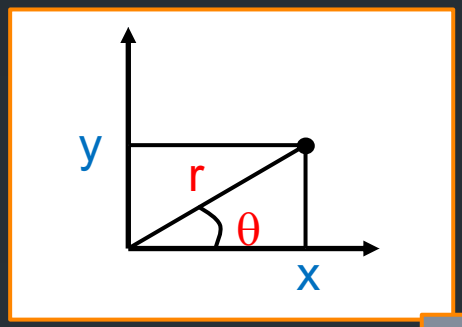




When curvilinear coordinates are used, the analytical expression of KEO can be extremely intricate (number of terms, complexity of the expression).

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)

How to get the KEO, $\hat{T}$?

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

$$\hat{T} = -\frac{\hbar^2}{2}\sum_{i,j}\frac{1}{\rho(\boldsymbol{Q})}\frac{\partial}{\partial Q^i}\rho(\boldsymbol{Q})\mathrm{G}^{ij}(\boldsymbol{Q})\frac{\partial}{\partial Q^j} + V_{extra}(\boldsymbol{Q})$$

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

Contravariant components of metric tensor

non-Euclidean volume element

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

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

$$\hat{T} = \frac{1}{2}\sum_{i,j} M_{ij}\vec{\hat{\boldsymbol{P}}}_i^{\dagger}\cdot\vec{\hat{\boldsymbol{P}}}_j$$

M is diagonal for Jacobi vectors: $M_{ij} = \frac{1}{\mu_i}\delta_{ij}$

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

[1] B. Podolsky, Phys. Rev. 32, 812 (1928).
[2] A. Nauts and X. Chapuisat, Mol. Phys. 55, 1287 (1985).
[3] J. Laane et al.,JMS 1982, 91, p286
[4] D. Lauvergnat et A. Nauts, JCP 116, p8560 (2002).
[5] X. Chapuisat, C. Iung, Phys. Rev. A 45, 6217–6235 (1992).
[6] F. Gatti, C. Iung Phys. Rep. 484 1–69 (2009).
[7] M. Ndong, L. Joubert-Doriol, H.-D. Meyer, A. Nauts, F. Gatti, D. Lauvergnat, JCP 136, p034107, (2012).

Numerical vs Analytical KEO

- Analytical KEO (TANA):
  - Sum of products of 1D-functions => analytical integrations
  - Restricted to some "kind" of coordinates: polyspherical ones

    ⇒Some flexibility (vector definitions, subsystems ...)

    ⇒Few transformations are possible (without loosing the sum of product structure)
  - Jacobi, Radau coordinate types

- Numerical KEO (TNUM):
  - No analytical expression: nD-numerical integrations.
  - Numerical but exact **G(Q)** values
  - High flexibility: It is very easy to add coordinates transformations

    ⇒z-matrix, polyspherical

    ⇒ linear combinations, curvilinear normal modes

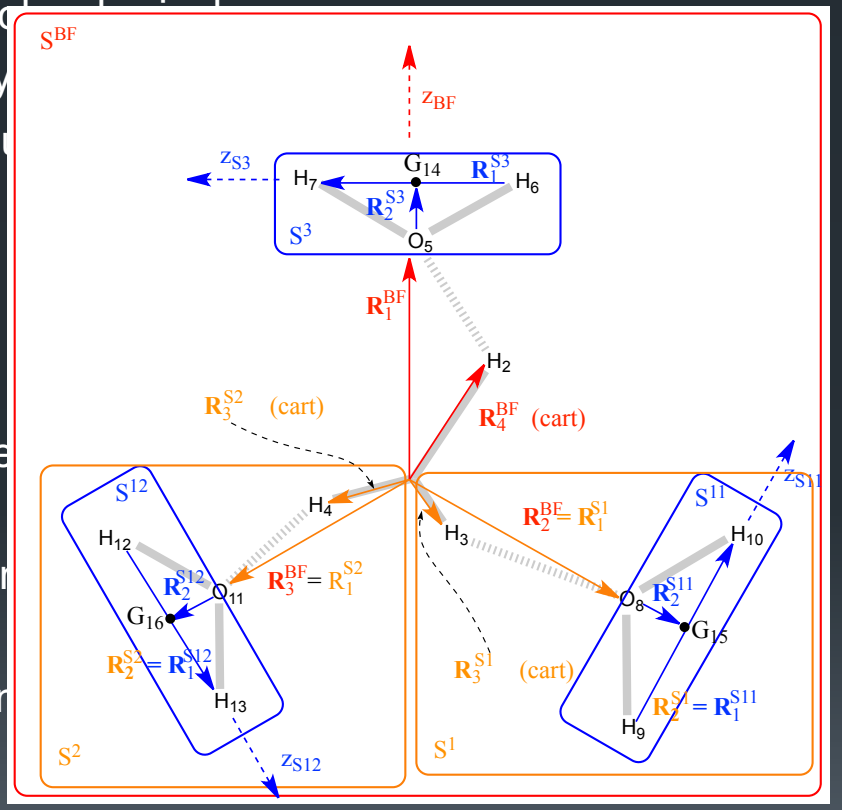
    ⇒Reaction Path (RPH)

    ⇒....

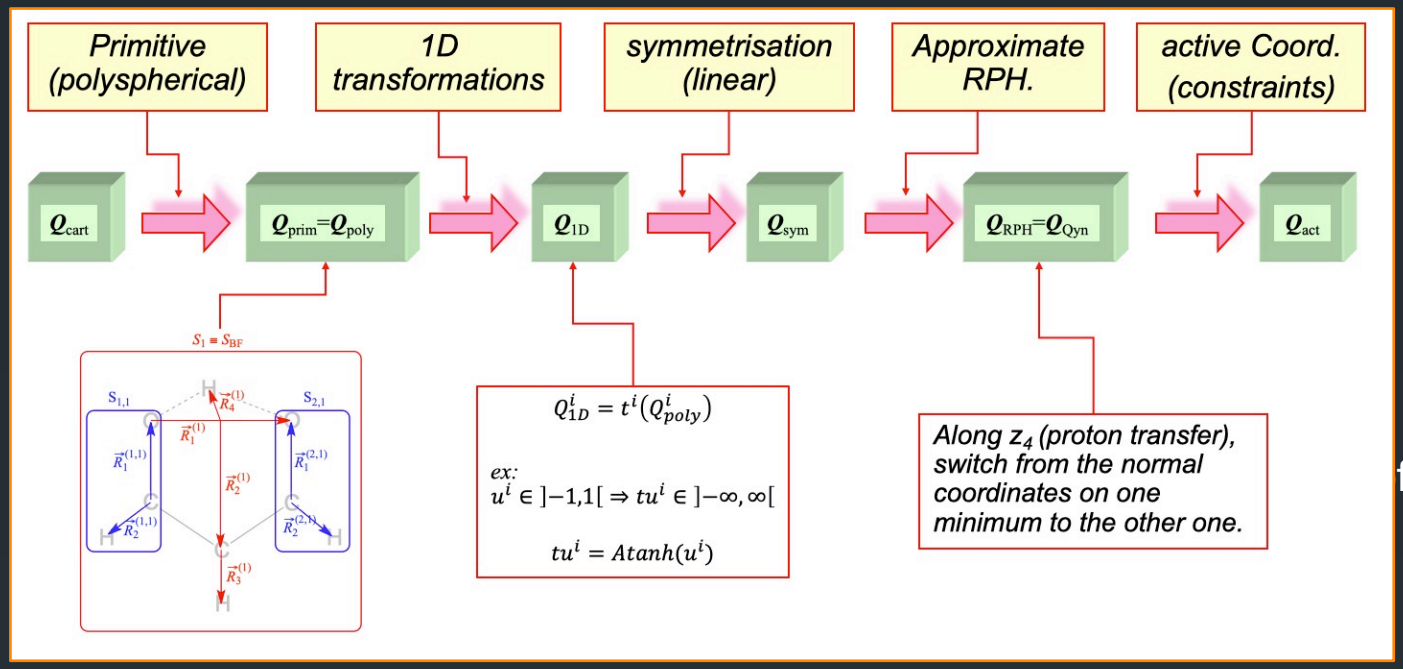
Numerical vs Analytical KEO

- Analytical KEO (TANA):
  - Sum of products of 1D-functions => analytical integrations
  - Restricted to some “kind” of coordinates: po
    - ⇒Some flexibility (vector definitions, subsy
    - ⇒Few transformations are possible (witho structure)
  - Jacobi, Radau coordinate types

- Numerical KEO (TNUM):
  - No analytical expression: nD-numerical inte
  - Numerical but exact **G(Q)** values
  - High flexibility: It is very easy to add coordi
    - ⇒z-matrix, polyspherical
    - ⇒ linear combinations, curvilinear normal r
    - ⇒Reaction Path (RPH)
    - ⇒....



KEO (vibration, rotation): 4741 terms in 23 seconds
Largest difference on ***G***(***Q***) is 10^{-15} au (~10^{-10} cm-1)



f product

- Numerical KEO (TNUM):
  - No analytical expression: nD-numerical integrations.
  - Numerical but exact **G(Q)** values
  - High flexibility: It is very easy to add coordinates transformations

    ⇒z-matrix, polyspherical

    ⇒ linear combinations, curvilinear normal modes

    ⇒Reaction Path (RPH)

    ⇒....

Coordinates: summary

Good coordinates help to reduce the coupling between modes

1. It enables to chose a good "primitive" basis along each coordinate
2. Even with good coordinates, the direct-product basis and grid sizes grow exponentially!!
3. The optimal choice is not obvious: ☹️
   - good for V, but bad for the KEO (or the reverse)
   - good at low energy and bad at high E
   - Try a set of coordinates, run a calculation ... try again^{n} ... 😒

Cartesian coordinates can be good, when a compact basis set can be found:

- The atomic basis sets are used in Cartesian coordinates!!

Overview:

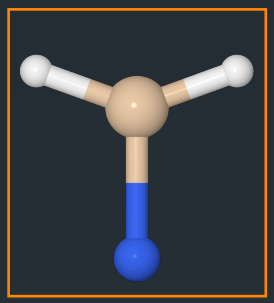
1. Chose a good model / approximation :
   - The Born-Oppenheimer separation of the electrons and nuclei
   - Adiabatic separation between fast and slow motions
   - Eckart conditions: good vibration/rotation separation
   - Do we need all degrees of freedom?

2. Chose a good set of nuclear (atomic) coordinates :
   - Choose coordinates well adapted to the process (rotation, dissociation ...)
   - Kinetic energy operator, $\widehat{T}$

3. Chose a compact basis set (grid) :
   - Basis set well adapted to the process
   - With direct-products, the basis or the grid sizes grow exponentially!

Do we need the direct-product form?

- In 2D: for the 2 Si-H stretches of H_2SiN:



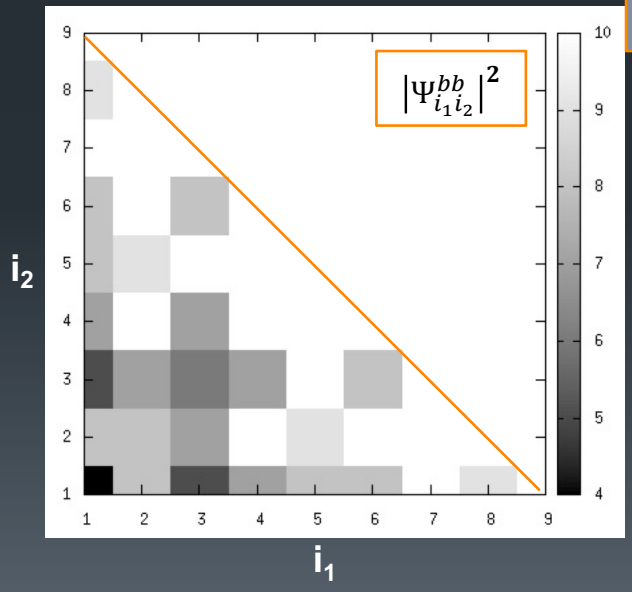
$$\Psi_I(Q_1,Q_2) = \sum_{i_1,i_2} \Psi^{bb}_{i_1 i_2} \cdot \boldsymbol{b}^1_{i_1}(Q_1) \cdot \boldsymbol{b}^2_{i_2}(Q_2)$$

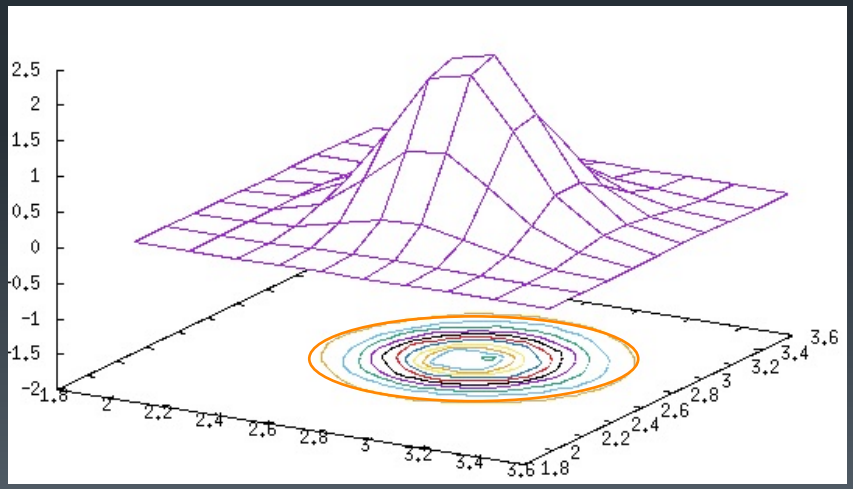
ZPE = 2261.4 cm^{-1}

E_1, E_2 = 2202.0, 2226.8 cm^{-1}

To converge these 3 levels, we need 9 basis functions (HO) and 9 grid points for each coordinate. => 81 2D-basis functions and 81 grid points

Vibrational ground state





Potential: D. Lauvergnat, M. L. Senent, L. Jutier, and M. Hochlaf JCP 135, 074301 (2011)

1st Smolyak scheme in 1D: useless!!

	B_0^1	B_1^1	B_2^1	...	B_ℓ^1
Basis, B_ℓ^1	$\{b_1^1\}$	$\{b_1^1, b_2^1\}$	$\{b_1^1, b_2^1, b_3^1\}$	...	$\{b_1^1, b_2^1, \dots, b_{\ell+1}^1\}$

$$\Psi^{\mathrm{L}} = \boldsymbol{B}_{\mathrm{L}}^1 \cdot \Psi = \sum_{i_1=1}^{L+1} \Psi_{i_1}^b \, . \, b_{i_1}^1$$

The relation between ℓ and the number of basis functions can be any increasing sequence.

$$\Psi^{\mathrm{L}} = \boldsymbol{B}_0^1 \cdot \Psi + (\boldsymbol{B}_1^1 - \boldsymbol{B}_0^1) \cdot \Psi + (\boldsymbol{B}_2^1 - \boldsymbol{B}_1^1) \cdot \Psi + \cdots (\boldsymbol{B}_L^1 - \boldsymbol{B}_{L-1}^1) \cdot \Psi$$

$$\Psi^{\mathrm{L}} = \Delta\boldsymbol{B}_0^1 \cdot \Psi + \Delta\boldsymbol{B}_1^1 \cdot \Psi + \Delta\boldsymbol{B}_2^1 \cdot \Psi + \cdots \Delta\boldsymbol{B}_{\mathrm{L}}^1 \cdot \Psi$$

$$\Psi^{\mathrm{L}} = \sum_{\ell=0}^{L} \Delta\boldsymbol{B}_\ell^1 \cdot \Psi$$

Can have more than one elements

	$\Delta B_0^1 = B_0^1$	ΔB_1^1	ΔB_2^1	...	ΔB_ℓ^1
Basis, ΔB_ℓ^i	$\{b_1^1\}$	$\{b_2^1\}$	$\{b_3^1\}$	...	$\{b_{\ell+1}^1\}$

1st Smolyak scheme in 2D

ΔB_2^2 $\ell_2 = 2$	$\{b_1^1\}\otimes\{b_3^2\}$	$\{b_2^1\}\otimes\{b_3^2\}$	$\{b_3^1\}\otimes\{b_2^2\}$
ΔB_1^2 $\ell_2 = 1$	$\{b_1^1\}\otimes\{b_2^2\}$	$\{b_2^1\}\otimes\{b_2^2\}$	$\{b_3^1\}\otimes\{b_2^2\}$
ΔB_0^2 $\ell_2 = 0$	$\{b_1^1\}\otimes\{b_1^2\}$	$\{b_2^1\}\otimes\{b_1^2\}$	$\{b_3^1\}\otimes\{b_1^2\}$
$\otimes$	$\Delta B_0^1 = \{b_1^1\}$ $\ell_1 = 0$	$\Delta B_1^1 = \{b_2^1\}$ $\ell_1 = 1$	$\Delta B_2^1 = \{b_3^1\}$ $\ell_1 = 2$

- Without constraint, we obtain a direct-product with 9 (3x3) 2D-basis functions.
- With a constraint: $\ell_1 + \ell_2 \leq 2$

1st Smolyak schemes in 2D

ΔB_2^2 $\ell_2 = 2$	$\{b_1^1\}\otimes\{b_3^2\}$		
ΔB_1^2 $\ell_2 = 1$	$\{b_1^1\}\otimes\{b_2^2\}$	$\{b_2^1\}\otimes\{b_2^2\}$	
ΔB_0^2 $\ell_2 = 0$	$\{b_1^1\}\otimes\{b_1^2\}$	$\{b_2^1\}\otimes\{b_1^2\}$	$\{b_3^1\}\otimes\{b_1^2\}$
$\otimes$	$\Delta B_0^1 = \{b_1^1\}$ $\ell_1 = 0$	$\Delta B_1^1 = \{b_2^1\}$ $\ell_1 = 1$	$\Delta B_2^1 = \{b_3^1\}$ $\ell_1 = 2$

- Without constraint, we obtain a direct product with 3x3 2D-basis functions.

- With a constraint: $\ell_1 + \ell_2 \leq 2$, we obtain a basis set with 6 2D-basis functions.

Smolyak Scheme: 1st summary:

- This is equivalent to a selection (in terms of excitations) of the basis functions.

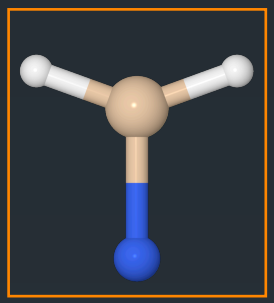
- The Smolyak scheme, with this selection ($|\boldsymbol{\ell}| = \sum \ell_k \leq L$) and with a simple sequence ($nb^k_{\ell_k} = 1 + \ell_k$), the number of basis functions is $NB = \frac{(n+L)!}{n! \cdot L!}$.

- The Smolyak scheme can be use also for the grid => NB and NQ do not grow exponentionaly with n.

- One can use on L for the basis (L_B) and another one (larger) for the grid (L_G).

Do we need the direct-product form? NO

- In 2D: for the 2 Si-H stretches of H_2SiN:



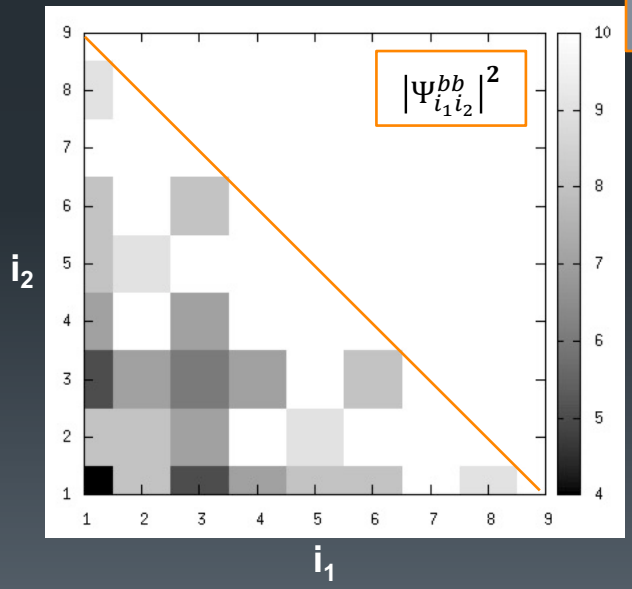
$$\Psi_I(Q_1,Q_2) = \sum_{i_1,i_2} \Psi^{bb}_{i_1 i_2} \cdot \boldsymbol{b}^1_{i_1}(Q_1) \cdot \boldsymbol{b}^2_{i_2}(Q_2)$$

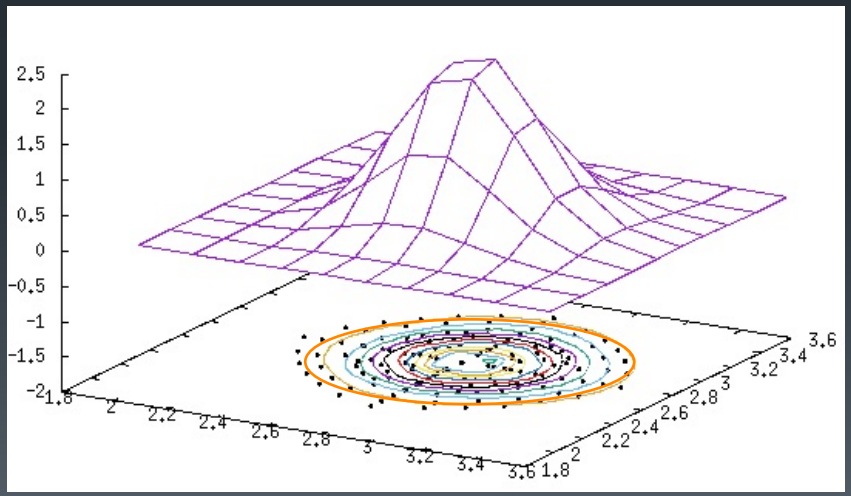
ZPE = 2261.4 cm^{-1}

E_1, E_2 = 2202.0, 2226.8 cm^{-1}

To converge these 3 levels, we need 9 basis functions (HO) and 9 grid points for each coordinate. => 81 2D-basis functions and 81 grid points

Vibrational ground state





Potential: D. Lauvergnat, M. L. Senent, L. Jutier, and M. Hochlaf JCP 135, 074301 (2011)

Back to the origin: **2** Smolyak schemes

$$|\boldsymbol{\ell}| = \sum \ell_k$$

- 1st Scheme:

  In term of "difference"

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{0\le|\boldsymbol{\ell}|\le L} \Delta\boldsymbol{S}_{\ell_1}^1 \otimes \cdots \Delta\boldsymbol{S}_{\ell_n}^n$$

expansion

- 2d Scheme:

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{L-n+1\le|\boldsymbol{\ell}|\le L} D_{\boldsymbol{\ell}} \cdot \boldsymbol{S}_{\ell_1}^1 \otimes \cdots \boldsymbol{S}_{\ell_n}^n$$

$$(-1)^{L-|\boldsymbol{\ell}|} C_{n-1}^{L-|\boldsymbol{\ell}|}$$

$$\sum_{-1\le|\boldsymbol{\ell}|\le L} D_{\boldsymbol{\ell}} \cdot \left|\Psi^{S_{\ell_1}^1 \otimes \cdots S_{\ell_n}^n}\right\rangle$$

МАТЕМАТИКА

С. А. СМОЛЯК

КВАДРАТУРНЫЕ И ИНТЕРПОЛЯЦИОННЫЕ ФОРМУЛЫ НА ТЕНЗОРНЫХ ПРОИЗВЕДЕНИЯХ НЕКОТОРЫХ КЛАССОВ ФУНКЦИЙ

(Представлено академиком А. Н. Колмогоровым 17 VIII 1962)

$$\| I \otimes \ldots \otimes I - \sum_{\nu_1+\ldots+\nu_s \leqslant q} \theta_{\nu_1} \otimes \ldots \otimes \theta_{\nu_s} \| \leqslant C(A, B, s, \alpha) \frac{q^{s-1}}{2^{\alpha q}}.$$

The scheme can be used on a grid ($\mathbf{S}_{\ell_i}^i = \mathbf{g}_{\ell_i}^i$) or on the basis set ($\mathbf{S}_{\ell_i}^i = \mathbf{B}_{\ell_i}^i$).

Back to the origin: **2** Smolyak schemes

$$|\boldsymbol{\ell}| = \sum \ell_k$$

- 1st Scheme:

  In term of "difference"

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{0 \le |\boldsymbol{\ell}| \le L} \boldsymbol{\Delta S}_{\ell_1}^1 \otimes \cdots \boldsymbol{\Delta S}_{\ell_n}^n$$

$$\boldsymbol{\Delta S}_{\ell_\mathrm{i}}^\mathrm{i} = \begin{cases} \boldsymbol{S}_0^\mathrm{i} & \text{for } \ell_\mathrm{i} = 0 \\ \boldsymbol{S}_{\ell_\mathrm{i}}^\mathrm{i} - \boldsymbol{S}_{\ell_{i-1}}^\mathrm{i} & \text{for } \ell_\mathrm{i} > 0 \end{cases}$$

$$|\Psi\rangle = \sum_{0 \le |\boldsymbol{\ell}| \le L} \left| \Psi^{\boldsymbol{\Delta S}_{\ell_1}^1 \otimes \cdots \boldsymbol{\Delta S}_{\ell_n}^n} \right\rangle$$

expansion

- 2d Scheme:

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \boldsymbol{S}_{\ell_1}^1 \otimes \cdots \boldsymbol{S}_{\ell_n}^n$$

$$D_{\boldsymbol{\ell}} = (-1)^{L-|\boldsymbol{\ell}|} C_{n-1}^{L-|\boldsymbol{\ell}|}$$

$$|\Psi\rangle = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \left| \Psi^{\boldsymbol{S}_{\ell_1}^1 \otimes \cdots \boldsymbol{S}_{\ell_n}^n} \right\rangle$$

The scheme can be used on a grid ($\mathbf{S}_{\ell_\mathrm{i}}^\mathrm{i} = \mathbf{g}_{\ell_\mathrm{i}}^\mathrm{i}$) or on the basis set ($\mathbf{S}_{\ell_\mathrm{i}}^\mathrm{i} = \mathbf{B}_{\ell_\mathrm{i}}^\mathrm{i}$).

Back to the origin: **2** Smolyak schemes

$$|\boldsymbol{\ell}| = \sum \ell_k$$

- 1st Scheme:

  In term of "difference"

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{0 \le |\boldsymbol{\ell}| \le L} \boldsymbol{\Delta S}_{\ell_1}^1 \otimes \cdots \boldsymbol{\Delta S}_{\ell_n}^n$$

$$\boldsymbol{\Delta S}_{\ell_\mathrm{i}}^\mathrm{i} = \begin{cases} \boldsymbol{S}_0^\mathrm{i} & \text{for } \ell_\mathrm{i} = 0 \\ \boldsymbol{S}_{\ell_\mathrm{i}}^\mathrm{i} - \boldsymbol{S}_{\ell_{i-1}}^\mathrm{i} & \text{for } \ell_\mathrm{i} > 0 \end{cases}$$

$$|\Psi\rangle = \sum_{0 \le |\boldsymbol{\ell}| \le L} \left| \Psi^{\boldsymbol{\Delta S}_{\ell_1}^1 \otimes \cdots \boldsymbol{\Delta S}_{\ell_n}^n} \right\rangle$$

expansion

- 2d Scheme:

$$\boldsymbol{S}_L^{1\ldots n} = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \boldsymbol{S}_{\ell_1}^1 \otimes \cdots \boldsymbol{S}_{\ell_n}^n$$

$$D_{\boldsymbol{\ell}} = (-1)^{L-|\boldsymbol{\ell}|} C_{n-1}^{L-|\boldsymbol{\ell}|}$$

$$|\Psi\rangle = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \left| \Psi^{\boldsymbol{S}_{\ell_1}^1 \otimes \cdots \boldsymbol{S}_{\ell_n}^n} \right\rangle$$

Instead of **one large** direct-product,
a (**large**) **sum** of **small** direct-products.

2^d Smolyak scheme in 2D

- Basis set: $nb^i_{\ell_i} = 1 + \ell_i$ constraints: $1 \leq \ell_1 + \ell_2 \leq 2$

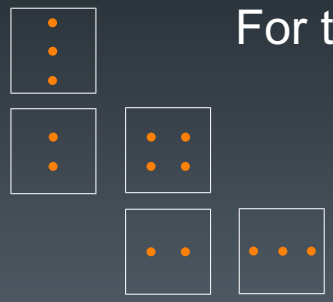
S^2_2 $\ell_2 = 2$	$\{b^1_1\}\otimes\{b^2_1, b^2_2, b^2_3\}$ **1**	~~$\{b^1_1, b^1_2\}\otimes\{b^2_1, b^2_2, b^2_3\}$~~	~~$\{b^1_1, b^1_2, b^1_3\}\otimes\{b^2_1, b^2_2, b^2_3\}$~~
S^2_1 $\ell_2 = 1$	$\{b^1_1\}\otimes\{b^2_1, b^2_2\}$ **-1**	$\{b^1_1, b^1_2\}\otimes\{b^2_1, b^2_2\}$ **1**	~~$\{b^1_1, b^1_2, b^1_3\}\otimes\{b^2_1, b^2_2\}$~~
S^2_0 $\ell_2 = 0$	~~$\{b^1_1\}\otimes\{b^2_1\}$~~ **0**	$\{b^1_1, b^1_2\}\otimes\{b^2_1\}$ **-1**	$\{b^1_1, b^1_2, b^1_3\}\otimes\{b^2_1\}$ **1**
$\otimes$	$S^1_0 = \{b^1_1\}$ $\ell_1 = 0$	$S^1_1 = \{b^1_1, b^1_2\}$ $\ell_1 = 1$	$S^1_2 = \{b^1_1, b^1_2, b^1_3\}$ $\ell_1 = 2$

2D-basis functions:

$b^1_1.b^2_1$
$b^1_1.b^2_2$ $b^1_1.b^2_3$
$b^1_2.b^2_1$ $b^1_3.b^2_1$
$b^1_2.b^2_2$

~~$b^1_2.b^2_2$~~
~~$b^1_1.b^2_3$~~
~~$b^1_3.b^2_1$~~

For the grid



Smolyak Scheme in 14D

Example in 14D: $L_B=L_G=9$ ($nq_{\ell_k}^k = nb_{\ell_k}^k = 1 + \ell_k$):

	NB	NQ
Direct product	10^{14}	10^{14}
Smolyak	**817 190**	**~124 10^6**

about 8 10^5 times smaller

2^d Smolyak scheme: computer representation

- Ψ on the basis functions:

$$\begin{bmatrix} b_1^x . b_1^y \\ b_1^x . b_2^y \\ b_2^x . b_1^y \\ b_1^x . b_3^y \\ b_2^x . b_2^y \\ b_3^x . b_1^y \end{bmatrix} \Rightarrow \Psi = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0.5 \\ 0 \end{bmatrix}$$

We need a mapping

- Ψ on the Smolyak basis rep.:

ℓ_x, ℓ_y	00	01	10	02	11	20
basis functions	$[b_1^x . b_1^y]$	$\begin{bmatrix} b_1^x . b_1^y \\ b_1^x . b_2^y \end{bmatrix}$	$\begin{bmatrix} b_1^x . b_1^y \\ b_2^x . b_1^y \end{bmatrix}$	$\begin{bmatrix} b_1^x . b_1^y \\ b_1^x . b_2^y \\ b_1^x . b_3^y \end{bmatrix}$	$\begin{bmatrix} b_1^x . b_1^y \\ b_2^x . b_1^y \\ b_1^x . b_2^y \\ b_2^x . b_2^y \end{bmatrix}$	$\begin{bmatrix} b_1^x . b_1^y \\ b_2^x . b_1^y \\ b_2^x . b_1^y \end{bmatrix}$
Ψ^{ℓ_x,ℓ_y}	$[1]$	$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0.5 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$
D_{ℓ_x,ℓ_y}	0	-1	-1	1	1	1

WF are stored on the basis set
No memory problem (almost)

With 2^d Smolyak scheme, the computer size (basis or grid) of a WF can be very large.
⇒ A WF is never stored on the full representation (only one term), even for operation on a WF.

2^d Smolyak scheme: operations on $|\Psi\rangle$

$$|\Psi\rangle = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \left| \Psi^{\boldsymbol{S}^1_{\ell_1} \otimes \cdots \boldsymbol{S}^n_{\ell_n}} \right\rangle$$

Wave function (mapping)

$$\Psi^B \Leftrightarrow \Psi^G \quad \overset{\forall \boldsymbol{\ell}}{\Rightarrow} \quad \Psi^{\boldsymbol{B}^1_{\ell_1} \otimes \cdots \boldsymbol{B}^n_{\ell_n}} \Leftrightarrow \Psi^{\boldsymbol{g}^1_{\ell_1} \otimes \cdots \boldsymbol{g}^n_{\ell_n}}$$

Basis ⇔ Grid

$$\langle \Phi | \Psi \rangle = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \left\langle \Phi^{\boldsymbol{S}^1_{\ell_1} \otimes \cdots \boldsymbol{S}^n_{\ell_n}} \middle| \Psi^{\boldsymbol{S}^1_{\ell_1} \otimes \cdots \boldsymbol{S}^n_{\ell_n}} \right\rangle$$

Scalar product

$$\hat{O}|\Psi\rangle = \sum_{L-n+1 \le |\boldsymbol{\ell}| \le L} D_{\boldsymbol{\ell}} \cdot \hat{O} \left| \Psi^{\boldsymbol{S}^1_{\ell_1} \otimes \cdots \boldsymbol{S}^n_{\ell_n}} \right\rangle$$

Operator action: standard action on small direct-products

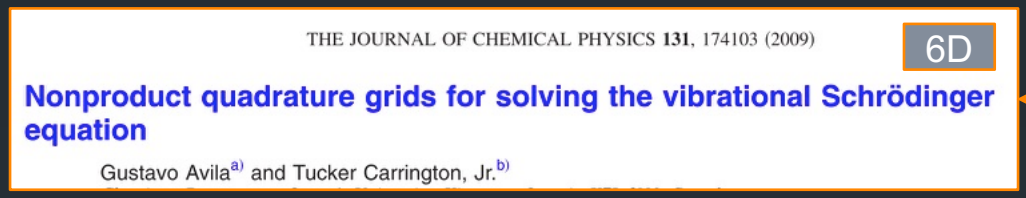
On the Smolyak sum, all operations are almost independent !!

⇒ parallelization: openmp, MPI (Ahai Chen)

Almost no communication except:

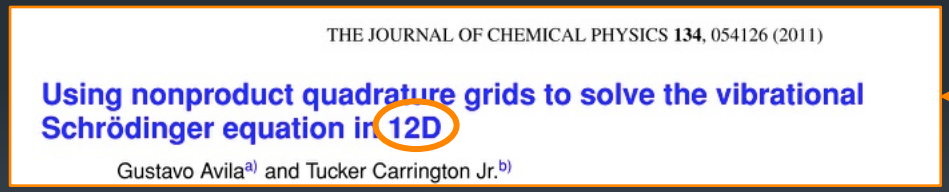
- transformation from the Smolyak representation to the basis one (mapping)

Smolyak Scheme: applications

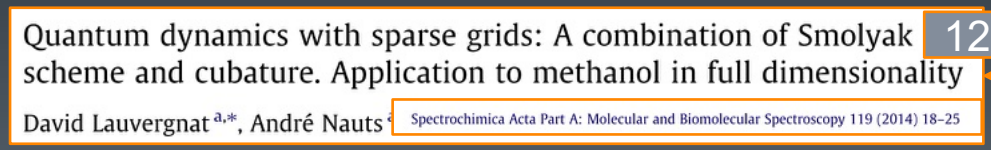


Stretches of SF_6
"rigid" system

$HO\text{-}NO_2$
"floppy" system



CH_3CN
"rigid" system

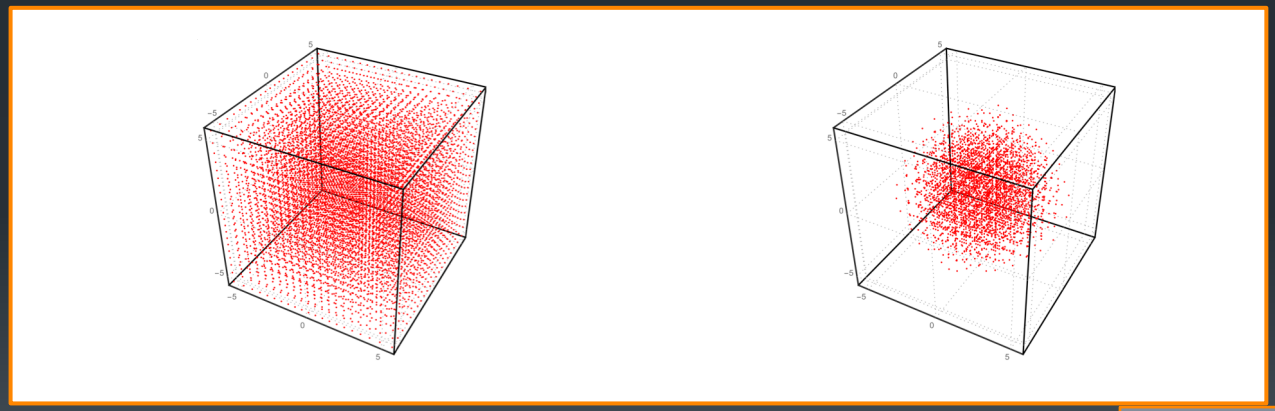


$CH_3\text{-}OH$
"floppy" system

+ other papers

Smolyak Scheme: Summary

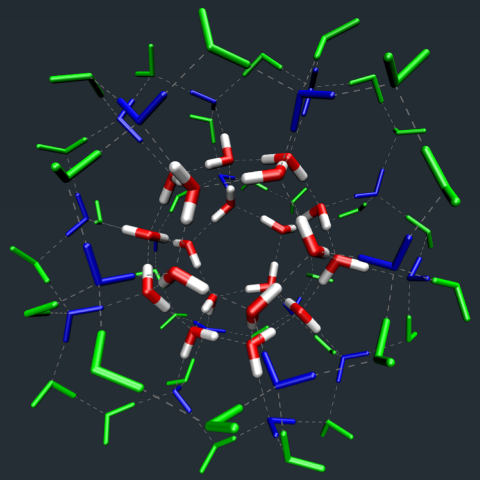
- The $G^i_{\ell_i}$ and the corresponding basis, $B^i_{\ell_i}$, are not necessary in 1D:
  - Spherical harmonics can be used
  - Other DP basis/Grid
- With those sparse grids (HO basis set), the edge or the corner of a cube (hyper) can be avoided.
  - Example 3D, with avec L_G=5 et B=4



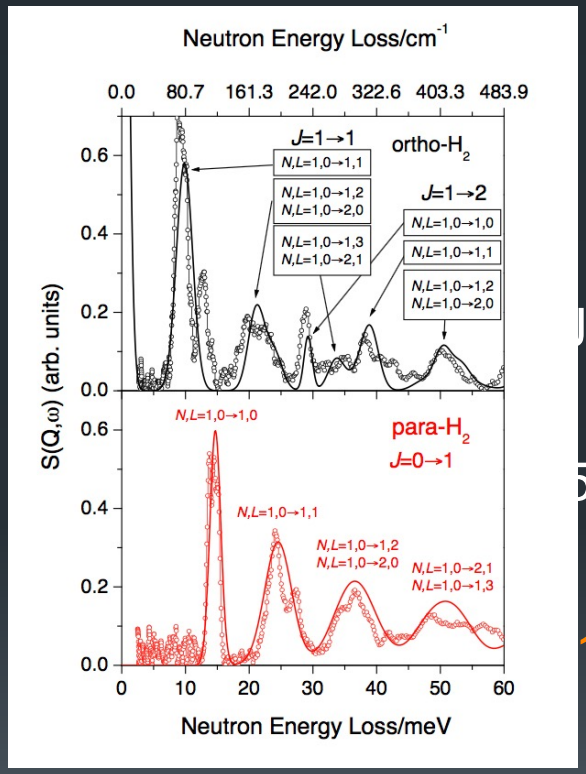
- Polynomial Scaling in *n* of degree *L*
- System / bath separation ⇒ Several *L* (L_{sys} and L_{bath})

with $nb^i_{\ell_i} = nq^i_{\ell_i} = 1 + \ell_i$

$H_2@(H_2O)_n$:



- Experimental transitions (cm^{-1}):

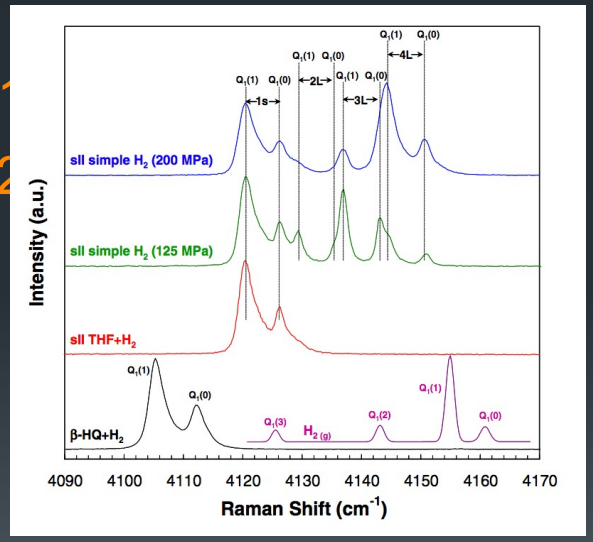


=1, 3x

6.6 122

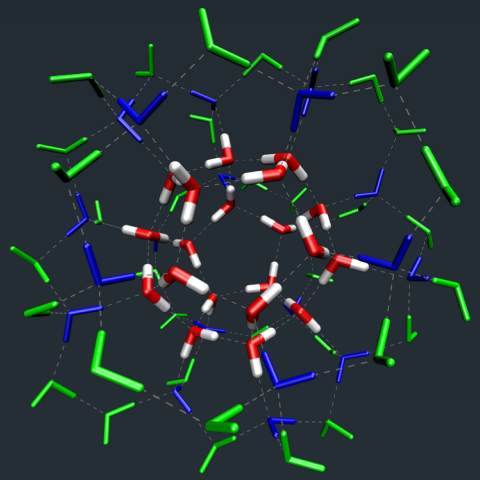
56.2

161.2)



[1] L. Ulivi, M. Celli, A. Gianiassi, A. J. Ramirez-Cuesta, D. J. Bull, and M. Zoppi, Phys. Rev. B **76**, 161401 2007
[2] T.A. Strobel et al. Chemical Physics Letters 478 (2009) 97–109

$H_2@(H_2O)_n$:



- Experimental transitions (cm^{-1}):
  - Translations [1]
    71,0 80,2 101.1
  - Rotations [1] (gas: J=1, 3x 118.4. J=2, 5x 354.2)
    J=1, ortho: 110.0 116.6 122.1
    J=2, para: 343.2 – 356.2
  - Vibration [2] (gas: 4161.2)
    ν = 4126

[1] L. Ulivi, M. Celli, A. Gianiassi, A. J. Ramirez-Cuesta, D. J. Bull, and M. Zoppi, Phys. Rev. B **76**, 161401 2007
[2] T.A. Strobel et al. Chemical Physics Letters 478 (2009) 97–109

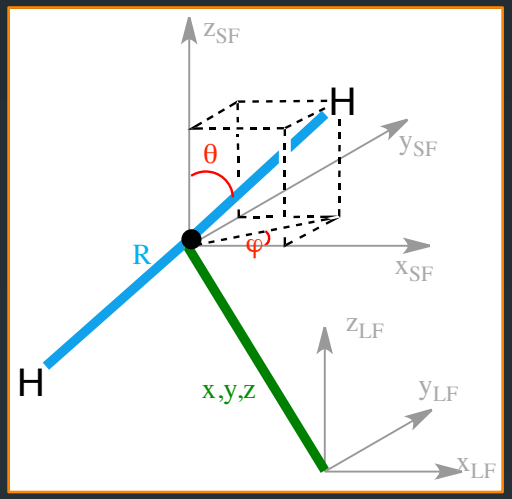
Models (Crystal geometry: 1st shell + other shells)

- Hamiltonian:

$$\hat{H}_{6D} = \frac{1}{2\,mH_2}\left(\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2\right) + \frac{1}{mH\,R^2}\hat{L}^2 + \frac{1}{2\,\mu H_2}\hat{P}_R^2 + V(x, y, z, \theta, \varphi, R)$$

- Potentials (frozen cage):
  - SPC/E, 5D: translation + rotation
  - Valiron 5D (+ adiabatic separation => vibrational shift) or 6D
    Ab intio (CCSD(T)) with 2 body terms

Enables to check our numerical implementation

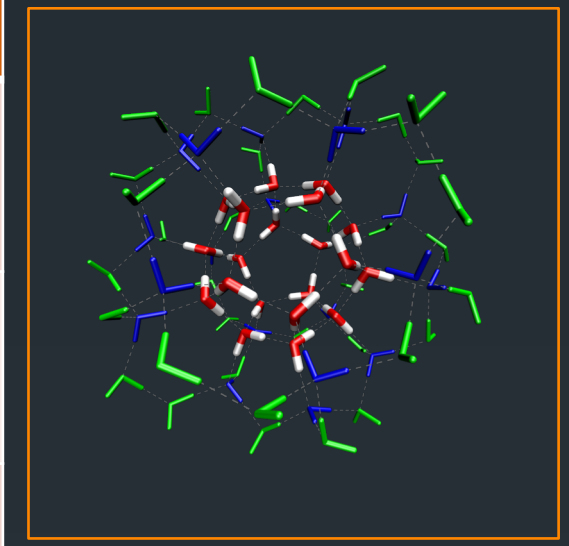


- Base / grids with Smolyak scheme (L_B, L_G) :
  - Translation: $HO_{ix}(x)$, $HO_{iy}(y)$, $HO_{iz}(z)$
  - Rotation: $Y_\ell^m(\theta, \varphi)$
  - Vibration H_2: $HO_{iR}(R)$

2D-basis set and 2D-Grid (Lebedev)

Rigid cage: 6D + cluster size

cm^{-1}	Exp.	6D $H_2@(H_20)_{20}$	6D $H_2@(H_20)_{40}$	6D $H_2@(H_20)_{76}$
Trans.	71.0 80.2 101.1	66.8 76.1 93.3	66.5 75.5 92.5	66.2 75.3 92.3
Rotation ortho, L=1	110.0 116.6 122.1	85.4 121.2 147.6	93.5 121.2 140.2	**97.7** 118.4 **137.7**
ν $\Delta\nu$	 -34/-37	4120.9 -40.2	4119.4 -41.7	4119.2 -41.9



Smolyak parameters : L_B=6 and L_G=7

NB=8246 and NQ=460 000.

3h30 on 12 cores (3h for the PES evaluation on the grid).

Remarks, with a single direct product:

NB~2.0 10^6 and NQ~6.4 10^6

DL et al. JCP 150, 154303 (2019)
Potential: P. Valiron et al., JCP 129, 134306 (2008)

Translation: $nb^T(\ell_T) = 1 + 2\ell_T$

Rotation: $j_{max}(\ell_R) = \ell_R$

Vibration: $nb^V(\ell_V) = 1 + 3\ell_V$

Models with flexible cage

- Potentials:
  - SPC/E (H_2-H_2O potential) + SPC/Fw (H_2O-H_2O potential)

The full potential is used (no harmonic approximation)

- Cage:
  - Only the first shell (20 water molecules) is flexible.

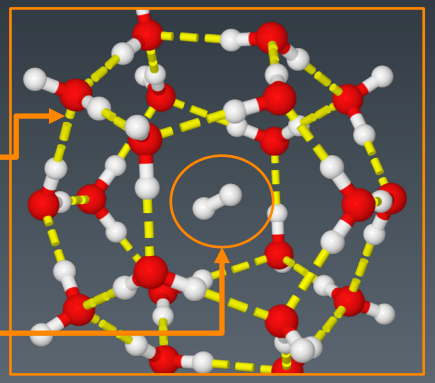
⇒ Separation between the vibrations and the translation-rotation modes of the waters.
⇒ The KEO is simple

- Cage coordinates (normal modes):
  - Full normal modes: to reduce the coupling between all cage modes (no quadratic couplings)

- Base / grids :
  - Cage basis sets: $HO_k(Q_i)$
  - System (H_2) / Bath (H_2O) separation

Bath: water molecules with $L_{Bath} << L_B$

System: H_2 motions with L_B/L_G



Fexible cage: 5+48D

cm^{-1}	Exp.	5+0D $H_2@(H_20)_{20+20}$ L_B=3	5+48D $H_2@(H_20)_{20+20}$ L_B=3, B=2	5+48D $H_2@(H_20)_{20+20}$ L_B=3, B=3
Trans.	71.0 80.2 101.1	83.7 88.6 100.0	85.7 90.6 103.5	85.9 90.6 103.0
Rotation ortho, L=1	110.0 116.6 122.1	109.4 125.1 131.6	**107.0** **122.6** **129.0**	**107.1** **122.6** **129.0**
NB NQ			$9.7\ 10^4$ $54\ 10^6$	$2.1\ 10^5$ $121\ 10^6$

With one large direct-product: NB~$5\ 10^{58}$

17 h with 12MPI threads

Smolyak parameters : L_B=3 (L_G=L_B+1), L_{BBath}=2 and L_{BBath}=3

Translation: $nb^T(\ell_T) = 1 + 3\ell_T$

Rotation: $j_{max}(\ell_R) = 2\ell_R$

Cage (bath): $nb^B(\ell_B) = 1 + B\ell_B$ (*B*=2 or 3)

Perspectives

- Applications

- Clathrates:
  - Several H_2 in large cages
  - H_2 tunneling between cages
  - CH_4 or CO_2 in a cage
- Application on reactive scattering
  - with L. Dupuy and Y. Scribano
  - ANR coord. Y. Scribano

Smolyak scheme:

- MPI/OpenMP parallelization
- Propagation scheme

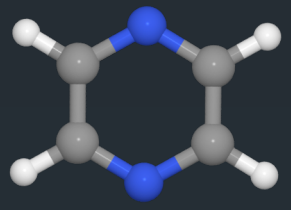
  => Time-Dependent basis
- Spectroscopy: difficulties with large density of states

Some tunneling effect!!

Thanks

Test on Pyrazine vibronic model

Several simulations with MCTDH from 4D to 24D[1]



- Vibronic model between the S_1 and S_2 states[1]:

$$\mathrm{H} = \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \mathbf{I} \sum_{i=1}^{n} \frac{\omega_i}{2} \left(\hat{P}_i^{\,2} + Q_i^{\,2} \right) + \begin{pmatrix} 0 & \lambda Q_1 \\ \lambda Q_1 & 0 \end{pmatrix} + \sum_{i=2}^{n} \begin{pmatrix} k_i^1 & 0 \\ 0 & k_i^2 \end{pmatrix} Q_i$$

- Primitive basis sets and grids:
  Harmonic oscillator (HO) + gauss Hermite quadrature

- Initial WP: gaussian WP (first nD-basis function) on S_2

- Smolyak parameters ($L_B = L_G$ up to 7):

$nb_{\ell_i}^i = nq_{\ell_i}^i = 1 + 4\ell_i$ i=1,2

$nb_{\ell_i}^i = nq_{\ell_i}^i = 1 + 3\ell_i$ i=3,4

$nb_{\ell_i}^i = nq_{\ell_i}^i = 1 + 2\ell_i$ i>4 (bath modes)

Parameters optimized for the 4D model

1) G. Worth, H.-D. Meyer, and L.S. Cederbaum.JCP 109 (1998), 3518

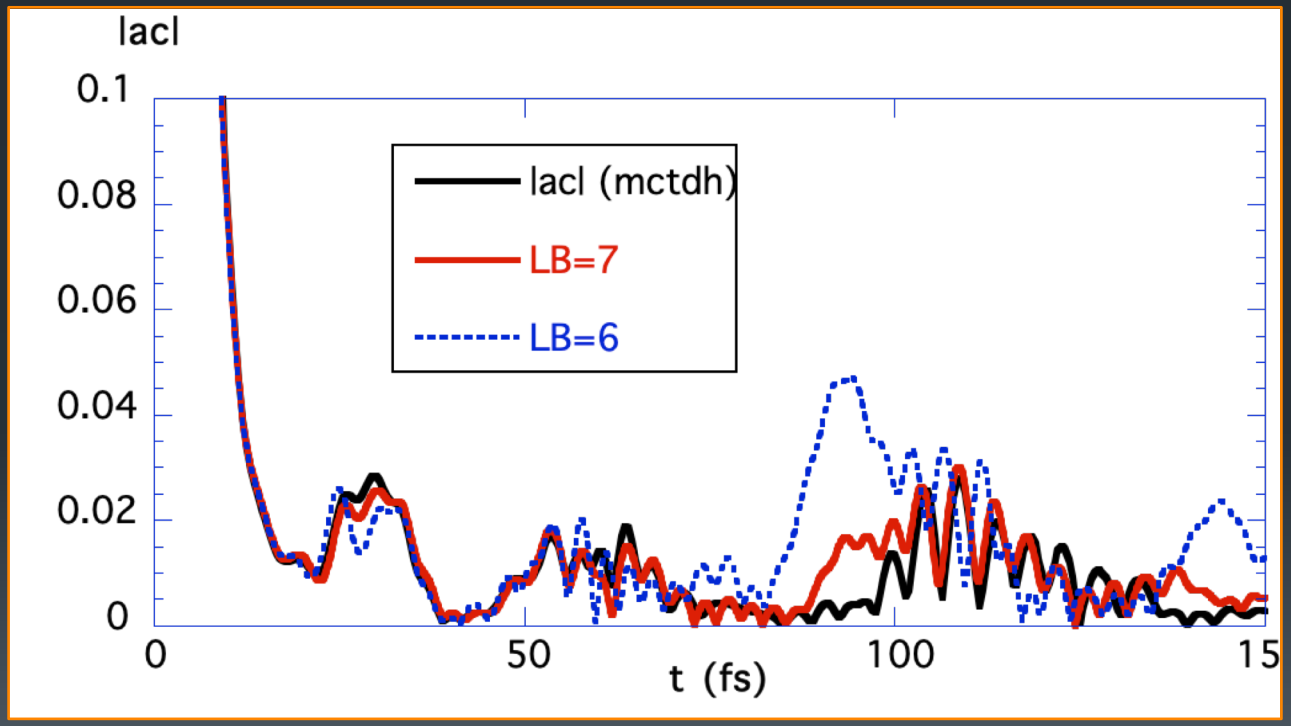
Pyrazine in 4+8D: autocorrelation function

Propagation with Chebyshev scheme, with 10 fs time step.

Autocorrelation function every 0.1 fs.

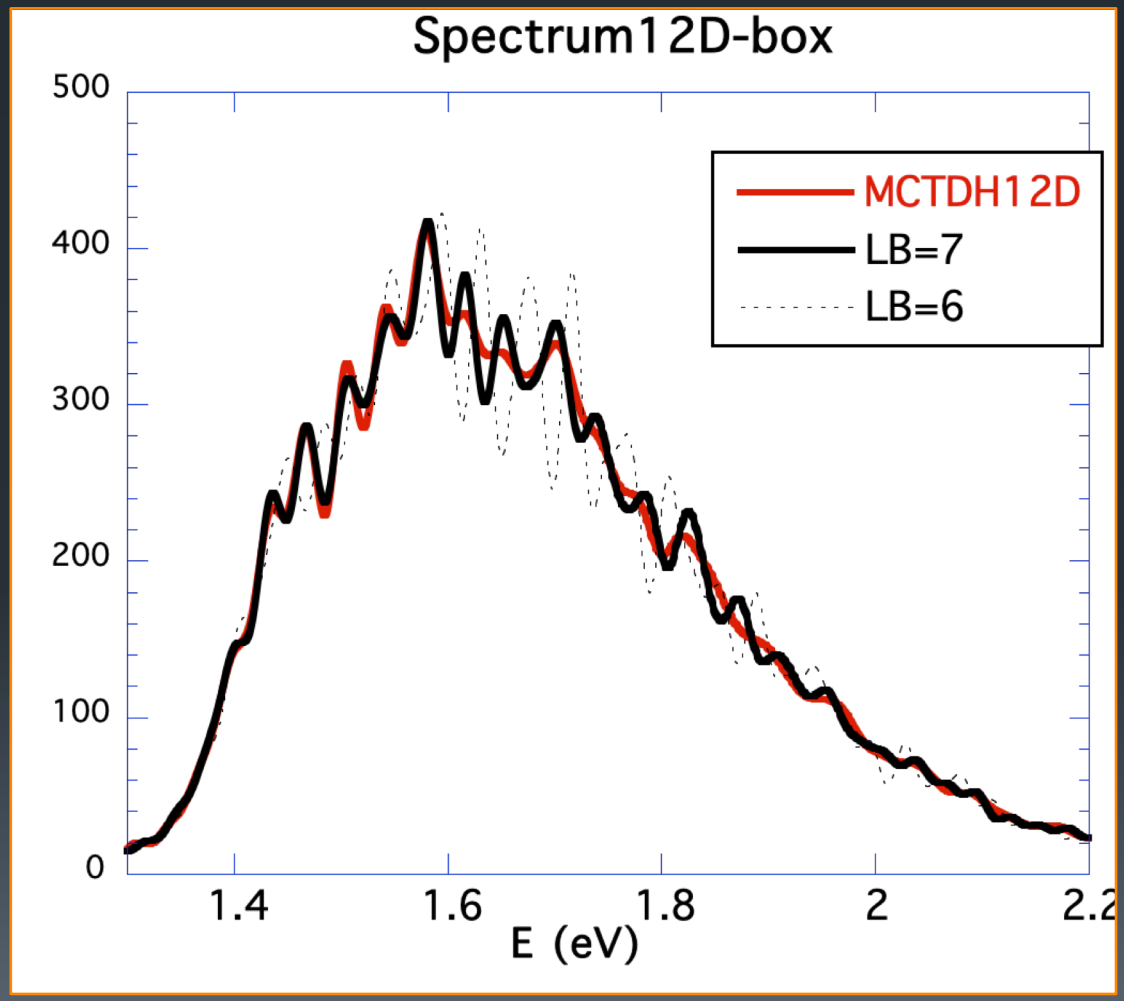
For LB=7
NB=4. 10^6
NQ=53. 10^6
HPsi>: 178s (3 cores)
cheby: 147
Total Time: 116h

Direct product:
NB= 10^{15}



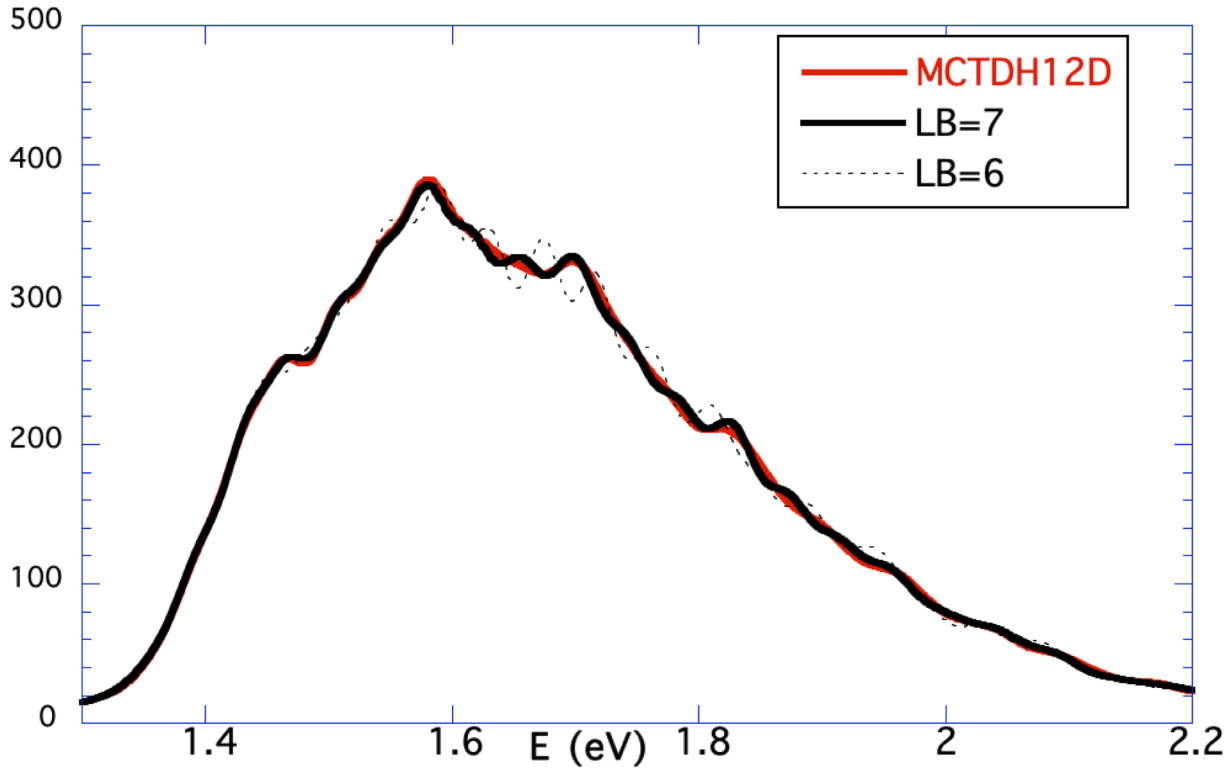
Comparison with MCTDH is not perfect, but ...

Pyrazine in 4+8D: spectrum

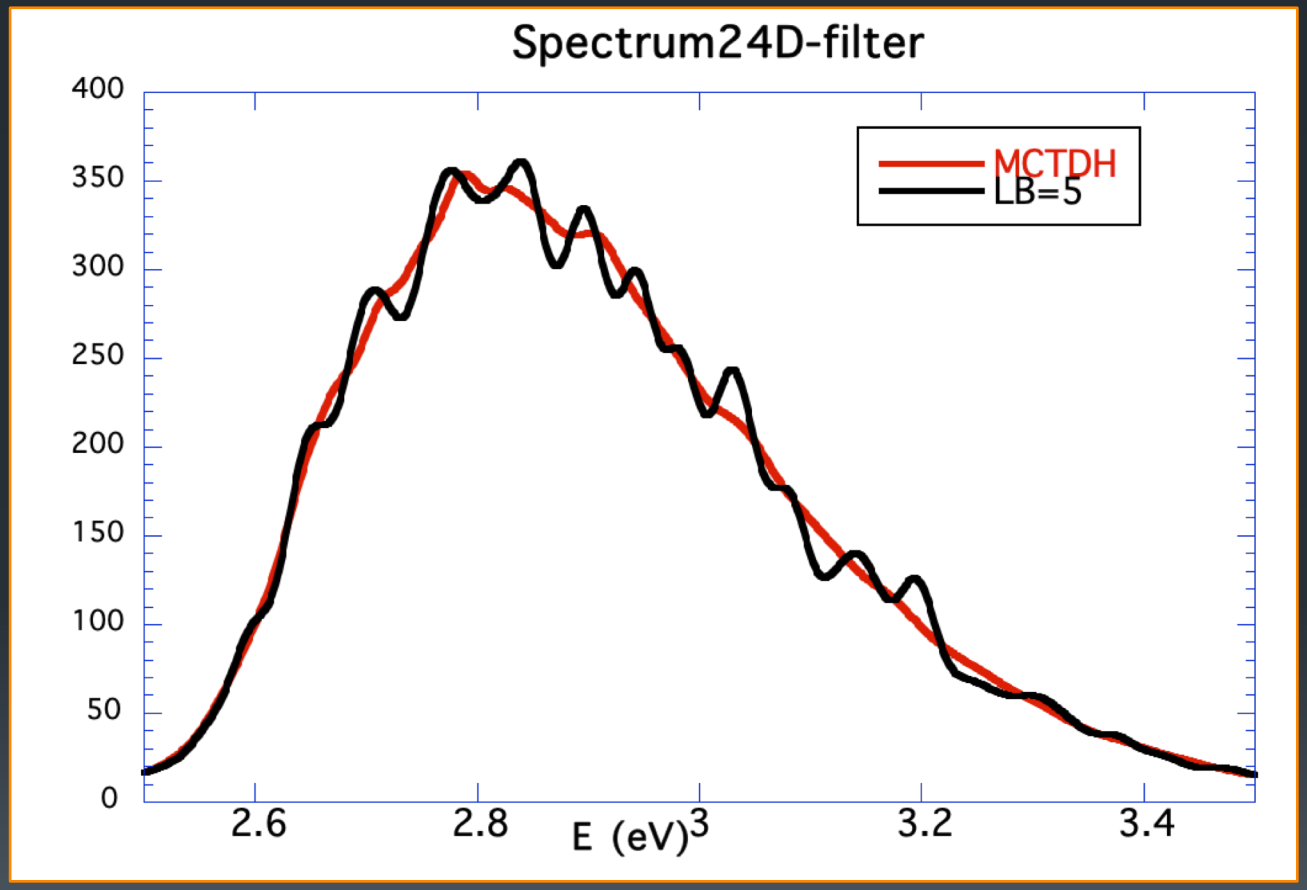


Comparison with MCTDH is not perfect, but ...

Pyrazine in 4+8D: spectrum with a filter



Pyrazine in 4+20D: spectrum with a filter



NB=4M
NQ=26M
HPsi>: 185s (3 cores)
cheby: 113
Total Time: 93h

Comparison with MCTDH is not perfect, but the principal features are reproduced

Modèles 5D/6D avec ELVIBROT :

- Base (non-produit direct) :
  - Translation : $HO_{ix}(x)$, $HO_{iy}(y)$, $HO_{iz}(z)$ et $ix \leq 1 + B \cdot \ell_x$ (id y,z)
  - Rotation : $Y_\ell^m(\theta, \varphi)$ et $\ell \leq B_{rot} \cdot \ell_{rot}$
  - Vibration : $HO_{iR}(R)$ et $iR \leq 1 + B_R \cdot \ell_R$

Sélection : $\ell_x + \ell_y + \ell_z + \ell_{rot}\ (+\ell_R) \leq L_B$

plus une sélection similaire pour les grilles (paramètre L_G)

- Exemple 3D (x, y, z)

avec : $L_B = 2$ et $B = 1$

Nb fonctions :

$N_B = 10$

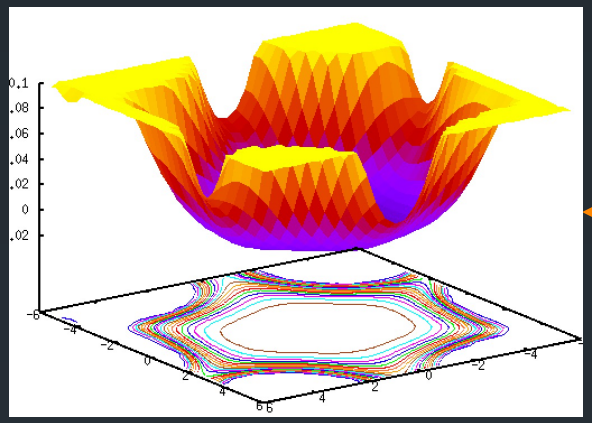
$N_B = (1+2)^3$ (produit direct)

- En général nD et B=1:

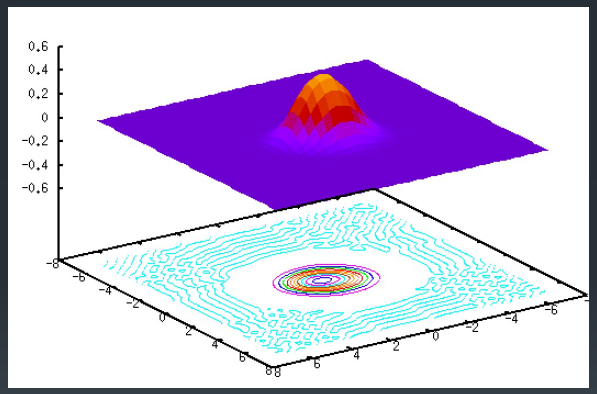
$$N_B = \frac{(n + L_B)!}{n! \cdot L_B!}$$

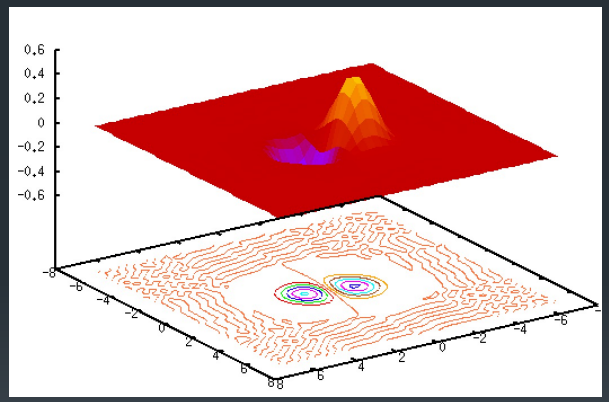
L =	$\ell_x + \ell_y + \ell_z$	i_x, i_y, i_z
0	0 + 0 + 0	1 , 1 , 1
1	1 + 0 + 0 0 + 1 + 0 0 + 0 + 1	2 , 1 , 1 1 , 2 , 1 1 , 1 , 2
2	2 + 0 + 0 0 + 2 + 0 0 + 0 + 2 0 + 1 + 1 1 + 0 + 1 1 + 1 + 0	3 , 1 , 1 1 , 3 , 1 1 , 1 , 3 1 , 2 , 2 2 , 1 , 2 2 , 2 , 1

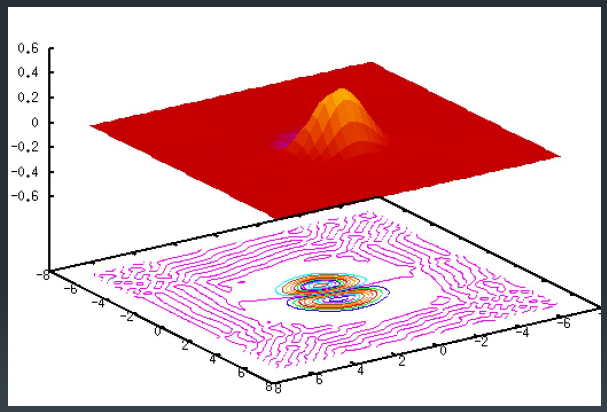
Potentiel + états 2D (x,y)



Potentiel (z=0)







Fonctions d'ondes

Résultats théoriques (5D) :

cm^{-1}	Exp.	DVR+contrac. Bačić[1]	MCTDH[2]	ElVibRot conv: 10^{-3}
ZPE*	/	-447.84	-447.07	-448.20
Trans.	71.0 80.2 101.1	74.45 74.67 97.54	74.25 74.37 97.21	74.15 74.38 97.18
Rotation ortho, L=1	110.0 116.6 122.1	109.00 121.70 128.10	110.08 119.23 127.12	108.98 119.39 128.12

- NonDP :

L_B=4, L_G=5

$nb_x^{max} = 17$ (HO)

$\ell^{max} = 8$

N_B= 4 065

N_Q= 90 588

- DP :

N_B= 397 953

$N_Q \simeq 10^6$

- DVR:

$nb_x^{max} = 20$ (sin)

$\ell^{max} = 5$

N_B= 14 855 après contraction

Base trop petite ?

1) M. Xu, F. Sebastianelli and Z. Bačić, JCP 2008, 128, 244715
2) Valdés PCCP V13 p2935 2011

Résultats théoriques, 6D :

Pot. Bowman (basé sur du CCSD(T)-F12)

cm^{-1}	Exp.	ElVibRot 3 corps cluster	ElVibRot 3 corps cristal	ElVibRot 2 corps cristal
Trans.	71.0 80.2 101.1	92.25 98.20 125.59	89.90 98.90 114.63	62.59 75.37 90.34
Rotation ortho, L=1	110.0 116.6 122.1	72.63 132.34 168.82	97.55 117.04 137.49	96.24 119.98 137.10

- NonDP : L_B=5, L_G=6

B_t=4, B_{rot}=2, B_R=3

N_B= 28 076
N_Q= 891 060

- Effet de la géométrie de la cage important.

Minimum du cluster $H_2@(H_2O)_{20}$ différent dans le cristal !

Prise en compte d'autres molécules d'eau (vers le cristal) : en projet
Prise en compte de la flexibilité de la cage : faible (< 5 cm^{-1})

Primitive basis set

Basis sets are adapted to the coordinates and orthonormal.

$$\int b_u(q) b_v(q) d\tau = \delta_{uv}$$

- Periodic coordinate (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 basis

How to represent Ψ in nD?

1. Expansion on a basis in 1D:

$$\Psi(Q_1) = \sum_{i_1=1}^{nb_1} \Psi_{i_1}^{b}\, \mathrm{b}_{i_1}(Q_1)$$

2. Expansion on a basis in 2D:

$$\Psi(Q_1, Q_2) = \sum_{i_2=1}^{nb_2} \sum_{i_1=1}^{nb_1} \Psi_{i_1 i_2}^{bb}\, \mathrm{b}_{i_2}(Q_2)\, \mathrm{b}_{i_1}(Q_1)$$

Double sum: $nb_1 \times nb_2$ terms

3. Expansion on a basis in nD:

$$\Psi(\mathbf{Q}) = \sum_{\mathrm{I}=1}^{\mathrm{NB}} \Psi_{I}^{bb\ldots b}\, \mathrm{B}_{\mathrm{I}}(\mathbf{Q})$$

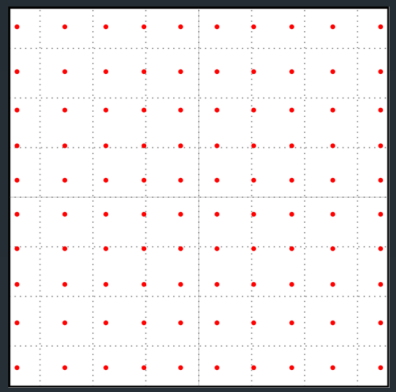
I is a collective index: $\{i_1, i_2 \ \ldots \ i_n\}$

$NB = nb_1 \times nb_2 \ldots nb_n$

in 6D : NB ~ 10^6
in 9D : NB ~ 10^9
The "curse" of dimensionality

How to represent Ψ in nD?

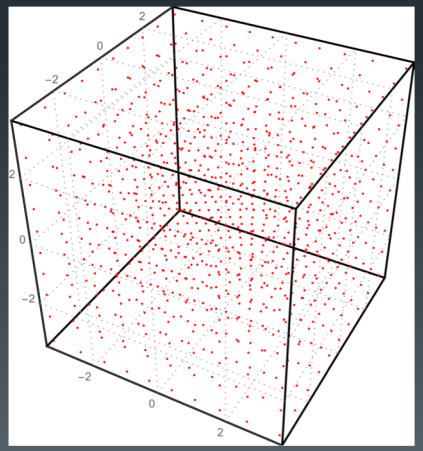
1. Expansion on a grid in 2D:



$$G_{DP}^{2D} = G_{\ell_1}^{1} \otimes G_{\ell_2}^{2}$$

Number of grid points: $NQ = nq_1 \times nq_2$

2. Expansion on a grid in 3D:



$$G_{DP}^{3D} = G_{\ell_1}^{1} \otimes G_{\ell_2}^{2} \otimes G_{\ell_3}^{3}$$

Number of grid points: $NQ = nq_1 \times nq_2 \times nq_3$

in 6D : NQ ~ 10^6
in 9D : NQ ~ 10^9
The "curse" of dimensionality

How to represent Ψ in nD?

On a basis, $|\mathrm{B_I}\rangle$ and / or on a grid :

$$\begin{bmatrix} \Psi_1^B \\ \Psi_2^B \\ \vdots \\ \Psi_{\mathrm{NB}}^B \end{bmatrix} \Leftrightarrow \begin{bmatrix} \Psi_1^G \\ \Psi_2^G \\ \vdots \\ \Psi_{NQ}^G \end{bmatrix}$$

$\Psi_U^G = \Psi(\mathbf{Q}_U)$

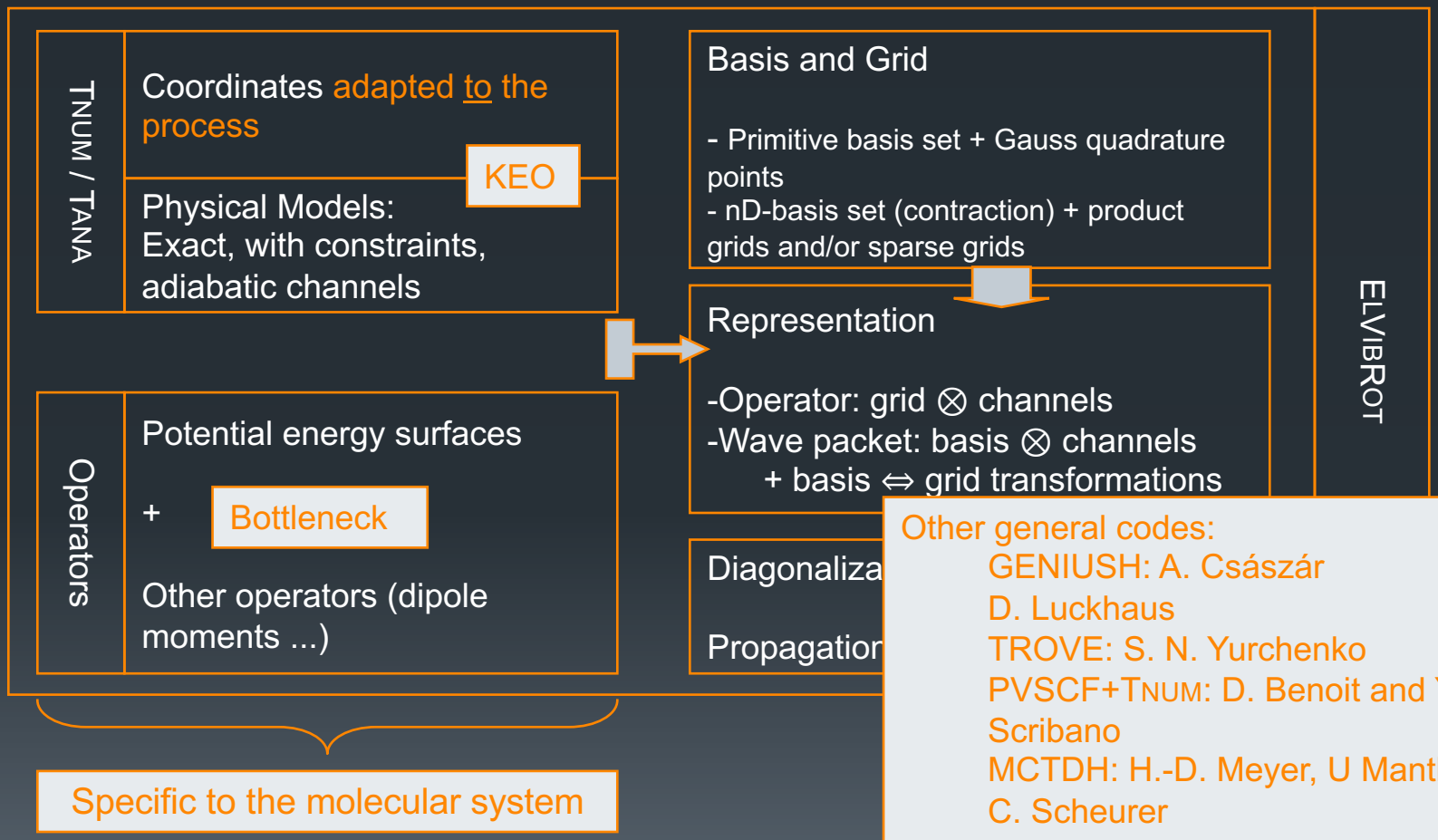
How can we reduce NB and NQ?

$$\Psi_I^B = \langle \mathrm{B_I} | \Psi \rangle$$

Multidimensional integrals

$$\Psi(\mathbf{Q}) = \sum_{\mathrm{I}=1}^{\mathrm{NB}} \Psi_I^B \, \mathrm{B_I}(\mathbf{Q})$$

Overview: Quantum dynamics



1st Smolyak schemes in 1D!!!

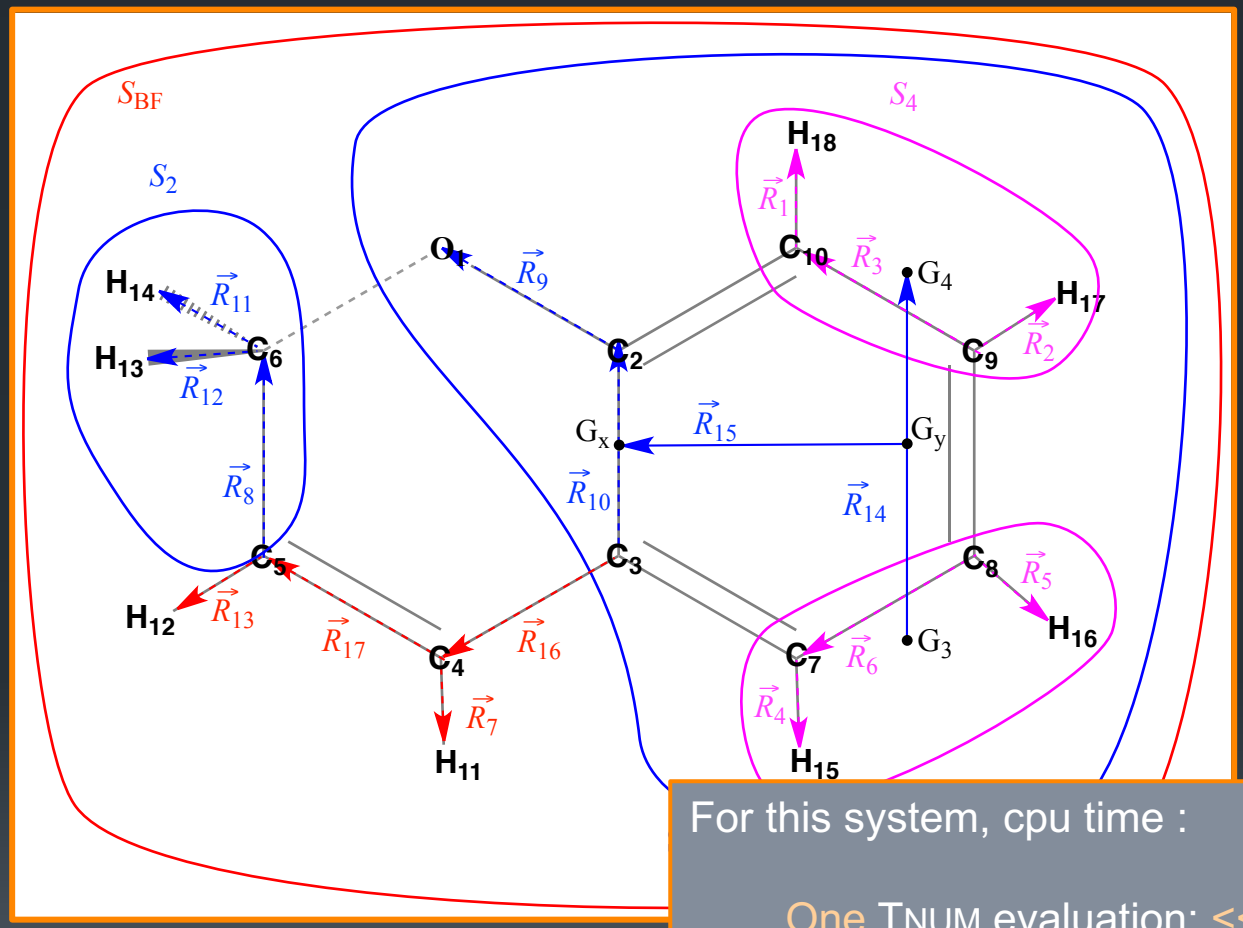
- Basis set/grid: $nb_\ell^1 = 1 + \ell$

	$\boldsymbol{S_0^1}$	$\boldsymbol{S_1^1}$	$\boldsymbol{S_2^1}$
Basis, $S_\ell^1 = \boldsymbol{B_\ell^1}$	$\{b_1^1\}$	$\{b_1^1, b_2^1\}$	$\{b_1^1, b_2^1, b_3^1\}$
Grid, $S_\ell^1 = \mathbf{G_\ell^1}$	$\{Q_{1,0}^1\}$	$\{Q_{1,1}^1, Q_{2,1}^1\}$	$\{Q_{1,2}^1, Q_{2,2}^1, Q_{3,2}^1\}$

$$\boldsymbol{\Delta S_{\ell_i}^i} = \begin{cases} \boldsymbol{S_0^i} & \text{for } \ell_i = 0 \\ \boldsymbol{S_{\ell_i}^i} - \boldsymbol{S_{\ell_{i-1}}^i} & \text{for } \ell_i > 0 \end{cases}$$

	$\boldsymbol{\Delta S_0^1 = S_0^1}$	$\boldsymbol{\Delta S_1^1}$	$\boldsymbol{\Delta S_2^1}$
Basis, $\Delta \boldsymbol{B_\ell^i}$	$\{b_1^1\}$	$\{b_2^1\}$	$\{b_3^1\}$
Basis, $\Delta \boldsymbol{G_\ell^i}$	$\{Q_{1,0}^1\}$	$\{Q_{1,1}^1, Q_{2,1}^1\}$-$\{Q_{1,0}^1\}$	$\{Q_{1,2}^1, Q_{2,2}^1, Q_{3,2}^1\}$-$\{Q_{1,1}^1, Q_{2,1}^1\}$

Comparison: numerical / analytical KEO



We can get the analytical expression of KEO of the benzopyran (48D) using polysherical coordinates with TANA.

For a given geometry the metric tensor (G) obtained analytically and numerically are identical. The largest difference is 10^{-18} au (~10^{-12} cm^{-1})

For this system, cpu time :

One TNUM evaluation: << 1 s
One TANA calculation: 32 s

For this system, number of terms (MCTDH format): 5809

Example: Benzopyrane

```
2.2857496219414603d-005 |1   q^-1 |3   qs*dq |7   q^-1*dq*q |8   qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |3   qs*dq |7   q^-1 |8   dq*q*qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |3   qs*dq |7   q^-1 |8   q^2*qs^-1 |9   dq*sin
-2.2857496219414603d-005 |1   q^-1 |3   qs*dq |7   q^-1 |8   qs |9   dq*sin
2.2857496219414603d-005 |1   q^-1 |5   qs*dq |6   cos |7   q^-1*dq*q |8   qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |5   qs*dq |6   cos |7   q^-1 |8   dq*q*qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |5   qs*dq |6   cos |7   q^-1 |8   q^2*qs^-1 |9   dq*sin
-2.2857496219414603d-005 |1   q^-1 |5   qs*dq |6   cos |7   q^-1 |8   qs |9   dq*sin
2.2857496219414603d-005 |1   q^-1 |5   q*qs^-1 |6   sin*dq |7   q^-1*dq*q |8   qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |5   q*qs^-1 |6   sin*dq |7   q^-1 |8   dq*q*qs |9   cos
-2.2857496219414603d-005 |1   q^-1 |5   q*qs^-1 |6   sin*dq |7   q^-1 |8   q^2*qs^-1 |9   dq*sin
-2.2857496219414603d-005 |1   q^-1 |5   q*qs^-1 |6   sin*dq |7   q^-1 |8   qs |9   dq*sin
-4.5714992438829206d-005 |1   q^-1 |7   q^-1 |8   q^3*qs^-2 |9   dq^2
-4.5714992438829206d-005 |1   q^-1 |7   q^-1 |8   q |9   dq^2
```

... and many more lines .....

Tana example