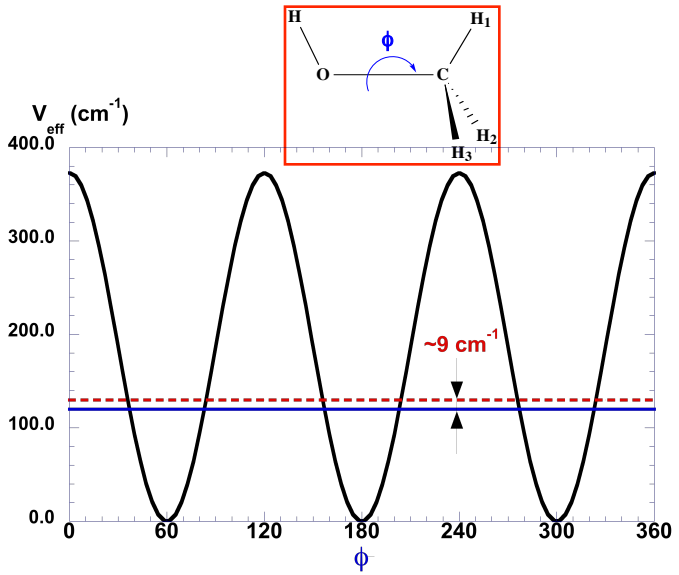
Quantum dynamics with sparse grids: a combination of Smolyak scheme and cubature

Application on methanol



This work is done with A. Nauts (Louvain-La-Neuve)

ANR

LCP UCL Université catholique de Louvain — Université Paris Sud — cnrs

Quantum Dynamics with full grid representation

- To calculate $\hat{H}|\Psi\rangle$, we need two representations:

on the grid and on a basis, $|\chi_I\rangle$

Grid representation

$$\begin{bmatrix} \Psi(q_1) \\ \Psi(q_2) \\ \vdots \\ \Psi(q_{Nq}) \end{bmatrix} \Leftrightarrow \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{Nb} \end{bmatrix}$$

Basis representation

The transformations have to be done as fast as possible with a grid as small as possible

$$\begin{cases} C_I = \langle \chi_I | \Psi \rangle \\ \Psi(q) = \sum_{I=1}^{Nb} C_I \chi_I(q) \end{cases}$$

Two bottle-necks: The basis se
- For the basis, one needs sor
- For the grid, one needs anot

They are ways to overcome these difficulties:

- Use multimode representations as in most VSCF approaches
- Expand the operators as sums of products like in MCTDH

Basis sets:

1) Primitive basis sets :

- Harmonic Oscillator (HO), Fourier, ...

2) Multidimensional basis-set:

- Calculation impossible with a direct-product basis.
  Ex: in 11D, **~10^{11}** basis functions!!

- Selection in terms of excitations or the degree of the multidimensional polynomials
  Ex : the 11D-basis functions are kept when Excitation(B_I) ≤ L_B

Selection equivalent to the:
-Pruned basis set of T. Carrington

Basis sets:

1) Primitive basis sets :

- Harmonic Oscillator (HO), Fourier, ...

2) Multidimensional basis-set:

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  Ex: in 11D, **~10^{11}** basis functions!!

- Select … e multidimensional polyno…

  Excitation(B_l) ≤ L_B

In 11D, with L_B=9 (equivalent to nb=10)

The total number of basis functions is:

167 960

Selection equivalent to the:
-Pruned basis set of T. Carrington

Grids

1) Grid associated with a primitive basis:

- Gaussian quadrature (1D) :

$$\boldsymbol{Q}^{i}_{nq_i}$$

For the coordinates, i, nq_i grid points

2) Grid associated with a multidimensional basis:

Direct-product grid (DPG) :
impossible: **~10^{11}** grid points!!

$$\boldsymbol{Q}^{nD}_{NQ} = \boldsymbol{Q}^{1}_{nq_1} \otimes \boldsymbol{Q}^{2}_{nq_2} \cdots \otimes \boldsymbol{Q}^{n}_{nq_n}$$

=> We need sparse grids

Smolyak multidimensionnal grid

$$\mathcal{Q}^{nD}_{L_{smol}} = \sum_{L_{smol}-n+1 \le |\ell| \le L_{smol}} (-1)^{L_{smol}-|\ell|} C^{L_{smol}-|\ell|}_{n-1} \cdot \mathcal{Q}^{1}_{\ell_1} \otimes \mathcal{Q}^{2}_{\ell_2} \cdots \otimes \mathcal{Q}^{n}_{\ell_n}$$

$$|\ell| = \sum_{i=1}^{n} \ell_i$$

The Smolyak parameter, L_{smol}, enables to increase the size of the grid

$$\mathcal{Q}^{i}_{\ell_i} = \mathcal{Q}^{i}_{nq(\ell_i)}$$

1D quadrature

How to chose $nq(\ell_i)$ in 1D?

1. $nq = \ell+1$
2. $nq = 2\ell+1$
3. $nq = 2^{\ell}+1$
4. Series ℓ

- $L_{smol} \geq L_B$ (excitations)
- $nq(\ell)$ has to be adapted to the selected basis functions
- Nested grids:
  The grid points of the level ℓ-1 are included in the level ℓ.
  Ex: Clenshaw-Curtis or Kronrod-Patterson quadrature

S.A. Smolyak *Soviet Mathematics Doklady*, 1963, 4, 240.
Avila, G.; Carrington, T. JCP, 2009, 131, pp174103 (6D 12D)
V. Gradinaru, SIAM J. Numer. Anal., 2008, 46, p103.
J. Burkardt : http://people.sc.fsu.edu/~jburkardt/presentations

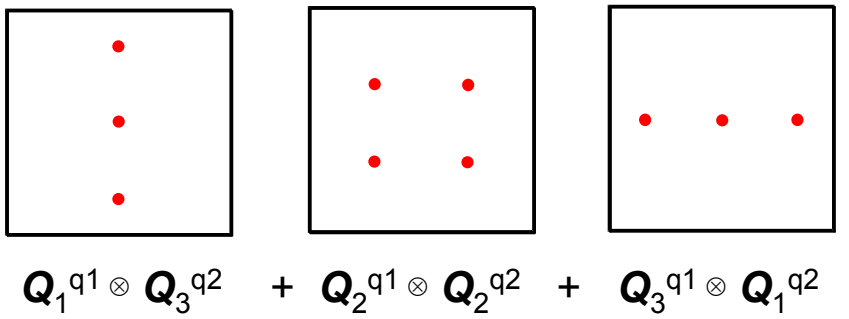
Smolyak grid in 2D

$$\boldsymbol{Q}_{L_{smol}}^{q_1,q_2} = \sum_{L_{smol}-2+1 \le |\ell| \le L_{smol}} (-1)^{L_{smol}-|\ell|} C_{2-1}^{L_{smol}-|\ell|} \cdot \boldsymbol{Q}_{\ell_1}^{q_1} \otimes \boldsymbol{Q}_{\ell_2}^{q_2}$$

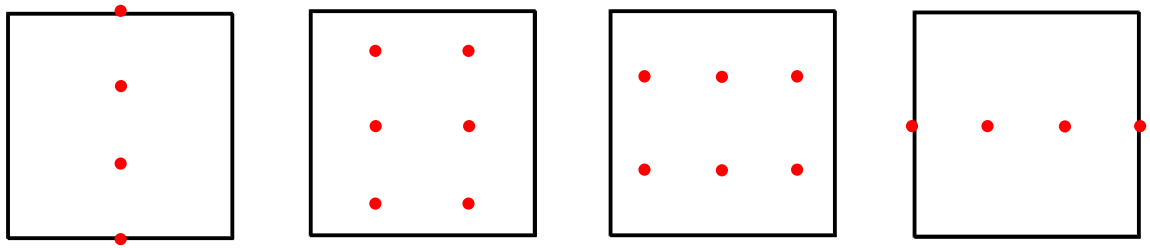
$$|\ell| = \sum_{i=1}^{2} \ell_i$$

- In 2D (n=2) with L_{smol}=3

$\|\ell\|$	ℓ_1 ℓ_2	nq_1 nq_2
2	0 2	1 3
	1 1	2 2
	2 0	3 1
3	0 3	1 4
	1 2	2 3
	2 1	3 2
	3 0	4 1



$$\boldsymbol{Q}_1^{q1} \otimes \boldsymbol{Q}_3^{q2} + \boldsymbol{Q}_2^{q1} \otimes \boldsymbol{Q}_2^{q2} + \boldsymbol{Q}_3^{q1} \otimes \boldsymbol{Q}_1^{q2}$$



$$\boldsymbol{Q}_1^{q1} \otimes \boldsymbol{Q}_4^{q2} + \boldsymbol{Q}_2^{q1} \otimes \boldsymbol{Q}_3^{q2} + \boldsymbol{Q}_3^{q1} \otimes \boldsymbol{Q}_2^{q2} + \boldsymbol{Q}_4^{q1} \otimes \boldsymbol{Q}_1^{q2}$$

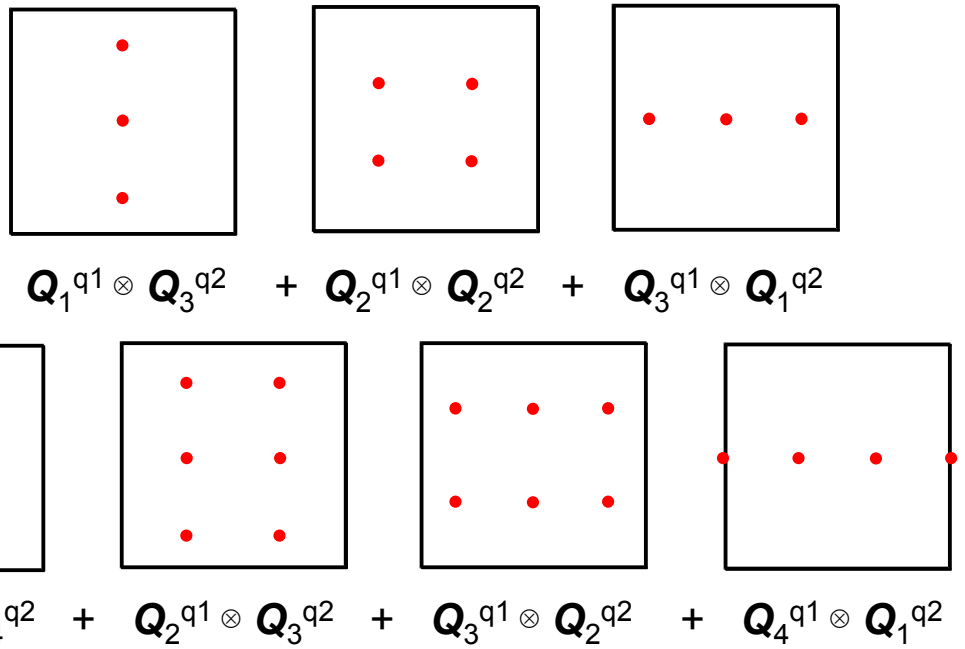
Smolyak grid in 2D

$$\boldsymbol{Q}_{L_{smol}}^{q_1,q_2} = \sum_{L_{smol}-2+1 \le |\ell| \le L_{smol}} (-1)^{L_{smol}-|\ell|} C_{2-1}^{L_{smol}-|\ell|} \cdot \boldsymbol{Q}_{\ell_1}^{q_1} \otimes \boldsymbol{Q}_{\ell_2}^{q_2}$$

- In 2D (n=2) with $L_{smol}=3$

$$|\ell| = \sum_{i=1}^{2} \ell_i$$

$\lvert\ell\rvert$	ℓ_1 ℓ_2	nq_1 nq_2
2	0 2	1 3
	1 1	2 2
	2 0	3 1
3	0 3	1 4
	1 2	2 3
	2 1	3 2



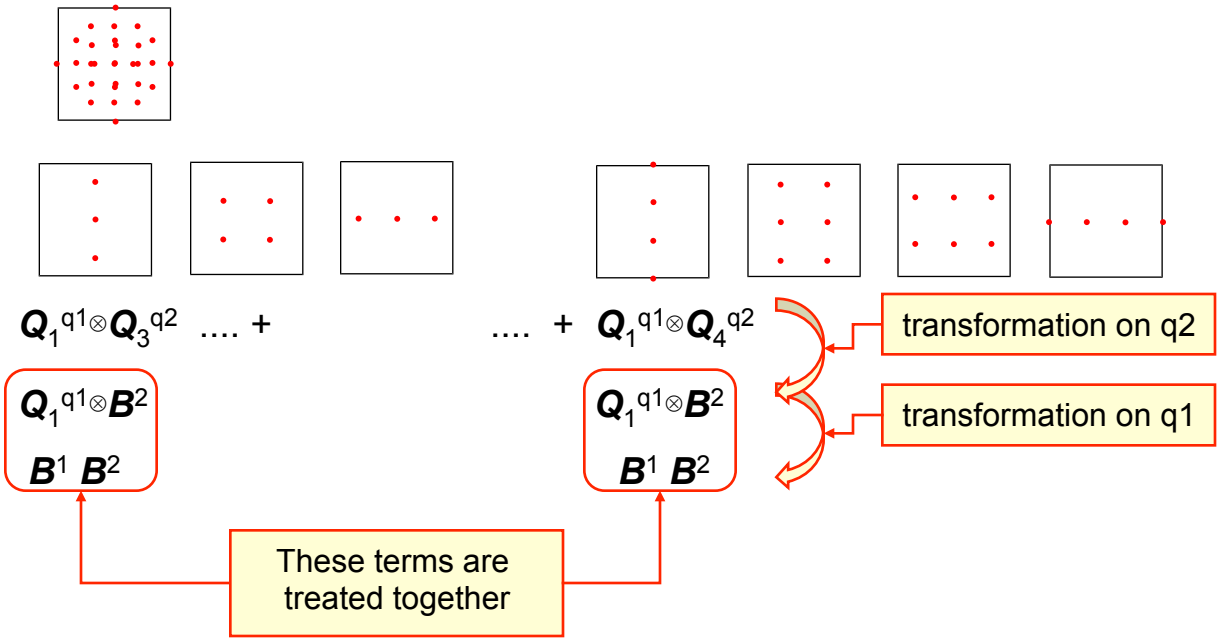
- Usual DP grid: NQ = 4^2 = 16
- Smolayk grid: NQ = 30

Smolyak grid: implementation

$$\mathcal{Q}^{nD}_{L_{smol}} = \sum_{L_{smol}-n+1 \le |\ell| \le L_{smol}} (-1)^{L_{smol}-|\ell|} C^{L_{smol}-|\ell|}_{n-1} \cdot \mathcal{Q}^1_{\ell_1} \otimes \mathcal{Q}^2_{\ell_2} \cdots \otimes \mathcal{Q}^n_{\ell_n}$$

1. As a full nD grid:
   Too many operations (NQ x NB)
2. Each direct-product grid is treated separately with sequential transformations (one coordinate after the other)
   Some transformations are done several times
3. Global sequential transformations
   Each equivalent partial transformations is done once
4. Use of nested grids

$$\mathcal{Q}_{\ell_{i-1}} \subset \mathcal{Q}_{\ell_i}$$



In the the usual imlementation, the $\mathcal{Q}_\ell$ are 1D-grids

We want to extend the use of Smolyak scheme with nD-grids (cubature....)

Avila, G.; Carrington, T. JCP, 2009, 131, pp174103

Cubature rules

- Cubature rules are multidimensional extensions of the usual 1D-gaussian quadrature.

$$\int \dots \int F(\boldsymbol{q})\rho(\boldsymbol{q})\,d\boldsymbol{q} \approx \sum_{K}^{Nq} F(\boldsymbol{q}_K) w_K$$

- q_K are the multidimensional grid points and the W_K are the corresponding weights.
  They are associated with multivariate orthogonal polynomials (nD).

- A given cubature rule with Nq points, can integrate exactly all nD-polynomials with a degree ≤ $d=2L_B$
- No simple procedure to get the grid points and weights.
- Rules are tabulated: one rule for each n and L_B.

Not all rules are known!

For nD Hermite polynomials (HO)

L_B	$(d=2L_B)$	0	1	2	3	4	5	6
2D	DP	1	4	9	16	25	36	49
	cubature	1	3	8	/	/	/	/
3D	DP	1	8	27	64	125	216	343
	cubature	1	4	14	45	77	151	/

A.H. Stroud et al, Gaussian Quadrature Formulas, Prentice–H, 1966.

R. Cools, J. Complexity 19 (2003) 445

J. Burkardt : http://people.sc.fsu.edu/~jburkardt

Smolyak grid and cubature rules

$$\boldsymbol{Q}^{nD}_{L_{smol}} = \sum_{L_{smol}-n+1 \le |\ell| \le L_{smol}} (-1)^{L_{smol}-|\ell|} C^{L_{smol}-|\ell|}_{n-1} \cdot \boldsymbol{Q}^{1}_{\ell_1} \otimes \boldsymbol{Q}^{2}_{\ell_2} \cdots \otimes \boldsymbol{Q}^{n}_{\ell_n}$$

The $\boldsymbol{Q}_\ell$ are nD-grids: Ideally, they are cubatures, but not all of them are available (tabulated)!!
Therefore the $\boldsymbol{Q}_\ell$ are:

1. Cubature if available
2. Direct-product grids
3. Another Smolyak grids (with L=ℓ)

Example, in 11D

L_{smol}	NQ Smol. 11x1D	NQ Smol. (3D)3x2D	NQ PD
9 (nq=10)	20 160 075 167958 G	**6 067 148** 589 G	**10^{11}**

Spectre de torsion du méthanol

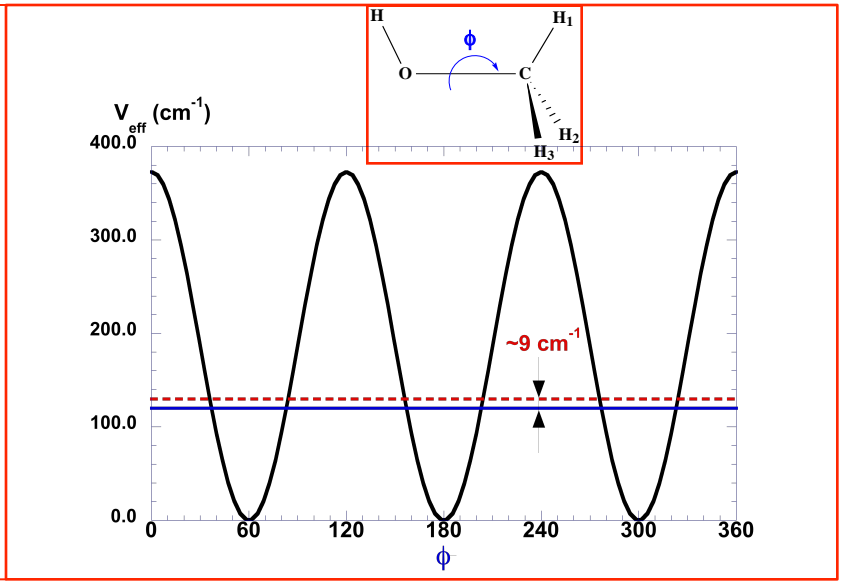
The 1D spectroscopic model works well:[1]

$$\boldsymbol{T}(\phi) = B\,\partial^2/\partial\phi^2$$

$$V(\phi)=\sum V_k \cos(k\phi) / 2$$

$B \approx -27.6\ cm^{-1}$

$V_3 \approx 373\text{-}374\ cm^{-1}$ et $V_6 \approx -0.8\ cm^{-1}$



[1] Lees… JCP 1968, 48, p5299 ; Wang… JCP 1998, 109 p 10795

[2] Stern ... JMS 67 (1977) 244

[3] Muñoz-Caro ... CPL 273 (1997) 135

[4] Fehrensen ... JCP 119 (2003) 5534

[5] Blasco ... CPL 373 (2003) 344

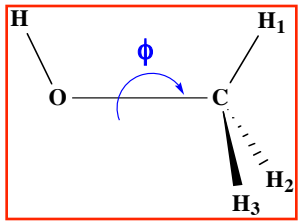
[6] Bowman ... J. Phys. Chem. A 2007, 111, 7317-7321

υ_{12}	Sym. (cm^{-1})	Exp.[2]	*1*D flexible[3]	*1+11*D RPH[4]	*1+11*D HADA[5]	RPH [6] Multimode
0	a_1	**0.0**	**0.0**	***0.0***	**0.0**	**0.0**
	e	**9.1**	**9.7**	***8.2***	**10.5**	**8.7**
1	e	208.9	199.2	*216.7*	204.7	205.3
	a_2	294.7	289.1	*297.8*	298.6	267.0
2	a_1	353.0	337.5	*363.5*	350.9	388.2
	e	510.3	498.3	*517.2*	518.6	509.3

Basis set and grid

Molecule with 12 degree of freedoms, but

- We want to separate the torsion from the 11 other modes
- For the torsion: a 1D-contracted Fourier basis with 48 grid points
- For the 11 other modes:
  The basis functions are selected in terms of excitations
  We use the Smolyak scheme with n=4 (3D,3D,3D,2D)



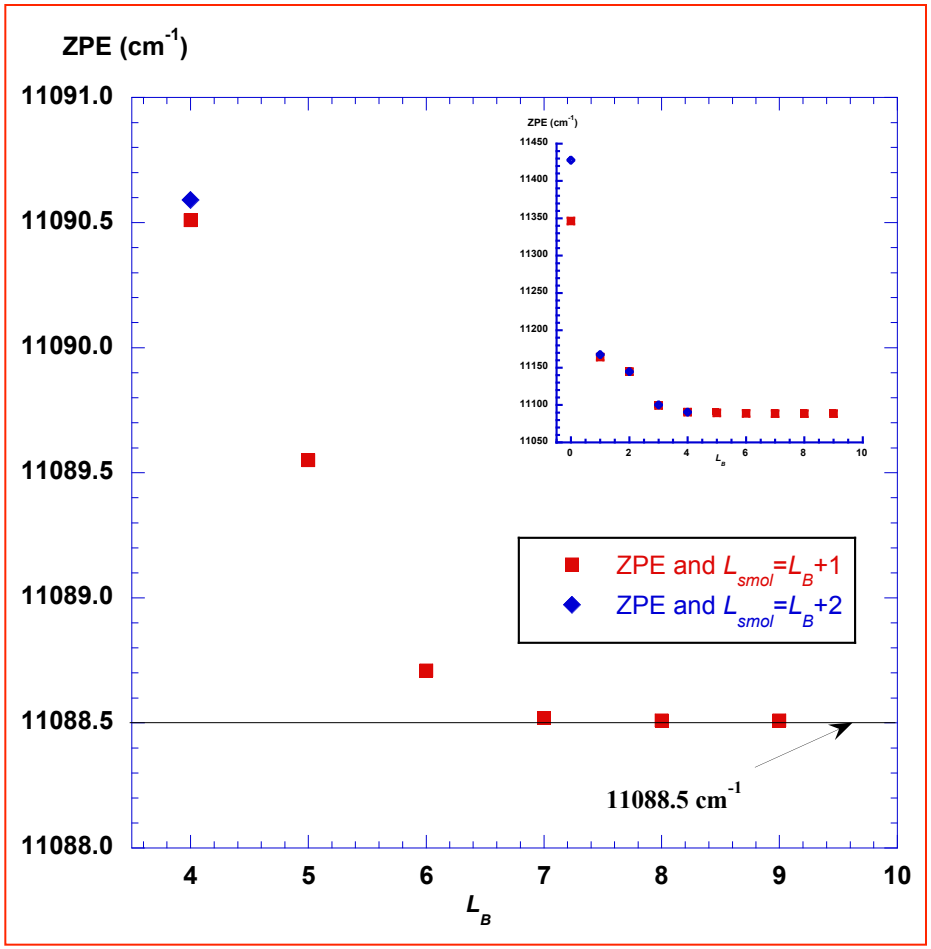
Q^i, i:	1	2	3	4	5	6	7	8	9	10	11	12 (torsion)
$\boldsymbol{B}^u$	$\boldsymbol{B}^1$ (Smolyak)											$\boldsymbol{B}^2$
$\boldsymbol{B}^{u,v}$	$\boldsymbol{B}^{1,1}$			$\boldsymbol{B}^{1,2}$			$\boldsymbol{B}^{1,3}$			$\boldsymbol{B}^{1,4}$		
Primitive Basis sets	HO	HO	HO	HO	HO	HO	HO	HO	HO	HO	HO	Contracted Fourier

Zero point energy

L_B	NB	L_{smol}	NQ
5	4 368	6	132 786
7	31 824	8	1 845 519
9	4 031 040	10	892 360 032

The Hamiltonian has 91 terms
=> Huge memory 605 GB

The calculations are long (12 days for L_B=9)!



Torsion levels

υ_{12}	sym	Exp.	12D-RPH MULTIMODE	12D ElVibRot L_B=5 with L_{smol}=7	12D ElVibRot L_B=6 with L_{smol}=8
0	a_1	0.0	0.0	11089.55	11088.71
	e	9.1	8.7	9.15, 9.15	9.14, 9.15
1	e	208.9	205.3	205.34	205.34
	a_2	294.7	267.0	290.70	290.70
2	a_1	353.0	388.2	347.49	347.49
	e	510.3	509.3	503.56	503.54
3	e	751.0	762.3	741.83	741.80
	a_2	1046.7	1017.8	1034.48	1034.47

Conclusions et perspectives

- ✓ The current implementation (Smolyak + cubature) enables to perform 12D-calculations
- ✓ Larger calculations are doable:

  15D, L_B =7, L_{smol}=9 => NB=170 544 and NQ=47.10^6 => cpu(G⇔B)=8 min

  18D, L_B =7, L_{smol}=9 => NB=480 700 and NQ=166.10^6 => cpu(G⇔B)=? min

  48D, L_B =3, L_{smol}=4 => NB= 20 825 and NQ= 815 814

Difficulties:

- ➢ Large grid and TNUM:

  The number of terms of numerical KEO grows as $n^2/2$

  ⇒ It requires a large amount of memory (disc)

  ⇒ Use of analytical expressions with TANA (less flexibility).

Improvements:

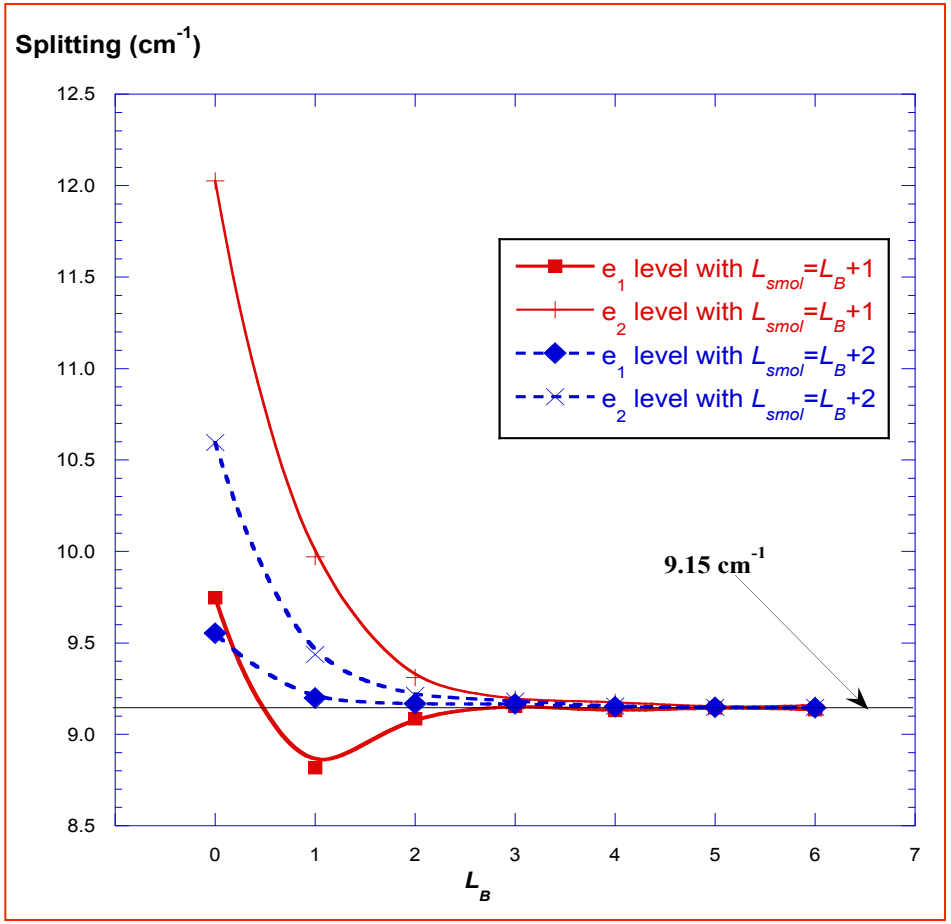
- ➢ Obtain cubature rules more systematically (help!)

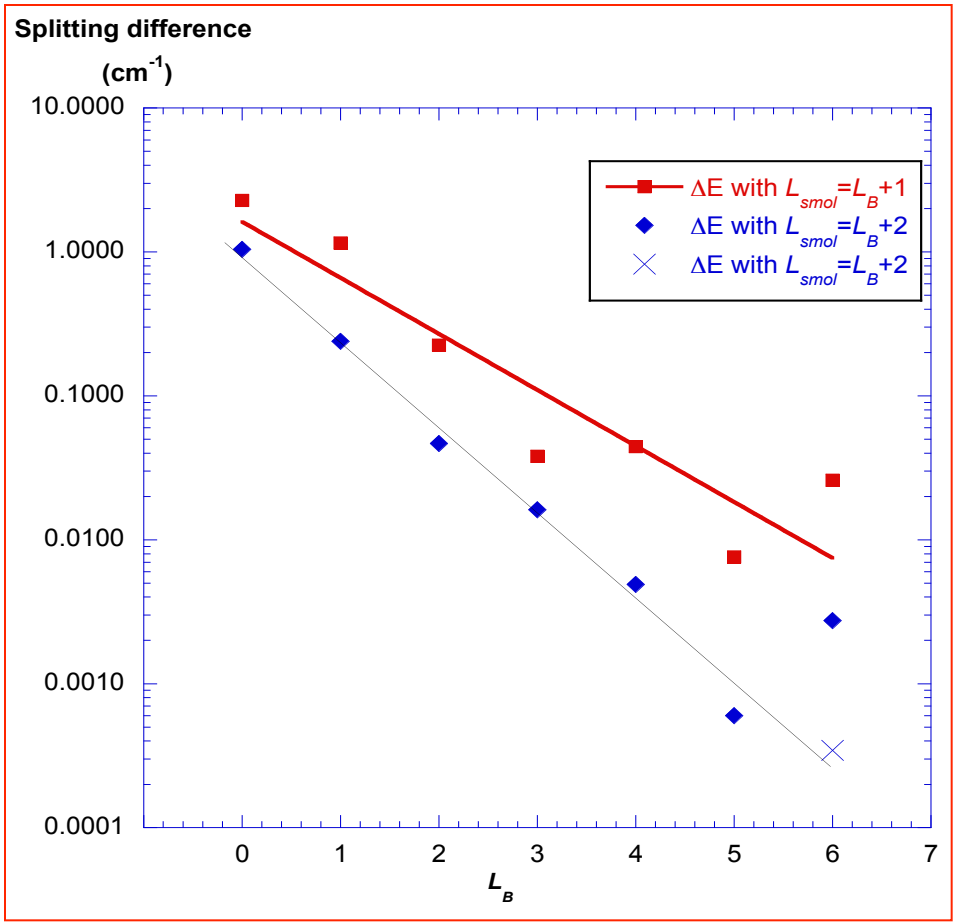
  If possible nested ones

- ➢ Implementation of the globally sequential transformations

  For a start, without a nested scheme

Tunneling splitting

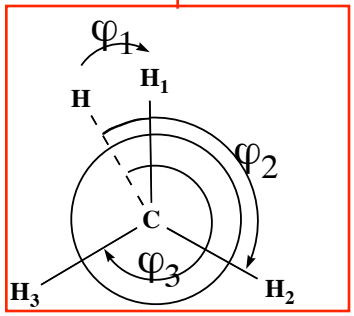




Coordinnates: TNUM

Primitive (z-matrix) | Symmetrization (linear) | Flexible Coord. | Normal Coord. | active Coord. (constraints)

$\mathbf{q}_{cart}$ → $\mathbf{q}_{prim} \equiv \mathbf{q}_{zmat}$ → $\mathbf{q}_{sym}$ → $\mathbf{q}_{flex}$ → $\mathbf{q}_{NM} \equiv \mathbf{q}_{dyn}$ → $\mathbf{q}_{act}$



$$\begin{cases} \phi_a = \frac{1}{3}(\varphi_1 + \varphi_2 + \varphi_3) \\ \phi_{e1} = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_3) \\ \phi_{e2} = \frac{1}{\sqrt{6}}(2\varphi_1 - \varphi_2 - \varphi_3) \end{cases}$$

$$Q^i_{flex} = Q^i - Q^i_{opt}(\phi_a)$$

Normal coordinates (11) with all coordinates except ϕ_a.

Use of the average metric tensor, ***G***, and the hessian matrix, to preserve the symmetry.

Freq (cm^{-1}) : 1061.2 1180.8 (x2) 1277.6 1484.0 1517.5 (x2) 3021.6 3093.0 (x2) 3845.7

KEO withTNUM

Nomber of terms : (n+1)(n+2)/2

in 12D : 91 terms!