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)
Quantum Dynamics with full grid representation

- To calculate $\hat{H} \ket{\Psi}$, we need two representations:
  on the grid and on a basis, $\ket{\chi_i}$

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

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

Two bottle-necks: The basis set grows exponentially
  • For the basis, one needs some contraction schemes (relatively easy)
  • For the grid, one needs another approach than the usual direct-product grid

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) \(\leq L\_B\)

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

1) Primitive basis sets:

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

2) Multidimensional basis-set:

- Calculation impossible with a direct-product basis.
  
  \[ \text{Ex: in 11D, } \sim 10^{11} \text{ basis functions!!} \]

- Selection in terms of excitations or the degree of the multidimensional polynomials
  
  \[ \text{Excitation}(B_i) \leq L_B \]

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

  The total number of basis functions is:

  \[ 167,960 \]
1) Grid associated with a primitive basis:
   - Gaussian quadrature (1D):

2) Grid associated with a multidimensional basis:
   
   Direct-product grid (DPG):
   impossible: ~$10^{11}$ grid points!!

$Q^i_{nq_i}$

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

$Q_N = Q_{nq_1} \otimes Q_{nq_2} \cdots \otimes Q_{nq_n}$

For the coordinates, $i$, $nq_i$ grid points

$\Rightarrow$ We need sparse grids
The Smolyak parameter, $L_{smol}$, enables to increase the size of the grid.

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

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

$Q_{L_{smol}}^{nD} = \sum_{L_{smol} - n + 1 \leq |\ell| \leq L_{smol}} (-1)^{L_{smol} - |\ell|} C_{n-1}^{L_{smol} - |\ell|} \times \bigotimes_{i=1}^{n} Q_{\ell_i}^{1} \otimes Q_{\ell_i}^{2} \cdots \otimes Q_{\ell_i}^{n}$
Smolyak grid in 2D

\[ Q_{L_{smol}}^{q_1, q_2} = \sum_{L_{smol} - 2 + 1 \leq \ell \leq L_{smol}} (-1)^{L_{smol} - |\ell|} C_{2-1}^{L_{smol} - |\ell|} Q_{\ell_1}^{q_1} \otimes Q_{\ell_2}^{q_2} \]

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

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

| \( |\ell| \) | \( \ell_1 \) \( \ell_2 \) | \( nq_1 \) \( nq_2 \) |
|---|---|---|
| 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 |

\[ Q_1^{q_1} \otimes Q_3^{q_2} + Q_2^{q_1} \otimes Q_2^{q_2} + Q_3^{q_1} \otimes Q_1^{q_2} \]

\[ Q_1^{q_1} \otimes Q_4^{q_2} + Q_2^{q_1} \otimes Q_3^{q_2} + Q_3^{q_1} \otimes Q_2^{q_2} + Q_4^{q_1} \otimes Q_1^{q_2} \]
Smolyak grid in 2D

\[ Q_{L_{smol}}^{q_1, q_2} = \sum_{L_{smol} - 2 + 1 \leq |\ell| \leq L_{smol}} (-1)^{|\ell|} C^{L_{smol} - |\ell|}_{2-1} \cdot Q_{\ell_1}^{q_1} \otimes Q_{\ell_2}^{q_2} \]

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

| | \(|\ell|\) | \(\ell_1 \) | \(\ell_2 \) | \(nq_1 \) | \(nq_2 \) |
|---|---|---|---|---|---|
| 2 | 02 | 1 | 3 |
| | 11 | 2 | 2 |
| | 20 | 3 | 1 |
| 3 | 03 | 1 | 4 |
| | 12 | 2 | 3 |
| | 21 | 3 | 2 |

- Usual DP grid: \( NQ = 4^2 = 16 \)
- Smolayk grid: \( NQ = 30 \)
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
   \( Q_{\ell_{i-1}} \subset Q_{\ell_i} \)

In the usual implementation, the \( Q_\ell \) 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.

\[
\int \cdots \int F(q) \rho(q) dq \approx \sum_{K} F(q_K) W_K
\]

- \(q_K\) 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 \(N_q\) points, can integrate exactly all nD-polynomials with a degree \(\leq d=2L_B\)
- 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)

<table>
<thead>
<tr>
<th>(L_B)</th>
<th>((d=2L_B))</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D DP</td>
<td>1</td>
<td>4</td>
<td>9</td>
<td>16</td>
<td></td>
<td>25</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>cubature</td>
<td>1</td>
<td>3</td>
<td>8</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>3D DP</td>
<td>1</td>
<td>8</td>
<td>27</td>
<td>64</td>
<td>125</td>
<td>216</td>
<td>343</td>
<td></td>
</tr>
<tr>
<td>cubature</td>
<td>1</td>
<td>4</td>
<td>14</td>
<td>45</td>
<td>77</td>
<td>151</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>


J. Burkardt : http://people.sc.fsu.edu/~jburkardt
Smolyak grid and cubature rules

\[ Q_{nD}^{L_{\text{smol}}} = \sum_{L_{\text{smol}}-n+1 \leq |\ell| \leq L_{\text{smol}}} (-1)^{L_{\text{smol}}-|\ell|} C_{\ell}^{L_{\text{smol}}-1} \otimes Q_{\ell_1}^{1} \otimes Q_{\ell_2}^{2} \cdots \otimes Q_{\ell_n}^{n} \]

The \( Q_\ell \) are nD-grids: Ideally, they are cubatures, but not all of them are available (tabulated)!! Therefore the \( Q_\ell \) are:

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

**Example, in 11D**

<table>
<thead>
<tr>
<th>( L_{\text{smol}} )</th>
<th>NQ Smol. 11x1D</th>
<th>NQ Smol. (3D)3x2D</th>
<th>NQ PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (nq=10)</td>
<td>20 160 075 G</td>
<td>6 067 148 G</td>
<td>589 G</td>
</tr>
</tbody>
</table>

\( 10^{11} \)
The 1D spectroscopic model works well:[1]

\[ T(\phi) = B \frac{\partial^2}{\partial \phi^2} \]

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

\[ B \approx -27.6 \text{ cm}^{-1} \]

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

---

[2] Stern … JMS 67 (1977) 244
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)

<table>
<thead>
<tr>
<th>$Q^i$, i:</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12 (torsion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B'^{\mu}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B'^{\mu,v}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B'^{i,1}$</td>
<td>$B'^{i,2}$</td>
<td>$B'^{i,3}$</td>
<td>$B'^{i,4}$</td>
<td>$B^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primitive Basis sets</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td>HO</td>
<td></td>
</tr>
<tr>
<td>Contracted Fourier</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Zero point energy

The Hamiltonian has 91 terms => Huge memory 605 GB

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

<table>
<thead>
<tr>
<th>$L_B$</th>
<th>NB</th>
<th>$L_{smol}$</th>
<th>NQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4368</td>
<td>6</td>
<td>132786</td>
</tr>
<tr>
<td>7</td>
<td>31824</td>
<td>8</td>
<td>1845519</td>
</tr>
<tr>
<td>9</td>
<td>4031040</td>
<td>10</td>
<td>892360032</td>
</tr>
</tbody>
</table>

![Graph showing ZPE (cm⁻¹) vs. $L_B$]
## Torsion levels

<table>
<thead>
<tr>
<th>$\nu_{12}$</th>
<th>sym</th>
<th>Exp.</th>
<th>12D-RPH MULTIMODE</th>
<th>12D $L_B=5$ with $L_{\text{smol}}=7$</th>
<th>12D $L_B=6$ with $L_{\text{smol}}=8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$a_1$</td>
<td>0.0</td>
<td>0.0</td>
<td>11089.55</td>
<td>11088.71</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>9.1</td>
<td>8.7</td>
<td>9.15, 9.15</td>
<td>9.14, 9.15</td>
</tr>
<tr>
<td>1</td>
<td>$e$</td>
<td>208.9</td>
<td>205.3</td>
<td>205.34</td>
<td>205.34</td>
</tr>
<tr>
<td></td>
<td>$a_2$</td>
<td>294.7</td>
<td>267.0</td>
<td>290.70</td>
<td>290.70</td>
</tr>
<tr>
<td>2</td>
<td>$a_1$</td>
<td>353.0</td>
<td>388.2</td>
<td>347.49</td>
<td>347.49</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>510.3</td>
<td>509.3</td>
<td>503.56</td>
<td>503.54</td>
</tr>
<tr>
<td>3</td>
<td>$e$</td>
<td>751.0</td>
<td>762.3</td>
<td>741.83</td>
<td>741.80</td>
</tr>
<tr>
<td></td>
<td>$a_2$</td>
<td>1046.7</td>
<td>1017.8</td>
<td>1034.48</td>
<td>1034.47</td>
</tr>
</tbody>
</table>
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$\leftrightarrow$B)=8 min
18D, $L_B = 7$, $L_{smol} = 9$ => NB=480 700 and NQ=166.10^6 => cpu(G$\leftrightarrow$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

Splitting ($cm^{-1}$)

- $e_1$ level with $L_{smol} = L_B + 1$
- $e_2$ level with $L_{smol} = L_B + 1$
- $e_1$ level with $L_{smol} = L_B + 2$
- $e_2$ level with $L_{smol} = L_B + 2$

Splitting difference ($cm^{-1}$)

- $\Delta E$ with $L_{smol} = L_B + 1$
- $\Delta E$ with $L_{smol} = L_B + 2$
- $\Delta E$ with $L_{smol} = L_B + 2$

$9.15 \ cm^{-1}$
**Coordinates: TNUM**

- **Primitive (z-matrix):** $q_{prim} = q_{zmat}$
- **Symmetrization (linear):** $q_{sym}$
- **Flexible Coord.**
- **Normal Coord.**
- **active Coord. (constraints)**

**KEO with TNUM**

**Number of terms:** $(n+1)(n+2)/2$

**in 12D:** 91 terms!

- Normal coordinates (11) with all coordinates except $\phi_a$.
- 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