Non-product Smolyak quadrature grids for computing spectra: how and why?.

Gustavo Avila and Tucker Carrington

Chemistry Department
Queen's University

June 18, 2011

I. SOME INTRODUCTORY FACTS

1) The variational method is the most reliable method to resolve the (ro)vibrational Schrodinger equation and therefore to compute accurately the (ro)vibrational spectra of a molecule.

2) The literature dealing with the variational calculation of the spectra of two-, three- and four-atom molecules is extensive.

3) For five- and six-atom molecules the number of articles begins to decrease dramatically. For molecules with more than six atoms the number of works where the variational method is rigorously used is extremely small.

4) The amount of experimental (ro)vibrational data of large molecules is extensive.

II. THE CHALLENGE

For thirty years different research groups have developed new ideas in order to make computationally feasible the calculation of the (ro)vibrational spectra of large molecules with the variational method.

In the following two talks we will describe a new scheme.

III. THE ONE DIMENSIONAL (1D) PROBLEM

Suppose we want to calculate variationally some of the lowest eigenstates of the 1D dimensional Hamiltonian

$$\hat{H}(x) = \frac{\omega}{2}\left(-\frac{d^2}{dx^2} + x^2\right) + V_{\rm anhar}(x).$$

1) We define a basis set of 1D harmonic functions

$$\mid n\rangle = P_n(x)\exp\left(-\frac{1}{2}x^2\right), \ \text{ with } \ n = 0, 1, 2, 3, \cdots, b,$$

where $P_n(x)$ is a normalized Hermite polynomial.

2) We calculate the elements of the H matrix

$$\langle n' \mid \hat{H} \mid n \rangle = \int P_{n'}(x) \hat{H}(x) P_n(x) \exp\left(-x^2\right) dx,$$

The potential matrix elements are calculated using $N \geq b + 1$ Gauss-Hermite quadrature points

$$\langle n' \mid V \mid n \rangle = \sum_{k=1}^{N} w_k P_{n'}(x_k) V(x) P_n(x_k) + \mathrm{err}(N),$$

until $\mathrm{err}(N)$ is small enough for a given value of b.

3) We diagonalize the H matrix for $b = 1, 2, 3, \cdots$ with sizes (2×2), (3×3), $(4 \times 4) \cdots$ until the lowest eigenenergies converge to a given accuracy.
EVEN IN THE WORST CASE the number of basis set functions $b + 1 < 200$ and the number of Gauss quadrature points $N < 200$.

1D VARIATIONAL CALCULATIONS ARE COMPUTATIONALLY EASY.

IV. THE TWELVE DIMENSIONAL (12D) PROBLEM: PRODUCT BASIS SET+PRODUCT GAUSS GRID

Suppose we want to calculate some of the lowest eigenstates of the 12D dimensional Hamiltonian

$$\hat{H}(x_1, \cdots, x_{12}) = \sum_{c=1}^{12} \frac{\omega_c}{2} \left(-\frac{\partial^2}{\partial x_c^2} + x_c^2 \right) \quad + \quad V_{\mathrm{anhar}}(x_1, \cdots, x_{12}).$$

1) We define a 12D product basis set of $(b+1)^{12}$ basis functions by multiplying 1D harmonic functions

$$
\begin{aligned}
|\, n_1 \cdots n_{12}\rangle &= P_{n_1}(x_1)\cdots P_{n_{12}}(x_{12})\exp\left(-\frac{1}{2}\sum_{c=1}^{12} x_c^2\right), \\
\text{with } n_c &= 0,1,2,3,\cdots,b \text{ for } c = 1,\cdots,12.
\end{aligned}
$$

2) We calculate the elements of the H matrix

$$\langle n_1' \cdots n_{12}' \mid \hat{H} \mid n_1 \cdots n_{12} \rangle =$$

$$\int \cdots \int P_{n_1'}(x_1) \cdots P_{n_{12}'}(x_{12}) \hat{H}(x_1, \cdots, x_{12})$$

$$\times P_{n_1}(x_1) \cdots P_{n_{12}}(x_{12}) \exp\left(- \sum_{c=1}^{12} x_c^2 \right) dx_1 \cdots dx_{12}.$$

The potential matrix elements are calculated using $N^{12} \geq (b+1)^{12}$ Gauss-Hermite quadrature points

$$\langle n'_1 \cdots n'_{12} \mid V(x_1, \cdots, x_{12}) \mid n_1 \cdots n_{12} \rangle =$$
$$\sum_{k_1=1}^{N} \cdots \sum_{k_{12}=1}^{N} w_{k_1} \cdots w_{k_{12}} P_{n'_1}(x_1) \cdots P_{n'_{12}}(x_{12})$$
$$V(x_1, \cdots, x_{12}) P_{n_1}(x_1) \cdots P_{n_{12}}(x_{12}) + \mathrm{err}(N),$$

until $\mathrm{err}(N)$ is small enough for a given value of b.

3) We diagonalize H for $b = 1, 2, 3, \cdots$ with sizes (4096×4096), $([5.3 \times 10^5] \times [5.3 \times 10^5])$, $([1.7 \times 10^7] \times [1.7 \times 10^7]) \cdots$ until the lowest eigenenergies converge to a given accuracy.

Even in the best case $b = 10$ and the number of basis set functions is $(b+1)^{12} > 10^{12}$ and the number of quadrature points is $N^{12} > 10^{12}$.

Considering that the V matrix is non-sparse (in some cases the T matrix is also non-sparse):

1) We have to calculate a Hamiltonian matrix of dimensions $10^{12} \times 10^{12}/2$=0.5 YB for direct diagonalization (*the combined space of all computer hard drives in the world does not amount to even one yottabyte*) **(problem in memory)**

2) We have to make $\sim 10^{12\times 3} = 10^{36}$ operations **(problem in computer time)**.

3) We have to calculate vectors with sizes of 10^{12}=8000 GB for iterative eigensolvers **(problem in memory)**

CONCLUSION: **The variational method scheme described for 1D is not suitable with 12 dimensions** $\Longrightarrow$
"Curse of the dimensionality" for both the product basis set and the quadrature grid.

V. THE PRODUCT BASIS SET+PRODUCT GAUSS GRID SCHEME: WHY IS SO EXPENSIVE?

With this scheme we are considering:

1) **The only way to represent accurately the wavefunctions** is by expanding them in terms of $(b+1)^D$ product basis functions

$$\Phi = \sum_{n_1=0}^{b} \cdots \sum_{n_D=0}^{b} C_{n_1,\cdots,n_D} \phi_{n_1 \cdots n_D} + \mathrm{err}(b).$$

2) **The integrands must be written as linear combinations of** $(2N-1)^D$ monomials $x_1^{l_1} \cdots x_D^{l_D}$ as

$$\Phi_{n_1' \cdots n_D'} V(x_1, \cdots, x_D) \Phi_{n_1 \cdots n_D} = \sum_{l_1=1}^{2N-1} \cdots \sum_{l_D=1}^{2N-1} A_{l_1,\cdots,l_D} x_1^{l_1} \cdots x_D^{l_D} + \mathrm{err}(N).$$

These two assumptions are not necessarily true.

One way to effectively reduce the number of product basis set functions

If the product basis set functions are the eigenfunctions of $\hat{H}_0$ and $\hat{H} = \hat{H}_0 + \hat{H}'$ $(\hat{H}' < \hat{H}_0)$ we can prune the product basis set by selecting those product basis functions with zeroth-order energies $E^0_{n_1 \cdots n_D} \leq T$ by using a restriction like

$$\sum_{c=1}^{D} \alpha_c n_c \leq b.$$

$\Longrightarrow$ **THIS TALK**.

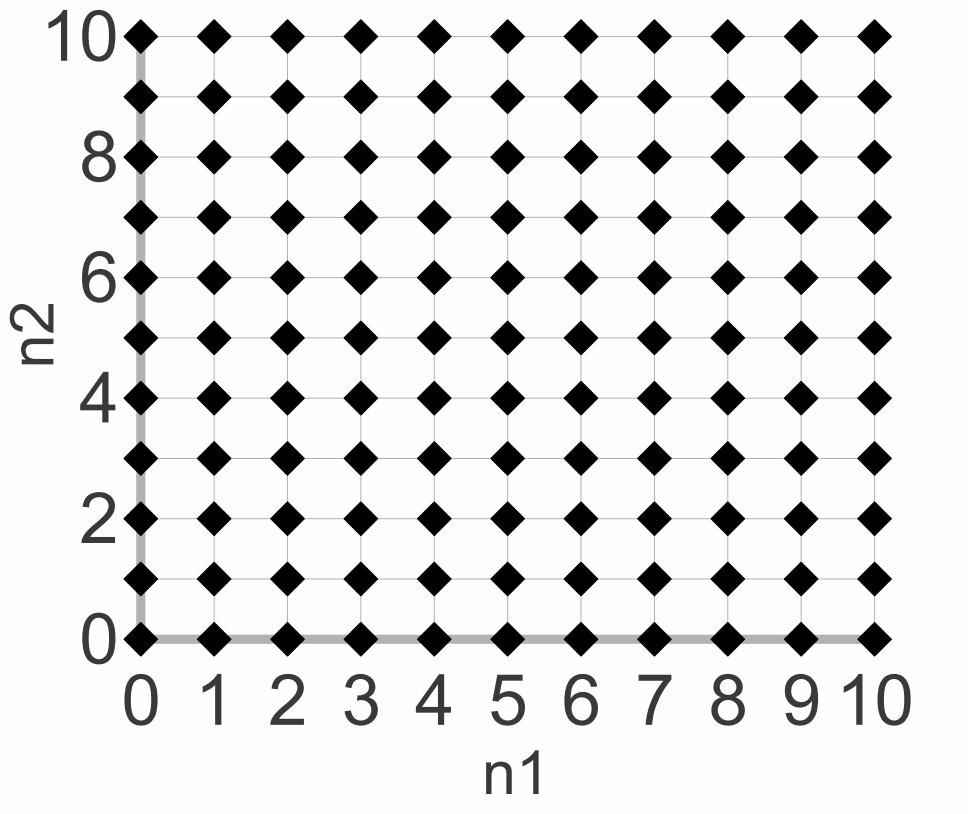

Figure 1: Product basis set $n_1 \leq 10$ and $n_2 \leq 10$.

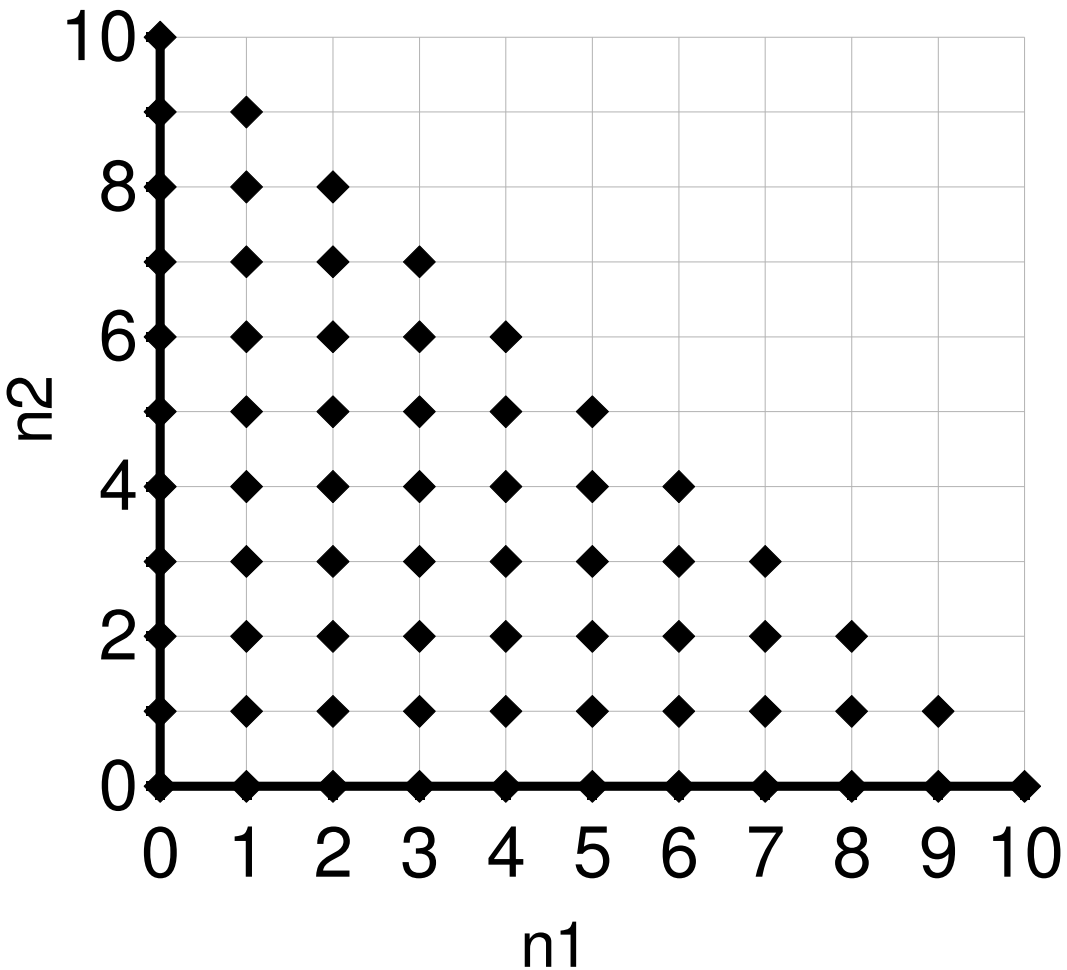

Figure 2: Pruned basis set $n_1 + n_2 \leq 10$.

Since we can reduce the number of basis set functions we can also reduce the number of quadrature points.

One way to effectively reduce the number of product quadrature points is to employ non-product quadrature grids as Smolyak. This works when an efficient pruning condition is possible and the potential is smooth enough $\Longrightarrow$ **THIS TALK**.

VI. PRUNED PRODUCT BASIS SET + NON-PRODUCT GRIDS SCHEME

This scheme enables us to partially overcome the "Curse of dimensionality" when **the wavefunctions can be accurately represented in a pruned product basis set and the potential is smooth enough.**

Why?

A) Because we can expand accurately the wavefunctions in terms of $\sim \frac{(b+D)!}{b!D!}$ basis functions ($\sim (b+1)^D$ with a product basis set).

B) Because we can expand accurately the integrands in terms of $\sim \frac{(d+D)!}{d!D!}$ **necessary** monomials $x_1^{l_1} \cdots x_D^{l_D}$ with $l_1 + \cdots + l_D \leq d$ ($\sim (d+1)^D$ with a product Gauss grid).

For large dimensional systems $D \geq 5$

$$\frac{(b+D)!}{b!D!} << (b+1)^D, \text{ with} \frac{(d+D)!}{d!D!} << (d+1)^D$$

Table 1: Number of monomials of degree up to d (necessary) and number of total monomials (useless+necessary) exactly integrated by a product 12D Gauss grid of $(Int(d/2)+1)^D$ points, $0 \leq l_1 + l_2 + ... + l_{12} \leq d$.

d	good	total	PG points
	$\frac{(d+D)!}{d!D!}$	$(d+1)^D$	
3	4.55×10^2	1.68×10^7	4.10×10^3
5	6.19×10^3	2.18×10^9	5.31×10^5
7	5.04×10^4	6.87×10^{10}	1.68×10^7
9	2.94×10^5	1.00×10^{12}	2.44×10^8
11	1.35×10^6	8.92×10^{12}	2.18×10^9
13	5.20×10^6	5.67×10^{13}	1.38×10^{10}
15	1.74×10^7	2.81×10^{14}	6.87×10^{10}
17	5.19×10^7	1.16×10^{15}	2.82×10^{11}
19	1.41×10^8	4.10×10^{15}	1.00×10^{12}
21	3.55×10^8	1.29×10^{16}	3.14×10^{12}
23	8.34×10^8	3.65×10^{16}	8.92×10^{12}
25	1.85×10^9	9.54×10^{16}	2.33×10^{13}

CONCLUSIONS

1) Product Gauss quadrature grids are too good **if the basis product set can be pruned and the potential is smooth**: they exactly integrate the set of necessary monomials and a larger number of useless monomials.

2) Non-product quadrature grids are designed to **exactly integrate only the set of necessary monomials** and therefore they have a lesser number of quadrature points that the smallest Gauss product grid that can exactly integrate **the same set of necessary monomials**.

Example

Table 2: Total number of non-product Smolyak quadrature points for 12D considering at least degree $0 \leq l_1 + ... + l_{12} \leq d$.

d	$w(x) = \exp(-x^2)$	PG
3	25	4096
7	2097	1.68×10^7
11	47529	2.18×10^9
15	585033	6.87×10^{10}
19	4.87×10^6	10^{12}
23	3.05×10^7	8.91×10^{12}
27	1.53×10^8	5.70×10^{13}
31	6.35×10^8	2.81×10^{14}

3) **Within non-product quadrature grids the Smolyak quadrature grids are a attractive option since:**

A) All the effort is 1D: to calculate sequences of quadrature rules $Q^i(x_c)$ $(i = 1, \cdots, i_c^{max})$, $c = 1, \cdots, D$.

B) We can consider different 1D weight functions.

C) Different definitions of the set of necessary monomials $0 \leq f(l_1, l_2, ..., l_D) \leq d$ can be used.

D) No limits for D. No limits for d.

E) They have structure.

In the next talk we present a example applied to the calculation of the vibrational levels of the C_2H_4 molecule, a 12D case.