Using a non-product Smolyak quadrature grid to compute the vibrational spectrum of C_2H_4

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June 18, 2011

I. THE HAMILTONIAN AND THE BASIS SET

Watson Hamiltonian for $J = 0$

$$\hat{H}_W = -\frac{1}{2}\sum_{k=1}^{D}\omega_k\frac{\partial^2}{\partial {q_k}^2} + V(q_1, \cdots, q_D) + \frac{1}{2}\sum_{\alpha,\beta}\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta - \frac{1}{8}\sum_{\alpha}\mu_{\alpha\alpha}.$$

The vibrational wavefunctions are expanded in a pruned product basis set of harmonic basis functions $\phi_n(q_c)$, $n = 0, \cdots, b$ and $c = 1, \cdots, 12$

$$\Phi_i = \sum_{0 \le n_1 + \cdots + n_{12} \le b} C^i_{n_1,\cdots,n_{12}}\phi_{n_1}\cdots\phi_{n_{12}} + \mathrm{err}(b),$$

II. THE POTENTIAL

In this work we used the quartic force field in *curvilinear symmetry coordinates* determined by Martin *et al* at the ab initio level of theory CCSD(T)/cc-pVTZ

$$\hat{V}^{CC}(S_1, \cdots, S_{12}) = \sum_{i}^{12}\sum_{j\leq i}^{12} F_{i,j}^{CC} S_i S_j + \sum_{i}^{12}\sum_{j\leq i}^{12}\sum_{k\leq j}^{12} F_{i,j,k}^{CC} S_i S_j S_k + \sum_{i}^{12}\sum_{j\leq i}^{12}\sum_{k\leq j}^{12}\sum_{l\leq k}^{12} F_{i,j,k,l}^{CC} S_i S_j S_k S_l.$$

This potential was morsified in order to improve the representation of the anharmonicity of the potential for the C−H stretch coordinates.

The non-product quadrature we propose can be used with general potentials, a force field is not necessary.

III. THE NON-PRODUCT SMOLYAK QUADRATURE GRID

Since the product basis set can be pruned and the potential is smooth the integrands to evaluate can be accurately expanded in terms of a restricted set of monomials $q_1^{l_1} \cdots q_{12}^{l_{12}}$ as

$$\begin{aligned} &\Phi_{n_1' \cdots n_{12}'} V(q_1, \cdots, q_{12}) \Phi_{n_1 \cdots n_{12}} \\ = &\sum_{0 \le l_1 + \cdots + l_D \le d} A_{l_1, \cdots, l_{12}} q_1^{l_1} \cdots q_{12}^{l_{12}} + \mathrm{err}(d) \end{aligned}$$

Therefore, **Our goal is to find the smallest non-product Smolyak quadrature grid that can integrate the restricted set of monomials**

$$q_1^{l_1} \cdots q_{12}^{l_{12}}, \text{ with } 0 \le l_1 + \cdots + l_{12} \le 2b + p.$$

p is an appropriate maximum degree for a Taylor expansion of the potential.

Non-product Smolyak quadrature grids are built by

A) Selecting sequences of 1D quadrature rules Q_c^i with increasing maximum accuracies d_i, $i = 1, \cdots, K$ for every coordinate $c = 1, \cdots, D$

$$\{Q_c^1, Q_c^2, Q_c^3 \cdots, Q_c^K\}, \text{with } {}^c d_1 \leq^c d_2 \leq^c d_3 \cdots \leq^c d_K.$$

$$
\begin{aligned}
Q_c^1 \quad & \text{exactly integrates all the monomials } x_c^l,\ l = 0, \cdots, {}^c d_1, \\
Q_c^2 \quad & \text{exactly integrates all the monomials } x_c^l,\ l = 0, \cdots, {}^c d_2, \\
Q_c^3 \quad & \text{exactly integrates all the monomials } x_c^l,\ l = 0, \cdots, {}^c d_3, \\
& \vdots \\
Q_c^K \quad & \text{exactly integrates all the monomials } x_c^l,\ l = 0, \cdots, {}^c d_K.
\end{aligned}
$$

B) Combining product quadrature grids with different maximum accuracies ${}^{c}d_i$ for every 1D coordinate

$$S(D,H) = \sum_{D \le i_1 + \cdots + i_D \le H} C_{i_1,\cdots,i_D} \, Q_1^{i_1} \otimes \cdots \otimes Q_D^{i_D}.$$

Properties of the Smolyak algorithm:

1) If one of the product quadrature grids $Q_1^{i_1} \otimes \cdots \otimes Q_D^{i_D}$ within $S(D, H)$ exactly integrates a given monomial $x_1^{l_1} \cdots x_D^{l_D}$ the non-product Smolyak quadrature grid $S(D, H)$ can exactly integrate that monomial $\Longrightarrow$

with $D \leq i_1 + \cdots + i_D \leq H$ and ${}^c d_i \geq 2i - 1$ the Smolyak quadrature grid integrates exactly all the monomials

$$x_1^{l_1} \cdots x_D^{l_D}, \text{ with } 0 \leq l_1 + \cdots l_D \leq 2K - 1,$$
$$K = H - D + 1.$$

2) If the points of the quadrature rules are nested $Q^1(x) \subset Q^2(x) \subset \cdots \subset Q^{K-1}(x) \subset Q^K(x)$ the Smolyak quadrature grid is the result of pruning a product quadrature grid

$$S(D,H)w(x_1,\cdots,x_D)F(x_1,x_2,\cdots x_D)$$
$$= \sum_{k_1}^{N_1} \sum_{k_2}^{N_2^{max}(k_1)} \cdots \sum_{k_D}^{N_D^{max}(k_1,k_2,\cdots,k_{D-1})} w^S(k_1,k_2,\cdots,k_D)F(x_1,x_2,\cdots x_D).$$

This property is very important: non-product Smolyak grids made from nested quadratures have structure.

The following sequence of nested Hermite quadrature rules for C_2H_4 was used

$$\begin{aligned} i &= 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, \cdots \\ N_i &= 1, 3, 3, 7, 9, 9, 9, 9, 17, 19, 19, 19, 31, 33, 41, 41, \cdots \\ d_i &= 1, 5, 5, 7, 15, 15, 15, 15, 17, 29, 29, 29, 31, 33, 61, 61, \cdots . \end{aligned}$$

Therefore, as ${}^c d_i \geq 2i - 1$

$$2K - 1 \geq 2b + p,$$

we exactly integrate all the necessary monomials in the integrands (with $0 \leq l_1 + \cdots + l_{12} \leq 2p + p$) in addition to monomials with $0 \leq l_1 + \cdots + l_{12} > 2b + p$.

With $b = 11$ and $p = 4$, $H^{min} = 25$ and the non-product Smolyak grid has 1.5×10^8 points.

The smallest product Gauss grid that exactly integrates the same set of necessary monomials (with $0 \leq l_1 + \cdots + l_{12} \leq 2b + p = 26$) has 5.7×10^{13} points.
This means a reduction of 5 orders of magnitude: The variational calculation of the vibrational levels of 12D systems is feasible using non-product Smolyak quadrature grids and pruned product basis sets.

IV. ADVANTAGES OF NON-PRODUCT SMOLYAK QUADRATURE GRIDS

A) Matrix-vector products $v_2 = Hv_1$ with pruned product basis sets can be calculated sequentially as

$$v_2(n'_1, \cdots, n'_{12}) = \sum_{k_{12}} \phi_{n'_1}(q_{k_1}) \cdots \sum_{k_1} \phi_{n'_{12}}(q_{k_{12}}) w(k_1, \cdots, k_{12})$$

$$\times V(q_{k_1}, \cdots, q_{k_{12}}) \sum_{n_1} \phi_{n_1}(q_{k_1}) \cdots \sum_{n_{12}} \phi_{n_{12}}(q_{k_{12}}) v_1(n_1, \cdots, n_{12}),$$

since non-product Smolyak quadrature grids made from nested quadratures have structure. The number of operations scales with D as $\sim M^{D+1}$ (M is the maximum number of operations in 1D). This scheme can be also applied to the kinetic operator.

B) We integrate the complete operator (potential or kinetic) and not an approximation up to $2, 3, 4, 5, \cdots$ body terms as MULTIMODE.

V. RESULTS

Results were calculated using the exact Watson Hamiltonian. The pruned basis set was restricted to $n_1 + \cdots + n_{12} \leq 11$ and $H = 25$. The total number of pruned product basis functions was 1.4×10^6. Vibrational energies up to 4100 cm^{-1} were converged to less than 0.5 cm^{-1}.

assignation	$E_{b=11}$	Exp
ν_{10}	821.74	825.93
ν_8	926.81	939.86
ν_7	947.22	948.9
ν_4	1025.93	1025.69
ν_6	1223.76	1222
ν_3	1341.37	1343.54
ν_{12}	1440.20	1442.47
ν_2	1623.53	1625.4
$2\nu_{10}$	1655.51	1662
$\nu_8 + \nu_{10}$	1751.09	1767
$\nu_7 + \nu_{10}$	1775.36	1781

assignation	$E_{b=11}$	Exp
$\nu_4 + \nu_{10}$	1849.44	1854
$2\nu_8$	1855.72	1881
$\nu_7 + \nu_8$	1869.38	1889
$2\nu_7$	1895.21	1900
$\nu_4 + \nu_8$	1949.81	1958
$\nu_4 + \nu_7$	1964.46	1965
$\nu_6 + \nu_{10}$	2040.33	2048
$2\nu_4$	2049.11	2046
$\nu_3 + \nu_{10}$	2165.84	2173
$3\nu_{10}$	2494.40	2504
$2\nu_3$	2680.89	2685
$3\nu_7$	2843.78	2854
$2\nu_{12}$	2872.07	2877
$\nu_2 + \nu_3$	2957.97	2962
$\nu_6 + \nu_8 + \nu_{10}$	2977.94	2993.29
ν_{11}	2983.94	2988.64
ν_1	3019.66	3022.03

assignation	$E_{b=11}$	Exp
$\nu_2 + \nu_{12}$	3072.84	3079
$\nu_3 + \nu_8 + \nu_{10}$	3091.06	3109.32
ν_5	3076.72	3083.36
$2\nu_{10} + \nu_{12}$	3094.98	3104.33
ν_9	3098.04	3104.89
$2\nu_2$	3238.35	3239
$\nu_2 + 2\nu_{10}$	3267.96	3276.2
$\nu_7 + \nu_8 + \nu_{12}$	3297.05	3327.3
$\nu_2 + 2\nu_8$	3462.02	2496.9
$\nu_6 + \nu_{10} + \nu_{12}$	3473.49	3480.1
$\nu_2 + 2\nu_7$	3504.29	3514.4
$\nu_2 + 2\nu_4$	3665.61	3658.7
$\nu_8 + 2\nu_{12}$	3790.03	3810.97
$\nu_{10} + \nu_{11}$	3800.77	3809
$\nu_1 + \nu_{10}$	3833.60	3842
$\nu_6 + \nu_8 + 2\nu_{10}$	3806.95	3825.05
$\nu_2 + \nu_{10} + \nu_{12}$	3885.22	3892.46

assignation	$E_{b=11}$	Exp
$\nu_8 + \nu_{11}$	3903.97	3921
$\nu_9 + \nu_{10}$	3918.63	3928
$\nu_3 + \nu_8 + 2\nu_{10}$	3926.66	3946.82
$\nu_7 + \nu_{11}$	3924.07	3931
$\nu_6 + \nu_7 + \nu_8 + \nu_{10}$	3929.23	3948.59
$3\nu_{10} + \nu_{12}$	3929.63	3944.31
$\nu_1 + \nu_8$	3939.54	3954
$\nu_7 + \nu_9$	4039.00	4047
$\nu_2 + 2\nu_6$	4042.32	4049.50
$\nu_7 + 2\nu_{10} + \nu_{12}$	4043.17	4057.72
$4\nu_4$	4087.53	4076

V. CONCLUSION AND FUTURE WORK

The calculation of the vibrational spectra of molecules with six or more atoms using rigorously the variational method can be feasible using the pruned product basis sets+non-product Smolyak quadrature grids made from nested quadratures+iterative eigensolvers scheme.

An alternative to this work would be to use the Smolyak algorithm to interpolate the vibrational wavefunctions instead of integrating the basis functions. In this case we should abandon the variational method and use the different finite-differences method because we no longer have integrals over basis functions.

APPENDIX Considering the pruning condition

$$\Phi_i = \sum_{0 \le n_1 + \cdots + n_{12} \le b} C^i_{n_1,\cdots,n_{12}} \phi_{n_1} \cdots \phi_{n_{12}} + \mathrm{err}(b) = \sum_{0 \le l_1 + \cdots + l_{12} \le b} T^i_{l_1,\cdots,l_{12}} q_1^{l_1} \cdots q_{12}^{l_{12}} + \mathrm{err}(b),$$

and the expansion of the potential as

$$V = \sum_{0 \le l_1 + \cdots + l_{12} \le p} D^i_{l_1,\cdots,l_{12}} q_1^{l_1} \cdots q_{12}^{l_{12}} + \mathrm{err}(p).$$