A Convivial outlook at the generalized mean field configuration interaction method - CONVIVIAL 2.0: Theory and Implementation

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Plan

- The GMFCI method for nuclear motion

Philosophy and practice

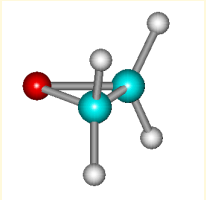
- The CONVIVIAL interface

Demo of this blackbox device and a glimpse at what is inside (dance party theorem)

- Prospects: electrons-nuclei GMFCI

Quantum chemistry without Born-Oppenheimer surfaces

A heptatomic interstellar molecule: C_2H_4O



H^{eff} order 1

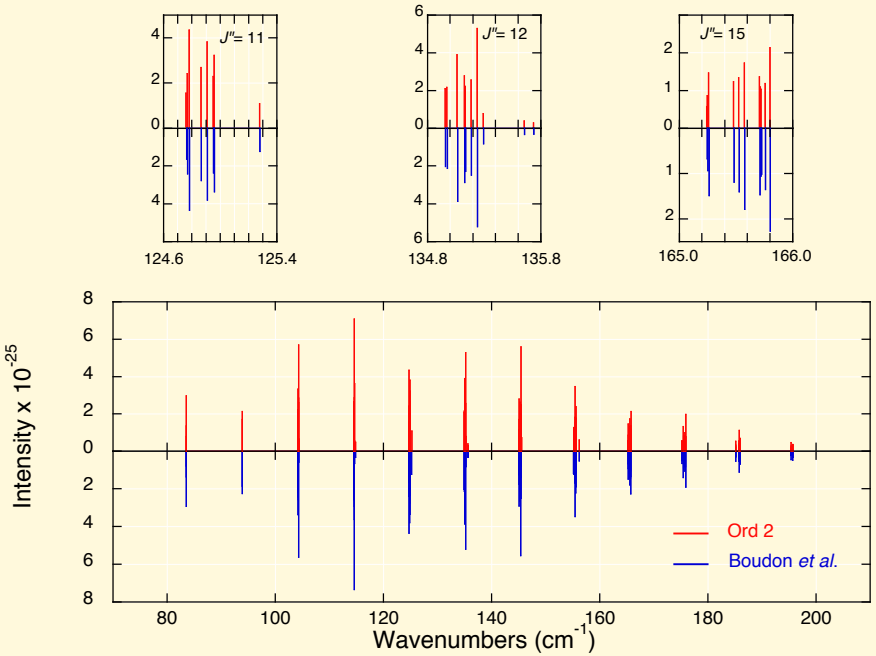
VSCF/ VSCFCI(ν_1-ν_6-ν_9-ν_{13}, ν_3-ν_5-ν_{12}; 34072, 17000)/ VSCFCI(ν_1-ν_6-ν_9-ν_{10}-ν_{13}-ν_{15}; 19464)/ VCI

Assignment		Gaz phase IR		Liquid phase Raman	Solid Phase amorphous	Solid Phase crystalline		Computed VMFCI	type of motion
	ν_1	-	3018	3005	3011	3024	3005	2919	ν_{s,CH_2}
	ν_2	1497	1498	1490	1492	1481-1495	-	1497	σ_{CH_2}
A_1	ν_3	1270	1270	1266	1267	1266-1268	1266	1272	Ring breath.
	ν_4	-	1148	1120	-	1119 -1129	1147	1123	ω_{CH_2}
	ν_5	877	877	867	856	857-875	854	879	Ring deform.
	ν_6	-	ia	3063	3073	3050-3051	3073	3032	ν_{as,CH_2}
A_2	ν_7	ia	ia	(1345)	1043	1043-1046	1046	1149	τ_{CH_2}
	ν_8	1020	ia	807	821	837-851	818	1019	ρ_{CH_2}
	ν_9	-	3006	3005	3001	2996-3006	2995	2913	ν_{s,CH_2}
B_1	ν_{10}	1470	1472	-	1467	1455-1467	1467	1468	σ_{CH_2}
	ν_{11}	-	1151	1150	1169	1159-1169	1152	1125	ω_{CH_2}
	ν_{12}	822	840	867	-	816-825	859	823	Ring deform.
	ν_{13}	3065	3065	3063	3061	3062-3075	3058	3041	ν_{as,CH_2}
B_2	ν_{14}	-	1142	1150	-	1146 -1161	1160	1147	τ_{CH_2}
	ν_{15}	808	821	-	794	794 -798	796	794	ρ_{CH_2}

D. Bégué, C. Pouchan, N. Gohaud, P. Cassam-Chenaï, J. Liévin, J. Chem. Phys. **127**, 164115 (2007).

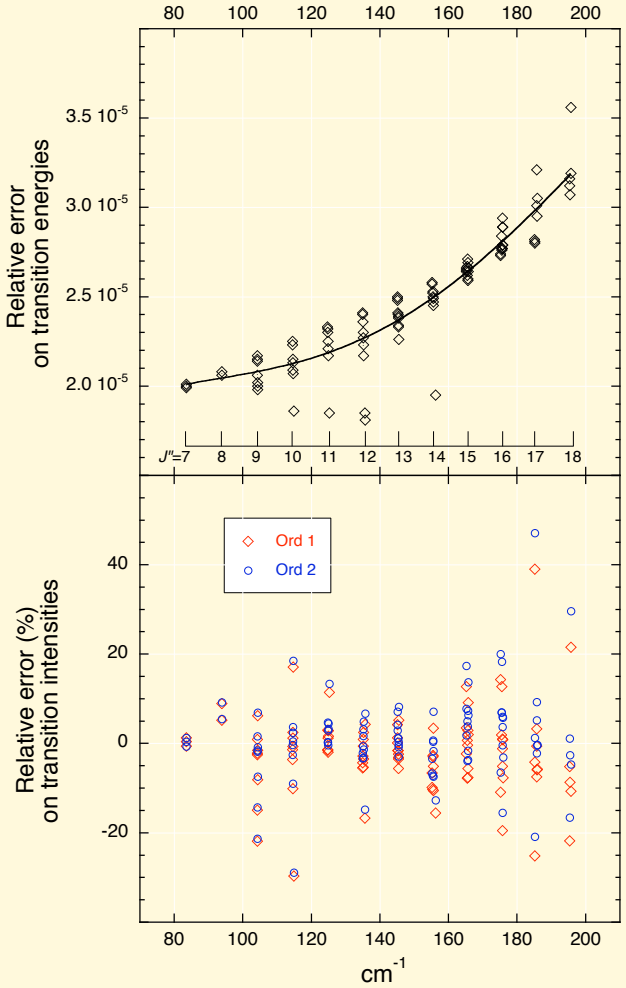
Application: CH_4 forbidden spectrum

$I_j = \{\theta, \phi, \psi\}$, H^{eff} order 4, μ^{eff} order 2



Spectre R(7-18) experimental (SOLEIL Synchrotron, V. Boudon et al. 2010)

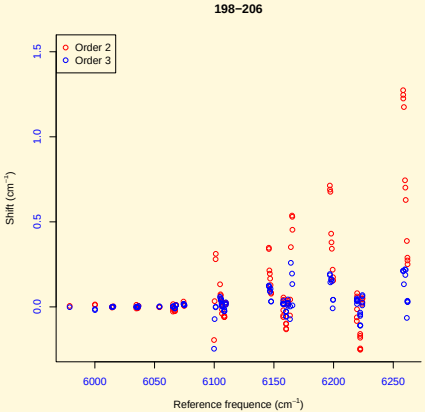
Spectre R(7-18) calculated (CONVIV code, P. Cassam-Chenaï et al.)

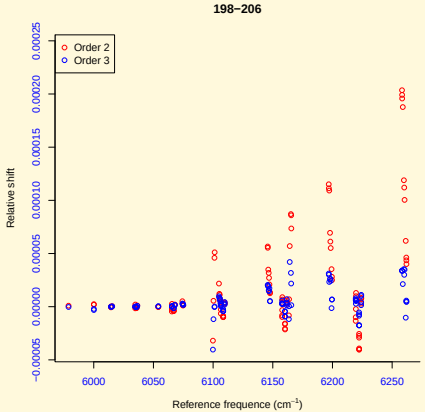


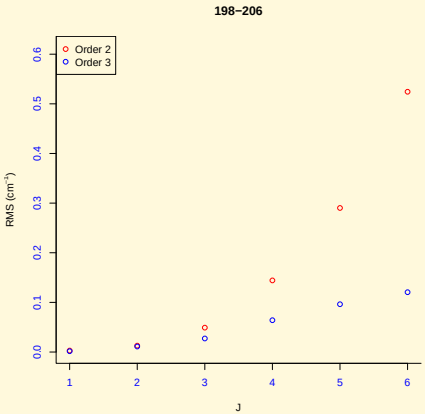
- Purely *ab initio* Ro-vibrational treatment: no scaling
- Average relative error on line positions: $2.46 * 10^{-5}$
- Average relative error on line intensities: 5.93%
(Average relative experimental uncertainties: 10.62%)

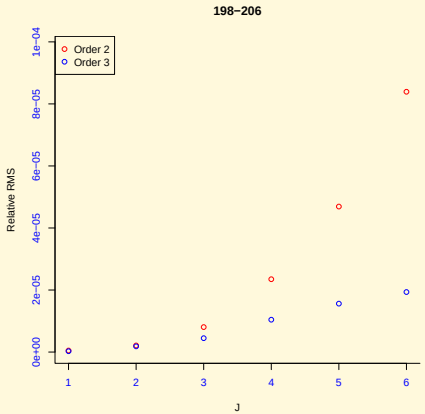
CH_4: $2\nu_3$ region - Comparison with M. Rey

Quasi degenerate GMFCI: 9 vibrational sublevels



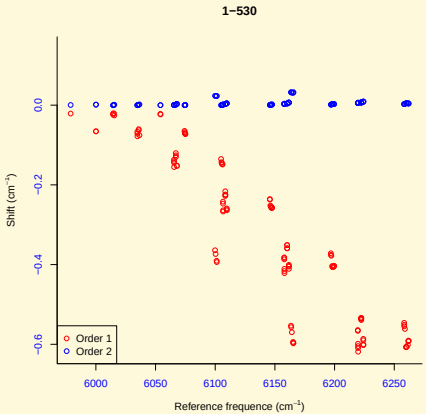


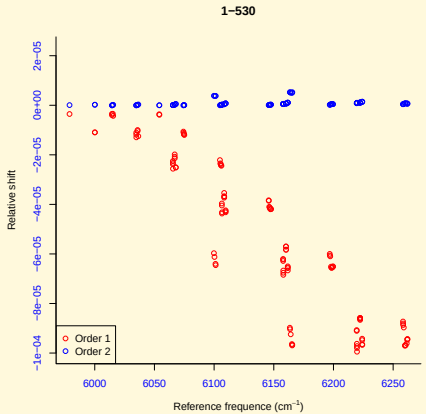


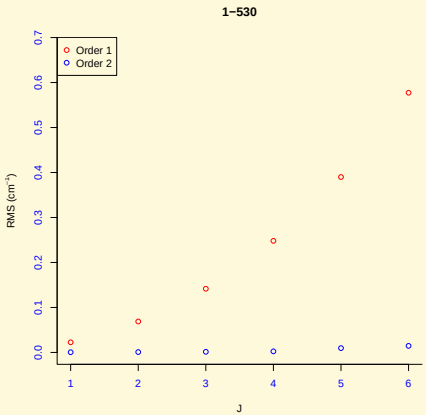


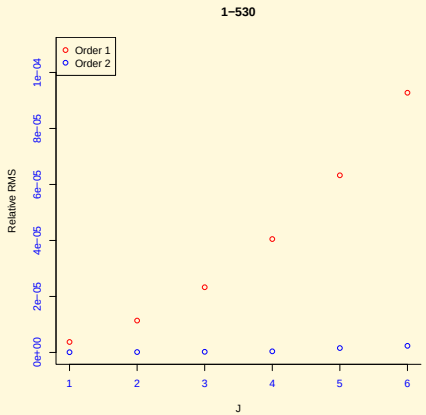
CH_4: $2\nu_3$ region - Comparison with M. Rey

Quasi degenerate GMFCI: $P_0 - P_5 = 530$ vibrational sublevels









Generalized Mean Field Configuration Interaction - I

- Q_i: degrees-of-freedom (dof) ex: normal coord. or group of dof
ex: 3 Euler angles, set of all electronic dof's

- P_i: associated group of conjugate momenta operators

- H: Hamiltonian of the system of distinguishable dof

$$H = \sum_{i_1} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1,i_2} h_{i_1 i_2}(Q_{i_1}, P_{i_1}) h_{i_1 i_2}(Q_{i_2}, P_{i_2}) + \cdots + h_{1\ldots n}(Q_1, P_1) \cdots h_{1\ldots n}(Q_n, P_n)$$

Consider a partition of the n Q_i into q sets $I_1, I_2, \cdots, I_q$, of respectively $p_1, p_2, \cdots, p_q$ elements,

$$(I_1, I_2, \cdots, I_q) = (\{i_1^1, i_2^1, \cdots, i_{p_1}^1\}, \{i_1^2, i_2^2, \cdots, i_{p_2}^2\}, \cdots, \{i_1^q, i_2^q, \cdots, i_{p_q}^q\}).$$

For each contraction, I_j, we define a partial Hamiltonian,

$$H_j = \sum_{i_1 \in I_j} h_1(Q_{i_1}, P_{i_1}) + \sum_{\{i_1,i_2\} \subset I_j} h_{i_1 i_2}(Q_{i_1}, P_{i_1}) h_{i_1 i_2}(Q_{i_2}, P_{i_2}) + \cdots + h_{i_1^j \ldots i_{p_j}^j}(Q_{i_1^j}, P_{i_1^j}) \cdots h_{i_1^j \ldots i_{p_j}^j}(Q_{i_{p_j}^j}, P_{i_{p_j}^j}),$$

Generalized Mean Field Configuration Interaction - II

The eigenvalue equation for I_j is : $[H_j^{eff} - \epsilon_j]\Phi_j = 0$, with:

- order 0: Usual contraction method Hamiltonian

$$H_j^{eff} = H_j$$

- order 1: MFCI Hamiltonian

$$H_j^{eff} = H_j + \langle \prod_{I_k \neq I_j} \phi_{V_k} | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k} \rangle$$

- order 2: GMFCI Hamiltonian

$$H_j^{eff} = H_j + \langle \prod_{I_k \neq I_j} \phi_{V_k} | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k} \rangle$$

$$+ \sum_{(V'_1,\ldots,V'_{j-1},V'_{j+1},\ldots) \neq (V_1,\ldots,V_{j-1},V_{j+1},\ldots)} \frac{\langle \prod_{I_k \neq I_j} \phi_{V_k} | H - H_j | \prod_{I_k \neq I_j} \phi_{V'_k} \rangle \langle \prod_{I_k \neq I_j} \phi_{V'_k} | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k} \rangle}{\sum_{k \neq j} E_{V_k} - E_{V'_k}}$$

- can be developed to arbitrary order for any observable

GMFCI flexibility

- Hierarchical contraction scheme
- Active basis function truncation scheme

$$\langle \Psi_m | H_j^{eff} | \Psi_n \rangle_{m,n} \cdot \langle \Psi_n | \Phi_j \rangle_n = \epsilon_j \langle \Psi_n | \Phi_j \rangle_n$$

$$\Psi_n = \prod_{J_k \subseteq I_j} \phi_{v_k} \; such\ that \sum_{k/J_k \subseteq I_j} E_{v_k} \leq E^{max}(j)$$

- Generalized mean field order
- Spectator basis function truncation scheme

for GMF of order, $Ord > 1$:

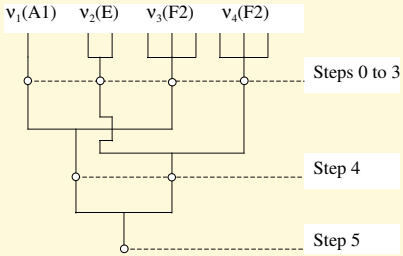
$$(V'_1, \ldots, V'_{j-1}, V'_{j+1}, \ldots) \; such\ that \sum_{k \neq j} E_{V'_k} \leq E^{max}(Ord)$$

Flexibility: contraction hierarchy

Particular cases

- The partition, $(\{1\},\{2\},\cdots,\{n\})$, corresponds to the VSCF method.
- The partition, $(\{1,2,\cdots,n\})$, corresponds to the VCI method.

General case: example CH_4



- Combinatorics: n-steps, m-mode MFCI calculation

$$N(m,n) = \sum_{m=m_0\geq m_1\geq\cdots\geq m_{n-1}\geq sup(2,m_n)} \prod_{i=0}^{n-1} \left(\sum_{k=0}^{m_{i+1}} (-1)^{m_{i+1}-k} \frac{k^{m_i}}{(m_{i+1}-k)!\ k!} \right)$$

- Ex. $N(9,1) = 21147$

Artefactual symmetry breaking in VSCF-based methods

Table 3
Low lying vibrational levels of methane, calculated using SPECTRO and MULTIMODE, and compared with experiment

Symmetry	Level	SPECTRO	MM-T	MM-M	Expt. [15]
A_1	*zpe*	9625.83	9635.61	9633.45	
	$\nu_4(T)$	1304.24	1297.97	1298.13	1310.76
	$\nu_2(E)$	1523.49	1518.77	1518.84	1533.33
	$2\nu_4$	2599.73	2570.62	2568.16	2587.04
	$2\nu_4(T)$	2600.17	2595.21	2594.81	2614.26
	$2\nu_4(E)$	2600.21	2601.91	2601.93	2624.62
	ν_1	2902.58	2915.33	2907.31	2916.48
	$\nu_3(T)$	2997.64	3013.25	3008.70	3019.49
	$2\nu_2$	3047.73	3034.38	3034.68	3063.65
	$2\nu_2(E)$	3053.93	3041.10	3041.19	3065.14
	$2\nu_1$	5781.65	5811.47	5781.59	5790.00
	$2\nu_3$	5936.79	5995.14	5985.21	5968.10
	$2\nu_3(T)$	5936.99	6038.48	6013.33	6004.60
	$2\nu_3(E)$	5966.74	6042.67	6032.57	6043.80
B_2	$\nu_4(T)$	1306.33	1300.33	1300.43	1310.76
	$\nu_3(T)$	2998.51	3021.15	3016.64	3019.49
B_1	$\nu_4(T)$	1306.31	1300.39	1300.49	1310.76
	$\nu_3(T)$	2998.61	3021.23	3016.59	3019.49
A_2	$\nu_2(E)$	1525.83	1521.31	1521.33	1533.33

The calculations using MULTIMODE involve two distinct potentials: (i) Taylor expansion (MM-T) of the normal coordinates; (ii) Morse-like expansion (MM-M) of symmetric normal coordinates. Experimental values are included to demonstrate the good prediction of MM-M for the splitting of the overtones. The overtones from SPECTRO are not reliable (see text).

R. Burcl, S. Carter, N. C. Handy, Chem. Phys. Lett. **373**, 357-365 (2003).

Flexibility: active basis truncation

The GMFCI equation is solved in the space spanned by product functions,

$$\phi_{V_j}(Q^j_{i_1}, \cdots, Q^j_{i_{p_j}}) = \prod_{i \in I_j} \phi_{v_i}(Q_i),$$

truncated on energy criteria.

Energies in cm^{-1} of the vibrational levels of ozone for different truncation schemes

		{1,2,3} truncated at:			{{1,3},{2}} truncated at:		
Ass.	irreps.	5000 cm^{-1}	7000 cm^{-1}	9000 cm^{-1}	5000 cm^{-1}	7000 cm^{-1}	9000 cm^{-1}
ZPE	A1	1453.58	1453.54	1453.54	1453.54	1453.54	1453.54
0 1 0	A1	698.87	698.84	698.82	698.83	698.82	698.82
0 0 1	B1	1045.00	1044.27	1044.06	1044.06	1044.04	1044.04
1 0 0	A1	1103.26	1102.61	1102.50	1102.51	1102.50	1102.50
0 2 0	A1	1395.19	1395.08	1395.03	1395.13	1395.03	1395.02
0 1 1	B1	1740.00	1726.86	1726.37	1726.62	1726.32	1726.30
1 1 0	A1	1802.22	1793.84	1793.58	1793.72	1793.54	1793.53
0 0 2	A1	2093.04	2063.51	2061.63	2061.62	2061.26	2061.25
0 3 0	A1	2094.95	2088.80	2088.68	2088.87	2088.68	2088.66
1 0 1	B1	2143.40	2114.68	2112.96	2112.80	2112.52	2112.51
2 0 0	A1	2212.84	2200.47	2200.13	2200.37	2200.07	2200.06

Flexibility: Mean field order 0 versus 1

	Harmonic level	MSP-ord0	MSP-ord1	MSP-ord1-SCF	Converged
ν_4	1345	1356	1295	1318	1309
ν_2	1570	1567	1527	1532	1528
$2\nu_4$	2691	2714	2591	2638	2588
$2\nu_4$	2691	2719	2597	2643	2610
$2\nu_4$	2691	2719	2597	2643	2622
ν_1	3036	3013	2972	2972	2925
ν_3	3157	3214	3176	3062	3027
$2\nu_2$	3141	3131	3051	3061	3051
$2\nu_2$	3141	3134	3054	3064	3054
$3\nu_4$	4036	4079	3896	3966	3868
$3\nu_4$	4036	4087	3905	3974	3905
$3\nu_4$	4036	4088	3905	3974	3915
$3\nu_4$	4036	4088	3906	3974	3929
$3\nu_2$	4711	4694	4573	4588	4573
$3\nu_2$	4711	4699	4579	4594	4579
$3\nu_2$	4711	4699	4579	4594	4579

Wave numbers in cm^{-1} of the vibrational levels of methane calculated for different MSP-methods. MSP-ord0 goes in the wrong direction for modes 3 and 4 MSP-ord1-SCF always go in the right direction and modes 1 and 2 are closer to the converged value than with MSP-ord0. (HO modal basis set with quantum number less than 10. Order 0 rotational corrections).

Flexibility: Mean field order

$I_1 = \{\theta, \phi, \psi\}$: Euler angles , $I_2 = \{Q_1, \ldots, Q_9\}$: normal coords

Energies in cm^{-1} of methane rotational levels in its vibrational ground state

	Van Vleck Perturbation[a]			Our method[b]			STDS[c]
	ord2	ord4	ord6	ord0	ord2	ord4	
$J = 1$	10.59973	10.44174	10.44237	10.63296	10.48010	10.48008	10.481648
$J = 2$	31.79918	31.32521	31.32439	31.89887	31.43746	31.43742	31.442121
	31.79918	31.32521	31.32463	31.89887	31.43772	31.43769	31.442387
$J = 3$	63.59837	62.65041	62.64064	63.79775	62.86645	62.86635	62.875779
	63.59837	62.65041	62.64162	63.79775	62.86749	62.86742	62.876841
	63.59837	62.65041	62.64285	63.79775	62.86879	62.86877	62.878169

[a] X. G. Wang et E. L. Sibert, Spectrochimica Acta A, **58** (2002) 863. 12 force constants adjusted on experiment.

[b] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003). Purely *ab initio* results.

[c] C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transfer **59**, 471-480 (1998). From an effective Hamiltonian accurate to 10^{-5} cm^{-1} .

Spectator basis truncation

$$
\begin{aligned}
D_{fz}(Y) = \lambda_{fz}(Y)\big[&\theta_1(\Pi_x\Pi_y + \Pi_y\Pi_x) + i\theta_2\Pi_z(\Pi_x^2 - \Pi_y^2) \\
&+\theta_3(\Pi_x^2 + \Pi_y^2)(\Pi_x\Pi_y + \Pi_y\Pi_x) + \theta_4\Pi_z^2(\Pi_x\Pi_y + \Pi_y\Pi_x)\big] \\
&+\theta_5\Pi_x\lambda_{fz}(Y)\Pi_y + i\theta_6\Pi_z\lambda_{fz}(Y)(\Pi_x^2 - \Pi_y^2) \\
&+i\theta_7(\Pi_x\lambda_{fz}(Y)(\Pi_z\Pi_x + \Pi_x\Pi_z) - \Pi_y\lambda_{fz}(Y)(\Pi_y\Pi_z + \Pi_z\Pi_y)) \\
&+\theta_8(\Pi_x^2 + \Pi_y^2)\lambda_{fz}(Y)(\Pi_x\Pi_y + \Pi_y\Pi_x) + \theta_9\Pi_z^2\lambda_{fz}(Y)(\Pi_x\Pi_y + \Pi_y\Pi_x) \\
&+\theta_{10}((\Pi_z\Pi_x + \Pi_x\Pi_z)\lambda_{fz}(Y)(\Pi_y\Pi_z + \Pi_z\Pi_y) + \textit{hermitic conjugate}.
\end{aligned}
$$

	number of spectator=vibrational functions		
Coefficients	$2070 \equiv 10091\text{cm}^{-1}$	$4141 \equiv 11506\text{cm}^{-1}$	$8281 \equiv 13063\text{cm}^{-1}$
θ_1	$+4.52262 * 10^{-6}$	$+4.52245 * 10^{-6}$	$+4.52238 * 10^{-6}$
θ_2	$+2.71041 * 10^{-8}$	$+2.71023 * 10^{-8}$	$+2.71024 * 10^{-8}$
θ_3	$-3.30689 * 10^{-10}$	$-3.30668 * 10^{-10}$	$-3.30678 * 10^{-10}$
θ_4	$+1.35661 * 10^{-10}$	$+1.35642 * 10^{-10}$	$+1.35631 * 10^{-10}$
θ_5	$-1.48633 * 10^{-9}$	$-1.56091 * 10^{-9}$	$-1.58940 * 10^{-9}$
θ_6	$-1.91565 * 10^{-9}$	$-1.91320 * 10^{-9}$	$-1.91270 * 10^{-9}$
θ_7	$+1.42382 * 10^{-9}$	$+1.42378 * 10^{-9}$	$+1.42347 * 10^{-9}$
θ_8	$-1.61201 * 10^{-10}$	$-1.61187 * 10^{-10}$	$-1.61187 * 10^{-10}$
θ_9	$+5.12521 * 10^{-11}$	$+5.12559 * 10^{-11}$	$+5.12536 * 10^{-11}$
θ_{10}	$+1.28183 * 10^{-10}$	$+1.28178 * 10^{-10}$	$+1.28179 * 10^{-10}$

ZPE Convergence in CH4 VMFCI scheme

	ZPE in cm^{-1} (nb. bf)			
step type	ν_1 (10 bf)	ν_3 (220 bf)	ν_2 (120 bf)	ν_4 (680 bf)
MSP-VMFCI	97 36.817797	9 817.832496	9 830.213859	9 828.829953
MSP-VMFCI	972 4.937053	9721 .80854	972 4.971052	972 4.624952
MSP-VMFCI	9721.4 92681	9721 .614393	9721 .617023	9721 .613361
MSP-VMFCI	9721.4 94016	9721.489 747	9721.4 94231	9721.4 93759
MSP-VMFCI	9721.4893 35	9721.489 504	9721.489 515	9721.489 508
MSP-VMFCI	9721.4893 34	9721.48932 8	9721.4893 35	9721.4893 34
MSP-VMFCI	9721.489327	9721.489327	9721.489327	9721.489327
VMFCI($\nu_1-\nu_3$;48000)	9704.716 970 (1781 bf)		97 21.489327	97 21.489327
VMFCI($\nu_1-\nu_3$;22000)	9704.716 970 (330 bf)		9704.716 867	9704.716 590
VCI(18349)	9698.84 1643 (52096 bf)			

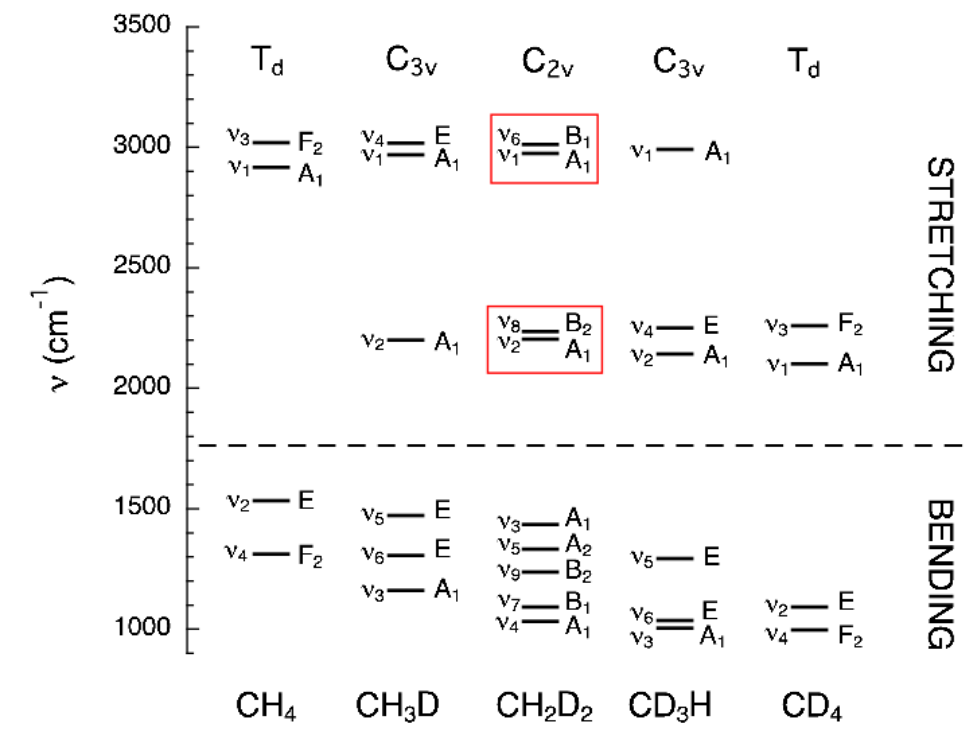
179,520,000 HO product basis functions at step 0.

ZPE-lowering criterium

ZPE after 2-mode contractions for CH_2D_2
(ZPE VSCF $8460.04 cm^{-1}$)

$\{\{1\}^\infty,\{2\}^\infty\}$	$\{\{1\}^\infty,\{3\}^\infty\}$	$\{\{1\}^\infty,\{4\}^\infty\}$	$\{\{1\}^\infty,\{5\}^\infty\}$	$\{\{1\}^\infty,\{6\}^\infty\}$	$\{\{1\}^\infty,\{7\}^\infty\}$
8459.91	8459.74	8460.02	8459.81	8447.97	8459.85
$\{\{1\}^\infty,\{8\}^\infty\}$	$\{\{1\}^\infty,\{9\}^\infty\}$	$\{\{2\}^\infty,\{3\}^\infty\}$	$\{\{2\}^\infty,\{4\}^\infty\}$	$\{\{2\}^\infty,\{5\}^\infty\}$	$\{\{2\}^\infty,\{6\}^\infty\}$
8459.93	8458.98	8460.03	8459.77	8460.03	8460.00
$\{\{2\}^\infty,\{7\}^\infty\}$	$\{\{2\}^\infty,\{8\}^\infty\}$	$\{\{2\}^\infty,\{9\}^\infty\}$	$\{\{3\}^\infty,\{4\}^\infty\}$	$\{\{3\}^\infty,\{5\}^\infty\}$	$\{\{3\}^\infty,\{6\}^\infty\}$
8459.82	8453.51	8460.04	8460.03	8460.01	8459.83
$\{\{3\}^\infty,\{7\}^\infty\}$	$\{\{3\}^\infty,\{8\}^\infty\}$	$\{\{3\}^\infty,\{9\}^\infty\}$	$\{\{4\}^\infty,\{5\}^\infty\}$	$\{\{4\}^\infty,\{6\}^\infty\}$	$\{\{4\}^\infty,\{7\}^\infty\}$
8459.93	8460.04	8460.00	8460.02	8460.00	8459.97
$\{\{4\}^\infty,\{8\}^\infty\}$	$\{\{4\}^\infty,\{9\}^\infty\}$	$\{\{5\}^\infty,\{6\}^\infty\}$	$\{\{5\}^\infty,\{7\}^\infty\}$	$\{\{5\}^\infty,\{8\}^\infty\}$	$\{\{5\}^\infty,\{9\}^\infty\}$
8459.93	8460.01	8459.99	8460.04	8460.03	8460.03
$\{\{6\}^\infty,\{7\}^\infty\}$	$\{\{6\}^\infty,\{8\}^\infty\}$	$\{\{6\}^\infty,\{9\}^\infty\}$	$\{\{7\}^\infty,\{8\}^\infty\}$	$\{\{7\}^\infty,\{9\}^\infty\}$	$\{\{8\}^\infty,\{9\}^\infty\}$
8459.99	8460.04	8459.90	8460.02	8460.04	8460.03

A basis set of 10 HO per degree of vibration has been used for the VSCF calculation, so that there are 100 product functions in the basis set of the 2-mode contractions.


3500
3000
2500
2000
1500
1000
ν (cm⁻¹)
Td
C3v
C2v
C3v
Td
ν3 — F2
ν1 — A1
ν4 — E
ν1 — A1
ν6 — B1
ν1 — A1
ν1 — A1
ν2 — A1
ν8 — B2
ν2 — A1
ν4 — E
ν2 — A1
ν3 — F2
ν1 — A1
STRETCHING
ν2 — E
ν4 — F2
ν5 — E
ν6 — E
ν3 — A1
ν3 — A1
ν5 — A2
ν9 — B2
ν7 — B1
ν4 — A1
ν5 — E
ν6 — E
ν3 — A1
ν2 — E
ν4 — F2
BENDING
CH4
CH3D
CH2D2
CD3H
CD4

CONVIVIAL interface

"Make hierarchy" black box facilities

1 • Start from an initial partition

2 • Is the partition made of a single contraction ?

$YES \rightsquigarrow$ **STOP**

$NO \rightsquigarrow$ **SCF run:**
iterate the partition until ZPE differences are less than tolerance

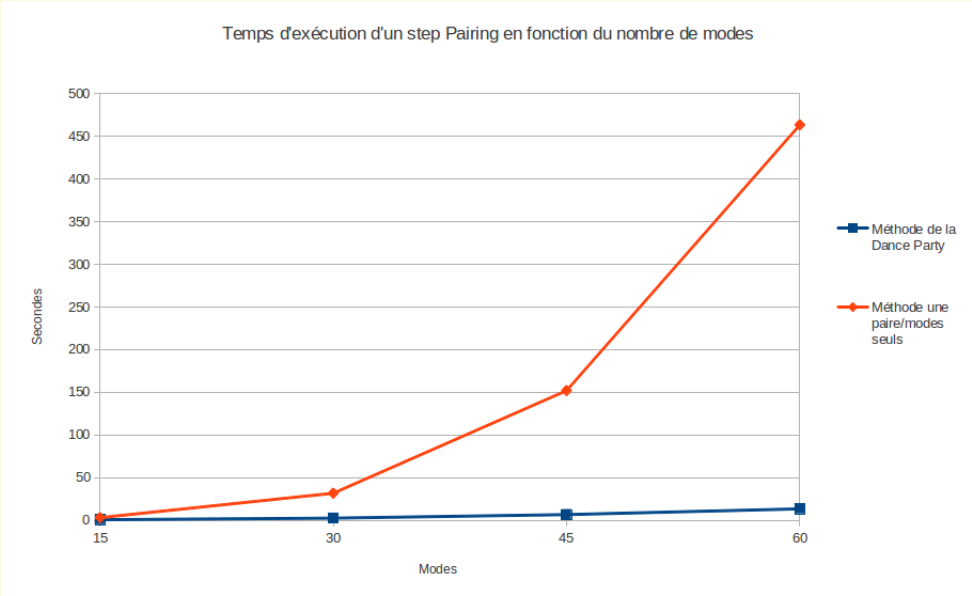
3 • Find best partition into disjoint pairs using the ZPE lowering criterium

Make pairing: Use the dance party theorem to scan all possible partitions into pairs (plus possibly one single dancer if odd number of contractions)

4 • Loop back to 2

CONVIVIAL interface

“Dance Party Theorem” speed up



Comparaison de l’algorithme de la soirée dansante et de l’algorithme standard pour la sélection des meilleures contractions d’un ensemble de modes vibrationnels (jusqu’à 60 i.e. molécule de 22 atomes).
Mémoire d’A. De Oliveira, Polytech’ Nice.

CONVIVIAL interface

Electron-Nuclei MFCI

1 • Start from an effective electronic Hamiltonian

$$\hat{H}^{eff}(\vec{R}^e) = -\frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r}_i^{\,e}} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i^{\,e}-\vec{r}_j^{\,e}\|} + \langle\psi_0(Q)| - \frac{1}{2}\Delta_Q + \frac{\sqrt{\mu_{ab}}Z_aZ_b}{|\xi^0_{ab}+Q|}$$
$$-\sum_{i=1}^{p}\frac{Z_a}{\sqrt{(r^e_{i_x})^2+(r^e_{i_y})^2+(r^e_{i_z}-r^0_{a_z}-\frac{\sqrt{\mu_{ab}}Q}{m_a})^2}} + \frac{Z_b}{\sqrt{(r^e_{i_x})^2+(r^e_{i_y})^2+(r^e_{i_z}-r^0_{b_z}+\frac{\sqrt{\mu_{ab}}Q}{m_b})^2}}|\psi_0(Q)\rangle_Q.$$

⋆ $\psi_0(Q) = \delta(Q_0)$ ↦ clamped nuclei approximation

⋆ $\psi_0(Q)$ = GS of a Kratzer potential ↦ vibrationally averaged Hamiltonian

⇝ Obtain a basis set of electronic approximate eigenstates $\phi_i(\vec{R}^e)$ (not $\phi_i(\vec{R}^e, Q)$ like in BO)

2 • Keep the same partition?

YES ⇝ **solve an effective vibrational Hamiltonian and loop back to** 1
PES known analytically, but actually integrals calculated directly

$$\hat{H}^{eff}(Q) = -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} + \frac{\sqrt{\mu_{ab}}Z_aZ_b}{|\xi^0_{ab}+Q|} + \langle\phi_0(\vec{R}^e)| - \frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r}_i^{\,e}} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i^{\,e}-\vec{r}_j^{\,e}\|}$$
$$-\sum_{i=1}^{p}\frac{Z_a}{\sqrt{(r^e_{i_x})^2+(r^e_{i_y})^2+(r^e_{i_z}-r^0_{a_z}-\frac{\sqrt{\mu_{ab}}Q}{m_a})^2}} + \frac{Z_b}{\sqrt{(r^e_{i_x})^2+(r^e_{i_y})^2+(r^e_{i_z}-r^0_{b_z}+\frac{\sqrt{\mu_{ab}}Q}{m_b})^2}}|\phi_0(\vec{R}^e)\rangle_{\vec{R}^e},$$

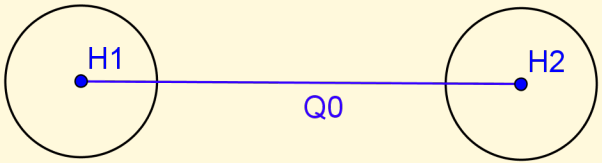
Electron-Nuclei MFCI

2 • Keep the same partition?

$NO \rightsquigarrow$ **Electron-Nuclei CI in direct product basis set :**

$$\{\psi_j(Q)\phi_i(\vec{R}^e)\}_{(j,i)}$$

$PB \rightsquigarrow$ **Core atomic orbitals unsuited to describe vibrationally averaged molecular clouds:**



Electron-Nuclei MFCI

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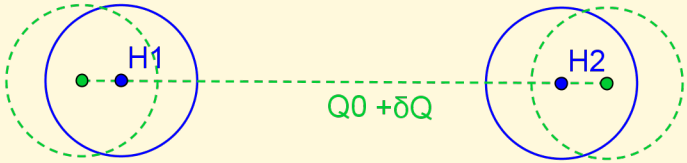

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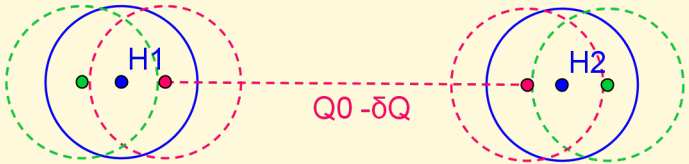

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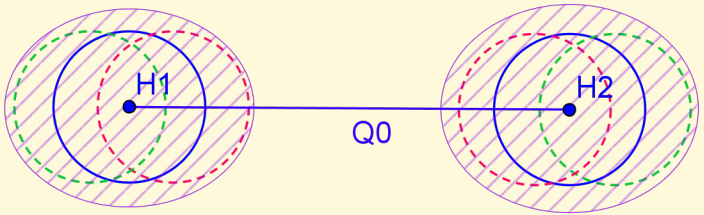


Electron-Nuclei MFCI

2 • Keep the same partition?

NO ⇝ **Electron-Nuclei CI in direct product basis set :**

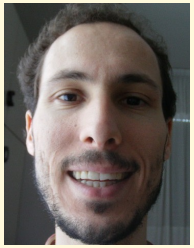
$$\{\psi_j(Q)\phi_i(\vec{R}^e)\}_{(j,i)}$$

RESULTS ⇝ $\mathbf{H_2}$, $m \in \{0,\cdots,15\}$, $n \in \{0,\cdots,8255\}$

Electron-nuclei CI			Bubin et al. CPL **477** (2009) p12		
E (Hartree)	Δ E (Hartree)	$\bar{\nu}$ (cm^{-1})	E (Hartree)	Δ E (Hartree)	$\bar{\nu}$ (cm^{-1})
-1.164025	0.0	0.0	-1.1640250308	0.0	0.0
-1.14506 4	0.018961	4161. 458	-1.1450653721	0.0189596588	4161.1641150762
-1.1271 64	0.036861	809 0.054	-1.1271779357	0.0368470951	8087.0026185542
-1.1102 68	0.053757	117 98.298	-1.1103404789	0.0536845519	11782.3972407646
-1.094 292	0.069733	153 04.624	-1.0945391728	0.0694858581	15250.3830854109
-1.078 985	0.085040	18 664.123	-1.0797694464	0.0842555844	18491.9633315277
-1.06 4068	0.099957	21 938.026	-1.0660372354	0.0979877954	21505.8352764667
-1.04 9672	0.114353	2 5097.583	-1.0533607612	0.1106642696	24287.9997764010
-1.03 5673	0.128352	2 8170.001	-1.0417730365	0.1222519944	26831.2113965306
-1.0 21788	0.142237	3 1217.413	-1.0313253816	0.1326996492	29124.2065912310
-1.0 07688	0.156337	3 4312.005	-1.0220923942	0.1419326367	31150.6131126623

Acknowledgements

Amine Ilmane



Guillaume Rousseau

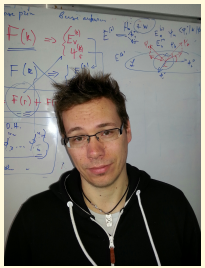
Alexandra De Oliveira

Bingbing Suo

Yann Bouret

Frédéric Patras

Manfred Schocker



Michael Rey

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