# CONVIVIAL: a graphical user interface for performing vibrational mean field configuration interactions

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## The Vibrational Mean Field Configuration Interaction method

$$H = \sum_{i_1} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1, i_2} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_n(Q_1, P_1, Q_2, P_2, \cdots, Q_n, P_n)$$

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

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

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

$$H_j = \sum_{i_1 \in I_j} h_1(Q_{i_1}, P_{i_1}) + \sum_{\{i_1, i_2\} \subset I_j} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_{p_j}(Q_{i_1^j}, P_{i_1^j}, Q_{i_2^j}, P_{i_2^j}, \cdots, Q_{i_{p_j}^j}, P_{i_{p_j}^j}),$$
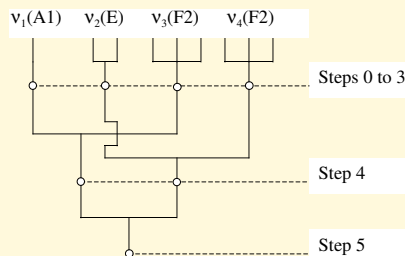
The mean-field equation for $I_j$ is :

$$[H_j + \langle \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) \rangle - \epsilon_j] \Phi_j = 0$$

## 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 $CH_4$

# 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 | |
| | $v_4(T)$ | 1304.24 | 1297.97 | 1298.13 | 1310.76 |
| | $v_2(E)$ | 1523.49 | 1518.77 | 1518.84 | 1533.33 |
| | $2v_4$ | 2599.73 | 2570.62 | 2568.16 | 2587.04 |
| | $2v_4(T)$ | 2600.17 | 2595.21 | 2594.81 | 2614.26 |
| | $2v_4(E)$ | 2600.21 | 2601.91 | 2601.93 | 2624.62 |
| | $v_1$ | 2902.58 | 2915.33 | 2907.31 | 2916.48 |
| | $v_3(T)$ | 2997.64 | 3013.25 | 3008.70 | 3019.49 |
| | $2v_2$ | 3047.73 | 3034.38 | 3034.68 | 3063.65 |
| | $2v_2(E)$ | 3053.93 | 3041.10 | 3041.19 | 3065.14 |
| | $2v_1$ | 5781.65 | 5811.47 | 5781.59 | 5790.00 |
| | $2v_3$ | 5936.79 | 5995.14 | 5985.21 | 5968.10 |
| | $2v_3(T)$ | 5936.99 | 6038.48 | 6013.33 | 6004.60 |
| | $2v_3(E)$ | 5966.74 | 6042.67 | 6032.57 | 6043.80 |
| $B_2$ | $v_4(T)$ | 1306.33 | 1300.33 | 1300.43 | 1310.76 |
| | $v_3(T)$ | 2998.51 | 3021.15 | 3016.64 | 3019.49 |
| $B_1$ | $v_4(T)$ | 1306.31 | 1300.39 | 1300.49 | 1310.76 |
| | $v_3(T)$ | 2998.61 | 3021.23 | 3016.59 | 3019.49 |
| $A_2$ | $v_2(E)$ | 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).

# VMFCI Convergence with the number of iterations

**Minimal symmetry preserving contraction scheme:**
$\{1\}^{n+1}, \{2,3\}^{n+1}, \{4,5,6\}^{n+1}\{7,8,9\}^{n+1}$, where $n$ is the step number

| | | Step 0 | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 | Step 6 |
|---|---|---|---|---|---|---|---|---|
| $CMu_4$ | $\nu_1$ | 8607.17 | 8562.01 | 8610.13 | 8599.51 | 8604.15 | 8602.97 | 8603.43 |
| | $\nu_2$ | 4301.54 | 4346.44 | 4303.40 | 4308.75 | 4304.61 | 4305.25 | 4304.85 |
| | $\nu_3$ | 9269.15 | 8434.91 | 8502.39 | 8430.60 | 8439.83 | 8433.05 | 8434.18 |
| | $\nu_4$ | 3279.51 | 3465.49 | 3407.24 | 3424.15 | 3418.05 | 3419.79 | 3419.17 |
| $CH_4$ | $\nu_1$ | 297 2.15 | 297 1.39 | 2972 .30 | 2972.2 1 | 2972.24 | 2972.24 | 2972.24 |
| | $\nu_2$ | 152 7.48 | 153 4.05 | 1532 .21 | 1532 .47 | 1532.4 0 | 1532.41 | 1532.41 |
| | $\nu_3$ | 3 176.01 | 30 62.09 | 30 65.73 | 3061 .53 | 3061 .74 | 3061.5 8 | 3061.60 |
| | $\nu_4$ | 12 95.15 | 132 0.08 | 131 7.25 | 1318 .18 | 1318.0 6 | 1318.1 0 | 1318.09 |
| $CD_4$ | $\nu_1$ | 2113.93 | 2113.72 | 2114.00 | 2113.98 | 2113.98 | 2113.98 | 2113.98 |
| | $\nu_2$ | 1088.49 | 1091.96 | 1091.26 | 1091.36 | 1091.34 | 1091.35 | 1091.34 |
| | $\nu_3$ | 2343.19 | 2280.99 | 2282.47 | 2280.73 | 2280.80 | 2280.75 | 2280.75 |
| | $\nu_4$ | 989.36 | 1003.08 | 1001.93 | 1002.32 | 1002.28 | 1002.29 | 1002.29 |
| $CT_4$ | $\nu_1$ | 1731.74 | 1731.65 | 1731.79 | 1731.78 | 1731.78 | 1731.78 | 1731.78 |
| | $\nu_2$ | 892.24 | 894.65 | 894.24 | 894.30 | 894.29 | 894.29 | 894.29 |
| | $\nu_3$ | 1996.59 | 1952.17 | 1953.05 | 1952.00 | 1952.04 | 1952.01 | 1952.01 |
| | $\nu_4$ | 851.69 | 861.39 | 860.70 | 860.93 | 860.91 | 860.91 | 860.91 |

A basis set of 10 HO has been used for each degree of vibration, with no truncation. The degree of vibration labelled by, 1, corresponds to the vibrational mode $\nu_1$, those labelled by 2 and 3 to the doubly degenerate mode $\nu_2$, $4, 5, 6$ and $7, 8, 9$, to the triply degenerate modes $\nu_3$ and $\nu_4$, respectively

# VMFCI versus traditional contractions

| | Harmonic level | MSP-CI | MSP-VMFCI | MSP-VSCFCI | Converged |
|---|---|---|---|---|---|
| $\nu_4$ | 1345 | 1356 | 1295 | 1318 | 1309 |
| $\nu_2$ | 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 |
| $\nu_1$ | 3036 | 3013 | 2972 | 2972 | 2925 |
| $\nu_3$ | 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-CI goes in the wrong direction for modes 3 and 4 MSP-VSCFCI always go in the right direction and modes 1 and 2 are closer to the converged value than with MSP-CI. (HO modal basis set with quantum number less than 10. Order 0 rotational corrections).

# Contraction-truncation effectiveness

The VMFCI 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**

| Ass. | irreps. | {1,2,3} truncated at: | | | {{1,3},{2}} truncated at: | | |
|------|---------|-----------------------|---------------|---------------|---------------------------|---------------|---------------|
| | | 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 |

# ZPE-lowering criterium

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

| $\{\{1\}^\infty, \{2\}^\infty\}$ | $\{\{1\}^\infty, \{3\}^\infty\}$ | $\{\{1\}^\infty, \{4\}^\infty\}$ | $\{\{1\}^\infty, \{5\}^\infty\}$ | $\{\{1\}^\infty, \{6\}^\infty\}$ | $\{\{1\}^\infty, \{7\}^\infty\}$ |
|---|---|---|---|---|---|
| 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.
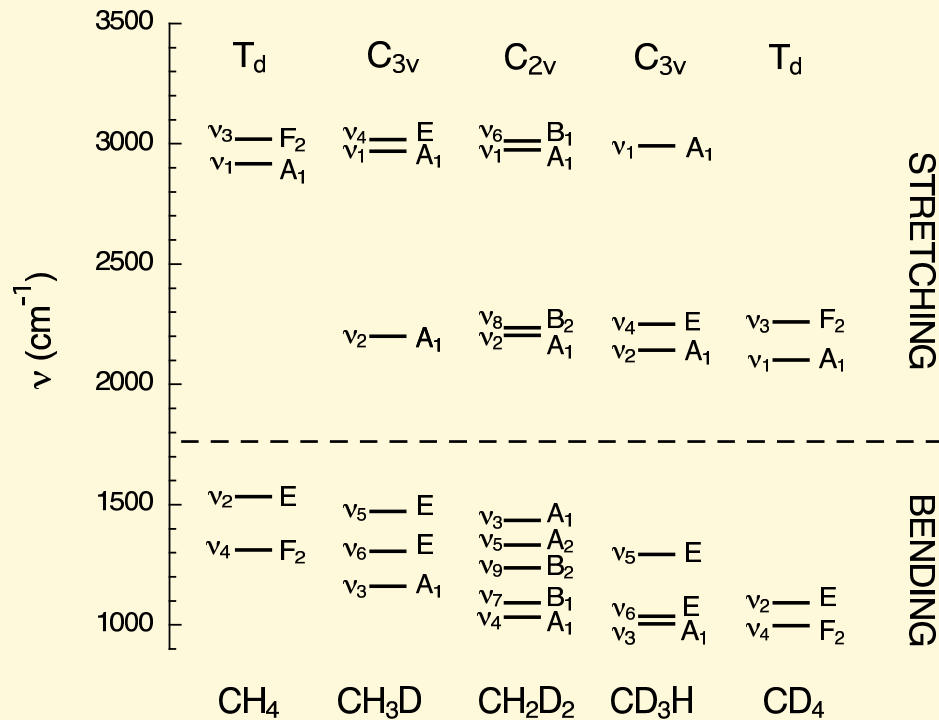
# A heptatomic interstellar molecule: $C_2H_4O$
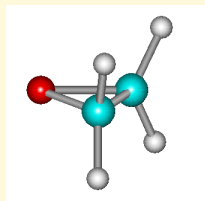


VSCF/
VSCFCI($\nu_1$-$\nu_6$-$\nu_9$-$\nu_{13}$, $\nu_3$-$\nu_5$-$\nu_{12}$; 34072, 17000)/
VSCFCI($\nu_1$-$\nu_6$-$\nu_9$-$\nu_{10}$-$\nu_{13}$-$\nu_{15}$; 19464)/
VCI

| Assignment | | Gaz phase IR | | Liquid phase Raman | Solid Phase amorphous | crystalline | | Computed VMFCI | type of motion |
|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | $\nu_1$ | - | 3018 | 3005 | 3011 | 3024 | 3005 | 2919 | $\nu_{s,CH_2}$ |
| | $\nu_2$ | 1497 | 1498 | 1490 | 1492 | 1481-1495 | - | 1497 | $\sigma_{CH_2}$ |
| | $\nu_3$ | 1270 | 1270 | 1266 | 1267 | 1266-1268 | 1266 | 1272 | Ring breath. |
| | $\nu_4$ | - | 1148 | 1120 | - | 1119 -1129 | 1147 | 1123 | $\omega_{CH_2}$ |
| | $\nu_5$ | 877 | 877 | 867 | 856 | 857-875 | 854 | 879 | Ring deform. |
| $A_2$ | $\nu_6$ | - | ia | 3063 | 3073 | 3050-3051 | 3073 | 3032 | $\nu_{as,CH_2}$ |
| | $\nu_7$ | ia | ia | (1345) | 1043 | 1043-1046 | 1046 | 1149 | $\tau_{CH_2}$ |
| | $\nu_8$ | 1020 | ia | 807 | 821 | 837-851 | 818 | 1019 | $\rho_{CH_2}$ |
| $B_1$ | $\nu_9$ | - | 3006 | 3005 | 3001 | 2996-3006 | 2995 | 2913 | $\nu_{s,CH_2}$ |
| | $\nu_{10}$ | 1470 | 1472 | - | 1467 | 1455-1467 | 1467 | 1468 | $\sigma_{CH_2}$ |
| | $\nu_{11}$ | - | 1151 | 1150 | 1169 | 1159-1169 | 1152 | 1125 | $\omega_{CH_2}$ |
| | $\nu_{12}$ | 822 | 840 | 867 | - | 816-825 | 859 | 823 | Ring deform. |
| $B_2$ | $\nu_{13}$ | 3065 | 3065 | 3063 | 3061 | 3062-3075 | 3058 | 3041 | $\nu_{as,CH_2}$ |
| | $\nu_{14}$ | - | 1142 | 1150 | - | 1146 -1161 | 1160 | 1147 | $\tau_{CH_2}$ |
| | $\nu_{15}$ | 808 | 821 | - | 794 | 794 -798 | 796 | 794 | $\rho_{CH_2}$ |

# Watson-Eckart Hamiltonian decomposition I

$$H_{watson}(X, Y) = H_0(X) + \varepsilon H_1(X, Y)$$

- Ex. $X$
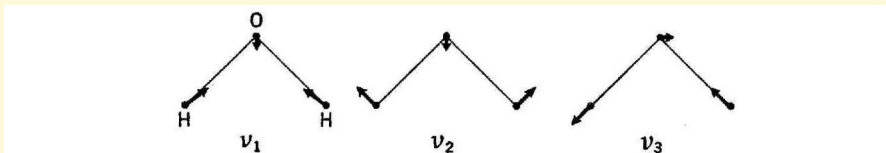


Example: Normal modes of vibration of the water molecule in mass-weighted coordinates. To represent actual relative motions in space, the arrows representing displacements of the oxygen atom should be only one-fourth as long as here shown.

- Ex. $Y$ Euler angles
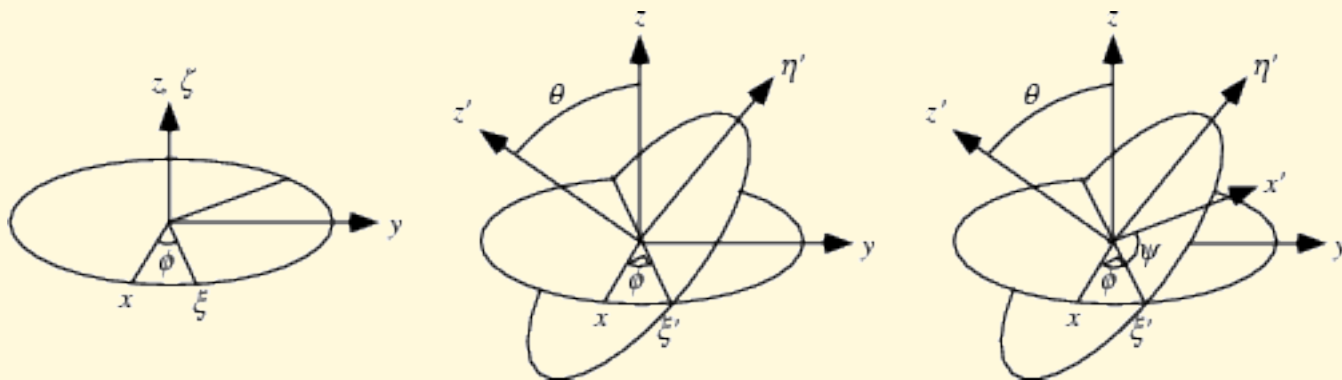
## Watson-Eckart Hamiltonian decomposition II

$$H_{watson}(X, Y) = H_0(X) + \varepsilon H_1(X, Y)$$

where, $X = [(Q_i)_i, (P_k)_k]$, and $Y$, denotes the Euler angles in the Eckart frame and their conjugate momenta.

$$H_0(X) = \tfrac{1}{2} \vec{P}^T \cdot \vec{P} + V_{BO} - \tfrac{1}{8} Tr(\mu) + \tfrac{1}{2} \vec{\pi}^T \mu \vec{\pi}$$

$$\varepsilon H_1(X, Y) = \tfrac{1}{2} (\vec{\Pi} - 2\vec{\pi})^T \mu \vec{\Pi}$$

## Rayleigh-Schrödinger perturbation theory . . .

$$H_N(\varphi_0 + \varepsilon \psi_1 + \varepsilon^2 \psi_2 + \cdots) =$$
$$(\lambda_0 + \varepsilon \lambda_1 + \varepsilon^2 \lambda_2 + \cdots).(\varphi_0 + \varepsilon \psi_1 + \varepsilon^2 \psi_2 + \cdots)$$

# . . . generalised for a module over a non-commutative ring

- $A = \sum_{n_x,n_y,n_z} \mathbb{C} \; \Pi_x^{n_x} \; \Pi_y^{n_y} \; \Pi_z^{n_z}$

- $\forall \; i \neq 0, \; \varepsilon^i \; \lambda_i \; \in \; A$

- $\forall \; i \neq 0, \; \varepsilon^i \; \psi_i = \sum_k a_k \; \varphi_k$ where the $(\varphi_k)_k$ are the eigenfunctions of $H_0$ associated to the eigenvalues $(\mu_k)_k$ and the $(a_k)_k$ are elements of the ring $A$.

$$\lambda_0 = \mu_0,$$

$$\varepsilon^1 \; \lambda_1 = \langle \varphi_0 | \varepsilon H_1 | \varphi_0 \rangle,$$

$$\varepsilon^2 \; \lambda_2 = \sum_{k \neq 0} \frac{\langle \varphi_0 | \varepsilon H_1 | \varphi_k \rangle \langle \varphi_k | \varepsilon H_1 | \varphi_0 \rangle}{\mu_0 - \mu_k},$$

$$\varepsilon^3 \, \lambda_3 \; = \; \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)(\mu_0 - \mu_{k'})}$$

$$- \sum_{k\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)^2},$$

$$\varepsilon^4 \, \lambda_4 \; = \; \sum_{k,k',k''\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_{k''}\rangle\langle\varphi_{k''}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)(\mu_0 - \mu_{k'})(\mu_0 - \mu_{k''})}$$

$$- \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)(\mu_0 - \mu_{k'})^2}$$

$$- \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)^2(\mu_0 - \mu_{k'})}$$

$$- \sum_{k,k'\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_{k'}\rangle\langle\varphi_{k'}|\varepsilon H_1|\varphi_0\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)^2(\mu_0 - \mu'_k)}$$

$$+ \sum_{k\neq 0} \frac{\langle\varphi_0|\varepsilon H_1|\varphi_k\rangle\langle\varphi_0|\varepsilon H_1|\varphi_0\rangle^2\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{(\mu_0 - \mu_k)^3}.$$

# Speed of convergence with the order of the perturbation

| | 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$^{-1}$ .

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

|  | Carter/Bowman[a] | Wang/Carrington[b] | Wang/Sibert[c] | Cassam-Chenaï/Liévin[d] | Exp.[e] |
|---|---|---|---|---|---|
| $J = 1$ | 10.47 | 10.430 | 10.44237 | 10.48165 | 10.481648 |
| $J = 2$ | N/A | N/A | 31.32439 | 31.44213 | 31.442121 |
|  | N/A | N/A | 31.32463 | 31.44240 | 31.442387 |
| $J = 3$ | N/A | N/A | 62.64064 | 62.87581 | 62.875779 |
|  | N/A | N/A | 62.64162 | 62.87689 | 62.876841 |
|  | N/A | N/A | 62.64285 | 62.87824 | 62.878169 |
| $J = 4 - 18$ | N/A | N/A | N/A | largest relative difference $2.10^{-5}$ | |

[a] S. Carter et J. M. Bowman, J. Phys. Chem. **A104**, 2355 (2000). MULTIMODE using Lee, Martin and Taylor PES.

[b] X. G. Wang et T. Carrington,J. Chem. Phys **121**, 2937 (2004). CI calculation using Schwenke PES.

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

[d] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003). VMFCI using Lee, Martin and Taylor PES + generalised perturbation with 1 parameter related to the equilibrium distance scaled by a factor 1.0002535.

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

## Effective dipole moment

- "first order correction to the wave function" $\varepsilon\psi_1 = \sum\limits_{k \neq 0} \frac{|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{\mu_0 - \mu_k}$,

- dipole moment: $\mu_f = \sum\limits_{\alpha = x,y,z} \lambda_{f\alpha}\mu_\alpha, \quad \lambda_{f\alpha}(Y), \quad \mu_\alpha(X)$

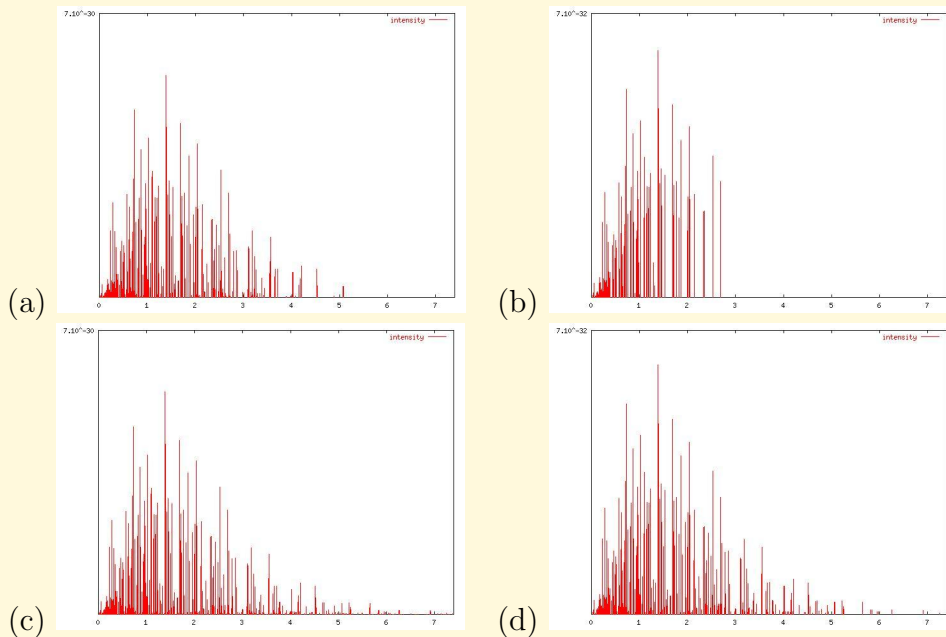- "first order effective dipole moment" $\langle\phi_0 + \varepsilon\psi_1|\mu_f|\phi_0 + \varepsilon\psi_1\rangle$

- Spherical top: $\langle\phi_0|\mu_\alpha|\phi_0\rangle = 0 \rightsquigarrow \quad \langle\phi_0|\mu_f|\varepsilon\psi_1\rangle + hc$

- Watson formula

$$\lambda_{f\alpha} \sum\limits_{k \neq 0} \frac{\langle\varphi_0|\mu_\alpha|\varphi_k\rangle\langle\varphi_k|\varepsilon H_1|\varphi_0\rangle}{\mu_0 - \mu_k} + hc$$

$$= \theta(\lambda_{fx}(\Pi_y\Pi_z + \Pi_z\Pi_y) + \lambda_{fy}(\Pi_x\Pi_z + \Pi_z\Pi_x) + \lambda_{fz}(\Pi_y\Pi_x + \Pi_x\Pi_y))$$

# Comparison with HITRAN at 500K



P. Cassam-Chenaï, J. Quant. Spectrosc. Radiat. Transfer **82**, 251-277 (2003).

Q-Branch of the vibrational ground state of methane at 500K.
Comparison of the extrapolation from HITRAN for $^{12}CH_4$ (a) and $^{13}CH_4$ (b) with *ab initio* calculated spectra for $^{12}CH_4$ (c) and $^{13}CH_4$ (d). Units as in HITRAN, intensities in [cm$^{-1}$ / (molecule . cm$^{-2}$)], wave numbers in cm$^{-1}$ . Isotopic abundances: 0.988274 for $^{12}CH_4$, 0.0111031 for $^{13}CH_4$ .

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Y. Bouret, P. Cassam-Chenaï