

The Vibrational Mean-Field Configuration Interaction method: theory and applications

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The vibrational mean field configuration interaction (VMFCI) method [1, 2] is an efficient variational approach for calculating the vibrational anharmonic spectrum of non trivial molecules [3], for which standard methods are facing with the huge size of the configuration interaction (CI) matrices to be diagonalized. The VMFCI approach encompass both the VSCF and full VCI techniques as special cases, but it especially introduces a hierarchical contraction of the vibrational degrees of freedom, and allows a mean-field treatment at each step of the contraction scheme. The resulting basis sets are very compact and can then be truncated according to energy thresholds without significative loss of accuracy on the end results.

The formalism of the VMFCI method will be presented and its implementation in the CONVIV Fortran 90 program will be discussed. The efficiency and the flexibility of the method will be demonstrated on water, ozone and methane as test systems [1, 2] and its ability for tackling larger systems will be illustrated on ethylene oxyde (C₂H₄O), a heptatomic molecule of astrophysical interest [3].

[1] P. Cassam-Chenaï and J. Liévin, *Int. J. Quantum Chem.*, **93**, 245 (2003).

[2] P. Cassam-Chenaï and J. Liévin, *J. Comput. Chem.*, **27**, 628 (2006).

[3] D. Bégué, N. Gohaud, C. Pouchan, P. Cassam-Chenaï and J. Liévin, submitted.