

# The generalized mean field configuration interaction method: how far a direct product wave function ansatz can go.

P. Cassam-Chenaï

*Laboratoire J. A. Dieudonné, CNRS - Université Nice Sophia Antipolis,  
Faculté des Sciences, Parc Valrose, Nice 06100, France.*

---

## Abstract

The generalized mean field configuration interaction (GMFCI) method is a very general method to solve a molecular Schrödinger equation. It encompasses in a unified formalism both variational and perturbative existing techniques, and, more importantly, empowers the users to optimally combine them in order to reduce the computational effort for a given accuracy goal. It has been applied successfully to molecules of astrobiological interest such as ethylene oxide, or of atmospheric interest such as methane.

In the first part of this talk, the GMFCI theory will be recalled with historical insights into its early development in the 1990's in collaboration with Prof. J. Liévin. Demonstrations of its effectiveness will be provided on several examples. Then, we will present two recent important developments of the theory. The first one is the extension of the perturbative treatment to deal with quasi-degenerate zero-order states. The second part of the talk will illustrate on the  $2\nu_3$ -band of methane, how to tune up the order of perturbation and the size of the quasi-degenerate space to minimize computational cost. The second one is the extension of the variational treatment to include both nuclear and electronic molecular degrees of freedom, and go beyond the adiabatic approximation. The last part of the talk will illustrate on dihydrogen how far a direct product wave function can go in the non-adiabatic case, the GMFCI method being able to provide the best direct product of a full-CI-type electronic wave function times a full-CI-type vibrational wave function with respect to the energy lowering criterium. We will also report on electron-nuclear CI calculations in basis sets made of such direct product functions, which are still particular cases of GMFCI calculations.

---

## References

- [1] P. Cassam-Chenaï and J. Liévin, *Int. J. Quantum Chem.* **93**, 245-264 (2003).
- [2] P. Cassam-Chenaï, J. Liévin, *Journal of Computational Chemistry* **27**, 627-640 (2006).
- [3] P. Cassam-Chenaï, A. Ilmane, *J. Math. Chem.* **50**, 652-667 (2012).
- [4] P. Cassam-Chenaï and J. Liévin, *J. Mol. Spectrosc.* **291**, 77-84 (2013).
- [5] P. Cassam-Chenaï, G. Rousseau, Y. Bouret, M. Rey, A. Ilmane, *Application of quasi-degenerate perturbation theory to the calculation of rotational energy levels of methane vibrational polyads*, hal preprint hal-01099480.
- [6] P. Cassam-Chenaï, B. Suo, W. Liu, *Decoupling electrons and nuclei without the Born-Oppenheimer approximation: The Electron-Nuclei Mean-Field Configuration Interaction Method*, hal preprint hal-00804101.