# Orbital optimization in selected configuration interaction

Yann Damour[1]

Supervisors: Anthony Scemama[1], Pierre-François Loos[1] and Fabris Kossoski[1]

[1]Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, France




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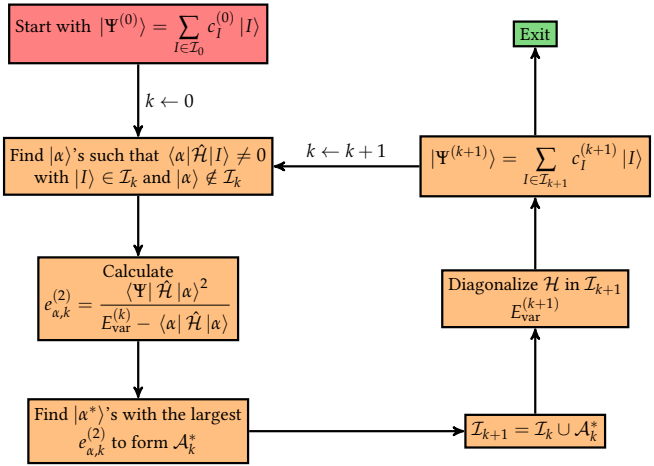
# CIPSI

CIPSI, *Configuration Interaction using a Perturbative Selection made Iteratively*:[1]




[1] B. Huron, J. P. Malrieu, P. Rancurel, J. Chem. Phys. 1973, 58, 5745–5759.

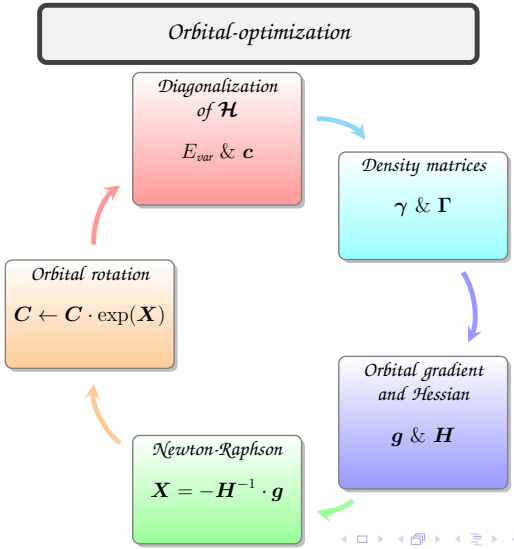
# Orbital optimization

How to minimize the CI energy of a given wave function ?

$$E_{\text{var}}(\boldsymbol{c}, \boldsymbol{X}) = \langle \Psi | \, e^{\hat{X}} \hat{\mathcal{H}} e^{-\hat{X}} \, | \Psi \rangle$$

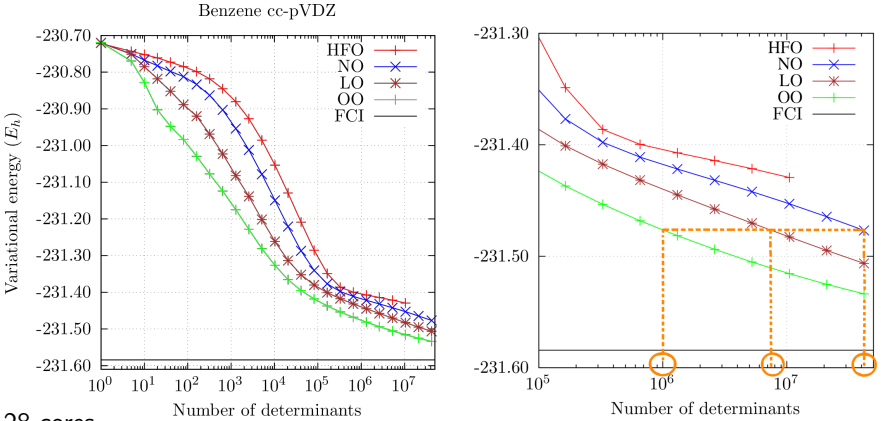
- $\boldsymbol{X}$ orbitals parameters
- $\hat{X}$ operator producing a rotation matrix when exponentiated

*F. Kossoski, A. Marie, A. Scemama, M. Caffarel, Michel and P. F. Loos, J. Chem. Theory Comput. 2021, 17, 8, 4756–4768*



# Benzene cc-pVDZ

CIPSI calculations with different kinds of MOs:




- 10 $\times$ 128 cores
- Natural: 44 $\times 10^6$ determinants $\sim$ 31h
- Local: 7 $\times 10^6$ determinants $\sim$ 5h
- Optimized: 1 $\times 10^6$ determinants $\sim$ 0.3h

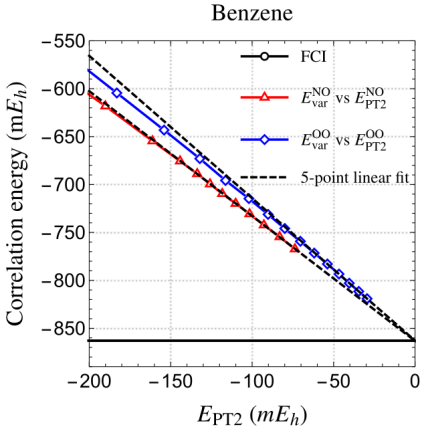
# FCI extrapolation

- When FCI energy is unreachable, it can be extrapolated

The PT2 energy computed during the CIPSI provides an estimate of the missing correlation energy:

$$E_{\text{PT2}} = \sum_{\alpha \in \mathcal{A}} e_\alpha^{(2)} \tag{1}$$

- For large enough wave functions: $E_{\text{FCI}} \approx E_{\text{var}} + E_{\text{PT2}}$
- $E_{\text{var}} = f(E_{\text{PT2}}) \approx \beta E_{\text{PT2}} + E_{\text{FCI}}$



# Conclusion

- Method provides more compact wave functions
  - Tested on 12 cyclic molecules, 16-32 times smaller wave functions with OOs compared to NOs
    *Damour, Véril, Kossoski, Caffarel, Jacquemin, Scemama and Loos, J. Chem. Phys. 155, 134104 (2021)*
  - More accurate extrapolations to the FCI energy
  - Allows to consider larger Hilbert spaces/systems
- Code implemented in QUANTUM PACKAGE
- Works for all methods for which the density matrices are available (ex: pCCD) and excited states

# Acknowledgments

Anthony Scemama

Pierre-François Loos

Fabris Kossoski