

Orbital optimization in selected configuration interaction

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Abstract

The obtention of very accurate solutions of the Schrödinger equation remains nowadays a challenge in theoretical chemistry. The natural improvement of the configuration interaction (CI) and coupled cluster (CC) methods by increasing the maximal excitation degree rapidly becomes prohibitive, with a growing number of neglectable contributions. By performing a sparse exploration of the Hilbert space, selected CI methods are good candidates to provide a solution to this problem.

The code used for this poster is available in the open-source software QUANTUM PACKAGE, freely accessible on Github at <https://quantumpackage.github.io/qp2/>. The plugin for the orbital optimization is also available on Github at https://github.com/Ydrnan/qp_plugins_damour/tree/dev.

CIPSI

CIPSI, *Configuration Interaction using a Perturbative Selection made Iteratively*, [1] [2] is a selected CI algorithm, which selects iteratively the most energetically-important determinants of the Hilbert space using a perturbative criterion. The process is illustrated in fig. 1.

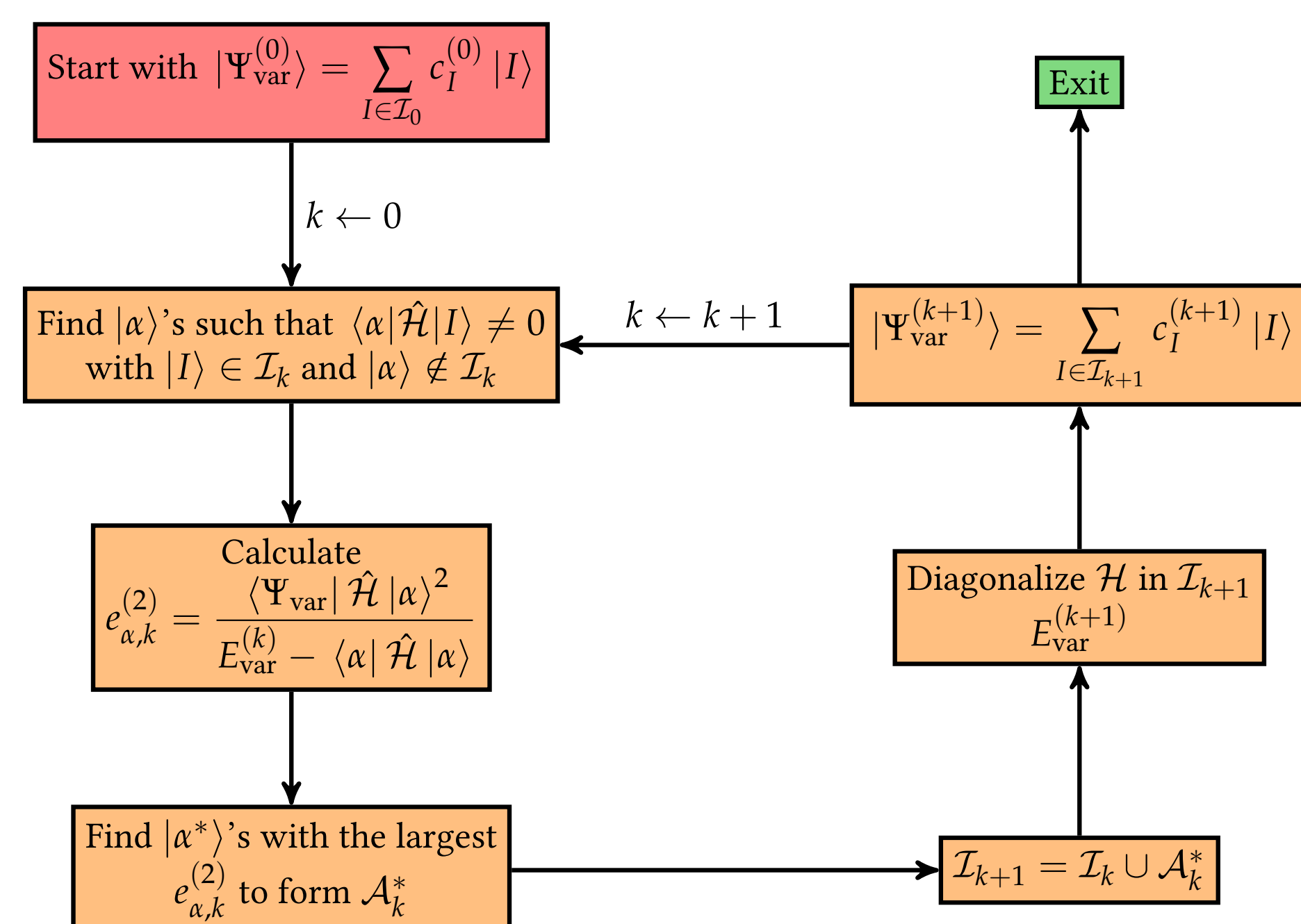


Figure 1. CIPSI algorithm

Orbital optimization

The variational energy, E_{var} , of a truncated CI wave function, Ψ_{var} , is not invariant under orbital rotations. Hence, it can be written with the introduction of some orbital rotation parameters \mathbf{X} , with $\mathbf{X} \cdot \mathbf{X}^\dagger = \mathbf{1}$, [3]

$$E_{\text{var}}(\mathbf{c}, \mathbf{X}) = \langle \Psi_{\text{var}} | e^{\hat{\mathbf{X}}} \hat{\mathcal{H}} e^{-\hat{\mathbf{X}}} | \Psi_{\text{var}} \rangle. \quad (1)$$

Both the CI coefficients, \mathbf{c} , and orbital rotation parameters, \mathbf{X} , have to be optimized to minimize the electronic energy. Since they are coupled, this is done by optimizing them alternatively. The process is illustrated in fig. 2. [4]

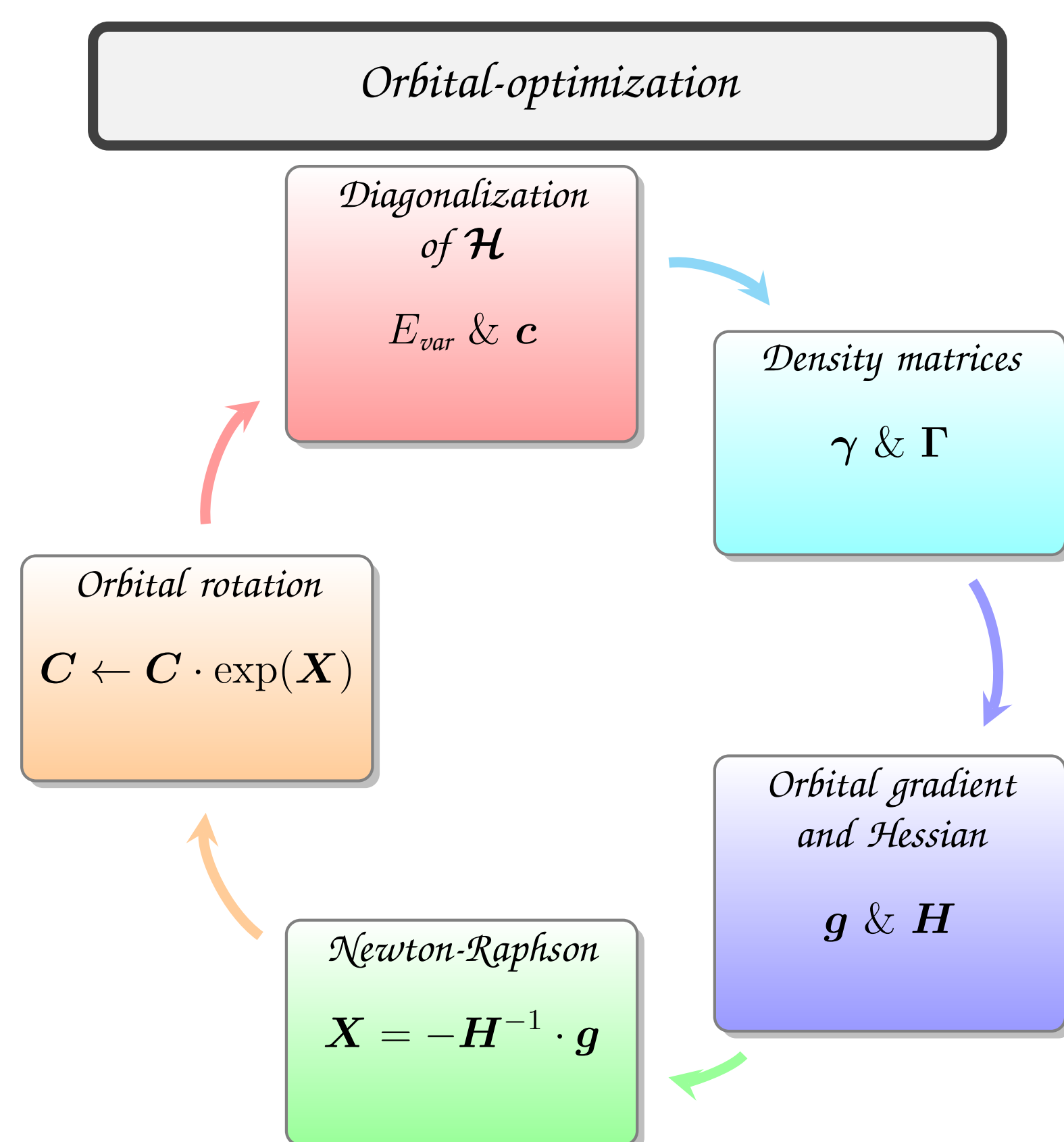


Figure 2. Orbital optimization, the gradient and the hessian can be obtained by differentiating analytically the energy with respect to the orbital rotations parameters [5]

The optimization process can be done for a given set of determinants. But in general, we found that it was more efficient to:

- 1 start from a small CIPSI wave function,
- 2 optimize the orbitals of the previous step, as seen in fig. 2,
- 3 perform a new CIPSI step to increase the size of the wave function (typically twice larger),
- 4 go back to 2 and repeat the process until the gain in energy during the optimization process becomes smaller than the aimed accuracy, which is typically about 1 mE_h.

Results

The results of the orbital optimization are illustrated in fig. 3. For a wave function of a given size, the variational energy obtained using the optimized orbitals is lower than the ones obtained with the Hartree-Fock, natural or local orbitals. Thus, with the optimized orbitals one can obtain the same variational energy than with these orbitals, with significantly less determinants in the wave function.

Since the energy is obtained by diagonalizing the matrix representation of the Hamiltonian, and the standard Davidson diagonalization scales as $\mathcal{O}(\text{Number of determinants}^{3/2})$, orbital optimization leads to a massive reduction of the computational cost to reach a given accuracy.

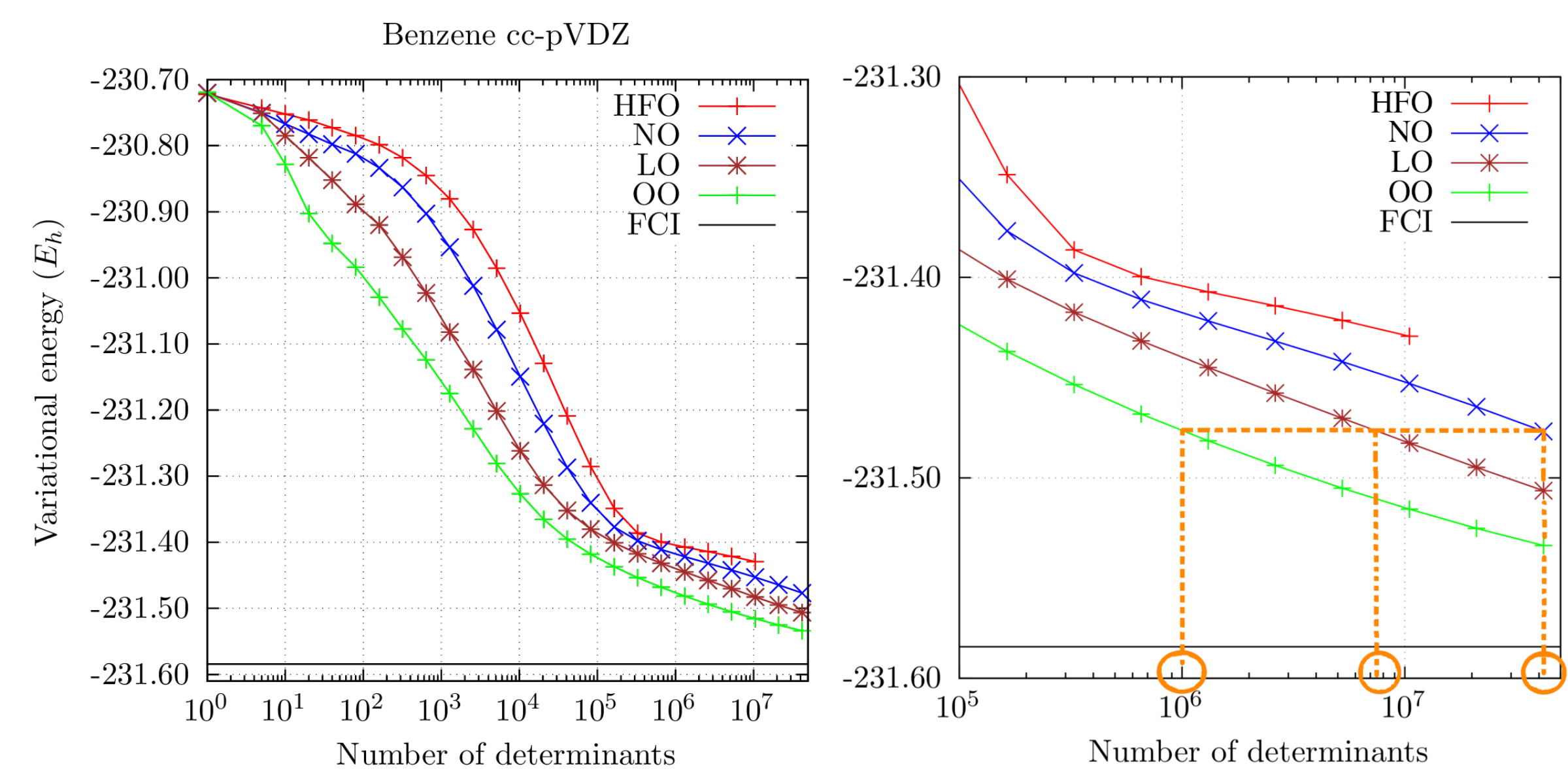


Figure 3. Benzene/cc-pVDZ, evolution of the variational energy in CIPSI calculations using different kinds of orbitals, Hartree-Fock (HFO), natural (NO), local (LO) and optimized (OO). Right: Zoom of the left panel. The natural orbitals were obtained from a CIPSI calculation using Hartree-Fock orbitals and at least 10 millions determinants in the wave function. The local orbitals were obtained from the Foster-Boys localization method. [6] The optimized orbitals were obtained by optimizing the local orbitals.

FCI extrapolation

Even if the FCI energy is unreachable in most cases, it can be obtained by extrapolation. In the CIPSI algorithm, an estimate of the missing correlation energy is given by the second-order perturbative energy. This energy is computed within Epstein-Nesbet perturbative theory

$$E_{\text{PT2}}^{(k)} = \sum_{\alpha \in A_k} e_{\alpha,k}^{(2)}. \quad (2)$$

For large enough wave functions, $E_{\text{FCI}} \approx E_{\text{var}} + E_{\text{PT2}}$, so $E_{\text{var}} = f(E_{\text{PT2}}) \approx \beta E_{\text{PT2}} + E_{\text{FCI}}$ and E_{FCI} can be obtained by extrapolating to $E_{\text{PT2}} = 0$ by using a linear regression.

Since the orbital optimization leads to lower variational energy for a given size of the wave function compared to Hartree-Fock, natural and local orbitals, the E_{PT2} is closer to 0. Hence, the distance for the extrapolation of E_{FCI} is smaller, as we can see in fig. 4. Consequently, the extrapolation is more precise and it allows to reach higher accuracy and to consider bigger systems.

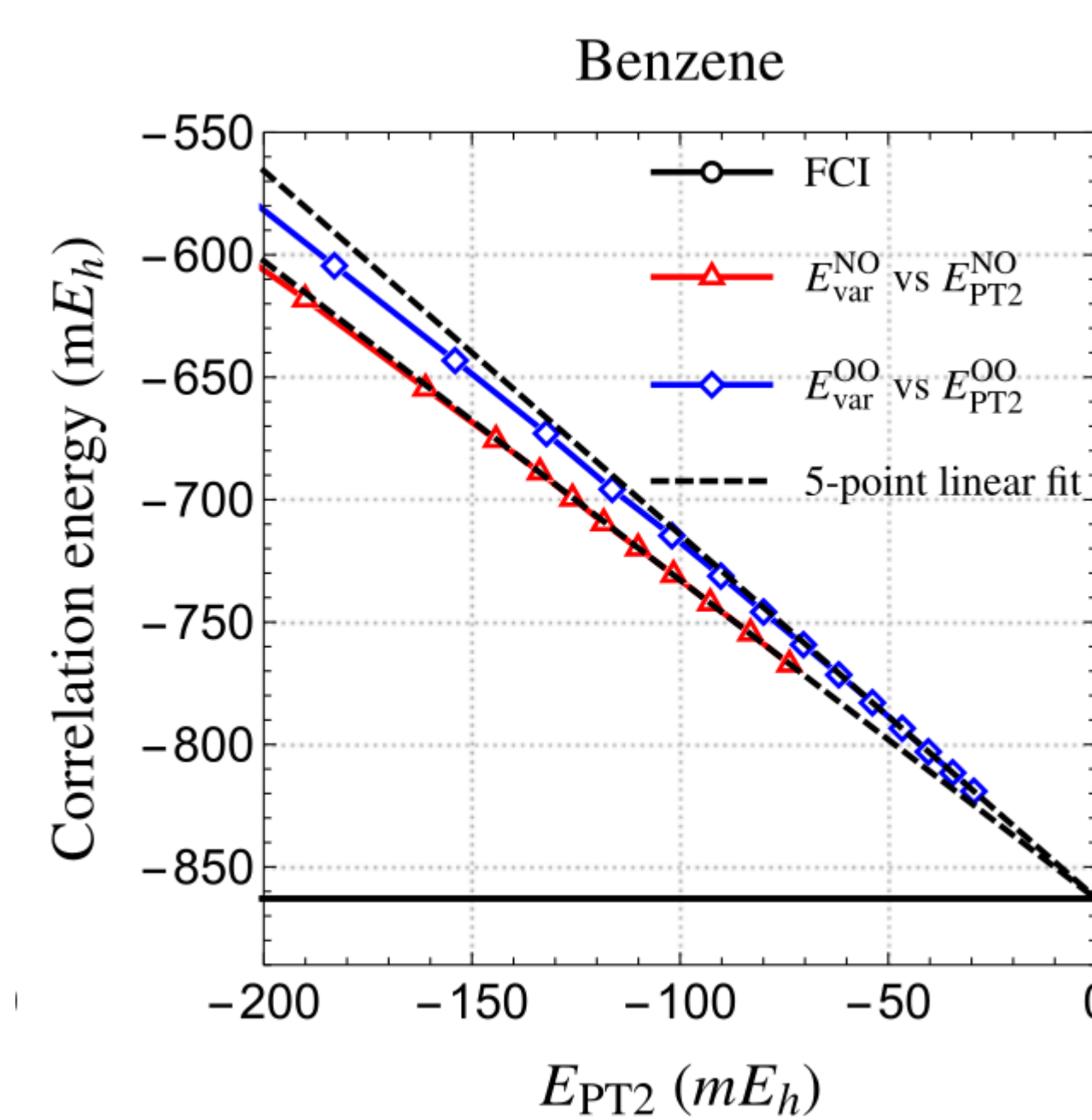


Figure 4. Benzene/cc-pVDZ, evolution of the correlation energy $E_{\text{corr}} = E_{\text{var}} - E_{\text{HF}}$ as function of E_{PT2} , for the natural orbitals (NO) and the optimized orbitals (OO). [7]

Conclusion

The aim of the orbital optimization is to provide more accurate energies. Thus, orbital optimization should enable to treat larger systems, with a smaller computational cost than with the usual natural or local orbitals. In fact, the orbital optimization works not only for the selected CI methods but for all the methods where the density matrices are available. In addition, the use of state-average density matrices enables to do the same thing for multistate calculations and to aim for more accurate excitation energies.

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