Local pyscf Documentation

Release 0.0

Artem Pulkin

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Contents

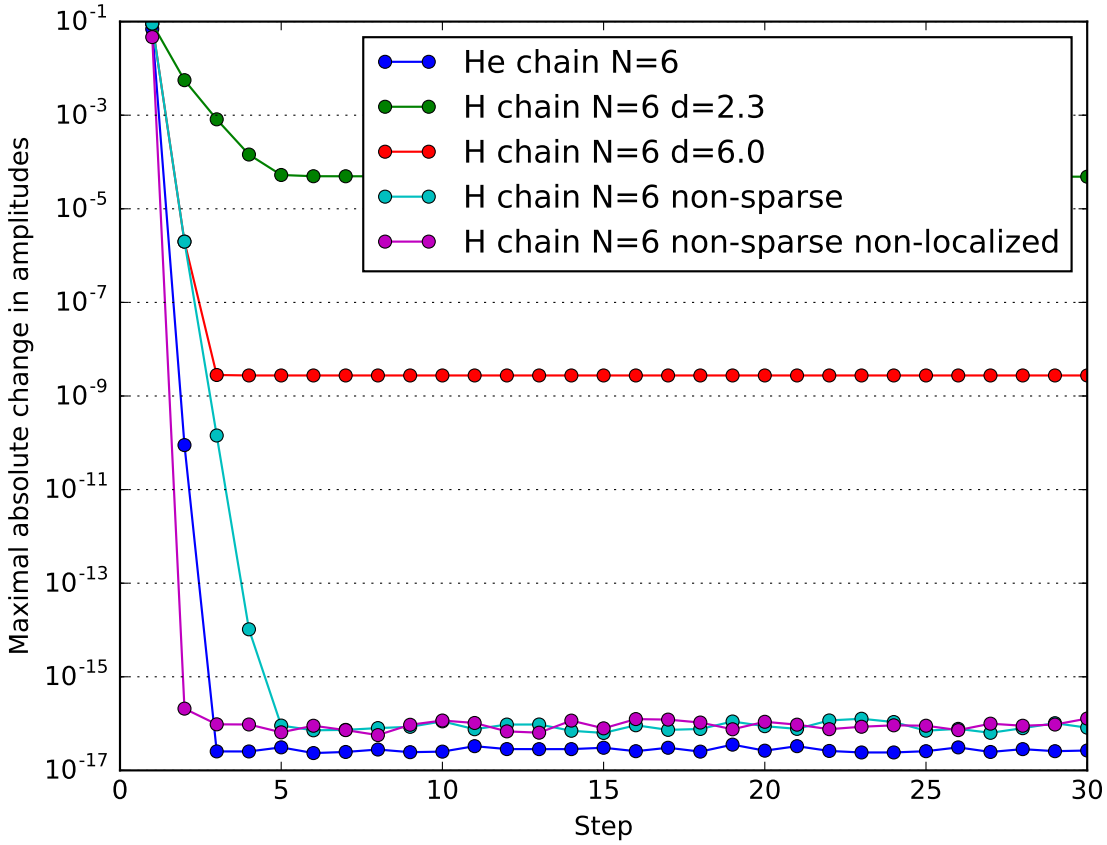
Contents:

CHAPTER 1

Local MP2 by Pulay and Saebo

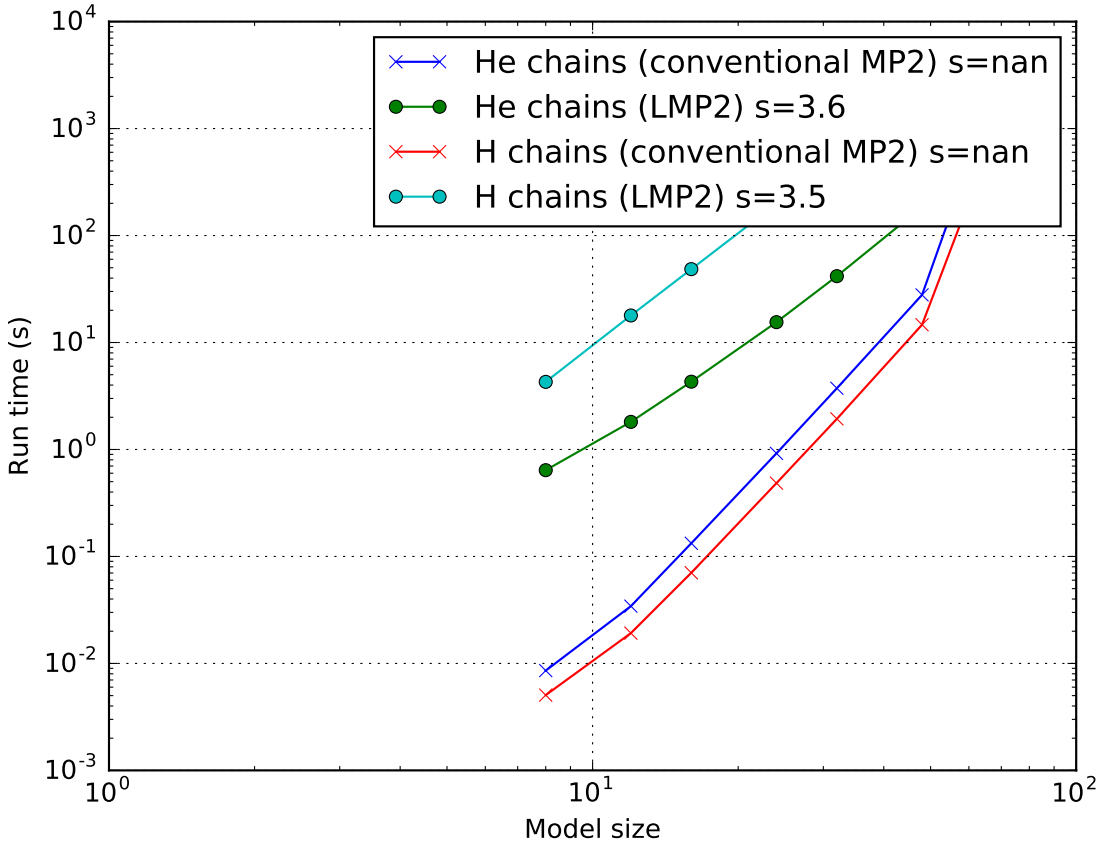
1.1 Convergence

The study of how the amplitude error decreases with iterations.



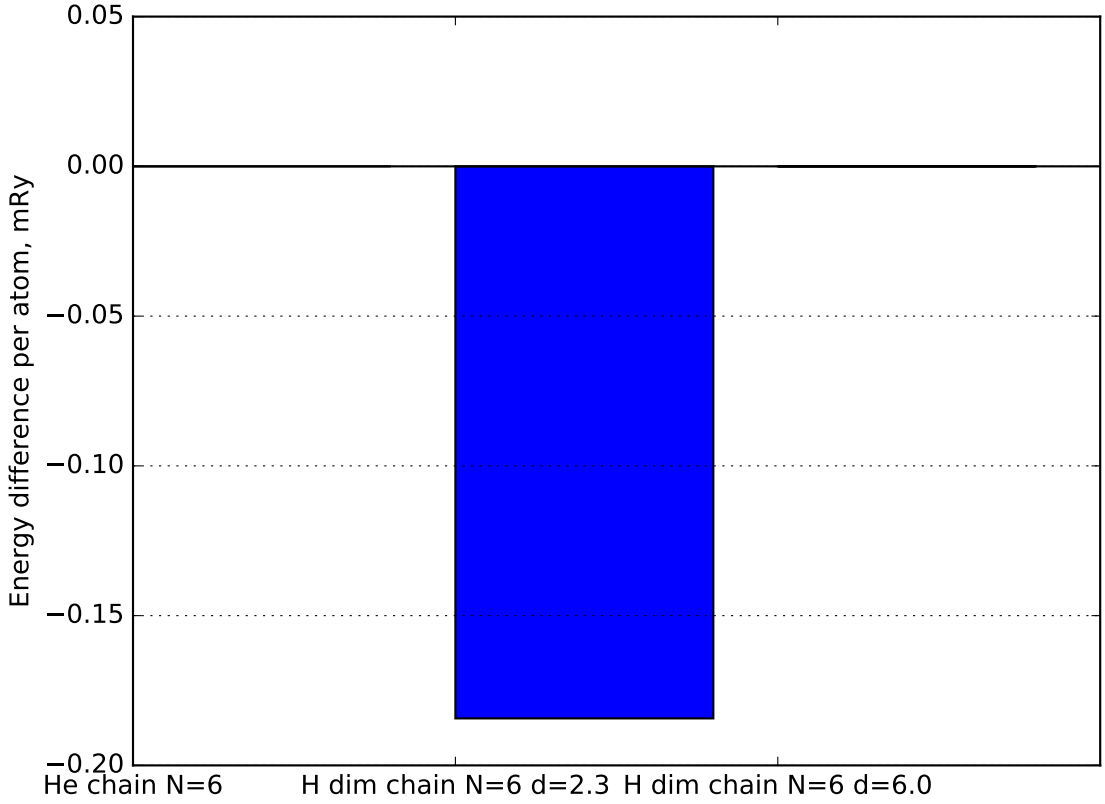
1.2 Complexity

The study of how the calculation time scales with the model increase. The expected problem complexity in conventional MP2 is $O(N^5)$ while this implementation of local MP2 should scale as $O(N^3)$ where N is the number of atoms in the system.



1.3 Errors in MP2 energies

Energies obtained with LMP2 compared to conventional MP2.


0.05
0.00
−0.05
−0.10
−0.15
−0.20
Energy difference per atom, mRy
He chain N=6
H dim chain N=6 d=2.3
H dim chain N=6 d=6.0

CHAPTER 2

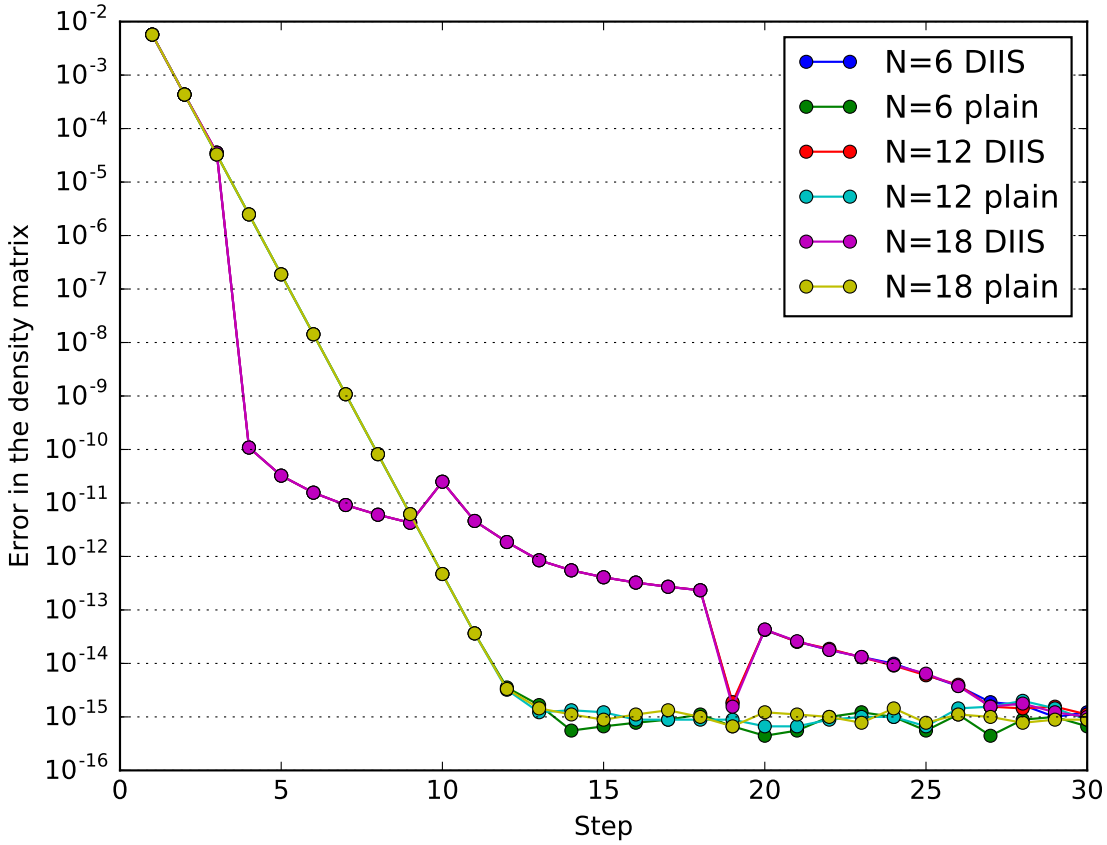
Divide-conquer HF by Kobayashi and Nakai

2.1 Case 1: Helium chains

The simplest case of closed-shell non-interacting systems assembled into a single model. The Helium atoms are arranged into chains with 6A spacing.

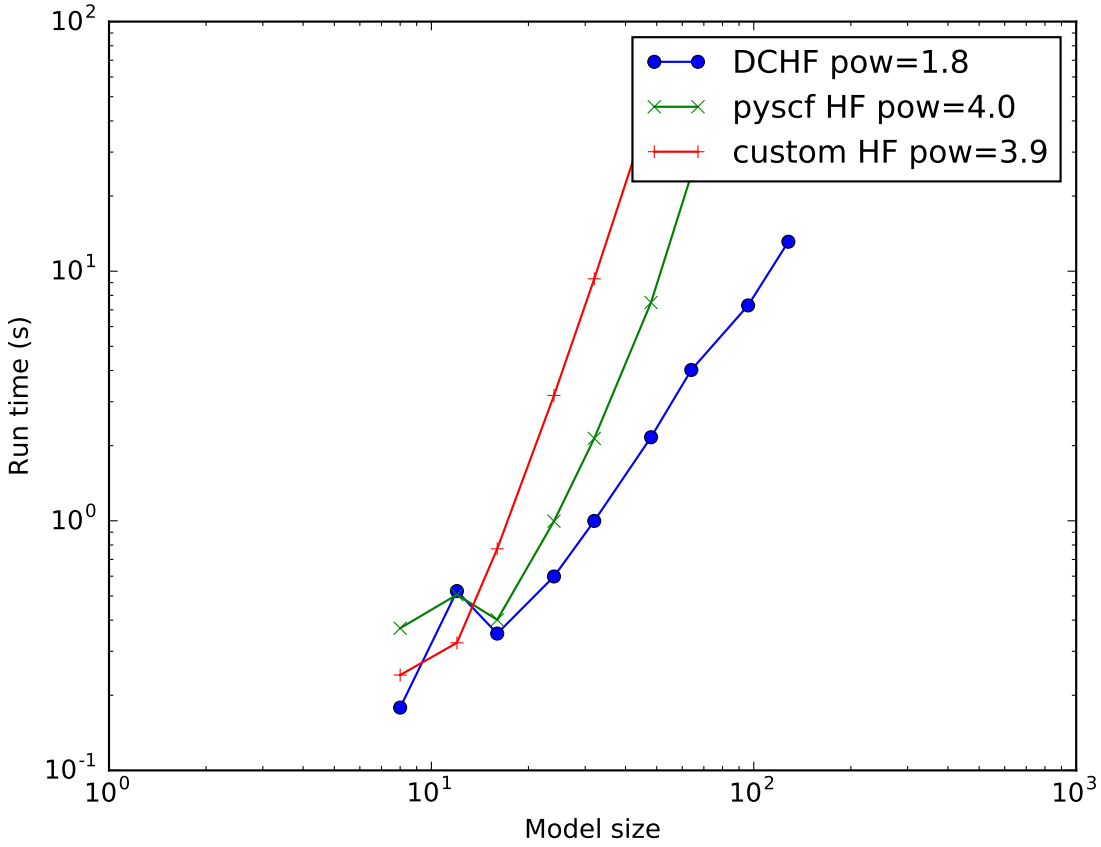
2.1.1 Convergence

The study of how the error in density matrix elements decreases with iterations; N is the number of Helium atoms in the model.



2.1.2 Complexity

The study of how the calculation time scales with the model increase. The expected problem complexity in conventional HF is $O(N^4)$ while this implementation of DC-HF should scale as $O(N^2)$ where N is the number of atoms in the system.



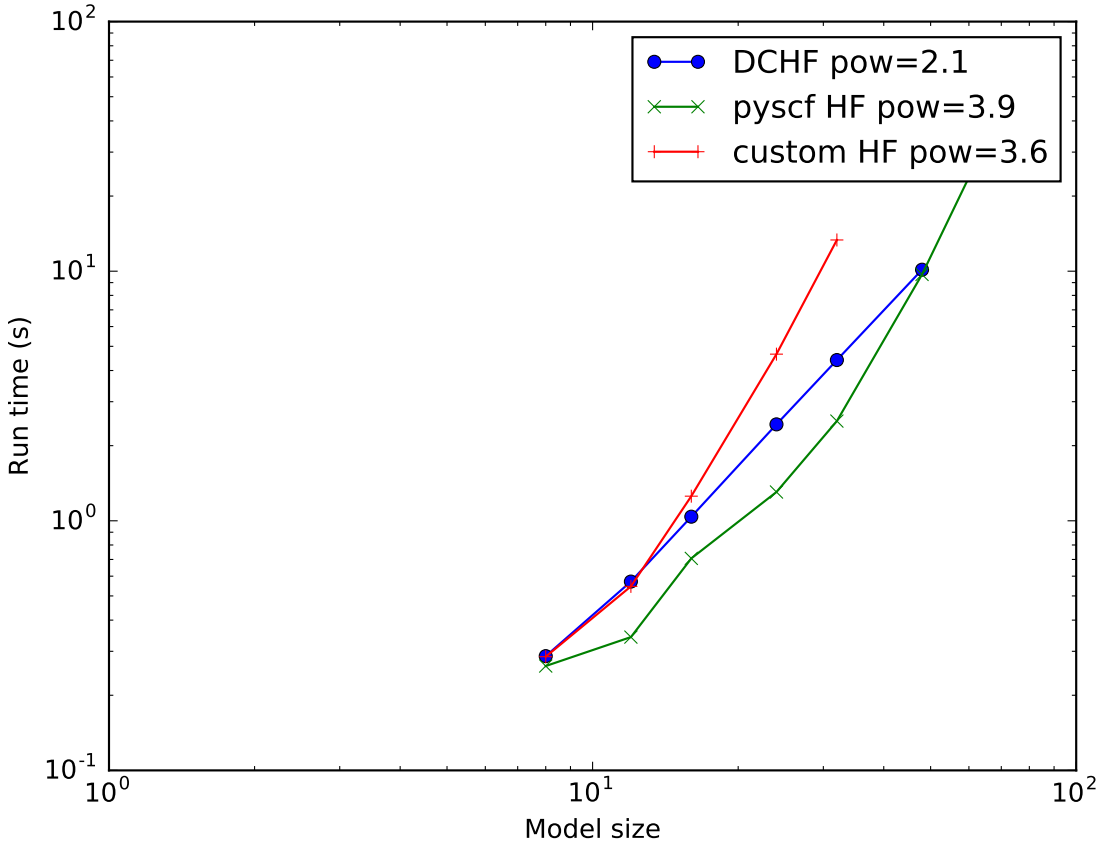
2.2 Case 2: Hydrogen dimer chains

Study of 1D dimerized chains of hydrogen atoms where the minimal distance between nearest neighbours is 1.4A and the maximal distance is 2.3A.

2.2.1 Complexity

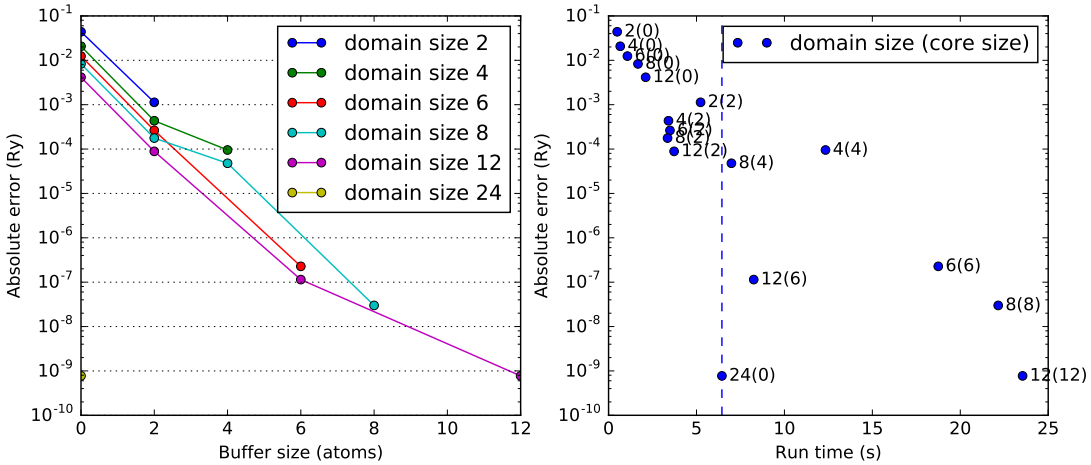
The subject model is split into domains with 4 atoms in the core region and 2 atoms in the buffer region at both sides of the domain (the 4(2) configuration).

The complexity is expected to be reduced from $O(N^4)$ of conventional HF to $O(N^2)$ for this implementation.



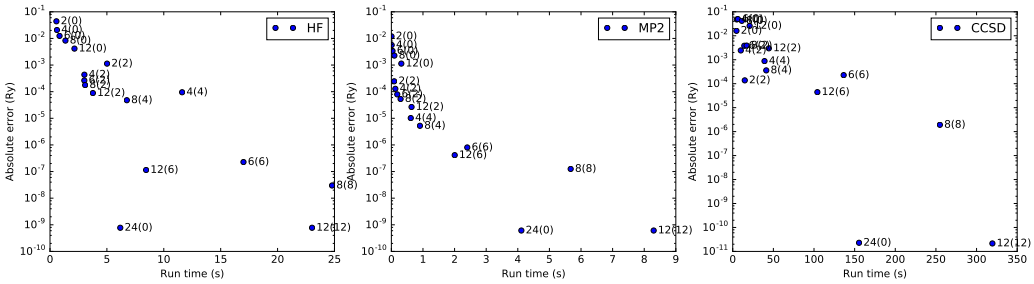
2.2.2 Domain size dependence

Errors in HF energies (compared to conventional HF) as a function of the domain size, buffer size and run time. The size of the chain considered is $N = 24$.

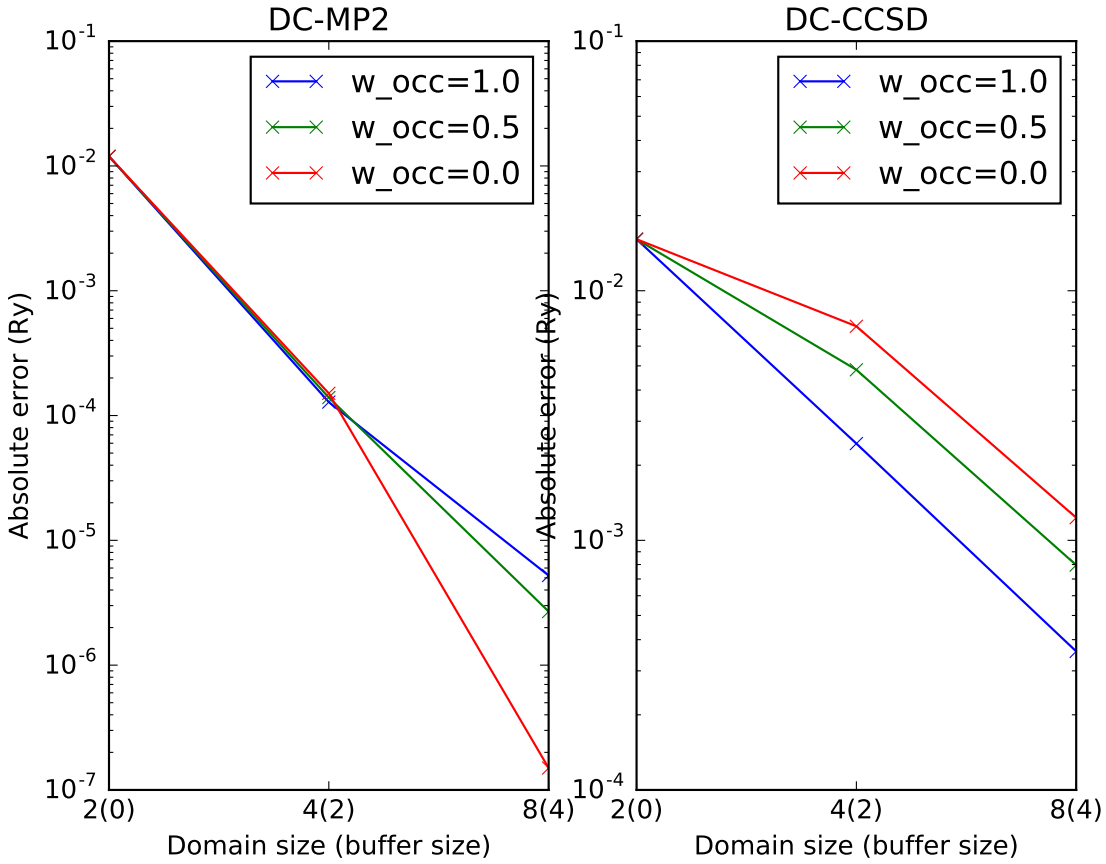


2.2.3 MP2 and CCSD energy corrections

Errors in total energies E_{HF} (HF) and E_{corr} (MP2, CCSD; compared to conventional approaches) as a function of the domain size, buffer size and the run time. The chain size is $N = 24$.



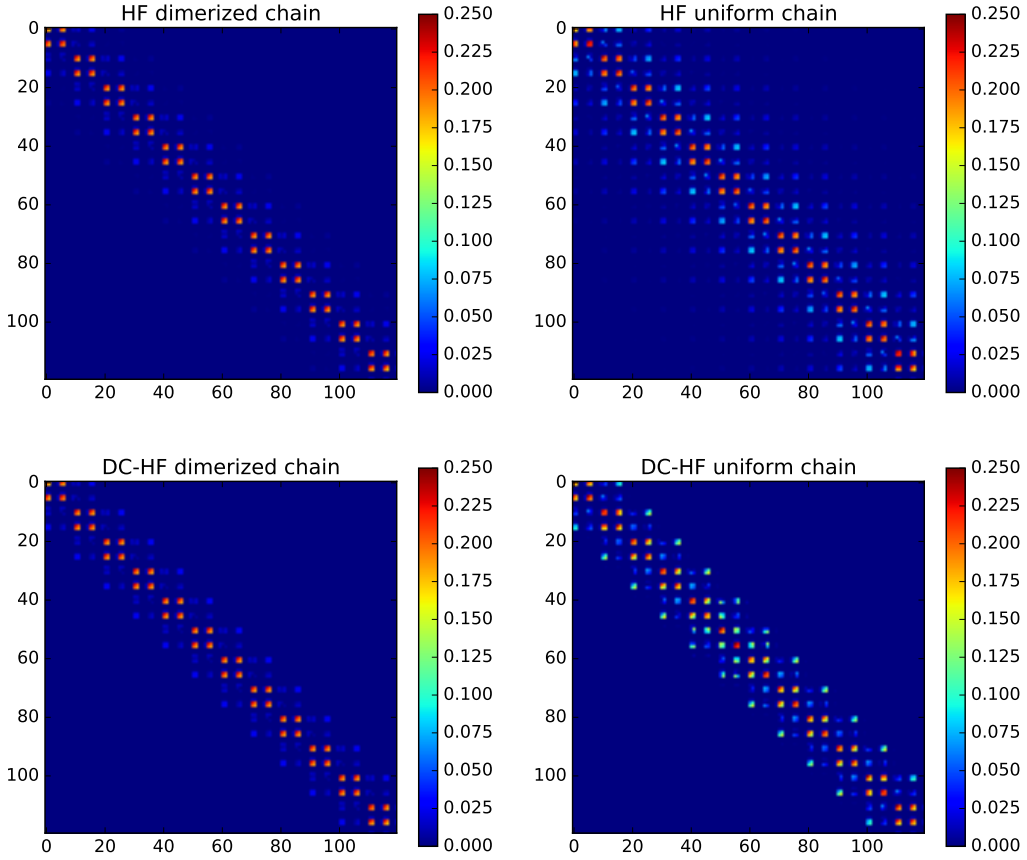
The errors slightly depend on the theory parameter w_{occ} as shown on the following plot.



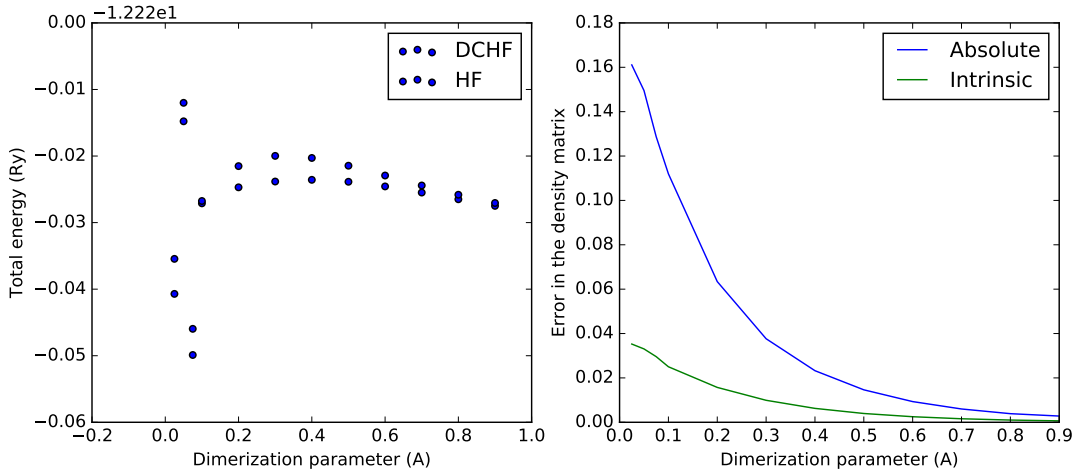
2.2.4 Difficult cases

The DC-HF essentially assumes locality of molecular orbitals. The more molecular orbitals extend, the larger error will be. The dimerization in hydrogen chains prevents delocalization of orbitals. Once the spacing between nearest hydrogens becomes equal, the orbitals become delocalized and the approximation fails. The following two plots

demonstrate absolute values of density matrixes (color) obtained from a conventional HF calculation and DC-HF for both dimerized and uniform chains.



The following two plots demonstrate how the total energy and the errors in DC-HF density matrix behave on the change of dimerization parameter, the difference between the maximal and the minimal distance between nearest neighbours in the chain. The minimal distance is kept constant at 1.4A.

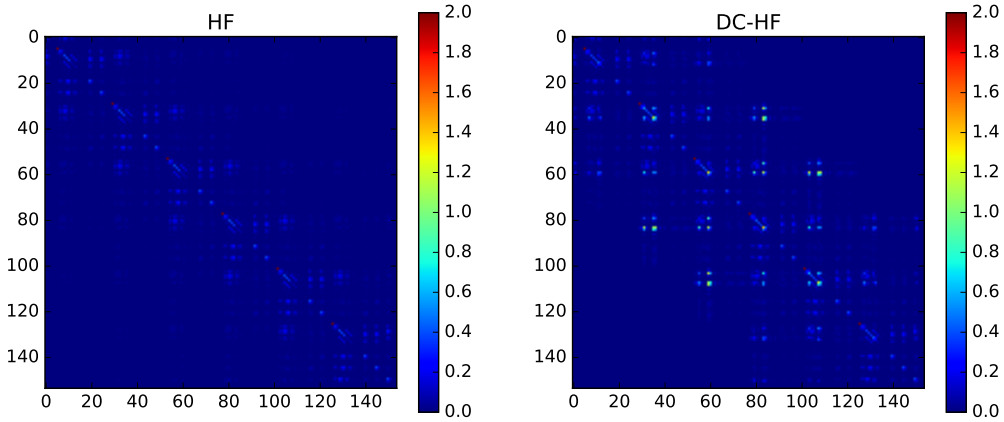


2.3 Case 3: Linear alkanes

The benchmark model is C_6H_{14} split into 6 clusters.

2.3.1 Basis set: cc-pvdz

The density matrix comparison:



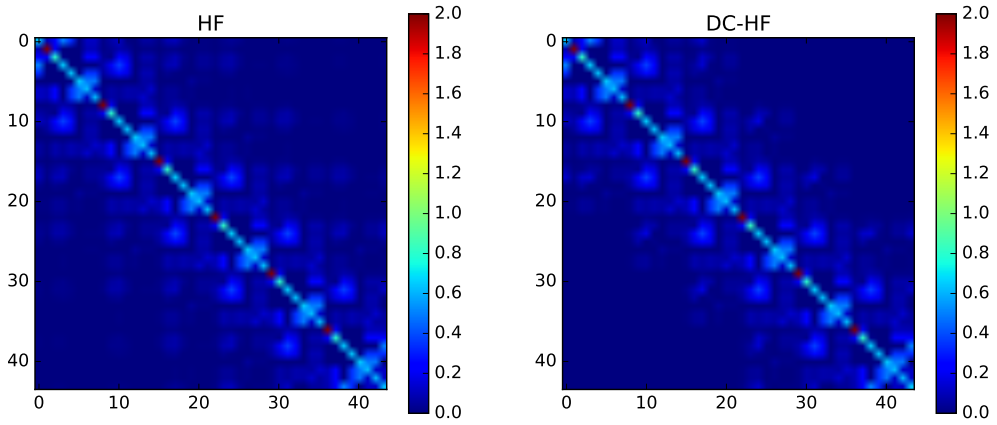
DM error: 1.27165943285

DM intrinsic error: 0.00862713587552

Energy diff: 0.769603364653

2.3.2 Basis set: sto3g

The density matrix comparison:



DM error: 0.0747824565832

DM intrinsic error: 0.0108856898115

Energy diff: 0.0193028866541

CHAPTER 3

Indices and tables

- genindex
- modindex
- search