

# A Subquadratic, Pair Atomic Resolution of the Identity-Based SOS-AO-MP2 Implementation in ADF

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We present a production level implementation of pair atomic resolution of the identity (PARI)[1] based second-order Møller–Plesset perturbation theory (MP2) in the Slater type orbital (STO) based Amsterdam Density Functional (ADF)[2] code[3]. Furthermore, we describe a subquadratically scaling, atomic orbital based spin-opposite-scaled (SOS)[4] MP2 approach with a very small prefactor[3], being order- $N$  in memory. Due to a worst-case scaling of  $\mathcal{O}(N^3)$ , our implementation is very fast for small- as well as for medium- and large-sized systems and shows an exceptionally early crossover to canonical, global density fitting based SOS-MP2. We report wall clock times for computations on realistic three-dimensional molecules and show, that triple- $\zeta$  quality calculations on molecules of several hundreds of atoms are only a matter of a few hours on a single compute node. In all considered cases, the computational bottleneck is the SCF, whereas the post-SCF energy correction can be calculated to the price of a few SCF cycles.

To demonstrate the accuracy of our implementation, we report systematic benchmark results for dimerization energies and relative conformational energies. Our results show mean absolute deviations to canonical, basis set extrapolated MP2 reference values of less than 1 kcal/mol when STO basis sets of triple- $\zeta$ -quality are used.

## References

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