

# Density Fitting in Explicitly Correlated Electronic Structure Theory

Andy May

*School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK*

## Abstract

Accurate quantum chemical calculations are limited to small molecules partly owing to the poor convergence of orbital based methods. One solution to this problem is to use explicitly correlated electronic structure theories [1]. These methods give very accurate energies for small molecules, but become computationally difficult for larger systems. The problem arises from the need to compute three- and four-electron integrals, which are both complicated and extremely numerous. The R12 methods developed by Kutzelnigg and Klopper [2–4] use Resolution of Identity (RI) to approximate these integrals and have allowed calculations on chemically significant problems.

In this work we develop a version of MP2-R12 theory for an arbitrary correlation factor and derive recurrence relations for the integrals needed when the correlation factor is a frozen Gaussian geminal [5]. We show that the accuracy of MP2-R12 methods can be greatly improved by replacing the conventional  $r_{12}$  factor with a function of  $r_{12}$  better able to describe the shape of the correlation hole. It is shown that the errors associated with using linear  $r_{12}$  (rather than something better) are at least an order of magnitude greater than the errors associated with RI or other approximations in the MP2-R12 class of methods. The impact on our aim to do accurate quantum chemistry in reasonably compact orbital basis sets is assessed.

## References

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