

Pair-Atomic Resolution-of-the-Identity

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The resolution-of-the-identity (RI) approximation [1, 2], or the density-fitting approximation, is today accepted as an efficient way to approximate the four-center two-electron integrals of the electron-electron Coulomb repulsion contribution appearing in Hartree-Fock and DFT. In the last two decades similar approximations have received significant attention also for the general application to four-center two-electron integrals, as for example for the exact exchange [3] and various correlated wave-function methods [4, 5]. For small to medium sized systems the extension of the RI approximation to general four-center two-electron integrals gives speed-ups comparable with that of the Coulomb repulsion contribution, at negligible loss of computational accuracy, whereas for larger systems the cost of these methods becomes increasingly expensive. The steep increase in computational cost is due to the non-local nature of the fitting procedures used today [6], in which a product of two basis functions (pair product) are approximated by auxiliary basis functions spanning the whole molecular system. As the size of the molecular system grows, the number of auxiliary functions included in an approximation of each pair-product increases proportionally.

In this presentation, we explore the pair-atomic resolution-of-the-identity (PARI) approximation, in which each pair-product is approximated by auxiliary basis functions centered only on the two parent atoms of the two basis-functions forming the pair product. We demonstrate the computational efficiency of the PARI approximation applied to the exact exchange contribution, and discuss both the accuracy of the presented results as well as the prospects for further extensions of this scheme to correlated wave-function treatment.

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