

Linear Scaling Density Fitting using Cholesky Decomposition

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The essence of density fitting (DF) is the exploitation of linear dependence in the direct product space of atomic orbitals (AOs). Specifically, products of AOs are expanded in an auxiliary basis set according to

$$\chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) \approx \sum_J \phi_J(\mathbf{r})C_{\mu\nu}^J \quad (1)$$

Like AO basis sets, auxiliary basis sets are usually composed of (Gaussian) functions centered on the nuclei. The auxiliary basis set is thus distributed over the entire molecule, making the fitting procedure nonlocal in general.

The computational cost of the fit is formally cubic with respect to system size, although prescreening gives essentially quadratic scaling in practice. Different techniques have been suggested to reduce the computational scaling to linear, including local fitting metrics and domain fitting. An alternative approach based on the inherent locality of auxiliary basis sets derived from Cholesky decompositions of subblocks of the molecular integral matrix is presented. It is demonstrated that only auxiliary functions centered on the same two nuclei as the AOs are needed to give an accurate fit. Leading to a trivially linear-scaling calculation of fitting coefficients, this procedure offers complete error control provided that two-center auxiliary functions are included.