Automatic generation of auxiliary basis sets for density fitting

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Density fitting, or the resolution of the identity approach, is a powerful method used to accelerate density functional theory, Hartree–Fock, and post-Hartree–Fock calculations in large orbital basis sets (OBSs). While compact auxiliary basis sets (ABSs) have been painstakingly optimized for standard OBSs for the calculation of single-point energies as well as geometry optimizations, the accuracy of these standard ABSs is unknown *a priori* for the reproduction of properties other than the total energy, as well as for non-standard OBSs. Because of these features, automatic schemes for obtaining ABSs are highly enticing, as they enable the use of the DF/RI approach for applications for which specialized ABSs have not been published. I will present the automatic algorithm I recently described in reference 1. At variance to the preceding automatic generators by Yang *et al.* [2], Aquilante *et al.* [3], and Stoychev *et al.* [4], the algorithm of reference 1 is applicable to any type of atomic OBS, employs only spherical auxiliary functions, and reproduces ABSs with a level of accuracy controlled by a single input parameter: the Cholesky decomposition threshold ϵ. The simple use of the method and the excellent accuracy of the generated ABSs are promising for future applications of the method.

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[1] S. Lehtola, Straightforward and accurate automatic auxiliary basis set generation for molecular calculations with atomic orbital basis sets, J. Chem. Theory Comput. **17**, 6886 (2021).

[2] R. Yang, A. P. Rendell, and M. J. Frisch, Automatically generated Coulomb fitting basis sets: design and accuracy for systems containing H to Kr., J. Chem. Phys. **127**, 074102 (2007).

[3] F. Aquilante, L. Gagliardi, T. B. Pedersen, and R. Lindh, Atomic Cholesky decompositions: a route to unbiased auxiliary basis sets for density fitting approximation with tunable accuracy and efficiency., J. Chem. Phys. **130**, 154107 (2009).

[4] G. L. Stoychev, A. A. Auer, and F. Neese, Automatic generation of auxiliary basis sets, J. Chem. Theory Comput. **13**, 554 (2017).