New atomic basis sets from coupled cluster primitives

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Notwithstanding the well-known flaws and shortcomings of configuration interaction (CI) theory, the vast majority of the basis sets currently used were constructed subjected to CI methods. The main objective of the present work is the generation of new basis sets based on primitives tailored for coupled cluster (CC) theory, targeting the description of valence electron correlation in both atomic and molecular systems. Gausisan primitive sets in each angular momentum shell are generated and extended until the incremental addition of a function grants an improvement below a certain energy threshold per electron. In shells with occupied orbitals, the primitives sets are constructed based on the Legendre polynomial expansion proposed by Petersson et al, [1] with the goal of convergence of the SCF energy. These primitive sets are subsequently augmented by polatization/correlating functions of higher angular momentum based on even-tempered expansions, enlarged in the same fashion as in the lower *l*-shells.[2]

[1] G. A. Petersson, S. Zhong, J. A. Montgomery, M. J. Frisch, *J. Chem. Phys.* **118**, 1101 (2003).
[2] D. Feller, K. Ruedenberg, *Theoret. Chim. Acta.* **52**, 231 (1979); M. W. Schmidt, K. Ruedenberg, *J. Chem. Phys.* **71**, 3951 (1979).