

New primitive Gaussians based on per electron energy convergence criteria

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Abstract: Even the simplest electronic structure calculation depend on the proper choice of two parameters, namely level of theory and basis set, and they can be equally important in obtaining meaningful and accurate answers. Notwithstanding the central role of correlation energy in high-accuracy calculations, Pople-style[1] and correlation consistent,[2] arguably the most popular basis sets, are based on theories with well-known deficiencies in the description of the correlation phenomenon. The former is optimized at the SCF level, that is, it does not come from a correlated method, while the latter depends on truncated configuration interaction (CISD) calculations, a non-size extensive method. On the other hand, coupled cluster (CC) not only does not suffer from these drawbacks but also surpasses CI analogs in their capacity of recovering correlation energy.[3] However, CC methods had not been employed in the development of new basis sets until recently, where they were used in conjunction with the atomic natural orbital (ANO) procedure to generate superior contraction coefficients from the primitives found in the correlation consistent bases.[4] These primitive sets are constructed by the addition of Gaussian functions that recover approximately the same amount of correlation energy, and it is assumed that the same number of primitives is suitable to treat all atoms in a given row of the periodic table. Here, we turn to a convergence criterion that is based on the energy improvement per electron, instead of the total energy recovery per additional primitive. The *sp* primitives are calculated from an optimized degree 5 Legendre polynomial for improved convergence,[5] while the polarization functions (*d* and higher angular momentum) come from optimized even-tempered expansions at the MBPT(2) level, which are shown to yield very similar results to CCSD(T) in terms of optimized exponents. The new primitive sets are converged within each angular momentum shell to a predetermined energy threshold per electron in the total CCSD(T) energy upon addition of extra functions for a given angular momentum.

References

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