High precision calculations on relativistic and QED energy of a-few-electron systems

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Abstract

For a-few-electron systems the exponentially correlated Gaussian (ECG) wave functions are able to provide the nonrelativistic energy converged to the submicrohartree level. However, the convergence of expectation values of relativistic and QED operators in the ECG basis is much slower than the convergence of the nonrelativistic energy. The slow convergence of the singular operators is directly related to the fact that the Gaussian type wave functions do not reproduce the interparticle cusps. Methods correcting this deficiency will be the main topic of the presented work. It will be shown that the accuracy of the expectation values of the singular operators like $\delta(\mathbf{r})$, p^4, and $P(1/r^3)$ can be improved by 2-3 orders of magnitude compared to that achievable from the traditional approach. Benchmark results for selected atomic and molecular systems will be presented. In particular, thanks to the increased accuracy, tiny relativistic and QED corrections to the helium dimer interaction energy can be reliably estimated.