Explicitly-correlated Gaussian geminals in electronic structure calculations

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Explicitly-correlated basis functions, i.e., functions containing an explicit dependence on the inter-electronic distance \( r_{12} \), can describe the electron-electron cusps in the wave functions much better than products of orbitals for a given size of basis set, but the costs of calculations are significantly higher in the former case. Explicitly-correlated functions have been the main tool for investigations of two-electron system since the early days of quantum mechanics. In 1960s, Boys and Singer [1, 2] introduced the basis set of Gaussian-type geminals (GTG), i.e., functions with an \( \exp(-r_{12}^2) \) dependence, later proved to be complete [3, 4]. For \( \text{H}_2 \), such functions give results competitive [5, 6] with those produced by the best alternative approaches, and at the same time GTGs can be applied to many-electron systems. GTGs can be used to represent pair functions in many-body perturbation theory (MBPT) and coupled-cluster (CC) methods in the so-called first-quantized approach [7–9]. For small molecules, the GTG basis appears to be able to reach accuracies higher than other approaches that are currently available. In particular, it has been possible to compute a helium dimer potential [10–12] which predicts thermophysical properties of helium so well that it has been used to calibrate some measurement standards. GTGs have been applied to molecules containing a dozen or so electrons [13], but such calculations are very time consuming due to the necessity of exponent optimization [14]. An alternative explicitly-correlated approach applicable to many-electron systems was proposed by Kutzelnigg and Klopper [15]. In this approach, \( r_{12} \) appears linearly, multiplied by products of orbitals, but the integrals are computed approximately by inserting resolutions of identity. Recently, the two approaches were merged in a sense in the so-called F12 method which uses a linear combination of GTGs instead of the \( r_{12} \) factor [16, 17].