Explicitly correlated Slater-type geminal theory

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The use of the resolution of the identity (RI) in explicitly correlated electronic structure theory has transcended the restriction to small molecules breaking up many-electron integrals into sums of products of two-electron integrals [1]. The recent progresses in the field are mainly on improving the accuracy and efficiency of such decompositions using auxiliary basis set (ABS) [2], complementary auxiliary basis set (CABS) [3], density fitting (DF) [4,5], and numerical quadratures (QD) [6]. For a given correlation factor, f_{12}, these methods require two-electron integrals for the operators, f_{12}, $-(\nabla_1^2 f_{12}) - (\nabla_1 f_{12})\cdot(\nabla_1 - \nabla_2)$, $-(\nabla_1 f_{12})\cdot(\nabla_1 f_{12})$, $r_{12}^{-1} f_{12}$, f_{12}^2, and so on, but no higher-rank operators arise. Most of the explicitly correlated treatments to date have employed either of the linear r_{12} function and a linear combination of Gaussian-type functions, for which the necessary integrals are calculated in closed form algebraic expressions.

More recently, we have shown that all of the necessary integrals for the Slater-type correlation factor [7] can be calculated from the special function,

$$G_m(T,U) = \int_0^1 dt t^{2m} \exp[-Tt^2 + U(1-t^{-2})] \quad (m = -1,0,1,...),$$

and excellent results can be obtained by the resulting Slater-type geminal (STG) method. Some authors have also reported the efficiency of the correlation factor shortly after [8,9]. My talk will concern the computational details of STG and some benchmark results involving weak interactions of simple molecules.

References

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