QMC over Slater type orbitals: Coulomb resolution.

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Abstract

Here, exponential type orbital basis sets, in particular Slater type orbitals (STO) or Coulomb Sturmians are considered for molecules.

In a limited number of cases, the well-known Neumann expansion suffices to obtain two-electron integrals in analytic closed forms. These include all atomic and diatomic Coulomb energy terms, because this expansion then leads to finite sums (often limited to a single term) as a result of orthogonality relations. However, very few two-center exchange integrals and no three- or four- center terms are amenable to such closed forms.

In the cases where no completely analytical expression is available, work analogous to the resolution of the identity, namely the Coulomb resolutions [1] have led P. Gill to approximate separations involving products of one-electron integrals obtained involving a potential arising from Poisson's equation.

The purpose of this work is to investigate the accuracy of such resolutions, as applied to three- and four- center integrals, from which they eliminate the cumbersome orbital translations. The approach is versatile, in that basis function types can be changed very easily (even can be switched to gaussians) and without changing the entire algorithm. Various choices can be made for the potential, subject to the restrictions described here. Several choices are compared and numerical accuracy is investigated.

Keywords:
Analytical two-electron integrals, STO, Coulomb Sturmians, Coulomb resolutions.

Presentation at the CESTC 2009, Hungary 25-28 spetember 2009.

References

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