Integrals over effective core potentials

Robert A. Shaw‡, J. Grant Hill
Department of Chemistry, University of Sheffield, S3 7HF
‡rashaw1@sheffield.ac.uk

The innermost electrons in atoms are not strongly perturbed by the electrons on nearby atoms. They can therefore be approximated well by a fixed potential, called an effective core potential (ECP).

Depending on the number of electrons frozen, this can greatly increase the efficiency of quantum chemical calculations without significant loss in accuracy. In fact, ECPs can be made to include relativistic effects. As these can be very important, especially for heavy atoms, they may even improve results.

The integrand will disappear for most combinations of the parameters, allowing many integrals to be avoided.

We have shown that it is rigorously enveloped by a spherical gaussian with exponent $p$, whose centre, $r_0$, is found by solving the equation below. In fact, it is accurate enough to be used to evaluate integrals below a given threshold.

Calculations are about 40 times faster than conventional algorithms. Both the prefactor and exponent of the scaling with system size are reduced.

The resulting algorithm is numerically stable across all arguments, due to the tightness of the prescreening bound. Importantly, a single approach is used for all arguments.

The integrals can be reduced to recursion on three soluble base integrals. This can then be unrolled a priori by a combinatorial search over a network.

This can then be used in combination with an algebraic simulator, leaving a minimal number of arithmetic operations on known quantities. Optimised code can then be generated for all integrals up to a given total angular momentum.

For example, from the network above, we get the algebraic expression:

$$<125> = \langle uu \rangle H_2 + \langle uu \rangle G_4 + \langle uu \rangle G_6 + \langle uu \rangle G_8$$

which simplifies to giving the following:

References