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SHORT COMMENT

Comment on "numerical treatment of two-center overlap integrals"

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Abstract The subject paper by H. Safouhi (J Mol Model 12:213–220, 2006) presents a scheme based on a nonlinear convergence acceleration transformation for the numerical evaluation of two-center overlap integrals of Slater-type orbitals. In this comment we argue that there is no reason to adopt such an approach, as well-known methods for these integrals are substantially superior both in speed and in accuracy.

Keywords Slater-type orbitals · Overlap integrals · Numerical evaluation of overlap integrals

A recent paper by Safouhi [1] starts from the erroneous premise that "two-center [Slater-type-orbital-STO] overlap integrals are... difficult to evaluate to a level of high accuracy". Safouhi's premise relies on the undisputed fact that the conversion of the STO overlap integral to its Fourier integral representation, as found in work by Weniger and Steinborn [2], yields an infinite-range one-dimensional integral with an oscillatory integrand, and direct evaluation of this Fourier integral is, indeed, difficult. The approach of Safouhi's paper is to introduce a nonlinear convergence accelerator to extrapolate a value of the oscillatory integral from the contributions of its first few lobes.

The reason this approach is flawed is that entirely satisfactory direct-space methods are available for STO overlap integrals, and these methods are inherently, by orders of magnitude, both more efficient and more accurate than the numerical methods advocated in the paper under discussion. It may be worth noting that excessive oscillation is often a signal indicating the inadvisability of using a Fourier representation; in the present application, the oscillations become ever stronger as the value of the overlap integral tends toward zero with increasing internuclear separation.

Complete direct-space methods for STO overlap integrals were first presented more than 50 years ago [3], and good methods for evaluating the one-dimensional integrals occurring therein became widely known after Corbató [4] showed in 1956 how the integrals known as B_n could be obtained stably from the easily computed spherical Bessel functions i_n. With some organizational improvements made by the present author in 1960 [5], these methods have been found to be both sufficiently rapid and sufficiently accurate, so that there is no need to try to coax good results from a formulation that is clearly nonoptimal.

To illustrate the accuracy and effectiveness of the established methods for STO overlap integrals, we used our existent computer programs to reproduce all the integrals in Safouhi's Table 3. Our computations can be run at any desired precision; we started by obtaining integrals guaranteed to have twelve correct significant digits. Comparing with the presumably authentic values, labelled [13–16] in Table 3, we found negligible discrepancies (1 in the final place) in lines 4, 8, 11, 18, and 24, a two-digit discrepancy in line 25, and gross errors in the entries on lines 22 and 26 (the respective accurate values are 0.100640064×10^{-5} and $-0.115825653\times10^{-3}$). No agreement at all was obtained for lines 14–17 until we noticed that the data were for different input than given in the table. When we changed the ζ_1 values (labelled ξ_1 in the table) for these lines to the respective values 10, 30, 10, 10, we observed negligible

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discrepancies for lines 14, 16, 17, and a last-place discrepancy of 9 units for line 15.

We then repeated the integral computation at standard double-precision arithmetic (somewhat less precise than the above-described reference computations); we found that all the integrals of Table 3 were reproduced with absolute errors less than 10^{-10} hartree.

Looking next at the values from the numerical treatment, labelled $\overline{D}$ in Table 3, we note that correction of the "authentic literature values" reduced the apparent error in the $\overline{D}$ results, but that some (e.g. lines 17 and 25) still exhibit absolute errors as large as 10^{-5} hartree. Such errors are far too large for serious work, and are not consistent with the claim of "a highly accurate algorithm".

Considering now matters of efficiency, the direct-space computation involves (for an integral with indices *n, l, n′, l′*) a set of auxiliary integrals A_k and B_k with $0 \le k \le n+n'$, and the formation of a sum of products of the generic form $c_{kk'}A_kB_{k'}$. The coefficients $c_{kk'}$ have values that depend on the quantum numbers but not the real-valued parameters, and can be read from a reference table. For the integrals of Table 3, the sums have an average of 60 terms, thus requiring a total of about 180 computer operations. The work needed to make A_k and B_k depend on the parameter values, but a rough estimate of the average number of operations required for the set of A_k and B_k for an entry of Table 3 is about 450. Combining these operation counts (and increasing by another 10%), we estimate some 700 computer operations per table entry when obtained by standard direct-space methods.

The numerical treatment described by Safouhi involves Gauss-Legendre quadrature of order 48 for each of a sufficient number of lobes of an oscillatory integrand, repeated for integrands containing spherical Bessel functions j_λ of approximately $(l+l')/2$ different λ values. The data of Safouhi's Table 4 suggest that an average of seven lobes might be adequate; from Table 3 we deduce that an average of five λ values would occur. These data indicate that 48×7×5 integrand evaluations would be needed; each integrand evaluation [cf. Safouhi's Eq. (13)] involves at least ten elementary operations plus the evaluation of a Bessel function; a reasonable overall operations count for an integrand evaluation cannot be less than 20. Ignoring the overhead involved in the convergence–accelerating transformation, and also that in conversion from B-functions to STOs, the complete numerical evaluation of an entry in Table 3 must require of the order of 48×7×5×20, or nearly 35,000 operations. This is nearly two orders of magnitude more than would be needed for the direct approach.

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