Direct evaluation of overlap integrals between Slater-type-orbitals

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We derive direct single-stage numerical evaluation of the electronic overlap integral between arbitrary atomic orbitals (including STOs). Integration is over cartesian co-ordinates, and replaces previous sums over 'special' functions. The results, in Mathematica 10 and Maple 18, agree with the literature to ~ 8 digits. We briefly discuss possible use in quantum chemistry, including accuracy, algorithmic suitability and operating-system machine-implementation as an intrinsic function.

I. INTRODUCTION

Single-centre electronic orbitals,
\[ \psi_{nlm}(r) = F_{nl}(r, \alpha) Y_{ml}(r), \] (1)
are building blocks in the quantum description of atoms, molecules, and, hence in general of matter. In Eq(1) \( F_{nl}(r) \) is a radial function, \( Y_{ml} \) is a solid harmonic, and \( Y_{ml} \) the familiar spherical (surface) harmonic. We state that vital parts of Molecular Quantum Mechanics can be built with the overlap integral
\[ I(\mathbf{R}) = I(r, n, l, m, n', l', m') = \int dr \psi_{nlm}^*(r) \psi_{n'l'm'}(r - \mathbf{R}) \] (2)
where vector \( \mathbf{R} \) is the spatial separation of the two orbital centres. Important normalised \( F_{nl}(r) \) are the Gaussian-
\[ F_{nl}(r) = e^{-\beta r^2} \] (3)
and Slater-type-orbitals (STOs)
\[ F_{nl}(r, \alpha) = F_{nl}(x, y, z, \alpha) = \frac{(2\alpha)^{n+1/2}}{(2n)!} r^{n-1-l} e^{-\alpha r}, \]
\[ r = r(x, y, z) = \sqrt{x^2 + y^2 + z^2} \] (4)
where \( \alpha \) is a screening constant. The STO is accepted as physically superior to the GTO, but numerical evaluation of its \( I(\mathbf{R}) \) is more difficult; both have previously used special and associated functions, including: Fourier, Bessel, Laguerre, Gegenbauer, Gaunt, Hobson, .. . We shall next evaluate the \( I(\mathbf{R}) \) for STOs, as a direct single-stage integration, with no summations over 'special' functions.

II. ANALYSIS

From Eq(1) and Eq(2) we have
\[ \psi_{n'l'm'}(r - \mathbf{R}) = F_{n'l'}(|r - \mathbf{R}|, \alpha') Y_{m'l'}(r - \mathbf{R}), \] (5)
which is valid for arbitrary \( F(r) \) and, with cartesian vectors \( r(x, y, z) \) and \( R(X, Y, Z) \), will use
\[ |r - \mathbf{R}| = r' = r'(x, y, z) = \sqrt{(x - X)^2 + (y - Y)^2 + (z - Z)^2}. \] (6)

Also, we use the cartesian solid-harmonic\(^{1,2} \) in Eq(5)
\[ F_{nl}(x, y, z, \alpha) = Y_{ml}(x, y, z) = \left[ \frac{(2l+1)(l+m)!(l-m)!}{4\pi} \right]^{1/2} \]
\[ \sum_{k=0}^{[(l-m)/2]} (-i)^k \frac{(x - iy)^{k+m} (x - iy)^k z^{l-m-2k}}{2^{2k+m} k! (l-m-2k)!}, \]
\[ l = 0, 1, 2, .. ; m = -l..+l \] (7)

Thus with Eqs(5,6,7) in Eq(2) we have
\[ I = I(X, Y, Z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz F_{nl}(x, y, z, \alpha) Y_{ml}(x, y, z) \]
\[ F_{n'l'}(x - X, y - Y, z - Z, \alpha') Y_{m'l'}(x - X, y - Y, z - Z) \] (8)

The \( I(X, Y, Z) \) of Eq(8) can be evaluated by direct numerical computation and is valid for arbitrary orbitals specified by \( F_{nl}(r) \); this is our desired solution.

For the case of an STO (8) becomes
\[ I = I(X, Y, Z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \]
\[ \frac{(2\alpha)^{n+1/2}}{(2n)!} r^{n-1-l} e^{-\alpha r} Y_{ml}(x, y, z) \]
\[ \frac{(2\alpha')^{n'+1/2}}{(2n')!} r'^{n'-1-l'} e^{-\alpha' r'} Y_{m'l'}(x - X, y - Y, z - Z), \]
\[ r = \sqrt{x^2 + y^2 + z^2} \quad r' = \sqrt{(x - X)^2 + (y - Y)^2 + (z - Z)^2} \] (9)

III. NUMERICAL RESULTS

We use Mathematica 10 and Maple 18 to calculate Eq(9). Each integral in the table below contains a
comma (e.g. -0.117413789, 53804531) whose left figures agree with literature values\(^3\)\(^{-10}\): this is typically 8 digits. These data are collected in\(^9\),\(^10\).

IV. DISCUSSION

Our overlap integrals for STOs Eq(9) agree with the literature to \(\sim 8\) digits. We ask active experts (quantum chemists/physicists and computer-aware numerical-analysts) if our direct evaluation Eq(10) could be useful.

Present methods, (sums over special function, SS) e.g.\(^3\)\(^{-10}\), to calculate Eq(9) are acceptable, so our proposed direct integration (DI) should consider *inter alia*:

- What minimum accuracy is needed for quantum molecular calculations? If >8 digits, then SS and DI give different values and we must ask.

- Which of SS and DI is more accurate (suitable)? It would be wrong to automatically assume that the established SS is more accurate: SS and DI are different methods needing expert comparison. Along with accuracy we would like DI to have suitable and natural notation for its purpose, so we ask.

- How would DI handle/evaluate any of the several integrals (of which the overlap is but one) occurring in quantum molecular mechanics? We sketch evaluation of coulomb \((ab|cd)\), 'the two-electron, four centre integral, one of the greatest problems in quantum chemistry'\(^{11}\):

\[
(ab|cd) = (12|34) = \int \frac{d1 \, d2 \, \psi_a(r1) \psi_b(r1)^* \psi_c(r2) \psi_d(r2)^*}{r_{12}},
\]

where

\[
\psi_a(r1) = \psi_{n_a l_m a}(\alpha_a, x1, y1, z1), \quad d1 = dx1 \, dy1 \, dz1,
\]

\[
r_{12} = |R + r2 - r1| = \sqrt{(X + x2 - x1)^2 + (Y + y2 - y1)^2 + (Z + z2 - z1)^2},
\]

etc., and is evaluated in Mathematica 10 in the same way used for overlap Eq(9).

V. REFERENCES

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| n l m n' l' m' α α' R θ Φ     | integral Eq(9) | ref |
|---|---|---|---|---|---|---|---|
| 1 0 0 2 1 0 10 2 1.4 0 0 | -0.117413789,53804531 | 3 |
| 2 1 0 5 2 0 2 0.3 1.4 0 0 | -0.23323008,22624455-2 | 3 |
| 3 2 0 3 2 0 7.5 2.5 5 π/3 2π/3 | -0.68034002,4312253-4 | 4 |
| 3 2 1 3 2 0 9.7 6.4 0.3 π/9 3π/4 | 0.013735076.44 | 5 |
| 8 0 0 8 0 0 5 1 1 0 0 | 0.0107437341.23348333 | 6 |
| 10 7 1 8 1 1 3 3 10 0 0 | 0.23447835,22183802-2 | 7 |
| 1 0 0 1 0 0 10 10 1.4 0 0 | 0.66799473,05543532-4 | 8 |
| 2 1 0 2 1 0 2 2 1.4 0 0 | -0.10074038,66530121 | 8 |

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