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2E01 Molecular calculations with the Slater-type orbitals

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Introduction In recent molecular physics and theoretical chemistry, most people use basis sets consisting of Gaussian-type orbitals (GTO). However, it is well known that GTO, $\exp(-\alpha r^2)$, have, at least, two serious defects; i.e., (a) they have no cusp at $r = 0$ and (b) decay too fast at $r \to \infty$. In contrast with GTO, the Slater-type orbitals (STO) have the right cusp and long distance behavior. It is clear that STO should be the natural choice for molecular calculations, but the fact that they lead to difficult integrals have seriously hindered their use in this field. Recently, two of us (R.L. and J. F. R) showed that the difficult integrals (which are the four-center electron-repulsion integrals, ERI) can be calculated with using the so-called STO-NG expansion with an enough precision [1]. They developed a computer program named as SMILES2003 for the molecular calculations with using STO as basis functions [2]. The accompanying coordinate expansion (ACE) algorithm developed by one of us (K. I.) is capable to compute such integrals extremely fast [3]. We revised the SMILES2003 to SMILES2007 with using the ACE algorithm for the four-center ERI.

Table I. Speeding up ratio for the individual ERI by the ACE algorithm

ERI type	SMILES 2003	SMILES 2007	Parallel	Total effect
(1s1s|1s1s)	1 .62 ms	992 μs	117 μs	14 times faster
(2p2p|2p2p)	20 .8 ms	4 .74 ms	212 μs	98 times faster
(3d3d|3d3d)	454 ms	18 .6 ms	614 μs	740 times faster
(4f4f|4f4f)	18 .8 s	50 ms	4 .0 ms	4700 times faster
(5g5g|5g5g)	68 .7 s	84 ms	27 ms	2500 times faster
(6h6h|6h6h)	260 s	236 ms	149 ms	1700 times faster

Computation time was measured with a HITAC sr11000 computer.
The 64 processors were used for the parallel computation
For all four-center computation, the STO-12G expansion is used for 1s-, 2p-, and 3d-type STO, the STO-11G is used for 4f- and 5g-type STO, and the STO-10G is for 6h-type STO.

Table I shows that the speeding-up ratio in the computation time from as in SMILES2003 to as in SMILES2007. The parallel version of SMILES2007 is extremely efficient, as seen in Table I.

Table II shows the total computation time for several molecules with using the parallel version of SMILES2007. We are now tractable to the computation of middle-sized molecules like adenine with the STO as basis functions, as seen in Table II.

Table II. Total computation time of the four-center ERIs over STOs for several molecules

Molecule Basis (# of STOs)	SMILES 2007 single processor	Parallel computation with 64 processors
Methanol CH_3OH (18 electrons; C_s)		
VB1 (62 STOs)	79 sec.	3.6 sec. (22 times faster)
VB2 (130 STOs)	990 sec.	35 sec. (28 times faster)
VB3 (244 STOs)	7928 sec.	270 sec. (29 times faster)
Benzene C_6H_6 (42 electrons D_{2h})		
VB1 (150 STOs)	789 sec.	44 sec. (18 times faster)
VB2 (300 STOs)	8699 sec.	410 sec. (21 times faster)
Adenine $C_5H_5N_5$ (70 electrons; C_s)		
VB1 (220 STO2)	19490 sec.	1095 sec. (19 times faster)
VB2 (425 STOs)	201128 sec.	8698 sec. (23 times faster)

The basis set of VB1 is a “triple-zeta + polarization”

The VB2 is a “quadruple zeta + double polarization”

The VB3 is a “quintuple zeta + triple polarization”

We may conclude that we have now an efficient tool to compute molecules with STO.

The next will be the geometry optimization of molecules. We need derivatives of molecular integrals for such purpose. We derive the derivatives of one-electron integrals and present them at the meeting.

References

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