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Algorithm for the four-index transformation of primitive molecular integrals stored in triples

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Summary. We present an algorithm for the evaluation of the operators J^{ij} and K^{ij} as well as for the full four-index transformation from primitive molecular integrals stored in partially reordered sets of triples $(pq\,|\,rs)$, $(pr\,|\,qs)$, $(ps\,|\,qr)$ rather than in canonical order.

Key word: Integral transformation

1 Introduction

It is well known that the conventional routines for building Coulomb and exchange operators from the stored primitive electron repulsion integrals such as they are implemented in Hartree–Fock programs should not be used when a large number of operators from a set of molecular orbitals or the so-called full four-index transformation of the molecular integrals is needed. In connection with multireference and configuration interaction calculations either one of the following situations may arise. If N is the total number of orbitals, $p, q, r \ldots$ designate indices or labels of the basis functions (AOs) and $i, j, k \ldots$ molecular orbitals (MOs) with expansion coefficients $C(i, p)$, then a number of Coulomb operators $J^{ij} \equiv (ij\,|\,pq)$ and exchange operators $K^{ij\pm} \equiv 0.5[(pi\,|\,jq) \pm (pj\,|\,iq)]$ in terms of a restricted set of M MOs ($i, j = 1, \ldots, M \leqslant N$, often $M \ll N$) may be required in the AO basis ("two-index integral transformation") or transformed to the MO basis ("four index transformation"). Following Saunders and van Lenthe [1] we speak of a partial transformation if only an incomplete list of transformed integrals is required, e.g. a selection of Coulomb or exchange operators. The construction of all possible Coulomb operators in the MO basis, i.e. the transformation of an integral list over N AOs to M MOs is termed "full transformation" even if $M < N$. Special algorithms have been developed to this purpose which reduce the number of operations considerably, because instead of the construction of one operator at a time by multiplication of the repulsion integrals with density matrix elements corresponding to an N^6 step typical for Hartree–Fock programs the efforts are proportional to N^5 when two or more consecutive multiplications with orbital expansion coefficients are carried out [1–8]. For rapid transformation the primitive integrals should be arranged in suitable order. If the orbital labels are not stored together with the integrals this is usually the so-called canonical order. Saunders and van Lenthe [1] propose a slightly different ordering which allows a more efficient program structure.

We take the opportunity of the sixtieth birthday of Prof. Werner Kutzelnigg to present an alternative method which we have used for several years already without the intention of publishing. Following an idea of Meyer and Ahlrichs (see [9] and ref. 7 therein) instead of the canonical order the integrals can be stored in triples together with their labels, as will be explained in more detail below. This method which is frequently used among the pupils of Kutzelnigg has several advantages: Depending on the algorithm of integral evaluation certain preparatory steps need be carried out only once and the length of the integral file can considerably be reduced when small integral triples are omitted. Furthermore it allows efficient construction of the Fock operator when doing Hartree–Fock calculations. Therefore a fast method for the integral transformation is desirable.

2 The integral program

Our integral program is a very fast combination of the HONDO formalism by Dupuis et al. [10] and King and Dupuis [11] for cartesian Gaussian basis functions (delivering the integrals in l-shell packages) and the integral storage by triples. As usual in HONDO an outer set of loops running over the different shells is combined with loops over the primitive functions or contractions within each shell (a shell consists of all basis functions with the same center, orbital exponents, contraction scheme and angular momentum quantum number). The basis functions need not be chosen symmetry adapted. Instead equivalent sets of integrals are calculated only once and given an appropriate weight (as a consequence after construction in the AO basis the operators must be symmetrized). Each record of the integral file consists of the four labels of the basis functions $p \geqslant q \geqslant r \geqslant s$ and the three integrals $R_1 = (pq\,|\,rs)$, $R_2 = (pr\,|\,qs)$ and $R_3 = (ps\,|\,qr)$. The integral triples can be thought of as constructed in a fourfold loop; they would then be ordered in the same way. Because of multiple storage of integrals with identical labels the total number of integrals is slightly larger than in canonical order. However, because of the use of shells and of equivalences and because small integral triples are omitted, not all possible triples are stored and the stored triples are not strictly ordered.

For the present application in contrast to Ahlrichs' original proposal the three integrals of each triple must be multiplied with the following factors: 1 if all orbital labels are different; 1/2 if $p = q$, $q = r$ or $r = s$; 1/4 if $p = q$ and $r = s$; 1/6 if $p = q = r$ or $q = r = s$; 1/24 if all four labels are identical. This is equivalent to dividing by $(1 + \delta_{pq})(1 + \delta_{rs})(1 + \delta_{pq,rs})$ and omitting identical integrals.

3 Preparation of the integral files

Given a file of primitive integrals before transformation the following preparations have to be carried out:

- Construct an integral file (A-file) which is arranged strictly in the order of the first and second label. This means that the values of p must increase monotonously and the same must be true for the q within constant p. The ordering of the r and s labels as well as the completeness of the triples is irrelevant.

- Construct an integral file (B-file) which is arranged in the order of the first and third label, p and r.

This task can be accomplished easily with a sorting routine (e.g. Quicksort). Ordering of the whole integral file can be broken down to ordering of all integral triples belonging to the same largest shell label (the outermost loop of the integral program). Thus, the size of the largest block of integrals to be ordered is proportional to N^3. At the same time premultiplication of the integrals with the factors discussed in the preceding section can be carried out, if not already done in the integral program. Ordering techniques have been introduced by Yoshimine [12] in the context of configuration interaction calculations, however applied rather to the list of symbolic matrix elements than to the electron repulsion integrals.

4 Integral transformation

Integral transformation consists of two consecutive two-index transformations, first the construction of operators in terms of MOs and second the transformation of these operators to MO basis.

The first step where the crucial reduction of floating point multiplication operations (FPMOs) can be achieved is shown below in FORTRAN-like notation; $+=$ means to add the right-hand side to the sum at the left. Six $M \times N$ matrices UX, UY, VX, VY, WX, WY and a second set of orbital coefficients $D(i, p) = 0.5 * C(i, p)$ $(i = 1, \ldots, M,\ p = 1, \ldots, N)$ must be provided.

```
     DO 100  all pairs of labels $N \geqslant x \geqslant y \geqslant 1$
     Initialize matrices $UX, UY, VX, VY, WX, WY$ to zero.
C    Processing of the primitive integrals: $2M$ FPMOs per integral.
     DO 20  Read all integral triples with labels $x$ and $y$ from the A file.
     $A1 = (xy|rs)$,          $A2 = (xr|ys)$,              $A3 = (xs|yr)$
     DO 10  $i = 1, M$
     $A1R = A1 * C(i, r)$,    $A2R = A2 * C(i, r)$,        $A3R = A3 * C(i, r)$
     $A1S = A1 * C(i, s)$,    $A2S = A2 * C(i, s)$,        $A3S = A3 * C(i, s)$
     $UX(i, r) += A2S$,       $VX(i, r) += A1S + A3S$,     $WX(i, r) += A1S - A3S$
     $UX(i, s) += A3R$,       $VX(i, s) += A1R + A2R$,     $WX(i, s) += A1R - A2R$
     $UY(i, r) += A3S$,       $VY(i, r) += A1S + A2S$,     $WY(i, r) += A1S - A2S$
10   $UY(i, s) += A2R$,       $VY(i, s) += A1R + A3R$,     $WY(i, s) += A1R - A3R$
20   CONTINUE
     DO 40  Read all integral triples with labels $x$ and $y$ from the B file.
     $B1 = (xq|ys)$,          $B2 = (xy|qs)$,              $B3 = (xs|qy)$
     DO 30  $i = 1, M$
     $B1Q = B1 * C(i, q)$,    $B2Q = B2 * C(i, q)$,        $B3Q = B3 * C(i, q)$
     $B1S = B1 * C(i, s)$,    $B2S = B2 * C(i, s)$,        $B3S = B3 * C(i, s)$
     $UX(i, q) += B1S$,       $VX(i, q) += B2S + B3S$,     $WX(i, q) += B2S - B3S$
30   $UY(i, s) += B1Q$,       $VY(i, s) += B2Q + B3Q$,     $WY(i, s) += B2Q - B3Q$
40   CONTINUE
C    Second multiplication: $N^3$ FPMOs per operator.
     DO 80  all MO pairs $M \geqslant i \geqslant j \geqslant 1$
     DO 60  $t = 1, x$
     $J^{ij}(x, t) += C(i, y) * UX(j, t) + C(j, y) * UX(i, t)$
     $K^{ij+}(x, t) += D(i, y) * VX(j, t) + D(j, y) * VX(i, t)$
     $K^{ij-}(x, t) += D(i, y) * WX(j, t) - D(j, y) * WX(i, t)$
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60   CONTINUE
     DO 70  $t = 1, y$
     $J^{ij}(y,t) + = C(i,x) * UY(j,t) + C(j,x) * UY(i,t)$
     $K^{ij+}(y,t) + = D(i,x) * VY(j,t) + D(j,x) * VY(i,t)$
     $K^{ij-}(y,t) + = D(i,x) * WY(j,t) - D(j,x) * WY(i,t)$
70   CONTINUE
80   CONTINUE
100  CONTINUE
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After this step either the diagonal elements of the matrices (which are all arranged as triangles) must be multiplied by 2 and then the operators can be stored away or if desired the second two-index transformation may be carried out. If $M < N$, transformation of a number of both Coulomb and exchange operators may be required. The full transformation, on the other hand, can of course be restricted to Coulomb operators. The transformation is performed along the lines of a method explained by Saunders [1], reducing the number of FPMOs proportional to N^2 to the account of FPMOs proportional to N. Moreover, as the ordered set of all operators J^{ij} transformed to MO basis contains every integral twice, storage and computing time can be saved if only $[ij]$ elements of the $[ij]$th operatror are transformed and stored consecutively in the case of the full transformation ($[ij] = i(i-1)/2 + j$; $i \geqslant j$). This procedure automatically arranges the transformed integrals $(ij|kl)$ in canonical order. For Coulomb operators the synthesis of both ideas goes as follows (remember that the diagonal elements have not been doubled):

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     DO 200  $[ij] = 1,\ [MM]$   (all operators $J^{ij}$; $i \geqslant j$)
C    $iN^2/2 + i^2N$ FPMOs per operator in the $i$th row.
     DO 180  $k = 1, i$
     Initialize auxiliary vector $Z(N)$ to zero.
     DO 120  $t = 1, N$
     DO 120  $t' = 1, t$
120  $Z(t) + = J^{ij}(t,t') * C(k,t')$
     DO 160  $t = 1, N$
     DO 140  $l = 1, k$
140  $IF([kl] \leqslant [ij])$  $(ij|kl) + = C(l,t) * Z(t)$
     DO  150 $l = k, i$
150  $IF([lk] \leqslant [ij])$  $(ij|lk) + = C(l,\ t) * Z(t)$
160  CONTINUE
180  CONTINUE
200  CONTINUE
```

5 Discussion

If $M \ll N$ processing of the primitive integrals is the slowest step; if $M \approx N$ the second part of the first two-index transformation and the transformation of the operators to MO basis are most expensive. It may be a disadvantage of this algorithm that in the first step two integral files are needed simultaneously (the original file can be discarded if the construction of single operators using density matrix elements is reformulated such that the new files can be processed) and that storage for a number of not too small auxiliary matrices as well as for the transformed operators must be provided. When only Coulomb operators are desired, e.g. in CASSCF calculations or for the full transformation, only those operations need be carried out which involve the matrices UX, UY, thus considerably reducing computational and storage requirements. Furthermore, main storage can be saved if the above transformation is segmented and only part of the operators constructed at a time. Of course this requires multiple processing of the integral files. Our formalism works even when only the set of all operators $O^{ij}, j \leqslant i$, with fixed i is evaluated simultaneously. While the number of passes is less than $M/2$, say, this is still faster than repeated construction of single operators.

The various available integral transformation algorithms have all more or less the same performance, always proportional to N^5 or N^4M and only the coefficients differ. Although it was not the aim of the present work to compete in speed with other algorithms we shall discuss the important contributions and compare the coefficients of the leading terms with the method of Werner and Meyer (WM, [8]) which has the same performance as the formalism proposed by Saunders and van Lenthe for partial transformation [1]. Processing the primitive integrals requires $2ZM$ FPMOs for Coulomb operators only (WM $2ZM$), $(10/3)ZM$ FPMOs for exchange operators (WM $2ZM$) and $4ZM$ FPMOs if both Coulomb and exchange operators are evaluated simultaneously (WM $3ZM$). Here Z is the total number of processed integrals, $(1/8)N^4 + (1/4)N^3$ in the case of canonical storage or $(1/8)N^4 + (3/4)N^3$ when all integrals are stored in triples; M is the number of involved MOs.

The second step of the first two-index transformation requires N^3 FPMOs per operator J, K^+ or K^- (WM N^3 for J operators, $(4/3)N^3$ for quadratic K operators). Here we can no longer profit from the reduced length of the integral list. FPMOs can be saved if only nonvanishing MO coefficients are processed. Of course only the desired operators need be evaluated. This applies also to the second two-index transformation yielding $M \times M$ matrices, where $(1/2)N^2M + NM^2$ FPMOs are required per operator (WM $(28/24)N^3M(M+1)$ for all operators).

For the full four-index transformation (Coulomb operators only) our method requires $(28/24)N^5$ FPMOs, about 10% slower than the fast formalism by Saunders and van Lenthe [1] which needs only $(25/24)N^5$ FPMOs. Partial transformations: For the construction of all Coulomb operators with M orbitals we need about $0.25MN^4 + 0.5M^2N^3 + 2MN^3$ FPMOs (WM $0.25MN^4 + 1.25M^2 N^3 + 1.75MN^3$), for all exchange operators $0.42MN^4 + M^2N^3 + 3.5MN^3$ FPMOs (WM $0.25MN^4 + 1.67M^2N^3 + 1.17MN^3$), and for all Coulomb plus exchange operators $0.5MN^4 + 1.5M^2N^3 + 4.5MN^3$ FPMOs (WM $0.38MN^4 + 2.92M^2N^3 + 3.67MN^3$).

Our algorithm has hitherto not been implemented on computers equipped with parallel or vector processors. Since it consists essentially of the same steps as are carried out in constructing electron repulsion operators (read stored molecular integrals, multiply with constants and add them to certain storage positions) it is expected to perform on such machines like a Hartree–Fock program.

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