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Integral Transformations. A Bottleneck in Molecular Quantum Mechanical Calculations*

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Two matrix manipulations encountered in molecular calculations are

$$O_{ij} = \sum_{p=1}^{n} \sum_{q=1}^{n} W_{ip} W_{jq} A_{pq} \tag{1}$$

and

$$T_{ijkl} = \sum_{p=1}^{n} \sum_{q=1}^{n} \sum_{r=1}^{n} \sum_{s=1}^{n} W_{ip} W_{jq} W_{kr} W_{ls} B_{pqrs} \,. \tag{2}$$

Here A_{pq} and B_{pqrs} are integrals for the same expansion set, A_{pq} being a general one-electron integral and B_{pqrs} a two-electron integral. The length of the expansion set is n. The expansion coefficients W_{ip} define symmetry or molecular orbitals. The above equations define the one-electron transformation and the two-electron transformation, respectively. At first glance the one-electron transformation appears to be proportional to n^4, i.e., for each of the n^2 matrix elements, n^2 operations are required. Similarly, the two-electron transformation appears to be proportional to n^8. The two-electron case constitutes one of the few remaining time consuming segments in *ab initio* molecular calculations. The effect of this bottleneck can be minimized by transforming only unique integrals, by using the method of partial sums, and finally by taking advantage of the structure of the coefficient matrix. When these techniques are used, the one-electron transformation in the worst case is proportional to n^3. A reduction from n^8 to n^5 is realized for the two-electron transformation. One slight problem remains, redundant expansion integrals are required. The purpose of this note is to introduce a method which eliminates the redundancy problem. An algorithm is given which requires unique expansion integrals sequentially.

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Inspection of Eq. (1) leads one to the realization that

$$O_{ij} = O_{ji}\,, \tag{3}$$

provided

$$A_{pq} = A_{qp}\,. \tag{4}$$

For energy calculations involving the Born–Oppenheimer Hamiltonian this is true and only one-half the n^2 transformed integrals are unique. An even greater reduction is realized in the two-electron case, since

$$\begin{aligned} B_{pqrs} &= B_{qprs} \\ &= B_{pqsr} \\ &= B_{qpsr} \\ &= B_{rspq} \\ &= B_{srpq} \\ &= B_{rsqp} \\ &= B_{srqp}\,. \end{aligned} \tag{5}$$

The symmetry of the transformed integrals is identical and approximately $n^4/8$ integrals are unique.

The method of partial sums[1] can be used to further reduce the computational effort. For the one electron case, the matrix

$$\mathbf{O} = \mathbf{W}^{+}\mathbf{A}\mathbf{W} \tag{6}$$

is calculated in two steps:

$$\mathbf{C} = \mathbf{A}\mathbf{W}, \qquad (\mathbf{C})_{pj} = \sum_{q=1}^{n} W_{jq}A_{pq} \tag{7}$$

and

$$\mathbf{O} = \mathbf{W}^{+}\mathbf{C}, \qquad (\mathbf{O})_{ij} = \sum_{q=1}^{n} W_{iq}C_{qj}\,. \tag{8}$$

Although a storage area is required for the partial sum matrix **C** calculation of **O** is proportional to n^3 rather than n^4. For the two-electron case the n-dependence is reduced from n^8 to n^5. This is accomplished in the following manner; a first partial sum is calculated for fixed p, q, r and all l:

$$D(pqr/l) = \sum_{s=1}^{n} W_{ls}B_{pqrs}\,. \tag{9}$$

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[1] Many of the ideas were reviewed for the author by Prof. E. R. Davidson.

A second partial sum is accumulated for fixed p and q and all k and l:

$$E(pq/kl) = \sum_{r=1}^{n} W_{kr} D(pqr/l). \tag{10}$$

The third partial sum is accumulated for fixed p and all j, k and l:

$$F(p/jkl) = \sum_{q=1}^{n} W_{jq} E(pq/kl). \tag{11}$$

Finally the integral matrix T is accumulated for all i, j, k and l (subject to the symmetry conditions mentioned above)

$$T_{ijkl} = \sum_{p=1}^{n} W_{ip} F(p/jkl). \tag{12}$$

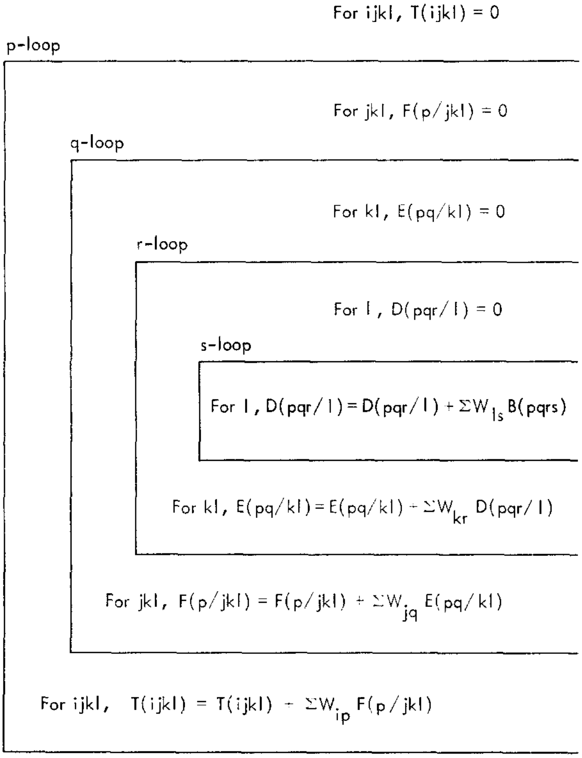

FIG. 1. Loop structure of partial sums method for the two-electron transformation.

Calculation of each partial sum is proportional to n^5, hence the complete process is proportional to n^5. The algorithm is one of the many [1–3] which is proportional to n^5, it is particularly useful when the number of transformed orbitals is considerably less than the number of expansion functions. For this case the computational effort is proportional to mn^4, where m is the number of transformed orbitals. The loop structure of the algorithm is given schematically in Fig. 1.

Use of the uniqueness and the method of partial sums has resulted in great reductions of computational effort. It would seem the limit has been attained, but further reductions can be realized. Clearly any reduction in n, the number of expansion functions, will yield great savings. To a lesser degree the reduction of m, the number of transformed orbitals, can also be helpful. The latter is generally recognized as a theoretical problem and will not be considered here. The final reduction is realized not as a direct reduction of the number of expansion functions, but as a reduction by partitioning of the expansion set. Partitioning is possible when the coefficient matrix contains disjoint subsets. For atoms, s-functions and p-functions can be partitioned since the transformed orbitals contain no common expansion functions. Transformation to symmetry orbitals is another example, functions are partitioned into subsets which contain common (and no external) expansion functions. For the one-electron case

$$\mathbf{O}^{ab} = \mathbf{W}_a \mathbf{A}^{ab} \mathbf{W}_b\,, \tag{13}$$

two types of one-electron transformations are possible

$$\begin{aligned} t&:\quad a = b,\\ s&:\quad a \neq b. \end{aligned} \tag{14}$$

Here a and b denote subsets. The two-electron case

$$\mathsf{T}^{abcd} = \mathbf{W}_a^{+}\mathbf{W}_b^{+}\mathsf{B}^{abcd}\mathbf{W}_c\mathbf{W}_d\,, \tag{15}$$

yields six transformations

$$\begin{aligned} ttt&:\quad a = b = c = d,\\ tts&:\quad a = b,\quad c = d,\quad a \neq c,\\ tss&:\quad a = b,\quad c \neq d,\\ sts&:\quad a \neq b,\quad c = d,\\ sst&:\quad a \neq b,\quad c \neq d \quad \text{but} \quad a = c \quad \text{and} \quad b = d,\\ sss&:\quad a \neq b \neq c \neq d. \end{aligned} \tag{16}$$

Although more programming effort is required for transformation by blocks, the savings are enormous. Rather than the n^5 proportionality a k^5 dependence is realized, k being the largest number of functions in a subset.

The one shortcoming of the methods mentioned is *all require random access of the expansion integrals*. This is extremely troublesome in the two-electron case where the basic two-electron integrals cannot be contained in fast computer storage. We have developed an algorithm which does not require these integrals randomly. In fact, if properly ordered the integrals can be used sequentially. For the one-electron case, the symmetrix matrix $\mathbf{A}$ ($\equiv \mathbf{A}^{aa}$) is rewritten as

$$\mathbf{A} = \mathbf{A}_1 + \mathbf{A}_1{}^{+}, \tag{17}$$

where

$$\begin{aligned} (A_1)_{ij} &= A_{ij}/(1 + \delta_{ij}) \qquad i \geqslant j \\ &= O \qquad\qquad\qquad\quad i < j. \end{aligned} \tag{18}$$

The one-electron transformation is, therefore,

$$\begin{aligned} \mathbf{O} &= \mathbf{W}^{+}\mathbf{A}\mathbf{W} \\ &= \mathbf{W}^{+}\mathbf{A}_1\mathbf{W} + \mathbf{W}^{+}\mathbf{A}_1{}^{+}\mathbf{W} \\ &= \mathbf{W}^{+}\mathbf{P} + \mathbf{P}^{+}\mathbf{W}, \end{aligned} \tag{19}$$

where

$$\mathbf{P} = \mathbf{A}_1\mathbf{W}; \qquad P_{pi} = \sum_{q=1}^{n} W_{iq}(\mathbf{A}_1)_{pq} = \sum_{q=1}^{p} W_{iq}A_{pq}/(1 + \delta_{pq}).$$

Notice the elements A_{pq} are required sequentially. The general formula for the one electron transformation is

$$O_{ij}^{ab} = \sum_{p=1}^{n_a} \sum_{q=1}^{*} (1 + \delta_{ab}\delta_{pq})^{-1} A_{pq}(W_{ip}W_{jq} + \delta_{ab}W_{jp}W_{iq}),$$

where

$$\begin{aligned} * &= n_b\,;\, a \neq b \\ &= p;\, a = b. \end{aligned}$$

Using the same technique, the general formula for the two-electron transformation is rewritten as

$$\begin{aligned} T_{ijkl}^{abcd} = \sum_{p=1}^{n_a} \sum_{q=1}^{*} \sum_{r=1}^{**} \sum_{s=1}^{***} & [(1 + \delta_{ab}\delta_{pq})(1 + \delta_{cd}\delta_{rs})(1 + \delta_{ac}\delta_{pr}\delta_{bd}\delta_{qs})]^{-1} \\ & \times B_{pqrs}[W_{ip}W_{jq}W_{kr}W_{ls} + \delta_{ab}W_{iq}W_{jp}W_{kr}W_{ls} + \delta_{cd}W_{ip}W_{jq}W_{ks}W_{lr} \\ & + \delta_{ab}\delta_{cd}W_{iq}W_{jp}W_{ks}W_{lr} + \delta_{ac}\delta_{bd}W_{ir}W_{js}W_{kp}W_{lq} \\ & + \delta_{ac}\delta_{bd}\delta_{ab}W_{ir}W_{js}W_{kq}W_{lp} + \delta_{ac}\delta_{bd}\delta_{cd}W_{is}W_{jr}W_{kp}W_{lq} \\ & + \delta_{ac}\delta_{bd}\delta_{ab}\delta_{cd}W_{is}W_{jr}W_{kq}W_{lp}], \end{aligned} \tag{20}$$

the limits being

$$\begin{array}{rll} * & = n_b\,; & a \neq b \\ & = p; & a = b, \\ ** & = n_c\,; & a \neq c \\ & = p; & a = c \quad \text{and} \quad b = d, \\ *** & = n_d\,; & \left.\begin{array}{l} c \neq d \\ c = d \end{array}\right\} \quad \begin{array}{l} \text{if } a = c \text{ and } b = d, \text{ the sum will also terminate when} \\ \quad p = r \text{ and } q = s. \end{array} \\ & = r; & \end{array}$$

Notice the integral B_{pqrs} is required only once. The explicit formulas for the method of partial sums are given in the Appendix[2].

The effect of one of the few remaining bottlenecks in molecular quantum mechanical calculations, integral transformation, has been reduced by orders of magnitude. The new algorithm presented is particularly useful since basic integrals are required sequentially. Efficient methods [4] have been developed for obtaining the desired order, so it would seem the limit has been reached. A shortcoming of the method should be mentioned, the algorithm requires random access of the partial sums, hence at least D, E and F (see Appendix) must remain in fast computer memory.

APPENDIX

The new algorithm requires different partial sum formulas. For the six block types, the formulas are

<u>*sss*</u>:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{n_d} W_{ls} B_{pqrs}^{abcd},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{n_c} W_{kr} D(pqr/l),$$

$$F(p/jkl) = F(p/jkl) + \sum_{q=1}^{n_b} W_{jq} E(pq/kl),$$

$$T_{ijkl}^{abcd} = T_{ijkl}^{abcd} + \sum_{q=1}^{n_a} W_{ip} F(p/jkl);$$

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[2] Subroutines for each type are available on request.

sts:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{r} (1 - \delta rs)^{-1} W_{ls} B_{pqrs}^{abcc},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{n_c} W_{kr} D(pqr/l) + W_{lr} D(pqr/k),$$

$$F(p/jkl) = F(p/jkl) + \sum_{q=1}^{n_b} W_{jq} E(pq/kl),$$

$$T_{ijkl}^{abcc} = T_{ijkl}^{abcc} + \sum_{p=1}^{n_a} W_{ip} F(p/jkl);$$

tss:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{n_d} W_{ls} B_{pqrs}^{aacd} (1 + \delta_{pq})^{-1},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{n_c} W_{kr} D(pqr/l),$$

$$F(q/jkl) = F(q/jkl) + \sum_{q=1}^{p} W_{jq} E(pq/kl),$$

$$T_{ijkl}^{aacd} = T_{ijkl}^{aacd} + \sum_{p=1}^{n_a} W_{ip} F(p/jkl) + W_{jp} F(p/ikl);$$

tts:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{r} W_{ls} B_{pqrs}^{aacc} [(1 + \delta_{pq})(1 + \delta_{rs})]^{-1},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{n_c} W_{kr} D(pqr/l) + W_{lr} D(pqr/k),$$

$$F(p/jkl) = F(p/jkl) + \sum_{q=1}^{p} W_{jq} E(pq/kl),$$

$$T_{ijkl}^{aacc} = T_{ijkl}^{aacc} + \sum_{p=1}^{n_a} W_{ip} F(p/jkl) + W_{jp} F(p/ikl);$$

sst:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{*} W_{ls} B^{abab}_{pqrs} (1 + \delta_{pr}\delta_{qs})^{-1},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{n_a} W_{ks} D(pqr/l),$$

$$F(p/jkl) = F(p/jkl) + \sum_{q=1}^{n_b} W_{jq} E(pq/kl),$$

$$T^{abab}_{ijkl} = T^{abab}_{ijkl} + \sum_{p=1}^{n_a} W_{ip} F(p/jkl) + W_{kp} F(p/lij),$$

$$* = n_b \quad \text{until} \quad p = r \quad \text{and} \quad q = s;$$

ttt:

$$D(pqr/l) = D(pqr/l) + \sum_{s=1}^{*} (1 + \delta_{pq})(1 + \delta_{rs})(1 + \delta_{pr}\delta_{qs})^{-1} B^{aaaa}_{pqrs} W_{ls},$$

$$E(pq/kl) = E(pq/kl) + \sum_{r=1}^{p} W_{kr} D(pqr/l) + W_{lr} D(pqr/k),$$

$$F(p/kjl) = F(p/jkl) + \sum_{q=1}^{p} W_{jq} E(pq/kl),$$

$$T^{aaaa}_{ijkl} = T^{aaaa}_{ijkl} + \sum W_{ip} F(p/jkl) + W_{jp} F(p/ikl) + W_{kp} F(p/lij) + W_{lp} F(p/kij),$$

$$* = r \quad \text{until} \quad p = r \quad \text{and} \quad q = s.$$

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