

Simplifications in the Generation and Transformation of Two-Electron Integrals in Molecular Calculations

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Abstracts

Approximate numerical linear dependence among the columns of the two-electron integral matrix and the positiveness of the Coulomb operator are exploited in order to reduce the number of integrals that need to be calculated when a numerical accuracy is given by the machine in use or by the choice of the investigator. Numerical results presented indicate that the method leads to an algorithm for carrying out the two-electron integral four-index transformation which in practice can be achieved in a small fraction ($\sim \frac{1}{5}-\frac{1}{3}$) of the time required to generate the integrals by one of the fastest available Gaussian integral programs, Almlöf's MOLECULE. This effectively removes one of the major bottlenecks of computational quantum chemistry.

La dépendance linéaire numérique approximative entre les colonnes de la matrice formée des intégrales à deux électrons et la positivité de l'opérateur de Coulomb ont été exploitées pour réduire le nombre d'intégrales à calculer pour une précision numérique donnée par l'ordinateur ou par le choix du chercheur. On présente des résultats numériques, qui indiquent que notre méthode mène à un algorithme pour la transformation à quatre indices des intégrales à deux électrons, qui ne requiert qu'une petite fraction ($\sim \frac{1}{5}-\frac{1}{3}$) du temps nécessaire pour générer les mêmes intégrales par un des programmes pour des orbitales gaussiennes les plus rapides, le MOLECULE de Almlöf. Ceci enlève d'une façon efficace une des difficultés principales des calculs de la chimie quantique.

Die approximative numerische lineare Abhängigkeit zwischen den Spalten der von Zweielektronenintegralen gebildeten Matrix und die Positivität des Coulomboperators werden ausgenutzt um die Anzahl der Integrale zu reduzieren, die für eine von der Rechenmaschine oder dem Forscher gegebene Genauigkeit gebraucht werden. Die vorgelegenen numerischen Ergebnisse zeigen, dass die Methode zu einem Algorithmus für die Vierindextransformation der Zweielektronenintegrale führt, der in der Praxis ausgeführt werden kann in einem Bruchteil ($\sim \frac{1}{5}-\frac{1}{3}$) der Zeit, die mit einem der schnellsten gausschen Integralprogramme, dem Almlöf'schen MOLECULE, für die Erzeugung der Integrale gebraucht wird. Dadurch wird eine der wichtigsten Schwierigkeiten in quantenchemischen Berechnungen beseitigt.

Introduction

The vast number of two-electron integrals that need to be considered in large *ab initio* molecular calculations can be arranged in the form of a Hermitian positive definite matrix whose rows and columns are labeled by products of two orbitals, which we call a *distribution*. The properties of this matrix seem not to have been generally exploited. Reid [1] and Fox [2] have recently attempted to replace the Coulomb potential by an inner projection in Löwdin's sense [3]. This idea is used here to develop a particularly simple means of reducing the com-

putational effort in determining and storing two-electron integrals. Preliminary computations indicate that a reduction in computing effort may result which leads to an appropriate N^3 behavior in the number of two-electron integrals needed, and a corresponding N^4 behavior in the four-index integral transformation, for a basis of N orbitals. These results indicate that it is possible to achieve a very substantial reduction in the computation and transformation of two-electron integrals, which has for many years been the major bottleneck of *ab initio* quantum chemistry.

Theory

We shall consider the general case of an orbital basis $\{\phi_k(\mathbf{r})\}$ ($k = 1, 2, \dots, N$) with corresponding distributions $(\phi_k^*(\mathbf{r})\phi_l(\mathbf{r}))$ ($k = 1, 2, \dots, N$, $l = 1, 2, \dots, k$). This basis will often form a basis for a reducible representation of some group G , and it will be worthwhile to exploit these symmetry properties. However, to avoid cluttering the algorithm with a profusion of symmetry indices, we shall defer symmetry considerations until later in this section. The two-electron integrals form a matrix \mathbf{V} , defined by

$$V_{ij,kl} = \int \int \phi_i^*(1)\phi_j(1)(1/r_{12})\phi_k^*(2)\phi_l(2) d\tau_1 d\tau_2 \\ = (ij|kl) \quad (1)$$

where the second line is the usual Mulliken notation. Since it is positive definite, the magnitude of every element is less than the largest diagonal element. This is seen simply by considering a 2×2 block, $\begin{Bmatrix} a & c \\ c & b \end{Bmatrix}$, for which the determinant $ab - c^2$ is positive, which in turn implies that $|c| < \max(a, b)$. In addition, it may be decomposed by means of the Cholesky [4] procedure into a product of a lower triangular matrix \mathbf{L} and its adjoint,

$$\mathbf{V} = \mathbf{L}\mathbf{L}^\dagger \quad (2)$$

This decomposition always exists provided \mathbf{V} is positive definite, and as Wilkinson [4] has shown, the algorithm for the construction of \mathbf{L} is numerically exceedingly stable. To simplify notation, we use a capital letter to represent the two letters in a distribution index. The form of the algorithm for construction of \mathbf{L} which is most convenient for our purposes is as follows. For $J = 1, 2, \dots, M$, where M is the index of the last row, set

$$L_{JJ} = \left(V_{JJ} - \sum_{K=1}^{J-1} L_{JK}^2 \right)^{1/2} \quad (3)$$

and

$$L_{IJ} = \left(V_{IJ} - \sum_{K=1}^{J-1} L_{IK}L_{JK} \right) / L_{JJ} \quad (I = J+1, \dots, M) \quad (4)$$

omitting the summations when the upper limit is zero. When applying this to the two-electron integral matrix, we introduce the following modifications of the algorithm.

(1) First obtain all diagonal elements of \mathbf{V} , that is, the integrals $(pq|pq)$, and arrange these in nonincreasing order, keeping a record of the original order.

(2) Select the first of the reordered diagonal elements V_{11} , which is of course now the largest, and compute

$$L_{11} \leftarrow V_{11}^{1/2}$$

(3) Obtain the entire column (or equivalently, row) of two-electron integrals, V_{I1} ($I = 1, 2, \dots, M$).

(4) Set

$$L_{I1} \leftarrow V_{I1}/L_{11} \quad (I = 2, \dots, M)$$

(5) Update the stored diagonal elements by

$$V_{II} \leftarrow V_{II} - L_{I1}L_{I1} \quad (I = 2, \dots, M)$$

(note that this would set $V_{11} \leftarrow 0$).

The algorithm now proceeds cyclically, where at step J , V_{JJ} is the largest remaining diagonal element, and we perform (6)–(9):

(6) $L_{JJ} \leftarrow V_{JJ}^{1/2}$.

(7) Obtain the partial column V_{IJ} ($I = J + 1, \dots, M$).

(8) Obtain L_{IJ} according to Eq. (4) for $I = J + 1, \dots, M$.

(9) Update the stored diagonal elements by

$$V_{II} \leftarrow V_{II} - L_{IJ}^2 \quad (I = J + 1, \dots, M).$$

The procedure stops at step $J = \nu$ when all the remaining updated diagonal elements V_{II} fall below some specified tolerance δ , which need not be smaller than the accuracy of the original two-electron integrals. The matrix \mathbf{V} then contains no further information of numerical significance, and ν is its effective numerical rank. We have thus achieved a representation of \mathbf{V} in terms of a truncated lower triangular matrix \mathbf{L} , from which the *entire* \mathbf{V} may be regenerated according to

$$V_{IJ} = \sum_{K=1}^{\min(I,J,\nu)} L_{IK}L_{JK} \quad (5)$$

The significance of this result is the fact that the numerical rank ν of the two-electron integral matrices used in actual calculations turns out to be considerably smaller than its maximum possible value, which is $\frac{1}{2}N(N+1)$.

The Cholesky decomposition is equivalent to a particular form of an inner projection procedure [3]. If V is a positive definite operator, and P is a projection operator onto a subspace in the domain of V , then we have

$$0 \leq V^{1/2}PV^{1/2} = V' \leq V \quad (6)$$

The left equality holds only if $P = 0$ and the right equality only if $P = 1$. Suppose we consider the distributions $\{\phi_k(\mathbf{r})\phi_l(\mathbf{r})\}$ as a set of functions $\{h_K\}$ and introduce another set of functions $\{g_K\}$ in the domain of V . We can then construct a projection operator

$$P = V^{1/2} |g\rangle \langle g| V |g\rangle^{-1} \langle g| V^{1/2} \quad (7)$$

which gives

$$V' = V |g\rangle \langle g| V |g\rangle^{-1} \langle g| V \quad (8)$$

Clearly, for the applications here, the inverse matrix in this equation is very large, and direct inversion is impractical. If however the functions g_K are such that $\langle g|V|g\rangle$ is *diagonal*, then taking the inverse is trivial. We can obtain such a set of functions by the following obvious modification of the Gram-Schmidt procedure for orthogonalization of a set of functions:

$$g_K = h_K - \sum_{I=1}^{K-1} g_I \langle g_I | V | h_K \rangle \langle g_I | V | g_I \rangle^{-1/2} \quad (K = 1, 2, \dots, M) \quad (9)$$

The summation is omitted if the upper limit is zero. Matrix elements of V' are then easily obtained from Eq. (8) as

$$\langle h_I | V' | h_J \rangle = \sum_{K=1}^{\min(I,J)} \frac{\langle h_I | V | g_K \rangle}{\langle g_K | V | g_K \rangle^{1/2}} \frac{\langle g_K | V | h_J \rangle}{\langle g_K | V | g_K \rangle^{1/2}} \quad (10)$$

which is analogous to Eq. (5). From this point of view, the orthogonalization (9) is continued until the subtraction produces a negligibly small result, which arises if the functions h are approximately linearly dependent. Closer examination shows that the two factors in the summation in Eq. (10) are nothing but L_{IK} and L_{JK} , and the derivation using the inner projection reveals the important result that the matrix V regenerated from Eq. (5) is actually the matrix V' , which means that average values computed from these two-electron integrals will be lower bounds to the results obtained using the original two-electron integral matrix.

The decomposition given by Eq. (5) is particularly convenient for many applications because it defines *all* the two-electron integrals in terms of two quantities which each depend only on the two indices of each distribution, rather than on four. Thus, if a change of orbital basis is to be made by

$$\psi_k = \sum_j \phi_j C_{jk} \quad (11)$$

then L can be transformed by

$$L'_{kl,K} = \sum_i \sum_j C_{ik}^* L_{ij,K} C_{il} \quad (12)$$

so that all the two-electron integrals in the basis ψ can be obtained directly from the transformed tables L' using Eq. (5). The time-consuming four-index two-electron integral transformation, which for large basis sets has been the most

expensive part of many molecular calculations, is thus reduced to two-index transformations of a limited set of arrays $\{L_{ij,K}\}$.

Treatment of Symmetry

We now proceed to examine how symmetry properties of the orbital basis can be implemented and exploited in our method. Normally the basis set is chosen to span a reducible representation of the point group involved. In applications to atoms and linear molecules, the basis sets can generally be chosen to have the symmetry of irreducible representations of the corresponding point groups. The two-electron integral matrix then symmetry blocks according to the distribution symmetries, which are given by the direct product of the symmetries of the two orbitals in the distribution. For point groups having only one-dimensional representations, the distribution direct product can contain only one representation when the individual orbitals are symmetry adapted. A two-electron integral $(pq|rs)$ is then necessarily zero unless the representation of (pq) is the same as that of (rs) . The symmetry properties of the basis can then be conveniently described by an array $\text{IR}(I)$ giving the representation number of orbital I , and a multiplication table, $\text{MULT}(\text{IR}(I), \text{IR}(J))$, giving the representation number of the direct product of $\text{IR}(I)$ and $\text{IR}(J)$. The multiplication table will be symmetric, with a unit diagonal, corresponding to the totally symmetric representation which by convention is given the number one. Since the group is closed, each representation will appear no more than once in each row and column of the multiplication table. The table then provides a convenient method for checking whether an integral is necessarily zero: $(pq|rs)$ is zero by symmetry if $\text{MULT}(\text{MULT}(\text{IR}(p), \text{IR}(q)), \text{MULT}(\text{IR}(r), \text{IR}(s))) \neq 1$, or equivalently, if $\text{MULT}(\text{IR}(p), \text{IR}(q)) \neq \text{MULT}(\text{IR}(r), \text{IR}(s))$. The point groups of atoms and linear molecules contain multidimensional representations, for which the direct product does not decompose into a single representation, and this would apparently invalidate the above scheme for such cases. In fact, it is possible to retain all symmetry information relevant for determining whether or not an integral is vanishing by a suitable modification of the basis and the table MULT , and we show how to achieve this in the Appendix.

For other point groups containing multidimensional representations, the use of MULT does not appear to offer any utility, since the fact that the direct product decomposition into a sum of representations shows that a given two-electron integral will contain contributions from several symmetry blocks, and this may introduce a substantial complication into the programming. In the following, we suggest a possible solution to this problem.

Following Löwdin's [5] discussion of group algebra, we introduce the projection and shift operators P_{km}^α defined by

$$P_{km}^\alpha = \frac{l_\alpha}{h} \sum_R \Gamma_{km}^\alpha(R) P_R^{-1} \quad (13)$$

where l_α is the dimension of representation α , h is the order of the group, $\Gamma(R)$ is a representation matrix, and P_R is the symmetry operation corresponding to

group element R , such that $P_R^{-1}\phi(\mathbf{r}) = \phi(P_R\mathbf{r})$. These operators satisfy

$$P_{km}^{\alpha\dagger} = P_{mk}^{\alpha} \quad (14)$$

have the basic multiplication rule

$$P_{km}^{\alpha} \times P_{nl}^{\beta} = \delta^{\alpha\beta} \delta_{kl} P_{nm}^{\alpha} \quad (15)$$

and for $k = l$, they are projection operators satisfying the resolution of the identity,

$$1 = \sum_{\alpha} \sum_k P_{kk}^{\alpha} \quad (16)$$

Taking the trace of these for a given representation gives the familiar character projection operator.

$$\begin{aligned} \mathcal{P}^{\alpha} &= \sum_k P_{kk}^{\alpha} \\ &= \frac{l_{\alpha}}{h} \sum_R \chi^{\alpha}(R) P_R^{-1} \end{aligned} \quad (17)$$

For an arbitrary function Φ , we have

$$\Phi_{km}^{\alpha} = P_{km}^{\alpha} \Phi \quad (18)$$

and

$$P_R \Phi_{km}^{\alpha} = \sum_n \Phi_{kn}^{\alpha} \Gamma_{nm}^{\alpha}(R) \quad (19)$$

Making use of the turnover rule and the multiplication rule, we find that matrix elements between the functions (18) for any operator Ω in the group of the Hamiltonian are given by

$$\langle \Phi_{km}^{\alpha} | \Omega | \Psi_{ln}^{\beta} \rangle = \delta^{\alpha\beta} \delta_{mn} \langle \Phi | \Omega | \Psi_{lk}^{\alpha} \rangle \quad (20)$$

These results are now to be applied to the two-electron integrals. The reader will note that the integral $((qp)^* | rs) = (pq | rs)$ satisfies the requirements for a general scalar product which allows application of the turnover rule, and applying the results (14) and (20), we have

$$\begin{aligned} (P_{km}^{\alpha}(pq) | P_{ln}^{\beta}(rs)) &= \delta^{\alpha\beta} \delta_{mn} (pq | P_{lk}^{\alpha}(rs)) \\ &= \delta^{\alpha\beta} \delta_{mn} (P_{kl}^{\alpha}(pq) | rs) \end{aligned} \quad (21)$$

and

$$\begin{aligned} (pq | rs) &= \left(pq | \sum_{\alpha} \sum_k P_{kk}^{\alpha}(rs) \right) \\ &= \sum_{\alpha} \sum_k (pq | P_{kk}^{\alpha}(rs)) \\ &= \sum_{\alpha} (pq | \mathcal{P}^{\alpha}(rs)) \end{aligned} \quad (22)$$

The symmetry adapted distributions $P_{km}^\alpha(pq)$ are thus noninteracting between different representations and also between different columns of the same representation. Our algorithm for the generation of the Cholesky decomposition is well suited to the above. Since a *row* of integrals is required at each step, we see that we can compute $P_{kk}^\alpha(pq)$, which by Eq. (19) is just a sum of distributions, say, $(p'q')$, so we compute the row $(p'q'|rs)$ for fixed α, k, p and q , and all (rs) . We repeat these for all k and α , thus generating at each step M a sequence of elements $L_{pq,M}^{\alpha k}$ which we store *sequentially* according to $((\alpha, k), k = 1, l_\alpha, \alpha = 1, 2, \dots)$, omitting those (α, k) combinations for which $P_{km}^\alpha(pq)$ is identically zero. Clearly, the maximum number of pairs (α, k) is equal to the order of the group. When the distribution tables are to be recombined, we have

$$(pq|rs) = \sum_{\alpha} \sum_k \sum_M L_{pq,M}^{\alpha k} L_{rs,M}^{\alpha k} \quad (23)$$

This result appears to be more complicated than that in Eq. (5). However, since all that we have done is to introduce symmetry blocking from the start, no more work is involved. From the last line of Eq. (22), we see that we could have worked in terms of the \mathcal{P}^α instead of the P_{kk}^α , which would remove the k summation in Eq. (23). However, use of the P_{kl}^α offers a particular advantage in that they produce linearly independent functions for different columns l . If we use the character projection operators \mathcal{P}^α , then, in general, a number of the $\mathcal{P}^\alpha(pq)$ will be linearly dependent, but this will not show up until we have evaluated integrals over them and begun construction of the tables \mathbf{L} . The reader may recall that a similar situation exists for angular momentum projections of N -electron Slater determinants. For the case of spin, the path diagram rule allows generation of linearly independent projections using the character projection operator, but for orbital angular momentum projections, no such rule is known, and the projected determinants will usually be linearly dependent.

The above treatment requires application of the group operators P_R to each of the distributions, and therefore to each of the functions in the basis. It is thus clear that we could advantageously choose to symmetry adapt the basis from the start, although we are well aware that this generally introduces a symmetry restriction into the calculation which prevents complete flexibility in a variational calculation. If we do so, however, then we see immediately that the α summation in Eq. (23) need only include those terms for which $\Gamma^\alpha \subset \Gamma^p \times \Gamma^q \cap \Gamma^r \times \Gamma^s$. Thus in O_h , the most complicated direct product is $t_{1g} \times t_{1g} \sim a_{2g} + e_g + t_{1g} + t_{2g}$, so that the α summation includes 4, instead of 10, representations, and together, the α, k summations include 10, instead of 48, inner summations.

So far we have gained numerical experience only with the simpler point groups and the atomic and linear molecule cases described in the Appendix, and these will be discussed in more detail in the next section. Implementation for the more complicated point groups requires a larger programming effort in that representation matrices must be computed (or stored as permanent information

in the program) and that the effect of P_R on a basis function must be known. This requires rather detailed specification of geometry and also of basis function properties, and should be implemented with an integral program which is capable of producing an arbitrary row of two-electron integrals on demand. It is going to be a matter of experiment and experience to decide whether P_{kk}^α or \mathcal{P}^α is the more effective operator to use. The latter requires computation of many more rows of integrals, but eliminates the k summation in Eq. (23).

Applications

The success of our proposal depends upon numerical experience—how large is the numerical rank of the two-electron integral matrix in an actual calculation? In the following, we drop symmetry indices and write the decomposition (23) in the form

$$(pq|rs) = \sum_{K=1}^{\nu} L_{pq,K} L_{rs,K} \quad (24)$$

The first observation is that computation of all the required columns of \mathbf{L} , which hereafter will be referred to as tables, requires knowledge of the diagonal elements $(pq|pq)$ of the two-electron integral matrix, as well as ν columns of the lower triangle. This entails $(\nu+1)(N(N+1)/2 - \frac{1}{2}\nu)$ integrals for N basis functions, which may be considerably fewer than the $N^4/8$ in the full matrix. The tables \mathbf{L} may then be used as above to generate the *full* matrix. Existing methods for estimation of integrals may of course be used to reduce the number $(\nu+1)(N(N+1)/2 - \frac{1}{2}\nu)$ even further. Several such schemes have been proposed, particularly for Gaussian type orbital (GTO) basis sets, and we shall discuss some of them here for completeness.

Clementi [6] introduced the adjoined function technique, which replaces the fixed linear combination of GTO's, called a contracted GTO (CGTO), normally used for the basis functions, by a single GTO chosen by a least squares criterion. Four such adjoined functions are then used to estimate the value of an integral $(pq|rs)$ which would normally require a fourfold summation over the contraction coefficients and integrals over the primitive GTO's. Very small integrals can then be discarded; for small integrals the adjoined function integral can be used. Larger integrals can be calculated accurately from the fourfold summation. This procedure has been implemented in the well known IBMOL programs.

Wilhite and Euwema [7] proposed replacing the product of CGTO's in a distribution (pq) by a single GTO chosen to conserve the total charge and the center of charge and provide the best least squares fit to the distribution. If p and q are themselves primitive GTOs, this can of course be done exactly, since the product of two Gaussian functions is itself a Gaussian. In addition, they suggested neglect of all two-electron integrals for which the corresponding overlap integral of one of the charge distributions is smaller than a specified tolerance, but not zero on symmetry grounds, with simultaneous neglect of all one-electron integrals involving the same pair of functions. The two methods combined give a

very significant reduction in the number of two-electron integrals to be evaluated. In addition, they offer two important advantages over the adjoined function technique. First, neglect of the integral $(pq|rs)$ is based on the charge distribution (pq) or (rs) , leading to elimination of entire rows and columns of the two-electron integral matrix on the basis of a single test. Second, the charge conservation requirement in practice allows substantially larger cutoff tolerances than are otherwise required to obtain the same total error in an SCF total energy.

A similar idea was investigated earlier by Monkhorst and Harris [8], who proposed evaluation of the difficult multicenter integrals over Slater-type orbitals (STO) by expanding the distribution (pq) as a sum of GTOs where the expansion coefficients and orbital exponents could, for example, be determined by a nonlinear least squares procedure. Their interest was in producing all the multicenter two-electron integrals accurately, and numerical experience showed that rather long expansions would be required to evaluate the integrals to an accuracy sufficient for molecular total energy calculations. However, for approximating or neglecting small integrals, their method should be quite useful, since multicenter integrals over STOs are otherwise time consuming and difficult to evaluate. The older Harris and Michels programs for diatomic two-electron integrals over STOs [9] produced tables of integration points characteristic of each distribution, so that the integrals could be obtained by the summation given in Eq. (24). However, the basis size is limited because up to 1300 points are required in each table for 4–6 figure accuracy, and up to 2600 for 7–9 figure accuracy. The input–output (I/O) involved in manipulating the tables to combine them pairwise to produce the integrals simply becomes prohibitive for large basis sets.

Ohno and coworkers [10] have recently implemented in their JAMOL SCF and COMICAL CI programs a modification of Löwdin's symmetric orthonormalization due to Kashiwagi and Sasaki [11], which allows transforming to a basis in which a larger number of integrals become small enough to be neglected. In an SCF calculation of cobalt porphine complex recently completed by them, the number of integrals which had to be calculated was reduced to around 1% of the total number.

None of the above methods give a direct estimate of the error introduced in the calculations due to the approximation or neglect of small integrals. The authors have thus reasonably chosen to make test calculations with different cutoff tolerances in order to determine typical relationships between the error in computed total energies and the cutoff tolerance. Gianinetti [12] has given attention to the production of upper and lower bounds to approximated two-electron integrals as a step in this direction. Some caution is certainly required, for as Clementi pointed out in a panel discussion at the Sanibel conference some years ago, even though two-electron integrals generally follow the order four-center < three-center < two-center < one-center by size, the net contribution of each type to the total energy is about the same, simply because the number of integrals in each type is the reverse of the above order.

A crude estimate of the error in the total energy due to approximation and neglect of small integrals may be obtained as follows. In a closed-shell SCF calculation, the two-electron integral contribution to the total energy is given by

$$E_2 = \sum_{p \leq q} P_{pq} D_{pq}$$

where

$$P_{pq} = \sum_{p \leq q} \mathcal{P}_{pqrs} D_{rs}$$

$$\mathcal{P}_{pqrs} = \{(pq|rs) - (1/4)(ps|rq) - (1/4)(pr|qs)\} / (1 + \delta_{pq,rs})$$

and

$$D_{pq} = \sum_k C_{pk} C_{qk} / (1 + \delta_{pq})$$

C is of course the matrix of orbital expansion coefficients. Suppose that the maximum error in a supermatrix element \mathcal{P}_{pqrs} due to approximation or neglect is $\pm \delta$ ($\delta > 0$). Then the corresponding error in E_2 is

$$\delta E_2 = \sum_{r \leq s} \sum_{p \leq q} D_{pq} \delta D_{rs} \leq \left\{ \sum_{r \leq s} |D_{rs}| \right\}^2 \delta$$

We have implemented this simple test in Almlöf's MOLECULE SCF program [13] and compared the results with the true error, to see if this might be a useful guide. In practice, this gives $\delta E_2 \approx 10^4 \delta - 10^6 \delta$, while the actual error is of the order of $10^1 \delta$.

The separability of the two-electron integrals afforded by the decomposition (24) can be utilized to advantage in certain applications. For example, in calculational methods which compute total energies directly from the two-electron reduced density matrix Γ , the most time-consuming step of the process is the trace operation,

$$E_2 = \sum_p \sum_q \sum_r \sum_s (pq|rs) \Gamma_{pqrs}$$

Using Eq. (24), this becomes

$$\begin{aligned} E_2 &= \sum_K \sum_p \sum_q L_{pq,K} \sum_r \sum_s L_{rs,K} \Gamma_{pqrs} \\ &= \sum_K \sum_p \sum_q L_{pq,K} M_{pq,K} \end{aligned}$$

The low rank of the K summation makes precomputation of the tables **M** particularly convenient, since only one row of Γ is required at one time, so that core requirements amount to three one-electron matrices. The elements $L_{pq,K}$ generally decrease for increasing K , and it may therefore be reasonable in early

iterations of a calculation to include only the first few terms in the K summation. This effectively allows increasing the integral accuracy as convergence is reached, while saving at the beginning stages where high accuracy may not be important. In addition, the low numerical rank of \mathbf{L} offers a compact representation of the two-electron integrals, so that the data handling required is reduced. This is important when one realizes that in large basis SCF calculations, about 80% of the time utilized in a single iteration is taken up by reading the integrals from external storage.

Utilization of the separability of the two-electron integrals for construction of the Fock matrix and total energy in SCF calculations is clearly of interest. Unfortunately, neither the \mathcal{P} supermatrix, not the \mathcal{K} supermatrix, defined by

$$\mathcal{K}_{pqrs} = \frac{1}{2}\{(ps|rq) + (pr|qs)\}/(1 + \delta_{pq,rs})$$

which is required for the simpler types of open-shell SCF calculations, are positive definite. An alternative Cholesky decomposition for symmetric non-positive definite matrices may exist in the form

$$\mathbf{V} = \mathbf{L}\mathbf{d}\mathbf{L}^\dagger$$

where \mathbf{L} is real lower triangular with a unit diagonal and \mathbf{d} is real and diagonal. The existence of this decomposition depends upon the absence of zeroes on the diagonal of \mathbf{d} . Thus for our purposes, when such an element would be discarded anyway since it makes no contribution to \mathbf{V} , the decomposition can be performed on \mathcal{P} and \mathcal{K} . The elements of \mathbf{d} can be both positive and negative, and the criterion for stopping the decomposition would then have to be based on the absolute value of d_{KK} . However, we do not have assurance that only a limited portion of \mathbf{L} and \mathbf{d} may actually be required to obtain a satisfactory numerical representation of \mathbf{V} and as Wilkinson [4] points out, the decomposition for nonpositive definite matrices enjoys none of the numerical stability of that for positive definite matrices. This is however a point worth investigating further, for as noted above, if the supermatrices \mathcal{P} and \mathcal{K} can be represented by a fraction, say one-tenth, of the data required for the supermatrices themselves, then an effective tenfold decrease in the SCF iteration time will have been achieved. And, of course, the partial summation technique may be applied to the sums over \mathcal{P} and \mathcal{K} supermatrix elements for the construction of the Fock matrix and total energy.

The supermatrices are attractive since they reduce the number of integrals required in the presence of symmetry, for the multiplication by elements of the density matrix forces $\Gamma_p \times \Gamma_q = \Gamma_r \times \Gamma_s = \Gamma_1$, which for one-dimensional representations implies that $\Gamma_p = \Gamma_q$ and $\Gamma_r = \Gamma_s$. However, we shall now demonstrate that it is possible to work directly with the tables \mathbf{L} in order to construct the Fock matrix and the total energy. We follow the notation of Roothaan [24], except that we normalize the open-shell eigenvectors to unity instead of to f , the fractional occupation number. The Fock matrix for a closed shell, a single open shell, and certain classes of several open shells each having

different symmetry but degenerate with the others, can be written in the form

$$\mathbf{F} = \mathbf{h} + \mathbf{P} - \mathbf{Q} + \mathbf{R}$$

When the eigenvectors are divided into closed, open, and virtual sets,

$$\mathbf{C} = [\mathbf{C}^c \mathbf{C}^o \mathbf{C}^v]$$

and the occupation numbers specified by

$$\mathbf{n} = \text{diag} (1, 1, 1, \dots, f, f, f, \dots, 0, 0, 0)$$

the various density matrices are given by

$$\mathbf{D}^o = f \mathbf{C}^o \mathbf{C}^{o\dagger}$$

$$\mathbf{D}^c = \mathbf{C}^c \mathbf{C}^{c\dagger}$$

$$\mathbf{D}^T = \mathbf{D}^c + \mathbf{D}^o$$

$$= \mathbf{C} \mathbf{n} \mathbf{C}^\dagger$$

The matrices required for \mathbf{F} can then be constructed according to

$$\mathbf{R} = (\mathbf{S} \mathbf{D}^T \mathbf{Q} + \mathbf{Q} \mathbf{D}^T \mathbf{S})$$

$$P_{pq} = [2(pq | rs) - (ps | rq)] D_{rs}^T$$

$$Q_{pq} = [2\alpha(pq | rs) - \beta(ps | rq)] D_{rs}^o$$

$$\alpha = (1 - a)/(1 - f)$$

$$\beta = (1 - b)/(1 - f)$$

where \mathbf{S} is the overlap matrix and the couplings parameters a and b are tabulated by, e.g., Roothaan [24] and Guest and Saunders [25]. The total energy is given by

$$E = 2 \text{tr} \mathbf{h} \mathbf{D}^T + \text{tr} \mathbf{P} \mathbf{D}^T - (1 - f) f \text{tr} \mathbf{Q} \mathbf{D}^o$$

Considering first the computation of P_{pq} , we employ Eq. (24) to obtain

$$\begin{aligned} P_{pq} &= \sum_K \sum_r \sum_s [2L_{pq,K} L_{rs,K} D_{rs}^T - L_{ps,K} L_{rq,K} D_{rs}^T] \\ &= \sum_K \sum_m n_m [2L_{pq,K} (\sum_r b_{rm,K} C_{rm}) - b_{pm,K} b_{qm,K}] \end{aligned}$$

where

$$b_{pm,K} = \sum_r L_{rp,K} C_{rm}$$

A similar procedure for Q_{pq} gives

$$Q_{pq} = \sum_K \sum_m^{\text{open}} n_m \left[2\alpha L_{pq,K} \left(\sum_r b_{rm,K} C_{rm} \right) - \beta b_{pm,K} b_{qm,K} \right]$$

This clearly requires only one \mathbf{L}_K matrix in core, and only a vector of N elements indexed by the first subscript of \mathbf{b}_K is needed since each term in the m summation can be accumulated in P_{pq} and Q_{pq} as it is formed. The storage requirements are essentially that of \mathbf{L}_K , \mathbf{P} , \mathbf{Q} , and \mathbf{C} , and the density matrices are not required at this stage. It should also be noted that the m summation runs only over occupied orbitals because of the factors n_m . Once \mathbf{P} and \mathbf{Q} are computed, \mathbf{D}^T , \mathbf{D}° , \mathbf{R} , \mathbf{F} , and E can be constructed and the secular problem $\mathbf{F}\mathbf{C}' = \mathbf{S}\mathbf{C}'\epsilon$ solved. Actually, even the construction of \mathbf{R} , which requires four matrix multiplications, can be avoided if the matrix chosen to remove the overlap matrix in the secular problem is taken to be the \mathbf{C} used to construct \mathbf{P} , \mathbf{Q} , \mathbf{D}^T , and \mathbf{D}° . A simple calculation shows that

$$(\mathbf{C}^\dagger \mathbf{F} \mathbf{C})_{pq} = (\mathbf{C}^\dagger (\mathbf{h} + \mathbf{P}) \mathbf{C})_{pq} + (n_p + n_q - 1)(\mathbf{C}^\dagger \mathbf{Q} \mathbf{C})_{pq}$$

However, if this is done, it is advisable to reorthonormalize the eigenvectors \mathbf{C} every few iterations to ensure that $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1}$. This choice offers the additional advantages that \mathbf{S} need not be used at all to construct \mathbf{F} , and neither \mathbf{D}^T nor \mathbf{D}° need ever be calculated, for we have

$$\begin{aligned} \text{Tr } \mathbf{P} \mathbf{D}^T &= \text{Tr } \mathbf{P} \mathbf{C} \mathbf{n} \mathbf{C}^\dagger \\ &= \text{Tr } \mathbf{n} \mathbf{C}^\dagger \mathbf{P} \mathbf{C} \\ &= \sum_m n_m (\mathbf{C}^\dagger \mathbf{P} \mathbf{C})_{mm} \end{aligned}$$

where the last matrix product is computed like a structure of \mathbf{F} . A similar result is obtained for the term in E involving \mathbf{Q} . Turning to the work involved in forming P and Q by the two methods, we see that working directly with the two-electron integrals could require up to $\frac{1}{2}N^2(N+1)^2$ operations for each matrix if all integrals were nonzero. Using the distribution tables requires for M occupied orbitals about νMN^3 operations for P and Q together. This could be considerably more than in the other method, but there are other factors to consider. First, the amount of I/O required to obtain the tables \mathbf{L}_K is expected to be considerably less than that for retrieval of the nonzero integrals with their four indices packed into a word. Second, unpacking of the integral indices is unnecessary, and third, the dot products required to compute $b_{pm,K}$ and each term inside the K and m summations for P_{pq} can be optimized since the quantities needed for them are in core.

Having touched upon some of the possible applications of the integral representation, we turn now to some specific numerical examples which bear out our hope that the numerical rank of the two-electron integral matrix is indeed small.

We have in operation both the Harris–Michels diatomic STO integral program, and the MOLECULE GTO integral program. Neither of these is suited to “black box” production of a single two-electron integral $(pq|rs)$ on demand. The former, as previously noted, is based on a distribution table concept already and the latter requires a great deal of precomputation, producing simultaneously

all two-electron integrals corresponding to the different m_l components of the four functions in an integral. In addition, the MOLECULE program employs twofold symmetry operations (allowing groups up to order $2^3 = 8$ having one-dimensional representations) to produce either \mathcal{P} and \mathcal{K} supermatrix elements, or ordinary two-electron integrals, directly over symmetry-adapted combinations of CGTOs. The necessary symmetry projections are carried out entirely within the program itself, the only input information being which coordinates change sign under the symmetry operations. The precomputations carried out during the integral generation make the MOLECULE integral perhaps the fastest Gaussian integral program available to date, and the fact that symmetry is included from the start eliminates the need for any intermediate symmetry transformation, and greatly speeds the SCF calculations since they are automatically symmetry-blocked. In addition, having the integrals already in the form of supermatrix elements eliminates the need for special case checking and index manipulations required when the Fock matrix is constructed directly from ordinary two-electron integrals.

We have therefore used both of these programs to produce two-electron integrals which are used as input to the program we have written to implement the distribution table production and integral transformation outlined above. The integrals are first sorted by rows onto a direct-access file for each distribution symmetry block in turn. The diagonal elements are simultaneously saved in core for use in step (3) of the algorithm which saves one complete reading of the integrals. The diagonal elements are then sorted into descending order and steps (2)–(9) are carried out. Each such cycle requires retrieval of one row of the two-electron integrals from the direct-access file. The tables **L** for all distributions belonging to the symmetry block being processed are held in core, and are the major core requirement of the method. So far these have not filled up before the requested tolerance δ was reached, although this may happen for larger basis sets than we have yet used. Removal of this restriction will require direct-access storage and retrieval of the tables, since all the previously computed tables are required in each cycle to perform the summation in Eq. (4) and this additional I/O will prove to be the most time-consuming part of each step. Once the tolerance has been reached, the tables can be saved on sequential external storage, and the next symmetry block begun. The division of the procedure into consideration of single distribution symmetries at a step is useful in that it not only reduces the size of the tables required and allows easy restart at the beginning of any symmetry block, but can also reduce the amount of direct access storage required. The latter is accomplished by retrieving onto the direct-access file only those integrals belonging to the symmetry block being processed. This however will generally require a larger number of complete passes through the original randomly-ordered integral file, and the choice then is installation dependent.

Once the tables are complete, they can be recombined to produce all the original integrals if desired, as would be the case if only those required to compute the tables had initially been calculated. It is worth remarking here that

all those integrals which were used to calculate the tables **L** will be generated *exactly* by Eq. (5), while all others will be in error by a quantity not larger than the cutoff tolerance specified. They can also be transformed, again stepping by symmetry block, to obtain a set of transformed tables which can be used to produce integrals over a new set of orbitals, as in Eqs. (11) and (12). The most efficient algorithms for this integral transformation to date are based on an N^5 procedure introduced by Yoshimine [14], for which improvements have been proposed by several authors [15], but which still are N^5 algorithms. The number of operations (multiplication + addition + array indexing) required to compute the tables **L** is about $\frac{1}{2}N(N+1)\frac{1}{2}\nu^2 - \frac{1}{3}\nu^3$. The maximum value of ν is $\frac{1}{2}N(N+1)$, giving a maximum of $\frac{1}{48}N^6$ operations, but a more probable value of ν is N , giving about $\frac{1}{4}N^4$ operations. Transformation of a single table is equivalent to transforming a single one-electron integral array, which takes about $\frac{1}{2}N^3$ operations. The table transformation is thus, at worst, $\frac{1}{4}N^5$ (when $\nu = \frac{1}{2}N(N+1)$), and more likely to be of the order of $\frac{1}{2}N^4$ (when $\nu = N$). Multiplication of the distribution tables to obtain the transformed integrals requires $\nu N^4/8$ operations, at worst $\frac{1}{16}N^6$, and more probably $\frac{1}{8}N^5$. Thus it might seem that this approach to the integral transformation problem is not going to produce any improvement over existing methods. However, it must be remembered that there is a great deal of extra overhead involved in the actual programming, and things like loop initialization, array indexing, and I/O take a heavy toll. Furthermore, it is not necessary to actually carry out the table multiplication for all the transformed integrals. Since the tables **L** form a lower triangular matrix (if appropriately ordered), it is worthwhile for each (pq) to save the index K of the last nonzero $L_{pq,K}$ and the largest of these for the various K values. The summation (5) need not then proceed to ν , but only to the lower of the last K values in $L_{pq,K}$ and $L_{rs,K}$. An upper bound to the sum, and, therefore, to $(pq|rs)$, can be obtained by multiplying the two maximum elements together times the number of terms in the sum. If this is below the tolerance for saving integrals, the sum can be omitted. Finally, since the transformation is essentially a series of one-electron integral transformations (albeit with different symmetry properties than the overlap and one-electron Hamiltonian matrices), core and I/O requirements are reduced, and fewer loops are required. It should thus be quite clear that we must simply put the method into practice, and see what the timings actually are.

We present results for two calculations in Tables I and II. The first is a calculation on the CO molecule, using the Harris-Michels diatomic STO program. In order to allow detailed comparisons, the timing of several steps in the calculation has been given. For the reasons noted above, the process begins with all the two-electron integrals available in random order on external storage in large blocks with accompanying packed indices. For each distribution symmetry in turn, the first step is sorting of these integrals into row order on the direct-access file. If a sufficient number of records is available on the direct-access file, the sort can be accomplished with one pass through the integral file by writing chained records for each row of integrals. The present version uses a simpler

TABLE I. Timing and other data for the CO molecule^a.

Distribution Symmetry	Integral Sort Time (sec)	Number of Distributions	Number of Tables	Fraction of Integrals Needed	Calculation of Distribution Tables (sec)	Table Transformation (sec)	Table Merging (Eq. 24) (sec)
σ	43.8	243	83	0.566	10.9	39.9	44.8
π	15.8	144	62	0.674	3.7	8.5	3.2
δ	12.4	64	30	0.714	0.5	1.7	0.2

^a The basis set consists of 34 STOs (18σ , 8π , and 8π), and integrals were evaluated with the 1300-point Harris-Michels diatomic integral program. The calculations were carried out on a CDC 6400 computer, using the FTN 3 compiler, OPT = 2 (highest optimization level). Table tolerance was set at 10^{-10} . Of the 17890 unique integrals which are not zero by symmetry, 94.9% of the transformed integrals were larger than 10^{-10} . The number of integrals over STOs lying in each order of magnitude range is as follows: $1288 < 10^{-7} < 8467 < 10^{-6} < 2334 < 10^{-5} < 3780 < 10^{-4} < 7046 < 10^{-3} < 14998 < 10^{-2} < 26441 < 10^{-1} < 14276 < 10^0 < 2333 < 10^1$. The total time for the calculation below was 223.7 sec (including the π symmetry twice), while the original integral calculation took 902.7 sec.

TABLE II. Timing and other data for the benzene (C_6H_6) molecule^a.

Distribution Symmetry	Integral Sort Time (sec)	Number of Distributions	Number of Tables	Fraction of Integrals Needed	Calculation of Distribution Tables (sec)	Table Transformation (sec)	Table Merging (Eq. 24) (sec)
a_{1g}	4.5	140	81 (49)	0.821 (0.576)	4.5 (2.2)	8.9 (5.8)	13.3 (8.9)
b_{1g}	4.1	112	70 (38)	0.857 (0.561)	2.6 (1.2)	3.9 (2.1)	6.7 (4.4)
b_{2g}	3.5	48	36 (22)	0.934 (0.702)	0.4 (0.2)	0.9 (0.6)	0.7 (0.6)
b_{3g}	3.5	42	29 (17)	0.899 (0.640)	0.3 (0.1)	0.7 (0.4)	0.6 (0.4)
a_{1u}	4.2	122	74 (43)	0.843 (0.579)	3.3 (1.6)	4.9 (2.9)	9.2 (5.8)
b_{1u}	4.1	112	63 (32)	0.806 (0.488)	2.3 (0.9)	3.8 (1.9)	6.8 (3.9)
b_{2u}	3.5	48	32 (19)	0.884 (0.630)	0.3 (0.2)	1.0 (0.6)	0.8 (0.6)
b_{3u}	3.5	42	25 (15)	0.831 (0.581)	0.2 (0.1)	0.7 (0.4)	0.6 (0.4)

^a The basis set consists of (C3,1/H 3) GTOs contracted to (C2,1/H 1), giving 36 CTGOs in all. In D_{2h} symmetry, these form symmetry blocks of order (9, 6, 2, 1, 9, 6, 2, 1). The integrals were evaluated using MOLEUCLE and all those larger than 10^{-10} were saved. The calculations were carried out on a CDC 6400 computer, using the FTN 4.5 compiler, OPT = 2, which produces code executing about 30% faster than programs compiled with the FTN 3 compiler. Table tolerance was set first at 10^{-10} , then to 10^{-6} ; results in parentheses correspond to the latter. Computation of the 9870 \mathcal{P} and \mathcal{X} supermatrix elements required 390.9 sec, and computation of the 34187 two-electron integrals required 397.8 sec; all integrals were larger than 10^{-10} and were retained. The number of integrals over symmetry-adapted CTGOs lying in each order of magnitude range is as follows: $3 < 10^{-8} < 17 < 10^{-5} < 193 < 10^{-4} < 1590 < 10^{-3} < 7172 < 10^{-2} < 13984 < 10^{-1} < 9258 < 10^0 < 1970 < 10^1$. Of the 34187 transformed integrals, 32531 (28587) were larger than 10^{-10} (10^{-6}) and were saved; this corresponds to 95.2% (83.6%) of the total number. The number of transformed integrals lying in each order of magnitude range is as follows: $10^{-5} < 3107 < 10^{-4} < 2914 < 10^{-3} < 7549 < 10^{-2} < 9643 < 10^{-1} < 4652 < 10^0 < 722 < 10^1$. The total time required for the steps below was 123.0 (89.4) sec.

method which may require more than one pass through the integral list, since entire rows are collected in core before writing them out as single records. This inefficiency will soon be removed from the program. The next step is the construction of the distribution tables, and we indicate in Tables I and II how many of these are required for a specified accuracy. The computed tables are written as individual records on a sequential file for retrieval in the next step. For the transformation, only one table is required at a time, and we have used this to dynamically reduce the core assigned to the job. This is simply a practical matter which reduces the cost, increases the job priority, and is beneficial to concurrent users of the machine. The transformed tables are also written as individual records on a sequential file, and are retrieved into core for the final step, which is the table multiplication of Eq. (24) to produce the transformed integrals. For the purposes of this test, the tolerance for the table accuracy and for retaining integrals has been set to 10^{-10} , which is considerably smaller than generally required in practice, and since the 1300-point diatomic integral program was used, is smaller than warranted by the accuracy of the original integrals. We have also shown in Tables I and II the number of integrals lying within each order of magnitude range. It is clear from these figures that very few of the integrals are small enough to be approximated or discarded according to the methods discussed earlier. Nevertheless, it is interesting to note that the rank ν is of the order of $\frac{1}{3}$ to $\frac{1}{2}$ the size of the matrix, so that only that fraction of the original integrals actually need have been calculated.

The second example is a calculation on the benzene molecule at the experimental geometry with a small GTO basis set. The MOLECULE program system was used, and the table construction and transformation has been carried out at two different tolerances (10^{-10} and 10^{-6}) to illustrate the savings that can be made by reducing the accuracy. This is particularly convenient for propagator methods which directly compute energy differences, for an accuracy of 10^{-5} in the transformed two-electron integrals will be more than adequate for most purposes.

We have in operation two other integral transformation programs, one written by one of us (N.H.F.B.), and the other by Roos [16] as part of the MOLECULE CI system. Neither of these exploit symmetry to the fullest, while the new program does. Thus, while we have checked the results of the new transformation method against these two older programs, we feel that a direct comparison of timings would be unfair. Instead, it is more interesting to compare the total transformation time, including the distribution table construction and integral sorting, against the time required to generate the original integrals. In both these examples, the transformation has been accomplished in 25–35% of the time for the basic integrals! We thus feel confident that the use of the distribution table method as proposed here will effectively remove the major bottleneck of computational quantum chemistry—the two-electron integral transformation. By implementing the method with a black box integral generator, it will also be possible to reduce the number of two-electron integrals which must be calculated in the first place by a substantial factor, while still allowing

any of the approximation schemes discussed earlier. Preliminary experience with even larger basis sets indicates that the most time-consuming step in the current program is the retrieval of the integrals from random order into row order on a direct-access file, which may take up to 75% of the total time. It is clear that implementation of the program with a black box integral generator stands to considerably reduce the time required, since the sorting procedure is eliminated, and the rows of two-electron integrals generated need not be saved on external storage during table generation. Further, since in a row of integrals, two of the four functions in each integral are unchanged, any necessary quantities involving them may be precomputed for the entire row.

Winograd's Identity

In this section, we introduce an identity apparently first noted rather recently by Winograd [17] which can effectively cut the work involved in the Cholesky decomposition, in the table multiplications for regeneration of the integrals, and in the two-index transformations, by a factor of nearly 50%. Since this result seems not to be widely known, we include it here in the hope of furthering awareness of it. Winograd observed that a matrix multiplication $A = BC$ can be written in the form

$$A_{ij} = \sum_{k=1}^{N/2} (B_{i,2k-1} + C_{2k,j})(B_{i,2k} + C_{2k-1,j}) - (\xi_i + \eta_j)$$

where

$$\xi_i = \sum_{k=1}^{N/2} B_{i,2k-1}B_{i,2k}$$

and

$$\eta_j = \sum_{k=1}^{N/2} C_{2k-1,j}C_{2k,j}$$

We have assumed N even here; the case of N odd is obviously trivially handled by adding the term $B_{iN}C_{Nj}$ to the first and replacing the upper limits by $(N-1)/2$. The matrix multiplication can then be carried out with $\frac{1}{2}N^3 + N^2$ multiplications and $3N^3/2 + 2N(N-1)$ additions, compared to the usual N^3 and $N^3 - N^2$, respectively. Brent [18] has carried out an error analysis for use of the Winograd identity in matrix multiplication, Gaussian elimination, and the Cholesky decomposition, and shown that, provided scaling is applied (this takes about N^2 operations), the algorithm is almost as accurate as the usual summation of N terms. We have not yet included this in our program, but it is clear from the timing statistics in Tables I and II that the improvement can be expected to be substantial.

Conclusions

The distribution table concept for the representation of two-electron integrals has the potential of reforming the methods we are accustomed to using for

their generation and transformation. Harris [9] has, in particular, long been an advocate of such methods. The data reduction involved, and the partial summation technique may, in a number of applications, make use of the numerous two-electron integrals themselves unnecessary. The two-electron reduced density matrix, which is also positive definite, can be represented in a similar fashion, and the reduced computation necessary, since the full two-matrix need not be produced, should make density matrix methods much more attractive. The two-electron density matrix is in fact an excellent candidate for this method, since it is known to have a high density of very small eigenvalues whose physical effects can generally be discarded. The fact that fewer two-electron integrals will need to be calculated may add incentive to the search for better orbitals, even if their integrals are more difficult to compute. STOs are the most noteworthy example of this. However, there are a number of local exchange programs available which are capable of producing quite cheaply numerical molecular orbitals which closely resemble the exact SCF orbitals. Rigorous evaluation of orbital and total energies from local exchange models is not generally possible without having the difficult exchange integrals at hand, and the orbitals cannot usually be used for more extensive calculations unless the associated two-electron integrals are available. Thus, the distribution table idea combined with, perhaps, recent work by Chang [19] on the evaluation of multicenter integrals from numerical orbitals, may be an idea worth pursuing.

The program for computing the distribution tables, transforming them, and producing transformed integrals, has been written very carefully with the goal of both efficiency and portability, and we expect to make it available to the public through the Quantum Chemistry Program Exchange at Indiana University.

Appendix

We consider here symmetry properties in atoms and linear molecules for orbitals built up from linear combinations of products of radial functions and complex spherical harmonics Y_{lm} . For linear molecules, we assume that the orbitals are eigenfunctions of \hat{l}_z , i.e., having fixed m values, and for atoms, as well as eigenfunctions of the inversion operator, we assume an eigenvalue $\text{MOD}(l, 2)$ where MOD is the usual modulus function. Hence a two-electron integral $(pq|rs)$ is zero unless $m_p - m_q = m_s - m_r$, and when inversion symmetry is present, $\text{MOD}(l_p + l_q, 2) = \text{MOD}(l_r + l_s, 2)$. We next observe that if $(pq|rs) \neq 0$, then we have

$$(pq|sr) = \begin{cases} 0 & (\text{if } m_r \neq m_s) \\ (pq|rs) & (\text{if } m_r = m_s) \end{cases}$$

This allows storage of the integrals according to the usual triangle conditions $p \geq q$, $r \geq s$, and $(pq) \geq (rs)$, where (pq) is computed as $\max(p, q) \times (\max(p, q) + 1)/2 + \min(p, q)$, provided that the requirement on the m values is checked on retrieval. Taking the complex conjugate of the two orbitals in a distribution and reversing their order preserves the m symmetry condition but

introduces a possible phase factor, $(pq|s^*r^*) = \pm(pq|rs)$. The usual definitions of spherical harmonics according to Condon and Shortley [20], Slater [21], Rose [22], and others result in the lower sign if one of the m_r, m_s is zero because of the inclusion of the phase factor $(-1)^m$ for $m < 0$ in Y_{lm} . Following Harris [23], we omit this phase factor and obtain the upper sign, allowing storage of both integrals in the same location without requiring time-consuming checks for a possible sign change.

As noted earlier, the multiplication table for a point group containing only one-dimensional representations is symmetric with a unit diagonal corresponding to the totally symmetric representation. The multiplication table for an atom or linear molecule obtained by considering the m value of a distribution as a representation index is not symmetric since for (pq) we have $m = m_q - m_p$, while (qp) has $m = -m_q + m_p$. However, if we define a symmetry index for each orbital p according to

$$\text{IR}(p) = 1 + \text{MOD}(l_p, 2) + 4|m_p| - \begin{cases} 0 & (m_p < 0) \\ 2 & (m_p \geq 0) \end{cases}$$

for atoms, and

$$\text{IR}(p) = 1 + 2|m_p| - \begin{cases} 1 & (m_p > 0) \\ 0 & (m_p \leq 0) \end{cases}$$

for linear molecules, we can compute a symmetric multiplication table

$$\begin{aligned} \text{MULT}(\text{IR}(p), \text{IR}(q)) &= \text{MULT}(\text{IR}(q), \text{IR}(p)) \\ &= 1 + \text{MOD}(l_p + l_q, 2) + 4|m_p - m_q| - \begin{cases} 0 & (m_p < m_q) \\ 2 & (m_p \geq m_q) \end{cases} \end{aligned}$$

and

$$\begin{aligned} \text{MULT}(\text{IR}(p), \text{IR}(q)) &= \text{MULT}(\text{IR}(q), \text{IR}(p)) \\ &= 1 + 2|m_p - m_q| - \begin{cases} 1 & (m_p > m_q) \\ 0 & (m_p \leq m_q) \end{cases} \end{aligned}$$

for the two cases, respectively. MULT must be computed only for $\text{IR}(p) \geq \text{IR}(q)$. Provided that we always characterize the symmetry of a distribution (pq) by maintaining $p \geq q$ and referencing $\text{MULT}(\text{IR}(p), \text{IR}(q))$, we can then correctly identify all those integrals $(pq|rs)$ which are zero by symmetry. For the integrals which survive the test using MULT, reference must still be made to the m values to determine whether $(pq|rs)$ or $(pq|sr)$ was stored in the event that $m_r \neq m_s$ since only one of the two can be nonzero. For linear molecules with maximum $m = M$, we obtain $2M + 1$ orbital symmetries, and the highest distribution symmetry produced is $4M + 1$. For atoms with maximum $l = L$, the corresponding figures are $4L + 2$ and $8L + 2$. The multiplication table must then have $4M + 1$ and $8L + 2$ rows, respectively.

The symmetry blocking for atoms obtained with this scheme is substantial. For a typical basis containing s , p , and d orbitals, there are 18 symmetry blocks

of two-electron integrals, each of which may be transformed separately. It should also be noted that the atomic symmetry classification given here holds equally well for spherical harmonic mixtures $s + d + g + \dots$ and $p + f + h + \dots$ which are met in, e.g., unrestricted Hartree-Fock calculations. Finally, the description of the basis symmetry via the symmetric multiplication table allows the integrals to be used directly in the MOLECULE program system which was written for the special case of point groups containing only twofold symmetry operations provided that appropriate dimensional modifications are made to accommodate the large number of symmetries ($8L + 2$) as opposed to the original maximum of 8 arising in D_{2h} symmetry.

One final comment should be made here. The equivalence between the integrals $(pq|s^*r^*)$ and $(pq|rs)$ means that in practice it is only necessary to compute one of them, and we have arranged to do this in both the Harris-Michels diatomic program and the atomic integral program written by one of us (N.H.F.B.). We have generally maintained a symmetry-packed list of two-electron integrals in core storage in which only the unique integrals are kept, and as integrals are retrieved, the indices are checked to find which of the above two is required. However, when using the MOLECULE SCF program, both integrals are saved with their associated indices, making it possible to read small blocks into core during construction of the Fock matrix. In principle, one could then arrange to skip the table construction and transformation steps for one of either (pq) or (p^*q^*) when these are different, and then to compute the two possible indices when a transformed integral is regenerated by the table multiplication. The ordering ($p \geq q$) generally results in having unequal numbers of distributions in the two equivalent groups, so that special programming is necessary to compensate for this. We have chosen not to do so since we anticipate that the major application will be to polyatomic molecules where one generally does not have such equivalences.

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