COLOPHON

The attached paper has no connection with my current research in Computer Science and Digital Documents. It is another in a series of experiments to see how long it takes me to re-build electronic versions of my published early papers as properly re-typeset 'PDF Normal' rather than just as a bitmap scan.

This particular paper appeared in the journal "Chemical Physics Letters" (Elsevier) in 1973. It is available online (to subscribers) as a scanned bitmap PDF via: `http://www.sciencedirect.com/`

The text was acquired by scanning the paper from the original Proceedings and then using Omnipage OCR on the resulting TIFF files. The paper was then re-typeset using UNIX *troff* suite to set up the correct typeface (Times) and to get the line and page breaks as accurate as possible.

The equations and tables were re-set using the *troff* pre-processors *eqn* and *tbl* respectively.

The time taken to rebuild this paper was about 2 hours.

FAST ASSEMBLY OF FOCK MATRICES UTILISING SYMMETRY PROPERTIES OF THE BASIS SET

David F. BRAILSFORD and Jane HYLTON*

Department of Mathematics, University of Nottingham, Nottingham NG7 2RD, UK

Received 10 November 1972

A method of assembling the elements of the Fock matrix is described which is a modification of that due to Dacre. Lists of symmetry equivalent one-electron integrals are used as pointers to abbreviate the process of collecting two-electron integrals into the Fock matrix.

In the original POLYATOM [1] scheme for storage of one- and two-electron integrals, lists of integral labels and corresponding integral values are produced. A label consists of indices, representing the basis functions that appear in the integral, and a marker tag (which takes the value 1, 2 or 3). A label with a marker tag of 1 will be referred to as a *sublist head*, since it is representative of a set of integrals which are equal because of the geometrical symmetry of the basis set. Underneath the sublist head we have the *sublist body*. This consists of labels for integrals which are equal to the sublist head (marker = 2) or equal to minus the value of the sublist head integral (marker = 3). In early implementations of the scheme, this symmetry information was only used to cut down integral evaluation times. It was not used to aid the setting up of the Fock matrix for the SCF process.

In 1970 a scheme was proposed by Dacre [2] for storing only the sublist heads of the two-electron integral list and for using this smaller list to set up the Fock matrix. This leads to a large saving in the space required to store the list and the time to read it, when the problem possesses symmetry. The total length of the two-electron integral list for a basis set of N members is $\frac{1}{8}N(N+1)(N^2+N+2)$. The reduced size of the list, when only sublist heads are stored, can be calculated by group theoretical arguments [3].

In the Dacre scheme, sublist heads are stored, together with a factor m which represents, essentially, how many times a two-electron integral label permutes into itself under the operations of the symmetry group of the basis functions. The value of the integral to be stored has to be divided by the factor m as explained by Dacre. Then the two-electron Coulomb and exchange matrices are obtained from the formulae

$$J_{ij} = \sum_k G_k \hat{J}_{i'j'} , \qquad K_{ij} = \sum_k G_k K_{i'j'} ,$$

where G_k is a symmetry operation of the basis set's symmetry group. The effect of the summation is to accumulate in J_{ij}, after multiplication by any necessary phase factors, all those $J_{i'j'}$, whose subscripts $i'j'$ transform into ij on application of the operation G_k. The summation is over all operations of the symmetry group. Thus the complete two-electron matrices are obtained from the partial matrices $\hat{J}_{ij}$, $\hat{K}_{ij}$ built up from sublist head integrals, by applying each symmetry operation, in turn, to every element of the matrices, and summing over all symmetry operations.

The computer implementation of Dacre's scheme requires that the full symmetry transformation table for the basis functions be available at the two-electron matrix set up stage. It does not make use of the fact that if J_{ij} and J_{kl} are symmetry related elements, then they are equal, so that once one of them has

* Present address: Department of Molecular and Quantum Biology, University of Tennessee Medical Unit, Memphis, Tennessee 38103, USA.

been calculated from the partial matrix it is not necessary to calculate the other. Utilising this property decreases the time taken to build the complete two-electron matrices from the partial ones and, as will be shown below, avoids the necessity for having the table of symmetry operations available at this stage.

A scheme has been devised and implemented which calculates the partial two-electron matrices, as in the Dacre scheme, but which then calculates a complete matrix element and sets all symmetry related elements equal to this value without further calculation. To minimise the number of passes through this procedure, the Coulomb and exchange partial matrices are first combined to give a partial two-electron Fock matrix contribution.

$$\hat{F}_{ij} = 2\hat{J}_{ij} - \hat{K}_{ij}$$

and the procedure then operates on this matrix to give

$$F_{ij} = 2J_{ij} - K_{ij} .$$

It is important to remember that a necessary requirement for this scheme of partial matrix set up, using sublist head integral values, is that all symmetry operations on the basis set must induce only a permutation of the members of the set. Symmetry operations which transform basis functions into linear combinations of themselves are not permitted. Equally, the set of transformations chosen must have no effect on the nuclei, other than permuting identical nuclei among themselves. Elder [4], in a recent paper, discusses these points and shows how to make full use of the nuclear symmetry when this is higher than that of the basis set. But, for our present scheme, the symmetry operations used must be those that are common to the nuclei and the basis functions.

If one-electron integrals are stored as in the POLYATOM scheme, storing all $\frac{1}{2}N(N+1)$ of them together with their labels, then those matrix elements F_{ij} which are related by symmetry, and are therefore equal in value, are indicated by the one-electron labels list. For example, if integrals $\langle i \mid j \rangle$ and $\langle k \mid l \rangle$ are equal by symmetry, then

$$J_{ij} = J_{kl} , \quad K_{ij} = K_{kl} , \quad F_{ij} = F_{kl} .$$

In this way the one-electron labels list can provide pointers indicating which elements of F must be equal by symmetry. However, we must remember that

$$F_{ij} = \sum_k G_k \hat{F}_{i'j'} ,$$

which requires a sum over all valid symmetry operations, even if several of these give rise to identical contributions. Thus if, instead of actually applying each symmetry operation to every element $\hat{F}_{ij}$ (as in the Dacre scheme), we are now going to combine all symmetry related matrix elements, with appropriate phase factors ±1, as indicated by the one-electron labels list, then we must multiply each term by the number of times it would be generated in scanning the symmetry transformation table. This number, m', will be equal for every member of a given sublist in the one-electron integral labels list, and is given by $m' = p_1/p_2$ where p_1 is the total number of symmetry operations and p_2 is the number of members in the given sublist. It is now necessary only to add together all symmetry related elements of $\hat{F}_{ij}$, multiply the result by m' and set all symmetry related elements of $\hat{F}_{ij}$ to this value. Hence we use two types of integer factor in our scheme. The first is Dacre's m factor which *divides* the two-electron integral value. The second is the *multiplying* factor m' which has just been described.

Table 1 shows comparative timings for complete calculations on various molecules using the OPIT program [5] on an ICL 1906A computer. In this program the SCF operation is performed many times as the basis set is optimised. For example the time quoted for the CH_2 calculation represents 100 separate calls of the SCF routine. In nearly every example, significantly faster times are achieved than those obtained from the Dacre scheme. As might be expected, the improvement will be most noticeable for large symmetric molecules employing big basis sets.

We thank Dr. P.D. Dacre and Dr. M. Elder for helpful communication of results prior to publication. The award of an SRC studentship to Jane Hylton is gratefully acknowledged.

Table 1
Comparative mill (central processor) times, on a 1906A computer, for complete runs of the OPIT program using 3 different schemes of Fock matrix set up

	1906A mill time for complete run of OPIT program (seconds)			Symmetry group of basis functions	No. of symmetry operations	No. of basis functions
	a)	b)	c)			
CH_2	22.9	21.3	21.3	C_{2v}	2	5
CH_4	173.6	136.4	99.7	T_d	24	6
C_2H_6	704.1	313.5	278.5	D_{3d}	12	11
HF	469.8	338.4	313.8	C_{3v}	6	6
F_2	916.3	532.7	447.3	D_{3d}	12	11

[a] Original OPIT program using POLYATOM scheme of storing all the integrals.
[b] Modified OPIT program storing only sublist head integrals and using the Dacre scheme for building up the two-electron part of Fock matrix.
[c] This work.

References

[1] I.G. Csizmadia, J. Moskowitz, M.C. Harrison and B.T. Sutcliffe, Theoret. Chim. Acta 6 (1966) 191.
[2] P.D. Dacre, Chem. Phys. Letters 7 (1970) 47.
[3] D.F. Brailsford and G.G. Hall, Intern. J. Quantum Chem. 5 (1971) 657.
[4] M. Elder, Intern. J. Quantum Chem., to be published.
[5] J.C. Packer and D.F. Brailsford, Computer Phys. Commun. 5 (1973) to be published.