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# Computer Programs for Electronic Wave-Function Calculations

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## I. INTRODUCTION

THE purpose of this paper is to describe several digital computer programs that have turned out to be extremely useful in applications to atomic and molecular physics. The whole set of these programs could be rewritten by an experienced programmer in less than half a year, working from the information given here.

These programs carry out some of the crucial computational processes in a general procedure for solving the many-electron Schrödinger equation for atoms and molecules. There are three relatively independent stages of calculation:

Stage A: choice of some finite set of basis orbitals and evaluation of all one- and two-electron integrals over this set for operators in the many-electron Hamiltonian. In Sec. II the simplest program of this kind is described—it computes one-center integrals for general atomic orbitals of the exponential class. General programs for two-center integrals are much more complicated, and cannot be produced except as a separate major research project. The only workable methods for multicenter integrals at present appear to be those using Gaussian basis orbitals, originally proposed by Boys.[1] Analysis needed for an efficient Gaussian program is presented by Harris in an accompanying paper.[2]

Stage B: matrix Hartree–Fock calculation, in the basis of orbitals chosen in Stage A. The program described in Sec. III carries out calculations by the unrestricted Hartree–Fock method or by the truncated Hartree–Fock method (method of symmetry and equivalence restrictions[3]) in open-shell configurations. The truncated method differs in some cases from the traditional Hartree–Fock method,[4] but it has the advantage of simplicity of programming, and no case has yet been found in which the results are significantly different from the traditional method.[5]

Stage C: configuration interaction. Such a wide range of methods are available here, and there is so little useful experience with adequate computations, that it would be premature to prescribe a definite procedure. In most methods, the one- and two-electron integrals must be transformed to the basis of orthonormal Hartree–Fock orbitals. A general program for doing this is described in Sec. IV. It is relatively easy, given the transformed two-electron integrals, to carry out an extensive survey of correlation effects, using second-order perturbation theory after removing degeneracies or near degeneracies.[3,6] The bulk of the effort in such a computation goes into transforming the two-electron integrals.

## II. ATOMIC INTEGRALS[7]

By including enough basis orbitals from the class

$$\eta_a = N_a r^{A+l_a} \exp\,(-z_a r) Y(l_a, m_a; \theta, \phi)\;, \qquad (1)$$

where $A$ is an integer, $z_a$ is any positive number, and $Y$ is a normalized spherical harmonic, it is possible to obtain atomic wave functions of arbitrary accuracy.

It is necessary to compute all integrals of the form

$$(Q|ab) = \int d\tau_1 \eta_a^*(1) Q(1) \eta_b(1)\;, \qquad (2)$$

$$(ab|cd) = \int d\tau_1 \int d\tau_2 \eta_a^*(1) \eta_b(1) (1/r_{12}) \eta_c(2) \eta_d^*(2)\;. \qquad (3)$$

The operator $Q$ is either $-\frac{1}{2}\nabla^2$, $1/r$, or unity.

The program requires, for each different value of $l$, lists of $A$, $z_a$ for the basis orbitals. Output (to auxiliary memory for use by later programs) consists for the one-electron operators of strings of matrices written as linear arrays. The matrices are symmetrical, so for each $l$ value in increasing order there is a lower

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[1] S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).

[2] F. E. Harris, Rev. Mod. Phys. **35**, 558 (1963).

[3] R. K. Nesbet, Ph.D. Dissertation, University of Cambridge, 1954 (unpublished); Proc. Roy. Soc. (London) **A230**, 312 (1955).

[4] R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).

[5] R. K. Nesbet and R. E. Watson, Ann. Phys. (N. Y.) **9**, 260 (1960). Different variants of the Hartree-Fock method are compared for the $^2S$ ground state of Li.

[6] R. K. Nesbet, J. Chem. Phys. **32**, 1114 (1960).

[7] The formulas used here are due to S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950), programmed for the EDSAC I by S. F. Boys and V. E. Price. The program described here was written for Whirlwind II at MIT by R. K. Nesbet, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, April 15, 1955, p. 38. This program was recoded for the IBM 704 by R. E. Watson.

triangular list, in order 11, 21, 22, 31, etc. The two-electron integrals can be expressed in terms of

$$(ab|cd)^k = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_a(1) R_b(1) \times (r_<^k / r_>^{k+1}) R_c(2) R_d(2) \,, \tag{4}$$

where

$$R_a(1) = N_a r^{A+l_a} \exp\,(-z_a r) \tag{5}$$

is a normalized radial function, and $r_>$, $r_<$ are, respectively, the greater and lesser of $r_1$, $r_2$.

Given $l_a$, $l_b$, $l_c$, $l_d$ there are, in general, several independent integrals $(ab|cd)^k$ with different values of $k$. The conditions to be satisfied are $|l_a - l_b| \leq k \leq l_a + l_b$, $|l_c - l_d| \leq k \leq l_c + l_d$, $l_a + l_b + k$ even, $l_c + l_d + k$ even. Each block of integrals with fixed $l_a$, $l_b$, $l_c$, $l_d$ is computed and stored separately, with the integrals in each block in the canonical sequence of increasing "numbers" ($a\ b\ c\ d$), where $a \geq b$, $c \geq d$, $(ab) \geq (cd)$, with all indices $a$ considered to greater than all indices $b$ if $l_a > l_b$, etc. Thus, within the $(ss|ss)^0$ block the order is $1s1s|1s1s$, $2s1s|1s1s$, $2s1s|2s1s$, $2s2s|1s1s$, etc. Within the $(ds|pp)^2$ block the order is $1d1s|1p1p$, $1d1s|2p1p$, $1d1s|2p2p$, $\cdots$, $1d2s|1p1p$, $1d2s|2p1p$, etc. For convenience, the convention $l_a \geq l_b$, $l_c \geq l_d$, $(l_a l_b) \geq (l_c l_d)$ is maintained. When several values of $k$ occur, the integrals $(ab|cd)^k$ are stored together (in order of increasing $k$ in the current 704/7090 program). The integral blocks needed for Hartree–Fock calculations are themselves arranged in a canonical sequence, described in Sec. III.

Define the function $T(x,y) \equiv x!/y^{x+1}$ by the recurrence formula

$$T(0,y) = 1/y \,, \tag{6}$$

$$T(x+1,y) = [(x+1)/y]T(x,y) \,. \tag{7}$$

Then integrals of type $(Q|ab)$ are given, except for normalization constants, by

$$(1|ab) = T(A + B + 2l + 2, z_a + z_b) \,,$$

$$\left(\frac{1}{r}|ab\right) = T(A + B + 2l + 1, z_a + z_b) \,,$$

$$(-\tfrac{1}{2}\nabla^2|ab) = \tfrac{1}{2}\begin{bmatrix} z_a z_b T(A + B + 2l + 2, z_a + z_b) \\ -(Az_b + Bz_a)T(A + B + 2l + 1, z_a + z_b) \\ + ABT(A + B + 2l, z_a + z_b) \end{bmatrix}, \tag{8}$$

where $l_a = l_b = l$.

Integrals of type $(ab|cd)^k$ are given, except for normalization constants, by

$$(ab|cd)^k = \sum_{r=0}^{M+1} \frac{(M+1)!}{(M+1-r)!} \frac{1}{u^{r+1}} \times T(P + Q + 3 - r, u + v) + \sum_{s=0}^{N+1} \frac{(N+1)!}{(N+1-s)!} \frac{1}{v^{s+1}} \times T(P + Q + 3 - s, u + v) \,, \tag{9}$$

where

$$M = P - k, P = A + B + l_a + l_b, u = z_a + z_b \,,$$
$$N = Q - k, Q = C + D + l_c + l_d, v = z_c + z_d \,. \tag{10}$$

Equation (9) can be written in the form $\sum_r V_M(r,u)\,T(\cdots)$ where $V_M$ is defined by the recurrence formula

$$V_M(0,u) = 1/u \,,$$
$$V_M(r+1,u) = [(M - r)/u]V_M(r,u) \,. \tag{11}$$

The computer program consists of subroutines for recurrence formulas (7) and (11), together with a subroutine which counts through all independent combinations of indices $a$, $b$, $c$, $d$ taking account of the selection rules on $l_a$, etc. The normalization constants

$$N_a = (1|aa)^{-1/2} \tag{12}$$

are computed in a separate initial cycle. The one-electron integrals are multiplied by $N_a N_b$ and the two-electron integrals by $N_a N_b N_c N_d$ as they are computed.

### III. MATRIX HARTREE–FOCK METHOD[8]

The technique used is a straightforward generalization of Roothaan's closed-shell method.[9] A computer program for Roothaan's method written by Meckler for Whirlwind II[10] was a valuable source of ideas for utilizing auxiliary memory and for the use of the

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[8] The main SCF program (iterative matrix method incorporating the truncated Hartree–Fock method for general open shell systems) was originally programmed for EDSAC I by R. K. Nesbet, Ph.D. dissertation, University of Cambridge (1954). The SCF program was recoded for Whirlwind II at MIT by R. K. Nesbet, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, October 15, 1955, p. 4, with some major modifications in technique. This program was recoded for the IBM 704/7090 at the National Bureau of Standards by A. Beam, P. Walsh, and J. D. Waggoner under the supervision of E. Haynesworth. The **A** matrix program was originally programmed for Whirlwind II by R. K. Nesbet, Summary Report No. 42, Project Whirlwind, Digital Computer Laboratory, MIT, April–June, 1955. This program (in the version used for current work) was recoded for the IBM 704/7090 by R. K. Nesbet.

[9] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[10] A. Meckler, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, July 15, 1953, p. 46 and Jan. 15, 1955, p. 36.

density matrix rather than the individual orbitals in a convergence criterion.

The matrix unrestricted Hartree–Fock equations in canonical form[4] are

$$\sum_{b=1}^{M} [(\mathcal{H}_0|ab) - \epsilon_i(1|ab)]x_{bi} = 0, i = 1,\cdots,M\,, \quad (13)$$

where

$$(\mathcal{H}_0|ab) = (K|ab) + \sum_{i=1}^{N}\sum_{c=1}^{M}\sum_{d=1}^{M} x_{ci}x_{di}R(ab|cd)\,, \quad (14)$$

where

$$R(ab|cd) = (ab|cd) - (ac|bd) \quad (15)$$

in the notation of Eq. (3), and $K$ is the one-electron operator in the original many-electron Hamiltonian. There are $M$ basis orbitals $\eta_a$ and $N$ occupied self-consistent orbitals out of the $M$fold orthonormal set

$$\phi_i = \sum_{a=1}^{M} \eta_a x_{ai}\,. \quad (16)$$

All coefficients and matrix elements can be assumed to be real, and the operators are assumed to be Hermitian. The basis orbitals are, in general, not orthonormal.

In the truncated Hartree–Fock method,[3,4] coefficients $x_{ai}$ vanish unless $\phi_i$ and $\eta_a$ belong to the same symmetry species $\lambda$ (e.g., $l$ for spherical symmetry, $L$–$S$ coupling) and subspecies $\mu$ (e.g., $m_l$, $m_s$), with respect to the symmetry group used to define shell structure. Moreover, the coefficients are the same for all orbitals $\phi_i(\lambda\mu)$ with the same indices $(i\lambda)$ [e.g., $(nl)$ in $L$–$S$ coupling], independent of the subspecies index $\mu$. Thus, Eqs. (13) are solved for only one subspecies $\mu_0$ for each species $\lambda$, or more generally, the equation solved is a weighted average over the different subspecies.[4] Thus, in Eq. (14), indices $a$ and $b$ refer to orbitals with a common value of $\lambda$, say, $\lambda_\alpha$, and a fixed subspecies index $\mu_0(\lambda_\alpha)$. Indices $c$ and $d$ also refer to orbitals with a common value of $\lambda$, say, $\lambda_\beta$, but there will be contributions from all of the different subspecies $\mu_\beta$ that represent occupied orbitals of the set $(i\lambda_\beta)$.

When there are several occupied shells (different indices $i$) of orbitals of the same symmetry species $\lambda_\beta$, with the same shell structure in the sense that the occupied subspecies $\mu(i\lambda)$ are the same, the set of such shells will be denoted by index $\beta$. Thus, $\beta$ determines a symmetry species $\lambda_\beta$, a set of subspecies $\mu(\beta)$, and a set of orbital indices (principal quantum numbers) $i(\beta)$. If there are other sets of occupied orbitals of the same symmetry species $\lambda_\beta$ but with different shell structure in the sense that a different set of subspecies $\mu$ are occupied, these will be denoted by different values of the index $\beta$. Thus, for the $^2S$ state of Li, configuration $1s^22s$, $M_S = \frac{1}{2}$, $\beta$ has two values, with $\lambda_1 = l = 0$, $\mu(1) = \{(m_l,m_s)\} = [(0,\frac{1}{2}), (0,-\frac{1}{2})]$, $i(1) = \{n\} = [1]$; and $\lambda_2 = l = 0$, $\mu(2) = [(0,\frac{1}{2})]$, $i(2) = [2]$. In the unrestricted Hartree–Fock method, $\beta$ for this example would also have two values but with a different meaning. Since the state is spherically symmetrical, $l$ is still a good quantum number, but $m_s$ subspecies are split (spin polarized), so for the two values of index $\beta$, $\lambda_1 = l = 0$, $\mu(1) = [(0,\frac{1}{2})]$, $i(1) = [1,2]$; $\lambda_2 = l = 0$, $\mu(2) = [(0,-\frac{1}{2})]$, $i(2) = [1]$. Strictly speaking, in this last example, $\lambda$ has become the index pair $(l,m_s)$ and the symmetry species are not degenerate in $m_s$. The group of $\mathcal{H}_0$ is the spatial rotation group with no spin symmetry.

This analysis makes it possible to write the second term of Eq. (14) in the simplified form

$$\sum_{\beta} \underset{(\lambda_\beta)}{\sum_{c}\sum_{d}} \Big[\sum_{i(\beta)} x_{ci}x_{di}\Big]\Big[\sum_{\mu(\beta)} R(a\mu_0,b\mu_0|c\mu,d\mu)\Big]\,. \quad (17)$$

Since $x_{ci}x_{di}$ is symmetrical in indices $(cd)$, the $R$ integrals can by symmetrized in these indices, and the summation is carried out only over independent index pairs $(cd)$, with the convention that $c \geq d$ (lower triangle of a symmetric matrix). Quantities with indices $(cd)$ are stored in the computer in linear arrays indexed by increasing values of $(cd)$ for $c \geq d$, counted separately for each value of $\beta$. Note that $\lambda(c) = \lambda(d) = \lambda_\beta$ always. With this convention, Eq. (14) becomes

$$(\mathcal{H}_0|ab) = (K|ab) + \sum_{\beta}\sum_{(cd)_\beta} \rho^{\beta}(cd)A^{\beta}(ab|cd)\,, \quad (18)$$

where

$$\rho^{\beta}(cd) = \sum_{i(\beta)} (2 - \delta_{cd})x_{ci}x_{di} \quad (19)$$

and

$$A^{\beta}(ab|cd) = \sum_{\mu(\beta)} [(a\mu_0,b\mu_0|c\mu,d\mu) - \tfrac{1}{2}\,(a\mu_0,c\mu|b\mu_0,d\mu) - \tfrac{1}{2}\,(a\mu_0,d\mu|b\mu_0,c\mu)]\,. \quad (20)$$

The coding of Eq. (18) is trivial, since each element $(\mathcal{H}_0|ab)$ is obtained by adding to the fixed element $(K|ab)$ the scalar product of the variable "vector" $\rho^\beta(cd)$ with the fixed "vector" $A^\beta(ab|cd)$, the $(ab)$ row of a supermatrix, summing on the "index" $(cd)$. The $A$ matrix can be stored in auxiliary memory and brought into fast memory by block transfer, one row at a time.

As initial data the SCF program requires the fixed matrices $(K|ab)$ and $(1|ab)$, the fixed supermatrix $A(ab|cd)$, and an approximation to the variable matrix $\rho(cd)$. In each iterative cycle, $(\mathcal{H}_0|ab)$ is constructed from Eq. (18) and Eqs. (13) are solved. The method used to deal with the overlap matrix $(1|ab)$ will be described below. Starting from an estimated matrix $\rho(cd)^{(0)}$ three cycles are carried out in succession to give

$$\begin{array}{ll} \rho(cd)^{(1)} & \\ \rho(cd)^{(2)}\,, & \Delta(cd)^{(2)} \\ \rho(cd)^{(3)}\,, & \Delta(cd)^{(3)}\,, \end{array} \tag{21}$$

where $\Delta^{(n)} = \rho^{(n)} - \rho^{(n-1)}$. This gives an extrapolated value for each matrix element

$$\rho^{(\infty)} = \rho^{(3)} + (\Delta^{(3)})^2/(\Delta^{(2)} - \Delta^{(3)})\,, \tag{22}$$

which is taken as $\rho(cd)^{(0)}$ for the next sequence of three cycles, unless $|\Delta^{(3)}/(\Delta^{(2)} - \Delta^{(3)})|$ becomes larger than some fixed number, in which case $\rho^{(\infty)}$ is estimated by $\rho^{(3)} + \Delta^{(3)}$ for the particular element in question.

This extrapolation process has been very satisfactory in practice. It is, of course, an essential part of a fully automatic computer program. The extrapolation method is based on the observation that the error in successive estimates of $\rho(cd)$ tends to oscillate or to increase or decrease geometrically.[11] All of these cases are covered by the formula (with complex $\alpha$)

$$\rho^{(m)} = \rho^{(\infty)} + e^{\alpha m}\,. \tag{23}$$

Then

$$\begin{aligned} \Delta^{(m+1)} &= e^{\alpha m}(e^{\alpha} - 1)\,, \\ \Delta^{(m+2)} &= e^{\alpha m + \alpha}(e^{\alpha} - 1)\,, \end{aligned}$$

which, when solved for $e^{\alpha m}$ and substituted into Eq. (23) gives Eq. (22).

The convergence criterion is

$$\sum_{(cd)} [\Delta(cd)]^2 < \text{crit}\,, \tag{24}$$

for some fixed criterion, usually $\sim 10^{-8}$.

Before the iterative process begins a Schmidt transformation matrix $(M|ab)$ is constructed from the overlap matrix $S = (1|ab)$, where $M$ is a triangular matrix that satisfies

$$MSM^T = I\,. \tag{25}$$

A method has been devised by which $S$ is replaced element by element by $M$ without the use of additional storage space, where $S$ is a string of lower triangles of symmetric matrices and $M$ is a string of triangular matrices.[12]

At each cycle of the iterative process, the matrix $\mathcal{H}_0$ of Eq. (13) is constructed and then transformed into

$$\mathcal{H}_0' = M\mathcal{H}_0 M^T\,, \tag{26}$$

whose eigenvectors $y_{bi}$ satisfy

$$\sum_{b=1}^{M} (\mathcal{H}_0'|ab) y_{bi} = \epsilon_i y_{ai}\,. \tag{27}$$

Highly efficient standard computer programs[13] are available for solving Eqs. (27). The eigenvectors of Eq. (13) are computed by the transformation

$$x_{ai} = \sum_b (M^T|ab) y_{bi} = \sum_b (M|ba) y_{bi}\,. \tag{28}$$

Both Eqs. (26) and (28) can be coded to replace the transformed matrix or vectors element by element without using additional working space. Transformations with a triangular matrix are, of course, more rapid than transformations with a square matrix. It should be noted that the large supermatrix $A(ab|cd)$ is not transformed at any stage in the calculation—this would be a very slow process compared with two- or one-index transformations.

A special program is used to construct the $A$ matrix. In general, given indices $\lambda_\alpha$, $\lambda_\beta$ as defined above, the summation over subspecies index $\mu$ indicated in Eq. (20) reduces to a formula that can be symbolized by

$$\begin{aligned} A^{\beta}(\alpha|\beta) = \sum_{\sigma} C_D^{\sigma} D^{\sigma}(\lambda_\alpha,\lambda_\beta) &+ \sum_{\sigma'} C_X^{\sigma'} X^{\sigma'}(\lambda_\alpha,\lambda_\beta) \\ &+ \sum_{\sigma'} C_X^{\sigma'} X^{\sigma'}(\lambda_\alpha,\lambda_\beta) \end{aligned} \tag{29}$$

where $D^{\sigma}(\lambda_\alpha,\lambda_\beta)$ is a "direct" integral from the block $(\lambda_\alpha\lambda_\alpha|\lambda_\beta\lambda_\beta)$, and $X^{\sigma'}$ is an "exchange" integral from the block $(\lambda_\alpha\lambda_\beta|\lambda_\alpha\lambda_\beta)$, with terminology as in Sec. II. The indices $\sigma$ or $\sigma'$ have the same meaning as the quantum number $k$ in Sec. II: In general, an integral $(a\mu_a,b\mu_b|c\mu_c,d\mu_d)$ can be written as a linear combination of integrals $(ab|cd)^{\sigma}$, where $\sigma$ indexes the linearly independent integrals arising from all possible combinations of subspecies indices $\mu_a$, $\mu_b$, etc. The coefficients $C_D^{\sigma}$ and $C_X^{\sigma'}$ are obviously independent of the individual orbital indices $a$, $b$, $c$, $d$. They depend only

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[11] This is a standard method of converting a first-order iterative procedure into a second-order one. See D. R. Hartree, *Numerical Analysis* (Oxford University Press, New York, 1952), pp. 196–197. C. W. Scherr [J. Chem. Phys. **23**, 569 (1955)] reported geometrical convergence in an LCAO calculation. The present author had noted such things as oscillatory geometrical divergence in work on excited states of butadiene, Proc. Roy. Soc. (London) **A230**, 322 (1955).

[12] R. K. Nesbet (to be published).

[13] Jacobi method subroutines written by F. J. Corbato have been used in both the Whirlwind and IBM 704/7090 programs described here.

on the symmetry species indices $\lambda_\alpha$, $\lambda_\beta$, and on the set of subspecies indices $\mu(\beta)$. They are obtained by writing each of the integrals in Eq. (20) as a linear combination of the independent parameters $D^\sigma$ or $X^{\sigma\prime}$, and then summing the coefficients over the set $\mu(\beta)$.

The $A$-matrix program requires the $C_D$, $C_X$ coefficients as input data. It then uses the canonical sequence of two-electron integrals, described in Sec. II, to construct the $A$ matrix, using Eq. (29). The direct and exchange integral blocks are themselves in a canonical sequence, as follows:

$$(\lambda_1\lambda_1|\lambda_1\lambda_1),(\lambda_2\lambda_1|\lambda_2\lambda_1),(\lambda_2\lambda_2|\lambda_1\lambda_1),(\lambda_2\lambda_2|\lambda_2\lambda_2),\text{etc.} \quad (30)$$

This is the sequence of symmetric pairs $(\lambda_\alpha\lambda_\beta)$, with $X(\lambda_\alpha,\lambda_\beta)$ before $D(\lambda_\alpha,\lambda_\beta)$.

### IV. TRANSFORMATION OF INTEGRALS[14]

The symmetric one-electron matrices $(1|ab)$, $(K|ab)$, and $(\mathcal{H}_0|ab)$ are transformed to the basis of self-consistent orbitals $\phi_i$ by the SCF program, after convergence is reached. In the unrestricted or closed shell case, the Hartree–Fock energy is given by the well-known formula

$$H_{00} = \tfrac{1}{2}\sum_{i=1}^{N}[(\mathcal{H}_0|ii) + (K|ii)] . \quad (31)$$

The $\mathcal{H}_0$ matrix is constructed from the vectors obtained in the last iteration and then contracted with the *same* vectors, to ensure that Eq. (31) is an identity independent of the extent to which the iterative process has converged.[4]

The transformation of two-electron integrals to the basis of orthonormal self-consistent orbitals is a much more tedious process, and it requires special organization for efficiency. Fortunately, only those two-electron integrals required for a particular configuration interaction calculation need be computed.

The transformation to be considered is

$$(ij|kl)^\sigma = \sum_a\sum_b\sum_c\sum_d x_{ai}x_{bj}x_{ck}x_{dl}(ab|cd)^\sigma . \quad (32)$$

The integral $(ab|cd)^\sigma$ is unchanged by interchanging $a$ and $b$, by interchanging $c$ and $d$, or by interchanging $(ab)$ and $(cd)$, if by convention orbitals of different symmetry species are counted in different sequences (see Sec. II). Then from the symmetry of $(ab|cd)^\sigma$,

$$(ij|kl)^\sigma = \sum_{(ab)\geq(cd)}\sum \times\left[\begin{array}{l} \quad\{x_{ai}x_{bj} \oplus x_{bi}x_{aj}\}\{x_{ck}x_{dl} \oplus x_{dk}x_{cl}\} \\ \oplus\{x_{ci}x_{dj} \oplus x_{di}x_{cj}\}\{x_{ak}x_{bl} \oplus x_{bk}x_{al}\}\end{array}\right](ab|cd)^\sigma , \quad (33)$$

where

$$\begin{aligned} F(ab) \oplus F(ba) &= F(aa) , & a &= b \\ &= F(ab) + F(ba) & a &\neq b \end{aligned}$$

and

$$\begin{aligned} F[ab,cd] &\oplus F[cd,ab] \\ &= F[ab,ab] , & (ab) &= (cd) \\ &= F[ab,cd] + F[cd,ab] ; & (ab) &\neq (cd) . \quad (34) \end{aligned}$$

Here the index pairs are ordered by the rules

$$(ab) > (cd) \text{ if } a > c \text{ or if } a = c, b > d .$$

By convention, $a \geq b$ and $c \geq d$ always.

This establishes a simple ordering of the integrals if by convention $(ab) \geq (cd)$ always. Then $(abcd) > (a'b'c'd')$ is similarly defined. When the basis orbitals have symmetry properties that define a number of blocks of independent integrals, the standard ordering of integrals is preserved within each block, while the blocks are treated independently of each other. Here a block of integrals is designated by the series of symmetry species indices $(\lambda_a\lambda_b|\lambda_c\lambda_d)$.

The coefficients $x_{ai}$ of Eq. (16) vanish unless $\phi_i$ and $\eta_a$ belong to the same symmetry species. The integrals do not depend explicitly on subspecies indices, and subspecies are assumed to be equivalent to each other, i.e., $x_{ai}$ does not depend on subspecies. Thus, the transformation is applied to the independent quantities $(ab|cd)^\sigma$, not to the integrals

$$(a\mu_a,b\mu_b|c\mu_c,d\mu_d).$$

For counting purposes orbitals are numbered serially [counting only one orbital $(i\lambda)$ from the set $(i\lambda\mu)$, since subspecies are equivalent], with orbitals $\eta_0\cdots\eta_{n_0-1}$ or $\phi_0\cdots\phi_{n_0-1}$ in symmetry species 0, orbitals $\eta_{n_0}\cdots\eta_{n_0+n_1-1}$ or $\phi_{n_0}\cdots\phi_{n_0+n_1-1}$ in symmetry species 1, etc. Then the orbitals of symmetry species $\lambda$ have indices running from

$$\underline{a}_\lambda = \sum_{t=0}^{\lambda-1} n_t$$

through

$$\bar{a}_\lambda = \underline{a}_\lambda + n_\lambda - 1 .$$

Hence a single block of integrals is completely speci-

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[14] The program for transforming two-electron integrals is based on unpublished work by S. F. Boys. The first version of the present program was written by R. K. Nesbet, Ph.D. dissertation, University of Cambridge, 1954, subsequently recoded for Whirlwind II, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, April 15, 1955, p. 41, and again recoded for the IBM 704/7090, in both cases by R. K. Nesbet.

fied by two sets of four numbers, $(\underline{a}\ \underline{b}\ \underline{c}\ \underline{d})$ and $(\bar{a}\ \bar{b}\ \bar{c}\ \bar{d})$. These numbers determine the orbitals in both $(ij|kl)^\sigma$ and $(ab|cd)^\sigma$ by the conditions $\underline{a} \leq a, i \leq a$, etc.

The integral transforming program includes a counting subroutine that performs the following operations:

Given $(\underline{a}\ \underline{b}\ \underline{c}\ \underline{d})$ and $(\bar{a}\ \bar{b}\ \bar{c}\ \bar{d})$ and some ordered set of four integers $(a\ b\ c\ d)_s$ with $\underline{a} \leq a \leq \bar{a}$, etc., replace $(a\ b\ c\ d)_s$ by the next bracket $(a\ b\ c\ d)_{s+1}$ in sequence, with indices in the same specified range. If $(a\ b\ c\ d) = \bar{a}\ \bar{b}\ \bar{c}\ \bar{d}$, transfer control to a specified exit.

Another subroutine constructs the quantity

$$x_{ai}x_{bi} \oplus x_{bi}x_{aj} \tag{35}$$

defined by Eq. (34). If the two indices $i$ and $j$ do not refer to the same symmetry species the $\oplus$ operation is suppressed.

The transformation of Eq. (33) is broken up into two stages. First a semitransformation is performed.

$$\begin{aligned}(ij|cd)^\sigma = &\sum_{(ab)\geq(cd)} \{x_{ai}x_{bj} \oplus x_{bi}x_{aj}\}(ab|cd)^\sigma \\ &+ \sum_{(ab)<(cd)} \{x_{ai}x_{bj} \oplus x_{bi}x_{aj}\}(cd|ab)^\sigma ,\end{aligned} \tag{36}$$

if both index pairs $(ij)$ and $(kl)$ refer to the same two symmetry species. Otherwise,

$$(ij|cd)^\sigma = \sum_{(ab)} \{x_{ai}x_{bj} \oplus x_{bi}x_{aj}\}(ab|cd)^\sigma . \tag{37}$$

Given $(ij)$ the matrix $(ij|cd)^\sigma$ is built up in fast memory. The much larger matrix $(ab|cd)$ is read through serially, by block transfers from auxiliary storage if necessary, for each value of $(ij)$. The four indices $(a\ b\ c\ d)$ are stepped up serially by the counting subroutine and are used to compute

$$\{x_{ai}x_{bj} \oplus x_{bi}x_{aj}\}(ab|cd)^\sigma \tag{38}$$

and

$$\{x_{ci}x_{dj} \oplus x_{di}x_{cj}\}(ab|cd)^\sigma , \tag{39}$$

which are the contributions of $(ab|cd)^\sigma$ to $(ij|cd)^\sigma$ and $(ij|ab)^\sigma$, respectively. There is no contribution to $(ij|ab)^\sigma$ when $(ij)$ and $(kl)$ refer to different pairs of symmetry species.

From $(ij|cd)^\sigma$ all integrals $(ij|kl)^\sigma$ with $(ij) \geq (kl)$ are computed by the formula

$$(ij|kl)^\sigma = \sum_{(cd)} \{x_{ck}x_{dl} \oplus x_{dk}x_{cl}\}(ij|cd)^\sigma . \tag{40}$$

When there are several different values of the index $\sigma$ (see Sec. III), basis integrals $(ab|cd)^\sigma$, $(ab|cd)^{\sigma\prime}$, $\cdots$ are stored consecutively, so the count through $(ab|cd)$ is incremented by one to obtain transformed blocks $(ij|kl)^\sigma$ in order.

## V. APPLICATIONS

The versatility of these programs can be seen from a summary of work done with them. The programs of Secs. III and IV have been used with many different sources of integrals for different purposes: for configuration interaction calculations on atomic carbon and $CH_4$, with Gaussian basis orbitals[15]; for Pariser-Parr calculations, with empirical parameters for the basic integrals[16]; for diatomic molecular calculations, with two-center integrals evaluated by a program not described here[17]; by atomic hyperfine structure calculations using the integral program of Sec. II[18]; for various other atomic calculations, with the same integral program[19]; and for an approximate nuclear Hartree–Fock calculation with integrals computed by special FORTRAN programs.[20] The atomic integral program of Sec. II is used as an auxiliary to all *ab initio* molecular calculations, since it is necessary to carry out atomic and molecular calculations of comparable accuracy to establish the asymptotic limit of potential curves.

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[15] See references 3 and 6.

[16] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 322 (1955); J. Chim. Phys. 750 (1962); Bunel, Chalvet, Daudel, Nesbet, and Paradejordi, C. R. Acad. Sci. (Paris) **252**, 2890 (1961).

[17] R. K. Nesbet, Rev. Mod. Phys. **32**, 272 (1960); P. Merryman, C. M. Moser, and R. K. Nesbet, J. Chem. Phys. **32**, 631 (1960), and later papers on excited states of CO with H. Lefebvre-Brion and C. M. Moser; other published work includes calculations on $N_2$, LiH, $Li_2$, HF, and HCl.

[18] R. K. Nesbet, Phys. Rev. **118**, 68 (1960); more recent work with these programs is reported in a series of papers by N. Bessis, H. Lefebvre-Brion, and C. M. Moser.

[19] R. K. Nesbet and R. E. Watson, Phys. Rev. **110**, 1073 (1958); Ann. Phys. (N. Y.) **9**, 260 (1960); R. E. Watson, Phys. Rev. **119**, 170 (1960), and later papers, some with A. J. Freeman.

[20] N. Ullah, Ph. D. dissertation, Boston University, 1962 (unpublished); N. Ullah and R. K. Nesbet, Nucl. Phys. **39**, 239 (1962).