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THE ALCHEMY LINEAR MOLECULE INTEGRAL GENERATOR

by

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Science & Engineering Research Council

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1. INTRODUCTION

For many years it has been recognised that electron-molecule acattering processes could be calculated within the framework of R-matrix or other variational reaction theories by modifying existing quantum chemistry configuration interaction (CI) computer program packages. However, attempts to implement this idea have shown that the quality of the results obtained depends sensitively on the extent to which the discrete molecular orbital basis used is able to represent the scattering continuum. The region of Hilbert space which is spanned is dependent on the amount of linear dependence which is tolerable within the orbital basis and, therefore, effectively on the accuracy with which the undsrlying atomic integrals may be computed. The compromise which must be made between obtaining the integrals to a high degree of accuracy while keeping the computational time to within reasonable limits has meant that it has been possible to obtain accurate scattering phase ehifts only for a narrcw range of scattering energies. This range is typically from threshold to about 1.0 Rydberg when using an analytio Slater orbital basis.

The present integral package is designed to reduce this limitaticn. Although the STO integral generator from the IBM CI Program ALCHEMY is the starting point of the new code the techniques employed to restrict the integration domain to the finite R-matrix region are entirely different from those used by Kendrick and Buckley[1]. In addition many new facilities have been added. Before listing these features it may be helpful to summarise the salient sepects of R-matrix theory for electron-molecule scattering.

The application of R-matrix theory to molecular processes involves the division of configuration space into distinct internal and external

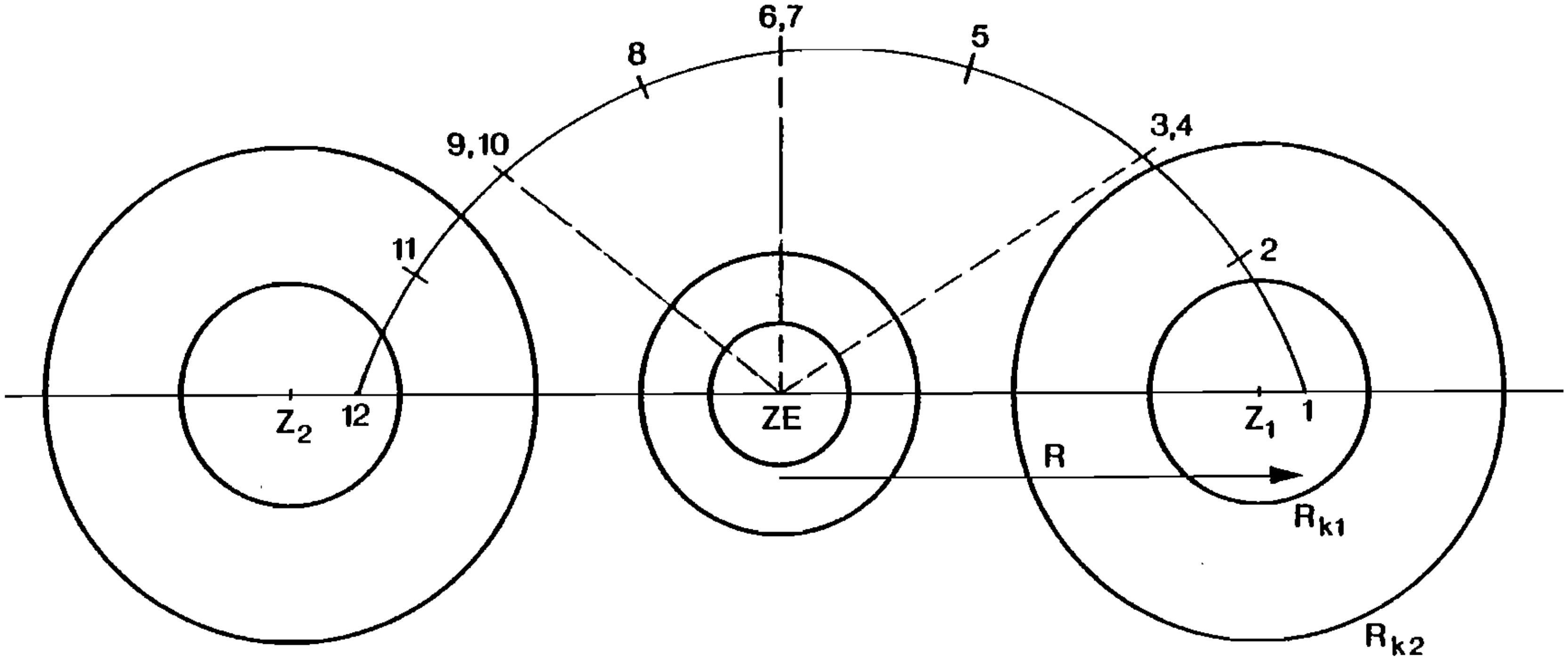

Fig. 13

used and to provide an overall view of the program structure. Comments within the source listing should be consulted for finer details about the program. The next two sections deal with the generation of quadrature weights and nodes and with the calculation of boundary amplitudes and continuum molecular orbitals.

The input data to the integral package is essentially the same as that for the original IBM bound state code and therefore the notes prepared by B. Liu[5] should be consulted. However, for convenience, the entire input data will be described in this report including some details of parameters controlling the integration mesh generation since these were not described in detail in the original notes and will possibly have to be varied in scattering calculations. In appendices we provide sample input data, a summary of disk files used and installation details.

2. THE ALCHEMY LINEAR MOLECULE INTEGRAL PACKAGE

The present program has been developed from the ALCHEMY Slater integral generator for linear molecules, SCFWFORD, written by B. Liu of IBM, San Jose[5]. The basic algorithms used in the original package have not been modified. However, as outlined in the introduction, the options available have been considerably expanded and the package is now suitable for computing all integrals required in scattering calculations within the R-matrix, variational or hybrid formalisms. Apart from permitting the integrals to be computed over a finite region of space, it is now possible to use basis functions which are defined numerically to represent the continuum.

The overall structure and operation of the program may most easily be seen by refering to figs.1(a) and 1(b). Figure 1(a) illustrates the subroutine calling structure in the initial stages of the computation and shows the set-up of the dynamic core allocation scheme and the reading and printing of the control and input data. The calculation may cycle over sets of input parameters; this operation is the principal role of the subroutine DRIVER.

The basic supervisory program in the package is LINTP which is an entry point of subroutine LINT. Figure 1(b) illustrates the subroutines called directly by LINTP. Subroutines lower down the calling tree are shown only for the initial section which is concerned with processing the input data and producing those fundamental arrays (mostly pointer arrays) which are used extensively throughout the rest of the package. Each of the required integral types are then computed in turn and written to disk files. The integral computation sections are followed by an integral renormalisation section which is necessary because integrals over a finite region are initially computed without renormalising the basis functions -

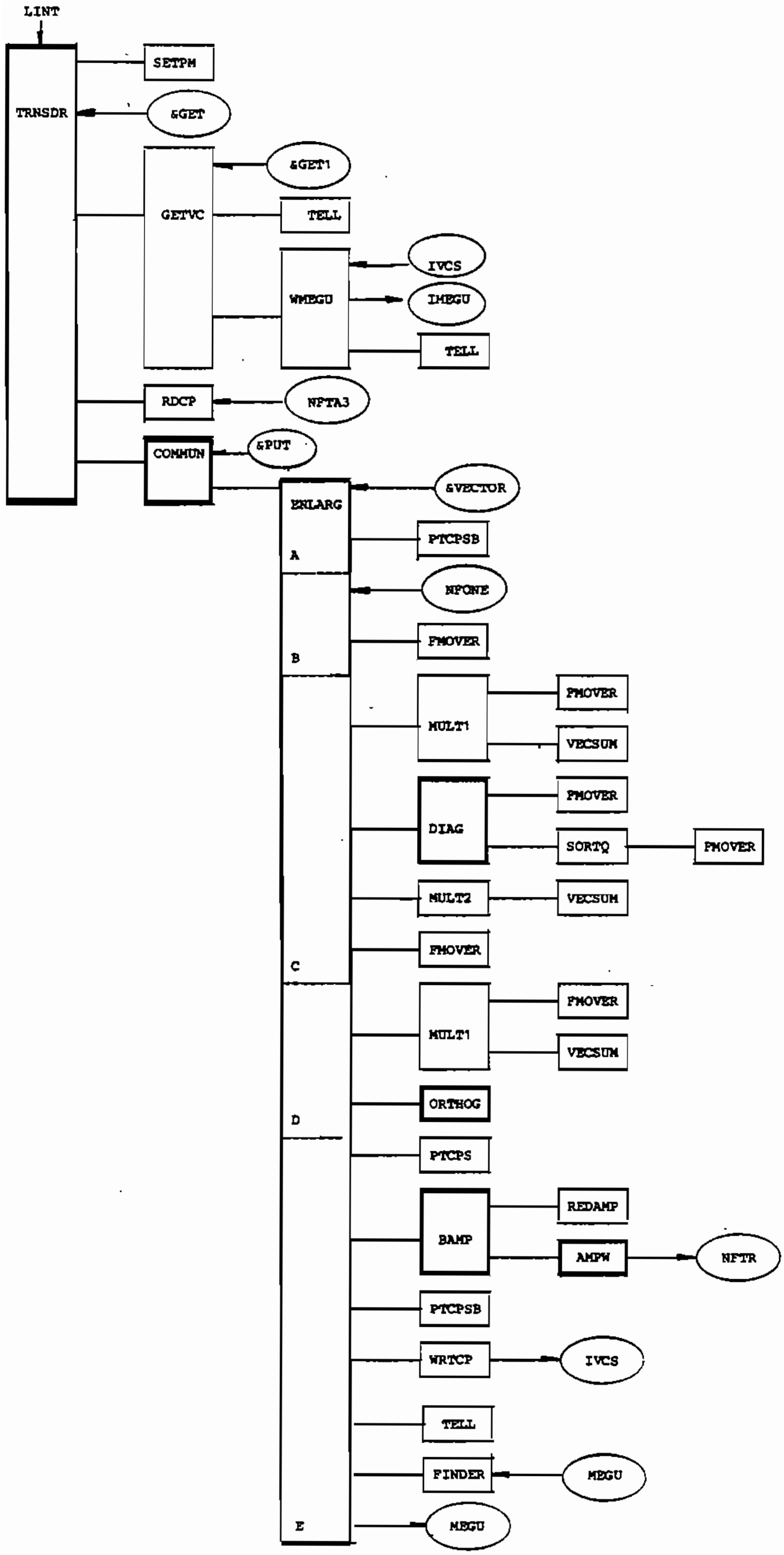
LINT
TRNSDR
SETPM
&GET
GETVC
&GET1
TELL
WMEGU
IVCS
IMEGU
TELL
RDCP
NFTA3
COMMUN
&PUT
ENLARG
&VECTOR
A
PTCPSB
NPONE
B
FMOVER
MULT1
FMOVER
VECSUM
DIAG
FMOVER
SORTQ
FMOVER
MULT2
VECSUM
FMOVER
C
MULT1
FMOVER
VECSUM
ORTHOG
D
PTCPS
BAMP
REDAMP
AMPW
NFTR
PTCPSB
WRTCP
IVCS
TELL
FINDER
MEGU
E
MEGU

Fig.9

3. COULOMB AND HYBRID INTEGRALS

The two-electron Coulomb and Hybrid integrals involve either two or three centres and are characterised by two one-centre distributions and by a one-centre and a two-centre charge distribution, respectively.

(a) Coulomb:

$$\iint d\tau_1 \, d\tau_2 \, \Omega_a(1) \frac{1}{r_{12}} \Omega_b^*(2) \tag{1}$$

(b) Hybrid:

$$\iint d\tau_1 \, d\tau_2 \, \Omega_a(1) \frac{1}{r_{12}} \Omega_{bc}^*(2) \tag{2}$$

In general the two-centre charge distribution, Ω_{bc}, may be written in terms of the basis functions χ as

$$\Omega_{bc}(1) \equiv \chi_b^*(\vec{r}_1) \, \chi_c(\vec{r}_1) \tag{3}$$

$$= R_b(r_1) \, R_c(r_1) \, Y_b^*(\hat{r}_1) \, Y_c(\hat{r}_1) \tag{4}$$

using the centre labels to also represent the quantum numbers of the basis state. For STO basis functions

$$R_b(r) = N_b \, r^{n_b-1} \, e^{-\zeta_b r} \tag{5}$$

where $N_b = [(2n_b)!]^{-1/2} \, (2\zeta_b)^{n_b+1/2}$. (6)

Using the analysis outlined by McLean[6], it is straightforward to show that the radial distribution functions may be written as

$$D_{aa}^{LM}(r) = R^a_{n_1\ell_1}(r) \, R^a_{n_2\ell_2}(r) \, \frac{1}{\sqrt{4\pi}} \, G^{\ell_1 \, L \, \ell_2}_{m_1 \, M \, m_2} \tag{7}$$

and

$$D_{bc}^{LM}(r) = \frac{1}{\sqrt{2\pi}} \, \delta_{M,m_4-m_3} \int_{-1}^{+1} dx R_{n_3\ell_3}(r_b) R_{n_4\ell_4}(r_c) \mathscr{P}_L^M(x) \times \mathscr{P}_{\ell_3}^{m_3}(\cos\theta_b) \mathscr{P}_{\ell_4}^{m_4}(\cos\theta_c) \tag{8}$$

where

$$\mathscr{P}_\ell^m(x) = C_{\ell m} P_\ell^m(x) \tag{9}$$

$$C_{\ell m} = \left[\frac{2\ell+1}{2} \, \frac{(\ell-m)!}{(\ell+m)!} \right]^{1/2} \tag{10}$$

and

$$G^{\ell_1 \, L \, \ell_2}_{m_1 \, M \, m_2} = 2^{3/2} \int_0^1 dx \, \mathscr{P}_{\ell_1}^{m_1}(x) \mathscr{P}_L^M(x) \mathscr{P}_{\ell_2}^{m_2}(x) \tag{11}$$

$P_\ell^m(x)$ is the usual associated Legendre function as defined by Messiah[7].

Potential functions may be defined in terms of the radial distributions by

$$F^{LM}(r) = \sqrt{4\pi} \, r^L \int_r^\infty dr' \, r'^{-L+1} D^{LM}(r') \tag{12}$$

where centre labels have been suppressed.

The required Coulomb and Hybrid integrals are then given by

$$I_{a;bc} = \sum_L \int_0^\infty F_{aa}^{LM}(r) \, F_{bc}^{LM}(r) dr \, . \tag{13}$$

The one-centre potential function may be written in the case of STO basis functions as

$$F_{aa}^{LM}(r) = N_1 N_2 \, G^{\ell_1 \, L \, \ell_2}_{m_1 \, M \, m_2} \, r^{n_1+n_2} \, A_{n_1+n_2-L-1}\left[(\zeta_1+\zeta_2)r\right] \tag{14}$$

where the auxiliary integral, $A_n(x)$, is given by

$$A_n(x) = \int_1^\infty dy \, y^n \, e^{-xy} \tag{15}$$

and may be simply evaluated using the method of Wahl et al[8].

To evaluate Coulomb and Hybrid integrals within a finite region it should be noted that long-range contributions to the integrals can only

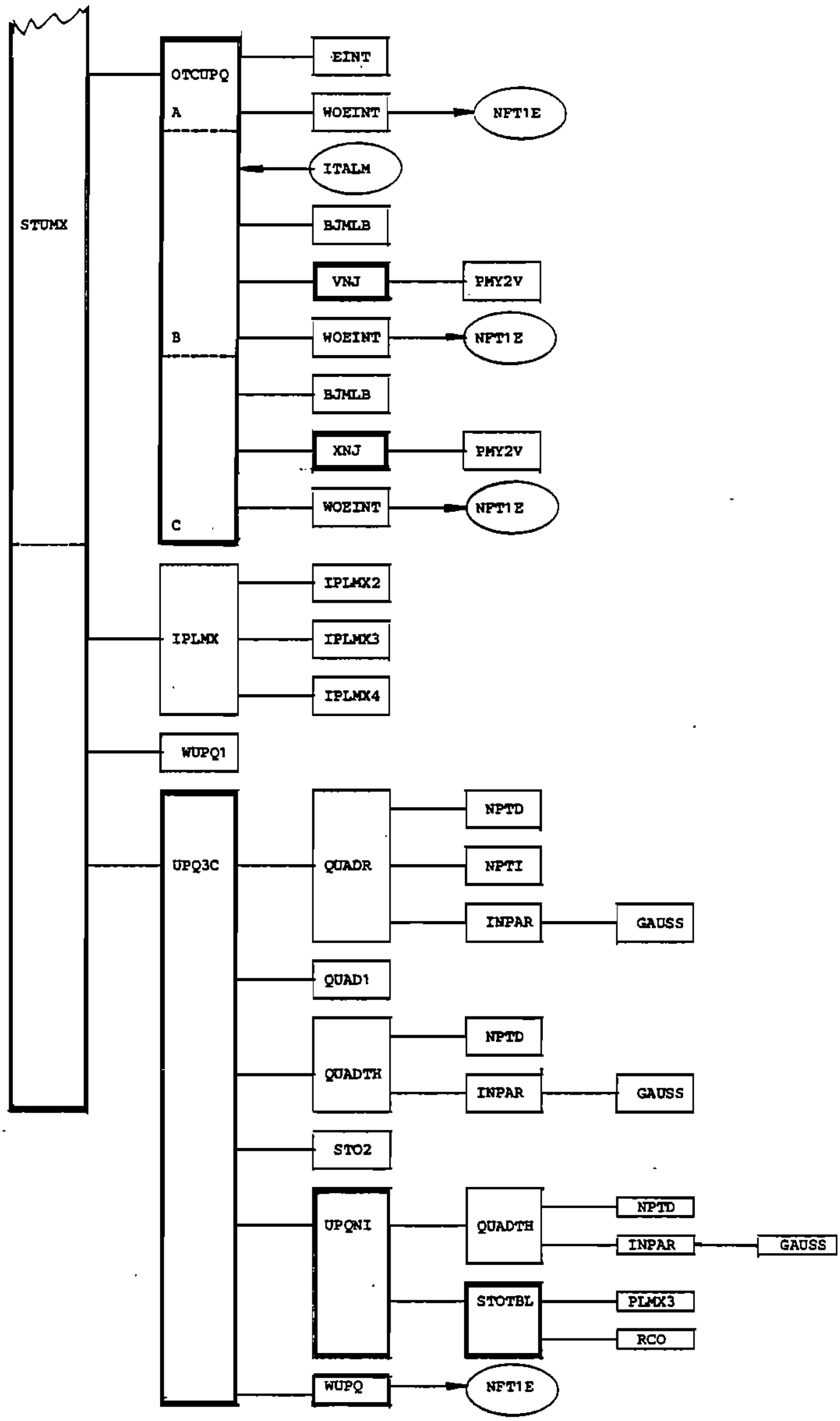
STUMX
OTCUPQ
A
B
C
EINT
WOEINT
NFT1E
ITALM
BJMLB
VNJ
PMY2V
WOEINT
NFT1E
BJMLB
XNJ
PMY2V
WOEINT
NFT1E
IPLMX
IPLMX2
IPLMX3
IPLMX4
WUPQ1
UPQ3C
QUADR
NPTD
NPTI
INPAR
GAUSS
QUAD1
QUADTH
NPTD
INPAR
GAUSS
STO2
UPQNI
QUADTH
NPTD
INPAR
GAUSS
STOTBL
PLMX3
RCO
WUPQ
NFT1E

Fig.7

435ABF

RSRQ

This subroutine is analogous to OCPQRQ, setting up pointer arrays to enable the two-centre (in general) distributions given by eq.(8) to be computed.

CHINT

This subroutine performs the numerical integration over the potential functions given by eq.(13) and carries out the summation over orbital angular momenta, L, to give the required integrals. If the basis functions in the one-centre distribution are STO's, the corresponding potential function is determined analytically according to eq.(14). The auxiliary A-integral, eq.(15), is computed by recursion; for diffuse basis functions in R-matrix calculations the value of $F_{GG}^{LM}(R)$ is computed using eq.(14) [R is the R-matrix radius] and subtracted from $F_{GG}^{LM}(r)$.

FRSR

The second potential function, $F_{bc}^{LM}(r)$, is computed by the two-dimensional quadrature implied by eqs.(8) and (12). The algorithm employed is

$$F_{bc}^{LM}(r_i) = \sum_{j=1}^{N_i} W_{r_j'} r_i \left(\frac{r_i}{r_j'}\right)^{L-1} \left[\frac{1}{\sqrt{4\pi}} D_{bc}^{LM}(r_j')\right] + \left(\frac{r_i}{r_{i-1}}\right)^{L} F_{bc}^{LM}(r_{i-1}) \qquad (16)$$

denoting r' quadrature weights and nodes by Wr_j' and r_j' respectively. The r-points, r_i, are chosen so that $r_i < r_{i-1}$.

QUADTH

Determines the angular x-integration weights, w_{x_j}, and nodes, x_j, used to evaluate eq.(8). Note that the radial nodes, r_i', were computed by QUADR, and chosen to cover each subinterval of the primary r-mesh used to evaluate the integrals of eq.(13).

STOTBL

Computes a table of basis function values, $R_{n_p \ell_p}(r_p) \times \mathcal{P}_{\ell_p}^{m_p}(\cos\theta_p)$, corresponding to a specific pair of (r',x)-values. Only those basis functions which can form suitable distributions are evaluated. If the basis function is found to correspond to a numerical continuum function, subroutine RCO is called to provide the required value. Associated Legendre functions are obtained by calling subroutine PLMX3.

FPQR

In cases where the one-centre potential is required for numerical continuum functions, FPQR is called to perform the required numerical integration. In fact

$$\begin{pmatrix} \ell_1 & L & \ell_2 \\ G_{m_1} & M & m_2 \end{pmatrix}^{-1} F_{GG}^{LM}(r) = r \int_r^R dr' \left(\frac{r}{r'}\right)^{L-1} R_{n_1\ell_1}(r') R_{n_2\ell_2}(r') \qquad (17)$$

is computed using an algorithm analogous to eq.(16).

WCHINT

The final phase of the calculation, deleting those integrals with a magnitude less than a specified threshold value, and grouping the remainder, with their corresponding labels, into buffer loads is performed by WCHINT. The integrals are then written to the disk file associated with unit NFT2E.

The header on each output record gives the number of symmetries, the total number of integrals, and the number of integrals for each symmetry.

The remaining subroutine calls are largely to initialisation or other subsidiary entry points. Table 2 lists each subroutine used in this section together with its entry point identifiers. Entry points QUAD, and WRINT are called directly from LINT.

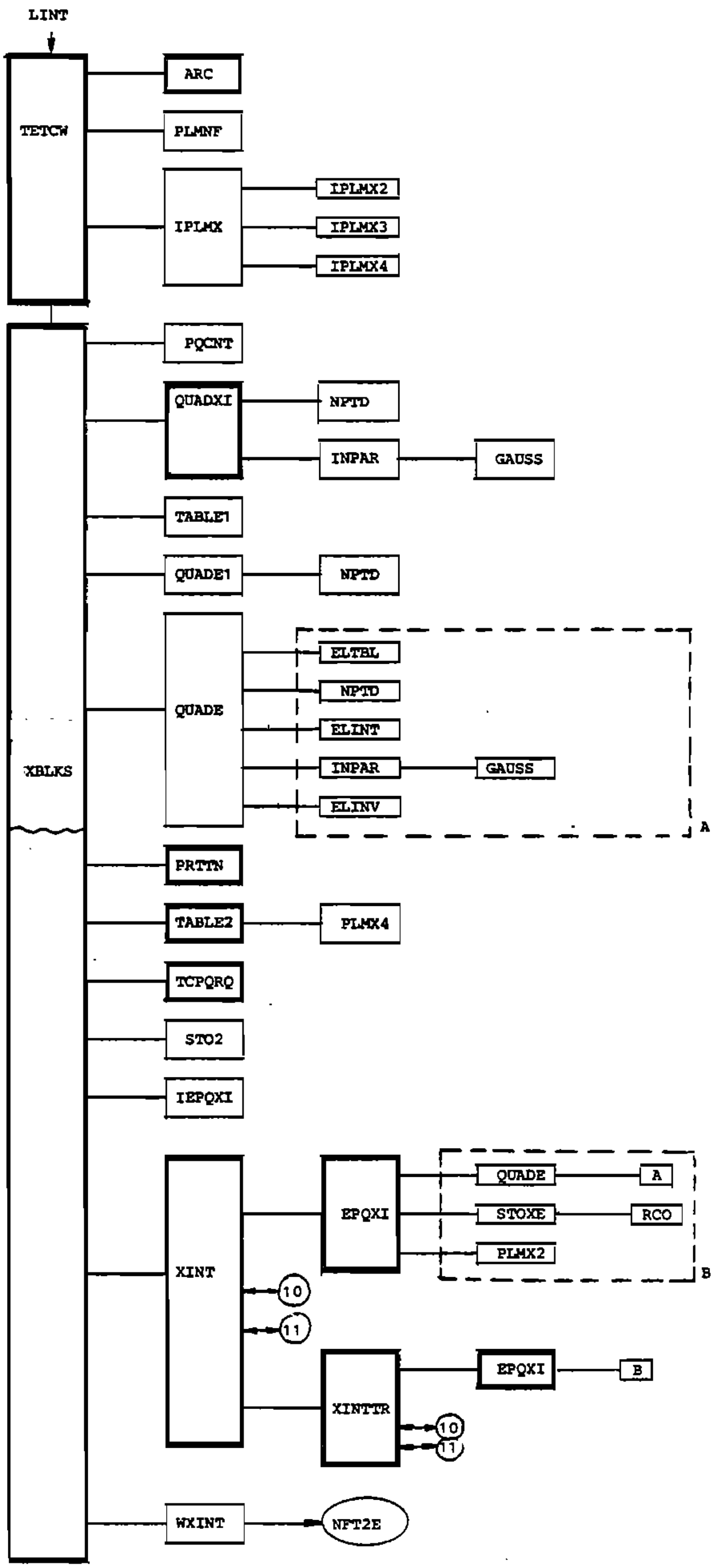
LINT
TETCW
ARC
PLMNF
IPLMX
IPLMX2
IPLMX3
IPLMX4
XBLKS
PQCNT
QUADXI
NPTD
INPAR
GAUSS
TABLE1
QUADE1
NPTD
QUADE
ELTBL
NPTD
ELINT
INPAR
GAUSS
ELINV
A
PRTTN
TABLE2
PLMX4
TCPQRQ
STO2
IEPQXI
XINT
EPQXI
QUADE
A
STOXE
RCO
PLMX2
B
10
11
XINTTR
EPQXI
B
10
11
WXINT
NFT2E

Fig.5

OCINT

The one-centre integrals are evaluated in OCINT using the expression given in eq.(20). If necessary, long range contributions are estimated using eq.(23) and subtracted. The angular coefficients, G, are passed from the first section of subroutine TEOCW.

EINT

Computes the auxiliary E-integral given by eq.(24).

5. EXCHANGE INTEGRALS

The exchange integrals are defined as those two-electron integrals which involve two two-centre charge distributions.

$$I_{pqrs} = \iint d\tau_1 d\tau_2 \Omega_{pq}(1) \frac{1}{r_{12}} \Omega^*_{rs}(2) \qquad (25)$$

In general, therefore, between 2 and 4 distinct centres might be involved. The reduction of the integrals (25) to a computable form has been described by McLean[6] and hence only the most significant points will be summarised here.

The integral (25) is simplified by a technique analogous to that employed for the Coulomb/Hybrid integrals; the major difference is that rather than using a spherical coordinate system with origin located on the centre of the one-centre charge distribution, it is now necessary to use a prolate spheroidal coordinate system with foci at centres p and q. Figure 4 illustrates the coordinate system, with origin at the midpoint of pq.

$$\xi = \frac{r_p + r_q}{2R}$$

$$\eta = \frac{r_p - r_q}{2R} \qquad (26)$$

$$\phi = \tan^{-1}(y/x)$$

An STO basis function located on centre p may then be written in the form

$$\chi_p(\vec{r}_p) = N_p\, R^{n_p - 1} (\xi+\eta)^{n_p - 1} e^{-R\zeta_p(\xi+\eta)} \mathscr{P}^{m_p}_{\ell_p}\left(\frac{1+\xi\eta}{\xi+\eta}\right) \Phi_p(\phi) \qquad (27)$$

where

$$\Phi_p(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad . \qquad (28)$$

A charge distribution on centres a,b may then be written as

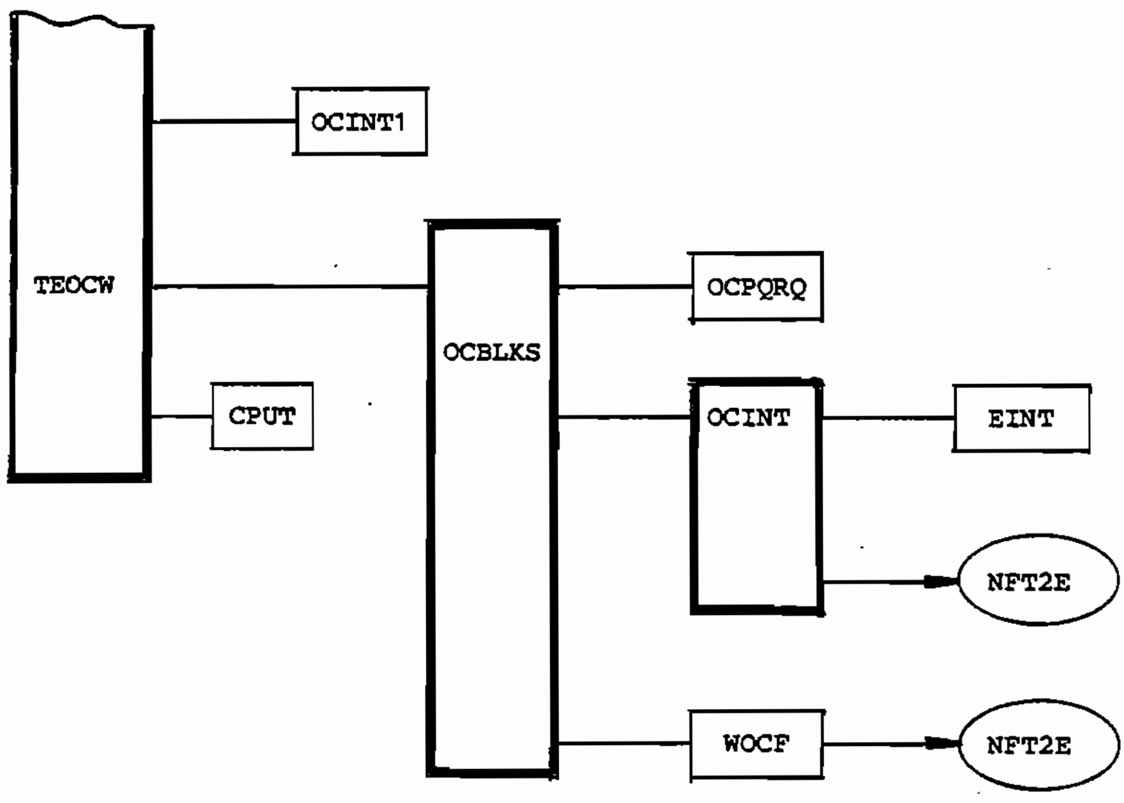
TEOCW
OCINT1
CPUT
OCBLKS
OCPQRQ
OCINT
EINT
NFT2E
WOCF
NFT2E

Fig.3

tribution of the required type and sets up pointer arrays for locating these basis functions during the integral calculation.

XINT

This subroutine performs the x-integration of eq.(31) to yield the required exchange integrals in the case where centres p,q are not identical to the r,s centre pair. The potential functions, E, may be read or written to temporary disk files associated with units 10 and 11 during the calculation.

XINTTR

Performs the same function as XINT in the case that the pq pair is identical to the rs-centre pair.

EPQXI

Two-centre potential functions, E, are computed using eqs.(32), (33) by this subroutine. The integration proceeds upwards from the lower limit point x=1, otherwise the organisation of the calculation is exactly similar to that used in the Coulomb/Hybrid calculation. Basis functions at specific elliptic coordinates are obtained via calls to STOXE; the computation does not depend therefore on whether the values being returned correspond to STO functions or to a numerical function determined externally by RCO.

WXINT

Integral labels are generated in routine WXINT. These and the computed integrals are then written to the disk file associated with unit NFT2E. Integrals with magnitude less than a specified threshold value (THRINT) are deleted.

PLMX4

This routine computes a table of unnormalised associated Legendre functions, each entry being multiplied by two weighting factors. The second factor is raised to the power corresponding to the order of the Legendre function.

The remaining subroutine calls in this section are either initialisation calls or calls to the routines used to generate the various quadrature formulae used. The latter subroutines will be considered further in section 9 of this memorandum.

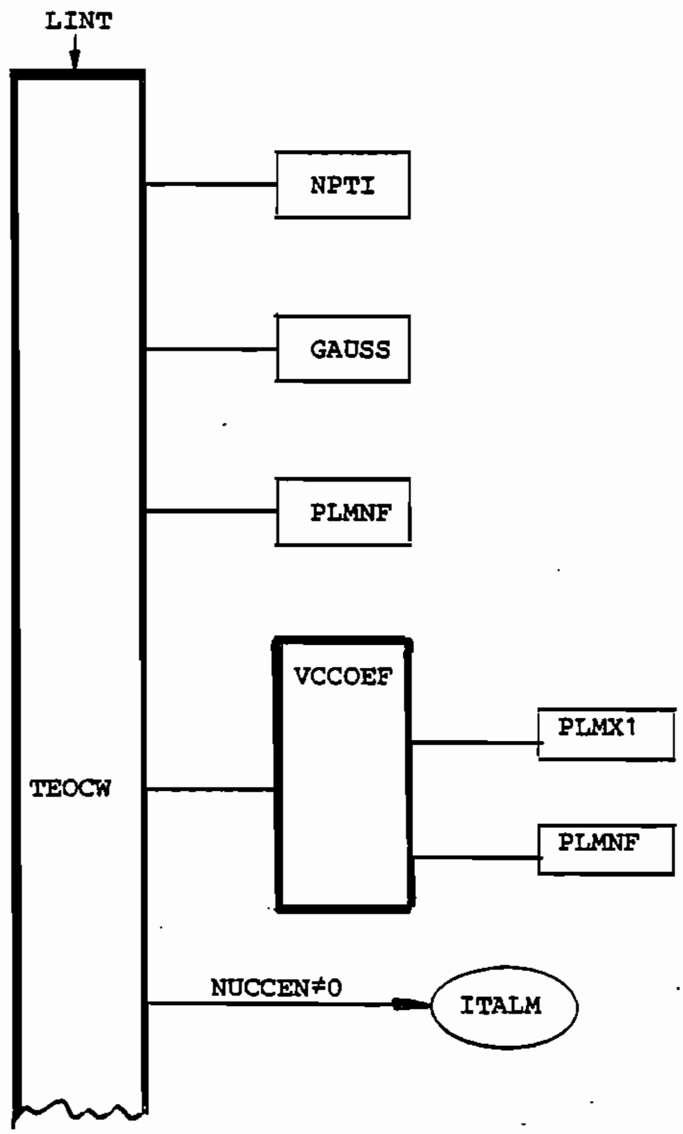
LINT
TEOCW
NPTI
GAUSS
PLMNF
VCCOEF
PLMX1
PLMNF
NUCCEN≠0
ITALM

Fig.2a

6.2 Two-centre integrals

Three types of two-centre one-electron integrals need be considered:

(i) overlap;

(ii) nuclear attraction; a, b distinct, c coincident with a or b;

(iii) nuclear attraction; a, b identical, c distinct.

All are most conveniently treated by using the spheroidal coordinate system introduced for exchange integrals taking the distinct centres as foci (see fig.4).

The overlap integrals may then be written in the form

$$S_{12} = \delta_{m_1m_2} N_{n_1\ell_1} N_{n_2\ell_2} (R)^{n_{12}+1} \sum_{i,j} d_{ij} \, A_i(R\zeta_{12}) B_j^{00}(-R\bar{\zeta}_{12}) \tag{44}$$

where

$$\bar{\zeta}_{12} = \zeta_1 - \zeta_2 \tag{45}$$

and integral B is given by

$$B_j^{m\ell}(\beta) = \frac{(\ell-m)!}{(\ell+m)!} \int_{-1}^{+1} d\eta \; \eta^j (1-\eta^2)^{m/2} P_\ell^m(\eta) e^{\beta(\eta-1)} \tag{46}$$

and R is half the separation of centres 1 and 2. The coefficients d_{ij} appearing in eq.(44) are defined by

$$(\xi + \eta)^{n_1} (\xi - \eta)^{n_2} \mathscr{P}_{\ell_1}^{m_1}\left(\frac{1+\xi\eta}{\xi+\eta}\right) \mathscr{P}_{\ell_2}^{m_2}\left(\frac{1-\xi\eta}{\xi-\eta}\right) \equiv \sum_{ij} d_{ij} \, \xi^i \eta^j . \tag{47}$$

It is clear that a similar result to eq.(44) will hold for the nuclear attraction integrals of type (ii). The power of R will be reduced by one in (44) and also the exponent n_1 or n_2 on the left hand side of (47) will be reduced by one depending on whether 1 or 2 is the attracting centre respectively.

Similarly for type (iii) nuclear attraction integrals, assuming b is

the centre of attraction

$$U_{aa}^{b} = \delta_{m_1m_2} N_{n_1\ell_1} N_{n_2\ell_2} R^{n_{12}} \sum_{ij} d'_{ij} \, A_i(R\zeta_{12}) \, B_j^{00}(-R\zeta_{12}) \tag{48}$$

and

$$(\xi + \eta)^{n_{12}-1} \mathscr{P}_{\ell_1}^{m_1}\left(\frac{1+\zeta\eta}{\zeta+\eta}\right) \mathscr{P}_{\ell_2}^{m_2}\left(\frac{1+\zeta\eta}{\zeta+\eta}\right) \equiv \sum_{ij} d'_{ij} \, \xi^i \eta^j . \tag{49}$$

There will clearly be no long-range contributions to these two-centre integrals when the charge distribution involved is two-centred - however case (iii) given by eqs.(48) and (49) will have long-range contributions when centre a corresponds to the scattering centre G. It is essential that these long-range contributions to the integral are computed in a spherical coordinate system with an origin located on G. It can then be shown that

$$U_{GG}^{C} = \sum_{L} \frac{1}{\sqrt{2L+1}} \begin{Bmatrix} 1 \\ (-1)^L \end{Bmatrix} \left(\frac{r_c}{a}\right)^L N_{n_1\ell_1} N_{n_2\ell_2} G_{m_1\,0\,m_2}^{\ell_1\,L\,\ell_2} \, a^{n_{12}} A_{n_{12}-L-1}(\zeta_{12}a) \tag{50}$$

where the upper factor in the braces is to be taken if centre C is to the right of G, and the lower is to be used if it is to the left.

6.3 Three-centred nuclear attraction integrals

These integrals are treated by introducing a spherical coordinate system with the origin located on the attracting centre C. The two-centred charge distribution must then be expanded about this point in complete analogy with the case already considered for Coulomb/Hybrid integrals. It is found that

$$U_{ab}^{C} = F_{ab}^{00}(r=0) \equiv \int_0^\infty dy \; y \int_{-1}^{+1} dx \; \chi_a \, \chi_b \tag{51}$$

where F is the potential function defined by eq.(12).

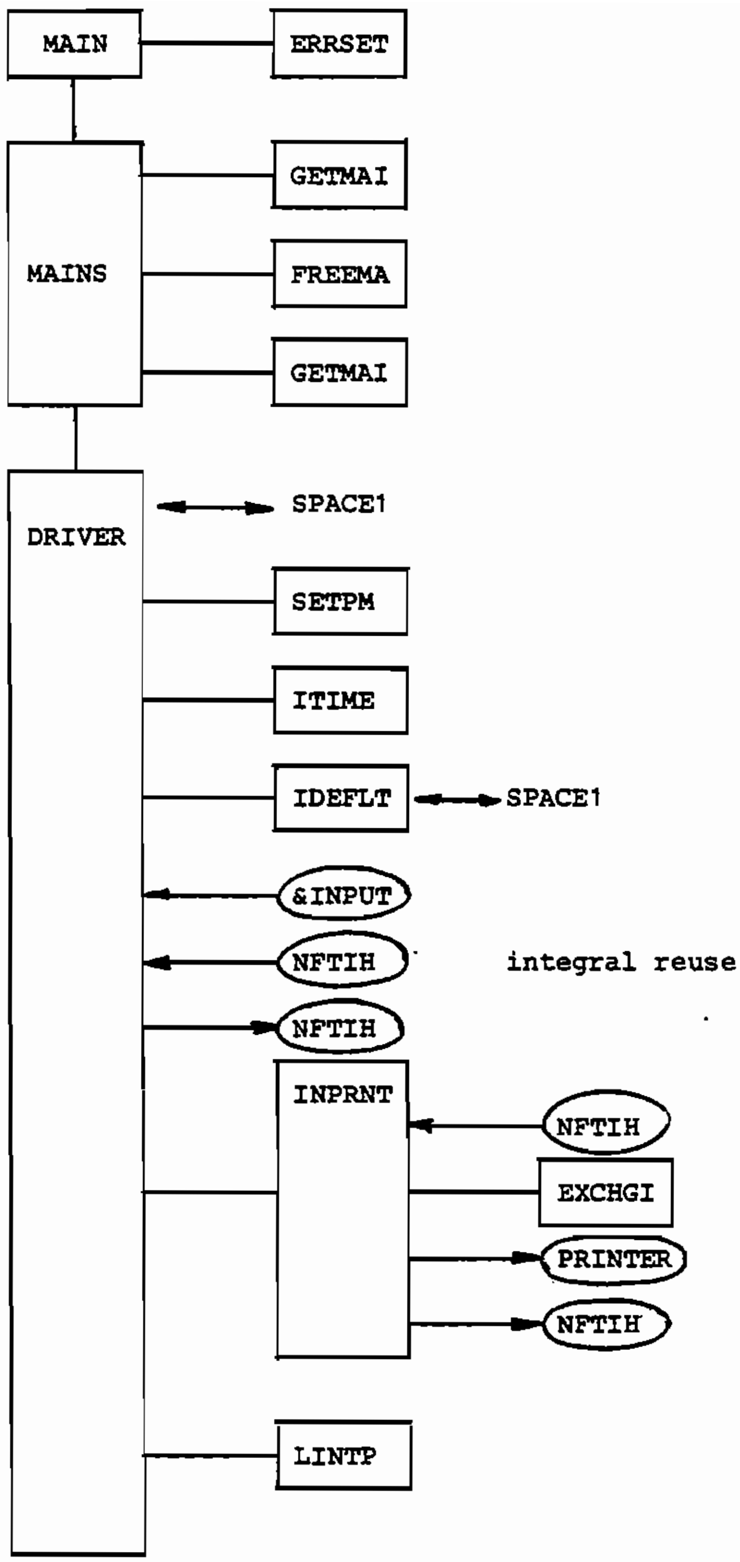
MAIN
ERRSET
MAINS
GETMAI
FREEMA
GETMAI
DRIVER
SPACE1
SETPM
ITIME
IDEFLT
SPACE1
&INPUT
NFTIH
integral reuse
NFTIH
INPRNT
NFTIH
EXCHGI
PRINTER
NFTIH
LINTP

Fig.1a

subroutine. The calculation is divided into three sections corresponding to (A) one-centre integrals, (B) two-centre integrals with a one-centre charge distribution, (C) two-centre integrals with a two-centre charge distribution as indicated in fig.7. The methods used are identical to those for overlap integrals. In R-matrix calculations, the Gaunt coefficients G required in eq.(50) are read from disk file ITALM.

UPQ3C

The looping over centres and symmetries is combined in this subroutine which supervises the 3-centre nuclear attraction integral computation. Note that nuclear attraction integrals carry the type label 3 in addition to the sequence number of the attracting centre.

UPQNI

Performs the two-dimensional integration of eq.(51) and so evaluates the three-centre nuclear attraction integrals.

WUPQ

This subroutine computes block and integral labels before writing the three-centre nuclear attraction integrals to disk file NFT1E.

WOEINT

Writes one- and two-centre one-electron integrals to the disk file attached to unit NFT1E.

7. PROPERTY AND NUMERICAL ONE-ELECTRON INTEGRALS

The integrals of this class are defined as one-electron integrals (involving between one and three centres) of the form

$$I_{ab,k} = \int d\tau_1 \, \Omega_{ab}(1) \, O_k \, . \tag{54}$$

Ω_{ab} is the usual one- or two-centred charge distribution while the operator O_k may take either the form

$$O_k = r_k^n (1-x_k^2)^{1/2} \, x_k^j \, P_\ell^m(x_k) \, \Phi_m(\phi_k) \, , \tag{55}$$

where $x_k = \cos\theta_k$ or alternatively

$$O_G^k = \frac{1}{|\vec{r}_G - \vec{r}_k|} \, . \tag{56}$$

By taking a spherical coordinate system with the origin located on the property centre the evaluation of the integrals (54) is easily reduced to a two-dimensional quadrature.

7.1 Program details

Property integrals and numerical one-electron integrals are calculated by separate calls to the same group of subroutines from subroutine LINT. This calling sequence is shown schematically in fig.8 and the subroutines involved listed in Table 6.

True property integrals involving operators of the form given in eq.(55) are computed over the infinite domain and carry the type label 4. The full block header label is an octet of numbers of the form 4 n i j k ℓ m 0. The operation of this section is controlled by the switch IFLINT(5). Of course for the integral to be convergent the value of the parameter n must satisfy n > - 1. Integrals are written to the disk file attached to unit IOEU.

TABLE 3. TWO-ELECTRON ONE-CENTRE INTEGRAL SUBROUTINE LIST

Entry Points

1.	EINT			
2.	OCBLKS			
3.	OCPQRQ	IOCPQ		
4.	TEOCW			
5.	WOCI	OCINT1	OCINT	WOCF

TABLE 4. EXCHANGE INTEGRAL SUBROUTINE LIST

Entry Points

1.	ARC	ELTBL	ELINT	ELINV		
2.	GAUSS					
3.	IEPQXI	EPQXI				
4.	INPAR					
5.	IPLMX					
6.	NPTD	NPTI				
7.	PLMNF					
8.	PLMX2	IPLMX2				
9.	PLMX4	IPLMX4				
10.	PQCNT					
11.	PRTTN					
12.	QUADXE	QUADXI	QUADE1	QUADE		
13.	INCO	RCO	TRCO	BRCO		
14.	STO1	STO2	STOXE	STOTB	SBLOCH	STOTBL
15.	TABLE1	TABLE2				
16.	TCPQRQ					
17.	TETCW					
18.	WRXINT	WXINT				
19.	XBLKS					
20.	XINT					
21.	XINTTR					

TABLE 5. SLATER ONE-ELECTRON INTEGRAL SUBROUTINE LIST

Entry Points

1.	BJMLB					
2.	EINT					
3.	GAUSS					
4.	INPAR					
5.	IPLMX					
6.	NPTD	NPTI				
7.	OTCUPQ					
8.	PLMX3	IPLMX3				
9.	PMY2V					
10.	PMY2V2	PMY2V3	PMY2V4			
11.	QUAD	QUAOR	QUAD1	QUADTH		
12.	STO1	STO2	STOXE	STOTB	SBLOCH	STOTBL
13.	STPQ					
14.	STUMX					
15.	UPQNI					
16.	UPQ3C					
17.	WNJ	VNJ	XNJ	WNJ1		
18.	WOEINT	IWOE				
19.	WUPQ	WUPQ1				

TABLE 6. PROPERTY INTEGRAL SUBROUTINE LIST

Entry Points

1.	GAUSS					
2.	INCO	RCO	TRCO	BRCO		
3.	INPAR					
4.	IOEOP	OEOP1	OCOEOP			
5.	IPLMX					
6.	NPTD	NPTI				
7.	OCOEME					
8.	OEINT					
9.	OEMXLP					
10.	OTPQRQ					
11.	PLMX2	IPLMX2				
12.	PLMX3	IPLMX3				
13.	QUAD	QUADR	QUAD1	QUADTH		
14.	SORTOP					
15.	STO1	STO2	STOXE	STOTB	SBLOCH	STOTBL
16.	WOEMX	WOEMX1				
17.	WOEMX2					

8. RENORMALISATION, BOUNDARY AMPLITUDES AND MOLECULAR ORBITALS

8.1 Integral renormalisation

All integrals computed in previous sections of the program have been calculated with basis functions normalised over all space. In R-matrix calculations these must be renormalised to the volume of the R-matrix internal region. This implies that those integrals which have been computed from truncated basis functions must be multiplied by factors equal to the inverse square root of the corresponding (truncated) diagonal overlap matrix element in order to form a correctly normalised integral. Hence, for example,

$$S^R_{12} = S^{-1/2}_{11}\, S^{-1/2}_{22}\, S_{12}, \tag{57}$$

where labels 1 and 2 correspond to complete sets of basis function quantum numbers and the value on the left corresponds to the correctly normalised overlap element.

8.2 Continuum molecular orbital generation

Several options exist within the program for generating continuum molecular orbitals by orthogonalisation techniques. The target molecular orbitals are first read in. This is followed by a Schmidt orthogonalisation, symmetry by symmetry, of the continuum basis functions with respect to the target orbitals. The continuum orbitals which result may then be symmetric orthogonalised amongst themselves. Alternatively the entire set of functions may be Schmidt orthogonalised. In both cases the linear dependence of the generated orbital set is monitored (orbitals are deleted if they would lead to normalisation errors) and may be restricted to be less than some specified value.

In cases where numerical orbitals which already form an orthonormal set with the target orbitals are used it is possible to generate effective

molecular orbital wavefunctions in the standard ALCHEMY format without any orthogonalisation. The resultant molecular orbital set may be output in a variety of formats including that of a standard ALCHEMY molecular orbital dumpfile.

8.3 Boundary amplitudes

Once an orthonormal set of molecular orbitals including continuum orbitals is available the construction of boundary amplitudes according to eq.(16b) of Burke et al[10] is straightforward. Note that the amplitude definition contains the $(2a)^{-1/2}$ factor as well as the orbital angular momentum projection of the radial molecular orbital wavefunction on the R-matrix boundary.

In large calculations there are considerable advantages to the use of partitioning techniques and the introduction of an optical potential. This aspect has been emphasised by Nesbet[4] (see also Oberoi and Nesbet[13,14]). With these considerations in mind it is possible to perform an orthogonal transformation on the generated molecular orbital set so that only one orbital for each asymptotic channel has a non-zero boundary amplitude. This transformation is included as an option within the code.

8.4 Program details

The calling sequence of the subroutines involved in the generation of continuum molecular orbitals and in the computation of boundary amplitudes is illustrated in fig.9. The corresponding subroutine names and entry points are listed in Table 7.

TRNSDR

The target molecular orbitals are input by subroutine TRNSDR either

APPENDIX C. INSTALLATION DETAILS

The special programming features used in this package imply that it will only run correctly on a computer with IBM compatible architecture. It is currently implemented on the NAS 7000 computer at the Daresbury Laboratory.

1. Source Code

   File NB.DARLAB.TAILMY.FORT

   (May be archived)

2. Load module

   NO.LOAD(TAILV)

3. JCL

   (i) for compilation: NB.DARLAB.TAILMY.FORT(COMP)

   (ii) for link editing: NB.DARLAB.TAILMY.FORT(LINK)

Input and output files corresponding to the examples given in Appendix A may be found in the archived files NB.DARLAB.TAILMY.DATA and NB.DARLAB.TAILMY.TEXT.

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9. QUADRATURE AND TRANSFORMATION ROUTINES

The efficiency of the program depends ultimately on the speed and accuracy with which various numerical integrations can be performed. As a consequence rather elaborate procedures have been adopted for generating the quadrature nodes and weights. Six subroutines are involved: QUAD, QUADXE, INPAR, GAUSS, ARC, NPTD. The entry point names associated with these routines are listed in Table 8. The logical structure of the two major routines, QUAD and QUADXE, is quite involved and therefore will be briefly described here. The underlying physical picture which should be kept in mind during this discussion is as follows.

The appropriate integration mesh for use in a particular integral calculation is determined by the effective potential seen by an electron at each spatial point. For example in the case of a homonuclear molecule, the dominant feature is the occurrence of the nuclear singularities (at a radial distance, $r = r_N$, say). In some region which may typically extend up to 0.5 Bohr either side of this point the effective potential will be rapidly varying and be dominated by the static componente. Most integration mesh points therefore must be concentrated in this region and should be distributed symmetrically about the singularity. At smaller radial distances the potential will be strong but nearly constant and consist of an approximately equal mixture of exchange and statio components. Beyond the nuclear region the exchange and static components will again be comparable. At still larger radial distances ($> 2\ r_N$) the exchange components will be decaying rapidly and the static component will tend to assume a smoothly varying multipolar character. Hence both the outer two regions will require fewer mesh points than the nuclear region.

QUAD

This routine generates integration formulae used for Coulomb/Hybrid,

numerical one-electron and property integral calculations. The two major entry points are QUADR, which generates formulae for tha radial integrations, and QUADTH which generates the angular theta mesh. Recall that a spherical coordinate system is used with origin located on one of the centres and that between one and three centres may be involved in the integral.

QUADR

Input data controlling the computation of the radial mesh is of three types

(i) centre data

RNUC specifies the characteristic range associated with the charge distribution on the centre i.e. the region about the nuclear singularity where the static potential dominates

DRNUC gives the number of integration points per unit path length in the region associated with the centre

(ii) IRIP an array of data determining the order of Gauss formulae to be used in various subintervals

(iii) DRIP an array of data determining distance scales and the positioning of the transformation points within a subinterval

The mesh is determined for the interval between each pair of centres in turn and then for the region beyond the last centre. For each pair of centres r_{k_i} and $r_{k_{i+1}}$ (see fig.10) the number of integration subranges into which the interval is divided depends essentially on the size of the intermediate region, denoted by r_A.

(a) $r_A < r'_0$

Then in the case of Coulomb integrals two subintervals are created

TABLE A2

```
// EXEC FGG,LIBRARY='NO.LOAD',MEMBER=TAILV,REGION=1999K,TIME=(29,59)
//G.FT08F001 DD DSN=NB.N2SGP3.DATA,DISP=SHR,UNIT=3330-1,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(2,2),RLSE)
//G.FT08F002 DD DSN=NB.N2SGP4.DATA,UNIT=3330-1,DISP=SHR,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(6,6),RLSE),
//  VOL=SER=DL0298
//G.FT09F001 DD DSN=NB.N2SGP5.DATA,UNIT=3330,DISP=SHR,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(1,1),RLSE),
//   VOL=SER=DNPL33
//G.FT10F001 DD DSN=&&DUMM3,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(5,5),RLSE)
//G.FT11F001 DD DSN=&&DUMM4,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(5,5),RLSE)
//G.FT12F001 DD DSN=&&KAT12,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(50,90),RLSE)
//G.FT13F001 DD DSN=&&KAT13,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(90,90),RLSE)
//G.FT15F001 DD DSN=&&KAT14,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(90,90),RLSE)
//G.FT21F001 DD DSN=NB.N2SGPO.DATA,UNIT=3330,VOL=SER=DNPL33,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(10,10),RLSE),
//  DISP=SHR
//G.FT22F001 DD DSN=NB.N2SGPLA.DATA,UNIT=3330-1,VOL=SER=DL0298,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(1,1),RLSE),
// DISP=SHR
//G.FT27F001 DD DSN=NB.V2.STON2N,DISP=SHR
//G.FT29F001 DD DSN=QKV.N2FUN.SG0243.DATA,DISP=SHR
//G.SYSIN DD *
 &INPUT
    NAME='N2 NESBET SIGMA-G (S, D, G WAVES) 22-POLES (COUPLED),2 CORRELATN
  GEONUC= -1.034,1.034,0.0,  NEF=86,  NNUC=3,
  NLMK=1,0,0,1, 1,0,0,2, 1,0,0,1, 1,0,0,2, 2,0,0,1, 2,0,0,2,
       2,0,0,1, 2,0,0,2, 2,1,0,1, 2,1,0,2, 2,1,0,1, 2,1,0,2,
       3,2,0,1, 3,2,0,2, 2,1,1,1, 2,1,1,2, 2,1,1,1, 2,1,1,2,
       3,2,1,1, 3,2,1,2,
        1,0,0,3,  2,0,0,3,  3,0,0,3,  4,0,0,3,  5,0,0,3,  6,0,0,3,
        7,0,0,3,  8,0,0,3,  9,0,0,3, 10,0,0,3, 11,0,0,3, 12,0,0,3,
       13,0,0,3, 14,0,0,3, 15,0,0,3, 16,0,0,3, 17,0,0,3, 18,0,0,3,
       19,0,0,3, 20,0,0,3, 21,0,0,3, 22,0,0,3,
        3,2,0,3,  4,2,0,3,  5,2,0,3,  6,2,0,3,  7,2,0,3,  8,2,0,3,
        9,2,0,3, 10,2,0,3, 11,2,0,3, 12,2,0,3, 13,2,0,3, 14,2,0,3,
       15,2,0,3, 16,2,0,3, 17,2,0,3, 18,2,0,3, 19,2,0,3, 20,2,0,3,
       21,2,0,3, 22,2,0,3, 23,2,0,3, 24,2,0,3,
        5,4,0,3,  6,4,0,3,  7,4,0,3,  8,4,0,3,  9,4,0,3, 10,4,0,3,
       11,4,0,3, 12,4,0,3, 13,4,0,3, 14,4,0,3, 15,4,0,3, 16,4,0,3,
       17,4,0,3, 18,4,0,3, 19,4,0,3, 20,4,0,3, 21,4,0,3, 22,4,0,3,
       23,4,0,3, 24,4,0,3, 25,4,0,3, 26,4,0,3,
```



```
ZETA=6.21292, 6.21292, 9.36827, 9.36827, 1.46786, 1.46786,
     2.24642, 2.24642, 1.52853, 1.52853, 3.33678, 3.33678,
     1.93500, 1.93500,
     1.52853, 1.52853, 3.33678, 3.33678, 2.43700, 2.43700,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,


  NUCCEN=3,
  IBLOCH=0, BBLOCH=0.0, RMATR=10.00,NUCCEN=3, IFLOUT=0,0,
  IFLSYM=1,IFLINT=7*0,             IPRINT=5*0,2*0,0, LREC=6300,
  ICF=1,ICFP=1,
 &END
 &GET
  NSYM=2,
  NBF=14,6, NOB=9,5,
  ITVCI=1,
 &END
 &GETI
    IVCS=27, NIND=9,
    IND=1,0,1,3, 1,0,6,6, 1,0,9,9, 1,0,4,5, 1,0,7,8,
        1,1,1,1, 1,1,3,4, 1,1,2,2, 1,1,5,5,
    NBASE=0
 &END
 &PUT
  CHARG=7.0,7.0,0.0, NBF=80,6, NOB=31,5, NSYM=2,
  TPROJ=-1.0D0,  ITVCI=0, IORTHO=1,NFONE=9,
  MEGU=21,ISTOST=1,
 &END
```

total interval involved in the integration is πR. This interval may be split into up to four segments depending on the location of the centres and on the most important regions covered by the associated charge distributions. The most general case occurs if there are centres located both to the right and left of the coordinate origin on ZE and the integration arc intersects the important regions of both charge distributions. This case is illustrated in fig.13.

The first case to be considered is that when R is small. Only the charge-distribution associated with ZE is deemed relevant and there is no subdivision of the full integration arc. Input parameters define the number of Gaussian points to be used per unit arc length.

In other cases the distance between each centre and the integration arc must be determined. If no centres are close to the integration path there again is no subdivision of the interval. Variable $D = |Z_k - R|$ for centre k, is used to linearly scale the number of mesh points per unit arc length corresponding to the region associated with centre k. Having determined the subintervals and numbers of grid points, subroutine INPAR is again called to transform the Gauss-Legendre weights and nodes thus constructing the compound quadrature formula.

QUADXI

This routine is used to construct the ξ-integration mesh used in the evaluation of exchange integrals. The overall structure and most of the detailed logic used is identical to that employed in routine QUADR and therefore need not be repeated here. Between two and four centres may be involved. Apart from the fact the charge distributions are all assumed to be two-centred and short-ranged, differences arise from QUADR only because of the different integration variable.

QUADE

This entry point of subroutine QUADXE is used to determine the η-integration mesh used in the exchange integral calculation. The routine has a similar structure to QUADTH the differences resulting from the fact that the integration path is elliptical rather than circular. To handle the geometric problem of determining elliptic arc lengths subroutine ARC with entry points ELTBL, ELINT and ELINV is used. An initial call to ARC sets up a compound integration rule based on the 2-point Gauss-Legendre formula for the 0 to π interval. Using this rule, ELTBL is called to set up a table of arc lengths corresponding to each multiple of $\pi/32$. Entry ELINT may then be used to determine the arc length subtended by any two angles by linear interpolation on the arc-length table. This process is inverted by entry ELINV. The division of the η-arc length into sub-intervals according to the proximity of the various charge-distributions follows the pattern established by QUADTH. Once the intervals, orders and transformation points have been established, INPAR is again called to generate the required weights and nodes.

MEGU 1; 1; I*4; 27

Unit for the output of the generated molecular orbital vectors in the case that ITVCI<1

NBF NSYM; 21; I*4; 21*0

Number of basis functions in the generated vector set for each of the NSYM symmetries

NBFT 1; 1; I*4; 0

Total number of basis functions (summed over symmetries) in the generated set of molecular orbitals

NPBF NBFT; 150; I*4;

Array giving for each of the complete set of output basis functions, the corresponding basis function sequence number within a given symmetry set

NFONE 1; 1; I*4; 9

Unit number from which overlap matrix elements are to be read in subroutine ENLARG in order to perform the orthogonalisation of the molecular orbitals

NOB NSYM; 21; I*4; 21*0

Number of molecular orbitals which are to be constructed (including the target orbitals) for each symmetry in the output molecular orbital set

NSYM 1; 1; I*4;

Number of symmetries in the generated set of molecular orbitals

LTRB 1; 1; I*4; 449

Number of coefficients to be written in each output record of the generated set of molecular orbitals. The complete record size will be (LTRB*2+1)*4 bytes

TPROJ 1; 1; R*8; 1.0D-5

The smallest eigenvalue of the molecular orbital overlap matrix which is to be retained; orbitals which are more linearly dependent are deleted

If TPROJ = -1.D0 all orbitals are retained

The scattering centre should be first followed by nuclear centres in order of decreasing nuclear charge. The code will force G to be first.

IPROPU 1; 1; I*4; 9

Unit number for output of property integrals

PRNAME (2,20); (2,20); R*8; '   '

Property names each having a maximum of 16 characters.

I2PCDE (8,20); (8,20); I*2;

Octets, each specifying a one-electron property operator, of the form

4, n, i, j, k, l, |m|, 0

$$r_k^n \cos^j\theta_k \sin^i\theta_k \, P_\ell^{|m|}(\cos\theta_k) \, \frac{1}{\sqrt{2\pi}} \, e^{i|m|\theta_k}$$

k identifies the centre which acts as coordinate origin

ITALM 1; 1; I*4; 21

Unit for scratch storage of Legendre function integrals computed by VCCOEF

NFTR 1; 1; I*4; 22

Unit for the output of boundary amplitudes

NFTC 1; 1; I*4; 29

Unit for the input of data defining the numerical continuum basis functions

NFTIH 1; 1; I*4; 8

Unit for the output of data defining the run

NFT1E 1; 1; I*4; 13

Unit for the output of one-electron integrals. The integral labels may not be symmetry-ordered and the integrals themselves will not be renormalised.

NFT1I 1; 1; I*4; 9

Unit for the output of one-electron integrals. Labels will correspond to symmetry-ordered basis functions as required in other ALCHEMY program modules.

NFT2E 1; 1; I*4; 12

Unit for the output of two-electron integrals. Labels will correspond to the order in which the basis-functions were input and may not be symmetry-ordered.

NFT2I 1; 1; I*4; 8

Unit for the output of two-electron integrals. Labels will correspond to symmetry-ordered basis functions as required by other ALCHEMY programs.

THINT 1; 1; R*8; 5.0D-8

Delete all two-electron integrals with magnitude less than THINT

IFLOUT 2; 2; I*4; 2*0

Print switch for integration mesh data

IFLOUT(1) unused

IFLOUT(2) =0 no printout

=1 print primary radial integral subranges and orders and secondary orders

=2 as 1 plus print angular subranges and orders

Switch applies to all numerical integrals

IXORD 1; 1; I*4; 1

=1 order centres in two-electron exchange integral calculation according to decreasing Z-coordinates

=-1 order centres according to increasing Z-coordinates

LREC 1; 1; I*4; 7200

Maximum length in bytes for a logical output record of integrals

NFTA3 — 1; 1; I*4; 21

Unit number from which target molecular orbitals are to be read

NOB — NSYM; 21; I*4; 21*0

Number of target molecular orbitals for each symmetry

NSYM — 1; 1; I*4;

Number of different symmetries in the input set of target molecular orbitals (NSYM<21)

VCIN — NT; 1700; R*8;

Packed array of target molecular orbital coefficients - read if ITVCI=0

$$NT = \sum_{L=1}^{NSYM} NOB(L)*NBF(L)$$

10.4 Namelist &GET1

This namelist is read in by subroutine GETVC in the case that ITVCI=1. It contains control variables for the selection of target molecular orbital coefficients from a dumpfile attached to unit IVCS. The selected orbitals are written as the first file on unit IMEGU.

CGU — (2, number of basis functions); (2,150); R*8;

Array used when dealing with a dumpfile containing vector co-efficients in $D_{\infty v}$ format. For details refer to the source listing of subroutine WMEGU. There are two entries for each basis function giving the sign with which it enters into the corresponding g- and u-symmetrised basis functions. The other member of the pair is defined by array MT. A zero is entered for basis functions on the central atom of a molecule with an odd number of nuclei.

IFLSYM — 1; 1; I*4; 0

Switch indicating the type of vector coefficients in the dumpfile i.e. $C_{\infty v}$, $D_{\infty h}$. Normally only the default is used implying $C_{\infty v}$ storage.

IVCS — 1; 1; I*4; 27

Unit of the dumpfile from which the target molecular orbital coefficients are to be selected

IND — (4,NIND); (4,100); I*4;

NIND quartets (a,b,c,d) which define the target molecular orbitals which are to be selected

a — the set number

b — symmetry type

c — starting orbital } orbital sequence numbers

d — final orbital } orbital sequence numbers

MT — number of basis functions; 150; I*4;

Pointer array used in conjunction with CGU in the $D_{\infty h}$ case. Each entry of MT refers to a basis function and gives the serial number (using the serialisation within a symmetry class established by input to the integral program) of the basis function which is to be associated with that function in a symmetrised basis function.

NBASE — 1; 1; I*4; 0

A base number by which all the orbital set numbers in IND are incremented

NIND — 1; 1; I*4;

The number of quartets in array IND used to select the required molecular orbital coefficients

10.2 Integration Mesh Parameters

Many parameters must be passed to the quadrature generating subroutines QUAD and QUADXE. In general the default values provided by data statements in the code will be adequate; however in scattering calculations involving very diffuse Slater orbitals or highly oscillatory numerical continuum functions some may need to be adjusted.

Two independent sets of parameters are entered for subroutine QUAD; one set is used for the Coulomb/Hybrid calculation, the other for property and numerical one-electron integrals. For this reason the external variable names of the first set will be used in the following description and related to the second set in a later section.

Parameters relating to the radial integration meshes generated by subroutine QUAD

DRIP 10; 15; R*8;

DRIP(1)	AR	number of Gauss points per unit interval to be used in the internal region between centre regions
DRIP(2)	BR	exponent determining the weighting to be given to an interval in the internal region when determining the number of integration points Typically for an interval Δr in the central region the number of points will be $\Delta n = a_r \times (\Delta r)^{b_r}$
DRIP(3)	CR	fraction determining the position of the transformation point within a subrange
DRIP(4)	DR	exponent determining the weighting to be given to the internal region when partially included in a subrange extending into a centre region

DRIP(5)	RMIN	centres which are closer together than this distance are regarded as identical
DRIP(6)	RMAX	the distance between the centre farthest from the origin and the largest radial mesh point ("infinity")
DRIP(7)	P1	determines the fraction of centre region grid points of the primary radial mesh which are to correspond to secondary radial grid subranges with NG1-order Gauss formulae
DRIP(8)	RCINF	the distance of the transformation point in the last (highest radial grid points) subrange from the start of the subrange
DRIP(9)	RTHR	parameter determining the division of the interval between centres into subranges by setting the scale. Variables r_2' and r_4' of section 9 correspond to 2 and 4 times RTHR, respectively
DRIP(10)	RTHRL	the distance between the boundary of the centre region furthest from the origin and the initial point of the final "semi-infinite" subrange

The remaining 5 entries of array DRIP are unused.

The column following the variable name corresponds to the internal variable most closely related (not necessarily identical!) to the external variable.

IRIP 7; 15; I*4;

IRIP(1)	NRINF	Order of the Gauss formula to be used in the outermost radial subrange
IRIP(2)	DNRMN2	The internal region between centre regions is

generated (assuming the orders are identical)

DTHIP(8)	R01	minimum radius of the inner region associated with the centre located at the origin
DTHIP(9)	R02	minimum radius for the outer part of the region associated with the centre at the origin

The remaining entries of DTHIP are unused.

ITHIP	10; 15; I*4;	
ITHIP(1)	DNTMNI	minimum number of integration points for an arc in the region associated with the centre at the origin
ITHIP(2)	DNTMXI	maximum number of integration points for an arc in the region associated with the centre at the origin
ITHIP(3)	DNTMNO	minimum order Gauss formula to be used in non-centre regions
ITHIP(4)	DNTMXO	maximum order Gauss formula to be used in non-centre regions
ITHIP(5)	DNTMNF	minimum order formula to be used for a complete arc which does not intersect centre regions
ITHIP(6)	DTMX1	maximum number of integration points for the non-centre sector of the quadrant which has a centre subrange (centres on one side of the origin)
ITHIP(7)	DTMX2	maximum number of integration points for a quadrant which has no centre subrange (centres on one side of the origin)
ITHIP(8)	DTMX3	maximum number of intgration points in a non-centre sector when there are centres on both sides of the origin
ITHIP(9)	DTMX4	maximum order formula in a non-centre region for a quadrant having no centre-subrange when there are centres located on both sides of the origin
ITHIP(10)	DNTMNR	minimum number of integration points in a non-centre region

The remaining entries of ITHIP are unused.

Centre parameters

DIPNUC(3,I)	RTHUC(I)	basic region size to be associated with centre I
DIPNUC(4,I)	ATHNUC(I)	maximum number of integration points per unit interval in the region associated with the centre
DIPNUC(5,I)	CTHNUC(I)	maximum value of the factor determining the position of the transformation point in a subrange including the centre region

Parameters relating to the radial integration meshes generated by subroutine QUADXB

These parameters are completely analogous to those passed to subroutine QUAD and hence it suffices to establish the correspondence between the two sets.

DXIIP 10; 15; R*8;

Determines the integration subranges and should be compared to array DRIP

IXIIP 7; 15; I*4;

Determines the orders for the primary and secondary ξ quadratures. Compare with array IRIP

Differences are due entirely to the coordinate definitions (i.e. $R \leftrightarrow \xi$). This is also true for the centre parameters.

DIPNUC(6,I)	RXNUC(I)
DIPNUC(7,I)	DXNUC(I)

generated (assuming the orders are identical)

DTHIP(8)	R01	minimum radius of the inner region associated with the centre located at the origin
DTHIP(9)	R02	minimum radius for the outer part of the region associated with the centre at the origin

The remaining entries of DTHIP are unused.

ITHIP	10; 15; I*4;	
ITHIP(1)	DNTMNI	minimum number of integration points for an arc in the region associated with the centre at the origin
ITHIP(2)	DNTMXI	maximum number of integration points for an arc in the region associated with the centre at the origin
ITHIP(3)	DNTMNO	minimum order Gauss formula to be used in non-centre regions
ITHIP(4)	DNTMXO	maximum order Gauss formula to be used in non-centre regions
ITHIP(5)	DNTMNF	minimum order formula to be used for a complete arc which does not intersect centre regions
ITHIP(6)	DTMX1	maximum number of integration points for the non-centre sector of the quadrant which has a centre subrange (centres on one side of the origin)
ITHIP(7)	DTMX2	maximum number of integration points for a quadrant which has no centre subrange (centres on one side of the origin)
ITHIP(8)	DTMX3	maximum number of intgration points in a non-centre sector when there are centres on both sides of the origin
ITHIP(9)	DTMX4	maximum order formula in a non-centre region for a quadrant having no centre-subrange when there are centres located on both sides of the origin
ITHIP(10)	DNTMNR	minimum number of integration points in a non-centre region

The remaining entries of ITHIP are unused.

Centre parameters

DIPNUC(3,I)	RTNUC(I)	basic region size to be associated with centre I
DIPNUC(4,I)	ATHNUC(I)	maximum number of integration points per unit interval in the region associated with the centre
DIPNUC(5,I)	CTHNUC(I)	maximum value of the factor determining the position of the transformation point in a subrange including the centre region

Parameters relating to the radial integration meshes generated by subroutine QUADXE

These parameters are completely analogous to those passed to subroutine QUAD and hence it suffices to establish the correspondence between the two sets.

DXIIP 10; 15; R*8;

Determines tha integration subranges and should be compared to array DRIP

IXIIP 7; 15; I*4;

Determines the orders for the primary and secondary ξ quadratures. Compare with array IRIP

Differences are due entirely to the coordinate definitions (i.e. $R \leftrightarrow \xi$). This is also true for the centre parameters.

DIPNUC(6,I)	RXNUC(I)
DIPNUC(7,I)	DXNUC(I)

10.2 Integration Mesh Parameters

Many parameters must be passed to the quadrature generating subroutines QUAD and QUADXE. In general the default values provided by data statements in the code will be adequate; however in scattering calculations involving very diffuse Slater orbitals or highly oscillatory numerical continuum functions some may need to be adjusted.

Two independent sets of parameters are entered for subroutine QUAD; one set is used for the Coulomb/Hybrid calculation, the other for property and numerical one-electron integrals. For this reason the external variable names of the first set will be used in the following description and related to the second set in a later section.

Parameters relating to the radial integration meshes generated by subroutine QUAD

DRIP 10; 15; R*8;

DRIP(1)	AR	number of Gauss points per unit interval to be used in the internal region between centre regions
DRIP(2)	BR	exponent determining the weighting to be given to an interval in the internal region when determining the number of integration points Typically for an interval Δr in the central region the number of points will be $\Delta n = a_r \times (\Delta r)^{b_r}$
DRIP(3)	CR	fraction determining the position of the transformation point within a subrange
DRIP(4)	DR	exponent determining the weighting to be given to the internal region when partially included in a subrange extending into a centre region

DRIP(5)	RMIN	centres which are closer together than this distance are regarded as identical
DRIP(6)	RMAX	the distance between the centre farthest from the origin and the largest radial mesh point ("infinity")
DRIP(7)	F1	determines the fraction of centre region grid points of the primary radial mesh which are to correspond to secondary radial grid subranges with NG1-order Gauss formulae
DRIP(8)	RCINF	the distance of the transformation point in the last (highest radial grid points) subrange from the start of the subrange
DRIP(9)	RTHR	parameter determining the division of the interval between centres into subranges by setting the scale. Variables r_2' and r_4' of section 9 correspond to 2 and 4 times RTHR, respectively
DRIP(10)	RTHRL	the distance between the boundary of the centre region furthest from the origin and the initial point of the final "semi-infinite" subrange

The remaining 5 entries of array DRIP are unused.

The column following the variable name corresponds to the internal variable most closely related (not necessarily identical!) to the external variable.

IRIP 7; 15; I*4;

IRIP(1)	NRINF	Order of the Gauss formula to be used in the outermost radial subrange
IRIP(2)	DNRMN2	The internal region between centre regions is

NFTA3 1; 1; I*4; 21

Unit number from which target molecular orbitals are to be read

NOB NSYM; 21; I*4; 21*0

Number of target molecular orbitals for each symmetry

NSYM 1; 1; I*4;

Number of different symmetries in the input set of target molecular orbitals (NSYM<21)

VCIN NT; 1700; R*8;

Packed array of target molecular orbital coefficients - read if ITVCI=0

$$NT = \sum_{L=1}^{NSYM} NOB(L)*NBF(L)$$

10.4 Namelist &GET1

This namelist is read in by subroutine GETVC in the case that ITVCI=1. It contains control variables for the selection of target molecular orbital coefficients from a dumpfile attached to unit IVCS. The selected orbitals are written as the first file on unit IMEGU.

CGU (2, number of basis functions); (2,150); R*8;

Array used when dealing with a dumpfile containing vector coefficients in $D_{\infty v}$ format. For details refer to the source listing of subroutine WMEGU. There are two entries for each basis function giving the sign with which it enters into the corresponding g- and u-symmetrised basis functions. The other member of the pair is defined by array MT. A zero is entered for basis functions on the central atom of a molecule with an odd number of nuclei.

IFLSYM 1; 1; I*4; 0

Switch indicating the type of vector coefficients in the dumpfile i.e. $C_{\infty v}$, $D_{\infty h}$. Normally only the default is used implying $C_{\infty v}$ storage.

IVCS 1; 1; I*4; 27

Unit of the dumpfile from which the target molecular orbital coefficients are to be selected

IND (4,NIND); (4,100); I*4;

NIND quartets (a,b,c,d) which define the target molecular orbitals which are to be selected

a the set number

b symmetry type

c starting orbital } orbital sequence numbers

d final orbital }

MT number of basis functions; 150; I*4;

Pointer array used in conjunction with CGU in the $D_{\infty h}$ case. Each entry of MT refers to a basis function and gives the serial number (using the serialisation within a symmetry class established by input to the integral program) of the basis function which is to be associated with that function in a symmetrised basis function.

NBASE 1; 1; I*4; 0

A base number by which all the orbital set numbers in IND are incremented

NIND 1; 1; I*4;

The number of quartets in array IND used to select the required molecular orbital coefficients

The scattering centre should be first followed by nuclear centres in order of decreasing nuclear charge. The code will force G to be first.

IPROPU 1; 1; I*4; 9

Unit number for output of property integrals

PRNAME (2,20); (2,20); R*8; '   '

Property names each having a maximum of 16 characters.

I2PCDE (8,20); (8,20); I*2;

Octets, each specifying a one-electron property operator, of the form

4, n, i, j, k, l, |m|, 0

$$r_k^n \cos^j\theta_k \sin^i\theta_k \, P_\ell^{|m|}(\cos\theta_k) \frac{1}{\sqrt{2\pi}} e^{i|m|\theta_k}$$

k identifies the centre which acts as coordinate origin

ITALM 1; 1; I*4; 21

Unit for scratch storage of Legendre function integrals computed by VCCOEF

NFTR 1; 1; I*4; 22

Unit for the output of boundary amplitudes

NFTC 1; 1; I*4; 29

Unit for the input of data defining the numerical continuum basis functions

NFTIH 1; 1; I*4; 8

Unit for the output of data defining the run

NFT1E 1; 1; I*4; 13

Unit for the output of one-electron integrals. The integral labels may not be symmetry-ordered and the integrals themselves will not be renormalised.

NFT1I 1; 1; I*4; 9

Unit for the output of one-electron integrals. Labels will correspond to symmetry-ordered basis functions as required in other ALCHEMY program modules.

NFT2E 1; 1; I*4; 12

Unit for the output of two-electron integrals. Labels will correspond to the order in which the basis-functions were input and may not be symmetry-ordered.

NFT2I 1; 1; I*4; 8

Unit for the output of two-electron integrals. Labels will correspond to symmetry-ordered basis functions as required by other ALCHEMY programs.

THINT 1; 1; R*8; 5.0D-8

Delete all two-electron integrals with magnitude less than THINT

'IFLOUT 2; 2; I*4; 2*0

Print switch for integration mesh data

IFLOUT(1) unused

IFLOUT(2) =0 no printout

=1 print primary radial integral subranges and orders and secondary orders

=2 as 1 plus print angular subranges and orders

Switch applies to all numerical integrals

IXORD 1; 1; I*4; 1

=1 order centres in two-electron exchange integral calculation according to decreasing Z-coordinates

=-1 order centres according to increasing Z-coordinates

LREC 1; 1; I*4; 7200

Maximum length in bytes for a logical output record of integrals

MEGU 1; 1; I*4; 27

Unit for the output of the generated molecular orbital vectors in the case that ITVCI<1

NBF NSYM; 21; I*4; 21*0

Number of basis functions in the generated vector set for each of the NSYM symmetries

NBFT 1; 1; I*4; 0

Total number of basis functions (summed over symmetries) in the generated set of molecular orbitals

NPBF NBFT; 150; I*4;

Array giving for each of the complete set of output basis functions, the corresponding basis function sequence number within a given symmetry set

NFONE 1; 1; I*4; 9

Unit number from which overlap matrix elements are to be read in subroutine ENLARG in order to perform the orthogonalisation of the molecular orbitals

NOB NSYM; 21; I*4; 21*0

Number of molecular orbitals which are to be constructed (including the target orbitals) for each symmetry in the output molecular orbital set

NSYM 1; 1; I*4;

Number of symmetries in the generated set of molecular orbitals

LTRB 1; 1; I*4; 449

Number of coefficients to be written in each output record of the generated set of molecular orbitals. The complete record size will be (LTRB*2+1)*4 bytes

TPROJ 1; 1; R*8; 1.0D-5

The smallest eigenvalue of the molecular orbital overlap matrix which is to be retained; orbitals which are more linearly dependent are deleted

If TPROJ = -1.D0 all orbitals are retained total interval involved in the integration is πR. This interval may be split into up to four segments depending on the location of the centres and on the most important regions covered by the associated charge distributions. The most general case occurs if there are centres located both to the right and left of the coordinate origin on ZE and the integration arc intersects the important regions of both charge distributions. This case is illustrated in fig.13.

The first case to be considered is that when R is small. Only the charge-distribution associated with ZE is deemed relevant and there is no subdivision of the full integration arc. Input parameters define the number of Gaussian points to be used per unit arc length.

In other cases the distance between each centre and the integration arc must be determined. If no centres are close to the integration path there again is no subdivision of the interval. Variable $D = |Z_k - R|$ for centre k, is used to linearly scale the number of mesh points per unit arc length corresponding to the region associated with centre k. Having determined the subintervals and numbers of grid points, subroutine INPAR is again called to transform the Gauss-Legendre weights and nodes thus constructing the compound quadrature formula.

QUADXI

This routine is used to construct the ξ-integration mesh used in the evaluation of exchange integrals. The overall structure and most of the detailed logic used is identical to that employed in routine QUADR and therefore need not be repeated here. Between two and four centres may be involved. Apart from the fact the charge distributions are all assumed to be two-centred and short-ranged, differences arise from QUADR only becaus of the different integration variable.

QUADE

This entry point of subroutine QUADXE is used to determine the η-integration mesh used in the exchange integral calculation. The routine has a similar structure to QUADTH the differences resulting from the fact that the integration path is elliptical rather than circular. To handle the geometric problem of determining elliptic arc lengths subroutine ARC with entry points ELTBL, ELINT and ELINV is used. An initial call to ARC sets up a compound integration rule based on the 2-point Gauss-Legendre formula for the 0 to π interval. Using this rule, ELTBL is called to set up a table of arc lengths corresponding to each multiple of $\pi/32$. Entry ELINT may then be used to determine the arc length subtended by any two angles by linear interpolation on the arc-length table. This process is inverted by entry ELINV. The division of the η-arc length into subintervals according to the proximity of the various charge-distributions follows the pattern established by QUADTH. Once the intervals, orders and transformation points have been established, INPAR is again called to generate the required weights and nodes.

TABLE A2

```
// EXEC FGG,LIBRARY='NO.LOAD',MEMBER=TAILV,REGION=1999K,TIME=(29,59)
//G.FT08F001 DD DSN=NB.N2SGP3.DATA,DISP=SHR,UNIT=3330-1,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(2,2),RLSE)
//G.FT08F002 DD DSN=NB.N2SGP4.DATA,UNIT=3330-1,DISP=SHR,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(6,6),RLSE),
//  VOL=SER=DL0298
//G.FT09F001 DD DSN=NB.N2SGP5.DATA,UNIT=3330,DISP=SHR,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(1,1),RLSE),
//   VOL=SER=DNPL33
//G.FT10F001 DD DSN=&&DUMM3,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(5,5),RLSE)
//G.FT11F001 DD DSN=&&DUMM4,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(CYL,(5,5),RLSE)
//G.FT12F001 DD DSN=&&KAT12,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(50,90),RLSE)
//G.FT13F001 DD DSN=&&KAT13,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(90,90),RLSE)
//G.FT15F001 DD DSN=&&KAT14,UNIT=3330,VOL=SER=DNPL33,DISP=(NEW,DELETE),
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(90,90),RLSE)
//G.FT21F001 DD DSN=NB.N2SGP0.DATA,UNIT=3330,VOL=SER=DNPL33,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(10,10),RLSE),
//  DISP=SHR
//G.FT22F001 DD DSN=NB.N2SGPLA.DATA,UNIT=3330-1,VOL=SER=DL0298,
// DCB=(RECFM=VBS,BLKSIZE=6400,BUFNO=1),SPACE=(TRK,(1,1),RLSE),
// DISP=SHR
//G.FT27F001 DD DSN=NB.V2.STON2N,DISP=SHR
//G.FT29F001 DD DSN=QKV.N2FUN.SG0243.DATA,DISP=SHR
//G.SYSIN DD *
 &INPUT
    NAME='N2 NESBET SIGMA-G (S, D, G WAVES) 22-POLES (COUPLED),2 CORRELATN
  GEONUC= -1.034,1.034,0.0,  NEF=86,  NNUC=3,
  NLMK=1,0,0,1, 1,0,0,2, 1,0,0,1, 1,0,0,2, 2,0,0,1, 2,0,0,2,
       2,0,0,1, 2,0,0,2, 2,1,0,1, 2,1,0,2, 2,1,0,1, 2,1,0,2,
       3,2,0,1, 3,2,0,2, 2,1,1,1, 2,1,1,2, 2,1,1,1, 2,1,1,2,
       3,2,1,1, 3,2,1,2,
        1,0,0,3,  2,0,0,3,  3,0,0,3,  4,0,0,3,  5,0,0,3,  6,0,0,3,
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       13,0,0,3, 14,0,0,3, 15,0,0,3, 16,0,0,3, 17,0,0,3, 18,0,0,3,
       19,0,0,3, 20,0,0,3, 21,0,0,3, 22,0,0,3,
        3,2,0,3,  4,2,0,3,  5,2,0,3,  6,2,0,3,  7,2,0,3,  8,2,0,3,
        9,2,0,3, 10,2,0,3, 11,2,0,3, 12,2,0,3, 13,2,0,3, 14,2,0,3,
       15,2,0,3, 16,2,0,3, 17,2,0,3, 18,2,0,3, 19,2,0,3, 20,2,0,3,
       21,2,0,3, 22,2,0,3, 23,2,0,3, 24,2,0,3,
        5,4,0,3,  6,4,0,3,  7,4,0,3,  8,4,0,3,  9,4,0,3, 10,4,0,3,
       11,4,0,3, 12,4,0,3, 13,4,0,3, 14,4,0,3, 15,4,0,3, 16,4,0,3,
       17,4,0,3, 18,4,0,3, 19,4,0,3, 20,4,0,3, 21,4,0,3, 22,4,0,3,
       23,4,0,3, 24,4,0,3, 25,4,0,3, 26,4,0,3,
ZETA=6.21292, 6.21292, 9.36827, 9.36827, 1.46786, 1.46786,
     2.24642, 2.24642, 1.52853, 1.52853, 3.33678, 3.33678,
     1.93500, 1.93500,
     1.52853, 1.52853, 3.33678, 3.33678, 2.43700, 2.43700,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,
     0.0000, 0.0000, 0.0000, 0.0000, 0.0000, 0.0000,


   NUCCEN=3,
   IBLOCH=0, BBLOCH=0.0, RMATR=10.00,NUCCEN=3, IFLOUT=0,0,
   IFLSYM=1,IFLINT=7*0,           IPRINT=5*0,2*0,0, LREC=6300,
   ICF=1,ICFP=1,
  &END
  &CET
   NSYM=2,
   NBF=14,6, NOB=9,5,
   ITVC1=1,
  &END
  &GET1
     IVCS=27, NIND=9,
     IND=1,0,1,3, 1,0,6,6, 1,0,9,9, 1,0,4,5, 1,0,7,8,
         1,1,1,1, 1,1,3,4, 1,1,2,2, 1,1,5,5,
     NBASE=0
  &END
  &PUT
   CHARG=7.0,7.0,0.0, NBF=80,6, NOB=31,5, NSYM=2,
   TPROJ=-1.0D0,  ITVCI=0, IORTHO=1,NFONE=9,
   MEGU=21,ISTOST=1,
  &END
```

9. QUADRATURE AND TRANSFORMATION ROUTINES

The efficiency of the program depends ultimately on the speed and accuracy with which various numerical integrations can be performed. As a consequence rather elaborate procedures have been adopted for generating the quadrature nodes and weights. Six subroutines are involved: QUAD, QUADXE, INPAR, GAUSS, ARC, NPTD. The entry point names associated with these routines are listed in Table 8. The logical structure of the two major routines, QUAD and QUADXE, is quite involved and therefore will be briefly described here. The underlying physical picture which should be kept in mind during this discussion is as follows.

The appropriate integration mesh for use in a particular integral calculation is determined by the effective potential seen by an electron at each spatial point. For example in the case of a homonuclear molecule, the dominant feature is the occurrence of the nuclear singularities (at a radial distance, $r = r_N$, say). In some region which may typically extend up to 0.5 Bohr either side of this point the effective potential will be rapidly varying and be dominated by the static components. Most integration mesh points therefore must be concentrated in this region and should be distributed symmetrically about the singularity. At smaller radial distances the potential will be strong but nearly constant and consist of an approximately equal mixture of exchange and static components. Beyond the nuclear region the exchange and static components will again be comparable. At still larger radial distances ($> 2\ r_N$) the exchange components will be decaying rapidly and the static component will tend to assume a smoothly varying multipolar character. Hence both the outer two regions will require fewer mesh points than the nuclear region.

QUAD

This routine generates integration formulae used for Coulomb/Hybrid,

numerical one-electron and property integral calculations. The two major entry points are QUADR, which generates formulae for the radial integrations, and QUADTH which generates the angular theta mesh. Recall that a spherical coordinate system is used with origin located on one of the centres and that between one and three centres may be involved in the integral.

QUADR

Input data controlling the computation of the radial mesh is of three types

(i) centre data

RNUC specifies the characteristic range associated with the charge distribution on the centre i.e. the region about the nuclear singularity where the static potential dominates

DRNUC gives the number of integration points per unit path length in the region associated with the centre

(ii) IRIP an array of data determining the order of Gauss formulae to be used in various subintervals

(iii) DRIP an array of data determining distance scales and the positioning of the transformation points within a subinterval

The mesh is determined for the interval between each pair of centres in turn and then for the region beyond the last centre. For each pair of centres r_{k_i} and $r_{k_{i+1}}$ (see fig.10) the number of integration subranges into which the interval is divided depends essentially on the size of the intermediate region, denoted by r_A.

(a) $r_A < r'_0$

Then in the case of Coulomb integrals two subintervals are created

APPENDIX C. INSTALLATION DETAILS

The special programming features used in this package imply that it will only run correctly on a computer with IBM compatible architecture. It is currently implemented on the NAS 7000 computer at the Daresbury Laboratory.

1. Source Code

   File NB.DARLAB.TAILMY.FORT

   (May be archived)

2. Load module

   NO.LOAD(TAILV)

3. JCL

   (i) for compilation: NB.DARLAB.TAILMY.FORT(COMP)

   (ii) for link editing: NB.DARLAB.TAILMY.FORT(LINK)

Input and output files corresponding to the examples given in Appendix A may be found in the archived files NB.DARLAB.TAILMY.DATA and NB.DARLAB.TAILMY.TEXT.

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15. I. Shavitt. The method of configuration interaction. In: Methods of Electronic Structure Theory, ed. H.F. Schaefer III (New York: Plenum Press, 1977) p.204.
16. A.D. McLean and M. Yoshimine, IBM J. of Research & Development 9 (1965) 203.

8. RENORMALISATION, BOUNDARY AMPLITUDES AND MOLECULAR ORBITALS

8.1 Integral renormalisation

All integrals computed in previous sections of the program have been calculated with basis functions normalised over all space. In R-matrix calculations these must be renormalised to the volume of the R-matrix internal region. This implies that those integrals which have been computed from truncated basis functions must be multiplied by factors equal to the inverse square root of the corresponding (truncated) diagonal overlap matrix element in order to form a correctly normalised integral. Hence, for example,

$$S^R_{12} = S^{-1/2}_{11}\, S^{-1/2}_{22}\, S_{12}, \tag{57}$$

where labels 1 and 2 correspond to complete sets of basis function quantum numbers and the value on the left corresponds to the correctly normalised overlap element.

8.2 Continuum molecular orbital generation

Several options exist within the program for generating continuum molecular orbitals by orthogonalisation techniques. The target molecular orbitals are first read in. This is followed by a Schmidt orthogonalisation, symmetry by symmetry, of the continuum basis functions with respect to the target orbitals. The continuum orbitals which result may then be symmetric orthogonalised amongst themselves. Alternatively the entire set of functions may be Schmidt orthogonalised. In both cases the linear dependence of the generated orbital set is monitored (orbitals are deleted if they would lead to normalisation errors) and may be restricted to be less than some specified value.

In cases where numerical orbitals which already form an orthonormal set with the target orbitals are used it is possible to generate effective

molecular orbital wavefunctions in the standard ALCHEMY format without any orthogonalisation. The resultant molecular orbital set may be output in a variety of formats including that of a standard ALCHEMY molecular orbital dumpfile.

8.3 Boundary amplitudes

Once an orthonormal set of molecular orbitals including continuum orbitals is available the construction of boundary amplitudes according to eq.(16b) of Burke et al[10] is straightforward. Note that the amplitude definition contains the $(2a)^{-1/2}$ factor as well as the orbital angular momentum projection of the radial molecular orbital wavefunction on the R-matrix boundary.

In large calculations there are considerable advantages to the use of partitioning techniques and the introduction of an optical potential. This aspect has been emphasised by Nesbet[4] (see also Oberoi and Nesbet[13,14]). With these considerations in mind it is possible to perform an orthogonal transformation on the generated molecular orbital set so that only one orbital for each asymptotic channel has a non-zero boundary amplitude. This transformation is included as an option within the code.

8.4 Program details

The calling sequence of the subroutines involved in the generation of continuum molecular orbitals and in the computation of boundary amplitudes is illustrated in fig.9. The corresponding subroutine names and entry points are listed in Table 7.

TRNSDR

The target molecular orbitals are input by subroutine TRNSDR either

TABLE 3. TWO-ELECTRON ONE-CENTRE INTEGRAL SUBROUTINE LIST

Entry Points

1.	EINT			
2.	OCBLKS			
3.	OCPQRQ	IOCPQ		
4.	TEOCW			
5.	WOCI	OCINT1	OCINT	WOCF

TABLE 4. EXCHANGE INTEGRAL SUBROUTINE LIST

Entry Points

1.	ARC	ELTBL	ELINT	ELINV		
2.	GAUSS					
3.	IEPQXI	EPQXI				
4.	INPAR					
5.	IPLMX					
6.	NPTD	NPTI				
7.	PLMNF					
8.	PLMX2	IPLMX2				
9.	PLMX4	IPLMX4				
10.	PQCNT					
11.	PRTTN					
12.	QUADXE	QUADXI	QUADE1	QUADE		
13.	INCO	RCO	TRCO	BRCO		
14.	STO1	STO2	STOXE	STOTB	SBLOCH	BTOTBL
15.	TABLE1	TABLE2				
16.	TCPQRQ					
17.	TETCW					
18.	WRXINT	WXINT				
19.	XBLKS					
20.	XINT					
21.	XINTTR					

TABLE 5. SLATER ONE-ELECTRON INTEGRAL SUBROUTINE LIST

Entry Points

1.	BJMLB					
2.	EINT					
3.	GAUSS					
4.	INPAR					
5.	IPLMX					
6.	NPTD	NPTI				
7.	OTCUPQ					
8.	PLMX3	IPLMX3				
9.	PMY2V					
10.	PMY2V2	PMY2V3	PMY2V4			
11.	QUAD	QUADR	QUAD1	QUADTH		
12.	STO1	STO2	STOXE	STOTB	SBLOCH	STOTBL
13.	STPQ					
14.	STUMX					
15.	UPQNI					
16.	UPQ3C					
17.	WNJ	VNJ	XNJ	WNJ1		
18.	WOEINT	IWOE				
19.	WUPQ	WUPQ1				

TABLE 6. PROPERTY INTEGRAL SUBROUTINE LIST

Entry Points

1.	GAUSS					
2.	INCO	RCO	TRCO	BRCO		
3.	INPAR					
4.	IOEOP	OEOP1	OCOEOP			
5.	IPLMX					
6.	NPTD	NPTI				
7.	OCOEME					
8.	OEINT					
9.	OEMXLP					
10.	OTPQRQ					
11.	PLMX2	IPLMX2				
12.	PLMX3	IPLMX3				
13.	QUAD	QUADR	QUAD1	QUADTH		
14.	SORTOP					
15.	STO1	STO2	STOXE	STOTB	SBLOCH	STOTBL
16.	WOEMX	WOEMX1				
17.	WOEMX2					

subroutine. The calculation is divided into three sections corresponding to (A) one-centre integrals, (B) two-centre integrals with a one-centre charge distribution, (C) two-centre integrals with a two-centre charge distribution as indicated in fig.7. The methods used are identical to those for overlap integrals. In R-matrix calculations, the Gaunt coefficients G required in eq.(50) are read from disk file ITALM.

UPQ3C

The looping over centres and symmetries is combined in this subroutine which supervises the 3-centre nuclear attraction integral computation. Note that nuclear attraction integrals carry the type label 3 in addition to the sequence number of the attracting centre.

UPQNI

Performs the two-dimensional integration of eq.(51) and so evaluates the three-centre nuclear attraction integrals.

WUPQ

This subroutine computes block and integral labels before writing the three-centre nuclear attraction integrals to disk file NFT1E.

WOEINT

Writes one- and two-centre one-electron integrals to the disk file attached to unit NFT1E.

7. PROPERTY AND NUMERICAL ONE-ELECTRON INTEGRALS

The integrals of this class are defined as one-electron integrals (involving between one and three centres) of the form

$$I_{ab;k} = \int d\tau_1 \, \Omega_{ab}(1) \, O_k \ . \tag{54}$$

Ω_{ab} is the usual one- or two-centred charge distribution while the operator O_k may take either the form

$$O_k = r_k^n (1-x_k^2)^{1/2} \, x_k^j \, P_\ell^m(x_k) \, \Phi_m(\phi_k) \ , \tag{55}$$

where $x_k = \cos\theta_k$ or alternatively

$$O_G^k = \frac{1}{|\vec{r}_G - \vec{r}_k|} \ . \tag{56}$$

By taking a spherical coordinate system with the origin located on the property centre the evaluation of the integrals (54) is easily reduced to a two-dimensional quadrature.

7.1 Program details

Property integrals and numerical one-electron integrals are calculated by separate calls to the same group of subroutines from subroutine LINT. This calling sequence is shown schematically in fig.8 and the subroutines involved listed in Table 6.

True property integrals involving operators of the form given in eq.(55) are computed over the infinite domain and carry the type label 4. The full block header label is an octet of numbers of the form 4 n i j k ℓ m 0. The operation of this section is controlled by the switch IFLINT(5). Of course for the integral to be convergent the value of the parameter n must satisfy $n > -1$. Integrals are written to the disk file attached to unit IOEU.

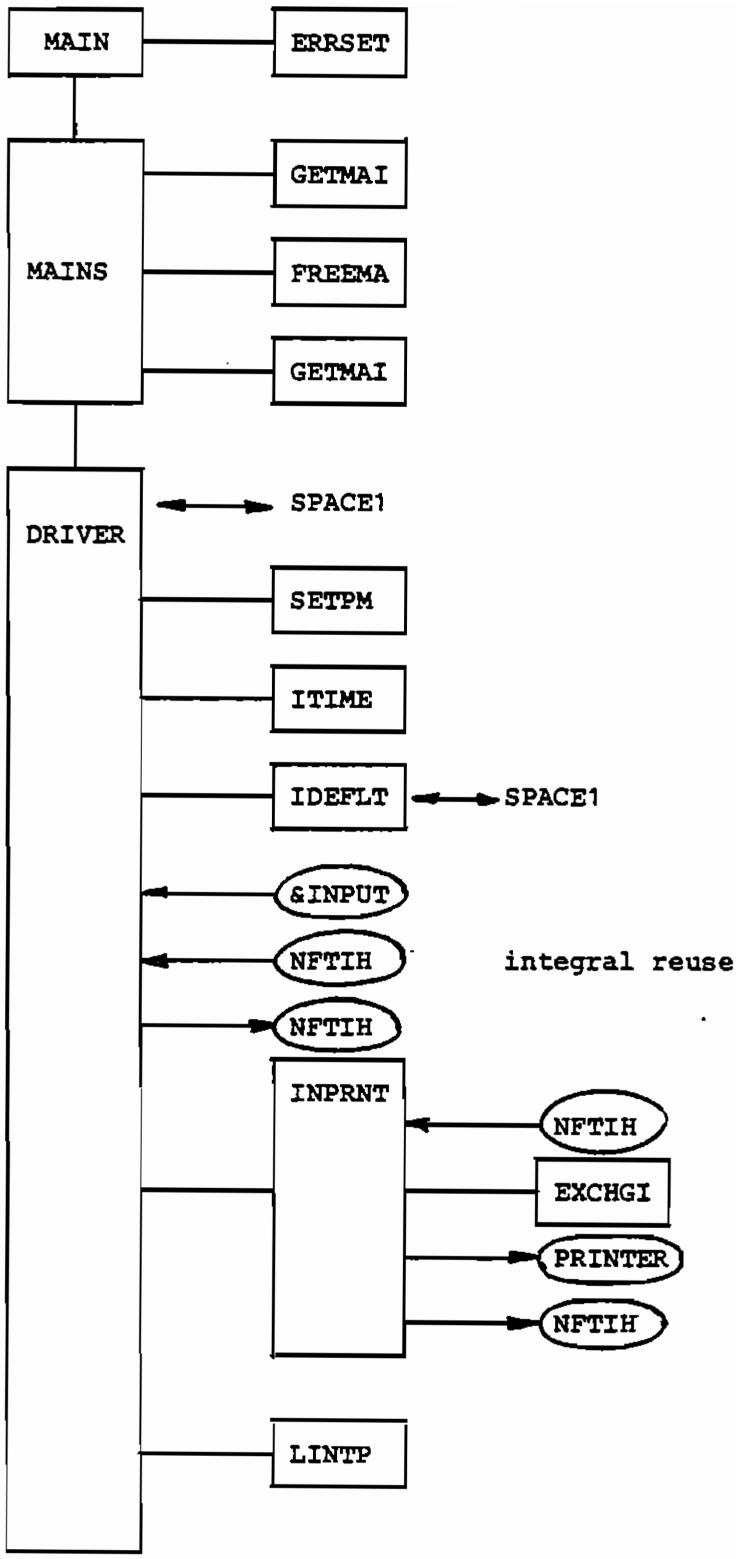

MAIN
ERRSET
MAINS
GETMAI
FREEMA
GETMAI
DRIVER
SPACE1
SETPM
ITIME
IDEFLT
SPACE1
&INPUT
NFTIH
integral reuse
NFTIH
INPRNT
NFTIH
EXCHGI
PRINTER
NFTIH
LINTP

Fig.1a

6.2 Two-centre integrals

Three types of two-centre one-electron integrals need be considered:

(i) overlap;

(ii) nuclear attraction; a, b distinct, c coincident with a or b;

(iii) nuclear attraction; a, b identical, c distinct.

All are most conveniently treated by using the spheroidal coordinate system introduced for exchange integrals taking the distinct centres as foci (see fig.4).

The overlap integrals may then be written in the form

$$S_{12} = \delta_{m_1m_2} N_{n_1\ell_1} N_{n_2\ell_2} (R)^{n_{12}+1} \sum_{i,j} d_{ij}\, A_i(R\zeta_{12}) B_j^{00}(-R\bar{\zeta}_{12}) \qquad (44)$$

where

$$\bar{\zeta}_{12} = \zeta_1 - \zeta_2 \qquad (45)$$

and integral B is given by

$$B_j^{m\ell}(\beta) = \frac{(\ell-m)!}{(\ell+m)!} \int_{-1}^{+1} d\eta\, \eta^j (1-\eta^2)^{m/2} P_\ell^m(\eta) e^{\beta(\eta-1)} \qquad (46)$$

and R is half the separation of centres 1 and 2. The coefficients d_{ij} appearing in eq.(44) are defined by

$$(\xi+\eta)^{n_1}(\xi-\eta)^{n_2} \mathscr{P}_{\ell_1}^{m_1}\left(\frac{1+\xi\eta}{\xi+\eta}\right) \mathscr{P}_{\ell_2}^{m_2}\left(\frac{1-\xi\eta}{\xi-\eta}\right) \equiv \sum_{ij} d_{ij}\, \xi^i \eta^j. \qquad (47)$$

It is clear that a similar result to eq.(44) will hold for the nuclear attraction integrals of type (ii). The power of R will be reduced by one in (44) and also the exponent n_1 or n_2 on the left hand side of (47) will be reduced by one depending on whether 1 or 2 is the attracting centre respectively.

Similarly for type (iii) nuclear attraction integrals, assuming b is

the centre of attraction

$$U_{aa}^b = \delta_{m_1m_2} N_{n_1\ell_1} N_{n_2\ell_2} R^{n_{12}} \sum_{ij} d'_{ij}\, A_i(R\zeta_{12})\, B_j^{00}(-R\zeta_{12}) \qquad (48)$$

and

$$(\xi+\eta)^{n_{12}-1} \mathscr{P}_{\ell_1}^{m_1}\left(\frac{1+\zeta\eta}{\zeta+\eta}\right) \mathscr{P}_{\ell_2}^{m_2}\left(\frac{1+\zeta\eta}{\zeta+\eta}\right) \equiv \sum_{ij} d'_{ij}\, \xi^i \eta^j . \qquad (49)$$

There will clearly be no long-range contributions to these two-centre integrals when the charge distribution involved is two-centred - however case (iii) given by eqs.(48) and (49) will have long-range contributions when centre a correeponds to the scattering centre G. It is essential that these long-range contributions to the integral are computed in a spherical coordinate system with an origin located on G. It can then be shown that

$$U_{GG}^C = \sum_L \frac{1}{\sqrt{2L+1}} \begin{Bmatrix} 1 \\ (-1)^L \end{Bmatrix} \left(\frac{r_c}{a}\right)^L N_{n_1\ell_1} N_{n_2\ell_2} G^{\ell_1\, L\, \ell_2}_{m_1\, 0\, m_2}\, a^{n_{12}} A_{n_{12}-L-1}(\zeta_{12}a) \qquad (50)$$

where the upper factor in the braces is to be taken if centre C is to the right of G, and the lower is to be used if it is to the left.

6.3 Three-centred nuclear attraction integrals

These integrals are treated by introducing a spherical coordinate system with the origin located on the attracting centre C. The two-centred charge distribution must then be expanded about this point in complete analogy with the case already considered for Coulomb/Hybrid integrals. It is found that

$$U_{ab}^C = F_{ab}^{00}(r=0) \equiv \int_0^\infty dy\, y \int_{-1}^{+1} dx\, \chi_a\, \chi_b \qquad (51)$$

where F is the potential function defined by eq.(12).

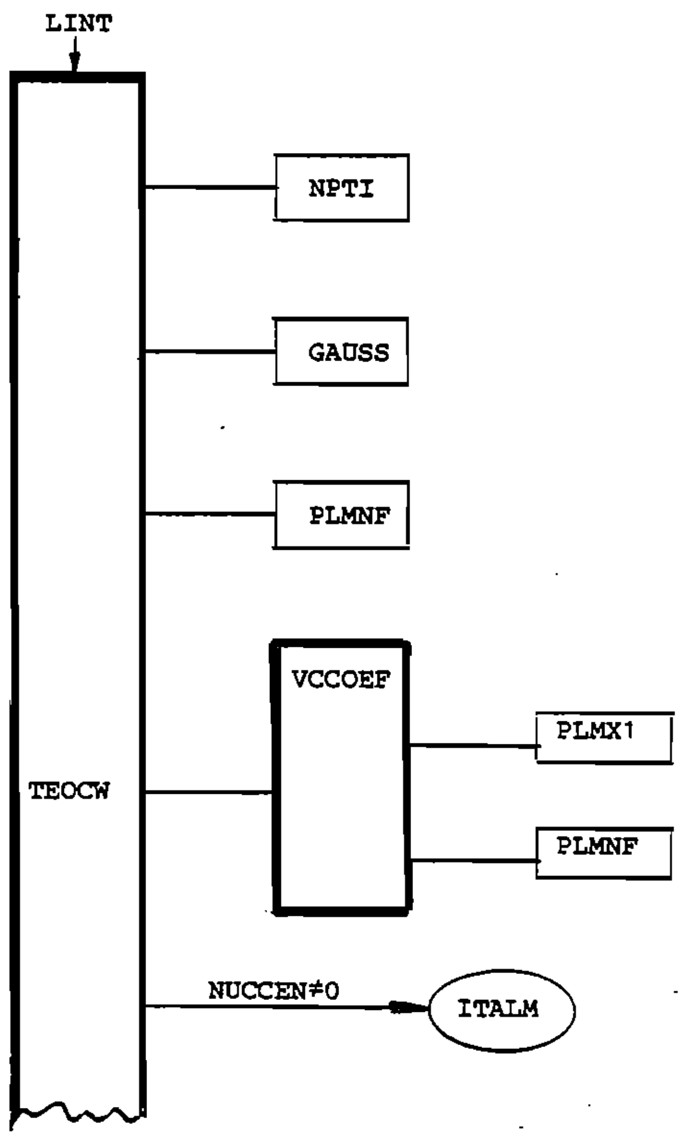

LINT
TEOCW
NPTI
GAUSS
PLMNF
VCCOEF
PLMX1
PLMNF
NUCCEN≠0
ITALM

Fig.2a

tribution of the required type and sets up pointer arrays for locating these basis functions during the integral calculation.

XINT

This subroutine performs the x-integration of eq.(31) to yield the required exchange integrals in the case where centres p,q are not identical to the r,s centre pair. The potential functions, E, may be read or written to temporary disk files associated with units 10 and 11 during the calculation.

XINTTR

Performs the same function as XINT in the case that the pq pair is identical to the rs-centre pair.

EPQXI

Two-centre potential functions, E, are computed using eqs.(32), (33) by this subroutine. The integration proceeds upwards from the lower limit point x=1, otherwise the organisation of the calculation is exactly similar to that used in the Coulomb/Hybrid calculation. Basis functions at specific elliptic coordinates are obtained via calls to STOXE; the computation does not depend therefore on whether the values being returned correspond to STO functions or to a numerical function determined externally by RCO.

WXINT

Integral labels are generated in routine WXINT. These and the computed integrals are then written to the disk file associated with unit NFT2E. Integrals with magnitude less than a specified threshold value (THRINT) are deleted.

PLMX4

This routine computes a table of unnormalised associated Legendre functions, each entry being multiplied by two weighting factors. The second factor is raised to the power corresponding to the order of the Legendre function.

The remaining subroutine calls in this section are either initialisation calls or calls to the routines used to generate the various quadrature formulae used. The latter subroutines will be considered further in section 9 of this memorandum.

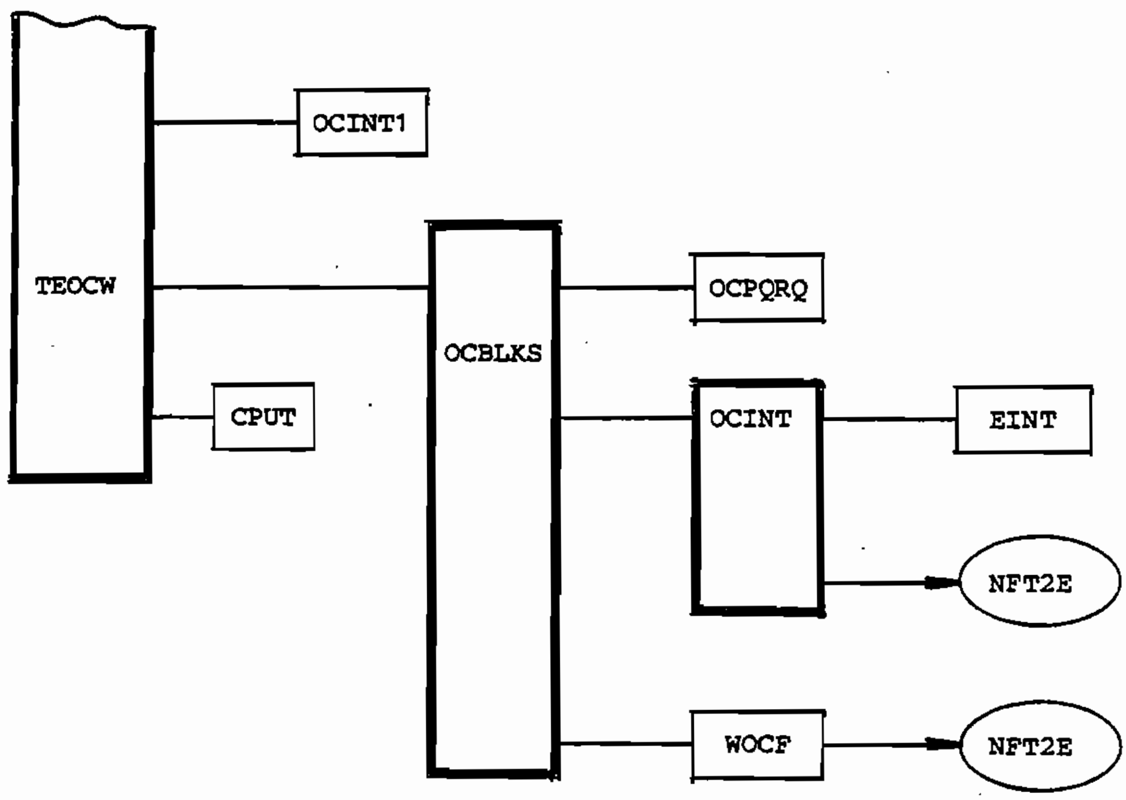

TEOCW
OCINT1
CPUT
OCBLKS
OCPQRQ
OCINT
EINT
NFT2E
WOCF
NFT2E

Fig.3

OCINT

The one-centre integrels are evaluated in OCINT using the expression given in eq.(20). If necessary, long range contributions are estimated using eq.(23) and subtracted. The angular coefficients, G, are passed from the first section of subroutine TEOCW.

EINT

Computes the auxiliary E-integral given by eq.(24).

5. EXCHANGE INTEGRALS

The exchange integrals are defined as those two-electron integrals which involve two two-centre charge distributions.

$$I_{pqrs} = \iint d\tau_1 d\tau_2 \Omega_{pq}(1) \frac{1}{r_{12}} \Omega^*_{rs}(2) \qquad (25)$$

In general, therefore, between 2 and 4 distinct centres might be involved. The reduction of the integrals (25) to a computable form has been described by McLean[6] and hence only the most significant points will be summarised here.

The integral (25) is simplified by a technique analogous to that employed for the Coulomb/Hybrid integrals; the major difference is that rather than using a spherical coordinate system with origin located on the centre of the one-centre charge distribution, it is now necessary to use a prolate spheroidal coordinate system with foci at centres p and q. Figure 4 illustrates the coordinate system, with origin at the midpoint of pq.

$$\xi = \frac{r_p + r_q}{2R}$$

$$\eta = \frac{r_p - r_q}{2R} \qquad (26)$$

$$\phi = \tan^{-1}(y/x)$$

An STO basis function located on centre p may then be written in the form

$$\chi_p(\vec{r}_p) = N_p R^{n_p - 1} (\xi+\eta)^{n_p - 1} e^{-R\zeta_p(\xi+\eta)} \mathscr{P}^{m_p}_{\ell_p}\left(\frac{1+\xi\eta}{\xi+\eta}\right) \Phi_p(\phi) \qquad (27)$$

where

$$\Phi_p(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad . \qquad (28)$$

A charge distribution on centres a,b may then be written as

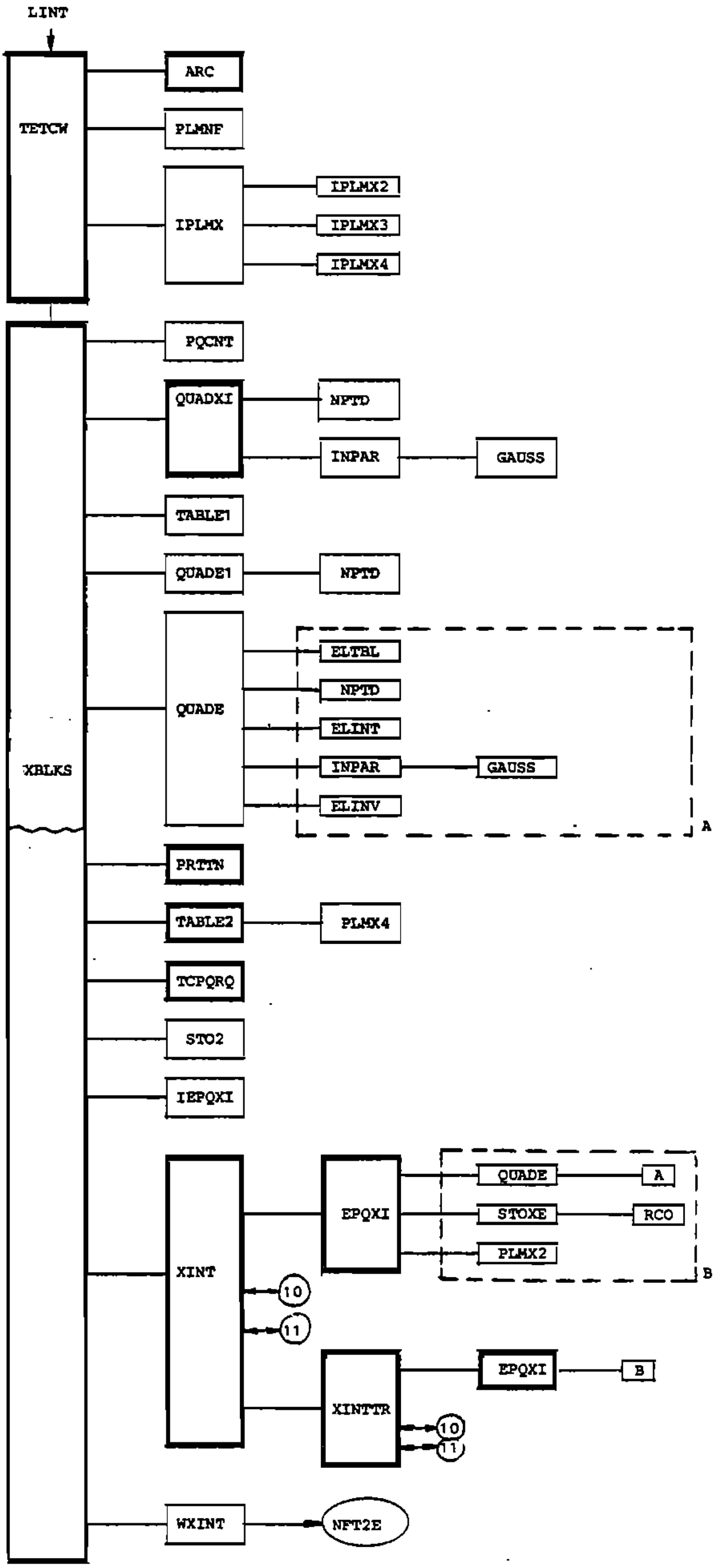

LINT
TETCW
ARC
PLMNF
IPLMX
IPLMX2
IPLMX3
IPLMX4
XBLKS
PQCNT
QUADXI
NPTD
INPAR
GAUSS
TABLE1
QUADE1
NPTD
QUADE
ELTBL
NPTD
ELINT
INPAR
GAUSS
ELINV
A
PRTTN
TABLE2
PLMX4
TCPQRQ
STO2
IEPQXI
XINT
EPQXI
QUADE
A
STOXE
RCO
PLMX2
B
10
11
XINTTR
EPQXI
B
10
11
WXINT
NFT2E

Fig.5

RSRQ

This subroutine is analogous to OCPQRQ, setting up pointer arrays to enable the two-centre (in general) distributions given by eq.(8) to be computed.

CHINT

This subroutine performs the numerical integration over the potential functions given by eq.(13) and carries out the summation over orbital angular momenta, L, to give the required integrals. If the basis functions in the one-centre distribution are STO's, the corresponding potential function is determined analytically according to eq.(14). The auxiliary A-integral, eq.(15), is computed by recursion; for diffuse basis functions in R-matrix calculations the value of $F^{LM}_{GG}(R)$ is computed using eq.(14) [R is the R-matrix radius] and subtracted from $F^{LM}_{GG}(r)$.

FRSR

The second potential function, $F^{LM}_{bc}(r)$, is computed by the two-dimensional quadrature implied by eqs.(8) and (12). The algorithm employed is

$$F^{LM}_{bc}(r_i) = \sum_{j=1}^{N_i} W_{r_j'} r_i \left(\frac{r_i}{r_j'}\right)^{L-1} \left[\frac{1}{\sqrt{4\pi}} D^{LM}_{bc}(r_j')\right] + \left(\frac{r_i}{r_{i-1}}\right)^{L} F^{LM}_{bc}(r_{i-1}) \qquad (16)$$

denoting r' quadrature weights and nodes by Wr_j' and r_j' respectively. The r-points, r_i, are chosen so that $r_i < r_{i-1}$.

QUADTH

Determines the angular x-integration weights, w_{x_j}, and nodes, x_j, used to evaluate eq.(8). Note that the radial nodes, r_i', were computed by QUADR, and chosen to cover each subinterval of the primary r-mesh used to evaluate the integrals of eq.(13).

STOTBL

Computes a table of basis function values, $R_{n_p \ell_p}(r_p) \times \mathcal{P}^{m_p}_{\ell_p}(\cos\theta_p)$, corresponding to a specific pair of (r',x)-values. Only those basis functions which can form suitable distributions are evaluated. If the basis function is found to correspond to a numerical continuum function, subroutine RCO is called to provide the required value. Associated Legendre functions are obtained by calling subroutine PLMX3.

FPQR

In cases where the one-centre potential is required for numerical continuum functions, FPQR is called to perform the required numerical integration. In fact

$$\begin{pmatrix} \ell_1 & L & \ell_2 \\ G_{m_1} & M & m_2 \end{pmatrix}^{-1} F^{LM}_{GG}(r) = r \int_r^R dr' \left(\frac{r}{r'}\right)^{L-1} R_{n_1\ell_1}(r') R_{n_2\ell_2}(r') \qquad (17)$$

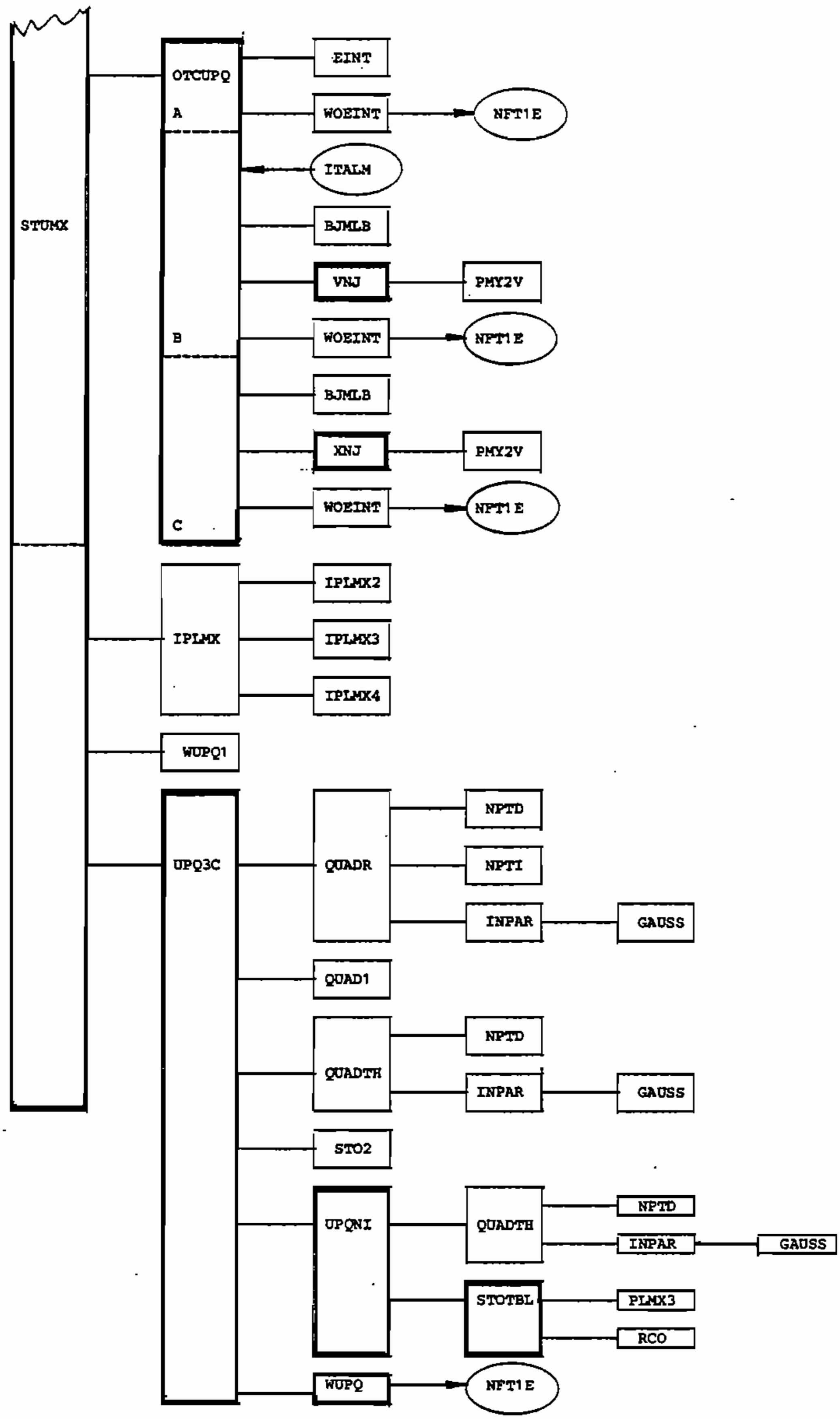
is computed using an algorithm analogous to eq.(16).

WCHINT

The final phase of the calculation, deleting those integrals with a magnitude less than a specified threshold value, and grouping the remainder, with their corresponding labels, into buffer loads is performed by WCHINT. The integrals are then written to the disk file associated with unit NFT2E.

The header on each output record gives the number of symmetries, the total number of integrals, and the number of integrals for each symmetry.

The remaining subroutine calls are largely to initialisation or other subsidiary entry points. Table 2 lists each subroutine used in this section together with its entry point identifiers. Entry pointa QUAD, and WRINT are called directly from LINT.



STUMX
OTCUPQ
A
B
C
EINT
WOEINT
NFT1E
ITALM
BJMLB
VNJ
PMY2V
WOEINT
NFT1E
BJMLB
XNJ
PMY2V
WOEINT
NFT1E
IPLMX
IPLMX2
IPLMX3
IPLMX4
WUPQ1
UPQ3C
QUADR
NPTD
NPTI
INPAR
GAUSS
QUAD1
QUADTH
NPTD
INPAR
GAUSS
STO2
UPQNI
QUADTH
NPTD
INPAR
GAUSS
STOTBL
PLMX3
RCO
WUPQ
NFT1E

Fig.7

435ABF

3. COULOMB AND HYBRID INTEGRALS

The two-electron Coulomb and Hybrid integrals involve either two or three centres and are characterised by two one-centre distributions and by a one-centre and a two-centre charge distribution, respectively.

(a) Coulomb:

$$\iint d\tau_1\, d\tau_2\, \Omega_a(1)\, \frac{1}{r_{12}}\, \Omega_b^*(2) \tag{1}$$

(b) Hybrid:

$$\iint d\tau_1\, d\tau_2\, \Omega_a(1)\, \frac{1}{r_{12}}\, \Omega_{bc}^*(2) \tag{2}$$

In general the two-centre charge distribution, Ω_{bc}, may be written in terms of the basis functions χ as

$$\Omega_{bc}(1) \equiv \chi_b^*(\vec{r}_1)\, \chi_c(\vec{r}_1) \tag{3}$$

$$= R_b(r_1)\, R_c(r_1)\, Y_b^*(\hat{r}_1)\, Y_c(\hat{r}_1) \tag{4}$$

using the centre labels to also represent the quantum numbers of the basis state. For STO basis functions

$$R_b(r) = N_b\, r^{n_b-1}\, e^{-\zeta_b r} \tag{5}$$

where $$N_b = [(2n_b)!]^{-1/2}\, (2\zeta_b)^{n_b+1/2}\ . \tag{6}$$

Using the analysis outlined by McLean[6], it is straightforward to show that the radial distribution functions may be written as

$$D_{aa}^{LM}(r) = R^a_{n_1\ell_1}(r)\, R^a_{n_2\ell_2}(r)\, \frac{1}{\sqrt{4\pi}}\, G^{\ell_1\ L\ \ell_2}_{m_1\ M\ m_2} \tag{7}$$

and

$$D_{bc}^{LM}(r) = \frac{1}{\sqrt{2\pi}}\, \delta_{M,m_4-m_3} \int_{-1}^{+1} dx R_{n_3\ell_3}(r_b) R_{n_4\ell_4}(r_c) \mathscr{P}_L^M(x)$$

$$\times\, \mathscr{P}^{m_3}_{\ell_3}(\cos\theta_b)\mathscr{P}^{m_4}_{\ell_4}(\cos\theta_c) \tag{8}$$

where

$$\mathscr{P}^m_\ell(x) = C_{\ell m} P^m_\ell(x) \tag{9}$$

$$C_{\ell m} = \left[\frac{2\ell+1}{2}\, \frac{(\ell-m)!}{(\ell+m)!}\right]^{1/2} \tag{10}$$

and

$$G^{\ell_1\ L\ \ell_2}_{m_1\ M\ m_2} = 2^{3/2}\int_0^1 dx\, \mathscr{P}^{m_1}_{\ell_1}(x)\mathscr{P}^{M}_{L}(x)\mathscr{P}^{m_2}_{\ell_2}(x) \tag{11}$$

$P^m_\ell(x)$ is the usual associated Legendre function as defined by Messiah[7].

Potential functions may be defined in terms of the radial distributions by

$$F^{LM}(r) = \sqrt{4\pi}\, r^L \int_r^\infty dr'\, r'^{-L+1} D^{LM}(r') \tag{12}$$

where centre labels have been suppressed.

The required Coulomb and Hybrid integrals are then given by

$$I_{a;bc} = \sum_L \int_0^\infty F^{LM}_{aa}(r)\, F^{LM}_{bc}(r) dr\ . \tag{13}$$

The one-centre potential function may be written in the case of STO basis functions as

$$F^{LM}_{aa}(r) = N_1 N_2\, G^{\ell_1\ L\ \ell_2}_{m_1\ M\ m_2}\, r^{n_1+n_2}\, A_{n_1+n_2-L-1}\left[(\zeta_1+\zeta_2)r\right] \tag{14}$$

where the auxiliary integral, $A_n(x)$, is given by

$$A_n(x) = \int_1^\infty dy\, y^n\, e^{-xy} \tag{15}$$

and may be simply evaluated using the method of Wahl et al[8].

To evaluate Coulomb and Hybrid integrals within a finite region it should be noted that long-range contributions to the integrals can only

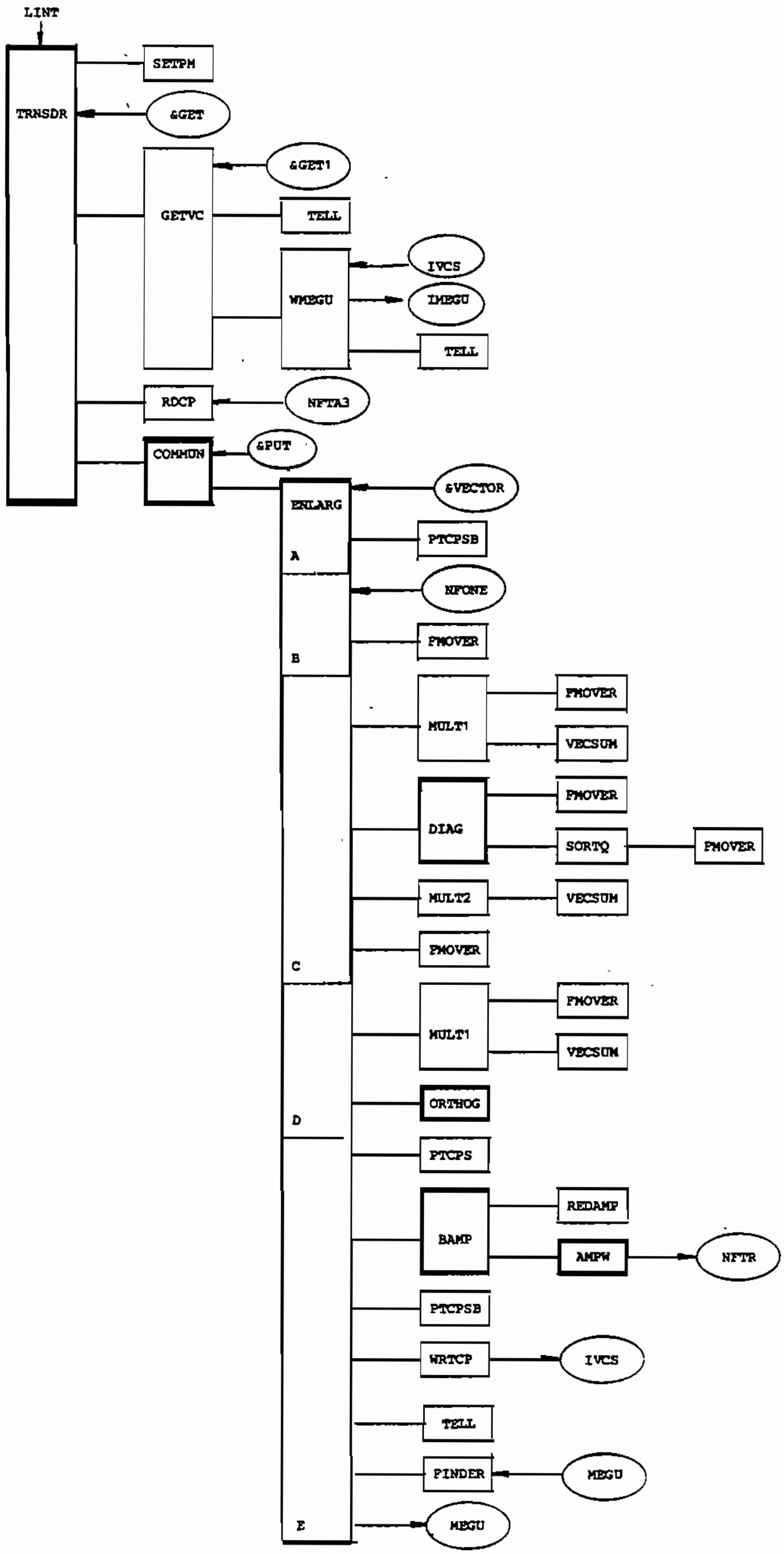

LINT
TRNSDR
SETPM
&GET
GETVC
&GET1
TELL
WMEGU
IVCS
IMEGU
TELL
RDCP
NFTA3
COMMUN
&PUT
ENLARG
A
B
C
D
E
&VECTOR
PTCPSB
NFONE
FMOVER
MULT1
FMOVER
VECSUM
DIAG
FMOVER
SORTQ
FMOVER
MULT2
VECSUM
FMOVER
MULT1
FMOVER
VECSUM
ORTHOG
PTCPS
BAMP
REDAMP
AMPW
NFTR
PTCPSB
WRTCP
IVCS
TELL
FINDER
MEGU
MEGU

Fig.9

used and to provide an overall view of the program structure. Comments within the source listing should be consulted for finer details about the program. The next two sections deal with the generation of quadrature weights and nodes and with the calculation of boundary amplitudes and continuum molecular orbitals.

The input data to the integral package is essentially the same as that for the original IBM bound state code and therefore the notes prepared by B. Liu[5] should be consulted. However, for convenience, the entire input data will be described in this report including some details of parameters controlling the integration mesh generation since these were not described in detail in the original notes and will possibly have to be varied in scattering calculations. In appendices we provide sample input data, a summary of disk files used and installation details.

2. THE ALCHEMY LINEAR MOLECULE INTEGRAL PACKAGE

The present program has been developed from the ALCHEMY Slater integral generator for linear molecules, SCFWFORD, written by B. Liu of IBM, San Jose[5]. The basic algorithms used in the original package have not been modified. However, as outlined in the introduction, the options available have been considerably expanded and the package is now suitable for computing all integrals required in scattering calculations within the R-matrix, variational or hybrid formalisms. Apart from permitting the integrals to be computed over a finite region of space, it is now possible to use basis functions which are defined numerically to represent the continuum.

The overall structure and operation of the program may most easily be seen by refering to figs.1(a) and 1(b). Figure 1(a) illustrates the subroutine calling struoture in the initial stages of the computation and shows the set-up of the dynamic core allocation scheme and the reading and printing of the control and input data. The calculation may cycle over sets of input parameters; this operation is the principal role of the subroutine DRIVER.

The basic supervisory program in the package is LINTP which is an entry point of subroutine LINT. Figure 1(b) illustrates the subroutines called directly by LINTP. Subroutines lower down the calling tree are shown only for the initial section which is concerned with processing the input data and producing those fundamental arrays (mostly pointer arrays) which are used extensively throughout the rest of the package. Each of the required integral types are then computed in turn and written to disk files. The intagral computation sections are followed by an integral renormalisation section which is necessary because integrals over a finite region are initially computed without renormalising the basis functions -

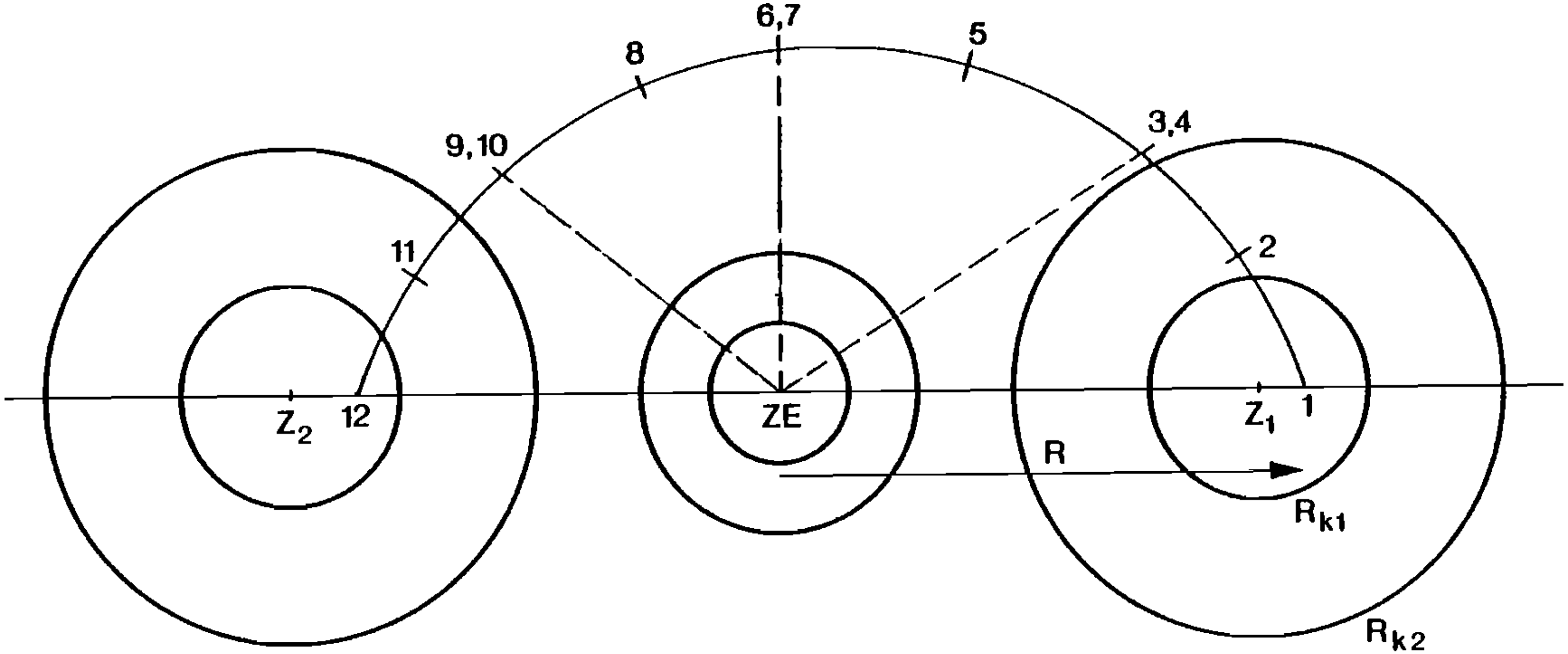


Fig. 13

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1. INTRODUCTION

For many years it has been recognised that electron-molecule scattering processes could be calculated within the framework of R-matrix or other variational reaction theories by modifying existing quantum chemistry configuration interaction (CI) computer program packages. However, attempts to implement this idea have shown that the quality of the results obtained depends sensitively on the extent to which the discrete molecular orbital basis used is able to represent the scattering continuum. The region of Hilbert space which is spanned is dependent on the amount of linear dependence which is tolerable within the orbital basis and, therefore, effectively on the accuracy with which the underlying atomic integrals may be computed. The compromise which must be made between obtaining the integrals to a high degree of accuracy while keeping the computational time to within reasonable limits has meant that it has been possible to obtain accurate scattering phase shifts only for a narrow range of scattering energies. This range is typically from threshold to about 1.0 Rydberg when using an analytic Slater orbital basis.

The present integral package is designed to reduce this limitation. Although the STO integral generator from the IBM CI Program ALCHEMY is the starting point of the new code the techniques employed to restrict the integration domain to the finite R-matrix region are entirely different from those used by Kendrick and Buckley[1]. In addition many new facilities have been added. Before listing these features it may be helpful to summarise the salient aspects of R-matrix theory for electron-molecule scattering.

The application of R-matrix theory to molecular processes involves the division of configuration space into distinct internal and external

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