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technical memorandum Daresbury Laboratory

A PROGRAM FOR OPTIMISING CONTINUUM SLATER TYPE ORBITALS FOR MOLECULAR
R-MATRIX CALCULATIONS

by

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In the R-matrix method for electron-molecule scattering it is necessary to have a set of continuum orbitals centered upon the molecular center-of-mass to represent the wavefunction of the scattered electron. In the codes supported at Daresbury these orbitals are constructed from a basis set of Slater type orbitals (STO). The program ORBOPT accepts as input a set of continuum STO's, and gives as output a new set adjusted so as to minimise their mutual linear dependence subject to given constraints on the parameters.

The STO's used are defined by

1) $\phi_i = A_i \, r^{N_i-1} \, e^{-\zeta_i r}$

with $i = 1, 2, \ldots n \leq 20$, with A_i determined from

2) $\int_0^a dr \; r^2 \, (\phi_i)^2 = 1$

where a is the radius of the R-matrix boundary; with N_i an integer $\lesssim 15$ and ζ_i any positive number $\gtrsim 1/2$, which limits correspond roughly to those imposed in practice by the modified ALCHEMY code used in the R-matrix calculations (they can be exceeded in ORBOPT, but this may void the warranty). The probability amplitude associated with the orbital ϕ_i is $r\phi_i$ which obtains its maximum at $r_i = N_i/\zeta_i$. The standard method of using ORBOPT consists of defining as input the principal quantum numbers N_i, the peak positions r_i, and the allowed variations in the peak positions $r_i^{\pm}$. The exponents ζ_i are then confined to lie within the limits

3) $N_i/(r_i + r_i^+) < \zeta_i < N_i/(r_i - r_i^-)$;

ORBOPT adjusts the set of ζ_i within this range to minimise the degree of linear dependence of the set of orbitals.

In the present application the "degree of linear dependence" is determined from the determinant D of the overlap matrix S of the STO's:

4) $S_{ij} = \int_0^a dr \; r^2 \, \phi_i \, \phi_j$.

The smaller the determinant D, the greater is the degree of linear dependence. This determinant is the product of the eigenvalues of the S-matrix. In the actual R-matrix calculation orthonormal continuum orbitals are constructed from linear combinations of the ϕ_i. If the expansion coefficients of any of the ϕ_i are too large - say, greater than 100 - the two-electron integrals entering the Hamiltonian matrix cannot be evaluated reliably because of round off error. In the symmetric orthonormalisation procedure the expansion coefficients are given by the components of the eigenvectors of the S-matrix. In this case only those eigenvectors can be used which correspond to eigenvalues which exceed a certain value (in practice, generally 10^{-5}). Thus it is intended that by maximising the product of the eigenvalues one will raise a few of the lowest eigenvalues above the cutoff value, and this expectation is fulfilled in execution. In the full R-matrix calculation one has the additional worry of the degree of linear dependence between the bound and continuum orbitals, but this short interactive program is not intended to deal with it.

The means by which the determinant D is maximised is quite simple. The n principal quantum numbers N_i are held fixed while the exponents ζ_i are allowed to vary between the predetermined limits. These limits define an n-dimensional rectangular prism Ω within which the vector $\underset{\sim}{\zeta}$ lies. The program calculates the N-dimensional gradient vector $\underset{\sim}{G} = \dfrac{\partial D}{\partial \underset{\sim}{\zeta}}$ at the initial value of $\underset{\sim}{\zeta}$. The vector $\underset{\sim}{\zeta}$ is then varied along the direction of $\underset{\sim}{G}$ until no additional increase in the determinant occurs. The value of $\underset{\sim}{G}$ at the new $\underset{\sim}{\zeta}$ can be then determined, and the process repeated indefinitely. The length of step along $\underset{\sim}{G}$ is at first taken to be 1/10 of the distance from the point $\underset{\sim}{\zeta}$ to the boundary of Ω. This step length is

used until the determinant decreases (or the boundary is reached); then one step backward is taken, the step length is divided by 10, and the process repeated (10 such iterations are made in the present version). As presently constructed the program evaluates Q ten separate times before printing out intermediate results. This can be varied as required. It is generally the case that little improvement occurs after four or five such intermediate results. The results printed on unit 6 are the principal quantum numbers N_i, the new values of the exponents ζ_i, the surface probability amplitudes $r\phi_i = A_i r^{N_i} e^{-\zeta_i r}$ associated with the new continuum orbitals on the R-matrix boundary sphere $r=a$, and the eigenvalues of the new overlap matrix S.

The program is designed to run interactively on the 170k TSO region of the Daresbury IBM 370/165. Units 5 and 6 are assigned to the terminal screen. Matrix diagonalization routines from the NAG library are employed. To execute ORBOPT it is suggested that a copy of 'CW.ORBOPT.FORT' be made on the user's own directory and that an object module ORBOPT.OBJ be then created by the command FORT ORBOPT. Some facilities to aid interactive execution reside on 'CW.CLIST'; 'CW.CLIST(TSET)' assigns units 5 and 6 to the terminal with definite blocksize and record length (this may be executed only once during a terminal session); 'CW.CLIST(NALGO)' loads the object module given as a positional parameter along with the NAG library and initiates execution. All required input is prompted in an obvious manner by ORBOPT with the required format specifications given in the prompt.

The author gives no guarantee that the new orbitals generated by ORBOPT will be superior to the original set in the sense of providing better results in an R-matrix calculation - in fact in some cases the contrary is true. The types of orbitals required in application are determined by the physics of the problem at hand, and a bad choice of an initial set will not be much improved by reducing linear dependence. However, to establish the convergence of an R-matrix calculation it is desirable to increase the number of orbitals which can be used. Generally ORBOPT will facilitate this by providing a new set of orbitals not too dissimilar to that given initially, but which provides a greater number of orthogonal combinations of STO's with sufficiently small coefficients.

The results of a sample execution are given below. Seven orbitals with the principal quantum numbers indicated are put in a sphere of radius 10 a.u. The first orbital, with $N=2$, is set initially to peak at 2 a.u., and its peak is allowed to vary between 0.7 and 3.5 a.u. The minimum, initial, and maximum values of zeta are printed after each peak specification is given.

It has been found that the results are relatively insensitive to the allowed peak variations assigned to intermediate orbitals. Adjacent orbitals "repel" each other, since any increase in mutual overlap must tend to decrease the value of the determinant. Thus it will be found that the greatest change occurs in the outermost orbital, whose peak is pushed out as far as possible. The innermost orbital on the other hand is invariably contracted, though if it is diffuse (as in this example) its peak will not be shifted much.

Figures 1 and 2 show respectively the old set of orbitals, and the new set of orbitals obtained after four passes of optimisation. It can be seen that the individual orbitals have not been greatly altered by optimisation. The improvement of linear independence is significant, however. The second lowest eigenvalue for the initial set is probably too

small for its eigenvector to be used in a calculation, whereas after

optimisation its magnitude would appear to be satisfactory.

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test
READY
nalgo orbopt
 R MATRIX RADIUS IN ATOMIC UNITS (F14.7)
10.00
 NUMBER OF ORBITALS LE 20 (I2) 99 TO STOP,98 NEW RADIUS
 7
 PRINCIPAL QUANTUM NUMBERS IN ORDER   (NP * I2)
 2 3 4 5 6 7 7
 ENTER 0 FOR DEFAULT PEAK SPACE OR 1 TO SPECIFY (I1)
 1
 DISTANCE FROM ORIGIN OF PEAK #   1   (F14.7)
2.00
 PLUS    F14.7
1.50
 MINUS   F14.7
0.30
ZMIN,ZETA,ZMAX        0.5714285D+00       0.10000000D+01      0.11764706D+01
 DISTANCE FROM ORIGIN OF PEAK #   2   (F14.7)
3.75
 PLUS    F14.7
2.00
 MINUS   F14.7
1.0
ZMIN,ZETA,ZMAX        0.52173913D+00      0.80000000D+00      0.10909091D+01
 DISTANCE FROM ORIGIN OF PEAK #   3   (F14.7)
4.50
 PLUS    F14.7
2.00
 MINUS   F14.7
2.00
ZMIN,ZETA,ZMAX        0.61538462D+00      0.88888889D+00      0.16000000D+01
 DISTANCE FROM ORIGIN OF PEAK #   4   (F14.7)
5.50
 PLUS    F14.7
2.00
 MINUS   F14.7
2.00
ZMIN,ZETA,ZMAX        0.66666667D+00      0.90909091D+00      0.14285714D+01
 DISTANCE FROM ORIGIN OF PEAK #   5   (F14.7)
7.50
 PLUS    F14.7
1.50
 MINUS   F14.7
2.50
ZMIN,ZETA,ZMAX        0.66666667D+00      0.80000000D+00      0.12000000D+01
 DISTANCE FROM ORIGIN OF PEAK #   6   (F14.7)
9.00
 PLUS    F14.7
2.00
 MINUS   F14.7
3.00
ZMIN,ZETA,ZMAX        0.63636364D+00      0.77777778D+00      0.11666667D+01
 DISTANCE FROM ORIGIN OF PEAK #   7   (F14.7)
11.00
 PLUS    F14.7
2.00
 MINUS   F14.7
4.00
ZMIN,ZETA,ZMAX        0.53846154D+00      0.63636364D+00      0.10000000D+01
 FIRST EVALUATION OF DETERMINANT      0.491699D-14
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FIRST EVALUATION OF DETERMINANT        0.491699D-14
N        ZETA        SURFACE AMPLITUDE      OVERLAP EIGENVALUES
   2    0.1000000D+01    0.5242377D-02       0.1371352D-05
   3    0.8000000D+00    0.6490370D-01       0.4426794D-04
   4    0.8888889D+00    0.9184298D-01       0.1386872D-02
   5    0.9090909D+00    0.1607322D+00       0.2295593D-01
   6    0.8000000D+00    0.3621191D+00       0.3271944D+00
   7    0.7777778D+00    0.5077505D+00       0.1517632D+01
   7    0.6363636D+00    0.6531132D+00       0.5130787D+01
VALUE OF DETERMINANT AFTER TEN STEPS IS        0.543559D-13
N        ZETA        SURFACE AMPLITUDE      OVERLAP EIGENVALUES
   2    0.1015967D+01    0.46692560D-02      0.3116447D-05
   3    0.8274443D+00    0.5547354D-01       0.8367491D-04
   4    0.9212424D+00    0.779553D-01        0.2113190D-02
   5    0.9319868D+00    0.1461534D+00       0.338350FD-01
   6    0.8285679D+00    0.3346400D+00       0.3650891D+00
   7    0.7600500D+00    0.5259173D+00       0.1596185D+01
   7    0.5725979D+00    0.7178283D+00       0.5002691D+01
ENTER 0 TO CONTINUE OR 1 TO TRY NEW SET OR STOP (I1)
0
VALUE OF DETERMINANT AFTER TEN STEPS IS        0.114838D-12
N        ZETA        SURFACE AMPLITUDE      OVERLAP EIGENVALUES
   2    0.1022560D+01    0.4423555D-02       0.3954689D-05
   3    0.8386312D+00    0.5197930D-01       0.1032680D-03
   4    0.9343653D+00    0.7283198D-01       0.2422411D-02
   5    0.9406054D+00    0.1410342D+00       0.3805398D-01
   6    0.8362278D+00    0.3274152D+00       0.3783800D+00
   7    0.7534468D+00    0.5326988D+00       0.1627483D+01
   7    0.5503661D+00    0.7401114D+00       0.4953553D+01
ENTER 0 TO CONTINUE OR 1 TO TRY NEW SET OR STOP (I1)
0
VALUE OF DETERMINANT AFTER TEN STEPS IS        0.147916D-12
N        ZETA        SURFACE AMPLITUDE      OVERLAP EIGENVALUES
   2    0.1024984D+01    0.4343272D-02       0.4284627D-05
   3    0.8427226D+00    0.5074956D-01       0.1108978D-03
   4    0.9391450D+00    0.7103599D-01       0.2538846D-02
   5    0.9433767D+00    0.1392582D+00       0.3957897D-01
   6    0.8386419D+00    0.3251515D+00       0.3829836D+00
   7    0.7510932D+00    0.5351176D+00       0.1638788D+01
   7    0.5426117D+00    0.7478411D+00       0.4935996D+01
ENTER 0 TO CONTINUE OR 1 TO TRY NEW SET OR STOP (I1)
0
VALUE OF DETERMINANT AFTER TEN STEPS IS        0.161428D-12
N        ZETA        SURFACE AMPLITUDE      OVERLAP EIGENVALUES
   2    0.1025844D+01    0.4315117D-02       0.4404799D-05
   3    0.8441718D+00    0.5031993D-01       0.1136591D-03
   4    0.9408353D+00    0.7040966D-01       0.2580562D-02
   5    0.9444162D+00    0.1386407D+00       0.4011730D-01
   6    0.8294538D+00    0.3243917D+00       0.3845841D+00
   7    0.7502663D+00    0.5359675D+00       0.1642772D+01
   7    0.5399086D+00    0.7505313D+00       0.4929827D+01
ENTER 0 TO CONTINUE OR 1 TO TRY NEW SET OR STOP (I1)
1
 NUMBER OF ORBITALS LE 20 (I2) 99 TO STOP,OR NEW RADIUS
00
READY
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Figure Captions:

Fig.1. Probability amplitudes $r\phi_i$ for the seven orbitals of the initial

set as a function of r.
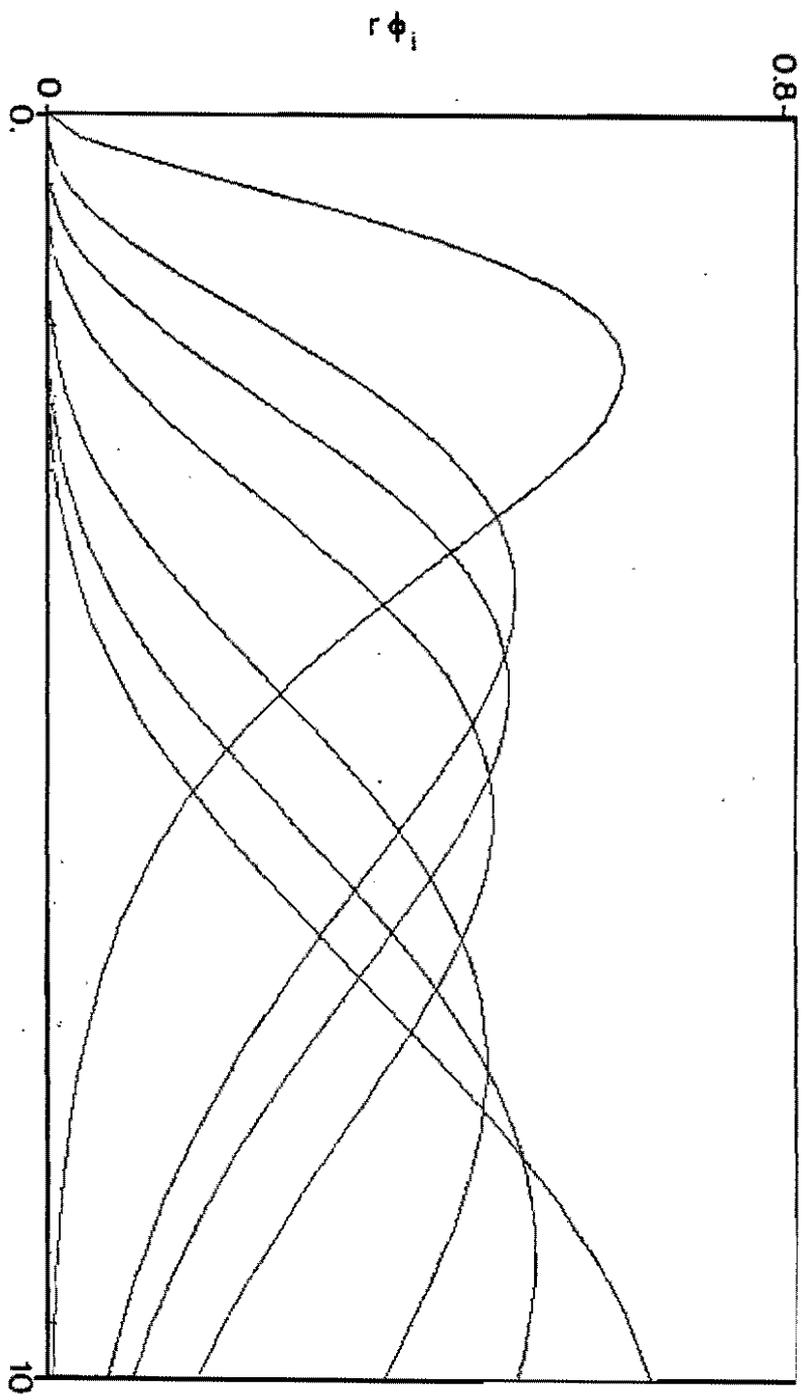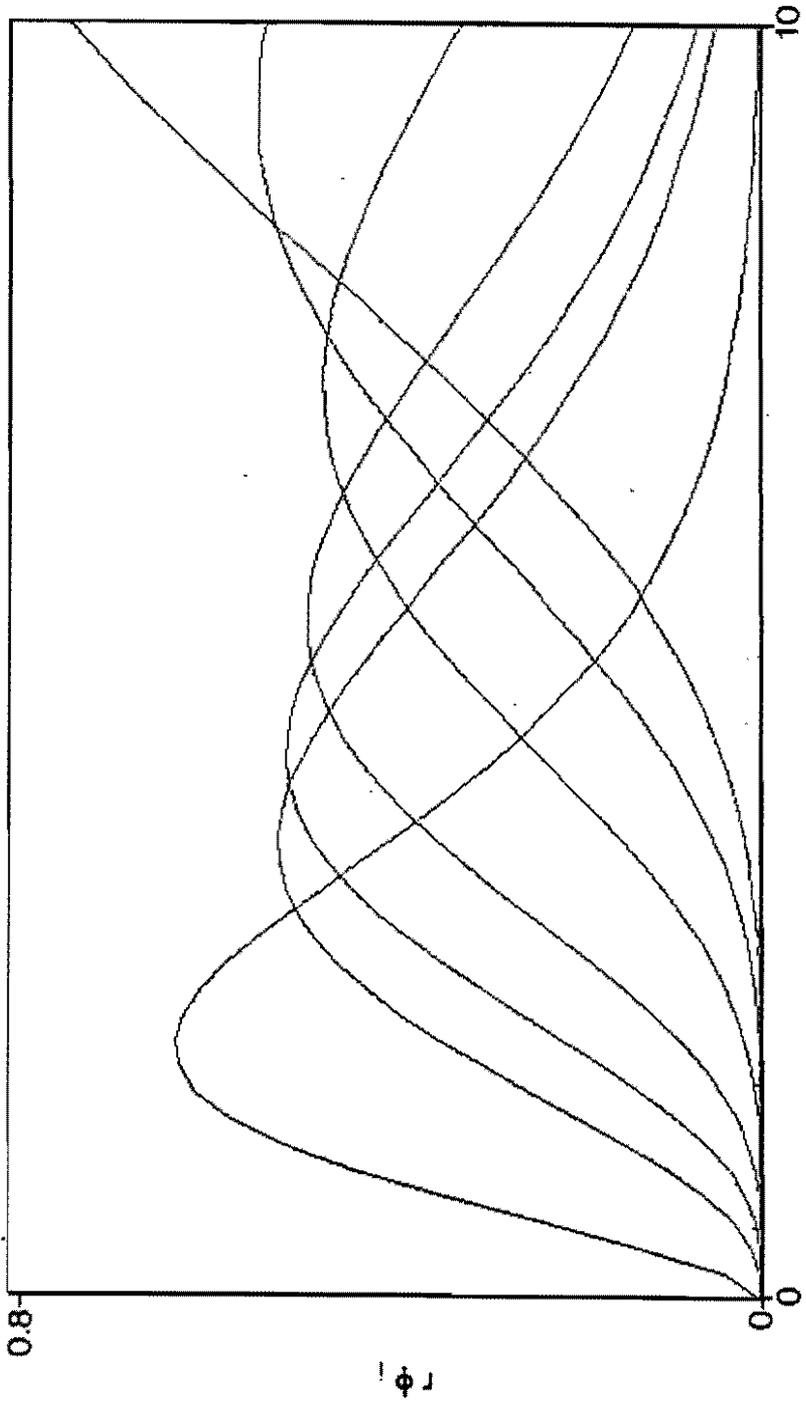
Fig.2. Probability amplitudes for the optimised set.

Fig.1

Fig. 2