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USER'S GUIDE TO PROGRAM RCN

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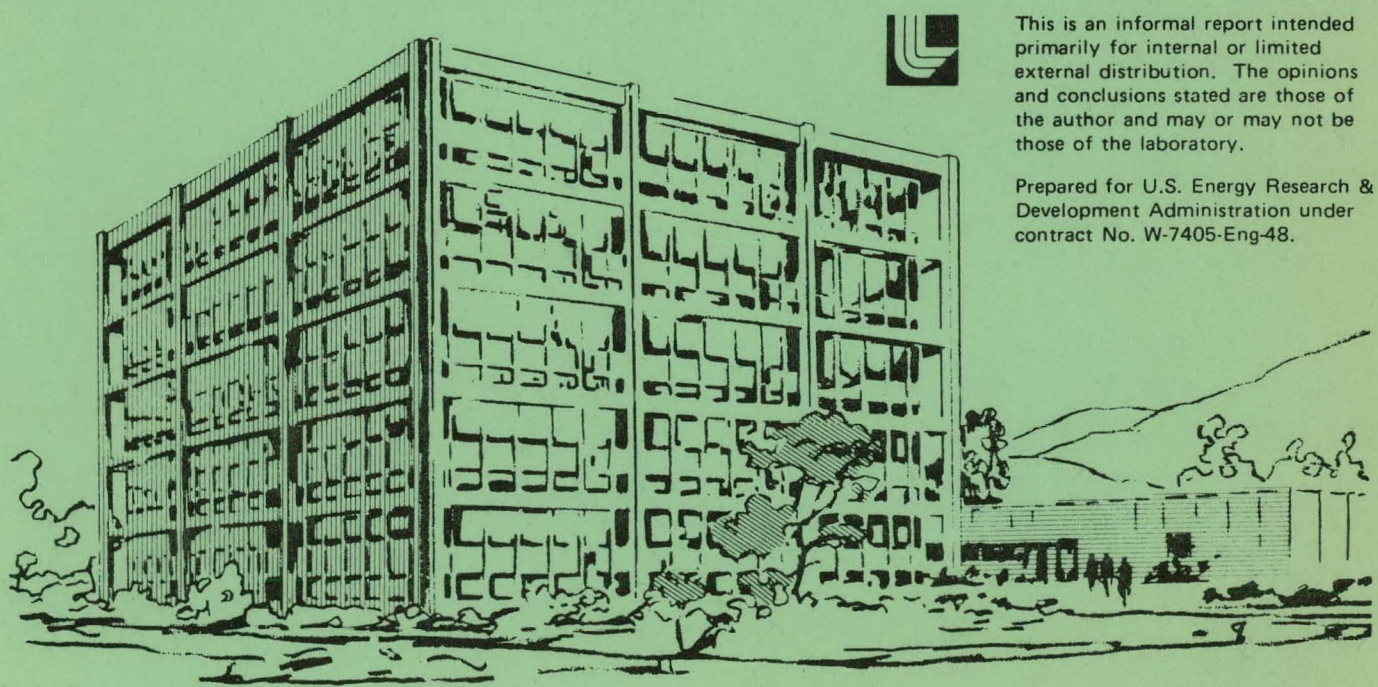

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DISCLAIMER

USER'S GUIDE TO PROGRAM RCN

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This is a set of three Fortran IV programs, RCN29, HFMOD7 and RCN229 based on the Herman-Skillman and Charlotte Froese Fischer programs, with extensive modifications and additions by R. D. Cowan, D. C. Griffin and K. L. Andrew at LASL. Modifications for running at LLL were made by Paul Renard.

The programs compute self-consistent-field radial wave functions and the various radial integrals involved in the computation of atomic energy levels and spectra. The codes RCN29 and RCN229 as obtained from LASL (March, 1975) were versions with some dimensions which were too small for continuum functions. These were changed as per Cowan's instructions so that the current LLL code should be the same as the large LASL version. Responsibility for any errors involving these dimension changes must rest with LLL. Other changes have been limited to those necessary to make the codes run on the LLL system. Two of us (Rajnak and Renard) make no pretense of understanding the detailed workings of the codes and Cowan should be contacted (Ext. 5139 at LASL) if any major changes are contemplated. The codes are also running at LBL and John Conway (Ext. 5141) may be able to help with some difficulties.

I. Program Descriptions

A. Overview[1]

These three programs can be run in a chain in any one of the following four combinations:

RCN29
RCN29/RCN229
RCN29/HFMOD7
RCN29/HFMOD7/RCN229

The primary input information is always to RCN29, and each program automatically provides input information to the succeeding program of the chain. Details of the programs will be described later; here we outline only the basic purpose of each program.

Program RCN29 calculates single-configuration radial wavefunctions for a spherically-symmetrized atom via any one of the following homogeneous-differential-equation approximations to the Hartree-Fock method.

(1) Hartree (H);

(2) Hartree-Fock-Slater (HFS), with any desired value of the coefficient for Slater's approximate exchange term, and either without or with (HFSL) Latter's tail cutoff in the central-field potential-energy function;

(3) Hartree-plus-statistical-exchange (HX);

(4) Hartree-Slater (HS).

Normally, the HX method is the only one used. (HX and HXR (see below) are the only methods which have been used at LLL. All others should be regarded as untested). Also calculated in each case are various radial integrals ($\langle r^m \rangle$, F^k, G^k, ζ) and the total energy E_{av} of the atom, including approximate relativistic and correlation energy corrections. Relativistic terms can be included in the differential equation (HXR) to give approximate relativistic wavefunction corrections for heavy atoms.[2] (See B 7 below). (Important for outer orbitals only if $Z \geq 54$, for inner orbitals if $Z > 35$.) Options are available to provide radial wavefunctions as input to either RCN229 or HFMOD7.

Program HFMOD7 calculates single-configuration Hartree-Fock radial wavefunctions corresponding to either the center-of-gravity energy of the configuration, or to any specified LS term of the configuration (provided the LS value of interest appears only once in that configuration). (We have computed only center-of-gravity energies at LLL but the LS term feature has been used at LBL). Radial integrals and E_{av} are calculated as in RCN, except that spin-orbit parameters are computed by the Blume-Watson method[3] instead of via the simple one-electron, central-field formula. Input is entirely from RCN29; output wavefunctions provide input to RCN229. Relativistic terms can be included in the HF equations if desired (HFR).

Program RCN229 accepts radial wavefunctions (for one or more different configurations of one or more atoms or ions) from either RCN29 or HFMOD7 and calculates multiple-configuration radial integrals: configuration-interaction Coulomb integrals (R^k) and spin-orbit integrals $\zeta_{\ell\ell'}$, and radial electric-dipole and electric-quadrupole integrals. In its most commonly used option, it automatically computes all quantities required for calculating energy levels and spectra of an atom, and creates a file PUNCHA which gives input in the exact form required by program RCG MOD 5 or 6, which performs these calculations.[4]

Computing Times

The following approximate computing times for RCN29 (HX or HXR) and HFMOD7 were obtained on the CDC 7600 at LASL.

	Time (sec)			
Config	HX	HXR	HX[a] + HF	HXR[b] + HFR
Ar I $3p^6$	5	6	4 + 3	2 + 4
Kr I $4p^6$	9	9	7 + 6	3 + 8
Xe I $5p^6$	11	12	9 + 12	4 + 15
Dy I $4f^{10}6s^2$	18	24	14 + 17	7 + 24
Rn I $6p^6$	17	21	13 + 26	7 + 33
U I $5f^36d7s^2$	20	27	15 + 54	8 + 62

[a]Time for SCF calc (TOLEND = $5 \cdot 10^{-8}$) + ZETA1

[b]Time for SCF calc (TOLEND = $5 \cdot 10^{-2}$) only

Running under ORDER at LLL the following times were obtained.

	HXR + HFR (min)
Pt I $4f^{14}5d^96s$ $4f^{14}5d^86s^2$ Au II $4f^{14}5d^96s$ $4f^{14}5d^86s^2$ Hg III $4f^{14}5d^96s$ $4f^{14}5d^86s^2$	.69 + 4.45

Pt I as above RCN229 .02 min.

U I 4 configurations HXR + HFR + RCN229 7.10 min.

Fe I, Nb II, Gd I, U I
3 configurations each
HXR(RCN2) + HFR(HFMOD7) + RCN229 10 minutes

Computing time for RCN229 is usually only a small fraction of the RCN29 or HFMOD7 time. However, if there are a large number of configurations on unit 2 (say, > 20) and the configurations in question are the ones with high serial number (i.e., near the end) read and rewind times can be uncomforably long, especially with a tape rather than disk unit.

File Sizes

The 1st data card gives decimal sizes for the disk files OUTP (the output file), PUNCHA (input for RCG), TAPE4 (a scratch file), TAPE2 (input to RCN229), TAPE7 (input to HFMOD7) and ENC (an encode/decode). When running under ORDER the size of OUTP is really determined by the COPY instruction on the ORDER card, PUNCHA contains essentially only values of radial integrals and is quite small.

For running U I $5f^3 6d 7s^2$ through all three programs, the following file sizes are necessary.

TAPE4	19000
TAPE2	5000
TAPE7	5000

TAPE4 rewinds between configurations so its size is determined by the configuration containing the largest number of shells. The number of wavefunctions on TAPE2 is controlled by the value of NORBPT on the control card. (See B2). As usually run only the 5 outermost orbitals of each configuration are written on TAPE2 so it is smaller than TAPE7. TAPE7 contains wavefunctions for each shell of each configuration so for actinides its size $\sim$ 5000 x # of configurations.

If HFMOD7 is not used, TAPE7 isn't needed. The size of TAPE4 increases to 30000 because a different write statement is used.

For U I $f^4 s^2$ and $f^3 ds$ 99p (continuum p) TAPE4 is 72000, TAPE2 is 7000.

ENC needs only a size of 10.

B. PROGRAM RCN29

1. Description

This is a Fortran IV program for the CDC 7600 for the calculation of radial wavefunctions of a spherically-symmetrized atom, corresponding to the center-of-gravity energy E_{av} of an electron configuration

$$(n_1\ell_1)^{w_1}\ (n_2\ell_2)^{w_2} \cdot \cdot \cdot \cdot (n_q\ell_q)^{w_q} \quad . \qquad (1)$$

Computed from these radial wavefunctions are the Coulomb integrals F^k and G^k and the spin-orbit integrals ζ_i, along with radial integrals required to give kinetic and electron-nuclear energies, and rough relativistic and correlation energy corrections to both the one-electron binding energies and total electronic binding energy E_{av}.

The program was originally (January, 1964) based on the Share program 1417 (ML HFSS) described by Herman and Skillman[5], and this reference may be used for a description of the integration mesh and basic numerical methods used in RCN29. However, except for the subroutine CROSYM and most of SCHEQ, the original program has been changed beyond recognition (including notational changes from SNL(M,I) and SNLO(I) to PNL(I,M) and PNLO(I), and redefinition of NNLZ from 100n + 10ℓ + const to 100n + ℓ). Options are still available for making calculations via the Hartree-Fock-Slater approximation used by Herman and Skillman either with or without Latter's tail-cut-off in the one-electron potential, using either Slater's original exchange coefficient $\frac{3}{2}$ or Kohn and Sham's modified value of 1 (or any other value). However, these approximations are all considered to be unsatisfactory, and the program is intended primarily for calculations via the Hartree-plus-statistical-exchange (HX) approximation[6] described in Phys. Rev. 163. 54 (1967), which should be consulted for theoretical discussions (except that the method of calculating correlation corrections has recently been modified). Still a further option is the HS approximation of Lindgren and Rosén.[7]

Program Outline

The program is all in Fortran IV and consists of a main program and ten subroutines.

RCN29

RCN29 is the main program. It handles all input, most output, controls the self-consistent-field iteration, and does much of the detailed calculation.

SCHEQ

SCHEQ integrates the one-electron radial wave equation, and controls the iteration on the one-electron eigenvalue E=EE(M) to give a radial wavefunction $P_{n\ell}(r) = rR_{n\ell}(r)$ = PNLO(I) = PNL(I,M) which satisfies the boundary conditions ar r = 0 and ∞. It also properly normalizes the function for either a bound electron (E < 0) or a free electron (E > 0); it will not handle the case E=0. The normalization for a free electron is likely to be inaccurate if E > 0.1 rydberg (because of too coarse an integration mesh) unless 0.1 EMX ≦ E ≦ EMX and very large dimensions are used for PNL, R, and other variables (see remarks below regarding continuum-wavefunction calculations).

SUBCOR

SUBCOR calculates a modified free-electron correlation energy for a specified electron density.

CROSYM

CROSYM solves a system of linear equations to provide a value of

$$AZ \equiv \left(r^{-\ell-1}P_{n\ell}\right)_{r=0} \qquad (2)$$

POWER

POWER computes values of $\langle r^m \rangle$ for $-3 \leq m \leq 6$ (except m = 5) for each orbital.

ZETA1

ZETA1 computes spin-orbit parameter values ζ from the central-potential formula

$$\zeta = \frac{\alpha^2}{2} \int_0^\infty P_{n\ell}^2(r) \, \frac{1}{r} \frac{dV}{dr} \, dr$$

using two different forms of the one-electron potential V; the right-hand one of the two values printed out is the one used in practice. Also computed and printed are the one-electron kinetic-plus-nuclear energy I, and the relativistic mass-velocity and Darwin corrections. (Actually, I is computed in RCN29, and only printed in ZETA1.)

SLI1

SLI1 computes and prints all Slater integrals F^k and G^k (in units of both rydbergs and cm^{-1}); it also computes overlap integrals and calls RCN3S.

RCN3S

RCN3S prints the overlap integrals, and calculates (from the F^k and G^k, with the aid of subroutine S3JOSQ) and prints the Coulomb interaction energy between each pair of electrons. It then calculates correlation-energy corrections, and (using values of I from ZETA1) calculates and prints one-electron binding energies and the total binding energy of the atom. (See Ref. 6 for equation). It also prints the single-configuration parameter values E_{av}, $F^k(ii)$, ζ_i, $F^k(ij)$, and $G^k(ij)$ required for the calculation of atomic energy levels; E_{av} (total binding energy) is given is rydbergs, all other parameter values are in kK (units of 1000 cm^{-1}).

S3JOSQ

S3JOSQ calculates the value of

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix}^2$$

where $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is a 3-j symbol.

FCTRL

FCTRL calculates the factorial of an integer A, required by S3JOSQ.

HFWRTP

HFWRTP interpolates the RCN wavefunctions to points on the logarithmic mesh used by HF, and writes on TAPE7 these wavefunctions and other input data for a Hartree-Fock calculation.

2. Input

Input consists of a card giving file sizes (see IA), a 13-card deck providing a starting estimate for the one-electron potential RU, a control card, and one configuration card for each configuration to be computed. (Additional cards are required if an LS-term HF calculation is to be done; see below). Normally, the potential cards (and to some extent the control cards) are universal, and are never changed from one run to the next.

(a) File sizes: The first card gives the sizes for the files OUTP, PUNCHA, TAPE4, TAPE2, TAPE7 and ENC. The format is FILE SIZE=6I10

(b) Potential Cards: Read at statement 195 of main program RCN29. These cards are identical (except for format) with Herman-Skillman's corresponding input, and contain values of their potential U(X) for some appropriate value of Z (e.g., Z = 18, 36, or 54: the value used is not particularly important). (All LLL runs have begun with the Ar potential).

(c) Control Card: Read at statement 200 of RCN29, and containing the following quantities

cols	format	variable	normal value HX only	HX + HF	HF only
1	I1	ITPOW	2	2	0
2	I1	IPTVU	0	0	0
3	I1	IPTEB	0	0	0
4-5	I2	NORBPT	-5	-5	-5
6	I1	IZHXBW	0	0	0
7-8	I2	IPHFWF	0	0	0
9-10	I2	IHF	0	2	1
11-15	F5.1	TOLSTB	1.0	1.0	1.0
16-20	F5.1	TOLKM2	1.0	1.0	1.0
21-30	E10.5	TOLEND	5.E-08	5.E-08	5.E-02[a]
31-40	E10.5	THRESH	1.E-11	1.E-11	1.E-05[a]
41-42	I2	KUTD	-2	-2	-2
43-45	I3	KUT1	0[b]	0[b]	0[b]
46	I1	IREL	0	0	0
47-48	I2	MAXIT	30	30	30
49-50	I2	NPR	0	0	0
51-55	F5.5	EXF10	1.0	1.0	1.0
56-60	F5.5	EXFM1	0.65	0.65	0.65
61-65	F5.5	EMX	0.0[c]	0.0[c]	0.0[c]
66-70	F5.5	CA0	0.5	0.5	0.5
71-75	F5.5	CORRF	0.0	0.0	0.0
76-80	F5.5	CA1	0.7	0.7	0.7

[a] Use 5.E-08 and 1.E-11 if IREL = 0 and HX relativisitic energy corrections to E_{av} are desired.

[b] Use IREL = 2 for HXR, IREL = 1 or 2 for HFR.

[c] See notes regarding continuum-wavefunction calculations, section B6.

The first seven quantities and NPR control the amount of printed output, as follows:

ITPOW
- $\geq$1 or $\geq$3, print SCF iteration information
- $\geq$2, call POWER to print $\langle r^m \rangle$

IPTVU
- $\geq$1, print F^k and G^k
- $\geq$2, print Coulomb interaction energies
- $\geq$3, print wavefunction overlap integrals
- $\geq$4, print HFS potentials (RU, RUEE, etc)
- $\geq$5, print HX potentials ($V^{n\ell}$)
- $\geq$6, in SCHEQ, print relativistic contribution to potential

IPTEB
- $\geq$1, print EE, JJJ, R(JJJ), AZ
- $\geq$2, print E_{kin}, etc

NORBPT
- <0, do not print wavefunctions
- >0, print first two and last NORBPT wavefunctions at every fifth mesh point
- $\geq$6, print continuum wavefunctions at every mesh point for configurations 1, 5, 10, 15, ...
- any, If IHF=0 write on TAPE 2 the last |NORBPT| wavefunctions (at least 4; if |NORBPT|=9, write all wavefunctions)

IZHXBW
- >0, in HF, calculate and print all quantities using HX input wavefunctions (primarily to give ζ calculated by Blume-Watson method).

IPHFWF
- >0, in HF, print last |IPHFWF| wavefunctions at every mesh point
- <0, same, except at only every fourth point
- $\pm$9, print all wavefunctions

IHF
- =0, signifies RCN calculation only; do not load HF program
- $\neq$0, RCN output wavefunctions are for input to HF (via TAPE7) rather than for RCN229 (via TAPE2)
- =1, skip all RCN calculations of radial integrals if IREL > 1; if IREL = 0 and TOLEND < 1.0E-4, call only ZETA1 (to calculate relativistic energy correction for HF E_{av})
- $\geq$2, carry out all RCN calculations (of F^k, G^k, ζ, E_{av})

NPR
- $\neq$0, diagnostic potentials and diagnostic wavefunctions are printed during the course of the RCN SCF iteration

The significance of the other input quantities is as follows:

TOLEND is the maximum permissible value of DELTA (change in the absolute value of RU) for ending the SCF iteration (RCN29, statements number 530-550, 705).

THRESH is the maximum permissible fractional change in the value of the eigenvalue E to end the eigenvalue iteration (SCHEQ, 805 and 205).

MAXIT is the maximum allowable number of SCF iterations; if convergence is not obtained, the calculation is continued for 4 more cycles with diagnostic printout (NPR.GT.0) (710-729).

EXF10 is the coefficient of Slater's exchange term for a HFS calculation with no tail cutoff (KUT = 1) or with tail cutoff (KUT = 0) (411-417). EXF10 = 1.5 is Slater's original value, EXF10 = 1.0 is Kohn and Sham's modified value.

EXFM1, CA0, and CA1 are values of k_1, k_3, k_2, respectively, for KUT = -1 [HX calculation; Reference 6, eqs. (13) - (14)].
EXFM1 = 0.0 will give a Hartree calculation for KUT = -1.
KUT = -2 gives a HS calculation.

If IREL = 0, relativistic terms are omitted from the differential equations (HX and HF); if IREL = 1 or 2, they are included (HXR and HFR); if IREL > 2, some diagnostic printouts will occur. (IREL = 2 is supposedly better for HX, but sometimes leads to instabilities present in HXR that are not present with IREL = 1; the difference lies only in numerical methods used in calculating dV/dr.

(d) Configuration Card: read at statement 213 of RCN29 and containing the following information:

cols	format	variable	significance
1	I1	NHFTRM	No. of LS terms for which HF calculations are to be made
2-5	I4	IZ	atomic number (fixed-point)
6-10	I5	NSPECT	1 + degree of ionization (1 = neutral, 2 = singly-ionized, etc)
11-28	3A6	CONF	BCD configuration label (e.g., CA I 4S 3D), for identification purposes only
31	1Pf1.0	ALFMIN	iteration control variables (normally left blank)
32	"	ALFMAX	
33-35	A3	NLBCD8	orbital specification (e.g., "^4S", "12D")
36-37	A2	WWNL8	occupation number (0^ or ^0 = 0, blank = 1, 1^ or ^1 = 1, 2^ or ^2 = 2, etc)
.	.	.	
.	.	.	
.	.	.	
68-70	A3	NLBCD8	"
71-72	A2	WWNL8	"
73-74	I2	KUT	Overrides value of KUT1 from control card for this configuration
75-80	F6.5	EE8	Eigenvalue of outermost orbital, for a free electron only. (EE8 must be > 0, and last punched value of NLBCD8 should be "99S", "99P", "99D", etc., and last value of WWNL8 must be blank or one.

For a continuum wavefunction $\varepsilon\ell$, punch 99ℓ (e.g., "99S", "99P", "99D", etc) at the appropriate place in cols 33-72, and punch the desired value of the kinetic energy ε (in rydbergs) in cols 75-80 (format F6.5).

For heavy elements ($Z > 70$), it may be necessary to decrease by an order of magnitude the values of TOLEND and THRESH punched on the control card. (This card is read at statement 200 of RCN29 main). (See Sect. E).

If NHFTRM (col 1 of the configuration card) is non-zero, then NHFTRM (or more, as required) additional cards must follow, containing the following information:

cols	format	variable	significance
1-7	7X	---	unused identification information (e.g., the configuration "PD", "P4^D", etc)
8-10	A3	TERM(I)	LS term identification (e.g., "1P" for ^{1}P, "3D" for ^{3}D, etc)
11-15	I5	NFG	No. of Slater parameters (F^k and G^k) involved in the diagonal energy matrix element for this LS term (excluding E_{av}).
21-29	F9.8	CFG(J,I)	Coef. f_k or g_k of the j^{th} F^k or G^k.
30	A1	FG(J,I)	"F" or "G", as appropriate.
31	I1	KFG(J,I)	Value of k.
33-35	A3	IFG(J,I)	Orbital codes; e.g., "^3P" and "^4D" for F^2(3p,4d) and G^k(3p,4d).
37-39	A3	JFG(J,I)	
41-59, 61-79	same as 21-39 for second and third F^k and G^k.		

Code dimensions limit this option to 9 terms/configuration and a total of 10 F^k and G^k integrals in the energy expression.

If more than three Slater parameters are involved in the expression for the energy of this LS term (relative to E_{av}), then the remaining coefficients and parameters are punched four to a card in cols 1-19, 21-39, 41-59, and 61-79. (If an HF calculation for the center-of-gravity energy is desired in addition to one or more calculations for specific LS terms, it is only necessary to fake an LS-term card with TERM = C-G, NFG = 1, CFG(1,I) = 0.0, IFG and JFG equal any two orbitals of the configuration.) None of this information is used in RCN29, but is simply passed on unchanged to the HFMOD7 program.

3. Calculational Procedure

After reading the input potential and control card, the following is done for each configuration card:

(a) If IZ > 0 but columns 11-16 are blank (first configuration card only), the output (see later) from IZ completed configurations done on previous runs is skipped over on TAPE2.

If IZ = 0, go back and read a new control card.

If IZ < 0, write EOF on TAPE2 and TAPE7 and exit.

If IZ > 0 and columns 11-16 are not all blank make a calculation as follows:

(b) Calculate the number of electrons in the atoms from

N = IZ + 1 - NSPECT ;

set up the heaviest rare gas core (ground configuration of Ne, Ar, Kr, Xe, Rn, or Z = 118) having no more than N electrons; modify or add to this core according to any values of NLBCD8/WWNL8 punched on the configuration card so as to obtain the final desired configuration (1); estimate a value of the eigenvalue for each orbital (unless EE8 is non-zero, in which case this value is used for the outermost orbital). [Decoding of WWNL8 (statements 230-233) and of NLBCD8 (237-242) is done partly via table look-up].

The ionization state punched in columns 6-10 of a configuration card is used only to find the rare-gas configuration from which to start in setting up the desired configuration. Negative numbers sometimes can be used to simplify the card punching. Fox example, the following two cards will produce exactly the same results for neutral germanium:

```
32    1    GE I    4P    4D        3D10    4S2    4P    4D
32   -3    GE I    4P    4D        4P      4D
```

The former starts with Ar I $3p^6$ and adds on 14 more electrons; the latter starts with Kr I $4p^6$, changes $4p^6$ to $4p^1$, and adds on $4d^1$. Note that if the previous rare gas did not include a filled shell (such as $3d^{10}$ and $4s^2$ above or $4f^{14}$) it must be included on the configuration card. If a filled shell which should have been included is omitted it is most easily seen by looking at the first line of the output. ION=(degree of ionization). If ION is not the expected value, a wrong configuration card is usually the source of the difficulty.

(c) A suitable starting atomic potential for the current value of Z is obtained by scaling the input potential (first configuration only) or the final SCF potential from the preceeding configuration, and a radial integration mesh is constructed.

(d) A SCF iteration is carried out by repeatedly (up to MAXIT times)

(1) integrating the differential equation to obtain a radial function PNL(I,M) for each orbital M,

(2) recalculating the potential RU from the PNL,

(3) comparing the PNL and/or RU with values from the preceding cycle, and revising as appropriate.

An HX calculation is started by first making an HFS calculation (KUT = 0) for at least two cycles to obtain approximate wavefunctions (required for the calculation of HX potential functions for use in the differential equation), and then automatically switching to HX (KUT = -1) when

DELTA <TOLKM2 (729-736). [To calculate via HFS only, make TOLKM2 = 0 on the control card; to calculate for two or more values of KUT in succession (in the order +1, 0, -1, -2), make TOLKM2 = TOLEND on the control card, KUT1 = 1 (or 0, if KUT = 1 is not desired), and KUTD = 0 if KUT = 0 is not desired (cf, statements 996-).

Stabilization of the iteration is via RU on early cycles (600-660), and on the PNL on later cycles (454-490). The control involves quantities ALFM(M), recomputed each cycle within the range ALFMIN to ALFMAX (normally 0.2 to 1.0);if the SCF iteration should fail to converge because of oscillatory instabilities (very unlikely), three things can be tried;

(1) decrease the values of ALFMIN and ALFMAX read in on the configuration card (see code near statement 215 for details);

(2) increase the value of TOLEND on the control card;

(3) on the card just before statement 708, increase the number "5.E-06", which is an upper bound on the fractional change allowed in the tail of each wavefunction.

(e) Using the final SCF radial wavefunctions PNL, various one-electron radial integrals (e.g., kinetic energy, electron-nuclear potential energy) are computed, the subroutines POWER, ZETA1, SLI1, and RCN3S are called, and output is written on the output file OUT1, and on output TAPE2, for use by the computer program RCN229, or (if IHF > 0) HFWRTP is called to convert from a linear to a logarithmic mesh and write wavefunctions on TAPE7 for use by program HFMOD7.

(f) If the values of TOLKM2, TOLEND, KUT, and KUTD so indicate, additional calculations are automatically made for the same configuration, but with different values of KUT [see under (d) above].

4. Input/Output Units

Data input and printed output are via files INP1 and OUT1, respectively. In addition, disk file TAPE2 or TAPE7 is used for output wavefunctions (input to RCN229 or HFMOD7, respectively), and disk file TAPE4 is used for temporary storage.

5. Output

The amount of printed output is controlled by the quantities ITPOW, IPTVU, IPTEB, NORBPT, IHF, and NPR punched on the control card, in ways described under B2. Provided NORBPT.GT.0, the first two and the last NORBPT radial wavefunctions are printed out. For each function the value is printed at every fifth mesh point in a two-column format (mesh points 1, 11, 21, 31, ... in the first column, and mesh points 6, 16, 26, 36 .... in the second column); the radius is printed only at mesh points 1, 11, 21, 31, ... If NORBPT.GT.5, continuum wavefunctions are printed in the above manner, and also at every mesh point in a ten-column format.

Interaction energies between two electrons, and one-electron and total binding energies (without corrections, and with relativistic and/or correlation corrections) are printed out on the final page; ALL VALUES ARE IN RYDBERGS.

The final line of each listing (except for timing information) contains the configuration identification, the number of parameters required for an energy-level calculation in the single-configuration approximation, and a list of the parameter values together with an integer code number:

0 = E_{av} = total binding energy (in rydbergs)

1 = $F^k(\ell_i\ell_i)$ (in units of 1000 cm^{-1})

2 = ζ_i (in units of 1000 cm^{-1})

3 = $F^k(\ell_i\ell_j)$ "

4 = $G^k(\ell_i\ell_j)$ "

The order of the parameters is the same as that required as input to program RCG.

Finally, if IHF = 0, then in the main program (statement 939) most of the important output information is written on TAPE2. The information includes a configuration serial number ("1" for the first configuration, and automatically made one greater for each succeeding configuration), the atomic number IZ and ionization stage ION (0 = neutral), and a number of wavefunctions which for the first configuration of given IZ and ION is determined by NORBPT, and which for later configurations is such as to delete any wavefunctions deleted from the first configuration. (The purpose here

is to delete most closed-shell wavefunctions, which are not needed by RCN229, so as to decrease required disk read/write and storage requirements in RCN229.

If IHF $\neq$ 0, then wavefunctions and other information required to start a HF calculation are written on TAPE7. If IHF > 1, the entire RCN calculation described above is carried out. If IHF = 1, most radial integrals are not computed--only the call of ZETA1 to calculate a relativistic energy correction for carryover to the HF program; if IREL > 0, the HF program calculates its own relativistic energy, and time can be saved by using TOLEND $\cong$ 0.05, so that the RCN SCF iteration is not carried to final convergence.

6. Continuum Functions

A continuum wavefunction is computed when the last orbital defined on the configuration card is singly occupied, has NLBCD8 = "99S", "99P", "99D", etc., and a positive eigenvalue (kinetic energy) EE8 (in rydbergs) has been punched in columns 75-80.

In columns 61-65 of the control card, a quantity EMX should be punched with a value equal (approximately) to the largest value of EE8 contained on any of the configuration cards. The action of EMX is to change the radial integration mesh R(I) which is set up: instead of $\Delta R \equiv R(I)-R(I-1)$ being doubled at mesh points 41, 81, 121, 161, ..., no further doubling is done after ΔR becomes $\geq \frac{1}{4\sqrt{EMX}}$. This insures that the mesh interval will not become so large but what there will still be about 10 mesh points within each half-wavelength of the continuum function, even at large R.

It is of course necessary that the dimension of the integration mesh be great enough, or that EMX be small enough, so that sufficiently large radii can be reached: the value of "F" printed via Format 97 of SCHEQ should not differ from unity by more than about 0.1. The required dimension is usually quite large: In place of the 641 points used for bound functions, 2201 points are used for continuum functions. Storage space was obtained by placing PNL and QQQ in RCN and PNL in RCN2 in large core memory. (Continuum wavefunctions cannot be handled by the HFMOD7 program, because the logarithmic radial mesh becomes much too coarse at large R.)

7. Relativistic Corrections[2]

Both RCN2 (the HX method) and HFMOD7 (the Hartree-Fock approach) provide the option of employing a method of approximating relativistic effects within the format of a non-relativistic calculation.[8] This is done by rewriting the non-relativistic one-electron differential equation for $P_{n_i \ell_i}$ as

$$\left\{ -\frac{d^2}{dr^2} + \frac{\ell_i(\ell_i+1)}{r^2} + V^i(r) - \frac{\alpha^2}{4}\left[\varepsilon^i - V^i(r)\right]^2 \right.$$

$$\left. - \delta_{\ell_i 0}\frac{\alpha^2}{4}\left[1 + \frac{\alpha^2}{4}\left(\varepsilon^i - V^i(r)\right)\right]^{-1}\left(\frac{dV^i}{dr}\right)\left[\frac{dP_i/dr}{P_i} - \frac{1}{r}\right]\right\} P_i(r) = \varepsilon^i P_i(r)$$

where α is the fine structure constant, r is in Bohr units and all energies are in rydbergs. $V^i(r)$ is an SCF central field potential such as that computed by the HX method. The spin-orbit term of the Pauli equation has been omitted to prevent the introduction of the quantum number j. Condon and Shortley[9] show that the term involving $[P_i'/P_i - 1/r]$ contributes only for s-states if the potential is purely Coulombic. This term is small for non-s-states in the HX or HF method and it has been neglected in this code. The factor

$$\left[1 + \frac{\alpha^2}{4}\left(\varepsilon^i - V^i(r)\right)\right]^{-1}$$

has been retained to avoid a $1/r^3$ singularity.

In RCN29, results obtained by solving the above equation with the HX method are labeled HXR while those obtained by the HF method in HFMOD7 are labeled HFR. Table I compares HX, HXR, HF and HFR calculations for one-electron binding energies of U I with Dirac-Fock and experimental results.[2] Table II makes a similar comparison for spin-orbit coupling constants. The details of the starting series for the solution to the above equation are given in the appendix.[2]

Table I One Electron Binding Energies, Center of Gravity, for U I $5f^3 6d 7s^2$ (ry)

	HF	HX	HXR	HFR	DF[a]	Exp[b]
1s	-7433	-7434	-8644	-8591	-8559	-8497
2s	-1302	-1302	-1630	-1619	-1612	-1599
2p	-1258	-1258	-1356	-1357	-1365	-1355
3s	-333.3	-333.8	-417.9	-415.0	-413.2	-407.8
3p	-311.9	-312.4	-341.1	-340.8	-342.5	-337.9
3d	-272.3	-272.8	-272.0	-271.6	-270.1	-266.3
4s	- 87.04	- 87.43	-110.2	-109.0	-108.6	-106.0
5s	- 20.12	- 20.34	- 25.71	- 25.28	- 25.15	- 23.8
6s	- 3.365	- 3.422	- 4.404	- 4.283	- 4.248	- 5.2
5f	- 1.269	- 1.356	- 0.740	- 0.663	- 0.704	---
6d	- 0.533	- .528	- 0.372	- 0.376	- 0.416	---
7s	- 0.333	- .338	- 0.414	- 0.403	- 0.398	---

a) J. B. Mann, private communication.
For $\ell \neq 0$, these values are $2j + 1$ weighted averages, except for 5f and 6d, where the $5f_-$ and $6d_-$ values are listed.

b) K. Siegbahn, et.al., ESCA; Atomic, Molecular & Solid-State Structure Studied by Means of Electron Spectroscopy (Almquist & Wiksells, Uppsala), 1967. Weighted averages are used as for DF.

Table II Spin Orbit Parameter Values $\zeta_{n\ell}$ (ry) for U I, $5f^3 6d 7s^2$

	HF[a]	HX[a]	HXR[a]	HFR[a]	DF[b]	Exp[c]
2p	132.8	133.5	200.0	199.1	187.8	185.3
3p	30.12	30.09	46.06	46.21	43.72	43.0
3d	4.927	4.943	5.333	5.327	5.293	5.17
4p	7.799	7.704	11.90	11.98	11.54	11.2
4d	1.166	1.151	1.246	1.264	1.288	1.23
4f	0.231	0.230	0.220	0.221	0.250	0.23
5p	1.761	1.839	2.813	2.701	2.763	3.2
5d	0.216	0.225	0.237	0.230	0.334	0.26
5f	0.0210	0.0206	0.0158	0.0165	---	---
6p	0.267	0.291	0.444	0.427	0.539	0.49
6d	0.0210	0.0161	0.0132	0.0138	---	---

a) Values computed via Blume-Watson method.

b) Values computed from $\zeta_{n\ell} \cong (E^{n\ell j+} - E^{n\ell j-}) \cdot 2/(2\ell + 1)$.

c) Ref b of Table I. Values computed as for DF.

C. PROGRAM HFMOD7 [D.C. Griffin and R.D. Cowan (November, 1974)]

1. Description

This is a Fortran IV program based on the well-known program of C. Froese-Fischer[10]. It has been extensively modified, to accept input from RCN29 and with the multi-configuration option removed, by D.C. Griffin [Thesis, Purdue University, (1970)]. Further modifications make possible inclusion of relativistic terms in the differential equation if IREL > 0 (Griffin, 1973), and incorporate a new method of stabilizing the SCF iteration[11].

Program Outline

The program consists of a main program and 42 subroutines, of which only a few of the more important ones will be described:

HFMOD7 is the main program, and does little except read a control card and call various subroutines.

DATA reads the input information which RCN29 has written on TAPE7 and sets up calculations accordingly.

SCF controls the self-consistent-field iteration for a given configuration (or for a given LS term of a given configuration). One iteration cycle consists of two parts: (1) A considerable number of calculations are made for different orbitals, in an order that depends on which orbital appears to be farthest from self consistency; (2) each orbital is recalculated once in the order from innermost to outermost subshell. [The iteration cycle in RCN29 consists of only this second phase and hence convergence requires many more cycles to reach self-consistency; the total number of orbital calculations is, however, approximately the same in RCN29 as in HFMOD7.]

SOLVE controls the iteration on the orbital eigenvalue to obtain a normalized radial function having positive initial slope and the correct number of nodes (= n-ℓ-1).

2. Input

The first card is blank if HFMOD7 is to be run. A 2 in column 1 will skip HFMOD7. (This feature was inserted when the three codes were overlayed as one and it is still there.)

Most of the input has already been discussed in the RCN29 writeup. Here we need describe only the HF control card (actually, two cards):

Columns	Format	Variable	Normal Value
1-10	E10.2	WFTOL	1.E-07
13-15	I3	NITER	15
38-40	F3.1	ACMIN	(default = 0.2)
43-45	I3	ISCACC	0
48-50	I3	ISENCD	0
53-55	I3	IGRANG	0
61-65	F5.0	TIMPM	(default = 280. sec)
68-70	I3	IPRINT	0
76-80	F5.3	HXFAC	0.95

Columns	Format	Variable	Normal Value
1-5	I5	NSLV	51
6-10	I5	ITERSL	0
11-15	F5.3	QNRNG	0.5
16-20	F5.3	FACHL	0.65
26-30	I5	IRCN	0

WFTOL is the maximum allowable absolute change in any wavefunction (at any mesh point) from one SCF cycle to the next before ending the iteration.

NITER is the maximum allowable number of SCF cycles. (If exceeded before WFTOL is satisfied, the calculation is ended, and no output written on TAPE2 for this case.)

ACMIN is the minimum allowed value of the acceleration factor (amount of trial function included in trial function for the next cycle).

If ISCACC = 0, the acceleration factor ACC(M) for each orbital will be automatically modified (between the limits ACMIN $\leq$ ACC $\leq$ 0.994) in an attempt to speed the SCF convergence. [Note that ACC in HFMOD7 is equal to 1-ALF of RCN29.]

ISENCD $\neq$ 0 deletes portion (1) of the calculation described under SCF.

IGRANG $\neq$ 0 excludes the off-diagonal Lagrangian multipliers ε_{ij}.

TIMPM is the maximum computational time allowed for RCN29 and HFMOD7 (in seconds) before exiting from HFMOD7 to load RCN229.

This feature was designed to allow one to get integrals from RCN229 between those configurations already completed before time runs out. Since one can either allow a long run time or restart the problem at LLL this really isn't needed. A large number like 1999 will avoid such an exit to RCN229 before the HFMOD7 calculation is complete.

If IPRINT $\neq$ 0, eigenvalue-iteration information is printed (for the outermost two orbitals only, if IPRINT = 1).

HXFAC determines the magnitude of the term that modifies the inhomogeneous differential equation to make it approximately homogeneous, to eliminate convergence difficulties.[11] If HXFAC > 0 and the atom is less than threefold ionized, this modification is used for the outermost two orbitals if they are singly occupied. (The pertinent code is in subroutine SOLVE following statement 4 and at statement 125.)

IRCN accomplishes the same thing as the variable IZHXBW of RCN29.

The remaining quantities on the second control card deal with calls of SOLVE1 and SLVIS1 (at the end of SCF, if ITERSL $\neq$ 0 and the above HXFAC is in effect for the outermost orbital) to make a diagnostic calculation of the shape of the normalization curve.
(Several variables not listed above are read from the control card, but are no longer used in the code.)

3. Input/Output Units

Control card input is via INP2; printed output via OUT2. Input from RCN29 is via TAPE7, and wavefunction output to RCN29 via TAPE2. Printed output is in somewhat different format from that of RCN29, but is basically the same in scope.

4. Miscellaneous

If no diagnostic norm curves are to be computed (ITERSL = 0) then subroutines SOLVE1 and SLVTST may be discarded. In any case, the code sections in SLVTST and HXPOT having to do with microfilm plotting (involving library subroutine PLOJB) should be deleted.

All plotting features have been commented out of the LLL version. Dummy subroutines were inserted where necessary. They all contain the statement DUMMY = 0 to facilitate finding them with TRIX.

This program was designed to handle only inhomogeneous differential equations, which excludes all configurations for which there are no exchange terms (namely, one-electron atoms, and s^2 configurations of helium-like ions.) An attempt has been made to overcome this limitation by a section of code at the beginning of subroutine HXPOT, but this feature has never been tested. A simple way of handling these configurations is to use RCN29 only (since HX gives exact HF results in these cases); if He-like configurations are to be passed on to RCN29, a simple procedure would be to let RCN29 write s^2 configurations directly to TAPE2 rather than passing them on to HF (and to delete the TAPE2 rewind at the beginning of HFM0D7).

D. PROGRAM RCN229

1. Description

This is a Fortran IV program for the CDC 7600 that reads information from the output TAPE2 of RCN29 or HFMOD7, calculates configuration-interaction radial Coulomb integrals R^k and electric dipole and quadrupole reduced matrix elements $P^{(k)}_{\ell\ell'} = \langle \ell \| r^{(k)} \| \ell' \rangle$ ($k = 1$ or 2), scales all energy-level-structure parameters F^k, G^k, R^k, ζ, and punches[12] a complete set of data input cards for making energy-level and spectrum calculations via program RCG Mod 5 or Mod 6. [Note: For HF wavefunctions, RCN229 output is useful mainly for center-of-gravity(not LS-term-dependent) calculations.]

Program Outline

The program consists of a main program RCN229 and eight subroutines.

RCN229 reads control cards and calls various subroutines accordingly.

OVER computes an overlap integral between two specified radial wavefunctions from the same or different configurations.

ZETA2 computes single-configuration or configuration-interaction spin-orbit parameters. The former are now computed by ZETA1 (of RCN), and the latter are usually so small as to be negligible; in practice this program is almost never used.

DIP computes electric dipole and quadrupole integrals $P^{(k)}_{\ell\ell'}$.

SLI2 computes configuration-interaction integrals $R^{(k)}$.

G5INP is a master program which calls SLI2 and DIP as appropriate, and prepares the input data decks for RCG.

S3J calculates 3-j symbols $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$.

S3JOSQ calculates values of

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix}^2$$

FCTRL calculates factorials of an argument A for use by S3J and S3JOSQ.

2. Input

Input consists of radial wavefunctions and other information written on TAPE2 by program RCN29 or by program HFMOD7 and of a G5INP card or one data card for each calculation to be made. The G5INP option is the one usually used. When the first three characters on the data card are "G5I", subroutines are not called directly but only via G5INP. Control is then transferred to subroutine G5INP, which de-codes the card according to the following format (statement 100):

Columns	Format	Variable	Normal Value
6-7	I2	NCMIN	0
8-10	I3	NCONF	# of configurations
11-20	2(I1,2I2)	NSCONF(3,2)	All zeros
21	I1	IABG	0
22	I1	IV	0
23-30	F8.5	EAV11	0.0
31-55	5F5.2	FACT(5)	1.00, 1.00, 1.00, 1.00, 1.00 or 0.85, 0.95, 0.85, 0.85, 0.85 or 0.67, 0.67, 0.67, 0.67, 0.67 etc.
56-59	I4	IMAG	0
60	I1	IQUAD	0
61-65	F5.0	ALF	0.0
66-70	5I1	IPRINT(5)	00000
73	I1	ICON	0
74	I1	ISLI	1 or 2
75	I1	IDIP	0

NCMIN is never used in practice. NCONF is the number of configurations computed.[13]

IV, IMAG, and IPRINT are quantities not used in RCN229, but simply transmitted unchanged to RCG. (If desired, they can be ignored here, and modified by hand repunching of the RCG control card.)

If IABG.GT.0, it is a signal that the effective-operator parameters α, β, γ, are to be included in the RCG calculation. Values of these parameters cannot easily be computed theoretically; hence, RCN229 simply leaves room at the proper places on the single-configuration parameter cards, where empirical parameter values can be inserted by hand [except that the number (ALF) punched in columns 61-65 of the control card will be punched for α].

EAV11 is the value desired for the center-of-gravity energy E_{av} of the first configuration (in units of 1000 cm^{-1}). It merely shifts the energy scale of all energy levels calculated by RCG.

FACT(5) are fudge factors to be applied to the theoretical values of the parameters $F^k(\ell_i,\ell_i)$, ζ_i, $F^k(\ell_i,\ell_j)$, $G^k(\ell_i\ell_j)$, $R^k(\ell_i\ell_j,\ell_i'\ell_j')$ respectively, to give scaled-down parameters for input to RCG. It is known empirically that computed energy-level intervals will agree better with experiment if the parameter values are 10-40% smaller than theoretical. Values of FACT of 0.85, 0.95, 0.85, 0.85, 0.50 are assumed by the code if zeroes are read in; for HX wavefunctions, values of 0.85, 0.95, 0.85, 0.85, 0.85 are about right for $\sim$ 10-fold ionized atoms with $Z \simeq 25$; values should probably be more like 0.75 for most neutral atoms; Cowan has previously estimated all five values = 2/3 as a good first guess for the actinides. The experience of Mark Fred[14] and K. Rajnak for U I is that when HFR is used, the factor is closer to .4 for the configuration interaction integrals, $\sim$ .9 for ζ_f, perhaps as low as .68 for ζ_d and $\sim$ 1.1 for ζ_p. The code requires a single factor for all ζ's.

IMAG = 1, 2, or 3 signifies that RCG is to calculate magnetic dipole spectra for configurations of the first, second, or both parities, respectively; IMAG is not used by RCN229, but is simply passed on to RCG.

If IQUAD = 1, 2, or 3, electric quadrupole spectra will be computed by RCG for the first, second, or both parities, and RCN229 computes and punches values of $P^{(2)}_{\ell\ell'}$ accordingly.

If ICON $\neq$ 0, the RCG-input control and configuration cards are not punched.

If ISLI
- = 0, print all SLI2 output
- = 1, omit restore and most printout
- = 2, omit all but final punched-card image (except that parameter values are unscaled)
- = 3, omit all printout

If IDIP
- $\geq$ 8, do not punch dipole cards
- $\geq$ 9, do not punch nor print

Other values of IDIP, in combination with ISLI > 4, provide some special-purpose options of no interest here.

If the G5INP option is not used, the data card is read as a string of 80 BCD characters at statement 200 of RCN229, and is then decoded according to a format appropriate to subroutines other than G5INP. The first three characters (columns 1-3 on the data card) specify the subroutine to be called, columns 11-20 contain the serial numbers of the two configurations to be used in the calculation, and columns 21-30 or 21-40 the radial wavefunctions to be selected. For example, if one wishes to calculate spin-orbit integrals $\zeta_{\ell\ell'}$ between members of the Rydberg series, the subroutine ZETA2 must be called. The input is then:

Column	
1-3	ZET
8-10	Atomic # (probably not used)
11-15	Serial number of first configuration
16-20	Serial number of second configuration
23-25 28-30 33-35 38-40	Orbitals to be used; in case of ZETA2, only the first two are involved: $n\ell$ and $n'\ell$ in 23-25 and 28-30 respectively.

A separate card is necessary for each pair of configurations. These spin-orbit integrals are not automatically calculated via the G5INP option so this is the only way to get them. For configurations involving $\zeta_{n\ell,n'\ell}$ between singly occupied shells $\zeta_{n\ell,n'\ell} \cong \sqrt{\zeta_{n\ell}\ \zeta_{n'\ell}}$ so this calculation is probably not necessary.[15] The G5INP option will give the required R^k integrals. If the G5INP option is not used a separate card calling the appropriate subroutine is necessary for each integral desired.

3. Calculational Procedure

In order for G5INP to properly prepare input decks for RCG, it is necessary that the pertinent configurations be arranged on TAPE2 in a specific order, and hence that the input configuration cards for RCN29 also be arranged in this order:

All configurations of given IZ and ION which are to be included in one RCG calculation must be arranged in succession. Usually the lowest-energy configuration is chosen as the first one; all configurations of this same parity follow, and then come all configurations of the opposite parity (if any). Within a given parity, all configurations which are members of a single Rydberg series (e.g., $3p^5 3d$, $3p^5 4d$, $3p^5 5d$,...) should be placed in succession. For any one configuration, the pertinent input data card for RCN29 should be punched so that all non-filled subshells (other than the outer, most-weakly-bound, singly-occupied subshell) are arranged in order of increasing n, and for given n in order of increasing ℓ. [If orbitals are not arranged this way, G5INP attempts to rearrange things but is not bug-proof.]

The calculational procedure is as follows:

(1) TAPE2 is searched to determine the number of configurations of each parity which have common values of IZ and ION, and which appear on the disk as successive configurations with no intervening configuration of different IZ nor ION.

(2) All subshells ℓ^w which are full ($w = 4\ell + 2$) in <u>all</u> configurations are ignored. The remaining subshells are arranged according to the requirements of RCG.

(3) The RCG control card is punched, containing the total number of subshells and the number of configurations of each parity [NSCONF(3,2)], among other things.

(4) The ℓ and w values are punched for each configuration.

(5) The single-configuration parameter values VPAR supplied by RCN29 or HFMOD7 (via TAPE2) are rearranged (if necessary--see parenthetical remark above), scaled by the factors FACT, and punched. [First parity only.]

(6) All possible configuration-interaction parameter values R^k are computed with the aid of calls to SLI2, and punched. [First parity.]

(7) If the value of IQUAD so indicates, values of the electric quadrupole reduced matrix element $P^{(2)}_{\ell\ell'}$ are computed (via DIP) and punched. [First parity.]

(8) If configurations of both parities are present, (5), (6) and (7) are repeated for the second parity, and then values of the electric dipole reduced matrix element $P^{(1)}_{\ell\ell'}$ are computed (via DIP) and punched.

(9) A card with "-99999999." in columns 21-30 is punched, to signal the end of an RCG calculation.

(10) TAPE2 is searched to see if there exist additional configurations of different IZ and/or ION. If so, items (2)-(9) are repeated for each such set of configurations.

(11) When TAPE2 has been exhausted (or the configuration with serial number NCMAX has been reached), a return is made to the main program, and a new input card read; a negative number in columns 8-10 results in an exit from the program.

4. Input/Output Units

Data input and printed output are via files INP3 and OUT3, respectively. In addition, PUNCHA is used for output punching, TAPE2 for input wavefunctions from RCN29 or HFMOD7. TAPE4 is defined on the program card of the current code but it is not actually needed. It is used in RCN29.

5. Output

Output includes file PUNCHA ready to be used directly as input to program RCG. (Such files may be used without change or they may be modified by hand in various obvious ways. For example, the print options in columns 66-70 may be modified; if one wishes to add or delete calculation of magnetic dipole spectra, this may be done simply by changing column 49 appropriately; if configurations of both parity were included in the RCN29 and RCN229 run but one wishes to include only the first parity in the RCG calculation, it is only necessary to insert zeroes in columns 16-20, and delete all configuration-definition and parameter-value cards for the second parity, and remove all electric dipole cards, etc.).

All information in PUNCHA is also printed via the output file OUT3, as is some additional detail regarding the calculation of the R^k and the $p^{(k)}_{\ell\ell'}$.

6. Autoionization Calculations

In certain cases, a calculation is also made of the radial contributions to Fano's Γ and q for autoionized states[16]. The code involved is that in G5INP, statements 600-660, and output is printed listings only. This calculation is made if:

(a) there is only one configuration of the first parity,
(b) there are at least three configurations[17] of the second parity,
(c) the outermost orbital of the last configuration (number NCX) is a continuum function ($\varepsilon > 0$), and
(d) the outermost subshell is singly occupied for all configurations of the second parity with the possible exception of the first one (configuration no. NCN).

Under these conditions it is assumed that:

(1) configuration NCN (the first configuration of the second parity) involves some levels lying above the first ionization limit, which can autoionize by configuration interaction with continuum states;

(2) all configurations following NCN are members of one or more Rydberg series, of which at least the last configuration (NCX) is a member of this series which lies in the continuum; and,

(3) that dipole transitions are possible from the lone configuration of first parity to all Rydberg-series configurations (and perhaps also to the autoionized configuration). A simple example is:

Al I	$3s^2 3p$	(odd parity)
"	$3s3p^2$	(even parity)
"	$3s^2 3d$	"
"	$3s^2 4d$	"
"	$3s^2 \varepsilon_1 d$	"
"	$3s^3 \varepsilon_2 d$	"
"	$3s^2 \varepsilon_3 d$	"

Absorption transitions from $3s^2 3p$ are possible to $3s3p^2$ and to all $3s^2$ nd and $3s^2 \varepsilon d$; all oscillator strengths are grossly modified as a result of configuration mixing of the $3s3p^2$ with each $3s^2 d$. Fano's Γ and q are measures of the width and shape of the autoionized discrete lines

$$3s^2 3p\ {}^2P \rightarrow 3s3p^2\ {}^2D.$$

The full width of an autoionized line at half-maximum (in the limit of large q or of q = 0) is

$$\Gamma = 2\pi < \phi_{LS} | H | \psi_E >^2 \quad , \qquad (8)$$

where ϕ is a basis function for one of the autoionized states and ψ_E is a basis function for a state of the continuum having energy E. For pure LS coupling conditions and Coulomb interactions,

$$\Gamma = 2\pi \langle \phi_{LS} | H | \psi_E \rangle^2$$

$$= 2\pi \left[\sum_k r_k R^k \right]^2 , \qquad (9)$$

where R^k is the appropriate radial integral (computed by SLI2) and r_k is the corresponding angular factor (computed later by RCG). Assuming there is only one value of k, or that one term in the sum is dominant and dropping all smaller terms,

$$\Gamma = 2\pi \, (r_k)^2 \, (R^k)^2 \qquad (10)$$

The quantities tabulated in the computer listings are the eigenvalue EE or ε of the valence electron; if EE < 0, the effective quantum number

$$n^* = \frac{Z^*}{(-EE)^{1/2}} , \qquad (Z^* = IØN + 1) \; ; \qquad (11)$$

a weighting factor

$$WT = \left[\frac{n^{*3}}{2Z^{*2}} \right]^{1/2} = \left[\frac{dE}{dn^*} \right]^{-1/2} \qquad (12)$$

equal to the inverse square root of the energy interval per bound configuration;

$$\text{"RKSC"} \equiv \begin{cases} WT.R^k & \text{(bound)} \\ R^k & \text{(free)} \end{cases} \text{ (rydbergs)}^{1/2}, \qquad (13)$$

where R^k is a configuration-interaction integral between configuration NCN and one of the Rydberg-series configurations; and

$$\text{"GAMMA/RKSQ"} \equiv \Gamma/(r_k)^2 = 2\pi \, (RKSC^2)_{max} \qquad (14)$$

Typically, values of r_k are like ± 0.5, so that values of Γ are like 1/4 of the numbers tabulated.

The value of q for an absorption transition from an initial state i to the autoionized discrete state ($\cong$ the unperturbed discrete state Φ) is

$$q = \frac{\text{(dipole mx. elem. to discrete state)}}{\pi\text{(dipole elem. to cont.) (interaction elem.)}}$$

$$= \frac{\langle i|r|\Phi\rangle}{\pi \langle i|r|\psi_E\rangle \langle\psi_E|H|\psi\rangle} \qquad (15)$$

$$\cong \frac{\langle i|r|\phi\rangle}{\pi \langle i|r|\psi_E\rangle \langle \psi_E|H|\phi\rangle}$$

For pure LS coupling, and again neglecting all but the largest term of the Coulomb-interaction matrix element,

$$q \cong \frac{\langle i_{LSJ}|r|\phi_{L'S'J'}\rangle}{\pi \langle i_{LSJ}|r|\psi_{EL'S'J'}\rangle \langle \psi_{EL'S'}|H|\phi_{L'S'}\rangle}$$

$$= \frac{\langle n\ell\|r\|n'\ell'\rangle \langle i_{LSJ}|r|\phi_{L'S'J'}\rangle_{ang}}{\pi \langle n''\ell''\|r\|n'''\ell'''\rangle \langle i_{LSJ}|r|\psi_{EL'S'J'}\rangle_{ang} r_k (R^k)_{max}} \qquad (16)$$

The quantities tabulated are

$$\text{"PDIPSC"} = \begin{cases} WT\cdot\langle n\ell\|r\|n'\ell'\rangle & \text{(bound)} \\ \langle n''\ell''\|r\|n'''\ell'''\rangle & \text{(free)} \end{cases}$$

$$= \text{radial dipole integrals (units of } e^2a_o^2/ryd^{1/2}) \qquad (17)$$

and

$$\text{"Q*RK"} \equiv \frac{q\, r_k \langle i_{LSJ}|r|\psi_{E\,L'S'J'}\rangle_{ang}}{\langle i_{LSJ}|r|\phi_{L'S'J'}\rangle_{ang}}$$

$$= \frac{\langle n\ell\|r\|n'\ell'\rangle}{\pi \langle n''\ell''\|r\|n'''\ell'''\rangle R^k} \quad \text{(dimensionless)}. \qquad (18)$$

The quantity r_k is again like ±1/2, so that inclusion of this factor would make q perhaps a factor 2 greater in magnitude than the number "Q*RK" tabulated in the computer listing. The values of $\langle m | r | m \rangle_{ang}$ can be anything from very small to something like $\sqrt{2}$; the ratio of the two values can thus be most any magnitude and either sign. However, for a strong discrete line and a strong continuum, the magnitude of the ratio probably would lie somewhere between 1/2 and 2, so that the value of q would be within a factor 2 or so of the computer output value.

E. Storage

1. RCN29

Storage requirements for an integration mesh of 2201 points and up to 25 orbitals is, on the CDC 7600, about as follows (number of 60-bit words, octal):

Fortran (including local variables and system/library)	102 K
common	44.5 K
LCM storage	160 K
I/O buffers	6 K
Total LCM image size	334.5 K

2. HFMOD7

Storage requirements for an integration mesh of 200 points (561 in HXWRTP) and up to 20 orbitals is, on the CDC 7600 (60-bit words, octal):

Fortran Code (local variables, system/library)	76 K
Common (Storage)	33.3 K
I/O Buffer	6 K
Total LCM Image	137.3 K

3. RCN229

Storage requirements for up to 50 configurations, eight orbitals per configuration (so far as the information written on TAPE2 is concerned), and 2201 mesh points for the CDC 7600 is about as follows (number of 60- bit words, octal):

Fortran Code (local variables; system/library)	56 K
Common (storage)	70 K
LCM (storage)	42.4 K
I/O Buffers	6 K
Total LCM Image	216.4 K

LASL storage is a few K less in all cases since I/O buffers are not in SCM at LASL.

F. Conversion to Other Computers

Conversion problems to other computers having a Fortran IV compiler should be minor but because the LLL time-sharing requires file-manipulation statements not required by other systems the LASL version of the code is probably an easier one to convert. The ENCODE/DECODE changes discussed below have been made in the LLL code.

In RCN29 (main program), there are ENCODE and DECODE statements at $\sim$ 223 and $\sim$ 237. These are concerned with memory-to-memory conversion of two words with format (I2, A1) to three characters of BCD information [stored in NLBCD(M)], or vice versa. With compilers not having ENCODE/DECODE statements it may be necessary to accomplish the conversion in each case via formated Write and Read statements involving tape or disk.

The SCF iteration must be carried out to very tight tolerance if one wishes to compute meaningful excitation energies by differencing values of E_{av} for two configurations, because many significant figures are lost in this difference ($\sim$ 6 or 7 significant figures for an actinide). This means that most calculations must be done to 9 or 10 significant figures. On machines using 60- or 64-bit basic floating-point word lengths, this is no problem. With the IBM 360 32-bit words (7 significant figures?), it may be necessary to define as double precision most variables, including RSATOM, QQ, RSQ, R, RU, RUEE, RUEXCH, PNL, EE, EI, EVEL, EDAR, V, EKIN, EEN, UEE, UEX, RSCORE, RSVALE, PNLO, XI, XJ, T, Q, RRYD, VPAR, F1, F2, XA, XB, EMN, RKP1, AO, A, B, ET2, ET3CR, and probably many others.

Conversion problems for RCN229 should be minor except for ENCODE/DECODE statements. These include format 19 (which was chosen for the 10-character word length of the CDC) and the following statement in RCN229 main,

and statements 100 and ∿ 178 of G5INP. No double-precision calculations should be necessary.

An end-of-file test on unit 2 at statement 111 of G5INP may have to be altered for non-CDC compilers.

G. Comments, Discussion and Warnings

1. Output

a. Continuum output from RCN229

The output from RCN229 gives R^k integrals involving a continuum function in both "ry" and "cm^{-1}". The units are really $ry^{1/2}$ and the conversion to cm^{-1} is made as if they were ry. Divide results in "cm^{-1}" by $\sqrt{R_\infty}$. The spectrum code RCG is designed to take output from RCN229 and make the appropriate correction. If this code is corrected, RCG must be changed also.

b. RCN2/SLI2 Output for Configuration Interactions of the General Form

$$\text{(Unprimed conf.)} \quad \cdots \ell_j^{w_j} \cdots \ell_x^{w_{x+1}} \cdots \ell_y^{w_y} \cdots \tag{1}$$

$$\text{(Primed conf.)} \quad \cdots \ell_j^{w_j} \cdots \ell_x^{w_x} \cdots \ell_y^{w_{y+1}} \cdots \tag{2}$$

with $\ell_x = \ell_y$, where $\ell_j^{w_j}$ is any unfilled subshell (lying either before the x subshell, as shown, between x and y, or following y).

In this case, configuration interaction Hamiltonian matrix elements

$$\langle \psi \mid H \mid \psi' \rangle \tag{3}$$

include not only the usual electron-electron Coulomb contributions

$$\left\langle \psi \mid \frac{2}{r_{ij}} \mid \psi' \right\rangle , \tag{4}$$

but also contributions from the one-electron terms of the Hamiltonian. The spin-orbit operator leads to contributions involving the spin-orbit CI radial parameter

$$\zeta_{x,y'} = \frac{\alpha^2}{2} \int_0^\infty \left(\frac{1}{r}\frac{dV}{dr}\right) P_x P_{y'} dr;$$

The angular coefficients will not be discussed here.

A lengthy derivation shows that the effect of the kinetic-energy and the electron-nuclear contributions to (3) is (for HF radial functions) to replace the ordinary R^o_d integral(s) in (4) by linear combinations of radial integrals similar to the ordinary R^k_d and R^k_e, except employing one radial function from (1) and three functions from (2) or vice versa, instead of two radial functions from each configuration. Consequently, for interactions of this type, SLI2 computes (and prints) four sets of radial integrals:

(A) $R^k_d(ab,c'd')$, $R^k_e(ab,c'd') \equiv R^k_d(ab,d'c')$,

(B) $R^k_d(ab, ad')$, $R^k_e(ab,ad')$,

(C) $R^k_d(c'b,c'd')$, $R^k_e(c'b,c'd')$,

(D) average of (B) and (C),

where either (ab,c'd') = (xx,x'y') or (yx,y'y') or (jx,j'y'). [The set (A) is the normal set; the sets (B) - (D) are these modified integrals].

The replacement for the normal R^o_d, made automatically by SLI2 in the output written on file PUNCHA, is as follows ($\ell=\ell_x=\ell_y$):

(I) In place of $R^o_d(xx,x'y')$,

$$\frac{1}{2}\left(\frac{2\ell+1}{4\ell+1}\right) \sum_{k>o} \begin{pmatrix} \ell & k & \ell \\ o & o & o \end{pmatrix}^2 R^k_d(xx,xy') + \frac{1}{4} \sum_k \begin{pmatrix} \ell & k & \ell \\ o & o & o \end{pmatrix}^2 R^k_e(x'x,x'y')$$

(II) In place of $R^o_d(yx,y'y')$,

$$\frac{1}{2}\left(\frac{2\ell+1}{4\ell+1}\right) \sum_{k>o} \begin{pmatrix} \ell & k & \ell \\ o & o & o \end{pmatrix}^2 R^k_d(y'x,y'y') + \frac{1}{4} \sum_k \begin{pmatrix} \ell & k & \ell \\ o & o & o \end{pmatrix}^2 R^k_e(yx,yy')$$

(III) In place of $R_d^o(jx,j'y')$,

$$\frac{1}{2}\sum_k \begin{pmatrix} \ell & j & k \\ o & o & o \end{pmatrix}^2 \left[\frac{R_e^k(jx,jy') + R_e^k(j'x,j'y')}{2}\right].$$

In the Rydberg-series case ($w_x = w_y = 0$), $P_j \cong P_{j'}$ so that this last expression is approximately

$$\frac{1}{2}\sum_k \begin{pmatrix} \ell & j & k \\ o & o & o \end{pmatrix}^2 R_e^k(jx,j'y');$$

in this case, SLI2 replaces $R_d^o(jx,j'y')$ by zero, and RCG (Mod 5 or 6 or 7) adds

$$\frac{w_j}{2}\begin{pmatrix} \ell & j & k \\ o & o & o \end{pmatrix}^2$$

(w_j is the occupation number of the j^{th} subshell to the angular coefficient calculated from (4) for R_e^k. [This makes the square CI block of the Hamiltonian matrix identical with each single-configuration block, except with F^k replaced by R_d^k, G^k replaced by R_e^k, and no analog of E_{av}].

c. Orthogonality integrals from HFR are $\sim .06$ for $\langle 1s|2s\rangle$ for U I but much smaller in HF. The code calculates the total binding energy E_{av} assuming these orthogonality integrals to be exactly zero.

d. Energies

HFMOD7 prints out 6 total energies when the relativistic option is not used.

ET = total nonrelativistic energy
ETR = total energy with relativistic correction
ETCO = total energy with correlation (method 1)
ETRCO = total energy with relativistic and correlation corrections
ETCN = total energy with correlation (method 2)
ETRCN = ETCN with addition of relativistic correction.

Method 1 is that described in Ref. 6, a modified free-electron-gas model, and method 2 is described in Appendix (I2).

e. Convergence in RCN29 Calculations

If TOLEND is too small a diagnostic print will result on the last 4 iteration cycles. (See pp 43a,b). The last line of such a print contains the iteration number (35 in eg.), timing information and DELTA, the change in the potential from the previous iteration cycle. If this is .000000 in all cases convergence is at least that good and probably sufficient for anything except differencing total binding energies.

This problem occurs with TOLEND = 5×10^{-8} for HXR runs on some, but not all, actinide configurations. Since the starting potential is derived from that of the previous configuration computed it sometimes even depends on the order in which the configurations are computed. TOLEND and THRESH can be increased by a factor of 10 or the number of SCF iterations can be increased. The increased output when the diagnostic print occurs may overflow the output file.

A 3 in col. 1 of the RCN29 Control Card will print the line containing DELTA for every iteration cycle so one can tell if oscillations are occuring. For some actinide configurations, particularly $5f^5 7s$ of U I, oscillations are large and DELTA is still > 1 instead of 10^{-7} after 30 iteration cycles. In this case better convergence can be obtained by narrowing the range of allowed changes in the potential from one cycle to the next. This is accomplished by punching values of ALFMIN and ALFMAX (col. 31 & 32) on the configuration card instead of using the default values. (See statement 213 of RCN29 MAIN). Experimentation shows that the best results for f^5s are obtained with ALFMIN = 9 and ALFMAX = 5. DELTA is still .000006 on iteration cycle 34 but oscillations have been eliminated. An increase in the number of iterations (MAXIT) on the control card should achieve convergence. For most purposes $\Delta = 6 \times 10^{-6}$ is sufficient.

There were several other actinide configurations where DELTA was $\sim 5 \times 10^{-6}$ on the 34th iteration cycle when the default values of ALFMIN and ALFMAX were used. Using values of 9 and 5 resulted in convergence (TOLEND = 5×10^{-7}) after only 30 iteration cycles.

Using IREL = 1 instead of IREL = 2 will speed convergence. The results are not the same in the 2 cases, however. For $5f^{10} 7p$ of CF II the difference is $\sim$ 7% in AZ for the 1s orbital, .1% in $F^2(f,f)$ and .3% in ζ_{5f}. IREL = 1 results in the larger values. Because of the larger AZ, IREL = 1 might be preferable but further comparisons are necessary for a clear cut choice. Both cases are approximations to Dirac-Fock results and any calculated values will require some kind of scaling to get agreement with empirical results.

```
135     RU,RUEE,RUEXCH
 -192.000000 -179.337026 -168.907386 -151.804158 -137.927864 -116.197034  -99.739199  -76.194956  -60.140748  -40.938821
  -29.783122  -17.183693  -10.909213   -5.449101   -3.319715   -1.771264   -1.236898    -.715218    -.428995    -.153317

     .000000   13.591042   24.226628   41.844177   55.859687   77.988443   94.663906  118.290355  134.731908  153.588977
  164.751227  177.319951  183.397751  188.566296  190.287677  191.405056  191.780255  191.970362  191.995834  191.999938

          .0    -.928067   -1.134014   -1.648334   -1.787551   -2.185477   -2.403105   -2.485311   -2.872656   -2.527798
   -2.534349   -2.503644   -2.306964   -2.015397   -1.607392   -1.176320   -1.017153    -.685580    -.424829    -.153255


035     1S      1.000C052   -9609.466143   R*VSELF,  R*VTOTAL,  R*VEFF,   (IF DIAGNOSTIC PRINT OUT-R*VS, R*VT, CALC. WVFN
, MOD. WVFN)
      .0C0000   1.564281    1.917790    1.997417    1.999934    2.000010    2.000010    2.000010    2.000010    2.000010
     2.0C0010   2.000010    2.000010    2.000010    2.000010    2.000010    2.000010    2.000010    2.000010    2.000010

*9936.000000 -180.068191 -170.138531 -153.203482 -139.297512 -117.428138 -100.893505  -77.318333  -61.128410  -42.040465
  -30.877876  -18.279279  -12.057888   -6.660078   -4.597966   -3.047477   -2.492489   -2.085453   -2.011051   -2.000152

          .0   7.553505    4.912757    1.277973     .272637     .010167     .000340     .000000     .000000     .000000
      .C0000        .0          .0          .0          .0          .0          .0          .0          .0          .0

          .0   7.553505    4.912757    1.277973     .272637     .010167     .000340     .000000     .000000     .000000
      .C0000        .0          .0          .0          .0          .0          .0          .0          .0          .0


035     2S      1.0000009   -1828.449315   R*VSELF,  R*VTOTAL,  R*VEFF,   (IF DIAGNOSTIC PRINT OUT-R*VS, R*VT, CALC. WVFN
, MOD. WVFN)
      .000000   .475145     .855583    1.507119    1.838882    1.988760    1.999407    2.000001    2.000002    2.000002
     2.000002   2.000002    2.000002    2.000002    2.000002    2.000002    2.000002    2.000002    2.000002    2.000002

*9936.000000 -179.460096 -169.347808 -152.522054 -138.903670 -117.373597 -100.890724  -77.321681  -61.131854  -42.047247
  -30.885934  -18.293222  -12.079502   -6.700512   -4.670981   -3.163500   -2.605914   -2.128828   -2.017583   -2.000223

          .0   1.716763   -1.188121   -4.330082   -4.052753   -1.682508    -.492002    -.029002    -.001392    -.000003
     -.000000    -.000000    -.000000          .0          .0          .0          .0          .0          .0          .0

          .0   1.716763   -1.188121   -4.330082   -4.052753   -1.682508    -.492002    -.029002    -.001392    -.000003
     -.000000    -.000000    -.000000          .0          .0          .0          .0          .0          .0          .0


035     2P      1.0000000   -1502.504695   R*VSELF,  R*VTOTAL,  R*VEFF,   (IF DIAGNOSTIC PRINT OUT-R*VS, R*VT, CALC. WVFN
, MOD. WVFN)
      .000000   .485373     .934830    1.565812    1.852325    1.987422    1.999139    1.999997    2.000000    2.000000
     2.000000   2.000000    2.000000    2.000000    2.000000    2.000000    2.000000    2.000000    2.000000    2.000000
```

```
*9936.000000 -179.017701 -168.521666 -151.249993 -137.336385 -115.489134  -98.977887  -75.449880  -59.305148  -40.311754
  -29.240774  -16.821391  -10.775613   -5.726560   -3.965150   -2.695787   -2.343880   -2.124103   -2.031195   -2.000582

          .0     .023895     -.026735     -.055098     -.002961      .081549      .038111     -.106263     -.068169      .145096
      .112482     -.195241     -.243629      .103703      .409580      .556278      .435135      .168738      .050931      .003445

          .0     .023895     -.026736     -.055098     -.002961      .081549      .038111     -.106263     -.068169      .145096
      .112482     -.195241     -.243629      .103703      .409580      .556278      .435135      .168738      .050931      .003445

 35 26.31   -.000000 226 -1  28   .68 1.00  .67  .67  .44  .44  .44  .30  .30  .30  .20  .30  .30  .30  .30  .30  .44  .3
0
```

DELTA

iteration number

The scale factors will just be different in the two cases. It is important to use the same value of IREL for comparison of different configurations, however.

f. AZ Values from HFR

When the relativistic correction is added to the HF equations P no longer goes like $r^{\ell+1}$ near the origin. Consequently, the initial slope AZ is not a measure of the electron density at the nucleus and the numbers in that column are meaningless. HXR solutions have been fit by a polynomial and in this case AZ is the coefficient of $r^{\ell+1}$.

2. Miscellaneous Comments

a. As written, continuum functions can be computed only in the HX code (RCN29). There's sufficient uncertainty in the continuum functions that doing HF on the bound states of the configuration is probably not worthwhile, although it could be done with relatively minor modifications.

b. It's best to keep the order of the shells on the configuration cards in order of increasing n and within a given n, increasing ℓ. When several configurations are being computed, empty shells need not be punched even though they occur in only part of the configurations, i.e., one can use

5F3 6D1 7S1 7P1

and 5F4 7S2

instead of 5F4 6D0 7S2 7P0

H. References

1. R. D. Cowan, "Programs RCN MOD29/HFMOD7/RCN2 MOD29", LASL, Nov. 1974, Unpublished.
2. R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am., in press.
3. M. Blume & R.E. Watson, Proc. Roy Soc. London, A270, 127, (1962).
4. RCG is a code written by Cowan to compute angular matrix elements and, given the appropriate radial integrals, diagonalize the energy matrices and compute the spectrum. RCGMOD5 is available at LLL as GFIVE and RCGMOD6 is available as RCGM6.

5. Herman and Skillman, Atomic Structure Calculations, Prentice Hall, 1963.
6. R. D. Cowan, "Atomic Self-Consistant-Field Calculations using Statistical Approximations for Exchange & Correlation," Phys. Rev. 163 54, 1967.
7. Lindgren & Rosen, Int. J. Quant. Chem. S5, 411 (1971); Phys. Scrip. 6, 109 (1972).
8. Bethe & Salpeter, Quantum Mechanics of One-and Two-Electron Atoms, Springer-Verlag, Berlin, 1957, Sect. 13, especially eq. (13.6) and paragraph following (13.11).
9. E. U. Condon & G. H. Shortley, The Theory of Atomic Spectra (Cambridge Univ. Press, New York, 1970) p.130.
10. C. Frose-Fischer, Can. J. Phys. 41, 1895 (1963); ANL-7404 (1968); Comp. Phys. Commun. 1, 151 (1969).
11. R. D. Cowan & J. B. Mann, Jr., J. Comput. Phys., 16, 160, (1974).
12. All numbers hereafter referred to as punched go into a file called PUNCHA which can then be punched or stored as desired.
13. This was added at LLL because an end of file was sometimes not written on TAPE2. The default is to 50 if NCONF = 0. If the EOF gets written the code will run properly with the default but putting in NCONF will ensure running even if the EOF is missing.
14. Mark Fred, ANL, private Communication.
15. W. C. Martin, Jack Sugar & Jack L. Tech, Phys. Rev. A6, 2022 (1972).
16. U. Fano, Phys. Rev. 124, 1866 (1961).
17. The version obtained from LASL required 4 configurations but this has been changed to 3.
18. E. Clementi, J. Chem. Phys. 38, 2248 (1963); 39, 175 (1963); 42, 2783 (1965).

I. Appendix:

1. Small-r Solution for the HXR Method

In trying to find a series solution of the differential equation for $P_j(r)$, we run into difficulty with the Darwin factor

$$\delta_{\ell 0}\,\frac{\alpha^2/4}{1 + (\varepsilon - V)\alpha^2/4} \cong \frac{r}{2Z}\left[\frac{\delta_{\ell 0}}{1 + (\varepsilon + 4/\alpha^2)r/2Z}\right] , \tag{1}$$

where we have taken $V = -2Z/r$ for small r. The quantity $\varepsilon + 4/\alpha^2 \geq -Z^2 + 274^2 \cong 274^2$ is so large that a series expansion of the factor in brackets in (1) is invalid at r_2 (on an integration mesh $r_j = jh$) for any practical value of h; for example, on a mesh commonly used for non-relativistic problems,[5] $h = 0.0022\, Z^{-1/3}$, the limitation $2r_2/\alpha^2 Z << 1$ requires $Z >> (0.0022 \cdot 274^2)^{3/4} = 46$. In order to be able to handle all values of Z (including Z as small as unity), we try using a fixed value

$$d \equiv d_{jh} = \frac{\delta_{\ell 0}}{1 + (\varepsilon + 4/\alpha^2)jh/2Z} . \tag{2}$$

Because of this approximation, there is no point in carrying series expansions beyond a couple of terms and so we assume

$$P \cong r^{\lambda+1} + a_1 r^{\lambda+2} \tag{3}$$

for the (unnormalized) radial function. Differentiating this expression we find

$$\frac{P'}{P} - \frac{1}{r} \cong \frac{1}{r}\,(\lambda + a_1 r) .$$

In the approximation $V \cong -2Z/r$, the Darwin term is

$$-\frac{r}{2Z}\,d\left(\frac{2Z}{r^2}\right)\frac{1}{r}\,(\lambda + a_1 r) = -\frac{d}{r^2}\,(\lambda + a_1 r) ,$$

and the differential equation for $P_j(r)$ becomes to second order

$$P'' = (\lambda + 1)\lambda r^{\lambda-1} + a_1(\lambda + 2)(\lambda + 1)r^{\lambda}$$
$$= \left[\frac{\ell(\ell + 1) - \alpha^2 Z^2 - d\lambda}{r^2} - \frac{2Z + \alpha^2 \varepsilon Z + da_1}{r}\right]\left[r^{\lambda+1} + a_1 r^{\lambda+2}\right] .$$

Equating coefficients of $r^{\lambda-1}$ gives

$$(\lambda + 1)\lambda = \ell(\ell + 1) - \alpha^2 Z - d\lambda$$

or

$$\lambda + 1 = \frac{1 - d}{2} + \left[\ell(\ell + 1) + \left(\frac{1 + d}{2}\right)^2 - \alpha^2 Z^2\right]^{1/2} , \qquad (4)$$

and equating coefficients of r^{λ} gives

$$a_1 = - \frac{(2 + \alpha^2\varepsilon)Z}{(\lambda + 2 + d)(\lambda + 1) - \ell(\ell + 1) + \alpha^2 Z^2} . \qquad (5)$$

In the small-Z limit, $d \cong 0$ and $|\alpha^2\varepsilon| \leq \alpha^2 Z^2 \cong 0$, and these expressions reduce to the usual non-relativistic results

$$\lambda + 1 = \ell + 1 \quad , \quad a_1 = - \frac{2Z}{2(\ell + 1)} \qquad (6)$$

On the other hand, for large Z and $\ell = 0$ (s electrons), $d \cong 1$ and (4) becomes

$$\lambda + 1 = [1 - \alpha^2 Z^2]^{1/2} , \qquad (7)$$

showing firstly that $\lambda < 0$ $(= \ell)$ and secondly that solutions are possible only for $Z \leq \alpha^{-1} \cong 137$--which is however not a serious restriction for our purposes.

2. Correlation Correction - Method 2

Electrons in atoms cannot move around as readily as free electrons because they are localized by their attraction to the nucleus; we would therefore expect correlation energies in atoms to be smaller in magnitude than those in a free-electron gas, especially at high densities. This is born out by the empirical observation [18] that in atoms

$$\bar{e}_c \equiv \frac{E_{av}^{exp} - (E_{av}^{HF} + E_r)}{N} \cong 0.08 \text{ Ryd/elec}, \qquad (8)$$

Instead of using the method of Reference 6, we here compute E_c as though we were adding electrons to the atom one at a time (in the order from most-strongly bound, 1s, to least-strongly bound), and compute the correlation energy of the i^{th} electron not from the average free-electron value $\bar{e}_c$, but from the incremental value e_c upon adding one more electron (Method 2).

The incremental correlation energy per electron is

$$e_c = \frac{d(N\bar{e}_c)}{dN} = \left[\frac{d(\rho\bar{e}_c)}{d\rho}\right]_{vol} = \frac{d(r_s^{-3}\bar{e}_c)}{d(r_s^{-3})}$$

$$= -\frac{r_s^4}{3}\frac{d(r_s^{-3}\bar{e}_c)}{dr_s}, \tag{9}$$

where r_s is the radius of a sphere whose volume is the average volume per electron:

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

In the low-density limit this gives

$$e_c = -\frac{r_s^4}{3}\left(\frac{-1}{1.142}\right)\frac{dr_s^{-4}}{dr_s} = \frac{4}{3}\left(\frac{-1}{1.142 r_s}\right) = \frac{4}{3}\bar{e}_c, \tag{10}$$

and in the high-density limit $\bar{e}_c \cong$ const we have

$$e_c = \bar{e}_c \tag{11}$$

As a semi-empirical interpolation formula between (10) and the high-density limit (11) + (8), we assume

$$e_c(r_s) = -\left[4(r_s + 9)^{1/2} + \frac{3}{4}\left(1.142\right)r_s\right]^{-1}. \tag{12}$$

We then take the correlation correction to the total binding energy E_{av} to be

$$E_c = \sum_{i=2}^{N}\int_0^\infty P_i^2(r)\, e_c^{\,i}(r_s)\, dr, \tag{13}$$

where $e_c^{\,i}$ is given by (12), and r_s is in turn given as a function of r by

$$r_s = \left[\frac{4\pi}{3}\sum_{j=1}^{i-1}\rho_j(r)\right]^{-1/3} = \left[\frac{1}{3r^2}\sum_{j=1}^{i-1}P_j^2(r)\right]^{-1/3}. \tag{14}$$

It may be noted that this final method (12) - (14) of computing E_c is more laborious than the method of Reference 6 because an integral has to be evaluated for N-1 electrons rather than only q subshells. However, the computing time required to obtain E_c is still small compared with the time required to obtain the SCF radial wavefunctions, and the gain in accuracy of computed energies is great enough to make the effort worthwhile.

II. Running the Codes

A. Availability and Compilation

The program segments, sample input and sample output are available in private files in photostore in the following directory sequences.

.049625:KR:COWAN:HF:CODE:RCN29S
.049625:KR:COWAN:HF:CODE:HFMOD7S
.049625:KR:COWAN:HF:CODE:RCN229S
.049625:KR:COWAN:HF:CODE:RCN

.049625:KR:COWAN:HF:SAMPLEIN:FENB
.049625:KR:COWAN:HF:SAMPLEIN:CONT

.049625:KR:COWAN:HF:SAMPLEOUT:FENBOUT
.049625:KR:COWAN:HF:SAMPLEOUT:CONTOUT

The first group contains the source codes for the three programs. Compilation produces the controlees. These are put into the "LIX" produced library file RCN which is the code to be run under ORDER. The SAMPLEIN and SAMPLEOUT directories contain sample input and output respectively.

The source codes are compiled and loaded via "PUTT". No system libraries other than the standard CLIB are needed. A sample execute line for compilation is

PUTT RCN29S LIST S #1 #2 / t v

where "LIST" will contain the compiler listing. Suitable choices for t and v are .4 and .5 respectively. "S" indicates the compile mode. The controlee RCN29 will be produced. Appropriate values for #1 and # 2 for the current versions of the three codes are

	#1	#2
RCN29S	112000	155000
HFMOD7S	106000	140000
RCN229S	72000	155000

B. Running the Codes

1. Running Separately

The codes may be run individually, constrained to the sequences in Section IA. RCN29 expects to find an input file named INP1 and a (blank)

output file named OUT1. It will generate, internally, additional output files PUNCHA, TAPE4, TAPE2, ENC and TAPE7. PUNCHA will contain data that was to be punched in the LASL version. Cards will not automatically be punched, however. This can be done via the utility routine PUNCH if desired. ENC is a short file not really used but expected to be present for the ENCODE/DECODE statement. The other files are used to output the data needed for HFMOD7 and/or RCN229. Upon completion OUT1 may be sent to the printer via ALLOUT. Execution is accomplished by

RCN29 / t v

HFMOD7 and RCN229 are run similarly, expecting input files INP2 and INP3 respectively and (blank) output files OUT2 and OUT3. However, TAPE4, TAPE2 and TAPE7 must also be present, with names switched to DAT4,DAT2, DAT7.

It is generally easier to run any sequence of the codes under ORDER. (See following section). Essentially what is done is that all TTY operation for creating files, switching names, etc., become commands to the ORDER controller.

2. Running under ORDER

RCN is currently a "LIX" produced library containing binary codes for RCN29, HFMOD7, and RCN229 and designed to be run under ORDER. The input file, which can have any name, contains both the ORDER cards and input to the codes being run. Control cards contain a * in column 1. The execute line is

ORDER input file / t v

RCN must also be on the machine.

Any sequence of the codes can be run by concatenating one or more of the following typical modules.

```
*ID          (first card in entire deck)
*XEQ X                        } Retrieves the controlee
*XEQMES RCN RCN29 DR.         } from library file.
*NXT         (card between separate jobs)
*XEQ COPY                     } Create output file OUT1 of length 50000
*XEQMES COPY OUT1 L 50000     } octal by copying COPY
*NXT
*XEQ RCN29                    } Execute controllee identified
*DATA INP1 A                  } Input file INP1 is generated via the DATA card
```

Data cards follow.

An additional sequence of cards is inserted to switch file names. (See sample input). The last job in the execute (*XEQ) stream should be ALLOUT to print output files OUT1, OUT2, and OUT3.

```
*NXT
*XEQ ALLOUT
*XEQMES HSP OUT1 OUT2 OUT3 BOX & ID
```

MCT can be used to store the output if desired. (See input file CONT). DESTROY is the nice-guy clean up stage.

C. Sample input

The next page lists a sample input, FENB, which runs (under ORDER) an HFR calculation for 3 configurations each of Fe, NB and U. The only changes necessary to run some other set of configurations not involving continuum functions are:

1. Account number, Box and ID on ORDER cards
2. Configuration cards
3. Replace 12, the first number, on G5INP card, by the number of configurations being computed.
4. If a large number of configurations are included in one calculation file sizes on the first card might need to be increased.

Note that the output file size is really determined by COPY statement on ORDER card.

The file CONT (see p. 54) lists a sample input for an ORDER run which includes continuum functions. Since HFMOD7 cannot handle continuum functions only RCN29 and RCN229 are used. Note the following differences from the previous input.

1. On the RCN29 control card IHF=0 instead of 2 since HF calculation is not being done; TOLEND and THRESH have been decreased to carry the HX calculation to convergence rather than just to provide starting wavefunctions for HFMOD7; IREL=1 instead of 2. The relativistic correction is included in either case. EMX, the maximum continuum energy, has been added to control card.

2. Continuum d orbitals are indicated by 99D on configuration cards and continuum energy has been added.

3. The number of configurations on the G5INP card has been changed from 12 to 4.

FENB

```
*ID   199YLD                                          RAJNAK          BOX Z69
*XEQ X
*XEQMES RCN RCN29 DR.
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ COPY
*XEQMES COPY OUT1 L 50000
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ RCN29
*DATA INP1 A
FILE SIZE=      50000      50000     150000     150000      50000        10
 1.00000 0.99094 0.98164 0.97218 0.96266 0.95311 0.94359 0.93413 0.92475  A I  1
 0.91549 0.90634 0.88844 0.87109 0.85429 0.83802 0.82227 0.80700 0.79220  A I  2
 0.77785 0.76393 0.75044 0.72473 0.70066 0.67816 0.65710 0.63732 0.61866  A I  3
 0.60097 0.58416 0.56814 0.55285 0.52427 0.49813 0.47416 0.45214 0.43184  A I  4
 0.41304 0.39553 0.37916 0.36377 0.34927 0.32262 0.29887 0.27789 0.25953  A I  5
 0.24348 0.22926 0.21645 0.20468 0.18376 0.18354 0.16493 0.14852 0.13412  A I  6
 0.12152 0.11053 0.10094 0.09255 0.08517 0.07866 0.07289 0.06311 0.05556  A I  7
 0.048    0.042    0.037   0.033    0.030    0.025    0.021    0.017    0.014    A I  8
 0.011    0.009    0.007   0.006    0.005    0.004    0.003    0.002    0.001    A I  9
 0.000                                                                          A I 10
                                                                                A I 11
                                                                                A I 12
                                                                                A I 13
2  -5     2  1.0  1.0     5.E-02     1.E-05-2    230    1.0  0.65  0.0 0.50 0.0  0.7
   26     1FEI 3D6 4S2              3D6   4S2
   26     1FEI 3P4 3D8 4S2          3P4   3D8   4S2
   26     1FEI 3S1 3D7 4S2          3S1   3D7   4S2
   41     2NB2 4D4                  4D4
   41     2NB2 4P4 4D6              4P4   4D6
   41     2NB2 4S1 4D5              4S1   4D5
   64     1GDI 4F7 5D1 6S2          4F7   5D1   6S2
   64     1GDI 5P4 4F7 5D3 6S2      5P4   4F7   5D3   6S2
   64     1GDI 5S1 4F7 5D2 6S2      5S1   4F7   5D2   6S2
   92     1U I 5F2 6D2 7S2          5F2   6D2   7S2
   92     1U I 6P4 5F2 6D4 7S2      6P4   5F2   6D4   7S2
   92     1U I 6S1 5F2 6D3 7S2      6S1   5F2   6D3   7S2
   -1
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE2 DAT2
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE4 DAT4
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE7 DAT7
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ X
*XEQMES RCN HFMOD7 DR.
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ COPY
*XEQMES OUT1 OUT2
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ HFMOD7
*DATA INP2 A

   1.E-07   10                                                  999,          0.95
  51        0.5 0.65
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ X

*XEQMES RCN RCN229 DR.
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ COPY
*XEQMES OUT1 OUT3
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ RCN229
*DATA INP3 A
G5INP   120 0 00 0 000          100  100  100  100  100   00     00000
       -1
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ ALLOUT
*XEQMES HSP OUT1 OUT2 OUT3 BOX Z69 CACL. ALPHA D
*NXT  199YLD                                          RAJNAK          BOX Z69
*XEQ DESTROY
*XEQMES INP1 INP2 INP3 DAT2 DAT4 DAT7
```

CONT

```
*ID   199YAM                                        RAJNAK          BOX Z69
*XEQ X
*XEQMES RCN RCN29 DR.
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ COPY
*XEQMES COPY OUT1 L 150000
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ RCN29
*DATA INP1 A
FILE SIZE=      50000      50000     150000     150000      50000        10
 1.00000 0.99094 0.98164 0.97218 0.96266 0.95311 0.94359 0.93413 0.92475  A I  1
 0.91549 0.90634 0.88844 0.87109 0.85429 0.83802 0.82227 0.80700 0.79220  A I  2
 0.77785 0.76393 0.75044 0.72473 0.70066 0.67816 0.65710 0.63732 0.61866  A I  3
 0.60097 0.58416 0.56814 0.55285 0.52427 0.49813 0.47416 0.45214 0.43184  A I  4
 0.41304 0.39553 0.37916 0.36377 0.34927 0.32262 0.29887 0.27789 0.25953  A I  5
 0.24348 0.22926 0.21645 0.20468 0.19376 0.18354 0.16493 0.14852 0.13412  A I  6
 0.12152 0.11053 0.10094 0.09255 0.08517 0.07866 0.07289 0.06311 0.05556  A I  7
 0.048   0.042   0.037   0.033   0.030   0.025   0.021   0.017   0.014    A I  8
 0.011   0.009   0.007   0.006   0.005   0.004   0.003   0.002   0.001    A I  9
 0.000                                                                    A I 10
                                                                          A I 11
                                                                          A I 12
                                                                          A I 13
2  -5    0  1.0  1.0    5.E-08    1.E-11-2   130   1.0  0.650.02  0.50 0.0  0.70
   92    1UI  5F3 6D1 7S1 7P1    5F3  6D1  7S1  7P1
   92    1UI  5F3 6D1 7P2        5F3  6D1  7P2
   92    1UI  5F3 6D1 7S1 99D    5F3  6D1  7S1 99D                          .005
   92    1UI  5F3 6D1 7S1 99D    5F3  6D1  7S1 99D                          .02
   -1
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE2 DAT2
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE4 DAT4
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES TAPE7 DAT7
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ X
*XEQMES RCN HFMOD7 DR.
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ COPY
*XEQMES OUT1 OUT2
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ HFMOD7
*DATA INP2 A
2
   1.E-07   10                                                1999.          0.95
  51       0.5 0.65
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ X
*XEQMES RCN RCN229 DR.
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ COPY
*XEQMES OUT1 OUT3
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ RCN229
*DATA INP3 A
G51NP    40 0 00 0 000          100  100  100  100  100   00     00000

      -1
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ ALLOUT
*XEQMES HSP OUT1 OUT3 BOX Z69 U CONTINUUM
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES OUT1 UCONT1
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ SWITCH
*XEQMES OUT3 UCONT
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ MCT
*XEQMES ELF WRS L T:COWAN:HF:OUTPUT FILE UCONT UCONT1 END
*NXT  199YAM                                        RAJNAK          BOX Z69
*XEQ DESTROY
*XEQMES INP1 INP3 DAT2 DAT4 DAT7
```

D. Sample Output

Typical sections from the output for the Fe configurations from the run of FENB follow. The entire output is in photostore as FENBOUT.

Output from the continuum calculation CONT is stored as CONTOUT and those sections which are different from the previous case are on pp 62-66. (Note section G1a to avoid errors in interpretation of R^k integrals).

The cancellation factor FRAC beside R^k integrals is defined as the ratio of the R^k integral to the same integral computed using the modulus of each wave function. A large factor indicates that only a small part of the integral has disappeared due to cancellation. Integrals with small concellation factors are expected to be much more sensitive to the exact form of the wavefunction than those with large cancellation factors.

The lines in the RCN29 output beginning with ***** are printed when the continuum function is close to convergence. The second number is the energy. I is the number of the mesh point and B1 is a normalization factor for the continuum function to correct for the fact that r does not go to ∞. It should be close to 1.

```
....INPUT....
 1.00000   .99094   .98164   .97218   .96266   .95311   .94359   .93413   .92475
   .91549   .90634   .88844   .87109   .85429   .83802   .82227   .80700   .79220
   .77785   .76393   .75044   .72473   .70066   .67816   .65710   .63732   .61866
   .60097   .58416   .56814   .55285   .52427   .49813   .47416   .45214   .43184
   .41304   .39553   .37916   .36377   .34927   .32262   .29887   .27789   .25953
   .24348   .22926   .21645   .20468   .19376   .18354   .16493   .14852   .13412
   .12152   .11053   .10094   .09255   .08517   .07866   .07289   .06311   .05556
   .04800   .04200   .03700   .03300   .03000   .02500   .02100   .01700   .01400
   .01100   .00900   .00700   .00600   .00500   .00400   .00300   .00200   .00100
      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0
      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0
      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0      -.0
      -.0      -.0
200-50-0 2  1.0  1.0*.00000E-02*.00000E-05-2 -0230-0 1.00   .65    .0   .50    .0   .70
....INPUT....
0  26    1FEI 3D6 4S2          ** 3D6  4S2                                  -0    -.0
```

OUT1 - from RCN2


```
1
   FEI 3D6 4S2              NCONF= 1    Z= 26    NCORES= 6    NVALES= 1    ION= 0    R(I)/X(I)= .29884981      CA1= .700
 TOLSTB=1.000   TOLK-2=1.00000   TOLEND= 5.0E-02   THRESH= 1.0E-05   KUT= 0    EXF=1.000   CORRF=   .0      CAO=  .500
ORCN MOD 29 (CDC)            MESH= 601   IDB= 601   RDB= 979.241   EMX=    .00   R(MESH)= 979.241     IREL= 2

OTIME=   5.431 SEC,        5.745,        5.757
....INPUT....
0  26    1FEI 3P4 3D8 4S2      ** 3P4  3D8  4S2                             -0    -.0
```



```
1
   FEI 3P4 3D8 4S2          NCONF= 2    Z= 26    NCORES= 6    NVALES= 1    ION= 0    R(I)/X(I)= .29884981      CA1= .700
 TOLSTB=1.000   TOLK-2=1.00000   TOLEND= 5.0E-02   THRESH= 1.0E-05   KUT= 0    EXF=1.000   CORRF=   .0      CAO=  .500
ORCN MOD 29 (CDC)            MESH= 601   IDB= 601   RDB= 979.241   EMX=    .00   R(MESH)= 979.241     IREL= 2

OTIME=   6.131 SEC,        6.444,       12.203
....INPUT....
0  26    1FEI 3S1 3D7 4S2      ** 3S1  3D7  4S2                             -0    -.0
```

OUT1 - from RCN2

OUT2 - from IOD7

1 HARTREE-FOCK WAVE FUNCTIONS FOR 26 FEI 3D6 4S2 HX INPUT NCONF= 1

DATA

	WAVE FUNCTION NL	QC	INITIAL ESTIMATES E(NL)	AZ(NL)	ACC
1	1S	2	526.8147	285.043	.5
2	2S	2	62.9968	87.101	.5
3	2P	6	54.8647	571.698	.5
4	3S	2	7.6410	33.004	.5
5	3P	6	5.1295	211.588	.5
6	3D	6	1.1467	156.675	.5
7	4S	2	.5607	8.244	.5

ENERGY = E(AVERAGE)+

RHO= -3.000 H= .0625 NO= 200 IREL= 2 HXFAC= .95 WFTOL= 1.0E-07 NITER=10 TIMPM= 999.0

I	TIME	WFTOL	DPM(J)	JDPM	NL	TYPE	1S	2S	2P	3S	3P	3D	4S
1	1.08	1.0E-07	2.7E-03	109	4S	1.0	.50	.50	.50	.50	.50	.50	.50
2	1.86	1.0E-07	3.2E-04	109	4S	1.0	.40	.40	.40	.50	.50	.50	.50
3	2.64	1.0E-07	4.1E-05	108	4S	1.0	.40	.40	.40	.40	.40	.40	.50
4	3.40	1.0E-07	5.1E-06	108	4S	1.0	.40	.40	.40	.40	.40	.40	.50
5	4.13	1.0E-07	6.2E-07	108	4S	1.0	.40	.40	.40	.40	.40	.40	.50
6	4.87	1.0E-07	8.8E-08	108	4S	1.0	.40	.40	.40	.40	.40	.40	.50

MATRIX OF ENERGY PARAMETERS

527.41723177	.0	.0	.0	.0	.0	.0
.0	64.91430361	.0	.0	.0	.0	.0
.0	.0	55.12606787	.0	.0	.0	.0
.0	.0	.0	8.53116445	.0	.0	.0
.0	.0	.0	.0	5.56360165	.0	.0
.0	.0	.0	.0	.0	1.16927142	.0
.0	.0	.0	.0	.0	.0	.52700992

ORTHOGONALITY INTEGRALS FOR 26 FEI 3D6 4S2 NCONF= 1

(NL)	(NL)	INTEGRAL
2S	1S	-.00360140
3S	1S	-.00131215
3S	2S	-.00122891
3P	2P	-.00091848
4S	1S	-.00027904
4S	2S	-.00024792
4S	3S	-.00009911

1 VALUES OF F AND G INTEGRALS FOR FE I 3D6 4S2 (CM-1) NCONF= 1

(2P, 2P)	F0=	852856.0		F2=	402285.2				
(2P, 3S)	F0=	324105.1							
(2P, 3S)	G1=	25733.6	FRAC= .524						
(2P, 3P)	F0=	313086.2		F2=	60733.6				
(2P, 3P)	G0=	23121.2	FRAC= .291	G2=	24261.4	FRAC= .757			
(2P, 3D)	F0=	265250.8		F2=	47302.3				
(2P, 3D)	G1=	33670.9	FRAC=1.000	G3=	19104.3	FRAC=1.000			
(2P, 4S)	F0=	84875.5							
(2P, 4S)	G1=	1128.7	FRAC= .507						
(3S, 3S)	F0=	243940.5							
(3S, 3P)	F0=	236896.6							
(3S, 3P)	G1=	157519.8	FRAC= .997						
(3S, 3D)	F0=	211468.7							
(3S, 3D)	G2=	91176.5	FRAC= .967						
(3S, 4S)	F0=	81492.5							
(3S, 4S)	G0=	2395.5	FRAC= .227						
(3P, 3P)	F0=	230477.5		F2=	115702.6				
(3P, 3D)	F0=	206267.5		F2=	96844.7				
(3P, 3D)	G1=	120470.8	FRAC= .959	G3=	72601.2	FRAC= .991			
(3P, 4S)	F0=	81227.5							
(3P, 4S)	G1=	3465.9	FRAC= .462						
(3D, 3D)	F0=	187542.1		F2=	85786.8		F4=	53190.4	
(3D, 4S)	F0=	79822.5							
(3D, 4S)	G2=	8139.9	FRAC= .774						
(4S, 4S)	F0=	62031.9							

1 26 FEI 3D6 4S2 NCONF= 1

NL	E(NL)	ECOR(NL)	AZ(NL)	N*	N*CR	1/R**3	1/R**2	MEAN VALUE OF 1/R	R	R**2
1S	527.417232	.082346	234.815262	.044	.044	.0	1378.5473	25.9536	.058464	.004597
2S	64.914304	.080727	71.641209	.124	.124	.0	130.6302	5.5727	.265751	.083320
2P	55.126068	.080990	512.549012	.135	.135	474.8071	40.8299	5.4541	.235015	.067780
3S	8.531164	.076953	26.563236	.342	.341	.0	18.6872	1.7306	.810633	.757169
3P	5.553602	.076486	185.925612	.424	.421	56.2787	5.5200	1.5863	.861139	.873271
3D	1.189271	.074191	147.210373	.917	.890	4.8898	2.0525	1.2239	1.091156	1.552446
4S	.527010	.052396	5.763581	1.377	1.314	.0	.9864	.3986	3.206820	11.998042

EC(OLD)= -1.974848 EC(NEW)= -1.683880 EREL= .0

ET= -2541.651469 ETR= -2541.651469 ETCO= -2543.626317 ETRCO= -2543.626317 ETCN= -2543.335349 ETRCN= -2543.335349

SPIN-ORBIT PARAMETER

ZETA(2P) =	63604.283 CM-1	=	.57960496 RYD
ZETA(3P) =	7519.280 CM-1	=	.06852073 RYD
ZETA(3D) =	408.781 CM-1	=	.00372509 RYD

SPIN-SPIN PARAMETERS

MO(2P, 2P) =	137.233 CM-1		
MO(3P, 3P) =	3.186 CM-1		
MO(3D, 3D) =	1.589 CM-1		
M2(3D, 3D) =	.865 CM-1		

RCG INPUT PARAMETERS

OFEI 3D6 4S2 4 -2543.3353 0 86.7868 1 53.1904 1 .4088 2

HF MOD 7 NCONFG= 1 TIME= 6.05, 6.06 SEC

OUT2 - from HFMOD7

OUT3 - fr CN229

```
1
...INPUT...
G5INP   120 0 00 0 000          100  100  100  100  100   00     00000

1RCN2---INPUT FOR RCG MOD 5

    1      3 3 30 0 000                        00 1000          00000     -0-0-0       2
 S 2     P 3     D 6
 S 2     P 4     D 8
 S 1     P 5     D 7

OFEI 3D6 4S2                        .0     85.78678    53.19037      .40878          .0     FR     FACT=  1.00  1.00  1.00
  1.00  1.00

OFEI 3P4 3D8 4S2                943.66989   116.63198    87.71727    54.44516     7.77254     FR     FACT=  1.00  1.00  1.00
  1.00  1.00
      .42670     98.41748   122.10450    73.79367

OFEI 3S1 3D7 4S2                784.91020    87.69064    54.43894      .42430    92.48082     FR     FACT=  1.00  1.00  1.00
  1.00  1.00

1RCN MOD 27

 EE,EEE=   -5.55360   -2.77680
 EE,EEE=   -1.24804   -3.40082

0 SLATER INTEGRALS FOR FEI 3D6 4S2              NCONF= 1              Z= 26   ION= 0     EXF=    .0          IREL= 2
                       FEI 3P4 3D8 4S2          NCONF= 2                      KUT=-6   CORRF=   .0        CLASS  0

0        K          RDK( 3P, 3P, 3D, 3D)                    FRAC        K          REK( 3P, 3P, 3D, 3D)                    FRAC
         -   ------------------------------------------      -----       -   ------------------------------------------      -----
         1     1.11270459 RYD  =   122105.2080 CM-1          .958        1     1.11270459 RYD  =   122105.2080 CM-1          .958
         3      .67144285 RYD  =    73682.3320 CM-1          .990        3      .67144285 RYD  =    73682.3320 CM-1          .990
0

0 EIGENVALUE CONTRIBUTION OF      .0 KK INCLUDED IN PARAMETER NUMBER  1

OFEI 3D6 4S2     -4 3D8 4S2      2   122.1052 5    73.6823 5
```

OUT3 - from RCN229

```
1RCN MOD 27

 EE,EEE=    -.53437    -.26718
 EE,EEE=   -2.45520   -1.49478

0 SLATER INTEGRALS FOR U I 6P4 5F2 6D4 7S      NCONF=11              Z= 92   ION= 0     EXF=    .0          IREL= 2
                   U I 6S1 5F2 6D3 7S      NCONF=12                      KUT=-5   CORRF=    .0          CLASS  0

0         K          RDK( 6S, 6D, 6P, 6P)                  FRAC        K          REK( 6S, 6D, 6P, 6P)                  FRAC

          1       .48510613 RYD  =     53234.2419 CM-1     .988         1       .48510613 RYD  =     53234.2419 CM-1     .988
0

0 EIGENVALUE CONTRIBUTION OF        .0 KK INCLUDED IN PARAMETER NUMBER  1


OU I 6P4 5F2 6D4 -1 5F2 6D3       1     53.2342 5


                    -99999999.0


OFINISHED G5INP
...INPUT...
          -1
```

1

UI 5F3 6D1 7S1 99D NCONF= 4 Z= 92 NCORES=18 NVALES= 1 ION= 1 R(I)/X(I)= .19611681 CA1= .700

TOLS-B=1.000 TOLK-2=1.00000 TOLEND= 5.0E-08 THRESH= 1.0E-11 KUT= 0 EXF=1.000 CORRF= .0 CAO= .500

ORCN MOD 29 (CDC) MESH=2201 IDB= 481 RDB= 80.310 EMX= .02 R(MESH)=3534.476 IREL= 1

0 2191 *****ZST,E,R,A1,B1,F,I= 1.000000 .020000 3516.401862 .00710954 .98137300 .99302289

0 2191 *****ZST,E,R,A1,B1,F,I= 1.000000 .020000 3516.401862 .00710954 .98137300 .99302289

0 2191 *****ZST,E,R,A1,B1,F,I= 1.000000 .020000 3516.401862 .00710954 .98137300 .99302289

NL	WNL	EE	AZ	(R-3)	(R-2)	(R-1)	(R+1)	(R+2)	(R+3)	(R+4)	(R+6)
1S	2	-8528.97826	5550.653	.0E+00	4.043E+04	1.226E+02	1.373E-02	2.643E-04	6.553E-06	1.988E-07	2.959E-10
2S	2	-1601.89293	2208.377	.0E+00	5.747E+03	2.897E+01	5.750E-02	3.935E-03	3.074E-04	2.709E-05	2.914E-07
2P	6	-1352.84683	38168.244	4.221E+04	7.921E+02	2.392E+01	5.355E-02	3.504E-03	2.713E-04	2.429E-05	2.818E-07
3S	2	-405.96172	1069.046	.0E+00	1.330E+03	1.066E+01	1.483E-01	2.520E-02	4.706E-03	9.568E-04	5.032E-05
3P	6	-335.41322	19916.868	9.711E+03	1.835E+02	9.164E+00	1.522E-01	2.680E-02	5.226E-03	1.117E-03	6.607E-05
3D	10	-269.49034	77735.551	1.258E+03	9.173E+01	8.628E+00	1.384E-01	2.235E-02	4.138E-03	8.660E-04	5.250E-05
4S	2	-104.30668	556.251	.0E+00	3.609E+02	4.643E+00	3.217E-01	1.168E-01	4.600E-02	1.949E-02	4.309E-03
4P	6	-80.87845	10320.491	2.510E+03	4.932E+01	4.036E+00	3.452E-01	1.351E-01	5.759E-02	2.652E-02	7.009E-03
4D	10	-55.73280	42737.251	2.953E+02	2.357E+01	3.672E+00	3.593E-01	1.484E-01	6.768E-02	3.377E-02	1.086E-02
4F	14	-29.91028	54503.127	6.789E+01	1.356E+01	3.349E+00	3.545E-01	1.469E-01	7.021E-02	3.826E-02	1.616E-02
5S	2	-24.04832	281.332	.0E+00	9.304E+01	2.092E+00	6.706E-01	5.025E-01	4.071E-01	3.537E-01	3.267E-01
5P	6	-16.64016	5043.324	5.938E+02	1.236E+01	1.796E+00	7.517E-01	6.337E-01	5.802E-01	5.725E-01	6.934E-01
5D	10	-8.42022	19135.353	5.649E+01	5.106E+00	1.487E+00	8.888E-01	8.965E-01	9.958E-01	1.211E+00	2.331E+00
6S	2	-4.35134	125.531	.0E+00	1.876E+01	8.878E-01	1.486E+00	2.465E+00	4.453E+00	8.704E+00	4.195E+01
6P	6	-2.50109	2009.596	9.415E+01	2.147E+00	7.041E-01	1.830E+00	3.764E+00	8.518E+00	2.110E+01	1.687E+02
5F	3	-1.10104	16134.591	5.200E+00	1.439E+00	9.001E-01	1.484E+00	2.704E+00	5.962E+00	1.576E+01	1.792E+02
6D	1	-.80371	4978.888	3.827E+00	4.511E-01	4.169E-01	3.030E+00	1.059E+01	4.194E+01	1.870E+02	9.140E+03
7S	1	-.85756	44.919	.0E+00	2.451E+00	3.278E-01	3.829E+00	1.639E+01	7.682E+01	3.921E+02	1.304E+04
	91				1.036E+05	7.656E+02	5.433E+01	8.142E+01	2.131E+02	7.877E+02	1.984E+04
	1				1.139E+03	8.413E+00	5.970E-01	8.947E-01	2.342E+00	8.656E+00	2.180E+02

NL	WNL	ZETA R*VI/(1+(E-V)/274**2) (RYD)	ZETA R*VI/(1+(E-V)/274**2) (CM-1)	ZETA -----(R*VI)----- (RYD)	ZETA -----(R*VI)----- (CM-1)	I (RYD)	EPS S	EVEL	EDAR	EVEL+EDAR	EREL
1S	2	.0	.0	.0	.0	-9651.43347	-8510.81640	13634.05308	11722.57313	-1911.480	-10422.28635
2S	2	.0	.0	.0	.0	-2490.51892	-1605.78439	-2297.22812	1725.78907	-571.439	-2177.22344
2P	6	169.45054	18595046.959	202.56444	22228877.016	-2257.06976	-1353.79647	-153.25472	5.64613	-153.255	-1507.05118
3S	2	.0	.0	.0	.0	-1047.96209	-410.97266	-548.60690	399.86809	-148.739	-559.71147
3P	6	37.67015	4133820.894	46.52162	5105157.673	-971.92891	-340.05817	-45.86959	1.36650	-45.870	-385.92777
3D	10	5.32842	584726.864	5.50062	603622.987	-926.80122	-273.13023	-11.54422	-.12325	-11.544	-284.67445
4S	2	.0	.0	.0	.0	-536.20315	-107.83852	-149.62017	107.95827	-41.662	-149.50042
4P	6	9.64600	1058525.833	12.01049	1317998.975	-495.97916	-84.17957	-12.81411	.35780	-12.814	-96.99369
4D	10	1.23206	135203.125	1.28082	140553.366	-462.15909	-58.79081	-3.41901	-.02804	-3.419	-62.20982
4F	14	.23217	25477.764	.23417	25696.912	-434.45905	-32.49012	-.87320	-.02018	-.873	-33.36332
5S	2	.0	.0	.0	.0	-285.08454	-25.67529	-38.37286	27.59607	-10.777	-36.45208

```
CONT ...N229

1RCN MOD 27

 EE,EEE=    -.30390    -.15195
 EE,EEE=     .00500    -.14945

0 SLATER INTEGRALS FOR UI   5F3 6D1 7P2        NCONF= 2          Z= 92   ION= 0     EXF= .650        IREL= 1
                    UI   5F3 6D1 7S1 99D      NCONF= 3                  KUT=-1   CORRF=  .0        CLASS 0

0        K        RDK( 7P, 7P, 7S,99D)                FRAC      K        REK( 7P, 7P, 7S,99D)                FRAC
         1      .20342403 RYD  =    22323.2058 CM-1    .796      1      .20342418 RYD  =    22323.2224 CM-1    .796
0

0 EIGENVALUE CONTRIBUTION OF       .0 KK INCLUDED IN PARAMETER NUMBER  1

0UI  5F3 6D1 7P2 -3 6D1 7S1      1    22.3232 5
```

```
1RCN MOD 27

 EE,EEE=     .00500     .00250
 EE,EEE=     .02000     .01250
       1.934233        1.958142        1.946187
        .217010         .217010         .217010
        .103193         .103193         .103193
        .104219         .104219         .104219
        .083934         .083934         .083934
        .064778         .064778         .064778

0 SLATER INTEGRALS FOR UI   5F3 6D1 7S1 99      NCONF= 3          Z= 92   ION= 0     EXF= .650          IREL= 1
                    UI   5F3 6D1 7S1 99      NCONF= 4                  KUT=-1   CORRF=   .0          CLASS 11

0        K          RDK( 5F,99D, 5F,99D)                    FRAC        K        REK( 5F,99D, 5F,99D)                    FRAC
         -   ------------------------------------------   -----        -   ------------------------------------------   -----

         0      1.94618715 RYD  =   213569.3421 CM-1     .178         1       .10421917 RYD  =   11436.7309 CM-1     .606
         2       .21700967 RYD  =    23814.0571 CM-1     .995         3       .08393357 RYD  =    9210.6446 CM-1     .846
         4       .10319288 RYD  =    11324.1087 CM-1    1.000         5       .06477770 RYD  =    7108.5306 CM-1     .932
0
       1.934233        1.958142        1.946187
        .217010         .217010         .217010
        .103193         .103193         .103193
        .104219         .104219         .104219
        .083934         .083934         .083934
        .064778         .064778         .064778
         -   ------------------------------------------   -----        -   ------------------------------------------   -----

         0      1.94618715 RYD  =   213569.3421 CM-1     .178         1       .10421917 RYD  =   11436.7308 CM-1     .606
         2       .21700967 RYD  =    23814.0570 CM-1     .995         3       .08393357 RYD  =    9210.6446 CM-1     .846
         4       .10319288 RYD  =    11324.1087 CM-1    1.000         5       .06477770 RYD  =    7108.5306 CM-1     .932
0
       1.934233        1.958142        1.946187
        .217010         .217010         .217010
        .103193         .103193         .103193
        .104219         .104219         .104219
        .083934         .083934         .083934
        .064778         .064778         .064778
         -   ------------------------------------------   -----        -   ------------------------------------------   -----

         0      1.94618715 RYD  =   213569.3421 CM-1     .178         1       .10421917 RYD  =   11436.7309 CM-1     .606
         2       .21700967 RYD  =    23814.0571 CM-1     .995         3       .08393357 RYD  =    9210.6446 CM-1     .846
         4       .10319288 RYD  =    11324.1088 CM-1    1.000         5       .06477770 RYD  =    7108.5306 CM-1     .932
0
         -   ------------------------------------------   -----        -   ------------------------------------------   -----

         0      1.94618715 RYD  =   213569.3421 CM-1     .178         1       .10421917 RYD  =   11436.7309 CM-1     .606
         2       .21700967 RYD  =    23814.0571 CM-1     .995         3       .08393357 RYD  =    9210.6446 CM-1     .846
         4       .10319288 RYD  =    11324.1088 CM-1    1.000         5       .06477770 RYD  =    7108.5306 CM-1     .932
```

```
0
0
  Z  KUT              CONF1                  CONF2              OVERLAP INTEGRAL          FRACTION
 --- ---  ------------------  ------------------  ------------------------  --------

  92  -1        UI  5F3 6D1 7S1 99    UI  5F3 6D1 7S1 99     (99D/99D)=  15.254966477      .003738
   3.00000    .31266   3.00000   1.00000   2.00000        .0    .01250  15.25497
   3.00000    .25180   3.00000   3.00000   2.00000        .0    .01250  15.25497
   3.00000    .19433   3.00000   5.00000   2.00000        .0    .01250  15.25497

0 EIGENVALUE CONTRIBUTION OF       .0 KK INCLUDED IN PARAMETER NUMBER  1

0UI  5F3 6D1 7S1 -3 6D1 7S1      6          .0 5    23.8141 5    11.3241 5    11.4367 5    9.2106 5
     7.1085 5
```

1

Z OVER	KUT	CA1 FR1	CA0	CONF1	CONF2	R INTEGRAL	REDUCED MUPOLE ELEMENT		FRAC	SIGMA SQ
92	-1	.70	.5C	UI 5F3 6D1 7S1 7P	UI 5F3 6D1 7P2	-4.033842	(7S//R1// 7P)=	4.03384 A0	-.9954	5.423961
-.838	-.989									
92	-1	.70	.5C	UI 5F3 6D1 7S1 7P	UI 5F3 6D1 7S1 99	-5.118339	(7P//R1//99D)=	7.23842 A0	-.4005	1.748493
-1.073	-.625									
92	-1	.70	.5C	UI 5F3 6D1 7S1 7P	UI 5F3 6D1 7S1 99	-4.541084	(7P//R1//99D)=	6.42206 A0	-.3643	1.374763
-1.061	-.596									

-99999999.0

	EE	N*	WT= RT(0.5*NST3/ZST2)	GAMMA/RKSQ	Q*RK	PI*(QRKSQ)/2	PDIPSC	RKSC(RYD)----	
3 6D1	-.303902	.0	.0	.0	.0	.0	4.03384	.0	.0
0	.0								
3 6D1	.005000	.0	.0	.26001	.872	1.194	7.23842	.203424	
3 6D1	.020000	.0	.0	.24540	1.012	1.608	6.42206	.197627	

OFINISHED G5INP

...INPUT...
-1

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