HARTREE-FOCK PROGRAM

BY

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CERTIFICATE

It is certified that the work contained in this dissertation was carried out and completed under my supervision.

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ABSTRACT

In the present research project we have installed and tested two computer programs for the calculations of atomic and molecular structure. The first program is for the Hartree-Fock multi configuration calculations of atom and ionized species. The objective of this program is to to solve the coupled integro-differential equation for radial wave functions to extract energy and multiplets of a configuration. The equations are being solved iteratively using self-consistent field method. The structure of the program is such that the frozen core approximation may be used. The program was originally designed for VAX-11-780, we have modified it for NEC-610. In order to check the performance of the program, we have performed ab-initio Hartree-Fock calculations for

1) $2p^6 3s$ ground state and $2p^6 3d$ excited state of sodium,
2) $3p^6 4s$ ground state of Potassium and
3) $4d^{10} 5s$ ground state of Cadmium.

The second program is based on Chebyshev polynomial fitting and is especially designed to extract the wavelengths from the experimentally recorded absorption/emission spectrum using known wavelength standards. The main advantage of this program is that it rejects automatically if a wavelength standard does not fit or miss identified. We have checked the validity of this program by calculating the unknown wavelength of experimental data of Krypton recorded at high resolution and high dispersion.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION OF HARTREE-FOCK METHOD

The micro realm of atomic structure has proved to be an exceedingly difficult problem even for simpler atoms with only a few electrons. As the number of electrons increases, the task of solving Schrodinger's equation becomes prohibitively complicated. Exact solutions are known only for one electron system. Some approximate but reliable methods were sought. Various successful attempts have been made for N=2. Hylleraas[1] was the first to reach a high degree of accuracy in the theoretical prediction of the ground state of two-electron system including Helium and the negative hydrogen ion. His calculations were based on the Variational Principle i.e in minimizing the energy given by a wave function with six parameters. Hylleraas found for E the value -2.90324 atomic units. Chandrashaker Elbert and Herzberg[2] recalculated the energy of the ground state by the Ritz Variation method, making use of a trial function with ten adjustable parameters and showed that their ground state energy, including the relativistic and mass polarization corrections was about 21.5 cm^{-1} higher than the observed value while the error of observation was of the order ± 5cm^{-1}. Later more accurate variational wave functions were obtained by Kinoshita[3] and by Perkeris[4]. So far the best approximated value is E=-2.90372437703 a.u. which is several orders more accurate than the experimental value. The excellent agreement between the theoretical and experimental results for helium verifies the accuracy of the quantum mechanical model. But the variational methods employed are exceedingly difficult to generalize to large systems; other more approximate methods are required.

Fortunately we have approximations which are good enough to give agreement with experiment, though with far larger errors than for the helium calculations. One such approximation is Hartree's[5] method of the self-consistent field. In this method we replace the instantaneous action of all the electrons of an atom on one of their number, which would result in a mechanical problem so difficult that it could not be solved, by the much simpler problem in which each electron is assumed to move in a central field produced by the nucleus, and the spherically averaged potential fields of each other electron. The wave function of an electron in such a spherical field is very similar to the hydrogenic function. Its dependence on angle is exactly the same, and the only difference is in the radial function $R_{nl}(r)$. Thus we can assume that the one-electron wave function or orbitals will have the same form as that for hydrogen atom wave function. Wave function for the N-electron atom can be constructed from these one orbitals by supposing that each electron move quite independently of the others only in an averaged manner. Hence the quantity $\psi^{*}\psi$, the probability density, where ψ is the N-electron wave function, should be a product of probability densities for the various electrons, as we should have for independent motion. This implies that the wave function should be a product of functions of the various electrons. Each orbital is assigned three quantum numbers n, l, m_l. The wave function does not depend on the spin quantum number m_s, but in accordance with Pauli's exclusion principle , we may assign no more than two electrons to a given set of (nlm_l) values, of which we assume that one has $m_s=1/2$, the other has $m_s=-1/2$. Using this representation of ψ, Hartree found the average value of the Hamiltonian. This average Hamiltonian is then varied with respect to one electron orbitals. This leads to a set of variational equations. The variational equations have the form of coupled integro-differential equations. In principle, a self consistent set of solutions can be obtained by iterative techniques.

The Hartree's representation, however, overlooks the fact that ψ must be an anti-symmetric function of the electron coordinates. This defect is remedied in the Hartree-Fock approach in which ψ is expressed in terms of determinantal wave function built up from single orbitals which automatically satisfy this anti-symmetry requirement.

1.2 CURVE FITTING

One of the most common problems in numerical analysis is to approximate a function for a set of experimental data. The approximating functions usually used are those involving linear combinations of simple functions. The functions most often encountered are;

(1) Monomials $\{x^i\}$, $i = 0,1,\ldots\ldots n$,
(2) Fourier functions $\{\sin kx, \cos kx\}$, $k = 0,1,\ldots n$,
(3) Exponentials $\left\{e^{b_i x}\right\}$, $i = 0,1,\ldots\ldots,n$.

Linear combinations of monomials lead to polynomials of degree n, $P_n(x)$,

$$P_n(x) = a_o + a_1x + a_2x^2 + \ldots\ldots\ldots + a_nx^n,$$

whereas, linear combinations of the fourier functions lead to approximations of the form,

$$g(x) = a_0 + \sum_{k=1}^{n} a_k \cos kx + \sum_{k=1}^{n} b_k \sin kx.$$

The widely used approximating functions are the algebraic polynomials $P_n(x)$, because they are easy to evaluate and their sums, products and differences are also polynomials. They can be differentiated and integrated with little difficulty, yielding other polynomials in both cases. But the problem with using such functions is that the error over an arbitrary interval [a,b], centered at 0 is extremely non-uniform, small near the center but growing very rapidly near the end points. Since any such arbitrary finite interval can be transformed to the interval [-1,1], (X in [a,b], Z in [-1,1]) it would seem more reasonable to look for other set of simple related functions that have their extreme values well distributed on the interval [-1,1]. If we approximate an arbitrary function using a linear combination of such functions, the error in the approximation will be distributed more evenly over the interval. In particular, we want to find approximations which are fairly easy to generate and which reduce the maximum error to the minimum value.

The cosine functions $\cos\theta$, $\cos 2\theta$, ...,$\cos n\theta$ appear to be good candidates. Each of the function has identical maximum and minimum values distributed regularly over an arbitrary interval, $0 \le \theta \le \pi$;in addition, the extreme value for two functions $\cos j\theta$, $\cos j\theta$, $j \neq k$, do not, in general, occur at the same values of Z. The cosine function requires an approximation for its numerical evaluation. A simpler and more useful form results from the transformation of $\cos n\theta$ on the interval $0 \le \theta \le \pi$ into an nth degree polynomial in Z on the interval [-1,1]. The set of polynomials $T_n(Z) = \cos n\theta$, n=0, 1, ..., generated from the sequence of cosine functions using the transformation $\theta = \cos^{-1}Z$ is known as Chebyshev polynomials.[6]

CHAPTER 2

MULTI-CONFIGURATION HARTREE-FOCK PROGRAM

2.1 INTRODUCTION

In the preceding chapter Hartree-Fock approach was introduced which was based on representing the total wave function ψ in terms of determinantal wave function. In its simplest form, the Hartree-Fock approximation treats only a single electronic configuration. In this case, ψ is represented by a linear combination of determinantal wave functions. Each of these corresponds to a different assignment of the electronic quantum numbers of the constituent spin-orbitals consistent with the symmetry of the chosen configuration. In the special case of a closed shell configuration, there is only one possible assignment of these quantum numbers and hence ψ is represented by a single determinantal wave function. In the configuration interaction representation which is an extension of the Hartree-Fock method, ψ is expanded in terms of the determinantal wave functions associated with more than one configuration. It is also assumed that the total wave function ψ is an eigen function of S^2 and L^2, that it can be constructed from one-electron functions ϕ_i and that each ϕ_i is a product of a spherical harmonic, a radial wave function depending on n and l quantum numbers and a spin function.

2.2 GENERAL DESCRIPTION

Assume that the total wave function $\psi(SL)$ for a ground state of an N-electron atom can be expressed in the form

$$\psi(SL) = \sum_{j=1}^{NCFG} c_j \Phi_j(n_1 l_1, n_2 l_2, \ldots\ldots, n_N l_N, SL),$$

where NCFG is the number of configurations and c_j is the weight of the configuration j. Other symbols have their usual meaning. Φ_j is an eigenfunction of S^2 and L^2 for a given configuration in a given coupling scheme, and $,\langle\Phi_i|\Phi_j\rangle = \delta_{ij}$. Φ_i are constructed from one-electron functions ϕ_i, which have the form

$$\phi_i = \frac{1}{r} P(n_i l_i;r)\ Y_{l_i}^{m_{l_i}}(\theta,\phi')\ \chi(1/2, m_{s_i}),$$

where,

$P(n_i l_i;r)$ are the radial wave functions,

$Y_{l_i}^{m_{l_i}}(\theta,\phi')$ are the spherical harmonics, and

$\chi(1/2, m_{s_i})$ are the usual spin function.

Expressions for the energy can be derived in terms of the unknown functions P(nl;r). When Φ(SL) is a single determinant simple rules given by Slater[7], for example may be used. But in complex systems the number of determinants that need to be considered may become exceedingly large, making this approach impractical. For a complex atom the energy expression contains many terms, most of which are independent of the LS term value of the state. An extremely useful concept is Slater's[7] average energy of the configuration which is denoted by Eav. It depends only on configuration and when all functions are normalized is given by

$$Eav = \sum_{i} q_i I(n_i l_i) + \sum_{i} q_i \left(\frac{q_i - 1}{2} \right) \sum_{k} a^{k}_{n_i l_i m_{l_i}; n_i l_i m_{l_i}} F^{k}(n_i l_i ; n_i l_i)$$

$$+ \sum_{i,j} q_i q_j \left(F^{0}(n_i l_i ; n_j l_j) + \sum_{k} b^{k}_{n_i l_i m_{l_i}; n_j l_j m_{l_j}} G^{k}(n_i l_i ; n_j l_j) \right)$$

Where q_i is the number of electrons in the shell i, coefficients a and b are defined as

$$a^{k}_{nlm_l;n'l'm_l'} = e^{k}(nlm_l;nlm_l) \text{ x } e^{k}(n'l'm_l';n'l'm_i'),$$

$$b^{k}_{nlm;n'l'm_l'} = \left[e^{k}(nlm_l;n'l'm_l') \right]^{1/2},$$

where e^k is given as

$$e^{k}_{nlm_l;n'l'm_l'} = (-1)^{[m+|m|+m'+|m|+(m-m')+|m-m'|]/2} \text{ x}$$

$$\sqrt{\frac{(k-|m-m'|)!}{(k+|m-m'|)!}} \sqrt{\frac{(2l+1)(l-|m|)!}{(l+|m|)!}} \sqrt{\frac{(2l'+1)(l'-|m'|)!}{(l'+|m'|)!}} \text{ x}$$

$$\frac{1}{2} \int_{-1}^{+1} P_{l}^{|m|}(\mu) \; P_{l'}^{|m'|}(\mu) \; P_{k}^{|m-m'|}(\mu) d\mu,$$

where $P_l^{|m|}(\mu)$'s are associated Legendre functions. Slater[7] has calculated these coefficients for various configurations. The Slater $F^k(n_i l_i;n_i l_i)$ and $G^k(n_i l_i;n_j l_j)$ integrals are given by

$$F^k(n_i l_i; n_i l_i) = \int_0^\infty P^2(n_i l_i; r)\frac{2}{r_1} Y^k(n_i l_i; n_i l_i; r_1)\,dr_1,$$

$$G^k(n_i l_i; n_j l_j) = \int_0^\infty P(n_i l_i; r_1)P(n_j l_j; r_1)\frac{2}{r_1} Y^k(n_i l_i; n_j l_j; r_1)\,dr_1,$$

where $Y^k(n_i l_i; n_j l_j; r_1)$ is given as

$$Y^k(n_i l_i; n_j l_j; r_1) = \int_0^{r_1} P(n_i l_i; r_2)P(n_j l_j; r_2)\left(\frac{r_2}{r_1}\right)^k dr_2$$

$$+ \int_r^\infty P(n_i l_i; r_2)P(n_j l_j; r_2)\left(\frac{r_1}{r_2}\right)^{k+1} dr_2.$$

The LS term energies can be expressed as

$$E(LS) = Eav + \Delta E(LS)$$

where $\Delta E(LS)$ is the deviation from the average energy and has several useful properties.

i) When a configuration admits only one term value, $\Delta E(LS)=0$. Therefore all configurations consisting only of complete groups, or complete groups plus one electron outside a complete group have $\Delta E(LS) = 0$.

ii) $\Delta E(l^n LS) = \Delta E(l^{4l+2-n} LS)$; that is, the deviations for electrons and holes are the same.

iii) For configurations consisting of several incomplete groups, ΔE is a sum of deviations from interactions within individual incomplete groups plus deviations from interactions between incomplete groups. For example, suppose the deviation for γL_1S_1 is known and the incomplete group $l^n(L_2S_2)$ is coupled to γL_1S_1 to produce a state $\gamma(L_1S_1).l^n(L_2S_2)LS$. Then

$\Delta E(\gamma(L_1S_1).l^n(L_2S_2)LS) = \Delta E(\gamma L_1S_1) + \Delta E(l^nL_2S_2)$ plus the deviation for the interaction between γL_1S_1 and $l^nL_2S_2$.

Combining the average energy with the deviations we get the expression for the total energy

$$E(\gamma LS) = \sum_i q_i I(n_il_i) + \sum_{i\geq j;k} a_{ijk}F^k(n_il_i,n_jl_j) + \sum_{i>j;k} b_{ijk}G^k(n_il_i,n_jl_j) \tag{2.1}$$

From the average energies, F^k, and G^k integrals two arrays A(I,J,K) and B(I,J,K) are then generated. The value of a_{ijk} is the coefficient of $Y^{2(k-1)}(j,j)$ in the potential function for wave function i, whereas the value of b_{ijk} is the coefficient of

$$Y^{|l_i-l_j|+2(k-1)}(i,j)\ P(n_jl_j;r)$$

in the exchange function for wave function i.

2.3 METHOD OF SOLUTION

The variational principle requires that energy given by (2.1) be stationary with respect to variations in each of the radial functions. An additional assumption that wave functions associated with a particular angular quantum number l form an orthonormal set can also be introduced. However if this assumption is made, then lagrange multipliers must be introduced into the variational procedure and consequently the orthogonality conditions result in off-diagonal energy parameters in the Hartree-Fock equations. These have the form

$$\frac{d^2P(nl;r)}{dr^2} + \left\{ \frac{2}{r}(Z - Y(r)) - \varepsilon_{nl,nl} - \frac{l(l+1)}{r^2} \right\} P(nl;r)$$

$$= \frac{2}{r} X(r) + \sum_{n'} \varepsilon_{nl,n'l} P(n'l;r),$$

where Y(r) and X(r) are known as Potential and Exchange functions[7] and have form

$$Y(r) = \sum_{n'l';k} A^k_{nl;n'l',k} Y^k(n'l';n'l';r_1)$$

$$X(r) = \sum_{n'l' \neq nl,k} B^k_{nl;n'l',k} Y^k(nl;n'l';r_1) P(n'l';r),$$

where

$$A_{nl,n'l',k} = \frac{\left(1+\partial_{nl,n'l'}\right) a_{nl,n'l',k}}{q_{nl}}$$

$$B_{nl,n'l',k} = \frac{b_{nl,n'l',k}}{q_{nl}}$$

and

$$\varepsilon_{nl,n'l'} = \frac{\lambda_{nl,n'l'}}{q_{nl}}$$

The equation has boundary conditions

$P(0) = P(\infty) = 0.$

The orthonormality condition

$$\int P(nl;r)\, P(n'l;r)\, dr = \delta_{nn'},$$

are applied only to functions within a configuration.When two incomplete groups with the same occupation number and the same angular quantum number l are present the off diagonal energy parameters are assumed to be zero which will not always lead to orthogonal wave functions.[9]

Introducing a logarithmic variable ,

$\rho = \log_e Zr$,

and defining,

$\overline{P}(nl;r) = P(nl;r)/r^{1/2}$,

the last equation can be written as

$$\frac{d^2\overline{P}}{d\rho^2} = \left\{ r^2\varepsilon_{nl,nl} + (l+1/2)^2 - 2r(Z-Y(r)) + \sum_{n'} \varepsilon_{nl,n'l} r^2 \right\} \overline{P}(nl;r) + 2r\overline{X}$$

[10,11]

This differential equation can be solved iteratively, i.e. by starting with an educated guess of the radial wave functions. The differential equation is repeatedly solved until the difference between the wave functions of two successive iterations becomes smaller than some required limit. The wave functions thus achieved are said to be self-consistent.[12] We may use the frozen core approximation, if we want to reduce the amount of computer time. This possibility has been materialized in the program by specifying the number of functions NIT to be iterated. If closed shell wave functions are to be frozen, they are not included in NIT. However, they do make part of NWF which stands for the total number of wave functions. The interdependence of all the functions has been taken into account; the program ensures that a function remains self-consistent on a subsequent change in any other function. The algorithm used is as follows,

1. Orthogonalize functions and determine $\epsilon_{nl;n'l}$.
2. Solve each differential equation in turn.
3. Orthogonalize and determine $\epsilon_{nl;n'l}$.

4. Search for and solve the differential equation with largest change.

5. Solve each differential equation in turn.

6. If largest tolerance $\geq$ SCF tolerance, double the tolerance.

In addition to determine the set of radial functions the energy matrix is also computed and if required the program can also determine a set of mixing coefficients which are components of an eigen vector of energy matrix.

2.4 SUMMARY OF SUBROUTINES

Fig 2.1 shows the flow chart of the program and various subroutines and functions called.

1)MAIN. The main program controls the overall calculation. It reads and stores data concerning the number of configuration, the number and type of electrons in each configuration, as well as the data associated with F^k, G^k, and R^k integrals.

2)ARRAY. It's purpose is to generate two arrays A and B from the basic data and the weights c_j for the configuration, which contain coefficients for the potential function and coefficients for exchange functions respectively.

3)WAVEFN. It's function is to have an initial estimate of the wave functions. Initial estimates can either be as input data, screened hydrogenic functions, or left the same as the results of a previous calculation still in memory. Estimates of the energy parameter $\epsilon_{nl,nl}$ and $a_0 = \frac{P}{r^{l+1}}$, $r \longrightarrow 0$ are also determined if these have been omitted from the input data. Arrays for r, r^2, and $r^{1/2}$ are also generated.

4)SCALE. This subroutine scales for a different Z using computed values of screening parameter.

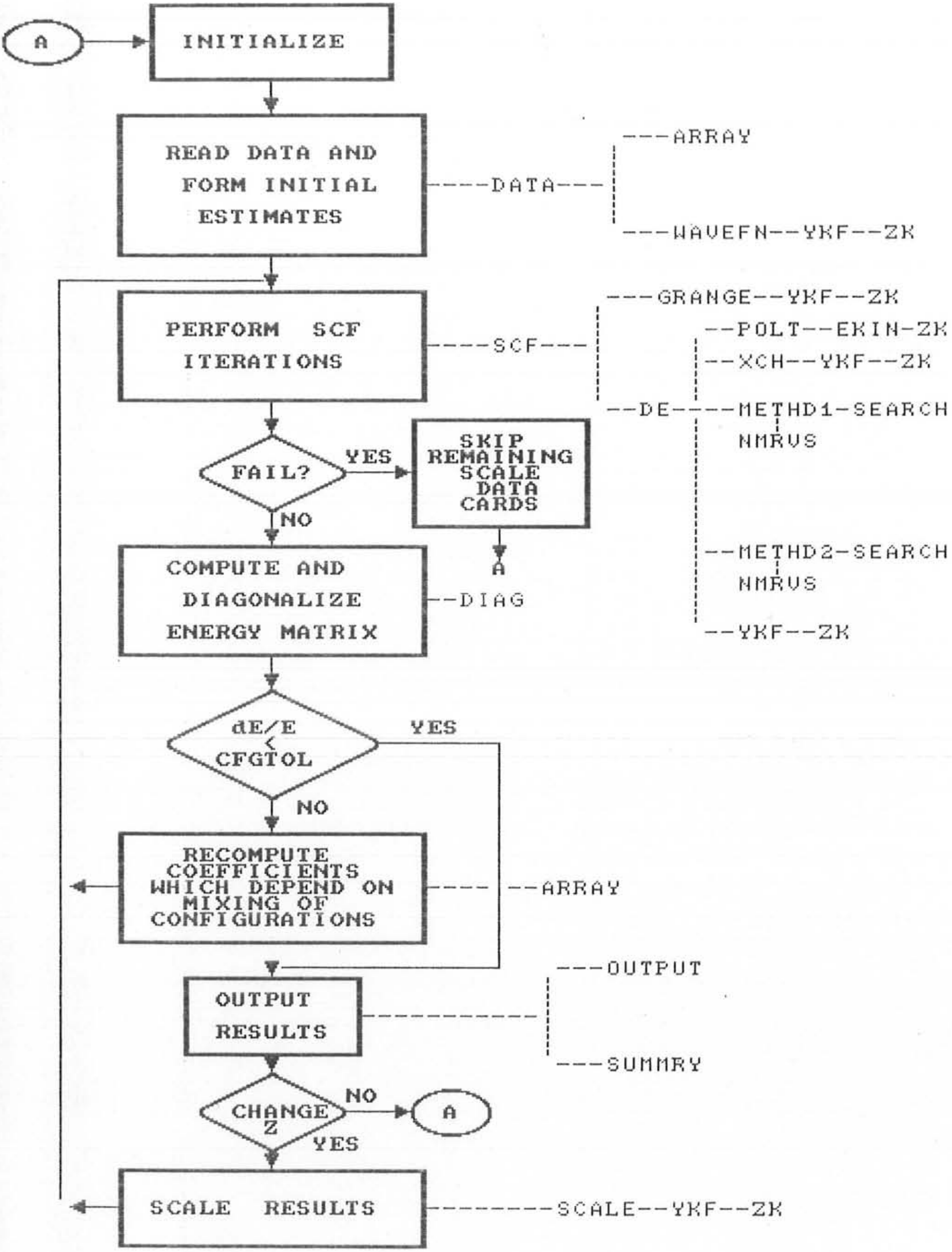


FIG 2.1 FLOWCHART OF PROGRAM AND CONTROL OF SUBROUTINES
(FUNCTION SUBPROGRAMS ARE NOT INCLUDED)

5)HWF. HWF function computes a value for an unnormalized hydrogenic function.

6)HNORM. This function subroutine computes the normalization constant for the hydrogenic function.

7)SCF. SCF subroutine determines self-consistent wave functions for a subset of the total number of wave function, namely the last NIT functions. The remaining core is allowed to remain fixed.

8)DE. This subroutine solves the differential equation for the wave function,

$$\overline{P}(nl;r) = P(nl;r)/r^{1/2}, \text{ namely}$$

$$\frac{d^2\overline{P}}{d\rho^2} = \left\{ r^2 \varepsilon_{nl,nl} + (1+1/2) - 2r(Z-Y(r)) \right\} \overline{P}(nl;r) + 2r\overline{X}$$

$$= F(r)\,\overline{P}_i + G(r),$$

where the potential function Y(r) and the exchange function $\overline{X}(r)$ are determined from current estimates. Two methods of solution are tried. If both fail, the exchange function is reduced by a factor of 7/8 and another attempt is made at obtaining a solution.

9)SEARCH. This subroutine searches for the largest point r_j for which $F(r_j)$ is positive. Then NJ $\geq$ 70 is selected as the point for joining the outward integration with a special tail procedure.

10)METHD1. METHD1 solves the differential equation by estimating a_0, adjusting the diagonal energy parameter $\varepsilon_{nl,nl}$ to satisfy the differential equation and boundary conditions, then adjusting a_0 to satisfy the normalization requirement and repeating the process. This method is suitable for core functions where exchange is relatively[10] unimportant.

11)METHD2. Solves the differential and variational equations of one or two orbitals simultaneously (k=1 or 2) and searches for acceptable solutions which are orthonormal.

12)NMRVS. Solves the differential equation,

$$Y'' = F(r)\,Y + G(r),$$

in two regions. In the first, the equation is integrated outward n_j steps by the Numerov method, then applies a tail procedure for a solution over the remainder of an appropriate range. The two solutions each satisfy one boundary condition and match at r_{nj}, though the differential equation may not be satisfied at this point. M is the number of points in the range of the solution and DELTA the difference at r_{nj+1} of the outward integration and the tail procedure.

13)POLT. The POLT subroutine computes a function $Y_i(r)$ such that $\frac{2\,Y_i(r)}{r}$ is the potential function.

14)XCH. Subroutine for computing the exchange function $\overline{X}_i(r)$ either with or without the contribution from off diagonal energy parameters.

15)ZK. This subroutine computes $Z^k(i,j;r)$.

16)YKF. Subroutine for computing $Y^k(i,j;r)$.

17)GRANGE. The GRANGE subroutine orthogonalizes, estimates and computes off diagonal energy parameters.

18)DIAG. The DIAG subroutine determines the energy matrix element $E_{ij} = (\phi_i|H|\phi_j)$ for the given configurations and, unless input data specifies otherwise, computes the eigenvalue ETOTAL and the corresponding eigenvector c_j.

19)EKIN. The EKIN function computes

$$< P_j \left| \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} - \varepsilon_{ij} \right| P_i >$$

$$= \int P_j \,\frac{2}{r}\Big(Y_i(r)P_i(r) + X_i\Big)\, dr,$$ [8]

where Y(r) and X(r) are the potential and exchange functions respectively.

20)FK. The FK function computes $F^k(i,j)$ integral.

21)GK. The GK function computes $G^k(i,j)$ integral.

22)RK. The RK function evaluates $R^k(i_1,i_2;j_1,j_2)$ integral.

23)OUTPUT. The output subroutine prints tables of the wave function $P_i(r)$ and if OUT = TRUE punches results in a form suitable for future input either as estimates or part of a frozen core. Orthogonality integrals are also printed as a possible check on the calculation.

24)SUMMRY. The SUMMARY subroutine summarizes all results in tabular form.

25)SM. SM is a function required for the determination of spin-orbit parameter.

26)SN. SN is a function required for the determination of spin-orbit parameter.

27)V. V is a function required for the determination of spin-orbit parameter.

28)DYK. Function subprogram used to compute $V^k(i,j)$.

29)QUAD. It integrates the function

$$\int X_i(r)\ Y_i(r)\ dr\ ,$$

by Simpson's rule.

30)QUADR. This function integrates

$$\int r^k P_i(r)\ P_j(r)\ dr,$$

by Simpson's rule.

31)QUADS. This function evaluates

$$\int \frac{1}{r^k} YK(r)\ P_i(r)\ P_j(r)\ \ dr,$$

by Simpson's rule.

2.5 DATA INPUT AND ENERGY CALCULATIONS FOR SINGLE CONFIGURATION

CARD ONE WITH ATOM, TERM, Z, NO, NWF, NIT, NCFG, NF, NG, NR and ORTHO,

in the format

(2A6,F6.0,I6,6I3,L3).

ATOM. Identifying label.

TERM. Identifying label.

Z. Atomic number.

NO. An estimate of the maximum number of points in the range of the outermost electron ≤ 220.

NWF. Number of wave functions ≤ 20.

NIT. Number of functions to be made self-consistent with the core to remain fixed.

NCFG. Number of configurations ≤ 7.

NF. Number of F^k integrals in the expression for the energy.

NG. Number of G integrals in the expression for the energy.

NR. Number of R^k integrals in the expression for the energy ≤ 10.

ORTHO. Logical variable if .FALSE. , only orbitals within a configuration will be made orthogonal, otherwise all orbitals will be made orthogonal.

CARD TWO WITH CONFIG1, CONFIG2, WT and WTL,

IN THE FORMAT,

(2A8,F10.8,L1).

CONFIG. Identifying label for the configuration.

WT. The weight for the configuration if omitted, all configurations have equal weight. The weights are normalized by the program.

WTL. Logical variable if .TRUE., then the weight is to be left unchanged from the previous case, otherwise the value of Wt is to be used.

CARD THREE WITH EL(I), N(I), L(I), S(I), METH(I), ACC(I), IND(I) and (QC(I,J), J=1,NCFG),

IN THE FORMAT

(A3,2I3,F6.2,I3,F3.1,I3,6F3.0).

EL. Identifying label for the electron.

N. Principal quantum number.

L. Angular quantum number.

S. Screening parameter.

METH. Methods to be used for solving the differential equation. Three methods used are

1. Method 1 solves a single boundary value problem for an acceptable solution which need not be normalized.
2. Method 2 solves a pair of equations connected by an orthogonality constraint (if does not exist) for acceptable solutions, orthonormal to first order.
3. Method 3 is a variation of method 1 which does not check whether the solution is acceptable.

ACC. Minimum accelerating factor.

IND. Indicator specifying the type of initial estimate,

-1. To be read as an input data.

0. Screened hydrogenic function.

1. Same as result already in memory.

QC. Number of electrons i in configuration j.

CARD FOUR FOR EACH M, M = 1,NF

WITH A, W, K, I1, J1, I2 and J2,

in the format,

(f12.8,A1,I1,1X,2I2,1X,2I2).

A. Coefficient of the F^k integral.

W. The character F.

K. Value of k.

$\left.\begin{array}{l}\mathrm{I1,J1.}\\ \mathrm{I2,J2.}\end{array}\right\}$ Ith wave function on the jth configuration.

CARD FIVE FOR EACH M = 1,NG

B, W, K, I1, J1, I2 and J2,

in the format

(f12.8,1X,I1,1X,3I2,1X,3I2).

B. Coefficient of the G^k integral.

W. The character G.

K. Value of k.

$\left.\begin{array}{l}\mathrm{I1,J1.}\\ \mathrm{I2,J2.}\end{array}\right\}$Ith wave function on the jth configuration.

CARD SIX FOR EACH M, M = 1,NR,

WITH D, K, I1, J1, I2, J2, I3 and J3,

in the format,

(f12.8,1X,I1,1X,3I2,1X,3I2).

D. The coefficient of R^k integral.

K. Value of k.

$\left.\begin{array}{l}\mathrm{I1,I2,J1.}\\ \mathrm{I3,J4,J2.}\end{array}\right\}$ Ith wave function on the jth configuration.

CARD SEVEN .

For each I,I = 1,NWF for which IND(I) = 1, the output data for a wave function $\overline{P}$ punched during some previous run by the output routine. This data is used to form an estimate for wave function I. If the value of Z on the punched input is not the same as that for the atom under consideration, a simple scaling procedure is used.

CARD EIGHT WITH OUT, PUNCH, NSCF, IC, ACFG and ID,

in the format

(2L3,2I3,F3.1,I3).

OUT. A logical variable if .TRUE., results will be printed and wave functions may be punched, otherwise neither printing nor punching will occur.

PUNCH. A logical variable if OUT = .T. and PUNCH = .T. the functions which were made self-consistent will be punched.

NSCF. Maximum number of SCF iterations allowed in configuration interaction iteration. If omitted will be set 5 by the program.

IC. Number of new estimates of wave functions to be determined between the recomputation of off-diagonal energy parameters and the doubling of SCF tolerance.

ACFG. An accelerating parameter to be applied to the weights after an energy diagonalization.

ID. If ID = 0, the energy matrix computed by the DIAG will be diagonalized and an eigenvalue and eigenvector determined, otherwise diagonalization is omitted.

CARD NINE WITH END, NEXT, ATOM, ZZ and (ACC(I), I = 1,NWF), in the format

(A1,I2,A6,F6.0,20F3.1).

END. If END = *, this signifies the end of a case, i.e, the next card is a card of type 1.

NEXT. If NEXT = 0, the next card is assumed to be a card of type 1. If NEXT = 1, the program will scale the results for P(nl;r), r, $\varepsilon_{nl,n'l'}$ and a_0 for atomic number ZZ, assuming a screened hydrogenic approximation and repeat the calculations for the new atom.

We have calculated the average energy for the configurations

i) Na in both ground and excited(3d) states.

ii) K ground state and

iii) Cd ground state.

All of these correspond to single configuration Hartree-fock method. Further there is only one electron in the outermost shell, therefore ψ is represented by a single determinantal wave function, also all of these have only one LS term. If more than one terms are possible then atomic properties are calculated for the term of highest multiplicity and within that multiplicity for the term with the highest allowed L value. Table 2.1 shows for each nl group

E	the diagonal energy parameter $\varepsilon_{nl,nl}$
AZ	the initial slope, $a_0(nl) = P(nl;r)/r^{l+1}, r \to 0$
SIGMA	the screening parameter,

$$\sigma_{nl} = Z - \frac{\left\langle r^H_{nl} \right\rangle}{\left\langle r_{nl} \right\rangle}$$

where $\left\langle r^H_{nl} \right\rangle$ is the mean radius of a hydrogenic radial function.

$\left\langle 1/_{R^3} \right\rangle$	the expectation value $\left\langle r^{-3}_{nl} \right\rangle$, $l > 0$
$\left\langle 1/_{R} \right\rangle$	the expectation value $\left\langle r^{-1}_{nl} \right\rangle$
$\left\langle R \right\rangle$	the expectation value $\left\langle r_{n} \right\rangle$
$\left\langle R^2 \right\rangle$	the expectation value $\left\langle r^{2}_{nl} \right\rangle$
ZETA(nl)	the spin-orbit parameter ζ_{nl} as defined by Blume and Watson[14]
M^K(nl,nl)	the orbit-orbit integral[14]

Orthogonality integrals, F and G integrals, kinetic energy, potential energy and ratio of both energies, calculated by the program. If Hartree-Fock problem had been solved exactly then the ratio of the potential energy of the atom to its kinetic energy would be exactly -2.0. Table 2.1

suggests that this ratio is usually -2.0 to at least seven decimal places. Fig 2.2. shows the wave functions of

i) Outermost 3s electron in Na ground state.

ii) Excited 3d-electron and 2p electron of Na, shaded area shows the spatial overlap between the d-electron and the core whose width is the the measure of auto ionization.

iii) Outermost 4s electron in K ground state.

iv) Outermost 5s electron in Cd ground state.

All quantities except spin-orbit parameter and orbit-orbit integral are in atomic units.(a.u).

HATREE-FOCK CALCULATIONS FOR NA(Z=11) TERM 3^2S

	CONFIGURATION	WEIGHT
1	SODIUM GROUND S	1.00

WAVE FUNCTION INITIAL ESTIMATES

NO. OF ELECTRONS IN CONFIGURATION

	nl	SIGMA	METH	ACC	OPT	1	2	3	4	5	6	7
1	1S	0.00	1	0.0	0	2						
2	2S	2.00	1	0.0	0	2						
3	2P	4.00	1	0.0	0	6						
4	3S	10.00	1	0.0	0	1						

ENERGY = E(AVERAGE) +
INITIAL ESTIMATES

nl	SIGMA	E(nl)	AZ(nl)	WAVE FUNCTION
1S	0.00	9316.114	1970.075	SCREENED HYDROGENIC
2S	2.00	2158.713	682.491	SCREENED HYDROGENIC
2P	4.00	2119.768	18719.733	SCREENED HYDROGENIC
3S	10.00	912.741	341.327	SCREENED HYDROGENIC

ORTHOGONALITY INTEGRALS FOR ATOM Z=11 TERM 3^2S

nl	nl	INTEGRAL
2S	1S	-0.00000001
3S	1S	0.00000000
3S	2S	-0.00000023

ATOM Z=11 TERM 3^2S

				MEAN VALUE OF					
nl	E(nl)	AZ(nl)	SIGMA	1/R**3	1/R	R	R**2	I(NL)	KE
1S	80.9569552	70.2903984	0.500	0.00000	10.60738	0.1428583	0.0274807	-60.40597560	56.2752406
2S	5.5940367	17.1634515	3.298	0.00000	1.86734	0.7790687	0.7314960	-13.6980725	6.8426303
2P	3.0362686	38.8468936	4.738	17.00478	1.69660	0.7984864	0.8221367	-12.7699292	5.8926271
3S	0.3642056	2.5799190	7.792	0.00000	0.30140	4.2087689	20.7049551	-3.0480879	0.2672952

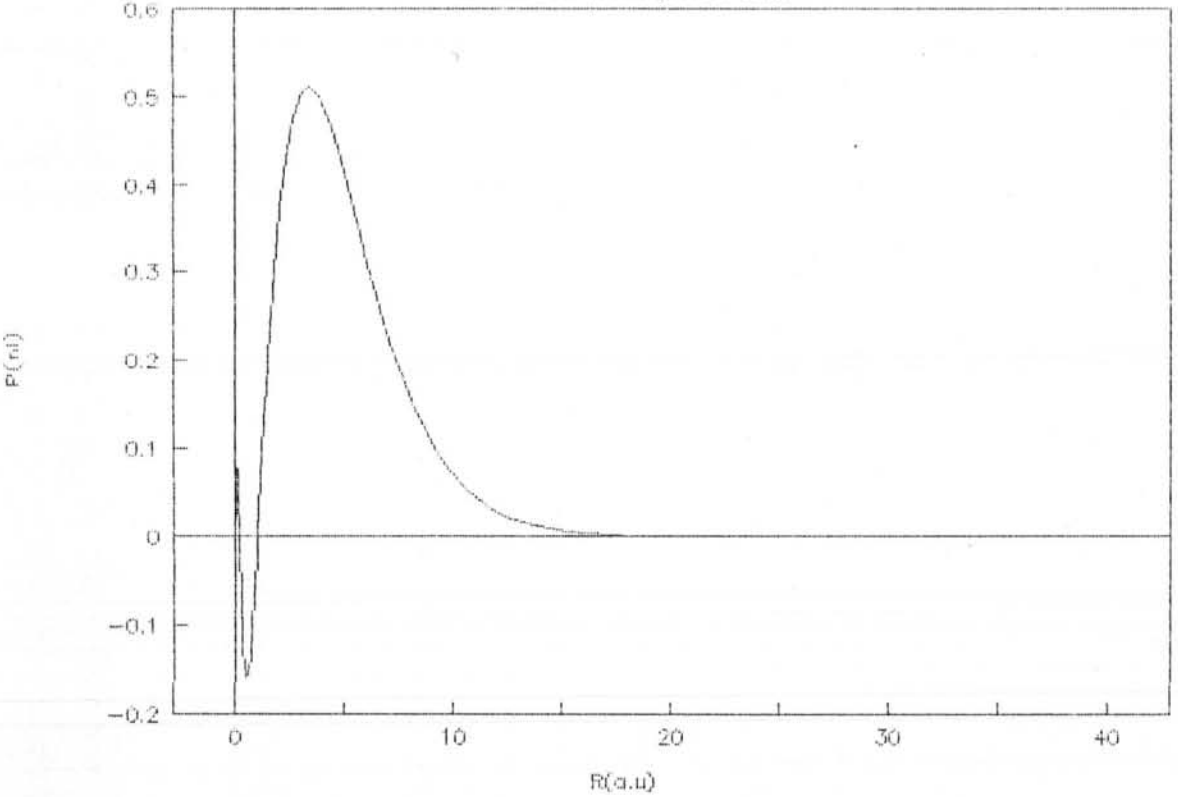
TOTAL ENERGY = -161.8589115 KINETIC ENERGY = 161.8587997 POTENTIAL ENERGY = -323.7177112 RATIO = 2.000000691

VALUES OF F AND G INTEGRALS

```
F0(1S,1S)  = 6.5882556
F0(1S,2S)  = 1.6578631
G0(1S,2S)  = 0.1224562
F0(2S,2S)  = 1.1674922
F0(1S,2P)  = 1.6731645
G1(1S,2P)  = 0.1884129
F0(2S,2P)  = 1.1598157
G1(2S,2P)  = 0.7016706
F0(2P,2P)  = 1.1612445
F0(1S,3S)  = 0.2966950
G0(1S,3S)  = 0.0026674
F0(2S,3S)  = 0.2866362
G0(2S,3S)  = 0.0071614
F0(2P,3S)  = 0.2864924
G1(2P,3S)  = 0.0098032
```

```
F2(2P,2P) = 0.5214068
```

Fig 2.2(i) Radial wave function of
3s electron in Na ground state



HARTEE-FOCK CALCULATIONS FOR NA EXCITED STATE 3^2D

	CONFIGURATION	WEIGHT
1	SODIUM EXCITED S	1.00

WAVE FUNCTION INITIAL ESTIMATES

NO. OF ELECTRONS IN CONFIGURATION

	nl	SIGMA	METH	ACC	OPT	1	2	3	4	5	6	7
1	1S	0.00	1	0.0	0	2.						
2	2S	2.00	1	0.0	0	2.						
3	2P	4.00	1	0.0	0	6.						
4	3D	10.00	1	0.0	0	1.						

ENERGY = E(AVERAGE) +
INITIAL ESTIMATES

nl	SIGMA	E(nl)	AZ(nl)	WAVE FUNCTION
1S	0.00	9312.114	1970.075	SCREENED HYDROGENIC
2S	2.00	2154.584	682.491	SCREENED HYDROGENIC
2P	4.00	2115.795	18719.733	SCREENED HYDROGENIC
3D	10.00	890.933	70646.867	SCREENED HYDROGENIC

ORTHOGONALITY INTEGRALS FOR ATOM Z= 11 TERM 3^2D

(nl)	(nl)	INTEGRAL
2S	1S	0.00000001

ATOM Z=11 TERM 3^2D

				MEAN VALUE OF					
nl	E(nl)	AZ(nl)	SIGMA	1/R**3	1/R	R	R**2	I(NL)	KE
1S	81.2961946	70.2900907	0.500	0.00000	10.60731	0.1428602	0.0274816	-60.4059271	56.2744833
2S	5.9239635	17.1593078	3.299	0.00000	1.86696	0.7791206	0.7314411	-13.6970788	6.8395305
2P	3.3709831	38.9051122	4.721	17.05091	1.69918	0.7962692	0.8159590	-12.7828823	5.9080711
3D	0.1113337	0.0682980	9.996	0.00260	0.11178	10.4589986	125.1330465	-1.1732955	0.0562525

TOTAL ENERGY = -161.7326293 KINETIC ENERGY = 161.7327069 POTENTIAL ENERGY = -323.4653363 RATIO = 1.999999520

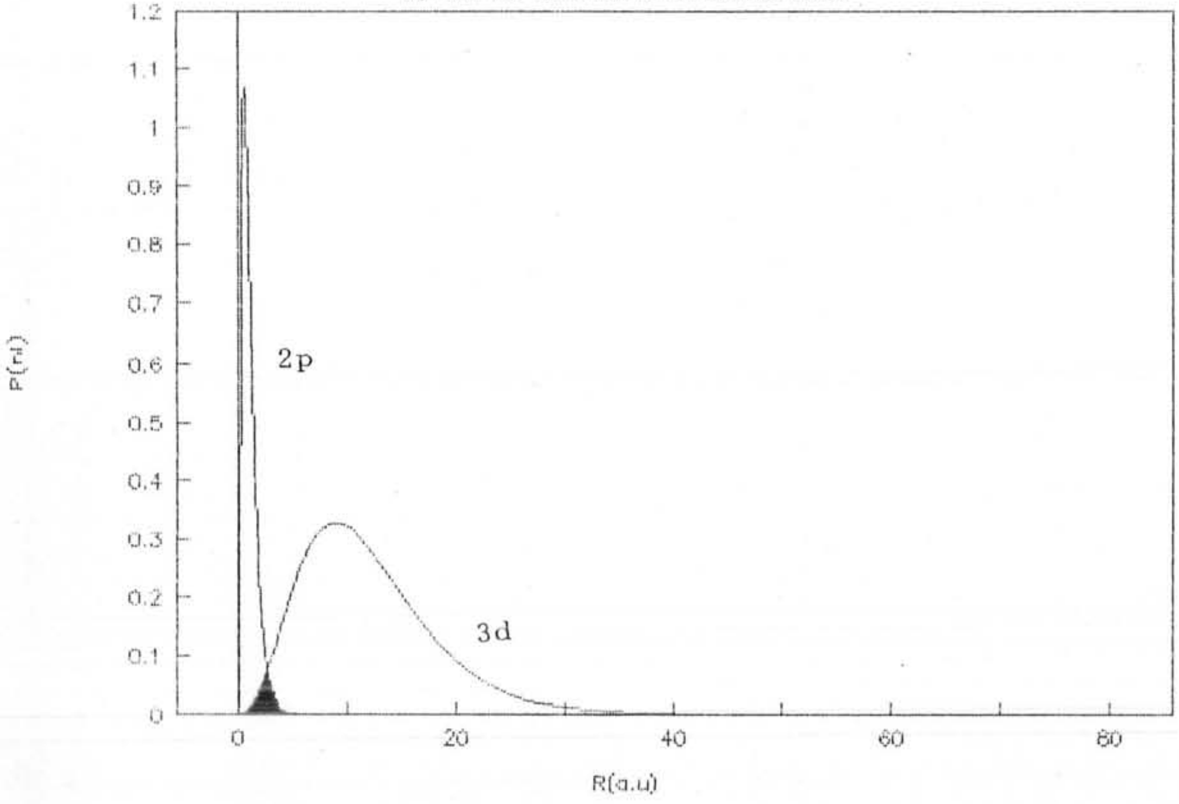
```
VALUES OF F AND G INTEGRALS

FO ( 1S, 1S ) = 6.5881875
FO ( 1S, 2S ) = 1.6575885
GO ( 1S, 2S ) = 0.1224044
FO ( 2S, 2S ) = 1.1673454
FO ( 1S, 2P ) = 1.6756771
G1 ( 1S, 2P ) = 0.1889438
FO ( 2S, 2P ) = 1.1609583
G1 ( 2S, 2P ) = 0.7025280
FO ( 2P, 2P ) = 1.1637353      F2 ( 2P, 2P ) = 0.5228715
FO ( 1S, 3D ) = 0.1117771
G2 ( 1S, 3D ) = 0.0000001
FO ( 2S, 3D ) = 0.1117725
G2 ( 2S, 3D ) = 0.0000634
FO ( 2P, 3D ) = 0.1117699
G1 ( 2P, 3D ) = 0.0001425      G3 ( 2P, 3D ) = 0.0000784
```

SPIN ORBIT PARAMETERS

SPIN-ORBIT PARAMETER (cm^{-1})

```
1 ZETA( 3D) =        0.013
```

Fig 2.2(ii) Radial wave functions of
2p and 3d electrons in Na excited state



HARTREE-FOCK CALCULATIONS FOR K(Z=19) TERM 4^2S

CONFIGURATION				WEIGHT
1	K	GROUND	S	1.000

WAVE FUNCTION INITIAL ESTIMATES

NO. OF ELECTRONS IN CONFIGURATION

	nl	SIGMA	METH	ACC	OPT	1	2	3	4	5	6	7
1	1S	0.00	1	0.0	0	2.						
2	2S	2.00	1	0.0	0	2.						
3	2P	4.00	1	0.0	0	6.						
4	3S	10.00	1	0.0	0	2.						
5	3P	12.00	1	0.0	0	6.						
6	4S	18.00	1	0.0	0	1.						

ENERGY = E(AVERAGE) +
INITIAL ESTIMATES

nl	SIGMA	E(nl)	AZ(nl)	WAVE FUNCTION
1S	0.00	9188.824	1970.075	SCREENED HYDROGENIC
2S	2.00	2046.067	682.491	SCREENED HYDROGENIC
2P	4.00	2004.657	18719.733	SCREENED HYDROGENIC
3S	10.00	831.135	341.327	SCREENED HYDROGENIC
3P	12.00	815.102	9758.344	SCREENED HYDROGENIC
4S	18.00	427.800	202.500	SCREENED HYDROGENIC

ORTHOGONALITY INTEGRALS FOR ATOM Z=19 TERM 4^2S

(nl)	(nl)	INTEGRAL
2S	1S	0.00000000
3S	1S	-0.00000001
3S	2S	-0.00000003
3P	2P	-0.00000009
4S	1S	0.00000002
4S	2S	0.00000002
4S	3S	0.00000005

ATOM Z=19 TERM 4^2S

				MEAN VALUE OF					
nl	E(nl)	AZ(nl)	SIGMA	1/R**3	1/R	R	R**2	I(NL)	KE
1S	267.0660647	161.6273378	0.588	0.00000	18.54736	0.0814665	0.0089134	-180.3708980	172.0289922
2S	28.9798883	46.4261912	3.472	0.00000	3.79771	0.3863893	0.1765933	-43.4927102	28.6636993
2P	23.0385317	213.7963655	4.691	151.80737	3.69703	0.3494267	0.1508008	-42.7733121	27.4702037
3S	3.4975506	15.2987338	8.429	0.00000	1.07486	1.2770584	1.8834682	-15.6081849	4.8141048
3P	1.9088398	65.1091937	10.300	12.95587	0.93901	1.4368481	2.4406634	-13.9970120	3.8442265
4S	0.2949507	2.9541522	14.423	0.00000	0.23659	5.2437293	31.5447375	-4.2306790	0.2645086

TOTAL ENERGY = -599.1647865 KINETIC ENERGY = 599.1646825 POTENTIAL ENERGY = -1198.3294690 RATIO = 2.000000174

VALUES OF F AND G INTEGRALS

```
F0 ( 1S, 1S ) =11.5410462
F0 ( 1S, 2S ) = 3.2960480
G0 ( 1S, 2S ) = 0.2864224
F0 ( 2S, 2S ) = 2.3427550
F0 ( 1S, 2P ) = 3.6246292
G1 ( 1S, 2P ) = 0.5538308
F0 ( 2S, 2P ) = 2.4520292
G1 ( 2S, 2P ) = 1.4413243
F0 ( 2P, 2P ) = 2.6180056
F0 ( 1S, 3S ) = 1.0210016
G0 ( 1S, 3S ) = 0.0291707
F0 ( 2S, 3S ) = 0.9290643
G0 ( 2S, 3S ) = 0.0539620
F0 ( 2P, 3S ) = 0.9386572
G1 ( 2P, 3S ) = 0.0671221
F0 ( 3S, 3S ) = 0.7064117
F0 ( 1S, 3P ) = 0.9325958
G1 ( 1S, 3P ) = 0.0452763
F0 ( 2S, 3P ) = 0.8485536
G1 ( 2S, 3P ) = 0.0422743
F0 ( 2P, 3P ) = 0.8594653
G0 ( 2P, 3P ) = 0.0546996
F0 ( 3S, 3P ) = 0.6653840
G1 ( 3S, 3P ) = 0.4420399
F0 ( 3P, 3P ) = 0.6304216
F0 ( 1S, 4S ) = 0.2345831
G0 ( 1S, 4S ) = 0.0010805
F0 ( 2S, 4S ) = 0.2311833
G0 ( 2S, 4S ) = 0.0018623
F0 ( 2P, 4S ) = 0.2315357
G1 ( 2P, 4S ) = 0.0023665
F0 ( 3S, 4S ) = 0.2237949
G0 ( 3S, 4S ) = 0.0057770
F0 ( 3P, 4S ) = 0.2225479
G1 ( 3P, 4S ) = 0.0093341
```

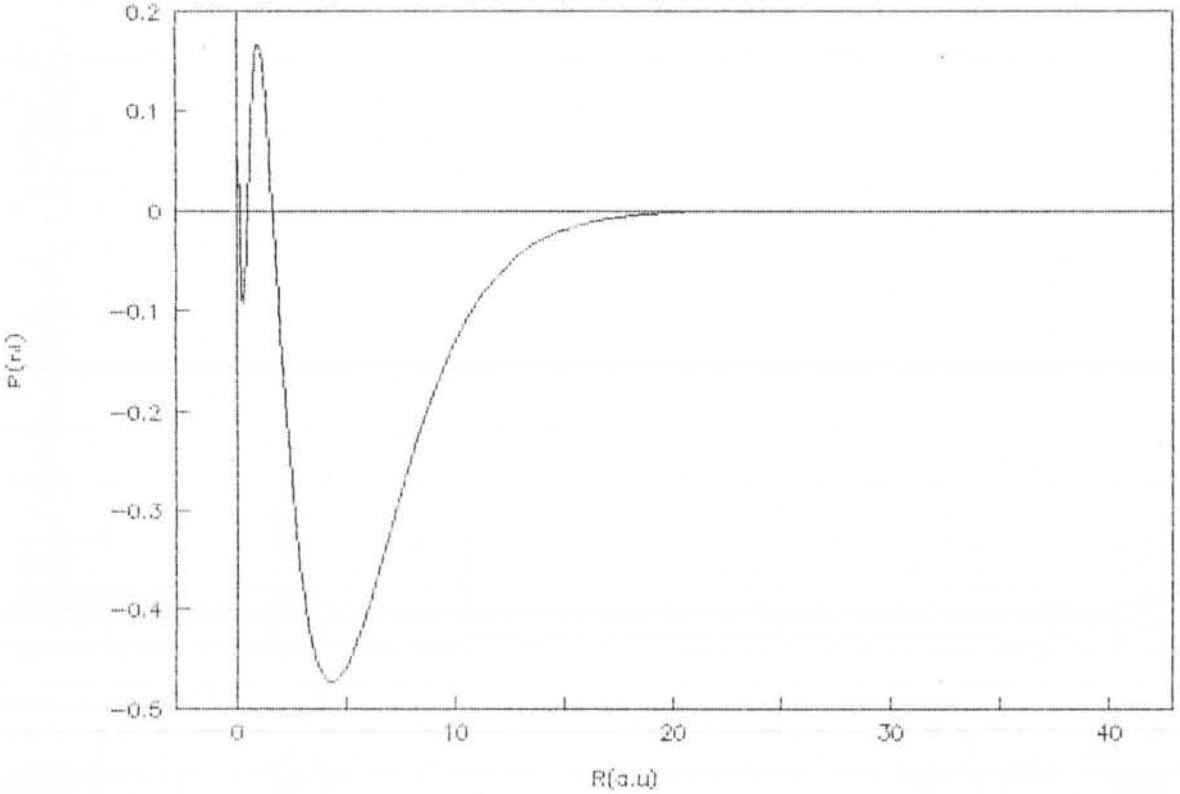
```
F2 ( 2P, 2P ) = 1.2251859
```

```
G2 ( 2P, 3P ) = 0.0559186
```

```
F2 ( 3P, 3P ) = 0.3169379
```

Fig 2.2(iii) Radial wave function of

4s electron in K ground state



HARTREE-FOCK CALCULATIONS FOR CD(Z=48) TERM 5^2S

	CONFIGURATION	WEIGHT
1	CD GROUND STATE	1.00

WAVE FUNCTION INITIAL ESTIMATES

NO. OF ELECTRONS IN CONFIGURATION

	(nl)	SIGMA	METH	ACC	OPT	1	2	3	4	5	6	7
1	1S	0.00	1	0.0	0	2.						
2	2S	2.00	1	0.0	0	2.						
3	2P	4.00	1	0.0	0	6.						
4	3S	10.00	1	0.0	0	2.						
5	3P	12.00	1	0.0	0	6.						
6	3D	18.00	1	0.0	0	10.						
7	4S	28.00	1	0.0	0	2.						
8	4P	30.00	1	0.0	0	6.						
9	4D	36.00	1	0.0	0	10.						
10	5S	46.00	1	0.0	0	2.						

ENERGY = E(AVERAGE) +

INITIAL ESTIMATES

nl	SIGMA	E(nl)	AZ(nl)	WAVE FUNCTION
1S	0.00	8898.608	1970.075	SCREENED HYDROGENIC
2S	2.00	1768.394	682.491	SCREENED HYDROGENIC
2P	4.00	1723.920	18719.733	SCREENED HYDROGENIC
3S	10.00	605.717	341.327	SCREENED HYDROGENIC
3P	12.00	586.453	9758.344	SCREENED HYDROGENIC
3D	18.00	547.449	59154.036	SCREENED HYDROGENIC
4S	28.00	234.491	179.056	SCREENED HYDROGENIC
4P	30.00	236.579	4729.198	SCREENED HYDROGENIC
4D	36.00	225.057	29475.444	SCREENED HYDROGENIC
5S	46.00	106.207	98.975	SCREENED HYDROGENIC

ORTHOGONALITY INTEGRALS FOR ATOM Z=48 TERM 5^2S

(nl)	(nl)	INTEGRAL
2S	1S	0.00000000
3S	1S	0.00000000
3S	2S	0.00000002
3P	2P	0.00000000
4S	1S	0.00000000
4S	2S	-0.00000007
4S	3S	-0.00000018
4P	2P	-0.00000007
4P	3P	-0.00000044
4D	3D	-0.00000078
5S	1S	0.00000000
5S	2S	-0.00000002
5S	3S	-0.00000026
5S	4S	-0.00000473

ATOM Z=48 TERM $5^{2}S$

				MEAN VALUE OF					
nl	E(nl)	AZ(nl)	SIGMA	1/R**3	1/R	R	R**2	I(NL)	KE
1S	1910.6299309	657.8011006	0.685	0.00000	47.47763	0.0317027	0.0013447	-1151.8241844	1127.1019128
2S	284.0129646	212.0905049	4.245	0.00000	10.84171	0.1371282	0.0221002	-285.5606883	234.8412253
2P	264.0933388	2751.9008145	5.384	3546.41691	10.81431	0.1173271	0.0167533	-284.9446479	234.1422126
3S	55.4167404	92.4191629	11.406	0.00000	3.89320	0.3689105	0.1553899	-119.6386278	67.2350680
3P	47.1939670	1244.0431860	13.385	637.42441	3.80254	0.3611193	0.1511142	-117.6765384	64.8455399
3D	32.1434645	3057.0539713	16.515	99.49483	3.64201	0.3334897	0.1318953	-114.5843009	60.2324100
4S	8.9008424	39.0406056	21.746	0.00000	1.48494	0.9141370	0.9451458	-55.0258479	16.2511051
4P	6.1068188	498.5358293	24.540	100.26239	1.36898	0.9803912	1.0996742	-51.5533925	14.1575081
4D	1.5272328	1037.0466172	31.228	9.90387	1.06423	1.2521038	1.8847954	-42.0134858	9.0695716
5S	0.5297378	9.2800205	36.417	0.00000	0.39039	3.2375194	12.1710598	-17.5501131	1.1886487

TOTAL ENERGY = -5465.1331415 KINETIC ENERGY = 5465.1273003 POTENTIAL ENERGY = -10930.2604419 RATIO = 2.000001069

VALUES OF F ANF G INTEGRALS

```
F0 ( 1S, 1S ) =29.6119930
F0 ( 1S, 2S ) = 9.2420295
G0 ( 1S, 2S ) = 0.8920594
F0 ( 2S, 2S ) = 6.5912803
F0 ( 1S, 2P ) =10.5474945
G1 ( 1S, 2P ) = 1.9566503
F0 ( 2S, 2P ) = 7.0447685
G1 ( 2S, 2P ) = 3.9642116
F0 ( 2P, 2P ) = 7.7679134        F2 ( 2P, 2P ) = 3.7021318
F0 ( 1S, 3S ) = 3.5943763
G0 ( 1S, 3S ) = 0.1549590
F0 ( 2S, 3S ) = 3.1515001
G0 ( 2S, 3S ) = 0.2362271
F0 ( 2P, 3S ) = 3.2186280
G1 ( 2P, 3S ) = 0.2948628
F0 ( 3S, 3S ) = 2.4355583
F0 ( 1S, 3P ) = 3.7518086
G1 ( 1S, 3P ) = 0.3274353
F0 ( 2S, 3P ) = 3.2402472
G1 ( 2S, 3P ) = 0.2347491
F0 ( 2P, 3P ) = 3.3336471
G0 ( 2P, 3P ) = 0.2958438        G2 ( 2P, 3P ) = 0.3203701
F0 ( 3S, 3P ) = 2.4611508
G1 ( 3S, 3P ) = 1.6120658
F0 ( 3P, 3P ) = 2.4928603        F2 ( 3P, 3P ) = 1.2599577
F0 ( 1S, 3D ) = 3.6410112
G2 ( 1S, 3D ) = 0.0149697
F0 ( 2S, 3D ) = 3.5063895
G2 ( 2S, 3D ) = 0.8004075
F0 ( 2P, 3D ) = 3.5487357
G1 ( 2P, 3D ) = 0.8287068        G3 ( 2P, 3D ) = 0.4754300
F0 ( 3S, 3D ) = 2.5439198
G2 ( 3S, 3D ) = 1.0503664
F0 ( 3P, 3D ) = 2.5797686        G3 ( 3P, 3D ) = 0.9148979
G1 ( 3P, 3D ) = 1.4156582
F0 ( 3D, 3D ) = 2.7237799        F2 ( 3D, 3D ) = 1.3637636
                                 F4 ( 3D, 3D ) = 0.8715615
F0 ( 1S, 4S ) = 1.4317798
G0 ( 1S, 4S ) = 0.0271901
F0 ( 2S, 4S ) = 1.3540934
G0 ( 2S, 4S ) = 0.0360927
F0 ( 2P, 4S ) = 1.3656926
G1 ( 2P, 4S ) = 0.0470113
F0 ( 3S, 4S ) = 1.2417579
G0 ( 3S, 4S ) = 0.0731233
F0 ( 3P, 4S ) = 1.2456360
G1 ( 3P, 4S ) = 0.0970607
F0 ( 3D, 4S ) = 1.2575990
G2 ( 3D, 4S ) = 0.0933364
F0 ( 4S, 4S ) = 0.9834943
F0 ( 1S, 4P ) = 1.3609320
G1 ( 1S, 4P ) = 0.0507997
```

```
F0 ( 2S, 4P ) = 1.2826304
G1 ( 2S, 4P ) = 0.0334143
F0 ( 2P, 4P ) = 1.2967139
G0 ( 2P, 4P ) = 0.0403225

F0 ( 3S, 4P ) = 1.1757869
G1 ( 3S, 4P ) = 0.0751509
F0 ( 3P, 4P ) = 1.1800159
G0 ( 3P, 4P ) = 0.0717858
F0 ( 3D, 4P ) = 1.1908785
G1 ( 3D, 4P ) = 0.0840928
F0 ( 4S, 4P ) = 0.9492346
G1 ( 4S, 4P ) = 0.6501771
F0 ( 4P, 4P ) = 0.9184933
F0 ( 1S, 4D ) = 1.0641168
G2 ( 1S, 4D ) = 0.0016658
F0 ( 2S, 4D ) = 1.0501422
G2 ( 2S, 4D ) = 0.0709562
F0 ( 2P, 4D ) = 1.0544768
G1 ( 2P, 4D ) = 0.0748431
F0 ( 3S, 4D ) = 0.9729201
G2 ( 3S, 4D ) = 0.0359127
F0 ( 3P, 4D ) = 0.9755160
G1 ( 3P, 4D ) = 0.0386036
F0 ( 3D, 4D ) = 0.9860556
G0 ( 3D, 4D ) = 0.0568758

F0 ( 4S, 4D ) = 0.8285444
G2 ( 4S, 4D ) = 0.3818391
F0 ( 4P, 4D ) = 0.8074265
G1 ( 4P, 4D ) = 0.5092127

F0 ( 4D, 4D ) = 0.7267250

F0 ( 1S, 5S ) = 0.3873893
G0 ( 1S, 5S ) = 0.0015319
F0 ( 2S, 5S ) = 0.3830120
G0 ( 2S, 5S ) = 0.0019915
F0 ( 2P, 5S ) = 0.3836641
G1 ( 2P, 5S ) = 0.0026108
F0 ( 3S, 5S ) = 0.3767528
G0 ( 3S, 5S ) = 0.0036220
F0 ( 3P, 5S ) = 0.3769680
G1 ( 3P, 5S ) = 0.0049325
F0 ( 3D, 5S ) = 0.3776299
G2 ( 3D, 5S ) = 0.0047806
F0 ( 4S, 5S ) = 0.3638482
G0 ( 4S, 5S ) = 0.0102096
F0 ( 4P, 5S ) = 0.3623099
G1 ( 4P, 5S ) = 0.0153445
F0 ( 4D, 5S ) = 0.3553171
G2 ( 4D, 5S ) = 0.0387228
F0 ( 5S, 5S ) = 0.2798667
```

```
G2 ( 2P, 4P ) = 0.0461829
```

```
G2 ( 3P, 4P ) = 0.0859786
```

```
G3 ( 3D, 4P ) = 0.0822176
```

```
F2 ( 4P, 4P ) = 0.4839859
```

```
G3 ( 2P, 4D ) = 0.0437416
```

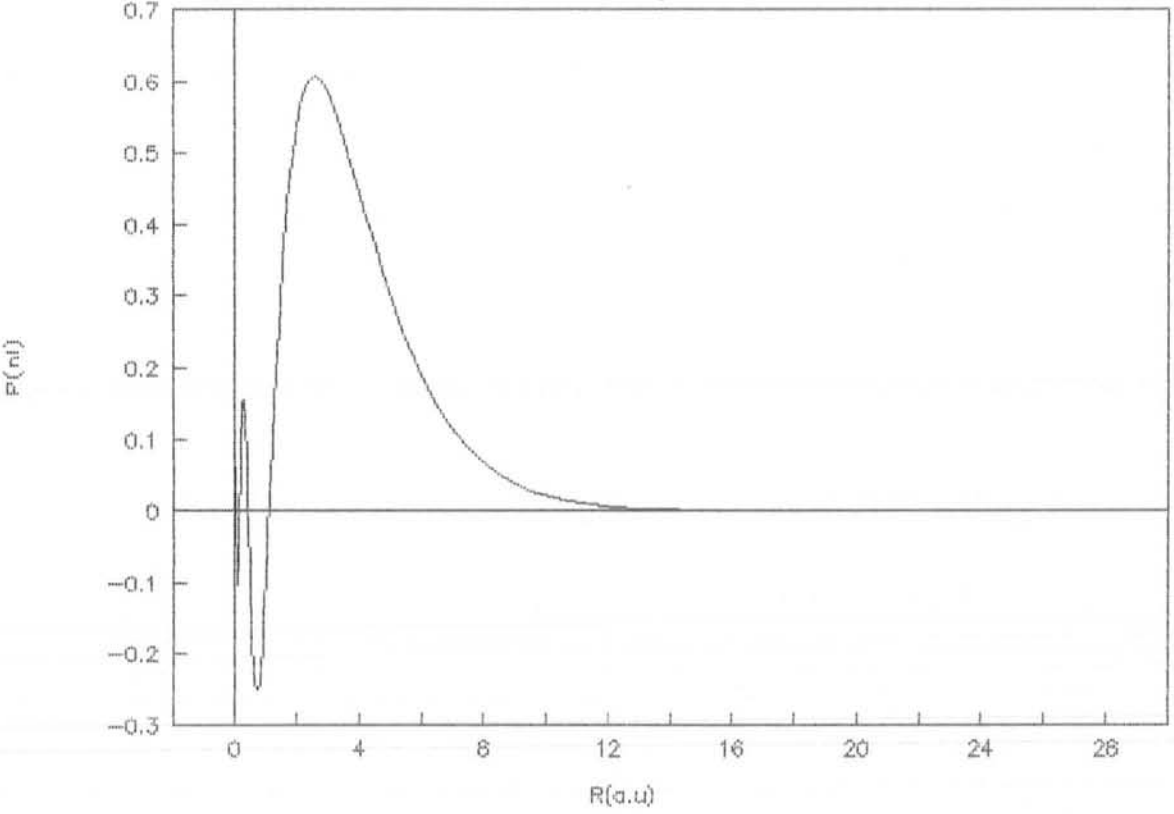
```
G3 ( 3P, 4D ) = 0.0399157
```

```
G2 ( 3D, 4D ) = 0.0664216
G4 ( 3D, 4D ) = 0.0507162
```

```
G3 ( 4P, 4D ) = 0.3116717
```

```
F2 ( 4D, 4D ) = 0.3621135
F4 ( 4D, 4D ) = 0.2364975
```

Fig 2.2(iv) Radial wave function of
5s electron in Cd ground state



CHAPTER 3

CURVE FITTING PROGRAM

3.1 INTRODUCTION

In chapter 1 it was described that the problem with using approximations based on monomials is that the error over an interval centered at 0 is extremely non-uniform, small near the center but growing very rapidly near the end points. It would seem more reasonable to use an approximating functions instead of powers of x, polynomials whose behavior over an interval centered at 0 would be in some sense uniform. We would hope that functions formed from combinations of these polynomials would exhibit a more uniform error behavior. Such functions were introduced in chapter 1 and are known as Chebyshev polynomials. Some properties of Chebyshev polynomials[6] are given below.

Fourier expression for orthogonality of Chebyshev polynomials is given by

$$\int_0^{\pi} \cos m\theta \cos n\theta \, d\theta = \begin{cases} 0 & m \neq n \\ \pi/2 & m = n \\ \pi & m = n = 0 \end{cases} \qquad (3.1)$$

$$= \int_{-1}^{+1} T_m(Z)\, T_n(Z) \frac{dZ}{\sqrt{1 - Z^2}} \, .$$

Using the trigonometric expressions

(1) $\cos(n+1)\theta + \cos(n-1)\theta = 2\cos\theta\cos n\theta$ (3.2)

(2) $\cos(m+n)\theta + \cos(m-n)\theta = 2\cos m\theta\cos n\theta,$ (3.3)

we arrive at the following relations

$$T_{n+1}(Z) + T_{n-1}(Z) = 2\,Z\,T_n(Z)\,, \tag{3.4}$$

$$T_{m+n}(Z) + T_{m-n}(Z) = 2\,T_m(Z)\,T_n(Z). \tag{3.5}$$

Eq. (3.4) is a three term recurrence relation. For $m = n$, Eq. (3.5) yields

$$T_{2n}(Z) = 2\,T_n^2(Z) - 1.$$

First 13 Chebyshev polynomials are given in table 3.1.

The n roots of $T_n(Z)$ are real, occur in the interval $[-1,1]$ and are given by

$$\lambda_i = \frac{\cos\left[(2i - 1)\pi\right]}{2\,n}\,, \quad i = 1,\dots,n.$$

A very useful property of these polynomials is that of all the polynomial of degree n with the coefficient of the nth power term equal to 1, the polynomial,

$$\phi_n(Z) = \frac{T_n(Z)}{2^{n-1}},$$

has the smallest upper bound for its absolute value on the interval $[-1,1]$.

3.2 PROGRAM DESCRIPTION

This program reads a set of data (X_i, Y_i). It linearly transforms the x-coordinate $a \le X \le b$ to Z-coordinate by using

$$Z = \frac{2X-b-a}{b-a}, \qquad X \text{ in } [a,b], \quad Z \text{ in } [-1,1]. \tag{3.6}$$

It finds the Chebyshev coefficients using table 3.1 and expands the polynomial in terms of chebyshev coefficients

$$f(Z)=C_0T(0,Z)+C_1T(1,Z)+C_2T(2,Z)+\dots\dots+C_nT(n,Z),$$

where n may take on values up to 12.

Table 3.1

$T_0(Z) = 1.$

$T_1(Z) = Z.$

$T_2(Z) = 2Z^2 - 1.$

$T_3(Z) = 4Z^3 - 3Z.$

$T_4(Z) = 8Z^4 - 8Z^2 + 1.$

$T_5(Z) = 16Z^5 - 20Z^3 + 5Z.$

$T_6(Z) = 32Z^6 - 48Z^4 + 18Z^2 - 1.$

$T_7(Z) = 64Z^7 - 112Z^5 + 56Z^3 - 7Z.$

$T_8(Z) = 128Z^8 - 256Z^6 + 160Z^4 - 32Z^2 + 1.$

$T_9(Z) = 256Z^9 - 576Z^7 + 432Z^5 - 120Z^3 + 9Z.$

$T_{10}(Z) = 512Z^{10} - 1280Z^8 + 1120Z^6 - 400Z^4 + 50Z^2 - 1.$

$T_{11}(Z) = 1024Z^{11} - 2816Z^9 + 2816z^7 - 1232Z^5 + 220Z^3 - 11Z.$

$T_{12}(Z) = 2048Z^{12} - 6144Z^{10} + 6912Z^8 - 3584Z^6 + 840Z^4 - 72Z^2 + 1.$

The program finds the coefficients $C_0, C_1, \ldots C_n$ using least square method which is as follows. If there are m number of observations and T_{ij} is the value of the polynomial T_j evaluated at ith point, our task is to choose $C_0, C_1, \ldots C_n$ that minimize the sum of squares,

$$S = \sum_{i=1}^{m} \left(f(Z_i) - \sum_{j=0}^{n} C_j \, T_{ij}\right)^2$$

S will be minimum when $\frac{\partial S}{\partial C_k} = 0$, where $k=0,1,..n$.This permits us to write

$$\sum_{j=0}^{n} C_j \sum_{i=1}^{m} T_{ik} \, T_{ij} = \sum_{i=1}^{m} T_{ik}\left(f(Z_i)\right)$$

Define $\mathbb{T}$ as the m x (n + 1) matrix containing T_{ij} in its ith row and jth column

$$\mathbb{T} = \begin{pmatrix} T_{10} T_{11} \ldots T_{1n} \\ \vdots \qquad \vdots \\ T_{m0} T_{m1} \ldots T_{mn} \end{pmatrix}$$

and also define the following column vectors

$$f(Z) = \left(f(Z_1) \ldots\ldots f(Z_m)\right)^t, \quad \mathbb{C} = \left(C_0 \ldots\ldots C_n\right)^t.$$

The system of normal equations can be written in the equivalent form

$$\mathbb{T}^t \mathbb{T} \, \mathbb{C} = \mathbb{T}^t f(Z)$$

which has the solution,

$$\mathbb{C} = \left(\mathbb{T}^t \mathbb{T}\right)^{-1} \mathbb{T}^t f(Z)$$

where the general element of $\mathbb{T}^t \mathbb{T}$ is given by $\sum_{i=1}^{m} T_{ik} T_{il}$.

For orthogonal polynomials, we have

$$\sum_{i=1}^{m} T_{ik} T_{il} = 0 \qquad \text{for } k \neq l$$

$$C = \frac{\sum_{i=1}^{m} T_{ij} f(Z_l)}{\sum_{i=1}^{m} T_{ij}^2} \qquad j=0,1,\ldots\ldots,n$$

After determining the coefficients $C_0\ C_1; C_2, \ldots\ldots, C_n$, it converts the coefficients of T to those of coefficients of Z i.e.

$$f(Z_i) = C_0 + C_1\ Z_i\ + \ldots\ldots\ldots + C_n\ Z_i^n$$

Finally above equation should be transformed to the original variable Z on the interval [a,b] using (3.7) to yield,

$$f(X) = C_0 + C_1 X + \ldots\ldots\ldots\ldots + C_n\ X^n$$

Then for each X, f(X) i,e wavelength is calculated. The program then prints the X-values, the wavelengths given and calculated ,the residuals i,e calculated minus given wavelength and the error in Y_i resulting from the errors in the coefficient which is given by

$$dY_i = \left[\sum_{i=0}^{n} (dC_i T_i)^2 \right]^{1/2}$$

where dC_i is the error in the coefficient of C. The error does not refer to the error of wavelength of the line but rather to the error in the accuracy of the polynomial fit at that point. The residuals of the fit are then plotted. Following this plot in the program, output is a statistical summary. Four measures of the scatter of the points about the least square fit and the quality of the fit are given. They are defined as follows ,where

ϵ_i = residual of the ith point.
w_i = weight of the ith point.
m = number of standards with non-zero weight.
n = number of coefficients used in the fit.

The standard deviation (for unit weight) is given by

$$= \left[\frac{\sum_{i=1}^{m} \epsilon_i^2 \; w_i}{m - n} \right]^{1/2}$$

[13]

The weighted standard deviation is

$$\left[\frac{m \quad \sum_{i=1}^{m} \epsilon_i^2 \; w_i}{m - n \sum_{i=1}^{m} w_i} \right]^{1/2}$$

The probable error = 0.6744898 x the weighted standard deviation.

Mean error of weighted mean is given by,

$$\left[\frac{\sum_{i=1}^{m} \epsilon_i^2 \; w_i}{m - n \sum_{i=1}^{m} w_i} \right]^{1/2}$$

It is a measure of the overall uncertainty of the fit, rather than the scatter of points about the mean. However, for most purposes, the ERROR column will be a more useful guide to the uncertainty of the fit at each standard.

If all measurements are expected to be equally accurate i,e all are of the same weight, subject only to random errors of measurements, then a histogram of the residuals for many observations should be a Gaussian distribution. The standard deviation of the sample is a measure of the width of this distribution. However, when relative weights are introduced, the problem is more complicated. If many observations of each weight are included, the distribution of all observations of any weight should be Gaussian, but relative widths of the Gaussian distributions should be inversely proportional to the square root of the weight of each Gaussian. The overall distribution of residuals is therefore a sum of Gaussians of different widths but the distribution of $\epsilon_i w_i$ should give the same distribution for all weights. The standard deviation for unit weight can be used to find the widths of the distributions of points of any weight, w, simply by multiplying the standard deviation for unit weight by $1/(w)^{1/2}$. As a crude check that the experimenter has a reasonable scale of widths, the program will divide the standards into two or three classes (high and low weights for two classes; high, medium and low weights for three classes). It then computes and prints the standard deviation (for unit weight) for each class. If enough points exist in each class for this number to be significant, then the standard deviation (for unit weight) should be approximately equal for all classes. If it varies considerably, the weight scale should be revised. Following these statistics if the fit is satisfactory, the coefficients of Chebyshev polynomials are listed, with their standard errors. If the magnitudes of the coefficients are all considerably larger than their errors, it may be desirable to increase the order of the polynomial.

3.3 SUMMARY OF SUBROUTINES

Main.	Main program reads input data and controls the overall calculations.
Waveno.	Converts wavelength to wave number.
Graph.	Does statistics and graphs the fit to standard.
Disp.	Tabulates and graphs the dispersion at each standard.
Extrap.	Identifies where the fit must be extrapolated for the unknowns.
Prepar.	Helps set up formats.
Cheby.	Controls iteration to find a fit to the standards.
Tcalc.	Transform X coordinate into Z and computes T for Chebyshev polynomials.
Tprint.	Prints chebyshev coefficients.
Abcalc.	Calculates A's and B's for matrix to be inverted for least-squares solution.
Horner.	Calculates Wave = SUM(X**(I-1)*C(I)).
Matinv.	Inverts the matrix to obtain least-squares solution and to allow computation of error from errors in coefficients of the solution.
Ercalc.	Calculates error in wavelength of unknowns due to errors in the fit.
Convrt.	Converts the coefficients of T to coefficients of powers of Z and coefficients of powers of Z to those of powers of X.
Funct1 & Funct2.	Their purpose is to find a least-square fit of the function other than polynomial.

3.4 DATA INPUT

CARD ONE WITH IDENT, TOLMIN, NMIN, NMAX, ITRMAX,

(JOP),I=1,10), MF, ACC, LREAD, LXFACT, DEC, JOPRPT and LFAC, in the format

(A72/F9.4,3I2,10I1,I6,F5.2,2I1,5A1,2I1).

IDENT. Used to label the spectrum.

TOLMIN. the largest acceptable difference between the calculated and observed Y-values, that is, the tolerance for fitting a data point to the polynomial. If the residual is greater than TOLMIN, the point is rejected.

NMIN & NMAX. These are the minimum and maximum values for the acceptable number of constants (N) in the fitting polynomial. Ordinarily, NMIN will be tried first, and if a fit cannot be obtained before rejecting ITRMAX points, N will be increased by one This will continue until N = NMAX has been tried. If still no fit has been obtained, the program prints an explanatory message and then goes to the next plate. If, however, it is decided to allow the machine to find the best value for N, the first attempt will be made with NMAX.

ITRMAX. This is the number of passes that will be made in trying to fit the points within the tolerance. It is one greater than the allowed number of points to be rejected while trying to fit the points.

JOP(I), I= 1,10 These ten options are used that permits arbitrary weighting of the data points, calculation of dispersion across the plate (dY/dX), rejection of points that deviate too widely from the probable error of the fit, conversion of air or vacuum wavelengths to wave numbers, automatic best adjustment of the degree of the polynomial, conversion of wave numbers to Lorentz units for the case of Zeeman spectrograms, placement of decimal points, curve fitting of functions other than polynomials, etc.

MF. The magnetic field intensity, in gauss, for Zeeman plates.

ACC. If it is preferred not to supply in advance an absolutely fixed value for TOL, the program will calculate a value based on the standard deviation of the fit The resultant TOLMIN will be taken as ACC times the standard deviation This is done by using JOP(2) option.

DEC. The number of decimal places to which results are outputted.

JOPRPT. If its value is '1' then fitting of function other than polynomial is done.

LFAC. This is an integer quantity that determines the degree of expansion of the vertical scale of the plot. Each line on a page of printed output will have a scaled width in X-units equal to AVSEP/LFAC, where AVSEP is the average separation between successive X-values.

CARD TWO WITH XI, Y(I)

in the format,

(F14.5,5X,F12.5).

XI. The value of standards, maximum number of which can be 385.

Y(I). The experimentally calculated value of wavelength ,its maximum number is also 385.

CARD THREE WITH W(J)

in the format

(10F5.0).

W(J). The value of weight assign to each standard.

CARD FOUR WITH ITERW

in the format

(I1).

Its value '1' will cause the program after a polynomial fit to the standards, to have a new fit for the same value of standards but different weighting.

CARD FIVE WITH UJ

in the format

(f14.5).

UJ. This card is used after the polynomial fit has been obtained to find Y-values for a given set of X-values.

3.5 MAIN FEATURES OF PROGRAM.

1) In order to obtain a more accurate solution of the normal equations the X-values are first reduced so as to lie in the range $-1 \leq X \leq 1$, and Chebyshev polynomials are used as the coordinate functions. After the fit has been obtained, the results are modified and for convenience re-expressed in terms of powers of X. Double precision arithmetic is used throughout.

2) The tolerance, TOLMIN, is the largest acceptable difference between the calculated and observed values of an X-Y data point or standard wavelength. If any difference exceed this tolerance, the standard that is most in error will be rejected and a new attempt at fitting will be made. One may specify how many passes (ITRMAX) should be made before giving up trying to fit the lines. Up to 20 tries may be made. That is up to 19 lines may be discarded, one at a time, while trying to fit the standards to within the designated tolerance. TOLMIN may either be specified in advance, or one may allow the computer to pick its own tolerance based on the standard deviation of the fit.

3) If ever the number of constants (N) specified for the polynomial equals or exceeds the number of standards remaining in a particular iteration, a message to that effect is written. In this case, of course, the fit should be exact and may or may not have meaning, depending upon the problem. In the case of an exact fit, the tolerance is internally set to 0.001 to prevent computer round-off error from showing up on the plot.

4) The residuals of the fit are plotted on a scale extending from minus TOL to plus TOL. If any residual exceeds the tolerance, the word OUT will be printed at the left or right edge of the plot, depending upon the sign of the residual.

5) A standard line that is discarded is not used in the succeeding trials at fitting, but it is still listed and identified by a double asterisk on the printout. Its new calculated wavelength is printed out to assist in its correct identification.

6) Ordinarily a weight of unity will be assigned to each standard. An arbitrary set of weights may, however, be supplied at object time.

7) It is essential that the set of standards be arranged in algebraically ascending or descending order.

2.6 ENERGY LEVEL CALCULATIONS FOR KRI

```
     SPECTRUM OF KR


 TOLERANCE       NMIN     NMAX                  ITRMAX     OPTIONS

    0.4000         1           3                   3       5312432001


     SPECTRUM OF KR
 THIS IS TRY NUMBER  1 WITH N =  3           SET NUMBER 1    THE TOLERANCE FOR THIS FIT IS     0.0067
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
    X    LAB.     CALC.  ERROR     RESID        WT    -TOL                        ZERO                      +TC
300.85  496.07  496.07 0.00546    -0.00010     1.00    .                          *
                                                       .                          .
                                                       .                          .
                                                       .                          .
226.20  471.23  471.22 0.00458     0.00064     1.00    .                          !  *
                                                       .                          .
200.54  462.71  462.70 0.00220     0.00164     1.00    .                          !     *
188.45  458.69  458.69 0.00211    -0.00673     1.00    .*                         !
180.67  456.12  456.11 0.00357     0.00372     1.00    .                          !              *
176.48  454.73  454.72 0.00463     0.00310     1.00    .                          !           *
173.48  453.73  453.73 0.00546    -0.00226     1.00    .                 *        !
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
 THE AVERAGE SEPARATION BETWEEN LINES =    21.2283 X-UNITS    LFAC = 1
 THE NUMBER OF STANDARDS MEASURED ON THIS PLATE =   7  SMDEVSQ = 7.697202E-05
 THE STANDARD DEVIATION (FOR UNIT WEIGHT) FROM 7 RESIDUALS = 0.0044  TESTN = 3.7074E-03
 THE WEIGHTED STANDARD DEVIATION =    0.0044       CTEST = 1.3938E-02
 THE PROBABLE ERROR = 0.0030   MEAN ERROR OF WEIGHTED MEAN = 0.0000
```

```
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
     SPECTRUM OF KR
 THIS IS TRY NUMBER  2 WITH N =  3            SET NUMBER 1     THE TOLERANCE FOR THIS FIT IS      0.0036
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
   X    LAB.   CALC.    ERROR   RESID      WT    -TOL                      ZERO                      +TOL
300.85 496.07 496.06 0.00339   0.00012     1.00    .                          !*                         .
                                                   .                          .                          .
                                                   .                          .                          .
                                                   .                          .                          .
226.20 471.23 471.23 0.00284  -0.00078     1.00    .                    *     !                          .
                                                   .                          .                          .
200.54 462.71 462.70 0.00136   0.00014     1.00    .                          !*                         .
188.45 458.69 458.69 0.00131  -0.00818 **  0.00    .                          !                          .
180.67 456.12 456.11 0.00222   0.00233     1.00    .                          !                *         .
176.48 454.73 454.72 0.00287   0.00176     1.00    .                          !            *             .
173.48 453.73 453.73 0.00339  -0.00357     1.00    .*                         !                          .
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
 THE AVERAGE SEPARATION BETWEEN LINES =    21.2283 X-UNITS    LFAC = 1
 THE NUMBER OF STANDARDS MEASURED ON THIS PLATE =  7 SMDEVSQ = 2.192573E-05
 THE STANDARD DEVIATION (FOR UNIT WEIGHT) FROM 6 RESIDUALS = 0.0027 TESTN = 2.2073E-03
 THE WEIGHTED STANDARD DEVIATION =    0.0027      CTEST = 1.3557E-02
 THE PROBABLE ERROR =  0.0018   MEAN ERROR OF WEIGHTED MEAN = 0.0000
```

```
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
     SPECTRUM OF KR
 THIS IS TRY NUMBER  3 WITH N =  3            SET NUMBER 1     THE TOLERANCE FOR THIS FIT IS      0.0005
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
   X    LAB.   CALC.    ERROR   RESID       WT      -TOL                      ZERO                      +TOL
300.85 496.07  496.07 0.00066  0.00000      1.00    .                          *                          .
                                                    .                          .                          .
                                                    .                          .                          .
                                                    .                          .                          .
226.20 471.23  471.22 0.00054  0.00006      1.00    .                          !  *                       .
                                                    .                          .                          .
200.54 462.71  462.71 0.00024 -0.00020      1.00    .                *         !                          .
188.45 458.69  458.69 0.00030 -0.00935 **   0.00    .                          !                          .
180.67 456.12  456.11 0.00051  0.00054      1.00    .                          !                         *.
176.48 454.73  454.73 0.00066 -0.00040      1.00    .       *                  !                          .
173.48 453.73  453.73 0.00066 -0.00600 **   0.00    .                          !                          .
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
 THE AVERAGE SEPARATION BETWEEN LINES =    21.2283 X-UNITS   LFAC = 1
 THE NUMBER OF STANDARDS MEASURED ON THIS PLATE = 7 SMDEVSQ = 4.948457E-07
 THE STANDARD DEVIATION (FOR UNIT WEIGHT) FROM 5 RESIDUALS = 0.0005  TESTN = 3.8530E-04
 THE WEIGHTED STANDARD DEVIATION =    0.0005    CTEST = 1.4059E-02
 THE PROBABLE ERROR =    0.0003   MEAN ERROR OF WEIGHTED MEAN = 0.0000
```

```
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
   TO OBTAIN A FIT WITH N =  3 AND TOLERANCE =     0.0005, WE WOULD HAVE TO REJECT MORE THAN  2 STANDARDS.
   WE ARE ACCEPTING THE LAST PRECEDING FIT THATFELL WITHIN A TOLERANCE,
   NAMELY TRY NUMBER  3 WITH N =  WITH N =  3
   THE COEFFICIENTS OF THE CHEBYSHEV POLYNOMIALS   AND THEIR ERRORS ARE AS FOLLOW
               1      4.7538613997D+02    -2.4354687359D-05
               2     -2.0669802961D+01     3.0478365959D-04
               3      1.4059282987D-02     5.7956304762D-04
   THE COEFFICIENTS TRANSFORMED INTO A POWER SERIES AND THEIR ERRORS ARE AS FOLLOWS


               1      3.9645590905D+02     9.6824313684D-03
               2      3.2892121541D-01    -7.6441109816D-05
               3      7.2714645449D-06     1.4987507387D-07
```

```
    SPECTRUM OF KR
 DY/DX FOR TRY NUMBER  3 WITH N    3             SET NUMBER 1              /DISPERSION PLOT/
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


300.85  496.07 0.33330    .
                          .
                          .
                          .
226.20  471.22 0.33221    .                                  *
                          .
200.54  462.71 0.33184    .                 *
188.45  458.69 0.33166    .         *
180.67  456.11 0.33155    .    *
176.48  454.73 0.33149    . *
173.48  453.73 0.33144    .*
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
 THE AVERAGE SEPARATION BETWEEN LINES =    21.2283 X-UNITS   LFAC = 1
```

```
  SPECTRUM OF KR

 X          LAMBDA        ERROR       SIGMA

330.10     505.82514     0.00000     197696.77534
329.80     505.72503     0.00000     197735.91240
329.60     505.65829     0.00000     197762.01210
328.45     505.27452     0.00000     197912.21474
327.73     505.03426     0.00000     198006.36702
324.05     503.80639     0.00000     198488.94582
323.85     503.73967     0.00000     198515.23811
323.30     503.55617     0.00000     198587.57665
322.53     503.29929     0.00000     198688.93630
316.70     501.35458     0.00000     199459.63282
150.75     446.20603     0.00000     224111.71788
 27.70     405.57261     0.00000     246564.97631
 26.35     405.12803     0.00000     246835.54863
 25.00     404.68348     0.00000     247106.69926
 23.10     404.05787     0.00000     247489.30193
 22.75     403.94263     0.00000     247559.90712
 22.55     403.87678     0.00000     247600.27055
 21.70     403.59692     0.00000     247771.95806
 21.00     403.36646     0.00000     247913.52181
 20.40     403.16893     0.00000     248034.98750
 19.80     402.97140     0.00000     248156.56904


THE NUMBER OF SPECTRAL  LINES  ON THIS PLATE=    21
```

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