CHAPTER IV

THE COHESIVE ENERGY CALCULATION WITH ANALYTICAL MODEL POTENTIALS

4.1 Wigner and Seitz[10,13]'s Numerical Calculation

The cellular method is utilized in the Wigner and
Seitz's calculation. The procedure requires the use of state
wave function near the bottom of the band which can be
written in the Bloch form

$$\Psi_{\vec{k}}(\vec{r}) \quad = \quad e^{i\vec{k}.\vec{r}} \quad u_o(\vec{r}) \quad . \qquad (4.1)$$

Equation (4.1) is an approximation of the true wave
function

$$\Psi_{\vec{k}}(\vec{r}) \quad = \quad e^{i\vec{k}.\vec{r}} \quad u_{\vec{k}}(\vec{r}) \quad , \qquad (4.2)$$

where $u_o(\vec{r})$ and $u_{\vec{k}}(\vec{r})$ are periodic within the atomic
cell. $u_o(\vec{r})$ satisfies the boundary condition (2.4).
Substituting the function $\Psi_{\vec{k}}(\vec{r})$ in (4.2) into the
Schrödinger equation (in atomic units), we get

$$(-\nabla^2 + V)u_{\vec{k}} - 2i\vec{k}.\vec{\nabla}u_{\vec{k}} \quad = \quad (E(\vec{k}) - k^2)u_{\vec{k}} , \qquad (4.3)$$

where $u_{\vec{k}}(\vec{r})$ can be expanded as a series in k

$$u_{\vec{k}}(\vec{r}) \quad = \quad \sum_{n=o}^{\infty} u_n(\vec{r})k^n \quad . \qquad (4.4)$$

The energy can be expressed in even powers of k , i.e.,

$$E(\vec{k}) = \sum_{n=o}^{\infty} E_{2n} k^{2n} \qquad . \qquad (4.5)$$

The odd powers of k are absent because of the inversion symmetry in $E(\vec{k})$. By replacing (4.4) and (4.5) into (4.3) and equating the coefficients of k^n, we obtain

$$(-\nabla^2 + V - E_o)u_o = 0 \qquad , \qquad (4.6a)$$

$$(-\nabla^2 + V - E_o)u_1 = 2i\hat{k}.\vec{\nabla}u_o \qquad , \qquad (4.6b)$$

$$(-\nabla^2 + V - E_o)u_2 = 2i\hat{k}.\vec{\nabla}u_1 + (E_2-1)u_o , \qquad (4.6c)$$

$$(-\nabla^2 + V - E_o)u_n = 2i\hat{k}.\vec{\nabla}u_{n-1} + (E_2-1)u_{n-2}$$

$$+ E_4 u_{n-4} + \cdots, \qquad (4.6d)$$

where $\hat{k}$ is the unit vector in the direction $\vec{k}$. These equations were first solved for the values of E_2, the effective mass, by Bardeen[18] and for E_4 by Silverman[30]. Since we are not interested in the band structure calculation, the procedure for obtaining E_2 and E_4 are omitted here, only their values are presented in table 4.2. Callaway[29], following Bardeen, Silverman and Brook[27], has found that the average energy per atom in state $\vec{k}$ is

$$E_b = E_o + E_k \qquad , \qquad (4.7)$$

where

$$E_k = \frac{2.21\ E_2}{r_s^2} + \frac{5.81\ E_4}{r_s^4} \ . \tag{4.8}$$

The value of E_o is obtained from (4.6a) which is of the same form as (2.1). This is due to the fact that according to either (4.1) or (4.2), $\Psi_o(\vec{r})$ is equal to $u_o(\vec{r})$ at $\vec{k} = 0$. Our problem at present is considered to have spherical symmetry and only the lowest state energy has been treated. For the sake of simplicity, we represent $\Psi_o(\vec{r})$ by $\Psi(\vec{r})$. The radial Schrödinger equation (2.3) is considered together with the boundary condition (2.4). It is convenient to let

$$f(r) = r\Psi(r) \ . \tag{4.9}$$

Substituting (4.9) into (2.3) , we obtain

$$\frac{d^2f}{dr^2} + (E - V(r)\ f(r) = 0 \ . \tag{4.10}$$

The boundary condition (2.4) becomes

$$\frac{df}{dr} = \frac{f}{r} \quad \text{at} \quad r = r_s. \tag{4.11}$$

In the calculation of the ground state energy for Na, Wigner and Seitz used Prokofjew's[15] analytical potential form. They started the calculation from the origin since the wave function must be zero there. Near $r = 0$, the

asymptotic wave function can be written explicitly as $r^{\ell+1}$, where ℓ is the angular momentum quantum number. This wave function form was used up to a distance $r = 0.025$ in step intervals of 0.005. The method of finite difference was used. The magnitude of the difference were increased by doubly the previous difference until the largest difference was 0.32. After obtaining the curve of function $f(r)$, condition (4.11) was then tested. If this was not fulfill, a new value of energy was tried. There is only one curve of $f(r)$ which would satisfy the condition. This value of r for which (4.11) is satisfied, is the atomic sphere radius r_s.

4.2 Heine-Abarenkov[31,32] Type Model Potentials with Parameter Determined by Cowley et.al[14]

The Hartree-Fock self-consistent potential in solid can be considered into two regions : A and B in fig.(4.1). In region A which is inside the sphere, the potential is very strong especially at the nucleus and decreases in the region of the core of atom. In region B, the remaining interstitial region, the potential varies slowly[33]. The best known strong model potential is the Prokofjew's potential for Na.
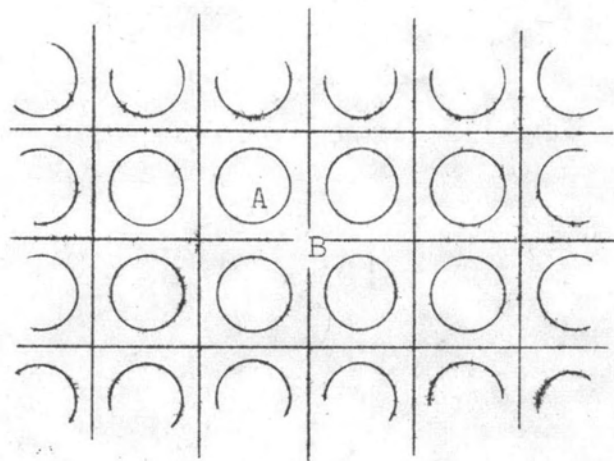
Fig. 4.1   The potential in two regions : the strong
            potential in A and the weak potential
            in B.

    The Heine-Abarenkov potential may be considered
as the potential in which the core acting on a valence
electron in an atom.   Instead of using the actual potential
in an atom, the psuedo-potential is considered.   The idea
of the psuedo-potential[33] will not be discussed here.   We
refer only to the form of the potential[32]

$$V_\ell(r) \;=\; -\frac{Z}{r} + \frac{(Z - Ar)}{r}\,\exp(-(r/R_M)^6) \qquad , \qquad (4.12)$$

here   Z   is the ionic charge. A and R_M are constants.
The potential in the form of   (4.12)   has the asymptofic
behavior for large r as $\frac{1}{r}$ and for small r, it
approaches a constant value. The psuedo-potential is. ,
however, not used in the cohesive energy calculation. The
form of potential to be used in the cohesive energy
calculation was introduced by Cowley et.al. and is as
follows

$$V_\ell(r) \;=\; -\frac{Z}{r} - \frac{(Z_N - Z)}{r} \exp(-\alpha_\ell r) \qquad , \qquad (4.13)$$

where Z_N and Z represent the nuclear and ionic charge
respectively. Since only the alkali metals are treated
here, Z is thus equal to one. α_ℓ is the parameter
which characterizes the ℓ -potential. For large r, the
potential in (4.13) has asymptotic form similar to those
of (4.12). Figure 4.2 shows graphically the four
different model potentials, the pure Coulomb potential,
the screened Coulomb potential, the Heine-Abarenkov type
model potential and the Cowley et.al.'s potential. Cowley
et.al. obtained the values of the parameter α_ℓ by using
the following numerical technique. One starts with the
observed energy levels of the atom and initial guess value
of α_ℓ . Then the radial Schrödinger equation is
integrated both outwards from the origin and inwards from
the infinity to match at a suitable point. As a result,

V(r)
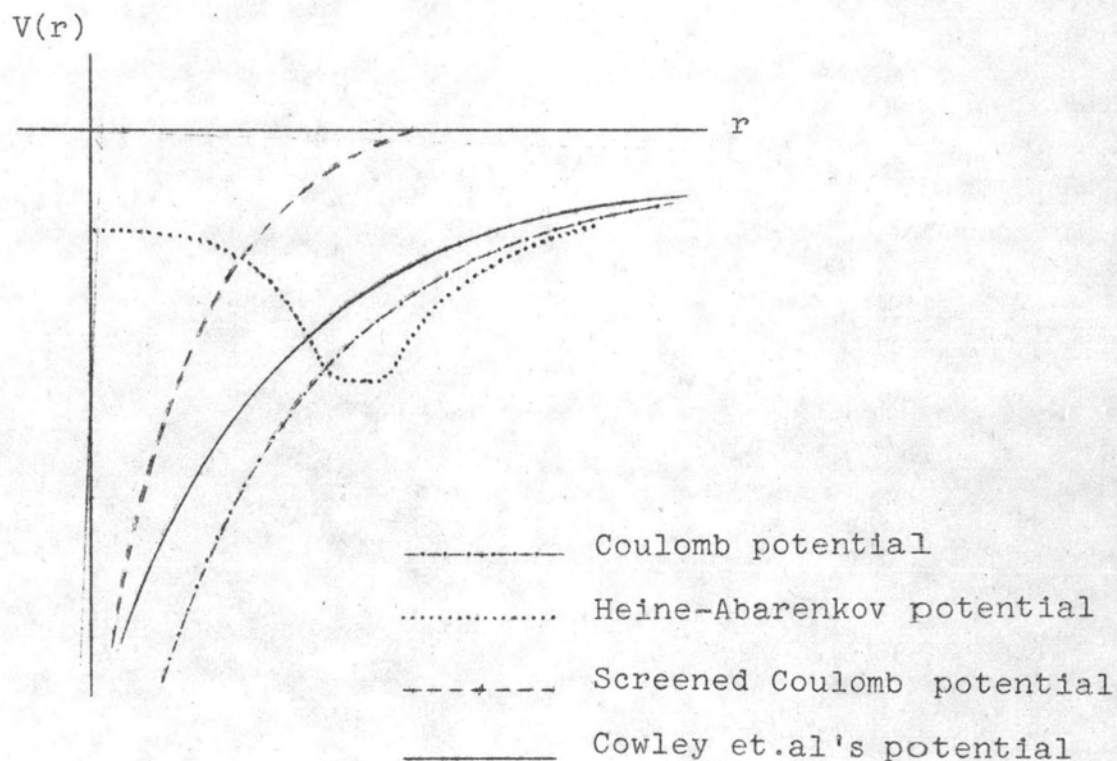
Fig. 4.2 Diagram showing four different type model potentials.

two values of the logarithmic derivative were obtained.
α_ℓ was adjusted until the two values were considerably
equal. This yielded the value of α_ℓ at that state. In
table 4.1 the values of α_ℓ for all states with given
ℓ are shown.

Element	α_s	α_p	α_d	Z_N
Li	2.1024	2.3397	2.0513	3
Na	2.3641	2.4063	2.0222	11
K	2.0545	2.1340	2.0044	19
Rb	2.4550	2.5550	2.3658	37
Cs	2.4333	2.5336	2.3814	55

Table 4.1[14] Fitted values of α_ℓ and nuclear
charge Z_N for alkali metals.

4.3 The Numerical Calculation of the Ground State Energy

The following diagram expresses the crude flow
chart use to calculate the lowest state energy for alkali
metals. It is not an actual flow chart in our program,
but is written for the purpose of the description.

```
                    ┌─────────────────────────────┐
                    │  input ℓ,α_ℓ,n,2_N,r_s       │
                    │  input initial energy        │
                    └─────────────────────────────┘
                                 │
                    ┌─────────────────────────────────────┐
                    │ compute asymptotic values of f(r)(WAVEFT)│
                    │            f_{1-5}                    │
                    └─────────────────────────────────────┘
   ┌──────────────┐                │
   │ set new trial│                │
   │   energy     │───────────────►│
   └──────────────┘     ┌──────────────────────┐
                        │ compute f''_{1-5} (FYY)│
                        └──────────────────────┘
                                 │
           ┌─────────────────────────────────────────┐
           │ compute other values of f(r) (YNEX1,YNEX2)│
           │              f_{6-765}                    │
           └─────────────────────────────────────────┘
                                 │
                             test boundary
                    No        condition
              ◄───────────   of f(r) at r_s
                               (WAVEFT)
                                 │ Yes
                              ┌──────┐
                              │ stop │
                              └──────┘
```
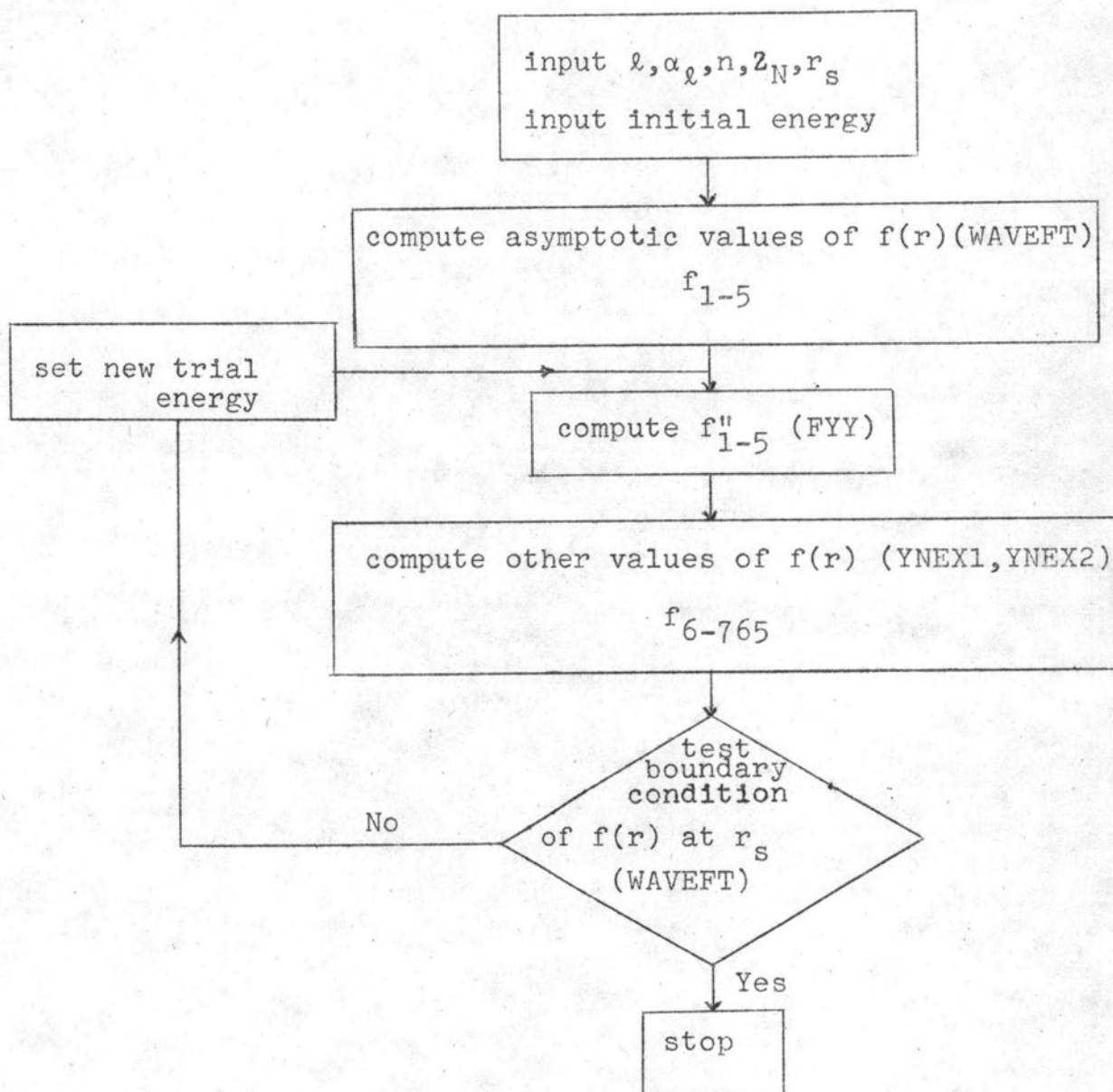
Details of the calculation can be divided into the following steps :

1) We can rewrite the Schrödinger equation (4.10) as

$$f''(r) = (V(r) - E)f(r) \qquad (4.14)$$

Making use of the boundary condition of the wave function,
i.e., it must be zero at the origin, we have

$$\Psi(0) \;=\; 0 \qquad\qquad ,$$

and from (4.9)

$$f(0) \;=\; f_1 \;=\; 0 \quad . \qquad\qquad (4.15)$$

f_1 is now used in place of $f(0)$. Substituting this into
(4.14), we get

$$f''(0) \;=\; 0 \qquad\qquad . \qquad\qquad (4.16)$$

2) Since the asymptotic form of the wave function is

$$\Psi(r) \;\sim\; r^{\ell}\, e^{-Z_N r/n} \qquad\qquad ,$$

where Z_N is the nuclear charge, n and ℓ are the
principal quantum number and angular momentum quantum
number respectively. The function $f(r)$ must be in the
form

$$f(r) \;\sim\; r^{\ell+1}\, e^{-Z_N r/n} \qquad\qquad , \qquad\qquad (4.17)$$

The above form of $f(r)$ is utilized in finding the four
successive values of $f(r)$, i.e., $f(\Delta r)$, $f(2\Delta r)$, $f(3\Delta r)$
and $f(4\Delta r)$ which will be denoted by f_2, f_3, f_4 and
f_5. Δr used here is equal to $2.5 \times 10^{-3}/2^8$. The second
derivatives of f_2 to f_5 are obtained from (4.14) by

substituting (4.13) for V(r) and picking the values of α_s and Z_N from the table 4.1. Here Z is equal to one since it is the ionic charge of all alkali metals. We make a guess about initial value of energy E. Equation (4.14) is now ready to be solved numerically.

3) The next forty values of f(r), f_6 to f_{45}, with the usage of the same Δr as in step 2 can be obtained by inserting some of $f_1 - f_5$ and its second derivative into the following equations[34,35] where h stands for Δr and N is started from 6.

$$f_{N+1} = f_N + f_{N-2} - f_{N-3} + 3h^2(f_N'' - \Delta f_N'' + \frac{5}{12}\Delta_2 f_N'' + \frac{17}{720}\Delta_4 f_N'' + \dots)$$

$$(4.18)$$

$$f_{N+1} = 2f_N - f_{N-1} + h^2(f_{N+1}'' - \Delta f_{N+1}'' + \frac{1}{12}\Delta_2 f_{N+1}'' - \frac{1}{240}\Delta_4 f_{N+1}''$$

$$- \frac{1}{240}\Delta_5 f_{N+1}'' + \dots) \qquad (4.19)$$

$$f_{N+1} = 2f_N - f_{N-1} + h^2(f_N'' + \frac{1}{12}\Delta_2 f_{N+1}'' - \frac{1}{240}\Delta_4 f_{N+2}'' + \dots) \quad (4.20)$$

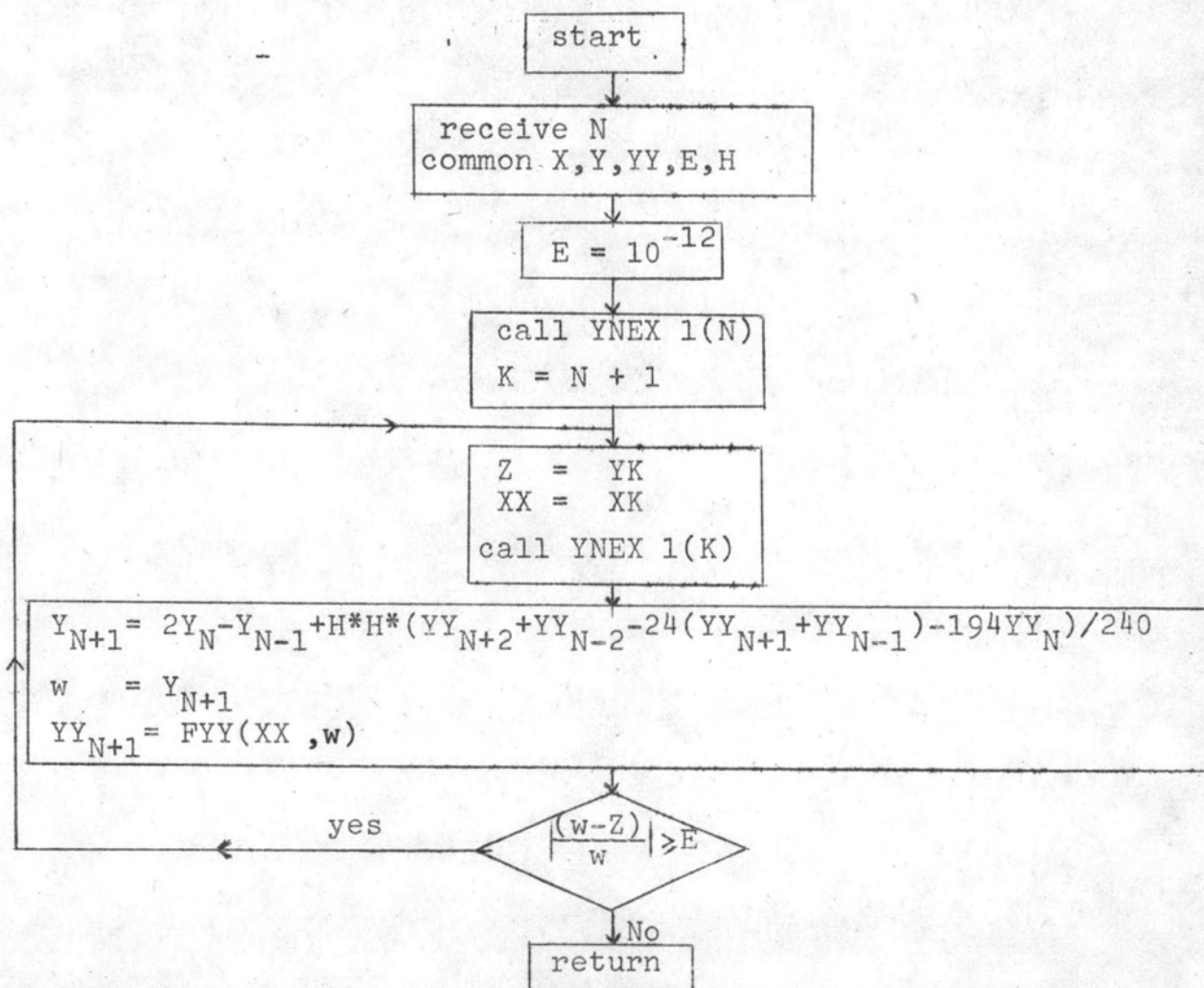Substituting $\Delta_r f_N - \Delta_r f_{N-1}$ for $\Delta_{r+1} f_N$, (4.18), (4.19) and (4.20) become

$$f_{N+1} = f_N + f_{N-2} - f_{N-3} + \frac{h^2}{720}(951 f_N'' + 156 f_{N-1}'' - 594 f_{N-2}''$$

$$-204 f_{N-3}'' + 51 f_{N-4}'') \qquad , \qquad (4.21)$$

$$f_{N+1} = 2f_N - f_{N-1} + \frac{h^2}{240}(18f''_{N+1} + 209f''_N + 4f''_{N-1} + 14f''_{N-2}$$

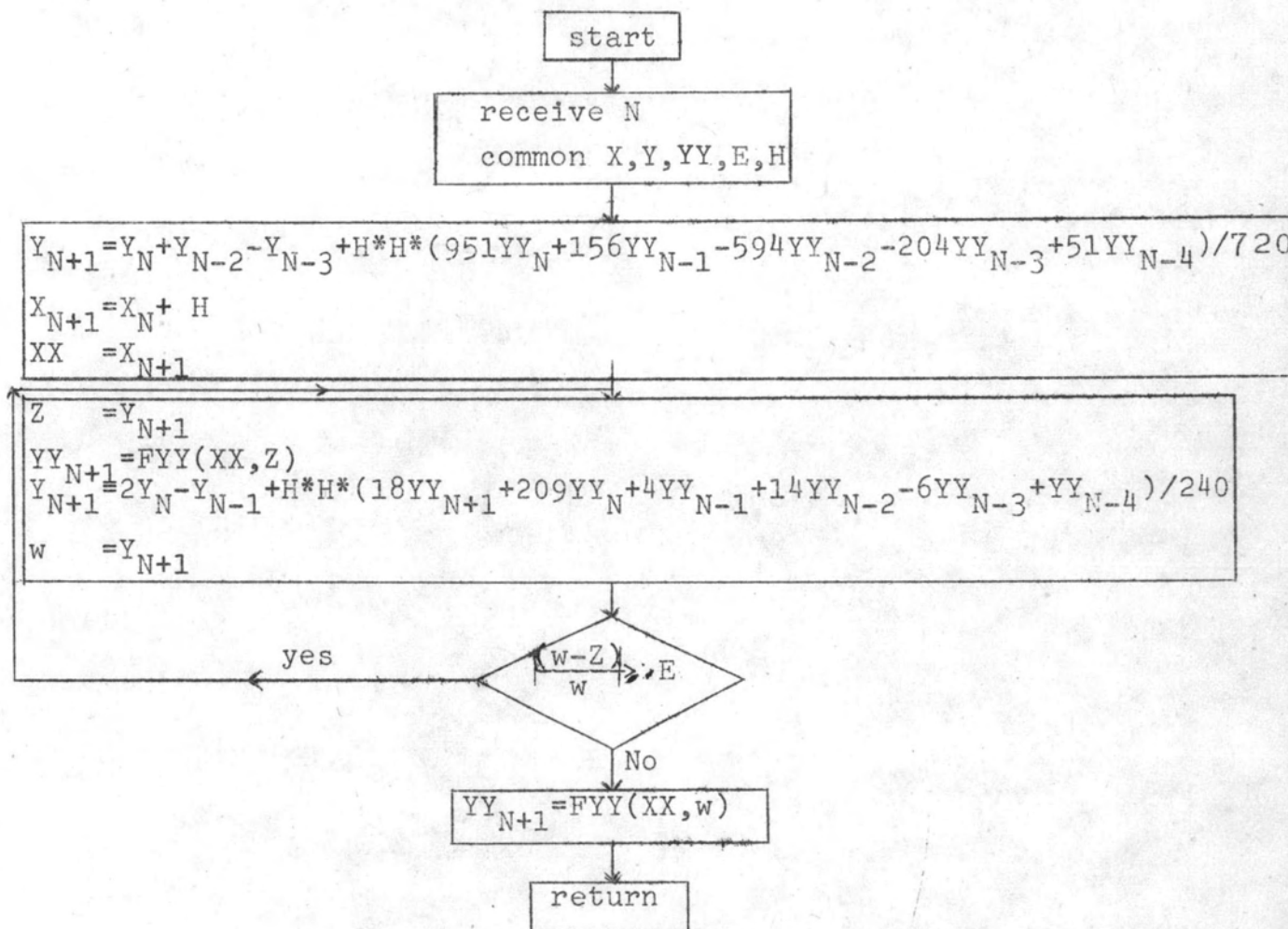$$- 6f''_{N-3} + f''_{N-4}) \qquad , \qquad (4.22)$$

$$f_{N+1} = 2f_N - f_{N-1} - \frac{h^2}{240}(f''_{N+2} + f''_{N-2} - 24(f''_{N+1} + f''_{N-1}) - 194f''_N) \quad (4.23)$$

respectively. Each value of $f(r)$ starts from f_6 have
to satisfy the following self-consistency program whose
flow chart is shown below. The complete program and
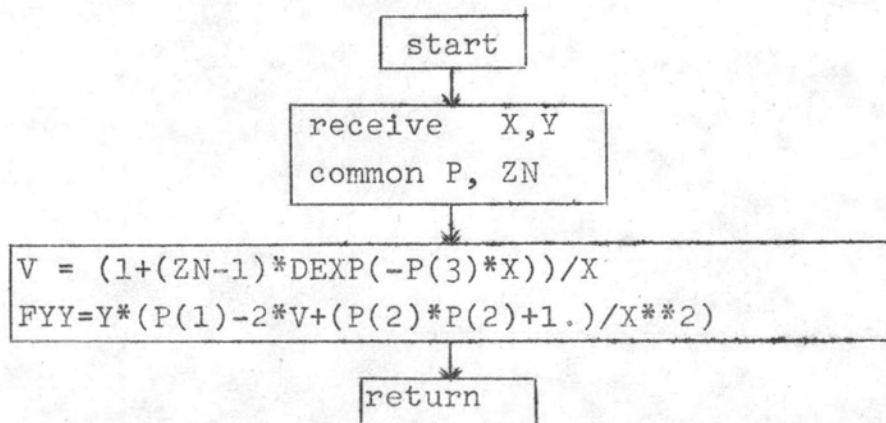the detail of symbols are presented in appendix C.

SUBROUTINE YNEX 2 (N)

```
                    ┌─────────────┐
                    │    start    │
                    └──────┬──────┘
                    ┌──────┴──────────┐
                    │ receive N       │
                    │ common X,Y,YY,E,H│
                    └──────┬──────────┘
                    ┌──────┴──────┐
                    │  E = 10^-12 │
                    └──────┬──────┘
                    ┌──────┴──────┐
                    │ call YNEX 1(N)│
                    │ K = N + 1   │
                    └──────┬──────┘
                    ┌──────┴──────┐
                    │ Z  =  YK    │
                    │ XX =  XK    │
                    │ call YNEX 1(K)│
                    └──────┬──────┘
```

$$Y_{N+1} = 2Y_N - Y_{N-1} + H*H*(YY_{N+2} + YY_{N-2} - 24(YY_{N+1} + YY_{N-1}) - 194YY_N)/240$$
$$w = Y_{N+1}$$
$$YY_{N+1} = FYY(XX, w)$$

```
      yes  ◄──── ◇ |（w-Z)/w| ≥ E ◇
                        │ No
                  ┌─────┴─────┐
                  │  return   │
                  └───────────┘
```

SUBROUTINE YNEX 1(N)

start

receive N
common X,Y,YY,E,H

$Y_{N+1}=Y_N+Y_{N-2}-Y_{N-3}+H*H*(951YY_N+156YY_{N-1}-594YY_{N-2}-204YY_{N-3}+51YY_{N-4})/720$

$X_{N+1}=X_N+H$

$XX=X_{N+1}$

$Z=Y_{N+1}$

$YY_{N+1}=FYY(XX,Z)$

$Y_{N+1}=2Y_N-Y_{N-1}+H*H*(18YY_{N+1}+209YY_N+4YY_{N-1}+14YY_{N-2}-6YY_{N-3}+YY_{N-4})/240$

$w=Y_{N+1}$

yes ← $\left(\dfrac{w-Z}{w}\right) \ge E$

No

$YY_{N+1}=FYY(XX,w)$

return

REAL FUNCTION FYY*8(X,Y)

start

receive X,Y
common P, ZN

$V = (1+(ZN-1)*DEXP(-P(3)*X))/X$

$FYY=Y*(P(1)-2*V+(P(2)*P(2)+1.)/X**2)$

return

4) When the forty values have been obtained, Δr_1 is then increased by doubling its size to find the next twenty values of $f(r)$ by the same procedure as mentioned in step 3 and this must be done eight times repeatedly by using $(\Delta r)_1 = 2(\Delta r)$, $(\Delta r)_2 = 2(\Delta r)_1, \ldots, (\Delta r)_8 = 2(\Delta r)_7$. The last values of r should be equal to 0.1. At the end of this step, we have f_1 to f_{205}.

5) After having the two hundred and five values of $f(r)$, we set the new $(\Delta r)_9$ as being double of $(\Delta r)_8$ and carry on the same process as in step 3 until f_{206} to f_{245} are obtained. We iterate the process fourteen times successively with $(\Delta r)_9 = 2(\Delta r)_8$, $(\Delta r)_{10} = 2(\Delta r)_9, \ldots,$ $(\Delta r)_{22} = 2(\Delta r)_{21}$. The last Δr should not be larger than one. Finally we get f_1 to f_{765}.

6) As a result, we acquire the values of the function $f(r)$ for different values of r at the fixed energy value referred to in step 3. The only thing we are interested in is the lowest state energy appropriate to an r_s. This is done by testing the slope of the obtained function $f(r)$ at the atomic sphere radius r_s which is fixed for each element. First of all, we interpolate the function to seek for $f(r_s)$ at r_s. Then two points in the neighbourhood of r_s are chosen, say $r_{s_1} = r_s - 10^{-12}$ and

$r_{s_2} = r_s + 10^{-12}$ and the interpolation is carried on until the values of $f(r_{s_1})$ and $f(r_{s_2})$ are obtained. Thereafter, the boundary condition to be satisfied at r_s becomes

$$\frac{f(r_s)}{r_s} - \frac{f(r_{s_2}) - f(r_{s_1})}{r_{s_2} - r_{s_1}} = 0 \qquad . \qquad (4.24)$$

We now suppose that at any energy E_n the left side of (4.24) is positive. This implies that the slope of the function which sets between $f(r_{s_2})$ and $f(r_{s_1})$) is smaller than the slope of function at r_s. We, therefore, vary E until the sign of the left side of (4.24) is negative, assuming that it is at E_m. It is obvious that the desirable value of E must lie within the range between E_n and E_m. The next trial value of E is taken to be half of E_n and E_m, and the process is iterated from the step 2 until (4.24) is satisfied. Thus the lowest state energy E_o of alkali metals are thus acquired and presented in table 4.2. With the inclusion of the correction terms, the cohesive energy is obtained through

$$S = E_b - I + E_c \qquad , \qquad (4.25)$$

where I is the ionization energy, E_b is defined by (4.7) and E_c is the sum of the exchange energy, the self-potential energy and the correlation energy which are given by (2.37), (2.38) and (2.41) respectively. The

values of the lowest state energy and the cohesive energy are shown to compare with those obtained by Callaway in table 4.2

	Li	Na	K	Rb	Cs
E_o	-0.6850	-0.6024	-0.4835	-0.4546	-0.4129
E_o^ℓ	-0.6832	-0.6113	-0.452	-0.444	-0.4156
E_2^ℓ	0.7305	1.022	1.149	1.10	1.197
E_4^ℓ	-0.0303	-0.0096	-0.3	-1.01	-1.85
r_s^ℓ	3.2	4.0	4.86	5.21	5.74
E_k	0.1560	0.1409	0.1044	0.0816	0.0704
E_b	-0.5290	-0.4615	-0.3791	-0.3730	-0.3425
E_c	-0.0106	-0.0253	-0.0353	-0.0383	-0.0420
I	-0.3963	-0.3777	-0.3190	-0.3070	-0.2862
$S^m = E_b - I + E_c$ (kcal/mole)	44.9471	34.2140	29.9186	32.7030	30.8322
$S^{\ell,m}$	43.5687	27.7465	22.2869	20.7376	22.2702
S^n	41.6187	26.2822	18.8589	20.6996	17.6663
$S^{\ell,n}$	46.2263	26.8244	18.8377	16.6034	17.3891
S(experiment)	36.5	26.0	22.6	18.9	18.8

ℓ These values are obtained from Callaway.[29]

m   These values contain the correction terms.

n   These values do not include the correction terms.

Table 4.2   The lowest state energy and the cohesive energy for alkali metals.