A thesis entitled

" ATOMIC AND IONIC ENERGIES AND ELECTRON DENSITIES "

submitted for the degree of
Master of Philosophy
in the

University of London

by
M. Suleman Yusaf

of
Imperial College London

1976

Abstract

Because of the central role of the hydrogenlike atoms in the so-called $1/Z$ (Z the atomic number) expansion of atomic and ionic binding energies, the first part of this thesis presents results, both analytic and numerical, for

(a) the X-ray scattering factor

(b) the momentum density

for the case when up to and including hundred shells are filled.

As the number of shells filled gets large, contact is established with asymptotic results for scattering factor obtained from the Thomas-Fermi theory. The accuracy of this approximate method is critically assessed. In connection with (b) the kinetic energy density is calculated for several shells filled and is again compared with the Thomas-Fermi result which is proportional to the 5/3rd power of the electron density.

The second part of the thesis is concerned with the electron densities and energies of atoms and ions, within a self- consistent framework. Results of Boyd on radial electron densities are referred to, but the main emphasis here is the binding energy as a function of N and N/Z (N the total number of electrons). Numerical data is used for this purpose, from Hartree and Hartree-Fock calculations. Specific results are given for the rare gas elements.

ACKNOWLEDGEMENTS

I would like to express my whole hearted gratitude to my supervisor, Professor N. H. March for his direction and encouragement throughout my studies.

I am also grateful to Dr. Peter Grout for his valuable guidance in the computer programming used in this work.

I am indebted to Southfields Trust for financial support during my studies.

CONTENTS

Introduction

Our main objective in this thesis is to clarify the range of validity of the Thomas-Fermi (TF) approximation. This we have achieved by studying different properties of atoms, for example X-ray scattering factors, binding energies, kinetic energy densities and charge densities. In each case we have finally made a comparison between the TF and the fully wave mechanical approach through Hartree-Fock-Slater calculations.

The outline of the thesis is as follows. Part A is about the X-ray scattering factor. Here we have made a detailed study of Fock's (1935) general expression for the electron density, and scattering factor and how it could be used to get results for increasing number of shells when only a pure coulomb field is considered. We have developed the TF scattering factor relation from the charge density and have solved for this scattering factor analytically as well as numerically. This can be represented by a universal curve independent of atomic number Z. Finally fully wave mechanical results are compared numerically with this TF result.

Part B is concerned with the momentum and kinetic energy densities. After giving a brief derivation of both the wave mechanical and the TF expressions we have applied these to hydrogenlike atomic systems. At the end of this part, we have put some emphasis on the electron density at the origin since it can be used in conjunction with an exact relation between density and its gradient (Steiner, 1963). We have also demonstrated how $\rho(0)$ is related to the density in momentum space when the momentum is sufficiently large.

In part C our interest is focussed on binding energies in atoms and ions. After out-lining the TF energy and 1/Z expressions we discuss the physical interpretation of the different terms involved. A relation between the binding energy and the sum of eigenvalues is derived. We have also discussed some approximate analytic fits and how they may be refined.

Finally a brief study of self-consistent charge densities is made in part D. Here we have studied the TF universal form in comparison with some of Boyd's (1976) data.

(A) X-ray scattering factor.

Our aim here is to study in some detail the electron density in a neutral hydrogenlike system, always assuming closed shells, having nuclear charge Ze and Z electrons. The reason for our interest in this problem is two-fold:

(i) The hydrogenic problem gives rise to the leading term in the so-called 1/Z expansion for atoms, which we shall discuss in detail in the second half of thesis.

(ii) For large Z, this study will enable us to test the range of validity of the Thomas-Fermi statistical theory applied to the hydrogenlike problem.

Later in the thesis, we shall also comment on the relation between the Thomas-Fermi selfconsistent density and the approximate densities derived, from the Hartree-Fock equations (Boyd, private communication).

(A.I) Fourier transform of electron density.

In order to implement the above programme, in which we wish to study quite a large number of closed shells, we shell find it helpful to calculate the coherent X-ray scattering factor defined by

$$f\,(\underline{k}) \;=\; \int \rho(\underline{r}) \,.\, e^{i\underline{k}.\underline{r}} \,.\, d\underline{r}\;, \qquad \text{(A.I.1)}$$

where $\rho(\underline{r})$ is the total electron density in the atomic system under consideration. Actually, below, we construct $\rho(\underline{r})$ by summing the density $\rho_n(\underline{r})$ for the nth closed shell over n' closed shells i.e

$$\rho(\underline{r}) \;=\; \sum_{n=1}^{n'} \rho_n(\underline{r}) \;, \qquad \text{(A.I.2)}$$

and correspondingly we define the scattering factor $f_n(\underline{k})$ for the nth closed shell by

$$f_n(\underline{k}) \;=\; \int \rho_n(\underline{r}) \,.\, e^{i\underline{k}.\underline{r}} \,.\, d\underline{r}. \qquad \text{(A.I.3)}$$

Since by Unsold's theorem $\rho_n(r)$ is spherical as long as the shell is fully closed, (see Pauling and Wilson, 1935) we can use Bauer's expansion of a plane wave in spherical waves, namely

$$e^{i\underline{k}.\underline{r}} \;=\; \sum_{l} i^{l} \,.\, (2l+1) \,.\, j_l(kr) \,.\, P_l(\mathrm{Cos}\ \theta)\;, \qquad \text{(A.I.4)}$$

where j_l is the usual spherical Bessel function, P_l the Legendre polynomial of order l, and θ is the angle between $\underline{k}$ and $\underline{r}$, to write

$$f_n(k) = 4\pi \int_0^\infty \varrho_n(r) \cdot \frac{\text{Sin }(kr)}{k\,r} \cdot r^2 \cdot dr \cdot \qquad \text{(A.I.5)}$$

(A.II) Fock's expression for scattering factor.

In what follows we shall use Fock's result (Fock, 1935) that the scattering factor $f_n(k)$ for the nth closed shell can be obtained in closed form in terms of Tschebyscheff polynomials and the Legendre polynomials already used above.

Fock's result is most compactly summarized in terms of a new variable X defined by

$$X = \frac{4\,p_n^2 - k^2}{4\,p_n^2 + k^2} , \qquad \text{(A.II.1)}$$

where p_n^2 is mean square momentum for nth shell. It can be shown from the calculation of the momentum density that

$$p_n^2 = \frac{Z^2}{n^2} ,$$

we have derived this value in Appendix 1. Fock's expression is given by

$$F_n(X) = \frac{1}{4n^2} \cdot T_n'(X) \cdot (1 + X)^2 \cdot [\, P_n'(X) - P_{n-1}'(X) \,] \qquad \text{(A.II.2)}$$

where $T_n'(X)$ denotes the derivative of the Tschebyscheff polynomial while $P_n'(X)$ is the derivative, of the Legendre polynomial of order n. This relation, it must be stressed, is valid for singly occupied levels and for a particular closed shell, when we are considering a pure coulomb field.

Before utilizing Fock's result for shells with larger n, it has been checked directly for the K, L and M shells. These are the only shells for which we have made explicit calculations of the electronic charge density $\rho_n(r)$. Calculations have been carried out from relations (A.I.5) and (A.II.2) separately and a comparison is thereby made.

(A.III) Calculation of scattering factor for K, L and M shells from electron density $\rho(r)$.

Putting the corresponding values of $\rho_n(r)$ for the K, L and M shells into equation (A.I.5) and evaluating the integral is straight forward. We have given a general solution for the integration of this type in Appendix 2*. We merely quote the final results below.

K-Shell $$f_1(k) = \frac{32}{(4 + C^2)^2}$$

L-Shell $$f_2(k) = \frac{4(2 - 3C^2 + C^4)}{(1 + C^2)^4}$$

M-Shell $$f_3(k) = \frac{2(9 - 48E^2 + 72E^4 - 28E^6 + 3E^8)}{(1 + E^2)^6}$$

where $E = 3/2\,C \ : \ C = k/Z$,

in the last step atomic units (Bohr radius $a_0 = 1$) having been used.

---

* Solution is given for the integrals

$$\text{(i)} \quad \int_0^\infty \sum_l a_l \cdot x^l \cdot \sin(Ex) \cdot e^{-x} \cdot dx$$

$$\text{(ii)} \quad \int_0^\infty t^m \cdot \sin(Ft) \cdot e^{-t} \cdot dt$$

Fock's results

Next we take Fock's general expression i.e equation (A.II.2). As the evaluation is fairly straight forward, we shall not give all the details, but merely a typical example.

The results we obtained are precisely half in magnitude of those we have given above using $\rho(r)$. This is because, as we remarked already, Fock's expression is derived for singly occupied levels where-as the charge densities we have used in equation (A.I.5) for direct calculations have been normalized for doubly occupied levels. In Appendix 3 we summarize the calculation of $f_3(k)$ from Fock's expression to show explicitly how the detail works out, even for $n = 3$ the detail is quite lengthy.

(A.IV) Thomas-Fermi scattering factor.

Numerical evaluation of the Fock's result is readily carried out with the aid of an electronic computer. But before going into details of this method it will be instructive to calculate the Thomas-Fermi (TF) scattering factor for hydrogenlike atoms.

The TF charge density for a pure coulomb field is defined as

$$\rho(r) = \begin{cases} \frac{8\pi}{3h^3}(2m)^{3/2}. \quad (E_f + \frac{Ze^2}{r})^{3/2}, & \text{for } r < \frac{Ze^2}{|E_f|} \\ 0 \quad \text{otherwise,} & \end{cases} \qquad \text{(A.IV.1)}$$

where h, m, e, Z, and r denote respectively Planck's constant, electron mass, electronic charge, atomic number and distance from nucleus. E_f being the total energy of the fastest electron.

The scattering factor for the total electron density $\rho(r)$ is already defined by equation (A.I.1) which has been modified to

$$f\ (k) = \int_0^{r_c} \rho(r) \cdot \frac{\text{Sin}\ (kr)}{kr} \cdot 4\pi r^2\, dr,$$

where $r_c = \dfrac{Z\ e^2}{|E_f|}$.

Putting in the value of $\rho(r)$ from equation (A.IV.1) we get

$$f\ (k) = \frac{32\pi^2}{3\ h^3} \cdot (2m)^{3/2} \int_0^{r_c} r^2\ (E_f + \frac{Z\ e^2}{r})^{3/2} \cdot \frac{\text{Sin}\ (kr)}{kr} dr.$$

Again substituting $r = r_c \cdot s$

where r_c is the maximum atomic radius, we obtain

$$f\ (k) = R \cdot \int_0^1 s^2 (E_f + \frac{Z\ e^2}{r_c\ s})^{3/2} \cdot \frac{\text{Sin}\ (k.r_c.s)}{k.r_c.s}\ r_c^3 \cdot ds,$$

where $R = \dfrac{32\pi^2}{3\ h^3} (2m)^{3/2}$.

Further simplification is possible if we put $k \cdot r_c = K$ where k, we recall, is equal to $\dfrac{4\pi\ \text{Sin}\ (\theta/2)}{\lambda}$, θ being the scattering angle for X-rays, and λ the X-ray wave length. Then we find

$$f\ (K) = R.r_c^3 \int_0^1 (E_f + \frac{Z\ e^2}{r_c\ s})^{3/2} \cdot \frac{\text{Sin}\ (Ks)}{Ks} \cdot s^2\ ds\ .$$

But in a pure coulomb field

$$|E_f| = \frac{Z\ e^2}{r_c}\ .$$

Therefore, being more explicit we can write

$$f(K) = R \cdot r_c^3 \cdot |E_f|^{3/2} \cdot \int_0^1 \left(\frac{1}{s} - 1 \right)^{3/2} \cdot \frac{\mathrm{Sin}\ (Ks)}{K\ s} \cdot s^2 \cdot ds.$$

Substituting value of r_c from above we get

$$f(K) = R \cdot \frac{(Z\ e^2)^3}{|E_f|^{3/2}} \cdot \int_0^1 \left(\frac{1}{s} - 1 \right)^{3/2} \cdot \frac{\mathrm{Sin}\ (Ks)}{K\ s} \cdot s^2 \cdot ds \quad ,$$

which we can express in the form

$$f(K) = R \cdot \frac{(Z\ e^2)^3}{|E_f|^{3/2}} \cdot G(K) \quad , \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (A.IV.2)$$

where

$$G(K) = \int_0^1 \left(\frac{1}{s} - 1 \right)^{3/2} \cdot \frac{\mathrm{Sin}\ (Ks)}{K\ s} \cdot s^2 \cdot ds \quad .$$

We shall come back to the evaluation of G(K) later but now we give attention to the other factors in equation (A.IV.2). Integration of equation (A.IV.1) over r and solving for E_f gives us

$$E_f = - \frac{Z^2}{N^{\frac{2}{3}}} \cdot \frac{1}{18^{\frac{1}{3}}} \cdot \frac{e^2}{a_o} \quad , \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} (A.IV.3)$$

(see, for example March, 1975) where N is total number of electrons present in the system. It is related to n', total number of closed shells in the system, by the following relation

$$N = n'(n' + 1)\ (2n' + 1)\ /\ 3$$

$$\text{since} \quad N = \sum_{n=1}^{n'} 2\ n^2 \quad ,$$

n being the principle quantum number. Putting back the value of N in equation (A.IV.3) we get

$$E_f = -\frac{Z^2 e^2}{a_o} \left(\frac{3}{n' \, (n'+1) \, (2n'+1)} \right)^{2/3} . \frac{1}{18^{\frac{1}{3}}} ,$$

and therefore

$$|E_f|^{3/2} = \frac{3 \, Z^3 . \, e^3}{n'(n'+1).(2n'+1) \, a_o^{3/2} . \, 18^{\frac{1}{2}}} . \qquad \underline{\qquad\qquad} (A.IV.4)$$

Hence the TF scattering factor can be written, after putting (A.IV.4) in (A.IV.2), as

$$f(K) = \frac{R. \, (Z \, e^2)^3 . \, n'(n' + 1)(2n' + 1) \, 18^{\frac{1}{2}} \, a_o^{3/2}}{Z^3 . \, e^3 . \, 3} . \, G(K) ,$$

and after simplification we obtain

$$f(K) = R \, . \, \frac{n'(n' + 1)(2n' + 1)}{3} . \, 18^{\frac{1}{2}} . \, e^3 . \, a_o^{3/2} G(K) . \qquad \underline{\qquad\qquad} (A.IV.5)$$

Substituting for R and using atomic units, which we shall employ in most of the calculations, i.e $m = e = h = 1$, equation (A.IV.5) is easily reduced to

$$f(K) = 5.0928 \, . \, \frac{n'(n' + 1)(2n' + 1)}{3} . \, G(K) . \qquad \underline{\qquad\qquad} (A.IV.6)$$

We can get a universal form out of this expression if we divide both sides by N. i.e

$$\frac{f(K)}{N} = 5.0928 \, . \, G(K) , \qquad \underline{\qquad\qquad} (A.IV.7)$$

where the right hand side is now independent of atomic number Z. A check can be made by putting $K = 0$ in equation (A.IV.7). Equation (A.I.1) for $K = 0$ gives us

$$f(0) = \int_0^\infty \rho(r) \, . \, d\underset{\sim}{r} = N \quad , \qquad \text{(A.IV.8)}$$

provided $\rho(r)$ is properly normalized for N electrons. Dividing both sides by N we get

$$\frac{f(0)}{N} = 1 \; .$$

$G(0)$ is evaluated and found equal to 0.1963. Therefore from equation (A.IV.7) we get

$$\frac{f(0)}{N} = 0.99971 \; .$$

Since the results from equations (A.IV.7) and (A.IV.8) agree with each other we can safely assume that our numerical as well as analytical solutions are correct at least at $K = 0$.

Numerically equation (A.IV.7) has been solved for different K's with the help of an electronic computer using Simpson's rule for numerical integration. We have listed the programme in Appendix 4. The results are recorded in Table I.

(A.V) Analytic solution of $G(K)$.

Though we have evaluated the integral $G(K)$ numerically, yet it is of some interest to examine whether a useful analytic solution can be found. $G(K)$ is defined by equation (A.IV.2). Expanding $\mathrm{Sin}(Ks)$ in powers of Ks

then yields

$$G(K) = \frac{1}{K} \int_0^1 \sum_{m=1}^{1} \frac{(-1)^{m-1} \,.\, K^{2m-1}}{(2m-1)!} \,.\, s^{2m-3/2} \,.\, (1-s)^{3/2} \,.\, ds \;. \qquad \text{\_\_\_\_\_\_\_(A.V.1)}$$

In terms of the Beta function defined as

$$\beta(m+1,n+1) = \int_0^1 t^m \,.\, (1-t)^n . \, dt$$

$$= \frac{\Gamma(m+1) \,.\, \Gamma(n+1)}{\Gamma(n+m+2)}$$

(see, for example, Bartlett and Fyfe, 1974) we can express G(K) as

$$G(K) = \frac{1}{K} \sum_{m=1}^{1} \frac{(-1)^{m-1} . K^{2m-1}}{(2m-1)!} \,.\, \frac{\Gamma(2m-\frac{1}{2}) . \; \Gamma(5/2)}{\Gamma(2m+2)} \;. \qquad \text{\_\_\_\_\_\_\_(A.V.2)}$$

We simplify the term

$$\frac{\Gamma(2m-\frac{1}{2}) \,.\, \Gamma(5/2)}{\Gamma(2m+2)} = \frac{3}{4(2m+1)} \quad \frac{\Gamma(2m+\frac{1}{2}) \,.\, \Gamma(\frac{1}{2})}{(2m-\frac{1}{2}) \,.\, \Gamma(2m+1)} \;.$$

Since in general

$$\Gamma(n+1) = n \,.\, \Gamma n \;.$$

Therefore in terms of the Beta function we get

$$\frac{\Gamma(2m-\frac{1}{2}) \,.\, \Gamma(5/2)}{\Gamma(2m+2)} = \frac{3 \,.\, \beta(2m+\frac{1}{2}, \frac{1}{2})}{4(2m+1).(2m-\frac{1}{2})} \;. \qquad \text{\_\_\_\_\_\_\_(A.V.3)}$$

Using the identity

$$\beta(n, \tfrac{1}{2}) = \beta(n, n) \,.\, 2^{2n-1}$$

we can write

$$\mathcal{B}(2m+\tfrac{1}{2},\tfrac{1}{2}) = \mathcal{B}(p,p)\,.\,2^{4m} ,$$

where $p = 2m+\tfrac{1}{2}$.

Equation (A.V.3) then becomes

$$\frac{\Gamma(2m-\frac{1}{2})\,.\,\Gamma(5/2)}{\Gamma(2m+2)} = \frac{3\,.\,\mathcal{B}(p,p)\,.\,2^{4m}}{4\,(2m+1)\,(2m-\frac{1}{2})} \,. \qquad \text{——————(A.V.4)}$$

Again we can make use of the definition of the Beta function to write (A.V.4) in integral form. We have

$$\mathcal{B}(p,p) = \int_0^1 [\,s\,(1-s)\,]^{p-1}.\;ds \,.$$

Putting $s = \sin^2 A$, therefore $ds = 2\sin A\,.\cos A\;dA$

it follows that

$$s(1-s) = \sin^2 A.\;\cos^2 A = \tfrac{1}{4}\sin^2(2A) \,.$$

For $s = 0$, $A = 0$; and for $s = 1$, $A = \pi/2$

therefore

$$\mathcal{B}(p,p) = \int_0^{\pi/2} [\,\sin(2A)/2\,]^{2p-2}.\;\sin(2A)\,.\,dA \,.$$

Substituting back $p = 2m+\tfrac{1}{2}$ we get

$$\mathcal{B}(p,p) = 2^{-2(2m-\frac{1}{2})}\int_0^{\pi/2} \sin^{4m}(2A)\;.\,dA$$

Using recurrence relation for integration of $\sin^n x$ we obtain

$$\mathcal{B}(p,p) = 2^{-4m+1} \cdot \frac{4m-1}{4\,m} \cdot \int_0^{\pi/2} \operatorname{Sin}^{4m-2}(2A) \cdot dA \quad .$$

We can carry on until, power $(4\,m - c) = 0$ whereby

$$\int_0^{\pi/2} \operatorname{Sin}^{0}(2A) \cdot dA = \pi/2$$

c is arbitrary constant and has even values $2,4,6, \ldots\ldots 4m$.

Ultimately we arrive at the result

$$\mathcal{B}(p,p) = 2^{-4m+1} \cdot \frac{(4m-1)(4m-3)\ldots\ldots.5.3.1}{4m\,(4m-2)(4m-4)\ldots4.2} \cdot \pi/2 \quad . \qquad \text{(A.V.5)}$$

Putting this back into equation (A.V.4) it follows that

$$\frac{\Gamma(2m-\frac{1}{2})\;.\;\Gamma(5/2)}{\Gamma(2m+2)} = \frac{3}{2}\;\frac{(4m-1)(4m-3)\ldots\ldots\ldots5.3.1}{4m\,(4m-2)\ldots\ldots\ldots4.2}\;\frac{\pi/2}{(2m+1)(2m-\frac{1}{2})}, \qquad \text{(A.V.6)}$$

which can be simplified to give

$$\frac{\Gamma(2m-\frac{1}{2})\,.\,\Gamma(5/2)}{\Gamma(2m+2)} = \frac{3}{2} \cdot \frac{(4m-1)^2(4m-3)^2\ldots.3^2.1^2}{(4m)!\;(2m+1)(2m-\frac{1}{2})} \cdot \pi/2$$

,

Inserting this finally into $G(K)$ i.e equation (A.V.2) we obtain the required analytic expression, namely

$$G(K) = \sum_{m=1}^{1} \prod_{q=1}^{21} \frac{(-1)^{m-1} \cdot K^{2m-2}}{(2m-1)!} \cdot \frac{3}{2} \cdot \frac{(4m-2q+1)^2}{(4m)!\;(2m+1)(2m-\frac{1}{2})} \cdot \pi/2. \qquad \text{(A.V.7)}$$

This exact solution of $G(K)$ has been numerically solved for different values of K and 1. The results are given in Table I.

Table I

Numerical and analytical solution of the TF scattering factor.

K	G(K)				f/Z	
(K = k.r_c)	Numerical	Analytical			Numerical	Analytical
		l = 6	l = 19	l = 30		l = 30
0.000	0.19627	0.19635	0.19635	0.19635	1.00000	0.99971
1.0	0.18972	0.19033	0.19033	0.19033	0.96621	0.96930
2.0	0.17289	0.17356	0.17356	0.17356	0.88048	0.88392
3.0	0.14877	0.14952	0.14952	0.14952	0.75766	0.76149
4.0	0.12191	0.12274	0.12271	0.12271	0.62087	0.62494
5.0	0.09652	0.09753	0.09732	0.09732	0.49154	0.49565
6.0	0.07540	0.07729*	0.07618	0.07618	0.38399	0.38798
7.0	0.05958		0.06034	0.06034	0.30344	0.30728
8.0	0.04858		0.04931	0.04931	0.24738	0.25114
9.0	0.04106		0.04181	0.04181	0.20912	0.21292
10.0	0.03565		0.03641	0.03641	0.18157	0.18544
11.0	0.03134		0.03212	0.03212	0.15962	0.16356
12.0	0.02887		0.02842	0.02842	0.14083	0.14475
13.0	0.02348		0.02522	0.02522	0.12461	0.12845
14.0	0.02180		0.02254	0.02254	0.11103	0.11479
15.0	0.01963		0.02035	0.02037	0.09999	0.10372
16.	0.01786		0.01839*	0.01860	0.09096	0.09473
17.0	0.01636			0.01710	0.08330	0.08709
18.0	0.01502			0.01577	0.07649	0.08030
19.0	0.01381			0.01455	0.07035	0.07411
20.0	0.01274			0.01347	0.06488	0.06858
21.0	0.01180			0.01252	0.06012	0.06376
22.0	0.01099			0.01170	0.05598	0.05960
23.0	0.01028			0.01099	0.05233	0.05599
24.0	0.00962			0.01037	0.04901	0.05283
25.0	0.00903			0.01010	0.04596	0.05145

* Beyond these values the solution's behaviour becomes unacceptable for that particular value of l.

We have examined the solution for three different values of 'l' when keeping K_{max} constant at 25.

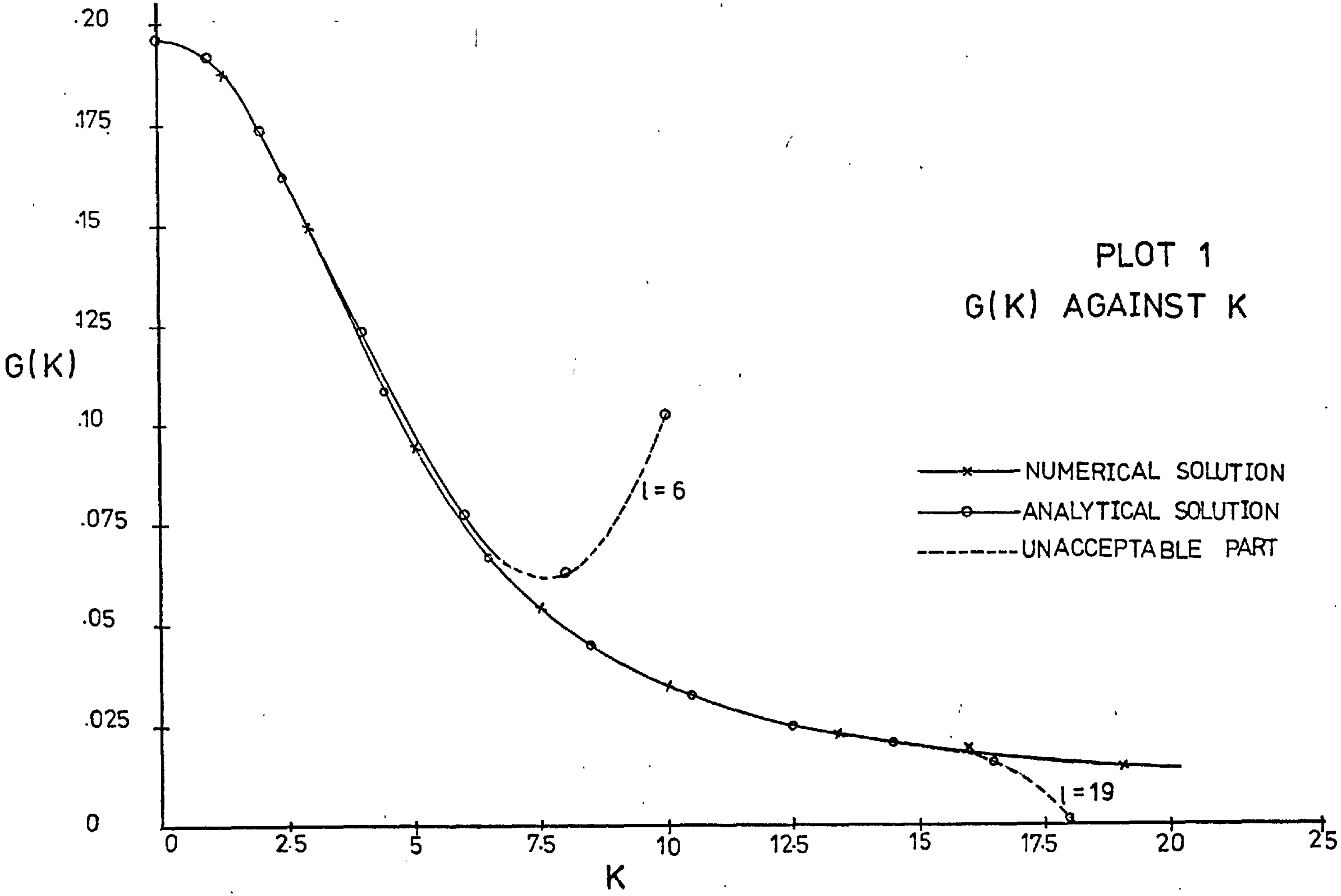
(i) l = 6 : As shown in plot 1 curve is smooth and in agreement with numerical solution curve, up to $K \leqslant 5$. But from there onwards it starts rising rapidly. In this region we cannot rely on the analytic solution.

(ii) l = 19 : This time, the curve remains smooth and acceptable until $K \leqslant 16$ (see plot 1). After that the curve begins to fall rapidly (dotted curve).

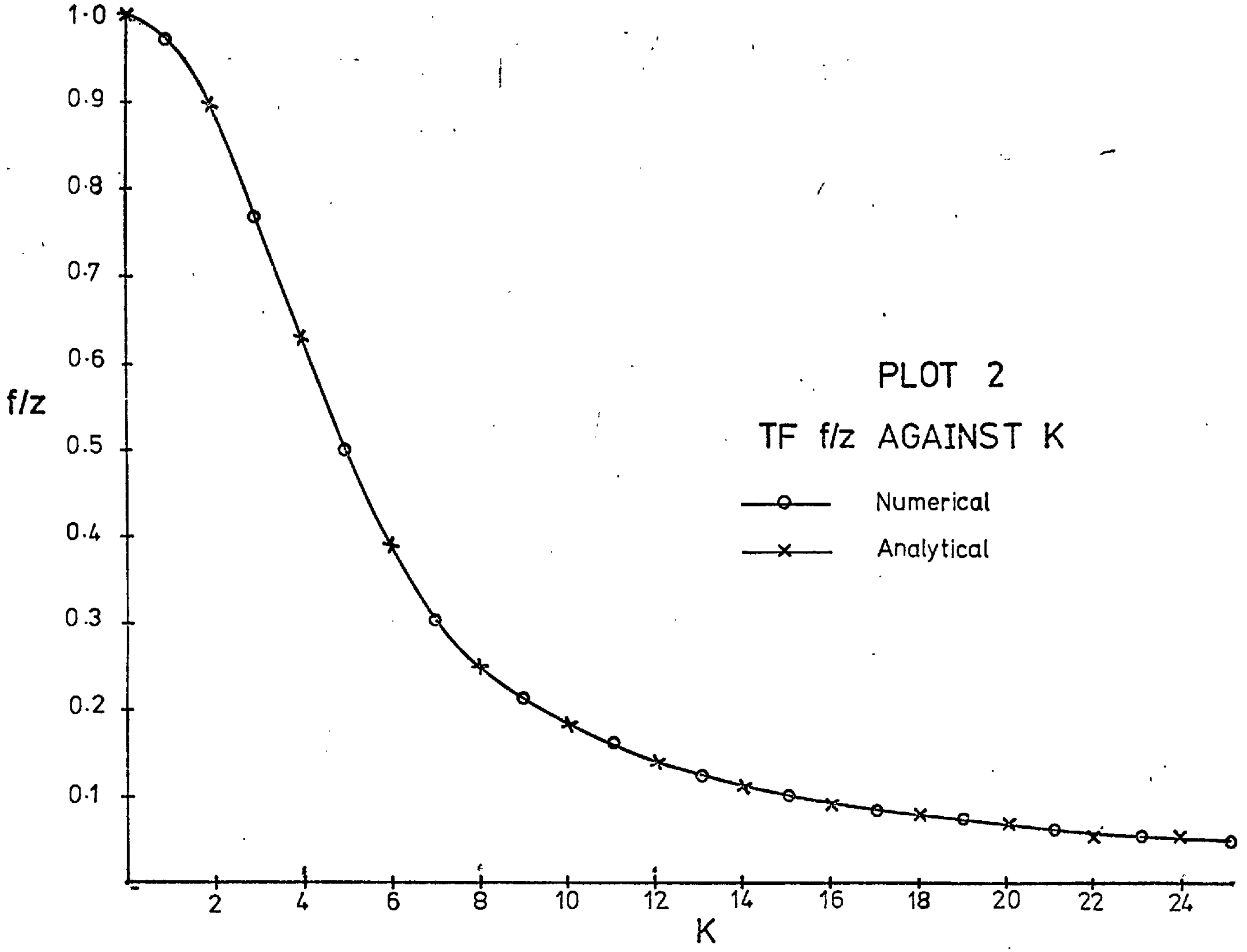
(iii) l = 30 : Here we see that the solution remains acceptable over the whole range of K (plot 2).

We have also found that for odd values of 'l' the curve ultimately finishes up (where the behaviour becomes unacceptable) as a rapidly decreasing curve, whereas if 'l' is chosen to be even the reverse is true. Table I allows us to draw one important conclusion about the analytic solution we have obtained.

To afford an acceptable solution we must take the value of 'l', total number of terms in the summation, more than the selected maximum value of K, otherwise the solution will start behaving differently before K becomes equal to K_{max}. This conclusion is demonstrated in the plots presented here.



PLOT 1
G(K) AGAINST K


PLOT 2
TF f/z AGAINST K
Numerical
Analytical
f/z
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
2
4
6
8
10
12
14
16
18
20
22
24
K

(A.VI) Numerical evaluation of Fock's general expression for scattering factor.

Now we come back to Fock's general expression for the atomic scattering factor given in equation (A.II.2). As mentioned earlier we shall examine it numerically for large n.

For use in the computer programme, what we require are recurrence relations for the Tchebyscheff and Legendre polynomials. Therefore we first derive the required forms of these as follows :

Into the definition of $T_n(X)$, namely

$$T_n(X) = \text{Cos}\,(n\,\text{Cos}^{-1} X)$$

let us substitute

$$X = \text{Cos}\,Y \quad .$$

Therefore

$$T_n(X) = \text{Cos}\,(nY) \quad . \qquad \text{\_\_\_\_\_\_\_\_(A.VI.1)}$$

Evidently

$$T_{n-1}(X) = \text{Cos}\left[(n-1)\,Y\right] \quad . \qquad \text{\_\_\_\_\_\_\_\_(A.VI.2)}$$

Taking the derivative of (A.VI.1) we obtain

$$T'_n(X) = \frac{dT_n}{dY} \cdot \frac{dY}{dX} \quad .$$

After substituting the values we get

$$T'_n(X) = \text{Sin}(nY).\, n \,.\, \frac{1}{(1-X^2)^{\frac{1}{2}}}$$

Similarly we find

$$T'_{n-1}(X) = \frac{\text{Sin}\left[(n-1)\,Y\right] .\ (n-1)}{(1-X^2)^{\frac{1}{2}}} \qquad \text{\_\_\_\_\_\_\_\_(A.VI.3)}$$

We now expand in the form

$$T'_{n-1}(X) = \frac{(n-1)}{(1-X^2)^{\frac{1}{2}}} \cdot \left[\text{Cos } Y \cdot \text{Sin } (nY) - \text{Cos } (nY). \text{ Sin } (Y) \right],$$

which is readily rewritten as

$$T'_{n-1}(X) = \frac{(n-1)}{(1-X^2)^{\frac{1}{2}}} \cdot \left[X \cdot \text{Sin } (nY) - T_n(X). \text{ Sin } Y \right] ,$$

more usefully

$$T'_{n-1}(X) = \frac{(n-1).X.\text{Sin}(nY)}{(1-X^2)^{\frac{1}{2}}} - (n-1).\ T_n(X) \qquad \text{(A.VI.4)}$$

since

$$\text{Sin } Y = (1 - X^2)^{\frac{1}{2}} .$$

Simplifying (A.VI.4) we find

$$\text{Sin } (nY) = \frac{T'_{n-1}(X) + (n-1).T_n(X)}{(n-1) \cdot X} . (1 - X^2)^{\frac{1}{2}} \qquad \text{(A.VI.5)}$$

Going back to equation (A.VI.2) where

$$T_{n-1}(X) = \text{Cos } ((n-1)Y)$$

expanding it into Cosine and Sine terms we find

$$T_{n-1}(X) = \text{Cos } Y \cdot \text{Cos}(nY) + \text{Sin } Y \cdot \text{Sin } (nY) ,$$

which is equivalent to

$$T_{n-1}(X) = X \cdot T_n(X) + (1 - X^2)^{\frac{1}{2}}. \text{ Sin } (nY) .$$

Solving this for Sin (nY) yields

$$\text{Sin}\ (nY) = \frac{T_{n-1}(X) - X \cdot T_n(X)}{(1 - X^2)^{\frac{1}{2}}} \tag{A.VI.6}$$

Comparing equations (A.VI.5) and (A.VI.6) we get

$$\frac{T_{n-1}(X) - X\, T_n(X)}{(1 - X^2)^{\frac{1}{2}}} = \frac{T'_{n-1}(X) + (n-1) . T_n(X)}{(n-1)\ X} \cdot (1 - X^2)^{\frac{1}{2}} . \tag{A.VI.7}$$

Sorting out the terms and multiplying both sides by a factor $\frac{(n-1)\ X}{(1-X^2)^{\frac{1}{2}}}$

we get

$$T'_{n-1}(X) = \frac{(n-1)\ X}{1 - X^2} \cdot T_{n-1}(X) - T_n(X) \left[\frac{(n-1)\ X^2}{1 - X^2} + (n-1) \right] .$$

Further simplification gives us

$$T'_{n-1}(X) = (n - 1) \cdot \frac{X \cdot T_{n-1}(X) - T_n(X)}{1 - X^2} .$$

Finally replacing (n-1) by n yields

$$T'_n(X) = n \cdot \frac{X \cdot T_n(X) + T_{n+1}(X)}{1 - X^2} . \tag{A.VI.8}$$

From this relation it is now easy to find $T'_n(X)$ for an arbitrary order n.

Legendre polynomials

The procedure for the Legendre polynomials is essentially the same, and we merely quote the final recurrence relation.

$$P_n'(X) = n \frac{X \cdot P_n(X) - P_{n-1}(X)}{(X^2 - 1)} \qquad \text{(A.VI.9)}$$

Putting values of $T_n'(X)$ from equation (A.VI.8) and of $P_n'(X)$ from (A.VI.9) back in equation (A.II.2) we get the required general expression of Fock in recurrence form, suitable for use in the computer programme (see Appendix 4).

Table II summarizes the results of the computer calculations for different shells. The symbols used in the programme are presenting the following physical quantities:

N : the total number of shells considered at a time. It corresponds to n' we have used above.

X : the parameter used in Fock's expression. Same as we have used above.

F : corresponds to f used above and represents the scattering factor for a particular shell, say the nth, for different values of K,

ADDF : the total scattering factor for all the shells is being added up in here up to the nth shell for different K's.

F/Z : the scattering factor per electron.

AK : corresponds to our $k = \frac{4\pi \sin \theta/2}{\lambda}$.

BK : corresponds to the K used in the TF theory.

```
N          X          F          ADDF        F/Z        BK          AK

1     1.000000   2.000000    2.000000   1.000000          0          0
       .882352   1.771626    1.771626    .885813   2.080083   1.000000
       .600000   1.280000    1.280000    .640000   4.160167   2.000000
       .280000    .819200     .819200    .409600   6.240251   3.000000
             0    .500000     .500000    .250000   8.320335   4.000000
      -.219512    .304580     .304580    .152290  10.400419   5.000000
      -.384615    .189349     .189349    .094674  12.480502   6.000000

2     1.000000   8.000000   10.000000   1.000000          0          0
       .980198   7.572309    9.562946    .956294   1.216440   1.000000
       .923076   6.433598    8.394190    .839419   2.432880   2.000000
       .834862   4.925255    6.838204    .683820   3.649321   3.000000
       .724137   3.414434    5.263596    .526359   4.865761   4.000000
       .600000   2.150400    3.922026    .392202   6.082201   5.000000
       .470588   1.227236    2.910596    .291059   7.298642   6.000000
       .342281    .624974    2.212267    .221226   8.515082   7.000000
       .219512    .270726    1.757049    .175704   9.731523   8.000000
       .104972    .084264    1.467384    .146738  10.947963   9.000000
             0          0    1.280000    .128000  12.164403  10.000000
      -.095023   -.027318    1.151074    .115107  13.380844  11.000000
      -.180327   -.027306    1.053508    .105350  14.597254  12.000000
      -.256505   -.016340     .972043    .097204  15.813725  13.000000

3     1.000000  18.000000   28.000000   1.000000          0          0
       .994270  17.423491   27.366308    .977308    .863054   1.000000
       .977311  15.797076   25.570393    .913246   1.726108   2.000000
       .949641  13.400044   22.900469    .817873   2.589163   3.000000
       .912195  10.610052   19.744395    .705156   3.452217   4.000000
       .866111   7.807998   16.498599    .589235   4.315271   5.000000
       .812710   5.298475   13.484900    .481603   5.178326   6.000000
       .753424   3.256852   10.905868    .389531   6.041380   7.000000
       .689655   1.770178    8.845577    .315913   6.904434   8.000000
       .622768    .793030    7.284442    .260158   7.767489   9.000000
       .554013    .225847    6.146789    .219528   8.630543  10.000000
       .494497   -.033433    5.331974    .190427   9.493598  11.000000
       .415162   -.107517    4.741902    .169353  10.356652  12.000000
       .346783   -.069395    4.295858    .153423  11.219706  13.000000
       .280000    .013495    3.935521    .140554  12.082761  14.000000
       .215268    .171591    3.623577    .129413  12.945815  15.000000
       .152941    .173855    3.339244    .119258  13.808869  16.000000
       .093254    .222076    3.073070    .109752  14.671924  17.000000
       .036351    .245904    2.822358    .100798  15.534978  18.000000
      -.017697    .249077    2.587793    .092421  16.398033  19.000000
      -.068333    .236879    2.371108    .084682  17.261087  20.000000

4     1.000000  32.000000   60.000000   1.000000          0          0
       .997780  31.313322   59.173760    .986229    .669432   1.000000
       .991150  29.331265   55.776232    .946303   1.338865   2.000000
       .980198  26.274103   53.048975    .884149   2.008298   3.000000
       .965050  22.455517   48.335170    .805586   2.677731   4.000000
       .945945  18.285011   43.044951    .717415   3.347164   5.000000
       .923077  14.100032   37.526646    .625444   4.016597   6.000000
       .896703  10.223190   32.017436    .533623   4.686030   7.000000
       .867200   6.897523   27.507877    .458464   5.355463   8.000000
       .834862   4.235369   23.326014    .388766   6.024896   9.000000
       .800000   2.271523   19.840075    .330667   6.694328  10.000000
       .762977    .957533   17.035207    .283920   7.363762  11.000000
       .724137    .191357   14.837939    .247299   8.033195  12.000000
       .683816   -.155392   13.142553    .219042   8.702628  13.000000
       .642305   -.214259   11.833351    .197227   9.372061  14.000000
       .600000   -.135219   10.383649    .173060  10.041494  15.000000
       .557093    .083219    9.962987    .166049  10.710927  16.000000
       .513877    .277529    9.244374    .154072  11.380360  17.000000
       .470588    .437012    8.602395    .143373  12.049793  18.000000
       .427438    .544085    8.010152    .133502  12.719226  19.000000
       .384615    .591765    7.454718    .124245  13.388659  20.000000
       .342281    .587033    6.932275    .115537  14.058091  21.000000
       .300578    .541387    6.444034    .107400  14.727524  22.000000
       .259621    .469625    5.993091    .099884  15.396957  23.000000
       .219512    .380476    5.582346    .093039  16.066390  24.000000
       .180327    .294310    5.213361    .086889  16.735823  25.000000
       .142150    .210316    4.885929    .081432  17.405256  26.000000
       .104972    .136399    4.598131    .076635  18.074689  27.000000

5     1.000000  50.000000  110.000000   1.000000          0          0
       .974500  33.564090   87.744028    .797672   2.734827   5.000000
       .901768   8.327205   48.888795    .444443   5.469655  10.000000
       .791750   -.274498   26.423030    .240209   8.204482  15.000000
       .657534    .031113   17.944787    .163134  10.939310  20.000000
       .511930    .900437   13.178439    .119804  13.674137  25.000000
```

```
                 X              F           ADDF            F/Z             BK             AK

6      1.000000000   72.000000000  182.000000000    1.000000000              0              0
        .986500342   55.454013152  154.582452451     .849354134    2.312262007    5.000000000
        .947036167   19.623442663   99.050375120     .544235578    4.624524015   10.000000000
        .884770738    1.391733498   55.768632433     .311915563    6.936786022   15.000000000
        .803912926    -.023480159   36.995850774     .203273905    9.249048029   20.000000000
        .739665927    1.530901779   27.724702349     .152333529   11.561310037   25.000000000
        .607020034     .937381644   21.248702349     .116751112   13.873572044   30.000000000
        .500534939     .002346166   16.734528717     .091783125   16.185834052   OPS

7      1.000000000   98.000000000  280.000000000    1.000000000              0              0
        .992217899   77.790160799  247.525287260     .884018883    2.002971773    5.000000000
        .969230769   36.476679380  175.136932834     .625489260    4.005943545   10.000000000
        .932075472    6.943165493  106.700146239     .500214878    6.008915318   15.000000000
        .882352941    -.758687740   69.920435546     .249715841    8.011887090   20.000000000
        .822004057    1.358090239   51.449047187     .183746597   10.014858863   25.000000000
        .753424658    2.185964783   40.472735960     .144545486   12.017830635   30.000000000
        .678688525     .773523459   32.101864217     .114649515   14.020802408   35.000000000
        .600000000    -.124247076   26.161080278     .093432430   16.023774181   40.000000000

8      1.000000000  128.000000000  408.000000000    1.000000000              0              0
        .995200676  106.453592386  370.544200135     .908196569    1.766746007    5.000000000
        .980950634   56.792933060  261.449797574     .689827935    3.533492013   10.000000000
        .957660997   17.713123294  188.392950768     .461747428    5.300238020   15.000000000
        .925925351     .340213363  123.570477701     .392868818    7.066984026   20.000000000
        .886662435     .060415533   88.638991545     .217252430    8.833730033   25.000000000
        .840704331    2.834243784   69.816261077     .171123189   10.600476039   30.000000000
        .739329804    2.416945822   56.538516237     .136697344   12.367222046   35.000000000
        .733422193     .532459715   46.161961493     .113142062   14.133968053   40.000000000
        .674149167    -.197069543   38.635224183     .094694177   15.900714059   45.000000000

9      1.000000000  162.000000000  570.000000000    1.000000000              0              0
        .996888565  139.360135674  527.619045482     .925647448    1.580408005    5.000000000
        .987654838   86.357355969  422.074038052     .740480769    3.160816010   10.000000000
        .972340789   34.306109812  301.186382856     .528397163    4.741224015   15.000000000
        .951351351    5.111535464  284.355355761     .359576063    6.321632020   20.000000000
        .925012493   -1.224339516  145.493663425     .255234497    7.902040026   25.000000000
        .893770492    2.044158736  112.740655693     .197790642    9.482448031   30.000000000
        .858130931    3.938226709   92.320839688     .161966473   11.062856036   35.000000000
        .818639798    2.351227676   76.491912454     .134196338   12.643264041   40.000000000
        .775364719     .264192241   63.847385266     .112012957   14.223672046   45.000000000
        .730377472    -.218841792   54.539360526     .095663089   15.804080051   50.000000000

10     1.000000000  200.000000000  770.000000000    1.000000000              0              0
        .997830939  176.453636334  722.735771550     .933617885    1.429652861    5.000000000
        .991622284  118.947384592  631.039793407     .780532139    2.859305722   10.000000000
        .981217793   56.862244176  451.821748499     .566731492    4.288958582   15.000000000
        .966827003   14.901332821  321.515562370     .418253977    5.718611443   20.000000000
        .948646317    -.735445710  229.094621977     .297525743    7.148264304   25.000000000
        .926870828     .110783494  174.355197182     .226694944    8.577917165   30.000000000
        .901763473    4.153488171  142.155138959     .164616939   10.007570026   35.000000000
        .873597725    4.588241817  119.280826307     .154910164   11.437222886   40.000000000
        .842653455    2.113550073  100.606322463     .130657562   12.866875747   45.000000000
        .809275773     .008804338   85.574279720     .111135428   14.296528608   50.000000000
        .773755656    -.139523857   74.287256325     .096476956   15.726181469   55.000000000

11     1.000000000  242.000000000 1012.000000000    1.000000000              0              0
        .998524247  217.659073275  959.884483557     .948502454    1.305170759    5.000000000
        .994110025  156.372011510  822.227896765     .812478159    2.610341517   10.000000000
        .986796162   85.293121421  644.679440070     .637035023    3.915512276   15.000000000
        .976640427   30.482952698  475.954338943     .470320542    5.220683035   20.000000000
        .963740151    3.277333959  346.561915350     .342452486    6.525853793   25.000000000
        .948210381   -1.713308653  261.360227627     .258853980    7.831024552   30.000000000
        .930150626    2.671404397  210.563521088     .208966720    9.136195311   35.000000000
        .909747292    5.307322907  176.984923037     .174886238   10.441366070   40.000000000
        .887120892    4.834906593  151.075013974     .149263611   11.746536828   45.000000000
        .862471119    1.762431161  129.354128251     .127320285   13.051707587   50.000000000
        .835953895    -.216335943  111.757910410     .113432718   14.356878346   55.000000000
        .807774455    -.136633405   98.293267759     .097127735   15.662049104   60.000000000
        .778104567     .932040559   87.952771084     .086909853   16.967219863   65.000000000
```

```
           X              F               ADDF          F/Z           GK            AK

 1  1.000000000    2.000000000      2.000000000 1.000000000             0             0
     .862350941    1.771626298      1.771626298  .565813149   2.080083823   1.000000000
     .600000000    1.280000000      1.280000000  .640000000   4.160167646   2.000000000
     .280000000     .819200000       .819200000  .409600000   6.240251469   3.000000000
              0     .500000000       .500000000  .250000000   8.320335292   4.000000000
    -.219512195     .334580657       .334580657  .152290303  10.400419115   5.000000000
    -.384615385     .184349112       .184349112  .094674556  12.480502938   6.000000000

11  1.000000000  242.000000000   1012.000000000 1.000000000             0             0
     .998502247  217.083675275    955.304455557  .945562454   1.305170759   5.000000000
     .994100025  150.372011510    832.227696765  .812478159   2.610341517  10.000000000
     .986790452   85.243127421    644.579443600  .637035023   3.915512276  15.000000000
     .976645427   36.482952098    473.964388943  .470320542   5.220683035  20.000000000
     .963743151    3.223389389    344.561815360  .342452406   6.525853793  25.000000000
     .948215552   -1.713310553    261.960227627  .253853980   7.831024552  30.000000000
     .930105626    2.671414397    210.563521088  .208766720   9.136195311  35.000000000
     .909747792    5.900822907    175.934923837  .174886298  10.441366070  40.000000000
     .887126892    4.834906893    151.375013874  .149283611  11.746536828  45.000000000
     .862471119    1.762411161    123.356128251  .127320235  13.051707587  50.000000000
     .835953935    -.216915943    111.757910410  .112432718  14.356878346  55.000000000
     .807774455    -.135533405     95.293257759  .097127735  15.662049104  60.000000000
     .778164567     .932049559     67.952771684  .086909853  16.967219863  65.000000000

21  1.000000000  382.000000000   6622.000000000 1.000000000             0             0
     .999407236  773.554433892   6223.184114219  .941329525   1.395600478  10.000000000
     .997990459  510.656307416   5225.517581299  .789114706   2.791200956  20.000000000
     .995430623  232.144151461   3972.397253459  .599378776   4.186801434  30.000000000
     .991900797   52.153330099   2847.016731368  .429933061   5.582401912  40.000000000
     .987527509   -6.052434350   2044.823992870  .308792509   6.978002391  50.000000000
     .982050119    4.925116493   1556.390956280  .235033367   8.373602869  60.000000000
     .975600607   21.539843247   1264.723014068  .190988072   9.769203347  70.000000000
     .968327742   17.853376636   1061.065535365  .160236867  11.164803825  80.000000000
     .960082825    4.525183992    896.229525264  .135341215  12.560404303  90.000000000
     .950943188   -1.547024711    763.671372424  .115323372  13.956004781 *  .10000E+03

31  1.000000000 1922.000000000  20832.000000000 1.000000000             0             0
     .999889285 1855.576449525  20251.464363735  .972132506    .952460951  10.000000000
     .999557213 1489.933202507  18624.147208356  .894016283   1.904921902  20.000000000
     .999004054 1062.758751733  16257.824816607  .780425538   2.857382852  30.000000000
     .998230026  632.319335357  13562.104439053  .651022679   3.809843803  40.000000000
     .997235791  238.855909210  10934.950238989  .524911208   4.762304754  50.000000000
     .996021959   77.426872241   8667.926231169  .416087039   5.714765705  60.000000000
     .994589330   -7.312908408   6899.466038175  .331195569   6.667226655  70.000000000
     .992938850   -8.705837179   5623.549594696  .259947643   7.619687606  80.000000000
     .991071686   22.493155564   4739.213272260  .227496797   8.572148557  90.000000000
     .988988821   46.229054114   4113.898940576  .197479788   9.524609508 *  .10000E+03
     .986691855   46.770633984   3634.598679965  .174471903  10.477070459 *  .11000E+03
     .984182221   29.426334611   3232.288023873  .155159391  11.429531409 *  .12000E+03
     .981465533    9.394153135   2873.560415359  .139242147  12.381992360 *  .13000E+03
     .978532559   -2.393087186   2574.729563467  .123594929  13.334453311 *  .14000E+03
     .975394185   -1.720262389   2319.639382823  .111349817  14.286914262 *  .15000E+03

41  1.000000000 3362.000000000  47642.000000000 1.000000000             0             0
     .999916635 3096.128635112  45329.545278419  .964055776   1.084389822  15.000000000
     .999665782 2383.122452261  41224.449396364  .855296364   2.168779643  30.000000000
     .999251617 1516.318324401  34654.330543257  .727384042   3.253169465  45.000000000
     .998667790  726.375913104  27615.349730563  .579655552   4.337559286  60.000000000
     .997912213  209.239944545  21301.731099575  .447120841   5.421949108  75.000000000
     .997015034   -5.865165788  16373.352213821  .343779905   6.506338929  90.000000000
     .995925721  -13.771774692  12935.455036426  .271513917   7.590728751 *  .10500E+03
     .994683810    9.482797398  10662.153055375  .223795392   8.675118573 *  .12000E+03
     .993273616   36.013016352   9116.440119813  .191353010   9.759508394 *  .13500E+03
     .991702738   69.633915215   7942.361019505  .166719723  10.843898216 *  .15000E+03

51  1.000000000 5202.000000000  91052.000000000 1.000000000             0             0
     .999967706 4929.313434400  89910.375917642  .976479110    .873813864  15.000000000
     .999850870 4179.515193731  86842.351224216  .909833602   1.747627727  30.000000000
     .999682395 3134.133564619  73325.633117873  .813907375   2.621441591  45.000000000
     .999435638 2007.833822269  63213.811539556  .694227603   3.495255455  60.000000000
     .999110613 1074.410594932  52393.216130926  .575475729   4.369069319  75.000000000
     .998730185  427.493319033  42539.048521404  .467195103   5.242883182  90.000000000
     .998272076   55.365234073  34343.348273151  .377189339   6.116697046 *  .10500E+03
     .997742665  -41.845703846  28037.516479255  .307329720   6.990510910 *  .12000E+03
     .997142181    4.203015267  23443.546323752  .257523150   7.864324774 *  .13500E+03
     .996476712   85.583555680  20175.612747739  .221594284   8.738138637 *  .15000E+03
     .995730393  131.623550561  17772.780125912  .195193737   9.611952501 *  .16500E+03
     .994930395  121.756750098  15871.620541610  .174313805  10.485766365 *  .18000E+03
```

```
61 1.000000000 7442.000000000 * .15506200E+06 1.000000000           0           0
    .999982590 7164.974015918 * .15249352E+06  .983435812  .731723439 15.000000000
    .999930362 6383.355331743 * .14519594E+06  .935696349 1.463446879 30.000000000
    .999843321 5233.556309882 * .13370691E+06  .862280336 2.195170318 45.000000000
    .999721477 3906.216321844 * .11958918E+06  .771234641 2.926893757 60.000000000
    .999564842 2682.307753583 * .10416289E+06  .671749979 3.658617197 75.000000000
    .999370433 1489.339385212 88798.421441711  .572663976 4.390340636 90.000000000
    .999147269  672.641542654 74613.956131264  .461187758 5.122064075 *  .10500E+03
    .998886374  178.270873467 62349.725967340  .402095458 5.853787514 *  .12000E+03
    .998591775  -33.815412544 52331.249042020  .337485989 6.585510954 *  .13500E+03
    .998261504  -48.694977991 44515.371416190  .287081112 7.31720P5
+03
    .997805594   34.557598635 38595.969380136  .248906691 8.048957832 *  .16500E+03
    .997498083  130.696744918 34134.522342232  .220134671 8.780681272 *  .18000E+03
    .997062014  186.215330390 30682.008339071  .197869293 9.512404711 *  .19500E+03
    .996593431  184.033933200 27806.657546439  .17971319610.244128150 *  .21000E+03
    .996090384  136.717370844 25436.391471882  .16404013510.975851590 *  .22500E+03
    .995552923   71.730531768 23258.008558067  .14999167111.707575029 *  .24000E+03

71 1.00000000010082.000000000 * .24367200E+06 1.000000000           0           0
    .999990449 9801.991581222 * .24067804E+06  .987713160  .629360889 15.000000000
    .999961796 8939.374743768 * .23139538E+06  .951930465 1.258761778 30.000000000
    .999914043 7779.564255445 * .21826605E+06  .895737104 1.888142667 45.000000000
    .999847192 6297.010533257 * .20073859E+06  .823806574 2.517523556 60.000000000
    .999761248 4726.136152481 * .18075130E+06  .741783257 3.146904444 75.000000000
    .999656216 3241.924580027 * .15974428E+06  .655570968 3.776285333 90.000000000
    .999532101 1972.657384389 * .13904977E+06  .570643217 4.405666222 *  .10500E+03
    .999338910 1004.953085492 * .11975997E+06  .491480263 5.035047111 *  .12000E+03
    .999225652  364.465513958 * .10263667E+06  .421206324 5.664428000 *  .13500E+03
    .999045336   24.444382408 88081.276057634  .361474753 6.293808889 *  .15000E+03
    .998844972  -30.507095396 76159.339752197  .312548589 6.923189778 *  .16500E+03
    .998625572  -35.423279078 66663.130270847  .273597829 7.552570667 *  .18000E+03
    .998387149   75.076021935 59229.376283312  .243070104 8.181951556 *  .19500E+03
    .998129715  184.781696268 53367.502949083  .219095764 8.811332445 *  .21000E+03
    .997853287  249.753467501 48695.755667034  .199841408 9.440713333 *  .22500E+03
    .997557878  256.355493177 44778.039545126  .18376358210.070094222 *  .24000E+03
    .997243597  212.010211243 41361.043881306  .16974065110.699475111 *  .25500E+03
    .996910192  139.832162534 38278.131371508  .15708875611.328856000 *  .27000E+03

81 1.00000000013122.000000000 * .36088200E+06 1.000000000           0           0
    .99999133312839.824153750 * .35746343E+06  .990527190  .552154167 15.000000000
    .99997733012022.555411391 * .34743938E+06  .962750654 1.104308333 30.000000000
    .99994699410753.735263487 * .33148015E+06  .918527805 1.656462500 45.000000000
    .999909324 9159.647134937 * .31052407E+06  .860735860 2.208616667 60.000000000
    .999858322 7391.797373951 * .28617039E+06  .792974974 2.760770833 75.000000000
    .999791991 5606.843322298 * .25954569E+06  .719209321 3.312925000 90.000000000
    .999722331 3946.833225719 * .23218864E+06  .643392154 3.865079167 *  .10500E+03
    .999637345 2522.382235865 * .20538548E+06  .569120880 4.417233333 *  .12000E+03
    .999541037 1414.541115625 * .18021057E+06  .499361496 4.969387500 *  .13500E+03
    .999433713  616.172032978 * .15744139E+06  .436269742 5.521541666 *  .15000E+03
    .999314467  143.130351373 * .13753974E+06  .381121114 6.073695833 *  .16500E+03
    .999184212  -73.933545569 * .12065943E+06  .334346101 6.625850000 *  .18000E+03
    .999042650  -97.172379530 * .10669586E+06  .295653042 7.178004166 *  .19500E+03
    .998863785   -6.594035552 95349.001345465  .264211029 7.730158333 *  .21000E+03
    .998725623  126.796150686 86200.389103687  .238860318 8.282312500 *  .22500E+03
    .998550170  247.819180454 78767.229920617  .218318536 8.834466666 *  .24000E+03
    .998360431  322.230584053 72605.687589458  .201355791 9.386620833 *  .25500E+03
    .998160412  337.331014630 67456.462110660  .186921105 9.938775000 *  .27000E+03
    .997950121  290.345347407 62370.105734162  .17421236210.490929166 *  .28500E+03
    .997735564  223.949779315 58712.654815540  .16269211211.043083333 *  .30000E+03
    .997500749  136.223306772 54875.518334941  .15205945011.595237500 *  .31500E+03

91 1.00000000016562.000000000 * .51069200E+06 1.000000000           0           0
    .99999042816278.182629467 * .50634941E+06  .992475734  .491808174 15.000000000
    .99998571215450.193531276 * .49352876E+06  .970308453  .983616348 30.000000000
    .99996785214145.830419481 * .47333830E+06  .934680405 1.475424522 45.000000000
    .99994284912469.451547167 * .45321422E+06  .867451136 1.967232696 60.000000000
    .99991070310556.756338127 * .42438710E+06  .831094012 2.459040870 75.000000000
    .999871415 8530.547522588 * .39223692E+06  .766253786 2.950849044 90.000000000
    .999824985 6546.237012226 * .35821819E+06  .701430862 3.442657218 *  .10500E+03
    .999771415 4718.437530786 * .32372944E+06  .633973499 3.934465392 *  .12000E+03
    .999710706 3140.527322127 * .29063875E+06  .567932827 4.426273566 *  .13500E+03
    .999641859 1871.451705642 * .25819904E+06  .505596619 4.918081740 *  .15000E+03
    .999567876  934.135052232 * .22900090E+06  .448412950 5.409889914 *  .16500E+03
    .999483757  317.290938776 * .20295138E+06  .397404675 5.901698087 *  .18000E+03
```

(A.VII) Plot of scattering factor.

We have plotted f/Z , i.e the scattering factor per electron for the different methods, namely, Fock's and both coulomb and self-consistent results from the TF method, against K. Very good numerical agreement was found between the TF coulomb results and Fock's results for $n' \geqslant 5$. We have also plotted results for $n' = 1$ (thin curve) . As n' goes from 1 to 5 the curve approches the TF curve and for $n' = 5$ it coincides with it to graphical accuracy.

We have also plotted the self-consistent TF data of X-ray scattering (see, for example, Pirenne, 1945). Another important curve we have drawn here is from self-consistent Hartree and Hartree-Fock calculations given by Berghuis,IJbertha, Haanappel and Potters (1955). We have plotted results for Ne, which is the only example of a closed shell atom, given in the above reference.

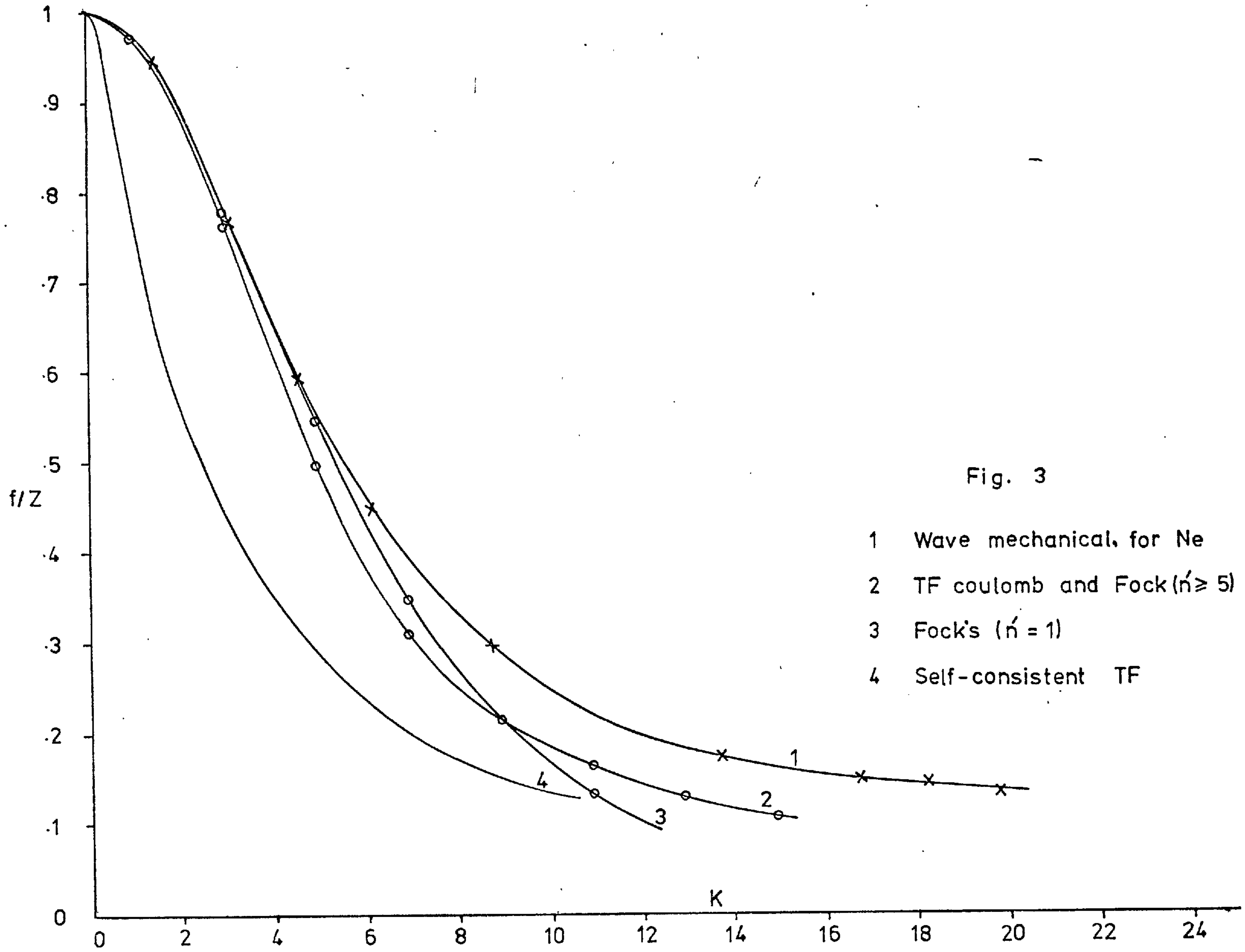

1
·9
·8
·7
·6
·5
f/Z
·4
·3
·2
·1
0
0
2
4
6
8
10
12
14
16
18
20
22
24
K
1
2
3
4
1 Wave mechanical, for Ne
2 TF coulomb and Fock (n′ ≥ 5)
3 Fock's (n′ = 1)
4 Self-consistent TF

Fig. 3

Conclusion

The main conclusion drawn from the above calculations of the scattering factor is that for hydrogenlike atoms the results of Fock and the TF theory agree to graphical accuracy if $n' \geqslant 5$ over quite a wide range of K. We expect however, since the TF density cuts off to zero at a finite radius, that the TF scattering factor will be in error at really large K.

(B) Momentum and kinetic energy densities.

In this section first we focus our attention on the momentum density, since it is directly related to the kinetic energy which we shall also study in some detail. Relations for wave mechanics and for the semi-classical TF theory are given along with the applications to hydrogenlike atoms and comparison is made between the results. Finally a relation is derived for the exact density at origin with comments on its relation to the momentum density for the limit of high momentum.

(B.I) The momentum density.

Here again we shall like to consider a pure coulomb field for evaluating the momentum density. We assume that $\psi_{n,l,m}(p)$ is the momentum wave function of an electron, n, l and m are respectively, principle, orbital and magnetic quantum numbers defining the electron state. The off-diagonal momentum density for the nth closed shell is defined by

$$\rho_n(p',p) = \sum_{lm} \psi^*_{nlm}(p') \cdot \psi_{nlm}(p) \,. \qquad \underline{\hspace{3cm}} \qquad (B.I.1)$$

The diagonal form of this density matrix for a pure coulomb field is given by

$$\rho_n(p,p) = \frac{8 \cdot p_n^5 \cdot n^2}{\pi^2 \cdot (p_n^2 + p^2)^4} \,, \qquad \underline{\hspace{3cm}} \qquad (B.I.2)$$

where p_n^2 is the mean square momentum for principle quantum number n. This has been evaluated in Appendix 1. The off-diagonal form is given by

$$\varrho_n(p',p) = \frac{8 \, . \, p_n^5}{\pi^2 \, (p_n^2 + p^2)^2 \, (p_n^2 + p'^2)^2} \quad \frac{n \, . \, \mathrm{Sin}(nQ)}{\mathrm{Sin} \; Q} \; .$$

Our Q here is equivalent to Fock's ω (see Fock, 1935). The momentum space density matrix $\varrho_n(\underset{\sim}{p}',\underset{\sim}{p})$ can be related to $\underset{\sim}{r}$ space density $\varrho_n(\underset{\sim}{r}',\underset{\sim}{r})$, essentially, through a Fourier transform. We then find the same angular dependence in $\underset{\sim}{r}$ space. Here $\varrho_n(p,p)$ is normalized only for singly occupied levels inside the shell i.e

$$4\pi \int_0^\infty \varrho_n(p,p) \, . \, p^2 . \, dp = n^2 \quad .$$

If the system contains n' closed shells then the total momentum density for the system is obviously

$$\varrho(p) = \sum_{n=1}^{n'} \varrho_n(p,p) \; .$$

Using equation (B.I.2) we find

$$\varrho(p) = \sum_{n=1}^{n'} \frac{8 \, . \, Z^5}{\pi^2 \, n^3 \left[\frac{Z^2}{n^2} + p^2 \right]^4} \qquad \text{\_\_\_\_\_\_\_\_(B.I.3)}$$

where we have substituted

$$p_n^2 = \frac{Z^2}{n^2}$$

as given in Appendix 1. At p = 0 the above relation (B.I.3) is simply written as

$$\varrho(0) = \frac{8}{\pi^2 \, . \, Z^3} \, . \, \sum_{n=1}^{n'} n^5 \quad ,$$

whereas at sufficiently large p, the explicit form of $\varrho(p)$ becomes

$$\varrho(p)\Big|_{\text{large } p} \sim \frac{1}{p^8} \cdot \frac{8\ Z^5}{\pi^2} \cdot \sum_{n=1}^{n'} \frac{1}{n^3} \cdot \qquad \text{(B.I.4)}$$

Equation (B.I.4) is related to $\varrho(r=0)$ which we shall discuss later on.

(B.II) Kinetic energy density.

(i) Wave mechanical relation.

The momentum is related to the kinetic energy by the following relation.

$$T = \left\langle \frac{p^2}{2\ m} \right\rangle \qquad \text{(B.II.1)}$$

where T is kinetic energy. Otherwise we can write it in terms of mean square momentum p_n^2, i.e

$$T = \frac{p_n^2}{2\ m}$$

since

$$\langle p^2 \rangle = p_n^2 \qquad \text{(see Appendix 1).}$$

We can also make use of Bohr's coulomb field energy relation and Virial theorem i.e

$$2\ T + V = 0$$

to write T as

$$T = \frac{Z^2}{2\ n^2} \cdot \frac{e^2}{a_0} \quad ,$$

where all the parameters have their usual meanings. The wave mechanical form of the kinetic energy density can be obtained from equation (B.II.1) by using the definition of the average square momentum, i.e

$$\left\langle \frac{p^2}{2\,m} \right\rangle = \int \psi^* \frac{p^2}{2\,m} \psi \, d\tau \quad .$$

Since the momentum p in quantum mechanics is represented by the operator $\frac{\hbar}{i} \nabla$, we have

$$\left\langle \frac{p^2}{2\,m} \right\rangle = - \frac{\hbar^2}{2\,m} \cdot \int \psi^* \nabla^2 \psi \; .d\tau \quad ,$$

which finally yields, by integrating by parts,

$$T = \frac{\hbar^2}{2\,m} \int |\nabla \psi|^2 \; . \, d\tau \quad . \text{\_\_\_\_\_(B.II.2)}$$

The kinetic energy per unit volume is therefore given by

$$t_r[\varrho] = \frac{\hbar^2}{2\,m} \cdot |\nabla \psi|^2 \quad . \text{\_\_\_\_\_\_\_(B.II.3)}$$

We shall use this relation when we study the application to hydrogenlike atoms later.

(ii) TF relation.

The TF approximation has its roots in statistical consideration of N free electrons moving in a volume v. The total kinetic energy in free electron theory is given by

$$T = N \cdot \int_0^{p_f} \frac{p^2}{2\,m} \cdot \frac{4.\pi.p^2}{4/3.\pi.p_f^3} \cdot dp \quad ,$$

where $\frac{p^2}{2\,m}$ is the kinetic energy of an electron with momentum p. The remainder of the integrand is simply the probability of an electron in the

Fermi gas having momentum of magnitude between p and $p+dp$. The first limitation of the TF theory, as is clear from the above argument is that it only holds for a system of non-interacting particles.

Integration of the above expression gives us the following result for T

$$T = \frac{3}{5} \cdot N \cdot \frac{p_f^2}{2\,m} ,$$

i.e the mean kinetic energy per particle is 3/5 of the Fermi energy E_f. Thus from the above result the kinetic energy per unit volume, say t, is given by

$$t = \frac{3}{5} \cdot \frac{N}{v} \cdot \frac{p_f^2}{2\,m} . \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_(B.II.4)}$$

Using the definition of phase space with occupied volume $\frac{4}{3}\pi p_f^3$, we can write electron density as

$$\rho(r) = \frac{2}{h^3} \cdot \frac{4\pi}{3} \cdot p_f^3(r)$$

where h is Planck's constant, h^3 being the volume of a basic cell in phase space which can hold 2 electrons with opposite spins. Using free electron relations locally we can write $\rho = N/v$, therefore

$$p_f = \left[\frac{N}{v} \cdot \frac{3\,h^3}{8\pi}\right]^{\frac{1}{3}} .$$

Putting it in equation (B.II.4), we obtain

$$t = \left[\frac{N}{v}\right]^{5/3} \cdot \frac{3\,h^2}{10\,m} \cdot \left(\frac{3}{8\pi}\right)^{\frac{2}{3}}$$

or in an inhomogeneous electron gas

$$t_r[\rho] = C_k \cdot \rho^{5/3}(r) \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_(B.II.5)}$$

where

$$C_k = \frac{3\,h^2}{10\,m} \cdot \left(\frac{3}{8\pi}\right)^{2/3}$$

(see, for example, March 1975). The above TF 5/3rd relation between $t_r[\rho]$ and charge density $\rho(r)$ has evidently been obtained by using free electron relations locally.

We can add a correction term arising from the density gradient in the inhomogeneous electron gas. This can be motivated through the wave mechanical relation for the kinetic energy of a single particle. In this case, assuming the ground state wave function ψ to be real, we can write

$$\psi = \rho^{\frac{1}{2}} .$$

Hence from (B.II.3) we have

$$t_r[\rho] = \frac{h^2}{8\,m} \cdot \frac{(\nabla\rho)^2}{\rho} .$$

This suggests the following type of correction to the TF kinetic energy density, namely

$$t_r[\rho] = C_k \cdot \rho(r)^{5/3} + \lambda \cdot \frac{h^2}{8\,m} \cdot \frac{(\nabla\rho)^2}{\rho} , \qquad \text{(B.II.6)}$$

which was first proposed by Von Weizscker, with $\lambda = 1$ as suggested by the above one-particle example. We now know from the later work of Kirznitz that λ is, in fact, 1/9.

The important thing is to compare equation (B.II.3) summed over occupied states and (B.II.5). This is done in the next section where we have applied each of these formulae to calculate the total kinetic energy for K, K+L and K+L+M shells of the hydrogenlike atoms.

(B.III) Application to hydrogenlike atomic systems.

(i) Wave mechanical results.

The normalized ground state wave functions for a system of Z electrons and nuclear charge Ze are taken from Pauling and Wilson (1935). The calculations needed to obtain the kinetic energy are straight forward. We need only the radial wave functions since we are considering the closed shell cases only. According to Unsold's theorem the angular parts of wave functions contribute either unity or a constant.

The exact relation (B.II.3) for the kinetic energy density is true for one particle only. But since we are interested in the closed shell contributions therefore we have to multiply it by a factor 2(2l+1), total number of states in a shell, where l is the orbital quantum number to get the total contribution of the closed orbital. To take account of this fact we write equation (B.II.3) again as

$$t_r[\rho] = \frac{\hbar^2}{2m} \cdot 2(2l+1) \cdot \left|\nabla \psi\right|^2 .$$

We also require the contribution to the total kinetic energy of the atom from the shell under consideration. This is obtained by integrating the above expression over the whole volume. Results for the exact kinetic energy density for K,L,M shells of a hydrogenlike system are summarized here.

K-shell	$1s^2$	$t_r[\rho] = E \cdot \frac{2}{\pi} \cdot e^{-2S}$
L-Shell	$2s^2$	$= E \cdot (S^2-8S+16) \cdot e^{-S}/(64\pi)$
	$2p^6$	$= E \cdot (S^2-4S+4)3 \cdot e^{-S}/(64\pi)$

M-Shell $3s^2$ $t_r = E \cdot (\frac{2}{3} S^2 - 10\, S + 27) \cdot e^{-\frac{2}{3} S} \cdot 2/(81^2 \cdot 3\pi)$

$3p^6$ $= E \cdot (S^2 - 12S + 18)^2 \cdot e^{-\frac{2}{3}S} \cdot 18/(81^2 \cdot 27\pi)$

$3d^{10}$ $= E \cdot (S^2 - 6S)^2 \cdot e^{-\frac{2}{3}S} \cdot 20/(81^2 \cdot 27\pi)$,

where $E = \frac{h^2}{2\,m} \cdot A^5$, $A = \frac{Z}{a_o}$, $S = A \cdot r$

The increase in the total kinetic energy of the atom as we add K, L and M shells one by one is as follows:

K-Shell $T_K = 2 \cdot E = \frac{Z^2 e^2}{a_o}$

K+L Shells $T_{K+L} = 4 \cdot E = 2 \cdot \frac{Z^2 e^2}{a_o}$

K+L+M Shells $T_{K+L+M} = 6 \cdot E = 3 \cdot \frac{Z^2 e^2}{a_o}$

These results are in agreement with the virial theorem.

(ii) TF results.

According to the TF relation, the kinetic energy density in an atom is proportional to the 5/3rd power of the charge density, equation (B.II.5).

In using this relation we note that we shall use the exact density obtained from the wave functions after proper normalization and not the TF charge density. Using the exact density we shall naturally get the best results for the TF approximation to the kinetic energy density. Another important point is that for the TF theory each shell is not treated separately as we did for the exact relation but rather all the shells present in the atom are treated together, since $\varrho(r)$ in the TF relation is the total charge density for N electrons. We record below the normalized densities for different cases considered,

K Shell $1s^2$ $$\varrho_K = A^3 \cdot \frac{2}{\pi} \cdot e^{-2S}$$

K+L Shells $1s^2+2s^2+2p^6$

$$\varrho_{K+L} = A^3 . \quad \left[2e^{-S} + \frac{1}{16}\left((2-S)^2 + S^2\right) \right] e^{-S}/\pi$$

K+L+M Shells $1s^2+2s^2+2p^6+3s^2+3p^6+3d^{10}$

$$\varrho_{K+L+M} = \frac{A^3}{\pi} \cdot \left[e^{-S}\left[2e^{-S} + \frac{1}{16}\left((2-S)^2+S^2\right)\right] + \frac{2}{81^2} \cdot e^{-\frac{2}{3}S}\left[\tfrac{1}{3}(27-18S+2S^2)^2 + 2(6-S)^2 S^2 + \tfrac{2}{3}S^4\right]\right].$$

The general TF expression for the total kinetic energy in terms of variable S can be written as

$$T = C_k \cdot \frac{1}{A^3} \int_0^\infty 4\pi S^2 \cdot \varrho^{5/3}(S) \cdot dS \cdot$$

Due to the lengthy expressions for the charge densities plus the 5/3 power, numerical integration has been used, combining Simpson's rule with an electronic computer. Omitting the details we merely record the results for the three cases:

K Shell $$T_K = 0.9179 \frac{Z^2 e^2}{a_o}$$

K+L Shells $$T_{K+L} = 1.88855 \frac{Z^2 e^2}{a_o}$$

K+L+M Shells $T_{K+L+M} = 2.87575 \frac{Z^2 e^2}{a_0}$

General behaviour of exact kinetic energy density $t_r[\rho]$.

Here we wish to comment on the general behaviour of the wave mechanical kinetic energy density. Hydrogenlike wave function has the form

$$\psi_n \sim e^{-\frac{Zr}{na_0}}$$

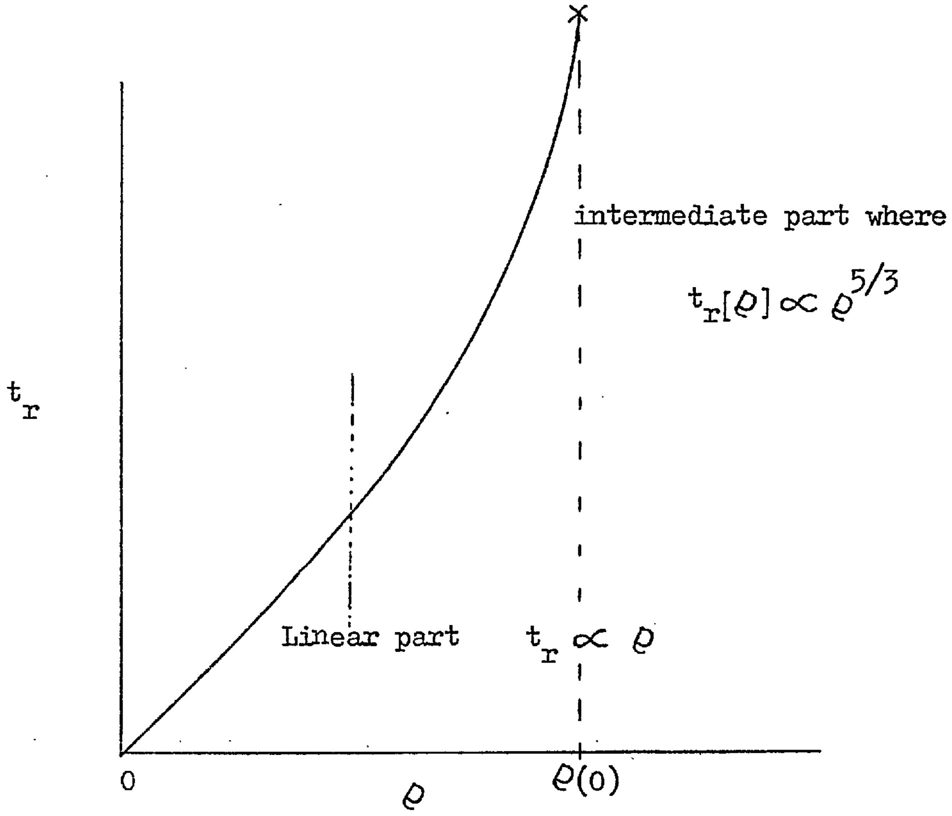
which means that at low density $\rho \to 0$, kinetic energy density $t_r[\rho]$ will be dominated by the last closed shell and at sufficiently large r, the highest value of n will dominate. This will lead to a linear relation between $t_r[\rho]$ and $\rho(r)$ i.e

$$t_r[\rho] \propto \rho(r) \quad .$$

The constant of proportionality will depend on the potential, since it will involve the energy E_n of last closed shell.

At high density, there will be a maximum $\rho(r)$ (the value of the density at the nucleus) beyond which one cannot go.

Between these two extremes the intermediate part of $t_r[\rho]$ ought to go like $\rho^{5/3}$, the dependence we obtain from the TF theory when a local relation is assumed. Graphically $t_r[\rho]$ is expected to behave as shown in in the diagram on next page. We attempted to obtain this behaviour from the results for the K,L and M shells given above. But the number of shells are not sufficient to show the exact $\rho^{5/3}$ region. The result we obtained was in the region of the linear part of the plot shown. To reach the intermediate region we would need to include more shells. But the density expressions already becoming quite complicated to deal with and therefore we did not proceed to include any higher shell .



Nevertheless from the above results for the K, L and M shells we can conclude that the TF approximation is a useful approximation to the exact kinetic energy of atoms, increasing in accuracy with the number of shells included.

(B.IV) Density at origin in hydrogenlike atoms.

The calculation of the density at the origin is of interest because there is an exact relation between the density and its gradient at the origin even for many interacting electrons (see Steiner, 1963). It is helpful in testing the approximate many electron wave functions. The normalized eigen functions for hydrogen-like system as given by Pauling and Wilson (1935) are usually written as

$$U_{n,l,m}(r,\theta,\phi) = R_{n,l}(r) \cdot Y_{l,m}(\theta,\phi)$$

The normalized radial wave function $R_{n,l}(r)$ is expressed as

$$R_{n,l}(r) = -\left[\left(\frac{2Z}{na_o}\right)^3 \cdot \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{\frac{1}{2}} \cdot e^{-\frac{1}{2}\sigma} \cdot \sigma^{l} \cdot L_{n+l}^{2l+1}(\sigma),$$

where

$\sigma = \frac{2}{n} S = \frac{2}{n} \frac{Z}{a_o} r$ and L denotes the associated Leguerre polynomials. The angular part of the wave function is given explicitly by

$$Y_{l,m}(\theta,\phi) = \frac{1}{(2\pi)^{\frac{1}{2}}} e^{im\phi}\left[\frac{(2l+1)(l+|m|)!}{2\,(l+|m|)!}\right]^{\frac{1}{2}} P_l^m(\text{Cos}\ \theta) .$$

It is assumed that the coordinate system has origin at the nucleus. But we know that the only functions which are non-zero at the nucleus have $l = 0$. Hence for $r = 0$ the radial wave function becomes

$$R_{n,0}(0) = -\left[\left(\frac{2}{n}\frac{Z}{a_o}\right)^3 \cdot \frac{(n-1)!}{2n(n!)^3}\right]^{\frac{1}{2}} L_n^1(0) .$$

We also have

$$L_n^1(0) = (-1) \frac{(n!)^2}{(n-1)!}$$

and rewriting the above expression leads to

$$R_{n,0}(0) = \frac{1}{2^{\frac{1}{2}}} \cdot \left(\frac{2}{n}\frac{Z}{a_o}\right)^{3/2} .$$

Similarly the angular part reduces to

$$Y_{0,0} = \frac{1}{(4\pi)^{\frac{1}{2}}} .$$

Therefore the normalized total wave function at the origin for the hydrogen-like atoms is given by

$$U_{n,0,0}(0) = \frac{1}{2(2\pi)^{\frac{1}{2}}} \cdot \left(\frac{2}{n}\frac{Z}{a_o}\right)^{3/2}$$

Since it is a real quantity the charge density is the square of the wave function i.e

$$U^2_{n,0,0}(0) \quad = \quad \frac{1}{8\pi} \left(\frac{2\,Z}{n\,a_o}\right)^3 \quad .$$

The total electron density at the origin for an atom with n' closed shells and with doubly occupied levels obviously becomes

$$\rho(0) \quad = \quad 2 \sum_{n=1}^{n'} U^2_{n,0,0}(0)$$

Simplification then yields the result

$$\rho(0) \quad = \quad \frac{2}{\pi}\,\frac{Z^3}{a_o^3} \sum_{n=1}^{n'} \frac{1}{n^3} \; . \qquad \underline{\hspace{3cm}}(\mathrm{B.IV.1})$$

We can relate $\rho(0)$ to the momentum density $\rho(p)$ at large p. From equations (B.IV.1) and (B.I.4) it is easy to show that

$$\left.\rho(p)\right|_{\text{large } p} \quad \simeq \quad \frac{4\,Z^2}{\pi\,p^8} \quad \rho(0) \qquad \underline{\hspace{3cm}}(\mathrm{B.IV.2})$$

A more important relation, as we remarked earlier, is due to Steiner (1963) linking $\rho(0)$ and $\left.\nabla\rho(r)\right|_{r=0}$. Steiner derived this relation from the result of Kato (1957), namely

$$\left.\frac{\partial\bar{\Psi}}{\partial r_n}\right|_{r_n=0} \quad = \quad -\,Z \left|\,\bar{\Psi}(r_1,r_2,r_3,\ldots\ldots\ldots r_n)\right|_{r_n=0} \; ,$$

where Ψ is the wave function of N electrons and $\bar{\Psi}$ is given by

$$\bar{\Psi} \quad = \quad \frac{1}{4\pi}\int_{\omega_n} \Psi(r_1,r_2,r_3,\ldots\ldots r_n)\; d\omega_n \quad ,$$

which represents the average of Ψ over a sphere of radius r_n. Steiner's result is then

$$\left.\frac{\partial\rho}{\partial r}\right|_{r=0} \quad = \quad 2\,.\,\frac{\rho(0)}{a_o} \qquad \underline{\hspace{3cm}}(\mathrm{B.IV.3})$$

Returning to equation (B.IV.1) we now analyze the term $\sum_{n=1}^{n'} \frac{1}{n^3}$. For $n' = 1$ we get

$$\rho(0) = \frac{2}{\pi} \frac{Z^3}{a_0^3} .$$

It is true for all the elements as long as the total number of electrons, N, present in the atom remain equal to 2. If n' becomes 2 the value of electron density at origin increases 9/8 times that of $n'=1$, i.e

$$\rho_{K+L}(0) = \rho_K(0) \frac{9}{8}$$

and holds always for $N = 10$. Similarly for $n' = 3$ we get

$$\rho_{K+L+M}(0) = \rho_K(0) \left(1+\frac{1}{8}+\frac{1}{27}\right)$$

where all the three shells are assumed to be closed. We can carry on for any number of shells by just following the above procedure .

We next make an estimate of the term $\sum_{n=1}^{n'} \frac{1}{n^3}$ for large n' . It is easy to show that for a large number of closed shells we can write, for neutral atoms only, that

$$Z \sim \frac{2\, n'^3}{3}$$

(we shall discuss this in detail below). From the above relation we get immediately

$$n' = \left(\frac{3}{2} Z\right)^{\frac{1}{3}} . \qquad \text{(B.IV.4)}$$

Estimate of $\sum_{n=1}^{n'} \frac{1}{n^3}$ is possible by finding the area under the curve for limits $m+\frac{1}{2}$ and $n'+\frac{1}{2}$ to take account of n' shells

$$\text{Area} = \int_{m+\frac{1}{2}}^{n'+\frac{1}{2}} \frac{1}{n^3}\, dn .$$

and adding the sum of the first m terms of the series. In this way, the summation is found to be ~ 1.2, by taking $m \sim 20$.

The formula for the area beyond the mth term suggests a correction term to this value of $O(Z^{-2/3})$ for large Z, but we have not pursued the matter further.

(C) Binding energies of atoms and ions.

(C.I) Binding energy expressions.

We shall give here the main outlines of the Thomas-Fermi binding energy relation, leaving out the details. We start with the TF charge density given already in part A when considering the TF scattering factor, for a pure coulomb field. But in general the TF relation for $\varrho(r)$ is given by

$$\varrho(r) = \begin{cases} \frac{8\pi}{3h^3}(2m)^{3/2} \cdot (E_f - V(r))^{3/2} & \text{for } |V(r)| > |E_f| \\ 0 & \text{otherwise,} \end{cases} \qquad \text{\_\_\_\_\_\_\_\_\_\_(C.I.1)}$$

E_f being the total energy of the fastest electron. Other parameters have their usual meanings. The usual substitution

$$E_f - V(r) = \frac{Z e^2}{r} \cdot \Phi(x) , \qquad \text{\_\_\_\_\_\_\_\_\_\_(C.I.2)}$$

leads to a description of the potential field in the ion in terms of the dimensionless function $\Phi(x)$. The length r is also usefully expressed in deminsionless form by putting

$$x.b = r ,$$

b being a constant of dimensions of length given by

$$b = \frac{1}{4}\left(\frac{9\pi^2}{2Z}\right)^{\frac{1}{3}} a_o$$

$$= \frac{0.8853}{Z^{\frac{1}{3}}} \cdot a_o \cdot \qquad \text{\_\_\_\_\_\_\_\_\_\_(C.I.3)}$$

From equations (C.I.1), (C.I.2) and (C.I.3) it follows that Φ satisfies the dimensionless Thomas-Fermi equation

$$\Phi'' = x^{-\frac{1}{2}} \cdot \Phi^{3/2} \quad ,$$

with the boundary conditions

$$\Phi(x_o) = 0 \quad , \quad \Phi(0) = 1 \quad \text{and} \quad x_o \Phi'(x_o) = -q = -(1-\tfrac{N}{Z})$$

where $\underline{q}$ is the degree of ionization, while x_o measures the ionic radius r_o through $b \cdot x_o = r_o$ (see, for example, March 1975).

Now we proceed to the binding energy relations. The total energy E is evidently given by

$$E = T + V \quad ,$$

where T is the kinetic and V the potential energy. V as usual consists of the sum of electron-nucleus and electron-electron contributions. In the TF theory these three contributions are

$$T = C_k \int \rho^{5/3}(r) \, d\underset{\sim}{r} \; , \quad V_{en} = -Z\, e^2 \int \frac{\rho(r)}{r} \, d\underset{\sim}{r}$$

$$\text{and} \quad V_{ee} = \frac{1}{2} \int \rho(r) \; V_e(r) \; d\underset{\sim}{r}$$

__________________(C.I.4)

where $V_e(r)$ is the electrostatic potential created by the electronic cloud $\rho(r)$. We recall that T given above has been derived by a local approximation, from the kinetic energy density of free electrons. Minimizing E with respect to variation in $\rho(r)$ subject to the normalization condition $\int \rho(r) \, d\underset{\sim}{r} = N$, the total number of electrons, that is

$$\delta (E + \lambda N) = 0 \quad ,$$

where λ is a Lagrange multiplier, it is straight forward to derive the relation

$$\frac{5}{3}\, C_k\, \varrho^{\frac{2}{3}}(r) = -\,(\,\lambda + V(r)\,)\,. \tag{C.I.5}$$

Comparing (C.I.1) and (C.I.5) we recognize that $E_f \equiv -\lambda$. We can also show from thermodynamics that λ is equivalent to chemical potential as well

$$\mu = \frac{\partial E}{\partial N} = -\lambda = -\,\frac{(Z-N)}{r_0}\, e^2 \;, \tag{C.I.6}$$

since $\varrho(r_0) = 0$. We shall need this value of λ later.

One way of proceeding to calculate energy is to find $\frac{dE}{dZ}$ at constant N/Z . Mathematically we have

$$\left(\frac{dE}{dZ}\right)\Big|_{N/Z} = \frac{\partial E}{\partial N}\,\frac{dN}{dZ} + \frac{\partial E}{\partial Z}\;. \tag{C.I.7}$$

Using equation (C.I.4) and (C.I.6) in (C.I.7) we arrive at the result

$$\left(\frac{dE}{dZ}\right)\Big|_{N/Z} = 4\left(\frac{2}{9\pi^2}\right)^{\frac{1}{3}} \left[\Phi'(0) + \left(1 - \frac{N}{Z}\right)^2 \frac{1}{x_0}\right] Z^{4/3}\, \frac{e^2}{a_0}$$

where $\Phi'(0)$ is the slope of $\Phi(x)$ at $x = 0$. Integrating the above expression with respect to Z we get the required relation for the total energy E as a function of N and Z, that is

$$E(N,Z) = 0.4841 \left[\Phi'(0) + \left(1 - \frac{N}{Z}\right)^2 \frac{1}{x_0}\right] Z^{\frac{7}{3}}\cdot \frac{e^2}{a_0}\;. \tag{C.I.8}$$

In general we can write

$$E(N,Z) = Z^{\frac{7}{3}}\, f\!\left(\frac{N}{Z}\right) \frac{e^2}{a_0}\;,$$

where $f(\frac{N}{Z})$ expresses the fact that $\Phi'(0)$ and x_0 depend only on N/Z.

A sketch of $f(\frac{N}{Z})$ was given by March and White (1972), using available numerical solutions of the TF equation. They have plotted the function

$$\frac{E(N,Z)}{Z^{\frac{7}{3}}} \left(\frac{N}{Z}\right)^{\frac{2}{3}} \equiv \left(\frac{N}{Z}\right)^{\frac{2}{3}} f\left(\frac{N}{Z}\right)$$

against $\frac{N}{Z} \geqslant .5$ with Z large. This was a more convenient form to plot than simply $f(\frac{N}{Z})$. The function itself has been calculated by different people: March and White (1972) used $\sim 1/Z$ expansion and worked out the energy coefficients $\epsilon_o(N)$, $\epsilon_1(N)$ and $\epsilon_2(N)$ for $2 \leqslant N \leqslant 10$ range. In general they obtained

$$\epsilon_n(N) \sim a_n N^{n+\frac{1}{3}}$$

for large N. 'a_o' has been calculated from first principle (Ballinger and March 1955), whereas a_1 and a_2 estimated by them by least-square fit of data on $\epsilon_1(N)/N$ and $\epsilon_2(N)/N^2$. Later on Dmitrieva and Plindov (1975) derived a_1 and a_2 from first principles. Recently March (1976) has proposed a modified value of the coefficient of $(\frac{N}{Z})^2$ given by them, arguing that by doing so one can get the correct isolated atom limit as well as excellent numerical agreement with the correct results over the whole range $0 \leqslant \frac{N}{Z} \leqslant 1$ by neglecting all the higher order terms.

The complete expression after the modification of March (1976) for the binding energy of a heavy ion up to third order is

$$E(N,Z) = -\left(\frac{3}{2}\right)^{\frac{1}{3}} N^{\frac{1}{3}} Z^2 \frac{e^2}{a_o} \left(1 - 0.4236\frac{N}{Z} + 0.0951\frac{N^2}{Z^2} \right). \tag{C.I.9}$$

We shall discuss this in more detail later and establish a connection between (C.I.9) and 1/Z theory.

Equation (C.I.9) contains the TF neutral atom binding energy as we shall now show. In equation (C.I.8) if we put $\frac{N}{Z} = 1$ and $\Phi'(0) = -1.58805$ from the TF solution for the isolated atom we get the binding energy as

$$E(Z,Z) = -\,0.7687 \; Z^{\frac{7}{3}} \, \frac{e^2}{a_0} \; . \qquad \text{(C.I.10)}$$

This result was first obtained by Milne (1927).

(C.II) $Z^{\frac{7}{3}}$ dependence from Bohr's formula.

We can obtain the $Z^{\frac{7}{3}}$ dependence in equation (C.I.10) from Bohr's formula for the energy level spectrum. The energy levels for principle quantum number n are given by

$$E_n = -\frac{Z^2}{2\,n^2} \, \frac{e^2}{a_0} \quad ,$$

since a closed shell of quantum number n can hold $2n^2$ electrons, the sum of the eigenvalues becomes

$$E_{nth} = -\; Z^2 \, \frac{e^2}{a_o} \; . \qquad \text{(C.II.1)}$$

For an atomic system of n' closed shells the total eigenvalue sum E_s is obviously given by

$$E_s = -\; Z^2 \, n' \frac{e^2}{a_0} \; . \qquad \text{(C.II.2)}$$

Now we must relate E_s to N, the total number of electrons. It is possible through n', since we have

$$N = \sum_{n=1}^{n'} 2\,n^2 = \frac{n'(n'+1)(2n'+1)}{3} \; . \qquad \text{(C.II.3)}$$

If n' is large, as for heavy ions and atoms, it follows from equation (C.II.3) that

$$N \simeq \frac{2\,n'^3}{3} , \qquad \text{\_\_\_\_\_\_\_\_\_\_(C.II.4)}$$

the result we used in the earlier calculation of the density at the origin when $Z = N$. Writing (C.II.4) more exactly by adding the next order we find

$$N = \frac{2\,n'^3}{3} + n'^2$$

and using (C.II.4) in the correction term we obtain

$$N = \frac{2\,n'^3}{3} + (\tfrac{3}{2}N)^{\frac{2}{3}} .$$

This yields the required relation between n' and N i.e

$$n' = (\frac{3}{2}N)^{\frac{1}{3}} \left[1 - (\frac{3}{2})^{\frac{2}{3}} N^{-\frac{1}{3}}\right]^{\frac{1}{3}} . \qquad \text{\_\_\_\_\_(C.II.5)}$$

Putting (C.II.5) back in (C.II.2) we find

$$E_s = - Z^2 (\frac{3}{2}N)^{\frac{1}{3}} \left[1 - (\frac{3}{2})^{\frac{2}{3}} N^{-\frac{1}{3}}\right]^{\frac{1}{3}} \frac{e^2}{a_0} .$$

For the neutral atom case $N = Z$ it follows that

$$E_s(Z,Z) = - (\frac{3}{2})^{\frac{1}{3}} Z^{\frac{7}{3}} \left[1 - (\frac{3}{2})^{\frac{2}{3}} Z^{-\frac{1}{3}}\right]^{\frac{1}{3}} \frac{e^2}{a_0} . \qquad \text{\_\_\_\_\_(C.II 6)}$$

Here we have considered only the over simplified case for n' closed shells in a neutral atom under the assumption of a pure coulomb field.

The coefficient of the leading term in (C.II.6) only involves the nuclear coulomb field felt by Z electrons. But the corresponding coefficient in the TF self consistent equation (C.I .10) obviously involves the screening effect of the electron distribution as well. Expanding equation (C.II.6) we get

$$E_s = -\left(\frac{3}{2}\right)^{\frac{1}{3}} Z^{\frac{7}{3}} \frac{e^2}{a_0} + Z^2 \frac{e^2}{2a_0} \qquad \text{———} (C.II.7)$$

where E_s has the $Z^{\frac{7}{3}}$ dependence of Milne's result but with a different coefficient. In addition to that we have got here a term proportional to Z^2 which we shall regard as correction term ΔE.

March (1976) obtained $Z^{\frac{7}{3}}$ exactly from the TF charge density i.e equation (C.I.1). Thus, using

$$\int \rho(r) \, d\underset{\sim}{r} = N$$

to find E_f as

$$E_f = -\frac{Z^2}{N^{\frac{2}{3}}} \cdot \frac{1}{18^{\frac{1}{3}}} \cdot \frac{e^2}{a_0}, \qquad \text{———} (C.II.8)$$

We have from equation (C.I.6)

$$-E_f = \frac{dE}{dN},$$

and therefore

$$\frac{dE}{dN} = \frac{Z^2}{N^{\frac{2}{3}}} \cdot \frac{1}{18^{\frac{1}{3}}} \cdot \frac{e^2}{a_0}.$$

Integrating this with respect to N yields

$$E_{TF}(Z,N) = -\left(\frac{3}{2}\right)^{\frac{1}{3}} Z^2 N^{\frac{1}{3}} \frac{e^2}{a_0}.$$

For the neutral atom case it follows immediately that

$$E_{TF}(Z,Z) = -\left(\frac{3}{2}\right)^{\frac{1}{3}} Z^{\frac{7}{3}} \frac{e^2}{a_0},$$

which is the leading term of equation (C.II.7).

(C.III) Relation between eigenvalue sum and binding energy.

We now go back to the TF binding energy expression (C.I.9) and form the sum of eigenvalues like (C.I.7). Equation (C.I.9) i.e self-consistent TF binding energy has been derived from

$$E = \int t_r[\varrho]\, \underset{\sim}{dr} + \int \varrho(r) \cdot V_N \cdot \underset{\sim}{dr} + \frac{1}{2}\int \varrho(r) \cdot V_e \cdot \underset{\sim}{dr} \ , \qquad \text{(C.III.1)}$$

whereas the sum of the eigenvalues is defined as

$$E_s = \sum_i \epsilon_i = \int t_r[\varrho]\ \underset{\sim}{dr} + \int \varrho \cdot (V_N + V_e) \cdot \underset{\sim}{dr} \ . \qquad \text{(C.III.2)}$$

From (C.III.1) and (C.III.2) we can easily find that

$$\begin{aligned} E_s &= E + \frac{1}{2}\int \varrho \cdot V_e \cdot \underset{\sim}{dr} \\ &= E + V_{ee} \ . \qquad \text{(C.III.3)} \end{aligned}$$

We can derive another relation between E_s and E if the atomic system is neutral and $Z \rightarrow \infty$. Using the relation

$$V_{en} = - 7\ V_{ee}$$

(see March, 1975) we obtain

$$V = -6\ V_{ee} \ .$$

Substituting this in equation (C.III.3) and making use of the virial theorem it is easy to derive

$$E_s = \frac{2}{3}\ E \ . \qquad \text{(C.III.4)}$$

Putting in the value of E for the TF theory from equation (C.I.10) and transferring it to Rydberg units gives us

$$E_s = -1.025 \; Z^{\frac{7}{3}} \quad \text{Rydbergs,}$$

which does not contain the correction term but this can be added for relatively light atoms. Here we assume that $\triangle E$ will have the Z^2 dependence as found earlier using Bohr's formula i.e equation (C.II.7). This will be investigated below.

With this, our analysis of the leading term in the energy expression is complete. It is essentially due to the coulomb field inside the atom between the electrons and the nucleus.

Study of correction term $\triangle E$.

We go back to the equation (C.II.7), where we have concluded that the correction term in the sum of eigenvalues is proportional to Z^2. If we take the Rydberg as the unit of energy, then the constant of proportionality becomes unity. Therefore the above arguement implies that a plot of $\triangle E$ against Z^2 should be a straight line with a slope 1.

To test this we must calculate $\triangle E$. Modifying equation (C.III.5) for relatively light atoms by adding the correction term $\triangle E$ we obtain

$$E_s = -1.025 \; Z^{\frac{7}{3}} + \triangle E \quad .$$

Thus

$$\triangle E = E_s + 1.025 \; Z^{\frac{7}{3}} \quad , \qquad \text{\_\_\_\_\_\_\_\_\_\_(C.III.6)}$$

where E_s is negative and available in the Hartree's calculations. Herman and Skillman (1963) have calculated Hartree-Fock-Slater self-consistent field results for energy eigenvalues and charge densities, normalized for each electron at each level. For our calculations we have to take sum of eigenvalues for all the electrons present in the level.

The results are not very different for either neutral atoms, or for singly or doubly ionized atoms. But since we are restricted to neutral atoms for the present calculations we have naturally used only neutral atom results from Herman and Skillman's numerical data. We have carried out numerical calculation up to $Z = 84$, The plot for this is shown below(Fig. 4). Except for Nd^{60} all the others lie more or less on a straight line of slope 0.94. We have also drawn the straight line with a slope of 1 as expected; the percentage error from the predicted slope being only 6 %.

Thus we conclude that the Hartree-Fock-Slater numerical results are satisfactorily in agreement with the theoretically predicted result that $\Delta E \propto Z^2$.

We have also examined ionization potentials, since these are useful in determining the binding energies of ions and atoms as previously shown by Foldy (1951), namely

$$E_b = \frac{1}{2} Z^{12/5} \frac{e^2}{a_o} + \sum_{Z=2}^{Z} I_Z - 1.278 \frac{e^2}{2\, a_o} .$$

However, the plot of ln I.P versus ln Z which we have given below(Fig. 5) shows a periodic variation and statistical arguments are obviously not applicable here.

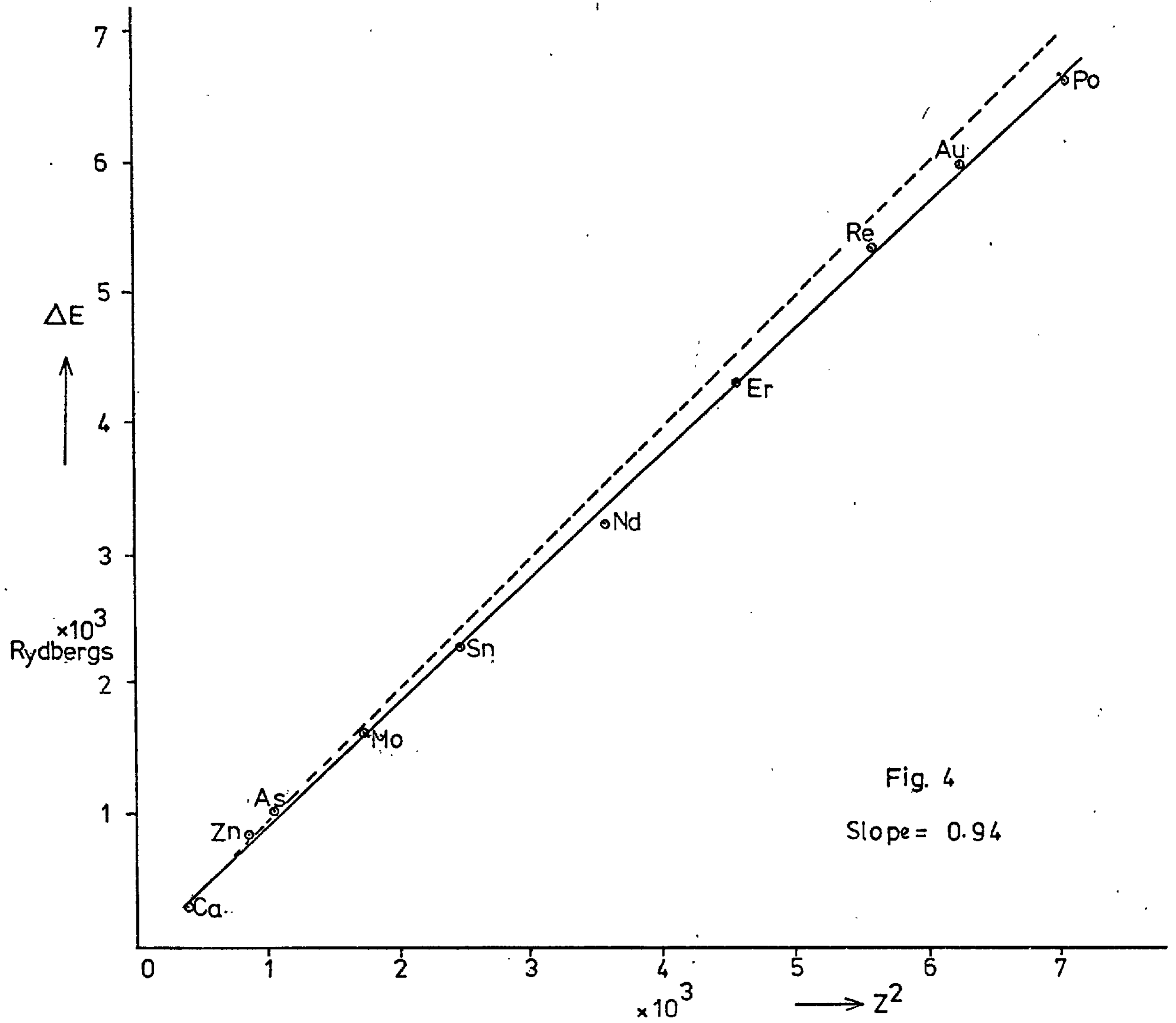


Fig. 4

Slope = 0.94

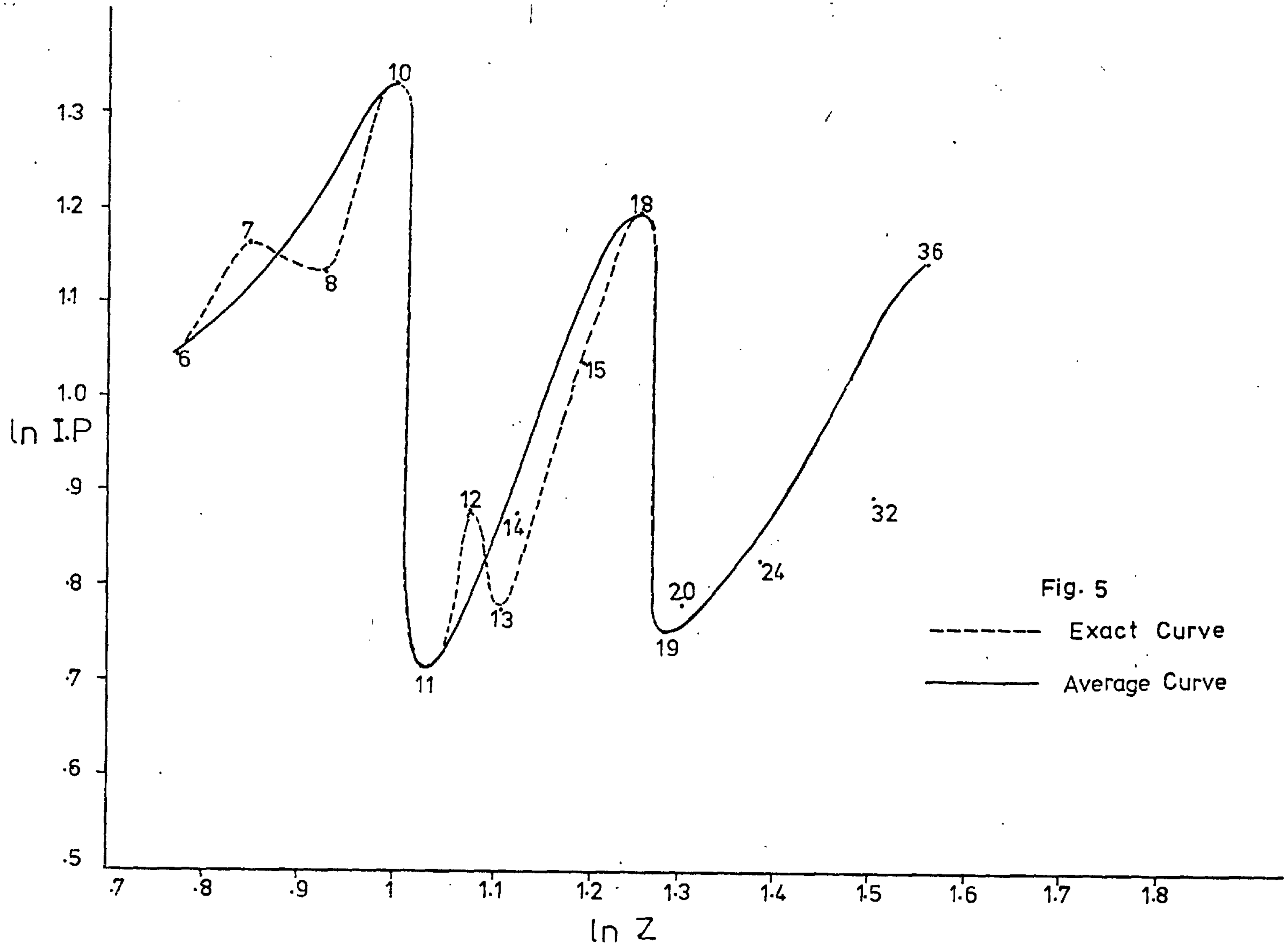

ln I.P
1.3
1.2
1.1
1.0
·9
·8
·7
·6
·5
ln Z
·7
·8
·9
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
6
7
8
10
11
12
13
14
15
18
19
20
24
32
36
Exact Curve
Average Curve

Fig. 5

(C.IV) Binding energies of atoms and ions by 1/Z expansion.

Kato (1951) gave the total energy of an ion with Ze as nuclear charge and N electrons, so called the 1/Z theory, given by

$$E\ (Z,N) \quad = \quad Z^2\ (\ \epsilon_0+\frac{1}{Z}\epsilon_1+\frac{1}{Z^2}\ \epsilon_2+\ \ldots\ldots) \quad , \quad \underline{\qquad}(C.IV.1)$$

with the condition that Z is quite large. N dependence is contained in the coefficients ϵ_m. Exchange and correlation effects both occur in ϵ_1, but the presence of correlation in ϵ_1 indicates a degenerate zero order state (Dmitrieva and Plindov, 1975). Coefficients ϵ_n in (C.IV.1) have been calculated by a number of groups for the ground states from N = 2 to 10 and one such table has been given by March and White(1972). According to them the general asymptotic form of coefficients is given, for large N and Z, by

$$\frac{1}{Z^m}\ \epsilon_m(N) \quad \propto \quad Z^{\frac{1}{3}}\ (\frac{N}{Z})^{m+\frac{1}{3}} \quad . \quad \underline{\qquad\qquad}(C.IV.2)$$

They argue that we can obtain Foldy's result, that for a relatively small Z the dependence is $Z^{12/5}$ rather than $Z^{\frac{7}{3}}$ as predicted by the TF theory. If we put m=0 and plot ln $\epsilon_m(N)$ against ln N it will be found that the slope is nearer 2/5 than 1/3. This then will give us the leading term in the energy expression as approximately proportional to $Z^{12/5}$, a result given earlier by Foldy. "Thus N is never large enough to yield the characteristic asymptotic dependence graphically", (March and White, 1972). Here we can find, at least in principle, the relation between the TF and 1/Z theory. We stress that as $\frac{N}{Z} \rightarrow 1$ for a large Z the TF theory is indeed giving us an approximate summation to all orders of the 1/Z expansion. It is useful to modify the expression (C.IV.1) and rewrite it in the following form

$$\frac{E\ (Z,N)}{Z^2\ \epsilon_o(N)} = 1 + \frac{\epsilon_1}{N\ \epsilon_o}\left(\frac{N}{Z}\right) + \frac{\epsilon_2}{N^2\ \epsilon_o}\left(\frac{N}{Z}\right)^2 + \ldots\ldots \qquad . \tag{C.IV.3}$$

The left hand side is a ratio of E_{exact} and $E_{coulomb}$ which we simply denote by $\phi\,(N, \frac{N}{Z})$. It is interesting to compare this expression with the asymptotic expression (C.I.9) we have given earlier. The coefficient $\epsilon_o(N)$ is obviously equivalent to $-\left(\frac{3}{2}\right)^{\frac{1}{3}}\ N^{\frac{1}{3}}$ which is also obtained if we use (C.IV.2) and put m = 0. But we must not forget that (C.I.9) is an asymptotic case of Z and N, whereas (C.IV.3) is a general expression for any value of Z and N ($Z \geqslant N$). If we put $N = Z$ in the asymptotic form we get back the result of the TF theory for neutral atom i.e (C.I.10), the correlation between the TF and 1/Z theory we described earlier. In brief it follows that $f(\frac{N}{Z})$ of the TF corresponds to $\phi(N,\frac{N}{Z})$ of 1/Z theory.

Rewriting equation (C.IV.3) as

$$\phi\,(N,\frac{N}{Z}) = 1 + \frac{\epsilon_1}{N\ \epsilon_o}\left(\frac{N}{Z}\right) + \frac{\epsilon_2}{N^2\epsilon_o}\left(\frac{N}{Z}\right)^2 + \ldots\ldots \quad ,$$

and using table 2 of March and White, (1972) we can obtain a set of equations each corresponding to each value of N. Physical study of the coefficients in this expression is also important. The coefficient of $\frac{N}{Z}$ term is simply the slope at the origin and it corresponds to $\phi'(0)$ quoted already in the TF theory. As long as we strictly follow the 1/Z theory, we can calculate any coefficient by the general expression (C.IV.2). But here we would like to consider a different technique for the evaluation of the coefficient of $(\frac{N}{Z})^2$.

It is assumed that the energy expression behaves reasonably even if we take only the first three terms. Therefore, we have only two unknown coefficients. The first of these is the coefficient of $\frac{N}{Z}$ which is usually taken from the $1/Z$ theory, whereas the next order coefficient, i.e of $\frac{N^2}{Z^2}$, is to be evaluated for the neutral atom case since the exact value of $\phi(N,\frac{N}{Z})$ is often known . In general we have

$$\phi(N,\tfrac{N}{Z}) \quad = \quad 1 + \frac{\epsilon_1}{N\,\epsilon_0} \; (\tfrac{N}{Z}) + b_2(N) \; (\tfrac{N}{Z})^2 \quad ,$$

where $b_2(N)$ is unknown. Substituting $N = Z$ and simplifying the equation we obtain

$$b_2(N) \quad = \quad \phi(N,1) \; - \; 1 \; - \; \frac{\epsilon_1}{N\,\epsilon_0} \qquad .$$

It follows that when $N \neq Z$ for other cases, $\phi(N,\frac{N}{Z})$ can be easily determined. The general expression, so called analytic fit, for any N and Z ($Z \geqslant N$) is given by

$$\phi(N,\tfrac{N}{Z}) \quad = \quad 1 - \frac{\epsilon_1}{N\,\epsilon_0} \; (\frac{N}{Z}) + \left[\phi(N,1) - 1 - \frac{\epsilon_1}{N\,\epsilon_0}\right] \quad (\frac{N}{Z})^2 . \qquad \text{(C.IV.4)}$$

In what follows we shall give some of the results due to the $1/Z$ theory and to the analytic expressions worked out from (C.IV.4), the refined method expression which we have described above.

<u>Atomic systems with N = 2.</u>

Weiss (1961) has given numerical results of E_{exact} for atomic systems with N = 2. We have recorded these and corresponding values of $\phi(2,\frac{N}{Z})$ in Table III.A below. One may fit the results with good accuracy by the following expression

$$\phi(2,\tfrac{N}{Z}) \quad = \quad 1 - 0.30272 \; (\tfrac{N}{Z}) + 0.02865 \; (\tfrac{N}{Z})^2 \quad . \qquad \text{(C.IV.5)}$$

But it does not exactly match the experimental values of $\phi(2,\frac{N}{Z})$ given in Table III. For example the expression gives us $\phi(2,\frac{1}{2}) = 0.8558$, whereas the experimental value given in table III is 0.8535 . The

Table III

Values of E_{exact} for different isoelectronic sequences.

Z	N = 2	N = 3		N = 4
	Weiss (1961)	Onello (1974)	Perkins (1976)	Weiss (1961)
2	- 2.90372			
3	- 7.27991		- 7.47807	
4	-13.65557		-14.32479	-14.66741
5	-22.03097	- 23.42145	-23.42471	-24.34915
6	-32.40625	- 34.77316	-34.77573	-36.53524
7	-44.78145	- 48.37492	-48.37728	-51.22358
8	-59.15660	- 64.22672	-64.22917	-68.41332
9		- 82.32858		
10		-102.68048		
11		-125.28242		
12		-150.13439		
13		-177.23639		
14		-206.58800		

improved analytical expression for N = 2 due to the refined method is as follows

$$\phi(2,\tfrac{N}{Z}) = 1 - 0.31250\ (\tfrac{N}{Z}) + 0.03843\ (\tfrac{N}{Z})^2 \quad . \tag{C.IV.6}$$

In Table IV.A we have given all the three sets of results i.e experimental (Weiss, 1961), analytic fits (C.IV.5) and (C.IV.6).

Table(IV.A)

$\phi(2, \frac{N}{Z})$ values for N = 2 from different methods.

N/Z	Experimental Weiss' result	Analytical	
		(C.IV.5)	(C.IV.6)
1	0.72593	0.72593	0.72593
2/3	0.80888	0.81092	0.80874
1/2	0.85347	0.85580	0.85335
2/5	0.88124	0.88349	0.88114
1/3	0.90017	0.90227	0.90010
2/7	0.91391	0.91584	0.91385
1/4	0.92432	0.92611	0.92427

We can see from the above Table (IV.A) that the improved method is working satisfactorily for the analytic expressions of $\phi(N,\frac{N}{Z})$, since the results are matching up to the third significant figure.

Atomic systems with $N = 3$.

J.F Perkins (1976) has provided the results of E_{exact} for the three electron systems for atomic numbers 3 to 8. We have calculated the corresponding values of $\phi(3,\frac{N}{Z})$ and recorded them in Table (IV.B) as experimental values. Another set of values for such a system has been worked out by Onello,(1974) up to $Z = 14$ (see Table III.B). But we would like to work with Perkins' data which is more recent.

The analytic fit we have found by the above method, suitable for three electron system and matches the Perkins' results, is given by

$$\phi(3,\tfrac{N}{Z}) = 1 - 0.30305 \left(\tfrac{N}{Z}\right) + 0.04165 \left(\tfrac{N}{Z}\right)^2 \quad . \qquad \text{\_\_\_\_(C.IV.7)}$$

Results for this expression are recorded below in Table(IV.B).

Table (IV.B)

N / Z	Experimental	Analytical
1	0.7386	0.7386
3/4	0.7958	0.7961
3/5	0.8329	0.8332
3/6	0.8587	0.8589
3/7	0.8775	0.8779
3/8	0.8921	0.8922

Atomic systems with N = 4.

Procedure is essentially the same. We just give the expression for the analytical fit and record the results in Table (IV.C).

$$\phi(4,\tfrac{N}{Z}) = 1 - 0.31186\,(\tfrac{N}{Z}) + 0.04523\,(\tfrac{N}{Z})^2 \ .$$

Table IV.C

N/Z	Experimental	Analytical
1	0.73337	0.73337
4/5	0.77917	0.77946
4/6	0.81189	0.81219
4/7	0.83630	0.83656
4/8	0.85516	0.85537

From the above three cases it seems that our improved method for analytic fits of $\phi(N,\frac{N}{Z})$ for different atomic systems is working very well. But unfortunately for the time being there is not enough experimental data, specially below $\frac{N}{Z} = .5$, for larger values of N and Z to find the range of validity of our method.

Plot between $\phi(N,\frac{N}{Z})$ and N/Z.

We have sketched $\phi(N,\frac{N}{Z})$ against N/Z for $N = 2,3$ and 4 from the above tables. It is obvious that at $\frac{N}{Z} = 0$, $\phi(N,\frac{N}{Z})$ is always unity. At the other end (where $\frac{N}{Z} = 1$) we see that the curves have diverged from each other and we get a pencil of curves for all values of N.

For $N \rightarrow \infty$ the value of $\phi(\infty,1)$ is found to be 0.674 and the coefficient of $(\frac{N}{Z})$ term for $N \rightarrow \infty$ has been given by Dmitrieva and Plindov, 1975, as − 0.4236, which is the slope at the origin. The analytic fit for asymptotic case is therefore found to be

$$\phi(\infty,N/Z) = 1 - 0.4236 \left(\frac{N}{Z}\right) + 0.0976 \left(\frac{N}{Z}\right)^2$$

which is very close to the f(N/Z) of the TF theory,(compare equation (C.I.9)). For comparison with other cases we have plotted this curve on the same graph, Fig. 6.

(C.V) Behaviour of the coefficient of $(\frac{N}{Z})$.

Before we close our discussion of the binding energies of atoms and ions we shall study briefly the behaviour of the coefficient of $(\frac{N}{Z})$, i.e $\frac{\epsilon_1(N)}{N\,\epsilon_0(N)}$, as N becomes large.

This has been calculated by different people with different methods. We have plotted the results from March and White, and Dmitrieva and Plindov. These are shown in Fig. 7.

One striking feature of this plot which we observe is that for N equal to 2,10,28 and 60 the values from different methods almost coincide to the graphical accuracy. These values of N corresponds to the closed shell cases, in which we are particularly interested.

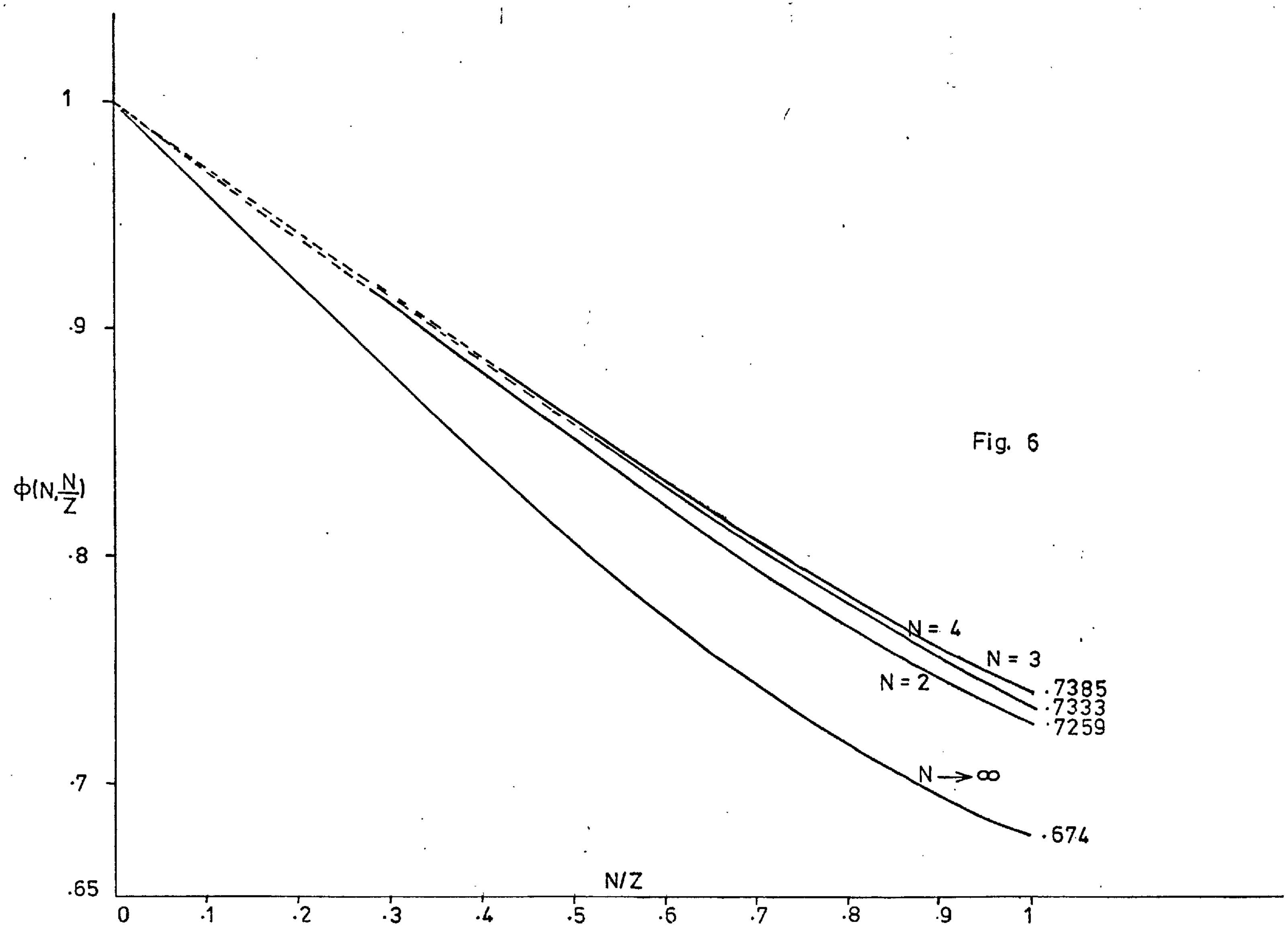


Fig. 6

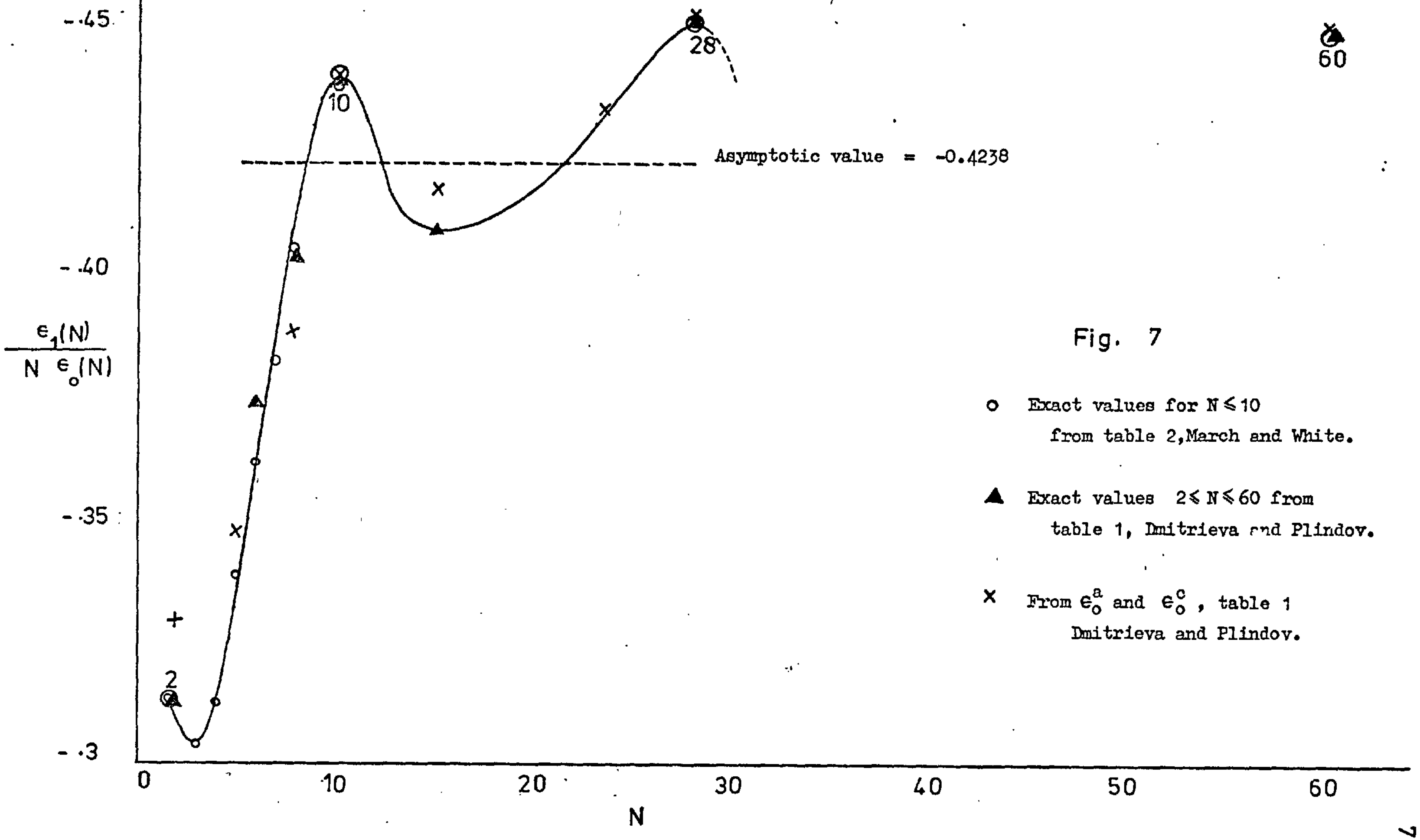
-.45
-.40
-.35
-.3
$\frac{\epsilon_1(N)}{N\ \epsilon_o(N)}$
0
10
20
30
40
50
60
N
2
10
28
60
Asymptotic value = -0.4238
○ Exact values for N ≤ 10 from table 2, March and White.
▲ Exact values 2 ≤ N ≤ 60 from table 1, Dmitrieva and Plindov.
× From ϵ_o^a and ϵ_o^c, table 1 Dmitrieva and Plindov.
+

Fig. 7

The general behaviour of the coefficient when $N > 10$ appears to be oscillatory. As N becomes larger the oscillations seem to die away and the value approaches the asymptotic value -0.4238. But it is far from realistic case because for $Z = 60$ the value is -0.45 which is somewhat different.

Earlier when $N \leq 10$ the sharp decrease in the value of the coefficient is quite understandable. Since we know that this coefficient corresponds to the slope of the potential function Φ in the TF theory, and because the filling of the second shell shields the outer electrons, the potential dies away, which gives rise to sharp decrease in slope.

(D) Electron densities.

Since the electron density is playing a major role in the TF approximation, we shall now examine this more closely by comparison with the wave-mechanical data of Boyd. We shall also refer to the analytic fit recently supplied by Boyd (private communication). Finally a few remarks will be made on the study of $\rho(r)$ we carried out for the rare gas elements from Herman and Skillman's data for Hartree and Hartree-Fock calculations.

(D.I) Spatial dependence of TF charge density.

The TF charge density has already been defined in equation (C.I.1). An equivalent form is

$$\rho(r) = \frac{8\pi}{3h^3} (2m)^{3/2} E_f^{3/2} \left[1 - \frac{V(r)}{E_f}\right]^{3/2} . \qquad \text{(D.I.1)}$$

We recall that it only holds in the region where $\frac{V}{E_f} < 1$. Beyond this region $\rho(r)$ is assumed to be zero (though wave mechanically wave function can leak through to the classically forbidden region). This TF relation gives a semi-classical approximation to the procedure of solving for the one-electron wave functions ψ_i in the self-consistent field and then forming the sum of the squares of these wave functions over the occupied levels, i.e

$$\rho(r) = \sum_i \psi_i^2 .$$

We have summarized above the details how the TF density is calculated from the TF differential equation, namely

$$\frac{d^2\Phi}{d\,x^2} = \frac{\Phi^{3/2}}{x^{\frac{1}{2}}} \quad ,$$

for which the asymptotic solution for large x is given by

$$\Phi(x) = \frac{144}{x^3} \qquad \text{(D.I.2)}$$

(see March, 1975). But this solution does not satisfy the boundary condition $\Phi(0) = 1$. Therefore the relation between $\rho(r)$ and r which we are going to derive will hold only for large r. From equation (C.I.2) we have

$$E_f - V(r) = \frac{Z\,e^2}{r}\Phi \; . \qquad \text{(D.I.3)}$$

Inserting value of Φ from (D.I.2) in here and after simplification we get

$$\left(1 - \frac{V}{E_f}\right)^{3/2} = \left[\frac{Z\,e^2}{r}\;\frac{144}{x^3}\;\frac{1}{E_f}\right]^{3/2} .$$

In terms of r defined as $r = b.x$, where $b = \frac{0.8853}{Z^{\frac{1}{3}}}\,a_o$, we can write

$$\left(1 - \frac{V}{E_f}\right)^{3/2} = \left[\frac{144\;b^3\,Z\,e^2}{E_f}\;\frac{1}{r^4}\right]^{3/2} . \qquad \text{(D.I.4)}$$

Using this result in equation (D.I.1) we get

$$\rho(r) = \frac{8\,\pi}{3\,h^3}\,(2m.\;144.\;b^3.\;Z\,e^2)^{3/2}\,\frac{1}{r^6} \; . \qquad \text{(D.I.5)}$$

Which precisely gives

$$\rho(r) \propto \frac{1}{r^6} \; .$$

If we take log of equation (D.I.5) we have

$$\ln\,\rho(r) = \ln A - 6\,\ln r \; , \qquad \text{(D.I.6)}$$

where $A = \frac{8\,\pi}{3\,h^3}\,(2m.\;144\;b^3\,Z\,e^2)^{3/2}$.

Mathematically it represents a straight line with slope − 6.

Thus the important result we got here is that the TF charge density for heavy atoms and at large r goes like r^{-6}. This is true for all atomic numbers, since A becomes independent of Z if we substitute the value of b. We have investigated this universal result numerically. We examined data from two available sources of the wave mechanically derived charge density for different elements.

(i) Boyd's results.

Recently Boyd has made detailed calculations of wave mechanical charge densities. In particular he has provided numerical data for D(r), defined as

$$D(r) = 4\pi r^2 \cdot \rho(r) \quad .$$

He has also obtained an analytic fit of his data for D(r), in the form

$$D(r) = \sum_i C_i \, . \, r^{n_i} \, . \, e^{-Z_i r}$$

(Boyd, private communication). This expansion can be used to calculate various one-electron properties.

His numerical data for D(r) is available for the elements up to Z = 54. We have studied the cases Kr^{36}, Zr^{40}, Ag^{47} and Xe^{54} to make comparison with the TF result (D.I.5). It is obvious that if $\rho(r)$ has dependence r^{-6}, then D(r) behaves as r^{-4}. Therefore we sketched the function r^{-4} against r and then plotted D(r) for the four elements given above on the same diagram. It was found that just before D(r) begins to decay exponentially which is always true after $r > r_c$, r_c being the atomic radius, there ex-ists a region where the behaviour of D(r) becomes comparable with the r^{-4} curve. It also turns out that the extent of this region is related to the atomic number and also that it moves towards larger r as Z increases.

(ii) Herman and Skillman calculations.

The second source of information about the charge density is that of Herman and Skillman. Results are available up to $Z = 104$, but we have restricted ourselves to the rare gas elements.

After the proper normalization check over the charge density given, we have plotted $\ln\rho(r)$ against $\ln r$ for Rn^{86}, Xe^{54} and Kr^{36}. It is shown below for Rn^{86}, Fig 8. At large r we find the expected region, the average of the last four points yielding a slope of almost -6.

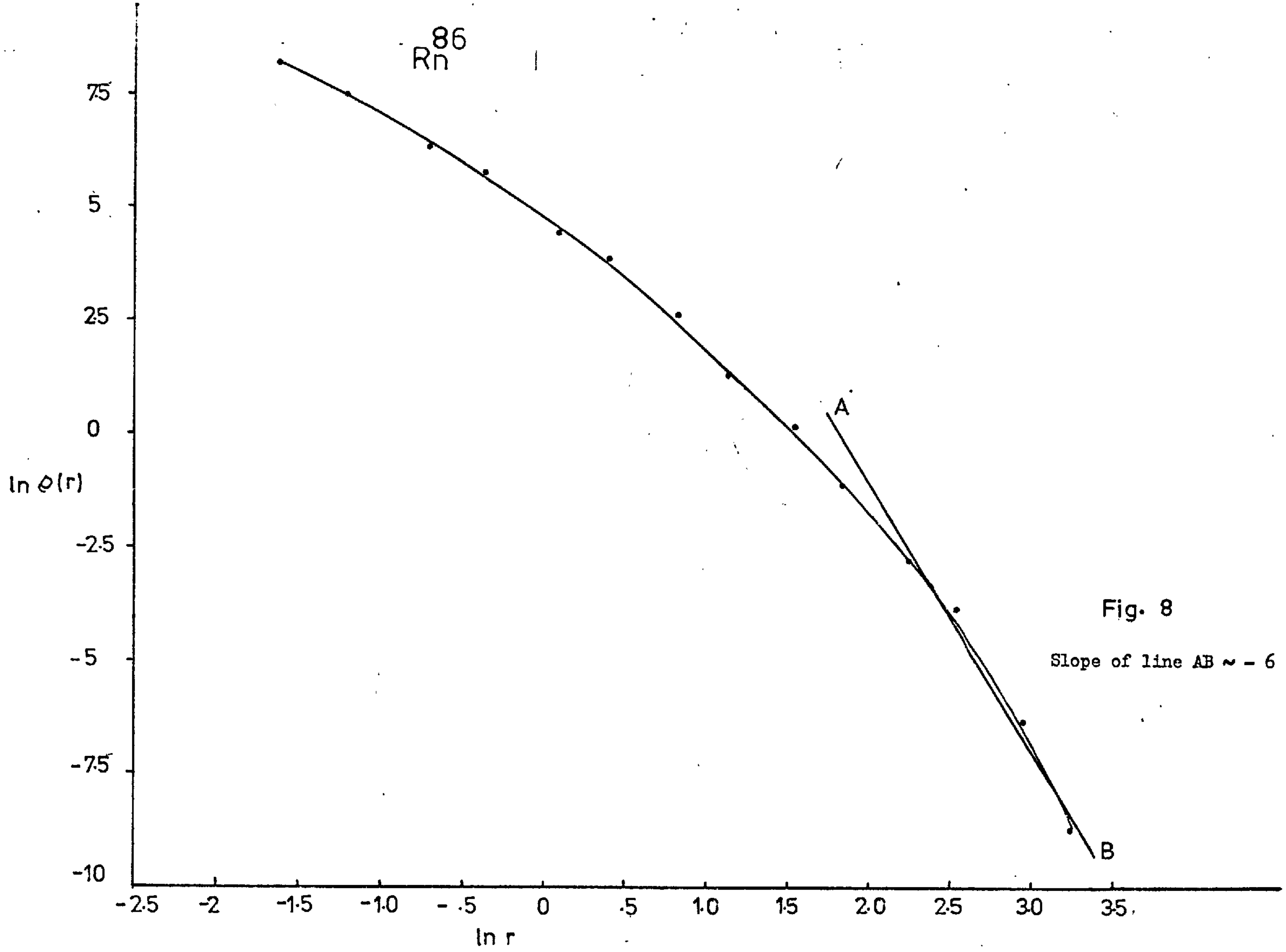


Fig. 8

Slope of line AB ~ - 6

CONCLUSION

It is well known that the TF theory is only valid for heavy ions (and is also, of course, non-relativistic, in the form used in this thesis).

The main objective here has been to understand more precisely the range of validity of the theory. This has been tackled by giving a lot of attention to the pure coulomb field case, for which the wave-mechanical solution is, of course, known exactly.

The most interesting result is that the X-ray scattering factor for the coulomb field case is accurately represented by the TF theory with a relatively small number of closed shells. This statement needs qualifying, in that, at large k, the TF scattering factor has spurious oscillations, arising from the cut-off of the electron density.

Some comparison of the self-consistent TF density with Hartree calculations is also made. The region of validity of the behaviour of $\rho(r)$ as r^{-6} is thereby clarified; it is useful in heavy atoms before one reaches the region of exponentially decaying wave functions.

In addition to these studies, some approximate analytic formulae are given for the binding energies of systems with a small number of electrons and an attempt is made again to relate these results to $1/Z$ expansions, and thereby to the TF theory.

References

Ballinger,R.A. and March,N.H (1955) Phil.Mag. 46, 246.

Bartlett,B,R. and Fyfe, D.J (1974) "Hand book of mathematical formulae" Denny publishers, London.

Berghuis, J., IJbertha,M.H, Potters,M. and others. (1955) Acta. Cryst. 8,478.

Boyd,R.J. (1976) J.Phys.B 9, NO.5. L69.

Dickinson,W.C. (1950) Phys.Rev. 80, 563.

Dmitrieva,I.K. and Plindov,G.I (1975) Phys.Letters, A55, 3.

Fermi, E. (1928) Z.fur Phys. 48, 73.

Feynman,R.P. (1939) Phys.Rev. 56, 340.

Foldy,L.L. (1951) Phys.Rev. 83, 397.

Fock,V. (1935) Z.fur.Phys. 98. 145.

Herman,F. and Skillman,S. (1963) Atomic structure calculations(Englewood. Cliffs, N,J; Prentice-Hall)

Kato,T. (1957) Commun. Pure Appl.Math.10, 151; (1951) J.Fac.Sci.Tokyo Univ. 16, 145.

March, N.H. (1976) J.Phys.B. 9, L_1.

March, N.H. and Murray,A.M. (1961) Proc.Roy.Soc. A261, 119.

March,N.H. and White,R.T. (1972) J.Phys.B. 5, 466.

Milne,E.A. (1927) Proc.Camb.Phil.Soc. 23, 794.

Miranda,C. (1934) Men.Acc.Italia. 5, 283.

Onello,J.S, Ford,L and Dalgarno,A. (1974) Phys.Rev. A10, 9.

Pauling,L. and Wilson,E.B. (1935) Introduction to quantum mechanics (New york: McGraw Hill).

Pirenne,M.H (1946) The diffraction of X-rays and electrons by free molecules (Combridge university press).

Perkins,J.F (1976) Phys.Rev. A13, 915.

Schiff,L.I. (1955) Quantum Mechanics, 2nd edition (New York: McGraw Hill).

Steiner,E. (1963) J.Chem.Phys. 39, 2365.

Stoddart,J.C. and March,N.H. (1967) Proc.Roy.Soc. A299, 279.

Thomas,L.H. (1926) Proc.Comb.Phil.Soc. 23, 542.

Weiss,A.W. (1961) Phys.Rev. 122, 1326.

Appendix 1

Calculation of mean square momentum.

Definition of average square momentum is given by

$$\langle p^2 \rangle = \frac{\int \psi^* \, p^2 \, \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

where ψ is momentum wave function of an electron in nth shell. Simplification yields

$$\langle p^2 \rangle = \frac{\int p^4 \rho_n(p,p) \, dp}{\int p^2 \rho_n(p,p) \, dp} \qquad \text{\_\_\_\_\_\_\_\_(App.1.1)}$$

Momentum density $\rho_n(p,p)$ is given already in equation (B.I.2). If we substitute $\frac{p^2}{p_n^2} = q^2$, we obtain

$$\int_0^\infty p^2 \rho_n(p,p) \, dp = \frac{8\,n^2}{\pi^2} \int_0^\infty \frac{q^2}{(1+q^2)^4} \, dq.$$

$$= \pi/32 \qquad \text{\_\_\_\_\_\_\_\_(App.1.2)}$$

and

$$\int_0^\infty p^4 \rho_n(p,p) \, dp = \frac{8\,n^2}{\pi^2} p_n^2 \int_0^\infty \frac{q^4}{(1+q^2)^4} \, dq.$$

$$= p_n^2 \cdot \pi/32 \qquad \text{\_\_\_\_\_\_\_\_(App.1.3)}$$

Using (App.1.2) and (App,1.3) in (App.1.1) we get

$$\langle p^2 \rangle = p_n^2$$

From the virial theorem we have $T = - E$ therefore

$$\frac{\langle p^2 \rangle}{2m} = \frac{Z^2}{2n^2}\frac{e^2}{a_o} \quad .$$

From where we obtain

$$p_n^2 = \frac{Z^2}{n^2}\frac{me^2}{a_o} \quad .$$

Since we are using atomic units in our most of the calculations therefore we can write

$$p_n^2 = \frac{Z^2}{n^2} \quad .$$

Appendix 2

General solution of the integrals involved in our scattering factor calculations.

General form of the integrals we deal with, in scattering factor calculations, is given by

$$I = \int_0^\infty \sum_{l = 1}^{n} a_l \, . \, x^l \, . \, \mathrm{Sin}(Ex) \, . \, e^{-x} . \, dx \quad ,$$

which we can write as

$$= - \mathrm{imag} \sum_{l=1}^{n} a_l \int_0^\infty x^l \, . \, e^{-(iE + 1)\, x} . \, dx \qquad .$$

Since

$$e^{-iEx} = \mathrm{Cos}\,(Ex) - i \, \mathrm{Sin}(Ex) \qquad .$$

Integration gives us

$$I = - \mathrm{imag} \sum_{l=1}^{n} a_l \, . \frac{l!}{(1 + iE)^{l+1}} \qquad .$$

Multiplying and dividing by $(1 - iE)^{l+1}$ on right hand side yields

$$I = - \mathrm{imag} \sum_{n=1}^{n} a_l \, . \, \frac{l!}{(1 + E^2)^{l+1}} \, . \, (1 - iE)^{l+1} \, .$$

Expanding $(1 - iE)^{l+1}$ for different values of l and choosing the imaginary terms only we obtain

$$(1 - iE)^2 = 2\,E$$

$$(1 - iE)^3 = 3\,E - E^3$$

$$(1 - iE)^4 = 4\,E - 4\,E^3$$

$$(1 - iE)^5 = 5\,E - 10\,E^3 + E^5$$

$$(1 - iE)^6 = 6E - 20E^3 + 6E^5 ,$$

etc.

Therefore solution of the integral I is given by

$$I = \frac{a_1 (1!)}{(1 + E^2)^2} \cdot 2E + \frac{a_2 (2!)}{(1 + E^2)^3} \cdot (3E - E^3) + \frac{a_3 (3!)}{(1 + E^2)^4} \cdot (4E - 4E^3) + \frac{a_4 (4!)}{(1 + E^2)^5} \cdot (5E - 10E^3 + E^5) + \ldots .$$

Appendix 3

Application of Fock's scattering factor expression to M-shell of hydrogen-like atom.

In the general expression of Fock for the scattering factor if we put $n = 3$, for M-shell, we get

$$F_3(X) = \frac{1}{36} \, . \, T_3'(X) \, . \, (1+X)^2 . \, \left[P_3'(X) - P_2'(X)\right] , \qquad \_\_\_\_\_\_\_\_ (App.3.1)$$

where Tshebysheff polynomial $T(X)$ is defined as

$$T_n(X) = \operatorname{Cos}\,(n \operatorname{Cos}^{-1} X) \; .$$

For $n = 3$ we get

$$T_3(X) = X\,(4\,X^2 - 3) \; ,$$

since $\operatorname{Cos} 3A = \operatorname{Cos} A \, . \, (4 \operatorname{Cos}^2 A - 3)$

where A corresponds to $\operatorname{Cos}^{-1} X$.

Derivative of $T_3(X)$ yields

$$T_3'(X) = 12\,X^2 - 3 \; . \qquad \_\_\_\_\_\_\_\_ (App.3.2)$$

Now take the Legendre polynomial from mathematical tables where

$$P_3'(X) = \frac{15}{2} X^2 - \frac{3}{2}$$

and $P_2'(X) = 3X$.

Putting the values back in equation (App.3.1) we obtain

$$F_3(X) = \frac{1}{8} \, (4X^2 - 1)(1 + X)^2 . \, (5X^2 + 2X - 1) \; . \qquad \_\_\_\_\_\_\_\_ (app.3.3)$$

X is defined as

$$X = \frac{4\,p_n^2 - k^2}{4\,p_n^2 + k^2}$$

where

$$p_n^2 = \frac{Z^2}{n^2} \quad .$$

For $n = 3$ we get

$$X = \frac{4\,Z^2 - 9\,k^2}{4\,Z^2 + 9\,k^2} \quad .$$

It would be more convenient if we put

$$\frac{k}{Z} = \frac{2}{3} \cdot E \quad ,$$

so that

$$X = \frac{1 - E^2}{1 + E^2} \quad . \qquad \text{\_\_\_\_\_\_\_\_\_\_(App.3.4)}$$

Therefore

$$(1 + X)^2 = \left(\frac{2}{1 + E^2}\right) \quad . \qquad \text{\_\_\_\_\_\_\_\_\_\_(App.3.5)}$$

Substituting (App.3.4) and (App.3.5) in equation (App.3.3) we get the final result

$$F_3(X) = \frac{1}{(1+E^2)6} \cdot \left(9 - 48E^2 + 72E^4 - 28E^6 + 3E^8 \right)$$

If we put $E = 0$ or $X = 1$ we get the expected normalization condition, i.e

$$F_3(X) = 9,$$

since Fock's expression is true for singly occupied levels. Above result is in agreement with the one obtained by using the charge density for M-shell and solving the Fourier transform, equation (A.I.1).

Appendix 4

Programmes used for different calculations involved in our work.

We provide the copies of different programmes used for the numerical calculation of different expressions. First we give G(K), the function involved in the TF scattering factor. It is solved from two different expressions. We have used Simpson's rule of numerical integration for equation (A.IV.7) and for the integrals involved in the calculation of kinetic energy for the hydrogenlike atoms. First of the following programmes corresponds to the evaluation of equation (A.IV.7) whereas the second one for the equation (A.V.7).

Programme 1

```
TBL 2⊢
3:
.0001→A⊢
4:
0→B⊢
5:
0→C⊢
6:
.0001→X⊢
7:
SIN (A*X)/(A*X)→
Y⊢
8:
Y*√(X*(1-X)↑3)→Z
⊢
9:
X+.05→X⊢
10:
SIN (A*X)/(A*X)→
Y⊢
11:
Y*√(X*(1-X)↑3)→Y
⊢
12:
Y+B→B⊢
13:
X+.05→X⊢
14:
IF 1<X+.05→X;
GTO 19⊢
15:
SIN (A*X)/(A*X)*
√(X*(1-X)↑3)→Y⊢
16:
IF 1<X+.05→X;
GTO 19⊢
17:
Y+C→C⊢
18:
GTO 9⊢
19:
X(Z+4*B+2*C+Y)*1
.6976→Z⊢
20:
PRT Z,A⊢
21:
A/X;Z→Y⊢
22:
PLT X,Y⊢
23:
A+1→A⊢
24:
IF 26<A;GTO 26⊢
25:
GTO 4⊢
26:
END ⊢
R129
```

Programme 2

```
                           C+1→C⊢
0:                         10:
SCL 0,20,0,.2⊢             IF 2B≤C;Z*X→Z;
1:                         GTO 12⊢
AXE 0,0,2.5,.05⊢           11:
2:                         GTO 8⊢
SFG 14⊢                    12:
3:                         Y-Z→Y⊢
0→A⊢                       13:
4:                         B+1→B⊢
0→Y⊢                       14:
5:                         IF 30≤B;PRT A,Y;
1→B⊢                       GTO 16⊢
6:                         15:
3π*(-1)↑(B-1)*A↑           GTO 6⊢
B↑2*A↑(-2)/(8*(2           16:
B-.5)*(2B+1))→X⊢           A+1→A⊢
7:                         17:
1→C;1→Z⊢                   IF 26≤A;GTO 19⊢
8:                         18:
2*(4B-2C+1)/((2B           GTO 4⊢
-C)*(4B-2C+2))→Z           19:
⊢                          END ⊢
```

We also like to give details about the computer programme used for the calculation of Fock's general expression of scattering factor. Function 'DERT' in the programme represents equation (A.VI.8), the recurrence relation for Tschebyscheff polynomials. Whereas the derivative of Legendre polynomial, equation (A.VI.9) is denoted by 'DERLN'. With these simplification the recurrence relation for Fock's expression (A.II.2) is given by

```
F  =  2.0 * DERT * (1-X)**2 *(DERLN1 - DERLN2)/
                              (4.0 * AN **2)
```

Factor of 2 is included in the above expression to make the relation true for doubly occupied levels.

We have used DO LOOP 3 to generate different values of M which corresponds to n', and of TZ which corresponds to atomic number Z. DO LOOP 1 is generating different values of k and K. Once the values of Z and k is fixed by the above do-loops we need to determine scattering factor . But Fock's relation determine F only for one shell at a time therefore we need to have a do-loop which carry on adding all F's till N become equal to M. This is done by do loop2. As soon as N = M we have asked to print the values of X,F,ADDF, FRATIO,BK,AK and N. Execution time for this programme was 25 seconds.

Computer programme for Fock's general expression of scattering factor.

```
      PROGRAM MAIN( INPUT, OUTPUT, TAPE5= INPUT, TAPE6= OUTPUT)
       DIMENSION T(110), P(110)
      WRITE(6,444)
 444  FORMAT('1',1X,'N',13X,'X',17X,'F',18X,'ADDF',15X,'F/Z',13X,'BK',
     114X,'AK')
      DO 3 M=1,101
      AM= FLOAT(M)
      TZ = AM*(AM+1.0)*(2.0*AM+1.0)/3.0
      WRITE(6,333) M
 333  FORMAT('0',I3)
      IF(M.LT.5) GO TO 10
      IF(M.LT.15) GC TO 20
      IF(M.LT. 40) GO TO 30
      INT= 15
- NAME - INT SAME AS STANDARD FUNCTION AND REMOVES FUNCTION FROM USE
      LIM= 4*M
      GO TO 100
  10  INT= 1
      LIM= 7*M
      GO TO 100
  20  INT= 5
      LIM= 6*M
      GO TO 100
  30  INT=10
      LIM= 5*M
 100  DO 1 J= 1,LIM,INT
      AK = FLOAT(J-1)
      BK= AK*((18.0/TZ)**(1.0/3.0))
      ADDF=0.0
      DO 2 N= 1,M
      AN= FLOAT(N)


      Z= 2.0*(AN**2)
      PN=TZ/AN
      X=(4.0*(PN**2)-(AK**2))/(4.0*(PN**2)+(AK**2))
      X2=X**2
      IF( AK .EQ. 0.0) GO TO 101
- IS FLOATING POINT EQUALITY TO BE EXPECTED
      CALL CMP(T,X,N+1)
      CALL LEP(P,X,N)
      DERT=AN*(X*T(N+1)-T(N+2))/(1.0-X2)
      DERLN1= AN*(X*P(N+1)-P(N))/(X2-1.0)
      IF( N .EQ. 1) P(N-1) = 1.0
      DERLN2= (AN-1.0)*(X*P(N)-P(N-1))/(X2-1.0)
      F = 2.0 *   DERT*(DERLN1+DERLN2)*(1.0+X)**2/(4.0*AN**2)
      GO TO 110
 101  F= Z
  110 ADDF=ADDF+F
      FRATIO = ADDF/TZ
      NMI= M-1
      IF(N.EQ.M)WRITE(6,222) X,F,ADDF,FRATIC,BK ,AK
 222  FORMAT(13X,F11.9,5X,F15.9,5X,F15.9,5X,F12.9,5X,F12.9,5X,F12.9)
  2   CONTINUE
1     CONTINUE
   3  CONTINUE
      STOP
      END
```