THOMAS-FERMI POTENTIAL

AND

PROBLEMS IN ATOMIC SPECTRA

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Contents

Chapter I	Introduction	1
(I)	Scope of the Work	1
(II)	Resumé of Previous Work	3
	Calculation of Atomic Potential and Energy Levels	3
	Thomas-Fermi Potential for Neutral Atoms and Positive Ions; Applications	7
Chapter II	Integration of Thomas-Fermi Equation for Positive Ions	14
Chapter III	Eigenvalues of Central Field Problems	20
(1)	Potential Field with One Minimum	
(II)	Potential Field with Two Minima	
Chapter IV	Energy Levels and Lowest States of the Atoms of the 7th Period of the Periodic Table	29
Chapter V	Quantum Defects of f States of Heavy Atoms	38
Chapter VI	Doublet Separations and Nuclear Magnetic Moments	41
	Calculations of Eigenfunctions and Comparison of Results	

Chapter VII	Negative Ions and Electron Affinities of Halogens	53
Appendix I	Fermi's Function for Positive Ions	57
Appendix II	Potentials in Various Ions of Uranium	58
Appendix III	Comparison of the Potentials of Fermi, Zwaan and This Thesis	
Appendix IV	The Ground State of Ce^{+++}	59
References		61

Notation

Throughout this thesis, unless otherwise mentioned, the atomic units of Hartree are used, i.e., ε and v are the total and the potential energy of an electron in units of the first ionization potential of hydrogen, ρ is length in units of the first Bohr radius of hydrogen.

CHAPTER I

Introduction

(I). Scope of the Work.

The present dissertation is concerned with a study of some problems in atomic spectra with the aid of the statistical potential of Thomas and Fermi.

A resumé of the contents of this thesis is given below:

In section II of this chapter, is given a review of previous work on the determination of atomic potentials and energy levels, and the Thomas-Fermi potentials for neutral atoms and positive ions and their applications.

In Chapter II, a more rigorous solution of the Fermi-Thomas differential equation for positive ions is given, and the result compared with the approximate solution of Fermi and Sommerfeld.

In Chapter III, the eigenvalue problem, that for a potential field having two unsymmetrical minima in particular, is solved by the method of Wentzel-Kramers-Brillouin. It leads to the quantum condition

$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - r}\, d\rho = (n - l - \tfrac{1}{2})\,\pi - \tan^{-1}\left[\tfrac{1}{4}\, e^{-2\int_{\rho_1}^{\rho_3}\sqrt{r-\varepsilon}\, d\rho} \tan\int_{\rho_3}^{\rho_4}\sqrt{\varepsilon - r}\, d\rho\right]$$

that finds interesting application in the calculations of certain energy levels and especially of the quantum defects of the f states of heavy atoms (Chapter V).

In Chapter IV, the building up of the outer incomplete electron shells of the atoms and ions of the elements of the 7th period of the periodic table is studied. Energy levels for 5f, 6d, 7s, 7p electrons of the various ions built upon the radon core are calculated by solving the wave equation with the statistical potential. The lowest states and electron configurations are predicted. Also the earlier work of Sugiura and Urey is shown to be erroneous.

In Chapter V, the result of Chapter IV for the two minima problem is applied to the calculation of the quantum defects of the f states of heavy elements. It accounts satisfactorily for the fact that the quantum defects of these states are all close to unity.

In Chapter VI, the wave functions are actually obtained by solving the radial wave equation with the Fermi potential. The doublet separations of $6p\ ^2P_{\frac{1}{2}} - 6p\ ^2P_{\frac{3}{2}}$ of Cs, $7p\ ^2P_{\frac{1}{2}} - 7p\ ^2P_{\frac{3}{2}}$ of the last alkaline atom $Z = 87$ are calculated. Also the values of the squares of the radial eigenfunctions $\psi^2(0)$, which enter in the theory of hyperfine structure separation, of $6s\ ^2S_{\frac{1}{2}}$ of Cs, and $7s\ ^2S_{\frac{1}{2}}$ of Tl are obtained. The results show better agreement with observed data than those of previous workers.

In Chapter VII, the question as to the existence of discrete spectrum due to negative ions is investigated. It is found that no negative ions possess two stationary states and hence there can be no discrete spectrum from negative ions. Also the electron affinities of the halogens are calculated; only a qualitative agreement is obtained with experimental data.

(II). Resume of Previous Work.

1° Determination of atomic potentials and energy levels.

Since the advent of the wave mechanics, much progress has been made in the theory of atomic spectra. In the case of the simplest of the atoms, hydrogen, the wave mechanics furnishes so complete and successful an account of energy levels, intensity of spectral lines, Zeeman and Stark effects, etc., that it is rarely paralleled in the history of physics. However, when an attempt is made to treat rigorously even the slightly more complicated atom than hydrogen, one encounters great mathematical difficulties. The problems that immediately present themselves are those connected with the energies of states, and the problem of calculating the energy of an atom is essentially a problem of many bodies. In wave mechanics, this involves the solution of the wave equations and the determination of the wave functions of the many-electron atoms. The Schrödinger equation for an atom of nuclear charge Z may be written

$$\left[\sum_i^Z \left(\Delta_i + \frac{2Z}{\rho_i} \right) + \varepsilon - \sum_{i,j \neq i}^{Z} \frac{2}{\rho_{ij}} \right] \Psi = 0 \qquad (I)$$

where Δ_i is the Laplace operator in the coordinates of the i th electron, $-\frac{2Z}{\rho_i}$ its potential energy due to the nuclear charge, $\frac{2}{\rho_{ij}}$ the energy of electrostatic interaction between the i th and the j th electrons, and ε the total energy of the system. An exact solution of this equation is not known, and in order to proceed at all approximations have to be made.

One way of attack is the method of self-consistent field due to Hartree[1]. The actual problem as represented by equation (1) is replaced by one which admits of solution. The many-electron problem is replaced by a one-electron problem with a central field for each electron. The Schrödinger equation for the system is then

$$\left[\sum_i^Z (\Delta_i - v_i) + \varepsilon \right] \Psi = 0 \qquad (2)$$

which is separable into Z equations, one for each electron, of the form

$$\Delta_i \Phi_i + (\varepsilon_i - v_i) \Phi_i = 0 \qquad (3)$$

where $\sum \varepsilon_i = \varepsilon$ and $\Psi = \prod_i \Phi_i$. Equation (3) is the wave equation of an electron in a field in which it has a potential energy v and a total energy ε. On the assumption of spherical symmetry in the field, this equation is separable into angular and radial parts, and the radial part of the solution $\frac{\psi}{\rho}$ is given by

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon - v - \frac{l(l+1)}{\rho^2} \right] \psi = 0 \qquad (4)$$

First a potential v is assumed and ε found by trial and error method until the solution ψ corresponding to these v and ε is zero at $\rho = 0$ and at infinity. The electron distribution of this particular electron given by ψ^2 is then calculated, and the sum of the charge distribution of all the electrons (Z in number in the case of a neutral atom, $Z - 1$ in the first ionized atom, etc.) found, and the resulting potential field due to this distribution of charge together with the nucleus is in turn calculated. Approximations of v are continued until the resulting calculated field agrees with the assumed potential v with which one starts. The field so obtained depends only on the degree of ionization of the atom and is otherwise a definite function of ρ involving no arbitrary constants. With this potential, a number of atomic problems which require a knowledge of v can be solved. This method is capable of giving results in good agreement with experimental data, but is of course laborious. In the absence, however, of other methods which are ready even to sacrifice great accuracy for ease of calculation, this method has been applied to problems of atomic states, X-ray scattering, etc., with success.

Another way of approach is that of Fues[2] dated back in the pre-wave-mechanical days. This method has been used by Sugiura and Urey[3] in calculating the potential field of atoms from empirical X-Ray data, and is now justified by wave mechanical considerations. In essence, the radial

phase integral of Sommerfeld is used

$$\int \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho = n_\rho \pi \qquad (5)$$

in which the azimuthal and radial quantum numbers k, n_ρ are replaced by half integers. On substituting empirical term values corresponding to different states n, l into this equation, it is possible to determine v by graphical methods. From the field so obtained, one can calculate the energy of other states or other quantities demanding a knowledge of v.

An entirely different way of obtaining the potential in an atom was then given independently by Thomas and Fermi, on the basis of the Fermi statistics. The theory was later extended by Fermi to positive ions. A short derivation of the Thomas-Fermi functions will be given in the next section.

With the potential in an atom or ion known, then the physical problem of determining the energy of an electron in that potential field reduces, in the wave mechanics, to the mathematical one of finding the eigenvalues of the wave equation of the electron. The wave equation (4), however, can be solved by elementary means only for a few happily simple forms of the potential v. In the case of a Coulomb field, the condition for negative eigenvalues leads to the well known Balmer formula. For an atom in which the potential field can not be expressed by simple analytical expressions, such as the Hartree field and Thomas-Fermi field, one

is often forced to resort to numerical methods to obtain the eigenvalues and the eigenfunctions, which are usually long and tedious.

An approximate method of solving wave equations has been developed by Wentzel[4], Brillouin[5], Kramers[6], and Swaan[7], and higher approximations have been given by Sommerfeld and Dunham[8]. Their results show that in the first approximation, the condition for eigenvalues is identical with the radial phase integral (5) in the classical quantum theory, except that here it leads to half integer quantization, a conclusion which the systematic applications of the Sommerfeld phase integral by Fues and others to the calculation of atomic levels forced one to draw even in the pre-wave-mechanical days. This Wentzel-Brillouin-Kramers method when applied to the Dirac equations leads in the first approximation also to correct results[9]. It will be used in the following chapters.

2° Statistical potentials of Thomas and Fermi and their applications.

The basic considerations of Thomas[10] and Fermi[11] are that the electrons in an atom, on account of their small mass, may be regarded as a completely degenerate gas and obey Fermi's statistics, according to which the distribution of electrons in the six-dimensional μ-space is uniform, with a density of one electron to each unit cell of the phase space of translation and rotation of a spinning electron.

Let V be the potential in an atom of nuclear charge Z. On the assumption of complete degeneracy, each cell in the μ phase space for which

$$\frac{p^2}{2m} - eV \leq 0 \qquad (1)$$

is filled up with two electrons while the rest of the phase space is empty.

For an electron whose positional coordinates lie between x, y, z, and $x+dx$, $y+dy$, $z+dz$, the amount of phase space available is

$$\frac{4}{3}\pi p^3 dx\, dy\, dz = \frac{4}{3}\pi (2me)^{\frac{3}{2}} V^{\frac{3}{2}} dx\, dy\, dz .$$

The number of cells in this space is

$$\frac{4\pi}{3h^3} (2me)^{\frac{3}{2}} V^{\frac{3}{2}} dx\, dy\, dz .$$

Two electrons are assigned to each cell, corresponding to the two oppositely directed spins of the electron. Hence the density of electron in ordinary space is

$$n = \frac{2^{\frac{7}{2}} \pi (me)^{\frac{3}{2}}}{3h^3} V^{\frac{3}{2}} \qquad (2)$$

which when put into Poisson's equation gives

$$\Delta V = \frac{2^{\frac{13}{2}} \pi^2 m^{\frac{3}{2}} e^{\frac{5}{2}}}{3h^3} V^{\frac{3}{2}} \qquad (3A)$$

This equation is solved subject to the conditions (i) that the field in the immediate neighbourhood of the nucleus is that due to the nucleus alone and (ii) that the total

number of electrons in the cloud is Z, i.e.,

$$\lim_{r\to 0} rV = Ze \tag{4A}$$

$$4\pi \int_0^\infty n r^2 dr = Z \,. \tag{5A}$$

Introducing $x = \gamma r$, $\varphi = \frac{rV}{Ze}$

where $$\gamma = \frac{2^{\frac{13}{3}} \pi^{\frac{4}{3}} m e^2}{3^{\frac{3}{3}} h^2} Z^{\frac{1}{3}}$$

equation (3A) and the boundary conditions (4A) and (5A) become

$$\frac{d^2\varphi}{dx^2} = \frac{\varphi^{\frac{3}{2}}}{x^{\frac{1}{2}}} \,. \tag{3}$$

$$\varphi(0) = 1 \tag{4}$$

$$\int_0^\infty \varphi^{\frac{3}{2}} \sqrt{x}\, dx = 1 \,. \tag{5B}$$

It can be easily shown that (5B) is equivalent to the condition

$$\varphi(\infty) = 0 \,. \tag{5}$$

Equation (3) subject to the conditions (4) and (5) has been solved numerically by Thomas, and Fermi, and an asymptotic solution is obtained by Sommerfeld[14].

In the case of positive ions[12] [13], the consideration is as follows: All cells in the phase space for which the total energy $\frac{p^2}{2m} - eV$ lies below a certain value, are each filled up with two electrons, while the rest of the phase space is empty. This limiting value of $\frac{p^2}{2m} - eV$ is determined by the total number of electrons in the electron cloud, it being zero for a neutral atom. In a positive ion, the number

of electrons in the cloud is less than the nuclear charge, and hence the greatest total energy must necessarily be negative. That is, only in that portion of the phase space for which

$$\frac{p^2}{2m} - eV \leq -e\alpha \tag{1'}$$

are the cells occupied; the rest of the phase space is not available. Introducing $v = V - \alpha$, we have for the density, instead of (2),

$$\begin{aligned} n &= \frac{2^{\frac{9}{2}}\pi (me)^{\frac{3}{2}}}{3h^3} v^{\frac{3}{2}}, & v > 0 \\ &= 0, & v < 0 \end{aligned} \tag{2'}$$

Instead of (3A) (4A) (5A), the Poisson equation and the boundary conditions are

$$\begin{aligned} \Delta v &= \frac{2^{\frac{13}{2}}\pi^2 m^{\frac{3}{2}} e^{\frac{5}{2}}}{3h^3} v^{\frac{3}{2}}, & r < r_0 \\ &= 0, & r > r_0 \end{aligned} \tag{3'A}$$

$$\lim_{r \to 0} rv = Ze \tag{4'A}$$

$$4\pi \int_0^{r_0} n r^2 dr = Z - z \tag{5'A}$$

which become, on introducing

$$x = \gamma r, \qquad \varphi = \frac{rv}{Ze}$$

$$\begin{aligned} \frac{d^2\varphi}{dx^2} &= \frac{\varphi^{\frac{3}{2}}}{x^{\frac{1}{2}}}, & x < x_0 \\ &= 0, & x > x_0 \end{aligned} \tag{3'}$$

$$\varphi(0) = 1 \tag{4'}$$

$$\int_0^{x_0} \varphi^{\frac{3}{2}} \sqrt{x}\, dx = 1 - \frac{z}{Z} \tag{5'B}$$

where z is the number of electrons removed.

Equation (5'B) becomes, on integration by parts,

$$-x_0\,\dot{\varphi}(x_0) = \frac{z}{Z} \qquad (5')$$

where

$$\varphi(x_0) = 0$$

Equations (3') subject to the conditions (4') and (5') have been solved numerically by an approximate method by Fermi. An asymptotic solution based on the same approximation has been obtained by Sommerfeld[14]. Fermi's solution of (3') is given in the appendix.

The justification for these statistical potentials is shown by the fact that they have found many successful applications, especially in the hands of Fermi and his school. In the following, a resume of some of the applications will be given.

i). Building up of electron subgroups.

From considerations of the angular momenta of the electrons, Fermi showed that the first s, p, d, f, shell should begin with the elements $Z = 1, 5, 21, 55$ respectively, as compared with the values $Z = 1, 5, 21, 58$ known from the theory of the periodic table.

ii). Calculations of X-rays $M_3(3d)$ terms[15].

Rasetti applied an approximate form of the Thomas-Fermi function to the calculation of M terms of different elements The Moseley curve obtained represents very satisfactorily the experimental data.

iii). Rydberg correction of optical s terms[11].

Fermi obtained the Rydberg corrections of s terms of differ-

ent elements by solving the wave equation by an approximate method. The agreement with optical data is satisfactory.

iv). Diamagnetic susceptibility [14].

Sommerfeld calculated the diamagnetic susceptibilities of atoms and ions by means of the Thomas-Fermi potential for neutral atoms and positive ions respectively. The agreement with experimental data is satisfactory for ions, but is poor for neutral atoms.

v). Total and successive ionization potential.

Milne [16], Baker [17], Sommerfeld [14,18] applied the statistical potential to the calculation of the total and successive ionization potentials of atoms, with fairly satisfactory results.

vi). Angular distribution of electrons scattered by mercury atom.

Hennenberg [19] applied the statistical potential to calculate the angular distribution of electrons scattered by mercury atoms. The theoretical result shows the maxima and minima as observed by Arnot and the agreement is best for electrons with energy of 800 electron volts.

vii). Electron density distribution in diatomic non-polar molecules.

Hund applied the method of Thomas and Fermi to the calculation of electron distribution in diatomic molecules. Approximate solutions of the differential equations arising were obtained, and the electron distribution calculated.

viii). Among the less successful applications of the statistical potential may be mentioned the following:

Gentile and Majorana[20] calculated the doublet separation $6p\ ^2P$ of Cs and Fermi[21] calculated the value of $\psi^2(0)$ for $6s\ ^2S$ of Cs, ψ being the radial wave function. In the first case the calculated value is 100 per cent higher than the observed value; and in the second case 60 per cent higher than the value obtained by the approximate formula of Goudsmit and by the numerical calculation of Nile[22]. Part of the discrepancy is due to the fact that the statistical potential is only approximate; but as Chapter IV of this thesis will show, a great part is due to the fact that they used a now obsolete method to obtain the potential distribution for the ion. For the potential of an electron in the field of an ion (singly charged), they used

$$V = \frac{Z-1}{r} e\varphi_0(\eta r) + \frac{e}{r}$$

where φ_0 is the Thomas-Fermi function for a neutral atom with nuclear charge $Z - 1$. This potential deviates, as will be shown later, appreciably from the actual potential in a region near the periphery of the atom. This region plays an important role when the eigenfunctions are actually calculated.

CHAPTER II

Integration of Thomas-Fermi Equation for Positive Ions

Fermi[12] and Sommerfeld[14] solved the equation

$$\frac{d^2\varphi}{dx^2} = \frac{\varphi^{\frac{3}{2}}}{x^{\frac{1}{2}}} \tag{1}$$

subject to the conditions

$$\varphi(0) = 1 \tag{2}$$

$$x_0 \dot{\varphi}(x_0) = -\frac{z}{Z} \tag{3}$$

in the following way. Let $\varphi_0(x)$ be the solution of equation (1) for the neutral atom, i.e., with the conditions $\varphi(0) = 1$, $\varphi(\infty) = 0$. Then $\varphi(x)$ is set

$$\varphi(x) = \varphi_0(x) - k\,\eta(x) \tag{4}$$

where k is a constant depending on $\frac{z}{Z}$ and η a function to be determined. On substituting (4) into (1), expanding in powers of $\frac{k\eta(x)}{\varphi_0(x)}$ and neglecting higher powers than the first, one obtains a linear differential equation for

$$\ddot{\eta} = \frac{3}{2}\sqrt{\frac{\varphi_0}{x}}\,\eta$$

with the boundary condition $\eta(0) = 0$. A solution of this equation with the arbitrary initial slope $\dot{\eta}(0) = 1$ is

$$\eta = (\varphi_0 + \frac{x\dot{\varphi}_0}{3}) \int_0^x \frac{dx}{(\varphi_0 + \frac{x\dot{\varphi}_0}{3})^2} .$$

Fermi solved this equation by numerical quadrature while Sommerfeld obtained an asymptotic expression of η. $\varphi(x)$ is then obtained from (4).

It is obvious that this method gives a good approximation to $\varphi(x)$ only in the region where $\frac{k\eta(x)}{\varphi_0(x)} \ll 1$; it can no longer be used in the neighbourhood of $x = x_0$ where $\varphi(x_0) = 0$ and $\frac{k\eta(x)}{\varphi_0(x)} \sim 1$. Hence the ionic radius x_0 determined by setting $\varphi_0(x) - k\eta(x) = 0$ together with the condition (3) is in error, although the magnitude of the error may not be great.

To obtain accurate solution of equation (1), it would be necessary to solve equation (1) for each particular value of $\frac{z}{Z}$. Instead, equation (1) is here solved for a few values of $\frac{z}{Z}$ by the method of difference equations (23). Let the argument x be divided into intervals ω, and $\Delta_1\ddot{\varphi}$ $\Delta_2\ddot{\varphi}$, ···· be the first, second differences of $\ddot{\varphi}$, ω being so chosen that the fourth difference $\Delta_4\ddot{\varphi}$ is smaller than the accuracy desired. An extension of the backward form of the Gregory-Newton formula leads to

$$\varphi_{n+1} = \varphi_n + \omega\dot{\varphi}_n + \frac{\omega^2}{2}\ddot{\varphi}_n + \frac{\omega^2}{6}\Delta_1\ddot{\varphi}_{n-1} + \frac{\omega^2}{8}\Delta_2\ddot{\varphi}_{n-1} + \frac{19\omega^2}{180}\Delta_3\ddot{\varphi}_{n-3} + \frac{3\omega^2}{32}\Delta_4\ddot{\varphi}_{n-4} + \cdots$$

$$\dot{\varphi}_{n+1} = \dot{\varphi}_n + \omega\ddot{\varphi}_n + \frac{\omega}{2}\Delta_1\ddot{\varphi}_{n-1} + \frac{5\omega}{12}\Delta_2\ddot{\varphi}_{n-1} + \frac{3\omega}{8}\Delta_3\ddot{\varphi}_{n-3} + \frac{251\omega}{720}\Delta_4\ddot{\varphi}_{n-4} + \cdots$$

The initial points $x_1, x_2, \cdots x_5$ and $\varphi_1, \varphi_2, \cdots \varphi_5$ are calculated from the series

$$\varphi(x) = 1 - \lambda x + \frac{4}{3}x^{\frac{3}{2}} - \frac{2}{5}\lambda x^{\frac{5}{2}} + \frac{1}{3}x^3 + \frac{3}{70}\lambda^2 x^{\frac{7}{2}} - \frac{2}{15}\lambda x^4 + \frac{4}{63}\left(\frac{2}{3} + \frac{\lambda^3}{16}\right)x^{\frac{9}{2}} + \cdots$$

$$\dot{\varphi}(x) = -\lambda + 2x^{\frac{1}{2}} - \lambda x^{\frac{3}{2}} + x^2 + \frac{3}{20}\lambda^2 x^{\frac{5}{2}} - \frac{8}{15}\lambda x^3 + \frac{2}{7}\left(\frac{2}{3} + \frac{\lambda^3}{16}\right)x^{\frac{7}{2}} + \cdots$$

which are obtained from equation (1) by successive approximation.

From these solutions of equation (1) for a few values of $\frac{z}{Z}$, one may plot the values of the initial slope $\lambda = \dot{\varphi}(0)$ as a function of $\frac{z}{Z}$, and the $\dot{\varphi}(0) = \lambda$ for other $\frac{z}{Z}$ can be obtained by interpolation. To obtain the solution $\varphi_B(x)$ for an initial slope λ_B corresponding to $\left(\frac{z}{Z}\right)_B$, it is noticed that within a small range of λ, one can obtain $\varphi_B(x)$ from a neighbouring solution $\varphi_A(x)$ which has been obtained by solving equation (1) for $\dot{\varphi}(o) = \lambda_A$, by means of the expression

$$\varphi_B(x) = \varphi_A(x) + (\lambda_B - \lambda_A) \frac{\delta \varphi}{\delta \lambda}(x)$$

where $\frac{\delta \varphi}{\delta \lambda}$ is determined as a function of x for values of λ in the neighbourhood of λ_A and λ_B.

By extending the calculation of Baker [17], the following tables are obtained.

TABLE I

x	φ (λ = 1.60)	$-\frac{\delta\varphi}{\delta\lambda}$	$\dot{\varphi}$ (λ = 1.60)	$-\frac{\delta\dot{\varphi}}{\delta\lambda}$
.10	.880	.101	1.008	1.031
.20	.790	.206	.807	1.086
.30	.717	.318	.676	1.154
.42	.642	.462	.563	1.252
.50	.600	.565	.505	1.326
.62	.544	.731	.436	1.449
.74	.495	.913	.382	1.588
.82	.466	1.044	.351	1.685
.90	.439	1.183	.325	1.791
1.06	.390	1.488	.282	2.024
1.14	.360	1.655	.264	2.150
1.22	.348	1.833	.248	2.287
1.30	.329	2.021	.234	2.429
1.38	.310	2.222	.222	2.583
1.46	.293	2.435	.211	2.747
1.54	.277	2.661	.201	2.954
	(λ = 1.589)		(λ = 1.589)	
1.65	.288	2.99	.1546	3.12
1.82	.263	3.56	.1361	3.49
2.01	.239	4.27	.1186	3.91
2.23	.215	5.15	.1027	4.41
2.46	.193	6.25	.0887	5.03
2.72	.172	7.65	.0762	5.76
3.00	.152	9.37	.0652	6.57
3.32	.133	11.62	.0556	7.70
3.67	.115	14.38	.0475	9.09
	(λ = 1.58856)	(λ = 1.589 — 1.58857)		(λ = 1.589 — 1.58857)
4.0	.1075	18.	.0368	10.
4.5	.0914	24.	.0292	12.8
5.0	.0783	31.	.0235	16.
5.5	.0677	38.4	.0192	19.
6.0	.0591	49.	.0158	22.5

TABLE I (continued)

x	$\varphi(\lambda=1.58856)$	$-\frac{\delta\varphi}{\delta\lambda}$ $(\lambda=1.58856-1.58857)$	$\dot{\varphi}$	$-\frac{\delta\dot{\varphi}}{\delta\lambda}$
6.5	.0519	60	.01313	26.0
7.0	.0459	73	.01106	30.6
7.5	.0408	88	.00938	33.6
8.0	.0354	102.5	.00802	37.0
8.5	.0327	123	.00690	42.3
9.0	.0295	145	.00598	47.0
9.5	.0267	169	.00523	52.0
10.0	.0242	196	.00458	57.6
10.5	.0221	225	.00403	63.5
11.0	.0202	257	.00357	69.5
11.5	.0185	294	.00319	76.2
12.0	.0167	342	.00306	83.5
12.5	.0154	375	.00276	91.5
13.0	.0141	420	.00251	100.5
13.5	.	475		109.5
14.0	.0118	530	.00210	1 9.4
15.0	.00987	653	.00180	141.0
	$(\lambda=1.58856)$	$(\lambda=1.588559-1.58856)$	$(\lambda=1.58856)$	$(\lambda=1.588559-1.58856)$
16	.00808	804	.00158	164.
17	.00658	1040	.00144	210.
18	.00520	1280	.00132	233.
19	.00392	1540	.00125	270.
20	.00269	1850	.00121	311.
21	.00149	2185	.00119	349.
22	.00031	2250	.00118	379.

Table I, Thomas-Fermi Function for Positive Ions.

TABLE II

$\frac{z}{Z}=x_0\dot{\varphi}(x_0)$	x_0	λ (Initial slope)
.0188	25.5	1.588559
.0270	22	1.588560
.0332	20	1.588562
.0367	19	1.588563
.0400	18	1.588564
.0460	17	1.588566
.0525	16	1.588570
.0583	15	1.588575
.0665	14	1.588582
.0763	13	1.588594
.0862	12	1.588609
.0992	11	1.588639
.117	10	1.588684

Table II, Initial Slopes of φ and Ionic Radii for ions of various degrees of ionization.

Table II is obtained from Table I by interpolation, and these two tables together will give the function for any ion.

As a comparison between the result obtained here and the approximate solutions of Fermi [12] and Sommerfeld [14], the values of x_0 for a few $\frac{z}{Z}$ are tabulated below:

TABLE III

$\frac{z}{Z}$	x_0 according to Sommerfeld	x_0 according to Fermi	x_0 according to Table II
.01	34.23	34.5	
.02	24.95	23.5	24.95
.03	20.54	20.0	21.0
.05	15.81	16.1	16.3
.08	12.18	12.1	12.6
.10	10.64	10.36	10.9

CHAPTER III

Eigenvalues of Central Field Problems

The energy of an electron in an atom is given by the Schrodinger equation

$$\Delta\Psi + (\varepsilon - v)\Psi = 0$$

where v is the potential energy of the electron. In a spherically symmetrical field, this equation may be separated and

$$\Psi = \frac{\psi(\rho)}{\rho} \Theta(\vartheta)\, \Phi(\varphi)$$

where

$$\Theta = \sqrt{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}}\, P_l^m(\cos\vartheta)$$

$$\Phi = \frac{1}{\sqrt{2\pi}}\, e^{im\varphi}$$

and $\psi(\rho)$ satisfies the equation

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon - v - \frac{l(l+1)}{\rho^2}\right]\psi = 0 \qquad (1)$$

The problem of finding the energies ε reduces to that of finding the eigenvalues ε of this differential equation.

An exact solution, however, of this equation is usually difficult, except for very simple forms of the function v. An approximate method due to Wentzel[4], Kramers[5], and Brillouin[6] is very helpful for this purpose, and will be used in what follows.

It is convenient to rewrite equation (1) in the ordinary units

$$\frac{d^2\psi}{dr^2} + \left(\frac{2\pi}{h}\right)^2\left[2m(E-V) - \left(\frac{h}{2\pi}\right)^2\frac{l(l+1)}{r^2}\right]\psi = 0$$

or, on putting

$$2m(E-V) - \left(\frac{\ell}{2\pi}\right)^2 \frac{l(l+1)}{r^2} = P^2$$

where P is the classical momentum,

$$\frac{d^2\psi}{dr^2} + \left(\frac{2\pi}{h}\right)^2 P^2 \psi = 0$$

Assume

$$\psi = e^{\frac{2\pi i}{h}\int y\, dr}$$

where y is expanded into a series with $\frac{h}{2\pi}$ as a parameter,

$$y = y_0 + \frac{h}{2\pi} y_1 + \left(\frac{h}{2\pi}\right)^2 y_2 + \cdots$$

Then substitution of the last two expressions into the differential equation gives, on comparing coefficients of $\frac{h}{2\pi}$, in the first approximation

$$\psi = \frac{c_1'}{\sqrt{P}} e^{\frac{2\pi i}{h}\int P\, dr} + \frac{c_2'}{\sqrt{P}} e^{-\frac{2\pi i}{h}\int P\, dr}$$

which, when transformation of the energy and distance to the atomic units is made, can be shown to take the form

$$\psi = \frac{c_1}{\sqrt{Q}} e^{i\int Q\, dp} + \frac{c_2}{\sqrt{Q}} e^{-i\int Q\, dp}$$

where $Q^2 = (\varepsilon - v)$ is the coefficient of ψ in the wave equation (1) written in the form

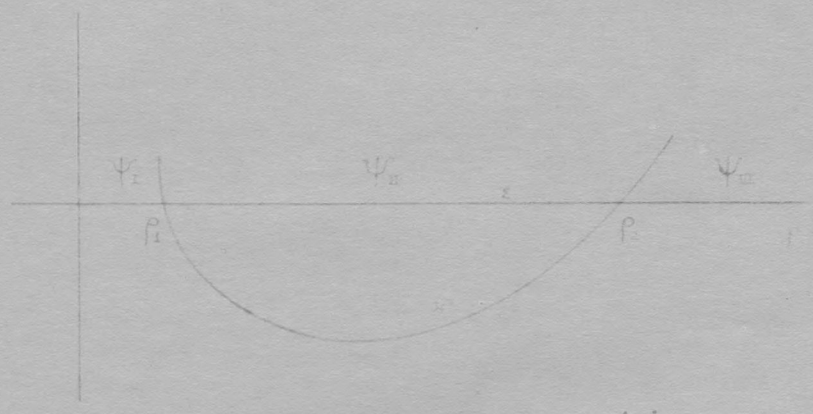
$$\frac{d^2\psi}{dp^2} + (\varepsilon - v)\psi = 0$$

The constants c_1, c_2 must be so chosen that for real values of r, ψ is real; and in the regions in which $Q^2 > 0$, i.e., classical motion is possible, ψ has an oscillatory character; while in the regions in which $Q^2 < 0$, i.e., motion is impossible classically, ψ is either a decreasing exponential

function, or a linear combination of increasing and decreasing exponential functions, according to the boundary conditions of the problem.

The eigenvalues ε are found in some cases by a consideration of the continuity and single-valuedness of the eigenfunction [8A], and in other problems, by a detailed consideration of the behavior of the function ψ at the points where $Q = 0$ [6,7,8]. From considerations on the complex ρ-plane, Kramers [6] and Zwaan [7] arrived at the following "connection formulae" which join an exponential function to an oscillatory function in the different regions.

Case I. For a potential x such that there is only one region of possible classical motion, as shown in the following figure



Potential field with one minimum

the wave functions ψ_I , ψ_{II} , ψ_{III} in the three regions $\rho < \rho_1$, $\rho_1 < \rho < \rho_2$, $\rho_2 < \rho$ are connected by the following formula

$$\frac{1}{2\sqrt{Q}} e^{-\int_{\rho}^{\rho_1} Q d\rho} \longleftrightarrow \frac{1}{\sqrt{Q}} \cos\left[\int_{\rho_1}^{\rho} Q d\rho - \frac{\pi}{4}\right] \equiv \frac{1}{\sqrt{Q}} \cos\left[\int_{\rho}^{\rho_2} Q d\rho - \frac{\pi}{4}\right] \longleftrightarrow \frac{1}{2\sqrt{Q}} e^{-\int_{\rho_2}^{\rho} Q d\rho} \qquad (6)$$

$$\psi_I \qquad \psi_{II_a} \qquad \psi_{II_b} \qquad \psi_{III}$$

where ψ_I vanishes when $\rho \to -\infty$, ψ_{III} vanishes when $\rho \to \infty$, and ψ_{II} has an oscillatory character.

The identity of the two expressions for ψ_{II} requires that

$$\frac{\dot{\psi}_{II_a}}{\psi_{II_a}} = \frac{\dot{\psi}_{II_b}}{\psi_{II_b}} .$$

From this it follows that

$$\tan\left[\int_{\rho_1}^{\rho} Q d\rho - \frac{\pi}{4}\right] = -\tan\left[\int_{\rho}^{\rho_2} Q d\rho - \frac{\pi}{4}\right]$$

This transcendental equation may be put in the form

$$\int_{\rho_1}^{\rho_2} Q \, d\rho = (n_\rho + \tfrac{1}{2})\pi \qquad (7)$$

where n_ρ is an integer. Remembering that our equation (2) is the radial part of the wave equation, we put in the radial quantum number $n-\ell-1$ for n_ρ . Thus equation (7) becomes

$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - v - \frac{\ell(\ell+1)}{\rho^2}} \, d\rho = (n-\ell-\tfrac{1}{2})\pi$$

which is exactly the "phase integral" of the classical quantum theory, with half integer quantum numbers. In order that this gives Balmer's formula in the case of

hydrogen, it is necessary to replace $l(l+1)$ by $(l+\frac{1}{2})^2$, and in all that follows, the equation will be used in the form

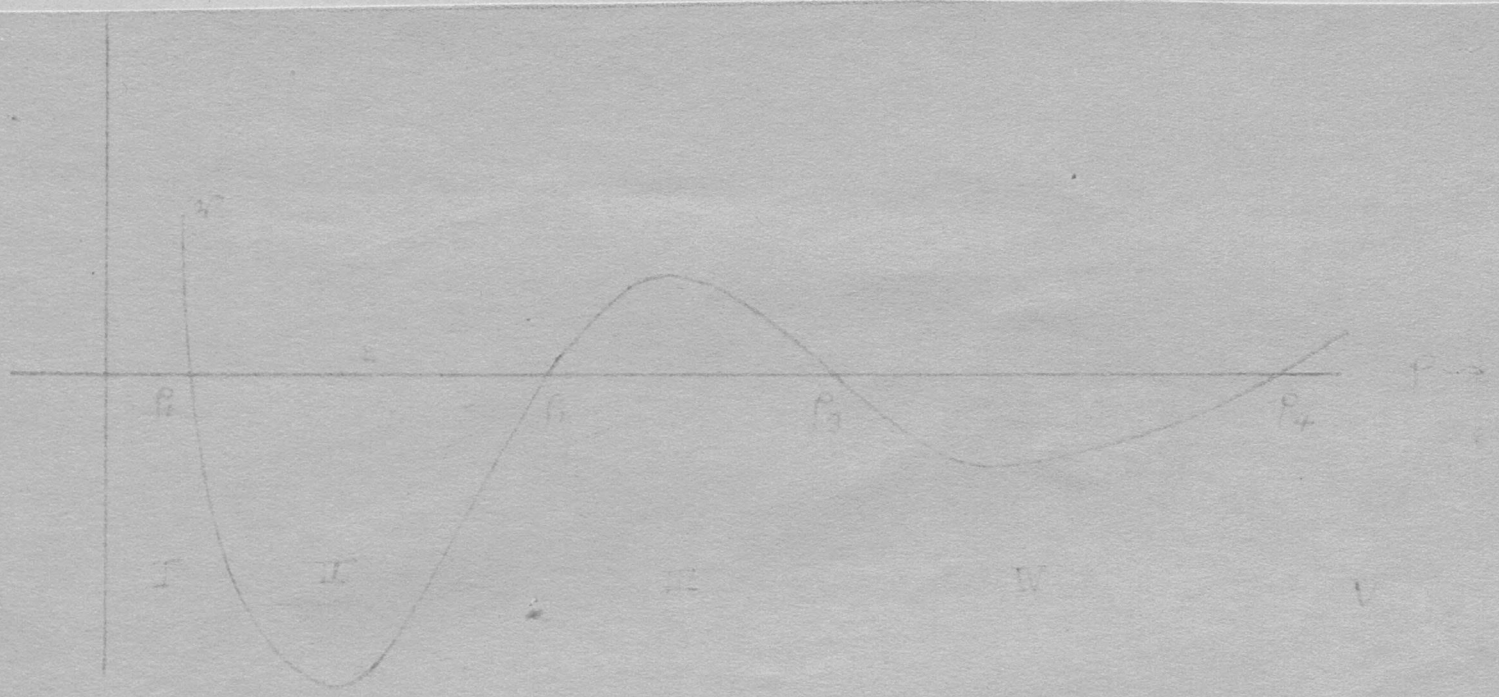
$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho = (n-l-\tfrac{1}{2})\pi \qquad (8)$$

The approximate wave functions in the different regions are given by (6), except for a multiplicative constant to be determined by normalization. By means of them the matrix element of any quantity U which is a function of ρ alone, may be calculated from the relation

$$U = \frac{\int \psi^2 U\, d\rho}{\int \psi^2 d\rho} \qquad (9)$$

where ψ stands for ψ_I, ψ_{II}, ψ_{III}, and $\frac{\psi_I}{\rho}$, $\frac{\psi_{II}}{\rho}$, $\frac{\psi_{III}}{\rho}$ are the radial wave functions in the three regions.

Case II. A case of considerable interest has not yet been treated in the literature, namely, one in which the potential field is such that there are two regions of possible classical motion separated by a potential hill.



Potential field with two minima

At ρ_1 , the exponential decreasing function in the region $\rho < \rho_1$

$$\psi_I = \frac{A}{\sqrt{Q}} e^{-\int_{\rho}^{\rho_1} Q\, d\rho}$$

is connected with the oscillatory function to the right of ρ_1

$$\psi_{II_a} = \frac{2A}{\sqrt{Q}} \cos\left[\int_{\rho_1}^{\rho} Q\, d\rho - \frac{\pi}{4}\right] .$$

At $\rho \geq \rho_2$, we have a linear combination of increasing and decreasing exponentials

$$\psi_{III_a} = \frac{D}{\sqrt{Q}} e^{\int_{\rho_2}^{\rho} Q\, d\rho} + \frac{E}{\sqrt{Q}} e^{-\int_{\rho_2}^{\rho} Q\, d\rho}$$

which are to be connected with the oscillatory functions to the left of ρ_2 ,

$$\psi_{II_b} = \frac{D}{\sqrt{Q}} \cos\left[\int_{\rho}^{\rho_2} Q\, d\rho + \frac{\pi}{4}\right] + \frac{2E}{\sqrt{Q}} \cos\left[\int_{\rho}^{\rho_2} Q\, d\rho - \frac{\pi}{4}\right]$$

$$= \frac{1}{\sqrt{Q}} \cos\left[\int_{\rho}^{\rho_2} Q\, d\rho - \frac{\pi}{4} + \delta\right]$$

where $$\tan\delta = \frac{D}{2E} \qquad (10)$$

The identity $\psi_{II_a} \equiv \psi_{II_b}$ requires that

$$\dot{\psi}_{II_a} / \psi_{II_a} = \dot{\psi}_{II_b} / \psi_{II_b}$$

from which follows

$$-\tan\left[\int_{\rho_1}^{\rho} Q\, d\rho - \frac{\pi}{4}\right] = \tan\left[\int_{\rho}^{\rho_2} Q\, d\rho - \frac{\pi}{4} + \delta\right]$$

or

$$\int_{\rho_1}^{\rho_2} Q\, d\rho = \left(n_\rho + \frac{1}{2}\right)\pi - \delta \qquad (11)$$

At ρ_4 , the decreasing function

$$\psi_V = \frac{B}{\sqrt{Q}} e^{-\int_{\rho_4}^{\rho} Q\, d\rho}$$

is connected with the oscillatory function to the left of ρ_4 .

$$\psi_{IV_a} = \frac{2B}{\sqrt{Q}} \cos\left[\int_{\rho}^{\rho_4} Q\, d\rho - \frac{\pi}{4}\right]$$

At ρ_3 , the linear combination

$$\psi_{III_b} = \frac{F}{\sqrt{Q}} e^{\int_{\rho}^{\rho_3} Q\, d\rho} + \frac{G}{\sqrt{Q}} e^{-\int_{\rho}^{\rho_3} Q\, d\rho}$$

is connected with

$$\psi_{IV_b} = \frac{F}{\sqrt{Q}} \cos\left[\int_{\rho_3}^{\rho} Q\, d\rho + \frac{\pi}{4}\right] + \frac{2G}{\sqrt{Q}} \cos\left[\int_{\rho_3}^{\rho} Q\, d\rho - \frac{\pi}{4}\right]$$

$$= \frac{1}{\sqrt{Q}} \cos\left[\int_{\rho_3}^{\rho} Q\, d\rho - \frac{\pi}{4} + \epsilon\right]$$

where $$\tan \epsilon = \frac{F}{2G} \qquad (12)$$

The identity $\psi_{IV_a} \equiv \psi_{IV_b}$ gives, as before,

$$\int_{\rho_3}^{\rho_4} Q\, d\rho = \left(n_\rho + \tfrac{1}{2}\right)\pi - \epsilon \qquad (13)$$

The relation between δ and ϵ is found from the fact that ψ_{III_a} and ψ_{III_b} are identical. Rewriting ψ_{III_b} in the form

$$\psi_{III_b} = \frac{F}{\sqrt{Q}} e^{-\int_{\rho_4}^{\rho} Q\, d\rho} e^{\int_{\rho_4}^{\rho_3} Q\, d\rho} + \frac{G}{\sqrt{Q}} e^{-\int_{\rho_4}^{\rho_3} Q\, d\rho} e^{\int_{\rho_4}^{\rho} Q\, d\rho}$$

and calling $e^{\int_{\rho_4}^{\rho_3} Q\, d\rho}$ α^2 , we have

$$\psi_{III_b} = \frac{F\alpha^2}{\sqrt{Q}} e^{-\int_{\rho_4}^{\rho} Q\, d\rho} + \frac{G}{\alpha^2\sqrt{Q}} e^{\int_{\rho_4}^{\rho} Q\, d\rho}$$

By comparison with ψ_{III_a}

$$\psi_{III_a} = \frac{D}{\sqrt{Q}} e^{\int_{\rho_2}^{\rho} Q\, d\rho} + \frac{E}{\sqrt{Q}} e^{-\int_{\rho_2}^{\rho} Q\, d\rho}$$

it follows that

$$F\alpha^2 = E \quad , \qquad \frac{G}{\alpha^2} = D \quad .$$

Hence, from the definitions (10) and (12), it follows that

$$\tan \delta = \frac{\cot \epsilon}{4\alpha^4} \quad . \tag{14}$$

The eigenvalue ε is then given by (11), (13), (14),

$$\begin{aligned} \int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho &= (n - l - \tfrac{1}{2})\pi - \delta \\ \int_{\rho_3}^{\rho_4} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho &= (n - l - \tfrac{1}{2})\pi - \epsilon \\ \tan\delta \tan\epsilon &= \frac{1}{4} e^{-2\int_{\rho_2}^{\rho_3} \sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}\, d\rho} \end{aligned} \tag{15}$$

or, on combining,

$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho = (n - l - \tfrac{1}{2})\pi - \tan^{-1}\left[\frac{1}{4} e^{-2\int_{\rho_2}^{\rho_3} \sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}\, d\rho} \tan \int_{\rho_3}^{\rho_4} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho\right] \tag{16}$$

This equation although highly complicated is of great importance for the calculation of the energy levels of the higher series, and explains the experimental fact that the quantum defects of the f states of all the heavier elements above gold (Z = 79) are almost unity. This will be shown in Chapter IV and V.

An immediate result of equation (15) is that when the two minima of the potential curve are exactly symmetrical, it follows that $\delta = \epsilon$ and

$$\delta = \pm \frac{1}{2\alpha^2}$$

which shows that to first approximation, each energy level is split up into two symmetrically about one which would exist if there were only one minimum. Furthermore, this splitting, which results from the resonance between the two energy states in the two regions, increases as the area under the potential hill decreases. This agrees with the result of Dennison and Uhlenbeck [24], in connection with the doubling of ammonia vibrational levels.

CHAPTER IV

The Energy Levels and Ground States of the Atoms of the 7th Period of the Periodic Table

The known elements of the 7th period of the periodic table are Ac, Th, Pa, and U. Their spectra have not yet been analyzed and our knowledge of their electron configurations in their normal states is very meagre. Since the statistical potential is a good approximation to the actual potential in heavy atoms, it is possible to study theoretically the normal configurations of these atoms and to calculate the approximate energy values of different states by the approximate method of solving the wave equation of the last Chapter. Such a calculation is particularly desirable since the conclusion drawn on erroneous reasoning by Sugiura and Urey [3] concerning the beginning of the 5f shell seemed to be generally accepted. In this chapter the method and result of the calculation of the energy values are given.

To calculate the energy of an electron in a certain state in an atom, the semi-classical idea is employed that the electron moves in the field of the nucleus and the rest of the electrons in the atom. Thus to calculate the arc spectra of an element, we solve the Schrodinger equation for the electron moving in the field of the singly ionized atom; to calculate the first spark spectra, the Schrödinger

equation for an electron in the field of the doubly ionized atom is solved, etc.. The energy of a state (n, l) is obtained by solving the radial wave equation

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon - v - \frac{l(l+1)}{\rho^2}\right]\psi = 0$$

In this equation, v is the potential energy of the optical electron in the field of the ion. For our calculation, the statistical potential for positive ions is used. Application of the Wentzel-Brillouin-Kramers method leads in the first approximation to the quantum condition:

$$\int_{\rho_1}^{\rho_2}\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\,d\rho = (n-l-\frac{1}{2})\pi \qquad (1)$$

in case there is only one region of possible classical motion for that particular eigenvalue ε ; or to the condition

$$\int_{\rho_1}^{\rho_2}\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\,d\rho = (n-l-\frac{1}{2})\pi - \tan^{-1}\left[\frac{1}{4}\,e^{-2\int_{\rho_2}^{\rho_3}\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\,d\rho}\tan\int_{\rho_3}^{\rho_4}\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\,d\rho\right] \qquad (2)$$

in case there are two regions of possible classical motion $\rho_1 < \rho < \rho_2$, $\rho_3 < \rho < \rho_4$, separated by a potential hill $\rho_2 < \rho < \rho_3$.

As the statistical potential is known in such a form that the "phase integrals" can not be integrated analytically, resort is made to numerical quadrature. Let us write the expression under the radical sign in the form $\varepsilon - \nu$ where

$$\nu = v + \frac{(l+\frac{1}{2})^2}{\rho^2} \qquad (3)$$

and

$$v = -\frac{2Z}{\rho}\varphi\left[\left(\frac{2^7}{9\pi^2}Z\right)^{\frac{1}{3}}\rho\right] - \frac{2z}{\rho_0} \quad , \quad \rho < \rho_0$$

$$= -\frac{2z}{\rho} \quad , \quad \rho > \rho_0 \qquad (4)$$

Z being the nuclear charge, $z = 1, 2, 3 \cdots$ for the calculation of energy of neutral, singly ionized, doubly ionized atom, etc., respectively, Q the Fermi function for positive ion $\frac{z}{Z}$. Here the assumption is made that the introduction of the optical electron into the ion does not disturb the field of the ion existing appreciably. This seems to be justified by the results obtained later. Fermi and others used, for the potential energy of an electron in the field of an ion, the expression

$$v = -\frac{2}{\rho}\left[1 + (Z-1)\varphi_0\left(\sqrt[3]{\tfrac{2^7}{9\pi}(Z-1)}\,\rho\right)\right] \qquad (5)$$

where $\varphi_0(\sqrt[3]{\ }\rho)$ is the Thomas-Fermi function for a neutral atom of nuclear charge (Z-1)e. This potential deviates, except for very small and very large values of ρ , from the actual potential as determined by equation (1) from empirical X-rays and optical data, to a much greater extent than the potential given by (4). The $Q = \rho^2 v$ curve for Ca^+ has been determined by Zwaan. A comparison of the potentials (4), (5) with that of Zwaan is given in Appendix III. Probably it is the use of the potential (5) that caused the results of Gentile, Majorana and Fermi to diverge so greatly from the known values (Chapter VI).

Below are given the $\nu = v + \frac{(l+\frac{1}{2})^2}{\rho^2}$ curves for the f


H
A
B
C
D
O
1
3
6
7
8
9
ρ →
ε1
ε2
ε3
ε4
χ
-1
-2
A. χ = v − (ℓ+½)²/ρ² for f states of U
B. " " U⁺
C. " " U⁺⁺
D. " " U⁺⁺⁺
H. " " Hg

Fig. 1

state of U, U^+, U^{++}, U^{+++} and Hg, which possess two minima the first of which can not be brought into the diagram without crowding the outer portions of the χ curves. For these elements, the χ curves for s, p, d states lie much more deeply in the diagram, while those for g, h--- states lie above those for the f states. They do not possess two regions of classical motions. For practical difficulty in drawing these other χ curves to scale, their position is represented by the schematic diagram (1A).

Thus it is seen that to calculate the energies of the f states of U and U^+ (and also Ac, Ac^+, Th, Th^+, Pa, Pa^+), it is necessary to use equation (2) obtained for the two minima problem. In any case, the energy ε is so determined that equation (1) or (2) is satisfied for the state n, l in question.

Another way of representing the same situation is to plot, instead of $\chi = v + \frac{(l+\frac{1}{2})^2}{\rho^2}$,

$$P = \varepsilon\rho^2 - (l+\tfrac{1}{2})^2 \quad , \qquad Q = \rho^2 v$$

separately. The Q curve for any ion can be calculated by means of equations (4). Its general shape, however, in the regions very close to and very far from the nucleus can be fixed even without the help of any particular v. In the immediate neighbourhood of the nucleus, the field is almost a Coulombian field corresponding to a central charge Ze, i.e., for very small ρ,

$$v \longrightarrow -\frac{2Z}{\rho} \quad .$$

At very great distance from the nucleus, the field is again

$P = \varepsilon\rho^2 - (\ell+\frac{1}{2})^2$, $Q = \rho^2 v$ for U

$P_1 = \varepsilon\rho^2 - (\ell+\frac{1}{2})^2$, $Q_1 = \rho^2 v$ for U^+

$Q_2 = \rho^2 v$ for U^{++}

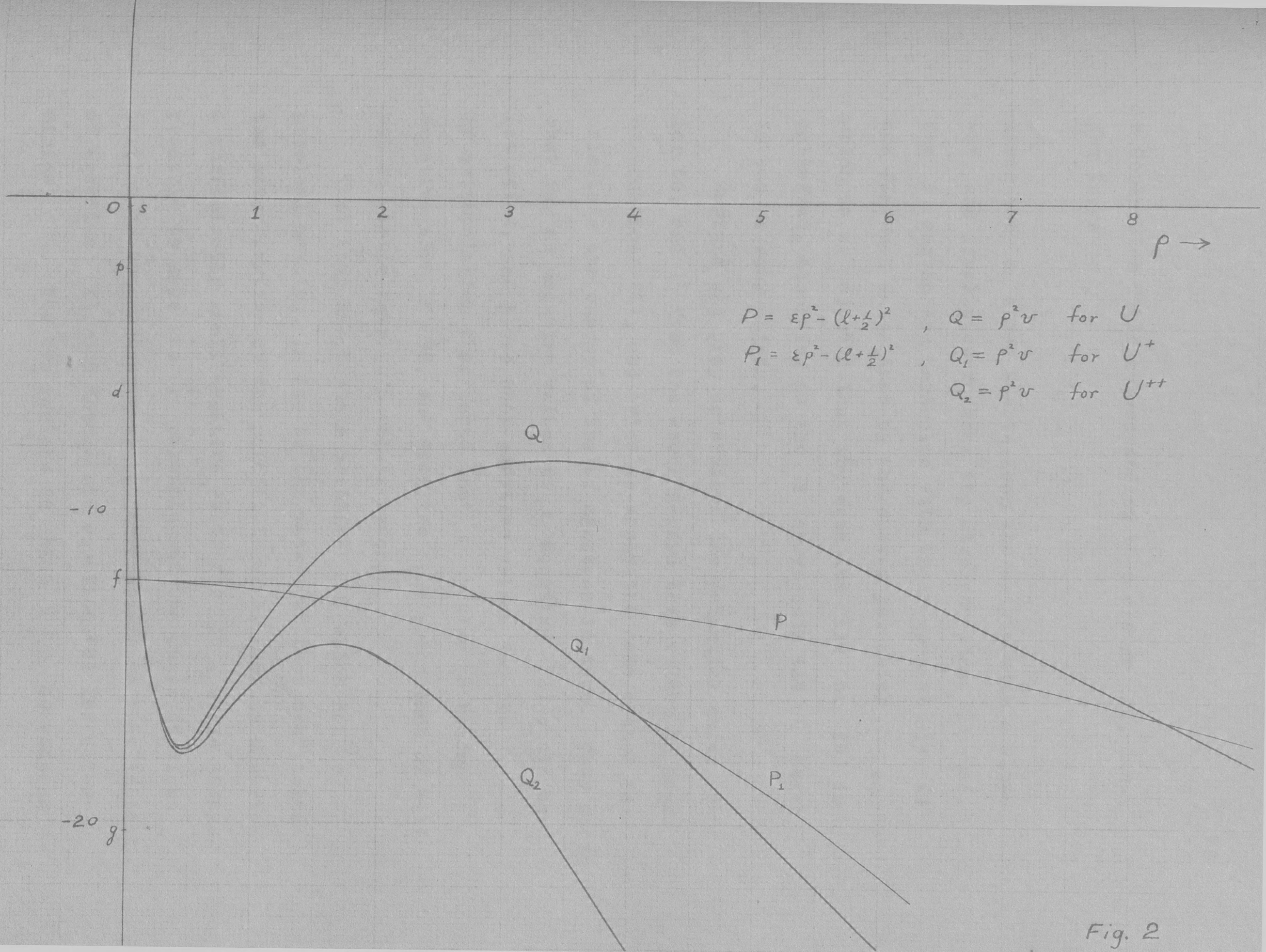


Fig. 2

a Coulombian field corresponding to a charge ze, i.e., for large ρ,

$$v = -\frac{2z}{\rho} .$$

Hence the Q curve starts from the origin with a slope $-2z$ and finally approaches the straight line $Q = -2z\rho$. The P curves are parabolas with their apex at $-(l + \frac{1}{2})$ and flatness determined by the energy parameter ε, which is so adjusted that the equation (1) or (2) is satisfied, according as the P curve cuts the Q curve in two or four points.

Sugiura and Urey determined the potential curve Q for Ac, and U from the known X-rays term values by means of equation (1), and tried to apply the same method to calculate the energy of the 5f electron in turn. They found that for no negative values of ε equation (1) could be satisfied, and hence took positive values for the ε. By extrapolation they found that ε begins to become negative when $Z = 95$, and drew the conclusion that 5f will not be stable until $Z = 95$ is reached.

That they had to take positive ε, which has no physical meaning, is due to the fact that they overlooked the outer portion of the potential curve. For by choosing a sufficiently small negative value for ε, it is always possible to make the P parabola cut the outer straight portion of the Q curve at two more points so that instead of equation (1), one should use equation (2) for determining ε. The two regions in which $P > Q$ correspond

exactly to the two regions of possible classical motion in figure 1.

For states with large ℓ, $(\ell > 4)$ the P curve will cut the Q curve in two points in the outer straight portion only, and in this case, equation (1) should be used again. Such states are then hydrogen like and equation (1) leads on integration immediately to a Balmer formula.

The actual computation consists in calculating:

i) the Fermi function $\varphi(1.1295 Z^{\frac{1}{3}} \rho)$ for values of ρ from .01 to ρ_0, where $\varphi(1.1295\, Z^{\frac{1}{3}} \rho_0) = 0$ and from where on the field is Coulombian,

ii) the v of equations (4) (the v's for the various ions of U are given in a table in the Appendix II),

iii) the $\eta = v + \frac{(\ell+\frac{1}{2})^2}{\rho^2}$ of equation (3), and

iv) plotting $\sqrt{\varepsilon - \eta}$ for a chosen ε and adjusting ε until equation (1) or equation (2) is satisfied.

The numerical quadrature in iv) can be rapidly carried out with the help of a planimeter. The following table gives the results of calculations for the energy of 5f, 6d, 7p, 7s electrons in the various ions of uranium. Calculations show that the energies of these states depend chiefly on the degree of ionization, and only to a small extent on the nuclear charge Z. Hence the relative position of these states in the other atoms of the 7th period is also represented by that in the corresponding ions of uranium.

	U^{+++++}	U^{++++}	U^{+++}	U^{++}	U^{+}	U^{+}	U
5f	-4.20	-3.22	-2.35	-1.45	- .70	-.256	-.0625
6d	-4.00	-3.15	-2.40	-1.70	-1.10	-.55	-.14
7s		-2.39	-1.85	-1.38	- .90	-.54	-.20
7p		-2.26	-1.75	-1.30	- .85	-.47	-.165

$\varepsilon = -\frac{\nu^2}{R}$ for the states of 5f, 6d, 7s, 7p in the various ions of Uranium

Although these results are obtained by the approximate method of Wentzel-Kramers-Brillouin of solving the wave equation with a Fermi field, they nevertheless give information as to which configuration can be expected to form the lowest state of the four heaviest atoms and their ions. They are given in the following table

	Neutral Atom	Singly Ionized	Doubly Ionized	3-Fold Ionized	4-Fold Ionized	5-Fold Ionized	6-Fold Ionized
Ac 89	$6d\ 7s^2$	$7s^2$ $6d\ 7s$	$7s$ $6d$				
Th 90	$6d^2\ 7s^2$	$6d\ 7s^2$ $6d^2\ 7s$	$6d\ 7s$ $6d^2$	$6d$			
Pa 91	$6d^3\ 7s^2$	$6d^2\ 7s^2$ $6d^3\ 7s$	$6d^2\ 7s$ $6d^3$	$6d^2$	$6d$		
U 92	$6d^4\ 7s^2$ $5f\ 6d^3\ 7s^2$	$6d^3\ 7s^2$ $6d^4\ 7s$ $5f\ 6d^3\ 7s$	$6d^3\ 7s$ $6d^4$ $5f\ 6d^3$	$6d^3$ $5f\ 6d^2$	$6d^2$ $5f\ 6d$	$6d$ $5f$	
93	$5f\ 6d^4\ 7s^2$ $5f\ 6d^3\ 7s^2$	$5f\ 6d^3\ 7s^2$ $5f\ 6d^4\ 7s$ $5f^2\ 6d^2\ 7s$	$5f\ \{6d^3\ 7s$ / $6d^4$ $5f^2\ \{6d^3\ 7s$ / $6d^2$	$5f\ 6d^3$ $5f^2\ 6d^2$	$5f\ 6d^2$ $5f^2\ 6d$	$5f\ 6d$ $5f^2$	$5f$

Outer electron configurations of atoms and ions of elements of the 7th period

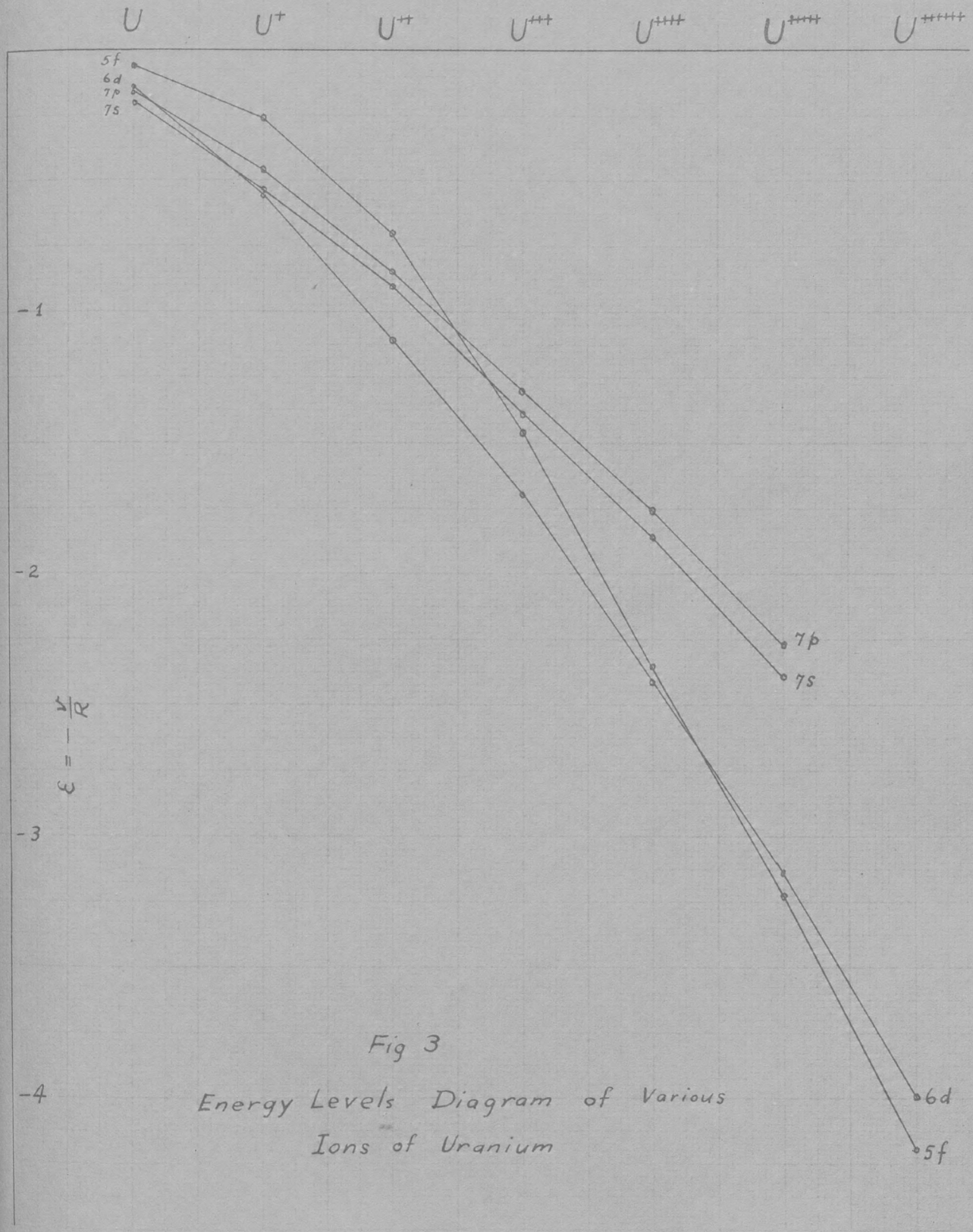


Fig 3

Energy Levels Diagram of Various Ions of Uranium

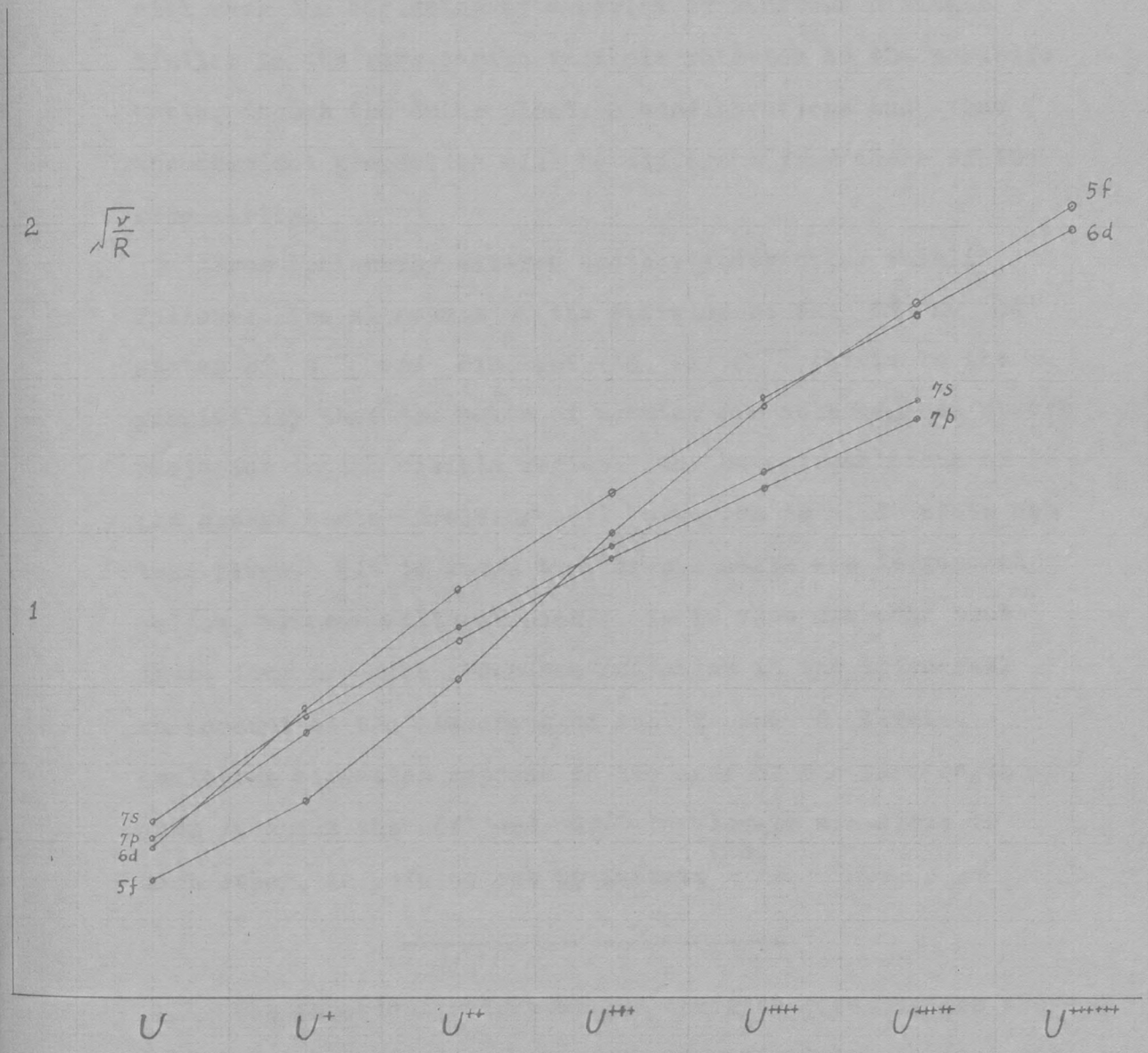


Fig. 3A

Moseley Diagram of Energy States of Uranium Ions

The interesting point is that, with uranium the 5f state begins to be prominent, and the element Z = 93, if it exists, would have at least one 5f electron. Hence it will mark the beginning of a series of fourteen elements similar to the rare earths in their relation to the periodic table, though the outer electron configurations and thus the chemical properties will be different from those of the rare earths.

From the energy diagram another interesting result follows: The closeness of the energies of the 5f and 6d states of U^{++++} and 5f6d and 6d of U^{+++} points to the possibility that the salts of uranium are colored, and absorb radiation in the visible region; for here transitions of the ground state involving an f electron to a d state can take place. (It is known that uranyl salts are in general yellow, uranous salt greenish). It is also probable that these ions may give resonance radiation in the infra-red, on account of the closeness of the f and d levels. Analogous situation happens in the case of the rare earth ions in which the $4f^2$ and $4f^{2-1}$ 5d levels are close to each other, as pointed out by Laporte (25).

The numerical values of the energies given in the above table must be regarded as a rough approximation, in fact, it is found, on comparison of calculated values with empirical data in spectra that have been analyzed, that the calculated

values of the energy are always too small. It is possible to find empirically the corrections that have to be applied to each level in each ion by carrying out similar calculations for corresponding ions whose term values are well established and comparing calculated and known results. This will be done separately and will not be included here.

CHAPTER V

The Quantum Defects of f States of Heavy Atoms

In the term-value tables of elements obtained from analysis of their spectra, it is a salient fact that the quantum defects of the f-states of all elements from H to Ba are all very small, of the order of magnitude .01. But from Au(Z = 79) on, the quantum defects of the 5f states are all very close to unity. This has led many authors to assign to them a principal quantum number 4, in spite of the fact that the 4-f shell has long been filled up before Au is reached [26]. This close proximity of the quantum defects to unity remains so far unexplained in a satisfactory manner. The quantum condition for the two-minima problem finds an interesting application in this connection and immediately accounts for the quantum defects of the f-states.

To calculate the quantum defects of the f-states of the elements Au, Hg, Tl, Pb, etc. one starts with the wave equation

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon - v - \frac{l(l+1)}{\rho^2} \right] \psi = 0$$

On calculating and plotting $\varkappa = v + \frac{(l+\frac{1}{2})^2}{\rho^2}$ it is found that $\varkappa$ has two regions of possible classical motion separated by a potential hill. The $\varkappa$ curves for the f-states of Hg and U are given in figure I of Chapter IV.

For the energy, it is necessary to use the condition

$$\int_{\rho_3}^{\rho_4}\sqrt{\varepsilon-\frac{2}{\rho}}\,d\rho=(n-l-\tfrac{1}{2})\pi-\tan^{-1}\Big[\tfrac{1}{4}e^{-2\int_{\rho_2}^{\rho_3}\sqrt{\frac{2}{\rho}-\varepsilon}\,d\rho}\tan\int_{\rho_1}^{\rho_2}\sqrt{\varepsilon-\frac{2}{\rho}}\,d\rho\Big] \qquad (1)$$

Here $\rho_1\ \rho_2$ and $\rho_3\ \rho_4$ have been interchanged. This is possible since the phase integrals $\int_{\rho_1}^{\rho_2}$, $\int_{\rho_3}^{\rho_4}$ play a symmetrical role in the derivation of the quantum condition. Here a great simplicity sets in, as the field in the region $\rho_3-\rho_4$ is Coulombian. The integral $\int_{\rho_3}^{\rho_4}$ can be evaluated directly giving

$$\int_{\rho_3}^{\rho_4}\sqrt{\varepsilon+\frac{2z}{\rho}-\frac{(l+\frac{1}{2})^2}{\rho^2}}\,d\rho=\frac{z^2\pi}{i\sqrt{\varepsilon}}-(l+\tfrac{1}{2})\pi \qquad (2)$$

writing

$$\tan^{-1}\Big[\tfrac{1}{4}e^{-2\int_{\rho_2}^{\rho_3}\sqrt{\frac{2}{\rho}-\varepsilon}\,d\rho}\tan\int_{\rho_1}^{\rho_2}\sqrt{\varepsilon-\frac{2}{\rho}}\,d\rho\Big]=\Delta\pi \qquad (3)$$

we have on combining (1) and (2)

$$\varepsilon=-\frac{z^2}{(n-\Delta)^2}$$

which is a Rydberg formula with a quantum defect Δ.

The value ε is adjusted so that equation (1) is satisfied, and then Δ calculated according to equation (3). It is found that for all the elements for Au($Z=79$) to U($Z=92$), the integral $\int_{\rho_1}^{\rho_2}\sqrt{\frac{2}{\rho}-\varepsilon}\,d\rho$ over the inner classical region varies from 1.0 to 1.2, and the potential hill is so large that $e^{-2\int_{\rho_2}^{\rho_3}\sqrt{\frac{2}{\rho}-\varepsilon}\,d\rho}$ varies from $\frac{1}{10000}$ to $\frac{1}{1000}$. A little consideration will hence show that $\Delta\sim 1$. The experimental values[27] of the quantum defects of these elements are listed below:

Z		Principal Quantum Number n	Effective Quantum Number $n^* = \sqrt{\frac{A}{\nu}}$	obs. Δ	calc. Δ
56	Ba	4	3.85	.15	0
79	Au	5	3.97	1.03	1.
80	Hg	5	3.97	1.03	1.
81	Tl	5	3.98	1.02	1.
82	Pb	5	3.96	1.04	1.
83	Bi	5			
84		5			
85		5			
86	Ru	5	3.98	1.02	1.
87		5			
88		5			
89	Ac	5			1.
90	Th	5			1.
91	Pa	5			1.
92	U	5			1.

The difference between the observed values and the expected value 1.00 of the quantum defects may be attributed to the effect of polarization of the atomic core which has been neglected, and the approximate nature of the calculation. The agreement is very satisfactory.

CHAPTER VI

Doublet Separation and Hyperfine Structure Separation

The Darwin-Pauli (28) equation of an electron in an electric field E can be written

$$\Delta\psi_3 + \frac{8\pi^2 m}{h^2}\left[(\varepsilon - eV)\left(1 - \frac{\varepsilon - eV}{2mc^2}\right) + \frac{eh^2}{16\pi^2 m^2 c^2}\left\{(E\cdot\nabla) + i[E\times\nabla]\sigma\right\}\right]\psi_3 = 0$$

$$\Delta\psi_4 + \frac{8\pi^2 m}{h^2}\left[(\varepsilon - eV)\left(1 - \frac{\varepsilon - eV}{2mc^2}\right) + \frac{eh^2}{16\pi^2 m^2 c^2}\left\{(E\cdot\nabla) + i[E\times\nabla]\sigma\right\}\right]\psi_4 = 0$$

where ψ_3 , ψ_4 are the two big components of the 4 ψ's. The term in $[E\times\nabla]\sigma$ is first given by Pauli and may be identified with the energy of spin-orbit interaction when the equation is applied to an electron in the field of the atom. This can be shown readily; for when the field is central, we have, on replacing $\frac{\partial}{\partial x}$ by $\frac{2\pi i}{h}p_x$ etc.,

$$\frac{ieh^2}{16\pi^2 m^2 c^2}[E\times\nabla]\sigma = \frac{ih^2}{16\pi^2 m^2 c^2}\cdot\frac{2\pi i}{h}\frac{1}{r}\frac{dV}{dr}[r\times p]\sigma$$

and $p = \frac{lh}{2\pi}$,

$$\frac{ieh^2}{16\pi^2 m^2 c^2}[E\times\nabla]\sigma = \frac{h^2}{16\pi^2 m^2 c^2}\frac{1}{r}\frac{dV}{dr}[r\times l]\sigma$$

The energy difference due to the two orientations of the spin is

$$\Delta W = \frac{h^2(l+\frac{1}{2})}{8\pi^2 m^2 c^2}\overline{\frac{1}{r}\frac{dV}{dr}}$$

This gives the doublet separation in the first approximation. Since throughout the present calculation, the atomic units are used, i.e.,

$$V = \frac{2\pi^2 me^4}{h^2}v, \qquad r = \frac{h^2}{4\pi^2 me^2}\rho ,$$

we have,

$$\Delta W = \frac{4\pi^4 m e^8 (l+\frac{1}{2})}{c^2 h^4} \overline{\frac{1}{\rho}\frac{dv}{d\rho}}$$

The separation in wave numbers is

$$\Delta \nu = \frac{\Delta W}{hc} = \frac{4\pi^4 m e^8}{c^3 h^5}(l+\frac{1}{2})\overline{\frac{1}{\rho}\frac{dv}{d\rho}}$$
$$= \frac{R\alpha^2}{2}(l+\frac{1}{2})\overline{\frac{1}{\rho}\frac{dv}{d\rho}} \qquad (1)$$

where $R = \frac{2\pi^2 m e^4}{h^3 c} = 109{,}737.42\ cm^{-1}$ and $\alpha = \frac{2\pi e^2}{hc}$, the Sommerfeld fine structure constant, and $R\alpha^2 = 5.82$.

To evaluate $\overline{\frac{1}{\rho}\frac{dv}{d\rho}}$, the matrix element

$$\overline{\frac{1}{\rho}\frac{dv}{d\rho}} = \frac{\int_0^\infty \psi^2 \frac{1}{\rho}\frac{dv}{d\rho} d\rho}{\int_0^\infty \psi^2 d\rho} \qquad (2)$$

is calculated, where ψ/ρ is the radial part of the wave function.

The wave function may be calculated by solving Schrödinger's equation for the electron in the field of the ion, namely,

$$\Delta \Psi + (\varepsilon - v)\Psi = 0$$

which separates and gives the radial equation

$$\ddot{\psi} + [\varepsilon - v - \frac{l(l+1)}{\rho^2}]\psi = 0$$

where ψ/ρ is the radial part of Ψ.

For a field such that there is only one region $\rho_1 < \rho < \rho_2$ of classical motion, the eigenvalues ε and the wave function may be calculated by means of Wentzel-Brillouin-Kramers approximation, namely

$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho = (n - l - \tfrac{1}{2})\pi$$

$$\psi^2 = \frac{1}{4\sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}} e^{-2\int_{\rho}^{\rho_1} \sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}\, d\rho}, \qquad \rho < \rho_1$$

$$= \frac{1}{\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}} \cos^2\left[\int_{\rho_1}^{\rho} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho - \frac{\pi}{4}\right], \quad \rho_1 < \rho < \rho_2 \qquad (5)$$

$$= \frac{1}{4\sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}} e^{-2\int_{\rho_2}^{\rho} \sqrt{\left|\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}\right|}}, \qquad \rho > \rho_2$$

for points not too close to ρ_1 and ρ_2.

In the neighbourhood of $\rho = \rho_1$, where $\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}} = 0$, the eigenfunction obtained by the W.-K.-B. method can not be used, for there the approximation is worst. In calculating the doublet separation, $\frac{1}{\rho}\frac{dv}{d\rho}$ is very large near the nucleus, and nearly all the contribution to the integral $\int \psi^2 \frac{1}{\rho}\frac{dv}{d\rho} d\rho$ comes from this region. Also in determining the hyperfine structure separation of ^2S states, the actual value of ψ/ρ at the nucleus $\psi/\rho(0)$ must be known. In both cases, it requires the eigenfunction to be determined accurately for small values of ρ. To achieve this, the approximation of Kramers (6), which neglects ε in comparison with the last terms in the coefficient of ψ in the wave equation and replaces v simply by $-\frac{2Z}{\rho}$, is not sufficiently good, for the effect of external screening is entirely neglected. Instead, Fermi's potential, being best near the nucleus, is used, and the region close to the nucleus is divided into small intervals for each of which the Fermi function φ is approximated by

$$\varphi = a - b\rho$$

where a , b are so chosen that for that interval, φ is closely given by the above expression. The wave equation then becomes

$$\ddot{\psi} + \left[-\varepsilon - 2Zb + \frac{2Za}{\rho} - \frac{l(l+1)}{\rho^2} \right] \psi = 0.$$

Writing $A = \varepsilon + 2Zb$, $B = Za$ and introducing the new variable $x = 2\sqrt{A}\,\rho$, the wave equation becomes

$$\frac{d^2\psi}{dx^2} + \left[-\frac{1}{4} + \frac{B}{\sqrt{A}\,x} - \frac{l(l+1)}{x^2} \right] \psi = 0.$$

The solution of this equation is the series

$$\psi(x) = k e^{-\frac{x}{2}} x^{l+1} \sum_r a_r x^r$$

where the coefficients a_r are given by the two-term recursion formula

$$a_r = \frac{r + l - \frac{B}{\sqrt{A}}}{r(r+2l+1)}\, a_{r-1}$$

ψ (x) can also be put in the form

$$\psi(x) = k e^{-\frac{x}{2}} x^{l+1} \sum_r \left[1 + x^r \prod_{r=1} \frac{r + l - \frac{B}{\sqrt{A}}}{r(r+2l+1)} \right]$$

The constant k is determined by a smooth joining of this solution with the W.-K.-B. solution in the oscillatory region.

At the outer root ρ_2 where $\sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}} = 0$ again, the W.-K.-B. solution fails, and the eigenfunction may be either obtained by smoothing over the singularity $\rho = \rho_2$, or by another solution of the wave equation appropriate for that region obtained as follows: Since the field is fairly Coulombian at great distance from the nucleus, the wave equation takes the simple form

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon + \frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2}\right]\psi = 0$$

On introducing the variable $x = 2\sqrt{-\varepsilon}\,\rho$, and writing

$$a = \frac{Z}{\sqrt{-\varepsilon}}$$

the equation becomes

$$\frac{d^2\psi}{dx^2} + \left[-\frac{1}{4} + \frac{a}{x} - \frac{l(l+1)}{x^2}\right]\psi = 0$$

The asymptotic behavior of ψ for large x has been studied by Whittaker (29), and the solution is called by him the confluent hypergeometric function. The particular solution which vanishes at infinity can be represented by the asymptotic series

$$W(x) = e^{-\frac{x}{2}} x^a \sum_\nu \left[1 + \frac{1}{x^\nu} \prod_{\nu=1} \frac{(l+\frac{1}{2})^2 - (a - \frac{2\nu-1}{2})^2}{\nu}\right]$$

To join this solution with the W.-K.-B. solution in the region of possible classical motion, i.e.,

$$\frac{1}{\sqrt[4]{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}} \cos\left[\int_\rho^{\rho_2} \sqrt{\varepsilon - v - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho - \frac{\pi}{4}\right] \longleftrightarrow \alpha W(2\sqrt{-\varepsilon}\,\rho),$$

the constant α is found (7) by the saddle point method and may be shown to be

$$\alpha = (2\pi\sqrt{-\varepsilon})^{\frac{1}{2}} e^{l+\frac{1}{2}} (a-l-\tfrac{1}{2})^{\frac{a-l-\frac{1}{2}}{2}} (a+l+\tfrac{1}{2})^{-\frac{a+l+\frac{1}{2}}{2}} \frac{1}{\Gamma(a-l)}$$

where Γ is the ordinary gamma function.

The calculations for the doublet separation of $6^2P_{\frac{1}{2}} - 6^2P_{\frac{3}{2}}$ of Cs, and $7^2P_{\frac{1}{2}} - 7^2P_{\frac{3}{2}}$ of the last alkalie ($Z = 87$) are carried out. Also the values of $\frac{\psi^2}{\rho^2}(0)$, where $\psi/\rho(0)$ is the radial eigenfunction at the nucleus, for the $6s\ ^2S_{\frac{1}{2}}$ state of Cs and $7s\ ^2S_{\frac{1}{2}}$ of Tl are calculated. The

calculations are rather involved and lengthy. The result is given below

	obs.	calc.
Doublet separation ($6p^2P$ of Cs)	554 cm^{-1}	390 cm^{-1}
Doublet separation ($7p^2P$ of $Z=87$	?	990 cm^{-1}

	Method of this paper	Goudsmit's formula
$(\psi/\rho)^2(0)$ for $6s\ ^2S_{\frac{1}{2}}$ of Cs	1.51×10^{25}	1.6×10^{25}
$(\psi/\rho)^2(0)$ for $7s\ ^2S_{\frac{1}{2}}$ of Tl	1.88×10^{25}	1.7×10^{25}

Fermi[21] has also calculated $(\psi/\rho)^2(0)$ for Cs and found 2.7×10^{25}. The value obtained by Breit[22] from Lande's approximate formula is 1.8×10^{25} while Nile[22] by numerical calculation found $(\psi/\rho)^2(0)$ $1.7\ (5) \times 10^{25}$. The better agreement obtained here than Fermi's justifies the form of the potential used in this manner, and the various solutions of the wave equation given above.

The eigenfunctions of the 6p, 6s of Cs, 7p of Z = 87, 7s of Tl are given in the following tables, together with the potential v and $\frac{1}{\rho}\frac{dv}{d\rho}$ in Cs and the element Z = 87, where

$$v = -\frac{2Z}{\rho}\varphi\left[\left(\frac{2^7}{9\pi^2}Z\right)^{\frac{1}{3}}\rho\right] - \frac{2Z}{\rho_0}, \quad \rho < \rho_0$$

$$v = -\frac{2Z}{\rho}, \quad \rho > \rho_0$$

and

$$\frac{1}{\rho}\frac{dv}{d\rho} = +\frac{1}{\rho^2}\left[v - 2Z\varphi\right], \quad \rho < \rho_0$$

$$\frac{1}{\rho}\frac{dv}{d\rho} = +\frac{2Z}{\rho^3}, \quad \rho > \rho_0$$

$7p^2P$ of $Z=87$

ρ	v	ψ	ψ^2	$\frac{1}{\rho}\frac{dv}{d\rho}$
.001		-.000 571	.000 000 35	172,200,000,000
.005		-.012 55	.000 157 5	1,337,000,000
.008		-.027 68	.000 765	
.010	16,260	-.039 28	.001 54	160,580,000
.012		-.051 5	.002 65	
.014		-.064 0	.004 10	
.016		-.076 0	.005 78	37,650,000
.018		-.083 4	.007 62	
.020	7,360	-.100 0	.010 00	17,950,000
.022		-.110 2	.012 14	
.024		-.119 0	.014 12	
.026		-.126 3	.015 92	
.028		-.130 9	.017 10	
.030	4,830	-.138 2	.019 10	5,200,000
.036		-.143 0	.020 40	
.040	3,445	-.139 2	.019 40	2,066,000
.05	2,622	-.111 2	.012 35	1,000,000
.06	2,084	-.062 4	.003 90	546,000
.08	1,433	.052 05	.002 71	224,000
.09	1,218	.102 9	.010 59	139,500
.10	1,052	.146 9	.021 55	96,700
.13	723	.201 3	.040 51	38,500
.15	581	.177 3	.031 42	23,050
.20	369.3	.001 6	.000 09	8,020
.25	250.8	-.176 7	.031 20	3,410
.30	180.3	-.281 1	.079 0	1,670
.35	135.1	-.273 3	.074 7	898
.40	150.1	-.177 3	.031 42	529
.45	82.7	-.054 7	.003 00	324
.50	66.3	.087 4	.007 64	207
.55	54.7	.219 8	.048 25	140
.60	45.4	.317 1	.100 7	95.9
.70	32.18	.436 8	.190 8	48.5
.80	24.07	.457 5	.209 5	27.6
.90	18.00	.340 5	.116 0	15.95
1.00	13.80	.208 0	.043 0	9.74
1.20	8.72	-.152 0	.023 0	4.15
1.40	5.962	-.439 5	.192 0	2.068
1.60	4.252	-.666 0	.444	1.118
1.80	3.132	-.807 0	.650	

$7p\ ^2P$ of $Z = 87$

ρ	v	ψ	ψ^2	$\frac{1}{r}\frac{dv}{d\rho}$
2.0	2.427	-.870	.755	.409
2.2	1.902	-.893	.798	
2.4	1.552	-.852 6	.727	
2.6	1.158	-.777	.602	
2.8	.952	-.694	.480	
3.0	.833	-.570	.325	.060 4
3.5	.694	-.242 2	.058 7	
4.0	.556	.133	.017 7	.025 8
4.5	.476	.452 5	.205 0	
5.0	.423	.735	.540	.016 0
5.5		1.099	1.214	
6.0		1.321	1.742	.009 25
6.5		1.562	2.435	
7.0		1.730	2.995	
7.5		1.870	3.50	
8.0		1.979	3.92	.003 94
8.5		2.040	4.15	
9.0		2.050	4.20	
9.5		2.030	4.10	
10.0		1.970	3.86	.002 00
11.0		1.823	3.30	
12.0		1.580	2.50	.001 156
13.0		1.300	1.69	
14.0		.960	.900	.000 73
15.0		.653	.427	
16.0		.430	.185	.000 49
17.0		.276	.076	

$$\int_0^\infty \psi^2 d\rho = 28.2$$

$6p\ ^2P$ of Cs

ρ	$-v$	ψ	ψ^2	$\frac{1}{\rho}\frac{dv}{d\rho}$
.001		.000 322	.000 000 103 6	109,060.000,000.
.005	20,140.	.007 20	.000 051 90	894,000,000.
.008		.017 0	.000 289	
.010	10,375.	.025 1	.000 629	102,000,000.
.012		.034 1	.001 067	
.014		.044 0	.001 934	
.016		.054 2	.002 94	24,080,000.
.018		.064 8	.004 20	
.020	4,928.3	.075 5	.005 70	12,050,000.
.025		.102 2	.010 42	
.030	3,122.3	.127 0	.016 10	3,356,000.
.035		.149 3	.022 25	
.04	2,243.3	.167 0	.027 76	1,340,500.
.05	1,716.3	.185 0	.034 35	740,000.
.06	1,371.3	.189 8	.036 06	360,000.
.08	954.3	.159 5	.025 4	138,000.
.10	708.3	.098 7	.009 75	64,750.
.15	399.6	-.117 0	.013 66	
.20	256.7	-.254 0	.064 40	
.25	178.2	-.271 0	.073 60	
.30	130.15	-.196 8	.038 75	
.35	98.70	-.065 5	.004 29	
.40	77.10	.074 7	.005 59	
.50	49.90	.315 0	.099 2	
.60	34.43	.433 6	.188 0	
.70	25.00	.436 0	.190 5	
.80	18.49	.349 5	.122 0	
.90	14.16	.201 0	.044 1	
1.00	11.14	.031 3	.000 98	
1.20	7.24	-.288 0	.082 8	
1.40	4.98	-.564 0	.318 3	
1.60	3.603	-.750	.561 5	
1.80	2.710	-.858	.736 4	
2.00	2.110	-.900	.810 0	
2.20	1.704	-.876	.769 0	
2.40	1.400	-.821	.675 0	
2.60	1.172	-.716	.512 3	
2.80	1.004	-.635	.403 0	
3.0	.881	-.515	.265	
3.5	.671	-.168	.028 3	

$6p\ ^2P$ of Cs

ρ	$-v$	ψ	ψ^2
4.0	.544 9	.202	.040 9
4.5	.465 4	.562	.316
5.0	.409 4	.860	.740
5.5	.368 6	1.158	1.342
6.0		1.371	1.882
6.5	$\frac{2}{\rho}$	1.580	2.495
7.0		1.738	3.020
7.5		1.860	3.460
8.0		1.940	3.770
8.5		2.000	4.00
9.0		2.020	4.09
9.5		2.030	4.12
10.0		2.020	4.08
10.5		1.995	3.98
11.0		1.954	3.82
12.0		1.795	3.22
12.5		1.684	2.84
13.0		1.555	2.42
14.0		1.27	1.62
15.0		1.020	1.04
16.0		.812	.66
17.0		.632 5	.40
18.0		.490	.24

$$\int_0^\infty \psi^2 d\rho = 32.1$$

$6s\,^2S$ of Cs

ρ	ψ	ψ^2	ρ	ψ	ψ^2
n.005	.082 5	.006 80	5.5	-1.610	2.59
.010	.106	.011 20	6.0	-1.696	2.87
.015			6.5	-1.732	3.00
.020	.096 0	.009 20	7.0	-1.740	3.02
.025			7.5	-1.712	2.93
.030	.042 5	.001 81	8.0	-1.66	2.75
.035			8.5	-1.574	2.47
.040	-.024 5	.000 60	9.0	-1.455	2.11
.05	-.091 4	.008 32	10.0	-1.140	1.30
.06	-.124	.015 4	11.0	- .846	.717
.08	-.181	.032 8	12.0	- .626	.391
.10	-.156	.024 25	13.0		
.15	.049 5	.002 45	14.0	- .318	.101
.20	.224	.050 0	15.0		
.25	.268	.071 9	16.0	- .181 5	.032 9
.30	.170 5	.029 0			
.35	.068 6	.004 71			
.40	- .080 4	.006 46			
.50	- .323	.104 0			
.60	- .415	.172 0			
.70	- .376	.141 0			
.80	- .250	.062 5			
.90	- .081 4	.006 61			
1.00	.106	.011 24			
1.20	.435	.188 2			
1.40	.645	.415			
1.60	.742	.550			
1.80	.740	.548			
2.00	.665	.441			
2.20	.530	.280 5			
2.40	.377	.143 8			
2.60	.195	.037 9			
2.80	.005 0	.000 025			
3.00	- .193 5	.037 35			
3.50	- .617	.380			
4.00	- .990	.979			
4.50	-1.275	1.621			
5.00	-1.469	2.150			

$$\int_0^\infty \psi^2 d\rho = 17.3$$

$Ts\ ^2S$ of Tl

ρ	ψ	ψ^2	ρ	ψ	ψ^2
.002					
.003	.065 25	.004 255	3.5	.123 6	.015 3
.005	.079 1	.006 26	4.0	.522	.272 2
.01	.088 5	.007 82	4.5	.874	.762 5
.02	.030 8	.000 95	5.0	1.179	1.390
.03	-.053 2	.002 83	5.5	1.418	2.010
.04	-.115 0	.013 25	6.0	1.595	2.550
.05	-.143 5	.020 60	6.5	1.718	2.95
.06	-.137 0	.018 75	7.0	1.805	3.26
.07	-.107 1	.011 48	7.5	1.850	3.42
.08	-.055 3	.003 06	8.0	1.860	3.46
.09	.001 22	.000 001 5	8.5	1.850	3.42
.10	.058 65	.003 45	9.0	1.820	3.315
.12	.151 6	.023 0	9.5	1.766	3.120
.14	.200 0	.040 0	10.0	1.682	2.835
.16	.201 5	.040 6			
.20	.098 7	.009 75	11.0	1.414	2.00
.35	-.098 5	.009 70	12.0	1.095	1.20
.30	-.247 0	.061 0	13.0	.828	.681
.35	-.294 2	.086 8	14.0	.637 5	.406
.40	-.251 7	.063 2	15.0	.482 6	.233
.45	-.143 1	.020 5	16.0	.368 6	.136
.50	-.009 27	.000 086			
.55	.124 9	.015 6			
.60	.248 0	.061 5			
.70	.407 8	.166 5			
.80	.449 0	.200 8			
.90	.390 0	.152 0			
1.00	.263 8	.069 5			
1.20	-.006 03	.000 036 4			
1.40	-.376 0	.141 5			
1.60	-.612 5	.375 0			
1.80	-.760 0	.577			
2.00	-.820 0	.672			
2.20	-.810 0	.655			
2.40	-.750 0	.561			
2.60	-.602 5	.363			
2.80	-.482 6	.233 3			
3.00	-.299 0	.089 3			

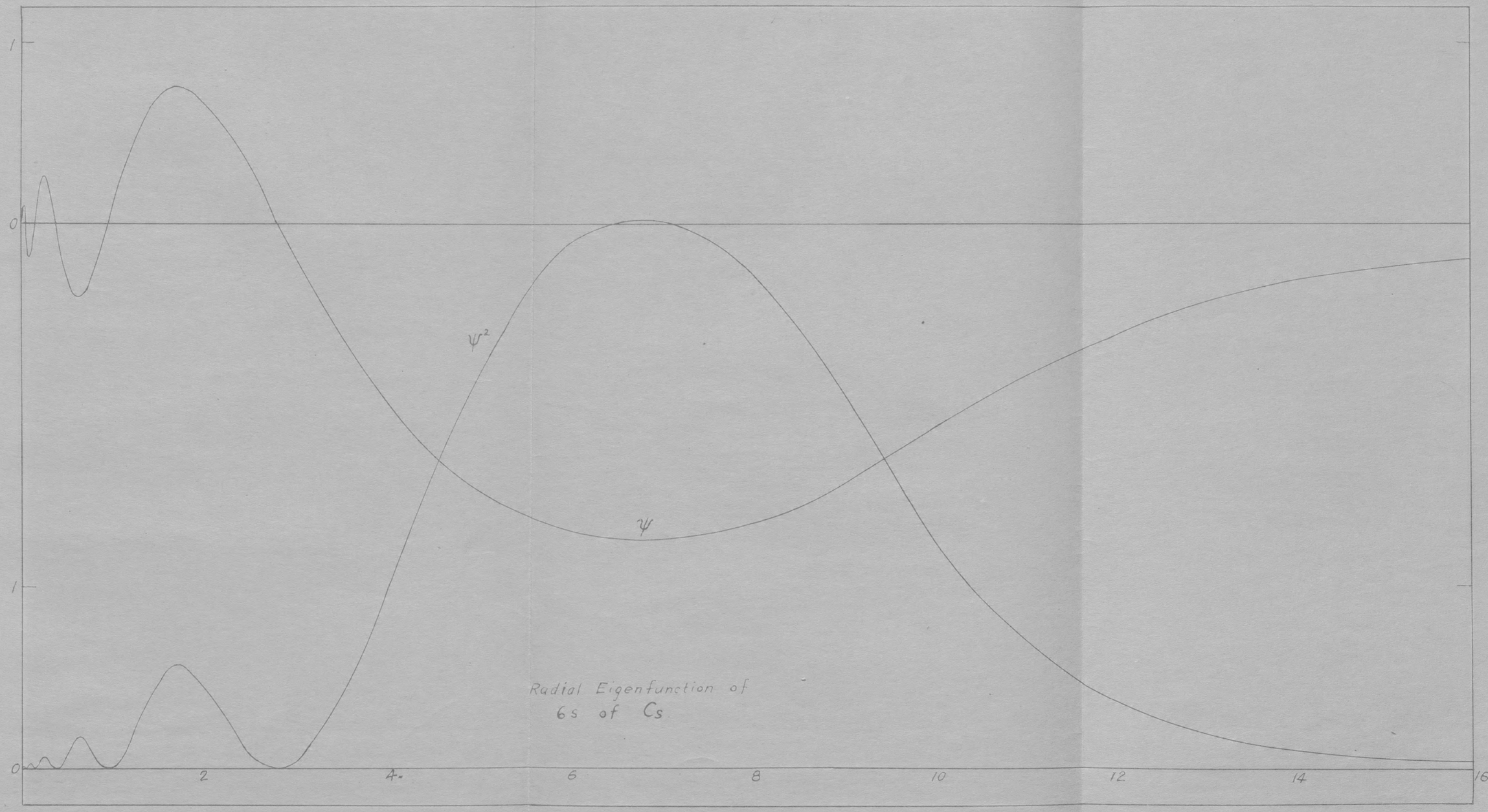
$\int_0^\infty \psi^2 d\rho = 22.6$



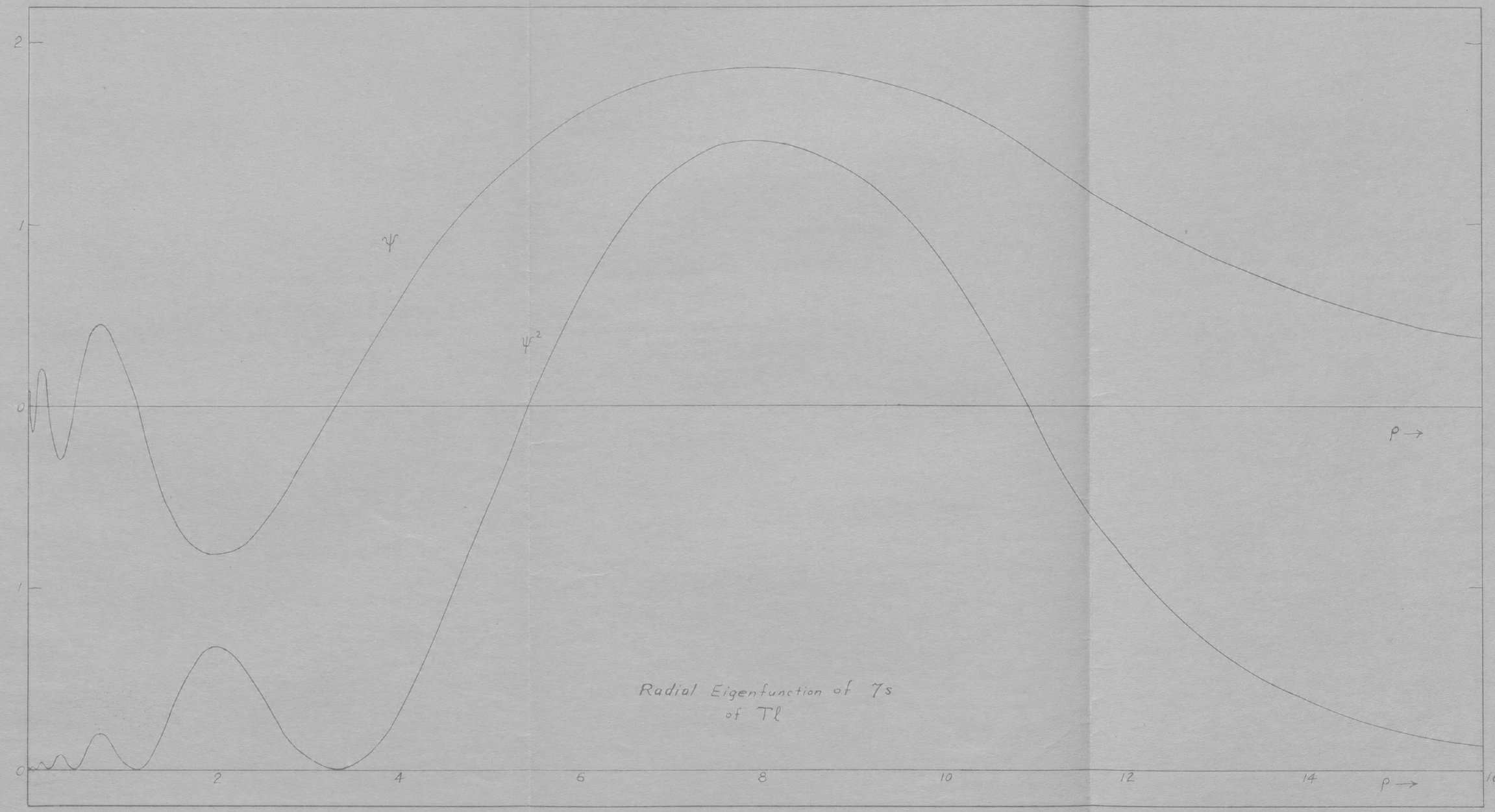
Radial Eigenfunction of 7p
of atom Z = 87



Radial Eigenfunction, of
6p of Cs



Radial Eigenfunction of
6s of Cs



Radial Eigenfunction of 7s
of Tl

CHAPTER VII

Negative Ions and Electron Affinities

It is well known that chemical elements, at the right of the periodic table, for example, the halogens, have great affinity for electron. The following problems naturally arise, namely

i) what elements will form stable negative ions, i.e., a neutral atom with an extra electron attached to it?

ii) whether there exist negative ions with more than one stationary state so that transition between them may give rise to a discontinuous spectrum?

iii) the energy values of the stationary states, especially the lowest one, if there be more than one, which gives the electron affinity of the atom.

At present an exact theoretical treatment of these questions is not known. An attempt is here made to study them in a qualitative way.

The wave equation of an electron in the field of a neutral atom is

$$\Delta\psi + (\varepsilon - v)\psi = 0$$

If the field be assumed to be spherically symmetrical, this equation can be separated and the radial wave function ψ/ρ is given by

$$\frac{d^2\psi}{d\rho^2} + \left(\varepsilon - v - \frac{l(l+1)}{\rho^2}\right)\psi = 0.$$

The question as to the stability of the negative ion and the existence of stationary states then reduces to that of finding negative eigenvalues of ε .

For heavy atoms, the statistical potential of Thomas and Fermi may be used in the wave equation. The effect of polarization of the atomic core by the last electron is relatively important in the case of negative ions. To take this into account, a term $\frac{\alpha}{\rho^4}$ must be added to the potential v , where α is a constant for the polarizability of the atomic core. The radial wave equation becomes

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon + \frac{2Z}{\rho}\varphi_0(\mu\rho) + \frac{\alpha}{\rho^4} - \frac{l(l+1)}{\rho^2}\right]\psi = 0$$

where φ_0 is the Thomas-Fermi potential for a neutral atom, and $\mu = \left(\frac{2^7}{9\pi^2}\ Z\right)^{\frac{1}{3}}$.

This equation can not be solved by elementary means on account of the mathematical form of φ_0 . Also for small ρ , the term $\frac{\alpha}{\rho^4}$ loses its significance and the polarizability effect can no longer be represented by $\frac{\alpha}{\rho^4}$. To obtain approximate values of ε , we may neglect the polarization of the atomic core, and solve the equation

$$\frac{d^2\psi}{d\rho^2} + \left[\varepsilon + \frac{2Z}{\rho}\varphi_0 - \frac{l(l+1)}{\rho^2}\right]\psi = 0$$

by the W.-K.-B. method, which leads to the quantum condition

$$\int_{\rho_1}^{\rho_2} \sqrt{\varepsilon + \frac{2Z}{\rho}\varphi_0 - \frac{(l+\frac{1}{2})^2}{\rho^2}}\, d\rho = (n - l - \tfrac{1}{2})\pi$$

There is an essential difference between this problem and that for a neutral atom or positive ions: for a study

of the function $\chi = -\frac{2Z}{\rho}\varphi_0 + \frac{(l+\frac{1}{2})^2}{\rho^2}$ shows that it possesses the following property

$\chi > 0$ for very small ρ

$= 0$ for $\rho = \rho_1$ where $\frac{2Z}{\rho_1}\varphi_0(\mu\rho_1) = \frac{(l+\frac{1}{2})^2}{\rho_1^2}$,

< 0 for $\rho_1 < \rho < \rho_2$

$= 0$ for $\rho = \rho_2$ where $\frac{2Z}{\rho_2}\varphi_0(\mu\rho_2) = \frac{(l+\frac{1}{2})^2}{\rho_2^2}$,

> 0 for $\rho > \rho_2$, since φ_0 decreases much more rapidly than $\frac{1}{\rho}$.

and $\chi \to 0$ from above, as $\rho \to \infty$.

This behavior of χ limits the eigenvalues ε to a finite number, while in the case of neutral atoms and positive ions, $\chi = -\frac{2Z}{\rho} + \frac{(l+\frac{1}{2})^2}{\rho^2}$ for large ρ and there is an infinite number of eigenvalues ε for each value of l .

By numerical quadrature, it is found that in the case of all the halogens F, Cl, Br, I, $Z = 85$, there exists only one negative ε for which the quantum condition, is satisfied, and that state of the extra electron corresponds in each case to the last place of the unclosed p-shell. This result shows that even in these strongly electronegative elements, there is only one stationary state, and hence no discrete spectrum of the negative ions.

The eigenvalues ε in electron volts for Cl, Br, I, $Z = 85$ are given below, together with the values obtained from the heads of the continuous absorption spectra of their negative ions.

	$\mathcal{E}$ obs.[30]	$\mathcal{E}$ calc.
Cl	3.84 volts	2.31 volts
Br	3.49	4.63
I	3.095	2.31
Z 85	?	2.72

The agreement between the observed values of electron affinity and the calculated values is not very close except for iodine. But considering the nature of the calculation the agreement is what can be expected. In fact the value of $\mathcal{E}$ for the last halogen (Z=85) whose discovery is recently claimed would be closer to the actual value than those of the lighter atoms, and it will be interesting if the electron affinity of this halogen be determined spectroscopically.

Appendix I

Fermi's Solution of Thomas-Fermi Equation (12) for Positive Ions

$$\varphi = \varphi_0 - k\eta$$

where φ_0 is the function for neutral atoms, and k a parameter depending on $\frac{z}{Z}$, z the number of electrons removed.

$\frac{z}{Z}$	k
.01	10^{-7}
.02	10^{-6}
.05	10^{-5}
.10	10^{-4}
.22	10^{-3}

x	$\eta(x)$	x	$\eta(x)$	x	$\eta(x)$	x	$\eta(x)$
.0	.00	1.4	2.23	8	103	20	2080
.1	.10	1.6	2.76	9	146	21	2480
.2	.21	1.8	3.36	10	201	22	2940
.3	.32	2.0	4.04	11	271	23	3460
.4	.44	2.5	6.1	12	359	24	4050
.5	.56	3.0	8.8	13	467	25	4710
.6	.70	3.5	12.3	14	598	26	5450
.7	.85	4.0	16.7	15	755	27	6280
.8	1.01	4.5	22.1	16	942	28	7210
.9	1.18	5.0	28.6	17	1160	29	8250
1.0	1.36	6.0	45.9	18	1420	30	9410
1.2	1.76	7.0	70.0	19	1730	31	10690

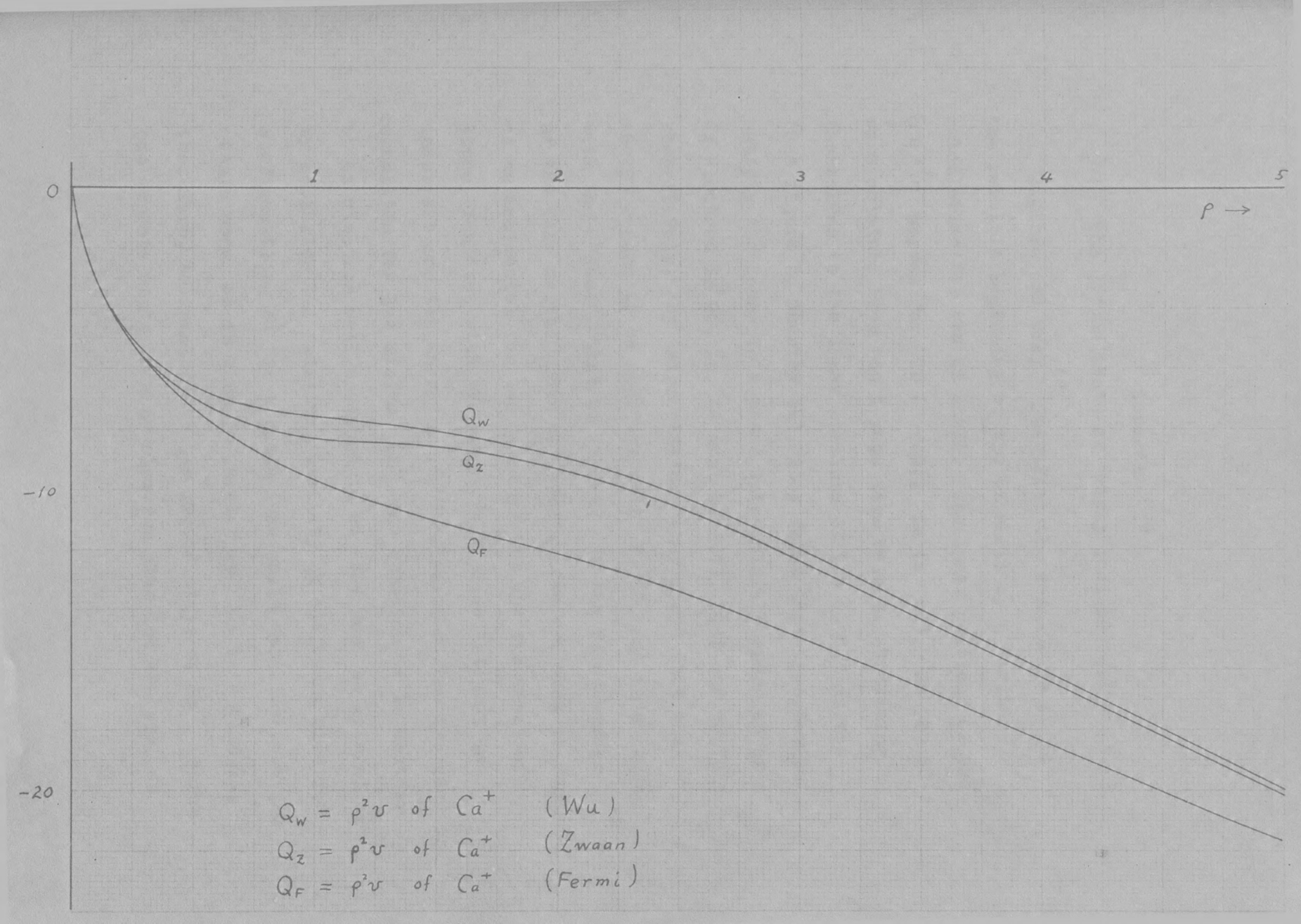
$$\eta = (\varphi_0 + \frac{x\dot{\varphi}_0}{3}) \int_0^x \frac{dx}{(\varphi_0 + \frac{x\dot{\varphi}_0}{3})^2}$$

Appendix II

Potential-v in various ions of U

ρ	$(Z=93)^{+++++}$	U^{++++}	U^{+++}	U^{++}	U^{+}	U
.01		17204.	17203.	17202.	17201.6	17200.	17200.
.02		8094.5	8093.4	8092.4	8091.6	8090.9	8090.3
.04	3665.6	3629.5	3628.4	3627.4	3626.6	3625.9	3625.3
.05	2798.6	2770.5	2769.4	2768.4	2767.6	2766.9	2766.3
.06	2223.6	2199.5	2198.4	2197.4	2196.6	2195.9	2195.3
.08	1527.6	1513.5	1512.4	1511.4	1510.6	1509.9	1509.3
.09	1303.6	1288.5	1287.4	1286.4	1285.6	1284.9	1284.3
.10	1123.6	1124.5	1123.4	1122.4	1121.6	1120.9	1120.3
.13	771.6	763.5	762.4	761.4	760.6	759.9	759.3
.15	620.64	614.46	613.40	612.4	611.56	610.9	610.3
.20	396.14	392.46	391.40	390.4	389.56	388.9	388.3
.25	270.64	266.46	265.4	264.4	236.56	262.9	262.3
.30	196.14	193.46	192.4	191.40	190.56	189.9	189.3
.35	148.64	145.96	145.20	144.20	143.36	142.7	142.1
.40	117.24	113.96	113.40	112.40	111.56	110.9	110.3
.45	92.44	90.66	89.65	88.65	87.81	87.12	86.55
.50	75.39	73.56	72.56	71.56	70.72	70.03	69.46
.55	62.82	61.21	60.20	59.20	58.36	57.67	57.10
.60	52.56	51.60	50.60	49.60	48.76	48.07	47.50
.70	39.14	37.46	36.50	35.50	34.66	33.97	33.40
.80	30.19	28.60	27.51	26.51	25.69	24.998	24.41
.90	23.90	22.52	21.54	20.54	19.76	19.068	18.44
1.00	19.58	18.43	17.44	16.45	15.66	14.968	14.400
1.20	14.22	13.10	12.14	11.15	10.335	9.658	9.100
1.40	11.17	10.09	9.130	8.177	7.390	6.718	6.152
1.60	9.24	8.228	7.300	6.363	5.575	4.908	4.350
1.80	8.00	7.030	6.146	5.200	4.423	3.768	3.328
2.00	7.10	6.176	5.331	4.436	3.670	3.020	2.508
2.20	6.416	5.567	4.791	3.879	3.135	2.490	1.948
2.40	5.849	5.0577	4.297	3.457	2.732	2.074	1.605
2.60		4.658	3.836	3.146	2.445	1.826	1.294
2.80			3.531	2.8925	2.2205	1.613	1.084
3.00				2.6920	2.0450	1.457	.935
3.50					1.7215	1.236	.688
4.00						1.020	.545
4.50						.9256	.4712
5.00							.4031
5.50							
6.00							.3343
6.50							.3096
7.00							

$v = -\frac{14}{\rho}$ $v = -\frac{12}{\rho}$ $v = -\frac{10}{\rho}$ $v = -\frac{8}{\rho}$ $v = -\frac{6}{\rho}$ $v = -\frac{4}{\rho}$ $v = -\frac{2}{\rho}$


1
2
3
4
5
0
ρ →
Q_W
Q_Z
Q_F
-10
-20
$Q_W = \rho^2 v$ of Ca^+ (Wu)
$Q_Z = \rho^2 v$ of Ca^+ (Zwaan)
$Q_F = \rho^2 v$ of Ca^+ (Fermi)

Appendix IV

The Ground State of Triply Ionized Cerium

Sugiura and Urey[3] justified the conclusion as to the possible beginning of the 5f shell by a similar calculation for the 4f shell. The inner portions of the $Q = \rho^2 v$ curves for Cs (Z=55), La (Z=57), Nd (Z=60) were obtained from the X-rays term values. Confining themselves to the inner portions of the $Q = \rho^2 v$ curves (See figure 2, Chapter IV), they found that in order to satisfy the Sommerfeld phase integral, the energies of a 4f electron in Cs, La, Nd must be 1.71, 0.25 and -0.70 respectively. By interpolation, they found that the energy begins to be negative with Z=58, and this agrees with the "fact" that Ce (Z=58) is the first member of the rare earth. This agreement, however, must be regarded as accidental for two reasons: i) the treatment of these f-states with the Sommerfeld phase integral is incorrect and the energy must be calculated from the quantum condition for two minima ii) the question as to whether a 4f electron will be found in an atom must be determined by comparing the relative stability of different electron configurations of the various ions built upon the rare gas atomic core, as is done in Chapter IV. It is desirable, therefore, to recalculate the ground state of Ce^{+++} which one expects would be a 4f electron plus the Xe core, as

the paramagnetic susceptibility calculated for this ground state ^2F agrees with the observed value.

On carrying out similar calculations as in Chapter IV, it is found that for Ce^{+++}, the energy of a 5d electron lies deeper than that of 4f.

$$\varepsilon\,(5d) = 1.65 \text{ approx.}$$

$$\varepsilon\,(4f) = 1.08 \text{ approx.}$$

This agrees with the result of Gibbs and White[31] from a study of the Moseley diagrams of these states of the isoelectric series of Cs, and is at variance with the magnetic data. The divergence from the magnetic data seems to point to the conclusion that the ground state of Ce^{+++} in the vapor state is 5d ^2D, while that in solid salts and even in solutions, is 4f ^2F, and the difference must be accounted for by the action of surrounding molecules in salts and solutions. The 4f ^2F state of Ce^{+++} has not yet been found[31] and a complete analysis of its spectrum Ce IV is very desirable.

Appendix V

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