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Statistical Potential of Atomic Ions

Paul S. Lee and Ta-You Wu
Department of Physics, National Tsing *Hua University, Hsinchu, Taiwan 300, R.O.C.*
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The equation for statistical potential $\phi(x,Z,z)$ for atomic ions of nuclear clarge Ze and Z $-z$ electrons has been integrated in high accuracy by means af computers. Tables are given for $\phi(x)$ for various values of the parameter z/Z, i.e. for ions of any atom to various degrees of ionization.

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I. Introduction

The Thomas-Fermi statistical potential for neutral atoms, $\phi_0(x)$, has been extended by Fermi [1] to positive atomic ions of nuclear charge Ze and $Z-z$ electrons. Approximate solutions have been obtained by Fermi [1], Sommerfeld [2], and Wu [3] for the potential $\phi(x;Z,z)$. The resultant potential $\phi(x;Z,z)$ has been applied by Wu [3,4,5] to a few problems in atomic spectra, namely, the beginning of the 5f shell in the neighborhood of the uranium atom in the periodic table; the quantum defects of the f states of the heavy atoms; the doublet separation of $6p^2P$ in Cs and $7p^2P$ in Fr. However, except for an account of these works in Gombus' book [6], the literature on the whole subject is limited.

As the early solutions of $\phi(x;Z,z)$ are all of an approximate nature, the integration of the Fermi equation has been carried out in the present work with great accuracy by means of a computer. The numerical algorithm used in the work is the well-known Runge-Kutta method. The step size is carefully chosen to optimize the integration yet be sufficiently small to guarantee convergence. Owing to the extreme sensitivity of the solution to the initial slope (as shall be illustrated later), especially for the neutral atom, and the large number of integration steps involved, the cumulative and truncation errors in the numerical integration are of major concern. In the present work, two independent approaches, one a direct integration and another a coordinate transformation with a transformed potential function, have been utilized to find the solution with virtually the same result. In addition, truncation error has been estimated during the integration to be on the order of 10^{-17} or less thus indicating a high accuracy result.

II. Fermi's theory

Consider an atom of nuclear charge Ze with z electrons removed. Let $U(r)$ be the potential at a distance r from the nucleus. The $Z-z$ electrons form a degenerate gas, the maximum total energy of an electron being negative,

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$$\frac{p^2}{2m} - eU = -eu < 0 \tag{1}$$

u being a positive constant.

The number density $n(r)$ in that part of the phase space that is filled up is

$$n(r) = \frac{8\pi}{3h^3}[2me]^{3/2}[U-u]^{3/2}. \tag{2}$$

The assumption is made that $U(r)$ and $n(r)$ obey the classical Poisson equation,

$$\nabla^2 U = -4\pi \cdot (-ne) = C(U-u)^{3/2} \tag{3}$$

where

$$\mathbf{C} = \frac{32}{3h^3}\pi^2 e[2me]^{3/2}$$

The constant u can be determined by considering the electrons being in a degenerate state. Their spatial distribution has a sharp boundary on a spherical surface $r = r_0$. That is, $n(r) = 0$, if $r \geq r_0$, so that $U(r) = u$, at $r = r_0$; and $U(r) = ze/r$, if $r \geq r_0$. Hence $u = ze/r_0$.

The radius r_0 is determined by the condition

$$4\pi \int_0^{r_0} n(r) \cdot r^2 dr = Z - z. \tag{4}$$

Equstion (3) is then

$$\Delta^2 U = \begin{cases} C(U - \frac{ze}{r_0})^{3/2}, & r \leq r_0 \\ 0, & r \geq r_0 \end{cases} \tag{5}$$

U(T) satisfies the condition,

$$\lim_{r \to 0}[rU] = \text{Ze}; \tag{6}$$

On introducing, the dimensionless variable, x, and the function $\phi(x)$ by

$$x = \mu r, \quad \phi(x) = \{r[U(r) - ze/r_0]\}/\{Ze\}, \tag{7}$$

where $\mu = ((128\ Z)/(4\pi^2)\}^{1/3}/\text{a}$, and a = first Bohr radius = $\{h/(2\pi e)\}^2/m$, equation (5) takes the form,

$$\frac{d^2\phi}{dx^2} = \begin{cases} \frac{1}{\sqrt{x}}\phi^{3/2}, & x \leq x_0 \\ 0, & x_0 \leq x. \end{cases} \tag{8}$$

where $x_0 = \mu r_0$, This is the Fermi equation. The boundary conditions (4), (5) and (6) are

$$\phi(0) = 1, \tag{9}$$

$$\phi(x_0) = 0, \tag{10}$$

and

$$\int_0^{x_0} \phi^{3/2}\sqrt{x}dx = 1 - \frac{z}{Z}. \tag{11}$$

The last two conditions lead to the relation

$$-x_0 \cdot \left(\frac{d\phi}{dx}\right)_{x_0} = \frac{z}{Z}. \tag{12}$$

The Fermi equation (8) is to be solved, for a given z/Z, under the boundary conditions (9), (10), and (12).

III. Solution of Fermi equation (8)

Fermi [1] solves (8) subject to (9),(10), (12) by setting

$$\phi(x) = \phi_0(x) - k \cdot \eta(x), \tag{13}$$

where $\phi_0(x)$ is the Thomas-Fermi function for neutral atoms (i.e., $\phi(x)$ for $z = 0$ with $\phi_0(\infty) = 0$, and k is a constant depending on z/Z. (13) is substituted into (8), $\phi(x)$ is expanded in powers of $k\eta/\phi_0$ and terms in powers higher than the first are neglected, thereby leading to a linear equation for $\eta(x)$.

$$\frac{d^2\eta}{dx^2} = \frac{3}{2} \cdot \left[\frac{\phi_0(x)}{x}\right]^{1/2} \cdot \eta, \tag{14}$$

with the boundary condition

$$\eta(0) = 0. \tag{15}$$

A solution of (14) with the arbitrary initial slope $\eta'(0) = 1$ is

$$\eta(x) = \left[\phi_0 + \frac{x}{3}\phi_0'\right] \int_0^x \frac{dx}{[\phi_0 + \frac{1}{3}(x\phi_0')]^2}. \tag{16}$$

Fermi [1] solves this equation by numerical integration and Sommerfeld obtains an asymptotic expression for $\eta(x)$. $\phi(x)$ is then obtained from (13).

Wu [3] points out an objection, in principle, of the above method, namely, that in the neighborhood of x_0 where $\phi(x_0) = 0$ (i.e. $k\eta(x) = \phi_0(x)$), the neglect of powers of $k\eta/\phi_0$ higher than the first is not valid precisely near x_0 which determines x_0 itself. He proposes to integrate equation (8) numerically for various initial slopes, $B = [d\phi/dx]_{x-0}$, leading to various solutions $\phi(x)$ which intersect the x-axis at various x = x_0 with slope

TABLE I. Thomas-Formi Potential of a Neutral Atom: $B = -1.58807102$

x	$\phi(x)$	x	$\phi(x)$	x	$\phi(x)$	x	$\phi(x)$
0.000	1.0000	2.0	0.2430	30.0	2.26E-03	300	4.73E-06
0.001	0.9985	2.5	0.1930	32.5	1.86E-03	325	3.78E-06
0.002	0.9969	3.0	0.1566	35.0	1.55E-03	350	3.08E-06
0.003	0.9955	3.5	0.1294	37.5	1.31E-03	375	2.54E-06
0.004	0.9940	4.0	0.1084	40.0	1.11E-03	400	2.12E-06
0.005	0.9925	4.5	9.19E-02	45.0	8.28E-04	450	1.53E-06
0.006	0.9911	5.0	7.88E-02	50.0	6.32E-04	500	1.14E-06
0.007	0.9897	5.5	6.82E-02	55.0	4.94E-04	600	6.84E-07
0.008	0.9882	6.0	5.94E-02	60.0	3.94E-04	700	4.45E-07
0.009	0.9868	6.5	5.22E-02	65.0	3.19E-04	800	3.07E-07
0.010	0.9854	7.0	4.61E-02	70.0	2.62E-04	900	2.213-07
0.020	0.9721	7.5	4.10E-02	75.0	2.18E-04	1000	1.65E-07
0.030	0.9593	8.0	3.66E-02	80.0	1.84E-04	2000	2.38E-08
0.040	0.9471	8.5	3.28E-02	85.0	1.56E-04	3000	7.68E-09
0.050	0.9352	9.0	2.96E-02	90.0	1.34E-04	4000	3.44E-09
0.060	0.9239	9.5	2.68E-02	95.0	1.15E-04	5000	1.85E-09
0.070	0.9129	10.0	2.43E-02	100.0	1 .OOE-04	6000	1.11E-09
0.080	0.9022	11.0	2.03E-02	110.0	7.72E-05	7000	7.22E-10
0.090	0.8919	12.0	1.71E-02	120.0	6.07E-05	8000	4.98E-10
0.100	0.8818	13.0	1.45E-02	130.0	4.87E-05	9000	3.58E-10
0.200	0.7931	14.0	1.25E-02	140.0	3.96E-05	10000	2.67E-10
0.300	0.7206	15.0	1.08E-02	150.0	3.27E-05	20000	3.86E-11
0.400	0.6596	16.0	9.42E-03	160.0	2.73E-05	30000	1.24E-11
0.500	0.6070	17.0	8.27E-03	170.0	2.31E-05	40000	5.58E-12
0.600	0.5612	18.0	7.30E-03	180.0	1.97E-05	50000	2.99E-12
0.700	0.5208	19.0	6.48E-03	190.0	1.69E-05	60000	1.80E-12
0.800	0.4849	20.0	5.78E-03	200.0	1.47E-05	70000	1.17E-12
0.900	0.4529	22.5	4.43E-03	225.0	1.06E-05	80000	8.06E-13
1.000	0.4240	25.0	3.47E-03	250.0	7.87E-06	90000	5.80E-13
1.500	0.3148	27.5	2.78E-03	275.0	6.03E-06	100000	4.32E-13

$[d\phi/dx](x=x_0)$, satisying the condition (12). Unfortunately, without computational help, the results obtained are neither extensive nor accurate [3].

In the present work, the program of Wu [3] is carried out with the help of a pentium 200 computer. The Fermi equation (8) is integrated for various values of the initial slope $B = [d\phi/dx]_{x=0}$. $\phi(x)$ decreases to zero at various corresponding values x_0. The results of the present work are collected together in Tables II and III. (More extensive results are not published here, but are available from the authors.)

The method used for the present work is the well-known 4-th order Runge-Kutta method. Due to the singular point of (8)at$x$ = 0, a series solution in powers of $\xi = x^{1/2}$ of the function $\phi(x)$ is sought at and near x = 0. The first few terms of the series are given as

TABLE II. Numerical Solution of Fermi-Thomas Equation.

- B	x0	$[d\phi/dx](x = x_0)$	z/Z
1.5880714	28.593	$-5.282E-4$	0.0151
1.5880720	23.932	$-9.317E-4$	0.0223
1.5880734	20.627	$-1.478E-3$	0.0305
1.5880785	16.923	$-2.683E-3$	0.0454
1.5880820	15.808	$-3.277E-3$	0.0518
1.5880880	14.613	$-4.113E-3$	0.0601
1.5881000	13.245	$-5.436E-3$	0.0720
1.5881100	12.530	$-6.346E-3$	0.0795
1.5881300	11.580	$-7.878E-3$	0.0912
1.5881900	10.094	$-1.137E-2$	0.1148
1.5882200	9.650	$-1.280E-2$	0.1235
1.5882500	9.297	$-1.409E-2$	0.1310
1.5883400	8.548	$-1.744E-2$	0.1491
1.5884800	7.826	$-2.174E-2$	0.1701
1.5887700	6.959	$-2.882E-2$	0.2006
1.5897500	5.689	$-4.579E-2$	0.2605
1.5950000	3.970	$-9.738E-2$	0.3866

TABLE III. Thomas-Fermi Potential of Positive Ione at Various Slope B.

$-B =$	1.588072	1.5880785	1.58810	1.58813	1.58825	1.58848	1.58877
$x_0 =$	23.932	16.923	13.245	11.580	9.297	7.826	6.959
x	ϕ	ϕ	ϕ	ϕ	ϕ	ϕ	ϕ
0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.005	9.925E-1	9.925E-1	9.925E-1	9.925E-1	9.925E-1	9.925E-1	9.925E-1
0.010	9.854E-1	9.854E-1	9.854E-1	9.854E-1	9.854E-1	9.854E-1	9.854E-1
0.025	9.657E-1	9.657E-1	9.657E-1	9.657E-1	9.657E-1	9.657E-1	9.657E-1
0.050	9.352E-1	9.352E-1	9.352E-1	9.352E-1	9.352E-1	9.352E-1	9.352E-1
0.075	9.075E-1	9.075E-1	9.075E-1	9.075E-1	9.075E-1	9.075E-1	9.075E-1
0.100	8.818E-1	8.818E-1	8.817E-1	8.818E-1	8.817E-1	8.817E-1	8.817E-1
0.200	7.931E-1	7.931E-1	7.931E-1	7.931E-1	7.931E-1	7.930E-1	7.930E-1
0.300	7.206E-1	7.206E-1	7.206E-1	7.206E-1	7.206E-1	7.205E-1	7.204E-1
0.400	6.596E-1	6.596E-1	6.595E-1	6.595E-1	6.595E-1	6.594E-1	6.593E-1
0.500	6.070E-1	6.070E-1	6.070E-1	6.070E-1	6.069E-1	6.068E-1	6.066E-1
0.600	5.612E-1	5.612E-1	5.611E-1	5.611E-1	5.610E-1	5.609E-1	5.607E-1
0.700	5.208E-1	5.208E-1	5.208E-1	5.208E-1	5.207E-1	5.205E-1	5.202E-1
0.800	4.849E-1	4.849E-1	4.849E-1	4.849E-1	4.848E-1	4.845E-1	4.842E-1
0.900	4.529E-1	4.529E-1	4.528E-1	4.528E-1	4.527E-1	4.524E-1	4.520E-1
1.000	4.240E-1	4.2403-l	4.240E-1	4.239E-1	4.238E-1	4.235E-1	4.231E-1
1.500	3.149E-1	3.1483-l	3.147E-1	3.147E-1	3.144E-1	3.1385-l	3.131E-1
2.000	2.431E-1	2.430E-1	2.429E-1	2.428E-1	2.423E-1	2.414E-1	2.402E-1
2.500	1.930E-1	1.930E-1	1.928E-1	1.926E-1	1.919E-1	1.905E-1	1.887E-1
3.000	1.567E-1	1.566E-1	1.564E-1	1.561E-1	1.551E-1	1.530E-1	1.505E-1
3.500	1.294E-1	1.293E-1	1.290E-1	1.286E-1	1.272E-1	1.243E-1	1.208E-1
4.000	1.084E-1	1.083E-1	1.079E-1	1.074E-1	1.054E-1	1.016E-1	9.678E-2
4.500	9.193E-2	9.179E-2	9.131E-2	9.065E-2	8.800E-2	8.295E-2	7.660E-2
5.000	7.878E-2	7.859E-2	7.798E-2	7.712E-2	7.369E-2	6.714E-2	5.894E-2
5.500	6.813E-2	6.789E-2	6.710E-2	6.600E-2	6.163E-2	5.330E-2	4.290E-2
6.000	5.938E-2	5.908E-2	5.809E-2	5.671E-2	5.122E-2	4.078E-2	2.782E-2
6.500	5.212E-2	5.175E-2	5.052E-2	4.880E-2	4.199E-2	2.912E-2	1.324E-2
7.000	4.603E-2	4.557E-2	4.406E-2	4.196E-2	3.362E-2	1.795E-2	
7.500	4.088E-2	4.032E-2	3.849E-2	3.593E-2	2.584E-2	7.015E-3	
8.000	3.649E-2	3.582E-2	3.360E-2	3.053E-2	1.844E-2		
8.500	3.271E-2	3.191E-2	2.927E-2	2.561E-2	1.126E-2		
9.000	2.945E-2	2.850E-2	2.536E-2	2.103E-2	4.187E-3		
9.500	2.661E-2	2.548E-2	2.180E-2	1.671E-2			
10.00	2.412E-2	2.280E-2	1.849E-2	1.257E-2			
10.50	2.193E-2	2.039E-2	1.539E-2	8.541E-3			
11.00	1.998E-2	1.821E-2	1.243E-2	4.574E-3			
11.50	1.826E-2	1.621E-2	9.578E-3	6.313E-4			
12.00	1.671E-2	1.437E-2	6.796E-3				
13.00	1.407E-2	1.103E-2	1.332E-3				
14.00	1.189E-2	8.018E-3					
15.00	1.006E-2	5.199E-3					
16.00	8.494E-3	2.479E-3					
17.00	7.125E-3						
18.00	5.902E-3						
19.00	4.787E-3						
20.00	3.749E-3						
21.00	2.762E-3						
22.00	1.807E-3						
23.00	8.691E-4						

$$\begin{aligned}\phi(x) = 1 &+ B\,\xi^2 + 4\cdot\xi^3/3 + 2B\,\xi^5/5 \text{ t } \xi^6/3 \text{ t } 3B^2\cdot\xi^7/70 \text{ t } 2\text{B}\cdot\xi^8/15 \\ &+2[7/3 - B^3/8]\,.\,\xi^9/63 + B^2\cdot\xi^{10}/175 \text{ t } B[31/15 \text{ t } 3B^3/32]\cdot\xi^{11}/99 \\ &+4[1/9 + B^3/35]\cdot\xi^{12}/45 \text{ t } B^2[557/700 - 3B^3/64]\cdot\xi^{13}/143 \\ &+B[32/33 - 232B^2/1155]\cdot\xi^{14}/168 \text{ t } [101/135 - 1123B^3/900 \\ &+7B^6/128]\cdot\xi^{15}/390 + \ldots.\end{aligned} \tag{17}$$

In the series solution, 15 terms are used to obtain the desired 10^{-17} or better accuracy. Runge-Kutta integration starts either the ξ^{15} terms $\geq 10^{-15}$ or $x > 0.0156$, for the range of B of interest. A major concern of the numerical integration is on the cumulative and the truncation errors. Since the Runge-Kutta method is known to hold a local truncation error proportional to $\delta^5\phi^{(5)}$ (or $\delta^5 y^{(5)}$, where 6 is the incremental and $\phi^{(5)}$ (or $y^{(5)}$) is the fifth derivative of the potential function), this quantity is routinely checked during the integration to keep the local truncation error small ($< 10^{-15}$). In addition, various value of δ has been used and the results compared to ensure convergence of solution with a proper integration step size.

Equation (8) is directly integrated until x reaches $x = x_p \approx 1$. In the range $x_p \geq x \geq 0$, the limited integration steps renders the error manageable. Beyond x_p, the required number, M, of integration steps increases rapidly and may become very large, especially near the neutral atom condition. This large M causes the cumulative error untraceable. For this reason, we shall divide the domain of integration, x, into two regions:

$$\text{(a) } 0 \leq x \leq x_p; \quad \text{(b) } x_p \leq x \leq x_0, \tag{18}$$

where $x_p = 1$ and x_O is where $\phi(x_O) = 0$ as in (10). For the region (b), we shall make the transformation

$$\varsigma = \varsigma_0 - 1/\sqrt{x}, \qquad \text{co} = 1/\sqrt{x_p}. \tag{19}$$

and introduce the Ansatz

$$y(\varsigma) = x^N \phi(x), \tag{20}$$

where N is a constant which ensures $y(\varsigma)$ converges as $x \to \infty$. The function y satisfies the equation

$$[\zeta_0 - \zeta]^5\,.\,y'' - (4\text{N t } 3)\cdot[\zeta_0 - \zeta]^4\,.\,y' - 4N(N \text{ t } 1)[\zeta_0 - \zeta]^3\,.\,y = 4[\zeta_0 - \zeta]^N \cdot y^{3/2}. \tag{21}$$

The value of N is found to be best chosen between -1 and 2. Equation (21) is to be integrated from $\varsigma = 0$ to $\varsigma = \varsigma_0$ (i.e. $x = x_p$ to ∞) with the boundary conditions matched at $\varsigma = 0$ utilizing the integrated values $\phi_q \equiv \phi(x_p)$ and the slope, $b = [d\phi/dx](x = x_p)$, at $x = x_p$ of the Fermi equation (8) (from x = 0, under $\phi(0) = 1$ and $B = [d\phi/dx]_{x=0}$, until $x = x_p$).

To match the boundary conditions, in the neighborhood of $\varsigma = 0$ (i.e. $\varsigma = 0$), equation (21) is solved for a sories solution (twelve terms, for accuracy) of y in terms of ς,

$$y = Ao + A_1 . \varsigma + A_2 \varsigma^2 + A_3 \cdot \varsigma^3 + \ldots, \tag{22}$$

under the boundary conditions:

$$y(\varsigma = 0) = x_p^N \cdot \phi_p, \quad y'(\varsigma = 0) = A_1 = \sqrt{x_p}[2x_p^{N+1} \cdot b + 2N x_p^N \cdot \phi_p]. \tag{23}$$

The method for the series solution is straightforward. The expression of the coefficients is very complex and will not be presented here, but is available from the authors. It suffices to say that the coefficients of ζ^k, $k \geq 2$, can all be expressed in terms of the first two coefficients because the Fermi equation (21) is a second order differential equation. Since ϕ_p and b are determined by $\phi(0)$ and $B.y(\zeta)$ is thus uniquely defined by $\phi(0)$ and B.

Use of the series solution (22) terminstes at $\varsigma = \varsigma_1 > 0$ and Runge-Kutta method is again used to solve equation (21) for $\varsigma > \varsigma_1$ similar to that as in $0 \leq x \leq x_p$.

Equation (8) is also directly integrated for the region (b), x $\geq x_p$. The use of (21) reduces M, the number of integration steps, significantly. Comparison of the results from these two approaches (i.e., by direct integradon of ϕ without reaking up the range of x into two regions (18) and by following through (18) to (21) shows that they are virtually identical. This shows that accumulated error of the numerical integration is small, and the results of the present work are accurate.

IV. Remarks

(1) The Thomas-Fermi potential $\phi_0(x)$ for neutral atoms ($z = 0$) is a special case of (9), (10), (11), (12), namely,

$$\phi_0(0) = 1; \ \phi_0(\infty) = 0; \ \int_0^\infty \phi_0^{3/2} . \sqrt{x} dx = 1. \tag{24}$$

In our work we were at the beginning concerned with the problem of accumulated error beyond, say, x = 1. We therefore re-integrated the Thomas-Fermi equaton (8) for various slopes $B_0 = [d\phi_0/dx]_{x=0}$, until we found $\phi_0(x)$ which approaches zero as x $\rightarrow \infty$. The result is given in Table I. Instead the result is slightly different from the approximate values of $\phi_0(x)$ obtained in the 1930's, before modern computers were available. The value of B_0 is found to be -1.5880710 > B_0 > -1.5880711, compared with the volue -1.58856 in the literature since the early 1930's.

(2) In obtaining the energy state of the arc spectrum of a neutral atom, one approximates the problem by solving the Schrodinger oquation of one electron in the field $V(r)$ of the nuclear charge Ze and the other $Z-1$ electrons. Before Fermi's potential for positive ions was known, $V(r)$ was approximated by

$$V_0(r) = \frac{Z-1}{r} e\phi_0(\mu r; Z-1) + \frac{e}{r}, \tag{25}$$

where $\phi_0(\mu r; Z-1)$ is the Thomas-Fermi potential for a neutral atom of nuclear charge $(Z-1)e$. A better approximation to $V(r)$ is

$$V_F(r) = \begin{cases} \frac{Ze}{r}\phi(\mu r) + \frac{e}{r_0} & , \ r \leq r_0 \\ \frac{e}{r} & , \ r_0 \leq r \end{cases} , \tag{26}$$

where $\phi(\mu r)$ is the potential for positive ion of nuclear charge Ze with $Z-1$ electrons. Although $V_0(r)$ and $V_F(r)$ have the same correct limiting behavior $\lim_{r\to 0}[rV] = Ze$, and $\lim_{r\to 0}[V] = e/r$, they differ appreciably, especially in the region $r = r_0$. This may account for the rather unsatisfactory calculated results based on the use of $V_0(r)$ in the early work [7], as pointed out by Wu [3].

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