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ANALYTIC PROPERTIES OF THE RELATIVISTIC THOMAS-FERMI EQUATION AND THE TOTAL ENERGY OF ATOMIC IONS *

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ABSTRACT

The analytic properties of solutions of the relativistic Thomas-Fermi equation which tend to zero at infinity are first examined, the neutral atom solution being a member of this class. A new length is shown to enter the theory, proportional to the square root of the fine structure constant.

This information is used to develop a perturbation expansion around the neutral atom solution, corresponding to positive atomic ions with finite but large radii. The limiting law relating ionic radius to the degree of ionization is thereby displayed in functional form, and solved explicitly to lowest order in the fine structure constant.

To embrace this knowledge of heavy positive ions, as well as results from the one-electron Dirac equation, a proposal is then advanced as to the analytic form of the relativistic total energy $E(Z,N)$ of an atomic ion with nuclear charge Ze and total number of electrons N. The fact that, for $N > 1$, the nucleus is known only to bind $Z+n$ electrons, where n is 1 or 2, indicates non-analyticity in the complex Z plane, represented by a circle of radius $Z \sim N$. Such non-analyticity is also a property of the non-relativistic energy derived from the many-electron Schrödinger equation. The relativistic theory, however, must also embody a second type of non-analyticity associated with the known property for $N = 1$ that the Dirac equation predicts electron-positron pair production when the electronic binding energy becomes equal to twice the electron rest mass energy. This corresponds to a second circle of non-analyticity in $E(Z,N)$, and hence to a Taylor-Laurent expansion of this quantity in the atomic number Z. The relation of this expansion to the Layzer-Bahcall series is finally discussed.

1. INTRODUCTION

It is fair to say that the properties of heavy positive atomic ions are well understood on the basis of the many-electron Schrödinger equation, which provides a satisfactory framework for a non-relativistic atomic theory. A central approach in this theory is provided by the so-called 1/Z expansion, Z being the atomic number. This expansion had its origins in the work of Hylleraas [1),2)] and was successfully exploited especially by Layzer [3)] and a number of later workers [4),5)]. Explicitly, one writes for the total energy E(Z,N) of an atomic ion with N electrons:

$$E(Z,N) = Z^2 \sum_{n=0}^{\infty} \epsilon_n Z^{-n} \qquad (1.1)$$

where the coefficients $\epsilon_n(N)$ are by now known to useful numerical accuracy for small n over a range corresponding to $N \lesssim 20$. Furthermore, as shown by March and White [6)], the asymptotic form of $\epsilon_n(N)$ for large N can be established from the Thomas-Fermi statistical theory; the later work of Dmietrieva and Plindov [7)], and of Tal and Levy [8)] pressing this point of view fully quantitatively for small n. Very recently, following work of Stillinger [9)] on the He-like ions with N = 2, we have shown from the known expansion of the Thomas-Fermi energy E(Z,N) about the neutral atom limit E(Z,Z) that the radius of convergence of the series (1.1) and its associated non-analyticity in the Z variable can be discussed quantitively in the limit of Z and N both large and $N/Z \leq 1$. [10)]

That some problems arise when one seeks the generalization of Eq.(1.1) within a fully relativistic framework has been clear for quite some time. In particular, the work of Layzer and Bahcall [11)] has been subjected to some criticism, for example by Ermolaev and Jones [12)], though the Layzer-Bahcall approach seems a plausible physical extension of Eq.(1.1) to include an expansion also in the fine structure constant $\alpha = e^2/\hbar c$. Thus, in the present paper, we shall attempt, on the basis of reasonable postulates, to effect an extension of the series (1.1) to take full account of the requirements of special relativity. Why such postulates are necessary is because we do not have at present a satisfactory relativistic theory for many interacting electrons [13)].

The outline of the paper is as follows. In Sec.II, we focus our attention immediately on the analytic properties of the solutions of the relativistic Thomas-Fermi theory [14),15)], relevant of course to the calculation of the

relativistic total energy E(Z,N) of heavy positive ions and neutral atoms [16),17)]. One important result that quickly emerges there is that the fine structure constant entering the Thomas-Fermi theory leads to the existence of a new length in this treatment, proportional to the square root of the fine structure constant. In Sec.III, the properties of the neutral atom solution are used to develop a perturbation method for positive atomic ions with large classical radius, which allows the functional form of the relation between degree of ionization $q = 1 - N/Z$ and classical radius to be established. To exemplify this functional relation, specific results are then presented to lowest order in the fine structure constant. In Sec.IV we briefly review the relation between our results for heavy positive ions and the predictions of the Dirac equation for N = 1. This discussion leads us, in Sec.V, to advance a proposal for an expansion of Laurent form in the atomic number Z, on the basis of two, physically based, postulates which in turn define the analyticity of E(Z,N) in the complex plane for atomic ions in relativistic theory. The relation of this Laurent expansion to the Layzer-Bahcall series is then established. Sec.VI constitutes a summary, with some suggestions as to the way in which future work might enable the present proposals to be confirmed or, if necessary, refined. In the appendices, some detailed mathematical investigation of specific solutions of the relativistic Thomas-Fermi theory are presented.

II. ANALYTIC PROPERTIES OF SOLUTIONS OF RELATIVISTIC THOMAS-FERMI EQUATION

In the Thomas-Fermi theory [18)], the self-consistent potential distribution in an atomic ion is determined by the solutions of the dimensionless Thomas-Fermi equation

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \qquad (2.1)$$

where the distance r from the atomic nucleus of charge Ze is measured by

$$r = bx \; ; \quad b = 0.88534\, a_0/Z^{1/3} \qquad (2.2)$$

with a_0 the Bohr radius $h^2/4\pi^2me^2$. The dimensionless quantity ϕ is converted to a self-consistent potential energy (relative to the chemical potential μ), by multiplying ϕ by $-Ze^2/r$.

When the requirements of special relativity are embodied into the Thomas-Fermi statistical theory, Eq.(2.1) is generalized to [14),15),18)]

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}\left(1 + \frac{\lambda\phi}{x}\right)^{3/2} \qquad (2.3)$$

where

$$\lambda = (4/3\pi)^{2/3}\alpha^2 Z^{4/3} \qquad (2.4)$$

In this section, we shall investigate the analytic properties of the solutions of Eq.(2.3) which tend to zero at infinity. The corresponding solutions of Eq.(2.1), given by Coulson and March [19)], can be expressed in the form

$$\phi(x) = \frac{144}{x^3}\left(1 - \frac{F_1}{x^c} + \frac{F_2}{x^{2c}} - \frac{F_3}{x^{3c}} + \cdots\right) \qquad (2.5)$$

where

$$c = (73^{1/2} - 7)/2 = 0.772 \quad , \qquad (2.6)$$

while $F_n = f_n F_1^n$, the numbers f_n being tabulated for $n \leq 10$. [20)] The Sommerfeld [21)] exact solution $144/x^3$, corresponding evidently to $F_1 = 0$ in Eq.(2.5), divides the $(\phi$-$x)$ plane into two regions; that below this Sommerfeld solution corresponding to positive F_1, and that above to negative F_1 as discussed by one of us elsewhere [22)]. Our first task below is to establish, for the relativistic Thomas-Fermi equation (2.3), that solution which effects the generalization of the Sommerfeld exact solution $144/x^3$, with asymptote corresponding to $x = 0$, to include the fine structure constant, reflected by $\lambda \neq 0$ in Eq.(2.3).

2.1 Generalization of Sommerfeld solution to include the fine structure constant

To effect this generalization, it will be useful to gain orientation as to the types of solution of Eq.(2.3) which tend to zero as x tends to infinity, by presenting a solution to first order in λ using, essentially, perturbation theory on the Sommerfeld solution $144/x^3$. To do this, we merely rewrite Eq.(2.3) first as an equation expressing the constancy of λ in space, namely

$$\lambda = \frac{x^2}{\phi^2}\left(\frac{\phi''}{x}\right)^{2/3} - \frac{x}{\phi} \quad . \qquad (2.7)$$

This Eq.(2.7) can clearly be re-expressed by the simultaneous differential equations for $\phi(\lambda,x)$ and, say $h(\lambda,x)$, given by

$$\left(\frac{x}{\phi}\right)\left[\left(\frac{\phi''}{x}\right)^{1/3} - \left(\frac{\phi}{x}\right)^{1/2}\right] = \frac{\lambda}{h(\lambda,x)} \qquad (2.8)$$

and

$$\left(\frac{x}{\phi}\right)\left[\left(\frac{\phi''}{x}\right)^{1/3} + \left(\frac{\phi}{x}\right)^{1/2}\right] = h(\lambda,x) \quad . \qquad (2.9)$$

Clearly, by substituting the Sommerfeld solution $144/x^3$ into Eq.(2.9) we obtain almost immediately

$$h(0,x) = x^2/6 \qquad (2.10)$$

and from this 'non-relativistic' approximation to h inserted into the right-hand side of Eq.(2.8) we can integrate to find the first-order perturbation solution to Eq.(2.3) as

$$\phi(\lambda,x) = \frac{144}{x^3}\left(1 + a_1\frac{\lambda}{x^4} + \cdots\right) \qquad (2.11)$$

where $a_1 = 3.12^3/76$. This solution for $\phi(\lambda,x)$ is developed systematically for the coefficients a_n in Appx1. We merely note here that (i) $\phi(\lambda,x) = (144/x^3)\, f(\lambda/x^4)$, and that $f(s)$ has a simple pole at a critical value s_c say, which in order of magnitude is about 10^{-2}. This evidently corresponds to a critical length $r_c = b\, x_c$ where

$$x_c = \text{constant}\ \lambda^{1/4}; \quad \text{constant} = 2.9045 \qquad (2.12)$$

yielding $r_c = 2.229\, a_0^{1/2}\, a_0 \approx 0.190\, a_0$. In Fig.1, the non-relativistic situation is compared and contrasted with the relativistic situation. From this figure, it can be concluded that, from the point of view of analytic properties, the non-zero fine structure constant results in the analogue of

the Sommerfeld solution $144/x^3$ of Eq.(2.1) having its asymptote at non-zero x, namely $x_c \propto \lambda^{1/4} \propto a^{1/2}$. This new 'length', we stress, is a fundamental mathematical property of the solution of the relativistic Thomas-Fermi equation (2.3).

In the next section, we use the knowledge of f(s), set out fully in Appx.1, to generate what is the relativistic analogue of (i) the Coulson-March solution (2.5) of Eq.(2.1) to include relativity, and (ii) the perturbation theory on this zeroth order neutral atom-type solution to treat positive ions with weak degree of ionization, i.e. with small q.

It is important, in concluding this section, to note that it is not physically significant to solve Eq.(2.3), in contrast to (2.1), for a point nucleus, as the electron density is not integrable [14)-17)]. This question of the (presumably weak) dependence of E(Z,N) on the choice of (a) nuclear radius and (b) the detailed model adopted for the proton distribution, will be discussed a little further later in the paper. For the present, however, we turn to discuss the relevance of the above generalization of the Sommerfeld solution to the determination of the self-consistent potential distribution in neutral atoms and positive ions in the relativistic Thomas-Fermi theory. Since numerical solutions are already available [17)], our purpose below is solely to clarify the analytic nature and functional dependence of these potential distributions reflected through $\phi(\lambda,x)$ satisfying Eq.(2.1).

III. ANALYTIC FORM OF SOLUTION OF RELATIVISTIC THOMAS-FERMI EQUATION FOR NEUTRAL ATOMS AND WEAKLY IONIZED SYSTEMS

We can show, with little difficulty, that the analogue of the Coulson-March solution (2.5) corresponding to $\lambda = 0$ has the form

$$\phi(\lambda,x) = \frac{144}{x^3} f(\lambda/x^4) \left(1 - \frac{F_1}{x^c} + \cdots\right) \tag{3.1}$$

whereas the series inside the final parenthesis in Eq.(3.1) has only non-integral inverse powers in Eq.(2.5). The non-zero value of λ in Eq.(2.3) will eventually introduce integral inverse powers of x into Eq.(3.1), but this will only occur at order $1/x^4$ and we need not go into detail for our present purposes.

Experience in relating q and the classical ionic radius x_0 in the non-relativistic case, using the positive ion boundary conditions

$$\phi(x_0) = 0 \tag{3.2}$$

$$x_0\phi'(x_0) = -q \tag{3.3}$$

leading to

$$qx_0^2 = 144\,(7 + c) \tag{3.4}$$

prompts us to write for the relativistic case, with ϕ_0 denoting the neutral atom solution:

$$\phi(\lambda,x) = \phi_0(\lambda,x) + k\eta \quad , \tag{3.5}$$

where $k\eta$ is to be treated as a perturbation on ϕ_0. Then in the non-relativistic case, η is found to satisfy the differential equation

$$\eta'' = \frac{3}{2}\left(\frac{\phi_0}{x}\right)^{1/2}\eta \quad . \tag{3.6}$$

For weak ionization, i.e. sufficiently small q, it is adequate in lowest order to impose the boundary conditions (3.2) and (3.3) after replacing ϕ_0 by the Sommerfeld solution $144/x^3$. Then one finds from Eq.(3.6) that

$$\eta \propto x^{4+x} \quad ; \text{ large x, small q} \tag{3.7}$$

and hence for the relativistic analogue we shall write

$$\phi(\lambda,x) = \frac{144}{x^3} f(\lambda/x^4) + k\,x^{4+c}\, g(\lambda/x^4) \; ; \tag{3.8}$$

f(0) and g(0) both being equal to unity.

In Appx.1 we set out an explicit perturbation equation relating g and f, without treating λ perturbatively, and imposing the boundary conditions we can generalize the limiting law (3.4) to read

$$G(\lambda/x_0^4) = qx_0^3 - 144\,(7 + c) \quad . \tag{3.9}$$

The function G is briefly considered in Appx.1, where it is shown that to first order in λ

$$G(\lambda/x_0^4) = \frac{2^{11}\cdot 3^5}{19\, x_0^4}\,\lambda\left[\frac{3c-25}{2c+3}\right] \tag{3.10}$$

which exemplifies the functional dependence in Eq.(3.8) through the explicit perturbative solution

$$qx_0^3 = 144\,(7+c) - 130756.6\,\frac{\lambda}{x_0} + \ldots \tag{3.11}$$

Should it prove of interest later, it will plainly be possible to (a) integrate Eq.(A1.2) for $f(s)$ numerically and (b) to use this numerical determination of $f(s)$ to numerically integrate Eq.(A1.13) for $g(s)$. For our present purposes the important conclusions are (i) the limiting length $x_c \propto \lambda^{1/4}$ and the new limiting law having the functional form (3.9), exemplified perturbatively in the explicit form (3.11).

Having established these properties of heavy atoms and positive ions from the relativistic Thomas-Fermi theory, the remainder of the paper is concerned with the way we might use them, in conjunction with the supposedly exact results from Dirac's one-electron equation, to advance a definite proposal as to the analytic structure in the (now complex) variable Z of the relativistic total energy $E(Z,N)$. Before doing so, we must summarize some results for $N = 1$ briefly in the following section.

IV. CONSEQUENCES FOR TOTAL RELATIVISTIC ENERGY E(Z,N) OF RESULTS FOR DIRAC EQUATION FOR N = 1

Here we take as a starting point the Dirac relativistic wave equation for one electron. The energy of the 1s level, which is $mc^2\,(1-Z^2\alpha^2)^{1/2}$ for a point nucleus, clearly vanishes at $Z_c = 137$ and becomes imaginary for larger Z.

The situation is changed when one treats a finite nucleus. As discussed, for example, by Zel'dovich and Popov [23], for non-zero nuclear radius R, each energy level changes continuously with increasing Z from mc^2 to $-mc^2$. The energy then becomes complex if Z is further increased.

In particular, for physival values of R, the critical value Z_c at which the 1s level merges into the lower continuum is around 170. This property that the energy levels change continuously until the lower continuum is reached is a characteristic of the long-range of the Coulomb potential.

We note here that the above behaviour of the energy is not unique to spin 1/2 Fermi particles; a similar situation obtains with the Klein-Gordon equation for particles with zero spin [24]. With bosons, however, further considerations involving Bose condensation change the physical picture [25),27] considerably. These remarks are especially relevant below since the relativistic Thomas-Fermi theory includes, of course, the Pauli Exclusion Principle but does not treat the kinetic energy operator in the manner characteristic of the Dirac theory.

The main point to be stressed here is that for very small R, there will plainly be non-analytic behaviour of the one-electron energy, reflected in the appearance of a term involving $\ln R$. The considerations of Zel'dovich and Popov [23] relate the Dirac level spectrum for $R = 0$ to the physically realistic case of finite nuclear radius. Though their work is specifically for $N = 1$, we shall see below that for large Z and N it is also essential to treat a finite nuclear radius.

V. TAYLOR-LAURENT EXPANSION OF TOTAL ENERGY E(Z,N) IN RELATIVISTIC ATOMIC THEORY

In this section we shall, on the basis of two postulates, develop a Taylor-Laurent expansion of the total energy $E(Z,N)$ of relativistic atomic ions in the complex Z plane.

The two basic postulates on which we found such an expansion are: (i) that there is a circle of non-analyticity in the complex Z plane which reflects the established fact that, for $N \geq 1$, it is not possible to bind to a nucleus of charge Ze more than one or at most two electrons beyond the neutral atom.

This circle of non-analyticity exists, therefore, for $Z \sim N$, and is not specifically, in fact, a consequence of special relativity; it is already present for the non-relativistic expansion (1.1). It is evidenced, for example, in the work of Stillinger [9] for two-electron ions treated by non-relativistic Schrödinger wave mechanics, and in our own work [10] on the non-relativistic theory for large Z and N in the limit $N/Z \lesssim 1$.

(ii) That, now specifically associated with special relativity, there is a second circle of non-analyticity in the complex Z plane.

The physical significance of such a singularity with $R \neq 0$ is that the nature of the 1s level changes from a true localized bound state to a vacuum polarization as the 1s level passes through the lower continuum, corresponding to Z, taking its critical value Z_c. This criterion is quite equivalent to that obtained by equating the electronic binding energy for one electron to $2mc^2$, the energy required to create an electron-positron pair.

This then is the basis of the postulate (ii); in the absence of a full relativistic theory of N interacting electrons, it is presently not possible to give more than a plausible physical basis for adopting such a postulate. In the end, of course, its validity or otherwise must rest on bringing its consequences into contact with experiment.

These two postulates (i) and (ii) above then lead, quite naturally, to a basic expansion for the total energy E(Z,N) in relativistic atomic theory.

5.1 Taylor-Laurent expansion related to that of Layzer and Bahcall

Fig.2 for $N > 1$ shows schematically the consequences of the postulates (i) and (ii) above. The circle labelled (ii) is a result, as we stressed, of the requirements of special relativity; we know that this circle must move away to infinity, for all N greater than or equal to unity, in the non-relativistic limit in which the fine structure constant α tends to zero. In contrast, the circle labelled (i) is present even in non-relativistic theory, and we know about its movement with varying N in non-relativistic theory from the work of Refs.9 and 10.

It follows, by referring to Fig.2, with the assumption that E(Z,N) is analytic in the shaded region between the circles (i) and (ii), that we can write the Taylor-Laurent expansion

$$E(Z,N,\alpha,R) = Z^2 \sum_{n=-\infty}^{\infty} \epsilon_n(N,\alpha,R) Z^{-n} \quad . \qquad (5.1)$$

In contrast to Eq.(1.1), which corresponds to analyticity of E(Z,N) in the shaded region of Fig.2(a), Eq.(5.1) involves both positive and negative powers of Z, and in addition non-zero values of α and R. Clearly $\epsilon_n(N,\alpha,R)$,

as we let first $\alpha \to 0$ and then R tends to zero, must reduce to the coefficient ϵ_n in Eq.(1.1) for n positive, and to zero for n negative.

From our previous discussion, for the special case $N = 1$, the coefficients $\epsilon_n(1,\alpha,R)$ are all zero for n positive. In the limit of large Z and N, the relativistic Thomas-Fermi theory can be brought into formal contact with Eq.(5.1) as discussed previously by Marconi and March [16].

However, our main purpose below is to demonstrate that Eq.(5.1) embraces the Layzer-Bahcall expansion

$$E_{LB}(Z,N) = Z^2 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} E_{nm}(N) \epsilon^m Z^{-n} \qquad (5.2)$$

with $\epsilon = \alpha^2 Z^2$. As written in Eq.(5.2), the coefficients $E_{nm}(N)$ also have a weak dependence on ϵZ in the Layzer-Bahcall formulation.

First of all, with neglect of this dependence of $E_{nm}(N)$ on ϵZ, Eq.(5.2) can readily be rearranged to take the form (5.1), the coefficients $\epsilon_n(N,\alpha,R)$ taking the form

$$\epsilon_{n=2p} = \sum_{t \geq \max[p,0]} E_{2t,-p+t}(N) \alpha^{2(t-p)} \qquad (5.3)$$

which is plainly valid for even n since p and t are integers or 0. For odd n we have the result

$$\epsilon_{n=2p+1} = \sum_{t \geq \max[p,0]} E_{2t+1,-p+t} \alpha^{2(t-p)} \quad . \qquad (5.4)$$

In Eqs.(5.3) and (5.4), the notation max [a,b] means the larger of a and b.

Returning at this point to the relativistic Thomas-Fermi theory, Marconi and March [16] demonstrate that this corresponds, for large N, to the coefficient $E_{nm}(N) \sim c^0_{nm}(N)^{n-\frac{2m}{3}-\frac{1}{3}}$ which clearly again relates, through Eqs.(5.3) and (5.4), with the series (5.1).

VI. SUMMARY AND FUTURE DIRECTIONS

The main proposal of the present paper is embodied in the Taylor-Laurent expansion (5.1). This followed an investigation of the analytic properties of the solutions tending to zero at infinity of the relativistic Thomas-Fermi equation, which are shown schematically in Fig.1. This, synthesized with the Dirac equation results for $N = 1$ led to the schematic form of $E(Z,N)$ in the complex plane implied by Fig.2. We have stressed that the existence of Eq.(5.1), as well as the correctness of Fig.2, is strongly favoured by physical arguments; namely the inability of a nucleus of charge Ze, for $N > 1$, to bind more than one or at most two states beyond the neutral atom. That is, it is the instability of negative ions in nature beyond singly and doubled charged states which is the essential physics underlying the existence of the circle labelled (i) in Fig.2. Secondly, we have argued from the Dirac ground state energy for $N = 1$ for the presence of the second non-analyticity reflected by circle (ii) in Fig.2. That this circle is sensitive to the non-zero nuclear radius is clear from the Dirac theory.

These postulates are then shown to embrace the Layzer-Bahcall expansion and, in our view, render the objections that have been voiced against it much less compelling than they have appeared to be hitherto. Experiments, for $N > 1$ and for various values of Z, will be of the essence in either confirming the postulates (i) and (ii) of this paper, or in indicating the directions in which these postulates may eventually need refining.

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APPENDIX 1

Solutions of relativistic Thomas-Fermi equation which tend to zero at infinity, and also for large radii positive ions.

If in Eq.(2.3) we write $x^3\phi$ as a new dependent variable, we are led to a differential equation solely dependent on the quantity $\lambda/x^4 = s$, which confirms the scaling property which one would infer from the series (2.11). As there, we choose to write explicitly

$$\phi = \frac{144}{x^3} f(s) \quad : \quad s = \lambda/x^4 \quad , \tag{A1.1}$$

and then we find the differential equation for $f(s)$ as

$$4s^2 f'' + 11sf' + 3f = 3f^{3/2} [1 + 144fs]^{3/2} \quad . \tag{A1.2}$$

We wish to solve this equation such that $f(s)$ reduces to the Sommerfeld exact solution of Eq.(2.1), namely $144/x^3$, in the limit λ tends to zero, i.e. $s = 0$. This solution has the small s expansion given in Eq.(2.1) and our purpose now is (i) to obtain higher terms in that expansion and (ii) to investigate the singular point of this solution $f(s)$.

Systematic determination of small s expansion of $f(s)$

From Eq.(2.11), a convenient independent variable is $a_1\lambda/x^4 \equiv a_1 s = t$ say. Then $f(s) \to F(t)$ and we seek the series solution

$$F(t) = \sum_{n=0}^{\infty} f_n t^n \tag{A1.3}$$

and substituting this in Eq.(A1.2) leads to a recurrence relation for the coefficients f_n. From Eq.(2.11) it is already clear that $f_0 = f_1 = 1$. For $n > 1$, the recurrence relation can be expressed in the form

$$f_n = \frac{6}{8n^2 + 14n - 3} H_n \quad , \tag{A1.4}$$

where, in terms of the binomial coefficients b_n given by

$$b_n = \binom{3/2}{n} = \frac{\Gamma(5/2)}{\Gamma(5/2-n)\,\Gamma(n+1)} \qquad \text{(A1.5)}$$

H_n has the form

$$H_n = b_1 \tilde{D}^1_{n-1} + \sum_{K=0}^{n-2} b_{n-K} D^{n-K}_K \quad : \quad n \geq 2 \qquad \text{(A1.6)}$$

Here

$$D^1_k = \frac{19}{9} \sum_{\ell=0}^{K} f_\ell f_{K-1} + \frac{1}{K c_0} \sum_{p=1}^{k-1} (K-2p) c_{K-p} D^1_p \qquad \text{(A1.7)}$$

and

$$D^n_k = \frac{1}{K c_0} \sum_{p=0}^{K-1} \left[(K-p)^n - p \right] c_{K-p} D^n_p \,, \quad n \geq 1 \,, \; K \geq 1 \qquad \text{(A1.8)}$$

where $D^n_0 = (c_0)^n$ and $D^0_k = \delta_{k0}$. Finally c_m is defined by

$$c_m = f_{m+1} + \frac{19}{9} \sum_{\ell=0}^{m} f_\ell f_{m-\ell} \qquad \text{(A1.9)}$$

From these results, we find explicitly the coefficients recorded in Table A1.1.

Expansion of f(s) around singular point

Having established the small s expansion of f(s), we next turn to a study of its behaviour around its singular point. We assume this to occur at $s = s_c$ and write, for $s \lesssim s_c$:

$$f(s) \sim \frac{A}{(s_c - s)^\gamma} \,. \qquad \text{(A1.10)}$$

Substituting this expression (A1.10) into Eq.(A1.2) we find the results:

$$\gamma = 1 \quad ; \quad A = s_c^{1/4} / 18.2^{1/2} \,. \qquad \text{(A1.11)}$$

Of course, the determination of s_c is only possible exactly by joining f(s) in Eq.(A1.10), valid near s_c, with the small s expansion. This will eventually require a numerical integration of Eq.(A1.2), but fortunately, as we shall see below, the singular behaviour determined by Eqs.(A1.10) and (A1.11) is already in evidence in the higher coefficients of the small s expansion.

To demonstrate this, we use the data in Table A1.1 to find the ratio $f_n/f_{n+1} \equiv R_n$, for $n \gtrsim 4$ say. R_n, even at $n = 4$, has already reached a limiting value of 0.958. At the largest values of n in Table A1.1 R_n has reached the limit 0.95838. Thus, from a well-known convergence property, the singular point, t_c say, of F(t) is given by

$$t_c = 0.95838 \quad ; \quad s_c = 0.014050 \qquad \text{(A1.12)}$$

which leads directly to Eq.(2.12) of the main text. This leads from Eq.(A1.11) to a value A = 0.013525 and hence we have settled the values of γ, s_c and A in Eq.(A1.10) to the accuracy specified above. It is of some interest to note that, if we write from Eq.(2.11) that $f_1 = 1 + a_1 s + \ldots = (1 - a_1 s)^{-1}$ then $a_1 \doteq s_c^{-1} = A^{-1}$, confirming that A and S_c are nearly equal, as demonstrated numerically above. Thus, f(s) is already determined to useful accuracy, without explicit numerical integration of the differential Eq.(A1.12).

Perturbation expansion about neutral atom solution

In Eq.(3.1) the above exact solution is used to construct an asymptotic solution of Eq.(2.3) tending to zero at infinity and valid at sufficiently large x. Our object in this section is to develop a perturbation expansion about that solution of the form (3.1) corresponding to the neutral atom. As discussed in the main text, this leads to $\phi(\lambda,x)$ expanded as in Eq.(3.7).

Therefore, we need a perturbation differential equation to determine the function $g(s)$, given the above knowledge of $f(s)$. This equation is found to take the form

$$s^2 g'' - (6+4c)s g' + (1+\tfrac{c}{4})(6+2c) g = 3\frac{g}{f}\left[4s^2 f'' + 11 s f' + 3f\right]\left[1 + \frac{144 s f}{1+144 s f}\right] . \tag{A1.13}$$

This equation will eventually require numerical integration, with $f(s)$ as input data, to determine $g(\lambda/x^4)$ in Eq.(3.8). Below we will content ourselves with the low order term in the series solution in s of $g(s)$, which will allow the determination of the function $G(\lambda/x_0^4)$ in Eq.(3.9) to lowest order in λ. Writing

$$g(s) = \sum_{n=0}^{\infty} g_n s^n \tag{A1.14}$$

we find g_1, by using the series in (2.11) for $f(s)$ as

$$\left[\frac{5}{2} - \frac{c}{2} - 9\right] g_1 = 3\left[144 + 11 a_1\right]$$

or

$$g_1 = -\frac{50976}{19(4c+6)} = 295.3184 . \tag{A1.15}$$

Using the boundary condition (3.2), we can write, before expanding f and g

$$-k = \frac{144}{x_0^{7+c}} \frac{f(\lambda/x_0^4)}{g(\lambda/x_0^4)} \tag{A1.16}$$

and imposing Eq.(3.3) we obtain further

$$G(\lambda/x_0^4) = 144 \frac{\lambda}{x_0^4}\left[4 f' - 4 \frac{f g'}{g}\right] + (7+c)144(f-1) = g x_0^3 - (7+c)144 \tag{A1.17}$$

which reduces to Eq.(3.4) for $\lambda = 0$. This equation demonstrates that its right-hand side is solely a function of λ/x_0^4 as expressed by Eq.(3.9) of the text. We now use the results

$$f'(s=0) = a_1 \quad ; \quad g'(s=0) = g_1 \tag{A1.18}$$

in Eq.(A1.17) to obtain Eq.(3.10).

Table A1.1

Explicit coefficients f_n for $n \leq 13$ in series solution (A1.3)

$f_0 = 1$ $\qquad$ $f_1 = 1$

$f_2 = \frac{538}{513}$ $\qquad$ $f_3 = \frac{4482296}{4099896}$

$f_4 = \frac{6033405354}{5287328379}$

Further coefficients have been obtained to the numerical accuracy given below:

$f_6 = 1.242296$ $\qquad$ $f_5 = 1.190519$

$f_8 = 1.352519$ $\qquad$ $f_7 = 1.296202$

$f_{10} = 1.472533$ $\qquad$ $f_9 = 1.411235$

$f_{12} = 1.603200$ $\qquad$ $f_{11} = 1.536469$

$f_{13} = 1.672814$

APPENDIX 2

Thomas-Fermi theory for non-zero nuclear radius

In this appendix, the effect of non-zero radius on the Thomas-Fermi theory of neutral atoms will be briefly considered.

Non-relativistic case

Starting with the non-relativistic case, we shall refer to two models:

(A) the protons are uniformly distributed within the nuclear radius R, and

(B) the less realistic model in which the total proton charge is uniformly smeared over the surface of a sphere of radius R.

Model (B)

From the work of one of us [22], on a model of almost spherical molecules like CH_4, we can adapt the results to the finite nucleus case to obtain the electronic energy E(Z,R) in the form

$$E(Z,R) = \frac{3}{7} Z V_1(R) + \frac{1}{7} Z R V_1'(R) - \frac{3}{7} \frac{Z^2 e^2}{R} \qquad (A2.1)$$

where $V_1 = -e\chi_1$, χ_1 being the total electrostatic potential inside R. Using the continuity of the nuclear electrostatic potential at R we find

$$E(Z,R) = \frac{3}{7} Z V_{1e}(R) + \frac{1}{7} Z R V_1'(R) \qquad (A2.2)$$

where the subscript e denotes the electronic contribution to V_1. As $R \to 0$ the second term on the right-hand side vanishes. No difficulty arises therefore in taking the limit $R \to 0$, by means of which we regain the well-known total energy of the neutral atom in the Thomas-Fermi theory [18].

Model (A)

Here the potential energy due to the proton distribution felt by an electron is quadratic in the distance r from the centre of the nucleus. With the appropriate scaling from V to ϕ, this term has simply to be added to the right-hand side of Eq.(2.1). Though, to our knowledge, the resulting self-

consistent solutions have not, so far, been obtained numerically by matching across the nuclear radius, we have no reason to expect more than minor quantitative changes from the conclusions drawn from the model (B) above.

In summary, this argument shows that the coefficients $\epsilon_n(N)$ in Eq.(1.1) will not vary in any important manner in non-relativistic heavy positive ions as the nuclear radius is increased from zero to its known value.

Relativistic results for bare Coulomb case

Though Hill et al. [17] have solved the relativistic Thomas-Fermi equation for model (A) numerically and have thereby calculated the total energy, we have not, so far, been able to make purely analytical progress. Therefore, below, we content ourselves with the study of the relativistic Thomas-Fermi electron density $\rho(r)$ given by

$$\rho = \text{constant} \left\{ \frac{(\mu - V)^2}{2mc^2} + \mu - V \right\}^{3/2} \qquad (A2.3)$$

where the constant is $(2m)^{3/2}\,(8\pi/3h^3)$, with

$$\left.\begin{aligned} V(r) &= -Ze^2/R && r < R \\ &= -Ze^2/r && r > R \end{aligned}\right\} . \qquad (A2.4)$$

This will lead to a non-self-consistent solution of Model (B).

Our aim is to study the non-analytic behaviour of the chemical potential, or equivalently the classical radius R_0 corresponding to $\rho(R_0) = 0$, i.e.

$$\mu = -Ze^2/R_0 \quad . \qquad (A2.5)$$

We notice that, as the nuclear radius $R \to 0$, $R/R_0 \to$ finite constant, D say. The leading non-analytic terms for D small then yield

$$D = \exp\left(-\frac{3\pi}{4}\frac{1}{Z^2\alpha^3}\right) \equiv \exp\left(-1/\lambda^{3/2}\right) \qquad (A2.6)$$

or

$$\mu = -\frac{Ze^2}{R}\exp\left(-1/\lambda^{3/2}\right) \quad . \qquad (A2.7)$$

displaying the fact that in relativistic Thomas-Fermi theory the non-zero nuclear radius is playing an essential role, in sharp contrast to the non-relativistic case discussed above.

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FIGURE CAPTIONS

Fig.1 Shows schematic form of solutions of Thomas-Fermi equations for (a) non-relativistic case, i.e. $\phi(0,x)$ and (b) relativistic case $\phi(\lambda,x)$.

In (a), the Sommerfeld exact solution of Eq.(2.1) divides the (ϕ,x) plane into two parts. The part where $\phi(x)$ is always below $144/x^3$ includes as a special case the neutral atom solution in which one has the second boundary condition $\phi(0,x = 0) = 1$ for a point nucleus. In case (b), the curve $(144/x^3)\, f(\lambda/x^4)$ has its asymptote at non-zero x, labelled x_c, which is proportional to $\lambda^{1/4}$. This reduces to the Sommerfeld solution $144/x^3$ in the limit λ tends to zero. There is therefore a length in relativistic Thomas-Fermi theory which is not in evidence in the non-relativistic limit. The neutral atom solution, now for a finite nucleus, in order to obtain a normalizable electron density, corresponds to a solution in which $\phi(\lambda,x)$ lies below the generalized Sommerfeld solution labelled $(144/x^3)\, f(\lambda/x^4)$.

Fig.2 Shows nature of singular points of total energy E(Z,N) in complex Z plane for (a) non-relativistic theory and (b) relativistic theory.

In (a), the circle shown at $Z \sim N$ contains a singular point which lies on the real axis. This circle has non-zero radius for all N greater than one and its radius tends precisely to N in the limit as both Z and N tend to infinity. For $N = 1$ such a circle is not present, as a bare Coulomb potential energy $-Ze^2/r$ inserted in the Schrödinger equation has, of course, an infinite number of bound states, for all $Z \neq 0$.

The proposal made in this paper as to the analytic structure of the relativistic energy E(Z,N) is illustrated schematically in Fig.2(b). This again is drawn for $N > 1$; for $N = 1$ there is only one circle, for a finite nucleus, corresponding to the singular behaviour of the Dirac one-electron energy at a value of $Z \sim 170$.

The outer circle (ii) for $N > 1$ reflects this same physical phenomenon, namely the lowest bound state crossing the lower continuum, with increasing Z. To date, the relative movement of the two circles with increasing Z and N is not known. The Taylor-Laurent expansion (5.1) is only valid in the shaded region enclosed between (i) and (ii).

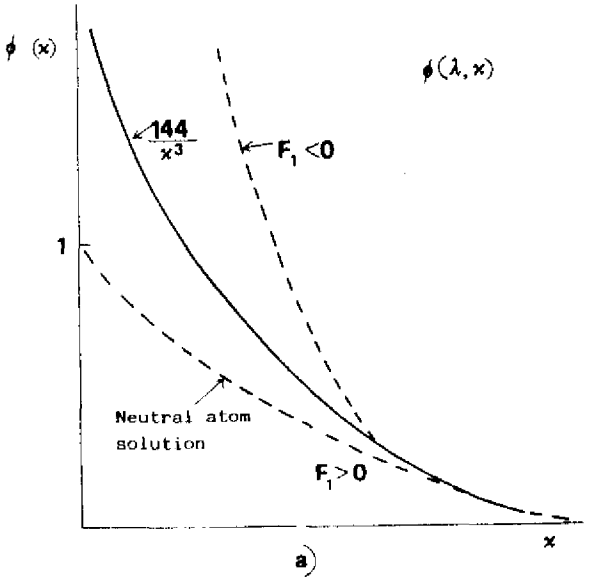

φ (x)
φ(λ, x)
144/x³
F₁ <0
1
Neutral atom solution
F₁ >0
x
a)

Fig.1(a)

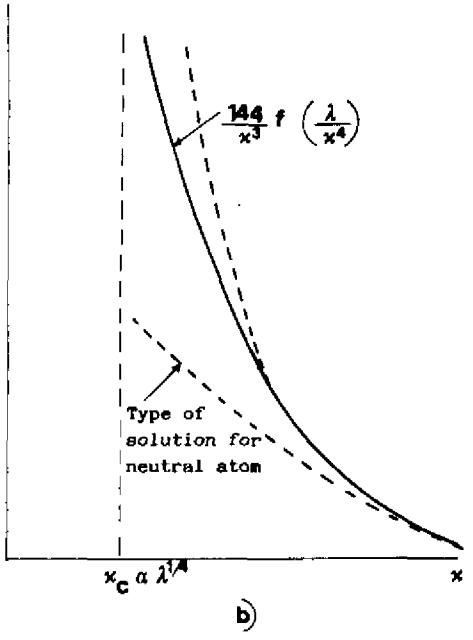
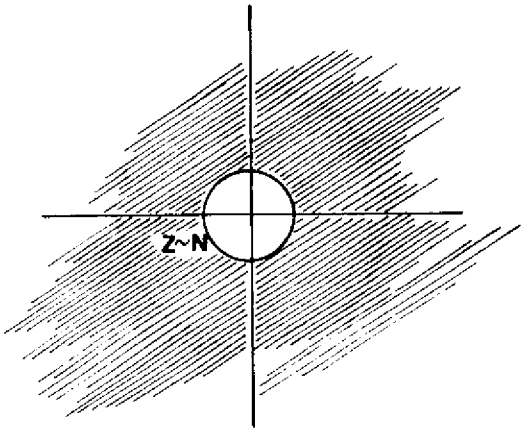
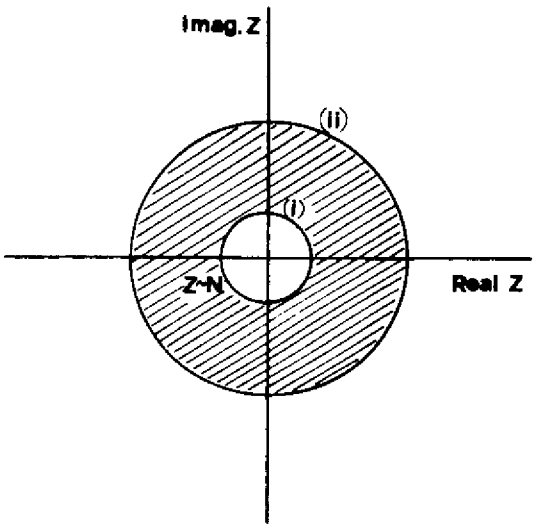

144/x³ f (λ/x⁴)
Type of solution for neutral atom
x_c α λ^1/4
x
b)

Fig.1(b)



a)

Fig.2(a)



b)

Fig.2(b)