

## **Approximate propagator for the radial Dirac problem.**

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### ABSTRACT

Two coupled first order differential equations derived for the atomic central field problem within the relativistic framework are transformed to integral equations through the use of approximate Wentzel-Kramers-Brillouin solutions. It is shown that a finite charge density can be derived for a relativistic form of the Fermi-Thomas atomic model by appropriate attention to the boundary conditions. A numerical solution for the effective nuclear charge in the Xenon atom is calculated and fitted to a rational expression.

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## 1. INTRODUCTION.

Per-Olov Löwdin had a long and lasting interest in the analytical methods of quantum mechanics and my tribute to his legacy involves an application of the Wentzel-Kramers-Brillouin (WKB) asymptotic approximation method. It was the subject of a contribution(1) by Löwdin to the Solid State and Molecular Theory Group created by John C. Slater at the Massachusetts Institute of Technology.

Our esteemed teacher looked with skepticism on the efforts by Yngve Öhrn and myself to make use of propagators but learned to accept and appreciate our results. We offered a derivation of the Fermi-Thomas central field model for atoms through a WKB-approach to the radial propagator in our book(2). I developed an integral equation for the general multichannel scattering problem(3) from the WKB solutions and have nourished a feeling that a similar attack could be used for the relativistic, two component, radial Dirac central field case. This paper delineates such an approach.

The next section establishes the basic formulation and is followed by the transformation to an integral equation form by means of the WKB-type solutions where all terms are retained. It is demonstrated that the quantization condition derives from the reciprocal kernel of the integral equation in the fourth part. There follows a derivation of the electron and energy densities for the relativistic central field model where it is shown that a Fermi-Thomas type screening function can be obtained without the disturbing singularity at the origin by observing proper boundary conditions. An example solution is computed for the Xenon atom and presented in the sixth section. A short review of the attempts towards a relativistic Fermi-Thomas theory concludes this paper.

## 2. PRELIMINARIES.

Condon and Shortley wrote *the* book(4) on atomic theory and I will use their equations for the radial components of the relativistic wave function for an electron in a central field(5). Thus I quote

$$\begin{aligned} -\mu c^2 F(r) + \text{ch} \left( \frac{dG(r)}{dr} + \frac{k}{r} G(r) \right) + U(r)F(r) &= WF(r); \\ +\mu c^2 G(r) - \text{ch} \left( \frac{dF(r)}{dr} - \frac{k}{r} F(r) \right) + U(r)G(r) &= WG(r); \end{aligned} \quad (1)$$

The quantum number  $k$  takes positive and negative integer values, the appropriate electron mass parameter is given by  $\mu$ , the energy parameter is  $W$ , and the central field potential energy is

$$U(r) = -\frac{e^2 Z(r)}{r} \quad (2)$$

where a general screening function is used instead of the pure Coulomb field from Condon and Shortley. The radial amplitudes,  $F$  and  $G$ , are the "small" and "large" components respectively. They define the radial density distribution as

$$\rho(r)dr = \left( |F(r)|^2 + |G(r)|^2 \right) dr \quad (3)$$

and a state has the degeneracy is  $2|k| = 2j + 1$ .

Early applications of WKB approximations to the Coulomb problem in Schrödinger theory demonstrated the necessity and expediency of the Kramers modification(6):

$$l(l+1) \Rightarrow \left( l + \frac{1}{2} \right)^2 \quad (4)$$

It holds that

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$$l = \begin{cases} k, & k > 0 \\ -k-1 & k < 0 \end{cases} \quad (5)$$

so that

$$l(l+1) = k(k+1) \Rightarrow \left(k + \frac{1}{2}\right)^2 \quad (6)$$

is the corresponding replacement for the Dirac case. Thus it is useful to introduce an auxiliary variable through the replacement

$$k = r\kappa(r) - \frac{1}{2} \quad (7)$$

Another substitution serves to simplify the equations. The combination  $W-U$  defines an additional function:

$$h(r) = \frac{1}{c}(W - U(r)) = \frac{1}{c}\left(W + \frac{e^2 Z(r)}{r}\right) \quad (8)$$

Atomic units, where  $\mu$ ,  $\hbar$ , and  $e$  equal unity, will be used. The basic equations will be used in the inhomogeneous form in order to prepare for the Green function formulation:

$$\begin{aligned} [h(r) + c]F(r) - \frac{dG(r)}{dr} - \kappa(r)G(r) &= \Phi(r) - \frac{G(r)}{2r}; \\ \frac{dF(r)}{dr} - \kappa(r)F(r) + [h(r) - c]G(r) &= -\frac{F(r)}{2r} + \Gamma(r); \end{aligned} \quad (9)$$

Notations  $\Phi$  and  $\Gamma$  are used for the source functions. These coupled first order differential equations will be transformed into integral equations with a WKB approach.

### 3.TOWARDS INTEGRAL EQUATIONS.

Approximate solutions to the homogeneous equations on the left-hand side of Eq. (9) are constructed in the WKB manner as

$$\left\{ \begin{array}{l} f^+(r) = \frac{1-i}{2} \left[ \frac{\kappa(r) + ip(r)}{\sqrt{p(r)(h(r)+c)}} \right] \exp[is(r)] \\ g^+(r) = \frac{1-i}{2} \left[ \frac{h(r)+c}{\sqrt{p(r)(h(r)+c)}} \right] \exp[is(r)] \end{array} \right\} \quad (10)$$

$$\left\{ \begin{array}{l} f^-(r) = \frac{1-i}{2} \left[ \frac{\kappa(r) - ip(r)}{\sqrt{p(r)(h(r)+c)}} \right] \exp[-is(r)] \\ g^-(r) = \frac{1-i}{2} \left[ \frac{h(r)+c}{\sqrt{p(r)(h(r)+c)}} \right] \exp[-is(r)] \end{array} \right\}$$

The phase integral  $s(r)$  has the derivative  $p(r)$  and it satisfies the secular equation

$$\left\{ \begin{array}{cc} h(r)+c & -\kappa(r) - ip(r) \\ -\kappa(r) + ip(r) & h(r) - c \end{array} \right\} = h^2(r) - c^2 - \kappa^2(r) - p^2(r) = 0 \quad (11)$$

General complex energy parameters  $W$  will be considered and it is useful to choose the branch of the function  $p(r)$  in the upper part of the complex plane. This means that the phase integral  $s(r)$  has an imaginary part which is increasing with  $r$ . Accordingly it holds that the upper set of functions of Eq. (10) vanish at large values of  $r$  while the lower set go to zero at the origin. The limiting form of  $p(r)$  at small  $r$ -values is seen to be

$$p(r) \xrightarrow{r \rightarrow 0} \frac{i}{r} \sqrt{\left(k + \frac{1}{2}\right)^2 - [Z(0)/c]^2} \quad (12)$$

and we conclude that

$$\left|k + \frac{1}{2}\right| \geq Z(0)/c \quad (13)$$

This relation will prove to be significant later.

Two auxiliary constructs are defined as

$$\begin{aligned} X(r) &= g^+(r)F(r) - f^+(r)G(r); \\ Y(r) &= g^-(r)F(r) - f^-(r)G(r); \end{aligned} \tag{14}$$

The inverse relation is

$$\begin{aligned} F(r) &= f^+(r)Y(r) - f^-(r)X(r); \\ G(r) &= g^+(r)Y(r) - g^-(r)X(r); \end{aligned} \tag{15}$$

and the reason for the rather arbitrary complex factor in Eq. (10) becomes clear. Differentiation of the functions (15) and usage of the basic equations (9) gives, after some algebra with primes indicating derivatives, that

$$\begin{aligned} \frac{dX(r)}{dr} &= g^+(r) \left\{ \frac{h'(r)}{2[h(r)+c]} - \frac{p'(r)}{2p(r)} - \frac{1}{2r} \right\} F(r) \\ &\quad + f^+(r) \left\{ \frac{h'(r)}{2[h(r)+c]} - \frac{p(r)+i\kappa(r)}{p(r)-i\kappa(r)} \left[ \frac{p'(r)}{2p(r)} + \frac{1}{2r} \right] \right\} G(r) \\ &\quad + f^+(r)\Phi(r) + g^+(r)\Gamma(r); \\ \frac{dY(r)}{dr} &= g^-(r) \left\{ \frac{h'(r)}{2[h(r)+c]} - \frac{p'(r)}{2p(r)} - \frac{1}{2r} \right\} F(r) \\ &\quad + f^-(r) \left\{ \frac{h'(r)}{2[h(r)+c]} - \frac{p(r)-i\kappa(r)}{p(r)+i\kappa(r)} \left[ \frac{p'(r)}{2p(r)} + \frac{1}{2r} \right] \right\} G(r) \\ &\quad + f^-(r)\Phi(r) + g^-(r)\Gamma(r); \end{aligned} \tag{16}$$

The significance of the Kramers correction is evident from the form with the logarithmic derivative of  $p(r)$ . Its singularity at the origin is cancelled by the Kramers term. The logarithmic derivative of the function  $c+h(r)$  is small except at the origin and its effect will be neglected here. Essential singularities occur for real energy parameter values at the so-called classical turning points where  $p(r)$  goes through zero. Their treatment lead to the Born-Sommerfeld quantization condition, the subject of the next section.

Boundary conditions requires that

$$X(r) = -\int_r^{\infty} dr' X'(r'); \quad Y(r) = \int_0^r dr' Y'(r'); \quad (17)$$

and combination with Eq. (15) provides the integral equation form

$$\begin{aligned} \begin{bmatrix} F(r) \\ G(r) \end{bmatrix} &= \int dr' \begin{bmatrix} f^+(r_>)f^-(r_<) & f^+(r_>)g^-(r_<) \\ g^+(r_>)f^-(r_<) & g^+(r_>)g^-(r_<) \end{bmatrix} \begin{bmatrix} \Phi(r') \\ \Gamma(r') \end{bmatrix} \\ &+ \int dr' \begin{bmatrix} f^+(r_>)f^-(r_<) & f^+(r_>)g^-(r_<) \\ g^+(r_>)f^-(r_<) & g^+(r_>)g^-(r_<) \end{bmatrix} \begin{bmatrix} 0 & \tilde{n}(r') \\ n(r') & 0 \end{bmatrix} \begin{bmatrix} F(r') \\ G(r') \end{bmatrix} \\ n(r) &= \frac{h'(r)}{2[h(r)+c]} - \frac{p'(r)}{2p(r)} - \frac{1}{2r} \\ r_> &= \max(r, r') \\ r_< &= \min(r, r') \end{aligned} \quad (18)$$

Equation (16) contains the information to relate the function  $\tilde{n}(r)$  to  $n(r)$  and it involves a factor, which changes when  $r'$  equals  $r$ . There seems to be no convenient way to express this in a compact way. Its importance arises in connection with the derivation of the Bohr-Sommerfeld quantization rule.

The matrix kernel in the integral equation (18) defines the zeroth order propagator or Green function for the central field Dirac problem:

$$\mathbf{G}_0(r, r'; W) = \frac{1}{c} \begin{bmatrix} f^+(r_>)f^-(r_<) & f^+(r_>)g^-(r_<) \\ g^+(r_>)f^-(r_<) & g^+(r_>)g^-(r_<) \end{bmatrix} \quad (19)$$

The energy parameter  $W$  is indicated explicitly and the notation for the smaller and larger of the radial arguments is used.

#### 4. BOHR-SOMMERFELD QUANTIZATION.

The zeroth order propagator has no isolated poles but exhibits a cut along the real energy axis for radial values where  $p(r)$  takes real values. A pole like structure is obtained from a Fredholm analysis of the integral equation(7). The only terms of concern arise from the logarithmic derivative of  $p(r)$ . It is assumed that there are two values of  $r$  where  $p(r)$  has zeroes for a given real energy. The addition of a small imaginary part to the energy causes small displacements of the zeroes and it is concluded that the forms

$$p(r) \cong \begin{cases} \sqrt{\alpha(r-a+i\eta)}, & |r-a| \text{ small} \\ \sqrt{\beta(b+i\eta'-r)}, & |b-r| \text{ small} \end{cases} \quad (20)$$

apply. The  $\eta$ 's are positive when the energy parameter is in the upper half of the complex plane and negative otherwise.

The relevant matrix kernel from the second term on the right hand side of Eq. (18) is expressed in terms of a couple of modified functions:

$$\begin{aligned} \tilde{f}^+(r) &= -\frac{1-i}{2} \left[ \frac{\kappa(r)-ip(r)}{\sqrt{p(r)(h(r)+c)}} \right] \exp[is(r)] \\ \tilde{f}^-(r) &= -\frac{1-i}{2} \left[ \frac{\kappa(r)+ip(r)}{\sqrt{p(r)(h(r)+c)}} \right] \exp[-is(r)] \end{aligned} \quad (21)$$

Thus we define

$$\mathbf{Q}(r, r') = \begin{cases} \begin{bmatrix} f^+(r)g^-(r') & f^+(r)\tilde{f}^-(r') \\ g^+(r)g^-(r') & g^+(r)\tilde{f}^-(r') \end{bmatrix} & r > r' \\ \begin{bmatrix} f^-(r)g^+(r') & f^-(r)\tilde{f}^+(r') \\ g^-(r)g^+(r') & g^-(r)\tilde{f}^+(r') \end{bmatrix} & r < r' \end{cases} \quad (22)$$

and consider the homogeneous integral equation

$$\begin{bmatrix} F(r) \\ G(r) \end{bmatrix} = \int dr' \mathbf{Q}(r, r') \begin{bmatrix} -\frac{p'(r')}{2p(r')} \\ 1 \end{bmatrix} \begin{bmatrix} F(r') \\ G(r') \end{bmatrix} \quad (23)$$

It should be appreciated here that the singularities at  $r'=a$  and  $r'=b$  makes the kernel of this equation practically separable of rank two. Fredholm theory shows that a solution to the homogeneous equation (23) requires a singular reciprocal kernel. Thus it holds that

$$\begin{aligned} 0 &= 1 - \int dr \left[ \text{Tr} \mathbf{Q}(r, r) \frac{p'(r)}{2p(r)} \right] \\ &+ \frac{1}{2} \int dr dr' \left[ \text{Tr} \mathbf{Q}(r, r) \frac{p'(r)}{2p(r)} \right] \left[ \text{Tr} \mathbf{Q}(r', r') \frac{p'(r')}{2p(r')} \right] \\ &- \frac{1}{2} \int dr dr' \left[ \frac{p'(r)}{2p(r)} \text{Tr} \mathbf{Q}(r, r') \mathbf{Q}(r', r) \frac{p'(r')}{2p(r')} \right] + \dots \end{aligned} \quad (24)$$

The second and the third term on the right hand side equal zero since the trace of the matrix kernel  $\mathbf{Q}(r, r)$  vanishes. The next term reduces when the explicit form is used,

$$\text{Tr} \mathbf{Q}(r, r') \mathbf{Q}(r', r) = -\exp[2is(r_>) - 2is(r_<)] \quad (25)$$

so that the essential condition is

$$0 = 1 + \int_0^\infty dr \exp[2is(r)] \frac{p'(r)}{2p(r)} \int_0^r dr' \exp[-2is(r')] \frac{p'(r')}{2p(r')} + \dots \quad (26)$$

Approximate evaluation of the integrals by means of the saddle point method<sup>8</sup> will be used. The integration over a small interval around the singular point at  $r=a$  comes out as follows(3):

$$\begin{aligned} \int_{r \approx a} dr \exp[-2is(r)] \frac{p'(r)}{2p(r)} &= \int_{r \approx a} dr \exp \left[ -2is(a) - \frac{4}{3} i \sqrt{\alpha(r-a+i\eta)^3} \right] \frac{1}{4(r-a+i\eta)} \\ &= -i \text{sgn}(\eta) \sqrt{\frac{\pi}{12}} \exp \left[ \frac{2}{3} - 2is(a) \right] \end{aligned} \quad (27)$$

A similar result for the other singular point gives the result that

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$$\begin{aligned}
 0 &= 1 + \exp\left[2is(b) - 2is(a) + \frac{4}{3} - \ln\left(\frac{\pi}{12}\right)\right] + \dots \\
 &= 1 + \exp\left[2is(b) - 2is(a) - 0.0068434\dots\right] + \dots
 \end{aligned}
 \tag{28}$$

and we learn that the Fredholm determinant is small when the Bohr-Sommerfeld quantization condition is satisfied:

$$2s(b) - 2s(a) = 2 \int_a^b dr p(r) = (2\nu + 1)\pi
 \tag{29}$$

Our analysis demonstrates that the integral equation approach offers an alternative to the differential equation methods for connection formulas across the turning points. The degeneracy between states with quantum number  $k$  and those with  $-k-1$  should be noticed here. The soluble case with a pure Coulomb field will not give the accurate energy eigenvalues here as is the case in the Schrödinger form. The quantization condition (29) gives the result

$$\begin{aligned}
 W &= c^2 \left\{ 1 + \frac{(Z/c)^2}{\left[ \nu + \frac{1}{2} + \sqrt{\left(k + \frac{1}{2}\right)^2 - (Z/c)^2} \right]^2} \right\}^{-1/2} \\
 &= c^2 - \frac{Z^2}{2n^2} - \frac{Z^4}{2c^2 n^4} \left( \frac{n}{\left|k + \frac{1}{2}\right|} - \frac{3}{4} \right) \dots
 \end{aligned}
 \tag{30}$$

$$n = \nu + \frac{1}{2} + \left|k + \frac{1}{2}\right|$$

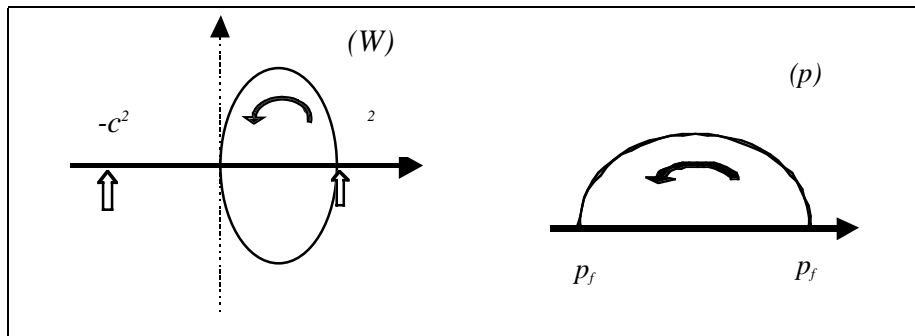
where the second order term differs from the correct result on account of the one half from the Kramers modification.

5. ELECTRON DENSITY DISTRIBUTION.

Propagator theory(2) provides an expression for the electron density in terms of an integral over the residues of the Green function at the poles corresponding to the occupied levels. Coulson suggested the equivalent procedure(9) of a contour integration in the complex energy plane. The present case calls for a contour that encloses the part of the spectrum that corresponds to bound electron states so it should include the part of the real axis between 0 and  $c^2$ . States with quantum number  $k$  are degenerate and thus the total radial density emanating from these states equals

$$\begin{aligned} \rho_k(r) &= \frac{2|k|}{2\pi i} \oint dW \text{Tr} \mathbf{G}_0(r, r; W) \\ &= \frac{2|k|}{2\pi i} \oint dW \left[ f^+(r) f^-(r) + g^+(r) g^-(r) \right] \\ &= -\frac{|k|}{\pi c} \oint dW \frac{h(r)}{p(r)} = -\frac{|k|}{\pi c} \oint dp \end{aligned} \quad (31)$$

An illustration of the path in the complex energy plane and its mapping onto the complex  $p$ -plane is offered in Fig. 1.



**Figure 1.** The left panel shows an example of an acceptable contour in the energy plane and the right panel gives its mapping onto the  $p$ -plane.

The integration gives the result

$$\rho_k(r) = \frac{2|k|}{\pi} \sqrt{\left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left( \frac{k + 1/2}{r} \right)^2} \quad (32)$$

The total radial density is obtained from a summation over quantum numbers  $k$  and its approximation with an integral:

$$\begin{aligned} \rho(r) &= \sum_k \rho_k(r) = \sum_j \left[ \rho_{-j-1/2}(r) + \rho_{j+1/2}(r) \right] \\ &= \sum_j \frac{2j+1}{\pi} \sqrt{\left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left[ \frac{j}{r} \right]^2} \\ &\quad + \sum_j \frac{2j+1}{\pi} \sqrt{\left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left[ \frac{j+1}{r} \right]^2} \\ &\cong \sum_j \frac{4j+2}{\pi} \sqrt{\left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left[ \frac{j+1/2}{r} \right]^2} \quad (33) \\ &= -\sum_j \frac{4r^2}{3\pi} \frac{\partial}{\partial j} \left\{ \left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left[ \frac{j+1/2}{r} \right]^2 \right\}^{3/2} \\ &\cong \frac{4r^2}{3\pi} \left\{ \left[ c + \frac{Z(r)}{cr} \right]^2 - c^2 - \left[ \frac{Z(0)}{cr} \right]^2 \right\}^{3/2} \end{aligned}$$

The lower limit of the integration is determined by the condition (13) and it secures that a self-consistent field can be sought from Poisson's equation,

$$\nabla^2 U(r) = -\frac{\rho(r)}{r^2} \quad (34)$$

which gives the equation for the screening function as

$$\frac{d^2 Z(r)}{dr^2} = \frac{4}{3\pi\sqrt{r}} \left[ 2Z(r) - \frac{Z^2(0) - Z^2(r)}{c^2 r} \right]^{3/2} \quad (35)$$

This simplifies to the regular Fermi-Thomas equation for infinitely large values of  $c$  and reduces to a well-known difficult form when the term in  $Z(0)$  is neglected(10).

The propagator gives a value for the sum of the energies of the one-electron states through the integral

$$\begin{aligned} \varepsilon_k(r) &= \frac{2|k|}{2\pi i} \oint W dW [Tr \mathbf{G}_0(r, r; W)] = -\frac{|k|}{\pi} \oint W dp \\ &= \frac{|k|}{\pi} \oint \left[ \frac{Z(r)}{r} - c\sqrt{p^2 + c^2 + \kappa^2} \right] dp \\ &= -\frac{Z(r)\rho_k(r)}{r} + \frac{|k|c}{\pi} \left[ c + \frac{Z(r)}{cr} \right]^2 \left\{ \xi_k(r) + \frac{1}{2} [1 - \xi_k^2(r)] \ln \frac{1 + \xi_k(r)}{1 - \xi_k(r)} \right\} \quad (36) \\ \xi_k(r) &\equiv \sqrt{1 - \frac{c^4 r^2 + c^2 (k + 1/2)^2}{[Z(r) + c^2 r]^2}} \end{aligned}$$

It is important to choose the branch of the square root with a positive real part in the integrations above. Summation over quantum numbers  $k$  proceeds as before with the result for the energy density that

$$\begin{aligned} \varepsilon(r) &= -\frac{Z(r)\rho(r)}{r} + \frac{cr^2}{2\pi} \left[ c^2 + \frac{Z^2(0)}{c^2 r^2} \right]^2 \left\{ \frac{\xi(r) + \xi^3(r)}{[1 - \xi^2(r)]^2} - \frac{1}{2} \ln \frac{1 + \xi(r)}{1 - \xi(r)} \right\} \quad (37) \\ \xi(r) &\equiv \sqrt{1 - \frac{c^4 r^2 + Z^2(0)}{[Z(r) + c^2 r]^2}} \end{aligned}$$

The first term in the energy density expression is the expectation value of the potential energy and it is concluded that the second one includes the kinetic energy

as well as the rest energy. The auxiliary variable  $\xi(r)$  can be expressed in terms of the density rather than the potential in the form

$$\xi(r) = \sqrt[3]{\frac{3\pi\rho(r)}{4c^3r^2}} / \sqrt{1 + \frac{Z^2(0)}{c^4r^2} + \left[\sqrt[3]{\frac{3\pi\rho(r)}{4c^3r^2}}\right]^2} \quad (38)$$

so that the energy may related directly to the density. It is also seen that this variable is small even for rather small values of the radius. An expansion of the energy density in inverse powers of  $c$  gives the result that

$$\begin{aligned} \varepsilon(r) = & -\frac{Z(r)\rho(r)}{r} \\ & + c^2\rho(r) \left\{ 1 + \frac{3}{10c^2} \left[ \frac{3\pi\rho(r)}{4r^2} \right]^{2/3} - \frac{1}{c^4} \left[ \frac{Z^2(0)}{r^2} + \frac{3}{56} \left[ \frac{3\pi\rho(r)}{4r^2} \right]^{4/3} \right] + \dots \right\} \end{aligned} \quad (39)$$

where the rest energy and the classical Fermi-Thomas kinetic energy density are readily recognized. The expansion is not valid near the origin and the last explicit term is not integrable over the range of radii.

## 6. THE CENTRAL FIELD.

Equation (35) does not exhibit the singularity at the origin that mars the form where  $Z(0)$  is omitted. A solution is not readily computed because a new condition appears. The argument of the root on the right hand side needs to be non-negative, that is

$$\begin{aligned}
 2Z(r) - \frac{Z^2(0) - Z^2(r)}{c^2 r} &\geq 0 \Rightarrow \\
 Z(r) + c^2 r - \sqrt{c^4 r^2 + Z^2(0)} &= Z(r) - \frac{Z^2(0)}{c^2 r + \sqrt{c^4 r^2 + Z^2(0)}} \geq 0;
 \end{aligned}
 \tag{40}$$

and thus it seems as if the screening function goes to an asymptotic inverse distance behavior. An expansion can be generated in the form

$$Z(r) = \frac{Z^2(0)}{2c^2 r} \left[ 1 + a_1 r^{-2/3} + a_2 r^{-4/3} + \dots \right]
 \tag{41}$$

for the large radius regime. The coefficients are rapidly increasing,

$$a_1 = \left[ \frac{3\pi c}{4Z(0)} \right]^{2/3}; \quad a_2 = \frac{40}{27} \left[ \frac{3\pi c}{4Z(0)} \right]^{4/3};
 \tag{42}$$

and the series is of little use presently. This asymptotic form ensures that the number of electrons in the system equals the nuclear charge.

Small radii suggest a series of the form

$$\begin{aligned}
 Z(r) &= Z(0) \left[ 1 + b_1 r + b_2 r^{3/2} + \dots \right] \\
 b_2 &= \frac{32\sqrt{2Z(0)}}{9\pi} \left[ 1 + \frac{Z(0)b_1}{c^2} \right]^{3/2}
 \end{aligned}
 \tag{43}$$

where  $b_1$  is negative and will be determined by the appropriate asymptotic behavior. An accurate representation of the non-relativistic Fermi-Thomas function can be found as a rational function of the variable  $\sqrt{r}$ . The present case, with the different form for large radii, does not seem to offer a similar approach.

Direct numerical integration is approached through a couple of transformations. The radius variable and the screening function are expressed in the traditional Fermi-Thomas scaled ones:

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$$r = xb; \quad b = \sqrt[3]{\frac{9\pi^2}{128Z(0)}}; \quad Z(r) = Z(0)\chi(x); \quad (44)$$

Thus we find from Eq. (34) that

$$\sqrt{x} \frac{d^2\chi(x)}{dx^2} = \left\{ \chi(x) - \frac{\beta}{x} [1 - \chi^2(x)] \right\}^{3/2}; \quad \beta = \frac{Z(0)}{2bc^2}; \quad (45)$$

and the atomic number occurs only in the parameter  $\beta$ . It has been convenient to replace Eq. (45) by a system of coupled first order differential equations with yet another independent variable:

$$\begin{aligned} x &= \xi^2; \\ \frac{d\chi(\xi)}{d\xi} &= \xi\varphi(\xi); \\ \frac{d\varphi(\xi)}{d\xi} &= 4 \left\{ \chi(\xi) - \frac{\beta}{\xi^2} [1 - \chi^2(\xi)] \right\}^{3/2}; \end{aligned} \quad (46)$$

A satisfactory solution requires that  $\varphi(\xi)$  is negative and that its derivative is positive. Integration by means of the numerical Runge-Kutta(11) stepping procedure starts from values  $\varphi(0)$  and  $\chi(0) = 1$  and ends when either of the two conditions is violated. A solution has been sought such that the screening function is as small as possible while still having a negative derivative. This will result in a finite radius for the charge distribution, a consequence that seems to be unavoidable in the present approximation. A similar situation occurs when Dirac exchange is included with the non-relativistic version(10).

An example calculation for  $Z=54$ , the Xenon atom, gives the result in Table 1. The "edge" of the charge distribution appears at 6.5 Bohr radii, well outside the normally accepted atomic radius. The screening function is well represented by the rational form

$$\chi(\xi) = \frac{1 + \sum_{j=1}^5 a_j \xi^j}{1 + \sum_{j=1}^7 c_j \xi^j} \quad (47)$$

with the coefficients from Table 2. There are no poles on the real, positive  $\xi$ -axis and the zeroes occur outside the range where the numerical solution is acceptable.

The initial value  $\varphi(0)$  was chosen as -3.12851 which gives  $d\chi(0)/dx = -1.564255$ , slightly less than the regular value for the Fermi-Thomas function, -1.588041. The two screening functions are close and differ significantly only at larger distances from the atomic nucleus.

**Table 1.** Result of integration of Eq. (46) for the Xenon atom where  $Z=54$ ,  $\beta=0.0061383$ ,  $b=0.936928$

$\xi$	$r$	$\chi(\xi)$	$\varphi(\xi)$
0.000	0.000000	1.000000	-3.128510
0.088	0.007256	0.988767	-2.788210
0.176	0.029022	0.958524	-2.458086
0.264	0.065300	0.914188	-2.146406
0.352	0.116089	0.860156	-1.858689
0.440	0.181389	0.800175	-1.598044
0.528	0.261201	0.737311	-1.365625
0.616	0.355523	0.673965	-1.161112
0.704	0.464356	0.611934	-0.983153
0.792	0.587701	0.552496	-0.829748
0.880	0.725557	0.496492	-0.698544
0.968	0.877924	0.444422	-0.587063
1.056	1.044802	0.396515	-0.492859
1.144	1.226191	0.352804	-0.413621
1.232	1.422092	0.313179	-0.347230
1.320	1.632503	0.277432	-0.291792

*Approximate propagator*

1.408	1.857426	0.245293	-0.245642
1.496	2.096860	0.216454	-0.207338
1.584	2.350805	0.190592	-0.175648
1.672	2.619261	0.167377	-0.149525
1.760	2.902228	0.146483	-0.128092
1.848	3.199706	0.127595	-0.110615
1.936	3.511696	0.110406	-0.096486
2.024	3.838196	0.094623	-0.085203
2.112	4.179208	0.079962	-0.076351
2.200	4.534731	0.066153	-0.069587
2.288	4.904765	0.052932	-0.064626
2.376	5.289310	0.040046	-0.061219
2.464	5.688367	0.027254	-0.059136
2.552	6.101934	0.014330	-0.058140
2.640	6.530013	0.001084	-0.057917

**Table 2.** Coefficients in the rational approximation for the screening function  $\chi(\xi)$  of Eq. (47).

$j$	$a_j$	$c_j$
1	0.606287	0.606287
2	-1.020611	0.543644
3	0.397868	0.0509944
4	-0.0577654	-0.0031777
5	0.0000232	-0.0216453
6	0	-0.0092576
7	0	0.0037789

## 7. SOME COMMENTS.

Several suggestions have been put forth for a relativistic generalization of the traditional Fermi-Thomas atomic model. It seems that Vallarta and Rosen(12) initiated this quest. They arrived at the expression for the electron density from the homogenous electron gas and could not then obtain the boundary condition (13), which was essential here to eliminate the singularity at the origin(13). Rudkjøbing(14) considered the spherical case and approximated the radial equations in a shell and obtained a density distribution dependent on the gradient of the potential in addition to the potential itself. His purpose was a study of relativistically degenerate stars and there seems to have been no atomic applications. Weizsäcker's(15) correction, based on the density gradient, has been introduced by Tomishima(16) in an effort to remove the singularity at the origin.

There are a couple of attempts to use the WKB approximation to the two component radial Dirac problem for screened Coulomb fields. Kosaka and Yonei(17) review these and apply the form offered by Goldberg and Pratt(18) for calculations of bound state orbitals in the potentials suggested by Tomishima(16). Their procedure is rather more involved than the present one.

The current effort demonstrates the necessity to include a proper coupling between the angular and radial behavior in order to obtain a reasonable charge density distribution in the Dirac case. This coupling manifests itself through the boundary condition on the Green function at the atomic nucleus as given by relation (13). A less satisfactory situation occurs far from the nucleus. It appears unavoidable to get a density with a finite radius. The effective nuclear charge will thus be zero outside this radius.

### *Approximate propagator*

The demonstration here of the efficacy of the integral formulation and the propagator techniques may be used in further attempts at approximating the more awkward terms in the electron-electron interactions, such as exchange and Breit terms(19), albeit giving rise to rather involved integrals.

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