Asymptotic Expansion of the Irregular Coulomb Function

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It is shown that the irregular Coulomb Function G_L can be expanded as an asymptotic power series in the energy, with coefficients which are expressible in terms of the modified Bessel function of the second kind. The form of the coefficients is the same as obtained by Yost, Wheeler, and Breit in an expansion of the regular function F_L with the modified Bessel function of the second kind replacing that of the first kind of the same order.

It has been shown in a previous note[1] that the expansion of the irregular Coulomb function for angular momentum zero can be made employing a series in powers of the energy, each term of the series being obtainable by replacement of the Bessel function I_ν by the Bessel function K_ν in a series occurring in the representation of the regular function.

In the present note a similar relationship is shown to hold for angular momenta greater than zero. Standard notation, a list of which is given in the previous note, will be used below. This notation is identical with that of Yost, Wheeler, and Breit.[2] The proof, as carried out in [I], depends on the possibility of rearranging the power series in ρ which represents Θ_0. The result of the rearrangement is a power series in $1/\eta^2$, *i.e.*, essentially in the energy. The coefficients are functions of the distance r and are expressed in terms of $K_\nu(x)$ the Bessel function of the second kind of imaginary argument, in the notation of Whittaker and Watson.[3] It will first be shown that for $L\neq 0$ a similar rearrangement of terms can be made.

The series Ψ_L can be rearranged in this manner, as may be seen from the fact that any power of ρ, ρ^s may be expressed as $(\rho\eta)^s/\eta^s$ and that, when the whole solution is substituted into Eq. (27) of YWB, there can be no connection when working in the $(\zeta,\ 1/\eta^2)$ variables between coefficients connecting powers of η differing by odd numbers. The same may be seen from Eqs. (19), (20) of YWB which give Ψ_L as

$$\Psi_L=\Sigma_{-L}{}^{\infty}a_j\rho^{j+L};\quad a_{-L}=1,\ a_{L+1}=0,$$
$$a_j=[2\eta a_{j-1}-a_{j-2}-p_L(2j-1)A_j]/[(j+L)(j-L-1)],\quad (1)$$

and here A_j is the coefficient of ρ^{j-L-1} in the series for Φ_L. The latter starts with 1 for $j=L+1$ and, as has been shown in YWB, it can be rearranged in terms of the variable x with the aid of even powers of $1/\eta^2$. The result of this reordering is the series on the right side of Eq. (33). The rearrangement would give also odd powers of $1/\eta$ unless the A_j are even or odd functions of η for even or odd values of $j-L-1$; this fact can be seen directly from the recurrence formula between the A_j which connects A_j with ηA_{j-1} and A_{j-2} by a linear relation. It is seen, on the other hand, that for $j=-L$ the quantity a_j is by definition even in η and that $j-L-1$ is in this case odd. Since p_L is odd in η the recurrence formula for a_j connects quantities of the same parity provided a_j is even or odd in η according as to whether $j-L$ is even or odd. A consideration of how a_{-L+1} follows from a_L shows that the construction of coefficients gives coefficients having a parity in η in accordance with the rule just mentioned. The value zero for a_{L+1} is consistent with a_{L+1} being odd in η as is in agreement with $L+1-(-L)$ being odd. It has thus been shown that only even powers $1/\eta$ occur in the result of rearranging Ψ_L in terms of x.

It will be seen next that the term in $\ln(2\rho)$ which multiplies Φ_L in the formula for Θ_L does not leave a term in $\ln\eta$ if Stirling's series for $\Gamma'(i\eta)/\Gamma(i\eta)$ is employed. The disappearance of $\ln\eta$ occurs because the combination

$$p_L\ln 2\rho+q_L,\quad (1.1)$$

contains $\Gamma'(i\eta)/\Gamma(i\eta)$ only in q_L as

$$p_L\,\mathrm{R.P.}[\Gamma'(i\eta)/\Gamma(i\eta)],$$

so that ln (2ρ) and Stirling's series combine in the same way independently of the value of L. The remaining part of q_L contributes to Θ_L the following amount

$$\mathrm{I.P.}(-)^{L+1}\frac{2^L}{(2L)!}\left\{\frac{2^{-L}}{2L+1}+\frac{2^{1-L}(i\eta-L)}{1!(2L)}+\cdots+\frac{2^{s+1-L}(i\eta-L)\cdots(i\eta-L+s)}{(s+1)!(2L-s)}+\cdots+\frac{2^L(i\eta-L)(i\eta-L+1)\cdots(i\eta+L-1)}{(2L)!1}\right\}\rho^{2L+1}\Phi_L.\quad (1.2)$$

The factor $\rho^{2L+1}=(x^2/8)^{2L+1}/\eta^{2L+1}$ is odd in η. The factor Φ_L can be expressed as a power series in $1/\eta^2$. The remaining factor is the imaginary part of a sum of products containing η in the form $i\eta$ only. It introduces therefore odd powers of η only. Taking into account the

* Assisted by the joint program of the ONR and the AEC.
[1] G. Breit and M. H. Hull, Jr., Phys. Rev. 80, 392 (1950), referred to as [I].
[2] Yost, Wheeler, and Breit, Phys. Rev. 49, 174 (1936), referred to as YWB.
[3] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1920), third edition, Chapter XVII.

factor η^{-2L-1} arising from ρ^{2L+1} it is seen that only even powers of η are brought in. The highest power of η in the sum of products is η^{2L} and therefore the imaginary part of the sum of products contributes only terms in η^{2L-1} and lower. The contributions of this part of q_L are seen to be confined to positive powers of $1/\eta^2$. The same holds for terms coming from $\Gamma'(i\eta)/\Gamma(i\eta)$ because the highest power of η in p_L is η^{2L+1} which is absorbed by ρ^{2L+1} to form $(x^2/8)^{2L+1}$ and because Stirling's series contributes terms in positive powers of $1/\eta^2$ only. An examination of the recurrence relation for the series for Ψ_L shows that here also there occur only positive powers of $1/\eta^2$ in the x, η representation. Thus $2\eta a_{j-1}$ can contribute to a_j at most η^{j+L} which is absorbed by ρ^{j+1}, the term $-a_{j-2}$ can contribute at most a power of η less by two than that coming from $2\eta a_{j-1}$. The quantity A_j, which is the coefficient of ρ^{j-L-1} in Φ_L, does not contain η to a power higher than η^{j-L-1}. The powers of η contained in p_LA_j are, therefore, no higher than $\eta^{j-L-1+(2L+1)}=\eta^{j+L}$ and this power of η is absorbed by ρ^{j+L} which is multiplied by a_j in Ψ_L. It may be concluded that all powers of $1/\eta^2$ occurring in the x, η representation with the introduction of the Stirling's series for $\Gamma'(i\eta)/\Gamma(i\eta)$ are positive or zero and that odd powers of $1/\eta$ are absent. The discussion so far is the equivalent of part A of the proof as conducted in [I].

The integral representation

$$Y_L=F_L+iG_L$$
$$=\frac{ie^{-i\rho}}{(2L+1)!C_L\rho^L}\int_0^\infty t^{-i\eta+L}(t+2i\rho)^{i\eta+L}e^{-t}dt \quad (2)$$

gives by the same deformation of the path as in [I]

$$G_L=(\Theta_L{}^{\mathrm{I}}+\Theta_L{}^{\mathrm{II}})/[(2L+1)C_L\rho^L], \quad (2.1)$$

with

$$\Theta_L{}^{\mathrm{I}}=[1/(2L)!]\int_0^\infty(\tau^2+\rho^2)^L \times\exp[-\tau-2\eta\tan^{-1}(\rho/\tau)]d\tau, \quad (2.2)$$

$$\Theta_L{}^{\mathrm{II}}=[e^{-\pi\eta}\rho^{L+1}/(2L)!]\int_0^1(1-u^2)^L \times\sin\left[-\rho u+\eta\ln\frac{1+u}{1-u}\right]du, \quad (2.3)$$

and

$$\Phi_L=C_L{}^{-2}[e^{-\pi\eta}/(2L+1)!] \times\frac{1}{2}\int_{-1}^{+1}(1-u)^{L-i\eta}(1+u)^{L+i\eta}e^{-i\rho u}du. \quad (2.4)$$

According to the reasoning presented in connection with Eqs. (10), (11), (12), (13) of [I] the result of arranging Θ_0 as a power series in $1/\eta^2$ gives coefficients which can be obtained from $\Theta_0{}^L$ by a symbolic expansion. This part of the proof in [I] applies in the present case without essential change. The form of Eq. (10) is changed but this circumstance is immaterial since it is only the possibility of obtaining the coefficient of η^{-2s} as $(1/s!)[\partial^s\Theta_L/\partial(\eta^{-2})^s]_{\eta=\infty}$ that is essential. It is thus seen that part C of the proof in [I] applies here also and that the series for Θ_L can be obtained by expanding

$$[\Theta_L]_{\mathrm{Symb}}=[1/(2L)!](x/2)^{2L+1}\int_0^\infty[v^2+(x/4\eta)^2]^L \times\exp\left[-\frac{vx}{2}-2\eta\tan^{-1}\frac{x}{4\eta v}\right]dv \quad (3)$$

in powers of $1/\eta^2$ under the integral sign, with the employment of the Taylor expansion for $\tan^{-1}(x/4\eta v)$.

A transformation of the integral representation for Φ_L given by Eq. (2.4) by means of the variable θ used in Eq. (14) of [I] and a consideration of the result as a sum of two parts arising from the presence of $e^{\pi\eta}$ and $e^{-\pi\eta}$ in $C_L{}^{-2}$ by deformation of the path of integration described in connection with Eq. (14′) of [I] yield

$$\Phi_L=(i/\pi x)(C_0{}^2/C_L{}^2)[x^{-2L}/(2L+1)!]\int_C(x^2+16\eta^2\zeta^2)^L \times\exp\left[-\frac{x\zeta}{2}-2\eta\tan^{-1}\frac{x}{4\eta\zeta}\right]d\zeta \quad (4)$$

where C is a contour around $\zeta=0$, taken counterclockwise and where it is understood that $\tan^{-1}(x/4\eta\zeta)$ should be expanded as a Taylor's series.

Comparison of Eq. (4) with Eq. (3) and employment of integral representations for K_ν, I_ν listed as Eqs. (17), (18) in [I] shows that

$$[\Theta_L]_{\mathrm{Symb}} =-(2L+1)(C_L{}^2/C_0{}^2)2^{-6L-1}x^{4L+2}\eta^{-2L}[\Phi_L]_{I\to K}, \quad (5)$$

where $I\to K$ indicates the replacement of all the I_ν by the K_ν. Since the recurrence formulas for the I_ν and the K_ν are the same in form, the replacement may be made in any form obtainable from Eq. (4) by expansion in powers of η^2 and employment of Eq. (18) of [I]. The coefficient,

$$C_L{}^2/C_0{}^2 =\frac{[1+\eta^2/L^2][1+\eta^2/(L-1)^2]\cdots[1+\eta^2/1^2]}{[1\cdot3\cdots(2L+1)]^2}. \quad (5.1)$$

Its limiting value for $\eta\to\infty$ is

$$(2\eta)^{2L}/[(2L+1)!]^2. \quad (5.2)$$

The limiting form of Eq. (5) for $\eta\to\infty$ is, therefore,

$$\mathrm{Lim}[\Theta_L/\Phi_L]=-[2K_{2L+1}(x)/I_{2L+1}(x)](x/2)^{4L+2}/[(2L)!(2L+1)!],$$

in agreement with Eqs. (32), (36) of YWB.

The right side of Eq. (5.1) can be obtained from the expression on the right side of Eq. (5.2) by multiplying the latter by the factor.

$$[1+L^2/\eta^2][1+(L-1)^2/\eta^2]\cdots[1+1^2/\eta^2],$$

whose presence cannot be inferred from the consideration of limiting forms for $\eta\rightarrow\infty$. This factor can be checked, however, by collecting all terms in $\ln x$ which are present in the $K_\nu(x)$.

The result of the consideration is that the employment of Stirling's asymptotic expansion for $\Gamma'(i\eta)/\Gamma(i\eta)$ in the formula for Θ_L, ordering of all terms according to powers of $1/\eta^2$ with coefficients expressed as functions of $x=(8\rho\eta)^{\frac{1}{2}}$ gives a series which is identical with the series obtainable by evaluating the right side of Eq. (5). The series in the I_ν may be obtained either by means of Eq. (4) and Eq. (18) of [I] or by means of Eq. (33) of YWB.

The integral representation reproduced as Eq. (2) of the present paper applies also to attractive fields. The quantity $\Theta_L{}^{II}$ may not be disregarded, however, in this case when one evaluates the coefficients of $1/\eta^{2s}$ in Θ_L because $e^{-\pi\eta}$ is infinite. The considerations do not apply, therefore, to attractive Coulomb Fields.

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Hartree Computation of the Internal Diamagnetic Field for Atoms*

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For an atom or monatomic ion in a magnetic field H there will be an induced shielding field $H'(0)$ at the the nucleus given by $H'(0)=(eH/3mc^2)v(0)$ where $v(0)$ is the electrostatic potential produced at the nucleus by the atomic electrons. Using the Thomas-Fermi model, Lamb put this expression into a calculable form. However, in modern nuclear induction and resonance absorption experiments it is important to have a more precise knowledge of the magnitude of this shielding field. In this paper computed values of $v(0)$ are given for all atoms and singly charged ions which have been treated by the Hartree or Hartree-Fock approximations to the self-consistent field method. By interpolation a list of $H'(0)/H$ values for all neutral atoms is given. Although it is impossible to check the accuracy of these values experimentally it is estimated from other evidence that they can be trusted to within five percent. An exception must be made, however, for the heaviest atoms where the relativity effect becomes appreciable, amounting to an estimated six percent correction to $H'(0)/H$ for $Z=92$. Finally, the usefulness of accurate values of the atomic shielding field in analyzing the total shielding field in molecules is discussed.

I. INTRODUCTION

IN the case of an atom or monatomic ion in an external magnetic field H, Larmor's theorem states that the motion of the atomic electrons in the field is the same (neglecting terms in H^2) as the motion before the existence of the field, except for the superposition of the Larmor precession. This creates a shielding field at the nucleus which, although always small compared with the external field, constitutes an important correction in the measurement of nuclear magnetic moments by the resonance method. Lamb[1] derived an expression for this shielding field, showing it to depend directly on the electrostatic potential $v(0)$ produced at the nucleus by the atomic electrons. Evaluating $v(0)$ on the basis of the Thomas-Fermi model he obtained for the ratio of induced to external field

$$H'(0)/H=-0.319\times10^{-4}Z^{4/3}. \qquad (1)$$

In the cases $Z=19$, 20, 26, 29, 37, 55, 74, and 80 where $v(0)$ was explicitly available from Hartree wave functions, Lamb showed that Eq. (1) is checked fairly well. This paper extends the computation of $v(0)$ and hence $H'(0)/H$ for all atoms and singly charged ions which have been treated by the Hartree or Hartree-Fock approximations to the self-consistent field method. The project was undertaken originally for a limited number of cases to determine the dependence of the shielding field $H'(0)$ on the state of ionization of an atom. The results indicated the possibility of just detecting a shift in nuclear resonance positions between an atom in a neutral and singly ionized state. However, with the subsequent discovery of larger shifts due to the effect of chemical binding (discussed below) it would be difficult to distinguish this small effect experimentally.

II. THEORY

Consider an atom with a spherically symmetrical charge distribution of radial charge density $\rho(r)$ in an external field H. As an element of volume we take a ring with axis passing through the nucleus and parallel to H, with cross section $rd\theta dr$ and perimeter $2\pi r\sin\theta$, so that its volume is $2\pi r^2\sin\theta d\theta dr$ and it will contain a

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[1] W. E. Lamb, Jr., Phys. Rev. 60, 817 (1941).