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High-Order Perturbation Theory for the Bound States of an Electron in a Screened Coulomb Potential

Gerald J. Iafrate*
Institute for Exploratory Research, Fort Monmouth, New Jersey 07703

and

Lawrence B. Mendelsohn†
Polytechnic Institute of Brooklyn, Brooklyn, New York

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The solution to the nonrelativistic Schrödinger equation for a bound electron in an attractive screened Coulomb potential is investigated using the large-Z (Z is nuclear charge) asymptotic expansion theory. Both the basic asymptotic and perturbation solutions are found. The problem of finding the kth order perturbation wave function and energy for any state is reduced to solving, recursively, a set of k linear algebraic equations in k unknowns. The asymptotic expansions for the energy and wave functions are presented to the tenth order in perturbation theory for the 1S state and to fifth order for the general n, $l=n-1$ quantum state. Results for the 2S states are also given. Comparison of the perturbation-theory results with those of numerical integrations for the energy show excellent agreement. It is shown that a finite screening radius gives rise to a *finite* number of bound states, a result which contradicts some recently published work. Application of the screened Coulomb potential model to intensity cutoffs in the spectra of solar and laboratory hydrogen plasmas is discussed.

I. INTRODUCTION

The problem considered here is that of an electron bound in an attractive screened Coulomb potential. This potential, commonly known as the Debye-Hückel potential in plasma physics and the Yukawa potential in nuclear physics, has the form

$$V(r) = -Ze^{-\lambda r}/r, \tag{1}$$

where Z is the nuclear charge and λ is the reciprocal of the Debye screening distance. Conventionally, the screened Coulomb potential result is derived by linearizing the Poisson-Boltzmann equation using the condition

$$V(r)/KT < 1 \tag{2}$$

thereby obtaining a solution in the high temperature, low density limit. Of all the many possible criteria for the validity of Debye-Hückel theory, the Frank-Thomson criteria,[1] which in effect states that the thermal energy must be an order of magnitude greater than the Coulomb energy, is the most conservative and can be written as

$$N_e \leq \tfrac{1}{2}(KT/4\pi a_0)^3, \tag{3}$$

where KT is in terms of large rydbergs and N_e is the electron density. This criteria gives a maximum N_e of about 5.42×10^{13} cm^{-3} at $T = 10^3$ K and goes to a value of about 5.42×10^{16} cm^{-3} at $T = 10^4$ K. Thus condition (3) is easily satisfied by most laboratory and astrophysical plasmas. In particular, in this paper we will study the bound states of a one-electron ion embedded in such a plasma.

The screened Coulomb effective potential can be obtained directly from Thomas-Fermi theory in a high-density, zero-temperature approximation thus enabling one to use it in describing electron impurity levels in solids.[2] This potential has also been shown to describe quasiparticle-quasiparticle interactions in a uniform electron gas, a result which follows rigorously from the random-phase approximation in the high-density long-wavelength limit.[3]

Since the Schrödinger equation for the screened Coulomb potential is not solvable analytically, previous investigations of this problem have employed first-order perturbation theory,[4] variational calculations[5, 6] and the actual numerical integration[7, 8] of the differential equation. In this paper, the large parameter asymptotic approach developed by one of the authors (L. B. M.)[9–11] is employed to obtain the wave functions and the perturbation-theory energy expansion to arbitrarily high order.

In Sec. II of the paper, the basic asymptotic expansion (the correct large-Z asymptotic expansion away from the neighborhood of the origin) is obtained to first order in Z^{-1} and the general form of the energy expansion is derived for any n, l quantum state.

In Sec. III, a large-Z solution is obtained in the neighborhood of the origin by solving the stretched differential equation (perturbation-theory equation). By demanding "good behavior" of the solution near the origin, the energy terms are immediately determined and the "matching condition" is automatically satisfied. After solving the Schrödinger equation recursively through a few orders in $\epsilon = \lambda/Z$, the truncation form for the solution becomes obvious and the solution near the origin can be found to *any* order of perturbation theory by solving a simple set of linear algebraic equations of the same order. In particular, results are obtained for the case $l = n - 1$ and for the 2S state. For the 1S state, calculations are carried through tenth order which show the oscillatory nature of the series. The asymptotic property is also clearly indicated. A comparison of the numerical results for the 1S, 2S, and 2P states for astrophysical values of λ is made with the numerical integration results of C. Rouse[7] and very good agreement is found. Our results for the ground state for semiconductor values of λ are also found to agree closely with the variational calculations of G. Harris[5] and the numerical integration results of V. Bonch-Bruevich[8] *et al.*

In Sec. IV, we discuss the problem of the number of bound states in a screened Coulomb potential. This problem is of importance if Debye-Hückel theory is to explain the disappearance of spectral lines originating from levels greater than $n = 16$ in the solar photosphere and from levels greater than $n = 40$ in the chromosphere. We show explicitly, employing a theorem derived by V. Bargmann[12] and J. Schwinger,[13] that for finite λ there are a finite number of bound states. In particular, for a given λ an upper bound to the number of bound states is found. This result contradicts the statements of C. Rouse[7] that an infinite number of bound states occur for a screened Coulomb potential. A lower bound to the number of bound states is found by re-examining the work of H. Margenau and M. Lewis.[6]

In Sec. V, it is observed that although the Debye-Hückel potential leads to a maximum value of occupied principal quantum number n, this value is much too large to explain the spectral anomalies. A possible explanation of the discrepancy is given as well as the way in which it may be resolved.

II. THE BASIC ASYMPTOTIC EXPANSION FOR THE SCREENED COULOMB POTENTIAL

The radial Schrödinger equation for an electron bound in a screened coulomb potential is

$$-\frac{1}{2}\frac{d^2\psi}{dr^2}-\frac{1}{r}\frac{d\psi}{dr}-Z\frac{e^{-\lambda r}}{r}\psi+\frac{\frac{1}{2}l(l+1)}{r^2}\psi=E\psi, \qquad (4)$$

where distances are expressed in terms of Bohr radii and the energy is in terms of large rydbergs (approximately 27.2 eV). The $\psi(r)$ in Eq. (4) is, of course, multiplied by the appropriate Legendre polynomial to bring in the correct angular dependence in the total wave function. In the large-Z expansion theory, the assumed solution to Eq. (4) is the formal asymptotic expansion

$$\psi(r)=e^{-ZS(r)}\sum_{m=0}^{\infty}a_m(r)Z^{-m}. \qquad (5)$$

Notice that the solutions obtained for the Schrödinger equation should reduce to the hydrogen solutions in the limit $\lambda \to 0$, that is

$$\psi \to e^{-Zr/n}\left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}(2Zr/n), \qquad (6)$$

and

$$E \to -\tfrac{1}{2}Z^2/n^2, \quad \text{as } \lambda \to 0. \qquad (7)$$

In order to obtain the proper form of the energy expansion, it is necessary to find a natural perturbation-theory expansion parameter. Transforming the radial Schrödinger equation [Eq. (4)] into stretched variables $\xi = Zr$ and expanding the exponential part of the screened Coulomb potential, one obtains the equation

$$-\frac{1}{2}\frac{d^2\Psi}{d\xi^2}-\frac{1}{\xi}\frac{d\Psi}{d\xi}-\frac{1}{\xi}\Psi+\sum_{t=1}^{\infty}B_{(t)}\left(\frac{\lambda}{Z}\right)^{(t)}\xi^{t-1}\Psi$$
$$+\left[\tfrac{1}{2}l\,(l+1)/\xi^2\right]\Psi=(E/Z^2)\Psi, \qquad (8)$$

$$\text{where } B_{(t)}=(-1)^{t+1}/t\,! \qquad (9)$$

Equation (8) represents the Schrödinger equation (in dimensionless form) for a one-electron ion perturbed simultaneously by the infinite sum of operators $(\lambda/Z)\xi^0$, $(\lambda/Z)^2\xi, \cdots$, $(\lambda/Z)^k\xi^{k-1}, \ldots$, etc. By treating each perturbation separately, we see that the expansion parameter for the ξ^{k-1} term is $\epsilon_{k-1} = (\lambda/Z)^k$. The total energy shift E_1 due to the ξ^0 term alone is

$$E_1 = \epsilon \qquad (10)$$

since the perturbation term is a constant. In a similar fashion, the energy shift E_2 due to ξ is written as

$$E_2 = E_{2,2}\epsilon^2 + E_{2,4}\epsilon^4 + E_{2,6}\epsilon^6 + \cdots , \qquad (11)$$

where the $E_{2,j}$'s are constants. In general for the ξ^{k-1} term, the energy shift is given by

$$E_k = E_{k,k}\epsilon^k + E_{k,2k}\epsilon^{2k} + E_{k,3k}\epsilon^{3k} + \cdots . \tag{12}$$

Then the energy E for the problem can be written as

$$E/Z^2 = E_0 + \sum_{k=1} E_k + \sum_{k=4} (\mathrm{CT})_k \epsilon^k , \tag{13}$$

where the $(\mathrm{CT})_k$ are cross terms arising from lower orders of perturbation theory. The (CT) sum starts at $k=4$ since first-order perturbation in ϵ is a constant. Therefore the conventional matrix element form for the energy sum does not give rise to cross terms for $k<4$. Upon collecting powers of ϵ, we find that

$$E/Z^2 = E_0 + \epsilon + E_{2,2}\epsilon^2 + E_{3,3}\epsilon^3 + [E_{4,4} + E_{2,4} + (\mathrm{CT})_4]\epsilon^4 . \tag{14}$$

Thus by inspecting Eq. (14) we see that $\epsilon = \lambda/Z$ is the natural perturbation-theory expansion parameter. Therefore the perturbation-theory expansion for the energy can be written as

$$E/Z^2 = \sum_{t=0}^{\infty} C_t \epsilon^t , \tag{15}$$

where the C_t are immediately discerned from Eq. (14). Note that treating the entire sum as the perturbation and then evaluating

$$Z^{-1} \int \psi_0^* \sum_{t=1}^{\infty} B_{(t)} \lambda^t r^{t-1} \psi_0 d^3 r , \tag{16}$$

where ψ_0 is the unperturbed wave function is equivalent to a first-order perturbation-theory calculation with unspecified perturbation parameter. Such a calculation has been performed by C. Smith[4] and is equivalent to considering only the diagonal terms of our sum. Thus his result E_S can be written as

$$E_S/Z^2 = E_0 + \epsilon + \sum_{j=2} E_{j,j}\epsilon^j . \tag{17}$$

Such a calculation will give the correct result for the first-three orders in ϵ. In fourth order, the term $E_{2,4}$ and $(\mathrm{CT})_4$ would be omitted in E_S. Thus in any order higher than the third, first-order unspecified parameter perturbation theory gives incorrect results for the coefficient of the appropriate power of ϵ. We shall see this explicitly later.

From the foregoing, it is seen that the solution to Eq. (8) can be expanded in powers of ϵ as

$$\Psi(\xi) = \sum_{j=0}^{\infty} \Psi_j(\xi)\epsilon^j , \tag{18}$$

where the energy expansion is given by Eq. (15). Also note that, due to the large-Z limiting procedure, when ξ is finite and Z is taken as large, $r = \xi/Z \to 0$ and the solution to Eq. (8) becomes the solution to Schrödinger's equation [Eq. (4)] near the origin. In addition, for the condition of Eq. (7) to be obeyed, we chose $C_0 = -\frac{1}{2}n^{-2}$.

Now that the form of the energy expansion has been found, attention is again focused on the solution to Eq. (4). Substituting Eq. (5) and Eq. (15) into Eq. (4), and canceling out the exponential on both sides, one obtains

$$\sum_{m=0}^{\infty} \Big(-\frac{1}{2} [Z^2(S')^2 a_m - Z(S'' a_m + 2S' a_m') + a_m''] + \frac{1}{r}(ZS' a_m + a_m') - Z \frac{e^{-\lambda r}}{r} a_m + \frac{1}{2}\frac{l(l+1)}{r^2} a_m - Z^2 \sum_{t=0}^{\infty} C_t a_m \frac{\lambda^t}{Z^t} \Big) Z^{-m} = 0. \tag{19}$$

Setting the coefficient of Z^2 equal to zero in Eq. (19), one obtains

$$[-\tfrac{1}{2}(S')^2 - C_0] a_0 = 0 . \tag{20}$$

From the value of C_0 above, S is immediately found to be

$$S = r/n . \tag{21}$$

By setting the coefficient of Z equal to zero, a first-order differential equation for a_0 is found to be

$$a_0'/a_0 = -1/r + n(e^{-\lambda r}/r) + n\lambda C_1 . \tag{22}$$

Equation (22) can be immediately integrated to get

$$a_0 = r^{n-1} \exp\{n[W(r) + \lambda C_1 r]\}, \tag{23}$$

$$\text{where}\quad W(r) = \sum_{i=1}^{\infty} (-1)^i \lambda^i r^i / i\, i\,! \tag{24}$$

Upon setting the coefficient of Z^{-j} equal to zero, the general lower-order (first-order) inhomogeneous recursive differential equation is found to be

$$a_{j+1}' + [(1/r) - n(e^{-\lambda r}/r) - n\lambda C_1] a_{j+1} = n\{\tfrac{1}{2} a_j'' + (a_j'/r) - [\tfrac{1}{2} l(l+1)/r^2] a_j\}$$

$$+n\sum_{r=0}^{j}[\lambda^{j-r+2}-C_{j-r+2}]a_r,$$

$$\text{with } j=0,1,2,\ldots. \tag{25}$$

The integrating factor for Eq. (25) is

$$\exp\left[\int(1/r-ne^{-\lambda r}/r-n\lambda C_1)dr\right]=1/a_0.$$

By multiplying through by the integrating factor, one reduces the formal solution of Eq. (25) to quadratures. For a_{j+1}, one gets

$$\begin{aligned}a_{j+1}=a_0(r)&\int^r dx(1/a_0(x))\\&\times\left\{n\left(\frac{1}{2}a_j''(x)+\frac{a_j(x)}{x}-\frac{1}{2}\frac{l(l+1)}{x^2}a_j(x)\right)\right.\\&\left.+n\sum_{r=0}^{j}[\lambda^{j-r+2}C_{j-r+2}a_r(x)]\right\}.\end{aligned} \tag{26}$$

For $j=0$, the result of integrating Eq. (26) is

$$\begin{aligned}a_1=a_0\{&\tfrac{1}{2}n^2[(e^{-\lambda r}/r)-n(e^{-2\lambda r}/r)]\\&+n^2\lambda(C_1-1)\ln r+n^2\lambda[C_1W(r)-B(r)]\\&+\lambda^2(\tfrac{1}{2}n^3C_1{}^2+nC_2)r+\tfrac{1}{2}nl(l+1)/r\},\end{aligned} \tag{27}$$

where $W(r)$ is given by Eq. (24) and

$$B(r)=\sum_{i=1}^{\infty}(-1)^i(2\lambda)^i r^i/i\,i\,! \tag{28}$$

Now that a_0 and a_1 have been found, the basic asymptotic expansion can be written to first order in $(1/Z)$. The result is

$$\begin{aligned}\psi(r)=r^{n-1}&\{\exp[-Zr/n+n(W-\lambda C_1)r]\}\\&\times\{1+Z^{-1}[\tfrac{1}{2}n^2(e^{-\lambda r}/r-ne^{-2\lambda r}/r)\\&+n^3\lambda(C_1-1)\ln r+n^3\lambda(C_1W-B)\\&+\lambda^2(\tfrac{1}{2}n^3C_1{}^2+nC_2)r+n\tfrac{1}{2}l(l+1)/r]+\ldots\}.\end{aligned} \tag{29}$$

In order to show that this solution goes over to the hydrogen solution, in the limit $\lambda\to 0$, note that $\psi(r)$ in Eq. (29) becomes

$$\begin{aligned}\psi_{(r)}=r^{n-1}e^{-Zr/n}&\{1+Z^{-1}[\tfrac{1}{2}n^2(1-n)/r\\&+\tfrac{1}{2}nl(l+1)/r]+\ldots\};\end{aligned} \tag{30}$$

for $n=1,\quad l=0,\quad \psi=e^{-Zr};$

$n=2,\quad l=0,\quad \psi=re^{-Zr/2}(1-2/Zr);$

$n=2,\quad l=1,\quad \psi=re^{-Zr/2}$

This demonstrates that the basic expansion carried to Z^{-1} gives the correct corresponding hydrogen solution for the above cases. In point of fact, carrying the process to all orders in Z^{-1} yields the correctly truncated solutions for all n, l states.[9]

We shall show through matching that $C_1=1$ and therefore no logarithmic divergence occurs in the basic asymptotic solutions [Eq. (29)]. In general, such a basic asymptotic expansion will give a good approximation to the wave function away from the origin. Thus if one is interested in the expectation values of observables that are not sensitive to the behavior of the wave functions near the origin, it would be reasonable to use expression (29) or for higher accuracy the basic asymptotic expansion with terms of higher order in $1/Z$. Such cases would exist when applying the large parameter technique to the problem of finding scattering amplitudes or when looking for $\langle r^m\rangle$ $(m>0)$ in bound state problems.

III. HIGH-ORDER PERTURBATION THEORY

In order to find the correct asymptotic expansion in the neighborhood of the origin, one must seek the solution to Eq. (8). Substituting Eq. (18) and Eq. (15) into Eq. (8), one obtains

$$\sum_{j=0}^{\infty}\left[\left(-\frac{1}{2}\Psi_j''-\frac{1}{\xi}\Psi_j'-\frac{1}{\xi}\Psi_j+\frac{1}{2}\frac{l(l+1)}{\xi^2}\Psi_j-C_0\Psi_j\right)\epsilon^j+\sum_{t=1}^{\infty}(B_{(t)}\xi^{t-1}-C_t)\Psi_j\epsilon^{t+j}\right]=0, \tag{31}$$

where the prime now indicates the derivative with respect to the variable ξ. Letting

$$\Psi_j(\xi)=e^{-\xi/n}b_j(\xi) \tag{32}$$

Eq. (31) becomes

$$\sum_{j=0}^{\infty}\left\{\left[-\frac{1}{2}b_j''+\left(\frac{1}{n}-\frac{1}{\xi}\right)b_j'+\frac{1/n-1}{\xi}b_j+\frac{\frac{1}{2}l(l+1)}{\xi^2}b_j\right]\epsilon^j+\sum_{t=1}^{\infty}(B_{(t)}\xi^{t-1}-C_t)b_j\epsilon^{t+j}\right\}=0. \tag{33}$$

Setting the coefficient of ϵ^0 equal to zero in Eq. (33) one gets

$$-\tfrac{1}{2}b_0'' + (1/n - 1/\xi)b_0' + [(1/n - 1)/\xi]b_0 + [\tfrac{1}{2}l(l+1)/\xi^2]b_0 = 0 \tag{34}$$

which is the familiar Laguerre differential equation. The solutions to Eq. (34), well behaved at the origin, are the Laguerre polynomials. Setting the coefficients of ϵ^k equal to zero, one obtains the second order, linear, inhomogeneous, recursive differential equation for the b_k as

$$-\frac{1}{2}b_k'' + \left(\frac{1}{n} - \frac{1}{\xi}\right)b_k' + \frac{1/n - 1}{\xi}b_k + \frac{1}{2}\frac{l(l+1)}{\xi^2}b_k + \sum_{w=0}^{k-1}[B_{(k-w)}\xi^{k-w-1} - C_{k-w}]b_w = 0, \quad \text{for } k \geqslant 1. \tag{35}$$

Equation (35) can be reduced to a first-order inhomogeneous equation by factoring out the homogeneous solution b_0.

Thus, in this regard, we let

$$b_k = b_0 u_k, \tag{36}$$

where $u_0 = 1$. Substituting Eq. (36) into Eq. (35), it can be seen that the differential equation reduces to

$$u_k'' + \left(\frac{2b_0'}{b_0} + \frac{2}{\xi} - \frac{2}{n}\right)u_k' = 2\sum_{w=0}^{k-1}[B_{(k-w)}\xi^{k-w-1} - C_{k-w}]u_w\,. \tag{37}$$

Using a suitable integrating factor, the solution to Eq. (37) is immediately reduced to quadratures. The result is

$$u_k = 2\sum_{w=0}^{k-1}\int^{\xi}dy[e^{2y/n}/y^2 b_0^{\,2}(y)]\int_{\infty}^{y}dx[B_{(k-w)}x^{k-w+1} - x^2C_{k-w}]b_0^{\,2}(x)u_w(x)e^{-2x/n} + \gamma_k, \tag{38}$$

where γ_k is an arbitrary constant of integration. Thus, for a given n, l state, where b_0 is specified as the appropriate Laguerre polynomial, the integral of Eq. (38) can immediately be evaluated.

To illustrate the method of solution, u_k is found to some order ($k = 5$) for the principal quantum number n with $l = n - 1$. In this case, $b_0 = \xi^{n-1}$

Putting b_0 into Eq. (38), the integral reduces to

$$u_k = 2\sum_{w=0}^{k-1}\int^{\xi}dy[e^{2y/n}/y^{2n}]\int_{\infty}^{y}dx[B_{(k-w)}x^{k-w-1} - C_{k-w}]x^{2n}u_w e^{-2x/n} + \gamma_k\,. \tag{39}$$

For $k = 1$, Eq. (39) can be immediately integrated to give

$$u_1 = (C_1 - 1)Q(\xi) + \gamma_1\,, \tag{40}$$

where $Q(\xi) = n\xi + n^3\ln\xi + \sum_{r=2}^{2n} n^{r+1}/(2n-r)!\,2^r(1-r)\xi^{r-1}$

and γ_1 is an arbitrary constant of integration. It may be chosen equal to $\frac{1}{2}n^2(2n-1)$. In so doing, it will be shown later that the matching condition with the basic solution is satisfied, although any nonzero choice of this constant in no way affects the values of the observables of the system.[14] It is also seen that the constants of integration for other orders are zero.

Demanding the good behavior of u_1 near the origin, one is forced to pick $C_1 = 1$. In doing so, we have automatically determined, self-consistently, the first-order correction to the energy expansion of Eq. (15). It should also be noticed that this choice of $C_1 = 1$ has removed the $\ln(r)$ singularity from the basic asymptotic solution of [Eq. (29)]. Thus for $k = 1$,

$$u_1 = \tfrac{1}{2}n^2(2n-1) \tag{41}$$

and $C_1 = 1$. (42)

In carrying the recursive process of Eq. (39) to second order we find that

$$u_2 = [C_2 + \tfrac{1}{4}n(2n+1)]\,Q(\xi) + \tfrac{1}{4}n\xi^2\ . \tag{43}$$

Thus for the perturbation wave function to be nonsingular at the origin, we see that

$$u_2 = \tfrac{1}{4}n\xi^2 \tag{44}$$

and $C_2 = -\tfrac{1}{4}n(2n+1)$. (45)

Continuing in the same way to third order, we find that

$$u_3 = (n^2/24)(6n^2 - 5n - 2)\xi^2 - (n/18)\xi^3 \tag{46}$$

and $C_3 = (n^2/12)(2n+1)(n+1)$. (47)

We can continue this process indefinitely and in any order we would find

$$u_k = (C_k - A_k)Q(\xi) + \phi_k(\xi) \tag{48}$$

with $\phi_k(\xi) = \sum_{j=2}^{k} B_{k,j}\,\xi^j$ (49)

and where $B_{k,j}$ are functions of principal quantum number n, A_k being a number. Thus by setting $C_k = A_k$ our solution is always nonsingular and the energy is determined. From the foregoing we demand that the solution for any order k be of the form

$$u_k \equiv \phi_k = \sum_{j=2}^{k} B_{k,j}\,\xi^j\ , \quad \text{where } k = 2, 3, 4, \ldots, \tag{50}$$

and substitute it into Eq. (37) with $b_0 = \xi^{n-1}$. For $k \geqslant 2$ one obtains

$$\sum_{l=0}^{k-2} (l+2)(l+1)B_{k,l+2}\,\xi^l + 2n\sum_{l=1}^{k-1} (l+1)B_{k,l+1}\,\xi^{l-1} - \frac{2}{n}\sum_{l=1}^{k-1} (l+1)B_{k,l+1}\,\xi^l = 2\sum_{w=0}^{k-1} [B_{(k-w)}\,\xi^{k-w-1} - C_{k-w}]u_w\,. \tag{51}$$

For $k = 2$, Eq. (51) reduces to

$$2B_{2,2} + 4nB_{2,2} - (4/n)B_{2,2}\xi = -\xi - 2C_2\ . \tag{52}$$

Setting powers of ξ equal to zero, one obtains the result that

$$B_{2,2} = \tfrac{1}{4}n \tag{53}$$

and $C_2 = -\tfrac{1}{4}n(2n+1)$ (54)

as expected from Eq. (44) and Eq. (45).

For $k > 2$, we obtain a power series in ξ as

$$[C_k + \tfrac{1}{2}n^2(2n-1)C_{k-1} + (2n+1)B_{k,2}] + \sum_{l=1}^{k-2} [(l+2)(l+2n+1)B_{k,l+2} - (2/n)(l+1)B_{k,l+1}]\,\xi^l$$
$$+ 2\left(\frac{(-1)^k}{k!} - \frac{kB_{k,k}}{n}\right)\xi^{k-1} + n^2(2n-1)\,\frac{(-1)^{k-1}\xi^{k-2}}{(k-1)!}$$

$$+2\sum_{w=2}^{k-1}\sum_{r=2}^{w} B_{w,r}\left(\frac{(-1)^{k-w}\xi^{k+r-w-1}}{(k-w)!}+C_{k-w}\xi^{r}\right)=0\,. \tag{55}$$

Upon setting powers of ξ in Eq. (55) to zero for a given k order, one can determine the $B_{k,l}$ and C_k explicitly from the resulting linear equations. The solution of this equation through fifth order ($k=5$) gives for the wave function and energy expansion

$$\begin{aligned}\Psi(\xi)=\xi^{n-1}e^{-\xi/n}\{&1+\tfrac{1}{2}n^2(2n-1)\epsilon+\tfrac{1}{4}n\xi^2\epsilon^2+[(n^2/24)(6n^2-4n-2)\xi^2-(n/18)\xi^3]\epsilon^3\\
&+[((n^3/96)(n+1)(8n+3)-(n^4/24)(2n-1)(n+1))\,\xi^2\\
&+((n/144)(8n+3)-(n^2/36)(2n-1))\xi^3+(n/96)(3n+1)\xi^4]\epsilon^4\\
&+[(n^4/2880)(n+1)((2n+3)(90n^3-75n^2-141n-12)-(2n+1)(60n^3-105n^2-30n))\xi^2\\
&+(n^3/4320)((2n+3)(90n^3-75n^2-141n-12)-(2n+1)(60n^3-105n^2-30n))\xi^3\\
&+(n^2/2880)(90n^3-75n^2-141n-12)\xi^4-(n/1800)(25n+3)\xi^5]\epsilon^5+\cdots\}\end{aligned} \tag{56}$$

and

$$\begin{aligned}E/Z^2=&-\tfrac{1}{2}(1/n^2)+\epsilon-\tfrac{1}{4}n(2n+1)\epsilon^2+(n^2/12)(2n+1)(n+1)\epsilon^3\\
&-(n^3/96)(n+1)(2n+1)(8n+3)\epsilon^4+[\,n^4(n+1)(2n+1)/2880]\\
&\times[15n(2n-1)(8n+3)-(2n+3)(90n^3-75n^2-141n-12)\\
&+(2n+1)(60n^3-105n^2-30n)]\epsilon^5+\cdots\,.\end{aligned} \tag{57}$$

For $k\geqslant 6$, a general form for the linear equations in k unknowns is found. In particular, for the 1S state, the equations are

$$C_k=-\tfrac{1}{2}C_{k-1}-3B_{k,2}, \tag{58a}$$

$$B_{k,2}-3B_{k,3}=0, \tag{58b}$$

$$-6B_{k,3}+20B_{k,4}=-2\sum_{j=2}^{k-2}C_{k-j}B_{j,2}\,, \tag{58c}$$

$$-2(l+1)B_{k,l+1}+(l+2)(l+3)B_{k,l+2}=-2\sum_{j=l}^{k=2}C_{k-j}B_{j,l}-2\sum_{j=2}^{l-1}(-1)^{-j+(l+1)}B_{j+k-(l+1),j}/(-j+l+1)!\,,$$

$$\text{for } 3\leqslant l\leqslant k-3, \tag{58d}$$

$$\begin{aligned}&-2(k-1)B_{k,k-1}+k(k+1)B_{k,k}\\
&\qquad=-(-1)^{k-1}/(k-1)!-2C_2B_{k-2,k-2}-2\sum_{j=2}^{k-3}(-1)^{-j+k-1}B_{j+1,j}/(-j+k-1)!\,,\end{aligned} \tag{58e}$$

$$kB_{k,k}=(-1)^k/k!+\sum_{j=2}^{k-2}(-1)^{-j+k}B_{j,j}/(k-j)! \tag{58f}$$

The results carried to tenth order for the wave function are given in Table I, whereas the energy expansion was found to be

$$E/Z^2 = -\tfrac{1}{2}(1/n^2) + \epsilon - (0.75)\epsilon^2 + (0.5)\epsilon^3 - (0.68750)\epsilon^4 + (1.31253)\epsilon^5 - (3.02090)\epsilon^6 \quad (59)$$

$$+ (7.88557)\epsilon^7 - (22.60230)\epsilon^8 + (69.76020)\epsilon^9 - (228.900)\epsilon^{10}.$$

TABLE I. The perturbation wave function coefficients for the 1S state carried out to tenth order. The meaning of k, l, and B_{kl} are understood from Eq. (50).

k	l	B_{kl}	k	l	B_{kl}
2	2	0.250 000	8	6	0.047 043
3	2	−0.041 670	8	7	0.008 317
3	3	−0.055 560	8	8	0.001 082
4	2	0.145 833	9	2	−19.486 200
4	3	0.048 611	9	3	−6.495 450
4	4	0.041 667	9	4	−2.398 490
5	2	−0.322 927	9	5	−0.633 315
5	3	−0.107 642	9	6	−0.144 426
5	4	−0.047 917	9	7	−0.026 766
5	5	−0.015 556	9	8	−0.003 962
6	2	0.788 211	9	9	−0.000 408
6	3	0.262 737	10	2	64.675 700
6	4	0.109 030	10	3	21.558 600
6	5	0.028 496	10	4	7.778 860
6	6	0.006 982	10	5	2.054 770
7	2	−2.125 640	10	6	0.470 371
7	3	−0.708 347	10	7	0.089 632
7	4	−0.279 693	10	8	0.014 211
7	5	−0.073 369	10	9	0.001 776
7	6	−0.016 452	10	10	0.000 149
7	7	−0.002 759			
8	2	6.219 840			
8	3	2.073 280			
8	4	0.788 264			
8	5	0.207 745			

For comparison purposes we now evaluate expression (16) to reproduce the first-order perturbation result of C. Smith. In so doing, we must evaluate

$$E/Z^2 = -\tfrac{1}{2}(1/n^2) + Z^{-1} \sum_{i=1}^{\infty} B_{(i)} \lambda^i \langle r^{i-1} \rangle_{n,l} . \quad (60)$$

The values for $\langle r^j \rangle$ can be found explicitly in many standard quantum-mechanics textbooks to $j = 4.$[15, 16] By using these values and the $B_{(i)}$ of Eq. (9), an explicit expression for Eq. (60) can be written in the leading terms as

$$E/Z^2 = -\tfrac{1}{2}(1/n^2) + \epsilon - \tfrac{1}{4}[3n^2 - l(l+1)]\epsilon^2 + (n^2/12)[5n^2 - 3l(l+1) + 1]\epsilon^3$$

$$- (n^2/192)[35n^2(n^2-1) - 30n^2(l+1)(l-1) + 3(l+2)(l+1)(l-1)]\epsilon^4 + \cdots . \quad (61)$$

For the state n, $l = n-1$, Eq. (61) reduces to

$$E_{n,n-1}/Z^2 = -\tfrac{1}{2}(1/n^2) + \epsilon - \tfrac{1}{4}n(2n+1)\epsilon^2 + (n^2/12)(2n+1)(n+1)\epsilon^3$$

$$- (n^3/192)\{(n+1)[35n(n-1) + 3(n-2)] - 30n^2(n-2)\}\epsilon^4 + \cdots . \quad (62)$$

Comparing Eq. (62) with the perturbation-theory result of Eq. (57), we see that the energy coefficients of the fourth order differ as expected (see Sec. II).

Now that the stretched solution, namely $\Psi(\xi)$, has been obtained for any n, $l = n-1$, we wish to examine the behavior of the basic asymptotic solution of Eq. (29) as compared to $\Psi(\xi)$. For the case of any n, $l=n-1$, with $C_1=1$ and $C_2=-(n/4)(2n+1)$, Eq. (29) reduces to

$$\psi(r)=r^{n-1}\{\exp[-Zr/n+Y(r)]\}$$
$$\times\{1+Z^{-1}[\tfrac{1}{2}n^2(e^{-\lambda r}/r-ne^{-2\lambda r}/r)+n^3\lambda(W-B)-\lambda^2n^2/4+\tfrac{1}{2}n^2(n-1)/r]+\cdots\}, \tag{63}$$

where $W(r)$ and $B(r)$ are given by Eqs. (24) and (28) and $Y(r)$ is given by

$$Y(r)=n\sum_{i=2}^{\infty}(-1)^i\lambda^ir^i/i\,i! \tag{64}$$

In order to relate the stretched solution to the basic asymptotic solution, we invoke the "matching principle" so often used in fluid mechanics.[17] For convenience in stating this principle, let us use the following nomenclature. Let $\psi_j(Z,r)$ represent the truncated basic asymptotic expansion after the Z^{-j} term and consider $\Psi_m(\epsilon,\xi)$ to be the truncated expansion after ϵ^m. One re-expresses $\psi_j(Z,r)$ in terms of the variables ϵ, ξ and $\Psi_m(\epsilon,\xi)$ in terms of Z, r. We then obtain

$$\psi_j(Z,r)\to\tilde{\psi}_j(\epsilon,\xi) \tag{65}$$

and
$$\Psi_m(\epsilon,\xi)\to\tilde{\Psi}_m(Z,r). \tag{66}$$

Truncating $\tilde{\psi}_j$ after mth order and $\tilde{\Psi}_m$ after jth order, we then define

$$[\tilde{\psi}_j(\epsilon,\xi)]_T=\tilde{\psi}_j \quad \text{(truncated expansion after } \epsilon^m \text{ term)} \tag{67}$$

and
$$[\tilde{\Psi}_m(Z,r)]_T=\tilde{\Psi}_j \quad \text{(truncated expansion after } Z^{-j} \text{ term).} \tag{68}$$

The "matching condition" is then stated as

$$[\tilde{\psi}_j]_T=[\tilde{\Psi}_m]_T. \tag{69}$$

Substituting $\xi=Zr$ in Eq. (63), one finds $\psi(r,Z)$ in terms of the stretched variables to be

$$\tilde{\psi}(\epsilon,\xi)=\xi^{n-1}e^{-\xi/n}\{1+\tfrac{1}{2}n^2(2n-1)\epsilon+\tfrac{1}{4}n\xi^2\epsilon^2+[(n^2/24)(6n^2-5n-2)\xi^2-(n/18)\xi^3]\epsilon^3+O(\epsilon^4)\}. \tag{70}$$

Comparing to the stretched solution which was found to be (including constants of integration γ_k)

$$\Psi(\epsilon,\xi)=\xi^{n-1}e^{-\xi/n}\{1+\gamma_1\epsilon+(\gamma_2+\tfrac{1}{4}n\xi^2)\epsilon^2+[\gamma_3+(n^2/24)(6n^2-5n-2)\xi^2-(n/18)\xi^3]\epsilon^3+O(\epsilon^4)\}. \tag{71}$$

We see that by choosing $\gamma_1=\frac{1}{2}n^2(2n-1)$, $\gamma_2=0$, and $\gamma_3=0$, the matching condition of Eq. (69) is satisfied to third order in ϵ. Thus for our problem, $j=1$ and $m=3$ are the appropriate values which satisfy the matching condition. In carrying the basic expansion to first order in $1/Z$, we have accounted for three orders of the perturbation-theory solution. It then follows for this nonsingular problem that the perturbation-theory result to any order can be obtained by keeping higher-order terms in the basic asymptotic expansion and re-expressing them in terms of stretched variables.

Since numerical calculations have been done for the $2S$ state, we have also obtained the perturbation-theory result explicitly for this case for purposes of comparison. The results obtained to fifth order are

$$\Psi=e^{-\xi/2}\{(\xi-2)+\gamma_1(\xi-2)\epsilon+(-2\xi^2+\tfrac{1}{2}\xi^3)\epsilon^2+[(\tfrac{14}{3}-2\gamma_1)\xi^2+(-\tfrac{7}{9}+\tfrac{1}{2}\gamma_1)\xi^3-\tfrac{1}{9}\xi^4]\epsilon^3$$
$$+[(\tfrac{14}{3}\gamma_1-\tfrac{121}{6})\xi^2+(-\tfrac{7}{9}\gamma_1+\tfrac{121}{36})\xi^3+(-\tfrac{19}{72}\gamma_1-\tfrac{121}{36})\xi^4+\tfrac{7}{48}\xi^5]\epsilon^4+[(124-\tfrac{121}{6}\gamma_1)\xi^2$$
$$+(-\tfrac{62}{3}+\tfrac{121}{36}\gamma_1)\xi^3+(\tfrac{11}{15}-\tfrac{19}{72}\gamma_1)\xi^4+(-\tfrac{106}{225}+\tfrac{7}{48}\gamma_1)\xi^5-\tfrac{53}{900}\xi^6]\epsilon^5+\cdots\} \tag{72}$$

and
$$E/Z^2=\tfrac{1}{8}+\epsilon-3\epsilon^2+7\epsilon^3-\tfrac{121}{4}\epsilon^4+186\epsilon^5+\cdots. \tag{73}$$

Upon multiplying Eqs. (57) and (73) by -2, the energy expansions, to fifth order in ϵ, for the $1S$, $2S$, and $2P$ states are put into the convenient form:

$$-2E_{1S}/Z^2 = 1 - 2\epsilon + (\tfrac{3}{2})\epsilon^2 - \epsilon^3 + (\tfrac{11}{8})\epsilon^4 - (\tfrac{21}{8})\epsilon^5 , \tag{74}$$

$$-2E_{2S}/Z^2 = (\tfrac{1}{4}) - 2\epsilon + 6\epsilon^2 - 14\epsilon^3 + (\tfrac{121}{2})\epsilon^4 - 372\epsilon^5 , \tag{75}$$

$$-2E_{2P}/Z^2 = (\tfrac{1}{4}) - 2\epsilon + 5\epsilon^2 - 10\epsilon^3 + (\tfrac{95}{2})\epsilon^4 - 138\epsilon^5 , \tag{76}$$

One observes from these results that a lower l state gives rise to a lower energy eigenvalue for the same principal quantum number $(|E_{2S}| > |E_{2P}|)$. Thus for the screened Coulomb potential problem, we obtain the well-known result that l degeneracy is no longer present.

TABLE II. The first-five partial sums of the large-Z energy expansion [Eqs. (74), (75), and (76)] are given for the 1S, 2S, and 2P energy states, and compared with the numerical results of Rouse (last column).

ϵ	S_0	S_1	S_2	S_3	S_4	S_5	$-2E_R/Z^2$
			1-S State				
0.001 996	1.000 000	0.996 008	0.996 014	0.996 014	0.996 014	0.996 014	0.996 012
	0.500 000	0.998 004[a]	0.996 011	0.996 014	0.996 014	0.996 014	
0.019 610	1.000 000	0.960 780	0.961 357	0.961 349	0.961 349	0.961 349	0.961 357
	0.500 000	0.980 390	0.961 068	0.961 353	0.961 349	0.961 349	
0.111 418	1.000 000	0.777 164	0.795 785	0.794 402	0.794 613	0.794 568	0.794 496
	0.500 000	0.888 582	0.789 474	0.795 093	0.794 508	0.794 591	
0.201 711	1.000 000	0.596 579	0.657 610	0.649 403	0.651 679	0.650 802	0.650 994
	0.500 000	0.798 289	0.627 094	0.653 505	0.650 540	0.651 240	
0.340 808	1.000 000	0.318 383	0.492 609	0.453 024	0.471 574	0.459 504	0.464 601
	0.500 000	0.659 192	0.405 497	0.472 817	0.462 299	0.465 539	
0.412 337	1.000 000	0.175 326	0.430 359	0.360 252	0.400 000	0.368 711	0.382 549
	0.500 000	0.587 663	0.302 842	0.395 306	0.380 306	0.384 355	
0.524 027	1.000 000	−0.048 053	0.363 853	0.219 953	0.323 638	b	0.274 604
	0.500 000	0.475 973	0.157 899	0.291 902	0.271 795		
0.722 204	1.000 000	−0.444 408	0.337 960	−0.038 727	0.335 335	•••	0.130 395
	0.500 000	0.277 796	−0.053 224	0.149 617	0.148 304		
0.895 596	1.000 000	−0.791 192	0.411 946	−0.306 404	•••	•••	0.050 131
	0.500 000	0.104 404	−0.189 623	0.052 771			
			2-S State				
0.000 996	0.250 000	0.248 008	0.248 914	0.248 014	0.248 014	0.248 014	0.248 012
	0.125 000	0.249 004	0.248 010	0.248 013	0.248 014	0.248 014	
0.009 619	0.250 000	0.230 762	0.231 317	0.231 305	0.231 505	0.231 305	0.231 306
	0.125 000	0.240 381	0.231 040	0.231 311	0.231 305	0.231 305	
0.050 448	0.250 000	0.149 104	0.164 374	0.162 577	0.162 968	0.162 847	0.162 880
	0.125 000	0.199 552	0.156 739	0.163 475	0.162 772	0.162 908	
0.085 321	0.250 000	0.079 357	0.123 036	0.114 340	0.117 546	0.115 865	0.116 476
	0.125 000	0.164 679	0.101 197	0.118 688	0.115 944	0.116 706	
0.131 586	0.250 000	−0.013 172	0.090 717	0.058 820	0.076 958	0.062 283	0.069 259
	0.125 000	0.119 414	0.038 773	0.074 769	0.067 888	0.069 620	
0.182 405	0.250 000	−0.114 810	0.084 820	−0.000 145	0.066 828	•••	0.033 272
	0.125 000	0.067 595	−0.014 995	0.042 337	0.033 416		
0.228 009	0.250 000	−0.206 017	0.105 910	−0.060 041	0.103 475	•••	0.012 997
	0.125 000	0.021 991	−0.050 054	−0.022 934	0.021 716		

TABLE II (*cont*)

ϵ	S_0	S_1	S_2	S_3	S_4	S_5	$-2E_R/Z^2$
			2-*P* State				
0.000 996	0.250 000	0.248 008	0.248 013	0.248 013	0.248 013	0.248 013	0.248 024
	0.125 000	0.249 004	0.248 010	0.248 013	0.248 013	0.248 013	
0.009 617	0.250 000	0.230 766	0.231 228	0.231 219	0.231 220	0.231 220	0.231 221
	0.125 000	0.240 383	0.230 997	0.231 224	0.231 220	0.231 220	
0.050 187	0.250 000	0.149 627	0.162 220	0.160 956	0.161 257	0.161 213	0.161 197
	0.125 000	0.199 813	0.155 923	0.161 588	0.161 106	0.161 235	
0.084 017	0.250 000	0.081 967	0.117 261	0.111 330	0.113 697	0.113 119	0.112 941
	0.125 000	0.165 983	0.099 613	0.114 295	0.112 513	0.113 408	
0.126 505	0.250 000	−0.003 011	0.077 007	0.056 762	0.068 927	0.064 457	0.064 015
	0.125 000	0.123 495	0.036 999	0.066 885	0.062 845	•••	
0.167 780	0.250 000	−0.085 560	0.055 191	0.007 960	0.045 601	0.027 253	0.028 150
	0.125 000	0.082 220	−0.015 185	0.031 576	0.026 781	•••	

[a] Bottom row indicates values obtained using averaging technique of Ref. 18.

[b] These terms are deleted since the series begins to diverge at these partial sums.

For various values of ϵ, Table II shows the perturbation-theory results of Eqs. (74), (75), and (76) as compared to the numerical results of Rouse.[7] It is seen that for small values of $\epsilon(\epsilon \sim 10^{-3})$ the perturbation-theory results agree with the numerical calculations to five significant digits, whereas for large values of $\epsilon(\epsilon \sim 10^{-1})$ significant accuracy is lost. However, by using a suitable averaging technique[18] which leads to another asymptotic series, each term of which represents an average of two consecutive terms in the original asymptotic expansion, it is seen that two to three place accuracy can be achieved for very large values of ϵ. For example, for the ground-state energy, using $\epsilon = 0.412\,337$, the agreement with Rouse using the averaged summation technique is to within 0.47%. The original summation value is only good to 3.75%. As we go to higher values of n, for a given ϵ, the perturbation theory naturally gets worse. For the 2S state using a value of $\epsilon = 0.182\,405$ the averaged summation gives a result to within 0.43% of Rouse's numerical calculation, a result which represents a considerable improvement over the original summation result.

We note that for the three states in which computations were performed, the total time consumed on the Burroughs 5500 digital computer to find the perturbation-theory wave functions and energy coefficients for all the values of ϵ listed in Tables I, II, and III was less than 2 min.

An additional comparison of the perturbation-theory tenth-order [Eq. (59)] results for the 1S state with the variational calculations of G. Harris[5] and the numerical work of V. Bonch-Bruevich[8] *et al.* is made in Table III for typical semiconductor values of λ. Since the quoted results of G. Harris are due to a three parameter variational wave function, they must give an upper bound to the correct energy value. Thus for $\epsilon = 0.250$ in Table III it is seen that the numerical result of V. Bonch-Bruevich falls outside this upper bound and therefore must be less accurate. Our results agree with G. Harris' to four significant digits using the averaged summation technique and are certainly superior to those of Bonch-Bruevich. Note also that in Table III for a value of $\epsilon = 0.8$ (hardly what one would consider a normal perturbation parameter value) a third-order result gives agreement with Harris to 14.6%.

Plotting the partial sums of Table III for $\epsilon = 0.3$ and $\epsilon = 0.4$, Fig. 1 illustrates the oscillatory and asymptotic behavior of the energy expansion. Since the energy expansions are oscillatory in nature, it then follows that, in the limit $\epsilon \to 0$, successive partial sums set upper and lower bounds on the true energy values.[19] In particular, examination of Fig. 1 for $\epsilon = 0.4$ indicates that the energy expansion begins to diverge at the partial sum S_8 (S_j denotes the sum of the first j terms). In fact, for any ϵ, the perturbation-theory expansion for the screened Coulomb potential is observed to be nonconvergent when carried to sufficiently high order. In this regard, in order to have a convergent perturbation-theory expansion within some radius of convergence ϵ_0, bound states for the perturbed problem must exist for any $|\epsilon| < \epsilon_0$. Moreover, since the screened Coulomb potential with $\epsilon = -|\epsilon|$ does not give rise to bound states (tunneling is present), it necessarily follows that the energy expansions are divergent but asymptotic.

TABLE III. Tabulation of calculated perturbation-theory (PT) energies [Eq. (59)] compared with the variational calculations of G. Harris (H) and the numerical calculations of V. Bonch-Bruevich *et al.* (B).

ϵ	$-2E_{\mathrm{PT}}/Z^2$	$-2E_H/Z^2$	$-2E_B/Z^2$
0.150	0.730 922[a] 0.730 921	0.730 920	...
0.250	0.582 039 0.581 821	0.581 830	0.581 25
0.300	0.516 637 0.515 285	0.515 270	...
0.400	0.383 227 0.396 147	0.396 750	...
0.500	0.253 904 0.294 921	0.296 230	0.296 20
0.600	0.302 200 0.213 100	0.212 660	...
0.667	0.308 643 0.172 838	...	0.164 80
0.700	0.322 138 0.157 069	0.143 660	...
0.800	−0.152 000 0.104 000	0.089 40	...

[a] For values of $0<\epsilon\leq 0.3$ the perturbation theory results are given to tenth order in ϵ, whereas for $\epsilon=0.4$, 0.5, and $0.6\leq\epsilon\leq 0.8$ the results are given, respectively, to eighth, fifth, and fourth order in ϵ only since the series [Eq. (59)] begins to diverge after these orders.

IV. THE NUMBER OF BOUND STATES IN A SCREENED COULOMB POTENTIAL

Recently there has been some controversy over whether there exists an infinite or finite number of bound states in a screened Coulomb potential. C. A. Rouse has asserted there are an infinite number of bound states. Other authors[8,20] claim there are a finite number of bound states but their arguments lack mathematical rigor. Actually, the question is easily resolved using the following theorem derived independently by J. Schwinger[13] and V. Bargmann[12] which states that "it is a fundamental property of any spherical potential $V(r)$ for which

$$\int_0^\infty dr\, r|V(r)| \tag{77}$$

exists there are only a finite number of bound states." The result of the proof is stated mathematically in terms of the inequality

$$N_l<[1/(2l+1)]\int_0^\infty dr\, r|V(r)|, \tag{78}$$

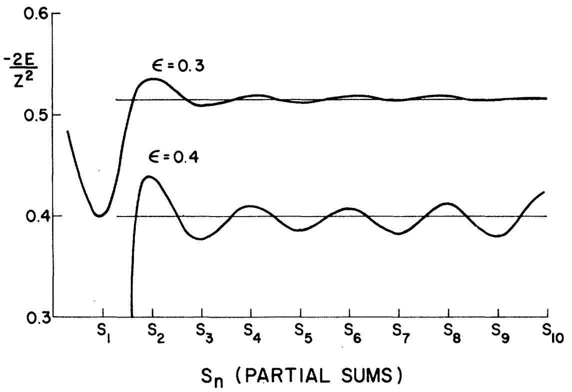

FIG. 1. The 1S energy state $(-2E/Z^2)$ is illustrated to tenth order in the perturbation theory for $\epsilon=0.3$ and $\epsilon=0.4$.

where N_l is the number of bound states with angular momentum l. When $V(r)=-Ze^{-\lambda r}/r$ is used in Eq. (78), we obtain

$$N_l<[1/(2l+1)]ZD/a_0, \tag{79}$$

where $D=1/\lambda$ and is usually referred to as the Debye screening radius. For S states, the resulting relation is

$$n^*<n_U^*=ZD/a_0, \tag{80}$$

where n_U^* represents an upper bound to the number of bound states. A close look at the proof by J. Schwinger which utilizes the integral form of the Schrödinger equation for the canonical problem of variable potential [$U(r)=\alpha V(r)$ where α is a variable constant] and zero energy indicates that the upper limit may be much higher (see Table IV) than the actual cutoff level. It should be noted that Rouse in his work[7] studied a much wider class of potentials than that given by Eq. (1) and for all the other forms of potential considered, his conclusion that there are an infinite number of bound states is born out anew by direct application of Eq. (78).

A lower bound on the value of n^* for the last allowed bound state for the screened Coulomb potential may be found by following a procedure analogous to that of H. Margenau and M. Lewis.[6] We perform a variational calculation using general hydrogenic state wave functions for arbitrary n and $l=n-1$ and with variation parameter $\mathfrak{Z}$ (instead of Z). We then minimize the variational energy E_v using

$$\partial E_v(n,\mathfrak{Z})/\partial\mathfrak{Z}=0. \tag{81}$$

We observe that the variational wave function with $l=n-1$ is orthogonal to all the *exact* wave functions corresponding to states of lower energy

TABLE IV. Calculation of the Debye radius from Eq. (87), and of n_L^* from Eq. (86) and n_U^* from Eq. (80) for various values of T and N_e. $R(\;)$ indicates the results for T and N_e reported by C. Rouse in Ref. 27, whereas $I(\;)$ represents the resulting T and N_e calculated by G. Ivanov-Kholodnyi *et al.* in Ref. 33.

	T (°K)	N_e (electrons/cc)	D (cm)	n_L^*	n_U^*
R(Photo)	5750	7.44×10^{12}	1.92×10^{-4}	164	36 282
R(Photo)	5150	5.44×10^{12}	2.13×10^{-4}	173	40 251
R(Chrom)	5150	1.51×10^{11}	1.28×10^{-3}	422	241 882
I (Chrom)	5000	1.00×10^{11}	1.55×10^{-3}	465	292 904

since all such exact wave functions contain Legendre polynomials with values of l ranging from 0 to $n-2$ while our variational wave function has an angular dependence given by a Legendre polynomial with $l=n-1$. Therefore E_v must be an upper bound to the n, $l=n-1$ state.[14] For a given n, states of higher l have a larger energy. Therefore E_v gives an upper bound to all energies of the nth level. We determine the last bound state n_v from

$$E_v(n_v,\mathfrak{Z})=0. \tag{82}$$

Combining Eq. (81) and Eq. (82), we eliminate $\mathfrak{Z}$, obtaining the result (details can be found in the Appendix)

$$(n_v)^2 \gtrsim 0.736ZD/a_0. \tag{83}$$

From the foregoing discussion it follows that the exact energy $E(n_v)$ for any lth level of a state with principal quantum number n_v satisfies

$$E(n_v) < E_v(n_v,\mathfrak{Z}) = 0. \tag{84}$$

From the way we have chosen n_v, $E_v(n_v+1,\mathfrak{Z})$ with $\mathfrak{Z}$ determined by Eq. (81) is certainly greater than zero. However, since $E_v(n_v+1,\mathfrak{Z})$ is an upper bound to $E(n_v+1)$, the fact that its greater than zero does not preclude $E(n_v+1)$ from being less than zero in which case the n_v+1 state is a bound state. It then follows from Eq. (84) that n_v represents a lower bound to the principal quantum number of the last occupied energy state n^*. Therefore we obtain

$$(n^*)^2 \geqslant (n_v)^2 \gtrsim (n_L^*)^2, \tag{85}$$

where

$$(n_L^*)^2 = 0.736ZD/a_0. \tag{86}$$

V. DISCUSSION OF SPECTRAL CUTOFFS AND PHYSICAL PROCESSES IN PLASMAS

The question of the number of bound states of a hydrogen atom immersed in a plasma is of importance in understanding the disappearance of spectral lines originating from energy levels with high principal quantum numbers. This phenomenon has been shown to occur both in laboratory discharge tubes[21, 22] and in solar observations.[23–27] In Ref. 22, the Balmer series is shown to have an abrupt cutoff at principal quantum number $n=20$. For observations in the photosphere, the various series appear to terminate at about $n=16$. For observations in the chromosphere, Mitchell,[24] using data obtained during eclipses finds lines originating from n as high as 37 in the Balmer series and from $n=40$ in the Paschen series. R. N. Thomas and R. G. Athay[25] find lines up to $n=31$ in the Balmer series of the chromosphere. Thus there appears to be some difference in the maximum bound state observed in the chromosphere by the authors cited. G. S. Ivanov-Kholodyni and G. M. Nikolskii[26] referring to other[23] chromospheric data state that "near the series limit the lines do not merge because of their broadening and convergence, but instead they disappear because of a rapid fall in intensity. As a result, we fail to observe the last few lines of the series even though their half-widths are smaller than the separation between them." We will refer to these observations later. The existence of a finite number of bound states is also of importance in order that the hydrogen partition function be finite.[28]

Using our results for n_L [Eq. (85)] and the expression for the Debye length[29]

$$D=6.91(T/N_e)^{1/2}\text{cm}, \tag{87}$$

where T is the temperature in °K and N_e is the electron density in cm^{-3} we evaluate n_L and n_U for the appropriate data in the chromosphere and photosphere in Table IV. Comparing these with the experimental values, it is observed that the results of the screened potential model are high by an order of magnitude. It is, therefore, concluded that the effect of electron screening alone in the screened Coulomb potential model does not adequately account for the rapid fall in intensity of the hydrogen spectral lines in this temperature and density region. As we go to higher electron densities ($N_e\sim10^{20}\ \text{cm}^{-3}$) such as occur in the plasma focus[30] and laser spark devices,[31] Debye shielding may become the dominant effect[6] in causing the spectral emission cutoffs. Of couse, the question of the validity of Debye theory then comes into play (see Sec. I).

In our use of the screened Coulomb model to describe a hydrogen atom embedded in a plasma, we have ignored the effect of the electric fields produced by the free protons (and electrons) on the atom. Such fields lower the maximum of the potential energy curve below zero and tunneling and ionization can occur for a high lying level. The ionization effect of a neighboring proton has been studied both by Unsöld[32] in a static approach and by G. S. Ivanov-Kholodnyi *et al.*[33] (IK) who obtain an expression for the fraction of time (Γ_n) spent by level n above the potential barrier. For $\Gamma_{n^*}=1$, the electron is ionized. They also show that including the effects of tunneling decreases n^* by 1. The expressions derived are, respectively,

$$\log_{10}N_e = 21.88 - 6\log_{10}n^*_{\text{Unsöld}} \tag{88}$$

and
$$\log_{10}N_e = 21.65 - 6\log_{10}(n^*_{\text{IK}}+1). \tag{89}$$

For the data in the chromosphere (see Table IV for data) they both give values of n^* of about 60 which appears to be much too large. The effect of the external field is also to cause a Stark Effect broadening of the levels which leads to a merging of the upper levels. This effect has been studied, using the first-order Stark Effect result for the maximum displacement of a level from its unperturbed energy by D. R. Inglis and E. Teller[34] (IT) and they obtain the result

$$\log_{10}N_e = 23.26 - 7.5\log_{10}n^*_{\text{IT}}, \tag{90}$$

where the field due to the electrons is also included. In fact, this equation was shown to give very good agreement with Mohler's experimental results. If we apply it to the chromospheric data, we obtain the value $n^*=41$ in perfect agreement with Mitchell's data. However, in the photosphere, values of 22 and 26 are found for the two sets of data given. Thus the error in n^* for the photosphere is far more than the 15% attributed to the Inglis-Teller formula by H. R. Griem.[35] Also this merging effect which is the basis of the Inglis-Teller formula does not appear to occur in the data of Schluter[22] or that of Ref. 26 as mentioned earlier.

In a future paper, a more systematic perturbation treatment including electric field effects and Debye screening simultaneously will be performed in the hope of better explaining the existing data. Certainly more experimental work is called for – especially on the dependence of n^* on temperature which is not at all included in the Inglis-Teller formula. Although this dependence is known to be weak, its functional form represents an important test of the validity of any accurate theory.

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APPENDIX. CALCULATION OF n_v

To obtain an upper bound for the n, $l=n-1$ state of the screened Coulomb potential, we choose as our variational trial wave function a general hydrogenic n, $l=n-1$ state wave function for arbitrary n and with variable charge $\mathfrak{Z}$ of the form

$$\psi_v = Cr^{n-1}e^{-\mathfrak{Z}r/n}Y_{n-1,m}(\theta,\phi). \tag{1A}$$

We then find the variational energy E_v to be

$$E_v(n,\mathfrak{Z}) = \mathfrak{Z}^2/2n^2 - Z\mathfrak{Z}[\mathfrak{Z}/(\mathfrak{Z}+nK)]^{2n}/n^2, \tag{2A}$$

where $K=\lambda/2$. Using the minimization condition

$$\partial E_v(n,\mathfrak{Z})/\partial\mathfrak{Z} = 0, \tag{3A}$$

we obtain the result

$$\mathfrak{Z} - Z\left(\frac{\mathfrak{Z}}{\mathfrak{Z}+nK}\right)^{2n}\left[1+2n\left(1-\frac{\mathfrak{Z}}{\mathfrak{Z}+nK}\right)\right] = 0. \tag{4A}$$

To find the last bound state with angular momentum $l=n-1$, we demand that

$$E_v(n_v,\mathfrak{Z}) = 0. \tag{5A}$$

Eliminating $\mathfrak{Z}$ from Eq. (5A) using Eq. (4A) with n set equal to n_v we obtain

$$(n_v)^2 = (2Z/\lambda)F, \tag{6A}$$

where

$$F = 2n_v[(2n_v-1)^{2n_v-1}/(2n_v)^{2n_v}]. \tag{7A}$$

To obtain a good estimate of F for n_v large we take logarithms of both sides of Eq. (7A) and then use Stirling's approximation giving

$$\ln F \simeq \ln(2n_v) + \ln[(2n_v-1)!] + (2n_v-1) - \ln[(2n_v)!] - 2n_v \tag{8A}$$

which results in

$$F \gtrsim e^{-1} \tag{9A}$$

and therefore

$$(n_v)^2 \gtrsim 0.736\, ZD/a_0 , \tag{10A}$$

where we have used $\lambda = a_0/D$. The reason for the greater than sign is that the use of Stirling's approximation gives a result for F [Eq. (9A)] which is below the exact value of Eq. (7A). Including the next term in the expansion for $\log x!$ would lead to a multiplying factor $[2n_v/(2n_v - 1)]^{1/2}$ on the right-hand side of Eq. (9A). For n_v's of astrophysical interest this factor has a value very close to 1.

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