

## Finite Electronic Partition Function from Screened Coulomb Interactions\*

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A definition of a finite partition function for bound electronic states is presented for a hydrogenic ion, with the associated problems of the fall in intensity of spectral lines and the lowering of the effective ionization potential. The partition function is partly based on numerical solutions of the Schrödinger equation (SE) with the complete screened Coulomb potential (CSCP), where the  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  states are considered. The CSCP is given by

$$V(r) = V_i(r) = -Ze^2 \left( \frac{1}{r} - \frac{1}{D+A} \right), \quad 0 \leq r \leq A$$

$$= V_o(r) = -Ze^2 \frac{D}{D+A} \frac{\exp[(A-r)/D]}{r}, \quad r \geq A$$

where  $D$  is the screening radius and  $A$  is the mean minimum radius of the ion atmosphere. The standard transformations  $x = 2Zr/\lambda a_0$  and  $E_\lambda = -Z^2 \mu e^4 / 2\hbar^2 \lambda^2$ , where  $\lambda$  is the CSCP quantum number, yield the standard form of the SE equation with  $\lambda$  in place of  $n$ . The numerical solutions are obtained with a nonlinear method that is both accurate and stable. Since the accurate numerical solutions do not yield an explicit maximum-bound principal quantum number, another property of the screened solutions is used to define a decreasing probability of an electron occupying a particular Coulomb eigenstate. The quantity derived is the relative probability of the screened to the unscreened Coulomb state, given by

$$\Phi_{n,l} = \frac{\lambda^{2l+1} N(\lambda, l, d, a)}{n^{2l+1} N(n, l)},$$

where the  $N$ 's are the normalizations in  $x$  space, calculated with variations of  $D$  and  $A$  only. This relative occupation probability of the bound state is used to modify the Boltzmann factor in the standard expression for the electronic partition function. Correlations with observations are discussed: there is excellent agreement with the fall in intensity of hydrogen lines in the solar atmosphere and good agreement with lines from laboratory hydrogen at 21°K. The effective ionization potential of hydrogen is calculated using the maximum detected level of hydrogen observed in the solar chromosphere. A simple analytical fit to the  $\Phi$  function and a useful approximate analytical expression for the screened Coulomb partition function are given.

### 1. INTRODUCTION

THE standard electronic partition function for bound states is given by

$$Q_{eb} = \sum_{i,j} \exp[-E_{i,j}/kT],$$

where the  $E_{i,j}$  are the energies of the bound states. From Coulomb interactions for a hydrogenic ion (neutral hydrogen will be an "ion" with zero charge),

$$Q_{eb} = \sum_n 2n^2 \exp[-E_n'/kT], \quad (1.1)$$

where  $n$  is the principal quantum number (q.n.);  $2n^2$  represents the degeneracies of the states; and  $E_n'$  is the energy of the state relative to the ground-state energy taken as zero, i.e.,  $E_n' \sim 1 - (1/n^2)$ .

Unfortunately, (1.1) diverges as  $n \rightarrow \infty$ . Relative to using screened Coulomb (SC) interactions of the bound electron to define a finite electronic partition function, the pioneering work of Ecker and Weizel<sup>1</sup> has been

followed by others<sup>2,3</sup> where a maximum bound principal quantum number, referred to as  $g^*$ , was the quantity sought. However, accurate numerical solutions of the Schrödinger equation (SE)<sup>4</sup> with the complete screened Coulomb (or attractive Yukawa) potential (CSCP)<sup>5</sup> show that, with a finite screening radius,  $D > 0$ , SC interactions do not yield a finite number of bound states.

The quantity that does decrease as  $D \rightarrow 0$  is the magnitude of the normalization integral when calculated with all other initial values remaining constant, except those depending on the quantum number itself. With this in mind, we will derive a quantity called the relative occupation probability of a bound electronic state, that will be equal to the ratio of the relative total probability of a state with finite screening radius, to that with an infinite screening radius (the standard Coulomb interaction). This will be used to modify the

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<sup>1</sup> G. Ecker and W. Weizel, *Ann. Physik* **17**, 126 (1956).

<sup>2</sup> H. Margenau and M. Lewis, *Rev. Mod. Phys.* **31**, 569 (1959); G. M. Harris, *Phys. Rev.* **125**, 1131 (1962); G. Ecker and W. Kröll, *Phys. Fluids* **6**, 62 (1963); C. R. Smith, *Phys. Rev.* **134**, A1235 (1964).

<sup>3</sup> C. A. Rouse, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (SERMA, Paris, 1964), Vol. I.

<sup>4</sup> C. A. Rouse, *Bull. Am. Phys. Soc.* **11**, 356 (1966); *J. Math. Phys.* **46**, 63 (1967).

<sup>5</sup> C. A. Rouse, *Phys. Rev.* **159**, 41 (1967).

Boltzmann factor—as is one of the common practices<sup>6</sup>—in the definition of a finite electronic partition function.

A recent survey of the problems of the partition function cutoff and the lowering of the ionization potential in plasmas—with a brief bibliography—are given in the appendix of the paper by Armstrong *et al.*<sup>7</sup> The reader is referred to this report (and its references) for discussions of other approaches to the problem of a finite electronic partition function (p.f.).

Section II of this report will discuss the definition of a finite electronic p.f. based upon the changes in the relative charge probability densities and the resulting changes in the relative normalizations of the screened, bound-state wave functions. Expressions for the *effective* maximum bound state and the maximum detected level will be derived. Section III will discuss correlations of the present solutions with observations of the fall in intensity of hydrogen lines (an unsolved problem), and the effective ionization potential of hydrogen. Finally, the Summary and Conclusions are given in Sec. IV.

## II. A FINITE SCREENED COULOMB ELECTRONIC PARTITION FUNCTION

It has been shown that the CSCP and Coulomb potential yield the same number of bound states.<sup>5</sup> However, what the CSCP solutions do yield that will be useful is the relative total probability of the state which varies with changes in  $D$  and  $A$ . In what follows, spin degeneracy will be omitted since it is well known to be 2.

### A. Brief Review of the Numerical Solutions

The complete screened Coulomb potential is given by<sup>8-10</sup>

$$V(r) \begin{cases} V_i(r) = -\frac{Ze^2}{\eta_0} \left( \frac{1}{r} - \frac{1}{D+A} \right), & 0 \leq r \leq A \\ V_0(r) = -\frac{Ze^2}{\eta_0} \frac{D}{D+A} \frac{\exp[(A-r)/D]}{r}, & r \geq A \end{cases} \quad (2.1)$$

where  $D$  is the screening length,  $A$  is the mean minimum radius of the ion atmosphere<sup>3,8</sup> and  $\eta_0$  is the dielectric constant of the medium.<sup>1-10</sup>

After the standard transformations<sup>11</sup>

$$x = 2Zr/a_0\lambda \quad (2.2)$$

<sup>6</sup> R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge, England, 1936).

<sup>7</sup> B. H. Armstrong, R. R. Johnston, P. S. Kelly, H. E. DeWitt, and S. G. Brush, in *Progress in High Temperature Physics and Chemistry*, edited by C. A. Rouse (Pergamon Press, Inc., New York, 1967), Vol. 1.

<sup>8</sup> H. Margenau and M. Lewis, Ref. 2; T. L. Hill, *An Introduction To Statistical Thermodynamics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1960).

<sup>9</sup> C. A. Rouse, *Bull. Am. Phys. Soc.* **9**, 731 (1964).

<sup>10</sup> C. A. Rouse, University of California Radiation Laboratory Report No. UCRL-12461, 1965 (unpublished).

<sup>11</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Com-

and

$$E_\lambda = -\frac{Z^2\mu e^4}{2\hbar^2 \lambda^2}, \quad (2.3)$$

the radial SE for a hydrogenic ion with the CSCP (with  $\eta_0=1.0$ ) becomes

$$\frac{d^2R}{dx^2} + \frac{2}{x} \frac{dR}{dx} - \left[ \lambda v(x) + b^2 + \frac{l(l+1)}{x^2} \right] R = 0, \quad (2.4)$$

with

$$v(x) \begin{cases} v_i(x) = -\left( \frac{1}{x} - \frac{1}{d+a} \right), & 0 \leq x \leq a \\ v_0(x) = -\frac{d}{d+a} \frac{\exp[(a-x)/d]}{x}, & x \geq a, \end{cases} \quad (2.5)$$

where  $d$  and  $a$  are the values of  $D$  and  $A$  in  $x$  space, and  $b^2$  is a constant to be designated. In the standard analytic Coulomb solutions,  $b^2 = \frac{1}{4}$ .

The numerical method of solution to (2.4) is that developed by the author.<sup>4</sup> The wave function  $R(x)$  and slope of the wave function,  $m(x) = dR/dx$ , are *simultaneously* expanded in a Taylor series between space steps, to the cubic terms, with the first and higher derivatives of the slope defined by the SE. Exact initial values are obtained from a series solution of the SE without  $\exp(-x/2)$  factored out. We write the series solution in the form

$$R(x) = x^l \phi(x), \quad (2.6)$$

with

$$\phi(x) = \sum \alpha_k x^k, \quad \alpha_0 \neq 0. \quad (2.7)$$

Letting  $(i)$  indicate the  $i$ th derivative, the initial values are given by

$$R_{n,l}^{(i)}(0) \equiv i! \alpha_{i-l}, \quad (2.8)$$

where  $\alpha_{i-l} = 0$  for  $i < l$ . From the series solution, the  $\alpha$ 's are equal to

$$\alpha_1 = -\frac{\lambda}{2(l+1)} \alpha_0$$

and

$$\alpha_{t+1} = \frac{b^2 \alpha_{t-1} - \lambda \alpha_t}{(t+1)(2l+2+t)}, \quad t \geq 1,$$

with

$$b^2 = \frac{1}{4} + \frac{\lambda}{d+a}.$$

In the present work, all numerical results are carried out with  $\alpha_0 = 1.0$  for  $i=l$ . Other values of  $\alpha_0$  will be considered below through physical considerations.

As described in Refs. 4, 5, and 9, solutions were

pany, Inc., New York, 1949); H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 33; C. W. Sherwin, *Introduction to Quantum Mechanics* (Holt, Rinehart, and Winston, Inc., New York, 1960); R. B. Leighton, *Principles of Modern Physics* (McGraw-Hill Book Company, Inc., New York, 1959).

sought for wave functions with the same shapes as the Coulomb wave functions; i.e., the same number of nodes. Consequently, we will use the standard Coulomb designations,  $R_{n,l}$ , for the corresponding CSCP wave functions with  $n$  and  $l$ , the standard Coulomb principal quantum number (q.n.) and angular momentum q.n., respectively. The CSCP q.n.  $\lambda$  will be a function of  $d$  and  $a$  as well as  $n$  and  $l$ . Consequently, whenever we write  $\lambda$  alone, the dependence on  $d$  and  $a$  are implied, or,  $\lambda \equiv \lambda_{n,l} \equiv \lambda_{n,l}(d,a)$ . We will refer to the  $1s$ ,  $2s$ ,  $2p$ , etc., states and/or wave functions with screening distance  $d(D)$  and minimum ion atmosphere radius  $a(A)$ . The eigenvalues will all be given in units of rydbergs divided by  $Z^2$ , or from (2.3)

$$\epsilon_\lambda \equiv \frac{E_\lambda 2\hbar^2}{Z^2 \mu e^4} = -\frac{1}{\lambda^2}. \quad (2.9)$$

From Eq. (2.2),

$$ZD/a_0 = \lambda d/2, \quad (2.10)$$

as the transformation to  $r$  space of the values of  $d$  assumed in Eq. (2.5).

## B. Derivation of the Relative Occupation Probability of a Screened Coulomb Bound State

### Normalization of Bound-State Wave Functions

We will first derive the necessary transformation of the radial normalization integral from  $x$  space to  $r$  space. The desired  $r$ -space normalization integral—the total probability of the state—is given by

$$\int_0^\infty r^2 (R_{n,l}(r))^2 dr = 1,$$

for the normalized radial wave functions,  $R_{n,l}(r)$ . But what is usually evaluated is<sup>11</sup>

$$\int_0^\infty x^2 (R_{n,l}(x))^2 dx = N(n,l). \quad (2.11)$$

Then  $N(n,l)$  is multiplied by  $(a_0 n/2Z)^3$  in order to obtain this value for the unnormalized wave function in  $r$  space, or,

$$\int_0^\infty r^2 \left[ R_{n,l} \left( \frac{2Zr}{na_0} \right) \right]^2 dr = \left( \frac{a_0 n}{2Z} \right)^3 N(n,l).$$

However, for any radial wave function of the form  $x^s \phi(x)$ , we substitute  $R_{n,l}(x) = x^l \phi_{n,l}(x)$  into (2.11) and obtain

$$\int_0^\infty x^{2l+2} (\phi_{n,l}(x))^2 dx = N(n,l), \quad (2.12)$$

where  $s=l$ . From Eq. (2.2),  $x = 2Zr/na_0$  and  $dx = (2Zdr/na_0)$ ; hence, the transformation of the left side

of (2.12) yields

$$\int_0^\infty r^{2l+2} \left[ \phi_{n,l} \left( \frac{2Zr}{na_0} \right) \right]^2 dr = \left( \frac{a_0 n}{2Z} \right)^{2l+3} N(n,l), \quad (2.13)$$

as the desired transformation, with  $\lambda = n$  as the screened Coulomb quantum number.

However, the magnitude of  $N(\lambda,l)$  calculated with  $\alpha_0 = 1.0$  gives this value a significance that is partly mathematical. Consequently, a physical argument is needed to fix a value to  $\alpha_0$ , the second constant in the general solution. This evaluation will now be presented in the next part of this section and observational correlations discussed in Sec. III.

### Evaluation of the Second Constant in the Solution

The evaluation of the second constant in the solution of the radial SE that is required to give a quantitative usefulness to the normalization integral is based on the requirement—as a basic assumption—that the relative charge probability density in  $r$  space,  $r^2(R_{n,s}(r))^2$ , be proportional to the relative charge probability density calculated in  $x$  space,  $x^2(R_{n,s}(x))^2$ , for  $s$  states.<sup>9</sup> Write the  $s$ -state wave function in  $x$  space that has initial value,  $R_{n,s}(0) = h$ , as  $R_{n,s}(x; h)$ . Then for  $h = 1.0$ ,

$$x^2 [R_{n,s}(x; 1.0)]^2 \sim \frac{r^2}{\lambda^2} [R_{n,s}(x; 1.0)]^2 \quad (2.14)$$

or

$$\lambda^2 x^2 [R_{n,s}(x; 1.0)]^2 \sim r^2 [R_{n,s}(x; 1.0)]^2.$$

Now, for any value of  $h$  different from 1.0,  $R_{n,s}(x; h) = h R_{n,s}(x; 1.0)$ . Hence, for  $h = 1/\lambda$ ,  $\lambda R_{n,s}(x; 1/\lambda) = R_{n,s}(x; 1.0)$ . Substituting this into the right side of Eq. (2.14), there obtains

$$x^2 [R_{n,s}(x; 1.0)]^2 \sim r^2 [R_{n,s}(x; 1/\lambda)]^2.$$

Hence, the relative charge probability densities for bound states in  $r$  space will be proportional to those calculated in  $x$  space if we choose the initial magnitudes of the Coulomb-type wave functions in  $r$  space to be equal to  $1/\lambda$ . Or, more specifically, we choose the second constant in the series  $x$ -space solutions to be  $\alpha_0 = 1.0$  and then the desired  $r$ -space solutions have  $\alpha_0 = 1/\lambda$  for all  $n$  and  $l$ .

### Definition of the Relative Occupation Probability of a Screened Coulomb Bound State

With  $\alpha_0 = 1/\lambda$ , the net effect on the magnitude of the normalization, Eq. (2.13), would be to divide the right side by  $\lambda^2$ . Therefore, the presently desired transformation of  $N(\lambda, l, d, a)$  calculated in  $x$  space leads to

$$\int_0^\infty r^{2l+2} (\phi_{n,l}(r; 1/\lambda))^2 dr = \left( \frac{a_0}{2Z} \right)^{2l+3} \lambda^{2l+1} N(\lambda, l, d, a), \quad (2.15)$$

where the square root of the right side is the standard normalization factor. In the CSCP solutions, for a given  $l$  and  $a$ , as  $d \rightarrow 0$ ,  $\lambda^{2l+1}N(\lambda)$  also  $\rightarrow 0$ .

Consequently, we define the relative total occupation probability of a screened Coulomb state, using (2.15), as

$$\Phi_{n,l}(\lambda, D, A) = \frac{\lambda^{2l+1}N(\lambda, l, d, a)}{n^{2l+1}N(n, l)}. \quad (2.16)$$

In the next part of this section, we will use this as a factor in the definition of an electronic p.f. But first we will discuss the numerical values of the charge probability densities, normalization integrals, and the above relative screened probability of a state being occupied.

#### Discussion of Numerical Results

We consider the  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  states with  $a=d$ ,  $a=0$ , and  $a=d/2$ . (The  $d$  in  $3d$  will be unambiguous.) We use space steps  $\Delta x=10^{-2}$  and  $\Delta x=10^{-3}$  in order to obtain four or more significant figure accuracy as was obtained in the linear study<sup>5</sup> with  $\Delta x=10^{-4}$ . With  $a=0$ , it was found necessary to use  $\Delta x=10^{-3}$  in order to obtain this desired accuracy. The maximum values of  $x$  used ranged from 10 to 25 as discussed in Ref. 4. All calculations were done on a CDC-3800 computer. With the linear system of equations,<sup>9</sup> the previous automatic search for one q.n. took about 12-15 min on a CDC-3600 computer using  $\Delta x=10^{-4}$ . With the present cubic system of equations,<sup>4,5</sup> twelve q.n.'s can be calculated in about 4-5 min—including printer time—using  $\Delta x=10^{-2}$ .

In Ref. 9 are shown plots of  $x^2(R_{n,s}(x))^2$  versus  $r/a_0$  for the  $1s$  and  $2s$  states. They show very clearly the changes in the values of the charge probability density

as the screening distance changes—when initial values of the wave functions are equal. Table I of the present report presents detailed information for the six states considered here from solutions in which  $ZD \approx 3a_0n^2/2 = \bar{r}_n$ , the mean position of the electron in the Coulomb  $s$  states. First note that for  $s$  states with  $a=d$ , the values of  $\Phi$  (see below) are approximately equal to  $1/e$  ( $=0.3679$ ). In addition, the magnitudes of their corresponding eigenvalues ( $\sim 1/\lambda^2$ ) are also decreased approximately by a factor of  $e$ .

Tables II, III, and IV give values of  $\Phi_{n,l}(\lambda)$  for the cases  $A=D$ ,  $A=0$ , and  $A=D/2$ , respectively. Some of these values are plotted in Figs. 1 and 2 as a function of  $u=(ZD/a_0n^2)$ . With the equivalence of  $\alpha_0=1.0$  in the series solutions, Eq. (2.7), for the Coulomb wave functions, the exact normalization integrals for said wave functions,  $N(n, l)$ , are equal to 2, 2, 2, 24, 9, and 720 for the  $1s$ ,  $2s$ ,  $3s$ ,  $2p$ ,  $3p$ , and  $3d$  states, respectively. The approximate values obtained numerically for these Coulomb wave function normalizations<sup>4</sup> by the trapezoidal rule, integrating to  $x_{\max}=20$  are 1.9<sup>(6)</sup>08; 1.9<sup>(4)</sup>1664; 1.99726920; 23.9995932; 8.99242730; and 719.816311, respectively.

The general property of interest concerning  $\Phi_{n,l}$  is that for a given relationship between  $a$  and  $d$ , the function  $\Phi_{n,l}$  is essentially independent of  $n$  and  $l$  for  $u=(ZD/a_0n^2) \geq 2$ . Furthermore, at  $u=1.5$ , the spread in values of  $\Phi_{n,l}$  for the states considered is only four units in the second significant figure, as is shown in Table I, last column. However, for larger values of  $n$ , this spread at  $u=1.5$  may increase. But since the low-lying states are the most important for most applications, this relatively small spread is very convenient: It suggests the possibility of simple analytic fits. For example, for  $u > 1.5$ ,  $\exp[-1.5/u]$  falls in the upper part of the “ $\Phi$  band”; and for  $u < 1.5$ ,  $\exp[-(1.5/u)^m]$ , with

TABLE I. Details of CSCP solutions where  $ZD \approx 3a_0n^2/2$ . CP stands for Coulomb potential. The relative occupation probability  $\Phi_{n,l}(\lambda)$  is discussed in Sec. II.

| State | $V$  | $d$   | $a$   | $\lambda_{n,l}$ | $(xR)_{\max}^2$     | $(xR)_{x=d}^2$       | $ZD/a_0$ | $\Phi_{n,l}(\lambda)$ |
|-------|------|-------|-------|-----------------|---------------------|----------------------|----------|-----------------------|
| 1s    | CP   | ...   | ...   | 1.0000          | 0.54134             | 0.44808 <sup>a</sup> | ...      | 1.0000                |
|       | CSCP | 1.802 | 1.802 | 1.6648          | 0.1979 <sup>b</sup> | 0.1681               | 1.5000   | 0.3933                |
|       | CSCP | 1.214 | 0     | 2.4676          | 0.1063              | 0.1016               | 1.4978   | 0.2764                |
| 2s    | CP   | ...   | ...   | 2.0000          | 0.38187             | 0.35694              | ...      | 1.0000                |
|       | CSCP | 3.55  | 3.55  | 3.3819          | 0.1360              | 0.1289               | 6.0030   | 0.3772                |
|       | CSCP | 2.483 | 0     | 4.8332          | 0.08221             | 0.08217              | 6.0004   | 0.2866                |
| 2p    | CP   | ...   | ...   | 2.0000          | 4.68880             | 3.21246              | ...      | 1.0000                |
|       | CSCP | 3.55  | 3.55  | 3.4014          | 0.5670              | 0.3946               | 6.0374   | 0.3630                |
|       | CSCP | 3.509 | 3.509 | 3.4200          | 0.5551              | 0.3911               | 6.0004   | 0.3597                |
| 3s    | CP   | ...   | ...   | 3.0000          | 0.30460             | 0.30238              | ...      | 1.0000                |
|       | CSCP | 5.3   | 5.3   | 5.0974          | 0.1079              | 0.1076               | 13.508   | 0.3728                |
| 3p    | CP   | ...   | ...   | 3.0000          | 1.37405             | 1.26514              | ...      | 1.0000                |
|       | CSCP | 5.3   | 5.3   | 5.1114          | 0.1658              | 0.1543               | 13.545   | 0.3650                |
| 3d    | CP   | ...   | ...   | 3.0000          | 115.649             | 65.5850              | ...      | 1.0000                |
|       | CSCP | 5.3   | 5.3   | 5.13175         | 4.657               | 2.654                | 13.599   | 0.3526                |

<sup>a</sup> CP results at  $3n^2/2 (=Z\bar{r}_n/a_0)$ .

<sup>b</sup> Maximum value printed out.



The value of  $ZD/a_0n^2$  where  $\Phi=1/e$  (above) certainly suggests the definition of an *effective* maximum bound state—we will call it  $n^*$ . From Fig. 1, the expression for  $n^*$  can be written

$$n^{*2} = CZD/a_0, \quad (2.18)$$

where  $C=0.67$  from solutions with  $A=D$ ;  $C=0.54$  from solutions with  $A=0$ ; and  $C=0.59$  from solutions with  $A=D/2$ .

What one means by the maximum detected level depends on two important experimental conditions, viz., the ability to resolve closely spaced spectral lines and the composition of the sample observed. With the present state of the art, we will note that if  $\Phi \approx 0.1$ , we obtain an expression given by

$$n_m^2 = ZD/a_0, \quad (2.19)$$

which corresponds to the upper limit of the expression obtained by Ecker and Weizel<sup>1</sup> for the maximum bound

TABLE IV. Relative occupation probabilities  $\Phi_{n,l}(\lambda)$  from CSCP solutions with  $a=d/2$ , for 1s and 2s states. [ $(ZD/a_0) = (\lambda d/2)$ , with  $\lambda_{n,l}$  from Ref. 5.]

| $\left(\begin{smallmatrix} d \\ a= \\ 2 \end{smallmatrix}\right)$ | 1s               |             | 2s                |             |
|---|------------------|-------------|-------------------|-------------|
|   | $\frac{ZD}{a_0}$ | $\Phi_{1s}$ | $\frac{ZD}{4a_0}$ | $\Phi_{2s}$ |
| $10^3$  | 501              | 0.997       | 251               | 0.995       |
| $10^2$  | 50.67            | 0.974       | 25.67             | 0.948       |
| 32  | ...              | ...         | 8.694             | 0.847       |
| 30  | 15.68            | 0.915       | ...               | ...         |
| 16  | 8.694            | 0.847       | 4.721             | 0.719       |
| 8   | 4.719            | 0.721       | 2.759             | 0.545       |
| 4   | 2.749            | 0.551       | 1.782             | 0.381       |
| 3   | 2.259            | 0.478       | ...               | ...         |
| 2   | 1.769            | 0.379       | 1.283             | 0.248       |
| 1   | 1.276            | 0.238       | 1.024             | 0.149       |
| 0.5   | 1.026            | 0.138       | ...               | ...         |

principal quantum number. We will also test this expression with observations.

Next, however, we will discuss the basic quantity sought in this investigation, namely, a definition of a finite electronic partition function based upon the screened Coulomb interaction of the bound electron with the nucleus.

### C. Definition of a Finite Electronic Partition Function

The right side of Eq. (2.15) describes the total probability of an hydrogenic state that has the second arbitrary constant of the solution set equal to  $1/\lambda$ , where  $\lambda$  is the CSCP quantum number for the state. And since the change from a Coulomb state to a screened Coulomb state reflects the interaction of a bound electron with the external particles of the ion atmosphere, the relative normalization of the screened Coulomb state will be of interest in expressing the relative probability that the bound electron in the  $n, l$  state will interact

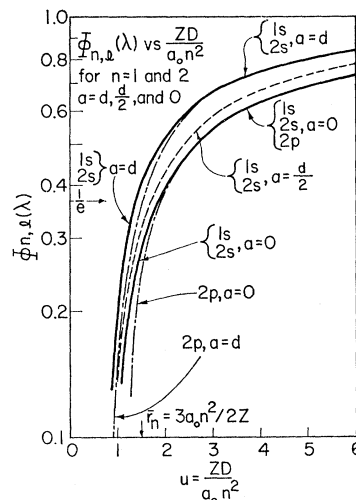


FIG. 1.  $\text{Log}_{10} \Phi_{n,l}(\lambda)$  versus  $ZD/a_0n^2$  from CSCP solutions with  $a=d, d/2$ , and 0, for 1s, 2s, and 2p states. The case  $a=d/2$  is shown only for 1s and 2s states. Note  $1/e \approx 0.368$ . The mean position of an electron in a Coulomb s state is  $3a_0n^2/2Z$ . Hence,  $u=1.5$  is the mean position for all s states. Note the small deviations of the p and d states at  $u=1.5$ .

with a neighboring particle or particles—or, a relative probability of finding an electron occupying that state. And since the screening of interest depends on the time-averaged positions of the neighboring particles, the mean effect on a system of particles will be expressed by a modification of the Boltzmann factor; or we define—for a given  $D$  and  $A$ —

$$Q_{eb}^{\text{CSCP}} = 2 \sum_{n,l} \Phi_{n,l}(\lambda, D, A) \exp[-E_{\lambda}'/kT], \quad (2.20)$$

where  $\Phi_{n,l}$  is the above function of the relative occupa-

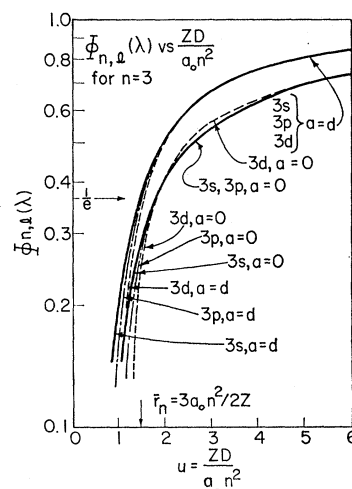


FIG. 2.  $\text{Log}_{10} \Phi_{n,l}(\lambda)$  versus  $ZD/a_0n^2$  from CSCP solutions with  $a=d$  and 0 for 3s, 3p and 3d states. The 3s solutions are near the 1s and 2s solutions shown in Fig. 1 for  $u \leq 1.5$ . The 3d curve with  $a=0$  was tested with more accurate calculations using  $\Delta x=10^{-4}$ , but the 3% difference between  $u=2$  and 3 was not altered.

tion of the CSCP state to the corresponding Coulomb state, and where the eigenvalues  $E_\lambda'$  are given relative to the ground-state energy taken as zero. From the results in Ref. 5, the standard Boltzmann factors will essentially remain unchanged except for states near the continuum, where the  $\Phi_{n,l}$  decreases very rapidly.

#### Magnitude of the CSCP Partition Function

With a given screening distance, we consider the approximate analytic  $\Phi$  function. We can obtain a value for a hydrogenic p.f. by either of three approaches, similar to those discussed by Fowler<sup>6</sup>:

- (1) Sum the terms in the p.f. until the value of the terms fall outside the accuracy desired.
- (2) Approximate the sum with an integration over the range  $n=0$  to  $n=\infty$ , using  $m=1$  between  $n=0$  and  $n=n^*$ ; and using  $m=2$  or 3 from  $n^*$  to  $\infty$ ; or
- (3) If  $n^*$  is equal to or less than, say, 10, sum from  $n=1$  to  $n=n^*$  and integrate the rest of the way.

The approximate integral form of the p.f. can be derived for the very useful hydrogenic approximation to the many-electron atom—analogue to that obtained by Fowler—by using the analysis of the gamma function given by Copson.<sup>12</sup> There results

$$Q_j^{e1} = \omega_j + 5.531 \times 10^{11} \omega_{j+1} (Z'D)^{3/2} \exp[-I_j/kT], \quad (2.21)$$

where  $\omega_j$  is the ground-state degeneracy of ion  $j$ , with charge  $j$  and with ionization potential  $I_j$ ; and  $Z'$  is the net core charge where  $Z' = j+1$ . In this derivation, 1.7 was used instead of 1.5 in the exponential term of Eq. (2.17) in order to obtain better agreement with solutions with  $A = D/2$  in the region where  $\Phi = 1/e$ .

#### Discussion

In any system where the total sum over states—the complete partition function—can be separated into translational, electronic, vibrational, etc., states, the above definition of  $Q_{eb}^{\text{CSCP}}$ , the bound electronic contribution, is a natural generalization that reflects the first-order interaction of the bound electron with the surrounding particles. Tolman,<sup>13</sup> in discussing the long-time behavior of nonisolated systems, derives an expression for the equilibrium probability  $P_n$  of finding any given state  $n$  with energy  $E_n$ , that is given by

$$P_n = \rho_{nn} = C' e^{-\beta E_n}, \quad (2.22)$$

where  $\rho_{nn}$  is the density matrix;  $C'$  and  $\beta$  are parameters having values independent of the state  $n$ ; and the quantities  $E_n$  are the true energies for the various energy eigenstates  $n$ . Of course in equilibrium,  $\beta = 1/kT$ . Now, however, in the CSCP interactions of bound states, the relative occupation  $\Phi$  represents a quantum analog of

$C'$  in (2.22). Note that with a given  $A$ , for bound states where  $D > \bar{r}_n$ ,  $\Phi$  is functionally independent of the state,  $n, l$ , but the magnitude of  $\Phi$  lies between 1 and about  $1/e$  for a finite screening distance  $D$ . Further, the  $\Phi$ 's cannot generally be normalized by setting  $Q_{eb} = 1.0$ . With systems of bound and free electrons in ionization equilibrium, normalization, if desired, for all the possible electronic states would have to be relative to

$$Q_{eb}^{\text{CSCP}} + Q_{ef}^{\text{FD}} = 1,$$

where  $Q_{ef}^{\text{FD}}$  is the p.f. for free and/or “mobile” electrons satisfying Fermi-Dirac statistics. At high densities, “mobile” electrons behaving as “free” particles have a classical analog in that a particle acted upon by no external forces and a particle upon which the sum of the external forces is zero, behave in the same manner.

Clearly, the partition function for bound electronic states given by Eq. (2.20) does not contradict any basic statistical mechanics—it generalizes the previous definition to one that reflects the mean interaction of bound electrons with neighboring particles. And the present modification is based on solutions of the SE. We can summarize by saying that  $\Phi_{n,l}(\lambda, D, A)$  represents the probability relative to that of an isolated atom (ion), for an electron to occupy the  $(n, l)$  bound electronic state with energy  $E_\lambda$  when the bound electron interacts with the nucleus and neighboring particles via a screened Coulomb potential, the screened Coulomb potential being characterized by an effective screening distance  $D$ ; by an effective mean minimum ion atmosphere radius  $A$  for the neighboring particles; and by a dielectric constant  $\eta$  for the first-order effect of neutral atoms or molecules. Here, of course, we have assumed  $\eta = 1.0$ .

In the next section we discuss observational correlations with the relative occupation probability of a screened Coulomb bound state.

### III. CORRELATION OF SOLUTIONS WITH OBSERVATIONS

A direct test of screened Coulomb effects is in the observations of relative line intensities such as those reported by Ivanov-Kholodni and Nikol'skii,<sup>14,15</sup> who report “. . . In prominence and chromospheric spectra, it has been found that near the series limit the lines do not merge because of 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.” It has been shown<sup>16</sup> that this “rapid fall in intensity” is indeed compatible

<sup>14</sup> G. S. Ivanov-Kholodni, G. M. Nikol'skii, and R. A. Gulyaev, *Astron. Zh.* **37**, 799 (1960) [English transl.: *Soviet Astron.—A. J.* **4**, 754 (1961)].

<sup>15</sup> G. S. Ivanov-Kholodni and G. M. Nikol'skii, *Astron. Zh.* **38**, 455 (1961) [English transl.: *Soviet Astron.—A. J.* **5**, 339 (1961)].

<sup>16</sup> C. A. Rouse, *Nature* **212**, 803 (1966).

<sup>12</sup> E. T. Copson, *Introduction to the Theory of Functions of a Complex Variable* (Oxford University Press, London, 1935).

<sup>13</sup> R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938).

TABLE V. The effective maximum bound state  $n^*$  and the last discrete level  $n_m$  at three points in the solar photosphere and one point in the chromosphere. The photospheric points are from a solar model ( $R$ ) and are compared with the Utrecht (1964) model of the photosphere ( $U$ ). The radius of the mean atomic volume is  $r_0$ , with  $n^{*2} = 0.59Zr_0/a_0$ , and  $n_m^2 = Zr_0/a_0$ .

|     | $h$<br>(km) | $T^a$<br>(°K) | $P_p$<br>(dyn/cm <sup>2</sup> ) | $\rho$<br>(g/cm <sup>3</sup> ) | $r_0$<br>(cm) | $n^*(r_0)$ | $n_m(r_0)$        |
|-----|-------------|---------------|---------------------------------|--------------------------------|---------------|------------|-------------------|
| $R$ | ...         | 5775          | 13.2                            | $2.66^{-7}$                    | $1.28^{-8}$   | 12         | 16                |
| $U$ | 46          | 5735          | 13.3                            | ...                            | ...           | ...        | ...               |
| $R$ | ...         | 5177          | 3.65                            | $2.24^{-7}$                    | $1.35^{-8}$   | 12         | 16                |
| $U$ | 104         | 5100          | 3.36                            | ...                            | ...           | ...        | ...               |
| $R$ | ...         | 4577          | 1.05                            | $1.85^{-7}$                    | $1.44^{-6}$   | 13         | 16.5 <sup>b</sup> |
| $U$ | 173         | 4590          | 1.18                            | ...                            | ...           | ...        | ...               |
| $R$ | ...         | 5150          | 0.11                            | $1.0^{-9}$                     | $8.22^{-6}$   | 30         | 39                |
| $U$ | 635         | 5125          | 0.14                            | ...                            | ...           | ...        | ...               |

<sup>a</sup> Note: The minimum temperature in the Utrecht model is  $4500 \pm 50^\circ\text{K}$  at  $h = 197$  km.

<sup>b</sup> Model predicts  $H_{17}$  as the maximum Balmer line in absorption. C. E. Moore, M. G. J. Minnaert, and J. Houtgast [Nat. Bur. Std. (U.S.) Monograph 61, (1966)], conclude that of the Balmer lines of hydrogen, "...  $H_{16}$ ,  $H_{16}$ , and  $H_{17}$  are measurable. The line  $H_{18}$  is certainly not seen; ..."

with the present relative occupation probabilities when applied to the disappearance of hydrogen lines in the solar photosphere as well as the chromosphere—provided that at low densities also, the effective screening distance is correlated with  $r_0$  and with the present CSCP solutions with  $A = D/2$ . The correlation of  $r_0$  with  $D$  at liquid or higher densities was expected,<sup>17–20</sup> but this is the first known evidence for this correlation at low densities.

Tables V and VI are the updated versions of Tables 1 and 2 in Ref. 16, that are based on the most recent solar model and ionization equilibrium equation of state (IEEOS) calculations.<sup>21</sup> In particular, the approximate analytical CSCP p.f. given in Eq. (2.28) was used in the IEEOS for the mixture. The tables are self-explanatory. The solar model was calculated as reported in Ref. 19 but with several recent improvements.

The references of Ref. 16 show that  $n^* = 12$  and  $n_m = 16$  are in agreement with these defined quantities in the solar photosphere; and  $n^* = 30$  and  $n_m = 39$  are the corresponding quantities in the chromosphere. Note in Table VI that the present screened Coulomb result for  $n_m$  in the chromosphere is in exact agreement with the value obtained with Mohler's empirical formula; and all formulas for  $n_m$  yield good agreement with Mitchell's chromospheric observations.<sup>22</sup>

<sup>17</sup> D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

<sup>18</sup> C. A. Rouse, *Astrophys. J.* **139**, 339 (1964).

<sup>19</sup> C. A. Rouse, (a) University of California Laboratory Report No. UCRL-7820, Rev. 1, 1964 (unpublished); (b) Rev. 1, Supplement, 1955 (unpublished); *Bull. Am. Phys. Soc.* **10**, 1 (1965).

<sup>20</sup> D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966).

<sup>21</sup> C. A. Rouse, (a) *Astrophys. J.* **134**, 435 (1961); (b) **135**, 599 (1962); (c) **136**, 636 (1962); (d) **136**, 665 (1962); (e) **137**, 1286 (1963). See also Ref. 18.

<sup>22</sup> S. A. Mitchell, *Astrophys. J.* **105**, 1 (1947).

TABLE VI. The effective maximum bound state calculated with the Debye radius DR, and the last discrete level  $n_m$ , calculated with the Inglis-Teller formula,  $n_m(I-T)$ , and with Mohler's empirical formula  $n_m(M)$ . Three points of Table I are shown here, where  $n^*(r_0)$  is repeated.

| $n^*(r_0)$ | DR <sup>b</sup><br>(cm) | $n^*(\text{DR})$ | $N_e$<br>(electrons/cc) | $n_m(I-T)^a$ | $n_m(M)$ |
|------------|-------------------------|------------------|-------------------------|--------------|----------|
| 12         | $9.04^{-5}$             | 101              | $1.65^{13}$             | 22           | 20       |
| 12         | $1.50^{-4}$             | 130              | $5.11^{12}$             | 26           | 24       |
| 30         | $9.03^{-4}$             | 318              | $1.51^{11}$             | 41           | 39       |

<sup>a</sup> Note: Inglis-Teller formula (*Astrophys. J.* **90**, 439 (1939)]:

$$7.5 \log n_m = 23.26 - \log N_e$$

Mohler's formula [*Astrophys. J.* **90**, 429 (1939)]:

$$7.5 \log n_m = 23.06 - \log N_e$$

<sup>b</sup> DR taken from *Nature* **212**, 803 (1966).

Finally, note that if the Debye radius is replaced by  $r_0$ , the upper limit of Ecker and Weizel's  $g^*$  would be in agreement with  $n_m$  in the present solar observations, but not with the same interpretation.

Further evidence of the effect of screening on the disappearance of the Balmer lines of hydrogen even at very low temperatures—demonstrating a dominate density dependence—is in the experimental results of Shrum.<sup>23</sup> With an electric discharge through nearly pure hydrogen at  $T = 21^\circ\text{K}$  and a pressure of 5 mm Hg, Shrum was just able to detect the  $H_{2-8}$  line in the Balmer series. Assuming that the pressure is given by  $P = NkT$ ,  $N$ , and  $r_0$  can be determined. With this  $r_0$ , the maximum detected level is given by  $n_m^2 = r_0/a_0$  and yields  $n_m \approx 9.4$  or 9. Considering that the electric field acts as an additional perturbation and multipole interactions have not been included in the present calculations, this value represents a good agreement with observation.

This latter agreement points up the fact that the derivation of the present  $\Phi$  function was not based upon the assumption of local thermal equilibrium. (The present screened Coulomb potential implies only a time-averaged effect of the neighboring particles.) One should also note that Berg, Ali, Lincke, and Griem<sup>24</sup> in their study of Stark profiles of hydrogen and helium lines from shock-heated plasmas, state that in dense plasmas with temperatures in the 1–10-eV range, "... Stark profiles depend almost exclusively on the electron density, and are only weak functions of the temperature."

Consequently, the fall in intensity of spectral lines and their Stark profiles give us probes for ion densities and electron densities, respectively—both essentially independent of an assumption of thermodynamic equilibrium.

As a final application, we consider the calculation of the observed ionization potential of hydrogen as an illustration of the lowering of the ionization potential

<sup>23</sup> G. M. Shrum, *Proc. Royal Soc. (London)* **A105**, 259 (1924). Also note the observations of R. W. Wood [*Proc. Roy. Soc. (London)* **97**, 455 (1920)] who wrote "If the pressure is gradually raised, the higher (Balmer) members disappear in succession..."

<sup>24</sup> H. F. Berg, A. W. Ali, R. Lincke, and H. R. Griem, *Phys. Rev.* **125**, 199 (1962).



of an atom due to screening. Since a depression of the continuum is equivalent to an increase in the energy of the ground state, let us consider the change in the ground-state energy. In the Appendix of Ref. 5, it is shown that for  $n \ll d$ , the energies of the low-lying levels of a hydrogenic atom (ion) are given by

$$E_{n,s} \approx -\frac{Z^2 \mu e^4}{2\hbar^2} \frac{1}{n^2} + \frac{Z \mu e^4}{\hbar^2} \frac{a_0}{(D+A)} \frac{\lambda}{n}. \quad (3.1)$$

Hence, the increase in the ground-state energy is given by

$$\Delta E_{n,s} \approx Z e^2 / (D+A), \quad (3.2)$$

since  $\lambda/n \approx 1$  and  $\hbar^2 = a_0 \mu e^2$ . Consequently, for large screening distances, the energies of all states with small  $n$  are increased by  $Z e^2 / (D+A)$ , approximately.

We now consider explicitly the energy change for the  $1s$  state. The maximum detected levels of hydrogen in the solar chromosphere<sup>21</sup> are about  $n_m = 38$  to 40; or, this indicates that for  $n_m = 38$ ,  $r_0 = n_m^2 a_0 = 1444 a_0$ . Substituting  $D = r_0$  and  $A = r_0/2$  into Eq. (3.2) one obtains

$$\Delta E_{1s} = e^2 / 1.5 r_0 = 1.256^{-2} \text{ eV}.$$

Then from Eq. (3.1),

$$E_{1s}(n_m = 38) \approx -\frac{\mu e^4}{2\hbar^2} + \frac{e^2}{1.5 r_0} = -13.592 \text{ eV}.$$

For  $n_m = 40$ , similar calculations lead to a ground-state energy of

$$E_{1s}(n_m = 40) = -13.594 \text{ eV}.$$

The accepted ionization potential for hydrogen is 13.595 eV. The reader is also referred to the recent calculations of Garcia and Mack<sup>25</sup> of the limiting hydrogen level using Dirac energies and a quantum-electrodynamical correction.

Another effect that would decrease the ionization potential is line broadening.<sup>8,26</sup> However, the only quantitative change in Eq. (3.1) would occur relative to states near the continuum where the energy added during a perturbation would free the electron, i.e., perturb it to a positive energy state. Otherwise, broadening of states near the continuum limit—particularly for states with  $\bar{r}_n \gg D$ —can only lead to merging of states. These merged bound states still contribute to the p.f. even if only with diminishing effect because of the “guillotining” due to  $\Phi_{n,i}$  in screened Coulomb interactions. Note that line broadening is completely consistent with the present results since the neighboring particles that produce line broadening are the same particles whose time-averaged effect lead to a screened

potential. This includes neutral particles through multipole interactions as well as charged particles.

#### IV. SUMMARY AND CONCLUSIONS

Some numerical solutions of the Schrödinger equation with the complete screened Coulomb potential have been presented with tables and graphs of relative occupation probabilities  $\Phi_{n,i}(\lambda, D, A)$ . Although the SE with a screened Coulomb potential is not analytic,  $\Phi$  can be described by a simple, analytic function for a wide range of interesting values of the screening distance  $D$ .

Since the screened Coulomb potential yields at least as many bound states as the Coulomb potential, the concept of a maximum bound principal quantum number is replaced by a definition of the relative occupation probability of a screened Coulomb state  $\Phi_{n,i}$ . An effective maximum bound state and a maximum detectable level are defined and correlated with the disappearance of hydrogen lines in the solar atmosphere and in laboratory hydrogen at 21°K.

This  $\Phi$  function is used to modify the Boltzmann factor in the standard form of the partition function for bound electronic states. This is analogous to the equilibrium probability of a state derived by Tolman for nonisolated systems.

The very good agreement with the maximum effective bound state and the maximum detected levels in the solar atmosphere and the good agreement with the disappearance of Balmer lines in very low temperature hydrogen support both the definition of the relative occupation probability derived here and the fact that the effective screening radius is correlated with the radius of the mean atomic volume at low densities as well as at high densities.

Furthermore, since the derivation of the screened occupation probability of a state is independent of any assumption of thermodynamic equilibrium, the present CSCP partition function would be useful for calculations of phenomena that deviate from local thermal equilibrium. The good agreements with the observed levels in the chromosphere and in laboratory  $H$  at 21°K support this.

Finally, the effect of screening on the lowering of the ionization potential of an atom is illustrated by the calculation of the observed ionization potential of hydrogen.<sup>27</sup>

<sup>27</sup> Note added in manuscript. The reader's attention is called to the fact that the basic theoretical argument used to derive the probability  $\Phi_{n,i}$  is that the electron-charge probability density should change under screening. This phenomenon—arrived at independently here for monatomic matter—appears to be measurable through the isomer shift (where the nucleus emits a gamma ray) with the Mössbauer effect. Note the following published reports:

(1) O. C. Kistner and A. W. Sunyer, Phys. Rev. Letters 4, 412 (1960).

<sup>25</sup> J. D. Garcia and J. E. Mack, J. Opt. Soc. Am. 55, 654 (1965).

<sup>26</sup> M. Baranger, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962); H. R. Griem, A. C. Kolb, and K. Y. Shen, Phys. Rev. 116, 4 (1959); H. R. Griem, *ibid.* 128, 515 (1962).

- (2) S. DeBenedetti, G. Lang, and R. Ingalls, *Phys. Rev. Letters* **6**, 60 (1961).
- (3) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).
- (4) J. H. Wood, *Phys. Rev.* **117**, 714 (1960).
- (5) D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, *Phys. Rev.* **135**, A1604 (1964).
- (6) R. Ingalls, *Phys. Rev.* **155**, 157 (1967).
- (7) R. Ingalls, H. G. Drickamer, and G. De Pasquali, *Phys. Rev.* **155**, 165 (1967).
- (8) I. B. Bersuker, V. I. Gol'danskii, and E. F. Makarov, *Zh. Eksperim. i Teor. Fiz.* **49**, 699 (1965) [English transl.: *Soviet Phys.—JETP* **22**, 485 (1966)].
- (9) J.-P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, *Phys. Rev. Letters* **17**, 809 (1966).
- (10) H. S. Möller and R. L. Mössbauer, *Phys. Letters* **24A**, 416 (1967).

Relative to the author's formulation to the ionization equilibrium equation of state at high densities [C. A. Rouse, *Astrophys. J.* **139**, 339 (1964); Naval Research Laboratory Report No. NRL 6594 (unpublished)], the experimental results reported in above references (5), (7), and (10) are of particular interest.

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## Relativistic Effects in Low-Energy Electron Scattering by Atoms\*

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Low-energy electron-scattering phase shifts and bound-state energies of neutral atomic potentials are computed using the Fredholm method. The relativistic and nonrelativistic results are compared. It is concluded that relativistic corrections to the phase shifts are unimportant for the potentials considered here.

### I. INTRODUCTION

RECENTLY,<sup>1,2</sup> it has been pointed out that relativistic effects in the scattering of low-energy electrons from heavy atoms can be significant. The reason for this seems to stem from the fact that for some atomic models the electron can penetrate far enough into the atom to be accelerated by the nuclear charge to a high speed. Under such circumstances, one might expect classically some modification of the elastic differential scattering cross section. That such reasoning also applies to a quantum-mechanical treatment has been demonstrated by Browne and Bauer,<sup>1</sup> who have numerically computed phase shifts and differential cross sections for several atomic-potential models, using Schrödinger's equation and the second-order relativistic wave equation.

It was later discovered<sup>3</sup> that for potentials representing singly charged atoms, the binding energy of the

valence electron was different for the relativistic and nonrelativistic equations. Thus, when the potential was adjusted so as to obtain the same values of the binding energy, the relativistic corrections to the low-energy scattering phase shifts were found to be unimportant. Qualitative arguments<sup>2</sup> based on effective-range theory tend to support the view that for neutral atoms regions of strong interaction need not lead to significant relativistic effects, provided only that there exist an ionic bound state of small binding energy.

In the present work, scattering amplitudes are computed for the Schrödinger and Dirac equations for the case of a neutral atomic potential, using the Fredholm method. These amplitudes are used to find both the phase shifts and bound states, and are of the form predicted by effective-range theory. The results (Sec. II) indicate that for a wide range of potentials, relativistic corrections to the phase shifts are unimportant for low-energy scattering; however, the binding energies, which were large compared to scattering kinetic energies, were significantly different in the relativistic and nonrelativistic treatments.

\* Research supported by the U. S. Army Research Office (Durham).

<sup>1</sup> H. N. Browne and E. Bauer, *Phys. Rev. Letters* **16**, 495 (1966).

<sup>2</sup> L. Spruch, *Phys. Rev. Letters* **16**, 1137 (1966).

<sup>3</sup> M. Rotenberg, *Phys. Rev. Letters* **16**, 969 (1966).