ELECTRONIC CHARGE DENSITY IN HELIUM IN THE FIRST ORDER SHIELDING APPROXIMATION*

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ABSTRACT

We have calculated the electronic charge density for the ground state of helium using the first order shielding approximation. The results are disappointing.

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I. Introduction

C. Schwartz[1] has calculated the first order correction to the electronic charge density in the ground state of Helium-like ions,[2] due to the interaction between the electrons. His result in atomic units for an ion of nuclear charge Z is[3]

$$\rho(r) = \frac{Z^3}{\pi} e^{-2Zr} \left[1 + \frac{\chi}{Z} \right] \tag{1}$$

where

$$\chi = -\frac{23}{16} - \frac{3}{4}\gamma - \frac{3}{4}\ln Zr - \frac{1}{2}e^{-2Zr} + \frac{5}{4}Zr + \frac{3}{8}\frac{1-e^{-2Zr}}{Zr} + \frac{3}{4}Ei(-2Zr) \tag{2}$$

and where

$$\gamma = .5772\ldots$$

$$Ei(-x) = -\int_x^\infty \frac{e^{-s}}{s}\,ds$$

In the derivation of (1) only the coulomb interaction between the electrons was treated as a perturbation. In the first order shielding approximation[4] one has as an additional perturbation the effect of the difference between the actual nuclear charge Z and an assumed nuclear charge ζ. In particular if we are interested in the expectation values of any operator W which does not depend explicitly on Z then if with $\zeta = Z$ one finds

$$\langle W \rangle = W_0(Z) + \frac{1}{Z} W_1(Z) \tag{3}$$

it is easy to show that in the first order shielding approximation one will find

$$\langle W \rangle = W_0(\zeta) + \frac{1}{\zeta} W_1(\zeta) + (Z-\zeta) \frac{dW_0(\zeta)}{d\zeta} \tag{4}$$

Following Dalgarno and Stewart[4] one then determines ζ so that the first order correction vanishes:

$$\frac{1}{\zeta} W_1(\zeta) + (Z-\zeta) \frac{dW_0(\zeta)}{d\zeta} = 0 \tag{5}$$

For our problem where $W = \frac{1}{2} [\delta(\underline{r}-\underline{r}_1) + \delta(\underline{r}-\underline{r}_2)$, $\underline{r}_1$ and $\underline{r}_2$ being the electronic coordinates, this means that <u>we will choose a different value of ζ for each value of $\underline{r}$</u> .

II. Calculational Procedure

Combining (1), (4) and (5) one finds the equation

$$Z - \zeta = \frac{x}{2\zeta\tau - 3} \equiv G(2\zeta\tau) \qquad (6)$$

which is to be solved to yield ζ as a function of τ for a given Z . Since G is a "universal function" of $y \equiv 2\zeta\tau$, the procedure is quite simple. For a given value of y one evaluates G . Then one uses (6) to determine ζ , whence one can determine τ from

$$\tau = y/2\zeta \qquad (7)$$

Unfortunately this procedure runs into difficulty because G is singular at y = 3 [5]. Referring to Figure I, which is a graph of G versus y , we could confine our attention to the "first branch" running from y=0 to y=3 , y=0 yielding r=0 and G=Z yielding $\tau = \infty$. However this seemed physically unsatisfactory because, as one readily sees, this would mean that

$$\rho(\tau) = \frac{\zeta^3}{\pi} e^{-2\zeta\tau} \qquad (8)$$

would be decreasing only as τ^{-3} as $\tau \to \infty$. On the other hand the second branch clearly yields $\zeta \to$ constant as $r \to \infty$.

Thus what we have chosen to do is to use the first branch for small values of r and the second branch for large values of r, bridging the discontinuity smoothly by eye.

III. Results and Discussion

The results for ρ (r) for Z = Z are shown in Figure II. The points are obtained in the way we have indicated while the smooth curve represents the analytic interpolation formula

$$\rho(r) = \sum_{i} A_i e^{-k_i r} \tag{9}$$

The values of the A_i and k_i are given in Table I.

To get some idea of the accuracy of our results we have computed the averages of some powers of r using (9) and defining

$$\langle r^n \rangle \equiv \int_0^\infty r^{n+2} \rho(r)\, dr \Big/ \int_0^\infty r^2 \rho(r)\, dr$$

The results, and their comparison with exact values and with values derived using the first-order shielding approximation are given in Table II. Clearly on all counts: theoretical (the singularity) and practical (agreement with exact values)[7], the results are rather disappointing.

Footnotes and References

1. C. Schwartz, Annals of Phys. 6, 156 (1959).
2. G. G. Hall, L. L. Jones, and D. Rees, Proc. Roy. Soc. (London) A283, 194 (1965) have derived analogous results for the state of He-like ions and for the ground state of Li-like ions.
3. Schwartz's paper contains a misprint. We have chosen to retain the "$\frac{1}{2}$" on the ~~right~~ Left hand side of equation (25) and to delete the "2" in equation (21). Schwartz (Table I) does the reverse. Incidentally, we have also rederived (1) using double perturbation theory. (See J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advances in Quantum Chemistry, edited by P. O. Löwdin (Academic Press Inc., New York 1964) footnote 9a, page 291.
4. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) A257, 534 (1960).
5. Another procedure one might use to determine ζ is to require that $\partial\rho/\partial\zeta = 0$ (See W. A. Sanders and J. O. Hirschfelder, J. Chem. Phys. 42, 2904 (1965)). However, this involves singularities at $2\zeta r = 3 \pm \sqrt{3}$ so we did not pursue it further.
6. See Table I W. A. Sanders and J. O. Hirschfelder, Footnote 6 and references given there.
7. Unfortunately, an accurate graph of ρ does not seem to be available in the literature, and an overall comparison might show our approximation to be better than the numbers in Table II suggest. For example, our $\rho(0)$ is identical to that given by the usual shielding approximation and is quite accurate .

TABLE I

i	1	2	3	4
A_i	.828	.52	.88	-.44
k_i	2.75	5.68	6.39	10.0

TABLE II

$\langle r^n \rangle$	This Approx.	Exact[6]	Shielding[6] Approx.
n = 2	1.43	1.19	1.17
n = 1	1.01	.92	.93
n = -1	1.57	1.69	1.69

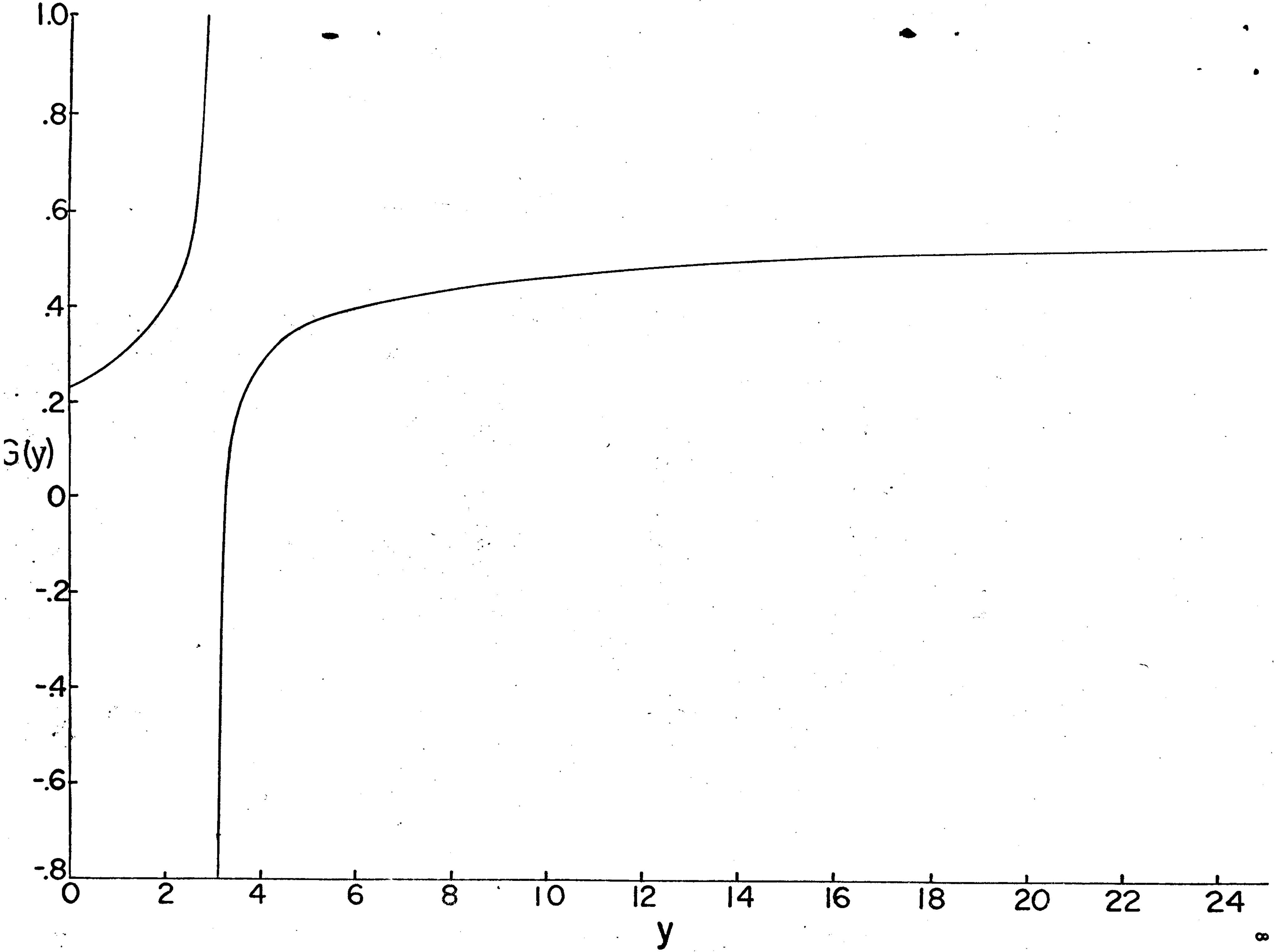

Fig. I

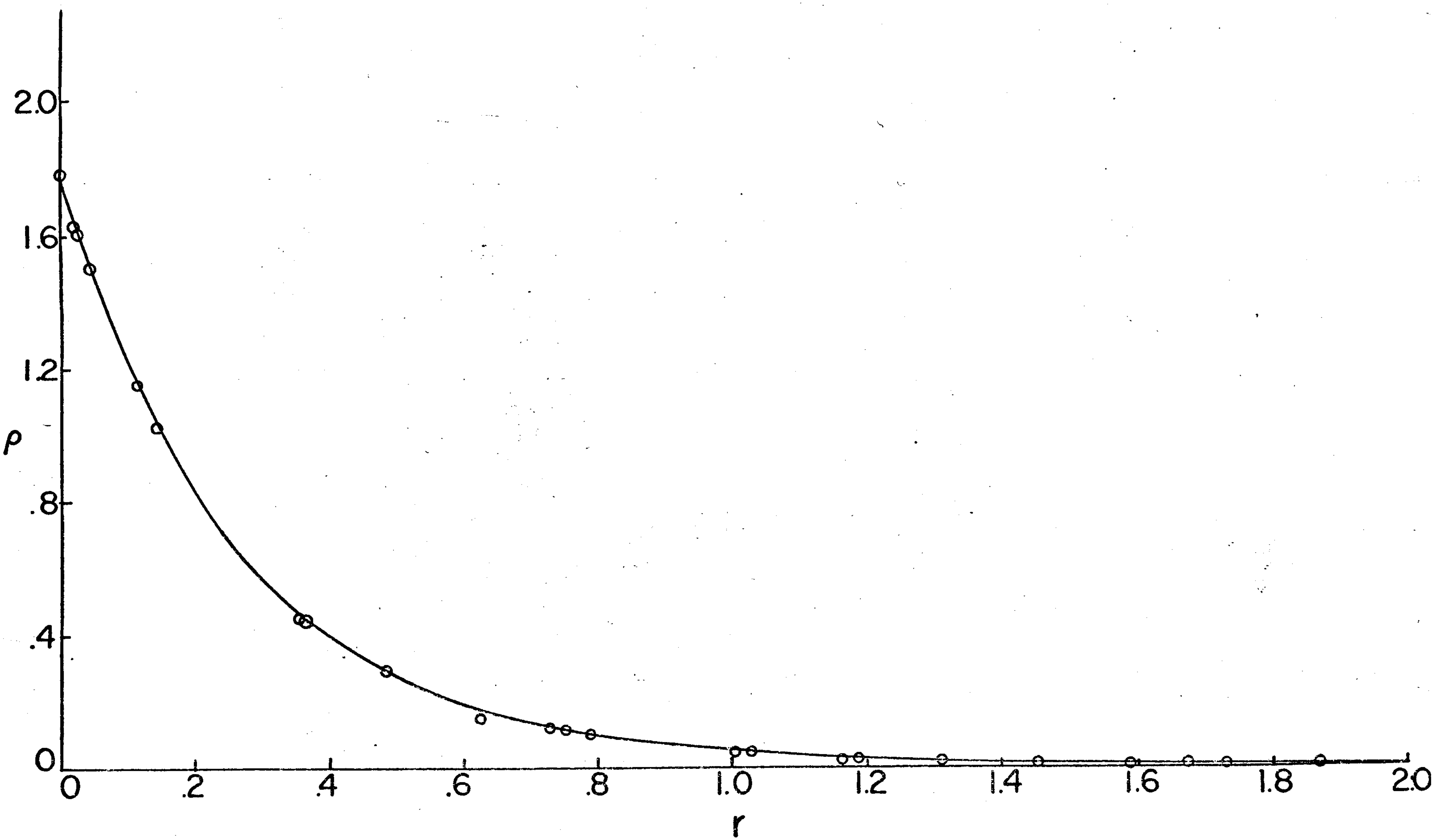

Fig. II