

# Asymptotic form at large $r$ of a third-order linear homogeneous differential equation for the ground-state electron density of the He atom

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## Abstract

In earlier work a linear differential equation satisfied by the Schwartz ground-state electron density  $\varrho(r)$  for (non-relativistic) He-like atomic ions with large atomic number  $Z$  has been derived. Here, we utilize the asymptotic expansion at large  $r$  given by Amovilli and March for the neutral He atom. We thereby show that a linear differential equation of the same general shape as that satisfied by the Schwartz  $\varrho(r)$  again emerges for the neutral He atom itself, in the asymptotic limit of large  $r$ . We argue that essential input into the final differential equation for the He ground-state electron density will be the ionization potential plus the atomic polarizability.

Going back at least to the early work of Hoffmann-Ostenhof and Hoffmann-Ostenhof [?], it is known that the ground-state density  $\varrho(r)$  of spherical atoms (eg Ne and Ar) falls off at sufficiently large  $r$  as

$$\varrho(r) \approx Nr^n \exp(-2\sqrt{2I}r) \quad : \quad r \rightarrow \infty, \quad (1)$$

where  $I$  is the ionization potential in atomic units.

Here we shall be concerned with the two-electron He atom ground-state density  $\varrho(r)$  and in particular with the ongoing search for the differential equation this  $\varrho(r)$  satisfies. A first step towards this objective was taken by Gál, March and Nagy [?]. These authors adopted as their starting point the study of Schwartz [?] who considered (always via the non-relativistic Schrödinger equation however!) the large atomic number  $Z$  limit of two-electron He-like ions of nuclear charge  $Ze$ . His result had the form

$$\varrho(r) = \frac{2Z^3}{\pi} \left[ 1 + \frac{2}{Z}\chi(r) \right] \exp(-2Zr), \quad (2)$$

where  $\chi(r)$  was calculated explicitly. The major finding in [?] was that  $\varrho(r)$  in eq. (??) satisfied exactly a third-order linear homogeneous differential equation (see eq. (??) below).

The motivation for reopening the search for such an exact differential equation for the neutral He atom itself, with  $Z = 2$  comes from the very recent study by two of us [?] of the long-range asymptotic behavior of  $\varrho(r)$  in this case. In particular, we take as the starting point of the present study the asymptotic, large  $r$  expansion given in eqs. (31)-(33) of [?].

We show below that the Amovilli-March (AM) large  $r$  form satisfies indeed a third-order linear homogeneous differential equation having precisely the same shape, but of course differs in fine details. As in [?] the form is explicitly

$$P_3(r)\varrho'''(r) + P_2(r)\varrho''(r) + P_1(r)\varrho'(r) + P_0(r)\varrho(r) = 0. \quad (3)$$

Treating the AM asymptotic form as exact, one is then led (see below) to the fact that the  $P_i(r)$  in eq. (??) are polynomials all with the highest power of  $r^3$ .

Of course, even if this proves the correct structure of any final differential equation for  $\varrho(r)$  for the He itself, the coefficients of the low-order terms will be changed.

Below we present an outline of the derivation of the form (??) from the AM asymptotic large  $r$  expansion of  $\varrho(r)$  [?] (see especially eqs. (31) - (34) ). In particular, eq. (31) yields, at large  $r$ :

$$\exp(2\sqrt{2I}r)\varrho(r) = g(r) = Ar^k \left[ 1 + \frac{C_1}{r} + \frac{C_2}{r^2} + \frac{C_3}{r^3} + O\left(\frac{1}{r^4}\right) \right]. \quad (4)$$

Differentiating eq.(??) three times then leads to the form

$$\varrho g''' = g \left[ \varrho''' + 6\sqrt{2I}\varrho'' + 24I\varrho' + 16I\sqrt{2I}\varrho \right]. \quad (5)$$

Using expression (??) for  $g$  and truncating expansion at  $r^{-3}$  we find the general form of eq. (??), where the polynomials have the form

$$P_3(r) = C_3 + C_2r + C_1r^2 + r^3, \quad (6)$$

$$P_2(r) = 6\sqrt{2I} \left[ C_3 + C_2r + C_1r^2 + r^3 \right], \quad (7)$$

$$P_1(r) = 24I \left[ C_3 + C_2r + C_1r^2 + r^3 \right] \quad (8)$$

and

$$P_0(r) = \left[ 16I\sqrt{2I}C_3 - k(k-1)(k-2) + 16I\sqrt{2I}C_2r + 16I\sqrt{2I}C_1r^2 + 16I\sqrt{2I}r^3 \right]. \quad (9)$$

Comparing eq. (??) with eq. (31) of [?], namely

$$\sqrt{\varrho(r)} \approx Mr^{\beta-1} \left[ 1 + \frac{A_1}{r} + \frac{A_2}{r^2} + \frac{A_3}{r^3} \right] \exp(-\sqrt{2I}r), \quad (10)$$

we obtain

$$C_1 = 2A_1, \quad (11)$$

$$C_2 = A_1^2 + 2A_2 \quad (12)$$

and

$$C_3 = 2(A_3 + A_1A_2). \quad (13)$$

It was shown in [?] that for He

$$A_1 = \frac{\beta(\beta-1)}{2[\sqrt{2I}(\beta-1)-1]}, \quad (14)$$

$$A_2 = \frac{A_1(\beta - 1)(\beta - 2)}{2[\sqrt{2I}(\beta - 2) - 1]}, \quad (15)$$

$$A_3 = \frac{A_2(\beta - 2)(\beta - 3)}{2[\sqrt{2I}(\beta - 3) - 1]} + \frac{\alpha}{2[\sqrt{2I}(\beta - 3) - 1]} \quad (16)$$

and

$$\beta = \frac{k}{2} + 1 = \frac{1}{\sqrt{2I}}. \quad (17)$$

Of course, while we expect the highest powers of  $r$  in polynomials  $P_i(r)$  entering eq. (??) will be derivable from the result (32) and (33) in [?], we shall not pursue the details further.

What we emphasize here is that such a differential equation as in eq. (??) will then be characterized by (i) the ionization potential  $I$  and (ii) the polarizability  $\alpha$ , which enters the AM coefficient  $A_3$  and consequently  $C_3$  occurring in eq. (??).

For the future, should it prove, as we conjecture, that the shape (??) is formally exact for the ground-state electron density of the He atom, then the small  $r$  expansion of  $\varrho(r)$  should also be invoked to fix the low-order terms in the polynomials  $P_i(r)$  entering eq. (??). In fact, from the study of Nagy and Sen [?], one has a relation between derivatives of  $\varrho(r)$  at the origin of the form

$$\bar{\varrho}'''(0) = Z \left[ -5\bar{\varrho}''(0) + 12Z^2\bar{\varrho}(0) + 4\eta_1(0) \right]. \quad (18)$$

The spherical average of the density can be written as

$$\bar{\varrho}(r) = \eta_0(r) + \sum_{l>0} r^{2l}\eta_l(r). \quad (19)$$

The last term in eq. (??) contains not the density itself, but only a part of the density: the part corresponding to  $l = 1$  that is, there is a contribution only from the 'p electron density' [?]. In this aspect eq. (??) differs from eq. (??) that contains only the density and its derivatives.

In summary, the shape (??) of the linear third-order homogeneous differential equation satisfied by the Schwartz limiting density (??) for He-like atomic ions with large atomic

number  $Z$  also follows from the AM asymptotic large  $r$  expansion for the ground state of the He atom itself. Then the AM result indicates that such a differential equation will be characterized by the ionization potential  $I$ , which should occasion no surprise due to the exact asymptotic result quoted in eq. (??), and also by the atomic polarizability  $\alpha$ . The origin of the dependence on  $\alpha$  can be traced back, through density functional theory, to the large  $r$  form of the exchange-correlation potential  $V_{xc}$  as  $-e^2/r - \alpha/2r^4$  [?,?].

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