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Long-range asymptotic behaviour of the ground-state electron density in He-like ions as a function of atomic number

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Abstract

From the early work of Hoffmann–Ostenhof, the electron density $\rho(r)$ for He-like ions at sufficiently large r has the form $Ar^n \exp(-2\sqrt{2I}r)$ where I is the ionization potential. A derivation of the relation between n and I is briefly presented. The non-relativistic ionization potential I is then calculated quantitatively from diffusion quantum Monte Carlo (DMC) calculations, as is the range of validity of the above asymptotic form for $Z \leqslant 2$. The above arguments are valid away from $Z = Z_c$, the critical atomic number 0.911 028 at which the ionization potential I tends to zero. Again analytic theory plus DMC is used at $Z = Z_c$ to quantify $\rho(r)$.

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1. Background and outline

It has been known since the work of Hoffmann–Ostenhof and Hoffmann–Ostenhof [1] that, in atomic units, the ground state density of rare gas atoms with spherical electron density $\rho(r)$ falls off at sufficiently large r as

$$\rho(r) \approx Ar^n \exp(-2\sqrt{2I}r) \quad (r \to \infty), \tag{1}$$

where I is the ionization potential.

Here, we are concerned solely with the non-relativistic two-electron He-like series of atomic ions with atomic number Z. In the early work of Schwartz [2] it was found that in the limit of large Z we have

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

where $\chi(r)$ was calculated explicitly. Subsequently, March and Pucci [3] used equation (2) with the Schwartz form of $\chi(r)$ to show that, again for sufficiently large Z, $\sqrt{2I} \approx Z - 5/8$, $n \approx -(3/4)Z^{-1}$ and $A = (2Z^3/\pi)[1 - (3/4Z)\ln Z + O(Z^{-1})]$.

Here we use non-relativistic density functional theory for the He-like series of atomic ions to first obtain the general relationship between n and I for arbitrary atomic number Z. If $V(r)$ is the one-body potential of DFT then the constant chemical potential equation reads [4]

$$\mu = \frac{\delta T_s[\rho]}{\delta\rho(r)} + V(r), \tag{3}$$

where $T_s[\rho]$ is the single-particle kinetic energy functional. While $T_s[\rho]$ is still unknown for general atomic system, for two-electron spin compensated cases like the He atom $T_s = T_W$ where the von Weizsäcker functional is given by [5]

$$T_W = \frac{1}{8}\int \frac{|\nabla\rho|^2}{\rho}\,\mathrm{d}\mathbf{r}. \tag{4}$$

Since the functional derivative entering equation (3) is readily derived from equation (4), one finds the well-known von Weizsäcker equation [5]

$$\mu = \frac{|\nabla\rho|^2}{8\rho} - \frac{\nabla^2\rho}{4\rho} + V(r). \tag{5}$$

We know from DFT that the self-interaction correction leads to $V(r)$ having the asymptotic form $-1/r$ as $r \to \infty$ for neutral atoms and to $(N - 1 - Z)/r$ for ions with N electrons [4]. Using spherical symmetry, plus the constancy of the chemical potential μ throughout the entire inhomogeneous electron density distribution $\rho(r)$ we readily find from equation (5) the result that

$$\frac{\partial V}{\partial r} = \frac{1}{4}\frac{\partial}{\partial r}\left(\frac{\rho''}{\rho}\right) + \frac{1}{4}\frac{\partial}{\partial r}\left(\frac{2\rho'}{r\rho}\right) - \frac{1}{8}\frac{\partial}{\partial r}\left(\frac{\rho'^2}{\rho^2}\right). \tag{6}$$

The outline of the paper is then as follows. In section 2 equations (6) and (1) will be combined to derive the index n in terms of atomic number Z and ionization potential I. The result will be compared with the March and Pucci limit $n \to -(3/4)Z^{-1}$ referred to above. Section 3 will focus attention on the asymptotic forms of differential equations giving the density amplitude. Then section 4 deals with the density amplitude $\sqrt{\rho}$ for Z near to the critical value Z_c at which $I \approx 0$. Section 5 treats the neutral He atom by including polarizability contribution.

2. Relation between index n in asymptotic form of density, the ionization potential I and the atomic number Z

Inserting the known asymptotic form (1) into equation (6), the RHS is evidently independent of the amplitude A and we find the following equation relating the exponent n to the ionization potential I:

$$n = \frac{2(Z-1)}{\sqrt{2I}} - 2 \quad (N = 2). \tag{7}$$

Equation (7) in the Schwartz limit ($Z \to \infty$) leads to

$$n = \frac{2(Z-1)}{Z - 5/8} - 2 = -\frac{3}{4Z} + O(Z^{-2}), \tag{8}$$

which recovers the March and Pucci limit [3] given above.

In order to quantify the asymptotic form (1) using equation (7) the non-relativistic ionization potential I is needed as a function of atomic number Z. To settle this matter,

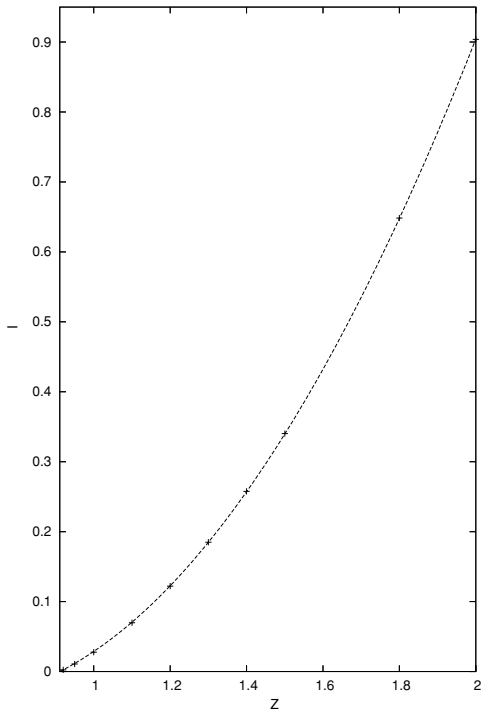

Figure 1. Plot of the DMC ionization potential I of He-like atomic ions in the range of nuclear charges between the critical value $Z_c = 0.911\,028$ and $Z = 2$. Data are in atomic units.

before proceeding to further analytic development in the later sections, we shall next present diffusion quantum Monte Carlo (DMC) (see, for example, [6]) calculations for (a) $I(Z)$ for Z from $Z_c = 0.911\,028$ to $Z = 2$ and (b) the range of r over which we can expect the asymptotic form (1), or its generalization near Z_c (see especially section 4).

In figure 1 we plot the ionization potential obtained by the difference between $-Z^2/2$, the energy of the one-electron ion in atomic units, and the DMC energy of the two-electron system. The difference between DMC energies and the exact values are within statistical error which was, in our calculation, smaller than 10^{-4} atomic units. A simple quadratic fit of such an ionization potential in terms of Z, in the range of figure 1, gives the following result:

$$I(Z) \approx 0.278(Z - Z_c) + 0.507(Z - Z_c)^2, \tag{9}$$

which will be considered in section 4.

Finally, in figure 2 we show the radius of the sphere which contains 99% of the total electron distribution against the nuclear charge Z. It is interesting to note that this radius at $Z = Z_c$ is an order of magnitude larger than that for helium.

3. Density amplitude differential equations in asymptotic regime

It is commonly accepted that the long-range behaviour of the density in an atom is determined by the solution of the differential equation [1, 7, 8]

$$-\frac{1}{2}\nabla^2\sqrt{\rho} + \left(I - \frac{Z^*}{r}\right)\sqrt{\rho} \approx 0 \quad (r \to \infty), \tag{10}$$

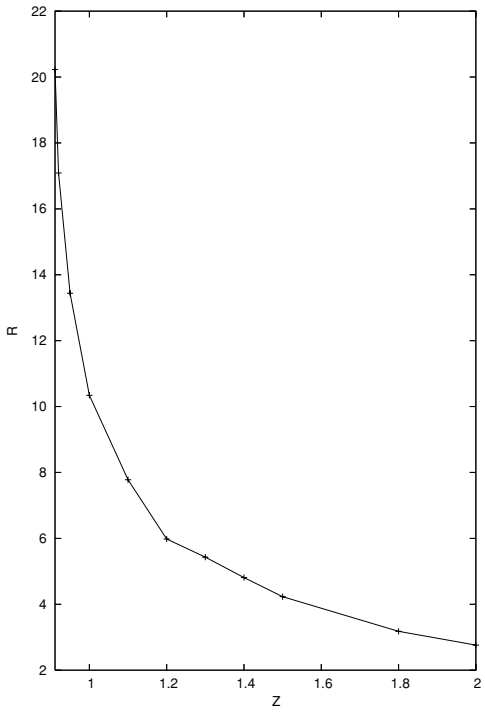

Figure 2. Plot of the radius R of the sphere containing 99% of total electronic charge for the He-like ions calculated with DMC in the range of atomic numbers between $Z_c = 0.911\,028$ and $Z = 2$. The radius is in bohr.

which, for a two-electron atom, is also the limiting form of the DFT Euler equation (3) as $r \to \infty$. Here, Z^* is an appropriate screened nuclear charge and is intended as the limit, for $r \to \infty$, of $-r(v_P + v_{KS})$, v_P and v_{KS} being, respectively, the Pauli and Kohn–Sham potentials [8]. In our case, namely two electrons in a Coulomb potential $-Z/r$, the screened nuclear charge Z^* is $Z - 1$ and equation (10) has two limiting forms for $Z = Z_c$ and for Z away from Z_c. When $Z = Z_c$, by writing

$$\sqrt{\rho(t^2)} = \frac{\phi(t)}{t} \quad (r = t^2) \tag{11}$$

we have for $\phi(t)$

$$t^2\phi'' + t\phi' - [8(1 - Z_c)t^2 + 1]\phi = 0, \tag{12}$$

which has the solution

$$\phi(t) = K_1(\sqrt{8(1 - Z_c)}t), \tag{13}$$

$K_1(x)$ being the modified Bessel function of the second kind of order 1 [10]. In large r regime, we can write

$$\sqrt{\rho(r)} \propto r^{-3/4} \exp[-\sqrt{8(1 - Z_c)}r], \tag{14}$$

with $K_1(x) \to \exp(-x)/\sqrt{2x/\pi}$ as $x \to \infty$, and the asymptotic expression already given by Hoffmann–Ostenhof *et al* [9] is recovered.

Away from $Z = Z_c$, instead, equation (10) can be transformed into the Wittaker equation [10]

$$W''_{k,m} + \left(-\frac{1}{4} + \frac{k}{x} + \frac{\frac{1}{4} - m^2}{x^2}\right) W_{k,m} = 0 \tag{15}$$

with $m = 1/2$. The asymptotic behaviour of a Whittaker function $W_{k,1/2}(x)$ is $x^k \exp(-x/2)$. Thus, starting from (10) and setting $\phi(r) = r\sqrt{\rho(r)}$ one has

$$\phi'' + \left[-2I + \frac{2(Z-1)}{r}\right]\phi = 0, \tag{16}$$

which reduces to (15) ($m = 1/2$) by the change of variable $t = 2\sqrt{2I}r$ and with $k = (Z-1)/\sqrt{2I}$. This leads to ($r \to \infty$)

$$\sqrt{\rho(r)} \propto r^{(Z-1)/\sqrt{2I}-1} \exp(-\sqrt{2I}r) \tag{17}$$

as already known from the early work of Hoffmann–Ostenhof and Hoffmann–Ostenhof [1].

The two limiting solutions (14) and (17) suggest, for the density amplitude at large r, a more general expression in the form

$$\sqrt{\rho(r)} = g(r) \exp(-\sqrt{2I}r), \tag{18}$$

with $g(r)$ satisfying the condition

$$\sqrt{\rho_c(r)} = \lim_{Z \to Z_c} g(r), \tag{19}$$

with $\exp(-\sqrt{2I}r)$ being 1 in this limit. In the next two sections we deal with the derivation of such a more general function $g(r)$.

4. Asymptotic density amplitude in range of atomic number near critical value Z_c

In order to describe the long-range behaviour of the electron density in a range of atomic numbers for the He-like ions, we want to determine the function $g(r)$ which gives the density amplitude as described at the end of the previous section. From the density amplitude equation (10) in the large r regime or equivalently the von Weiszäcker equation (5) we get

$$rg'' + (2 - 2\sqrt{2I}r)g' - 2(\sqrt{2I} + 1 - Z)g = 0, \tag{20}$$

which becomes Kummer's equation [10] in the variable $x = 2\sqrt{2I}r$, namely

$$x\phi'' + (2 - x)\phi' - a\phi = 0, \tag{21}$$

where $\phi(x) = \phi(2\sqrt{2I}r) = g(r)$ and $a = (\sqrt{2I} + 1 - Z)/\sqrt{2I}$. Equation (21) is solved by the Kummer special function $U(a, 2, x)$ [10]. Such a function is related to the density amplitude only in the limit of large r where $v_{xc}(r) \to -1/r$. A good starting point for this study is the integral form of U valid for $a > 1$ ($Z < 1$). More precisely

$$\Gamma(a)U(a, 2, x) = \int_0^\infty \mathrm{e}^{-xt}\left[\frac{t}{1+t}\right]^{a-1} \mathrm{d}t. \tag{22}$$

The function under integration is 0 at the origin and at infinity and becomes sharply peaked for large values of x. Because such x is large when r is large, we can recover the desired long-range regime by evaluating the integral using the saddle point method. We must expand the following function at the second order in t around the minimum t_0:

$$f(t) = -xt + (a-1)\ln\left[\frac{t}{1+t}\right] \approx f(t_0) + \frac{1}{2}f''(t_0)(t - t_0)^2. \tag{23}$$

Here we have

$$t_0 = \frac{1}{2}\left(-1 + \sqrt{1 + \frac{4(a-1)}{x}}\right) \tag{24}$$

and equation (22) becomes

$$\Gamma(a)\bar{U}(a,2,x) = \sqrt{\frac{2\pi}{-f''(t_0)}}\exp[f(t_0)] \quad (r \to \infty). \tag{25}$$

The density amplitude $\sqrt{\rho(r)}$ in equation (18) is then determined by the form

$$g(r) = A\Gamma(a)\bar{U}(a,2,2\sqrt{2I}r) \tag{26}$$

and is valid from the critical point $Z = Z_c$ to $Z \to 1^-$. A is a constant dependent on the atomic number Z. We can illustrate now how equation (25) works for different values of Z. Let us start from the critical point. At this point we have $Z = Z_c = 0.911\,028$, $I = 0$ and $a = \infty$. If we consider a large we can include the behaviour in the proximity of the critical point.

When $a \to \infty$ we have

$$\begin{aligned} t_0 &\approx \sqrt{\frac{a-1}{x}} \\ f(t_0) &\approx -2\sqrt{(a-1)x} \\ f''(t_0) &\approx -2\sqrt{\frac{x^3}{a-1}} \end{aligned} \tag{27}$$

and $g(r)$ becomes

$$\begin{aligned} g(r) &= A\sqrt{\frac{\pi\sqrt{a-1}}{\sqrt{x^3}}}\exp[-2\sqrt{(a-1)x}] \\ &= \frac{A}{2I}\sqrt{\frac{\pi}{2}\sqrt{\frac{1-Z}{2}}}r^{-3/4}\exp[-2\sqrt{2(1-Z)}r]. \end{aligned} \tag{28}$$

This equation, which reduces to that of Hoffman–Ostenhof *et al* [9] for $Z = Z_c$, is valid also in the neighbourhood of the critical point where $I \to 0$. The I factor in the denominator is absorbed by the constant A, equation (18) being normalized to some fraction of the total number of electrons. The set of equations above is valid when $4(a-1)/x \gg 1$ (see equation (24)). This essentially means that $(1-Z)/r \gg I$ for some large r for which the corresponding sphere contains about 99% of electrons. From equation (9) and figure 2, equation (28) should be valid in the region $Z_c \leqslant Z < 0.93$.

Now we can consider the different situation for which a is finite and r sufficiently large to determine $4(a-1)/x \ll 1$. This condition implies $(\sqrt{2I} + 1 - Z)/I \ll r$. As for the previous case we have

$$t_0 \approx \frac{a-1}{x} \qquad f(t_0) \approx -(a-1)[\ln x + 1 + \ln(a-1)] \qquad f''(t_0) \approx -\frac{2x^2}{a-1} \tag{29}$$

therefore

$$\begin{aligned} g(r) &= A\sqrt{\frac{\pi}{a-1}}(a-1)^{a-1}\,\mathrm{e}^{1-a}x^{-a} \\ &= A\sqrt{\frac{\pi}{a-1}}(a-1)^{a-1}\,\mathrm{e}^{1-a}[2\sqrt{2I}r]^{(Z-1)/\sqrt{2I}-1}, \end{aligned} \tag{30}$$

which relates to the Hoffman–Ostenhof and Hoffman–Ostenhof [1] result when the coefficient multiplying the factor involving $2\sqrt{2I}r$ is subsumed, say, into a constant B which is dependent on Z.

Table 1. Parameters entering equation (31) for the density amplitude of neutral He at large r.

Parameter	Value
$\sqrt{2I}$	1.344 46
β	0.743 79
A_1	0.070 87
A_2	− 0.004 24
$A_3(\alpha = 0)$	0.001 49
$A_3(\alpha = 0.3)$	− 0.035 70
$k(\alpha = 0.3)$	1.137 92

5. Inclusion of dipolar polarizability of He^+ for neutral He atom

If we include the dipolar polarizability of He^+ in the description of the long-range behaviour of the density, as shown by Almbladh and von Barth [11] and March [12], we must expand the pre-factor of the exponential term in (18) at least up to the third order in power of $1/r$, namely

$$\sqrt{\rho(r)} \approx k r^{\beta-1}\left[1 + \frac{A_1}{r} + \frac{A_2}{r^2} + \frac{A_3}{r^3}\right]\exp(-\sqrt{2I}r). \tag{31}$$

For $Z = 2$ we have via equation (7) $\beta = 1/\sqrt{2I}$. Neglecting at first the effect of the polarizability α the coefficients A_j are (exact solution of Kummer equation with $v_{xc} \to -1/r$)

$$A_1 = \frac{\beta(\beta-1)}{2[\sqrt{2I}(\beta-1)-1]} \qquad A_2 = \frac{A_1(\beta-1)(\beta-2)}{2[\sqrt{2I}(\beta-2)-1]} \qquad A_3 = \frac{A_2(\beta-2)(\beta-3)}{2[\sqrt{2I}(\beta-3)-1]}. \tag{32}$$

If α is considered, because $v_{xc} \approx -1/r - \alpha/2r^4$ [12], A_3 must be modified into

$$A_3 = \frac{A_2(\beta-2)(\beta-3)}{2[\sqrt{2I}(\beta-3)-1]} + \frac{\alpha}{2[\sqrt{2I}(\beta-3)-1]}. \tag{33}$$

By way of an example, α for He^+ has been estimated by means of sum rules (see, for example, [13]). These lead to $0.25 \leqslant \alpha \leqslant 0.33$ in atomic units. Final data to compute the density amplitude (31) are recorded in table 1.

The Kummer expansion (no polarizability) is rapidly convergent and the effect of α on A_3 is quite evident from table 1. Finally, we can define the constant k in equation (31) simply by choosing some large radius r_0 and calculating the ratio

$$k = \frac{\sqrt{\rho(r_0)}}{r_0^{\beta-1}\left[1 + \frac{A_1}{r_0} + \frac{A_2}{r_0^2} + \frac{A_3}{r_0^3}\right]\exp(-\sqrt{2I}r_0)}. \tag{34}$$

For $r_0 = 2$ atomic units in the neutral He atom, k is found to have the value 1.137 92. A plot of $r\sqrt{\rho(r)}$ from (31) compared with the corresponding DMC function is shown in figure 3. The agreement is remarkable.

6. Summary and future directions

Not withstanding the analytic intractability of the Schrödinger equation for the ground-state wavefunction of He-like ions, we have demonstrated here how a combination of analysis based on DFT and numerical simulations using DMC allows considerable analytic progress to be made on the long-range asymptotic behaviour of the electron density. Since the Schwartz

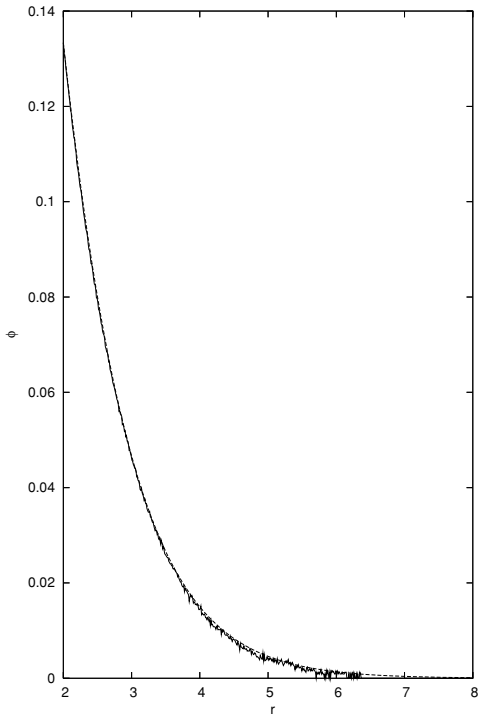

Figure 3. Comparison between the function $\phi(r) = r\sqrt{\rho(r)}$, relative to neutral helium, computed at DMC level (broken line) and from the theoretical expected behaviour (dashed line) following the derivation given in section 4. Data are in atomic units.

result (2) covers the large atomic number limit, the present study has focused especially on the range $Z_c \leqslant Z \leqslant 2$, where $Z_c = 0.911\,028$ is the critical value of Z in which the ionization potential I becomes zero.

The main achievement of the present study near the critical value Z_c is then embodied in equation (18) where $g(r)$ is given in equation (26), the corresponding ionization potential taking the form (9).

Furthermore, for the particular case of the neutral He atom with $Z = 2$, we have utilized the known long-range form of $V(r)$ in equations (5) and (6), namely

$$V(r) = -\frac{1}{r} - \frac{\alpha}{2r^4} + \cdots, \tag{35}$$

where α is the dipolar polarizability of the He^+ ion to derive the density amplitude $\sqrt{\rho(r)}$ in the form (31), where the coefficients A_1–A_3 are obtained in equations (32) and (33).

The importance of combining the above analytical studies with DMC is evidenced particularly in the figures giving the, essentially exact within statistical errors, non-relativistic ionization potential I from Z_c to the neutral He atom and in showing the dramatic increase in the importance of the long-range tail of $\rho(r)$ as Z_c is approached, the effect already being pronounced in the case of the hydrogen negative ion.

As to future directions, we believe it would be of particular interest to attempt some generalization of the present study to embrace the correlated one-particle density matrix $\gamma(r, r')$. While the one-body density matrix of DFT is essentially idempotent, the many-body

matrix γ must satisfy $\gamma^2 < \gamma$, corresponding to fractional occupation numbers of the natural orbitals, which bring $\gamma(r, r')$ into diagonal form. One limit especially connected with the present study is that in which r' say becomes very large, when $\gamma(r, r')$ takes the form

$$\gamma(r, r') \approx f(r)\rho(r')^{1/2} \tag{36}$$

at all r. We have characterized the density amplitude $\sqrt{\rho}$ at large argument rather fully in the present study. Obviously $f(r)$ must tend to $\sqrt{\rho(r)}$ as r also becomes sufficiently large. Knowledge of $f(r)$ for all r should be obtainable in the future from DMC and this seems a future project of some importance for the He-like ions.

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