Application of Benson's inequalities to the atomic electronic density

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In this work, several upper bound estimates for the atomic electronic density are derived by making use of Benson's inequalities. In some cases, it has been possible to compare the results obtained using Benson's inequalities with some bounds recently derived by other workers.

I. INTRODUCTION

Some time ago, Benson[1] proposed an elementary method which allowed a number of classical inequalities[2-4] to be derived. The basis of the method is as follows. If $P(u, x) > 0$ and $P(u,x)$ and $G(u,x)$ are continuously differentiable for x in $[a, b]$, then

$$P(u' - G_u P^{-1})^2 \geqslant 0, \tag{1}$$

$$P(u' - G_u P^{-1})^2 + 2u'G_u + 2G_x \geqslant \frac{d(2G)}{dx}, \tag{2}$$

$$\int_a^b [P(u')^2 + P^{-1}G_u^2 + 2G_x]dx \geqslant 2G(u(b),b) - 2G(u(a),a). \tag{3}$$

A subscript indicates the appropriate partial derivative. Despite the elementary nature of the above sequence of equations, Benson showed by judicious choice of the functions P and G that many interesting inequalities could be obtained.

A special case of Eq. (3) given by Benson is

$$P(u,x) = p(x); \quad G(u,x) = \tfrac{1}{2}u^2 g(x)p(x),$$

which leads to the result

$$\int_a^b [p(x)(u')^2 + \{p(x)g(x)^2 + (p(x)g(x))'\}u(x)^2]dx$$
$$\geqslant u(b)^2 p(b)g(b) - u(a)^2 p(a)g(a). \tag{4}$$

In the remainder of this paper, a simplified form of Eq. (4) will be utilized, namely,

$$\int_a^b [(u(x)')^2 + \{g(x)^2 + g(x)'\}u(x)^2]dx$$
$$\geqslant u(b)^2 g(b) - u(a)^2 g(a). \tag{5}$$

The main advantage of the above approach is that it provides a very straightforward approach to deriving bounds for the function u, given information on certain integrals involving u^2 and $(u')^2$. In some instances, however, the approach of Benson does not lead to the sharpest possible inequalities. This particularly appears to be the situation if additional information is known about the function $u(x)$. This point will be discussed further in the next section.

II. THEORY

In the present work, our interest is centered on the determination of bounds for the atomic electronic density. This topic has been the subject of recent interest,[5-12] particularly the determination of bounds for the asymptotic behavior. Considering the central role played by the electronic density in discussions of the static and dynamic behavior of matter, it is obviously very useful to know rigorous bounds for this fundamental quantity.

The following discussion will focus on the application of Eq. (5) to the electronic density for seven simple cases. The first couple of choices are selected in order to compare the resulting bounds with previous investigations. The last couple of cases examined are attempts to provide very sharp bounds for the electronic density.

The electronic density, which we will assume throughout to be radially symmetric, is defined by

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3...d\mathbf{r}_N,$$

where N is the number of electrons. Our results are restricted to atomic systems.

Case 1: $g = k$ (k is a constant).

If we set $g = k$, then the basic Benson inequality (5) becomes, on setting $a = 0$ and $u(a) = 0$,

$$ku(r_b)^2 \leqslant \int_0^{r_b} [u(x)']^2 dx + k^2 \int_0^{r_b} u(x)^2 dx. \tag{6}$$

If the optimum k is selected, then

$$u(r_b)^2 \leqslant 2\left[\int_0^{r_b} [u(x)']^2 dx \int_0^{r_b} u(x)^2 dx\right]^{1/2}. \tag{7}$$

which may be rewritten as

$$u(r)^2 < 2\left[\int_0^{\infty} [u(x)']^2 dx \int_0^{\infty} u(x)^2 dx\right]^{1/2}. \tag{8}$$

This special case of Benson's inequality has been known for some time.[13] The special case of Eq. (8) for $r = 0$ can be found in the book by Hardy *et al.*[2]

Employing the substitution

$$u(r) = r\rho(r)^{1/2} \tag{9}$$

and making use of the inequality, derived by Hoffmann-Ostenhof *et al.*,[5]

$$\int_0^{\infty} ([r\rho(r)^{1/2}]')^2 dr \leqslant \frac{T}{2\pi} \tag{10}$$

leads to the result

$$\rho(r) < (2NT)^{1/2}/2\pi r^2. \tag{11}$$

In Eq. (10) T is the total kinetic energy of the system. A slightly stronger result has been given by Hoffmann-Ostenhof *et al.*:[5]

$$\rho(r) \leqslant (2NT)^{1/2}/4\pi r. \tag{12}$$

For Eq. (8) we assume that $u(r)$ is continuous. No other as-

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sumptions on the function $u(r)$ are employed, although the additional requirement that the integrals appearing in Eq. (8) converge will be employed; otherwise the result is rather trivial. The stronger result obtained by Hoffmann-Ostenhof, Eq. (12), follows from the inequality

$$|u(r)|^2 \leqslant \left[\int_0^\infty [u(x)']^2 \, dx \int_0^\infty u(x)^2 \, dx \right]^{1/2}, \quad (13)$$

which requires the hypothesis $u(0) = 0$. This additional constraint allows the sharper inequality to be obtained, and can be observed to follow from a particular case of Block's inequalities[14,15]:

$$|u(r)|^2 \leqslant \frac{\tanh k\,(b-a)}{2k} \int_a^b \{ [u(x)']^2 + k^2 u(x)^2 \} dx, \quad (14)$$

which represents the uniform bound of the more general form of one of Block's inequalities:

$$|u(r)|^2 \leqslant \frac{\sinh k\,(r-a)\sinh k\,(b-r)}{k \sinh k\,(b-a)} \int_a^b \{ [u(x)']^2 + k^2 u(x)^2 \} dx. \quad (15)$$

Equations (14) and (15) are derived under the hypothesis

$$u(a) = u(b) = 0. \quad (16)$$

If, in place of Eq. (9), the substitution

$$u(r) = \rho(r)^{1/2} \quad (17)$$

is employed in Eq. (8), then bounds for the electronic density at the nucleus may be obtained, and these have been discussed elsewhere.[11] We note in passing that even for the case where $u(0) = 0$ is not assumed, the inequality that follows from Benson's Eq. (5), i.e., Eq. (6), can be given in slightly sharper form:

$$ku(r)^2 \leqslant \tfrac{1}{2}(1 + e^{-2kr}) \int_0^\infty \{ [u(x)']^2 + k^2 u(x)^2 \} dx, \quad (18)$$

which follows from an inequality of Block:

$$|u(r)|^2 \leqslant \frac{\cosh k\,(b-r)\cosh k\,(r-a)}{k \sinh k\,(b-a)} \int_a^b \{ [u(x)']^2 + k^2 u(x)^2 \} dx. \quad (19)$$

Case 2: $g' + g^2 = k^2 e^{-2\Gamma x}$ (Γ is a positive constant). The differential equation to be solved is

$$g(x)' + g(x)^2 = k^2 e^{-2\Gamma x}. \quad (20)$$

The standard approach to handle a differential equation of this form is to employ the substitution

$$g(x) = v(x)'/v(x). \quad (21)$$

Using Eq. (21), Eq. (20) is converted to

$$v(x)'' - k^2 e^{-2\Gamma x} v(x) = 0. \quad (22)$$

The change of variable $y(x) = k^2 e^{-2\Gamma x}$ converts Eq. (22) into a modified Bessel differential equation. The solution of Eq. (22) is (in terms of constants c_1 and c_2)

$$v(x) = c_1 I_0(\gamma e^{-\Gamma x}) + c_2 K_0(\gamma e^{-\Gamma x}), \quad (23)$$

where $\gamma = k/\Gamma$ and I_0 and K_0 are modified Bessel functions of the first and second kind, respectively. The constant c_2 must be zero if $v(x)$ is finite at $x \to \infty$. From Eq. (23) we have that

$$g(x) = -ke^{-\Gamma x} I_1(\gamma e^{-\Gamma x})/I_0(\gamma e^{-\Gamma x}). \quad (24)$$

From Benson's inequality, Eq. (5),

$$\frac{u(r_a)^2 k e^{-\Gamma r_a} I_1(\gamma e^{-\Gamma r_a})}{I_0(\gamma e^{-\Gamma r_a})}$$

$$< \int_{r_a}^\infty \{ [u(x)']^2 + k^2 e^{-2\Gamma x} u(x)^2 \} dx. \quad (25)$$

If we employ Eq. (9) and take advantage of the fact that the integrand in Eq. (25) is always positive, then

$$\rho(r) < \frac{I_0(\gamma e^{-\Gamma r})[2T + k^2 N \langle \Psi | e^{-2\Gamma r_1} | \Psi \rangle]}{4\pi r^2 k e^{-\Gamma r} I_1(\gamma e^{-\Gamma r})}. \quad (26)$$

From the asymptotic expansions for the modified Bessel functions of the first kind[16]:

$$I_0(z) \sim \frac{e^z}{(2\pi z)^{1/2}} \left[1 + \frac{1}{8z} + \frac{9}{128 z^2} + \cdots \right] \quad z \to \infty, \quad (27)$$

$$I_1(z) \sim \frac{e^z}{(2\pi z)^{1/2}} \left[1 - \frac{3}{8z} - \frac{15}{128 z^2} + \cdots \right] \quad z \to \infty, \quad (28)$$

it follows that Eq. (26) reduces to Eq. (11) in the limit $\Gamma \to 0$ when the optimum k is employed.

Hoffmann-Ostenhof *et al.*[5] have considered the problem of deriving bounds for expectation values involving exponential functions. Here we consider a different approach utilizing Sobolev's inequality.[17,18] Our bounds are restricted to expectation values of exponentially decreasing functions, and will allow us to express the expectation values in Eq. (26) in terms of the kinetic energy.

Using the Holder inequality, we have

$$\int e^{-kr} \rho(\mathbf{r}) d\mathbf{r} \leqslant \left\{ \int e^{-3/2 kr} d\mathbf{r} \right\}^{2/3} \left\{ \int \rho(\mathbf{r})^3 \, d\mathbf{r} \right\}^{1/3}. \quad (29)$$

Sobolev's inequality takes the form (in R^3)

$$\left\{ \int \phi(\mathbf{r})^6 \, d\mathbf{r} \right\}^{1/2} \leqslant c \left\{ \int |\nabla \phi(\mathbf{r})|^2 \, d\mathbf{r} \right\}^{3/2}, \quad (30)$$

where the constant $c = 4/3^{3/2} \pi^2$. If we substitute

$$\phi(\mathbf{r}) = \rho(\mathbf{r})^{1/2} \quad (31)$$

in Eq. (30), then

$$\int \rho(\mathbf{r})^3 \, d\mathbf{r} \leqslant c^2 \left\{ \int |\nabla \rho(\mathbf{r})^{1/2}|^2 \, d\mathbf{r} \right\}^3. \quad (32)$$

Hence,

$$\int e^{-kr} \rho(\mathbf{r}) d\mathbf{r} \leqslant c^{2/3} \left\{ \int e^{-3/2 kr} d\mathbf{r} \right\}^{2/3} \left\{ \int |\nabla \rho(\mathbf{r})^{1/2}|^2 \, d\mathbf{r} \right\}, \quad (33)$$

which simplifies on using

$$\int |\nabla \rho(\mathbf{r})^{1/2}|^2 \, d\mathbf{r} \leqslant 2T \quad (34)$$

to give

$$\int e^{-2\Gamma r} \rho(\mathbf{r}) d\mathbf{r} \leqslant \frac{16T}{27\Gamma^2} \left(\frac{2}{\pi^2} \right)^{1/3}. \quad (35)$$

We now make a simple evaluation of Eq. (35), using as a reference, the obvious result

$$\int e^{-2\Gamma r} \rho(\mathbf{r}) d\mathbf{r} \leqslant N. \quad (36)$$

For the hydrogen atom, $\rho(r) = e^{-2r}/\pi$, and hence

$$\int e^{-2\Gamma r}\rho(\mathbf{r})d\mathbf{r} = \frac{1}{(\Gamma+1)^3}. \tag{37}$$

The right-hand side of Eq. (35) becomes

$$\frac{8}{27\Gamma^2}\left(\frac{2}{\pi^2}\right)^{1/3} \sim 0.174\,03\,\Gamma^{-2} \text{ (in atomic units)},$$

and hence the bound in Eq. (35) is a fairly satisfactory approximation. The inequality for the case of the hydrogen atom is sharpest for $\Gamma=2$. Comparing Eqs. (35) and (36), we find that Eq. (35) is the better bound for $\Gamma > 0.417\,17$. For a general atom, Eq. (35) is superior to Eq. (36) when

$$0.348\,069T^{1/2}/N < \Gamma. \tag{38}$$

For He Eq. (35) is better than Eq. (36) if $\Gamma > 0.7109$ and for the Be atom, if $\Gamma > 1.130$.

Returning to Eq. (26), we may rewrite this bound using Eqs. (35) and (36):

$$\rho(r) < \frac{I_0(\gamma e^{-\Gamma r})T}{2\pi r^2 k e^{-\Gamma r}I_1(\gamma e^{-\Gamma r})}[1 + 0.174\,035\gamma^2], \tag{39}$$

or the alternative form,

$$\rho(r) < \frac{I_0(\gamma e^{-\Gamma r})[2T + k^2N]}{4\pi r^2 k e^{-\Gamma r}I_1(\gamma e^{-\Gamma r})}. \tag{40}$$

The optimum bound for Eq. (40) can be obtained by examining the limit $\Gamma \to 0$, which leads to

$$\rho(r) < (1/4\pi k r^2)[2T + k^2N].$$

Case 3: $g' + g^2 = k^2x^2$.

With the substitution $g(x) = v(x)'/v(x)$, the equation

$$g(x)' + g(x)^2 = k^2x^2 \tag{41}$$

is transformed into

$$x^2v(x)'' - k^2x^4v(x) = 0, \tag{42}$$

for which the solution is

$$v(x) = x^{1/2}[c_1I_{1/4}(\tfrac{1}{2}kx^2) + c_2K_{1/4}(\tfrac{1}{2}kx^2)]. \tag{43}$$

With the requirement that $v(x)$ remains finite as $x \to \infty$, we set $c_1 = 0$; hence

$$g(x) = \frac{1}{x} - \frac{kxK_{5/4}(\tfrac{1}{2}kx^2)}{K_{1/4}(\tfrac{1}{2}kx^2)}. \tag{44}$$

Since the integrand in Benson's inequality is positive for the present case, we obtain, using Eq. (9) and (10),

$$\rho(r) < \frac{K_{1/4}(\tfrac{1}{2}kr^2)[2T + Nk^2\langle\Psi|r_1^2|\Psi\rangle]}{4\pi kr^3K_{3/4}(\tfrac{1}{2}kr^2)}. \tag{45}$$

Case 4: $g' + g^2 = k^2/x$.

On making the substitution $g(x) = v(x)'/v(x)$, the solution of the Riccati equation

$$g(x)' + g(x)^2 = k^2/x \tag{46}$$

is, with $\beta = 2kx^{1/2}$,

$$g(x) = kI_0(\beta)/x^{1/2}I_1(\beta), \tag{47}$$

which leads to the bound

$$\rho(r) < \frac{I_1(\beta)[2T + Nk^2\langle\Psi|r_1^{-1}|\Psi\rangle]}{4\pi r^{3/2}kI_0(\beta)}. \tag{48}$$

It can be shown,[11] that a slightly sharper bound can be obtained when the additional hypothesis that $u(r)$ vanishes at

$r=0$ is employed. The resulting bound is

$$\rho(r) < \frac{I_1(\beta)[2T + Nk^2\langle\Psi|r_1^{-1}|\Psi\rangle]}{4\pi r^{3/2}k[I_0(\beta) + \{I_1(\beta)K_0(\beta)/K_1(\beta)\}]} \tag{49}$$

$$= \frac{I_1(\beta)K_1(\beta)[2T + Nk^2\langle\Psi|r_1^{-1}|\Psi\rangle]}{2\pi r}. \tag{49a}$$

For large values of β, the denominator of Eq. (49) behaves like $\sim 2I_0(\beta)$. Therefore, in this limit, Eq. (49) is a sharper bound by a factor of 2. In the limit $\beta \to 0$, the additional factor in the denominator approaches zero, and hence Eqs. (48) and (49) become equivalent in this limit. The superior result, Eq. (49), is a direct consequence of the additional assumption on $u(r)$.

Case 5: $g' + g^2 = k/x^2$.

The solution of the Riccati equation in this case is elementary:

$$g = m_1/x, \quad m_1 = \tfrac{1}{2} + \tfrac{1}{2}(1 + 4k)^{1/2}, \tag{50}$$

$$g = m_2/x, \quad m_2 = \tfrac{1}{2} - \tfrac{1}{2}(1 + 4k)^{1/2}. \tag{51}$$

If we employ Benson's inequality and Eq. (9), then each of Eqs. (50) and (51) leads to bound for $\rho(r)$. The sharper of the two bounds is

$$\rho(r) < \frac{[2T + kN\langle\Psi|r_1^{-2}|\Psi\rangle]}{2\pi r[(1 + 4k)^{1/2} - 1]}. \tag{52}$$

The optimum k, restricted to positive values, for Eq. (52) is

$$k = \Omega + \Omega^{1/2}, \tag{53}$$

where

$$\Omega = \frac{2T}{N\langle\Psi|r_1^{-2}|\Psi\rangle}. \tag{54}$$

It follows from the well-known inequality[19]

$$N\langle\Psi|r_1^{-2}|\Psi\rangle \leqslant 8T \tag{55}$$

that $\Omega \geqslant \tfrac{1}{4}$ and hence $k \geqslant \tfrac{3}{4}$. Equation (52) reduces to

$$\rho(r) < \frac{N\langle\Psi|r_1^{-2}|\psi\rangle[2\Omega + \Omega^{1/2}]}{2\pi r[(1 + 4\Omega + \Omega^{1/2})^{1/2} - 1]}. \tag{56}$$

Case 6: $g' + g^2 = -k/x^2$.

The constant k is positive. From Eqs. (50) and (51), it is obvious that $-\tfrac{1}{4}$ is the most negative factor that is possible. Benson's inequality becomes, on using Eq. (50),

$$\tfrac{1}{2}r_b\rho(r_b) - \tfrac{1}{2}r_a\rho(r_a) \leqslant \int_{r_a}^{r_b}\{[(r\rho(r)^{1/2})']^2 - \tfrac{1}{4}\rho(r)\}dr. \tag{57}$$

If we employ Eq. (10), Eq. (57) may be rewritten as

$$\int_{r_a}^{r_b}\frac{\rho(r)}{r^2}(4\pi r^2\,dr) \leqslant 8T + 8\pi[r_a\rho(r_a) - r_b\rho(r_b)], \tag{58}$$

which is a generalization (for a radially symmetric density) of the well-known result

$$\int\frac{\rho(\mathbf{r})d\mathbf{r}}{r^2} \leqslant 8T. \tag{59}$$

Since the integrand in Eq. (57) is not necessarily positive for all r, it is clearly not possible to add the terms

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$$\int_0^{r_a} \{([rp(r)^{1/2}]')^2 - \tfrac{1}{4}\rho(r)\}dr + \int_{r_b}^{\infty} \{([rp(r)^{1/2}]')^2$$
$$- \tfrac{1}{4}\rho(r)\}dr$$

to the right-hand side of the inequality. By way of example, consider the case of the hydrogen atom, for which this point can be resolved analytically. For the hydrogen atom, we have

$$([rp(r)^{1/2}]')^2 - \tfrac{1}{4}\rho(r) = \rho(r)(r - 3/2)(r - \tfrac{1}{2}). \quad (60)$$

The integrand is positive for all $r > 3/2$ for the hydrogen atom, and hence for this case,

$$\rho(r) \leqslant \frac{1}{\pi r}\left[T - \tfrac{1}{8}N\langle\Psi|r_1^{-2}|\Psi\rangle\right] \quad \text{for } r > 3/2. \quad (61)$$

Because of the importance of the region $r = 0 - 0.5$ a.u., where the integrand is positive [see Eq. (60)], it is straightforward to show that Eq. (61) actually holds for all r.

From Eq. (58), we have

$$\rho(r) \leqslant \frac{1}{8\pi r}\left\{8T - N\langle\Psi|r_1^{-2}|\Psi\rangle + \int_r^{\infty} 4\pi\rho(x)dx\right\}. \quad (62)$$

A bound for the last integral appearing in Eq. (62) can be obtained in the following manner. If we integrate the bound[5]

$$4\pi\rho(r) < \frac{1}{r^2}\left(\frac{T}{\alpha} + \frac{1}{2}\alpha N\right)(1 - e^{-2\alpha r}), \quad (63)$$

we obtain

$$4\pi\int_r^{\infty}\rho(x)\,dx < \left(\frac{T}{\alpha} + \frac{1}{2}\alpha N\right)(1 - E_2(2\alpha r))r^{-1}, \quad (64)$$

where α is an arbitrary positive parameter in Eq. (63) and $E_2(z)$ is an exponential integral.[16] Hence, Eq. (62) becomes

$$\rho(r) < 1/8\pi r$$
$$\times\{8T - N\langle\Psi|r_1^{-2}|\Psi\rangle$$
$$+ (1/2\alpha r)(2T + \alpha^2 N)(1 - E_2(2\alpha r))\}. \quad (65)$$

Case 7: $g' + g^2 = -k^2/x.$

The Riccati equation to be solved is

$$g(x)' + g(x)^2 = -k^2/x. \quad (66)$$

This may be converted into the following differential equa-

tion:
$$x^2 v(x)'' + k^2 x v(x) = 0. \quad (67)$$

The solution of Eq. (67) is, with $\beta = 2kx^{1/2}$,

$$v(x) = x^{1/2}[c_1 J_1(\beta) + c_2 Y_1(\beta)], \quad (68)$$

where J_n and Y_n are Bessel functions of the first and second kind, respectively. If $v(x)'$ is finite as $x \to 0$, then $c_2 = 0$. The function g is

$$g(x) = \frac{k}{x^{1/2}}\frac{J_0(\beta)}{J_1(\beta)}. \quad (69)$$

Because of the oscillatory nature of the Bessel functions, we impose the restriction that $\beta < 2.404\,825$ [the first zero of $J_0(\beta)$], i.e.,

$$r < 1.445\,79\,k^{-2}. \quad (70)$$

Benson's inequality with u given by Eq. (9) gives

$$\rho(r) < \frac{J_1(\beta)}{kr^{3/2}J_0(\beta)}\int_0^r\{([x\rho(x)^{1/2}]')^2 - k^2 x\rho(x)\}dx. \quad (71)$$

Using Eq. (10), Eq. (71) can be rewritten as

$$\rho(r) < \frac{J_1(\beta)}{4\pi kr^{3/2}J_0(\beta)}\left\{2T + \frac{k^2}{Z}V_{en} + k^2\int_r^{\infty}\rho(x)4\pi x\,dx\right\}, \quad (72)$$

where V_{en} is the electron-nuclear potential energy and Z is the nuclear charge. Both Eqs. (71) and (72) require the restriction given in Eq. (70).

A question of interest is whether or not a sharper form of Eq. (72) can be formulated. This can be answered in the affirmative, at least for one-electron systems. For the hydrogen atom, we have that

$$([rp(r)^{1/2}]')^2 - k^2 rp(r)$$
$$= \rho(r)[r - \{1 + \tfrac{1}{2}k^2 + \tfrac{1}{2}k[k^2 + 4]^{1/2}\}]$$
$$\times[r - \{1 + \tfrac{1}{2}k^2 - \tfrac{1}{2}k[k^2 + 4]^{1/2}\}]. \quad (73)$$

In this case, the integrand in Eq. (71) is positive for

$$r > 1 + \tfrac{1}{2}k^2 + \tfrac{1}{2}k[k^2 + 4]^{1/2} \quad (74)$$

and hence,

$$\rho(r) < \frac{J_1(\beta)}{4\pi kr^{3/2}J_0(\beta)}\left[2T + \frac{k^2}{Z}V_{en}\right]. \quad (75)$$

The range of r for which Eq. (75) may be applied is governed by both Eqs. (70) and (74); that is,

TABLE I. Bounds for $\rho(r)$ for the hydrogen atom.

Radial distance (atomic units)	Bounds for $\rho(r)$ (in atomic units)					
	Eq. (11)	Eq. (48)	Eq. (49)	Eq. (56)	Eq. (65)	Exact
0.1	0.1592×10^2	0.7958	0.7958	0.5872×10^1	0.2171×10^1	0.2606
0.2	0.3979×10^1	0.3979	0.3973	0.2936×10^1	0.9270	0.2134
0.3	0.1768×10^1	0.2653	0.2631	0.1957×10^1	0.5564	0.1747
0.4	0.9947	0.1989	0.1948	0.1468×10^1	0.3852	0.1430
0.5	0.6366	0.1592	0.1530	0.1174×10^1	0.2887	0.1171
0.6	0.4421	0.1326	0.1246	0.9787	0.2279	0.9587×10^{-1}
0.7	0.3248	0.1137	0.1042	0.8389	0.1865	0.7849×10^{-1}
0.8	0.2487	0.9947×10^{-1}	0.8878×10^{-1}	0.7340	0.1569	0.6427×10^{-1}
0.9	0.1965	0.8842×10^{-1}	0.7678×10^{-1}	0.6524	0.1347	0.5261×10^{-1}
1.0	0.1592	0.7958×10^{-1}	0.6722×10^{-1}	0.5872	0.1176	0.4308×10^{-1}
1.5	0.7074×10^{-1}	0.5305×10^{-1}	0.3929×10^{-1}	0.3915	0.7053×10^{-1}	0.1585×10^{-1}
2.0	0.3979×10^{-1}	0.3979×10^{-1}	0.2633×10^{-1}	0.2936	0.4970×10^{-1}	0.5830×10^{-2}

$$1 + \tfrac{1}{4}k^2 + \tfrac{1}{4}k[k^2 + 4]^{1/2} < r < 1.445\ 79\ k^{-2}. \qquad (76)$$

As a final remark on this case, we note that it is possible to derive an upper bound for the last integral appearing in Eq. (72) using an exponentially decreasing bound given by Hoffmann-Ostenhof et al.[5] The bound obtained requires information on the ionization potential.

Numerical results for some of the bounds discussed in this work are presented in Table I for the hydrogen atom. More detailed applications will be presented elsewhere. The value of k in each bound formula was optimized at each value of the radial coordinate r. The best bounds range from a factor of about 1.3 too high at medium range to about a factor of $3 \sim 4$ too high at both short and long range. At very long range, all the bounds give poor estimates because of the incorrect asymptotic behavior of the bounds as $r \rightarrow \infty$.

III. CONCLUSION

In this work, we have examined the application of Benson's inequalities to obtain upper bound estimates for the atomic electronic density. The bounds derived herein do not exhibit the correct long-range asymptotic behavior; that is, they do not decay exponentially as $r \rightarrow \infty$. Also, the bounds are not finite at $r = 0$. The problem of determining a reasonable bound which is both finite at the nucleus and decays exponentially for large r, is an unresolved problem. The few bounds for the electronic density which have been previously given in the literature, become infinite at $r = 0$. The exceptions are a recent bound derived by the author[11] and a bound derived specifically for $r = 0$ by Hoffmann-Ostenhof et al.[6]

The bounds derived in this work are satisfactory for values of r typically in the small to moderate range. Numerical applications will be discussed elsewhere.

For the situation were $g(x)' + g(x)^2$ is negative, only a limited number of functional forms have been examined. It is possible that a more judicious selection of the functional form of $g(x)' + g(x)^2$ would result in improved bounds.

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