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Investigation of an Inequality between Atomic Expectation Values *via* the Density Functional Theory

P. Csavinszky

Department of Physics and Astronomy, University of Maine, Orono, Maine 04469

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The present work investigates an inequality derived earlier by Gadre. The inequality involves the product of the expectation values of the radial distance and the inverse of the radial distance. Using the density-functional theory, and the Ne atom as an example, these quantities are calculated in three successive approximations. It is found that, in all three cases, the product of the expectation values satisfies the inequality of Gadre. The results are compared with a calculation of Gadre and Matcha, who have obtained the expectation values with the Thomas-Fermi equation. It is found that the density-functional approach leads to a tighter bound for the product of the expectation values than the approach based on the Thomas-Fermi equation. This is attributed to the power law decay of the solution of the Thomas-Fermi equation at large distances from the nucleus.

INTRODUCTION

The possibility of deriving a bound on one expectation value in terms of other expectation values *via* an inequality is an intriguing one. The feasibility of such a procedure has been recently demonstrated by Gadre,[1] and Gadre and Matcha,[2] who made use of theorems by Pólya and Szegö.[3]

One of the inequalities that Gadre and Matcha[2] have numerically investigated is given by

$$\frac{\langle r \rangle \langle 1/r \rangle}{Z^2} > \frac{9}{8}, \tag{1}$$

where $\langle r \rangle$ is the expectation value of the radial distance, $\langle 1/r \rangle$ is the expectation value of the inverse of the radial distance, and Z is the atomic number. This inequality has been derived earlier by Gadre,[1] with the sole assumption of a monotonously decreasing electron (number) density.

Gadre and Matcha[2] have investigated the value of the product $\langle r \rangle \langle 1/r \rangle / Z^2$ for atoms by resorting to the Thomas-Fermi (TF) equation.[4] The TF model has recently received extensive mathematical attention by Lieb,[5] and by Lieb and Simon,[6] who have established that it is the correct model of a neutral atom of atomic number Z in the $Z \to \infty$ limit. Gadre and Matcha[2] have found that the value of $\langle r \rangle \langle 1/r \rangle / Z^2$ is 5.72, whereas Eq. (1) predicts it to be merely greater than 1.125. This result shows that the bound obtained with Eq. (1) is not tight when expectation values based on the TF equation are used.

The present work makes use of the density-functional theory[7] to arrive at values of $\langle r \rangle$ and $\langle 1/r \rangle$. In the density-functional theory the basic variable is the electron (number) density, for which approximations may be made. One approximation that has been suggested[8] constructs the electron (number) density of an atom from hydrogen-like wave functions. This is the approach adopted in the present work in three successive stages of sophistication, using the Ne atom as an example.

In the first approximation, the »Z« in the 1s, 2s, and 2p wave functions is taken to be the same ($Z_1 = Z_2 = Z_3$). In the second approximation, the »Z« in the 1s wave function is different from the »Z« in the 2s and 2p wave functions, which latter two are taken to be the same ($Z_1 \neq Z_2 = Z_3$). In the third approximation, the »Z« in the 1s wave function differs from the »Z« in the 2s wave function which, in turn, differs from the »Z« in the 2p wave function ($Z_1 \neq Z_2 \neq Z_3$). In the second and third approximations, the 2s wave function is orthogonalized to the 1s wave function . With the electron (number) densities resulting from the above three approximations, the TF energy-density functional[4] is minimized with respect to the variational parameters Z_1, Z_2, Z_3, and the expectation values $\langle r \rangle$ and $\langle 1/r \rangle$ are computed.

THEORY

The TF energy-density functional (in atomic units[9]) is given[4] by

$$E[\rho] = E_k[\rho] + E_{ne}[\rho] + E_{ee}[\rho] , \tag{2}$$

where ρ is the electron (number) density,

$$E_k[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int_0^\infty \rho^{5/3} 4\pi r^2 \, dr \tag{3}$$

is the kinetic energy of the electrons,

$$E_{ne}[\rho] = -\int_0^\infty V_n \rho \, 4\pi r^2 \, dr \tag{4}$$

is the attractive (Coulomb) interaction energy between the nucleus of atomic number ζ and the N electrons ($\zeta = N$), and

$$E_{ee}[\rho] = -\frac{1}{2}\int_0^\infty V_e \rho \, 4\pi r^2 \, dr \tag{5}$$

is the repulsive (Coulomb) interaction energy among the N electrons.

In Eq. (4), the quantity

$$V_n = \frac{\zeta}{r} , \tag{6}$$

is the potential of the nucleus, while in Eq. (5) the quantity V_e is the potential of the electrons which, with the present three choices for ρ, is determined analytically from Poisson's equation,

$$\frac{d^2(rV_e)}{dr^2} = 4\pi\rho r , \tag{7}$$

by integrating it twice with the boundary condition

$$rV_e \to -N \quad \text{as} \quad r \to \infty . \tag{8}$$

ρ is such that the electron (number) density is (1) finite at the atomic nucleus, (2) it exhibits an exponential decay with r, and (3) its associated radial electron (number) density exhibits the shell structure of the Ne atom.

For the Ne atom of electron configuration $(1s)^2\ (2s)^2\ (2p)^6$, the electron (number) density is constructed as

$$\rho = \frac{1}{4\pi} [2R_{1s}\ (Z_1)^2 + 2R_{2s}\ (Z_1, Z_2)^2 + 6R_{2p}\ (Z_3)^2] , \tag{9}$$

where $R_{1s}(Z_1)$ and $R_{2p}(Z_3)$ are the radial parts of hydrogen-like radial wave functions, given[10] (in atomic units[9]) by

$$R_{1s}\ (Z_1) = 2Z_1^{3/2}\, e^{-Z_1 r} , \tag{10}$$

$$R_{2p}\ (Z_3) = \frac{1}{2\sqrt{6}} Z_3^{5/2}\, r\, e^{-1/2\,(Z_3 r)} , \tag{11}$$

while $R_{2s}(Z_1,Z_2)$ is the radial part of a hydrogen-like wave function $R_{2s}(Z_2)$, namely

$$R_{2s}\ (Z_2) = \frac{1}{2\sqrt{2}} Z_2^{3/2}\, (2 - Z_2 r) e^{-1/2\,(Z_2 r)} , \tag{12}$$

orthogonalized to a R_{1s} radial function.

This orthogonalized radial wave function $R_{2s}(Z_1,Z_2)$ is given by*

$$R_{2s}(Z_1,Z_2) = \overline{N}\ [R_{2s}{}^{un}\ (Z_2) + CR_{1s}\ (Z_1)] , \tag{13}$$

* The Gram-Schmidt procedure[11] has been used. The superscript *un* on $R_{2s}(Z_2)$ means unnormalized.

where the constant $\overline{N}$ is determined from the normalization condition,

$$\int_0^\infty R_{2s}\,(Z_1, Z_2)^2\, r^2\, dr = 1\,, \tag{14}$$

and the constant C is obtained from the orthogonality condition,

$$\int_0^\infty R_{1s}\,(Z_1)\, R_{2s}\,(Z_1, Z_2)\, r^2\, dr = 0\,. \tag{15}$$

Using Eq. (9), the minimum of Eq. (2) has been found by numerical integration (employing Simpson's rule[11]) in all three approximations. (In the first approximation $Z_1 = Z_2 = Z_3$. In the second approximation $Z_1 \neq Z_2 = Z_3$. In the third approximation $Z_1 \neq Z_2 \neq Z_3$). The results of the calculations are displayed in Tables I – III, and in Figures 1 – 3.

TABLE I.

Values of the variational parameters Z_1, Z_2, Z_3 *and the constants* C *and* $\overline{N}$ *in three approximations for the Ne atom.*

Approximation	Z_1	Z_2	Z_3	C	$\overline{N}$
1st	7.81	7.81	7.81	0	7.72
2nd	10.49	5.76	5.76	–0.0402	4.98
3rd	10.52	2.34	6.63	–0.120	1.28

TABLE II.

Values of the total energy E, *the energy components* E_k, E_{ne}, E_{ee} *(in atomic units*[9]*), and check on the virial theorem V.T.*

Approximation	E	E_k	E_{ne}	E_{ee}	V.T.
1st	–115.05	115.19	–312.40	82.15	–1.9988
2nd	–125.63	125.72	–317.29	65.95	–1.9993
3rd	–128.96	128.91	–320.49	62.62	–2.0004

TABLE III.

Atomic expectations values and their products (in atomic units[9]*), obtained in the three approximations for the Ne atom.*

Approximation	$\langle r \rangle / Z^{2/3}$	$\langle 1/r \rangle / Z^{4/3}$	$\langle r \rangle \langle 1/r \rangle / Z^2$
1st	1.24	1.45	1.80
2nd	1.65	1.47	2.43
3rd	2.16	1.49	3.21
TF equation*	3.19	1.79	5.72
SM equation	3.28	1.76	5.77

* The TF equation values are taken from Ref. 2.

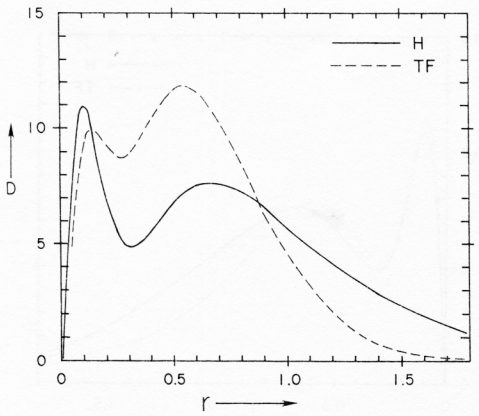

Figure 1. Comparison of the radial electron (number) density obtained in the first approximation for the Ne atom with the Hartree radial (number) density of Brown[12]. (D is measured in units of a_0^{-1} and r is measured in units of a_0).

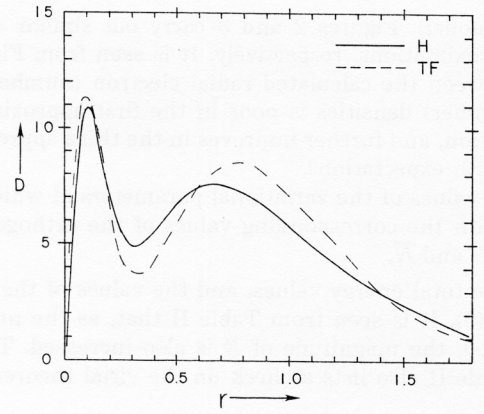

Figure 2. Comparison of the radial electron (number) density obtained in the second approximation for the Ne atom with the Hatree radial (number) density of Brown[12]. (D is measured in units of a_0^{-1}, and r is measured in units of a_0).

DISCUSSION

Figure 1 compares the radial electron (number) density,

$$D = 4\pi r^2 \rho \ , \tag{16}$$

obtained in the first approximation with the Hartree (H) radial electron (number) density of Brown.[12] (Consideration of the H density, instead of the Hartree-Fock (HF) density is called for since, as Dirac[13] has shown, the TF model is the semiclassical

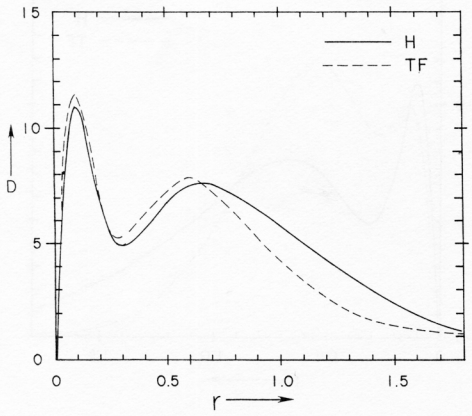

Figure 3. Comparison of the radial electron (number) density obtained in the third approximation for the Ne Atom with the Hatree radial (number) density of Brown[12]. (D is measured in units of a_o^{-1}, and r is measured in units of a_o).

equivalent of the H model). Figures 2 and 3 carry out similar comparisons for the second and third approximations, respectively. It is seen from Figures 1 – 3 that the overall agreement between the calculated radial electron (number) densities and the H radial electron (number) densities is poor in the first approximation, improves in the second approximation, and further improves in the third approximation. This finding is in agreement with expectations.

Table I shows the values of the variational parameters at which Eq. (2) attains its minimum, together with the corresponding values of the orthogonalization and normalization constants C and $\overline{N}$.

Table II shows the total energy values, and the values of the energy components defined in Eqs. (3) – (5). It is seen from Table II that, as the number of variational parameters is increased, the magnitude of E is also increased. This is in agreement with expectations. Table II also lists a check on the virial theorem,

$$\text{V.T.} = (E_{ne} + E_{ee})/E_k = -2 , \tag{17}$$

and shows that it is satisfied quite well.

Table III displays the values of $\langle r \rangle / Z^{2/3}$ and $\langle 1/r \rangle / Z^{4/3}$, together with the values of the product $\langle r \rangle \langle 1/r \rangle / Z^2$. The respective expectation values have been calculated from

$$\langle r^n \rangle = \int_0^\infty r^n \rho \, 4\pi r^2 dr, \tag{18}$$

with $n = 1$ and $n = -1$, respectively. Table III also displays the values of these quantities, obtained by Gadre and Matcha,[2] using the exact solution of the TF equation. It is seen from Table III that, in all three approximations considered in the present work,

the inequality of Gadre[1] is satisfied. It is also seen from Table III that the present energy-density functional approach leads to better bounds on the product $\langle r \rangle < 1/r > /Z^2$ than the approach based on the TF equation. These, and several other aspects of Table III, need to be discussed.

(1) One sees from Table III that the $\langle 1/r \rangle / Z^{4/3}$ values are nearly the same in all the three approximations considered while this is not the case for the $\langle r \rangle / Z^{2/3}$ values. To explain this finding, Eq. (18) has been evaluated for various intervals in r. The result of the computations is presented in Tables IV and V.

Table IV shows that the largest contribution to $\langle 1/r \rangle$ comes from distances close to the nucleus. In this region, the contribution to $\langle 1/r \rangle$ does not appear to change drastically as one moves from the first to the second and then to the third approxima-

TABLE IV

Contribution to $\langle 1/r \rangle$ *from various intervals in* r.

Interval in r	Contribution to $\langle 1/r \rangle$			
Approximation:	1st	2nd	3rd	SM eq.
[0, 0.5]*	23.76	23.87	25.46	20.49
[0. 1]	30.33	29.38	30.22	35.65
[0. 2]	31.24	31.64	31.53	37.21
[0. 3]	31.25	31.69	31.88	37.59
[0, 4]			32.01	37.72
[0. 5]			32.04	37.78
[0. 6]			32.05	37.80
[0, 7]				37.82
[0, 8]				37.83
[0, 9]				37.84

* The entry in the last column has been computed from Eq. (20) with the $x = y^2$ substitution.

TABLE V

Contribution to $\langle r \rangle$ *from various intervals in* r.

Interval in r	Contribution to $\langle r \rangle$			
Approximation:	1st	2nd	3rd	SM eq.
[0, 05]	1.24	0.68	0.83	0.87
[0, 1]	4.46	3.70	3.25	2.51
[0, 2]	5.75	7.41	5.60	5.55
[0, 3]	5.76	7.65	7.72	7.75
[0, 4]		7.66	9.21	9.30
[0, 5]			9.82	10.42
[0, 6]			9.99	11.26
[0, 7]			10.04	11.89
[0, 8]			10.05	12.39
[0, 12]				13.57
[0, 16]				14.16
[0, 20]				14.48
[0, 24]				14.69
[0, 28]				14.82
[0, 70]				15.24
[0, 110]				15.25

tion. Therein lies the explanation of why the values of $\langle 1/r \rangle / Z^{4/3}$ is nearly the same in all the three approximations considered. Table IV also reveals that distances from the nucleus, which are important for the third approximation, are less important for the first and second approximations. This finding has its origin in the fact that one of the variational parameters (Z_2) in the third approximation has a considerably smaller values than the value of any of the variational parameters in the first and second approximations. As a result, ρ decays slower with increasing r in the third approximation than it does in the other two approximations. Therein lies the explanation that there is a slight increase in the value of $\langle 1/r \rangle / Z^{4/3}$ as one moves from the first to the second and then from the second to the third approximation.

Table V shows that, relative to the $\langle 1/r \rangle$ case, distances considerably further away from the nucleus are important in contributing to $\langle r \rangle$. Table V also reveals that larger distances from the nucleus are important for the third approximation and not so important for the first and second approximations. This finding is explainable again by the fact that ρ in the third approximation decreases slower with increasing r than ρ in the first and second approximations. Therein lies the explanation of why the value of $\langle r \rangle / Z^{2/3}$ in Table III increases from the first to the second, and then again from the second to the third approximation.

(2) It is seen from Table III that the present energy-density functional approach leads to better bounds on the product $\langle r \rangle \langle 1/r \rangle / Z^2$ than the approach based[2] on the TF equation. To explain this finding, an analytical approximation of the solution of the TF equation by Sommerfeld[14] and March[15] (SM) is adopted for the evaluation of Eq. (18). The SM equation, which is accurate[16] to better than 3%, is given by

$$\phi = \left[1 + \left(\frac{x^3}{144} \right)^{\lambda/3} \right]^{-3/\lambda} \qquad \text{with } \lambda = 0.8034 , \tag{19}$$

in terms of which Eq. (18) can be evaluated as[2]

$$\langle r^n \rangle = (0.88534138)^n \, Z^{(3-n)/3} \int_0^\infty x^{(2n+1)/2} \, \phi(x)^{3/2} \, dx \tag{20}$$

The connection between the distance r and the dimensionless variable x, on the one hand, and the universal function ϕ and the electron (number) density ρ, on the other hand, is given (in a.u.) by the relations

$$x = r/\mu \tag{21}$$

with

$$\mu = 0.88534138 \, Z^{-1/3}, \tag{22}$$

and

$$\rho = \frac{z}{4\pi \mu^3} \left(\frac{\phi}{x} \right)^{3/2} . \tag{23}$$

Equation (20) has been evaluated for the same intervals in r as before, and the result of the computations is displayed in the last columns of Tables IV and V. Table IV shows that the region closer to the nucleus is again the most important one for $\langle 1/r \rangle$. Table V shows that distances quite far from the nucleus are important for $\langle r \rangle$. These are the distances that were unimportant for $\langle r \rangle$ in the first, second, and third approximations. The origin of this finding is attributed to the fact that, at large values of r, the asymptotic form of the SM equation is proportional to $1/r^3$. Consequently, the integrand in the expression for $\langle r \rangle$ decays slower with r than the integrand does in the first, second, and third approximations. This explains why the value of $\langle r \rangle$ is largest in the TF approximation.

CONCLUSIONS

It is found that the energy-density functional approach gives a better bound on the product of the expectation values of $\langle r \rangle / Z^{2/3}$ and $\langle 1/r \rangle / Z^{4/3}$ than the bound obtained by the TF equation. The fact that the TF value of $\langle r \rangle$ is significantly larger than the values of $\langle r \rangle$ obtained in the first, second, and third approximations is attributed to the power law decay of the TF electron (number) density. To put it another way, distances from the nucleus at which the exponentially decaying electron (number) densities associated with the first, second, and third approximations furnish negligible contributions to $\langle r \rangle$ are still important for contributions to the TF value of $\langle r \rangle$.

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SAŽETAK

Ispitivanje Gadreove nejednakosti s pomoću teorije funkcionala gustoće

P. Csavinsky

U radu se ispituje Gadreova nejednakost. Ona sadržava umnožak očekivanih vrijednosti za udaljenost od središta i recipročnu vrijednost te udaljenosti. Očekivane vrijednosti izračunane su s pomoću teorije funkcionala gustoće, u tri postupne aproksimacije. Za svaku od njih nađeno je da vrijedi Gadreova nejednakost. Rezultati su uspoređeni s Thomas-Fermijevim računima Gadrea i Matche. Nađeno je da pristup zasnovan na funkcionalu gustoće daje bolje granice za umnožak očekivanih vrijednosti nego Thomas-Fermijev model koji nerealno opisuje gustoću na velikim udaljenostima.