Relationships among the terms in the expansions of the kinetic- and exchange-correlation-energy density functionals

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With use of the Sobolev-Hölder inequalities, certain rigorous interrelationships among the leading terms in the expansions of the kinetic- and the exchange-correlation-energy density functionals have been derived. This work has also been extended to include some quasiclassical connections. All these relationships are inequalities that have been tested numerically with use of Hartree-Fock densities for 1806 neutral atoms and their ions.

I. INTRODUCTION

In two recent articles[1,2] some interesting connections, in terms of rigorous bounds, between the leading terms in the expansion of the kinetic and exchange-correlation-energy density functionals[3,4] were derived. These derivations were based on the three-dimensional Sobolev inequality[5,6]

$$\int |\nabla\phi(\mathbf{r})|^2 d\tau \geq 3(\pi/2)^{4/3}\left[\int |\phi(\mathbf{r})|^6 d\tau\right]^{1/3}, \quad (1)$$

for any normalized $\phi(\mathbf{r})$ such that $\int \phi(\mathbf{r})d\tau$ exists, and the Hölder inequality

$$\left|\int f(\mathbf{r})g(\mathbf{r})d\tau\right| \leq \left[\int |f(\mathbf{r})|^p d\tau\right]^{1/p}\left[\int |g(\mathbf{r})|^q d\tau\right]^{1/q} \quad (2)$$

where $f(\mathbf{r}),g(\mathbf{r})$ with $p \geq 1$ and $p^{-1}+q^{-1}=1$ are all real. Recently, Csavinszky and coworkers[7] have made some details investigations on the bounds in Refs. 1 and 2.

The spirit underlying the present work is to bring out additional interesting connections among the leading terms in the expansion of the kinetic and exchange-correlation-density functionals by employing the inequalities in Eqs. (1) and (2). The resulting inequalities were numerically investigated using 1806 Hartree-Fock atomic densities, obtained by numerically solving the "average-energy-of-the-configuration" Hartree-Fock equations.[8]

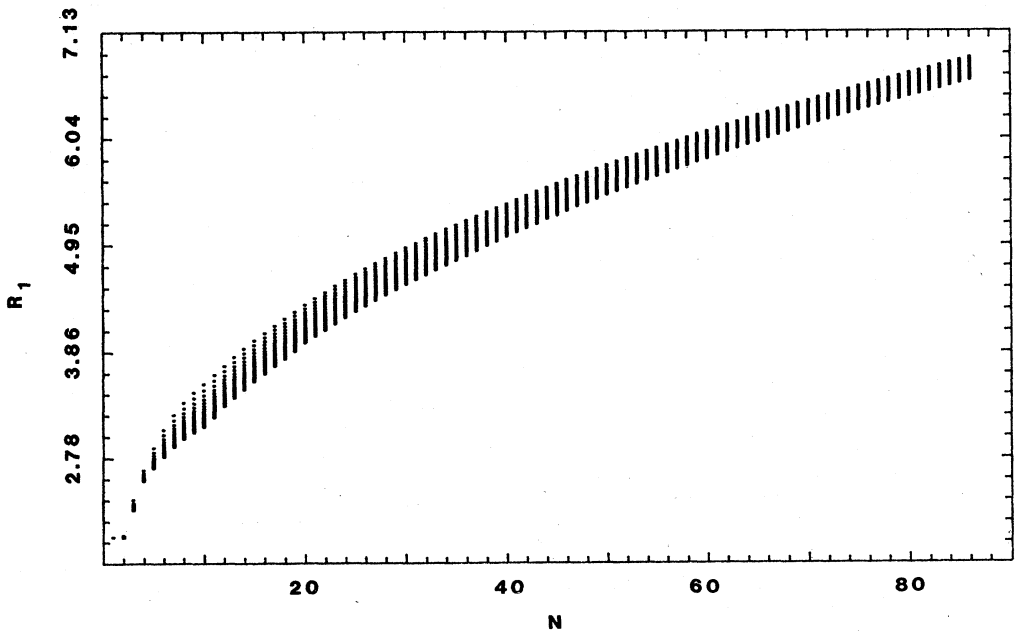

FIG. 1. Plot of R_1 against the number of electrons, N, for 1806 neutral atoms and their ions.

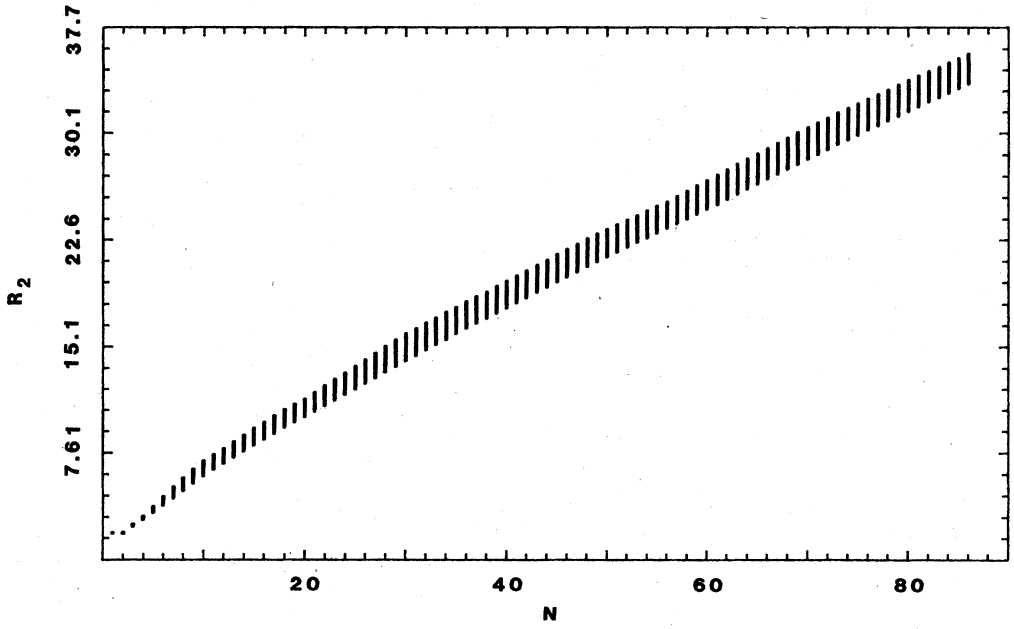

FIG. 2. Plot of R_2 against the number of electrons, N, for 1806 neutral atoms and their ions.

II. DERIVATIONS

A. Rigorous inequalities

As a prerequisite, we note the following inequalities, directly obtainable from the Hölder inequality (2):

$$\int \rho^2 d\tau \leq \left[N \int \rho^3 d\tau \right]^{1/2}, \tag{3}$$

$$\int \rho^2 d\tau \leq \left[\int \rho^{5/3} d\tau \right]^{5/4} \left[\int \rho^3 d\tau \right]^{1/4}, \tag{4}$$

and

$$\left[\int \rho^{5/3} d\tau \right]^2 \leq \left[\int \rho^{4/3} d\tau \right] \left[\int \rho^2 d\tau \right]. \tag{5}$$

Here $N = \int \rho \, d\tau$ represents the total number of electrons. The inequality[9]

$$T_W[\rho] \equiv \tfrac{1}{8} \int (\nabla\rho \cdot \nabla\rho)\rho^{-1} d\tau \leq T[\rho], \tag{6}$$

where $T_W[\rho]$ is the Weizsäcker[10] functional and $T[\rho]$ is the kinetic energy density functional, along with the inequalities given in Refs. 1 and 2, yields

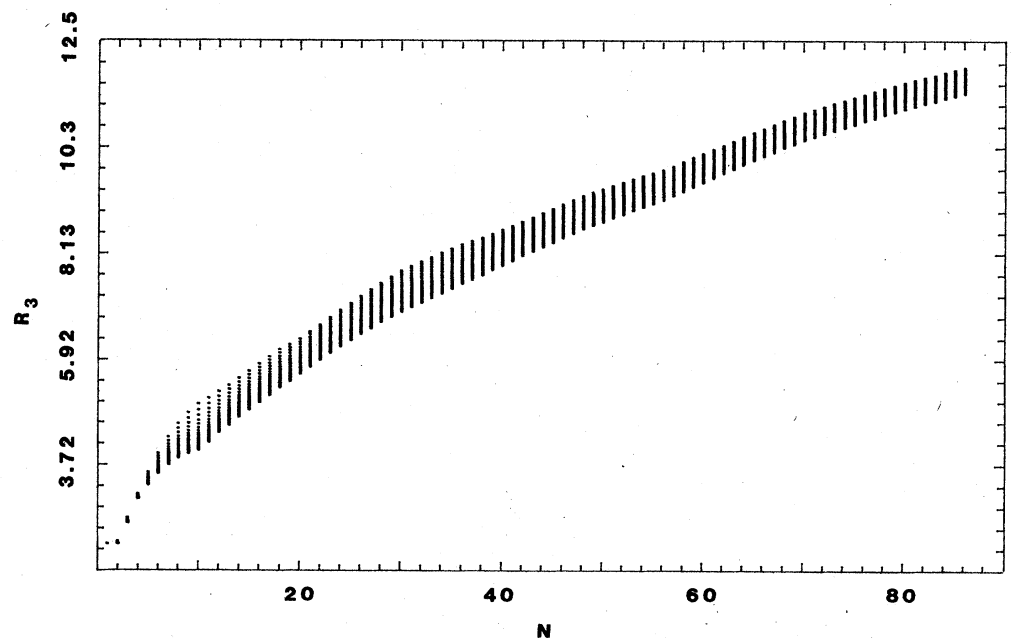

FIG. 3. Plot of R_3 against the number of electrons, N, for 1806 neutral atoms and their ions.

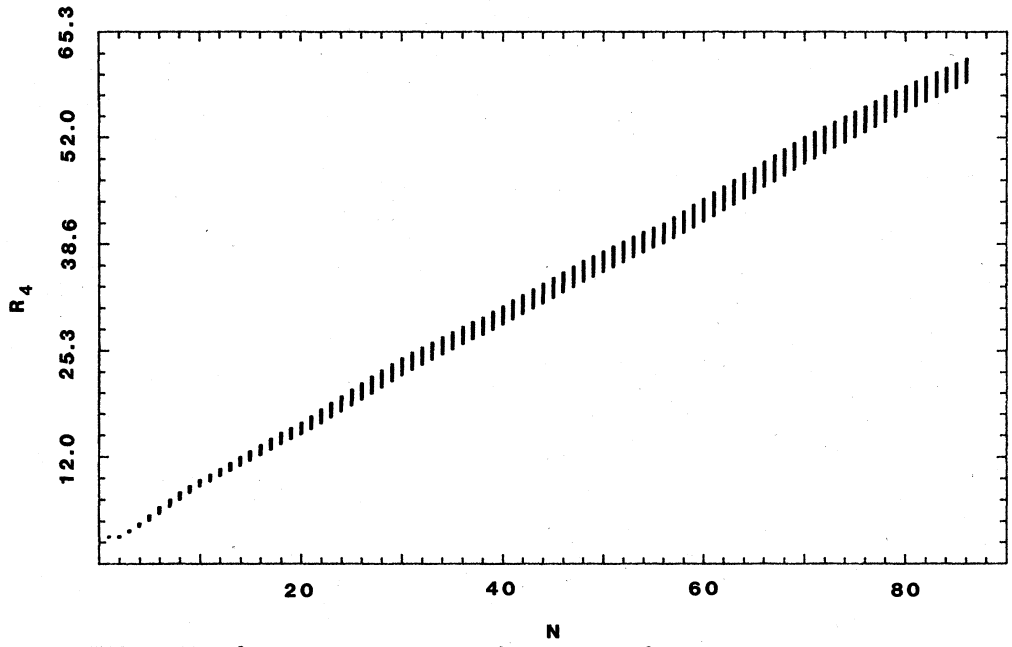

FIG. 4. Plot of R_4 against the number of electrons, N, for 1806 neutral atoms and their ions.

$$\left[\int \rho^3 d\tau\right]^{1/3} \leq \frac{8}{3(2\pi^2)^{2/3}} T_W \leq \frac{8}{3(2\pi^2)^{2/3}} T \ . \tag{7}$$

By means of the inequalities (3) through (4), several interesting rigorous relations can be derived.

A connection between the Weizsäcker term (as well as the total kinetic energy) and $\int \rho^2 d\tau$, which is an observable related to the intensity of the coherent (elastic) scattering of x rays by elements, has been shown by Hyman *et al.*[11] (The derivation given by Hyman *et al.* is in error; the correct derivation is supplied below.) From the inequalities (3), (6), and (7) it follows that

$$1 \leq \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2} N^{1/2} T_W^{3/2} \Big/ \int \rho^2 d\tau \equiv R_1$$
$$\leq \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2} N^{1/2} T^{3/2} \Big/ \int \rho^2 d\tau \equiv R_2 \ . \tag{8}$$

Equation (8) and the recent lower bound for $\int \rho^2 d\tau$ de-

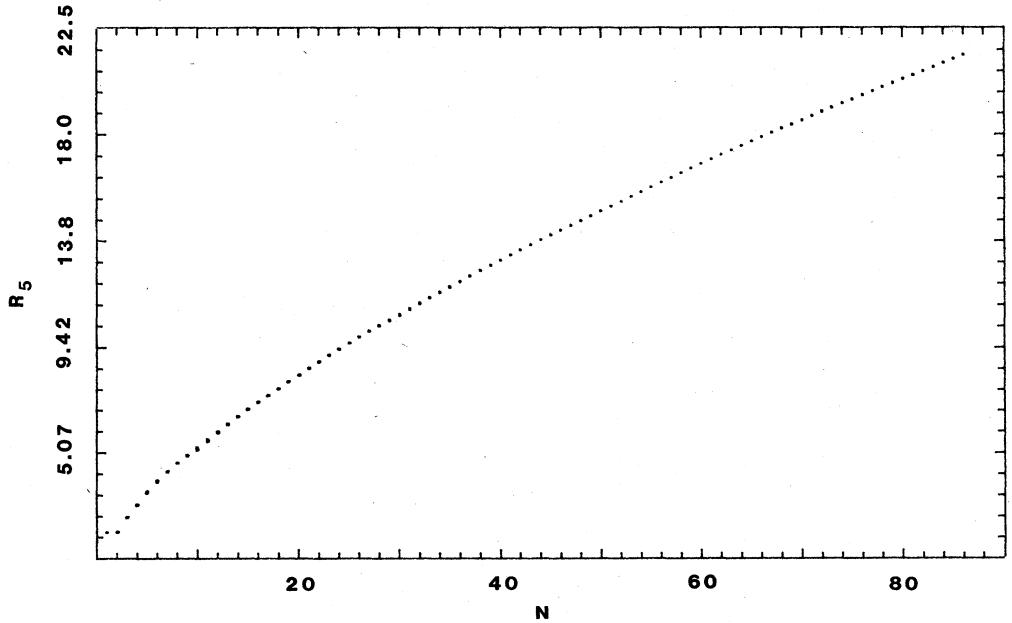

FIG. 5. Plot of R_5 against the number of electrons, N, for 1806 neutral atoms and their ions.

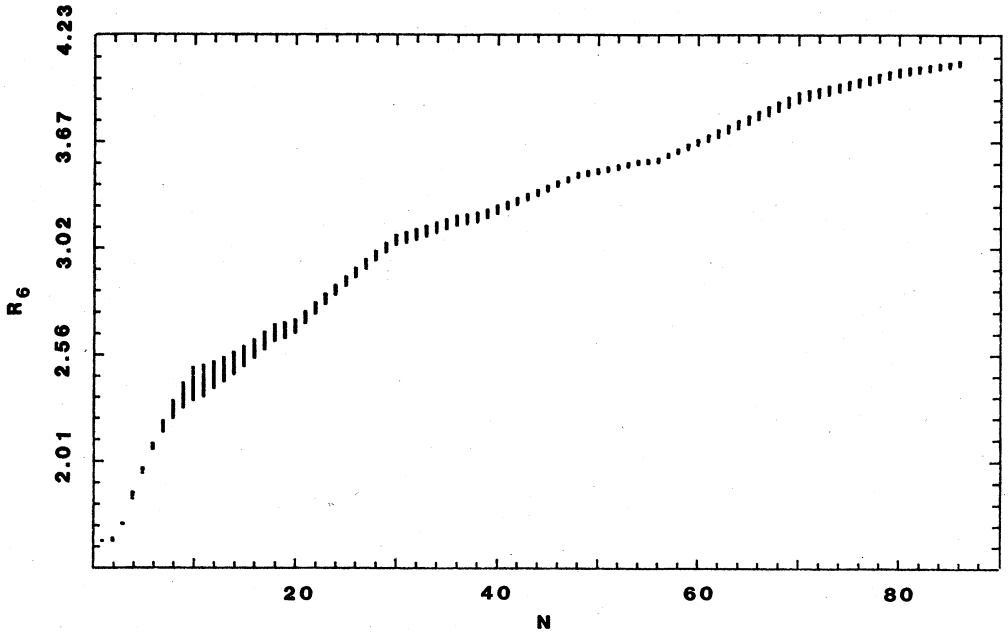

FIG. 6. Plot of R_6 against the number of electrons, N, for 1806 neutral atoms and their ions.

rived by Hyman *et al.*[12] yield

$$0.034N^{1/2}T^{3/2}\Big/\int\rho^2 d\tau \le R_1 \le R_2 \ . \tag{8'}$$

The inequalities (5), (3), and (8) (in the given order) lead to

$$\left[\int\rho^{5/3}d\tau\right]^2 \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2} N^{1/2}\int\rho^{4/3}d\tau\, T_W^{3/2} \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2} N^{1/2}\int\rho^{4/3}d\tau\, T^{3/2}\ , \tag{9}$$

which is easily transformed into

$$1 \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2}(c_{\rm TF}^2/c_{\rm ex})N^{1/2}K_0T_W^{3/2}/T_0^2 \equiv R_3 \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2}(c_{\rm TF}^2/c_{\rm ex})N^{1/2}K_0T^{3/2}/T_0^2 \equiv R_4 \tag{10}$$

where $T_0[\rho]=c_{\rm TF}\int\rho^{5/3}d\tau$, with $c_{\rm TF}=(\frac{3}{10})(3\pi^2)^{2/3}$ is the Thomas-Fermi kinetic energy functional and $K_0[\rho]=c_{\rm ex}\int\rho^{4/3}d\tau$, with $c_{\rm ex}=(\frac{3}{4})(3/\pi)^{1/3}$, is the negative of the Dirac-Slater[13] exchange energy density functional.

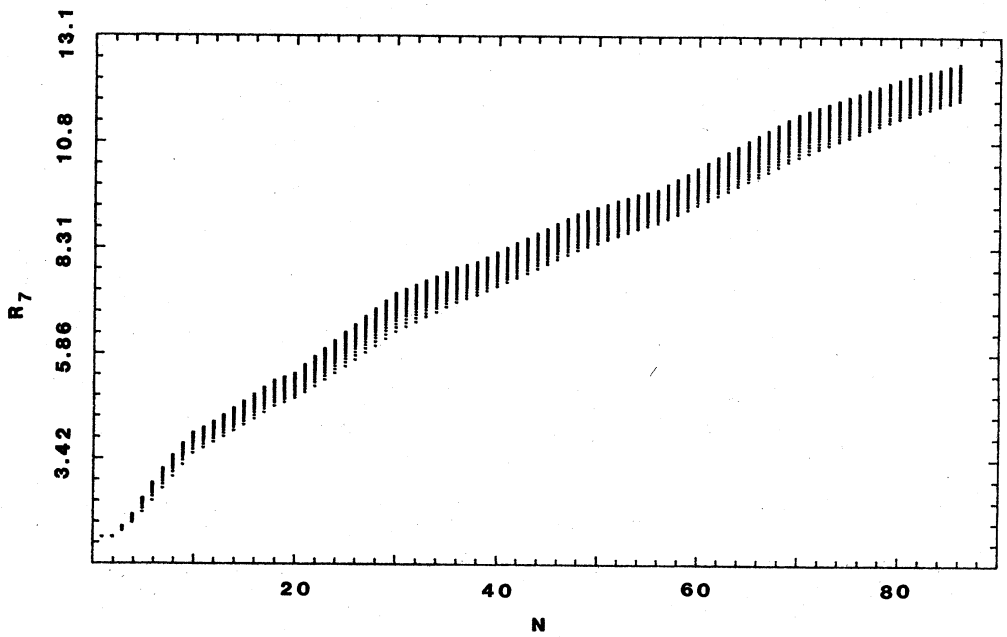

FIG. 7. Plot of R_7 against the number of electrons, N, for 1806 neutral atoms and their ions.

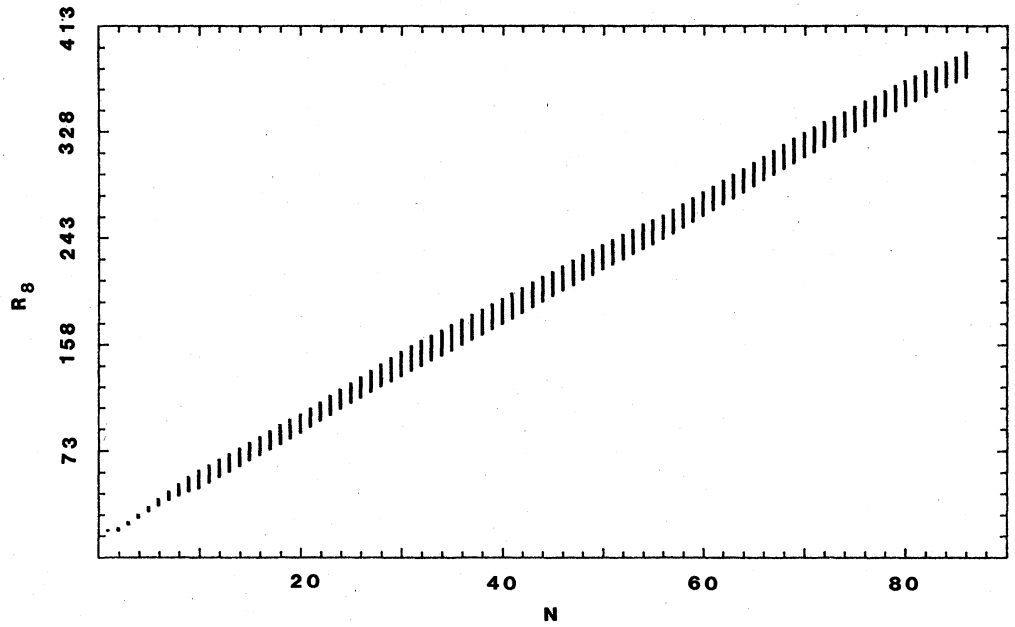

FIG. 8. Plot of R_8 against the number of electrons, N, for 1806 neutral atoms and their ions.

The inequality $T_0 \leq \frac{4}{5}(3N/2)^{2/3}T_W$ (obtained in Ref. 2 through successive applications of the Sobolev and Hölder inequalities) and the inequality (6) furnish a connection between T_0 and T:

$$1 \leq \tfrac{4}{5}(3N/2)^{2/3}T/T_0 \equiv R_5 \ . \tag{11}$$

At this point, a comparison between the inequality (11) and a recent bound due to Lieb and Thirring[14] is in order, namely,

$$1 \leq (4\pi)^{2/3}T/T_0 \equiv R_{\mathrm{LT}} \ . \tag{12}$$

While R_5 is smaller than R_{LT} (the Lieb-Thirring bound) for small N, R_{LT} is tighter than R_5 for values of $N > 12$. A combination of the inequalities (4), (5), and (7) yields

$$\begin{aligned} 1 &\leq \frac{8}{3(2\pi^2)^{2/3}} \frac{c_{\mathrm{TF}}^{5/3}}{c_{\mathrm{ex}}^{4/3}} K_0^{4/3} T_W/T_0 \equiv R_6 \\ &\leq \frac{8}{3(2\pi^2)^{2/3}} \frac{c_{\mathrm{TF}}^{5/3}}{c_{\mathrm{ex}}^{4/3}} K_0^{4/3} T/T_0 \equiv R_7 \ . \end{aligned} \tag{13}$$

Another interesting inequality which involves the value of

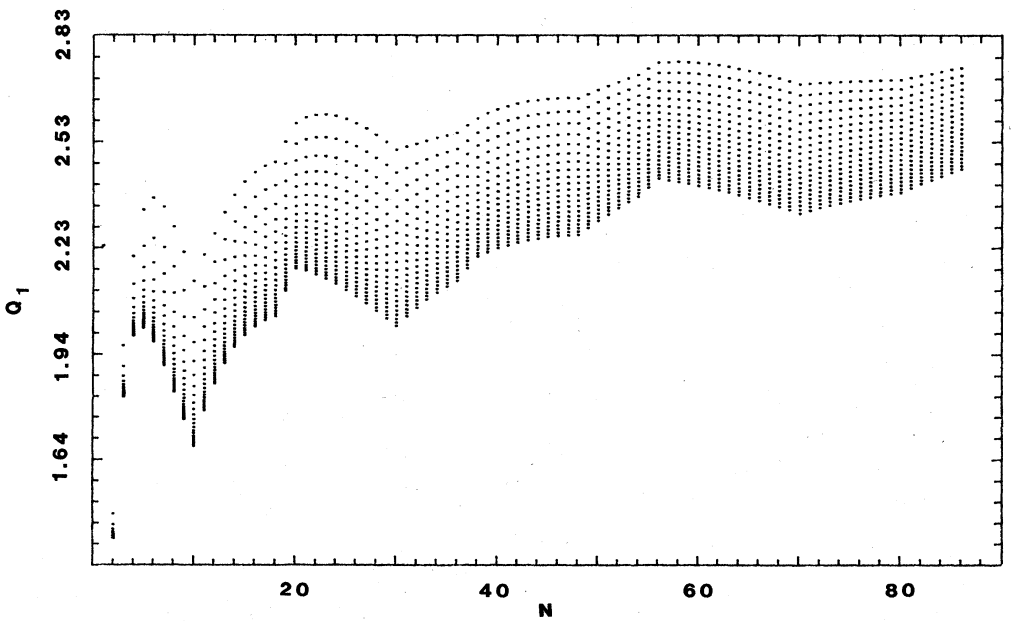

FIG. 9. Plot of Q_1 against the number of electrons, N, for 1806 neutral atoms and their ions.

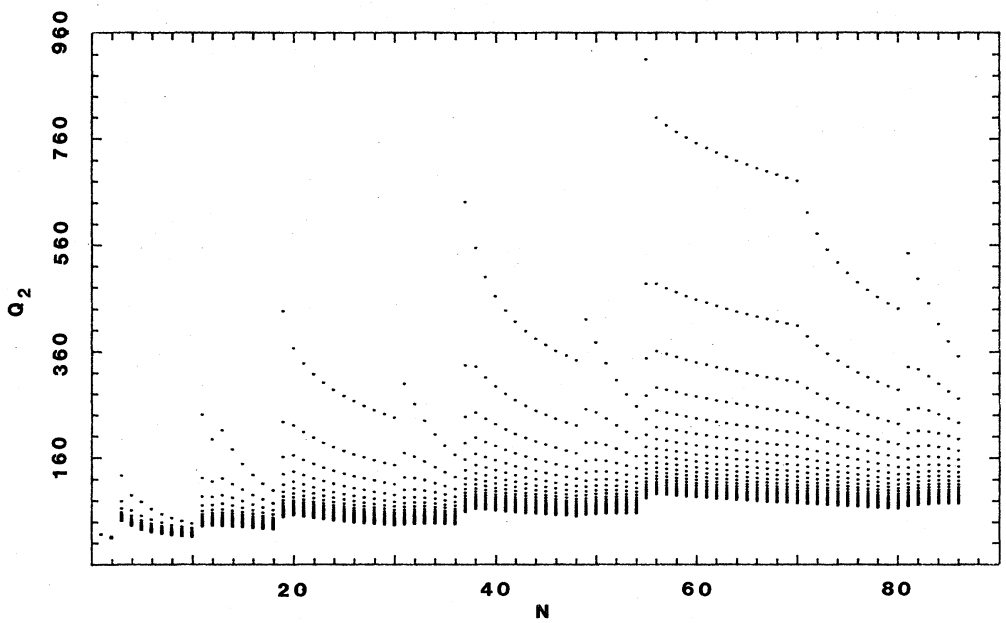

FIG. 10. Plot of Q_2 against the number of electrons, N, for 1806 neutral atoms and their ions.

the electron density at the nucleus $\rho(0)$ is

$$\int \rho^2 d\tau \leq \rho_{\max} \int \rho \, d\tau = \rho(0)N \ , \tag{14}$$

where the monotone decrement of the spherically averaged $\rho(\mathbf{r})$ for atoms is implicit,[15] i.e., the maximum value of $\rho(r)$ is equal to $\rho(0)$. Combining the above inequality with the inequality (5), we find

$$1 \leq \frac{c_{\mathrm{TF}}^2}{c_{\mathrm{ex}}} N\rho(0)K_0/T_0^2 \equiv R_8 \tag{15}$$

which provides a lower bound for $\rho(0)$. Lower bounds to the density are hard to determine and are very scarce in the literature; some recent work in this direction was done by King,[16] who computed several upper and lower bounds to $\rho(0)$ for the helium-isoelectronic sequence.

The ratios R_1 through R_8 provide some interesting rigorous connections between some of the energy density functionals. Apart from these rigorous bounds, it is possible to derive certain relationships on a quasiclassical basis, as done in the next section.

B. Quasiclassical inequalities

From the position and the momentum space transformations that form the theme of Ref. 17, we can show that

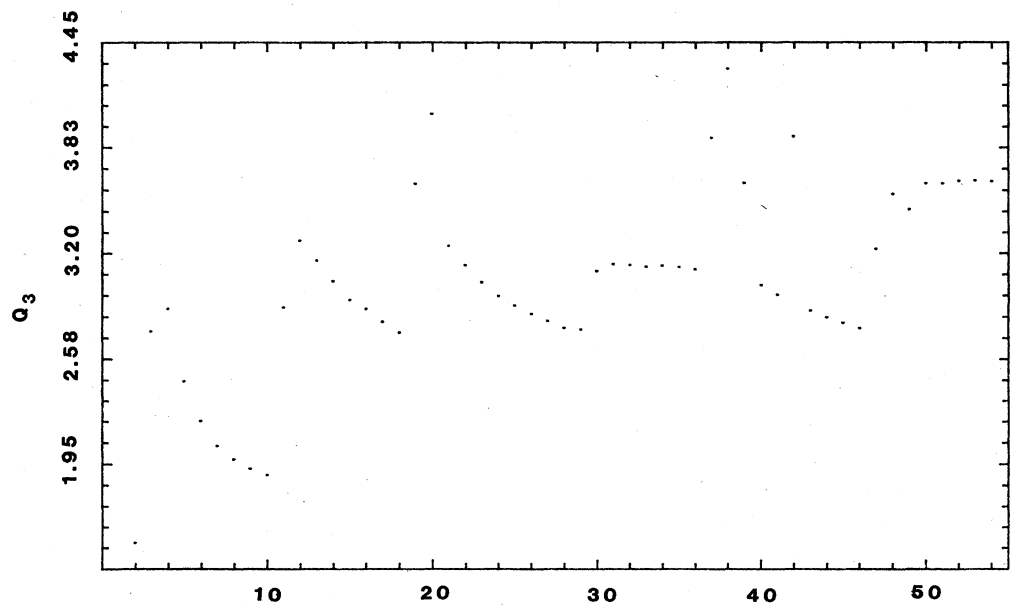

FIG. 11. Plot of Q_3 against the number of electrons, N, for 53 neutral atoms and their ions.

TABLE I. Numerically determined upper and lower limits to the ratios R_1 through R_8 and Q_1 through Q_3.[a]

$1.9610 \leq R_1 \leq 6.8858$
$1.9610 \leq R_2 \leq 35.904$
$2.0699 \leq R_3 \leq 11.984$
$2.0699 \leq R_4 \leq 62.024$
$1.8213 \leq R_5 \leq 21.384$
$1.5933 \leq R_6 \leq 4.0878$
$1.5933 \leq R_7 \leq 12.602$
$9.4184 \leq R_8 \leq 391.46$
$1.4151 \leq Q_1 \leq 2.7562$
$11.613 \leq Q_2 \leq 909.98$
$1.4862 \leq Q_3 \leq 4.2975$

[a]The inequalities R_1 through R_8, Q_1, and Q_2 are based on 1806 Hartree-Fock densities within the range $1 \leq N \leq 86$ and $N \leq Z \leq N+20$. The inequality Q_3 is based on the 53 Hartree-Fock densities within the range $2 \leq N = Z \leq 54$.

the following equalities hold *quasiclassically:*

$$\langle p \rangle_{\text{atomic}} = \pi K_0 \ , \tag{16}$$

and

$$\langle p^{-2} \rangle_{\text{atomic}} = \frac{3}{(3\pi^2)^{2/3}} \int \rho^{1/3} d\tau \ . \tag{17}$$

The above two relations become exact as the nuclear charge tends to infinity. Now, from the theory of distributions $\langle p^2 \rangle_{\text{per particle}} \geq (\langle p \rangle_{\text{per particle}})^2$ or $\langle p^2 \rangle_{\text{atomic}} \geq \langle p_{\text{atomic}} \rangle^2 / N$. With $\langle p^2 \rangle / 2 \equiv T$, and the quasiclassical equality (16), a quasiclassical bound is obtained:

$$1 \leq \frac{2NT}{\pi^2 K_0} \equiv Q_1 \ . \tag{18}$$

Noting that $N^2 \leq \langle p^2 \rangle \langle p^{-2} \rangle$, we obtain

$$1 \leq \frac{6}{(3\pi^2)^{3/2}} T \int \rho^{1/3} d\tau \equiv Q_2 \ . \tag{19}$$

Using $N^2 \leq \langle p \rangle \langle p^{-1} \rangle$ and the fact that $\langle p^{-1} \rangle = 2J(0)$ (exactly), $J(0)$ being the peak value of the Compton profile (which is an observable), we can rewrite (16) as

$$1 \leq 2\pi K_0 J(0) / N^2 \equiv Q_3 \ . \tag{20}$$

All the rigorous bounds R_1 through R_8 and the quasiclassical bounds Q_1 through Q_3 will be numerically tested in the next section.

III. NUMERICAL TESTS AND DISCUSSION

Each of the ratios R_1 through R_8 as well as Q_1 through Q_2 was tested individually for 1806 Hartree-Fock atomic ground-state densities within the range $1 \leq N \leq 86$, $N \leq Z \leq N+20$. The quasiclassical ratio Q_3 was tested using the Clementi-Roetti[18] neutral atom near Hartree-Fock densities and the corresponding theoretical Compton peak values recently obtained by Gadre *et al.*,[19] via a direct Fourier transformation of the Clementi-Roetti wave functions. This ratio was tested for the neutral atoms $2 \leq N = Z \leq 54$. Table I lists the various ratios and the numerical limits which we found for the above Hartree-Fock densities. Plots of the ratios R_1 through R_8 and Q_1 through Q_3 are displayed in Figs. 1—11. Even though the ratios provide interrelationships among some important density functional energy components, none of them are very tight for the Hartree-Fock densities, especially as N becomes large. The reason for this not-very-tight behavior is that several inequalities have been employed in succession to arrive at the final result. However, with the exception of the quasiclassical ratios Q_1 through Q_3, all the ratios tend to rise smoothly with N. The ratios R_2, R_4, and R_8 are of particular interest because of their linear behavior. The ratio R_5 is most interesting because it displays very little Z dependence. The ratio R_8 provides a lower bound to $\rho(0)$ which is not as tight as King's[16] highest lower bound for $N=2$. However, since R_8 is related to some simple integrals of powers of the density alone, certain simple mathematical inequalities enable one to connect the terms in the density expansions.

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