Weizsäcker energy of many-electron systems

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(Received 24 February 1994)

Rigorous lower bounds to the Weizsäcker energy T_W of a many-fermion system are derived by means of two and three radial expectation values. Some of them are of variational nature and others are founded on classical integral inequalities and a theorem which allows us to extend universally the validity of the bounds to T_W obtained for spherically symmetric densities. Also, rigorous and approximate upper bounds, in terms of a radial expectation value and the ionization potential, are encountered in the case of atomic systems by taking into account, at times, the properties of monotonicity of the electron density. The role of the expectation value $\langle r^{-2} \rangle$ is highly remarkable in the determination of the bounds. The bounds found in this work allow us to correlate rigorously the Weizsäcker energy with numerous fundamental and/or experimentally measurable quantities of the system, such as, e.g., the number of constituents, the diamagnetic susceptibility, the diamagnetic-shielding correction, and the softness kernel in the density-functional theory. Finally, just for checking the quality of both lower and upper bounds, numerical comparisons employing Hartree-Fock atomic densities are done in the whole Periodic Table.

I. INTRODUCTION

The Weizsäcker energy T_W given by [1–3]

$$T_W[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} = \frac{1}{2} \int [\nabla \rho^{1/2}(\mathbf{r})]^2 d\mathbf{r} \qquad (1)$$

(atomic units will be used through this paper) is a fundamental element not only in the Thomas-Fermi related theories of many-electron systems [4–6] to explain, e.g., the central and asymptotic behavior of the atomic charge density, the binding of atoms and molecules, and the stability of negative ions, but also in the general density-functional theory initiated by Hohenberg and Kohn [2,3]. Indeed, the Weizsäcker energy is, when multiplied by 1/9, the first order correction to the leading Thomas-Fermi kinetic-energy term T_0 in the gradient expansion of the exact kinetic-energy functional $T[\rho]$ and gives the kinetic energy of the inhomogeneity of the electron density $\rho(\mathbf{r})$ of the system [7–9].

Also the Weizsäcker energy together with the radial expectation value $\langle r^{-2} \rangle$ has been used to obtain different upper bounds to the electron density of atoms and ions [10–12].

Moreover, let us consider the normalized-to-unity and antisymmetric N-fermion wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \sigma_1, ..., \sigma_N)$, where $(\mathbf{r}_i, \sigma_i)$ denotes the space-spin coordinates of the ith-particle. Each particle may have available q spin states; so $\sigma \in \{1, 2, ..., q\}$, $q = 2$ for electrons. Then, the single-particle density is

$$\rho_\Psi(\mathbf{r}) = N \sum_\sigma \int |\Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N, \sigma_1, ..., \sigma_N)|^2$$
$$\times d\mathbf{r}_2 ... d\mathbf{r}_N$$

and the kinetic energy $T[\Psi]$ is [5]

$$T[\Psi] = N \sum_\sigma \int |\nabla_1 \Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N, \sigma_1, ..., \sigma_N)|^2$$
$$\times d\mathbf{r}_2 ... d\mathbf{r}_N .$$

It is not known, possibly it is uncomputable, the expression of this quantity in terms of the single-particle density. That is, the kinetic-energy density-functional $T[\rho_\Psi]$ does not bear an exact, known universal form. The Weizsäcker energy $T_W[\rho_\Psi]$ has been used to rigorously bound the exact kinetic energy $T[\Psi]$ in both sides. Indeed, it is fulfilled that

$$T_W[\rho_\Psi] \leq T[\Psi] \leq (4\pi)^2 N^2 T_W[\rho_\Psi] . \qquad (2)$$

The lower bound was found by Hoffmann-Ostenhof and Hoffmann-Ostenhof [13] and the upper bound was proved by Lieb [5]. The latter bound was improved by Zumbach [14] as follows:

$$T[\Psi] \leq \left[1 + (4\pi)^2 \left(\frac{N}{q} \right)^{2/3} \frac{9}{5^{2/3}} \right] T_W[\rho_\Psi] . \qquad (3)$$

So, since the exact evaluation of the Weizsäcker energy is practically impossible and to avoid uncontrolled approximations for this functional which are not very useful for the general theory, it is natural to obtain rigorous inequalities which involve $T_W[\rho]$ together with other density functionals of fundamental meaning for the system. As reviewed by Gadre and Pathak [15], it is known that

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$$T_W[\rho] \geq 3 \left(\frac{\pi^4}{2^7}\right)^{1/3} \left[\int \rho^3(\mathbf{r})d\mathbf{r}\right]^{1/3} , \qquad (4)$$

which was derived by use of the Sobolev inequality [5,16].

$$T_W[\rho] \geq \frac{5}{(12N)^{2/3}} T_0[\rho] , \qquad (5)$$

which illustrates the relative significance of the first two terms of the aforementioned gradient expansion of the kinetic-energy functional [17,18].

$$T_W[\rho] \geq \left(\frac{\pi}{12}\right)^2 \frac{\langle r^{-1}\rangle^3}{J[\rho]} , \qquad (6)$$

which links the Weizsäcker energy with the direct Coulomb energy functional $J[\rho]$ and the nucleus-electron attraction energy $\langle r^{-1}\rangle$ in an atomic system [19].

$$T_W[\rho] \geq \frac{1}{8} \langle r^{-2}\rangle \equiv L_1 , \qquad (7)$$

which was derived by Gadre and co-workers [16,20], and [12]. The symbol $\langle r^n\rangle$ denotes the nth-radial expectation value defined by

$$\langle r^n\rangle = \int r^n \rho(\mathbf{r})d\mathbf{r} = 4\pi \int_0^\infty r^{n+2}\rho(r)dr \equiv 4\pi\mu_{n+2},$$

which gives, apart from the factor 4π, the moment of $(n+2)$th-order of the spherically symmetric single-particle density $\rho(r)$, i.e., $\rho(r) \equiv \frac{1}{4\pi}\int_\Omega \rho(\mathbf{r})d\Omega$.

The radial expectation values $\langle r^n\rangle$ are not only analytically relevant because they completely characterize the single-particle density but they are physically meaningful. Indeed, they represent the diamagnetic-shielding correction $(n = -1)$ [21], the number of constituents of the system $(n = 0)$, the diamagnetic susceptibility $(n = 2)$ [22], the softness kernel in the density-functional theory $(n = 3)$ [23], and so on.

Here we will use the radial expectation values (moments) as the basic elements to rigorously bound the Weizsäcker energy from below and from above. First in Secs. II and III, we show and derive, respectively, the lower bounds to the Weizsäcker energy of general fermionic systems either variationally or by means of some classical integral inequalities (Sobolev, Hölder) together with a theorem (proved in the Appendix) which allows us to extend to general non-spherically-symmetric densities the validity of the lower bounds to $T_W[\rho]$ obtained for spherically-symmetric densities. Second, in Sec. IV, we find differently upper bounds to the Weizsäcker energy of atomic systems. Then, in Sec. V, just for checking the relative quality of the previous lower and upper bounds, a numerical comparison is carried out in a Hartree-Fock framework. Finally, some concluding remarks (Sec. VI) and some references are given.

II. LOWER BOUNDS: MAIN RESULTS

Here we collect the main lower bounds to the Weizsäcker energy $T_W[\rho]$ of a general fermionic system

that we have found in this work. Some are of variational nature and others are derived from various classical integral inequalities and the Theorem proved in the Appendix.

A. Variational bounds

We have variationally found that

1. Two-moments bounds

$$T_W \geq \frac{9}{8}\frac{N^2}{\langle r^2\rangle} \equiv L_2' , \qquad (8)$$

$$T_W \geq \frac{1}{2}\frac{\langle r^{-1}\rangle^2}{N} \equiv L_2 , \qquad (9)$$

where N is the number of constituents of the system. These two bounds were previously proved [16] only for spherically symmetric bound systems by use of a Redheffer inequality of Weyl type [24,25].

2. Three-moments bounds

$$T_W \geq \frac{1}{8}\langle r^{-2}\rangle \frac{1}{1 - \frac{\langle r^{-1}\rangle^2}{\langle r^{-2}\rangle N}} \equiv L_3' , \qquad (10)$$

$$T_W \geq \frac{1}{8}\langle r^{-2}\rangle \left[1 + \frac{4}{\frac{\langle r^{-2}\rangle\langle r^2\rangle}{N^2} - 1}\right] \equiv L_3 . \qquad (11)$$

B. Nonvariational bounds

They have been obtained by use of one, two, or three classical integral inequalities together with a theorem derived in the Appendix.

1. Two-moments bounds

According to their analytical origin, they may be classified in the two following types.

(a) *First type.* The starting point of these bounds is the above mentioned Redheffer's inequality or alternatively the Hölder inequality. They are given by

$$T_W \geq \frac{(\beta+1)^2}{32} \frac{\left\langle r^{\frac{\beta+1}{2}-3}\right\rangle^2}{\langle r^{\beta-3}\rangle} \qquad (12)$$

for $\beta > 0$. The cases $\beta = 1, 3$, and 5 give the variational one-moment and two-moments bounds expressed by the inequalities (7), (8), and (9), respectively. This allows us to conjecture that all the bounds (12) are not only rigorous but also the best possible ones.

(b) *Second type.* These bounds are obtained from the inequality (4) of Sobolev's origin and various variational bounds to the density functional $\omega_3 = \int \rho^3 d\mathbf{r}$ recently encountered in terms of two moments $\langle r^\alpha \rangle$ [26] (see also [27–30]) or a moment $\langle r^\alpha \rangle$ and a logarithmic moment $\langle r^\alpha \ln r \rangle$ [31,32]. The following three sets of bounds are found.

(i) If $\alpha > \beta > -2$, then

$$T_W \geq C_1(\alpha,\beta) \left(\frac{\langle r^\beta \rangle^{\alpha+2}}{\langle r^\alpha \rangle^{\beta+2}} \right)^{\frac{1}{\alpha-\beta}} \qquad (13)$$

with

$$C_1(\alpha,\beta) = 9 \frac{\pi^{2/3}(\alpha-\beta)^{5/3}}{2^{11/3}} \left[\frac{(6+3\beta)^{6+3\beta}}{(6+3\alpha)^{6+3\alpha}} \right]^{\frac{1}{3(\alpha-\beta)}}$$
$$\times \frac{1}{\left[B\left(\frac{3(2+\beta)}{2(\alpha-\beta)}, \frac{5}{2} \right) \right]^{2/3}} .$$

The symbol $B(x,y)$ denotes the Euler's β function.

In the cases $(\alpha,\beta) = (1,-1)$ and $(2,-1)$ one has the following interesting particular bounds:

$$T_W \geq 0.41733 \frac{\langle r^{-1} \rangle^{3/2}}{\langle r \rangle^{1/2}} , \qquad (14)$$

$$T_W \geq 0.44646 \frac{\langle r^{-1} \rangle^{4/3}}{\langle r^2 \rangle^{1/3}} , \qquad (15)$$

respectively. Moreover, in the cases that $\beta = 0$ or $\alpha = 0$ one has

$$T_W \geq C_1(0,m) \frac{N^{1+2/m}}{\langle r^m \rangle^{2/m}} . \qquad (16)$$

$0 \neq m > -2$, which leads to the following lower bounds

$$T_W \geq \begin{cases} 0.37494 \dfrac{\langle r^{-1} \rangle^2}{N} , & m = -1, \qquad (17) \\[2ex] 0.547353 \dfrac{N^3}{\langle r \rangle^2} , & m = 1, \qquad (18) \\[2ex] 0.59527 \dfrac{N^2}{\langle r^2 \rangle}, & m = 2. \qquad (19) \end{cases}$$

Although less accurate than the corresponding ones previously mentioned, these bounds generalize and complement them.

(ii) If $\beta < \alpha < -2$, then

$$T_W \geq C_2(\alpha,\beta) \left(\frac{\langle r^\alpha \rangle^{-(\beta+2)}}{\langle r^\beta \rangle^{-(\alpha+2)}} \right)^{\frac{1}{\alpha-\beta}} \qquad (20)$$

with

$$C_2(\alpha,\beta) = 9 \frac{\pi^{2/3}(\alpha-\beta)^{5/3}}{2^{11/3}} \left[\frac{(-6-3\beta)^{6+3\beta}}{(-6-3\alpha)^{6+3\alpha}} \right]^{\frac{1}{3(\alpha-\beta)}}$$
$$\times \frac{1}{\left[B\left(\frac{-3(2+\alpha)}{2(\alpha-\beta)}, \frac{5}{2} \right) \right]^{2/3}} .$$

(iii) If $\beta > -3$, then

$$T_W \geq C_3(\alpha,\beta) \langle r^\beta \rangle \exp \left[-(\beta+2) \frac{\langle r^\beta \ln r \rangle}{\langle r^\beta \rangle} - 1 \right] \qquad (21)$$

with

$$C_3(\alpha,\beta) = \frac{\pi^{1/3}}{2^4} (\beta+2)^{2/3} .$$

In the case that $\beta = 0$ one has

$$T_W \geq 0.481\,10 N \exp \left(-2 \frac{\langle \ln r \rangle}{N} \right) . \qquad (22)$$

2. Three-moments bounds

They belong to the two following types.

(a) *First type.* These bounds are derived from the Redheffer's inequality followed by an optimization procedure. They are given by

$$T_W \geq \frac{\langle r^{-2} \rangle}{32} \left(4 + \frac{[4 + \beta(\beta+4)] \left\langle r^{\frac{\beta}{2}-1} \right\rangle^2}{\langle r^\beta \rangle \langle r^{-2} \rangle - \left\langle r^{\frac{\beta}{2}-1} \right\rangle^2} \right); \quad \beta > -2 . \qquad (23)$$

Since $\langle r^\beta \rangle \langle r^{-2} \rangle \geq \langle r^{\frac{\beta}{2}-1} \rangle^2$, this bound improves the known lower bound (7) of Gadre and co-workers [16,20,12]. In addition, in the cases that $\beta = 0$ and 2, one obtains the variational three-moments bounds given by (10) and (11), respectively. Other interesting three-moments lower bounds can be found for bigger values of β. Let us just collect here those that correspond to the case $\beta = 4$:

$$T_W \geq \frac{\langle r^{-2} \rangle}{8} \left(1 + \frac{9}{\frac{\langle r^4 \rangle \langle r^{-2} \rangle}{\langle r \rangle^2} - 1} \right) . \qquad (24)$$

The three-moments bound (23) might be the best possible ones, although we have not been able to show it in general but only for $\beta = 0$ and 2.

(b) *Second Type.* These bounds are derived in three steps: (i) To use the Sobolev-origin inequality (4) in order to bound T_W by means of the functional ω_3, (ii) to use the Hölder inequality [33] in order to bound ω_3 by means of the number N of constituents of the system and any functional $\omega_b = \int \rho(\mathbf{r})^b d\mathbf{r}$ with $1 < b < 3$, and (iii) to use the known variational bounds to ω_b in terms of two radial moments $\langle r^\alpha \rangle$ [26] (see also [27–30]) or a radial moment $\langle r^\alpha \rangle$ and a logarithmic moment $\langle r^\alpha \ln r \rangle$ [32,34].

Among others, the following five sets of lower bounds are found.

(i) If $\alpha > \beta > -3(b-1)/b$, one has

$$T_W \geq K_1(\alpha,\beta,b) N^{-\frac{(3-b)}{3(b-1)}} \left[\frac{\langle r^\beta \rangle^{b(\alpha+3)-3}}{\langle r^\alpha \rangle^{b(\beta+3)-3}} \right]^{\frac{2}{3(b-1)(\alpha-\beta)}} \qquad (25)$$

with

$$K_1(\alpha,\beta,b) = \frac{3\pi^{2/3}}{2^{11/3}} \frac{(\alpha-\beta)^{\frac{2(2b-1)}{3(b-1)}} b^{\frac{2b}{3(b-1)}}}{\left[B\left(\frac{-3+3b+\beta b}{(\alpha-\beta)(b-1)}, \frac{2b-1}{b-1}\right)\right]^{2/3}}$$

$$\times \left[\frac{(-3+3b+b\alpha)^{3-3b-b\alpha}}{(-3+3b+b\beta)^{3-3b-b\beta}}\right]^{\frac{2}{3(b-1)(\alpha-\beta)}} . \tag{26}$$

An interesting particular case is that $b = 2, \beta = -1$, and $\alpha > -1$; then,

$$T_W \geq K_1(\alpha, -1, 2)N^{-1/3} \left[\frac{\langle r^{-1}\rangle^{2\alpha+3}}{\langle r^{\alpha}\rangle}\right]^{\frac{2}{3(\alpha+1)}} . \tag{27}$$

And for $\alpha = 2$, one has

$$T_W \geq 0.359\,451 N^{-1/3} \left(\frac{\langle r^{-1}\rangle^7}{\langle r^2\rangle}\right)^{2/9} . \tag{28}$$

(ii) If $\beta < \alpha < -3(b-1)/b$, then

$$T_W \geq K_2(\alpha,\beta,b)N^{-\frac{(3-b)}{3(b-1)}}$$

$$\times \left[\frac{\langle r^{\alpha}\rangle^{-b(\beta+3)+3}}{\langle r^{\beta}\rangle^{-b(\alpha+3)+3}}\right]^{\frac{2}{3(b-1)(\alpha-\beta)}} \tag{29}$$

with

$$K_2(\alpha,\beta,b) = \frac{3\pi^{2/3}}{2^{11/3}} \frac{(\alpha-\beta)^{\frac{2(2b-1)}{3(b-1)}} b^{\frac{2b}{3(b-1)}}}{\left[B\left(\frac{3-3b-\alpha b}{(\alpha-\beta)(b-1)}, \frac{2b-1}{b-1}\right)\right]^{2/3}}$$

$$\times \left[\frac{(3-3b-b\alpha)^{3-3b-b\alpha}}{(3-3b-b\beta)^{3-3b-b\beta}}\right]^{\frac{2}{3(b-1)(\alpha-\beta)}} . \tag{30}$$

A particular case is $b = 5/4, \alpha = -1, \beta = -2$,

$$T_W \geq 0.375\,341 N^{-7/3} \frac{\langle r^{-1}\rangle^{14/3}}{\langle r^{-2}\rangle^{4/3}} . \tag{31}$$

(iii) It is fulfilled that

$$T_W \geq 0.2083 \frac{\langle r^{-1}\rangle^2}{N} \left(1 - \frac{\langle r^{-1}\rangle^2}{N\langle r^{-2}\rangle}\right)^{1/3} . \tag{32}$$

(iv) If $\beta > -3(b-1)/b$, then

$$T_W \geq K_3(\beta,b) \frac{\langle r^{\beta}\rangle^{\frac{2b}{3(b-1)}}}{N^{\frac{3-b}{3(b-1)}}}$$

$$\times \exp\left[\frac{[-b(\beta+3)+3]2}{3(b-1)} \frac{\langle r^{\beta}\ln r\rangle}{\langle r^{\beta}\rangle} - \frac{2b}{3(b-1)}\right] \tag{33}$$

with

$$K_3(\beta,b) = \frac{3\pi^{2/3}}{2^{11/3}} \frac{b^{\frac{2b}{3(b-1)}}}{(b-1)^{\frac{2(2b-1)}{3(b-1)}}} \frac{(b(\beta+3)-3)^{2/3}}{\left[\Gamma\left(\frac{2b-1}{b-1}\right)\right]^{2/3}} .$$

In the case $\beta = 0$, one has

$$T_W \geq K_3(0,b)N \exp\left[-2\frac{\langle \ln r\rangle}{N} - \frac{2b}{3(b-1)}\right] . \tag{34}$$

(v) If $\beta < -3(b-1)/b$, then

$$T_W \geq K_4(\beta,b) \frac{\langle r^{\beta}\rangle^{\frac{2b}{3(b-1)}}}{N^{\frac{3-b}{3(b-1)}}}$$

$$\times \exp\left[\frac{[-b(\beta+3)+3]2}{3(b-1)} \frac{\langle r^{\beta}\ln r\rangle}{\langle r^{\beta}\rangle} - \frac{2b}{3(b-1)}\right] \tag{35}$$

with

$$K_4(\beta,b) = \frac{3\pi^{2/3}}{2^{11/3}} \frac{b^{\frac{2b}{3(b-1)}}}{(b-1)^{\frac{2(2b-1)}{3(b-1)}}} \frac{[-b(\beta+3)+3]^{2/3}}{\left[\Gamma\left(\frac{2b-1}{b-1}\right)\right]^{2/3}} .$$

III. LOWER BOUNDS: PROOFS

Let us prove the lower bounds described in the previous section.

A. Proof of the variational bounds

To prove the inequalities (8)–(11) we will look for extremals to the functional

$$\mathcal{F}(f) = \int \frac{|\nabla f(\mathbf{r})|^2}{f(\mathbf{r})} d\mathbf{r} \tag{36}$$

among all the positive definite functions $f(\mathbf{r})$ subject to the n moment restrictions

$$\int r^{\alpha_i} f(\mathbf{r}) d\mathbf{r} = \langle r^{\alpha_i}\rangle, i = 1,\ldots,n . \tag{37}$$

To do that, we write the corresponding variational equations as

$$\delta\left[\int \frac{|\nabla f|^2}{f} d\mathbf{r} - \sum_{i=1}^{n} \lambda_i \int r^{\alpha_i} f(\mathbf{r}) d\mathbf{r}\right] = 0 , \tag{38}$$

where λ_i are the Lagrange multipliers, i.e., the unknown parameters to be determined by means of the aforementioned restrictions. The differential equation to be solved is

$$\frac{|\nabla f|^2}{f^2} + 2\nabla\left(\frac{\nabla f}{f}\right) + \sum_{i=1}^{n} \lambda_i r^{\alpha_i} = 0 .$$

With the change $f(\mathbf{r}) \to y(\mathbf{r})$: $y(\mathbf{r}) = [f(\mathbf{r})]^{1/2}$ this equation transforms into

$$\nabla^2 y + \sum_{i=1}^{n} \frac{\lambda_i}{4} r^{\alpha_i} y = 0 .$$

(i) Let us first find the two-moments bounds (8) and (9). So, $n = 2$.

(1) If $\alpha_1 = 0$ and $\alpha_2 = 2$, the only solutions fulfilling the integrability conditions are

$$f(\mathbf{r}) = C^2_{n_1,n_2,n_3}\left(\prod_{i=1}^{3} H_{n_i}\left(x_i\left(\frac{-\lambda_1}{4}\right)^{1/4}\right)\right)$$
$$\times \exp\left[-x_i^2\left(\frac{-\lambda_1}{4}\right)^{1/2}/2\right]\right)^2 , \qquad (39)$$

where $(x_1, x_2, x_3) \in \mathbb{R}^3, \lambda_2 \in \mathbb{R}, \lambda_1 < 0, n_i \in \mathbf{N} \cup 0, i = 1,2,3$, and

$$\sum_{i=1}^{3}\left(n_i + \frac{1}{2}\right) = \left[-\lambda_2^2/(16\lambda_1)\right]^{1/2} .$$

The symbols $H_{n_i}(x)$ denote the Hermite polynomials of degree n_i. The values of $C^2_{n_1,n_2,n_3}$ and λ_1 are obtained by means of the restrictions (37) in this case. They are given by

$$(-\lambda_1/4)^{1/2} = \frac{N}{\langle r^2\rangle}\sum_{i=1}^{3}\left(n_i + \frac{1}{2}\right)$$

and

$$C^2_{n_1,n_2,n_3} = \frac{N^{5/2}}{\langle r^2\rangle^{3/2}}\left[\sum_{i=1}^{3}\left(n_i + \frac{1}{2}\right)\right]^{3/2}$$
$$\times \prod_{i=1}^{3}\left[2^{n_i}n_i!\sqrt{\pi}\right]^{-1} .$$

Then

$$\mathcal{F}(f) = \frac{N^2}{\langle r^2\rangle}4(n_1 + n_2 + n_3 + \tfrac{3}{2})^2 \qquad (40)$$

so that the only extremal which may supply a minimum is that corresponding to the case $n_1 = n_2 = n_3 = 0$. To show that $9N^2/(8\langle r^2\rangle)$ is indeed a minimum it is enough to prove that $\frac{\delta\mathcal{F}}{\delta f}$ exits and $\mathcal{F}(f)$ is a convex functional [35]. The former is trivial since the function does not vanish and the latter is shown in the Appendix. So the bound L_2' is proved.

(2) For $\alpha_1 = 0$ and $\alpha_2 = -1$ one can work similarly as in the previous case and finds that the minimum extremal is

$$f(\mathbf{r}) = \frac{C_0^2}{4\pi}\exp(-\sqrt{|\lambda_1|}r) \qquad (41)$$

with

$$\lambda_2^2 = 16|\lambda_1| , \qquad\qquad \lambda_1 < 0, \lambda_2 \geq 0 ,$$

and the values of C_0^2 and λ_1 are given by

$$C_0^2 = 4\frac{\langle r^{-1}\rangle^3}{N^2}; \qquad \sqrt{|\lambda_1|} = 2\frac{\langle r^{-1}\rangle}{N} ,$$

so that the bound L_2 readily follows. (ii) Let us now prove the three-moments bound (10) and (11). So, $n = 3$.

(1) In the particular case that $\alpha_1 = -1, \alpha_2 = 2$ and $\alpha_3 = 0$, the solution of our differential equation which minimizes $\mathcal{F}$ is

$$f(\mathbf{r}) = \frac{C_0^2}{4\pi}r^{-1+\sqrt{1-\lambda_2}}\exp(-2r\sqrt{-\lambda_3/4}) \qquad (42)$$

with $\lambda_2 \leq 0, \lambda_3 > 0$ and

$$\frac{1}{4}\lambda_3 = -\left[\frac{\lambda_3/4}{1+\sqrt{1-\lambda_2}}\right]^2 .$$

The values of the Lagrange multipliers are

$$\sqrt{1-\lambda_2} = \frac{1}{N\langle r^{-2}\rangle/\langle r^{-1}\rangle^2 - 1} ,$$

$$2\sqrt{-\lambda_3/4} = \frac{\langle r^{-2}\rangle}{N\langle r^{-2}\rangle/\langle r^{-1}\rangle - \langle r^{-1}\rangle} ,$$

$$C_0^2 = \frac{\langle r^{-2}\rangle}{\Gamma\left[1/(N\langle r^{-2}\rangle/\langle r^{-1}\rangle^2 - 1)\right]}$$
$$\times \left[\frac{\langle r^{-2}\rangle}{N\langle r^{-2}\rangle/\langle r^{-1}\rangle - \langle r^{-1}\rangle}\right]^{\frac{1}{N\langle r^{-2}\rangle/\langle r^{-1}\rangle^2 - 1}} .$$

Then, the bound L_3' given by (10) follows. (2) If $\alpha_1 = -2, \alpha_2 = 2, \alpha_3 = 0$, the solution of the differential equation which minimizes $\mathcal{F}$ is

$$f(\mathbf{r}) = \frac{C_0^2}{4\pi}r^{-1+\frac{1}{2}\sqrt{1-\lambda_1}}\exp(-r^2\sqrt{-\lambda_2/4}) \qquad (43)$$

with $\lambda_1 < 0, \lambda_2 < 0$ and

$$-\frac{1}{4}\lambda_3 = 2\sqrt{-\frac{1}{4}\lambda_2}\left(\frac{1}{2}\sqrt{1-\lambda_1}+1\right) .$$

The values of the Lagrange multipliers are

$$\frac{1}{4}\sqrt{1-\lambda_1} = \frac{1}{\langle r^{-2}\rangle\langle r^2\rangle/N^2 - 1} ,$$

$$\sqrt{-\frac{1}{4}\lambda_2} = \frac{\langle r^{-2}\rangle}{N}\frac{1}{\langle r^{-2}\rangle\langle r^2\rangle/N^2 - 1} ,$$

$$C_0^2 = \frac{2\langle r^{-2}\rangle}{\Gamma\left[1/(\langle r^{-2}\rangle\langle r^2\rangle/N^2 - 1)\right]}$$
$$\times \left[\frac{\langle r^{-2}\rangle}{N(\langle r^{-2}\rangle\langle r^2\rangle/N - 1)}\right]^{\frac{1}{\langle r^{-2}\rangle\langle r^2\rangle/N^2 - 1}} .$$

Then, the bound L_3 given by (11) follows.

B. Proof of the nonvariational two- and three-moments lower bounds of the first type

These bounds are given by the inequalities (12) and (23). To derive them we start from the following Redheffer's inequality of Weyl type valid for any absolutely continuous $u(r)$:

$$\int_0^\infty r^{m+n-1} u^2(r) dr \leq \frac{2}{m+n} \left\{ \int_0^\infty r^{2n} [u'(r)]^2 dr \right.$$

$$\left. \times \int_0^\infty r^{2m} u^2(r) dr \right\}^{1/2},$$

so that $-m < n \leq m+1$. Following Gadre and Chakravorty [12] we make the change $u(r) = r^k \sqrt{\rho(r)}, k = 1-n$, and obtain

$$T_W[\rho(r)] \geq \frac{(m-k+1)^2}{8} \frac{\langle r^{m+k-2} \rangle^2}{\langle r^{2m+2k-2} \rangle} - \frac{1}{2} k(k-1) \langle r^{-2} \rangle \tag{44}$$

(with $-m \leq k < m+1$), which is valid only for a spherically symmetric density $\rho(r)$. On the other hand, there is a theorem (see Appendix) which states that

$$T_W[\rho(\mathbf{r})] \geq T_W[\rho(r)] . \tag{45}$$

Then, in the case that $k = 0$ and with the change $m \to \beta = 2m+1$ the inequality (44) directly leads to the searched lower bound (12) for $\beta > 1$. To find the bound (12) for $\beta > 0$ we need the use of Hölder inequality [33]. To find the other inequality (23), we consider the inequality (44) for the general case in which k does not necessarily vanish. Then, by use of the change $(m,k) \to (\beta,x)$ so that $k = \frac{\beta}{4} + \frac{1}{2} - x$ and $m = \frac{\beta}{4} + \frac{1}{2} + x$ one has

$$T_W \geq \frac{\langle r^{\frac{\beta}{2}-1} \rangle^2}{\langle r^\beta \rangle} \frac{x^2}{2} - \frac{1}{2} \langle r^{-2} \rangle \left(\frac{\beta}{4} + 1 - x \right) \left(\frac{\beta}{4} - x \right) \tag{46}$$

with $\beta \geq -2$ and $x > 0$. Now, we optimize this inequality with fixed β by looking it as a function of x. This function has a maximum at

$$x = \frac{\beta+2}{4} \left(1 - \frac{\langle r^{\frac{\beta}{2}-1} \rangle^2}{\langle r^\beta \rangle \langle r^{-2} \rangle} \right)^{-1}$$

and the value of the function at this maximum is the searched lower bound (23).

C. Proof of the nonvariational two-moments bounds of the second type

Here we want to prove the inequalities (13), (20), and (21). To do that we start with the inequality (4), i.e.,

$$T_W \geq 3 \left(\frac{\pi^4}{2^7} \right)^{1/3} \omega_3^{1/3} \tag{47}$$

with $\omega_3 = \int \rho^3(\mathbf{r}) d\mathbf{r}$.

Then we use the variational lower bounds to the density functional $\omega_t, t > 1$, encountered by Dehesa et al. [26] in terms of two radial moments, $\langle r^\alpha \rangle$ and $\langle r^\beta \rangle$, and by Porras and Gálvez [34,32] in terms of a radial moment and a logarithmic moment, respectively. These bounds are given in the case $t = 3$ by the following.

If $\alpha > \beta > -2$, then

$$\omega_3 \geq F_1(\alpha,\beta) \left(\frac{\langle r^\beta \rangle^{\alpha+2}}{\langle r^\alpha \rangle^{\beta+2}} \right)^{\frac{1}{\alpha-\beta}} \tag{48}$$

with

$$F_1(\alpha,\beta) = \frac{27(\alpha-\beta)^5}{16\pi^2} \left(\frac{(6+3\beta)^{6+3\beta}}{(6+3\alpha)^{6+3\alpha}} \right)^{\frac{1}{\alpha-\beta}}$$

$$\times \frac{1}{\left[B\left(\frac{6+3\beta}{2(\alpha-\beta)}, \frac{5}{2} \right) \right]^2} .$$

The symbol $B(x,y)$ denotes the Euler's β function. If $\beta < \alpha < -2$, then

$$\omega_3 \geq F_2(\alpha,\beta) \left(\frac{\langle r^\alpha \rangle^{-(\beta+2)}}{\langle r^\beta \rangle^{-(\alpha+2)}} \right)^{\frac{1}{\alpha-\beta}} \tag{49}$$

with

$$F_2(\alpha,\beta) = \frac{27(\alpha-\beta)^5}{16\pi^2} \left(\frac{(-6-3\beta)^{6+3\beta}}{(-6-3\alpha)^{6+3\alpha}} \right)^{\frac{1}{\alpha-\beta}}$$

$$\times \frac{1}{\left[B\left(\frac{-(6+3\alpha)}{2(\alpha-\beta)}, \frac{5}{2} \right) \right]^2} .$$

If $\beta > -3$, then

$$\omega_3 \geq F_3(\beta) \langle r^\beta \rangle^3 \exp\left[-3(\beta+2) \frac{\langle r^\beta \ln r \rangle}{\langle r^\beta \rangle} - 3 \right] \tag{50}$$

with

$$F_3(\beta) = \frac{27}{32} \frac{(2+\beta)^2}{\pi^3} .$$

The combination of the inequality (47) with the inequalities (48), (49), and (50) produces the searched lower bounds (13), (20), and (21), respectively, in an easy manner.

D. Proof of the nonvariational three-moments bounds of the second type

Here we want to prove the inequalities (25), (29), (32), (33), and (35). We start from the inequality (4), i.e.,

$$T_W \geq 3 \left(\frac{\pi^4}{2^7} \right)^{1/3} \omega_3^{1/3} \tag{51}$$

Then, we use the Hölder inequality [33] which allows us to bound from below the quantity ω_3 by means of the number N of constituents of the system and any density functional ω_b, $1 < b < 3$, as follows:

$$\omega_3 \geq \left(\frac{\omega_b^2}{N^{3-b}} \right)^{\frac{1}{b-1}} . \tag{52}$$

Finally we take into account the following lower bounds

of the density functionals $\omega_t, t > 1$, in terms of two radial expectation values [26]:

(1) If $\alpha > \beta > -3(t-1)/t$, then

$$\omega_t \geq F_1(\alpha, \beta, t) \left[\frac{\langle r^\beta \rangle^{t(\alpha+3)-3}}{\langle r^\alpha \rangle^{t(\beta+3)-3}} \right]^{\frac{1}{\alpha-\beta}} \tag{53}$$

with

$$F_1(\alpha, \beta, t) = \frac{t^t (\alpha - \beta)^{2t-1}}{[4\pi B\{[t(\beta+3) - 3] / [(\alpha - \beta)(t-1)], (2t-1) / (t-1)\}]^{t-1}} \left\{ \frac{[t(\beta+3) - 3]^{t(\beta+3)-3}}{[t(\alpha+3) - 3]^{t(\alpha+3)-3}} \right\}^{\frac{1}{\alpha-\beta}} . \tag{54}$$

(2) If $\beta < \alpha < -3(t-1)/t$, then

$$\omega_t \geq F_2(\alpha, \beta, t) \left[\frac{\langle r^\alpha \rangle^{-t(\beta+3)+3}}{\langle r^\beta \rangle^{-t(\alpha+3)+3}} \right]^{\frac{1}{\alpha-\beta}} \tag{55}$$

with

$$F_2(\alpha, \beta, t) = \frac{t^t (\alpha - \beta)^{2t-1}}{[4\pi B\{[-t(\alpha+3) + 3] / [(\alpha - \beta)(t-1)], (2t-1) / (t-1)\}]^{t-1}} \left\{ \frac{[-t(\alpha+3) + 3]^{-t(\alpha+3)+3}}{[-t(\beta+3) + 3]^{-t(\beta+3)+3}} \right\}^{\frac{1}{\alpha-\beta}} . \tag{56}$$

Also, it is known that the density functionals $\omega_t, t > 1$, can be bounded from below [34,32] in terms of radial moments $\langle r^\alpha \rangle$ and a logarithmic moment $\langle r^\alpha \ln r \rangle$.

(3) If $\beta > -3(t-1)/t$, then

$$\omega_t \geq F_3(\beta, t) \langle r^\beta \rangle^t \exp \left([-t(\beta+3) + 3] \frac{\langle r^\beta \ln r \rangle}{\langle r^\beta \rangle} - t \right) \tag{57}$$

with

$$F_3(\beta, t) = \frac{t^t}{(t-1)^{2t-1}} \left[\frac{t(\beta+3) - 3}{4\pi \Gamma[(2t-1)/(t-1)]} \right]^{t-1} .$$

(4) If $\beta < -3(t-1)/t$, then

$$\omega_t \geq F_4(\beta, t) \langle r^\beta \rangle^t \exp \left([-t(\beta+3) + 3] \frac{\langle r^\beta \ln r \rangle}{\langle r^\beta \rangle} - t \right) \tag{58}$$

with

$$F_4(\beta, t) = \frac{t^t}{(t-1)^{2t-1}} \left[\frac{-t(\beta+3) + 3}{4\pi \Gamma[(2t-1)/(t-1)]} \right]^{t-1} ,$$

where $\Gamma(x)$ denotes the Gamma function. The combination of the inequalities (51) and (52) together with (53), (55), (57), and (58) readily leads to the searched lower bounds (25), (29), (33), and (35), respectively.

It remains to be proved the inequality (32). To obtain it we need the following result [34]:

$$\omega_{5/3} \geq \frac{5}{9(2\pi^2)^{2/3}} \frac{\langle r^{-1} \rangle^2}{N^{1/3}} \left(1 - \frac{\langle r^{-1} \rangle^2}{\langle r^{-2} \rangle} \right)^{1/3} . \tag{59}$$

Finally the combination of the inequalities (51) and (52) with $b = 5/3$ together with (59) allows us to find the searched lower bound given by (32).

IV. UPPER BOUNDS

Here we will describe and prove the upper bounds to the Weizsäcker energy $T_W[\rho_\Psi]$ in a state characterized by the Ψ wave function. The inequalities (62), (66), (68), and (72) given below are valid only for systems with a spherically symmetric single-particle density.

(A) For ions with a nuclear charge Z and a number N of electrons, it is fulfilled that

$$T_W \leq Z \langle r^{-1} \rangle - \epsilon N \tag{60}$$

in the approximation of infinite nuclear mass. The symbol ϵ denotes the first ionization potential.

To prove this bound, we use the following inequality of the electron density $\rho(\mathbf{r})$ found by the Hoffmann-Ostenhof [11] in the infinite-nuclear-mass approximation:

$$-\frac{1}{2} \nabla^2 \rho^{1/2}(\mathbf{r}) + \left[\epsilon + \frac{Z}{r} \right] \rho^{1/2}(\mathbf{r}) \leq 0 \tag{61}$$

$$\mathbf{r} \in \mathbb{R}^3, \rho^{1/2}(\mathbf{r}) \neq 0 .$$

The integration of this inequality multiplied by $\rho^{1/2}(\mathbf{r})$ over the whole space readily leads to (60).

(B) For fermionic systems with a kth-monotonic single-particle density with $k \geq 3$ (this is the case, e.g., of the heliumlike ions among the finite electronic systems [36]) one has that

$$T_W \leq \frac{1}{4}\frac{k-1}{k-2}\left\langle r^{-2}\right\rangle, \qquad k \geq 3 . \qquad (62)$$

It is interesting to remark that in the cases where $k = 3$ the bound is

$$T_W \leq \frac{1}{2}\left\langle r^{-2}\right\rangle \qquad (63)$$

and if the single-particle density $\rho(r)$ is completely monotone (i.e., when $k \to \infty$) [37,38] one has

$$T_W \leq \frac{1}{4}\left\langle r^{-2}\right\rangle . \qquad (64)$$

To derive these bounds we use a recent inequality [36] among the derivatives of the density $\rho(r)$ which has the property of monotonicity of order $k \geq 3$, i.e., such that $(-1)^k \rho^{(k)} \geq 0$. This inequality is

$$\rho''(r) \geq \frac{k-2}{k-1}\frac{[\rho'(r)]^2}{\rho(r)} . \qquad (65)$$

The integration of this inequality over the whole space and taking into account the definition (1) of the Weizsäcker energy allows us to find the searched bound (62).

(C) For systems with a log-convex density function $\rho(r)$, it is verified that

$$T_W \leq \frac{1}{4}\left\langle r^{-2}\right\rangle . \qquad (66)$$

To find this bound we start from the log-convexity condition of $\rho(r)$, i.e., that $d^2[\ln \rho(r)]/dr^2 \geq 0$, which leads to

$$\rho''(r) \geq \frac{[\rho'(r)]^2}{\rho(r)} . \qquad (67)$$

Operating with this inequality in a similar manner as described above for the inequality (65), one easily obtains the bound (66). It is worthwhile to remark that the bounds (64) and (66) are the same in spite of the different requirements of the single-particle density which they are founded on.

(D) There exist systems such that its single-particle density $\rho(r)$ does not possess a given order k of monotonicity but the related function $g(r) = \rho(r)/r^\alpha$, α real, does. This is, e.g., the case of most atoms in the Periodic Table [38,39]. Let us consider a many-body system such that the one-body density function $g(r) = \rho(r)/r^\alpha$, α being a known real parameter, is monotone of order k. Then, it is fulfilled that

$$T_W \leq \frac{\alpha+2}{8}\left[\frac{k-1}{k-2}(\alpha+1)-\alpha\right]\left\langle r^{-2}\right\rangle . \qquad (68)$$

In the case that $k = 3$ this bound reduces as

$$T_W \leq \frac{(\alpha+2)^2}{8}\left\langle r^{-2}\right\rangle , \qquad (69)$$

while in the completely monotonic case (i.e., for $k \to \infty$) one has

$$T_W \leq \frac{\alpha+2}{8}\left\langle r^{-2}\right\rangle . \qquad (70)$$

To prove these results we use the following known inequality [36]:

$$g''(r) \geq \frac{k-2}{k-1}\frac{[g'(r)]^2}{g(r)} . \qquad (71)$$

Again here, working with this inequality similarly as with (65) one is led to the bound (68).

(E) Some systems present a single-particle density $\rho(r)$ which is neither convex nor log convex but the related function $\rho(r)/r^\alpha$ is log convex for a certain real value of α. For example, this is the case in all atoms of the periodic table, except H and He where the electron density is log-convex [39,40].

Let us consider a many-body system such that its density function $g(r) = \rho(r)/r^\alpha$, α being a known real parameter, is logarithmically convex. Then, the Weizsäcker energy is bounded from above by

$$T_W \leq \frac{\alpha+2}{8}\left\langle r^{-2}\right\rangle . \qquad (72)$$

To find this bound we start from the log-convexity condition of $g(r)$, namely,

$$g''(r) \geq \frac{[g'(r)]^2}{g(r)} , \qquad (73)$$

and we operate as already done in the determination of the bound (66) from the inequality (67).

V. NUMERICAL TEST

Just for checking the quality of the bounds to the Weizsäcker energy obtained in this work, we use the near Hartree-Fock wave functions of Clementi-Roetti [41] and McLean-McLean [42] for all ground-state atoms with the nuclear charge $1 \leq Z \leq 92$. The numerical values of the Weizsäcker energy were calculated with these wave functions by Murphy-Wang [43] and dePristo-Kress [44].

We have performed numerical comparisons of some of the previous bounds and the Hartree-Fock values of the Weizsäcker energy. The results are shown in Figs. 1, 2, and 3. In Fig. 1, the Hartree-Fock value of the lower bounds of variational nature with one-moment $L_1 = \frac{\left\langle r^{-2}\right\rangle}{8}$, with two moments (i.e., $L_2 = \left\langle r^{-1}\right\rangle^2/(2Z)$ and $L_2' = 9Z^2/(8\left\langle r^2\right\rangle)$), and with three-moments [i.e., L_3 and L_3' given by (11) and (10)] respectively, are represented. The bounds are plotted by dotted (L_1), dashed-dotted (L_2), medium-dashed (L_2'), dashed (L_3), and long-dashed (L_3') lines, while the values of T_W are given by the continuous line in the figure. It is observed that (i) the bound L_2 is much more accurate than L_2', (ii) when we incorporate the moment $\left\langle r^{-2}\right\rangle$, the resulting variational bounds L_3 and L_3' get substantially improved, being always L_3' more accurate than L_3, and (iii) the one-moment bound L_1 is much better than the two-moments bounds L_2 and L_2' and, even more, it is of the same accu-
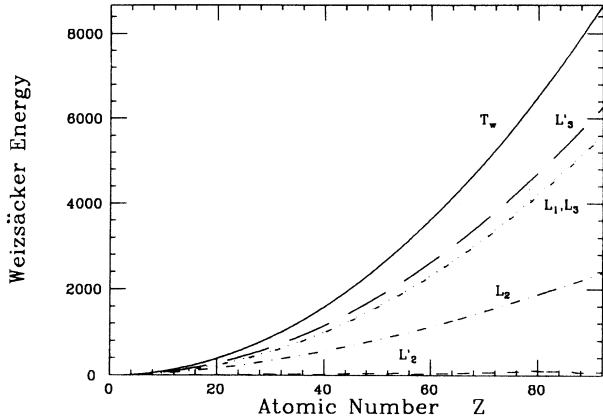
FIG. 1. Study of the accuracy of the variational lower bounds to the Weizsäcker energy T_W given by one (L_1), two $(L_2$ and $L_2')$, and three $(L_3$ and $L_3')$ radial expectation values $\langle r^\alpha \rangle$. The Hartree-Fock value (solid line) of T_W is compared to the values of L_1 (dotted line; it depends on $\langle r^{-2} \rangle$), L_2 (dashed-dotted line; it depends on Z and $\langle r^{-1} \rangle$), L_3 (short-dashed line; Z, $\langle r^{-2} \rangle$ and $\langle r^2 \rangle$) and L_3' (long-dashed line; Z, $\langle r^{-2} \rangle$ and $\langle r^{-1} \rangle$). Atomic units are used throughout.

racy as the three-moments bound L_3. Then, for a given number of moments $\langle r^\alpha \rangle$, the best lower bound to T_W is that corresponds to the moment(s) with lower order(s) α what is an indication that the Weizsäcker energy mainly depends on the electronic region of the density near the nucleus.

A similar study is done in Fig. 2 for the upper bounds to T_W of Schrödinger origin [to be denoted by $U_S = Z(\langle r^{-1} \rangle - \epsilon)$] and of kth-monotonic origin with $k = 3$ $(U_3 = \langle r^{-2} \rangle /2)$ and $k \to \infty$ $(U_\infty = \langle r^{-2} \rangle /4)$ found in this work. We observe that, in the whole Periodic Table, the Schrödinger upper bound U_S is much less accurate
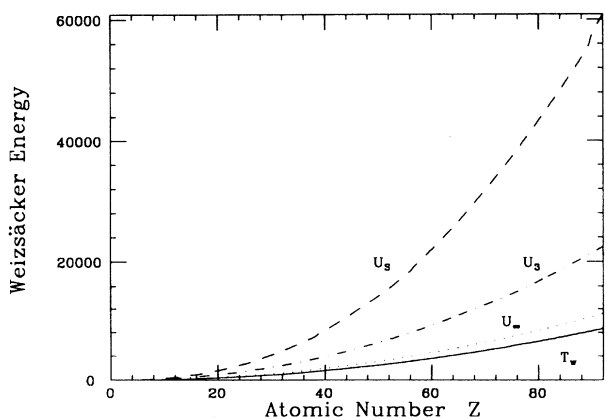

FIG. 2. Study of the accuracy of the upper bounds to the Weizsäcker energy T_W found in this work. The Hartree-Fock value of T_W (solid line) is compared to the values of the rigorous bound of Schrödinger origin U_S (dashed line) and the non-rigorous bounds of monotonic origin U_3 (dashed-dotted line) and U_∞ (dotted line).
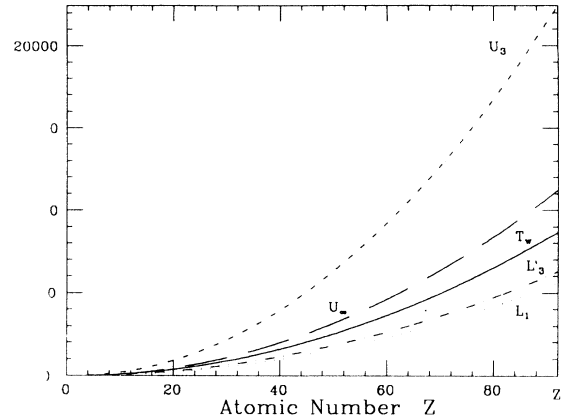
FIG. 3. Comparison of the upper bounds of monotonic origin U_3 (short-dashed line) and U_∞ (long-dashed line) with the variational lower bounds to T_w of one and three moments given by L_1 (dotted line) and L_3' (dashed-dotted line). The Hartree-Fock values of the Weizsäcker energy are given by the solid line. Atomic units are used throughout.

that the bounds of monotonic origin but, contrary to these, it is rigorous; in fact, to the best of our information, it is the only rigorous upper bound known in the literature.

Finally, in Fig. 3 we plot jointly the two upper bounds to the Weizsäcker energy with better accuracy (i.e., U_3 and U_∞) and the variational one-moment, and three-moments lower bounds (i.e., L_1 and L_3') together with the Hartree-Fock values of T_W. Keep in mind that both bounds L_1 and U_∞ depend only on the radial expectation value $\langle r^{-2} \rangle$.

It is striking that the complete monotonicity and the log-convexity approximations (both lead to the same upper bound as explained in Sec. IV) for the electron density produce so accurate upper bounds to the Weizsäcker energy of all atoms of the Periodic Table in spite of the known fact [37], [38], and [39] that they are generally violated except for H in the completely monotonic case and for H and He in the log-convex case. This observation, as well as the knowledge of the variational lower bound L_1, explains from a fundamental point of view (i.e., based on characteristics of the electron density) the approximate representation of the second-gradient correction $T_2 \equiv T_W/9$ to the total kinetic energy by means of the expression

$$T_2 = \frac{c_2}{72} \langle r^{-2} \rangle$$

(c_2 is usually determined empirically and found to be 1.84 for atoms), which has been done by several authors [16,45,46] when calculating the atomic kinetic-energy density functional.

VI. DISCUSSION AND CONCLUDING REMARKS

The relevant role played by the Weizsäcker energy T_W in the general density-functional theory (DFT) of many-

fermion systems [2,3,47] makes almost mandatory the search of relationships with as many fundamental and/or experimentally measurable quantities as possible. Since exact equations among them cannot be found in complex systems, it seems natural to look for relationships of inequality type.

The inequality approach to the Weizsäcker energy done in this work is founded on the moments around the origin of the single-particle density $\rho(\mathbf{r})$ which, apart from the constant 4π, are the radial expectation values $\langle r^n \rangle$. The reason to choose these quantities as the basic elements of our approach is twofold. Mathematically the knowledge of these expectation values (moments) of integer order may completely characterize $\rho(\mathbf{r})$. Physically they describe (some constants apart) numerous important quantities of the system under consideration as already mentioned.

The specific results of this approach are given by means of lower and upper bounds to T_W. Let us first consider the lower bounds. They are rigorous and they apply to all finite many-fermion systems and many of them to infinite systems, also. In addition to the one-moment bound L_1 given by Eq. (7), we have found variationally various two- and three-moments lower bounds previously denoted by L_2, L'_2, L_3, L'_3 which are given by Eqs. (8)–(11), respectively. Also, general sets of nonvariational two-moments and three-moments lower bounds have been described. To find the latter ones much use of the classical integral inequalities of functional analysis like those of Hölder, Sobolev, and Redheffer has been necessary; some of them are conjectured to be the best possible ones, although we have not been able to prove its variational origin.

The upper bounds found in this work are of a fully different origin. Apart from the bound given by Eq. (60), which is valid "only" for ions and comes out directly from the Schrödinger equation, the rest of upper bounds are valid for those femionic systems whose single-particle density or a related function possesses some monotonicity property (e.g., convexity, log-convexity, complete monotonicity, ...). The latter bounds are given in terms of the expectation value $\langle r^{-2} \rangle$ and the order of monotonicity of $\rho(\mathbf{r})$ of the related density function under consideration.

Finally, let us make some observations in view of these lower and upper bounds

(i) They set up numerous rigorous relationships of inequality type which involve the Weizsäcker energy together with other physical quantities (e.g., number of constituents, magnetic susceptibility, diamagnetic-shielding correction, softness kernel, ...) of the system, which would be difficult to obtain otherwise.

(ii) The expectation value $\langle r^{-2} \rangle$, which gives the strength of the angular-momentum dependent part of the kinetic energy, is shown to play an important role in bounding the Weizsäcker energy both

from below and from above; let us bring here for example, that

$$\frac{1}{8} \langle r^{-2} \rangle \le T_W \le \frac{1}{4} \langle r^{-2} \rangle \ ,$$

whose accuracy in neutral atoms is certainly striking as illustrated in Fig. 3. At this point, however, we should immediately say that, contrary to the lower bound $\langle r^{-2} \rangle /8$ (which is of variational origin), the upper bound $\langle r^{-2} \rangle /4$ was obtained under the complete-monotonicity hypothesis (which is only approximately satisfied, generally speaking). The reason of such so important role of $\langle r^{-2} \rangle$ is possibly that it takes best (with respect to the rest of the other possible expectation values of integer order) the electronic region near atomic nucleus.

(iii) The logarithmic expectation values $\langle r^\beta \ln r \rangle$ and specifically the mean logarithmic value $\langle \ln r \rangle$, (which determines [48,49] the high-energy behavior of the phase-shifts in electron-nucleus scattering at low angular momentum) are encountered to be good elements to bounding from below the Weizsäcker energy as illustrated by (21)–(34) and (33)–(35). One should say, for completeness, that these logarithmic values have been recently used to bound physical density functionals of the type $\omega_b = \int \rho^b(\mathbf{r}) d\mathbf{r}$ in many-electron systems [32,34], and [38] and to obtain novel uncertainty relationships in D-dimensional many body systems [50].

ACKNOWLEDGMENTS

APPENDIX

Here the following result is proved.

Theorem. The electron density $\rho(\mathbf{r})$ fulfills the inequality

$$T_W[\rho(\mathbf{r})] \ge T_W[\rho(r)] \ , \tag{A1}$$

where $\rho(r)$ is the spherical average of $\rho(\mathbf{r})$, i.e.,

$$\rho(r) = \frac{1}{4\pi} \int_\Omega \rho(\mathbf{r}) d\Omega \ .$$

Proof. First, we shall prove the following result. Let

$$\mathcal{F}[f] = \int \frac{|\nabla f(\mathbf{r})|^2}{f(\mathbf{r})} d\mathbf{r}, f \in \mathbb{X}$$

with

$$\mathbb{X} = \left\{ \begin{array}{l} f : \mathbb{R}^3 \to \mathbb{R} : f(\mathbf{r}) \ge 0; \frac{|\nabla f(\mathbf{r})|^2}{f(\mathbf{r})} \in L^2(\mathbb{R}^3); f = \partial_{x_i} f = 0 \\ \text{over the surface and } -2\frac{\nabla^2 f}{f} + \frac{|\nabla f|^2}{f^2} \in \mathbb{C}^{(0)}(\mathbb{R}^3) \end{array} \right\} \ .$$

The symbol $\mathbb{C}^{(0)}(\mathbb{R}^3)$ denotes the class of functions that are continuous on $\mathbb{R}^3$. Then $\mathcal{F}$ is a convex functional over $\mathbb{X}$.

This result follows the proposition 42.6 of Ref. [35]. A functional $\mathcal{G}[f]$ is convex over $\mathbb{X}$ if and only if the inequality

$$\mathcal{G}[f_1] - \mathcal{G}[f_2] - \int (f_1 - f_2)\frac{\delta\mathcal{G}[f_2]}{\delta f_2}d\mathbf{r} \geq 0 \qquad (A2)$$

is fulfilled for all f_1 and $f_2 \in \mathbb{X}$. Indeed, since

$$\int \frac{f_1\nabla^2 f_2}{f_2}d\mathbf{r} = -\int \frac{\nabla f_1\nabla f_2}{f_2}d\mathbf{r} + \int \frac{f_2|\nabla f_2|^2}{f_2^2}d\mathbf{r},$$

the inequality (A2) for the functional $\mathcal{F}$ transforms into

$$\int \frac{(f_2\nabla f_1 - f_1\nabla f_2)^2}{f_1 f_2^2}d\mathbf{r} \geq 0 ,$$

which is clearly fulfilled.

Second, for $\rho(\mathbf{r}) \in \mathbb{X}$, and $\rho(r) \in \mathbb{X}$, it is fulfilled that

$$\int [\rho(\mathbf{r}) - \rho(r)]\frac{\delta\mathcal{F}[\rho(r)]}{\delta\rho(r)}d\mathbf{r} = 0 .$$

Then, it easily follows that

$$\mathcal{F}[\rho(\mathbf{r})] - \mathcal{F}[\rho(r)] \geq 0.$$

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