

**Functional differentiation, line integration, and departures from homogeneity of the single-particle kinetic energy functional for one-dimensional systems of N fermions**

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Citation: *Journal of Mathematical Physics* **42**, 3361 (2001); doi: 10.1063/1.1379069

View online: <http://dx.doi.org/10.1063/1.1379069>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jmp/42/8?ver=pdfcov>

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# Functional differentiation, line integration, and departures from homogeneity of the single-particle kinetic energy functional for one-dimensional systems of $N$ fermions

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(Received 11 December 2000; accepted for publication 4 April 2001)

The differential virial theorem of March and Young for  $N$  fermions moving in a common one-dimensional potential energy  $V(x)$  is here combined with the Euler equation of density functional theory expressing the constancy of the chemical potential throughout the entire inhomogeneous particle density. The functional derivative of the single-particle kinetic energy is thereby expressed directly in terms of the kinetic energy density; a line integral being involved in establishing the connection. This result is then used to establish a formula measuring departures from simple homogeneity of the kinetic energy functional: a matter of current interest in density functional theory. Finally, the general theory of the functional derivative of the single-particle kinetic energy with respect to the particle density is exemplified for the case of harmonic confinement of fermions in one dimension.

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## I. BACKGROUND AND OUTLINE

Density functional theory is of considerable current interest in connection with atomic, molecular, and condensed matter physics.<sup>1-3</sup> The origins of the theory go back to Thomas<sup>4</sup> and Fermi,<sup>5</sup> whose work was formally completed by the theorem of Hohenberg and Kohn,<sup>6</sup> which states that the ground-state energy  $E$  of a many-fermion assembly of  $N$  interacting particles is a unique functional of the corresponding particle density  $n$ . Unfortunately, to date this functional remains unknown.

As background to the present study of the (single-particle) kinetic energy functional  $T_s[n]$  of  $N$  fermions moving independently in a one-dimensional common potential  $V(x)$ , let us write immediately the Thomas–Fermi (TF) approximation to the ground-state energy  $E_{\text{TF}}[n]$ , namely<sup>7</sup> (atomic units are used throughout)

$$E_{\text{TF}}[n] = \frac{\pi^2}{6} \int_{-\infty}^{\infty} n^3(x) dx + \int_{-\infty}^{\infty} n(x) V(x) dx. \quad (1)$$

The variational principle underlying the density functional theory may be expressed as

$$\delta(E - N\mu) = 0, \quad (2)$$

where  $\delta$  represents variation with respect to the particle density  $n(x)$  while  $\mu$  is a Lagrange multiplier taking care of the normalization condition

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$$\int_{-\infty}^{\infty} n(x) dx = N. \quad (3)$$

The physical significance of  $\mu$ , as Hulthén<sup>8</sup> pointed out, is that it represents the chemical potential, which is constant throughout the entire inhomogeneous fermion particle density  $n(x)$ . Applying the general result (2) to the approximate Thomas–Fermi functional in Eq. (1) yields the well-known result

$$\mu = \frac{\pi^2}{2} n^2(x) + V(x), \quad (4)$$

which involves semiclassical approximations and therefore comes into its own when the microscopic system under consideration has many states with large quantum numbers occupied. Bohr’s correspondence principle then assures us that in such a limit the predictions of a fully quantal theory will be usefully represented by semiclassical theory.

Generalizing Eq. (4) to such a formally exact quantal theory, one writes<sup>9</sup>

$$\mu = \frac{\delta T_s[n]}{\delta n(x)} + V(x). \quad (5)$$

Here  $T_s[n]$  is the so-called single-particle kinetic energy functional of density functional theory, and though a much simpler (one-body) problem than that of  $E[n]$  cited previously, it also remains an unknown functional to date. Obviously, by comparing Eqs. (4) and (5), we see that the functional derivative of the Thomas–Fermi kinetic energy in Eq. (1) (a “local” density approximation) is  $(\pi^2/2) n^2(x)$ .

It was von Weizsäcker<sup>10</sup> ( $W$ ) who first recognized the need to correct the Thomas–Fermi kinetic energy function(al) in Eq. (1) by introducing a kinetic energy term dependent on the density gradient. His so-called inhomogeneity kinetic energy,  $T_W$  say, will be written in the following in terms of a kinetic energy density  $t_W(x)$ , as

$$T_W = \int_{-\infty}^{\infty} t_W(x) dx, \quad t_W(x) = \frac{1}{8} \frac{(n'(x))^2}{n(x)}. \quad (6)$$

In an early attempt to synthesize density matrix theory with what is now called density functional theory, March and Young<sup>11</sup> derived an approximate form of  $T_s[n]$  which was the linear combination of  $T_W[n]$  and  $T_{TF}[n]$  given by  $T_W[n] + \gamma(N) T_{TF}[n]$ , where  $\gamma(1)=0$ , since the von Weizsäcker form (6) is the exact single-particle kinetic energy functional for one level only occupied. Baltin<sup>12,13</sup> subsequently made generalizations of such results relating to the single-particle kinetic energy functional  $T_s[n]$ . Searches for improved approximations to  $T_s[n]$  are continuing,<sup>14–16</sup> in order to use so-called “orbital-free” density functional theory, thereby bypassing the need to solve one-electron (Slater–Kohn–Sham) Schrödinger equations.<sup>17,18</sup> But even for formal properties of  $T_s[n]$ , such as its homogeneity or otherwise,<sup>19</sup> current interest remains, this area having been one of some controversy.<sup>20</sup> One of the purposes of this investigation is to settle the matter of (departures from simple) homogeneity of  $T_s[n]$  for  $N$  fermions in one dimension.<sup>21</sup>

The outline of the present study is then as follows. In Sec. II the Euler Eq. (5) of density functional theory is combined with the differential virial theorem of March and Young<sup>22</sup> to allow by a single integration the functional derivative  $\delta T_s[n]/\delta n(x)$  to be written in terms of the corresponding kinetic energy plus properties of the particle density  $n(x)$ . Section III is then concerned with using this result to discuss the homogeneity departures of the (formally exact)  $T_s[n]$  in one dimension for an arbitrary number of fermions. Section IV is devoted to exemplifying the formally exact results of Secs. II and III particularly for the (exactly soluble) case of harmonic confinement.<sup>23,24</sup> Section V constitutes a summary, and includes some proposals for possible further studies in the general area of the nonlocal kinetic energy functional  $T_s[n]$ . In the

Appendix, the “box” model of finite length  $L$  is considered for  $N$  fermions. The thermodynamic limit of this model, the so-called semi-infinite gas, has been discussed earlier by one of us in this Journal<sup>25</sup> and has in fact been treated in  $d$  dimensions. For  $d=1$ , the Appendix contains a generalization of the differential equation for a spherical Bessel function, which incorporates all inhomogeneities in  $n(x)$  due to the finite length  $L$  of the box.

## II. FORMALLY EXACT FUNCTIONAL DERIVATIVE OF SINGLE-PARTICLE KINETIC ENERGY IN TERMS OF KINETIC ENERGY AND PARTICLE DENSITIES

The March–Young<sup>22</sup> differential virial theorem reads, for kinetic energy density  $t_G(x)$  defined from the positive  $(\text{grad } \psi)^2$  wave function form:

$$t'_G(x) = -\frac{1}{2} n(x) \frac{dV(x)}{dx} + \frac{n'''(x)}{8}. \tag{7}$$

This exact result was derived from the equation of motion for the first-order density matrix, which was then solved by expansion around the diagonal element, which is just the particle density  $n(x)$ . The near-diagonal behavior of the density matrix is precisely determined by the kinetic energy density  $t_G(x)$  plus  $n(x)$ . An immediate check of Eq. (7) is to multiply both sides by  $x$ , and then to integrate over all  $x$  from  $-\infty$  to  $\infty$ . The left-hand side, after integration by parts, then gives the total kinetic energy, while the first term on the right-hand side is in magnitude half the virial of the force  $(-dV/dx)$ . Since the  $n'''(x)$  term in Eq. (7) makes no contribution, Eq. (7) contains correctly the (integral) quantum-mechanical virial theorem.

Following the force-balance equation approach used by Holas and March<sup>26</sup> in their derivation of the force  $-\nabla V_{xc}$  associated with the exchange–correlation potential  $V_{xc}(\mathbf{r})$  in terms of low-order density matrices, we rewrite Eq. (7) for the force  $(-dV/dx)$  acting on the  $N$  fermions occupying singly the levels generated by the common potential  $V(x)$ . Then

$$n(x) = \sum_{m=1}^N \psi_m^*(x) \psi_m(x), \tag{8}$$

where the normalized wave functions  $\psi_m(x)$  are, of course, generated by  $V(x)$ . One finds from Eq. (7) after multiplying by  $2/n(x)$ , the so-called force-balance equation

$$-\frac{dV(x)}{dx} = \frac{2 t'_G(x)}{n(x)} - \frac{n'''(x)}{4n(x)}. \tag{9}$$

Next we appeal to the Euler equation of density functional theory,<sup>9</sup> which is a statement of the constancy of the chemical potential  $\mu$  throughout the entire fermion particle density  $n(x)$ , however inhomogeneous this may be. With

$$T_s[n] = \int_{-\infty}^{\infty} t_G(x) dx \tag{10}$$

one has for the functional derivative of the single-particle kinetic energy  $T_s[n]$  the result quoted already in Eq. (5). Differentiating Eq. (5) with respect to  $x$  to exploit the constancy of  $\mu$ , one can evidently rewrite Eq. (9) as

$$\left( \frac{\delta T_s[n]}{\delta n(x)} \right)' = \frac{2 t'_G(x)}{n(x)} - \frac{n'''(x)}{4n(x)}. \tag{11}$$

We now proceed to integrate this Eq. (11) to obtain the desired expression for the functional derivative  $\delta T_s / \delta n(x)$ . The result, as is readily verified, can be expressed in the form

$$\frac{\delta T_s[n]}{\delta n(x)} = 2 \frac{t_G(x)}{n(x)} - \frac{n'^2(x)}{8n^2(x)} - \frac{n''(x)}{4n(x)} + 2 \int^x \frac{n'(s)}{n(s)} \left[ \frac{t_G(s) - t_W(s)}{n(s)} \right] ds \quad (12)$$

by repeated integration by parts. In Eq. (12) we have introduced the von Weizsäcker inhomogeneity kinetic energy density  $t_W(x)$  defined in Eq. (6). From there, the following functional derivative is readily calculated as

$$\frac{\delta T_W}{\delta n(x)} = \frac{1}{8} \left[ \frac{n'(x)}{n(x)} \right]^2 - \frac{n''(x)}{4n(x)}. \quad (13)$$

Using Eqs. (6) and (13) in Eq. (12) one reaches the general one-dimensional form of the functional derivative of  $T_s[n]$  as

$$\frac{\delta \{T_s[n] - T_W[n]\}}{\delta n(x)} = 2 \left[ \frac{t_G(x) - t_W(x)}{n(x)} \right] + 2 \int^x \frac{n'(s)}{n(s)} \left[ \frac{t_G(s) - t_W(s)}{n(s)} \right] ds, \quad (14)$$

which, for arbitrary  $N$ , is defined to within an  $N$ -dependent constant.

One immediate check of Eq. (14) is the case  $N=1$ , where  $T_s = T_W$  and  $t_G(x) = t_W(x)$ . Evidently Eq. (14) is trivially satisfied, with no arbitrary constant left for this special case [compare Eq. (13)].

Of course, for a general potential  $V(x)$ , the kinetic energy  $t_G(x)$  is not known solely in terms of the density  $n(x)$ . However, for the case of harmonic confinement, we shall return to Eq. (14) in Sec. IV.

### III. DEPARTURES FROM HOMOGENEITY OF THE SINGLE-PARTICLE KINETIC ENERGY FUNCTIONAL $T_s[n]$ FOR $N$ FERMIONS IN ONE DIMENSION

Having obtained  $\delta T_s / \delta n(x)$  in Eq. (14), let us now consider the departures from homogeneity of the single-particle kinetic energy functional  $T_s[n]$ . Since the work of Liu and Parr,<sup>20</sup> this has been an area of considerable interest (see, e.g., Ref. 19) and also some degree of controversy.<sup>21</sup>

Let us start from the customary definition of homogeneity. A functional  $F[n]$  is homogeneous of order  $\alpha$  in  $n(x)$  if

$$F[\lambda n] = \lambda^\alpha F[n]. \quad (15)$$

Let us immediately use the examples cited above of (a) Thomas–Fermi and (b) von Weizsäcker kinetic energies to explore the validity (or otherwise) of Eq. (15) when  $F$  becomes the single-particle kinetic energy functional  $T_s[n]$ .

#### A. Thomas–Fermi and von Weizsäcker functionals, $T_{TF}[n]$ and $T_W[n]$

Using Eq. (1),

$$T_{TF}[n] = \frac{\pi^2}{6} \int_{-\infty}^{\infty} n^3(x) dx$$

and hence  $T_{TF}[\lambda n] = \lambda^3 T_{TF}[n]$ . Therefore we see immediately that the functional  $T_{TF}[n]$  is homogeneous of order three.

Next let us consider again the von Weizsäcker functional already given in Eq. (6),

$$T_W[n] = \frac{1}{8} \int_{-\infty}^{\infty} \frac{(n'(x))^2}{n(x)} dx.$$

It follows immediately that  $T_W[\lambda n] = \lambda T_W[n]$  and hence  $T_W[n]$  is homogeneous of order one, as already emphasized by Liu and Parr.<sup>20</sup> This means, since  $T_W$  is the exact functional for  $N = 1$ , that for all confining potentials  $V(x)$  the single-particle kinetic energy  $T_s[n]$  has this exact homogeneity property in this special case.

**B. Example of harmonic confinement of an arbitrary number of fermions**

March, Senet, and Van Doren<sup>24</sup> have constructed the fully nonlocal single-particle kinetic energy  $T_s[n]$  for harmonic confinement of  $N$  fermions. We quote their functional here:

$$T_s[n] = T_W[n] + \int_{-\infty}^{\infty} dx \xi(x) t_{TF}(x), \tag{16}$$

where

$$t_{TF}(x) = \frac{\pi^2}{6} n^3(x). \tag{17}$$

In Eq. (16), the function  $\xi(x)$  is explicitly given in Ref. 24 as

$$\xi(x) = \xi(0) + \frac{3}{\pi^2} \int_0^x ds \frac{(n'(s))^3}{n^5(x)}. \tag{18}$$

Thus, introducing the kinetic energy term on the right-hand side of Eq. (1), it follows by inserting Eq. (18) into Eq. (16) that

$$T_s[n] = T_W[n] + \xi(0) T_{TF}[n] + \frac{3}{\pi^2} \int_{-\infty}^{\infty} dx t_{TF}(x) \int_0^x ds \frac{(n'(s))^3}{n^5(x)}. \tag{19}$$

But we have already discussed the order of homogeneity of  $T_{TF}$  and  $T_W$  in Sec. III A above, the orders being, respectively, three and one. The quantity  $\xi(0)$  is itself a weak function of  $N$ , tending rapidly to a constant as  $N$  becomes large. The order of the final term in Eq. (19) is unity, and hence it is clear that  $T_s[n]$  is not homogeneous. Thus it follows that while

$$\int_{-\infty}^{\infty} n(x) \frac{\delta T_s}{\delta n(x)} dx = T_s[n] \tag{20}$$

is true for  $N = 1$  (when  $T_s \equiv T_W$ ), for  $N$  arbitrary there are departures from homogeneity until  $N \rightarrow \infty$ , when  $T_s \rightarrow T_{TF}$  and the order of homogeneity tends to three (see Sec. III A).

Thus, having demonstrated departures from homogeneity for a specific potential energy  $V(x) = x^2/2$  representing harmonic confinement, it follows naturally that the general result (14) must reflect such departures, being true for arbitrary one-dimensional confining potentials  $V(x)$ .

**IV. ILLUSTRATIONS OF GENERAL EQUATION (14)**

In this section, we shall illustrate the functional derivative in Eq. (14) by reference to some specific cases. As a first example, let us take the two-level system, i.e.,  $N = 2$ , for an arbitrary confining potential  $V(x)$ .

**A. Two-level system with arbitrary confining potential  $V(x)$**

Here we work out explicitly the example for a given potential  $V(x)$  for two levels only occupied. We invoke the so-called Dawson–March<sup>27</sup> transformation in which the wave functions  $\psi_1(x)$  and  $\psi_2(x)$  associated with the two levels are written in terms of density “amplitude”  $\sqrt{n(x)}$  and phase  $\theta(x)$  as

$$\psi_1(x) = \sqrt{n(x)} \cos \theta(x), \quad \psi_2(x) = \sqrt{n(x)} \sin \theta(x), \quad (21)$$

leading, of course, to  $n(x) = \psi_1^2(x) + \psi_2^2(x)$ . It is then readily shown that the kinetic energy density  $t_G(x)$  is given by

$$t_G(x) = t_W(x) + \frac{1}{2} n(x) \left( \frac{d\theta(x)}{dx} \right)^2. \quad (22)$$

The phase  $\theta(x)$  is related to the particle density  $n(x)$  by the nonlinear pendulumlike equation, with eigenvalue  $\epsilon$ :

$$\theta''(x) + \frac{n'(x)}{n(x)} \theta'(x) + \epsilon \sin 2\theta(x) = 0. \quad (23)$$

Introducing Eq. (22) into Eq. (14) yields almost immediately

$$\frac{\delta(T_s - T_W)}{\delta n(x)} = (\theta'(x))^2 + \int^x \frac{n'(s)}{n(s)} (\theta'(s))^2 ds. \quad (24)$$

But multiplying Eq. (23) by  $\theta'(x)$  and using the result for  $n'(\theta')^2/n$  in Eq. (24) one can readily evaluate the integral to find, to within a constant of integration

$$\frac{\delta(T_s - T_W)}{\delta n(x)} = \frac{1}{2} (\theta'(x))^2 + \frac{\epsilon}{2} \cos 2\theta(x). \quad (25)$$

This result Eq. (25) is now to be compared with Eq. (B10) of Holas *et al.*,<sup>28</sup> namely

$$\frac{\delta(T_s - T_W)}{\delta n(x)} = \frac{1}{2} (\theta'(x))^2 + \frac{1}{2} \left( \theta''(x) + \frac{n'(x)}{n(x)} \theta'(x) \right) \tan \theta(x). \quad (26)$$

Again using Eq. (23) in the last term of this equation, it is readily verified that it agrees with our result Eq. (25) to within an additive constant. This completes the demonstration that Eq. (14) holds for all two-level systems with an arbitrary confining potential.

## B. Large $N$ limit with arbitrary confining potential $V(x)$

Here, from the studies, for example, of Lieb,<sup>29</sup> we know that the Thomas–Fermi method is asymptotically correct in the limit  $N \rightarrow \infty$ . Then, one can drop  $n''(x)$  in the difference between  $t_G$  and  $t$ , this being expressed precisely in

$$t_G(x) = t(x) + \frac{n''(x)}{4}, \quad (27)$$

and can neglect the von Weizsäcker contribution relative to the Thomas–Fermi kinetic energy. Equation (14) then simplifies to read

$$\frac{\delta T_{\text{TF}}}{\delta n(x)} = 2 \frac{t_{\text{TF}}}{n(x)} + 2 \int^x \frac{n'(s)}{n(s)} \frac{t_{\text{TF}}(s)}{n(s)} ds + (\text{constant}). \quad (28)$$

But from Eq. (1),  $t_{\text{TF}} = (\pi^2/6)n^3(x)$ , and hence Eq. (28) becomes

$$\frac{\delta T_{\text{TF}}}{\delta n(x)} = 2 \frac{t_{\text{TF}}}{n(x)} + \frac{\pi^2}{3} \int^x n'(s) n(s) ds = 3 \frac{t_{\text{TF}}(x)}{n(x)} + (\text{constant}), \quad (29)$$

which can be confirmed by direct appeal to Eqs. (1) and (4). Thus, for arbitrary potential  $V(x)$ , Eq. (14) is now confirmed asymptotically as  $N \rightarrow \infty$ .

**C. Harmonic confinement: Arbitrary number  $N$  of fermions**

The above-mentioned Thomas–Fermi example, applicable asymptotically in the limit of large  $N$ , has encouraged us to consider the harmonic confinement case treated in earlier work as a further example. Let us use the form of March, Senet, and Van Doren<sup>24</sup> for the kinetic energy density  $t(x)$ , namely [their Eq. (27)]:

$$t(x) = t_W(x) + \xi(x)t_{TF}(x). \tag{30}$$

Here  $\xi(x)$  is given by (18). Thus, it follows that

$$\xi'(x) = \frac{3}{\pi^2} \frac{(n'(x))^3}{n^5(x)}. \tag{31}$$

But differentiating Eq. (30) and substituting Eq. (31) for  $\xi'(x)$  and Eq. (17) yields

$$3\xi(x)t_{TF}(x) = \frac{n(x)}{n'(x)}[t'(x) - t'_W(x)] - \frac{1}{2} \frac{(n'(x))^2}{n(x)}. \tag{32}$$

Inserting this equation into Eq. (30) for  $t(x)$  and using Eq. (6), one finds

$$3t(x) + t_W(x) = \frac{n(x)}{n'(x)}[t'(x) - t'_W(x)]. \tag{33}$$

But from Eq. (16) of Ref. 24

$$\frac{t'(x)}{n'(x)} = N - \frac{x^2}{2} \tag{34}$$

and therefore

$$3t(x) + t_W(x) = n(x) \left[ N - \frac{x^2}{2} \right] - \frac{n(x)}{n'(x)} t'_W(x). \tag{35}$$

From here, and using Eq. (6)

$$t(x) + \frac{n(x)}{6}(x^2 - 2N) = -\frac{n''(x)}{12n(x)}, \tag{36}$$

or from Eq. (5)

$$\frac{3t(x)}{n(x)} + \frac{t_W(x)}{n(x)} + \frac{t'_W(x)}{n'(x)} = \frac{\delta T_s}{\delta n(x)} + K(N), \tag{37}$$

where  $K(N)$  is a constant depending on the number of fermions.

Now again using Eq. (6)

$$\frac{t'_W(x)}{n'(x)} = \frac{1}{4} \frac{n''(x)}{n(x)} - \frac{1}{8} \left( \frac{n'(x)}{n(x)} \right)^2 = -\frac{\delta T_W}{\delta n(x)}. \tag{38}$$

Thus Eq. (37) becomes

$$\frac{\delta T_s}{\delta n(x)} = -K(N) + \frac{3t(x)}{n(x)} + \frac{1}{4} \frac{n''(x)}{n(x)}, \quad (39)$$

which agrees with Eq. (35) of March, Senet, and Van Doren.<sup>24</sup> Thus

$$\left[ \frac{\delta T_s}{\delta n(x)} \right]' = 3 \frac{n(x)t'(x) - n'(x)t(x)}{n^2(x)} + \frac{1}{4} \frac{n(x)n'''(x) - n'(x)n''(x)}{n^2(x)} \quad (40)$$

and at this point we shall compare with the general Eq. (14) which yields by differentiation

$$\left[ \frac{\delta T_s}{\delta n(x)} \right]' = 2 \frac{t'_G(x) - t'_W(x)}{n(x)} + \left[ \frac{\delta T_W}{\delta n(x)} \right]'. \quad (41)$$

Using the two equalities in Eq. (38) the last term in Eq. (41) becomes

$$\left[ \frac{\delta T_W}{\delta n(x)} \right]' = \frac{2}{n(x)} \left[ t'_W(x) - \frac{n'''(x)}{8} \right]. \quad (42)$$

Returning to the harmonic oscillator, using Eq. (27) in Eq. (40) yields

$$\left[ \frac{\delta T_s}{\delta n(x)} \right]' = \frac{2}{n} (t'_G - t'_W) + \frac{2}{n} t'_W - \frac{n'''}{4n} + \left[ \frac{t'}{n} - \frac{3tn'}{n^2} - \frac{n'n''}{4n^2} \right]. \quad (43)$$

But the last term in brackets is readily seen to be zero using Eqs. (34) and (36). Therefore, Eq. (43) agrees completely with Eqs. (41) and (42), confirming once more the validity of the general Eq. (14).

## V. SUMMARY AND POSSIBLE FUTURE DIRECTIONS

What has been demonstrated here is that the combination of the differential virial theorem (7) of March and Young with the Euler equation (5) of density functional theory allows the explicit expression (14) to be obtained for the functional derivative  $\delta T_s/\delta n(x)$  of the single-particle kinetic energy  $T_s[n]$ . This Eq. (14) has, therefore, by measuring  $T_s[n]$ , and its kinetic energy density  $t_G(x)$ , from the von Weizsäcker counterparts  $T_W[n]$  and  $t_W(x)$ , respectively, bypassed the process of functional differentiation by recourse to a line integration. This allows, in principle, a much more straightforward route to the functional derivative of  $T_s[n]$ . Of course, the general form of  $[t_G(x) - t_W(x)]/n(x)$  is still lacking and therefore the illustrations of the validity of Eq. (14), set out in Sec. IV, have been either for models (e.g., harmonic confinement) or asymptotic for large particle number  $N$  but for arbitrary confining potential  $V(x)$ .

As to future directions, it would naturally be important to find other soluble models to add to the harmonic confinement example invoked extensively in Sec. IV. But in the case of a quite general potential  $V(x)$  and an arbitrary number of fermions, Eq. (14) may perhaps afford an approximate route to the functional derivative, and hence to the desired differential equation for the ground-state density  $n(x)$ , given  $V(x)$ . It is presently only for such models as harmonic confinement that such a differential equation exists [see also the Appendix, especially Eqs. (A10) and (A11)], as derived by Lawes and March<sup>23</sup> in this case. The fact that one has a line integration in the final term of Eq. (14) makes it tempting to contemplate inserting an approximation for  $[t_G(x) - t_W(x)]/n(x)$  in this term, possibly modeled on the harmonic confinement example already fully solved.

The final comments concern what has been until recently the vexed question of homogeneity of  $T_s[n]$ . The present argument, set out explicitly in Sec. III, and most precisely in Eq. (19) for admittedly the special case of harmonic confinement, can leave no possible doubt that  $T_s[n]$  in one-dimensional  $N$  fermion problems is a linear combination of terms with different scaling properties as the density  $n(x)$  goes to  $\lambda n(x)$ . Of course, in the case  $N=1$ , the von Weizsäcker

functional is the exact form of  $T_s[n]$  and from well-known arguments  $T_w[n]$  has homogeneity of order one. Again, in the asymptotic limit  $N \rightarrow \infty$ , the Thomas–Fermi kinetic energy functional in Eq. (1) is again homogeneous, but now of order three. For intermediate  $N$ , one must expect therefore departures from homogeneity, as clearly evidenced in the harmonic example set out in Eq. (19) where each of the three terms on the right-hand side has its own specific scaling properties with the parameter  $\lambda$ .

**ACKNOWLEDGMENTS**

It is a pleasure for N.H.M. to thank Professor J.A. Alonso for most generous hospitality during a visit to the University of Valladolid, which made possible this collaborative study. This work has been supported by the Spanish DGES (PB98-0370) and Junta de Castilla y León (CO2/199).

**APPENDIX: KINETIC ENERGY AND PARTICLE DENSITY FOR FREE MOTION IN A BOX OF LENGTH  $L$**

In this Appendix we will calculate  $t_G(x)$  and  $n(x)$  for  $N$  fermions occupying singly the free particle levels for confinement in a box of length  $L$ , with normalized eigenfunctions  $\psi_m(x) = \sqrt{2/L} \sin(m\pi x/L)$ . In this case the particle density  $n(x)$  is given by<sup>30</sup>

$$\begin{aligned} n(x) &= \frac{2}{L} \sum_{m=1}^N \sin^2 \left[ \frac{m\pi x}{L} \right] \\ &= \frac{1}{L} \left[ N - \frac{\cos \left[ \frac{(N+1)\pi x}{L} \right] \sin \left[ \frac{N\pi x}{L} \right]}{\sin \left[ \frac{\pi x}{L} \right]} \right] \\ &= \frac{1}{L} \left\{ N + \sin^2 \left[ \frac{N\pi x}{L} \right] - \cot \left[ \frac{\pi x}{L} \right] \sin \left[ \frac{N\pi x}{L} \right] \cos \left[ \frac{N\pi x}{L} \right] \right\}. \end{aligned} \tag{A1}$$

As  $N$  and  $L$  both tend to infinity in such a way that  $N/L$  tends to a finite value,  $n_0 \equiv k_f/\pi$  say, Eq. (A1) becomes

$$n(x) = n_0 \left[ 1 - \frac{\sin(2k_f x)}{2k_f x} \right] = n_0 [1 - j_0(2k_f x)], \tag{A2}$$

$k_f$  being the wave number of the Fermi gas in this limit and  $j_\ell(z)$  the spherical Bessel function of order  $\ell$ . This result (A2) is the special case corresponding to one dimension ( $d=1$ ) of the  $d$ -dimensional semi-infinite electron gas treated earlier by one of us in this Journal.<sup>25</sup>

The kinetic energy density corresponding to Eq. (A2) was also given in this earlier work in the “thermodynamic” limit discussed previously as

$$t(x) = t_0 + \frac{k_f^2}{2} [n(x) - n_0] + \frac{k_f^3}{\pi} \frac{j_1(2k_f x)}{2k_f x}. \tag{A3}$$

The generalization of Eq. (A3) before passing to the thermodynamic limit, in the  $(\text{grad } \psi)^2$  wave function form of the kinetic energy  $t_G(x)$  is evidently

$$t_G(x) = \frac{1}{2} \sum_{m=1}^N (\psi'_m(x))^2. \tag{A4}$$

Hence we find

$$\begin{aligned}
t_G(x) &= \frac{\pi^2}{L^3} \sum_{m=1}^N m^2 \cos^2\left(\frac{m\pi x}{L}\right) \\
&= \frac{\pi^2}{24L^3} \left\{ \frac{6}{\sin\left[\frac{\pi x}{L}\right]} \left( N + N^2 \sin^2\left[\frac{\pi x}{L}\right] \right) \cos\left[\frac{2N\pi x}{L}\right] \right. \\
&\quad \left. - 3 \frac{\cos\left[\frac{\pi x}{L}\right]}{\sin^3\left[\frac{\pi x}{L}\right]} \left( 1 - 2N^2 \sin^2\left[\frac{\pi x}{L}\right] \right) \sin\left[\frac{2N\pi x}{L}\right] + 2N(N+1)(2N+1) \right\}. \quad (\text{A5})
\end{aligned}$$

Except at the box “edges”  $x=0$  and  $L$ ,

$$t'_G(x) = \frac{n'''(x)}{8}, \quad (\text{A6})$$

from the March-Young virial result. Using Eq. (A5) explicitly one finds the integral of Eq. (A6) as

$$t_G(x) = \frac{\pi^2}{12L^3} N(N+1)(2N+1) + \frac{n''(x)}{8}. \quad (\text{A7})$$

Connection with the semi-infinite electron gas result<sup>25</sup> is readily established using the second-order differential equation for the spherical Bessel function.

This has stimulated us to construct a generalized differential equation for the exact density  $n(x)$  without invoking the thermodynamic limit. The argument goes as follows. Using the definition from Eq. (A1) that

$$S(x) = n(x) - \frac{N}{L} - \frac{1}{2L}, \quad (\text{A8})$$

where the last term is introduced to have a homogeneous equation [see Eq. (A10)] for  $S(x)$ , we have

$$\sin\left[\frac{\pi x}{L}\right] S(x) = -\frac{1}{2L} \sin\left[\frac{(2N+1)\pi x}{L}\right]. \quad (\text{A9})$$

From here it is very easy to prove that the function  $S(x)$  satisfies the following second-order linear differential equation

$$S''(x) + \left[ \frac{2\pi/L}{\tan\left[\frac{\pi x}{L}\right]} \right] S'(x) + \left[ \frac{4N(N+1)\pi^2}{L^2} \right] S(x) = 0, \quad (\text{A10})$$

which we will term a generalized spherical Bessel equation. If we consider now the thermodynamic limit in Eq. (A10) and we call  $S_0(x)$  the resulting function from  $S(x)$ , one can immediately prove that  $S_0(x)$  satisfies the following spherical Bessel equation:

$$S_0''(x) + \frac{2}{x} S_0'(x) + (2k_f)^2 S_0(x) = 0, \quad (\text{A11})$$

the solution of which is essentially given by (A2). It seems to us somewhat remarkable that the major “size effects” due to the finite length  $L$  of the box enter Eq. (A10) through the factor  $(2\pi/L)/\tan[\pi x/L]$  multiplying the first derivative of  $S(x)$ , the change in the coefficient  $S(x)$  for finite  $N$  being minor in comparison. As  $L \rightarrow \infty$  and  $N \rightarrow \infty$ , such that  $N/L$  tends to a finite limit  $n_0$ , the tangent factor with  $0 < x < L$  has a node at  $L/2$  for finite box length which moves out to infinity, and the factor  $2/x$  multiplying  $S'_0(x)$  in the spherical Bessel equation (A11) is recovered.

<sup>1</sup>*Density Functional Theory; Topics in Current Chemistry*, edited by R.F. Nalewajski (Springer, Berlin, 1996), Vols. 179–182.

<sup>2</sup>Á. Nagy, Phys. Rep. **298**, 1 (1998).

<sup>3</sup>*Density-Functional Theory of Molecules, Clusters and Solids*, edited by D.E. Ellis (Kluwer, Dordrecht, 1994).

<sup>4</sup>L.H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1926).

<sup>5</sup>E. Fermi, Z. Phys. **48**, 73 (1928).

<sup>6</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, 8864 (1964).

<sup>7</sup>See, for example, N.H. March, Adv. Phys. **6**, 1 (1957).

<sup>8</sup>L. Hulthén, Z. Phys. **95**, 789 (1935).

<sup>9</sup>See, for instance, R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

<sup>10</sup>C.F. von Weizsäcker, Z. Phys. **96**, 431 (1935).

<sup>11</sup>N.H. March and W.H. Young, Proc. Phys. Soc. London Sec. A **72**, 182 (1959).

<sup>12</sup>R. Baltin, Phys. Lett. **113A**, 121 (1985).

<sup>13</sup>R. Baltin, J. Phys. A **20**, 111 (1987).

<sup>14</sup>L.W. Wang and M.P. Teter, Phys. Rev. B **45**, 13196 (1992).

<sup>15</sup>M. Pearson, E. Smargiassi, and P.A. Madden, J. Phys.: Condens. Matter **5**, 3221 (1993); see also B.J. Jesson, M. Foley, and P.A. Madden, Phys. Rev. B **55**, 4941 (1997).

<sup>16</sup>F. Perrot, J. Phys.: Condens. Matter **6**, 431 (1994).

<sup>17</sup>J.C. Slater, Phys. Rev. **81**, 385 (1951).

<sup>18</sup>W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

<sup>19</sup>See, for example, G.K.-L. Chan and N.C. Handy, Phys. Rev. A **59**, 2670 (1999), and earlier references therein.

<sup>20</sup>S.B. Liu and R.G. Parr, Chem. Phys. Lett. **278**, 341 (1997).

<sup>21</sup>See also T. Gál, Phys. Rev. A **62**, 044501 (2000).

<sup>22</sup>N.H. March and W.H. Young, Nucl. Phys. **12**, 237 (1959).

<sup>23</sup>G.P. Lawes and N.H. March, J. Chem. Phys. **71**, 1007 (1979).

<sup>24</sup>N.H. March, P. Senet, and V.E. Van Doren, Phys. Lett. A **270**, 88 (2000).

<sup>25</sup>N.H. March, J. Math. Phys. **28**, 2975 (1987).

<sup>26</sup>A. Holas and N.H. March, Phys. Rev. A **51**, 2040 (1995).

<sup>27</sup>K.A. Dawson and N.H. March, J. Chem. Phys. **81**, 5850 (1984).

<sup>28</sup>A. Holas, N.H. March, Y. Takahashi, and C. Zhang, Phys. Rev. A **48**, 2708 (1993).

<sup>29</sup>E.H. Lieb, Rev. Mod. Phys. **53**, 603 (1981); **48**, 553 (1976).

<sup>30</sup>I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1994).