A form of the single-particle kinetic energy density of an inhomogeneous electron liquid from a combination of one-body potential and ground-state electron density

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Gál and March have recently proposed a form of the single-particle kinetic energy density in density functional theory in terms of the one-body potential $V(\mathbf{r})$ and the ground-state electron density $n(\mathbf{r})$ generated thereby. Here, with a minor modification of the GM form, examples are given for (a) harmonic trapping and (b) a bare Coulomb potential. The case of the He atom is also considered, via the Chandrasekhar variational wave function. Finally, the use of the semiempirical fine-tuned Hartree–Fock $n(\mathbf{r})$ for spherical atoms due to Cordero *et al.* is briefly referred to.

Keywords: differential virial; kinetic energy density; one-body potential

1. Introduction

Gál and March [1] have recently considered, via the virial theorem, forms of the single-particle kinetic energy density, denoted below by $t_{GM}(\mathbf{r})$, of density functional theory (DFT) [2]. One form these authors propose, which is a focal point below, is that

$$t_{GM}(\mathbf{r}) = \frac{1}{2}\frac{\delta T_s}{\delta n(\mathbf{r})}[3n(\mathbf{r}) + \mathbf{r}\cdot\nabla n(\mathbf{r})], \tag{1}$$

where T_s is the total single-particle kinetic energy functional. Using the Euler equation of DFT [2] in Equation (1), namely

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + V(\mathbf{r}) = \mu, \tag{2}$$

where μ is the constant chemical potential at every point in the inhomogeneous electron liquid under consideration, one immediately has that

$$t_{GM}(\mathbf{r}) = \left[\frac{\mu - V(\mathbf{r})}{2}\right][3n(\mathbf{r}) + \mathbf{r}\cdot\nabla n(\mathbf{r})]. \tag{3}$$

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We turn next to illustrate the use of Equation (3) on two simple, but important examples, when $V(\mathbf{r})$ is (a) a harmonic trapping potential $(1/2)kr^2 = (1/2)m\omega^2 r^2$, of much current interest in the experiments on cold quantum Fermion vapours [3–5] and (b) bare Coulomb confinement, which has played a significant role in obtaining analytical insight into the exchange energy density $\epsilon_x(\mathbf{r})$ and exchange-only potential $V_x(\mathbf{r})$ in non-relativistic Ne-like atomic ions in the limit of large atomic number Z [6,7].

2. Harmonic trapping

Minguzzi *et al.* [8] proved for an arbitrary number of closed shells generated by the harmonic potential $V(\mathbf{r}) = (1/2)m\omega^2 r^2$ that the ground-state density satisfies the differential equation

$$\frac{\hbar^2}{8m}\frac{\partial}{\partial r}\nabla^2 n + [(M+2)\hbar\omega - V(\mathbf{r})]\frac{\partial n}{\partial r} + \frac{3}{2}\frac{\partial V}{\partial r}n = 0 \tag{4}$$

for $M+1$ closed shells. Combining Equation (4) with a result of Howard *et al.* [9] that

$$\frac{\partial t_L}{\partial r} = -\frac{3}{2}\frac{\partial V}{\partial r}n - \frac{\hbar^2}{8m}\frac{\partial}{\partial r}\nabla^2 n, \tag{5}$$

one readily reaches the formula

$$\frac{t_L'(r)}{n'(r)} = \mu - V(r) \tag{6}$$

where $t_L = -\sum_j^{occ}\psi_j\nabla^2\psi_j$ and $\mu = (M+2)\hbar\omega$.

In Figure 1, we take the case of a single closed shell, i.e. $M = 0$. Then in atomic units ($m = 1$, $\hbar = 1$, $e = 1$, $4\pi\epsilon_0 = 1$) with $\omega = 1$, we have the ground-state electron density $n(r)$ as

$$n(r) = 2\pi^{-3/2}\exp(-r^2). \tag{7}$$

Curve (a) of Figure 1 shows the conventional gradient form t_g of kinetic energy density given by the von Weizsäcker expression [10] for the case of a single-level occupancy under discussion as

$$t_g = \frac{(\nabla n)^2}{8n} = \frac{1}{2}r^2 n(r), \tag{8}$$

the last part of Equation (8) following from Equation (7). Evidently, as curve (a) displays, t_g is zero at the origin $r = 0$, is everywhere positive, and integrates to $T_s = \int t_g\,d\mathbf{r} = (1/2)E = (3/2)\hbar\omega$, or 3/2 in the units of this example.

Turning from t_g in Equation (8) to t_{GM} from Equation (3) with n given by Equation (7), curve (b) of Figure 1 shows t_{GM} for comparison with t_g, both, of course, yielding by volume integration the known single-particle kinetic energy $T_s = 3/2$ a.u. cited above. To show that t_{GM} is non-trivially different from t_g, for example the Laplacian form t_L corresponding to the wave function definition
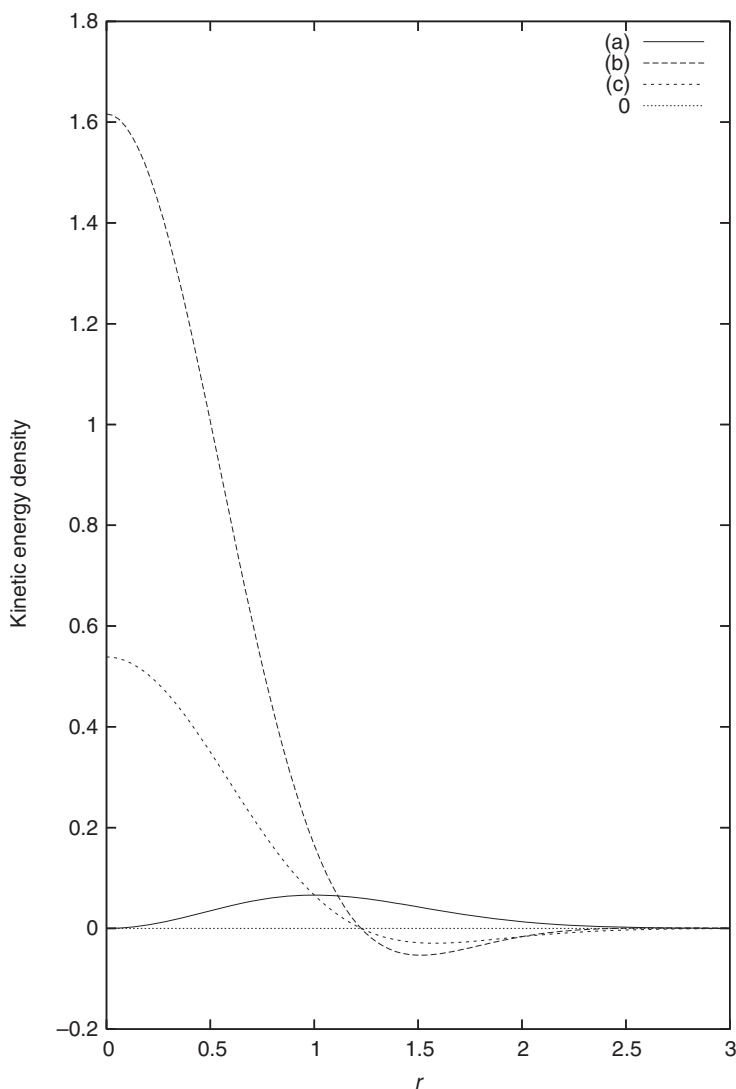
Figure 1. Plot of kinetic energy density functions against the distance from the centre of the harmonic trapping potential for a system of two non interacting electrons. Curve (a) refers to t_g, curve (b) to t_{GM} and curve (c) to the Laplacian of the electron density multiplied by the factor $-1/4$.

$-\psi\nabla^2\psi$ differs from t_g by

$$t_g = t_L + \frac{1}{4}\nabla^2 n, \tag{9}$$

we also depict in curve (c) of Figure 1 the shape of $\nabla^2 n$ again using Equation (7). This has a node at $r = \sqrt{3/2}$, which coincides with the first node of t_{GM} as seen in Figure 1. Thus, t_{GM} differs non-trivially from t_g, though both reproduce the correct value of T_s.

3. Closed shells generated by the bare Coulomb potential $-Ze^2/r$

In the earlier work, the present authors [11] have proved the following result for the derivative of t_g, which is valid for an arbitrary number of closed shells generated by $V(r) = -Ze^2/r$, namely, again in a.u.:

$$t'_g = \frac{1}{8}n''' - \frac{3}{4r^2}n' - \frac{3Z}{2r^2}n. \tag{10}$$

But for this Coulomb example, with e also set equal to unity, $\partial V/\partial r = Z/r^2$, and hence from Equation (10) we have that

$$\frac{3}{2}\left(\frac{\partial V}{\partial r}\right)n = \frac{1}{8}n''' - \frac{3}{4r^2}n' - t'_g. \tag{11}$$

Evidently, by dividing both sides of Equation (3) by $(3n + rn')$, and by differentiating with respect to r, $\partial V/\partial r$ can be removed from Equation (11), yielding a direct, if somewhat cumbersome, relationship for this Coulombic example, between t_g and t_{GM}, for any number of closed shells.

4. Example of helium atom

The DFT potential $V(r)$ for He is related to the exact correlated ground-state density $n(r)$ by

$$\nabla^2 n^{1/2} + 2[I - V(r)]n^{1/2} = 0, \tag{12}$$

which is equivalent to the usual von Weizsäcker [10] equation when written in terms of n rather than the density amplitude $n^{1/2}$ [12] appearing in Equation (12). I entering Equation (12) is the exact non-relativistic ionisation potential of He. Again, by constructing $\partial V/\partial r$ from Equation (3) in terms of t_{GM} and n, and from Equation (12) in terms of $n^{1/2}$, t_{GM} and t_g are related via the ground-state density of He. An approximate analytic form for n has been obtained for He by Howard *et al.* [13] from the Chandrasekhar variational wave function [14], and hence, by a straightforward numerical calculation t_g and t_{GM} can be compared, though now to a good approximation only because of the use of [14] for the ground-state wave function.

5. Conclusions and future directions

We have taken three examples to illustrate the application of the proposed kinetic energy density in Equation (3), motivated by [1]. These are (a) harmonic trapping, (b) bare Coulomb potential generating an arbitrary number of closed shells and (c) the He atom characterised by an approximate analytic density $n(r)$ [13] derived earlier from the wave function proposed by Chandrasekhar [14]. In each case, contact can be made between the well-established form t_g of kinetic energy density and the form (3) utilized here. As to the future direction, we first recommend the use of the semiempirical fine-tuned Hartree–Fock density of Cordero *et al.* [15], which has been shown to be of quantum Monte Carlo quality. Besides the, of course approximate, ground-state electron density thereby made possible, the conventional kinetic energy densities t_g and t_L can also be obtained for spherically symmetric atoms,

following Amovilli *et al.* [16]. Second, we stress that the seeds of a formula having resemblance to Equation (3) may be found in the study of Stoddart and March [17,18]. These authors calculated to all orders, in perturbation theory, the idempotent Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ when a potential $V(\mathbf{r})$ was 'switched on' to an initially uniform free electron gas. In [17], a formula for t_g was given in which a term proportional to $V(\mathbf{r})$ appeared, namely

$$t_g(\mathbf{r}) - t_0 = -V(\mathbf{r})\Sigma(\mathbf{r}), \tag{13}$$

where t_0 is the kinetic energy density of the homogeneous electron gas. Here, $\Sigma(\mathbf{r})$ is the series derived by Stoddart and March [17], namely

$$\Sigma(\mathbf{r}) = \sum_{j=1}^{\infty} \frac{j}{j+1} n_j, \tag{14}$$

where n_j is $O(V^j)$. March [19] obtained a closed expression for $\Sigma(\mathbf{r})$ for an arbitrary number of closed shells with harmonic trapping as

$$\Sigma(r) = \frac{3}{2V(r)} \int^r n(s)V'(s)\mathrm{d}s - \frac{n''(r)}{8V(r)} - \frac{n'(r)}{4rV(r)}, \tag{15}$$

with $V(r) = (1/2)kr^2$. This is readily shown to lead back to the correct result for t_g given when Equation (15) is inserted in Equation (13) for $t_g - t_0$, and then this is differentiated with respect to r.

We can add the further example of the Coulomb field for $\Sigma(r)$ to conclude this work. This then reads

$$\Sigma(r) = \frac{3}{2V(r)} \int^r n(s)V'(s)\mathrm{d}s - \frac{n''(r)}{8V(r)} + \frac{3}{4V(r)} \int^r \frac{n'(s)}{s^2}\mathrm{d}s. \tag{16}$$

This has evident similarity to the harmonic result (15) for $\Sigma(r)$, though the final terms of Equations (15) and (16) differ in detail. It would, of course, be of considerable interest for the future if the Stoddart and March series $\Sigma(r)$ entering Equation (13) $t_g - t_0$ could eventually be summed for an arbitrary potential $V(\mathbf{r})$.

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