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The three-dimensional kinetic energy density functional compatible with the exact differential equation for its associated tensor

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The kinetic energy density functional $t[n]$ of a system of electrons with density $n(\mathbf{x})$ moving independently in an effective one-body potential $V(\mathbf{x})$ can be written as the trace $\Sigma_{\alpha=1}^{3} t_{\alpha\alpha}$ of a tensor $t_{\alpha\beta}(\mathbf{x})$ field the divergence of which is shown to be related exactly to third derivatives of n and to the gradient of V. This relation is a "differential", i.e., pointwise valid refinement of the usual "integral" virial theorem. When the approximation is made that $t_{\alpha\beta}$ is a function of n and ∇n only, and when V is identified with the Kohn-Sham effective potential occurring in the Euler equation of the total energy minimization problem then V can be eliminated from both the tensor theorem and from the Euler equation whereby a set of differential equations for the dependence of $t_{\alpha\beta}$ on n and ∇n is obtained. These equations are solved exactly yielding finally the result that $t = \varkappa n^{5/3} + \lambda_w (\nabla n)^2/n$ with arbitrary constant $\varkappa$ and $\lambda_w = \hbar^2/(8m)$ is—within the assumption $t[n] \approx t(n,\nabla n)$—the only possible solution compatible with the tensor theorem. This indicates that corrections to the Thomas–Fermi–Weizsäcker functional should be done to the TF term, but not to the Weizsäcker term.

I. INTRODUCTION

For an electron gas with density $n(\mathbf{x})$ and particles moving independently in an effective one-body potential $V(\mathbf{x})$ the kinetic energy density functional $t[n]$ is usually approximated by a function of n and of its spatial derivatives

$$t[n] = \varkappa n^{5/3} + \lambda \frac{(\nabla n)^2}{n} + \eta \Delta n + \cdots , \tag{1}$$

where $\varkappa$, λ, and η are certain constants. The well-known Thomas–Fermi (TF) approximation is provided by $\lambda = 0$ and $\varkappa = \varkappa_{\mathrm{TF}} \equiv 3(3\pi^2)^{2/3} \hbar^2/(10m)$, see, e.g., the books of Gombás,[1] Lundqvist and March,[2] or the review articles of March,[3] Ghosh and Deb,[4] Parr,[5] and references therein.

The term $\sim (\nabla n)^2/n$ was first introduced by von Weizsäcker[6] with $\lambda = \lambda_w \equiv \hbar^2/(8m)$. Later on Kirzhnits,[7] and Kompaneets and Pavlovskii[8] found that λ_w should be diminished by a factor of 9 using quasiclassical expansion procedures and that the term $\sim \Delta n$ should be taken into account, at the same level of approximation. When the nonpositive definite form

$$t_1(\mathbf{x}) \equiv -\frac{\hbar^2}{2m} [\nabla^2 \Gamma(\mathbf{x},\mathbf{x}')]_{\mathbf{x}'=\mathbf{x}} \tag{2a}$$

is used for the kinetic energy density, $\Gamma(\mathbf{x},\mathbf{x}')$ being the first order density matrix, η has the value $-\hbar^2/(12m)$ in the Kirzhnits expansion. The positive definite expression

$$t_2(\mathbf{x}) \equiv \frac{\hbar^2}{2m} [\nabla \cdot \nabla' \Gamma(\mathbf{x},\mathbf{x}')]_{\mathbf{x}'=\mathbf{x}} \tag{2b}$$

can be shown to be the sum of t_1 and $(\hbar^2/4m)\Delta n$, see, e.g., Ref. 9, so that the factor η in a corresponding Kirzhnits expansion is $\hbar^2/(6m)$. Both t_1 and t_2 are equivalent with respect to calculation of the total kinetic energy $T = \int t_1[n] d^3x = \int t_2[n] d^3x$. In what follows we shall use the definition (2b) and omit the index 2 henceforth.

Higher order terms in Eq. (1) were given by Hodges[10] and Murphy.[11] In all these quasiclassical expansions, terms beyond the leading TF term were regarded as small corrections.

When the first two terms of Eq. (1) are taken into account, insertion of Hartree–Fock densities leads to kinetic energies which differ from the HF kinetic energy values by less than 1%, and agreement is still better when the fourth term of expansion (1) is included.[12]

However, local behavior of t is far less favorable, when $\lambda = \lambda_w/9$ is used, and the good global agreement of the kinetic energy turns out to arise from cancellation of local errors. This has been shown with the semiclassical expansion of expression t_1, Eq. (2a), in Ref. 13. Other authors[9,14,15] tested the corresponding expansion of t_2, Eq. (2b), however without taking care of the term $(\hbar^2/6m)\Delta n$. When densities are calculated self-consistently from the Euler equation corresponding to the minimization of the total energy functional $E[n]$, the Kirzhnits approximation shows unsatisfactory results even for the total energy itself when applied to atoms.[16,17] Moreover, the fourth term in the expansion (1) yields an infinite result for atoms.[11]

This approximation has been criticized also on theoretical grounds in earlier papers[16–19] and more recently[20–25] where it is claimed that the Weizsäcker term with the original value $\lambda = \lambda_w$ should be retained, whereas the coefficient $\varkappa_{\mathrm{TF}}$ should be modified or even the whole TF term be replaced by another expression.

In the present paper an approach is chosen which does not use semiclassical expansions. Especially, the density gradient will not be assumed to be small. The only approximation we shall make is the supposition that $t[n]$ can be represented as an ordinary function of n and ∇n. The principle of the following derivation rests on the requirement that $t[n]$ should be compatible with some exact quantum mechanical relation to be specified below. A well-known general theorem to be satisfied is the virial theorem. However, as was shown by Szasz *et al.*,[26] expression (1) obeys this theorem already for arbitrary coefficients $\varkappa$, λ, and η so that this

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theorem is not selective enough to fix the constants.

For one-dimensional systems there exists, however, a differential virial theorem[27,28] which connects exactly t, $n(x)$, and the potential $V(x)$ at every point x,

$$\frac{dt}{dx}=\frac{\hbar^2}{8m}\frac{d^3n}{dx^3}-\frac{n}{2}\cdot\frac{dV}{dx}. \tag{3}$$

From both the approximation that t is a positive definite function of $n,n'=dn/dx$ and $n''=d^2n/dx^2$ and from the requirement that t satisfies the differential virial theorem (3) exactly the most general solution is found to be[29]

$$t=\tilde{\varkappa}n^3+\frac{\hbar^2}{8m}\cdot\frac{n'^2}{n}, \tag{4}$$

where $\tilde{\varkappa}\geqslant 0$ is still arbitrary. The coefficient of the Weizsäcker term is fixed uniquely and identical with the original value λ_w. The detailed calculation made by the author yields also a term linear in n'' (with a coefficient which still depends on n and n'), however, the requirement that $t\geqslant 0$ for *arbitrary* density distributions rules out this term leaving expression (4).

It is the purpose of the present paper to draw corresponding conclusions for three-dimensional systems. Unfortunately, there is no differential virial theorem involving t as in the one-dimensional case. Rather, the three-dimensional analog of Eq. (3) is given by Eq. (9) below which connects the divergence of the kinetic energy density tensor $t_{\alpha\beta}$ [defined in Eq. (8) below] with third derivatives of n and with the gradient of V.[30] This exact relation can be exploited only if the additional assumption is made that each of the components $t_{\alpha\beta}$ can be approximated as a function of n and its derivatives, too.

We let t depend only on n and ∇n here. On the one hand, inclusion of second order derivatives would make calculations extremely tedious (as will be seen, already the case treated in this paper, is not simple). On the other hand, the result of the one-dimensional case gives rise to expect that second derivatives of n will occur only linearly also in the three-dimensional case, and therefore could be ruled out by the same arguments as above.

In the second section the differential equation for $t_{\alpha\beta}$ is derived more directly from the Schrödinger equation, alternatively to the derivation of Ref. 30 where this equation appears as a hypervirial theorem which is valid pointwise. In the third section the Euler equation of energy minimization is derived subject to the approximation that $t_{\alpha\beta}[n]\approx f_{\alpha\beta}(n,\nabla n)$. After the effective one-body potential $V(\mathbf{x})$ has been eliminated from both the Euler equation and from the differential equations determining $f_{\alpha\beta}$ (Sec. IV) a coupled system of new differential equations is obtained describing the dependence of the functions $f_{\alpha\beta}$ on n and on the components of ∇n. This system is solved exactly in Sec. V whereby the most general kinetic energy density is obtained which is compatible with (i) the prescribed dependence on n and ∇n and with (ii) the exact differential equations for the tensor divergence of $t_{\alpha\beta}$. Results are summarized and discussed in the last section.

II. THE DIFFERENTIAL EQUATION FOR THE KINETIC ENERGY DENSITY TENSOR

For a system of N (N even) fermions moving independently in an effective one-body potential $V(\mathbf{x})$ the ground state kinetic energy density of Eq. (2b) is given by

$$t(\mathbf{x})=2\cdot\frac{\hbar^2}{2m}\sum_{i=1}^{N/2}|\nabla\psi_i(\mathbf{x})|^2, \tag{5}$$

where each of the eigenfunctions $\psi_i(\mathbf{x})$ of the Hamiltonian

$$\hat{H}=-\frac{\hbar^2}{2m}\Delta+V(\mathbf{x}) \tag{6}$$

is occupied twice, according to the Pauli principle, up to a maximum energy.

$t(\mathbf{x})$ can be written as the trace

$$t(\mathbf{x})=\sum_{\alpha=1}^{3}t_{\alpha\alpha}(\mathbf{x}) \tag{7}$$

of the tensor field

$$t_{\alpha\beta}(\mathbf{x})=2\cdot\frac{\hbar^2}{4m}\sum_{i=1}^{N/2}\left(\frac{\partial\psi_i^*}{\partial x_\alpha}\frac{\partial\psi_i}{\partial x_\beta}+\frac{\partial\psi_i^*}{\partial x_\beta}\frac{\partial\psi_i}{\partial x_\alpha}\right) \tag{8}$$

($\alpha,\beta=1,2,3$). To avoid ambiguities below the Einstein convention of summation over repeated Greek indices is not adopted.

Let us call $t_{\alpha\beta}$ the kinetic energy density tensor which satisfies the differential equations ($\alpha=1,2,3$)

$$\sum_{\beta=1}^{3}\frac{\partial t_{\alpha\beta}}{\partial x_\beta}=\frac{\hbar^2}{8m}\sum_{\beta=1}^{3}\frac{\partial^3 n}{\partial x_\alpha\partial x_\beta\partial x_\beta}-\frac{n}{2}\cdot\frac{\partial V}{\partial x_\alpha}, \tag{9}$$

where

$$n=n(\mathbf{x})=2\sum_{i=1}^{N/2}\psi_i^*(\mathbf{x})\psi_i(\mathbf{x}) \tag{10}$$

is the ground state density of the system. Equation (9) was established by the author as a differential (i.e., valid pointwise) hypervirial theorem,[27] however, it can be derived more directly from the Schrödinger equation as follows.

When the conjugate complex of the Schrödinger equation with Hamiltonian (6) is differentiated with respect to x_α and multiplied by ψ_i the result is

$$-\frac{\hbar^2}{2m}\psi_i\Delta\left(\frac{\partial\psi_i^*}{\partial x_\alpha}\right)+\psi_i^*\psi_i\frac{\partial V}{\partial x_\alpha}+(V-E_i)\psi_i\frac{\partial\psi_i^*}{\partial x_\alpha}=0. \tag{11}$$

Multiply now the Schrödinger equation by $\partial\psi_i^*/\partial x_\alpha$ so that

$$-\frac{\hbar^2}{2m}\frac{\partial\psi_i^*}{\partial x_\alpha}\Delta\psi_i+(V-E_i)\psi_i\frac{\partial\psi_i^*}{\partial x_\alpha}=0, \tag{12}$$

and subtract Eq. (12) from Eq. (11). This yields

$$\frac{\partial\psi_i^*}{\partial x_\alpha}\Delta\psi_i-\psi_i\Delta\left(\frac{\partial\psi_i^*}{\partial x_\alpha}\right)=-\frac{2m}{\hbar^2}\psi_i^*\psi_i\frac{\partial V}{\partial x_\alpha} \tag{13}$$

which shows that the left-hand side is real since the right-hand side is.

Using definitions (8) and (10) we obtain by straightforward algebra

$$\sum_{\beta=1}^{3}\left(\frac{\partial t_{\alpha\beta}}{\partial x_\beta}-\frac{\hbar^2}{8m}\frac{\partial^3 n}{\partial x_\alpha \partial x_\beta \partial x_\beta}\right)$$
$$=\frac{\hbar^2}{4m}\sum_{i=1}^{N/2}\left[\frac{\partial\psi_i^*}{\partial x_\alpha}\Delta\psi_i-\psi_i\Delta\left(\frac{\partial\psi_i^*}{\partial x_\alpha}\right)\right.$$
$$\left.+\text{complex conjugate}\right]$$
$$=-\frac{\partial V}{\partial x_\alpha}\sum_{i=1}^{N/2}\psi_i^*\psi_i$$
$$=-\frac{n}{2}\cdot\frac{\partial V}{\partial x_\alpha} \tag{14}$$

because of Eq. (13).

III. EULER EQUATION WITH KINETIC ENERGY DENSITY DEPENDING ON n AND ∇n ONLY

When $V(\mathbf{x})$ is identified with the effective potential of the Kohn–Sham self-consistent equations then the functional derivative $\delta T[n]/\delta n(\mathbf{x})$ of the kinetic energy T of independent particles satisfies (see, e.g., the review article of Kohn and Vashishta contained in Ref. 2)

$$\frac{\delta T[n]}{\delta n}+V=\mu \tag{15}$$

with chemical potential μ.

Suppose now that the kinetic energy density t is approximated by a function of n and ∇n,

$$t=f\left(n,\frac{\partial n}{\partial x_1},\frac{\partial n}{\partial x_2},\frac{\partial n}{\partial x_3}\right) \tag{16}$$

so that t depends on $\mathbf{x}$ only indirectly via $n(\mathbf{x})$ and $\nabla n(\mathbf{x})$. It follows that the variation of T is given by

$$\delta T=\int \delta f(n,u_1,u_2,u_3)d^3x \tag{17}$$
$$=\int\left(\frac{\partial f}{\partial n}\delta n+\sum_{\alpha=1}^{3}\frac{\partial f}{\partial u_\alpha}\delta u_\alpha\right)d^3x,$$

where we have put

$$u_\alpha\equiv\frac{\partial n}{\partial x_\alpha}. \tag{18}$$

From Gauss' theorem we have that

$$\sum_{\alpha=1}^{3}\int\frac{\partial f}{\partial u_\alpha}\delta u_\alpha\, d^3x=\sum_{\alpha=1}^{3}\int\frac{\partial f}{\partial u_\alpha}\frac{\partial(\delta n)}{\partial x_\alpha}d^3x$$
$$=-\sum_{\alpha=1}^{3}\int\frac{\partial}{\partial x_\alpha}\left(\frac{\partial f}{\partial u_\alpha}\right)\delta n\, d^3x \tag{19}$$

since it is assumed that surface integrals vanish. When Eq. (19) is inserted into Eq. (17) the variation δT can be written

$$\delta T=\int\frac{\delta T}{\delta n}\delta n\, d^3x$$
$$=\int\left[\frac{\partial f}{\partial n}-\sum_{\alpha=1}^{3}\frac{\partial}{\partial x_\alpha}\left(\frac{\partial f}{\partial u_\alpha}\right)\right]\delta n\, d^3x \tag{20}$$

and therefore from Eq. (15), after performing the differentiation,

$$\frac{\partial f}{\partial n}-\sum_{\beta=1}^{3}u_\beta\frac{\partial^2 f}{\partial n\partial u_\beta}$$
$$-\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3}w_{\gamma\beta}\frac{\partial^2 f}{\partial u_\gamma\partial u_\beta}+V=\mu, \tag{21}$$

where

$$w_{\gamma\beta}\equiv\frac{\partial u_\gamma}{\partial x_\beta}=\frac{\partial^2 n}{\partial x_\beta\partial x_\gamma}. \tag{22}$$

IV. CONDITIONS ON THE KINETIC ENERGY DENSITY TENSOR BY ELIMINATION OF THE POTENTIAL

When the function $f(n,u_1,u_2,u_3)$ is specified, the differential Eq. (21) determines n from V and μ given. On the other hand, Eq. (9) is exact for the exact kinetic energy density tensor which, of course, is not known to us as a functional of n.

Once the exact kinetic energy density has been approximated by a function of n and of Δn, it is consistent to assume that all tensor components $t_{\alpha\beta}$ separately are approximately functions of n and Δn, too, i.e.,

$$t_{\alpha\beta}(\mathbf{x})\approx f_{\alpha\beta}[n(\mathbf{x}),u_1(\mathbf{x}),u_2(\mathbf{x}),u_3(\mathbf{x})], \tag{23}$$

where $f_{\alpha\beta}$ are still to be determined, and

$$f=\sum_{\alpha=1}^{3}f_{\alpha\alpha}. \tag{24}$$

With the assumption (23) Eq. (9) can be imposed as a condition to be satisfied exactly by the $f_{\alpha\beta}$.

Let us now eliminate V and μ from both Eqs. (9) and (21).

For this purpose Eq. (21) is differentiated with respect to x_α, multiplied with $-n/2$ and added to Eq. (9) the result being

$$\frac{n}{2}\frac{\partial}{\partial x_\alpha}\left[\frac{\partial f}{\partial n}-\sum_{\beta=1}^{3}\left(u_\beta\frac{\partial^2 f}{\partial n\partial u_\beta}-\sum_{\gamma=1}^{3}w_{\gamma\beta}\frac{\partial^2 f}{\partial u_\beta\partial u_\gamma}\right)\right]$$
$$+\sum_{\beta=1}^{3}\left(\frac{\hbar^2}{8m}\frac{\partial w_{\alpha\beta}}{\partial x_\beta}-\frac{\partial f_{\alpha\beta}}{\partial x_\beta}\right)=0. \tag{25}$$

These equations ($\alpha=1,2,3$), however, have to be satisfied for all density distributions whatever the potential may be since the latter does no longer occur in Eq. (25). Therefore, Eq. (25) are not differential equations which determine $n(\mathbf{x})$; rather they have to be regarded as relationships the functions f and $f_{\alpha\beta}$ have to obey for arbitrary values of n and all of its derivatives appearing in Eq. (25) at any fixed point in space. In other words, f and $f_{\alpha\beta}$ have to be determined such that Eq. (25) are satisfied identically with respect to n and its derivatives. This requirement leads to conditions on f and $f_{\alpha\beta}$ which we first want to state explicitly and then to exploit in the following sections of this paper.

After all differentiations in Eq. (25) have been performed, it can be conveniently rearranged in the form

$$G_\alpha^{(1)}+G_\alpha^{(2)}+G_\alpha^{(3)}+G_\alpha^{(4)}=0, \tag{26}$$

where

$$G_\alpha^{(1)}\equiv\frac{n}{2}u_\alpha\left(\frac{\partial^2 f}{\partial n^2}-\sum_{\beta=1}^{3}u_\beta\frac{\partial^3 f}{\partial u_\beta\partial n^2}\right)-\sum_{\beta=1}^{3}u_\beta\frac{\partial f_{\alpha\beta}}{\partial n}, \tag{27a}$$

$$G_\alpha^{(2)} \equiv -\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3}\left[\frac{n}{2}(w_{\alpha\beta}u_\gamma + w_{\beta\gamma}u_\alpha)\frac{\partial^3 f}{\partial n \partial u_\beta \partial u_\gamma} + w_{\beta\gamma}\frac{\partial f_{\alpha\beta}}{\partial u_\gamma}\right], \tag{27b}$$

$$G_\alpha^{(3)} \equiv -\frac{n}{2}\sum_{\nu=1}^{3}\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3} w_{\alpha\nu}w_{\beta\gamma}\frac{\partial^3 f}{\partial u_\nu \partial u_\beta \partial u_\gamma}, \tag{27c}$$

$$G_\alpha^{(4)} \equiv \frac{\hbar^2}{8m}\sum_{\beta=1}^{3}\frac{\partial w_{\alpha\beta}}{\partial x_\beta} - \frac{n}{2}\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3}\frac{\partial w_{\beta\gamma}}{\partial x_\alpha}\frac{\partial^2 f}{\partial u_\beta \partial u_\gamma}. \tag{27d}$$

These various expressions may be characterized as follows:

$G_\alpha^{(1)}$ does not contain second and/or higher derivatives of n,

$G_\alpha^{(2)}$ contains second derivatives linearly, since they do not occur in $f, f_{\alpha\beta}$, and no derivatives higher than second,

$G_\alpha^{(3)}$ is of second order with respect to second derivatives and has no derivatives higher than second,

$G_\alpha^{(4)}$ is linear with respect to third derivatives.

Since, however, Eq. (26) is to be an identity with respect to n and its derivatives and since f depends on n and u_α, but not on higher derivatives of n, it follows from the above characterization of the $G_\alpha^{(i)}$ that each of the four terms $G_\alpha^{(i)}$, $i = 1,2,3,4$, must vanish separately:

$$G_\alpha^{(i)} = 0 \quad (\alpha = 1,2,3). \tag{28}$$

V. SOLUTION OF THE DIFFERENTIAL EQUATIONS DETERMINING $f_{\alpha\beta}$

A. Evaluation of $G_\alpha^{(i)}=0$, $i=3,4$

It is convenient to start with Eqs. (27d) and (28). From the definition of $w_{\alpha\beta}$, Eq. (22), it is clear that

$$\frac{\partial w_{\alpha\beta}}{\partial x_\beta} = \frac{\partial w_{\beta\beta}}{\partial x_\alpha} \tag{29}$$

so that $G_\alpha^{(4)} = 0$ can be written in detail as follows:

$$\sum_{\beta=1}^{3}\left(\frac{\hbar^2}{8m} - \frac{n}{2}\frac{\partial^2 f}{\partial u_\beta^2}\right)\cdot\frac{\partial w_{\beta\beta}}{\partial x_\alpha} - n\sum_{\beta<\gamma}\sum\frac{\partial^2 f}{\partial u_\beta \partial u_\gamma}\frac{\partial w_{\beta\gamma}}{\partial x_\alpha} = 0, \tag{30}$$

where in the double sum over off-diagonal elements use has been made of the symmetry with respect to interchange of β with γ. For α fixed, all third derivatives of n are independent variables in Eq. (30), therefore Eq. (30) is identically satisfied only if

$$\frac{\partial^2 f}{\partial u_\beta^2} = \frac{\hbar^2}{4mn} \quad (\beta = 1,2,3) \tag{31}$$

and

$$\frac{\partial^2 f}{\partial u_\beta \partial u_\gamma} = 0 \quad (\beta \neq \gamma). \tag{32}$$

From the last equation we conclude that $\partial f/\partial u_\beta$ can depend at most on n and u_β,

$$\frac{\partial f}{\partial u_\beta} \equiv q_\beta(n, u_\beta) \tag{33}$$

and Eq. (31) yields

$$\frac{\partial q_\beta}{\partial u_\beta} = \frac{\hbar^2}{4mn} \tag{34}$$

which leads to

$$\frac{\partial f}{\partial u_\beta} = \frac{\hbar^2}{4mn}u_\beta + s_\beta(n), \tag{35}$$

where s_β is some function depending solely on the density.

Further integration yields

$$f = \frac{\hbar^2}{8m}\frac{u_\beta^2}{n} + s_\beta u_\beta + h_\beta \quad (\beta = 1,2,3), \tag{36}$$

where h_β is independent of u_β. Clearly, f must be the same function for all values of index β. Therefore, putting $\beta = 1$, we have from Eq. (35) that

$$\frac{\partial f}{\partial u_1} = \frac{\hbar^2}{4mn}u_1 + s_1(n), \tag{37}$$

on the other hand, from Eq. (36) with $\beta = 2$,

$$\frac{\partial f}{\partial u_1} = \frac{\partial h_2}{\partial u_1}, \tag{38}$$

whereby we obtain

$$\frac{\partial h_2}{\partial u_1} = \frac{\hbar^2}{4mn}u_1 + s_1 \tag{39}$$

leading to

$$h_2 = \frac{\hbar^2}{8mn}u_1^2 + s_1 u_1 + g(n, u_3). \tag{40}$$

Since h_2 is independent of u_2, and due to Eq. (39), g depends only on n and u_3.

Analogously, we find

$$\frac{\partial f}{\partial u_3} = \frac{\hbar^2}{4mn}u_3 + s_3 = \frac{\partial h_2}{\partial u_3} = \frac{\partial g}{\partial u_3} \tag{41}$$

and therefore, with $k(n)$ still indetermined,

$$g = \frac{\hbar^2}{8mn}u_3^2 + s_3 u_3 + k(n) \tag{42}$$

so that we finally obtain from Eqs. (36), (40), and (42),

$$f = \sum_{\alpha=1}^{3}\left(\frac{\hbar^2}{8mn}u_\alpha^2 + s_\alpha(n)u_\alpha\right) + k(n) \tag{43}$$

or

$$f = \frac{\hbar^2}{8m}\frac{(\nabla n)^2}{n} + \mathbf{s}(n)\cdot\nabla n + k(n). \tag{43'}$$

Expression (43) shows immediately that third derivatives of f with respect to density gradient components vanish so that $G_\alpha^{(3)} = 0$ is already satisfied by Eq. (43).

B. Evaluation of $G_\alpha^{(2)}=0$

Let us consider now Eq. (28) for $i = 2$ which reads

$$\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3} w_{\beta\gamma}\left[\frac{\hbar^2}{8mn}(u_\beta\delta_{\gamma\alpha} + u_\alpha\delta_{\gamma\beta}) - \frac{\partial f_{\alpha\beta}}{\partial u_\gamma}\right] = 0 \tag{44}$$

after

$$\frac{\partial^3 f}{\partial n \partial u_\beta \partial u_\gamma} = -\frac{\hbar^2}{4mn^2}\delta_{\gamma\beta}, \tag{45}$$

arising from Eqs. (31) and (32), has been inserted into Eq. (27b).

From $w_{\beta\gamma} = w_{\gamma\beta}$ [see Eq. (22)] we can perform the double sum over β and γ in Eq. (44) as follows:

$$\sum_{\gamma>\beta}\sum w_{\beta\gamma}(B_{\alpha\gamma\beta} + B_{\alpha\beta\gamma}) + \sum_{\beta} w_{\beta\beta}B_{\alpha\beta\beta} = 0\,, \tag{46}$$

where $B_{\alpha\beta\gamma}$ is the expression in the square brackets of Eq. (44). Under the restriction $\gamma>\beta$, the components $w_{\beta\gamma}$ are independent variables in the sense of Sec. IV. Therefore we conclude from Eq. (46) that

$$B_{\alpha\beta\gamma} + B_{\alpha\gamma\beta} = 0 \quad (\gamma>\beta)\,. \tag{47}$$

Each of the possible combinations of indices $\alpha,\beta,\gamma>\beta$ is easily seen to fall into one of the following cases according to which Eq. (47) leads to relations (48a)–(48e),

(a) α,β,γ all different:

$$\frac{\partial f_{\alpha\beta}}{\partial u_\gamma} + \frac{\partial f_{\alpha\gamma}}{\partial u_\beta} = 0\,, \tag{48a}$$

(b) $\alpha=\beta<\gamma$:

$$\frac{\partial f_{\alpha\alpha}}{\partial u_\gamma} + \frac{\partial f_{\alpha\gamma}}{\partial u_\alpha} = \frac{\hbar^2}{8mn}u_\gamma\,, \tag{48b}$$

(c) $\alpha\neq\beta=\gamma$:

$$\frac{\partial f_{\alpha\beta}}{\partial u_\beta} = \frac{\hbar^2}{8mn}u_\alpha\,, \tag{48c}$$

(d) $\alpha=\gamma>\beta$:

$$\frac{\partial f_{\alpha\alpha}}{\partial u_\beta} + \frac{\partial f_{\alpha\beta}}{\partial u_\alpha} = \frac{\hbar^2}{8mn}u_\beta\,, \tag{48d}$$

(e) $\alpha=\beta=\gamma$:

$$\frac{\partial f_{\alpha\alpha}}{\partial u_\alpha} = \frac{\hbar^2}{4mn}u_\alpha\,. \tag{48e}$$

Cases (b) and (d) can be comprised by stating that (48b) is valid for $\alpha\neq\gamma$.

Since $f_{\alpha\beta}$ equals $f_{\beta\alpha}$ by definition—see Eqs. (8) and (23)—we find from Eq. (48c), after interchanging α and β,

$$\frac{\partial f_{\alpha\beta}}{\partial u_\alpha} = \frac{\hbar^2}{8mn}u_\beta \quad (\alpha\neq\beta), \tag{49}$$

which together with Eqs. (48b) and (48d) yields

$$\frac{\partial f_{\alpha\alpha}}{\partial u_\beta} = 0 \quad (\alpha\neq\beta). \tag{50}$$

Therefore, $f_{\alpha\alpha}$ can depend only on n and u_α, so that integration of Eq. (48e) leads to

$$f_{\alpha\alpha} = \frac{\hbar^2 u_\alpha^2}{8mn} + k_\alpha(n)\,, \tag{51}$$

where k_α is a function of n only.

Comparison with Eqs. (24) and (43) shows that

$$k(n) = \sum_{\alpha=1}^{3} k_\alpha(n) \tag{52}$$

and

$$s_\alpha(n) = 0 \quad (\alpha = 1,2,3). \tag{53}$$

Furthermore, when Eqs. (48a) are written out, we obtain on account of the symmetry of $f_{\alpha\beta}$,

$$\frac{\partial f_{13}}{\partial u_2} + \frac{\partial f_{12}}{\partial u_3} = 0\,,$$
$$\frac{\partial f_{23}}{\partial u_1} + \frac{\partial f_{12}}{\partial u_3} = 0\,,$$
$$\frac{\partial f_{23}}{\partial u_1} + \frac{\partial f_{13}}{\partial u_2} = 0\,,$$

which has only the trivial solution

$$\frac{\partial f_{\alpha\beta}}{\partial u_\gamma} = 0 \quad (\alpha,\beta,\gamma \text{ all different}), \tag{54}$$

i.e., $f_{\alpha\beta}$ does not depend on u_γ, so that integration of Eq. (49) yields

$$f_{\alpha\beta} = \frac{\hbar^2}{8mn}u_\alpha u_\beta + k_{\alpha\beta}(n,u_\beta) \quad (\alpha\neq\beta). \tag{55}$$

However,

$$\frac{\partial f_{\alpha\beta}}{\partial u_\beta} = \frac{\hbar^2}{8mn}u_\alpha + \frac{\partial k_{\alpha\beta}}{\partial u_\beta} \tag{56}$$

which leads to

$$\frac{\partial k_{\alpha\beta}}{\partial u_\beta} = 0 \tag{57}$$

by comparison with Eq. (48c), so that $k_{\alpha\beta}$ is dependent at most on n.

Thus we obtain from Eqs. (51), (55), and (57) that for all values of α,β,

$$f_{\alpha\beta} = \frac{\hbar^2}{8mn}u_\alpha u_\beta + k_{\alpha\beta}(n) \tag{58}$$

with

$$k_{\alpha\alpha} = k_\alpha\,. \tag{59}$$

C. Evaluation of $G_\alpha^{(1)}=0$ and final result for the kinetic energy density and its associated tensor

We are now able to evaluate equation $G_\alpha^{(1)} = 0$. When expressions (58) and (59) are inserted in expression (27a) the above equation reads

$$nu_\alpha\frac{d^2}{dn^2}\sum_{\beta=1}^{3}k_{\beta\beta}(n) = 2\sum_{\beta=1}^{3}u_\beta\frac{dk_{\alpha\beta}(n)}{dn} \tag{60}$$

($\alpha = 1,2,3$). Equating coefficients of u_1,u_2, and u_3 we find

$$\frac{dk_{\alpha\beta}}{dn} = \frac{n}{2}\delta_{\alpha\beta}\frac{d^2}{dn^2}\sum_{\gamma=1}^{3}k_{\gamma\gamma}\,. \tag{61}$$

Putting $\alpha=\beta$ and summing over α yields

$$\frac{dk}{dn} = \frac{3n}{2}\cdot\frac{d^2k}{dn^2}\,, \tag{62}$$

where

$$k \equiv \sum_{\alpha=1}^{3}k_{\alpha\alpha}\,. \tag{63}$$

Equation (62) has the solution

$$k(n) = \varkappa n^{5/3} + K\,, \tag{64}$$

where $\varkappa$ and K are arbitrary constants of integration.

For $\alpha=\beta$, Eq. (61) then reads

$$\frac{dk_{\alpha\alpha}}{dn}=\frac{5}{9}\varkappa n^{2/3} \tag{65}$$

or

$$k_{\alpha\alpha}=\frac{\varkappa}{3}n^{5/3}+K_{\alpha\alpha}\,. \tag{66}$$

Due to Eqs. (63) and (64) the constants $K_{\alpha\alpha}$ have to satisfy

$$K=\sum_{\alpha=1}^{3}K_{\alpha\alpha}\,. \tag{67}$$

If $\alpha\neq\beta$, Eq. (61) clearly leads to

$$k_{\alpha\beta}=K_{\alpha\beta}=\text{const}\,, \tag{68}$$

so that Eqs. (66) and (68) can be comprised to

$$k_{\alpha\beta}(n)=\frac{\varkappa}{3}n^{5/3}\delta_{\alpha\beta}+K_{\alpha\beta}\,. \tag{69}$$

Of course, the constants $K_{\alpha\beta}$ must vanish,

$$K_{\alpha\beta}=0 \tag{70}$$

since $t_{\alpha\beta}$ and thus $f_{\alpha\beta}$ are zero if there is no density at all.

Thus we finally obtain from Eqs. (18), (58), (69), and (70)

$$f_{\alpha\beta}=\frac{\hbar^2}{8m}\cdot\frac{1}{n}\frac{\partial n}{\partial x_\alpha}\frac{\partial n}{\partial x_\beta}+\frac{\varkappa}{3}n^{5/3}\delta_{\alpha\beta} \tag{71}$$

and the kinetic energy density becomes

$$t\approx f=\sum_{\alpha=1}^{3}f_{\alpha\alpha}=\frac{\hbar^2}{8m}\frac{(\nabla n)^2}{n}+\varkappa n^{5/3}\,, \tag{72}$$

where $\varkappa$ remains still indetermined.

VI. SUMMARY AND CONCLUSION

It was the aim of this paper to find the most general positive definite expression for the ground state kinetic energy density t of an electron system under the condition that

(i) the tensor components $t_{\alpha\beta}[n]$, defined by Eq. (8) can be approximately described by functions $f_{\alpha\beta}(n,\nabla n)$ of the ground state density n and of its gradient alone.

(ii) The system of differential equations (9) which has to be satisfied by the exact tensor components $t_{\alpha\beta}$ is also satisfied by $f_{\alpha\beta}$.

Because of Eq. (7), condition (i) implies that t is approximated as function of n and ∇n.

After the potential was eliminated from the Euler equation (21) of the energy minimization problem and from Eqs. (9), the system (25) was obtained. This system has to be valid for any density distribution and therefore, must be regarded as to be satisfied identically with respect to n and its derivatives $\partial n/\partial x_\alpha$, etc. at any point x in space. Consequently, a coupled system of new differential equations (27a)–(27d) and (28) arises which determines the functions $f_{\alpha\beta}(n,\nabla n)$. The solution is calculated exactly in the fifth section, the result being

$$f_{\alpha\beta}=\frac{\hbar^2}{8m}\frac{1}{n}\frac{\partial n}{\partial x_\alpha}\frac{\partial n}{\partial x_\beta}+\frac{\varkappa}{3}n^{5/3}\delta_{\alpha\beta} \tag{71}$$

and thus

$$t\approx f=\frac{\hbar^2}{8m}\frac{(\nabla n)^2}{n}+\varkappa n^{5/3}\,. \tag{72}$$

The coefficient $\varkappa$ remains indetermined therefore this expression cannot be used for practical calculations. Yet we not only recovered the specific type of functions occurring in the approximation of t by a new, very general argument but also succeeded in fixing the Weizsäcker coefficient. The result strongly indicates that any corrections to approximations of the form (1) should be performed at the TF term, not at the Weizsäcker term which is in agreement with the conclusion drawn by other authors.[16,17,19–25] Especially, the arbitrariness of $\varkappa$ allows for a dependence on the electron number N such that $\lim_{N\to\infty}\varkappa(N)=\varkappa_{\mathrm{TF}}$.

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