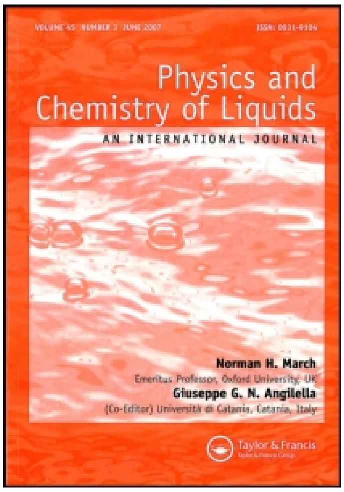

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REVIEW

Some pointers towards a future orbital-free density functional theory of inhomogeneous electron liquids

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Recent work by Gál and March has been concerned with a model two-electron atom in which electron-nuclear Coulomb attraction is replaced by harmonic confinement. Furthermore, the interfermion interaction $u(r_{12})$ between electrons at separation r_{12} is taken to be of inverse square form λ/r_{12}^2. With these model simplifications, it then proves possible to obtain an exact analytical expression for the ground-state energy density functional. Turning to current usage of density functional theory of inhomogeneous Fermion liquids, in terms of a one-body potential $V(\mathbf{r})$, the single-particle (s) kinetic energy functional $T_s[n]$ is next considered, for the experimentally interesting case of ultracold Fermion vapours which are magnetically trapped. This is again the case of harmonic confinement. Results for $T_s[n]$ for different dimensionalities have been obtained analytically for such systems and are summarized. The intimate relationship between this kinetic energy T_s and the exchange energy E_x is then exhibited, the off-diagonal density, or idempotent Dirac density matrix now being invoked. In turn this latter quantity can be related to the ground-state density $n(\mathbf{r})$ via a partial differential equation. Finally, some brief discussion is given of the, as yet unsolved, problem of the electron–electron correlation energy.

Keywords: density functional theory; inhomogeneous electron liquids

1. Background and outline

The forerunner of modern density functional theory (DFT) was the semi-classical method introduced independently more than eight decades ago by Thomas [1] and Fermi [2]. This method, of course approximate, can be considered as based on an energy functional $E_{\mathrm{TF}}[n]$ of the ground-state electron density $n(\mathbf{r})$ having the form [3]

$$E_{\mathrm{TF}}[n] = c_k \int \{n(\mathbf{r})\}^{\frac{5}{3}} d\mathbf{r} + \int n(\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + \tfrac{1}{2} e^2 \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'. \tag{1.1}$$

Writing the variation principle in the form

$$\delta[E_{\mathrm{TF}} - N\mu] = 0, \tag{1.2}$$

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where the variation δ is with respect to the density $n(\mathbf{r})$ in Equation (1.1), N is the total number of electrons while μ is the chemical potential which is constant everywhere in the inhomogeneous electron distribution of density $n(\mathbf{r})$. This ground-state density $n(\mathbf{r})$ can be determined self-consistently.

Dirac [4] added exchange to the TF energy (1.1) to obtain the TDF approximation

$$E_{\mathrm{TFD}}[n] = E_{\mathrm{TF}}[n] - c_{\mathrm{x}} \int \{n(\mathbf{r})\}^{\frac{4}{3}}\, \mathrm{d}\mathbf{r}, \tag{1.3}$$

and again the variational principle can be utilized to find the self-consistent ground-state density.

In this Thomas-Fermi-Dirac (TFD) theory, the constants c_{k} and c_{x} appearing in Equations (1.1) and (1.3), respectively, are determined from the theory of the homogeneous electron gas (HEG) as

$$c_{\mathrm{k}} = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} \tag{1.4}$$

and

$$c_{\mathrm{x}} = e^2\left(\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{1/3}. \tag{1.5}$$

Electron correlation being a formidable problem was clear from the fact that it took half a century from Dirac's work yielding the exchange energy in Equation (1.3) from the HEG used locally to the quantum Monte Carlo solution of this same HEG model for correlation energy, carried out by Ceperley and Alder [5]. No elegant analytic form of the correlation energy density $\epsilon_{\mathrm{c}}(\mathbf{r})$ comparable to the Dirac exchange form $-c_{\mathrm{x}}\{n(\mathbf{r})\}^{4/3}$ has as yet emerged. But as with kinetic and exchange in Equations (1.1) and (1.3), respectively, $\epsilon_{\mathrm{c}} \equiv \epsilon_{\mathrm{c}}[n(\mathbf{r})]$ in this local density description. The resulting energy functional has still the merit of universality.

However, it soon became clear, as summarized in detail in the writer's book [3], that the really serious approximation in this local density theory was in the TF kinetic energy $c_{\mathrm{k}}\int\{n(\mathbf{r})\}^{5/3}\mathrm{d}\mathbf{r}$, and that a return to symmetrised Hartree-like orbital equations offered a quantitative way forward.

Nevertheless, it is highly desirable for the future to return to orbital-free DFT as in the TFD method, but avoiding, of course, the too-drastic local density approximation of that latter approach. It is the purpose of the present article to stress some pointers towards a future orbital-free DFT.

The outline of the present study is then as follows. In Section 2, a model two-electron atom is treated in which an exact analytical expression, due to Gál and March has been obtained. Then, in Section 3, we return to the single-particle kinetic energy functional $T_{\mathrm{s}}[n]$, given in the TF method by $c_{\mathrm{k}}\int\{n(\mathbf{r})\}^{5/3}\mathrm{d}\mathbf{r}$ as in Equation (1.1). $T_{\mathrm{s}}[n]$ is exhibited for the important case studied experimentally of harmonically confined ultracold Fermion vapours. In Section 4, the idempotent Dirac density matrix, essentially the off-diagonal generalisation of the ground-state density $n(\mathbf{r})$, is the focal point. This is shown to lead to a formally exact integral equation to solve for the exchange-only potential of DFT, namely $V_{\mathrm{x}}(\mathbf{r})$. Section 5 considers the form of the partial differential equation for the Dirac density matrix in terms of the diagonal ground-state density $n(\mathbf{r})$. Section 6 then deals with some fairly general considerations relating to correlation energy in DFT: the outstanding unsolved problem at the time of writing. The article concludes with Section 7 which constitutes a summary, plus some proposals for future studies which should prove fruitful.

2. A two-electron spin-compensated 'model atom' for which the ground-state is known analytically

We move from the ground-state statistical method of TFD, completed in 1930, to the case of a 'model atom'. Ideally (see also Section 2.1), we would like to consider non-relativistic two-electron He-like atomic ions with nuclear charge Ze and therefore external potential $-Ze^2/r$, together with interfermion interaction $u(r_{12}) = e^2/r_{12}$. Except for the large Z limit treated briefly below, this problem remains unsolved, despite very accurate approximate treatments going back at least to Hylleraas [6].

But if one chooses a 'model atom' characterized by $V_{\text{ext}}(\mathbf{r}) = \frac{1}{2}kr^2 = \frac{1}{2}m\omega^2 r^2$ and $u(r_{12}) = \lambda / r_{12}^2$, then as Crandall *et al.* [7] demonstrated, the ground-state wave function can be obtained analytically. Using this wave function, Capuzzi *et al.* [8] quite recently derived an exact differential equation satisfied by the ground-state Fermion density $n(\mathbf{r})$, which naturally contained the harmonic force constant $k = m\omega^2$ and the strength λ of the inverse square interparticle interaction $u(r_{12})$ characterising this model atom. This equation reads

$$\frac{\hbar}{4m\omega} r n''(r) + \left(\frac{\hbar}{2m\omega} + \frac{3}{2}r^2\right) n'(r) + r\left(\frac{3}{2} - \alpha + \frac{2m\omega}{\hbar} r^2\right) n(r) = 0, \tag{2.1}$$

with $2\alpha = \left(\sqrt{1 + \frac{4m}{\hbar^2}\lambda} - 1\right)$, and has an exact solution in terms of hypergeometric functions [8].

Gál and March [9] have subsequently derived an exact energy density functional for the above model atom. The essential steps in their proof are summarized in Appendix A, and we merely quote their result immediately below:

$$E[n] = \int n(r) V_{\text{ext}}(r) \mathrm{d}\mathbf{r} + \frac{\hbar^2}{16m} \int \left[\frac{n'^2(r)}{n(r)} + \frac{r\, n'(r) n''(r)}{2\quad n(r)}\right] \mathrm{d}\mathbf{r} + \frac{3}{16}\hbar\omega \int \left[r^2 \frac{n'^2(r)}{n(r)} - 9n(r)\right] \mathrm{d}\mathbf{r}, \tag{2.2}$$

where $\hbar\omega$ is given in terms of $n(\mathbf{r})$ in Appendix A.

2.1. *Parallel equation for n(r, Z) for He-like atomic ions at large atomic number Z*

As already mentioned above, let us finish the present section by emphasising the parallel between Equation (2.1), which can be regarded as the Euler–Lagrange equation derivable, at least in principle, from the ground-state energy functional $E[n]$ given in Equation (2.2), and the ground-state density $n(r, Z)$ for non-relativistic He-like atomic ions in the limit of large Z. This quantity $n(r, Z)$ was obtained as Z tends to infinity in the pioneering work of Schwartz [10,11]. Subsequently Gál *et al.* [12] derived the differential equation satisfied by the Schwartz density $n(r, Z)$ as:

$$P_3(r)n'''(r) + P_2(r)n''(r) + P_1(r)n'(r) + P_0(r)n(r) = 0. \tag{2.3}$$

This linear, third-order and homogeneous differential equation has known [12] polynomials $P_i(\mathbf{r})$ multiplying the density $n(\mathbf{r})$ and its low-order derivatives. Naturally these polynomials $P_i(\mathbf{r})$ depend also on the (large) atomic number Z as a parameter. A key aim of DFT for the He-like atomic ions is to remove the constraint of large Z which limits the applicability of the non-relativistic Equation. (2.3).

3. A pointer towards the orbital-free single-particle kinetic energy functional in DFT

Equation (2.2) for the 'model 2-electron atom' of the previous section, being exact, evidently contains correlation kinetic energy in current DFT usage. But Slater–Kohn–Sham orbitals [13,14] were introduced to specifically remove the single-particle kinetic energy density functional approximation proportional to $\{n(\mathbf{r})\}^{5/3}$ made in Equation (1.1) summarising the TFD statistical method, valid therefore in the extreme large N limit, with N the number of electrons.

3.1. *Variational approach of March and Young*

March and Young [15; MY] in early work, constructed variational methods based on the first-order density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ already introduced by Dirac [4] in his study in which exchange was added to the TF Euler equation readily obtained by minimising Equation (1.1) with respect to the density n. To illustrate the approach of MY [15], let us write the one-dimensional 1D ansatz:

$$\gamma_{\mathrm{MY}}(x, x') = \frac{\partial y(x)}{\partial x}\frac{\partial y(x')}{\partial x'}\gamma_{\mathrm{model}}(y, y'), \tag{3.1}$$

where $\gamma_{\mathrm{model}}(x, x')$ is a chosen, known idempotent density matrix, while $y(x)$ is a scaling function which in turn is connected with the diagonal density. This ansatz corrected the TF single-particle kinetic energy 'density' (proportional to $n^3(x)$ in one dimension) by a term of the form introduced by von Weizsäcker [16], to obtain the single-particle kinetic energy density functional as

$$t_{\mathrm{MY}}(x) = \frac{N^2 - 1}{N^2} c_{\mathrm{k}}^{(d=1)}(n(x))^3 + t_{\mathrm{W}}(x), \tag{3.2}$$

the von Weizsäcker [16] form $t_{\mathrm{W}}(x)$ being given explicitly by

$$t_{\mathrm{W}}(x) = \frac{\hbar^2}{8m}\frac{(\partial n/\partial x)^2}{n(x)}. \tag{3.3}$$

Equation (3.2) has the merit that it recovers the TF single-particle kinetic energy in the limit $N \to \infty$, whereas it reduces to the correct von Weizsäcker form (3.3) for one-level occupancy ($N = 1$). The other point to be stressed concerning Equation (3.2) is that, in contrast to the TFD form in three dimensions given by the first term in Equation (1.3), the MY Equation (3.2) (also of course approximate) is not universal. In current usage [17] Equation (3.2) is non-universal because it contains explicitly the number of particles N, as well as functionals of $n(x)$ in this 1D example.

With this brief background, together with a reference to the extensive discussion in the book by Kryachko and Ludeña [18] we turn to an exact example of the single-particle kinetic energy functional, in the case again though of harmonic confinement, characterized by $V_{\mathrm{ext}}(\mathbf{r})$ as

$$V_{\mathrm{ext}}(\mathbf{r}) = \tfrac{1}{2}kr^2 = \tfrac{1}{2}m\omega^2 r^2. \tag{3.4}$$

It is then natural, in view of Equation (3.2), to start this example in 1D.

3.2. *Harmonic confinement of independent Fermions for an arbitrary number of closed shells in D dimensions*

For $D = 1$, March *et al.* [19] derived the single-particle (s) kinetic energy functional $T_{\mathrm{s}}^{(D)}[n]$ as

$$T_{\mathrm{s}}^{(1)}[n] = T_{\mathrm{W}}^{(1)}[n] + \int_{-\infty}^{\infty} \xi(x) t_{\mathrm{TF}}(x)\mathrm{d}x. \tag{3.5}$$

It was emphasized in [19] that the basic building blocks in the exact result (3.5) are the TF result $t_{\mathrm{TF}}^{(1)}(x) = (\pi^{2/6})n^3(x)c_{\mathrm{k}}^{(1)}n^3(x)$ and the von Weizsäcker form defined in Equation (3.3). Here $\xi(x)$ has the form

$$\xi(x) - \xi(0) = (3/\pi^2)\int_0^x \left[\{n'(s)\}^3 \big/ n^5(x)\right]\mathrm{d}x. \tag{3.6}$$

The *D*-dimensional generalisation of Equation (3.5) was given by Howard *et al.* [20]. Instead of quoting their result, let us, by way of illustration, refer to the numerical calculations of Howard and March [21] for $D = 2$. Their findings are summarised in Table 1 for this two dimensionality and for a variety of values for the number of closed shells, M. We have chosen to separate $T_{\mathrm{s}}^{(D)}$ into the sum of three parts:

$$T_{\mathrm{s}}^{(D)} = T_{\mathrm{sTF}}^{(D)} + \tfrac{1}{D}T_{\mathrm{W}}^{(D)} + T_{\mathrm{s}}^{(D)(\text{non-universal})}, \tag{3.7}$$

using the terminology introduced above. Returning to the $D = 1$ MY variational result (3.2) we would then write, paralleling Equation (3.7), the now

Table 1. Kinetic energy components for harmonic confinement as in Equation (3.7).

2D	T_{TF}	$\frac{1}{2}T_{\mathrm{W}}$	$T_{\text{non-univ}}$	$T_{\mathrm{s}} = T_{\mathrm{TF}} + \frac{1}{2}T_{\mathrm{W}} + T_{\text{non-univ}}$
M				
0	1/4	1/4	0	1/2
1	1.25	0.5193	0.7307	2.5
2	3.5	0.8132	2.6868	7
5	22.75	1.8028	20.9472	45.5
9	96.25	3.2840	92.966	192.5
14	310.	5.3029	304.6972	620

Note: *This is a modified table from Howard and March [21].

approximate form

$$T^{(1)}_{\mathrm{sMY}} = T^{(1)}_{\mathrm{TF}} + T^{(1)}_{\mathrm{W}} - \frac{1}{N^2} c_{\mathrm{k}}^{(D=1)} \int_{-\infty}^{\infty} \{n(x)\}^3 \mathrm{d}x, \tag{3.8}$$

the von Weizsäcker term having its original value motivated by the harmonic confinement form (3.7), for $D=1$. Evidently, the final (non-universal) term in Equation (3.8) reduces rapidly with increasing N compared with the original TF contribution.

4. The idempotent Dirac density matrix γ_s revisited

March and Young [22] utilized the so-called equation of motion for the Dirac density matrix γ_s in one dimension to derive the differential form of the virial theorem. They wrote the above equation of motion in the form, for a DFT potential $V(x)$ in one dimension, as

$$\frac{\partial^2 \gamma_s(x,x')}{\partial x^2} - \frac{\partial^2 \gamma_s(x,x')}{\partial x'^2} = \frac{2m}{\hbar^2}\left[V(x) - V(x')\right]\gamma_s. \tag{4.1}$$

Using sum and difference coordinates, MY proved the result

$$\frac{\partial t_s(x)}{\partial x} = -\frac{1}{2} n(x) \frac{\partial V}{\partial x} + \frac{\hbar^2}{8m} n'''(x), \tag{4.2}$$

where $t_s(x)$ here corresponds to the positive definite wave function form (grad $\psi(x))^2$ of the single-particle (s) kinetic energy per unit length.

Some three decades later, Holas and March [HM; 23] gave the three-dimensional (3D) generalisation of Equation (4.2), which we shall also utilize below. However, let us stress at this point that in 1D the MY differential virial theorem (DVT) in Equation (4.2) allows, given the physical boundary conditions that $t_s(x)$ at ± infinity is zero, the kinetic energy per unit length to be obtained solely from knowledge of $n(x)$ plus, however, the one-body force $-\partial V(x)/\partial x$. In fact, the force equation equivalent to Equation (4.2) evidently reads, in 1D:

$$-\frac{\partial V(x)}{\partial x} = \frac{2}{n(x)} \frac{\partial t_s(x)}{\partial x} + \frac{\hbar^2}{4mn(x)} n'''(x). \tag{4.3}$$

As HM [23] proved, it is this force equation which has a ready generalisation to 3D, as will be discussed further below. Entering this 3D equation is the Dirac idempotent density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$, related to the exchange energy density $\epsilon_x(\mathbf{r})$ according to Dirac [4] by

$$\epsilon_x(\mathbf{r}) = -\frac{e^2}{4} \int \frac{\gamma_s^2(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}'. \tag{4.4}$$

For doubly occupied energy levels the idempotency condition satisfied by the Dirac matrix γ_s takes the explicit form

$$\frac{\gamma_s(\mathbf{r},\mathbf{r}')}{2} = \int \left\{\frac{\gamma_s(\mathbf{r},\mathbf{r}'')}{2}\right\}\left\{\frac{\gamma_s(\mathbf{r}'',\mathbf{r}')}{2}\right\} \mathrm{d}\mathbf{r}''. \tag{4.5}$$

It will be important for what follows to emphasize the intimate connection between exchange and kinetic energy, as pointed out especially by March and Santamaria [24]. Explicit examples of this appear in Appendix B.

4.1. *Formally exact integral equation for the exchange-only potential $V_x(r)$ involving the Dirac matrix $\gamma_s(r,r')$*

The discussion summarized below had its motivation in the work of Della Sala and Görling [25]. These authors started out from orbital language, with the seemingly drastic assumption that the single Slater determinant built from Slater–Kohn–Sham (SKS) orbitals was equal to the corresponding Hartree–Fock (HF) determinant. It turns out that the earlier approximate study of the exchange-only, potential based on what seemed also a drastic 'denominator approximation', by Gritsenko and Baerends [26] led to precisely the same result as in [25]. The subsequent work of Howard and March [27], which was formally exact, completed these studies, when supplemented, as will be summarized in Appendix C, by the work of Joubert [28].

The integral equation of Howard and March [27], the derivation of which is referred to again in Appendix C, reads for the exchange-only potential $V_{\mathrm{x}}(\mathbf{r})$, which is formally related to the total exchange energy E_{x}:

$$E_{\mathrm{x}} = \int \epsilon_{\mathrm{x}}(\mathbf{r})\mathrm{d}\mathbf{r} \tag{4.6}$$

by

$$V_{\mathrm{x}}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}[n]}{\delta n(\mathbf{r})}: \tag{4.7}$$

$$\begin{aligned} V_{\mathrm{x}}(\mathbf{r}) = {} & \frac{2\epsilon_{\mathrm{x}}(\mathbf{r})}{n(\mathbf{r})} + \frac{1}{2n(\mathbf{r})}\int \mathrm{d}\mathbf{r}'\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}')^2 V_{\mathrm{x}}(\mathbf{r}') \\ & + \frac{e^2}{4n(\mathbf{r})}\int\int \mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}''\left[\frac{\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}')\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}'')\gamma_{\mathrm{s}}(\mathbf{r}'',\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}''|}\right] + \frac{P(\mathbf{r})}{n(\mathbf{r})}. \end{aligned} \tag{4.8}$$

In Equation (4.8), $P(\mathbf{r})$ was shown in [27] to satisfy the 'sum rule'

$$\int \mathrm{P}(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \tag{4.9}$$

and its explicit form has been considered further by Joubert [28]: see also Appendix C. The first term on the right-hand side of Equation (4.8) is the approximation to $V_{\mathrm{x}}(\mathbf{r})$ proposed in the pioneering work of Slater [13], namely

$$V_{\mathrm{x}}^{S\ell}(\mathbf{r}) = \frac{2\epsilon_{\mathrm{x}}(\mathbf{r})}{n(\mathbf{r})}, \tag{4.10}$$

which is determined solely by the Dirac matrix $\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}')$ with the (assumed) exact ground-state density $n(\mathbf{r})$ given by

$$\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}')\big|_{\mathbf{r}'=\mathbf{r}} = n(\mathbf{r}). \tag{4.11}$$

Hence, $V_{\mathrm{x}}^{S\ell}(\mathbf{r})$ is determined by $\gamma_{\mathrm{s}}(\mathbf{r},\mathbf{r}')$ through Equation (4.4), as discussed in the early works of Kleinman *et al.* [29,30].

A numerical example illustrating the integral equation (4.8) has been worked out by Howard and March [31] for the case of neon-like ions in the limit of large atomic number Z. In this limit, $\gamma_s(\mathbf{r},\mathbf{r}')$ can be calculated analytically using bare Coulomb wave functions.

4.2. *Relation of single-particle kinetic energy density t_s (r) to the Dirac density matrix $\gamma_s(r,r')$*

Returning to the point made above concerning the intimate relationship between $\epsilon_x(\mathbf{r})$, the exchange energy density, and the single-particle kinetic energy density $t_s(\mathbf{r})$ discussed briefly above, we note first that

$$t_s(\mathbf{r}) = \frac{\hbar^2}{2m} \nabla_{\mathbf{r}} \boldsymbol{\cdot} \nabla_{\mathbf{r}'} \gamma_s \nabla_{\mathbf{r}'}(\mathbf{r},\mathbf{r}')\bigg|_{\mathbf{r}'=\mathbf{r}}. \tag{4.12}$$

Dawson and March [DM; 32] thus obtained the 'von Weizsäcker-like' result that

$$t_s(\mathbf{r}) = \frac{\hbar^2}{16m} \int \frac{(\nabla_{\mathbf{r}} F(\mathbf{r},\mathbf{r}'))^2}{F(\mathbf{r},\mathbf{r}')}\, d\mathbf{r}', \tag{4.13}$$

where F is defined by

$$F(\mathbf{r},\mathbf{r}') = \gamma_s^2(\mathbf{r},\mathbf{r}'). \tag{4.14}$$

Thus, both $t_s(\mathbf{r})$ and $\epsilon_x(\mathbf{r})$ are determined by the Dirac $\gamma_s(\mathbf{r},\mathbf{r}')$, satisfying the equation of motion (compare the 1D analogue in Equation (4.1)):

$$\nabla_{\mathbf{r}}^2 \gamma_s - \nabla_{\mathbf{r}'}^2 \gamma_s = \frac{2m}{\hbar^2}[V(\mathbf{r}) - V(\mathbf{r}')]\gamma_s, \tag{4.15}$$

where $V(\mathbf{r})$ is the, as yet unknown, one-body potential of DFT.

Appendix B gives an explicit example of the intimate link between $\epsilon_x(\mathbf{r})$ and $t_s(\mathbf{r})$.

5. Differential equation for the Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$, given the ground-state electron density $n(\mathbf{r})$ from diffraction experiments or quantum Monte Carlo calculations

Equation (4.15) is the equation of motion of the idempotent Dirac density matrix γ_s in terms of a one-body potential $V(\mathbf{r})$. The objective of the present section is to set down a differential equation for $\gamma_s(\mathbf{r},\mathbf{r}')$, given that its diagonal element $\gamma_s(\mathbf{r},\mathbf{r})$ is equal to the exact ground-state density $n(\mathbf{r})$ of the molecule or cluster being considered. In principle, $n(\mathbf{r})$ is experimentally accessible via X-ray or electron diffraction measurements. Another route, but presently restricted to relatively small numbers of electrons, is via quantum Monte Carlo calculations.

For one- and two-level systems, a start has been made on the above programme by March and Suhai [33; MS]. Thus, for He_2, Be-like atomic ions, or the diatomic molecule LiH, one must solve the MS equation

$$[\nabla_r \gamma_s(\mathbf{r},\mathbf{r}')]^2 - \frac{\gamma_s \nabla_r \gamma_s \bullet \nabla_r n(\mathbf{r})}{n(\mathbf{r})} + \frac{2\gamma_s^2 t_s(\mathbf{r})}{n(\mathbf{r})} + \tfrac{1}{4} n(\mathbf{r}') \frac{(\nabla_r n)^2}{n(\mathbf{r})} - 2n(\mathbf{r}')t_s(\mathbf{r}) = 0, \tag{5.1}$$

subject to the idempotency condition (4.5). The main steps in the derivation of the above equation are recorded in Appendix D. Below, we outline a route which removes the restriction on the level occupancy. The starting point is the force equation for $-\partial V(\mathbf{r})/\partial\mathbf{r}$, where $V(\mathbf{r})$ is the still unknown potential of DFT [34]. This force equation was derived by HM [23], and can be viewed as the 3D generalisation of the DVT given by March and Young [22], cited in Equation (4.2). Rewriting this 1D result in the form (4.3) the 3D generalisation given by HM [23] reads

$$-\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}} = \frac{\mathbf{z}(\mathbf{r})}{n(\mathbf{r})} + \frac{\hbar^2}{4mn(\mathbf{r})}\frac{\partial}{\partial \mathbf{r}}\left(\nabla^2 n(\mathbf{r})\right). \tag{5.2}$$

Here, the components of the vector field $\mathbf{z}(\mathbf{r})$ are defined from the kinetic energy density tensor $t_{\alpha\beta}(\mathbf{r})$ by [23]

$$z_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial t_{\alpha\beta}(\mathbf{r})}{\partial r_\beta}. \tag{5.3}$$

In turn, $t_{\alpha\beta}(\mathbf{r})$ is defined from the idempotent Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ by

$$t_{\alpha\beta}(\mathbf{r}) = \frac{\hbar^2}{4m}\left(\frac{\partial^2}{\partial r'_\alpha r''_\beta}\gamma(\mathbf{r},\mathbf{r}') + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\gamma(\mathbf{r}',\mathbf{r}'')\right)_{\mathbf{r}''=\mathbf{r}'=\mathbf{r}}. \tag{5.4}$$

5.1. *Use of the force equation (5.3) in the equation of motion for the Dirac density matrix $\gamma_s(r,r')$*

The 3D equation of motion of the Dirac density matrix γ_s for a specified one-body potential $V(\mathbf{r})$ has already been cited in Equation (4.15). Dividing both sides of Equation (4.15) by γ_s, and then taking the gradient of the resulting equation with respect to the variable $\mathbf{r}$ yields the form

$$-\frac{\partial V(\mathbf{r})}{\partial r} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial \mathbf{r}}\left[\frac{\nabla^2_{\mathbf{r}}\gamma_s - \nabla^2_{\mathbf{r}'}\gamma_s}{\gamma_s}\right]. \tag{5.5}$$

Inserting the HM force Equation (5.2) into Equation (5.5) gives an equation characterized solely by the Dirac matrix γ_s, since this determines the vector field $\mathbf{z}(\mathbf{r})$ entering Equation (5.2) via Equations (5.3) and (5.4). The diagonal element $\gamma_s(\mathbf{r},\mathbf{r}) = n(\mathbf{r})$ is, of course, the essential input required, as stressed already.

To date, no application has been made of the above theory, set out here, to the writer's knowledge, for the first time. Appendix E proposes a possible semi-empirical application of this theory, making use of quantum crystallography.

6. Some rather general considerations on electron correlation: mainly in neutral atoms and atomic ions

Of course, the most difficult problem remaining currently in DFT is that of electron correlation. Even for the non-relativistic two-electron He-like atomic ions, with ground-state electron density $n(r,Z)$, the only analytic results due to Schwartz [10] are at large Z, say 92. Gál *et al.* [35] discussed the kinetic correlation energy $T_{\mathrm{corr}} \equiv T_{\mathrm{c}}$ following from Schwartz's work, when supplemented by the subsequent study of Hall *et al.* [36]. While their result for T_{c} is precise, later work [37] has discussed possible forms for the correlation kinetic energy functional $T_{\mathrm{c}}[n]$ for these He-like atomic ions at large Z. In this two-electron context, the fully solvable model atom considered in Section 2 also contains kinetic correlation energy, embodied in the functional displayed in Equation (2.2).

More generally, Alonso *et al.* [38] have exhibited correlation energies for light neutral atoms and for atomic ions, but using a combination of experiment and theoretical considerations. Their principal conclusion supports the earlier findings of March and Wind [39] for (lighter) neutral atoms that the major variable in determining these correlation energies is the number of electrons. This might mean that $E_{\mathrm{corr}}[n] \equiv E_{\mathrm{c}}[n] = \text{constant} \int n(\mathbf{r})\mathrm{d}\mathbf{r}$, or alternatively that the correlation energy functional is non-universal to an important degree i.e. $E_{\mathrm{c}} = E[n, N]$. If the former statement is useful beyond light atoms that would mean from the variational principle of DFT that the main effect of correlation is to make a shift in the (constant) chemical potential μ. Much more work is needed, of course, in this general area. Some recent relevant considerations on a number of important energy density functionals in widespread usage, bearing on the validity of their respective treatments of correlation are summarized in [40].

7. Summary and future directions

After a summary of substantial progress in treating two-electron atoms, including a model atom in which the correlated energy density functional is now completely known, as well as a differential equation for the exact ground-state electron density $n(\mathbf{r})$, attention has been focussed on a model form of the single-particle (s) kinetic energy functional $T_{\mathrm{s}}[n]$. The model considered has been motivated by experiments of DeMarco and Jin [41] on cold Fermion vapours in magnetic traps, the latter allowing changes in the effective dimensionality. These magnetic traps have motivated a full D-dimensional study of independent Fermions that are harmonically confined. In 1D, the building blocks are (i) the TF kinetic energy density proportional to $\{n(x)\}^3$ and (ii) the von Weizsäcker inhomogeneity kinetic energy density. However, $T_{\mathrm{s}}[n]$ for this model has a non-universal component which is explicitly known, and tends to zero relative to the TF component of $T_{\mathrm{s}}[n]$ as the level occupancy becomes large. Numerical results for this model in 2D due to Howard and March [21], are also briefly referred to. The universal part of $T_{\mathrm{s}}[n]$ in 2D and 3D contains a reduction of the von Weizsäcker term by the factor D^{-1}, leaving the 1D case unchanged.

Considerable attention is then given to the determination of the idempotent Dirac density matrix $\gamma_{\mathrm{s}}(\mathbf{r}, \mathbf{r}')$ [4] introduced in 1930, in which the diagonal element $\gamma_{\mathrm{s}}(\mathbf{r}, \mathbf{r})$ is fixed as the exact non-relativistic ground-state density $n(\mathbf{r})$ in the molecule under discussion. This matrix determines the exchange energy density $\epsilon_{\mathrm{x}}(\mathbf{r})$ via Equation (4.4). This is known analytically for one or two examples, the currently most important being for the non-relativistic 10-electron Ne-like series of atomic ions at large Z. While the corresponding exchange-only potential is also known for $Z = 92$ by numerical evaluation of the optimised exchange potential (OEP: [42,43]), its analytic determination awaits knowledge of the functional derivative $\delta t_s(\mathbf{r})/\delta n(\mathbf{r}')$, where $t_s[\mathbf{r}]$ is the single-particle kinetic energy density. While the above considerations on $\gamma_s(\mathbf{r}, \mathbf{r}')$ are based on first-principles theory, Appendix E briefly sets out a 'semi-empirical' approach to the determination of $\gamma_s(\mathbf{r}, \mathbf{r}')$ by means of X-ray diffraction: an area now termed quantum crystallography (Appendix E). Further work in this general area may lead to important progress in determining an idempotent $\gamma_s(\mathbf{r}, \mathbf{r}')$, which has the 'experimental' ground-state electron density as its diagonal.

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References

[1] L.H. Thomas, Proc. Camb. Philos. Soc. **23**, 542 (1926).
[2] E. Fermi, Z. Phys. **48**, 73 (1928).
[3] N.H. March, *Self-Consistent Fields in Atoms* (Pergamon, Oxford, 1975).
[4] P.A.M. Dirac, Proc. Camb. Philos. Soc. **26**, 376 (1930).
[5] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[6] E.A. Hylleraas, Z. Phys. **48**, 469 (1928).
[7] R. Crandall, R. Whitnell, and R. Bettega, Amer. J. Phys. **52**, 438 (1984).
[8] P. Capuzzi, N.H. March, and M.P. Tosi, J. Phys. A: Math. Gen. **38**, L439 (2005).
[9] T. Gál and N.H. March, J. Phys. B: At. Mol. Opt. Phys. **42**, 025001 (2009).
[10] C. Schwartz, Ann. Phys. (NY) **6**, 156 (1959).
[11] N.H. March, W.H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Dover, New York, 1995).
[12] T. Gál, N.H. March, and Á. Nagy, Chem. Phys. Lett. **305**, 429 (1999).
[13] J.C. Slater, Phys. Rev. **81**, 385 (1951).
[14] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[15] N.H. March and W.H. Young, Proc. Phys. Soc. (London) **72**, 182 (1958).
[16] C.F. von Weizsäcker, Z. Phys. **96**, 431 (1935).
[17] L. Delle Site, J. Phys. A: Math. Theor. **38 A**, 7893 (2005).
[18] E.S. Kryachko and E.V. Ludeña, *Energy Density Functional Theory of Many-Electron Systems* (Kluwer Academic Publishers, Dordrecht, 1990).
[19] N.H. March, P. Senet, and V.E. van Doren, Phys. Lett. **270 A**, 88 (2000).
[20] I.A. Howard, N.H. March, and L.M. Nieto, Phys. Rev. **66 A**, 054501 (2002).
[21] I.A. Howard and N.H. March, (2009) to be published.
[22] N.H. March and W.H. Young, Nucl. Phys. **12**, 237 (1959).
[23] A. Holas and N.H. March, Phys. Rev. **A 51**, 2040 (1995).
[24] N.H. March and R. Santamaria, Int. J. Quantum Chem. **39**, 585 (1991).
[25] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).
[26] O.V. Gritsenko and E.J. Baerends, Phys. Rev. **A 64**, 042506 (2001).
[27] I.A. Howard and N.H. March, J. Chem. Phys. **119**, 5789 (2003).
[28] D.P. Joubert, Phys. Rev. A (to be published).

[29] L. Kleinman, Phys. Rev. B **49**, 14197 (1994).
[30] A. Holas and N.H. March, Phys. Rev. B **55**, 1295 (1997).
[31] I.A. Howard and N.H. March, Mol. Phys. **103**, 1261 (2005).
[32] K.A. Dawson and N.H. March, J. Chem. Phys **81**, 5850 (1984).
[33] N.H. March and S. Suhai, Phys. Lett. A **360**, 665 (2007).
[34] See, for example, R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[35] T. Gál, N.H. March, and Á. Nagy, Chem. Phys. Lett. **305**, 429 (1999).
[36] G.G. Hall, L.L. Jones, and D. Rees, Proc. R. Soc. (London) A **283**, 1393 (1965).
[37] R. Lopez-Boada, Chem. Phys. Lett. **311**, 101 (2000).
[38] J.A. Alonso, N.H. March, N.A. Cordero, and A. Rubio, J. Phys. B: At. Mol. Opt. Phys. **36**, 2695 (2003).
[39] N.H. March and P. Wind, Mol. Phys. **77**, 791 (1992).
[40] C. Amovilli, F. Bogar, N.H. March and T. Gap, Phys. Lett. A **373**, 3158 (2009).
[41] B. DeMarco and D.S. Jin, Science **285**, 1703 (1999).
[42] R.T. Sharp and G.K. Horton, Phys. Rev. **90**, 317 (1953).
[43] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[44] N.H. March and R. Santamaria, Phys. Rev. A **38**, 5002 (1988).
[45] I.A. Howard, N.H. March, P. Senet, and V.E. van Doren, Phys. Rev. A **62**, 062512 (2000).
[46] N.H. March and Á. Nagy, Phys. Lett. A (to appear).
[47] S.T. Howard, J.P. Huke, P.R. Mallinson, and C.S. Frampton, Phys. Rev. B **49**, 7124 (1994).
[48] A. Holas and N.H. March, Phys. Rev. B **55**, 9422 (1997).

Appendix A

Essential steps in establishing the energy density functional (2.2) for the model atom with harmonic confinement and inverse square law interfermion interaction

Following Gál and March [9], we invoke the virial theorem to find that the single-particle kinetic energy functional, $T_s[n]$, satisfies

$$T_s[n] = -\frac{1}{2}\int n(r)\mathbf{r} \bullet \nabla \frac{\delta T_s[n]}{\delta n(\mathbf{r})}\,\mathrm{d}\mathbf{r}. \tag{A1}$$

Writing

$$E[n] = F[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{A2}$$

it follows, paralleling Equation (A1) that

$$F[n] = -\tfrac{1}{2}\int n(\mathbf{r})\mathbf{r} \bullet \frac{\nabla\delta F[n]}{\delta n(\mathbf{r})}\mathrm{d}\mathbf{r}. \tag{A3}$$

Utilising next the differential equation (2.1) of the main text, it follows after some manipulation [9] that $E[n]$ is given by Equation (2.2) for this model atom. It only remains to express $\hbar\omega$ in Equation (2.2) in terms of the interparticle strength λ, or equivalently α introduced after Equation (2.1). Then, since the explicit ground-state energy of this model is $E = (\alpha + 3)\hbar\omega$, it readily follows that

$$\hbar\omega = \frac{4}{\alpha + 3}\frac{F[n]}{\int n(\mathbf{r})}\,\mathrm{d}\mathbf{r}. \tag{A4}$$

Inserting Equation (2.1.4) into Equation (2.2) completes the functional $E[n]$.

Appendix B

Connections between kinetic and exchange energy densities

DM [32] used the idempotency condition (4.5) on the Dirac density matrix γ_s to obtain a form of single-particle kinetic energy density given by

$$t_s^{DM}(\mathbf{r}) = \frac{\hbar^2}{16m}\int \frac{(\nabla_{\mathbf{r}}F)^2}{F(\mathbf{r},\mathbf{r}')}\,d\mathbf{r}', \tag{B1}$$

where $F(\mathbf{r},\mathbf{r}') = \gamma_s^2(\mathbf{r},\mathbf{r}')$. For comparison, the Dirac form (4.4) of the exchange energy density reads

$$\epsilon_x(\mathbf{r}) = -\frac{e^2}{4}\int \frac{F(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{B2}$$

To attempt to pull Equations (B1) and (B2) together, March and Santamaria [44] defined generalized kernels $K(\mathbf{r},\mathbf{r}')$ and $X(\mathbf{r},\mathbf{r}')$ of $t_s^{DM}(\mathbf{r})$ and $\epsilon_x(\mathbf{r})$, respectively, via

$$t_s^{DM}(\mathbf{r}) = \int K(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{B3}$$

where

$$K(\mathbf{r},\mathbf{r}') = \frac{\hbar^2}{16m}\frac{(\nabla_{\mathbf{r}}F)^2}{F(\mathbf{r},\mathbf{r}')} \tag{B4}$$

and

$$\epsilon_x(\mathbf{r}) = \int X(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{B5}$$

$X(\mathbf{r},\mathbf{r}')$ being chosen explicitly from Equation (B2) to be given by

$$X(\mathbf{r},\mathbf{r}') = -\frac{e^2}{4}\frac{F(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{B6}$$

Evidently, inserting F from Equation (B6) into Equation (B4), $K(\mathbf{r},\mathbf{r}')$ is determined completely by the exchange kernel $X(\mathbf{r},\mathbf{r}')$.

A further connection between an exchange property and a functional derivative of the kinetic energy density has been established in the work of Howard *et al.* [45] on the exchange potential $V_x(\mathbf{r})$ in non-relativistic 10-electron Ne-like atomic ions at large atomic number Z. In [43], it was proved that

$$V_x(\mathbf{r}) = \sum_{i=1}^{3} V_x^{(i)}(\mathbf{r}). \tag{B7}$$

$V_x^{(i)}(\mathbf{r})$ is given explicitly in terms of the known electron density $n(\mathbf{r})$. But $V_x^{(i)}(\mathbf{r})$ for $i=2$ and 3 involve a functional derivative of the kinetic energy density t_s of the form $\delta t_s(s)/\delta n(\mathbf{r})$ which presently is not known, even though one has an explicit $\mathbf{r}$ space form of both t_s and n.

Appendix C

Some considerations related to the closure function $P(r)$ in the integral equation (4.8) for the exchange-only potential $V_x(r)$

The assumption that $P(\mathbf{r})=0$ in Equation (4.8) leads back to the approximate integral equation derived by Della Sala and Görling [25]. This approximation $\mathrm{P}=0$ must therefore be the consequence of their starting assumption that the Slater determinant of SKS orbitals is identical to the corresponding HF determinant.

Following the derivation of Equation (4.8) by Howard and March [27], and their proof that $P(\mathbf{r})$ satisfied the sum rule (4.9), March and Nagy [46] discussed various forms of $P(\mathbf{r})$ satisfying Equation (4.9). They emphasized especially the importance of choosing $P(\mathbf{r})$ to give back the OEP in [42] and [43].

Subsequent work by Joubert [28] has revealed some further results concerning $P(\mathbf{r})$ which may well allow more progress in this area.

Appendix D

Summary of main steps in the derivation of Equation (5.1) given by March and Suhai [33] for one- and two-level occupancies

For one-level occupancy as in the H_2 molecule or the He atom, the single-particle (s) Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$, with the exact ground-state density $n(\mathbf{r})$ as its diagonal element, is readily written as

$$\gamma_s(\mathbf{r},\mathbf{r}') = n(\mathbf{r})^{\frac{1}{2}} n(\mathbf{r}')^{\frac{1}{2}}. \tag{D1}$$

This is easily shown to satisfy the MS equation (5.1) by direct substitution.

More interesting therefore is the two-level case, appropriate say to the series of four-electron Be-like atomic ions or the heteronuclear diatomic molecule LiH. As demonstrated by DM [32], γ_s can be written in terms of the density amplitude already entering Equation (D1), together with a phase $\theta(\mathbf{r})$. The explicit form derived in [32] is

$$\gamma_s(\mathbf{r},\mathbf{r}') = n(\mathbf{r})^{\frac{1}{2}} n(\mathbf{r}')^{\frac{1}{2}} \cos[\theta(\mathbf{r}) - \theta(\mathbf{r}')]. \tag{D2}$$

The important property of $\theta(\mathbf{r})$ is that it is related to the ground-state density $n(\mathbf{r})$ by a non-linear pendulum-like eigenvalue equation [32]:

$$\nabla^2\theta(\mathbf{r}) + \frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \bullet \nabla\theta(\mathbf{r}) + \lambda \sin 2\theta(\mathbf{r}) = 0. \tag{D3}$$

The kinetic energy density $t_s(\mathbf{r})$ is given from Equation (D2) by

$$t_s(\mathbf{r}) = t_w(\mathbf{r}) + \tfrac{1}{2} n(\mathbf{r})(\nabla\theta(\mathbf{r}))^2, \tag{D4}$$

where the von Weizsäcker inhomogeneity kinetic energy is known explicitly as

$$t_w(\mathbf{r}) = \frac{\hbar^2}{8m}\frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})}. \tag{D5}$$

It is now a matter of fairly cumbersome manipulation to show again that, in this already quite complex two-level case, the MS equation (5.1) is satisfied. Since $t_s(\mathbf{r})$ is determined via Equation (D4) and the solution of equation (D3) for $\theta(\mathbf{r})$ for a given n, $t_s(\mathbf{r})$ is determined completely by $n(\mathbf{r})$ and hence the MS equation (5.1) relates the Dirac matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ directly to $n(\mathbf{r})$; albeit by a non-linear differential equation, which must be solved for the Dirac matrix γ_s satisfying the idempotency condition (4.5).

Appendix E

Quantum crystallography as a future route to derive an idempotent Dirac density matrix corresponding to a potential V(r) of DFT

It has become common practice among experimental crystallographers to fit their Bragg reflection X-ray data with basis sets in common use in theoretical chemistry.

But then, as for example in the experimental data analysis on formamide by Howard [47], the same basis set used to fit the electron density $n(\mathbf{r})$ is frequently used to construct an idempotent Dirac density matrix. Unfortunately, this is not of use in DFT: where the corresponding Dirac matrix γ_s must also satisfy Equation (5.5), as coming from a force $-\partial V(\mathbf{r})/\partial\mathbf{r}$ generated by the DFT one-body potential $V(\mathbf{r})$.

Prompted by the study of Howard [47] on formamide, Holas and March [48] have proposed a type of least squares constraint, which ties the Dirac matrix extracted using the quantum crystallographic procedure outlined above to the 'force equation' (5.5). It will be interesting in the future to attempt to impose such a 'potential-locality' constraint on the idempotent Dirac density matrix extracted from Bragg reflection X-ray data.