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Some problems in density functional theory

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Abstract
Though calculations based on density functional theory (DFT) are used remarkably widely in chemistry, physics, materials science, and biomolecular research and though the modern form of DFT has been studied for almost 60 years, some mathematical problems remain. From a physical science perspective, it is far from clear whether those problems are of major import. For context, we provide an outline of the basic structure of DFT as it is presented and used conventionally in physical sciences, note some unresolved mathematical difficulties with those conventional demonstrations, then pose several questions regarding both the time-independent and time-dependent forms of DFT that could benefit from attention in applied mathematics. Progress on any of these would aid in development of better approximate functionals and in interpretation of DFT.

Keywords Hohenberg–Kohn · Kohn–Sham · Density functional

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1 Introduction and overview

Our objective is to identify some outstanding questions relating to density functional theory (DFT), including finite-temperature, orbital-free, and time-dependent DFT.

DFT is a reformulation of the Hamiltonian description of quantum mechanics (e.g., Schrödinger equation) for calculation of properties of interest (e.g., ground-state energy, free-energy, etc.). As such, it is not an independent many-body theory, hence adds no physics. Instead, it offers a framework that is quite distinct from other approaches to the quantum mechanical many-body problem.

Some readers may not be familiar with the extensive DFT literature of the past sixty years. Therefore, we have organized our presentations regarding both time-independent and time-dependent DFT to begin with contextual overviews, Sects. 2 and 6, respectively. A generic but more abstract overview of the two is offered in Appendix 1.

By choice, our perspective for the two more physical overviews is the conventional one of the physical sciences (condensed matter physics, materials science, theoretical chemistry). In addition to being a fair representation of our expertise (and its limits), the conventional perspectives give a straightforward way to summarize known mathematical difficulties with those approaches (a consequence, among other things, of the different standards of proof typical of physical sciences compared to mathematics). Useful resources include Refs. [1–7].

Observe that our attention is restricted to quantum systems. The counterpart DFT for classical systems, e.g., atoms in liquid states [8], is an active area with problems of its own. It is not discussed here. Moreover, we restrict discussion to many-electron systems because they, overwhelmingly, comprise the quantum systems of interest in DFT.

Though our purpose is not a DFT review, it is important to note that DFT is, by now, the most widely used many-electron method by far. Its appeal and utility rest in several aspects. It reduces the many-degrees-of-freedom problem of other many-fermion formulations to a functional dependency on a single, physically observable scalar quantity, the electron number density. It provides a structure by which that density (time-independent or time-dependent, zero or nonzero temperature) can be generated by use of an auxiliary *non-interacting* many-electron system. That, in turn, provides highly advantageous computational cost-scaling with system size compared to other many-body ansätze. And it yields system-specific physical and chemical property values (energies, free energies, ionization potentials, . . . etc.). In detail, applications of DFT as a computational tool confront many technical and fundamental problems. Some of these are discussed in more detail below.

Before proceeding, some basic definitions are useful. We use Hartree atomic units, $\hbar = m_e = q_e = 1$ where $\hbar$ is Planck's constant divided by 2π, m_e is the electron mass, and q_e is the electron charge magnitude. We restrict consideration to non-relativistic

many-electron systems in an external potential such that the system total energy (free-energy) per unit volume is bounded below. The electron number density is $n(\mathbf{r})$; it is normalized to the number of electrons (or number per cell as the case may be), N_e.

The remainder of the paper is structured as follows. Section 2 summarizes time-independent DFT as presented conventionally along with the time-independent Kohn–Sham (KS) variational procedure. Section 3 then gives the known mathematical difficulties with those conventional approaches (both as to the underlying theorems and the KS procedure), and poses four questions about the scope and impact of those mathematical deficiencies. In Sect. 4, we summarize the so-called orbital-free formulation of KS DFT and pose six questions. Section 5 poses six questions on various other aspects of time-independent DFT (e.g., explicit number dependence, spin-density-functionals, spectral gap). Turning attention to time-dependent DFT (TDDFT), Sect. 6 summarizes conventional approaches to formulating TDDFT. Then, Sect. 7 discusses some fundamental issues of TDDFT proofs. We conclude with very brief remarks in Sect. 8.

Throughout, we formulate specific questions that are of current interest to the DFT community. About them, we believe the applied mathematics and mathematical physics community may be able to make some helpful progress.

2 Time-independent DFT—conventional presentation

As noted above, time-independent DFT conventionally is presented as a variational formalism within which the quantum mechanical energy of a many-particle (usually many-fermion) system can be determined. For a system at zero temperature, this refers to the ground state energy, while at nonzero temperature (called "finite temperature" in the physics literature) it refers to the thermodynamic free energy.

At the fundamental level, the problem is characterized by a Hamiltonian H for the system of interest plus an external potential coupling separately to each degree of freedom q_i, $V = \sum v_{\text{ext}}(q_i)$. The energy is therefore a functional of this external potential, $E = E[v_{\text{ext}}]$. Similarly, derived properties also are functionals of v_{ext}. For example, the local number density $n(\mathbf{r})$ is the functional derivative $n(\mathbf{r}) = \delta E[v_{\text{ext}}]/\delta v_{\text{ext}}(\mathbf{r})$. Therefore, one may use this to define $n(\mathbf{r} \mid v_{\text{ext}})$ as a functional of $v_{\text{ext}}(\mathbf{r})$. Via a Legendre transform, a functional of the density $F[n]$ can be constructed. In this way, the properties of the system of interest are characterized by the density for any external potential. The objective of time-independent DFT is to find this representation through the propositions that (i) there is a one-to-one relationship between $v_{\text{ext}}(\mathbf{r})$ and $n(\mathbf{r})$, and (ii) there exists a universal (i.e., independent of v_{ext}) functional $\mathcal{F}[n]$ such that the extremum (minimum) of $F[n] := \mathcal{F}[n] + \int \mathrm{d}\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$ occurs at $n_0(\mathbf{r})$ with $F[n_0]$ being the ground state energy for temperature T = 0 K or equilibrium free energy for T > 0 K.

Proofs of various forms of these propositions for many-electron systems at zero temperature were given by Hohenberg and Kohn (HK) [9] and refined by Levy [10] and Lieb [7]. From this work, there are three distinct functionals, Hohenberg–Kohn ($\mathcal{F}_{HK}$), Levy–Lieb ($\mathcal{F}_{\text{LL}}$), and Lieb ($\mathcal{F}_L$). We sketch the differences.

The HK argument established that for a non-degenerate ground state Ψ_0 and its density $n_0(\mathbf{r})$ from a particular $v_{\text{ext}}(\mathbf{r})$, there is a one-to-one mapping $v_{\text{ext}}(\mathbf{r}) \leftrightarrow n_0(\mathbf{r})$ and $E_0 = \mathcal{F}_{\text{HK}}[n_o] + \int \mathrm{d}\mathbf{r} n_0(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$. *On the assumption* that *every* $n(\mathbf{r})$ is associated with some $v_{\text{ext}}(\mathbf{r})$ as its ground-state ("ground-state interacting v-representability"), HK defined $\mathcal{F}_{\text{HK}}[n] := E[v_{\text{ext}}] - \int \mathrm{d}\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$ and the associated variation principle (see Ref. [7] at Eq. (3.10)). The difficulties with the HK functional are (i) it is not convex on the required density domain, (ii) it is difficult to define that domain, which is the space of ground-state $n(\mathbf{r})$, and it also is difficult to define the space of $v_{\text{ext}}(\mathbf{r})$ for which $H + V$ has a ground state, and (iii) not every density is ground-state interacting v-representable.

The Levy–Lieb functional [7, 10] removed both the interacting v-representability problem and the non-degenerate ground state restriction essentially by rearranging the ordinary Ritz variational principle into variation over equivalence classes by density, followed by variation over densities ("constrained search" in the DFT literature):

$$\begin{aligned} \mathcal{F}_{\text{LL}}[n] &:= \inf \left\{ \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \Big| \psi \mapsto n \right\} \\ E[v] &= \inf \{ \mathcal{F}_{\text{LL}}[n] + \int \mathrm{d}\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) | n \in \mathcal{I}_{N_e} \}. \end{aligned} \tag{1}$$

Here $\mathcal{I}_{N_e}$ is the set of properly normalized densities with finite von Weizsäcker kinetic energy; see Ref. [7]. The difficulty with $\mathcal{F}_{\text{LL}}[n]$ is that it also is not convex.

Lieb then defined a convex functional

$$\mathcal{F}_L[n] := \sup \{ E[v] - \int \mathrm{d}\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \} \tag{2}$$

with $v_{\text{ext}}(\mathbf{r})$ defined on a suitable space $(L^{3/2} + L^{\infty})$. (Aside: There is a typographical error in Lieb's Theorem 3.4 (i). It should say "$\tilde{F}(\rho)$ is not convex." Equivalently in our notation "$\mathcal{F}_{\text{LL}}[n]$ is not convex.")

For most physical scientists, Lieb's functional has been regarded as providing a firm mathematical foundation for DFT but a quotation from Lieb himself gives worthwhile perspective (notation transcribed): "Despite the hopes of HK,…it is not true that every $n(\mathbf{r})$ (even a "nice" $n(\mathbf{r})$) comes from the ground state of some single-particle potential $v_{\text{ext}}(\mathbf{r})$. This problem can be remedied by replacing the HK functional by the Legendre transform of the energy, as is done here. However, the new theory is also not free of difficulties, and these can be traced to the fact that the connection between $v_{\text{ext}}(\mathbf{r})$ and $n(\mathbf{r})$ is extremely complicated and poorly understood." 40 years later some of those challenges are unresolved.

Regarding the one-to-one mapping, the issue of $v_{\text{ext}}(\mathbf{r})$ in a suitable space is discussed by Lieb (his Remark (ii), page 255) in terms of densities that do not come from some $v_{\text{ext}}(\mathbf{r})$. Of specific concern are those otherwise proper densities "…that vanish on a nonempty open set." If v_{ext} belongs to $L^{3/2} + L^{\infty}$, then he asserts that such cannot be ground state densities by the unique continuation theorem. But parenthetically he adds "(Strictly speaking, this theorem is only known to hold for $v \in L^3_{loc}$ but it is believed to hold for $L^{3/2} + L^{\infty}$.)" The argument then goes that "if the set of allowed

vs can be extended properly to allow infinite vs, the existence of such ns may not have any particular importance. The question is very delicate, however ….” From a physical science perspective the question also is significant because $v \in L^{3/2} + L^{\infty}$ excludes the harmonic oscillator. We return to this below.

2.1 Conventional discussion of functional derivatives

As a practical tool for physical science, time-independent DFT almost always relies on the existence of functional derivatives of $F[n]$ to determine the equations used to solve for the optimizing density n_0. The existence and detailed properties of functional derivatives remain, therefore, among the crucial open issues for time-independent DFT. This is the context in which, after detailed discussion of the existence of continuous tangent functionals for $\mathcal{F}_L$ and $\mathcal{F}_{\mathrm{LL}}$, Lieb posed two questions “…whose answers we cannot give but that are obviously important for the theory.” Those two questions are about the occurrence of continuous tangent functionals and their relationship to v_{ext}. He did not discuss functional derivatives explicitly (in fact, the term does not appear). That was taken up by Englisch and Englisch [4, 5], who asserted that on the basis of Lieb’s results for continuous tangent functionals $\mathcal{F}_L$ has a proper functional derivative.

An example of how this is presented in the DFT community (from a treatise we respect and use) is on page 36 of Ref. [1]: “In summary: The functional derivative of $\mathcal{F}_L[n]$ exists for all ensemble v-representable densities and is identical with a potential v_{ext} …Moreover, for any other “reasonable” density n …one can find an ensemble v-representable density which is arbitrarily close to n, so that the functional derivative of $\mathcal{F}_L[n]$ again exists.”

The foregoing statement has been known not to be true since at least 2007; we defer further details to Sect. 3. What is significant here is that, in our experience, statements such as the foregoing are an authentic representation of the understanding of most of the physical science segment (the majority) of the DFT community. Generally it is held that Levy’s seminal insight [10], Lieb’s analysis [7], and Englisch and Englisch’s analysis [4, 5], together provided a reasonably sound resolution of the limitations of the original HK argument, save perhaps for some mathematical niceties that are tacitly assumed to be inconsequential. Thus, restrictions on allowable potentials are ignored for example and functional differentiation is done routinely.

More tersely, Mermin provided the analogue to the original HK proof for finite temperature [11]. Ensemble generalizations [12, 13] analogous with the conventional ground state treatment for $\mathcal{F}_{\mathrm{LL}}$ and $\mathcal{F}_L$ are obvious. Refinements and their extension for more general systems are described in Refs. [1, 7, 14, 15]. Additionally, it is the conventional view that the zero temperature results are subsumed by the appropriate limit from finite temperature except without some of the problems of the functional derivatives that the zero-temperature theory has [12].

It is safe to say that most of the attention in the DFT community is focused on overcoming the barriers to exploiting the many advantages to representing the original many-body problem in terms of the density rather than the external potential. A very recent “round-table” paper has many details [16].

2.2 Conventional time-independent Kohn–Sham procedure

The variational representation in terms of a density functional provides means for approximations that are not confined to limitations of other quantum mechanical many-body methods. Because, however, the proofs about $\mathcal{F}[n]$ in any of its forms provide no insight into its structure, the strategy for exploiting the variational representation is indirect, namely the Kohn–Sham (KS) scheme [17]. In it, $\mathcal{F}_{\rm LL}$ is decomposed into two pieces. Working at T = 0 K for simplicity, the KS strategy is to introduce an auxiliary non-interacting system with variational functional $\mathcal{E}_s := T_s + E_H + E_{\rm ext} + \int {\rm d}\mathbf{r} n(\mathbf{r}) v_{xc}(\mathbf{r})$ that has the same number density and same external potential as the physical interacting system. Here $T_s[n]$ is the non-interacting (KS) system kinetic energy. The additional potential v_{xc} required to maintain the same density eventually becomes identified as connected with exchange and correlation energies in the interacting system, hence the subscript "xc."

Remark In the conventional presentation, the variational functionals for both the interacting and auxiliary system usually are $\mathcal{F}_{\rm LL}$. This is expressed with admirable candor in Ref. [15], p. 36: "As a matter of principle, the subsequent development of the DFT formalism should therefore be based explicitly on the Lieb functional. We will nevertheless ignore the issue … and not distinguish between the various flavors …."

Introduction of the KS auxiliary system provides a definition for the exchange energy E_x in terms of a single-determinant of the KS one-body states ("orbitals"). Then, $\mathcal{F}_{\rm LL} + \int {\rm d}\mathbf{r} n(\mathbf{r}) v_{\rm ext}(\mathbf{r})$ can be rearranged so that the variational energy is

$$\begin{aligned} \mathcal{E}_{\rm LLKS}[n] := T_s[n] + E_H[n] \\ + E_x[n] + E_c[n] + E_{\rm ext}[n] \end{aligned} \tag{3}$$

with E_H the Hartree energy, E_c the DFT correlation energy, and $E_{\rm ext}$ the energy from the external potential (usually the Coulomb interaction with nuclei or ions).

Remark For those conversant with variational wave-function approaches, the KS-DFT correlation energy includes the difference between the interacting system and non-interacting system kinetic energies, $T[n]$ and $T_s[n]$. Explicit expressions for $E_{\rm xc}[n] = E_x[n] + E_c[n]$ are not known except for a few special cases. The majority of the papers that discuss "approximate density functionals" concern approximations to $E_{\rm xc}[n]$. We return to this below.

Variation of $\mathcal{E}_{\rm LLKS}[n]$ with respect to the density subject to conservation of total particle number then causes the functional derivative $v_{\rm xc} := \delta E_{\rm xc}/\delta n$ to appear as a local potential in the eigenvalue problem for the KS orbitals, along with the original $v_{\rm ext}$.

Remark (a) Notice that $\mathcal{F}_{\rm LL}$ conventionally is assumed to have well-defined functional derivatives (an assumption we already have highlighted). (b) The Kohn–Sham decomposition is extremely helpful because the non-interacting terms may be

expressed exactly with the use of the orbitals and because, for most systems of interest, the exchange-correlation energy, which still must be approximated, is only a small-magnitude correction to the non-interacting energy.

3 Mathematical difficulties with conventional time-independent DFT

3.1 Issues with conventional time-independent HK and LL functionals

Issue 1 The argument in Ref. [7] for the one-to-one correspondence between density and external potential in the first HK theorem depends on Lieb's *assumption*, discussed above, that the unique continuation theorem actually holds for the function space in which his argument is formulated. A version of unique continuation and a resulting HK theorem was given much more recently by Garrigue [18] but, as we understand it, for a different function space than used in Ref. [7]. Hence, the ground-state "HK theorem" that is used conventionally is not the one for which Garrigue provided a mathematically proper foundation and conversely. The issue of relevant spaces and corresponding conditions upon external potentials (including unique continuation) was studied at the same time by Lammert [19]. He gave several HK theorems, not just one. Again, there are function-space differences involved. His proofs are in Kato class spaces, for example, K_3. He noted explicitly that Lieb's proofs are in $L^{3/2}(\mathbb{R}^3) + L^{\infty}(\mathbb{R}^3)$ which is *not* in K_3 but then he says "K_3 nearly contains the Lieb class in some sense." For the thermal case, the only rigorous proofs of the one-to-one HK theorem seem to be in a finite-basis [20] or on a lattice [21]. For explicitly finite systems, the results for graphs are perhaps more perplexing from the conventional viewpoint, since the first HK theorem demonstrably does not hold [22] for those systems.

Question 1.1 *To what extent and in what ways are the mathematical deficiencies of the conventional justification of time-independent DFT consequential for its use? Put another way, where and how do those deficiencies manifest themselves? Do they matter for many physically realizable systems or are they important only for some limited, exotic (hopefully well-defined) cases?*

Remark In the context of Lammert's remark quoted above, our question amounts to asking about the detailed consequences of that function space relationship.

Question 1.2 *In what way or ways must the responses to Question 1.1 be modified for the thermal case?*

3.2 Issues with the conventional time-independent KS procedure

Briefly, at least two categories of mathematical difficulties with the conventional KS scheme are known. One is the v-representability problem: What are the conditions under which a density n can be associated uniquely with both an interacting and a non-interacting system constructed from it by the KS strategy? This seems to have been resolved (see Ref. [23]), but we are unsure on that point.

Issue 2 The other issue has drawn much attention. For the Lieb functional, neither Gateaux nor Frechet functional derivatives exist in general. It is known [24] that the supposed proof of Gateaux differentiability in Refs. [5] and [23] is incorrect. Reference [24] shows that differentiability can be rescued by imposition of subsidiary conditions about the density (which must be strictly greater than zero) *and* about the first and second derivatives of the parent ground-state wave function. This obviously is far from what is assumed in the conventional KS development, *vide supra*.

Remark Even if the conditions of Ref. [24] were to be met, it is not obvious to us that the resulting functional derivatives would have a straightforward operational relationship with those derivatives commonly used in the conventional DFT development.

Question 2.1 *To what extent and in what ways does the lack of the functional derivatives that are assumed to exist in conventional DFT manifest itself in the development and use of approximate functionals? Alternatively stated, can a prescription or protocol be provided (such as those used for manipulating the Dirac delta function and Heaviside unit step function in the physical sciences) to account for the consequences of the restrictions given in Ref.* [24]*, such that the conventional procedure could be made operationally valid?*

The only other cure to the functional derivative problem so far offered seems to be in Ref. [25] but that requires the use of quasi-densities.

Question 2.2 *Can a detailed scheme be provided whereby the quasi-densities of Ref.* [25] *and manipulations with them are related systematically to the physical densities (that are experimentally measurable quantities) used in conventional DFT?*

Remark Many rigorous results about physical densities are known and exploited in the development of approximate $E_{\rm xc}$ functionals. Connecting quasi-densities systematically to those properties is an essential pre-requisite therefore to any approach for using quasi-densities in some reformulation of DFT.

4 Issues in "orbital-free" time-independent DFT

We continue at $\mathrm{T} = 0\,\mathrm{K}$. Though the ordinary KS equation has a local potential $v_{\rm ext}(\mathbf{r}) + v_{\rm xc}(\mathbf{r})$, its self-consistent solution in a basis typically has computational costs that scale as N_e^3. This scaling is worsened by the introduction of approximations for $E_{\rm xc}[n]$ that depend explicitly on the KS single-particle orbitals. Though in principle one can find the KS potential for such an $E_{\rm xc}$ via what is called the optimized effective potential [1], the computational burden is so high that the conventional work-around is what is called "generalized KS" (gKS). It amounts to taking the variational derivative of $\mathcal{E}_{\rm LLKS}[n]$ with respect to the orbitals $\varphi_j(\mathbf{r})$. That worsens the computational burden because each orbital must be calculated from a separate, orbital-dependent potential in the gKS equation. Details are irrelevant here. To evade that bottleneck, one may express the non-interacting kinetic energy T_s as an explicit functional of the density, obviating the use of orbitals. Since $T_s[n]$ is not known in general as an explicit functional of $n(\mathbf{r})$, doing so requires a further approximation. This is called, slightly misleadingly,

orbital-free DFT (OFDFT). In fact, there is one orbital $\propto n^{1/2}(\mathbf{r})$. Approximating $T_s[n]$ is significantly more challenging than for $E_{\rm xc}$. OFDFT is an area of continuing fundamental and practical research; see Refs. [26–28].

Thus, ordinary KS calculations require accurate approximations for E_x and E_c, while the OFDFT form also requires an accurate approximation for $T_s[n]$. The range of systems of interest is enormous, yet there are few exact results to guide or inform development of those required approximations. Two routes are followed therefore. One is unabashedly pragmatic. Terms in $\mathcal{E}_{\rm LLKS}$ are written in some physically sensible form with parameters that then are fitted to relevant physical or chemical data (computed or measured). Such functional approximations (called "empirical" in the physics and chemistry literature) are not our priority. Our focus is on the second kind, developed by imposition of whatever set of exact properties is known as constraints. These approximations are formulated in the framework of the KS decomposition, so we give pertinent details next. We assume Coulombic systems.

As noted above, the desired functional is decomposed into the sum of a non-interacting kinetic energy, the classical Coulomb repulsion, and the external interaction energy, denoted above as $\mathcal{E}_s[n]$, and the remainder, $E_{\rm xc} = E_x[n]+E_c[n]$. Standard utilization of the KS decomposition invokes the explicit form of T_s, namely, for specified density n,

$$T_s[n] = \tfrac{1}{2} \min_{\phi \mapsto n} \int \mathrm{d}\mathbf{r}_1 ... \mathrm{d}\mathbf{r}_{N_e} \sum_i^{N_e} |\nabla_i \phi|^2 \tag{4}$$

with ϕ a properly normalized single Slater determinant. (Extension to T $>$ 0 K is by the corresponding 1-particle reduced density matrix.) This leads to the commonly seen expression

$$T_s\left[\{\varphi_i[n]\}\right] := \tfrac{1}{2} \sum_i f_i \int d\mathbf{r}\ |\nabla \varphi_i(\mathbf{r})|^2. \tag{5}$$

The f_i are the Fermi-Dirac occupation numbers for the KS orbitals φ_i and the domain of integration is $\mathbb{R}^3$ for finite systems (molecules, atoms) or the periodic volume in 3D periodic boundary conditions. Solving for the minimum of $\mathcal{F}$ leads to a self-consistent eigenvalue problem for each occupied $\varphi_i[n]$.

The OFDFT utilization of the KS decomposition eschews explicit use of the φ_i and instead constructs an approximate non-interacting kinetic energy $T_s[n]$ (non-interacting free energy) functional for use along with an approximate $E_{xc}[n]$. The $T_s[n]$ contribution to the total energy typically is substantially larger than the magnitude of $E_{\rm xc}$. Nonetheless, it is less well studied than the XC term, so the OFDFT approach has several significant unsolved problems regarding the properties and behavior of T_s.

Exact properties of various density functionals (especially XC) have been extremely useful in the construction and improvement of practical approximations. Thus, next we suggest several topics regarding which mathematicians may well be able to contribute to advancing OFDFT.

Issue 3 The structure and properties of $T_s[n]$ remain somewhat obscure. In OFDFT (for convenience here still at T = 0 K; there is an obvious finite T counterpart) there are two ways to formulate approximations for the Kohn–Sham kinetic energy T_s. To embody known properties, one-point approximations are written as

$$\begin{aligned} T_{s,1}[n] = T_{vW}[n] \\ + c_{TF} \int \mathrm{d}\mathbf{r}\, n^{5/3}(\mathbf{r}) \\ \times f_\theta \left(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \ldots \right) \end{aligned} \tag{6}$$

with the "enhancement factor" f_θ to be approximated. Here $c_{\mathrm{TF}} := \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$ and $f_\theta = 1$ makes that term the Thomas–Fermi kinetic energy,

$$T_{\mathrm{TF}} := c_{\mathrm{TF}} \int \mathrm{d}\mathbf{r}\, n^{5/3}(\mathbf{r}). \tag{7}$$

The first term is the von Weizsäcker kinetic energy,

$$T_{vW} := \frac{1}{8} \int \mathrm{d}\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \tag{8}$$

The Thomas–Fermi kinetic energy is exact for a homogeneous electron gas, while the von Weizsäcker kinetic energy is exact for a one-electron problem or a doubly occupied two-electron problem.

Remark There is a vast literature of exact results on the TF problem [29–33] and gradient expansion corrections thereto. [34–37]

Two-point approximations conventionally are written as augmentations to those two limiting cases,

$$\begin{aligned} T_{s,2}[n] = T_{vW}[n] + T_{\mathrm{TF}}[n] \\ + \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \mathcal{K}[n(\mathbf{r}), n(\mathbf{r}'); \mathbf{r}, \mathbf{r}'], \end{aligned} \tag{9}$$

with $\mathcal{K}$ to be approximated. At least one exact result is known about it [38]. It also is known that the sum of the last two terms must be ≥ 0 because $T_{vW} \leq T_s$ [39].

For reasons of computational speed and clarity of formulation, we have focused on one-point approximations. Except for the gradient expansion, some positivity conditions on the second term in Eq. (6), and some properties provable in the limit of infinite distance from a single atom, rather little is known to guide and shape such approximations. Practical barriers so far have led to no higher-order spatial derivative dependence than $\nabla^2 n$.

Question 3.1 *For a specified highest-order ν of spatial derivative dependence $\partial^\nu n / \partial \mathbf{r}^\nu$ of a one-point approximation, is there an underlying intrinsic property of T_s that*

makes such an approximation impossible in principle or subject to formidably difficult necessary and sufficient conditions?

Remark There are claims in the literature about maximum possible order; see Ref. [40] and references therein.

Issue 3 -continued It long has been conjectured that one-point approximations cannot yield atomic shell structure because they cannot reproduce the interference between orbitals that arises in the KS kinetic energy, Eq. (5). However, whether functionals employing higher-order derivatives, e.g., $\nabla^2 n$, that necessarily are sensitive to small deviations from a smooth density, could generate such structure is an unresolved issue.

Question 3.2 *Is the conjecture about the non-appearance of shell-structure in one-point approximations true and, if so, under what conditions?*

Remark Observe that this question is linked to **Question 3.1**.

Question 3.3 *If the answer to Question 3.2 is negative, does obtaining shell-structure in a one-point approximation implicate non-standard (e.g., improper signs) terms in the gradient expansion correction to the Thomas–Fermi kinetic energy?*

Remarks The subsidiary matter at issue here is whether terms can be implemented in a practical functional so as to generate the correct shell structure in the density rather than unphysical fluctuations. This relates to the observation, in several contexts, that the lowest-order gradient expansion correction to the Thomas–Fermi kinetic energy (proportional to $|\nabla n|^2$) might properly be negative, rather than positive, as is the case in the standard gradient expansion [34]. The contexts include the Airy or edge gas [41], the large-Z limit of neutral atoms [42], and imposition of the discontinuity in the Lindhard response function as a constraint upon the approximation [43]. This opens the possibility that shell structure could be induced because of the reduction in T_s as gradients are introduced in the density. However, to date, approximate functionals implementing a negative gradient expansion contribution to the kinetic energy while retaining overall stability fail to produce shell structure in self-consistent calculations.

Issue 3 continued An upper-bound to the KS kinetic energy T_s that has been conjectured but apparently never proved [44, 45] is

$$T_s \leq T_{\rm TF} + T_{vW}. \tag{10}$$

The inequality has been invoked in constructing OFDFT T_s approximations as a constraint. It can be rationalized [46] by taking the $N_e \to \infty$ limit of the finite-system inequality due to Gázquez and Robles [47]. However, their inequality involves a local-density approximation, hence is not an exact result.

In the development of approximate $T_s[n]$ functionals, for reasons of convenience, the conjectured inequality (10) usually is enforced locally, that is, as a constraint on the respective integrands in (10) for an approximation to T_s, to wit,

$$t_s(\mathbf{r}) \leq t_{\rm TF}(\mathbf{r}) + t_{vW}(\mathbf{r}). \tag{11}$$

Examples of violations of local satisfaction have been discussed recently [48].

Remark The gauge ambiguity in using densities such as in Eq. (11) is well understood in the DFT community.

Questions 3.4, 3.5, and 3.6 *Is the inequality* (10) *true and, if so, under what conditions? What are the provable implications of its use locally? Are those results different for* $\mathrm{T} > 0$ K *and if so, in what way(s)?*

5 Additional issues in time-independent density functional theory

It is standard practice (see, for example, Section 2.5 of Ref. [1]) to generalize from DFT to spin density functional theory (SDFT). Doing so exposes physically significant aspects of the exchange-correlation functional that are hard to access in the original non-spin-polarized formulation. We continue to limit discussion to $\mathrm{T} = 0$ K. In outline, the textbook argument goes as follows: Define the magnetization density $m(\mathbf{r}) := n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})$ ($n_\alpha =$ "up spin," $n_\beta =$ "down spin") and an external field of magnitude $B(\mathbf{r})$. For simplicity, take the $\mathbf{B}$ and magnetization directions to be aligned (though they may be parallel or anti-parallel). Then, to lowest-order in the field, the KS-decomposed Levy–Lieb functional, Eq. (3), becomes

$$\begin{aligned}\mathcal{E}_{\mathrm{LLKS}}[n,m] := {} & T_s[n] + E_H[n] \\ & + E_x[n,m] + E_c[n,m] + E_{\mathrm{ext}}[n] \\ & + \mu_0 \int \mathrm{d}\mathbf{r} m(\mathbf{r}) B(\mathbf{r}).\end{aligned} \tag{12}$$

Here μ_0 is the Bohr magneton. The conventional argument is that this is a straightforward extension of Levy–Lieb constrained search. That is, the usual Hamiltonian (sum of many-electron kinetic energy, electron–electron Coulomb interaction, and external potential) is augmented by a term linear in B. The KS decomposition and rearrangement gives Eq. (12) and variation then gives spin-dependent exchange and correlation potentials in two coupled KS equations, even for $B(\mathbf{r}) \to 0$.

Issue 4 However, Savin [49] has shown, by explicit example, that (12) is not bounded below for any finite B, so the textbook variational argument is not valid. Earlier it had been shown [50] that the SDFT spin-dependent potentials are not unique. Though that problem can be resolved [51], the resolution does not solve the lower-bound issue raised by Savin. Going beyond linear order in B supposedly provides the solution but that implicates current density functional theory [52] and it is not obvious that it resolves the issue of $B = 0$ SDFT legitimacy.

Question 4.1 *Is there a formulation of SDFT that resolves these issues and is connected unambiguously to the Levy–Lieb–Englisch formulation of the spin-independent theory?*

Issue 5 A fundamental problem of many-fermion physics is to predict the existence or absence of a spectral gap for a prescribed Hamiltonian, that is, to predict whether there is a nonzero energy interval between the ground- and first-excited stationary

states for that Hamiltonian. In a tour-de-force paper, Cubitt, Pérez-Garcia, and Wolf [53] showed that for a certain carefully described type of two-dimensional quantum spin system, the spectral gap problem can be mapped to the outcome of the Turing machine "halting problem." Given a well-specified input, it is provable that the question of whether a Turing machine will halt is undecidable. Therefore the question of whether a system with the type of Hamiltonian they defined is gapped or gapless also is undecidable. Note that this is subject to the logical limitation that, as defined by the authors [54], in the original proof "gapped" is not defined strictly as the negation of "gapless."

The direct calculation of spectral functions via DFT has not received much attention. Reference [55] does give one formulation with particular emphasis on degenerate states. Viewed broadly, since DFT is, in principle, an exact rendition of interacting many-electron quantum mechanics and the formalism discussed by Jacob and Kurth [55] is an exact result for the exact functional, a question arises.

Question 5.1 *Does spectral gap undecidability apply to exact DFT for degenerate many-electron systems, or does it fall into a different class of gapped systems?*

Issue 5 continued Suppose that spectral gap undecidability does apply for exact DFT. In practice, the theory is used with approximations, e.g., $E_x[n]$ and $E_c[n]$ in conventional KS calculations and, additionally, $T_s[n]$ in the orbital-free form of the KS procedure (*vide supra*). Those approximations introduce errors.

Question 5.2 *Can the errors from density functional approximations cause a proof of spectral gap undecidability in DFT to be nullified? For example, if the proof relies on halting a Turing machine, can such errors fortuitously halt a Turing machine, thus making the evaluation of the spectral gap decidable for degenerate states?*

Issue 6 Lieb, at the beginning of Section 4.A of Ref. [7], remarked that any mathematically satisfactory definition of the DFT variational functional "…must depend explicitly on the particle number N_e. This fact is unavoidable and frequently overlooked." Various examples of such dependence in practice were cataloged in Ref. [56]. Early investigations of approximations for $T_s[n]$ notably involved such dependence [47, 57–62]. Partly at least that was motivated by the possibility of generating shell structure from N_e dependence. The problem that explicit N_e-dependence could introduce, of course, is incompatibility with size consistency. (For two systems, A, B with ground state energies E_A, E_B, size consistency requires that the total energy of the aggregate in the limit of arbitrarily large separation between them be $E_{A+B} \rightarrow E_A + E_B$.) The conventional KS form of T_s includes the required N_e dependence explicitly by its sum over the kinetic energy of the occupied KS orbitals, c.f. Equation (5). Practical approximations for E_x and E_c either have no explicit N_e dependence or they pick up such dependence from use of the KS kinetic energy density in a dimensionless indicator function [63].

Question 6.1 *Are there formal structures by which N_e dependence could be incorporated systematically in approximations of useful quality for T_s (within OFDFT) and/or E_x, E_c without violation of size-consistency?*

Issue 7 Because of the differentiability issues discussed above (recall 3.2), interest recently has grown [64] in generating the time-independent KS potential directly by a bijective mapping $n(\mathbf{r}) \leftrightarrow v_{KS}(\mathbf{r})$, much as is done in time-dependent DFT, *vide infra*. The methodology is force-balance and continuity, i.e., use of the equations of motion of the physical current density and the density, respectively. In at least one demonstration calculation [65], the potential was derived for various systems and compared with, among others, simplified optimized effective potentials.

Question 7.1 *In the absence of an explicit variational density functional $E[n]$, how is a ground-state KS potential obtained by the force-balance scheme to be used to evaluate ground-state expectation values, particularly the ground state energy $E_0[n_0]$?*

Remark Opportunism from a physical science perspective would suggest using the v from force-balance to solve for $n(\mathbf{r})$ and use of that to evaluate $E[n]$ from some approximate $E_{\mathrm{xc}}[n]$. The motive is to avoid "density-driven error" [66], but the logical difficulty is, of course, that this procedure assumes that the inversion (bijection) is variationally related to the ground-state energy.

6 Time-dependent DFT conventional presentation

An extension of the DFT concepts to dynamical phenomena, time-dependent density functional theory (TDDFT), also is a very active research area. As just mentioned in the force-balance context, this approach relies on the existence of a bijective map between the time-dependent density $n(\mathbf{r}, t)$ (which may take on any initial value at $t = 0$) and the time-dependent external potential $v_{\mathrm{ext}}(\mathbf{r}, t)$, up to a constant.

At least from the physical scientist's perspective, proof of this mapping is fundamentally different in character and more complicated than the proofs for ground-state or finite-temperature DFT. See Ref. [67] and references therein to the original literature. One way to understand the distinction is that there is no straight-forward variational principle for the time-dependent case. An attempt to proceed analogously with standard procedure for the time-dependent Schrödinger equation by defining an action and varying it leads to causality problems [68].

The focus of time-dependent DFT therefore is almost entirely on the $n(\mathbf{r}, t) \leftrightarrow v_{\mathrm{ext}}(\mathbf{r}, t)$ mapping. For pure-states, the conventional TDDFT formulation was put forth first by Runge and Gross [69] with substantial refinements by van Leeuwen [70]. Their result was extended to general mixed states recently by Dufty, Luo, and Trickey [71]. In all of those cases, the systems were restricted to those with densities and potentials that are analytic in time for some domain about the initial time (an exception is the special case of linear response).

For context about the conventional perspective, it is worthwhile to outline the Runge–Gross [69] proof. It exploits the analyticity of the potentials by considering two potentials v_A, v_B that differ by more than a constant. At some order k, the time derivative of their difference is non-constant (because of analyticity):

$$v_{A,k}(\mathbf{r}) - v_{B,k}(\mathbf{r}) := \frac{\partial^k [v_A(\mathbf{r}, t) - v_B(\mathbf{r}, t)]}{\partial t^k}\bigg|_{t=t_0} \neq \text{constant}. \tag{13}$$

Then, they calculate the partial time derivative of the difference in the two quantum mechanical currents. If Eq. (13) is satisfied for $k = 0$, the current-difference time derivative is nonzero and the bijectivity result is trivial. If, however, $k > 0$, they take $k + 1$ current-difference derivatives and show that they correspond to the spatial gradient of the kth potential time derivative. By the equation of continuity, this is related to the $(k+2)$nd time derivative of the density difference $n_A(\mathbf{r}, t) - n_B(\mathbf{r}, t)$ and from there they show that this difference is nonzero provided that a certain surface integral vanishes. They argue that on physical grounds it must vanish. Counterexamples and ways to deal with them have been discussed [72–74].

We give this rather labored summary of the Runge–Gross argument to illustrate how very different TDDFT is, at least from the conventional physical science perspective, from time-independent DFT.

A quite different approach has been proposed by Ruggenthaler and van Leeuwen [75, 76]. It is based on an iterative solution to an equation relating the time-dependent density and external time-dependent potential that follows from the conservation laws for number density and momentum. There are two steps: relating existence and uniqueness of solutions to that equation to the corresponding statements of TDDFT, and proof of that existence and uniqueness. The method does not require analyticity of the density and external potential. While formulated for pure states, it can be extended directly to more general mixed states for both quantum and classical descriptions.

7 Some issues in time-dependent DFT

To get at the questions regarding TDDFT proofs, it is helpful to frame the problem rather generally. Consider two systems characterized by the Hamiltonians $H(t)$ and $H_1(t)$,

$$H(t) = K + U + V(t), \qquad H_1(t) = K + U_1 + V_1(t). \tag{14}$$

Here, K denotes the kinetic energy, U and U_1 are general many-body potentials, and V and V_1 are sums of single particle potentials

$$V(t) = \int \mathrm{d}\mathbf{r} v(\mathbf{r}, t)\widehat{n}(\mathbf{r}), \qquad V_1(t) = \int \mathrm{d}\mathbf{r} v_1(\mathbf{r}, t)\widehat{n}(\mathbf{r}). \tag{15}$$

The number density operator $\widehat{n}(\mathbf{r})$ is given by

$$\widehat{n}(\mathbf{r}) = \sum_{j=1}^{N} \delta\left(\mathbf{r} - \mathbf{q}_j\right), \tag{16}$$

where $\mathbf{q}_j$ is the position operator for the jth particle. The expectation value of some observable corresponding to an operator X is $\langle X \rangle = \mathrm{Tr}\rho X$, $\mathrm{Tr}\rho = 1$. The trace is taken over an arbitrary complete set of states defining the Hilbert space considered. The system state is represented by the positive, semi-definite Hermitian operator ρ

normalized to unity. The corresponding quantities for the second system have the same definitions but distinguished by the subscript 1.

The time-dependence of a state $\rho(t)$ is given by the Liouville–von Neumann equation

$$\partial_t \rho(t) = -i\left[H(t), \rho(t)\right], \qquad \rho(t=0) = \rho \tag{17}$$

where, without loss of generality, the initial time is taken to be $t = 0$. Accordingly, the number densities for the two systems are

$$n(\mathbf{r}, t \mid v) = \mathrm{Tr}\rho(t)\widehat{n}(\mathbf{r}) \equiv \langle \widehat{n}(\mathbf{r}); t\rangle, \tag{18}$$

$$n_1(\mathbf{r}, t \mid v_1) = \mathrm{Tr}\rho_1(t)\widehat{n}(\mathbf{r}) \equiv \langle \widehat{n}(\mathbf{r}); t\rangle_1. \tag{19}$$

The notation $n(\mathbf{r}, t \mid v)$ indicates that the density is a space-time functional of $v(\mathbf{r}, t)$, where for simplicity we have dropped the "ext." Also the subscript on the bracket $\langle \widehat{n}(\mathbf{r}); t\rangle_1$ indicates an average over $\rho_1(t)$ with dynamics generated by $H_1(t)$. Densities $n(\mathbf{r}, t)$ for which there exists a corresponding potential $v(\mathbf{r}, t)$ are called v-representable and their determination is the v-representability problem (*vide supra*).

As stated already, the objective of TDDFT is to show that for a given $n(\mathbf{r}, t)$ the corresponding external potential $v(\mathbf{r}, t)$ is unique, i.e., that there is a one-to-one mapping of the potential and density for the given Hamiltonian $H(t)$. If so, the mapping must hold as well for the Hamiltonian $H_1(t)$ with different $U_1, V_1(t)$. *It follows* that for the same choice of density there exists a unique external potential $v_1(t)$ such that $n_1(\mathbf{r}, t \mid v_1) = n(\mathbf{r}, t)$. Consequently,

$$n(\mathbf{r}, t \mid v) = n_1(\mathbf{r}, t \mid v_1). \tag{20}$$

This is the strongest statement of TDDFT (conditions for the initial state are required but details are not needed for this discussion). For the special case that system 1 consists of non-interacting particles, i.e., $U_1 = 0$, this result implies that the density of an interacting system can be reproduced by a non-interacting system with a different external potential. That representation is referred to as the Kohn–Sham form.

Issue 8 The TDDFT proof proposed by Ruggenthaler et al. starts with an exact representation for the functional relationship of the density and external potential resulting from the local macroscopic conservation laws for the density and momentum density, to wit

$$\begin{aligned}\partial_t^2 n(\mathbf{r}, t \mid v) = &\frac{1}{m}\partial_i\left[\partial_j t_{ij}(\mathbf{r}, t \mid v) + \right.\\ &\left. + n(\mathbf{r}, t \mid v)\partial_i v(\mathbf{r}, t)\right].\end{aligned} \tag{21}$$

(Subscripts i, j are coordinate indices. Repeated indices denote Einstein summation. We have left the mass dependence explicit for clarity, though for electrons in Hartree atomic units $m = m_e = 1$.) This is an *identity* relating the average density obtained from the Liouville equation for the dynamics evolved under the external potential $v(\mathbf{r}, t)$. Here $t_{jk}(\mathbf{r}, t \mid v)$ is the average momentum flux $t_{jk}(\mathbf{r}, t \mid v) =$

$Tr\rho(t \mid v)\widehat{t}_{jk}(\mathbf{r})$. The precise definition for the operator $\widehat{t}_{jk}(\mathbf{r})$ is known, and its average over the ensemble implies that it is a functional of $v(\mathbf{r}, t)$.

Now consider an arbitrary density $n(\mathbf{r}, t)$ and an external potential $w(\mathbf{r}, t)$ *defined* as the solution to the equation

$$\partial_t^2 n(\mathbf{r}, t) = \frac{1}{m}\partial_i \left[\partial_j t_{ij}(\mathbf{r}, t \mid w) + n(\mathbf{r}, t)\partial_i w(\mathbf{r}, t)\right]. \tag{22}$$

This is an equation for $w(\mathbf{r}, t)$ in terms of the given density. The functional $t_{ij}(\mathbf{r}, t \mid w)$ is unchanged, only its argument is different. Suppose (22) has a solution. Then, the Liouville equation with $w(\mathbf{r}, t)$ gives the exact conservation law corresponding to (21)

$$\begin{aligned}\partial_t^2 n(\mathbf{r}, t \mid w) = &\frac{1}{m}\partial_i \left[\partial_j t_{ij}(\mathbf{r}, t \mid w) + \right.\\ &\left. + n(\mathbf{r}, t \mid w)\partial_i w(\mathbf{r}, t)\right].\end{aligned} \tag{23}$$

The difference between (22) and (23) gives the relationship of $n(\mathbf{r}, t)$ and $n(\mathbf{r}, t \mid w)$

$$\partial_t^2 \phi(\mathbf{r}, t) = \partial_i \left(\phi(\mathbf{r}, t)\partial_i w(\mathbf{r}, t)\right) \tag{24}$$

where $\phi(\mathbf{r}, t) \equiv n(\mathbf{r}, t \mid w) - n(\mathbf{r}, t)$. At this point it is necessary to specify the initial conditions

$$n(\mathbf{r}, t = 0 \mid w) = n(\mathbf{r}, t = 0), \tag{25}$$

$$\partial_t n(\mathbf{r}, t \mid w)|_{t=0} = \partial_t n(\mathbf{r}, t)|_{t=0}, \tag{26}$$

or equivalently

$$\phi(\mathbf{r}, t = 0) = 0, \qquad \partial_t \phi(\mathbf{r}, t)|_{t=0} = 0. \tag{27}$$

Clearly, $\phi(\mathbf{r}, t) = 0$ is a solution to (24). However, Ruggenthaler and van Leeuwen claim that this is the *unique* solution. If true, the proof of TDDFT follows directly as indicated below.

Question 8.1 *Is there a proof of this assertion, i.e., that $\phi(r, t) = 0$ is the unique solution to (24)?*

Remark For a time-independent external potential, proof is straightforward using the method of separation of variables. However, that is not the case here. It would appear that this is a straightforward problem of classical analysis, yet to our knowledge its proof has not yet been demonstrated.

Let us assume that the proof has been provided and consider the consequences. At this point, the density $n(\mathbf{r}, t)$ in (22) still is arbitrary. Denote the solution to (22) for a given density as a functional of that density $w(\mathbf{r}, t) = w(\mathbf{r}, t \mid n)$. The specific functional is determined by the Hamiltonian through $t_{ij}(\mathbf{r}, t \mid w)$ but is otherwise universal, i.e., $w(\mathbf{r}, t \mid n)$ delivers an arbitrary density $n(\mathbf{r}, t)$ via solution to (22). Now choose that density to be the one associated with the conservation laws for the

Liouville equation with a different external potential $u(\mathbf{r}, t)$, i.e., $n(\mathbf{r}, t) \to n(\mathbf{r}, t \mid u)$, so that (21) becomes

$$\partial_t^2 n(\mathbf{r}, t \mid u) = \frac{1}{m} \partial_i [\partial_j t_{ij}(\mathbf{r}, t \mid u) + n(\mathbf{r}, t \mid u) \partial_i u(\mathbf{r}, t)] . \tag{28}$$

It follows from $\phi(\mathbf{r}, t) = 0$ that

$$n(\mathbf{r}, t \mid w) = n(\mathbf{r}, t) = n(\mathbf{r}, t \mid u). \tag{29}$$

Then, the identity (21) can be written as

$$\partial_t^2 n(\mathbf{r}, t) = \frac{1}{m} \partial_i \left[\partial_j t_{ij}(\mathbf{r}, t \mid u) + n(\mathbf{r}, t) \partial_i u(\mathbf{r}, t) \right]. \tag{30}$$

Consequently, $u(\mathbf{r}, t)$ is also a solution to (22). If, as assumed, that solution is unique, then $w(\mathbf{r}, t) = u(\mathbf{r}, t)$. Thus, the first part of TDDFT, that the potential associated with a given density is unique, is equivalent to uniqueness of the solution to (22). Also, since the solution provides the potential for any given density, this also implies existence of such a potential - v-representability.

The preceding analysis can be repeated for a system with a different two-particle potential $U \to U_1$. Then, the solution to (22) for system with U_1 gives an external potential for that system for any given density. Now choose that density to be the one for the system with U. The resulting unique external potential then reproduces that density from the system with U_1. The special case of $U_1 = 0$ gives the Kohn–Sham representation: an interacting system density can be represented by an appropriate non-interacting system.

In summary, the solution to (22) for a given density implies that the density is v-representable. Furthermore, if the solution is unique, then there is a one-to-one relationship between $n(\mathbf{r}, t \mid v)$ and the potential $v(\mathbf{r}, t)$. Finally, the density from a potential $v(\mathbf{r}, t)$ and pair interaction U can be generated from a different potential $v_1(\mathbf{r}, t)$ for a system with pair interaction U_1. A proof of these conditions of TDDFT therefore reduces to a proof of the existence and uniqueness of solutions to (22).

Question 8.2 *Can the existence and uniqueness of solutions to (22) be proven?*

Remark The basic equations of the preceding discussion of TDDFT are those of continuum mechanics and are of the same form regardless of their basis in quantum mechanics (pure or mixed states) or in classical mechanics. Only the explicit form for the macroscopic stress tensor functional $t_{ij}(\mathbf{r}, t \mid u)$ differs among the cases.

7.1 Issues with proposed answer to Question 8.2

An affirmative response to the Question 8.2 has been put forth but poses its own difficulties.

To proceed, first rewrite (22) in a notation similar to that of Ref. [75],

$$Qw(\mathbf{r},t) = q(\mathbf{r},t \mid w) - \partial_t^2 n(\mathbf{r},t) \tag{31}$$

where $q(\mathbf{r},t \mid w) \equiv \frac{1}{m}\partial_i \partial_j t_{ij}(\mathbf{r},t \mid w)$ and Q is the linear differential operator $Q \equiv -\frac{1}{m}\partial_i n(\mathbf{r},t)\partial_i$. Consider first the operator Q. For *appropriate homogeneous boundary conditions* Q is self-adjoint

$$(\psi, Q\psi) \equiv -\left(\psi, \frac{1}{m}\partial_i n(\mathbf{r},t)\partial_i \psi\right) = (Q\psi, \psi), \tag{32}$$

where the scalar product is for integrable functions over the system volume. Furthermore, its spectrum is positive

$$Q\psi \equiv -\frac{1}{m}\partial_i n(\mathbf{r},t)\partial_i \psi = \lambda\psi \tag{33}$$

$$(\psi, Q\psi) \equiv \frac{1}{m}(\partial_i \psi, n(\mathbf{r},t)\partial_i \psi) = \lambda(\psi,\psi) \geq 0, \tag{34}$$

for positive densities $n(\mathbf{r},t)$. Finally, $\lambda = 0$ is an eigenvalue with eigenvector $\psi = 1$ (or any constant). The right side of (31) is orthogonal to this zero eigenvector, so the Fredholm conditions are met for inverting Q

$$w(\mathbf{r},t) = Q^{-1}\left[q(\mathbf{r},t \mid w) - \partial_t^2 n(\mathbf{r},t)\right]. \tag{35}$$

Issue 9: A constructive approach to a solution to (35) can be attempted via iteration from an initial trial solution $w^{(0)}(\mathbf{r},t)$ and successive approximations,

$$w^{(n+1)}(\mathbf{r},t) = Q^{-1}\left[q\left(\mathbf{r},t \mid w^{(n)}\right) - \partial_t^2 n(\mathbf{r},t)\right], \tag{36}$$

or

$$w^{(n+1)}(\mathbf{r},t) = \mathcal{G} \circ w^{(n)}(\mathbf{r},t). \tag{37}$$

Here, $\mathcal{G}\circ$ denotes the nonlinear "map"

$$\mathcal{G} \circ x(\mathbf{r},t) = Q^{-1}\left[q(\mathbf{r},t \mid x) - \partial_t^2 n(\mathbf{r},t)\right]. \tag{38}$$

The convergence of the sequence $\left\{w^{(n)}\right\}$ follows if it can be established that $\mathcal{G}$ is a contraction mapping

$$\mathcal{G} \circ \left[w^{(n)}(\mathbf{r},t) - w^{(n-1)}(\mathbf{r},t)\right] \leq \left[w^{(n)}(\mathbf{r},t) - w^{(n-1)}(\mathbf{r},t)\right], \tag{39}$$

or equivalently

$$w^{(n+1)}(\mathbf{r},t) - w^{(n)}(\mathbf{r},t) \leq \left[w^{(n)}(\mathbf{r},t) - w^{(n-1)}(\mathbf{r},t)\right]. \tag{40}$$

Convergence, $w^{(n)}(\mathbf{r},t) \to w(\mathbf{r},t)$, implies that it is the desired solution to (35) and that it is a fixed point of $\mathcal{G}$

$$w(\mathbf{r},t) = \mathcal{G} \circ w(\mathbf{r},t). \tag{41}$$

These inequalities are measured with respect to some norm, e.g.,

$$\begin{aligned} &\|\mathcal{G} \circ \left[w^{(n)}(\mathbf{r},t) - w^{(n-1)}(\mathbf{r},t)\right] \| \\ &\quad \leq \left\| \left[w^{(n)}(\mathbf{r},t) - w^{(n-1)}(\mathbf{r},t)\right] \right\| . \end{aligned} \tag{42}$$

Questions 9.1 and 9.2 *What is an appropriate function space for analysis of the map $\mathcal{G}$? Can suitable bounds be found to establish that it is a contraction mapping?* See Ruggenthaler et al. [76] for the extent to which these issues have been addressed.

8 Concluding remarks

A striking feature of both time-independent DFT and time-dependent DFT is that they are formulated in terms of theorems that do not provide any mechanical recipe (e.g., perturbation theory) for constructing approximations. Therefore, even cursory examination of the literature on development of density functional approximations will convince one of the influence and value that bounds, limits, asymptotics and similar rigorously provable properties have had on such developments. What we have delineated here is, in a way, self-serving, in that we are certain we would be helped by having some answers to the questions posed. Leads to other questions of rigorous nature about DFT and TDDFT may be found in a recent "round-table" paper [16].

Our objective has been to provide a personal perspective of DFT and its limitations in foundation and application. The discussion of the time-independent case has been from the traditional variational formulation and the attendant, related difficulties in applications. This is the most common approach currently in use. The subsequent discussion of TDDFT has been from the force balance formulation and an elaboration of the basis for applications from a time-dependent Kohn–Sham single particle dynamics. The literature in both cases is extensive. We have highlighted selected specifics for attention. It is our hope that interested mathematicians will see opportunities for contributions based on tools typically not familiar to the DFT physical sciences community.

DFT is widely practiced across the most complex problems of physics, chemistry, and materials sciences, with growing use in biomolecular areas as well. Its popularity arises from the capacity to formulate approximations to questions for which other traditional many-body methods such as perturbation theory, small parameter expansions,

and simulations are limited. In application, typical DFT approximations are inherently uncontrolled in a technical sense. For example *a priori* error estimates are not given. But wide experience over more than a half-century has led to ever increasing intensity of use in spite of the remaining open problems. It is expected that the contributions sought here from the mathematical community will mostly strengthen the confidence in current approximations rather than to undermine or negate their continued practice.

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Declarations

Conflicts of interest On behalf of all authors, the corresponding author states that there is no conflict of interest. This paper has no associated data.

Appendix 1: Generic overview of DFT

Though most of what follows is completely generic to any quantum mechanical single-species system, our focus is on many-electron systems. We note, for example, that there is active work on nuclear many-body DFT; see Ref. [77] and references therein.

In the simplest case, the Hamiltonian describes N particles interacting pairwise (e.g., Coulomb interactions) subject to an external single-particle potential that couples to each particle, $v_{\text{ext}}(\boldsymbol{r})$. (Any possible time dependence is left implicit to simplify the notation here.) The states of interest (wave function, density matrix) are "extremal" states (e.g., ground state, mechanical equilibrium) that are fixed by conditions involving the Hamiltonian. Hence, those states are functionals of v_{ext}. Properties of interest (e.g., energy, free energy, magnetization, etc.) are expectation values of appropriate operators in these states; hence, they inherit a functional dependence on v_{ext}. In particular, the number density $n(\boldsymbol{r})$ defined in this way is a functional of v_{ext}, denoted $n(\boldsymbol{r}|v_{\text{ext}})$.

For reasons of insight and computational accessibility mentioned in the main text, it typically is preferable to express properties of interest as functionals of n rather than of v_{ext}. This change of variables can be implemented if there is a one-to-one relationship $v_{\text{ext}}(\boldsymbol{r}) \leftrightarrow n(\boldsymbol{r}|v_{\text{ext}})$, e.g., via a Legendre transformation (subject to certain conditions on the functional representing the property considered). The first task of DFT thus is to establish this bijective relationship of the density and external potential. Two complementary approaches have been used.

The first (historically) [9] is based on variational principles showing that the density associated with a given potential provides the extremum of a certain functional (or action in the time-dependent case). The convexity of the functional assures the uniqueness required. A second approach is based on the force balance for these states, or specifically, the conservation law for the local momentum density. Both approaches accomplish the goal formally, but without complete mathematical rigor. Specifically, the function space for $v_{\text{ext}}(\boldsymbol{r})$ and that for $n(\boldsymbol{r})$ have not been fully characterized within the proof. As detailed in the main text, this deficiency remains an open problem for all states considered: time-independent, time-dependent, ground state, and finite temperature.

The variational approach also requires conditions on the associated functional to allow functional differentiation. Existence of such functionals in general remains an open problem, related to the above-mentioned characterization of function spaces. The force balance approach does not require functional differentiation and thus avoids this difficulty.

Important practical problems remain after the bijectivity is proved. The first is to know the functional $n(\boldsymbol{r}|v_{\text{ext}})$, and the second is to know the corresponding functional for the desired property (e.g., energy, free energy, etc.). These two tasks do not arise as separate problems in the variational approach because the extremum of the functional is identified as the primary property of interest (e.g., ground state energy or free energy). In the force balance approach, the density can be calculated, but the dependence of a property of interest upon that density remains to be fixed.

In practice, the calculation of the density for a given potential is accomplished by a mapping of the DFT for the interacting particle system to that for a non-interacting system, the Kohn–Sham representation. In the variational formulation, this is straightforward once the existence of the functional derivative (or its equivalent) can be established. Once again, this can be done in the force balance approach without need for the functional derivative.

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