

Time-dependent generalized Kohn–Sham theory[★]

Roi Baer^{1,a} and Leeor Kronik^{2,b}

¹ Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

² Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

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Abstract. Generalized Kohn–Sham (GKS) theory extends the realm of density functional theory (DFT) by providing a rigorous basis for non-multiplicative potentials, the use of which is outside original Kohn–Sham theory. GKS theory is of increasing importance as it underlies commonly used approximations, notably (conventional or range-separated) hybrid functionals and meta-generalized-gradient-approximation (meta-GGA) functionals. While this approach is often extended in practice to time-dependent DFT (TDDFT), the theoretical foundation for this extension has been lacking, because the Runge–Gross theorem and the van Leeuwen theorem that serve as the basis of TDDFT have not been generalized to non-multiplicative potentials. Here, we provide the necessary generalization. Specifically, we show that with one simple but non-trivial additional caveat – upholding the continuity equation in the GKS electron gas – the Runge–Gross and van Leeuwen theorems apply to time-dependent GKS theory. We also discuss how this is manifested in common GKS-based approximations.

1 Introduction

Density functional theory (DFT) [1–6] is a powerful and versatile first-principles approach to the many-electron problem, in which the electron density, rather than the many-electron wave function, plays the central role. The fundamental tenet of DFT is the Hohenberg–Kohn theorem [7], which establishes a mapping between the time-independent external potential of the system and its ground-state electron density. This means that all the information pertaining to system properties is already encoded in the electron density, a physically accessible object that is far more simple than the many-electron wave function. DFT is inherently a ground-state theory, but fortunately an extension to time-dependent many-electron systems, known as time-dependent DFT (TDDFT) [8,9], has been established rigorously. The central tenet of TDDFT is the Runge–Gross theorem [10], which proves a similar mapping between the time-dependent external potential of the system and its time-dependent electron density, i.e., it shows that (given an initial condition) the time-dependent electron density

again contains all information with respect to the system properties. While slower to develop owing to both conceptual and computational challenges, TDDFT has also proven to be a first-principles approach of great value.

Both DFT and TDDFT are exact in principle, but nearly always approximate in practice, because the required “mapping” between the external potential and the electron density is only approximately known, except in very special cases. Originally, the overwhelming majority of practical DFT applications were based on the Kohn–Sham (KS) construct. In this approach, the Hohenberg–Kohn theorem is utilized to show that the ground state of the physical interacting-electron system can be mapped into the ground state of a system of fictitious non-interacting electrons that are subject to a common *multiplicative* external potential, such that the fictitious system has the same ground-state density as the real one. The mapping potential is a functional of the density and the mapping is expressed in the form:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}([n]; \mathbf{r}) + v_{xc}([n]; \mathbf{r}) \right] \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (1)$$

where ϵ_k and $\varphi_k(\mathbf{r})$ are KS eigenvalues and eigenstates, respectively, $n(\mathbf{r}) = \sum_k |\varphi_k(\mathbf{r})|^2$ is the electron density (with the summation extending over occupied states only), v_{ext} is the external potential, v_{H} – the Hartree potential – treats electrostatic interactions, and v_{xc} – the exchange-correlation potential – accounts

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^a e-mail: roi.baer@huji.ac.il

^b e-mail: leeor.kronik@weizmann.ac.il

for all many-body interactions beyond electrostatics. For simplicity, spin unpolarized notation and atomic units ($e = m = \hbar = 1$) are used throughout. Equation (1) constitutes a nonlinear eigenvalue problem, requiring a self-consistent solution for the charge density $n(\mathbf{r})$.

In most cases, the dependence of v_{xc} on the electron density is not known and needs to be approximated. Relatively simple approximations for v_{xc} rely on the electron density explicitly. Specifically, in the local density approximation (LDA), v_{xc} is a simple function of the density; In the generalized-gradient approximation (GGA) family of functionals, v_{xc} is a function of the density and its gradient. However, more advanced classes of approximation rely on orbital-dependent functionals [11], i.e., expressions that depend explicitly on the KS orbitals. Notable examples are meta-GGA (MGGA) functionals, which use the kinetic energy density,

$$\tau(\mathbf{r}) = \sum_k \frac{1}{2} |\nabla \varphi_k(\mathbf{r})|^2, \quad (2)$$

or hybrid functionals, which rely on Fock exchange integrals.

Use of orbital-dependent functionals triggers an immediate and serious difficulty: The exchange-correlation potential, v_{xc} , is defined within KS theory as the functional derivative of the exchange-correlation energy, E_{xc} , with respect to the density, i.e., $v_{xc} = \delta E_{xc} / \delta n$. But how is this derivative to be evaluated if E_{xc} is an orbital-dependent functional? One possibility is to think of the KS orbitals as being themselves functionals of the density. E_{xc} is then an implicit density functional and v_{xc} can be evaluated by using chain-rule variational calculus to take the implicit functional derivative, which leads to an integro-differential equation known as the optimized effective potential (OEP) equation [11–13]. The advantage of this procedure is that it is rigorously within KS theory, but the disadvantage is that it is computationally difficult. Therefore, from the very early days of orbital-dependent functionals most work proceeded by taking functional derivatives of E_{xc} directly with respect to the orbitals [14,15]. This procedure is clearly unsupported by KS theory and therefore at first glance appears to be no more than an uncontrolled approximation to it. However, Seidl et al. showed that in some cases this procedure can be rigorously justified within DFT by resorting to a *generalized* Kohn–Sham (GKS) theory, presented in detail in the next Section, in which the many-electron problem is mapped into a partially-interacting electron gas [16]. Furthermore, it is now well established that the GKS framework provides for greater flexibility that holds some advantages over the original KS theory, especially in the context of spectroscopy [17].

The time-dependent extension of equation (1) can be straightforwardly written in the form: [10]

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}, t) + v_{\text{H}}([n]; \mathbf{r}, t) + v_{xc}([n]; \mathbf{r}, t) \right] \varphi_k(\mathbf{r}, t) = i \frac{\partial}{\partial t} \varphi_k(\mathbf{r}, t). \quad (3)$$

Unlike in the time-independent case, the exchange-correlation potential is now generally a complicated functional of the density dependence on both space and time, as well as of the initial state of both the interacting and the non-interacting system (with some assumptions, e.g., that the density is non-zero almost everywhere) [18]. The uniqueness of the time-dependent Kohn–Sham potential is guaranteed by the Runge–Gross Theorem. Beyond uniqueness, van Leeuwen [19] later showed that, under some assumptions on the initial and boundary conditions, the time-dependent Kohn–Sham potential is in fact guaranteed to exist.

Usually, one of the above-discussed classes of approximations is employed also within TDDFT, using the additional assumption (known as the adiabatic approximation) that the exchange-correlation at a given time only depends on the electron density at that time. As in the time-independent theory, this can in principle be done within KS theory using, e.g., OEP procedures [20,21]. But here too, the more simple use within TDDFT of non-multiplicative potentials, whose form has been inherited from orbital-based derivatives in the ground state, has become increasingly popular and successful – see., e.g., references [17,22–30]. However, whereas for the ground-state this is justified by the above-mentioned generalization of KS theory [16], to the best of our knowledge no such generalization has been offered for either the Runge–Gross theorem or the van Leeuwen theorem. This is an untenable situation because it leaves an entire field of applications without proper theoretical foundations. Specifically, without the Runge–Gross theorem and the van Leeuwen theorem it remains unknown whether a unique time-dependent potential can indeed be mapped to a unique electron density and one does not know if reproduction of the time-dependent electron density suffices to retain the system information. Here, we remedy this problem by proving the missing generalization, based on the identification of appropriate conditions for its validity. We do so by providing a succinct overview of ground-state GKS theory, followed by its extension to the time-dependent case and discussion of important consequences for specific GKS maps.

2 Time-independent generalized Kohn–Sham theory

2.1 Formalism

We start our analysis by providing a short synopsis of GKS theory, based on the seminal work of Seidl et al. [16] (to which the reader is referred for complete details). In keeping with the spirit of the original proof, we shall not dwell on questions of existence, i.e., we will assume all relevant densities to be physically realizable.

As mentioned above, KS theory maps a many-electron system into a non-interacting electron system that yields the same ground state density. In GKS theory, one maps the real system to a *partially interacting* model system, but one that can still be represented by a single Slater determinant. Such an alternate mapping is achieved in

practice by defining an energy functional of the Slater determinant, $S[\Phi]$, or equivalently of the orbitals that comprise it, $S[\{\varphi_j\}]$, and an associated energy density functional, $F^s[n]$, obtained from the Slater determinant that minimizes $S[\cdot]$ while yielding a density $n(\mathbf{r})$, i.e.,

$$F^s[n] \equiv \min_{\{\varphi_j\} \rightarrow n(\mathbf{r})} S[\{\varphi_j\}]. \quad (4)$$

The minimizing orbitals, $\{\varphi_j\}$, comprise the model system and play a role similar to those of KS orbitals. According to the Hohenberg-Kohn theorem, [7] the total energy, E_{tot} , can be expressed as a sum of the potential energy owing to the external potential, $v_{\text{ext}}(\mathbf{r})$, in the form $\int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$, and an energy contribution that is a universal functional of the density, $F_{\text{HK}}[n]$. We can then define a “remainder energy” functional, $R^s[n]$, by the difference between $F_{\text{HK}}[n]$ and $F^s[n]$, which naturally depends on the initial choice of $S[\cdot]$. The total energy is then trivially given by:

$$E_{\text{tot}} = \min_n \left\{ \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F^s[n] + R^s[n] \right\}. \quad (5)$$

Minimizing over all densities using the orbitals that generate them, subject to the constraint that they integrate to the density $n(\mathbf{r})$, leads directly to the generalized KS equation:

$$\left(\hat{O}^S[\{\varphi_j\}] + v_{\text{ext}}(\mathbf{r}) + v_R(\mathbf{r}) \right) \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (6)$$

where

$$v_R(\mathbf{r}) \equiv \frac{\delta R^s[n]}{\delta n(\mathbf{r})} \quad (7)$$

is a multiplicative “remainder potential” and $\hat{O}^S[\{\varphi_j\}]$ is a generally non-multiplicative operator, obtained from the derivation by orbital of $S[\{\varphi_j\}]$, which depends on the choice of $S[\cdot]$, but not on $v_{\text{ext}}(\mathbf{r})$ or $v_R(\mathbf{r})$.

Before closing this sub-section, we define an equivalent phrasing of GKS theory, which we find below to be useful. It states that given a density $n(\mathbf{r})$, which is the ground state density of an interacting system of N electrons, there exist a unique potential $v(\mathbf{r})$ and corresponding set of orbitals $\varphi_k(\mathbf{r})$ ($k = 1, \dots, N$), which obey an equation of the general form:

$$\epsilon_k \varphi_k(\mathbf{r}) = \left(\frac{-\nabla^2}{2} + \hat{g}[\rho] + v(\mathbf{r}) \right) \varphi_k(\mathbf{r}), \quad (8)$$

such that

$$n(\mathbf{r}, t) = \sum_k |\varphi_k(\mathbf{r})|^2. \quad (9)$$

In the above equations $\rho(\mathbf{r}, \mathbf{r}') \equiv \sum_{k=1}^N \varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}')$, where the summation is over occupied states is the density matrix (DM). We define $\hat{g} \equiv \hat{O}^S[\{\varphi_j\}] + \nabla^2/2$ so as to focus on contributions to the non-multiplicative operator $\hat{O}^S[\{\varphi_j\}]$ other than the obvious kinetic energy one, and further define $v(\mathbf{r}) \equiv v_{\text{ext}}(\mathbf{r}) + v_R(\mathbf{r})$. Importantly, \hat{g} can be viewed as a functional of the DM, $\rho(\mathbf{r}, \mathbf{r}')$, corresponding to the Slater determinant Φ , rather than the Slater determinant itself. This is because there is a one-to-one correspondence (up to an uninteresting phase factor) between the two.

2.2 Examples of GKS maps

Both the KS and the GKS maps are formally exact, if the exact potential, $v_{xc}(\mathbf{r})$ or $v_R(\mathbf{r})$, is known. However, whereas there is only one KS map, there exist a multitude (indeed, an infinitude) of GKS maps, depending on the choice of $S[\Phi]$. The GKS approach and its versatility are best illustrated, then, by considering specific classes of GKS maps. Here, we elaborate on several such choices.

One class of GKS maps is obtained if one chooses $S[\Phi]$ to be the kinetic energy of the fictitious system, i.e., $\hat{T}\Phi$, where $\hat{T} = \sum_{i=1}^N (-\nabla_i^2/2)$. Straightforward derivation by orbital then shows that $\hat{O}^S[\{\varphi_j\}]$ is the usual single-particle kinetic energy operator, $-\nabla^2/2$, i.e., the first term in the KS equation. The “remainder” potential, $v_R(\mathbf{r})$, is then simply the sum of the Hartree and exchange-correlation terms of the KS equation. In other words, from this perspective the original KS scheme is “just” a special case of the GKS approach, obtained for this specific choice of $S[\Phi]$.

A different, more interesting case emerges if one chooses $S[\Phi]$ to be the sum of kinetic energy and Coulomb repulsion energy of the fictitious system, i.e., $\hat{T} + \hat{W}\Phi$, where $\hat{W} = 1/2 \sum_{i \neq j} 1/|\mathbf{r}_i - \mathbf{r}_j|$ [16]. Derivation then reveals that $\hat{O}^S[\{\varphi_j\}] = -\nabla^2/2 + v_H + \hat{v}_F$, i.e., is the sum of the single-particle kinetic energy operator and the Hartree-Fock operator, where

$$\hat{v}_F \varphi_k(\mathbf{r}) = - \sum_j \int d\mathbf{r}' \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (10)$$

The “remainder” potential, $v_R(\mathbf{r})$, can then be interpreted as a correlation potential. This particular GKS map can be thought of as a “Hartree-Fock-Kohn-Sham” equation, which is in principle exact. The original Hartree-Fock equation, then, is obtained as just another approximation within DFT, obtained under the rather crude approximation of $v_R(\mathbf{r}) = 0$.

Once Hartree-Fock theory is established as GKS theory, the road to incorporating hybrid functionals is wide open. Specifically, the choice $S[\Phi] = \hat{T} + a\hat{W}\Phi$, where $0 < a < 1$, leads to $\hat{O}^S[\{\varphi_j\}] = -\nabla^2/2 + av_H + a\hat{v}_F$, i.e., the sum of the single-particle kinetic energy operator, a fraction a of the Hartree potential, and the same fraction a of the Fock operator [31]. If $v_R(\mathbf{r})$ is approximated as the sum

of the complementary fraction of the Hartree potential, the complementary fraction of GGA exchange, and the full GGA correlation, an approximate GKS equation is obtained, in the form:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}([n]; \mathbf{r}) + a\hat{v}_F + (1-a)v_x^{\text{GGA}}(n); \mathbf{r} \right. \\ \left. + v_c^{\text{GGA}}(n); \mathbf{r} \right] \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (11)$$

which is precisely the definition of a conventional hybrid functional.

To obtain a range-separated hybrid functional, one can choose $S[\Phi] = \hat{T} + \hat{W}^{LR}\Phi$, where ‘‘LR’’ means that $\text{erf}(\gamma|\mathbf{r} - \mathbf{r}'|)/|\mathbf{r} - \mathbf{r}'|$ is used instead of $1/|\mathbf{r} - \mathbf{r}'|$, i.e., $\hat{W} = 1/2 \sum_{i \neq j} 1/|\mathbf{r}_i - \mathbf{r}_j|$ is the long-range Coulomb repulsion, where γ is a range-separation parameter. This yields $\hat{O}^S[\{\varphi_j\}] = -\nabla^2/2 + v_{\text{H}}^{LR} + \hat{v}_F^{LR}$ [17]. If $v_R(\mathbf{r})$ is then approximated as the sum of the short-range Hartree potential (designated by ‘‘SR’’) that is computed using $\text{erfc}(\gamma|\mathbf{r} - \mathbf{r}'|)/|\mathbf{r} - \mathbf{r}'|$, short-range GGA exchange, and full GGA correlation, one obtains the following approximate GKS equation:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}([n]; \mathbf{r}) + \hat{v}_F^{LR} + v_x^{\text{SR,GGA}}(n); \mathbf{r} \right. \\ \left. + v_c^{\text{GGA}}(n); \mathbf{r} \right] \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (12)$$

which is the definition of a simple range-separated hybrid functional.

Our final example is that of MGGA functionals, in which the exchange-correlation energy is approximated as

$$E_{xc}^{\text{MGGA}}[n] = \int dr f^{\text{MGGA}}(n(r), \nabla n(r), \tau(r)), \quad (13)$$

where τ is the kinetic energy density defined in equation (2) above and f^{MGGA} is an appropriate energy-density function. Here too, one rarely takes the functional derivative of equation (13) with respect to the electron density, as one should in KS theory, owing to the complications associated with the dependence on τ . Instead, one usually derives equation (13) by orbital, as first suggested by Neumann et al. [15]. The MGGA potential operator obtained that way can be expressed as

$$\hat{v}^{\text{MGGA}} = v^{\text{GGA}} + \hat{v}_\tau. \quad (14)$$

The first term is a multiplicative potential arising from explicit derivation of f^{MGGA} with respect to n , taking ∇n into account, exactly as done in a GGA functional. The second term is a non-multiplicative operator arising from explicit derivation of f^{MGGA} with respect to τ and is given by

$$\hat{v}_\tau = -\frac{1}{2} \nabla \mu(r) \nabla, \quad (15)$$

where $\mu(r) = \partial f^{\text{MGGA}}/\partial \tau$. Owing to the non-multiplicative nature of \hat{v}_τ , using equation (14) clearly violates KS theory. However, it can be justified within GKS theory by choosing

$$S[\Phi] = \hat{T}\Phi + E_{xc}^{\text{MGGA}}[\Phi]. \quad (16)$$

The first term in equation (16) is the expectation value of the kinetic energy in the Slater determinant, as before, and the second term is the MGGA energy expression of equation (13), now viewed as a functional of Φ because both n and τ only depend on the single-electron orbitals φ_i that comprise the Slater determinant Φ . $\hat{O}^S[\{\varphi_j\}]$ is immediately obtained as the sum of single-particle kinetic energy operator and the potential operator of equation (14). If the remainder potential is approximated to be the Hartree potential, the standard MGGA equation is obtained, in the form

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n]; \mathbf{r} + V^{\text{GGA}}([n]; \mathbf{r}) + \hat{v}_\tau \right] \varphi_k(\mathbf{r}) \\ = \epsilon_k \varphi_k(\mathbf{r}). \quad (17)$$

Thus, the choice of energy functional $S[\cdot]$ made in equation (16) is perhaps not as elegant as in the previous examples, as it cannot generally be expressed solely as an expectation value of a many-body operator on a Slater determinant, but is nevertheless well-defined and provides a rigorous GKS foundation for the MGGA potential derivation of Neumann et al. [15].

We note that additional GKS maps of practical importance can be obtained simply by combining some of the $S[\Phi]$ choices presented above. For example, combining $S[\Phi]$ corresponding to a fraction of Coulomb repulsion with $S[\Phi]$ corresponding to a (possibly different) fraction of long-range Coulomb repulsion will lead to a more general form of a range-separated hybrid functional, e.g., that given in reference [32]. Combining $S[\Phi]$ corresponding to a fraction of Coulomb repulsion with the complementary fraction of $S[\Phi]$ corresponding to MGGA will result in an MGGA-hybrid functional, e.g., those given in references [33,34].

Before closing this sub-section, we note that all the special cases studied here use ‘‘functional ingredients’’ that are easily alternatively phrased in terms of the density matrix (DM) as per equation (8) above. The electron density n is just the diagonal of the DM; Fock integrals as in equation (10) obviously involve the DM; and the kinetic energy density τ can be found using

$$\tau(\mathbf{r}) = \frac{1}{2} \lim_{\mathbf{r} \rightarrow \mathbf{r}'} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \\ \equiv \frac{1}{2} [\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}=\mathbf{r}'}. \quad (18)$$

3 Time-Dependent Generalized Kohn–Sham theory

3.1 Preliminaries

As mentioned in the introduction, time-independent KS or GKS theory relies on the variational principle, which cannot be used in the time-dependent case. The Runge–Gross theorem [10] broke through this barrier by proving that the single-particle potential leads to a given v -representable density that is uniquely determined. This was achieved by showing a one-to-one mapping between both quantities and the paramagnetic current density, defined below. However, the Runge–Gross theorem only considered multiplicative potentials and therefore only applies to KS theory.

Formal proof aside, naively if one wishes to use the formalism of equation (8) in time-dependent problem, the following “TD-GKS” equation can be phrased as:

$$i\dot{\varphi}_k(\mathbf{r}, t) = \hat{h}_{\mathbf{r}}(t)\varphi_k(\mathbf{r}, t) = \left(\frac{-\nabla^2}{2} + \hat{g}[\rho(t)] + v(\mathbf{r}, t) \right) \varphi_k(\mathbf{r}, t), \quad (19)$$

where $v(\mathbf{r}, t)$ is a given real time-dependent external potential, $\phi_k(\mathbf{r}, t)$ are time-dependent GKS orbitals that obey the standard integrability boundary conditions (sufficiently rapid decay as $r \rightarrow \infty$), for which the time-dependent GKS Hamiltonian $\hat{h}_{\mathbf{r}}(t)$ is Hermitean. The occupied orbitals obey an initial condition of being equal to a set of N orthonormal wave-functions:

$$\varphi_k(\mathbf{r}, t = 0) = \varphi_k^0(\mathbf{r}). \quad (20)$$

The time-dependent DM is defined as

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_{k=1}^N \varphi_k(\mathbf{r}, t) \varphi_k^*(\mathbf{r}', t). \quad (21)$$

Note that the operator $\hat{g}[\rho(t)]$ is “inherited” from the ground-state formalism as is and therefore does not introduce “memory effects”, i.e., does not depend on the history of the DM. Because the Hamiltonian is Hermitean the GKS orbitals remain orthonormal in time and the DM obeys the idempotency condition at each time t :

$$\int \rho(\mathbf{r}, \mathbf{r}', t) \rho(\mathbf{r}', \mathbf{r}'', t) d^3r' = \rho(\mathbf{r}, \mathbf{r}'', t). \quad (22)$$

Furthermore, the diagonal of the DM is the time-dependent particle density

$$n(\mathbf{r}, t) = \rho(\mathbf{r}, \mathbf{r}, t) = \sum_{k=1}^N |\varphi_k(\mathbf{r}, t)|^2 \quad (23)$$

for which the following condition holds at all times t :

$$\int n(\mathbf{r}, t) d^3r' = N. \quad (24)$$

Lastly, we can define the paramagnetic current density in the usual way, as

$$\mathbf{j}_P(\mathbf{r}, t) \equiv Im \sum_{k=1}^N \varphi_k^*(\mathbf{r}, t) \nabla \varphi_k(\mathbf{r}, t), \quad (25)$$

which can also be expressed in terms of the DM:

$$\mathbf{j}_P(\mathbf{r}, t) = Im [\nabla \rho(\mathbf{r}, \mathbf{r}', t)]_{\mathbf{r}=\mathbf{r}'}. \quad (26)$$

In order to use equation (19) and its associated definitions on a rigorous basis, rather than as a naive and unproven extension of the time-independent case, we must address the question of the uniqueness of the potential $v(\mathbf{r}, t)$ given the time-dependent density $n(\mathbf{r}, t)$, as well as its initial state $\varphi_k(\mathbf{r}, t = 0)$. We now show that this question is not trivial and in need of detailed proof and discussion.

3.2 The generalized Runge–Gross Theorem

Consider the evolution of the density in time-dependent GKS, given by equation (19), starting from the same initial state but under the influence of two different time-dependent potentials, $v_1(\mathbf{r}, t)$ and $v_2(\mathbf{r}, t)$, which differ by more than a time-dependent spatial constant. The question before us is whether the corresponding densities $n_1(\mathbf{r}, t)$ and $n_2(\mathbf{r}, t)$ can still be the same. In other words, the question is whether the mapping from potentials $v(\mathbf{r}, t)$ to densities $n(\mathbf{r}, t)$ is invertible. Following the logic of the proof of the original Runge–Gross theorem, we use the paramagnetic current density to show that even when time has only evolved infinitesimally, the answer is yes.

As a first step, we assume that both potentials are Taylor expandable as a function of t around $t = 0$. We consider differences between the two evolving systems, which we denote by δ , i.e., we consider potential differences $\delta v \equiv v_2 - v_1$, density matrix differences $\delta \rho = \rho_2 - \rho_1$, etc. We then claim that the TD-GKS equation shares the following property with the Schrödinger equation: If there exists an integer $m \geq 0$, such that $\frac{\partial^j}{\partial t^j} (\delta v(\mathbf{r}, t))_{t=0}$ is a spatial constant for $j = 1, \dots, m-1$ while $\frac{\partial^m}{\partial t^m} (\delta v(\mathbf{r}, t))_{t=0}$ is not a spatial constant, then $\left(\frac{\partial^{(m+1)}}{\partial t^{(m+1)}} \delta \mathbf{j}_P(\mathbf{r}, t) \right)_{t=0}$ is non-zero.

The proof of this Lemma is based on induction. Let us first consider the case $m = 0$. To compute the first time-derivative of the current, we note that by deriving equation (21) while using equation (19) we obtain:

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, \mathbf{r}', t) = i \left(\hat{h}_{\mathbf{r}}(t) - \hat{h}_{\mathbf{r}'}(t) \right) \rho(\mathbf{r}, \mathbf{r}', t). \quad (27)$$

Furthermore the initial condition

$$\delta\rho(\mathbf{r}, \mathbf{r}', t=0) = 0, \quad (28)$$

means that $\delta n(t=0) = 0$ and therefore:

$$\delta\hat{h}_{\mathbf{r}}(0) = \delta v(\mathbf{r}, 0). \quad (29)$$

Hence

$$\left(\frac{\partial}{\partial t}\delta\rho(\mathbf{r}, \mathbf{r}', t)\right)_{t=0} = i(\delta v(\mathbf{r}, 0) - \delta v(\mathbf{r}', 0))\rho(\mathbf{r}, \mathbf{r}', 0) \quad (30)$$

Using equation (26), the time derivative of the current density difference at $t=0$ is then:

$$\frac{\partial}{\partial t}(\delta\mathbf{j}_P(\mathbf{r}, t))_{t=0} = n(\mathbf{r}, 0)\nabla\delta v(\mathbf{r}, 0). \quad (31)$$

Hence, if $\nabla\delta v(\mathbf{r}, 0) \neq 0$, i.e. $\delta v(\mathbf{r}, 0) \neq c(0)$, then $\frac{\partial}{\partial t}(\delta\mathbf{j}_P(\mathbf{r}, t))_{t=0} \neq 0$ and the proof for $m=0$ is concluded.

Let us now assume that $m=1$, i.e., $(\delta v(\mathbf{r}, t))_{t=0} = c(0)$ but $\frac{\partial}{\partial t}(\delta v(\mathbf{r}, t))_{t=0} \neq c'(0)$. Under these assumptions $\delta v(\mathbf{r}, 0) - \delta v(\mathbf{r}', 0) = 0$ and therefore

$$\delta\hat{h}_{\mathbf{r}}(0) = \delta\hat{h}_{\mathbf{r}'}(0). \quad (32)$$

From equation (30)

$$\left(\frac{\partial}{\partial t}\delta\rho(\mathbf{r}, \mathbf{r}', t)\right)_{t=0} = 0, \quad (33)$$

which leads to

$$\left(\frac{\partial}{\partial t}\delta\hat{g}[\rho(t)]\right)_{t=0} = 0, \quad (34)$$

from which necessarily

$$\left(\frac{\partial}{\partial t}\delta\hat{h}_{\mathbf{r}}(t)\right)_{t=0} = (\delta\dot{v}(\mathbf{r}, t))_{t=0}. \quad (35)$$

This now allows us to consider the next derivative of the DM:

$$\begin{aligned} \frac{\partial^2}{\partial t^2}\rho(\mathbf{r}, \mathbf{r}', t) &= i(\dot{\hat{h}}_{\mathbf{r}}(t) - \dot{\hat{h}}_{\mathbf{r}'}(t))\rho(\mathbf{r}, \mathbf{r}', t) \\ &\quad + i(\hat{h}_{\mathbf{r}}(t) - \hat{h}_{\mathbf{r}'}(t))\dot{\rho}(\mathbf{r}, \mathbf{r}', t), \end{aligned} \quad (36)$$

from which, using equations (28), (32), and (33) we deduce that the DM difference at $t=0$ obeys

$$\left(\frac{\partial^2}{\partial t^2}\delta\rho(\mathbf{r}, \mathbf{r}', t)\right)_{t=0} = i(\delta\dot{v}(\mathbf{r}, 0) - \delta\dot{v}(\mathbf{r}', 0))\rho(\mathbf{r}, \mathbf{r}', 0). \quad (37)$$

Hence, from equation (19) the second derivative of the current density difference is:

$$\frac{\partial^2}{\partial t^2}\delta\mathbf{j}_P(\mathbf{r}, t)_{t=0} = (\nabla_{\mathbf{r}}\delta\dot{v}(\mathbf{r}, 0))n(\mathbf{r}, 0) \quad (38)$$

and thus $\frac{\partial^2}{\partial t^2}(\delta\mathbf{j}_P(\mathbf{r}, t))_{t=0} \neq 0$. The lemma is then fully proven by induction as follows. If we assume that the potential difference is non-zero only in the m^{th} derivative $\frac{\partial^m}{\partial t^m}\delta v(\mathbf{r}, t)$ then

$$\frac{\partial^j}{\partial t^j}\delta\hat{h}_{\mathbf{r}}(0) = 0, \quad j = 0, 1, \dots, m-1 \quad (39)$$

and

$$\frac{\partial^j}{\partial t^j}\delta\rho(\mathbf{r}, \mathbf{r}', 0) = 0, \quad j = 0, 1, \dots, m. \quad (40)$$

The corresponding derivatives of \hat{g} are then also zero and therefore

$$\left(\frac{\partial^m}{\partial t^m}\delta\hat{h}_{\mathbf{r}}(t)\right)_{t=0} = \left(\frac{\partial^m}{\partial t^m}\delta v(\mathbf{r}, t)\right)_{t=0} \neq 0. \quad (41)$$

It is then a matter of straightforward calculus to show that

$$\begin{aligned} \left(\frac{\partial^{m+1}}{\partial t^{m+1}}\delta\rho(\mathbf{r}, \mathbf{r}', t)\right)_{t=0} \\ = i\left(\frac{\partial^m}{\partial t^m}\delta v(\mathbf{r}, t) - \frac{\partial^m}{\partial t^m}\delta v(\mathbf{r}', t)\right)_{t=0}\rho(\mathbf{r}, \mathbf{r}', 0), \end{aligned} \quad (42)$$

from which the current density difference:

$$\frac{\partial^{m+1}}{\partial t^{m+1}}\delta\mathbf{j}_P(\mathbf{r}, t)_{t=0} = \left(\nabla_{\mathbf{r}}\frac{\partial^m}{\partial t^m}\delta v(\mathbf{r}, 0)\right)n(\mathbf{r}, 0), \quad (43)$$

must be different than zero. This concludes the proof.

In the original Runge–Gross theorem, the second step is to show that if $\left(\frac{\partial^{(m+1)}}{\partial t^{(m+1)}}\delta\mathbf{j}_P(\mathbf{r}, t)\right)_{t=0}$ is not zero everywhere then $\left(\frac{\partial^{(m+2)}}{\partial t^{(m+2)}}\delta n(\mathbf{r}, t)\right)_{t=0}$ is not zero everywhere either. We examine this statement in the GKS context by taking the first derivative of the time-dependent density. Using equations (23) and (19) we then obtain:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}_P(\mathbf{r}, t) + 2Im(\hat{g}_{\mathbf{r}}[\rho(t)]\rho(\mathbf{r}, \mathbf{r}', t))_{\mathbf{r}=\mathbf{r}'}. \quad (44)$$

If the second term on the right hand of the above equation is zero, the usual continuity equation is valid. The original proof of Runge and Gross for the relation between $\left(\frac{\partial^{(m+1)}}{\partial t^{(m+1)}}\delta\mathbf{j}_P(\mathbf{r}, t)\right)_{t=0}$ and $\left(\frac{\partial^{(m+2)}}{\partial t^{(m+2)}}\delta n(\mathbf{r}, t)\right)_{t=0}$ [10] can then be used as is and is not repeated here. Our two-step generalization of the Runge–Gross theorem is then complete, because overall if $v_i(\mathbf{r}, t)$ $i = 1, 2$

are two Taylor expandable potentials, leading through equations (19)–(23) to the same density to all orders in the Taylor expansion, i.e. $v_i(\mathbf{r}, t) \rightarrow n(\mathbf{r}, t)$, then necessarily $\delta v(\mathbf{r}, t) \equiv v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t) = c(t)$ where $c(t)$ is a purely time-dependent function. However, equation (44) reveals an important caveat, because in general, $\text{Im}(\hat{g}_{\mathbf{r}}[\rho(t)]\rho(\mathbf{r}, \mathbf{r}', t))_{\mathbf{r}=\mathbf{r}'}$ is not necessarily zero and therefore TD-GKS theory will not necessarily obey a the generalized Runge–Gross theorem. Naturally, mappings that cause additional terms to appear in the continuity equation also cause difficulties in the physical interpretation of single-particle currents and at the very least require a different definition of the paramagnetic current, if at all possible.

3.3 The generalized van Leeuwen theorem

By proving the generalization of the Runge–Gross theorem to time-dependent GKS theory, we have established the uniqueness of the GKS remainder potential, per a given choice of the GKS map. However, we have not established existence, i.e., whether a GKS remainder potential, reproducing the time-dependent density of the original system, can at all be found. Here, we achieve this goal for time-dependent GKS theory by generalizing the van Leeuwen theorem, [19] which (as mentioned in the introduction) has established existence for time-dependent KS theory.

Van Leeuwen’s proof starts by noting that the continuity equation is valid for both the original many-body system and the fictitious system that reproduces its density. As noted above, if the continuity equation is not obeyed the Runge–Gross theorem is not necessarily valid. Therefore, we shall continue to assume here that the continuity equation is obeyed for the time-dependent GKS system. Van Leeuwen’s original proof then proceeds by considering the time-derivative of the current, given as the expectation value of the commutator of the current density operator with the Hamiltonian:

$$\frac{\partial}{\partial t} j_{\alpha}(\mathbf{r}, t) = -n(\mathbf{r}, t) \frac{\partial}{\partial r_{\alpha}} v(\mathbf{r}, t) - i \left\langle \Psi(t) \left| \left[\hat{j}_{\alpha}, \hat{T} + \hat{W} \right] \right| \Psi(t) \right\rangle, \quad (45)$$

where $\alpha = x, y, z$, $v(\mathbf{r}, t)$ is the one-electron potential, \hat{T} and \hat{W} are the many-electron kinetic energy and Coulomb repulsion operators, respectively, and Ψ is the time-dependent many-electron wave function. Combining this equation with the continuity equation, an equation for the second derivative of the density is obtained:

$$\frac{\partial^2}{\partial t^2} n(\mathbf{r}, t) = \nabla \cdot [n(\mathbf{r}, t) \nabla v(\mathbf{r}, t)] + q(\mathbf{r}, t), \quad (46)$$

where

$$q(\mathbf{r}, t) = i \frac{\partial}{\partial r_{\alpha}} \left\langle \Psi(t) \left| \left[\hat{J}_{\alpha}(\mathbf{r}), \hat{T} + \hat{W} \right] \right| \Psi(t) \right\rangle. \quad (47)$$

If one then considers a system with different many-body operators, V' and W' , corresponding to one-electron and two-electron interactions, such that the same time-dependent density is obtained, then an analogous equation (46) is valid also for the new system in the form:

$$\frac{\partial^2}{\partial t^2} n(\mathbf{r}, t) = \nabla \cdot [n(\mathbf{r}, t) \nabla v'(\mathbf{r}, t)] + q'(\mathbf{r}, t), \quad (48)$$

where the prime indicates quantities of the new system. By subtracting equation (48) from equation (46) we obtain:

$$\nabla \cdot [n(\mathbf{r}, t) \nabla \omega(\mathbf{r}, t)] = \zeta(\mathbf{r}, t) \quad (49)$$

where $\omega(\mathbf{r}, t) = v(\mathbf{r}, t) - v'(\mathbf{r}, t)$ and $\zeta(\mathbf{r}, t) = q(\mathbf{r}, t) - q'(\mathbf{r}, t)$. Assuming that the initial state of both systems is such that they share the same density and time-derivative of the density, and assuming that $\omega(\mathbf{r}, t)$ vanishes at infinity, equation (49) can be shown to be a Sturm–Liouville problem possessing a unique solution for $\omega(\mathbf{r}, t)$. This means that given the time-dependent one-electron potential in one system, the time-dependent one-electron potential in the other one exists and can be found.

In the GKS approach, the original many-electron problem is mapped to a system that does not possess a two-body term but instead possesses a non-multiplicative one-body potential term, as in equation (8). This change in the form of the Hamiltonian modifies the form of the commutator of the current density operator with the Hamiltonian. Therefore equations (45)–(47) need to be reformulated for the GKS system. Straightforward algebra shows them to be given by:

$$\frac{\partial}{\partial t} j_{\alpha}(\mathbf{r}, t) = -n(\mathbf{r}, t) \frac{\partial}{\partial r_{\alpha}} v_R(\mathbf{r}, t) - i \left\langle \Psi(t) \left| \left[\hat{j}_{\alpha}, \hat{T} + \hat{G} \right] \right| \Psi(t) \right\rangle, \quad (50)$$

$$\frac{\partial^2}{\partial t^2} n(\mathbf{r}, t) = \nabla \cdot [n(\mathbf{r}, t) \nabla v_R(\mathbf{r}, t)] + q'(\mathbf{r}, t), \quad (51)$$

and

$$q'(\mathbf{r}, t) = i \frac{\partial}{\partial r_{\alpha}} \left\langle \Phi(t) \left| \left[\hat{J}_{\alpha}(\mathbf{r}), \hat{T} + \hat{G} \right] \right| \Phi(t) \right\rangle, \quad (52)$$

where, as before, v_R is the remainder potential and Φ is the Slater-determinant of GKS theory, and \hat{G} is the many-body operator corresponding to the non-multiplicative single-electron operator $\hat{g}[\rho]$. With these modified expressions for the GKS system, equation (49) is still obtained and therefore the existence of its solution is still guaranteed under the same, reasonably mild assumptions. Thus, as long as the continuity equation is obeyed in the GKS system, the van Leeuwen theorem is applicable, and the time-dependent remainder potential of GKS theory is not only guaranteed to be unique (up to a time-dependent constant) but also to exist.

3.4 Implications to special GKS maps

We conclude our presentation of time-dependent GKS theory by revisiting the special GKS schemes surveyed in Section 2.2 above and examining whether the caveat posed by equation (44) and the van Leeuwen theorem, namely the continuity equation, is of concern in practice.

Clearly, in the special case that is the original KS system a non-interacting electron gas is obtained and the continuity equation is trivially obeyed. For a GKS map based on a $\hat{g}_{\mathbf{r}}[\rho]$ that involves exchange integrals we find that:

$$\text{Im}(\hat{g}_{\mathbf{r}}[\rho(t)]\rho(\mathbf{r},\mathbf{r}'))_{\mathbf{r}=\mathbf{r}'} = \text{Im} \int d\mathbf{r}'' \frac{|\rho(\mathbf{r},\mathbf{r}'')|^2}{|\mathbf{r}-\mathbf{r}''|} = 0. \quad (53)$$

This result is easily generalized to a range-separated exchange integral. Therefore, for the important classes of the Hartree–Fock–Kohn–Sham equation, global hybrid functionals, and range-separated hybrid functionals, the continuity equation is obeyed and the generalized Runge–Gross and van Leeuwen theorems are satisfied.

Time-dependent MGGA theory is a more complicated case. It has already been pointed out [35,36] that the construction of a time-dependent MGGA equation based on the non-multiplicative potential of equation (14) leads to an equation that is neither gauge-invariant nor obeying the continuity equation. In the present formalism, this means that the second term in equation (44) is not identically zero. Therefore a further disadvantage of straightforward generalization of MGGA expressions into time-dependent DFT is that it is not protected by the generalized Runge–Gross theorem. Fortunately, using approaches inspired by time-dependent current–density functional theory [37], this can be remedied by replacing the kinetic energy density τ of equation (2) by the expression [35,36]:

$$\tau(\mathbf{r}) - \frac{|\mathbf{j}_P(\mathbf{r},t)|^2}{2n(\mathbf{r},t)}, \quad (54)$$

in all MGGA expressions. Thus, the caveat posed by equation (44) is not at all hypothetical. Its violation indicates difficulties in the definition of the paramagnetic current, [38,39] the resolution of which leads to further development and additional insights [40].

4 Conclusions

In conclusion, we have presented time-dependent generalized Kohn–Sham theory. We started by explaining that GKS theory is the rigorous basis for the use of non multiplicative potentials within DFT, as is the common practice with (conventional or range-separated) hybrid functionals or with meta-generalized-gradient-approximation (meta-GGA) functionals. Furthermore, we explicitly showed how these important classes of approximations can be derived from GKS considerations. We then provided a rigorous basis for time-dependent GKS theory. This was accomplished by showing that the Runge–Gross theorem and

the van Leeuwen theorem, which serve as the basis of time-dependent KS theory, apply to GKS theory too if an important caveat – upholding the continuity equation in the GKS electron gas – is met. We showed that this condition is not always obeyed in common GKS schemes and discussed it as a practical means of assessing and/or improving time-dependent GKS-based approximations.

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Author contribution statement

RB and LK developed the theory and wrote the paper jointly.

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