

Critique of the foundations of time-dependent density functional theory

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Abstract

The general expectation that, in principle, the time-dependent density functional theory (TDDFT) be an exact formulation of the time-evolution of an interacting N -electron system is critically reexamined. It is demonstrated that the previous TDDFT foundation, resting on four theorems by Runge and Gross (RG) [Phys. Rev. Lett. 52, 997(1984)], is invalid because undefined phase factors corrupt the RG action integral functionals. Our finding confirms much of a previous analysis by van Leeuwen [Int. J. Mod. Phys. B 15, 1969(2001)].

To analyze the RG theorems and other aspects of TDDFT, an utmost simplification of the KS concept has been introduced, in which the ground-state density is obtained from a single KS equation for one spatial (spin-less) orbital. The time-dependent (td) form of this radical Kohn-Sham (rKS) scheme, which has the same validity status as the ordinary KS version, has proved to be a valuable tool for analysis. The rKS concept is used to clarify also the alternative non-variational formulation of td KS theory. We argue that it is just a formal theory, allowing one to reproduce, but not predict the time-development of the exact density of the interacting N -electron system.

Besides the issue of the formal exactness of TDDFT, it is shown that both the static and time-dependent KS linear response equations neglect the particle-particle (p - p) and hole-hole (h - h) matrix elements of the perturbing operator. For a local (multiplicative) operator this does not lead to a loss of information due to a remarkable general property of local operators. Accordingly, no logical inconsistency arises with respect to DFT, because DFT requires any external potential to be local. For a general non-local operator the error resulting from the neglected matrix elements is of second order in the electronic repulsion.

I. INTRODUCTION

Over the last decade, time-dependent density functional theory (TDDFT) has become an extremely popular method to compute electronic excitation energies and response properties of ever bigger molecules and clusters (see, for example, Refs. [1–3]). The method and its foundations were already worked out in the nineteen eighties, primarily in papers by Zangwil and Soven [4], Runge and Gross [5], and Gross and Kohn [6]. More recently, various efficient computer codes have been developed [7–12] and made available as parts of major quantum chemistry program packages. At present, one witnesses intense activities worldwide aiming both at the further development of methodological aspects and the computational efficiency of the codes.

Besides the relatively modest computational expense, a major boost for the advancement of the method has been the assurance that TDDFT is a formally exact theory [13–15], that is, the TDDFT results would become exact if the exact time-dependent exchange-correlation (xc) potentials were available. In practice, of course, one always has to use approximate xc potentials, and therefore one has to be prepared for smaller or larger errors in the computational results. There is a widely held confidence that any problems encountered with the TDDFT method are only caused by imperfections of the underlying xc potentials, a belief prevailing even as some more severe problems became apparent, such as in the description of Rydberg excitations [10, 16], the treatment of extended π systems [17], the absence of double (and higher) excitations [18, 19], and the $1/R$ dependence of charge-transfer (CT) excitation energies [20–23]. These failures have triggered efforts to modify the xc potentials accordingly and thereby remedy the respective problems. Most of this work has been confined to the so-called adiabatic approximation, in which the time-dependence enters the xc functionals only via the time-dependent (td) density functions. But also the development of time- or energy-dependent xc functionals beyond the adiabatic approximation [19, 24, 25] has been envisaged.

On the other hand, TDDFT has never obtained a similarly accepted status of uncontested validity as the original (time-independent) density functional theory (DFT) developed by Hohenberg and Kohn (HK) [26] and by Kohn and Sham (KS) [27]. The foundations of TDDFT, as formulated by Runge and Gross (RG) in Ref. [5], have been constructed largely in terms analogous to the HK and KS concepts of DFT. However, elusive notions such as

td v -representability and non-interacting v -representability were clearly in need of further mathematical clarification [28–30]. More recently, the RG foundations of TDDFT were challenged by Rajagopal [31], van Leeuwen [32], and Harbola and Banerjee [33], after it was realized that the kernel of the xc functional in the RG formulation violates causality [34, 35]. A critical review of the RG action integral functionals by van Leeuwen [32, 36] revealed basic deficiencies. Presently, an alternative formulation of TDDFT, being essentially a KS-type approach without implying a variational principle of the HK type, is viewed as a valid foundation [34, 36–38].

In this paper we will take a new look at the foundations of TDDFT. For our review we use a simple analytical device, referred to as radical Kohn-Sham (rKS) formulation, which is as legitimate as the usual N -electron KS theory. Not obscured by intricacies such as td v -representability etc., the rKS concept allows us to analyze both the static DFT and TDDFT in an utmost transparent way. What we find, confirms van Leeuwen’s criticism of the RG foundation of TDDFT, but also proves the non-variational form of TDDFT illusory.

An outline of the paper is as follows. The starting point of our study (Sec. 2) is the observation that the TDDFT equations, more specifically, the time-dependent Kohn-Sham (KS) linear response (LR) equations, neglect matrix elements of the perturbing (external) potential of the h - h or p - p type, where h and p refer to occupied (hole) and unoccupied (particle) KS orbitals, respectively. Because the exact linear response depends on all matrix elements, the TDDFT results appear to be deficient irrespective of the choice of the xc potential. The same situation arises in the case of a static (time-independent) perturbation, as is analyzed in Sec. 3. Here the problem would even challenge the well-founded (time-independent) DFT. The resolution of that puzzle in Sec. 3 is a very instructive confirmation of the logical consistency of DFT. In Sec. 4 we introduce the rKS concept, in which the GS density is not determined from the density of N non-interacting electrons, but from a single KS equation for one (spin-less) particle. In Sec. 5 the rKS formulation is used to analyze the RG theorems and other aspects of TDDFT. A reader primarily interested in the issue of the validity of TDDFT might skip Secs. 2 and 3 and leap directly to Sec. 4. A summary of our results and some conclusions are given in the final Sec. 6.

II. COMPARISON OF EXACT AND KOHN-SHAM LINEAR RESPONSE

The TDDFT formalism has been presented in various ways in previous work [8, 12, 13, 15, 39] where the reader is referred to for an overview and further details. Because TDDFT (in linear response form) is similar to the time-dependent Hartree-Fock (TDHF) or random-phase approximation (RPA) [40–42], it is rewarding to consult also previous TDHF derivations (see, for example, Ring and Schuck [43]). A few basic notions pertinent to the ensuing discussion will be given in the following.

For an N -electron system (atom or molecule) having a non-degenerate ground state $|\Psi_0\rangle$ the (exact) ground state (GS) density matrix, γ , is given by

$$\gamma_{pq} = \langle \Psi_0 | c_q^\dagger c_p | \Psi_0 \rangle \quad (1)$$

Here the second-quantized operators $c_p^\dagger(c_p)$ are associated with one-particle states (spin-orbitals) ϕ_p . As a particular choice, we will consider the KS orbitals arising from the KS one-particle equations associated with the ground state of the system under consideration,

$$h^{KS}\phi_i(\mathbf{r}, s) = \left\{ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + J[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}) \right\} \phi_i(\mathbf{r}, s) = \epsilon_i \phi_i(\mathbf{r}, s) \quad (2)$$

Here \mathbf{r} and s denote spatial and spin variables, respectively, $v(\mathbf{r})$ is the one-particle operator for the electron-nuclei interaction, $J[\rho](\mathbf{r})$ is the Coulomb operator, and $v_{xc}[\rho](\mathbf{r})$ is the KS exchange-correlation potential. The exact GS density function, $\gamma(\mathbf{r})$, is obtained from the density matrix elements (1) according to

$$\gamma(\mathbf{r}) = \sum_{p,q} \sum_s \gamma_{qp} \phi_p^*(\mathbf{r}, s) \phi_q(\mathbf{r}, s) \quad (3)$$

By contrast to the exact density matrix, the KS density matrix, ρ , is derived from the KS determinant

$$|\Phi_0^{KS}\rangle = |\phi_1 \dots \phi_N| \quad (4)$$

according to

$$\rho_{pq} = \langle \Phi_0^{KS} | c_q^\dagger c_p | \Phi_0^{KS} \rangle \quad (5)$$

In the KS orbital representation assumed here the KS density matrix assumes the simple diagonal form

$$\rho_{pq} = \delta_{pq} n_p \quad (6)$$

where $n_p = 0, 1$ denote KS occupation numbers. The KS density function,

$$\rho(\mathbf{r}) = \sum_{p,q} \sum_s \rho_{qp} \phi_p^*(\mathbf{r}, s) \phi_q(\mathbf{r}, s) = \sum_k \sum_s |\phi_k(\mathbf{r}, s)|^2 n_k \quad (7)$$

is devised to reproduce the exact density function, that is, $\gamma(\mathbf{r}) \equiv \rho(\mathbf{r})$, provided the correct exchange-correlation potential is used in Eq. (2). Whereas, at least in principle, the exact and KS density functions are identical, the density matrices necessarily must differ. As is well recognized (see, for example, [13, 15]), the two entities differ with respect to a basic property: the KS density matrix, deriving from a single determinantal wave function, is idempotent, that is, $\rho^2 = \rho$, whereas the exact density matrix is not, $\gamma^2 \neq \gamma$.

To discuss the linear response (LR) theory let us consider an additional time-dependent (td) external (“driving”) potential of the form

$$\hat{u} = \hat{d} f(t) \quad (8)$$

where $\hat{d} = d(\mathbf{r})$ is a local (multiplicative) operator and $f(t)$ is a scalar time dependent function (vanishing for $t < 0$). In the notation of second quantization, the corresponding N -electron operator, $\hat{D} = \sum_i^N \hat{d}(i)$, can be written as

$$\hat{D} = \sum_{r,s} d_{rs} c_r^\dagger c_s \quad (9)$$

where $d_{rs} = \langle \phi_r | \hat{d} | \phi_s \rangle$ denote the one-particle matrix elements of \hat{d} . Now let us distinguish particle-hole (p - h) and h - p matrix elements, d_{ak}, d_{ka} , from p - p and h - h elements, d_{ab}, d_{kl} . Here and in the following we use the notation in which the subscripts a, b, c, \dots and i, j, k, \dots denote unoccupied (virtual) and occupied KS orbitals, respectively, while the subscripts p, q, r, \dots refer to the general case. As will be discussed below, the KS linear response contribution to the density depends only on the p - h (and h - p) matrix elements of the driving potential, whereas the exact linear response contribution is a linear function of all matrix elements.

Let us first inspect the exact case. Upon Fourier transformation the linear response of the exact density matrix can be written as (see, for example, [44])

$$\delta\gamma_{pq}(\omega) = \sum_{n \neq 0} \frac{\langle \Psi_0 | c_q^\dagger c_p | \Psi_n \rangle \langle \Psi_n | \hat{D} | \Psi_0 \rangle}{\omega - E_n + E_0 + i\eta} - \frac{\langle \Psi_0 | \hat{D} | \Psi_n \rangle \langle \Psi_n | c_q^\dagger c_p | \Psi_0 \rangle}{\omega + E_n - E_0 + i\eta} \quad (10)$$

Here $|\Psi_n\rangle$ and E_n denote excited energy eigenstates and eigenvalues of the original (undisturbed) Hamiltonian \hat{H} ; the complex infinitesimal $i\eta$ is required for the definiteness of the

Fourier transforms between the time and energy domain. For the special operator \hat{D} considered here, the transition moments appearing in the numerators on the right-hand side of Eq. (10) take on the form

$$\langle \Psi_n | \hat{D} | \Psi_0 \rangle = \sum_{p,q} d_{pq} \langle \Psi_n | c_p^\dagger c_q | \Psi_0 \rangle \quad (11)$$

and it is obvious that the p - p and h - h contributions, $\langle \Psi_n | c_a^\dagger c_b | \Psi_0 \rangle$ and $\langle \Psi_n | c_k^\dagger c_l | \Psi_0 \rangle$, need not vanish. Using many-body perturbation theory (MBPT) for $|\Psi_0\rangle$ and $|\Psi_n\rangle$ based on the familiar Møller-Plesset decomposition of \hat{H} (and adopting for a moment Hartree-Fock (HF) one-particle states) one may readily establish that non-vanishing contributions appear for the first time in second order. For example, one finds

$$\langle \Psi_n | c_a^\dagger c_b | \Psi_0 \rangle = O(2) \quad (12)$$

for single excitations deriving from the HF configurations $c_a^\dagger c_j | \Phi_0^{HF} \rangle$. An analogous result is found in the case of the h - h amplitudes. Moreover, the exact response comprises contributions arising from double (and higher) excitations, the corresponding p - p and h - h amplitudes being here even of first order.

Now let us turn to the KS response theory. In the formulation given by Gross and Kohn [6] (adopting here a slightly deviating notation) the linear response to the KS density function is given by

$$\delta\rho(\mathbf{r}, \omega) = \int \chi(\mathbf{r}, \mathbf{r}'; \omega) v_1^{eff}(\mathbf{r}', \omega) d\mathbf{r}' \quad (13)$$

Here

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{pq} \sum_{s,s'} (n_p - n_q) \frac{\phi_p^*(\mathbf{r}, s) \phi_q(\mathbf{r}, s) \phi_q^*(\mathbf{r}', s') \phi_p(\mathbf{r}', s')}{\omega - \epsilon_q + \epsilon_p + i\delta} \quad (14)$$

is referred to as the KS density-density response function and

$$v_1^{eff}(\mathbf{r}, \omega) = u(\mathbf{r}, \omega) + J[\delta\rho](\mathbf{r}) + \delta v_{xc}(\mathbf{r}, \omega) \quad (15)$$

is the first-order effective potential comprising the (Fourier transformed) external perturbation of Eq. (8), the (first-order) change of the Coulomb potential, $J[\delta\rho](\mathbf{r})$, and of the xc potential, $\delta v_{xc}(\mathbf{r}, \omega)$, the latter two contributions being linear expressions in $\delta\rho(\mathbf{r}, \omega)$.

Inserting the first part of $v_1^{eff}(\mathbf{r}, \omega)$, that is, the “driving” potential, $u(\mathbf{r}, \omega)$, in the rhs

of Eq. (13) yields

$$\int \chi(\mathbf{r}, \mathbf{r}'; \omega) u(\mathbf{r}', \omega) d\mathbf{r}' = \sum_{a,k} \sum_s \left(\frac{\phi_k^*(\mathbf{r}, s) \phi_a(\mathbf{r}, s)}{\omega - \epsilon_a + \epsilon_k + i\delta} d_{ak} - \frac{\phi_a^*(\mathbf{r}, s) \phi_k(\mathbf{r}, s)}{\omega + \epsilon_a - \epsilon_k + i\delta} d_{ka} \right) f(\omega) \quad (16)$$

Obviously, here the p - p and h - h matrix elements of \hat{d} have been projected out and only p - h (and h - p) matrix elements, d_{ak} , enter (as inhomogeneities) the linear KS response equations. As we have seen, the exact linear response to the density function, $\delta\gamma(\mathbf{r}, \omega)$, which may be written in a form analogous to Eq. (13),

$$\delta\gamma(\mathbf{r}, \omega) = \int \bar{\chi}(\mathbf{r}, \mathbf{r}'; \omega) u(\mathbf{r}', \omega) d\mathbf{r}' \quad (17)$$

is a linear function of all matrix elements, d_{pq} , of the perturbing potential. Here the exact density-density response function [6], $\bar{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$, is related to $\delta\gamma$ of Eq. (10) according to

$$\int \bar{\chi}(\mathbf{r}, \mathbf{r}'; \omega) d(\mathbf{r}') d\mathbf{r}' = \sum_{p,q} \sum_s \delta\gamma_{pq}(\omega) \phi_q^*(\mathbf{r}, s) \phi_p(\mathbf{r}, s) \quad (18)$$

This result evokes the question if equating $\delta\rho(\mathbf{r}, \omega)$ and $\delta\gamma(\mathbf{r}, \omega)$ is permitted at all. It seems that in the KS linear response equations the information associated with the p - p and h - h matrix elements of the external (driving) potential is lost and, thus, these equations have to be viewed as an approximation even in the case of an exact exchange correlation potential.

Let us inspect the situation in the more general and transparent matrix formulation of TDDFT (see, for example, [12, 15]). Here the KS response equations are written in the form of a matrix commutator relation,

$$\omega \delta\rho = [\mathbf{h}, \delta\rho] + [\delta\mathbf{h}, \rho] + [\mathbf{d}, \rho] \quad (19)$$

where \mathbf{h} and \mathbf{d} denote the matrix representations of the (unperturbed) KS Hamiltonian and the perturbing potential (time-independent part), respectively, and $\delta\mathbf{h}$ is the change of the KS Hamiltonian linear in $\delta\rho$. Note that due to the form of ρ the commutator $[\mathbf{d}, \rho]$ on the rhs of Eq. (19) projects out the p - p and h - h matrix elements of \mathbf{d} . Arranging the p - h and h - p matrix elements of $\delta\rho$ and of \hat{d} in columns (vectors),

$$\delta\underline{\rho} = \begin{pmatrix} \delta\rho_{ph} \\ \delta\rho_{hp} \end{pmatrix}, \quad \underline{d} = \begin{pmatrix} d_{ph} \\ d_{hp} \end{pmatrix} \quad (20)$$

the linear response equation for $\delta\rho$ takes on the familiar RPA form,

$$\begin{pmatrix} \omega - \mathbf{A} & -\mathbf{B} \\ -\mathbf{B}^* & -\omega - \mathbf{A}^* \end{pmatrix} \delta\rho = \underline{d} \quad (21)$$

The elements of the matrices \mathbf{A} and \mathbf{B} , being related to the functional derivatives of the Coulomb and xc potentials of the KS Hamiltonian, have been specified elsewhere (see, for example, Ref. [7], and Sec. 3). The information on the perturbing external potential enters the response equations (21) only via the vector \underline{d} . Thus, it is manifest that only the p - h and h - p matrix elements of the perturbing potential come into play. Does the neglect of the h - h and p - p matrix elements of the perturbing operator mean that TDDFT is not formally exact? The same problem occurs in the case of a time-independent (static) perturbation, and here it would even challenge the logical consistency of DFT itself, more specifically, the universality of the HK energy functionals. In the next Sec. 3 we will consider the static case and see how the apparent contradiction to the universality of the DFT functionals can be resolved.

III. TIME-INDEPENDENT KOHN-SHAM RESPONSE THEORY

In this section we consider the problem of the loss of the h - h and p - p matrix elements in the simpler static case of a (small) time-independent external perturbation, \hat{u} .

The linear KS response equations are obtained here as a special case ($\omega = 0$) of the more general time-dependent equations (19):

$$[\mathbf{h}, \delta\rho] + [\delta\mathbf{h}, \rho] + [\mathbf{u}, \rho] = \mathbf{0} \quad (22)$$

Likewise, these equations can be deduced via first-order perturbation theory for the ground state KS orbital, also referred to as coupled-perturbed Kohn-Sham (CPKS) theory (see Casida[13] and references therein). As above \mathbf{h} and \mathbf{u} denote the matrix representations of the unperturbed KS Hamiltonian and the perturbing potential, respectively. The KS density matrix, ρ , associated with the unperturbed ground state is diagonal, $\rho_{pq} = \delta_{pq}n_p$; $\delta\rho$ denotes the first-order change in the KS density matrix. Finally, $\delta\mathbf{h}$ is the matrix representation of the linear change of the KS Hamiltonian,

$$\delta h = J[\delta\rho](\mathbf{r}) + \delta v_{xc}(\mathbf{r}) \quad (23)$$

A basic assumption of the KS linear response theory is that the xc part of δh can be expanded according to

$$\delta v_{xc} = v_{xc}[\rho + \delta\rho] - v_{xc}[\rho] = \int \frac{\delta v_{xc}[\rho](\mathbf{r})}{\delta\rho(\mathbf{r}')} \delta\rho(\mathbf{r}') d\mathbf{r}' + O(\delta\rho^2) \quad (24)$$

in terms of $\delta\rho$ (and, possibly, gradients, $\nabla\delta\rho$, and higher derivatives). Here $\delta\rho$ is related to the first-order density matrix, $\delta\rho$, according to

$$\delta\rho(\mathbf{r}) = \sum_{a,k} \sum_s \{ \phi_k^*(\mathbf{r}, s) \phi_a(\mathbf{r}, s) \delta\rho_{ak} + \phi_a^*(\mathbf{r}, s) \phi_k(\mathbf{r}, s) \delta\rho_{ka} \} \quad (25)$$

Proceeding in the usual way, one now may evaluate the p - h and h - p matrix elements of δh ,

$$(\delta\mathbf{h})_{pq} = \int \delta h(\mathbf{r}) \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) d\mathbf{r} \quad (26)$$

which leads to linear expressions in the density matrix elements $\delta\rho_{rs}$:

$$(\delta\mathbf{h})_{pq} = \sum_{rs} M_{pq,rs} \delta\rho_{rs} \quad (27)$$

Here the index pairs, (pq) or (rs), are either of p - h or h - p type. Finally, introducing $\delta\mathbf{h}$ in that form in Eq. (22) one arrives at the desired KS linear response equations, reading in matrix form analogous to Eqs. (20,21),

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \underline{\delta\rho} = -\underline{u} \quad (28)$$

Here, the matrix elements of \mathbf{A} and \mathbf{B} are given by

$$A_{ak,bl} = (\epsilon_a - \epsilon_k)\delta_{ab}\delta_{kl} + M_{ak,bl}, \quad B_{ak,lb} = M_{ak,lb} \quad (29)$$

As in Eq. (20), the p - h and h - p matrix elements of $\delta\rho$ and u are arranged to form column vectors,

$$\underline{\delta\rho} = \begin{pmatrix} \delta\rho_{ph} \\ \delta\rho_{hp} \end{pmatrix}, \quad \underline{u} = \begin{pmatrix} u_{ph} \\ u_{hp} \end{pmatrix} \quad (30)$$

As in the td case, the perturbation enters the set of linear equations via the inhomogeneity vector, \underline{u} , in which the p - p and h - h matrix elements of \hat{u} are absent.

It appears that we are facing a paradox here: on the one hand, we have just applied a valid first-order perturbation theory to the density within the KS framework arriving at a seemingly deficient result; on the other hand, the full solution of the KS eigenvalue problem for the perturbed Hamiltonian must yield the exact density, so that also the result of first-order perturbation theory cannot be incorrect. The answer to this puzzle is that no information on the perturbing potential is lost in the absent p - p and h - h matrix elements provided that the perturbation is a local (multiplicative) operator [45]. This is due to a remarkable, though apparently not widely known property of local operators which may be stated as follows:

Theorem 1. A local operator, $v = v(\mathbf{r})$, is uniquely determined up to a constant by its p - h (and h - p) matrix elements with respect to a complete one-particle basis and an arbitrary partitioning of that basis into occupied (hole) and unoccupied (particle) one-particle states. A simple proof of this assertion is given in the Appendix. An interesting aspect here is that the proof assures merely the uniqueness (up to a constant) of the local operator but does not offer a way to reproduce the operator from its p - h matrix elements. It seems that for such a reconstruction one needs one of the diagonal blocks, that is, either h - h or p - p , in addition to the p - h block. Thus, the logical status of theorem 1 resembles that of the HK

and KS theorems which prove the existence of universal xc functionals but do not provide for means to construct the functionals.

Theorem 1 assures that the loss of the p - p and h - h matrix elements in the CPKS equations is no contradiction to the formal exactness of the theory, provided that the external potentials are local (multiplicative). Clearly, this observation applies also to the td KS linear response considered in Sec. 2. The restriction to local external (one-particle) potentials is a basic and well understood consistency requirement of DFT. The universality of the kinetic energy and xc functionals hinges on the condition that the external potential functionals are of the form

$$E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (31)$$

It should be recalled that quantum theory is essentially non-local, and many physically important interactions are not of the local type. For example, the interaction of electrons with an electromagnetic field involves the momentum operators, $\underline{p}_j = -i\nabla_j$. It is common practice, to apply the usual CPKS and TDDFT methods also for non-local external potentials (see, for example, [46–48]). In that case one should be aware that the loss of the p - p and h - h matrix elements of the external operator introduces indeed an error beyond the approximation for the functional, which is of second order in the Coulomb repulsion. In the td KS linear response this error affects only the transition moments. In particular, it destroys the equivalence between the so-called length and velocity forms of the transition moments, because the former is associated with a local operator and the latter with a non-local operator.

In principle, DFT can be extended to account for non-local external potentials as well. For this purpose the non-local potential must be incorporated “a priori” into the HK and KS formalism, that is, the HK and KS functionals have to be defined from the outset for the N -electron system under the action of the external potential. This would lead to modified functionals being now specific to the considered non-local potential. In other words, the functionals would depend on the respective non-local external potentials. An important example for the necessity to deal with non-local operators is the presence of magnetic fields. As a systematic approach referred to as current density functional theory (CDFT) one here considers functionals that depend not only on the density but also on the current density [49–51]. As another possibility of dealing with non-local external potentials, Gilbert [52] and Levy [53] have considered density-matrix dependent functionals.

Let us briefly inspect how the CPKS equations will change if the the xc potential depends directly on a non-local perturbing potential, u . Obviously, this would lead to an additional contribution to δh of the form

$$\delta\tilde{v}_{xc} = w[\rho, u](\mathbf{r}) \quad (32)$$

and, thus, to another inhomogeneity term in the linear response equation (28). Here ρ is the unperturbed GS density. Because the additional inhomogeneity contribution depends on u , the full information on u can be restored, reconciling the (first-order) result of the KS linear response with the exact result.

As a more general aspect, the non-local potential problem shows that the CPKS equations, while justified as a valid first-order perturbation theory for the KS approach to determine the ground state density of the system plus perturbation, may not be seen as physical response equations for the interacting N -electron system (in that case they should apply also to non-local perturbations). This admonishes us to be wary of the prospect that the td KS equations can describe the time evolution of the system in response to a td perturbation.

IV. A RADICAL KOHN-SHAM VERSION

The KS formulation is a clever way to transform the problem of finding the density minimizing the HK functional into the determination of the ground state of an associated non-interacting N -particle system. While providing a good basis for practical computational schemes, the usual KS formulation still does not achieve its full theoretical potential. In fact, one may proceed to a radical KS approach, in which the mapping of the exact density is not onto that of a non-interacting N -particle system but rather to the density of a single particle. Whereas such a radical KS formulation will be less suitable as a starting point for the approximate treatment of the exact ground state density, it may serve as a valuable analytical tool to clarify various aspects of DFT and, in particular, TDDFT. It should be noted that the idea of such an obvious extension of the usual KS approach is not new, though apparently little known. Already in 1984 it was used by Levy *et al.* [54] to discuss asymptotic properties of the xc potential.

In the usual (N -particle) KS formulation the kinetic energy contribution, $T[\rho]$, to the HK functional is substituted by the kinetic energy functional

$$T_S[\rho] = \sum_{i,s} \int \psi_i^*(\mathbf{r}, s) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r}, s) d\mathbf{r} \quad (33)$$

of a non-interacting N -particle system, the density being obtained according to

$$\rho(\mathbf{r}) = \sum_k \sum_s \psi_k^*(\mathbf{r}, s) \psi_k(\mathbf{r}, s) \quad (34)$$

as the density function associated with the Slater determinant $|\Phi\rangle = |\psi_1\psi_2\dots\psi_N|$ of orthonormal orbitals $\psi_i, i = 1, \dots, N$. As is well-known, the functional (33) can be made unambiguous using the Levy constrained search (LCS) definition [53] (see also Parr and Yang [55]):

$$T_S[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | -\frac{1}{2} \sum \nabla_i^2 | \Phi \rangle \quad (35)$$

where $\Phi \rightarrow \rho$ indicates that the search is over all Slater determinants yielding the given density ρ .

The deviation between the exact and the KS kinetic energy is accounted for in the KS exchange-correlation functional,

$$E_{xc}[\rho] = F_{HK}[\rho] - T_S[\rho] - J[\rho] \quad (36)$$

where

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \quad (37)$$

is the original HK functional (supposing here again the rigorous LCS definition); $J[\rho]$ denotes the classical electronic repulsion energy. Now the task of finding the minimum of the total energy functional,

$$E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} = E[\rho\{\psi_i\}] \quad (38)$$

under the constraint $\int \rho(\mathbf{r})d\mathbf{r} = N$ can be performed in orbital space (see Parr and Yang [55]). The corresponding variational procedure yields the well-known KS equations for the ground-state of a system of N non-interacting electrons moving in the effective potential

$$v^{eff}[\rho](\mathbf{r}) = v(\mathbf{r}) + J[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}) \quad (39)$$

where

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (40)$$

is the KS exchange-correlation potential. In this derivation a direct variation with respect to the orbitals ψ_i is implied for the explicit KS kinetic energy functional (first term on the r.h.s. of Eq. 38), whereas the chain rule $\delta/\delta\psi_i = \delta/\delta\rho \delta\rho/\delta\psi_i$ is used for the other terms. This is reflected in the more precise form, $E[\psi_i] = T_S[\psi_i] - T_S[\rho\{\psi_i\}] + E[\rho\{\psi_i\}]$, advocated for the functional underlying the KS equations (see Levy and Perdew [56]).

Let us emphasize that $v^{eff}[\rho](\mathbf{r})$ is a potential-functional, and Eqs. (39,40) have to be solved self-consistently. Self-consistency will be attained for the exact ground-state density, ρ_0 , where the KS equations with the potential $v^{eff}[\rho_0](\mathbf{r})$ reproduce ρ_0 .

As this rigorous derivation of the KS equations shows, there is nothing that would compel a density representation associated with N non-interacting electrons: any number of non-interacting electrons will be permissible, even $N = 1$. Indeed, we will demonstrate in the following how the entire line of arguments can readily be transferred to the representation of the density in terms of a single (spinless) particle.

Obviously, any N-electron (ground-state) density function, $\rho(\mathbf{r})$, can be represented by a one-particle wave function (orbital) according to

$$\rho(\mathbf{r}) = N|\phi(\mathbf{r})|^2 \quad (41)$$

where

$$\phi(\mathbf{r}) = \left(\frac{\rho(\mathbf{r})}{N}\right)^{1/2} \quad (42)$$

Such a representation is unique as long as $\rho(\mathbf{r}) \geq 0$ and $\rho(\mathbf{r}) \neq 0$ for finite values of $|\mathbf{r}|$. Obviously, this defines directly (that is, without invoking the concept of non-interacting v-representability) a 1-1 mapping of density functions and (real) orbitals. Next we can define a corresponding kinetic energy functional:

$$\tilde{T}_S[\rho] = N \int \phi(\mathbf{r})(-\frac{1}{2}\nabla^2)\phi(\mathbf{r}) d\mathbf{r} \quad (43)$$

Since the (real) orbital $\phi(\mathbf{r})$ is uniquely defined by $\rho(\mathbf{r})$, so is the kinetic energy. One may note that this is the well-known von Weizsäcker functional [57].

It is readily seen that this definition is consistent with the Levy constrained search procedure. The general form of an orbital reproducing the density $\rho(\mathbf{r})$ according to Eq. (41) reads

$$\psi(\mathbf{r}) = e^{ik(\mathbf{r})}\phi(\mathbf{r}) \quad (44)$$

where $k(\mathbf{r})$ is a real function. Clearly, the kinetic energy of ψ ,

$$\langle \psi | -\frac{1}{2}\nabla^2 | \psi \rangle = \frac{1}{2} \int (\nabla k(\mathbf{r}))^2 \phi(\mathbf{r})^2 d\mathbf{r} + \langle \phi | -\frac{1}{2}\nabla^2 | \phi \rangle \quad (45)$$

is larger than the kinetic energy of the real orbital ϕ , if $k(\mathbf{r}) \neq const.$ This means that the orbital minimizing the kinetic energy functional for a given density is (up to a constant phase) a real function. As a consequence, Eq. (42) relates densities and orbitals, and the kinetic energy functional (43) is uniquely defined at the orbital level. We may elaborate that point somewhat further by considering a system where the KS orbital cannot be chosen real, e.g. in the presence of an external magnetic field. Clearly, an orbital of the general form (44) is not determined by the density alone. In addition, one has to take into account the current density, $\mathbf{j} = \phi^2 \nabla k$, in order to obtain a unique definition of kinetic energy functional, now being a functional of both ρ and \mathbf{j} , at the orbital level. That is why a current density version of DFT must be used in the case of magnetic fields.

The next step is to introduce a correspondingly modified xc functional,

$$\tilde{E}_{xc}[\rho] = T[\rho] + V_{ee}[\rho] - \tilde{T}_S[\rho] - J[\rho] \quad (46)$$

so that the functional for the total energy can be written as

$$E[\rho] = \tilde{T}_S[\rho] + J[\rho] + \tilde{E}_{xc}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} \quad (47)$$

As in the usual KS approach, the variational search for the minimum of $E[\rho]$ under the constraint $\int \rho(\mathbf{r})d\mathbf{r} = N$ can equivalently be effected by a search in the space of (normalized) orbitals $\phi(\mathbf{r})$. The variation of $E[\rho\{\phi\}]$ with respect to $\phi(\mathbf{r})$ via

$$\rho(\mathbf{r}) = N|\phi(\mathbf{r})|^2 \quad (48)$$

leads to the single KS equation

$$\{-\frac{1}{2}\nabla^2 + v^{eff}[\rho](\mathbf{r})\}\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}) \quad (49)$$

for the ground-state of a single particle moving in the effective potential

$$v^{eff}[\rho](\mathbf{r}) = v(\mathbf{r}) + J[\rho](\mathbf{r}) + \tilde{v}_{xc}[\rho](\mathbf{r}) \quad (50)$$

where $\tilde{v}_{xc}[\rho](\mathbf{r})$ is the modified xc potential deriving from $\tilde{E}_{xc}[\rho]$,

$$\tilde{v}_{xc}[\rho](\mathbf{r}) = \frac{\delta\tilde{E}_{xc}[\rho]}{\delta\rho(\mathbf{r})} \quad (51)$$

Obviously, the single GS KS orbital has no direct physical meaning. It may be viewed as a kind of a mean orbital averaged over the $N/2$ spatial KS orbitals of the usual approach.

As the usual KS approach, the radical Kohn-Sham (rKS) formulation, established by Eqs. (48,49) is, in principle, exact. That is, one would obtain the exact ground-state density of the interacting N-electron system provided the exact energy functional were available. Of course, the usual N-electron KS formulation will be a better starting point for the use of approximative functionals, simply because its expression for the kinetic energy, Eq. (33), will give a better approximation to the full kinetic energy than the mean one-orbital term of Eq. (43). The actual benefit of the rKS variant is its potential as an analytical tool, and in the ensuing Sec. 5 we will use that tool to examine the foundations of TDDFT.

Let us emphasize once again that $\tilde{v}_{xc}[\rho](\mathbf{r})$ is a potential-functional and Eqs. (49,50) have to be solved self-consistently to yield the exact GS density, $\rho_0(\mathbf{r})$. As a consequence of the simple structure of the rKS equation (49), the xc potential for the exact GS density, $\rho_0(\mathbf{r})$, can be expressed according to

$$\tilde{v}_{xc}[\rho_0](\mathbf{r}) = \frac{1}{2\sqrt{\rho_0(\mathbf{r})}}\nabla^2\sqrt{\rho_0(\mathbf{r})} - v(\mathbf{r}) - J[\rho_0](\mathbf{r}) + \epsilon \quad (52)$$

Eq. (52) has been used to study features of the exact KS xc potential, such as the asymptotic behaviour [54]. A similar equation, arising in the ordinary KS treatment of 2-electron systems, was used to characterize 2-electron KS xc potentials [58–60].

While the rKS version introduced above is the simplest possible KS-type approach, other variants are conceivable in which the non-interacting system consists of $M = 2$ or more electrons (M might even be larger than N .) For example, in the case $M = 2$ any (reasonable) density can be derived from the KS determinant

$$|\Phi_0^{KS}\rangle = |\phi_{0\alpha}\phi_{0\beta}| \quad (53)$$

for two non-interacting spin- $\frac{1}{2}$ particles in the spin-orbitals, $\phi_{0\gamma} = \phi_0(\mathbf{r})\chi_\gamma(s)$, $\gamma = \alpha, \beta$, where the spatial orbital is given by

$$\phi_0(\mathbf{r}) = \left(\frac{2\rho_0(\mathbf{r})}{N}\right)^{\frac{1}{2}} \quad (54)$$

Whereas the rKS formulation is purely spatial, spin degrees-of-freedom come into play in these M -electron KS variants for $M \geq 2$.

V. REVIEW OF TIME-DEPENDENT DFT

A. Time dependent radical Kohn-Sham theory

Having established the rKS formulation for the static case, we may now use this tool to analyze td density functional theory.

Let us consider a td external potential, $\hat{U}(t) = \sum u(\mathbf{r}_i, t)$, supposed to be static for $t \leq 0$, that is, $u(\mathbf{r}, t) = v(\mathbf{r})$ for $t \leq 0$ and let the system be in the ground state (of the static Hamiltonian) at $t = 0$. The solution of the td N -electron Schrödinger equation,

$$i \frac{\partial}{\partial t} \Psi(t) = \left(\hat{T} + \hat{V} + \hat{U}(t) \right) \Psi(t) \quad (55)$$

where \hat{T} and \hat{V} denote the kinetic energy and the electron repulsion operator, respectively, gives rise to an associated td density function, $\rho = \rho(\mathbf{r}, t)$ with $\rho(\mathbf{r}, 0) = \rho_0(\mathbf{r})$. As in the static case, the time development of the density can be assigned to a td orbital by generalizing Eq. (42):

$$\phi(\mathbf{r}, t) = \left(\frac{\rho(\mathbf{r}, t)}{N} \right)^{1/2} \quad (56)$$

This is trivial. The non-trivial issue is, of course, whether one can establish a Schrödinger-type equation at the single-orbital level that would allow one to *predict* the time-development of the density. Because inevitably any (non-stationary) wave function evolving according to a td Schrödinger equation picks up a time- and space-dependent phase, the orbital must be written in the general form,

$$\psi(\mathbf{r}, t) = e^{ik(\mathbf{r}, t)} \phi(\mathbf{r}, t) \quad (57)$$

where $k(\mathbf{r}, t)$ is a real-valued phase function, and $\phi(\mathbf{r}, t)$ is given by Eq. (56).

Supposing the Runge-Gross (RG) theorems valid in their original form, they will apply as well to the rKS formulation. Then there is a single td KS equation of the form,

$$i \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left\{ -\frac{1}{2} \nabla^2 + u(\mathbf{r}, t) + J[\rho](\mathbf{r}) + \tilde{v}_{xc}[\rho](\mathbf{r}, t) \right\} \psi(\mathbf{r}, t) \quad (58)$$

governing the time evolution of $\psi(\mathbf{r}, t)$ and, thus, of $\rho(\mathbf{r}, t) = N|\psi(\mathbf{r}, t)|^2$. Here

$$\tilde{v}_{xc}[\rho](\mathbf{r}, t) = \frac{\delta \tilde{A}_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)} \quad (59)$$

is the td xc potential associated with the rKS modification of the RG td xc functional, $\tilde{A}_{xc}[\rho(t)]$. The RG theorems assure that such a td xc potential exists, so that, in principle,

the time development of the density can be determined exactly via Eq. (58). In practice, of course, one has to resort to approximations such as the widely used adiabatic local density approximation (ALDA). Here one uses the ordinary static DFT xc potentials, depending on time only via the instantaneous density function, $\rho = \rho(\mathbf{r}, t)$.

In the rKS version the RG theorems suggest that one can, at least in principle, condense the full N -electron td Schrödinger equation into a one-orbital td KS equation. Can this be true? As a step towards an answer let us inspect how the fourth RG theorem, establishing an analogy to the KS concept in the time-independent DFT, works in the rKS case.

B. The Runge-Gross theorems

The KS equations have been invented as a means for determining the minimum of the HK energy functional and thus the exact ground-state density of the interacting N -electron system. In TDDFT the role of the KS equations is daringly expanded: their time-dependent form is believed to govern, at least in principle, also the exact time evolution of the density of the interacting N -electron system. The basis for that claim has been laid in a series of four theorems in a famous article by Runge and Gross [5], in the following referred to as RG. Let us critically review their arguments.

The first theorem (RG1) is the td analogue of the first HK theorem. It establishes a one-to-one correspondence between td density functions, $\rho(\mathbf{r}, t)$, and td external potentials, $u[\rho](\mathbf{r}, t)$, which, in turn, via the td Schrödinger equation,

$$i\frac{\partial}{\partial t}\Psi[\rho](t) = \left(\hat{T} + \hat{V} + \hat{U}[\rho](t)\right)\Psi[\rho](t) \quad (60)$$

determine the exact td N -electron wave functions, $\Psi[\rho](t)$ (up to a purely time-dependent phase).

The third theorem (RG3) is the analogue to the second HK theorem. Instead of the HK energy functional, one considers the action integral defined according to

$$A[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \Psi[\rho](t) \rangle \quad (61)$$

where $\hat{H}(t) = \hat{T} + \hat{V} + \hat{U}(t)$ is the td Hamiltonian of the considered system. We may leave any problems in this definition (see Ref. [36]) at that and go on further to the fourth theorem (RG4). In analogy to the ordinary KS approach, one introduces a kinetic-energy

action functional,

$$S_0[\rho] = \int_{t_0}^{t_1} dt \langle \Phi[\rho](t) | i \frac{\partial}{\partial t} - \hat{T} | \Phi[\rho](t) \rangle \quad (62)$$

for non-interacting particles. Here it is supposed that for a given td density function, $\rho(\mathbf{r}, t)$, there exists a unique state (Slater determinant), $\Phi[\rho](t)$, of the non-interacting electron system. The functional $S_0[\rho]$ is defined in analogy to the full kinetic energy action functional,

$$S[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i \frac{\partial}{\partial t} - \hat{T} | \Psi[\rho](t) \rangle \quad (63)$$

for the original interacting electron system. As in the time-independent KS approach, $S_0[\rho]$ replaces $S[\rho]$, the remainder, $S[\rho] - S_0[\rho]$, being transferred into the exchange-correlation part, $A_{xc}[\rho]$, of the full action functional (61). Everything seems to be completely analogous to the time-independent case.

However, there is a problem, clearly to be seen in the focus of the rKS formulation. Here the non-interacting state, $\Phi[\rho](t)$, becomes a one-particle state of the general form of Eq. (57),

$$\psi[\rho](\mathbf{r}, t) = e^{ik(\mathbf{r}, t)} \left(\frac{\rho(\mathbf{r}, t)}{N} \right)^{1/2}$$

so that the S_0 functional reads

$$\tilde{S}_0[\rho] = \int_{t_0}^{t_1} dt \int d\mathbf{r} \psi^*(\mathbf{r}, t) \left(i \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2 \right) \psi(\mathbf{r}, t) \quad (64)$$

While the modulus of $\psi(\mathbf{r}, t)$ is completely determined by the density $\rho(\mathbf{r}, t)$, the phase function $k(\mathbf{r}, t)$ is not. Clearly, the value of $\tilde{S}_0[\rho]$ depends manifestly on this phase function, but there is no way of determining it (completely) from the given density. This means that the functional S_0 is ill-defined at the orbital level. There are (infinitely) many orbital trajectories for a given td density, each yielding a different value for the S_0 functional.

Let us consider the latter argument in somewhat greater detail. Inserting the form (57) of the orbital in the integrand of the $S_0[\rho]$ functional one readily obtains

$$\langle \psi | i \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2 | \psi \rangle = \langle \phi | \frac{1}{2} \nabla^2 | \phi \rangle - \frac{1}{2} \langle \phi | (\nabla k)^2 | \phi \rangle - \langle \phi | \dot{k} | \phi \rangle \quad (65)$$

This means that besides the density here also the gradient of the phase function, $\nabla k(\mathbf{r}, t)$, and the time derivative, $\dot{k}(\mathbf{r}, t)$, is needed. In fact, the latter information can be derived from the density to a certain extent if, as an additional requirement, one takes into account

that the orbital not only is to reproduce the density, but also to fulfill a td Schrödinger equation (SE) of the form

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \{-\frac{1}{2}\nabla^2 + w(\mathbf{r}, t)\}\psi(\mathbf{r}, t) \quad (66)$$

where $w(\mathbf{r}, t)$ is a local td potential yet to be determined. Therefore, the continuity equation

$$\frac{d}{dt}\phi^2 + \nabla\mathbf{j} = 0 \quad (67)$$

applies to the orbital, where the current density is given by

$$\mathbf{j} = \phi^2\nabla k \quad (68)$$

As a consequence, it is possible to determine ∇k from ρ and $\dot{\rho}$, respectively. (A mathematical complication may arise here due to the requirement that $\nabla \times (\mathbf{j}/\phi^2)$ must vanish.) Further, if ∇k is given (at any time), then also $k(\mathbf{r}, t)$ is determined, though only up to a purely time-dependent function, $\alpha(t)$. Thus we have established in a direct way a mapping $\rho(t) \rightarrow \psi[\rho](t)$, which is uniquely defined up to a purely td phase, $e^{i\alpha(t)}$. But as Eq. (65) clearly shows, the latter indefiniteness of the phase prevents the S_0 functional to become well-defined. The time integral $\int \dot{\alpha}(t)dt$ on the r.h.s. of Eq. (65) leads to a completely undetermined constant in the definition of the S_0 functional. Note that this does not mean just a uniform shift of the S_0 values, which of course would drop out in a variational search for stationary points. The S_0 functional can assume any value for a given density $\rho(t)$.

So far we have not specified the local potential $w(\mathbf{r}, t)$ in Eq. (66), but only assumed that such a potential exists, e.g., as a consequence of the first RG theorem (RG1) applied to the non-interacting KS system (of one electron). Remarkably, in the rKS version the $\rho(t) \rightarrow w(t)$ mapping can be obtained in a direct way (thereby proving the one-orbital td v-representability of any “reasonable” density), allowing us even to give an explicit expression for $w(\mathbf{r}, t)$. This is achieved by inserting the ansatz (57) in the SE (66). Separating the real and imaginary parts yields the following two equations:

$$w(\mathbf{r}, t) = \frac{\nabla^2\phi}{2\phi} - \frac{1}{2}(\nabla k)^2 - \dot{k} \quad (69)$$

and

$$\dot{\phi} + \nabla k\nabla\phi + \frac{1}{2}\nabla^2 k\phi = 0 \quad (70)$$

Obviously, the latter equation reproduces the continuity equation (67), whereas the former gives an explicit expression for the local td potential, $w(\mathbf{r}, t)$. Since both ∇k and k result from ρ as discussed above, $w(\mathbf{r}, t)$ is determined by ρ (more precisely, by ρ , $\dot{\rho}$, and $\ddot{\rho}$) up to a purely time-dependent function, namely $-\dot{\alpha}(t)$. As easily seen, the explicit form of the potential is of no avail to determine $\alpha(t)$. Even if the value of $\alpha(t)$ was given (or fixed) at an initial time, it cannot be determined for later times by solving the td SE (66) due to the corresponding indefiniteness of $w(\mathbf{r}, t)$.

So inevitably the rKS formulation calls our attention to the problem of the undetermined purely time-dependent phase functions corrupting the RG action integral functionals. The phase problem arises not only in the functionals of the non-interacting KS system but already in the functional (61) for the original interacting N -electron system. When one consults the RG paper [5] with regard to this issue, one finds that the phase problem, being correctly discussed in the beginning of the paper, gets lost in the matrix element $\langle \Phi(t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{W} - \hat{V}(t) | \Phi(t) \rangle$ after Eq. (11). Here $\hat{V}(t)$ is the external td potential of the physical system under consideration ($\hat{U}(t)$ in our notation). Erroneously, RG mistake $\hat{V}(t)$ for $\tilde{V}(t)$ (i.e. $\tilde{U}[\rho](t)$ in our notation), that is, the potential associated with the RG1 mapping, $\rho(t) \rightarrow \tilde{V}(t)$. The latter potential contains an undefined td function $C(t)$ that would cancel the term arising from the time derivative of the phase function in $\Phi(t)$. (Later TDDFT papers and virtually all review articles inconspicuously leap over the phase problem in the action integral functionals.)

Whereas there is still wide-spread confidence in the RG foundations of TDDFT, their breakdown due to the phase problem has been clearly analyzed and expressed by R. van Leeuwen already several years ago [32, 36]. In his 2001 review article [36] he draws the following conclusion: “*We therefore conclude that time-dependent density-functional theory can not be based on the usual variational principle, and indeed attempts to do so have led to paradoxes.*” Let us note that besides the phase problem, van Leeuwen also analyzed correctly the non-stationarity of the RG action integral functionals, exposing another fault line in the original RG argumentation. But why have van Leeuwen’s revelations not triggered stronger shock waves in the TDDFT community and beyond? Apparently because by the time of van Leeuwen’s analysis the leading actors in the field had come to the conclusion that the KS equations could be established directly without the necessity of resorting to a variational principle [34, 61]. Sharing that conviction, van Leeuwen communicated the

reassuring message that TDDF is valid, though only in a new shape featuring the so-called Keldysh Green's function technique [62]. In the ensuing subsection 5.C, we will have a closer look at the non-variational KS theory.

Before proceeding let us note that recently Cohen and Wasserman [30] have attempted to restore and generalize the original RG formulation by introducing a time-dependent analog of the LCS concept. This development can also be tried using the rKS analysis, which, as will be reported elsewhere [63], uncovers unexpected, presumably irreparable, problems underneath a seemingly faultless formal solution.

C. Kohn-Sham equations without a variational principle?

In the derivation of the static KS equations three elements are essential: *i*) a universal energy functional (HKI); *ii*) a variational principle for the exact ground-state density (HKII); and *iii*) a functional for the kinetic energy of non-interacting electrons defined at the orbital level (KS). Runge and Gross have pursued a strictly analogous approach in order to establish a basis for TDDFT. As first analyzed by van Leeuwen and corroborated here, this endeavor must be viewed as foundered in each of the three essentials.

But is there a different way to derive td KS equations? Within the TDDFT community, the generally accepted view is that there is such a route based entirely on the mappings established by the RG1 theorem. Indeed, the first RG theorem does offer a shortcut to KS-type equations. Applying RG1 to the case of non-interacting N electrons, there is the mapping

$$\rho(\mathbf{r}, t) \longrightarrow w[\rho](\mathbf{r}, t) \quad (71)$$

so that the td KS-type equations

$$i\frac{\partial}{\partial t}\psi_j(\mathbf{r}, t) = \{-\frac{1}{2}\nabla^2 + w[\rho](\mathbf{r}, t)\}\psi_j(\mathbf{r}, t), \quad j = 1, \dots, N \quad (72)$$

allow one to calculate the density $\rho(\mathbf{r}, t)$ from the orbitals $\psi_j(\mathbf{r}, t)$. The KS potential in Eq. (72) can be written in a more familiar form,

$$w[\rho](\mathbf{r}, t) = u(\mathbf{r}, t) + J[\rho](\mathbf{r}, t) + v_{xc}[\rho](\mathbf{r}, t) \quad (73)$$

where $u(\mathbf{r}, t)$ is the external td potential of the system under consideration. Apparently, Eq. (73) serves as a definition of an xc potential-functional $v_{xc}[\rho](\mathbf{r}, t)$ by subtracting two

known potentials from the unknown KS potential-functional $w[\rho](\mathbf{r}, t)$ (see Refs. [37, 38, 64]). At least formally, everything looks as one would expect. But is this already the solution? Once more, the rKS formulation allows for a closer inspection of what we have got, because here the potential $w[\rho](\mathbf{r}, t)$ can be given in an explicit form.

Indeed, as the analysis of Sec. 5.B has shown, for a given density $\rho(\mathbf{r}, t)$ there exists a single-particle td SE (Eq. 66),

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \left\{-\frac{1}{2}\nabla^2 + w[\rho](\mathbf{r}, t)\right\}\psi(\mathbf{r}, t) \quad (74)$$

with the td local potential (Eq. 69),

$$w[\rho](\mathbf{r}, t) = \frac{\nabla^2\phi}{2\phi} - \frac{1}{2}(\nabla k)^2 - \dot{k} \quad (75)$$

which is determined by the density up to a purely td function $(-\dot{\alpha}(t))$. Let us note that the indefinite td function does not affect the resulting density and, thus, is no longer relevant in the present context. Eq. (75) together with the prescription to determine $k(\mathbf{r}, t)$ from $\rho(t)$ and $\dot{\rho}(t)$ via the continuity equation can be seen as a direct (constructive) proof of the RG1 theorem in the non-interacting (one-electron) case. But it should be clear that Eqs. (74,75) do not yet offer a method to determine the time-development of the exact density of the interacting N -electron system, $\rho_0(\mathbf{r}, t)$. They hold for any density, and the question is how can $\rho_0(\mathbf{r}, t)$ be determined without knowing it beforehand and using it to construct the potential $w[\rho_0](\mathbf{r}, t)$. (In the case of 2-electron systems, such a construction of $w[\rho_0](\mathbf{r}, t)$ from $\rho_0(t)$ obtained otherwise was presented, for example, by Hessler et al. [65] and Lein and Kümmel [66].)

At this point it is instructive to inspect the more transparent case of static DFT. Let us assume for a moment that there is no second Hohenberg-Kohn theorem (HKII) and, thus, no variational principle. As above, however, one has a shortcut to KS-type equations (now applying the HKI mapping to the non-interacting system). In the rKS variant, the corresponding single KS-type equation can explicitly be constructed (by inserting the ansatz (42) in the one-particle Schrödinger equation):

$$\left\{-\frac{1}{2}\nabla^2 + w[\rho](\mathbf{r})\right\}\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}) \quad (76)$$

Here the potential

$$w[\rho](\mathbf{r}) = \frac{\nabla^2\sqrt{\rho}}{2\sqrt{\rho}} + c \quad (77)$$

is determined by the density $\rho(\mathbf{r}) = N\phi(\mathbf{r})^2$ (up to a constant c). Eqs. (76,77) show that any (reasonable) density is non-interacting (one-electron) v -representable. But, clearly, the potential-functional $w[\rho](\mathbf{r})$ of Eq. (77) as such is of no avail for determining the exact ground-state density, ρ_0 . According to the successive steps,

$$\rho(\mathbf{r}) \longrightarrow w[\rho](\mathbf{r}) \longrightarrow (\text{Eq. 76}) \longrightarrow \phi(\mathbf{r}) \longrightarrow \rho(\mathbf{r})$$

any density $\rho(\mathbf{r})$ will only reproduce itself. Obviously, the KS potential-functional (77) is trivial, i.e. without physical meaning.

By contrast, in the variationally derived KS equation (49) the potential-functional $v^{eff}[\rho](\mathbf{r}) = v(\mathbf{r}) + J[\rho](\mathbf{r}) + \tilde{v}_{xc}[\rho](\mathbf{r})$ according to Eq. (50) is of completely different type. The density will change in the course of the iterative solution of the KS equation and will (eventually) converge to the exact (or approximate) ground-state density ρ_0 . Only for ρ_0 , the KS equation (with $v^{eff}[\rho_0](\mathbf{r})$) will reproduce the initial density ρ_0 . At this “fixed-point”, the potentials deriving from the non-trivial and trivial functional become identical (up to a constant),

$$w[\rho_0](\mathbf{r}) = v(\mathbf{r}) + J[\rho_0](\mathbf{r}) + \tilde{v}_{xc}[\rho_0](\mathbf{r}) + c \quad (78)$$

as can be seen by comparing Eqs. (52) and (77).

Eq. (78) holds only for $\rho_0(\mathbf{r})$, but $w[\rho](\mathbf{r})$, $J[\rho](\mathbf{r})$, and $\tilde{v}_{xc}[\rho](\mathbf{r})$ are universal potential-functionals, so that any density can be turned into a fixed-point if the external potential, $v_{ext}[\rho]$, is chosen accordingly:

$$w[\rho](\mathbf{r}) = v_{ext}[\rho](\mathbf{r}) + J[\rho](\mathbf{r}) + \tilde{v}_{xc}[\rho](\mathbf{r}) + c \quad (79)$$

Obviously, $v_{ext}[\rho](\mathbf{r})$ can be identified with the potential-functional associated with the HKI mapping for the interacting N -electron system. For the exact ground-state density of the original system, ρ_0 , the potential-functional yields of course

$$v_{ext}[\rho_0](\mathbf{r}) = v(\mathbf{r}) \quad (80)$$

Eq. (79) can be read in two ways. On the one hand, it can be used to define $v_{ext}[\rho](\mathbf{r})$ in terms of $w[\rho](\mathbf{r})$, $J[\rho](\mathbf{r})$, and $\tilde{v}_{xc}[\rho](\mathbf{r})$, as we have done just now. But one may as well suppose the external potential-functional $v_{ext}[\rho](\mathbf{r})$ as established by the HKI theorem, which then offers the possibility to define the (non-trivial) xc potential-functional $v_{xc}[\rho](\mathbf{r})$. This shows that, apart from the v -representability problem, the HKI mappings for the interacting

(N -electron) and the non-interacting (one-electron) systems establish the existence of a non-trivial xc potential-functional [36, 67], which in turn can be used in the KS equation in the familiar way, that is, together with the given one-particle potential $v(\mathbf{r})$ of the considered system. What one gets is formally equivalent to the variationally derived result (Eqs. 49,50): a KS equation with the exact ground-state density ρ_0 as fixed-point, thereby offering the possibility of determining ρ_0 by a self-consistency procedure. At this point, the only difference between the variational and the mapping based derivation is that in the former the iterative procedure represents a well-defined search for a minimum on an energy surface, whereas in the latter approach the final step amounts to an *ad hoc* fixed-point equation, for which the possibility of a converging self-consistency procedure has to be shown. One should not expect such a proof be possible without recourse to the HKII theorem, that is, the existence of a minimum of the energy functional at the exact ground-state density. In other words, the mapping derivation of the KS equation is valid only because, wittingly or unwittingly, the HKII variational principle is in the background.

Now we may come back to the time-dependent case. Variationally derived KS equations lacking, one can, nevertheless, establish a “non-trivial” xc potential-functional in analogy to Eq. (79):

$$w[\rho(t)](\mathbf{r}, t) = v_{ext}[\rho(t)](\mathbf{r}, t) + J[\rho(t)](\mathbf{r}, t) + v_{xc}[\rho(t)](\mathbf{r}, t) \quad (81)$$

where $v_{ext}[\rho(t)]$ and $w[\rho(t)]$ denote the potential-functionals established via the RG1 theorem (analogue to HKI) for the interacting (N -electron) and non-interacting (one-electron) system, respectively. Let us note that for the exact density trajectory, $\rho_0(\mathbf{r}, t)$, of the interacting N -electron system with the external potential $u(\mathbf{r}, t)$ the RG1 potential-functional gives

$$v_{ext}[\rho_0(t)](\mathbf{r}, t) = u(\mathbf{r}, t) \quad (82)$$

Again, we may use the non-trivial xc potential-functional $v_{xc}[\rho(t)](\mathbf{r}, t)$ in the (radical) KS equation together with $u(\mathbf{r}, t)$, giving rise to the one-orbital td KS equation

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \left\{-\frac{1}{2}\nabla^2 + u(\mathbf{r}, t) + J[\rho(t)](\mathbf{r}, t) + v_{xc}[\rho(t)](\mathbf{r}, t)\right\}\psi(\mathbf{r}, t) \quad (83)$$

which is “correct” only for the exact density $\rho_0(\mathbf{r}, t)$. In the latter case the effective potential in Eq. (83) becomes identical to the trivial KS potential-functional of Eq. (75) taken at the exact density $\rho_0(\mathbf{r}, t)$,

$$v^{eff}[\rho_0(t)](\mathbf{r}, t) = u(\mathbf{r}, t) + J[\rho_0(t)](\mathbf{r}, t) + v_{xc}[\rho_0(t)](\mathbf{r}, t) = w[\rho_0](\mathbf{r}, t) \quad (84)$$

and the KS equation with the potential $w[\rho_0](\mathbf{r}, t)$ reproduces $\rho_0(\mathbf{r}, t)$, that is, the exact density $\rho_0(\mathbf{r}, t)$ is a fixed-point of the td KS equation (83). Again, everything looks very similar to the static case, and one might be tempted to acquiesce in this status. However, as we will argue below, the td KS Eq. (83) does by no means offer a method to determine the exact density: it can reproduce $\rho_0(\mathbf{r}, t)$, but not predict it.

At this point it is helpful to distinguish two distinct modes of solving the td KS equation(s), namely (i) a potential-functional (PF) propagation mode, in which the instantaneous potential, $v^{eff}[\rho(t)]$, changes with the (instantaneous) density $\rho(t)$; and (ii) a trajectory mode supposing a predetermined density in a given time interval.

Let us first consider the PF propagation mode and assume the ideal case that the exact xc potential-functional is given and the propagation can start from the exact static ground-state density, $\rho_0(\mathbf{r})$, at $t = 0$. This means one would solve Eq. (83) by time-propagation “along” the exact density trajectory $\rho_0(t)$, for which the effective potential reduces to that obtained from the trivial KS potential functional (see Eq. 84). Miraculously, one would not need to know the xc potential functional at all since already the trivial KS potential-functional, via $w[\rho_0]$, would do the job. The catch is that the propagation does not work. There is a problem associated with the mapping $\rho(t) \rightarrow w[\rho(t)]$ (Eq. 71) being “non-local” in time (or non-instantaneous). What does this mean? An instantaneous potential-functional, for example, is the Hartree potential, $J[\rho(t)](\mathbf{r}, t)$: the density at a given time t determines the Hartree potential at the same moment t . But the situation is not as simple in the case of the KS potential-functional. This can be seen by inspecting again the KS potential-functional (75) of the rKS formulation. The first contribution on the r.h.s. of Eq. (75) is instantaneous; the second term, depending on the gradient of the phase function $k(\mathbf{r}, t)$, requires the first time-derivative of the density, $\dot{\rho}(t)$ according to the discussion in Sec. V.B; and the third term, being the time-derivative of the phase function, $\dot{k}(\mathbf{r}, t)$, can only be determined if the 2nd time-derivative of the density, $\ddot{\rho}(t)$, is available. A similar temporal non-locality must be expected for $v_{xc}[\rho(t)]$ and $v_{ext}[\rho(t)]$.

What is the consequence of this temporal non-locality for the time-propagation according to Eq. (83)? Obviously, the 2nd time-derivative of the density is not determined by the development through a given time t (“past” or “history”) so that the potential at the time t is undefined unless one takes into account the density beyond that point (“future”) in form of the 2nd derivative. To see this more clearly let us consider a general propagation scheme

on a time grid. The step generating the wave function at time t_{n+1} from that at t_n reads

$$\psi(t_{n+1}) = \psi(t_n) - i \Delta t \hat{h}^{KS}(t_n) \psi(t_n) \quad (85)$$

Due to the presence of a temporal non-local potential-functional, the determination of $\hat{h}^{KS}(t_n)$ requires the 2nd derivative of $\psi(t)$ at t_n , numerically given by the three-point formula

$$\ddot{\psi}(t_n) = \frac{1}{\Delta t^2} (\psi(t_{n+1}) - 2\psi(t_n) + \psi(t_{n-1})) \quad (86)$$

These equations show that in order to determine the wave function at the point t_{n+1} one already needs to know the wave function at that point, thwarting the possibility of a stringent propagation. Perhaps one could view Eqs. (85,86) as implicit equations for $\psi(t_{n+1})$ to be solved by iteration? But there is no *a priori* guarantee that such a procedure would lead to a self-consistent solution. As another possible way out, one might think of using the approximation, $\ddot{\psi}(t_n) \sim \ddot{\psi}(t_{n-1})$, in the sense of a predictor-corrector approach. In practice, this may succeed for a while, but, lacking a corrector step, one will sooner or later lose track of the actual solution. One may compare the situation to the problem of predicting the trajectory, say, of a missile using Newton's equations without knowing the actual force. The knowledge of the trajectory, $\mathbf{r}(t)$, including velocity and acceleration, through a given time allows one to extrapolate a probable trajectory beyond that point, but not predict the actual trajectory.

The problem with the PF propagation becomes even more distinct when the 2nd time derivative of the density is discontinuous. As any td SE, the td KS equation is of first order in time. Supposing a continuous td potential, the first derivative of the wave function will be continuous as well. But the 2nd derivative need not be continuous, and, in fact, discontinuities will usually be encountered whenever the perturbation $u(t)$ is turned on, say, at $t = 0$. In the latter case, it is quite obvious that one would need the 2nd derivative at t^+ (future) side of the point t for the purpose of propagation. To be more specific, assume a system in the unperturbed ground state for $t < 0$. Consider a td perturbation of the form $u(t) \sim t\theta(t)$, or even $u(t) \sim \theta(t)$. In both cases, the density behaves as $\delta\rho(t) \sim ct^2\theta(t)$ for small times, that is, the 2nd derivative vanishes for $t < 0$ and is $\sim 2c$ for $t = 0$. Clearly, the propagation step at $t=0$ requires the 2nd derivative at 0^+ .

But what about the trajectory mode of solving the td KS equation? Let us suppose some "trial" density (trajectory) $\rho(t)$ in a time interval $t_i \leq t \leq t_f$. Then of course also

$v^{eff}[\rho(t)]$ is determined in that interval, and the td KS equation can be solved like any ordinary td differential equation, yielding a new, usually distinct, density trajectory $\tilde{\rho}(t)$ in the considered interval. Obviously, this process can be iterated establishing a kind of a self-consistency procedure. Will it eventually lead to the desired fixed-point solution, $\rho_0(t)$? That is the question. Lacking a proof, the possibility of convergence of the fixed-point iteration must be considered as unfounded. The situation differs from that in the static case, where the self-consistency procedure is equivalent to the search for the minimum of the energy functional, shown to exist according to the HKII theorem or the Levy constrained search definition. Without a corresponding variational or stationarity principle, the td fixed-point iteration scheme cannot be expected to be convergent.

It should be noted that the trajectory and the PF propagation modes are, in fact, related. Choosing a (quasi) infinitesimal time interval, say, the interval $[t_n, t_{n+1}]$ between two successive grid points, the self-consistency procedure for the trajectory mode becomes equivalent to iteratively solving Eqs. (85,86) for $\psi(t_{n+1})$. This means that both modes of treating the td KS equation must be expected to fail as a method to predict the desired fixed-point solution for the same reason, that is, the absence of a variational principle in the td case.

To conclude, the td KS equations do not provide a method for *predicting* the exact density $\rho_0(t)$ of the interacting N -electron system. They would allow one to *reproduce* the time-development of the density at the orbital level, provided the td density is already given, e.g., from a solution of the full N -electron td Schrödinger equation, which is of course without practical use. In view of this analysis, the “causality problem” in the TDDFT linear response equations is to be seen from a new perspective. Rather than being the consequence of improperly defined xc functionals, as van Leeuwen and others have supposed, the problem seems to reflect a basic inadequacy of the formally correct, but not predictive td KS equations. The shortcut to td KS equations based entirely on the RG1 mappings between densities and potentials does not suffice to establish physical equations-of-motion. A suitable variational principle seems to be indispensable for this end.

Let us add that at the formal level of td KS theory the distinction between predictive and merely reproductive equations is well concealed and easy to overlook. In particular, the essentially mathematical, that is, acausal nature of the RG1 mappings between td densities and potentials, supposing beside $\rho(t)$ both the first and second time derivatives, has become apparent only by the explicit construction within the rKS framework.

D. Linear response in the adiabatic approximation

So far we have used the rKS concept as a tool to analyze some basic aspects of the TDDFT approach. Let us finally take a view at the structure of the results to be expected at the linear response (LR) level of the theory.

Using the adiabatic approximation for the td xc potential-functional, both in the usual and radical KS versions, leads to the RPA-like equations given by Eq. (21), where the blocks of the secular matrix, \mathbf{A} and \mathbf{B} , are constant (ω -independent) matrices. The excitation energies, $\omega_m = E_m - E_0$, are obtained as the eigenvalues of the pseudo-eigenvalue problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \underline{x}_m \\ \underline{y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \underline{x}_m \\ -\underline{y}_m \end{pmatrix} \quad (87)$$

The transition moment associated with the $0 \rightarrow m$ transition derives from the corresponding (specifically normalized) pseudo-eigenvector components according to

$$\langle \Psi_m | \hat{D} | \Psi_0 \rangle = \sum_{a,k} (x_{ak,m}^* d_{ak} + y_{ka,m}^* d_{ka}) \quad (88)$$

The manifold of excitations obtained from these equations is determined by the configuration space of the secular matrix block \mathbf{A} (note that the RPA pseudo-eigenvalues occur in pairs having positive and negative values, respectively). For the ordinary KS approach this means that the excitation manifold is that of the p - h or single excitations (with respect to the GS KS determinant). Here each spatial p - h configuration gives rise to 4 (primitive) spin states, from which one singlet and three (degenerate) triplet states can be formed. Let $n_o = N/2$ and n_v denote the number of occupied and virtual spatial KS orbital. Then the KS LR excitation manifold comprises $4n_on_v$ solutions. The full excitation manifold of N interacting electrons is, of course, much larger, because double and higher excitations come into play. It is thought that the restriction to single excitations is a consequence of the adiabatic approximation and the missing double and higher excitations would be accounted for by going beyond that approximation. Supposing that the exact td xc potential-functional, $v_{xc}[\rho](\mathbf{r}, t)$, exists, one would arrive at the same type of equations as in Eq. (21), but now with ω -dependent matrices, $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$. In principle, this could lead to an enhanced excitation manifold.

Let us now inspect the excitation manifold in the rKS case. The LR equations within the adiabatic approximation have the same structure (Eq. 21) as those of the usual KS

approach, but there is only one occupied spatial KS orbital ($n_o = 1$). As a consequence, the excitation manifold comprises only n_v excitations, that is, the excitations out of a single (average) KS orbital. Moreover, any spin degrees-of-freedom are missing, and, even if one assigns the n_v spatial excitations to singlets, any triplet excitations are absent. We have argued that the td treatment in the rKS framework is as legitimate or not legitimate as the usual KS approach. This means that here the hypothetical non-adiabatic td xc potential-functional, $\tilde{v}_{xc}[\rho](\mathbf{r}, t)$, must not only account for the double and higher excitations but has to restore already the single excitation manifold. A generation of triplet excitations appears to be completely impossible, because the density function $\rho(\mathbf{r}, t)$ and, thus, $\tilde{v}_{xc}[\rho](\mathbf{r}, t)$, does not bear information on the spin degrees-of-freedom. Let us note that the absence of triplets in the rKS version does not constitute an inconsistency with the N -particle KS case. In principle, the standard KS approach too does not allow for triplets, because the perturbing td potential has to be local, and a local potential cannot excite triplets from a singlet ground state. This fact is often suppressed because, in a technical sense, the usual TDDFT LR equations do yield triplet excitations (albeit with vanishing intensities). In the rKS scheme triplet excitations are neither accessible basically nor technically.

As was noted in Sec. 4, the rKS variant is only the limiting case of more general M -electron KS schemes, where the number M of non-interacting electrons may even exceed N . In the latter case the adiabatic approximation would produce more single excitations than the original interacting N -electron system, which would mean that the non-adiabatic td xc potentials must eliminate spurious solutions introduced at the adiabatic level of theory.

This shows that the well-known excitation manifold or “counting” problem of the LR form of TDDFT is further aggravated in the rKS (and M -electron KS) variants. Whereas it cannot be excluded that a hypothetical energy dependent xc potential beyond the adiabatic approximation might restore the single-excitation manifold of the ordinary KS scheme and, moreover, generate double and higher excitations, it appears more convincing to see this problem as an indication of the invalidity of the TDDFT equations.

VI. SUMMARY AND CONCLUSIONS

In this paper we have critically reexamined the foundations of TDDFT. In particular, we have addressed the question whether TDDFT is, in principle, exact. What have we learned to judge that issue? Let us summarize the three main results of our investigation.

First, we have observed that an error is introduced both in the td and static KS linear response theory if the perturbing (external) potential is given by a non-local operator. This error, resulting from the neglect of the h - h and p - p matrix elements of the perturbing operator in the KS response equations, is of second order in the electronic repulsion. Yet for a local (multiplicative) potential no logical inconsistency arises, because the absence of h - h and p - p matrix elements does not imply a loss of information of the local operator. As stated in Theorem 1 of Sec. 3, this is a remarkable general property of local operators. It is a well-known consistency requirement of DFT that the external potentials must be local. One can also extend the HK and KS approach to general non-local potentials, but that would require the incorporation of the non-local potentials already in the definition of the HK functional, $F_{HK}[\rho]$, and, accordingly, in the KS xc potential, $v_{xc}[\rho]$. As a consequence, the functionals would no longer be universal but depend on the respective non-local potentials.

The problem of the non-local operators reminds us that the KS LR equations cannot be viewed as having an unconditional physical meaning. In fact, their validity derives from the underlying theory. The CPKS equations, for instance, are founded on a valid first-order perturbation theory for the KS equations for the perturbed N -electron system. In the td case the validity of the response equations would presuppose that the time-dependent extension of the KS equations be correct, that is, the td KS equations establish a formally exact approach to the time-development of the N -electron density.

Secondly, we have discussed an utmost simplification of the KS concept, referred to as radical Kohn-Sham (rKS) approach. Here the ground-state density is obtained from a single one-particle KS equation supposing a correspondingly modified xc potential. In principle, the rKS form of the theory is as legitimate as the usual N -particle KS approach. Whereas the ordinary KS approach will certainly be better suited for developing practical computational schemes, it is not inconceivable that the rKS variant will have some computational potential as well. More importantly though, the rKS formulation represents a useful pedagogical and analytical tool, and as such it has been used here to elucidate basic aspects of DFT and

TDDFT.

In the td extension of the rKS approach, having the same validity status as the ordinary td KS theory, a single td one-particle KS equation, though involving a possibly very complicated td xc potential, would allow us to determine exactly the time-development of the density function of the full interacting N -electron system, thus bypassing the N -electron time-dependent Schrödinger equation. Given the richness of the phase relations of the full N -electron wave function, the spin degrees-of-freedom, even the permutation symmetry, all the wealth of information seemingly absent in a one-particle orbital or the one-particle density function, the possibility of predicting the exact time-development at a fictitious one-particle level must appear fantastic. But this is what TDDFT implies. Is that expectation justified? Guided by the rKS approach, in the third step, we have critically reexamined the RG foundation of TDDFT. What has become apparent here is a phase problem corrupting the definitions of the RG action integral functionals, as already recognized and analyzed by van Leeuwen in a different way [36]. Our findings fully confirm van Leeuwen’s conclusion that the RG foundation of TDDFT, based on analogues to the HKI, HKII, and KS theorems, is invalid.

Yet there is an alternative way of introducing the KS equations of TDDFT without invoking a variational principle, as formulated by Gross, van Leeuwen and others. Once again, this idea can be analyzed at the rKS level. The mere existence of one-particle KS type equations *reproducing* the exact td density is almost a triviality within the rKS framework. But these equations do not allow one to *predict* the exact density $\rho_0(t)$ of the interacting N -electron system. Due to the temporal non-locality of the KS potential-functionals, explicitly seen at the rKS level, the usual time-propagation schemes for solving the td KS equations cannot be applied. Moreover, a possible self-consistent procedure based on successive “trajectory mode” solutions of the KS equations within a definite time interval cannot be expected to succeed as the question of convergence is completely unfounded. As we have argued, the common cause for these failures is the absence of an underlying variational principle. The concept of a shortcut to td KS equations based entirely on the RG1 mappings between densities and potentials, dispensing with a variational principle, must be seen as an illusion.

Given the original RG foundation of TDDFT invalid and the design of a KS theory without a variational principle unfounded, one should face the possibility that the idea of TDDFT, that is, the idea of a formally exact method for predicting the time-development

of an interacting N -electron system at the orbital level, must be abandoned. The TDDFT approach (in linear response form) was first introduced 25 years ago as an analogue to TDHF (or RPA) before any attempts at a rigorous foundation had been made. Without the RG theorems or another viable justification, the theory would be set back to the status it had in its beginning: an empirically “corrected” version [17] of the RPA. While TDDFT (LR) may afford an improvement over the RPA description, it cannot escape the RPA limitation of being an approximate method for singly excited states.

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APPENDIX: MATRIX REPRESENTATION OF LOCAL OPERATORS

For matrix representations of local one-particle operators the following uniqueness theorem holds:

Theorem: If two local operators, $v(\mathbf{r})$ and $w(\mathbf{r})$, have the same p - h matrix elements with respect to an arbitrary partitioning of a (complete) one-particle basis into hole(h) and particle(p) states, they can differ only by a constant λ , that is, $w(\mathbf{r}) = v(\mathbf{r}) + \lambda$.

Proof: Let $\phi_s(\mathbf{r})$, $s = 1, 2, \dots$, denote the functions (orbitals) of a one-particle basis and assume a partitioning of the orbitals such that $\phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r})$ are referred to as occupied or hole states and $\phi_{n+1}(\mathbf{r}), \phi_{n+2}(\mathbf{r}), \dots$ as unoccupied or particle states. Consider two local operators $v(\mathbf{r})$ and $w(\mathbf{r})$ having the same p - h matrix elements,

$$\langle \phi_a | v | \phi_k \rangle = \langle \phi_a | w | \phi_k \rangle, \quad k \leq n, \quad a > n \quad (\text{A.1})$$

This means that the p - h matrix elements of the difference operator, $\lambda(\mathbf{r}) = w(\mathbf{r}) - v(\mathbf{r})$ vanish:

$$\lambda_{ak} = \langle \phi_a | w - v | \phi_k \rangle = 0, \quad k \leq n, \quad a > n \quad (\text{A.2})$$

Now consider the n functions $\lambda(\mathbf{r})\phi_l(\mathbf{r})$, $l \leq n$. These functions may be expanded in terms of the basis functions,

$$\lambda(\mathbf{r})\phi_l(\mathbf{r}) = \sum_{s=1}^{\infty} \lambda_{sl} \phi_s(\mathbf{r}) \quad (\text{A.3})$$

$$= \sum_{k=1}^n \lambda_{kl} \phi_k(\mathbf{r}), \quad l \leq n \quad (\text{A.4})$$

yielding finite linear combinations as a consequence of Eq. (A.2). Obviously, the latter equations can be brought to diagonal form by a suitable unitary transformation:

$$\lambda(\mathbf{r})\tilde{\phi}_k(\mathbf{r}) = \tilde{\lambda}_{kk}\tilde{\phi}_k(\mathbf{r}), \quad k \leq n \quad (\text{A.5})$$

This means that all transformed diagonal matrix elements must be equal, $\tilde{\lambda}_{kk} = \lambda$, $k \leq n$, and the difference potential is constant: $\lambda(\mathbf{r}) \equiv \lambda$.

The proof given here shows that the theorem can also stated as follows: Any local operator with vanishing p - h matrix elements with respect to a complete basis set and an arbitrary partitioning into p and h states must be a constant. An apparent objection is: What about

a diagonal representation of the operator? The answer is that local operators cannot be diagonalized properly, that is, in the Hilbert space of l^2 functions.

An interesting question arising in this context is if it is possible to reconstruct a local operator $v(\mathbf{r})$ (up to a constant), if only its p - h matrix elements are given. It seems that this is not possible except for the special case $n = 1$ (one occupied state). Let us first inspect the case $n = 1$ and let $\phi_1(\mathbf{r})$ be the single h orbital. Expanding $v(\mathbf{r})\phi_1(\mathbf{r})$ yields

$$v(\mathbf{r})\phi_1(\mathbf{r}) = v_{11}\phi_1(\mathbf{r}) + \sum_{a=2}^{\infty} v_{a1}\phi_a(\mathbf{r}) \quad (\text{A.6})$$

where $v_{pq} = \langle \phi_p | v | \phi_q \rangle$ denote the matrix elements of $v(\mathbf{r})$. Dividing this expression by $\phi_1(\mathbf{r})$ yields an explicit representation

$$v(\mathbf{r}) = v_{11} + \sum_{a=2}^{\infty} v_{a1}\phi_a(\mathbf{r})\phi_1(\mathbf{r})^{-1} \quad (\text{A.7})$$

which reconstructs $v(\mathbf{r})$ in terms of the p - h matrix elements v_{a1} up to a constant, being here the (single) h - h matrix element, v_{11} .

In obvious generalization of the case $n = 1$ one may proceed as follows. Let there be n occupied orbitals, $\phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r}), n > 1$. Expanding the products, $v(\mathbf{r})\phi_i(\mathbf{r})$, gives

$$v(\mathbf{r})\phi_i(\mathbf{r}) = \sum_{k=1}^n v_{ki}\phi_k(\mathbf{r}) + \sum_{a=n+1}^{\infty} v_{ai}\phi_a(\mathbf{r}), \quad i \leq n \quad (\text{A.8})$$

where the summation on the rhs has been split into h and p parts. As in the proof above, the h - h block of the v matrix can be diagonalized by a suitable unitary transformation, yielding

$$v(\mathbf{r})\tilde{\phi}_i(\mathbf{r}) = \tilde{v}_{ii}\tilde{\phi}_i(\mathbf{r}) + \sum_{a=n+1}^{\infty} \tilde{v}_{ai}\phi_a(\mathbf{r}), \quad i \leq n \quad (\text{A.9})$$

Here \tilde{v}_{ai} denote the transformed p - h matrix elements of $v(\mathbf{r})$. Dividing these equations by the respective transformed occupied orbital, $\tilde{\phi}_i(\mathbf{r})$, leads to n different representations of $v(\mathbf{r})$,

$$v(\mathbf{r}) = \tilde{v}_{ii} + \sum_{a=n+1}^{\infty} \tilde{v}_{ai}\phi_a(\mathbf{r})\tilde{\phi}_i(\mathbf{r})^{-1}, \quad i \leq n \quad (\text{A.10})$$

However, this does not solve the problem because the transformed p - h matrix elements, \tilde{v}_{ai} cannot be determined without diagonalization of the h - h block of the v matrix, that is, without the knowledge of the h - h matrix elements. Thus, it appears that one encounters a similar situation as in the theoretical foundation of DFT, where the Hohenberg-Kohn theorem states the existence of an universal xc functional without any constructive means.

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- [1] D. Sundholm, Chem. Phys. Lett. **302**, 480 (1999).
- [2] F. Furche, R. Ahlrichs, A. Sobanski, C. W. F. Vögtle, and S. Grimme, J. Am. Chem. Soc. **122**, 1717 (2000).
- [3] A. Dreuw, B. D. Dunietz, and M. Head-Gordon, J. Am. Chem. Soc. **124**, 12070 (2002).
- [4] A. Zangwil and P. Soven, Phys. Rev. A **21**, 1561 (1980).
- [5] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- [6] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).
- [7] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).
- [8] C. Jamorski, M. E. Casida, and D. R. Salahub, J. Chem. Phys. **104**, 5134 (1996).
- [9] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **103**, 9347 (1995).
- [10] D. J. Tozer and N. C. Handy, J. Chem. Phys. **109**, 10180 (1998).
- [11] A. Görling, H. H. Heinze, S. P. Ruzankin, M. Staufer, and N. Rösch, J. Chem. Phys. **110**, 2875 (1999).
- [12] R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **109**, 8218 (1998).
- [13] M. E. Casida, in *Recent Advances in Density Functional Theory, Part I*, edited by D. P. Chong (World Scientific, Singapore, 1995).
- [14] M. Petersilka, U. J. Grossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
- [15] S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999).
- [16] M. E. Casida and D. R. Salahub, J. Chem. Phys. **113**, 8918 (2000).
- [17] Z.-L. Cai, K. Sendt, and J. R. Reimers, J. Chem. Phys. **117**, 5543 (2002).
- [18] D. J. Tozer and N. C. Handy, Phys. Chem. Chem. Phys. **2**, 2117 (2000).
- [19] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, J. Chem. Phys. **120**, 5932 (2004).
- [20] D. J. Tozer, R. D. Amos, N. C. Handy, B. Roos, and L. Serrano-Andrés, Mol. Phys. **97**, 859 (1999).
- [21] A. Dreuw, J. L. Weisman, and M. Head-Gordon, J. Chem. Phys. **119**, 2943 (2003).
- [22] A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. **126**, 4007 (2004).
- [23] A. L. Sobolewski and W. Domcke, Chem. Phys. **294**, 73 (2003).
- [24] N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. **89**, 023002 (2002).
- [25] C. A. Ullrich and K. Burke, J. Chem. Phys. **121**, 28 (2004).

- [26] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).
- [27] W. Kohn and L. J. Sham, Phys. Rev. **140**, A 1133 (1965).
- [28] H. Kohl and R. M. Dreizler, Phys. Rev. Lett. **56**, 1993 (1986).
- [29] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).
- [30] M. H. Cohen and A. Wasserman, Phys. Rev. A **71**, 032515 (2005).
- [31] A. K. Rajagopal, Phys. Rev. A **54**, 3916 (1996).
- [32] R. van Leeuwen, Phys. Rev. Lett. **80**, 1280 (1998).
- [33] M. K. Harbola and A. Banerjee, Phys. Rev. A **60**, 5101 (1999).
- [34] E. K. U. Gross, C. A. Ulrich, and U. J. Gossmann, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum Press, New York, 1995), vol. 337 of *NATO ASI, Ser. B*.
- [35] E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory*, edited by R. F. Nalewajski (Springer, New York, 1996).
- [36] R. van Leeuwen, Int. J. Mod. Phys. B **14**, 1969 (2001).
- [37] H. H. Heinze, F. D. Sala, and A. Görling, J. Chem. Phys. **116**, 9524 (2002).
- [38] K. Burke, J. Werschnik, and E. K. U. Gross, J. Chem. Phys. **123**, 062206 (2005).
- [39] E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).
- [40] A. D. McLachlan and M. A. Ball, Rev. Mod. Phys. **36**, 844 (1964).
- [41] A. Dalgarno and G. A. Victor, Proc. R. Soc. **A291**, 291 (1966).
- [42] D. J. Rowe, Rev. Mod. Phys. **40**, 153 (1968).
- [43] P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer, Heidelberg, 2000).
- [44] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Mc Graw-Hill, New York, 1971).
- [45] M. Head-Gordon, 2004, private communication.
- [46] M. Bühl, M. Kaupp, O. L. Malkina, and V. G. Malkin, J. Comput. Chem. **20**, 91 (1999).
- [47] F. Neese, J. Chem. Phys. **115**, 11080 (2001).
- [48] I. Tunell, Z. Rinkevicius, O. Vatrás, P. Salek, T. Helgaker, and H. Ågren, J. Chem. Phys. **119**, 11024 (2003).
- [49] S. K. Ghosh and A. K. Dhara, Phys. Rev. A **38**, 1149 (1988).
- [50] G. Vignale, M. Rasolt, and D. J. W. Geldart, Adv. Quantum Chem. **21**, 235 (1990).
- [51] S. M. Colwell and N. C. Handy, Chem. Phys. Lett. **217**, 271 (1994).

- [52] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).
- [53] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).
- [54] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).
- [55] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press - Clarendon Press, New York, Oxford, 1989).
- [56] M. Levy and J. P. Perdew, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).
- [57] C. F. von Weizsäcker, Z. Physik **96**, 431 (1935).
- [58] C.-O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).
- [59] M. A. Buijse, E. J. Baerends, and J. G. Snijders, Phys. Rev. A **40**, 4190 (1989).
- [60] C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).
- [61] A. Görling, Int. J. Quant. Chem. **69**, 265 (1998).
- [62] L. V. Keldysh, Sov. Phys. JETP **20**, 1018 (1965).
- [63] J. Schirmer and A. Dreuw, 2006, to be published.
- [64] M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
- [65] P. Hessler, N. P. Maitra, and K. Burke, J. Chem. Phys. **117**, 72 (2002).
- [66] M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005).
- [67] E. K. U. Gross and A. Görling, 2006, private communication.