

***N*-representability and stationarity in time-dependent density-functional theory**Morrel H. Cohen¹ and Adam Wasserman²¹*Department of Physics and Astronomy, Rutgers University, 126 Frelinghuysen Road, Piscataway, New Jersey 08854-8019, USA and Department of Chemistry, Princeton University, Washington Road, Princeton, New Jersey 08544-1009, USA*²*Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854-8087, USA*

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To construct an *N*-representable time-dependent density-functional theory, a generalization to the time domain of the Levy-Lieb (LL) constrained-search algorithm is required. That the action is only stationary in the Dirac-Frenkel variational principle eliminates the possibility of basing the search on the action itself. Instead, we use the norm of the partial functional derivative of the action in the Hilbert space of the wave functions in place of the energy of the LL search. The electron densities entering the formalism are *N*-representable, and the resulting universal action functional has a unique stationary point in the density at that corresponding to the solution of the Schrödinger equation. The original Runge-Gross (RG) formulation is subsumed within the current formalism. Concerns in the literature about the meaning of the functional derivatives and the internal consistency of the RG formulation are allayed by clarifying the nature of the functional derivatives entering the formalism.

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I. INTRODUCTION

Density-functional theory (DFT) now provides the conceptual, theoretical, and computational framework for the study of the ground-state properties of a vast array of quantum-mechanical systems at all levels of aggregation from atomic to macroscopic. The foundations for the contemporary theory of chemical reactivity emerge naturally from DFT as well [1–3]. The essential elements of DFT are the Hohenberg-Kohn (HK) theorems [4], the Kohn-Sham (KS) equations [5], and the Levy-Lieb (LL) constrained-search algorithm [6,7] which together with the Harriman-Zumbach-Masche (HZM) construction [8] introduces *N*-representable densities into DFT, accurate approximate functionals [9], and powerful computational algorithms [10].

As defined through the LL algorithm, the density functional $E[n]$ has a unique global minimum at the ground-state density within the space \mathcal{N} of all allowable [7] electron densities $n(\mathbf{r})$. This variational principle of DFT stands in one-to-one correspondence with the Rayleigh-Ritz variational principle for the time-independent Schrödinger equation and provides the same generality to the derivation of the KS equations.

Following the ground-breaking HK paper, a series of steps was taken toward a time-dependent density-functional theory (TDDFT) [11,12] which culminated in a more general formulation by Runge and Gross (RG) [13]. TDDFT is now being routinely applied to the calculation of excitation energies of atoms and molecules [14], as well as various physical properties within the linear response regime [15] and beyond it [16] (see Ref. [17] for a survey of recent applications).

In parallel to this success, discussions regarding the foundations of the theory continue to take place [17]. In their original work, Runge and Gross [13] employed the quantum-mechanical action integral (from here on the RG action) to derive time-dependent Kohn-Sham equations through the Dirac-Frenkel variational principle [18]. It was later argued

[19] that the RG action led to paradoxes when calculating response functions because these must be causal, whereas second functional derivatives of the RG action were thought to be symmetric. This “symmetry-causality paradox” was resolved first by Rajagopal [20], who introduced an action based on the time path introduced by Jackiw and Kerman [21], and subsequently by van Leeuwen [22], who reformulated TDDFT replacing the RG action by a Keldysh action [23]. The RG, Jackiw-Kerman, and Keldysh actions are defined *only* for time-dependent *v*-representable (TDVR) densities, and, regarded as functionals *only* of the density, are not stationary at the density of the solution of the time-dependent Schrödinger equation [12,19,22,24,25]. Such a lack of stationarity is a decided inconvenience, but even within TDVR TDDFT stationarity can be restored by recognizing that the density and external potential can be treated as independent functions [26]. Nevertheless, for reasons analogous to those applying to the ground-state theory, it is important to generalize the definition of the action functional to hold for time-dependent *N*-representable (TDNR) densities. More explicitly, Mearns and Kohn [27] have shown that small, time-dependent additions to the ground-state density need not be *v*-representable in first order. A suitable generalization can be effected by constructing a constrained-search algorithm for TDDFT analogous to the LL algorithm for DFT.

Apart from restoring stationarity to the action in TDDFT, *N*-representability is important because, as in DFT, accurate solution of the KS equations requires iteration to self-consistency. The most convenient starting densities may well not be *v*-representable, nor may the densities be at intermediate stages of the computational algorithms. It is then essential to have an action functional and KS potentials defined for *N*-representable densities both as a matter of principle and for practical reasons.

In this paper we formulate an *N*-representable TDDFT based on the Dirac-Frenkel variational principle in which the

RG action functional is stationary with respect to n at that unique n derivable from the solution of the time-dependent Schrödinger equation. We establish a one-to-one invertible map between all densities in a time-dependent generalization of \mathcal{N} and wave functions by use of the norm of the partial functional derivative [28] of the RG action in the Hilbert space of the wave functions. Insertion of that map into the action defines the action functional. The Runge-Gross formulation of TDVR is subsumed within this TDNR TDDFT, and the desired stationarity and generality are achieved.

In Sec. II, we begin by reviewing two topics central to our later developments, the Dirac-Frenkel variational principle and the action and its total and partial derivatives. Via Sec. II we introduce our notation for wave functions, operators, functional derivatives, Hilbert spaces, and more general function spaces. We also introduce the notion of mapping between abstract spaces as central to the formulation of TDDFT, following Dreizler and Gross for DFT [29]. In Sec. III, we recapitulate the RG formulation of v -representable TDDFT and show explicitly that its unnecessary limitation to the density generated by that v which enters the Hamiltonian destroys the stationarity of the action functional. We also provide an explicit explanation of why there are no inconsistencies in the functional derivatives entering the theory and why second functional derivatives of the RG action with respect to the density are not symmetric. Up to this point, our paper has concerned itself with the clarification of existing work on v -representable TDDFT. In Sec. IV, we turn to the problem of establishing a satisfactory N -representable TDDFT. We begin by stating a set of criteria that such a theory must meet. Next, we review existing proposals [26,30] and show that they do not meet all of the criteria. Finally, we develop the principal result of this paper, a constrained-search algorithm that meets all of the criteria. We close with a brief summary of our results in Sec. V.

II. BACKGROUND AND NOTATION

A. The Dirac-Frenkel variational principle

Consider a finite system of electrons and nuclei containing N electrons. Ignoring nuclear kinetic energy, keeping the nuclei fixed, and discarding the internuclear interaction energy as an irrelevant constant, the system Hamiltonian becomes

$$\hat{\mathcal{H}}[v] = \hat{T} + \hat{W} + \hat{V}[v] = \hat{H} + \hat{V}[v]. \quad (1)$$

In Eq. (1), \hat{T} is the electron kinetic-energy operator and \hat{W} the electron-electron interaction operator. The operator $\hat{V}[v]$ is the energy of interaction of the electrons with a time-dependent external potential $v(\mathbf{r}, t)$,

$$\hat{V}[v] = \int d\mathbf{r} v(\mathbf{r}, t) \hat{n}(\mathbf{r}). \quad (2)$$

In Eq. (2), $\hat{n}(\mathbf{r})$ is the electron-density operator. $v(\mathbf{r}, t)$ is comprised of the potential energy of an electron in the fixed nuclear electrostatic potential plus that in a time-dependent potential generated by sources external to the system. For

each time t in the interval (t_0, t_1) under consideration, the \mathbf{r} dependence of $v(\mathbf{r}, t)$ must meet the conditions imposed by Lieb [7]. In addition, we impose the requirement that

$$v(\mathbf{r}, t) \rightarrow 0, \quad r \uparrow \infty, \quad \forall t \in (t_0, t_1) \quad (3)$$

to eliminate irrelevant phase factors in the wave functions (see also Ref. [31]). The time dependence of v must meet certain implicit integrability conditions discussed below. Such acceptable potentials lie in the space \mathcal{V} . The space $\mathbb{R}^3 \times (t_0, t_1)$ is the support on which the elements v of \mathcal{V} are defined. As indicated by our notation, $\hat{V}[v]$ is a linear functional of v , Eq. (2), and so, consequently, is $\hat{\mathcal{H}}[v]$, Eq. (1).

The wave functions $\Phi(t)$ of the N -electron system are time-dependent, normalized, antisymmetric functions of the N space and spin coordinates of the electrons,

$$\|\Phi(t)\| = (\Phi(t), \Phi(t)) = 1, \quad \forall t \in (t_0, t_1). \quad (4)$$

They satisfy the time-dependent Schrödinger equation (atomic units are used throughout)

$$i\partial_t \Phi(t) = \hat{\mathcal{H}}[v] \Phi(t). \quad (5)$$

Once the initial condition

$$\Phi(t_0) = \Phi_0 \quad (6)$$

is imposed, $\Phi(t)$ is unique,

$$\Phi(t) = \mathcal{T}_L \exp \left[-i \int_{t_0}^t dt' \hat{\mathcal{H}}[v] \right] \Phi_0. \quad (7)$$

In Eq. (7) \mathcal{T}_L is the time-ordering operator, later to the left. Equation (7) defines implicitly the conditions that $v(t)$, $\Phi(t)$, and Φ_0 must meet. In addition to those conditions which were specified by Lieb [7], $\Phi(t)$ must be differentiable in time. The set of such functions that are solutions of Eq. (5) for all v in \mathcal{V} form a Hilbert space Φ . They are supported in Φ on the space τ , which is the product of (t_0, t_1) with the configuration and spin space \mathcal{S} of the N electrons,

$$\tau = \mathcal{S} \times (t_0, t_1). \quad (8)$$

All scalar products like the norm entering Eq. (4) are defined on \mathcal{S} .

Equations (5) plus (6) implicitly, and (7) explicitly, define a mapping $M_1: \mathcal{V} \rightarrow \Phi$. M_1 is surjective; Φ contains no element that is not associated with an element of \mathcal{V} [33]. That M_1 is injective as well, i.e., one-to-one and therefore bijective or invertible, can be seen as follows. Suppose there is a v' and therefore a \hat{V}' which yields the same Φ as solution of Eq. (5) as do v and \hat{V} . Subtracting the two Schrödinger equations leads to

$$(\hat{V}' - \hat{V})\Phi = \int d\mathbf{r} [v'(\mathbf{r}, t) - v(\mathbf{r}, t)] \hat{n}(\mathbf{r}) \Phi(t) = 0, \quad (9)$$

which implies that v' must equal v under the conditions on the \mathbf{r} dependence of v required for the analogous proof for the time-independent problem (cf. Ref. [7] and p. 5 of Ref. [29]). Thus M_1^{-1} exists and $\Phi \leftrightarrow \mathcal{V}$ is one-to-one. Φ can then be regarded as a functional of v , $\Phi[v]$, or v one of Φ , $v[\Phi]$.

Let us now expand the Hilbert space Φ to Ψ which contains all functions Ψ that meet the conditions imposed on Φ including $\Psi(t_0)=\Phi_0$, except that the Ψ need not satisfy Eq. (5). The Dirac-Frenkel variational principle states that Ψ satisfies Eq. (5) if and only if

$$(\delta\Psi, (i\partial_t - \hat{H}[v])\Psi) = 0, \quad (10a)$$

$$(\delta\Psi(t), \Psi(t)) = 0, \quad \forall t. \quad (10b)$$

B. The action and its total and partial functional derivatives

We can now define the usual quantum-mechanical action functional $A[\Psi, v]$ on the space $\Psi \times \mathcal{V}$,

$$A[\Psi, v] = \int_{t_0}^{t_1} dt (\Psi, (i\partial_t - \hat{H}[v])\Psi). \quad (11)$$

$A[\Psi, v]$ is stationary only at $\Phi[v]$ in Ψ with respect to variations $\delta\Psi, \delta\Psi^*$ taken at *constant* v , given that $\Psi(t_0) = \Phi_0 \forall \Psi \in \Psi$, and requiring as well that [34]

$$(\delta\Psi(t_1), \Psi(t_1)) = 0, \quad (12)$$

a less severe restriction than that of Eq. (10b). The functional gradient of $A[\Psi, v]$ along Ψ^* (v is fixed),

$$\Theta_{\Psi^*} = \partial_{\Psi^*} A[\Psi, v] = (i\partial_t - \hat{H}[v])\Psi, \quad (13)$$

thus vanishes in Ψ at $\Phi[v]$, yielding the time-dependent Schrödinger equation. Note the use in Eq. (13) of ∂_{Ψ^*} as a symbol for a partial functional derivative. We now clarify the nature of such a derivative. The action is a functional of two functions defined in two different spaces. Accordingly, it does not fit simple examples of functionals used to define Fréchet and Gâteaux derivatives [28–32], which restrict the functions on which they are defined to a single Banach space (in the case of a Fréchet derivative), or normed space (in the case of a Gâteaux derivative). The Gâteaux derivative has been regarded as a generalization of the concept of the partial derivative of a function [28]. Similarly, the Fréchet derivative has been regarded as a generalization of a total derivative [28]. In our case, the properties of the action are such that taking derivatives only with respect to n meets the criteria for a Fréchet derivative despite the fact that it is a partial functional derivative. In the following we shall use the terminology *partial functional derivative* to refer to derivatives with respect to a single function of functionals of more than one function. When, however, we map the potential in the action back to the density or vice versa so that the action becomes a functional only of a single function, we shall refer to the functional derivative taken with respect to that single function as a *total functional derivative*. The total differential could then be represented as a linear combination of partial functional derivatives times the corresponding differentials of the respective functions.

III. v -REPRESENTABLE TDDFT

A. v -representability and stationarity of the RG action

We can recast the arguments of RG [13] as follows. Restrict the argument Ψ of $A[\Psi, v]$ in Eq. (11) to lie in Φ , the space of v -representable wave functions $\Phi[v']$, defining an action functional

$$A[\Phi, v] = \int_{t_0}^{t_1} dt (\Phi, (i\partial_t - \hat{H}[v])\Phi) \quad (14)$$

on the space $\Phi \times \mathcal{V}$. Stationarity of $A[\Psi, v]$ implies stationarity of $A[\Phi, v]$, i.e., that its partial functional derivative vanishes,

$$\partial_{\Phi^*} A[\Phi, v] = 0, \quad (15)$$

since $\Phi \subset \Psi$ and the stationary point of $A[\Psi, v]$ is in Φ .

$A[\Phi, v]$ can be established as a functional of v alone by inserting in $A[\Phi, v]$ that $\Phi[v']$ for which $v' = v$,

$$A[v] = A[\Phi[v], v]. \quad (16)$$

The stationarity condition (15) then implies that the total functional derivative of $A[v]$ is $-n$,

$$\delta_{v(r,t)} A[v] = \delta_{v(r,t)} A[\Phi[v], v] = -n(\mathbf{r}, t), \quad (17)$$

a generalization of the Hellmann-Feynman theorem [35]. The total functional derivative (17) does not vanish, obviously. It is only the partial functional derivative (15) which yields stationarity [26].

To go on to the density functional $A[n, v]$ requires establishing that the map $M'_2: \Phi \rightarrow \mathcal{N}_v$,

$$n(\mathbf{r}, t) = (\Phi(t), \hat{n}(\mathbf{r})\Phi(t)), \quad (18)$$

is one-to-one and invertible. In Eq. (18), $n(\mathbf{r}, t)$ is the time-dependent electron density, and the symbol \mathcal{N}_v stands for the subset of all such v -representable densities contained in \mathcal{N} , the time-dependent generalization of the space of densities of DFT [7]. All $n(\mathbf{r}, t)$ in \mathcal{N} and \mathcal{N}_v obey the initial condition

$$n(\mathbf{r}, t_0) = n_0(\mathbf{r}) = (\Phi_0, \hat{n}(\mathbf{r})\Phi_0). \quad (19)$$

Equation (18) defines what is meant by the phrase TDVR; a TDVR density is derivable via Eq. (18) from the solution Φ of the Schrödinger equation (5) for some v in \mathcal{V} . Demonstrating the invertibility of M'_2 directly, however, is non-trivial. The HZM construction [8] shows that $\Psi \rightarrow \mathcal{N}$ is many-to-one.

RG followed an alternative path. Substituting Eq. (7) into Eq. (18) defines a map $M_3 = M_1 M'_2: \mathcal{V} \rightarrow \mathcal{N}_v$. They then showed by a pretty argument that M_3 is one-to-one and invertible for all potentials $v(t)$ that possess a Taylor expansion in time about t_0 converging for all $t \in (t_0, t_1)$. Van Leeuwen [25] has pointed out that it is sufficient for a Taylor series to exist about a set of points $t_i \in (t_0, t_1)$ for which the radii of convergence overlap to cover (t_0, t_1) . $M_2'^{-1}: \mathcal{N}_v \rightarrow \Phi$ can then be constructed as $M_3^{-1} M_1$. Substitution of $M_2'^{-1}$, that is, $\Phi[n]$, into $A[\Phi, v]$, then yields the desired functional $A[n, v]$. $A[n, v]$ is stationary with respect to variation of n at fixed v [26], that is, its partial functional derivative vanishes,

$$\partial_n A[n, v] = 0. \quad (20)$$

It is important to recognize that $A[n, v]$ is defined for all n generated via Eqs. (7) and (18) from some v' , which can be varied independently of v . It is only at the stationary point that $v' = v$.

B. Time-dependent Kohn-Sham equations

Substitution of both M_2^{-1} and M_3^{-1} , i.e., $\Phi[n]$ and $v[n]$, into $A[\Phi, v]$ then yields a functional $A[n]$ of n only (for a given initial state [36]), the RG action functional. One thus has the option of using n or v as the independent variable in the functional. Van Leeuwen [25] gives a simple and elegant argument for the construction of the TDKS equations from $A[n]$ without invoking stationarity in \mathcal{N}_v . Switching now to $A[n]$ from $A[v]$, we carry out a Legendre transformation to

$$B[n] = A[n] + \int_{t_0}^{t_1} dt \int d\mathbf{r} v(\mathbf{r}, t; [n]) n(\mathbf{r}, t). \quad (21)$$

From Eq. (21), it follows that

$$\delta_{n(\mathbf{r}, t)} B[n] = v(\mathbf{r}, t). \quad (22)$$

The TDKS equations [25] follow from Eq. (23).

Consider a system of noninteracting electrons denoted by subscript s which move in an external potential $v_s(\mathbf{r}, t)$, starting from a single determinantal state Φ_{0s} at t_0 . v_s is a functional of their electron density, $v_s[n_s]$. The HZM construction [8] allows identification of $n_s(\mathbf{r}, t)$ with the density of the interacting system,

$$n_s(\mathbf{r}, t) \equiv n(\mathbf{r}, t), \quad \forall \mathbf{r}, t \in (t_0, t_1). \quad (23)$$

Thus v_s can be regarded as a functional of n . Combining

$$\delta_{n(\mathbf{r}, t)} B_s[n] = v_s(\mathbf{r}, t) \quad (24)$$

with Eq. (22) leads to

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) - \delta_{n(\mathbf{r}, t)} (A - A_s). \quad (25)$$

The usual rearrangements in $A - A_s$ in turn lead to

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{XC}(\mathbf{r}, t), \quad (26)$$

$$v_H(\mathbf{r}, t) = \int d\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (27)$$

$$v_{XC}(\mathbf{r}, t) = -\delta_{n(\mathbf{r}, t)} A_{XC}[n], \quad (28)$$

$$A_{XC}[n] = \int_{t_0}^{t_1} dt \{ [(\Psi, i\partial_t \Psi) - (\Psi_s, i\partial_t \Psi_s)] - [(T - T_s) - (W - W_H)] \}. \quad (29)$$

T is the kinetic energy and W the energy of electron-electron interaction of the interacting electrons in state $\Phi[n]$. T_s is the kinetic energy of the noninteracting electrons in state $\Phi_s[n]$. W_H is the Hartree approximation to W using $\Phi[n]$ or equivalently $\Phi_s[n]$.

It is at this point that concern about the meaning of the functional derivative defining v_{XC} , Eq. (28), arises in the literature [12,19,22,24,25]. Since in Sec. IV we shall base our development of N -representable TDDFT on the RG action and since the above-mentioned concern raises doubts about the validity of doing this, we now summarize the debate and show why the RG action is perfectly suitable for the developments of Sec. IV.

C. The symmetry-causality dilemma

Taking the functional derivative of Eq. (26) with respect to n results in [37]

$$\chi^{-1}(\mathbf{r}, t; \mathbf{r}', t') = \chi_s^{-1}(\mathbf{r}, t; \mathbf{r}', t') + f(\mathbf{r}, t; \mathbf{r}', t'), \quad (30)$$

where

$$\chi(\mathbf{r}, t; \mathbf{r}', t') = -\frac{\delta n(\mathbf{r}, t)}{\delta v(\mathbf{r}', t')}, \quad (31)$$

$$\chi_s(\mathbf{r}, t; \mathbf{r}', t') = -\frac{\delta n(\mathbf{r}, t)}{\delta v_s(\mathbf{r}', t')}, \quad (32)$$

$$f(\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta [v_H + v_{XC}](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} = \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{XC}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}. \quad (33)$$

From Eqs. (18) and (7), the well-known retarded character of the time dependence of the susceptibilities χ and χ_s follows; they vanish if $t' > t$. Their inverses $\chi^{-1}(\mathbf{r}, t; \mathbf{r}', t')$ and $\chi_s^{-1}(\mathbf{r}, t; \mathbf{r}', t')$ entering Eq. (30) are retarded as well. Yet

$$f_{XC}(\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta v_{XC}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} = -\frac{\delta^2 A_{XC}[n]}{\delta n(\mathbf{r}', t') \delta n(\mathbf{r}, t)} \quad (34)$$

is formally a second derivative of $A_{XC}[n]$ according to Eq. (28). van Leeuwen [22,25] assumes that, as f_{XC} is a second functional derivative, it must be symmetric in \mathbf{r}, t and \mathbf{r}', t' . Such symmetry is inconsistent with the retarded nature of χ^{-1} and χ_s^{-1} in Eq. (30). van Leeuwen [22,25] describes this inconsistency as a ‘‘paradox’’ and develops TDVR TDDFT from the Keldysh action instead of the RG action to avoid it. The second functional derivatives remain symmetric on the Keldysh time contour but become retarded when mapped into real time.

Gross, Dobson, and Petersilka [19], on the other hand, suppose that Eq. (30) holds and that $f_{XC}(\mathbf{r}, t; \mathbf{r}', t')$ must be retarded and not symmetric in \mathbf{r}, t and \mathbf{r}', t' . They then conclude by supposing from Schwarz’s lemma [39] that (1) $f_{XC}(\mathbf{r}, t; \mathbf{r}', t')$ cannot be a second functional derivative and (2) the exact $v_{XC}[n]$ cannot therefore be a functional derivative. They conclude further that this in turn is in contradiction to the principle of stationary action which leads to v_{XC} as a functional derivative.

To complicate matters further, Harbola and Banerjee [38] have argued that there is no symmetry-causality dilemma because while χ is causal, χ^{-1} is symmetric. Amusia and Shaginyan [41], while not disagreeing with this conclusion, have argued that, in contrast, it is possible to construct a

causal χ^{-1} as well. Harbola [42] has responded that Ref. [41] itself implies a causality in the potential as a functional of the density. van Leeuwen, however, has argued that χ^{-1} must be rigorously causal in analogy with the properties of discrete lower triangular matrices [25], an argument which does not take into account the fact that χ^{-1} is not a smooth function of $t-t'$ but contains both a δ function and the second derivative of a δ function at $t=t'^+$. We show in Appendix A that $\chi^{-1}(t-t')$ is causal, consisting of those singular functions at $t=t'^+$ plus a smooth causal function of $(t-t')$, so that the dilemma remains.

D. A way out of the dilemma

We conclude that in the context of TDDFT at the RG level, χ^{-1} is causal. The most forceful argument that the causality of χ^{-1} imposes a symmetry-causality dilemma via Eq. (30) is that of Gross, Dobson, and Petersilka [19]. The flaw in their reasoning is the supposition that Schwarz's lemma can be applied to the functionals of TDDFT. Throughout all of density-functional theory, the Fréchet definition [28] of the functional derivative was implicitly used. In the present instance, the functional derivatives of Eqs. (20), (22), (24), and (25) are all Fréchet derivatives. Taking a second derivative simply involves a single iteration of the Fréchet operation [28]. For the first derivative to exist, both the functional and the function space must meet smoothness criteria. The first derivative remains a functional, which for the second derivative to exist, must remain smooth. This condition is implicitly assumed for $v_{XC}[n]$ in all of DFT and TDDFT, and we presume it here as well. We conclude that all of the second functional derivatives encountered in TDDFT are perfectly well defined iterations of the Fréchet derivative operation. These include

$$\chi(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta^2 A[v]}{\delta v(\mathbf{r}',t')\delta v(\mathbf{r},t)} \quad (35)$$

and χ_s as well as f_{XC} . All have a retarded dependence on t and t' and are decidedly not symmetric in \mathbf{r},t and \mathbf{r}',t' . Similarly, χ^{-1} and χ_s^{-1} can be expressed as second derivatives, e.g.,

$$\chi^{-1}(\mathbf{r},t;\mathbf{r}',t') = -\frac{\delta v(\mathbf{r},t)}{\delta n(\mathbf{r}',t')} = \frac{\delta^2 B[n]}{\delta n(\mathbf{r}',t')\delta n(\mathbf{r},t)}, \quad (36)$$

have retarded time dependence (Appendix A), and are not symmetric in \mathbf{r},t and \mathbf{r}',t' .

We therefore agree with the main conclusion of Amusia and Shaginyan [40,41] and Harbola and Banerjee [38,42] that there is no conflict between the symmetry and the causality. However, the way out of the dilemma is not by finding symmetry in the inverse response functions, but by recognizing that second functional derivatives need *not* be symmetric functions of the time variables. To understand how this asymmetry can come about in a second functional derivative, consider that functionals are defined on three levels. First, there is the space on which the functions are defined; second, there is the function space on which the functionals are defined; and third, there is the definition of the functional. For

example, $A[v]$ is defined through Eq. (11) and the map M_1 , on the function space \mathcal{V} within which the potentials v are supported on $\mathbb{R}^3 \times (t_0, t_1)$. For the total functional derivative $\delta A[v]/\delta v(\mathbf{r},t)$ to exist and equal $-n(\mathbf{r},t)$, first \mathcal{V} must be smooth enough that variations $\delta v(\mathbf{r},t)$ exist which can be taken continuously to zero. Following Lieb [7], we have defined \mathcal{V} for this to be the case. Second, the functional $A[v]$ must be smooth enough that the resulting variation in it, $\delta A[v]$, exists, is linear in $\delta v(\mathbf{r},t)$, and goes continuously to zero with $\delta v(\mathbf{r},t)$. $A[v]$ meets that criterion. The functional derivative $\delta A[v]/\delta v(\mathbf{r},t)$ is then defined through Fréchet's theory of linear functionals [28]. Similarly, for $\delta n(\mathbf{r},t)/\delta v(\mathbf{r}',t') = \delta^2 A[v]/\delta v(\mathbf{r}',t')\delta v(\mathbf{r},t)$ to exist, $n(\mathbf{r},t)$ need only meet the smoothness criterion as a functional of v , which it does through the definition of \mathcal{N}_v .

The requirement for the applicability of Schwarz's lemma, that the second derivative be invariant with respect to interchange of the order of differentiation, is that the first level of support, the space on which the function is defined, be unchanged by the first functional differentiation. That is not the case here, and Schwarz's lemma does not apply. In $A[v]$, v is supported on $\mathbb{R}^3 \times (t_0, t_1)$, but in $n[v]$, the first derivative, v is supported on $\mathbb{R}^3 \times (t_0, t)$ precluding the applicability of Schwarz's lemma (see also the discussion in Appendix B). If $t' > t$ in $\delta^2 A[v]/\delta v(\mathbf{r}',t')\delta v(\mathbf{r},t)$, it must vanish, destroying symmetry while remaining a well-defined second functional derivative [28]. In the Keldysh action functional used by van Leeuwen [22,25], the time-ordered contour on which the action is defined provides the support for the time dependence of the potential v . Functional differentiation of the Keldysh action does not modify this support, and so the second functional derivative remains symmetric in that support. Transformation from the Keldysh time contour back to real time introduces the asymmetry without changing the fact that a second functional derivative was taken. Thus, van Leeuwen has, in effect, proved that second functional derivatives need not be symmetric. We conclude that all functional derivatives in the RG formulation are well defined, both first and second, and that Eq. (30), a relation among second functional derivatives, contains no inconsistencies. One thus has a choice—one can base TDVR TDDFT on the RG action or on the Keldysh action. How to generalize the Keldysh action so as to provide a basis for TDNR TDDFT is not now clear. Accordingly, we choose to base our development of TDNR TDDFT on the RG action.

IV. N-REPRESENTABLE TDDFT

The HZM construction [8] establishes that at each time t , there is an infinite set of wave functions $\Psi(t)$ which yield any preset $n(\mathbf{r},t)$ in \mathcal{N} via the mapping $M_2: \Psi \rightarrow \mathcal{N}$,

$$n(\mathbf{r},t) = (\Psi(t), \hat{n}(\mathbf{r})\Psi(t)) \quad (37)$$

with $n(\mathbf{r},t_0) = n_0(\mathbf{r})$, Eq. (19). The task in constructing an N -representable TDDFT is to select a single member of that set so that M_2 becomes one-to-one and invertible, i.e., to find $M_2^{-1}: \mathcal{N} \rightarrow \Psi$. M_2^{-1} should meet the following four criteria. (1) It should be universal; (2) it should require searching

only in Ψ and not in Ψ and \mathcal{V} ; (3) it should subsume the mapping $M_2'^{-1}$ of v -representable TDDFT; and (4) it should provide a stationarity principle.

A. Previous work

Apart from formulations applicable to special classes of potentials [43], there are two proposals for the formulation of NR TDDFT. That of Kohl and Dreizler [30] does not meet criterion 2 and, as a consequence, cannot meet criterion 4 either. That of Ghosh and Dhara [26] does not produce N -representability, only v -representability. Their Theorem 4 can be restated as defining the map $M_{\text{GD}}: \mathcal{N} \rightarrow \Psi$,

$$\Psi[n] = \arg\{\text{stat}_{\Psi \rightarrow n} B[\Psi]\}. \quad (38)$$

However, since in Eq. (38) one searches only for a *stationary* point of $B[\Psi]$ in Ψ , one is allowed to relax the subsidiary condition (37) by a Legendre transformation. Equation (38) then becomes

$$\Psi[n] = \arg\left\{\text{stat}_{\Psi}\left(B[\Psi] - \int_{t_0}^{t_1} dt \int d\mathbf{r} \Lambda(\mathbf{r}, t) n(\mathbf{r}, t)\right)\right\}. \quad (39)$$

Now, the Lagrange multiplier $\Lambda(\mathbf{r}, t)$ will exist if and only if $n(\mathbf{r}, t)$ is v -representable, in which case Eq. (39) becomes

$$\Psi[n] = \arg\{\text{stat}_{\Psi} A[\Psi, \Lambda]\} \quad (40)$$

with $\Lambda \subset \mathcal{V}$, a potential. Thus, the map defined by Eq. (38) is identical to the map $M_2'^{-1}: \mathcal{N}_v \rightarrow \Phi$ defined by RG. Equations (38)–(40) should therefore be rewritten with $\Phi[n]$ replacing $\Psi[n]$. What Ghosh and Dhara have actually accomplished is to find a simpler and more direct proof of v -representability than the original proof of RG.

B. Our approach

We note that the stationary point $\Phi[n]$ of $B[\Psi]$ in Eq. (38) is unique in the subspace Φ_n ($\Psi \rightarrow n$) of Ψ for $n \subset \mathcal{N}_v$. The partial functional derivative of $A[\Psi, v]$, its gradient in Φ_n , vanishes uniquely there,

$$\partial_{\Psi^*} A[\Psi, v]_{v,n} = \partial_{\Psi^*} B[\Psi]_n = (i\partial_t - \hat{H})\Psi = 0, \quad (41)$$

$$n \subset \mathcal{N}_v, \quad \Psi = \Phi[n].$$

Thus the magnitude squared of the gradient,

$$\int_{t_0}^{t_1} dt (\partial_{\Psi^*} A, \partial_{\Psi^*} A)_{v,n} = \int_{t_0}^{t_1} dt (\partial_{\Psi^*} B, \partial_{\Psi^*} B)_n, \quad (42a)$$

has a unique minimum there as well. As the search can be restricted to normalized Ψ 's without penalty, it follows from Eq. (42a) that

$$\int_{t_0}^{t_1} dt (\partial_{\Psi^*} A, \partial_{\Psi^*} A)_{v,n} = \int_{t_0}^{t_1} dt (\Psi, (i\partial_t - \hat{H})^2 \Psi) \quad (42b)$$

holds as well because of the consequent Hermiticity of $i\partial_t$.

On the other hand, no such minimum can exist in the magnitude of the gradient for an N -representable $n \subset \mathcal{N}$ which is not v -representable. A similar situation exists in time-independent DFT. A minimum exists in the functional $E[\Psi] = (\Psi, \hat{H}\Psi)$ for $\Psi \rightarrow n$ if and only if n is v -representable. If we suppose that a minimum exists under the constraint of fixed n for n not v -representable, the constant can be eliminated by a Legendre transformation. The Lagrange multiplier then simply adds to the external potential contradicting the hypothesis that n is not v -representable as in the arguments associated with Eqs. (38)–(40). For a general N -representable n , there is only an infimum in both $(\Psi, \hat{H}\Psi)$ and $(\Psi, \hat{H}\Psi)$ at the same point. The Levy-Lieb constrained-search algorithm makes use of this infimum to define the density functional for N -representable densities:

$$E[n] = \inf_{\Psi \rightarrow n} E[\Psi], \quad (43a)$$

$$\Psi[n] = \arg\{\inf_{\Psi \rightarrow n} E[\Psi]\}. \quad (43b)$$

An analogous constrained-search algorithm can be constructed for TDDFT from the magnitude of the gradient [44]:

$$\begin{aligned} \Psi[n] &= \arg\left\{\inf_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt (\partial_{\Psi^*} A, \partial_{\Psi^*} A)_{v,n}\right\} \\ &= \arg\left\{\inf_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt (\partial_{\Psi^*} B, \partial_{\Psi^*} B)_n\right\} \\ &= \arg\left\{\inf_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt (\Psi, (i\partial_t - \hat{H})^2 \Psi)\right\}, \end{aligned} \quad (44a)$$

$$A[n, v] = \int_{t_0}^{t_1} dt (\Psi[n], (i\partial_t - \hat{H}[v])\Psi[n]). \quad (44b)$$

We note that the quantity over which the search in Eq. (42a) is done corresponds to the time integral of the McLachlan functional for \hat{H} [45] widely used in formulations of semi-classical dynamics [46]. The proposed constrained-search algorithm expressed in Eqs. (44a) and (44b) meets all of the criteria imposed above. (1) It is universal, not involving v . (2) It requires searching only in Ψ . (3) It subsumes v -representable n for which the infimum becomes a minimum and yields the condition

$$(i\partial_t - \hat{H})^2 \Psi = 0 \quad \text{such that } \Psi \rightarrow n, \quad (45)$$

which yields the same Ψ as Eq. (38) or, ultimately, Eq. (5). Finally, (4) it provides a stationarity principle since n in Eq. (44b) can be varied independently of v , and the corresponding partial functional derivative vanishes via Eq. (13),

$$\partial_n A[n, v] = 0. \quad (46)$$

Stationarity in TDDFT plays the role that minimality does in DFT regarding error reduction.

V. SUMMARY

An N -representable time-dependent DFT has been established, and a time-dependent analog of the Levy-Lieb constrained-search algorithm has been proposed. The central quantity in this search is the norm of the partial functional derivative of the Runge-Gross action in the Hilbert space of wave functions. The proposed constrained search meets all of the requirements we pose: it is universal, requires searching only in one Hilbert space, subsumes Runge-Gross v -representability, and provides a stationarity principle.

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APPENDIX A: CAUSALITY OF χ_s^{-1} AND χ^{-1}

As stated in Secs. III C and III D, there is a substantial spread of opinion in the literature with regard to the time dependence of χ_s^{-1} and χ^{-1} , differing as to whether it is causal or symmetric. We argue here that it is unequivocally causal, with local singularities at $t=t'^+$. It is easiest to see this explicitly for the χ_s of the uniform electron gas, which has the form $\chi_s(|\mathbf{r}-\mathbf{r}'|, t-t')$, from space-time uniformity. Accordingly, it is diagonalized by Fourier transforming on space and time yielding the eigenvalues $\chi_s(\mathbf{q}, \omega-i\delta)$, $\delta \downarrow 0$. The wave vector \mathbf{q} is introduced by the Fourier transform on $\mathbf{r}-\mathbf{r}'$, the frequency ω is introduced by that on $t-t'$, and δ is introduced by the causality of χ_s , $\chi_s(|\mathbf{r}-\mathbf{r}'|, t-t')=0$, $t > t'^+$.

The explicit form of $\chi_s(\mathbf{q}, \omega-i\delta)$ is known [47]. When continued to the entire complex angular frequency plane in the process of inverting the Fourier transform on time, its only singularities are a second-order pole at infinity and bounded branch cuts just above the real axis. For $q < 2k_F$ (k_F is the Fermi wave number), there is one bounded branch cut at $z = \omega + i\delta$, with $|\omega| \leq (\hbar/2m)(2k_{Fq} + q^2)$; for $q > 2k_F$ there are two, with $(\hbar/2m)(-2k_{Fq} + q^2) \leq |\omega| \leq (\hbar/2m)(2k_{Fq} + q^2)$. $\chi_s(\mathbf{q}, \omega)$ has no zeros away from the branch cuts.

χ_s^{-1} is also uniform in space and time and therefore diagonalized by Fourier transformation. Its eigenvalues are simply

$$\chi_s^{-1}(\mathbf{q}, \omega) = 1/\chi_s(\mathbf{q}, \omega). \quad (A1)$$

The second-order pole in $\chi_s(\mathbf{q}, \omega)$ at $\omega = \infty$ yields the following behavior in $\chi_s^{-1}(\mathbf{q}, \omega)$ at ∞ :

$$\chi_s^{-1}(\mathbf{q}, \omega) \xrightarrow[\delta \rightarrow 0]{|\omega| \rightarrow \infty} A_s(\mathbf{q})\omega^2 + B_s(\mathbf{q}) + \frac{C_s(\mathbf{q})}{\omega^2} + \dots, \quad (A2)$$

$$A_s(\mathbf{q}) = -\frac{m}{nq^2},$$

$$B_s(\mathbf{q}) = \frac{2E_F}{5n} \left[3 + \frac{5\hbar^2 q^2}{8mE_F} \right],$$

$$C_s(\mathbf{q}) = \frac{16E_F^2 q^2}{175nm} \left[3 + 35 \frac{\hbar^2 q^2}{8mE_F} \right],$$

where n is the number of electrons per unit volume and m is the electron mass. Thus χ_s^{-1} has the form

$$\begin{aligned} \chi_s^{-1}(\mathbf{q}, t-t') = & -A_s(\mathbf{q})\delta''((t-t')^+) + B_s(\mathbf{q})\delta((t-t')^+) \\ & + \chi_s^{-1}(\mathbf{q}, t-t')'. \end{aligned} \quad (A3)$$

In Eq. (A3), δ'' is the second derivative of the delta function. $(\chi_s^{-1})'$ arises from the branch cut(s) and is rigorously causal because the locations of the branch cuts in $\chi_s^{-1}(\mathbf{q}, z)$ are identical to those of $\chi_s(\mathbf{q}, z)$, being in the upper half z plane.

The principal change in passing from $\chi_s(\mathbf{q}, \omega)$ to $\chi(\mathbf{q}, \omega)$ for the uniform electron gas is that the free-particle excitations are replaced by quasiparticle excitations which have finite lifetime except at $q=0$. This causes the branch cuts to extend to infinity, but causes no change in the formal structure of $\chi^{-1}(\mathbf{q}, t-t')$ which is given by Eq. (A3) with modification of $A_s(\mathbf{q})$ to $A(\mathbf{q})$, etc.

For a nonuniform extended system for which the excitation spectrum forms continua, be the system ordered or disordered, there is no change in formal structure of $\chi_s^{-1}(\mathbf{r}, \mathbf{r}'; t-t')$ and $\chi^{-1}(\mathbf{r}, \mathbf{r}'; t-t')$. Each contains the local contributions $\delta''((t-t')^+)$ and $\delta((t-t')^+)$ as well as nonlocal retarded contributions. For finite systems that have at least one discrete excitation associated with a transition from the ground state to a bound excited state, there is a change. Each eigenvalue of $\chi_s(\mathbf{r}, \mathbf{r}'; \omega)$ or $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ switches from $+\infty$ to $-\infty$ as the pole at $z = \omega + i\delta$ with $\hbar\omega$ equal to that discrete excitation energy is crossed. This forces the existence of a zero between discrete excitation energies or between the highest discrete excitation energy and the continuum threshold. Each such zero gives rise to a pole in the corresponding eigenvalue of $\chi^{-1}(\mathbf{r}, \mathbf{r}'; z)$ or $\chi_s^{-1}(\mathbf{r}, \mathbf{r}'; z)$ at the same z . Upon Fourier transform to the time domain $\chi^{-1}(\mathbf{r}, \mathbf{r}'; t-t')$ and $\chi_s^{-1}(\mathbf{r}, \mathbf{r}'; t-t')$ each contains a causal contribution from the pole which oscillates with angular frequency corresponding to the excitation energy for $t \geq t'$ and vanishes for $t' > t$.

In conclusion, the causality of $\chi(\mathbf{r}, \mathbf{r}'; t-t')$ and $\chi_s(\mathbf{r}, \mathbf{r}'; t-t')$ forces the eigenvalues of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ and $\chi_s(\mathbf{r}, \mathbf{r}'; \omega)$ to have singularities only in the upper half complex-frequency plane. The corresponding eigenvalues of $\chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega)$ and $\chi_s^{-1}(\mathbf{r}, \mathbf{r}'; \omega)$ can therefore also have singularities only in the upper half plane apart from the second-order pole at ∞ . This arises from the fact that ω enters χ and χ_s only in the combination $\omega - i\delta$, $\delta \downarrow 0$, which does not change when their eigenvalues are inverted to obtain χ^{-1} and χ_s^{-1} . Those quantities must therefore always be of the form

$$\hat{\chi}^{-1}(t-t') = \hat{A}\delta''((t-t')^+) + \hat{B}\delta((t-t')^+) + \hat{\chi}^{-1}(t-t')', \quad (A4)$$

where $\hat{\chi}^{-1}(t-t)'$ is nonlocal and causal in time.

APPENDIX B: SECOND FUNCTIONAL DERIVATIVE ASYMMETRY

In Sec. III below Eq. (36), we have pointed to the modification of the support of $v(\mathbf{r}, t)$ in $n[v]$ by the first functional derivative of $A[v]$ with respect to v as the origin of the asymmetry of its second derivative χ . Alternatively, one can preserve the support on which the function $v(\mathbf{r}, t)$ is defined, but then the second level of definition, the function space on which the functional is defined, must change. Consider, for example, the map $M_1: \mathcal{V} \rightarrow \Phi$, Eq. (7), which, together with Eq. (18) defines the map $M_3: \mathcal{V} \rightarrow \mathcal{N}_v$, $n=n[v]$. A more explicit expression of that map would be

$$n = n[\hat{\mathcal{H}}[v]], \quad (\text{B1})$$

according to Eq. (7), in which $v(\mathbf{r}, t)$ is supported on (t_0, t) . However, Eq. (7) can be rewritten as

$$\Phi(t) = \mathcal{T}_L \exp \left[-i \int_{t_0}^{t_1} dt' \tilde{\mathcal{H}}_t[v] \right] \Phi_0, \quad (\text{B2})$$

where

$$\tilde{\mathcal{H}}_t[v] = \begin{cases} \hat{\mathcal{H}}[v], & t' \in (t_0, t), \\ 0, & t' \in (t, t_1). \end{cases} \quad (\text{B3})$$

Thus, by changing the operator space on which the argument of the functional, now the operator $\tilde{\mathcal{H}}_t[v]$, is defined, we have formally restored the support of v to (t_0, t_1) . However, that does not eliminate the asymmetry; it trivially shifts the location of its origin, viz.,

$$\frac{\delta n(\mathbf{r}, t)}{\delta v(\mathbf{r}', t')} = \frac{\delta n(\mathbf{r}, t)}{\delta \hat{\mathcal{H}}_t} \frac{\delta \hat{\mathcal{H}}_t}{\delta v(\mathbf{r}', t')} = 0, \quad t' > t. \quad (\text{B4})$$

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