N-Representability and stationarity in time-dependent density functional theory

Morrel H. Cohen\textsuperscript{1,2} and Adam Wasserman\textsuperscript{3}

\textsuperscript{1}Department of Physics and Astronomy, Rutgers University, 126 Frelinghuysen Rd., Piscataway, NJ 08854-8019, USA
\textsuperscript{2}Department of Chemistry, Princeton University, Washington Rd., Princeton, NJ 08544-1009, USA
\textsuperscript{3}Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Rd., Piscataway, NJ 08854-8087, USA

(Dated: October 22, 2018)

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 new 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.

PACS numbers:

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\textsuperscript{4,5,6}. The essential elements of DFT are the Hohenberg-Kohn (HK) theorems\textsuperscript{4}, the Kohn-Sham (KS) equations\textsuperscript{5,6}, the Levy-Lieb (LL) constrained search algorithm\textsuperscript{7}, which together with the Harriman-Zumbach-Masche (HZM) construction\textsuperscript{8} introduces N-representable densities into DFT; accurate approximate functionals\textsuperscript{8}; and powerful computational algorithms\textsuperscript{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 \(\mathcal{N}\)-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 towards a time-dependent density-functional theory (TDDFT)\textsuperscript{11,12}, which culminated in a more general formulation by Runge and Gross (RG)\textsuperscript{13}. TDDFT is now being routinely applied to the calculation of excitation energies of atoms and molecules\textsuperscript{14}, as well as various physical properties within the linear response regime\textsuperscript{15} and beyond it\textsuperscript{16} (see ref.\textsuperscript{17} for a survey of recent applications).

In parallel to this success, discussions regarding the foundations of the theory continue to take place\textsuperscript{17}. In their original work, Runge and Gross\textsuperscript{13} employed the quantum-mechanical action integral (hereon the RG action) to derive time-dependent Kohn-Sham equations through the Dirac-Frenkel variational principle\textsuperscript{18}. It was later argued\textsuperscript{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\textsuperscript{20}, who introduced an action based on the time path introduced by Jackiw and Kerman\textsuperscript{21}, and subsequently by van Leeuwen\textsuperscript{22}, who reformulated TDDFT replacing the RG action by a Keldysh action\textsuperscript{23}. The RG, Jackiw-Kerman, and Keldysh actions are defined only for time-dependent \(\nu\)-representable densities (TDVR). and, regarded as functionals only of the density, are not stationary at the density of the solution of the time-dependent Schrödinger equation\textsuperscript{12,14,22,24,25,26}. 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\textsuperscript{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 densities (TDNR). More explicitly, Mearns and Kohn\textsuperscript{27} have shown that small, time-dependent additions to the ground-state density need not be \(\nu\)-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 \( 22 \) 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 Section 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 Section 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 Section 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 Section 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 \( 24,31 \) and show that they do not meet all of the criteria. Finally, we develop the principal result of this paper, a constrained search algorithm which meets all of the criteria. We close with a brief summary of our results in Section V.

II. BACKGROUND AND NOTATION

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

\[
\hat{H}[v] = \hat{T} + \hat{W} + \hat{V}[v] = \hat{H} + \hat{V}[v].
\]

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 \( v(\mathbf{r}, t) \),

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

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 \( r \)-dependence of \( v(\mathbf{r}, t) \) must meet the conditions imposed by Lieb \( 7 \). In addition, we impose the requirement that

\[
v(\mathbf{r}, t) \rightarrow 0 , \; \mathbf{r} \uparrow \infty , \; \forall \; t \in (t_0, t_1)
\]

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 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 \( \hat{H}[v] \), 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,

\[
||\Phi(t)|| = (\Phi(t), \Phi(t)) = 1 \; , \; \forall \; t \in (t_0, t_1)
\]

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

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

Once the initial condition

\[
\Phi(t_0) = \Phi_0
\]

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

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

In Eq. (7), \( \mathcal{T}_L \) is the time-ordering operator, later to the left. Eq. (4) defines implicitly the conditions which \( v(t), \Phi(t), \text{and } \Phi_0 \) 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 which are solutions of Eq. (4) for all \( v \) in \( \mathcal{V} \) form a Hilbert space \( \Phi \). They are supported in \( \Phi \) on the space \( \tau \), which is the product of \( (t_0, t_1) \) with the configuration and spin space \( \mathcal{S} \) of the \( N \)-electrons,

\[
\tau = \mathcal{S} \times (t_0, t_1)
\]
All scalar products like the norm entering Eq. (1) are defined on $S$.

Eqs. (5) plus (6) implicitly, and (7) explicitly, define a mapping $M_1 : \mathcal{V} \to \Phi$. $M_1$ is surjective. $\Phi$ contains no element which is not associated with an element of $\mathcal{V}$.

That $M_1$ is injective as well, i.e. one-to-one and therefore bijective or invertible, can be seen as follows. Suppose $M$ has a solution of Eq. (5) as does $\Phi$, thus $\Psi$ can then be regarded as a functional of $A$.

The action functional is defined on $\mathcal{V}$.

We now clarify symbol for a partial functional derivative. We now clarify symbol for a partial functional derivative.

Thus vanishes in $\Phi$ at $\Phi_v$, yielding the time-dependent Schrödinger equation. Note the use in Eq. (13) of $\Theta_{\Psi_v}$ 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, 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.

Similarly, the Fréchet derivative has been regarded as a generalization of a total derivative. 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

#### 1. v-representability and stationarity of the RG action

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

$$A[\Phi, v] = \int_{t_0}^{t_1} dt \left[ \Psi \left[ i \partial_t - \hat{H}[v] \right] \Psi \right]$$

(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,

$$\partial_{\Psi_v} A[\Phi, v] = 0$$

(15)

since $\Phi \subset \Psi$ and the stationary point of $A[\Psi, v]$ is in $\Phi$. $A[\Phi, v]$ can be established as a functional of $v$ alone by inserting in $A[\Phi, v]$ that $\Phi[v']$ for which $v' = v$,

$$A[v] = A[\Phi[v], v]$$

(16)

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

$$\delta_v A[v] = \delta_v A[\Phi[v], v] = -n(r, t)$$

(17)

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

To go on to the density-functional, $A[n, v]$, requires establishing that the map $M^*_v : \Phi \to N_v$,

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

(18)
is one-to-one and invertible. In Eq. (18), \( n(r, t) \) 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 [5]. All \( n(r, t) \) in \( \mathcal{N} \) and
\( \mathcal{N}_v \) obey the initial condition
\[ n(r, t_0) = n_0(r) = (\Phi_0, \hat{n}(r)\Phi_0) \quad . \] (19)

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

RG followed an alternative path. Substituting Eq. (7)
to Eq. (18) defines a map \( M_3 = M_1M'_2 : \mathcal{V} \rightarrow \mathcal{N}_v \).
They then show by a pretty argument that \( M_3 \) is one-to-one and invertible for all potentials \( v(t) \) which 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 \( (t_0, t_1) \). \( M_3^{-1} : \mathcal{N}_v \rightarrow \Phi \) can then be constructed
as \( M_3^{-1}M_1 \). Substitution of \( M_3^{-1} \), that is \( \Phi[n] \)
to \( A[\Phi, v] \), 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 \( v' = v \).

2. **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 \( \Phi_0 \)), 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
\[ B[n] = A[n] + \int_{t_0}^{t_1} dt \int dr \; v(r, t; [n])n(r, t) \quad . \] (21)

From Eq. (21), it follows that
\[ \delta n(r, t) B[n] = v(r, t) \quad . \] (22)

The TDKS equations [25] follow from (22).

Consider a system of non-interacting electrons denoted
by subscript \( s \) which move in an external potential
\( v_s(r, t) \), starting from a single determinantal state \( \Phi_{0s} \)
at \( t_0 \). \( v_s \) is a functional of their electron density, \( v_s[n_s] \).
The HZM construction [5] allows identification of \( n_s(r, t) \)
with the density of the interacting system,
\[ n_s(r, t) \equiv n(r, t) \quad , \quad \forall r, t \in (t_0, t_1) \quad . \] (23)

Thus \( v_s \) can be regarded as a functional of \( n \). Combining
\[ \delta n(r, t) B_s[n] = v_s(r, t) \quad , \] (24)
with Eq. (22) leads to
\[ v_s(r, t) = v(r, t) - \delta n(r, t)(A - A_s) \quad . \] (25)

The usual rearrangements in \( A - A_s \) in turn lead to
\[ v_s(r, t) = v(r, t) + v_0(r, t) + v_{XC} (r, t) \quad , \] (26)
\[ v_0(r, t) = \int dr' \frac{n(r', t, t)}{|r - r'|} \quad , \] (27)
\[ v_{XC} (r, t) = -\delta n(r, t)A_{XC}[n] \quad , \] (28)
\[ A_{XC}[n] = \int_{t_0}^{t_1} dt \left\{ \left[ \Psi, i\partial_t \Psi \right] - \left[ \Psi_s, i\partial_t \Psi_s \right] \right\} - \left[ (T - T_s) - (W - W_n) \right] \quad . \] (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 \( \Phi_s[n] \). \( W_n \) 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 Section IV we shall base our development of \( \mathcal{N} \)-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 Section IV.

3. **The symmetry-causality dilemma**

Taking the functional derivative of Eq. (28) with respect to \( n \) results in [37]
\[ \chi^{-1}(r, t; r', t') = \chi_s^{-1}(r, t; r', t') + f(r, t; r', t') \quad , \] (31)
where
\[ \chi(r, t; r', t') = -\frac{\delta n(r, t)}{\delta v(r', t')} \quad , \] (32)
\[ \chi_s(r, t; r', t') = -\frac{\delta n(r, t)}{\delta v_s(r', t')} , \quad (33) \]

\[ f(r, t; r', t') = \frac{\delta [u_n + v_{\text{xc}}](r, t)}{\delta n(r', t')} = \frac{\delta (t - t')}{|r - r'|} + \frac{\delta v_{\text{xc}}(r, t)}{\delta n(r', t')} \quad (34) \]

From Eqs. 18 and 41, the well known retarded character of the time dependence of the susceptibilities \( \chi \) and \( \chi_s \) follows; they vanish if \( t' > t \). Their inverses \( \chi^{-1}(r, t; r', t') \) and \( \chi_s^{-1}(r, t; r', t') \) entering Eq. 31 are regarded as well. Yet

\[ f_{\text{xc}}(r, t; r', t') = \frac{\delta v_{\text{xc}}(r, t)}{\delta n(r', t')} = \frac{\delta^2 A_{\text{xc}}[n]}{\delta n(r', t') \delta n(r, t)} \quad (35) \]

is formally a second derivative of \( A_{\text{xc}}[n] \) according to Eq. 28. Van Leeuwen 22, 25 assumes that, as \( f_{\text{xc}} \) is a second functional derivative, it must be symmetric in \( r, t \) and \( r', t' \). Such symmetry is inconsistent with the retarded nature of \( \chi^{-1} \) and \( \chi_s^{-1} \) in Eq. 31. 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. 31 holds and that \( f_{\text{xc}}(r, t; r', t') \) must be retarded and not symmetric in \( r, t \) and \( r', t' \). They then conclude by supposing from Schwarz’s lemma 34 that (1) \( f_{\text{xc}}(r, t; r', t') \) cannot be a second functional derivative and that (2) the exact \( v_{\text{xc}}[n] \) 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 \( v_{\text{xc}} \) as a functional derivative.

To complicate matters further, Harbola and Banerjee 23, 33 have argued that there is no symmetry-causality dilemma because while \( \chi \) is causals, \( \chi^{-1} \) is symmetric. Amusia and Shaginyan 11, while not disagreeing with this conclusion, have argued that, in contrast, it is possible to construct a causal \( \chi^{-1} \) as well. Harbola 12 has responded that reference 11 itself implies a causality in the potential as a functional of the density. van Leeuwen, however, has argued that \( \chi^{-1} \) must be rigorously causal in analogy with the properties of discrete lower triangular matrices 22, an argument which does not take into account the fact that \( \chi^{-1} \) is not a smooth function of \( t - t' \) but contains both a delta function and the second derivative of a delta 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.

We conclude that in the context of TDDFT at the RG level, \( \chi^{-1} \) is causal. The most forceful argument that the causality of \( \chi^{-1} \) imposes a symmetry-causality dilemma via Eq. 31 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. 28, 29, 31 and 35 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 \( v_{\text{xc}}[n] \) 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

\[ \chi(r, t; r', t') = \frac{\delta^2 A[v]}{\delta v(r', t') \delta v(r, t)} \quad (36) \]

and \( \chi_s \) as well as \( f_{\text{xc}} \). All have a retarded dependence on \( t \) and \( t' \) and are decidedly not symmetric in \( r, t \) and \( r', t' \). Similarly, \( \chi^{-1} \) and \( \chi_s^{-1} \) can be expressed as second derivatives, e.g.

\[ \chi^{-1}(r, t; r', t') = -\frac{\delta v(r, t)}{\delta n(r', t')} = \frac{\delta^2 B[n]}{\delta n(r', t') \delta n(r, t)} \quad (37) \]

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

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 \( \delta A[v]/\delta v(r, t) \) to exist and equal \( -n(r, t) \), first \( \mathcal{V} \) must be smooth enough that variations \( \delta v(r, t) \) 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 \( \delta v(r, t) \), and goes continuously to zero with \( \delta v(r, t) \). \( A[v] \) meets that criterion. The functional derivative \( \delta A[v]/\delta v(r, t) \) is then defined through Fréchet’s theory of linear functionals 28. Similarly, for \( \delta n(r, t)/\delta v(r', t') = \delta^2 A[v]/\delta v(r', t') \delta v(r, t) \)
to exist, \(n(r, t)\) 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 \(\mathbb{R}^3 \times (t_0, t_1)\) precluding the applicability of Schwarz’s lemma (see also the discussion in Appendix B). If \(t' > t\) in \(\delta^2 A[v]/\delta v(r', t')\delta v(r, t)\), it must vanish, destroying symmetry while remaining a well-defined second functional derivative. In the Keldysh action functional used by van Leeuwen \([22, 25]\), the time-ordered contour on which the action is defined, be unchanged by the first functional differentiation. The requirement for the applicability of Schwarz’s lemma (see also the discussion in Appendix B) one searches only for a stationary point of \(B[\Psi] \in \mathcal{N}_v\), one is allowed to relax the subsidiary condition \([48]\) by a Legendre transformation. Eq. (39) then becomes

\[
\Psi[n] = \text{ARG} \left\{ \text{STAT}_\Psi \left[ B[\Psi] - \int_{t_0}^{t_1} dt \int dr \Lambda(r, t)n(r, t) \right] \right\} \tag{40}
\]

Now, the Lagrange multiplier \(\Lambda(r, t)\) will exist if and only if \(n(r, t)\) is \(v\)-representable, in which case Eq. (11) becomes

\[
\Psi[n] = \text{ARG} \left\{ \text{STAT}_\Psi A[\Psi, \Lambda] \right\} \tag{41}
\]

with \(\Lambda \subset \mathcal{V}\), a potential. Thus, the map defined by Eq. (39) is identical to the map \(M^{j-1}_v : \mathcal{N}_v \to \mathcal{N}_v\) defined by RG. Eqs. (39)–(41) 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.

**Our approach**

We note that the stationary point \(\Phi[n]\) of \(B[\Psi]\) in Eq. (39) is unique in the subspace \(\Phi_n\) \((\Psi \to n)\) of \(\Psi\) for \(n \subset \mathcal{N}_v\). The partial functional derivative of \(A[\Psi, v]\), its gradient in \(\Phi_n\), vanishes uniquely there,

\[
\partial_{\Psi} A[\Psi, v]_{v, n} = \partial_{\Psi} B[\Psi]_n = \left[ i\partial_t - \hat{H} \right] \Psi = 0 ; \quad n \subset \mathcal{N}_v, \Psi = \Phi[n] \tag{42}
\]

Thus the magnitude squared of the gradient,

\[
\int_{t_0}^{t_1} dt \left( \partial_{\Psi} A, \partial_{\Psi} A \right)_{v, n} = \int_{t_0}^{t_1} dt \left( \partial_{\Psi} B, \partial_{\Psi} B \right)_{n} \tag{43a}
\]

has a unique minimum there as well. As the search can be restricted to normalized \(\Psi\)’s without penalty, it follows from eq. (13a) that

\[
\int_{t_0}^{t_1} dt \left( \partial_{\Psi} A, \partial_{\Psi} A \right)_{v, n} = \int_{t_0}^{t_1} dt \left( \Psi, [i\partial_t - \hat{H}]^2 \Psi \right) \tag{43b}
\]

holds as well because of the consequent hermiticity of \(i\partial_t\).

**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.) as well. That of Ghosh and Dhara \([29]\) does not produce \(N\)-representability, only \(v\)-representability. Their Theorem 4 can be restated as defining the map \(M_{GD} : \mathcal{N} \to \Psi\),

\[
\Psi[n] = \text{ARG} \left\{ \text{STAT}_{\Psi \to n} B[\Psi] \right\} \tag{39}
\]

However, since in Eq. (39) one searches only for a stationary point of \(B[\Psi] \in \Psi\), one is allowed to relax the subsidiary condition \([48]\) by a Legendre transformation. Eq. (39) then becomes

\[
\Psi[n] = \text{ARG} \left\{ \text{STAT}_{\Psi} \left[ B[\Psi] - \int_{t_0}^{t_1} dt \int dr \Lambda(r, t)n(r, t) \right] \right\} \tag{40}
\]

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 \(n(r, t)\) in \(\mathcal{N}\) via the mapping \(M_2 : \Psi \to \mathcal{N}\),

\[
n(r, t) = (\Psi(t), \delta(\Psi(\tau))(t)) \; , \tag{38}
\]

with \(n(r, t_0) = n_0(r)\). 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 \(M_2^{-1} : \mathcal{N} \to \Psi\). \(M_2^{-1}\) should meet the following four criteria. 1.) It should be universal; 2.) it should require searching only in \(\Psi\) and not in \(\Psi\) and \(\Psi\); 3.) it should subsume the mapping \(M_2^{-1}\) of \(v\)-representable TDDFT; and 4.) it should provide a stationarity principle.
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 \( E[\Psi] = \langle \Psi, \hat{H}\Psi \rangle \) 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. (40), (41). 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:

\[
E[n] = \text{INF}_{\Psi \rightarrow n} E[\Psi] ; \quad \text{(44a)}
\]

\[
\Psi[n] = \text{ARG} \{ \text{INF}_{\Psi \rightarrow n} E[\Psi] \} \quad \text{(44b)}
\]

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

\[
\Psi[n] = \text{ARG} \left\{ \text{INF}_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt \left( \partial_{\Psi} A, \partial_{\Psi} A \right)_{v,n} \right\}
= \text{ARG} \left\{ \text{INF}_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt \left( \partial_{\Psi} B, \partial_{\Psi} B \right)_{n} \right\} \quad \text{(45a)}
= \text{ARG} \left\{ \text{INF}_{\Psi \rightarrow n} \int_{t_0}^{t_1} dt \left( \Psi, [i\partial_t - \hat{H}]^2 \Psi \right) \right\} ;
\]

\[
A[n, v] = \int_{t_0}^{t_1} dt \left( \Psi[n], [i\partial_t - \hat{H}] \Psi[n] \right) \quad \text{(45b)}
\]

We note that the quantity over which the search in Eq. (43) is done corresponds to the time-integral of the McLachlan functional for \( \hat{H} \) widely used in formulations of semiclassical dynamics. The proposed constrained search algorithm expressed in Eqs. (44a, 45a) meets all of the criteria imposed above: 1.) It is universal, not involving \( v \). 2.) It requires searching only in \( \Psi \). 3.) It subsumes \( v \)-representable \( n \) for which the infimum becomes a minimum and yields the condition

\[
(i\partial_t - \hat{H})^2 \Psi = 0 \quad \text{s.t.} \quad \Psi \rightarrow n , \quad \text{(46)}
\]

which yields the same \( \Psi \) as Eq. (39) or, ultimately Eq. (15). Finally, 4.) it provides a stationarity principle since \( n \) in Eq. (45a) can be varied independently of \( v \), and the corresponding partial functional derivative vanishes via Eq. (13),

\[
\partial_n A[n, v] = 0 . \quad \text{(47)}
\]

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 wavefunctions. 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.

APPENDIX A: CAUSALITY OF \( \chi_s^{-1} \) AND \( \chi^{-1} \)

As stated in Section III.3 and III.4, there is a substantial spread of opinion in the literature with regard to the time dependence of \( \chi_s^{-1} \) and \( \chi^{-1} \), 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 \( \chi_s \) of the uniform electron gas, which has the form \( \chi_s([r - r'] , t - t') \), from space-time uniformity. Accordingly, it is diagonalized by Fourier transforming on space and time yielding the eigenvalues \( \chi_s(q, \omega - i\delta), \delta \downarrow 0 \). The wave-vector \( q \) is introduced by the Fourier transform on \( r - r' \), the frequency \( \omega \) is introduced by that on \( t - t' \), and \( \delta \) is introduced by the causality of \( \chi_s \), \( \chi_s([r - r'], t - t') = 0, t > t' \).

The explicit form of \( \chi_s(q, \omega - i\delta) \) is known. 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 wavenumber), there is one bounded branch cut at \( z = \omega + i\delta \), with \( |\omega| \leq \frac{h}{2m}(2k_F q + q^2) \); for \( q > 2k_F \) there are two, with \( \frac{h}{2m}(-2k_F q + q^2) \leq |\omega| \leq \frac{h}{2m}(2k_F q + q^2) \). \( \chi_s(q, \omega) \) has no zeros away from the branch cuts.

\( \chi_s^{-1} \) is also uniform in space and time and therefore diagonalized by Fourier transformation. It’s eigenvalues are simply

\[
\chi_s^{-1}(q, \omega) = 1/\chi_s(q, \omega) . \quad \text{(A1)}
\]

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

\[
\chi_s^{-1}(q, \omega) \rightarrow \frac{A_s(q) \omega^2 + B_s(q) \omega^2}{\delta} + ... \quad \text{(A2)}
\]

\[
|\omega| \rightarrow \infty
\]

\[
\delta \rightarrow 0
\]
\[ A_s(q) = -\frac{m}{nq^2} \]
\[ B_s(q) = \frac{2E_F}{5n} \left[ 3 + \frac{5\hbar^2q^2}{8mE_F} \right] \]
\[ C_s(q) = \frac{16E_F^2q^2}{175nm} \left[ 3 + \frac{35\hbar^2q^2}{8mE_F} \right] \]

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

\[ \chi_s^{-1}(q, t - t') = -A_s(q)\delta''((t - t')^+) + B_s(q)\delta((t - t')^+) + \chi_s^{-1}(q, t - t')' \]

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

The principal change in passing from \( \chi_s(q, \omega) \) to \( \chi(q, \omega) \) for the uniform electron gas is that the free-particle excitations are replaced by quasi-particle 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 \( \chi^{-1}(q, t - t') \) which is given by (A3) with modification of \( A_s(q) \) to \( A(q) \), etc.

For a non-uniform extended system for which the excitation spectrum forms continua, be the system ordered or disordered, there is no change in formal structure of \( \chi_s^{-1}(q, t - t') \) and \( \chi_s^{-1}(q, r; t - t') \). Each contains the local contributions \( \delta''((t - t')^+) \) and \( \delta((t - t')^+) \) as well as non-local retarded contributions. For finite systems which 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 \( \chi_s(r, r'; \omega) \) or \( \chi(r, r'; \omega) \) 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 \( \chi^{-1}(r, r'; z) \) or \( \chi_s^{-1}(r, r'; z) \) at the same \( z \). Upon Fourier transform to the time-domain \( \chi_s^{-1}(r, r'; t - t') \) and \( \chi_s^{-1}(r, r'; t - t') \) each contains a causal contribution from the pole which oscillates with angular frequency corresponding to the excitation energy for \( t > t' \) and vanishes for \( t' > t \).

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

\[ \hat{\chi}^{-1}(t - t') = \hat{A}\delta''((t - t')^+) + \hat{B}\delta((t - t')^+) + \hat{\chi}^{-1}(t - t')' \]

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

**APPENDIX B: SECOND-FUNCTIONAL DERIVATIVE ASYMMETRY**

In section III below Eq. (B7), we have pointed to the modification of the support of \( v(r, t) \) 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, \( \chi \). Alternatively, one can preserve the support on which the function \( v(r, t) \) 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 \( M_1: \mathcal{V} \to \Phi \), Eq. (7), which, together with Eq. (13) defines the map \( M_3: \mathcal{V} \to \mathcal{N}_v, n = n[v] \). A more explicit expression of that map would be

\[ n = n[\hat{\mathcal{H}}_t[v]] \]

according to Eq. (4), in which \( v(r, t) \) is supported on \( (t_0, t) \). However, Eq. (4) can be rewritten as

\[ \Phi(t) = T_L \exp \left[ -i \int_{t_0}^{t_1} dt' \hat{\mathcal{H}}_t[v] \right] \Phi_0 \]

where

\[ \hat{\mathcal{H}}_t[v] = \hat{\mathcal{H}}[v] \]

Thus, by changing the operator space on which the argument of the functional, now the operator \( \hat{\mathcal{H}}_t[v] \), 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

\[ \frac{\delta n(r, t)}{\delta v(r', t')} = \frac{\delta \mathcal{H}_t}{\delta \hat{\mathcal{H}}_t} = 0 \]

\[ t' > t \]

**ACKNOWLEDGMENTS**

We are grateful to Kieron Burke for critical and stimulating discussions in response to which Appendix B was added to the paper. We thank Neepa Maitra for calling relevant references to our attention. We also thank A.K. Rajagopal for bringing his pioneering work on the symmetry-causality paradox to our attention. This research was supported in part by ONR grant N00014-01-1-0365, ONR/DARPA grant N00014-01-1-1061 and NSF grant no. CHE-9875091.
[1] R. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York (1989).
[2] P. Geerlings, F. De Proft, and W. Langenaeker, Chem. Rev. **103**, 1793 (2003).
[3] M.H. Cohen and A. Wasserman, Israel J. Chem. **43**, 219 (2003).
[4] P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964).
[5] W. Kohn and L.J. Sham, Phys. Rev. **140A**, 1133 (1965).
[6] M. Levy, Proc. Nat. Acad. Sci. USA **76**, 6062 (1979); Phys. Rev. A **26**, 1200 (1982).
[7] E.H. Lieb, in *Physics as Natural Philosophy*, eds. A. Shimony and J. Feshbach, (MIT Press, Cambridge), p.111 (1982); Int. J. Quant. Chem. **24**, 243 (1983); in *Density Functional Methods in Physics*, NATO ASI Series B123, ed. R.M. Dreizler and J. da Providencia, Plenum, New York (1985), p.31.
[8] J.E. Harriman, Phys. Rev. A **24**, 680 (1980); G. Zumbach and K. Masche, Phys. Rev. A**28**, 544 (1983); erratum, Phys. Rev. A **29**, 1585 (1984).
[9] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965); J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[10] R. Car and M. Parinello, Phys. Rev. Lett. **55**, 2471 (1985).
[11] See the review by Gross, et al., ref. [12], for a brief historical survey.
[12] E.K.U. Gross, C.A. Ullrich, and U.J. Gossmann, in *Density Functional Theory, NATO ASI Series B337*, ed. E.K.U. Gross and R.M. Dreizler, Plenum Press, New York (1995), p.149.
[13] E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[14] M.E. Casida, in *Recent Advances in Density Functional Methods*, ed. D.P. Chong, p. 155 (World Scientific, Singapore, 1995); M. Petersilka, U.J. Gossmann, and E.K.U. Gross, Phys. Rev. Lett. **76**, 1212 (1996); H. Appel, E.K.U. Gross, and K. Burke, Phys. Rev. Lett. **90**, 043005 (2003).
[15] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[16] J.F. Dobson, M.J. Bunner, and E.K.U. Gross, Phys. Rev. Lett. **79**, 1905 (1997).
[17] N.T. Maitra, K. Burke, and E.K.U. Gross, and R. van Leeuwen, in *Reviews in Modern Quantum Chemistry: A celebration of the contributions of R.G. Parr*, ed. K. Sen, (World Scientific, 2001).
[18] J. Frenkel, Wave Mechanics, Clarendon, Oxford, 1934; P.A.M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930); S.I. Sawada, R. Heather, B. Jackson, and H. Metiu, J. Chem. Phys. **83**, 3009 (1985); F.Y. Hansen, N.E. Henriksen, and G.D. Billing, J. Chem. Phys. **90**, 3060 (1989).
[19] E.K.U. Gross, J.F. Dobson, and M. Petersilka, in *Density Functional Theory*, ed. F. Najlaewski, Springer, Berlin (1996).
[20] A.K. Rajagopal, Phys. Rev. A **54**, 3916 (1996); in "Electron Density Functional Theory: Recent Progress and New Directions", eds. J. F. Dobson, G. Vignale, and M.P. Das, p.217, Plenum Press (1998).