Reply to "Comment on 'Critique of the foundations of time-dependent density functional theory' "

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Abstract

In the preceding Comment, Maitra, van Leeuwen, and Burke (MLB) attempt to refute our criticism of the foundations of TDDFT (see Phys. Rev. A **75**, 022513 (2007)). However, their arguments miss the essence of our position. This is partly due to an ambiguity concerning the present status of the time-dependent (TD) Kohn-Sham (KS) equations. Based on the first Runge-Gross (mapping) theorem, the TD KS equations have to be established as a fixed-point iteration scheme for potential-functionals (PF-FPI). Here, however, the convergence of the FPI is not assured. On the other hand, time-propagation of the TD KS equations in their PF-FPI form fails because these equations do not represent physical equations-of-motion. MLB present a construction of the exact exchange-correlation (xc) potential, apparently contradicting one of our findings. We explain that their construction is explicitly based on the solution of the TD Schrödinger equation, and, for this reason, does not address our objections, let alone refute them.

In a recent paper [1], henceforth referred to as I, we have shown that time-dependent density functional theory (TDDFT) is lacking a valid foundation. In the preceding Comment, Maitra, van Leeuwen, and Burke (MLB) claim that they can falsify one of our two main arguments, affecting the viability of time-propagation in the TDDFT context. However, partly due to an ambiguity with regard to the so-called mapping derivation of the time-dependent (TD) Kohn-Sham (KS) equations, their demonstration fails to challenge the essence of our position, as we will explain in the following.

Before addressing the central issue, let us rectify two misunderstandings brought up in the first paragraph of the Comment, concerning (i) the problems of the Runge-Gross (RG) action-integral functionals, and (ii) the use of non-local (external) potentials in DFT or TDDFT. The latter point, being the topic of Secs. 2 and 3 in I, is not at all intended as a critique of DFT (or TDDFT). On the contrary, it is a highly instructive confirmation of the logical consistency of DFT in view of an apparent contradiction. Second, we fully agree that the failure of the RG action-integral functionals [2] was recognized previously, as has been clearly stated in I (see Refs. 32 and 36). However, the breakdown of the original RG foundation of the TD KS equations is not widely known outside the inner TDDFT community. Moreover, the problem of the RG functionals is by no means resolved by the Keldysh action [3], as insinuated by MLB and others. Lacking an $i\partial_t$ term, the Keldysh action functional cannot be used to establish TD equations. Without the RG action-integral functionals, one has to rely entirely on the first RG theorem (RG1), an essentially mathematical theorem mapping TD densities to TD potentials. In view of the enormity of the claim (an approach to the time-evolution of quantum many-particle systems without phase information), one may rightly wonder whether this can succeed.

Unfortunately, the "mapping foundation" of TDDFT, based entirely on the RG1 theorem [2], has not been spelled out completely and transparently in the literature, let alone analyzed critically. Besides other problems, a common source of confusion arises from not always distinguishing clearly between potential-functionals and potentials. A potential-functional, such as the Kohn-Sham potential-functional (PF),

$$v_S : n(\boldsymbol{r}, t) \rightarrow v_S[n(t)](\boldsymbol{r}, t) \tag{1}$$

is a a function of functions, that is, a recipe to construct a (time-dependent) potential $u(\boldsymbol{r}, t)$ for a given density $n(\boldsymbol{r}, t)$. Here and in the following, we adopt the notation used

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by MLB; the KS PF was referred to as $w[\rho(t)](\boldsymbol{r}, t)$ in I. While the KS PF is trivial as a potential-functional, the specific potential

$$v_S(\boldsymbol{r}, t) = v_S[n_0(t)](\boldsymbol{r}, t) \tag{2}$$

associated with the exact TD density, $n_0(\boldsymbol{r}, t)$, of the interacting N-electron system under consideration is a highly non-trivial TD potential. Using it in the TD KS equation for a single orbital (assuming here the radical Kohn-Sham (rKS) version),

$$i\frac{\partial}{\partial t}\psi(\boldsymbol{r}, t) = \{-\tfrac{1}{2}\nabla^2 + v_S(\boldsymbol{r}, t)\}\psi(\boldsymbol{r}, t) \tag{3}$$

would allow one to determine the time-evolution of the exact one-particle density $n_0(\boldsymbol{r}, t)$. However, the question is not whether such a potential exists and could be used to solve the TD KS equation in the familiar way (that is, by time-propagation). Indeed, the existence of $v_S(\boldsymbol{r}, t)$ is almost a triviality, as was demonstrated in I for the rKS version. The actual problem is how to determine $v_S(\boldsymbol{r}, t)$ (and thereby $n_0(\boldsymbol{r}, t)$) without somehow solving the full TD N-electron Schrödinger equation. Here, the KS PF (1) is obviously of no help. We have called it trivial because it is completely unspecific (void of physical significance) and applies to any given TD density. The information necessary to generate the TD potential associated with a given TD density (trajectory) $n(\boldsymbol{r}, t)$ has to be extracted from the density trajectory itself. To determine the respective potential at a given time t, the density $n(\boldsymbol{r}, t)$, and its 1st and 2nd time-derivatives, $\dot{n}(\boldsymbol{r}, t)$, $\ddot{n}(\boldsymbol{r}, t)$, are needed, as we have shown in Sec. 5 of I.

So what actually is the mapping foundation of the TD KS equations? The procedure offered here [4] is essentially a fixed-point iteration scheme for the desired density $n_0(\boldsymbol{r}, t)$, resting on the following three equations (in rKS formulation):

$$v_{xc}[n(t)](\boldsymbol{r}, t) \equiv v_S[n(t)](\boldsymbol{r}, t) - v_H[n(t)](\boldsymbol{r}, t) - v_{ext}[n(t)](\boldsymbol{r}, t) \tag{4}$$

$$i\frac{\partial}{\partial t}\psi(\boldsymbol{r}, t) = \{-\tfrac{1}{2}\nabla^2 + v(\boldsymbol{r}, t) + v_H[n(t)](\boldsymbol{r}, t) + v_{xc}[n(t)](\boldsymbol{r}, t)\}\psi(\boldsymbol{r}, t) \tag{5}$$

$$n(\boldsymbol{r}, t) = N|\psi(\boldsymbol{r}, t)|^2 \tag{6}$$

The first equation (Eq. 81 in I) serves as a definition of the (non-trivial) exchange-correlation (xc) PF. Here $v_{ext}[n(t)](\boldsymbol{r}, t)$ is the "external" PF established by RG1 for N interacting electrons. For a given TD density $n(\boldsymbol{r}, t)$ this PF yields the TD potential recovering

$n(\boldsymbol{r},t)$ when used in the interacting N-electron TD Schrödinger equation. In particular,

$$v_{ext}[n_0(t)](\boldsymbol{r},t) = v(\boldsymbol{r},t) \tag{7}$$

where $v(\boldsymbol{r},t)$ is the specific external potential of the system under consideration. In a similar way the (trivial) KS PF, $v_S[n(t)](\boldsymbol{r},t)$, established by the RG1 mapping for the non-interacting KS system (or directly according to Eq. 75 of I), yields a potential that will recover $n(\boldsymbol{r},t)$ when used in the TD KS equation (3); $v_H[n](\boldsymbol{r},t)$ denotes the Hartree PF.

By using the non-trivial xc PF in the KS equation (5) one obtains a fixed-point itera-tion (FPI) scheme with the desired $n_0(\boldsymbol{r},t)$ as the fixed-point. This becomes particularly transparent by expressing $v_{xc}[n(t)]$ according to Eq. (4):

$$i\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = \{-\tfrac{1}{2}\nabla^2 + v_S[n(t)](\boldsymbol{r},t) + v(\boldsymbol{r},t) - v_{ext}[n(t)](\boldsymbol{r},t)\}\psi(\boldsymbol{r},t) \tag{8}$$

If and only if $n(\boldsymbol{r},t) \equiv n_0(\boldsymbol{r},t)$, the two latter potentials on the rhs cancel each other (see Eq. 7), and the KS equation with the remaining potential, $v_S[n_0(t)](\boldsymbol{r},t) = v_S(\boldsymbol{r},t)$, will yield the fixed-point density $n_0(\boldsymbol{r},t)$. At the fixed-point (and only here), Eq. (4) turns into a relation between the (exact) xc and KS potentials, as given by Eq. C(1) of the Comment.

However, as it stands, this is just an *ad hoc* fixed-point iteration scheme. To qualify as a method for determining $n_0(\boldsymbol{r},t)$, the question of convergence must be settled, at least in principle. But so far there is no proof of the feasibility of convergence (not to be dismissed as "numerical convergence" in actual computations). So even if one had the exact xc PF, $v_{xc}[n(t)]$, this would be of no avail to determine the fixed-point solution, because one cannot expect the FPI (referred to as "trajectory mode solution" in I) to converge. The situation here is completely different from static DFT, where FPI is the standard method to deter-mine the ground-state density $n_0(\boldsymbol{r})$. In static DFT, by contrast, the variational principle according to the second Hohenberg-Kohn theorem [5] assures the convergence of the FPI as a means of finding the existing minimum of the energy functional.

In the TDDFT community, the lack of a proof of convergence for the TD KS fixed-point iteration has never been seen as a problem. To the best of our knowledge, the problem has not even been mentioned in the TDDFT literature. There was no reason to worry about the TD FPI at all because there was an apparent silver bullet: direct time-propagation of the TD KS equation (5). By starting from the exact static ground-state density $n_0(\boldsymbol{r})$ at the onset of the TD interaction, say at $t = 0$, it was believed that one could propagate the

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initital KS orbital(s) through a given time by supplying the required density argument in $v_{xc}[n(t)](\boldsymbol{r}, t)$ (and $v_H[n(t)](\boldsymbol{r}, t)$) on the fly via Eq. (6). While this would work for instantaneous potential-functionals (as those used in the adiabatic approximation), in general, PFs cannot be expected to be instantaneous. As we have explicitly shown in I, the KS PF $v_S[n(t)](\boldsymbol{r}, t)$, required in the definition (4) of $v_{xc}[n(t)](\boldsymbol{r}, t)$, depends on the 2nd time-derivative of the density, which undermines the possibility of propagation. The eventuality that the PFs appearing in the TD KS equations are non-instantaneous in the described sense has never been seen and addressed before. The inescapable conclusion of that finding is that the TD KS equations, as established by the RG1 mapping theorem, do not represent physical equations-of-motion amenable to time-propagation: The silver bullet is an illusion.

To avoid possible misunderstanding, the dependence on the 2nd time-derivative of the density (and thus on the infinitesimal "past" and "future" of the density at a given time t) pertains to the PFs, $v_S[n(t)]$, $v_{ext}[n(t)]$, and $v_{xc}[n(t)]$, and, more specifically, to the information required to construct a potential at a given time t from the respective PF. We do *not* claim that this applies to the potentials, $v_S(\boldsymbol{r}, t)$ or $v_{xc}(\boldsymbol{r}, t)$, themselves. As a matter of fact, $v_S(\boldsymbol{r}, t)$ or $v_{xc}(\boldsymbol{r}, t)$ can be determined *directly* by somehow solving the full TD Schrödinger equation (FTDSE) for the original N-electron system. We do not at all deny that such a direct FTDSE-based determination of the potentials can do perfectly well without 2nd time-derivatives of the wave function or the density. An example of a direct approach was presented in I. For the exact TD density $n_0(\boldsymbol{r}, t)$, obtained by solving the FTDSE (e.g. by time-propagation from a specified initial state), $v_S(\boldsymbol{r}, t)$ could be determined by inserting the density as argument in the explicitly available (trivial) KS PF, $v_S(\boldsymbol{r}, t) = v_S[n_0(t)](\boldsymbol{r}, t)$. (This way of determining $v_S(\boldsymbol{r}, t)$ from $n_0(\boldsymbol{r}, t)$ is also referred to as the inversion of the TD KS equation.) In the final inversion step, being based only on the density information, the 2nd time-derivative of the density is required, which, of course, causes no problem here as the density trajectory is available anyway, along with its 1st and 2nd time-derivatives.

At this point MLB think they can refute us, namely, by demonstrating that the exact xc potential $v_{xc}(\boldsymbol{r}, t)$ can be determined without recourse to 2nd derivatives of the density, that is, by a procedure depending only on the past. The problem is that their procedure is of the direct type, manifestly based on solving the FTDSE, as we will explain below. Obviously, we have no objections to such a direct construction of the exact xc or KS potentials, but it should by no means be confused with a genuine density-functional approach.

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MLB begin their specific argumentation with a "simple counter-example" which allegedly arises if the rKS scheme is applied to a TD one-electron system and leads to an "absurd conclusion." But what MLB imply here is simply due to a misconception. For any one-electron system, the rKS and external PFs become identical, so that they cancel in Eq. 8, yielding the regular one-particle SE with the given TD potential $v(\boldsymbol{r}, t)$, exactly as is to be expected: no dependence on $\ddot{n}(\boldsymbol{r}, t)$, whatsoever. Alternatively, according to Eq. 4, we have $v_{xc}[n(t)](\boldsymbol{r}, t) = -v_H[n(t)](\boldsymbol{r}, t)$, just as demanded by MLB.

Now let us inspect the derivations along Eqs. C(2-11) in the Comment (C), where MLB demonstrate the possibility to construct the exact xc potential, more precisely the combined Hartree and xc potential, $v_{HXC}(\boldsymbol{r}, t) = v_{xc}(\boldsymbol{r}, t) + v_H(\boldsymbol{r}, t)$, without recourse to 2nd time-derivatives of the density. But as can readily be seen, this construction is based on solving the FTDSE. Here, the key is to note that the Sturm-Liouville type Eq. C(4), underlying the construction of $v_{HXC}(\boldsymbol{r}, t)$, depends explicitly on the quantity (Eq. C2)

$$q(\boldsymbol{r}, t) = \langle \Psi(t)|\hat{q}(\boldsymbol{r})|\Psi(t)\rangle$$

that is, an expectation value involving the N-electron TD wave function $\Psi(t)$. This makes apparent that the construction of the xc potential at a given time t along Eqs. C(2) to C(5) depends on the TD N-electron wave function $\Psi(t)$ at t.

Since, according to Eq. C(4), $v_{HXC}(\boldsymbol{r}, t)$ (at a given time t) is completely determined by $\Psi(t)$ (and the density $n(t)$, being itself determined by $\Psi(t)$), one might devise a time-propagation scheme for $v_{HXC}(\boldsymbol{r}, t)$ based on time-propagation of $\Psi(t)$. The time-propagation of $v_{HXC}(\boldsymbol{r}, t)$ could then be used in the propagation of the TD KS equations, of which the first step has been specified in Eq. C(6). Like the underlying time-propagation of $\Psi(t)$, the (concomitant) time-propagations of $v_{HXC}(\boldsymbol{r}, t)$ and the TD KS equations are viable procedures, depending only on the previous (past) time steps and the initial wave function. Of course, this is not what MLB want to do. Nevertheless, apparently unnoticed, their procedure is based on providing the wave function at the respective times t, not via time-propagation, to be sure, but using a Taylor expansion of $\Psi(t)$ at $t = 0$, as we will explain in the following.

Obviously, MLB expand $v_{HXC}(\boldsymbol{r}, t)$ in a Taylor expansion at $t = 0$. This can be seen in Eq. C(9), specifying the linear term at $t = \Delta t$,

$$v_{HXC}(\boldsymbol{r}, \Delta t) = v_{HXC}(\boldsymbol{r}, 0) + \partial_t v_{HXC}(\boldsymbol{r}, 0)\Delta t$$

To evaluate the potential at $t = 2\Delta t$ the Taylor expansion has to be expanded through the quadratic term, $2\partial_t^2 v_{HXC}(\boldsymbol{r}, 0)\Delta t^2$, and so forth, with the respective time arguments $\Delta t, 2\Delta t, 3\Delta t, \ldots$. At this point it is important to observe that the expansion of $v_{HXC}(\boldsymbol{r}, t)$ at $t = 0$, is directly related to the corresponding Taylor expansion of the TD wave function $\Psi(t)$. The first step, spelled out in Eq. C(8), establishes $\partial_t \Psi(0) = -i\hat{H}(0)\Psi(0)$, which readily leads to the commutator expression on the rhs of Eq. C(8). In the general kth time step, the k-th time-derivative of $q(\boldsymbol{r}, t)$ can be written in a form involving multiple commutators of $\hat{q}(\boldsymbol{r})$, $\hat{H}(0)$, and time derivatives of $\hat{H}(t)$ at $t = 0$, sandwiched by $\Psi_0 = \Psi(0)$ (see text after Eq. C11). Obviously, these multiple commutators arise from terms of the kind $\hat{H}(0)^k|\Psi_0\rangle$ with increasingly higher powers of $\hat{H}(0)$ and higher time-derivatives $\partial_t^k \hat{H}(0)$. The $k = 2$ term is given explicitly in the unnumbered equation following Eq. C(11). To conclude, in each time step of their time-propagation of the KS equation, MLB use a higher derivative of $\Psi(t)$ at $t = 0$, generated by applying successively higher powers of the Hamiltonian to $\Psi(0)$. Evidently, this is a way of solving the TD Schrödinger equation.

Let us note that a Taylor expansion of $\Psi(t)$ at $t = 0$ means a severe restriction compared to time-propagation, as it presupposes that the TD Hamiltonian, and thus the wave function, is analytic at all times. In any case, what MLB have shown (or could have shown more stringently using time-propagation) is that the exact xc potential can be constructed directly, and then used in a regular time-propagation scheme for the TD KS equations, if the N-electron wave-function $\Psi(t)$ is at hand. We have no objections to that result, it simply misses the point. What MLB should have shown is that one can construct the xc potential at t if only the exact density is available at t or prior to t. The latter proof will not be possible, we believe, because one cannot expect that a mathematical mapping theorem such as RG1 will result in physical equations-of-motion, amenable to time-propagation. At some point that deficiency has to emerge.

The status of the TD KS equations as physical equations-of-motion has always been seen as self-evident. But after the failure of the RG action-integral functionals and their stationarity principles, this can no longer be taken for granted. Surprisingly, this issue has been addressed nowhere in the TDDFT literature, let alone clarified. There is no such thing as a second founding paper (of the theorem-proof type), filling the void after the breakdown of the original RG foundation. Even more disconcerting is that the PF-FPI concept, while well-known in the inner TDDFT community, has not been fully disclosed or analyzed in

the literature so far. What is offered instead is rather misleading (see, for example, the authoritative review article by Marquardt and Gross [6]). It is insinuated, partly by not clearly distinguishing between the levels of PFs and potentials, that a non-trivial xc PF can be obtained by just subtracting the Hartree PF and the given external potential $v(\boldsymbol{r}, t)$ from the trivial KS PF. While the TD KS equations then assume the familiar, reassuring shape of physical equations-of-motion, apparently amenable to time-propagation after making a good guess for the xc PF, the actual problems of the underlying mapping-based FPI scheme are simply ignored.

Let us summarize: (1) After the breakdown of the original foundation based on the RG action-integral functionals, the TD KS equations have to be established as a fixed-point iteration scheme for potential-functionals (PF-FPI) based on the Runge-Gross (RG1) mapping theorem. In I we have shown that the PF-FPI concept is not valid because the convergence of the FPI is not assured. The apparent way out (time-propagation of the TD KS equations in their PF-FPI form) fails because these equations do not represent physical equations-of-motion. This emerges from the necessity to provide 2nd time-derivatives of the density in the xc or KS PF. (2) A direct construction of the xc potential at some t, based on the solution of the full time-dependent Schrödinger equation (FTDSE), is always possible, and does not, of course, depend on 2nd time derivatives, as MLB show. Using this xc potential in the KS equations will reproduce the exact density $n_0(\boldsymbol{r}, t)$. Obviously, such a direct Kohn-Sham potential (DKSP) scheme is little more than a detour to determine the exact density by ultimately solving (or approximating) the FTDSE. It certainly does not constitute a density-functional method. (3) Upon close inspection, it is seen that the construction of the xc potential given by MLB is based on the solution of the FTDSE (in this case, by a Taylor expansion of the wave function at $t = 0$). For this reason, our objections to the present TDDFT foundations have not been addressed, let alone refuted.

In conclusion, the status of TDDFT as an in-principle rigorous approach to the time-evolution of an interacting many-electron system, must still be considered as completely unfounded. In view of this situation, a major effort should be made to ultimately clarify the question as to whether one can derive predictive equations-of-motion formulated entirely in terms of densities, that is, without recourse to the wealth of phase information governing the time-evolution of the many-electron wave functions. It is highly questionable whether one will be able to derive density-based physical equations-of-motion at all, but it will be

next to impossible to do so without a valid variational (or stationary) principle. As MLB have made reference to a piece of world literature, it may be allowed to respond by alluding to another famous text [7], which might not be unrelated to the present state of TDDFT.

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