Differentiation of density functionals that conserves the normalization of the density

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The formula for differentiation of functional $A[\rho]$ with respect to $\rho(\mathbf{r})$ while keeping the normalization $\int \rho(\mathbf{r})d\mathbf{r}$ of $\rho(\mathbf{r})$ fixed is derived, and basic properties arising from it are concerned. The results are then generalized for time-dependent theories. One of the essential consequences of normalization conservation for functional differentiation, namely, that it ruins the symmetry in $\mathbf{r}$ of multiple derivatives, is shown to give the resolution of the causality paradox of response functions in time-dependent density-functional theory. The formula for the differentiation of functionals $A[\rho]$ that conserves the shape of $\rho(\mathbf{r})$ is also presented.

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I. INTRODUCTION

Functional differentiation plays an essential role in density-functional theory [1,2], where the particle density takes the place of the wave function of traditional quantum mechanics as the basic variable. For determining the ground-state density $\rho(\mathbf{r})$ of an N-particle quantum system in an external field $v(\mathbf{r})$, density-functional theory has its own variational principle, based on the second Hohenberg-Kohn theorem [3], which says that the energy functional

$$E_v[\rho]=F[\rho]+\int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \tag{1}$$

where $F[\rho]$ is a functional determined by the type of interaction between the particles, takes its minimum over N-particle densities for the real density of the ground-state system, from which it follows that variations of $E_v[\rho]$ which conserve the particle number

$$N=\int \rho(\mathbf{r})d\mathbf{r} \tag{2}$$

must vanish for the ground-state density of the system (N,v):

$$\delta_N E_v[\rho]=0, \tag{3}$$

that is,

$$\frac{\delta E_v[\rho]}{\delta_N \rho(\mathbf{r})}=0 \tag{4}$$

[$\delta/\delta_N\rho(\mathbf{r})$ denotes functional differentiation with respect to $\rho(\mathbf{r})$ while keeping N fixed]. However, no formula for carrying out number-conserving functional differentiations $\delta/\delta_N\rho(\mathbf{r})$ explicitly is known. To bypass this problem, a Lagrange multiplier μ is introduced to ensure the fulfilment of Eq. (2), thereby resolving the constraint on the variations in Eq. (3), giving

$$\delta\left\{E_v[\rho]-\mu\left(\int \rho(\mathbf{r})d\mathbf{r}-N\right)\right\}=0, \tag{5}$$

from which

$$\frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})}=\mu \tag{6a}$$

or

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}+v(\mathbf{r})=\mu \tag{6b}$$

arises, which, if knowing $F[\rho]$, can be used formally to get $\rho(\mathbf{r};\mu)$; then, using Eq. (2), μ can be determined, thus obtaining the ground-state density of the system (N,v). Though having this procedure, embodied in Eq. (6) with Eq. (2), it is, of course, still an open question as to what extent the direct use of Eq. (4) means an alternative. Apart from the problem of getting the ground-state density for a given $v(\mathbf{r})$, N conservation in density-functional theory is substantial in general, as density-functional theory concerns changes in the distribution of a given number of particles induced by changes in the external potential acting on the particles. N conservation also appears in the case of using a functional $A_N[\rho]$ which is an exact expression for a density functional $A[\rho]$ for a given particle number N, that is,

$$A[\rho_N]=A_N[\rho_N], \tag{7}$$

e.g., the Weizsäcker or the Thomas-Fermi expression for the noninteracting kinetic energy functional, where generally

$$\frac{\delta A[\rho_N]}{\delta\rho(\mathbf{r})}\neq\frac{\delta A_N[\rho_N]}{\delta\rho(\mathbf{r})}, \tag{8}$$

but

$$\frac{\delta A[\rho_N]}{\delta_N\rho(\mathbf{r})}=\frac{\delta A_N[\rho_N]}{\delta_N\rho(\mathbf{r})} \tag{9}$$

is the correct relationship. Recent attempts to resolve the controversy about the homogeneity relation [4–7] for the kinetic energy density functional by using number-conserving functional differentiations $\delta/\delta_N\rho(\mathbf{r})$ instead of unconstrained ones $\delta/\delta\rho(\mathbf{r})$ [5] have also drawn attention to the problem of not knowing how to carry out differentiation with respect to $\rho(\mathbf{r})$ while keeping $\int\rho(\mathbf{r})d\mathbf{r}$ fixed. In this paper this question will be answered by deriving the formula of number-conserving functional differentiation. The essential properties of this differentiation will be considered, and the results will be generalized for time-dependent theories, by which the causality paradox of time-dependent density-functional theory [8,9] will also be resolved.

II. DERIVATION OF THE FORMULA AND ESSENTIAL CONSEQUENCES

The basis for the derivation is the separation of the dependence on $N=\int\rho(\mathbf{r})d\mathbf{r}$ in $\rho(\mathbf{r})$ by [10]

$$\rho(\mathbf{r})=N\frac{g(\mathbf{r})}{\int g(\mathbf{r}')d\mathbf{r}'},\tag{10}$$

with the use of which the functional

$$A[g,N]=A\left[N\frac{g}{\int g}\right]\tag{11}$$

results, given a functional $A[\rho]$. This $A[g,N]$ can be considered as a two-variable functional, the partial derivative of which with respect to $g(\mathbf{r})$, provided $A[\rho]$ is differentiable with respect to $\rho(\mathbf{r})$, can be written, applying the chain rule of functional differentiation, as

$$\left(\frac{\delta A[g,N]}{\delta g(\mathbf{r})}\right)_N=\int\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\left(\frac{\delta\rho(\mathbf{r}')}{\delta g(\mathbf{r})}\right)_N d\mathbf{r}',\tag{12}$$

where

$$\left(\frac{\delta\rho(\mathbf{r}')}{\delta g(\mathbf{r})}\right)_N=\frac{N}{\int g(\mathbf{r}'')d\mathbf{r}''}\left(\delta(\mathbf{r}'-\mathbf{r})-\frac{g(\mathbf{r}')}{\int g(\mathbf{r}'')d\mathbf{r}''}\right)\tag{13}$$

from Eq. (10). Here $g(\mathbf{r})$, of course, can be $\rho(\mathbf{r})$ itself, for which $N=\int\rho(\mathbf{r})d\mathbf{r}$. Since $A[g,N]\big|_{g=\rho}=A[\rho]$ and any variations of $g(\mathbf{r})$ at $\rho(\mathbf{r})$ conserve the normalization N of $\rho(\mathbf{r})$, for $g=\rho$, $[\delta/\delta g(\mathbf{r})]_N$ is $\delta/\delta_N\rho(\mathbf{r})$, that is,

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}=\left(\frac{\delta A[g,N]}{\delta g(\mathbf{r})}\right)_N\Bigg|_{g=\rho},\tag{14}$$

so Eq. (13) yields

$$\frac{\delta\rho(\mathbf{r}')}{\delta_N\rho(\mathbf{r})}=\delta(\mathbf{r}'-\mathbf{r})-\frac{\rho(\mathbf{r}')}{N}\tag{15}$$

and Eq. (12) gives

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}=\int\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r}')}{\delta_N\rho(\mathbf{r})}d\mathbf{r}'.\tag{16}$$

From Eqs. (15) and (16), finally,

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}=\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}-\frac{1}{N}\int\rho(\mathbf{r}')\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}d\mathbf{r}',\tag{17}$$

the formula searched, arises. It is worth pointing out that the essence of solving the problem of differentiation $\delta/\delta_N\rho(\mathbf{r})$ lies in finding expression (15) for $\delta\rho(\mathbf{r}')/\delta_N\rho(\mathbf{r})$ [the relation between $\delta\rho(\mathbf{r}')/\delta_N\rho(\mathbf{r})$ and $\delta\rho(\mathbf{r}')/\delta\rho(\mathbf{r})=\delta(\mathbf{r}'-\mathbf{r})$], the key for it being the recognition of the connection exhibited by Eq. (14). It is also worthy of note that, while $\int[\delta\rho(\mathbf{r}')/\delta\rho(\mathbf{r})]d\mathbf{r}'=1$, from Eq. (15),

$$\int\frac{\delta\rho(\mathbf{r}')}{\delta_N\rho(\mathbf{r})}d\mathbf{r}'=0,\tag{18}$$

so multiplying Eq. (17) by $\delta\rho(\mathbf{r})/\delta_N\rho(\mathbf{r}')$, after integration,

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r}')}=\int\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta_N\rho(\mathbf{r}')}d\mathbf{r}\tag{19}$$

arises, which is analogous to the relation

$$\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}=\int\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta\rho(\mathbf{r}')}d\mathbf{r}$$

of unconstrained functional differentiation. A verification of formula (17) (maybe the only obvious one) is given by applying it to the simple case of the functional $f(N)$, the derivative $\delta f(N)/\delta_N\rho(\mathbf{r})$ of which is expected to be zero since $f(N)$ depends on $\rho(\mathbf{r})$ only through N:

$$\frac{\delta f(N)}{\delta_N\rho(\mathbf{r})}=\frac{\partial f(N)}{\partial N}-\frac{1}{N}\int\rho(\mathbf{r}')\frac{\partial f(N)}{\partial N}d\mathbf{r}'=0.$$

Equation (17) is in agreement with an argument by Parr and Bartolotti [11], who concluded, decomposing $\rho(\mathbf{r})$ into N and a shape function $\sigma(\mathbf{r})$, which is normalized to 1, that the difference of the $\delta/\delta_N\rho(\mathbf{r})$ derivative and the $\delta/\delta\rho(\mathbf{r})$ derivative of a functional is independent of $\mathbf{r}$.

Considering the generally accepted [10,11,14] view on number-conserving functional differentiation in density-functional theory—namely, that a $\delta/\delta_N\rho$ derivative is determined only up to an arbitrary constant—it is important to examine why, in fact, a unique formula could have been derived. The above view comes from the following reasoning: a functional derivative being defined by

$$\delta A[\rho]=\int\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r})d\mathbf{r}\tag{20}$$

and for N-conserving variations

$$\int\delta_N\rho(\mathbf{r})d\mathbf{r}=0,\tag{21}$$

for N-conserving variations of a functional:

$$\delta_N A[\rho]=\int\left(\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}+C\right)\delta_N\rho(\mathbf{r})d\mathbf{r},\tag{22}$$

thus, $\delta A[\rho]/\delta_N\rho(\mathbf{r})$ is defined only up to an arbitrary constant. [Note that ''constant'' here means independence of $\mathbf{r}$, but not of $\rho(\mathbf{r})$: that is, an arbitrary, purely functional dependence on $\rho(\mathbf{r})$ is allowed.] The fault in this logic is that it assumes that the definition Eq. (20) becomes

$$\delta_N A[\rho] = \int \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})} \delta_N \rho(\mathbf{r}) d\mathbf{r} \tag{23}$$

for defining $\delta A[\rho]/\delta_N \rho(\mathbf{r})$. However, from Eq. (20), only

$$\delta_N A[\rho] = \int \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \delta_N \rho(\mathbf{r}) d\mathbf{r} \tag{24}$$

arises for N-conserving variations, which is in accordance with the rigorously derived Eq. (16), and Eq. (23), which is justified by Eq. (19), but not trivial, has to be considered only as a property of number-conserving functional differentiation, that is, a necessary but not sufficient condition for $\delta A[\rho]/\delta_N \rho(\mathbf{r})$. So one could ask the question, how can then a $\delta/\delta_N \rho$ derivative be defined? The answer is that a $\delta/\delta_N \rho$ derivative is that part of an unconstrained $\delta/\delta\rho$ derivative which, for an arbitrary variation $\delta\rho(\mathbf{r})$ of $\rho(\mathbf{r})$, gives the variation of a functional that is due to the N-conserving variation part of $\delta\rho(\mathbf{r})$ $[\delta_N \rho(\mathbf{r})]$. To see this, decompose the full variation of $\rho(\mathbf{r})$ as

$$\delta\rho(\mathbf{r}) = \delta N \frac{g(\mathbf{r})}{\int g(\mathbf{r}')d\mathbf{r}'} + N \delta \frac{g(\mathbf{r})}{\int g(\mathbf{r}')d\mathbf{r}'}, \tag{25}$$

in accordance with Eq. (10). The second part in Eq. (25) is nothing else than $\delta_N \rho(\mathbf{r})$ for $g = \rho$,

$$\begin{aligned} \delta_N \rho(\mathbf{r}) &= N \delta \frac{g(\mathbf{r})}{\int g(\mathbf{r}')d\mathbf{r}'}\bigg|_{g=\rho} \\ &= \int \left\{ \delta(\mathbf{r}-\mathbf{r}') - \frac{\rho(\mathbf{r})}{N} \right\} \delta\rho(\mathbf{r}') \\ &= \int \frac{\delta\rho(\mathbf{r})}{\delta_N \rho(\mathbf{r}')} \delta\rho(\mathbf{r}'), \end{aligned} \tag{26}$$

and the first part gives that part of $\delta\rho(\mathbf{r})$ where only the normalization of $\rho(\mathbf{r})$ is varied, and its shape is conserved: $\delta_\sigma \rho(\mathbf{r})$. Inserting Eq. (26) into Eq. (24) yields, with the use of Eq. (16),

$$\delta_N A[\rho] = \int \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})} \delta\rho(\mathbf{r}) d\mathbf{r}, \tag{27}$$

which is precisely what was stated above. [Note that, as arbitrary variations $\delta\rho(\mathbf{r})$ are allowed in Eq. (27), the kind of ambiguity, exhibited by Eq. (22), that is involved in the use of Eq. (23) to determine $\delta/\delta_N \rho$ derivatives is not present with Eq. (27).] Further, since

$$\delta A[\rho] = \delta_\sigma A[\rho] + \delta_N A[\rho], \tag{28}$$

$$\begin{aligned} \delta_\sigma A[\rho] &= \int \frac{1}{N} \int \rho(\mathbf{r}') \frac{\delta A[\rho]}{\delta \rho(\mathbf{r}')} d\mathbf{r}' \, \delta\rho(\mathbf{r}) d\mathbf{r} \\ &= \delta N \frac{1}{N} \int \rho(\mathbf{r}') \frac{\delta A[\rho]}{\delta \rho(\mathbf{r}')} d\mathbf{r}'; \end{aligned} \tag{29}$$

that is, as, analogously to Eq. (27),

$$\delta_\sigma A[\rho] = \int \frac{\delta A[\rho]}{\delta_\sigma \rho(\mathbf{r})} \delta\rho(\mathbf{r}) d\mathbf{r}, \tag{30}$$

$$\frac{\delta A[\rho]}{\delta_\sigma \rho(\mathbf{r})} = \frac{1}{N} \int \rho(\mathbf{r}') \frac{\delta A[\rho]}{\delta \rho(\mathbf{r}')} d\mathbf{r}', \tag{31}$$

which is the formula of shape-conserving functional differentiation. An unconstrained, or full, derivative can thus be written as the sum of two component derivatives:

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta A[\rho]}{\delta_\sigma \rho(\mathbf{r})} + \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})}. \tag{32}$$

For $\rho(\mathbf{r})$, Eq. (31) gives

$$\frac{\delta \rho(\mathbf{r}')}{\delta_\sigma \rho(\mathbf{r})} = \frac{\rho(\mathbf{r}')}{N}. \tag{33}$$

Equation (31), of course, can also be obtained from Eq. (25), via

$$\delta_\sigma \rho(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N} \delta N. \tag{34}$$

It is worthy of mention, finally, that the two Euler equations (4) and (6) are derivable from Eqs. (27) and (24), respectively.

For number-conserving differentiation of functionals composed from two functionals there are rules analogous to the corresponding rules of unconstrained functional differentiation—namely, for the sum of two functionals,

$$\frac{\delta(A+B)}{\delta_N \rho(\mathbf{r})} = \frac{\delta A}{\delta_N \rho(\mathbf{r})} + \frac{\delta B}{\delta_N \rho(\mathbf{r})}; \tag{35}$$

for the product of two functionals,

$$\frac{\delta(AB)}{\delta_N \rho(\mathbf{r})} = \frac{\delta A}{\delta_N \rho(\mathbf{r})} B + A \frac{\delta B}{\delta_N \rho(\mathbf{r})}; \tag{36}$$

and the chain rule for $\delta/\delta_N \rho(\mathbf{r})$,

$$\frac{\delta A[b(\mathbf{r}')]}{\delta_N \rho(\mathbf{r})} = \int \frac{\delta A}{\delta b(\mathbf{r}')} \frac{\delta b(\mathbf{r}')}{\delta_N \rho(\mathbf{r})} d\mathbf{r}'; \tag{37}$$

as can be seen with the use of Eq. (16) or Eq. (17) itself.

From Eq. (17) a substantial property of $\delta/\delta_N \rho$ derivatives follows straightaway:

$$\int \rho(\mathbf{r}) \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})} d\mathbf{r} = 0 \tag{38}$$

for arbitrary functional $A[\rho]$ $\delta/\delta_N \rho$ differentiable in $\rho(\mathbf{r})$. Equation (38), of course, gives a negative answer to whether the problem about the homogeneity relation [4] for the kinetic energy functional, mentioned before, can be eliminated simply by replacing $\delta/\delta\rho(\mathbf{r})$ with $\delta/\delta_N \rho(\mathbf{r})$; though it has to be mentioned, this can be seen without Eq. (17) as well, simply by examining the case of one-electron densities $\rho_1(\mathbf{r})$ using

$$\frac{\delta T_W[\rho]}{\delta_N\rho(\mathbf{r})}=\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{r})}+c[\rho]$$

and making use of Eq. (9), since

$$\begin{aligned}\int\rho_1(\mathbf{r})\frac{\delta T[\rho_1]}{\delta_N\rho(\mathbf{r})}d\mathbf{r}&=\int\rho_1(\mathbf{r})\frac{\delta T_W[\rho_1]}{\delta_N\rho(\mathbf{r})}d\mathbf{r}\\&=\int\rho_1(\mathbf{r})\frac{\delta T_W[\rho_1]}{\delta\rho(\mathbf{r})}d\mathbf{r}+c[\rho_1]\\&\quad\times\int\rho_1(\mathbf{r})d\mathbf{r}\\&=T_W[\rho_1]+c[\rho_1]=T[\rho_1]+c[\rho_1]\end{aligned}$$

(in the third equality the first-degree homogeneity of the Weizsäcker functional [12] $T_W[\rho]$ is used). Now, having Eq. (17), $c[\rho]$ is known:

$$\frac{\delta T_W[\rho]}{\delta_N\rho(\mathbf{r})}=\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{r})}-\frac{T_W[\rho]}{N};\tag{39}$$

that is, $-c[\rho_1]$ is $T_W[\rho_1]$ itself. Equation (39) is, of course, valid for arbitrary differentiable functional homogeneous of degree 1.

Another essential consequence of the formula Eq. (17) is that the second derivative $\delta^2A[\rho]/\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')$ is not symmetric in $\mathbf{r}$ and $\mathbf{r}'$, which can be seen easily with the help of Eq. (38): while applying Eq. (38) to the functional $\delta A[\rho]/\delta_N\rho(\mathbf{r}')$ gives

$$\int\rho(\mathbf{r})\frac{\delta^2A[\rho]}{\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')}d\mathbf{r}=0,\tag{40}$$

differentiation $\delta/\delta_N\rho(\mathbf{r}')$ of Eq. (38) yields

$$\int\rho(\mathbf{r})\frac{\delta^2A[\rho]}{\delta_N\rho(\mathbf{r}')\delta_N\rho(\mathbf{r})}d\mathbf{r}=-\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r}')}\tag{41}$$

[use of Eqs. (37), (36), (15), and (38) itself can be made]. Of course, $\delta^2A[\rho]/\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')$ can be expressed explicitly by applying Eq. (17) successively:

$$\begin{aligned}&\frac{\delta^2A[\rho]}{\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')}\\&=\frac{\delta^2A[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}-\frac{1}{N}\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\\&\quad-\frac{1}{N}\left(\int\rho(\mathbf{r}'')\frac{\delta^2A[\rho]}{\delta\rho(\mathbf{r}'')\delta\rho(\mathbf{r}')}d\mathbf{r}''\right.\\&\quad\left.+\int\rho(\mathbf{r}'')\frac{\delta^2A[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'')}d\mathbf{r}''\right)\\&\quad+\frac{1}{N^2}\left(\int\rho(\mathbf{r}'')\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}'')}d\mathbf{r}''\right.\\&\quad\left.+\int\int\rho(\mathbf{r}'')\rho(\mathbf{r}''')\frac{\delta^2A[\rho]}{\delta\rho(\mathbf{r}'')\delta\rho(\mathbf{r}''')}d\mathbf{r}''d\mathbf{r}'''\right),\end{aligned}\tag{42}$$

from which it shows that the second term ruins the symmetry in $\mathbf{r}$ and $\mathbf{r}'$. This asymmetry can be exhibited by the commutator

$$\left[\frac{\delta}{\delta_N\rho(\mathbf{r})},\frac{\delta}{\delta_N\rho(\mathbf{r}')}\right]=-\frac{1}{N}\left(\frac{\delta}{\delta\rho(\mathbf{r})}-\frac{\delta}{\delta\rho(\mathbf{r}')}\right)\tag{43}$$

or

$$\left[\frac{\delta}{\delta_N\rho(\mathbf{r})},\frac{\delta}{\delta_N\rho(\mathbf{r}')}\right]=-\frac{1}{N}\left(\frac{\delta}{\delta_N\rho(\mathbf{r})}-\frac{\delta}{\delta_N\rho(\mathbf{r}')}\right);\tag{44}$$

that is, the difference between the second functional derivatives at $\mathbf{r}$, $\mathbf{r}'$ and $\mathbf{r}'$, $\mathbf{r}$ is determined by the difference between the first functional derivatives at $\mathbf{r}$ and $\mathbf{r}'$. For the exchange-correlation part of the energy density functional, the second functional derivative of which plays an essential role in linear response theory [8], e.g., Eq. (43) gives

$$\frac{\delta^2E_{\mathrm{xc}}[\rho]}{\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')}-\frac{\delta^2E_{\mathrm{xc}}[\rho]}{\delta_N\rho(\mathbf{r}')\delta_N\rho(\mathbf{r})}=-\frac{1}{N}[\nu_{\mathrm{xc}}(\mathbf{r})-\nu_{\mathrm{xc}}(\mathbf{r}')],\tag{45}$$

which means that the difference in the second derivative of $E_{\mathrm{xc}}[\rho]$ due to the interchange of its $\mathbf{r}$ variables is characterized by the difference in the exchange-correlation potential $\nu_{\mathrm{xc}}(\mathbf{r})$ at the two points.

An important question is the case of continous functionals $A[\rho]$ which cannot be differentiated for $\rho(\mathbf{r})$ of a given N, $\rho_N(\mathbf{r})$, but have right and left functional derivatives

$$\left.\frac{\delta A[\rho_N]}{\delta\rho(\mathbf{r})}\right|_{N+}\Big/\left.\frac{\delta A[\rho_N]}{\delta\rho(\mathbf{r})}\right|_{N-},$$

that is, derivatives coming from differentiating $A[\rho]$, at $\rho_N(\mathbf{r})$, only over the ''half-space'' of $\rho(\mathbf{r})$'s for which $\int\rho(\mathbf{r})d\mathbf{r}\geqslant N/\int\rho(\mathbf{r})d\mathbf{r}\leqslant N$, e.g., the fractional particle number generalization of the energy functional $E_\nu[\rho]$ or the exchange-correlation part of it, $E_{\mathrm{xc}}[\rho]$ [13,14]. For this case, as can be seen easily, the formula Eq. (17) becomes

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}=\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\right|_{N+}-\frac{1}{N}\int\rho(\mathbf{r}')\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\right|_{N+}d\mathbf{r}'\tag{46a}$$

or

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r})}=\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\right|_{N-}-\frac{1}{N}\int\rho(\mathbf{r}')\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\right|_{N-}d\mathbf{r}'.\tag{46b}$$

If both $\delta A[\rho]/\delta\rho(\mathbf{r})|_{N+}$ and $\delta A[\rho]/\delta\rho(\mathbf{r})|_{N-}$ exist, from Eqs. (46a) and (46b),

$$\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\right|_{N+}-\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r})}\right|_{N-}=\frac{1}{N}\int\rho(\mathbf{r}')\left(\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\right|_{N+}-\left.\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}')}\right|_{N-}\right)d\mathbf{r}'=C[\rho], \quad (47)$$

that is, independent of $\mathbf{r}$, e.g., giving Eq. (9) of [14] for the above-mentioned generalization of $E_{\mathrm{xc}}[\rho]$. It is a basic property of $\delta/\delta_N\rho(\mathbf{r})$ that for $\rho(\mathbf{r})$ where the $\delta/\delta\rho(\mathbf{r})$ derivatives of different functionals differ by only functionals independent of $\mathbf{r}$, it gives the same derivative. It also has to be mentioned here that Eq. (17) is applicable for arbitrary functional $A[\rho]$ differentiable along a path defined by $\int\rho(\mathbf{r})d\mathbf{r}=N$ since $A[\rho_N]$ can be extended from the domain of $\rho_N(\mathbf{r})$'s to an ''unconstrained'' set of $\rho(\mathbf{r})$'s to get a functional $A'[\rho]$ $\delta/\delta\rho(\mathbf{r})$ differentiable for $\rho_N(\mathbf{r})$, a natural extension of $A[\rho_N]$ being its constant shifting

$$A'[\rho]:=A\left[N\frac{\rho}{\int\rho}\right] \quad (48)$$

($A'[\rho]$ being constant for $\rho(\mathbf{r})$'s of the same shape), to which Eq. (17) can be applied, giving $\delta A[\rho_N]/\delta_N\rho(\mathbf{r})$ on the basis of Eq. (9):

$$\frac{\delta A[\rho_N]}{\delta_N\rho(\mathbf{r})}=\frac{\delta A'[\rho_N]}{\delta_N\rho(\mathbf{r})}=\frac{\delta A'[\rho_N]}{\delta\rho(\mathbf{r})}-\frac{1}{N}\int\rho(\mathbf{r}')\frac{\delta A'[\rho_N]}{\delta\rho(\mathbf{r}')}d\mathbf{r}', \quad (49)$$

this way justifying Eq. (17) as the formula for number-conserving differentiation and not ''just'' the relation between $\delta/\delta_N\rho(\mathbf{r})$ and $\delta/\delta\rho(\mathbf{r})$.

Having the formula for $\delta/\delta_N\rho(\mathbf{r})$, the connection between the methods behind Eqs. (4) and (6) can be examined closely. Writing Eq. (4) in the form

$$\frac{\delta E_\nu[\rho]}{\delta\rho(\mathbf{r})}=\frac{1}{N}\int\rho(\mathbf{r}')\frac{\delta E_\nu[\rho]}{\delta\rho(\mathbf{r}')}d\mathbf{r}' \quad (50)$$

shows that Eq. (4) leads to the same method as Eq. (6) [with Eq. (2)]: from Eq. (50), $\delta E_\nu[\rho]/\delta\rho(\mathbf{r})=c$, independent of $\mathbf{r}$, so $c=(1/N)\int\rho(\mathbf{r})c\,d\mathbf{r}$, that is, $\int\rho(\mathbf{r})d\mathbf{r}=N$, the constraint for c. Comparing Eq. (50) with Eq. (6),

$$\mu=\frac{1}{N}\int\rho(\mathbf{r})\frac{\delta E_\nu[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}, \quad (51)$$

which, of course, can be obtained from Eq. (6) as well but not uniquely. With Eq. (17), Eq. (4) is also derivable from Eq. (6) as $\delta/\delta_N\rho(\mathbf{r})$ gives zero for $\mathbf{r}$-independent $\delta/\delta\rho(\mathbf{r})$ derivatives. With the separation of the ν-independent part in Eq. (4), using

$$\frac{\delta V_{\mathrm{ext}}[\rho]}{\delta_N\rho(\mathbf{r})}=\nu(\mathbf{r})-\frac{V_{\mathrm{ext}}[\rho]}{N}, \quad (52)$$

with $V_{\mathrm{ext}}[\rho]=\int\rho(\mathbf{r})\nu(\mathbf{r})d\mathbf{r}$, the equation

$$\frac{\delta F[\rho]}{\delta_N\rho(\mathbf{r})}+\nu(\mathbf{r})=\frac{1}{N}\int\rho(\mathbf{r}')\nu(\mathbf{r}')d\mathbf{r}' \quad (53)$$

arises for determining $\rho(\mathbf{r})$ for given N and $v(\mathbf{r})$. Real use of Eq. (53) could be made by getting expressions directly for $\delta F[\rho]/\delta_N\rho(\mathbf{r})$ [for which Eq. (38) is a condition], not through the formula (17). However, obtaining the energy, Eq. (1), would still remain a problem, unless only the noninteracting kinetic energy functional $T_s[\rho]$, a major part in $F[\rho]$, is kept $\delta/\delta_N\rho(\mathbf{r})$ differentiated in Eq. (4):

$$\frac{\delta T_s[\rho]}{\delta_N\rho(\mathbf{r})}+\nu_{\mathrm{KS}}(\mathbf{r})=\frac{1}{N}\int\rho(\mathbf{r}')\nu_{\mathrm{KS}}(\mathbf{r}')d\mathbf{r}', \quad (54)$$

since the relation

$$T_s[\rho]=-\tfrac{1}{2}\int\rho(\mathbf{r})\mathbf{r}\cdot\nabla\frac{\delta T_s[\rho]}{\delta_N\rho(\mathbf{r})}d\mathbf{r}, \quad (55)$$

arising from the corresponding relation [15] with $\delta/\delta\rho(\mathbf{r})$, makes it possible to get $T_s[\rho]$ from $\delta T_s[\rho]/\delta_N\rho(\mathbf{r})$. Also, Eq. (55) gives a condition on $\delta T_s[\rho]/\delta_N\rho(\mathbf{r}),\delta/\delta_N\rho$ differentiating it:

$$\frac{\delta T_s[\rho]}{\delta_N\rho(\mathbf{r})}=-\frac{1}{2}\mathbf{r}\cdot\nabla\frac{\delta T_s[\rho]}{\delta_N\rho(\mathbf{r})}-\frac{T_s[\rho]}{N}-\tfrac{1}{2}\int\rho(\mathbf{r}')\mathbf{r}'\cdot\nabla'\frac{\delta^2 T_s[\rho]}{\delta_N\rho(\mathbf{r})\delta_N\rho(\mathbf{r}')}d\mathbf{r}' \quad (56)$$

[with Eq. (55)], which can be considered as the first equation of a hierarchy obtainable by $\delta/\delta_N\rho$ differentiating Eq. (55) successively, like in the case of $\delta/\delta\rho$ differentiation [16]. Equation (56) [with Eq. (55)] and

$$\int\rho(\mathbf{r})\frac{\delta T_s[\rho]}{\delta_N\rho(\mathbf{r})}d\mathbf{r}=0 \quad (57)$$

can be used as constraints to get expressions for $\delta T_s[\rho]/\delta_N\rho(\mathbf{r})$, e.g., like described in [17] for $T_s[\rho]$. Note that similar considerations hold for any part of $F[\rho]$ which scales homogeneously in coordinates, such functionals being obtainable from (the gradients of) their functional derivatives [15].

In the Kohn-Sham formulation of density-functional theory [18,19], the problem of not knowing the noninteracting kinetic energy functional $T_s[\rho]$ is eliminated by minimizing

$$E_\nu[u_1,\ldots,u_N]=T_s[u_1,\ldots,u_N]+F[\rho]-T_s[\rho]+V_{\mathrm{ext}}[\rho], \quad (58)$$

where

$$\rho(\mathbf{r})=\sum_{i=1}^{N}u_i^*(\mathbf{r})u_i(\mathbf{r}) \quad (59)$$

and

$$T_s[u_1,\ldots,u_N]=\int\sum_{i=1}^{N}u_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)u_i(\mathbf{r})d\mathbf{r},\tag{60}$$

to get the ground-state density, instead of $E_v[\rho]$ itself, yielding the so-called Kohn-Sham equations

$$-\tfrac{1}{2}\nabla^2u_i(\mathbf{r})+\nu_{\mathrm{KS}}(\mathbf{r})u_i(\mathbf{r})=\varepsilon_iu_i(\mathbf{r}),\quad i=1,\ldots,N,\tag{61}$$

with

$$\nu_{\mathrm{KS}}(\mathbf{r})=\frac{\delta(F[\rho]-T_s[\rho]+V_{\mathrm{ext}}[\rho])}{\delta\rho(\mathbf{r})},\tag{62}$$

for the minimum $\{u_i(\mathbf{r})\}_{i=1}^N$. In the derivation of Eq. (61), the condition (2) is ensured by the normalization of $u_i(\mathbf{r})$ $(i=1,\ldots,N)$, N being fixed; thus, the differentiation in Eq. (62) is unconstrained; though adding $[(-1/N)\int\rho(\mathbf{r}')v_{\mathrm{KS}}(\mathbf{r}')d\mathbf{r}']u_i(\mathbf{r})$ to both sides of Eq. (61),

$$-\tfrac{1}{2}\nabla^2u_i(\mathbf{r})+\nu_{\mathrm{KS}}^N(\mathbf{r})u_i(\mathbf{r})=\varepsilon_i^Nu_i(\mathbf{r}),\quad i=1,\ldots,N,\tag{63}$$

arises, where

$$\begin{aligned}\nu_{\mathrm{KS}}^N(\mathbf{r})&=\frac{\delta(F[\rho]-T_s[\rho]+V_{\mathrm{ext}}[\rho])}{\delta_N\rho(\mathbf{r})}\\&=\nu_{\mathrm{xc}}^N(\mathbf{r})+\nu_J^N(\mathbf{r})+\nu^N(\mathbf{r}),\end{aligned}\tag{64}$$

with

$$\nu_{\mathrm{xc}}^N(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta_N\rho(\mathbf{r})},\tag{65}$$

$$\nu_J^N(\mathbf{r})=\frac{\delta J[\rho]}{\delta_N\rho(\mathbf{r})}=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'-\frac{2J[\rho]}{N}\tag{66}$$

(for particles with Coulomb interaction), and

$$\nu^N(\mathbf{r})=\nu(\mathbf{r})-\frac{1}{N}\int\rho(\mathbf{r}')\nu(\mathbf{r}')d\mathbf{r}',\tag{67}$$

for which

$$\int\rho(\mathbf{r})\nu_{\mathrm{KS}}^N(\mathbf{r})d\mathbf{r}=0,\tag{68}$$

yielding

$$T_s=\sum_{i=1}^N\varepsilon_i^N.\tag{69}$$

Of course, without Eq. (17), Eq. (63) with potential $v_{\mathrm{KS}}^N(\mathbf{r})$ giving Eq. (68), hence Eq. (69), could also be constructed, but having Eq. (17), $v_{\mathrm{KS}}^N(\mathbf{r})$ has obtained physical meaning: Eq. (64).

III. GENERALIZATION FOR TIME-DEPENDENT CASES

The formula and basic properties of number-conserving functional differentiation having been derived, it is an important question how they can be generalized to functions ρ which have variables which are not involved in the integration in the number-conserving constraint—that is, for which that constraint holds pointwise—as time-dependent densities, on which, of course, time-dependent density-functional theory (TDDFT) [20,8,9] is based. TDDFT, for which the time-dependent generalization of the Hohenberg-Kohn theorems [20] forms the ground, concerns systems of given number of particles whose density distribution changes in time due to a time-dependent external potential $v(\mathbf{r},t)$, giving $\delta/\delta_N\rho$ differentiation a substantial importance. In this section, therefore, the results of the previous section will be generalized to include time dependence. For more generality, a time-dependent particle number $N(t)$ can also be allowed, with which the number-conserving, more precisely, $N(t)$-conserving, constraint:

$$\int\rho(\mathbf{r},t)d\mathbf{r}=N(t),\tag{70}$$

which, of course, includes the case $N(t)=N=$const.

The starting point, again, is the separation of the normalization N in ρ:

$$\rho(\mathbf{r},t)=N(t)\frac{g(\mathbf{r},t)}{\int g(\mathbf{r}',t)d\mathbf{r}'}.\tag{71}$$

Along the lines described in the previous section, with the use of Eq. (71), as the time-dependent generalization of Eqs. (15) and (16),

$$\frac{\delta\rho(\mathbf{r}',t')}{\delta_N\rho(\mathbf{r},t)}=\delta(\mathbf{r}'-\mathbf{r})\,\delta(t'-t)-\frac{\rho(\mathbf{r}',t')}{N(t')}\,\delta(t'-t)\tag{72}$$

and

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r},t)}=\int\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}',t')}\frac{\delta\rho(\mathbf{r}',t')}{\delta_N\rho(\mathbf{r},t)}d\mathbf{r}'dt'\tag{73}$$

can be obtained, from which

$$\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r},t)}=\frac{\delta A[\rho]}{\delta\rho(\mathbf{r},t)}-\frac{1}{N(t)}\int\rho(\mathbf{r}',t)\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}',t)}d\mathbf{r}'.\tag{74}$$

From Eq. (74), then, rules similar to Eqs. (35)–(37) ($\mathbf{r},t$ in the place of $\mathbf{r}$) follow for the number-conserving differentiation of functionals composed from two functionals. Equation (38) also holds t-wise,

$$\int\rho(\mathbf{r},t)\frac{\delta A[\rho]}{\delta_N\rho(\mathbf{r},t)}d\mathbf{r}=0,\tag{75}$$

while for a second $\delta/\delta_N\rho$ derivative:

$$\frac{\delta^2 A[\rho]}{\delta_N\rho(\mathbf{r},t)\,\delta_N\rho(\mathbf{r}',t')} = \frac{\delta^2 A[\rho]}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')} - \frac{1}{N(t')}\frac{\delta A[\rho]}{\delta\rho(\mathbf{r},t)}\delta(t-t') - \frac{1}{N(t)}\int \rho(\mathbf{r}'',t)\frac{\delta^2 A[\rho]}{\delta\rho(\mathbf{r}'',t)\,\delta\rho(\mathbf{r}',t')}d\mathbf{r}''$$
$$-\frac{1}{N(t')}\int \rho(\mathbf{r}'',t')\frac{\delta^2 A[\rho]}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}'',t')}d\mathbf{r}'' + \frac{1}{N(t)N(t')}\Bigg(\int \rho(\mathbf{r}'',t')\frac{\delta A[\rho]}{\delta\rho(\mathbf{r}'',t')}d\mathbf{r}''\,\delta(t-t')$$
$$+\int\int \rho(\mathbf{r}'',t)\rho(\mathbf{r}''',t')\frac{\delta^2 A[\rho]}{\delta\rho(\mathbf{r}'',t)\,\delta\rho(\mathbf{r}''',t')}d\mathbf{r}''d\mathbf{r}'''\Bigg), \qquad (76)$$

from which

$$\left[\frac{\delta}{\delta_N\rho(\mathbf{r},t)},\frac{\delta}{\delta_N\rho(\mathbf{r}',t')}\right] = -\frac{1}{N(t)}\left(\frac{\delta}{\delta\rho(\mathbf{r},t)} - \frac{\delta}{\delta\rho(\mathbf{r}',t')}\right)\times\delta(t-t'). \qquad (77)$$

The commutator, Eq. (77), shows how the N-conserving constraint ruins the symmetry of functional differentiation in $\mathbf{r}$, t, though, as can be expected, purely in t $(\mathbf{r}=\mathbf{r}')$ the symmetry remains. This property gives the resolution of a long-standing paradox in TDDFT concerning the exchange-correlation kernel, illustrating the physical relevance of number-conserving functional differentiation.

In TDDFT the density response function $\delta\rho(\mathbf{r}',t')/\delta v(\mathbf{r},t)$ determines the density variations $\delta\rho(\mathbf{r},t)$ of an N-particle system generated by first-order variations of the external potential $v(\mathbf{r},t)$. Because of causality, for times t later than t', $\delta\rho(\mathbf{r}',t')/\delta v(\mathbf{r},t)$ must vanish:

$$\frac{\delta\rho(\mathbf{r}',t')}{\delta\nu(\mathbf{r},t)} = 0, \quad t>t'. \qquad (78)$$

Causality for the inverse of $\rho[v]$, the existence of which [20] gives the basis of TDDFT, means that

$$\frac{\delta\nu(\mathbf{r}',t')}{\delta_N\rho(\mathbf{r},t)} = 0, \quad t>t'. \qquad (79)$$

In $\delta v(\mathbf{r}',t')/\delta_N\rho(\mathbf{r},t)$, N conservation is essential as the particle number N is fixed when defining $\rho[v]$, so its derivative is also determined only for given N: $\delta\rho_N(\mathbf{r}',t')/\delta v(\mathbf{r},t)$; thus, it has to be inverted with an N-conserving constraint on $\rho(\mathbf{r},t)$. Of course, $v[\rho]$ can be extended to all ρ's, but even in this case the physically relevant differentiation for which causality can be required is the N-conserving functional differentiation. The external potential $v(\mathbf{r},t)$ acting on an interacting particle system is connected with the effective potential of the corresponding noninteracting system with the same $\rho(\mathbf{r},t)$ as the interacting one [20,21], the time-dependent correspondent of the Kohn-Sham potential, $v_{\rm KS}(\mathbf{r},t)$, the concept of which is essential for the practical use of TDDFT, by

$$\nu_{\rm KS}(\mathbf{r},t) = \nu(\mathbf{r},t) + \int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta A_{\rm xc}[\rho]}{\delta\rho(\mathbf{r},t)} \qquad (80)$$

(in the case of a Coulomb interaction between the particles), where the second term is the functional derivative of the Hartree part of the action functional $A[\rho]$ [20], on which the variational principle of TDDFT for determining $\rho(\mathbf{r},t)$ is based, and the third term comes from the exchange-correlation part of $A[\rho]$. Differentiation of Eq. (80) leads to a paradox [8,9] if the fact that not the usual differentiation procedure applies under N conservation, which ruins the symmetry of unconstrained functional differentiation, is ignored, since in the case of symmetric second functional derivatives, that is, practically neglecting N conservation, the causality requirement on $v[\rho]$, and also on $v_{\rm KS}[\rho]$, is in conflict with the symmetry of the second derivative of $A_{\rm xc}[\rho]$. This paradox, which has induced much effort to find a resolution of it [22,23], however, cancels out automatically by correctly taking N conservation into account as in the $\delta/\delta_N\rho$ derivative of Eq. (80),

$$\frac{\delta\nu_{\rm KS}(\mathbf{r}',t')}{\delta_N\rho(\mathbf{r},t)} = \frac{\delta\nu(\mathbf{r}',t')}{\delta_N\rho(\mathbf{r},t)} + \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{N}\int\frac{\rho(\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|}\times d\mathbf{r}''\,\delta(t-t') + \frac{\delta^2 A_{xc}[\rho]}{\delta_N\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')}, \qquad (81)$$

the second derivative

$$\frac{\delta^2 A_{\rm xc}[\rho]}{\delta_N\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')} = \frac{\delta^2 A_{\rm xc}[\rho]}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')} - \frac{1}{N}\int\rho(\mathbf{r}'',t)\frac{\delta^2 A_{\rm xc}[\rho]}{\delta\rho(\mathbf{r}'',t)\,\delta\rho(\mathbf{r}',t')}d\mathbf{r}'' \qquad (82)$$

is not symmetric in its space-time arguments:

$$\frac{\delta^2 A_{\rm xc}[\rho]}{\delta_N\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')} - \frac{\delta^2 A_{\rm xc}[\rho]}{\delta_N\rho(\mathbf{r}',t')\,\delta\rho(\mathbf{r},t)} = -\frac{1}{N}\int\left(\rho(\mathbf{r}'',t)\frac{\delta^2 A_{\rm xc}[\rho]}{\delta\rho(\mathbf{r}'',t)\,\delta\rho(\mathbf{r}',t')} - \rho(\mathbf{r}'',t')\frac{\delta^2 A_{\rm xc}[\rho]}{\delta\rho(\mathbf{r}'',t')\,\delta\rho(\mathbf{r},t)}\right)d\mathbf{r}'' \qquad (83)$$

(not even in time purely); thus, requiring causality, Eq. (79), yields no contradiction, and simply gives a condition for $A_{\rm xc}[\rho]$:

$$\frac{\delta^2 A_{\mathrm{xc}}[\rho]}{\delta_N \rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')} = -\frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{N}\int \frac{\rho(\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|} \times d\mathbf{r}''\,\delta(t-t') \quad \text{for } t>t'. \quad (84)$$

The second derivative of $A_{\mathrm{xc}}[\rho]$, the exchange-correlation kernel, plays a key role in linear response theory [8] and in calculating excitation energies via TDDFT [24]. Equation (81) exhibits the fact that the physically relevant second derivative is the mixed derivative, Eq. (82), instead of a full unconstrained second derivative. Note that, though, according to Eq. (24), a variation of a functional $A[\rho]$ due to a number-conserving variation of its variable ρ is determined by its unconstrained derivative; in theoretical practice, the arbitrariness of variations $\delta\rho$ is substantial, therefore, number conservation needs to be forced out by a number-conserving functional derivative, on the basis of Eq. (27).

IV. SUMMARY

The main result of the paper is Eq. (17), which is a general mathematical formula for differentiating a functional $A[\rho]$ with respect to $\rho(\mathbf{r})$ while keeping the normalization $\int \rho(\mathbf{r})d\mathbf{r}$ of $\rho(\mathbf{r})$ fixed, as such giving a case in functional analysis when a constrained functional differentiation is managed to be treated explicitly, showing how the usual differentiation procedure of functionals alters due to this constraint, and Eq. (17) is essential for the determination of changes in a quantity which is dependent on some density distribution (mass, charge, or particle distribution, e.g.), if conservation of the normalization of the distribution (total mass, total charge, particle number) is needed. With Eq. (27) a correct formal definition has been presented for a number-conserving functional derivative, elucidating a long-standing false view in density-functional theory—namely, that these functional derivatives are ambiguous by definition. Also, the formula of shape-conserving functional differentiation, Eq. (31), where change in the normalization of $\rho(\mathbf{r})$ is allowed only, has been obtained. Two substantial properties of number-conserving functional differentiation, which illustrate its essential difference from unconstrained differentiation well, are that $\delta/\delta_N\rho(\mathbf{r})$ derivatives multiplied by $\rho(\mathbf{r})$ integrate to zero [Eq. (38)] and that second $\delta/\delta_N\rho(\mathbf{r})$ derivatives are asymmetric in their $\mathbf{r}$ arguments, Eq. (43). After generalizing the results to involve time dependence, Eqs. (72)–(77), the latter property, more precisely that an N conservation ruins the symmetry of multiple $\delta/\delta\rho(\mathbf{r})$ derivatives in their $\mathbf{r}$ arguments, has been shown to resolve the causality paradox of time-dependent density-functional theory concerning the exchange-correlation kernel, Eqs. (79)–(83), illustrating the real presence of number-conserving functional differentiation in density-functional theory.

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