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On the role of second number-conserving functional derivatives

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Abstract

It is found that number-conserving second derivatives, of functional differentiation constrained to the domain of functional variables $\rho(x)$ of a given norm $\int \rho(x)\,dx$, are not obtained via two successive number-conserving differentiations, contrary to the case of unrestricted second derivatives. Investigating the role of second number-conserving derivatives, with the density-functional formulation of time-dependent quantum mechanics in focus, it is shown how number-conserving differentiation handles the dual nature of the Kohn–Sham potential arising in the practical use of the theory. On the other hand, it is pointed out that number-conserving derivatives cannot resolve the causality paradox connected with the second derivative of the exchange-correlation part of the action density functional.

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Constraints on the changes of different distributions in some space appear in almost all fields of physics. Those constraints have to be taken into account in the physical relations and equations valid over the (restricted) distribution domain. In most of the cases in modern physics, those relations involve functional differentiation, which leads to the need for a proper inclusion of constraints into it. For that proper inclusion, in [1,2], an analytical formula for constrained functional differentiations, for a wide class of constraints, namely,

$$\int f\bigl(\rho(x)\bigr)\,dx = K, \tag{1}$$

has been given

$$\frac{\delta F[\rho]}{\delta_K \rho(x)} = \frac{\delta F[\rho]}{\delta\rho(x)}\bigg|_K - \frac{f^{(1)}(\rho(x))}{K}\int \frac{f(\rho(x'))}{f^{(1)}(\rho(x'))}\frac{\delta F[\rho]}{\delta\rho(x')}\bigg|_K dx', \tag{2}$$

which simplifies to [1]

$$\frac{\delta F[\rho]}{\delta_N \rho(x)} = \frac{\delta F[\rho]}{\delta\rho(x)}\bigg|_N - \frac{1}{N}\int \rho(x')\frac{\delta F[\rho]}{\delta\rho(x')}\bigg|_N dx' \tag{3}$$

for number-conservation, $\int \rho(x)\,dx = N$. $\frac{\delta F[\rho]}{\delta\rho(x)}|_K$ in Eqs. (2) and (3) is determined by

$$\int \frac{\delta F[\rho]}{\delta\rho(x)}\bigg|_K \Delta_K\rho(x)\,dx = D[\rho;\Delta_K\rho] \tag{4}$$

(required for all K-conserving changes in $\rho(x)$, $\Delta_K\rho(x)$), with $D[\rho;.]$ a K-restricted Fréchet differential, or the K-restricted Gâteaux differential (for linear $f(\rho)$'s), at $\rho(x)$ [3] (so $\frac{\delta F[\rho]}{\delta\rho(x)}|_K$ can be the unrestricted derivative $\frac{\delta F[\rho]}{\delta\rho(x)}$ if that exists) [4]. Very recently, two applications, a physical [5] and a formal [6] one (in ultrathin-film dynamics and in spin-density-functional theory, respectively), have been given, which has stimulated the reexamination of an important question in the density-functional-theory (DFT) [7] formulation of time-dependent nonrelativistic quantum mechanics [8,9] (possibly answerable by number-conserving differentiation [1]), namely, the causality problem [9,10] connected to the exchange-correlation kernel $\frac{\delta^2 A_{xc}[\rho]}{\delta\rho(\vec{r},t)\delta\rho(\vec{r}',t')}$, which is the second derivative of the exchange-

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correlation part of the action functional $A[\rho]$ of the theory. In that problem, the symmetry in the space–time arguments of $\frac{\delta^2 A_{\mathrm{xc}}[\rho]}{\delta\rho(\vec{r},t)\delta\rho(\vec{r}',t')}$, appearing as a part of the derivative of the Kohn–Sham potential,

$$v_{\mathrm{KS}}(\vec{r},t)=v(\vec{r},t)+\frac{\delta J[\rho]}{\delta\rho(\vec{r},t)}+\frac{\delta A_{\mathrm{xc}}[\rho]}{\delta\rho(\vec{r},t)} \tag{5}$$

(with $v(\vec{r},t)$ the external potential and J the classical electrostatic Coulomb repulsion energy of the system of identical charged particles), with respect to the time-dependent particle density distribution $\rho(\vec{r},t)$,

$$\frac{\delta v_{\mathrm{KS}}(\vec{r}',t')}{\delta\rho(\vec{r},t)}=\frac{\delta v(\vec{r}',t')}{\delta\rho(\vec{r},t)}+\frac{\delta^2 J[\rho]}{\delta\rho(\vec{r},t)\delta\rho(\vec{r}',t')}+\frac{\delta^2 A_{\mathrm{xc}}[\rho]}{\delta\rho(\vec{r},t)\delta\rho(\vec{r}',t')}, \tag{6}$$

is in contradiction with the causality requirement on time-dependent external potentials, saying that the external potential that governs the time-evolution of a given $\rho(\vec{r},t)$, at time t', must be independent of $\rho(\vec{r},t)$ with $t>t'$, that is,

$$\frac{\delta v_{\mathrm{ext}}(\vec{r}',t')}{\delta\rho(\vec{r},t)}=0 \quad \text{for } t>t'. \tag{7}$$

In [1], a possible resolution of the above contradiction has been proposed. It was pointed out there that since the time-evolution of $\rho(\vec{r},t)$ is under a number-conservation constraint,

$$\int\rho(\vec{r},t)\,d\vec{r}=N, \tag{8}$$

differentiations with respect to $\rho(\vec{r},t)$ in time-dependent DFT have to be taken under that constraint, therefore the right equation instead of Eq. (6) is

$$\frac{\delta v_{\mathrm{KS}}(\vec{r}',t')}{\delta_N\rho(\vec{r},t)}=\frac{\delta v(\vec{r}',t')}{\delta_N\rho(\vec{r},t)}+\frac{\delta^2 J[\rho]}{\delta_N\rho(\vec{r},t)\delta\rho(\vec{r}',t')}+\frac{\delta^2 A_{\mathrm{xc}}[\rho]}{\delta_N\rho(\vec{r},t)\delta\rho(\vec{r}',t')}, \tag{9}$$

or, precisely (as $A[\rho]$ is also defined only for $\rho(\vec{r},t)$'s of Eq. (8)),

$$\frac{\delta v^N_{\mathrm{KS}}(\vec{r}',t')}{\delta_N\rho(\vec{r},t)}=\frac{\delta v(\vec{r}',t')}{\delta_N\rho(\vec{r},t)}+\frac{\delta^2 J[\rho]}{\delta_N\rho(\vec{r},t)\delta_N\rho(\vec{r}',t')}+\frac{\delta^2 A_{\mathrm{xc}}[\rho]}{\delta_N\rho(\vec{r},t)\delta_N\rho(\vec{r}',t')}, \tag{10}$$

where

$$v^N_{\mathrm{KS}}(\vec{r},t):=v(\vec{r},t)+\frac{\delta J[\rho]}{\delta_N\rho(\vec{r},t)}+\frac{\delta A_{\mathrm{xc}}[\rho]}{\delta_N\rho(\vec{r},t)} \tag{11}$$

(the N-conservation constraint on the differentiation of $\int\rho(\vec{r},t)v(\vec{r},t)\,d\vec{r}\,dt$ yielding $v(\vec{r},t)$ in Eq. (11) is trivially relaxable). It has to be emphasized that the proper account for N-conservation is especially important, as N-conservation is not just a simple norm-fixation of the density distribution in space but it forces the whole time-evolution of $\rho(\vec{r},t)$ to a fixed particle number (that is, N-conservation is pointwise in t), embracing basically two constraints, namely, $\int\rho(\vec{r},t)\,d\vec{r}=N(t)$ and $N(t)=\text{const}$. A substantial consequence of the formula Eq. (2), or more precisely, of its generalization [1,2]

$$\frac{\delta F[\rho]}{\delta_{K(t)}\rho(x,t)}=\left.\frac{\delta F[\rho]}{\delta\rho(x,t)}\right|_{K(t)}-\frac{f^{(1)}(\rho(x,t))}{K(t)}\int\frac{f(\rho(x',t))}{f^{(1)}(\rho(x',t))}\left.\frac{\delta F[\rho]}{\delta\rho(x',t)}\right|_{K(t)}dx' \tag{12}$$

for t-dependent constraints $\int f(\rho(x,t))\,dx=K(t)$, is that second $\frac{\delta}{\delta_N\rho(x,t)}$ derivatives are not symmetric in their (x,t) arguments,

$$\left[\frac{\delta}{\delta_N\rho(x,t)},\frac{\delta}{\delta_N\rho(x',t')}\right]=-\frac{1}{N}\left(\frac{\delta}{\delta_N\rho(x,t)}-\frac{\delta}{\delta_N\rho(x',t')}\right)\delta(t-t'), \tag{13}$$

which suggests a possible resolution of the causality problem, leading to the condition

$$\frac{\delta^2(J+A_{\mathrm{xc}})[\rho]}{\delta_N\rho(\vec{r},t)\delta_N\rho(\vec{r}',t')}=-\frac{1}{N}\left(\frac{\delta(J+A_{\mathrm{xc}})[\rho]}{\delta_N\rho(\vec{r},t)}-\frac{\delta(J+A_{\mathrm{xc}})[\rho]}{\delta_N\rho(\vec{r}',t')}\right)\delta(t-t') \quad \text{for } t'>t \tag{14}$$

from the causality condition

$$\frac{\delta v_{\mathrm{ext}}(\vec{r}',t')}{\delta_N\rho(\vec{r},t)}=0 \quad \text{for } t>t' \tag{15}$$

applied on $v^N_{\mathrm{KS}}(\vec{r},t)$ and $v(\vec{r},t)$ in Eq. (10). Thus, the question to be answered here: does N-conservation bring enough additional structure into functional differentiation to handle the causality of external potentials? For the answer, the following important property of second N-conserving derivatives is needed:

$$\int\rho(x',t')\frac{\delta^2 F[\rho]}{\delta_N\rho(x,t)\delta_N\rho(x',t')}\,dx'=-\frac{\delta F[\rho]}{\delta_N\rho(x,t)}\delta(t-t'). \tag{16}$$

To obtain Eq. (16), integrate over x' Eq. (13) multiplied by $\rho(x',t')$, and make use of the basic relation [1]

$$\int\rho(x,t)\frac{\delta F[\rho]}{\delta_N\rho(x,t)}\,dx=0, \tag{17}$$

or simply $\frac{\delta}{\delta_N\rho}$-differentiate the above equation. With the help of Eq. (16), then

$$\frac{\delta(J+A_{\mathrm{xc}})[\rho]}{\delta_N\rho(\vec{r},t)}=0 \tag{18}$$

(containing only one time variable!) follows from the condition Eq. (15) applied in Eq. (10). Eq. (18) would mean that the exchange-correlation potential is equal in space (up to an additive constant) to the classical Coulomb potential $\frac{\delta J[\rho]}{\delta\rho(\vec{r},t)}$, which is obviously not true, therefore the answer to the above