

Reply to the comment by M Biagini on generalized density functional theory

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REPLY TO COMMENT

Reply to the comment by M Biagini on generalized density functional theory

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Abstract. The two exchange–correlation potentials that derive from a variation of the exchange–correlation energy for full and averaged electron–electron coupling strengths, respectively, are shown to be identical, which invalidates the conclusions of M Biagini presented in the preceding comment.

The essence of the preceding comment consists in the conclusion that the two exchange–correlation potentials $V_{xc}^{Frit}(\mathbf{r}, \sigma)$ and $V_{xc}^{K-S}(\mathbf{r}, \sigma)$ that are implicitly defined through

$$\delta E_{xc} = \sum_{\sigma} \int V_{xc}^{Frit}(\mathbf{r}, \sigma) \delta \rho_{\sigma}(\mathbf{r}) d^3r \tag{1}$$

and

$$\delta \bar{E}_{xc} = \sum_{\sigma} \int V_{xc}^{K-S}(\mathbf{r}, \sigma) \delta \rho_{\sigma}(\mathbf{r}) d^3r \tag{2}$$

respectively cannot be identical. The quantity \bar{E}_{xc} denotes the exchange–correlation energy averaged over the full range of the coupling strength λ ($0 \leq \lambda \leq 1$), whereas E_{xc} is just the exchange–correlation energy at full coupling strength ($\lambda = 1$). Apart from its apparent plausibility, there seem to be reasons for Biagini’s statement being correct. Nevertheless, the two potentials do, in fact, agree, as will be proven in the following.

I first want to justify my notation concerning the exchange–correlation energy E_{xc} . If one subdivides the pair density $\rho_{2n\sigma'\sigma}(\mathbf{r}', \mathbf{r})$ in some eigenstate Ψ_n of the N -electron system according to

$$\rho_{2n\sigma'\sigma}(\mathbf{r}', \mathbf{r}) = \rho_{n\sigma'}(\mathbf{r}')\rho_{n\sigma}(\mathbf{r}) + \tilde{\rho}_{2n\sigma'\sigma}(\mathbf{r}', \mathbf{r}) \tag{3}$$

the electron–electron interaction energy can be cast as

$$\langle V_{e-e} \rangle^{(n)} = V_c^{(n)} + E_{xc}^{(n)} \tag{4}$$

where

$$V_c^{(n)} = \frac{1}{2} \iint \frac{\rho_n(\mathbf{r}')\rho_n(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3r' d^3r \tag{5}$$

and

$$E_{xc}^{(n)} = \frac{1}{2} \sum_{\sigma', \sigma} \iint \frac{\tilde{\rho}_{2n\sigma'\sigma}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3r' d^3r \tag{6}$$

with $\rho_n(\mathbf{r})$ denoting the total charge density of the system in that eigenstate. Since $V_c^{(n)}$ is commonly referred to as the ‘classical Coulomb interaction energy’, $E_{xc}^{(n)}$ includes the effects of exchange and correlation and should therefore be termed accordingly. The above subdivision of $\langle V_{e-e} \rangle^{(n)}$ is a matter of principle and should not depend on specific aspects of density functional theory. Within the framework of the latter one performs the familiar thought experiment in which one gradually scales down the electron–electron interaction by a factor λ and simultaneously turns on spin-dependent potentials $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ that ensure the conservation of the spin-resolved charge densities $\rho_{n\sigma}(\mathbf{r})$. The N -electron Hamiltonian that refers to the situation for $0 \leq \lambda \leq 1$ leads to a λ -dependence of the n th eigenstate and, as a result, to a λ -dependent pair density. One can then define an average exchange–correlation energy \bar{E}_{xc} by replacing $\tilde{\rho}_{2n\sigma'}(\mathbf{r}', \mathbf{r})$ in equation (6) with its λ -averaged analogue. As can be shown by using the Hellmann–Feynman theorem, the following equation holds:

$$E_n^{Frit} = E_n^{K-S} \quad (7)$$

where

$$E_n^{Frit} = \langle T_{e-e} \rangle^{(n)} + \langle V_{ext} \rangle^{(n)} + V_c^{(n)} + E_{xc}^{(n)} \quad (8)$$

and

$$E_n^{K-S} = \langle T_0 \rangle^{(n)} + \langle V_{ext} \rangle^{(n)} + V_c^{(n)} + \bar{E}_{xc}^{(n)} \quad (9)$$

with $\langle T_0 \rangle^{(n)}$ denoting the kinetic energy of the non-interacting N -electron system having the same densities $\rho_{n\sigma}(\mathbf{r})$ as the original one whose kinetic energy is denoted by $\langle T_{e-e} \rangle^{(n)}$. Furthermore, we have abbreviated the interaction with the external (nuclear) potential as $\langle V_{ext} \rangle^{(n)}$, i.e.

$$\langle V_{ext} \rangle^{(n)} = \int \rho_n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3r.$$

In the following we shall confine ourselves to discussing the ground state ($n = 0$) only since the essential claim of Biagini’s paper consists in stating a fundamental contradiction between my approach and the Hohenberg–Kohn–Sham theory of the N -electron ground state.

We subject the ground-state wavefunction Ψ_0 to a slight distortion and write the new wavefunction in the form

$$\Psi'_0 = \Psi_0 + \eta_0 \delta\Psi_0 \quad (10)$$

with η_0 being a positive quantity that is small compared to unity, and $\delta\Psi_0$ just some function normalized to unity and orthogonal to Ψ_0 .

Since Ψ_0 can uniquely be mapped onto a Slater determinant Φ_0 made up of the N lowest-lying Kohn–Sham orbitals $\psi_{i\sigma}(\mathbf{r})$, Ψ_0 can generally be cast as

$$\Psi_0 = \Phi_0 + \tilde{\Psi}_0 \quad (11)$$

where $\tilde{\Psi}_0 = \tilde{\Psi}_0(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is non-orthogonal to Φ_0 and has the property

$$N \int \left[\Phi_0^* \tilde{\Psi}_0 + \Phi_0 \tilde{\Psi}_0^* + |\tilde{\Psi}_0|^2 \right] d^4x_2 \dots d^4x_N = \tilde{\rho}_{0\sigma}(\mathbf{r}) = 0.$$

That is, $\tilde{\Psi}_0$ does not contribute to the one-particle densities $\rho_{0\sigma}(\mathbf{r})$. (Note that we have abbreviated \mathbf{r} together with the spin variable $\sigma (= \pm 1)$ as \mathbf{x} , so $\int \dots d^4x$ refers to a real-space integration including a spin summation.) If Ψ'_0 is generated as a ground-state wavefunction of a perturbed Hamiltonian, we can again partition this function according to equation (11):

$$\Psi'_0 = \Phi'_0 + \tilde{\Psi}'_0 \quad (12)$$

where Φ'_0 is now made up of orbitals $\psi'_{i\sigma}(\mathbf{r})$ which we write in the form

$$\psi'_{i\sigma}(\mathbf{r}) = \psi_{i\sigma}(\mathbf{r}) + \delta\psi_{i\sigma}(\mathbf{r}). \quad (13)$$

From equation (10) we have

$$\delta\rho_{0\sigma}(\mathbf{r}) = \eta_0 N \int [\Psi_0^* \delta\Psi_0 + \text{CC}] d^4x_2 \dots d^4x_N.$$

That is,

$$\delta\rho_{0\sigma}(\mathbf{r}) \propto \eta_0. \quad (14)$$

On the other hand, it follows from equation (13) and the properties of Φ'_0 that

$$\delta\rho_{0\sigma}(\mathbf{r}) = \sum_i^{(N_\sigma)} [\psi_{i\sigma}^* \delta\psi_{i\sigma} + \text{CC}]. \quad (15)$$

Similarly, we obtain for the changes of E_0^{Frit} and E_0^{K-S} associated with the distortion $\Psi_0 \rightarrow \Psi'_0$

$$\begin{aligned} \delta E_0^{Frit} = & \sum_{\sigma} \sum_i^{(N_\sigma)} \left[\int \delta\psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^{Frit}(\mathbf{r}, \sigma) \right) \right. \\ & \left. \times \psi_{i\sigma}(\mathbf{r}) d^3r + \text{CC} \right] + \delta\tilde{T}_0 \end{aligned} \quad (16)$$

and

$$\begin{aligned} \delta E_0^{K-S} = & \sum_{\sigma} \sum_i^{(N_\sigma)} \left[\int \delta\psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^{K-S}(\mathbf{r}, \sigma) \right) \right. \\ & \left. \times \psi_{i\sigma}(\mathbf{r}) d^3r + \text{CC} \right] \end{aligned} \quad (17)$$

where $V_H(\mathbf{r})$ denotes the familiar Hartree potential, and \tilde{T}_0 in equation (16) is defined by

$$\tilde{T}_0 = \langle T_{e-e} \rangle^{(0)} - \langle T_0 \rangle^{(0)}$$

which is generally a positive quantity. (See, e.g., Fritsche (1986).) In deriving equations (16) and (17) we have made use of the definitions (1) and (2).

We now consider the changes δE_0^{Frit} and δE_0^{K-S} associated with a subset of distorted functions Ψ'_0 that leave \tilde{T}_0 unchanged. (As regards this point, see Fritsche (1993).) This can be achieved by generating eigenfunctions Ψ'_0 in a perturbed potential $V_{ext}(\mathbf{r}) + \gamma v_{Pert}(\mathbf{r})$ where γ is some dimensionless strength parameter. As we change γ we simultaneously change the electron–electron coupling strength λ appropriately so that $\delta\tilde{T}_0 = 0$. (Note that \tilde{T}_0 increases (at constant γ) as λ becomes larger, but decreases (at fixed λ) when the nuclear potentials are made more attractive.) For this subset of distorted functions expressions (16) and (17) become formally identical then, except that equation (16) contains $V_{xc}^{Frit}(\mathbf{r}, \sigma)$ in place of $V_{xc}^{K-S}(\mathbf{r}, \sigma)$ in equation (17). By construction, the functions $\psi_{i\sigma}(\mathbf{r})$ in equation (17) guarantee that

$$\delta E_0^{K-S} = 0 \quad (18)$$

to first order in η_0 . If we rewrite equation (16) for the subset of functions (defined by $\delta\tilde{T}_0 = 0$) in the form

$$\delta E_0^{Frit} = \sum_{\sigma} \sum_i^{(N_{\sigma})} \left[\int \delta \Psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^{K-S}(\mathbf{r}, \sigma) \right) \times \Psi_{i\sigma}(\mathbf{r}) \, d^3r + \text{CC} \right] + \sum_{\sigma} \int (V_{xc}^{Frit}(\mathbf{r}, \sigma) - V_{xc}^{K-S}(\mathbf{r}, \sigma)) \delta \rho_{0\sigma}(\mathbf{r}) \, d^3r$$

and use equation (18) we arrive at

$$\delta E_0^{Frit} = \sum_{\sigma} \int (V_{xc}^{Frit}(\mathbf{r}, \sigma) - V_{xc}^{K-S}(\mathbf{r}, \sigma)) \delta \rho_{0\sigma}(\mathbf{r}) \, d^3r.$$

Since E_0^{K-S} and E_0^{Frit} are alternative expressions for the same quantity, δE_0^{Frit} must also have the property

$$\delta E_0^{Frit} = 0 \tag{19}$$

to first order in η_0 . Because of equation (14) it follows then that

$$V_{xc}^{Frit}(\mathbf{r}, \sigma) = V_{xc}^{K-S}(\mathbf{r}, \sigma) \tag{20}$$

as opposed to what is claimed in Biagini’s paper.

The salient point of the above derivation consists in the observation that $\delta\tilde{T}_0$ can be made zero to first order in η_0 for an infinite subset of functions Ψ'_0 . We can rewrite expression (8) in the form

$$E_0^{Frit} = E_0^{K-S} + (E_{xc} - \bar{E}_{xc}) + \tilde{T}_0. \tag{21}$$

Since we have quite generally

$$\delta E_0^{Frit} \propto \eta_0^2$$

and

$$\delta E_0^{K-S} \propto \eta_0^2$$

to lowest order in η_0 , we can see from equations (1), (2), (20) and (21) that $\delta\tilde{T}_0$ will in general be proportional to η_0^2 to lowest order in η_0 for functions Ψ'_0 that do not belong to the above subset. The Kohn–Sham (KS) equations result from the requirement that the changes of the total energy vanish to first order in η_0 , and hence the occurrence of a finite $\delta\tilde{T}_0 \propto \eta_0^2$ has no effect on the final form of the KS equations.

In contradiction to Biagini’s claim we thus arrive at the conclusion that the finiteness of \tilde{T}_0 and its actual dependence on $\rho_{0\sigma}(\mathbf{r})$ do not give rise to a difference between the potentials $V_{xc}^{Frit}(\mathbf{r}, \sigma)$ and $V_{xc}^{K-S}(\mathbf{r}, \sigma)$.

Biagini’s conclusion rests on his equation (15) which in the present notation reads

$$V_{xc}^{Frit}(\mathbf{r}, \sigma) = V_{xc}^{K-S}(\mathbf{r}, \sigma) + \frac{\delta\tilde{T}_0[\rho]}{\delta\rho_{0\sigma}(\mathbf{r})}. \tag{22}$$

I have repeatedly pointed out (see, e.g., Fritsche 1995) that functional derivatives such as those on the right-hand side of this equation are mathematically meaningless in the context of density functional theory. This becomes immediately obvious when one writes down its definition more explicitly (see, e.g., Gelfand and Fomin 1963):

$$\frac{\delta\tilde{T}_0[\rho]}{\delta\rho_{0\sigma}(\mathbf{r})} = \lim_{\substack{\tau \rightarrow 0 \\ |\delta\rho_{0\sigma}(\mathbf{r})|_{max} \rightarrow 0}} \left[\left(\tilde{T}_0[\rho_{0\sigma}(\mathbf{r}) + \delta\rho_{0\sigma}(\mathbf{r})] - \tilde{T}_0[\rho_{0\sigma}(\mathbf{r})] \right) / \int_{\tau(\mathbf{r})} \delta\rho_{0\sigma}(\mathbf{r}') \, d^3r' \right] \tag{23}$$

where $\delta\rho_{0\sigma}(\mathbf{r}')$ is different from zero only within the volume τ around a fixed point \mathbf{r} . (Note that it is inadmissible to allow $\delta\rho_{0\sigma}(\mathbf{r})$ to be also finite outside τ , because the integral would then only contain part of the information on $\delta\rho_{0\sigma}(\mathbf{r})$ whereas $\tilde{T}_0[\rho_{0\sigma}(\mathbf{r}) + \delta\rho_{0\sigma}(\mathbf{r})]$ contains inevitably the full information, and hence one could not expect the quotient on the right to converge to a unique function of \mathbf{r} .)

Since

$$\int [\rho_{0\sigma}(\mathbf{r}') + \delta\rho_{0\sigma}(\mathbf{r}')] d^3r' = \int \rho_{0\sigma}(\mathbf{r}') d^3r' = N_\sigma$$

we have

$$\int_{\tau(\mathbf{r})} \rho_{0\sigma}(\mathbf{r}') d^3r' = 0. \quad (24)$$

Hence, the denominator on the right-hand side of equation (23) is always exactly zero as a result of the wavefunction representability of the original and distorted charge densities. Biagini implies without justification that the additional function on the right-hand side of equation (22) exists and is non-vanishing. In contrast, our considerations lead to

$$\delta\tilde{T}_0 \propto \eta_0^2$$

and

$$\delta\rho_{0\sigma} \propto \eta_0$$

so we have

$$\lim_{\eta_0 \rightarrow 0} \frac{\delta\tilde{T}_0}{\delta\rho_{0\sigma}} = 0.$$

The above objection against functional derivatives applies to the standard definition of $V_{xc}^{K-S}(\mathbf{r}, \sigma)$ as well. As follows from the derivation of the KS equations by varying the total energy expression (9), one needs $\delta\bar{E}_{xc}^{(0)}$ in the form

$$\delta\bar{E}_{xc}^{(0)} = \sum_{\sigma} \int V_{xc}^{K-S}(\mathbf{r}', \sigma) \delta\rho_{0\sigma}(\mathbf{r}') d^3r'. \quad (25)$$

If one assumes $\delta\rho_{0\sigma}(\mathbf{r}')$ for some spin direction σ to be non-vanishing only within a volume $\tau(\mathbf{r})$ and to be identically zero for the other spin direction, equation (25) reduces to

$$\delta\bar{E}_{xc}^{(0)} = \int_{\tau(\mathbf{r})} V_{xc}^{K-S}(\mathbf{r}', \sigma) \delta\rho_{0\sigma}(\mathbf{r}') d^3r'. \quad (26)$$

In a case where $\delta\rho_{0\sigma}(\mathbf{r}')$ would not integrate to zero within τ , equation (26) could be recast as

$$\delta\bar{E}_{xc}^{(0)} = V_{xc}^{K-S}(\bar{\mathbf{r}}, \sigma) \int_{\tau(\mathbf{r})} \delta\rho_{0\sigma}(\mathbf{r}') d^3r' \quad (27)$$

where $\bar{\mathbf{r}}$ denotes an appropriately chosen point within the volume $\tau(\mathbf{r})$. One could then divide this equation by the integral on the right-hand side and let τ go to zero. The result would, in fact, be identical with the standard definition of $V_{xc}^{K-S}(\mathbf{r}, \sigma)$. However, since $\delta\rho_{0\sigma}(\mathbf{r}')$ does integrate to zero, one cannot define a point \mathbf{r} because it is generally defined through

$$V_{xc}^{K-S}(\bar{\mathbf{r}}, \sigma) = \int_{\tau(\mathbf{r})} V_{xc}^{K-S}(\mathbf{r}', \sigma) \delta\rho_{0\sigma}(\mathbf{r}') d^3r' / \int_{\tau(\mathbf{r})} \delta\rho_{0\sigma}(\mathbf{r}') d^3r'$$

where the denominator on the right-hand side equals zero.

One is hence led to conclude that $V_{xc}^{K-S}(\mathbf{r}', \sigma)$ cannot be defined by the functional derivative of \tilde{E}_{xc} , but should rather be defined by equation (26), which, however, is not justifiable within conventional density functional theory. Since $\delta\tilde{E}_{xc}^{(0)}$ is primarily connected to $\delta\tilde{\rho}_{20\sigma'\sigma}(\mathbf{r}', \mathbf{r})$, it is not at all clear whether there is such a potential $V_{xc}^{K-S}(\mathbf{r}', \sigma)$ that interconnects the correlated pair-density variation with $\delta\rho_{0\sigma}(\mathbf{r}')$. Also in this respect Biagini's comment gives the rather misleading impression that this problem would solely be a matter of concern within my generalized density functional scheme. In completing the list of debatable statements made in Biagini's comment, I want to emphasize that my approach to constructing $V_{xc}^{(n)}(\mathbf{r}, \sigma)$ from functions $\Gamma_n(\mathbf{x}'', \mathbf{x}', \mathbf{x})$ which Biagini is referring to, is very explicitly dealt with in a recent article (Fritsche 1995) where I have described a possible way of proving the existence of such functions.

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