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Fux, Samuel; Jacob, Christoph R.; Neugebauer, Johannes; Visscher, Lucas; Reiher, Markus

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Response to “Comment on ‘Accurate frozen-density embedding potentials as a first step towards a subsystem description of covalent bonds’”

[J. Chem. Phys. 135, 027101 (2011)]

Samuel Fux,¹ Christoph R. Jacob,^{2,a)} Johannes Neugebauer,^{3,b)} Lucas Visscher,⁴ and Markus Reiher¹

¹Laboratorium für Physikalische Chemie, ETH Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

²Center for Functional Nanostructures, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Str. 1a, 76131 Karlsruhe, Germany

³Gorlaeus Laboratories, Leiden Institute of Chemistry, Universiteit Leiden, 2300 RA Leiden, The Netherlands

⁴Amsterdam Center for Multiscale Modeling, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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With our recent paper,¹ we contribute to the development of improved approximations to the functional derivative of the nonadditive kinetic energy,

$$v_T[\rho_1, \rho_2](\mathbf{r}) = \frac{\delta T_s^{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1(\mathbf{r})} = \frac{\delta T_s[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}(\mathbf{r})} - \frac{\delta T_s[\rho_1]}{\delta \rho_1(\mathbf{r})}, \quad (1)$$

which is of central importance in subsystem density-functional theory and in the closely related frozen-density embedding (FDE) scheme. This potential $v_T[\rho_1, \rho_2](\mathbf{r})$ is a bifunctional of the densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ of the active and of the frozen subsystem, respectively. Different strategies are possible for approximating $v_T[\rho_1, \rho_2]$ in practical calculations, e.g., by approximating either the noninteracting kinetic energy $T_s[\rho]$ in Eq. (1) or the bifunctional $T_s^{\text{nadd}}[\rho_1, \rho_2]$ as a whole.

For many applications of the FDE scheme $T_s^{\text{nadd}}[\rho_1, \rho_2]$ itself is actually not needed. The electron density as well as all molecular properties that directly depend on it are determined by $v_T[\rho_1, \rho_2]$. As Wesolowski points out in his comment, previous work has shown that the accuracy of a given approximation $\tilde{T}_s^{\text{nadd}}[\rho_1, \rho_2]$ (where the tilde is used to denote the approximate bifunctional) does not, in general, correlate with the accuracy of its functional derivative $\tilde{v}_T[\rho_1, \rho_2]$. Consequently, we focus on developing approximations for $v_T[\rho_1, \rho_2]$ and not for $T_s^{\text{nadd}}[\rho_1, \rho_2]$. We consider this strategy, which is also well-known for exchange–correlation potentials (see, e.g., Ref. 5), to be most promising.

To study the bifunctional $v_T[\rho_1, \rho_2]$, we implemented a numerical inversion procedure to accurately calculate $v_T[\rho_1^0, \rho_2^0](\mathbf{r})$ for a given pair of densities $\rho_1^0(\mathbf{r})$ and $\rho_2^0(\mathbf{r})$. In Ref. 1, we applied this procedure to obtain accurate reference potentials $v_T[\rho_1^0, \rho_2^0](\mathbf{r})$ for particular choices of $\rho_1^0(\mathbf{r})$ and $\rho_2^0(\mathbf{r})$ in a representative set of model systems. These accurate reference potentials are then compared to those obtained from

popular approximations for the bifunctional $\tilde{v}_T[\rho_1^0, \rho_2^0](\mathbf{r})$ in order to identify the reason for their shortcomings, in particular the dramatic failure for subsystems connected by covalent bonds.^{2–4} Of course, such a strategy will only provide limited information on the bifunctional $v_T[\rho_1, \rho_2]$. However, our paper clearly demonstrates that already this limited information provides valuable insights, which can serve as guidance for constructing improved approximations to the bifunctional $v_T[\rho_1, \rho_2]$ in future work.

Since points (iii) and (iv) of Wesolowski’s comment are not concerned with Ref. 1, we will start by discussing points (i), (ii), and (v). Concerning points (i) and (ii), we would like to emphasize that—as the title of Ref. 1 clearly indicates—our goal was to provide accurate reference potentials that could serve as a first step towards improved approximations for $v_T[\rho_1, \rho_2]$. This represents a valid and actually very important goal in itself. Therefore, the criticism that practical calculations would also require the knowledge of $T_s^{\text{nadd}}[\rho_1, \rho_2]$ misses the point of our paper.

In point (v), which is the only part of his comment that is directly related to the results of our paper, Wesolowski questions the soundness of our numerical inversion procedure. We vigorously stress that this severe accusation is not corroborated by any data. In fact, the numerical accuracy of our inversion procedure, as well as its limitations are discussed in great detail in Sec. III of our paper. Therefore, Wesolowski’s statement that our target densities are not likely to possess nodes is puzzling to us, considering that Figures 1 to 4 (insets c and e) in our paper clearly show their nodal structure, whereas the reconstructed densities (shown in the same figures) do not possess nodes.

Wesolowski suggests that the accurate nonadditive kinetic energies, calculated as described in his point (ii), could be used for an additional verification. Two tests are proposed in his point (ii.2). First, Wesolowski claims that the total kinetic energy obtained with our accurate $T_s^{\text{nadd}}[\rho_1, \rho_2]$ should be compared to the one from the supermolecular calculation. Such a comparison is, however, pointless, since the latter is used to define our accurate $T_s^{\text{nadd}}[\rho_1, \rho_2]$. Therefore, the two

^{a)}Electronic mail: christoph.jacob@kit.edu.

^{b)}Electronic mail: j.neugebauer@chem.leidenuniv.nl.

TABLE I. Accurate nonadditive kinetic energies (in eV) for the model systems considered in Ref. 1.

	(H ₂ O) ₂	FHF ⁻	BH ₃ NH ₃	C ₂ H ₆
$T_s^{\text{nadd}}[\rho_1, \rho_2]$	1.283	7.253	8.190	21.276

will always be equal. Second, he insists that we should verify that our accurate $T_s^{\text{nadd}}[\rho_1, \rho_2]$ are larger than zero. As can be seen from Table I, this is obviously the case.

The remaining points (iii) and (iv) of Wesolowski's comment are actually not concerned with Ref. 1 at all, but discuss earlier work by two of us⁶ and by himself and co-workers.⁷ Nonetheless, we would like to take the opportunity to clarify these issues.

In the former paper,⁶ the exact behavior of the kinetic-energy component $v_T[\rho_1, \rho_2]$ of the embedding potential was investigated in the limit of a large separation between the subsystems ("long-distance limit"), and exact expressions at the active and at the frozen subsystem were derived. We then showed that at the frozen subsystem, this exact limit is not described correctly by any of the existing approximations for $v_T[\rho_1, \rho_2]$ and proposed a correction that enforces the correct form.

In the latter paper,⁷ Wesolowski and co-workers followed up on our work and investigated a closely related limit, the embedding potential at the nuclear cusps. Using ideas similar to those of Ref. 6, they proposed an approximation for $v_T[\rho_1, \rho_2]$ that enforces the correct behavior at the nuclei by employing the von Weizsäcker expression. Wesolowski and co-workers approximate $T_s^{\text{nadd}}[\rho_1, \rho_2]$ as an explicit density functional, whereas in Ref. 6 the potential $v_T[\rho_1, \rho_2]$ is approximated as an implicit density functional (see below for details). Even though the former might be preferable from a theoretical point of view, the performance of the two approximations, in practice, will have to be assessed. We intend to present such a comparison elsewhere.

In his comment, Wesolowski objects to our statement that the approximation for $v_T[\rho_1, \rho_2]$ proposed in Ref. 6,

$$\tilde{v}_T^{\text{Ref. 6}}[\rho_1, \rho_2](\mathbf{r}) = \frac{\delta \tilde{T}_s^{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1(\mathbf{r})} + v_T^{\text{corr}}[\rho_1, \rho_2](\mathbf{r}), \quad (2)$$

where $\tilde{T}_s^{\text{nadd}}[\rho_1, \rho_2]$ is an existing approximation to the non-additive kinetic energy and $v_T^{\text{corr}}[\rho_1, \rho_2](\mathbf{r})$ is a correction that enforces the correct long-distance limit,

$$v_T^{\text{corr}}[\rho_1, \rho_2](\mathbf{r}) = -\exp\left[-\left(\frac{\rho_1(\mathbf{r})}{\alpha \rho_2(\mathbf{r})}\right)^2\right] \times \left(v_2^{\text{nuc}}(\mathbf{r}) + \int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}^{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1(\mathbf{r})} + \frac{\delta \tilde{T}_s^{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1(\mathbf{r})} \right), \quad (3)$$

is an (implicit) bifunctional of the densities ρ_1 and ρ_2 . Note that, in contrast to what is claimed in Wesolowski's comment, $v_T^{\text{corr}}[\rho_1, \rho_2]$ does not correct for errors in the exchange–correlation functional (for details, see Ref. 6).

Obviously, the right-hand side of Eq. (3) depends on the density functions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. Therefore, we consider Wesolowski's notation to drop this dependence on ρ_1 and ρ_2 on the left-hand side and to refer to this correction as the "function $v_T^{\text{corr}}(\mathbf{r})$ " confusing and highly misleading. However, the correction of Ref. 6 depends, in addition to the densities ρ_1 and ρ_2 , on the nuclear potential $v_2^{\text{nuc}}(\mathbf{r})$. As given in Eq. (3), our correction is thus obviously a functional of ρ_1 and ρ_2 that in addition contains the nuclear potential $v_2^{\text{nuc}}(\mathbf{r})$. Therefore, it is not a function as suggested by Wesolowski, but could be better described as a tri-functional $v_T^{\text{corr}}[\rho_1, \rho_2, v_2^{\text{nuc}}](\mathbf{r})$, even though its functional dependence on the potential may have a trivial form. Once the nuclear potential is chosen appropriately, Eq. (3) reduces to a bifunctional.

Clearly, we are considering a system-dependent correction if we insert the nuclear Coulomb potential for $v_2^{\text{nuc}}(\mathbf{r})$. But as is actually pointed out in Wesolowski's comment, also $v_2^{\text{nuc}}(\mathbf{r})$ can be interpreted as a true density functional by means of the first Hohenberg–Kohn theorem. In the limiting case of two infinitely separated subsystems considered in Ref. 6 it could, for instance, be directly obtained by inspecting the cusps of $\rho_2(\mathbf{r})$ ("Bright-Wilson argument"). Of course, such a procedure is not of any interest for practical calculations, since the nuclear charges and positions are known beforehand. Nevertheless, this argument shows that Eq. (3) can be understood as a system-independent bifunctional of the densities ρ_1 and ρ_2 .

Finally, we want to stress that the rather subtle question whether or not the correction proposed in Ref. 6 is an implicit bifunctional is completely unrelated to the contents of Ref. 1. It further bears no relevance for the usefulness or the accuracy of this correction in practical calculations, which was demonstrated in Refs. 2 and 6.

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