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Addition/Correction

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Correction to "Performance of the Density Matrix Functional Theory in the Quantum Theory of Atoms in Molecules"

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Recently, we analyzed the performance of several density matrix functional theory (DMFT) based exchange−correlation functionals in the quantum theory of atoms in molecules (QTAIM).[1] One of these functionals is the third Piris natural orbital functional (PNOF3),[2] that we erroneously stated as follows

$$\rho_2^{\mathrm{xc}}(\mathbf{r}_1;\,\mathbf{r}_2) = \sum_{i,j} f(n_i,\,n_j)^{\mathrm{PNOF3}} \chi_{ij}(\mathbf{r}_1)\,\chi_{ij}(\mathbf{r}_2) \tag{1}$$

where $\chi_{ij}(\mathbf{r})$ is an abbreviature for $\chi_i^*(\mathbf{r})\,\chi_j(\mathbf{r})$,

$$f^{\mathrm{PNOF3}}(n_i,n_j) = 2(n_i n_j)^{1/2} - 2n_i(1-n_j)\delta_{i,j} + 2[(1-n_i)(1-n_j)]^{1/2}\lambda_{i,j} \tag{2}$$

$$\lambda_{i,j} = \begin{cases} 1, & i,\,j \le N/2 \text{ and } i \ne j \\ 0, & \text{otherwise} \end{cases} \tag{3}$$

χ_i are the natural molecular orbitals, $0 \le n_i \le 1$ their populations, and N the number of electrons. The above formula does not satisfy the sum rule

$$\iint \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\rho_2^{\mathrm{xc}}(\mathbf{r}_1;\mathbf{r}_2) = N \tag{4}$$

nor the asymptotic limits $\delta^{\mathrm{A,B}} \to 0$ and $V_{\mathrm{xc}}^{\mathrm{AB}} \to 0$ when the distance between two fragments in the molecule, A and B, tends to infinity. As a direct consequence of this mistake, the data (lines or points) relative to the PNOF3 functional in Figures 1−5 are also wrong, and the comments within the text that refer to it, mostly negative, are not true.

We sincerely apologize for this mistake that may have negatively affected the scientific community about the benefits and virtues of the PNOF3 functional, and thank Prof. Mario Piris for noticing this error. Prof. Piris has also read our article with great interest, making us to know that the true PNOF3 functional cannot be formally represented according to eq 1. Actually, the fourth Piris functional (PNOF4),[3] which has been implemented in our promolden code, is representable by means of eq 1, satisfies the sum rule (eq 4), and offers very promising results that will be published elsewhere.

REFERENCES

(1) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, U.K., 1990.
(2) Piris, M. *Int. J. Quantum Chem.* **2006**, *106*, 1093.
(3) Piris, M.; Matxain, J. M.; López, X.; Ugalde, J. M. *J. Chem. Phys.* **2010**, *133*, 111101.

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