

Trushin *et al.* Reply: In their Comment [1], Shahi and Perdew point out that plots along the bond axis of the CO molecule of deviations between ground-state electron densities from approximate electronic structure methods and from CCSD(T) (coupled cluster singles doubles with perturbative triples) calculations are not sufficient to assess the quality of electron densities from approximate electronic structure methods in general. We agree with this point. Figure 3 in the main text in our Letter [2] and Fig. 8 in Supplemental Material display this difference to demonstrate that the self-consistent random phase (scRPA) method yields electron densities of high quality, which supports the main message of our Letter that the scRPA yields exchange-correlation potentials that are almost exact. We did not intend to make general judgments on the quality of electron densities of approximate electron structure methods.

Shahi and Perdew evaluate in their comment the error measure $\Delta\rho(z) = \int dxdy|\rho(\mathbf{r}) - \rho^{\text{CCSD(T)}}(\mathbf{r})|$ with ρ denoting the approximate density to be evaluated and with $\rho^{\text{CCSD(T)}}$ being the reference CCSD(T) density. This is a meaningful error measure for the CO molecule; however, an analysis of a single molecule is a narrow basis for drawing general conclusions. We, therefore, reevaluated our data and calculated for 49 molecules [3] the error measures $\Delta\rho = \int d\mathbf{r}|\rho(\mathbf{r}) - \rho^{\text{CCSD(T)}}(\mathbf{r})|$, $\Delta V_{\text{ext}} = \int d\mathbf{r}v_{\text{ext}}(\mathbf{r})\rho^{\text{CCSD(T)}}(\mathbf{r}) - \int d\mathbf{r}v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})$, ΔU , and the sum $\Delta V_{\text{ext}} + \Delta U$, with ΔU being the difference of the Coulomb energies of the densities ρ and $\rho^{\text{CCSD(T)}}$. Furthermore, we calculated for nine molecules the difference of the dipole moments from approximate methods with the CCSD(T) reference dipole moments. The same computational setup as in the main Letter [2] was used; i.e., all calculations employ aug-cc-pwCV5Z orbital basis sets. The geometries of the considered molecules correspond to those of the W4-17 dataset [4]. The error measure $\Delta\rho$ has been used before by us in Ref. [5], the error measures ΔV_{ext} and ΔU in Ref. [6].

Table I shows the error measure $\Delta\rho$ that directly refers to the difference of the densities and is not compromised by error cancellations between different spatial regions. The corresponding mean errors decrease in the order $\text{HF} > \text{PBE} > \text{r}^2\text{SCAN} > \text{scRPA}$. The same order is found for the mean absolute errors (MAEs) of dipole moments displayed in Fig. 1. This suggests that among the considered methods scRPA yields the most accurate electron

TABLE I. Mean error measures (in a.u.) across 49 molecules.

	$\Delta\rho$	ΔV_{ext}	ΔU	$\Delta V_{\text{ext}} + \Delta U$
HF	0.282	0.436	0.186	0.260
PBE	0.147	0.054	0.053	0.036
r ² SCAN	0.070	0.072	0.032	0.054
scRPA	0.060	0.097	0.052	0.047

densities followed by r²SCAN and PBE, while HF leads to the least accurate densities. This finding is in agreement with Ref. [7]. However, the picture changes if the weighted error measures ΔV_{ext} , ΔU , and $\Delta V_{\text{ext}} + \Delta U$ are considered; the corresponding MAEs are ordered $\text{HF} > \text{scRPA} > \text{r}^2\text{SCAN} > \text{PBE}$, $\text{HF} > \text{PBE} \approx \text{scRPA} > \text{r}^2\text{SCAN}$, and $\text{HF} > \text{r}^2\text{SCAN} > \text{scRPA} > \text{PBE}$, respectively.

The error measures ΔV_{ext} , ΔU , and $\Delta V_{\text{ext}} + \Delta U$ are affected by error cancellations between different spatial regions and, therefore, might be considered as less meaningful for judging the quality of an approximate electron density itself. However, when evaluating energies with approximate densities, such energy-related measures are relevant. For a complete analysis of why density functional approximations lead to higher accuracies when evaluated with the HF density instead of the corresponding self-consistent density [8], the error measures considered here are not sufficient. For the SCAN functional, an analysis of this point can be found in Ref. [9]; to answer this question in further detail, all contributions to the total energy would have to be compared to reference data from KS inversion.

Data availability—The data supporting the results of this study are openly available [10].

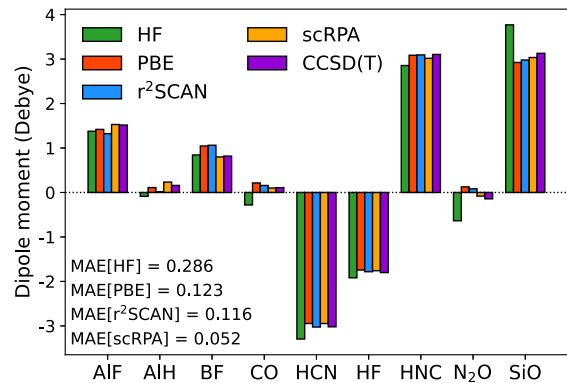


FIG. 1. Dipole moments from the HF method and from the density-functional methods PBE, r²SCAN, and scRPA in comparison to CCSD(T) reference values.

Egor Trushin^{1,2}, Steffen Fauser¹, Andreas Mölkner¹, Jannis Erhard¹, and Andreas Görling^{1,2,*}

¹Lehrstuhl für Theoretische Chemie

Universität Erlangen-Nürnberg

Egerlandstrasse 3, D-91058 Erlangen, Germany

²Erlangen National High Performance Computing Center (NHR@FAU)

Martensstrasse 1, D-91058 Erlangen, Germany



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*Contact author: andreas.goerling@fau.de

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[3] The list of 49 molecules includes AlF, AlH, AlH₃, allene, B₂H₆, BF, BH₃, c-HCOH, c-N₂H₂, C₂H₂, C₂H₄, C₂H₆,

CH₂C, CH₂NH, CH₃F, CH₃NH₂, CH₄, CO, CO₂, cyclopropene, F₂, H₂, H₂CO, H₂O, HCCF, HCN, HCNO, HF, HNC, HCNO, HN₃, HOCN, HOF, HONC, HOOH, ketene, methanol, N₂, N₂H₄, N₂O, NH₂F, NH₂OH, NH₃, oxirene, propyne, SiH₄, SiO, t-HCOH, and t-N₂H₂.

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