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Authors

Bates, Jefferson E
Heiche, Maximillian C
Liang, Jiashu
et al.

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Erratum: "Harnessing the meta-generalized gradient approximation for time-dependent density functional theory" [J. Chem. Phys. 137, 164105 (2012)]

Jefferson E. Bates,[1] Maximillian C. Heiche,[1] Jiashu Liang,[2] and Filipp Furche[3]
[1] *Appalachian State University, Department of Cheimstry and Fermentation Sciences, 525 Rivers Street, Boone, NC 28608, USA*
[2] *Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA*
[3] *University of California, Irvine, Department of Chemistry, 1102 Natural Sciences II, Irvine, CA 92697-2025, USA*

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We recently determined that Eq. (55), one of the equations reporting the implementation of current-density corrected meta-generalized gradient approximation (cMGGA) density functionals in Ref. 1, is missing a multiplicative factor of 1/2. The correct equation reads

$$[(\mathbf{A}-\mathbf{B})(\mathbf{X}-\mathbf{Y})]_{\mu\nu\sigma} \leftarrow \frac{1}{4}\sum_g w_g\, c\mathbf{A}_\sigma^{\mathrm{XC\ cMGGA}}(\mathbf{r}_g) \times [\chi_\mu(\mathbf{r}_g)\nabla\chi_\nu(\mathbf{r}_g) - \nabla\chi_\mu(\mathbf{r}_g)\chi_\nu(\mathbf{r}_g)]\,. \quad (55)$$

While the other equations contained in the publication are unaffected by this error, the cMGGA excitation energies and optical rotations (ORs) should be replaced by the values reported below and provided in the updated supplementary material of Ref. 1. While some of the changes are significant, the conclusions of the paper still hold after correction of these values.

The original implementation in TURBOMOLE [2] was corrected accordingly and has been released in version V7.6. One of us (J. L.) independently confirmed the implementation of Eq. (55). This implementation is part of Q-Chem Version 5.4[3].

a. AEX Benchmark Comparing the previous and present current-dependent implementations for cTPSS and cTPSSh over the entire AEX benchmark, the correction resulted in a shift to larger excitation energies by 0.03 eV on average, though the largest change was approximately 0.2 eV for the $^3\Pi$ state of NH. The correction tends to reduce the effect of the current-dependence and hence leads to slightly larger excitation energies than originally reported. For Pyridone-lactam and OMpCA, the values reported in 2012 were too large due a convergence issue, and the corrected values of the excitation energies display an even smaller effect of including the current-density response than the originally reported ones, in line with the other singlet excitations included in the AEX test set. The statistical error analysis for TPSS, TPSSh, cTPSS, and cTPSSh compared to experiment shows little change due to the corrections, see Tables II (corrected) and III (corrected). Individual results for the benchmark set using cTPSS and cTPSSh are available in the corrected Supporting Information of Ref. 1.

b. Optical Rotations The corrected ORs are displayed in Table IV (corrected). The current-free results were re-confirmed except for two cases whose ground-state solution was not fully converged. As in the original publication, all results were computed in units of $\deg\cdot[\mathrm{dm}\cdot(\mathrm{g/cc})]^{-1}$, utilizing the length gauge, and obtained at the sodium D-line of 589.3 nm.

The effect of the corrections is small for most systems considered here, with the exception of bisnoradamantan-2-one, whose (c)TPSS ORs are significantly more negative than reported previously, while the hybrid results for (c)TPSSh are slightly more positive. The overall conclusion that cMGGAs provide ORs with an accuracy comparable to that of GGAs remains unaffected.

c. Testing Strategy We briefly outline a method to help ascertain the correctness of MGGA and cMGGA implementations using the one- and two-electron limit and an existing GGA implementation which was used to check the present results. By construction, the generalized Kohn-Sham kinetic energy density $\hat{\tau}$, Eq. (14), reduces to the von Weizsäcker kinetic energy density in the limit of one-electron systems and two-electron singlets. Thus, the substitution

$$\hat{\tau}_\sigma \to \tau_{W\sigma} = \frac{1}{8}\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma}$$

in Eq. (28) produces a GGA whose energy functional is identical to the corresponding cMGGA one in this limit. While the resulting GGA generally yields KS potentials, virtual orbitals, and orbital rotation Hessians different from the MGGA and cMGGA ones, the total energy, density, and all properties derived from them are identical. In particular, the above substitution enables the calculation of cMGGA excitation energies for one-electron systems and two-electron singlets using a GGA code.

Additional tests performed included (i) calculation of the second-order correction of the MGGA excitation energy treating the current density response as a perturbation, and calculation of the velocity form of the transition dipole moment $\boldsymbol{\mu}_{0n,v}$ from integration of the transition current density on the molecular integration grid and the (converged) excitation energy Ω_{0n} according to

$$\boldsymbol{\mu}_{0n,v} = -\frac{1}{\Omega_{0n}}\int dx\, \mathbf{j}_{P,0n}(x). \quad (1)$$

TABLE II (corrected). AEX benchmark set mean errors (ME), mean absolute errors (MAE), standard deviations (SD), and maximum positive (MPD) and maximum negative (MND) deviations for seven functionals using def2-TZVP basis sets. All values are in eV. TPSS, PBE, B3LYP and PBE0 were taken from Ref. 65 of the original paper, TPSSh was recomputed for this Note.

Method	ME	MAE	SD	MND	MPD
cTPSS	–0.26	0.33	0.33	–1.05 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.34 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
TPSS	–0.21	0.33	0.36	–1.05 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.79 (NH $1\,{}^{3}\Pi$)
PBE	–0.33	0.40	0.49	–1.14 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.74 ($\mathrm{NO_3}$ $1\,{}^{2}\mathrm{E}'$)
cTPSSh	–0.11	0.25	0.29	–0.85 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.50 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
TPSSh	–0.08	0.27	0.32	–0.84 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.73 (NH $1\,{}^{3}\Pi$)
B3LYP	–0.08	0.21	0.28	–0.73 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.42 (Benzene $1\,{}^{1}\mathrm{B}_{1u}$)
PBE0	0.01	0.25	0.30	–0.66 (quinoline $1\,{}^{3}\mathrm{A}'$)	0.63 (CuH $2\,{}^{1}\Sigma^{+}$)

TABLE III (corrected). Performance of TPSS and TPSSh and their current-dependent versions for AEX subsets of 86 singlet, 10 triplet, and 13 spin-unrestricted excited states using def2-TZVP basis sets. See Table II (corrected) for further explanations. All values are in eV. BPK radical is benzophenone ketyl radical.

Subset	Method	ME	MAE	SD	MND	MPD
Singlets	cTPSS	–0.26	0.33	0.33	–1.05 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.34 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
	TPSS	–0.24	0.31	0.33	–1.05 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.37 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
	cTPSSh	–0.11	0.25	0.29	–0.85 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.50 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
	TPSSh	–0.08	0.24	0.29	–0.84 (p-Benzoquinone $1\,{}^{1}\mathrm{B}_{1g}$)	0.54 ($\mathrm{NH_3}$ $1\,{}^{1}\mathrm{A}_2''$)
Triplets	cTPSS	–0.53	0.54	0.25	–0.91 (Acrolein $1\,{}^{3}\mathrm{A}''$)	0.04 ($\mathrm{CS_2}$ $3\,{}^{3}\mathrm{A}$)
	TPSS	–0.50	0.51	0.24	–0.88 (Acrolein $1\,{}^{3}\mathrm{A}''$)	0.05 ($\mathrm{CS_2}$ $3\,{}^{3}\mathrm{A}$)
	cTPSSh	–0.48	0.49	0.20	–0.72 (Acrolein $1\,{}^{3}\mathrm{A}''$)	0.01 ($\mathrm{CS_2}$ $3\,{}^{3}\mathrm{A}$)
	TPSSh	–0.45	0.46	0.20	–0.69 (Acrolein $1\,{}^{3}\mathrm{A}''$)	0.02 ($\mathrm{CS_2}$ $3\,{}^{3}\mathrm{A}$)
Unrestricted	cTPSS	0.17	0.24	0.25	–0.27 (BPK $2\,{}^{2}\mathrm{A}$)	0.59 (NH $1\,{}^{3}\Pi$)
	TPSS	0.21	0.27	0.28	–0.26 (BPK $2\,{}^{2}\mathrm{A}$)	0.79 (NH $1\,{}^{3}\Pi$)
	cTPSSh	0.20	0.22	0.19	–0.09 (ScO $1\,{}^{2}\Pi$)	0.55 (NH $1\,{}^{3}\Pi$)
	TPSSh	0.24	0.26	0.21	–0.06 (ScO $1\,{}^{2}\Pi$)	0.73 (NH $1\,{}^{3}\Pi$)

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TABLE IV (corrected). Frequency-dependent optical rotations of 13 structurally rigid chiral molecules evaluated at 589.3 nm using the aug-cc-pVDZ basis sets. Experimental and CCSD results were taken from Ref. 66 of the 2012 publication, while the results for the other functionals were calculated for this work. The reported MAEs do not include (1S,4S)-norbornenone, as its OR is 2 orders of magnitude larger than the other systems. TPSSh results (without currents) for compounds in boldface were also corrected.

Compound	TPSS	cTPSS	TPSSh	cTPSSh	CCSD	Expt.
(1R,2S,5R)-cis-pinane	14.6	15.0	13.3	13.6	8.8	23.3
(1S,2S,5S)-trans-pinane	7.3	7.5	4.8	4.9	–0.7	–15.9
(1S,3R,4R)-endo-isocamphane	–12.7	–12.7	–11.0	–11.0	–9.8	6.6
(1S,3R,4R)-exo-isocamphane	3.9	4.0	5.6	5.7	6.4	15.8
(1R,5R)-α-pinene	37.7	38.7	43.0	43.9	44.1	51.6
(1R,5R)-β-pinene	–38.4	–39.7	–26.9	–27.8	–0.9	23.1
(1R,4S)-camphenilone	–68.3	–70.1	–61.5	–62.9	–49.8	–72.3
(1R,5S)-nopinone	–2.4	–2.2	–3.2	–3.2	–8.3	39.9
(1R,4S)-1-methylnorbornanone	–31.4	–32.1	–29.5	–30.1	–19.0	–45.5
(1R,3S,6S,7R)-2-brendanone	39.5	41.8	40.1	41.9	55.8	46.6
(1R,3R,5R,7R)-bisnoradamantan-2-one	–36.1	–33.8	–16.2	–13.9	19.5	–78.4
(1S,4R)-norbornanone	–6.4	–6.8	–4.8	–5.2	–7.6	29.8
(1S,4S)-norbornenone	–1583	–1631	–1322	–1358	–740.4	–1146
MAE (vs Expt.)	28.7	28.0	26.1	25.5	27.4	
MAE (vs CCSD)	12.2	12.2	8.2	8.4	0	