

# Response to “Comment on ‘Regularized SCAN functional’” [J. Chem. Phys. 151, 207101 (2019)]

Cite as: J. Chem. Phys. 151, 207102 (2019); <https://doi.org/10.1063/1.5128484>

Submitted: 19 September 2019 . Accepted: 31 October 2019 . Published Online: 26 November 2019

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<https://doi.org/10.1063/1.5128484>

In their comment,<sup>16</sup> Mejía-Rodríguez and Trickey benchmarked the performance of our recently proposed regularized form<sup>1</sup> of the SCAN<sup>2</sup> functional in terms of reproducing the energetic and geometric properties of isolated molecules and simple solids. Their work confirms that rSCAN does improve on the numerical instability of the original SCAN functional, while retaining the remarkable accuracy of SCAN in most respects but also retaining its peculiar overmagnetization.<sup>16</sup> The notable exception is an increase in the error of predicted formation enthalpies of isolated molecules, as demonstrated on the G3/99X set.<sup>3,4</sup>

Formation enthalpies are a stringent test of any *ab initio* theory, as they measure small energy differences in relatively large total energies, calculated in atomic systems characterized by vastly different chemical environments, as well as curvature information on the molecular potential energy surface, responsible for the accurate estimation of vibrational contributions. As Mejía-Rodríguez and Trickey showed in their comment, on a molecular test set, rSCAN remains accurate for geometrical parameters and vibrational frequencies, suggesting that the molecular potential energy surface is well reproduced. We attribute the increased discrepancy in formation enthalpies with respect to SCAN to errors in the atomic and molecular energies predicted by rSCAN.

It is interesting to note that the magnitude of the mean error in formation enthalpies predicted by rSCAN is very close to the mean absolute deviation figure (−12.5 kcal/mol and 12.9 kcal/mol, respectively), indicating a systematic error. Also notable is the fact that for structural isomers among the G3/99X set, the deviations of formation enthalpies are, in general, close to each other for a given chemical formula. To illustrate this, we collected all compositions from the G3/99X set where more than one structural

isomers are presented in Table I. Using the deviations of standard enthalpies of formation reported by Mejía-Rodríguez and Trickey at the most converged, “NWChem Huge” grid, we calculated the mean absolute deviation around their mean. Users should be alert to the fact that rSCAN differs from SCAN<sup>2</sup> and SCAN-L<sup>5</sup> for molecular formation enthalpies on the most commonly used test set, but apparently not for relative intermolecular energies. Further study will be necessary to establish the errors in benchmark sets which do not use reference atomic energies, such as the GMTKN55<sup>6</sup> or W4-11-RE<sup>7</sup> set.

Csonka *et al.* suggested that comparing the enthalpies of formation without the free atom references would be a more fair benchmark of density functionals and illustrated this statement by applying a set of atomic corrections for a number of functionals, reducing the mean absolute errors in the enthalpies of formation significantly.<sup>8</sup> Perdew *et al.* showed that the atomic energy shift arises due to errors in the spin-dependence of the correlation energy functional.<sup>9</sup> To further explore the idea that the molecular potential energy surfaces and the relative energies are comparable across SCAN, SCAN-L, and rSCAN, we determined sets of atomic correction parameters for each functional that minimize the mean square deviation of standard enthalpies of formation values for the entire G3/99X set based on the deviation figures listed in the comment by Mejía-Rodríguez and Trickey. As a baseline, we also present the performance of the PBE functional reproduced from the work of del Campo *et al.*<sup>10</sup> Table II shows the effect of these atomic correction parameters on the mean deviation and mean absolute deviation. The deviations of the corrected enthalpies of formation are reduced significantly for all three functionals with their mean values being very close to each other, implying that the errors are largely due to the incorrectly predicted relative differences between isolated

**TABLE I.** Mean absolute deviation around the mean of standard enthalpies of formation (kcal/mol) calculated using the SCAN exchange-correlation functional and two variants of it for structural isomers of given chemical formulas in the G3/99X set. The data were reused from the comment by Mejia-Rodriguez and Trickey.

| Chemical formula                             | SCAN | SCAN-L | rSCAN |
|--|------|--------|-------|
| CH <sub>2</sub>                              | 6.07 | 4.24   | 6.50  |
| SiH <sub>2</sub>                             | 4.93 | 4.66   | 4.92  |
| C <sub>3</sub> H <sub>4</sub>                | 1.22 | 1.33   | 1.39  |
| C <sub>3</sub> H <sub>6</sub>                | 0.91 | 0.12   | 0.91  |
| C <sub>4</sub> H <sub>6</sub>                | 1.37 | 1.47   | 1.60  |
| C <sub>4</sub> H <sub>8</sub>                | 0.78 | 0.41   | 0.00  |
| C <sub>4</sub> H <sub>10</sub>               | 0.24 | 0.25   | 0.21  |
| C <sub>5</sub> H <sub>8</sub>                | 2.11 | 0.27   | 2.02  |
| CNO <sub>2</sub> H <sub>3</sub>              | 0.84 | 0.45   | 1.64  |
| C <sub>2</sub> O <sub>2</sub> H <sub>4</sub> | 0.79 | 1.15   | 0.00  |
| C <sub>2</sub> NH <sub>7</sub>               | 0.14 | 0.25   | 0.43  |
| C <sub>2</sub> OH <sub>4</sub>               | 0.71 | 1.16   | 0.27  |
| C <sub>2</sub> OH <sub>6</sub>               | 0.84 | 0.75   | 0.21  |
| C <sub>2</sub> SH <sub>6</sub>               | 0.36 | 0.64   | 0.46  |
| C <sub>3</sub> OH <sub>8</sub>               | 1.13 | 1.01   | 0.46  |
| C <sub>4</sub> OH <sub>4</sub>               | 4.02 | 2.64   | 3.60  |
| COH <sub>3</sub>                             | 1.62 | 1.04   | 0.80  |
| C <sub>5</sub> H <sub>12</sub>               | 0.56 | 0.53   | 0.48  |
| C <sub>6</sub> H <sub>8</sub>                | 0.23 | 0.51   | 0.32  |
| C <sub>6</sub> H <sub>14</sub>               | 0.63 | 0.49   | 0.57  |
| C <sub>10</sub> H <sub>8</sub>               | 0.30 | 1.04   | 0.19  |
| C <sub>4</sub> OH <sub>10</sub>              | 1.22 | 1.00   | 0.53  |
| C <sub>4</sub> OH <sub>6</sub>               | 0.28 | 0.12   | 0.52  |
| C <sub>4</sub> OH <sub>8</sub>               | 1.15 | 0.70   | 0.97  |
| C <sub>4</sub> N <sub>2</sub> H <sub>4</sub> | 5.00 | 3.74   | 4.76  |
| C <sub>4</sub> C <sub>1</sub> H <sub>9</sub> | 0.19 | 0.10   | 0.22  |
| C <sub>5</sub> OH <sub>10</sub>              | 0.06 | 0.30   | 1.16  |
| C <sub>6</sub> F <sub>2</sub> H <sub>4</sub> | 0.16 | 0.05   | 0.15  |

and chemically bonded atoms, with rSCAN (without the correction) being the poorest performer. To ensure that the reduction in error is not due to over-fitting, we also obtained atomic corrections by fitting using five sets comprising 70 randomly selected molecules, and averaging over the resulting corrected deviations of the rest of the G3/99X set, and also repeating the same procedure with 35 random molecules.

**TABLE II.** Mean absolute deviation (mean deviation) of standard enthalpies of formation (kcal/mol) after applying atomic corrections, which were fitted using the entire G3/99X set, or samples of 70 and 35 randomly selected molecules averaged in a cross-validation fashion.

| Fitting               | PBE          | SCAN       | SCAN-L     | rSCAN        |
|-----------------------|--------------|------------|------------|--------------|
| No correction         | 21.2 (−20.7) | 4.9 (−3.4) | 5.7 (2.2)  | 12.9 (−12.5) |
| Entire G3/99X         | 2.9 (−0.1)   | 2.5 (0.2)  | 2.9 (−0.3) | 2.4 (0.3)    |
| Cross-validation (70) | 3.9 (−0.5)   | 3.1 (0.4)  | 3.7 (0.3)  | 2.9 (0.1)    |
| Cross-validation (35) | 3.9 (0.6)    | 3.5 (0.7)  | 4.2 (−0.4) | 3.2 (−0.3)   |

**TABLE III.** Equilibrium lattice constants (Å) of a selection of metallic and semiconductor solids (a subset of “LC20” in Ref. 2) computed using the rSCAN functional. Experimental values, corrected for zero point anharmonic expansion, were taken from Ref. 11 and reference SCAN values from Ref. 2.

|       | Li    | Na    | Ag    | C     | Si    | SiC   | LiF   | MgO   |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Expt. | 3.451 | 4.207 | 4.063 | 3.555 | 5.422 | 4.348 | 3.974 | 4.188 |
| SCAN  | 3.460 | 4.190 | 4.079 | 3.550 | 5.424 | 4.349 | 3.980 | 4.206 |
| rSCAN | 3.469 | 4.244 | 4.102 | 3.554 | 5.440 | 4.351 | 3.974 | 4.202 |

**TABLE IV.** Dissociation energies (meV/monomer) of a few low-energy water hexamer conformations, the equilibrium bond length (Å), bond angle, and dipole moment (Debye) of the water molecule. Reference hexamer dissociation values are computed by CCSD(T),<sup>12</sup> while the geometry of the water molecule is from Ref. 13 and its dipole moment from Ref. 14. SCAN values were obtained from Ref. 15.

|       | Prism | Cage | Book | Chair | $r_{\text{OH}}$ | $\theta_{\text{HOH}}$ | $\mu$ |
|-------|-------|------|------|-------|-----------------|-----------------------|-------|
| Ref.  | 348   | 346  | 339  | 332   | 0.957           | 104.5°                | 1.855 |
| SCAN  | 377   | 376  | 370  | 360   | 0.961           | 104.5°                | 1.847 |
| rSCAN | 359   | 358  | 356  | 348   | 0.959           | 104.5°                | 1.846 |

Based on these observations and the comment, we conclude that the calculated values of standard enthalpies of formation of molecules using all three functionals may contain systematic errors, which are comparable in SCAN and SCAN-L and significantly larger in rSCAN. These may be attributed to energy shifts of the free atom reference values, and empirical correction of the atomic energies counterbalances this effect, improving the performance of all three functionals to comparable levels. We argue that molecular energetic comparisons, such as reaction energies or relative stability of isomeric structures, remain accurate for the studied functionals, with the caveat that they are not referenced to isolated atom energies.

After the publication of the original article, we discovered a programming mistake in our plane-wave implementation of the rSCAN functional. After correcting the error, we have recomputed the benchmark results we presented in our original paper, which remained unchanged, except some lattice constant values in Table III and some calculated properties of the water molecule in Table IV in Ref. 1. The corrected values are presented here in Tables III and IV.

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