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Comment on "Regularized SCAN functional" [J. Chem. Phys. 150, 161101 (2019)]

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I. INTRODUCTION

Recently, Bartók and Yates[1] presented modest modifications of the Strongly Constrained and Appropriately Normed (SCAN) exchange-correlation (XC) functional.[2] Motivated by numerical instabilities caused by the SCAN XC potential in generalized Kohn-Sham calculations, their changes allowed them to generate SCAN pseudopotentials. Their modifications are the addition of a small positive constant to the denominator of the iso-orbital indicator α, subsequent rescaling of α, and a 7-parameter fit to the SCAN switching function $f_x(\alpha)$ for $\alpha < 2.5$. That "regularized" SCAN (rSCAN) XC functional performed comparably to SCAN on a small sample of solids and molecules. Bartók and Yates therefore hypothesized that rSCAN "…should improve the stability of any density functional theory (DFT) implementation where the XC functionals need to be represented on a grid."

We have examined that hypothesis with all-electron molecular calculations and projector augmented wave (PAW) solid calculations. In both, the tests were against much larger *de facto* standard databases than Ref. 1 used. We also did comparisons with the deorbitalized SCAN version, SCAN-L.[3,4] The molecular calculations used a locally modified NWChem,[5] while the crystalline calculations used locally modified VASP 5.4.4.[6]

II. RESULTS AND OBSERVATIONS

Molecular comparison - Molecular calculations used the def2-tzvpp basis set[7] and five prespecified grid refinements: `COARSE`, `MEDIUM`, `FINE`, `XFINE`, and `HUGE`. Table I shows the mean absolute errors (MAEs) for heats of formation (G3/99X set[8]), bond lengths (T96-R set[9]), and harmonic vibrational frequencies (T82-F set[9]) obtained with HUGE. Results for lower quality grids are presented in Table S1 of the supplementary material.

The most important point is that rSCAN does not reproduce SCAN performance for heats of formation with the MAE with respect to experiment worse than that from some generalized-gradient-approximation (GGA) functionals such as BLYP[10] (9.49 kcal/mol) or NCAP[11] (5.96 kcal/mol), but better than PBE[12] (21.38 kcal/mol) (see the supplementary material). In contrast, the SCAN bond length and vibrational frequency MAEs are very well reproduced by rSCAN. Importantly, therefore, rSCAN appears to preserve the molecular potential energy surface shape.

SCAN grid sensitivity is alleviated markedly with rSCAN. Using the `COARSE` grid with rSCAN achieves the same convergence with respect to grid density as with the `XFINE` grid for SCAN. Observe that the reported SCAN sensitivity is very similar to that obtained in Refs. 13 and 14. rSCAN is slightly more sensitive to grid refinement than many GGA, but equally as sensitive as the SOGGA11[15] functional (see the supplementary material). Note that vibrational frequencies are expected to be more sensitive when second functional derivatives, not available in NWChem for metaGGAs, are used.

Crystalline comparison - Bulk calculations with VASP used the same PAWs and settings as in our previous work[4] and the same 55-solid test set. Table II summarizes the results. In a seemingly striking contrast to the molecular heats of formation comparison, the rSCAN MAE for crystalline cohesive energies is better than the SCAN MAE. However, the solid-molecule comparison is not quite as severe as might appear. If heats of formation are re-expressed per atom, the rSCAN MAE is worse than that of SCAN by about 0.04 eV/atom, about twice the magnitude of the cohesive energy MAE difference. A part of this difference is related to a slightly different behavior of rSCAN for regions $\alpha \approx 0$, a consequence of the α rescaling. For lattice constants, the rSCAN MAE is worse than the SCAN result but

TABLE I. Mean absolute errors, with respect to experiment, of SCAN, rSCAN, and SCAN-L for heats of formation (kcal/mol), bond lengths (Å), and vibrational frequencies (cm^{-1}). NWChem `HUGE` grids were used.

	SCAN	rSCAN	SCAN-L
Heats of formation	4.93	12.89	5.66
Bond lengths	0.009	0.009	0.011
Vibrational frequencies	31.1	31.1	28.8

TABLE II. Performance of SCAN and rSCAN XC functionals for the solid state test set. Mean absolute errors are tabulated.

	SCAN	rSCAN
Lattice parameters (Å)	0.025	0.032
Bulk moduli (GPa)	7.0	6.0
Cohesive energies (eV/atom)	0.30	0.28

both MAEs are small on a fractional basis. For the bulk modulus, the rSCAN MAE is superior to the SCAN result.

Both the SCAN and rSCAN calculations used PBE PAWs.[4] It is conceivable that this procedural inconsistency (which at present is inescapable in VASP) could bias the results in such a way as to yield a false equivalence of the two functionals. To dismiss that possibility, atomization energies of four small molecules, CO, CO_2, ClF_3, and CF_4, were computed both with VASP and different PAWs and with NWChem (def2-qzvpp basis sets, HUGE grid) with all electrons. VASP calculations were done on a 15 × 15 × 15 $Å^3$ cell with an 800 eV kinetic energy cutoff and corrected for dipole-dipole interactions. Three PAWs were used, labeled according to VASP manual conventions as "Default," "Hard," and "GW." The energy cutoffs for the "GW" sets are modestly above the corresponding "Default" cutoffs but well below the "Hard" cutoffs. Table III shows the results. Observe first that for the all-electron calculations, the difference between the rSCAN and SCAN atomization energies of these molecules ranges over 0.186–0.379 eV (4.3–8.7 kcal/mol). Second, the difference between rSCAN and SCAN atomization energies is about the same for each PAW. However, both functionals are sensitive to the choice of the PAW. The GW type PAWs consistently yield results comparable to the all-electron case.

Deorbitalization comparison - Elsewhere,[16] we showed that SCAN-L,[4] the deorbitalized SCAN form, does not over-magnetize bcc Fe. Both SCAN and rSCAN do over-magnetize. Thus, the comparison of rSCAN and SCAN-L sensitivities to grid spacing and PAW choice is merited. Table I shows that on the molecular test sets, SCAN-L has the same grid quality sensitivity as SCAN.

SCAN, rSCAN, and SCAN-L are similarly sensitive to the PAW choice. However, SCAN-L seems to require harder PAWs than SCAN or rSCAN. Depending upon the PAW used, the atomization energies (per atom) varied up to 0.132, 0.114, and 0.116 eV/atom for SCAN, rSCAN, and SCAN-L, respectively. However, the comparison between the PAW results closest to the all-electron results (italicized values in Table III) shows larger variations for SCAN-L (−0.036 eV/atom) than for SCAN (−0.015 eV/atom) or rSCAN (0.006 eV/atom).

TABLE III. SCAN, rSCAN, and SCAN-L atomization energies (eV) obtained with different PAWs in VASP. NWChem all-electron results are also shown. Results closest to the all-electron ones are italicized.

	PAW	CO	CO_2	ClF_3	CF_4
SCAN	Default	10.833	16.625	6.107	20.457
	Hard	11.010	16.976	*5.971*	20.697
	GW	*11.040*	*17.021*	6.118	*20.885*
	All-electron	11.030	17.028	6.032	20.845
rSCAN	Default	11.041	17.040	6.218	20.746
	Hard	11.201	17.331	6.261	21.138
	GW	*11.228*	*17.383*	*6.316*	*21.256*
	All-electron	11.216	17.373	6.292	21.231
SCAN-L	Default	10.848	16.582	5.897	19.397
	Hard	*10.975*	16.749	*6.010*	*19.918*
	GW	11.036	*16.879*	5.871	*19.979*
	All-electron	11.004	16.856	6.155	20.124

Observations - SCAN, rSCAN, and SCAN-L are not fully interchangeable. The seemingly minor changes from SCAN to rSCAN do alleviate the SCAN grid sensitivity but have a nontrivial consequence; the balance between molecular and solid thermochemistry accuracy in SCAN is impaired in rSCAN. SCAN-L, which on its face is a major change of SCAN than rSCAN, actually retains the thermochemical balance but changes the magnetization behavior and increases sensitivity to the PAW choice.

SUPPLEMENTARY MATERIAL

See the supplementary material for tables with full results.

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