Meta-GGA Performance in Solids at Almost GGA Cost

Daniel Mejía-Rodríguez and S.B. Trickey
Center for Molecular Magnetic Quantum Materials, Quantum Theory Project, Department of Physics, University of Florida, Gainesville, FL 32611
(Dated: 27 Aug. 2020)

A recent modification, \(r^2\)SCAN, of the SCAN (strongly constrained and appropriately normed) meta-GGA exchange-correlation functional mostly eliminates numerical instabilities and attendant integration grid sensitivities exhibited by SCAN. Here we show that the successful deorbitalization of SCAN to SCAN-L (SCAN with density Laplacian dependence) carries over directly to yield \(r^2\)SCAN-L. A major benefit is that the high iteration counts that hindered use of SCAN-L are eliminated in \(r^2\)SCAN-L. It therefore is a computationally much faster meta-GGA than its orbital-independent antecedent. Validation data for molecular heats of formation, bond lengths, and vibrational frequencies (G3/99X, T96-R, T82-F test sets respectively) and on lattice constants, and cohesive energies (for 55 solids) and bulk moduli (for 40 solids) are provided. In addition, we show that the over-magnetization of bcc Fe from SCAN persists in \(r^2\)SCAN but does not appear in \(r^2\)SCAN-L, just as with SCAN-L.

Setting and Motivation - Recognition of chemically significant electron density inhomogeneities by use of an indicator function (usually denoted \(\alpha\); see below) is the critical mechanism by which a meta-GGA exchange-correlation (XC) functional improves upon a generalized gradient approximation (GGA). The most successful meta-GGA so far (see [4] and references therein), is SCAN, the strongly constrained and appropriately normed functional [2, 9]. Its success is attributed to enforcement upon it of all known rigorous constraints which a meta-GGA can meet, together with calibration to the energies of certain primitive physical systems (the “appropriate norms”; see Supplemental Material to Ref. [2]).

Despite its successes, SCAN introduced a numerical problem and exacerbated a methodological challenge. We defer discussion of the methodological issue briefly. The numerical problem has two elements. SCAN exhibits high sensitivity to numerical integration grid density. Handling that requires extremely dense, hence costly, grids. The other element is instability of self-consistent field convergence that is hard to foresee, hence control, for a given system (especially in periodic solids).

Those two numerical issues with SCAN were addressed by Bartók and Yates [4] by a simple renormalization of the denominator of \(\alpha\), a rescaling, and replacement of the SCAN switching function \(f(\alpha)\) with a smoother seventh-degree polynomial for \(\alpha < 2.5\). The resulting revised SCAN (rSCAN) is far better behaved computationally than SCAN. rSCAN preserves both the good molecular bond lengths and vibrational frequencies performance of SCAN. Unfortunately, rSCAN does not preserve the good performance of SCAN for benchmark molecular heats of formation [5]. In periodic solids, SCAN and rSCAN are about the same for lattice constants and cohesive energies on a 55 solid test set [6] and for bulk moduli on a 44 solid set [7].

Very recently Furness et al. [8] have shown that the shortcomings of rSCAN stem from the fact that its regularization resulted in violation of several constraints satisfied by SCAN. They adopted the smooth switching function strategy of rSCAN combined with modifications to restore compliance with all but one of the constraints satisfied in SCAN. The result, their regularized-restored SCAN functional or \(r^2\)SCAN, recovers the strong performance trends of SCAN relative to molecular and solid data sets while maintaining the numerical stability of rSCAN.

The \(r^2\)SCAN combination of accuracy and stability opens an opportunity for equally improved response to the methodological challenge. That comes from the regularized chemical region detector

\[
\alpha(\mathbf{r}) := \frac{\tau_s - \tau_W}{\tau_T F + \eta \tau_W},
\]

Here \(\tau_s = (1/2) \sum f_j |\nabla \phi_j(\mathbf{r})|^2\) is the positive-definite Kohn-Sham (KS) kinetic energy density in terms of the KS orbitals \(\phi_j\) and occupations \(f_j\), \(\tau_W\) and \(\tau_T F\) are the von Weizsäcker and Thomas-Fermi kinetic energy densities respectively, and \(\eta = 10^{-3}\) is a small regularization parameter. The original \(\alpha\) has \(\eta = 0\). Obviously the orbital dependence of the XC energy introduced by \(\alpha\) disqualifies SCAN or \(r^2\)SCAN from being used in orbital-free DFT. Worse, that orbital-dependence makes an ordinary KS calculation almost prohibitively costly because it necessitates an optimized effective potential calculation [11] at every SCF step. Usual practice to evade that cost is to do generalized-KS (gKS) calculations. The gKS Euler equation follows from variation of the density functional approximation with respect to the orbitals, not the density. For meta-GGA and higher-rung functionals the KS and gKS equations are not equivalent [13, 14].

We addressed this challenge by deorbitalization [15–17]. The deorbitalized version of SCAN, SCAN-L, differs from SCAN only in using an approximate orbital-independent approximation for \(\tau_s\) in the original \(\alpha\) to give \(\alpha[n, \nabla n, \nabla^2 n]\) (with \(n\) the electron number density). De-
orbitalization restores use of the KS equation. Furthermore, a SCAN-L calculation should be much faster than SCAN. In practice that advantage oft-times went unrealized because numerical instabilities caused very slow SCF convergence. Experience [18] suggested that the problem might be rooted in the $\nabla^2 n$ dependence. By deorbitalizing $r^2$SCAN into $r^2$SCAN-L, we show here that much of the problem actually was inherited from SCAN.

**Procedure and Results**

The deorbitalization of $r^2$SCAN used precisely the same deorbitalized $\tau_n$ form and parametrization as was used for SCAN-L in Refs. [15, 16]. Molecular calculations were done with a locally modified developers’ version of the NWChem code [19]. Similarly, the periodic solid calculations were done with a locally modified version of VASP 5.4.4 [20, 21]. Note the remarks about coding in the VASP meta-GGA trunk in Ref. [16]. As in that reference, we did calculations with coding implemented in that trunk (to check unambiguously against the VASP results of Ref. [8]) and coding in the GGA trunk (to ascertain optimal speed-up from the deorbitalization). Basis sets, cutoffs, and other matters of technique were as documented in [15, 16] with one exception, the PAWs, documented below.

Table I summarizes the results for the molecular test sets in the form of mean absolute errors (MAEs) with respect to experimental heats of formation (G3/99X set [22]), bond lengths (T96-R set [23]), and harmonic vibrational frequencies (T82-F set [22]) obtained with the NWChem huge grid. For lower-density grids, Table I shows the mean absolute deviation (MAD) and maximum absolute deviation (MAX) with respect to the huge grid results.

Table II confirms the necessity of very dense numerical integration grids for both SCAN and SCAN-L. Even the xFine preset grid yields deviations above 1 kcal/mol and 30 cm$^{-1}$ (bond lengths are less problematic). In contrast, $r^2$SCAN and $r^2$SCAN-L results are well-converged with the medium and fine grid presets. This is a major improvement both in reliability as well as in performance, since numerical integration easily can become a computational bottleneck. See below regarding calculation of $\nabla^2 n$ on the integration grid in the context of a Gaussian-type orbital (GTO) basis.

It is important to note the disentanglement of instabilities due to the functional form versus the Laplacian-dependence. It now is clear that SCAN-L exhibits roughly the same stability difficulties as SCAN because their common structure. However, the highly stable $r^2$SCAN-L shows thermochemical deviations about three times larger than those for $r^2$SCAN on a given preset grid. This residual grid sensitivity seems directly attributable to the Laplacian-dependence of $r^2$SCAN-L.

Different from the setup described in [16], the periodic solid calculations in VASP used the “no-suffix” PAW datasets instead of the GW ones. (Discussion of this choice is below.) Since the PAW datasets used here are softer than the GW sets, we lowered the kinetic energy cutoff to 600 eV. The k-point sampling density was increased to match that reported in [8] by using the KSPACING=0.1 keyword.

Table III shows MAEs with respect to experimental results for three crystalline test sets [16]: 55 equilibrium lattice constants (with cubic or hexagonal symmetry), 40 bulk moduli (cubic symmetry), and 55 cohesive energies. Zero-point effects were removed from experimental lattice parameters and bulk moduli. Similar to the molecular case, Table III shows that deorbitalization of $r^2$SCAN is achieved with the same success as with SCAN. (Note that the values in that table are not directly comparable with our previous reports [5, 16] because of the PAW dataset change.) In both cases, lattice parameters are well-treated. Predictions of bulk moduli and cohesive energies with both deorbitalized functionals show large percentage deviations, but the deviation magnitudes are nonetheless quite small (large percentage error in a small quantity). Some physics also is involved. Part of the cohesive energy MAE difference between $r^2$SCAN-L and $r^2$SCAN comes from the different electronic configurations found for the W atom. $r^2$SCAN-L, SCAN, and SCAN-L all find an 6s5d5 valence when the configuration is unconstrained, while $r^2$SCAN finds the correct 6s5d4 configuration.

The total time needed to converge the 660 single-point calculations (12 per each solid) was used as a surrogate measure of the speed and stability of each functional. Consistent with expectations, the total times relative to the SCAN benchmark were 0.924 for $r^2$SCAN, 0.438 for SCAN-L, and 0.272 for PBE [24]. In other words, $r^2$SCAN-L computational cost in a plane-wave basis is almost as inexpensive as a standard GGA functional, even though numerical demands associated with the Laplacian-dependence remain.

There is an important caveat. The SCF stability of all the approximate functionals, as measured by the number of iterations needed for convergence, can be degraded by use of the GW PAW datasets. The Laplacian-dependent functionals are significantly worse in this regard than the orbital-dependent ones. What one sees with some, but not all, of the GW datasets is erratic SCF convergence. In those cases, near-SCF-convergence from iteration steps $N - 1$ to $N$ often is followed by drastic worsening at step $N + 1$. Exploration of the origins of this behavior is outside the scope of the present work.

Despite the fact that SCAN-L inherits many properties from SCAN, SCAN-L avoids the over-magnetization of simple elemental solids such as bcc Fe [25]. We therefore tested $r^2$SCAN and $r^2$SCAN-L in bcc Fe at the experimental lattice constant (2.86 Å). As with SCAN and rSCAN, $r^2$SCAN predicts the magnetic moment of bcc Fe to be 2.63 $\mu_B$/atom. $r^2$SCAN-L lowers that to 2.27 $\mu_B$/atom, in line with other GGA functionals and SCAN-
TABLE I. Performance of SCAN, \( r^2 \text{SCAN} \), and \( r^2 \text{SCAN-L} \) for heats of formation (kcal/mol), bond lengths (Å), and vibrational frequencies (cm\(^{-1}\)) at various grid densities. Mean absolute errors with respect to experiment from the NWChem \textsc{huge} grid calculations are in \textbf{boldface}. For the lower-density grids, mean absolute deviation and maximum absolute deviation (in parenthesis), with respect to those \textsc{huge} results are shown.

|                     | SCAN     | SCAN-L   | \( r^2 \text{SCAN} \) | \( r^2 \text{SCAN-L} \) |
|---------------------|----------|----------|------------------------|------------------------|
| Heats of formation  | 4.93     | 5.66     | 4.49                   | 5.30                   |
| coarse              | 5.92 (26.61) | 5.12 (22.02) | 0.40 (1.80) | 0.81 (5.90) |
| medium              | 2.31 (15.56) | 2.36 (14.63) | 0.09 (0.54) | 0.22 (1.19) |
| fine                | 0.73 (4.25) | 0.88 (4.59) | 0.01 (0.09) | 0.04 (0.22) |
| xfine               | 0.23 (1.42) | 0.36 (1.90) | 0.00 (0.02) | 0.01 (0.07) |
| Bond lengths        | 0.009     | 0.011     | 0.010                  | 0.011                  |
| coarse              | 0.001 (0.016) | 0.001 (0.014) | 0.000 (0.003) | 0.001 (0.006) |
| medium              | 0.001 (0.006) | 0.001 (0.006) | 0.000 (0.002) | 0.000 (0.001) |
| fine                | 0.000 (0.004) | 0.000 (0.004) | 0.000 (0.000) | 0.000 (0.001) |
| xfine               | 0.000 (0.004) | 0.000 (0.003) | 0.000 (0.000) | 0.000 (0.001) |
| Vib. frequencies    | 31.1      | 28.8      | 30.9                   | 25.6                   |
| coarse              | 24.2 (150.5) | 24.1 (183.0) | 7.5 (71.2) | 7.0 (55.9) |
| medium              | 18.4 (330.2) | 21.7 (156.4) | 2.1 (21.1) | 2.1 (22.0) |
| fine                | 10.5 (100.0) | 14.8 (130.5) | 1.3 (11.6) | 1.4 (12.9) |
| xfine               | 3.6 (32.1) | 5.1 (39.9) | 0.5 (3.9) | 0.6 (4.2) |

TABLE II. Mean absolute error comparison for SCAN, SCAN-L, \( r^2 \text{SCAN} \), and \( r^2 \text{SCAN-L} \) XC functionals for the solid state test sets.

|                     | SCAN     | SCAN-L   | \( r^2 \text{SCAN} \) | \( r^2 \text{SCAN-L} \) |
|---------------------|----------|----------|------------------------|------------------------|
| Lattice parameters  | 0.034     | 0.038     | 0.037                   | 0.039                   |
| Bulk moduli [GPa]   | 7.4       | 8.8       | 6.0                     | 8.9                     |
| Cohesive energies [eV/atom] | 0.21 | 0.21     | 0.20                   | 0.33                   |

Summary - The slow (sometimes extremely so) SCF convergence and numerical sensitivities of SCAN-L originate mostly in structural characteristics of SCAN. The removal of those provided by \( r^2 \text{SCAN} \) leads to a similarly well-behaved deorbitalized version, \( r^2 \text{SCAN-L} \). Except for the elemental 3d solid magnetization discrepancy, \( r^2 \text{SCAN-L} \) replicates the behavior of \( r^2 \text{SCAN} \) on major molecular and solid benchmarks. \( r^2 \text{SCAN-L} \) additionally provides a pure KS treatment (hence enables band-gap and optical excitation comparison with gKS results from \( r^2 \text{SCAN} \)), and should, in most cases support significantly faster solid calculations than \( r^2 \text{SCAN} \), on the time scale of an ordinary GGA. Further speedup of molecular calculations from \( r^2 \text{SCAN-L} \) in a GTO basis will require addressing the remaining computational bottleneck, calculation of \( \nabla^2 n \) from GTO second-derivatives on the integration grid (rather than directly as in a plane-wave code.) Nonetheless calculations with \( r^2 \text{SCAN-L} \) with the \textsc{medium} NWChem grid are as fast as those with SCAN with the \textsc{xfine} grid.

This work was supported by U.S. Dept. of Energy Energy Frontier Research Center grant DE-SC 0019330.

SUPPLEMENTAL MATERIAL

Detailed molecular test set results obtained with \( r^2 \text{SCAN} \) and \( r^2 \text{SCAN-L} \), as well as the detailed results for the periodic solid test sets for all functionals, can be found in the supplementary material [20].

[1] E. B. Isaacs and C. Wolverton, Phys. Rev. Mat. 2, 063801 (2018).
[2] J. Sun, A. Ruzsinszky, and J.P. Perdew, Phys. Rev. Lett. 115, 036402 (2015).
[3] J. Sun, R.C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M.L. Klein, and J.P. Perdew, Nature Chemistry 8, 831 (2016).
[4] A. P. Bartók and J. R. Yates, J. Chem. Phys. 150, 161101 (2019).
[5] D. Mejía-Rodríguez and S.B. Trickey, J. Chem. Phys. 151, 207101 (2019).
[6] H. Peng, Z.-H. Yang, J.P. Perdew and J. Sun, Phys. Rev. X 6, 041005 (2016).
[7] F. Tran, J. Stelzl and P. Blaha, J. Chem. Phys. 144, 204120 (2016).
[8] James W. Furness, Aaron D. Kaplan, Jinliang Ning, John P. Perdew, and Jianwei Sun, arXiv 2008.03374v1, 11 Aug. 2020.
[9] M. Städele, J.A. Majewski, P. Vogl and A. Görling, Phys. Rev. Lett. 79, 2089 (1997).
[10] T. Grabo, T. Kreibich and E.K.U. Gross, Molec. Eng. 7, 27 (1997).
[11] T. Grabo, T. Kreibach, S. Kurth, and E.K.U. Gross, in Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation, V.I. Anisimov ed. (Gordon and Breach, Tokyo, 2000) 203.
[12] A. Heßelmann and A. Görling, Chem. Phys. Lett. 455, 110 (2008) and refs. therein.
[13] Z.H. Yang, H. Peng, J. Sun, and J.P. Perdew, Phys. Rev. B 93, 205205 (2016).
[14] J.P. Perdew, W. Yang, K. Burke, Z. Yang, E.K.U. Gross, M. Scheffler, G.E. Scuseria, T.M. Henderson, I.Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Görling, Proc. Nat. Acad. Sci. (USA) 114, 2801 (2017).
[15] D. Mejía-Rodríguez and S.B. Trickey, Phys. Rev. A 96, 052512 (2017).
[16] D. Mejía-Rodríguez and S.B. Trickey, Phys. Rev. B 98, 115161 (2018).
[17] F. Tran, P. Kovacs, L. Kalantari, G.K.H. Madsen, and P. Blaha, J. Chem. Phys. 149, 144105 (2018).
[18] “Laplacian-based generalized gradient approximations for the exchange energy”, Antonio C. Cancio and Chris E. Wagner, arXiv 1308.3744.
[19] E. Aprà, E.J. Bylaska, W.A. de Jong, N. Govind, K. Kowalski, T.P. Straatsma, M. Valiev, H.I.J. van Dam, Y. Alexeev, J. Anchell, V. Anisimov, F.W. Aquino, R. Atta-Fynn, J. Autschbach, N.P. Bauman, J.C. Becca, D.E. Bernholdt, K. Bhaskaran-Nair, S. Bogatko, P. Borowski, J. Boschen, J. Brabec, A. Bruner, E. Cauët, Y. Chen, G.N. Chuev, C.J. Cramer, J. Daily, M.J.O. Deegan, T.H. Dunning Jr., M. Dupuis, K. G. Dyall, G.I. Fann, S.A. Fischer, A. Fonari, H. Frúchtl, L. Gagliardi, J. Garza, N. Gauwande, S. Ghosh, K. Glaesemann, A. W. Götz, J. Hammond, V. Helms, E.D. Hernes, K. Hirao, S. Hirata, M. Jacquelin, L. Jensen, B.G. Johnson, H. Jönsson, R.A. Kendall, M. Klemm, R. Kobayashi, V. Konkov, S. Krishnamoorthy, M. Krishnan, Z. Lin, R.D. Lins, R.J. Littlefield, A.J. Logsdail, K. Lopata, W. Ma, A.V. Marenich, J. Martín del Campo, D. Mejía Rodríguez, J.E. Moore, J.M. Mullin, T. Nakajima, D.R. Nascimento, J.A. Nichols, P.J. Nichols, J. Nieplocha, A. Otero-de-la-Roza, B. Palmer, A. Panyala, T. Pirojsirikul, B. Peng, R. Peverati, J. Pittner, L. Pollack, R.M. Richard, P. Sadayappan, G.C. Schatz, W.A. Shelton, D.W. Silverstein, D.M.A. Smith, T.A. Soares, D. Song, M. Swart, H.L. Taylor, G. S. Thomas, V. Tipparaju, D.G. Truhlar, K. Tsemekhman, T. Van Voorhis, Á. Vázquez-Mayagoitia, P. Verma, O. Villa, A. Vishnu, K.D. Vogiatzis, D. Wang, J.H. Weare, M.J. Williamson, T.L. Windus, K. Wolinski, A.T. Wong, Q. Wu, C. Yang, Q. Yu, M. Zacharias, Z. Zhang, Y. Zhao, and R.J. Harrison, J. Chem. Phys. 152, 184102 (2020).
[20] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[21] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[22] L.A. Curtiss, K. Raghavachari, P.C. Redfern, and J.A. Pople, J. Chem. Phys. 106, 1063 (1997); L.A. Curtiss, P.C. Redfern, K. Raghavachari, and J.A. Pople, J. Chem. Phys. 114, 108 (2001).
[23] V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P Perdew, J. Chem. Phys. 119 12129 (2003); V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P Perdew, J. Chem. Phys. 121 11507 (2004).
[24] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996); erratum ibid. 78, 1396 (1997).
[25] D. Mejía-Rodríguez, and S.B. Trickey, Phys. Rev. B 100, 041113(R) (2019).
[26] Citation to Supplemental Material here.