Performance comparison of math xmlns="http://www.w3.org/1998/Math/MathML">msup>mrow>mi>r/mi>/mrow>mn>2/mn>/msup>mi>SCAN/mi>/math> and SCAN metaGGA density functionals for solid materials via an automated, high-throughput computational workflow

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Performance comparison of r²SCAN and SCAN metaGGA density functionals for solid materials via an automated, high-throughput computational workflow

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Computational materials discovery efforts utilize hundreds or thousands of density functional theory (DFT) calculations to predict material properties. Historically, such efforts have performed calculations at the generalized gradient approximation (GGA) level of theory due to its efficient compromise between accuracy and computational reliability. However, high-throughput calculations at the higher metaGGA level of theory are becoming feasible. The Strongly Constrained and Appropriately Normed (SCAN) metaGGA functional offers superior accuracy to GGA across much of chemical space, making it appealing as a general-purpose metaGGA functional, but it suffers from numerical instabilities that impede it's use in high-throughput workflows. The recently-developed r²SCAN metaGGA functional promises accuracy similar to SCAN in addition to more robust numerical performance. However, its performance compared to SCAN has yet to be evaluated over a large group of solid materials. In this work, we compared r²SCAN and SCAN predictions for key properties of approximately 6,000 solid materials using a newly-developed high-throughput computational workflow. We find that r²SCAN predicts formation energies more accurately than SCAN and PBEsol for both strongly- and weakly-bound materials and that r²SCAN predicts systematically larger lattice constants than SCAN. We also find that r²SCAN requires modestly fewer computational resources than SCAN and offers significantly more reliable convergence. Thus, our large-scale benchmark confirms that r²SCAN has delivered on its promises of numerical efficiency and accuracy, making it a preferred choice for high-throughput metaGGA calculations.

I. INTRODUCTION

Density functional theory (DFT) has emerged as the most widely-used computational method for predicting material properties in recent decades [1]. Hundreds of thousands of DFT calculations now populate materials databases such as the Materials Project [2], NOMAD [3], or OQMD [4, 5], laying the foundation for a new era of data-driven materials discovery [6].

The vast majority of these calculations employ the Perdew-Burke-Ernzerhof (PBE) [7] generalized gradient approximation (GGA) [8] functional, due to its popularity among researchers and its efficient compromise between high accuracy and high performance across a wide variety of chemistries and properties. However, as a semi-local GGA functional, PBE and its variants such as PBEsol [9] have well-documented and systematic errors related to electron self-interaction [1, 10] and fail to capture medium- and long-range dispersion [1, 11]. These errors compromise their predictive accuracy for many properties of interest. Specifically, PBE systematically under-predicts the magnitude of formation energies (i.e., under-binds) [12], slightly over-predicts lattice

parameters [12, 13], and severely under-predicts semiconductor bandgaps [12, 14, 15]. In principle, higher levels of theory such as metaGGA DFT functionals can capture medium-range dispersion interactions and should exhibit smaller self-interaction errors than GGA functionals such as PBE [10]. However, metaGGA functionals have historically been either too specific to selected properties or chemistries and/or too computationally demanding to be feasible for high-throughput calculations across the entire periodic table.

The challenge of generality was addressed by Sun and co-workers via development of the Strongly Constrained and Appropriately Normed (SCAN) [16] functional. This non-empirical metaGGA functional has been shown to be substantially more accurate than PBE for predicting lattice constants and ground-state structures of solids [13, 17–20], and modestly more accurate for semiconductor bandgaps [12, 15, 21]. SCAN predicts formation energies more accurately than PBE for strongly-bound compounds, but less accurately than PBE for weakly-bound compounds (e.g., intermetallics) [12]. Researchers have also noted that SCAN underpredicts some lattice parameters compared to experiment [12, 21] and identified shortcomings in SCAN's predictions of the magnetic moments of ferromagnetic systems [12, 21–25], the ground-state polymorphs of selected binary com-

pounds [13], and the bulk moduli of crystalline solids and water ice [21, 26]. Nevertheless, the generally superior accuracy of SCAN compared to PBE across many chemical systems and properties makes it appealing as a general-purpose functional for solids. However, it has a higher computational cost than PBE (by a factor of about 5 [12, 27]), and suffers from numerical instability. This numerical instability in particular makes it impractical to reliably and efficiently perform automated, high-throughput calculations with SCAN.

To mitigate the computational challenge, Furness and co-workers recently introduced r²SCAN [28], a modification of the original SCAN functional with substantially improved numerical stability, allowing calculations to converge much more reliably than in the original SCAN functional. This improved stability is achieved by utilizing a smoother switching function to interpolate between the slowly-varying and single-orbital density limits, and by relaxing one of the 17 theoretical constraints satisfied by the original SCAN functional (specifically, the fourth order gradient expansion constraint for exchange GE4X [28, 29]). These changes result in a smoother potential energy surface free of discontinuities. Compared to previous efforts to mitigate numerical difficulties in SCAN [27, 30], r²SCAN satisfies a greater number of theoretical constraints and was shown to largely preserve the accuracy of SCAN when benchmarked against several hundred molecular properties and 20 solid lattice constants [28]. Hence, it would appear that the arrival of r²SCAN has at last created a general-purpose, numerically-robust metaGGA functional. However, its accuracy compared to SCAN has yet to be demonstrated for a large group of solid materials.

To further promote progress towards high-throughput metaGGA DFT calculations for solids, in this work we compare the formation energies, cell volumes, and electronic structures of approximately 6,000 solid materials calculated in r²SCAN and SCAN by means of an automated, high-throughput workflow. We show that r²SCAN achieves comparable or even improved accuracy compared to SCAN and reaches convergence much more reliably for this large and diverse set of calculations.

II. METHODOLOGY

A. Automated workflow for metaGGA calculations

DFT calculations were carried out using a two-step workflow comprising an initial GGA structure optimization followed by a structure optimization with the SCAN [16] or r²SCAN [28] metaGGA functionals, coupled with automatic error correction logic (see Figure 1). The purpose of the initial GGA structure optimization was to generate an initial guess of the structure and charge density at lower computational cost, thereby speeding up the subsequent metaGGA calculation. Performing two optimizations in series also makes the calcu-

lation more robust to changes in the size or shape of the unit cell, as elaborated further in Section S1 [31]. SCAN calculations used PBE [7] for the initial GGA optimization, while r²SCAN calculations employed the PBEsol [9] functional, which is a variant of PBE tuned to predict solid lattice constants with greater accuracy. Since the purpose of the initial GGA calculation is simply to accelerate the metaGGA optimization, the final metaGGA result should not be particularly sensitive to the choice of GGA functional.

We employed the Vienna ab initio Simulation Package (VASP) [32, 33], version 6.1.1 with custom patches for r²SCAN, in conjunction with projector-augmented wave (PAW) pseudopotentials [34] and a plane-wave energy cutoff of 680 eV. Note that r²SCAN is officially available in VASP as of version 6.2. k-point grids were generated automatically by VASP using KSPACING values ranging from 0.22 to 0.44 Å^{-1}, which were determined from the GGA-estimated bandgap of each material based on the work of Wisesa et al. [35]. Plane-wave energy cutoff and k-point density settings were selected such that formation energies converged within approximately 1 meV/atom for a benchmark set of 21 materials (listed in Section S1 [31]) and were selected to be conservatively high. All calculations used pseudopotentials from the "PBE PAW datasets version 54" set released in September 2015; a list of the specific POTCAR symbols used for each element is provided in Section S9 [31, 36]. Although these pseudopotentials were developed for use with the PBE functional, their use with SCAN is common practice because no SCAN-specific pseudopotentials are available for use in VASP. Additional details related to development of our computational workflow are provided in the Supplemental Material [31, 37–39].

B. Selection of materials

The dataset we analyze below includes 6,307 distinct materials, comprising 412 elements, 5,297 binary materials, and 598 ternary materials whose elemental compositions cover the majority of the periodic table (see Figure S24). We first screened the Materials Project Database [38] for materials that were within 20 meV of the convex energy hull and had 20 or fewer sites, resulting in a set of approximately 45,000 materials. We retrieved PBE-relaxed structures for each of these from the Materials Project REST API [38], which we used as starting structures in our computational workflow. From this set, we prioritized elements, ground states, and materials close to the convex energy hull and performed metaGGA calculations for as many materials as possible within the computational resources available to our project. We were able to complete approximately 8,000 and 25,000 materials using SCAN and r²SCAN, respectively. We observed considerably more reliable convergence with r²SCAN than with SCAN (as discussed further below), which allowed us to complete calculations
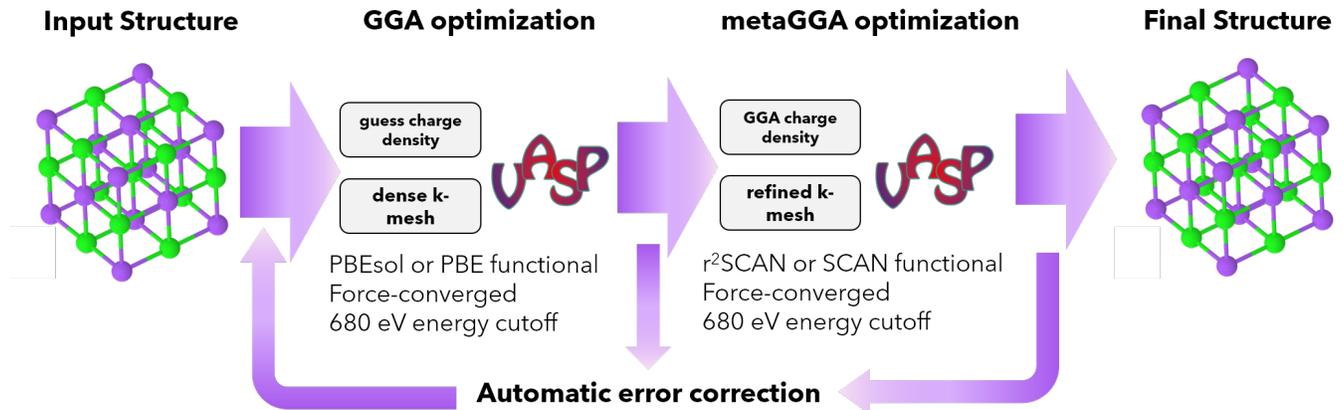
FIG. 1. Automated workflow for metaGGA calculations. The input structure is used to construct an initial guess of the charge density for the GGA optimization using a GGA functional. A high k-point density is used in this step. The output charge density from the GGA optimization is used as the initial guess in the subsequent metaGGA optimization using either r^{2}SCAN or SCAN. The bandgap estimated from the GGA calculation is used to refine the k-point density for the metaGGA optimization, where metals have the highest k-point density and semiconductors or nonmetals have lower k-point density. Automated error correction routines adjust settings and restart calculations that fail for well-defined reasons, improving reliability.

for more materials with this functional. Among these SCAN and r^{2}SCAN calculations, there are 6,307 materials (including 5,895 non-elemental solids) for which both SCAN and r^{2}SCAN calculations were completed. 5,466 of these materials correspond to structures reported in the Inorganic Crystal Structure Database (ICSD) [40], indicating that they represent experimentally-confirmed structures. We use this set of materials to compare the properties predicted by the two functionals. We note that the ≈ 1,700 materials for which we completed SCAN but not r^{2}SCAN calculations do not indicate cases where r^{2}SCAN failed to converge. Rather, after completing our SCAN calculations we chose to prioritize calculations slightly differently for r^{2}SCAN, and hence some materials originally completed in SCAN were not attempted in r^{2}SCAN.

III. RESULTS AND DISCUSSION

A. Relative comparison of r^{2}SCAN vs SCAN

1. Formation Energy

Computed formation energies predicted by r^{2}SCAN and SCAN are summarized in Figure 2a. In an extensive benchmark of the original SCAN functional, Isaacs and Wolverton [12] observed that SCAN formation energies were somewhat more accurate for strongly-bound compared to weakly-bound materials, where 'strongly-bound' materials are those with formation energies ≤ -1 eV/atom and 'weakly-bound' materials are those with formation energies between 0 and -1 eV/atom. We adopt the same categories here to facilitate comparison with this prior work. By this definition, our data con-

tains 1,428 and 4,317 strongly- and weakly-bound materials, respectively. We exclude any materials containing U, Np, or Pu (150 materials), because many exhibited exceptionally large differences in formation energy between the two functionals. For these cases, we found that r^{2}SCAN-predicted formation energies were substantially more accurate than SCAN-predicted energies compared to experiment. However, since these calculations were performed without spin-orbit coupling, the results must be interpreted with caution and we do not consider them in detail here. Further discussion is provided in Section S4 [31, 41].

Overall, r^{2}SCAN and SCAN predicted similar formation energies for most materials within both the strongly- and weakly-bound categories, as indicated by the fact that the median difference in formation energy was only -5 meV/atom. Nevertheless, there were substantial differences for many materials. For 95% of strongly-bound materials, $\Delta H_f^{\text{r}^2\text{SCAN}}$ differed from ΔH_f^{SCAN} by ≈ -135 to $+170$ meV/atom, while for weakly-bound materials, the 95th-percentile difference in formation energy was ≈ -105 to $+115$ meV/atom. Although the absolute differences in formation energy were similar for strongly- and weakly-bound materials, in *relative* terms they are much more significant for weakly-bound materials, since the magnitude of ΔH_f for weakly-bound materials is smaller by definition. Reassuringly, we find that in spite of these apparently large relative differences in predicted ΔH_f for weakly-bound materials, r^{2}SCAN has a lower average error compared to experiment by every measure(see Section III B 1).

In Section S7 [31] we analyze how differences in r^{2}SCAN and SCAN formation energies relate to specific chemistries. Among strongly- and weakly-bound materials, the largest positive differences (i.e., materials for
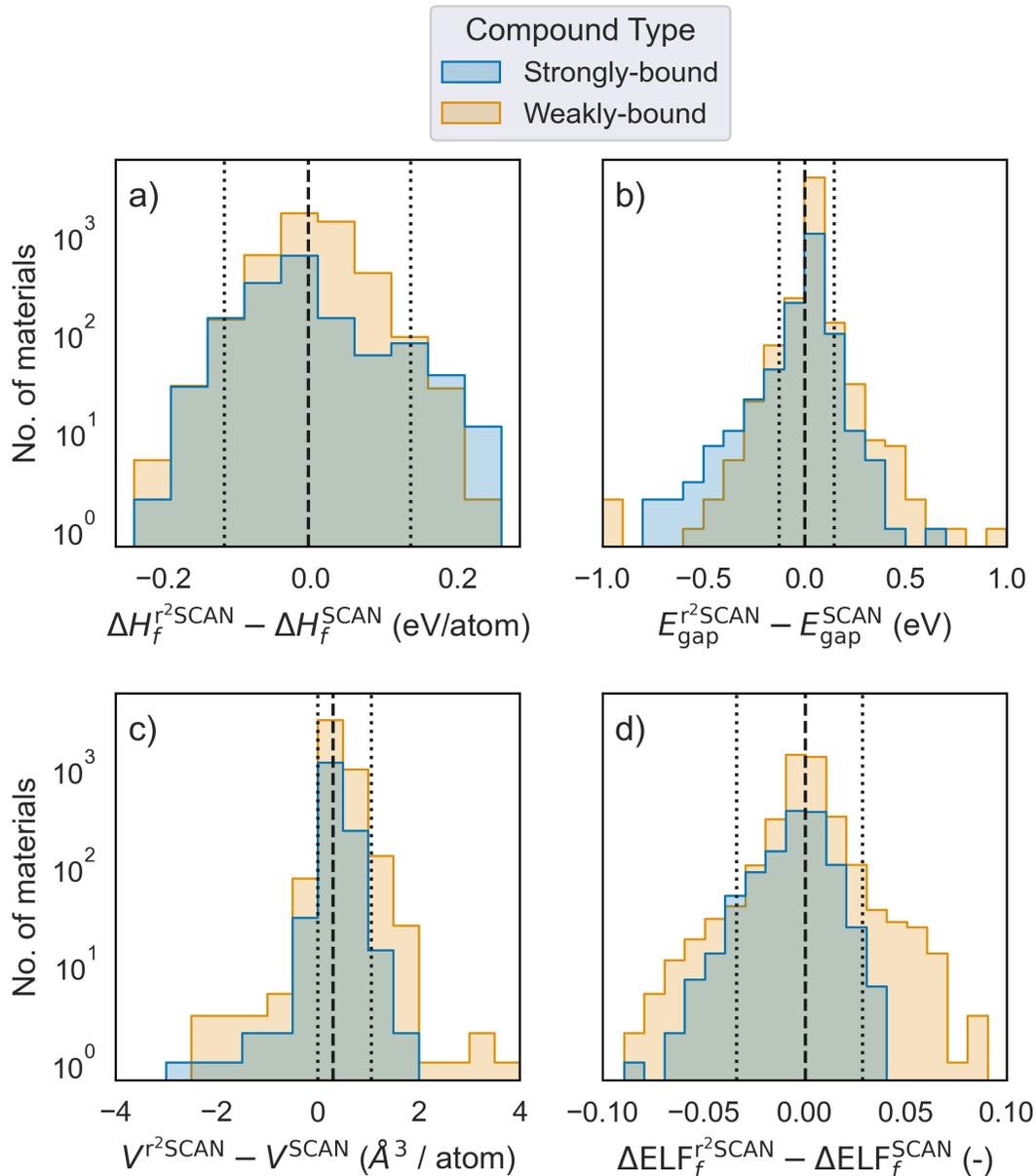
FIG. 2. Changes in a) formation energy, b) bandgap, c) cell volume, and d) formation electron localization function ($\Delta\mathrm{ELF}_f$; see Section S5 [31]) when computed in r²SCAN vs SCAN. Note that the y axis is logarithmic. Dashed and dotted vertical lines represent the median differences and two-sided 95th percentile differences, respectively, across both material categories.

which $\Delta H_f^{\mathrm{r^2SCAN}}$ was less negative than $\Delta H_f^{\mathrm{SCAN}}$) were materials containing Pt or Au, while Co, Ni, Rh, and Pd-containing materials also tended to have less negative $\Delta H_f^{\mathrm{r^2SCAN}}$. On the other hand, the largest negative differences in formation energy were observed for Cs, Pa, Br and Bi-containing materials. It is unclear why the largest differences in formation energy are associated with materials containing these particular elements. The major difference in construction between r²SCAN and SCAN (the change in switching function and in the formulation of the gradient expansion for exchange) have the greatest effect in regions of slowly-varying electron density which

would be encountered in metallic compounds [42]. Since the compounds with large positive differences tend to contain (transition) metals, it is possible these elements happen to be particularly sensitive to the different formulation of exchange. For the negative differences, a possible explanation may be that intermediate van der Waals interactions in the elemental Cs, Pa, Br and Bi phases are less captured by r²SCAN than SCAN [42]. In general, however, differences in elemental energies do not explain our observations. For pure elements, the difference in electronic energy between r²SCAN and SCAN grows systematically larger with the atomic number (Fig-

ure S28), hence one might expect materials containing heavier elements to exhibit the largest differences in formation energy. This is not what we observed: formation energies of materials show no such systematic trend (Figure S29 and S30). Since the formation energy of a material is calculated by subtracting the energies of elemental references from that of the material, it would appear that the sometimes substantial differences in formation energy predicted by r^{2}SCAN and SCAN are attributable to different energies of the materials rather than the elemental references.

2. Bandgaps

GGA DFT functionals are known to systematically and significantly underestimate bandgaps, and this shortcoming is only slightly mitigated by SCAN [12]. Nevertheless, it is instructive to examine whether r^{2}SCAN-predicted bandgaps differ substantially from those predicted by SCAN (Figure 2b). For strongly and weakly bound materials, r^{2}SCAN bandgaps were within ± 0.15 eV of SCAN-predicted bandgaps for 95% of materials studied. r^{2}SCAN was slightly more likely to predict a smaller bandgap than SCAN for strongly-bound materials and a larger bandgap than SCAN for weakly-bound materials.

Qualitative agreement between the r^{2}SCAN and SCAN predicted metallic character of materials is arguably more relevant than the quantitative bandgap predictions. Out of 5,895 materials for which we computed bandgaps, there were 73 cases ($\approx 1\%$, listed in Table S4) in which r^{2}SCAN predicted metallic character (zero bandgap) when SCAN predicted non-metallic character or vice versa. In six of these cases, the predictions differed by $\gtrsim 1$ eV. Manual inspection of the density of states (DOS; see Section S2 [31, 43]) for the materials with the largest discrepancies indicates that they represent edge cases in which the band occupancies are particularly sensitive to the exchange energy. For example, the material Sb$_2$F$_{13}$, was a notable outlier where r^{2}SCAN predicted a metallic material rather than the large-gap insulator predicted by SCAN, due to a small amount of ferromagnetism in the r^{2}SCAN case shifting the Fermi level into the valence band. Thus, the subtle differences in construction between r^{2}SCAN and SCAN can occasionally result in large differences in predicted bandgaps. However, this example represents a fictitious, unphysical material, since the originating crystal structure file was found to have omitted hydrogens when compared against the original publication. We emphasize, that we observed these large discrepancies in only $\approx 0.1\%$ of materials in our dataset, and that they may be partially attributable to recently-identified changes in the way VASP computes the Fermi level.

3. Lattice Volumes

r^{2}SCAN systematically predicted larger lattice volumes for many materials than SCAN, and this systematic difference was observed to a similar extent across both material categories (Figure 2c). Specifically, the median volumes per atom predicted by r^{2}SCAN were 1.4% and 1.8%, (0.2 - 0.3 Å^3/atom) larger than the SCAN predicted volumes for strongly-bound and weakly-bound materials, respectively. The systematically larger lattice volumes predicted by r^{2}SCAN compared to SCAN may be fortuitous, since SCAN was previously shown to under-predict experimental lattice volumes by an average of 0.11 Å^3/atom [12]. We will examine the accuracy of SCAN and r^{2}SCAN lattice volumes compared to experiment in a later section.

4. Electron Localization

To evaluate the consistency between r^{2}SCAN and SCAN in a more general way, we next present differences in the electronic structure predicted by the two functionals. Both r^{2}SCAN and SCAN incorporate information about the kinetic energy density into their calculation of the exchange and correlation energies by means of the iso-orbital indicator $\alpha = \frac{\tau - \tau_{\mathrm{W}}}{\tau_{\mathrm{unif}}}$ or $\bar{\alpha} = \frac{\tau - \tau_{\mathrm{W}}}{\tau_{\mathrm{unif}} + \eta \tau_{\mathrm{W}}}$ for SCAN and r^{2}SCAN, respectively, where τ is the positive kinetic energy density, τ_{W} and τ_{unif} are the limiting kinetic energies of a single orbital and uniform electron gas, respectively and $\eta=0.001$ is a regularization parameter [10, 28]. The calculated value of the exchange and correlation energies depends on the value of the iso-orbital indicator, and hence on the bonding regime (e.g. localized/covalent or delocalized/metallic). This ability to adjust for different local electronic environments is a major reason for the superior accuracy of r^{2}SCAN and SCAN compared to GGA [12], and also explains why SCAN requires much smaller Hubbard U values than GGA functionals to accurately predict formation energies of transition metal oxides [44].

r^{2}SCAN differs from SCAN primarily in that 1) it uses $\bar{\alpha}$ instead of α as the iso-orbital indicator (see definitions above) and 2) it uses a different 'switching function' to adjust the value of the exchange-correlation enhancement factor, F_{xc}, for different values of $\bar{\alpha}$ [28]. The iso-orbital indicator is closely related to the electron localization function (ELF), which is equal to $(1 + \alpha^2)^{-1}$ [16, 28] and ranges from 0 to 1, where a value of 0.5 corresponds to an electron gas and 1 corresponds to highly localized (covalent) bonding [45]. Since both α and $\bar{\alpha}$ and hence the value of F_{xc} are directly related to ELF, in Figure 2d we present the difference in 'formation ELF', $\Delta\mathrm{ELF}_f$, predicted by r^{2}SCAN and SCAN. $\Delta\mathrm{ELF}_f$ is calculated by analogy to the formation energy (see 3), and represents the degree to which the average amount of electron localization around each atom in a material differs from that in the corresponding elemental references. By con-

struction, the formation ELF must fall between 0 and 1. However, because high electron localization occurs only in a relatively small fraction of the volume occupied by a crystal (e.g., near the nuclei or along a covalent bond), average values for an entire atomic basin are typically small. An example illustrating the local value of ELF in a crystal structure is provided in Section S5 [31, 46–48]. In our dataset, the median values of $\Delta\mathrm{ELF}_f$ were 0.034 and 0.036 (dimensionless) for r^{2}SCAN and SCAN, respectively. These values are 10-20% larger than the median $\Delta\mathrm{ELF}_f$ calculated by PBEsol (0.030), indicating that the two metaGGA functionals predict larger changes in electronic structure during compound formation than GGA.

Figure 2d shows that broadly speaking, $\Delta\mathrm{ELF}_f$ values predicted by r^{2}SCAN and SCAN are similar for both categories of materials (as indicated by the differences being centered around 0). There is a slight skew towards r^{2}SCAN predicting smaller $\Delta\mathrm{ELF}_f$ (i.e., less change in localization between elements and compounds) than SCAN, with differences of -0.033 to $+0.028$ defining the 95th percentile of all materials. However in relative terms (i.e., $\left| \frac{\Delta\mathrm{ELF}_f^{\mathrm{r^2SCAN}} - \Delta\mathrm{ELF}_f^{\mathrm{SCAN}}}{\Delta\mathrm{ELF}_f^{\mathrm{SCAN}}} \right|$) these changes were quite large, with a median relative change of 16% and a 95th percentile relative change of 82%. Hence, while r^{2}SCAN and SCAN predict similar $\Delta\mathrm{ELF}_f$ in aggregate, subtle absolute differences in their respective prediction of ELF may result in large relative changes for specific materials.

By definition, the difference in DFT energy between the two functionals when evaluated on the same density (and Kohn-Sham orbitals) is equal to the difference in their exchange and correlation energy, which is a complex function of not only the ELF, but also the density, density gradient, and kinetic energy density [10, 28] which are themselves products of previous self-consistent iterations. Hence, it is difficult to relate changes in $\Delta\mathrm{ELF}_f$ directly to changes in DFT or formation energy. Figure 2a suggests that the large relative shifts in $\Delta\mathrm{ELF}_f$ that we observe between r^{2}SCAN and SCAN do not lead to commensurately large shifts in ΔH_f. For comparison, the median and 95th percentile relative changes in the electronic energy (i.e., the DFT energy) from SCAN to r^{2}SCAN were 26% and 32%, respectively, while the median and 95th percentile changes in ΔH_f were 6.5% and 54%. Nevertheless, Figure 2d shows that differences in $\Delta\mathrm{ELF}_f$ tended to be larger for weakly-bound materials compared to strongly-bound materials, and this fact could be related to the larger relative changes in formation energy that we observed for weakly-bound materials (see above).

B. Experimental benchmarks

1. Formation Energy

Having examined how material properties predicted by r^{2}SCAN differ from those of SCAN, we now turn our attention to how accurately r^{2}SCAN and SCAN predict experimental formation energies, volumes, and bandgaps. Predictions by the PBEsol GGA functional [9], executed with the same settings as the first step of the automated workflow (see Section II A) are shown as an additional point of comparison. We note that since experimental benchmarking was not the primary objective of this work, the materials we evaluate in this section are dictated primarily by the calculations we generated rather than through deliberate selection. Complementary efforts are underway by other research groups [42] to benchmark r^{2}SCAN against experimental data using carefully-curated sets of materials presented in previous studies [12, 17].

Figure 3a shows the mean absolute error (MAE) in formation energy for 986 materials. Experimental energies for these materials were obtained from the `expt_formation_enthalpy_kingsbury` dataset distributed with Matminer [49], which associates formation energies with specific crystal structures, allowing us to match our computed data with high confidence. Additional details about the dataset are provided in Section S8 [31, 40, 50–55].

For the majority of materials studied, the MAE in formation energy predicted by metaGGA functionals was $\approx$80-120 meV/atom. Strikingly, r^{2}SCAN formation energies had approximately 20% and 15% lower MAEs than SCAN for strongly- and weakly-bound materials, respectively, even though r^{2}SCAN is less theoretically exact (i.e., r^{2}SCAN relaxes the fourth order gradient expansion constraint for exchange that is satisfied by SCAN [28]). Although surprising from a theoretical standpoint, other recent studies have also reported greater accuracy of r^{2}SCAN compared to SCAN. For example, r^{2}SCAN was found to predict cohesive energies and bulk moduli of solids more accurately than SCAN [56].

We observed in Section III A that despite many materials having similar formation energies, there were a number of outlying materials for which $|\Delta H_f^{\mathrm{r^2SCAN}} - \Delta H_f^{\mathrm{SCAN}}| \geq$ 100-200 meV/atom or more. To evaluate the implications of such large differences, we examined the accuracy vs. experiment of all strongly- or weakly-bound materials for which $|\Delta H_f^{\mathrm{r^2SCAN}} - \Delta H_f^{\mathrm{SCAN}}| \geq 50$ meV/atom. There are 665 such materials in the entire dataset, of which we have experimental data for 345. Among this group of outliers, $\Delta H_f^{\mathrm{r^2SCAN}}$ is more accurate than $\Delta H_f^{\mathrm{SCAN}}$. Specifically, the mean error for r^{2}SCAN was -43.8 meV/atom, while the mean error for SCAN was -55.8 meV/atom, and the MAEs were 90.2 and 134.9 meV/atom for r^{2}SCAN and SCAN, respectively.

Comparing the metaGGA functionals to PBEsol, we
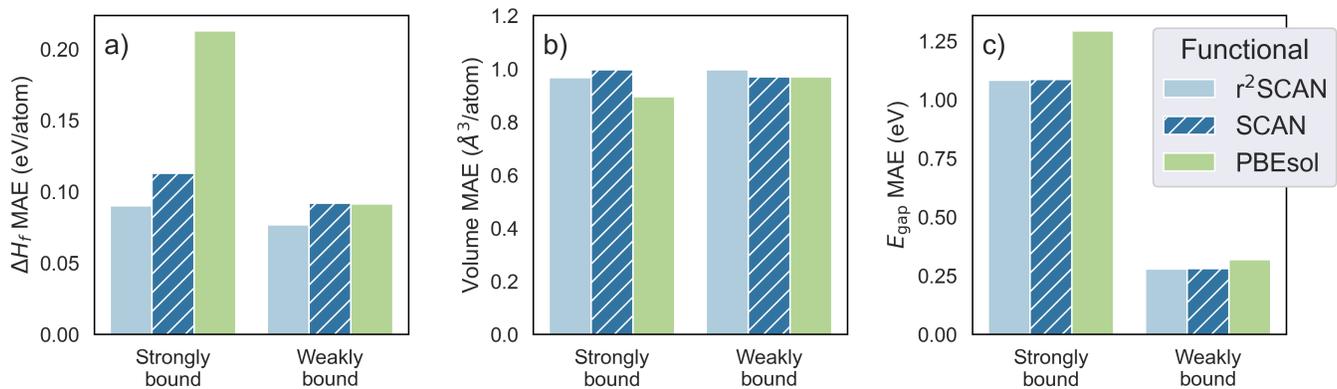
FIG. 3. Mean absolute error compared to experiment in a) formation energy (n=986 materials) b) cell volume (n=4,974 materials), and c) bandgap (n=582 materials) computed with r^{2}SCAN, SCAN, or PBEsol.

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note that for strongly-bound materials, both r^{2}SCAN and SCAN predicted formation energy much more accurately than PBEsol. This finding is similar to the previous observation by by Isaacs and Wolverton [12] that SCAN outperforms PBE for strongly-bound materials. For weakly-bound materials, however, SCAN was slightly less accurate than PBEsol (also consistent with previous findings [12]), whereas r^{2}SCAN was more accurate. Hence, r^{2}SCAN predicted formation energy more accurately than SCAN or PBEsol for all material categories. This is a fortuitous result: it appears that the regularization procedure used to create r^{2}SCAN not only enhances numerical stability but also improves accuracy in one of the few areas in which SCAN was less accurate than PBE. This suggests that the greater smoothness of the r^{2}SCAN potential energy surface is beneficial to accuracy as well as computational reliability, as elaborated by Furness et al. [29, 42].

2. Lattice Volume

Figure 3b summarizes the performance of the three functionals for predicting cell volume using experimental data obtained from the Inorganic Crystal Structure Database (ICSD) [40]. For strongly-bound materials, PBEsol has the lowest MAE of 0.89 Å^3/atom, followed by r^{2}SCAN (0.97 Å^3/atom) and SCAN (1.0 Å^3/atom). For weakly-bound materials, PBEsol and SCAN predict volume with a similar MAE of 0.97 Å^3/atom, while r^{2}SCAN has a slightly higher MAE of 1.0 Å^3/atom. Overall, neither metaGGA functional shows a clear and significant improvement in lattice volume prediction compared to PBEsol. Although surprising considering that SCAN lattice constants were shown to be more accurate than PBE (albeit underpredicted, whereas PBE lattice constants were overpredicted) [12], it is important to remember that PBEsol was developed specifically to reproduce solid lattice constants with high accuracy.

3. Bandgap

The errors in predicted bandgap are shown in Figure 3c for 582 materials that were present in both our dataset and the experimental `expt_gap_kingsbury` dataset in Matminer [49]. Compilation of the bandgap data is described in more detail in Section S8 [31].

For strongly-bound materials, the MAE in predicted bandgap was nearly identical between r^{2}SCAN and SCAN at 1.078 and 1.081 eV, respectively. The same was true for weakly-bound materials; although in this case the MAE was much lower at ≈0.28 eV. Although the MAEs for both metaGGA functionals were considerable, they were ≈0.21 eV and 0.04 eV lower than the PBEsol MAE for strongly- and weakly-bound materials, respectively.

C. Computational performance and reliability

Finally, we used the large amount of computed data we generated to develop a qualitative understanding of the relative computational demands and reliability of r^{2}SCAN and SCAN. In Figure 4a we present the relative performance of r^{2}SCAN, SCAN, and PBEsol in terms of 1) total CPU time, 2) total number of ionic steps and 3) total number of self consistent field (SCF) cycles (summed over all ionic steps) required to reach convergence. We note that this was not a rigorous computational benchmark, because the starting structures for the GGA and metaGGA stages of the workflow were not identical. As described in Section II A, each starting structure was optimized using equivalent VASP settings using both 1) PBE followed by SCAN and 2) PBEsol followed by r^{2}SCAN. All calculations were carried out on the Cori supercomputer at the National Energy Research Scientific Computing Center (Berkeley, CA); however the parallelization settings (i.e., number of nodes, cores, and multiprocessing tasks) varied slightly among
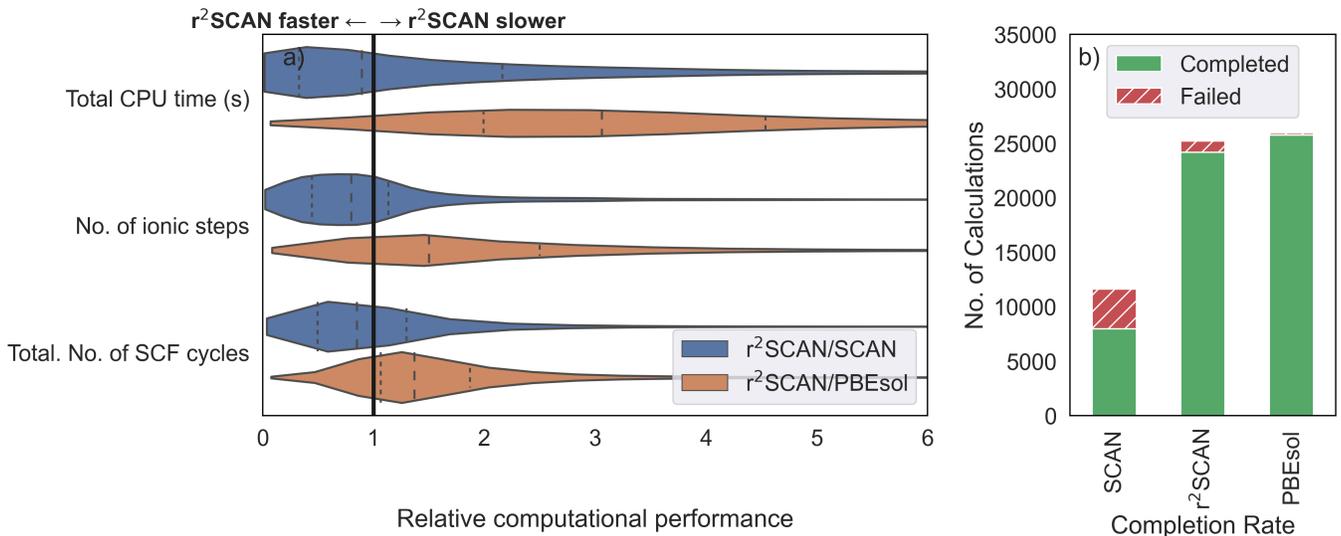
FIG. 4. a) Relative computational performance of r²SCAN compared to SCAN (blue) or PBEsol (orange), demonstrating that computational time required for r²SCAN is smaller than SCAN but larger than PBEsol. Each variable is plotted as the ratio of the value in the r²SCAN calculation divided by the value in the corresponding SCAN or PBEsol calculation. Dashed lines inside each violin represent the quartiles of the distribution. b) Completion rate of calculations carried out using each density functional.

calculations. As such, the information in Figure 4 should not be considered a definitive representation of the relative computational demands of these functionals, but rather a qualitative representation of their performance over a large and diverse set of materials.

As shown in the figure, r²SCAN required approximately 0.5-2x the CPU time to converge as SCAN, and 0.5-1x the number of ionic and electronic steps. Compared to PBEsol, r²SCAN required 2-4x the CPU time, 1-3x the number of ionic steps, and 1-2x the number of total SCF cycles. Our results here are largely consistent with a previous rigorous benchmark for CPU time based on single-point calculations, which showed that r²SCAN required approximately 0.9x of the CPU time as SCAN and approximately 4x as much as PBE. [57] Our finding that fewer ionic steps are required is consistent with a study by Ning and co-workers [58] which found r²SCAN to generate smoother potential energy surfaces (facilitating convergence) compared to SCAN. Thus, modestly fewer ionic steps and modestly less CPU time are required to converge r²SCAN than SCAN, but both functionals require considerably more computational resources than PBEsol.

Time required for convergence does not tell the whole story, however, because the data in Figure 4a reflect only *successful* calculations, and hence mask the much more reliable convergence of r²SCAN. Among approximately 11,000 and 25,000 total calculations we attempted with SCAN and r²SCAN, respectively, we observed a completion rate of 96% for r²SCAN, but only 69% for SCAN (Figure 4b). Among the incomplete SCAN calculations, we estimate that at least 25% failed due to unrecoverable errors, whereas the remaining calculations may have sim-

ply run out of wall time, which was limited to 48 hours in our work. Again, although these failure statistics do not represent a rigorous comparison of the two functionals (for example, the SCAN convergence rate may improve somewhat with very long wall time), they qualitatively highlight the generally much more reliable convergence of r²SCAN compared to SCAN, which was a key objective of its development [28]. Furthermore, it is noteworthy that for weakly-bound compounds, PBEsol predicted only modestly less accurate formation energies than r²SCAN, while consuming less than half the computational resources and offering extremely reliable convergence. Hence, PBEsol may still be considered an excellent choice for computing many properties of interest.

IV. SUMMARY AND OUTLOOK

In summary, we have compared r²SCAN and SCAN predictions for key properties of approximately 6,000 solid materials. We find that r²SCAN predicts substantially similar formation energies, bandgaps, and degrees of electron localization as the original SCAN functional, but predicts systematically larger lattice constants. r²SCAN is found to predict formation energies more accurately than SCAN and PBEsol for both strongly- and weakly-bound materials, while r²SCAN and SCAN calculated bandgaps are virtually identical and modestly more accurate than those predicted by PBEsol. For materials containing U, Np or Pu, r²SCAN predicts formation energies that are substantially different from and considerably more accurate than those predicted by SCAN. The reason for this is not clear, and

could arise from a fortuitous cancellation of errors related to the lack of spin-orbit-coupling in our calculations and/or as a consequence of the smoother potential energy surface generated by r^{2}SCAN. With respect to computational reliability, we find that r^{2}SCAN requires modestly fewer computational resources than SCAN, but offers much more reliable convergence. Thus, our large-scale benchmark confirms that r^{2}SCAN has delivered on its promises of numerical efficiency and accuracy [28], making it an ideal choice for high-throughput metaGGA calculations.

V. DATA AVAILABILITY

All data referenced herein are publicly available on Figshare [59] and will be integrated into the Materials Project database [38] in the near future. Our computational workflow has been implemented into the pymatgen [36], custodian [36], and atomate [60] packages as of versions 2020.12.3, 2021.1.8, and 0.9.6, respectively, for readers wishing to utilize it in their own work.

VI. ACKNOWLEDGEMENTS

VII. AUTHOR CONTRIBUTIONS

Ryan Kingsbury: Conceptualization, Software, Methodology, Data Curation, Formal Analysis, Writing - Original Draft, Writing - Review & Editing. Ayush Gupta: Formal Analysis, Writing - Review & Editing. Christopher Bartel: Conceptualization, Writing - Review & Editing. Jason Munro: Methodology, Writing - Review & Editing. Shyam Dwaraknath: Conceptualization, Methodology, Writing - Review & Editing, Supervision. Matthew Horton: Conceptualization, Methodology, Writing - Review & Editing, Supervision. Kristin Persson: Conceptualization, Writing - Review & Editing, Supervision, Funding Acquisition.

VIII. COMPETING INTEREST STATEMENT

The authors declare no competing financial interests.

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