Analysis of Over-magnetization of Elemental Transition Metal Solids from the SCAN Density Functional

Daniel Mejía-Rodríguez* and S.B. Trickey†
Quantum Theory Project, Department of Physics, University of Florida, Gainesville, FL 32611
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Recent investigations have found that the strongly constrained and appropriately normed (SCAN) meta-GGA exchange-correlation functional significantly over-magnetizes elemental Fe, Co, and Ni solids. For the paradigmatic case, bcc Fe, the error relative to experiment is \( \approx 23\% \). Comparative analysis of magnetization results from SCAN and its deorbitalized counterpart, SCAN-L, leads to identification of the source of the discrepancy. It is not from the difference between Kohn-Sham (SCAN-L) and generalized Kohn-Sham (SCAN) procedures. The key is the iso-orbital indicator \( \alpha \) (the ratio of the local Pauli and Thomas-Fermi kinetic energy densities). Its deorbitalized counterpart, \( \alpha_L \), has more dispersion in both spin channels with respect to magnetization in an approximate region between 0.6 Bohr and 1.2 Bohr around an Fe nucleus. The overall effect is that the SCAN switching function evaluated with \( \alpha_L \) reduces the energetic disadvantage of the down channel with respect to up compared to the original \( \alpha \), which in turn reduces the magnetization. This identifies the cause of the SCAN magnetization error as insensitivity of the SCAN switching function to \( \alpha \) values in the approximate range \( 0.5 \lesssim \alpha \lesssim 0.8 \) and an oversensitivity for \( \alpha \gtrsim 0.8 \).

Transition metals generally - and Fe particularly - are central to both practical applications and to the development of improved exchange-correlation (XC) approximations for use in density functional calculations. A pertinent example of the latter role is the generalized gradient approximation (GGA) \(^{1,2}\) breakthrough that gave the right ground-state crystal structure and magnetic order for elemental Fe\(^3\). In light of that importance, some results from a very sophisticated meta-GGA functional are quite provocative.

To summarize, recently Fu and Singh\(^4\) showed that the Strongly Constrained and Appropriately Normed (SCAN)\(^5,6\) meta-GGA XC functional over-magnetizes bcc Fe by \( \approx 23\% \) (saturation magnetization at experimental lattice parameter \( m(\alpha_{\text{exp}}) = 2.63\mu_B \) for SCAN vs. 2.13\(\mu_B\) from experiment). This result is strikingly different from the behavior found from other meta-GGA functionals (e.g. TPSS\(^7\) or a typical GGA (e.g. PBE\(^8\)). Both give close to the experimental magnetization.

For hcp Co and fcc Ni, Fu and Singh found SCAN over-magnetization by 14\% and 13\% respectively. Therefore they cautioned against using SCAN for predicting magnetic properties and materials.

Others have obtained similar results. For example, Jana et al.\(^9\) found that SCAN over-magnetizes bcc Fe by 20\%, fcc Co by 4\%, and fcc Ni by 8\%. Isaacs and Woverton\(^10\) found 19\% (bcc Fe), 8\% (hcp Co), and 14\% (fcc Ni). Based on local moment calculations they also found that “…the average maximum magnetic moment within SCAN is 12\% larger than that found within PBE.” Data from Ekholm et al.\(^11\) correspond to excesses of 25\% for bcc Fe, 9.5\% for hcp Co, and 28\% for fcc Ni. In the ordered 50-50 FePt alloy, Romero and Verstraete\(^12\) found that SCAN gave \( \approx 12\% \) over-magnetization on the Fe site compared to 3\% overage from PBE. In Fe–3C, Fu and Singh found SCAN give nearly 30\% over-magnetization per three-iron-atom formula unit.

Presumably the differences between calculated over-magnetization values for elemental Fe, Co, and Ni (compared for the same crystalline phases) trace to differences in computational parameters and technique and to the intrinsic sensitivity of magnetization calculations. Nevertheless, the trend is completely clear. SCAN over-magnetizes elemental transition metal solids. Given the other broad successes of SCAN (e.g. Ref.\(^10\) and references therein), the discrepancy is noteworthy.

The issue raised is the source of the discrepancy: what within the SCAN functional leads to such a strikingly different magnetization behavior compared to other semi-local functionals? With the aid of SCAN-L\(^13,14\), our deorbitalized version of SCAN, we can resolve the issue and, as well, provide insight perhaps useful for the development of better meta-GGA functionals.

A few definitions are useful. SCAN uses the so-called iso-orbital indicator
\[
\alpha(\mathbf{r}) := (\tau_s - \tau_W)/\tau_{TF}.
\]
Here \( \tau_s = (1/2) \sum |\nabla \varphi_j(\mathbf{r})|^2 \) is the positive-definite Kohn-Sham (KS) kinetic energy density in terms of the KS orbitals \( \varphi_j \), and \( \tau_W \) and \( \tau_{TF} \) are the von Weizsäcker and Thomas-Fermi kinetic energy densities respectively. The numerator of \( \alpha \) is the Pauli KE density. It vanishes for the case of a single-orbital system, one of the ways that \( \alpha \) enables a functional to distinguish chemically different bonding regions. The deorbitalized SCAN, SCAN-L, differs only in using an approximate orbital-independent \( \alpha|n, \nabla n, \nabla^2 n| \) with \( n \) the electron number density.

Turning to analysis, first we can eliminate the possibility that the SCAN magnetization discrepancies arise from limitations of computational technique. The possible issue is that PAW data sets do not exist for SCAN (nor for other meta-GGAs). Thus the VASP calculations\(^15,16\) here and earlier\(^3,4,10,11\) used PBE PAWs instead. However, in addition to those calculations, two groups\(^4,11\) also did post-scf all-electron calculations with...
the WIEN2k code\textsuperscript{17} and PBE spin densities and found the same distinctive over-magnetization trend for SCAN.

Therefore the issue originates structurally in SCAN. An obvious question is whether SCAN-L, which uses the same structure as SCAN, inherits the over-magnetization. Table \ref{tab:results} shows results of VASP\textsuperscript{15} calculations (with PAWs\textsuperscript{16} and other parameters as in Ref.\textsuperscript{14}). SCAN and SCAN-L give very different magnetizations. Consistent with prior results summarized above, in our calculations SCAN gives an overly stable bcc Fe structure (fixed spin moment energy $|E_{mag}| = 1100$ meV below zero moment at calculated equilibrium lattice parameter) compared to PBE (564 meV) that is over-magnetized, $m_{sp} = 2.60\mu_B$. Fig. 1 (the counterpart to Fu and Singh’s calculated post-scf with bcc Fe spin densities from PBE).

![Figure 1](image1.png)

**FIG. 1.** Fixed spin-moment energy versus magnetic moment for bcc Fe at $a_{exp}$ from PBE, SCAN, SCAN-L, TPSS, TPSS-L, and modSCAN. Dots show minimum FSM energy values. Experimental value from Ref. 4. Fig. 1 shows the dramatic difference in FSM energy as a function of magnetization for SCAN compared to other functionals (put aside, for now, the curve labeled “mod-SCAN”). In contrast to the SCAN magnetization, SCAN-L reduces both $|E_{mag}|$ and $m_{sp}$ to the point of being essentially the same as the PBE results.

The orbital independence of SCAN-L leads to a multiplicative XC potential and use of the ordinary Kohn-Sham (KS) procedure. The orbital-dependent SCAN XC potential, in contrast, almost always is used in the generalized Kohn-Sham (gKS) context. One might suspect that the magnetization discrepancy is a consequence of this procedural difference. However, $m_{sp}(a_{calc})$ values from the TPSS functional\textsuperscript{1}, which requires gKS, and its deorbitalized version, TPSS-L, which uses KS, do not exhibit the remarkable difference of the SCAN vs. SCAN-L case. TPSS and TPSS-L deliver $m_{sp}$ values indistinguishable from each other and from the PBE result (see Figure 1).

The only other difference between SCAN and SCAN-L is the distinction between $\alpha$ and $\alpha_L$. In most cases, $\alpha \approx \alpha_L$ is very accurate, but there can be small regions where their difference is noticeable\textsuperscript{13,18}. That is critical to the present analysis. Fig. 2 shows the ratio of the angularly averaged $\alpha_L$ to $\alpha$ for various magnetizations as a function of distance from the Fe nucleus in bcc Fe (cal-

![Figure 2](image2.png)

**FIG. 2.** Ratio of angularly averaged $\alpha_L / \alpha$ for spin-up (above) and spin-down (below) as function of radial distance from Fe nucleus (evaluated with bcc Fe PBE densities).

![Figure 3](image3.png)

**FIG. 3.** Angularly averaged $\alpha$ (above) and $\alpha_L$ (below) as a function of radial distance from a Fe nucleus (evaluated with bcc Fe PBE densities). Spin-up plots are in the left column, spin-down in the right.

Key distinctions to note include the fact that below about $r = 0.9$ bohr, $\alpha_L$ is smaller than $\alpha$ for both spins, with particularly strong reduction on $0.6 \lesssim r \lesssim 0.8$ bohr. It also important that the ratios for both spins exhibit some dispersion with respect to $m_{sp}$, especially on the same $0.6 \lesssim r \lesssim 0.8$ bohr region. Fig. 3 shows that such
dispersion is present in both spin channels of $\alpha_L$, but only in the spin-down channel of $\alpha$. Moreover, $\alpha_{L,\text{down}}$ is more dispersed than $\alpha_{\text{down}}$.

The dominant $\alpha$-dependent contribution to exchange in SCAN and SCAN-L is from the switching function $f_x(\alpha)$ that distinguishes regions of $\alpha < 1$ and $\alpha > 1$. An important bit of analysis is that it has been shown that modifications to make $f_x$ smoother around $\alpha \approx 1$ have negligible effect on SCAN structural and energetic predictions\(^{19}\). Our calculations confirm similarly little effect of those modifications upon $m_{sp}$ and $E_{\text{mag}}$.

Fig. 4 shows the angularly averaged switching function as a function of radial distance evaluated with $\alpha$ and $\alpha_L$ for both spin channels. One sees that on $0.6 \lesssim r \lesssim 0.9$ bohr or so, the $\alpha_L$ values separate the up and down-spin points on the $f_x(\alpha)$ curve more than $\alpha$ itself. In particular, because the down-spin ratio $\alpha_L$ to $\alpha$ is below the up-spin ratio in that radial domain, the down-spin exchange energy density $e_{x,\text{down}}$ contributes more to the full $e_x$ for SCAN-L compared to SCAN. The dispersion ordering with respect to magnetization of $\alpha_{L,\text{up}}$ values is reversed compared to $\alpha_{L,\text{down}}$. That is, for up spin, greatest magnetization has the least reduction (largest $(\alpha_{L,\text{up}})/(\alpha_{\text{up}})$) while for down spin, greatest magnetization has greatest reduction (least $(\alpha_{L,\text{down}})/(\alpha_{\text{down}})$). Added to this is the fact that the up-spin $\alpha$ is almost insensitive to $m_{sp}$, hence so is the up-spin $e_x$, which is not the case for $\alpha_L$.

In the immediately adjacent region, $0.9 \lesssim r \lesssim 1.2$ bohr, $\alpha_{\text{down}} > \alpha_{\text{up}}$ and $\alpha_{L,\text{down}} > \alpha_{L,\text{up}}$. However, the $\alpha_{L,\text{sp}}$ are closer together. Again, the result is that $e_{x,\text{down}}$ contributes more to the full $e_x$ for SCAN-L than for SCAN also in this region.

The net result is small but significant changes in the densities of states. Fig. 5 shows that, relative to SCAN, SCAN-L shifts the up-spin occupied states up a little, thereby reducing the magnetization energy and leaving their population slightly reduced. Meanwhile, the down-spin state energies are somewhat lowered, corresponding to enhanced $e_{x,\text{down}}$ and their population therefore goes up.

Since discrepancies of $\alpha_L$ with respect to $\alpha$ identify the region $0.6 \lesssim r \lesssim 1.2$ bohr as critical, we consider how to modify the SCAN switching function to respond to the actual orbital-dependent $\alpha$ values on that region. The deorbitalized $\alpha_L$ values for up and down spin are more separated than the original $\alpha$ in the $0.6 \lesssim r \lesssim 0.9$ bohr region (region A), but closer together in the $0.9 \lesssim r \lesssim 1.2$ bohr one (region B). Another important fact is that $\alpha$ and $\alpha_L$ values in both such regions are below 1, but get closer to 1 in region B. The task therefore is to bring the values of the switching function for $\alpha_{sp}$ closer to the ones for $\alpha_{\text{down}}$ in region B, while separating the values of the switching function in region A. This amounts to saying that sensitivity of the switching function to small changes in its argument needs to be reduced around 0.8 $\lesssim \alpha \lesssim 1$ and then increased for $\alpha \lesssim 0.8$.

For $\alpha < 1$ (see eqs. (58)-(60) in Ref. 14), the switching function is $f_x(\alpha) = \exp[-c_{Lx}\alpha/(1-\alpha)]$ with $c_{Lx} = 0.667$. A crude way to probe the desired sensitivity change for region B is to increase $c_{Lx}$ from 0.667 to 1. Doing so yields the “modSCAN” results in Table I. Clearly $m_{sp}$ is greatly improved, while $E_{\text{mag}}$ is bettered only somewhat. Those betterments come at the expense of degrading the $\alpha_{\text{calc}}$. Further improvements might be achieved by changes in $f_x$ sensitivity for both regions A and B. This can only be accomplished if $c_{Lx}$ is made a function of $\alpha$. The switching function for $\alpha \leq 1$ is plotted in Fig. 6, along with the “modSCAN” modification and a possible variable $c_{Lx}$. This variable $c_{Lx}$ achieves the

![FIG. 4. Left: Angularly averaged SCAN switching function, $f_x(\alpha)$, as function of radial distance from Fe nucleus (evaluated with bcc Fe PBE spin densities). Right: Angularly averaged SCAN-L switching function $f_x(\alpha_L)$ radial behavior for same density.](image)

![FIG. 5. bcc Fe densities of states for SCAN and SCAN-L.](image)

<table>
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<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$m_{sp}$ (μB/atom)</th>
<th>$E_{\text{mag}}$ (meV/atom)</th>
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<td>modSCAN</td>
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<tr>
<td>SCAN-L</td>
<td>2.81</td>
<td>2.05</td>
<td>-568</td>
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</table>

TABLE I. Calculated bcc Fe lattice parameters, saturation magnetizations, and FSM energies for various XC functionals at $\alpha_{\text{calc}}$. regSCAN values were taken from Ref. 19.
TABLE II. Co and Ni calculated saturation magnetizations and FSM energies for various XC functionals at $\alpha_{\text{exp}}$.

<table>
<thead>
<tr>
<th></th>
<th>$m_{sp}$ (µB/atom)</th>
<th>$E_{\text{mag}}$ (meV/atom)</th>
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<tr>
<td>fcc Ni</td>
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<td>PBE</td>
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<td>-60</td>
</tr>
<tr>
<td>SCAN</td>
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<td>-137</td>
</tr>
<tr>
<td>modSCAN</td>
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<td>-157</td>
</tr>
<tr>
<td>SCAN-L</td>
<td>0.67</td>
<td>-74</td>
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</table>

desired effect on the bcc Fe and hcp Co magnetizations but not on fcc Ni nor bcc V. Further pursuit of modifications of that sort is far beyond the scope of the present investigation.

Table II shows the calculated saturation magnetization and FSM energies for hcp Co and fcc Ni. For Co, SCAN-L reduces $m_{sp}$ relative to SCAN by about 9%, and modSCAN by about 3%. But this is only diagnostic, not a remedy: For Ni the SCAN-L reduction is 14% but modSCAN actually worsens by 3%. What is made clear is the importance of more carefully contrived switching-functions in improved metaGGA functionals. The switching-function can be directly linked to issues in the numerical integration sensitivity, the self-consistent field stability and, as we have seen, over-magnetization. To that point, we note that the Tao and Mo metaGGA XC functional, which uses a very different switching function, does not give over-magnetization.

Note also that the SCAN parameter values are determined, among other constraints, by appropriate norms, but that none of them is a spin-polarized case. As a consequence, SCAN relies solely on the spin-scaling relations for its magnetization predictions. A new or augmented set of norms may be more generally appropriate.

FIG. 6. SCAN switching function $f_{x}(\alpha)$.

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* dmejiarodriguez@ufl.edu
† trickey@qtp.ufl.edu