Shortcomings of meta-GGA functionals when describing magnetism

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Sequences recent studies have shown that SCAN, a functional belonging to the meta-generalized gradient approximation (MGGA) family, leads to significantly overestimated magnetic moments in itinerant ferromagnetic metals. However, this behavior is not inherent to the MGGA level of approximation since TPSS, for instance, does not lead to such severe overestimations. In order to provide a broader view of the accuracy of MGGA functionals for magnetism, we extend the assessment to more functionals but also to antiferromagnetic solids. The results show that to describe magnetism there is overall no real advantage in using a MGGA functional compared to GGAs. For both types of approximation, an improvement in ferromagnetic metals is necessarily accompanied by a deterioration (underestimation) in antiferromagnetic insulators, and vice versa. We also provide some analysis in order to understand in more detail the relation between the mathematical form of the functionals and the results.

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I. INTRODUCTION

The local density approximation [1] (LDA) and generalized gradient approximation [2,3] (GGA) of density functional theory [4,5] (DFT) usually provide a fair description of the magnetism in itinerant ferromagnetic (FM) 3d metals, albeit a slight overestimation of the magnetic moment can be obtained (see, e.g., Refs. [5–7]). On the other hand, the LDA and GGA are inaccurate for antiferromagnetic (AFM) insulators, where the 3d electrons are more localized and the self-interaction error (SIE) [8] present in LDA and GGA is more important. As a consequence, the atomic moment around the transition-metal atom in AFM systems is clearly underestimated [9].

The exchange-correlation (xc) functionals of the meta-GGA (MGGA) level of approximation [10,11] should in general be more accurate since they use an additional ingredient, the kinetic-energy density (KED), which makes it possible to remove a portion of the SIE [12]. The strongly constrained and appropriately normed (SCAN) MGGA functional proposed recently by Sun et al. [13] was constructed in such a way that it satisfies all the 17 known mathematical constraints that can be imposed on a MGGA functional and was appropriately normed, i.e., made accurate, for particular systems. The SCAN functional has been shown to be accurate for both molecules and solids [13–16], including systems bound by noncovalent interactions provided that a dispersion term is added [17–19]. On the other hand, it has been realized that SCAN leads to magnetic moments in bulk FM Fe, Co, and Ni that are by far too large [16,20–24]. The overestimation of the magnetic moment with SCAN has also been observed in alloys [25,26] and surface systems [27].

Nevertheless, this overestimation of magnetic moments is not inherent to the MGGA, since other MGGA functionals like TPSS [28], revTPSS [29], and TM [30] lead to values similar to PBE [20,23,31]. Interestingly, Mejía-Rodríguez and Trickey [24] showed that SCAN-L, a deorbitalized version of SCAN they proposed in Refs. [32,33], leads to a magnetic moment which is similar to PBE, while the results for the geometry and binding energy of molecules and solids stay close to the original SCAN [32–34].

Regarding the general performance of MGGA functionals for magnetism in solids, a few questions remain. For instance, not that many results for the atomic magnetic moment in AFM systems have been reported. Recent tests on various oxides have shown that SCAN underestimates the moment in some cases like MnO or Fe2O3 but overestimates it in MnO2 [35,36]. In Refs. [37,38], the FM and AFM phases of VO2 were studied with numerous functionals including TPSS, revTPSS, MGGA_MS0 [39], MGGA_MS2 [40], and SCAN. It was shown that the latter three functionals lead to moments that are larger than those predicted by TPSS and revTPSS, especially for the AFM phase. Comparisons with reference Monte-Carlo results for the AFM phase of VO2 indicate that MGGA_MS0, MGGA_MS2, and SCAN should be more accurate [37,38]. In Ref. [41], the high-Tc superconductor parent compound La2CuO4 were studied with TPSS, revTPSS, and SCAN, the latter giving a value of the moment of the Cu atom in good agreement with experiment, while a clear underestimation is obtained with TPSS and revTPSS. A recent study by Zhang et al. has shown that SCAN underestimates the atomic magnetic moment in MnO, FeO, CoO, and NiO [42]. Finally, it has been reported that SCAN leads to a magnetic moment in AFM α-Mn that is much larger than with PBE [43].

Despite these results for FM and AFM systems, what is missing is a more systematic study of the relative performance of MGGA functionals for magnetism. In particular,
besides SCAN and (rev)TPSS, not much is known about the performance of other MGGA functionals. It is also not fully clear to which extent an increase (e.g., with respect to PBE) of the moment in FM solids with a given MGGA necessarily translates into an increase for AFM solids. In the present work, a more systematic comparison of MGGA functionals for magnetism is presented. FM and AFM systems are considered, as well as nonmagnetic (NM) ones. The latter may be wrongly described as magnetic with DFT methods [22,44]. The search for a possible magnetic ground state for the supposedly NM systems is restricted to FM.

The paper is organized as follows. A description of the methods is given in Sec. II. In Sec. III, the results are discussed, while Sec. IV provides some analysis of the results. Finally, Sec. V gives the summary of this work.

### II. METHODS

Among the plethora of MGGA functionals that exist [45], we selected a few representatives of various types: empirical vs nonempirical, old standard vs modern, general purpose vs specialized for a particular property. These are the following: BR89 [46], TPSS [28], revTPSS [29], MGGA_MS2 [40], MVS [47], SCAN [13], TM [30], HLE17 [48], SCAN-L [32,33], and TASK [49]. Here, we just mention that HLE17 consists in a simple empirical rescaling of TPSS exchange and correlation, which are multiplied by 1.25 and 0.5, respectively, in order to achieve better results for the band gaps of solids and excitation energies of molecules [48]. The very recent TASK from Aschebrock and Kümmel [49], which is an explicit functional of the electron density. The mBJLDA potential [32,51,52] by replacing \( \rho_{\sigma} \) by an orbital-free (and thus necessarily approximate) expression that depends on \( \rho_{\sigma}, \nabla \rho_{\sigma}, \) and \( \nabla^2 \rho_{\sigma} \), and is thereby turned into a \( \nabla^2 \rho_{\sigma} \)-MGGA, which is an explicit functional of the electron density. The BR89 exchange functional of Becke and Roussel, which was proposed as an accurate approximation to the Hartree-Fock exchange energy [46], depends on both \( \rho_{\sigma} \) and \( \nabla^2 \rho_{\sigma} \). BR89, which is combined in this work with LDA correlation [50], is tested since it differs radically from the other MGGAs in terms of construction. Therefore, it may be interesting to see the results obtained with such a functional.

For comparison, the results obtained with the \( (t_\sigma, \nabla^2 \rho_{\sigma}) \)-dependent modified Becke-Johnson (mBJLDA) potential [53], LDA [50], and the two GGAs PBE [54] and HLE16 [55] are also shown. HLE16 was constructed specifically for band gaps in a similar way as HLE17, by rescaling the exchange and correlation parts (with 1.25 and 0.5, respectively) of the highly parameterized GGA HCTH/407 [56]. The mBJLDA potential was also proposed specifically for band gap calculations, for which it is currently the most accurate semilocal method [57-59].

The calculations were performed with the all-electron WIEN2k code [60,61], which is based on the linearized augmented plane-wave (LAPW) method [62-64]. Among the functionals, HLE17 and TASK were taken from the library of exchange-correlation functionals Libxc [65,66]. The MGGA functionals are not implemented self-consistently in WIEN2k, i.e., only the total energy can be calculated. Nevertheless, it is still possible to calculate the magnetic moment without the corresponding MGGA potential by using only the total energy. The fixed spin-moment (FSM) method [67] (used for a part of the calculations presented in Refs. [22–24]) can be used to calculate the magnetic moment of FM systems. The FSM method can not be applied to AFM systems, nevertheless, in the same spirit, the atomic moment can to some extent be constrained to have a chosen value. This can be done by adding and subtracting a constant shift \( C \) to the spin-up and spin-down xc potentials (of a given GGA functional), respectively, inside the LAPW sphere surrounding a transition-metal atom:

\[
\psi_{\sigma}^{\text{GGA}}_{xc,\text{shift,}\sigma}(r) = \psi_{xc,\sigma}(r) + \sigma C,
\]

where \( \sigma = 1 (-1) \) for spin-up (spin-down) electrons. Supposing that for an atom the spin-up electrons are the majority, a negative (positive) \( C \) should increase (decrease) the magnitude of the spin magnetic moment. Obviously, in order to keep the AFM state, shifts \( C \) of the same magnitude but with opposite signs have to be applied to the transition-metal atoms with opposite sign of the magnetic moment. As with the FSM method for FM solids, the variational principle is used: For a given GGA functional, the spin atomic moment is the one obtained at the value of \( C \) which leads to the lowest total energy.

The fact that MGGA functionals are applied non-self-consistently also means that for both the FSM and C-shift methods the xc potential corresponding to another functional, typically a GGA, has to be used to generate the orbitals \( \psi_{\sigma} \). In a recent study [68] we showed that the non-self-consistent calculation of band gaps with MGGAs can be done accurately, provided that an appropriate GGA potential to generate the orbitals is chosen. The criterion to choose the potential was based on the variational principle; among a plethora of GGA potentials, the one that is chosen is the one yielding orbitals that lead to the lowest total MGGA energy. As expected, these optimal orbitals also lead to band gaps that are the closest to the true MGGA band gaps obtained self-consistently from another code. That just means that in order to reproduce the true (i.e., self-consistent) MGGA results, one should use GGA orbitals which, according to the variational principle, are the closest to the MGGA orbitals. In the present study, the GGA orbitals that are used are those recommended in Ref. [68], namely RPBE [69] (for TPSS, revTPSS, MGGA_MS2, SCAN, TM, and SCAN-L, EV93PW91 [3,70] (for MVS), and mRPBE [68] (for HLE17). For TASK and BR89, not considered in Ref. [68], the orbitals generated by the GGAs HCTH/407 and PBE potentials (among all GGA potentials that we have tried, those listed in Ref. [68]), respectively, lead to the lowest total energy. Therefore, in the present study the TASK and BR89 functionals have been calculated with the HCTH/407 and PBE orbitals, respectively.

In order to validate our procedure, the magnetic moments obtained self-consistently with the VASP [71] and GPAW codes [72,73], both are based on the projector augmented wave
LDA magnetic moment is smaller by the value obtained at the experimental lattice constant, the far from the experimental one. For instance, compared to if a functional leads to an inaccurate lattice constant that is constant on the magnetic moment. It can be non-negligible of the AFM solids presented in Sec.III were obtained using the gradient of the electron density. The atomic moments called basin) is delimited by a surface with zero flux in the QTAIM as implemented in the CRITIC2 code [77,78]. Fe, Fu and Singh [22,23] considered the effect of the lattice NM, seven FM, and nine AFM solids. We mention that for the calculations. The set is divided into five listed in Table I along with their experimental geometry constants, so that it would not make sense to calculate a property at such inaccurate geometry.

The solids that are considered for the present study are shown in Table I along with their experimental geometry [79,80] used for the calculations. The set is divided into five NM, seven FM, and nine AFM solids. We mention that for Fe, Fe and Singh [22,23] considered the effect of the lattice constant on the magnetic moment. It can be non-negligible if a functional leads to an inaccurate lattice constant that is far from the experimental one. For instance, compared to the value obtained at the experimental lattice constant, the LDA magnetic moment is smaller by \( \sim 0.2 \mu_B \) when it is calculated at the corresponding LDA lattice constant. For the present work, no optimization of the geometry was done, i.e., the calculations were performed at the same (experimental) geometry with all functionals. The reasons are the following. First, the effect of geometry and functional on the magnetic moment would be entangled, which would lead to a more complicated analysis and discussion of the results. Second, some of the tested functionals lead to extremely poor lattice constants, so that it would not make sense to calculate a property at such inaccurate geometry.

### III. RESULTS

#### A. Choice of orbitals and atomic region

Before discussing the relative performance of the functionals, we show in Table II some results for MnO, FeO, CoO, and NiO in order to illustrate the influence of self-consistency and choice of integration region (i.e., definition of the atom) on the spin atomic magnetic moment \( \mu_S \). As mentioned in Sec. II and discussed in more detail in Ref. [68], the GGA RPBE potential is the optimal one for the MGGA TPSS and SCAN. The importance of using the orbitals generated by the RPBE potential is visible in the case of CoO; compared to using the PBE orbitals (the usual default choice) \( \mu_S \) is larger by about 0.1 and 0.2 \( \mu_B \) for TPSS and SCAN, respectively. Such differences are not negligible, and in fact we can also see that using the RPBE orbitals brings the WIEN2K results into agreement with those obtained self-consistently with VASP and GPAW codes. We just note that for NiO there is a discernible discrepancy between VASP and the two other codes. After looking into this issue, we came to the conclusion that the problem may be due to VASP projectors that are unadapted for the particular case of NiO. For MnO, FeO, and NiO, using either PBE or RPBE orbitals does not matter at all. Indeed, we found that in the case of CoO the optimal potential is mRPBE. Of the AFM solids, the AFM order leads to a lowering of the symmetry (second indicated space group).

| Solid     | \( a \)  | \( b \)  | \( c \)  | \( \alpha \) | \( \beta \) | \( \gamma \) |
|-----------|---------|---------|---------|------------|-----------|-----------|
| NM        |         |         |         |            |           |           |
| Sc(194)   | 3.309   | 3.309   | 5.273   | 90         | 90        | 120       |
| V(229)    | 3.028   | 3.028   | 3.028   | 90         | 90        | 90        |
| Y(194)    | 3.652   | 3.652   | 5.747   | 90         | 90        | 120       |
| Pd(225)   | 3.881   | 3.881   | 3.881   | 90         | 90        | 90        |
| Pt(225)   | 3.916   | 3.916   | 3.916   | 90         | 90        | 90        |
| Fe(229)   | 2.867   | 2.867   | 2.867   | 90         | 90        | 90        |
| Co(194)   | 2.507   | 2.507   | 4.070   | 90         | 90        | 120       |
| Ni(225)   | 3.523   | 3.523   | 3.523   | 90         | 90        | 90        |
| FeCo(221) | 2.857   | 2.857   | 2.857   | 90         | 90        | 90        |
| ZrZr\(_2\) (227) | 7.396 | 7.396 | 7.396 | 90 | 90 | 90 |
| Zr(1/8,1/8,1/8), Zn(1/2,0,0) | | | | | | |
| YFe\(_2\) (227) | 7.363 | 7.363 | 7.363 | 90 | 90 | 90 |
| Y(1/8,1/8,1/8), Fe(1/2,0,0) | | | | | | |
| Ni\(_2\)Al(221) | 3.568 | 3.568 | 3.568 | 90 | 90 | 90 |
| Ni(1/2,1/2,0), Al(0,0,0) | | | | | | |

| AFM       |         |         |         |            |           |           |
|-----------|---------|---------|---------|------------|-----------|-----------|
| Cr\(_2\)O\(_3\) (167,146) | 4.953 | 4.953 | 13.588 | 90         | 90        | 120       |
| Cr(0,0,0.3475), O(0.3058,0.1,4) | | | | | | |
| Fe\(_2\)O\(_3\) (167,146) | 5.035 | 5.035 | 13.747 | 90         | 90        | 120       |
| Fe(0,0,0.35534), O(0.3056,0.1,4) | | | | | | |
| MnO (225,166) | 4.445 | 4.445 | 4.445 | 90         | 90        | 90        |
| FeO (225,166) | 4.334 | 4.334 | 4.334 | 90         | 90        | 90        |
| CoO (225,166) | 4.254 | 4.254 | 4.254 | 90         | 90        | 90        |
| NiO (225,166) | 4.171 | 4.171 | 4.171 | 90         | 90        | 90        |
| CuO (15,14) | 4.684 | 3.423 | 5.129 | 90         | 99.54     | 90        |
| Cu(1/4,1/4,0), O(0,0,0.4184,1/4) | | | | | | |
| Cr\(_2\)Sb(194,164) | 4.122 | 4.122 | 5.464 | 90         | 90        | 120       |
| Cr\(_2\)Sb\(_2\) (58,14) | 6.028 | 6.874 | 3.272 | 90         | 90        | 90        |
| Cr(0,0,0), Sb(0.1835,0.3165,0.32) | | | | | | |

The solids that are considered for the present study are shown in Table I along with their experimental geometry [79,80] used for the calculations. The set is divided into five NM, seven FM, and nine AFM solids. We mention that for Fe, Fe and Singh [22,23] considered the effect of the lattice constant on the magnetic moment. It can be non-negligible if a functional leads to an inaccurate lattice constant that is far from the experimental one. For instance, compared to the value obtained at the experimental lattice constant, the LDA magnetic moment is smaller by \( \sim 0.2 \mu_B \) when it is calculated at the corresponding LDA lattice constant. For the present work, no optimization of the geometry was done, i.e., the calculations were performed at the same (experimental) geometry with all functionals. The reasons are the following. First, the effect of geometry and functional on the magnetic moment would be entangled, which would lead to a more complicated analysis and discussion of the results. Second, some of the tested functionals lead to extremely poor lattice constants, so that it would not make sense to calculate a property at such inaccurate geometry.
TABLE II. Spin atomic magnetic moment $\mu_S$ (in $\mu_B$) of AFM MnO, FeO, CoO, and NiO. The results in the first three columns were obtained with WIEN2k using different atomic sphere sizes (their radii, in bohr, are indicated) for calculating $\mu_S$. The results in the last three columns were obtained with three different codes and using the Bader volume for calculating $\mu_S$. The WIEN2k results for the MGGAs were obtained with the $C$-shift method [Eq. (1)] and using either the RPBE or PBE (results in parenthesis) orbitals. All VASP and GPAW results were obtained self-consistently. The calculations were done at the geometry specified in Table I.

|     | WIEN2K | VASP | GPAW |
|-----|--------|------|------|
| MnO | Small sphere | Medium sphere | Large sphere |
| Sphere radius | 2.05 | 2.25 | 2.45 |
| PBE | 4.19 | 4.31 | 4.38 |
| TPSS | 4.21 | 4.33 | 4.40 |
| SCAN | 4.32 | 4.44 | 4.51 |
| FeO | Small sphere | Medium sphere | Large sphere |
| Sphere radius | 2.00 | 2.20 | 2.40 |
| PBE | 3.39 | 3.45 | 3.48 |
| TPSS | 3.43 | 3.49 | 3.53 |
| SCAN | 3.53 | 3.59 | 3.63 |
| CoO | Small sphere | Medium sphere | Large sphere |
| Sphere radius | 1.95 | 2.15 | 2.35 |
| PBE | 2.42 | 2.45 | 2.45 |
| TPSS | 2.45 | 2.50 | 2.51 |
| SCAN | 2.55 | 2.59 | 2.61 |
| NiO | Small sphere | Medium sphere | Large sphere |
| Sphere radius | 1.90 | 2.10 | 2.30 |
| PBE | 1.38 | 1.38 | 1.37 |
| TPSS | 1.47 | 1.47 | 1.46 |
| SCAN | 1.62 | 1.62 | 1.61 |

calculations were done with three different radii for the atomic sphere, which were chosen to lie within a reasonable range from a physical point of view, in particular not too small in order to avoid core leakage. The value of $\mu_S$ calculated from within the sphere varies the most for MnO; from the smallest sphere (2.05 bohr) to the largest (2.45 bohr) $\mu_S$ increases by about 0.2 $\mu_B$, which is rather significant. On the other hand, there is no change in $\mu_S$ for NiO (since Ni has the largest nuclear charge $Z$ and therefore the most localized 3d electrons), but of course reducing the sphere size further would at some point lead to a decrease of the magnetic moment. For FeO and CoO, the variation of $\mu_S$ is intermediate between MnO and NiO. The other important point to note is that in all cases the magnetic moment obtained with the largest sphere agrees with the one obtained using the Bader volume.

Since the Bader volume is uniquely defined and the corresponding $\mu_S$ agrees with the value obtained with the largest LAPW atomic sphere, using it as the atomic region to calculate $\mu_S$ can be considered as a pretty sound choice. Therefore, the comparison of the functionals for the atomic magnetic moment in AFM solids will be based on the values obtained with the Bader volume.

B. Comparison of functionals

1. Ferromagnetic solids

We start the discussion on the comparison of the functionals with the FM solids. The results for the spin magnetic moment $\mu_S$ (per formula unit) are shown in Table III. It is known that the GGAs (and sometimes also the LDA) slightly overestimate the magnitude of $\mu_S$ in itinerant metals like Fe, Co, or Ni [5,6]. For these systems, the overestimation with LDA and the standard GGA PBE is in the range 0.05–0.2 $\mu_B$. The other GGA considered in this work, HLE16, leads to unpredictable results, since it yields a moment that is much larger (by 0.5 $\mu_B$) than the one predicted by PBE for Fe, but to identical values for Ni, while the increase is 0.1 $\mu_B$ for Co. However, such behavior with HLE16 is not that surprising since, as shown in Ref. [57] and discussed in Sec. IV, it has a strong enhancement factor that leads to an xc potential with very large oscillations and therefore possibly unexpected results. The results obtained for the compounds show that LDA and PBE are accurate for FeCo but overestimate $\mu_S$ for YFe$_2$ and significantly for ZrZn$_2$ and Ni$_3$Al. However, for the latter two systems spin fluctuations, which require a treatment beyond standard DFT, are supposed to significantly reduce the measured moment (see discussion in Ref. [91] for ZrZn$_2$ and in Refs. [92,93] for Ni$_3$Al). The results with HLE16 are again disparate; compared to PBE, $\mu_S$ is increased for FeCo and ZrZn$_2$ but reduced for YFe$_2$ and Ni$_3$Al. HLE16 leads to the best agreement with experiment for YFe$_2$ but to the worst for ZrZn$_2$.

Turning to the results obtained with the MGGAs, we mention again that several studies have already reported that SCAN, which is highly successful in solid-state physics for total-energy calculations [15–17,19,94,95], clearly overestimates the magnetic moment in itinerant metals [16,20–24]. Those studies considered mostly Fe, Co, and Ni. For the intermetallic ferromagnets considered here, the overestimation of $\mu_S$ with SCAN is also substantial. In fact, among all xc
TABLE III. Spin magnetic moment $\mu_S$ (in $\mu_B$ per formula unit) of FM solids. The experimental values for Fe, Co, and Ni are also spin magnetic moments. The results in parenthesis for FeCo are the atomic moments (defined according to the Bader volume) on Fe and Co. The results for the MGGA functionals were obtained with the FSM method. The calculations were done at the geometry specified in Table I. The largest discrepancies with respect to experiment are underlined.

| Method      | Fe   | Co   | Ni   | FeCo | YFe$_2$ | ZrZn$_2$ | Ni$_3$Al |
|-------------|------|------|------|------|---------|----------|----------|
| LDA         | 2.20 | 1.59 | 0.62 | 4.51 | 2.76    | 1.75     | 3.20     |
| PBE         | 2.22 | 1.62 | 0.64 | 4.55 | 2.81    | 1.75     | 3.38     |
| HLE16       | 2.74 | 1.73 | 0.64 | 4.77 | 3.06    | 1.71     | 2.91     |
| mBJLDA      | 2.51 | 1.69 | 0.73 | 4.60 | 2.87    | 1.73     | 3.60     |
| TPSS        | 2.23 | 1.65 | 0.66 | 4.63 | 2.86    | 1.77     | 3.66     |
| revTPSS     | 2.29 | 1.67 | 0.68 | 4.67 | 2.89    | 1.79     | 3.71     |
| MGGA_MS2    | 2.30 | 1.74 | 0.73 | 4.80 | 2.96    | 1.84     | 3.81     |
| MVS         | 2.71 | 1.80 | 0.76 | 4.88 | 3.01    | 1.87     | 3.69     |
| SCAN        | 2.63 | 1.79 | 0.76 | 4.86 | 2.99    | 1.87     | 3.88     |
| TM          | 2.25 | 1.68 | 0.69 | 4.69 | 2.89    | 1.79     | 3.67     |
| HLE17       | 2.67 | 1.72 | 0.65 | 4.74 | 3.02    | 1.71     | 3.60     |
| TASK        | 2.75 | 1.83 | 0.76 | 4.91 | 3.02    | 1.89     | 3.45     |
| SCAN-L      | 2.13 | 1.65 | 0.68 | 4.62 | 2.85    | 1.77     | 3.26     |
| BR89        | 2.45 | 1.67 | 0.66 | 4.64 | 2.86    | 1.78     | 3.74     |
| Expt.       | 1.98 | 2.05 | 1.52 | 2.05 | 1.58   | 1.55     | 1.62     |

$^a$Ref. [81].
$^b$Ref. [82].
$^c$Ref. [83].
$^d$Ref. [84].
$^e$Ref. [85].
$^f$Ref. [86].
$^g$Ref. [87].
$^h$Refs. [88,89].
$^i$Ref. [90].
FIG. 1. Magnetic energy $\Delta E_{\text{tot}}$ as a function of the magnetic moment $\mu_S$ in Fe (a), Ni (b), ZrZn$_2$ (c), and Ni$_3$Al (d).

We now turn to NM solids but consider only elemental transition metals. In Table V we present those cases for which DFT can predict a FM ground state instead of the experimental NM ground state. Note that Refs. [22,24] reported that all functionals except HLE16 and HLE17, there is a clear correlation between the magnetic moment and magnetic energy; the functionals leading to the largest values of $\mu_S$ (TASK, SCAN, and MVS) also lead to the largest values of $\Delta E_{\text{tot}}$. This trend was observed in Refs. [22–24] and is connected with the magnetic susceptibility. However, HLE16 and HLE17 do not really follow this trend. For instance, for Ni and YFe$_2$ HLE16 gives the smallest magnetic moment but the largest value for $\Delta E_{\text{tot}}$. Similar observations can be made with HLE17.

Figure 1 shows $\Delta E_{\text{tot}}$ as a function of $\mu_S$ in the cases of Fe, Ni, ZrZn$_2$, and Ni$_3$Al. As discussed above, a larger magnetic moment usually corresponds to a deeper minimum. However, we can see that this is not really the case with the HLE16 and HLE17 functionals for Ni and Ni$_3$Al.

2. Nonmagnetic solids

We now turn to NM solids but consider only elemental transition metals. In Table V we present those cases for which DFT can predict a FM ground state instead of the experimental NM ground state. Note that Refs. [22,24] reported that
SCAN leads to a FM ground state for V and Pd. As we can see, in many cases disagreement with experiment is obtained. The worst cases are Sc and Pd for which all methods except LDA lead to a nonzero magnetic moment. LDA gives \( \mu_S = 0 \) and \( \mu_S < 0.1 \mu_B \) for Sc and Pd, respectively. For the other systems, the functionals which usually lead to the correct NM state are LDA, PBE, TPSS, revTPSS, TM, and BR89. They were giving the least overestimations of the magnetic moment in FM systems. Note that the GGA HLE16 leads to extreme values, 2.86 \( \mu_B \), in FM systems. Note that the GGA HLE16 leads to the deepest minimum, which was also the case for several of the FM solids, as seen above. SCAN leads to a very shallow minimum but a quite large moment of 0.55 \( \mu_B \), while SCAN-L and the other common MGGAIs retain a NM state.

We mention that we also considered the possibility of an AFM ground state in Mo instead of the NM one. Mo belongs to the same group as Cr which is (incommensurate) AFM. By using a simple cubic two-atom CsCl cell, one functional, HLE16, leads to an AFM ground state with an atomic moment of 0.54 \( \mu_B \) in the Bader volume. The other functionals lead to the correct NM phase.

3. Antiferromagnetic solids

The results for the spin atomic moment \( \mu_S \) in AFM solids are shown in Table VI. We mention again that the Bader volume is used for the region defining the atomic moment. We also mention that for a comparison with experiment there is a possible non-negligible orbital contribution \( \mu_L \) to the experimental value, and estimates are given in the caption of Table VI.

It is well known that LDA and PBE have the tendency to underestimate the moment in AFM oxides, as we observe here for most oxides. An exception is Cr\(_2\)O\(_3\), since the LDA/PBE results lie in the range of the experimental values. In the cases of FeO and CoO, it is not possible to make a quantitative comparison with experiment since the range of experimental values and estimations for \( \mu_L \) are large. For the intermetallic compounds CrSb and CrSb\(_2\), where the magnetic moment on the Cr atom is considered (note that in CrSb\(_2\) the moment on the Sb atom is nonzero but tiny), PBE seems to lead to good agreement for CrSb, but to a very large overestimation of \( \sim 0.8 \mu_B \) for CrSb\(_2\). Such an overestimation by PBE for CrSb\(_2\) has already been noted by Kuhn et al. [136], who showed that by adding an on-site Hubbard correction to the Cr atom, using the around mean field (AMF) version of PBE + \( U \) [137] with \( U = 2.7 \) eV and \( J = 0.3 \) eV, leads to a reduction of the moment from 2.57 to 2.03 \( \mu_B \) (inside the Cr atomic sphere of radius 2.32 bohr). We could reproduce this trend with PBE + \( U(AMF) \) (we get \( \mu_B = 2.34 \mu_B \) inside the Bader volume). However, when using the fully localized limit (FLL) [137] variant of PBE + \( U \) (with same \( U \) and \( J \)) the moment increases by \( \sim 0.5 \mu_B \) with respect to PBE, and therefore worsens the agreement with experiment. These results with PBE + \( U \) are not surprising since DFT + \( U(AMF) \) is known to be better adapted than DFT + \( U(FLL) \) for (near)-metallic systems which are not as correlated as TM oxides [138,139].

Compared to PBE, the GGA HLE16 significantly increases the magnetic moment for all systems except CuO, for which the PBE and HLE16 moments are curiously identical. The increase in \( \mu_S \) is the largest for CrSb and CrSb\(_2\), where it is clearly above 1 \( \mu_B \). Actually, among all methods HLE16 leads to (nearly) the largest value of \( \mu_S \) for all systems except CoO, NiO, and CuO.

As observed in Sec. III B 1 for the FM solids, the MGGAIs TPSS, revTPSS, TM, SCAN-L, and BR89 lead to results that are relatively similar to PBE in most cases. These functionals lead to moments that are moderately larger than PBE, and the largest increase (\( \sim 0.2 \mu_B \)) occurs for Fe\(_2\)O\(_3\), CrSb, and CrSb\(_2\) with BR89. For the AFM solids considered here there is

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**Table V.** Spin magnetic moment \( \mu_S \) (in \( \mu_B \) per formula unit) of (supposedly) NM solids. A nonzero \( \mu_S \) means a FM ground state. The results for the MGGA functionals were obtained with the FSM method. The calculations were done at the geometry specified in Table I.

| Method      | Sc   | V    | Y    | Pd   | Pt  |
|-------------|------|------|------|------|-----|
| LDA         | 0.00 | 0.00 | 0.00 | 0.08 | 0.01|
| PBE         | 0.41 | 0.00 | 0.00 | 0.24 | 0.00|
| HLE16       | 2.86 | 0.78 | 2.86 | 0.36 | 0.51|
| mBILDA      | 0.53 | 0.00 | 0.00 | 0.39 | 0.47|
| TPSS        | 0.39 | 0.00 | 0.00 | 0.29 | 0.01|
| revTPSS     | 0.37 | 0.01 | 0.01 | 0.30 | 0.00|
| MGGA_MS2    | 0.58 | 0.02 | 0.56 | 0.44 | 0.00|
| TASK        | 0.69 | 0.00 | 0.71 | 0.41 | 0.55|
| SCAN        | 0.62 | 0.55 | 0.60 | 0.44 | 0.08|
| TM          | 0.37 | 0.00 | 0.00 | 0.34 | 0.00|
| HLE17       | 0.86 | 0.61 | 0.76 | 0.38 | 0.42|
| TASK        | 0.80 | 0.64 | 0.79 | 0.43 | 0.37|
| SCAN-L      | 0.49 | 0.01 | 0.46 | 0.26 | 0.00|
| BR89        | 0.50 | 0.00 | 0.00 | 0.36 | 0.04|

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FIG. 2. Magnetic energy \( \Delta E_{\text{tot}} \) as a function of the magnetic moment \( \mu_S \) in V.
TABLE VI. Calculated spin atomic magnetic moment $\mu_S$ of the transition-metal atom (in $\mu_B$ and defined according to the Bader volume) of AFM solids compared to experimental values of the total atomic magnetic moment $\mu_S + \mu_L$. The orbital moment $\mu_L$ is estimated to be in the range 0.6–1 $\mu_B$ for FeO [108–111], 1–1.6 $\mu_B$ for CoO [108–118], 0.3–0.45 $\mu_B$ for NiO [108,110,114,117,119], and much smaller in other oxides. No values of $\mu_L$ for CrSb and CrSb$_2$ could be found in the literature. The results for the MGGA functionals were obtained with the C-shift method [Eq. (1)]. The calculations were done at the geometry specified in Table I. The values which are in clear disagreement with experiment are underlined.

| Method       | MnO  | FeO  | CoO  | NiO  | CuO  | Cr$_2$O$_3$ | Fe$_2$O$_3$ | CrSb | CrSb$_2$ |
|--------------|------|------|------|------|------|------------|------------|------|---------|
| LDA          | 4.33 | 3.42 | 2.38 | 1.20 | 0.12 | 2.53       | 3.42       | 2.74 | 2.64    |
| PBE          | 4.39 | 3.48 | 2.45 | 1.37 | 0.37 | 2.62       | 3.61       | 2.90 | 2.75    |
| HLE16        | 4.69 | 3.67 | 2.59 | 1.45 | 0.37 | 3.13       | 4.08       | 4.10 | 4.04    |
| mBILDA       | 4.57 | 3.64 | 2.72 | 1.74 | 0.72 | 2.74       | 4.14       | 4.24 | 4.23    |
| TPSS         | 4.41 | 3.52 | 2.50 | 1.46 | 0.45 | 2.63       | 3.74       | 2.97 | 2.81    |
| revTPSS      | 4.42 | 3.53 | 2.51 | 1.46 | 0.45 | 2.64       | 3.78       | 3.00 | 2.84    |
| MGGA_MS2     | 4.48 | 3.59 | 2.56 | 1.58 | 0.59 | 2.71       | 3.95       | 3.10 | 2.95    |
| MVS          | 4.55 | 3.66 | 2.64 | 1.60 | 0.47 | 2.76       | 4.07       | 3.44 | 3.28    |
| SCAN         | 4.53 | 3.62 | 2.60 | 1.60 | 0.57 | 2.73       | 4.01       | 3.32 | 3.18    |
| TM           | 4.42 | 3.53 | 2.52 | 1.49 | 0.48 | 2.64       | 3.78       | 2.96 | 2.79    |
| HLE17        | 4.62 | 3.65 | 2.63 | 1.56 | 0.49 | 2.92       | 4.05       | 3.83 | 3.74    |
| TASK         | 4.63 | 3.70 | 2.67 | 1.60 | 0.50 | 2.90       | 4.18       | 3.71 | 3.61    |
| SCAN-L       | 4.43 | 3.50 | 2.49 | 1.50 | 0.48 | 2.65       | 3.71       | 2.96 | 2.79    |
| BR89         | 4.47 | 3.53 | 2.44 | 1.42 | 0.43 | 2.69       | 3.81       | 3.12 | 2.98    |
| Expt.        | 4.58 | 3.32 | 4.2 | 4.6 | 3.35 | 3.8 | 3.98 | 1.9 | 2.2 | 2.76 | 2.44 | 4.17 | 4.22 | 3.0 | 1.94 |

basically no case where a MGGA leads to a moment smaller than the PBE value, whereas there were many cases for the FM systems. All other MGGA lead to magnetic moments that are increased further, and the largest values of $\mu_S$ (disregarding the HLE16 results) are obtained in most cases by either TASK (MnO, FeO, and Fe$_2$O$_3$), HLE17 (Cr$_2$O$_3$, CrSb, and CrSb$_2$), or mBILDA (CoO, NiO, and CuO).

Due to the large uncertainties in the experimental values, a quantitative ranking of the theoretical methods is hardly possible. Overall, we can say that MGGA perform better than standard PBE. However, in some cases TPSS, revTPSS, TM, SCAN-L, and BR89 seem to be too weak, with magnetic moments that are still too small compared to experiment. On the other hand, HLE17 and TASK, as well as the GGA HLE16, lead to moments that are by far too large for Cr$_2$O$_3$ and the weakly correlated systems CrSb and CrSb$_2$. For the latter the overestimation of $\mu_S$ is in the range 1–2 $\mu_S$ with all functionals except PBE + $U$(AMF).

Finally, as already seen for the FM solids, HLE16 behaves erratically, since it leads to one of the smallest moments for CuO but to the largest moment for some of the other AFM systems.

IV . DISCUSSION

A quite general observation that can be made from the results presented in Sec. III B is that if a MGGA functional increases (let us say with respect to PBE) magnetism in a system, then it will most likely do it in other magnetic systems, too. However, clear exceptions were noted with HLE16 and HLE17, which lead to rather erratic results. The other general conclusion is that all tested MGGA lead in most cases to magnetic moments which are larger than the PBE values. In order to provide insight for some of the results, for instance by establishing a relation between the mathematical form of the xc functional and the magnetic moment $\mu_S$, we consider the xc magnetic energy density

$$\Delta \epsilon_{xc}(r) = \epsilon_{xc}^{(AFM)}(r) - \epsilon_{xc}^{(NM)}(r),$$

(3)
where $\epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow}, \nabla \rho_{\uparrow}, \nabla \rho_{\downarrow}, \nabla^2 \rho_{\uparrow}, \nabla^2 \rho_{\downarrow}, t_1, t_2)$ is the xc-energy density defined as follows:

$$E_{xc} = \int \epsilon_{xc}(\mathbf{r}) d^3 r. \quad (4)$$

In Eq. (3), $\epsilon_{xc}^{AFM}$ and $\epsilon_{xc}^{NM}$ were calculated in the (A)FM and NM phases, respectively. $\Delta\epsilon_{xc}$ is expected to be overall negative in magnetic systems.

Figure 3 shows the difference in $\Delta\epsilon_{xc}$ between SCAN and SCAN-L ($\Delta\epsilon_{xc}^{SCAN-L} - \Delta\epsilon_{xc}^{SCAN}$) in the cases of the FM systems Fe and FeCo. Note that for a meaningful comparison, $\epsilon_{xc}^{FM}$ is calculated at the same value of $\mu_S$ for both functionals (2.0 and 4.5 $\mu_B$ for Fe and FeCo, respectively). As discussed in Sec. III B, SCAN-L reduces $\mu_S$ with respect to its parent SCAN. According to Fig. 3, this is mainly due to the large values of $\Delta\epsilon_{xc}^{SCAN-L} - \Delta\epsilon_{xc}^{SCAN}$ close to the atoms where $\Delta\epsilon_{xc}^{SCAN-L}$ is overall less negative than $\Delta\epsilon_{xc}^{SCAN}$ (this was checked by integrating only over the atomic region). The contribution to the integral of $\Delta\epsilon_{xc}^{SCAN-L} - \Delta\epsilon_{xc}^{SCAN}$ follows the 3d electron density, which in Fe has its maximum already at 0.5 bohr and quickly decays beyond 1.5 bohr, as shown in Fig. 4. The contribution from the interstitial region is one order of magnitude smaller and has opposite sign (negative), which is due to reverse polarization of the 4s electrons [84,85]. Note that in general the difference $\Delta\epsilon_{xc}^{F1} - \Delta\epsilon_{xc}^{F2}$ around an atom between two functionals $F1$ and $F2$ is not uniformly positive or negative; there are lobes (which differentiate orbitals) with opposite signs. This is visible for the Co atom in FeCo, for instance. Of course, which lobes are the most visible also depends on the plane that is chosen for the plot. In Ref. [24] the case of Fe was explained by looking in detail at the differences between the iso-orbital indicator $\alpha_\sigma$ and its deorbitalized version $\alpha_{L,\sigma}$ (defined later) in the region around the nucleus corresponding to a sphere with a radius of 1.5 bohr, i.e., where $\Delta\epsilon_{xc}^{SCAN-L} - \Delta\epsilon_{xc}^{SCAN}$ is largest. Later in the text we also provide a more detail discussion on the difference between $\alpha_\sigma$ and $\alpha_{L,\sigma}$ in Fe.

The MGGA MVS, SCAN, HLE17, and TASK, and the GGA HLE16 lead to magnetic moments and magnetic energies that are usually clearly larger than the PBE value. For these functionals Fig. 5 shows for Fe the corresponding xc magnetic energy density in comparison to the one obtained with PBE. We can see that the empirical HLE16 and HLE17 functionals behave in a similar way and lead to a xc...
magnetic energy density that is more negative than PBE in larger regions of space (the red regions) and with different orientations of the lobes compared to the other functionals. However, it is important to mention that these differences between HLE16/HLE17 and the other functionals are actually mostly due to their corresponding xc potential (i.e., to self-consistency effects), which lead to different shape/occupation of the orbitals. This is demonstrated in Fig. 6 which compares \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{HLE17} \) when \( \Delta E_{xc}^{HLE17} \) is calculated with the density and KED obtained from either the mRPBE or the PBE potential. Very different patterns are obtained, and in the latter case \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{HLE17} \) is very similar to \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{MVS} \) or \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{SCAN} \), for instance. Nevertheless, despite the seemingly large influence of the density/KED on \( \Delta E_{xc}^{HLE17} \), the results for \( \mu_S \) and \( \Delta E_{tot} \) change little. Indeed, using the density/KED generated from the PBE potential leads to \( \mu_S = 2.71 \) \( \mu_B \) and \( \Delta E_{tot} = -1441 \) meV/f.u., which is quite similar to the results from Tables III and IV obtained with the mRPBE density/KED (\( \mu_S = 2.67 \) \( \mu_B \) and \( \Delta E_{tot} = -1491 \) meV/f.u.). Besides HLE16/HLE17, TASK and TPSS (or TM which is similar) lead to negative regions that dominate the most and the least, respectively. This corroborates with the magnetic moment that is among the largest (smallest) with TASK (TPSS/TM).

Taking Ni as an example, Fig. 7 shows \( \Delta E_{xc} \) as a function of \( \mu_S \). The shape and order of magnitude of the curves look rather similar to those of the total magnetic energy \( \Delta E_{tot} \) [see Fig. 1(b)], which indicates that the other terms (kinetic energy and Coulomb) play a less important role. However, note that the magnitude of \( \Delta E_{xc} \) is about 50 meV/f.u. larger than \( \Delta E_{tot} \). As already seen with \( \Delta E_{tot} \), the HLE16 and HLE17 functionals behave very differently from the other functionals. They lead to a minimum of the \( \Delta E_{xc} \) curve which is at a much smaller value of the magnetic moment, however this effect is much less pronounced for the total magnetic energy \( \Delta E_{tot} \) [Fig. 1(b)].

Figures 8 and 9 show \( \Delta E_{xc} \) in the AFM systems CrSb and NiO. As for the FM systems, the difference \( \Delta E_{xc}^{SCAN-L} - \Delta E_{xc}^{SCAN} \) in CrSb and NiO evidences the fact that SCAN leads to larger atomic moments than SCAN-L, since \( \Delta E_{xc}^{SCAN-L} \) is overall more negative than \( \Delta E_{xc}^{SCAN} \) on the transition-metal atoms. For CrSb on Fig. 9, we can see that \( \Delta E_{xc}^{SCAN-L} - \Delta E_{xc}^{SCAN} \) is mostly positive on the Cr atom. In the case of HLE17, the regions corresponding to positive and negative values are in this plane (visually) roughly equal; nevertheless, around the Cr atoms the positive values of \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{HLE17} \) clearly dominate and represent about 70% of the integrated value (which is positive) of \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{HLE17} \) in the unit cell. In the case of TASK, the positive region largely dominates in this plane. We note again that HLE16, HLE17, and TASK lead to atomic moments of 4.10, 3.83, and 3.71 \( \mu_B \), respectively, which are much larger than 2.90 \( \mu_B \) from PBE. As discussed above for FM Fe, the magnitude of \( \Delta E_{xc}^{PBE} - \Delta E_{xc}^{F} \) is the smallest for TPSS, which leads to a magnetic moment, 2.97 \( \mu_B \), very close to PBE.

It may also be interesting to compare the mathematical form of the xc-enhancement factor \( F_{xc} \) of the various
FIG. 9. Difference $\Delta \epsilon_{xc}^{PBE} - \Delta \epsilon_{xc}^F$ between the xc magnetic energy density within a (110) plane in CrSb obtained with PBE and another functional $F$. The AFM state corresponds to a Cr (left atoms) atomic moment of $\mu_S = 3.0 \mu_B$ (defined according to the Bader volume). Blue and red regions correspond to negative and positive values, respectively. The regions with the most intense blue/red colors correspond to absolute values above 0.01 Ry/bohr$^3$.

FIG. 10. $r_s$, $s$, and $\alpha$ for $\sigma = \uparrow$ (majority spin) as a function of the distance $d$ for FM Fe plotted along the direction from (0,0,0) to (1/2,1/2,1/2) or (1/2,1/2,0).

have rather extreme shapes; both the value of $F_{xc}$ and its derivative $\partial F_{xc}/\partial s$ are the largest. Such particular shapes of $F_{xc}$ lead to xc potentials with very large oscillations [57] and therefore erratic and somehow unpredictable behavior. We also note that among the MGGAs, TPSS, revTPSS, and TM have the weakest dependency on $\alpha$ and behave nearly like GGAs. In contrast to them, $F_{xc}$ from the TASK functional has by far the strongest variation with respect to $\alpha$, so that starting at some value of $\alpha$ it becomes the smallest enhancement factor among all those considered in this work. As discussed below, this particular behavior of the enhancement factor of TASK, as well as the ones from SCAN and MVS which show a similar feature, is related to the large magnetic moments obtained with these functionals. Actually, for these three functionals, as well as HLE16 for small values of $s$, Fig. 11 shows that $\partial F_{xc}/\partial s$ is also negative. The $r_s$ dependency of the LDA and TASK enhancement factors are also particular; depending on the value of $s$ and/or $\alpha$, they increases faster than for all other functionals.

As a side note, we mention that a few additional calculations were done by combining exchange of one functional (e.g., SCAN) with correlation of another functional (e.g., TPSS). From the results (not shown), we concluded that the choice of correlation has a rather minor effect on the magnetic moment.

functionals, which is defined as

$$F_{xc}(\mathbf{r}) = \frac{\epsilon_{xc}^{LDA}(\mathbf{r})}{\epsilon_{xc}(\mathbf{r})},$$

where (in spin-unpolarized formulation) $\epsilon_{xc}^{LDA} = -(3/4)(3/\pi)^{1/3} \rho^{4/3}$ is the exchange energy density from LDA [1]. $F_{xc}$ is usually expressed as a function of the Wigner-Seitz radius $r_s = (3/(4\pi \rho))^{1/3}$, reduced density gradient $s = (\nabla \rho)/(2(3\pi^2)^{1/3} \rho^{4/3})$, and iso-orbital indicator $\alpha = (t - t^W)/t^{TF}$, where $t^{TF} = (3/10)(3\pi^2)^{1/3} \rho^{5/3}$ and $t^W = (\nabla \rho)^2/(8 \rho)$ are the Thomas-Fermi [140,141] and von Weizsäcker [142] KED, respectively.

In order to give an idea of the typical values of $r_s$, $s$, and $\alpha$ encountered in dense solids, and to make a relationship with the enhancement factors, Fig. 10 shows plots of these quantities in FM Fe. Here, $r_s$ ranges from 0 to 2, $s$ from 0 to 1, and $\alpha$ from 0.5 to 2.5.

Figure 11 shows $F_{xc}$ plotted as a function of $s$, $\alpha$, or $r_s$ for all functionals except SCAN-L and BR89. These two functionals depend on $\nabla^2 \rho$, which does not allow a direct comparison with the other functionals. We can see that the enhancement factors of the GGA HLE16 and MGGA HLE17
MGGAs can be very different to each other in terms of enhancement factor and xc magnetic energy density. Thus, the details of the mechanism leading to an increase of the magnetic moment (with respect to PBE) may also differ from one functional to the other. For instance, the two MGGAs HLE17 and TASK lead (albeit not always with HLE17) to large magnetic moments, despite having extremely different analytical forms. As discussed above and in Ref. [24], the analytical form of a functional for densities close to the \( \rho \) of these three MGGAs are negative (see Fig. 11), which leads to two desirable features: (a) the presence of a field-counteracting term in the potential (as with exact exchange) and (b) a derivative discontinuity that is larger and therefore leads to more accurate band gaps. However, in the present context, magnetism, a negative value of \( \partial F_x/\partial \alpha \) does not seem to be beneficial. Thus, MGGAs with such negative \( \partial F_x/\partial \alpha \) to a certain extent mimic exact exchange, which also leads to too large magnetic moments in FM metals [143,144]. It was argued that a negative slope \( \partial F_x/\partial \alpha \) increases the nonlocal character of the MGGA exchange [49]. A possible way to cure the over-magnetization problem of TASK or SCAN would be to combine the exchange component with a more compatible (and most likely more advanced) correlation component. In the case of exact exchange, \textit{ab initio} correlations can solve some of the problems of exact exchange.

Mejía-Rodríguez and Trickey [24] provided an explanation for the smaller moment obtained with SCAN-L compared to SCAN. Here, a similar explanation is provided but with an emphasis on the importance of \( \partial F_{xc}/\partial \alpha \) as discussed above.
FIG. 12. Spatial average of \( r_{\sigma}, s_{\sigma}, \alpha_{\sigma}, \) and \( \alpha_{L,\sigma} \) inside a sphere of radius 1.25 bohr centered on the atom in Fe plotted as a function of \( \mu_S, \sigma = \uparrow \) corresponds to the majority spin.

Compared to \( \alpha_{\sigma} \), the deorbitalized \( \alpha_{L,\sigma} \) is smaller in magnitude for both spins, as shown in Fig. 12. Another important difference can be noted; for the majority spin \( \sigma = \uparrow, (\alpha_{L,\uparrow}) \) increases with \( \mu_S \) instead of decreasing, while for the minority spin, the increase for small values of \( \mu_S \) is strongly reduced. Therefore, by substituting \( \alpha_{\sigma} \) by \( \alpha_{L,\sigma} \) in TASK, SCAN, or MVS, the effect on the exchange splitting due to \( \partial F_{xc}/\partial \alpha \) is strongly suppressed (or maybe even reversed), which explains the reduction of magnetism. Actually, a deorbitalization of TPSS leads to very small change in the results (see Ref. [24]), which is due to the very weak dependency of TPSS on \( \alpha \).

SCAN-L has been shown to be more appropriate than SCAN for magnetic and nonmagnetic itinerant metals [24]. However, the \( \nabla^2 \rho \) dependency of SCAN-L may also carry practical disadvantages, since implementations of this family of functionals are less common than for \( t \)-MGGA. Furthermore, the third and fourth derivatives of the density, that are required for the potential, may lead to numerical problems [32,145–147]. Therefore, it would be interesting to find a \( t \)-dependent alternative to SCAN-L, that is, a slightly modified SCAN that leads to minimal changes for the geometries and binding energies but reduces the magnetic moment. Mejía-Rodríguez and Trickey [24] reported such attempts, which were apparently unsuccessful. Our numerous own attempts have all remained unsuccessful, as well. The most simple ones consist of just changing the value of one of the parameters in SCAN. Among them, \( c_{1s} \) for instance, can be used to vary the switching function and thus the magnetic moment (see Ref. [24]). By increasing the value of \( c_{1s} \) above \( \sim 2.5 \) \( (c_{1s} = 0.667 \text{ in SCAN}) \), the magnetic moments of Fe, Co, and Ni get smaller and approach to some extent the SCAN-L values. As discussed above, a negative slope \( \partial F_{xc}/\partial \alpha \) favors a large moment. Since an increase of \( c_{1s} \) makes \( \partial F_{xc}/\partial \alpha \) less negative for values of \( \alpha \) below 1, this should be (one of) the main reason(s) why the moments are smaller. However, with such values for \( c_{1s} \), the errors for the lattice constant and cohesive energy (results now shown) are larger (by \( \sim 50\% \)) than SCAN. Another strategy that we have considered consists of slightly modifying the expression of \( \alpha \) in SCAN. Numerous expressions have been tried, but none of them was useful to achieve our goal. A modification of \( \alpha \) can work for a system, but not for another. Thus, the construction of a \( t \)-MGGA with similar performance as SCAN-L seems far from trivial, as already reported by Mejía-Rodríguez and Trickey [24].

V. SUMMARY

The focus of this work has been on the description of magnetism in solids with MGGA functionals. FM, NM, and AFM systems have been considered. The goal was to provide an overview of the reliability of MGGA and the possible improvement with respect to standard GGA functionals like PBE. The most important observations are the following. In the vast majority of cases, the tested MGGA functionals lead to a magnetic moment that is larger than the value obtained with LDA and PBE. This means that for the considered FM systems, which are itinerant metals, the agreement with experiment can only be worse than with LDA and PBE, which are known to already slightly (or even strongly when spin fluctuations are important) overestimate the magnetic moment in FM solids. Consistent with this trend, a certain number of NM metals can be wrongly described as FM with MGGA and already with PBE in some cases. In the case of the AFM oxides with localized 3d electrons, using a MGGA leads to a more realistic value of the atomic moment, since PBE leads to too small moments. Only in the case of Cr2O3 the LDA and PBE values seem to be within the experimental range. Concerning the weakly correlated AFM CrSb and CrSb2, PBE is in agreement with experiment for the former but strongly overestimates the moment for the latter. Therefore, using a MGGA does not really seem to be beneficial for such systems.

The MGGA that we have considered can be split into two groups. Those which give results that are qualitatively similar to PBE, namely BR89, TPSS, revTPSS, TM, and SCAN-L. They lead to reasonable results for metals but clearly underestimate the atomic magnetic moment in the AFM transition-metal oxides. The other group consists of
TASK, HLE17, SCAN, MVS, and MGGA_MS2, which lead to sizeably larger moments. For the FM metals, TASK, SCAN, and MVS lead in many cases to the largest magnetic moments and therefore the largest disagreement with experiment. They also lead to a nonzero magnetic moment for the NM metals that we have considered. For the AFM systems, TASK, HLE17, as well as the mBJLDA potential and the GGA HLE16 lead to the largest values of the atomic moment. As just mentioned above, this is beneficial for the transition-metal HLE17, as well as the mBJLDA potential and the GGA alks that we have considered. For the FM metals, TASK, also lead to a nonzero magnetic moment for the NM metals.

Magnetic moments. Actually, we deduced that a negative derivative of the enhancement factor should contribute to making the magnetic moment larger, since the iso-orbital indicator of the majority (minority) spin decreases (increases) with the moment, leading to an enhanced exchange splitting.

On a more technical side, we have also discussed the choice of the GGA potential for generating the orbitals plugged into the MGGA functionals. We have shown that when an appropriate GGA potential is chosen, the results are very close to those obtained (from another code) self-consistently. We also pointed out the importance of choosing an atomic volume for the magnetic moment in AFM systems that is large enough, for which we used the basin as defined in Bader’s QTAIM.

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