

Magnetizabilities at Self-Interaction-Corrected Density Functional Theory Level

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Abstract: Using a recent high-quality ab initio coupled cluster benchmark set for magnetizabilities, we assess the performance of a set of density functionals, representing different levels of complexity, from the local density approximation (LDA), via generalized gradient approximations (GGA's) to kinetic energy density including meta-GGA's. The effect of self-interaction correction (SIC) is remarkable and, in most cases, leads to a significant error reduction, revealing the sensitivity of magnetizability toward a physically sound exchange-correlation potential.

1. Introduction

The static magnetizabilities are computed from the exchange-correlation potential as a second-order response of a molecule to an external magnetic field, as the second derivative of the energy with respect to the magnetic field, evaluated at zero field strength:

$$\xi = -\frac{d^2E}{dB^2}\Big|_{B=0}$$

It is thus the magnetic-field equivalent of polarizability in an electric field. A negative value for the magnetizability implies a diamagnetic molecule, a class that encompasses most closed-shell, neutral species. The few exceptions include the paramagnetic ozone and boron monohydride,^{1–3} BH. Experimentally, measuring absolute magnetizabilities is something of a challenge. Vibrational effects are also large,^{4,5} which makes a direct comparison to computed values less straightforward. Recently, Lutnæs et al. published a careful benchmark set for magnetizabilities⁴ (and rotational *g* tensors), computed at the coupled-cluster singles, doubles, and perturbative triples, CCSD(T)⁶ level, using large, gauge-including basis sets. They compared their CCSD(T) values against several levels of density functional theory (DFT)^{7,8}

and concluded that all of the tested functionals show significant differences with respect to the ab initio values. Other studies have also shown that magnetizabilities are relatively insensitive to electron correlation effects, and already Hartree–Fock (HF) theory^{9,10} usually performs adequately. Therefore, it is somewhat awkward that most density functionals, which naturally capture more of the correlation than HF, actually perform worse in predicting this property.

Standard exchange-correlation functionals suffer from an unphysical self-interaction of the electrons. An immediate consequence of the Coulomb self-interaction error (SIE) is to raise the energies of occupied orbitals. As is well known, the highest occupied molecular orbital (HOMO) in exact DFT would correspond exactly to the negative of the ionization potential.¹¹ In approximate DFT, this is seldom the case. Thus, band gaps are usually much too small, and in some cases, it is even impossible to satisfy the aufbau principle. For anions, the HOMO energy often becomes positive, implying unbound electrons. In an attempt to minimize the self-interaction, orbitals become too diffuse, an especially problematic artifact for unpaired electrons¹² and dissociation of radicals.¹³ SIE has also been found to cause problems in the evaluation of polarizabilities, the electric field counterpart of magnetizabilities.¹⁴

Lutnæs et al. found that hybrid functionals that incorporate a portion of exact “HF” exchange improve the magnetizabilities. A further improvement was found by employing the optimized effective potential (OEP) approach.^{15–20} By

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treating the exchange part in this manner, an orbital-dependent nonlocality is introduced. One effect of this is to reduce the self-interaction error of the functional.²¹ Correcting for self-interaction has previously been shown to be beneficial for computing nuclear magnetic resonance (NMR) parameters^{22–24} and magnetization.²⁵ In the field of computational NMR, the Malkin correction²⁶ seems to mimic self-interaction correction to a degree, often improving the results.^{22,27} Also, calculation of polarizabilities benefits from self-interaction correction, especially within the OEP-SIC formalism.^{28,29} Therefore, it is of interest to see how explicitly self-interaction-corrected DFT (SIC-DFT) performs for magnetizabilities.

Here, we assess the performance of several density functionals, representing various levels of complexity, starting from the local density approximation³⁰ (LDA). Of the generalized gradient approximation³¹ (GGA) family, we include the Swart–Solà–Bickelhaupt³² (SSB-D) functional, recently presented as a good all-round functional, well suited for, among other properties, reliable spin state energetics. Thus, it is of interest to see how well this functional performs for the somewhat related property of magnetizability. SSB-D is to a large part based on the nonempirical Perdew–Burke–Ernzerhof (PBE) functional³³ and its modification OPBE, which uses Handy–Cohen optimized exchange, OPTX.³⁴ PW91,^{35,36} closely related to PBE, PBEsol, a reformulation of PBE which satisfies exact conditions more relevant for solids than molecules³⁷ (while still being nonempirical), for magnetic properties the tuned Keal-Tozer KT2,³⁸ and the popular BP86^{39,40} functionals are also benchmarked.

The meta-GGA functionals go beyond the GGA approximation by also taking the orbital-dependent kinetic energy density and/or the Laplacian of the electron density as an input parameter. This allows for a more complete emulation of the “true” functional, for example, by satisfaction of a fuller range of known physical properties. Potentially, ingredients important also for magnetizabilities would be included. Here, we test two common representatives of this level of theory, the nonempirical Tao–Perdew–Staroverov–Scuseria⁴¹ (TPSS) and the semiempirical Minnesota group functional M06-L⁴² (which has been found to work well for chemical shieldings⁴³) noting that neither uses the Laplacian in their functional form.

Model density functional potentials have been designed for providing a correct asymptotic behavior, another feature most traditional functionals fail to accomplish. Here, we use three of these exchange–correlation potentials: the van Leeuwen and Baerends⁴⁴ (LB94), the more recent statistical average of orbital potentials⁴⁵ (SAOP), and the gradient-regulated asymptotic correction⁴⁶ (GRAC-LB) methodologies. The potentials have been shown to improve upon the description of response properties, especially excitation energies and polarizabilities.^{47–49} We note that SAOP in particular has been suggested to perform reasonably well for NMR chemical shifts.⁵⁰

2. Computational Details

All computations were performed with the Amsterdam Density Functional (ADF) code,^{51–53} version 2009.01 (snapshot r21439); the self-interaction-corrected calculations were performed with a modified local version. The polarized quadruple- ζ QZ4P Slater-type orbital (STO) basis set⁵⁴ was used in all cases unless otherwise noted, with extra diffuse fit functions added (via the AddDiffuseFit keyword). For a further improvement in basis set convergence, the gauge-including atomic orbitals (GIAO) formalism,^{55–62} was employed. This is currently not exploitable at the meta-GGA level within the code used. Therefore, the GIAO corrections for TPSS and M06-L were taken from the PBE calculations, simply using the ratio of standard and gauge-origin-corrected magnetizabilities:

$$\xi(\text{mGGA, GIAO}) = \xi(\text{mGGA, standard}) \times \frac{\xi(\text{PBE, GIAO})}{\xi(\text{PBE, standard})}$$

The reader should be aware that the same gauge origin dependence for PBE and the kinetic energy density incorporating meta-GGA's is only a for the purpose necessary assumption. We note that in general, gauge-invariance can be satisfied also within the meta-GGA framework.⁶³

The magnetizabilities were computed perturbationally, neglecting the current density, using the standard implementation in ADF^{22,23,64} for LDA and GGA's; for details, we refer the reader to the original papers. We note that here we only report the mean magnetizabilities from the magnetizability tensor, and thus, the direction of the magnetic field does not affect the results. The self-interaction corrections were computed self-consistently, using the Perdew–Zunger⁶⁵ (PZ) scheme with the Krieger–Li–Iafrate^{66,67} (KLI) approximation of the exact optimized potential^{15–20} (OEP). The PZ SIC removes one-electron self-interaction completely and many-electron self-interaction efficiently.¹³ The orbitals were localized using the Boys–Foster procedure,^{68,69} which has been found to be suitable in this context.⁷⁰ GRAC-LB requires an estimate of the ionization potential; these were obtained from the National Institute of Standards and Technology (NIST) Chemistry WebBook. The molecular geometries were taken from ref 4. Default convergence and accuracy parameters were used, with the following tighter exceptions: The integration accuracy parameter was set to 7.5; the self-consistent field (SCF) equations were converged to a threshold of 10^{-8} au.

3. Results and Discussion

3.1. Basis Set Convergence. Magnetic properties show a notoriously slow convergence with respect to basis set size, due to the gauge-origin issue.⁷¹ The use of gauge-including atomic orbitals (GIAO's), also known as London atomic orbitals (LAO's), alleviates this problem significantly. In this section, we perform an initial assessment of the basis set convergence, using both standard Slater-type basis sets and the GIAO formalism. The computations have been performed with the SSB-D functional, and four representative molecules from the benchmark set were chosen: CH₂O (formaldehyde),

Table 1. Magnetizabilities (in SI units, 10^{-30} J T $^{-2}$) Using Different Basis Sets for Four Molecules, Computed at the SSB-D Level^a

	bf's for C	CH ₂ O		H ₂ S		LiF		OCS	
		normal	GIAO	normal	GIAO	normal	GIAO	normal	GIAO
DZ	4s2p	−395.2	−124.4	−531.4	−466.8	−394.7	−212.6	−1974.3	−598.6
DZP	4s2p1d	−196.1	−117.0	−459.3	−464.0	−343.9	−209.0	−1314.4	−591.6
TZP	5s3p1d	−147.4	−112.8	−455.6	−452.3	−262.1	−195.3	−1133.3	−572.0
TZ2P	5s3p1d1f	−144.5	−112.1	−454.5	−452.5	−260.5	−195.1	−1115.2	−571.5
frozen core	4s3p1d1f	−188.2	−88.1	−454.7	−421.9	−337.5	−181.3	−1495.0	−538.7
QZ4P	7s4p2d2f	−110.7	−108.3	−455.3	−456.3	−198.9	−196.5	−640.7	−569.6

^a The second column shows the size of the basis set as the number of basis functions for carbon (bf's for C). Both normal and GIAO calculations are reported.

H₂S, LiF, and OCS. The standard basis sets in ADF,⁵⁴ of increasing size, were employed: DZ, DZP, TZP, TZ2P, ZORA-QZ4P. The results are summarized in Table 1.

As can be seen from Table 1, the convergences of the GIAO calculations are, as expected, much better than for the standard procedure. For all molecules, the GIAO calculations appear reasonably converged at the singly polarized triple- ζ , TZP level. We also tested the effect of using a frozen-core approach, where the lowest energy orbitals are not allowed to change during the SCF. This approach is unusable when computing magnetizabilities, showing the importance of core orbitals for this property. With the TZ2P basis set, the GIAO results for the frozen core approach differ from the all-electron calculations by $14\text{--}33 \times 10^{-30}$ J T $^{-2}$ for the four molecules above.

We also assessed the even-tempered ET-QZ+5P basis set (8s6p3d2f bf's for C) but experienced problematic linear dependency issues for some molecules. In general, for molecules without issues, the GIAO results compared to QZ4P are very small. The following calculations have been performed using the QZ4P basis set in connection with the GIAO formalism. We estimate that the error compared to the complete basis set limit is roughly $\pm 2 \times 10^{-30}$ J T $^{-2}$.

3.2. Performance of the Standard Functionals. Lutnæs et al. included the following molecules in their benchmark set:⁴ hydrogen fluoride (HF), carbon monoxide (CO), nitrogen (N₂), water (H₂O), hydrogen cyanide (HCN), hyperfluorous acid (HOF), ozone (O₃), ammonia (NH₃), formaldehyde (CH₂O), methane (CH₄), ethylene (C₂H₄), aluminum monofluoride (AlF), methyl fluoride (CH₃F), cyclopropene (C₃H₄), fluoroacetylene (FCCH), cyanogen fluoride (FCN), hydrogen sulfide (H₂S), methinophosphide (HCP), formyl fluoride (HFCO), ketene (H₂C=O), lithium fluoride (LiF), lithium hydride (LiH), nitrous oxide (N₂O), carbonyl sulfide (OCS), difluoride monoxide (OF₂), ethylene oxide (H₄C₂O), phosphorus mononitride (PN), and sulfur dioxide (SO₂). Here, we study the same molecules, using the original CCSD(T)-optimized structures.

Tables 2 and 3 show the magnetizabilities, as computed with the different functionals benchmarked here, relative to the CCSD(T) data. Table 4 summarizes the error statistics; following Lutnæs et al., we excluded ozone (O₃) from the statistics, due to its complex multireference character, which renders even the CCSD(T) value of 121.5×10^{-30} J T $^{-2}$ somewhat unreliable; at the MCSCF level, the magnetizability has been found to be appreciably lower,⁷² 97.8×10^{-30} J T $^{-2}$.

The values for LDA, PBE, and KT2 agree well with the corresponding values computed by Lutnæs et al., which shows the expected result that close to the (GIAO) basis set limit; there is no real difference in performance between Gaussian- and Slater-type orbitals. Further, we used the Perdew–Wang³⁰ (PW92) formulation of LDA correlation, instead of the Vosko–Wilk–Nusair⁷³ (VWN) formulation; the differences are negligible.

We start by giving an overview of the combined error statistics for the functionals, after which a more detailed analysis of representative molecules is provided.

Let us first consider the nonempirical functionals at each of the three represented rungs of the DFT ladder.⁷⁴ The performance of LDA is unsatisfactory, with a mean absolute relative error (MARE) of 3.7% and a standard deviation from the benchmark data of 11.5×10^{-30} J T $^{-2}$. Surprisingly, PBE, at the next rung, improves the results very weakly, if at all, as already commented upon in ref 4. PBEsol, tuned for solids, is actually just as good (or bad). Only at the third ladder do we see an improvement; TPSS performs quite well overall, having the smallest errors of all the functionals without self-interaction correction. We also note the smallest error, compared to CCSD(T), for ozone. Thus, the added flexibility of the meta-GGA formulation compared to GGA's does seem to capture more of the physics relevant also for magnetizabilities. This is encouraging, adding to the repertoire of the wide range of chemistry and physics, this fully nonempirical functional has previously been found to perform well for.^{75–82}

Replacing the standard PBE exchange by OPTX exchange notably degrades the magnetizabilities; all statistical error measures of OPBE are worse than those of PBE. The SSB-D functional, which largely is an interpolation of PBE and OPBE, shows for magnetizabilities a performance between those of PBE and OPBE. The MARE of 4.0% is closer to that of OPBE, while the standard deviation of 9.8×10^{-30} J T $^{-2}$ is closer to that of PBE. SSB-D, which has been shown to harvest the “best of both worlds” for other properties, the worlds being PBE and OPBE, is thus not a clear improvement over either when it comes to magnetizabilities. It is, however, not worse than its major constituents either, showing that its parametrization is sound. The performance of PW91 is very close to that of PBE, as expected due to their similarity. The magnetizabilities obtained with BP86 are also very similar. Of the GGA's, KT2 is still the best performer and together with TPSS the only functional that exceeds Hartree–Fock quality.

Table 2. Magnetizabilities (in SI units, 10^{-30} J T $^{-2}$) for the Lutnæs et al. Benchmark Set⁴ Using Hartree–Fock (from ref 4), LDA, and Different GGA Functionals^a

molecule	CCSD(T)	HF	LDA	PBE	PBEsol	OPBE	SSB-D	KT2	PW91	BP86
HF	-176.4	3.7	-4.9	-3.3	-3.7	0.8	0.1	-0.2	-3.1	-2.7
CO	-209.5	5.0	3.0	4.4	4.4	10.2	8.8	0.8	4.2	4.9
N ₂	-205.2	2.4	4.2	6.1	5.9	13.0	11.8	1.0	6.2	6.5
H ₂ O	-235.1	3.8	-6.2	-3.2	-4.1	1.7	1.1	0.0	-3.3	-2.6
HCN	-271.8	-8.3	6.3	7.6	7.9	17.7	13.6	1.4	7.4	7.6
HOF	-235.4	-9.2	6.8	8.6	7.1	11.0	12.2	8.2	9.2	8.2
O ₃	121.5	459.0	75.0	64.6	67.1	66.8	54.9	19.5	65.9	62.1
NH ₃	-290.3	2.9	-7.9	-3.0	-4.8	1.3	0.5	-0.4	-2.7	-1.5
CH ₂ O	-127.4	-12.1	31.6	22.5	26.3	20.7	19.1	9.3	22.4	19.3
CH ₄	-316.9	3.2	-12.8	-3.6	-7.8	0.3	1.5	0.5	-3.1	-1.5
C ₂ H ₄	-345.6	-9.1	14.2	14.8	14.7	20.4	18.9	9.8	15.9	15.0
AlF	-394.5	-4.9	-1.4	-2.1	-1.1	1.3	-1.2	1.8	-1.7	0.4
CH ₃ F	-315.7	-2.3	0.1	4.4	1.9	5.6	7.9	7.8	5.0	4.1
C ₃ H ₄	-478.9	0.9	14.2	19.1	16.3	23.0	25.0	21.2	21.7	19.2
FCCH	-441.6	-10.6	2.9	4.3	3.3	11.9	9.3	1.4	5.0	3.9
FCN	-370.0	-8.0	4.4	5.4	5.0	10.4	8.1	2.7	5.8	5.5
H ₂ S	-455.1	2.3	-11.9	-4.4	-7.8	1.3	-1.1	-1.8	-3.3	-2.1
HCP	-492.8	-18.7	14.7	13.3	14.9	22.5	19.4	4.3	13.0	13.3
HFCO	-307.2	-4.3	10.2	10.2	10.6	13.6	11.5	7.7	10.4	10.9
H ₂ C ₂ O	-423.9	-8.7	-4.1	2.2	-1.3	7.1	8.1	1.7	4.4	3.0
LiF	-195.5	4.6	-1.1	-0.9	-0.9	2.0	-1.0	-1.2	0.2	-1.9
LiH	-127.2	1.9	-8.9	-7.9	-8.5	-8.2	-8.4	-10.0	-8.7	-6.1
N ₂ O	-339.1	-3.7	4.4	7.3	-6.3	12.7	11.5	8.5	8.2	6.8
OCS	-584.1	-13.4	7.1	9.2	8.4	16.5	14.5	8.0	10.1	9.3
OF ₂	-247.1	-24.5	27.6	26.8	25.8	27.4	29.2	21.8	27.8	26.1
H ₄ C ₂ O	-535.2	-9.6	5.4	11.9	7.9	15.1	16.4	14.2	13.8	12.4
PN	-308.2	4.4	23.2	23.7	24.9	33.9	27.7	11.1	23.0	23.4
SO ₂	-314.3	12.5	19.0	20.4	-4.4	30.3	24.0	17.3	20.5	22.0

^a DFT values computed with the QZ4P basis set; values shown are relative to the CCSD(T)/aug-cc-pCV[TQ]Z reference data.**Table 3.** Magnetizabilities (in SI units, 10^{-30} J T $^{-2}$) for the Lutnæs et al. Benchmark Set⁴ Using Different meta-GGA's and Model Potentials, Computed with the QZ4P Basis Set^a

molecule	CCSD(T)	TPSS	M06-L	LB94	SAOP	GRAC
HF	-176.4	-1.9	2.4	2.3	2.8	-1.1
CO	-209.5	-0.4	2.3	25.6	5.3	6.2
N ₂	-205.2	2.0	6.5	29.7	7.6	8.0
H ₂ O	-235.1	-1.1	3.9	2.0	2.6	-0.5
HCN	-271.8	-0.3	7.0	29.2	9.0	8.9
HOF	-235.4	-0.4	-9.2	18.5	12.0	8.4
O ₃	121.5	4.5	-25.1	187.6	48.4	59.2
NH ₃	-290.3	0.1	5.3	-1.3	1.0	-1.8
CH ₂ O	-127.4	-5.1	-15.7	46.0	5.8	19.1
CH ₄	-316.9	0.5	3.2	-11.3	-5.1	-3.4
C ₂ H ₄	-345.6	-4.8	-5.9	33.9	16.1	14.4
AlF	-394.5	-10.2	-15.3	17.5	-8.6	0.7
CH ₃ F	-315.7	-8.6	-14.1	1.0	4.8	4.2
C ₃ H ₄	-478.9	-7.9	-22.0	24.8	18.2	18.4
FCCH	-441.6	-16.1	-16.1	21.9	6.5	5.0
FCN	-370.0	-9.7	-25.5	23.4	7.3	5.9
H ₂ S	-455.1	0.3	0.0	0.5	-5.9	-0.5
HCP	-492.8	-2.6	6.0	50.2	8.4	14.1
HFCO	-307.2	-8.5	-22.6	27.2	7.3	11.0
H ₂ C ₂ O	-423.9	-19.1	-41.1	17.1	0.9	2.1
LiF	-195.5	-2.2	-0.4	13.1	2.4	1.5
LiH	-127.2	-7.0	-6.2	13.8	-5.0	-1.7
N ₂ O	-339.1	-5.4	-22.4	21.4	9.9	6.7
OCS	-584.1	-12.0	-42.0	28.2	4.8	8.9
OF ₂	-247.1	5.4	-18.7	44.6	25.3	26.1
H ₄ C ₂ O	-535.2	-10.8	-18.8	10.6	12.5	12.0
PN	-308.2	8.9	12.0	62.5	11.5	24.8
SO ₂	-314.3	0.2	-26.4	50.0	9.7	22.5

^a The values are shown relative to the CCSD(T)/aug-cc-pCV[TQ]Z reference data.

The other meta-GGA studied, the empirical M06-L, performs quite poorly for magnetizabilities. Of the normal

Table 4. Statistical Error Analysis for the Density Functional Methods Studied^a

method	ME	MAE	MaxE	MRE	MARE	SD
Hartree–Fock	-3.7	7.2	-24.5	1.1%	2.5%	8.4
LDA	5.2	9.6	31.6	-2.0%	3.7%	11.5
PBE	7.2	9.3	26.8	-2.4%	3.4%	9.5
PBEsol	5.0	8.7	26.3	-1.8%	3.3%	10.3
OPBE	12.0	12.6	33.9	-3.9%	4.4%	10.4
SSB-D	10.7	11.5	29.2	-3.4%	4.0%	9.8
KT2	5.4	6.4	21.8	-1.6%	2.3%	7.3
PW91	7.7	9.6	27.8	-2.5%	3.5%	9.6
BP86	7.5	8.9	26.1	-2.5%	3.2%	8.9
TPSS	-4.3	5.6	-19.1	1.3%	1.7%	6.3
M06-L	-10.1	13.7	-42.0	2.9%	4.2%	14.8
LB94	22.3	23.2	62.5	-8.1%	8.4%	17.9
SAOP	6.2	8.0	25.3	-2.0%	2.7%	7.5
GRAC	8.1	8.8	26.1	-2.8%	3.1%	8.5

^a Hartree–Fock results from ref 4. Mean error (ME), mean absolute error (MAE), maximum error (MaxE), mean relative error (MRE), mean absolute relative error (MARE), and standard deviation (SD) are shown. Except for the relative errors, units are 10^{-30} J T $^{-2}$.

functionals tested here and in ref 4, it is actually the worst, with the largest maximum error, largest spread in errors, and largest mean absolute errors. The parametrization for the functional thus appears unsuitable for this property. One can note, however, that for the highly multiconfigurational ozone, M06-L performs reasonably, being on par with TPSS and KT2. This suggests the possibility that the true nonlocality entering, indirectly, via the orbital-dependent kinetic energy density does capture more of the relevant correlation also for difficult multireference species. A data set of one molecule is naturally too small for any conclusions; a more rigorous study should be performed.

Table 5. Magnetizabilities (in SI units, 10^{-30} J T $^{-2}$) for the Lutnæs et al. Benchmark Set⁴ Using SIC-DFT, Computed with the QZ4P Basis Set^a

molecule	LDA	PBE	PBEsol	OPBE	SSB-D	KT2	PW91	BP86	LB94	SAOP	GRAC
HF	6.9	4.8	5.3	5.6	3.0	−1.1	5.0	4.3	2.8	8.2	0.7
CO	8.4	2.9	3.9	1.0	0.9	−6.6	3.6	−0.4	1.8	−2.2	−10.9
N ₂	7.2	1.9	2.8	0.5	1.1	−7.5	2.7	−1.3	−0.7	−3.0	−9.9
H ₂ O	9.3	7.0	7.9	7.9	5.2	1.1	8.2	8.6	5.8	9.2	0.5
HCN	9.4	4.3	5.4	4.2	5.0	−3.6	0.8	5.0	2.4	−0.8	−6.5
HOF	12.2	5.8	7.1	3.5	0.2	−8.0	6.3	4.8	5.3	7.8	4.6
O ₃	−48.2	−66.4	−66.1	−83.5	−75.9	−89.1	−62.1	−78.7	−95.3	−85.7	−61.9
NH ₃	10.3	8.4	9.1	9.4	5.4	2.4	8.9	8.3	9.0	7.3	−2.4
CH ₂ O	3.9	−3.2	−1.7	−8.1	−4.7	−9.9	−2.6	−8.0	−9.5	−17.1	−1.8
CH ₄	4.0	3.3	3.0	3.9	2.6	0.2	3.6	4.7	6.7	−2.8	−9.7
C ₂ H ₄	17.7	12.1	13.2	10.2	12.0	6.5	13.1	11.1	13.5	8.3	4.3
AlF	21.6	12.3	15.6	9.4	8.2	7.8	13.4	11.6	19.4	3.3	0.5
CH ₃ F	5.2	2.7	3.0	1.7	0.6	−1.6	2.9	3.2	4.8	3.3	4.5
C ₃ H ₄	17.8	12.1	13.1	10.6	11.9	8.0	13.5	12.1	15.5	8.4	13.8
FCCH	11.9	4.8	6.3	2.7	2.2	−2.8	5.7	2.9	8.5	2.4	0.0
FCN	9.4	2.8	4.1	0.9	−0.5	−6.8	−8.4	−0.1	4.4	−0.9	−5.0
H ₂ S	10.5	6.6	7.3	7.0	2.4	−2.0	7.4	6.6	12.4	−2.0	−2.7
HCP	17.3	6.9	9.5	4.2	5.2	−1.9	8.6	1.3	10.5	−7.4	−13.0
HFCO	9.4	3.3	4.6	1.1	−1.4	−7.6	4.3	0.1	4.8	−4.5	−7.2
H ₂ C ₂ O	4.9	−1.6	−1.1	−5.2	−4.3	−9.5	1.1	−2.2	6.2	−9.2	−6.3
LiF	8.0	5.7	6.4	6.3	3.1	−1.3	6.2	4.2	6.9	8.1	3.3
LiH	9.9	8.9	8.8	7.7	9.2	8.5	9.2	8.0	13.3	2.6	−6.0
N ₂ O	1.5	−4.0	−3.4	−6.0	−6.1	−10.5	−3.0	−6.4	−1.8	−4.2	−3.2
OCS	4.3	−5.3	−3.3	−6.7	−8.5	−15.5	−3.5	−9.6	−1.0	−19.9	−13.7
OF ₂	23.6	12.1	14.2	5.9	1.0	−11.4	13.2	9.1	7.5	8.6	9.3
H ₄ C ₂ O	16.3	10.9	11.5	9.5	6.7	1.3	12.2	11.3	14.5	8.8	12.0
PN	6.7	−1.9	−0.8	−6.1	−5.8	−18.7	−0.5	−9.2	−3.8	−22.8	−30.3
SO ₂	4.3	−5.3	−3.5	−8.1	−9.6	−17.0	−2.5	−11.4	−3.3	−23.5	−23.1

^a Values are shown relative to the CCSD(T)/aug-cc- pCV[TQ]Z reference data.

Of the three model potentials studied, the older LB94 is surprisingly weak. Of all DFT methods studied, it shows the largest deviations from the reference data. The GRAC-LB and especially SAOP potentials, on the other hand, perform quite well. There seems to be, however, no advantage of using SAOP or GRAC-LB compared to well-performing standard functionals. Indirectly, it shows that a correct asymptotic behavior of the potential is not, as such, sufficient for obtaining good magnetizabilities; this has previously been noted also for excitation energies.⁸³ It should be noted that in ref 4 the Coulomb attenuated CAM-B3LYP,⁸⁴ with improved asymptotic behavior over the original B3LYP,^{85,86} did improve magnetizabilities.

The molecules where correlation is most important, measured as the largest relative errors of HF compared to CCSD(T), are, in decreasing order, O₃ (378%), OF₂ (9.9%), CH₂O (9.5%), SO₂ (−4.0%), HOF (3.9%), and HCP (3.8%). One could expect that for these, at least, DFT methods would outperform HF. We first consider LDA and the GGA's as well as the three model potentials for which this is *not* the case. For ozone, there is a clear improvement but the errors in general are still very large at the DFT level. For OF₂, the absolute error is of the same magnitude. It is however consistently of opposite sign, thus indicating an overcorrection. This overcorrection is even more serious in the case of CH₂O, where the absolute errors are significantly larger than for Hartree–Fock. For LDA and all the GGA's, these two molecules are, after O₃, the most problematic of the moderately correlated molecules. For all of these, the triple excitations are also significant. Coupled cluster with single and double excitations, CCSD,⁸⁷ is still in error by 3.3% (OF₂), 3.4% (CH₂O), and 39% (O₃).⁴

Nevertheless, problems at the DFT level are also observed for the molecules where triple excitations are not important. For SO₂, most functionals actually increase the absolute error. HOF and HCP still exhibit the same trend, with the DFT functionals providing roughly the same absolute error as HF but of opposite sign.

The situation changes when investigating the above subset of molecules at the TPSS level. The very good agreement between TPSS and CCSD(T) for ozone was already commented on. For the other molecules with an important correlation contribution, TPSS provides an improvement over Hartree–Fock that brings the magnetizabilities much closer to the CCSD(T) reference, with relative errors ranging from −0.1% (SO₂) to 4.0% (CH₂O). For all of these molecules, TPSS also clearly outperforms KT2, which again suggests that the added completeness in the description of exchange and correlation at the meta-GGA level is important.

The subset of molecules where the correlation contribution to magnetizability is very small, 1% or less, consists of C₃H₄ (−0.2%), H₂S (−0.5%), CH₃F (0.7%), CH₄ (−1.0%), and NH₃ (−1.0%). With the exception of C₃H₄, all of these are described quite well by DFT, which suggests that where exchange only is important DFT does not overshoot the correlation correction and thus works well. The case of C₃H₄, where the HF value is closest to the CCSD(T) reference data, is special, with DFT errors being quite large, between −3.0% for LDA up to −5.2% for the GGA's and model potentials. TPSS again performs best but is still in error by 1.7%. Studying the convergence for this molecule in the series HF → CCSD → CCSD(T) reveals that correlation effects *are* present but hidden by the fact that going from CCSD to CCSD(T) brings the value back toward the HF value. For

Table 6. Statistical Error Analysis for the Self-Interaction-Corrected Density Functional Methods Studied, Computed with the QZ4P Basis Set^a

method	ME	MAE	MaxE	MRE	MARE	SD
SIC-LDA	10.1	10.1	23.6	−3.4%	3.4%	5.7
SIC-PBE	4.4	6.0	12.3	−1.5%	2.1%	5.4
SIC-PBESol	5.5	6.5	15.6	−1.9%	2.2%	5.5
SIC-OPBE	2.7	6.3	10.6	−0.9%	2.0%	5.9
SIC-SSB-D	1.7	4.7	12.0	−0.6%	1.6%	5.7
SIC-KT2	−4.0	6.6	−18.7	1.4%	2.4%	7.2
SIC-PW91	4.8	4.8	13.5	−1.7%	2.2%	5.9
SIC-BP86	2.5	6.1	12.1	−0.8%	2.2%	6.9
SIC-LB94	5.8	7.3	19.4	−1.7%	2.5%	6.7
SIC-SAOP	−1.3	7.7	−23.5	0.4%	2.8%	10.0
SIC-GRAC	−3.6	7.6	−30.3	1.3%	2.5%	9.8

^a Mean error (ME), mean absolute error (MAE), maximum error (MaxE), mean relative error (MRE), mean absolute relative error (MARE), and standard deviation (SD) are shown. Except for the relative errors, units are $10^{-30} \text{ J T}^{-2}$.

the other “low correlation” molecules, the magnetization consistently becomes (slightly) more negative when correlation is described more completely in the ab initio series. Correlation is thus present in cyclopropene (still to a relatively small degree), but its various effects cancel.

Another anomaly that is worth mentioning is LiH. For this four-electron molecule, the correlation effect is quite small, −1.5%, and the triples contribution negligible. Despite this, all functionals, save GRAC-LB, perform poorly. The reason could be that for LiH, the potential energy surface is very shallow⁷² and small changes in geometry, although energetically insignificant, could have a notable effect on magnetizability. Thus, the errors for this molecule could be somewhat artificial. We discuss this in more detail in the following section.

3.3. Effect of Self-Interaction Correction. Almost all contemporary functionals and all functionals studied in the previous section including the model potentials⁸⁸ suffer from an unphysical self-interaction of the electrons. Also, TPSS, even if it describes the hydrogen atom correctly in this regard,

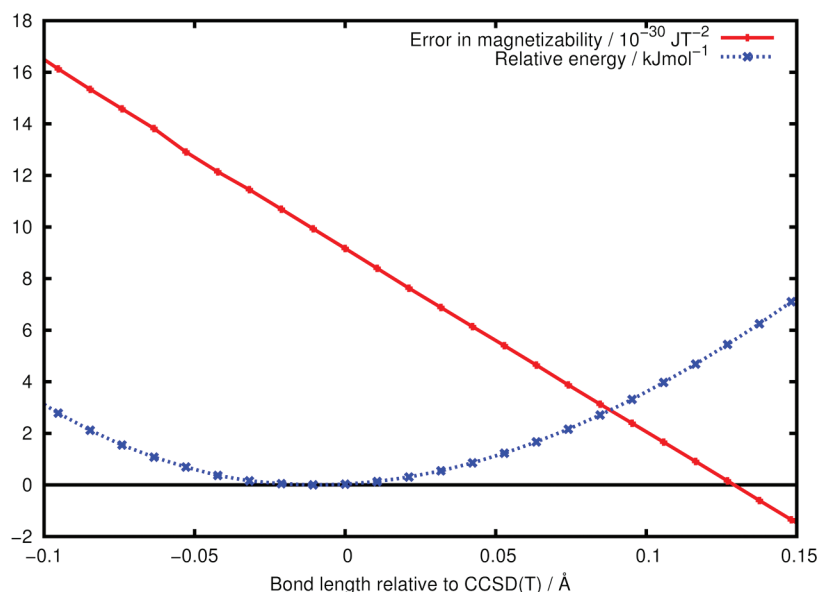
suffers from many-electron self-interaction,⁷⁵ an effect more complicated to quantify than “simple” one-electron self-interaction.^{89,90} In this section, we study the influence of (approximately) removing self-interaction from the standard functionals considered in the previous section. Table 5 shows the magnetizabilities computed at the SIC-DFT level, and Table 6 summarizes the error statistics.

We again start with a general overview of the error statistics. For SIC-LDA, both the mean error and the mean absolute error actually increase compared to standard LDA. The mean absolute relative error is slightly decreased. The errors become much more systematic, however, with the standard deviation halved. For all molecules except ozone, SIC-LDA now provides consistently too positive magnetizabilities.

All of the GGA’s, with one exception, gain a substantial error reduction from SIC. The standard deviation drops below $6 \times 10^{-30} \text{ J T}^{-2}$ for most functionals and the mean absolute relative error to around 2%; SIC-SSB-D is now the most accurate functional, with a MRE of −0.6% and a MARE of 1.6%. The one exception is SIC-KT2, with a performance almost identical to that of standard KT2. SIC does affect the KT2 values too, but overall the correction is too large; the mean error changes from $+5.4 \times 10^{-30}$ to $-4.0 \times 10^{-30} \text{ J T}^{-2}$. As the parent functional was already explicitly tuned for magnetic properties, the increased accuracy observed for the other functionals is absent.

Of the model potentials, SIC-LB94 performs significantly better than its parent and is now almost on par with the GGA’s. Still, there is no advantage in using LB94 over normal functionals. Neither SIC-SAOP nor SIC-GRAC-LB represent improvements over their uncorrected versions.

Looking at ozone, we observe a dramatic change when doing the SIC correction. The magnetizability, at all SIC levels, is lowered significantly and instead of being much too positive compared to CCSD(T) becomes not nearly positive enough. This can be related to the effect that despite

**Figure 1.** Magnetizability as a function of the bond length relative to the CCSD(T) value of 1.596 Å (red curve) and relative energy (blue curve), computed at the SIC-SSB-D/QZ4P level.

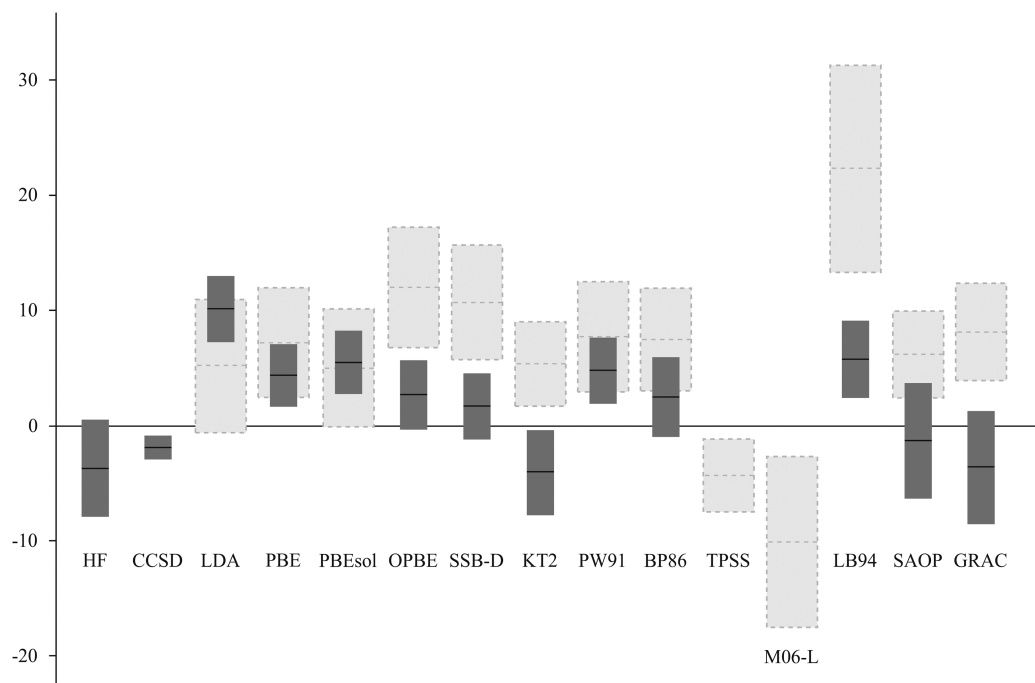


Figure 2. Mean errors and standard deviations of magnetizabilities (in SI units, $10^{-30} \text{ J T}^{-2}$) at different levels of theory. Light-gray boxes represent uncorrected, self-interaction including functionals; dark-gray boxes self-interaction-corrected (or self-interaction free) methods. The boxes are centered at the mean error of the method, and the vertical size of the boxes correspond to the standard deviation, both relative to the CCSD(T)/aug-cc-pCV[TQ]Z reference data from ref 4.

its many drawbacks, the self-interaction error present in standard functionals mimics static correlation, with the effect that DFT usually works quite well for mild multireference species; with the SIE removed, this advantageous side effect also disappears.^{34,21,91–96}

For CH_2O and OF_2 , the two other molecules with a significant contribution from the triple excitations in wave function theory, SIC-DFT performs remarkably well, although the description of CH_2O is still somewhat lacking. The exception is again SIC-KT2, where, in effect, only the sign of the error changes.

For the other molecules in the benchmark set, SIC-DFT almost consistently reduces the error at the GGA level. A somewhat surprising exception here is water, for which SIC-DFT in all cases performs notably worse than uncorrected DFT. The error for LiH also increases slightly but as discussed in the previous section could be artificial. Figure 1 shows how the error in magnetizability, compared to the CCSD(T) reference, evolves with a change of the bond length, computed at the SIC-SSB-D level, along with the relative energy. The sensitivity of the magnetizability toward the bond length is striking: with distortions between -0.05 and $+0.05 \text{ \AA}$ around the equilibrium bond length computed at CCSD(T) level, the energy difference is minute but the error in magnetizability drops from 13 to $5.6 \times 10^{-30} \text{ J T}^{-2}$.

Thus, using nonhybrid SIC-DFT, reliable magnetizabilities are obtainable. SIC-SSB-D provides the best overall performance. For self-interaction-corrected condensed matter studies,^{97,98} SIC-PBEsol could be a good choice. It would also be interesting to see how meta-GGA's would perform with SIC applied to them. The possibility of a further error reduction for, e.g., TPSS is appealing.

4. Summary and Conclusions

We studied the performance of several functionals and model exchange-correlation potentials for magnetizabilities using the recent high-quality reference set by Lutnæs et al. Of the standard functionals, without self-interaction correction, we find that the nonempirical TPSS meta-GGA performs very well, having a mean relative error (MRE) of only 1.3% and a standard deviation (SD) of $6.3 \times 10^{-30} \text{ J T}^{-2}$ compared to the reference CCSD(T) set with a mean value of magnetizability of $-324 \times 10^{-30} \text{ J T}^{-2}$. TPSS correlation is self-interaction free, and the exchange part is notably more physically correct in this respect compared to LDA and GGA's,⁷⁵ which with the results of the SIC functionals presented in this work suggests a reason for the good performance of this meta-GGA. Pending a rigorous implementation of gauge-independent magnetizabilities at the meta-GGA level, the reader should consider the values reported here somewhat preliminary though. Of the GGA's, KT2 performs best. The SSB-D functional exhibits a performance between that of its major constituents, PBE and OPBE. The model potentials LB94, SAOP, and GRAC-LB, designed for providing a correct asymptotic behavior, do not outperform standard functionals; LB94 performs quite poorly, and SAOP and GRAC-LB perform no better than normal functionals.

Correcting for the electron self-interaction present in the functionals leads to a significant reduction of the errors in almost all cases. With self-interaction correction, the best GGA studied here, SIC-SSB-D, provides a MRE of only -0.6% , a MAE of $4.7 \times 10^{-30} \text{ J T}^{-2}$, and a SD of $5.7 \times 10^{-30} \text{ J T}^{-2}$. Further, other GGA's closely follow. Notably, SIC leads to a significant reduction of the SD at LDA and

most GGA levels. Figure 2 summarizes the presented results, with the mean errors and standard deviations of both the standard and the self-interaction corrected methods depicted graphically.

Overall, DFT methods *can* be used to get reliable magnetizabilities. To achieve this level of quality, in addition to using a suitable functional, a minimum requirement is an all-electron polarized triple- ζ quality basis set, employed within a gauge-independent formalism.

It is perhaps fair to say that magnetizability is a second-order property not only mathematically, even with its direct relation to bulk permeabilities and susceptibilities, and to the spontaneous ordering of molecules in a magnetic field. This underappreciation is probably partly due to the experimental difficulties associated with the measurement of magnetizabilities. This could, of course, be seen as an excellent opportunity for chemical theory and computation to excel, especially as reliable computations can be performed at the “pure” DFT level, without costly Hartree–Fock exchange, as shown here. The good performance of the nonempirical meta-GGA TPSS and the SIC including GGA’s and conversely the poor performance of standard DFT methods further suggest that magnetizability could be used as a guiding property when designing new density functionals as it seems to be a quite sensitive measure of a correct description of the underlying physics and chemistry.

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