First-Principles Calculation of Transition Metal Hyperfine Coupling Constants with the Strongly Constrained and Appropriately Normed (SCAN) Density Functional and its Hybrid Variants

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Abstract: Density functional theory (DFT) is used extensively for the first-principles calculation of hyperfine coupling constants in both main-group and transition metal systems. As with many other properties, the performance of DFT for hyperfine coupling constants is of variable quality, particularly for transition metal complexes, because it strongly depends on the nature of the chemical system and the type of approximation to the exchange-correlation functional. Recently, a meta-generalized-gradient approximation (mGGA) functional was proposed that obeys all known exact constraints for such a method, known as the Strongly Constrained and Appropriately Normed (SCAN) functional. In view of its theoretically superior formulation a benchmark set of complexes is used to assess the performance of SCAN for the challenging case of transition metal hyperfine coupling constants. In addition, two global hybrid versions of the functional, SCANh and SCAN0, are described and tested. The values computed with the new functionals are compared with experiment and with those of other DFT approximations. Although the original SCAN and the SCAN-based hybrids may offer improved hyperfine coupling constants for specific systems, no uniform improvement is observed. On the contrary, there are specific cases where the new functionals fail badly due to a flawed description of the underlying electronic structure. Therefore, despite these methodological advances, systematically accurate and system-independent prediction of transition metal hyperfine coupling constants with DFT remains an unmet challenge.

Keywords: hyperfine coupling; density functional theory; spectroscopy; hybrid functionals

1. Introduction

Advancements in the theoretical framework for the calculation of electron paramagnetic resonance (EPR) parameters on the basis of Kohn–Sham density functional theory (DFT) [1], combined with the continuous improvement in the quality of approximate exchange–correlation functionals [2,3], have significantly expanded the scope of DFT calculations beyond simplistic considerations of potential energy surface features, enabling their tight integration with experimental spectroscopy in modern research [4–6]. The ability to compute with reasonable accuracy all properties relevant for EPR spectroscopy, i.e., g-values, hyperfine coupling constants, and zero-field splitting parameters, is well established for organic and main-group molecules. On the other hand, it is well documented that the performance of DFT for EPR parameters of transition metal systems is inconsistent and highly system-dependent [4]. Although it is usually possible to identify a DFT-based methodological approach that provides results of useful accuracy for a specific EPR property in a chemically closely related class of transition metal complexes, any given functional thus selected is rarely equally successful when applied to different systems. This limited transferability means that in DFT calculations of EPR

parameters for transition metal complexes one often relies on fortuitous cancellation of different errors with possibly distinct physical origins and non-transparent methodological causes. Thus, if one is restricted by choice or practical necessity to use DFT instead of rigorous wave function based methods for predicting EPR parameters in transition metal systems, the choice of functional is typically dictated by experience accumulated in previously published studies of related systems or by performing an initial benchmarking study. Among the EPR parameters that react most sensitively to the choice of computational methodology are hyperfine coupling constants [7–14].

Hyperfine coupling refers to the interaction between unpaired electrons and magnetic nuclei, i.e., between the electron spin $\hat{S}$ and the nuclear spin $\hat{I}$ ($\hat{H} = \hat{S}\mathbf{A}\hat{I}$). The hyperfine coupling tensor for a given nucleus N consists of three contributions, the isotropic Fermi contact term (A^{FC}), the anisotropic spin–dipolar (A^{SD}), and the spin–orbit coupling (SOC) contributions (A^{SO}):

$$A(N) = A^{FC} + A^{SD} + A^{SO} \tag{1}$$

The Fermi contact term arises from non-vanishing spin density at the point of the nucleus:

$$A^{FC}(N) = \frac{4\pi}{3} g_e g_N \beta_e \beta_N \langle S_z \rangle^{-1} \rho^{\alpha-\beta}(\mathbf{R}_N) \tag{2}$$

In the above equation g_e and g_N are the g-factors of the electron and the nucleus, and β_e and β_N are the electronic and nuclear magnetons. The product $g_e g_N \beta_e \beta_N$ is commonly abbreviated as P_N and is a scaling factor (with units MHz au^{-3}) fixed for a given nucleus. $\langle S_z \rangle$ is the expectation value of the z component of the total spin and $\rho^{\alpha-\beta}(\mathbf{R}_N)$ is the spin density at the position of nucleus N. The spin dipolar part of the hyperfine tensor describes the magnetic dipole interaction of the magnetic nucleus with the electron magnetic moment:

$$A^{SD}_{kl}(N) = \frac{1}{2} P_N S_z^{-1} \sum_{\mu,\nu} P^{\alpha-\beta}_{\mu,\nu} \langle \varphi_\mu | \mathbf{r}_N^{-5}(\mathbf{r}_N^2 \delta_{kl} - 3\mathbf{r}_{N,k}\mathbf{r}_{N,l}) | \varphi_\nu \rangle \tag{3}$$

where $\mathbf{r}_N = \mathbf{r} - \mathbf{R}_N$ and $P^{\alpha-\beta}_{\mu,\nu}$ is the spin density matrix with the indices denoting basis functions. Finally, spin–orbit coupling gives rise to the second-order contribution to the hyperfine coupling tensor. This can be obtained with the mean-field approximation to the SOC operator (SOMF) [15] as:

$$A^{SO}_{kl}(N) = -\frac{1}{S} P_N \sum_{\mu,\nu} \frac{\partial P^{\alpha-\beta}_{\mu,\nu}}{\partial \hat{I}_k} \langle \varphi_\mu | \hat{z}_l^{SOMF} | \varphi_\nu \rangle \tag{4}$$

Practical applications of DFT for the calculation of hyperfine coupling tensors have met with mixed success. For organic radicals usually good results can be obtained with a variety of density functionals in conjunction with basis sets that are developed specifically for the calculation of EPR properties. The picture is different for transition metal systems, where the quality of computed hyperfine coupling tensors varies widely with the nature of the chemical system, the oxidation state of the metal, and the choice of functional. The presence of multiple exchange-coupled transition metal centers introduces additional layers of complication that will not be discussed here [16–18].

The Fermi contact term depends on how a given functional describes core (s orbital) spin polarization induced by unpaired d orbital spin density and, hence, it is sensitive to the quality of the electronic structure description afforded by a particular density functional for a given transition metal complex. Modern functionals typically underestimate core spin polarization, often significantly [7]. Dipolar coupling is principally determined by the spin density distribution in the valence region. Thus it already becomes clear that a functional needs to provide a very balanced description of the core and valence electronic structure and spin density distribution to perform well for both A^{FC} and A^{SD}. Moreover, the A^{SO} term can have heightened importance for transition metal complexes compared

to organic systems, even for first-row transition metal complexes, introducing additional challenges for DFT.

Certain patterns in terms of performance may be identified with respect to the distinct families of density functionals. In the generalized gradient approximation (GGA) to DFT, the density and its gradient are employed. In meta-GGA (mGGA) functionals the Laplacian of the density or the local kinetic energy density are included. Hybrid functionals utilize a GGA or mGGA functional as starting point and incorporate a percentage of exact (Hartree–Fock) exchange, typically empirically adjusted. Double-hybrid functionals incorporate in addition a second-order perturbation term. The underestimation by DFT of core spin polarization can be partly counteracted by admixture of exact exchange in hybrid functionals. However, this is an ad hoc fix that may introduce other problems, for example related to spin contamination, and adversely affect contributions to hyperfine coupling other than the Fermi contact term. Thus, although hybrid functionals are generally considered superior to GGA functionals for specific families of compounds, their use does not automatically guarantee a balanced treatment of the physically diverse contributions to the hyperfine coupling tensor and hence cannot achieve uniformly higher accuracy. Local hybrids with variable position-dependent admixture of exact exchange are being developed as a potential way forward [13]. Nevertheless, it is important to seek improvements in the theoretical method already at the GGA and mGGA levels so that reliance on error cancellation by selective inclusion of exact exchange is minimized or altogether avoided.

The development of new density functionals is being pursued along conceptually distinct approaches [19–21]. One of them adopts the empirical adjustment of several parameters against datasets so that a functional reproduces as well as possible known values for a series of reference systems. Typically, the reference values are various types of energetics; spectroscopic parameters are seldom, if ever, used to guide the optimization of the empirical parameters. An alternative approach emphasizes the necessity of obeying known constraints and physical conditions (such as various upper/lower bounds, exact limiting cases and scaling relationships) on the assumption that a functional which is able by construction to obey as many as possible of these constraints and is able to converge to the correct answers for limiting cases should in principle be describing the actual physics of a system in a fundamentally superior manner. This in turn leads to the expectation of improved results for all kinds of properties. One of the latest functionals to be constructed along the lines of this non-empirical approach is the strongly constrained and appropriately normed (SCAN) functional by Sun, Ruzsinszky, and Perdew [22]. SCAN is an mGGA functional and the first to obey all known exact constraints (17 in total) that can apply to a density functional of this type. In addition, it is either exact or nearly exact for a set of "appropriate norms" that include rare-gas atoms and non-bonded interactions [22].

Studies that examined the performance of SCAN and certain derivative functionals have already indicated that it performs well for a variety of energy-related properties, usually surpassing previous GGA and mGGA approaches [22–31]. However, it is unclear whether these advances also translate into improved description of the physical mechanisms that give rise to the distinct contributions to hyperfine coupling. In the present study the performance of SCAN is tested for the challenging case of transition metal hyperfine coupling tensors using a reference set of transition metal complexes that cover most of the 3d elements. Moreover, two hybrid versions of the functional that incorporate either 10% or 25% of Hartree–Fock exchange (SCANh and SCAN0) are defined and assessed. The results are compared to experiment as well as to representative GGA, meta-GGA, and hybrid-meta-GGA functionals. In addition, a series of methodological considerations regarding the applicability of SCAN are examined.

2. Results

2.1. Reference Set of Transition Metal Systems

For the purposes of the present study a set of small first-row transition metal containing molecules is used. The compounds almost cover the complete 3d series and are selected because they have

experimentally known and resolved hyperfine coupling constants and have been employed previously in analogous evaluations of theoretical methods [10,32]. The compounds used along with their total spin states are: ScO ($S = 1/2$), TiF$_3$ ($S = 1/2$), [V(H$_2$O)$_6$]$^{2+}$ ($S = 3/2$), [VO(H$_2$O)$_5$]$^{2+}$ ($S = 1/2$), MnF ($S = 2$), MnO$_3$ ($S = 1/2$), [Mn(H$_2$O)$_6$]$^{2+}$ ($S = 5/2$), Mn(CO)$_5$ ($S = 1/2$), [Fe(CO)$_5$]$^{+}$ ($S = 1/2$), NiH(CO)$_3$ ($S = 1/2$), [Ni(mnt)$_2$]$^{-}$ ($S = 1/2$), [Cu(NH$_3$)$_4$]$^{2+}$ ($S = 1/2$), [Cu(dtc)$_2$] ($S = 1/2$), and [Cu(en)$_2$]$^{2+}$ ($S = 1/2$), where mnt = maleonitriledithiolate, dtc = dithiocarbamate, and en = ethylenediamine. For completeness, it is noted that the isotopes and nuclear spins assumed here are: ^{45}Sc ($I = 7/2$), ^{47}Ti ($I = 5/2$), ^{51}V ($I = 7/2$), ^{55}Mn ($I = 5/2$), ^{57}Fe ($I = 1/2$), ^{61}Ni ($I = 3/2$), and ^{63}Cu ($I = 3/2$). The default values implemented in the ORCA program package [33] were employed for the scaled nuclear g-values P_N.

2.2. Performance of SCAN in Comparison With Other Density Functionals

To place the performance of SCAN in context, Table 1 compares the detailed hyperfine parameters obtained by SCAN with those obtained using standard density functionals, the GGA BP86 [34,35], the mGGA TPSS [36], its hybrid version TPSSh (10% exact exchange) [37], B3LYP (20% exact exchange) [38,39], BHandHLYP (50% exact exchange), and CAM-B3LYP (range-dependent exact exchange from 19% to 65%) [40]. The table includes results from hybrid versions of SCAN that will be discussed in more detail in the following section. In all cases appropriate core-property CP(PPP) basis sets [41] with extensive polarization and a highly flexible inner-core subset of s-type functions were used (see Computational Details). The table includes experimental values for the hyperfine coupling constants. In some cases, experimental values are also available for the distinct contributions to the hyperfine tensor (A^{FC} and A^{SD}) and these are also listed in the respective columns. It is noted that the HFC components are listed in all cases from smaller to larger absolute value. The computed total values reported in Table 1 incorporate the spin-orbit coupling contributions (A^{SO}), which are only significant for Cu and secondarily for Ni complexes. The A^{SO} values are listed for all compounds and functionals in Table A1 of Appendix A.

Table 1. Hyperfine coupling constants (in MHz) computed with different density functionals.

Compound	Functional	A_{11}	A_{22}	A_{33}	A^{FC}	$A_{11}{}^{SD}$	$A_{22}{}^{SD}$	$A_{33}{}^{SD}$
ScO	BP86	1923.2	1923.2	1981.8	1943.3	−19.3	−19.3	38.6
	TPSS	1766.1	1766.1	1825.7	1786.5	−19.6	−19.6	39.3
	TPSSh	1763.5	1763.5	1825.1	1784.6	−20.3	−20.3	40.6
	B3LYP	1970.0	1970.0	2031.2	1991.0	−20.1	−20.1	40.2
	BHandHLYP	1932.1	1932.1	2000.5	1955.6	−22.5	−22.5	45.1
	CAM-B3LYP	2024.0	2024.0	2087.2	2045.6	−20.8	−20.8	41.7
	SCAN	−218.3	−218.3	−328.3	−252.1	35.2	35.2	−70.5
	SCANh	−230.1	−230.1	−342.2	−264.5	35.8	35.8	−71.7
	SCAN0	−247.7	−247.7	−363.2	−283.2	36.8	36.8	−73.6
	Exp. [42]	1922	1922	1997	1947	−25	−25	50
TiF$_3$	BP86	−210.9	−210.9	−241.6	−223.1	9.4	9.4	−18.7
	TPSS	−195.8	−195.8	−224.2	−206.9	8.8	8.8	−17.6
	TPSSh	−181.1	−181.1	−210.2	−192.6	8.9	8.9	−17.9
	B3LYP	−183.7	−183.7	−217.8	−197.5	10.2	10.2	−20.4
	BHandHLYP	−143.1	−143.1	−178.5	−158.3	10.1	10.1	−20.3
	CAM-B3LYP	−175.7	−175.7	−208.0	−187.2	10.5	10.5	−20.9
	SCAN	34.0	34.1	84.1	48.1	−16.2	−14.9	31.1
	SCANh	34.9	35.2	86.4	49.4	−15.3	−16.4	31.7
	SCAN0	36.0	37.0	89.9	51.1	−15.9	−16.7	32.6
	Exp. [43]	−178	−178	−199	−185	7	7	−14

Table 1. *Cont.*

Compound	Functional	A_{11}	A_{22}	A_{33}	A^{FC}	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}
$[V(H_2O)_6]^{2+}$	BP86	−170.5	−170.5	−170.8	−161.2	0.0	0.0	−0.1
	TPSS	−179.8	−179.8	−180.0	−171.6	0.0	0.0	−0.1
	TPSSh	−191.9	−191.9	−192.1	−183.4	0.0	0.0	−0.1
	B3LYP	−169.4	−169.4	−169.7	−159.4	0.1	0.1	−0.1
	BHandHLYP	−202.2	−202.2	−202.6	−191.4	0.1	0.1	−0.1
	CAM-B3LYP	−162.1	−162.1	−162.3	−158.1	0.0	0.0	−0.1
	SCAN	−230.4	−230.4	−230.7	−223.4	0.1	0.1	−0.2
	SCANh	−236.7	−236.7	−237.1	−229.5	0.1	0.1	−0.2
	SCAN0	−245.1	−245.1	−245.4	−237.4	0.1	0.1	−0.2
	Exp. [44]	−247	−247	−247				
$[VO(H_2O)_5]^{2+}$	BP86	−162.4	−163.3	−471.0	−252.3	97.1	96.4	−193.5
	TPSS	−179.8	−180.5	−485.8	−270.4	97.2	96.7	−193.9
	TPSSh	−204.5	−205.0	−514.5	−295.5	98.1	97.8	−195.9
	B3LYP	−178.8	−179.1	−503.2	−271.8	101.2	101.0	−202.1
	BHandHLYP	−269.2	−272.8	−599.0	−361.4	102.7	99.5	−202.2
	CAM-B3LYP	−175.4	−175.9	−489.0	−273.6	101.7	101.2	−202.9
	SCAN	−215.6	−216.0	−500.4	−299.3	90.9	90.4	−181.2
	SCANh	−238.9	−239.6	−527.1	−323.1	91.8	91.1	−183.0
	SCAN0	−275.4	−276.7	−568.0	−360.0	93.0	91.7	−184.7
	Exp. [45]	−208	−208	−547				
MnF	BP86	433.5	433.5	495.1	444.3	−14.7	−14.7	29.3
	TPSS	413.8	413.8	478.8	432.7	−16.1	−16.1	32.1
	TPSSh	397.3	397.3	467.2	417.0	−17.3	−17.3	34.5
	B3LYP	443.0	443.0	507.1	441.8	−16.5	−16.5	32.9
	BHandHLYP	457.2	457.2	525.3	430.7	−18.7	−18.7	37.4
	CAM-B3LYP	402.3	402.3	464.2	423.7	−17.9	−17.9	35.7
	SCAN	492.4	492.4	547.4	511.2	−13.7	−13.7	27.5
	SCANh	478.7	478.7	537.9	498.5	−14.8	−14.7	29.5
	SCAN0	459.9	459.9	525.5	480.8	−16.1	−16.1	32.3
	Exp. [46]	430	430	466	442	−12	−12	24
MnO$_3$	BP86	1818.4	1818.4	2124.9	1934.2	−96.9	−96.9	193.7
	TPSS	1750.4	1750.4	2040.1	1859.4	−92.0	−91.9	183.9
	TPSSh	1590.3	1590.4	1916.6	1712.5	−104.4	−104.4	208.8
	B3LYP	1520.0	1520.0	1917.6	1667.8	−128.5	−128.4	256.9
	BHandHLYP	1366.2	1366.2	1607.1	1455.8	−75.9	−75.9	151.9
	CAM-B3LYP	1427.9	1427.9	1874.9	1586.5	−147.2	−147.2	294.4
	SCAN	1714.2	1714.3	2016.3	1828.5	−97.2	−97.1	194.4
	SCANh	1502.8	1502.9	1877.0	1642.9	−121.8	−121.7	243.5
	SCAN0	1163.6	1164.1	1656.6	1346.2	−162.8	−162.3	325.1
	Exp. [47]	1532	1532	1775	1613	−81	−81	162
$[Mn(H_2O)_6]^{2+}$	BP86	−162.0	−162.2	−162.2	−159.2	0.1	0.0	0.0
	TPSS	−173.2	−173.4	−173.4	−170.4	0.1	−0.1	−0.1
	TPSSh	−187.7	−188.0	−188.0	−185.1	0.2	−0.1	−0.1
	B3LYP	−163.7	−163.9	−163.9	−161.3	0.1	−0.1	−0.1
	BHandHLYP	−197.4	−197.7	−197.7	−195.5	0.2	−0.1	−0.1
	CAM-B3LYP	−165.1	−165.3	−165.3	−162.9	0.1	−0.1	−0.1
	SCAN	−221.7	−222.1	−222.1	−219.0	0.2	−0.1	−0.1
	SCANh	−229.7	−230.1	−230.1	−227.1	0.3	−0.1	−0.1
	SCAN0	−240.3	−240.7	−240.7	−238.0	0.3	−0.1	−0.1
	Exp. [48]	−245	−245	−245				

Table 1. *Cont.*

Compound	Functional	A_{11}	A_{22}	A_{33}	A^{FC}	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}
$Mn(CO)_5$	BP86	−80.9	−81.0	202.5	12.0	−95.9	−96.0	191.8
	TPSS	−79.2	−79.3	195.9	11.6	−92.9	−93.0	185.9
	TPSSh	−83.4	−83.5	190.7	7.2	−92.7	−92.8	185.5
	B3LYP	−81.7	−81.8	201.7	11.1	−96.3	−96.4	192.7
	BHandHLYP	−74.2	−74.3	176.8	9.9	−85.7	−85.8	171.5
	CAM-B3LYP	−83.1	−83.2	207.9	15.5	−96.8	−96.9	193.7
	SCAN	−109.1	−109.2	161.0	−19.4	−90.7	−90.8	181.5
	SCANh	−106.4	−106.5	160.9	−17.5	−89.8	−89.9	179.7
	SCAN0	−96.2	−96.4	162.5	−9.9	−87.0	−87.2	174.2
	Exp. [49]	−86	−86	190	6	−92	−2	194
$[Fe(CO)_5]^+$	BP86	−15.2	−15.3	36.5	0.6	−18.1	−18.1	36.1
	TPSS	−14.9	−14.9	36.1	1.0	−17.7	−17.7	35.5
	TPSSh	−16.9	−17.0	34.9	−1.0	−18.1	−18.2	36.3
	B3LYP	−17.4	−17.5	36.4	−1.5	−19.2	−19.2	38.4
	BHandHLYP	−21.5	−21.5	32.2	−6.3	−19.7	−19.8	39.5
	CAM-B3LYP	−20.8	−20.9	37.2	−1.7	−19.6	−19.6	39.2
	SCAN	−19.5	−19.5	31.7	−3.1	−17.5	−17.6	35.1
	SCANh	−21.3	−21.3	30.4	−4.8	−17.8	−17.8	35.6
	SCAN0	−23.7	−23.8	28.5	−7.3	−18.2	−18.2	36.4
	Exp. [50]	−17	−17	28	−2	−15	−15	30
$NiH(CO)_3$	BP86	50.7	50.7	−88.1	12.8	50.1	50.2	−100.3
	TPSS	49.5	49.6	−91.3	11.0	50.8	50.8	−101.5
	TPSSh	52.6	52.6	−94.1	15.2	53.9	54.0	−107.9
	B3LYP	55.3	55.3	−95.0	21.7	57.2	57.2	−114.3
	BHandHLYP	46.9	46.9	−107.7	36.1	67.6	67.6	−135.2
	CAM-B3LYP	77.4	77.5	−95.5	25.1	59.8	59.8	−119.7
	SCAN	59.8	59.9	−91.7	17.2	53.9	53.9	−107.8
	SCANh	69.0	69.1	−88.3	27.2	56.7	56.8	−113.5
	SCAN0	81.4	81.5	−83.3	43.0	61.0	61.0	−122.0
	Exp. [51]	53	53	−79				
$[Ni(mnt)_2]^-$	BP86	−9.4	−11.1	47.7	24.7	−30.1	−25.7	55.8
	TPSS	−16.3	−17.2	45.3	19.5	−31.8	−26.4	58.2
	TPSSh	−16.6	−17.3	45.7	23.4	−26.4	−34.8	61.2
	B3LYP	−13.8	−16.0	41.1	26.8	−24.6	−33.6	58.2
	BHandHLYP	6.3	−13.5	35.2	23.9	−12.4	−15.4	27.8
	CAM-B3LYP	−0.9	−11.1	75.8	28.0	−24.7	−36.1	60.8
	SCAN	1.1	1.8	70.1	38.9	−27.9	−32.9	60.8
	SCANh	0.1	−2.4	69.4	40.4	−27.5	−36.7	64.3
	SCAN0	1.8	−8.6	64.8	43.9	−24.3	−41.1	65.4
	Exp. [52]	<6	9	45				
$[Cu(NH_3)_4]^{2+}$	BP86	−11.1	−11.1	−516.4	−264.4	206.2	206.2	−412.5
	TPSS	−6.9	−7.0	−542.6	−266.0	213.5	213.4	−426.9
	TPSSh	−25.7	−25.7	−593.7	−308.7	229.9	229.8	−459.7
	B3LYP	−18.6	−18.6	−584.0	−324.1	240.7	240.7	−481.4
	BHandHLYP	−2.7	−2.8	−618.4	−388.1	288.1	288.0	−576.1
	CAM-B3LYP	−67.4	−67.4	−755.9	−342.0	250.8	250.7	−501.4
	SCAN	−48.8	−50.5	−684.6	−326.4	239.7	238.0	−477.7
	SCANh	−66.0	−67.8	−734.3	−363.0	254.1	252.2	−506.3
	SCAN0	−76.6	−77.8	−782.4	−401.4	273.2	271.8	−545.0
	Exp. [53]	−27	−27	−586				

Table 1. *Cont.*

Compound	Functional	A_{11}	A_{22}	A_{33}	A^{FC}	$A_{11}{}^{\text{SD}}$	$A_{22}{}^{\text{SD}}$	$A_{33}{}^{\text{SD}}$
[Cu(dtc)$_2$]	BP86	−45.5	−50.0	−393.6	−199.2	132.9	129.8	−262.7
	TPSS	−46.6	−50.5	−413.9	−207.7	139.4	136.7	−276.1
	TPSSh	−74.3	−78.7	−468.2	−251.1	151.5	148.3	−299.8
	B3LYP	−78.3	−83.8	−479.8	−264.5	157.9	154.1	−312.0
	BHandHLYP	−111.8	−116.5	−627.2	−376.4	214.7	211.1	−425.7
	CAM-B3LYP	−133.6	−139.4	−606.1	−319.2	171.1	165.9	−337.0
	SCAN	−97.5	−100.6	−510.5	−271.7	153.3	151.1	−304.4
	SCANh	−116.5	−120.2	−556.7	−305.9	165.2	162.5	−327.7
	SCAN0	−137.3	−141.4	−624.4	−353.6	186.0	182.9	−368.9
	Exp. [54]	−107	−125	−476				
[Cu(en)$_2$]$^{2+}$	BP86	−43.4	−43.5	−536.3	−279.3	197.3	196.2	−393.5
	TPSS	−41.5	−41.6	−560.6	−283.8	204.3	203.2	−407.5
	TPSSh	−66.2	−66.5	−617.6	−330.9	220.4	218.9	−439.3
	B3LYP	−64.5	−64.8	−619.4	−348.7	231.2	229.7	−460.9
	BHandHLYP	−58.8	−58.9	−681.9	−423.4	282.4	281.6	−564.1
	CAM-B3LYP	−105.3	−107.1	−773.3	−370.3	242.9	240.7	−483.6
	SCAN	−91.1	−91.9	−695.1	−351.9	226.9	225.8	−452.7
	SCANh	−113.5	−113.9	−752.2	−393.9	241.9	240.9	−482.9
	SCAN0	−128.9	−130.0	−13.8	−439.4	263.8	262.6	−526.4
	Exp. [55]	−78	−82	−602				

The picture emerging from the data in Table 1 is largely congruent with established experience from spectroscopy-oriented DFT applications in the sense that no single functional is a clearly superior performer across the board. TPSSh provides results closest to experiment for several compounds, SCAN or one of its hybrids for others, while BP86 also performs well in specific cases. There is no example for which TPSS is the best performing functional. The performance of the closely related functionals B3LYP, BHandHLYP and CAM-B3LYP, which differ in the percentage of global or range-dependent exact exchange, is not sufficiently systematic to allow for specific trends to be established. Overall, the variation in results and functional performance is so large that we prefer to refrain from reporting average errors. Such metrics cannot accurately reflect the deviations in individual components of the hyperfine and would be dominated by outliers, and therefore are not considered reliable in guiding method selection for properties where the performance of DFT functionals is unsystematic.

Going through the list of molecules one can see that BP86 is the "best" functional for ScO. TPSS and TPSSh both underestimate the magnitude of the hyperfine coupling constants, principally because they underestimate the Fermi contact term A^{FC}. Interestingly, both functionals yield almost identical values, suggesting that the exact exchange included in the hybrid TPSSh has absolutely no effect on core spin polarization. This is consistent with the fact that the sequence of B3LYP, BHandHLYP, and CAM-B3LYP hybrids perform similarly despite their fundamentally different exact exchange admixture. However, the most surprising result for this molecule concerns the SCAN functional, which diverges drastically from the other functionals and fails spectacularly to approximate the experimental values even qualitatively. If only the Fermi contact term would be different, then this problem could be attributed to a flawed description of core spin polarization. However, the spin-dipolar parameters are also qualitatively different from other methods, indicating that the origin of the problem is in the description of the valence electronic configuration itself. Indeed, by inspecting in detail the electronic structure of ScO as obtained from the different functionals, it is confirmed that whereas all other functionals place the sole unpaired electron in an s valence orbital, SCAN converges to a solution where the unpaired electron resides instead in a d orbital ($3d_{xy}$). It was confirmed with additional calculations that this is not a technical issue of converging to a local minimum during the self-consistent field procedure, but it is indeed intrinsically how SCAN describes this molecule.

Therefore, the divergence of this method for ScO is due to the fundamentally different description of the ground-state electronic structure.

A similar type of problem is encountered in the next compound of the test set, TiF_3. In this case CAM-B3LYP and TPSSh yield hyperfine coupling values closest to experiment. In contrast to all other functionals that describe the spin density as distributed in a hybrid sd orbital with predominant d character, SCAN yields a solution where the electron resides entirely in a pure d_{z^2} orbital of Ti with no s orbital contribution. Thus, for both ScO and TiF_3 SCAN fails simply due to the description of the valence region, something that comes across also from the fact that the A^{SD} values from SCAN are qualitatively different from those of all other functionals. This behavior hints at a potentially more general problem of the method, which would require closer scrutiny in dedicated future studies of transition metal systems.

In a way that is representative of the notorious unpredictability of DFT, SCAN, and its hybrid variants provide good hyperfine coupling constants for the next two compounds, $[V(H_2O)_6]^{2+}$ and $VO(H_2O)_5]^{2+}$, with TPSSh being the second-best. The success of SCAN for $[V(H_2O)_6]^{2+}$ appears to be in the description of core polarization because of the larger A^{FC} term. However, in the anisotropic vanadyl complex $[VO(H_2O)_5]^{2+}$ the role of A^{SD} also becomes important and in this case the divergence of SCAN from the other functionals affects the total values in a negative way as the component of largest magnitude is suppressed compared to TPSSh.

^{55}Mn hyperfine coupling constants are widely employed for probing the electronic structure of inorganic systems and biological cofactors, so they have received extensive attention in the experimental and computational literature [16–18,56–68]. The performance of different functionals for the four small Mn compounds of the present set highlights why careful benchmarking on a series of closely related complexes is always required for meaningful applications of DFT in this field. Focusing only on the values of the hyperfine coupling constants and how they compare with experiment, the best performing functional turns out to be BP86 for MnF, TPSSh, and B3LYP for MnO_3, SCAN (and even more so, SCAN0) for $[Mn(H_2O)_6]^{2+}$, and TPSSh again for $Mn(CO)_5$. In no case can the results be considered very good; the hyperfine coupling values in the more anisotropic systems reveal starkly the importance of getting right both the A^{FC} and the A^{SD} terms, which none of the functionals appears to achieve reliably. Interestingly, SCAN-based functionals are again the best performing methods for a hexa-aquo complex, similarly to the vanadium case. For the carbonyl compound $Mn(CO)_5$ SCAN produces an A^{FC} term with inverted sign, i.e., opposite spin polarization compared to the other functionals, which results in deviating total values for the hyperfine coupling despite the fact that the A^{SD} terms are rather similar for all methods.

The next two molecules, $[Fe(CO)_5]^+$ and $NiH(CO)_3$, are examples where all methods are reasonably well-behaved and do not produce widely varying values in absolute terms for the hyperfine coupling constants. The picture is somewhat different for $[Ni(mnt)_2]^-$. Here SCAN deviates more strongly from the other methods, even though there are no qualitative differences in the description of the electronic structure.

Finally, it proves difficult yet again to single out a specific density functional for the three copper complexes $[Cu(NH_3)_4]^{2+}$, $[Cu(dtc)_2]$, and $[Cu(en)_2]^{2+}$, since the experimental values are approximated with different degrees of success by different methods in each case. The difficulty of the problem is compounded in the case of copper by the fact that A^{SO} terms become comparable in magnitude to the other components of the hyperfine interaction (Table A1). It is noteworthy that SCAN deviates significantly from experiment and from the best performing TPSSh functional in the case of $[Cu(NH_3)_4]^{2+}$, a simple system often used for method calibration purposes. For $[Cu(dtc)_2]$ and $[Cu(en)_2]^{2+}$ TPSSh and SCAN perform well, but neither method succeeds in reproducing the experimental hyperfine coupling constants quantitatively.

2.3. Performance of Hybrid Variants of SCAN

The results presented above suggest that there is no one clearly superior functional that can be used reliably across all systems investigated in the present study. In terms of the role of exact exchange, the series of B3LYP, BHandHLYP, and CAM-B3LYP functionals show no definitive trend, given that the effect of the variation in exact exchange within this family of functionals depends on the compound. A methodological point that does emerge, however, is that the comparison between the mGGA functional TPSS and its hybrid variant TPSSh with 10% exact exchange is usually in favor of the latter. Therefore, admixture of exact exchange appears to be beneficial for this type of functional. This prompted us to investigate whether hybrid versions of SCAN might also offer improved performance for the property of interest. For this purpose we define two functionals, SCANh with 10% exact exchange and SCAN0 with 25% exact exchange, in direct analogy with the exact exchange percentages and the nomenclature used for the well-known TPSSh and PBE0 [69] non-empirical hybrid functionals. SCAN0 has been previously described by Hui and Chai [29], who similarly based the choice of 25% exact exchange on the construction of PBE0 as derived from the parent PBE GGA approximation [70,71]. We hypothesize that the lower percentage of exact exchange used in the TPSSh functional [37] might be more appropriate for a hybrid version of SCAN given the common mGGA nature of the underlying formalisms.

Compared to the values obtained with the original definition of SCAN, the exact exchange in the hybrid versions can be seen to affect all components of the hyperfine coupling. Importantly, the nature of the electronic structure that is predicted for each compound is not altered, therefore SCANh and SCAN0 do not afford a correct description of ScO and TiF_3, failing in exactly the same way as the parent SCAN. The results for the two vanadium compounds demonstrate vividly that the admixture of exact exchange primarily shifts the predicted values instead of uniformly reducing the overall errors. For $[V(H_2O)_6]^{2+}$ SCANh improves on SCAN and SCAN0 yields even better results that reproduce experiment very well. However, the corresponding results for $[VO(H_2O)_5]^{2+}$ suggest that this agreement is fortuitous, since the increase in exact exchange in this case leads to increasing deviations from experiment.

The results for the four manganese compounds in general improve with the hybrid versions. SCAN0 is the best performing SCAN-based functional for MnF, $[Mn(H_2O)_6]^{2+}$, and $Mn(CO)_5$, but MnO_3 presents a notable exception. For this compound SCANh performs best, on par with TPSSh, but further increase of exact exchange in SCAN0 leads to significant deviations due to deterioration in the description of the valence orbitals. For the late transition metal complexes of the reference set (Fe, Ni, and Cu) it can be concluded that the hybrid versions of SCAN either do not improve on the original or result in progressively worse agreement with experiment, an observation that holds for all copper complexes. Overall, there is no support from the present data that a global hybrid version of SCAN may be preferable for the prediction of hyperfine coupling constants.

2.4. Basis Set Dependence of SCAN Results

A technical point worth considering, particularly in view of the qualitative failure of SCAN for specific compounds of the present test set, is the possibility of increased sensitivity to the basis set employed in the calculation of hyperfine coupling constants. For this reason, all SCAN calculations were repeated with a different basis set that is appropriate for the target property, namely the aug-cc-pVTZ-J basis set of Hedegård, Kongsted, and Sauer [72]. The results, reported in Table 2, show no qualitative differences compared to the CP(PPP) results of Table 1. Importantly, the electronic structure obtained by SCAN for the problematic cases ScO and TiF_3 remains invariant to the choice of basis set, and hence the Fermi contact terms for both compounds remain qualitatively incorrect.

Table 2. Hyperfine coupling constants (in MHz) computed with SCAN and the aug-cc-pVTZ-J basis set.

Compound	A_{11}	A_{22}	A_{33}	A^{FC}	$A_{11}{}^{SD}$	$A_{22}{}^{SD}$	$A_{33}{}^{SD}$
ScO	−199.8	−199.8	−299.9	−230.2	31.8	31.8	−63.7
TiF$_3$	27.3	28.1	79.9	42.3	−17.1	−15.1	32.2
[V(H$_2$O)$_6$]$^{2+}$	−222.2	−222.2	−222.5	−214.7	0.1	0.1	−0.2
[VO(H$_2$O)$_5$]$^{2+}$	−206.4	−206.8	−503.3	−293.3	94.5	94.0	−188.5
MnF	402.0	402.0	478.5	428.4	−21.3	−21.3	42.6
MnO$_3$	1800.2	1800.2	2081.7	1909.4	−89.8	−89.8	179.6
[Mn(H$_2$O)$_6$]$^{2+}$	−210.8	−211.2	−211.2	−207.2	0.3	−0.2	−0.2
Mn(CO)$_5$	−90.4	−90.5	183.4	1.4	−91.6	−91.7	183.4
[Fe(CO)$_5$]$^+$	−17.1	−17.1	34.5	−0.4	−17.6	−17.6	35.3
NiH(CO)$_3$	53.0	53.0	−100.2	9.2	54.1	54.2	−108.3
[Ni(mnt)$_2$]$^-$	−6.0	−7.2	59.5	29.3	−31.2	−27.2	58.4
[Cu(NH$_3$)$_4$]$^{2+}$	−63.2	−65.1	−721.2	−349.2	247.5	245.5	−493.0
[Cu(dtc)$_2$]	−118.9	−121.6	−544.6	−298.5	157.7	156.1	−313.8
[Cu(en)$_2$]$^{2+}$	−104.6	−105.0	−731.7	−374.5	234.9	234.2	−469.1

3. Discussion and Conclusions

The present study was motivated by the expectation that the ability of the recently reported SCAN density functional to satisfy all known formal constraints and physical limits for a meta-GGA method might lead to better performance compared to previous density functional approximations for the theoretically and computationally challenging case of transition metal hyperfine coupling constants. SCAN and selected standard GGA, mGGA, and hybrid-mGGA functionals were compared on a selection of small 3d transition metal compounds with well-characterized hyperfine coupling constants. The results suggest that the formal superiority of SCAN does not translate into a clear and uniform advantage in terms of practical applications for the property under investigation.

There are cases where SCAN performs better than BP86 GGA and the TPSS mGGA functionals, approaching or exceeding the performance of the hybrid-mGGA TPSSh despite the absence of exact exchange mixing. This is observed for both vanadium complexes of the test set, [V(H$_2$O)$_6$]$^{2+}$ and [VO(H$_2$O)$_5$]$^{2+}$, as well as for Mn(CO)$_5$, [Fe(CO)$_5$]$^+$, [Cu(dtc)$_2$], and [Cu(en)$_2$]$^{2+}$, and to a lesser extent for NiH(CO)$_3$. This is already an encouraging result and implies that the fundamental physics of the hyperfine coupling interaction captured by SCAN are likely improved over those of older exchange–correlation functionals. On the other hand, there are cases where SCAN underperforms significantly compared to other functionals, such as for [Ni(mnt)$_2$]$^-$ and [Cu(NH$_3$)$_4$]$^{2+}$. The most worrying situation is however encountered for two seemingly trivial examples, ScO and TiF$_3$. Here SCAN fails entirely to provide meaningful results for the hyperfine coupling constants because it describes the electronic structure of these molecules in a fundamentally distinct way compared to other functionals. No other method tested here displays instances of this type of electronic structure error in the present test set, despite the occasional poor performance of any given functional for the values of the hyperfine coupling constants themselves.

The SCAN functional has inspired a series of recent studies that investigated the definition of simple hybrid as well as double-hybrid functionals using SCAN as the basic mGGA component [28,29,31]. As an example, SCAN0 [29], a hybrid with 25% exact exchange, has been reported to offer improved performance for a variety of properties, including reaction energetics of late transition metal systems [31]. In this vein, we additionally studied for the spectroscopic property of interest the performance of the already described SCAN0 functional, and of the SCANh functional defined in the present study, a hybrid with 10% exact exchange. The results for the hyperfine coupling constants show that the inclusion of exact exchange shifts the predicted values by affecting core and valence spin polarization, but no clear and uniform benefit emerges: the hybrid versions may or may not perform better than SCAN in cases where SCAN is underperforming, but they also result in larger deviations in cases where SCAN already provides values that compare well with experiment. In other words, no systematic

reduction of errors in hyperfine coupling constants can be observed upon mixing of exact exchange. This, of course, does not exclude the possibility that hybrid or double-hybrid SCAN-based functionals may systematically outperform the parent mGGA for other properties. Importantly, both hybrid versions of SCAN fail in exactly the same way as the parent functional for the problematic cases of ScO and TiF_3.

The origin of these errors cannot be safely deduced from the present limited results, but the potential for this type of behavior in transition metal systems implies that SCAN needs to be evaluated more extensively in terms of its performance for the electronic structure, valence orbital description and spin-state energetics of transition metal systems before any demanding applications to spectroscopic properties. SCAN obviously offers an important platform for further methodological improvements. Additionally, with careful evaluation SCAN itself or one of its hybrid reformulations may prove useful in applications for specific transition metal ions and types of ligand environment. Nevertheless, it appears that the advanced formalism does not translate directly in improved results for hyperfine coupling interactions, suggesting that there is significant room for improvement for this property even at the level of new functional forms. Empirical benchmarking of different functionals for chemically related systems persists as the only pragmatic approach for achieving reasonably reliable predictions of transition metal hyperfine coupling constants from density functional theory.

4. Computational Details

All quantum chemical calculations reported in this work were performed with the ORCA package. The BP86, TPSS, TPSSh, B3LYP, BHandHLYP, CAM-B3LYP, and SCAN functionals were used as implemented in the program, while SCANh and SCAN0 were defined manually using appropriate parameters for the mixing of exact (Hartree–Fock) exchange. Geometries for all compounds were obtained from tightly converged optimizations that employed the TPSS functional with the D3 dispersion corrections [73] in conjunction with Becke–Johnson damping [74]. Geometry optimizations used the def2-TZVP basis sets [75] for all atoms and fully decontracted def2/J auxiliary basis sets [76]. Very fine integration grids (Grid6) and tight energy convergence criteria were applied throughout. A common set of geometries were used for the calculation of hyperfine coupling constants with the different functionals because calculations on selected cases showed that functional-specific geometries are not associated on average with improvements in the final predicted hyperfine coupling constants for any given method; exactly the same conclusion was reached in previous studies that investigated the performance of DFT for hyperfine coupling in transition metal complexes [10]. The core-property basis sets CP(PPP) [41] and the property-optimized aug-cc-pVTZ-J basis sets [72] were used for the transition metals in the calculation of spectroscopic parameters. These calculations employed the spin-orbit mean-field approximation and were performed with increased radial integration grids overall (IntAcc 6) and with further increased integration accuracy (SpecialGridIntAcc 12) specifically for the transition metal atoms.

Conflicts of Interest: The author declares no conflict of interest.

Appendix A

Spin-orbit coupling is a minor contributor to the hyperfine coupling for most, but not all, compounds in this study. Its importance is more obvious for the heavier elements of the series and becomes crucial for copper compounds, for which the magnitude of A^{SO} is comparable to that of the other two components. Table A1 presents the spin-orbit contributions to the metal hyperfine coupling tensor for all compounds and all functionals discussed in this study. With respect to SCAN and its hybrid variants, it can be seen that the admixture of exact exchange has limited effects and clear trends emerge only for the heavier metals (Ni and Cu), where the increase in exact exchange from SCAN

to SCANh and SCAN0 is systematically accompanied with increased magnitude of the individual A^{SO} components.

Table A1. Spin-orbit contributions to hyperfine coupling (MHz) computed with all functionals discussed in the present work.

Compound	Functional	A_{11}^{SO}	A_{22}^{SO}	A_{33}^{SO}
ScO	BP86	−0.8	−0.8	−0.1
	TPSS	−0.8	−0.8	−0.1
	TPSSh	−0.9	−0.9	−0.1
	B3LYP	−0.9	−0.9	−0.1
	BHandHLYP	−1.0	−1.0	−0.2
	CAM-B3LYP	−0.7	−0.7	−0.1
	SCAN	−1.4	−1.4	−5.8
	SCANh	−1.4	−1.4	−6.0
	SCAN0	−1.2	−1.2	−6.5
TiF$_3$	BP86	2.8	2.8	0.2
	TPSS	2.3	2.3	0.2
	TPSSh	2.5	2.5	0.2
	B3LYP	3.6	3.6	0.1
	BHandHLYP	5.1	5.1	0.1
	CAM-B3LYP	1.0	1.0	0.1
	SCAN	2.1	0.8	5.0
	SCANh	0.8	2.2	5.3
	SCAN0	0.8	2.6	6.3
[V(H$_2$O)$_6$]$^{2+}$	BP86	−9.3	−9.3	−9.5
	TPSS	−8.2	−8.2	−8.4
	TPSSh	−8.5	−8.5	−8.7
	B3LYP	−10.0	−10.0	−10.2
	BHandHLYP	−10.9	−10.9	−11.1
	CAM-B3LYP	−4.0	−4.0	−4.0
	SCAN	−7.1	−7.1	−7.1
	SCANh	−7.3	−7.3	−7.4
	SCAN0	−7.8	−7.8	−7.9
[VO(H$_2$O)$_5$]$^{2+}$	BP86	−7.2	−7.4	−25.2
	TPSS	−6.6	−6.8	−21.5
	TPSSh	−7.1	−7.2	−23.1
	B3LYP	−8.2	−8.3	−29.2
	BHandHLYP	−10.4	−0.9	−35.4
	CAM-B3LYP	−3.4	−3.5	−12.4
	SCAN	−7.2	−7.1	−19.8
	SCANh	−7.6	−7.6	−21.0
	SCAN0	−8.4	−8.4	−23.2
MnF	BP86	3.8	3.8	21.5
	TPSS	−2.8	−2.8	14.0
	TPSSh	−2.4	−2.4	15.7
	B3LYP	17.7	17.7	32.4
	BHandHLYP	45.2	45.2	57.3
	CAM-B3LYP	−3.6	−3.6	4.8
	SCAN	−5.1	−5.1	8.7
	SCANh	−5.1	−5.1	9.9
	SCAN0	−4.8	−4.8	12.4

Table A1. *Cont.*

Compound	Functional	A_{11}^{SO}	A_{22}^{SO}	A_{33}^{SO}
MnO$_3$	BP86	−19.0	−19.0	−3.1
	TPSS	−17.1	−17.0	−3.3
	TPSSh	−17.8	−17.8	−4.8
	B3LYP	−19.4	−19.4	−7.2
	BHandHLYP	−13.6	−13.6	−0.5
	CAM-B3LYP	−11.4	−11.4	−6.0
	SCAN	−17.1	−17.1	−6.6
	SCANh	−18.2	−18.2	−9.5
	SCAN0	−19.8	−19.8	−14.6
[Mn(H$_2$O)$_6$]$^{2+}$	BP86	−2.9	−3.0	−3.0
	TPSS	−2.9	−2.9	−2.9
	TPSSh	−2.8	−2.8	−2.8
	B3LYP	−2.6	−2.6	−2.6
	BHandHLYP	−2.1	−2.1	−2.1
	CAM-B3LYP	−2.3	−2.3	−2.3
	SCAN	−3.0	−3.0	−3.0
	SCANh	−2.8	−2.8	−2.8
	SCAN0	−2.6	−2.6	−2.6
Mn(CO)$_5$	BP86	3.0	3.0	−1.3
	TPSS	2.1	2.1	−1.6
	TPSSh	2.1	2.1	−2.0
	B3LYP	3.6	3.6	−2.2
	BHandHLYP	1.6	1.6	−4.7
	CAM-B3LYP	−1.8	−1.8	−1.2
	SCAN	1.0	1.0	−1.1
	SCANh	1.0	1.0	−1.3
	SCAN0	0.7	0.7	−1.9
[Fe(CO)$_5$]$^+$	BP86	2.2	2.2	−0.3
	TPSS	1.8	1.8	−0.3
	TPSSh	2.2	2.2	−0.4
	B3LYP	3.2	3.2	−0.5
	BHandHLYP	4.6	4.6	−0.9
	CAM-B3LYP	0.5	0.5	−0.3
	SCAN	1.1	1.1	−0.3
	SCANh	1.3	1.3	−0.4
	SCAN0	1.7	1.7	−0.6
NiH(CO)$_3$	BP86	−12.2	−12.2	−0.6
	TPSS	−12.2	−12.2	−0.8
	TPSSh	−16.6	−16.6	−1.5
	B3LYP	−23.5	−23.5	−2.3
	BHandHLYP	−56.8	−56.8	−8.6
	CAM-B3LYP	−7.5	−7.5	−1.0
	SCAN	−11.3	−11.3	−1.2
	SCANh	−14.9	−14.9	−2.1
	SCAN0	−22.5	−22.5	−4.2
[Ni(mnt)$_2$]$^-$	BP86	−4.0	−10.0	−32.8
	TPSS	−3.9	−10.3	−32.4
	TPSSh	−13.6	−5.9	−38.9
	B3LYP	−15.9	−9.1	−43.9
	BHandHLYP	−5.2	−22.1	−16.5
	CAM-B3LYP	−4.3	−3.0	−13.0
	SCAN	−9.9	−4.2	−29.6
	SCANh	−12.8	−6.1	−35.2
	SCAN0	−17.8	−11.5	−44.6

Table A1. *Cont.*

Compound	Functional	$A_{11}{}^{SO}$	$A_{22}{}^{SO}$	$A_{33}{}^{SO}$
$[Cu(NH_3)_4]^{2+}$	BP86	47.0	47.0	160.4
	TPSS	45.6	45.6	150.3
	TPSSh	53.1	53.1	174.6
	B3LYP	64.8	64.8	221.4
	BHandHLYP	97.2	97.3	345.7
	CAM-B3LYP	23.9	23.9	87.5
	SCAN	37.8	37.9	119.5
	SCANh	42.8	42.9	135.0
	SCAN0	51.7	51.8	164.0
$[Cu(dtc)_2]$	BP86	20.8	19.4	68.3
	TPSS	21.7	20.6	69.8
	TPSSh	25.3	24.1	82.6
	B3LYP	28.3	26.6	96.7
	BHandHLYP	49.9	48.8	174.9
	CAM-B3LYP	14.5	13.8	50.0
	SCAN	21.0	20.1	65.6
	SCANh	24.2	23.2	76.8
	SCAN0	30.3	29.3	98.1
$[Cu(en)_2]^{2+}$	BP86	38.6	39.6	136.5
	TPSS	38.1	39.0	130.7
	TPSSh	44.3	45.5	152.6
	B3LYP	53.0	54.2	190.2
	BHandHLYP	82.2	82.9	305.6
	CAM-B3LYP	22.1	22.5	80.7
	SCAN	33.9	34.2	109.5
	SCANh	38.4	39.0	124.6
	SCAN0	46.8	46.9	152.1

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