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Density Functional Theory Predictions of Isotropic Hyperfine Coupling Constants

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The reliability of density functional theory (DFT) in the determination of the isotropic hyperfine coupling constants (hfccs) of the ground electronic states of organic and inorganic radicals is examined. Predictions using several DFT methods and 6-31G*, TZVP, EPR-III and cc-pVQZ basis sets are made and compared to experimental values. The set of 75 radicals here studied was selected using a wide range of criteria. The systems studied are neutral, cationic, anionic; doublet, triplet, quartet; localized, and conjugated radicals, containing ^{1}H, ^{9}Be, ^{11}B, ^{13}C, ^{14}N, ^{17}O, ^{19}F, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{33}S, and ^{35}Cl nuclei. The considered radicals provide 241 theoretical hfcc values, which are compared with 174 available experimental ones. The geometries of the studied systems are obtained by theoretical optimization using the same functional and basis set with which the hfccs were calculated. Regression analysis is used as a basic and appropriate methodology for this kind of comparative study. From this analysis, we conclude that DFT predictions of the hfccs are reliable for B3LYP/TZVP and B3LYP/EPR-III combinations. Both functional/basis set scheme are the more useful theoretical tools for predicting hfccs if compared to other much more expensive methods.

Introduction

Electron paramagnetic resonance (EPR) spectroscopy is the most important tool for the study of paramagnetic systems.[1] The interaction between magnetic nuclei and unpaired electrons is represented by the hyperfine tensor, which can be factored into both an isotropic (spherically symmetric) and anisotropic (dipolar) term. The isotropic term depends on the Fermi contact interaction of the unpaired electron with a determined nucleus. Therefore, it is a purely local property, that is, it is very sensitive to the spin density at the nucleus position. On the other hand, the anisotropic term can be obtained from the classical expression of two interacting magnetic dipoles, and its value mainly depends on the overall spin distribution. For this reason, the calculated values for anisotropic constants are rather less method-dependent than the isotropic ones, and often they reasonably agree with the experimental data. As a consequence, it will be much more difficult to compute the isotropic hyperfine coupling constant (hfcc) in quantitative agreement with the experimental data than the corresponding dipolar term. In fact, this magnetic molecular property is one of the most challenging tasks in computational chemistry.[2] In contrast, the anisotropic hyperfine tensor terms can usually be easily computed.[2−4] The three main factors influencing the hfcc values are the radical geometry, the electron correlation and one-electron basis set.[5]

The assignment of the isotropic hfccs to different magnetic nuclei in each paramagnetic species is an important task for EPR spectroscopy. Moreover, EPR can help to characterize the structure of chemical species with unpaired electrons. For these systems, theoretical calculations provide very important source of information allowing to obtain both, the molecular geometry and the hfcc values. Many efforts have been devoted to the calculation of hyperfine couplings in order to carry out a correct assignment of the experimental data. Given its local character it constitutes a fair test for the quality of the wave function employed. For this reason it has received a great deal of attention from theoretical chemists and EPR spectroscopists[6a−m] for many years, in particular, from our laboratory.[6n−s]

One concern which immediately arises is the adequacy of the standard quantum chemical calculations for the treatment of hfccs, in particular when a high accuracy is required and when the size of the system is considerably large. The spin densities have been commonly calculated by semiempirical methods, particularly Pople's INDO,[7] due to the well-known deficiencies of ab initio Hartree−Fock (HF) methods.[2,3,8−10] At present, post-HF methodologies, that is, correlated ab initio molecular orbital methods, such as multiconfiguration self-consistent field (MCSCF),[11] multireference configuration interaction (MRCI),[12] or coupled cluster (CC) techniques,[13] are imperatively needed for an adequate description of the hyperfine structure of radicals. Moreover, extremely large basis sets are needed to obtain a good description of the spin densities at the nucleus. In the review of Chipman,[14] a compilation of these methods is given. Malkin et al.[15] and Huang et al.[12] include wide documentation of some of these methods as well as the comparison among them. For the above reasons, these calculations are highly demanding in computational time, and thus, restricting their application to very small radicals.

Density functional theory (DFT) methodology is a very promising alternative to post HF methods due to several features characterizing DFT. First, DFT methods partly include electron correlation through the exchange-correlation functional, leading to accurate values of spin densities with considerably lower computational time. Its favorable scaling, in comparison with correlated MO methods, allows one to obtain spin densities for much larger size radicals by using a much lesser expensive basis set. However, the bibliographic DFT data related to the calculation of radical spin densities show an important dispersion in the exchange functional, the correlation functional and basis sets employed. In addition to the previous reviews of Malkin et al.[15] and Barone,[8a] to our knowledge, the works of Batra et al.,[16] Janoschek,[17] Cohen et al.,[18] Zakrassov et al.,[19] and Nguyen

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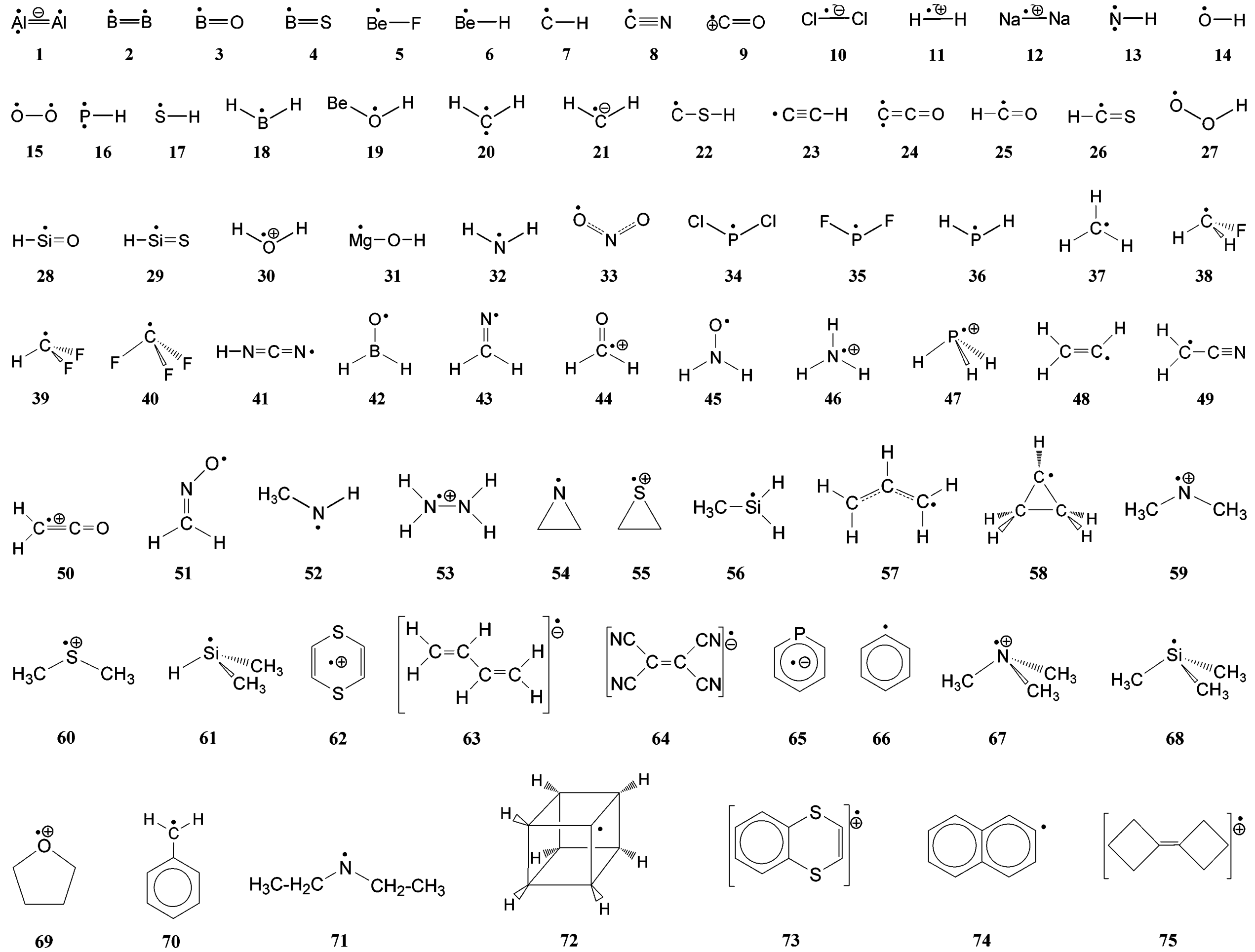

Figure 1. Geometrical structures of the selected radicals.

et al.[20] constitute the largest analysis in the comparison of experimental and DFT hyperfine data. Batra et al. analyze 17 radicals employing two hybrids functional namely BLYP and B3LYP with 6-31G* and 3-21G* basis sets and concluding that B3LYP/6-31G* with a geometrical optimization at either B3LYP/6-31G* or UHF/3-21G* is the best combination to obtain ^{1}H hyperfine coupling constants. For other nuclei, the authors indicate that a dependence with the functional used is noticeable although no detailed study were not carried out. In Janoschek's study, 20 radicals were analyzed using the very expensive cc-pVQZ Dunning's basis set. The main conclusion of this study is that B3LYP/cc-pVQZ calculations yield values closer to the experimental hfccs. However, the calculation time with this basis set is extremely high for medium size radicals and is forbidden for larger ones. In the work of Cohen et al., various functional and basis sets are tested. These authors studied 11 radicals analyzing only second-row nuclei. In the study of Zakrassov et al., only the a_{iso} of nitrogen nuclei is analyzed, for 16 large size nitroxide type radicals. They concluded that the B3LYP and B1LYP methods with a 6-31G(d) basis set can be used for the predictions of molecular magnetic properties. Finally, in the Nguyen's papers the hfccs of the ^{31}P nucleus from a set of 35 radicals are analyzed by using the B3LYP hybrid functional with the DFT-optimized valence triple-ζ basis, TZVP, and some variants in which tight *s*-functions are added to the core orbital. The values obtained for the hfccs of ^{31}P nucleus are reasonably accurate.

The aim of this paper is to investigate the performance of different DFT methods to predict, with a certain degree of accuracy, the isotropic hyperfine coupling constants of organic and inorganic radicals containing nuclei of first, second and third row elements of the Periodic Table. We will use other results obtained at high-level ab initio calculations as a suitable reference. This goal will be basically performed using a statistical analysis by comparing the calculated hfccs with the experimental ones. However, no specific radical is discussed.

We have considered a set of 75 paramagnetic species with a wide variety of nuclei, electronic states, and total charge. The basic criteria in the selection of the studied radicals have been the number and variety of hfccs of nuclei included in each radical and its well-established assignment. The set studied comprises neutral, cationic, anionic; doublet, triplet, quartet; localized and conjugated radicals. The studied nuclei and the their corresponding nuclear spin (in parentheses) were: ^{1}H ($I = {}^{1}/_{2}$), ^{9}Be ($I = {}^{3}/_{2}$), ^{11}B ($I = {}^{3}/_{2}$), ^{13}C ($I = {}^{1}/_{2}$), ^{14}N ($I = 1$), ^{17}O ($I = {}^{5}/_{2}$), ^{19}F ($I = {}^{1}/_{2}$), ^{23}Na ($I = {}^{3}/_{2}$), ^{25}Mg ($I = {}^{5}/_{2}$), ^{27}Al ($I = {}^{5}/_{2}$), ^{29}Si ($I = {}^{1}/_{2}$), ^{31}P ($I = {}^{1}/_{2}$), ^{33}S ($I = {}^{3}/_{2}$), and ^{35}Cl ($I = {}^{3}/_{2}$). The geometry of selected radicals are depicted in Figure 1, and ordered taking into account the number of nuclei that range from diatomic species up to the largest molecule, **75**, [bicyclobutylidene (C_8H_{12})], which has 20 nuclei. The first 17 diatomic species are ordered by alphabetical order and three, four, five, ... nuclei. Only for H_2^+ and HNCN radicals the experimental hfccs are not known. However, both systems have been theoretically very well studied at the highest level; see ref 50 and ref 80, respectively. We have included both radicals due to their extraordinary interest from astrophysical and theoretical points of view. For some of the larger radicals only the ^{1}H hfccs are known experimentally and thus, the hfccs of other nuclei are theoretically predicted in this study.

Theoretical Approach

The isotropic hyperfine coupling constant for a nucleus N is given by

$$a_{\mathrm{iso}}(N) = \frac{\mu_0}{3} g_e g_N \beta_e \beta_N \langle S_z \rangle^{-1} \rho(N) \tag{1}$$

where μ_o is the permeability of vacuum, g_e and g_N are the corresponding electronic and nuclear g factor; β_e is the Bohr magneton, β_N is the nuclear magneton of nucleus N; $\langle S_z \rangle$ is the mean value of S_z in the current electronic state, and $\rho(N)$ is the Fermi contact integral for nucleus N whose value is given by the expression

$$\rho(N) = \sum_{\mu\nu} P_{\mu\nu}^{\alpha\beta} \langle \phi_\mu(r_{kN}) | \delta(r_{kN}) | \phi_\nu(r_{kN}) \rangle \tag{2}$$

$P_{\mu\nu}^{\alpha\beta}$ is an element of the one-electron spin density matrix, ϕ denotes the atomic basis functions, and δ is the Dirac delta operator.

Substituting the corresponding constants in (1) the following conversion factors for the different nuclei is obtained (a_{iso} in Gauss):

$$a_{\mathrm{iso}}(N) = 142.770 \langle S_z \rangle^{-1} g_N \rho(N) \tag{3}$$

In the above expression $\rho(N)$ is expressed in au. The value of $\langle S_z \rangle$ depends on the electronic states of the analyzed radicals: $^1/_2$, 1, $^3/_2$, etc., for doublet, triplet, quartet, etc., states.

In the work of Nguyen et al.,[20] the conversion values reported between $a_{\mathrm{iso}}(N)$ in Gauss and $\rho(N)$ in au for nuclei ^{1}H, ^{13}C, ^{19}F, and ^{31}P (all of them with $I = {}^1/_2$) and for doublet states ($S = {}^1/_2$), are the correct ones. However, for nuclei ^{14}N ($I = 1$), ^{17}O ($I = {}^5/_2$), ^{33}S ($I = {}^3/_2$) and ^{35}Cl ($I = {}^3/_2$) and also for doublets states, the reported conversion values [$a_{\mathrm{iso}}(^{14}\mathrm{N}) = 57.6\rho(^{14}\mathrm{N})$, $a_{\mathrm{iso}}(^{17}\mathrm{O}) = -43.3\rho(^{17}\mathrm{O})$, $a_{\mathrm{iso}}(^{33}\mathrm{S}) = 40.8\rho(^{33}\mathrm{S})$, and $a_{\mathrm{iso}}(^{35}\mathrm{Cl}) = 52.1\rho(^{35}\mathrm{Cl})$] are erroneous. The correct values are [$a_{\mathrm{iso}}(^{14}\mathrm{N}) = 115.3\rho(^{14}\mathrm{N})$, $a_{\mathrm{iso}}(^{17}\mathrm{O}) = -216.3\rho(^{17}\mathrm{O})$, $a_{\mathrm{iso}}(^{33}\mathrm{S}) = 119.7\rho(^{33}\mathrm{S})$, and $a_{\mathrm{iso}}(^{35}\mathrm{Cl}) = 156.5\rho(^{35}\mathrm{Cl})$]. These mistakes are probably due to an accidental confusion between electronic states (S) and nuclear spin (I).

Computational Details

As it is well-known, DFT methods tend to describe more accurately valence effects than core effects, thus leading to an underestimated spin polarization. Addition of some HF restores the equilibrium between different contributions thus leading to much more improved hfccs. For this reason, we focused our attention on the hybrid DFT methods. We have studied the performance of several DFT approaches, mainly B3LYP, B3P86, and B3PW91 hybrid methods. These are the methods most widely used for investigating neutral, cationic, and anionic paramagnetic species. B3LYP approach is a hybrid method including the Becke's three parameter exchange functional[21] with the nonlocal correlation functional of Lee, Yang, and Parr.[22] The other hybrid DFT methods, namely B3P86 and B3PW91, include the same exchange functional and a different correlation functional. In the first one, B3P86, the electron correlation is accounted for by means of the nonlocal functional proposed by Perdew and Wang,[23] while the second one, B3PW91, includes the Perdew's gradient-corrected functional.[24]

Computations were performed using four basis sets of contracted Gaussian functions, namely 6-31G*,[25,26] TZVP,[27] EPR-III,[28] and cc-PVQZ.[29−31] The first of them, 6-31G*, is a small basis sets with a quality double-ζ plus polarization and a contraction scheme for the first-row elements of (10s4p1d)/[3s2p1d]. TZVP is a DFT-optimized valence triple-ζ basis. EPR-IIII is larger, and it has been optimized for the computation of hyperfine coupling constants by DFT methods. EPR-III is a triple-ζ basis including diffuse functions, double d-polarizations, and a single set of f-polarization functions. Also in this case, the s-part is improved to better describe the nuclear region: (6,2)/[4,2] for H and (11,7,2,1)/[7,4,2,1] for B to F. Unfortunately, this basis set is only available for the first and second row elements and for this reason, it has not been used for calculating hfccs of radicals containing heavier atoms. The last basis sets used in this work, the Dunning's correlation-consistent polarized valence quadruple-ζ basis set, cc-pVQZ, is formed from a contraction of (27, 9, 3, 2, 1) to [5, 4, 3, 2, 1] for the second row. A set of six Cartesian Gaussian functions is used for 6-31G*, whereas the correlation-consistent basis sets employ pure angular momentum sets of five d and seven f functions.

We have also done a prospective analysis by using other hybrid functionals such as B1B96, B1LYP, MPW1PW91, G961LYP, BHandH, and BHandHLYP. The first one includes the Becke's one-parameter hybrid functional with Becke's 1996 correlation functional.[32] The second one uses the previous exchange functional reported and the LYP correlation functional implemented by Adamo and Barone.[33] The third one is the functional proposed by Barone and Adamo using a modified one-parameter Perdew−Wang exchange and Perdew−Wang91 correlation functionals.[34] The fourth one uses exchange functional reported by Gill in 1996 and LYP correlation functional.[35] The fifth one is half-and-half functional, including HF and LSDA exchange functionals and Becke88[36] and LYP correlation functionals.[22] For these latter functionals, the optimized geometries and hfcc were computed using the 6-31G* basis set.

In this study, we determined the hfccs for 75 radicals after optimizing their geometry for their ground states using different functionals and basis sets. Furthermore, many of these radicals, mainly the smaller ones, have been previously calculated with other theoretical calculations, thus permitting a productive comparison. Because of its extremely high computational cost for medium and large size radicals, we only used cc-pVQZ basis set for analyzing the behavior of the most popular B3LYP functional. Prospective analysis also carried out indicates that the other functionals (B3P86, PB3PW91) give rise to very similar optimized geometrical parameters. Thus, the following input scheme, B3LYP/cc-pVQZ//B3LYP/cc-pVQZ, was employed for radicals **1**−**63**, while the B3LYP/cc-pVQZ//B3LYP/6-31G* (**64**−**73**) and B3LYP/cc-pVTZ//B3LYP/6-31G* (**74**−**75**) inputs were used for the others.

All computations were performed using Gaussian packages (G98 version A.7[37] and G03 version B6[38]). Both packages were used indistinctly, but in the case of EPR-III basis sets, we used only G98-A7, due to anomalous results detected in the G03 suite for this basis set. The spin-unrestricted theory was employed. The effects of vibrational averaging on the calculated hfccs have not been considered in this study.

Results and Discussion

Geometries. In this investigation, the geometrical optimization of all the radicals (**1**−**75**) employing the three hybrid functionals (B3LYP, B3P86, B3PW91) and the (6-31G*, TZVP, EPR-III and cc-PVQZ) basis sets, was performed *self-consistently* within the same density functional framework as that in which the hyperfine coupling constants were calculated.

The optimized geometries of the radicals investigated do not differ dramatically from one method to another and from one

TABLE 1: Electronic Ground States and Total Energies (au) of the Studied Species at the (A) B3LYP/6-31G*//B3LYP/6-31G*, (B) B3LYP/TZVP//B3LYP/TZVP, (C) B3LYP/EPR-III//B3LYP/EPR-III and (D) B3LYP/cc-pVQZ//B3LYP/cc-pVQZ Theoretical Levels

no.	radical	state	A	B	C	D	no.	radical	state	A	B	C	D
1	Al_2^-	$^4\Sigma_g$	−484.829734	−484.862087		−484.883864	**39**	F_2CH	$^2A'$	−238.305477	−238.416313	−238.435926	−238.433546
2	B_2	$^3\Sigma_g$	−49.408478	−49.422466	−49.425872	−49.425595	**40**	F_3C	$^2A'$	−337.551023	−337.698829	−337.730246	−337.726897
3	BO	$^2\Sigma$	−100.024137	−100.063897	−100.073959	−100.074481	**41**	HNCN	$^2A''$	−148.127242	−148.182946	−148.198195	−148.198398
4	BS	$^2\Sigma$	−422.969846	−423.001999		−423.018180	**42**	H_2BO	$^2B_2$	−101.248878	−101.288724	−101.298229	−101.299442
5	BeF	$^2\Sigma$	−114.610356	−114.646895	−114.668999	−114.672634	**43**	H_2CN	$^2B_2$	−93.982443	−94.017793	−94.026849	−94.027221
6	BeH	$^2\Sigma$	−15.261042	−15.260682	−15.267150	−15.267604	**44**	H_2CO^+	$^2B_2$	−114.106614	−114.148519	−114.160113	−114.160749
7	CH	$^2\Pi$	−38.479163	−38.495898	−38.499182	−38.499050	**45**	H_2NO	$^2A'$	−131.082451	−131.145334	−131.158535	−131.157961
8	CN	$^2\Sigma$	−92.711747	−92.744004	−92.752695	−92.752666	**46**	NH_3^+	$^2A_2''$	−56.184377	−56.210911	−56.215321	−56.216905
9	CO^+	$^2\Sigma$	−112.793565	−112.834407	−112.846307	−112.846407	**47**	PH_3^+	$^2A_1$	−342.780514	−342.808311		−342.823868
10	Cl_2^-	$^2\Sigma_u$	−920.451905	−920.513474		−920.544484	**48**	CH_2CH	$^2A'$	−77.901208	−77.933449	−77.941373	−77.941998
11	H_2^+	$^2\Sigma_g$	−0.598151	−0.609489	−0.609888	−0.610513	**49**	H_2CCN	$^2B_1$	−132.094668	−132.142359	−132.155086	−132.155390
12	Na_2^+	$^2\Sigma_g$	−324.397992	−324.417717		−324.436749	**50**	H_2CCO^+	$^2B_1$	−152.251902	−152.306771	−152.321712	−152.322110
13	NH	$^3\Sigma$	−55.219437	−55.243549	−55.231921	−55.247606	**51**	H_2CNO[c]	$^2A'$	−169.179622	−169.245157	−169.261843	−169.261876
14	OH	$^2\Pi$	−75.723455	−75.766092	−75.761159	−75.772306	**52**	CH_3NH[d]	$^2A''$	−95.190860	−95.229666	−95.239687	−95.240783
15	O_2	$^3\Sigma_g$	−150.320042	−150.381179	−150.394540	−150.394138	**53**	$NH_2NH_2^+$ [e]	$^2B_{2g}$	−111.576022	−111.624873	−111.635946	−111.638429
16	PH	$^3\Sigma$	−341.877168	−341.901417		−341.913641	**54**	C_2H_4N[f]	$^2B_1$	−133.268323	−133.314393	−133.327257	−133.328354
17	SH	$^2\Pi$	−398.740028	−398.769329		−398.784583	**55**	$C_2H_4S^+$ [g]	$^2B_1$	−476.457345	−476.505759		−476.531643
18	BH_2	$^2A_1$	−25.934712	−25.945008	−25.947519	−25.948170	**56**	CH_3SiH_2[h]	$^2A'$	−330.558694	−330.597644		−330.616080
19	BeOH	$^2A'$	−90.566760	−90.601642	−90.622329	−90.625036	**57**	CH_2CHCH_2[i]	$^2A_2$	−117.260354	−117.306857	−117.316815	−117.317759
20	CH_2	$^3B_1$	−39.150020	−39.168169	−39.171483	−39.171775	**58**	$(CH_2)_2CH$[j]	$^2A'$	−117.213456	−117.256569	−117.267149	−117.268646
21	CH_2^-	$^2B_1$	−39.128901	−39.183187	−39.198253	−39.187600	**59**	$(CH_3)_2N$[k]	$^2B_1$	−134.509485	−134.558662	−134.571388	−134.573339
22	CSH	$^2A'$	−436.734957	−436.777971		−436.800058	**60**	$(CH_3)_2S^+$ [l]	$^2B_1$	−477.699102	−477.750127		−477.779255
23	C_2H	$^2\Sigma$	−76.604282	−76.635494	−76.643235	−76.643103	**61**	$(CH_3)_2SiH$[m]	$^2A'$	−369.884861	−369.938835		−369.962138
24	C_2O	$^3\Sigma$	−151.257555	−151.313811	−151.329299	−151.328379	**62**	$C_4H_4S_2^+$ [n]	$^2B_{3u}$	−950.899488	−950.991334		−951.047456
25	HCO	$^2A'$	−113.850171	−113.897334	−113.909200	−113.908830	**63**	$C_4H_6^-$ [o]	^2A_u	−155.940389	−156.021516	−156.045376	−156.039462
26	HCS	$^2A'$	−436.804175	−436.843537		−436.864489	**64**	$C_6N_4^-$ [p]	$^2B_{2g}$	−447.631188	−447.790487	−447.750474	−447.831036[a]
27	HOO	$^2A''$	−150.899157	−150.968749	−150.983592	−150.982496	**65**	$C_5H_5P^-$ [q]	$^2B_1$	−534.856130	−534.955672		−534.991978[a]
28	HSiO	$^2A'$	−365.262583	−365.318261		−365.342540	**66**	C_6H_5[r]	$^2A_1$	−231.561282	−231.635693	−231.659666	−231.660334[a]
29	HSiS	$^2A'$	−688.250274	−688.296443		−688.325218	**67**	$(CH_3)_3N^+$ [s]	$^2A_1$	−174.197430	−174.252830	−174.268280	−174.260229[a]
30	H_2O^+	$^2B_1$	−75.958808	−75.997688	−76.004856	−76.005996	**68**	$(CH_3)_3Si$[t]	$^2A'$	−409.210970	−409.280122		−409.307583[a]
31	MgOH	$^2\Sigma$	−275.906991	−275.944627		−275.982914	**69**	$C_4H_8O^+$ [u]	^2B	−232.118585	−232.193533	−232.215714	−232.218301[a]
32	NH_2	$^2B_1$	−55.872619	−55.902023	−55.888278	−55.908962	**70**	$C_6H_5CH_2$[v]	$^2B_1$	−270.915143	−271.006816	−271.030723	−271.031939[a]
33	NO_2	$^2A_1$	−205.072206	−205.153208	−205.175789	−205.173868	**71**	$(CH_3CH_2)_2N$[w]	$^2A''$	−213.143322	−213.217119	−213.237885	−213.224126[a]
34	PCl_2	$^2B_1$	−1261.758543	−1261.836796		−1261.889679	**72**	C_8H_7[x]	$^2A_1$	−308.785905	−308.875574	−308.902934	−308.904265[a]
35	PF_2	$^2B_1$	−541.040028	−541.156464		−541.200316	**73**	$C_8H_6S_2^+$ [y]	$^2B_1$	−1104.562405	−1104.699547		−1104.768839[a]
36	PH_2	$^2B_1$	−342.504214	−342.530996		−342.545639	**74**	$C_{10}H_7$[z]	$^2A'$	−385.205128	−385.321738	−385.361943	−385.335675[b]
37	CH_3	$^2A_2''$	−39.838292	−39.857211	−39.861205	−39.861983	**75**	$C_8H_{12}^+$ [aa]	$^2B_{1u}$	−311.714166	−311.805550	−311.836113	−311.817279[b]
38	FCH_2	$^2A'$	−139.064267	−139.129694	−139.142863	−139.141721							

[a] B3LYP/cc-pVQZ//B3LYP/6-31G*. [b] B3LYP/cc-pVTZ//B3LYP/6-31G*. [c] Formaldiminoxyl. [d] Methylaminyl. [e] Hydrazine. [f] 1-Aziridinyl. [g] Thiirane. [h] Methylsilyl. [i] Allyl. [j] Cyclopropyl. [k] Dimethylaminyl. [l] Dimethyl sulfide. [m] Dimethylsilyl. [n] 1,4-Dithiin. [o] Butadiene. [p] Tetracyanoethene. [q] Phosphabenzene. [r] Phenyl. [s] Trimethylamine. [t] Trimethylsilyl. [u] Tetrahydrofuran. [v] Benzyl. [w] Diethylaminyl. [x] Cubyl. [y] Benzo-1,4-dithiin. [z] 2-Naphthyl. [aa] Bicyclobutylidene.

basis set to another. Although geometry plays an important role in the calculation of hfccs, the selected radicals present well-defined geometries for the ground states. We have summarized in Table 1 the energies of the ground states of the 75 species using B3LYP method and with the four basis sets considered, as well as the corresponding electronic state and the empirical formula. To avoid any confusion among several isomers, the names of compounds **51**−**75**, are included. Table 1 shows that when the size of the basis set increases, the energy of the determined species is lower. However, the lowest energy does not always correspond to the Dunning's basis set, because Barone's basis set has a similar size.

Isotropic Hyperfine Coupling Constants. The calculated hfccs at the different levels of theory for B3LYP method with the four basis sets are summarized in Table 2, and in supplementary Tables 1 and 2, for B3P86 and B3PW91 respectively, with 6-31G*, TZVP, and EPR-III basis sets. In general, all DFT methods investigated yield values similar to the experimental ones for ^1H nuclei, whereas large differences for the second- and third row nuclei are found.

The hfccs (a_{iso}) given in Gauss are summarized in Table 2. For each radical, the nuclei are presented in the same order as the empirical formula of the radical (see Figure 1). For those species with nonequivalent atoms, additional information on that atom is included to identify it. Table 2 has 10 columns, the first one corresponds to the number of the radical, the second one is the empirical formula, and the third one contains the nuclei with their isotopic mass. Five theoretical hfcc values appear in the column of theoretical a_{iso}. Four columns (A−D) contain the values obtained with the four basis sets considered (6-31G*, TZPV, EPR-III, and cc-pVQZ). The last column, theoretical a_{iso}, shows the corresponding values obtained at high level ab initio calculation from the bibliography using different methods (see top of Table 2). In the last column of Table 2, the experimental hfccs are given and their references are summarized. The sign of those a_{iso} is not determined when an experimental EPR spectrum is analyzed. The corresponding sign is assigned in agreement with high level theory. The sign obtained for the hfccs of ^{29}Si is an error in the version G03 of the Gaussian program; however, it is correct in the G98 version.

The values obtained with the larger basis set (cc-pVQZ) are poorer for several atoms as ^{11}B in radical **2**, ^{13}C in radical **7**, ^{14}N and ^1H in radical **13**, ^{17}O in radicals **14**, **15**, and **25**, one of the ^{13}C atoms in radicals **57** and **70**, and one of the ^{14}N atoms in radical **71**. For some radicals, we do not obtain the same hfcc values using the same input scheme (contraction scheme and size basis sets) as Janoschek's paper,[17] this disagreement being significant for radicals **15**, **24**, and **37**. On the other hand, the deficiency of very large basis sets in the obtention of accurate hfcc values has been already pointed out.[134] We think that large basis sets reproduce the valence electrons well; however, they can be deficient in the electron core representation. This last

TABLE 2: Theoretical Hyperfine Coupling Constants (G) of Studied Radicals at the (A) B3LYP/6-31G*//B3LYP/6-31G*, (B) B3LYP/TZVP//B3LYP/TZVP, (C) B3LYP/EPR-III//B3LYP/EPR-III, and (D) B3LYP/cc-pVQZ//B3LYP/cc-pVQZ Levels and (E) Other Theoretical Results

			a_{iso}(theoretical)					experimental	
no.	radical	nuclei	A	B	C	D	E	a_{iso}	ref
1	Al_2^-	^{7}Al	−11.6	−6.8		−12.5	−7.9[a]	8.2	40
2	B_2	^{11}B	9.9	4.2	5.3	1.7	4.4[b]	5.4	41
3	BO	^{11}B	375.9	398.4	384.4	385.9	381.3[c]	365.7	42
		^{17}O	−0.2	−4.1	−4.2	−4.6		5.0	43
4	BS	^{11}B	289.6	304.8		293.7	291.5[c]	284.0 (Ne)	44
								292.0 (Ar)	
		^{33}S	0.4	1.5		1.0			
5	BeF	^{9}Be	−111.0	−119.3	−108.0	−108.7	−100.2[d]	104.9	45
		^{19}F	71.1	84.8	92.0	91.4	70.7[d]	81.7	
6	BeH	^{9}Be	−74.3	−78.3	−72.6	−73.4	−67.9[d]	71.1	6e, 46
		^{1}H	68.7	63.5	73.0	69.6	73.1[d]	69.2	
7	CH	^{13}C	16.8	14.8	19.0	9.0	20.0[e]	16.8	48
		^{1}H	−18.3	−17.1	−16.9	−16.0	−17.3[e]	20.6	
8	CN	^{13}C	183.9	214.6	207.7	201.6	205.2[c]	209.8	49
		^{14}N	−6.4	−7.5	−6.7	−7.7	−6.7[c]	4.5	
9	CO^+	^{13}C	495.3	587.8	569.3	566.5		561.3	43
		^{17}O	11.1	10.2	9.9	9.5		6.6	
10	Cl_2^-	^{35}Cl	26.3	32.7		28.4	28.9[f]	38.9	49
							31.0[g]		
11	H_2^+	^{1}H	347.2	320.7	346.2	328.5	323.7[h]	333.7	50
12	Na_2^+	^{23}Na	112.1	150.1		169.4	142.7[i]	157.0	51
13	NH	^{14}N	6.0	4.5	4.8	2.0	6.0[j]	6.9	52
		^{1}H	−21.0	−20.5	−20.1	−18.9	−24.3[j]	23.6	
14	OH	^{17}O	−18.3	−8.6	−15.7	−1.5	−17.5[k]	18.3	53
		^{1}H	−24.4	−24.2	−23.4	−22.3	−24.5[k]	25.5	54
15	O_2	^{17}O	−15.1	−10.3	−13.9	−5.8	−13.9[c]	19.6	55
16	PH	^{31}P	22.1	53.9		31.4	45.4[l]	44.7	56
		^{1}H	−13.1	−11.0		−11.0	−17.6[l]	17.4	
17	SH	^{33}S	7.6	15.6		8.9			57
		^{1}H	−16.0	−14.0		−13.6	−13.6[c]	23.2	
18	BH_2	^{11}B	145.0	130.7	127.0	123.8	119.89[m]	127.7	58
		^{1}H	14.0	13.5	14.4	13.7	10.35[m]	13.56	
19	BeOH	^{9}Be	−103.6	−109.0	−98.3	−98.7	−93.5[n]	94.20	59
		^{17}O	−15.7	−21.9	−20.1	−20.0	−18.5[n]		
		^{1}H	1.5	2.7	1.6	1.4	2.5[n]	<1.8	
20	CH_2	^{13}C	95.5	82.4	82.1	75.2	84.1[o]		
		^{1}H	−5.2	−4.8	−4.5	−4.3	−7.9[o]	7.2	2a
21	CH_2^-	^{13}C	33.0	20.7	29.4	16.0	27.1[p]	21.0	58
		^{1}H	−16.9	−14.8	−13.7	−14.0	−16.6[p]	−16.0	
22	CSH	^{13}C	21.7	16.6		10.9	17.5[q]	17.09	60
		^{33}S	13.9	12.5		13.5	13.7[q]		
		^{1}H	97.9	92.0		95.5	89.0[q]	103.7	
23	C_2H	^{13}C	348.2	390.7	378.7	374.3	375.6[c]	362.0	14
		$^{13}C_{(H)}$	72.9	82.9	81.2	83.5	80.7[c]	76.0	
		^{1}H	21.7	19.2	19.7	18.8	18.8[c]	18.0	
24	C_2O	^{13}C	16.7	12.0	14.2	8.1	14.2[c]	15.7	61
		$^{13}C_{(O)}$	−2.7	−8.5	−7.1	−8.1	−6.9[c]	10.7	
		^{17}O	−7.8	−5.1	−6.7	−3.2			
25	HCO	$^{1}H_{\alpha}$	129.3	124.5	135.4	136.8	122.4[q]	138.8	62
								126.3	63
		^{13}C	152.2	142.7	138.5	129.6	134.7[q]	134.7	64
								130.2	65
		^{17}O	−11.6	−10.5	−12.5	−8.1	−9.9[q]	−15.1	66
26	HCS	^{1}H	45.7	45.6		45.1	41.8[r]	45.5	67, 68
		^{13}C	117.2	110.1		100.8	93.3[r]		
		^{33}S	5.0	6.5		5.2	8.8[r]		
27	HOO	^{1}H	−9.3	−9.1	−9.1	−8.7	−10.42[s]	9.78	67, 68
		$^{17}O_{(HO)}$	−18.1	−12.0	−17.4	−6.1	−21.9[s]		
		^{17}O	−11.2	−8.2	−9.1	−5.7	−12.1[s]		
28	HSiO	^{1}H	154.1	149.5		153.4	141.7[q]	161.0	69
								160.5	70
		^{29}Si	−170.8	−186.3		−190.8	−210.9[q]	237.3	70
		^{17}O	−6.2	−3.0		−1.2	−4.7[q]		
29	HSiS	^{1}H	114.1	111.8		115.7	112.5[q]	119.8	71
		^{29}Si	−161.3	−169.3		−175.7	−194.3[q]		
		^{33}S	2.6	5.4		3.1	1.1[q]		
30	H_2O^+	^{1}H	−25.1	−25.7	−25.0	−23.7	−23.8[t]	26.1	72
		^{17}O	−31.0	−16.0	−23.1	−8.5	−20.6[t]	29.7	
31	MgOH	^{25}Mg	−91.8	−111.6		−103.7	−102.7[u]	108.7(Ne)	59
								111.6(Ar)	
		^{17}O	−26.7	−38.2		−29.1	−22.8[u]		
		^{1}H	7.9	8.8		7.1	5.4[u]	4.2 (Ne)	
								3.6 (Ar)	
32	NH_2	^{14}N	11.9	7.8	10.1	5.3	8.6[v]	9.95	73
		^{1}H	−23.1	−22.3	−21.5	−20.4	−22.6[v]	23.98	
33	NO_2	^{14}N	53.4	52.4	51.7	50.7	52.7[w]	54.7	66, 74
		^{17}O	−14.5	−16.9	−19.4	−14.6	−20.4[w]	16.8 21.8	
34	PCl_2	^{31}P	32.7	66.2		56.4	71.8[a]	68.3	75
		^{35}Cl	2.3	3.2		2.6	0.7[a]	0.40	
50	H_2CCO^+	^{1}H	−21.7	−20.1	−20.6	−19.6	−20.1[hh]	20.7−21.1	92
		$^{13}C_{CH_2}$	33.2	21.0	23.1	15.7			
		$^{13}C_{CO}$	−14.4	−19.7	−18.7	−18.7			
		^{16}O	−6.9	−3.7	−5.4	−2.0			
51	H_2CNO	$^{1}H_{cis}$	28.0	28.7	31.3	29.8	25.1[ii]	26.2	93
		H_{trans}	5.8	7.1	7.4	7.0	2.6[ii]	2.8	93
		^{13}C	24.7	32.5	31.9	32.9	37.5[ii]		
		^{14}N	30.1	29.4	29.6	27.6	28.4[ii]	33.3	93
		^{17}O	−18.1	−14.1	−17.9	−9.8	−22.5[ii]	∼22.8	94
52	CH_3NH	^{13}C	−10.9	−12.5	−11.6	−11.5	−12.3[jj]		95
		$^{1}H_{CH_3}$	30.7	30.7	33.8	32.3	29.6[jj]	34	
		^{14}N	13.6	9.2	11.3	6.8	7.8[jj]	13	
		^{1}H	−22.0	−21.3	−20.7	−19.7	−21.2[jj]	22	
53	$NH_2NH_2^+$	^{14}N	10.3	6.7	7.7	5.1		11.0	96
		^{1}H	−16.2	−15.7	−15.7	−15.0		10.4	
54	C_2H_4N	^{13}C	−7.9	−9.0	−8.6	−8.4			
		^{1}H	27.8	29.6	32.0	30.7		30.70	97
		^{14}N	12.1	8.5	10.7	6.1		12.52	
55	$C_2H_4S^+$	^{13}C	−2.4	−2.7		−2.6			
		^{1}H	15.3	15.1		16.3		16.1	98
		^{33}S	8.7	15.0		11.5			
56	CH_3SiH_2	^{13}C	5.9	6.5		6.9[oo]			
		$3\,^{1}H$	8.2	8.2		8.2[oo]		7.98	99
		^{29}Si	−150.5	−162.0		−160.7[oo]	−184.2[kk]	181.0	100
		$2\,^{1}H$	13.5	14.3		16.6[oo]	6.0	11.82	99
57	CH_2CHCH_2	$2\,^{13}C_{(CH_2)}$	28.2	17.0	18.3	13.2	18.6[c]	21.9	14
		$^{13}C_{(CH)}$	−17.5	−16.3	−16.0	−14.9	−16.0[c]	17.2	
		$2\,^{1}H_{trans}$	−16.5	−14.8	−15.2	−14.6	−14.4[c]	14.8	
		$2\,^{1}H_{cis}$	−15.8	−14.0	−14.3	−13.8	−13.5[c]	13.5	
		$^{1}H_{CH}$	5.0	4.3	4.4	4.5	4.2[c]	4.2	
58	$(CH_2)_2CH$	$2\,^{13}C$	−6.3	−7.2	−6.8	−6.8	−7.3[ll]		
		$4\,^{1}H$	22.7	23.2	25.0	18.9	18.2[ll]	23.5	100
		$^{13}C_{CH}$	108.8	95.5	93.6	87.7	116.9[ll]	95.9	
		$^{1}H_{\alpha}$	−6.0	−5.0	−5.3	−5.0	−5.7[ll]	6.7	
59	$(CH_3)_2N$	^{13}C	−10.3	−11.9	−11.2	−11.9			
		^{1}H	25.7	25.6	27.9	26.6		27.36	101
		^{14}N	15.9	10.6	12.5	8.2		14.78	
60	$(CH_3)_2S^+$	^{13}C	−4.5	−5.6		−4.7			
		$^{1}H_{(av)}$	21.2	21.2		22.1		20.4	98
		^{33}S	12.4	18.5		14.6			
61	$(CH_3)_2SiH$	^{13}C	8.2	9.1		9.0			
		$^{1}H_{(av)}$	7.4	7.3		7.6		7.19	99
		^{29}Si	−147.4	−161.1		−157.3		183.0	
		$^{1}H_{\alpha}$	17.2	18.3		19.1		16.99	
62	$C_4H_4S_2^+$	^{13}C	2.3	−0.2		−0.5			
		^{1}H	−3.3	−2.9		−2.9		2.82	102
		^{33}S	6.2	7.9		7.2		9.84	
63	$C_4H_6^-$	$2\,^{13}C_{CH_2}$	19.3	9.5	8.0	7.2	8.5[mm]		
		$2\,^{13}C_{CH}$	−0.5	−2.6	−1.0	−3.0	−2.9[mm]		
		$4\,^{1}H$	−11.5	−9.7	−8.2	−9.0	7.0[mm]	7.62	103
		$2\,^{1}H$	−2.7	−2.6	−2.5	−2.4	−0.6[mm]	2.79	
64	$C_6N_4^-$	$2\,^{13}C$	11.2	5.1	6.0	3.4[oo]			
		$4\,^{13}C_{CN}$	−8.3	−9.7	−9.2	−8.9[oo]		9.45	
		^{14}N	2.0	1.1	1.5	0.8[oo]		1.57	104
65	$C_5H_5P^-$	$2\,^{13}C_o$	7.7	3.1		2.8[oo]			
		$2\,^{13}C_m$	−6.7	−6.3		−5.8[oo]			
		$^{13}C_p$	16.7	9.3		7.2[oo]		12.0	105
		$2\,^{1}H_o$	−5.1	−4.1		−4.1[oo]		3.7	
		$2\,^{1}H_m$	0.9	0.5		0.6[oo]		<1	
		$^{1}H_p$	−9.6	−8.2		−8.0[oo]		7.6	
		^{31}P	26.6	33.6		31.1[oo]		35.6	
66	C_6H_5	^{13}C	131.7	134.8	131.6	129.3[oo]			
		$2\,^{13}C_o$	1.4	5.0	5.2	5.3[oo]			
		$2\,^{13}C_m$	15.3	17.2	16.7	16.6[oo]			
		$^{13}C_p$	−2.8	−2.3	−2.2	−2.2[oo]			
		$2\,^{1}H_o$	17.3	17.8	19.3	18.0[oo]		17.43	106
		$2\,^{1}H_m$	5.9	5.6	6.2	5.8[oo]		6.25	
		$^{1}H_p$	2.0	2.0	2.0	2.1[oo]		2.04	
67	$(CH_3)_3N^+$	^{13}C	−8.7	−10.1	−10.6	−9.0[oo]			
		^{1}H	28.3	28.0	31.2	27.9[oo]		28.2	107
		^{14}N	18.7	14.8	16.7	10.9[oo]		14−18	
68	$(CH_3)_3Si$	^{13}C	11.0	12.2		12.4[oo]			
		$^{1}H_{(av)}$	6.6	6.4		6.5[oo]		6.28	99
		^{29}Si	−145.0	−160.0		−159.2[oo]		181	
69	$C_4H_8O^+$	$2\,^{13}C_{CO}$	−8.5	−10.4	−9.8	−10.0[oo]			
		$2\,^{13}C_{CC}$	−0.8	−1.1	−1.0	−1.0[oo]			
		$2\,^{1}H_{ax(\beta)}$	88.0	82.2	97.1	90.6[oo]		89.0	108
		$2\,^{1}H_{eq(\beta)}$	39.1	39.2	43.4	40.5[oo]		40.0	
		$2\,^{1}H$	4.2	4.6	5.1	4.6[oo]			

TABLE 2 (Continued)

			a_{iso}(theoretical)					experimental	
no.	radical	nuclei	A	B	C	D	E	a_{iso}	ref
35	PF_2	^{31}P	72.2	96.2		72.1	89.24^{y}	84.8	76
		^{19}F	47.0	29.5		19.6	32.8^{y}	32.6	
36	PH_2	^{31}P	45.0	74.7		60.4	74.9^{x}	77.4	77
		^{1}H	−15.4	−13.3		−12.9	-17.2^{x}	17.5	
37	CH_3	^{13}C	44.4	27.0	28.6	19.9	29.2^{c}	27.0	78
		^{1}H	−25.3	−22.7	−23.0	−21.9	-21.8^{c}	25.0	
38	FCH_2	^{19}F	73.2	51.3	52.1	44.7	64.7^{y}	64.3	79
		^{13}C	62.3	50.9	56.4	40.0	54.2^{y}	54.8	
		^{1}H	−16.7	−18.3	−19.0	−17.7	-21.5^{y}	21.1	
39	F_2CH	^{19}F	71.8	72.9	77.2	62.4	86.5^{y}	84.2	79
		^{13}C	152.8	146.8	143.4	137.6	147.4^{y}	148.8	
		^{1}H	22.7	21.6	23.8	23.1	18.2^{y}	22.2	
40	F_3C	^{19}F	133.9	133.4	138.3	125.6	151.1^{y}	142.4	79
		^{13}C	258.9	274.0	264.5	261.3	266.7^{y}	271.6	
41	HNCN	^{1}H	−16.8	−16.3	−16.0	−15.2	-18.20^{z}		
		$^{14}N_{(HN)}$	9.8	6.6	7.8	4.9	8.92^{z}		
		^{13}C	−20.0	−21.2	−20.7	−19.1	-25.00^{z}		
		$^{14}N_{(CN)}$	6.3	3.3	4.6	1.8	4.64^{z}		
42	H_2BO	^{1}H	111.9	114.3	126.6	121.2	71.8^{aa}	130.0	81
		^{11}B	−26.4	−27.8	−26.5	−26.4	-19.3^{aa}	30.0	
		^{17}O	−19.0	−9.7	−14.6	−3.8	-19.3^{aa}		
43	H_2CN	^{1}H	78.4	77.5	84.8	81.3	74.2^{bb}	83.2	82
		^{13}C	−23.6	−25.7	−24.5	−24.4	27.8^{bb}	28.9	
		^{14}N	10.0	6.2	8.2	8.1	9.2^{bb}	9.2	
44	H_2CO^+	^{1}H	118.0	120.0	131.3	125.9	134.2^{cc}	132.74	83
		^{13}C	−30.1	−35.1	−33.5	−33.2	-34.6^{cc}	38.89	
		^{17}O	−21.4	−9.8	−15.4	−3.5	-14.5^{cc}		
45	H_2NO	^{1}H	−5.9	−13.0	−14.3	−10.7	-10.99^{dd}	10.53	84
		^{14}N	12.8	5.2	5.5	5.4	10.10^{dd}	9.67	
		^{17}O	−18.1	−12.9	−17.2	−8.3	-27.00^{dd}		
46	NH_3^+	^{14}N	18.7	13.3	14.8	9.9	18.2^{ee}	19.6	85, 86
		^{1}H	−27.1	−27.1	−26.9	−25.5	-26.0^{ee}	27.4	
47	PH_3^+	^{31}P	349.7	383.4		367.2	427.7^{ff}	419.6	87
		^{1}H	3.7	5.0		5.5		<2.1	
48	CH_2CH	$^{13}C_{(CH_2)}$	−7.0	−5.3	−4.9	−4.0	-5.71^{gg}	8.55	78, 88− 90
		$^{1}H_{cis}$	59.9	59.7	65.0	62.2	51.81^{gg}	68.5	
		$^{1}H_{trans}$	36.5	38.2	41.7	39.9	29.79^{gg}	34.2	
		^{13}C	121.9	109.6	107.7	101.5	124.32^{gg}	107.6	
		$^{1}H_{(CH)}$	15.1	15.1	17.1	16.3	10.88^{gg}	13.3	
49	H_2CCN	^{1}H	−22.1	−20.0	−20.5	−19.5		20.98	91
		$^{13}C_{(CH_2)}$	31.8	22.4	23.9	16.8			
		$^{13}C_{(CN)}$	−20.0	−21.9	−20.9	−19.5			
		^{14}N	4.8	2.7	3.5	1.5		3.51	
		$2^{1}H$	−1.1	−1.1	−1.1	-1.1^{oo}			
		^{17}O	−25.3	−16.3	−20.9	-11.3^{oo}			
70	$C_6H_5CH_2$	$^{13}C_1$	−14.4	−14.1	−13.7	-13.2^{oo}	-13.7^{c}	14.45	109
		$^{13}C_o$	11.6	7.4	7.7	6.5^{oo}			
		$^{13}C_m$	−8.2	−7.0	−7.0	-6.8^{oo}			
		$^{13}C_p$	12.3	7.7	8.2	6.7^{oo}			
		$^{1}H_o$	−6.0	−5.4	−5.5	-5.7^{oo}	-5.24^{c}	5.15	110
		$^{1}H_m$	2.6	2.3	2.3	2.7^{oo}	2.22^{c}	1.79	110
		$^{1}H_p$	−6.8	−6.2	−6.5	-6.5^{oo}	-6.15^{c}	6.18	110
		$^{13}C_{CH_2}$	32.0	19.0	20.4	15.1^{oo}	20.9^{c}	24.45	109
		$^{1}H_{CH_2}$	−18.3	−16.2	−16.6	-16.0^{oo}	-15.75^{c}	16.30	110
71	$(CH_3CH_2)_2N$	$^{13}C_{CH_3}$	−9.8	−11.4	−10.7	-10.0^{oo}			
		$6^{1}H$	−0.7	−0.6	−0.7	-0.7^{oo}			
		$^{13}C_{CH_2}$	−0.5	−0.8	−0.8	-0.7^{oo}			
		$4^{1}H$	37.8	37.0	41.0	36.8^{oo}		36.9	101
		^{14}N	14.8	10.4	12.2	6.9^{oo}		14.3	
72	C_8H_7	$^{13}C_\alpha$	88.0	88.1	85.7	82.1^{oo}			
		$3^{13}C_\beta$	−5.4	−5.7	−5.0	-5.4^{oo}			
		$3^{13}C_\gamma$	9.7	11.0	10.8	10.6^{oo}			
		$^{13}C_\delta$	5.3	7.3	7.2	7.4^{oo}			
		$3^{1}H_\beta$	7.4	7.0	7.9	7.6^{oo}		8.2	111
		$3^{1}H_\gamma$	11.7	11.4	12.7	12.0^{oo}		12.4	
		$^{1}H_\delta$	5.7	5.8	6.3	6.1^{oo}		6.3	
73	$C_8H_6S_2^+$	$^{13}C_{2,3}$	2.7	0.5		-0.4^{oo}			
		$^{13}C_{5,8}$	−1.6	−1.6		-1.1^{oo}			
		$^{13}C_{6,7}$	1.6	0.5		0.4^{oo}			
		$^{13}C_{9,10}$	2.2	−0.1		-0.8^{oo}			
		$^{1}H_{2,3}$	−3.4	−3.1		-2.9^{oo}		3.32	102
		$^{1}H_{5,8}$	0.1	0.0		-0.3^{oo}		0.20	
		$^{1}H_{6,7}$	−1.3	−1.1		-1.3^{oo}		1.06	
		$^{32}S_{1,4}$	5.8	7.6		6.4^{oo}		9.35	
74	$C_{10}H_7$	$^{13}C_1$	1.2	4.9	5.1	5.8^{pp}			
		$^{13}C_2$	135.8	135.5	132.4	124.1^{pp}			
		$^{13}C_3$	2.8	5.8	5.9	6.2^{pp}			
		$^{13}C_4$	15.1	16.9	18.2	15.7^{oo}			
		$^{13}C_{others}$	<1.7	<1.5	<1.4	$<1.5^{pp}$			
		$^{13}C_9$	16.8	18.7	18.2	17.2^{pp}			
		$^{13}C_{10}$	−2.3	−2.1	−2.1	-1.7^{pp}			
		$^{1}H_3$	15.4	15.9	17.2	15.3^{pp}		15.7^{qq}	112
		$^{1}H_1$	19.6	20.1	21.8	19.5^{pp}		19.7^{qq}	
		$^{1}H_4$	5.6	5.3	5.9	5.4^{pp}		5.8	
		$^{1}H_{others}$	<0.6	<0.7	<0.7	$<0.6^{pp}$			
75	$C_8H_{12}^+$	$2^{13}C_\alpha$	15.8	7.3	8.3	2.2^{pp}			
		$4^{13}C_\beta$	−4.9	−5.7	−5.2	-5.2^{pp}			
		$2^{13}C_\gamma$	−0.2	−0.2	−0.2	-0.2^{pp}			
		$8^{1}H_\beta$	28.3	28.8	31.3	28.5^{pp}	27.6^{nn}	26.2	113
		$4^{1}H_\gamma$	2.1	2.4	2.6	2.3^{pp}	3.4^{nn}	2.7	

[a] HFSDCI (Contracted)/aug-cc-pVTZ at $r_e = 2.589$ Å.[40]

[b] MCSCF−RU at experimental geometry (3.005 au).[114]

[c] B3LYP/cc-pVQZ//B3LYP/cc-pVQZ.[17]

[d] FCI/4321 at experimental geometry (2.538 au).[115]

[e] B3LYP/augTZ2P′ at $r_e = 1.122$ Å.[116]

[f] Reference 17 at $r_e = 2.717$ Å.

[g] Reference 17 at $r_e = 2.630$Å.

[h] SAC-CI,[132] with [3,1] Dunning's basis.[133]

[i] CISD.[121]

[j] MRSCF-RU with vibrationally averaged values of a_{iso}.[114]

[k] UCCD(ST) using the experimental geometry.[88]

[l] UQCISD/6-311+G(2df,p)//UQCISD/6-311G(d,p).[5]

[m] Reference 120.

[n] CCSD(T).[118]

[o] SD-CI level. The (10s, 5p, 1d/8s, 1p) [8s, 4p, 1d/6s, 1p] was used.[2a] The geometry of ref 119 was employed.

[p] GC-LSDA.[107]

[q] B3LYP/6-311++G**//MP2/6-311++G**.[124]

[r] CCSD(T)/ucsp6-311++(3df,3pd)//CCSD(T)/cc-pVQZ.[123]

[s] CCSD(T)/TZ2P.[122]

[t] CISD.[2a]

[u] Reference 122.

[v] MRSDCI.[121]

[w] Reference 125.

[x] UQCISD/6-311+G(2d,p)//UQCISD/6-311G(d,p).[129]

[y] QCISD(T)/TZP−//UMP2/TZVP.[138]

[z] Reference 80.

[aa] SD-CI. The (10s, 5p, 1d/8s, 1p) primitive basis was used.[2a] The optimal geometry of ref 130 was employed.

[bb] MRD-CI/B_K//MCSCF-ACPF.[127]

[cc] PBE0 model.[126]

[dd] QCISD(T).[84]

[ee] Reference 107.

[ff] UQCISD(T)/6-311+ G(2df,p)//UQCISD/6-311G(d,p).[5]

[gg] CCSD(T).[116]

[hh] MP2(FC)/6-311G(d,p)//UMP2(FULL)/6-311G(d,p).[128]

[ii] UQCISD(T)/[7421/521]//UQCISD/6-311+G(2df, p).[94]

[jj] SAC−CI/STO*p*(GTO).[134]

[kk] UHF/TZP.[136]

[ll] UMP2/DZP//UMP/DZP. [129]

[mm] UHF with (10s,6p)[5s,4p] basis set for C and (5s)[3s] for H.[137]

[nn] B3LYP/6-311G*//B3LYP/6-31G*.[131]

[oo] B3LYP/cc-pVQZ//B3LYP/6-31G*.

[pp] B3LYP/cc-pVTZ//B3LYP/6-31G*.

[qq] The assignment of the experimental hfccs of protons 1 and 3 of radical **74** has been exchange taking into account the present theoretical calculation.

point is essential in the calculation of the Fermi contact term. An additional *s*-tight function to any standard basis brings about a small improvement of the hfccs due to the best representation of the atomic core.

Regression Analysis. Regression analysis of the calculated hfccs is summarized in Table 3. Several points must to be taken into account when the data of Table 3 and supplementary Tables 1 and 2 are analyzed. It is important to bear in mind the strong dependence of the various error analysis terms on the nature of the data set. As was pointed by Cramer et al.[39] the errors are larger for nuclei which the hfccs span a much larger range than for any other nuclei with a shorter hfccs range. Although the error expressed in a percentage basis could be coherent and intuitive, however this procedure gives rise to serious difficulties with hfccs that are very small or near to zero.

For this reason, we have chosen the regression analysis as the most simple and useful methodology to compare large set of calculated hfccs with their corresponding experimental hfcc data. Moreover, it is important to consider that the regression analysis indicates more about the coherence of predicted hfccs than about their accuracy. For the theoreticists, the main objective is to obtain a quantitative agreement between calculated and experimental data. It will be a proof of the quality of the employed wave functions and of the correct physical description of the studied system. For EPR experimentalists, however, it is of basic importance to carry out a correct

TABLE 3: Regression Analysis for Predictions of hfccs (G)

calculation scheme	*N*	R^2	slope	intercept	MAD[a]	range
		All Nuclei[b]				
B3LYP/6-31G*//B3LYP/6-31G*	174	0.9907	0.922	1.55	6.43	559.7
B3LYP/TZVP//B3LYP/6/31G*	174	0.9952	1.004	−1.66	4.72	559.7
B3LYP/TZVP//B3LYP/TZVP	174	0.9952	1.005	−1.66	4.66	559.7
B3LYP/EPR-III//B3LYP/EPR-III	127	0.9988	1.023	−0.90	3.02	559.7
B3LYP/cc-pVQZ//B3LYP/cc-pVQZ	174	0.9954	0.980	−2.46	5.41	559.7
B3P86/6-31G*//B3P86/6-31G*	174	0.9908	0.906	0.99	6.92	559.7
B3P86/TZVP//B3P86/6-31G*	174	0.9948	0.985	−2.67	5.45	559.7
B3P86/EPR-III//B3P86/EPR-III	127	0.9982	0.998	−1.77	5.77	559.7
B3PW91/6-31G*//B3PW91/6-31G*	174	0.9899	0.904	1.26	7.21	559.7
B3PW91/TZVP//B3PW91/6-31G*	174	0.9947	0.984	−2.96	5.75	559.7
B3PW91/EPR-III//B3PW91/EPR-III	127	0.9976	1.001	−1.83	3.91	559.7
		First Row (^{1}H)				
B3LYP/6-31G*//B3LYP/6-31G*	87	0.9982	0.977	1.00	2.30	333.5
B3LYP/TZVP//B3LYP/6/31G*	87	0.9983	0.933	0.57	2.77	333.5
B3LYP/TZVP//B3LYP/TZVP	87	0.9985	0.935	0.87	2.43	333.5
B3LYP/EPR-III//B3LYP/EPR-III	63	0.9985	1.025	0.18	2.17	333.5
B3LYP/cc-pVQZ//B3LYP/cc-pVQZ	87	0.9970	0.982	0.16	2.05	333.5
B3P86/6-31G*//B3P86/6-31G*	87	0.9952	0.955	0.45	3.04	333.5
B3P86/TZVP//B3P86/6-31G*	87	0.9973	0.898	0.87	3.48	333.5
B3P86/EPR-III//B3P86/EPR-III	63	0.9981	0.995	0.37	2.10	333.5
B3PW91/6-31G*//B3PW91/6-31G*	87	0.9945	0.958	0.69	3.28	333.5
B3PW91/TZVP//B3PW91/6-31G*	87	0.9968	0.903	0.82	3.36	333.5
B3PW91/EPR-III//B3PW91/EPR-III	63	0.9978	0.998	0.69	2.39	333.5
		Second Row (^{9}Be, ^{11}B, ^{13}C, ^{14}N, ^{17}O, ^{19}F)				
B3LYP/6-31G*//B3LYP/6-31G*	69	0.9947	0.950	3.58	6.67	559.7
B3LYP/TZVP//B3LYP/6-31G*	69	0.9987	1.062	−3.66	5.56	559.7
B3LYP/TZVP//B3LYP/TZVP	69	0.9988	1.066	−4.14	4.66	559.7
B3LYP/EPR-III//B3LYP/EPR-III	64	0.9990	1.026	−2.17	3.82	559.7
B3LYP/cc-pVQZ//B3LYP/cc-pVQZ	69	0.9980	1.028	−6.51	6.97	559.7
B3P86/6-31G*//B3P86/6-31G*	69	0.9954	0.937	2.21	6.44	559.7
B3P86/TZVP//B3P86/6-31G*	69	0.9976	1.044	−6.01	7.13	559.7
B3P86/EPR-III//B3P86/EPR-III	64	0.9984	1.005	−4.02	5.12	559.7
B3PW91/6-31G*//B3PW91/6-31G*	69	0.9955	0.936	2.62	6.34	559.7
B3PW91/TZVP//B3PW91/6-31G*	69	0.9980	1.046	−6.70	6.95	559.7
B3PW91/EPR-III//B3PW91/EPR-III	64	0.9985	1.006	−3.99	4.85	559.7
		Third Row (^{23}Na,^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{33}S, ^{35}Cl)				
B3LYP/6-31G*//B3LYP/6-31G*	18	0.9939	0.821	−5.38	25.38	419.2
B3LYP/TZVP//B3LYP/6-31G*	18	0.9931	0.888	3.89	11.39	419.2
B3LYP/TZVP//B3LYP/TZVP	18	0.9945	0.881	4.67	11.13	419.2
B3LYP/cc-pVQZ//B3LYP/cc-pVQZ	18	0.9945	0.876	0.31	15.22	419.2
B3P86/6-31G*//B3P86/6-31G*	18	0.9926	0.817	−7.19	27.89	419.2
B3P86/TZVP//B3P86/6-31G*	18	0.9940	0.891	2.15	12.03	419.2
B3PW91/6-31G*//B3PW91/6-31G*	18	0.9909	0.812	−7.80	29.32	419.2
B3PW91/TZVP//B3PW91/6-31G*	18	0.9958	0.886	0.51	12.76	419.2

[a] MAD (mean absolute deviation), defined as $(1/N)\sum_i^N |a_{\mathrm{iso}}(\mathrm{calcd}) - a_{\mathrm{iso}}(\mathrm{expt})|$. [b] In the case of the EPR-III basis set, only ^{1}H, ^{9}Be, ^{11}B, ^{13}C, ^{14}N, ^{17}O, and ^{19}F nuclei have been parametrized.

assignment of the measured magnetic parameters, irrespective of the quantitative agreement between calculated and experimental values. In this sense, a regression analysis will permit us to discern which is the best combination of functionals and basis sets between a wide variety of possible ones. This will avoid the indiscriminate use of a nonadequate theoretical methodology for this task and a very probable erroneous assignment of the measured hfccs.

For comparison sake, we consider this regression analysis divided in three parts. In the first one, we consider all the nuclei for all the calculations that were carried out. Then, we consider only the proton nuclei (^{1}H), the second row nuclei (Be, B, C, N, O, and F) and finally the third row nuclei (Mg, Al, Si, P, S, and Cl). The main results of this regression analysis can be seen in Table 3. In Figures 2−5, we depicted only the linear regression representing the calculated a_{iso}(G) vs experimental a_{iso}(G) for B3LYP functional with the four different basis sets considered, 6-31G*, TZVP, EPR-III, and cc-pVQZ. We note that Figure 5 includes B3LYP/cc-pVQZ//B3LYP/6-31G* for **64**−**73** radicals and B3LYP/cc-pVTZ//B3LYP/6-31G* for **74** and **75** radicals. In each figure, we represent the points for the corresponding hfcc values, the bisectrice (dotted line) and the slope of linear regression (solid line). Moreover, to clarify the above representation, we enclose an amplified area ranging from 0 to 50 G, in which many data are included. The complete results of linear regression analysis for all functional/basis set combinations here considered are given in Table 3. This table contains four well-defined parts, corresponding to the regression analysis of all nuclei, the proton, second row nuclei, and third row nuclei, respectively. The first column shows the calculation scheme, the second one gives the number of points (*N*) considered for the regression analysis, and the rest of the columns correspond to the results of this analysis: correlation coefficient (R^2), slope, intercept, mean absolute deviation (MAD), and data range. The MAD only considers the absolute value, so that all deviations are converted to positive numbers, added, and then averaged. We have defined the employed MAD for our calculations in the bottom of Table 3.

In general, all DFT methods investigated yield hfccs close to experimental values. For all nuclei the numbers of hfcc values

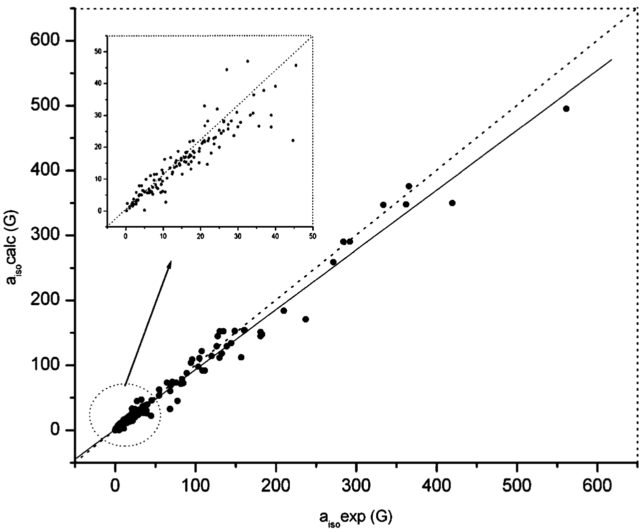

Figure 2. Linear regression representing the predicted hfccs for all nuclei subset with B3LYP/6-31G*//B3LYP/6-31G*. The inset expands the region from 0 to 50 G.

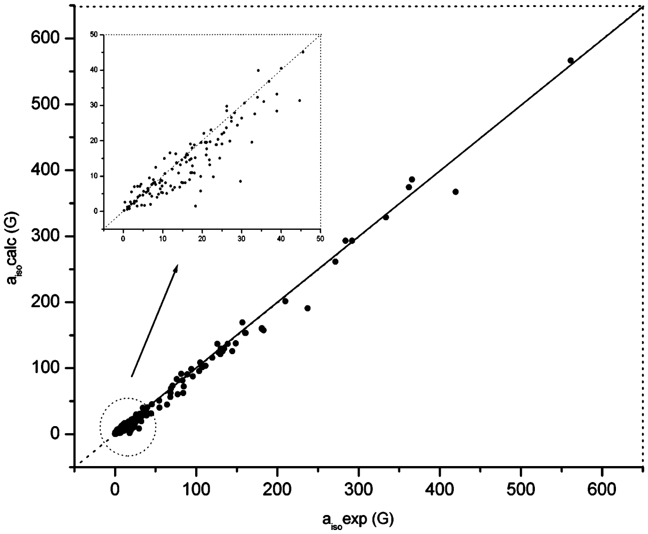

Figure 3. Linear regression representing the predicted hfccs for all nuclei subset with B3LYP/TZVP//B3LYP/TZVP. The inset expands the region from 0 to 50 G.

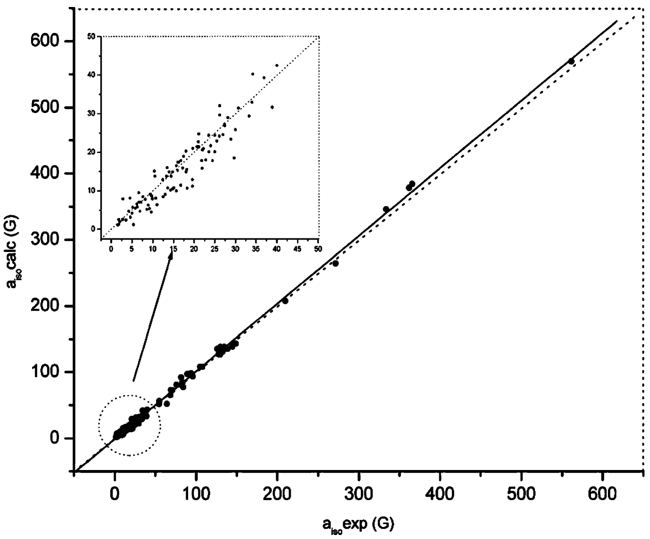

Figure 4. Linear regression representing the predicted hfccs for proton (^{1}H) and the second row nuclei subsets with B3LYP/EPR-III//B3LYP/EPR-III. The inset expands the region from 0 to 50 G.

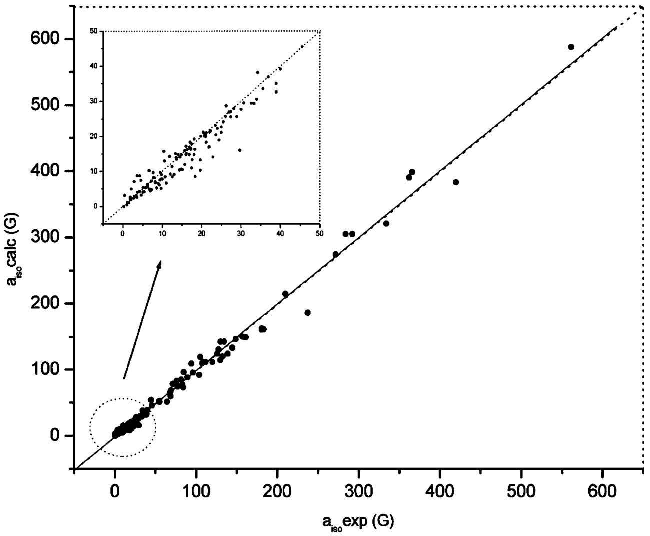

Figure 5. Linear regression representing the predicted hfccs for all nuclei subset with B3LYP/cc-pVQZ//B3LYP/cc-pVQZ. The inset expands the region from 0 to 50 G.

are 174 excepting for EPR-III basis sets, because this basis did not include atoms of the second row. All the R^2 values are higher than 0.99. When the regression analysis is only performed for protons, the number of points for statistics is reduced by half and this reduction also occurs when the analysis is carried out on the second row. The third row of nuclei only contributes with 18 values for the regression analysis.

From the analysis of Table 3 several points should be singled out for comments:

(a) Considering all nuclei, the slopes are close to 1.0 excepting the case of B3LYP, B3P86 and B3PW91 functionals with the small basis set 6-31G*, where the slopes are, however, higher than 0.90. This slope improves a great amount when TZPV basis sets are used. We can also conclude that the optimization of the geometry is less important, because the difference between B3LYP/TZPV//B3LYP/6-31G* and B3LYP/TZPV//B3LYP/TZPV is very small in the slope, intercept, and MAD. For this reason, we have not optimized the geometries with TZPV basis set for the other two functionals (B3P86 and B3PW91). The best values are obtained using the EPR-III basis set for the three functionals. The slopes obtained are very close to one, the intercept is near to zero, and the MAD is smaller. Because the range of the compared hfccs is very wide, 559.7 G, the results for this basis set can be considered to be excellent.

(b) For protons, the regression analysis indicates that the calculated hfccs are fitted better than when all nuclei are considered. The number of computed ^{1}H hfccs (87 values) is a half than those here considered (174 values) and for EPR-III basis set only 63 values are obtained. The correlation coefficients are higher than 0.995 and the slopes improve in each case except for TZVP results. The improvement is particularly notable in the intercept with values lower than 1.00 and MAD lower than 3.5 G. The above conclusions for all nuclei are very similar in this case. The range is also notably wide (333.5 G).

(c) For the second row, the number of values is less than the half of values for all nuclei (69 and 64 for EPR-III), and the regression analysis fits well. Although the intercept and the MAD present higher values, the range is the same for all nuclei subset. Finally, the analysis for the third-row is limited to 6-31G*, TZPV and cc-pVQZ basis sets and the results are poorer, may be, because the number of values is only 18. The regression analysis gives rise to slopes from 0.8 to 0.9, and we think that the values considered give rise to a nonsignificant statistic. However, for three nuclei of the third-row, ^{29}Si, ^{31}P, and ^{33}S, we have carried out a more complete analysis using B3LYP/TZVP//B3LYP/6-31G* scheme with 155 values and obtaining a good agreement between calculated and experimental data.[129,139]

Conclusions

This is the most significant attempt carried out to date in order to compare theoretical and experimental a_{iso} values using DFT methods. For this data set of 75 diverse radicals, 174 experimental hfccs are available for 14 different nuclei. The most accurate theoretical predictions are obtained from B3LYP/EPR-III//B3LYP/EPR-III (^{1}H and second row nuclei).

Density functional theory provides reliable predictions of the hfcc values of radicals even when large basis sets are not used. Even though the three hybrid functionals considered in this work give similar values, the B3LYP seems to be the best functional for computing hfccs.

The influence of the basis set appears to be more important than the hybrid functional used. Although, EPR-III is an excellent basis set for calculating hfccs, however for large molecules, smaller basis sets as 6-31G* and TZPV are a good alternative. The geometries of radicals are not very sensitive to the size of the basis set used in the geometry optimization. However, the conformational changes play an important role in the computation of hfccs of some radicals.[139]

The cc-pVQZ basis set is not a good candidate to compute hfccs, because other smaller basis sets give rise to similar or closer values to the experimental ones. The combination of the B3LYP functional with a TZPV basis set results in an excellent predictor of hfccs for radicals of moderate and large sizes. For very large radicals, the use of 6-31G* basis set brings about a drastic reduction of computing time in the geometry optimization and also predicts good values of hfccs, as was reported by Batra et al.[16]

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Supporting Information Available: Supplementary Table 1, containing the calculated hfccs with input schemes B3P86/6-31G*//B3P86/6-31G*, B3P86/TZVP//B3P86/6-31G*, and B3P86/EPR-III//B3P86/EPR-III and supplementary Table 2, containing the calculated hfccs with input schemes B3PW91/6-31G*//B3PW91/6-31G*, B3PW91/TZVP//B3PW91/6-31G*, and B3PW91/EPR-III//B3PW91/EPR-III. This material is available free of charge via the Internet at http://pubs.acs.org.

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