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Relativistic Density-Functional Computations of the Chemical Shift of ^{129}Xe in Xe@C_{60}

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Relativistic contributions to the chemical shift of ^{129}Xe in Xe@C_{60} have been computed by means of a two-component relativistic density functional approach. It is demonstrated that in all-electron calculations the scalar relativistic effects are moderate, of the order of 20 ppm depending on the basis set used, and tend to increase the chemical shift. The spin−orbit coupling induced contributions are small (a few ppm) and negative in all but two cases. The basis set dependence of the results is pronounced. In contrast to nonrelativistic Hartree−Fock studies of Xe@C_{60}, which strongly underestimate the experimental value of 179.24 ppm with respect to Xe gas, [61−72 ppm, *Chem. Phys. Lett*. **1997**, *275*, 14; 103 ppm, present work], our DFT results systematically overestimate the xenon shift (relativistically, ≥246 ppm). The large difference between the present nonrelativistic DFT results and the Hartree−Fock data can serve as an estimate of the important contributions due to electron correlation. Compared to the chemical shift range of ^{129}Xe (≈7000 ppm) the chemical shift in Xe@C_{60} is not large, and sizable relative errors can therefore be expected from currently feasible computations. Many comparatively small effects, with opposite signs, contribute to the final result and must therefore not be neglected.

1. Introduction

The noble gas ^{3}He can be introduced into C_{60} as well as higher fullerenes and detection of its NMR spectrum has had many important consequences for fullerene chemistry. Specifically, ^{3}He has been used as a probe for following, for example, fullerene Diels−Alder reactions,[1] reduction of C_{60} and C_{70},[2] the separation of isomers of C_{84},[3] along with other fundamental investigations.[4−11] The only other noble gas isotope easily observable with NMR is ^{129}Xe, with a spin of $^1/_2$. However, measuring the NMR spectrum of Xe@C_{60} has proved to be difficult. Only recently have researchers managed to incorporate enough ^{129}Xe into the cage and obtain a sufficiently enriched sample of ^{129}Xe@C_{60} to determine the chemical shift as being 179.24 ppm with respect to xenon gas.[12] The NMR chemical shift of ^{129}Xe is very sensitive to changes in environment with a range of more than 7000 ppm, making it a challenging case for computational studies. At the same time, this suggests that it would be an ideal probe to help advance the understanding of fullerene chemistry, provided that experimental difficulties could be overcome. Already, ^{129}Xe NMR spectroscopy is one of the most powerful tools available to study the local structure of porous materials, for example zeolites,[13,14] glasses,[15] polymers[16] as well as proteins in solution[17] and liquid crystals.[18]

Previous theoretical investigations have been successful in reproducing the chemical shifts of He@C_{60} along with He@C_{70}.[19] Calculated values at the HF/TZP(He)/DZ(C) level of −8.7 and −24.0 ppm are in agreement with the experimental values of −6.3 and −28.8 ppm for the aforementioned fullerenes. However, subsequent calculations failed to accurately predict the chemical shift of Xe@C_{60}, yielding values of 72 ppm using the DZP(Xe)/6-31G**(C) basis and 61 ppm using a [5s4p1d] basis for C and a well-tempered basis on Xe, contracted and augmented to [15s13p9d3f].[20] The computational method (Hartree−Fock) neglected electron correlation along with relativistic effects. The latter are known to be substantial for tellurium and iodine, the neighboring elements in the periodic table. In this study we aim to address the importance of these contributions by using the scalar and spin−orbit coupled relativistic approaches within the framework of density functional theory. Furthermore, we will investigate the sensitivity of the chemical shift with respect to the size of the basis set used.

2. Methodology, Computational Details

Most computations have been carried out with the Amsterdam density functional (ADF) program package.[21−23] It incorporates a modified (by one of us, J.A.) version of the code developed by Wolff et al.[24] for the two-component relativistic computation of nuclear shielding constants, based on the zeroth-order regular approximation (ZORA) Hamiltonian.[25,26] The modifications that have been made do not affect the results obtained with the program but implement a significantly better scaling of the computational time with increasing system size. This was in particular necessary to carry out the frozen-core computations including spin−orbit coupling for Xe@C_{60}.

The shielding constant σ_A for a nucleus A within the relativistic ZORA formalism consists of four terms:

$$\sigma_A = \sigma_A^D + \sigma_A^P + \sigma_A^{SO} + \sigma_A^{GC} \tag{1}$$

Here, σ_A^D is the diamagnetic shielding, and σ_A^P is the paramagnetic one. These two terms are also present in a nonrelativistic or a scalar (i.e., one-component) ZORA calculation. σ_A^{SO} denotes the spin−orbit induced terms due to the two-component analogues of the Fermi-contact (FC) and the spin-dipole (SD) operators. It is important to note that, due to the different shapes of the orbitals obtained from a variational two-component calculation, σ_A^D and σ_A^P are also somewhat different when comparing with scalar relativistic calculations. Finally, σ_A^{GC} denotes gauge correction terms obtained from the implemented GIAO (gauge including atomic orbitals[27−29]) formalism in a

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finite basis. For Xe@C_{60} a “natural” gauge origin is the Xe nucleus, which has been adopted in all calculations.

The comparatively expensive two-component relativistic computations of the chemical shift have not been carried out for all the computational models but for a representative subset, because during the course of this work it became obvious that the spin−orbit coupling induced effects are small.

In the present calculations we have mainly employed two different scalar-ZORA optimized geometries that were obtained with the Vosko−Wilk−Nusair[30] (VWN) local density approximation (LDA) functional, and with the Becke−Perdew (BP)[31−33] generalized gradient approximation (GGA) density functional. For Xe, a core including the shells 1s to 4p (36 electrons) has been kept frozen and a TZ2P basis was used in the geometry optimizations. For C, a 1s frozen core and a DZP basis has been employed. Xe@C_{60} affords two different C−C bond lengths. The present results are 1.436/1.385 Å for ZORA-VWN, and 1.450/1.396 Å for ZORA-BP, respectively. Because the LDA often tends to yield somewhat too short C−C bond distances, whereas the BP GGA has a tendency to yield somewhat too long C−C bonds, it can be assumed that these two geometries bracket the one that would be obtained with more accurate density functionals. Using different geometries with otherwise the same settings in the computations illustrates the geometry dependence of the ^{129}Xe chemical shift. During the optimizations with ADF, the icosahedral symmetry of Xe@C_{60} could not be fully employed, therefore we have carried out the optimizations in D_5 symmetry. The resulting C−C bond distances differ only very slightly among each other, and the computed ^{129}Xe-shielding tensors have been confirmed to afford only very minor anisotropies of less than 0.1 ppm (which is at the chosen limit of the numerical accuracy for the ADF NMR computations) due to a slight deviation from the ideal I_h symmetry.

We have also carried out nonrelativistic geometry optimizations of C_{60} using the aforementioned computational settings. For VWN and BP the two different bond lengths are 1.436/1.384 and 1.449/1.395 Å, respectively. The geometry of the fullerene cage is very little affected by the presence of the noble gas. This has also been found in ref 34. A comparison of the bond lengths obtained in ref 34 for C_{60} with an LDA functional (not further specified) and the 6-31G** basis (1.442/1.392 Å) shows deviations of less than 0.01 Å compared to our results.

For further comparison of different functionals and their influence on the molecular geometry, additional computations have been carried out with the Turbomole program package.[35−37] With the latter, a geometry optimization in I_h symmetry has been performed for Xe@C_{60}, employing the B3LYP hybrid density functional[38] and the default TZVP basis for C and Xe. For Xe, a 46-electron ECP[39] has been used to account for scalar relativistic effects. The resulting C−C bond lengths are 1.453/1.393 Å, quite close to the ZORA-BP result. For comparison, the geometry obtained with Turbomole with the BP functional and the TZVP basis is 1.456/1.402 Å. These results are also in excellent agreement with the 6-31G**/B3LYP results of ref 34 for C_{60} (1.453/1.395 Å). A Hartree−Fock optimization with the TZVP basis set yields 1.436/1.384 Å, on the other hand, which is closer to the ZORA-VWN result obtained with ADF. Unfortunately, because of the different basis sets (Slater type vs Gaussian) and the different relativistic approaches employed in the computations, the results from the two programs are not directly comparable. At the B3LYP optimized geometry, nonrelativistic calculations of the ^{129}Xe shift have additionally been carried out with Turbomole, employing for xenon the all-electron TZV basis available in the Turbomole basis set collection, augmented with the polarization function of the TZVP xenon ECP basis. ADF NMR computations based on the B3LYP geometry have also been performed for a direct comparison.

The VWN LDA, the BP GGA and, for comparison, in one case also the popular revPBE (Perdew−Burke−Ernzerhof[40−43]) GGA have been applied in the single point computations that precede the relativistic nuclear shielding determination. The explicit form of these Kohn−Sham potentials does not enter the shielding expression in the chosen (“uncoupled”) approach [except for the σ_A^{GC}, which are, however, a few ppm at most in our calculations. In principle, the Kohn−Sham potential also enters the shielding through its occurrence in the ZORA operators, but with negligible effects for different choices for the density functional]. However the choice of the density functional implicitly, but strongly, influences the results by affecting the orbital shapes and their energies. The latter is also true for NMR computations with the B3LYP functional, but in addition there occurs a direct shielding contribution from the solution of the coupled perturbed Kohn−Sham equations. The same holds for the Hartree−Fock (HF) method.

To determine the sensitivity of the ^{129}Xe-shifts with respect to the quality of the basis set, we have carried out a number of calculations varying the size of the basis set, nonrelativistically and relativistically, including or excluding spin−orbit (SO) coupling. The chemical shifts have been described as a “valence property” in the sense that, even though the integrals that contribute to the shielding tensor are mainly obtained from the near-nuclear regions, the chemical shift contributions often result mainly from the core tails of the valence (and outer core) orbitals. Therefore, a reasonable value of the chemical shift can often also be obtained from frozen-core calculations that are (at least after the program modifications that we have implemented) significantly cheaper than all-electron ones. A comparison of all-electron with frozen-core computations is therefore also made in the next section.

Generally, the ADF nonrelativistic computations have been carried out with the same relativistic basis set that has been used for the ZORA computations, to eliminate basis set effects from the estimate of relativistic effects. At the same time, it is also true that a relativistic basis set is not necessarily flexible enough to be useful for a nonrelativistic computation. This is only of concern regarding the Xe basis as the basis for the light element C is the same in both cases. The new QZ4P ZORA ADF basis is considered[44] to offer enough flexibility for both relativistic and nonrelativistic computations and we have confirmed that the trend from nonrelativistic to scalar relativistic results is the same for this basis as it is for the somewhat smaller TZ2P basis.

It is important to note that in the ADF computations Slater basis functions were employed, whereas Gaussian basis sets were utilized in the Turbomole computations. The acronyms TZP, TZVP, etc., refer to the nomenclature used in the respective basis set databases for each program.

3. Results and Discussion

3.1 Binding Energies. Interaction energies (with respect to free C_{60} and Xe) were computed with ADF for the two optimized geometries. Using the VWN LDA functional, the binding energy was computed as being −23.6 kcal/mol (BSSE uncorrected) and −7.4 kcal/mol (BSSE corrected). Similar results were reported in the literature, employing the 3-21G basis set.[34] The BP GGA yielded bonding energies of 9.7 kcal/mol

TABLE 1: Calculated NMR Chemical Shifts of ^{129}Xe in Xe@C_{60} (ppm)[a,b]

computational Settings				δ (Xe)		
basis for C[c]	basis for Xe[c]	geometry	functional	NR	scalar	SO
SZ (1s)	DZ (4d)	VWN	BP	117.20[f,g]	111.87	108.87
SZ	DZ	VWN	BP	149.24[f]	162.63	163.56
DZP (1s)	TZP (4p)	VWN	VWN	224.69[f,h]	221.49	
DZP (1s)	TZP (4p)	VWN	BP	201.82[f,i]	199.87	
DZP (1s)	TZ2P (4d)	VWN	VWN	217.89[f]	214.52	211.63
DZP (1s)	TZ2P (4d)	VWN	BP	194.94[f]	192.91	190.49
DZP	TZ2P	VWN	VWN	262.39[f]	281.34	279.06
DZP	TZ2P	VWN	BP	237.10[f]	254.63	252.73
DZP	TZ2P	BP	BP	229.14[f]	247.40	246.00
DZP	TZ2P	B3LYP	VWN	248.31[f]	267.37	
DZP	TZ2P	B3LYP	BP	224.28[f]	241.45	
TZVP	TZVP	B3LYP	BP[d]	276.03		
TZVP	TZVP	B3LYP	B3LYP[d]	226.05		
TZVP	TZVP	B3LYP	HF[d]	102.73		
DZP	TZ2P	BP	RevPBE	231.32[f]	250.52	249.27
TZP	TZ2P	BP	BP	243.32[f]	264.00	
DZP	QZ4P	BP	BP	270.36[f]	292.38	298.63
TZP	QZ4P	BP	BP	265.89[f]	286.97	

[a] With respect to the free atom. NR = nonrelativistic, scalar = relativistic scalar ZORA, SO = relativistic scalar + relativistic spin−orbit ZORA. NMR computations carried out with ADF unless noted otherwise. [b] Current experimental value: 179.24 ppm.[12] [c] Frozen core in parentheses. [d] Turbomole NMR computation with NR all-electron basis. [f] With ZORA basis. [g] Using NR basis 113.10 ppm. [h] Using NR basis 246.02 ppm. [i] Using NR basis 221.49 ppm.

TABLE 2: Individual Contributions to the ^{129}Xe Shielding Constant in Xe and Xe@C_{60}, Obtained from ADF Calculations[a]

	^{129}Xe atom	Xe@C_{60}	δ(^{129}Xe)
Nonrelativistic			
σ^D	5646.66	5640.68	5.98
σ^P	0.00	−231.12	231.12
total σ	5646.66	5409.56	237.10
Scalar ZORA			
σ^D	5578.34	5572.52	5.82
σ^P	82.15	−166.65	248.80
total σ	5660.50	5405.87	254.63
Spin−Orbit ZORA			
σ^D	5581.76	5575.92	5.84
σ^P	79.91	−170.00	249.91
σ^{SO}	747.46	750.48	−3.02
total σ	6409.13	6156.40	252.73

[a] The data correspond to the DZP/TZ2P/VWN/BP entry in Table 1. Small σ^{GC} contributions are included in the individual σ^P, σ^{SO} terms of the molecule.

(BSSE uncorrected) and 27.2 kcal/mol (BSSE corrected). Our GGA results are comparable with Hartree−Fock data from the literature. At this level Xe@$C_{60}$was found to be destabilized by 25.0 kcal/mol[34,45] (BSSE uncorrected, 3-21G basis) and 36.3 kcal/mol (BSSE corrected, 3-21G basis)[34] or 36.6 kcal/mol[20] (BSSE corrected, 6-31G** (C) and DZP (Xe) basis). Our GGA results are also very similar to the B3LYP data of ref 34 of 20.8 kcal/mol (BSSE uncorrected) and 31.3 kcal/mol (BSSE corrected), which in turn are very similar to the Hartree−Fock results quoted above. Our LDA values, on the other hand, are comparable with MP2 binding energies of −17.1 kcal/mol (BSSE uncorrected) and −5.4 kcal/mol (BSSE corrected)[20] and other LDA values of −21.1 kcal/mol (BSSE uncorrected) and −9.2 kcal/mol (BSSE corrected).[34,45] With the available limited set of data data at hand we do not want to speculate about specific defects in the functionals related to a description of dispersion effects vs other approximations in the treatment of correlation in comparison with the MP2 method. However, it becomes obvious that electron correlation plays an important role for the interaction between Xe and C_{60}—a fact that is very strongly visible in the results for the ^{129}Xe chemical shift, which will be discussed next.

3.2. Xe Chemical Shift and Relativistic Effects. In Table 1 the results of our NMR calculations are summarized. With the exception of the first two entries, all of our DFT computations overestimate the chemical shift of ^{129}Xe in Xe@C_{60}. In comparison, the Hartree−Fock results by Bühl et al.,[20] which exclude electron correlation by definition, strongly underestimate the xenon shift in comparison with the recent experimental result. We have included a Hartree−Fock computation in our study as well, leading to the same trend. The basis set used for the first two computations are small and the results they give are not meaningful. However, it is instructive to show the large basis set dependence of the calculated observable as well as the effect of core contributions.

The chemical shift, according to our computational results, is determined by a deshielding change in the paramagnetic contribution to the Xe shielding as compared with the free atom, whereas the diamagnetic contribution to the shielding remains almost the same, within a range of about 10 ppm. It should be noted at this point that, according to the way the ZORA shielding tensor has been defined and split into paramagnetic and diamagnetic contributions in the original paper by Wolff et al.,[24] the “paramagnetic” term is not always zero for atoms because of the presence of a function $\mathcal{K}(r) = 2c^2/(2c^2 - V(r))$, with V being the Kohn−Sham potential, in the respective matrix elements. However, in the nonrelativistic case, where $c \rightarrow \infty$, $\mathcal{K} \rightarrow 1$, the paramagnetic contribution evaluates to zero for spherical atoms. Only the sum of the two contributions is physically meaningful. In the two-component (including spin−orbit coupling) ZORA computations, there is the additional σ_A^{SO} term. The diamagnetic and in particular the paramagnetic shielding values are also affected by the change of the orbital shapes and energies due to the variational inclusion of the electronic spin−orbit (SO) coupling. Based on our computational results, the SO contributions to δ(^{129}Xe) are generally rather small. The total σ_A^{SO} for the atom and for Xe@C_{60} are large in comparison to the tiny net effects on the chemical shifts. They are about +750 ppm in the all-electron calculations, depending on the method and basis set used, but nearly completely cancel when the chemical shift is evaluated. The resulting δ^{SO} are therefore of the same magnitude (a few ppm) as the SO induced changes of δ^P and δ^D. Table 2 lists the respective contributions for one of the cases of Table 1. The results are representative for the other cases.

It is interesting to note that the scalar relativistic contributions to the nuclear shielding of ^{129}Xe are small in the ZORA DFT computations. The relativistic increase of the ^{129}Xe shielding constant of 763 ppm (for the atom, Table 2, BP functional) is almost exclusively caused by the SO contributions. It appears that the total xenon shielding (6409 ppm in our computations) is underestimated when compared with reference values from the literature. For the Xe atom we obtain essentially the same shielding constant as listed in Table 2 (within 1 ppm difference) when the Xα functional is employed instead. In comparison, Feiock et al. have in 1969 reported numerical four-component and nonrelativistic Xα computations of the shielding constants of atoms and obtained 7042 (relativistic), and 5996 (nonrelativistic) ppm, respectively, for xenon.[46] This four-component result is close to the 6958 ppm of ref 47 obtained with a Dirac Hartree−Fock program. The included corrections due to a finite nuclear radius are less than −30 ppm. However, the nonrelativistic result of ref 46 of 5996 ppm does not agree with the nonrelativistic HF result of 5327 ppm of ref 47, nor with a recently published nonrelativistic Hartree−Fock reference value of 5642 ppm (point nucleus).[48] The recommended near basis-set-limit four-component value of ref 48 obtained with a Gaussian nucleus model is 6938 ± 21 ppm. Correlation effects have been found to be negligible for rare gas atomic shieldings in this work. Our present nonrelativistic results are very close to the one of ref 48; however the relativistic increase appears to be somewhat too small. It is possible that this is caused by the numerical integration that is applied in the ADF code to calculate the necessary matrix elements, or it is caused by the ZORA approximation to relativity itself. However, previous experience with the computation of ZORA chemical shifts and spin−spin coupling constants indicates that such missing contributions, if existing, are likely to be of importance mainly for the absolute shielding, but not at all, or much less for "chemical" properties such as the chemical shift or spin−spin coupling constants.[24,49,50]

To summarize the preceding paragraphs, it can be seen from Table 1 that the relativistic corrections to $\delta(^{129}\mathrm{Xe})$ in Xe@C_{60} are moderate to small. In particular, the total SO effects on the chemical shift, often found to be of high importance in the NMR of heavy atomic systems,[50] are almost negligible when the general level of accuracy of the DFT calculations is considered. The scalar relativistic effects are not negligible but are also not large enough to drastically improve upon the nonrelativistic results. In fact, they do not have the "desired" sign since in the all-electron calculations they cause an increase of $\delta(^{129}\mathrm{Xe})$.

3.3. Basis Set Dependence and Influence of the Frozen Core Approximation. It turns out that the frozen core calculations are not capable of reproducing the scalar relativistic increase of the ^{129}Xe-shift that is obtained from the all-electron calculations. A slight *decrease* of $\delta(^{129}\mathrm{Xe})$ is obtained instead. This is most likely due to the missing flexibility of the valence orbitals' core tails in the Xe basis sets, rather than due to contributions from the core orbitals themselves. Unlike the all-electron basis sets, the ADF ZORA frozen core basis sets for xenon probably do not contain enough steep functions that are required to compute reliable scalar relativistic effects on the shielding tensor. It can be seen that the basis set dependence of the results is quite pronounced when the nonrelativistic results obtained with the nonrelativistic basis are compared with those from the ZORA basis set for Xe, resulting in differences of ∼20 ppm. The ZORA basis here yields "better" results in comparison with the experimental value of 179.24 ppm.

The basis set dependence of the results in Table 1 is generally very pronounced. This could probably be expected, taking the small magnitude of the xenon shift with respect to its whole chemical shift range of more than 7000 ppm into account. Rather subtle changes in the electronic structure must therefore result in comparatively large *relative* changes of the ^{129}Xe chemical shift in Xe@C_{60}, which is also likely to be the reason that the DFT results are so different from the earlier Hartree−Fock data. Compared to the total Xe shift range, the absolute error with both methods is not large. It is interesting to note that the agreement with experiment worsened when more flexible basis sets were employed in the computations. Our best computed result should have been obtained at the ZORA spin−orbit level with the GGA functional and the carbon TZP/Xe QZ4P basis set. However, the (too costly) spin−orbit result can be expected to exceed the experimental value by some 100 ppm. We have previously found[51] that the QZ4P basis set yields too large chemical shifts for heavy atoms, and usually the TZ2P basis performs much better in comparison with experiment. Whether this is due to a fortuitous error cancellation or because the TZ2P basis is better optimized is not clear at this time. The TZ2P basis on Xe still yields too large ^{129}Xe shifts by approximately 70 ppm.

Table 1 also demonstrates that by choosing the "right" unflexible basis, in particular for xenon (DZ or frozen cores), it is easy to obtain a computational result that is close to the experimental one. This is, of course, rather well-known regarding the computation of many properties but perhaps particularly true for NMR observables due to their sensitivity. Here, for instance, a neglect of relativistic effects would yield results that are closer to experiment, while (provided one can transfer these effects between DFT and Hartree−Fock computations) improving the Hartree−Fock data.

3.4. Discussion of Approximations in Chemical Shift Computations. It is known that many popular "standard" density functionals often predict a too small HOMO−LUMO gap for compounds of main group elements. The inverse HOMO−LUMO gap enters directly the expressions for the paramagnetic and the SO shielding tensor that, as we have seen above, determine the ^{129}Xe chemical shift in Xe@C_{60}. Therefore, the fact that the present results overestimate the xenon shift can tentatively be attributed to such deficiencies in the applied density functionals. This is corroborated by the large difference between the BP and the B3LYP results obtained with Turbomole (Table 1). It is likely that certain semiempirical correction schemes for the orbital energy differences that have been proposed in the literature[52] would lead to significantly smaller chemical shifts for the studied compound, as they tend to lead to smaller paramagnetic contributions. At the same time, more systematic improvements in the density functionals must also lead to the same trend, for instance, to correct for self-interaction errors, as we have previously done for a number of difficult cases.[53] Unfortunately, Xe@C_{60} is at this time out of range for such computations because of the requirements regarding the size of the auxiliary basis that would have to be used in the ADF code to calculate the Coulomb potential. The comparison of the BP with the revPBE results in Table 1 indicates that no significant improvement would be obtained with other common, not self-interaction free non-hybrid GGAs.

Regarding the comparison of different functionals that we have employed in the computations, it is first of all important to note that the GGA calculations systematically yield smaller xenon shifts than the LDA computations. A very strong effect (toward the experimental value) is further seen from a comparison of BP with B3LYP. A similar trend can be seen for a comparison of different geometries (VWN vs BP vs B3LYP) at otherwise the same computational approximations. If these trends continue toward the hypothetical exact density functional, better agreement with experiment can indeed be expected in the future. The very high importance of the treatment of electron correlation is demonstrated in Table 1 by comparing the DFT and Hartree−Fock values.

Another source of error is most likely the neglect of solvent effects. We have performed a few computations that included the COSMO[54,55] continuum solvent model with a dielectric constant of 2.284 for benzene, the solvent used in the experiments. A further increase of the xenon shift of the order of magnitude of 10 ppm has been found. However, we do not regard these results as being meaningful because this model just covers the electrostatic contribution to the solvent effects and has furthermore not yet been consistently implemented in ADF for use with NMR computations. The results are therefore not listed in Table 1. We mention them here to illustrate that solvent effects can also easily amount to a few 10 ppm, with yet unknown sign.

To estimate the magnitude of dispersion effects on $\delta(^{129}\mathrm{Xe})$, Bühl et al.[20] have performed a nonrelativistic MP2 calculation of the chemical shift of Xe in a Xe−benzene complex by employing the same Xe−C distance as found in the endohedral compound. A deshielding of 15 ppm was found, in contrast to Hartree−Fock calculations that predicted virtually no effect on the Xe shielding. Recently published scalar relativistic ZORA DFT calculations on the same complex "qualitatively agree with those of Bühl et al."[56] The authors of the latter paper have plotted the chemical shift for a range of Xe−benzene distances. The graphics allow estimation of a ^{129}Xe chemical shift of approximately 20−40 ppm for Xe−C distances found for Xe@C_{60}. We have performed scalar relativistic LDA and GGA calculations following the recipe of Bühl et al. and obtained 32.3 and 36.0 ppm, respectively, for the Xe shift, in agreement with the results of ref 56. Again, the results are strongly dependent on the level by which electron correlation is treated. However, in contrast to the binding energies the LDA and GGA results are in good agreement with each other. They predict an even larger chemical shift for xenon than the MP2 calculations, whereas Hartree−Fock predicts almost no interaction between Xe and benzene.[20] Our nonrelativistic GGA result is 30.0 ppm, indicating that relativistic effects are rather small also in this case.

The effects from vibrations have been neglected in the calculations. We have tried to gauge the importance of vibrational corrections to $\delta(^{129}\mathrm{Xe})$ by displacing the xenon atom within the C_{60} cage by 0.05 and 0.2 Å for the BP geometry. The chemical shift was calculated using scalar ZORA (BP functional) and the all-electron TZ2P and DZP basis sets for xenon and carbon. The chemical shift increased by 0.37 and 5.28 ppm for the smaller and larger displacement, respectively. The crude model of a one-dimensional harmonic oscillator is applied to the Xe atom vibrating in a fixed C_{60} cage. On the basis of the relative energy for the 0.05 Å displaced geometry with respect to the equilibrium geometry, a vibrational amplitude ($\sqrt{\langle R_{\mathrm{Xe}}{}^{2}\rangle}$) of 0.03 Å for the ground state and 0.05 Å for the first vibrationally excited state can be expected, along with a $\nu = 0 \rightarrow 1$ excitation energy of the magnitude 10^2 cm^{-1}. From this model we estimate the vibrational corrections to $\delta(^{129}\mathrm{Xe})$ to be positive and rather small. However, there might be larger effects from deformation vibrations of the C_{60} cage (with frequencies of 3×10^2 cm^{-1} and larger[57]).

In conclusion, we find from our computational results, and by comparison to earlier and present Hartree−Fock data as well as the current experimental value, and by discussing probable sources of errors, that there are many "small" contributions of the order of a few 10 to some 100 ppm to the chemical shift of ^{129}Xe in Xe@C_{60} that are of different sign and must all be considered to make theoretical predictions with confidence. In this study we have focused on the contributions arising from relativity and from electron correlation. We have found that scalar relativistic effects are moderate whereas those arising from spin−orbit coupling are negligible. Effects due to electron correlation are found to be substantial.

4. Summary

We have presented the first relativistic study of the ^{129}Xe chemical shift in Xe@C_{60}, considering both scalar relativistic effects and spin−orbit coupling. The results are intended to serve as a reference study for the magnitude of the scalar and spin−orbit relativistic effects regarding the investigated observable. Additionally, the applicability of frozen-core computations has been critically evaluated. In summary, the scalar relativistic corrections to $\delta(^{129}\mathrm{Xe})$ are not negligible (about +20 ppm, or 11% of the experimental value) and must thus be considered for a quantitative comparison with the experimental result. The corrections due to spin−orbit coupling, on the other hand, are found to be rather small. Contrary to Hartree−Fock computations of $\delta(^{129}\mathrm{Xe})$ in Xe@C_{60}, the DFT results overestimate the xenon shift. This is likely due to deficiencies in the applied approximate density functionals, together with large positive contributions due to electron correlation.

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