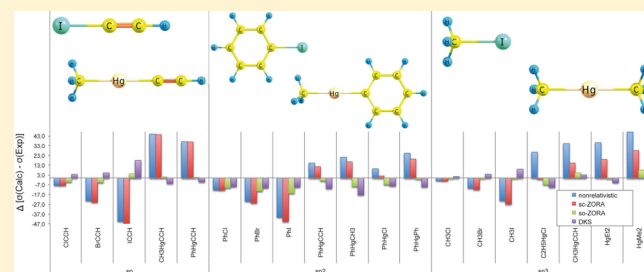


The Influence of a Presence of a Heavy Atom on ^{13}C Shielding Constants in Organomercury Compounds and Halogen Derivatives

Artur Wodyński,[†] Adam Gryff-Keller,[‡] and Magdalena Pecul^{*,†}[†]Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland[‡]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland

S Supporting Information

ABSTRACT: ^{13}C nuclear magnetic resonance shielding constants have been calculated by means of density functional theory (DFT) for several organomercury compounds and halogen derivatives of aliphatic and aromatic compounds. Relativistic effects have been included through the four-component Dirac–Kohn–Sham (DKS) method, two-component Zeroth Order Regular Approximation (ZORA) DFT, and DFT with scalar effective core potentials (ECPs). The relative shieldings have been analyzed in terms of the position of carbon atoms with respect to the heavy atom and their hybridization. The results have been compared with the experimental values, some newly measured and some found in the literature. The main aim of the calculations has been to evaluate the magnitude of heavy atom effects on the ^{13}C shielding constants and to check what are the relative contributions of scalar relativistic effects and spin–orbit coupling. Another object has been to compare the DKS and ZORA results and to check how the approximate method of accounting for the heavy-atom-on-light-atom (HALA) relativistic effect by means of scalar effective core potentials on heavy atoms performs in comparison with the more rigorous two- and four-component treatment.



1. INTRODUCTION

Nuclear magnetic resonance (NMR) shielding constants (and related to them chemical shifts) are among the most important spectroscopic parameters used in chemistry and biology, as they provide valuable insight into the electronic structure of systems under study.¹ The basic (nonrelativistic) theory for these parameters was formulated in a series of landmark papers in the 1950s by Ramsey,^{2–5} and nowadays nonrelativistic *ab initio* calculations of these properties are a routine task. However, NMR shielding constants exhibit strong relativistic effects: first, they are magnetic properties and therefore inherently relativistic phenomena,⁶ and second, the associated property operators probe the electron density in the core region, where relativistic effects tend to be the most pronounced. As a consequence, relativistic effects affect not only the shielding constants of heavy nuclei (like ^{129}Xe , ^{183}W , ^{195}Pt , or ^{199}Hg) but also of light nuclei (^1H , ^{13}C , ^{15}N) in proximity of heavy atoms. The latter phenomenon manifests itself as a so-called heavy-atom-on-light-atom (HALA) effect.⁷

The relativistic effects can be divided into scalar (spin-free) and spin–orbit coupling effects. Both contribute, to different degrees, to the HALA effects on the chemical shifts, but the factors on which their relative magnitude depends are not fully investigated. A systematic study of this problem has been carried out for chemical shifts of the carbon nuclei in the α position to the heavy atom.⁸ However, very approximate methods have been used to account for the relativistic effects, since implementations of two- and four-component relativistic

Hamiltonians for the shielding constants were not available at the time. Nowadays, the situation has changed, and therefore we decided to revisit the subject and carry out a systematic study of scalar and spin–orbit contributions to the HALA effect on carbon chemical shifts using the density functional approach with the two-component Zeroth Order Regular Approximation (ZORA) Hamiltonian. The calculated chemical shifts are compared with experimental results and the results obtained with the four-component Dirac–Coulomb Hamiltonian.

Our other aim is to check how the most widespread (and the most approximate) method of accounting for relativistic effects—through the use of relativistic effective core potentials (ECPs)—performs in comparison to explicitly relativistic methods. This is motivated by the fact that scalar effective core potentials are commonly used nowadays in calculations of the shielding constants of light nuclei (proton, carbon, nitrogen) in the proximity of the heavy atoms, especially in organometallic compounds,^{9–12} allowing one to perform calculations of NMR spectra for sizable systems containing fourth and fifth row elements, but they have never been optimized for calculations of the shielding constants (or magnetic properties in general), and their use is based on the assumption of a similar performance to that for the energy. ECPs have been constructed by fitting their form to match the numerical relativistic orbitals^{13,14} or to reproduce the spectral

Received: October 24, 2012

properties obtained by all-electron calculations.^{15–17} Furthermore, most applications of ECPs (including the one used in the present work) pose some problems with gauge invariance.¹⁸ The numbers of ECP calculations will be compared with scalar ZORA results, since ECPs parametrized to include the spin–orbit coupling effects,¹⁹ as far as we know, have never been implemented for the calculations of the shielding constants.

The molecules under study are selected organomercury compounds (CH_3HgCCH , PhHgCCH , PhHgCH_3 , PhHgPh , PhHgCl , $\text{C}_2\text{H}_5\text{HgCl}$, $\text{Hg}(\text{C}_2\text{H}_5)_2$) and halogen derivatives of aliphatic (CH_3X , $\text{C}_2\text{H}_5\text{X}$, XCCH , $\text{X} = \text{Cl}$, Br , I) and aromatic (PhX , $\text{X} = \text{Cl}$, Br , I) compounds. It is known that for systems which can be described as having hybridization with a strong s character, the spin–orbit coupling effects are important, especially for nuclei which are immediate neighbors of the heavy atoms.^{20–22} Therefore, the chosen systems contain carbon atoms of different hybridizations and in different positions with respect to the heavy atom (halogen or mercury).

The paper is organized as follows. After the description of experimental and computational details, we discuss the calculated heavy atom on light atom (HALA) effects on the ^{13}C relative shielding constants, comparing the results obtained when modeling the relativistic effects using DKS and ZORA Hamiltonians (the latter with the two-component term including the spin–orbit effects and in one-component form without the spin–orbit effects) with experimental results. Next, we examine the performance of ECPs, comparing the scalar relativistic term as received from the ECP calculations with the scalar term from the ZORA calculations. The results are discussed in order of increasing number of bonds between the carbon nucleus and the heavy atom. After the discussion of relativistic effects, some other factors which may influence the comparison with experimental results are discussed, i.e., solvents effects as estimated by means of conductor-like screening model (COSMO), vibrational effects, and the effects of using different exchange–correlation functionals. Finally, a summary and main conclusions are presented.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

2.1. NMR Experimental Details. The ^{13}C chemical shift data for halogenobenzenes have been taken from the free-access database,²³ whereas the data for aliphatic halides,^{24,25} CH_3HgCCH ,²⁶ PhHgCH_3 ,²⁷ PhHgCl ,²⁷ $\text{Hg}(\text{CH}_3)_2$,²⁸ $\text{Hg}(\text{C}_2\text{H}_5)_2$,²⁸ and $\text{C}_2\text{H}_5\text{HgCl}$ ²⁸ have been found in the indicated literature sources. The ^{13}C NMR chemical shifts for PhHgCCH and PhHgPh have been measured as part of this work.

Commercially available phenylmercury chloride and diphenylmercury (Aldrich) have been used in measurements and synthesis without purification. Ethynylphenylmercury (PhHgCCH) has been synthesized from phenylmercury chloride and acetylene using the literature procedure.²⁶

Approximately 0.1 M solutions for NMR measurements have been prepared directly in 5 mm outer-diameter NMR tubes by weighing an appropriate amount of solute and dissolving it in 0.6 mL of CDCl_3 . All measurements have been performed at the temperature stabilized at 25 °C using a 500 MHz VNMR spectrometer working at $B_0 = 11.7$ T. The ^{13}C chemical shifts have been referenced to the carbon signal of the solvent assuming $\sigma(\text{CDCl}_3) = 77.0$ ppm. The 1D ^{13}C NMR spectra as well as 2D ^1H -detected ^{13}C NMR spectra have been acquired using the standard spectrometer software and parameter sets. Each time, the number of scans has been adjusted to obtain $S/N > 5$ for the weakest signal in the recorded spectrum.

2.2. Computational Details. Geometry. The geometric parameters of the isolated molecules under study have been obtained by means of geometry optimization carried out using ZORA DFT²⁹ (spin–orbit coupling included, called so-ZORA through the paper) as implemented in the ADF³⁰ program with the ADF version of the BP86 exchange–correlation functional (composed of VWN³¹+Becke88³² and Perdew86³³ functionals) and the TZ2P basis set. Frozen core included 1s for carbon, 1s to 4d for mercury, 1s to 2p for chlorine, 1s to 3d for bromine, and 1s to 4p for iodine. Test calculations for PhHgCCH by means of scalar-only ZORA show the variation of the bond lengths in comparison to the spin–orbit ZORA of about 0.005 Å for $R(\text{HgC}_\alpha)$ and 0.001 Å for $R(\text{C}_{\text{ipso}}\text{C}_{\text{orto}})$ and $R(\text{C}_{\text{orto}}\text{C}_{\text{meta}})$; therefore for consistency we have decided to perform all geometry optimization including spin–orbit coupling. The same geometry parameters (obtained by spin–orbit ZORA calculation) have been used for all calculations (DKS, ZORA, ECP) of shielding constants in order to separate the effects of using different computational models on the molecular geometry and the shielding constants.

Another set of geometry parameters (used for estimating solvent effects) has been obtained using the same electron structure model as above and the conductor-like screening model (COSMO^{34–37}). Dielectric constants of 4.8 and 46.7 have been employed to describe CHCl_3 and DMSO, respectively, and the cavity has been built from the default van der Waals radii.

DKS Calculations of the Shielding Constants. The four-component Dirac–Kohn–Sham calculations of the shielding constants have been carried out using the implementation available in the ReSpect program (version 3.1.0).³⁸ Restricted magnetic balance has been ensured by transformation of the Dirac Hamiltonian,^{39,40} and gauge invariant atomic orbitals (GIAOs) have been employed. The generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE⁴¹); triple- ζ uncontracted pc-2 Gaussian basis set of Jensen^{42,43} for carbon, hydrogen, and chlorine; and Dyall's⁴⁴ triple- ζ for mercury, bromine, and iodine basis set have been used. The calculated shielding constants (obtained using DKS and other employed methods) have been converted into relative shielding constants using benzene as a reference ($\Delta_{\text{rel}}\sigma = \sigma - \sigma_{\text{benzene}}$).

ZORA Calculations of the Shielding Constants. The NMR shielding constants have been calculated using DFT as implemented in the ADF program at the spin–orbit, scalar ZORA (scaled-ZORA variant, called sc-ZORA through the paper) and nonrelativistic levels, with a standard PBE and Perdew, Burke, and Ernzerhof functional with Adamo and Barone's HF exchange contribution (PBE0).⁴⁵ We have used the standard Slater basis set available in the ADF³⁰ program: TZP (triple- ζ with one polarization function) with GIAOs. In one set of calculations, the conductor-like screening model (COSMO) with the same set of parameters as for geometry optimization has been applied to include solvent effects.

ECP Calculations of the Shielding Constants. The effective core potential results have been obtained using the Gaussian 03 program.⁴⁶ We have used the PBE functional and the upc-2 basis set for carbon and hydrogen and two effective core potentials, MWB60¹⁶ and MDF60¹⁷ (the standard version available in Gaussian program, coming with the (8s8p7d)/[6s6p4d] valence basis set), for mercury. Additionally, we have performed calculations with nonrelativistic MHF60⁴⁷ ECP to

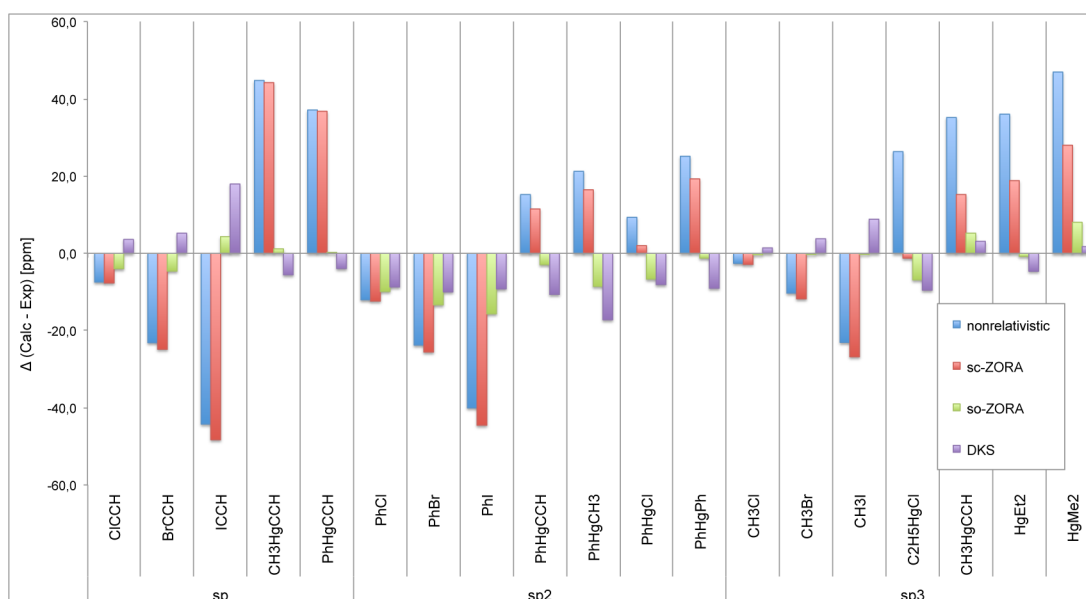


Figure 1. A comparison of the calculated relative shielding constants [ppm] for carbon directly bonded with the heavy atom with the experimental data (differences between experimental and calculated data; both with benzene as a reference) for nonrelativistic DFT, sc-ZORA, so-ZORA, and DKS.

estimate scalar relativistic effects as rendered by the relativistic ECPs.

Calculations of Vibrational Corrections of the Shielding Constants. The vibrational corrections have been obtained using the Dalton 2011⁴⁸ program at the nonrelativistic level. We have used the PBE functional and the upc-2 basis set for carbon, hydrogen, and chlorine and the dyall.v3z basis set for bromine, iodine, and mercury. The calculations have been performed at a temperature of 300 K, using a geometry step of 0.05 Å for numerical differentiation.

3. RESULTS

3.1. Performance of Different Methods of Modeling the HALA Effect. In this subsection, we will discuss how the relative ^{13}C shieldings (with benzene as a reference) obtained by means of DKS and ZORA-DFT compare with the experimental data. No environmental or vibrational effects are included in this set of calculations. The relevant numerical values can be found in the Supporting Information (Tables S1–S6).

3.1.1. The Relative Shielding Constants of the Carbon Nuclei Directly Bonded with the Heavy Atom. The comparison of the ^{13}C relative shielding constants calculated using various computational methods with the experimental results is shown in Figure 1, where deviations from the experimental results are displayed for each method and each compound under study. Inspection of these results shows that in most cases so-ZORA reproduces the experimental results very well. The agreement is good for carbons with the sp hybridization in the systems containing mercury and for the sp³ hybridization for the series of CH_3X where $\text{X} = \text{Cl}, \text{Br}, \text{I}$. A poorer agreement is observed for the phenyl ipso position in PhHgCH_3 , PhHgCl , $\text{Hg}(\text{CH}_3)_2$, and the PhX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) series, where the so-ZORA relative shieldings are smaller than the experimental ones.

Interestingly, the agreement with experimental results is usually slightly worse for the four-component calculations than for ZORA. As a rule, it appears as if DKS overestimated the

relativistic effects. Apparently, there is a cancellation of errors in the ZORA calculations of relative shielding constants of ^{13}C nuclei in immediate proximity of a heavy atom. It is particularly noticeable for sp and sp² hybridization (for systems containing mercury). However, for the PhX series where there are substantial differences between ZORA and experimental results, DKS leads to a somewhat better agreement with experimental results.

The magnitude of the spin–orbit effect (as estimated by comparison of the so-ZORA and sc-ZORA results) and consequently the performance of scalar ZORA in comparison with experimental results depends strongly on carbon hybridization. The spin–orbit coupling affects the shieldings of the sp-hybridized α carbons by as much as 20–52 ppm (the sign of the spin–orbit term depends on type of the heavy nucleus: it is positive for halides and negative for mercury). The scalar terms (negative in this case) are smaller: for example, for systems containing carbon with sp hybridization, the scalar terms are less (in terms of the absolute values) than -4 ppm (the biggest one is found for ICCH), and in many cases they are negligible in comparison with the spin–orbit term.

For carbon nuclei with the sp² hybridization directly bonded to the heavy atoms (occupying the ipso position in the benzene ring in the systems under study), large differences between the experimental relative shielding constants and the sc-ZORA results are observed again. This is particularly striking in the case of halogen derivatives, especially PhI, where the difference amounts to about 50 ppm. This is again a result of the fact that the scalar effects are small (in most cases at most about -5 ppm) in comparison with the spin–orbit term. On the other hand, even inclusion of the spin–orbit term at the ZORA level of theory only partially improves the agreement with experimental results (still, a difference of about 15.7 ppm is observed for PhI), so apparently the relativistic effects are not described fully by ZORA. As already mentioned, in the case of PhI, the use of DKS improves further the agreement with experimental results (the difference between DKS and experimental data is about 9.2 ppm). Inclusion of solvent

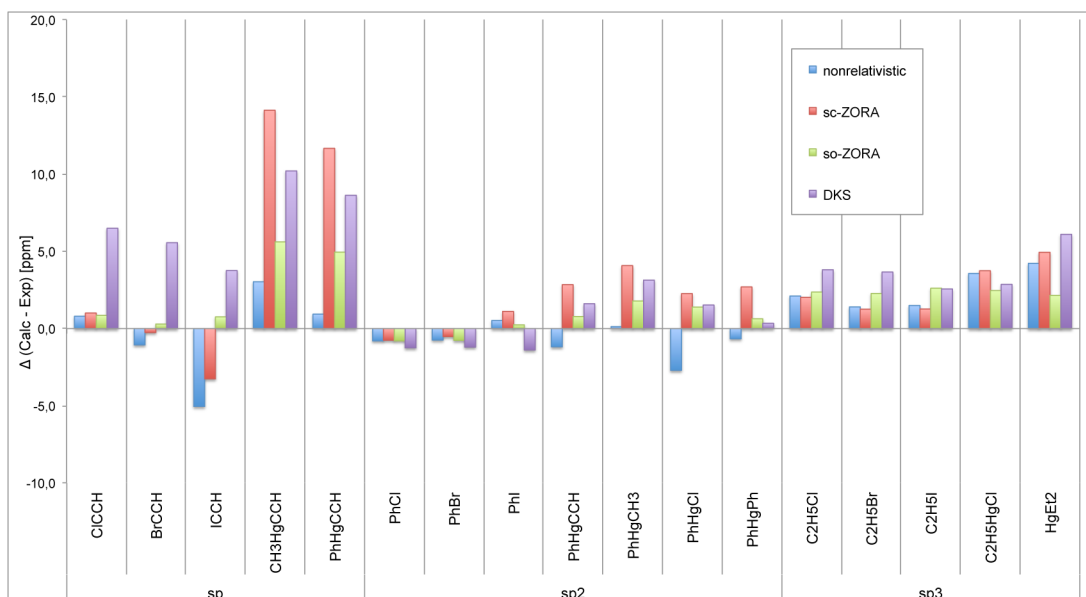


Figure 2. A comparison of the calculated relative shielding constants [ppm] for carbon bonded with the heavy atom with two bonds with the experimental data (differences between experimental and calculated data; both with benzene as a reference) for nonrelativistic DFT, sc-ZORA, so-ZORA, and DKS.

effects additionally improves agreement with experimental results, but the effects are rather small (0.8 ppm for PhI, see Table S7).

For monosubstituted benzenes containing mercury, the spin–orbit terms are smaller (between -8.7 ppm and -25.0 ppm) but still larger than the scalar terms (inclusion of only the scalar terms improves very little the agreement of the computational results with the experimental ones). In this case, the so-ZORA relative shieldings are smaller than the experimental ones, and this tendency is even more pronounced for the DKS results.

Among the results for the sp^2 carbons in the α position, the smallest differences between the DKS, so-ZORA, and sc-ZORA results are observed for PhHgCl and PhCl. It is due to small values of the SO terms. In the case of PhHgCl, it may be a consequence of electronegativity of the substituent bounded with mercury, since strong dependence of the SO term in ^{13}C shielding on the substituent electronegativity has been observed before for CH_3HgX ($\text{X} = \text{CN}, \text{Cl}, \text{CH}_3, \text{SiH}_3$) systems¹⁰ in perturbational calculations carried out on top of the non-relativistic electron density. In the case of PhCl, a small value of the SO term is due to the small nuclear charge of Cl, as discussed for example by Vaara et al.⁸

Now, the relative shielding constants of the carbon nuclei with sp^3 hybridization will be discussed. We do not include in this section the results for PhHgCH₃, because no experimental data are available (the computed results will be used in the discussion of scalar terms in next subsection) and omit the series of $\text{C}_2\text{H}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) because the trends are similar to those for the CH_3X series.

For the molecules of this class containing mercury, the relativistic effects (as calculated using ZORA) span the range of about 40 ppm, and the differences between so-ZORA results and the experimental data vary from about -1 ppm for $\text{Hg}(\text{C}_2\text{H}_5)_2$ to about 8 ppm for $\text{Hg}(\text{CH}_3)_2$. In this series of compounds, the use of DKS instead of ZORA reduces in some cases (e.g., $\text{Hg}(\text{CH}_3)_2$) the discrepancy with experimental results. The spin–orbit term for $\text{C}_2\text{H}_5\text{HgCl}$ is very small in

comparison with the scalar one, similarly to that for another molecule under study containing the HgCl moiety, PhHgCl (see above). The differences between HALA effects calculated using sc-ZORA and so-ZORA (i.e., the spin–orbit coupling effects) are substantial (except for $\text{C}_2\text{H}_5\text{HgCl}$), but unlike for sp and sp^2 carbon nuclei, the scalar terms are comparable or even bigger than the spin–orbit terms and of the same sign.

For the CH_3X series, the trends are similar to those for PhX, but the relativistic effects are generally smaller. The biggest spin–orbit term is observed, as expected, for CH_3I (about 26 ppm), and it has an opposite sign to the scalar term.

3.1.2. The Relative Shielding Constants of the Carbon Nuclei in β Position to the Heavy Atom. The differences between the experimental and calculated relative shielding constants of carbon nuclei separated by two bonds from the heavy atom are shown in Figure 2. As expected, the relativistic effects are smaller than for carbon in the α position to the heavy atom (here, they reach about 6 ppm). Again, a marked difference in the magnitude of the spin–orbit effect (and therefore in the performance of different computational methods) can be observed for the carbon nuclei of different hybridizations.

For carbon atoms in β positions with the sp hybridization, the results computed using different methods vary significantly (the differences can reach 9 ppm), although, because of smaller relativistic effects, they are much less scattered in comparison with the shieldings of the sp carbons directly bonded with the heavy atoms. Again, so-ZORA seems to perform slightly better than DKS. The SO terms, as calculated using ZORA, are much smaller for the β carbon nuclei than for the α carbon nuclei, amounting to about 8 ppm (in the absolute value). The scalar terms have the same sign as the spin–orbit terms for BrCCH and ICCH but not for CH_3HgCCH and PhHgCCH. For the latter two molecules, the scalar terms are larger (in terms of absolute values) than the SO ones, so the variation of the performance of the different computational methods originates partially from different rendering of the scalar terms.

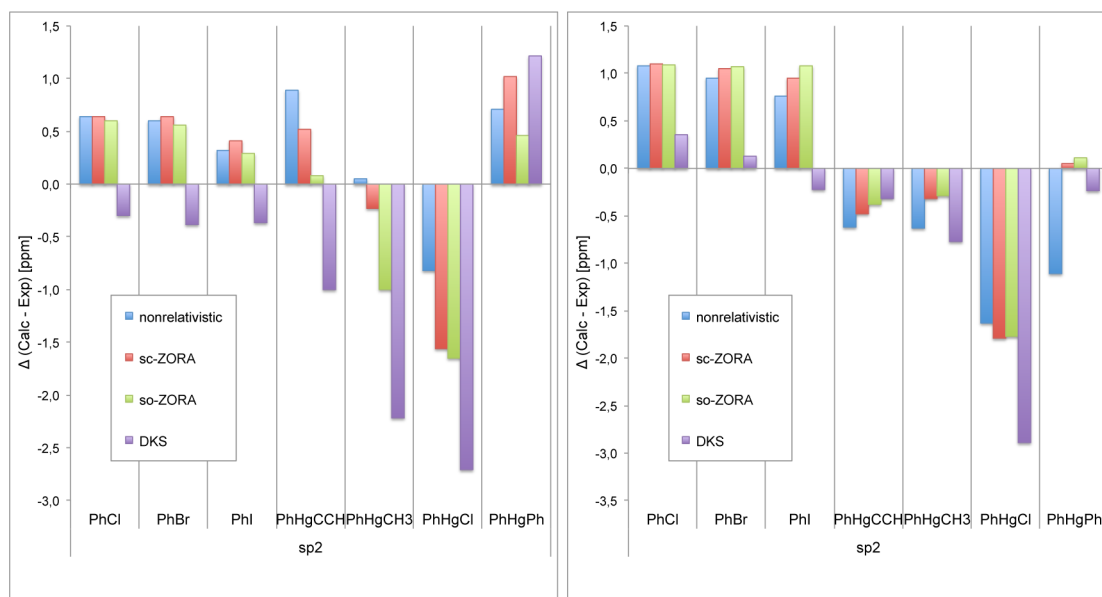


Figure 3. A comparison of the calculated relative shielding constants [ppm] for carbon bonded with the heavy atom with three or four bonds with the experimental data (differences between experimental and calculated data; both with benzene as a reference) for nonrelativistic DFT, sc-ZORA, so-ZORA, and DKS.

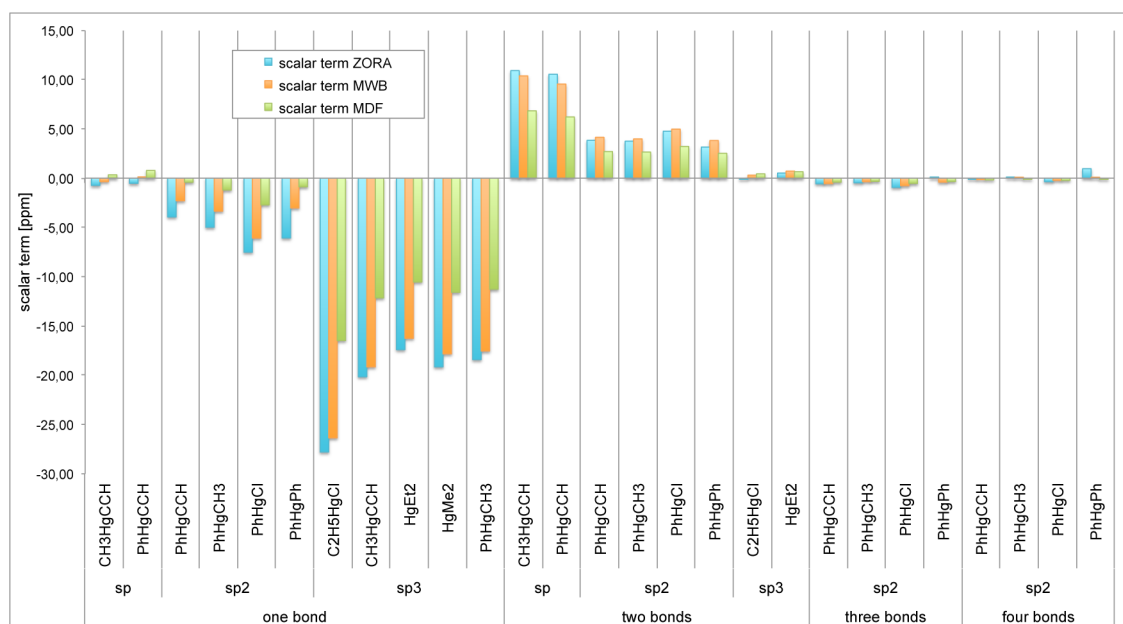


Figure 4. A comparison of the scalar effects calculated with the ZORA method and ECP methods.

In the case of the carbon atoms with the sp^2 hybridization in the benzene ring (separated by two bonds from the heavy atom, therefore in *ortho* position to it), the relativistic effects do not exceed 4.1 ppm (for molecules containing mercury), and they are negligible for halide derivatives. Generally, DKS seems to perform worse than so-ZORA, but the differences are less than 1.7 ppm.

For the carbon atoms with the sp^3 hybridization in the β position, the discrepancies between the so-ZORA results and experimental results do not exceed 3 ppm. (Inclusion of the solvent effects by means of COSMO leads to slightly larger differences of 4–4.5 ppm.) The DKS method again works worse than so-ZORA, especially for $Hg(C_2H_5)_2$. For C_2H_5HgCl , the relativistic effects are relatively small (especially

the scalar contribution). Generally, the SO term dominates over the scalar one, and they have opposite signs.

3.1.3. The Relative Shielding Constants of the Carbon Nuclei Separated from the Heavy Atom by Three or Four Bonds. The carbon atoms separated from the heavy nuclei by three or four bonds in the molecules under study are all in the phenyl ring (in the *meta* or *para* position), and thus all have the sp^2 hybridization. For relative shielding constants of the carbon nuclei in the *meta* positions, the HALA effects are small, not exceeding -1 ppm, as shown in Figure 3. For all *meta* carbon nuclei, the scalar terms are on the same order of magnitude as the spin–orbit terms or even bigger (as in the case of $PhHgCl$), and in the case of molecules containing mercury (except $PhHgPh$) the scalar and SO terms have the same signs (for the

series of PhX, they have opposite signs, but in this case, the relativistic terms are negligible, i.e., between 0 ppm and -0.2 ppm). In most cases, using DKS leads to underestimation of the experimental results (only for PhHgPh the opposite trend is observed), and the results are, on average, in worse agreement with experimental results than the so-ZORA results.

In the case of the relative shielding constants of the carbon nuclei in the para position, the observations are similar as for the meta position (except that for the para carbon nuclei, the spin-orbit term is negligible in comparison with the scalar term), and again for PhHgCl we observe a relatively large difference between so-ZORA or DKS and the experimental result (about 1.8 ppm for so-ZORA). The relativistic effects are very small, so no reliable conclusions about the performance of different methods in rendering them can be drawn.

3.1.4. Reproduction of the Scalar Effects by the Effective Core Potentials. In this subsection, we will discuss how the effective core potentials reproduce the scalar relativistic effects on the ^{13}C relative shielding constants in comparison with a more rigorous treatment by means of ZORA. (At the DKS level, we have at present no means to divide the total relativistic effect into scalar and spin-orbit contributions.) The ZORA scalar term is calculated as a difference between the sc-ZORA result and the nonrelativistic result obtained with the same basis set. It should be taken into account that the comparison is affected by different basis sets employed: Slater orbitals in ZORA and Gaussian orbitals in ECP calculations. The comparison is limited to MWB60 and MDF60 because, for this series, nonrelativistic ECP (MHF60) is available for Hg, allowing one to calculate the scalar relativistic term as a difference between the results obtained with the relativistic and nonrelativistic ECPs. Only the systems containing mercury are considered, since for halogen atoms MHF60 is not available and the usage of a full atomic basis on halogens leads to a nonphysical bias.

The comparison of the scalar relativistic effects on the relative carbon shielding constants calculated using different approaches is shown in Figure 4. In the case of carbon bonded directly to mercury, the scalar effect (always negative) changes significantly with decreasing s character of the carbon hybridization. For carbon with the sp hybridization, the scalar terms are generally negligible (between 0 ppm and -1 ppm). For carbon with sp^2 hybridization, they are more significant (especially for PhHgCl where the scalar term is about -7.5 ppm). The effective core potential parametrized with respect to the scalar two-component approximation to the Dirac equation (MWB60) reproduces the sc-ZORA term well for this class of shieldings, but MDF60 renders only from 18% (in the case of PhHgCCH) to 44% (in the case of PhHgCl) of the MWB60 result. For the relative shielding constants of the carbon nuclei with the sp^3 hybridization, the scalar effects are the biggest among all discussed systems (for $\text{C}_2\text{H}_5\text{HgCl}$, the scalar term is as large as -28 ppm), and generally MWB60 reproduces the sc-ZORA results quite well (although all MWB60 results are underestimated in comparison with sc-ZORA ones). Again, a substantial difference between the MWB60 and MDF60 scalar terms is observed (MDF60 reproduces about 63–65% of the MWB60 term). We have performed additional calculations for selected molecules with a more recent version of MDF60¹⁹ and obtained results much closer to MWB60; thus the observed difference is most likely a consequence of different fitting procedures employed to obtain the two ECPs.

In the case of the relative shielding constants of the carbon atoms bonded with mercury with two bonds, the scalar effect decreases with decreasing s character of the carbon hybridization, unlike for the carbon α atoms. The largest scalar terms (about 11 ppm) are observed for the sp hybridization, smaller (3–5 ppm) for the sp^2 hybridization, and smaller still (less than 1 ppm) for the sp^3 hybridization. For the sp hybridization, MWB60 underestimates the sc-ZORA term, but not significantly (by about 0.5–1 ppm), and for sp^2 it leads to a slight overestimation of the ZORA scalar term. Almost all scalar terms for the carbon atoms in the β position have positive signs. Similarly as for the α carbon shieldings, the MDF60 scalar terms are smaller than the MWB60 scalar terms (from 65 to 67%).

In the case of the relative shieldings of the carbon nuclei separated by three or four bonds from the heavy atom, the scalar terms are negligible (less than 1 ppm), and they will not be discussed any further.

3.2. The Influence of the Factors Other than the Relativistic Effects on the Quality of the Results. In the previous subsection, we focused on how different methods of accounting for the relativistic effects perform for the carbon shielding constants. In this subsection, we will discuss briefly other factors which may cause a difference between theoretical and experimental results, namely the effect of choosing different exchange-correlation functionals, solvents effects (as estimated by means of the COSMO model), and vibrational effects.

3.2.1. Comparison of Hybrid and Nonhybrid Functionals. All results discussed so far have been obtained using the PBE GGA functional. This has been done to ensure consistency with the DKS calculations, since hybrid functionals are not available yet in the ReSpect program. To check whether including exact exchange improves the agreement with experimental results, we have carried out so-ZORA calculations with the PBE0 hybrid functional. The root-mean-square deviation (RMSD) between theoretical and experimental results is 4.54 ppm and 4.24 ppm for PBE and PBE0, respectively, for the set of 53 relative shielding constants under study (see Tables S9 and S10 in the Supporting Information). The biggest differences between PBE and PBE0 are observed for the shieldings of the carbons directly bonded with the heavy atoms (between 0.3 ppm and 10.5 ppm, but in most cases more than 3.5 ppm). Thus, we can conclude that the inclusion of the hybrid component (going from PBE to PBE0) should not influence materially the conclusions concerning the relativistic effects.

3.2.2. Estimation of Solvent Effects. The results presented so far did not include solvent effects, even though most of the experimental chemical shifts have been measured in solutions. We have decided therefore to estimate solvent effects at the so-ZORA level using the COSMO model (both during geometry optimization and calculation of shielding constants). For most of the systems under study, they do not exceed ± 1.5 ppm (see Tables S7 and S8 in the SI). The largest solvent effects are predicted for $\text{C}_2\text{H}_5\text{I}$ (about -4.2 ppm) and for PhHgCH₃ and PhHgCCH (about 3.9 ppm and 3.0 ppm, respectively). RMSD for the computational results obtained for the isolated molecules is 4.60 ppm, and for molecules in solution modeled by means of COSMO, it is 5.00 ppm, so actually the calculations without accounting for the environmental effects lead to better agreement with the experimental data. The continuum model does not seem to be a suitable tool for the purpose, and using more elaborate solvent models is at present beyond our means.

3.2.3. Estimation of Vibrational Effects. The vibrational effects can be sizable for shielding constants,⁴⁹ and it is worthwhile to check how large they are in comparison with the relativistic effects. The calculations have been performed at the nonrelativistic level because, so far, only for this level of theory is the appropriate methodology implemented.⁴⁹ Calculations have been performed for all systems containing halides and for selected organomercury compounds.

Inclusion of a vibrational term leads to deshielding of carbon nuclei, for halides not exceeding -4.5 ppm (except for β carbon in the C_2H_5X series where they are about -7 ppm). Large vibrational effects have been predicted for four shielding constants in organomercury compounds (about -22 ppm for $Hg(CH_3)_2$, about -17 ppm and -20 ppm for the α and β positions, respectively, in $PhHgCCH$, and 15 – 30 ppm for the α position in $Hg(C_2H_5)_2$). However, it should be stressed that a comparison of the relativistic (so-ZORA) and nonrelativistic results of test calculations for CH_3I and $Hg(CH_3)_2$ with deformed geometry indicates that while for halide derivatives the vibrational term is nearly additive with the relativistic term, this is not the case for organomercury compounds. Numerical derivatives of ^{13}C shielding with respect to the bond length (calculated with the displacement of 0.01 Å) are similar for the so-ZORA and Schrödinger Hamiltonians in the case of CH_3I (for R_{IC} displacement, it is -109.5 ppm/Å and -112.5 ppm/Å and for R_{CH} displacement, -44.0 ppm/Å and -60.5 ppm/Å for the so-ZORA and Schrödinger Hamiltonians, respectively), but for $Hg(CH_3)_2$ they differ significantly (for R_{HgC} displacement it is 0.5 ppm/Å and -5.5 ppm/Å and for R_{CH} displacement, 3 ppm/Å and 1.5 ppm/Å for the so-ZORA and Schrödinger Hamiltonians, respectively).

To conclude, in most cases, the vibrational terms should not influence materially the conclusions concerning the relativistic effects, especially for the relative shielding constants where the vibrational correction for the compound under study should partially cancel out with that for benzene (about -3.2 ppm). For organomercury systems, the vibrational terms calculated at the nonrelativistic level are large, but the comparison of the bond length shielding derivatives calculated at relativistic and nonrelativistic levels indicates that they are not reliable. Calculation of the vibrational effects at the relativistic level is our future goal.

4. SUMMARY AND CONCLUSIONS

The ^{13}C nuclear magnetic resonance relative shielding constants have been calculated by means of density functional theory (DFT) for several organomercury compounds and halogen derivatives of aliphatic and aromatic compounds. The relativistic effects have been included through the four-component Dirac–Kohn–Sham (DKS) method, two-component Zeroth Order Regular Approximation (ZORA) DFT, and scalar effective core potentials (ECPs). The relative shielding constants have been analyzed in terms of the carbon hybridization and the position of carbon atoms with respect to the heavy atom. The results have been compared with the experimental values, some measured for the first time in this work and some found in the literature. The main conclusions can be summarized as follows.

The magnitude of relativistic effects on carbon chemical shifts depends strongly on the position of the carbon nucleus with respect to the heavy nucleus, the charge of the heavy nucleus, and type of carbon hybridization. The biggest relativistic contributions to chemical shifts are observed for

the carbon nuclei directly bonded with the heavy atoms (they amount to 50 ppm). For the carbon nuclei in the β position, the relativistic terms do not exceed 6 ppm and are below 1.3 ppm for carbon nuclei separated from the heavy nucleus by three or four bonds. Predictably, the relativistic contributions for the carbon nuclei directly bonded with halide depend strongly on the charge of the halide nucleus (they range from about 2 ppm for the systems containing chlorine to about 25 ppm for systems containing iodine for carbon with the sp^2 and sp^3 hybridization, and from 4 ppm to about 49 ppm for carbon with the sp hybridization).

Relativistic contributions tend to be the biggest for the carbon nucleus with the sp hybridization (even about 50 ppm for α carbons). In the case of a carbon atom directly bonded with the heavy nucleus, the relativistic contribution is the smallest (up to about 30 ppm) for the sp^2 hybridization and up to about 40 ppm for sp^3 . For the β position, the relativistic contributions for the sp^2 carbon nucleus are of the same order of magnitude as for the carbon with the sp^3 hybridization—i.e., less than 2 ppm (only for $PhHgCl$ is the relativistic contribution slightly bigger, about 4 ppm).

The relativistic contributions calculated at the ZORA level have been split into the scalar and spin–orbit terms. In the case of ^{13}C atoms with the sp and sp^2 hybridization bonded directly to the heavy nuclei, the scalar term is small in comparison with the spin–orbit coupling term, but for sp^3 it is comparable with the spin–orbit coupling term (for the systems containing mercury). For carbon in the β position, the scalar terms are of the same order of magnitude as the spin–orbit coupling terms. In most cases, the scalar terms have the opposite sign to the spin–orbit terms for the systems containing halides (only for carbon with the sp hybridization in the β position the opposite trend is observed), and for the systems containing mercury they have the same sign. An atypically small spin–orbit term has been observed for the systems containing the $HgCl$ moiety.

Three methods of including relativistic effects at several levels of theory have been examined. Inspection of the results shows that so-ZORA usually reproduces the experimental results very well, in most cases better than DKS, so it appears as if DKS overestimated the relativistic effects. However, for a few cases (especially for carbon in the α position in PhX) in which so-ZORA does not perform satisfactorily, DKS leads to a better agreement with the experimental data. These observations are confirmed by statistical analysis (see Table 1) for the shieldings of carbon in the α position, where the relativistic effects are the largest. The slope values confirm that the DKS method overestimates the experimental data (by about 10%) and that

Table 1. Statistical Analysis of the Calculated Relative Shielding Constants for Carbon Directly Bonded with the Heavy Atom against the Experimental Data

	slope	RMSD [ppm]	R^2
nonrel	0.87	27.61	0.811
sc-ZORA	0.84	24.71	0.847
so-ZORA	1.03	6.69	0.993
so-ZORA ^a	1.02	5.30	0.995
DKS	1.10	8.15	0.995
DKS ^b	1.08	6.50	0.997
MWB	0.83	26.52	0.822

^aExcluded results for $PhBr$ and PhI . ^bExcluded results for $ICCH$ and $PhHgCH_3$.

so-ZORA performs much better in this respect (it overestimates experimental results only by about 2%). The correlation between the calculated and the experimental data is very high for so-ZORA and DKS results. RMSD for DKS is slightly bigger (about 8.15 ppm) than for so-ZORA (6.69 ppm), showing a poorer agreement of the DKS results with experimental data, which is only partially improved by exclusion of the results differing more than 2*RMSD (6.50 ppm).

The scalar terms calculated with MWB ECP agree well with the scalar ZORA results, whereas MDF underestimates these terms. Because of the scalar-only character of the employed ECP methods, they lead to good agreement with the experimental data only for carbon, where the spin-orbit term is very small; otherwise there is scarcely any improvement over the nonrelativistic calculations (compare the RMSD and R^2 parameters in Table 1).

The solvent effects on the chemical shifts as obtained using COSMO are usually small: for most of the systems under study, they do not exceed ± 1.5 ppm, and they are never bigger than 3–4 ppm. The choice of a nonhybrid functional PBE instead of hybrid functional PBE0 does not lead to large errors and should not influence materially the conclusions concerning the relativistic effects. Vibrational effects seem small for halide derivatives. They may be sizable for organomercury compounds, but our preliminary tests indicate that they should be evaluated by means of a relativistic method, which is at present outside our means.

■ ASSOCIATED CONTENT

■ Supporting Information

Calculated ^{13}C shielding constant of benzene (Table S1), relative shielding constants used for the graphs exhibited in the paper (Tables S2–S6), relative shielding constants calculated with and without accounting for solvent effect (Tables S7 and S8), relative shielding constants calculated with PBE and PBE0 functionals (Tables S9 and S10), and vibrational corrections at the nonrelativistic level (Tables S11 and S12). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mpecul@chem.uw.edu.pl

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has received support from the Polish Ministry of Science and Higher Education via the No. N N204 148565 grant and from the Wrocław Centre for Networking and Supercomputing through a grant of computer time. MPD/2010/4 project, realized within the MPD programme of Foundation for Polish Science, cofinanced from European Union, Regional Development Fund, is acknowledged for a fellowship to A.W. The project has been carried out with the use of CePT infrastructure financed by the European Union—the European Regional Development Fund within the Operational Programme “Innovative economy” for 2007–2013.

■ REFERENCES

- (1) Kaupp, M.; Bühl, M.; Malkin, V. G. *Calculation of NMR and EPR Parameters. Theory and Applications*; Wiley-VCH: Weinheim, Germany, 2004.
- (2) Ramsey, N. F. *Phys. Rev.* **1950**, *77*, 567–567.
- (3) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699–703.
- (4) Ramsey, N. F. *Phys. Rev.* **1951**, *83*, 540–541.
- (5) Ramsey, N. F. *Phys. Rev.* **1952**, *86*, 243–246.
- (6) Saue, T. *Adv. Quantum Chem.* **2005**, *48*, 383–405.
- (7) Pyykkö, P.; Görling, A.; Röscher, N. *Mol. Phys.* **1987**, *61*, 195.
- (8) Vaara, J.; Malkina, O. L.; Stoll, H.; Malkin, V. G.; Kaupp, M. *J. Chem. Phys.* **2001**, *114*, 61–71.
- (9) Kaupp, M.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1995**, *235*, 382–388.
- (10) Kaupp, M.; Malkina, O. L. *J. Chem. Phys.* **1998**, *108*, 3648–3659.
- (11) Berger, S.; Bock, W.; Frenking, G.; Jonas, V.; Mueller, F. *J. Am. Chem. Soc.* **1995**, *117*, 3820–3829.
- (12) Kaupp, M. *Chem.—Eur. J.* **1996**, *2*, 348–358.
- (13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.
- (14) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.
- (15) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. *Mol. Phys.* **1993**, *80*, 1431–1441.
- (16) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.
- (17) Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H.; Schwerdtfeger, P.; Pitzer, R. *Mol. Phys.* **1993**, *78*, 1211–1224.
- (18) van Wüllen, C. *J. Chem. Phys.* **2012**, *136*, 114110.
- (19) Figgen, D.; Rauhut, G.; Dolg, M.; Stoll, H. *Chem. Phys.* **2005**, *311*, 227–244.
- (20) Kaupp, M. *Relativistic Electronic Structure Theory. Part 2. Applications*; Elsevier: Amsterdam, 2004; p 552.
- (21) Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem.—Eur. J.* **1998**, *4*, 118–126.
- (22) Wodyński, A.; Repiský, M.; Pecul, M. *J. Chem. Phys.* **2012**, *137*, 014311.
- (23) SDBSWeb, National Institute of Advanced Industrial Science and Technology. <http://riodb01.ibase.aist.go.jp/sdbs/>.
- (24) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Org. Chem.* **1980**, *45*, 4936–4947.
- (25) Jackowski, K.; Gryff-Keller, A.; Sas, W.; Szczeciński, P. *Pol. J. Chem.* **1996**, *70*, 221–230.
- (26) Sebal, A.; Wrackmeyer, B. *Spectrochim. Acta, Part A* **1982**, *38*, 163–173.
- (27) Michel, E.; Perie, J.; Lattes, A. *J. Organomet. Chem.* **1981**, *204*, 1–12.
- (28) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Hurst, N. W.; Mallinson, L. G.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1978**, 872–876.
- (29) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322–328.
- (30) ADF2010; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands. <http://www.scm.com>.
- (31) Vosko, S.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (32) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (33) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824. Erratum: Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.
- (34) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396–408.
- (35) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (36) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- (37) Klamt, A.; Jonas, V. *J. Chem. Phys.* **1996**, *105*, 9972–9981.
- (38) Malkin, V. G.; Malkina, O. L.; M. Repiský, S. Komorovský, Malkin, I.; Malkin, E.; Arbuznikov, A. V.; Kaupp, M.; Ruud, K. *ReSpect program*, version 3.1.0; 2011.
- (39) Komorovský, S.; Repiský, M.; Malkina, O.; Malkin, V. G.; Ondk, I. M.; Kaupp, M. *J. Chem. Phys.* **2008**, *128*, 104101–104115.
- (40) Komorovský, S.; Repiský, M.; Malkina, O. L.; Malkin, V. G. *J. Chem. Phys.* **2010**, *132*, 154101.

- (41) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (42) Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113–9125.
- (43) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 3502–3502.
- (44) Dyall, K. G. *Theor. Chem. Acc.* **2004**, *112*, 403–409.
- (45) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (46) Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (47) Häussermann, U. Unpublished report, 1988.
- (48) Dalton2011, a molecular electronic structure program (2011). <http://www.daltonprogram.org>.
- (49) Ruud, K.; Astrand, P.-O.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*, 2668–2683.