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Relativistic effects in the NMR spectra of compounds containing heavy chalcogens

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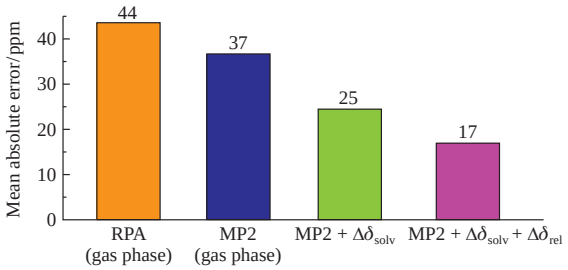
An accurate and efficient prediction of the NMR spectra of organoelement compounds containing heavy elements is on the cutting edge of the modern chemistry. Reviewed herewith are the relativistic effects provided by heavy chalcogens on light and heavy nuclei (accordingly, HALA and HAHA effects), which play a major role in the interpretation of the NMR spectra of vitally important chalcogen-containing compounds and should certainly be taken into account for practical purposes.



Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an efficient tool for structural elucidation of organic and biological molecules with a special emphasis on stereochemical aspects. Theoretical prediction of NMR parameters is of major importance providing a new guide into molecular structure and chemical reactivity. Recent advances in computational NMR (see reviews[1–13] and those on a relativistic level[14–17]) provided a profound impact on the calculation of chemical shifts and spin-spin coupling constants, two basic NMR parameters which could be derived from experimental NMR spectra.

Turning back to history, the nonrelativistic theories of magnetic resonance parameters were formulated by Ramsey in the early 1950s.[18,19] Since then a vast amount of computational approaches to NMR parameters based on the nonrelativistic many-electron Schrödinger equation for NMR properties have been thoroughly developed and coded. Among them are well-known approaches such as either those based on the first-principles (so-called *ab initio* methods), namely, a second-order polarization propagator approach (SOPPA)[20–22] and its modifications SOPPA(CC2)[23] and SOPPA(CCSD),[24] coupled clusters methods CC2,[25] CCSD,[26] CCSD(T),[27,28] and the Møller–Plesset perturbation theory (MPPT)[29] or those based on the approximate Kohn–Sham density functional theory (DFT).[30–33] However, the above approaches together with some on a semiempirical level, be it employed under the properly chosen conditions, are capable to provide a qualitative description of the NMR spectra of compounds containing only light elements. On the other hand, molecules incorporating heavy nuclei exhibit so-called relativistic effects to be treated within the framework of relativistic quantum mechanics.

Formally speaking, the relativistic effects are pure theoretical phenomena, which arise from a difference between the levels of physical grounds of the problem. It means that there is no way to measure relativistic effects by only resorting to experiment, let it be considered in NMR problem, or in somewhat else. Relativistic effects in a particular property, including NMR parameters, can be estimated only from a difference between the property value calculated within the relativistic theory and that calculated within the nonrelativistic theory.

The relativistic approach to many-electron problems, including the ones of NMR spectra, should be used when the system has electrons with the average orbital speed close to the speed of light. According to the Bohr model, the average speed of 1*s* electron equals to *Z*, with *Z* being the nuclear charge (in a.u.). Thus, the main marker, which signifies about the possible importance of the relativistic effects, is the nuclear charge *Z* being not much

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smaller than the speed of light. For example, for the first-to-third row elements the ratios Z/c are too small to be treated on relativistic grounds, so that these elements should be referred to as light elements. For example, this ratio for Hg is 0.58 a.u. to indicate the 'heaviness' of this nucleus. Indeed, the most pronounced relativistic effect for Hg consists in the fact that 1*s* radial orbital is shrinked by about 23% in comparison to that in the non-relativistic representation.[34]

The types of relativistic effects, resulting in the alternation of NMR parameters in comparison with nonrelativistic consideration in molecules containing heavy elements, could be derived from a quasirelativistic many-body Breit–Pauli Hamiltonian.[35,36] There are two most significant types of relativistic effects, namely, so-called scalar effects, whose operators do not contain an electronic spin variable, and spin-orbit relativistic effects, whose operators depend on the electronic spin.

Scalar effects could be defined as the sum of mass–velocity and Darwin corrections. In its turn, the mass–velocity correction arises due to a relativistic increase of the electron mass, alternating the kinetic energy of an electron, while the Darwin correction originates in the 'smearing' of the moving electron, resulting in a change of its potential energy. Spin-orbit effect originates in the interaction of an electron spin with its own angular momentum in relation to the position of the nucleus (one-electron effect), with its own angular momentum in relation to the position of another electron (two-electron spin-same-orbit effect), or with the angular momentum of another electron in relation to its own position (two-electron spin-other-orbit effect). Generally speaking, the spin-orbit interactions result in the spin-orbit splitting of orbitals, those with parallel and antiparallel spins relative to electron angular momentum, which makes spin to be no longer a proper quantum number.

The relativistic effects can also be spitted up in the sense of their inner/external origin. Herewith, attention will be paid to the so-called HAHA and HALA effects. The acronym HAHA stands for the Heavy Atom on Heavy Atom effect, being of the inner-origin type and corresponding to a heavy-atom (relativistic) effect on the heavy-atom's own NMR parameters. On the other hand, the HALA effect, as it will be used henceforth, refers to a Heavy-Atom effect on Light-Atom NMR parameters and represents the external-origin type effect. It is essential that in the molecules containing heavy elements not taking into account relativistic effects at appropriate level of theory cannot be compensated by using whatever high accuracy correlated *ab initio* nonrelativistic approaches.

The general relativistic theory of NMR chemical shifts was developed by Fukui *et al*.,[37] Pyykkö *et al*.,[38,39] Fukuda *et al*.,[40,41] Morishima *et al*.[42] and some others.[43–45] The relativistic grounds of NMR spin-spin coupling constants were also reported by Aucar *et al*.,[46] Oprea *et al*.[47] and many others.[48–50]

The development of relativistic approaches to the calculation of magnetic resonance parameters is of considerable current importance. However, four-component relativistic methods are extremely computationally demanding. Among the most widespread four-component methods for the calculation of NMR parameters are the relativistic random phase approximation (RRPA) or time-dependent Dirac–Hartree–Fock (TD-DHF) method[46,51–57] and time-dependent relativistic four-component density functional theory (TD-RDFT) method or time-dependent Dirac–Kohn–Sham (TD-DKS) method.[49,50,58,59] A detailed description of relativistic four-component methods as applied to the calculation of NMR parameters can be found in reviews by Xiao *et al*.,[43] Cheng *et al*.,[60] Rusakova *et al*.[17] and others.[61,62]

Currently, two-component approaches to NMR properties are much more popular owing to their much lower computational demands as compared to the four-component methods. However, note that the two-component relativistic methods are only approximate relativistic methods involving a complicated formalism that can badly suffer from singularities.[53] The two-component methods have been thoroughly investigated; see, for example, comprehensive reviews by Autschbach[15] and Sun *et al*.[63] with the latter being devoted to the two-component methods of calculation of NMR parameters and considering in detail two-component Hamiltonians including both exact (*e.g.*, X2C) and approximate (*e.g.*, A2C) procedures. The most popular among the family of A2C methods is the so called Zeroth-Order Regular Approximation (ZORA).[64–71]

The main idea of this review was to provide a timely general insight into the relativistic HAHA and HALA effects of heavy chalcogens (selenium and tellurium) in the NMR chemical shifts and spin-spin coupling constants with concentrating mainly on practical computational approaches and paying not too much attention to pure theoretical aspects.

Relativistic effects in the NMR parameters of heavy chalcogens

Nowadays the synthesis of organoselenium and organotellurium compounds is rapidly progressing in parallel with the development of their practical applications in biochemistry,[72–79] radiopharmaceutics[80,81] and microelectronics.[82] The ^{77}Se and ^{125}Te NMR spectroscopy is a highly efficient tool for the structural elucidation of organoselenium and organotellurium compounds. An accurate prediction of ^{77}Se and ^{125}Te NMR spectra is an inseparable part of modern NMR spectroscopy in the chalcogen chemistry.

The main trends in selenium and tellurium chemical shifts and spin-spin coupling constants have very much in common, being different only in scale. The width of a chemical shift scale is about 3000 ppm for selenium and more than 7000 ppm for tellurium. The spin-spin coupling constants involving tellurium are two or three times larger than those involving selenium.[83] In spite of a vast amount of published data on experimental ^{77}Se and ^{125}Te NMR chemical shifts,[83–91] it is not much known about their computational prediction and the experimental data have not been confirmed computationally. The main reason of this situation is the 'heaviness' of these nuclei, which requires computationally expensive relativistic approaches together with special relativistic basis sets.

Theoretical results on ^{77}Se NMR shielding constants and chemical shifts were published against the available experimental data obtained without taking into account relativistic effects. Thus, Wilson[92] used a mixed hybrid generalized gradient approximation (GGA)[93] to calculate ^{77}Se NMR absolute shielding constants in organoselenium molecules including SeH_2, SeCO, H_2CSe, CSe_2, SeF_6, and MeSeH at the nonrelativistic level. In the calculations,[92] the localized orbital/local origin method (LORG)[94] was used to account for the gauge origin problem. Basically, this mixed hybrid GGA scheme showed much better performance in the calculation of ^{77}Se NMR absolute shielding constants, as compared to conventional DFT methods, though demonstrating some lower level of accuracy as compared to experiment. As it could be easily estimated, the absolute deviations of nonrelativistic DFT-LORG chemical shifts from their experimental values in six organoselenium compounds[92] vary in a range of 100 to 300 ppm, and the mean absolute percentage error (MAPE) in that series is about 20–30%. The selenium chemical shifts in the same series of compounds were also presented by Schreckenbach *et al*.,[95] who used a nonrelativistic DFT method in combination with the gauge-including atomic orbitalts (GIAO)[96–100] method to take into account the gauge origin problem. The found deviation of calculated selenium chemical shifts from experiment was practically of the

same magnitude, providing the MAPE of about 23%. Obviously, these results do not comply with modern standards for the accuracy of quantum-chemical calculations.

The benchmark nonrelativistic chemical shifts in the same six compounds obtained *via* the GIAO-MP2 and GIAO-CCSD methods were reported by Bühl *et al.*[101] and Schreckenbach *et al.*[95] As follows from their results, the relative deviations of chemical shifts from experiment for the most part of considered molecules do not exceed 20% for GIAO-MP2 and 6% for the GIAO-CCSD methods. The nonrelativistic GIAO-CCSD results for a narrow range of selenium chemical shifts[95] were consistent with experimental data. However, in some cases, unaccounted factors such as relativistic effects can provide substantial contributions to selenium chemical shifts. First, this is due to not quite successful cancellation of relativistic effects at the stage of evaluating the chemical shift of a given nucleus as difference between the shielding constant of the nucleus in a reference compound (in which relativism can play a very substantial role) and that in the compound of interest.

In general, despite a seemingly high accuracy provided in simple cases by high-precision nonrelativistic methods, one should not regard the chemical shifts of heavy nuclei (^{77}Se and ^{125}Te in particular) obtained *via* these methods to be the reliable ones because there might be a very successful cancellation of unaccounted relativistic factors suddenly showing themselves up in the final results.

Indeed, dealing with the fourth-row element selenium, one should expect the manifestation of relativistic effects in the second-order magnetic properties of selenium compounds like ^{77}Se NMR absolute shielding constants and those converted into chemical shifts. Thus, Malli and Froese[102] estimated the relativistic correction to ^{77}Se NMR absolute shielding constant of dimethyl selenide at 300 ppm. More recently, Lantto *et al.*[103] used a fully relativistic four-component Dirac procedure at the DFT level and the two-component Breit–Pauli perturbation theory (BPPT)[104] to produce the relativistic ^{77}Se NMR shielding surfaces of carbon diselenide. The general conclusion was that the contribution from the relativistic effects to ^{77}Se NMR shielding parameters amounts to about 13% as compared to the nonrelativistic data.

Nakanishi *et al.*[105] evaluated relativistic effects in ^{77}Se NMR absolute magnetic shielding tensors within ZORA at the DFT level in a series of 40 small selenoinorganics. Relativistic effects were shown to give about several dozens of parts per million in the range of several hundreds of parts per million, which roughly totals to 10% of their nonrelativistic values. Similar conclusions were reached earlier.[106–108] Ruud *et al.*[109] reported a relativistic correction of 265.4 ppm to the ^{77}Se NMR shielding constant of SeF_6 calculated at the four-component relativistic DFT level, which is ~20% of the nonrelativistic coupled-cluster result of about 1250 ppm. A relativistic correction of 246 ppm to the ^{77}Se NMR shielding constant in the SeH_2 molecule was evaluated by Jaszuński and Olejniczak[110] with the Dirac–Coulomb Hamiltonian at the Hartree–Fock and spin-DFT levels, which is about 10% of the total value of 2447 ppm; the latter was evaluated as the sum of the nonrelativistic coupled-cluster value and Dirac–Hartree–Fock relativistic correction.

In view of a marked breakthrough in the theory of magnetic resonance parameters,[1,5,37–39,46,112,113] a thorough development of practical computational approaches to ^{77}Se NMR chemical shifts has now become affordable. Rusakov *et al.*[114,115] analyzed the main factors affecting the accuracy of calculations of ^{77}Se shielding constants (methods and basis sets, relativistic corrections and solvent effects) and proposed versatile computational procedures for the ^{77}Se NMR chemical shifts of medium-sized organoselenium compounds. Thus, Rusakov *et al.*[114] discussed practical aspects, such as basis set convergence, applicability of locally dense basis set schemes (LDBS),[116–118] solvent effects and relativistic corrections in the calculation of ^{77}Se NMR shielding constants in 18 open-chain and heterocyclic organoselenium compounds (including dimethyl selenide as a standard). The computational scheme proposed[114] combines the *ab initio* correlated GIAO-MP2 approach for the basic nonrelativistic values obtained both in gas and liquid phases and four-component RPA for taking into account relativistic effects.

Thus, the convergence of the two most popular groups of relativistic Dyall basis sets,[119–127] namely, valence dyall.v*X*z and diffuse valence dyall.av*X*z (*X* = 2, 3 and 4) uncontracted basis sets placed on all atoms (Se, C and H) in the calculation of ^{77}Se NMR isotropic absolute shielding constant of dimethyl selenide at nonrelativistic GIAO-RPA and GIAO-MP2 levels of theory, has been studied.[114] The choice of the Dyall family of basis sets used in this study resulted from the fact that the former was optimized from the relativistic calculations within the framework of the full four-component Dirac equation, which mostly suits the aims of relativistic calculation of ^{77}Se NMR chemical shifts. In addition, the performance of different LDBS procedures for the calculation of ^{77}Se NMR shielding constants has been investigated. Based on these results, the most reliable accurate and economic LDBS scheme, implying the dyall.av3z basis set on selenium and on α-atoms and dyall.av2z on the rest of atoms, was recommended. The relativistic corrections to ^{77}Se NMR shielding constants obtained within the four-component relativistic RPA scheme as implemented in the DIRAC program package[128] are about 230–260 ppm (some 15% of the total selenium shielding constants) and the ones transformed to a selenium chemical shifts scale are in a range of 20–30 ppm (about 5% of the total selenium chemical shifts).

The most efficient computational protocol for the practical calculations of ^{77}Se NMR chemical shifts of medium-sized organoselenium compounds[114] provides the results that can be characterized by a mean absolute error of only 17 ppm. Provided that selenium chemical shifts are spanned over a range of about 2500 ppm, the MAPE can be easily estimated in this case at 0.7% (Figure 1). The performance of the non-hybrid fully relativistic four-component GIAO-DFT schemes employing different nonrelativistic exchange-correlation functionals for the calculation of ^{77}Se NMR shielding constants and chemical shifts in the above representative series of organoselenium compounds has been investigated.[115]

Figure 2 shows that almost all GIAO-DFT methods (with the only exception of LDA or SVWN[129–131]) perform noticeably better than GIAO-RPA with the most reliable results for the functionals B3LYP,[132,133] KT2,[134] PBE,[135,136] and PBE0[137,138] (MAE 34–36 ppm), as compared to GIAO-RPA (MAE 47 ppm). This result was attributed to the fact that correlation effects are of major importance in the reproduction of experimental ^{77}Se NMR

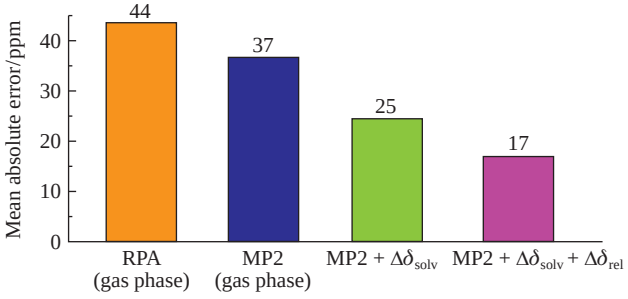


Figure 1 Mean absolute errors of ^{77}Se NMR chemical shifts in organoselenium compounds calculated at the GIAO-MP2 level taking into account solvent and relativistic effects in comparison with the nonrelativistic GIAO-MP2 and GIAO-RPA gas phase results. Reproduced from ref. 114 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

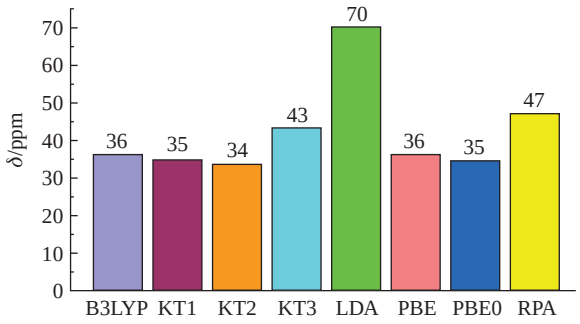


Figure 2 Mean absolute errors of ^{77}Se NMR chemical shifts calculated in the benchmark series of reference organoselenium compounds at the four-component DFT and RPA levels *versus* experimental data. Reproduced from ref. 115 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

chemical shifts, so that uncorrelated RPA demonstrates noticeably poor performance even at the four-component relativistic level.[115] The best result was achieved with NMR-oriented KT2 functional of Keal–Tozer[134] characterized by a fairly small MAE of only 34 ppm for the span of about 1700 ppm (< 2%).

Rusakov and Krivdin[115] had claimed that there were still other very important accuracy factors, which remained fallen out from the consideration. These factors are the relativistic geometry factor (the effect of relativistic geometry optimization as compared to nonrelativistic optimization) and vibrational corrections. Keeping this in mind, they performed the benchmark calculations of ^{77}Se NMR chemical shifts in six relatively small organoselenium compounds $Se(SiH_3)_2$, Me_2SeCl_2, Me_2SeO, C_4H_4Se (selenophene), $C_2H_2N_2Se$ (1,2,3-selenadiazole) and C_4H_4SSe (1,2-thiaselenin).

To study the effect of relativistic geometry factor on the accuracy of calculated ^{77}Se NMR chemical shifts, two series of the four-component relativistic calculations have been performed.[115] Namely, two sets of geometric parameters optimized at the four-component relativistic B3LYP/dyall.av3z level and at the one-component nonrelativistic level were employed using the same functional and the same basis sets. It followed that the effect of relativistic geometry does not exceed 6 ppm in an absolute value, being in average of about 1–2 ppm, so that it can be neglected in most cases. The only exception from this trend was provided by bistrimethylgermyl selenide, where relativistic geometrical effect totaled to as much as 20 ppm, noticeably improving the agreement of calculated ^{77}Se NMR chemical shift with experiment. This can be explained by the heavy surrounding of a selenium atom by two germanium atoms, which could be 'heavy enough' to cause scalar relativistic effects on geometrical parameters to come into play. The best result in this study was obtained within the non-hybrid four-component GIAO-KT2 scheme with taking into account solvent, vibrational and relativistic geometry factor corrections. It provided MAE of only 20 ppm and MAPE of about 4% for ^{77}Se NMR chemical shifts evaluated in the above organoselenium compounds. As could be estimated from the data of this study, pure four-component GIAO-KT2 calculations without additional corrections provided MAE of about 30 ppm and MAPE of about 8%. Thus, the contribution of relativistic effects to ^{77}Se NMR chemical shifts is about 5% of the total chemical shifts, while relativistic contributions to absolute ^{77}Se NMR shielding constants are expected to be approximately 10–15% of the total shielding constants.

A reasonable question, which could arise at this point, concerns the role of relativistic effects on the tellurium atom as a heavier analogue of selenium. Unfortunately, to date this issue is not investigated sufficiently well because of unaffordable computational costs when dealing with organotellurium molecules. Moreover, organotellurium molecules of interest are biologically active organotellurium species. Indeed, tellurium chemical shifts in such compounds could not simply be considered at the relativistic level of theory using modern computational capabilities. However, some scarce publications on the computational research of ^{125}Te NMR spectra in relatively small tellurium compounds have appeared in the literature. The first and solid steps to the relativistic computation of ^{125}Te NMR chemical shifts in the real-life organotellurium compounds, potential precursors of biologically active molecules have already been made.

The pioneering calculations of tellurium shielding constants and chemical shifts at the two-component relativistic ZORA-LDA level in combination with GIAO formalism have been reported by Ruiz-Morales *et al.*[139] for organic and inorganic tellurium compounds with ^{125}Te NMR chemical shifts covering a range of about 3000 ppm. An important aspect of this work is raising a question about the rate of cancellation of relativistic effects for the tellurium chemical shifts. Thus, for example, in the $TeMe_4$ molecule, the relativistic part of the absolute tellurium shielding constant accounts for about 170 ppm resulting in the tellurium chemical shift scale of about 11 ppm. However, for $[TeCl_6]^{2-}$ the situation turns out to be reversal with relativistic effects on tellurium shielding constant resulting in 57 ppm. At this, relativistic correction to the tellurium chemical shift is about 125 ppm. So far, this question is still open, and more wide statistical sampling is needed. The MAPE of tellurium chemical shifts in the 16 molecules studied is about 75% in relation to experimental results while the mean absolute error (MAE) is as much as 180 ppm.

Hayashi *et al.*[140] reported relativistic effects in ^{125}Te NMR chemical shifts in 45 compounds covering a range of about 4000 ppm. Relativistic effects were evaluated using a two-component spin-orbit ZORA Hamiltonian within the GIAO-BLYP[133,141] and GIAO-OPBE[142] approaches. The agreement of calculated tellurium chemical shifts with the experimental values was found. In particular, for the structures optimized within the relativistic two-component ZORA-OPBE method, the MAPEs for the tellurium chemical shifts were 20% for ZORA-OPBE and 23% for ZORA-BLYP.

Other two-component quasi-relativistic approaches to the calculation of tellurium shielding constants are revealed to be much less utilized than those based on ZORA formalism. In particular, Hada *et al.*[143,144] used a quasi-relativistic two-component method based on the second-order Douglas–Kroll–Hess transformed relativistic Hamiltonian[145] (including spin-free relativistic, one- and two-electron spin-orbit and relativistic magnetic interaction terms) within the framework of the generalized unrestricted Hartree–Fock method (GUHF)[41,146] to calculate ^{125}Te NMR magnetic shielding constants and chemical shifts in four representative compounds TeH_2, TeF_6, $TeMe_4$ and $TeMe_2Cl_2$. Relativistic effects were found to be 1300–1500 ppm for the tellurium shielding constants and –20 to 160 ppm for the tellurium chemical shifts. The MAPE for chemical shifts in this series accounts to 32%, as compared to experimental data. According to published data,[139,140,143,144] the two-component approaches can provide not a very high accuracy of calculated ^{125}Te NMR chemical shifts in relation to experiment.

Although the MAPEs are not very high and the methods employed are quite different, yet one can find an approximate measure of the relativistic effects on the NMR shielding constant of tellurium atom. Thus, according to Hayashi *et al.*,[140] a relativistic correction to shielding constants of tellurium varies in a range of 10–20% (excluding some specific molecules) relative to the total relativistic values, while Hada *et al.*[144] reported a value of about 30%.

However, Rusakova *et al.*[147] calculated the relativistic corrections to ^{125}Te NMR magnetic shielding constants and chemical shifts at the four-component fully relativistic GIAO-DFT level.

For the correct description of tellurium chemical shifts, they also took into consideration less essential factors, such as solvent and vibrational effects, maintaining a balance between the level of approximation and computational effort. The main goal was to approve the methodology of calculation of tellurium shielding constants at the four-component relativistic GIAO-DFT level taking into account many accuracy factors.

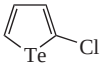
Attention was also focused on different LDBS schemes, which are of crucial importance when concerning molecules containing heavy nuclei like tellurium. The appropriate LDBS scheme was recommended.[147] It implies the dyall.av4z basis set on the tellurium atom, dyall.av3z on α-atoms and dyall.av2z on the rest of atoms.

The performance of different exchange-correlation functionals was examined both within the four-component relativistic and non-relativistic GIAO-DFT approaches in the calculation of tellurium chemical shifts in representative organotellurium open-chain and heterocyclic compounds. The most accurate results were obtained at both levels of theory when using KT2, PBE0 and B3LYP functionals. The PBE0 functional provides the smallest MAPE of about 6% at the four-component relativistic level and 20% at the nonrelativistic level of theory (Table 1).

Table 1 indicates that the average relativistic corrections to tellurium chemical shifts amount to 22% in relation to their total values calculated at the full four-component relativistic DFT-PBE0 level taking into account solvent and rovibrational corrections of 8 and 6%, respectively. Within this series, the MAPEs gradually decrease from 24% for the nonrelativistic level to 4% for the full four-component relativistic level with all corrections taken into account (Figure 3).

The total relativistic corrections $\Delta\sigma_{rel}$ to ^{125}Te NMR shielding constants evaluated in a series of 14 organotellurium compounds (including dimethyl telluride as a standard) amount to 661–1030 ppm, which is about 25–35% of the total relativistic values. In the ^{125}Te NMR chemical shift scale, the relativistic corrections $\Delta\delta_{rel}$ are about 17–369 ppm, which is 26% of their total relativistic values in average. In comparison with selenium chemical shifts, it follows that the role of relativistic effects in tellurium shifts is much more essential. To be more precise, the contribution of relativistic effects to selenium shielding constants is about 10–15%, while it is 25–35% for tellurium shielding constants. Converted into a chemical shift scale, the portion of relativistic effects in selenium shifts is about 5–10%, whereas this portion for tellurium shifts can be estimated at 20–30%.

Table 1 GIAO-PBE0 calculated ^{125}Te NMR chemical shifts (ppm) in organotellurium compounds using dimethyl telluride as a standard.[a]

Compound	Solvent	δ_{nonrel}	$\Delta\delta_{rel}$	$\Delta\delta_{solv}$	$\Delta\delta_{vib}$	δ_{total}	Experimental
Et_2Te	C_6D_6	293	38	–2	20	349	374
$(CH_2{=}CH)_2Te$	C_6D_6	455	113	15	–13	570	534
$(MeC{\equiv}C)_2Te$	C_6D_6	242	107	36	–61	324	338
Me_2TeBr_2	PhMe	567	230	138	–45	890	858
	$(CD_3)_2CO$	597	161	71	–22	807	782
	$(CD_3)_2CO$	696	181	78	–39	916	905

[a] All data are taken from ref. 147; the calculated chemical shifts of diethyl and divinyl tellurides are conformationally averaged.

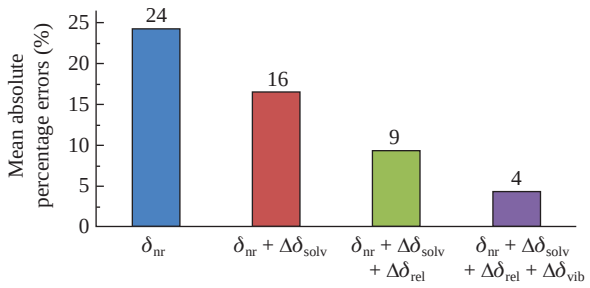


Figure 3 Mean absolute percentage errors of ^{125}Te NMR chemical shifts in organotellurium compounds calculated at the GIAO-PBE0 level taking into account solvent, relativistic and vibrational corrections in comparison with experiment. Reproduced from ref. 147 with permission of American Chemical Society provided *via* Copyright Clearance Center.

Note that relativistic effects also play a significant role in the mechanism of the nuclear spin-spin coupling involving at least one heavy nucleus, as discussed by Autschbach.[16] Obviously, relativistic effects in spin-spin coupling constants involving one heavy nucleus should be more pronounced than those in chemical shifts of that element. This is because there is no cancellation of relativistic effects, as it takes place when evaluating chemical shifts as a difference between the shielding constant of a heavy element in a standard and that in the test compound. For spin–spin coupling constants involving two heavy elements, relativistic effects could result in a contribution of more than an order of magnitude.

Aucar[57,148] considered the relativistic calculations of spin-spin coupling constants involving heavy chalcogens in the simple hydrides XH_2 (X = O, S, Se, Te and Po) and demonstrated that relativistic effects could substantially contribute to and even dominate in a spin-spin coupling mechanism.

At present, spin-spin coupling constants involving selenium or tellurium nuclei, ^nJ(Se,X) or ^nJ(Te,X), with X being one of the common NMR nuclei, ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{77}Se, ^{129}Xe, or ^{195}Pt, are scarcely investigated computationally. This is in spite of the fact that a plenty of experimental data is present in the literature (for example, Luthra *et al.*[149] concentrated on selenium and tellurium species). However, recent breakthrough in the computer engineering and quantum chemical software has advanced a considerable progress in using high-level theoretical approaches to calculate J-tensors involving selenium and tellurium.

A noticeable breakthrough was made by Gomez, Romero and Aucar[57] in 2002. They considered the one-bond $^1J(^{77}Se,^1H)$ and $^1J(^{125}Te,^1H)$ spin-spin coupling constants in the small molecules of SeH_2 and TeH_2, at the RPA level of theory with both Dirac–Fock and Hartree–Fock wave functions. Transformed to Hertz, the values obtained therein for $^1J(^{77}Se,^1H)$ and $^1J(^{125}Te,^1H)$ at the nonrelativistic RPA level were 105.6 and –325.8 Hz, while those obtained at the four-component RPA level were 57.8 and 82.8 Hz, respectively.[57] Based on these results, one could estimate relativistic effects for these simplest one-bond selenium– and tellurium–hydrogen spin-spin coupling constants at –47.8 and +408.6 Hz, respectively, which are approximately –80% and 500% of their total relativistic RPA values. Even based on these preliminary data obtained at the RPA level of theory, which is known to suffer from triplet instabilities,[150,151] the conclusion about the crucial importance of relativistic effects in $^nJ(^{77}Se,X)$ and $^nJ(^{125}Te,X)$ could be already made at this point. Some examples of the relativistic calculations of spin-spin coupling constants of selenium and tellurium with non-hydrogen NMR nuclei (such as fluorine or tellurium) could be found.[152,153]

Rusakov *et al.*[154,155] calculated the one-bond spin-spin coupling constants involving selenium in selenium heterocycles and their parent open-chain selenides at the SOPPA(CC2) and SOPPA(CCSD) levels taking into account relativistic corrections evaluated both at the RPA and DFT levels of theory in comparison with experimental data.

The one-bond selenium–carbon spin-spin coupling constants were calculated[154] in a series of 13 reference compounds. The nonrelativistic spin-spin coupling constants $^1J(^{77}Se,^{13}C)$ were calculated *via* the most accurate *ab initio* polarization propagator

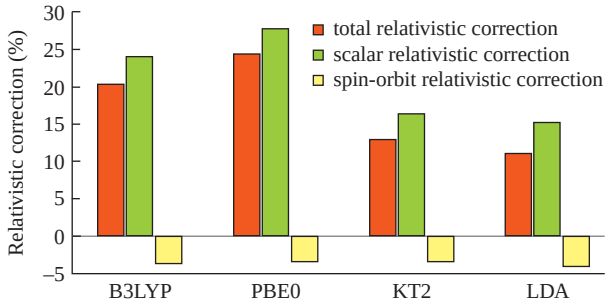


Figure 4 Relativistic corrections to the total values of ^1J(Se,C) calculated for organoselenium compounds at the four-component DFT level using different functionals. Reproduced from ref. 154 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

method, SOPPA(CC2), using decontracted Sauer's aug-cc-pVTZ-J basis set for selenium and coupled carbons and decontracted Dunning's cc-pVDZ basis sets for the rest of atoms. The relativistic corrections to $^1J(^{77}Se,^{13}C)$ spin-spin coupling constants were calculated at the four-component DFT level using exchange-correlation functionals.

From the analysis of these data, it was found that total relativistic corrections evaluated at the DFT level were essential for the one-bond $^1J(^{77}Se,^{13}C)$ couplings contributing to about 15–25% of their total relativistic values depending on the functional used. Figure 4 indicates that the B3LYP and PBE0 functionals give essentially larger total relativistic corrections than those calculated with KT2 and LDA functionals.

Published data[154] indicated that the most reliable results were obtained within the SOPPA(CC2) scheme in combination with the relativistic corrections calculated within the four-component DFT-B3LYP scheme, providing the MAPE of about 4%. The PBE0, KT2 and LDA functionals in the four-component DFT calculations resulted in the MAPEs of about 6, 12 and 15%, respectively. Figure 5 illustrates the excellent agreement with experimental results.

Another relativistic study of spin-spin coupling constants involving selenium nuclei was performed by Rusakova *et al.*[155] One-bond spin-spin coupling constants involving selenium of seven different types, $^1J(^{77}Se,X)$ with X = ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P and ^{77}Se, were calculated in a representative series of 14 organoselenium compounds at the SOPPA(CCSD) level taking into account relativistic corrections evaluated within the four-component RPA and DFT approaches (Table 2).

As expected, the largest contribution of total relativistic effect is manifested by $^1J(^{77}Se,^{77}Se)$ reaching almost 120% of the total calculated value of $^1J(^{77}Se,^{77}Se)$. Indeed, under these circumstances, the calculation of $^1J(^{77}Se,^{77}Se)$ at any nonrelativistic level without taking into account relativistic effects makes no sense.

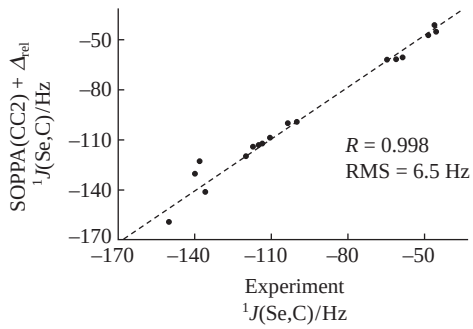


Figure 5 Correlation plot of ^1J(Se,C) calculated in a series of organoselenium compounds calculated at the SOPPA(CC2) level taking into account total relativistic corrections calculated at the four component DFT-B3LYP level *versus* experiment. Reproduced from ref. 154 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

Table 2 Spin-spin coupling constants of different types $^1J(^{77}Se,X)$ with X = ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P and ^{77}Se calculated at the SOPPA(CCSD) level taking into account DFT-PBE0 relativistic corrections.[a]

Compound	Coupling constant	SOPPA (CCSD)	Relativistic DFT-PBE0 correction, Δ_{rel}	SOPPA (CCSD) + Δ_{rel}	Experiment
H_2Se	$^1J(^{77}Se,^1H)$	107.96	–34.83	73.13	60.8
MeSeH	$^1J(^{77}Se,^{13}C)$	–34.02	–10.27	–44.29	(–)48.3
F_3CSeNH_2	$^1J(^{77}Se,^{15}N)$	62.39	2.90	65.29	60.1
Me_2SeF_2	$^1J(^{77}Se,^{19}F)$	395.27	161.10	556.37	634.0
SeF_6	$^1J(^{77}Se,^{19}F)$	–1360.17	–60.57	–1420.74	(–)1423.0
$F_2Se{=}O$	$^1J(^{77}Se,^{19}F)$	–834.47	84.66	–749.81	(–)837.0
F_2SeO_2	$^1J(^{77}Se,^{19}F)$	–1385.92	–32.25	–1418.17	(–)1580.0
$EtSeSiMe_3$	$^1J(^{77}Se,^{29}Si)$	72.86	23.77	96.63	107.3
$MeSePMe_2$	$^1J(^{77}Se,^{31}P)$	–222.52	9.01	–213.51	(–)205±6
$MeSePOMe_2$	$^1J(^{77}Se,^{31}P)$	–259.80	–36.55	–296.35	(–)367.9
$Me_3P{=}Se$	$^1J(^{77}Se,^{31}P)$	–747.05	–70.28	–817.33	(–)684.0
$F_3P{=}Se$	$^1J(^{77}Se,^{31}P)$	–1265.79	–177.46	–1443.25	(–)1490.0
$Cl_3P{=}Se$	$^1J(^{77}Se,^{31}P)$	–1104.58	–44.36	–1148.94	(–)1065.0
MeSeSeMe	$^1J(^{77}Se,^{77}Se)^b$	–14.35	100.46	86.11	20.0

[a] Data from ref. 155 including experimental values. All couplings and relativistic corrections are given in Hz. [b] Conformationally averaged.

A surprisingly large contribution of total relativistic correction (about 50%) was also found for $^1J(^{77}Se,^1H)$. This is even more surprising because, in this case, the total relativistic correction is of an opposite sign to the total value of $^1J(^{77}Se,^1H)$. According to Table 2, relativistic corrections to other spin-spin coupling constants do not exceed 30% of their total values. In particular, relativistic corrections to $^1J(^{77}Se,^{13}C)$ and $^1J(^{77}Se,^{29}Si)$ are about 20–25%.

It was also found[155] that within both nonrelativistic SOPPA (CCSD) without any corrections and SOPPA(CCSD) with taking into account relativistic corrections levels, the $^1J(^{77}Se,^{77}Se)$ coupling constant demonstrates a marked Karplus-type dihedral angle dependence with respect to the mutual orientation of selenium lone pairs providing a powerful tool for a stereochemical analysis of organoselenium compounds (Figure 6).

Like in the case of selenium couplings, experimental data for tellurium coupling constants, $^nJ(^{125}Te,X)$ with X = ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{77}Se, *etc.*, have been reported (see, for example, ref. 149). There is rather less quantitative information on spin-spin coupling constants involving tellurium than it can be found for selenium couplings. In particular, experimental spin-spin coupling constants involving tellurium have not been yet examined computationally, and there are no systematic studies of quantitative trends in tellurium spin-spin coupling constants. However, recent break-

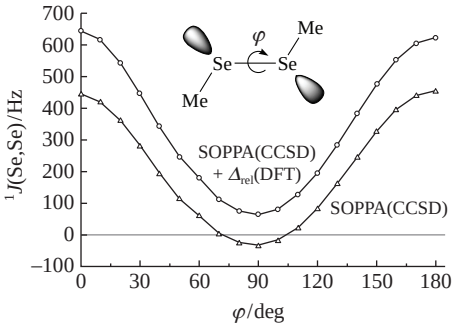


Figure 6 Dihedral angle dependence of $^1J(^{77}Se,^{77}Se)$ in dimethyl diselenide calculated at the nonrelativistic SOPPA(CCSD) level of theory with and without taking into account relativistic effects at the four-component DFT-PBE0 level. The value of $\varphi = 0°$ is adopted for the synperiplanar orientation of Se–Me bonds. Reproduced from ref. 155 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

through in the computing chemistry has advanced a considerable progress in high-level theoretical approaches to calculate tellurium *J*-tensors.[152,153]

In particular, a high-level computational study of geminal and vicinal couplings $^{n}J(^{125}\text{Te},^{1}\text{H})$, n = 2, 3, has been reported recently.[158] This was a correlated calculation of geminal and vicinal tellurium–hydrogen spin-spin coupling constants in the medium-sized organotellurium molecules at the level of SOPPA (CCSD) with taking into account relativistic, vibrational and solvent effects. The relativistic effects calculated at the ZORA-B3LYP level have been found to be ~20–25% of their nonrelativistic values while vibrational and solvent corrections appeared to be negligible. A special 'relativistic' av3z-J basis set for tellurium was presented.[158] It was derived from the relativistic Dyall's basis set, dyall.av3z, and specifically optimized for the correlated calculations of spin-spin coupling constants involving tellurium.

The results of the calculation of one-bond tellurium–carbon spin-spin coupling constants have been reported by Rusakova *et al*.[159] The hybrid computational scheme was used throughout this study, which involved the SOPPA method for obtaining basic nonrelativistic values in combination with the four-component DFT-PBE0 method for taking into account relativistic corrections.

A crucial parameter of the enormously time-consuming correlated calculations of NMR chemical shifts and spin-spin coupling constants is the LDBS scheme, which should be chosen thoroughly and correctly. Thus, the performance of different LDBS schemes,[159] implying Sauer's av3z-J[158] and different Dyall's dyall.*x*v3z[120,160] (with *x* being 'a', 'c', 'ac' and none) basis sets on tellurium, triple-zeta Sauer's aug-cc-pVTZ-J basis set[157] on α-carbons, and Dunning's cc-pVDZ basis sets[161] on the rest of atoms was investigated in the calculation of $^{1}J(^{125}\text{Te},^{1}\text{H})$ in four representative organotellurium compounds. It was found that the inclusion of core functions into basis set worsens the agreement of theoretical values with experiment. Indeed, it follows that the most reliable results are provided by those LDBS schemes, which imply av3z-J or dyall.v3z or dyall.av3z basis sets on tellurium within the above computational scheme. Calculated corrections together with full theoretical values against experimental data are given in Table 3.

Figure 7 shows the relative errors[159] of theoretical $^{1}J(^{125}\text{Te},^{13}\text{C})$ values compared to experimental data. Consideration for relativistic corrections calculated at the DFT level drastically diminish relative errors for all four compounds from ~50 to about 2–8% with the most striking effect for tellurophene (~2%). Vibrational corrections and solvent effects are much less pronounced with the former increasing the agreement of theoretical data with experiment by 1–2%.

Based on the data in Table 3, one can estimate relative contributions from the effects of each type. Thus, relativistic effects result in the contribution to $^{1}J(^{125}\text{Te},^{13}\text{C})$ of about 45–50% with

Table 3 Spin-spin coupling constants $^{1}J(^{125}\text{Te},^{13}\text{C})$ in four reference organotellurium compounds calculated at the SOPPA level with relativistic (Δ_{rel}), solvent (Δ_{solv}) and vibrational (Δ_{vib}) corrections calculated at the DFT-PBE0 level.[a]

Molecule	SOPPA	Δ_{rel}	Δ_{solv}	Δ_{vib}	Total	Experiment
$TeMe_2$	73.31	70.60	–6.58	9.50	146.83	158 (C_6D_6)
$Te(CF_3)_2$	201.24	195.50	–	16.46	413.20	423.2 (neat)
$Te(C{\equiv}CH)_2$	288.73	292.24	4.85	19.59	605.41	538.5 (C_6D_6)
	159.60	137.31	–2.11	10.76	305.56	302.4 $(CD_3)_2CO$

[a] All data are taken from ref. 159. All couplings and their contributions are given in Hz.

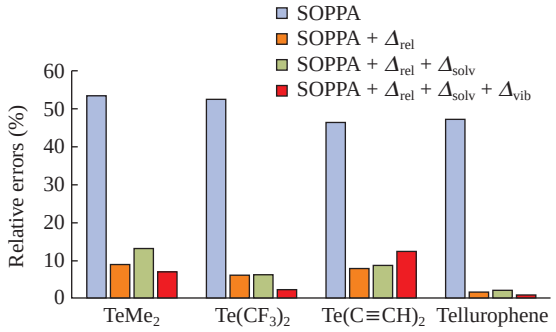


Figure 7 Relative errors of calculated $^{1}J(^{125}\text{Te},^{13}\text{C})$ spin-spin coupling constants in four representative organotellurium compounds with respect to experiment. Reproduced from ref. 159 with permission of John Wiley & Sons, Inc. provided *via* Copyright Clearance Center.

respect to the total theoretical values, which are 2–3 times larger than 15–25% for $^{1}J(^{77}\text{Se},^{13}\text{C})$. In the case of the one-bond $^{1}J(^{125}\text{Te},^{13}\text{C})$ and $^{1}J(^{77}\text{Se},^{13}\text{C})$, this ratio does really confirm the assumption by Luthra.[83] In this series of compounds, other types of corrections were found insignificant with solvent corrections of no higher than 4% and vibrational corrections in a range of 3–6%.[159]

The influence of the so-called 'relativistic geometry factor' in the tellurium–carbon spin-spin coupling constants is also of interest. A comparison of $^{1}J(^{125}\text{Te},^{13}\text{C})$ in the series of four organotellurium compounds calculated within the prime hybrid computational scheme (SOPPA + DFT-PBE0 corrections) at different equilibrium geometries as compared to experiment was performed. The equilibrium geometries were obtained at the DFT-B3LYP level of theory using the fully relativistic four-component approach with the Dirac–Coulomb Hamiltonian (not taking into account Breit interaction), the four-component Levy–Leblond nonrelativistic scheme, the 10c limit scheme and the usual one-component nonrelativistic method of optimization. The comparison was made with the results obtained using the MP2/dyall.av3z optimization as compared to experimental data to show no marked effect of 'relativistic' geometry.

Heavy atom effect on the NMR parameters of light atoms induced by heavy chalcogens

Versatile and highly efficient tools for the prediction of the NMR parameters of light nuclei based on nonrelativistic high-accuracy *ab initio* approaches or DFT have been developed and widely utilized in common practice. However, the results of such predictions might sometimes fail for the compounds containing one or more heavy chalcogens (selenium or tellurium).

It is well known that shielding and spin-spin coupling constants are highly sensitive to the presence of heavy atoms[162–166] due to different HALA effects,[167–173] *i.e.*, the effects of a heavy atom (HA) on the nuclear shielding of a light atom (LA) or spin-spin coupling constant between two LAs. The HALA effects in the nuclear shielding and spin-spin coupling constants involving light atoms can be described within a two-component representation, originating in the third-order perturbation energy corrections,[174] containing different combinations of hyperfine interaction operators, so that there are different types of HALA effects.[37,42]

Theoretically, two conceptually different HALA effects could generally be extracted from the perturbational approach, namely, the spin-free HALA (SF-HALA) effects, originating in the scalar relativistic effects on heavy atom, and, on the other hand, the spin-orbit HALA (SO-HALA) effects, originating in the spin-orbit interactions on the heavy atom. According to Kaupp,[168] SF-HALA effects on NMR parameters may be significant for NMR properties of compounds containing 5*d* and 6*p* elements

and beyond, while SO-HALA effects become important somewhat higher in the Periodic Table, starting from the 4th period.

The main mechanism of the SO-HALA effect on nuclear shielding constants of light atoms can be rationalized.[169] In the presence of an external magnetic field, the spin-orbit operators of heavy nucleus can mix singlet and triplet states and thus induce spin polarization. This polarized spin density will interact with the nuclear magnetic moment of a light nucleus by a Fermi-contact mechanism. The mechanism of the SO-HALA effect in spin-spin coupling constants is slightly more complicated than that in the shielding constants. Briefly, spin polarization induced by the heavy atom interferes with the Fermi-contact mechanism of light nuclei spin-spin coupling, resulting in the additional effective fields at the sites of the light nucleus.

Many factors can influence the SO-HALA effect on both NMR parameters, and some of them are very similar to those of the FC/SD spin-spin coupling mechanism between heavy nucleus and the light nuclei under consideration. These are (1) the rate of involvement of the valence *s*-orbitals of LA in the HA–LA bonding chain;[168,169] (2) the energy gap between the highest occupied and the lowest unoccupied molecular orbitals;[168,169] (3) the heaviness (atomic number) of HA and the number of HA lone pairs;[168,170,175] (4) the balance between σ–σ and π–π interactions between HA and LA;[171,176,177] and (5) the covalence of bonds between the HA and LA.[171,176,177]

To the best of our knowledge, except for several communications (*e.g.*, refs. 147 and 165), there are no publications on the SO-HALA effect on NMR parameters in compounds containing heavy chalcogens.

Recently, a thorough investigation into the SO-HALA effect on the shielding constants of carbon nuclei in the α- and β-positions to heavy *p*-elements was reported.[175] The test compounds were the monosubstituted ethanes $C_\beta H_3–C_\alpha H_2–XH_n$, the monosubstituted ethenes $C_\beta H_2=C_\alpha H–XH_n$ and the monosubstituted ethynes $C_\beta H\equiv C_\alpha–XH_n$, where X is a 13–17 Group *p*-element. These compounds were chosen to cover the different types of hybridization of α- and β-carbons, which are related to the magnitude of the SO-HALA effect.[168,169] The methyl tellurides Me_nTe (n = 2, 4, 6) were also used to investigate the consecutive diminishing of the SO effects on the heavy tellurium atom with an increase in its oxidation state. The latter in its turn is expected to result in an overall diminishing of the efficiency of the SO-HALA effect on the chemical shifts of α-carbons.[168,170] The calculations[175] were performed within the GIAO-DFT approach using dyall.av3z basis sets on all atoms employing the KT2 exchange-correlation functional specifically developed to predict NMR parameters.

Apart from the well-known revised Normal Halogen Dependences for the 17th Group elements (F, Cl, Br, I and At),[178–184] the so-called Chalcogen, Pnictogen, Tetrel and Triel Dependences were established for the α-carbon NMR shielding constants in the compounds containing 16th (O, S, Se, Te and Po), 15th (N, P, As, Sb and Bi), 14th (C, Si, Ge, Sn and Pb) and 13th (B, Al, Ga, In and Tl) Group elements, respectively.[175] As an example, the chalcogen dependences covering sulfur, selenium, tellurium and polonium in the series of monosubstituted ethanes, ethenes and ethynes are shown in Figure 8.

Commonly, chalcogen dependences are much less pronounced than normal halogen dependences while pnictogen dependences are even less pronounced than chalcogen ones. In particular,[175] the chalcogen dependence for *sp*-hybridized carbons is about two times weaker while the pnictogen dependence is about five times weaker than the normal halogen dependence. The weakening of the dependences on going from 17th to 14th Group elements is attributed to the decreasing number of lone electron pairs, which are expected to be the most powerful source of spin-orbit perturbations in the SO-HALA mechanism.[39,170] This problem was

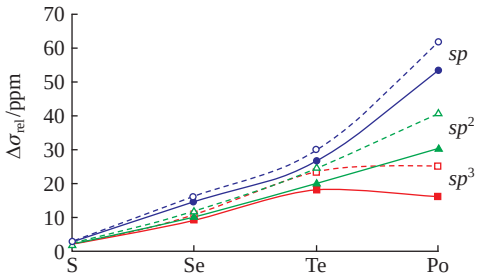


Figure 8 Chalcogen dependences of the total relativistic corrections to the α-carbon shielding constants (solid lines) and pure spin-orbit corrections (dashed lines) obtained for the compounds containing 16th Group elements. Reproduced from ref. 175 with permission of John Wiley and Sons, Inc. provided *via* Copyright Clearance Center.

Table 4 Calculated ^{13}C NMR isotropic shielding constants and chemical shifts (ppm) in comparison with experiment.[a]

Compound	σ_{nonrel}	σ_{rel}	$\Delta\sigma_{rel}$	$\Delta\sigma_{SO}$	δ_{nonrel}	δ_{rel}	Experiment
Me_2Te	184.6	208.7	24.1	27.2	1.8	–21.4	–21.5
Me_4Te	157.5	163.3	5.8	7.5	28.9	24.0	20.6
Me_6Te	148.8	146.2	–2.6	4.0	37.6	41.1	37.1

[a] Data are taken from ref. 175. In all calculations, methyl groups are conformationally averaged.

investigated[175] in a series of tellurium-containing compounds. Table 4 summarizes ^{13}C shielding constants and chemical shifts of dimethyl telluride, tetramethyl telluride and hexamethyl telluride in comparison with experimental data.

Table 4 shows that total relativistic corrections to ^{13}C NMR shieldings and their SO parts noticeably diminish on decreasing the number of the lone electron pairs on tellurium by a factor of 7 on going from dimethyl to hexamethyl telluride. As a consequence, there is a dramatic disagreement of ^{13}C NMR nonrelativistic chemical shift of dimethyl telluride with experiment (1.8 against –21.5 ppm), while relativistic chemical shift exactly reproduces experiment (–21.4 against –21.5 ppm). In tetramethyl and hexamethyl tellurides, the values of δ_{nonrel} and δ_{rel} are sufficiently closer to each other than those in dimethyl telluride to indicate the weakening of relativistic effects with decreasing the number of the lone electron pairs on tellurium.

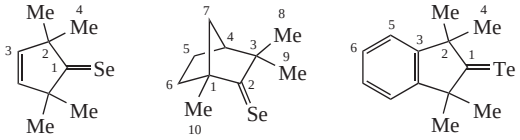
Relativistic corrections to chemical shifts of β-carbons were found small (up to several ppm) as compared to α-carbons (up to several dozens of ppm). For example, in the selenium and tellurium series $C_\beta H_3–C_\alpha H_2–XH$, $C_\beta H_2=C_\alpha H–XH$ and $C_\beta H\equiv C_\alpha–XH$ with X = Se or Te, the magnitudes of the HALA effect on shielding constants of β-carbons are 0.9, 1.5 and 2.3 ppm for C_{sp^3}, C_{sp^2} and C_{sp} in the selenium series and –0.6, 2.0 and 3.2 ppm for C_{sp^3}, C_{sp^2} and C_{sp} in the tellurium series, respectively.[175] The most pronounced SO-HALA effect is observed for *sp*-hybridized α- and β-carbons, while the smallest one is found for sp^3 carbons. This is consistent with the expected diminishing of the SO-HALA mechanism efficiency on decreasing the *s*-character of LA in the HA–LA bonding.[168,169]

Insignificant HALA effects on the chemical shifts of carbons in the β- and, especially, γ-positions to a heavy atom were reported. The natural question arises: does the insignificance of the SO-HALA effect (or HALA effect in the general case) on β- and γ-carbons hold for all types of compounds? The current investigations of the SO-HALA effect on the chemical shifts of light NMR nuclei separated by more than one bond from the heavy atom are very scarce, so that no definite answer could be found to that question.

A factor affecting the SO-HALA shielding is the hyperconjugative interactions from the bonding or antibonding orbitals involving light NMR atom. In this connection, Neto *et al.*[185]

performed a qualitative orbital analysis of SO matrix elements to predict the type of compounds where the large SO-HALA effect on chemical shifts of ^{13}C atoms directly bonded to heavy halogen could be expected. Compounds with strong hyperconjugative interactions involving $\sigma^*_{C–X}$ orbital (X = halogen) like halogen-substituted cyclohexanes and pyranes, provide good examples where such effects could be manifested. However, these issues have not received much attention, and only very few papers reported on the hyperconjugative aspect of the HALA effect on ^{13}C shieldings (*e.g.*, see ref. 186).

Rusakov *et al.*[187] reported a high-level computational study of compounds where large SO-HALA effects on shielding constants of distant carbons might show up. The carbon shielding constants of seleno- and telluroketones **1**–**3** containing sp^2-hybridized heavy Se and Te atoms have been examined within the high-correlated nonrelativistic GIAO-CCSD/dyall.av2z/6-311+G(2d,1p) method in combination with solvent, vibrational and relativistic corrections. Solvent corrections were calculated within the nonrelativistic GIAO-KT2/dyall.av3z approach while total relativistic corrections to carbon shieldings were obtained within the four-component GIAO-KT2/dyall.av3z approach (Table 5).



1 **2** **3**

Table 5 shows that the agreement of calculated results with experiment is very good providing deviations of chemical shifts of α (C^1), β (C^2) and γ (C^3 and C^4) carbons from their experimental values of 1.1, 3.2, –1.9 and 0.9 ppm, respectively, resulting in the MAPE of about 2.5%. Note that a pure nonrelativistic CCSD scheme gives the MAPE of 8.1% for the set of the three test compounds. Taking into account the solvent corrections at the GIAO-KT2 level reduces the MAPE from 8.1 to 8.0%. Finally, accounting for the relativistic GIAO-KT2 corrections dramatically reduces MAPE to 2.7%. Based on this finding, it was suggested[187] that GIAO-KT2 relativistic corrections may be represented as the reliable estimations of the HALA effect, especially in the absence of experimental data.

As expected, Table 5 indicates that HALA effect on α-carbon (α-HALA) is the largest one reaching –13.4 ppm. However, the most interesting unexpected observation is that the magnitude of the HALA effect on chemical shifts of the long-range β- and γ-carbons is far from being negligible. Indeed, according to Table 5, the β-HALA effect on the chemical shift of C^2 is 5.8 ppm while the γ-HALA effect on C^4 is –4.0 ppm! These noticeable long-range effects manifest a deviation from the widespread opinion that the long-range β- and γ-HALA effects on chemical shifts of carbon atoms do not play an essential role in the prediction and interpretation of ^{13}C NMR spectra.

The calculated absolute values[187] of HALA corrections to γ-carbons in rigid compounds **1**–**3** strongly depend on the dihedral

Table 5 Calculated ^{13}C NMR chemical shifts of α-, β- and γ-carbons (ppm) in 2,2,5,5-tetramethyl-3-cyclopentene-1-selone as compared to experiment.[187]

Atom	Type of effect	δ_{CCSD}	$\Delta\delta_{solv}$ ($CDCl_3$)	$\Delta\delta_{vib}$	$\Delta\delta_{rel}$	δ_{tot}	Experiment[a]
C^1	α	311.2	1.9	–3.7	–13.4	296.0	294.9
C^2	β	65.1	0.8	0.2	5.8	71.9	68.7
C^3	γ	136.1	0.0	–0.7	–0.7	134.7	136.6
C^4	γ	33.9	–0.2	0.6	–4.0	30.3	29.4

[a] See references cited in ref. 187.

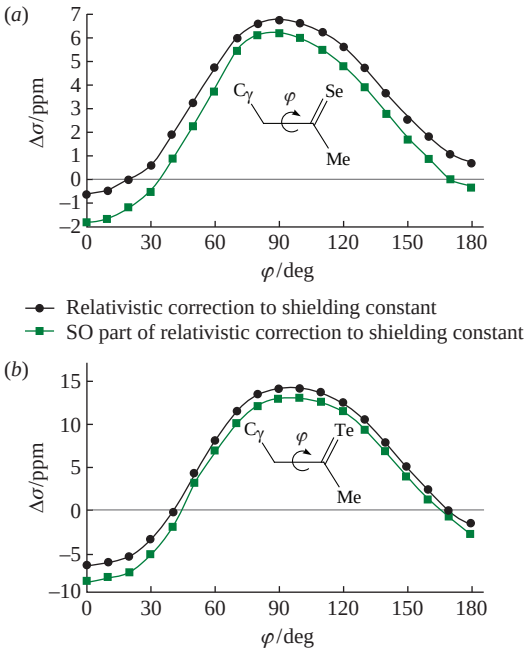


Figure 9 Dihedral angle dependence of the HALA effect on shielding constant of γ-carbon in (*a*) butane-2-selenone and (*b*) butane-2-tellurone calculated at the GIAO-KT2/dyall.av3z level. Reproduced from ref. 187 with permission of Taylor & Francis Group provided *via* Copyright Clearance Center.

angle $X–C^α–C^β–C^γ$, as illustrated in Figure 9. Total relativistic corrections (*i.e.*, total γ-HALA effects) calculated using the four-component Dirac–Kohn–Sham Hamiltonian[49,50,188,189] are shown as black lines while γ-SO-HALA corrections calculated at the two-component Barysz–Sadlej–Snijders level are shown in green.

Figure 9 demonstrates that the SO contribution to the shielding constant of γ-carbons is responsible for the bell-like dihedral angle dependence of the whole HALA effects in butane-2-selenone and butane-2-tellurone. The MO analysis[187] showed that contributions to the SO shielding tensor from the low-laying MOs remain almost unchanged on going ϕ from 0 to 90°, while the HOMO→LUMO and HOMO-1→LUMO magnetic couplings determine the most part of the change of SO correction.

Unlike well-documented HALA effects on NMR chemical shifts, very few papers were devoted to the HALA effect in spin-spin coupling constants between two light nuclei,[191–197] and especially in compounds containing heavy chalcogens.[191] As an example, Rusakova *et al.*,[198] investigated the HALA effect referred to as the Indirect Relativistic Effect (IRE) on the one-bond and germinal carbon–hydrogen spin-spin coupling constants. The IREs induced by the atoms of the fourth (X = C, Si, Ge, Sn, Pb), fifth (X = N, P, As, Sb) and sixth (X = O, S, Se, Te) main group elements were evaluated at the four-component DFT-PBE0 level of theory. In particular, for the chalcogen series MeXH with X = O, S, Se, Te, the relativistic indirect bridge effect was about 7–11% of the total values of $^2J(X–^{13}C–C–^1H)$ coupling constants.

Computational remarks on the relativistic calculations of NMR parameters

Based on our experience, we would like to report available information on the computational aspects of the relativistic calculations of NMR parameters. This can be helpful on the long way of attenuation of computational approaches to the accurate prediction of NMR spectra of compounds containing heavy elements.

Relativistic effects in NMR parameters are usually evaluated as the differences between the values obtained from the relativistic two- or four-component Hamiltonians and those obtained from the nonrelativistic Schrödinger Hamiltonian or some approximate

Hamiltonians derived from a relativistic or quasi-relativistic approach at the nonrelativistic limit. Relativistic NMR parameters could be evaluated within a number of state-of-the-art computational packages. The following list includes only the most widely used program packages while local or poorly known programs are not mentioned.

ADF[199–201] is a powerful Amsterdam Density Functional quantum chemistry package. It allows one to calculate NMR parameters at both two-component relativistic and nonrelativistic levels of RPA and TD-DFT methods using LDA and GGA functionals. Within this package, relativistic calculations of NMR parameters are performed at the two-component level within the ZORA-DFT approximation (either including or not including spin-orbit coupling). The ADF program makes use of the Slater-type basis set functions, which are known to describe the nearby nuclear region within the most accuracy. Integrated in ADF code, special relativistic basis sets of different quality have been specially optimized at the ZORA level of theory. The most profound and convenient tool of the ADF program package is the Localized Molecular Orbital module, which makes it possible to analyze separate contributions to nuclear spin-spin coupling or nuclear shielding tensors from different pairs of orbitals and, as a consequence, to extract orbital contributions to different types of relativistic effects.

DALTON[202] is the quantum chemical program package named in the honor of John Dalton, the founder of the atomic structure theory. In the NMR domain, this program at the most part can be involved into the nonrelativistic calculations of magnetic resonance parameters. To be more precise, within a nonrelativistic (Schrödinger) picture, the spin-spin coupling constants and shielding constants (chemical shifts) can be evaluated within the TD-HF,[54–56] TD-MCSCF,[203–205] TD-DFT,[206] SOPPA(MP2),[20–22] SOPPA(CC2)[23] and SOPPA(CCSD)[24] approaches. However, the last versions of DALTON provide calculations of the first- and second-order relativistic corrections within the Linear Response Elimination of Small Component (LRESC) scheme,[207] and third-order relativistic corrections, including third-order paramagnetic scalar and spin-orbit terms within quadratic response approach.

DIRAC[128] is the program for atomic and molecular direct iterative relativistic all-electron calculations, which computes NMR properties using relativistic or quasi-relativistic quantum chemical methods. The NMR parameters can be calculated within the relativistic four-component RPA and four-component DFT approaches using four-component Dirac–Coulomb or Dirac–Coulomb–Gaunt Hamiltonians. The Gaunt term[208] is responsible for the two-electron spin-orbit interactions. There is also a vast amount of the two-component approaches to NMR properties, which are included in this code. Among those are ones of the exact type, such as X2C,[209–211] X2Cmmf[212] and BSS[190,213–215] and ones of the approximate type, such as ZORA, DKH1[216,217] and DKH2.[218,219] Different schemes of gradual exception of relativism are also envisaged, making it possible to extract the different types of relativistic corrections. Pure nonrelativistic calculations of NMR parameters within variational approaches, such as RPA and DFT, are also provided by the DIRAC package.

ReSpect[220] is the Relativistic Spectroscopy quantum chemical program package with a completely parallelized code, which is aimed at fast and reliable prediction of spectroscopic properties (including NMR shielding and spin-spin coupling tensors) of closed- and open-shell molecules containing heavy elements. The program is based on the full four-component Dirac–Hartree–Fock and Dirac–Kohn–Sham theories, employing in-built all-electron basis sets suitable for relativistic calculations of all elements in the Periodic Table.

Undoubtedly, treating NMR parameters at the relativistic level of theory implies the usage of specially chosen basis sets. Preferably, all of them should be relativistically optimized and whenever possible unconstructed. However, if it is not physically achievable, propagation of relativistic perturbations must be described in an explicit way. On the other hand, they should also inherit the peculiarities of the basis sets specifically constructed for the calculations of spin-spin couplings and nuclear shielding constants. In addition, the balance between the accuracy and compactness must be maintained implying maximum compactness at a given level of accuracy.

The family of correlation-consistent polarized valence basis sets (aug)-cc-pV*n*Z (*n* is the number of primitive functions used to describe a valence orbital, 'aug' stands for 'augmented by diffuse functions', optional) was introduced by Dunning, Jr. *et al*.[221,222] These basis sets comply with the modern standards of nonrelativistic correlated calculations of chemical shifts and representing the sequence of sets systematically approaching to the complete basis set limit. For relativistic calculations, the Dunning's family of basis sets was extended to (aug)-cc-pV*n*Z-DK.[223–226] In this notation, 'DK' stands for Douglas–Kroll–Hess Hamiltonian, the latter used in optimization of the relativistic family of Dunning's basis sets. The (aug)-cc-pV*n*Z-DK basis sets have been developed only for limited series of heavy elements, mainly for transition metals. Generally, these Dunning's basis sets, which are suitable for the calculation of nuclear shielding constants, do not perform likewise well for spin-spin coupling constants. As was noticed by Schulman and Kaufman,[227] the s-type functions with very large exponents are of utmost importance for the convergence of the Fermi contact term. Thus, based on Dunning's basis sets, Enevoldsen *et al*.[21] started the developing of aug-cc-pV*n*Z-J series, characterized by additional tight s-type functions, which would fit well for the calculations of spin-spin coupling constants. As far as we know, there is no systematical development of Sauer's family of basis sets in relativistic domain, the only Sauer's basis set for tellurium atom, av3z-J, has been introduced recently.[158]

Specially for relativistic molecular calculations, the family of relativistic basis sets dyall(a)v*n*z was developed by Dyall.[119–127] These basis sets, being relativistically energy-optimized to roughly satisfy the correlation-consistent philosophy introduced by Dunning and co-workers, are strongly recommended for relativistic NMR calculations.

As mentioned above, the ADF program package uses its own in-built basis set library, which comprises relativistic and nonrelativistic Slater-type basis sets. In particular, for relativistic ZORA NMR calculations, all-electron ZORA/QZ4P basis set, as well as some of the nonrelativistic ones including AUG/ASZ, AUG/ADZ and AUG/ATZ2P, can be used.

In the last decade, the construction of relativistic basis sets, which are free from variational prolapse problem,[228,229] has received much attention. The recent achievements in solving this problem were reported by Teodoro *et al*.,[230,231] who proposed special relativistic prolapse-free (RPF) Gaussian basis sets of Quadruple-ζ quality, (aug-)RPF-4Z, for *s*-, *p*- and *d*-elements. The atomic and molecular calculations of the fundamental molecular properties (bond lengths and vibrational frequencies) were attested within the coupled cluster approach using quadruple-ζ quality RPF basis sets, resulting in a half-time-saving of CPU time in comparison to corresponding calculations with Dyall's v4z basis sets. These basis sets are essentially recent, so that there is no experience of their application to the calculation of NMR parameters.

It is worth mentioning other polarization-consistent basis sets developed especially for the NMR calculations, namely, Jensen's basis sets, (aug)-pcS-*n* (herewith, $n = 0, 1, 2, \ldots, n$, stands for the number plus one of Gaussian primitives for the valence orbital) for shielding constants[232–234] and (aug)-pcJ-*n* for spin-spin coupling constants.[235] These basis sets have been designed for the non-

relativistic DFT calculations of NMR parameters; unfortunately, there is no extension of these basis sets to the relativistic domain until now.

The above basis sets are well-known and suitable for either relativistic or nonrelativistic calculations of NMR parameters. However, there are many nonrelativistic basis sets, which are not particularly designed for NMR calculations. Here it is impossible to describe them, so that the reader is kindly advised to visit the Environmental Molecular Sciences Laboratory (EMSL) Basis Set Library.[236,237] Some key information is also given in recent review by Rusakov and Krivdin,[11] where the contemporary nonrelativistic quantum chemical calculations of spin-spin coupling constants are considered.

Conclusions

A systematic study of the accuracy factors of the quantum-chemical calculations of NMR parameters, *i.e.*, chemical shifts (nuclear shielding constants) and nuclear spin-spin coupling constants, are of prime importance. In spite of the reliability of the well-established nonrelativistic computational protocols for the prediction of NMR parameters of compounds containing only light elements, the accurate and efficient prediction of the NMR spectra of heavy nuclei is of considerable interest for the modern organoelement chemistry. Relativistic effects provided by heavy chalcogens on light and heavy nuclei (resulting in HALA and HAHA effects, respectively) play a major role in the interpretation of the NMR spectra of vitally important chalcogen-containing compounds, and they should be taken into account for practical purposes.

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