Theor Chem Acc (2016) 135:201
DOI 10.1007/s00214-016-1952-3

REGULAR ARTICLE

Relativistic and electron correlation effects on NMR J-coupling of Sn and Pb containing molecules

C. A. Giménez[1] · **A. F. Maldonado**[1] · **G. A. Aucar**[1]

Received: 1 December 2015 / Accepted: 17 July 2016 / Published online: 2 August 2016

Abstract We studied the influence of relativistic and electron correlation effects on NMR J-couplings in the following set of heavy-atom containing molecules: XY_4 and H_3XXH_3 ($X = $ Sn, Pb; $Y = $ H, F, Cl, Br, I). We applied two formalisms, the relativistic polarization propagator approach at random phase level of approach (RelPPA-RPA) and density functional theory (DFT) with functionals as implemented in the DIRAC code. We have chosen four functionals that have different amount of HF exchange (PBE0, B3LYP, BLYP, BP86). For those molecular systems, results of calculations with BLYP functional have the best performance as compared with available experimental data. As was previously found for magnetic shieldings in other molecular systems we are able to show here that DFT functionals must be modified in order to obtain reliable results of NMR J-coupling within the relativistic regime. We can state that there is a non-linear dependence among both, electron correlation and relativistic effects that should be introduced in the functionals. The functionals implemented in the DIRAC code are standard nonrelativistic ones which were parameterized with data taken from light-atom containing molecules. This explains why they are not able to properly introduce relativistic effects on NMR parameters, like J-coupling constant. Lastly we show that in the analysis of J-couplings for the family of compounds mentioned above, one must consider the effects of a third heavy-atom that is close to the J-coupled atoms of the same molecule, specially for ^nJ(H–H). This kind of effect is similar to the newest and so called heavy-atom effect on vicinal heavy atoms, HAVHA, proposed for the NMR-shielding constant. Such effects are among the most important relativistic effects in the family of compounds studied in this work.

Keywords Spin-spin coupling · Relativistic effects · DFT · Electron correlation

1 Introduction

NMR spectroscopic parameters are among the most useful tool to understand the electronic structure of atoms and molecules. When the systems under study contain heavy atoms, meaning atoms which belong to the fifth row of the Periodic Table or below, one must include relativistic effects on calculations of such magnetic parameters in order to obtain reliable results. In the last years an increasing amount of reviews and texbooks were published concerning the importance of relativity in quantum chemistry [1–6].

Indirect nuclear spin-spin J-coupling is one of the most important NMR spectroscopic parameter due to its high sensitivity, the possibility of routine measurements, and its ability to provide useful data about the geometry as well as the electronic structure of molecular compounds. It is a property of the electronic system (it does not depend on the external magnetic fields) and represents

---

Published as part of the special collection of articles "CHITEL 2015 - Torino - Italy".

✉ A. F. Maldonado
aleoml@yahoo.com.ar

C. A. Giménez
mail@carlosagimenez.com

G. A. Aucar
gaaucar@conicet.gov.ar

[1] Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina & Institute of Modelling and Innovation of Technology, IMIT, Corrientes, Argentina

the electron-mediated magnetic interaction of two nuclear magnetic moments. Consequently, calculations of NMR parameters based on first-principles theory are of high importance to help with the interpretation of experimental data and may provide reliable predictions.

The chemistry and physics of compounds that contain heavy elements can be modified qualitatively and quantitatively by relativity. Valence orbitals of heavy-atoms are influenced directly by relativistic effects, not only by a cascade of relativistic effects on core orbitals that propagate out to the valence shell. For that reason, some molecular properties like J-couplings with heavy atoms are not easy to reproduce computationally. Reliable calculations of J-coupling constants that include heavy nuclei have some important theoretical requirements to be fulfilled by the computational model; being among the most importants the introduction of relativistic effects, electron correlation and convergence of basis sets. It was recently suggested that the electron correlation and relativistic effects are not additive and they must be treated as accurate as possible in the calculations.

In the last twenty years an increasing number of works were published focused on J-coupling constant in heavy-atom containing molecules [7–12]. Those studies are based on semi-empirical and *ab initio* methods, including relativistic and electron correlation effects as well as solvent effect on the one- and two-bonds J-coupling calculations. It was found that relativistic effects may increase the value of J-couplings in more than two times as compared with their nonrelativistic values when heavy-atoms are involved. On the other hand, if one wants to include electron correlation with wavefunction-based methods this quickly becomes too much expensive because it has an awkward scaling behaviour. This is why there is an ever increasing interest in developing theoretical schemes for improving the treatment of relativistic and electron correlation effects on magnetic molecular properties.

The most reliable way to include the relativity on NMR properties calculations is to start with a four-component relativistic Dirac theory and then to calculate them using second order perturbation theory expressions [13] or the polarization propagator formalism [14]. Both of them reach the same analytical expression at the random phase approximation (RPA) and they were used in J-coupling calculations since more than seventeen years ago [13, 15].

One of the main characteristic of calculations of NMR parameters within the relativistic level is the fact that some contributions come from excitation to negative energy states. This means that those parameters are dependent on the description of the basis set of small components of the four-component wave function. The common way to improve such basis set is expanding the size of the basis set via the unrestricted kinetic balance prescription (UKB) or using some special basis set that depend on magnetic field [16], the restricted magnetic balance prescription (RMB). For J-coupling calculations, the restricted kinetic balance prescription (RKB) can be safely used, because the contribution that arise from the virtual excitations to negative-energy states are vanishingly small [15].

Density functional theory, DFT, is one of the method of choice when one wants to calculate NMR spectroscopic parameters in medium-size heavy-atom containing molecules. This is because the problem of describing accurately the electron correlation is taken by exchange-correlation functionals. So, DFT based methods can include electron correlation at an affordable computational cost. For the calculation of molecular properties some two-component DFT and wave function based methods are available, [2, 17–20] though not all of them were tested for tin and lead containing molecules. They were developed in order to assess the study of medium-size systems or to analyze nonrelativistic-like electronic mechanisms that may explain tendences or absolute values of NMR magnetic shieldings [21, 22]. It is therefore of interest to evaluate whether different DFT functionals are valuable tool for quantitative predictions of NMR properties of tin and lead.

In 2009 Repisky and co-wokers published the first four-component DFT implementation for the calculation of indirect nuclear spin-spin couplings based on the matrix formulation of the Dirac-Kohn-Sham method using the restricted magnetically balanced basis (mDKS-RMB) [23]. The method provides an alternative to existing approximate two-component methods with transformed Hamiltonians for relativistic calculations of spin-spin coupling constants of heavy-atom containing systems and was tested in XH_4 (X = Si, Ge, Sn, Pb) molecular systems with BP86 functional. The use of RMB basis allow to actually eliminate the problems associated with summation over negative energy states and thus to avoid additional approximations and the strong basis set dependence.

The zeroth order regular approximation (ZORA) method [24–26] is used with some functionals to calculate magnetic properties. In order to learn on the performance of DFT methods for getting quantitative predictions of ^{119}Sn NMR properties, Bagno et al. carried out calculations in several molecular systems using DFT with Becke 88 exchange [27] plus the Perdew 86 correlation [28] functional as implemented in the Amsterdam density functional (ADF) code, [29] in which frozen-core, as well as all-electron Slater basis sets are available for all atoms of interest. Relativistic effects were included by means of the ZORA scheme adding spin-orbit effects [9]. Moncho and Autschbach studied the performance for NMR indirect nuclear spin-spin coupling in heavy metal compounds with such approach combined with both, nonhybrid and hybrid density functional theory. They found a reasonably good performance of the hybrid functional PBE0 in the computations of J-coupling constant with heavy metal atoms [10].

For the properties studied here solvent effects are very often important when heavy elements are involved. In particular for metal-ligand couplings of complexes where the metal has open coordination sites that may be accessible by solvent molecules [30, 31]. In a recent article Demissie et al. showed the importance of including both relativistic and solvent effects in the analysis of organometallic complexes in order to obtain reasonable agreement between experimental data and calculated values for the chemical shifts and spin-spin coupling constants [32]. They performed four-component relativistic calculations of the NMR parameters at the Dirac-Kohn-Sham density functional level of theory using hybrid functionals. They found that using the B3LYP functional J-coupling constants are in much better agreement with the experimental values than that J-couplings calculated with BP86. This finding is more pronounced for J-couplings involving tin. It is then interesting to study the performance of different functionals on the J-coupling calculations in molecules containing heavy-atoms.

In this article we show results of one-bond J-coupling constant calculations, ^{1}J(X–Y), in the family of compounds XY_4 (X = Sn, Pb; Y = H, F, Cl, Br, I) applying both, the polarization propagator approach (PPA) and the DFT formalisms with four different functionals within relativistic (RelPPA) and nonrelativistic frameworks. We found important relativistic effects on such a property as can be expected, as well as important electron correlation effects also when the substituent halogen atom becomes heavier. A large dependence among both effects must be highlighted. This means that relativity has an strong influence on the electron correlation effect. We also analyzed the effect of a heavy atom on the one-, two- and three-bond J-couplings in molecular systems like H_3XXH_3 (X = Sn, Pb).

The structure of this article is as follows. We first give an schematic overview of the methods applied. Then we show results of tin and lead NMR J-couplings for XY_4 (X = Sn, Pb; Y = H, F, Cl, Br, I) molecular systems. Using these results together with some experimental values we are able to analyze the performance of the different functionals and the RelPPA formalism at RPA level of approach. The likely relationship among electron correlation and relativistic effects, and the effect of a heavy atom on the one-, two- and three-bond J-couplings in H_3XXH_3 molecular systems are then analyzed in the next subsections. The last section is devoted to highlight the main findings of our work.

2 Theoretical models

As mentioned above we applied two different formalisms for calculating NMR J-couplings within a theoretical four-component relativistic level, being them the RelPPA approach and the DFT formalism with four different functionals as implemented in DIRAC code, *e.g.* PBE0, B3LYP, BLYP and BP86.

2.1 Relativistic polarization propagator

Any static second-order molecular property can be studied applying the relativistic (Rel) formalism of polarization propagators. [6, 14, 33] Nonrelativistic (NR) methods can be safely employed when only light atoms are involved. The first implementation of the RelPPA method for the calculations of J-coupling tensors at RPA level of approach was published more than seventeen years ago [13, 15]. One advantage of this approach follows the fact that NR values can be obtained directly from relativistic calculations making c, the speed of light, scale to infinity.

For J-coupling constants, the *fully* relativistic expressions can be written as

$$\mathbf{J}_{MN} = \frac{e^2\hbar^2}{h}\gamma_M\gamma_N \left\langle\left\langle \frac{\boldsymbol{\alpha}\times\mathbf{r}_M}{r_M^3}; \frac{\boldsymbol{\alpha}\times\mathbf{r}_N}{r_N^3} \right\rangle\right\rangle \tag{1}$$

where $\mathbf{J}_{MN}$ refers to the indirect $\mathbf{J}$ coupling tensor between nuclei M and N; $\gamma_{M(N)}$ is the magnetogyric ratio of the $M(N)$ coupled nucleus, $\mathbf{r}_{M(N)} = (\mathbf{r} - \mathbf{R}_{M(N)})$, $\mathbf{R}_{M(N)}$ is the position of the nucleus $M(N)$ and α is a vector composed of 4×4 Dirac matrices. The expression above is fully relativistic given that retardation effects are not to be included due to their comparative (with respect to the leading relativistic effects) small contributions [34, 35]. From this equation one observes that only one electronic mechanism is involved in the spectroscopic parameter. There is also no distinction between dia and paramagnetic terms [33].

The reduced coupling constant, $\mathbf{K}_{MN}$ is more useful for the analysis of this molecular property because it does not depend on the magnetogyric ratios of the coupled nuclei. It is defined as

$$\mathbf{K}_{MN} = \frac{4\pi^2\mathbf{J}_{MN}}{h\gamma_M\gamma_N} \tag{2}$$

All terms in Eq. (1) can be calculated at different levels of approach depending on the fluctuation potential, *i.e.*, pure zeroth order approach (PZOA), consistent first order or random phase approximation (RPA), second order polarization propagator approach (SOPPA), etc. The fluctuation potential represents the difference between the Coulomb and the self consistent field (SCF) potential. This means that at RPA level, electron correlation is introduced to first order in the fluctuation potential, though the actual expressions are accidentally the same as those obtained by the coupled Hartree–Fock scheme [6]. At the moment, only the relativistic RPA level, RelPPA–RPA has been implemented in the DIRAC code [36].

2.2 Density functional theory with different functionals

When applying the Kohn-Sham density functional theory, one assumes that the exact universal exchange-correlation functional is not known, so that it needs to be modeled based on given grounds. The usual prescription for doing that is to design them to best reproduce experimental values of some properties. So, a good performance of a particular functional for the calculations of a given property cannot be assumed to be the same for another property.

There are several exchange-correlation functionals, *i.e.* semiempirical like the B3LYP [37, 38], BLYP, BP86 [27, 28] and the non-empirical PBE0 functional [39] based on the PBE with 25 % of exact exchange. All of these non local functionals include the exchange term of Becke [27]. BLYP and B3LYP use the functional correction of Lee, Yang and Parr [37] and the BP86 use the Perdew 86 [28] correlation funcional. PBE0 mixes the PBE exchange energy with Hartree-Fock exchange energy in a set of 3 to 1 ratio. This last ratio means that the inclusion of the exact exchange can be made mixing 25 % of exact exchange with 75 % of GGA exchange. The B3LYP include 20 % of exact exchange and BLYP and BP86 functional do not include it at all.

In the DIRAC code standard nonrelativistic functionals are used. Some studies about electron kinematics, potential energy, bond lengths, vibrational frequencies and binding energies of diatomic molecules indicate that relativistic corrections to the exchange-correlation functionals have a negligible effect on spectroscopic constants, at least for non-heavy-atom-containing compounds [40–42]. However in the last few years it was shown that relativistic effects are quite important for obtaining good results in the calculation of specific molecular properties with the four-component (4c) DFT formalism, and so they must be taken into account [43–45].

Earlier studies of molecular properties have shown that calculations performed with 4c-DFT schemes give smaller values of the NMR shielding constants of heavy atoms in molecules [43–49]. In addition, hybrid functionals containing exact HF exchange lead to smaller reductions as compared to GGA/BP86, and therefore they give results which are in better agreement with HF, especially PBE0 which has a larger percentage of HF exchange than B3LYP. For J-coupling constant a reasonable agreement with few experiments were found for the same functional [10].

3 Computational details

All calculations were carried out using DIRAC program [36]. The geometries of tetrahedral XY_4 (X = Sn, Pb; Y = H, F, Cl, Br, I) model compounds were obtained either from experimental data [50] or from calculations. In Table 1 we especify which molecular geometries were optimized. The bond lengths of the H_3XXH_3 molecules were taken from Ref. [51].

Table 1 Experimental/optimized geometries. d $(X-Y)$ bond distances in Angstroms (Å)

Molecule	*Y*				
	H	*F*	Cl	Br	*I*
SnY_4	1.711[a]	1.854[b]	2.2804[a]	2.487[b]	2.709[b]
PbY_4	1.743[a]	1.934[b]	2.360[a]	2.513[b]	2.738[b]

[a] Experimental geometry taken from Ref. [50]

[b] Theoretically optimized geometry

The geometry optimization was carried out at relativistic level with Dyall.cv3z [52] basis set and Dirac-Hartree-Fock Hamiltonian. Finite-size nuclear model of a Gaussian-type and uncontracted basis sets were used. The basis set for small components of the four-component wave function were obtained from the large components applying the RKB prescription.

J-coupling calculations in XY_4 (X = Sn, Pb; Y = H, F, Cl, Br, I) molecular systems were performed with the RelPPA formalism at RPA level of approach. It includes electron correlation till first order. We also carried out DFT calculations taking four functionals that include different amount of HF exchange: PBE0 (25 %), B3LYP (20 %), BLYP and BP86 (0 %). In order to get nonrelativistic values, the speed of light was multiplied by an scaling factor of 20 (c = 137.0359998 au). Doing this we obtain values that are equivalent to that of the NR limit with the same scheme of calculation. Dyall's basis sets [52] were chosen for the whole set of systems, and the cc-pVTZ basis set [53, 54] were used for H, F and Cl atoms. The small components were generated applying the RKB prescription because it is well know that J-coupling does not dependent of the negative-energy space.

Calculations in H_3XXH_3 molecular systems were carried out with the BLYP functional because, as will be shown in Sect. 4.1, it has the lowest mean deviation for tin/lead-atom containing molecules.

3.1 Grid quality and basis set convergence

Due to we looked for values of J-couplings as accurate as possible, we focused the study of different variables involved in highly accurate calculations like grid quality, basis set convergence and the prescription used to obtain the small component basis set from the large components. All of our tests were performed within the 4c-DFT level of approach, with BLYP and B3LYP functionals for PbI_4 molecule because this is the heaviest system studied in this work.

When heavy elements are included in the response calculations, special attention should be paid to the grid quality. For that reason some calculations for J(Pb–I) were performed using B3LYP functional and Dyall.cv3z basis set with respect to grid quality appliying different threshold for the the maximum error in the numerical integrations of the radial part (eLind) using the scheme proposed by Lindh et al. [55]. The angular part is handled by a set of highly accurate Lebedev grids (gLeb). We carried out the first calculation with eLind= 10^{-3} and gLeb = 10 (debug, very poor grid); for the second eLind=10^{-11} and gLeb = 35 (coarse grid); and for the third eLind = 2.0 10^{-15} and gLeb = 64 (ultrafine grid). We found a difference that is close to 27 Hz in J-coupling values among debug and coarse quality, but among coarse and ultrafine the difference is vanishingly small. The threshold chosen for all calculations was eLind=10^{-13} and gLeb = 41 and this grid quality is good enough to obtain reliable results for J-coupling constants for all systems studied in this work.

On the other hand, basis set convergence was also tested to be sure about reliability of results. Fig. 1 shows how the values of J(Pb–I) calculated with BLYP functional depends on the basis set of Dyall basis sets (cv2z, cv3z and cv4z). The difference among the J values obtained with cv2z and cv3z basis sets is quite large (473 Hz, meaning close to 23 %), but going from cv3z to cv4z basis sets such a difference is only of 35 Hz (meaning close to 2 %) of the J(Pb–I) value. This shows a good convergence. A similar behaviour was found for calculations using B3LYP functional, although its best result is different.

Even when the difference among the values obtained using cv3z and cv4z basis sets is not negligible, we have to keep in mind that it corresponds to the heaviest system. So we assume that for the rest of the lighter systems the use of the cv3z basis set is good enough to obtain reliable results. Then we used it for all calculations.

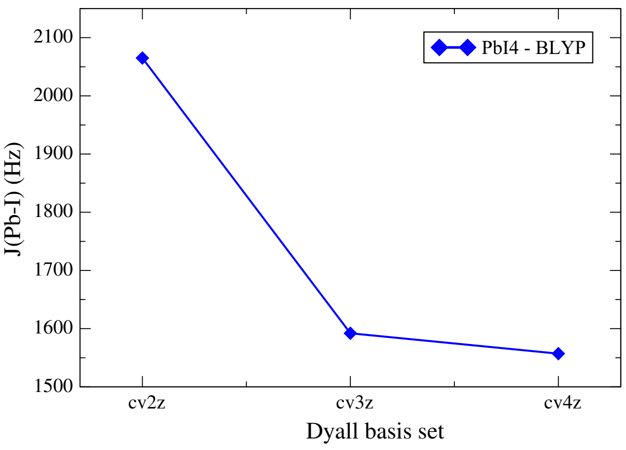

Fig. 1 Basis set convergency for J(Pb–I; PbI_4) with the functional BLYP

We also tested the convergence of basis sets after using both prescription, the RKB and the UKB. It is known that the application of RKB does not give good results when the summation over negative energy states is considered. This fact should not be very important for J-coupling calculations due to the fact that the contribution of the diamagnetic term is usually small (compared with the values of the paramagnetic term); what happens for J-couplings between two heavy nuclei is something that shall be checked. The difference among results of J(Pb–I) calculated with the B3LYP functional using both prescription is only 0.5 Hz, but the time demanding for calculations using the UKB prescription is 20 % larger than that using RKB. This is why we used the RKB prescription in all calculations of this work.

4 Results and discussion

4.1 RelPPA-RPA vs DFT calculations

In Tables 2 and 4 we show the value of one-bond J-couplings ^{1}J(Sn/Pb–Y) in Sn/PbY_4 model compounds (Y = H, F, Cl, Br, I) at the PPA-RPA level of approach, in addition to four different DFT functionals. The DFT functionals are sorted acording to Jacob's ladder [56], meaning acording to an increasing order in exchange-correlation functionals. In those Tables the reduced coupling constants, K(Sn/Pb–Y) are also shown.

In Table 2 we show results of relativistic and NR calculations of J(Sn–Y) and K(Sn–Y) for the family of SnY_4 (Y = H, F, Cl, Br, I) molecular systems at PPA-RPA and DFT level of approachs. We also show some experimental and theoretical values taken from the literature of J(Sn–Y). The values at RPA level are very different from those obtained with the four DFT schemes, though the DFT values are close each other. All of them are not so close to the experimental values, especially in the case of $SnBr_4$ molecule.

The absolute values of J(Sn–Y) at RelPPA-RPA level are larger than the NR ones, for all systems under study here, with variations close to 40 %. The exception happens for fluorine atom where the variation is close to 30 %. This means that relativistic effects on J-couplings are slightly dependent on the substituent heavy-atom, though its total value depends on the central heavy atom. On the other hand, the absolute value of 4c-DFT depends on what functional is used and also they have different behaviours depending on the halogen substituent. Relativistic values are larger than the NR ones for H, F and Cl atom, but they are smaller for Br and I atoms. In particular for SnI_4 molecule results of calculations with BLYP and BP86 are much

Table 2 One-bond J- and K-couplings, ^{1}J(Sn–*Y*) [Hz] and ^{1}K(Sn–*Y*) [10^{19} T^{2} J^{-1}] within relativistic and NR frameworks using PPA and DFT formalisms

Coupling	Rel		$J^{exp/theo}$	NR	
	J	K		J	K
Sn–H					
RPA	−2410.86	535.23	−1930[a]	−1694.15	376.11
PBE0	−1699.18	377.23		−1300.13	288.64
B3LYP	−1816.73	403.33		−1363.41	302.69
BLYP	−1732.24	384.57		−1342.55	298.05
PB86	−1542.65	342.48	−1549.5[b]	−1203.64	267.22
Sn–F					
RPA	1075.99	−253.78		842.13	−198.62
PBE0	4476.28	−1055.76		3135.43	−739.51
B3LYP	4837.36	−1140.92		3297.75	−777.79
BLYP	5380.35	−1268.99		3805.05	−897.44
PB86	5484.40	−1293.53		3889.57	−917.38
Sn–Cl					
RPA	444.60	−1006.24	470[c]	310.19	−702.04
PBE0	607.71	−1375.39		473.31	−1071.35
B3LYP	616.70	−1395.75		486.48	−1101.02
BLYP	606.11	−1371.78		505.12	−1143.20
BP86	611.25	−1383.41	535.5[b]	504.54	−1141.90
Sn–Br					
RPA	2909.40	−2383.45	920[d]	2031.40	−1664.17
PBE0	2590.41	−2122.13		2492.67	−2042.06
B3LYP	2373.49	−1944.42		2496.68	−2045.34
BLYP	1961.70	−1607.07		2444.25	−2002.39
BP86	2063.07	−1690.12	1633.3[b]	2462.17	−2017.07
Sn–I					
RPA	3228.16	−3557.37	940[c]	2315.33	−2551.45
PBE0	1637.14	−1804.09		2519.40	−2776.34
B3LYP	1193.52	−1315.23		2472.84	−2725.01
BLYP	473.94	−522.27		2343.95	−2582.98
BP86	625.97	−689.80	505.8[b]	2388.11	−2631.65

[a] Experimental value taken from Ref. [57]; [b] Calculated value taken from Ref. [9]; [c] Experimental value taken from Ref. [58]; [d] Experimental value taken from Ref. [59]

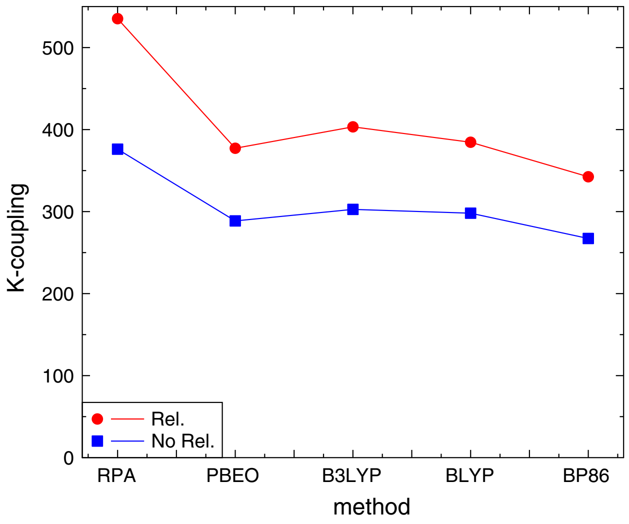

Fig. 2 Calculated K(Sn–H) (10^{19} T^{2} J^{-1}) reduced coupling within different DFT functionals and the RelPP-RPA approach for SnH_4 system

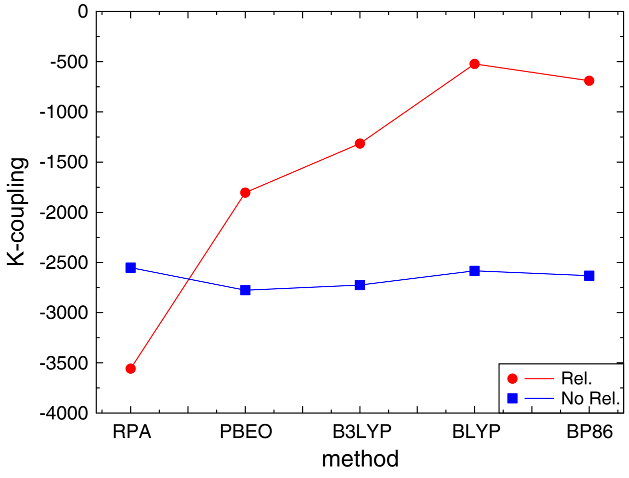

Fig. 3 Calculated K(Sn–I) (10^{19} T^{2} J^{-1}) reduced coupling within different DFT functionals and the RelPP-RPA approach for SnI_4 system

smaller than the corresponding NR values. This means that the description of relativistic effects strongly depend on the functionals.

It is nicely seen that electron correlation makes all K-couplings more negative, though when relativistic 4c-DFT functionals are considered the electron correlation of systems that contain the heavier halogen substituents makes such couplings more positive.

It is also worth to mention that results of J-couplings with PBE0 and B3LYP are closer each other as compared with the others. Then it seems that the amount of exchange-correlation is very important to account for relativistic and electron correlation effects. In Fig. 2 we show relativistic and NR values of the reduced coupling constant K(Sn–H), for the SnH_4 molecule, as a function of the different methods used for the calculations. The Hartree-Fock exchange percentage decreases from left to right, being PBE0 the largest, with 25 %. The difference among relativistic and NR values remains almost constants for different calculational schemes, which means that the electron correlation is not greatly affected by the relativity in this system. On the other hand in Fig. 3 we show the values of the reduced coupling constant, K(Sn–I), for the SnI_4 molecule calculated with different schemes. In opposition to what happens in the SnH_4 molecule, the

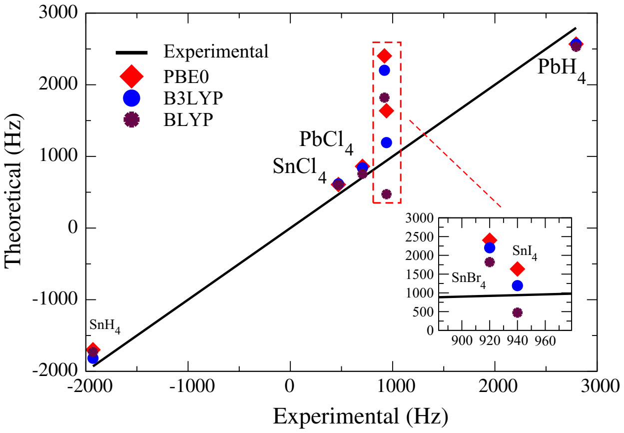

Fig. 4 Experimental vs DFT theoretical values for J(Sn–*Y*) in SnY_4 ($Y = $ H, F, Cl, Br, I) molecular systems

differences between relativistic and NR values vary highly with the method applied, and also with the functional. This means that when the weight of the molecule increases (due to the substituent halogen atom) the electron correlation has different behaviour. For the substituent fluorine and chlorine relativistic effects are different to those obtained for bromine and iodine. This suggests that there are some dependence among relativistic and electron correlation effects, and this must be taken into account when the weight of the molecule grows up.

Within the NR domain the electron correlation effects are different from those obtained within the relativistic regime. In other words, the introduction of relativity modifies the amount of electron correlation that is included in the J-coupling constants. This is clearly shown in Figs. 2 and 3, where the results of calculations using different functionals have similar behaviour for lighter systems, but they are quite different when the molecules become heavier.

How good are the performance of different functionals? To answer this inquire we should compare their results with experimental values. There are not many experimental data for the family of molecular systems studied in this work, though some of them are available. In Fig.4 we compare experimental with theoretical values of J(Sn–*Y*) in the family of SnY_4 ($Y = $ H, Cl, Br, I) molecular systems. PbH_4 and $PbCl_4$ (unsigned) values are also included. Which are the functionals that best reproduce such experimental values? We show there that they are BLYP and B3LYP, though this is not the case for all systems, especially for the $SnBr_4$ molecule.

In Table 3 we show the mean deviations of J(Sn–*Y*) couplings with respect to the experimental data for different schemes of calculations and within the relativistic level. RelPPA-RPA calculations have the largest mean deviation, reaching more than twice the corresponding 4c-DFT values. Of the four different functionals, the lowest mean deviation correspond to the BLYP functional, with very close value to the corresponding B3LYP and BP86 ones as one may expect using results of Fig 4. The PBE0 functional contains the largest HF exchange percentage, and this is the one that posses the largest mean deviation. If we include the two experimental (unsigned) values corresponding to lead-atom containing molecules the mean deviation of BLYP functional decreases to 366 Hz.

Table 3 Mean deviation for relativistic J(Sn–*Y*) (in Hz) calculations

J(Sn–Y)	RPA	PBE0	B3LYP	BLYP	BP86
Δ_{mean}	1196	684	492	460	496

Results of relativistic and NR calculations of J(Pb–*Y*) and K(Pb–*Y*) ($Y = $ H, F, Cl, Br, I) in PbY_4 molecular systems with some experimental and theoretical values are shown in Table 4. As in the case of the tin-atom containing molecules, it is observed that the absolute values of RelPPA-RPA are larger than those corresponding to the NR regime. It is also observed that there are very large variations between relativistic and NR values of J(Pb–*Y*). Such variations reach more than twice and up to four times the corresponding NR values.

The behavior of the results of calculations with the different functionals is very different from those obtained with RelPPA-RPA method. For PbH_4, PbF_4 and $PbCl_4$ molecules, the relativistic absolute values are larger than the corresponding NR ones. However for $PbBr_4$ molecule the PBE0 and B3LYP functionals (with larger percentage of HF exchange) give relativistic absolute values that are larger than the NR ones (more negative) but the results with BLYP and BP86 functionals give lower absolute values for the same molecule (more positive). Finally, in the case of the PbI_4 molecule, all relativistic DFT values are more positive than the NR ones, even with a change of the sign when different functionals are applied. These results are related, as in the case of tin-atom containing molecules, to the fact that electron correlation effects are linked to relativistic effects and this becomes important when the weight of the molecule grows up.

Our results are in very good agreement with those reported previously by other authors that also worked within a relativistic level and with the same functionals used in this work [10, 23].

If one wants to improve the final results of the J-coupling calculations there are some different effects that shall be considered, like the solvent effect and the finite nuclear size. Unfortunately DIRAC code uses only point magnetic moment distribution model and we must estimate the magnitud of the different effects based on previous works.

Table 4 One-bond J- and K-couplings, $^{1}J(Pb–Y)$ [Hz] and $^{1}K(Pb–Y)$ [10^{19} T^2 J^{-1}] within Relativistic and NR frameworks using PPA and DFT formalisms

Coupling	Rel		$J^{exp/theo}$	NR	
	J	K		J	K
Pb–H					
RPA	4128.61	1647.70	2793.8[a]	1535.68	612.87
PBE0	2536.48	1012.29	2900.8[b]	1160.78	463.26
B3LYP	2699.31	1077.28		1232.60	491.92
BLYP	2491.91	994.50		1188.66	474.38
BP86	2187.16	872.88	2345.3[c]	1065.80	425.35
Pb–F					
RPA	−3198.07	−1355.94		−763.99	−323.92
PBE0	−8009.12	−3395.76		−2892.05	−1226.19
B3LYP	−8345.87	−3538.53		−3020.52	−1280.66
BLYP	−8259.83	−3502.05		−3443.46	−1459.98
BP86	−8432.37	−3575.20		−3527.55	−1495.63
Pb–Cl					
RPA	−772.88	−3144.50	705.0[d]	−233.37	−949.47
PBE0	−861.30	−3504.22	−762.8[b]	−400.20	−1759.17
B3LYP	−841.31	−3422.86		−412.71	−1679.13
BLYP	−757.15	−3080.47		−430.70	−1752.33
BP86	−769.71	−3131.54		−432.38	−1628.23
Pb–Br					
RPA	−4122.30	−6543.96		−1580.17	−2508.44
PBE0	−2702.31	−4289.79		−2123.62	−3371.14
B3LYP	−2234.14	−3546.59		−2138.64	−3394.99
BLYP	−1390.95	−2208.07		−2139.25	−3395.96
BP86	−1543.57	−2450.34		−2140.64	−3398.17
Pb–I					
RPA	−4165.66	−8252.07		−1901.25	−3766.33
PBE0	−458.31	−907.90		−2309.71	−4575.48
B3LYP	341.42	676.34		−2296.12	−4548.56
BLYP	1591.96	3153.62		−2240.31	−4437.99
BP86	1375.39	2724.62		−2262.43	−4481.82

[a] The experimental value used in Ref. [10] has been extrapolated from $Pb(CH_3)_3H$ and $Pb(CH_3)_2H_2$; [b] Calculated valuetaken from Ref. [10]; [c] Calculated value taken from Ref. [23]; [d] Experimental value taken from Ref. [60]

For couplings involving one of the heaviest (sixth row) NMR nuclei and a light nucleus, early studies of Autschbach show that a reduction in the isotropic coupling due the finite nuclear size is of the order of 10 % or less. For TlI molecule, with basis set TZ2P3 at the ZORA spin-orbit PBE0 level of theory calculated with point nuclei and with the Gaussian nuclear model, the isotropic coupling constant is reduced in 4.5 % [61]. For TlBr molecule such a reduction is of 5.6 %, and these percentages would be similar for the J(Pb–Y) molecular systems.

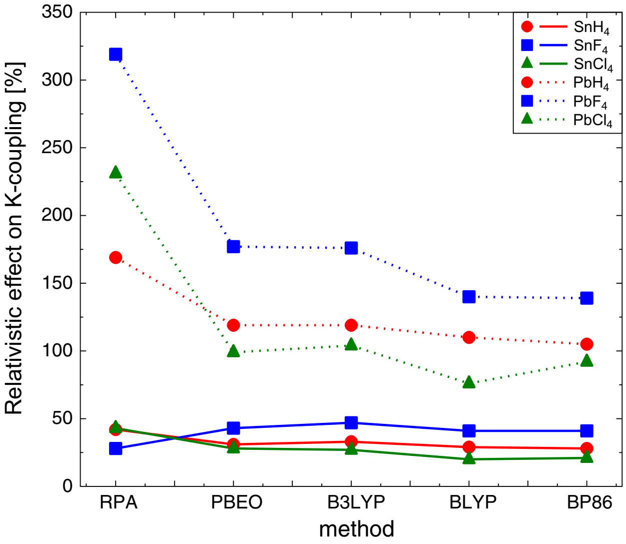

Fig. 5 Relativistic effects (%) on the reduced coupling constant, K, in Sn/PbY_4 (Y = H, F, Cl) model compounds with different scheme of calculations

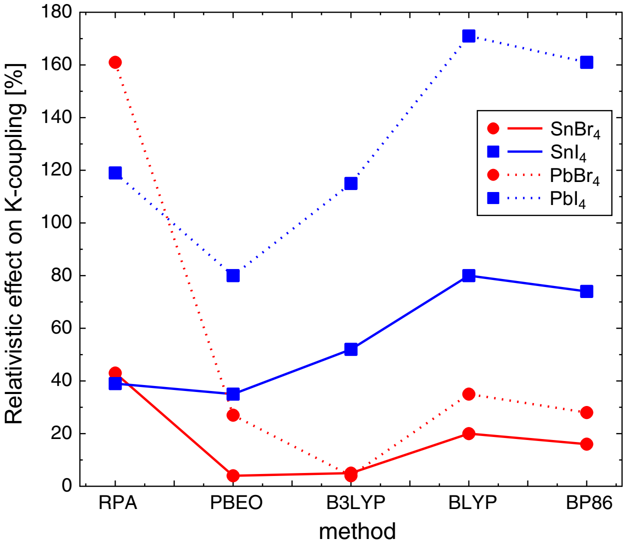

Fig. 6 Relativistic effects (%) on the reduced coupling constant, K, in Sn/PbY_4 (Y = Br, I) model compounds with different scheme of calculations

On the other hand the solven effect on heavy atom NMR spin-spin coupling constants can be very substantial and it was reported previously. Autschbach and Ziegler showed that DFT calculations of a number of solvated Hg and Pt complexes increase the isotropic couplings and yield reasonable agreement with experimental data obtained from solution [30]. Recently Demissie and co-workers studied the importance of including both relativistic and solvent effects in the analysis of organometallic complexes in order to obtain reasonable agreement between experimental data and calculated values for spin-spin coupling constants. They found that solvent effects improve the coupling constants calculations and yield a better agreement with the experimental values specially for B3LYP functional [32].

The nuclear size and solven effect usually produce opposite modifications of the J-coupling values, and the qualitative analysis of this work would not be modified without including them.

4.2 Relativistic and electron correlation effects

Relativistic effects of a response property, like the reduced coupling constant K($X - Y$), are usually estimated as a difference between the values within both regimes, relativistic and NR, and then compared with the nonrelativistic value. The percentual value gives the importance of this effect.

$$\Delta K(X - Y) = \frac{K(X - Y)^{\mathrm{Rel}} - K(X - Y)^{\mathrm{NR}}}{K(X - Y)^{\mathrm{NR}}} \times 100\,\% \qquad (3)$$

Figures 5 and 6 show the values of relativistic effects of the reduced coupling constant, K($X - Y$), for Sn and Pb central atoms and all substituents halogen atoms for the different schemes of calculation. Figure 5 shows values of relativistic effects for light substituent atoms (H, F, Cl). It is observed that the behaviour is similiar for all different functionals used, meaning that relativistic effects are not quite important for lighter molecules of the family of compounds studied here, and also the fact that they do not have an strong influence on correlation effects. On the other hand, for lead-atom containing molecules relativistic effects are quite large. In this case the RelPPA-RPA values reach a percentage of variation that is larger than 300 %. Figure 6 shows the relativistic effects for the heavier substituent halogen atoms (Br, I). The behaviour becomes completely different according to the scheme of calculation. For $SnBr_4$ and $PbBr_4$ molecules some functional gives relativistic values larger than the NR ones, in absolute value (like PBE0), but in other cases it follows the opposite tendency (like BLYP). The percentage of relativistic effects, also in absolute value, are very different depending on the functional used. For iodine substituent atom the behaviour is more pronounced and results of calculations with the whole set of functionals give very different values. For PbI_4 molecule all NR values are negative, but according to the functional applied in the calculations the relativistic results can be positive or negative, showing a strong dependence on the method. This may be due to the fact that when relativistic effects become important they would largely affect the electron correlation, and so a strong dependence among both effects do appears.

For the first three set of molecular systems, XY_4 ($X =$ Sn, Pb; $Y =$ H, F, Cl) we found that relativistic effects grow up when the electron correlation is included, with the exception of RelPPA-RPA values in the SnF_4 molecule. For heavier systems, like $SnBr_4$ and $PbBr_4$, the behaviour does not follow the same tendency, and for PbI_4 the behaviour is completely different of the other systems. This can be attributed to the fact that, for heavier systems the functionals used do not include relativistic effects in a proper maner, and also the likely case in which an strong dependence among relativistic and electron correlation effects do appears.

Table 5 Bond lenght (Å) and J-coupling constants (Hz) in H_3X–XH_3 molecules ($X =$ Sn, Pb) with BLYP functional

H_3X–XH_3	d(X–X)	^{1}J(X–X)	^{1}J(X–H)	^{2}J(H–H)	^{3}J(H–H)[a]
H_3Sn–SnH_3	2.855	2052.48	−1442.45	20.89	16.71
SnH_4			−1732.24	19.81	
H_3Pb–PbH_3	3.015	3533.64	1827.14	33.69	11.63
PbH_4			2491.91	38.74	

[a] Vicinal H–H coupling in cis position, in the cis/trans isomerism

4.3 J-coupling constant in H_3X-XH_3 molecules

Table 5 shows results of J-coupling constant for H_3X–XH_3 model compunds ($X =$ Sn, Pb) with the BLYP functional. In Sect. 4.1 we have shown that for such functional the lowest mean deviation is obtained for tin/lead-atom containig molecules. The second column shows the bond lengths d(X–X) taken from Ref. [51] and in the next columns ^{1}J(X–X), ^{1}J(X–H), ^{2}J(H–H) and ^{3}J(H–H) (in cis position, in the cis/trans isomerism) coupling constants are shown.

The bond lengths d(Sn–Sn) and d(Pb–Pb) are close each other being the difference of only 0.16 Å, although the different weight of the bonded atoms.

The ^{1}J(Sn–Sn) coupling value is quite different to the ^{1}J(Pb–Pb). The latter is almost two times larger than the corresponding ^{1}J(Sn–Sn) value, which shows that the J-coupling constant is strongly affected by the relativistic effects when heavy atoms are involved.

On the other hand, the ^{1}J(X–H) couplings are very different when the hydrogen atom is bonded to tin or lead atoms. The ^{1}J(Pb–H) value is around 400 Hz larger (in absolute value) than the corresponding ^{1}J(Sn–H) value. This can be compared with the results obtained for SnH_4 and PbH_4 molecules. Table 5 shows that ^{1}J(Sn–H) is 290 Hz (17 %) smaller, in absolute value, when such coupling is compared among SnH_4 and H_3Sn–SnH_3. In the same manner the ^{1}J(Pb–H) value is also reduced in 664 Hz (27 %) when we compare PbH_4 and H_3Pb–PbH_3. This means that there exist an important effect of the second heavy atom belonging to the same molecule that affect the coupling ^{1}J(X–H) and this is enhanced when the X atom becomes heavier.

A similar analysis can be performed for geminal couplings, ^{2}J(H–H). For the $H_3Pb–PbH_3$ molecule the ^{2}J(H–H) value is 60 % larger than the same coupling in $H_3Sn–SnH_3$ system, showing an important effect of the intermediate heavy-atom on the coupling of light atoms. This can be compared with a similar effect that was found for nuclear magnetic shieldings, named as HAVHA effect [62–64]. This is a very important relativistic effect. In the same table is also observed that this effect is much more important in XH_4 molecules. The geminal ^{2}J(H–H) coupling for PbH_4 is 100 % larger than the corresponding coupling in the SnH_4 molecule.

An important difference is also observed for the vicinal ^{3}J(H–H) coupling of the two system under study. In this case when the tin atom is replaced by the lead atom, the total value decreases around 30 %. This shows the appearance of an important effect of the central atom on the vicinal H–H coupling, meaning the existence of a heavy atom effect when such atom is in the path of the H–H coupling.

5 Concluding remarks

In this work we have studied the indirect J- and K-coupling constant in heavy-atom containing molecules of the families XY_4 and H_3XXH_3 (X = Sn, Pb; Y = H, F, Cl, Br, I). To do this we applied two different formalisms, the polarization propagator approach at random phase level of approximation (PPA-RPA) and the density functional theory (DFT) formalism with four different functionals. We worked within the relativistic and the NR frameworks. In all cases we analyzed the relationship among relativistic and electron correlation effects in the above mentioned molecular systems.

We tested some possible source of error in calculations to obtain reliable results, *e. g.* grid quality, basis set convergence and the prescription used to obtain the small component basis set from the large component basis set of the four-component wave function. We did not include some other minor effects that could improve the final results, like nuclear size of the dipole moments and solvent effect, but they must not modify our main conclusions.

It is better to analyze K-couplings due to its independence with the magnetogyric constants. We found that the absolute values of one-bond K-couplings ^{1}K(Sn–Y), in the family of XY_4 (X = Sn and Pb; Y = H, F, Cl, Br, I) model compounds, obtained by using PPA-RPA within the relativistic framework are always larger than the NR ones. It is nicely seen that within the NR framework: (1) all values of K, calculated with different functionals are close each other for each pair of central and halogen atoms and (2) they are positive for Y = H but become negative and more negative as the halogen increase its weight. There is a similar pattern within the relativistic domain though it changes when Y = Br and I. In these last cases K is negative though become more positive in the sequence PBE0, B3LYP, BP86 and BLYP, meaning more positive as the HF exchange-correlation diminish in the functional. In the special case of PbI_4 system it happens that the one-bond K(Pb–I) is negative for the PBE0 functional but it changes it sign for all others.

Then we can conclude that relativistic effects do modify the size and sign of the electron correlation that shall be included in calculation of K-couplings when the halogen belongs to the fourth or the fifth row of the Periodic Table. In such cases it appears that electron correlation contribution (the difference DFT-RPA) is positive, being it negative for all other cases. We mean, the electron correlation effects are negative within the NR framework for all functionals and also within the relativistic framework though till chlorine, and more important (in absolute value) in this regime. On the other hand, relativistic effects are negative for all one-bond Sn/Pb–Y (Y = F, Cl, Br, I) K-couplings at RPA level of approach. When electron correlation is included applying DFT such a behavior is modified when the halogen is I. In the case of Br such a behavior depends with the functional.

Another finding is related with the way the amount of exchange-correlation included in the functional do affects the final values of the J-couplings. All coupling values calculated with PBE0 and B3LYP functionals are close each other but the PBE0 values are not so close to the experimental ones. On the other hand, the lower mean deviation of theoretical values as compared with the experimental values is found for the BLYP functional, with very close values corresponding to B3LYP and BP86 functionals.

All these findings suggest that relativity highly affect the electron correlation for K-coupling constants in the heaviest systems like SnI_4, $PbBr_4$ and PbI_4; and also that for such systems the functionals applied in this study do not include relativistic effects in a proper maner.

Lastly, we found the existence of an important effect due to the heavy atom in H_3XXH_3 (X = Sn, Pb) molecular systems on the geminal ^{2}J(H–H) and vicinal ^{3}J(H–H) coupling constant that can reach 100 % when the tin atom is replaced by the lead atom. This effect may be similar to that of HAVHA effect lately well described for the nuclear magnetic shieldings.

Acknowledgments We gratefully acknowledge support from the Argentinian Agency for promotion of Science and Technology, FONCYT (grant PICT 2012-1214).

References

1. Pyykko P (1988) Chem Rev 88:563
2. Autschbach J, Ziegler T (2002) Encycl NMR 9:306
3. Dyall KG, Fægri K (2009) Introduction torelativistic quantum chemistry. Oxford University Press, New York

4. Reiher M, Wolf A (2009) Relativistic quantum chemistry. Wiley-VCH, Weinheim
5. Liu W (2010) Mol Phys 108:1679
6. Aucar GA, Romero RH, Maldonado AF (2010) Int Rev Phys Chem 29:1
7. Lobayan RM, Aucar GA (1998) J Mol Struct (Theochem) 452:13
8. Enevoldsen T, Visscher L, Saue T, Jensen HJ Aa (2000) J Oddershede J Chem Phys 112(8):3493
9. Bagno A, Casella G, Saielli G (2006) J Chem Theory Comput 2:37
10. Moncho S, Autschbach J (2010) J Chem Theory Comput 6:223
11. Zheng S, Autschbach J (2011) J Autschbach Chem Eur J 17:161
12. Autschbach J (2014) Encyclopedia of analytical chemistry. Wiley, Hoboken
13. Visscher L, Enevoldsen T, Saue T, Jensen HJ Aa (1999) J Oddershede J Comput Chem 20:1262
14. Aucar GA, Oddershede J (1993) J Oddershede Int J Quantum Chem 47:425
15. Aucar GA, Saue T, Visscher L, Jensen H J Aa (1999) J Aa Jensen J Chem Phys 110:6208
16. Komorovsky S, Repisky M, Malkina OL, Malkin Ondík VG, Kaupp M, Malkin Ondík I (2008) J Chem Phys 128:104104
17. Maeda H, Ootani Y, Fukui H (2008) J Chem Phys 128:129903
18. Seino J, Hada M (2010) J Chem Phys 132:174105
19. de Dios AC, Jameson CJ (2012) J Jameson Annu Rep NMR Spectrosc 77:1
20. Xiao Y, Sun Q, Liu W (2012) Theo Chem Acc 131:1080
21. Melo JI, Ruiz de Azúa MC, Giribet CG, Aucar GA, Romero RH (2003) J Chem Phys 118:471
22. Vaara J (2007) Phys Chem Chem Phys 9:5399
23. Repisky M, Komorovsky S, Malkina OL, Malkin VG (2009) Chem Phys 356:236
24. Chang C, Pelissier M, Durand M (1986) Phys Scr 34:394
25. van Lenthe E, Baerends EJ, Snijders JG (1993) J Chem Phys 99:4597
26. van Lenthe E, Baerends EJ, Snijders JG (1994) J Chem Phys 101:9783
27. Becke AD (1988) Phys Rev A 38(6):3098
28. Perdew JP (1986) Phys Rev B 33(12):8822
29. Amsterdam Density Functional (ADF) (2006) ADF2006, SCM. Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. http://www.scm.com
30. Autschbach J, Ziegler T (2001) J Am Chem Soc 123:3341
31. Sutter K, Truflandier LA, Autschbach J (2011) Chem Phys Chem 12:1448
32. Demissie TB, Kostenko N, Komorovsky S, Repisky M, Isaksson J, Bayer A, Ruud K (2015) J Phys Org Chem 28:723
33. Aucar GA (2014) Phys Chem Chem Phys 16:4420
34. Romero RH, Aucar GA (2002) Phys Rev A 65:53411
35. Romero RH, Aucar GA (2002) Int J Mol Sci 3:914
36. Visscher L, Jensen H. J. Aa, Bast R, Saue T (2013) DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13, http://www.diracprogram.org
37. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
38. Becke AD (1993) J Chem Phys 98:5648
39. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Phys Rev B 46:6671
40. Mayer M, Häberlen OD, Rösch N (1996) Phys Rev A 54:4775
41. Varga S, Engel E, Sepp W-D, Fricke B (1999) Phys Rev A 59:4288
42. Varga S, Fricke B, Nakamatsu H, Mukoyama T, Anton J, Geschke D, Heitmann A, Engel E, Bastug T (2000) J Chem Phys 112:3499
43. Arcisauskaite V, Melo JI, Hemmingsen L, Sauer SPA (2011) J Chem Phys 135:044306
44. Roukala J, Maldonado AF, Vaara J, Aucar GA, Lantto P (2011) Phys Chem Chem Phys 13:21016
45. Maldonado AF, Aucar GA (2014) J Phys Chem A 118:7863
46. Bühl M, Kaupp M, Malkina OL, Malkin VG (1999) J Comput Chem 20:91
47. Sanders LK, Oldfield E (2001) J Phys Chem A 105:8098
48. Auer AA, Gauss J, Stanton JF (2003) J Chem Phys 118:10407
49. Tossell JA (2004) Phys Chem Miner 31:41
50. Kagaku B (1984) Handbook of chemistry, 3rd edn. Maruzen Company, Tokyo
51. Schleyer P v R, Kaupp M, Hampel F, Bremer M, Mislowt K (1992) J Am Chem Soc 114:6791
52. Dyall KG (2006) Theor Chem Acc 115:441
53. Dunning TH Jr (1989) J Chem Phys 90:1007
54. Woon DE, Dunning TH Jr (1993) J Chem Phys 98:1358
55. Lindh R, Malmqvist PA, Gagliardi L (2001) Theor Chem Acc 106:178
56. Perdew JP, Ruzsinszky A, Tao J, Staroverov VN, Scuseria GE, Csonka GI (2005) J Chem Phys 123(6):062201
57. Schumann C, Dreeskamp HJ (1970) J Dreeskamp Magn Reson 3:204
58. Sharp RR (1972) J Chem Phys 57:5321
59. Sharp RR (1974) J Chem Phys 60:1149
60. Hawk RM, Sharp RR (1974) J Chem Phys 60:1009
61. Autschbach J (2009) Chem Phys Chem 10:2274
62. Maldonado AF, Aucar GA (2009) Phys Chem Chem Phys 11:5615
63. Melo JI, Maldonado A, Aucar GA (2011) Theor Chem Acc 129:483
64. Maldonado AF, Aucar GA, Melo JI (2014) J Mol Model 20:2417