Nuclear charge-distribution effects on the NMR spectroscopy parameters

Alejandro F. Maldonado,[a] Carlos A. Giménez, and Gustavo A. Aucar[b]
Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovation on Technology, IMIT, Corrientes, Argentina

(Received 4 April 2012; accepted 30 May 2012; published online 14 June 2012)

We present here a systematic study about the influence of the size and type of nuclear charge-distribution models (Gaussian and point-like) on the NMR spectroscopic parameters, the nuclear magnetic shielding σ and the indirect nuclear spin J-coupling. We found that relativistic effects largely enhance the nuclear charge-distribution effects (NChDE) on those parameters being them quite sensitive to the nuclear model adopted for calculations. Results for two rare gas atoms (Kr, Rn) and few molecular systems like HX, (X = Br, I, At), CH_4, SnH_4, $SnIH_3$, SnI_2H_2, and $PbIH_3$ are presented. J-couplings are more sensitive than shieldings in both, relativistic and non-relativistic (NR) regimes. The highest effect (close to 11% of variation in relativistic calculations with that two different nuclear models) is observed for J(Pb–I) in $PbIH_3$. A similar effect is found for J(Pb–H) in the same molecule, close to 9%. The NChDE for σ(Sn) in $SnI_{4-n}H_n$ with n = 1, 2 is as large as few ppm (between 3 and 8.56 ppm). For J(Sn–H) in this set of molecules, it goes from 37 Hz for SnH_4 to 54 Hz for SnI_2H_2. Furthermore, we found that the vicinal NChDE is very small though not zero. For ^{1}J(Sn–H) in $SnIH_3$, the NChDE of iodine is close to 2 Hz (0.1%). We also studied the NChDE on the ground state electronic energies of atoms and molecules. We found that these effects are only important within the relativistic regime but not within the NR one. They are in good agreement with previous works. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4729253]

I. INTRODUCTION

The NMR spectroscopic parameters are among the most influenced by relativity.[1,2] Relativistic effects can be larger than two times for the shielding of lead, σ(Pb) in PbH_3I molecule[3] and larger than nine times for the indirect J-coupling between hydrogen and iodine, J(HI) in HI molecule.[4]

For heavy-atom containing molecules there are few different effects that may contribute to the total relativistic effects on shieldings: (i) the heavy-atom effect on heavy atoms, HAHA, which is important for nuclear magnetic shieldings of heavy atoms;[3,5–7] they are mainly dependent on core-electrons,[6] (ii) the heavy-atom effect on light atoms, HALA, is mainly of spin-orbit, SO, type,[8,9] and (iii) the heavy-atom effect on vicinal heavy atoms,[7] which seems to be different of both, HAHA and HALA, though its basic mechanism is still not well understood.[3] Then one is led to consider that the nuclear charge-distribution, NChD, model can have a measurable influence on accurate theoretical calculations of magnetic shieldings of heavy atoms.

For the J-coupling NMR spectroscopic parameter, and within the non-relativistic (NR) domain, the Fermi contact electronic mechanism is usually the main one. It highly depends on the electronic density at the nuclear site. Moreover, within the relativistic domain the wave function is of a four-component type and the so called small components could contribute to large electron densities at the nuclear site. Then one should also consider that it can depend on the model applied to describe the NChD. The nuclear size effects, NSE, on both NMR spectroscopic parameters do consist of two different effects: (i) the nuclear charge distribution effect, NChDE, and (ii) the magnetic moment distribution effect, MMDE.

All this underlies on the increasing interest for the analysis of NSE on NMR spectroscopic parameters. Few of them were recently published. Calculations of the nuclear magnetic shielding with two different nuclear models were presented in Ref. 10 for He and Ne isoelectronic systems at quasi-relativistic level based on the Douglas-Kroll-Hess (DKH) approach. They also were applied to noble gas atoms.

Concerning J-couplings, Autschbach *et al.* applied the relativistic zeroth-order regular approach (ZORA), combined with both nonhybrid and hybrid density functional to calculate them in heavy metal compounds.[11,12] The atomic nuclei were represented by Gaussian-type charge distributions, because the effect of the nucleus representation has been found significant for heavy metal spin-spin coupling calculations.

One of the first studies on NChDE was carried out by Visscher and Dyall.[13] They calculated the ground state electronic energy of atoms with different nuclear models. They found significant differences only when nuclear models changes from point-like to finite size; the values for different finite-size nuclear models are close to each other.

The NSE was also studied in relation with other topics. Dirk Andrae published a review on the effects of different nuclear charge distribution models in electronic structure calculations of atoms and molecules.[14] He reviewed the use of finite nucleus models in standard quantum chemical electronic structure programs and gave a proposal to detect differences between physical properties obtained with various finite

[a]E-mail: aleoml@yahoo.com.ar.
[b]E-mail: gaa@unne.edu.ar.

nucleus models, specially on the total energy shifts and also on energy differences in hydrogen-like atoms. Dzuba *et al.* studied the effects of the nuclear model on the fine and hyperfine structure in different atoms,[15–17] and Andrae *et al.* also studied the effect of different NChD on relative energies of atomic terms.[14]

Gauss-type basis set were developed for calculation of relativistic electron densities at the position of finite-sized nuclei and also the dependence of the contact density with it.[18,19] This contact density can be used in the Mössbauer spectroscopy. The isomer shift on nuclear γ-resonance transitions is a parameter which depends on the charge (NChD) of the resonating atom. It arises in the Coulomb interaction between nuclear and electronic charge distributions. In the last few years, some studies had emphasized the importance of the inclusion of relativity and electron correlation on the Mössbauer spectroscopy, and within it, the NChDE on the isomer shift.[20–22]

The effect of a finite-size nuclear model for both nuclear charge and magnetic moment distributions on the calculated hyperfine coupling constants (HFCC) was recently studied by Malkin *et al.*[23] They used a relativistic four-component method based on density functional theory (DFT). It is an extension of previous works based on the second order scalar Douglas-Kroll-Hess (DKH-2) DFT level, which showed remarkable effect for HFCC of ^{199}Hg.[24] In the last article, they showed that for some diatomic molecules containing Hg and Cd, the main NSE on HFCC arise from the nuclear charge distribution (see Table V of Ref. 23).

The NSE on nuclear magnetic shielding were also included in recent calculations by Hamaya *et al.* on halogen halides.[25] They proposed a scheme with a finite-size nuclear model though applied only to the calculation of shieldings in HX molecular systems. Kita and Tachikawa have also analysed the nuclear quantum effect on molecular magnetic properties such as nuclear magnetic shielding constant and the molecular magnetic susceptibility in some small molecules.[26] They have found that the NSE may be important in those systems when the nuclei are heavy. In the same vein, Arcisauskaite *et al.* published last year an article with a brief consideration of the NSE on shielding constants in HgL_2 (L = Cl, Br, I, CH3) model compounds.[27] They used a finite Gaussian-type nuclear model for the Coulomb potential of the nuclei and found that the effect is larger in four-component calculations as compared with ZORA; this effect increases with the atomic number of the coordinating atom.

At the moment, there is no any *full* relativistic and *ab initio* wave function-based study of the complete NSE (NChDE + MMDE) on NMR spectroscopic parameters. Based on the recent results of HFCC, we assume that the NChD shall be the main contributor to the total NSE on magnetic shieldings and J-couplings.

In this article, we want to answer the following questions: (i) Are the electronic energies sensitive to the nuclear model used for describing the charge-distribution of nuclei in heavy-atom containing molecules? (ii) Do the type and size of nuclear charge-distribution models have any influence on the molecular magnetic properties values, like the NMR spectroscopic parameters, which can be measurable?

We shall assume that both the inter-electron and electron-nucleus interactions are instantaneous electrostatic interactions in the Dirac equation, and we will consider the interaction of an electron with a point-nucleus at rest as monopolar-monopolar. Then this last interaction can be described by a Coulombic operator

$$V = -\frac{Ze^2}{r}. \tag{1}$$

This approximation is good enough for light atoms but becomes non-adequate for heavy atoms. In such a case, one should modify the nuclear model. If one adopts a finite nuclear model, the singularity in the nuclear site is avoided. The asymptotic behavior for $r \to \infty$ is the same in both cases.

In Sec. II, we shall give a brief description of the nuclear charge-distribution model used in our work and the theory of relativistic polarization propagators. It is necessary to give in some detail how a Gaussian-type nuclear model can be expressed and what parameters we shall consider to modify the size of such nuclear model. Basis sets and codes used are described in Sec. III. The analysis of the NChDE on ground state energies and the two NMR spectroscopic parameters, J-couplings and shieldings, are given in Sec. IV. We will also show that one can throw away the small-small integrals without the loss of accuracy in the calculations. Finally, the main conclusions of this work are exposed in Sec. V.

II. THEORY

A. Nuclear charge-distribution models

The time-independent Dirac equation for electrons in a static potential due to nuclei can be written within the Born-Oppenheimer approximation[28] as

$$c(\boldsymbol{\alpha}\cdot\mathbf{p})\Psi + (\beta mc^2 + V)\Psi = E\Psi, \tag{2}$$

where $\boldsymbol{\alpha}$ and β are 4×4 matrices in a given representation and V is the nucleus-electron potential. Then, the relativistic wave function is a four-spinor with components that can be written as two-spinors usually known as *large* and *small*

$$\Psi(\mathbf{r}) = \begin{pmatrix} \Psi^L(\mathbf{r}) \\ \Psi^S(\mathbf{r}) \end{pmatrix}. \tag{3}$$

In terms of the basic spinors, the Dirac wave function is written as

$$\Psi(\mathbf{r}) = \begin{pmatrix} F_i(r)\chi_{\kappa,m_j}(\vartheta,\varphi) \\ iG_i(r)\chi_{-\kappa,m_j}(\vartheta,\varphi) \end{pmatrix}, \tag{4}$$

where $F_i(r)$ and $G_i(r)$ correspond to the radial part of the large (L) and small (S) components, respectively, and $\chi_{\kappa,m_j}(\vartheta,\varphi)$ corresponds to the angular part. The equations are valid for one-electron systems in a central potential but can be extended easily to N-electron systems given that neither the electron-electron interactions nor the inhomogeneities do affect the short range behavior of that functions.

According to the nuclear model used for describing its charge distribution, the radial functions of the wave functions are very different.[29] The Gaussian charge distribution assumes a charge concentration that decreases exponentially with the distance to the center of the nucleus, though never

becomes exactly zero. The Gaussian charge density can be written as

$$\rho_G(r) = \rho_{G,0} e^{-\lambda r^2}, \tag{5}$$

where $\rho_{G,0}$ is fixed through normalization condition

$$\rho_{G,0} = Ze\left(\frac{\lambda}{\pi}\right)^{\frac{3}{2}}; \lambda = \frac{3}{2\langle R^2\rangle}. \tag{6}$$

With this, the potential energy operator is

$$V_{G,0} = -\frac{Ze}{r} erf\left(\sqrt{\lambda} r\right), \tag{7}$$

where $erf(x)$ denotes the error function

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \tag{8}$$

It represents the probability that a measurement error will be between $-x$ and x.

The main parameter used for describing this Gaussian-type charge-distribution is the nuclear radius R which can be obtained from

$$R = 0.836A^{1/3} + 0.57, \tag{9}$$

where A is the mass number and the values are given in Fermi units (1 fm $= 10^{-15}$ m).[30]

Solutions of the Dirac equation are limited when the point-like charge distribution is considered. With this nuclear model, the atoms should have atomic number $Z \leq c$ (in a.u.), which means that the maximum atomic number is $Z_{max} \approx 137$. A nonsingular electron-nucleus potential energy operator allows us to overcome this limit if an atomic nucleus of a finite size is used[29]

$$\gamma = \sqrt{\kappa^2 - \frac{v_{-1}^2}{\hbar^2 c^2}} = \begin{cases} \sqrt{\kappa^2 - \frac{v_{-1}^2}{\hbar^2 c^2}} & \text{point-like,} \\ |\kappa| & \text{finite-size,} \end{cases} \tag{10}$$

where γ is the exponent of the radial functions expansions

$$F_i(r) = r^{\gamma-1} \sum_{i=0}^{\infty} a_i r^i e^{-\rho r}, \tag{11}$$

$$G_i(r) = r^{\gamma-1} \sum_{i=0}^{\infty} b_i r^i e^{-\rho r}. \tag{12}$$

$\kappa = \pm(j + \frac{1}{2})$ and v_{-1} is the first term of the general expansion of the potential energy operator given by

$$V_{nuc} = \sum_{n=-1}^{\infty} v_n r^n. \tag{13}$$

For point-like charges $v_{-1} = -Ze^2$, and 0 for finite-size nuclei. We are thus aware that there is an important qualitative difference depending on whether a singular Coulomb potential or a finite attractive potential is employed in the description of a relativistic Dirac atom.

For the calculation of NMR spectroscopic parameters, different nuclear models can be used. The two most common are the point-like and the Gaussian models. One may also consider some other models which were used until few years ago, as the homogeneous charge-distribution and the Fermi's distribution models. They do not introduce significant differences on the electronic energies when compared with the Gaussian charge-distribution model.[13]

The point-like NChD model presents many problems for wave function calculations in regions close to the nuclear site due the existence of a singularity in the origin. Very large basis sets are necessary in order to represent the short-range behavior of the radial functions. This problem can be overcome applying the *circle approximation* where the region near the nuclei is neglected.[31] The Gaussian model does avoid this problem.

We will consider the Gaussian model as expressed by

$$\rho(r) = Ze\left(\frac{m\lambda}{\pi}\right)^{3/2} e^{-m\lambda r^2}, \tag{14}$$

where Z is the atomic number, r is the distance from the center of the nuclei, and λ is a parameter depending on the nuclear radius

$$\lambda = 1.50(0.5217721 \times 10^5/\bar{R}_N)^2 \text{bohr}^{-2},$$

$$\bar{R}_N = \langle r^2\rangle^{1/2} \approx (0.836A^{1/3} + 0.57) fm.$$

This is the definition of R implemented in the DIRAC code and that is the reason why we used it.

When $m \to \infty$, one obtains the point-like model. Therefore, the effects of the nuclear size on the NMR spectroscopic parameters can straightforwardly be obtained.

B. Relativistic polarization propagator

Any static second-order molecular property, i.e., properties which arise from the second-order correction to the energy depending on two external static fields, can be calculated by using polarization propagators. The equation which relates the correction to the energy with propagators is as follows:[1]

$$E^2_{PQ} = 1/2 Re\langle\langle H^P; H^Q\rangle\rangle_{E=0}, \tag{15}$$

where H^P and H^Q are interaction Hamiltonians which describe the external perturbations to the system whose response (through molecular properties) one is interested to calculate and analyse.

The interaction of an N-electron system with an external magnetic field is accounted for by the minimal coupling prescription, $\mathbf{p} \to \mathbf{p} - \frac{e}{c}\mathbf{A}$, leading to the introduction of the perturbative Hamiltonian

$$H_1 = ec\boldsymbol{\alpha} \cdot \mathbf{A}, \tag{16}$$

where $\mathbf{A} = \mathbf{A}_M + \mathbf{A}_\mathbf{B}$ is the sum of the nuclear and the external vector potentials

$$\mathbf{A}_M = \frac{1}{c^2} \frac{\boldsymbol{\mu}_M \times \mathbf{r}_M}{r_M^3} \tag{17}$$

and

$$\mathbf{A}_B = \frac{1}{2}\mathbf{B} \times \mathbf{r}_G = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{R}_\mathbf{G}). \tag{18}$$

$\mathbf{R}_G$ is the gauge origin, $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M$, and $\mathbf{r}$ and $\mathbf{R}_M$ are the coordinates of the positions of the electron and the nucleus M, respectively. Then Eq. (16) can be written as

$$H_{1,M} = ec\boldsymbol{\alpha} \cdot \left\{ \frac{1}{c^2} \frac{\boldsymbol{\mu}_M \times \mathbf{r}_M}{r_M^3} + \frac{1}{2}\mathbf{B} \times \mathbf{r}_G \right\}$$
$$= -\frac{e}{c}\hbar\gamma_M \mathbf{I}_M \cdot \left(\frac{\boldsymbol{\alpha} \times \mathbf{r}_M}{r_M^3} \right) - ec\mathbf{B} \cdot (\boldsymbol{\alpha} \times \mathbf{r}_G). \quad (19)$$

From Eqs. (15), (16) and (19), the second-order perturbative correction to the energy is written as

$$E^{(2)} = \frac{1}{2} Re \langle\langle H_1; H_1 \rangle\rangle$$
$$= \frac{1}{2}\frac{e\hbar}{c}^2 \sum_{MN} \gamma_M \gamma_N \mathbf{I}_M \cdot Re \left\langle\left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_M}{r_M^3}; \frac{\boldsymbol{\alpha} \times \mathbf{r}_N}{r_N^3} \right\rangle\right\rangle \cdot \mathbf{I}_N$$
$$+ \frac{e^2\hbar}{2} \sum_M \gamma_M \mathbf{I}_M \cdot Re \left\langle\left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_M}{r_M^3}; \boldsymbol{\alpha} \times \mathbf{r}_G \right\rangle\right\rangle \cdot \mathbf{B}. \quad (20)$$

The *fully* relativistic expressions of the NMR spectroscopic parameters are obtained as

$$\mathbf{J}_{MN} = \frac{e^2\hbar^2}{h} \gamma_M \gamma_N \left\langle\left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \frac{\alpha \times \mathbf{r}_N}{r_N^3} \right\rangle\right\rangle \quad (21)$$

and

$$\sigma_M = e^2 \left\langle\left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle\right\rangle. \quad (22)$$

J_{MN} is the indirect J-coupling between nuclei M and N, and σ_M refers to the nuclear magnetic shielding of the nucleus M. Given that retardation effects will not be included due to its comparative (with respect to the leading relativistic effects) small contributions, the expressions above are fully relativistic.[32,33] From these equations, one observes that only one electronic mechanism is involved in each of both NMR spectroscopic parameters. There is also no distinction between diamagnetic and paramagnetic terms.[34]

III. COMPUTATIONAL DETAILS

All calculations of both NMR spectroscopic parameters were performed with DIRAC (Ref. 35) program package in a cluster of 9 nodes of Sun Fire X2200 M2 with two dual-core processors each.

For NR calculations, the speed of light was taken as 10 times c (c = 137.0 359 998 a.u.). For the model compounds, the experimental geometries were taken from Ref. 36 and optimized geometries ($SnIH_3$, SnI_2H_2, $PbIH_3$) were taken from Ref. 3. The gauge origin was fixed at the position of the heavy nucleus. Both NChD models, i.e., point-like and Gaussian, were used in all calculations.

Magnetic properties calculations were carried out at RPA level of approach, which means consistent at first order in electron correlation within the polarization propagator approach. The small components of the basis set were generated applying the unrestricted kinetic balance (UKB) prescription for the four-component shielding calculations.[7] For J-coupling calculations, the restricted kinetic balance (RKB) prescription was applied due to the fact that the contributions of the virtual excitations to the negative energy states are vanishingly small.[34] Sadlej's basis sets were chosen in most cases[37] and several more tight and diffuse Gaussian functions were included to get converged results. The scheme for including more Gaussian functions was the usual one: (i) tight basis functions were added to s, p, d, f, and g (only for Pb atom) blocks with exponents related as $\alpha_{i+1}/\alpha_i = 3$ from the largest exponent of each block; (ii) diffuse basis functions were not necessary to include shielding calculations in the d and f blocks because they do not change the shielding values significantly, but they were necessary in J-coupling calculations following the same scheme mentioned above from the lowest exponent of each block.

Faegri's basis sets[38] were used for Kr, Rn, At, and Pb nucleus with more tight and diffuse basis functions added following the scheme mentioned above. For HX (X = Br, I, At) molecular systems, in J-coupling calculations, Dyall-cVTZ (Ref. 39) basis set was used for the halogen atom X, and for the H atom the aug-cc-pVTZ-Jun3 basis set was used and taken from Ref. 40.

The whole basis sets with all previous considerations and all geometrical parameters used in calculations are given as the supplementary material.[41]

IV. RESULTS AND DISCUSSION

In order to learn on the sensitivity of different molecular properties with the NChD model, we shall first analyse results of calculations of ground state electronic energies of atoms and molecules. Then we will deal with results of calculations of NMR spectroscopic parameters. All of them were carried out at both levels, relativistic and NR.

The parameter λ of the Gaussian nuclear model is dependent of R. Even though there are few different empirical expressions for R, we use only that of Eq. (9) because we are first interested on the leading corrections due to the NChDE.

A. Dependence of atomic and molecular energies from the NChD models

In Table I, we show how much the electronic energies are influenced by the nuclear model and their dependence with the regime within which the calculations were performed.

No significant differences were found in full relativistic calculations with both NChD models on the Kr rare gas atom (~0.025 a.u.). However, for Rn atom which belongs to the sixth row of the periodic table, the energy difference is quite larger (~8.072 a.u.), though it is still very small in percentage (0.034%). For molecular systems, the differences of ground state energies are very small (lower than 1 a.u.) even for systems containing three heavy atoms belonging to the fifth row of the periodic table, like SnI_2H_2, and close to 6 a.u. for $PbIH_3$, which is smaller than the value of 8.073 a.u. which was obtained for Rn. In the case of SnI_nH_{4-n} (n = 1, 2), the differences are observed in the fifth digit or close to 0.0030%. As it also shown in Table I, those differences are much less important for all atomic and molecular systems studied in this work, when calculations are performed within the NR regime.

TABLE I. Ground state electronic energies of atoms and molecules calculated with different nuclear models at relativistic and NR levels. All values are given in a.u.

	Relativistic		NR	
System	Point-like model	Gaussian model	Point-like model	Gaussian model
Kr	−2788.897 964	−2788.874 940	−2752.406 592	−2752.391 091
	−2788.884 840[a]	−2788.860 624[a]		
Rn	−23 613.037 162	−23 604.964 873	−21 880.844 676	−21 879.907 258
	−23 611.19 283[a]	−23 602.10 425[a]		
CH_4	−40.229 045	−40.229 041	−40.213 213	−40.213 210
SnH_4	−6178.461 373	−6178.299 824	−6026.592 481	−6026.520 048
	−6176.291 511[b]	−6176.128 089[b]		
$SnIH_3$	−13 293.792 784	−13 293.399 188	−12 945.792 923	−12 945.625 636
SnI_2H_2	−20 409.127 149	−20 408.501 505	−19 892.059 178	−19 891.788 081
$PbIH_3$	−28 039.956 738	−28 033.935 913	−26 457.022 634	−26 456.264 449

[a]Taken from Ref. 13.
[b]Taken from Ref. 13 for Sn atom.

B. Dependence of NMR parameters with the inclusion of LL, LS, and SS bielectronic integrals

Calculations of molecular properties within the relativistic regime may include the large and also the small component contributions to the bi-electronic integrals, as separated terms. The large-large (LL), large-small (LS), and small-small (SS) bi-electronic integrals can be considered in calculations. Their contributions can also be splitted up in three blocks.

In Table II, the importance of such contributions for relativistic J(H–I) in HI molecular system are shown. Both NChD models (Gaussian and point-like) were used to represent the nuclear charge-distribution.

When LS integrals are only included in the calculation of DHF wave functions, the value of J-coupling increases around 7% (∼18 Hz). When those integrals are also considered in the response block of calculations (LL + LS in both, the wave function and response), that value increases only few Hz: less than 1% (∼2 Hz).

On the other hand, when SS integrals are included in the two blocks, no significant differences were obtained as compared with calculations including both LL and LS integrals. This means that the inclusion of SS integrals is not important in four-component calculations of such magnetic properties. This fact is also independent of the specific nuclear model. It is interesting to observe that the difference of the results obtained when considering one or the other of the NChD models is independent on whether one includes or not the LS or SS integrals (∼5 Hz).

The same kind of analysis for $\sigma(X)$ in HX model compounds (X = Br, I, At) are shown in Table III. In this case, the wave functions were calculated using LL + LS bi-electronic integrals for the reason mentioned above.

When LS bi-electronic integrals are included in the response part of calculations, a variation that range between 1.1% and 1.5% appears for shieldings. Moreover, when SS integrals are included, the variation becomes vanishingly small as it happens for the J-coupling case. Results (in percentages) are exactly the same for both NChD models. Still, for At the inclusion of SS integrals modify $\sigma(At)$ in less than 0.03%.

From previous results, one can state that the inclusion of LS and SS bi-electronic integrals must be performed with care, i.e., bi-electronic integrals should be included with a given criterium on both, the wave function and the specific response property calculations (LL + LS / LL + LS or LL + LS + SS / LL + LS + SS).

Hereafter, all results of our calculations for both magnetic properties include only LL and LS bi-electronic integrals on both calculation steps: the wave function and response.

TABLE II. Relativistic contributions to the J-couplings J(H–I) in HI molecular system, obtained at RPA level.

DHF[a]	RPA[b]	J(H–I)	
		Gaussian	Point-like
LL	LL	−257.38	−262.27
LL + LS	LL	−275.69	−280.49
LL + LS	LL + LS	−277.62	−282.46
LL + LS + SS	LL	−275.57	−280.38
LL + LS + SS	LL + LS	−277.51	−282.34
LL + LS + SS	LL + LS + SS	−277.59	−282.43

[a]Bi-electronic integrals included in the Dirac-Hartree-Fock (DHF) step.
[b]Bi-electronic integrals included in the property calculation step.

TABLE III. Dependence of $\sigma(X)$ in HX (X = Br, I, At) molecular systems with the inclusion of different bi-electronic integrals. Calculations obtained at RPA level.

Atom (X)	Response	$\sigma(X)$	
		Gaussian	Point-like
Br	LL	2973.16	2973.62
	LL + LS	2937.11	2937.54
	LL + LS + SS	2937.10	2937.52
I	LL	5931.08	5939.02
	LL + LS	5836.97	5844.59
	LL + LS + SS	5836.77	5844.37
At	LL	18 266.63	18 906.73
	LL + LS	18 067.74	18 701.52
	LL + LS + SS	18 064.12	18 697.64

TABLE IV. Nuclear magnetic shieldings (ppm) in different atomic and molecular systems calculated at relativistic and NR levels using different nuclear models.

	Relativistic		NR	
System	Point-like	Gaussian	Point-like	Gaussian
Kr	3568.17	3567.16	3241.36	3241.34
Rn	20 095.75	19 523.68	10 681.75	10 681.43
HBr				
Br	2937.54	2937.11	2633.69	2633.67
H	34.95	34.95	29.92	29.92
HI				
I	5844.59	5836.97	4546.48	4546.39
H	45.96	45.96	30.46	30.46
HAt				
At	18 701.52	18 067.74	8809.19	8808.42
H	73.27	73.21	30.12	30.12
CH_4				
C	193.80	195.61	193.87	193.86
H	30.88	31.04	30.91	30.91
SnH_4				
Sn	4131.70	4126.14	3280.16	3280.16
H	27.46	27.48	27.84	27.84
$SnIH_3$				
Sn	4078.97	4075.96	3104.45	3104.44
I	6692.44	6687.95	5501.28	5500.12
H	31.33	31.33	31.38	31.38
SnI_2H_2				
Sn	4168.84	4162.59	3018.54	3018.29
I	6319.40	6312.16	5190.00	5189.75
H	33.81	33.81	33.79	33.79
$PbIH_3$				
Pb	14 063.93	13 262.22	6612.50	6611.36
I	6599.39	6584.89	5568.74	5568.70
H	27.42	27.42	31.11	31.11

C. Nuclear charge-distribution effects on the NMR spectroscopic parameters

In Table IV, the nuclear magnetic shielding for two rare gas atoms and other nuclei in different molecular systems are shown.

For Kr atom, the difference of the shieldings calculated within the relativistic domain for the two different NChD models is only 1 ppm. In the case of Rn atom that difference increases considerably till 572.07 ppm. Such a difference is vanishingly small within the NR domain. This means that the value of σ(Rn) calculated with a finite NChD differs around 3% with respect to its value obtained with a point-like nuclear model.

For the set of molecular systems we are considering, such differences are important only for atoms belonging to the sixth row of the periodic table. This is the case for At in HAt and Pb in $PbIH_3$, where variations of 3.4% and 5.7% are obtained, respectively, within the relativistic regime. The last two columns correspond to the NR values and show that there are no significant differences between the values calculated with different NChD models even for the heavier atoms like Pb, At, and Rn.

TABLE V. J-coupling results, within the relativistic and NR domain. All values are given in Hz.

	Relativistic		NR	
System	Point-like	Gaussian	Point-like	Gaussian
HBr				
H–Br	− 52.24	− 51.75	12.70	12.83
HI				
H–I	282.52	− 277.62	− 32.87	− 32.36
CH_4				
C–H	160.22	160.21	159.36	159.35
H–H	− 27.27	− 27.27	− 27.25	− 27.25
SnH_4				
Sn–H	− 2696.49	− 2659.81	− 1946.65	− 1933.88
H–H	10.55	10.53	2.09	2.09
$SnIH_3$				
Sn–H	− 2966.54	− 2926.30	− 2130.70	− 2116.72
Sn–I	2134.16	2066.21	963.68	951.16
H–I	28.58	28.18	28.23	28.03
H–H	25.69	25.67	13.24	13.23
SnI_2H_2				
Sn–H	− 3998.34	− 3944.34	− 2854.53	− 2835.81
Sn–I	2219.42	2151.20	1138.71	1124.74
H–I	32.49	32.07	33.79	33.54
H–H	78.15	78.12	50.47	50.47
$PbIH_3$				
Pb–H	5765.16	5246.88	2088.56	2058.96
Pb–I	− 3213.83	− 2864.25	− 822.47	− 805.40
H–I	24.75	24.56	26.54	26.35
H–H	91.68	89.57	17.20	17.18

On the other hand, results of J-coupling calculations for all molecular systems considered in this work are shown in Table V. One can observe that its dependence with the NChD model is more important than that for shieldings, even within the NR regimen (though less pronounced).

In the bottom lines of Table V, we show the values of J-couplings between atoms belonging to the $PbIH_3$ model compound. The NChDE at relativistic level are more pronounced when the Sn atom is replaced by the Pb atom. The ^{1}J(Pb–H) coupling decreases ∼518 Hz (9%) from the point-like to Gaussian model, while ^{1}J(Pb–I) coupling enhances ∼350 Hz (11%). It represents a larger percentage of variation as compared with ^{1}J(Sn–I) in $SnIH_3$ (3%).

In Fig. 1, we show the percentile dependence of J-couplings with both, the nuclear models at relativistic and NR levels, and the weight of the coupled nuclei. In all cases, the percentage of variation is larger when relativity is included. This is clear when J(Sn–H) or J(Sn–I) are compared with its corresponding J(Pb–H) and J(Pb–I) couplings and is also observed when comparing J(Sn–H) with J(Sn–I) or when one or two hydrogen atoms are replaced by iodine in $SnH_{4-n}I_n$, though much less pronounced.

We can also observe that variations of both couplings ^{1}J(X–H) and ^{1}J(X–I) when X = Sn → X = Pb, are almost the same when considered within the relativistic or NR levels. All these mean that (i) relativity enhances the NChDE, or in other words the NChDE is larger when each or both of the

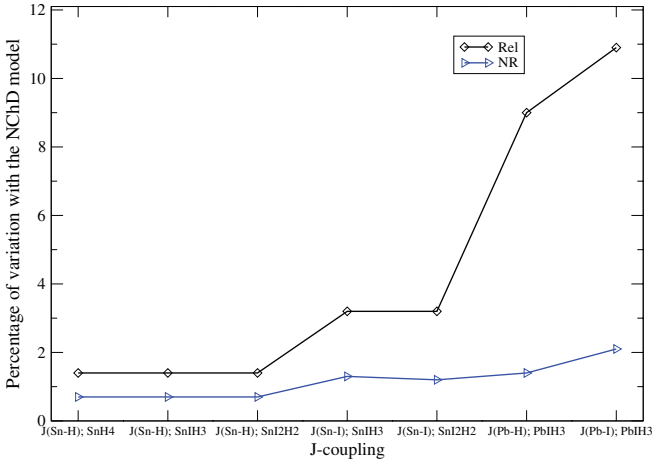

FIG. 1. Percentile variation of J-couplings in SnH_4, $SnIH_3$, SnI_2H_2, PbH_4, and $PbIH_3$ model compounds within both, the relativistic and NR domain.

coupled atoms are heavier, and (ii) the NChDE is mainly a local effect.

D. Dependence of J-couplings of hydrogen halides with the Gaussian exponents of the NChD model

As we have shown above, J-couplings are quite sensitive to the NChD model within the relativistic regime. For this reason, it would be a useful tool for studying such effects in more detail. We had done it starting with its value for a Gaussian model and making the Gaussian exponent goes to infinity to reach the limit of the point-like model. We used the expression

$$\rho(r) = Z\left(\frac{m\lambda}{\pi}\right)^{3/2} e^{-m\lambda r^2}, \tag{23}$$

where m is a factor that modifies the Gaussian exponent. As this factor is increased, the Gaussian NChD model goes to the point-like NChD model.

In Fig. 2, we show the relativistic values of J(I–H; IH) as a function of the factor m. The variation of J when m goes from 1 to 10 is $\Delta J_{HI}/J_{HI}^{m=1} = (J_{HI}^{m=1} - J_{HI}^{m=10})/J_{HI}^{m=1} \approx 1.54\%$ with $\Delta J_{HI} = 4.29$ Hz. When m goes from 1 to 100, the variation of J is $\Delta J_{HI}/J_{HI}^{m=1} = (J_{HI}^{m=1} - J_{HI}^{m=100})/J_{HI}^{m=1} \approx 1.74\%$ and $\Delta J_{HI} = 4.84$ Hz. This means that the most significant variation of J appears when the Gaussian exponent increases one order of magnitude. After that, there are no significant differences of the values of J with Gaussian model with respect to the point-like model.

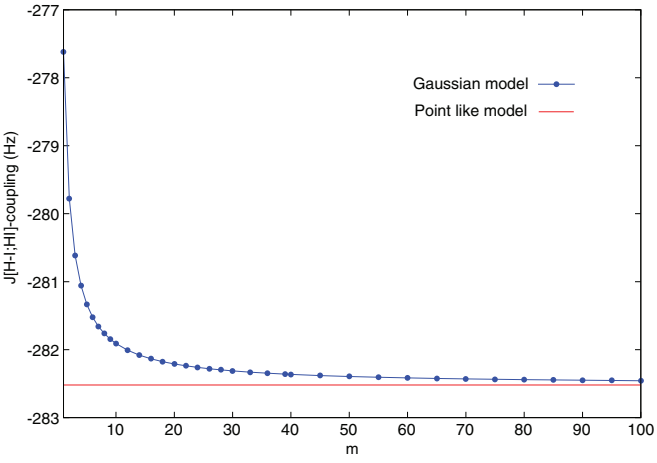

FIG. 2. J(H–I) values in the HI model compound with different nuclear Gaussian exponents for the iodine atom.

TABLE VI. J-couplings within relativistic and NR domains for HX (X = Br, I) systems using different nuclear Gaussian exponents.

	Relativistic			NR		
Molecule	1 λ	100 λ	Point-like	1 λ	100 λ	Point-like
HBr	− 51.75	− 52.24	− 52.24	12.83	12.70	12.70
HI	− 277.62	− 282.46	− 282.52	− 32.36	− 32.86	− 32.87

In Fig. 2, it is also observed that when the factor m goes to infinity the value of the J-coupling goes to the results of a point-like nuclear model as it should. Even though this could be predicted in advance without doing any calculation, this method will help us to learn about how large the effect of the NChD model of each nuclei on the others is when analysing J-couplings.

A similar pattern is obtained within the NR level. Then, that behavior is independent of the small components of the Dirac wave functions. This is a remarkable result.

In Table VI, the values of J-couplings for the HX (X = Br, I) molecules within relativistic and NR domain are shown, for both nuclear models and also in the limit of the point-like model ($m = 100$), only for the X atom.

For HBr, the variation of J is $\Delta\ J_{HBr}/J_{HBr}^{m=1} = (J_{HBr}^{m=1} - J_{HBr}^{m=100})/J_{HBr}^{m=1} \approx 0.95\%$ and $\Delta\ J_{HBr} = 0.49$ Hz. These values are smaller than those corresponding to the HI molecular system and it shows that the NChDE are more important when the atoms are heavier as shown also in Sec. IV C.

We obtained the same pattern within the NR regime as shown in Fig. 2. Then the m dependence of J(HI) is not affected by the inclusion of the small components of the wave functions.

E. NChDE on both NMR spectroscopic parameters due to the environment

If we consider the NChDE on the shielding of iodine, σ(I), we found that its values increase from lighter to heavier systems. From the results shown in Table IV, we obtain that $\Delta\sigma(I) = 4.49$ ppm (0.067%) for $SnIH_3$, 7.24 ppm (0.22%) for SnI_2H_2, and 14.5 ppm (0.22%) for $PbIH_3$. These results are in line with that previously obtained by Arcisauskaite *et al.*[27] for HgX_2 (X = Cl, Br, and I) systems.

As shown in Table V, the J-couplings ^{1}J(Sn–H) in SnH_4, $SnIH_3$, and SnI_2H_2 model compounds are not much dependent on the nuclear model within the relativistic domain (36.68 Hz, 40.24 Hz, and 54.00 Hz of variation, respectively). Such variations represent almost the same percentage (1.36%), which means that such particular coupling, ^{1}J(Sn–H), has a small but sizeable dependence with the environment. Quite a similar behavior is observed within the NR regime where the percentage is 0.66%.

TABLE VII. J(Sn–I), J(Sn–H), and J(H–I) couplings in $SnIH_3$ system within the relativistic and NR domain using different nuclear Gaussian exponents.

	Relativistic					NR				
	$1\lambda_I$		$100\lambda_I$		Point-like	$1\lambda_I$		$100\lambda_I$		Point-like
Coupling	$1\lambda_{Sn}$	$100\lambda_{Sn}$	$1\lambda_{Sn}$	$100\lambda_{Sn}$		$1\lambda_{Sn}$	$100\lambda_{Sn}$	$1\lambda_{Sn}$	$100\lambda_{Sn}$	
J(Sn–I)	2066.21	2099.48	2111.95	2144.87	2134.16	951.16	956.97	957.62	963.47	963.68
J(Sn–H)	− 2926.30	− 2971.16	− 2924.45	− 2971.13	− 2966.54	− 2116.72	− 2130.48	− 2116.72	− 2130.47	− 2130.70
J(H–I)	28.18	28.20	28.52	28.52	28.58	28.03	28.03	28.22	28.23	28.23

This is not the case for ^{1}J(Sn–I). For the $SnIH_3$ model compound, it varies ∼68 Hz (3.2%). Such a system has two heavy atoms (belonging to the fifth row of the periodic table). For a three heavy atom containing molecule, like SnI_2H_2, the variation of the J-coupling ^{1}J(Sn–I) is almost exactly the same (68.22 Hz). Then the NChDE is a local one in this case and it may not depend on vicinal (heavy) atoms.

Another feature we wanted to analyse in more detail was the influence of the NChD model of vicinal atoms on J-couplings. In Table VII, we show results of J-coupling calculations in the $SnIH_3$ molecular system as a function of the m factor for the nuclear exponents of two nuclei, iodine and tin.

In columns 2 and 3, results of J(Sn–I), J(Sn–H), and J(H–I) calculations are shown, with $m = 1$ and $m = 100$ for Sn atom and $m = 1$ for I atom. In columns 4 and 5, the corresponding values with $m = 100$ for the iodine atom are also shown. Point-like values are given in column 6. At the bottom, we show results of calculations within the NR domain with the same values of m.

If we want to analyse the vicinal atom effect on the J-coupling value of a couple of atoms, we have to see the variations of the value when the third atom changes its nuclear model from Gaussian to point-like. The vicinal atom effect on J(Sn–H) can be calculated as

$$\left[\frac{\Delta J(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1}}{J^{m_{\mathrm{I}}=1}(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1}}\right]_R$$

$$= \left[\frac{J^{m_{\mathrm{I}}=100}(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1} - J^{m_{\mathrm{I}}=1}(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1}}{J^{m_{\mathrm{I}}=1}(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1}}\right]_R, \quad (24)$$

where R means the relativistic regime.

For $m_{\mathrm{Sn}} = 1$, we obtain $[\Delta\mathrm{J(Sn–H)}/\mathrm{J}^{m_{\mathrm{I}}=1}(\mathrm{Sn}-\mathrm{H})_{m_{\mathrm{Sn}}=1}]_R$ = 1.85 Hz/−2926.30 Hz (∼−0.1%) and for $m_{\mathrm{Sn}} = 100$, the variation is vanishingly small. So the NChDE of iodine on ^{1}J(Sn–H) is quite small though close to 2 Hz. At NR level such effect is not observed.

On the other hand, the effect of the NChD model of tin atom on the J(H–I) value at relativistic level is ($m_{\mathrm{I}} = 1$): $[\Delta\mathrm{J(H–I)}/\mathrm{J}^{m_{\mathrm{Sn}}=1}(\mathrm{H}-\mathrm{I})_{m_{\mathrm{I}}=1}]_R$ = 0.02 Hz/28.18 Hz (∼0.1%) and for $m_{\mathrm{I}} = 100$ there is no variation. At NR level there is no variation on the J(H–I).

As we have shown above, at relativistic level, the vicinal atom effect on the J-coupling values is more important than the NR one, although the effect is very small.

V. CONCLUSIONS

We have studied the influence of two nuclear charge-distribution models (point-like and Gaussian) and the size of the Gaussian one, on both NMR spectroscopic parameters, J-couplings and shieldings. Few rare gas atoms and molecules containing Sn and Pb atoms were chosen as models.

In line with what was previously published for atoms by other authors, we found that ground state energies of atoms and molecules are not much influenced by the NChD model, though this effect is higher within the relativistic regime and so, higher for the heavier systems. In the NR case, there are no significant differences on such ground state energies.

Relativistic calculations show that, for atomic systems like the rare gas Rn atom, the variation of the nuclear magnetic shieldings when considering both NChD models are close to 3%. In the case of molecular systems, those variations amount 3.4% for At in HAt and 5.7% for Pb atom in $PbIH_3$. The differences are vanishingly small for lighter atoms.

On the other hand, J-couplings are more sensitive than σ with the NChD model. It varies around 3.2% for molecular systems containing two or three heavy atoms which belong to the fifth row of the periodic table. For heavier systems like $PbIH_3$ (one atom belonging to the sixth row of the periodic table) such variation reaches 11% for J(Pb–I).

In addition to that it has been shown here that the NChDE of vicinal heavy atoms on J-couplings are quite small but not zero: the NChDE of iodine on ^{1}J(Sn–H) $\simeq$ 2 Hz for $SnIH_3$. It will be interesting to learn more on this effect for heavier systems and progress on this matter is undertaken in our lab.

Within the NR regime the pattern of J-coupling dependence with the NChD model is almost the same as for the relativistic one, though the percentage of variation is much smaller. This means that relativity enhances the NChDE of the NMR J-couplings. For both J(Pb–H) and J(Pb–I), we found a factor of enhancement close to 6. In the case of shieldings, we did not find any variation within the NR regime but within the relativistic regime it grows till 5.7% for σ(Pb) in $PbIH_3$.

Another (though expected) finding was that the inclusion of the LL + LS two-electron integrals are important for the calculation of NMR spectroscopic parameters but not the two-electron integrals of SS-type.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the Argentinian National Research Council for Science and Technology (CONICET, PIP 11220090100654/2010).

[1]G. A. Aucar, R. H. Romero, and A. F. Maldonado, Int. Rev. Phys. Chem. **29**, 1 (2010).
[2]P. Pyykkö, Chem. Rev. **112**, 371 (2012).
[3]J. I. Melo, A. Maldonado, and G. A. Aucar, Theor. Chem. Acc. **129**, 483 (2011).
[4]A. Maldonado, C. A. Giménez, and G. A. Aucar, Chem. Phys. **395**, 75 (2012).
[5]U. Edlund, T. Lejon, P. Pyykkö, T. K. Venkatachalam, and E. Buncel, J. Am. Chem. Soc. **109**, 5982 (1987).
[6]P. Lantto, R. H. Romero, S. S. Gómez, G. A. Aucar, and J. Vaara, J. Chem. Phys. **125**, 184113 (2006).
[7]A. F. Maldonado and G. A. Aucar, Phys. Chem. Chem. Phys. **11**, 5615 (2009).
[8]P. Pyykkö, A. Görling, and N. Rösch, Mol. Phys. **61**, 195 (1987).
[9]M. Kaupp, O. L. Malkina, V. G. Malkin, and P. Pyykkö, Chem.-Eur. J. **4**, 118 (1998).
[10]R. Fukuda, M. Hada, and H. Nakatsuji, J. Chem. Phys. **118**, 1015 (2003).
[11]J. Autschbach, ChemPhysChem **10**, 2274 (2009).
[12]S. Moncho and J. Autschbach, J. Chem. Theory Comput. **6**, 223 (2010).
[13]L. Visscher and K. G. Dyall, At. Data Nucl. Data Tables **67**, 207 (1997).
[14]D. Andrae, Phys. Rep. **336**, 413 (2000).
[15]V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, J. Phys. B **17**, 1953 (1984).
[16]V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 1399 (1987).
[17]V. A. Dzuba and V. V. Flambaum, Phys. Rev. A **62**, 052101 (2000).
[18]R. Mastalerz, R. Lindh, and M. Reiher, Chem. Phys. Lett. **465**, 157 (2008).
[19]R. Mastalerz, P. Widmark, P. O. Roos, R. Lindh, and M. Reiher, J. Chem. Phys. **133**, 144111 (2010).
[20]M. Filatov, J. Chem. Phys. **127**, 084101 (2007).
[21]M. Filatov, Coord. Chem. Rev. **253**, 594 (2009).
[22]S. Knecht, S. Fux, R. van Meer, L. Visscher, M. Reiher, and T. Saue, Theor. Chem. Acc. **129**, 631 (2011).
[23]E. Malkin, M. Repiský, S. Komorovský, P. Mach, O. L. Malkina, and V. G. Malkin, J. Chem. Phys. **134**, 044111 (2010).
[24]E. Malkin, I. Malkin, O. L. Malkina, V. G. Malkin, and M. Kaupp, Phys. Chem. Chem. Phys. **8**, 4079 (2006).
[25]S. Hamaya, H. Maeda, and H. Fukui, J. Chem. Phys. **129**, 224103 (2008).
[26]Y. Kita and M. Tachikawa, Comput. Theor. Chem. **975**, 9 (2011).
[27]V. Arcisauskaite, J. I. Melo, L. Hemmingsen, and S. P. A. Sauer, J. Chem. Phys. **135**, 044306 (2011).
[28]M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).
[29]M. Reiher and A. Wolf, *Relativistic Quantum Chemistry* (Wiley-VCH, 2009).
[30]W. R. Johnson and G. Soff, At. Data Nucl. Data Tables **33**, 405 (1985).
[31]K. G. Dyall and K. Fægri, *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, 2009).
[32]R. H. Romero and G. A. Aucar, Phys. Rev. A **65**, 53411 (2002).
[33]R. H. Romero and G. A. Aucar, Int. J. Mol. Sci. **3**, 914 (2002).
[34]G. A. Aucar, T. Saue, L. Visscher, and H. J. Aa. Jensen, J. Chem. Phys. **110**, 6208 (1999).
[35]L. Visscher, H. J. Aa. Jensen, T. Saue, S. Dubbilard, R. Bast, K. G. Dyall, U. Ekström, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Sałek, and J. Sikkema, DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC 08, University of Southern Denmark, Odense, 2008, see http://dirac.chem.sdu.dk.
[36]L. E. Sutton, *Tables of Interatomic Distances and Configurations in Molecules and Ions* (The Chemical Society, London, 1995).
[37]A. J. Sadlej, Theor. Chim. Acta **79**, 123 (1991).
[38]K. Fægri, private communication; see also http://folk.uio.no/knutf/bases/one.
[39]K. G. Dyall, Theor. Chem. Acc. **108**, 335 (2002).
[40]J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and R. H. Romero, J. Chem. Phys. **118**, 471 (2003).
[41]See supplementary material at http://dx.doi.org/10.1063/1.4729253 for basis sets used for each nuclei.