


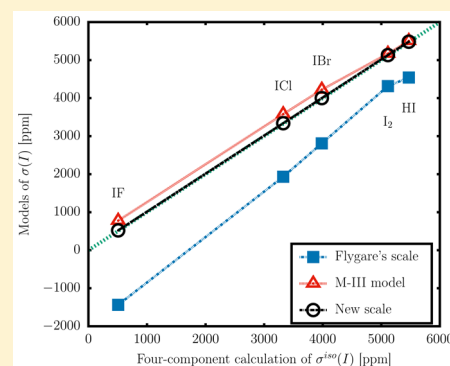
1 Role of Spin-Dependent Terms in the Relationship among Nuclear 2 Spin-Rotation and NMR Magnetic Shielding Tensors

3 I. Agustín Aucar,[†] Sergio S. Gomez,[†] Claudia G. Giribet,[‡] and Gustavo A. Aucar^{*,†} 

4 [†]Instituto de Modelado e Innovación Tecnológica, CONICET, and Departamento de Física, FCENA-UNNE, Avda. Libertad 5460,
 5 W3404AAS Corrientes, Argentina

6 [‡]Instituto de Física de Buenos Aires, CONICET, and Departamento de Física, FCEN-UBA, Ciudad Universitaria, C1428EGA Buenos
 7 Aires, Argentina

8 **ABSTRACT:** The broadly accepted procedure to obtain the experimental
 9 absolute scale of NMR magnetic shieldings, σ , is well-known for nonheavy
 10 atom-containing molecules. It was uncovered more than 40 years ago by the works
 11 of Ramsey and Flygare. They found a quite accurate relationship among σ and the
 12 nuclear spin-rotation constants. Its relativistic extension was very recently
 13 proposed, although it has an intrinsic weakness because a new SO-S two-
 14 component term needs to be considered. We show how to overcome this
 15 problem. We found that $(\nu_Y^S - \nu_Y^{\text{atom},S})$ generalizes the SO-S term, where $\nu_Y^S =$
 16 $\langle\langle [((r - r_Y) \times \alpha) / (|r - r_Y|^3)]; S^{(4)} \rangle\rangle$, $r - r_Y$ is the electron position with respect to
 17 the position of nucleus Y , and $S^{(4)}$ is the four-component total electron spin. When
 18 including this new term, one finds that the best of our relativistic Flygare-like
 19 models fits quite well with the results of the most accurate method available at the
 20 moment. We also show that the difference among the parallel component of
 21 $\sigma(\text{Xe})$ in XeF_2 and $\sigma(\text{Xe})$ of the free atom is almost completely described by that
 22 new term.



23 **U**ntil the past few years, one of the best ways to obtain by
 24 experiments the absolute value of the nuclear magnetic
 25 shielding of a nucleus Y , σ_Y , was to apply the long-standing
 26 Flygare's relationship.¹ This situation changes dramatically
 27 when the relativistic Dirac's theory of electrons is applied to
 28 describe magnetic atomic and molecular properties. That
 29 famous Flygare's relation is not valid any longer. The most
 30 important deviations are found when heavy-atom-containing
 31 molecules are considered, but they are also non-negligible in
 32 molecular systems that contain only light atoms. Wasylishen
 33 and coworkers had proven it experimentally by measuring the
 34 parallel component of the shielding tensors of xenon
 35 difluoride.²

36 Many years were devoted to the search of new strategies that
 37 could help to overcome this problem. The first important step
 38 forward was the finding of the proper relativistic expression of
 39 the nuclear spin-rotation tensor (M), recently published by two
 40 groups.^{3,4} Then, the next step shall be to look for a new
 41 Flygare-type relationship that should be valid within the
 42 relativistic framework. Even though, at first sight, a similar
 43 relation among the relativistic spin-rotation (SR) and shielding
 44 tensors seems difficult to obtain, few models were recently
 45 proposed.⁵⁻⁷ The most accurate of them has a two-component
 46 spin-orbit (SO) term.⁷

47 The application of those models to linear molecules gave
 48 results that are close to the current most exact values (obtained
 49 from four-component methods) but not in all cases (see ref 7).
 50 So, the new SO term seems to be one of few other unknown
 51 terms that must be considered. Where shall we look to get

52 better matching? Are there some more subtle physical reasons
 53 for those differences? How do we go one step further in the
 54 development of more accurate relativistic Flygare-type models?

55 We give some answers to these inquiries. We shall show that
 56 the SO term is the leading order contribution of the complete
 57 spin-dependent (SD) contribution that must be included in
 58 Flygare-type models to obtain more accurate results.

59 Ramsey first, and afterward Flygare, proposed a relationship
 60 among σ_Y and M_Y tensors of a nucleus in a molecule, which
 61 allows to indirectly obtain "experimental" values of absolute
 62 shieldings using experimental SR constants^{1,8-10} together with
 63 highly accurate calculations. This nonrelativistic (NR) relation
 64 links the paramagnetic contribution to σ_Y and the electronic
 65 contribution to M_Y according to

$$\begin{aligned} \sigma_Y^{\text{NR-para}} &= \frac{m_p}{g_Y} M_Y^{\text{NR-elec}} \otimes I \\ &= \frac{m_p}{g_Y} (M_Y^{\text{NR}} - M_Y^{\text{nuc}}) \otimes I \end{aligned} \quad (1)$$

66 Atomic units were used in the last expression and shall be used
 67 throughout this work, where m_p is the proton mass, g_Y is the
 68 nuclear g -value of nucleus Y , and I is the tensor of molecular
 69 moment of inertia with respect to the center of mass (CM) at
 70

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71 the equilibrium geometry. Equation 1 explicitly shows that the
72 M_Y tensor can be expressed as the sum of two terms: one
73 electronic and one nuclear. The $M_Y^{\text{NR-elec}}$ tensor is the linear
74 response that takes account of two external potentials
75 originated in (i) the total electronic orbital angular momentum
76 centered in the molecular CM and (ii) the nuclear magnetic
77 moment of nucleus Y . Besides, eq 1 is valid only when the
78 gauge origin (GO) of the magnetic potential is located at that
79 CM.

80 Another finding of Flygare and coworkers was a relationship
81 between the diamagnetic contribution to σ of a nucleus in a
82 molecule, $\sigma_Y^{\text{NR-dia}}$, when the GO is placed at the nucleus position
83 Y , and the shielding of that nucleus in the free atom, $\sigma_Y^{\text{atom,NR}}$
84 (which has only diamagnetic contributions within the NR
85 domain). They first found that $\sigma_Y^{\text{NR-dia}}$ can be approximated as
86 the sum of $\sigma_Y^{\text{atom,NR}}$ and another tensor that only depends on the
87 nuclear positions at equilibrium (the first term in equation 6 of
88 ref 9, which includes our M_Y^{nuc} as part of it; see ref 3).^{9,10}
89 Applying this relation, they found that the average (isotropic)
90 values are more accurate than the individual tensor elements. In
91 further works, they improved the last relation by using an atom
92 dipole model including two other terms: a dipole one, in
93 general quite small, and a quadrupole term.^{1,11}

94 It is important to highlight here that although Flygare found
95 this relation taking the center of rotation and the GO positions
96 in the SR and shielding tensors (respectively) at the position of
97 nucleus Y ,⁹ it also happens that when the CM is considered as
98 the center of rotation for the SR tensor and also as GO for the
99 magnetic potential in the shielding tensor, Flygare's diamag-
100 netic approach can be expressed as (it can be shown following
101 the arguments of ref 3) $\sigma_Y^{\text{NR-dia}} \cong \sigma_Y^{\text{atom,NR}} + \frac{m_p}{g_Y} M_Y^{\text{nuc}} \otimes I$.

102 Because the Flygare's quadrupole term appears only for
103 individual tensor elements of $\sigma_Y^{\text{NR-dia}}$ (it does not contribute to
104 the isotropic diamagnetic shielding), ignoring this term may
105 introduce significant errors in the approximation of the tensor
106 elements of $\sigma_Y^{\text{NR-dia}}$. So the isotropic diamagnetic shielding can
107 accurately be reproduced as the sum of $\sigma_Y^{\text{atom,NR}}$ and $M_Y^{\text{nuc-iso}}$ (in
108 ppm), whereas only fair estimations will be obtained for the
109 individual tensor elements if the quadrupole term is ignored.¹¹

110 From these considerations, one obtains the well-known
111 Flygare's relationship

$$\begin{aligned} \sigma_Y &= \sigma_Y^{\text{NR-para}} + \sigma_Y^{\text{NR-dia}} \\ &\approx \frac{m_p}{g_Y} M_Y^{\text{NR}} \otimes I + \sigma_Y^{\text{atom,NR}} \end{aligned} \quad (2)$$

113 which is restricted to rigid rotor molecules in their equilibrium
114 geometry. The approximation is generally more accurate for the
115 isotropic than for each individual tensor element.

116 As mentioned above, few recent works have shown that such
117 a relationship is broken within the relativistic regime.^{3-6,12} In
118 our search for generalizing Flygare's NR relationship, we have
119 proposed three increasingly accurate relativistic theoretical
120 models.⁷ Such models were related to a few previous ones, such
121 as those of Malkin and coworkers⁵ and Xiao and coauthors.⁶
122 However, the aim of the present work is to go one important
123 step further.

124 The most accurate of the above-mentioned models is the M-
125 III one, which was defined as

$$\sigma_Y^{\text{M-III}} = \frac{m_p}{g_Y} M_Y \otimes I + \sigma_Y^{\text{atom}} + \frac{1}{2} \sigma_Y^{\text{SO-S}} \quad (3)$$

This model includes terms that are formally the same as those
of the original Flygare's relationship plus the new SO term. The
second term of eq 3 is the free atomic shielding, which includes
both its "paramagnetic-like" (e-e) and "diamagnetic-like" (e-p)
relativistic values.¹³ Again, isotropic values shall be more
accurate than the individual tensor elements due to Flygare's
approach to diamagnetic contributions.

One can expect that the model M-III shall fail when higher
order effects are not vanishingly small. So, a more accurate
model shall be obtained when the SO-S term is replaced by its
four-component counterpart.

In the special case of linear molecules, the first term of the
right-hand side of eq 3 will not have parallel components
(where the main line of the molecular geometry is parallel). In
ref 7, we studied the accuracy of the M-III model. With such an
aim we analyzed the (e-e) part of the perpendicular
components of $\sigma_Y^{\text{M-III}}$ of eq 3. We studied how close $\frac{1}{2} \sigma_{L,Y}^{\text{SO-S}}$
and $\sigma_{L,Y}^{(e-e)} - \frac{m_p I}{g_Y} M_{L,Y}^{(e-e)} - \sigma_Y^{\text{atom}(e-e)}$ are in a series of linear
molecules. The last difference was coined $\Delta \sigma_{L,Y}^{\text{II}}$ because it is
the difference between $\sigma_{L,Y}^{(e-e)}$ and $\sigma_{L,Y}^{\text{II}(e-e)}$ (see ref 7). Such a
difference may be due to relativistic higher order terms, not
included in the SO-S one.

How do we get such terms? Let us start from the definition
of the relativistic electronic contribution to the SR tensor.³ It is
known that

$$\begin{aligned} M_Y^{\text{elec}} &= M_Y^L + M_Y^S \\ &= \frac{g_Y}{2m_p c} \left\langle \left\langle \frac{(\mathbf{r} - \mathbf{r}_Y) \times \boldsymbol{\alpha}}{|\mathbf{r} - \mathbf{r}_Y|^3}; (\mathbf{r} - \mathbf{r}_{\text{CM}}) \times \mathbf{p} \right\rangle \right\rangle \otimes I^{-1} \\ &\quad + \frac{g_Y}{2m_p c} \left\langle \left\langle \frac{(\mathbf{r} - \mathbf{r}_Y) \times \boldsymbol{\alpha}}{|\mathbf{r} - \mathbf{r}_Y|^3}; \mathbf{S}^{(4)} \right\rangle \right\rangle \otimes I^{-1} \\ &= \frac{g_Y}{m_p} \left[\frac{1}{2c} (\boldsymbol{\nu}_Y^L + \boldsymbol{\nu}_Y^S) \right] \otimes I^{-1} \end{aligned} \quad (4)$$

where $\mathbf{r} - \mathbf{r}_Y$ are the electronic position operators and $\boldsymbol{\alpha}$ stands
for the Dirac matrices. The linear responses $\boldsymbol{\nu}_Y^L$ and $\boldsymbol{\nu}_Y^S$ are
associated with M_Y^L and M_Y^S , respectively. The SO-S mechanism
arises from $M_Y^{\text{S}(e-e)}$.⁷

To generalize the SO-S term to a four-component
expression, the same methodology used previously in ref 14
will be applied here. This scheme is related to the Dyall
formalism,¹⁵ where the Dirac-Coulomb-Breit Hamiltonian is
splitted into two Hamiltonians, that is, one that is spin-free
(SF) and another one that is SO-dependent. From this
separation, we are able to define a four-component SO
mechanism for σ_Y

$$\sigma_Y^{\text{SD}} = \sigma_Y - \sigma_Y^{\text{SF}} \quad (5)$$

where σ_Y^{SF} is the shielding tensor obtained when considering the
SF Hamiltonian.

A similar definition can be applied to the linear response $\boldsymbol{\nu}_Y^{\text{S}}$
of the second term of eq 4,

$$\boldsymbol{\nu}_Y^{\text{S-SD}} = \boldsymbol{\nu}_Y^{\text{S}} - \boldsymbol{\nu}_Y^{\text{S-SF}} \quad (6)$$

Replacing $\frac{1}{2} \sigma_Y^{\text{SO-S}}$ with $\frac{1}{2c} \boldsymbol{\nu}_Y^{\text{S-SD}(e-e)}$ in eq 3, we obtain

$$\sigma_Y^{\text{M-IV}} = \frac{m_p}{g_Y} \mathbf{M}_Y \otimes \mathbf{I} + \sigma_Y^{\text{atom}} + \frac{1}{2c} \nu_Y^{\text{S-SD(e-e)}} \quad (7)$$

where only (e-e) rotations are considered in $\nu_Y^{\text{S-SD}}$ because they (and not the (e-p) ones) give rise to the SO-S term as a leading order correction.¹⁶ We should also mention here that for linear molecules the first term has null parallel component.

Now we shall compare the performance of M-III and M-IV models on a set of linear molecules, HX (X = F, Cl, Br, I, At), XF, IX (X = Cl, Br, I), and XeF₂, and see which one is the best. Four-component calculations of both, σ_Y and \mathbf{M}_Y tensor elements were performed at the RPA level of approach of the polarization propagator formalism with Dirac–Coulomb Hartree–Fock wave functions, employing a developmental version of the DIRAC14 program package.¹⁷ Gaussian-type nuclear models were employed in all calculations.

To fulfill Flygare’s prescription for the relation of eq 1, the GO was placed at the molecular CM for the calculation of σ_Y . Furthermore, to perform a four-component calculation of σ_Y^{atom} , an electron was added to the halogen free-atoms. Calculations of open-shell structures are not available in the DIRAC code.

Experimental internuclear distances for molecules in their gaseous phase were considered and taken from refs 18 (all compounds but IF) and 19 (only IF). For HAt, an optimized internuclear distance was used (1.720284558 Å).

All calculations were performed using large uncontracted Gaussian basis sets and the common gauge-origin (CGO) approach. The NR Dunning’s aug-cc-pCVSZ basis set was used for hydrogen, fluorine, and chlorine atoms,²⁰ whereas for Br, I, Xe, and At, the dyall.acv4z²¹ basis set was employed. In all cases the restricted kinetic balance prescription (RKB) was used, although calculations of few selected molecules were also performed using the unrestricted kinetic balance prescription (UKB).¹³ This is because to evaluate the performance of our models, it is enough to consistently use RKB with a huge basis set and also because the differences found applying UKB are such that the accuracy of our models does not vary.

In Figure 1 we show the performance of SO-S and S-SD contributions versus $\Delta\sigma_{\perp,Y}^{\text{II}}$. It gives us an insight into how

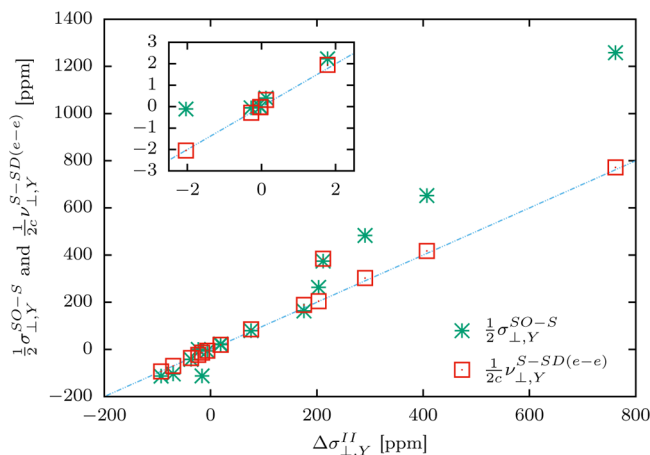


Figure 1. Comparison of the matching of $\frac{1}{2}\sigma_{\perp,Y}^{\text{SO-S}}$ and $\frac{1}{2c}\nu_{\perp,Y}^{\text{S-SD(e-e)}}$ with $\Delta\sigma_{\perp,Y}^{\text{II}}$, where Y represents each nucleus of all the compounds studied in the present work. The agreement between $\Delta\sigma_{\perp,Y}^{\text{II}}$ and $\frac{1}{2c}\nu_{\perp,Y}^{\text{S-SD(e-e)}}$ is by far better than that with $\frac{1}{2}\sigma_{\perp,Y}^{\text{SO-S}}$ for all Y in all compounds, except for At in HAt.

important the S-SD term is. It also shows that the difference between $\Delta\sigma_{\perp,Y}^{\text{II}}$ and $\frac{1}{2}\sigma_{\perp,Y}^{\text{SO-S}}$ arises from higher order terms.

The replacement of $\frac{1}{2}\sigma_{\perp,Y}^{\text{SO-S}}$ by $\frac{1}{2c}\nu_{\perp,Y}^{\text{S-SD(e-e)}}$ greatly improves the behavior of the M-III model. The subtraction between $\frac{1}{2c}\nu_{\perp,Y}^{\text{S-SD(e-e)}}$ and $\Delta\sigma_{\perp,Y}^{\text{II}}$ has nearly the same value for each nucleus Y in different molecules. Such a subtraction is close (in ppm) to 0.1 when Y = F, 0.2 for Cl, 1 for Br, 9 for I, and 172 for At. So, the remaining difference seem to be of atomic nature. We then evaluated the term $\frac{1}{2c}\nu_{\perp,Y}^{\text{atom,S-SD(e-e)}}$ and found the following values (in ppm): 0.0029 for X = F, 0.0299 for X = Cl, 0.9324 for X = Br, 8.2424 for X = I, 1.1477 for X = Xe, and 171.7071 for X = At. They have a remarkable similarity with those given above.

There is an error that comes from the fact that we have calculated $\sigma^{\text{atom(e-e)}}(Y^-)$ instead of $\sigma^{\text{atom(e-e)}}(Y)$ (see Table 1). In all cases, $\sigma^{\text{atom(e-e)}}(Y^-)$ are larger by few ppm than the values of $\sigma_{\perp,Y}^{(e-e)} - \frac{m_p I}{g_Y} \mathbf{M}_{\perp,Y}^{(e-e)} - \frac{1}{2c} \nu_{\perp,Y}^{\text{S-SD(e-e)}}$ and $\sigma_{\parallel,Y}^{(e-e)} - \frac{1}{2c} \nu_{\parallel,Y}^{\text{S-SD(e-e)}}$. The worst results were found for At, where the parallel and perpendicular components of $\sigma_{\text{At}}^{(e-e)} - \frac{m_p}{g_Y} \mathbf{M}_{\text{At}}^{(e-e)} \otimes \mathbf{I} - \frac{1}{2c} \nu_{\text{At}}^{\text{S-SD(e-e)}}$ have values that are close to 10 390 ppm, where $\sigma^{\text{atom(e-e)}}(\text{At}^-) \cong 10\,563$ ppm. Then, we propose a model that includes all of these considerations

$$\sigma_Y^{\text{M-V}} = \frac{m_p}{g_Y} \mathbf{M}_Y \otimes \mathbf{I} + \sigma_Y^{\text{atom}} + \frac{1}{2c} (\nu_Y^{\text{S}} - \nu_Y^{\text{atom,S}}) \quad (8)$$

For linear molecules this equation is written as

$$\begin{aligned} \sigma_{\perp,Y}^{\text{M-V}} &= \frac{m_p I}{g_Y} M_{\perp,Y} + \sigma_Y^{\text{atom}} + \frac{1}{2c} (\nu_{\perp,Y}^{\text{S}} - \nu_{\perp,Y}^{\text{atom,S}}) \\ \sigma_{\parallel,Y}^{\text{M-V}} &= \sigma_Y^{\text{atom}} + \frac{1}{2c} (\nu_{\parallel,Y}^{\text{S}} - \nu_{\parallel,Y}^{\text{atom,S}}) \end{aligned} \quad (9)$$

Our M-V model has a few important advantages: (i) the restrictions of considering only the SD and (e-e) parts of ν_Y^{S} are not needed any more; (ii) from calculations we find that $\nu_Y^{\text{S(e-p)}} \cong \nu_Y^{\text{atom,S(e-p)}}$ and $\nu_Y^{\text{S-SF(e-e)}} \cong \nu_Y^{\text{atom,S-SF(e-e)}}$. Therefore, $\nu_Y^{\text{S}} - \nu_Y^{\text{atom,S}} \cong \nu_Y^{\text{S-SD(e-e)}} - \nu_Y^{\text{atom,S-SD(e-e)}}$ and (iii) the application of the linear response within the elimination of small components (LRESC) model to $\frac{1}{2c}(\nu_Y^{\text{S}} - \nu_Y^{\text{atom,S}})$ gives, as the leading order contribution, $\frac{1}{2}\sigma_Y^{\text{SO-S}}$.

In Table 1 we compare results of the (e-e) contributions to the shieldings of nuclei in ionized free atoms (except for Xe) and the differences between four-component calculations of shieldings of the nucleus in molecules, SR constants, and the S-SD terms. Also, the differences when replacing the S-SD terms by $\nu_Y^{\text{S(e-e)}} - \nu_Y^{\text{atom,S(e-e)}}$ are shown. We see that the values of the tensor elements of $\sigma_Y^{(e-e)} - \frac{m_p}{g_Y} \mathbf{M}_Y^{(e-e)} \otimes \mathbf{I} - \frac{1}{2c} (\nu_Y^{\text{S(e-e)}} - \nu_Y^{\text{atom,S(e-e)}})$ are closer to $\sigma_Y^{\text{atom(e-e)}}$ than the elements of $\sigma_Y^{(e-e)} - \frac{m_p}{g_Y} \mathbf{M}_Y^{(e-e)} \otimes \mathbf{I} - \frac{1}{2c} \nu_Y^{\text{S-SD(e-e)}}$. So, the M-V model is more accurate than the M-IV one.

What is the behavior of the M-V model in the NR limit? We scaled the speed of light several times in all calculations of the (e-e) contributions, and its results are summarized as

Table 1. Comparison of $\sigma_Y^{\text{atom}(e-e)}(Y^-)$ with the Difference among the Calculated (e-e) Parts of Shielding, the SR Constant and the S-SD Term, or the $\nu^S - \nu^{\text{atom},S}$ One^a

Mol	Y	b	c	d	e	$\sigma_Y^{\text{atom}(e-e)}$
HBr	Br	525.6652	526.6818	525.4341	526.4220	526.5790
BrF	Br	525.2953	526.1843	525.8365	526.8936	526.5790
IBr	Br	524.2390	525.2110	525.5713	526.5569	526.5790
HI	I	1906.8889	1915.2733	1907.1891	1915.5107	1915.7296
IF	I	1906.1397	1914.2449	1907.9397	1916.4363	1915.7296
ICl	I	1905.0742	1913.3050	1907.0292	1915.4419	1915.7296
IBr	I	1903.9301	1912.1788	1906.9541	1915.3500	1915.7296
I ₂	I	1903.1371	1911.4018	1906.6010	1914.9608	1915.7296
XeF ₂	Xe	2024.6561	2025.7857	2024.7760	2026.0695	2026.0618 ^f
HAt	At	10390.5182	10562.5504	10390.2688	10562.0430	10563.0186

^aAll values are given in ppm. b $\sigma_{\perp,Y}^{(e-e)} - \frac{m_p I}{g_Y} M_{\perp,Y}^{(e-e)} - \frac{1}{2c} \nu_{\perp,Y}^{\text{S-SD}(e-e)}$. c $\sigma_{\perp,Y}^{(e-e)} - \frac{m_p I}{g_Y} M_{\perp,Y}^{(e-e)} - \frac{1}{2c} (\nu_{\perp,Y}^{\text{S}(e-e)} - \nu_{Y^-}^{\text{atom},\text{S}(e-e)})$. d $\sigma_{\parallel,Y}^{(e-e)} - \frac{1}{2c} \nu_{\parallel,Y}^{\text{S-SD}(e-e)}$. e $\sigma_{\parallel,Y}^{(e-e)} - \frac{1}{2c} (\nu_{\parallel,Y}^{\text{S}(e-e)} - \nu_{Y^-}^{\text{atom},\text{S}(e-e)})$. f $\sigma_{\text{Xe}}^{\text{atom}(e-e)}$ was calculated as such (not ionized) because it has a closed-shell structure.

Table 2. Four-Component Calculations of the Isotropic Parameters, M , σ^{atom} , ν^S , $\nu^{\text{atom},S}$, and σ , at RPA Level of Approach^{a,b}

Mol	Y	$\frac{2}{3} \frac{m_p I}{g_Y} M_{\perp,Y}$	σ_Y^{atom}	$\frac{1}{2c} \nu_Y^{\text{S,iso}}$	$\frac{1}{2c} \nu_{Y^-}^{\text{atom},\text{S}}$	$\sigma_Y^{\text{M-V,iso}}$	σ_Y^{iso}
HF	F	-57.9462	480.3801	2.0197	2.0608	422.3927	415.8361
ClF	F	210.9556	480.3801	1.7950	2.0608	691.0699	683.9108
BrF	F	291.9238	480.3801	-6.9508	2.0608	763.2923	756.7222
IF	F	375.8094	480.3801	-56.3174	2.0608	797.8113	790.7507
		[375.8150]	[482.3759]	[-56.4510]	[1.9266]	[799.8132]	[793.7221]
XeF ₂	F	-31.9061	480.3801	-2.2784	2.0608	444.1348	438.4208
		[-31.9027]	[482.3759]	[-2.4125]	[1.9266]	[446.1340]	[440.4896]
HCl	Cl	-192.3764	1132.2008	13.8434	13.9431	939.7247	934.1685
ClF	Cl	-1598.3155	1132.2008	13.2515	13.9431	-466.8064	-473.7810
ICl	Cl	25.7220	1132.2008	-7.3600	13.9431	1136.6197	1129.3206
HBr	Br	-482.9111	3355.2831	130.3628	133.3157	2869.4190	2865.2450
		[-482.9190]	[3439.9540]	[121.1226]	[124.0756]	[2954.0819]	[2948.7345]
BrF	Br	-3569.1870	3355.2831	94.3739	133.3157	-252.8456	-258.1816
IBr	Br	-388.0969	3355.2831	156.9831	133.3157	2990.8537	2983.1190
HI	I	-902.1302	6406.4582	511.0723	541.2102	5474.1901	5469.7790
		[-902.1781]	[6803.6769]	[495.7096]	[525.8491]	[5871.3594]	[5866.5947]
IF	I	-5630.2973	6406.4582	278.0488	541.2102	512.9994	507.5656
		[-5630.9135]	[6803.6769]	[262.6546]	[525.8491]	[909.5689]	[903.8078]
ICl	I	-2827.5506	6406.4582	294.2667	541.2102	3331.9641	3326.0317
IBr	I	-2184.7155	6406.4582	310.5022	541.2102	3991.0347	3984.5477
I ₂	I	-1236.6301	6406.4582	494.2027	541.2102	5122.8205	5112.9888
XeF ₂	Xe	-3609.8499	6619.4386 ^c	562.4590	570.4629 ^c	3001.5848	2999.2927
		[-3609.9578]	[7020.7966] ^c	[546.6925]	[554.6929] ^c	[3402.8383]	[3400.2130]
HAt	At	-146.9260	18778.8819	2797.5863	3662.3453	17767.1969	17762.6035
		[-147.4289]	[19193.0912]	[2761.4493]	[3626.2449]	[18180.8666]	[18175.7059]

^aRKB prescription was used in all calculations, but between brackets are the UKB calculations. ^bAll values in ppm. ^c $\sigma^{\text{atom}}(\text{Xe})$ and $\nu^{\text{atom},\text{S}}(\text{Xe})$ were calculated as such (not Xe⁻) because it has a closed-shell electronic structure.

(1) For all studied systems, the SD values of σ_Y , σ_Y^{atom} , M_Y^L , M_Y^S (and therefore also ν_Y^L and ν_Y^S), and $\nu_Y^{\text{atom},\text{S}}$ go to zero as c scales to ∞ . This behavior is fine because they arise only within the relativistic domain.

(2) The SF contribution to M_Y^S , ν_Y^S , and $\nu_Y^{\text{atom},\text{S}}$ also goes to zero as $c \rightarrow \infty$.

Some remarks concerning the isotropic contributions of both properties need to be made. As was pointed out in ref 7, the M-II and M-III models match each other when isotropic values of shieldings of nuclei in linear molecules are considered. This occurs because $\sigma_Y^{\text{S}^{\text{O-S,iso}}}$ is zero for linear molecules,²² but $\frac{1}{2c} \nu_Y^{\text{S-SD}(e-e),\text{iso}}$ and $\frac{1}{2c} (\nu_Y^{\text{S}(e-e),\text{iso}} - \nu_Y^{\text{atom},\text{S}(e-e)})$ are not zero.

In Table 2 we show the values of

$$\sigma_Y^{\text{M-V,iso}} = \frac{2}{3} \frac{m_p I}{g_Y} M_{\perp,Y} + \sigma_Y^{\text{atom}} + \frac{1}{2c} (\nu_Y^{\text{S,iso}} - \nu_{Y^-}^{\text{atom},\text{S}}).$$

In addition, a good agreement between $\sigma_{\perp,Y}^{\text{M-V}(e-e)}$ and $\sigma_{\perp,Y}^{(e-e)}$ and also between $\sigma_{\parallel,Y}^{\text{M-V}(e-e)}$ and $\sigma_{\parallel,Y}^{(e-e)}$ is found. The differences are of <1 ppm for the parallel tensor elements of all nuclei in all compounds (<0.8% of difference in all studied cases, except for F in HF where the difference is of 0.1365 ppm against $\sigma_{\parallel,\text{F}}^{(e-e)} = 8.2395$ ppm and Br in BrF, where the difference is of 0.3146 ppm while $\sigma_{\parallel,\text{Br}}^{(e-e)} = 2.7290$ ppm). For the perpendicular elements, the greatest difference in their (e-e) contributions occurs for I₂, and it is ~4.3278 ppm (4.5% of difference with respect to $\sigma_{\perp,\text{I}}^{(e-e)}$, which is 96.0347 ppm); all other perpendicular

273 elements give a percentage difference of <0.75%. Therefore, the
274 main differences between $\sigma_Y^{M-V,iso}$ and σ_Y^{iso} in Table 2 are due to
275 their (e-p) contributions.

276 In the special case of XeF₂, it is well known that there is a
277 difference between $\sigma_{\parallel,Y}$ of the nuclei in the molecule and σ_Y^{atom}
278 of that nuclei in free atoms (Y = Xe and F). This was an
279 indication that Flygare's relation is broken when heavy atoms
280 are considered. Flygare's NR relation states that for a nucleus Y
281 in a linear molecule, $\sigma_{\parallel,Y}^{NR,para}$ is zero and $\sigma_Y^{atom,NR,para}$ is also zero.
282 In addition, it holds that $\sigma_{\parallel,Y}^{NR,dia} \cong \sigma_Y^{atom,NR,dia} = \sigma_Y^{atom,NR}$.

283 What happens within the relativistic domain? We shall
284 analyze the (e-e) and (e-p) contributions to the shieldings. The
285 calculations of the (e-p) part at RPA level give: $\sigma_{\parallel}^{(e-p)}(\text{Xe:XeF}_2)$
286 = 4599.7948 ppm, whereas $\sigma^{atom(e-p)}(\text{Xe}) = 4593.3768$ ppm. It
287 is seen that there is only a small difference between them, that
288 is, 6.4180 ppm. For fluorine a difference of 18.9435 ppm is
289 found. The differences in both cases are probably due to
290 quadrupole terms.¹¹

291 The relativistic (e-e) contribution has a large difference with
292 its NR counterpart. Within the relativistic regime $\sigma_Y^{atom(e-e)}$ and
293 $\sigma_{\parallel,Y}^{(e-e)}$ are both different from zero. In the case of Xe in XeF₂,
294 $\sigma_{\parallel}^{(e-e)}(\text{Xe}) = 1388.2505$ ppm, while $\sigma^{atom(e-e)}(\text{Xe}) = 2026.0618$
295 ppm, being its difference of -637.8113 ppm. We assume that
296 the mechanism responsible for this difference is related with
297 $\nu_{\parallel}^{S(e-e)} - \nu_{atom,S(e-e)}$. Its RPA value for Xe in XeF₂ and the atomic
298 Xe is -637.8190 ppm. In the case of fluorine in XeF₂ the
299 difference among $\sigma_{\parallel}^{(e-e)}(\text{F})$ and $\sigma^{atom(e-e)}(\text{F}^-)$ is 19.3646 ppm,
300 whereas $\frac{1}{2c}\nu_{\parallel}^{S(e-e)}(\text{F:XeF}_2) - \frac{1}{2c}\nu_{atom,S(e-e)}(\text{F}^-)$ is 19.5146 ppm.

301 Therefore, $\sigma_{\parallel}(\text{Xe:XeF}_2) - \sigma^{atom}(\text{Xe}) \cong \nu_{\parallel}^{S(e-e)} - \nu_{atom,S(e-e)}$, and
302 this is because the (e-p) parts of $\sigma_{\parallel}^{(e-p)}$ and $\sigma^{atom(e-p)}$ are very
303 close each other.

304 To summarize, we have shown here that the best of our
305 relativistic Flygare-like models must include new four-
306 component terms: ν^S and $\nu_{atom,S}$. These terms are more general
307 than the previously used two-component SO-S term. This one
308 can be obtained as the leading order relativistic correction of
309 the LRESC expansion of $\nu_Y^{S(e-e)} - \nu_Y^{atom,S(e-e)}$.

310 The new M-V model is our best to obtain the absolute value
311 of σ in light- and heavy-atom-containing molecules. We applied
312 it to a family of XY and HX (X, Y = F, Cl, Br, I, At) linear
313 molecules, reaching accurate fittings with benchmark values of
314 σ .

315 In addition we answered the inquiry first proposed in 2004
316 by the work of Wasylshen and coauthors concerning the large
317 difference between the parallel component of the NMR
318 shielding tensor of Xe in XeF₂ and that of the Xe free atom.
319 It is almost completely explained through the introduction of
320 the new ν^S term.

321 ■ AUTHOR INFORMATION

322 Corresponding Author

323 *E-mail: gaucar@conicet.gov.ar.

324 ORCID

325 Gustavo A. Aucar: 0000-0003-2547-2330

326 Notes

327 The authors declare no competing financial interest.

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