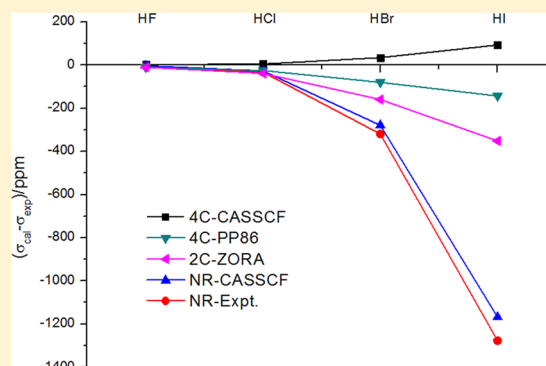


New Experimental NMR Shielding Scales Mapped Relativistically from NSR: Theory and Application

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ABSTRACT: The recently proposed relativistic mapping between nuclear magnetic resonance (NMR) shielding and nuclear spin-rotation (NSR) coupling tensors [*J. Chem. Phys.* **2013**, *138*, 134104] is employed to establish new experimental (more precisely, experimentally derived) absolute shielding constants for H and X in HX (X = F, Cl, Br, and I). The results are much more accurate than the old “experimental” values that were based on the well-known nonrelativistic mapping. The relativistic mapping is very robust in the sense that it is rather insensitive to the quality of one-particle basis sets and the treatment of electron correlation. Relativistic effects in the NSR coupling constants are also elucidated in depth.



1. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is the most powerful experimental technique for determining the electronic and molecular structures of molecular systems. Yet, absolute NMR shieldings cannot be measured accurately. Instead, they are usually translated^{1,2} from the nuclear spin-rotation (NSR) coupling constants that can be determined accurately through hyperfine splittings of molecular rotational spectra. This translation has been made possible by the following identity for connecting the electronic paramagnetic contributions to the NMR ($\sigma_{vu,eq}^{K,p}(\text{“exp”})$) and NSR ($M_{uv,eq}^{K,p}(\text{exp})$) tensors at the equilibrium (eq) geometry:

$$\begin{aligned}\sigma_{vu,eq}^{K,p}(\text{“exp”}) &= -\frac{I_{vv}^0}{2g_K\mu_n}M_{uv,eq}^{K,p}(\text{exp}) \\ &= -\frac{I_{vv}^0}{2g_K\mu_n}(M_{uv,eq}^{K,p}(\text{exp}) - M_{uv,eq}^{K,d}(\text{NR}))\end{aligned}\quad (1)$$

where I^0 , g_K , and μ_n are the principle inertia tensor, nuclear g factor, and nuclear magneton, respectively. Using the experimentally measured value for $M_{uv,eq}^{K,p}(\text{exp})$ and the theoretically calculated values for the diamagnetic contributions $M_{uv,eq}^{K,d}(\text{NR})$ and $\sigma_{vu,eq}^{K,d}(\text{NR})$, one would obtain the so-called “experimental” NMR shielding $\sigma_{vu,eq}^{K,p}(\text{“exp”})$:

$$\sigma_{vu,eq}^K(\text{“exp”}) = \sigma_{vu,eq}^{K,p}(\text{“exp”}) + \sigma_{vu,eq}^{K,d}(\text{NR})\quad (2)$$

This relation 1 was established by Ramsey already in 1950³ and later on was explored more thoroughly by several people.^{4–7} It has been in use until today. However, the relation holds only in the nonrelativistic limit (nrl), implying that the so-obtained “experimental” NMR shielding is nonrelativistic in

nature. In other words, a fully relativistic experimental measurement of M^K is translated into a nonrelativistic value for σ^K , which necessarily breaks down for heavy atoms. As a matter of fact, even for atoms like C to F bonded to light ligands, relativistic effects (ca. 2–5 ppm) are already 1 order of magnitude larger than the error bars in σ^K (typically 0.5 ppm) propagated from the uncertainties in the experimental measurements of M^K . Therefore, a relativistic mapping between NMR and NSR is highly desired. This can be made possible only if the relativistic theories of both NMR and NSR tensors are formulated rigorously and their internal relationship is then identified. Fortunately, all of these have been achieved very recently.^{8–14} The present account aims to demonstrate that the proposed “direct relativistic mapping” (vide post) is indeed very robust, and the resulting new experimental (more precisely, experimentally derived) NMR shielding scales are highly accurate.

2. THEORY

All equations, including eqs 1 and 2, are written in the System International atomic units. The nuclear (R_u , $u = x, y, z$) and electronic (r_u) coordinates refer to the body-fixed frame (BFF) of reference, with the origin placed at the nuclear center of mass (NCM) along the principal axes of inertia. The inertia tensors I^0 , I' , and I'' required here for nonlinear molecules are defined in eqs 33, 29 and 34 in ref 9, respectively, whereas the inertia numbers I^0 , I' and I'' for linear molecules aligning on the z axis are defined in eqs 27, 26, and 28 in ref 10, respectively. The charge and mass of nucleus K are denoted as

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Z_K and m_K , respectively. The Einstein summation convention over repeated indices is always employed.

2.1. Relativistic Theory for NSR: Rovibrational Corrections. The NSR tensor M^K is a parameter for defining the effective NSR Hamiltonian

$$H_{\text{NSR}} = I_{Ku} M_{uv}^K J_v \quad (3)$$

where \vec{I}_K is the spin operator for nucleus K and \vec{J} is the molecular angular momentum operator with the nuclear spin excluded. Without going into detail, the vibrationally averaged tensor M^K can, in the adiabatic approximation, be calculated as (see eq 124 in ref 10):

$$M_{uv}^K = \langle i_{\text{vib}}^{00}(Q_k) | M_{uv}^K(Q_k) | i_{\text{vib}}^{00}(Q_k) \rangle_{Q_k} \quad (4)$$

where i_{vib}^{00} is the vibrational part of the zeroth order rovibronic state $|i_{\text{rot}}^{00}\rangle \otimes |i_{\text{vib}}^{00}\rangle \otimes |i_{\text{ele}}^{00}\rangle$ under consideration, and the integration is to be carried out over the normal vibrational coordinates Q_k . The electronic state $|i_{\text{ele}}^{00}\rangle$ with energy $E_e(Q_k)$ can first be obtained by solving the electronic Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) equation with the clamped nuclei. The rotational state $|i_{\text{rot}}^{00}\rangle$ of quantum number J can then be calculated at the equilibrium geometry under the rigid rotor approximation. The vibrational state $|i_{\text{vib}}^{00}\rangle$ is finally obtained by solving the nuclear Schrödinger-like equation

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial(Q_k)^2} + T_{\text{cor}} + E_e(Q_k) + V_j + V_{\text{ad}}(Q_k) \right] |i_{\text{vib}}^{00}\rangle = E_{\text{ev}}^{00} |i_{\text{vib}}^{00}\rangle \quad (5)$$

where the first term is the nuclear kinetic energy operator, to which T_{cor} is a correction due to the vibrational angular momentum $J_{\text{vib}}^{\text{vib}}$. For nonlinear molecules $T_{\text{cor}} = 1/2 J_u^{\text{vib}} (I'^{-1})_{uv} J_v^{\text{vib}}$ [see eq 63 in ref 9], while for linear molecules $T_{\text{cor}} = 1/2 I'^{-1} [(J_x^{\text{vib}})^2 + (J_y^{\text{vib}})^2]$ [see eq 72 in ref 10]. The fourth term V_j arises from the centrifugal effect of the molecular rotation. For nonlinear molecules $V_j = 1/2 J_u [I'^{-1} - (I^0)^{-1}]_{uv} J_v$ [see eq 63 in ref 9], while for linear molecules $V_j = 1/2 [I'^{-1} - (I^0)^{-1}] (J_x^2 + J_y^2)$ [see eq 72 in ref 10]. The last term $V_{\text{ad}}(Q_k)$ collects all the diagonal adiabatic corrections (including the mass polarization, Watson potential, inverse-inertia-weighted spin–orbit, spin–spin and orbit–orbit interactions, etc.). To a good accuracy, the T_{cor} and $V_{\text{ad}}(Q_k)$ terms can be neglected, leading to

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial(Q_k)^2} + E_e(Q_k) + V_j \right] |i_{\text{vib}}^{00}\rangle = E_{\text{ev}}^{00} |i_{\text{vib}}^{00}\rangle \quad (6)$$

Instead of solving eq 6 exactly via, e.g., the finite-element technique,¹⁵ one can think of a perturbation theory^{16,17} by expanding $E_e(Q_k)$ around $Q_k = 0$ and taking the Harmonic oscillator as zeroth order. The first order corrections to $|i_{\text{vib}}^{00}\rangle$ arise solely from V_j and the third order derivatives of $E_e(Q_k)$. Therefore, to second order in Q_k , M_{uv}^K (eq 4) can be calculated as

$$M_{uv}^K = M_{uv,\text{eq}}^K + (\delta_{vj}^K)_{uv} \quad (7)$$

For diatomic molecules to be investigated here, only the perpendicular component of δ_{vj}^K is relevant, which can be written out explicitly¹⁸

$$\delta_{vj}^{K,\perp} = \left(\nu + \frac{1}{2} \right) \left(\frac{B_e}{\omega_e} \right) \left(\frac{d^2 M^{K,\perp}}{d\xi^2} \right) \bigg|_{\xi=0} - \frac{d^3 E_e / d\xi^3|_{\xi=0}}{d^2 E_e / d\xi^2|_{\xi=0}} \frac{dM^{K,\perp}}{d\xi} \bigg|_{\xi=0} + 4(J^2 + J) \left(\frac{B_e}{\omega_e} \right)^2 \frac{dM^{K,\perp}}{d\xi} \bigg|_{\xi=0} \quad (8)$$

$$B_e = \frac{1}{4\pi c I^0}, \quad \omega_e = \frac{1}{2\pi c \sqrt{I^0}} \sqrt{\frac{d^2 E_e}{d\xi^2} \bigg|_{\xi=0}}, \quad I^0 = \frac{m_1 m_2}{m_1 + m_2} r_0^2, \quad \xi = \frac{r - r_0}{r_0} \quad (9)$$

2.2. Relativistic Theory for NSR: $M_{uv}^K(Q_k)$. Having discussed briefly the rovibrational corrections δ_{vj}^K (eq 7), the NSR tensor $M_{uv}^K(Q_k)$ at an arbitrary geometry Q_k needs to be specified. The rigorous formulation must be based on the body-fixed relativistic molecular Hamiltonian transformed exactly from that in the laboratory frame of reference. Detailed derivations of $M_{uv}^K(Q_k)$ have been presented in ref 9 for nonlinear molecules and ref 10 for linear molecules. It is composed of three terms, viz.,

$$M_{uv}^K(Q_k) = M_{uv}^{K,\text{dn}}(Q_k) + M_{uv}^{K,\text{de}}(Q_k) + M_{uv}^{K,\text{p}}(Q_k) \quad (10)$$

where $M_{uv}^{K,\text{dn}}(Q_k)$ is the nuclear diamagnetic term and is simply a constant for a given geometry:

$$M_{uv}^{K,\text{dn}}(Q_k) = D_{\text{nn,C(SSO)},uv}^{11(K)} + D_{\text{nn,B(SOO)},uv}^{11(K)} \quad (11)$$

$$D_{\text{nn,C(SSO)},uv}^{11(K)} = - \sum_{L(L \neq K)} \frac{g_K \mu_n \gamma_K Z_L}{m_K c^2} \varepsilon_{uvv'} \frac{R_{KL,w}}{R_{KL}^3} A_{v'v}^{(K)}, \quad \gamma_K = 1 - \frac{Z_K m_p}{g_K m_K} \quad (12)$$

$$D_{\text{nn,B(SOO)},uv}^{11(K)} = \sum_{L(L \neq K)} \frac{g_K \mu_n Z_L}{m_L c^2} \varepsilon_{uvv'} \frac{R_{KL,w}}{R_{KL}^3} A_{v'v}^{(L)} \quad (13)$$

$$A_{uv}^{(K)} = \begin{cases} -m_K \varepsilon_{uv'w} R_{Kv}^0 (I'^{-1})_{vv'} & \text{for nonlinear molecules} \\ -m_K \varepsilon_{uzv} z_K^0 I'^{-1} & \text{for linear molecules} \end{cases} \quad (14)$$

The two terms of eq 11 stem from the nucleus–nucleus Coulomb spin-same-orbit and Breit spin-other-orbit interactions, respectively. γ_K and ε_{uvw} are the respective Thomas precession¹⁹ and Levi-Civita permutation symbol.

The second term in eq 10 is the electronic diamagnetic term arising from the electron–nucleus Coulomb spin-same-orbit interaction

$$M_{uv}^{K,\text{de}}(Q_k) = \langle i_{\text{ele}}^{00} | D_{\text{ne,C(SSO)},uv}^{11(K)} | i_{\text{ele}}^{00} \rangle \quad (15)$$

$$D_{\text{ne,C(SSO)},uv}^{11(K)} = - \sum_i \frac{g_K \mu_n \gamma_K}{m_K c^2} \varepsilon_{uvv'} \frac{r_{iK,w}}{r_{iK}^3} A_{v'v}^{(K)} \quad (16)$$

while the last term in eq 10 is the electronic paramagnetic term

$$M_{uv}^{K,\text{p}}(Q_k) = \frac{\langle i_{\text{ele}}^{00} | D_{\text{u}}^{01(K)} | a_{\text{ele}}^{00} \rangle \langle a_{\text{ele}}^{00} | D_{\text{v}}^{10} | i_{\text{ele}}^{00} \rangle}{E_i^{00} - E_a^{00}} + \text{c.c.} \quad (17)$$

$$D_u^{01(K)} = \sum_i \frac{g_K \mu_n}{c r_{iK}^3} (\vec{r}_{iK} \times \vec{\alpha}_i)_u \quad (18)$$

$$D_v^{10} = -\sum_i \left(l_{iv} + \frac{\Sigma_{iv}}{2} + j_v^{\text{vib}} \right) B_I + D_{\text{ne,G(O)},v}^{10} \quad (19)$$

$$l_{iv} = [(\vec{r}_i - \vec{R}_{\text{NCM}}) \times \vec{p}_i]_v, j_v^{\text{vib}} = -i \eta_{kl}^v Q_k \frac{\partial}{\partial Q_l} \quad (20)$$

$$B_I = \begin{cases} (I'^{-1})_{vv} & \text{for nonlinear molecules} \\ I'^{-1} & \text{for linear molecules} \end{cases} \quad (21)$$

$$D_{\text{ne,G(O)},v}^{10} = \sum_{iK} \frac{Z_K}{m_K c} \frac{\alpha_{iu}}{r_{iK}} A_{uv}^{(K)} \quad (22)$$

The first term of D^{10} (eq 19) describes the coupling between the electronic orbit motion and the molecular rotation and is the leading term. The second term of D^{10} describes the coupling between the electronic spin and the molecular rotation and is of $O(c^{-2})$ in a relative sense. The third term accounts for the Coriolis coupling. It vanishes identically for diatomic molecules, for the quantity η_{kl}^v [see eq 31 of ref 9] is antisymmetric and hence vanishes for $k = l = 1$. In the case that the electronic wave function $|i_{\text{ele}}^{00}\rangle$ does not vary greatly nearby the equilibrium, this term is also very small for a polyatomic molecule.²⁰ The $D_{\text{ne,G(O)}}^{10}$ term (eq 22) arises from the Gaunt interaction between the electrons and nuclei. It is formally on the same order as the spin term in D^{10} (eq 19).^{9,10} However, the Dirac matrix $\vec{\alpha}_i$ therein has an opposite parity as $\vec{r}_{iK} \times \vec{\alpha}_i$ in $D^{01(K)}$ (eq 18): The former is odd, whereas the latter is even. On the other hand, the $D^{01(K)}$ operator is highly localized in the vicinity of nucleus K . In this region, the electronic wave functions $|i_{\text{ele}}^{00}\rangle$ and $|a_{\text{ele}}^{00}\rangle$ have well-defined local parities. Therefore, it can be expected that each electronic transition $|i_{\text{ele}}^{00}\rangle \rightarrow |a_{\text{ele}}^{00}\rangle$ may have an appreciable contribution, but their sum tends to vanish due to opposite signs. This is indeed the case here: The Gaunt term (eq 22) contributes only a few Hz for H in HX ($X = \text{F, Cl, Br, I}$) and ca. 25 Hz for the halogen atoms (see Table 1). These are smaller than other contributions by 4 orders of magnitude (*vide post*). Therefore, D_v^{10} (eq 19) can safely be approximated as

$$D_v^{10} = -\sum_i j_{iv} B_I, j_{iv} = l_{iv} + \frac{1}{2} \Sigma_{iv} \quad (23)$$

Note in passing that the smallness of the electron–nucleus Gaunt/Breit term was also anticipated^{12,13} and later confirmed¹⁴ by Aucar et al. However, their argument in terms of the slow motion of the nucleus is invalid: This term has the same dependence on the nuclear mass as the electron spin term in D^{10} (eq 19), but the latter is not small. In reality, the overall smallness of the Gaunt/Breit term is dictated by the mismatch in the parity, while its relative magnitude (nucleus dependence) is mainly determined by the nuclear g-factor g_K instead of the nuclear mass m_K in the governing parameter $g_K Z_K / m_K$. As clearly seen from Table 1, among the halogen atoms, Cl has the smallest g factor and hence the least contribution from the electron–nucleus Gaunt term.

2.3. Relativistic Mapping between NMR and NSR. To establish a formal relation between the NMR and NSR tensors, we start with the apparent identity for the electronic paramagnetic terms

Table 1. Contributions of the Electron-Nucleus Gaunt Term (eq 22) to the NSR Coupling Constants (M_{eq}^{\pm} in kHz) of H and X in HX Calculated at the Experimental Equilibrium Distances with PP86 and BasL^a

	M_{H}	g_{H}	$Z_{\text{H}}/m_{\text{H}}$	$(g_{\text{H}} Z_{\text{H}})/m_{\text{H}}$
HF	0.0061	5.586	0.99	5.54
HCl	0.0022	5.586	0.99	5.54
HBr	0.0016	5.586	0.99	5.54
HI	0.0012	5.586	0.99	5.54
	M_{X}	g_{X}	$Z_{\text{X}}/m_{\text{X}}$	$(g_{\text{X}} Z_{\text{X}})/m_{\text{X}}$
HF	0.0382	5.258	0.47	2.49
HCl	0.0049	0.548	0.49	0.27
HBr	0.0254	1.404	0.44	0.62
HI	0.0258	1.125	0.42	0.47

^a g_K , Z_K , and m_K are the nuclear g factor, charge, and mass, respectively.

$$\sigma_{vu,\text{eq}}^{K,p} = \sigma_{vu,\text{eq}}^{K,\text{SR},p} + \Delta_{vu,\text{eq}}^{K,p} \sigma_{vu,\text{eq}}^{K,\text{SR},p} = -\frac{I_{vv}^0}{2g_K \mu_n} M_{uv,\text{eq}}^{K,p} \quad (24)$$

$$\Delta_{vu,\text{eq}}^{K,p} = \sigma_{vu,\text{eq}}^{K,p} - \sigma_{vu,\text{eq}}^{K,\text{SR},p} \quad (25)$$

which holds if the gauge origin of the external vector potential is placed at the NCM. We then replace the theoretical $M_{uv,\text{eq}}^{K,p}$ in eq 24 with the experimental $M_{uv,\text{eq}}^{K,p}(\text{exp})$

$$M_{uv,\text{eq}}^{K,p}(\text{exp}) = M_{uv,\text{eq}}^{K,\text{exp}}(\text{exp}) - M_{uv,\text{eq}}^{K,d}, \quad M_{uv,\text{eq}}^{K,d} = M_{uv,\text{eq}}^{K,\text{dn}} + M_{uv,\text{eq}}^{K,\text{de}} \quad (26)$$

so as to obtain

$$\sigma_{vu,\text{eq}}^{K,p}(\text{exp}) = \sigma_{vu,\text{eq}}^{K,\text{SR},p}(\text{exp}) + \Delta_{vu,\text{eq}}^{K,p}, \quad \sigma_{vu,\text{eq}}^{K,\text{SR},p}(\text{exp}) = -\frac{I_{vv}^0}{2g_K \mu_n} M_{uv,\text{eq}}^{K,p}(\text{exp}) \quad (27)$$

The desired experimental NMR shielding can then be obtained as

$$\sigma_{vu,\text{eq}}^{K,\text{exp}}(\text{exp}) = \sigma_{vu,\text{eq}}^{K,p}(\text{exp}) + \sigma_{vu,\text{eq}}^{K,d} \quad (28)$$

where $\sigma_{vu,\text{eq}}^{K,d}$ is again the calculated diamagnetic term. Any four-component (4C) relativistic formulation (for a recent review, see ref 21) of NMR shielding can be employed here, provided that it has an explicit diamagnetism. However, only the EFUT (external magnetic field-dependent unitary transformation) approach⁸ allows for a direct evaluation^{9,10} of $\Delta_{vu,\text{eq}}^{K,p}$ (eq 25), viz.,

$$\Delta_{vu,\text{eq}}^{K,p} = \langle i_{\text{ele}}^{00} | \sum_i \frac{(\vec{r}_{iK} \times \vec{\alpha}_i)_u}{c r_{iK}^3} | i_{\text{ele}}^{10} \rangle + \text{c.c.} \quad (29)$$

$$= \frac{\langle i_{\text{ele}}^{00} | \sum_i \frac{(\vec{r}_{iK} \times \vec{\alpha}_i)_u}{c r_{iK}^3} | a_{\text{ele}}^{00} \rangle \langle a_{\text{ele}}^{00} | \Delta D_v^{10} | i_{\text{ele}}^{00} \rangle}{E_i^{00} - E_a^{00}} + \text{c.c.} \quad (30)$$

$$\Delta D_v^{10} = \frac{1}{2} \sum_i \left[(\beta_i - 1) l_{i,v} + \left(\beta_i - \frac{1}{2} \right) \Sigma_{i,v} \right] \quad (31)$$

where $|i_{\text{ele}}^{10}\rangle$ represents the linear response of the electronic wave function to the differential perturbation ΔD_v^{10} (eq 31) and can formally be written in a sum-over-state form (eq 30). In contrast, for other formulations of NMR shielding, the difference $\Delta_{vu,\text{eq}}^{K,p}$ between the electronic paramagnetic con-

Table 2. Individual Contributions to the NSR Coupling Constants (M_{eq}^{\perp} in kHz) of H and X in HX Calculated at the Experimental Equilibrium Distances with LDA and BasL^a

	$D_{\text{nn,C(SSO)}}^{11b}$	$D_{\text{nn,B(SSO)}}^{11c}$	$M_{\text{eq}}^{\perp,\text{ded}}$	$M_{\text{eq},+}^{\perp,e}$	$M_{\text{eq},-}^{\perp,f}$	M_{eq}^{\perp}
$M_{\text{H}}, \text{NR-LDA}$						
HF	−412.262	−26.631	409.581 (408.399)	−44.631 (−42.688)		−73.943 (−73.182)
HCl	−289.884	−10.174	288.746 (288.518)	−29.439 (−30.637)		−40.750 (−42.176)
HBr	−436.673	−6.791	435.859 (435.612)	−25.197 (−26.224)		−32.802 (−34.076)
HI	−449.267	−4.345	448.708 (448.308)	−20.116 (−21.045)		−25.019 (−26.349)
$M_{\text{H}}, 4\text{C-LDA}$						
HF	−412.262	−26.631	409.580 (408.396)	−45.456 (−43.498)	0.014 (0.015)	−74.755 (−73.979)
HCl	−289.884	−10.174	288.748 (288.521)	−31.719 (−32.889)	0.023 (0.021)	−43.006 (−44.405)
HBr	−436.673	−6.791	435.933 (435.686)	−35.660 (−36.259)	0.048 (0.046)	−43.142 (−43.991)
HI	−449.267	−4.345	448.803 (448.412)	−44.464 (−44.365)	0.057 (0.052)	−49.216 (−49.513)
$M_{\text{X}}, \text{NR-LDA}$						
HF	−2.532	−52.520	2.509 (2.325)	349.886 (369.507)		297.343 (316.780)
HCl	−0.006	−2.037	0.006 (0.006)	55.946 (63.622)		53.908 (61.585)
HBr	−0.033	−3.821	0.033 (0.030)	303.928 (314.499)		300.108 (310.676)
HI	−0.010	−2.080	0.010 (0.009)	364.588 (376.840)		362.507 (374.759)
$M_{\text{X}}, 4\text{C-LDA}$						
HF	−2.532	−52.520	2.508 (2.323)	349.538 (369.098)	0.013 (0.010)	297.006 (316.379)
HCl	−0.006	−2.037	0.006 (0.006)	55.963 (63.588)	0.001 (0.001)	53.926 (61.551)
HBr	−0.033	−3.821	0.033 (0.030)	305.459 (314.620)	0.005 (0.002)	301.643 (310.798)
HI	−0.010	−2.080	0.010 (0.009)	367.242 (376.799)	−0.001 (−0.007)	365.160 (374.710)

^aThe BasS results are in parentheses. ^bEquation 12. ^cEquation 13. ^dEquation 15. ^eEquation 17 only with positive energy states. ^fEquation 17 only with negative energy states.

tributions to the NMR and NSR tensors has to be evaluated with the definition (eq 25). We shall call the combination of eq 28 with eq 30 (EFUT) “direct relativistic mapping,” whereas that of eq 28 with 25 will be “indirect relativistic mapping.” If the experimental absolute shielding $\sigma_{\text{nu,eq}}^{\text{K}}(\text{exp})$ (eq 28) is the sole target, the former is more advantageous than the latter, for then only one set of coupled-perturbed equations²² need to be solved for $|\tilde{r}_{\text{ele}}^{10}\rangle$, which converges very fast. Moreover, the contributions from the negative energy states (NES) can be treated in an uncoupled manner.²³ If both the NSR and NMR tensors are wanted, the indirect relativistic mapping is instead recommended even for EFUT, for which eqs 25 and 30 yield identical results, provided that the coupled-perturbed equations for NSR and NMR are sufficiently convergent. The very crucial point is whether the quantity $\Delta_{\text{vu,eq}}^{\text{K,p}}$ is really stable with respect to both the one- and N -particle basis sets. It will be shown here that it is indeed the case (see also ref 11, where an “indirect relativistic mapping” was employed). In essence, it is the explicit use of the experimental $M_{\text{uv,eq}}^{\text{K,p}}(\text{exp})$ (eq 26) in the mapping (eq 28) that will minimize the truncation errors in the one- and N -particle basis sets inherent in the theoretical $M_{\text{uv,eq}}^{\text{K,p}}$.

Equation 28 reduces to the well-known expression (eq 2) in the nonrelativistic limit.⁹ Close inspections reveal that the new experimental shielding $\sigma_{\text{vu,eq}}^{\text{K}}(\text{exp})$ (eq 28) has three relativistic corrections to the old $\sigma_{\text{vu,eq}}^{\text{K}}(\text{exp})$ (eq 2):

- $\Delta_{\text{A}} = \Delta_{\text{vu,eq}}^{\text{K,p}}$, relativistic effect in the paramagnetic mapping (eq 24)
- $\Delta_{\text{B}} = \sigma_{\text{vu,eq}}^{\text{K,d}} - \sigma_{\text{vu,eq}}^{\text{K,d}}(\text{NR})$, relativistic effect in the NMR diamagnetism
- $\Delta_{\text{C}} = I_{\text{vv}}^0/2g\mu_{\text{n}}[M_{\text{uv,eq}}^{\text{K,d}} - M_{\text{uv,eq}}^{\text{K,d}}(\text{NR})]$, relativistic effect in the NSR diamagnetism

The new and old experimental shieldings are hence related as

$$\sigma_{\text{vu,eq}}^{\text{K}}(\text{exp}) = \sigma_{\text{vu,eq}}^{\text{K}}(\text{exp}) + \Delta_{\text{A}} + \Delta_{\text{B}} + \Delta_{\text{C}} \quad (32)$$

It will be shown that the Δ_{A} correction predominates over Δ_{B} and Δ_{C} and that, for good reasons, all three corrections are rather insensitive to the quality of the one-particle basis sets and the treatment of electron correlation.

Note in passing that for linear molecules, eqs 24–32 hold only for the xx and yy components of the shielding. The zz component of the shielding has to be calculated directly. Specifically, the zz component of Δ_{A} reads

$$\Delta_{\text{zz,eq}}^{\text{K,p}} = \sigma_{\text{zz,eq}}^{\text{K,p}}(4\text{C}) - \sigma_{\text{zz,eq}}^{\text{K,p}}(\text{NR}) = \sigma_{\text{zz,eq}}^{\text{K,p}}(4\text{C}) \quad (33)$$

The last equality stems from the fact that the zz component of the paramagnetic shielding vanishes for linear molecules in the nrl. Additional rovibrational and temperature corrections should further be added to the so-obtained shielding $\sigma_{\text{vu,eq}}^{\text{K}}(\text{exp})$ the equilibrium geometry. However, they are out of the present scope.

3. COMPUTATIONAL DETAILS

The above formulations are completely general, in the sense that both linear and nonlinear molecules can be handled with any methods. As a first pilot application to the diatomic molecules of ^1HX ($\text{X} = ^{19}\text{F}, ^{35}\text{Cl}, ^{79}\text{Br}, ^{127}\text{I}$), we consider here the coupled-perturbed Dirac–Kohn–Sham scheme. In this case, eq 29 reduces to

$$\Delta_{\text{vu,eq}}^{\text{K,p}} = \langle i^{00} | \frac{(\vec{r}_{\text{K}} \times \vec{a})_{\text{u}}}{cr_{\text{K}}^3} | a^{00} \rangle C_{\text{ai}}^{10,\text{v}} + \text{c.c.} \quad (34)$$

where $|i^{00}\rangle$ and $|a^{00}\rangle$ are the unperturbed occupied and virtual orbitals, while the first order coefficients $C_{\text{ai}}^{10,\text{v}}$ are determined^{22,23} by

$$[(\varepsilon_{\text{a}}^{00} - \varepsilon_{\text{i}}^{00})\delta_{ij} + 2K_{\text{ai,bj}}]C_{\text{bj}}^{10,\text{v}} = -G_{\text{ai}}^{10,\text{v}} \quad (35)$$

Under the adiabatic noncollinear local density approximation (LDA),^{24–27} i.e.,

Table 3. NSR Coupling Constants (M_{eq}^{\perp} in kHz) of H and X in HX^a

	4C-LDA	4C-PP86	4C-RPA ^b	$M^{\perp}(\text{exp})$	δ_{ν}^c	$M_{\text{eq}}^{\perp}(\text{exp})^d$
	M_{H}					
HF	-74.75 [-2.57]	-77.39 [-5.20]	-71.82 [0.37]	-71.128(24) ^e	1.06	-72.188(24)
HCl	-43.01 [-0.78]	-44.25 [-2.02]	-44.03 [-1.80]	-41.877(139) ^f	0.35	-42.227(139)
HBr	-43.14 [-2.14]	-45.26 [-4.26]	-45.98 [-4.98]	-41.27(31) ^g	-0.27	-41.00(31)
HI	-49.22 [-1.02]	-52.25 [-4.06]	-60.44 [-12.24]	-49.22(22) ^h	-1.03	-48.19(22)
SD	1.79	4.06	6.67			
	M_{X}					
HF	297.01 [18.45]	333.17 [54.61]	321.24 [42.68]	307.637(20) ^e	29.08	278.557(20)
HCl	53.93 [2.63]	58.46 [7.17]	54.43 [3.13]	53.829(53) ^f	2.53	51.299(53)
HBr	301.64 [22.70]	325.44 [46.49]	279.85 [0.90]	290.83(8) ^g	11.88	278.95(8)
HI	365.16 [24.72]	391.86 [51.42]	322.62 [-17.83]	351.1(3) ^h	10.66	340.44(30)
SD	19.19	44.27	23.19			

^aDeviations from experiment (last column) are in brackets. Experimental uncertainties are in parentheses. SD: standard deviations. ^bRef 13.

^cRovibrational corrections according to eq 8. ^dRovibrationally corrected. ^eRef 38. ^fRef 39. ^gRef 40. ^hRef 41.

$$E_{\text{xc}} = \int \varepsilon(\rho, s) d\vec{r}, s = |\vec{M}|, \vec{M}(\vec{r}') = \langle i|\beta\vec{\Sigma}\delta(\vec{r} - \vec{r}')|i\rangle \quad (36)$$

the coupling matrix K and the force $G_{ai}^{10,\nu}$ read

$$K_{ai,bj} = \left(a^{00}\beta\Sigma_u i^{00} \left| \frac{\partial^2 \varepsilon}{\partial s^2} [\rho^{00}, s^{00}] \delta(\vec{r} - \vec{r}') \right| j^{00}\beta\Sigma_u b^{00} \right) \quad (37)$$

$$G_{ai}^{10,\nu} = \langle a^{00}|\Delta d^{10,\nu}|i^{00}\rangle + \langle a^{00}|V_{\text{ind},m}^{10,\nu}|i^{00}\rangle \quad (38)$$

$$\Delta d^{10,\nu} = \frac{1}{2}(\beta - 1)[(\vec{r} - \vec{R}_{\text{NCM}}) \times \vec{p}]_{\nu} + \frac{1}{2}\left(\beta - \frac{1}{2}\right)\Sigma_{\nu} \quad (39)$$

Note that, for closed-shell systems, the first order density $\rho^{10}(\vec{r})$ vanishes due to time reversal symmetry²³ and hence does not contribute to both the coupling and the force. The second term of eq 38 arises from the first order magnetization density $M_{u,m}^{10,\nu}$ solely through the magnetic balance of EFUT:⁸

$$\langle a^{00}|V_{\text{ind},m}^{10,\nu}|i^{00}\rangle = \left(a^{00}\beta\Sigma_u i^{00} \left| \frac{\partial^2 \varepsilon}{\partial s^2} [\rho^{00}, s^{00}] \delta(\vec{r} - \vec{r}') \right| M_{u,m}^{10,\nu} \right) \quad (40)$$

$$M_{u,m}^{10,\nu}(\vec{r}') = -\frac{1}{2c} \langle i^{00}|\gamma_s \varepsilon_{wuv}(\vec{r} - \vec{R}_{\text{NCM}})_w \delta(\vec{r} - \vec{r}')|i^{00}\rangle \quad (41)$$

It can be proven (cf. Appendix A) that $M_{u,m}^{10,\nu}(\vec{r})$ actually vanishes for linear molecules. Numerical experimentations reveal that this induced term (eq 40) contributes also very little to the isotropic shieldings of nonlinear molecules (e.g., less than 10^{-10} (10^{-5}) ppm for Sn in SnH_4 of T_d (C_1) symmetry). Therefore, it can safely be neglected. Then, only the first term of eq 38 contributes to the force.

Both the VWN5 parametrization²⁸ of the local density approximation (LDA) and the PP86 parametrization^{29,30} of the generalized gradient approximation (GGA) were adopted in the ground state calculations in conjunction with the finite Gaussian nuclear models.³¹ Both standard and exceedingly large basis sets were considered to check the basis set dependence. The former (denoted as BasS) were the Huzinaga–Kutzelnigg IGLO-III sets³² for H to Cl and the

Faegri sets³³ for Br and I, whereas the latter (denoted as BasL) were taken from ref 23 (Basis-B therein). The experimental equilibrium distances (0.9169, 1.2746, 1.4145, and 1.6090 Å for HF to HI)³⁴ were used. All of the calculations were carried out with the BDF (Beijing density functional) program package.^{35–37}

4. RESULTS AND DISCUSSION

4.1. Calculated NSR Coupling Constants. The individual contributions to the perpendicular NSR coupling constants of

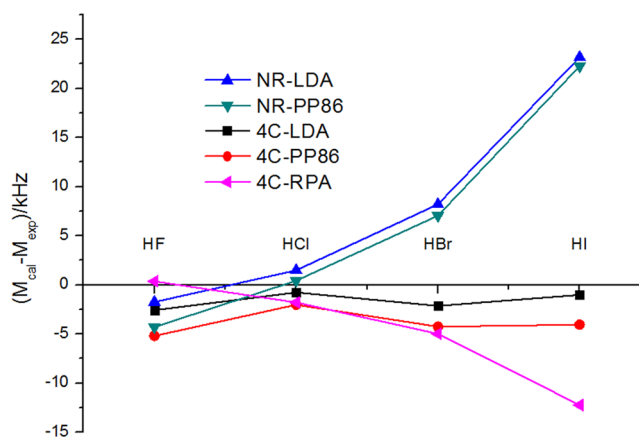


Figure 1. Deviations of theoretical from experimental NSR coupling constants of H in HX.

H and X in HX ($X = \text{F, Cl, Br and I}$) are first calculated at the LDA level, with the results given in Table 2. Note first that the $D_{\text{nn,C(SSO)}}^{11(K)}$ (eq 12) and $M^{K,\text{de}}$ (eq 15) terms are very similar in magnitude but opposite in sign. Actually, they should cancel each other precisely^{9,12} when calculated at the LDA equilibrium distances, leaving $D_{\text{nn,B(SSO)}}^{11(K)}$ (eq 13) the solely diamagnetic term. Noticeably, this nuclear diamagnetic term is smaller in magnitude than the electronic paramagnetic term $M^{K,p}$ (eq 17). It is also interesting to see that the NES have very little contributions to the electronic paramagnetic term. Moreover, relativistic effects are very small for X but significant for H in HX: Relativity increases the coupling constants of H by 1.1%, 5.5%, 31.5%, and 96.7% going from F to I. Similar findings are also observed at the PP86 (not documented) and the RPA (random phase approximation)¹³ levels. All of these stem from the peculiar behaviors of the $D^{01(K)}$ (eq 18) and D^{10} (eq 23)

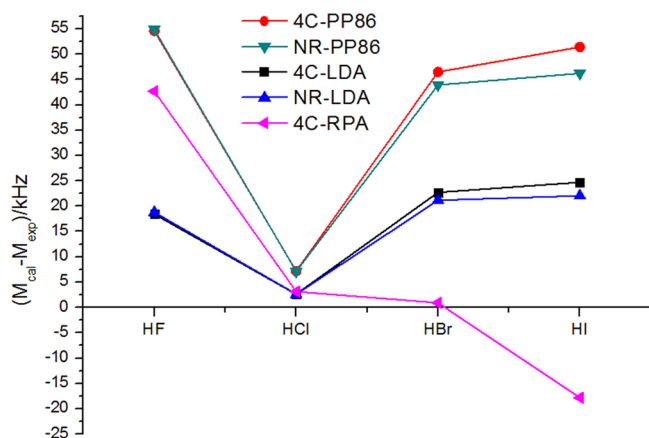


Figure 2. Deviations of theoretical from experimental NSR coupling constants of X in HX.

operators. The former is effective only in the vicinity of nucleus K , such that the matrix elements $D_{ia}^{01(K)}$ are only large for innermost atom-like orbitals i . The latter can be rewritten as

$$D_v^{10} = -\sum_i \left[(\vec{r}_i - \vec{R}_K) \times \vec{p}_i + \frac{1}{2} \Sigma_i \right] B_I - \sum_i [(\vec{R}_K - \vec{R}_{NCM}) \times \vec{p}_i]_v B_I \quad (42)$$

$$= -\sum_i f_{iv}^{(K)} B_I - \sum_i [(\vec{R}_K - \vec{R}_{NCM}) \times \vec{p}_i]_v B_I \quad (43)$$

Since atomic core orbitals are approximate eigenfunctions of the angular momentum $\vec{J}_i^{(K)}$, it is clear that the first term of eq 43 does not contribute much. The second term also contributes

Table 5. The Three Relativistic Corrections (Δ_A , Δ_B , and Δ_C in ppm) Which Brings $\sigma_{eq}^K(\text{exp})$ (2) to $\sigma_{eq}^K(\text{exp})$ (28)^a

method	HF	HCl	HBr	HI
hydrogen atom				
Δ_A LDA	−0.011 (−0.010)	−0.013 (−0.014)	−0.234 (−0.224)	−1.662 (−1.598)
Δ_A PP86	−0.011 (−0.011)	−0.013 (−0.014)	−0.245 (−0.234)	−1.725 (−1.648)
Δ_B LDA	0.000 (0.000)	0.000 (0.000)	−0.036 (−0.035)	−0.055 (−0.057)
Δ_B PP86	0.001 (0.001)	0.000 (0.002)	−0.023 (−0.022)	−0.029 (−0.031)
Δ_C LDA	0.000 (−0.001)	0.001 (0.001)	0.048 (0.048)	0.080 (0.087)
Δ_C PP86	−0.001 (−0.001)	0.000 (0.000)	0.035 (0.033)	0.049 (0.056)
Δ_{ABC} LDA	−0.011 (−0.011)	−0.012 (−0.012)	−0.222 (−0.211)	−1.637 (−1.567)
Δ_{ABC} PP86	−0.012 (−0.011)	−0.014 (−0.012)	−0.233 (−0.222)	−1.705 (−1.623)
halogen atom				
Δ_A LDA	4.359 (4.267)	31.129 (29.702)	305.200 (299.976)	1221.240 (1217.507)
Δ_A PP86	4.422 (4.328)	31.338 (29.889)	306.122 (300.873)	1224.161 (1220.558)
Δ_B LDA	0.073 (0.073)	0.928 (0.921)	11.790 (11.756)	51.603 (51.567)
Δ_B PP86	0.074 (0.073)	0.933 (0.926)	11.812 (11.778)	51.673 (51.637)
Δ_C LDA	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Δ_C PP86	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Δ_{ABC} LDA	4.433 (4.340)	32.057 (30.623)	316.990 (311.731)	1272.842 (1269.074)
Δ_{ABC} PP86	4.496 (4.401)	32.272 (30.815)	317.934 (312.651)	1275.834 (1272.195)

^aThe BasS results are in parentheses.

Table 4. Calculated Isotropic Shielding Constants (σ in ppm) of H and X in HX with BasL^a

method	HF	HCl	HBr	HI
σ_H				
NR-LDA	29.15 (29.42)	30.69 (30.89)	30.88 (30.98)	31.04 (31.28)
4C-LDA	29.28 (29.55)	31.45 (31.65)	35.10 (35.03)	42.93 (42.61)
NR-PP86	29.88 (30.20)	31.49 (31.66)	31.91 (31.98)	32.17 (32.37)
4C-PP86	30.02 (30.34)	32.32 (32.48)	36.54 (36.40)	45.19 (44.74)
NR-CASSCF ^b	28.84	30.82	31.03	31.57
4C-CASSCF ^c	28.97 (28.96)	31.58 (31.58)	35.25 (35.07)	43.46 (42.90)
4C-CASSCF ^d	28.98 (28.98)	31.65 (31.64)	35.66 (35.44)	44.59 (43.93)
δ^e	−0.04 [0.23]	0.08 [0.43]	1.03 [1.13]	1.72 [1.13]
σ_X				
NR-LDA	415.34 (415.32)	951.79 (955.39)	2604.51 (2602.37)	4490.52 (4491.20)
4C-LDA	419.83 (419.72)	983.80 (986.08)	2918.97 (2913.19)	5756.20 (5758.04)
NR-PP86	410.48 (410.26)	938.32 (941.91)	2567.49 (2565.74)	4425.40 (4428.55)
4C-PP86	415.02 (414.72)	970.41 (972.63)	2881.03 (2875.65)	5686.76 (5691.25)
NR-CASSCF ^b	422.53	968.55	2682.09	4661.91
4C-CASSCF ^c	427.01 (426.94)	1000.56 (999.24)	2996.54 (2992.91)	5927.59 (5928.75)
4C-CASSCF ^d	427.07 (426.99)	1000.64 (999.27)	2995.63 (2992.00)	5923.27 (5924.61)
δ^e	1.98[3.80]	5.02[7.33]	34.60[38.55]	93.31[102.73]
NR-CCSD(T) ^f	419.3	961.3		
4C-CCSD(T) ^g	423.78 (423.71)	993.31 (991.99)		
4C-CCSD(T) ^h	423.84 (423.76)	993.39 (992.02)		
δ^i	−1.25[0.57]	−2.23[0.08]		

^aThe BasS-GIAO results are in parentheses. ^bRef 45. ^cEstimated with NR-CASSCF and eq 44. ^dEstimated with NR-CASSCF and eq 45. ^eDeviations of BasL-4C-CASSCF^d [BasL-4C-CASSCF^b] from $\sigma_{eq}^K(\text{exp})^c$ in Table 7. ^fRef 47. ^gEstimated with NR-CCSD(T) and eq 44. ^hEstimated with NR-CCSD(T) and eq 45. ⁱDeviations of BasL-4C-CCSD(T)^h [BasL-4C-CCSD(T)^g] from $\sigma_{eq}^K(\text{exp})^d$ in Table 7.

Table 6. Individual Contributions to $\Delta_A = (2\Delta^{\perp,p} + \Delta^{\parallel,p})/3$ for I in HI (σ in ppm and M in kHz)^a

terms	l_{LL}	l_{SS}	Σ_{LL}	Σ_{SS}	total
the strict ratios between $\sigma^{\perp,p}$, $M^{\perp,p}$, and $\Delta^{\perp,p}$					
$\sigma^{\perp,p}$	1/2	-1/2	1/2	-1/2	
$M^{\perp,p} \times C$	1/2	1/2	1/4	1/4	
$\Delta^{\perp,p}$	0	-1	1/4	-3/4	
LDA					
$\sigma^{\perp,p}$	-1560.46 (-1600.26)	585.47 (582.42)	996.42 (992.99)	-228.34 (-225.46)	-206.91 (-250.31)
$M^{\perp,p}$	373.63 (383.16)	140.18 (139.45)	-119.29 (-118.88)	-27.34 (-26.99)	367.18 (376.74)
$\Delta^{\perp,p}$	0.00 (0.00)	1170.94 (1164.84)	498.21 (496.50)	-342.51 (-338.18)	1326.64 (1323.15)
PP86					
$\sigma^{\perp,p}$	-1671.61 (-1702.25)	586.78 (583.70)	997.37 (993.28)	-229.25 (-226.34)	-316.71 (-351.61)
$M^{\perp,p}$	400.24 (407.58)	140.49 (139.76)	-119.40 (-118.91)	-27.45 (-27.10)	393.88 (401.32)
$\Delta^{\perp,p}$	0.00 (0.00)	1173.56 (1167.40)	498.68 (496.64)	-343.88 (-339.52)	1328.36 (1324.53)
LDA					
$\Delta^{\parallel,p} = \sigma^{\parallel,p}$	288.97 (289.82)	585.40 (582.35)	364.44 (359.52)	-228.41 (-225.53)	1010.40 (1006.15)
PP86					
$\Delta^{\parallel,p} = \sigma^{\parallel,p}$	285.78 (285.50)	586.72 (583.64)	372.54 (369.82)	-229.32 (-226.42)	1015.71 (1012.54)
LDA					
Δ_A	96.32 (96.61)	975.76 (970.68)	453.62 (450.84)	-304.47 (-300.63)	1221.23 (1217.49)
PP86					
Δ_A	95.26 (95.17)	977.94 (972.81)	456.64 (454.37)	-305.69 (-301.82)	1224.15 (1220.53)

^aThe common gauge is placed at the nuclear center of mass when calculating σ . The BasS results are in parentheses. l_{LL} and Σ_{LL} denote the large-large component contributions to the respective orbital angular momentum and spin terms in D_v^{10} (23). l_{SS} and Σ_{SS} are the corresponding contributions from the small-small components. $C = -(I^0/(2g_K\mu_n)) = -4.17654$.

very little because it has an opposite parity with $D^{01(K)}$ (eq 18), just like the previously discussed Gaunt term (eq 22). In short, only atomic core orbitals that are strongly distorted by neighborhood heavy atoms can have significant contributions to NSR coupling constants. This is the case for H in HX but not for the halogen atoms. The NES are also of atomic nature²³ and hence do not contribute significantly.

The calculated NSR coupling constants can also be compared with other theoretical¹³ and experimental^{38–41} values, see Table 3. The deviations of the calculated results from the rovibrationally corrected experimental values are further depicted in Figure 1 for the hydrogen atom and Figure 2 for the halogen atoms. It is clearly seen that LDA outperforms both PP86 and RPA for the systems investigated here.

4.2. New Experimental NMR Absolute Shielding Scales. The calculated isotropic shielding constants for H and X in HX are given in Table 4. The EFUT ansatz⁸ is used here. It is seen that, when combined with the magnetically balanced²³ gauge-including atomic orbitals (GIAO) for distributed gauge origins,⁴³ the standard basis sets (BasS) yield virtually identical shielding constants as the exceedingly large basis sets (BasL). In contrast, the BasS results for the NSR coupling constants (cf. Table 2) still differ discernibly from the BasL ones, indicating that the rotational London atomic orbitals⁴⁴ should also be included in the relativistic NSR calculations. Unlike the NSR constants, relativistic effects are significant for the shielding constants of both H and X in HX, e.g., 38.3% for H and 28.2% for I in HI. The uncertainty in the theoretical shielding constants arises mainly from the treatment of electron correlation. If we assume that the interplay between relativity and correlation not covered by LDA/PP86 is negligible, the theoretical shielding constants for HX can be estimated as follows

$$\sigma(\text{theory}) \approx \sigma(\text{NR-HL}) + \sigma(4\text{C-LDA}) - \sigma(\text{NR-LDA}) \quad (44)$$

$$\approx \sigma(\text{NR-HL}) + \sigma(4\text{C-PP86}) - \sigma(\text{NR-PP86}) \quad (45)$$

where the first term represents a high-level (HL) nonrelativistic (NR) calculation. Taking the nonrelativistic CASSCF (complete active space self-consistent field)⁴⁵ and CCSD(T) (coupled-cluster with singles and doubles and perturbative triples)^{46,47} results for $\sigma(\text{NR-HL})$, accurate theoretical values can be obtained, denoted respectively as 4C-CASSCF and 4C-CCSD(T) in Table 4.

The most interesting point here is whether the proposed relativistic mapping (eq 28) between NMR and NSR is robust or not. To show this, we present the three relativistic corrections in eq 32 in Table 5. It is first seen that the Δ_A correction (eq 24) predominates over Δ_B and Δ_C . Second, the overall corrections $\Delta_{ABC} = \Delta_A + \Delta_B + \Delta_C$ are indeed dependent only weakly on the exchange-correlation functional and basis set. More specifically, the dependence of Δ_{ABC} on the functional and basis set is less than 0.1 ppm for the hydrogen atom, whereas for the halogen atoms, the dependence of Δ_{ABC} on the functional (basis set) amounts to 0.1 (0.1), 0.2 (1.4), 0.9 (5.3), and 3.0 (3.8) ppm going from F to I. Note in particular that such weak dependence is not fortuitous. As can be seen from Table 6, for both $\sigma^{\perp,p}$ and $M^{\perp,p}$, there exists a large dependence on the functional and basis set in the large-large component contributions to the orbital angular momentum term in D_v^{10} (eq 23). However, such contributions to Δ_A (eq 24) vanish identically. All the other contributions to $\sigma^{\perp,p}$, $\sigma^{\parallel,p}$, and $M^{\perp,p}$ are only weakly dependent on the functional and basis set. As a direct result, Δ_A is also weakly dependent on the functional and basis set.

Table 7. Experimental Isotropic Shielding Constants ($\sigma_{\text{eq}}(\text{exp})$ in ppm) of H and X in HX Mapped from Experimental NSR Coupling Constants ($M_{\text{eq}}^{\perp}(\text{exp})$ in kHz, See the Last Column of Table 3)

method	HF	HCl	HBr	HI
σ_{H}				
$M_{\text{eq}}^{\perp}(\text{exp})$	-72.19	-42.23	-41.00	-48.19
$M_{\text{eq}}^{\perp}(\text{NR})^a$	-29.45 (-29.31)	-11.20 (-11.31)	-7.83 (-7.61)	-5.17 (-4.90)
$\sigma_{\text{eq}}^{\perp}(\text{exp})^b$	11.18 (11.21)	16.05 (15.99)	21.45 (21.60)	36.20 (36.43)
$\sigma_{\text{eq}}^{\perp}(\text{NR})^a$	21.58 (21.28)	20.88 (20.50)	20.56 (19.95)	20.45 (19.69)
$\sigma_{\text{eq}}(\text{exp})^b$	29.03 (28.75) ^f	31.58 (31.16) ^g	34.86 (34.34) ^g	44.58 (43.98) ^g
Δ_{ABC}^c	-0.012 (-0.011)	-0.014 (-0.012)	-0.23 (-0.22)	-1.71 (-1.64)
$\sigma_{\text{eq}}(\text{exp})^d$	29.02 (28.74)	31.57 (31.15)	34.63 (34.12)	42.88 (42.34)
$\delta[\sigma_{\text{eq}}(\text{exp})]^e$	0.01	0.07	0.20	0.19
σ_{X}				
$M_{\text{eq}}^{\perp}(\text{exp})$	278.56	51.30	278.95	340.44
$M_{\text{eq}}^{\perp}(\text{NR})^a$	-52.55 (-52.54)	-2.04 (-2.04)	-3.82 (-3.82)	-2.08 (-2.08)
$\sigma_{\text{eq}}^{\perp}(\text{exp})^b$	-92.00 (-92.00)	-281.27 (-281.27)	-727.41 (-727.41)	-1430.56 (-1430.56)
$\sigma_{\text{eq}}^{\perp}(\text{NR})^a$	481.93 (480.11)	1150.86 (1148.69)	3128.04 (3125.95)	5507.84 (5505.73)
$\sigma_{\text{eq}}(\text{exp})^b$	420.59 (418.78) ^h	963.34 (961.18) ⁱ	2643.10 (2641.01) ⁱ	4554.13 (4552.02) ⁱ
Δ_{ABC}^c	4.50 (4.43)	32.27 (32.06)	317.93 (316.99)	1275.83 (1272.84)
$\sigma_{\text{eq}}(\text{exp})^d$	425.09 (423.21)	995.61 (993.23)	2961.03 (2958.00)	5829.97 (5824.86)
$\delta[\sigma_{\text{eq}}(\text{exp})]^e$	0.01	0.28	0.21	1.25

^aNonrelativistic PP86 (LDA) with BasL. ^bMapped according to eq 2.

^cSee Table 5. ^dMapped according to eq 32 or equivalently eq 28.

^eUncertainties of $\sigma_{\text{eq}}(\text{exp})^d$ inherited from those of $M_{\text{eq}}^{\perp}(\text{exp})$ in Table 3. ^f28.84 ppm from ref 46. ^g32 (32.2) ppm for H in HCl, 37 (36.8) ppm for H in HBr, and 46 (45.2) ppm for H in HI from ref 51 before (after) the present rovibrational corrections. The atom dipole approximation was adopted to obtain the diamagnetic term in ref 51. ^h421.40 from ref 46. ⁱ952 (964.6) ppm for Cl, 2617 (2645.7) ppm for Br, and 4510 (4551.8) ppm for I from ref 51 before (after) the present rovibrational corrections. The atom dipole approximation was adopted to obtain the diamagnetic term in ref 51.

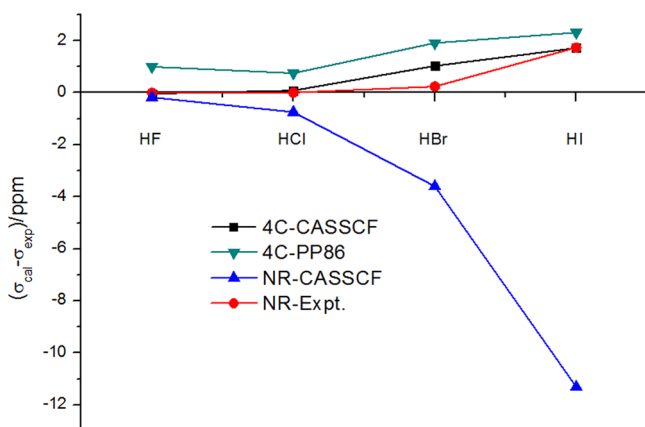


Figure 3. Deviations of theoretical from experimental NMR shielding constants of H in HX.

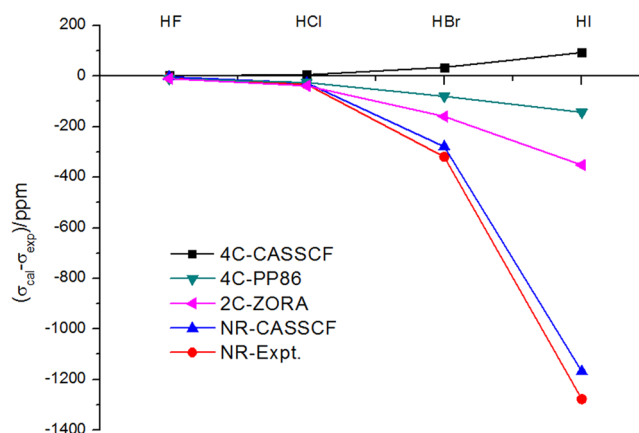


Figure 4. Deviations of theoretical from experimental NMR shielding constants of X in HX.

Given such a robust relativistic mapping between NSR and NMR, accurate⁴⁸ experimental (more precisely, experimentally derived) NMR absolute shielding scales can now be established for H and X in HX, see Table 7. As can be seen from Figures 3 and 4, they are indeed very close to the best theoretical values (4C-CCSD(T)^c or 4C-CASSCF^c in Table 4) estimated according to eq 45. In contrast, the old “experimental” shieldings $\sigma_{\text{eq}}(\text{exp})$ mapped according to the nonrelativistic relation 2 are far off, amounting to 4.5 ppm already for F in HF and even to 1276 ppm for I in HI. They are actually very close to the nonrelativistic values for the halogen atoms. Yet, for the hydrogen atom, the $\sigma_{\text{eq}}(\text{exp})$ values are close to the relativistic instead of the nonrelativistic values (see Figure 3). It sounds like that the nonrelativistic mapping (eq 2) is “nonrelativistic for heavy atoms but relativistic for (very) light atoms,” a sort of “inverse relativity.” This peculiarity arises from the fact that $\sigma_{\text{eq}}(\text{exp})$ for hydrogen inherits some relativistic effects from the experimental $M_{\text{eq}}^{\perp}(\text{exp})$. Specifically, in the case of H in HI, the inherited relativistic effect in $\sigma_{\text{eq}}(\text{exp})$ amounts to $[M_{\text{eq}}^{\perp}(4\text{C-LDA}) - M_{\text{eq}}^{\perp}(\text{NR-LDA})] * [(-I^0)/(2g_H\mu_n)] * 2/3 = (-24.20) * (-0.84142) * 2/3 = 13.57$ ppm (see Table 2), which is just the difference (13.01 ppm) between $\sigma_{\text{eq}}(\text{exp})$ (44.58 ppm) and NR-CASSCF (31.57 ppm). This effect amounts to 43% of the NR-CASSCF value! In contrast, in the case of I in HI, the so-inherited relativistic effect is only -7.38 ppm, leading to the NR-CASSCF value (4661.91 ppm) differing from $\sigma_{\text{eq}}(\text{exp})$ (4554.13 ppm) by only 2.4%. Here, it is the relativistic mapping Δ_{ABC} (1276 ppm, Table 5) that is important. Undoubtedly, for solid predications, the present relativistic mapping should be applied to both light and heavy atoms.

Two additional remarks are in order. First, while approximate relativistic methods are very useful for relative shieldings,⁴⁹ they cannot be used for absolute shieldings. For instance, the ZORA (zeroth order regular approximation) absolute shieldings⁵⁰ are quite off (see also ref 11). Second, the present $\sigma_{\text{eq}}(\text{exp})$ values are very close to the previous results,^{46,51} as they should be.

5. CONCLUSION

It has been demonstrated that the recently proposed relativistic mapping between NMR and NSR is very robust: By taking as input experimental NSR coupling constants as well as intermediate quantities evaluated at a low level of theory, accurate NMR absolute shielding scales can be obtained. The corresponding nonrelativistic mapping that has been in use for

more than 6 decades has thereby become obsolete, especially for atoms other than the lightest ones, say, H to Be. Yet, for routine applications, the use of rotational London atomic orbitals in the NSR calculations needs to be considered. Work along this direction is being carried out in our laboratory.

A. $M_{U,M}^{10,V}$ VANISHES FOR LINEAR MOLECULES

To show that $M_{U,M}^{10,V}(\vec{r})$ (eq 41) vanishes pointwise for linear molecules, we calculate it for an arbitrary point $\vec{r}_0 = (x_0, y_0, z_0)$. Without a loss of generality, x_0 can be set to zero. Therefore, $M_{U,M}^{10,V}(\vec{r}_0)$ is proportional to

$$\langle i^{00} | \gamma_5 \delta(x) \delta(y - y_0) \delta(z - z_0) | i^{00} \rangle \quad (46)$$

For the mirror reflection U with respect to the yz plane, we have

$$\begin{aligned} & \langle i^{00} | \gamma_5 \delta(x) \delta(y - y_0) \delta(z - z_0) | i^{00} \rangle \\ &= \langle i^{00} | U \gamma_5 U^{-1} \delta(x) \delta(y - y_0) \delta(z - z_0) U^{-1} | i^{00} \rangle \end{aligned} \quad (47)$$

$$= \langle i^{00} | (-\gamma_5) \delta(x) \delta(y - y_0) \delta(z - z_0) | i^{00} \rangle = 0 \quad (48)$$

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Notes

The authors declare no competing financial interest.

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