Nuclear Magnetic Resonance Chemical Shift in an Arbitrary Electronic Spin State

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We present a general and systematic electronic structure theory of the nuclear magnetic resonance shielding tensor and the associated chemical shift for paramagnetic atoms, molecules, and nonmetallic solids. The approach is for the first time rigorous for an arbitrary spin state as well as arbitrary spatial symmetry and is formulated without reference to spin susceptibility. The leading-order magnetic-field dependence of shielding is derived. The theory is demonstrated by first principles calculations of organometallic molecules.

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Nuclear magnetic resonance (NMR) [1,2] is the principal analytical tool for the structure and dynamics of microsystems in chemistry and materials science, with a wealth of applications in applied fields such as biology and medicine. NMR is typically applied on closed-shell molecules and solids, while systems with unpaired electrons are routinely investigated with electron spin resonance (ESR) [3,4]. NMR of paramagnetic, open-shell states [5] (PNMR) is nevertheless gaining importance in, e.g., systems with integer electron spin S or small hyperfine coupling (HFC), where ESR information is scarce.

The theory of closed-shell NMR parameters, the shielding tensor $\boldsymbol{\sigma}_K$ and the spin-spin coupling tensor $\boldsymbol{J}_{KL}$, where K and L denote paramagnetic nuclei, was established in the seminal papers by Ramsey [6]. Reviews of the current theory and electronic structure methods of the calculation of these parameters are given in Refs. [7–9]. In contrast, the field of first-principles theory and calculations of PNMR parameters is still in its infancy. Unlike the Ramsey theories that consider a pure electronic state, in PNMR a thermally populated ensemble of electronic Zeeman states is involved.

The first consistent quantum-chemical calculations of the PNMR chemical shift $\delta = \sigma_{\text{ref}} - \sigma$, with σ and σ_{ref} the isotropic shielding constant in the investigated and reference molecules, respectively, were published for the doublet electronic state in Ref. [10]. This work included the nonrelativistic (NR), $\mathcal{O}(\alpha^2)$ limit [11] composed of an orbital contribution analogous to the closed-shell case [6] as well as temperature-dependent hyperfine terms arising from the average Fermi contact (FC) and spin-dipole (SD) interaction in the Zeeman-split ground-state multiplet. While the SD term is a second-rank anisotropic contribution, the FC term gives rise to the isotropic contact shift [12]. Moon and Patchkovskii [13] presented a theory for $S = \frac{1}{2}$ states featuring the spin-orbit (SO) interaction contributions via the electronic Zeeman effect as parametrized with the g tensor, introducing effects such as the anisotropic contact and isotropic pseudocontact terms [14]. The latter is of central importance for the structure determination in paramagnetic metallo-organic molecules. The present authors [15] introduced SO corrections to the HFC tensor, $\boldsymbol{A}$ (Ref. [16]), and presented calculations of the thus extended Moon-Patchkovskii theory for main-group radicals and $S = \frac{1}{2}$ metallocenes.

An approximate *a posteriori* extension to the $S > \frac{1}{2}$ case [17] solved for the spin states in the presence of the Zeeman and zero-field splitting (ZFS) Hamiltonians, and formulated δ via the intermediate observable of spin susceptibility [5]. Ref. [17] was limited to cylindrically symmetric systems.

Here we derive a rigorous and systematic *a priori* theory for PNMR shielding for arbitrary S and spatial symmetry, where no assumptions about the magnitudes of ZFS and g tensor components or the mutual orientation of their principal axes are necessary. This leads to a formal expression for $\boldsymbol{\sigma}$ similar in spirit to that of Ref. [13], requiring solving for the electronic sublevels in the limit of vanishing magnetic field $\boldsymbol{B}_0$. We formulate the leading-order, quadratic field dependence of $\boldsymbol{\sigma}$. The field-independent part of the PNMR chemical shift is demonstrated by density-functional theory (DFT) calculations on metallocenes and a nonaxial model compound.

We adopt the starting point of Moon and Patchkovskii and equate the shielding term in the NMR spin Hamiltonian with a Boltzmann average of electronic energy terms bilinear in $\boldsymbol{B}_0$ and the nuclear spin $\boldsymbol{I}$:

$$\gamma \sum_{\epsilon\tau} B_{0,\epsilon} \sigma_{\epsilon\tau} I_\tau = \frac{\sum_n E_n(\boldsymbol{B}_0, \boldsymbol{I}) \exp[-W_n(\boldsymbol{B}_0, \boldsymbol{I})/kT]}{\sum_n \exp[-W_n(\boldsymbol{B}_0, \boldsymbol{I})/kT]}, \tag{1}$$

where ϵ, τ denote Cartesian components, γ is the gyromagnetic ratio of the investigated nucleus, and n denotes the relevant electronic states that consist of the ground-state spin multiplet as well as those of any low-lying excited electronic states. $E_n = \langle n|E|n\rangle$ is an expectation value of energy, which can be expanded in a power series of the components of $\boldsymbol{B}_0$ and $\boldsymbol{I}$ as [18]

$$E_n(\boldsymbol{B}_0, \boldsymbol{I}) = E_n^{(0,0)} + \sum_\mu E_n^{(\mu,0)} B_{0,\mu} + \sum_\tau E_n^{(0,\tau)} I_\tau + \sum_{\mu\tau} E_n^{(\mu,\tau)} B_{0,\mu} I_\tau + \frac{1}{2}\sum_{\mu\nu} E_n^{(\mu\nu,0)} B_{0,\mu} B_{0,\nu} + \frac{1}{2}\sum_{\mu\nu\tau} E_n^{(\mu\nu,\tau)} B_{0,\mu} B_{0,\nu} I_\tau + \ldots \quad (2)$$

$$E_n^{(\mu\nu,\ldots,\tau)} = \left(\frac{\partial^m E_n}{\partial B_{0,\mu}\partial B_{0,\nu}\ldots\partial I_\tau}\right)_{\boldsymbol{B}_0=0=\boldsymbol{I}}. \quad (3)$$

Equation (2) is limited to terms up to linear in $\boldsymbol{I}$.

An expansion similar to that of E_n can be applied to W_n, with an important simplification. The NMR signal is caused by transitions between the Zeeman states of the nuclear spin that occur at a much longer time scale than the electronic transitions that establish the equilibrium population distribution among the states n. Consequently, we may omit from W_n the terms referring to $\boldsymbol{I}$, leaving $W_n^{(\mu\nu\ldots,0)}$ in the Boltzmann factors of Eq. (1).

We multiply both sides of Eq. (1) by the partition function $\sum_n \exp[-W_n(\boldsymbol{B}_0, 0)/kT]$ to obtain [19]

$$\gamma\sum_{\epsilon\tau} B_{0,\epsilon}\sigma_{\epsilon\tau} I_\tau \sum_n \exp[-W_n(\boldsymbol{B}_0, 0)/kT] = \sum_n E_n(\boldsymbol{B}_0, \boldsymbol{I}) \exp[-W_n(\boldsymbol{B}_0, 0)/kT]. \quad (4)$$

The leading term in the expansion of W_n is by far the largest [20] and we may approximate

$$\exp[-W_n(\boldsymbol{B}_0, 0)/kT] \approx e^{-W_n^{(0,0)}/kT}\left\{1 - \frac{1}{kT}\left[\sum_\mu W_n^{(\mu,0)} B_{0,\mu} + \frac{1}{2}\sum_{\mu\nu} W_n^{(\mu\nu,0)} B_{0,\mu} B_{0,\nu} + \ldots\right] + \frac{1}{2(kT)^2}\left[\sum_\mu W_n^{(\mu,0)} B_{0,\mu} + \ldots\right]^2 - \ldots\right\}. \quad (5)$$

Finally, $\sigma_{\epsilon\tau}$ can be written as a power series in $\boldsymbol{B}_0$, as [21]

$$\sigma_{\epsilon\tau} = \sigma_{\epsilon\tau}^{(0)} + \frac{1}{3!}\sum_{\mu\nu} \sigma_{\epsilon\tau\mu\nu}^{(2)} B_{0,\mu} B_{0,\nu} + \ldots. \quad (6)$$

Only even powers appear due to time-reversal invariance.

The coefficients of the expansion (6) may now be solved for order by order from Eq. (4) [22]. For the field-independent shielding we obtain, as in Ref. [13],

$$\sigma_{\epsilon\tau}^{(0)} = \frac{1}{\gamma}\langle E^{(\epsilon,\tau)}\rangle_0 - \frac{1}{\gamma kT}\langle W^{(\epsilon,0)} E^{(0,\tau)}\rangle_0, \quad (7)$$

$$\langle A\rangle_0 = \frac{\sum_n \langle n|A|n\rangle \exp[-W_n(0,0)/kT]}{\sum_n \exp[-W_n(0,0)/kT]}. \quad (8)$$

A lengthy expression deposited in EPAPS [23] is obtained for the leading-order, quadratic $\boldsymbol{B}_0$-dependence.

At this point the separate notation for W and E is no longer required and these quantities may be associated with the ESR spin Hamiltonian

$$H_{\mathrm{ESR}} = -\gamma \boldsymbol{B}_0 \cdot (\boldsymbol{1} - \boldsymbol{\sigma}_{\mathrm{orb}}) \cdot \boldsymbol{I} + \mu_{\mathrm{B}} \boldsymbol{B}_0 \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{A} \cdot \boldsymbol{I} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}, \quad (9)$$

including the nuclear and electronic spin-Zeeman, as well as HFC and ZFS terms, in the respective order. $\boldsymbol{S}$ is the effective electron spin operator and μ_B is the Bohr magneton. $\langle E^{(\epsilon,\tau)}\rangle_0/\gamma$ in Eq. (7) for the field-independent shielding tensor $\boldsymbol{\sigma}^{(0)}$ may be identified with the orbital shielding tensor $\sigma_{\epsilon\tau}^{\mathrm{orb}}$, in complete analogy with the Ramsey theory for closed-shell systems. The temperature-dependent hyperfine shielding part becomes

$$-\frac{1}{\gamma kT}\langle E^{(\epsilon,0)} E^{(0,\tau)}\rangle_0 = -\frac{\mu_B}{\gamma kT}\sum_{ab} g_{\epsilon a} A_{b\tau}\langle S_a S_b\rangle_0, \quad (10)$$

involving, as compared to the doublet case reported in Refs. [13,15,17], a generalized product of $\boldsymbol{g}$ and $\boldsymbol{A}$.

In the $S = \frac{1}{2}$ case and in the absence of low-lying electronically excited states, it is trivial to evaluate $\langle S_a S_b\rangle_0 = \frac{1}{3}S(S+1)\delta_{ab}$, leading to earlier results [13,15]. In the presence of a nonvanishing ZFS tensor $\boldsymbol{D}$, the expectation value of the electron spin components is obtained with n in Eq. (8) labeling the eigenfunctions and eigenvalues of $\boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}$. $|n\rangle$ may be expanded in terms of the $2S+1$ eigenstates $|m_S\rangle$ of S_z as

$$\langle n|S_a S_b|n\rangle = \sum_{m_S, m_S'} C_{n,m_S'}^{\star} C_{n,m_S}\langle m_S'|S_a S_b|m_S\rangle. \quad (11)$$

This is a rigorous theory for the ground-state spin multiplet of arbitrary S, regardless of the spatial symmetry of the investigated molecular or solid-state system, such as axial [17]. In particular, we avoid using the spin susceptibility as an intermediate observable [5,17] and express $\boldsymbol{\sigma}$ solely in terms of the ESR spin Hamiltonian parameters. The essential point is that the expression for $\boldsymbol{\sigma}$ is always evaluated at $\boldsymbol{B}_0 = \boldsymbol{0}$, i.e., with the ZFS term alone determining the the Zeeman sublevels n. Erroneous use of finite $\boldsymbol{B}_0$, e.g., in an attempt to study the field dependence of $\boldsymbol{\sigma}$ (*vide infra*), would result in $\boldsymbol{\sigma}$ having an unphysical imaginary part. In that case special assumptions such as the coincidence of the principal axes of $\boldsymbol{g}$ and $\boldsymbol{D}$ in cylindrical spatial symmetry will render the error invisible. Our theory is genuinely free from this artifact. Any significant thermally excited states belonging to other than the ground-state Zeeman multiplet must naturally be accommodated in the summation over n.

$\boldsymbol{\sigma}^{\mathrm{orb}}$, $\boldsymbol{g}$, and $\boldsymbol{A}$ obtained at any consistent level of theory may be used in Eq. (7). In particular, Refs. [15,17] expand $\boldsymbol{g}$ and $\boldsymbol{A}$ as

$$\boldsymbol{g} = (g_e + \Delta g_{\mathrm{iso}})\mathbf{1} + \boldsymbol{\Delta}\tilde{\boldsymbol{g}} \tag{12}$$

$$\boldsymbol{A} = (A_{\mathrm{con}} + A_{\mathrm{PC}})\mathbf{1} + \boldsymbol{A}_{\mathrm{dip}} + \boldsymbol{A}_{\mathrm{dip},2} + \boldsymbol{A}_{\mathrm{as}}. \tag{13}$$

$\boldsymbol{g}$ consists of the $\mathcal{O}(\alpha^0)$ free-electron g_e factor and the $\mathcal{O}(\alpha^2)$ g shift tensor $\boldsymbol{\Delta g}$, the isotropic and anisotropic parts of which are Δg_{iso} and $\boldsymbol{\Delta}\tilde{\boldsymbol{g}}$, respectively. The HFC tensor contains the $\mathcal{O}(\alpha^2)$, NR contribution $A_{\mathrm{con}}\mathbf{1} + \boldsymbol{A}_{\mathrm{dip}}$ as well as the $\mathcal{O}(\alpha^4)$ relativistic SO term $A_{\mathrm{PC}}\mathbf{1} + \boldsymbol{A}_{\mathrm{dip},2} + \boldsymbol{A}_{\mathrm{as}}$ divided into the respective isotropic, symmetric anisotropic, and antisymmetric anisotropic contributions. Retaining up to $\mathcal{O}(\alpha^4)$ terms, the contributions arising from $\sum_{ab} g_{\epsilon a} A_{b\tau} \langle S_a S_b \rangle_0$ [Eq. (7)] are listed in Table I. The result generalizes the previously [15] presented doublet-case terms due to the fact that $\langle S_a S_b \rangle_0$ contains also an anisotropic symmetric contribution for higher multiplicities.

The result for the $\mathcal{O}(B_0^2)$ field dependence [23] consists of thermal averages of terms involving the leading-order field dependence of $\boldsymbol{\sigma}^{\mathrm{orb}}$ $[E^{(\epsilon\mu\nu,\tau)}]$, $\boldsymbol{g}$ $[W^{(\epsilon\mu\nu,0)}]$, $\boldsymbol{A}$ $[E^{(\mu\nu,\tau)}]$, and susceptibility $W^{(\mu\nu,0)}$. As alluded to above, it does not correspond to averaging the product of field-independent $\boldsymbol{g}$ and $\boldsymbol{A}$ at finite field, as in Ref. [17].

We interfaced the evaluation of Eq. (7) to the ORCA [24] molecular electronic structure package. The code uses Gaussian orbital basis sets and allows spin-unrestricted DFT calculation of the necessary $\boldsymbol{g}$ [25], $\boldsymbol{A}$ [26], and $\boldsymbol{D}$ [27] tensors using both generalized gradient approximation (GGA) and hybrid functionals. $\boldsymbol{\sigma}^{\mathrm{orb}}$ [15] was obtained using similar methods from GAUSSIAN 03 (Ref. [28]).

TABLE I. Order in the fine structure constant α and tensorial ranks of the hyperfine shielding terms in paramagnetic substances in both doublet and higher-multiplicity spin states.

			Tensorial rank[a]	
Term in $\sigma_{\epsilon\tau}$	Number	Order	$S = \frac{1}{2}$	$S > \frac{1}{2}$
$g_e A_{\mathrm{con}} \langle S_\epsilon S_\tau \rangle_0$	1	$\mathcal{O}(\alpha^2)$	0	0, 2
$g_e \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	2	$\mathcal{O}(\alpha^2)$	2	0, 2, 1
$g_e A_{\mathrm{PC}} \langle S_\epsilon S_\tau \rangle_0$	3	$\mathcal{O}(\alpha^4)$	0	0, 2
$g_e \sum_b A_{b\tau}^{\mathrm{dip},2} \langle S_\epsilon S_b \rangle_0$	4	$\mathcal{O}(\alpha^4)$	2	0, 2, 1
$g_e \sum_b A_{b\tau}^{\mathrm{as}} \langle S_\epsilon S_b \rangle_0$	5	$\mathcal{O}(\alpha^4)$	1	2, 1
$\Delta g_{\mathrm{iso}} A_{\mathrm{con}} \langle S_\epsilon S_\tau \rangle_0$	6	$\mathcal{O}(\alpha^4)$	0	0, 2
$\Delta g_{\mathrm{iso}} \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	7	$\mathcal{O}(\alpha^4)$	2	0, 2, 1
$A_{\mathrm{con}} \sum_a \Delta\tilde{g}_{\epsilon a} \langle S_a S_\tau \rangle_0$	8	$\mathcal{O}(\alpha^4)$	2, 1	0, 2, 1
$\sum_{ab} \Delta\tilde{g}_{\epsilon a} A_{b\tau}^{\mathrm{dip}} \langle S_a S_b \rangle_0$	9	$\mathcal{O}(\alpha^4)$	0, 2, 1	0, 2, 1

[a]Rank-0, 2, and 1 contributions correspond to the isotropic shielding constant and anisotropic symmetric as well as antisymmetric terms, respectively.

Calculations were carried out for the metallocenes [29] $NiCp_2$, $CrCp_2$ ($S = 1$), VCp_2 ($S = \frac{3}{2}$), and $MnCp_2$ ($S = \frac{5}{2}$) as well as a hypothetical, nonaxially symmetric chromium complex $[Cr(en)_2NH_3Br]^{2+}$ in the spin states $S = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$. The details and results have been deposited in EPAPS [23]. According to Fig. 1, the NR contact term is responsible for the experimental ^{13}C shift trends in metallocenes. The results for $\boldsymbol{\sigma}^{\mathrm{orb}}$ and the hyperfine terms that contribute to the isotropic shift in the doublet case (Table I), are in good qualitative agreement [23] with the approximate theory and DFT calculations of Ref. [17]. Hence, the presently generalized, nondiagonal $\langle \boldsymbol{SS} \rangle_0$ in Eq. (10) does not dramatically change terms 1, 3, 6, and 9. The range of DFT data obtained [23] indicates that the accuracy of the current functionals does not yet allow a one-to-one comparison with the experiment. More importantly, the "nondoublet" contributions to the isotropic shift (terms 2, 4, 7, and 8) are nonvanishing and amount up to a few ppm each, equally large as the pseudocontact term 9. In fact, the generalization of the NR dipolar shift (term 2) equals -196 ppm for $^3NiCp_2$ as a result of the large anisotropy of $\boldsymbol{D}$ at the PBE0 level [23]. Corresponding changes are seen in the shielding anisotropy [23], where the nondoublet terms (1, 3, and 6) contribute due to the ZFS interaction.

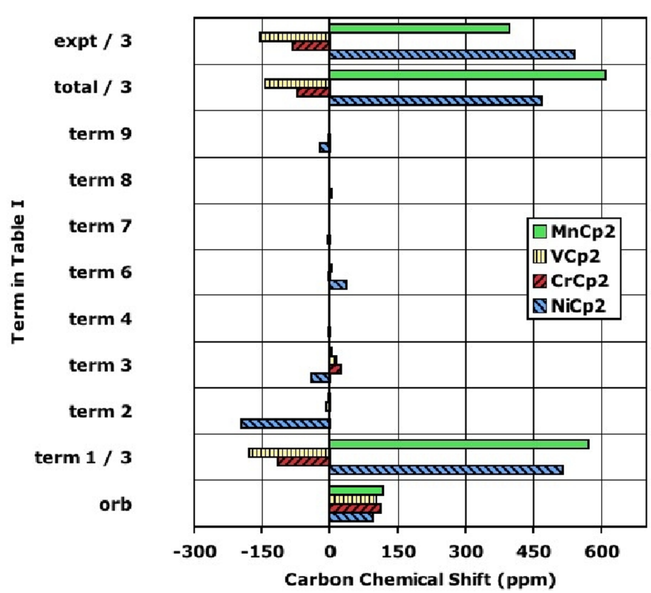

FIG. 1 (color online). Calculated (PBE0 [30]) ^{13}C NMR chemical shift contributions in the metallocenes $^3NiCp_2$, $^3CrCp_2$, $^4VCp_2$, and $^6MnCp_2$ at 298 K, averaged over the equivalent nuclei and numbered according to Table I. The NR contact shift (term 1) as well as the total and experimental shifts have been divided by three in the figure. Each experimental datum is an average of the solution [31–33] and solid-state [34,35] results.

The effect of spatial symmetry can be assessed by imposing artificially coaxial $\boldsymbol{g}$ and $\boldsymbol{D}$ for the nonaxial $[Cr(en)_2NH_3Br]^{2+}$. Compared to the full analysis [23], axial symmetry increases the total $^{13}C_{11}$ chemical shift by 0.5 ppm for the quartet state, due to changes in hyperfine terms 2, 4, and 7–9. The almost orbitally degenerate $S = \frac{5}{2}$ state experiences a larger change of 44 ppm.

In conclusion, we have presented a systematic and rigorous first principles theory for the PNMR nuclear shielding $\boldsymbol{\sigma}$ in arbitrary spin state and spatial symmetry in terms of the ESR spin Hamiltonian parameters and not involving spin susceptibility. For higher than doublet states, the resulting expression for the field-independent $\boldsymbol{\sigma}^{(0)}$ contains the product of the electronic Zeeman and nuclear HFC interactions in the eigenstates of the ZFS Hamiltonian. The leading-order, quadratic magnetic-field-dependence of $\boldsymbol{\sigma}$ involves the field-dependence coefficients of the underlying g, $\boldsymbol{A}$, orbital shielding, and susceptibility tensors, and is to be evaluated in the limit of vanishing $\boldsymbol{B}_0$, similarly to $\boldsymbol{\sigma}^{(0)}$. DFT calculations of PNMR chemical shifts in high-spin metallocenes indicate significant contributions to chemical shift and shielding anisotropy not present in doublet systems. Assumption of axial symmetry is also shown to potentially lead to errors in the analysis of nonaxial systems. We believe that the present theory will be valuable in the prediction and analysis of PNMR data in various fields both in solid state and molecular science.

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