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Alessandro Soncini, and Willem Van den Heuvel

Citation: The Journal of Chemical Physics **138**, 021103 (2013); doi: 10.1063/1.4775809
View online: https://doi.org/10.1063/1.4775809
View Table of Contents: http://aip.scitation.org/toc/jcp/138/2
Published by the American Institute of Physics

Communication: Paramagnetic NMR chemical shift in a spin state subject to zero-field splitting

Alessandro Soncini[a] and Willem Van den Heuvel
School of Chemistry, The University of Melbourne, Victoria 3010, Australia

(Received 16 December 2012; accepted 30 December 2012; published online 10 January 2013)

We derive a general formula for the paramagnetic NMR nuclear shielding tensor of an open-shell molecule in a pure spin state, subject to a zero-field splitting (ZFS). Our findings are in contradiction with a previous proposal. We present a simple application of the newly derived formula to the case of a triplet ground state split by an easy-plane ZFS spin Hamiltonian. When kT is much smaller than the ZFS gap, thus a single non-degenerate level is thermally populated, our approach correctly predicts a temperature-independent paramagnetic shift, while the previous theory leads to a Curie temperature dependence. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4775809]

The nuclear magnetic resonance (NMR) chemical shift in molecular species with an open-shell electronic structure is mainly governed by a term known as the "paramagnetic shift," a temperature-dependent term arising from the internal magnetic fields generated by the unpaired spin and unquenched orbital moments of the thermally populated Zeeman-split electronic degenerate ground state. Despite the increasingly central role played by paramagnetic NMR in the elucidation of the structure of metallo-proteins,[1] and in the investigation of the spin dynamics in novel magnetic materials,[2] only quite recently rigorous theories have been developed for the *ab initio* calculation of the paramagnetic NMR chemical shift.[3–6]

Of particular relevance in this respect is the work of Moon and Patchkovskii,[3] that of Pennanen and Vaara,[4] and that of Van den Heuvel and Soncini.[5,6] Moon and Patchkovskii[3] derived an expression for the paramagnetic shielding tensor of a spin doublet state in terms of its g- and A-tensors. This treatment was extended by Pennanen and Vaara[4] to arbitrary spin states, in the limit of weak spin-orbit coupling, and later generalised by us to a theory that is valid for arbitrary strength of spin-orbit coupling, and arbitrary size of the degenerate manifold.[5,6] In Ref. 4 the authors also proposed a general formula for the paramagnetic shielding tensor of a spin state subject to zero-field splitting (see Eq. (10) in Ref. 4). In this Communication we present an alternative derivation of this formula, based on the general theory of NMR chemical shift we have recently developed.[5,6] Interestingly, we obtain a result that differs from that proposed in Ref. 4. In the last part of this Communication we point out the difference, and argue for the correctness of our proposal by way of a simple example.

We consider a molecule in the frozen nuclei approximation (also known as the "solid state limit" of NMR[7,8]). Assuming that the zero-field splitting in the degenerate ground state is much smaller than the energy separating the ground state from excited states and assuming that these excited states are not thermally accessible, the shielding tensor $\boldsymbol{\sigma}$ can be divided in two parts: $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{p}} + \boldsymbol{\sigma}^{\mathrm{r}}$, the first part representing the "paramagnetic shift," which is due entirely to the (quasi-)degenerate ground state and which can be calculated from knowledge of the ground-state wave functions only; the second part representing the "Ramsey term," which is the only term in case of a non-degenerate ground state. These terms are distinguished by the fact that in the limit of vanishing zero-field splitting of the ground state $\boldsymbol{\sigma}^{\mathrm{r}}$ is temperature independent while $\boldsymbol{\sigma}^{\mathrm{p}}$ is proportional to $1/T$. The present Communication will consider the effect of a zero-field splitting on $\boldsymbol{\sigma}^{\mathrm{p}}$.

The electronic Hamiltonian consists of two parts: $H = H_0 + V$. Here V is the perturbation due to the applied magnetic field and the magnetic field arising from the magnetic moments of the nuclei. H_0 is the Hamiltonian in the absence of these fields, but including all other relevant electronic interactions. This means that H_0 includes those interactions that are responsible for the zero-field splitting of the ground state. If the ground manifold consists of ω states $|\psi_{\lambda a}\rangle$, eigenstates of H_0 with energies E_λ, an expression of H_0 valid within this manifold is

$$H_0 = \sum_{\lambda,a}^{\omega} E_\lambda \, |\psi_{\lambda a}\rangle\langle\psi_{\lambda a}|.$$

Here the index λ counts the energy levels of the manifold, and the index a labels a basis in case E_λ is degenerate. For our present purpose, the term V consists of two perturbations that combined give rise to paramagnetic shielding: the electronic Zeeman interaction $V_{\mathrm{z}} = -\mathbf{m}\cdot\mathbf{B}$, and the hyperfine coupling $V_{\mathrm{hf}} = \boldsymbol{\mathcal{F}}\cdot\boldsymbol{\mu}$, where $\mathbf{m}$ is the electronic magnetic moment, $\mathbf{B}$ is the applied field, $\boldsymbol{\mathcal{F}}$ is the hyperfine field, and $\boldsymbol{\mu}$ is the nuclear magnetic moment.[9]

A general formula for the shielding tensor was proposed in Ref. 6, to which the reader is referred for more details:

$$\sigma_{ij} = \left.\frac{\partial^2 F}{\partial B_i \partial \mu_j}\right|_0. \tag{1}$$

Here F is the electronic Helmholtz free energy of the full Hamiltonian $H = H_0 + V$. Evaluation of Eq. (1) and retention of the temperature-dependent paramagnetic part only

[a]Electronic mail: asoncini@unimelb.edu.au.

lead to[6]

$$\sigma^{\mathrm{p}}_{ij} = \left\langle \int_0^\beta e^{wH_0} m_i e^{-wH_0} \mathcal{F}_j dw \right\rangle_0, \tag{2}$$

where $\langle\cdot\rangle_0$ stands for the thermal average in the canonical ensemble of H_0 and $\beta = 1/kT$. The expression Eq. (2) can now be easily integrated[6] leading to an exact sum-over-states formula:

$$\sigma^{\mathrm{p}}_{ij} = \frac{1}{Q_0}\sum_\lambda e^{-\beta E_\lambda}\left[\beta \sum_{a,a'} \langle\psi_{\lambda a}|m_i|\psi_{\lambda a'}\rangle\langle\psi_{\lambda a'}|\mathcal{F}_j|\psi_{\lambda a}\rangle + 2\sum_{\lambda'\neq\lambda}\sum_{a,a'} \frac{\langle\psi_{\lambda a}|m_i|\psi_{\lambda' a'}\rangle\langle\psi_{\lambda' a'}|\mathcal{F}_j|\psi_{\lambda a}\rangle}{E_{\lambda'} - E_\lambda}\right]. \tag{3}$$

Here $Q_0 = \sum_{\lambda,a} e^{-\beta E_\lambda}$ is the partition function.

Our aim here is to rewrite Eq. (3) for the case of a pure spin ground multiplet split as a result of spin-orbit coupling. In molecules composed of light atoms the spin-orbit coupling is often a small perturbation, whose effect can be treated to good accuracy in the lowest order of perturbation theory. It is then a well known result[10] that such treatment leads to a spin Hamiltonian:

$$H = \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} + \mu_{\mathrm{B}}\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}.$$

In the notation used in this Communication, we thus have

$$H_0 = \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}, \quad m_i = -\mu_{\mathrm{B}}\sum_j g_{ij}S_j,$$

$$\mathcal{F}_i = \frac{1}{g_I\mu_{\mathrm{N}}}\sum_j A_{ji}S_j,$$

where the indices label the Cartesian directions x, y, z and we have used $\boldsymbol{\mu} = g_I\mu_{\mathrm{N}}\mathbf{I}$ to convert between the nuclear magnetic moment and the nuclear spin.

The states to be used in Eq. (3) can then be easily found by diagonalizing H_0 in the space of $2S+1$ spin basis states $|SM\rangle$. Naturally the eigenfunctions will depend on the zero-field splitting tensor $\mathbf{D}$. For the moment we leave the latter unspecified and denote the eigenfunctions generically by $|S\,\lambda a\rangle$. Now applying Eq. (3) gives

$$\sigma^{\mathrm{p}}_{ij} = -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{1}{Q_0}\sum_{kl} g_{ik}A_{lj}\sum_\lambda e^{-\beta E_\lambda} \times\left[\beta\sum_{a,a'}\langle S\,\lambda a|S_k|S\,\lambda a'\rangle\langle S\,\lambda a'|S_l|S\,\lambda a\rangle + 2\sum_{\lambda'\neq\lambda}\sum_{a,a'}\frac{\langle S\,\lambda a|S_k|S\,\lambda' a'\rangle\langle S\,\lambda' a'|S_l|S\,\lambda a\rangle}{E_{\lambda'} - E_\lambda}\right]. \tag{4}$$

Equation (4) represents the main result of this Communication.

Equation (4) has to be compared with the formula proposed by Pennanen and Vaara in Ref. 4. Their Eq. (10) reads

$$\sigma^{\mathrm{p}}_{ij} = -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{1}{kT}\sum_{kl} g_{ik}A_{lj}\langle S_k S_l\rangle_0, \tag{5}$$

which can be written more explicitly by performing the thermal average over the eigenfunctions of H_0:

$$\begin{aligned}\sigma^{\mathrm{p}}_{ij} &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{\beta}{Q_0}\sum_{kl} g_{ik}A_{lj}\sum_\lambda e^{-\beta E_\lambda}\sum_a\langle S\,\lambda a|S_k S_l|S\,\lambda a\rangle \\ &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{\beta}{Q_0}\sum_{kl} g_{ik}A_{lj}\sum_\lambda e^{-\beta E_\lambda} \\ &\quad\times\sum_{\lambda',a,a'}\langle S\,\lambda a|S_k|S\,\lambda' a'\rangle\langle S\,\lambda' a'|S_l|S\,\lambda a\rangle.\end{aligned} \tag{6}$$

Clearly, Eqs. (4) and (6) are not equal. In fact, only in the special case $\mathbf{D} = 0$, i.e., in the absence of zero-field splitting, the two expressions Eqs. (4) and (6) lead to the same formula for the paramagnetic shielding tensor:

$$\boldsymbol{\sigma}^{\mathrm{p}} = -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{1}{kT}\frac{S(S+1)}{3}\mathbf{gA}.$$

In every other case we argue that the correct formula is given by Eq. (4). Note that σ^{p}_{ij} can be expressed in a form that is only similar to Eq. (5), if we take the thermal average of a different operator:

$$\sigma^{\mathrm{p}}_{ij} = -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{1}{kT}\sum_{kl} g_{ik}A_{lj}\left\langle\int_0^\beta e^{\tau H_0}S_k e^{-\tau H_0}S_l\,d\tau\right\rangle_0. \tag{7}$$

Finally, to illustrate the difference between the results presented in this Communication and previous works, and to argue for the correctness of our proposal, we consider the simple but very common case of a triplet state with an axial zero-field splitting $H_0 = DS_z^2$, and axial g- and A-tensors:

$$\mathbf{g} = \begin{pmatrix} g_\perp & 0 & 0\\ 0 & g_\perp & 0\\ 0 & 0 & g_\parallel\end{pmatrix}, \qquad \mathbf{A} = \begin{pmatrix} A_\perp & 0 & 0\\ 0 & A_\perp & 0\\ 0 & 0 & A_\parallel\end{pmatrix}.$$

The eigenstates of H_0 are simply the $|SM\rangle$ (with $S=1$), which we further denote by their M value alone. Thus we have two energy levels: $|0\rangle$ at energy 0 and $|\pm 1\rangle$ at energy D. On evaluating the newly proposed Eq. (4) we find

$$\begin{aligned}\sigma^{\mathrm{p}}_\perp &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{2g_\perp A_\perp}{D}\frac{1-e^{-\beta D}}{1+2e^{-\beta D}},\\ \sigma^{\mathrm{p}}_\parallel &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{2g_\parallel A_\parallel}{kT}\frac{e^{-\beta D}}{1+2e^{-\beta D}}.\end{aligned} \tag{8}$$

Previously proposed Eq. (5) on the other hand predicts

$$\begin{aligned}\sigma^{\mathrm{p}}_\perp &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{g_\perp A_\perp}{kT}\frac{1+e^{-\beta D}}{1+2e^{-\beta D}},\\ \sigma^{\mathrm{p}}_\parallel &= -\frac{\mu_{\mathrm{B}}}{g_I\mu_{\mathrm{N}}}\frac{2g_\parallel A_\parallel}{kT}\frac{e^{-\beta D}}{1+2e^{-\beta D}},\end{aligned} \tag{9}$$

which disagrees with Eq. (8) on the value of $\sigma^{\mathrm{p}}_\perp$. Note that $\sigma^{\mathrm{p}}_\parallel$ is the same in both theories only because of the specific axial symmetry of this system, implying that the ZFS Hamiltonian commutes with the component of the spin operator along the axial direction. That the formula for $\sigma^{\mathrm{p}}_\perp$ in Eq. (9) must be wrong can be deduced by considering the low-temperature limit $kT \ll D$ for $D > 0$ (easy-plane ZFS anisotropy). In

this situation the ground state is $|0\rangle$ and is the only populated state of the system. Therefore, the shielding should be temperature-independent. Equation (9), however, predicts a Curie behaviour in this limit:

$$\sigma_{\perp}^{\mathrm{p}} \to -\frac{\mu_{\mathrm{B}}}{g_I \mu_{\mathrm{N}}} \frac{g_{\perp} A_{\perp}}{kT}.$$

The correct limit is obtained from Eq. (8) and is indeed a constant:

$$\sigma_{\perp}^{\mathrm{p}} \to -\frac{\mu_{\mathrm{B}}}{g_I \mu_{\mathrm{N}}} \frac{2 g_{\perp} A_{\perp}}{D}.$$

A.S. acknowledges support from the Early Career Researcher Grant (ECR 2012) from the University of Melbourne.

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