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On the relation between a common gauge origin formulation and the GIAO formulation of the NMR shielding tensor

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Abstract. In this article the formal equivalence between the "gauge including atomic orbitals" (GIAO) and the simpler common gauge (cg) formulations of the nuclear magnetic resonance (NMR) shielding tensor is proven. To be able to give this proof, one has to assume exactly solved zeroth order quantum mechanical equations and complete basis sets. The proof of the equivalence has been known in the literature for some time (e.g. S.T. Epstein 'The variation method in quantum chemistry', Academic Press, 1974). However, our approach has the advantage that, by comparing the GIAO and cg methods, it provides insight into the para- and diamagnetic contributions of the shielding. Thus, it yields justification for qualitative analysis schemes that have been used to explain trends in chemical shifts. Our formal proof is based on density functional theory. However, it is argued that very similar arguments should apply to other levels of theory as well.

Key words: NMR shielding – Gauge including atomic orbitals – GIAO – Common gauge origin – Density functional theory

Introduction

The shielding (chemical shift) tensor of nuclear magnetic resonance (NMR) spectroscopy is one of the most important spectroscopic properties in chemistry [1]. The theoretical description of the shielding based on quantum mechanical methods has seen a strong development within the last decade or so [2, 3, 4].

Almost all modern approaches to the shielding use some method with a distributed origin for the gauge of the magnetic field. This is necessary to avoid the – nonphysical – dependence of calculated properties on the coordinate origin or, more generally, on the gauge of the magnetic vector potential. This dependence vanishes, of course, if the quantum mechanical equations have been solved exactly. It can, however, have serious consequences if this is not the case, for instance for finite basis sets.

One of the most popular and at the same time most accurate methods for avoiding this gauge dependence is the so-called 'gauge including atomic orbitals' (GIAO, originally known as 'gauge *invariant* atomic orbitals') method [5, 6]. This method goes back to London [7], and the GIAOs are sometimes called 'London orbitals'.

The aim of the present paper is to show and discuss the equivalence of the GIAO formulation of the shielding with the simpler and more straightforward common gauge (cg) approach. This equivalence holds only in the limit of infinite basis sets and exactly solved zeroth order (magnetic field free) quantum mechanical equations, which we will assume.

In the following we will restrict ourselves to the shielding tensor based on uncoupled density functional theory (DFT) [3, 8, 9, 10]. However, an extension to other levels of theory should be possible, and the approach should be very similar in these cases. Hence, the results of the given paper should be much more generally applicable.

The formal equivalence of the GIAO and cg formulations of the shielding has already been shown for the Hartree-Fock approximation some time ago. For instance, Epstein [11] discusses it by noting that both approaches become equivalent to the exact Hartree-Fock solution in the limit of complete basis sets. Of course, for DFT, a very similar path could be followed to establish the proof. Our approach in this paper is, however, different. Here we discuss and prove the equivalence of the two formulations using the respective analytical expressions of the shielding tensor. This approach has the disadvantage that it is impossible to transfer directly its results to other magnetic properties. It has, however, the clear advantage that it yields a deeper understanding of the different terms that are present in the GIAO method. Such an understanding is helpful if one attempts to

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relate calculated shieldings to the electronic structure of the molecule at hand, and to base qualitative and quantitative interpretations on these relationships [10, 12, 13, 14, 15, 16, 17].

Theory, derivations

In the following, we will use atomic units throughout. The speed of light, c, is in these units equal to the inverse of the fine structure constant, or approximately equal to 137.

Throughout this article we will understand products of two vectors (for instance "**rs**") as tensor products that result in a second-rank tensor; dot products and cross products will be marked explicitly (as "$\mathbf{a} \cdot \mathbf{b}$" and "$\mathbf{c} \times \mathbf{d}$", respectively).

Kohn-Sham DFT

As mentioned in the introduction, we will base the following discussions on non-relativistic Kohn-Sham DFT [18, 19, 20]. In this section, a brief introduction to DFT shall be given. It will be restricted to the equations that are necessary for the subsequent discussions.

The fundamental property in DFT is the electronic density, ρ. DFT is based on an exact expression for the total electronic energy of the n-electron system as a functional of the density [18, 20]:

$$E[\rho] = \sum_i^n \int d\mathbf{r}_1 \Psi_i^* \left(\frac{\mathbf{p}^2}{2} + V_N(\mathbf{r}) \right) \Psi_i + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_{XC}[\rho] \quad (1)$$

where $\mathbf{p}$ is the electronic momentum operator. As mentioned, the energy $E[\rho]$ is a functional of the electron density, ρ, Eq. (1). Further, the $\{\Psi_i\}$ form a set of n orthonormal one-electron functions, called the Kohn-Sham (KS) orbitals. They are usually expanded into a set of $2M$ basis functions $\{\chi_\mu\}$ with expansion coefficients $\{d_{\mu i}\}$:

$$\Psi_i = \sum_\mu^{2M} d_{\mu i} \chi_\mu \quad (2)$$

We assume these basis functions to be atomic orbitals (AO). Each AO is centred on one particular nucleus. The density follows from the KS orbitals [19, 20] as

$$\rho = \sum_i^n \Psi_i^* \Psi_i \quad (3)$$

The first term in Eq. (1) describes the interaction of the electronic density with the external nuclear potential, $V_N(\mathbf{r})$, as well as the kinetic energy of a model system with exactly the same electron density, but without electron-electron interactions [18, 20]. The next term in Eq. (1) describes the Coulomb interaction of the electron density with itself. Finally, $E_{XC}[\rho]$ is the exchange-correlation (XC) energy functional.

The energy expression in Eq. (1) allows the derivation of effective one-electron equations for the KS orbitals, the KS equations [19, 20]

$$f\Psi_i = \varepsilon_i \Psi_i \ , \quad (4)$$

where

$$f(\mathbf{r}) = \frac{\mathbf{p}^2}{2} + V_N(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{XC}(\rho, \mathbf{r}) = \frac{\mathbf{p}^2}{2} + V_{KS}(\mathbf{r}) \quad (5)$$

and

$$V_{XC}(\rho, \mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho} \quad (6)$$

The XC potential V_{XC} of Eq. (6) is the functional derivative of the XC energy with respect to the electron density. The third term in Eq. (5) is the Hartree (or Coulomb) potential, i.e. the electrostatic potential of the electron density. In the second equation at Eq. (5), we have combined the XC, Coulomb, and nuclear potentials into the total KS potential V_{KS}. The KS equations, Eqs. (5) and (6), have to be solved self-consistently for the KS orbitals. Equations (4) and (5) apply in a similar form to Hartree-Fock theory if one replaces the XC potential by the exchange potential.

DFT-GIAO shielding tensor

In the following, we shall state the formulas for the (all-electron) DFT-GIAO shielding tensor. We will avoid any derivations; these can be found in the original literature [8, 10, 21, 22, 23, 24, 25] or the reviews [3, 4, 12].

A GIAO $\chi_\alpha(\mathbf{B}, \mathbf{r})$ follows from the corresponding field-free, zeroth order basis function $\chi_\alpha(\mathbf{r})$ (Eq. 2) by

$$\chi_\alpha(\mathbf{B}, \mathbf{r}) = \exp\left[-\frac{i}{2c} (\mathbf{B} \times \mathbf{R}_\alpha) \cdot \mathbf{r} \right] \chi_\alpha(\mathbf{r}) \quad (7)$$

Thus, a field-dependent phase factor is assigned to each basis function. This removes any dependence of expectation values on the gauge origin.

The shielding tensor, σ, a second rank tensor, is usually divided into its dia- and paramagnetic parts

$$\sigma = \sigma^d + \sigma^p \quad (8)$$

where one requires the diamagnetic part to depend on the zero-order, unperturbed density only. This separation is, in general, not unique because only the total shielding is an observable. It can, however, be made unique within a given approach. For GIAO, this is achieved by the additional requirement that the dia- and paramagnetic shieldings be gauge invariant by themselves [26]. Then we find for the DFT-GIAO shielding

$$\sigma_{GIAO} = \sigma^d_{GIAO} + \sigma^p_{GIAO} \quad (9)$$

where (*st* tensor component)

$$\sigma^{d}_{GIAO,st} = \sigma^{d,1}_{st} + \frac{1}{c}\sum_{i}^{occ} n_i \sum_{\lambda v}^{2M} d_{\lambda i} d_{vi} \times \left\langle \chi_\lambda \left| \left[\frac{\mathbf{r}_v}{2} \times (\mathbf{R}_v - \mathbf{R}_\lambda) \right]_s h_i^{01} \right| \chi_v \right\rangle \quad (10)$$

and

$$\sigma^{p}_{st} = \frac{1}{c}\sum_{i}^{occ} n_i \sum_{\lambda,v}^{2M} d_{\lambda i} d_{vi} \left\langle \chi_\lambda \left| \frac{1}{2} (\mathbf{R}_\lambda \times \mathbf{R}_v)_s h_t^{01} \right| \chi_v \right\rangle + \sigma^{p,oc-oc}_{st} + \sigma^{p,oc-vir}_{st} \quad (11)$$

The different contributions are given by

$$\sigma^{d,1}_{st} = \frac{1}{c^2}\sum_{i}^{occ} n_i \sum_{v}^{2M} d_{vi} \times \left\langle \Psi_i \left| \frac{1}{2r_N^3} (\mathbf{r}_N \cdot \mathbf{r}_v \delta_{st} - r_{N_s} \cdot r_{v_t}) \right| \chi_v \right\rangle \quad (12)$$

$$\sigma^{p,oc-oc} = \sum_{i,j}^{occ} n_i \mathbf{S}^1_{ij} \langle \Psi_i | \mathbf{h}^{01} | \Psi_j \rangle \quad (13)$$

and

$$\sigma^{p,oc-vir} = 2\sum_{i}^{occ} n_i \sum_{a}^{vir} \mathbf{u}^1_{ai} \langle \Psi_i | \mathbf{h}^{01} | \Psi_a \rangle \quad (14)$$

The last two equations describe the paramagnetic occupied-occupied and occupied-virtual shielding contributions, respectively. In Eqs. (13) and (14)

$$\mathbf{u}^1_{ai} = \frac{\mathbf{F}^1_{ai} - \varepsilon^0_i \mathbf{S}^1_{ai}}{\varepsilon^0_i - \varepsilon^0_a} \quad (15)$$

and

$$\mathbf{S}^1_{pj} = \frac{1}{c}\sum_{\lambda,v}^{2M} d_{\lambda p} d_{vj} \left\langle \chi_\lambda \left| \frac{\mathbf{r}}{2} \times (\mathbf{R}_v - \mathbf{R}_\lambda) \right| \chi_v \right\rangle \quad (16)$$

are the first order occupied-virtual and occupied-occupied coefficients, respectively. They have three Cartesian components each. Further,

$$\mathbf{h}^{01} = \frac{i}{c}\frac{\mathbf{r}_N}{r_N^3} \times \mathbf{p} \quad (17)$$

is the first order magnetic operator and

$$\mathbf{F}^1_{ai} = \frac{1}{c}\sum_{v}^{2M} d_{vi} \left\langle \Psi_a \left| \frac{-\mathbf{r}_v}{2} \times \nabla \right| \chi_v \right\rangle + \frac{1}{c}\sum_{\lambda,v}^{2M} d_{\lambda a} d_{vi} \times \left\langle \chi_\lambda \left| \left[\frac{\mathbf{r}}{2} \times (\mathbf{R}_v - \mathbf{R}_\lambda) f(0,\mathbf{r}) \right] \right| \chi_v \right\rangle \quad (18)$$

where $f(0, \mathbf{r})$ is the field-free Kohn-Sham operator of Eq. (5). In Eqs. (10), (11), (12), (13), (14), (15), (16), (17) and (18), the following notation has been used: n_i is the occupation number of the MO Ψ_i ($n_i = 2$ for occupied MOs in the closed shell case), $\mathbf{R}_v$ is the position of the nucleus where the AO χ_v is located, $\mathbf{r}_N = \mathbf{r} - \mathbf{R}_N$ is the electronic position operator relative to the NMR active nucleus N, likewise $\mathbf{r}_\lambda = \mathbf{r} - \mathbf{R}_\lambda$ is the electronic position relative to the centre of the AO χ_λ, and the $d_{\lambda a}$ are the zeroth-order expansion coefficients of Eq. (2).

For the sake of this article, let us rewrite σ_{GIAO} of Eq. (9) as

$$\sigma_{GIAO} = \sigma^{d,1} + \sigma^{p,oc-oc} + \sigma^{p,oc-vir} + \mathbf{T} \quad (19)$$

where we have combined the second term in Eq. (10) with the first term in Eq. (11) to yield a "rest", **T**. This "rest", a second rank tensor, is normally split up into its diamagnetic and paramagnetic parts, according to Eqs. (10) and (11), respectively [26]. It is recombined here to

$$\mathbf{T} = \frac{1}{c}\sum_{i}^{occ} n_i \sum_{\mu,v}^{2M} d_{\mu i} d_{vi} \left\langle \chi_\mu \left| \left[\frac{\mathbf{r}}{2} \times (\mathbf{R}_v - \mathbf{R}_\mu) \right] \mathbf{h}^{01} \right| \chi_v \right\rangle \quad (20)$$

Note that the different vectors in Eq. (20), but also in Eqs. (13) and (14) are connected by tensor products.

The discussion will now mainly focus on the last term, **T** of Eq. (20). However, before that we wish to introduce, in the next section, the common gauge origin formulation of the shielding [26].

Shielding tensor, common gauge formulation

The shielding tensor

$$\sigma_{cg} = \sigma^{d}_{cg} + \sigma^{p}_{cg} \quad (21)$$

is much simpler in the common gauge (cg) formulation [26] than in the GIAO scheme, Eqs. (9), (10), (11), (12), (13), (14), (15), (16), (17), (18), (19) and (20). Thus, we have

$$\sigma^{p}_{cg} = 2\sum_{i}^{occ} n_i \sum_{a}^{vir} \mathbf{u}^{1,cg}_{ai} \langle \Psi_i | \mathbf{h}^{01} | \Psi_a \rangle \quad (22)$$

and (*st* tensor component)

$$\sigma^{d,st}_{cg} = \frac{1}{c^2}\sum_{i}^{occ} n_i \left\langle \Psi_i \left| \frac{1}{2r_N^3} (\mathbf{r}_N \cdot \mathbf{r}\delta_{st} - r_{N_s} \cdot r_t) \right| \Psi_i \right\rangle \quad (23)$$

where

$$\mathbf{u}^{1,cg}_{ai} = \frac{\mathbf{F}^{1,cg}_{ai}}{\varepsilon^0_i - \varepsilon^0_a} \quad (24)$$

and

$$\mathbf{F}^{1,cg}_{ai} = \frac{1}{c}\left\langle \Psi_a \left| \left[-\frac{\mathbf{r}}{2} \times \nabla \right] \right| \Psi_i \right\rangle \ . \quad (25)$$

Note that the cg paramagnetic shielding tensor, σ^{p}_{cg}, has exclusively occupied-virtual terms, Eq. (22).

Next we intend to show the equivalence of the two formulations, starting from the GIAO scheme. The derivation will be based on a completeness relation for the zero order, unperturbed Kohn-Sham orbitals of Eq. (4).

Completeness relation. The "rest" term of the GIAO formulation

We note that the GIAO "rest" term, **T** of Eq. (20) resembles in its structure $\sigma^{p,oc-oc}$ of Eq. (13) and also $\sigma^{p,oc-vir}$ of Eq. (14). However, **T** consists so far of only one integral, while the said paramagnetic tensors contain products of two integrals. Our strategy will be to insert a unity operator into **T** by means of the completeness relation. In this way we will change **T** to contain a sum over products of two integrals.

A completeness relation [27] for the orthonormal Kohn-Sham orbitals $|\Psi_p\rangle$ (see Kohn-Sham DFT above) is given by

$$\hat{I} = \sum_{p}^{all} |\Psi_p\rangle\langle\Psi_p| \tag{26}$$

The unity operator $\hat{I}$ of Eq. (26) contains an infinite sum that runs over *"all = occupied + virtual"* zero order Kohn-Sham orbitals. The relation in Eq. (26) is only true in the limit of complete basis sets and exactly solved Kohn-Sham equations, Eq. (4), which we will assume.

To be able to apply this equation we have to reformulate **T** of Eq. (20). This is required to enable us to separate the "p" sum (Eq. 26) from the "μ" and "v" sums of Eq. (20). For this purpose, we split **T** as follows:

$$\mathbf{T} = \mathbf{T}_\mu + \mathbf{T}_v \tag{27}$$

$$= \frac{1}{c}\sum_{i}^{occ} n_i \sum_{\mu}^{2M} d_{\mu i}\left\langle \chi_\mu \middle| \left[\frac{\mathbf{r}}{2} \times (-\mathbf{R}_\mu)\right]\mathbf{h}^{01}\middle|\Psi_i\right\rangle + \frac{1}{c}\sum_{i}^{occ} n_i \sum_{v}^{2M} d_{vi}\left\langle \Psi_i \middle| \left[\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right]\mathbf{h}^{01}\middle|\chi_v\right\rangle \tag{28}$$

It turns out that $\mathbf{T}_\mu$, the first term in Eqs. (27) and (28), is already in a form to apply the completeness relation of Eq. (26). In this term, both the vector $\mathbf{R}_\mu$ and the atomic orbital $\langle\chi_\mu|$ would end up within the same integral after the transformation, and the sums over the molecular orbitals "p" and over the coefficients μ can be separated. However, the second term in Eqs. (26) and (27), $\mathbf{T}_v$, needs further treatment first.

To reformulate $\mathbf{T}_v$, let us consider for the moment just one integral out of the double sum of Eq. (28). Thus, we define a new second-rank tensor

$$\mathbf{I}_{iv} = \left\langle \Psi_i \middle| \left[\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right]\mathbf{h}^{01}\middle|\chi_v\right\rangle \tag{29}$$

where the operator $\mathbf{h}^{01}$ has been defined earlier in Eq. (17). Note that this operator is anti-Hermitian in the given form. Then (*st* tensor component)

$$I_{iv}^{st} = -\frac{1}{c}\left\langle \Psi_i \middle| \left[\left(\frac{\mathbf{r}_N}{r_N^3} \times \nabla\right)_t \left(\frac{1}{2}\overset{\downarrow}{\mathbf{r}} \times \mathbf{R}_v\right)_s\right]\chi_v\middle|\right\rangle - \left\langle \chi_v \middle| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right)_s h_t^{01}\middle|\Psi_i\right\rangle \tag{30}$$

$$= I_{iv}^{dia,st} + I_{iv}^{para,st} \tag{31}$$

The array ("$\overset{\downarrow}{\mathbf{q}}$") in the first term of Eq. (30) marks where the differential operator works. An operator without this array is always thought to work on all terms to the right of it. Equations (30) and (31) define the dia- and paramagnetic parts of $\mathbf{I}_{iv}$.

Diamagnetic shielding

We shall now treat $\mathbf{I}_{iv}^{dia}$ of Eqs. (30) and (31) a little further. We note also that $\mathbf{I}_{iv}^{para}$ has the same form as $\mathbf{T}_\mu$ of Eqs. (27) and (28). It shall turn out shortly that the part of **T** containing $\mathbf{I}_{iv}^{dia}$ will combine with the first part of the GIAO diamagnetic shielding tensor, Eq. (12), to result in the diamagnetic shielding tensor of the common gauge formulation, Eq. (23).

The operator of $\mathbf{I}_{iv}^{dia}$ is (in components)

$$-(\mathbf{r}_N \times \nabla)_t \left(\overset{\downarrow}{\mathbf{r}} \times \mathbf{R}\right)_s = \mathbf{r}_N \cdot \mathbf{R}\delta_{st} - r_{N_s} R_t \tag{32}$$

(This can easily be verified by 'brute force' differentiation.) Using Eqs. (32), (31), (30), (28) and (27) to put everything back together, we get for the diamagnetic part of the "rest" **T** (*st* tensor component)

$$T_{st}^{dia} = \frac{1}{c}\sum_{i}^{occ} n_i \sum_{v}^{2M} d_{vi} I_{iv}^{dia,st} = \frac{1}{c^2}\sum_{i}^{occ} n_i \sum_{v}^{2M} d_{vi} \times \left\langle \Psi_i \middle| \frac{1}{2r_N^3}(\mathbf{r}_N \cdot \mathbf{R}_v\delta_{st} - r_{N_s}R_{v_t})\middle|\chi_v\right\rangle \tag{33}$$

Finally, we find (from Eqs. 33, 12, and 23) that

$$\sigma_{GIAO}^{d,1} + \mathbf{T}_{GIAO}^{dia} = \sigma_{cg}^{d} \tag{34}$$

That is, we were able to show how the diamagnetic shielding tensor of the common gauge formalism relates to the GIAO scheme. It remains to treat the paramagnetic terms.

Paramagnetic shielding, occupied-occupied terms

At this point, we need to come back to **T** of Eq. (20). We shall now collect everything that is left over after the previous manipulations:

$$\mathbf{T}^{para} = \mathbf{T} - \mathbf{T}^{dia} = \mathbf{T}_\mu + \mathbf{T}_v^{para} \tag{35}$$

$\mathbf{T}_\mu$ had been defined previously in Eqs. (27) and (28); the paramagnetic term of $\mathbf{T}_v$ is defined through Eq. (35). It is given as

$$\mathbf{T}_v^{para} = \frac{1}{c}\sum_{i}^{occ} n_i \sum_{v}^{2M} d_{vi}\mathbf{I}_{iv}^{para} \tag{36}$$

Thus (from Eqs. 27, 28, 30, 31, 35 and 36),

$$\mathbf{T}^{para} = \frac{2}{c}\sum_{i}^{occ} n_i \sum_{\mu}^{2M} d_{\mu i}\left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2} \times \mathbf{R}_\mu\right]\mathbf{h}^{01}\middle|\Psi_i\right\rangle \tag{37}$$

We are now at a point where the completeness relation of Eq. (26) can be applied. We insert the unity operator of Eq. (26) into the integrals of Eq. (37) above, and get

$$\mathbf{T}^{para} = \frac{2}{c}\sum_{i}^{occ} n_i \sum_{p}^{all}\sum_{\mu}^{2M} d_{\mu i} \times \left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu\right] \middle| \Psi_p \right\rangle \langle \Psi_p | \mathbf{h}^{01} | \Psi_i \rangle \tag{38}$$

This expression is immediately split up again into occupied-occupied and occupied-virtual terms. We achieve the splitting by dividing the "p" sum as follows:

$$\mathbf{T}^{para} = \mathbf{T}^{para}_{oc-oc} + \mathbf{T}^{para}_{oc-vir} \tag{39}$$

where we have defined two new terms, the occupied-occupied and occupied. d-virtual contributions to $\mathbf{T}^{para}$, respectively, as

$$\mathbf{T}^{para}_{oc-oc} = \frac{2}{c}\sum_{i,j}^{occ} n_i \sum_{\mu}^{2M} d_{\mu i} \left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu\right] \middle| \Psi_j \right\rangle \times \langle \Psi_j | \mathbf{h}^{01} | \Psi_i \rangle \tag{40}$$

and

$$\mathbf{T}^{para}_{oc-vir} = \frac{2}{c}\sum_{i}^{occ} n_i \sum_{a}^{vir}\sum_{\mu}^{2M} d_{\mu i} \left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu\right] \middle| \Psi_a \right\rangle \times \langle \Psi_a | \mathbf{h}^{01} | \Psi_i \rangle \tag{41}$$

We shall delay the discussion of $\mathbf{T}^{para}_{oc\text{-}vir}$ for the moment and concentrate now only on $\mathbf{T}^{para}_{oc\text{-}oc}$.

We can rewrite this expression in Eq. (40) by using the anti-Hermitian and Hermitian properties of $\mathbf{h}^{01}$ and $(\mathbf{r}\times\mathbf{R}_\mu)$, respectively. In this way, we get

$$\begin{aligned}\mathbf{T}^{para}_{oc-oc} &= \frac{1}{c}\sum_{i,j}^{occ} n_i \sum_{\mu}^{2M} d_{\mu i}\left\{ \left\langle \chi_\mu \middle| -\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu \middle| \Psi_j \right\rangle \times \langle \Psi_j | \mathbf{h}^{01} | \Psi_i \rangle \right. \\ &\quad \left. - \left\langle \Psi_j \middle| -\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu \middle| \chi_\mu \right\rangle \langle \Psi_i | \mathbf{h}^{01} | \Psi_j \rangle \right\} \qquad (42)\\ &= \frac{1}{c}\sum_{i,j}^{occ} n_i \sum_{\mu,v}^{2M} d_{\mu i} d_{vj} \left\langle \chi_\mu \middle| -\frac{\mathbf{r}}{2}\times (\mathbf{R}_v - \mathbf{R}_\mu) \middle| \chi_v \right\rangle \times \langle \Psi_j | \mathbf{h}^{01} | \Psi_i \rangle \qquad (43)\end{aligned}$$

We obtained the last expression in Eq. (43) by noting that the "i" and "j" sums run over the same range. Therefore, we have exchanged i and j in the second term of Eq. (42) to get Eq. (43). From Eq. (43) we observe

$$\mathbf{T}^{para}_{oc-oc} = -\sigma^{p,oc-oc} \tag{44}$$

(cf. Eqs. 13 and 16). This means that the occupied-occupied contribution to $\mathbf{T}^{para}$ cancels the occupied-occupied contribution to the paramagnetic shielding tensor. This is necessary – and could have been anticipated – because the paramagnetic shielding tensor in the common gauge formulation lacks the occupied-occupied terms completely; see Eq. (22).

Paramagnetic shielding, occupied-virtual terms

We are now only left with the occupied-virtual contribution to $\mathbf{T}^{para}$. The sum of this term and the occupied-virtual paramagnetic shielding tensor $\sigma^{p,oc-vir}_{GIAO}$ of Eq. (14) should yield the paramagnetic shielding of the common gauge formulation. Thus, we have yet to show that

$$\mathbf{T}^{para}_{oc-vir} + \sigma^{p,oc-vir}_{GIAO} = \sigma^{p}_{cg} \tag{45}$$

The proof of Eq. (45) requires some fairly lengthy and tedious algebra, which we intend to deliver next. For that purpose, let us repeat the relevant equations at this point. We had

$$\sigma^{p,oc-vir} = 2\sum_{i}^{occ} n_i \sum_{a}^{vir} \mathbf{u}^1_{ai} \langle \Psi_i | \mathbf{h}^{01} | \Psi_a \rangle \tag{14}$$

for the GIAO shielding, as well as

$$\mathbf{T}^{para}_{oc-vir} = \frac{2}{c}\sum_{i}^{occ} n_i \sum_{a}^{vir}\sum_{\mu}^{2M} d_{\mu i} \left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu\right] \middle| \Psi_a \right\rangle \times \langle \Psi_a | \mathbf{h}^{01} | \Psi_i \rangle \tag{41}$$

and finally

$$\sigma^{p}_{cg} = 2\sum_{i}^{occ} n_i \sum_{a}^{vir} \mathbf{u}^{1,cg}_{ai} \langle \Psi_i | \mathbf{h}^{01} | \Psi_a \rangle \tag{22}$$

for the cg paramagnetic shielding. We note that all three tensors have the same occupied-virtual sums. Further, the second integral is the same in all three cases (apart from a minus sign in Eq. 41). Thus, it is sufficient to consider only one term out of each sum, and for this one term, only the respective coefficients in front of the $\langle \Psi_i | \mathbf{h}^{01} | \Psi_a \rangle$ integrals.

We shall concentrate for now only on the GIAO shielding. Here, the coefficients are

$$\mathbf{t}_{ai} = \frac{2}{c}\sum_{\mu}^{2M} d_{\mu i} \left\langle \chi_\mu \middle| \left[-\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu\right] \middle| \Psi_a \right\rangle \tag{46}$$

for $\mathbf{T}^{para}_{oc-vir}$ of Eq. (41), as well as $\mathbf{u}_{ai}$ of Eq. (15) for $\sigma^{p,oc-vir}$. It turns out to be necessary to treat the latter first. Recall that $\mathbf{u}^1_{ai}$ was given as follows:

$$\mathbf{u}^1_{ai} = \frac{\mathbf{F}^1_{ai} - \varepsilon^0_i \mathbf{S}^1_{ai}}{\varepsilon^0_i - \varepsilon^0_a} \tag{15}$$

with $\mathbf{S}^1_{ai}$ and $\mathbf{F}^1_{ai}$ defined in Eqs. (16) and (18), respectively. Let us rewrite these matrix operators somewhat. We get

$$\mathbf{S}^1_{ai} = \frac{1}{c}\sum_{\mu} d_{\mu a} \left\langle \chi_\mu \middle| -\frac{\mathbf{r}}{2}\times \mathbf{R}_\mu \middle| \Psi_i \right\rangle + \frac{1}{c}\sum_{v} d_{vi} \left\langle \Psi_a \middle| \frac{\mathbf{r}}{2}\times \mathbf{R}_v \middle| \chi_v \right\rangle \tag{47}$$

and

$$\mathbf{F}^1_{ai} = \mathbf{F}^{1,cg}_{ai} + \mathbf{F}^{T}_{ai} + \mathbf{F}^{\mu v}_{ai} \tag{48}$$

where

$$\mathbf{F}^{T}_{ai} = \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| \frac{\mathbf{R}_v}{2} \times \nabla \right| \chi_v \right\rangle \tag{49}$$

and

$$\mathbf{F}^{\mu v}_{ai} = \frac{1}{c}\sum_{\mu}^{2M} d_{\mu a}\left\langle \chi_\mu \left| \left(-\frac{\mathbf{r}}{2} \times \mathbf{R}_\mu\right) f(0,\mathbf{r}) \right| \Psi_i \right\rangle + \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) f(0,\mathbf{r}) \right| \chi_v \right\rangle \tag{50}$$

The second and third terms in Eq. (48) are defined through Eqs. (49) and (50), respectively, and the first term in Eq. (48), $\mathbf{F}^{1,cg}_{ai}$, has been defined earlier in Eq. (25). $\mathbf{F}^{1,cg}_{ai}$ is, in fact, what we are aiming for. We use the splitting of the GIAO $\mathbf{F}^1$ matrix (Eq. 48), to further rewrite $\mathbf{u}^1_{ai}$. Thus

$$\begin{aligned}\left(\varepsilon^0_i - \varepsilon^0_a\right)\mathbf{u}^1_{ai} &= \mathbf{F}^1_{ai} - \varepsilon^0_i \mathbf{S}^1_{ai} \\ &= \mathbf{F}^{1cg}_{ai} + \mathbf{D}\end{aligned} \tag{51}$$

This equation defines **D**, the difference between the GIAO and the common gauge formulations. From Eqs. (47), (48), (49), (50) and (51) we find for **D**

$$\begin{aligned}\mathbf{D} = \mathbf{F}^{T}_{ai} &+ \frac{1}{c}\sum_{\mu}^{2M} d_{\mu a}\left\{\left\langle \chi_\mu \left| \left(-\frac{\mathbf{r}}{2} \times \mathbf{R}_\mu\right) f(0,\mathbf{r}) \right| \Psi_i \right\rangle - \varepsilon^0_i \left\langle \chi_\mu \left| -\frac{\mathbf{r}}{2} \times \mathbf{R}_\mu \right| \Psi_i \right\rangle\right\} \\ &+ \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\{\left\langle \Psi_a \left| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) f(0,\mathbf{r}) \right| \chi_v \right\rangle - \varepsilon^0_i \left\langle \Psi_a \left| \frac{\mathbf{r}}{2} \times \mathbf{R}_v \right| \chi_v \right\rangle\right\}\end{aligned} \tag{52}$$

The second term in Eq. (52) vanishes exactly since the Ψ_i were assumed to be solutions to the Kohn-Sham equations, Eq. (4):

$$\left\{f(0,\mathbf{r}) - \varepsilon^0_i\right\}|\Psi_i\rangle = 0 \tag{53}$$

and we are left with the following expression for **D**:

$$\begin{aligned}\mathbf{D} = &\frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| \frac{\mathbf{R}_v}{2} \times \nabla \right| \chi_v \right\rangle \\ &+ \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right)\left(f(0,\mathbf{r}) - \varepsilon^0_i\right) \right| \chi_v \right\rangle\end{aligned} \tag{54}$$

From Eq. (45), all that is now left to show is

$$-\left(\varepsilon^0_i - \varepsilon^0_a\right)\mathbf{t}_{ai} + 2\mathbf{D} \stackrel{!}{=} 0 \tag{55}$$

(see Eq. 46 for $\mathbf{t}_{ai}$, and Eqs. 51, 52, 53 and 54 otherwise). To prove Eq. (55), we mainly have to treat the "difference", **D**, even further.

This is done in the following. In **D**, there are terms – let us call them $\mathbf{D}_a$ – as follows:

$$\mathbf{D}_a = \left\langle \Psi_a \left| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) f(0,\mathbf{r}) \right| \chi_v \right\rangle \tag{56}$$

The operator $f(0, \mathbf{r})$ is Hermitian, and we can write

$$\mathbf{D}_a = \left\langle \chi_v \left| f(0,\mathbf{r})\left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) \right| \Psi_a \right\rangle \tag{57}$$

where $f(0,\mathbf{r})$ is working on everything to the right of it. We know, of course, that

$$f(0,\mathbf{r}) = -\frac{\nabla^2}{2} + V_{KS} \tag{58}$$

(Eq. 5), and that ∇^2 does not commute with the position operator **r** in Eq. (57). Further, V_{KS} is the total Kohn-Sham potential, Eq. (5). In the given context, it is only relevant that V_{KS} commutes with **r**. Calculating the operator in Eq. (57), we have

$$\nabla^2\left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) = \nabla \cdot \left\{\nabla \otimes \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right)\right\} \tag{59}$$

(The tensor product has been shown explicitly in this equation.) With some easy algebra, we get for this operator

$$\nabla^2\left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) = -\mathbf{R}_v \times \nabla + \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right)\nabla^2 \tag{60}$$

This is the commutation worked out. Putting it back into the integral $\mathbf{D}_a$ of Eq. (57), we get

$$\mathbf{D}_a = \left\langle \chi_v \left| \frac{\mathbf{R}_v}{2} \times \nabla \right| \Psi_a \right\rangle + \left\langle \chi_v \left| \left(\frac{\mathbf{r}}{2} \times \mathbf{R}_v\right) f(0,\mathbf{r}) \right| \Psi_a \right\rangle \tag{61}$$

For the second integral, we can use again that the zero order orbitals are exact solutions to the Kohn-Sham equations (cf. Eqs. 4 and 53):

$$\left(f(0,\mathbf{r}) - \varepsilon^0_a\right)|\Psi_a\rangle = 0 \tag{62}$$

In this way, we obtain for $\mathbf{D}_a$ (making use of the anti-Hermitian properties of the first operator in Eq. 61):

$$\mathbf{D}_a = \left\langle \Psi_a \left| -\frac{\mathbf{R}_v}{2} \times \nabla \right| \chi_v \right\rangle + \varepsilon^0_a \left\langle \chi_v \left| \frac{\mathbf{r}}{2} \times \mathbf{R}_v \right| \Psi_a \right\rangle \tag{63}$$

This can now go back into **D** of Eq. (54), and into Eq. (55) that still has to be proven. We get

$$\begin{aligned}\mathbf{D} = &\frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| \frac{\mathbf{R}_v}{2} \times \nabla \right| \chi_v \right\rangle \\ &+ \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \Psi_a \left| -\frac{\mathbf{R}_v}{2} \times \nabla \right| \chi_v \right\rangle \\ &+ \frac{1}{c}\sum_{v}^{2M} d_{vi}\left\langle \chi_v \left| \frac{\mathbf{r}}{2} \times \mathbf{R}_v \right| \Psi_a \right\rangle \left(\varepsilon^0_a - \varepsilon^0_i\right)\end{aligned} \tag{64}$$

The first two terms in Eq. (64) cancel exactly. The remaining third term, put into Eq. (55), cancels exactly the $\mathbf{t}_{ai}$ term, Eq. (46). This proves Eq. (55). Therefore, it also proves Eq. (45), and completes the proof of equivalence between the common gauge and GIAO formulations of the shielding.

Summary and conclusions

At this point, let us summarize the lengthy derivations that were the main focus of this paper.

We started from the GIAO formulation of the NMR shielding tensor, Eqs. (7), (8), (9), (10), (11), (12), (13), (14), (15), (16), (17), (18), (19) and (20). It would probably be much more difficult to give the same proof, starting from the common gauge formulation of Eqs. (21), (22), (23), (24) and (25). All the derivations focused on the somewhat obscure "rest" term of Eq. (20). Normally, this term is numerically small, according to experience. Further, it is distributed over the diamagnetic and paramagnetic shieldings such that each one of them is gauge invariant each by itself [10, 21, 26].

For the purpose of this article, however, we split the rest term in a different fashion. First, we extracted a diamagnetic contribution out of it, Eqs. (30), (31), (32) and (33). This term, when added to the GIAO diamagnetic shielding, resulted in the diamagnetic shielding of the common gauge scheme, Eq. (34).

The remainder could apparently be called paramagnetic. This paramagnetic part of the "rest" turned out to be suitable for the insertion of an identity operator. We use for this identity the completeness relation of Eq. (26). We wish to stress again that we assumed at this point a *complete* set of orthonormal Kohn-Sham orbitals, i.e. a complete basis set, and exactly solved Kohn-Sham equations, Eq. (4).

The completeness relation contains a sum over *all* molecular orbitals, Eq. (38). The sum can be split up into a sum over occupied MOs plus an infinite sum over unoccupied MOs, Eqs. (39), (40) and (41). Easy manipulation shows that the occupied-occupied part cancels the occupied-occupied contribution of the GIAO paramagnetic shielding. This was necessary and expected because the common gauge formulation lacks this type of contributions.

All that we were left with at this point was an occupied-virtual tensor, Eq. (41). Fairly lengthy manipulations proved that the sum of this term and the respective contribution to the GIAO paramagnetic shielding resulted in the paramagnetic shielding tensor of the common gauge case. These manipulations were mainly concerned with calculating commutators between the GIAO phase factors and the unperturbed Kohn-Sham operator, cf. Eqs. (59) and (60). Use was made again of the assumption that the Kohn-Sham equations Eq. (4) had been solved exactly for the Kohn-Sham orbitals.

The dia- and paramagnetic parts of the "rest" term that were employed in this paper, Eq. (35), amount in general to large contributions of opposite signs. Consequently, they cancel almost exactly. These terms are left out in the GIAO formulation but included into the cg shielding expression. This is part of the reason that GIAO schemes, along with other distributed-origin methods like IGLO [28, 29], are more accurate then the simple cg method.

In summary, the GIAO and common gauge formulations of the shielding are identical (as they should be) in the limit of complete (infinite) basis sets. Otherwise, they may – and will – show differences [26, 30, 31, 32] with the GIAO scheme being the more accurate method.

Finally, we should point out that while we have restricted ourselves to one particular level of theory, Kohn-Sham DFT, there is no reason to believe that a very similar proof could not be designed for other methods including, for instance, Hartree-Fock theory. Thus, the conclusions of this paper should be applicable beyond the field of DFT.

The derivations illustrate again that and how the separation of the shielding tensor into dia- and paramagnetic parts is not unique – even though it can, of course, be defined uniquely for a given method. Practically, this is not a problem, though, since only the *total* shielding is an observable quantity. On the other hand, occupied-virtual terms are prominently present in the GIAO as well as the cg formulations of the shielding, Eqs. (14) and (22), respectively. This gives additional credibility to an analysis method that has been used by us as well as others for some time [13, 14, 15, 16, 17, 23]. In these analysis schemes, trends in chemical shifts are related to the electronic structure by considering the dominant occupied-virtual couplings in the calculated (GIAO) paramagnetic shielding tensor.

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