

Degenerate Perturbation Theory for Electronic g Tensors: Leading-Order Relativistic Effects

Zilvinas Rinkevicius,* Katia Julia de Almeida, Cornel I. Oprea, Olav Vahtras, and Hans Ågren

Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, SE-10691 Stockholm, Sweden

Kenneth Ruud

Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

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Abstract: A new approach for the evaluation of the leading-order relativistic corrections to the electronic g tensors of molecules with a doublet ground state is presented. The methodology is based on degenerate perturbation theory and includes all relevant contributions to the g tensor shift up to order $\mathcal{O}(\alpha^4)$ originating from the one-electron part of the Breit–Pauli Hamiltonian—that is, it allows for the treatment of scalar relativistic, spin–orbit, and mixed corrections to the spin and orbital Zeeman effects. This approach has been implemented in the framework of spin-restricted density functional theory and is in the present paper, as a first illustration of the theory, applied to study relativistic effects on electronic g tensors of dihalogen anion radicals X_2^- ($X = F, Cl, Br, I$). The results indicate that the spin–orbit interaction is responsible for the large parallel component of the g tensor shift of Br_2^- and I_2^- , and furthermore that both the leading-order scalar relativistic and spin–orbit corrections are of minor importance for the perpendicular component of the g tensor in these molecules since they effectively cancel each other. In addition to investigating the g tensors of dihalogen anion radicals, we also critically examine the importance of various relativistic corrections to the electronic g tensor of linear molecules with Σ -type ground states and present a two-state model suitable for an approximate estimation of the g tensor in such molecules.

I. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is an important experimental technique designed for the investigation of compounds with unpaired electrons. The information content of this technique is obtained by measurements of molecular parameters related to the Zeeman effect—that is, the electronic g tensor, the hyperfine coupling constants, and the zero-field splitting constants.^{1–3} These parameters play a central role in the interpretation of EPR measurements and are often connected to the electronic and geometrical structure of the systems analyzed using empirical relationships.^{2,3} This holds in particular for classes of species with well-established empirical “molecular structure–Zeeman effect

parameter” relationships, while for more complex systems, the empirical approach often encounters difficulties and can lead to multiple interpretations of the experimental results. One way to enhance the quality of the interpretation of EPR spectra and to overcome the ambiguity introduced by the use of empirical relationships is to incorporate quantum chemical modeling of the molecular parameters into the analysis.^{2,3} This combined approach for extracting information from EPR measurements is already now commonly in use^{2,3} and is expected to become even more prominent with the improved applicability of quantum chemistry methods to larger molecular systems of experimental interest.

A multitude of approaches for evaluating electronic g tensors of molecules has been developed and presented in the literature in recent years.^{4–20} These methods range from sophisticated ab initio approaches such as multiconfigurational self-consistent field (MCSCF) response theory^{6,17} to various density functional theory (DFT) based formalisms.^{7,8,10,12–14,16,18,19} The accuracy and applicability of these methodologies have been intensively studied and recipes for accurate calculations of electronic g tensors of organic radicals and first-row transition metal complexes have been suggested in several recent publications.^{10,12,14,16} Despite these achievements, only a few works^{8,9,13,18–26} have targeted compounds containing heavy elements, and relativistic effects on electronic g tensors have been studied in detail primarily for diatomics and other small compounds, such as the uranium hexafluoride anion,²¹ to mention one prominent example. In the domain of density functional theory, a few attempts have been made at including relativistic effects in the evaluation of the electronic g tensors. Following the pioneering work of van Lenthe et al.,⁸ the majority of DFT methods^{8,13} capable of computing relativistic g tensors have been based on the two-component Kohn–Sham approach, in which the reduced two-component Hamiltonian is obtained by applying the zeroth-order regular approximation (ZORA)^{27–30} or the Douglas–Kroll (DK)³¹ transformation. The first implementations of two-component DFT methods for the evaluation of electronic g tensors were restricted to molecules with doublet ground states, since Kramer’s doublet symmetry could then be utilized in the determination of the electronic g tensor components. This restriction was lifted only recently, when Malkin et al.¹⁸ implemented a spin-polarized Douglas–Kroll Kohn–Sham formalism which can handle molecules with arbitrary ground states. Despite the obvious advantages of two-component electronic structure methods, these methods have until now only been applied to systems consisting of a few atoms. The only exception from this unfortunate trend is van Lenthe’s ZORA formalism,⁸ which allows for the rapid evaluation of the electronic g tensors in molecules with doublet ground states, and this approach has been applied many times in studies of compounds containing heavy elements.^{32–34}

An alternative to the two-component DFT approaches is a one-component formalism in which the relativistic corrections to the electronic g tensor are treated on an equal footing to the nonrelativistic g tensor itself—that is, via perturbation theory expansions. Here, the term “non-relativistic g tensor” is understood as the g tensor composed of the free-electron g factor, $g_e \approx 2.0023$, and g tensor shifts of order $\mathcal{O}(\alpha^2)$, i.e., $\vec{g}_{\text{NR}} = g_e \vec{1} + \Delta\vec{g}(\mathcal{O}(\alpha^2))$. Consequently, the leading-order relativistic corrections to the g tensor are contributions to the g tensor shift of order $\mathcal{O}(\alpha^4)$, where α is the fine-structure constant, which is approximately 1/137 in the atomic unit system used throughout this paper. However, this approach has been exploited only at the ab initio theory level¹⁷ due to the lack of density functional theory implementations capable of handling arbitrary perturbations beyond second order. We recently extended our spin-restricted open-shell density functional response theory from the linear³⁵ to the quadratic level,³⁶ and this opens the way for

computing the leading-order relativistic corrections to the electronic g tensors using perturbation theory at the DFT level for the first time. In this paper, we apply degenerate perturbation theory (DGPT) for molecules with a doublet ground state to derive formulas for evaluating electronic g tensors in which relativistic corrections are accounted for, and employ linear and quadratic response functions as well as their residues to determine the different contributions to the g tensor appearing in the formalism at the level of spin-restricted density functional theory. The computational procedure proposed in this work extends previous simplified treatments of relativistic corrections to the electronic g tensor developed by Manninen, Vaara, and Ruud,¹⁷ and corrects conceptually as well as computationally deficiencies in that formalism. Apart from describing the formalism, we also present the results of electronic g tensor calculations for the series of dihalogen anion radicals X_2^- ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). In addition to testing the performance of the perturbational DFT treatment of relativistic electronic g tensors, we also resolve contradictions between the works of Manninen et al.¹⁷ and Malkin et al.¹⁸ regarding the dominant physical mechanism responsible for the large parallel g tensor shift of the dihalogen anion radicals.

The paper is organized in the following way. First, we give a detailed description of the relativistic electronic g tensor methodology based on degenerate perturbation theory, and we subsequently describe the computational details and discuss the results obtained for the dihalogen anion radicals. Finally, we draw some conclusions and outline some prospects for further applications of the formalism presented here.

II. Theory

Experimentally, observed EPR spectra are usually analyzed using a phenomenological spin Hamiltonian approach^{1–3} in which the Zeeman effect is described as

$$\hat{\mathcal{H}}_{\text{SH}} = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} \quad (1)$$

where $\mu_B = 1/2$ is the Bohr magneton and \vec{g} is the electronic g tensor of the molecule, which mediates the interaction between the effective spin \vec{S} and a static external magnetic field \vec{B} . In the special case of a molecule with a single unpaired electron, the effective spin \vec{S} can be rewritten in terms of the Pauli matrices $\vec{S} = 1/2\vec{\sigma}$, and the spin Hamiltonian becomes a 2×2 matrix

$$\hat{\mathcal{H}}_{\text{SH}} = \frac{\mu_B}{2} \vec{B} \cdot \vec{g} \cdot \vec{\sigma} \quad (2)$$

Consequently, the eigenvalues of $\hat{\mathcal{H}}_{\text{SH}}$ can readily be determined in a basis of two-dimensional spinors, leading to the well-known expression of Abraham and Bleaney³⁷ for the Zeeman splitting

$$\Delta E = \mu_B \sqrt{\vec{B} \cdot \vec{G} \cdot \vec{B}} \quad \text{and} \quad \vec{G} = \vec{g} \vec{g}^T \quad (3)$$

where we have introduced the so-called symmetric G tensor \vec{G} , which is measured in typical EPR experiments. Despite the fact that the G tensor is directly obtained from experi-

ment, the theoretical and experimental results are usually analyzed and discussed in terms of the electronic \vec{g} tensor which, being defined via three g factors with corresponding principal axes, is a more convenient quantity for interpretation. The electronic g tensor can be computed from the G tensor according to eq 3 in a two-step procedure: the first step is the diagonalization of the \vec{G} tensor, which determines the principal values and axes of this tensor; the second step involves the computation of the three g factors (diagonal components of the g tensor) as the positive square root of the principal values of the G tensor followed by an appropriate assignment of the principal axis to the \vec{g} components. This procedure is not only used to extract the electronic g tensor from experimental data, but is also employed in theoretical calculations for transforming the nonsymmetric \vec{g} into its diagonal form. Therefore, both the \vec{G} and \vec{g} tensors are equally suitable for a description of the Zeeman effect, and the selection of the specific tensor form depends only on convenience in the particular situation, as the G tensor always can be reduced to the electronic g tensor and vice versa, according to the procedure described above.

Before proceeding with the derivation of formulas for the evaluation of the relativistic g tensors, we briefly outline the connection between the spin Hamiltonian and the quantum mechanical treatment of the Zeeman effect in systems with ground states that in the absence of a magnetic field are described by a Kramers doublet pair $|0\rangle = (|0\rangle|0\rangle)$. In this case, the Zeeman interaction Hamiltonian is a 2×2 matrix

$$\hat{H}_Z = \mu_B (\vec{L} + 2\vec{S}) \cdot \vec{B} \quad (4)$$

where the angular momentum \vec{L} and electronic spin \vec{S} can be expanded in the basis of Pauli matrices

$$\vec{L} = \frac{1}{2} \vec{\Lambda} \cdot \vec{\sigma} \quad \text{and} \quad \vec{S} = \frac{1}{2} \vec{\Sigma} \cdot \vec{\sigma} \quad (5)$$

We observe that the Pauli matrices together with the unit matrix form a complete basis in the linear space of 2×2 matrices; for traceless operators, the expansion in eq 5 is the most general one. Taking into account the properties of the Zeeman interaction operator and the Kramers doublet pair, the Zeeman splitting can be written as the difference between the eigenvalues of \hat{H}_Z^{20}

$$\Delta E = \mu_B \sqrt{2\vec{B} \cdot \text{tr}((\vec{L} + 2\vec{S})(\vec{L} + 2\vec{S})) \cdot \vec{B}} \quad (6)$$

Comparing this definition of the Zeeman splitting with the one obtained in the spin-Hamiltonian approach (see eq 3) and requiring that the equality between the left-hand sides of both equations is fulfilled for all strengths of the magnetic field B , we obtain the following expression for calculating the G tensor

$$\vec{G} = (\vec{\Lambda} + 2\vec{\Sigma})(\vec{\Lambda} + 2\vec{\Sigma})^T \quad (7)$$

which, according to eq 3, allows us to define the electronic g tensor as

$$\vec{g} = \vec{\Lambda} + 2\vec{\Sigma} \quad (8)$$

From these equations it is evident that the \vec{G} and \vec{g} tensors are defined solely by the expansion tensors of the angular momentum \vec{L} and electronic spin \vec{S} operators, $\vec{\Lambda}$ and $\vec{\Sigma}$, and the task of computing the electronic g tensor reduces to the determination of the $\vec{\Lambda}$ and $\vec{\Sigma}$ tensors for a given approximate Hamiltonian using a selected ab initio or density functional theory method.

In this paper, we apply degenerate perturbation theory to the Kramers doublet pair in order to obtain formulas for evaluating the $\vec{\Lambda}$ and $\vec{\Sigma}$ tensors. The starting point for our derivation is the construction of the Kramers doublet pair $|0\rangle$ as a row matrix from two degenerate doublet wave functions, $|^20; 1/2\rangle$ and $|^20; -1/2\rangle$, which are eigenfunctions of the ordinary nonrelativistic Hamiltonian \hat{H}_0 , the total spin \hat{S}^2 and the spin projection \hat{S}_z operators, which satisfy the set of equations

$$\begin{aligned} \hat{H}_0 |^2S+10; m\rangle &= E_0 |^2S+10; m\rangle \\ \hat{S}^2 |^2S+10; m\rangle &= S(S+1) |^2S+10; m\rangle \\ \hat{S}_z |^2S+10; m\rangle &= m |^2S+10; m\rangle \end{aligned}$$

where for a doublet state $S = 1/2$ and $m = 1/2, -1/2$, respectively. We here consider all one-electron spin- and external field-dependent operators as well as other relevant one-electron operators of order $\mathcal{O}(\alpha^2)$ in the Breit–Pauli Hamiltonian as perturbations. These operators were also considered as perturbations by Manninen et al.,¹⁷ but we include in addition also the two-electron part of the spin–orbit operator, which was omitted in ref 17. Using these operators and their combinations, we will determine corrections to the Zeeman interaction eq 4 to $\mathcal{O}(\alpha^4)$ by applying degenerate perturbation theory (a brief account of this formalism is given in Appendix A).

At the nonrelativistic limit, i.e. order $\mathcal{O}(\alpha^0)$, the Zeeman effect is described by the spin and orbital Zeeman effect operators only (see Table 1, in which a detailed description of the operators included in the perturbation operator \hat{V} is given), and for an orbitally nondegenerate doublet state we thus obtain the following contributions to the Zeeman effect from first-order DGPT

$$\mathbf{H}_{SZ} = \langle 0 | \hat{H}_{SZ} | 0 \rangle = \mu_B \sum_{k=x,y,z} B_k [\Sigma_{SZ}]_{kk} \sigma_k = \mu_B \sum_{k=x,y,z} B_k \sigma_k \quad (9)$$

$$\mathbf{H}_{OZ} = \langle 0 | \hat{H}_{OZ} | 0 \rangle = \frac{\mu_B}{2} \sum_{k=x,y,z} B_k [\Lambda_{OZ}]_{kk} \sigma_k = 0 \quad (10)$$

which indicates that the magnetic moment of the molecule is defined by the spin of the unpaired electron in the molecule only. Therefore, at this level of approximation, the g tensor is $\vec{g} = 2\vec{\Sigma}_{SZ} = 2\vec{1}$, and the molecule behaves as a free electron in a magnetic field. After adding the quantum electrodynamic correction to the magnetic moment of the electron we retrieve the well-known form of the g tensor of the free electron, namely $\vec{g} = g_e \vec{1}$. The so-called g tensor

shift, $\Delta\vec{g} = \vec{g} - g_e\mathbf{1}$, thus vanishes, indicating that the influence of the other electrons in the molecule on the unpaired electron is neglected. At the lowest-order relativistic treatment, i.e., $\mathcal{O}(\alpha^2)$, which is usually considered in the derivation of the conventional formalism for nonrelativistic electronic g tensors, we obtain two corrections to the spin-Zeeman effect from first-order DGPT

$$\begin{aligned}\mathbf{H}_{\text{RMC}} &= \langle 0 | \hat{H}_{\text{SZKE}} | 0 \rangle \\ &= \mu_B \sum_{k=x,y,z} B_k [\Sigma_{\text{RMC}}]_{kk} \sigma_k \\ &= \mu_B \sum_{k=x,y,z} {}^{00}\Omega_{\text{SZKE}} B_k \sigma_k\end{aligned}\quad (11)$$

$$\begin{aligned}\mathbf{H}_{\text{GC}} &= \langle 0 | \hat{H}_{\text{GC}(1e)} | 0 \rangle \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{GC}}]_{kl} \sigma_l \\ &= \mu_B \sum_{k,l=x,y,z} B_k [{}^{00}\Omega_{\text{GC}(1e)}]_{kl} \sigma_l\end{aligned}\quad (12)$$

Taking into account the relationship between the electronic g tensor and the $\vec{\Sigma}$ tensor (see eq 8), the terms described above in the $\vec{\Sigma}$ expansion can readily be associated with the so-called mass velocity, $\Delta\vec{g}_{\text{RMC}} = 2\vec{\Sigma}_{\text{RMC}}$, and gauge, $\Delta\vec{g}_{\text{GC}} = 2\vec{\Sigma}_{\text{GC}}$, terms in the electronic g tensor shift. The remaining $\mathcal{O}(\alpha^2)$ corrections to the spin-Zeeman effect can be retrieved from second-order DGPT by combining the spin-Zeeman operator \hat{H}_{SZ} with the mass velocity \hat{H}_{MV} , one-electron Darwin \hat{H}_{DW} , and the one- and two-electron spin-orbit, $\hat{H}_{\text{SO}(1e)}$ and $\hat{H}_{\text{SO}(2e)}$, operators, which are all included in the perturbation \hat{V} (see Table 1 for details). However, all these corrections vanish as \hat{H}_{SZ} , being a pure spin operator, gives zero matrix elements between the electronic ground and excited states of the molecule. Therefore, at $\mathcal{O}(\alpha^2)$ only two corrections to the spin-Zeeman effect exist, namely the mass velocity and gauge corrections, if we assume that the perturbation \hat{V} has the form defined in Table 1. Applying a similar procedure to the orbital Zeeman effect, we obtain one nonvanishing correction of $\mathcal{O}(\alpha^2)$ which originates from second-order DGPT, in which the orbital Zeeman effect operator \hat{H}_{OZ} is coupled to the spin-orbit interaction operators

$$\begin{aligned}\mathbf{H}_{\text{OZ/SO}} &= \langle 0 | \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SO}} + \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZ}} | 0 \rangle \\ &= \frac{\mu_B}{2} \sum_{k=x,y,z} B_k [\Lambda_{\text{SO}}]_{kl} \sigma_l \\ &= \frac{\mu_B}{2} \sum_{k,l=x,y,z} B_k \left(4 \sum_{n>0} \frac{[{}^{0n}\Omega_{\text{OZ}}]_{kl} [{}^{n0}\Omega_{\text{SO}}]_{li}}{E_0 - E_n} \right) \sigma_l\end{aligned}\quad (13)$$

where \hat{H}_{SO} includes both the one- and two-electron spin-orbit operators, $\hat{H}_{\text{SO}(1e)}$ and $\hat{H}_{\text{SO}(2e)}$, with the combined matrix element denoted as ${}^{nn'}\Omega_{\text{SO}} = {}^{nn'}\Omega_{\text{SO}(1e)} + {}^{nn'}\Omega_{\text{SO}(2e)}$. We have in eq 13 also inserted the explicit form of the reduced resolvent operator \hat{R} (see Appendix A) as well as matrix elements of the \hat{H}_{OZ} and \hat{H}_{SO} operators. Summing up all $\mathcal{O}(\alpha^2)$

corrections to the spin and orbital Zeeman effects, and extracting the corresponding contributions to the $\vec{\Lambda}$ and $\vec{\Sigma}$ tensors, we can according to eq 8 write the g tensor shifts as

$$\begin{aligned}\Delta\vec{g}(\mathcal{O}(\alpha^2)) &= \Delta\vec{g}_{\text{SO}} + \Delta\vec{g}_{\text{RMC}} + \Delta\vec{g}_{\text{GC}} \\ &= \vec{\Lambda}_{\text{SO}} + 2\vec{\Sigma}_{\text{RMC}} + 2\vec{\Sigma}_{\text{GC}}\end{aligned}\quad (14)$$

which differs from the commonly used one only by having omitted the two-electron part of the gauge-correction term. We have here intentionally excluded the two-electron gauge operator from the perturbation operator \hat{V} in our derivation, as the g tensor shift arising from this operator usually is considered to be negligible and therefore in most cases can be safely neglected (recently, an alternative view on the importance of the one- and two-electron gauge corrections to the g tensor shift has been discussed by Patchkovskii et al.³⁸). Another reason for excluding this operator from our treatment stems from its two-electron nature, which makes the evaluation of the matrix elements a nontrivial task especially in the case of density functional theory. The same difficulties are also encountered in the computation of the $\Delta\vec{g}_{\text{SO}}$ term in the g tensor shift, which involves the two-electron spin-orbit operator $\hat{H}_{\text{SO}(2e)}$. However, in this case the two-electron part of $\Delta\vec{g}_{\text{SO}}$ cannot be neglected, as this contribution along with its one-electron counterpart dominates the electronic g tensor shift of most molecules composed of main-group elements. One way to overcome this difficulty is to employ an effective one-electron spin-orbit operator in which the spin-orbit interaction screening effect of $\hat{H}_{\text{SO}(2e)}$ is accounted for in an approximate manner. This approach would not only allow us to simplify the evaluation of the matrix elements but also to resolve the conceptional difficulty in the implementation of the $\Delta\vec{g}_{\text{SO}}$ term in density functional theory, as the formation of the two-particle density matrix, which is required for the computation of the two-electron part, can be avoided. In this paper, we will employ the atomic mean field approximation (AMFI)³⁹ for handling the two-electron spin-orbit operator matrix elements, as this method is well established and has previously been extensively used in computations of the electronic g tensor shifts^{10,15,16,20,23–25} in the Kohn–Sham formalism. The choice of using the AMFI approximation is not only motivated by our desire to avoid problems associated with the construction of the two-particle density matrix in DFT but also dictated by current limitations in our quadratic response code, which cannot handle Breit–Pauli two-electron spin-orbit operators in the evaluation of several of the leading-order relativistic corrections to the electronic g tensor.

Having settled the treatment of the $\hat{H}_{\text{SO}(2e)}$ operator in the calculation of $\Delta\vec{g}_{\text{SO}}$, let us now briefly review the computational cost of the various terms included in eq 14. An inspection of eqs 11–13 reveals that the most computationally expensive part of the $\Delta\vec{g}(\mathcal{O}(\alpha^2))$ evaluation is the determination of the spin-orbit contribution $\Delta\vec{g}_{\text{SO}}$, which requires the solution of a set of linear response equations. The remaining contributions to the g tensor shift are, on the other hand, straightforwardly evaluated as expectation values of the corresponding one-electron operators, and their computational cost is negligible compared to $\Delta\vec{g}_{\text{SO}}$. We note that spin-unrestricted and spin-restricted density functional linear response formalisms have been imple-

Table 1. List of Breit–Pauli Hamiltonian Operators Included in Perturbation \hat{V} and Their Matrix Elements in Degenerate Perturbation Theory

label	order	operator description	$\langle n \hat{H} n\rangle^{a,b,c}$	${}^{nn'}\Omega$ or $[{}^{nn'}\Omega]_k$ or $[{}^{nn'}\Omega]_{kl}^{c,d,e}$
\hat{H}_{SZ}	α^0	spin-Zeeman effect	$\mu_B {}^{nn'}\Omega_{SZ} \sum_{k=x,y,z} B_k \sigma_k$	$\delta_{nn'}$
\hat{H}_{OZ}	α^0	orbital Zeeman effect	$\mu_B \sum_{k=x,y,z} 1B_k [{}^{nn'}\Omega_{OZ}]_k$	$\langle n \sum_i [l_{iO}]_k n'\rangle$
\hat{H}_{SZKE}	α^2	mass-velocity correction to spin-Zeeman effect	$\mu_B {}^{nn'}\Omega_{SZKE} \sum_{k=x,y,z} B_k \sigma_k$	$\alpha^2 \langle n \sum_i \nabla_i^2 [s_i]_z n'\rangle$
\hat{H}_{OZKE}	α^2	mass-velocity correction to orbital Zeeman effect	$\mu_B \sum_{k=x,y,z} 1B_k [{}^{nn'}\Omega_{OZKE}]_k$	$\frac{\alpha^2}{2} \langle n \sum_i [l_{iO}]_k \nabla_i^2 n'\rangle$
$\hat{H}_{GC(1e)}$	α^2	one-electron gauge correction to Zeeman effect	$\mu_B \sum_{k,l=x,y,z} B_k [{}^{nn'}\Omega_{GC(1e)}]_{kl} \sigma_l$	$\frac{\alpha^2}{2} \left\langle n \left \sum_{i,N} \frac{\delta_k(\vec{r}_{iN} \vec{r}_{iO}) - [r_{iN}]_k [r_{iO}]_l}{r_{iN}^3} [s_i]_z \right n' \right\rangle$
$\hat{H}_{SO(1e)}$	α^2	one-electron spin–orbit	$\sum_{k=x,y,z} [{}^{nn'}\Omega_{SO(1e)}]_k \sigma_k$	$\frac{\alpha^2}{2} \left\langle n \left \sum_{i,N} Z_N \frac{[l_{iN}]_k}{r_{iN}^3} [s_i]_z \right n' \right\rangle$
$\hat{H}_{SO(2e)}$	α^2	two-electron spin–orbit	$\sum_{k=x,y,z} [{}^{nn'}\Omega_{SO(2e)}]_k \sigma_k$	$-\frac{\alpha^2}{2} \left\langle n \left \sum_{i \neq j} \frac{[l_{ij}]_k [s_i]_z + 2[l_{ij}]_k [s_j]_z}{r_{ij}^3} \right n' \right\rangle$
\hat{H}_{MV}	α^2	mass velocity	${}^{nn'}\Omega_{MV} \mathbf{1}$	$-\frac{\alpha^2}{8} \langle n \sum_i \nabla_i^2 n'\rangle$
\hat{H}_{DW}	α^2	one-electron Darwin	${}^{nn'}\Omega_{DV} \mathbf{1}$	$\frac{\pi \alpha^2}{2} \langle n \sum_{i,N} Z_N \delta(\vec{r}_{iN}) n'\rangle$

^a Matrix element between two Kramer doublet states: $|n\rangle$ and $|n'\rangle$, which are constructed from degenerate doublet wave functions. ^b Here, we denoted Bohr magneton as $\mu_B = 1/2$. ^c Here, we use two notations for vector \vec{A} components, namely A_k or $[A]_k$, and one distinctive notation for tensor \vec{T} components $[T]_{kl}$. ^d Reduced matrix element, which is computed as high spin diagonal of $\langle n|\hat{H}|n\rangle$ i.e., $\langle n; 1/2|\hat{H}|n; 1/2\rangle$. Detailed description of reduced matrix elements is given in Appendix B. ^e In definitions of reduced matrix elements, we employed following standard notations: Z_N is the charge of nucleus N ; $[s]_z$ is the z component of spin of electron i ; \vec{r}_{iN} is the position of electron i with respect to nucleus N ; \vec{r}_{ij} is the position of electron i with respect to electron j ; \vec{r}_{iO} is the position of electron i with respect to gauge origin; \vec{l}_{iO} , \vec{l}_{iN} , and \vec{l}_{ij} are the angular momentum of electron i evaluated around the position of the gauge origin O , nucleus N , or electron j , respectively.

mented in various quantum chemistry programs in recent years,^{10,12,14,35} and the evaluation of the nonrelativistic electronic \vec{g} tensors, $\vec{g}_{NR} = \vec{g}_e \mathbf{1} + \Delta\vec{g}(\mathcal{O}(\alpha^2))$, is therefore now becoming widely accessible. In this work, we will employ the spin-restricted density functional response formalism derived in ref 35 for evaluating the contributions to the electronic \vec{g} tensor shift described above as well as higher-order terms (vide infra), as this approach is free from the spin contamination problem appearing in spin-unrestricted DFT approaches. This choice is motivated not only by the ability of the spin-restricted formalism to provide the pure spin states required by degenerate perturbation theory but

also by the availability of a spin-restricted quadratic density functional response code,³⁶ which is needed for the evaluation of several of the $\mathcal{O}(\alpha^4)$ contributions to the electronic \vec{g} tensor shift.

The leading-order relativistic corrections to the electronic \vec{g} tensor is derived from degenerate perturbation theory by applying the same procedure as for the ordinary $\mathcal{O}(\alpha^2)$ contributions to $\Delta\vec{g}$, although one in this case needs to go beyond the second-order DGPT in order to retrieve all relevant contributions to the $\vec{\Sigma}$ and $\vec{\Lambda}$ tensors. Since the perturbation \hat{V} in this formalism only involves operators to

$\mathcal{O}(\alpha^2)$, the first corrections to the Zeeman effect of $\mathcal{O}(\alpha^4)$ will appear at second order of degenerate perturbation theory. Let us first consider the more complex case of the spin-Zeeman effect, to which we obtain two scalar relativistic corrections from second-order DGPT

$$\begin{aligned}\mathbf{H}_{\text{RMC/SR}} &= \langle 0 | \hat{H}_{\text{SZKE}} \hat{R} \hat{H}_{\text{SR}} + \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{SZKE}} | 0 \rangle \\ &= \mu_B \sum_{k=x,y,z} B_k [\Sigma_{\text{RMC/SR}}]_{kk} \sigma_k \\ &= \mu_B \sum_{k,l=x,y,z} B_k \left(2 \sum_{n>0} \frac{0n \Omega_{\text{SZKE}}^{n0} \Omega_{\text{SR}}}{E_0 - E_n} \right) \sigma_k \quad (15)\end{aligned}$$

$$\begin{aligned}\mathbf{H}_{\text{GC/SR}} &= \langle 0 | \hat{H}_{\text{GC(1e)}} \hat{R} \hat{H}_{\text{SR}} + \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{GC(1e)}} | 0 \rangle \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{GC/SR}}]_{kl} \sigma_k \\ &= \mu_B \sum_{k,l=x,y,z} B_k \left(2 \sum_{n>0} \frac{0n \Omega_{\text{GC(1e)}}^{n0} \Omega_{\text{SR}}}{E_0 - E_n} \right) \sigma_l \quad (16)\end{aligned}$$

which originate from the coupling of \hat{H}_{SR} with the operators defined by \mathbf{H}_{RMC} and \mathbf{H}_{GC} . We have here introduced the combined \hat{H}_{SR} operator, which is responsible for the bulk part of the scalar relativistic corrections to \hat{H}_0 , and includes the \hat{H}_{MV} and \hat{H}_{DW} operators. Its reduced matrix element is defined as ${}^{nn'}\Omega_{\text{SR}} = {}^{nn'}\Omega_{\text{MV}} + {}^{nn'}\Omega_{\text{DW}}$. Apart from the scalar relativistic corrections to the spin-Zeeman effect described above, the second-order DGPT also gives rise to spin-orbit corrections

$$\begin{aligned}\mathbf{H}_{\text{RMC/SO}} &= \langle 0 | \hat{H}_{\text{SZKE}} \hat{R} \hat{H}_{\text{SO}} + \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SZKE}} | 0 \rangle \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{RMC/SO}}]_{kl} \sigma_l \\ &= \mu_B \sum_{k,l=x,y,z} B_k \left(2i \sum_{j=x,y,z} \epsilon_{kjl} \sum_{n>0} \frac{0n \Omega_{\text{SZKE}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{E_0 - E_n} \right) \sigma_l \quad (17)\end{aligned}$$

$$\begin{aligned}\mathbf{H}_{\text{GC/SO}} &= \langle 0 | \hat{H}_{\text{GC(1e)}} \hat{R} \hat{H}_{\text{SO}} + \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{GC(1e)}} | 0 \rangle \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{GC/SO}}]_{kl} \sigma_l \\ &= \mu_B \sum_{k,l=x,y,z} B_k \times \\ &\quad \left(2i \sum_{j,j'=x,y,z} \epsilon_{jj'l} \sum_{n>0} \frac{0n \Omega_{\text{GC(1e)}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{E_0 - E_n} \right) \sigma_l \quad (18)\end{aligned}$$

in which instead of operators responsible for scalar relativistic effects, the spin-orbit interaction operator is coupled with \hat{H}_{SZKE} and $\hat{H}_{\text{GC(1e)}}$. Here, we only consider doublet states in the derivation of the spin-orbit corrections to the spin-Zeeman effect and therefore neglect the contributions arising from quartet states in the DGPT expressions involving two or more electronic spin-dependent operators. This approximation is used throughout

this paper and applied in the derivation of all contributions to the electronic g tensor shift which feature more than one spin-dependent operator. In addition to this approximation, we have also in the two latter equations, as well as other equations given below, employed the commutation and anticommutation relations of the Pauli matrices to reduce the equations to a final form featuring only a single Pauli matrix. From these four corrections to the spin-Zeeman effect, we can readily identify the second-order DGPT contributions to the $\vec{\Sigma}$ tensor of $\mathcal{O}(\alpha^4)$, which can be interpreted as the spin-orbit, $\vec{\Sigma}_{\text{RMC/SO}}$ and $\vec{\Sigma}_{\text{GC/SO}}$, and scalar relativistic, $\vec{\Sigma}_{\text{RMC/SR}}$ and $\vec{\Sigma}_{\text{GC/SR}}$, corrections to the lower-order terms, $\vec{\Sigma}_{\text{RMC}}$ and $\vec{\Sigma}_{\text{GC}}$, in the $\vec{\Sigma}$ tensor expansion.

In addition to these four corrections to the spin-Zeeman effect, two nonvanishing corrections are also obtained from third-order DGPT. One of these corrections is the so-called higher-order spin-orbit correction to the spin-Zeeman effect which only depends on the \hat{H}_{SO} and \hat{H}_{SZ} operators

$$\begin{aligned}\mathbf{H}_{\text{SZ/SO}} &= \langle 0 | \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SZ}} \hat{R} \hat{H}_{\text{SO}} | 0 \rangle - \\ &\quad \frac{1}{2} \{ \langle 0 | \hat{H}_{\text{SZ}} | 0 \rangle, \langle 0 | \hat{H}_{\text{SO}} \hat{R}^2 \hat{H}_{\text{SO}} | 0 \rangle \} \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{SZ/SO}}]_{kl} \sigma_l \\ &= \mu_B \sum_{k,l=x,y,z} B_k \left(\sum_{n>0} \frac{0n \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{(E_0 - E_n)^2} + \right. \\ &\quad \left. \sum_{n>0} \frac{0n \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{(E_0 - E_n)^2} - \right. \\ &\quad \left. 2\delta_{kl} \sum_{j=x,y,z} \sum_{n>0} \frac{0n \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{(E_0 - E_n)^2} \right) \sigma_l \quad (19)\end{aligned}$$

In the above equation, as well as other similar equations, only the terms from third-order perturbation theory which give nonvanishing contributions to the final results are kept. The other contribution is of mixed “scalar relativistic/spin-orbit” nature and involves the \hat{H}_{SR} operator in addition to the \hat{H}_{SO} and \hat{H}_{SZ} operators

$$\begin{aligned}\mathbf{H}_{\text{SZ/SO/SR}} &= \langle 0 | \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SZ}} \hat{R} \hat{H}_{\text{SR}} + \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{SZ}} \hat{R} \hat{H}_{\text{SO}} | 0 \rangle \\ &= \mu_B \sum_{k,l=x,y,z} B_k [\Sigma_{\text{SZ/SR}}]_{kl} \sigma_l \\ &= \mu_B \sum_{k,l=x,y,z} B_k \left(2i \sum_{j=x,y,z} \epsilon_{kjl} \sum_{n>0} \frac{0n \Omega_{\text{SR}}^{n0} \Omega_{\text{SO}}^{n0} \Omega_{\text{SO}}^{n0}}{(E_0 - E_n)^2} \right) \sigma_l \quad (20)\end{aligned}$$

At $\mathcal{O}(\alpha^4)$ in degenerate perturbation theory, a total of six corrections to the spin-Zeeman effect with nonvanishing

contributions to the $\vec{\Sigma}$ tensor is obtained, whereas in the work of Manninen et al.,¹⁷ which employed conventional perturbation theory, only two corrections to the spin-Zeeman effect (see eqs 21–24 of ref 17), corresponding to the $\mathbf{H}_{\text{RMC/SR}}$ and $\mathbf{H}_{\text{GC/SR}}$ terms in our formalism, were obtained.

Let us now turn to the less complicated case of the orbital Zeeman effect, for which the application of DGPT leads to only three nonvanishing corrections of $\mathcal{O}(\alpha^4)$. One of these corrections arises from second-order DGPT and involves a kinetic energy correction to the orbital Zeeman effect operator \hat{H}_{OZKE} coupled to the spin–orbit operator in a similar fashion as in the $\mathbf{H}_{\text{OZ/SO}}$ case

$$\begin{aligned}\mathbf{H}_{\text{OZKE/SO}} &= \langle \mathbf{0} | \hat{H}_{\text{OZKE}} \hat{R} \hat{H}_{\text{SO}} + \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZKE}} | \mathbf{0} \rangle \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k [\Lambda_{\text{SO/KE}}]_{kl} \sigma_l \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k \left(4 \sum_{n>0} \frac{[{}^{0n}\Omega_{\text{OZKE}}]_k [{}^{n0}\Omega_{\text{SO}}]_l}{(E_0 - E_n)^2} \right) \sigma_l\end{aligned}\quad (21)$$

The two remaining corrections are of a more complex nature and are obtained from third-order DGPT. One of these describes the scalar relativistic effects on the lower-order $\mathbf{H}_{\text{OZ/SO}}$ correction and is defined as

$$\begin{aligned}\mathbf{H}_{\text{OZ/SO/SR}} &= \langle \mathbf{0} | \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SR}} + \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SO}} + \\ &\hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZ}} | \mathbf{0} \rangle + \langle \mathbf{0} | \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{SO}} + \\ &\hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SR}} \hat{R} \hat{H}_{\text{OZ}} + \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SR}} | \mathbf{0} \rangle - \\ &\frac{1}{2} \{ \langle \mathbf{0} | \hat{H}_{\text{SR}} | \mathbf{0} \rangle, \langle \mathbf{0} | \hat{H}_{\text{SO}} \hat{R}^2 \hat{H}_{\text{OZ}} + \hat{H}_{\text{OZ}} \hat{R}^2 \hat{H}_{\text{SO}} | \mathbf{0} \rangle \} \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k [\Lambda_{\text{SO/SR}}]_{kl} \sigma_l \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k \times \\ &\left(2 \sum_{n,m>0} \frac{{}^{0n}\Omega_{\text{SR}}([{}^{nm}\Omega_{\text{OZ}}]_k [{}^{m0}\Omega_{\text{SO}}]_l + [{}^{nm}\Omega_{\text{OZ}}]_k [{}^{m0}\Omega_{\text{SO}}]_l)}{(E_0 - E_n)(E_0 - E_m)} + \right. \\ &2 \sum_{n,m>0} \frac{{}^{m0}\Omega_{\text{SR}}([{}^{0n}\Omega_{\text{OZ}}]_k [{}^{nm}\Omega_{\text{SO}}]_l + [{}^{0n}\Omega_{\text{SO}}]_k [{}^{nm}\Omega_{\text{OZ}}]_l)}{(E_0 - E_n)(E_0 - E_m)} + \\ &2 \sum_{n,m>0} \frac{{}^{nm}\Omega_{\text{SR}}([{}^{0n}\Omega_{\text{OZ}}]_k [{}^{m0}\Omega_{\text{SO}}]_l + [{}^{0n}\Omega_{\text{SO}}]_k [{}^{m0}\Omega_{\text{OZ}}]_l)}{(E_0 - E_n)(E_0 - E_m)} - \\ &\left. 4 \sum_{n>0} \frac{{}^{00}\Omega_{\text{SR}}([{}^{0n}\Omega_{\text{OZ}}]_k [{}^{n0}\Omega_{\text{SO}}]_l)}{(E_0 - E_n)^2} \right) \sigma_l\end{aligned}\quad (22)$$

whereas the last contribution describes the spin–orbit effect on the same lower-order correction $\mathbf{H}_{\text{OZ/SO/SR}}$ and has the form

$$\begin{aligned}\mathbf{H}_{\text{OZ/SO/SO}} &= \langle \mathbf{0} | \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SO}} + \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZ}} \hat{R} \hat{H}_{\text{SO}} + \\ &\hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{SO}} \hat{R} \hat{H}_{\text{OZ}} | \mathbf{0} \rangle \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k [\Lambda_{\text{SO/SO}}]_{kl} \sigma_l \\ &= \frac{\mu_{\text{B}}}{2} \sum_{k,l=x,y,z} B_k \times \\ &\left(2i \sum_{j,j'=x,y,z} \epsilon_{jj'l} \sum_{n,m>0} \frac{[{}^{0n}\Omega_{\text{OZ}}]_k [{}^{nm}\Omega_{\text{SO}}]_l [{}^{m0}\Omega_{\text{SO}}]_{j'}}{(E_0 - E_n)(E_0 - E_m)} + \right. \\ &2i \sum_{j,j'=x,y,z} \epsilon_{jj'l} \sum_{n,m>0} \frac{[{}^{0n}\Omega_{\text{SO}}]_j [{}^{nm}\Omega_{\text{OZ}}]_k [{}^{m0}\Omega_{\text{SO}}]_{j'}}{(E_0 - E_n)(E_0 - E_m)} + \\ &\left. 2i \sum_{j,j'=x,y,z} \epsilon_{jj'l} \sum_{n,m>0} \frac{[{}^{0n}\Omega_{\text{SO}}]_l [{}^{nm}\Omega_{\text{SO}}]_{j'} [{}^{m0}\Omega_{\text{OZ}}]_k}{(E_0 - E_n)(E_0 - E_m)} \right) \sigma_l\end{aligned}\quad (23)$$

From the last three equations we can identify the corresponding contributions to the $\vec{\Lambda}$ tensor of $\mathcal{O}(\alpha^4)$, which are all corrections to the lower-order contribution to $\vec{\Lambda}_{\text{SO}}$. More specifically, the spin–orbit correction is retrieved from $\mathbf{H}_{\text{OZ/SO/SO}}$, whereas the active and passive scalar relativistic corrections are obtained from $\mathbf{H}_{\text{OZ/KE/SO}}$ and $\mathbf{H}_{\text{OZ/SO/SR}}$, respectively. The expression for the leading-order relativistic corrections to the g tensor shift can thus be summarized as

$$\begin{aligned}\Delta \vec{g}(\mathcal{O}(\alpha^4)) &= \Delta \vec{g}_{\text{SO/KE}} + \Delta \vec{g}_{\text{SO/SR}} + \Delta \vec{g}_{\text{SO/SO}} + \Delta \vec{g}_{\text{RMC/SR}} + \\ &\Delta \vec{g}_{\text{RMC/SO}} + \Delta \vec{g}_{\text{GC/SR}} + \Delta \vec{g}_{\text{GC/SO}} + \Delta \vec{g}_{\text{SZ/SR}} + \Delta \vec{g}_{\text{SZ/SO}} \\ &= \vec{\Lambda}_{\text{SO/KE}} + \vec{\Lambda}_{\text{SO/SR}} + \vec{\Lambda}_{\text{SO/SO}} + 2\vec{\Sigma}_{\text{RMC/SR}} + 2\vec{\Sigma}_{\text{RMC/SO}} + \\ &2\vec{\Sigma}_{\text{GC/SR}} + 2\vec{\Sigma}_{\text{GC/SO}} + 2\vec{\Sigma}_{\text{SZ/SR}} + 2\vec{\Sigma}_{\text{SZ/SO}}\end{aligned}\quad (24)$$

where we have included all contributions to the $\vec{\Lambda}$ and $\vec{\Sigma}$ tensors of $\mathcal{O}(\alpha^4)$ according to eq 8. The relativistic g tensor can thus be defined as

$$\vec{g} = \vec{g}_{\text{NR}} + \Delta \vec{g}(\mathcal{O}(\alpha^4)) = g_e \vec{1} + \Delta \vec{g}(\mathcal{O}(\alpha^2)) + \Delta \vec{g}(\mathcal{O}(\alpha^4))\quad (25)$$

and includes the nonrelativistic g tensor corrected by $\Delta \vec{g}(\mathcal{O}(\alpha^4))$, which contains all the leading-order relativistic corrections. A detailed inspection of the various terms appearing in $\Delta \vec{g}(\mathcal{O}(\alpha^4))$ indicates that the contributions to the g tensor shift can be separated into three clearly distinct types: (1) passive and active scalar relativistic corrections to $\Delta \vec{g}(\mathcal{O}(\alpha^2))$: $\Delta \vec{g}_{\text{SO/SR}}$, $\Delta \vec{g}_{\text{RMC/SR}}$, $\Delta \vec{g}_{\text{GC/SR}}$, and $\Delta \vec{g}_{\text{SO/KE}}$; (2) spin–orbit corrections to $\Delta \vec{g}(\mathcal{O}(\alpha^2))$: $\Delta \vec{g}_{\text{SO/SO}}$, $\Delta \vec{g}_{\text{RMC/SO}}$, and $\Delta \vec{g}_{\text{GC/SO}}$; (3) various corrections to the spin-Zeeman effect, involving the \hat{H}_{SZ} operator directly, namely $\Delta \vec{g}_{\text{SZ/SR}}$ and $\Delta \vec{g}_{\text{SZ/SO}}$.

The formulas in eq 24 for the evaluation of the relativistic g tensor contains the full range of relativistic effects originating from various one-electron operators in the Breit–Pauli Hamiltonian and provides a complete treatment of these effects in the g tensor shift to $\mathcal{O}(\alpha^4)$ for the selected form of perturbations \hat{V} (see Table 1 for details). In the previous work by Manninen et al.,¹⁷ only scalar relativistic contributions to the g tensor shift $\Delta \vec{g}(\mathcal{O}(\alpha^4))$ were included—that is, the $\Delta \vec{g}_{\text{SO/SR}}$, $\Delta \vec{g}_{\text{RMC/SR}}$, $\Delta \vec{g}_{\text{GC/SR}}$, and $\Delta \vec{g}_{\text{SO/KE}}$ terms, and thus only a partial description of the

leading-order relativistic corrections to the electronic g tensor was considered in that work. Furthermore, in ref 17 all contributions to $\Delta\vec{g}(\mathcal{O}(\alpha^4))$ which involved two or more electronic spin-dependent operators were also neglected. The formalism presented here has similarities to the “two-step” approach by Bolvin,²⁰ which includes the scalar relativistic corrections self-consistently and the spin–orbit corrections to the orbital and spin–Zeeman effect via a few-state model. More specifically, the ${}^2\vec{\Sigma}$ and ${}^2\vec{\Lambda}$ tensor in Bolvin’s definition of the g tensor (see eq 26 of ref 20) can be identified as $\Delta\vec{g}_{\text{SZ/SO}}$ and the sum of $\Delta\vec{g}_{\text{SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$, respectively. A detailed comparison of the contributions to the g tensor in the two approaches for the case of linear molecules are given in Appendix C. Since the “two-step” approach accounts for scalar relativistic effects self-consistently, this approach implicitly handles passive scalar relativistic contributions to the g tensor, which in our methodology is designated as $\Delta\vec{g}_{\text{SO/SR}}$ and $\Delta\vec{g}_{\text{SZ/SR}}$ in the expression for the g tensor shift. The methodology presented here can thus be considered a generalization, in different ways, of previous work^{17,20} using perturbation theory to treat relativistic corrections to the g tensor. It provides a new and tractable formalism for handling leading-order scalar relativistic, spin–orbit and mixed corrections to the g tensor shifts.

Before discussing the results of our g tensor calculations for the F_2^- , Cl_2^- , Br_2^- , I_2^- molecules including the relativistic corrections, we will comment on the usage of linear and quadratic response functions for the evaluation of various DGPT contributions to the electronic g tensor. A comparison of the DGPT expressions for evaluation of $\Delta\vec{g}(\mathcal{O}(\alpha^2))$ and $\Delta\vec{g}(\mathcal{O}(\alpha^4))$, and more specifically their orbital parts, with the spectral representation of linear and quadratic response functions, allows us to identify the corresponding response functions for computation of $\Delta\vec{g}_{\text{SO}}$ as well as other contributions to the electronic g tensor, with the exception of the $\Delta\vec{g}_{\text{SO/SO}}$ and $\Delta\vec{g}_{\text{SZ/SO}}$ contributions, which cannot be defined by conventional response functions.

After now having established the applicability of response functions in DGPT calculations of electronic g tensors, we would also like to address one important practical point in the determination of linear and quadratic response functions involving triplet operators, which are an important part of calculations of the electronic g tensor. In linear and quadratic response functions of open-shell molecules, where only one of the perturbations is of triplet spin symmetry, the excited-state manifold is spanned by singlet excitations from the ground state. However, the perturbation operator itself retain its triplet nature and, consequently, its gradient, which enters the response equations, must be evaluated using the corresponding spin density, but not the total densities. Neglecting this fact is equivalent to reducing all triplet operators to singlet operators and leads, as we will show here, to an unphysical behavior. Unfortunately, because the generalizations required for triplet perturbations in open-shell molecules was implemented only recently for linear response functions,⁶ and are applied here for the first time for quadratic response functions, the results of ref 17 suffer from this error. This lead in ref 17 to the conclusion that the scalar relativistic corrections are responsible for the large parallel g tensor shift

in heavy dihalogen anion radicals, contrary to the findings of Malkin et al.,¹⁸ as well as to Bolvin’s results²⁰ obtained for other diatomic systems containing heavy elements, which both indicated that the spin–orbit interaction is responsible for this effect.

III. Computational Details

Calculations of nonrelativistic g tensors of the dihalogen anion radicals, as well as the leading-order relativistic corrections to them, have been carried out using the methodology described in the previous section. The contributions to $\Delta\vec{g}(\mathcal{O}(\alpha^2))$ and $\Delta\vec{g}(\mathcal{O}(\alpha^4))$ have been computed using spin-restricted density functional linear and quadratic response functions with the exception of the $\Delta\vec{g}_{\text{SO/SO}}$ and $\Delta\vec{g}_{\text{SZ/SO}}$ terms, for which we employed the sum-overstates (SOS) approach due to limitations in our density functional response code.^{35,36} Apart from the DFT calculations, we have also carried out calculations at the spin-restricted open-shell Hartree–Fock (ROHF) level in order to demonstrate the importance of an appropriate treatment of triplet operators for the $\Delta\vec{g}_{\text{SO}}$, $\Delta\vec{g}_{\text{RMC/SR}}$, $\Delta\vec{g}_{\text{GC/SR}}$, and $\Delta\vec{g}_{\text{SO/SR}}$ contributions to the g tensor shift, which were investigated previously in ref 17. In all calculations we used the AMFI approximation for the evaluation of the $\hat{H}_{\text{SO}(2e)}$ operator matrix elements. For the matrix elements of the gauge-dependent operators, we employed a gauge origin centered at the electronic charge centroid of the molecule. For all calculations we used the geometries of the X_2^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) anion radicals from the work of Manninen et al.,¹⁷ with the bond lengths in F_2^- , Cl_2^- , Br_2^- and I_2^- being 1.8916, 2.5570, 2.7943, and 3.1478 Å, respectively. These bond lengths were also used by Malkin et al.,¹⁸ thus facilitating a direct comparison of our results with those of refs 17 and 18. Following the same reasoning, we employed a large uncontracted Huzinaga basis set (denoted here as HIVu, the details on this basis set can be found in ref 17), which was used to calculate the relativistic g tensor of the dihalogen anions by Manninen et al.¹⁷ at the ROHF level. The HIVu basis set is furthermore sufficiently large to obtain near basis-set limit results for the dihalogen anion radicals.¹⁷ In order to test the dependence of the g tensors and their relativistic corrections on the choice of exchange–correlation functional, we have carried out calculations using the local density Dirac–Vosko–Wilk–Nusair⁴⁰ (LDA), gradient-corrected Becke–Lee–Yang–Parr^{41,42} (BLYP) and hybrid Becke3–Lee–Yang–Parr^{40–44} (B3LYP) functionals. All calculations of linear and quadratic response functions as well as their residues were carried out using individually adjusted convergence thresholds, typically 10^{-8} for the response functions and 10^{-12} for the wave function, to ensure 0.01 ppm accuracy for each of the nonrelativistic as well as the leading-order relativistic contributions to electronic g tensor shift. All calculations were performed using a development version of the DALTON program.⁴⁵

IV. Results and Discussion

Dihalogen anion radicals are homonuclear diatomics with 15 valence electrons of which, in the $|\text{X}^2\Sigma_u^+\rangle$ ground state,^{46,47}

Table 2. Results of Nonrelativistic ($\mathcal{O}(\alpha^2)$) Calculations of Electronic g Tensor Shifts in Dihalogen Anion Radicals^a

molecule	method	Δg_{\parallel} (in ppm)			Δg_{\perp} (in ppm)				
		RMC	GC	total	RMC	GC	SO(1e) ^b	SO(2e) ^b	total
F ₂ [−]	ROHF	−396	134	−262	−396	255	19558	−6195	13222
	LDA	−403	134	−269	−403	269	28605	−8920	19551
	BLYP	−402	134	−268	−402	269	26093	−8128	17831
	B3LYP	−402	134	−269	−402	266	24963	−7804	17024
	BP86 ^c	−448	144	−304	−448	282	23949	—	23783
	ROHF ^d	−425 ^e	—	−425	−454 ^e	—	15152 ^f	—	14698
	MRCI ^d	−425 ^e	—	−425	−454 ^e	—	18406 ^f	—	17952
	ROHF ^g	−558 ^h	165 ^h	−393	−558 ^h	316 ^h	24150	—	23908
	MCSCF ^g	−493 ^h	150 ^h	−343	−493 ^h	293 ^h	22318	—	22118
	ROHF	−286	154	−132	−286	272	31204	−5644	25546
Cl ₂ [−]	LDA	−305	155	−150	−305	302	52846	−9360	43483
	BLYP	−302	154	−148	−302	302	51164	−9071	42092
	B3LYP	−300	155	−145	−300	296	46864	−8342	38518
	BP86 ^c	−321	156	−165	−321	305	48828	—	48812
	ROHF ^d	−311 ^e	—	−311	−429 ^e	—	33255 ^f	—	32826
	MRCI ^d	−311 ^e	—	−331	−429 ^e	—	41669 ^f	—	41240
	ROHF ^g	−366 ^h	153 ^h	−213	−366 ^h	311 ^h	41524	—	41469
	MCSCF ^g	−362 ^h	153 ^h	−209	−362 ^h	310 ^h	46004	—	45952
	ROHF	−310	266	−44	−310	451	112335	−10690	101786
	LDA	−331	264	−67	−331	501	202592	−18894	183867
Br ₂ [−]	BLYP	−326	263	−63	−326	499	197890	−18486	179576
	B3LYP	−326	265	−61	−326	490	178645	−16749	162060
	BP86 ^c	−326	258	−68	−326	506	188684	—	188864
	ROHF ^g	−371 ^h	251 ^h	−120	−371 ^h	498 ^h	152050	—	152178
	MCSCF ^g	−371 ^h	251 ^h	−120	−371 ^h	498 ^h	151615	—	151742
	ROHF	−307	341	34	−307	552	196220	−12340	184125
	LDA	−326	336	10	−326	619	377954	−23561	354687
	BLYP	−319	333	14	−319	616	369651	−23096	346852
	B3LYP	−320	337	17	−320	604	330512	−20689	310107
	BP86 ^c	−312	324	12	−312	633	348526	—	348847
I ₂ [−]	ROHF ^g	−348 ^h	306 ^h	−42	−348 ^h	604 ^h	282883	—	283139
	MCSCF ^g	−348 ^h	306 ^h	−42	−348 ^h	604 ^h	302450	—	302706

^a ROHF and DFT (LDA, BLYP and B3LYP functionals) calculations performed using Huz-IVu basis set. ^b The spin-orbit contribution to nonrelativistic g tensor i.e. $\Delta \vec{g}_{\text{SO}}$ is splitted into one- and two-electron parts and $\vec{H}_{\text{SO}(2e)}$ matrix elements entering $\Delta \vec{g}_{\text{SO}(2e)}$ computed using AMFI approximation. ^c Unrestricted DFT calculations from ref 17 with BP86 exchange-correlation functional. ^d ROHF and MCSCF calculations from refs 46 and 47. ^e Sum of first-order contributions, i.e., $\Delta g_{\text{RMC}} + \Delta g_{\text{GC}}$, where the last term includes both one- and two-electron parts. ^f Sum of second order spin-orbit contributions, i.e., $\Delta g_{\text{SO}(1e)} + \Delta g_{\text{SO}(2e)}$. ^g ROHF and MCSCF calculations from ref 17 ^h Computed using restricted-unrestricted approach, i.e., spin polarization is accounted for in these calculations.

14 electrons are distributed between the $\sigma_{\text{g(u)}}$ and $\pi_{\text{g(u)}}$ orbitals and the single unpaired electron is located in a σ_{u} orbital (the typical valence electronic configuration is $\sigma_{\text{g}}^2 \sigma_{\text{u}}^2 \sigma_{\text{g}}^2 \pi_{\text{u}}^4 \pi_{\text{g}}^4 \sigma_{\text{u}}^1$). The electronic structure and magnetic properties of the two lightest members of this family, F₂[−] and of Cl₂[−], have been extensively investigated by ab initio methods and the behavior of their electronic g tensors are well understood.^{46,47} In contrast, the influence of relativity on the electronic g tensor of the heavier members of this anion family still remains an open question and two different views on the dominating mechanism of the relativistic corrections have been presented in the literature. On the basis of the results of MCSCF response theory calculations of $\mathcal{O}(\alpha^4)$ contributions to the electronic g tensors, Manninen et al.¹⁷ advocated that the major relativistic corrections to the g tensors of Br₂[−] and I₂[−] are of scalar relativistic nature arising from the $\Delta \vec{g}_{\text{RMC/SR}}$ and $\Delta \vec{g}_{\text{GC/SR}}$ contributions to the g tensor shift. In contrast, a recent two-component DFT study by Malkin et al.¹⁸ indicated that the relativistic effects to the electronic g tensors of Br₂[−] and I₂[−] are governed by higher-order spin-orbit corrections and that scalar relativistic effects are of minor importance. These disparate views on the influence of relativity on the electronic g tensors, and the inherent simplicity of the magnetic coupling responsible for the

nonrelativistic g tensors, make the family of dihalogen anion compounds attractive as a test suite for validating the formalism developed in this paper for evaluating electronic g tensors.

A. Nonrelativistic g Tensors of the X₂[−] (X = F, Cl, Br, I) Anion Radicals. Before we go into an analysis of the relativistic effects on the electronic g tensors of the X₂[−] (X = F, Cl, Br, I) anion radicals, we first briefly discuss the nonrelativistic electronic g tensors and the interactions responsible for the parallel and perpendicular components of the g tensor shifts. The results of our DFT response calculations for the contributions of $\mathcal{O}(\alpha^2)$ to $\Delta \vec{g}$, along with available results of previous ab initio and DFT calculations, are given in Table 2. As for other linear molecules, the parallel component of the electronic g tensor g_{\parallel} of X₂[−] (X = F, Cl, Br, I), deviates only slightly from the free electron g factor, as the spin-orbit contribution is negligible (see eq 14). The g_{\parallel} values are therefore entirely defined by the balance between two small contributions: the relativistic mass-velocity and gauge corrections to the spin-Zeeman effect, i.e. $[\Delta g_{\text{RMC}}]_{\parallel}$ and $[\Delta g_{\text{GC}}]_{\parallel}$. Overall, our DFT results agree very well with the BP86 results of Manninen et al.,¹⁷ while our ROHF results gives systematically smaller $[\Delta g_{\text{RMC}}]_{\parallel}$ and $[\Delta g_{\text{GC}}]_{\parallel}$ (in terms of absolute values) compared

to their ROHF results. We rationalize this difference between these two virtually identical ROHF calculations by the fact that the restricted–unrestricted⁴⁸ formalism was used to compute these two contributions in ref 17. That is, in addition to the expectation values of the \hat{H}_{RMC} and $\hat{H}_{\text{GC}(1e)}$ operators, the spin polarization contributions have been also computed. By comparing their and our results, we estimate that spin polarization mostly influences the relativistic mass-velocity contribution $[\Delta g_{\text{RMC}}]_{\parallel}$, whereas the gauge correction $[\Delta g_{\text{GC}}]_{\parallel}$ shows a significantly less pronounced dependence on spin polarization. Furthermore, the importance of spin polarization is reduced for the heavier members of the X_2^- anion family (the estimated spin polarization contribution to $[\Delta g_{\text{RMC}}]_{\parallel}$ is around 41% for F_2^- and only around 13% for I_2^- , see Table 2 and ref 17). On the basis of these findings, we conclude that spin polarization can play a significant role for the nonrelativistic g_{\parallel} values of F_2^- and Cl_2^- (a detailed discussion of spin polarization effects in radicals with Σ -type ground states can be found in ref 49). Despite this, we choose to neglect spin polarization effects in the evaluation of the relativistic g tensors, as these effects cannot be accounted for systematically for all contributions included in the relativistic g tensor (see eq 25). Both our ROHF results as well as those of Manninen et al.¹⁷ systematically underestimate the Δg_{\parallel} values compared to those obtained by Bruna and Grein^{46,47} for F_2^- and Cl_2^- , indicating that the two-electron part of $[\Delta g_{\text{GC}}]_{\parallel}$, which have been accounted for in their work, is fairly large (in terms of absolute values) and almost cancel its one-electron counterpart for F_2^- and Cl_2^- . In this respect, it is worth noting that the conventional view that the two-electron part of the gauge correction $\Delta \vec{g}_{\text{GC}}$ is small and thus can be neglected does not hold for these dihalogen anion radicals. In this particular case, a more appropriate procedure would be to compute or neglect both contributions as suggested by Patchkovskii et al. in their recent work³⁸ on the evaluation of two-electron gauge corrections to electronic g tensors. However, in order to demonstrate the relativistic effects on $\Delta \vec{g}_{\text{GC}}$, we kept its one-electron part in our calculations. These results underscore the importance of a balanced description of first order (in the perturbation theory sense) contributions to Δg_{\parallel} in linear molecules. To summarize, the g_{\parallel} components of the X_2^- ($X = F, Cl, Br, I$) compounds deviate at $\mathcal{O}(\alpha^2)$ only slightly from the free-electron g factor and is defined by the subtle balance between mass-velocity and gauge corrections to the spin-Zeeman effect. A comparative analysis of our results and those of Bruna and Grein corroborates the findings by Patchkovskii et al.³⁸ that the widely accepted view about the magnitude of the gauge correction to the spin-Zeeman effect cannot be considered trustworthy, and that the two-electron part of this correction actually can be a very important contribution to nonrelativistic g_{\parallel} of linear molecules. Therefore, in cases when the second-order spin–orbit contribution vanishes or is comparable to the first-order contributions, both the one- and two-electron parts of the gauge correction to the spin-Zeeman effect should be considered, and one cannot a priori assess the relative importance of these parts.

In contrast to g_{\parallel} , the perpendicular component of the electronic g tensor g_{\perp} differs significantly from the free-electron g factor for all dihalogen anion radicals, and this deviation increases dramatically when going from F_2^- to I_2^- (see Table 2). The behavior of g_{\perp} for the dihalogen anion radicals is governed by the dominating second-order spin–orbit contribution $\Delta \vec{g}_{\text{SO}}$, and the first-order contributions, which determine g_{\parallel} , are negligible for this component of the nonrelativistic g tensor. However, we note that the first-order contributions show a similar trend as for g_{\parallel} , with the exception of the Br_2^- and I_2^- anion radicals, for which the gauge contribution $[\Delta g_{\text{GC}}]_{\perp}$ becomes larger than the mass-velocity contribution $[\Delta g_{\text{RMC}}]_{\perp}$. For the dominant second-order one- and two-electron spin–orbit contributions, $[\Delta g_{\text{SO}(1e)}]_{\perp}$ and $[\Delta g_{\text{SO}(2e)}]_{\perp}$, our ROHF and DFT values agree well with previous MRCI and BP86 results (see Table 2), demonstrating the good performance of spin-restricted density functional response theory. We also note that there is only a moderate dependence of $[\Delta g_{\text{SO}}]_{\perp}$ on the exchange–correlation functionals used in the calculations. It is worth noting that the magnetic coupling, which gives rise to the spin–orbit contributions to g_{\perp} in the X_2^- radicals, is particularly simple—the major contribution originates from the $|1^2\Pi_u\rangle$ ($\pi_u \leftarrow \sigma_u$) excited state. Therefore, an accurate description of g_{\perp} can be achieved by considering a single excited state for the electronic g tensor shift (a detailed discussion of this topic is presented in Appendix C, where a two-state model for evaluating the electronic g tensor in linear molecules is derived). According to Bruna and Grein,^{46,47} the ratio between the angular momentum matrix element $\langle X^2\Sigma_u^+ | \hat{H}_{\text{OZ}} | 1^2\Pi_u \rangle$ and the $|X^2\Sigma_u^+ \rangle \rightarrow |1^2\Pi_u \rangle$ excitation energy remains almost constant going from F_2^- to Cl_2^- and, consequently, the increase of the spin–orbit matrix element $\langle X^2\Sigma_u^+ | \hat{H}_{\text{SO}} | 1^2\Pi_u \rangle$ determines the changes in Δg_{\perp} . According to our calculations, the same trend holds relatively well also for Br_2^- and I_2^- and, consequently, the ratio between Δg_{\perp} for two members of the dihalogen anion family is approximately equal to the ratio between their spin–orbit matrix elements $\langle X^2\Sigma_u^+ | \hat{H}_{\text{SO}} | 1^2\Pi_u \rangle$, although this correspondence between ratios is most accurate for neighboring X_2^- radical pairs, such as F_2^- and Cl_2^- , or Br_2^- and I_2^- . The perpendicular component of the nonrelativistic electronic g tensor of the X_2^- ($X = F, Cl, Br, I$) radicals can thus be rationalized by a two-state model as suggested by Bruna and Grein.^{46,47} As the spin–orbit interaction plays a major role for the perpendicular component of the g tensor shift, it is interesting to look at the importance of the one- and two-electron spin–orbit contributions. A quick inspection of Table 2 reveals that the two-electron spin–orbit contribution to Δg_{\perp} is only important for F_2^- (around 31% of the $[\Delta g_{\text{SO}(1e)}]_{\perp}$ contribution) and Cl_2^- (around 18% of the $[\Delta g_{\text{SO}(1e)}]_{\perp}$ contribution), whereas the importance of this contribution decreases for the heavier members of this anion family. In fact, $[\Delta g_{\text{SO}(2e)}]_{\perp}$ amounts only to about 10% and 6% of the $[\Delta g_{\text{SO}(1e)}]_{\perp}$ contribution (in absolute value) for Br_2^- and I_2^- , respectively. In agreement with previous work on the dihalogen compounds,¹⁰ we find that the neglect of the two-electron spin–orbit contribution to g_{\perp} for the two

Table 3. Leading-Order Relativistic Contributions to the g Tensor Shift of Dihalogen Anion Radicals^a

molecule	method	Δg_{\parallel} (in ppm)					Δg_{\perp} (in ppm)					
		RMC/SR	GC/SR	SZ/SO	SO/SO	total	RMC/SR	GC/SR	SO/SR	SO/KE	SZ/SO	total
F_2^-	ROHF	-0.29	0.02	-151.68	75.84	-76.11	-0.29	0.42	60.56	-3.87	-75.84	-19.02
	LDA	-0.27	0.01	-297.52	148.76	-149.02	-0.27	0.40	88.18	-4.63	-149.00	-65.32
	BLYP	-0.27	0.01	-260.90	130.45	-137.71	-0.27	0.39	79.96	-4.06	-130.58	-54.56
	B3LYP	-0.28	0.02	-238.16	119.08	-119.34	-0.28	0.40	76.50	-4.14	-119.20	-46.44
	ROHF ^b	-143.74	25.12	—	—	-118.62	-143.74	25.00	97.59	-13.22	—	-34.37
Cl_2^-	ROHF	-0.81	-0.01	-778.10	389.05	-389.87	-0.81	2.52	580.88	-3.98	-389.77	188.84
	LDA	-0.83	-0.01	-1915.82	957.91	-958.75	-0.83	2.50	947.70	-8.24	-958.93	-17.80
	BLYP	-0.84	-0.01	-1790.36	895.18	-896.03	-0.84	2.45	909.30	-7.41	-896.14	7.36
	B3LYP	-0.84	-0.01	-1533.14	766.57	-767.42	-0.84	2.49	843.74	-6.93	-767.39	71.07
	ROHF ^b	-2140.66	374.72	—	—	-1765.94	-2140.66	374.12	814.78	-104.12	—	-1055.88
Br_2^-	ROHF	-4.95	-0.14	-14528.38	7264.19	-7269.28	-4.95	25.91	13605.86	-6.72	-7271.93	6348.17
	LDA	-4.22	-0.34	-37932.00	18966.00	-18970.56	-4.22	25.20	23362.54	-43.58	-18986.20	4353.74
	BLYP	-4.16	-0.32	-35848.66	17924.33	-17928.81	-4.16	24.66	22639.70	-37.96	-17943.42	4678.82
	B3LYP	-4.44	-0.26	-30265.44	15132.72	-15137.42	-4.44	25.24	20711.50	-33.44	-15148.84	5550.02
	ROHF ^b	-44733.01	7759.88	—	—	-36973.13	-44733.01	7803.51	17532.21	-2587.48	—	-21984.77
I_2^-	ROHF	-12.52	-1.29	-63648.60	31824.30	-31838.11	-12.52	92.51	67229.06	52.63	-31858.20	35503.48
	LDA	-9.25	-2.11	-172355.92	86177.96	-86189.32	-9.25	90.18	118863.22	-77.49	-86269.74	32596.92
	BLYP	-9.12	-2.07	-160874.78	80437.39	-80448.58	-9.12	87.94	115020.68	-57.81	-80523.06	34518.63
	B3LYP	-10.11	-1.86	-135532.26	67766.13	-67778.10	-10.11	90.17	104979.68	-40.53	-67838.30	37180.91
	ROHF ^b	-253913.11	43944.08	—	—	-209969.03	-253913.11	43919.74	83520.87	-15425.12	—	-141897.62

^a ROHF and DFT (LDA, BLYP, and B3LYP functionals) calculations performed using Huz-IVu basis set. ^b ROHF calculation results from ref 17.

heaviest members of the X_2^- compounds is well justified, whereas this is not the case for the two lightest members.

To summarize, the nonrelativistic g tensor of the dihalogen anion radicals behaves similar to the g tensor of other linear molecules consisting of main group elements—that is, the parallel component of the g tensor is close to the free-electron g factor and the perpendicular component deviates significantly from the free-electron g factor, and this deviation depends almost exclusively on the magnitude of the spin–orbit coupling between the $|X^2\Sigma_u^+ \rangle$ ground state and the $|1^2\Pi_u \rangle$ excited state.

B. Leading-Order Relativistic Corrections to the g Tensors of X_2^- ($X = F, Cl, Br, I$) Anion Radicals. The calculated leading-order relativistic corrections to the electronic g tensors of the dihalogen anion radicals are presented in Table 3. We start the analysis of the results by first considering the scalar relativistic contributions to $\Delta\bar{g}(\mathcal{O}(\alpha^4))$, which have already been considered by Manninen et al.¹⁷ A quick inspection of the $\Delta\bar{g}_{RMC/SR}$ and $\Delta\bar{g}_{GC/SR}$ contributions reveals that these passive scalar relativistic corrections give negligible contributions to the parallel and perpendicular components of the g tensor shift for the entire dihalogen anion family, and even for the heaviest member of these compounds I_2^- , it only constitutes about 0.1–2% of the corresponding nonrelativistic contributions, $\Delta\bar{g}_{RMC}$ and $\Delta\bar{g}_{GC}$, from which these corrections originate (see eqs 15 and 16). A similar situation is also encountered in the case of the active scalar correction to $[\Delta g_{SO}]_{\perp}$, namely $[\Delta g_{SO/KE}]_{\perp}$, which is numerically insignificant and does not exceed 0.1% of $[\Delta g_{SO}]_{\perp}$ for I_2^- . In contrast, $[\Delta g_{SO/SR}]_{\perp}$ is nonnegligible and increases from about 0.06 to 118.9 ppt going from F_2^- to I_2^- , depending somewhat on the choice of exchange–correlation functional. For Br_2^- and I_2^- , this correction accounts for an increase of about 13% and 35% of the g tensor shift compared to the nonrelativistic Δg_{\perp} , respectively. Consequently, only $\Delta\bar{g}_{SO/SR}$ gives a sizable contribution to Δg_{\perp} and is thus responsible for the enhancement of this component in Br_2^- and I_2^- , whereas in the case

of Δg_{\parallel} , all corrections are negligible. We thus conclude that for compounds consisting of main group elements, scalar relativistic corrections to the nonrelativistic g tensor, given by the $\Delta\bar{g}_{RMC/SR}$, $\Delta\bar{g}_{GC/SR}$ and $\Delta\bar{g}_{SO/KE}$ terms in eq 24, can safely be neglected, as contributions arising from these corrections are in general small. For radicals containing heavy elements, on the other hand, passive scalar relativistic corrections to the spin–orbit term in the nonrelativistic g tensor, namely $\Delta\bar{g}_{SO/SR}$, is significant and must be accounted for in calculations of the electronic g tensor of such species.

These findings on the importance of the leading-order scalar relativistic corrections to the electronic g tensors of the dihalogen anion radicals are in marked contrast to the results of ref 17 and is due to the incorrect ROHF and MCSCF response code used in that work, as also noted in the previous section in the case of the second-order spin–orbit contribution to the nonrelativistic g tensor shift. In order to highlight the impact of this difference in calculations of the relativistic corrections, we have tabulated our recomputed ROHF values of the $\Delta\bar{g}(\mathcal{O}(\alpha^4))$ contributions together with the results of ref 17 in Table 3. A direct comparison of these results reveals significant differences. For example, for the case of Cl_2^- , the scalar relativistic correction to $[\Delta g_{RMC}]_{\perp}$ is in ref 17 found to be about -2.14 ppt, i.e., roughly 6 times larger than $[\Delta g_{RMC}]_{\perp}$ itself, whereas our calculations predict the scalar relativistic correction to $[\Delta g_{RMC}]_{\perp}$ to be -0.08 ppt, i.e., about 0.2% of $[\Delta g_{RMC}]_{\perp}$. We will therefore not consider the results of Manninen et al.¹⁷ in the remaining discussion.

Let us now turn to the next type of relativistic corrections to the electronic g tensor shift, namely the various spin–orbit corrections, which were omitted in ref 17 but which have been considered in part by Bolvin in connection with the “two-step” formalism.²⁰ The spin–orbit corrections to the mass-velocity and gauge terms in $\Delta\bar{g}(\mathcal{O}(\alpha^2))$, $\Delta\bar{g}_{RMC/SO}$ and $\Delta\bar{g}_{GC/SO}$, vanish for the dihalogen anion radicals and are therefore not tabulated in Table 3. We point out that

$\Delta\vec{g}_{\text{RMC/SO}}$ is a traceless antisymmetric tensor (see eqs 24 and 17) and does not contribute to the total isotropic g tensor shift of any molecule, not only in the specific case of X_2^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). The $\Delta\vec{g}_{\text{GC/SO}}$, on the other hand, is in general expected to give nonnegligible contributions of $\mathcal{O}(\alpha^4)$ to $\Delta\vec{g}$, whereas in the case of dihalogen anion radicals it is numerically insignificant due to the structure of the excited states in these systems. In addition to these corrections, the so-called higher-order spin-orbit correction to the orbital Zeeman effect, $\Delta\vec{g}_{\text{SO/SO}}$, also appears to $\mathcal{O}(\alpha^4)$. This correction gives a positive contribution to Δg_{\parallel} (see Table 3), but vanishes for Δg_{\perp} . The $\Delta\vec{g}_{\text{SO/SO}}$ can thus be interpreted as the higher-order counterpart of $\Delta\vec{g}_{\text{SO}}$, which requires two spin-orbit operators to mediate the interaction of the electrons with the external magnetic field via the \hat{H}_{OZ} operator. The data in Table 3 shows that $[\Delta g_{\text{SO/SO}}]_{\parallel}$ increases from 0.1 to 86.2 ppt going from the lightest to the heaviest members of the dihalogen anion radicals family, and already for Cl_2^- it is several times bigger than the nonrelativistic Δg_{\parallel} . However, since $[\Delta g_{\text{SO/SO}}]_{\parallel}$ is positive, it cannot be responsible for the large negative Δg_{\parallel} observed experimentally in the Br_2^- and I_2^- radicals and it therefore only has a screening effect—in fact, it effectively moderates other large negative relativistic corrections to Δg_{\parallel} (vide infra).

In order to identify these large negative contributions, let us turn to the last class of relativistic corrections to the g tensor included in the DGPT approach, the corrections that depend explicitly on the spin-Zeeman operator (the last two terms in eq 24). The first of these contributions, $\Delta\vec{g}_{\text{SZ/SR}}$, is similar to $\Delta\vec{g}_{\text{RMC/SO}}$ in the sense of being an antisymmetric traceless tensor that does not contribute to the total g tensor shift. $\Delta\vec{g}_{\text{SZ/SO}}$, on the other hand, gives rise to sizable contributions to both components of $\Delta\vec{g}$ ($\mathcal{O}(\alpha^4)$) (see Table 3). For linear molecules with a Σ -type ground state, this correction is distributed in a 2:1 ratio between Δg_{\parallel} and Δg_{\perp} as required by molecular symmetry (see Appendix C for details). The $[\Delta g_{\text{SZ/SO}}]_{\parallel}$ is of moderate size for F_2^- and Cl_2^- , but for the heaviest members of the dihalogen anion radical family, it increases significantly, being -18.97 and -86.18 ppt for Br_2^- and I_2^- , respectively. $\Delta\vec{g}_{\text{SZ/SO}}$ is therefore one of the largest (in terms of absolute values) relativistic corrections to the electronic g tensor shift and is responsible for the large negative parallel component of the g tensor shift of Br_2^- and I_2^- . This result is in agreement with the findings of Malkin et al.,¹⁸ which indicated that the spin-orbit effects determine Δg_{\parallel} in these radicals, since $\Delta\vec{g}_{\text{SZ/SO}}$ originates from the spin-orbit interaction operator and is interpreted as a higher-order spin-orbit correction to the spin-Zeeman effect (see eq 19).

Let us now examine the collective effect of all these corrections to $\Delta\vec{g}$ for the dihalogen anion radicals. For the parallel component of the g tensor, two relativistic corrections, $[\Delta g_{\text{SZ/SO}}]_{\parallel}$ and $[\Delta g_{\text{SO/SO}}]_{\parallel}$, are significant and they obey the relationship $[\Delta g_{\text{SZ/SO}}]_{\parallel} \approx -1/2[\Delta g_{\text{SO/SO}}]_{\parallel}$. The total relativistic correction to Δg_{\parallel} is therefore negative and approximately equal to $1/2[\Delta g_{\text{SZ/SO}}]_{\parallel}$, and it is dominated almost exclusively by higher-order spin-orbit interaction contributions to the spin and orbital Zeeman effects. The collective relativistic correction to Δg_{\parallel} becomes nonnegligible

already for Cl_2^- , and it increases steeply going to the heavier members of the dihalogen anion radical family. In this respect, it is worth to note that the nonrelativistic formalism for evaluating electronic g tensors fails already for Δg_{\parallel} of Cl_2^- , and an account of higher-order spin-orbit corrections to the Zeeman effect becomes essential for a correct prediction of Δg_{\parallel} . The higher-order spin-orbit corrections thus become competitive in magnitude compared to the nonrelativistic contributions to the g tensor shift even in molecules containing relatively light elements if the lower-order spin-orbit correction $\Delta\vec{g}_{\text{SO}}$ vanishes. For the perpendicular component of the g tensor shift of the dihalogen anion radicals, we encounter a different situation as both scalar-relativistic and spin-orbit corrections give sizable contributions to Δg_{\perp} in this case. However, $[\Delta g_{\text{SO/SR}}]_{\perp}$ and $[\Delta g_{\text{SZ/SO}}]_{\perp}$ are of comparable magnitude but bear the opposite sign, and the total relativistic correction to Δg_{\perp} is consequently relatively small, reflecting the fact that $[\Delta g_{\text{SO/SR}}]_{\perp}$ increases more rapidly compared to $[\Delta g_{\text{SZ/SO}}]_{\perp}$ when going from F_2^- to I_2^- . Thus, the leading-order relativistic correction to the perpendicular component of the g tensor shift is of moderate size and, for example in the case of I_2^- , is responsible for an increase of Δg_{\perp} by roughly 10–11% compared to the nonrelativistic Δg_{\perp} value. In contrast to Δg_{\parallel} , the relativistic correction to Δg_{\perp} must therefore be accounted for in molecules consisting of the heaviest elements in the periodic table.

Before concluding the discussion of the leading-order relativistic corrections to the electronic g tensors, we would like to consider in more detail a computational aspect of the evaluation of $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$. These contributions are computed using a sum-overstates approach, including up to 15 excited states of $|^2\Pi_u\rangle$ type in the perturbation theory summation of the $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$ corrections. As expected, for all dihalogen anion radicals, a single excited state dominates the contribution to $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$, and this contribution accounts for more than 99% of the total value of the computed corrections for all X_2^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) compounds. Thus, our SOS expansion for $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$ corrections are well converged and including more excited states in the SOS expansion is not expected to change these values further. We would like to stress, however, that the good convergence of the SOS expansion is specific to the dihalogen anion radicals and is not necessarily transferable to other molecular systems, and thus one should carefully check the convergence of the SOS expansion when evaluating the $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$ corrections in order to avoid introducing significant errors in the determination of the electronic g tensor shifts. We would also like to point out that the approximate relation between $[\Delta g_{\text{SZ/SO}}]_{\parallel}$ and $[\Delta g_{\text{SO/SO}}]_{\parallel}$, i.e., $[\Delta g_{\text{SZ/SO}}]_{\parallel} \approx -1/2[\Delta g_{\text{SO/SO}}]_{\parallel}$, only holds for dihalogen anion radicals, as the reduced matrix elements of the orbital angular momentum between the $|^2\Pi_u\rangle$ states for these molecules obeys $[{}^m\Omega_{\text{OZ}}]_z$ ($n \neq m$) vanish and $[{}^m\Omega_{\text{OZ}}]_z \approx 1$, indicating that the $|^2\Pi_u\rangle$ states are dominated by contributions from pure p_x and p_y atomic orbitals. Considering the complications described above in the computation of the $\Delta\vec{g}_{\text{SZ/SO}}$ and $\Delta\vec{g}_{\text{SO/SO}}$ corrections to electronic g tensor shifts, it is evident that the determination

Table 4. Nonrelativistic and Relativistic g Tensor Shifts of X_2^- ($X = F, Cl, Br, I$) and Their Dependence on the Exchange-Correlation Functional^a

molecule	method	$\Delta g_{ }$ (in ppt)			Δg_{\perp} (in ppt)			molecule	method	$\Delta g_{ }$ (in ppt)			Δg_{\perp} (in ppt)		
		nonrel ^a	rel ^b	total	nonrel ^a	rel ^b	total			nonrel ^a	rel ^b	total	nonrel ^a	rel ^b	total
F_2^-	ROHF	-0.26	-0.08	-0.34	13.22	-0.02	13.20	Cl_2^-	ROHF	-0.13	-0.39	-0.52	25.55	0.19	24.74
	LDA	-0.27	-0.15	-0.42	19.55	-0.07	19.48		LDA	-0.15	-0.96	-1.11	43.48	-0.02	43.46
	BLYP	-0.27	-0.13	-0.40	17.83	-0.06	17.77		BLYP	-0.15	-0.90	-1.05	42.09	0.01	42.10
	B3LYP	-0.27	-0.12	-0.39	17.02	-0.05	16.97		B3LYP	-0.15	-0.77	-0.92	38.52	0.07	35.59
	BP86 ^c	-0.30	—	-0.30	23.78	—	23.78		BP86 ^c	-0.17	—	-0.17	48.81	—	48.81
	ROHF ^d	-0.43	—	-0.43	14.70	—	14.70		ROHF ^d	-0.31	—	-0.31	32.83	—	32.83
	MRCI ^d	-0.43	—	-0.43	17.95	—	17.95		MRCI ^d	-0.31	—	-0.31	41.24	—	41.24
	BP86/DK-1e ^e	0.18 ^f	—	0.18	17.18 ^f	—	17.18		BP86/DK-1e ^e	0.18 ^f	—	0.18	39.88 ^f	—	39.88
	BP86/DK-2e ^e	-0.62 ^f	—	-0.62	16.28 ^f	—	16.28		BP86/DK-2e ^e	-0.92 ^f	—	-0.92	38.38 ^f	—	38.38
	expt ^g	—	—	-0.52	—	—	16.18		expt ^g	—	—	-1.72	—	—	13.81
Br_2^-	expt ^h	—	—	-0.32	—	—	19.08	I_2^-	expt ^h	—	—	-0.82	—	—	42.18
	ROHF	-0.31	-7.27	-7.58	101.79	6.35	108.14		ROHF	0.03	-31.84	-31.83	184.13	35.50	219.63
	LDA	-0.33	-18.97	-19.30	183.39	4.35	187.74		LDA	0.01	-86.19	-86.18	354.69	32.60	387.29
	BLYP	-0.33	-17.93	-18.26	179.58	4.68	184.26		BLYP	0.01	-80.44	-80.43	346.85	34.52	381.37
	B3LYP	-0.33	-15.14	-15.47	162.06	5.55	167.61		B3LYP	0.02	-67.77	-67.75	310.11	37.18	347.29
	BP86 ^c	-0.01	—	-0.01	188.86	—	188.86		BP86 ^c	0.01	—	0.01	348.85	—	348.85
	BP86/DK-1e ^e	0.18 ^f	—	0.18	178.58 ^f	—	178.58		BP86/DK-1e ^e	0.28 ^f	—	0.28	369.98 ^f	—	369.98
	BP86/DK-2e ^e	-17.82 ^f	—	-17.82	151.68 ^f	—	151.68		BP86/DK-2e ^e	-75.62 ^f	—	-75.62	243.68 ^f	—	243.68
	expt ^h	—	—	-23.22	—	—	171.78		expt ^h	—	—	-143.92	—	—	307.68

^a Nonrelativistic g tensor shifts evaluated according to eq 14. Computation carried out at ROHF and at DFT level (LDA, BLYP, and B3LYP functionals) in Huz-IVu basis set. ^b Relativistic g tensor shifts evaluated according to eqs 14 and 24. Computation carried out at ROHF and at DFT level (LDA, BLYP, and B3LYP functionals) in Huz-IVu basis set. ^c Unrestricted DFT calculations from ref 17 with BP86 exchange-correlation functional. ^d ROHF and MCSCF calculations from refs 46 and 47. ^e Douglas–Kroll one- and two-component calculation results from ref 18. The one-component results denoted as DK-1e and two-component results denoted as DK-2e, respectively. ^f Total contribution to electronic g tensor shift, includes relativistic effects. ^g Experimental data for F_2^- and Cl_2^- obtained in neon⁵⁰ and argon⁵¹ matrices, respectively. ^h Experimental data from NaX ($X = F, Cl, Br, I$) host crystal.⁵¹

of these correction is the most difficult part of calculating $\Delta \vec{g}(\mathcal{O}(\alpha^4))$, as it requires a detailed knowledge of the excited states domain structure and a careful consideration of the sum-overstates expansion convergence.

To summarize, of the $\mathcal{O}(\alpha^4)$ contributions to $\Delta \vec{g}$ defined in eq 24, only the scalar relativistic and spin–orbit corrections $\Delta \vec{g}_{SO/SR}$, $\Delta \vec{g}_{SO/SO}$, and $\Delta \vec{g}_{SZ/SO}$, are important and need to be included in the calculation of electronic g tensors of compounds containing Br or I atoms, or other heavy elements. Another important aspect to note in the evaluation of the relativistic corrections to $\Delta \vec{g}$ is the large differences between the corrections obtained in the ROHF and DFT calculations. These differences are likely to be due to the triplet instability problem that is often encountered in Hartree–Fock calculations involving triplet perturbations. The ROHF method can therefore not be recommended for calculations of relativistic corrections to electronic g tensors, and if one wants to pursue the ab initio track, MCSCF response theory will probably be required.

In Table 4, we have collected the nonrelativistic and relativistic g tensor shifts of the dihalogen radicals together with the previous one-component and two-component Douglas–Kroll DFT results of Malkin et al.,¹⁸ as well as available experimental data. The most striking effect of the relativistic corrections to $\Delta \vec{g}$ is observed for the parallel component of the g tensor shift, which increases by several orders of magnitude compared to its nonrelativistic value for the heaviest members of the dihalogen anion radicals family considered here. The relativistic effects are less pronounced on the perpendicular component of the g tensor shift, and amounts only to an increase by 10–11% compared to its nonrelativistic value for I_2^- . Our DFT results are in good agreement with the two-component Douglas–Kroll DFT

results of Malkin et al.¹⁸ (denoted as BP86/DK-2e in Table 4) for both components of the electronic g tensor shift. This result is as expected, as both methods account for the scalar relativistic and spin–orbit corrections to the nonrelativistic g tensors. The only difference between our results and those of Malkin et al.¹⁸ is observed for Δg_{\perp} of Br_2^- and I_2^- , where our DGPT approach produces systematically larger Δg_{\perp} values compared to the BP86/DK-2e method. This discrepancy is most likely caused by a different balance between the scalar-relativistic and spin–orbit corrections featured in these two approaches. Another interesting point to note is that the one-component Douglas–Kroll DFT method of Malkin et al.¹⁸ (denoted as BP86/DK-1e in Table 4), which includes only leading-order scalar relativistic corrections, fails to correctly predict the increase of $\Delta g_{||}$ going from F_2^- to I_2^- . This result is in agreement with our findings that the scalar relativistic effects are negligible for the parallel component of the g tensor shift of the dihalogen anion radicals and that the results of Maninnen et al.,¹⁷ which contradicts this statement, is caused by computational artifacts. Finally, we would like to point out that a comparison of the BP86/DK-1e and BP86/DK-2e results obtained in ref 18 indicates that the inclusion of higher-order spin–orbit corrections effectively reduces the magnitude of Δg_{\perp} on Br_2^- and I_2^- , and the same effect is also observed in our calculations (see the $[\Delta g_{SO/SR}]_{\perp}$ and $[\Delta g_{SZ/SO}]_{\perp}$ corrections in Table 3). Our DGPT approach therefore predicts a behavior of the g tensor shifts of the dihalogen anion radicals in agreement with the two-component Douglas–Kroll DFT approach, and both these very different methodologies give a consistent picture of the physical mechanisms responsible for the dominant relativistic corrections to the electronic g tensor of these compounds.

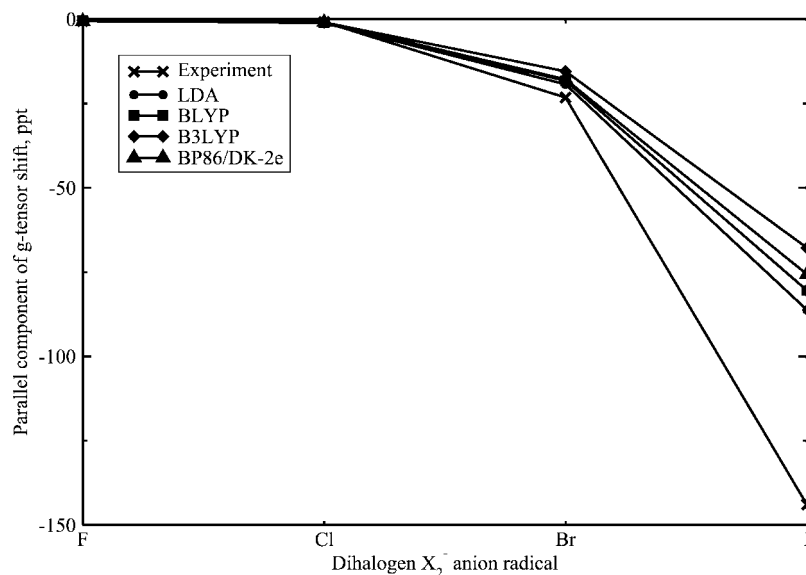


Figure 1. Parallel component of the electronic g tensor shift of dihalogen anion radicals.

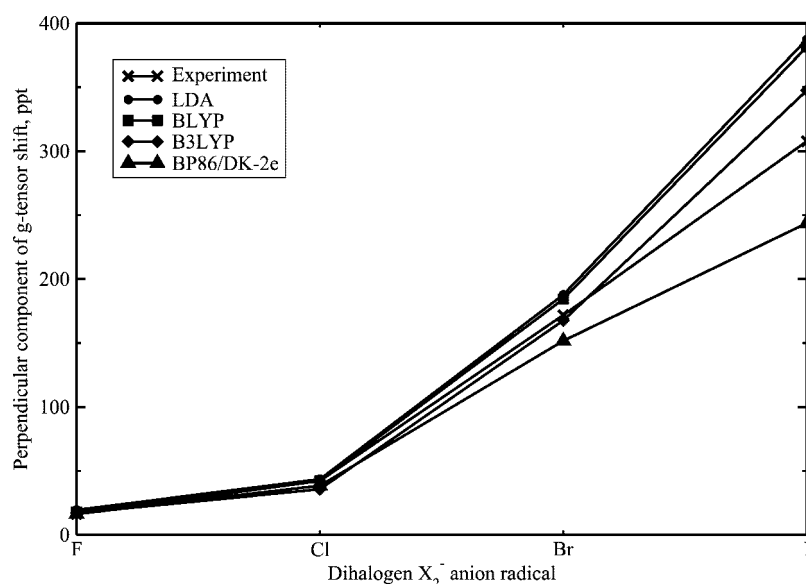


Figure 2. Perpendicular component of the electronic g tensor shift of dihalogen anion radicals.

Let us now turn to an assessment of the performance of the DGPT approach with respect to available experimental data. In Figure 1, we have plotted the parallel component of the g tensor shift for all dihalogen anion radicals obtained with the LDA, BLYP, and B3LYP functionals along with the BP86/DK-2e results of ref 18 as well as experimental data. From this plot it is evident that the DGPT approach reproduces the experimentally observed trend in $\Delta g_{||}$ for the whole series of dihalogen anion radicals independently of the choice of exchange-correlation functional. The best agreement with the experimental results is obtained using the LDA functional, as it consistently gives the smallest $|X^2\Sigma_u^+ \rangle \rightarrow |1^2\Pi_u \rangle$ excitation energies and in this way facilitates the enhancement of the $[\Delta g_{SZ/SO}]_{||}$ and $[\Delta g_{SO/SO}]_{||}$ corrections (see Table 3). The BLYP and B3LYP functionals systematically predict smaller (in terms of absolute values) $\Delta g_{||}$ values for all X_2^- ($X = F, Cl, Br, I$) compounds. The BLYP results are in close agreement with the BP86/DK-2e results of Malkin et al.¹⁸ The accuracy of the DGPT approach

in predicting $\Delta g_{||}$ is satisfactory for the first three members of the dihalogen anion radical family, but we underestimate $\Delta g_{||}$ of I_2^- approximately by a factor of 2 (in terms of absolute values), as can be seen from Figure 1. This discrepancy between theory and experiment is most likely caused by the complete neglect of environmental effects in our calculations, which play an important role in electronic g-tensor shifts as have been observed for the lightest members of the dihalogen anions family (see Bruna and Grein's MRCI and ROHF results in refs 46 and 47).

The perpendicular components of the g tensor shift of the X_2^- ($X = F, Cl, Br, I$) compounds are plotted in Figure 2. As for $\Delta g_{||}$, Δg_{\perp} obtained with the DGPT approach qualitatively reproduce the experimental data for the whole series of dihalogen anion radicals, independently of the choice of exchange-correlation functional employed in the calculations. Of the different exchange-correlation functionals, B3LYP has the closest agreement with experiment as well as to the results of ref 18. LDA in this case systematically overesti-

mates Δg_{\perp} , whereas BLYP gives results in between LDA and B3LYP. The difference in performance of the exchange-correlation functionals for the parallel and perpendicular components of the g tensor shift does not allow us to select a functional most suited for evaluating the relativistic g tensor using the DGPT approach. However, based on the good performance of the B3LYP functional for Δg_{\perp} in X_2^- ($X = F, Cl, Br, I$), we prefer this exchange-correlation functional over BLYP or LDA, as it provides more consistent results for the electronic g tensor shifts and excitation energies in the dihalogen anion radicals and is expected to give results of similar quality also for other compounds containing Br or I atoms. To summarize, the DGPT approach presented in this paper in combination with spin-restricted open-shell density functional theory is capable of predicting the leading-order relativistic corrections to the electronic g tensors of dihalogen anion radicals as well as providing a clear picture of the physical mechanisms responsible for the observed relativistic effects. The DGPT approach is thus an attractive alternative approach to the two-component approach developed by Malkin et al.¹⁸ for the calculation of relativistic g tensors in molecules containing heavy elements.

V. Conclusions

The current work is a step in the development of perturbation theory based approaches for the calculation of the leading-order relativistic corrections to electronic g tensors. The approach developed here is based on degenerate perturbation theory and is formulated for molecules with an orbitally nondegenerate doublet ground state. The approach accounts for all relativistic corrections of $\mathcal{O}(\alpha^4)$ to the electronic g tensor, arising from the one-electron part of the Breit–Pauli Hamiltonian—that is, the scalar relativistic and spin–orbit corrections to the spin- and orbital-Zeeman effects. The formalism developed is in its present form limited to molecules with a doublet ground state, but it can relatively easily be extended to handle systems with ground states of different multiplicity by substituting the conventional Pauli matrices with generalized Pauli matrices, and rederiving the final expression for each term in eq 24. The DGPT approach can be implemented at the *ab initio* or density functional level of theory, provided that the selected method is capable of producing pure spin states. In this work, we have implemented this approach at the spin-restricted open-shell density functional theory level, as our main aim is to investigate large molecular systems containing heavy elements, which are beyond the reach of conventional *ab initio* methods such as MCSCF. In addition to the full DGPT formalism, we have also developed a simplified two-state model for the approximate calculation of electronic g tensors of linear molecules including leading-order relativistic corrections. We believe that both approaches will become useful tools for the investigation and analysis of EPR spectra of compounds containing heavy elements, where an account of relativistic effects is of critical importance.

The application of the DGPT approach to the dihalogen anion radicals shows that the leading-order relativistic corrections allows us to explain the variation of both g tensor shift components in these compounds, and we achieve

satisfactory agreement between theory and available experimental data. The results obtained indicate that the spin–orbit interaction is responsible for the large negative parallel component of the g tensor shift in Br_2^- and I_2^- and that both scalar relativistic and spin–orbit effects are important for the perpendicular components of these two radicals. These findings are in a good agreement with the results of Malkin et al.¹⁸ and also demonstrate that the conclusions of Manninen et al.¹⁷ are incorrect due to an incorrect handling of triplet operators in their calculations. The controversy about the dominant physical mechanism responsible for the g tensor shift of the dihalogen anion radicals has thus been resolved.

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Appendix A: Degenerate Perturbation Theory for Computation of Molecular Properties

In open-shell molecular systems described by a nonrelativistic Hamiltonian, the ground state along with the excited states are degenerate with respect to the total electronic spin degrees of freedom, and consequently the evaluation of electronic spin-dependent properties, such as electronic g tensors, requires the application of a perturbation theory which can handle degeneracies of this kind. One such approach is the degenerate perturbation theory developed by Löwdin in the middle of the previous century.⁵² In this approach, the degeneracy of the unperturbed states is tackled by employing the reduced resolvent operator technique, which effectively splits states of the molecular system into sets of nondegenerate state domains and ensures that the perturbation theory summations are free from divergences caused by the degeneracies. The original formulation of DGPT by Löwdin focused on the evaluation of various corrections to the electronic energy of a degenerate ground state, and little attention has been given to the treatment of molecular properties in this approach. In order to extend this approach, we have, in the spirit of response theory,⁵³ reformulated the DGPT equations in a form more convenient for the direct computation of arbitrary molecular properties in the presence of a perturbation \hat{V} .

Collecting all degenerate substates of the ground-state into a row matrix $|0\rangle = (|^{2S+1}0; -m\rangle |^{2S+1}0; -m+1\rangle \dots |^{2S+1}0; m\rangle)$, and defining the conjugated state as a column matrix $\langle 0| = (\langle ^{2S+1}0; -m| \langle ^{2S+1}0; -m+1| \dots \langle ^{2S+1}0; m|)^T$, we can in analogy with ordinary response theory expand a molecular property given by an operator \hat{A} as

$$\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} + \mathbf{A}^{(2)} + \dots \quad (\text{A.1})$$

where we instead of the conventional response functions have introduced response matrices which span the degenerate

substates manifold. From the Löwdin expressions for evaluating first-, second-, and third-order corrections to the energy of the degenerate ground state, we can write down the following expressions for determining the zeroth-, first-, and second-order response matrices

$$\begin{aligned} \mathbf{A}^{(0)} &= \langle \mathbf{0} | \hat{A} | \mathbf{0} \rangle \\ \mathbf{A}^{(1)} &= \langle \mathbf{0} | \hat{A} \hat{R} \hat{V} + \hat{V} \hat{R} \hat{A} | \mathbf{0} \rangle \\ \mathbf{A}^{(2)} &= \langle \mathbf{0} | \hat{A} \hat{R} \hat{V} \hat{R} \hat{V} | \mathbf{0} \rangle - \frac{1}{2} \{ \mathbf{V}^{(0)}, \langle \hat{\mathbf{0}} | \hat{A} \hat{R}^2 \hat{V} | \mathbf{0} \rangle \} + \\ &\langle \mathbf{0} | \hat{V} \hat{R} \hat{A} \hat{R} \hat{V} | \mathbf{0} \rangle - \frac{1}{2} \{ \mathbf{A}^{(0)}, \langle \hat{\mathbf{0}} | \hat{V} \hat{R}^2 \hat{V} | \mathbf{0} \rangle \} + \langle \mathbf{0} | \hat{V} \hat{R} \hat{V} \hat{R} \hat{A} | \mathbf{0} \rangle - \\ &\frac{1}{2} \{ \mathbf{V}^{(0)}, \langle \mathbf{0} | \hat{V} \hat{R}^2 \hat{A} | \mathbf{0} \rangle \} \end{aligned} \quad (\text{A.2})$$

where we have introduced the reduced resolvent operator \hat{R} , which projects out the ground-state manifold from the perturbation theory summations and is defined in terms of the unperturbed Hamiltonian \hat{H}_0 of the system as

$$\hat{R} = \frac{\hat{1} - |\mathbf{0}\rangle\langle\mathbf{0}|}{E_0 - \hat{H}_0} \quad (\text{A.3})$$

These expressions for evaluating the property \mathbf{A} are in general applicable to open-shell molecular systems with a ground state of arbitrary multiplicity and allow us to treat the degeneracy with respect to spin degrees of freedom in a uniform way at different orders in the perturbation theory expansion. Furthermore, for electronic spin-independent operators \hat{A} and \hat{V} , the response matrices reduce to a diagonal form and, for each $|^{2S+1}0; m\rangle$ component of the degenerate ground state, the response matrix elements become identical to the ordinary response functions for evaluating static molecular properties.

Appendix B: Reduced Matrix Elements for Doublet States

In this Appendix we present the details underlying the different reduced matrix elements of the spin rank one operators, such as the spin-orbit operator, appearing in Table 1. The matrix element between two Kramer's doublet states, $|\mathbf{n}\rangle$ and $|\mathbf{n}'\rangle$, for these operators can be expanded in terms of reduced matrix elements ${}^{nn'}\Omega_k$ and the Pauli matrices which, together with the two-dimensional unit matrix, form a complete basis in the space of two-dimensional square matrices

$$\langle \mathbf{0} | \hat{H} | \mathbf{0} \rangle = \sum_{k=x,y,z} {}^{nn'}\Omega_k \sigma_k \quad (\text{B.1})$$

The reduced matrix elements ${}^{nn'}\Omega_k$ entering the above equation can be determined by comparing the corresponding nonvanishing matrix elements on the right- and left-hand sides, i.e.

$$\langle {}^2n; m | \hat{H}_k | {}^2n'; m' \rangle = {}^{nn'}\Omega_k [\sigma_k]_{mm'} \quad (\text{B.2})$$

and inserting the explicit expression for the $\langle {}^2n; m | \hat{H}_k | {}^2n'; m' \rangle$ and $[\sigma_k]_{mm'}$ matrix elements. In order to accomplish this task, we transform all quantities in the latter equality into spherical coordinates, and further

reduce the \hat{H} matrix elements by applying the Wigner-Eckart theorem in spin space

$$\langle {}^2n; m | \hat{H} | {}^2n'; m' \rangle = \sum_{\mu=-1,0,1} (-1)^\mu \langle {}^2n | \hat{H}_{-\mu}(\vec{s}) | {}^2n' \rangle C_{m'm\mu}^{(1/2)1(1/2)} \quad (\text{B.3})$$

where $C_{m'm\mu}^{j_1 j_2 j_3}$ are Clebsch-Gordan coefficients and $\langle {}^2n | \hat{H}_{-\mu}(\vec{s}) | {}^2n' \rangle$ are the reduced matrix elements which are independent of the spin projection quantum numbers. The operator in this expression refers in spin space to the operator as a whole, and the remaining index μ refers only to the spatial part (e.g., the orbital angular momentum part of the spin-orbit operator). A detailed discussion of the evaluation of matrix elements of this kind can be found in ref 54. In order to compute the matrix elements $\langle {}^2n | \hat{H}_{-\mu}(\vec{s}) | {}^2n' \rangle$, we have for convenience selected the high-spin reference states components, $|^2n; ^1/2\rangle$ and $|^2n'; ^1/2\rangle$, and this choice leads to the following expression for this matrix element

$$\langle {}^2n | \hat{H}_{-\mu}(\vec{s}) | {}^2n' \rangle = \langle {}^2n; \frac{1}{2} | \hat{H}_{-\mu}(s_0) | {}^2n'; \frac{1}{2} \rangle C_{(1/2)0(1/2)}^{(1/2)1(1/2)} \quad (\text{B.4})$$

which in turn allows us to obtain the final expression for evaluating the operator \hat{H} matrix elements in spherical coordinates

$$\begin{aligned} \langle {}^2n; m | \hat{H}_\mu | {}^2n'; m' \rangle \\ = \sum_{\mu=-1,0,1} (-1)^\mu \langle {}^2n; \frac{1}{2} | \hat{H}_{-\mu}(s_0) | {}^2n'; \frac{1}{2} \rangle C_{m'm\mu}^{(1/2)1(1/2)} / C_{(1/2)0(1/2)}^{(1/2)1(1/2)} \end{aligned} \quad (\text{B.5})$$

Taking this result into account, we can rewrite eq B.2, which defines the reduced matrix element ${}^{nn'}\Omega_k$ in Cartesian coordinates system, into an equivalent equation in spherical coordinates

$$\langle {}^2n; \frac{1}{2} | \hat{H}_{-\mu}(s_0) | {}^2n'; \frac{1}{2} \rangle C_{m'm\mu}^{(1/2)1(1/2)} / C_{(1/2)0(1/2)}^{(1/2)1(1/2)} = {}^{nn'}\Omega_{-\mu} [\sigma_\mu]_{mm'} \quad (\text{B.6})$$

Since the values of $[\sigma_\mu]_{mm'}$ can be easily obtained from the relationship

$$\frac{1}{2} [\sigma_\mu]_{mm'} = C_{m'm\mu}^{(1/2)1(1/2)} / 2 C_{(1/2)0(1/2)}^{(1/2)1(1/2)} \quad (\text{B.7})$$

we can after some algebraic manipulations write the reduced matrix elements used in the $\langle n | \hat{H} | n' \rangle$ expansion as

$${}^{nn'}\Omega_\mu = \langle {}^2n; \frac{1}{2} | \hat{H}_\mu(s_0) | {}^2n'; \frac{1}{2} \rangle \quad (\text{B.8})$$

in spherical coordinates, or as

$${}^{nn'}\Omega_k = \langle {}^2n; \frac{1}{2} | \hat{H}_k(s_z) | {}^2n'; \frac{1}{2} \rangle \quad (\text{B.9})$$

in Cartesian coordinates. These reduced matrix elements can be found in Table 1.

Appendix C: Two-State Model for Electronic g Tensors of Linear Molecules

The behavior of the electronic g tensors in linear molecules with a doublet ground state of $|^2\Sigma\rangle$ type is frequently

Table 5. Comparison of g Tensor Shift of Dihalogen Anion Radicals (in ppt) Obtained Using Full DGPT and “Two-State” Approaches^a

molecule	functional	two-state model		DGPT		molecule	functional	two-state model		DGPT	
		$\Delta g_{ }$	Δg_{\perp}	$\Delta g_{ }$	Δg_{\perp}			$\Delta g_{ }$	Δg_{\perp}	$\Delta g_{ }$	Δg_{\perp}
F_2^-	LDA	-0.15	20.51	-0.42	19.48	Cl_2^-	LDA	-0.96	47.38	-1.11	43.46
	BLYP	-0.13	18.75	-0.40	17.77		BLYP	-0.88	47.52	-1.05	42.10
	B3LYP	-0.12	17.91	-0.39	16.97		B3LYP	-0.75	42.93	-0.92	35.59
Br_2^-	LDA	-18.76	188.43	-19.30	187.74	I_2^-	LDA	-85.56	339.76	-86.18	387.29
	BLYP	-17.62	181.97	-18.26	184.26		BLYP	-79.57	329.51	-80.43	381.37
	B3LYP	-14.97	168.48	-15.47	167.61		B3LYP	-67.20	307.63	-67.75	347.29

^a DFT (LDA, BLYP, and B3LYP functionals) calculations performed using Huz-IVu basis set.

governed by a single excited $|^2\Pi\rangle$ type state, which gives the dominant contribution to both the perpendicular and parallel components of the electronic g tensor shift. This feature of the electronic g tensor of linear molecules has been observed many times in theoretical investigations of diatomics consisting of main group elements,^{5,11,15,47} and recently similar trends have been verified also for diatomics containing heavy elements.²⁰ In view of these findings, a simple two-state model for an approximate estimation of the electronic g tensor shift in linear molecules is desirable, as it not only allows us to predict the magnitude of the electronic g tensor shift but also provides valuable insight into the physical mechanisms responsible for this shift.

We will start the development of the two-state model by assuming that the bulk part of the parallel and perpendicular components of the g tensor is defined by the contribution from a single $|^2\Pi\rangle$ type state, which is one of the low-lying excited states in linear molecules. Similarly to Bolvin,²⁰ we will represent the orbitally doubly degenerate $\{^2\Pi$ state as two complex components $|^2\Pi_+\rangle$ and $|^2\Pi_-\rangle$. Under these conditions, we will apply degenerate perturbation theory for evaluating the relativistic electronic g tensor shift, taking into account only the $|^2\Sigma\rangle$ ground state and one $|^2\Pi\rangle$ excited state. As prescribed by the DGPT formalism, we first form a Kramers pair for the ground state $|\Sigma\rangle = (|^2\Sigma; 1/2\rangle|^2\Sigma; -1/2\rangle)$ and two row vectors for the $|^2\Pi\rangle$ state, namely $\langle\Pi_+| = (|^2\Pi_+; 1/2\rangle|^2\Pi_+; -1/2\rangle)$ and $\langle\Pi_-| = (|^2\Pi_-; 1/2\rangle|^2\Pi_-; -1/2\rangle)$. Taking into account only passive scalar relativistic and spin-orbit corrections to the orbital and spin-Zeeman interactions, i.e., limiting the perturbation operator to $\hat{H}_{SZ}, \hat{H}_{OZ}, \hat{H}_{SR} = \hat{H}_{MV} + \hat{H}_{DW}$ and $\hat{H}_{SO} = \hat{H}_{SO(1e)} + \hat{H}_{SO(2e)}$, we will obtain nonvanishing contributions to the electronic g tensor shift (see eqs 14 and 24) from $\Delta\vec{g}_{SO}$, $\Delta\vec{g}_{SO/SR}$, $\Delta\vec{g}_{SO/SO}$, and $\Delta\vec{g}_{SZ/SO}$. Before proceeding with the actual computation of these contributions to the g tensor shift, let us introduce the following definitions of the orbital Zeeman effect and energy-weighted spin-orbit interaction matrix elements between the $|^2\Sigma\rangle$ and $|^2\Pi\rangle$ states:

$$\langle\Sigma|\hat{H}_{OZ}|^2\Pi_{\pm}\rangle = \mu_B \sum_{k=x,y,z} B_k [^{\Sigma\Pi_{\pm}}\Omega_{OZ}]_k = \mu_B (B_x L \pm iB_y L) \mathbf{1} \quad (C.1)$$

$$\langle\Pi_{\pm}|\hat{R}\hat{H}_{SO}|\Sigma\rangle = \sum_{k=x,y,z} \frac{[^{\Pi_{\pm}\Sigma}\Omega_{SO}]_k \sigma_k}{E_{\Sigma} - E_{\Pi}} = \frac{\eta}{2} (\sigma_x \mp i\sigma_y) \quad (C.2)$$

The expressions for the \hat{H}_{OZ} and \hat{H}_{SO} operator matrix elements are chosen in agreement with the notation used by Bolvin²⁰ in

order to facilitate a direct comparison between the g tensor shift formulas obtained in ref 20 for linear molecules. For the nonrelativistic g tensor, $\Delta\vec{g}_{SO}$ gives a nonvanishing contribution only to the perpendicular g tensor shift component Δg_{\perp} (see eqs 13 and 14)

$$\Delta g_{\perp} = [\Lambda_{SO}]_{xx} = 4 \left(\frac{[^{\Sigma\Pi_+}\Omega_{OZ}]_x [^{\Pi_+\Sigma}\Omega_{SO}]_x}{E_{\Sigma} - E_{\Pi}} + \frac{[^{\Sigma\Pi_-}\Omega_{OZ}]_x [^{\Pi_-\Sigma}\Omega_{SO}]_x}{E_{\Sigma} - E_{\Pi}} \right) = 4\eta L \quad (C.3)$$

Therefore, in agreement with the conventional g tensor formalism, our two-state model predicts that only the perpendicular component of the nonrelativistic g tensor of linear molecules deviates significantly from the free-electron g factor. The leading-order relativistic corrections to the electronic g tensor shift are obtained from the remaining contributions to $\Delta\vec{g}$ considered in this two-state model, namely $\Delta\vec{g}_{SO/SR}$, $\Delta\vec{g}_{SO/SO}$, and $\Delta\vec{g}_{SZ/SO}$.

Let us first consider the spin-orbit induced contributions to the g tensor shift of $\mathcal{O}(\alpha^4)$. One of these contributions is the pure spin-orbit correction to the electronic Zeeman effect, i.e., $\Delta\vec{g}_{SZ/SO}$, which gives contributions to both the parallel and perpendicular components of the electronic g tensor shift, according to eqs 19 and 24

$$\Delta g_{\perp} = 2[\Sigma_{SZ/SO}]_{xx} = -4 \left(\frac{[^{\Sigma\Pi_+}\Omega_{SO}]_y [^{\Pi_+\Sigma}\Omega_{SO}]_y}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[^{\Sigma\Pi_-}\Omega_{SO}]_y [^{\Pi_-\Sigma}\Omega_{SO}]_y}{(E_{\Sigma} - E_{\Pi})^2} \right) = -2\eta^2 \quad (C.4)$$

$$\Delta g_{||} = 2[\Sigma_{SZ/SO}]_{zz} = -4 \left(\frac{[^{\Sigma\Pi_+}\Omega_{SO}]_x [^{\Pi_+\Sigma}\Omega_{SO}]_x}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[^{\Sigma\Pi_-}\Omega_{SO}]_x [^{\Pi_-\Sigma}\Omega_{SO}]_x}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[^{\Sigma\Pi_+}\Omega_{SO}]_y [^{\Pi_+\Sigma}\Omega_{SO}]_y}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[^{\Sigma\Pi_-}\Omega_{SO}]_y [^{\Pi_-\Sigma}\Omega_{SO}]_y}{(E_{\Sigma} - E_{\Pi})^2} \right) = -4\eta^2 \quad (C.5)$$

whereas the other contribution is the higher-order spin-orbit correction to the orbital Zeeman effect, i.e., $\Delta\vec{g}_{SO/SO}$ and affects only the parallel component of the g tensor (see eqs 23 and 24)

$$\Delta g_{\parallel} = [\Lambda_{\text{SO/SO}}]_{zz} = 2i \sum_{jj'=x,y,z} \epsilon_{jj'z} \frac{[\sum^{\Pi(+,-)} \Omega_{\text{SO}}]_j [\sum^{\Pi(+,-)} \Omega_{\text{OZ}}]_z [\sum^{\Pi(+,-)} \Omega_{\text{SO}}]_{j'}}{(E_{\Sigma} - E_{\Pi})^2} = 2i \left(\frac{[\sum^{\Pi+} \Omega_{\text{SO}}]_x [\sum^{\Pi+} \Omega_{\text{SO}}]_y}{(E_{\Sigma} - E_{\Pi})^2} - \frac{[\sum^{\Pi+} \Omega_{\text{SO}}]_y [\sum^{\Pi+} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} - \frac{[\sum^{\Pi-} \Omega_{\text{SO}}]_x [\sum^{\Pi-} \Omega_{\text{SO}}]_y}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[\sum^{\Pi-} \Omega_{\text{SO}}]_y [\sum^{\Pi-} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} \right) = 2\eta^2 \quad (\text{C.6})$$

We have here explicitly inserted the values of the reduced orbital Zeeman effect operators between the complex components of the $l^2\Pi$ state, which are equal to $[\sum^{\Pi+} \Omega_{\text{OZ}}]_z = \pm 1$ and $[\sum^{\Pi+} \Omega_{\text{OZ}}]_x = 0$, respectively. This selection of values for the reduced orbital Zeeman effect operator matrix elements between the complex $l^2\Pi$ state components is well justified for a $l^2\Pi$ state dominated by pure p_x and p_y atomic orbitals (see ref 20), and according to our quadratic response double residue calculations of $[\sum^{\Pi(+,-)} \Omega_{\text{OZ}}]_z$ type matrix elements holds very well for all investigated dihalogen anion radicals. Collecting these contributions to the electronic g tensor shift, which represent the spin-orbit effects on the g tensor, we obtain the following expression for the perpendicular and parallel components of $\vec{\Delta g}$ in linear molecules

$$\Delta g_{\perp} = 4\eta L - 2\eta^2 \quad \text{and} \quad \Delta g_{\parallel} = -2\eta^2 \quad (\text{C.7})$$

which are equivalent to those obtained by Bolvin (see eq 39) in ref 20). Therefore, the two-state model presented here, which deals with spin-orbit interaction-induced contributions, is identical to the “two-step” approach developed by Bolvin²⁰ if a single $l^2\Pi$ state is used in both models for linear molecules, and contributions from quartet states are neglected in the “two-step” approach.

Finally, let us examine another aspect of the two-state model, namely the treatment of the passive scalar-relativistic effects, which are accounted for by the inclusion of the $\vec{\Delta g}_{\text{SO/SR}}$ term in the g tensor shift evaluation formulas. The $\vec{\Delta g}_{\text{SO/SR}}$ only affects the perpendicular component of the g tensor shift, as this contribution corrects $\vec{\Delta g}_{\text{SO}}$, and gives rise to the following contribution according to eqs 22 and 24):

$$\Delta g_{\perp} = [\Lambda_{\text{SO/SR}}]_{xx} = 4 \left(\frac{[\sum^{\Pi+} \Omega_{\text{SR}}] [\sum^{\Pi+} \Omega_{\text{OZ}}]_x [\sum^{\Pi+} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} + \frac{[\sum^{\Pi-} \Omega_{\text{SR}}] [\sum^{\Pi-} \Omega_{\text{OZ}}]_x [\sum^{\Pi-} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} + \frac{\sum^{\Sigma} \Omega_{\text{SR}} [\sum^{\Pi+} \Omega_{\text{OZ}}]_x [\sum^{\Pi+} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} + \frac{\sum^{\Sigma} \Omega_{\text{SR}} [\sum^{\Pi-} \Omega_{\text{OZ}}]_x [\sum^{\Pi-} \Omega_{\text{SO}}]_x}{(E_{\Sigma} - E_{\Pi})^2} \right) = 4\eta L \zeta \quad (\text{C.8})$$

where we have introduced the energy-weighted reduced matrix element of the \hat{H}_{SR} operator

$$\zeta = \frac{\Pi_{\pm} \Pi_{\pm} \Omega_{\text{SR}} - \sum^{\Sigma} \Omega_{\text{SR}}}{E_{\Sigma} - E_{\Pi}} \quad (\text{C.9})$$

The passive scalar-relativistic correction is thus expected to be of similar magnitude as the higher-order spin-orbit correction to Δg_{\perp} , i.e., $4L\eta\zeta \approx 2\eta^2$ and this approximate equality can be expected to hold for most linear molecules. Combining the scalar-relativistic contribution to $\vec{\Delta g}$ with the previously described spin-orbit contribution, we obtain the final expression for evaluating electronic g tensor shifts of linear molecules in the two-state model:

$$\Delta g_{\perp} = 4\eta L(1 + \zeta) - 2\eta^2 \quad \text{and} \quad \Delta g_{\parallel} = -2\eta^2 \quad (\text{C.10})$$

It is clear that the scalar-relativistic and spin-orbit corrections to Δg_{\perp} almost cancel each other and that Δg_{\perp} becomes roughly equal to the nonrelativistic g tensor shift value, i.e., $\Delta g_{\perp} \approx 4\eta L$. In view of these findings, we emphasize that scalar relativistic effects only play a minor role in the electronic g tensor in linear molecules and that the spin-orbit interaction is responsible for the large negative parallel g tensor shift in linear molecules containing heavy elements. A similar conclusion about the importance of the spin-orbit contribution to Δg_{\parallel} has previously been obtained both theoretically and numerically by Bolvin,²⁰ as well as observed by Malkin et al. in their density-functional, two-component Douglas-Kroll calculations on the dihalogen anion radicals.¹⁸

Finally, before concluding the discussion of the two-state model for evaluating electronic g tensors in linear molecules with $l^2\Sigma$ type ground state, we would like to validate the approach for the dihalogen anion radicals. The electronic g tensor shift computed using the two-state model and the full DGPT treatment according to eq 25 are tabulated in Table 5. The results show that the two-state model results deviate from the ones obtained using a full DGPT treatment by on average 10%, and the largest deviation is observed for BLYP in the I_2^- radical anion. On the basis of this limited test example set, we can recommend the two-state model for estimating electronic g tensors in linear molecules, since these g tensors are dominated by the contribution from the singly excited $l^2\Pi$ state. Furthermore, this model can easily be generalized to a multistate model following the derivation above if the linear molecule features several $l^2\Pi$ states with significant contributions to the g tensor shift. We believe the two-state model will be useful in the analysis of EPR spectra of linear molecules and help quantify different effects responsible for the g tensor shift in molecules of this kind.

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