Calculation of Electronic g-Tensors Using a Relativistic Density Functional Douglas−Kroll Method

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We present a novel scheme to calculate electronic **g**-tensor values of doublet-state systems within a density functional method and discuss the implementation and results of first applications. The method employs two-component eigenfunctions of the Kohn−Sham equation where spin−orbit effects are taken into account self-consistently. Therefore, the **g**-tensor can be treated as first-order property with respect to the perturbation by external magnetic field alone. The Zeeman energy splitting, an inherently relativistic effect, is naturally and transparently determined by the two-component ground-state wave function (Kramers doublet) without invoking virtual states. Abandoning the widely accepted perturbative treatment of the spin−orbit term makes the present method also applicable to molecular systems with considerable spin−orbit interaction. Conceivable improvements of the method performance are proposed and discussed.

I. Introduction

Electron paramagnetic resonance (EPR) spectrosopy is widely employed to study radicals, coordination compounds, and solid materials characterized by the presence of unpaired electrons.[1−3] EPR spectra are helpful for clarifying interrelations between electronic and structural features of various molecular systems relevant to physical, chemical, and biological problems. Along with the hyperfine coupling constants, the **g**-tensor is one of the fundamental EPR parameters. Nevertheless, **g**-tensors attracted significant attention of the research community that deals with high-level quantum-chemical calculations only during the past few years.[4−17]

Several factors induced these recent theoretical activities. First, amazing progress in the computer hardware and software drastically enhanced the power of *first-principles* electronic structure calculations. Complex molecular systems can now be treated at the level of realistic models and computational results can be achieved with an accuracy close to that of experimental methods. This breakthrough enhanced the interest in calculating "properties" in general. Second, during the past decade experience has been accumulated with calculations of features that characterize the response of molecules to a magnetic field, foremost the response measured by nuclear magnetic resonance.[18] Third, the advent of the high-field (high-frequency) EPR technique (e.g., W-band, 95 GHz; F-band, 150 GHz) opened the way to resolve **g**-tensor components of much smaller anisotropy than by using conventional (X-band, 9 GHz) spectrometers.[19−21] This novelty is of particular importance for spectra of organic radicals: there, at common lower fields, only slightly split **g**-tensor components usually overlap with the hyperfine structure. Resolved **g**-tensor components were demonstrated to furnish very delicate (often unique) details of the structure of radical species and their environment as well as of the local behavior of their wave functions.[19−21] It is no surpise that semiempirical electronic structure calculations striving for precise **g**-tensor values of organic radicals again became frequently cited[22,23] after a relatively long quiet period that followed the era of semiempirically calculated magnetic resonance parameters.[1,3,24]

Recent high-level computations of **g**-tensor components using wave function methods have been initiated by Lushington et al. at the restricted open-shell Hartree−Fock (ROHF)[4] and multireference configuration interaction (MRCI)[5] levels. A response approach for calculating the **g**-tensor based on a combined perturbation treatment of the orbital Zeeman effect and spin−orbit interaction was developed.[7] Applications of this method (e.g., to medium-size organic radicals[8]) resulted in a rather encouraging accuracy already at the ROHF level. Density functional (DF) calculations of electronic **g**-tensors were pioneered by van Lenthe et al.[16] and by Schreckenbach and Ziegler.[10] One more DF tool to calculate **g**-tensors was implemented very recently.[13]

All the schemes mentioned, except that of van Lenthe,[16] share the feature of perturbational description of spin−orbit interactions. Such a treatment of spin−orbit effects is attractive because conventional quantum chemical codes operating with real (one-component) solutions are readily available. Nevertheless, the applicability of perturbational approaches can be questioned in at least two aspects. First, these methods generally require the summation over (formal) electronic excitations characterized by energies and spatial behavior of virtual (unoccupied) states; the accuracy of these features is usually not very high and the sum over states has to be truncated at some point, without a guarantee of rapid convergence, when the excited states are ordered with respect to the energy.[3,23] Second, perturbation theory is accurate

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only for small spin−orbit interactions. However, deviation of **g**-values from the free-electron value g_e is essentially a relativistic (spin−orbit) phenomenon in systems with quenched orbital momentum. Relativistic effects are known to grow roughly as the square of the atomic number Z.[25] Thus, deficiencies of the perturbation approach can become non-negligible already in molecules of rather light atoms.[10]

A fruitful assumption is that scalar relativistic (mass-velocity and Darwin) effects are of only minor importance for **g**-tensors of molecules of light elements. This leads to the idea of confining the calculation of the **g**-tensor to two-component wave function formalism, with spin−orbit interactions included self-consistently and scalar relativistic interactions neglected. In such a general Hartree−Fock (GHF) approach,[9] **g**-tensors of small inorganic radicals are calculated with errors of about 5×10^{-4} compared to experiment.[9] This accuracy is better than in the DF approach[10] and almost as good as in demanding MRCI calculations,[5] but for systems that contain heavy elements this promising GHF approach would need to be improved. Accounting for often mandatory scalar relativistic and computationally expensive electron correlation effects would significantly restrict the size of species tractable by this method.

One can build an efficient approach for calculating **g**-tensors on the basis of a DF method that partly takes correlation effects into account and goes beyond the common one-component ("nonrelativistic") formulation. In a fully relativistic four-component Dirac method, the perturbation operator for calculating electron Zeeman splitting in an applied magnetic field reads rather simple.[3] This approach to the **g**-tensor has first been implemented in the framework of the Dirac scattered-wave Xα (DSW-Xα) method.[26] Its applications to $\mathrm{Ga}_n\mathrm{As}_m$ clusters showed qualitative agreement with experiment.[14,15] Unfortunately, the crude muffin-tin approximation of the electronic potential used in a SW scheme represents a serious obstacle to precise calculations of **g**-values, as required, e.g., for organic radicals.

If one abandons this shape approximation of the potential and turns from the four-component Dirac method with both electronic and positronic solutions to a two-component Kohn−Sham method (which describes only electronic states), one arives at probably the most attractive formulation of the **g**-tensor problem to date. In such a method the eigenfunctions include spin−orbit and scalar relativistic effects self-consistently. Thus, only the applied magnetic field needs to be considered as a perturbation. This feature makes schemes, such as those applicable to both light and heavy (e.g., transition metal) molecular systems, in a rather economic fashion. Also, a transparent rationalization of the calculated **g**-values in terms of the (spin-)density distribution of the singly occupied molecular orbital (SOMO) becomes possible. A DF scheme to calculate **g**-tensors, like that just outlined, has been implemented within the zeroth-order regular approximation (ZORA)[16] and recently validated for radicals containing a metal atom[17] and for transition metal complexes of biological relevance.[27−29]

In the following, we communicate on the development, implementation, and benchmark applications of a novel scheme for DF calculations of **g**-tensors which is also based on two-component solutions of Kohn−Sham (KS) equations but uses an alternative formalism by Douglas and Kroll (DK).[30−32] The implementation is undertaken in the parallel program PARAGAUSS,[33] and the **g**-tensor module is a part of the latest release of this code.[34] Our approach to **g**-tensor calculations, based on a variationally stable relativistic DF method,[32] is applicable to doublet states of systems without restricitions in type, since heavy elements with a large spin−orbit interaction may be treated as well. Furthermore, the present approach affords a direct relation of **g**-values to the ground-state wave function, the accuracy of which can be improved in a systematic way, if required.

The paper is organized as follows. In section II, we describe the formalism including the newly derived expression for the DK Zeeman Hamiltonian. In section III, we describe computational details. In section IV, we discuss this methodology, the importance of various contributions to the spin−orbit interaction as well as the computational parameters involved, and we compare calculated results for touchstone radicals to those of other relevant calculations and experiment. We summarize the conclusions in section V.

II. Method

We have chosen the two-component Douglas−Kroll Kohn−Sham approach to relativistic density functional theory with self-consistent account of spin−orbit interaction as framework for **g**-tensor calculations. In this way, we will avoid the drawbacks of the double-perturbation approach which is inherently limited to molecular species of rather light atoms. To this end, we need to (i) define the form of the Zeeman Hamiltonian $\hat{H}^Z$ that describes the energy change of molecular systems in the presence of an external magnetic field $\vec{B}$ and (ii) relate the matrix elements of $\hat{H}^Z$ to parameters of the "experimental" spin Hamiltonian $\hat{H}$ in order to derive expressions for the components of the **g**-matrix.

A. Zeeman Hamiltonian in the Two-Component Douglas−Kroll Kohn−Sham Method. The Hamiltonian of the four-component Dirac−Kohn−Sham method can be written using the effective one-particle potential v_{eff} which describes the interaction in a many-electron system:[31]

$$\hat{H}^{\mathrm{D}} = c\vec{\alpha}\cdot\vec{p} + \beta c^2 + v_{\mathrm{eff}} \tag{1}$$

Here $\vec{p}$ is the mechanical momentum, c is the speed of light, and $\vec{\alpha}$, β are the Dirac 4×4 matrixes. $\hat{H}^{\mathrm{D}}$ describes electronic ($E > 0$) as well as positronic ($E < 0$) solutions. The positronic solutions are irrelevant in chemistry; rather, they cause significant complications. One way to get rid of the positronic solutions is to carry out a unitary DK transformation U of the Dirac Hamiltonian $\hat{H}^{\mathrm{D}}$:

$$\hat{H}^{\mathrm{DK}}_{(4)} = U\hat{H}^{\mathrm{D}}U^{\dagger} = U\begin{pmatrix} c^2 + v_{\mathrm{eff}} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -c^2 + v_{\mathrm{eff}} \end{pmatrix}U^{\dagger} = \begin{pmatrix} \hat{H}^{DK}_{(2)} & 0 \\ 0 & \hat{H}^{-\mathrm{DK}}_{(2)} \end{pmatrix} \tag{2}$$

here, the Pauli matrixes $\vec{\sigma} = (\sigma_x,\sigma_y,\sigma_z)$ are introduced. U decouples (with the accuracy to all orders) the four-component equation into two two-component equations: an electronic one, $\hat{H}^{\mathrm{DK}}_{(2)}\Psi_{(2)} = E\Psi_{(2)}$, and a positronic one, $\hat{H}^{-\mathrm{DK}}_{(2)}\Psi^{-}_{(2)} = E^{-}\Psi^{-}_{(2)}$. Note that solutions of $\hat{H}^{\mathrm{DK}}_{(4)}$ and $\hat{H}^{\mathrm{D}}$, Ψ^{DK} and Ψ, respectively, are related to each other via the transformation U:

$$\Psi^{\mathrm{DK}} = U\Psi \equiv \Psi^{U} \tag{3}$$

When calculating expectation values of operators one has to take this, so-called, *picture change* into account.[35]

For the first-order energy change ΔE^Z of a system

$$\hat{H}_0{}^{\mathrm{D}}\Psi_0 = E_0\Psi_0 \tag{4}$$

caused by a Zeeman perturbation $\hat{H}^{\mathrm{D,Z}}$,

$$(\hat{H}_0{}^{\mathrm{D}} + \hat{H}^{\mathrm{D,Z}})\Psi = (E_0 + \Delta E^{\mathrm{Z}})\,\Psi \tag{5}$$

a naive approach based on the DK wave function Ψ_0^U (mixed pictures) would lead to erroneous result:

$$\Delta\tilde{E}^{\mathrm{Z}} = \langle\Psi_0^U|H^{\mathrm{D,Z}}|\Psi_0{}^U\rangle \simeq 0 \tag{6}$$

This reflects the fact that the Zeeman operator,

$$\hat{H}^{\mathrm{D,Z}} = \begin{pmatrix} 0 & \vec{\sigma}\cdot\vec{A} \\ \vec{\sigma}\cdot\vec{A} & 0 \end{pmatrix} \tag{7}$$

which perturbs the Dirac Hamiltonian $\hat{H}_0{}^{\mathrm{D}}$, is off-diagonal (odd), and nonzero matrix elements can only appear between the electronic and the positronic solutions. $\hat{H}^{\mathrm{D,Z}}$ has been derived from eq 1 via the common minimal substitution to a (gauge-invariant) momentum

$$\vec{p} \rightarrow \vec{\pi} = \vec{p} + \vec{A}/c \tag{8}$$

In this way, one introduces the magnetic field $\vec{B}$ via

$$\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r}) \tag{9}$$

Within the DK formalism the correct expression for the first-order energy change ΔE^{Z} in the external magnetic field $\vec{B}$ as described by $\hat{H}^{\mathrm{D,Z}}$ is

$$\Delta E^{\mathrm{Z}} = \langle\Psi_0^U|U\hat{H}^{\mathrm{D,Z}}U^{\dagger}|\Psi_0^U\rangle \tag{10}$$

Obviously, the transformation of the Dirac Zeeman operator $\hat{H}^{\mathrm{D,Z}}$ to DK one $\hat{H}^{\mathrm{Z}} \equiv U\hat{H}^{\mathrm{D,Z}}U^{\dagger}$ is obligatory.

In the present implementation,[31,32] $\hat{H}^{\mathrm{DK}}_{(4)}$ is diagonal up to second-order in (v_{eff}/E)

$$\hat{H}^{\mathrm{DK,1}}_{(4)} = U_1U_0\hat{H}^{\mathrm{D}}U_0{}^{\dagger}U_1{}^{\dagger} = \begin{pmatrix} \hat{H}^{\mathrm{DK,1}}_{(2)} & \mathcal{O}[(v_{\mathrm{eff}}/E)^2] \\ \mathcal{O}[(v_{\mathrm{eff}}/E)^2] & \hat{H}^{\mathrm{DK,1}}_{(2)} \end{pmatrix} \tag{11}$$

Thus, the transformation $U = U_1U_0$ of the Dirac Zeeman operator $\hat{H}^{\mathrm{D,Z}}$ is required to get $\hat{H}^{\mathrm{Z}}$. The free-electron Foldy−Wouthyusen transformation

$$U_0 = A_p(1 + \beta R_p) = A_p(1 + K_p\beta\vec{\alpha}\cdot\vec{p}) = A_p\begin{pmatrix} \mathbf{1} & K_p\vec{\sigma}\cdot\vec{p} \\ -K_p\vec{\sigma}\cdot\vec{p} & \mathbf{1} \end{pmatrix} \tag{12}$$

can be expressed in a simple analytical form. Here, the relativistic generalization of the kinetic energy

$$E_p = c\sqrt{p^2 + c^2} \tag{13}$$

includes the rest mass term and

$$A_p = \sqrt{(E_p + c^2)/2E_p} \tag{14}$$

$$K_p = c/(E_p + c^2) \tag{15}$$

$$R_p = K_p(\vec{\alpha}\cdot\vec{p}) \tag{16}$$

are relativistic kinematic factors. If matrix elements are to be calculated via a completely consistent picture for both $\hat{H}^{\mathrm{Z}}$ and the wave functions, the considerably more complicated unitary transformation U_1 has to be applied[31,32]

$$U_1 = \sqrt{1 + W_1{}^2} + W_1 \tag{17}$$

$$W_{1;p,p'} = A_p\left(R_p\frac{v_{\mathrm{eff};p,p'}}{E_p + E_p{}'} - \frac{v_{\mathrm{eff};p,p'}}{E_p + E_{p'}}R_{p'}\right)A_{p'} \tag{18}$$

As first approximation, which permits computation of the major contributions to the expectation value $\langle\Psi_0^U|U\hat{H}^{\mathrm{D,Z}}U^{\dagger}|\Psi_0^U\rangle$, one employs the transformation U_0 only, so that

$$\Delta E^{\mathrm{Z}} \simeq \langle\Psi_0^U|U_0\hat{H}^{\mathrm{D,Z}}U_0{}^{\dagger}|\Psi_0^U\rangle \tag{19}$$

This is the approximation chosen in the present work. Note that the last expression can be rewritten as

$$\langle\Psi_0^U|U_0\hat{H}^{\mathrm{D,Z}}U_0{}^{\dagger}|\Psi_0^U\rangle = \langle U_0{}^{\dagger}\Psi_0^U|\hat{H}^{\mathrm{D,Z}}|U_0{}^{\dagger}\Psi_0^U\rangle \tag{20}$$

to reflect the equivalence of applying the transformation either to the operator or to the wave function.

Let us consider the transformation $\hat{H}^{\mathrm{D,Z}} \rightarrow \hat{H}^{\mathrm{DK,Z}}_{(2)} = \mathscr{L}_+U_0\hat{H}^{\mathrm{D,Z}}U_0{}^{\dagger}\mathscr{L}_+{}^{\dagger}$, (here, $\mathscr{L}_+$ simply projects out the electronic part of the 4×4 matrix) in more detail using eq 12:

$$\begin{aligned}\hat{H}^{\mathrm{DK,Z}}_{(2)} &= \mathscr{L}_+U_0\hat{H}^{\mathrm{D,Z}}U_0{}^{\dagger}\mathscr{L}_+{}^{\dagger} \\ &= \mathscr{L}_+A_p\begin{pmatrix} \mathbf{1} & K_p\vec{\sigma}\cdot\vec{p} \\ -K_p\vec{\sigma}\cdot\vec{p} & \mathbf{1} \end{pmatrix}\begin{pmatrix} 0 & \vec{\sigma}\cdot\vec{A} \\ \vec{\sigma}\cdot\vec{A} & 0 \end{pmatrix} \times \\ &\qquad \begin{pmatrix} \mathbf{1} & -K_p\vec{\sigma}\cdot\vec{p} \\ K_p\vec{\sigma}\cdot\vec{p} & \mathbf{1} \end{pmatrix}A_p\mathscr{L}_+{}^{\dagger}\end{aligned} \tag{21}$$

Therefore,

$$\hat{H}^{\mathrm{Z}} \equiv \hat{H}^{\mathrm{DK,Z}}_{(2)} = A_p[K_p(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A}) + (\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})K_p]A_p \tag{22}$$

K_p and ($\vec{\sigma}\cdot\vec{p}$) commute because K_p is a function of p^2 which commutes with the components of $\vec{p}$. With the help of the Pauli relation, we write

$$(\vec{\sigma}\cdot\vec{p})\,(\vec{\sigma}\cdot\vec{A}) = \vec{p}\cdot\vec{A} + i\vec{\sigma}\cdot(\vec{p} \times \vec{A}) \tag{23}$$

Employing $\vec{p} = -i\nabla$ and

$$\vec{B} = \nabla \times \vec{A} \tag{24}$$

we obtain for any wave function Ψ:

$$\begin{aligned}[(\vec{\sigma}\cdot\vec{p})\,(\vec{\sigma}\cdot\vec{A})]\,\Psi &= [\vec{p}\cdot\vec{A} + \vec{\sigma}\cdot\vec{B} - \vec{\sigma}\cdot(\vec{A} \times \nabla)]\Psi = \\ &\quad [\vec{\sigma}\cdot\vec{B} + \vec{A}\cdot\vec{p} - i\vec{\sigma}\cdot(\vec{A} \times \vec{p})]\Psi\end{aligned} \tag{25}$$

Here the relation $\vec{p}\cdot\vec{A}\Psi = (\vec{p}\cdot\vec{A})\Psi + \vec{A}\cdot\vec{p}\Psi$ was used, where parentheses indicate that $\vec{p}$ acts only on $\vec{A}$. The term $(\vec{p}\cdot\vec{A})\Psi$ vanishes since we invoke the Coulomb gauge $\nabla\vec{A} = 0$. The relation $\vec{B} = \nabla \times \vec{A}$, eq 24, was used to obtain the term $\vec{\sigma}\cdot\vec{B}\Psi$. The operator $\vec{A}\cdot\vec{p}$ yields

$$\vec{A}\cdot\vec{p} = \frac{1}{2}(\vec{B} \times \vec{r})\cdot\vec{p} = \frac{1}{2}\vec{B}\cdot(\vec{r} \times \vec{p}) = \frac{1}{2}\vec{B}\cdot\vec{L} \tag{26}$$

with $\vec{L} = \vec{r} \times \vec{p}$. For the third tem we have with eq 24

$$\vec{\sigma}\cdot(\vec{p} \times \vec{A}) = \frac{1}{2}\vec{\sigma}\cdot[(\vec{B} \times \vec{r}) \times \vec{p}] = \frac{1}{2}(\vec{\sigma}\cdot\vec{r})\,(\vec{B}\cdot\vec{p}) - \frac{1}{2}(\vec{\sigma}\cdot\vec{B})\,(\vec{r}\cdot\vec{p}) \tag{27}$$

Similarly, for the second term of eq 22 we obtain

$$(\vec{\sigma}\cdot\vec{A})\,(\vec{\sigma}\cdot\vec{p})\Psi = [\vec{A}\cdot\vec{p} + i\vec{\sigma}\cdot(\vec{A}\times\vec{p})]\Psi \tag{28}$$

and we can apply analogous chain of transformations such as for simplification of eq 25.

The Zeeman Hamiltonian, eq 22, reads

$$\hat{H}^{Z} = \frac{c}{2E_p}\vec{\sigma}\cdot\vec{B} + A_p[K_p(\vec{A}\cdot\vec{p}) + (\vec{A}\cdot\vec{p})K_p]A_p \tag{29}$$
$$- iA_p[K_p\vec{\sigma}\cdot(\vec{A}\times\vec{p}) - \vec{\sigma}\cdot(\vec{A}\times\vec{p})K_p]A_p$$

We substitute eqs 26 and 27 to obtain finally:

$$\hat{H}^{Z} = \frac{c}{2E_p}\vec{\sigma}\cdot\vec{B} + \frac{1}{2}A_p[K_p(\vec{L}\cdot\vec{B}) + (\vec{L}\cdot\vec{B})K_p]A_p + \frac{1}{2}A_p\{K_p[(\vec{\sigma}\cdot\vec{B})(\vec{r}\cdot\nabla) - (\vec{\sigma}\cdot\vec{r})(\vec{B}\cdot\nabla)] - [(\vec{\sigma}\cdot\vec{B})(\vec{r}\cdot\nabla) - (\vec{\sigma}\cdot\vec{r})(\vec{B}\cdot\nabla)]K_p\}A_p \tag{30}$$

The first term $\vec{\sigma}\cdot\vec{B}$ is the electron *spin Zeeman* interaction, the next term $\vec{L}\cdot\vec{B}$ describes the *orbital Zeeman* interaction due to the orbital motion of the electron in the magnetic field $\vec{B}$.[3] The last term is reminiscent of the spin−orbit Zeeman gaugecorrection term;[3] we neglected it in the following. In fact, assuming that K_p commutes with the brackets, this term equals to zero. We note here in passing, that the issue of gauge invariance of the DK Zeeman Hamiltonian is complicated: the wave functions in practical calculations do not correspond *exactly* to any particular picture because not all terms of the total DK Hamiltonian are treated on the same footings. For instance, an accurate relativistic description of the kinetic energy and nuclear attraction interactions by applying both U_0 and U_1 transformations is straightforward.[31] However, relativistic effects on the exchange−correlation potential become quite complicated already when introduced by the free-electron transformation U_0 and thus are usually neglected in practical calculations.[36]

Alternatively to the above procedure, one can derive a Zeeman operator $\hat{H}^{Z}$ linear in the external magnetic field $\vec{B}$ within the DK formalism if one applies a *field-dependent* DK transformation $U(\vec{B})$ to the Dirac−Kohn−Sham Hamiltonian

$$\hat{H}^{D}(\vec{B}) = c\vec{\alpha}\cdot\vec{\pi} + \beta c^2 + v_{\mathrm{eff}} \tag{31}$$

where the field $\vec{B}$ is introduced via the gauge-invariant mechanical momentum $\vec{\pi}$, eq 8. This way to define the DK Zeeman operator has the advantage of removing the (partial) inconsistency of the approach just outlined connected to the application of a DK transformation independent of the magnetic field to obtain a Zeeman operator *dependent on magnetic field*. All necessary algebra has already been given above; the only difference is that we now use the canonical momentum $\vec{\pi}$ everywhere instead of $\vec{p}$.

As before, we limit ourselves to the free-electron transformation U_0:

$$U_0(\vec{B}) = A_\pi(1 + K_\pi\beta\vec{\alpha}\cdot\vec{\pi}),\quad U_0^{\dagger}(\vec{B}) = (1 + \vec{\alpha}\cdot\vec{\pi}\beta K_\pi)A_\pi \tag{32}$$

where the relativistic energy E_π and kinematic factors A_π, K_π are defined as in eqs 13−15:

$$E_\pi = c\sqrt{(\vec{\alpha}\cdot\vec{\pi})^2 + c^2},\quad A_\pi = \sqrt{(E_\pi + c^2)/2E_\pi},\quad K_\pi = c/(E_\pi + c^2) \tag{33}$$

With these settings the Dirac Hamiltonian transformed to a DK form by $U_0(\vec{B})$

$$\hat{H}^{\mathrm{DK}}_{(4)}(\vec{B}) = U_0(\vec{B})\hat{H}^{D}(\vec{B})U_0^{\dagger}(\vec{B}) \tag{34}$$

in a two-component form, after elimination of the positronic solutions, reads:

$$\hat{H}^{\mathrm{DK}}_{(2)}(\vec{B}) = E_\pi + A_\pi v_{eff}A_\pi + A_\pi K_\pi\vec{\sigma}\cdot\vec{\pi}v_{\mathrm{eff}}\vec{\sigma}\cdot\vec{\pi}K_\pi A_\pi \tag{35}$$

For the valence electrons that define the **g**-tensors, the kinetic energy is small compared to the rest energy. Therefore, the expression for the relativistic energy E_π, eq 33, can be expanded in a power series of $[(\vec{\sigma}\cdot\vec{\pi})/c]$:

$$E_\pi = c^2 + \frac{1}{2}(\vec{\sigma}\cdot\vec{\pi})^2 - \frac{1}{8c^2}(\vec{\sigma}\cdot\vec{\pi})^4 + \mathcal{O}((\vec{\sigma}\cdot\vec{\pi})^6) \tag{36}$$

Inserting E_π in the Hamiltonian $\hat{H}^{\mathrm{DK}}_{(2)}(\vec{B})$, one obtains:

$$\hat{H}^{\mathrm{DK}}_{(2)}(\vec{B}) = c^2 + \frac{1}{2}(\vec{\sigma}\cdot\vec{\pi})^2 - \frac{1}{8c^2}(\vec{\sigma}\cdot\vec{\pi})^4 + A_\pi v_{\mathrm{eff}}A_\pi + A_\pi K_\pi\vec{\sigma}\cdot\vec{\pi}v_{\mathrm{eff}}\vec{\sigma}\cdot\vec{\pi}K_\pi A_\pi \tag{37}$$

Neglecting the dependence of the kinematic factors A_π, K_π on the magnetic field and collecting only the terms linear in $\vec{B}$ yields

$$\hat{H}(\vec{B}) = \frac{1}{2c}[(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A}) + (\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})] - \frac{1}{8c^3}[(\vec{\sigma}\cdot\vec{p})^2((\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A}) + (\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})) + \mathrm{hc}] + \frac{1}{c}A_pK_p[(\vec{\sigma}\cdot\vec{p})v_{eff}(\vec{\sigma}\cdot\vec{A}) + (\vec{\sigma}\cdot\vec{A})v_{eff}(\vec{\sigma}\cdot\vec{p})]K_pA_p \tag{38}$$

The first item of $\hat{H}(\vec{B})$ corresponds to the Pauli form of the Zeeman Hamiltonian $\hat{H}^{Z}$ (eq 22), and the second and third terms are corrections of the order p^2/c^2 and v_{eff}/c^2, respectively, and are usually ignored.[3] If we follow this strategy, we obtain the Zeeman Hamiltonian in the form

$$\hat{H}^{Z} = \frac{1}{2c}[(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A}) + (\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})] = \frac{1}{2c}(\vec{\sigma} + \vec{L})\cdot\vec{B} \tag{39}$$

It differs from that defined by eq 22 by the absence of the kinematic factors only. Note that the relativistic corrections due to the kinematic factors are *small* and essentially *isotropic* for the systems considered in the present study, thus they do not affect the calculated splitting of **g**-tensor components.

To finalize eq 30, we correct for small quantum electrodynamics effects (thus far neglected) by introducing a factor $g_e/2$ in the electron spin Zeeman term; $g_e = 2.002319$ is the g-factor of free electrons.[3] Finally, the DK Zeeman operator $\hat{H}^{Z}$ with only spin and orbital Zeeman contributions retained, becomes

$$\hat{H}^{Z} = \frac{g_e c}{4E_p}\vec{\sigma}\cdot\vec{B} \tag{40}$$

$$+ \frac{1}{2}A_p[K_p(\vec{L}\cdot\vec{B}) + (\vec{L}\cdot\vec{B})K_p]A_p \tag{41}$$

In the four-component Dirac picture, the Zeeman operator is represented by one term only;[3] in the DK approach, it splits into groups of terms, like in those in eqs 40 and 41. This is convenient to analyze the effects responsible for the energy splitting in a magnetic field. The purely relativistic nature of the Zeeman interaction follows immediately from eqs 40 and 41 and the definitions of E_p, A_p, and K_p, eqs 13−15: $\lim_{c\to\infty} (\hat{H}^Z) = 0$. This result once again emphasizes the necessity of a relativistic treatment of magnetic interactions.

Finally, we give the expression for the derivatives of the DK Zeeman Hamiltonian with respect to the components B_k^0, $k = x, y, z$ of a uniform magnetic field $\vec{B}^0$:

$$\frac{\partial \hat{H}^Z}{\partial B_k^0} = \frac{g_e c}{4E_p}\sigma_k + \frac{1}{2}A_p(K_pL_k + L_kK_p)A_p \tag{42}$$

This eq 42 will be used in the following subsection as well as in the calculations of **g**-tensors presented in section IV.

B. Relation of Zeeman Hamiltonian to Spin Hamiltonian. EPR spectroscopy deals with the transition between levels split at most by a few cm^{-1}. Hence only levels that are (nearly) degenerate without a magnetic field are of immediate interest. A common representation of such a group of levels after application of a magnetic field rests on the concept of an "effective spin" $\tilde{S} = (n/2)\vec{\sigma}$. The latter is a fictitious angular momentum such that the degeneracy of the group of levels involved is set equal to $(2\tilde{S} + 1)$, the same as that in an ordinary spin multiplet.[1] For example, a Kramers doublet with just two levels ($n = 1$) is assigned an effective spin $\tilde{S} = {}^1/_2$. The EPR **g**-tensor (which actually is not a tensor but merely a matrix[1]) parametrizes the interaction between the external magnetic field $\vec{B}^0$ and the effective spin $\tilde{S}$. For doublet states the spin Hamiltonian $\hat{H}$ reads

$$\hat{H} = \mu_B\vec{B}^0\boldsymbol{\cdot}\mathbf{g}\boldsymbol{\cdot}\tilde{S} \tag{43}$$

Here, μ_B is the Bohr magneton, $\mu_B = e\hbar/2mc$, or in atomic units, $\mu_B = {}^\alpha/_2$ (with $\alpha = {}^1/_c$ being the fine structure constant); e and m are the charge and mass of an electron, respectively, and $\hbar$ is Planck's constant. In terms of the spin Hamiltonian, the ground-state energy change ΔE in the field $\vec{B}^0$ is[1]

$$\begin{aligned}\Delta E &= \mu_B[(B_x^0g_{xx} + B_y^0g_{yx} + B_z^0g_{zx})^2 + (B_x^0g_{xy} + B_y^0g_{yy} + \\ &\qquad B_z^0g_{zy})^2 + (B_x^0g_{xz} + B_y^0g_{yz} + B_z^0g_{zz})^2]^{1/2} \\ &= \mu_B[\sum_{k,l}B_k^0B_l^0\sum_{\alpha}g_{k\alpha}g_{l\alpha}]^{1/2} = \mu_B[\sum_{k,l}B_k^0B_l^0G_{kl}]^{1/2}\end{aligned} \tag{44}$$

Here, $\mathbf{G} = \mathbf{g}\mathbf{g}^T$, a *true* tensor widely used in the experimental determination of **g**-values,[1,2] has been introduced. After diagonalization, **G** furnishes the main axes and the main components of the **g**-"tensor" via $g_{kk} = \sqrt{G_{kk}}$. Note that according to the spin Hamiltonians employed for interpreting experimental data,[1,3] only the energy contribution linear in the magnetic field is needed. Therefore, the **g**-tensor components are related to the experimental energy splitting ΔE as follows:

$$G_{kl} = \sum_{\alpha}g_{k\alpha}g_{l\alpha} = \frac{1}{2\mu_B^2}\frac{\partial^2(\Delta E)^2}{\partial B_k^0\partial B_l^0}|_{\vec{B}^0=0} \tag{45}$$

The energy defined as ΔE^Z, eq 10, can be calculated, thus connecting theory and EPR experiment by $\Delta E^Z = \Delta E$. Note that **G** is defined here completely generally as the response of the Zeeman splitting ΔE in the magnetic field $\vec{B}^0$. The price to be paid for this advantage is the requirement to work with at least two-component eigenfunctions that become *complex*.[25]

For a Kramers doublet ground state one can assume that the two spinors of the unpaired electron degenerate in the absence of a magnetic field completely determine the magnetic Hamiltonian, since the Zeeman interaction is usually much smaller than the energy difference between the ground and excited levels.[1] Commonly, this is a good assumption in a spin-restricted DF treatment. Without a magnetic field, a DF calculation yields two degenerate solutions, formally connected to each other by time-reversal symmetry. In the spin-restricted case, the spinors of the paired electrons are also connected to each other by time-reversal symmetry. Since all of them are occupied, they do not contribute to the matrix elements of the corresponding KS determinants of the magnetic Hamiltonian.[37] Therefore, the only nonzero contributions emerge from the two degenerate spinors of the unpaired electron, i.e., from the Kramers pair Φ_1, Φ_2 obtained at $\vec{B}^0 = 0$. Due to its relation with the **g**-matrix, it is more convenient to discuss the square of the energy change $\Delta E^Z(\vec{B}^0)$ in the field $\vec{B}^0$ described by $\hat{H}^Z$, eq 10, in terms of the standard first-order perturbation treatment. For a case of doubly degenerate states one has

$$\begin{aligned}(\Delta E^Z)^2 = [\langle\Phi_1|\,\hat{H}^Z|\Phi_1\rangle - \langle\Phi_2|\,\hat{H}^Z|\Phi_2\rangle]^2 + \\ 4\langle\Phi_1|\,\hat{H}^Z|\Phi_2\rangle\,\langle\Phi_2|\,\hat{H}^Z|\Phi_1\rangle\end{aligned} \tag{46}$$

or after taking the second derivative:

$$\begin{aligned}G_{kl} &= \frac{1}{2\mu_B^2}\frac{\partial^2\,(\Delta E^Z)^2}{\partial B_k^{\,0}\partial B_l^{\,0}}|_{\vec{B}^0=0} \\ &= \frac{1}{\mu_B^2}(\Phi_{11}^k\Phi_{11}^l - \Phi_{11}^k\Phi_{22}^l - \Phi_{11}^l\Phi_{22}^k + \Phi_{22}^k\Phi_{22}^l + \\ &\qquad 2\Phi_{12}^k\Phi_{21}^l + 2\Phi_{12}^l\Phi_{21}^k)\end{aligned} \tag{47}$$

G_{kl} is a first-order property as it can be expressed in terms of the first derivatives of the energy, eq 47. To obtain eq 47, the Hellmann−Feynman relation $\Phi_{ij}^k \equiv \partial/\partial B_k^0\ \langle\Phi_i|\hat{H}^Z|\Phi_j\rangle_{\vec{B}^0=0} = \langle\Phi_i|\partial\hat{H}^Z/\partial B_k^0|_{\vec{B}^0=0}|\Phi_j\rangle$ was used. It is valid for Φ_i, Φ_j independent of $\vec{B}^0$ as solutions of the Hamiltonian without a magnetic field. The linear approximation of the 2×2 Zeeman Hamiltonian $\hat{H}^Z$ defined by its matrix elements

$$H_{ij}^{\ Z} = \sum_k B_k^0\Phi_{ij}^k \tag{48}$$

can be compared to the spin Hamiltonian derived from eq 43:

$$\hat{H} = \frac{1}{4c}\sum_{kl}B_k^0g_{kl}\sigma_l \tag{49}$$

Therefore, the (real) values g_{kl} can be expressed in terms of the matrix elements Φ_{ij}^{k} as $g_{kx} = 4c\ \mathrm{Re}\Phi_{12}^k = 4c\ \mathrm{Re}\Phi_{21}^k$, $g_{ky} = -4c\ \mathrm{Im}\Phi_{12}^k = 4c\ \mathrm{Im}\Phi_{21}^k$, and $g_{kz} = 4c\ \mathrm{Re}\Phi_{11}^k = -4c\ \mathrm{Re}\Phi_{22}^k$.

To calculate the **g**-values, the code PARAGAUSS[34] has been extended by new types of integrals $\langle\chi_i^{l,a,\alpha}|\partial\hat{H}^Z/\partial B_k^0|\chi_{\mathrm{j}}^{l\prime,b,\beta}\rangle$ over primitive Gaussian functions $\chi_i^{l,a,\alpha}$ of angular momemtum l and exponent α located at center a. These integrals are symmetry adapted according to the irreducible representation of the appropriate double group, multiplied by contraction coeffiecients and combined into molecular integrals Φ_{ij}^{k}. The integration to account for relativistic kinematic factors, eq 42, was carried out, before the contraction step, by means of a transformation into (approximate) momentum space as usually done in the DK approach.[31,38] The complete procedure of calculating Φ_{ij}^{k} was coded and parallelized in line with that available in PARAGAUSS for calculating dipole integrals.[33]

III. Computational Details

All-electron calculations have been carried out using the program PARAGAUSS,[33,34] a newly developed parallel implementation of the linear combination of Gaussian-type orbitals fitting-functions DF (LCGTO−FF-DF) method.[39] The two-component relativistic wave functions[32,36] of a Kramers doublet representing an unpaired electron were employed to calculate **g**-tensors as explained in the previous section. Restricted open-shell Kohn−Sham (ROKS) approximation has been adopted. Gradient-corrected (GGA) exchange[40] and correlation[41] functionals (BP) were used in the **g**-tensor calculations and for the geometry optimization. For comparison, **g**-tensors were also computed in the local density approximation (LDA), with the Vosko−Wilk−Nusair (VWN) exchange-correlation (XC) functional.[42]

Two different Gaussian-type basis sets are used in the LCGTO−FF-DF method: one to describe the KS orbitals and another to represent the charge density when calculating the classical Coulomb (Hartree) interaction between electrons. In **g**-tensor calculations, the following specially constructed orbital basis sets were used that ensure the accuracy of *g*-values to better than 10^{-4}: (13s,8p,7d) for C, N, O, F; (8s,5p,1d) for H. For the former atoms, a (13s,8p) basis set[43] was extended by 7 d-exponents, identical to the p-exponents (except for the smallest one). For H, the analogous procedure was applied to derive 5 p-exponents from the s-exponents,[43] (except for the three most diffuse ones); the polarization d exponent of H was set to 1.0. The initial orbital basis sets for 3d-[44] and 4d-atoms[45] were extended in a similar fashion to obtain the following sets of primitive basis functions: Ti (15s,11p,6d,5f); Rh, Pd (18s,13p,9d,8f,8g). This considerable extension of basis sets mainly reflects an *indirect* sensitivity of *g*-values to basis completeness: the additional functions with $l+1$ or even $l+2$ (where l is the maximum angular momentum of the occupied atomic orbitals) are required only for the special transformations when calculating the relativistic contribution to the electron−electron Hartree interactions.[36] In the code, these transformations precede the basis contraction step. Thus, one can considerably reduce the computational effort using very compact contractions for the most expensive exponents with $l+1$ and $l+2$. In the present work we use the following contractions: [5s,4p,1d] for H; [8s,7p,3d] for C, N, O, F; [10s,11p,6d,1f] for Ti; [10s,12p,9d,3f,1g] for Pd, Rh: they were shown to cause deviation of the calculated *g*-values by less than 1×10^{-5}. The auxiliary fitting basis sets were constructed in a standard fashion by doubling the s- and p-exponents of the orbital basis functions;[39] they were augmented by standard sets of 5 p- and 5 d-type polarization functions.[39]

To test the present method for **g**-tensor calculations and the implementation in PARAGAUSS, two sets of inorganic and organic radicals were calculated: (i) CO^+, CN, NO_2, NF_2, HCO, C_3H_5, TiF_3, RhC, PdH; (ii) phenyl (Ph) C_6H_5, biphenyl radical anion (BPh^-) $C_6H_5-C_6H_5^-$, 1,4-benzoquinone radical anion (BQ^-) $C_6H_4O_2^-$, and tetramethyl-1,4-benzoquinone radical anion (duroquinone, DQ^-) $C_6(CH_3)_4O_2^-$. Set (i) allows a critical comparison with both experimental **g**-tensors[46−52] and results of other high-level calculations.[5,6,9,10,13,16,17] Experimental equilibrium geometries were used for molecules of the set i, except those for TiF_3[16] and C_3H_5,[10] which for consistency were taken from the cited calculations. The *z*-axis was always oriented along the main symmetry axis; the molecules belonging to point group C_{2v} (NO_2, NF_2) were located in the *yz*-plane. For set ii of organic radicals, *first-principles* calculated data are scarce.[8] But these radicals with very small **g**-tensor anisotropy[53−55] are indispensable to establish the performance of the new **g**-tensor tool for prototypes of biologically important EPR-active *organic* species. Geometric parameters of these radicals were optimized at the GGA BP level. The planar organic radicals were oriented in the *xy*-plane with the substituting $-C_6H_5$ or O groups or the missing H atom pointing along the *x*-axis. A common gauge origin at the center of mass has been employed.

IV. Results and Discussion

In Table 1 the calculated **g**-tensor values for a series of benchmark doublet-state radicals are presented and compared with results of other high-level calculations and experimental data. The computed *g*-components reproduce the experimental numbers for the main-group molecules in this touchstone set i: the relative shifts Δg of the main **g**-components, their signs, and the general trends traced from the EPR spectra. Transition metal radicals exhibit a somewhat less favorable situation which we address below in some detail. Let us begin with the main-group species.

The calculated spin Zeeman shift $\Delta\sigma$, eq 40, is essentially negligible for molecules of light atoms. Thus, the overall shift values Δg are defined alone by the orbital Zeeman contribution ΔL, eq 41. The present calculations systematically overestimate the **g**-tensor anisotropy for main-group molecules. This manifests an overestimation of the spin−orbit interaction as the driving force of **g**-shifts. This spin−orbit overestimation in the spin−orbit coupled DK method is known[56] for the commonly used restriction of the DK transformation to the nuclear potential only (i.e., neglecting the two-electron spin−orbit coupling terms).[30,31,57] Recently, an improved relativistic treatment of the Hartree part of the electron−electron interaction has been suggested and implemented in the code PARAGAUSS.[36] (The underlying transformation is partly carried out in a numeric fashion which requires a specially augmented orbital basis set described in section III.) For molecules without very heavy atoms, this alternative treatment does not cause significant changes of common observables.[36] However, **g**-tensor values are much more sensitive to the relativistic electron−electron terms. The leading orbital Zeeman contribution ΔL to **g**-shifts has been reduced in absolute value by as much as 30% (or more) for all radicals under study when the Hartree potential was affected by the relativistic transformation. Thus, the accuracy of the calculated **g**-tensor components for molecules composed of very light atoms has been improved *considerably* and *systematically* at the present level of approximation that uses wave functions obtained with Hartree part of the two-electron spin−orbit couplings taken into account.[36] Nevertheless, as follows from atomic calculations, even accounting for electron−electron spin−orbit terms still causes a slight overestimation of the spin−orbit splitting for p-orbitals.[56] This is the rationalization for overestimation of the **g**-tensor anisotropy in the main-group molecules.

Another part of the electron−electron interaction is the XC potential. Although it is smaller in magnitude than the Hartree contribution, it should also be subjected to the relativistic transformation to obtain further improved two-component wave functions when determining *g*-values. Work in this direction is

TABLE 1: Calculated and Experimental $\Delta g \times 10^5$ Values of Small Test Molecules

species	component	exp.[a]	MRCI[b]	ROHF[c]	GHF[d]	DF[e]	DF[f]	DF[g]	present
CO^+	$\perp$	−240	−238	−125	−280	−313	−246		−350
	$\parallel$		−18	−18	−4	−14	−9		−22
CN	$\perp$	−200			−198	−251			−270
	$\parallel$				−6	−14			−20
NO_2	*xx*	390	357	259	337	416	340	500	472
	yy	−1130	−1030	−708	−1101	−1372	−1123	−1600	−1513
	zz	−30	−54	−57	−62	−76	−69	−60	−72
NF_2	*xx*	−10			−45	−74	−62		−37
	yy	620			565	762	629		1027
	zz	280			289	468	393		603
HCO	*xx*	150			207	275	228	330	303
	yy	0			−18	−27	−22	−20	−20
	zz	−750			−686	−947	−748	−1230	−1076
C_3H_5	*xx*	0				−12	−7		−13
	yy	80				77	60		96
	zz	40				66	50		76
TiF_3	$\perp$	−11130					−2658	−7970	−4526
	$\parallel$	−1110					−112	−100	−28
RhC	$\perp$	5178						5028	4680
	$\parallel$	158						−202	−173
PdH	$\perp$	29088						29478	24735
	$\parallel$	−3732						−2772	−1818

[a] CO^+,[46] CN,[47] NO_2,[48] NF_2 (cited from ref 10), HCO,[49] C_3H_5,[50] TiF_3,[51] RhC,[52] PdH.[52] [b] MRCI.[5] [c] ROHF.[6] [d] GHF.[9] [e] One-component UKS.[10] [f] One-component UKS.[13] [g] Two-component ROKS (ZORA).[16,17]

in progress. One can also profit from using special relativistic exchange−correlation functionals modified due to relativistic kinematics of the electrons and, probably more important in the present context, due to the Breit contribution to the electron−electron interaction. Such functionals are now available at both LDA and GGA levels.[58] Notwithstanding very minor effect of these relativistic corrections on many molecular observables,[59] a notable alteration of so sensitive indicator as **g**-tensor is anticipated.

One more potential measure for improving the precision of calculated *g*-values in the present implementation is to go beyond the ROKS approach, taking spin polarization effects into account. Spin polarization effects were estimated within a one-component DF method to *systematically decrease* the absolute Δg values by as much as 20% (HCO, NO_2), making results for already light molecules notably more accurate.[16] In all **g**-tensor calculations with self-consistent treatment of spin−orbit interaction reported so far, spin polarization effects have been neglected. This is a principal limitation because spin−orbit interactions eliminate spin as a “good” quantum number. Fortunately, there exists a way to partly overcome this limitation: a very recent implementation of the so-called noncollinear spin density functional (NCSDF) approach in the spin−orbit part of PARAGAUSS showed promising results for energies.[32] Also, our first attempts of using a SOMO from a NCSDF calculation together with its fictitious Kramers partner in an otherwise standard calculation of the **g**-tensor within the present ROKS scheme gave encouraging restults. For instance, the largest Δg_{yy} shift of NO_2 has been reduced in absolute value (improved) by more than 10% in such a NCSDF evaluation. Spin polarization effects on **g**-tensors calculated in a two-component NCSDF method employing properly constructed determinantal wave functions have yet to be quantified.

As already mentioned, the gauge origin in this work has been chosen in the center of the nuclear charges (masses). A test displacement of the gauge origin for the CO^+ radical by 2 au along the *z* axis, a typical uncertainty, resulted in a variation of $g_\perp$ by less than 10^{-5}. The effect for other radicals in Table 1 was of the same order. This change is even below the commonly achieved experimental accuracy. Therefore, the unphysical feature of the gauge dependence of calculated *g*-values is of minor importance when very good basis sets are employed as done in the present calculations. Further test studies have shown that gauge effects may also be neglected for organic radicals of moderate size (Table 2). However, measures to ensure gauge invariance may become relevant for large asymmetric molecules.

TABLE 2: Calculated and Experimental $\Delta g \times 10^5$ Values of Organic Radicals

species	component	exptl[a,b]	calcd
C_6H_5	*xx*	−2 ± 50	−16
(Ph)	*yy*	−92 ± 50	−129
	zz	108 ± 50	72
$C_6H_5{-}C_6H_5^-$	*xx*	107 ± 2	142
(BPh^-)	*yy*	32 ± 2	46
	zz	−5 ± 2	−13
$C_6(CH_3)_4O_2^-$	*xx*	438 ± 5	711
(DQ^-)	*yy*	291 ± 5	357
	zz	−14 ± 5	−28
$C_6H_4O_2^-$	*xx*	473 ± 5	907
(BQ^-)	*yy*	306 ± 5	362
	zz	−6 ± 5	−30

[a] Ph,[53] BPh^-,[54] and DQ^-.[55] [b] Experimental data for BQ^- corrected for hydrogen-bond effect with isopropyl alcohol solvent, assuming that they are the same as for DQ^- when the latter is compared to an absolutely water-free solution in 2-methyltetrahydrofuran.[55]

For molecules of main-group elements (Table 1), the calculated deviations from experimental **g**-values are of similar size as in other computations.[5,6,9,10,13,16] For the most thoroughly studied gas-phase NO_2 and matrix-isolated HCO molecules, the present Δg values are very close to those of the methodologically similar ZORA DF approach.[16] (The still remained difference is mainly a consequence of neglecting two-electron XC spin−orbit couplings in the present work.) The latter two sets of *g*-shifts are slightly larger in absolute values than in a perturbative DF procedure,[10] probably due to the inclusion of spin polarization in the latter scheme. All three sets of DF *g*-shifts consistently overestimate the experimental values. The two-component GHF method[9] performs better for Δg, but it slightly underestimates the experimental shifts. Inspection of Table 1 shows that the data for the other main-group molecules confirm these trends as *systematic*: DF methods (except that by Malkina et al.[13]) overestimate Δg-values, and the GHF method tends to slightly underestimate them. This is an encouraging message because the systematic deviations can be reduced step by step when improvements of the **g**-tensor calculations are possible in a rigorous fashion, like in the present method.

As discussed elsewhere,[9−13,16,17] transition metal radicals represent more critical cases for calculations of **g**-tensors than main-group systems. Our results for TiF_3, RhC, and PdH (Table 1) are in line with previously calculated data for d-metal molecules: the agreement with experiment is qualitative and general features of EPR line splittings are reproduced. A key difference is the lack of the systematic overestimation of the **g**-tensor anisotropy. One can try to get an explanation based again on the analysis of spin−orbit effects in atoms as described at the DK level with two-electron spin−orbit couplings. Indeed, for d (and f) atomic states the spin−orbit effects are shown to be slightly but systematically *underestimated* compared to those computed at the most accurate four-component Dirac level.[56] When a transition metal atom is present in a radical, both p and d states of the constituting atoms contribute to the *g*-shift. Depending on the relative weights of both contributions, the overall effect may be either an overestimation or and underestimation, with the latter being probably more common for SOMO with a notable d character (see Table 1).

One can invoke further effects which may well cause difference in d-metal molecules. It is, for instance, the influence of the XC potential on the precision of the computed *g*-values. As for comparison of the LDA vs GGA calculations, the latter resulted in a slight reduction of the **g**-tensor anisotropy (by 5−10%) for essentially all molecules listed in Tables 1 and 2. This is an improvement for the main-group molecules, but not for the d-metal species. The **g**-tensor calculated for TiF_3 features the worst agreement with experiment, no matter whether LDA or GGA is used. Obviously, this is an indication of a general situation that the commonly used XC potentials are still far from optimal for describing very delicate magnetic response properties (and thus electronic structure details) of transition metal systems. More specifically, complexes in the electron configuration $3d^1$, like TiF_3, are probably less accurately described by common XC potentials due to the known deficiency of these methods to reproduce proper electron localization, in particular in such compact states as 3d. If this is indeed an important reason, one can hope to reach a significant improvement by employing DF approaches corrected for self-interaction.[60]

Organic radicals (Table 2) also furnish a critical test for the precision and reliability of **g**-tensor calculations because the involved anisotropy of **g**-tensors is small. Thus, small uncertainties in the geometry would translate into variations of the **g**-tensor which are comparable to the anisotropy. Furthermore, environmental effects on **g**-tensors of organic radicals, which are commonly studied in matrixes, often can be seen in measured **g**-shifts but are hard to model. Notwithstanding the small *g*-shifts observed for hydrocarbon and benzoquinone anion radicals of medium size, the present method is able to reproduce not only the signs, but also the relative values of the measured **g**-tensor components. The whole variety of the conceivable improvements discussed above is also applicable to these biologically relevant organic radicals. Important for future applications is the finding that tiny changes of EPR line positions caused by the formation of intermolecular hydrogen bonds of organic molecules are almost quantitatively reproduced within the present DF method.[61]

V. Conclusions

We developed a novel scheme for calculating EPR **g**-tensor values of doublet-state systems within a relativistic DF method and presented its implementation as well as first applications. The formalism is based on the two-component eigenfunctions of the Kohn−Sham equations which include spin−orbit effects self-consistently. Therefore, the **g**-tensor can be considered as first-order property with respect to the perturbation by the external magnetic filed alone. The Zeeman energy splitting, an inherently relativistic effect, is naturally and transparently determined by the two-component ground-state wave function without invoking virtual states. Since the widely accepted perturbative treatment of spin−orbit interaction is avoided, the method is also applicable to molecular systems with spin−orbit interaction of considerable strength.

Test calculations of **g**-tensors for small inorganic main-group and transition metal molecules as well as organic radicals demonstrated that the present method exhibits an accuracy sufficient for successful assigning and interpreting EPR spectra. This statement holds even without the further conceivable improvements proposed for the newly implemented scheme. The most important and straightforward future developments of PARAGAUSS for EPR calculations comprise an extension of the relativistic treatment of the exchange−correlation interaction and the inclusion of spin polarization effects. Implementation of both improvements is under way.

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