Calculation of Electronic *g*-Tensors using Coupled Cluster Theory[†]

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A scheme for the calculation of the electronic *g*-tensor at the coupled cluster (CC) level is presented. The reported implementation employs an effective one-electron spin−orbit operator, allows the inclusion of arbitrary excitations in the cluster operator, and offers various options concerning the treatment of orbital relaxation and choice of reference determinants. In addition, the use of gauge-including atomic orbitals (GIAOs) is possible to overcome the gauge origin problem. Benchmark calculations for the NH ($^3\Sigma^-$) radical reveal the importance of electron correlation effects for the accurate prediction of the *g*-shift as well as the slow basis set convergence of such calculations, which is only marginally improved by using GIAOs. CC singles and doubles results for the *g*-tensor are furthermore used to validate various functionals often used in density functional theory calculations. At least for radicals containing only light elements, the B3LYP hybrid functional appears to be the best among the four functionals tested in the present work.

Introduction

Due to recent advances in high magnetic field and pulse techniques, electron paramagnetic resonance (EPR) spectroscopy has found renewed interest from both experiment and theory.[1,2] The electronic *g*-tensor, which appears in the phenomenological EPR Hamiltonian, accounts for the molecular Zeeman effect and describes the splitting of the $(2S + 1)M_S$ magnetic sublevels of an electronic state with total spin S in the presence of an external homogeneous magnetic field **B**. The theory of the *g*-tensor has been well understood since the 1950s, with the most general treatment in terms of density and transition density matrices given by McWeeny.[3,4] A thorough theoretical treatment was provided later also by Harriman.[5] The main point of these theoretical descriptions has been that the dominant contribution to the electronic *g*-tensor is due to spin−orbit coupling (SOC) of the spatially nondegenerate ground state with excited states, which introduces some angular momentum in the ground state. This mixing induces a magnetic dipole which interacts with the external magnetic field and, in this way, modifies the interaction of the intrinsic magnetic moment due to the unpaired electron(s) with the external magnetic field. The molecular information is thus contained in the *g*-shift, that is, the deviation of the molecular *g*-value from the corresponding free-electron *g*-value.

Following some early and pioneering work by Moores and McWeeny,[6] Lushington and Grein were the first to present calculations of the electronic *g*-tensors complete to second order.[7−10] They used for their implementation a truncated sum over states (SOS) approach together with restricted open-shell Hartree−Fock (ROHF) and multireference configuration-interaction (MR-CI) wave functions and obtained satisfactory agreement with experimental results. However, the computational cost of their approaches did not allow application to larger molecules. Consequently, approaches based on density functional theory (DFT) were pursued and became rather popular in the mid 1990s. Apart from some early work using a Hartree−Fock−Slater approach,[11] the first modern DFT implementation for the calculation of electronic *g*-tensors was reported in 1997 by Schreckenbach and Ziegler (SZ).[12] Their approach was applicable within the local spin density (LSD) and generalized gradient approximations (GGA)[13] and enforced gauge origin independence through the use of gauge-including atomic orbitals (GIAOs).[14−16] A very similar method was presented somewhat later by Malkina et al.,[17] who, however, used a common gauge origin approach together with an atomic mean-field (AMFI) approximation[18] for the SOC. The work by SZ was critized as not taking proper care of the spin-other-orbit (SOO) interactions, thus leading to an overestimation of the SOC effects. A more recent analysis of the problem[19] confirmed this statement and furthermore led to the conclusion that the approach chosen by SZ also introduces exchange contributions of the wrong sign. A coupled perturbed self-consistent field treatment of electronic *g*-tensors was presented in ref 20, thereby making calculations at the unrestricted Hartree−Fock (UHF) and at the DFT level using hybrid functionals possible. However, the lack of either accurate experimental gas-phase or accurate theoretical reference data did not allow for an unambiguous assessment of the relative merits of pure versus hybrid density functionals. More recently, some effort has been devoted to the identification and development of suitable functionals for the calculation of the electronic *g*-tensor.[21−23]

While the so-far discussed approaches are based on a perturbative ansatz concerning both SOC and the external magnetic field, it should be mentioned that also some effort has been devoted to the formulation and implementation of schemes which include SOC straight from the beginning in a self-consistent manner. Noteworthy in this context are the implementations using the zeroth-order regular approximation

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by van Lenthe et al.,[24,25] that at the Douglas−Kroll−Hess level by Neyman et al.,[26] but also the full four-component calculations by Quiney and Belanzoni.[27]

Turning back to the more conventional quantum chemical schemes, recent years have witnessed the development of schemes for the calculation of *g*-tensors using second-order multireference perturbation theory (MR-PT2),[28−31] though still in the framework of truncated SOS schemes. SOS-based MR-CI calculations have been recently reported by Marian and co-workers[32,33] and one of us,[34−36] while a linear response treatment at the multiconfigurational SCF (MCSCF) level has been presented by Vahtras et al.[37−39] Noteworthy in the present context is also the work of Bolvin,[40] who used an alternative approach based on a formula proposed by Gerloch and McMeeking to compute electonic *g*-tensors for MR-PT2 and coupled cluster models. A further step forward has been the development of a linear response MRCI implementation for the calculation of the electronic *g*-tensor.[41] However, orbital relaxation effects were not included but may provide a significant contribution to the *g*-tensors computed at the CI level.

While, in this way, useful tools for the computation of electronic *g*-tensors are available and corresponding calculations have turned out useful for the interpretation of EPR spectra, reliable high-accuracy treatments are so far scarce. However, such calculations are mandatory for establishing the accuracy which can be achieved in lower-level treatments and for judging the importance of electron correlation effects for the accurate prediction of electronic *g*-tensors.

The standard choice for highly accurate quantum chemical calculations of energies and properties nowadays is coupled cluster (CC) theory,[42−45] which provides a systematic and efficient treatment of electron correlation and, at the same time, unlike corresponding configuration interaction methods, ensures size consistency. The high accuracy of CC calculations, in particular, when the computations involve higher excitations,[46−52] is amply documented in the literature.[53−64] We just emphasize here the quantitative agreement that can be reached with experiment in the case of modern computational thermochemistry[54−58] and in the accurate prediction of molecular geometries[62,63] and properties related to rotational spectroscopy.[64] Treatment of second-order properties is possible in CC theory using linear response theory[65,66] or, in other words, second-derivative techniques.[67−74] Such methods have been developed within the last two decades and successfully applied to the computation of vibrational and NMR properties.[71,72] Application of CC second-derivative techniques to the computation of electronic *g*-tensors, however, has not been reported so far, mainly due to the fact that most CC implementations are restricted to closed-shell cases. The developments in our groups, however, always comprised corresponding implementations for high-spin open-shell systems, preferably treated using UHF reference functions.[72,74]

In the present work, we will explore the possibility to compute the electronic *g*-tensor at the CC level and there investigate the effect of higher excitations, basis set convergence, as well as the issue of orbital relaxation. As our present implementation will take advantage of an effective one-electron SOC operator (see the following section), the reported calculations are primarily not intended to provide high-accuracy results for comparison with experiment. The latter anyways should include additional vibrational corrections and, and in addition, reliable experimental values are scarce for the small molecules investigated in the present work. The scope of the current investigation rather is to provide reference values for low-level treatments at the DFT level and, in this way, to help in the calibration of these often-used and pragmatic tools in the prediction of EPR parameters.

Theory

The effective spin-Hamiltonian for the interaction of the electronic magnetic moment with an external magnetic field **B** is given by[5]

$$H_{\mathrm{spin}} = \mu_{\mathrm{B}} \mathbf{B}^{\mathrm{T}} \mathbf{g} \mathbf{S} \qquad (1)$$

with **S** as the electronic spin, μ_{B} as the Bohr magneton, and **g** as the electronic *g*-tensor. The latter is more properly referred to as the *g*-matrix, as only $\mathbf{g}^{\mathrm{T}}\mathbf{g}$ is a true second-rank tensor, but we will retain in the following the usually adopted naming convention. On the basis of eq 1, the computational recipe for the *g*-tensor takes the form[20]

$$\mathbf{g} = \frac{1}{\mu_{\mathrm{B}}} \left(\frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{S}} \right)_{\mathbf{B},\mathbf{S}=0} \qquad (2)$$

The *g*-tensor itself can be in a second step decomposed in its various contributions

$$\mathbf{g} = g_{\mathrm{e}} \mathbf{l} + \Delta \mathbf{g}_{\mathrm{pso}} + \Delta \mathbf{g}_{\mathrm{dso}} + \Delta \mathbf{g}_{\mathrm{rmc}} \qquad (3)$$

in this way reflecting the different physical origin of the contributions. The first term is simply the free-electron value[75]

$$g_{\mathrm{e}} = 2.002319304386(20) \qquad (4)$$

The second, so-called paramagnetic spin−orbit (pso) term is a true second-order contribution and results from the interaction of the following two first-order contributions to the Hamiltonian

$$h_{\mathrm{B}} = \mu_{\mathrm{B}} \mathbf{B}^{\mathrm{T}} \cdot \mathbf{l}_{\mathrm{O}} \qquad (5)$$

$$h_{\mathrm{so}} = \frac{\alpha^2}{2} \sum_A Z_A^{\mathrm{eff}} \frac{\mathbf{S}^{\mathrm{T}} \cdot \mathbf{l}_A}{|\mathbf{r} - \mathbf{R}_A|^3} \qquad (6)$$

Note that we give here the perturbed Hamiltonians in the form of the corresponding one-electron operators and, at the same time, invoke a one-electron approximation for the SOC operator. The two-electron SOC term, which in a rigorous treatment needs to be considered,[76] is here accounted for by replacing in eq 6 the nuclear charges Z_A by effective charges Z_A^{eff}.[77,78] With these remarks, the first perturbed Hamiltonian describes the interaction with an external magnetic field **B**. The electronic angular momentum $\mathbf{l}_{\mathrm{O}}$ is here defined with respect to an arbitrary origin $\mathbf{R}_{\mathrm{O}}$, usually referred to as the gauge origin. The second Hamiltonian accounts for the spin−orbit interactions and involves the electronic spin **S**, the angular momentum $\mathbf{l}_A$ defined with respect to the nuclear position $\mathbf{R}_A$ as the origin, the electronic coordinate **r**, and the fine-structure constant α. The sum in eq 6 runs over all nuclei in the molecule.

Unlike Δg_{pso}, the last two contributions to the electronic *g*-tensor in eq 3 are given as simple expectation values. The diamagnetic spin−orbit (dso) contribution (sometimes referred to as gauge correction) is due to the following second-order perturbed Hamiltonian

$$h_{\text{dso}} = \frac{\alpha^3}{4}\sum_A Z_A^{\text{eff}} \frac{[(\mathbf{r} - \mathbf{R}_A)^T\cdot\mathbf{r}](\mathbf{S}^{\text{T}}\cdot\mathbf{B}) - (\mathbf{S}^{\text{T}}\cdot\mathbf{r})[(\mathbf{r} - \mathbf{R}_A)^{\text{T}}\cdot\mathbf{B}]}{|\mathbf{r} - \mathbf{R}_A|^3} \tag{7}$$

while the last term in eq 3 accounts for the relativistic mass corrections (rmc) and is determined with

$$h_{\text{rmc}} = -\frac{\alpha^3}{2}\mathbf{p}^2\mathbf{S}^{\text{T}}\cdot\mathbf{B} \tag{8}$$

as the perturbed Hamiltonian. In eq 8, **p** represents the electronic momentum.

To summarize the discussion so far, the quantum chemical calculation of the electronic g-tensor requires the evaluation of one true second-order contribution (Δg_{pso}) and of two first-order contributions (Δg_{dso} and Δg_{rmc}) for which the perturbed Hamiltonian is second order. In the following, we will outline how these terms can be computed within CC theory.

In CC theory,[42−45] the wave function is given by the following exponential ansatz[79,80]

$$|\Psi\rangle = \exp(T)|0\rangle \tag{9}$$

where $|0\rangle$ is a single-determinantal reference function (usually, but not necessarily, the HF wave function) and T is the cluster operator

$$T = T_1 + T_2 + T_3 + ... \tag{10}$$

$$T_m = \frac{1}{m!^2}\sum_{i,j,k,...}\sum_{a,b,c,...} t_{ijk\cdots}^{abc\cdots} a^+ i b^+ j \cdots \tag{11}$$

with the amplitudes $t_{ijk\cdots}^{abc\cdots}$ as the unknown wave function parameters. Note that we here use a second-quantization formulation with p^+ and q referring to creation and annihilation operators, respectively. In addition, we invoke the usual convention that indices $i, j, k,...$ label occupied spin orbitals and indices $a, b, c,...$ virtual spin orbitals.

Using the ansatz in eq 9 for the wave function, the energy is obtained after insertion into the Schrödinger equation and premultiplication with $\exp(-T)$ from the left by projection onto the reference determinant

$$E = \langle 0|\exp(-T)H\exp(T)|0\rangle \tag{12}$$

while equations for the determination of the amplitudes are then obtained by projection onto excited determinants $\Phi_{ij\cdots}^{ab\cdots}$

$$0 = \langle\Phi_{ij\cdots}^{ab\cdots}|\exp(-T)H\exp(T)|0\rangle \tag{13}$$

In the last two equations, H refers to the molecular Hamiltonian in second quantization. Note that the CC ansatz in principle involves no approximation, and in fact, the inclusion of all possible excitations in the cluster operator corresponds to the well-known full configuration interaction limit. Applicability, however, dictates the use of additional approximations in CC calculations, which can be obtained by restricting T to certain excitation classes. CC singles and doubles (CCSD)[81] thus refers to $T = T_1 + T_2$, CC singles, doubles, and triples (CCSDT)[47−49] to $T = T_1 + T_2 + T_3$, and so forth. Use of string-based many-body techniques[50] nowadays allows the incorporation of arbitrary excitations in CC calculations, though the inclusion of higher excitations renders the computation rather costly.

For the efficient treatment of molecular properties in CC theory, it is advantageous to introduce the following energy functional

$$\tilde{E} = \langle 0|(1 + \Lambda)\exp(-T)H\exp(T)|0\rangle \tag{14}$$

where Λ is a de-excitation operator[82,83] defined similarly as the cluster operator

$$\Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3 + ... \tag{15}$$

with

$$\Lambda_m = \frac{1}{m!^2}\sum_{i,j,k,...}\sum_{a,b,c,...} \lambda_{abc\cdots}^{ijk\cdots} i^+ a j^+ b \cdots \tag{16}$$

This energy functional is simply the CC energy augmented by the CC equations given in eq 13 multiplied by Lagrange multipliers $\lambda_{abc\cdots}^{ijk\cdots}$. Unlike the CC energy itself, the functional given in eq 14 can be made stationary, and this can be exploited to simplify the calculation of properties. The stationarity conditions are the original CC equations for the amplitudes and an additional set of linear equations

$$\langle 0|(1 + \Lambda)(\exp(-T)H\exp(T) - E)|\Phi_{ij\cdots}^{ab\cdots}\rangle = 0 \tag{17}$$

often referred to as Λ equations, which determine the Lagrange multipliers $\lambda_{abc\cdots}^{ijk\cdots}$.

For first-order properties, differentiation with respect to the corresponding perturbation x yields[84]

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \langle 0|(1 + \Lambda)\exp(-T)\frac{\mathrm{d}H}{\mathrm{d}x}\exp(T)|0\rangle \tag{18}$$

For second-order properties further differentiation with respect to a second parameter y leads to[85]

$$\begin{aligned}\frac{\mathrm{d}^2E}{\mathrm{d}x\mathrm{d}y} = {} & \langle 0|(1 + \Lambda)\exp(-T)\frac{\mathrm{d}^2H}{\mathrm{d}x\mathrm{d}y}\exp(T)|0\rangle + \\ & \langle 0|\frac{\mathrm{d}\Lambda}{\mathrm{d}y}\exp(-T)\frac{\mathrm{d}H}{\mathrm{d}x}\exp(T)|0\rangle + \\ & \langle 0|(1 + \Lambda)\left[\exp(-T)\frac{\mathrm{d}H}{\mathrm{d}x}\exp(T), \frac{\mathrm{d}T}{\mathrm{d}y}\right]|0\rangle\end{aligned} \tag{19}$$

In the case of the electronic g-tensor, x and y refer to the external magnetic field **B** and the electronic spin **S**. The first term in eq 19 allows the calculation of dso and rmc contributions; the second and third term are needed for the pso term.

While the formula for the first-order properties does not involve any perturbed wave function parameters, determination of second-order properties requires the perturbed cluster and Λ operator. In principle, it is possible to obtain expressions for second-order properties that do not contain the perturbed Λ operators. However, the expression given in eq 19 appears advantageous for the calculation of the electronic *g*-tensor, in the same way as that for the calculation of NMR chemical shifts, and the perturbed wave function parameters need to be determined solely for one of the two perturbations, namely, the magnetic field **B** with its three components. Alternatively, the perturbed equations could be solved solely for the spin–orbit perturbation.

The perturbed cluster and Λ amplitudes are obtained from solving the following equations

$$0 = \langle \Phi_{ij\cdots}^{ab\cdots} | \exp(-T) \frac{\mathrm{d}H}{\mathrm{d}x} \exp(T) | 0 \rangle + \langle \Phi_{ij\cdots}^{ab\cdots} | \left[\exp(-T) H \exp(T), \frac{\mathrm{d}T}{\mathrm{d}x} \right] | 0 \rangle \quad (20)$$

and

$$0 = \langle 0 | \frac{\mathrm{d}\Lambda}{\mathrm{d}y} (\exp(-T) H \exp(T) - E) | \Phi_{ij\cdots}^{ab\cdots} \rangle + \langle 0 | (1 + \Lambda) \left(\exp(-T) \frac{\mathrm{d}H}{\mathrm{d}y} \exp(T) + \left[\exp(-T) H \exp(T), \frac{\mathrm{d}T}{\mathrm{d}y} \right] - \frac{\mathrm{d}E}{\mathrm{d}y} \right) | \Phi_{ij\cdots}^{ab\cdots} \rangle \quad (21)$$

that are obtained by differentiating the unperturbed CC and Λ equations, respectively.

There are a few further remarks necessary. First, the given expressions are usually recast using a density matrix formulation.[71,86] Such a formulation is advantageous for the actual implementation. We are not repeating the corresponding discussion here and instead refer the reader to the literature,[69,71,86] where detailed expressions for the density matrices are given. A second issue is that we have so far not dealt with orbital relaxation or, in other words, the question of how the molecular orbitals are allowed to respond to the perturbation. As single excitations can take care of orbital relaxation effects in a satisfactory manner,[87] two options exist. The first results in the so-called "orbital-relaxed" approach in which the orbitals are allowed to respond to the applied perturbation and consequently the corresponding coupled perturbed HF equations[88] (or, alternatively, the corresponding *Z*-vector equations)[89] need to be solved. In the second, so-called "orbital-unrelaxed" approach, the orbitals are kept frozen in the presence of the perturbation. With respect to the given formula for first and second derivatives of the energy, we note that the orbital relaxation contribution, if included, is part of the perturbed Hamiltonian within the second-quantization notation. We will refrain from discussing the corresponding details further and again refer to the literature for details about how orbital relaxation are treated in actual calculations.[71,86] Finally, we comment on the open-shell issue, which is of relevance for calculations of the electronic *g*-tensor. For high-spin open-shell cases, with which we are dealing in the following exclusively, approaches with a single Slater determinant as the reference function are appropriate. The common choices are here either UHF or ROHF reference determinants, and both choices will be made in the following. The actual CC treatment is then the usual spin–orbital-based one and leads to wave functions which are not spin eigenfunctions.[90] However, the amount of spin contamination is usually small, so that the use of spin-restricted or spin-adapted CC approaches[91−97] seems to be unnecessary.

The described scheme for the calculation of electronic *g*-tensors at the CC level has been implemented in the existing CC second-derivative module of the quantum chemical program package CFour.[102] This implementation allows calculations at the CCSD level,[81] while CCSDT,[47−49] CCSDTQ,[50] and so forth calculations are possible using the interface to the open-shell CC second-derivative module[74] of the MRCC package.[103]

To be somewhat more specific about our implementation, the starting point has been our CC code for NMR chemical shift calculations,[68−70,73,74] which has been in a first step extended for UHF reference functions. For the calculation of electronic *g*-tensors, this code needs to be modified in a second step such that (a) in the property calculation, the usual unperturbed and perturbed density matrices are replaced by the corresponding spin density matrices, (b) the individual shielding tensors, obtained with the spin density matrices are scaled by Z_A^{eff} and summed, and (c) the additional relativistic mass correction contribution is considered, which is simply given via the expectation value of the kinetic energy operator obtained again with the spin density matrix instead of the usual density matrix.

If desired, GIAOs[14−16] can be used. However, it should be noted that their use is restricted to orbital-relaxed calculations, as it is still unclear how perturbation-dependent basis functions can be applied within orbital-unrelaxed schemes.

Computational Details

Calculations have been performed with the following four tasks in mind: (a) analysis of the convergence of the computed electronic *g*-tensor within the usual CC hierarchy ranging from CCSD up to CCSDTQ, (b) investigation of the importance of orbital relaxation effects, (c) analysis of the basis set convergence in CC calculations of electronic *g*-tensors, and (d) comparison of CC results (as reference values) for a number of small radicals (CN ($^2\Sigma^+$), CO^+ ($^2\Sigma^+$), BO ($^2\Sigma^+$), NH ($^3\Sigma^-$), OH^+ ($^3\Sigma^-$), H_2O^+ ($^2B_1$), CH_3 ($^2A''$), O_2 ($^3\Sigma_g^-$), O_3^- ($^2B_1$), CO_2^- ($^2A_1$), H_2CO^+ ($^2B_2$), NO_2 ($^2A_1$), NF_2 ($^2A''$), and NF_3^+ ($^2A''$)) with corresponding data obtained in HF and DFT calculations.

For the first two issues, calculations have been performed for the NH radical ($^3\Sigma^-$). The computations have been carried out at the CCSD, CCSDT, and CCSDTQ levels using the aug-cc-pVDZ basis.[98,99] The orbital-unrelaxed calculations employed either a UHF or ROHF reference function, while the orbital-relaxed calculations always started with a UHF reference. The gauge origin has been chosen in all calculations at the corresponding center of the electronic charge. All calculations have been furthermore carried out for a NH distance of 1.957794 bohr. The basis set convergence was investigated using again NH as an example. Corresponding orbital-relaxed calculations have been performed here using the aug-cc-pVXZ and aug-cc-pCVXZ basis set hierarchies[98−101] with X = D, T, Q, 5, and 6.

For the fourth task, calculations have been carried out at orbital-unrelaxed and orbital-relaxed CCSD levels using a UHF reference together with the aug-cc-pVTZ basis set.[98,99] The gauge origin has been again chosen for all calculations at the center of the electronic charge. The computations have been carried out using the following geometries: CN, $r(\mathrm{CN}) = 2.214$ bohr; CO^+, $r(\mathrm{CO}) = 2.098581$ bohr; BO, $r(\mathrm{BO}) = 2.276975$ bohr; NH, $r(\mathrm{NH}) = 1.957794$ bohr; OH^+, $r(\mathrm{OH}) = 1.944566$ bohr; H_2O^+, $r(\mathrm{OH}) = 2.089322$ bohr, $\angle(\mathrm{HOH}) = 109.62°$; CH_3, $r(\mathrm{CH}) = 2.038109$ bohr; O_2, $r(\mathrm{OO}) = 2.298896$ bohr; O_3^-, $r(\mathrm{OO}) = 2.608628$ bohr, $\angle(\mathrm{OOO}) = 115.98°$; CO_2^-, $r(\mathrm{CO}) = 2.368817$ bohr, $\angle(\mathrm{OCO}) = 133.88°$; H_2CO^+, $r(\mathrm{CO}) = 2.282000$ bohr,

TABLE 1: Effect of Higher Excitation, Choice of Reference Determinant, And Treatment of Orbital Relaxation in CC Calculations of the Electronic g-Shift (relative to the g-value of the free electron, in ppm) for NH ($^3\Sigma^-$)[a]

reference	orbital relaxation	component	HF	CCSD	CCSDT	CCSDTQ
UHF	orbital-relaxed	Δg_{xx}	1081.0	1313.8	1329.3	1330.8
		Δg_{zz}	−110.7	−106.2	−106.0	−106.0
UHF	orbital-unrelaxed	Δg_{xx}		1320.9	1329.6	1330.7
		Δg_{zz}		−105.8	−106.0	−106.0
ROHF	orbital-unrelaxed	Δg_{xx}		1327.7	1329.9	1330.7
		Δg_{zz}		−105.8	−106.0	−106.0

[a] All calculations have been performed using the aug-cc-pVDZ basis and a NH distance of 1.957794 bohr.

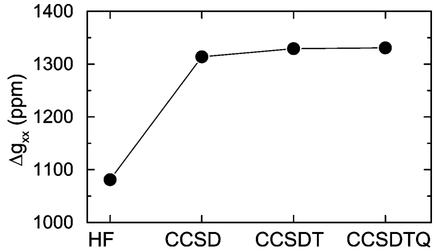

Figure 1. Convergence of the computed Δg_{xx} component of NH ($^3\Sigma^-$) with inclusion of higher exictations in the cluster operator.

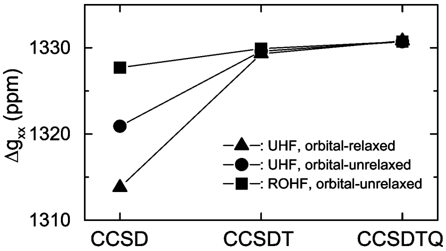

Figure 2. Effect of orbital relaxation and reference determinant on the computed Δg_{xx} component of NH ($^3\Sigma^-$).

r(CH) = 2.078000 bohr, ∠(HCO) = 117.85°; NO_2, r(NO) = 2.257132 bohr, ∠(ONO) = 134.32°; NF_2, r(NF) = 2.561195 bohr, ∠(FNF) = 103.575°; and NF_3^+, r(NF) = 2.479935 bohr. The DFT calculations have been carried using the local spin density functional in the parametrization V of Vosko, Wilk, and Nusair (VWN5),[104] the gradient-corrected BP86 functional,[105,106] and the B3LYP hybrid functional.[105,107,108] Furthermore, the TPSSh functional[109] has been employed as a member of the meta-GGA family of functionals that has shown good performance for hyperfine couplings.[110] The corresponding calculations have been carried out with the ORCA program,[111] making use of large grids and tight SCF convergence (keywords Grid7 and VeryTightSCF).

In all calculations, the effective one-electron spin−orbit operator suggested by Koseki et al.[77,78] has been used. The effective nuclear charges were 1.0 for H, 2.75 for B, 3.60 for C, 4.55 for N, 5.60 for O, and 6.75 for F.

Results and Discussion

Table 1 summarizes the various results for the electronic g-shift (relative to the g-value of the free electron) of the NH radical as obtained in HF, CCSD, CCSDT, and CCSDTQ calculations using the aug-cc-pVDZ basis and the different options concerning the choice of the reference determinant and treatment of orbital relaxation. The convergence of the CC results with inclusion of higher excitations is also illustrated in Figure 1 for the Δg_{xx} component. Figure 2 documents the performance of the orbital-relaxed and orbital-unrelaxed schemes as well as the influence of the choice of reference function on the results for the same component. First of all, it is seen from Table 1 and Figure 1 that electron correlation effects are quite substantial for the xx-component of the g-shift of NH. While the HF result amounts to about 1081 ppm, the converged CC result is about 1331 ppm, thus indicating a correlation contribution of about 250 ppm. The major fraction of the correlation effects is recovered already at the CCSD level, and thus, CCSD seems to be a good choice for the more routine determination of the electronic g-shift at the CC level. Inclusion of triple and quadruple excitations has, with about 16 and 2 ppm, respectively, only a rather small effect and seems to be only warranted if quantitative accuracy is needed and other issues such as basis set convergence and inclusion of vibrational corrections are adequately dealt with. It should be noted that we focus here solely on Δg_{xx}. For the zz-component, the situation is different; due to symmetry reasons, the only contribution is here the isotropic relativistic mass correction. The latter is not very demanding from a computational point of view, as also seen in Table 1. With respect to the treatment of orbital relaxation, we note, as clearly seen from Figure 2, that the orbital-unrelaxed scheme seems to perform slightly better. However, both schemes converge, as it should be, to the same limit, and the differences between them decrease with increasing excitation level. Nevertheless, triple- and quadruple-excitation contributions are for the unrelaxed approach with 9 and 1 ppm, slightly smaller than those in the corresponding orbital-relaxed calculations. An explanation here might be that the coupled perturbed HF treatment of orbital relaxation effects is only of limited accuracy and in some way suffers from the shortcomings of the UHF reference. Noteworthy here is, in particular, the notorious spin contamination issue. These problems are clearly avoided when reverting to the orbital-unrelaxed scheme. Furthermore, we note that the use of a ROHF reference might be preferred over the choice of an UHF reference. The convergence with respect to excitation level is here even faster, with triple- and quadruple-excitation contributions amounting to only 2 and 1 ppm, respectively.

Table 2 and Figure 3 illustrate the basis set convergence in the calculation of the electronic g-shift. Only the results for the xx-component of NH are reported here as again the calculation of Δg_{zz} poses no challenge. Comparison of the aug-cc-pVXZ and aug-cc-pCVXZ series indicates that the convergence with the latter is somewhat faster. However, the differences are not too pronounced, and thus, it can be concluded that core-polarizing functions are not essential for the accurate prediction of the electronic g-shift. On the other side, basis set convergence appears to be rather slow. The double-ζ results are far off from the basis set limit, with errors of about 200 (aug-cc-pVDZ) and 175 ppm (aug-cc-pCVDZ). The error is substantially reduced when using the triple-ζ sets, though the errors still amount to 70 and 50 ppm, respectively. Only the quadruple-ζ and quintuple-ζ results come close to the basis set limit, with remaining deviations of 25 and 15 (aug-cc-pVXZ) and 5 and 3 ppm (aug-cc-pCVXZ), respectively, from the sextuple-ζ values.

TABLE 2: Basis Set Convergence in CCSD Calculations of the Electronic *g*-Shift (Δg_{xx} component, in ppm) of NH ($^3\Sigma^-$)[a]

	unrelaxed		relaxed		GIAO	
cardinal number	aug-cc-pVXZ	aug-cc-pCVXZ	aug-cc-pVXZ	aug-cc-pCVXZ	aug-cc-pVXZ	aug-cc-pCVXZ
D	1320.9	1354.0	1313.8	1345.8	1319.4	1351.6
T	1465.4	1488.8	1451.5	1473.3	1453.3	1475.0
Q	1511.3	1521.6	1495.5	1504.8	1495.8	1505.2
5	1530.7	1533.7	1514.1	1516.5	1514.3	1516.6
6	1536.6	1537.9	1519.7	1520.6	1519.8	1520.6

[a] Compared are results from orbital-unrelaxed and orbital-relaxed calculations with those using GIAOs. All calculations have been carried out for a NH distance of 1.957794 bohr.

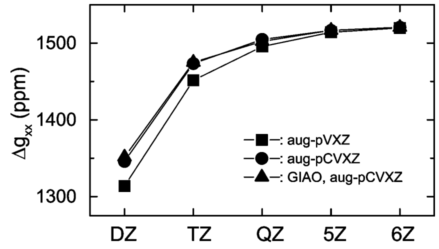

Figure 3. Basis set convergence in CCSD calculations of the Δg_{xx} component of NH ($^3\Sigma^-$).

It can be now argued that the use of GIAOs might improve the convergence to the basis set limit significantly, as seen in NMR chemical shift calculations.[16] However, the use of GIAOs, as shown in Table 2, does not really improve the convergence. The reason might be simply that the NMR chemical shift is a local molecular property while the *g*-tensor is a global property. This also is probably the reason why the gauge origin problem is significantly less pronounced for the electronic *g*-tensor, and common gauge origin calculations, as carried out also in the present work, are sufficient. It should be furthermore noted that a similar study concerning basis set convergence has been previously reported using the linear response MRCI approach.[41] With the cc-pVXZ basis sets, similarly slow convergence was found. The cc-pV5Z value of 1463 ppm for Δg_{xx}, however, can be considered in reasonable agreement with the present CCSD results.

Finally, we will turn to our comparison with HF and DFT results. The CC values, obtained at either the orbital-relaxed or orbital-unrelaxed CCSD level using the same geometry and basis set as those in the HF and DFT calculations, serve here as a reference. Table 3 summarizes the corresponding results for the chosen radicals. First of all, the comparison again demonstrates the importance of electron correlation effects for the reliable prediction of electronic *g*-tensors as the corresponding corrections are, in many cases, substantial. Noteworthy here are, for example, the Δg_{xx} value for CO^+ (electron correlation contribution of 627 ppm, 24% of the total value), the Δg_{xx} component for OH^+ (714 ppm, 17% of the total value), the Δg_{yy} result for H_2O^+ (3544 ppm, 21% of the total value), and the Δg_{yy} and Δg_{zz} components for O_3^- (−5708 and −5435 ppm, respectively, 32 and 51% of the total values). On the other hand, orbital-unrelaxed and orbital-relaxed CCSD values differ by much less. The difference is typically around 100 ppm or less, though substantially larger deviations of around 2000 ppm are seen in the case of O_3^-. It should be furthermore noted that electron correlation contributions are not negligible for those components for which the spin−orbit contributions vanish due to symmetry. The corresponding tensor elements, for example, the Δg_{zz} component in the case of linear molecules, are usually rather small, but the electron correlation correction can amout here quickly to about 30%. As examples, we note here the CN, CO^+, and BO radicals, while the corresponding components for OH^+ and NH seem to be more or less unaffected by correlation effects.

The judgment of the corresponding DFT results is not straightforward as there are no clear trends. In many cases, the DFT calculations tend to overestimate the electron correlation contributions (defined in the following with respect to the HF results), but there are also examples for which DFT underestimates those corrections. In a few examples, the correction has even the wrong sign, that is, the DFT results show in comparison to CCSD a larger error than HF. The LSD approximation with the VWN5 functional in most cases (e.g., Δg_{xx} of CN, NH, OH^+, O_3^-, and NF_3^+) overestimates the magnitude of the correlation corrections. Overall, the VWN5 results cannot be considered very accurate, with a mean absolute deviation of about 340 ppm from the orbital-unrelaxed CCSD values for our test set. LSD is, in this way, much better than HF but still far away from being reliable. The behavior of the gradient-corrected BP86 functional is somewhat more erratic. No clear trend is seen. There are cases where the correction is overestimated (e.g., the Δg_{xx} components of CN, O_2, and O_3^-) but also cases with an underestimation (e.g., Δg_{xx} for NH) and those with a wrong sign (e.g., Δg_{xx} for OH^+ and Δg_{yy} for H_2O^+). The statistical measures indicate for BP86 a significantly worse performance than that for LSD, with a mean absoute deviation of about 510 ppm. Even more severe problems are found for the TPSSh functional (mean absolute deviation of 575 ppm), which therefore also cannot be recommended. A surprisingly good performance, however, is seen for the B3LYP hybrid functional. It seems that the inclusion of HF exchange damps the overestimation of the correlation effects and leads to rather reliable predictions. The mean absolute deviation is here about 230 ppm and, thus, in an acceptable range. Larger deviations are only seen for H_2O^+, which seems anyways to be a notoriously difficult case. The good performance of B3LYP in our test calculations is also supported by the good performance of B3LYP found in several application studies,[112] provided that an accurate approximation to the spin−orbit coupling operator is used.[19] However, we emphasize that our findings so far only hold for light-element radicals and that no recommendation is given for open-shell transition-metal complexes. For these compounds, the *g*-shifts are up to 3 orders of magnitude larger, and all theoretical approaches tested so far turned out to have problems.

Conclusions and Outlook

In the present work, we have reported on a scheme for the calculation of electronic *g*-tensors using CC methods for the treatment of electron correlation effects. Our approach exploits available analytic second-derivative techniques and thus, unlike some earlier schemes at the MRCI level, can be characterized as a true response theory treatment. From our extensive set of calculations for the NH ($^3\Sigma^-$) radical, we conclude the following:

TABLE 3: Comparison of HF, DFT, and CCSD Results for the Electronic g-Shift (relative to the g-value of the free electron, in ppm) for Various Radicals[a]

		CCSD		HF	DFT			
molecule	component	unrelaxed	relaxed		VWN5	BP86	B3LYP	TPSSh
CN ($^2\Sigma^+$)	Δg_{xx}	−2151	−2151	−2237	−2103	−2009	−2193	−1959
	Δg_{zz}	−124	−126	−81	−132	−132	−134	−131
CO^+ ($^2\Sigma^+$)	Δg_{xx}	−2598	−2576	−3225	−2674	−2585	−2656	−2535
	Δg_{zz}	−125	−125	−63	−132	−133	−133	−131
BO ($^2\Sigma^+$)	Δg_{xx}	−1870	−1833	−2113	−1938	−1893	−1857	−1872
	Δg_{zz}	−60	−61	−27	−63	−65	−68	−66
NH ($^3\Sigma^-$)	Δg_{xx}	1465	1451	1133	1546	1237	1363	979
	Δg_{zz}	−105	−105	−109	−106	−104	−106	−104
OH^+ ($^3\Sigma^-$)	Δg_{xx}	4119	4101	3405	4216	3262	3704	2582
	Δg_{zz}	−173	−173	−178	−174	−171	−174	−171
H_2O^+ ($^2B_1$)	Δg_{xx}	−188	−188	−155	−188	−189	−188	−195
	Δg_{yy}	16667	16550	13123	17622	11447	13574	9331
	Δg_{zz}	4940	4905	4052	5433	4407	4681	3851
CH_3 ($^2A''$)	Δg_{xx}	−84	−85	−84	−87	−87	−89	−95
	Δg_{zz}	646	636	506	761	634	649	540
O_2 ($^3\Sigma_g^-$)	Δg_{xx}	2669	2853	3498	2526	2408	2677	2384
	Δg_{zz}	−199	−201	−232	−190	−190	−199	−195
O_3^- ($^2B_1$)	Δg_{xx}	−706	−662	−1502	455	−473	−555	−550
	Δg_{yy}	18062	20276	23770	16545	15286	18429	15250
	Δg_{zz}	10668	12376	16103	9127	8696	11032	9198
CO_2^- ($^2A_1$)	Δg_{xx}	840	914	1048	777	704	932	864
	Δg_{yy}	−5104	−5176	−5709	−4860	−4687	−5122	−4803
	Δg_{zz}	−779	−758	−927	−636	−661	−716	−726
H_2CO^+ ($^2B_2$)	Δg_{xx}	6172	6270	5806	6015	5519	5910	5199
	Δg_{yy}	144	145	662	14	28	91	38
	Δg_{zz}	721	945	3093	1264	−663	24	667
NO_2 ($^2A_1$)	Δg_{xx}	3596	3677	4278	3392	3323	3628	3361
	Δg_{yy}	−11728	−11952	−12588	−12219	−11208	−11837	−10522
	Δg_{zz}	−762	−730	−1195	−651	−663	−695	−702
NF_2 ($^2B_1$)	Δg_{xx}	−699	−694	−1038	−617	−627	−667	−682
	Δg_{yy}	6704	6832	5757	7446	6661	6988	6106
	Δg_{zz}	3766	3858	2889	4466	4117	4126	3817
NF_3^+ ($^2A_2''$)	Δg_{xx}	−2010	−1990	−3667	−1335	−1557	−1806	−1869
	Δg_{zz}	5178	5440	4020	6084	5648	5914	5352

[a] All calculations have been carried out using the aug-cc-pVTZ basis and with the axes of the Cartesian coordinate system given by the principal axes.

(a) Electron correlation effects turn out to be quite substantial, and in this way, HF calculations should be considered unreliable even qualitatively. This finding is also confirmed in calculations for a larger set of small radicals.

(b) The basis set convergence in the calculation of the electronic g-tensor is rather slow and necessitates the use of at least triple-ζ sets. The use of GIAOs solves the gauge origin problem, though it improves the basis set convergence only marginally.

(c) Differences in the treatment of orbital relaxation ("orbital-unrelaxed" versus "orbital-relaxed") as well as in the choice of reference functions (UHF versus ROHF) turn out to have only a small influence on the CC results. Nevertheless, there might be exceptions, in particular, in those cases where severe problems with the reference function are encountered.

As a first application of our newly developed CC techniques, we report on a validation of various functionals in DFT calculations of the electronic g-tensor. Here, the comparison leads to a clear recommendation in favor of the B3LYP hybrid functional, while the performance of the BP86 and TPSSh functionals is disappointing. Nevertheless, these conclusions are so far only valid for radicals containing light elements only, and it might be an interesting task to carry out a similar validation for a set including transition-metal compounds.

The present work should be considered only as a first step. For routine application, an efficient implementation using lower-order scaling CC methods[113−115] might be of interest as, in this way, applications to "real" chemical problems will become possible. On the other side, a rigorous treatment of spin−orbit interactions including the two-electron contribution should be aimed at. While at the DFT level cost arguments favor or even necessitate the use of approximate one-electron spin−orbit operators, the same is not true at the CC level. High-level CC calculations with a rigorous treatment of spin−orbit interactions then might provide reliable reference values for small molecules and might, in this way, stimulate some interest in gas-phase EPR investigations. However, such high-accuracy treatments also need to consider vibrational effects, possibly along the same lines as those in ref 116 for the calculation of NMR chemical shifts. Another issue that we would like to mention here is that the present scheme for the calculation of electronic g-tensors opens also the possibility to compute electronic spin−rotation tensors, which are of relevance for high-resolution gas-phase spectroscopy of small radicals. The close relationship between the electronic spin−rotation and the electronic g-tensor, as outlined, for example, in ref 117, can be exploited here and, in this way, lead, for the first time, to high-accuracy quantum chemical prediction of this spectroscopic parameter.

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