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Complete to second-order *ab initio* level calculations of electronic *g*-tensors

G.H. Lushington, F. Grein

Department of Chemistry, University of New Brunswick, B.S. #45222, Fredericton,
N.B., E3B 6E2, Canada

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Abstract. The electronic g-tensors for NO_2, CO^+ and H_2O^+ are calculated at the restricted open-shell Hartree–Fock (ROHF) level using the Rayleigh–Schrödinger perturbation approach. All known first- and second-order contributions have been evaluated, including the relativistic mass correction, one- and two-electron spin Zeeman gauge correction terms, and one- and two-electron second-order terms. Substantial code development has been necessary, including an integral routine for computing the two-electron spin-Zeeman gauge correction term.

Calculations have been done using triple zeta and quadruple zeta basis sets with additional polarization and semi-diffuse functions. Effective gauge invariance is obtained by placing the gauge origin at the molecule's electronic charge centroid. Excited state energies in the sum-over-states expansion are expressed using determinantal energies, thus avoiding the non-uniqueness of ROHF eigenvalues.

Our results successfully reproduce trends in gas phase g-shifts ($\Delta g = g - g_e$). However, discrepancies between our calculated g-shifts and experimental ones, sometimes on the order of 50%, point to the need for a correlated treatment.

Key words: Electronic g-tensor – Zeeman effect – Gauge invariance – Hartree–Fock wavefunctions – Magnetic properties

1 Introduction

The focus of electron spin resonance (ESR) spectroscopy is the study of microwave resonance phenomena in paramagnetic molecules. The observed resonance involves transitions between different m_s levels of the same molecular spin state, which are split by the magnetic field ($\boldsymbol{B}$) of the ESR spectrometer. This splitting, known as the electronic Zeeman effect, may be parametrized by electronic g-tensors (g) as follows

$$\Delta E = \mu_B \boldsymbol{S} \cdot g \cdot \boldsymbol{B}, \tag{1}$$

where μ_B is the Bohr magneton and $\boldsymbol{S}$ is the molecule's spin angular momentum vector.

Although g-tensors are perhaps the most fundamental of all ESR parameters, they have been the subject of surprisingly few *ab initio* studies [1–4].

The approaches used for g-tensor calculations include Rayleigh–Schrödinger perturbation theory (RSPT) [1–5], finite perturbation theory (also called Hartree–Fock perturbation theory) [3, 5] and Green's function techniques [6]. Despite the success of finite perturbation theory in chemical shift calculations [7, 8], it has not displayed any particular advantage when applied to the g-tensor problem [3, 5]. Instead, the consensus generally favours the Rayleigh–Schrödinger approach [1–5].

The RSPT g-tensor expansion is constructed from selected Breit–Pauli operators. The expansion is dominated by the spin–Zeeman interaction, which contributes in first-order. Also included in first-order are the relativistic mass correction to the spin–Zeeman ($\Delta g_{\mathrm{RMC-SZ}}$, not to be confused with the relativistic mass correction to kinetic energy), and one- and two-electron gauge terms ($\Delta g_{\mathrm{GC-SZ}}(1e)$ and $\Delta g_{\mathrm{GC-SZ}}(2e)$). Second-order contributions ($\Delta g_{2o}(1e)$ and $\Delta g_{2o}(2e)$) involve the mixing of the orbital Zeeman interaction with one- and two-electron spin–orbit interactions.

No previous g-tensor calculations have included all such correction terms. Hayden and McCain [1] and Ishii et al. [3] incorporated only second-order terms. Lushington et al. [4] used only one-electron contributions. The work of Moores and McWeeny [2] encompassed all terms except $\Delta g_{\mathrm{RMC-SZ}}$.

In this work, we have calculated the electronic g-tensors for NO_2, CO^+ and H_2O^+ at the Hartree–Fock level using an RSPT expansion complete to second-order. This has required the derivation and implementation of integral code for the two-electron spin–Zeeman gauge correction term ($\Delta g_{\mathrm{GC-SZ}}(2e)$), described in detail elsewhere [9].

For these calculations, we have exploited a technique of non-arbitrary gauge selection to attain approximately gauge invariant results, and have used large basis sets with polarization and semi-diffuse functions.

A basis set study is provided for NO_2.

2 Theory

As Eq. (1) implies, the crux of the electronic Zeeman effect involves an interaction of the external magnetic field ($\boldsymbol{B}$) with an electron's spin ($\boldsymbol{S}$). For a free electron, the effect can be described by the simple Hamiltonian

$$H_{\mathrm{Zeeman}} = g_e \mu_B \boldsymbol{S} \cdot \boldsymbol{B}, \tag{2}$$

where $g_e = 2.002319$ is the free-electron g-value.

For electrons in a bound environment, however, this simple description is perturbed by various other magnetic effects. As a result, the proportionality may deviate somewhat from g_e and, except in isotropic cases (such as isolated atoms), the effect becomes directionally dependent. The magnetic perturbations causing this include spin–spin and spin–orbit coupling, and the interactions of the external field with nuclear spin and electron orbital motion. In practice, however, nuclear spin effects are usually determined separately as hyperfine coupling. As well, the spin–spin interaction is only present in systems with at least two unpaired electrons. Therefore, the electronic Zeeman effect for molecules with one unpaired electron can be described by the spin Hamiltonian

$$H_{\mathrm{Zeeman}} = H'_{\mathrm{SZ}} + H'_{\mathrm{OZ}} + H'_{\mathrm{SO}}. \tag{3}$$

In the above, H'_{SZ} describes interactions between field and electron spin magnetic moment, H'_{OZ}, relates the mixing of the field with the orbital magnetic moment, and H'_{SO} accounts for spin–orbit coupling.

Such interactions are expressed at a non-relativistic level in terms of Breit–Pauli operators, derived by reducing the Breit equation to the second Pauli limit. H'_{SZ} interactions are described by a spin–Zeeman operator (H_{SZ}), and one- and two-electron gauge corrections ($H_{\mathrm{GC-SZ}}(1\mathrm{e})$ and $H_{\mathrm{GC-SZ}}(2\mathrm{e})$). Similarly, H'_{SO} is modelled by one- and two-electron spin–orbit operators ($H_{\mathrm{SO}}(1\mathrm{e})$ and $H_{\mathrm{SO}}(2\mathrm{e})$), while H'_{OZ} translates to the non-relativistic H_{OZ} operator.

One also finds that including a relativistic mass correction ($H_{\mathrm{RMC-SZ}}$) to the spin–Zeeman interaction can sometimes play an important role in describing the electronic Zeeman behaviour [4, 10]. A similar correction may be made to H_{OZ} [11], but it has been found to have negligible contribution [12].

In summary, the Hamiltonian necessary for a proper description of the electronic Zeeman effect in a doublet molecule includes the following interactions:

$$\begin{aligned} H_{\mathrm{Zeeman}} = {} & H_{\mathrm{SZ}} + H_{\mathrm{RMC-SZ}} + H_{\mathrm{GC-SZ}}(1\mathrm{e}) + H_{\mathrm{GC-SZ}}(2\mathrm{e}) \\ & + H_{\mathrm{SO}}(1\mathrm{e}) + H_{\mathrm{SO}}(2\mathrm{e}) + H_{\mathrm{OZ}}. \end{aligned} \tag{4}$$

Expressions for these operators are given elsewhere [11].

In the Rayleigh–Schrödinger approach, H_{Zeeman} is treated as a perturbation to the zeroth-order (Hartree–Fock) Hamiltonian

$$H = H_0 + H_{\mathrm{Zeeman}} \tag{5}$$

and energetic contributions may be expanded to nth-order. $H_{\mathrm{SO}}(1\mathrm{e})$, $H_{\mathrm{SO}}(2\mathrm{e})$ and H_{OZ} do not contribute in first-order, hence we have

$$\begin{aligned} E^{(1)} = {} & \langle \Psi_0 | H_{\mathrm{SZ}} | \Psi_0 \rangle + \langle \Psi_0 | H_{\mathrm{RMC-SZ}} | \Psi_0 \rangle + \langle \Psi_0 | H_{\mathrm{GC-SZ}}(1\mathrm{e}) | \Psi_0 \rangle \\ & + \langle \Psi_0 | H_{\mathrm{GC-SZ}}(2\mathrm{e}) | \Psi_0 \rangle, \end{aligned} \tag{6}$$

while second-order contributions include

$$\begin{aligned} E^{(2)} = {} & 2 \sum_n \langle \Psi_0 | H_{\mathrm{SO}}(1\mathrm{e}) | \Psi_n \rangle \langle \Psi_n | H_{\mathrm{OZ}} | \Psi_0 \rangle / (E_n - E_0) \\ & + 2 \sum_n \langle \Psi_0 | H_{\mathrm{SO}}(2\mathrm{e}) | \Psi_n \rangle \langle \Psi_n | H_{\mathrm{OZ}} | \Psi_0 \rangle / (E_n - E_0), \end{aligned} \tag{7}$$

where Ψ_0 is the ground state Hartree–Fock wavefunction of energy E_0, and E_n is the determinantal energy of a singly excited configuration Ψ_n. Note that double excitations do not contribute to the sum-over-states expansion since, although they can be mixed by the two-electron spin–orbit operators, the corresponding orbital Zeeman matrix element is zero.

Third-order contributions have also been derived [13], but are small compared to first- and second-order terms [14].

Since g-tensors are independent of spin and field, one factors $\boldsymbol{S}$ and $\boldsymbol{B}$ out of Eqs. (6) and (7). This leaves the following expression for elements of the electronic g-tensor:

$$\begin{aligned} g^{\mathrm{ab}} = {} & g_{\mathrm{e}} \delta^{\mathrm{ab}} + \Delta g_{\mathrm{RMC-SZ}} \delta^{\mathrm{ab}} + \Delta g^{\mathrm{ab}}_{\mathrm{GC-SZ}}(1\mathrm{e}) + \Delta g^{\mathrm{ab}}_{\mathrm{GC-SZ}}(2\mathrm{e}) \\ & + \Delta g^{\mathrm{ab}}_{2\mathrm{o}}(1\mathrm{e}) + \Delta g^{\mathrm{ab}}_{2\mathrm{o}}(2\mathrm{e}), \end{aligned} \tag{8}$$

where $a, b \in \{x, y, z\}$, δ is the Kronecker delta and g_e (the free-elecron g-factor) is the expectation value of the spin-field reduced spin–Zeeman term. All Δg contributions are described explicitly elsewhere [4].

3 Computation

The ground state g-tensors of three radicals have been studied in this work, including NO_2 ($^2A_1$), H_2O^+ ($^2B_1$) and CO^+ ($^2\Sigma^+$). Hartree–Fock wavefunctions were obtained with the HONDO-8 package [15]. Calculation of one-electron integrals was done with the MAGOPS package of Dykstra and Augspurger [16]. The EAGLE program of Chandra, Buenker, Marian and Hess [17–19] was used to generate two-electron spin–orbit integrals. All supplementary computation, including our newly derived and implemented code for $\Delta g_{GC-SZ}(2e)$ [20], was done with GSTEPS, the suite of FORTRAN programs developed during this research.

For NO_2, g-tensors produced with several basis sets were compared, including the STO-4G basis of Stewart [21], the split valence $(8s, 4p) \rightarrow [3s, 2p]$ MIDI-4 basis [22], the Huzinaga–Dunning $(10s, 6p) \rightarrow [5s, 4p]$ set [23], the Huzinaga–Dunning set with additional two-membered polarization functions [24], and the $(10s, 6p, 4d) \rightarrow [5s, 3p, 2d]$ basis by Sadlej [25].

For CO^+ and H_2O^+, we have used the $(12s, 7p) \rightarrow [7s, 4p]((6s) \rightarrow [4s]$ for H) basis sets devised by Thakkar et al. [26], supplemented with $(1s, 2p, 3d)((1s, 2p)$ for H) polarization and diffuse valence functions of Liu and Dykstra [27].

For the basis set study on NO_2, the molecule's experimental geometry ($R_{NO} = 2.25612$ bohr, $\angle_{ONO} = 133.8°$) was used. In addition, a calculation was done with Sadlej's basis using a geometry ($R_{NO} = 2.18856$ bohr, $\angle_{ONO} = 136.8°$) optimized for that basis. For CO^+ and H_2O^+ the geometries used ($R_{CO} = 2.10723$ bohr for CO^+ and $R_{OH} = 1.88099$ bohr, $\angle_{HOH} = 109.4°$ for H_2O^+) were those optimized for Thakkar et al.'s basis.

Some Breit–Pauli operators are gauge dependent. The expectation value of the operator may therefore vary depending on the selection of an origin (gauge) of the coordinate system. The size of this dependence for a gauge shift from $\boldsymbol{C} = (0, 0, 0)$ bohr to $\boldsymbol{C} = (1, 1, 1)$ bohr is calculated according to an expression derived in one of our prior papers [4].

The proper choice of gauge origin is an important consideration for our calculations. Luzanov et al. [28] have given a theoretical rationale to suggest that the ideal location of gauge is given by the molecule's electronic charge centroid (x_e, y_e, z_e), where

$$x_e = (1/N)\langle\Psi|\sum_{i=1}^{N} x_i|\Psi\rangle. \tag{9}$$

This choice had previously been demonstrated, for moderately gauge dependent calculations, to yield a good approximation to gauge invariant results [29–31].

Therefore, in all of our calculations the gauge origin was chosen to reside at the electronic charge centroid (ECC) of the molecule. Coordinate systems were chosen such that NO_2 and H_2O^+ lie in the yz-plane, with the z-axis aligned on the molecule's principal symmetry axis.

At the Hartree–Fock level, the most appropriate method for describing the manifold of excited states Ψ_n in Eq. (7) is by varying the occupancy of the ground state orbitals. For the excitation $\chi_r \rightarrow \chi_s$, the spin–orbit interaction becomes

$$\langle\Psi_0|H_{SO}|\Psi_n\rangle = \langle\Psi_0|H_{SO}|\Psi_r^s\rangle = \langle\chi_r|H_{SO}|\chi_s\rangle \tag{10}$$

and the excitation energy is best described in terms of determinantal energies

$$E_0 - E_n = E_0 - E_r^s = \langle \Psi_0 | H_0 | \Psi_0 \rangle - \langle \Psi_r^s | H_0 | \Psi_r^s \rangle . \tag{11}$$

4 Results and discussion

The treatment described above does not account for intermolecular interactions, as are sometimes important in solid or liquid state ESR determination. As a result, it is expected that our model should be best suited to the description of gas phase g-tensor data. These were obtained from spin rotation data [32–35] using the Curl equation [36]. For comparison, Ne matrix isolation data for NO_2 [37] and CO^+ [33] will also be provided.

In Table 1, our calculated Δg-values for NO_2, CO^+ and H_2O^+ are presented and compared with both spin rotation and matrix isolation data. In general, the calculated values reflect the trends in experimental numbers. In the case of H_2O^+, the computed values are in good agreement with the spin rotation data, except for Δg^{xx} where the signs disagree. For NO_2 and CO^+, the calculated g-shifts are all of the correct sign; however Δg^{xx}- and Δg^{yy}-values are only 49–58% the size of corresponding gas phase values. Overall, the results leave some question of the method's ability to consistently reproduce experiment.

In Table 2, a basis set study is presented for NO_2. In all cases except the last, the experimental geometry of NO_2 is used.

It is seen that the STO-4G basis set leads to results in excellent, but rather fortuitous, agreement with experimental values. They also compare reasonably well with the results of Moores and McWeeny [2], who used a similar approach and identical basis to compute g-shifts for NO_2. Part of the difference between their and our results is due to their omission of $\Delta g_{\mathrm{RMC-SZ}}$. It is difficult to trace the source of any further discrepancy, however, as they did not provide a complete breakdown of contributions.

Table 1. Comparison of calculated vs. experimental g-shifts (all values in ppm)

		Calculated[a]	Gas phase[b]	Neon matrix isolation[c]
NO_2	Δg^{xx}	2257	3900	3300
	Δg^{yy}	– 6597	– 11300	– 10300
	Δg^{zz}	– 474	– 300	700
CO^+	Δg^{xx}	– 1175	– 2400	– 3200
	Δg^{yy}	– 1175	– 2400	– 3200
	Δg^{zz}	– 176	—	– 1400
H_2O^+	Δg^{xx}	– 324	200	—
	Δg^{yy}	16361	18800	—
	Δg^{zz}	4402	4800	—

[a] NO_2 calculations done with [5s 3p 2d] basis of Sadlej [25]. Optimized geometries are used in each case

[b] Derived from spin rotation data. Refs. [32, 35] for NO_2, [33] for CO^+ and [34] for H_2O^+

[c] Ref. [37] for NO_2 and [33] for CO^+

Table 2. Calculated vs. experimental g-shifts for NO_2 (all values in ppm)

	Δg^{xx}	Δg^{yy}	Δg^{zz}
STO-4G [21]	3714	− 11503	− 307
MIDI-4 [22]	4011	− 10166	− 336
H–D [23]	3799	− 10067	− 371
H–D + 2*d* [23, 24]	2733	− 8002	− 477
Sadlej [25]	2762	− 7162	− 471
Sadlej [25] (optimized geometry)	2257	− 6597	− 474
Moores and McWeeny [2][b]	3460	− 10274	− 218
Exp. [32, 35]	3900	− 11300	− 300

[a] All calculations use experimental geometry except as noted

[b] Not including $\Delta g_{\mathrm{RMC-SZ}}$. Different geometry ($R_{\mathrm{NO}} = 2.243$ bohr, $\angle_{\mathrm{ONO}} = 133.9°$)

Compared to STO-4G, larger basis sets give g-shifts with poorer agreement with experiment. Addition of d-functions yields sharply reduced $|\Delta g^{xx}|$ and $|\Delta g^{yy}|$ values (20–30% lower), but substantially larger $|\Delta g^{zz}|$ (by about 50%).

As reported previously [4], one may observe a large geometry dependence in these calculations. For NO_2, the change of geometries from the experimental to the optimized ($\Delta R_{\mathrm{NO}} = 0.07$ bohr, $\Delta\angle_{\mathrm{ONO}} = 2.9°$) produces a change in Δg^{xx} from 2762 to 2257 ppm, and Δg^{yy} from − 7162 to − 6597 ppm.

In Table 3, the contributions to g-tensor elements of NO_2, CO^+ and H_2O^+ are broken down into component terms. It is well known that one-electron spin–orbit mixing dominates the g-tensor of all molecules, except those composed of only very light atoms [38]. This is reproduced in Table 3 by the large one-electron second-order term. The two-electron second-order term is also very important. In each case, its weight is consistently between 30% and 40% of the corresponding one-electron value. This ratio is compatible with previous findings for NO_2 [3] and with spin–orbit coupling data on first-row molecules [39]. Two-electron terms contribute negatively compared to their corresponding one-electron terms. This fits the general interpretation whereby one-electron integrals describe electronic interaction with nuclei, while corresponding two-electron terms give the effect of electron–electron shielding on the former.

First-order corrections are usually smaller than their second-order counterparts. As has been stressed in a previous paper [4], however, the first-order terms are useful in fine tuning the g-shifts. This is especially true for cases where second-order effects are small or zero [38]. An example of this in the present work is Δg^{zz} for NO_2, experimentally found to have a negative shift of around 300 ppm. Even for larger basis sets, second-order contributions are insufficient to account for this shift, hence necessitating the first-order terms. For CO^+, the second-order contribution to Δg^{zz} is zero. In this case, any net Δg^{zz} experimentally observed must be explained by first-order terms.

As has been predicted elsewhere [4, 11] our study of gauge dependence finds the problem to be diminished through use of larger basis sets. In Fig. 1, the change in NO_2 g-tensor elements for a gauge transformation from $\boldsymbol{C} = (0, 0, 0)$ to $\boldsymbol{C} = (1, 1, 1)$ bohr for several basis sets is shown. We find that the gauge dependence decreases in a largely monotonic fashion with basis set improvement.

The small gauge dependences represent a significant improvement over our previous work [4]. Both one- and two-electron effects are now included in the

Table 3. Contributions to the g-tensor elements of NO_2, CO^+ and H_2O^{+a} (all values in ppm)

		NO_2^b	CO^+	H_2O^+
Δg_{RMC-SZ}		− 287	− 192	− 287
Δg_{GC-SZ} (1e)	(xx)	260	198	98
	(yy)	234	198	201
	(zz)	139	92	200
Δg_{GC-SZ} (2e)	(xx)	− 191	− 115	− 135
	(yy)	− 57	− 115	− 153
	(zz)	− 164	− 76	− 156
Δg_{2o} (1e)	(xx)	3389	− 1556	0
	(yy)	− 9627	− 1556	23326
	(zz)	− 278	0	6591
Δg_{2o} (2e)	(xx)	− 914	503	0
	(yy)	3140	503	− 6716
	(zz)	116	0	− 1946
Total	Δg^{xx}	2257	− 1175	− 324
	Δg^{yy}	− 6597	− 1175	16361
	Δg^{zz}	− 474	− 176	4402

[a] All geometries optimized

[b] NO_2 calculations done with [5s3p2d] basis of Sadlej [25]

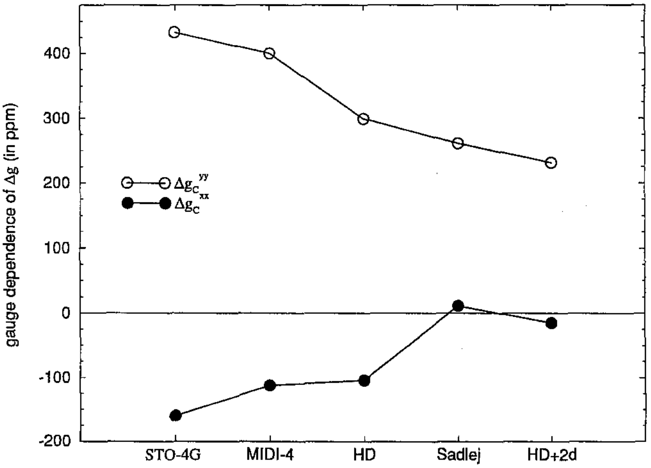

Fig. 1 Gauge dependence of Δg for NO_2 using selected basis sets. All values expressed in ppm, and given for a gauge transformation from $C = (0,0,0)$ to $C = (1,1,1)$ bohr. Experimental geometry used

calculation, and determinantal energies are employed in the second-order gauge expansion. As a result, these gauge dependence values are likely more reliable than previous determinations. While prior findings [4] had assigned disproportionately large gauge dependences to the Huzinaga–Dunning basis, our improved description places the H–D results within the expected trend.

Comparison of the two different polarized basis sets (Sadlej [25] and H–D + 2*d* [23, 24]) proves interesting. The Sadlej basis has four primitive *d*'s (contracted to two functions), compared to only two added to the H–D set. The H–D set, however, has more flexibility among valence *p*'s ([4*p*] versus [3*p*]).

From Fig. 1, we find that the H–D + 2*d* basis provides a slightly lower gauge dependence than Sadlej's, especially for Δg_c^{yy} (231 ppm versus 269 ppm). Therefore, while our previous work valued the importance of polarization functions, we now find valence flexibility to be important as well.

In general, the results of the gauge dependence study are encouraging. In none of the calculations is the gauge dependence larger than 5% of the size of the corresponding *g*-tensor element. Coupled with our choice of the ECC as gauge, our results may be considered to be effectively gauge invariant.

5 Conclusions

The focus of this work has been to produce quality *ab initio* calculations of electronic *g*-tensors. Our RSPT treatment, complete to second-order in all pertinent magnetic interactions, seems to provide the best description, to date, of the electronic Zeeman effect.

For all but very small molecules, the one-electron second-order terms are adequate to give a qualitative estimate of *g*-tensors. In order to better approximate experimental data, however, inclusion of other contributions becomes important. The two-electron second-order, for example, exerts a strongly moderating influence on the corresponding one-electron contribution. As well, first-order terms are important in explaining net shifts in *g*-tensor elements where the second-order contribution is small or zero.

Our results for three molecules suggest that this method reproduces qualitative trends in the available gas phase ESR data. Our most reliable calculations, those with large polarized basis sets, expose discrepancies of up to 50% between experiment and theory. This shortcoming can probably be attributed to the absence of electron correlation in our treatment. Bündgen et al. [40] have found differences of about 10% between correlated and uncorrelated values for the first-order terms. Correlation effects on second-order terms, under current investigation [41], are considerably larger.

Nonetheless, to the best of our knowledge our calculations represent the most complete and reliable treatment of electronic *g*-tensors to date. We have improved our previous results [4] through the incorporation of all necessary two-electron contributions, including the two-electron spin-Zeeman gauge correction terms for which we have recently derived and implemented computer code [9, 20].

Another improvement has been the use of ROHF wavefunctions which, unlike UHF, do not suffer from spin contamination. This has required the use of determinantal energies in the denominator of sum-over-states expansions rather than the non-unique Fock matrix eigenvalues.

The final refinement involves a practical elimination of gauge dependence in the calculations. The effect of a gauge shift from $\boldsymbol{C} = (0, 0, 0)$ to $\boldsymbol{C} = (1, 1, 1)$ bohr can generally be reduced to below 4% of the corresponding *g*-shift. Specifying the computational origin at the molecule's electronic charge centroid should therefore offer a good approximation to fully gauge invariant results.

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