Calculation of molecular $g$-tensors by sampling spin orientations of generalised Hartree-Fock states

Shadan Ghassemi Tabrizi, R. Rodríguez-Guzmán and Carlos A. Jiménez-Hoyos

ABSTRACT

The variational inclusion of spin–orbit coupling in self-consistent field (SCF) calculations affords single-determinant wave functions that completely break spin symmetry. The individual components of the molecular $g$-tensor are commonly obtained from separate SCF solutions that align the magnetic moment along one of the three principal tensor axes. However, this strategy raises the question if energy differences between solutions are relevant, or how convergence is achieved if the principal axis system is not determined by molecular symmetry. The present work resolves these issues by a simple two-step procedure akin to the generator coordinate method (GCM). First, the orientation of the magnetic moment is constrained in generalised Hartree-Fock (GHF) calculations. Then, non-orthogonal configuration interaction between GHF determinants yields a Kramers doublet for the calculation of the complete $g$-tensor. Alternatively, diagonalisation in a basis spanned by spin rotations of a single GHF determinant results in qualitatively correct $g$-tensors by eliminating errors related to spin contamination.

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1. Introduction

The $g$-tensor $g$ is a fundamental quantity in the phenomenological description of electron paramagnetic resonance (EPR) spectra of molecules with unpaired electrons. The spin Hamiltonian $\hat{H}_S$,

$$\hat{H}_S = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S},$$

defines the magnetic-field ($\mathbf{B}$) dependent Zeeman splitting of a Kramers doublet in terms of an $\mathbf{S} = \frac{1}{2} \text{ pseudo-spin } \mathbf{\tilde{S}}$ [1]. In molecules with light atoms (through the $3d$ series) the pseudo-spin is usually perturbatively related to a true electronic spin $S = \frac{1}{2}$ in the absence of spin–orbit coupling (SOC). However, Eq. (1) is not restricted to such cases [1,2].

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To interpret spectra in terms of electronic structure, quantum-chemical calculations of \( g \)-tensors must consider SOC as the main cause of deviations from the isotropic free-electron \( g \)-value, \( g_e \approx 2.0023193 \). A multitude of methods (see, e.g. Refs. [3–5] for additional literature), includes the coupled-perturbed treatment of SOC by Hartree Fock (HF) theory or — more commonly — Kohn–Sham (KS) density functional theory (DFT) [6,7], as well as generally more accurate ab initio methods, such as coupled-cluster theory [8], complete active space self-consistent field (CASSCF) [9,10], and multi-reference configuration interaction [11,12]. In the spin–orbit state-interaction (SOSI) procedure, the full Hamiltonian (including SOC) is diagonalised in a few selected nonrelativistic or scalar relativistic CASSCF solutions. The \( g \)-tensor for the resulting Kramers doublet is calculated from Eq. (4) (see Theory section below) [9,10]. When mixing between multiple nonrelativistic states is strong, SOC should be treated in a one-step procedure to calculate the Kramers doublet [13]; this applies to systems with heavy atoms. Dynamic correlation is often of minor importance for \( g \)-tensors [9] but may be captured by multi-reference perturbation theory [5,9,14]. DMRG-CASSCF can handle larger active spaces than traditional CASSCF, thereby enabling \( g \)-tensor calculations in challenging strongly correlated systems [4,15], e.g. multinuclear transition-metal clusters [4].

Despite such progress, simple and reliable low-scaling approaches, preferably with a mean-field cost and broadly applicable, are still of high interest. Two- or four-component (2c, 4c) HF or DFT approaches meet these requirements. By treating SOC self-consistently, higher-order spin–orbit effects are implicitly accounted for, which are important for \( g \)-tensors in 4d, 5d or actinide complexes [3,16–19]. Commonly, the SCF is converged for different orientations of the magnetic moment to derive each \( g \)-tensor component from the expectation value \( \langle \hat{\mu} \rangle \) in the respective SCF solution [20]. In rhombic molecules, three solutions with \( \langle \hat{\mu} \rangle \) aligned along the principal axes \( x \), \( y \) and \( z \) afford the principal \( g \)-components [20]. This approach is hence called 3SCF [3]. However, for lower molecular symmetry, up to six different SCF solutions are needed to determine all components. In such cases, solutions with \( \langle \hat{\mu} \rangle \) pointing along the Cartesian axes or bisectors could be sought [20], although enforcing convergence onto a desired \( \langle \hat{\mu} \rangle \) orientation will generally require the imposition of constraints (see below).

The fact that each \( g \)-component is determined from a separate SCF solution has raised conceptual questions [21]. In the presence of SOC, the three different solutions are in general not symmetry related and therefore not degenerate. In other words, an energy anisotropy with respect to different orientations of \( \langle \hat{\mu} \rangle \) or \( \langle \hat{S} \rangle \) exists. This anisotropy was quantitatively explored for a few \( \hat{S} = \frac{1}{2} \) systems in Ref. [22] and does not demand a vaguely hypothesised [21] revision of the foundations of EPR spectroscopy. It is however not clear if the anisotropy affects \( g \)-tensor predictions from mean-field calculations. Note that a similar conceptual issue does not arise when the full \( g \)-tensor is calculated from a single Kramers doublet [9,10,23]: the physically relevant quantities [2] \( G = gg^T \) (Eq. (4) below) and \( \det(g) \) are determined unequivocally when based on a qualitatively correct CASSCF or full configuration interaction (FCI) wave function. That is, the tensor \( G \) that defines the field-dependent splitting in the limit \( B \to 0 \), and the prediction of the sense of precession of the magnetic moment defined by the sign of \( \det(g) \), are unambiguous.

This work proposes a conceptually simpler and more broadly applicable mean-field approach that is closely related to 3SCF. It is based on configuration interaction in a manifold of constrained HF solutions with different orientations of \( \langle \hat{\mu} \rangle \). Alternatively, the directions of spin \( \langle \hat{S} \rangle \) or orbital-angular momentum \( \langle \hat{L} \rangle \) could be constrained. We discuss \( \langle \hat{\mu} \rangle \)-constrained optimisation based on a Thouless parametrisation of GHF-type Slater determinants along with an optimisation library that can handle nonlinear constraints. Diagonalisation in this manifold yields a single Kramers doublet that determines all components of a qualitatively correct \( g \)-tensor. Alternatively, a suitable manifold can be spanned by spin rotations of a single GHF solution. Where required, orbital degeneracies can be treated adequately by considering orientational manifolds associated with several configurations that break point-group symmetry.

### 2. Theory and computations

The spin Hamiltonian of Eq. (1) generically describes a tensorial linear field-induced splitting, that is, the lifting of Kramers degeneracy. A connection to electronic-structure theory is established by identifying the electronic Zeeman term, Eq. (2), as the cause of the splitting,

\[
\hat{H}_{\text{Zeeman}} = -B \cdot \hat{\mu},
\]

where \( \hat{\mu} = \mu_B (g_e \hat{S} + \hat{L}) \) is the electronic magnetic moment. The Kramers pair comprises two time-reversal conjugate states, \( | \Phi \rangle \) and \( | \Phi \rangle \equiv \Theta | \Phi \rangle \), where \( \Theta \) is the time-reversal operator. Let \( \mu = (\mu_x, \mu_y, \mu_z) \) denote the \( 2 \times 2 \) matrices of the three Cartesian components in the Kramers-pair basis. Up to a constant factor, the components of \( g \) represent the coefficients in an expansion of \( \mu = (\mu_x, \mu_y, \mu_z) \) in terms of Pauli spin...
matrices [2]. The specific values of these components generally depend on the definition of pseudospin functions, meaning the establishment of a one-to-one correspondence between pseudospin states \(| \uparrow \rangle, | \downarrow \rangle\) and electronic states \(| \Phi \rangle, | \Phi \rangle\) [1,2]. However, the symmetric Abragam-Bleaney tensor \([2,24]\) \( \mathbf{G} = \mathbf{g} \mathbf{g}^T \) is an invariant [2] that defines the splitting \(\Delta E\), Eq. (3),

\[
\Delta E = \mu_B \sqrt{\sum_{m,n} B_mB_n G_{mn}},
\]

resulting from the diagonalisation of \(\hat{H}_{\text{Zee}}\) in the basis \(| \Phi \rangle, | \Phi \rangle\). The elements \(G_{mn}(m,n = x,y,z)\) of \(\mathbf{G}\) were derived by Gerloch and McMeeking [24],

\[
G_{mn} = 2 \sum_{\nu = \Phi, \bar{\Phi}} \sum_{w = \Phi, \bar{\Phi}} \langle \nu | \tilde{\mu}_m | w \rangle \langle w | \tilde{\mu}_n | \nu \rangle.
\]

Diagonalisation of \(\mathbf{G}\) amounts to a rotation to its principal-axis system. The square roots of the eigenvalues yield the principal values of the diagonal tensor \(\mathbf{g} = \text{diag}(g_x, g_y, g_z)\), \(g_n = \sqrt{G_n}\). Strictly speaking, each individual value is only defined up to a sign, \(g_n = \pm \sqrt{G_n}\) (see below). We report shifts \(\Delta g_n = g_n - g_{c}\) in ppm \((10^{-6})\). The outlined approach was advocated by Bolvin [9] who also cited earlier applications of Eq. (4). It is a standard recipe applied in conjunction with SOSI between non-relativistic or scalar relativistic CASSCF solutions [10].

The quantity \(\text{det}(\mathbf{g})\) is another invariant, meaning that it is unchanged by arbitrary unitary transformations among pseudospin functions. Its sign corresponds to the sign of the product \(g_x g_y g_z\) [1,2] and defines the sense of precession of \(| \tilde{\mu} \rangle\), which is relevant for the absorption of circularly polarised radiation [2]. Although the signs of the individual principal components are not meaningful for the prediction of any property, they can be conventionally fixed by a simple procedure: increase the SOC strength stepwise from zero, where pseudospin and true spin are equivalent (thus, \(g = g_z\)); the pseudospin functions are successively updated by a Bloch [25]/des Cloizeaux [26] perturbative connection to the respective functions at the previous step until a realistic SOC strength is reached. This describes the adiabatic-connection strategy of Chibotaru [1]; see also Ref. [27] for simple applications in a different context, including \(S > \frac{1}{2}\) systems. Alternatively, high molecular symmetry anchors the adiabatic connection and fixes the signs of all principal \(g\)-values [1,28]. However, ambiguities in the definition of pseudospin functions are of no concern here. In our test set of light molecules, SOC effects are weak, keeping pseudospin closely related to true spin. Hence, all principal \(g\)-values are positive. Besides, rhombic symmetry determines the principal-axis system.

On the other hand, we consider orbitally degenerate states in two artificial tetrahedral model systems \((\text{CH}_4^+, \text{CuF}_4^{2-})\). We show that a GCM approach (explained below) can describe the first-order SOC-induced level splitting of orbitally degenerate states, where pseudospin is unrelated to true spin, and negative \(g\)-values may ensue. Tetrahedral symmetry enforces isotropy, \(g_x = g_y = g_z\) [28]. The sign of \(g_x g_y g_z\) corresponds to the sign of the quotient \(g_x g_z / g_y\) [23],

\[
\frac{g_x g_z}{g_y} = -i \frac{\langle \mu_x \mu_z - \mu_z \mu_x \rangle_{ab}}{\langle \mu_y \rangle_{ab}},
\]

where \(a,b = 1,2\) is an arbitrary index combination for a non-zero element \(\langle \mu_y \rangle_{ab}\) of the \(2 \times 2\) matrix \(\langle \mu_y \rangle\). Eq. (5) adheres to the usual Condon-Shortley phase convention.

The 3SCF procedure outlined in the Introduction was first applied in the frame of GHF calculations [20] that included one- and two-electron spin–orbit terms. It was later also applied in quasi-relativistic 2c-DFT [19,29,30] or 4c-Dirac-KS calculations [17]. Our present focus is on GHF, which breaks spin symmetry by independently expanding the \(\uparrow\) and \(\downarrow\) spin components of molecular orbitals \(\psi_i\) in terms of spatial basis functions \(\phi_i\),

\[
\psi_i = \left( \sum_j C_{ij}^\downarrow \phi_j \right) \left( \sum_k C_{ik}^\uparrow \phi_k \right),
\]

with generally complex coefficients \(C_{ij}^\downarrow\) and \(C_{ik}^\uparrow\). GHF solutions occur only in specific situations in nonrelativistic systems [31], but are the rule when SOC is included [32].

Besides the one-electron SOC term, the quasi-relativistic Breit-Pauli Hamiltonian contains spin-same-orbit (SSO) and spin-other-orbit (SOO) two-electron terms. The burden on memory and computation times [33] incurred by SSO and SOO integrals is often alleviated by a mean-field approximation [34]. However, for ultimate simplicity, we account for two-electron SOC only implicitly through the effective nuclear charges \(Z_{\text{eff}}(K)\) of Koseki et al. [35] in the one-electron SOC term, which we deem adequate for semi-quantitative accuracy. The accuracy of a \(Z_{\text{eff}}(K)-\text{SOC}\) treatment was assessed in Ref. [7]. For a larger test set, \(g\)-shifts usually deviated by ~10% from results based on a spin–orbit mean-field approximation. Note that five one- and two-electron terms contributing to \(g\)-shifts were explicitly considered in coupled-cluster calculations in Ref. [36]. Although a \(Z_{\text{eff}}(K)-\text{SOC}\) treatment was not pursued in that work, the provided data on the one-electron spin–orbit contributions allow us to estimate that errors do not significantly
exceed 10%.

$$\hat{H}_{\text{SOC}} = \frac{\alpha^2}{2} \sum_{i,K} Z_{\text{eff}}(K) r_{ik}^{-3} (\mathbf{r}_k \times \hat{\mathbf{p}}_i) \cdot \hat{\mathbf{s}}_i.$$  \hspace{1cm} (7)

In Eq. (7), $\alpha$ is the fine-structure constant, and $i$ and $K$ are electron and nuclear indices, respectively. $\hat{H}_{\text{SOC}}$ is added to the nonrelativistic electronic Hamiltonian $\hat{H}_0$, $\hat{H} = \hat{H}_0 + \hat{H}_{\text{SOC}}$.

If the principal axis system is known, 3SCF relies on solutions $|\Phi_n\rangle$ that align the magnetic moment along the principal unit vectors $\mathbf{n} = x, y, z$.

$$\frac{\langle \Phi_n | \hat{\mathbf{p}} | \Phi_n \rangle}{\langle \Phi_n | \hat{\mathbf{p}} | \Phi_n \rangle} = \mathbf{n}.$$  \hspace{1cm} (8)

In rhombic systems, $|\Phi_n\rangle$ will usually have self-consistent symmetry that enforces perfect alignment between magnetic moment and spin, that is, $\langle \Phi_n | \hat{S} | \Phi_n \rangle \propto \mathbf{n}$ (see Results section). An ‘effective’ $g$-value for a given direction is equated to the component of $\hat{\mathbf{p}}$ along $\mathbf{n}$,

$$\sqrt{n^T \cdot \mathbf{G} \cdot \mathbf{n}} = |\langle \Phi_n | \mathbf{n} \cdot \hat{\mathbf{p}} | \Phi_n \rangle|.$$ \hspace{1cm} (9)

Eq. (9) may also be used when $\mathbf{n}$ is not a principal tensor axis [20]. This applies to molecules of low symmetry, where the principal-axis system is not known \textit{a priori}. If $\mathbf{n}$ is indeed a principal axis, $g_n$ (assumed positive; $\mathbf{n} = x, y, z$) is obtained from Eq. (10),

$$g_n = |\langle \Phi_n | \mathbf{n} \cdot \hat{\mathbf{p}} | \Phi_n \rangle|.$$ \hspace{1cm} (10)

The 3SCF approach is schematically illustrated in Figure 3.

As an alternative to 3SCF, Cherry et al. [3] applied Eq. (4) based on one selected SCF solution, e.g. $|\Phi_x\rangle$, $|\Phi_z\rangle$. They explained that $g$-tensor components corresponding to perpendicular directions are strongly affected by spin contamination: for the UHF solution ($\hat{H}_{\text{SOC}} = 0$), $g_x = g_z$, but $g_x \neq g_y$. A quasi-restricted ansatz [37] avoids this complication but becomes equivalent to ROHF for $\hat{H}_{\text{SOC}} = 0$, thus missing important spin-polarisation effects [3,19]. A simple \textit{a posteriori} correction scheme was proposed for spin-contamination errors in $g$-tensors from completely unrestricted mean-field states [3] here corresponding to GHF but becomes ill-defined unless SOC is relatively weak. Besides, the resulting $g$-tensor depends on the choice of the specific GHF solution, albeit moderately [3]. Lastly, this scheme does not attempt to generate a qualitatively correct Kramers pair.

In the present work, we use a generator coordinate method (GCM) ansatz, Eq. (11), for the ground state,

$$|\Psi\rangle = \int d\Omega |\Phi_\Omega\rangle f(\Omega).$$ \hspace{1cm} (11)

We create a superposition of constrained HF solutions $|\Phi_\Omega\rangle$ with different spherical orientations $\Omega = (\theta, \phi)$ of $|\hat{\mathbf{p}}\rangle$ (or, $|\hat{\mathbf{S}}\rangle$ or $|\hat{\mathbf{L}}\rangle$). The linear coefficients $f(\Omega)$ are obtained using the variational principle by solution to the Griffin-Hill-Wheeler (GHW) equation,

$$\int d\Omega [\hat{H}(\Omega, \Omega') - ES(\Omega, \Omega')] f(\Omega') = 0,$$ \hspace{1cm} (12)

with $\hat{H}(\Omega, \Omega') = \langle \Phi_\Omega | \hat{H} | \Phi_{\Omega'} \rangle$ and $S(\Omega, \Omega') = \langle \Phi_\Omega | \hat{S} | \Phi_{\Omega'} \rangle$.

In practical calculations, Eq. (12) is discretised by a numerical sampling of the three-dimensional set of $|\hat{\mathbf{p}}\rangle$ orientations. The GHW equation then becomes equivalent to a non-orthogonal configuration interaction (NOCI) problem, which can be solved as a standard generalised eigenvalue problem for the Kramers doublet of interest. We emphasise, however, that the GCM ansatz of Eq. (11) implies the existence of a smooth, square-integrable function $f(\Omega)$. Note that, in the absence of SOC, the GCM ansatz of Eq. (11) by sampling all possible spin orientations of a UHF state becomes equivalent to a spin-projection ansatz (applied in a projection-after-variation framework, PAV, as opposed to variation-after-projection used in Projected Hartree–Fock theory [38]). The spin-projected HF state has, by construction, no spin contamination and correctly yields a vanishing $g$-shift. This prompted us to also study an alternative to converging GHF for different $|\hat{\mathbf{p}}\rangle$ orientations: spanning a basis from spin rotations of a single GHF solution eliminates spin-contamination errors (see Results section).

It is straightforward to set up the NOCI problem, Eq. (13), in terms of Hamiltonian and overlap matrices, $\mathbf{H}$ and $\mathbf{S}$,

$$\mathbf{HC} = \mathbf{SCE},$$ \hspace{1cm} (13)

where $\mathbf{E}$ is a diagonal energy matrix. The evaluation of matrix elements $\hat{H}(\Omega, \Omega')$ between non-orthogonal Slater determinants [39–41] is explained in detail in Ref. [42]. Matrix elements of time-even operators, e.g. $\hat{H} = \hat{G}^{-1} \hat{H} \hat{G}$, are zero between time-reversal conjugates, if $\hat{G}^2 = -1$ [2]. Thus, Kramers partners are orthogonal, $\langle \Phi | \hat{S} | \Phi \rangle = 0$, and do not couple, $\langle \Phi | \hat{H} | \Phi \rangle = 0$. For some of the larger spaces that we consider, the NOCI basis displays near linear dependencies, which we remove [43] based on a threshold of $10^{-8}$ for the eigenvalues of $\mathbf{S}$. Two columns $\{\mathbf{v}, \hat{\mathbf{v}}\}$ of the solution matrix $\mathbf{C}$ represent
the Kramers doublet \{|\Phi\rangle, |\bar{\Phi}\rangle\} of interest (the doubly-degenerate ground state, unless noted otherwise) and are used to calculate \textbf{G} from Eq. (4), based on NOCI-basis representations \(\mu_n (n = x, y, z)\) of the magnetic moment. Due to orthogonality, \(|\Phi\rangle |\bar{\Phi}\rangle = 0\), matrix elements \(|\langle \Phi| \hat{w} |\bar{\Phi}\rangle\) require special attention; here we are interested in the one-electron operator \(\hat{w} = n \cdot \hat{\mu}\). Eq. (14) was adopted from Ref. [3],

\[
|\langle \Phi| \hat{w} |\bar{\Phi}\rangle\rangle = \frac{1}{N} \sum_{k=1}^{N} \det(w_k). \tag{14}
\]

\(N\) is the number of electrons and \(w_k\) is an \(N \times N\) matrix with elements

\[
(w_k)_{ij} = \begin{cases} w_{ij}, & \text{if } k = i \\ s_{ij}, & \text{else,} \end{cases}
\tag{15}
\]

and \(w_{ij} = \langle \psi_i| \hat{w} |\bar{\psi}_j\rangle\) is a matrix element between occupied molecular orbitals in \(|\Phi\rangle\) and \(|\bar{\Phi}\rangle\); \(s_{ij} = \langle \psi_i| \bar{\psi}_j\rangle\) is the respective overlap.

One- and two-electron integrals are read from the Gaussian programme [44]. GHF and GCM calculations are run with our set of Matlab programmes. Gradient-based constrained optimisation to obtain SCF solutions is detailed in Appendix A. In our small test systems, the centres of nuclear charge, electronic charge or spin are detailed in Appendix A. In our small test systems, based constrained optimisation to obtain SCF solutions very modest gaugedependence [9].

We start with an exemplary discussion of various aspects of the GCM strategy for the \(H_2O^+\) radical. This molecule (and all others in the test set) lies in the \(xz\)-plane, with \(z\) being a rotational axis, see Figure 1.

Three UHF solutions \(|\Xi_n\rangle\) with spin projection \(M = \frac{1}{2}\) along \(n = x, y, z\) are degenerate, due to intact spin symmetry when \(\hat{H}_{SOC} = 0\). Taking these determinants as initial guess yields GHF solutions \(|\Phi_x\rangle\), \(|\Phi_y\rangle\), and \(|\Phi_z\rangle\), respectively, when considering the full Hamiltonian \(\hat{H} = \hat{H}_0 + \hat{H}_{SOC}\) that breaks spin symmetry. Even the conventional unconstrained SCF algorithm based on building and diagonalising a Fock matrix straightforwardly achieves convergence onto these three inequivalent GHF solutions.

Each of the three Kramers pairs \(|\Phi_n\rangle, |\bar{\Phi}_n\rangle\) separately spans the two-dimensional irreducible representation (irrep) \(E_1/2\) of the \(C_{2v}\) double group of the Hamiltonian. \(E_1/2\) is the only fermionic irrep of \(C_{2v}^+\) [47]. The \(C_{2v}\) group consists of combinations of the operations of the ordinary \(C_{2v}\) group of \(H_0\) with corresponding spin rotations. Each of the separate three GHF solutions partially breaks \(C_{2v}\). Their self-consistent symmetry [48–50] is isomorphic to the magnetic group \(C_{2h}^+\) \((C_2^+)\).

This notation [51] implies that a unitary \(C_{2h}^+\) subgroup of \(C_{2v}\) commutes with the Fock operator (or, equivalently, the single-particle density matrix), while the remaining unitary operations of \(C_{2h}^+\) must be combined with \(\Theta\) to represent self-consistent symmetries. The nontrivial self-consistent symmetry operations listed in Table 1 are different between \(|\Phi_x\rangle\), \(|\Phi_y\rangle\), and \(|\Phi_z\rangle\) (see Appendix B for further comments). The described symmetry properties hold true for all molecules in our test set (but see the footnote to Table 2 for a minor caveat on \(NO_2\)). Consequently, \(\langle \hat{S}_z = \mu \rangle\) and \(|\bar{\mu}\rangle\) are collinear, that is, parallel or antiparallel, \(|\Phi_n\rangle |\hat{S}| |\Phi_n\rangle \propto n, (|\Phi_n\rangle |\hat{L}| |\Phi_n\rangle \propto n, and (|\Phi_n\rangle |\hat{\mu}| |\Phi_n\rangle \propto n| dealing with the corresponding strong-correlation problem at a mean-field cost. This yields qualitatively correct Kramers doublets and \(g\)-tensors.

3. Results and discussion

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Figure 1. GHF energy surface, including SOC contributions, for H$_2$O$^+$. The distance from the origin (the centre of nuclear charge) for an orientation $n$ of the magnetic moment is proportional to the energy difference with respect to the global minimum $E_x = \langle \Phi_x | \hat{H} | \Phi_x \rangle$. See main text for further details; for energies, see Table 1 or Table 2. The energy curves for orientations $n$ in one of the coordinate planes ($xy$, red; $xz$, green; $yz$, blue) lie almost perfectly on the plotted surface.

For a general orientation $n$, these three vectors are not collinear, because the respective constrained GHF solution has no self-consistent symmetry. Due to the comparatively small orbital momentum $\langle \Phi_n | \hat{L} | \Phi_n \rangle$, spin and magnetic moment are still closely (though not perfectly) aligned.

It is simple to check that all three solutions $|\Phi_n\rangle$ are of GHF type and have non-collinear spin densities [52,53] (but note that even genuine GHF solutions can have collinear spin densities in specific cases [32]). The GHF character $\gamma_n$ that we define in Eq. (16) is rather small. For H$_2$O$^+$ we find $\gamma_x = 2.2 \times 10^{-5}$, $\gamma_y = 1.6 \times 10^{-5}$ and $\gamma_z = 2.2 \times 10^{-5}$. $|\Phi_n\rangle$ and $|\Xi_n\rangle$ belong to different components of $E_{1/2}$ and therefore have zero overlap.

$$E(n) = \langle \Phi_n | \hat{H} | \Phi_n \rangle \approx n^T \cdot M \cdot n,$$

(17)

with $M = \text{diag}(E_x, E_y, E_z)$. When parametrising $n$ in terms of polar angles $(\vartheta, \phi)$,

$$n = (\cos \phi \sin \vartheta, \sin \phi \sin \vartheta, \cos \vartheta)^T,$$

(18)

the MAE function takes the explicit form of Eq. (19),

$$E(\vartheta, \phi) \approx (E_x \cos^2 \phi + E_y \sin^2 \phi) \sin^2 \vartheta + E_z \cos^2 \vartheta.$$

(19)

The surface defined by the distance of $E(\vartheta, \phi) - \text{min}(E_x, E_y, E_z)$ from the coordinate origin is plotted in Figure 1 for H$_2$O$^+$. The MAE surface defines a non-degenerate GHF manifold, that is, a set of states that are nearly degenerate and unrelated by symmetry, except for opposite orientations $n$ and $(-n)$, which define Kramers pairs, $\{|\Phi_n\rangle, |\Phi_{-n}\rangle\}$. Curves connecting 100 data points
(not shown individually) for rotating \( \mathbf{n} \) in the three coordinate planes lie almost perfectly on the surface. We checked that this also holds for arbitrary \( \mathbf{n} \) (data not shown). Note that a state with arbitrary \( \mathbf{n} \neq \mathbf{x}, \mathbf{y}, \mathbf{z} \) is not in general a stationary point of the unconstrained HF energy functional and cannot therefore be converged unless constraints are imposed. The suggestion by Jayatilaka [20] to fix \( \mathbf{n} \) by including the Zeeman term of Eq. (2) self-consistently and gradually reducing its magnitude towards convergence, is not as well-defined as our present constrained optimisation, which is essentially a black-box procedure.

If \( \mathbf{n} \) defined the orientation of \( \hat{\mathbf{S}} \) rather than \( \hat{\mathbf{\mu}} \), a surface plot visually indistinguishable from Figure 1 would be obtained, due to the small relative magnitude of \( \hat{\mathbf{L}} \). Yet, \( \hat{\mathbf{L}} \) is quantitatively important for \( g \)-shifts. For several of the systems in our test set, separate spin- and orbital-momentum contributions were analysed in Ref. [9].

Energy profiles for additional systems (CN, CO\(_2\)\(^-\) and MgF) are displayed in Figure 2. Fully unconstrained GHF stability analyses [57] on \( |\Phi_1\rangle \), \( |\Phi_2\rangle \) and \( |\Phi_3\rangle \) confirm that only the lowest-energy solution is a minimum, while the remaining two are saddle points. For H\(_2\)O\(^+\), \( |\Phi_4\rangle \) is the minimum; \( |\Phi_2\rangle \) and \( |\Phi_3\rangle \) are first- and second-order saddle points, respectively, with a corresponding number of negative orbital-Hessian eigenvalues (with small magnitudes of \( \sim 10^{-8}\)a.u.). In addition, there are two small positive eigenvalues for \( |\Phi_4\rangle \) and one for \( |\Phi_3\rangle \).

For \( H_{SOC} \rightarrow 0 \), Hessian eigenvectors belonging to small-magnitude eigenvalues become zero-modes (Goldstone modes) that signal broken continuous symmetry. For example, \( |\Xi_2\rangle \) breaks spin-rotational symmetry about axes \( x \) or \( y \). On the other hand, as noted, a constrained solution \( |\Phi_n\rangle \) for arbitrary \( \mathbf{n} \) is not a stationary point

### Table 1.

| Symmetries | \( E \) | \( \Delta \alpha_x \) | \( \Delta \beta_y \) | \( \Delta \gamma_z \) |
|------------|--------|----------------|----------------|----------------|
| \( \exp(-i\hat{\mathbf{L}} \cdot \hat{\mathbf{\delta}}_{xz}) \) | \(-75.658 \times 10^3\) | 15 | 11,278 | 0 |
| \( \exp(-i\hat{\mathbf{L}} \cdot \hat{\mathbf{\delta}}_{xz}) \) | \(-75.658 \times 10^3\) | 15 | 11,278 | 0 |

### Table 2.

| MOLECULAR PHYSICS |
|-------------------|
| **Table 2.** UHF and GCM(6, UHF) energies (in Hartree, h); SOC not included. For GHF solutions \( |\Phi_1\rangle \), \( |\Phi_2\rangle \) and \( |\Phi_3\rangle \), with SOC included, energy differences are given with respect to UHF. For GCM(6) and GCM(48), energy differences are given with respect to GCM(6, UHF). All differences in \( 10^{-6} \) h. |
| **CO** | \( |\Phi_1\rangle \) | \( |\Phi_2\rangle \) | GCM(6, UHF) | GCM(6) | GCM(48) \( a \) |
| \( -112,303,992,73 \) | \(-2.77\) | \(-2.69\) | \(-2.73\) | \(-3.04\) | \( D = 20 \) |
| \( -92,234,197,34 \) | \(-0.83\) | \(-0.79\) | \(-0.85\) | \(-2.07\) | \( D = 20 \) |
| \( -299,142,482,33 \) | \(-15.53\) | \(-15.54\) | \(-15.55\) | \(-15.55\) | \( D = 12 \) |
| \( -204,108,535,36 \) | \(-7.47\) | \(-7.54\) | \(-8.09\) | \(-8.12\) | \( D = 20 \) |
| \( -253,260,924,96 \) | \(-15.30\) | \(-15.22\) | \(-15.33\) | \(-15.33\) | \( D = 16 \) |
| \( -187,651,597,05 \) | \(-5.26\) | \(-5.27\) | \(-5.27\) | \(-5.27\) | \( D = 14 \) |
| \( -224,438,474,81 \) | \(-12.19\) | \(-11.50\) | \(-11.45\) | \(-12.38\) | \( D = 20 \) |
| \( -75,658,027,77 \) | \(-3.58\) | \(-3.52\) | \(-3.48\) | \(-3.48\) | \( D = 12 \) |
| \( -113,566,339,13 \) | \(-3.46\) | \(-3.40\) | \(-3.34\) | \(-3.40\) | \( D = 20 \) |

\( a \) D denotes the reduced basis dimension after removal of near linear degeneracies in GCM(48). \( b \) There is a slightly lower UHF solution in NO\(_2\) \( E = -204.10855905 \) h that breaks \( C_{2v} \) symmetry. If the latter UHF solution is used as an initial guess for GHF (including SOC), then each of the three GCM Kramers pairs breaks \( C_{2v} \) symmetry, which would require including symmetry partners in the GCM basis to obtain a rhombic \( g \)-tensor. Our analysis is for simplicity based on symmetry-conserving UHF and GHF solutions.
of the unconstrained energy functional. In the limit $\hat{H}_{\text{SOC}} \to 0$, the size of the MAE surface shrinks to zero and the GHF manifold becomes a spin-rotation manifold of the UHF solution that spans states $|S, M = \pm \frac{1}{2}, \frac{3}{2}, \ldots, S_{\text{max}}\rangle$. Diagonalisation of $\hat{H}_0$ in this space yields a pure $S = \frac{1}{2}$ level and thus amounts to PAV spin projection.

Table 1 also includes $g$-tensors calculated from Eq. (4) for each of the three separate pairs $\{|\Phi_n\rangle, |\Phi_n\rangle\}$. As each Kramers pair preserves $C_2$ symmetry, the three different respective $g$-tensors are diagonal in the axis system of Figure 1. Appendix B explains why the principal component $g_\|$ that belongs to the direction $\mathbf{n}$ of $\hat{\mu}$ coincides with the 3SCF result of $g_\| = |\langle \Phi_n| \mathbf{n} \cdot \hat{\mu} |\Phi_n\rangle|$. On the other hand, the two orthogonal components are unreasonable when compared to 3SCF (or GCM, FCI, or experiment, see below). This problem was traced to spin contamination [3], which can be quantified in terms of the difference between $\langle \hat{S}^2 \rangle$ and its ideal value of $S(S+1)$ in the absence of SOC. Even when $\hat{H}_{\text{SOC}} = 0$, spin contamination yields an anisotropic $g$-tensor with non-zero $g$-shifts. As an example, we obtain $\Delta g_\| = 0$ and $\Delta g_\perp = -15433$ ppm for $\text{H}_2\text{O}^+$ from Eq. (4) based on the UHF solution $|\Xi_2\rangle$. This error is of the same magnitude as experimental $g$-shifts. Cherry et al. [3] proposed to subtract the quantity $\frac{\Delta g_\|}{2} \left[ (S^2) - S(S+1) \right]$, which must be multiplied by an appropriate phase factor, from cross-elements $\langle \Phi_n| \mathbf{n}' \cdot \hat{\mu} |\Phi_n\rangle$ in Eq. (4), where $\mathbf{n}' \cdot \mathbf{n} = 0$. By construction, this correction yields exactly $g = g_\|$ for $\hat{H}_{\text{SOC}} \to 0$, provided that $|\Phi_n\rangle$ becomes a real UHF determinant $|\Xi_n\rangle$ (with no orbital momentum) in this limit. Such an a posteriori correction would not be adequate for strong SOC, when spin is not an approximate symmetry anymore.

The fact that $g = g_\| = g_\perp$ is also obtained by eliminating contaminating spin states from $|\Xi_n\rangle$ suggests a more elegant and general strategy. A simple approximate spin-projection scheme consists in diagonalisation of $\hat{H}_0$ in the basis of six determinants oriented along the vertices of an octahedron, $\mathbf{n} = \pm \mathbf{x}, \pm \mathbf{y}, \pm \mathbf{z}$. For the molecules in the present set, this GCM(6,UHF) approach yields $\Delta g \ll 1$ ppm; in some cases, $\Delta g$ is as small as $10^{-6}$ ppm. In other words, GCM(6,UHF) affords essentially pure $S = \frac{1}{2}$ doublets. This observation prompted us to proceed similarly with three GHF Kramers doublets $\{|\Phi_n\rangle, |\Phi_n\rangle\}$ and their Kramers partners, where SOC is included self-consistently. However, it is not entirely correct to motivate this GCM(6) approach in terms of an approximate restoration of spin symmetry to remove spin-contamination errors in the $g$-tensor. This aspect is elucidated in a later section on diagonalisation in a manifold of spin rotations (Figure 3).

Table 3 compares $g$-shifts from our 3SCF and GCM(6) calculations and from a denser sampling (GCM(48), explained below) with 3SCF data from Ref. [20] and experimental values. Various factors contribute to the generally modest differences between the two 3SCF sets, e.g. small differences in molecular structures, or the treatment of relativistic effects. While we employ an effective one-electron SOC operator (Eq. (7)), additional relativistic terms were explicitly considered in Ref. [20]. A trend favouring GCM(6) over 3SCF in terms of agreement with experimental data cannot be discerned, because predictions from both methods are quite similar.

To probe if GCM(6) sufficiently samples the manifold of orientations of $\hat{\mu}$, we generated a larger basis by constraining $\langle \hat{\mu} |$ to point towards the vertices of an icosahedron. The icosahedral grid was arbitrarily rotated with respect to the molecule to avoid equivalences between grid points due to molecular symmetry. However, only six instead of twelve constrained GHF calculations are needed, because two GHF solutions with $\hat{\mu}$ pointing to diametrically opposite vertices of the icosahedron comprise a Kramers pair. This basis of dimension 12 does not span a representation of the molecular double group. Therefore, a Kramers doublet resulting from diagonalization in this space does not span an irreps.
calculate the Abragam-Bleaney tensor $G$ from Eq. (4). The principal Kramers partners (time-reversal conjugate states) span a six-dimensional NOCI problem. The resulting Kramers doublet is used to calculate the Abragam-Bleaney tensor $G$ from Eq. (4). The principal $g$-values are obtained from the principal values of $G$, that is, $g_n = \pm \sqrt{\gamma_n}$. Usually, $g$-values are positive, $g_n = \sqrt{\gamma_n}$. However, in contrast to 3SCF, the GCM approach allows to determine $\mathrm{sign}(g_x g_y g_z)$, see Eq. (5).

Table 3. Experimental $g$-shifts (in ppm; molecules lie in the $yz$-plane and $z$ is a rotational symmetry axis) are compared to 3SCF results from Ref. [20] and to our present 3SCF, GCM(6) and GCM(48) results.

|   | $\Delta g$ | Exp. | 3SCF [20] | 3SCF | GCM(6) | GCM(48) |
|---|------------|------|-----------|------|--------|--------|
| CO$_2^+$ | $\perp$ | $-2400/-3000$ | $-2798$ | $-2992$ | $-2260$ | $-2260$ |
|   | $\parallel$ | $-1200/-1400$ | $-42$ | $0$ | $-2$ | $-1$ |
| CN | $\perp$ | $-2000$ | $-1983$ | $-2003$ | $-1738$ | $-1736$ |
|   | $\parallel$ | $-700$ | $-63$ | $-1$ | $-6$ | $-1$ |
| MgF | $\perp$ | $-1300$ | $-1314$ | $-1839$ | $-1814$ | $-1815$ |
|   | $\parallel$ | $-300$ | $20$ | $2$ | $2$ | $2$ |
| NO$_2$ | $x$ | $3900$ | $3368$ | $4762$ | $5229$ | $5240$ |
|   | $y$ | $11,300$ | $11,008$ | $12,642$ | $12,838$ | $12,839$ |
|   | $z$ | $-300$ | $-623$ | $-1070$ | $-281$ | $-280$ |
| NF$_2$ | $x$ | $-100$ | $-447$ | $-747$ | $-258$ | $-258$ |
|   | $y$ | $6200$ | $5649$ | $6112$ | $6556$ | $6558$ |
| CO$_2^-$ | $x$ | $700/800$ | $805$ | $1190$ | $1396$ | $1397$ |
|   | $y$ | $-4800/-5700$ | $-4767$ | $-5976$ | $-5987$ | $-5988$ |
|   | $z$ | $-500/-710$ | $-571$ | $-741$ | $-450$ | $-450$ |
| O$_3^-$ | $x$ | $200/1300$ | $-597$ | $-743$ | $-307$ | $-307$ |
|   | $y$ | $14,700/-16,200$ | $17,933$ | $21,108$ | $23,530$ | $23,529$ |
|   | $z$ | $10,000/9700$ | $10,945$ | $13,650$ | $15,755$ | $15,755$ |
| H$_2$O$_2^+$ | $x$ | $200$ | $-229$ | $-15$ | $-41$ | $-41$ |
|   | $y$ | $18,800$ | $12,704$ | $13,751$ | $15,706$ | $15,718$ |
|   | $z$ | $4800$ | $3306$ | $3830$ | $4078$ | $4078$ |
| H$_2$CO$_2^+$ | $x$ | $4600$ | $5472$ | $5871$ | $6020$ | $6016$ |
|   | $y$ | $-800$ | $927$ | $799$ | $233$ | $234$ |
|   | $z$ | $200$ | $2976$ | $2977$ | $4629$ | $4628$ |

Figure 3. Schematic representation of 3SCF and GCM(6) approaches for $g$-tensor calculations. In 3SCF, GHF solutions $|\Phi_x\rangle$, $|\Phi_y\rangle$, $|\Phi_z\rangle$ with the magnetic moment pointing along $x$, $y$ or $z$ (the principle axes in rhombic molecules), are converged. Each principal $g$-value is given by the expectation value of the respective component of the magnetic moment, Eq. (10). In GCM(6), $|\Phi_x\rangle$, $|\Phi_y\rangle$ and $|\Phi_z\rangle$ and their Kramers partners (time-reversal conjugate states) span a six-dimensional NOCI problem. The resulting Kramers doublet is used to calculate the Abragam-Bleaney tensor $G$ from Eq. (4). The principal $g$-values are obtained from the principal values of $G$, that is, $g_n = \pm \sqrt{\gamma_n}$. Usually, $g$-values are positive, $g_n = \sqrt{\gamma_n}$. However, in contrast to 3SCF, the GCM approach allows to determine $\mathrm{sign}(g_x g_y g_z)$, see Eq. (5).

of $C_{2v}^\ast$ or $C_{\infty v}$. Consequently, the $g$-tensor will deviate (slightly) from its correct symmetry. For $C_{2v}$ molecules we therefore additionally include ‘symmetry partners’, which are determinants obtained from the application of one of the operations $\exp(-i\pi \hat{S}_z) \times \hat{C}_2$, $\exp(-i\pi \hat{S}_z) \times \hat{\sigma}_{yz}$, $\exp(-i\pi \hat{S}_y) \times \hat{\sigma}_{xz}$ of $C_{2v}^\ast$. The remaining operations of $C_{2v}^\ast$ (not listed here) are associated with additional $2\pi$ spin rotations about an arbitrary axis, which just introduces a factor of $(-1)$. Diagonalization in the basis of 48 determinants, GCM(48), thus restores $C_{2v}^\ast$ symmetry. Note that PAV restoration of point-group symmetry in the frame of NOCI was extensively discussed in a different context in Ref. [58]. In linear molecules, we restore $\hat{J}_z = \hat{S}_z + \hat{L}_z$ symmetry only approximately. To this end, $\hat{U} = \exp(-i\phi \hat{J}_z)$ rotates the twelve original determinants by $\phi = 2\pi k/4$, $k = 0, 1, 2, 3$, about the molecular axis. Although this only explicitly restores $C_{4v}$ symmetry, it still guarantees a perfectly axial $g$-tensor, $g =$
diag}(g_L,g_L,g_L). A threshold of $10^{-8}$ for the eigenvalues of the overlap matrix is applied to remove near linear dependencies in the GCM(48) basis. The basis dimensions $D$ after removal of near linear dependencies are collected in Table 2. For H$_2$O$^+$, all $g$-tensor components from GCM(48) differ by only a few ppm from GCM(6). Even with denser spherical grids (e.g. a Lebedev-Laikov grid [59] with 146 points) and a smaller threshold of $10^{-10}$ to define linear dependencies, there are still only $D = 12$ states and the $g$-tensor remains unchanged to within ppm accuracy. In summary, GCM(6) sufficiently samples the nearly degenerate manifold of orientations of spin or magnetic-moment. This is even true when encountering significant UHF spin contamination. For example, the CN radical has $\langle \hat{S}^2 \rangle = 0.9949$ in UHF, versus $\langle \hat{S}^2 \rangle = 0.7577$ for H$_2$O$^+$, where the ideal value is $S(S + 1) = \frac{3}{4}$. For CN, the GCM(48) energy is lower by $\gg 10^{-10}$ compared to GCM(6), while the energy difference is $< 10^{-3}$ for H$_2$O$^+$. However, the GCM(6) $g$-shifts are similarly well converged in both cases.

As to the relevance of energy differences between $|\Phi_x\rangle$, $|\Phi_y\rangle$, and $|\Phi_z\rangle$, we checked that they have a negligible effect on $g$-tensors by setting the diagonal elements of the GCM(6) matrix to zero. This causes changes of $\ll 1$ ppm in all components. One may even exclude $\hat{H}_{SOC}$ from the NOCI problem without affecting $g$-tensors to a relevant degree, as long as SOC is self-consistently included in GHF. We however cannot exclude that a consideration of MAE and the related inclusion of $\hat{H}_{SOC}$ in the NOCI step will make a sizable difference in systems with strong SOC. As an artificial example, we scaled up SOC by a factor of 100 in H$_2$O$^+$. When SOC is included in the NOCI step, this yields $g_x = 1.5976$, $g_y = 3.1973$ and $g_z = 1.7899$, versus $g_x = 1.5978$, $g_y = 3.1972$ and $g_z = 1.7901$ when SOC is not included in the NOCI step. In this example, the differences in $g$-shifts are on the order of 1000 ppm, but relative differences are still small. We like to emphasise that MAE, though not important for the present test set, does not pose a conceptual problem in the GCM approach, and it is generally recommended to include SOC in the NOCI diagonalisation.

### 3.1. Diagonalisation in a manifold of spin rotations

The fact that spin contamination strongly affects $g$-tensors calculated from a single GHF Kramers doublet $|\Phi_n\rangle$, $|\Phi_n\rangle$ [3] suggests to proceed like in a projective elimination of contaminating spin states. With a projector parametrised by three Euler angles [38,60], spin projection corresponds to an SU(2) integration. However, as SOC breaks spin symmetry, direct projection to obtain a pure $S = \frac{1}{2}$ state from $|\Phi_n\rangle$ is not adequate. It is still possible to apply the spin rotations that make up the grid-discretised projector (where each rotation operation is weighted by an element of the Wigner rotation matrix, which is not needed here) to span a spin-rotation basis from $|\Phi_n\rangle$. (Incidentally, this approach is similar in spirit to applying separate localised spin rotations to molecular fragments to span a GCM basis that correctly describes dissociation, where local spin is not a good quantum number, except at an infinite separation of fragments [61]). In the limit $\hat{H}_{SOC} \to 0$, diagonalisation in this basis will yield a pure $S = \frac{1}{2}$ state that could be obtained directly by applying the respective spin projector to the HF wave function; higher-lying NOCI solutions represent contaminating spin states.

The following efficient SU(2) integration grids appear useful: a Lebedev-Laikov [59]/trapezoid grid combination [62], grids based on the proper symmetry operations of symmetric polyhedra [63], or Coxeter grids [64]. Figure 4 illustrates the second option [62]. A selected GHF solution in H$_2$O$^+$ is arbitrarily spin-rotated, so that the resulting GHF-type determinant does not have any self-consistent symmetry. This excludes orthogonality with respect to any of the other determinants in the basis, except the respective Kramers partner, which facilitates the calculation of matrix elements. Next, spin rotations corresponding to the 60 proper symmetry operations of an arbitrarily oriented icosahedron are applied to this reference determinant. Lastly, Kramers partners are included to restore time-reversal symmetry. The resulting basis of dimension $D = 120$ contains many near linear dependencies (that we remove) and does not rigorously span a $C_{2v}^*$ representation. We however deliberately choose to not include point-group partners to assess the diagonalisation of $\hat{H}_0 + \hat{H}_{SOC}$ in a manifold of spin rotations independent of molecular symmetry.

The $g$-shifts resulting from GCM(x,120), GCM(y,120) and GCM(z,120), which work on a basis of GHF solutions $|\Phi_x\rangle$, $|\Phi_y\rangle$ and $|\Phi_z\rangle$, respectively, are given in Table 4. The deviations of $g$-tensors from perfect rhombicity are in all cases extremely small (not detailed) and the dependence on the choice of the GHF reference is modest. The results are quite similar to GCM(6) and show that a Kramers doublet that yields a reasonable $g$-tensor can be obtained based on just a single GHF solution. Somewhat unfortunately, GCM(x,120) and GCM(y,120) noticeably break axial symmetry in linear molecules (see, e.g. CO$^+$). This problem is absent in GCM(z,120). All results are well converged with respect to the grid size (larger Lebedev-Laikov/trapezoid grids cause changes $< 1$ ppm), grid orientation, as well as the arbitrary spin rotation of the GHF solution (cf. Figure 4(b)). In most cases, even a smaller grid, e.g.
Figure 4. Spanning a spin-rotation NOCI basis. A GHF solution with spin in some direction (the red arrow in (a) represents $\langle \Phi_1 | \hat{S}_x | \Phi_1 \rangle = a \times x$) is arbitrarily spin rotated (b). An arbitrarily oriented icosahedron (c) defines a spin-projection grid in terms of spin rotations corresponding to proper symmetries of the icosahedron. This yields 60 states with spin orientations marked by blue points on a sphere (d). Including Kramers partners doubles the number of determinants; points in (e) are connected by lines to guide the eye.

replacing the icosahedron in Figure 4(c) by an octahedron, is sufficient. We however found that no reasonable results can be obtained when restricting the spin-rotation basis to just six states.

For spin rotations from $|\Phi_1\rangle$, the overall shape of the energy surface is different, compare Figure 1 to Figure 5(a). As the spin-rotated GHF-type states are unrelaxed (with the exception of $|\Phi_1\rangle$ and $|\bar{\Phi}_1\rangle$), the energy dispersion on the diagonal of the NOCI matrix $H$ is about two orders of magnitude larger than energy differences for self-consistent (fully relaxed) GHF states employed in GCM(6) or GCM(48). Here, the energy anisotropy is crucially important for $g$-shifts. Neglecting the energy dispersion affords an almost pure $S = \frac{1}{2}$ NOCI solution ($\Delta g < 10^{-3}$ ppm), which would become a pure spin state if we also neglected the unimportant off-diagonal elements of $\hat{H}_{SOC}$. GCM based on several optimised GHF solutions and GCM in a spin-rotation space of a single GHF solution can overall be regarded as two complementary approaches that yield rather similar $g$-tensors for our test set.

3.2. Comparison with FCI

It is difficult to judge the suitability of experimental $g$-values for a direct comparison with quantum-chemical calculations that cannot consider all (possibly minor) complicating aspects. While magnetic contributions from molecular rotations must be subtracted from gas-phase data to yield intrinsic electronic properties, EPR measurements in the solid state are influenced by the environment (commonly a noble-gas matrix), which is another source of uncertainties. Besides, molecular vibrations may affect $g$-tensors, but are rarely considered (the present work is no exception). As an unambiguous benchmark for the intrinsic accuracy of 3SCF or GCM, we therefore ran FCI calculations on CN, CO$^+$, H$_2$O$^+$. The number of electronic configurations was reduced by working with an UNO active space, with frozen 1s cores, see Theory section. The effects of the basis truncation (UNO or FC-UNO) in 3SCF and GCM(6) are detailed in Table 5. With few exceptions, most notably the dramatic change in the $g_y$ component in NO$_2$, UNO (or FC-UNO) and full orbital-space results are reasonably similar.

For the selected three molecules, we compare FC-UNO 3SCF and GCM(6) to FCI in Table 6. A clear trend in favour of either 3SCF or GCM(6) is not apparent, but the semi-quantitative agreement with FCI is encouraging and corroborates that both approaches are reasonable. GCM and FCI also agree reasonably well in the energetic stabilisation of the ground state brought about by SOC. Specifically, the difference between GCM(6,UHF) and GCM(6) energies is $1.26 \times 10^{-6}$h for CO$^+$, $3.05 \times 10^{-7}$h for CN and $2.04 \times 10^{-6}$h for H$_2$O$^+$. 
Table 4. g-shits (in ppm) from a diagonalisation of $\hat{H}_0 + \hat{H}_{\text{SOC}}$ in a manifold of spin rotations of GHF solutions $|\Phi_0\rangle$, $|\Phi_1\rangle$ or $|\Phi_2\rangle$. $\hat{D}$ denotes the reduced basis dimension (see main text).

|          | GCM(x,120) | GCM(y,120) | GCM(z,120) |
|----------|------------|------------|------------|
| CO⁺      | x          | −2001      | −1689      | −1689      |
|          | y          | −1689      | −2001      | −1689      |
|          | z          | −1         | −1         | −1         |
|          |  $\hat{D}$ | 70         | 70         | 76         |
| CN       | x          | −1336      | −1326      | −1337      |
|          | y          | −1326      | −1336      | −1337      |
|          | z          | −1         | −1         | −1         |
|          |  $\hat{D}$ | 70         | 70         | 70         |
| MgF      | x          | −1701      | −1678      | −1678      |
|          | y          | −1678      | −1701      | −1678      |
|          | z          | −2         | −2         | −2         |
|          |  $\hat{D}$ | 38         | 38         | 38         |
| NO₂      | x          | 4043       | 3358       | 3335       |
|          | y          | −10,625    | −10,438    | −10,627    |
|          | z          | 36         | 34         | −670       |
|          |  $\hat{D}$ | 64         | 70         | 70         |
| NF₂      | x          | −495       | −89        | −92        |
|          | y          | 5837       | 5391       | 5838       |
|          | z          | 3004       | 3009       | 2816       |
|          |  $\hat{D}$ | 64         | 64         | 64         |
| CO₂⁻     | x          | 1116       | 1305       | 1305       |
|          | y          | −5118      | −5161      | −5118      |
|          | z          | −290       | −290       | −545       |
|          |  $\hat{D}$ | 64         | 64         | 64         |
| O₃⁻      | x          | −495       | −99        | −115       |
|          | y          | 16,130     | 14,438     | 16,146     |
|          | z          | 9352       | 9380       | 8820       |
|          |  $\hat{D}$ | 76         | 76         | 76         |
| H₂O⁺     | x          | −27        | −35        | −53        |
|          | y          | 15,831     | 13,460     | 15,836     |
|          | z          | 3984       | 4007       | 3608       |
|          |  $\hat{D}$ | 44         | 38         | 38         |
| H₂CO⁺    | x          | 5466       | 5619       | 5632       |
|          | y          | 1          | 574        | 7          |
|          | z          | 4743       | 4740       | 2668       |
|          |  $\hat{D}$ | 64         | 64         | 64         |

versus differences in the ‘nonrelativistic’ and ‘relativistic’ FCI energies of $1.03 \times 10^{-6}h$, $2.55 \times 10^{-7}h$ and $2.01 \times 10^{-6}h$, respectively. In summary, GCM(6) predicts qualitatively correct g-tensors at a mean-field cost. It should be noted however that the lack of dynamical electron correlation in GCM(6) would represent a limitation for the description of other systems not treated here, where GCM(6) may not be expected to provide satisfactory results.

3.3. Orbitally degenerate states

We lastly demonstrate how a GCM approach can be applied to nonrelativistic ground states with orbital degeneracy. The combined spin and orbital degeneracies are lifted through first order by SOC, leading to g-shifts that are by several orders of magnitude larger than in the foregoing examples. As two artificial yet illustrative examples with orbital degeneracies, we construct tetrahedral CH₄⁺ (bond length 1.07 Å) and CuF₄²⁻ species (1.92 Å). Both would be subject to Jahn–Teller distortions. Chibotaru and Ungur studied $T_d \rightarrow D_{4h}$ and $T_d \rightarrow D_{2h}$ deformations in CuCl₄²⁻ [23]. Using a CASSCF-SOSI procedure, they found that $g_x g_z/g_y$ (Eq. (5)) is negative for a $T_d$ structure. We consider only $T_d$ configurations but indicate how near orbital degeneracies for small structural deviations from perfect $T_d$ symmetry could be treated in the frame of GCM.

Tetrahedral CH₄⁺ has a nonrelativistic $^2T_1$ ground state, as expected from the $t_1$ highest occupied molecular orbital (HOMO) in neutral CH₄. Orbital degeneracy constitutes a multi-reference problem. UHF indeed strongly breaks symmetry, $T_d \rightarrow C_{3v}$: one H atom has Mulliken charge and spin densities of $+0.46$ and $+0.44$, respectively, with $+0.27$ and $+0.02$ on the remaining three H atoms. We used an STO-6G basis, which permits a direct comparison between NOCl and FCI. UNOs from a larger basis set are not adequate, because UHF breaks point-group symmetry. Therefore, FCI solutions in a symmetry-broken UNO space would break symmetry too. SOC splits the six-fold degenerate $^2T_1$ level into a four-fold degenerate ground state (irrep $F_{12}$ in $T_d^p$ [47]) and a doubly-degenerate excited state. We are interested in the latter, which can be treated in terms of $\tilde{S} = \frac{1}{2}$. The ground state, on the other hand, formally represents an $\tilde{S} = \frac{3}{2}$ system. The described splitting pattern is in accord with the SOC splitting of an atomic term, $^2L \rightarrow L_{3/2} \oplus L_{1/2}$: the more-than-half-filled valence shell of the central C atom in CH₄⁺ leads to a negative effective SOC constant [65] that energetically favours $\tilde{S} = \frac{3}{2}$ over $\frac{1}{2}$. This quartet, which could also be termed $\tilde{J} = \frac{3}{2}$, results from the coupling between $S = \frac{1}{2}$ and a pseudo-orbital momentum $[2] \tilde{L} = 1$. FCI predicts a splitting of $0.12 \times 10^{-3}h$ between $\tilde{S} = \frac{3}{2}$ and $\tilde{S} = \frac{1}{2}$ levels and yields an isotropic g-tensor for $\tilde{S} = \frac{3}{2}$, $g = 0.438$. From Eq. (5) we checked that the g-value is positive. This result suggests a qualitative explanation by the Landé formula,

$$
g_f = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}.
$$

Setting $S = \frac{3}{2}$, and replacing $L$ by $\tilde{L} = 1$ and $J$ by $\tilde{S} = \frac{1}{2}$ in Eq. (20), yields $g_S = \frac{3}{2}$, in semi-quantitative agreement with FCI.

A result that agrees well with FCI is obtained by diagonalising $\tilde{H} = \tilde{H}_0 + \tilde{H}_{\text{SOC}}$ in a basis of determinants that approximately spans the nonrelativistic $^2T_1$ ground state. Such a basis comprises all $T_d^p$ and Kramers partners of a symmetry-broken UHF solution with arbitrary spin orientation. Slightly depending on the spin orientation in the respective UHF reference, the resulting perfectly isotropic g-tensor does not deviate by more than $\approx 0.05$ from the FCI result.
The MAE surface (cf. caption to Figure 1) for spin rotations of the GHF solution $|\Phi_k\rangle$ in H$_2$O$^+$ is plotted in (a). Due to the transformation properties of spin operators under spin rotations, the direction dependence of the expectation value of $\hat{H}_{SOC}$ (Eq. (7)) is exactly described by Eq. (19), where $E_x \equiv \langle \Phi_k | \hat{H} | \Phi_k \rangle = -75.65802777$ (Table 2), $E_y \equiv \langle \Phi_k | e^{i\pi \hat{S}_y} \hat{H} e^{-i\pi \hat{S}_y} | \Phi_k \rangle = -75.65802592$, and $E_z \equiv \langle \Phi_k | e^{i\pi \hat{S}_z} \hat{H} e^{-i\pi \hat{S}_z} | \Phi_k \rangle = -75.65802814$. Curves (b), (c), and (d) are shown in the same colours as in (a) and have a perfect cosine form [in (b), $\phi$ is the angle with respect to the z-axis for a spin rotation about the y-axis, yielding $|\Phi_k\rangle$ for $\phi = \pi/2$, etc.].

The described $T^*_d$ projection is ill-defined for a geometrically distorted structure. A simple solution to this problem reverts to the GCM approach of probing a manifold of $\langle \hat{\mu} \rangle$ or $\langle \hat{S} \rangle$ orientations, as proposed in previous sections. However, due to the multi-reference character, we must sample such manifolds separately for each of the four symmetry-broken solutions. Each such manifold could be followed adiabatically along a distortion coordinate. On the other hand, for strongly distorted structures, a single manifold associated with the energetically favoured UHF solution should be appropriate.

For CH$_4^+$, we build a basis by orienting spin in each of the four equivalent symmetry-broken UHF solutions along one of the four C–H bond directions. Including Kramers partners, spin points to one of the eight vertices of a cube, see Figure 6. Diagonalisation in the full basis of dimension $D = 32$, which spans a representation of $T^*_d$, yields a splitting of $0.13 \times 10^{-3}\hbar$ between $\tilde{S} = \frac{3}{2}$ and $\tilde{S} = \frac{1}{2}$ levels. This splitting and the isotropic $g = 0.471$ for the $\tilde{S} = \frac{1}{2}$ level are in reasonable agreement with FCI. Basing the described strategy on GHF (including SOC) instead of UHF (without SOC) does not cause significant changes.

The 3SCF approach is not suitable for the present problem, because it is intrinsically incapable of describing the coupling between spin and pseudo-orbital momentum. The same applies to working in a spin-rotation manifold of a single symmetry-broken UHF solution: GCM(8), in contrast to GCM(32), neither describes orbital degeneracy nor does it afford an isotropic $g$-tensor.

For CuF$_4^{2-}$, basis sets def2-SVP [66,67] on Cu and jun-cc-pVDZ [68] on F were used. Orbital degeneracy in CuF$_4^{2-}$ is signalled by UHF symmetry-breaking, $T_d \rightarrow C_{2v}$; six degenerate UHF solutions differ in the distribution of charge- and spin-densities over two pairs of F-atoms. However, symmetry breaking is far less pronounced than in CH$_4^+$. Consequently, energetic barriers
Table 6. Experimental g-shifts (in ppm) are compared to 3SCF, GCM(6) and FCI in an FC-UNO active space.

|       | Exp. | 3SCF | GCM(6) | FCI  |
|-------|------|------|--------|------|
| CO⁺   |      | -2992| -2260  | -2777| -1972|
|       |      | -2003| -1738  | -1866| -1349|
| NO₂   | x    | 4762 | 5239   | 4493 | 4447 |
|       | y    | -12,642| -12,838| -3566| -3738|
|       | z    | -1070| -281   | -356 | -270 |
| NF₂   | x    | -747 | -258   | -571 | -192 |
|       | y    | 6121 | 6556   | 6203 | 6379 |
|       | z    | 3110 | 3412   | 3023 | 3170 |
| CO₂⁻  | x    | 1190 | 1396   | 1457 | 1440 |
|       | y    | -5976| -5987  | -2222| -2371|
|       | z    | -741 | -450   | -314 | -221 |
| O₃⁻   | x    | -743 | -307   | -392 | -175 |
|       | y    | 21,108| 23,530| 19,567| 20,234|
|       | z    | 13,650| 15,755| 12,074| 12,384|
| H₂O⁺  | x    | -15  | -41    | -13  | -35  |
|       | y    | 13,751| 15,706| 13,584| 14,256|
|       | z    | 3830 | 4078   | 3958 | 4161 |
| H₂CO⁺ | x    | 5871 | 6020   | 5654 | 5741 |
|       | y    | 799  | 233    | 697  | 224  |
|       | z    | 2977 | 4629   | 3427 | 4519 |

successively choose one of the six UHF solutions and orient the spin along one of the four bond directions. With such an initial guess, \( \langle \hat{S} \rangle \) is constrained along the given direction in GHF. This overall affords two sets of 12 GHF solutions related by \( T_d^* \). These are not two sets of 24 solutions related by \( T_d^* \) because for the chosen constraint directions, GHF preserves a mirror symmetry, leaving two F atoms equivalent. Finally, Kramers partners are included to span a GCM(48) basis, which yields the isotropic \( g = -1.898 \). The negative sign was established from Eq. (5). Chibotaru and Ungur calculated \( g \approx -2 \) for a tetrahedral configuration of CuCl₄²⁻ [23], which provides confidence that our present result for CuF₄²⁻ is at least semi-quantitatively correct. (Due to limitations of system size in our in-house code, we did not pursue calculations on CuCl₄⁻.) A space spanned by \( T_d^* \)

Figure 6. GCM(32) basis in tetrahedral CH₄⁺. For each of the four equivalent symmetry-broken UHF solutions (\( T_d \to C_3v \), the distinct H-atom is shown in green) a spherical manifold of spin orientations is sampled with eight grid points (vertices of a cube). Without SOC, all 32 states are degenerate, due to spin- and point-group symmetry. In the symmetry group of the full Hamiltonian (including SOC), the eight determinants represented by green arrows (spin parallel or antiparallel to the distinct C–H bond direction) and the remaining 24 determinants are separately related by operations of the double group or by time-reversal \( \hat{\Theta} \). The basis of 32 states overall furnishes a representation of \( T_d^* \) and maintains time-reversal symmetry.

Table 5. 3SCF and GCM(6) g-shifts with either the full cc-pVTZ basis, an UNO active space, or an UNO active space with frozen 1s cores (FC-UNO).

|       | 3SCF | GCM(6) |
|-------|------|--------|
| CO⁺   |       |        |
|       |       |        |
| CN    |       |        |
|       |       |        |
| NO₂   |       |        |
|       |       |        |
| NF₂   |       |        |
|       |       |        |
| CO₂⁻  |       |        |
|       |       |        |
| O₃⁻   |       |        |
|       |       |        |
| H₂O⁺  |       |        |
|       |       |        |
| H₂CO⁺ |       |        |

separating the six configurations in CuF₄²⁻ are of the same order of magnitude as SOC energies. An arbitrary constrained GHF solution (including SOC) cannot generally be attributed to one of six manifolds. In other words, manifolds are not strictly separate. We can nevertheless pursue a similar strategy as in CH₄⁺. We
and Kramers partners of a single arbitrary GHF solution yields a very similar $g$-value, with a slight dependence on the constraint orientation $\langle \hat{S} \rangle$. As explained for $\text{CH}_4^+$, the latter symmetry-projection strategy would not be feasible for distorted structures. As a general caveat we note that in specific cases, the action of a double-group operation on a determinant can be equivalent to the action of $\Theta$. In such situations, duplicates must be removed from the basis spanned by double-group and Kramers partners. This complication can be avoided by choosing an orientation $\langle \hat{S} \rangle$ unrelated to symmetry elements of the molecule. We lastly remark that negative $g$-values are an indication of strong coupling between spin and orbital degrees of freedom. Thus, pseudospin differs qualitatively from true electronic spin [23]. A single determinant cannot describe these features. Just as in $\text{CH}_4^+$, 3SCF is inadequate to calculate $g$-tensors in a tetrahedral configuration of $\text{CuF}_4^{2-}$. Besides, 3SCF cannot in principle predict the sign of $g$-values. Our GCM approach demonstrates that such multi-reference problems can still be handled qualitatively correctly at a mean-field cost.

4. Conclusions

We have explored different strategies for the calculation of molecular $g$-tensors based on non-orthogonal configuration interaction (NOCI) between GHF determinants. Two complementary strategies inspired by the generator coordinate method (GCM) were explored to span the basis: (i) sampling a spherical manifold of $\langle \hat{\mu} \rangle$ or $\langle \hat{S} \rangle$ orientations in terms of nearly degenerate GHF solutions, including SOC self-consistently, (ii) applying spin rotations to a single GHF solution.

For a set of small orbitally nondegenerate main-group radicals, the first approach requires just three GHF Kramers pairs. Predictions of $g$-tensors from the respective GCM(6) are similar to the common 3SCF strategy, but GCM(6) is conceptually more appealing: it yields a complete $g$-tensor from a single qualitatively correct Kramers pair. A qualitatively correct mean-field approximation to the Kramers-doublet ground state could become important when optimising geometries or calculating vibrational frequencies in the presence of SOC. The GCM approach is not restricted to three inequivalent GHF solutions that represent stationary points in rhombic molecules. In fact, a non-degenerate orientational manifold can be sampled arbitrarily densely by constraining the directions of $\langle \hat{\mu} \rangle$ or $\langle \hat{S} \rangle$. This essentially removes the need to know the principal axes a priori and would straightforwardly allow to treat molecules with lower symmetry.

The non-degeneracy of the different GHF solutions is implicitly incorporated through NOCI. We observed that the energy dispersion of the constrained manifold is essentially irrelevant for $g$-tensors in our test set with weak SOC. On the other hand, when generating the basis from spin rotations of a single GHF solution, without relaxation of rotated states, the energy dispersion is crucial to obtain reasonable $g$-tensors.

A UNO active space permitted a rigorous evaluation of 3SCF and GCM against FCI. GCM agrees rather well with FCI but does not represent a quantitative improvement over 3SCF. On the other hand, two tetrahedral model systems, $\text{CH}_4^+$ and $\text{CuF}_4^{2-}$, have served to demonstrate that GCM is also applicable to systems where orbital degeneracies are lifted through first order by SOC, leading to large $g$-shifts. The 3SCF single-determinant approach intrinsically fails in these cases, whereas GCM predicts qualitatively correct isotropic $g$-tensors, even including negative $g$-values in $\text{CuF}_4^{2-}$.

We believe that studies of larger systems with more pronounced SOC effects, particularly transition-metal complexes, would be worthwhile. However, such systems pose additional challenges and may display significant dynamic correlation, which the present GHF-based GCM approach is missing. Finally, NOCI in a basis of nearly degenerate constrained GHF solutions could also be used to parameterise spin Hamiltonians for $\hat{S} > \frac{1}{2}$ systems in terms of zero-field splitting and $g$-tensors. This could represent an alternative and conceptually attractive way for calculations of a wider range of EPR parameters at a mean-field cost.

Note

1. In low-symmetry systems, the $g$-tensor has in principle nine independent components. However, it is always possible to eliminate the three antisymmetric components by pseudospin rotations, see Ref. [1].

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Appendices

Appendix A. Gradient-based optimisation including magnetisation constraints

Parts of this section closely follow chapter 3.5 of Ref. [42]. Note that transformations between the original non-orthogonal atomic-orbital (AO) basis and an orthogonal AO (OAO) basis (we use Löwdin symmetric orthogonalisation) are necessary to avoid a costly transformation of two-electron integrals from the AO to the OAO basis. However, for ease of presentation, we assume that all integrals are given in the OAO basis. We trust that the reader can determine when a transformation from AO to OAO (or vice versa) is necessary in practice (see, e.g. Ref. [43]).

In Eq. (A1), a Thouless rotation $e^{\hat{Z}}$ relates $|\Phi\rangle$ to an initial guess $|\Phi^0\rangle$,

$$|\Phi\rangle = A e^{\hat{Z}} |\Phi^0\rangle,$$

(A1)

where

$$\hat{Z} = \sum_{v \in \text{virt}} \sum_{o \in \text{occ}} Z_{vo} \hat{c}_v^\dagger \hat{c}_o,$$

(A2)

and $A$ is a normalisation constant. The product $\hat{c}_v^\dagger \hat{c}_o$ of fermionic creation and annihilation operators transfers an electron from an occupied to a virtual orbital. Thouless parameters $Z_{vo}$ represent the unconstrained optimisation parameters and can be collected in a complex matrix $Z$ of dimension $(M - N) \times N$, where $M$ is the total number of single-electron basis functions (twice the number of spatial basis functions), and $N$ is the number of electrons. The essence of GHF consists in minimising the single-determinant energy $E = \langle \Phi | \hat{H} | \Phi \rangle$, which requires an optimisation with respect to $Z$.

An initial set of molecular orbitals (MOs) that define $|\Phi^0\rangle$ is provided in terms of OAO expansion coefficients in the columns of $O_{\text{occ}}^0$ ($an M \times N$ matrix). The combined set of occupied and virtual MOs is a unitary $M \times M$ matrix, $O^0 = (O_{\text{occ}}^0 O_{\text{virt}}^0)^\dagger$. In the first iteration, we set $Z = 0$ and $O = O^0$. The GHF determinant $|\Phi\rangle$ is completely characterised (up to an irrelevant phase) by its density matrix $\rho$,

$$\rho = O_{\text{occ}} O_{\text{occ}}^\dagger.$$

(A3)

In the GHF energy expression, Eq. (A4),

$$E = \langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \text{Tr} [\rho (\mathbf{F} + \mathbf{h})] + V_{\text{nuc}},$$

(A4)

$\mathbf{F}$ is the Fock matrix, $\mathbf{h}$ is the core Hamiltonian, which includes $\hat{H}_{\text{SOC}}$, Eq. (7), and $V_{\text{nuc}}$ is the nuclear-repulsion energy (a constant).

In the following, we explain the calculation of the global energy gradient with respect to $Z$. Eqs. (A5)–(A10) describe the Thouless rotation (Eq. (A1)) of $O^0$ into $O$ in each optimisation step. Lower triangular matrices $L (N \times N)$ and $M [(M - N) \times (M - N)]$ are obtained by Cholesky decomposition, Eqs. (A5) and (A6):

$$1 + Z^T Z = L L^T,$$

(A5)

$$1 + Z^* Z^T = M M^T.$$
Following Eqs. 3.45 and 3.47 in Ref. [42], we form the intermediate $O$,

$$\langle 0 | O_{\text{occ}} | 0 \rangle = \langle 0 | O_{\text{occ}} | 0 \rangle + \sum_{v=1}^{M-N} Z_{v0} (O_{\text{virt}})^v_v, \quad (A7)$$

$$\langle 0 | O_{\text{virt}} | 0 \rangle = \langle 0 | O_{\text{virt}} | 0 \rangle - \sum_{\sigma=1}^{N} Z_{v0} (O_{\text{occ}})^{\sigma}_v, \quad (A8)$$

where $\langle 0 | O_{\text{occ}} | 0 \rangle$ denotes the $o$-th column of $O_{\text{occ}}$, etc. Eqs. (A9) and (A10) represent the orthonormalisation of $O$ to yield a unitary $O$,

$$\langle 0 | O_{\text{occ}} | 0 \rangle = \sum_{k=1}^{N} (L^{-1})_{lk} (O_{\text{occ}})^{km}, \quad (A9)$$

$$\langle 0 | O_{\text{virt}} | 0 \rangle = \sum_{k=1}^{M-N} (M^{-1})_{lk} (O_{\text{virt}})^{km}. \quad (A10)$$

The global gradient vector $G$ is defined in terms of variations of the GHF energy, Eq. (A11), caused by Thouless rotations from the reference state $|\Phi\rangle$.

$$\delta E = \sum_{v=1}^{N} \frac{\delta E}{\delta Z_{v0}} \delta Z_{v0} + \text{c.c.}$$

$$= - \sum_{v=1}^{N} (G_{v0} \delta Z_{v0}^* + \text{c.c.})$$

$$= -2 \sum_{v=1}^{N} (\text{Re}(G_{v0}) \text{Re}(\delta Z_{v0}) + \text{Im}(G_{v0}) \text{Im}(\delta Z_{v0})) \quad (A11)$$

On the other hand, the local gradient $G_{\text{loc}}$ is defined with respect to Thouless rotations from the present determinant $|\Phi\rangle$ (which determines $\rho$ and $F$). Its matrix form is given in Eq. (A12):

$$G_{\text{loc}} = (\rho - 1)F\rho. \quad (A12)$$

The transformation of $G_{\text{loc}}$ (computed in the OAO basis) to the MO basis of the global reference $|\Phi\rangle$ yields the global gradient, Eq. (A13):

$$G = (O_{\text{occ}}^{\dagger})^0 G_{\text{loc}} O_{\text{occ}}^0. \quad (A13)$$

To reduce the number of iterations needed to reach convergence, we found it very useful to rescale the global gradient by dividing each element $G_{v0}$ by the square root of the corresponding virtual-occupied orbital-energy difference.

To constrain the magnetic moment to point along a general direction $n$, we construct an orthonormal system of three-dimensional unit vectors, $(n, n', n'')$, and demand:

$$\langle \Phi | n' \cdot \mu | \Phi \rangle = \text{Tr} [\rho (n' \cdot \mu)] = 0, \quad (A14)$$

$$\langle \Phi | n'' \cdot \mu | \Phi \rangle = \text{Tr} [\rho (n'' \cdot \mu)] = 0. \quad (A15)$$

(To instead constrain the spin direction, replace $\mu$ by $\hat{S}$.) The local gradients for the two constrained quantities are obtained by replacing $F$ in Eq. (A12) by $n' \cdot \mu$ or $n'' \cdot \mu$. The global gradients are again obtained by transforming to the MO basis of the global reference (cf. Eq. (A13)). To speed up convergence, the global constraint gradients are also divided by the square root of the orbital-energy difference.

The GHF energy $E$ and the global energy gradient $G$, as well as the values of the two constrained quantities and their respective global gradients, and an initial MO set $O^0$ (occupied and virtual orbitals) are passed to the fmincon function in Matlab [69]. The separation into real and imaginary parts (Eq. (A11)) is required for fmincon, which optimises with respect to a set of real-valued variables.

**Appendix B. Connection between 3SCF and the Kramers-pair formalism for E1/2 doublets in C2v**

As stated in the Results section, for all molecules in our test set (excluding CH4 and CuF42–), one of the three principal components of the $g$-tensor calculated for a single Kramers pair $|\Phi_n\rangle, |\Phi_{\bar{n}}\rangle$ based on Eq. (4), coincides with the 3SCF result, that is, $g_n = \langle \Phi_n | n \cdot \mu | \Phi_n \rangle$ (n = x, y, z). In the following, we rationalise this observation by tracing it to the fact that the cross-term of $n \cdot \mu$ between Kramers partners vanishes, $\langle \Phi_{\bar{n}} | n \cdot \mu | \Phi_{\bar{n}} \rangle = 0$, due to symmetry.

All molecules in our set have either $C_{2v}$ symmetry or $C_{2v}$ is a subgroup of their molecular point group. From the three symmetry elements for each solution listed in Table 1, two arbitrarily chosen elements generate the self-consistent symmetry group $C_{2v}(C_{2v}^0)$. Each of the three solutions has a distinct symmetry group, which is however in all cases isomorphic to $C_{2v}(C_{2v}^0)$. For example, the (unitary) $C_2$ operation of the group $C_{2v}(C_{2v}^0)$ corresponds to elements $\exp(-i\pi \hat{S}_z) \times \hat{\sigma}_{yz}$, $\exp(-i\pi \hat{S}_z) \times \hat{\sigma}_{xz}$ or $\exp(-i\pi \hat{S}_z) \times \hat{\sigma}_{yx}$ for $|\Phi_n\rangle$ or $|\Phi_{\bar{n}}\rangle$, respectively, where $\{\hat{E}, \hat{C}_2, \hat{\sigma}_{yx}, \hat{\sigma}_{yz}\}$ are the usual $C_{2v}$ elements of the nonrelativistic Hamiltonian $\hat{H}_0$. The $C_{2v}(C_{2v}^0)$ symmetry implies that each pair $|\Phi_n\rangle, |\Phi_{\bar{n}}\rangle$ spans E1/2 in the group $C_{2v}$. In other words, the Kramers pairs do not break the $C_{2v}$ symmetry of the Hamiltonian including SOC. (This is not true for arbitrary orientations $n$, which do not yield GHF states with any self-consistent symmetry.) $E_{1/2}$ is the only fermionic irreducible representation in $C_{2v}$ [in a fermionic representation, a $2\pi$ spin rotation about an arbitrary axis introduces a factor of $(-1)$]. On the other hand, operators like $\hat{S}, \hat{I}$, or $\mu$ span bosonic representations. As an example, when dealing with $|\Phi_n\rangle$, we attribute the Mulliken label $A_2$ to an operator that is symmetric (label A) with respect to $\exp(-i\pi \hat{S}_x) \times \hat{\sigma}_{yz}$ and antisymmetric (subscript 2) with respect to both $\exp(-i\pi \hat{S}_x) \times \hat{\sigma}_{xz}$ and $\exp(-i\pi \hat{S}_y) \times \hat{C}_2$.

Based on the foregoing symmetry analysis, we can now deduce that the cross-term of $n \cdot \mu$ vanishes. For $|\Phi_n\rangle$, $n \cdot \mu$ transforms as $A_2$, while the other two (orthogonal) components of $\mu$ (that is, $n' \cdot \mu$ and $n'' \cdot \mu$) transform as $B_1$ and $B_2$. As stated, $|\Phi_n\rangle, |\Phi_{\bar{n}}\rangle$ span E1/2, but the two components of E1/2 cannot be coupled by an A2 operator (cf. Clebsch-Gordan coefficients for $C_{2v}$ given in Ref. [47]); thus, $\langle \Phi_{\bar{n}} | n' \cdot \mu | \Phi_{\bar{n}} \rangle = 0$. In contrast, different components of E1/2 can indeed be connected by $B_1$ or $B_2$ operators. Therefore, in general, $\langle \Phi_{\bar{n}} | n' \cdot \mu | \Phi_{\bar{n}} \rangle \neq 0$, if $n' \cdot n' = 0$. 