Relativistic exact two-component coupled-cluster calculations of electronic g-factors for heavy-atom-containing molecules pertinent to search of new physics

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Exact two-component (X2C) coupled-cluster calculations of electronic g-factors for heavy-atom-containing small molecules pertinent to search of new physics Beyond the Standard Model (BSM) is reported. A magnetic-field-dependent unitary transformation of the Dirac Hamiltonian has been adopted to enable a simple inclusion of the quantum electrodynamics correction to the free-electron g-factor in the four-component formulation. The X2C transformation is subsequently employed to eliminate the positronic degrees of freedom to enhance computational efficiency without significant loss of accuracy. The relationship of the present scheme to alternative four- and two-component formulations is discussed. To demonstrate the accuracy and usefulness of the present X2C scheme, we report coupled-cluster calculations for electronic g-factors of representative heavy-metal-containing small molecules including those relevant to precision spectroscopic search of BSM physics.

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I. INTRODUCTION

Precision measurement of heavy-atom-containing small molecules is a promising approach to search for fundamental physics Beyond the Standard Model (BSM).[1–6] An important line of research here is to search for electron electric dipole moment (eEDM) originating from charge-conjugation and parity symmetry violation through precision measurement of atoms and molecules. Molecular species containing a heavy atom with strong spin-orbit coupling and a light atom or a functional group with high electronegativity exhibit gigantic effective internal electric fields.[7–22] They thus feature high sensitivity in the eEDM measurement. Recent updates of the upper bound for the eEDM value have been obtained from precision spectroscopy of diatomic molecules.[23–26] Experimental measurements using YbF[7,23,27] and ThO[24,26,28–30] take advantage of the high density of neutral molecules in molecular beam experiments, while those using molecular ions such as HfF^+ and ThF^+ exploit long coherence time of ions within an ion trap.[25,31–34] Heavy-atom-containing linear triatomic molecules such as YbOH have also been proposed as promising candidates for the search of eEDM,[35] in which the use of vibrational excited levels of the degenerate bending modes enables efficient polarization of a molecule using applied external electric fields.

Precision measurements of molecular eEDM-sensitive states require precise knowledge about electrical and magnetic properties for these states. Determination of these properties relies on high resolution spectroscopic studies.[27,34,36–47] Meanwhile, electronic-structure calculations are being used to predict these parameters and/or to facilitate experimental analysis.[9,13,14,48–57] Quantum-chemical calculations of molecular properties are sensitive to treatments of electron correlation. Molecular states of interest in the eEDM measurements are usually doublet or high-spin triplet states, whose wavefunctions are dominated by a single determinant; electron correlation in these electronic states are dynamic in nature. Coupled-cluster (CC) methods[58,59] that can provide accurate treatments of dynamic correlation thus have been widely used. Relativistic CC calculations in combination with the four-component Dirac-Coulomb Hamiltonian or relativistic two-component Hamiltonians have been shown to provide useful results for electric dipole moments, electronic g-factors, and magnetic hyperfine coupling constants for heavy-atom containing small molecules.

A motivation of the present work is to incorporate quantum electrodynamics (QED) correction to the free-electron g-factor into relativistic four-component and two-component formulations for ab initio calculations of electronic g-factors. Since many eEDM-sensitive states, e.g., the $^3\Delta_1$ states of ThO, HfF^+, and ThF^+, exhibit small electronic g-factor values, the inclusion of the QED correction to the free-electron g-factor plays an important role in accurate calculations of electronic g-factors for these molecular states. It is also essential to include this correction for accurate calculations of shifts of electronic g-factors relative to the free-electron g-factor.[60] In the non-relativistic formulation for electronic g-factors with perturbative treatment of spin-orbit coupling, the QED correction to free-electron g-factor has been included by scaling the non-relativistic spin Zeeman interaction with the ratio of the exact value of 2.002319304362(15)[61] for the free-electron g-factor and the value of two. Its importance has been demonstrated using the comparison of high-accuracy CC calculations of molecules containing first-row elements with the corresponding experimental values.[60] Skripnikov and Titov have used the form of thus-scaled non-relativistic spin Zeeman interaction in relativistic two-component calculations of electronic g-factors and have obtained promising results.[50] Nevertheless, development of an approach based on the Dirac Hamiltonian would be of significant interest. Calculations of electronic g-factors using the four-component Dirac-Coulomb Hamiltonian[62–65] and exact two-component theory[66,67] have been reported. The inclusion of the QED correction to the free-electron g-factor in these relativistic formulations have not been discussed so far. A challenge might be that it is not straightforward to apply the scaling factor in the original Dirac Hamiltonian. We mention than more approximate two-component approaches such as zeroth-order regular approximation and low-order Douglas-Kroll-Hess methods for calculations of electronic g-factors have been developed mostly for density-functional theory calculations.[68–72] The present work aims at rigorous treatments of relativistic and electron-correlation effects and will be focused on four-component and exact two-component formulations and CC calculations.

In this paper, we present a simple scheme for incorporating the QED correction to the free-electron g-factor into the four-component formulation for electronic g-factors, hereby employing a unitarily-transformed Hamiltonian originally developed by Kutzelnigg[73] and extensively studied by Liu and coworkers in calculations of nuclear magnetic resonance shielding tensors.[74,75] Subsequently, we apply the exact two-component (X2C) transformation[76–78] for focusing on the electronic degrees of freedom. The present X2C formulation have been used together with an X2C atomic mean-field spin-orbit approach[79] and the recent implementation of X2C-CC analytic derivative techniques[80] to perform calculations of electronic g-factors. Theory and computational details are presented in Section II and III. The X2C results for several representative molecules are reported in Section IV and compared with corresponding four-component results, available computational results in the literature, as well as experimental values. We have also compared Kramers unrestricted Hartree-Fock (KUHF) and Kramers restricted open-shell HF (KROHF) based calculations to demonstrate the relevance of a relativistic analogue to the spin contamination in these open-shell

CC calculations. Finally, a summary and an outlook is given in Section V.

II. THEORY

A. Four-component and exact two-component theory for electronic g-factors using a unitary transformation scheme

The Dirac Hamiltonian in the presence of a uniform external magnetic field can be written as a sum of the field-independent Hamiltonian H_0 and the interaction with the magnetic field H_1

$$H = H_0 + H_1. \tag{1}$$

H_0 can be written in a block form as

$$H_0 = \begin{pmatrix} V & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & V - 2c^2 \end{pmatrix}, \tag{2}$$

in which c is the speed of light, $\vec{\sigma}$ is the vector of Pauli spin matrices, $\vec{p}$ is the momentum operator, and V represents the electron-nucleus electrostatic interaction. The SI-based atomic units have been used. Within the minimum-coupling principle, H_1 is an "odd" operator appearing in the off-diagonal block of the Dirac Hamiltonian

$$H_1 = \begin{pmatrix} 0 & c\vec{\sigma}\cdot\vec{A} \\ c\vec{\sigma}\cdot\vec{A} & 0 \end{pmatrix}, \tag{3}$$

with the vector potential for the uniform external magnetic field $\vec{A}$ given by

$$\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}. \tag{4}$$

$\hat{H}_1$ can be equivalently written as

$$H_1 = \vec{B}\cdot\vec{H}_B, \tag{5}$$

with $\vec{H}_B$ given by

$$\vec{H}_B = \begin{pmatrix} 0 & \frac{1}{2}c\vec{\sigma} \times \vec{r} \\ \frac{1}{2}c\vec{\sigma} \times \vec{r} & 0 \end{pmatrix}. \tag{6}$$

The Dirac Hamiltonian gives a free-electron g-factor value of two. Note that the non-relativistic spin-Zeeman term is given by $\vec{s} \cdot \vec{B}$ with $\vec{s} = \frac{1}{2}\vec{\sigma}$. The quantum electrodynamics (QED) correction to the free-electron g-factor can readily be included in the non-relativistic theory by replacing a factor of two with the exact value of the free-electron g-factor $g_e = 2.002319304362(15)$ in this equation, leading to $\frac{1}{2}g_e\vec{s} \cdot \vec{B}$. However, it is not straightforward to incorporate this into the Dirac Hamiltonian by scaling the Pauli spin matrices in Eq. 6.

To address this problem, we apply a magnetic-field-dependent unitary transformation to the Dirac Hamiltonian as originally proposed by Kutzelnigg.[73] The transformed Hamiltonian $\widetilde{H}$ is given by

$$\widetilde{H} = e^{-\tau} H e^{\tau} = \widetilde{H}_0 + \widetilde{H}_1 + \cdots , \tag{7}$$

$$\tau = \begin{pmatrix} 0 & -\frac{1}{2c}\vec{\sigma} \cdot \vec{A} \\ \frac{1}{2c}\vec{\sigma} \cdot \vec{A} & 0 \end{pmatrix}. \tag{8}$$

The field-independent part of the transformed Hamiltonian is identical to that of the untransformed one

$$\widetilde{H}_0 = H_0. \tag{9}$$

The expansion of $\widetilde{H}$ features a non-terminating field-dependent series. For calculations of g-factors, we focus our discussion on the terms linear in magnetic field given by

$$\widetilde{H}_1 = H_1 + [H_0, \tau] = \vec{B} \cdot \vec{\widetilde{H}}_B, \tag{10}$$

in which the magnetic interaction now appears on the diagonal blocks of the transformed Hamiltonian with $\vec{\tilde{H}}_B$ taking the form

$$\vec{\tilde{H}}_B = \begin{pmatrix} \frac{1}{2}(\vec{l}+2\vec{s}) & 0 \\ 0 & -\frac{1}{2}(\vec{l}+2\vec{s}) \end{pmatrix} \;,\; \vec{l} = \vec{r}\times\vec{p} \;,\; \vec{s} = \frac{1}{2}\vec{\sigma}. \tag{11}$$

The unitary transformation scheme has been developed to elucidate the origin of the diamagnetic contribution to second-order magnetic properties including magnetizability and nuclear magnetic resonance shielding tensors in four-component relativistic theories,[73] where it is shown to be equivalent to Gordon decomposition of current density.[81] In-depth studies of this scheme in computations of second-order magnetic properties together with other explicit magnetic balance conditions[74,75,82,83] have been reported. It is straightforward to include the QED correction to the free-electron g-factor in the same way as in the non-relativistic theory, by replacing the factor of two in front of $\vec{s}$ in Eq. (11) with g_e. The corrected $\widetilde{H}_B$ is given by

$$\vec{\tilde{H}}_B = \begin{pmatrix} \frac{1}{2}(\vec{l}+g_e\vec{s}) & 0 \\ 0 & -\frac{1}{2}(\vec{l}+g_e\vec{s}) \end{pmatrix}. \tag{12}$$

Eqs. (9), (10), and (12) together define the four-component one-electron Hamiltonian for the present scheme. The two-electron instantaneous Coulomb interaction commutes with this unitary transformation and thus is not affected. We mention that the unitary transformation does not commute with the Gaunt term[84] or gauge transformation with distributed gauge origins,[85] and thus introduces extra field-dependent two-electron integrals when used together with the Gaunt term or gauge-including atomic orbitals.

To enhance computational efficiency without significant loss of accuracy, the matrix representation of the above four-component Hamiltonian in terms of kinetically balanced basis sets is transformed into the two-component formulation using the exact two-component (X2C) transformation[76,86] and its analytic-gradient formulation.[87,88] The resulting "electrons-only" two-component Hamiltonian, with the two-electron spin-orbit coupling contributions included using an atomic mean-field spin-orbit approach (X2CAMF),[79] is used together with the two-electron Coulomb interaction in subsequent many-electron treatments. The "picture change"[89] of the magnetic interaction has been fully taken into account in the present X2C scheme.

B. Relationship to alternative approaches

The scheme developed by Skripnikov and Titov uses the non-relativistic Zeeman interaction $\frac{1}{2}(L_z + g_e s_z)$ in two-component relativistic calculations.[50] Since $\frac{1}{2}(L_z + g_e s_z)$ is the same as the large-large block of the present four-component transformed Hamiltonian in Eqs. (10) and (12), the scheme of Skripnikov and Titov corresponds to the neglect of the picture-change effects in the present X2C formulation. The present scheme thus features a more rigorous treatment and also provides a justification for the scheme of Skripnikov and Titov using the non-relativistic operator. Because picture-change effects are in general small for valence properties,[89] the present X2C results for g-factors are expected to agree closely with those in Ref.[50].

The use of basis sets with restricted magnetic balance (RMB)[83]

$$\phi_p^{\mathrm{L}} = \sum_\mu C_{\mu p}^{\mathrm{L}} f_\mu \ , \ \phi_p^{\mathrm{S}} = \sum_\mu C_{\mu p}^{\mathrm{S}} \frac{\vec{\sigma}\cdot\vec{p} + \vec{\sigma}\cdot\vec{A}}{2c} f_\mu, \tag{13}$$

is a plausible alternative to the present approach. The unperturbed and first-order Hamiltonian matrix then can be written as

$$H_0^{\mathrm{RMB}} = H_0 \ , \ H_1^{\mathrm{RMB}} = \begin{pmatrix} 0 & H_1^{\mathrm{LS,RMB}} \\ (H_1^{\mathrm{LS,RMB}})^\dagger & H_1^{\mathrm{SS,RMB}} \end{pmatrix}, \tag{14}$$

in which

$$(H_1^{\mathrm{LS,RMB}})_{\mu\nu} = \frac{1}{2}\langle f_\mu|\vec{B}\cdot(\vec{l}+2\vec{s})|f_\nu\rangle \rightarrow \frac{1}{2}\langle f_\mu|\frac{1}{2}\vec{B}\cdot(\vec{l}+g_e\vec{s})|f_\nu\rangle, \tag{15}$$

$$(H_1^{\mathrm{SS,RMB}})_{\mu\nu} = -\frac{1}{2}\langle f_\mu|\vec{B}\cdot(\vec{l}+2\vec{s})|f_\nu\rangle \rightarrow -\frac{1}{2}\langle f_\mu|\vec{B}\cdot(\vec{l}+g_e\vec{s})|f_\nu\rangle. \tag{16}$$

Similar to calculations of NMR shield tensors,[75] Eq. (14) and (16) is expected to work as well as the unitary transformation scheme for calculations of electronic g-factors. Note that additional field-dependent two-electron integrals are required in calculations using the RMB basis sets, while the unitary transformation scheme using a common gauge origin requires no field-dependent two-electron integrals. In the present calculations of small molecules, the dependence of computed results with respect to gauge origin plays an insignificant role. We focus the present work on the simpler unitary transformation scheme.

We should mention that it is also possible to perform separation of spin-dependent and spin-independent terms for the magnetic-field dependent terms in the matrix representation of the original Dirac Hamiltonian [Eq. (3)] in terms of kinetically balanced basis sets[90] and subsequently include the QED correction to the free-electron g-factor. The term linear in magnetic field in the matrix representation of Eq. (3) in terms of kinetically balanced basis sets

$$\phi_p^{\mathrm{L}} = \sum_\mu C_{\mu p}^{\mathrm{L}} f_\mu \ , \ \phi_p^{\mathrm{S}} = \sum_\mu C_{\mu p}^{\mathrm{S}} \frac{\vec{\sigma}\cdot\vec{p}}{2c} f_\mu. \tag{17}$$

can be written as

$$H_1 = \begin{pmatrix} 0 & H_1^{\mathrm{LS}} \\ H_1^{\mathrm{SL}} & 0 \end{pmatrix}, \tag{18}$$

with matrix elements of H_1^{LS} and H_1^{SL} given by

$$\begin{aligned}
(H_1^{\mathrm{LS}})_{\mu\nu} &= \frac{1}{2}\langle f_\mu|(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})|f_\nu\rangle && (19)\\
&= \frac{1}{2}\langle f_\mu|\vec{B}\cdot(\frac{1}{2}\vec{l}+2\vec{s})-i\vec{\sigma}\cdot(\vec{p}\times\vec{A})|f_\nu\rangle && (20)\\
&\rightarrow \frac{1}{2}\langle f_\mu|\vec{B}\cdot(\frac{1}{2}\vec{l}+g_e\vec{s})-ig_e\vec{s}\cdot(\vec{p}\times\vec{A})|f_\nu\rangle && (21)\\
(H_1^{\mathrm{SL}})_{\mu\nu} &= \frac{1}{2}\langle f_\mu|(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A})|f_\nu\rangle && (22)\\
&= \frac{1}{2}\langle f_\mu|\vec{B}\cdot\frac{1}{2}\vec{l}+i\vec{\sigma}\cdot(\vec{p}\times\vec{A})|f_\nu\rangle && (23)\\
&\rightarrow \frac{1}{2}\langle f_\mu|\vec{B}\cdot\frac{1}{2}\vec{l}+ig_e\vec{s}\cdot(\vec{p}\times\vec{A})|f_\nu\rangle && (24)
\end{aligned}$$

Since a four-component theory based on Eqs. (18) is equivalent to the “matrix form” of the unitary transformation scheme (UTm) as developed in Ref. 74, the performance of Eqs. (18) is expected to be similar to unitarily transformed Hamiltonian for four-component calculations of electronic g-factors. The use of a magnetic balance condition thus is optional for four-component calculations of first-order magnetic properties, although it is necessary to use a magnetic balance condition for four-component calculations of second-order magnetic properties using finite basis-set representation. On the other hand, the X2C transformation of magnetic-field-dependent four-component Hamiltonian requires a full solution of the one-electron Dirac equation. Therefore, the use of Eqs. (18) in the X2C transformation introduces noticeable errors in a finite basis-set representation compared with the use of unitarily transformed Hamiltonian [Eqs. (10) and (12)], which will be demonstrated using numerical results in Section IV.

III. COMPUTATIONAL DETAILS

While the formulations in the previous section are generally applicable for calculations of g-factors, the present calculations are focused on a parallel component $G_{||}$ of a linear molecule. $G_{||}$ is defined as as a first derivative of the electronic energy with respect to the z-component of the field strength of a uniform external magnetic field[13,51]

$$G_{||} = \frac{2}{\Omega}\frac{\partial E_{\mathrm{ele}}}{\partial B_z}|_{\vec{B}=0}, \tag{25}$$

in which Ω represents the z-component of total angular momentum. The CFOUR program package[79,80,91–93] has been used in all the computations presented here. We compare X2CAMF KUHF results for $G_{||}$ in the $^3\Delta_1$ states of HfF$^+$, ThF$^+$, and ThO using the unitarily transformed Hamiltonian with the corresponding four-component Dirac-Coulomb results to demonstrate the accuracy of the X2CAMF scheme. The experimental equilibrium bond lengths of 1.809 Å,[40] 1.987 Å,[43] and 1.840 Å[39] for HfF$^+$, ThF$^+$, and ThO have been used in these calculations. The uncontracted correlation-consistent triple-zeta basis sets for Th (33s29p20d13f4g1h),[94] F (10s5p2d1f) and O (10s5p2d1f)[95] as well as the uncontracted Dyall's valence triple-zeta basis set for Hf (30s24p15d11f2g)[96] have been used in these KUHF calculations.

X2CAMF-KUHF-based coupled-cluster singles and doubles (CCSD)[97] and CCSD augmented with a non-iterative triples correction [CCSD(T)][98] calculations have then been performed to obtain electron-correlation contributions to $G_{||}$'s using the recent implementation of analytic X2CAMF-CCSD and CCSD(T) gradients.[80] Basis-set effects have been studied using systematically enlarged basis sets. The uncontracted Dyall's triple-zeta (30s24p15d11f2g) and quadruple-zeta (34s30p19d13f3g2h) basis sets for Hf have been used and are denoted as the TZ and QZ sets. The s-, p-, d-, f-type functions of the QZ set are further combined with g-, h-, and i-type correlating functions of the cc-pwCV5Z-PP basis set[99] to form a 5Z (34s30p19d13f4g3h2i) set. Correlation-consistent polarized core-valence triple- and quadruple-zeta basis sets for Th[94] have been used in the fully uncontracted form and are denoted as the TZ (33s29p20d13f4g1h) and QZ (37s34p24d15f7g4h1i) sets. Note that, since the basis sets are fully decontracted, the exponents of the d- and f-type core-correlating functions of the cc-pwCVTZ set fall into the range of the primitive functions and thus are removed. The uncontracted cc-pVTZ, cc-pVQZ, and cc-pV5Z of O and F have been used for O and F and are denoted as TZ, QZ, and 5Z sets, respectively. Forty-six core electrons of Hf (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d electrons of Hf), sixty core electrons of Th (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f electrons of Th), the F and O 1s orbitals, and virtual orbitals with orbital energies greater than 100 Hartree have been kept frozen in CCSD and CCSD(T) calculations.

We also compare KUHF- and KROHF-based calculations for electronic g-factors of ThO, ThF^+, ThF, and ThCl using the uncontracted ANO-RCC basis sets.[100,101] We have performed X2CAMF-KROHF calculations using fractional occupation numbers to obtain the orbitals, i.e., we have used an occupation number of 0.5 for the open-shell $\sigma_{1/2}$ and $\delta_{3/2}$ orbitals in these HF calculations. The equilibrium bond lengths of 2.029 Å and 2.501 Å determined in the experimental study[52] have been used for ThF and ThCl. Because we have not implemented analytic CC gradients for the Kramers restricted open-shell HF reference functions yet, the electron-correlation contributions have been obtained using an orbital-unrelaxed finite-difference scheme. We have carried out finite differentiation of KUHF- and KROHF-CCSD correlation energies with the magnetic-field perturbation included in the

Fock matrices. A two-point formula with field strengths of ±0.001 a.u have been used.

IV. RESULTS AND DISCUSSIONS

A. Benchmark studies of the accuracy of the X2CAMF scheme, electron-correlation contributions, and basis-set effects

As shown in Table I, the X2CAMF Kramers unrestricted Hartree-Fock results are in close agreement with the corresponding results obtained from the parent four-component Dirac-Coulomb calculations. The largest discrepancy amounts to only 0.0002 in the case of ThF^+. This demonstrates the reliability of the X2CAMF scheme. The inclusion of the QED correction to the free-electron g-factor plays an important role in these calculations. Since the absolute values of g-factors for these molecular states are small, the X2CAMF calculation using $g_e = 2$ as given in Table I introduces significant errors. The results obtained from X2CAMF calculations using kinetic balance basis sets without the field-dependent unitary transformation are summarized as "X2CAMF(KB)" in Table I. They exhibit around 10% deviation compared with the X2CAMF results using the unitary transformation as well as with the four-component Dirac-Coulomb results. Although the errors are not too large, it underlies the importance of using a magnetic balance condition in X2C calculations of electronic g-factors.

As expected, the electron correlation contributions play significant roles for calculations of $G_{||}$. As shown in Table II, in the case of HfF^+, the electron-correlation contribution (the difference between CCSD(T) and HF results in Table II) amounts to more than 50% of the total value. For ThF^+ and ThO, the effects are even more important, e.g., the HF results for ThO have a wrong sign and the major cancellation between HF and electron-correlation contributions renders it challenging to obtain accurate results. On the other hand, since the triples correction [the difference between CCSD(T) and CCSD results] amount to only 0.001, it is likely that high-level correlation contributions beyond CCSD(T) is smaller and the treatment of electron correlation has converged to a reasonable accuracy at the CCSD(T) level of theory.

The basis-set effects have been taken into account by using systematically enlarged basis sets and performing extrapolation to estimate the basis-set-limit values for the electron-correlation contributions.[102] The basis-set effects beyond triple-zeta basis sets play a relatively minor role in these calculations of electronic g-factors. The basis-set errors of triple-zeta basis sets amount to around 10% of the total value for HfF^+ and ThF^+. In the case of ThO, the ratio is around 20% because of the major cancellation between HF and electron-correlation contributions, although the absolute value of 0.0008 remains small.

B. Comparison between KUHF- and KROHF-based calculations

As spin-dependent properties, the computed electronic g-factors are expected to be sensitive to the breaking of Kramers symmetry. As shown in Table III, the Kramers unrestricted calculations show a relativistic analogue of spin contamination. In the calculations for the $X^2\Delta_{3/2}$ states of ThF and ThCl, the KUHF values of $G_{||}$ amount to 0.810 and 0.776, which substantially deviate from the spin-free value of 1.0 and the experimental values of 1.075 and 1.130. The ROHF values of 1.024 and 1.068 are significantly closer to the experimental values and also reproduce the relative shift between ThF and ThCl fairly well. On the other hand, the inclusion of electron correlation at the CCSD level largely corrects the contamination problem in KUHF-based calculations. The KUHF-CCSD and KROHF-CCSD calculations have produced similar results for ThF and ThCl. We have similar observation for ThF^+ and ThO. Namely, KUHF and KROHF results differ substantially, while the KUHF-CCSD and KROHF-CCSD results closely agree with each other.

The KROHF results for ThF^+, ThF, and ThCl are quite close to the KROHF-CCSD ones; the electron-correlation contributions in KROHF-CCSD calculations are smaller than those in KUHF-CCSD calculations for these molecules. On the other hand, the electron-correlation contribution obtained from the KROHF-CCSD calculation for ThO is even larger than that in the corresponding KUHF-CCSD calculation; it is in general necessary to include electron correlation to obtain qualitatively correct results for electronic g-factors. Nevertheless, the ROHF calculations for electronic g-factors seem to perform better than the KUHF calculations in general. It would also be of interest to develop relativistic analogues of spin-adapted CCSD methods[103–106] or the partially spin-adapted[107,108] and spin-restricted[109,110] CCSD.

C. Comparison with previous calculations and experiments

The computed $G_{||}$ values in the present work are in good agreement with previous computations. The present results of 0.0117 and 0.035 for HfF^+ and ThF^+ are consistent with the values of 0.0115/0.0127 and 0.034 reported in Refs.[13,15,51]. The computed value of 0.0117 for HfF^+ is in close agreement with the experimental value of 0.0118. The computed value of 0.035 in the case of ThF^+ is in reasonable agreement with but underestimate the measured value of 0.048(2). It might be interesting to investigate the contributions from the rotational g-factor, which has been demonstrated to contribute about 6% to the g-factor of ThO by Petrov *et al.*[48]

The computed value of 0.0040 for ThO amounts to around half of the experimental value of 0.0088(10). We have also studied the contribution from the Gaunt term to this g-factor (Table I) and found that its magnitude is smaller than 0.0002. Considering the convergence of electron-correlation and basis-set effects and the small magnitude of the Gaunt-term contribution, this discrepancy of a factor of 2 between computation and experiment seems to merit further study. The present value of 0.0040 for ThO is also smaller than the previous computational values of 0.007 or 0.005 in Ref.[50]. The calculations presented in Table II have used Kramers unrestricted HF wave functions as the reference functions, while the values of 0.007 and 0.005 have been obtained using averaged of configuration HF or the orbitals obtained from HF calculations of the closed-shell $^1\Sigma_1$ state. Our present KROHF-CCSD results in Table III are consistent with the corresponding CCSD value of 0.003 in Ref.[50]. On the other hand, the calculations in Ref.[50] have provided a (T) correction of 0.003, which are significantly larger than the (T) correction of 0.001 in the KUHF-CCSD(T) calculations in Table II. These deviations necessitate further study to include high-level correlation contributions beyond CCSD(T)[111,112] in the present calculations.

V. SUMMARY AND OUTLOOK

A simple scheme based on a magnetic-field-dependent unitary transformation of the Dirac Hamiltonian has been developed to include the quantum electrodynamics correction to the free-electron g-factor in four-component and exact two-component (X2C) calculations of electronic g-factors. The accuracy of the X2C approach is validated with comparison with the corresponding results obtained using the parent four-component method. It will be of interest to combine computed and measured electronic g-factors to analyze the compositions of the excited-state wave functions in heavy-atom-containing small molecules being used in the eEDM search, for example, to understand the coupling between excited states of YbF[55] and YbOH. It might also be of interest to extend the applicability of the present formulation to larger molecules by using gauge-including atomic orbitals.

VI. ACKNOWLEDGEMENT

The work has been supported by the National Science Foundation, under Grant No. PHY-2011794. The computations have been carried out at Advanced Research Computing at Hopkins (ARCH) core facility (rockfish.jhu.edu), which is supported by the National Science Foundation (NSF) under grant No. OAC-1920103.

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TABLE I. $G_{||}$ for the $^3\Delta_1$ states of HfF^+, ThF^+, and ThO computed at the Kramers unrestricted Hartree-Fock level using uncontracted correlation-consistent triple-zeta basis sets for Th, F and O as well as the uncontracted Dyall's valence triple-zeta basis set for Hf. A g_e value of 2.002319304362 has been used throughout unless noted otherwise.

	HfF^+	ThF^+	ThO
X2CAMF	0.00467	0.0074	-0.0057
X2CAMF($g_e = 2$)	0.00697	0.0097	-0.0034
X2CAMF(KB)	0.00397	0.0067	-0.0063
Dirac-Coulomb	0.00465	0.0072	-0.0058
Dirac-Coulomb-Gaunt	0.00426	0.0071	-0.0059

TABLE II. $G_{||}$ for the $^3\Delta_1$ states of HfF^+, ThF^+, and ThO computed using the X2CAMF scheme and comparison with experimental values as well as previous calculations. A g_e value of 2.002319304362 has been used in these calculations.

	HfF^+	ThF^+	ThO
HF/TZ	0.0047	0.0074	-0.0057
CCSD/TZ	0.0097	0.0326	0.0021
CCSD(T)/TZ	0.0101	0.0305	0.0032
HF/QZ	0.0045	0.0072	-0.0057
CCSD/QZ	0.0103	0.0371	0.0027
CCSD(T)/QZ	0.0107	0.0330	0.0037
HF/5Z	0.0045	/	/
CCSD/5Z	0.0108	/	/
CCSD(T)/5Z	0.0112	/	/
CCSD(T)/∞Z	0.0117	0.0348	0.0040
Experiment	0.0118[31,51]	0.048(2)[34]	0.0088(10)[48]
Previous theory	0.0115[51], 0.0127[15]	0.034[13]	0.007/0.005[50]

TABLE III. $G_{||}$ for the $^3\Delta_1$ states of ThF^+, and ThO and the $X^2\Delta_{3/2}$ states of ThF and ThCl computed using the X2CAMF scheme and the uncontracted ANO-RCC basis sets. A g_e value of 2.002319304362 has been used in these calculations.

		ThF^+	ThO	ThF	ThCl
KUHF	HF	0.0073	-0.0057	0.810	0.776
	CCSD	0.0298	0.0016	1.051	1.098
KROHF	HF	0.0215	0.0123	1.024	1.068
	CCSD	0.0308	0.0019	1.045	1.086
Experiment		0.048(2)[34]	0.0088(10)[48]	1.075(4)[52]	1.130(4)[52]