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# The Cotton-Mouton effect of neon and argon: A benchmark study using highly correlated coupled cluster wave functions

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The Cotton-Mouton effect (magnetic field induced linear birefringence) has been studied for neon and argon using state-of-the-art coupled cluster techniques. The coupled cluster singles, doubles and triples (CCSDT) approach has been used to obtain static benchmark results and the CC3 model with an approximate treatment of triple excitations to obtain frequency-dependent results. In the case of neon the effect of excitations beyond triples has also been estimated via coupled cluster calculations including quadruple excitations (CCSDTQ), pentuple excitations (CCSDTQP), etc. up to the full configuration-interaction level. The results obtained for the anisotropy of the hypermagnetizability $\Delta\eta(\omega)$, the molecular property that determines the magnetic field induced birefringence of spherically symmetric systems, are $\Delta\eta=2.89$ a.u. for neon and $\Delta\eta=24.7$ a.u. for argon, with a negligible effect of frequency dispersion. For neon we could estimate an absolute error on $\Delta\eta$ of 0.1 a.u. The accuracy of these results surpasses that of recently reported experimental data. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1805491]

## I. INTRODUCTION

When linearly polarized electromagnetic radiation traverses a region of space where a magnetic induction field perpendicular to its direction of propagation exists, it acquires an ellipticity. This is the result of a linear birefringence, or anisotropy of the refractive index, $\Delta n=n_{\parallel}-n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ refer to the refractive indices parallel and perpendicular to the applied magnetic field. The effect was first observed in fluids almost a century ago, and has been given the name Cotton-Mouton effect (CME), after the scientists who first performed a systematic detailed investigation.[1–3] A fundamental contribution to the theoretical understanding of the effect was given by Buckingham and Pople.[4] A comprehensive discussion of the theoretical foundations and practical aspects, including a thorough account of the literature from the discovery of the effect to the end of last century can be found in Ref. 5.

During the last ten to fifteen years there has been a growing interest in the CME, both theoretically and experimentally. The CME of helium was calculated in 1991 by Bishop and Pipin,[6,7] using explicitly correlated wave functions, giving an accuracy that exceeded by several orders of magnitude that of an experiment performed the same year by Cameron and co-workers.[8] The CME of neon was measured in 1991 also by the same group.[9] The following year Bishop and Cybulski,[10] using second-order Møller-Plesset perturbation theory (MP2), and Jaszuński and co-workers,[11] using multiconfigurational self-consistent-field (MCSCF) response, calculated an effect more than twice as large as the one observed by Cameron and co-workers. The CME of argon has been measured by Carusotto and co-workers[12] and it is in good agreement with both the MP2 calculation of Bishop and Cybulski[10] and the MCSCF response estimate of Jaszuński, Jørgensen, and Rizzo.[13]

Recently Muroo and co-workers have performed a new experimental investigation of the CME for helium, neon, and argon.[14] Previous data for helium and argon were confirmed. For neon the discrepancy between calculations and experiment was only partly resolved as the reported experimental results still had large error bars. The large difference between the experimental and the calculated CME for neon has thus been present for the last thirteen years, a rather unique occurrence in a field where theory and experiment have otherwise reached reasonable agreement.

In the last two decades noticeable advancements have been made in *ab initio* methods for studying higher-order nonlinear optical response properties. Coupled cluster (CC) theory,[15–19] in particular, nowadays represents an accurate and powerful tool for predicting the properties for systems of increasing complexity. The development of hierarchies of electronic structure models and basis sets has allowed to efficiently monitor the effect of multiple excitations in the cluster amplitudes, and coupled cluster response theory[20] has evolved to become an extremely appealing and accurate method to account for electron correlation effects in the cal-

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culation of frequency-dependent higher-order properties. Furthermore, CC models which consider triple excitations have been demonstrated to be the methods of choice for obtaining quantitative accuracy. Among these, CC singles and doubles (CCSD) (Ref. 21) with a noniterative correction for triple excitations—CCSD(T) (Ref. 22)—is currently the most popular choice for structural studies and prediction of static properties. For frequency-dependent properties, however, iterative approximations such as the CC3 model[23,24] have been proven an adequate approximation to the full treatment of triple excitations at the CCSD triples (CCSDT) level.[25–27]

Successful efforts have been made to provide analytical derivatives for models beyond the CCSD and CCSD(T) level of theory.[28–30] For example, in Ref. 30 highly accurate nuclear magnetic shieldings have been obtained for a series of diatomic and triatomic molecules by means of analytic second derivatives for the full CCSDT model. Extension to first and second analytic derivatives for general coupled cluster schemes[31,32] within the framework of a string-based many-body formalism[33] represents the most recent progress.

In the present contribution, we report a determination of the CME of neon and argon using the Hartree-Fock self-consistent-field (HF-SCF), MP2, CCSD, CCSD(T), CC3, and CCSDT electronic structure models by finite (electric) field techniques based on the analytic determination of magnetizabilities.[34] The use of various hierarchies of correlation-consistent basis sets up to quintuple-$\zeta$ level ensures the benchmark quality of the results. The effect of excitation levels beyond triples is analyzed in some detail for neon, where for basis sets of d-aug-cc-pVDZ quality static CME results with full inclusion of quadruple [CCSDT quadruples (CCSDTQ)] and quintuple excitations [CCSDTQ pentuples (CCSDTQP)] in the cluster operator as well as at the full configuration-interaction (FCI) level were obtained. For the d-aug-cc-pVTZ basis, results of corresponding CCSDTQ calculations are also given. It should be noted that these are the first calculations where fourth derivatives of higher-order CC as well as FCI energies are computed.

CC3 first-order properties,[28,35,36] excitation energies,[37–39] transition moments,[39] linear,[40–42] and quadratic[41,43–45] response properties have been calculated at several instances where a proper account of electron correlation effects has proven to be of importance. Very recently the first implementation of CC3 cubic response functions has been completed.[46,47] In the present work CC3 quadratic and cubic response theory is used for a detailed study of the dispersion of the CME. Calculations have been carried out for a wavelength of 632.8 nm, employing basis sets of up to t-aug-cc-pV5Z quality for neon and d-aug-cc-pV5Z quality for argon. As a result, we obtain estimates for the CME of neon and argon gas where electron correlation and dispersion effects are accounted with an accuracy higher than currently provided by experiment.

## II. THEORY

In a Cotton-Mouton experiment the observable is the ellipticity acquired by a linear polarized light beam in the birefringent medium. For weak field strengths, the ellipticity is proportional to the anisotropy of the refractive index $\Delta n = n_{\parallel} - n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ refer, respectively, to the refractive indices parallel and perpendicular to the external applied magnetic induction field **B**.

Buckingham and Pople[4] showed that the anisotropy of the refractive index in a diamagnetic system can be expressed as

$$\Delta n = \frac{1}{4\pi\epsilon_0}\frac{27B^2}{2V_m}{}_mC(\omega), \tag{1}$$

if $V_m$ is the molar volume, $\omega$ the laser frequency, and $\epsilon_0$ the vacuum permittivity. For closed shell atoms the so-called Cotton-Mouton constant ${}_mC(\omega)$ becomes[5] ($z$ arbitrary)

$${}_mC(\omega) = \frac{2\pi N_A}{27}\Delta\eta(\omega) = \frac{2\pi N_A}{27}[\eta_{zzzz}(\omega) - \eta_{zzxx}(\omega)], \tag{2}$$

where $N_A$ is Avogadro's number and $\Delta\eta$ is the anisotropy of the hypermagnetizability $\eta$. The tensor $\eta$ can be defined through a perturbative expansion of the frequency-dependent electric dipole polarizability $\alpha(-\omega;\omega)$ in the external (static) magnetic induction field **B**.[48] The second-order term in the expansion of $\alpha(-\omega;\omega)^{\mathbf{B}}_{\alpha\beta} - \alpha(-\omega;\omega)^{0}_{\alpha\beta}$ determines the hypermagnetizability $\eta$:

$$\eta(-\omega;\omega,0,0)_{\alpha\beta\gamma\delta} = \frac{\partial^2\alpha(-\omega;\omega)_{\alpha\beta}}{\partial B_\gamma \partial B_\delta}. \tag{3}$$

It contains two contributions,[5,49] a paramagnetic ($\eta^p_{\alpha\beta\gamma\delta}$) and a diamagnetic ($\eta^d_{\alpha\beta\gamma\delta}$) term, which, in the notation of analytic response theory,[50,51] can be written as

$$\eta^p_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0) = -\langle\langle \mu^e_\alpha;\mu^e_\beta,\mu^m_\gamma,\mu^m_\delta\rangle\rangle_{\omega,0,0}, \tag{4}$$

$$\eta^d_{\alpha\beta\gamma\delta}(-\omega;\omega,0) = \langle\langle \mu^e_\alpha;\mu^e_\beta,\xi^d_{\gamma\delta}\rangle\rangle_{\omega,0}, \tag{5}$$

$$\eta_{\alpha\beta\gamma\delta}(\omega) = \eta^p_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0) + \eta^d_{\alpha\beta\gamma\delta}(-\omega;\omega,0), \tag{6}$$

i.e., as a combination of a quadratic and a cubic response function. The electric dipole operator $\mu^e_\alpha$, is given as

$$\mu^e_\alpha = -\sum_i r^G_{i,\alpha}, \tag{7}$$

where $r^G_{i,\alpha}$ is the $\alpha$ component of the position operator for electron $i$, and the superscript $G$ denotes the choice of the gauge origin, $r^G_{i,\alpha} = r_{i,\alpha} - R_{G,\alpha}$ if $R_{G,\alpha}$ is the $\alpha$ component of the gauge origin. The magnetic dipole operator $\mu^m_\alpha$ is given as

$$\mu^m_\alpha = -\tfrac{1}{2}\sum_i l^G_{i,\alpha}, \tag{8}$$

where $l^G_{i,\alpha} = \epsilon_{\alpha\beta\gamma} r^G_{i,\beta} p_{i,\gamma}$ is the $\alpha$ component of the angular momentum operator for electron $i$, $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita alternating tensor and $p_{i,\gamma}$ is the $\gamma$ component of the linear momentum operator. Finally, $\xi^d_{\alpha\beta}$ denotes the diamagnetic magnetizability operator

$$\xi^d_{\alpha\beta} = -\tfrac{1}{4}\sum_i [(r^G_i)^2\delta_{\alpha\beta} - r^G_{i,\alpha} r^G_{i,\beta}]. \tag{9}$$

The change of the anisotropy $\Delta\eta(\omega)$ when the origin changes from $R_G$ to $R'_G = R_G + O_G$ has been discussed, for example,

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by Cybulski and Bishop.[52] The CME can easily be seen to be gauge-origin independent following the procedure outlined in Ref. 53 and discussed in detail in Ref. 54. The interested reader will find a discussion of this aspect in the Appendix.

The dependence on the gauge origin is nonphysical and vanishes for exact states, whereas it occurs in general in approximate calculations, where finite basis sets are used. The gauge-origin dependence can be removed in finite basis-set calculations by the use of gauge-including atomic orbitals (GIAO's), also known as London atomic orbitals (LAOs).[55–57] For atoms, choosing the gauge-origin at the nucleus is equivalent to the use of GIAO's.

Equation 3 provides a first clue on a possible pathway to the *ab initio* study of the CME in isolated systems. The frequency-dependent electric dipole polarizability can be computed in the presence of the perturbation due to a magnetic induction field, and the hypermagnetizability is obtained by finite difference. This approach, applied by Cybulski and Bishop in Ref. 52, unfortunately resorts to complex algebra, as the perturbation is purely imaginary, and is not available in a more general context of standard electronic structure codes where wave functions are usually constrained to be real. We therefore use a different finite-field approach introduced in the CME studies in Ref. 34, where the magnetizability $\xi$ is calculated in the presence of the external electric field $\mathbf{F}$. The static hypermagnetizability $\eta_{\alpha\beta\gamma\delta}$ is then obtained using numerical differentiation as

$$\eta_{\alpha\beta\gamma\delta}=\left(\frac{\partial^2\xi_{\gamma\delta}}{\partial F_\alpha \partial F_\beta}\right)\Bigg|_{\mathbf{F}=0}. \tag{10}$$

This technique is exploited in the present work to obtain the static hypermagnetizabilities from magnetizabilities obtained as analytical second derivatives for HF-SCF, MP2, CCSD, CCSD(T), CC3, CCSDT, CCSDTQ, and higher excitation wave functions. In these calculations the derivatives are—unless noted differently—obtained with orbital relaxation effects included, i.e., the Hartree-Fock orbitals are allowed to relax to the applied fields. This approach is used in the following to obtain benchmark values for the static limit of the birefringence.

The magnetic field induced birefringence may also be obtained from analytic calculations of the frequency-dependent quadratic and cubic response functions in Eqs. (5) and (4). The analytic evaluation of the quadratic response function has been available since the beginning of the 1990s at the HF-SCF and MCSCF level,[58] and later at the CC2, CCSD,[59] CC3,[43] and DFT (Ref. 60) levels, whereas cubic response was first coded at HF-SCF and MCSCF level[61] in 1996, and is nowadays available at the CC2, CCSD,[62] and DFT levels.[63] In the present work, we employ a newly implemented analytical quadratic and cubic response code[46,47] for CC3 to obtain the frequency-dependent hypermagnetizability anisotropies. In these calculations, orbital relaxation is not included to avoid artifacts from the uncorrelated frequency-dependence of the Hartree-Fock orbitals.

For atoms the evaluation of the CME in terms of quadratic and cubic response functions may be reduced to the calculation of the Cauchy moments $S(-2n)$ and the dipole-dipole-quadrupole hyperpolarizability dispersion coefficients $B(2n)$.[4,6,7] This technique is not used here, as the Cauchy Moments $S(-2n)$ and the dipole-dipole-quadrupole dispersion coefficients $B(2n)$, are currently only available for the CC2 and CCSD models.[64,65]

## III. COMPUTATIONAL DETAILS

As described above, the calculations of the static hypermagnetizabilities of neon and argon have been carried out at the HF-SCF, MP2, CCSD, CCSD(T), CC3, and CCSDT levels using analytically evaluated magnetizabilities[30,32,66–68] together with a finite electric field approach. In these calculations, the molecular orbitals are allowed to relax with respect to both the electric and the magnetic field. Particular care has been taken to ensure numerical stability. While in previous studies of hypermagnetizabilities[34,69,70] an electrical field strength of 0.01 a.u. was used and derivatives were obtained using a simple three-point procedure, field strengths of 0.0001 a.u. together with sufficiently tight convergence thresholds both in the HF-SCF and the coupled cluster calculations are employed in the present work.[71]

As a result the calculated hypermagnetizabilities are numerically stable to at least four decimal digits for neon, and at least three decimal digits for argon. The finite-field calculations were carried out using a local version of the ACESII program package,[72] while the CCSDTQ, CCSDTQP, and FCI calculations were performed using a string-based many-body code[31–33] interfaced to ACESII.

Both the static and frequency-dependent hypermagnetizabilities were also calculated from analytic quadratic and cubic response functions (for CC methods with unrelaxed orbitals) for HF-SCF, CC2, CCSD, and CC3 using a local version of the DALTON package.[73]

A wide range of correlation consistent basis sets, ranging from double $\zeta$ to quintuple $\zeta$ and from singly augmented to triply augmented, was employed.[74,75] For neon and argon, we present results obtained also with the t-aug-cc-pCVXZ (X = T,Q) core-valence sets.[74–77] Unless otherwise stated, no frozen-core approximation has been used, i.e., all electrons were correlated.

## IV. RESULTS AND DISCUSSION

### A. Neon

In Tables I–IV the results for the static hypermagnetizability components $\eta_{zzzz}$ and $\eta_{zzxx}$ and the anisotropy $\Delta\eta$ are given for neon. In Table I static MP2, CCSD, CCSD(T), CC3, and CCSDT results are given using the orbital-relaxed finite field approach. Table II gives CCSD, CCSDT, CCSDTQ, CCSDTQP, and FCI results using the same finite-field approach and the d-aug-cc-pVDZ and (up to CCSDTQ) d-aug-cc-pVTZ basis sets. In the latter set of calculations the occupation of the $1s^2$ core has been kept frozen. For comparison, orbital-unrelaxed results are also given for the d-aug-cc-pVDZ basis set in Table II.

Tables III and IV report results using the CCS, CC2, CCSD, and CC3 coupled cluster hierarchy based on analytical calculations of the quadratic and cubic response function together with the corresponding analytic HF-SCF values.

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TABLE I. Neon. The static hypermagnetizabilities $\eta_{zzzz}(0;0,0,0)$ and $\eta_{zzxx}(0;0,0,0)$, and the anisotropy $\Delta\eta(0)=\eta_{zzzz}(0;0,0,0)-\eta_{zzxx}(0;0,0,0)$ computed using a finite electric field approach, analytically evaluated magnetizabilities, and orbital-relaxation included.

| | MP2 | | | CCSD | | | CCSD(T) | | | CC3 | | | CCSDT | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Basis | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −1.6220 | −2.1343 | 0.5123 | −1.5472 | −2.0422 | 0.4950 | −1.6054 | −2.1071 | 0.5017 | −1.6401 | −2.1423 | 0.5022 | −1.6128 | −2.1139 | 0.5011 |
| aug-cc-pVTZ | −2.1671 | −3.1330 | 0.9659 | −2.0147 | −2.9465 | 0.9318 | −2.1223 | −3.0754 | 0.9531 | −2.1710 | −3.1284 | 0.9575 | −2.1261 | −3.0788 | 0.9527 |
| aug-cc-pVQZ | −2.6665 | −4.1586 | 1.4921 | −2.4382 | −3.8618 | 1.4235 | −2.5912 | −4.0590 | 1.4677 | −2.6585 | −4.1374 | 1.4789 | −2.5916 | −4.0584 | 1.4668 |
| aug-cc-pV5Z | −2.9501 | −5.0191 | 2.0691 | −2.6719 | −4.6271 | 1.9552 | −2.8562 | −4.8843 | 2.0281 | −2.9374 | −4.9858 | 2.0484 | −2.8541 | −4.8801 | 2.0260 |
| d-aug-cc-pVDZ | −3.6748 | −5.2841 | 1.6093 | −3.4655 | −5.0105 | 1.5450 | −3.6445 | −5.2353 | 1.5908 | −3.7566 | −5.3659 | 1.6094 | −3.6631 | −5.2566 | 1.5935 |
| d-aug-cc-pVTZ | −3.4367 | −5.6705 | 2.2338 | −3.1402 | −5.2559 | 2.1157 | −3.3605 | −5.5606 | 2.2001 | −3.4685 | −5.6962 | 2.2277 | −3.3668 | −5.5672 | 2.2004 |
| d-aug-cc-pVQZ | −3.2336 | −5.8147 | 2.5811 | −2.9119 | −5.3291 | 2.4173 | −3.1315 | −5.6570 | 2.5255 | −3.2345 | −5.7950 | 2.5605 | −3.1325 | −5.6564 | 2.5238 |
| d-aug-cc-pV5Z | −3.0483 | −5.9618 | 2.9135 | −2.7403 | −5.4505 | 2.7102 | −2.9485 | −5.7888 | 2.8403 | −3.0447 | −5.9277 | 2.8830 | −2.9474 | −5.7849 | 2.8375 |
| t-aug-cc-pVDZ | −3.9270 | −5.6555 | 1.7285 | −3.6920 | −5.3463 | 1.6543 | −3.8860 | −5.5927 | 1.7068 | −4.0109 | −5.7421 | 1.7312 | −3.9077 | −5.6190 | 1.7113 |
| t-aug-cc-pVTZ | −3.1159 | −5.9727 | 2.8568 | −2.8408 | −5.5272 | 2.6864 | −3.0470 | −5.8561 | 2.8091 | −3.1508 | −6.0033 | 2.8524 | −3.0533 | −5.8633 | 2.8100 |
| t-aug-cc-pVQZ | −3.0174 | −5.9383 | 2.9210 | −2.7187 | −5.4376 | 2.7189 | −2.9232 | −5.7755 | 2.8522 | −3.0201 | −5.9179 | 2.8978 | −2.9242 | −5.7748 | 2.8506 |
| t-aug-cc-pV5Z | −3.0110 | −5.9749 | 2.9639 | −2.7074 | −5.4607 | 2.7533 | −2.9119 | −5.8006 | 2.8887 | | | | | | |

Table III gives the static and Table IV the corresponding frequency-dependent results for a wavelength of 632.8 nm.

### 1. Basis-set convergence

Since basis-set convergence is similar in the orbital-relaxed and the orbital-unrelaxed calculations and basically independent of the frequency argument of $\eta$, we will discuss this aspect only for the static orbital-relaxed results. In Figs. 1 and 2 the basis-set convergence of the $\eta_{zzzz}$ and $\eta_{zzxx}$ components is shown for the electronic structure methods HF-SCF, MP2, CCSD, CCSD(T), CC3, and CCSDT. For both hyperpolarizability components and for all augmentation levels the convergence is basically monotonic with increasing cardinal number.

For $\eta_{zzzz}$ the singly augmented basis sets converge from above, whereas the doubly and triply augmented basis sets converge from below. In particular the triply augmented basis sets converge fast. From the results in Table I the CCSD(T)/t-aug-cc-pV5Z result may be estimated to be $<0.01$ a.u. away from the basis-set limit result (judged and estimated by the corresponding difference between the X=Q and X=5 result). The basis-set convergence for $\eta_{zzxx}$ is similar to that of $\eta_{zzzz}$, except that the convergence for all augmentation levels is from above. It appears that the CCSD(T)/t-aug-cc-pV5Z result is $<0.03$ a.u. away from the basis-set limit (again judged by the difference between the X=Q and X=5 result). For $\Delta\eta$ we may expect the CCSD(T)/t-aug-cc-pV5Z result to not differ more than $\approx 0.05$ a.u. from the basis-set saturated value.

### 2. Convergence in the electron-correlation treatment

In Table II CCSD, CCSDT, CCSDTQ, CCSDTQP, and FCI results are given for the doubly augmented basis sets with cardinal numbers X=D, T. They clearly show that electron-correlation effects beyond CCSDT can be neglected for the orbital-relaxed approach. For both $\eta_{zzzz}$ and $\eta_{zzxx}$ the difference between the CCSDT/d-aug-cc-pVDZ and FCI/d-aug-cc-pVDZ results is $<0.01$ a.u. and therefore of no importance for the accuracy we are aiming at in this investigation. The CCSDT results may thus be viewed as basically identical to the fully correlated hypermagnetizability results for neon. Comparison of the CCSDT and CCSD results shows that including triples leads to an increase of the anisotropy by 3%–5%, slightly increasing with the cardinal number X and the augmentation level.

### 3. Orbital-relaxed vs orbital-unrelaxed results

Of particular interest in this study is a comparison of orbital-relaxed (Table I) and orbital-unrelaxed (Table III) results. The CCSD orbital-unrelaxed results for both the parallel and perpendicular component of the hypermagnetizability are about 5%–10% larger in absolute terms than their relaxed counterparts. These percentages are approximately five times smaller at the CC3 level.

A further reduction by a factor of 2 appears when triple excitations are rigorously included at the CCSDT level, cf. CCSDT/d-aug-cc-pVDZ results in the orbital-relaxed and orbital-unrelaxed approximations in Table II. Inclusion of

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TABLE II. Neon. The static hypermagnetizabilities $\eta_{zzzz}(0;0,0,0)$ and $\eta_{zzxx}(0;0,0,0)$, and the anisotropy $\Delta\eta(0)=\eta_{zzzz}(0;0,0,0)-\eta_{zzxx}(0;0,0,0)$ computed using a finite electric field approach, analytically evaluated magnetizabilities, and the frozen core approximation.

| | d-aug-cc-pVDZ | | | | | | d-aug-cc-pVTZ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Orbital-relaxed | | | Orbital-unrelaxed | | | Relaxed | | |
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| CCSD | −3.4666 | −5.0121 | 1.5455 | −3.8068 | −5.4205 | 1.6137 | −3.1481 | −5.2679 | 2.1198 |
| CCSDT | −3.6642 | −5.2582 | 1.5939 | −3.6944 | −5.2942 | 1.5997 | −3.3743 | −5.5786 | 2.2043 |
| CCSDTQ | −3.6604 | −5.2536 | 1.5932 | −3.6598 | −5.2531 | 1.5932 | −3.3739 | −5.5782 | 2.2043 |
| CCSDTQP | −3.6571 | −5.2499 | 1.5928 | −3.6566 | −5.2493 | 1.5927 | | | |
| FCI | −3.6568 | −5.2496 | 1.5927 | | | | | | |

higher excitations leads (as expected) to a further decrease in the differences between the orbital-relaxed and-unrelaxed results, see again Table II.[78]

#### 4. All-electron calculation in valence basis sets

The results reported in Table I have been obtained with valence basis sets in the all-electron calculations. This may lead to an unbalanced description of the core effect. For example in all-electron calculations of equilibrium geometries using a cc-pVTZ basis artificially large core effects have been observed.[19] For higher cardinal numbers this artificial large core effect tends to vanish as the description of the core-valence region improves. To investigate the consequences of using valence basis sets in all-electron calculations we report in Table III also all-electron results obtained using the t-aug-cc-pCVTZ and t-aug-cc-pCVQZ core-valence basis sets. For $\eta_{zzzz}$ the difference between all-electron CCSD values using the t-aug-cc-pCVTZ and the t-aug-cc-pVTZ basis sets is only $\approx 0.032$ a.u. For the quadruple-$\zeta$ basis sets (t-aug-cc-pCVQZ and t-aug-cc-pVQZ) the difference lowers to $\approx 0.014$ a.u., i.e. about half of the difference for X=T. For the quintuple-$\zeta$ basis sets we expect the differences to become again smaller.

#### 5. Dispersion

The frequency dispersion of the hypermagnetizability tensor components and of the anisotropy can be determined by comparing the data of Table IV computed for a wavelength of 632.8 nm with the corresponding static results of Table III. Both $\eta_{zzzz}$ and $\eta_{zzxx}$ have for this wavelength a similar and very small frequency dependence. At the CC3/t-aug-cc-pV5Z level the difference between 632.8 nm and the static limit is for $\eta_{zzzz}$ and $\eta_{zzxx}$, respectively, only 0.0634 a.u. and 0.0651 a.u. For the anisotropy (i.e., the difference between these two components) the dispersion thus basically vanishes. The same trend is seen also for the lower-level models in the coupled cluster hierarchy.

The two measurements of the CME of neon reported in the literature have been performed at wavelengths of 514.5 nm (Ref. 9) and 790 nm,[14] respectively. Due to the small effect of dispersion seen at 632.8 nm, the frequency dependence may be also safely neglected for these frequencies.

#### 6. Best estimates for $\Delta\eta$

We will now derive ''best estimates'' for the hypermagnetizability anisotropy aiming at a total accuracy of 0.1 a.u. The CCSDT results were shown to reproduce the FCI results to within 0.01 a.u. for both components of the hypermagnetizability. Our starting point will thus be the CCSDT/d-aug-cc-pV5Z result in Table I, i.e., $\Delta\eta(0)=2.8375$ a.u. To this value we add the difference between the CCSD(T) results in the same table obtained with the t-aug-cc-pV5Z (2.8887 a.u.) and the d-aug-cc-pV5Z (2.8403 a.u.) basis sets. This leads to a value of $\Delta\eta(0)=2.8859$ a.u. Basis set effects beyond t-aug-cc-pV5Z, the largest source of uncertainty in the present study, are significantly below 0.1 a.u. The same is expected for the relativistic effects which have been neglected in the present work. All the other sources of error, correlation effects beyond triples, convergence of orbital-relaxed and orbital-unrelaxed approaches, the fact that valence basis sets were used in all-electron calculations, each estimated to be lower than $\approx 0.01$ a.u., have no significant effect and the final estimate of the static anisotropy $\Delta\eta(0)$ is thus $\approx 2.89$ a.u. with an absolute error that can be conservatively estimated to be of 0.1 a.u. This value should be compared to the CC3/t-aug-cc-pV5Z value of $\approx 2.91$ a.u. in Table III, giving a correlation error in CC3 of $\approx 0.02$ a.u.

As discussed above, the dispersion of the anisotropy can be neglected and our final estimate of the $\Delta\eta$ is thus $\approx 2.89$ a.u. (with an absolute error of 0.1 a.u.) for both the wavelengths of 514.5 and 790 nm.

With the exception of relativistic effect, not considered at this stage, these best estimates should account for all possible contributions to the observable in the CME of neon, and should then be as accurate as it is possible to obtain with current available state-of-the-art techniques.

### B. Argon

The hypermagnetizability results for argon are given in Tables V–VII. Parallel to Table I for neon, Table V includes the static hypermagnetizabilities $\eta_{zzzz}(0;0,0,0)$ and $\eta_{zzxx}(0;0,0,0)$ and the anisotropy $\Delta\eta(0)=\eta_{zzzz}(0;0,0,0)-\eta_{zzxx}(0;0,0,0)$, obtained using a finite-field approach in the MP2, CCSD, CCSD(T), CC3, and CCSDT models. Tables VI and VII include the hypermagnetizabilities $\eta_{zzzz}(-\omega;\omega,0,0)$, $\eta_{zzxx}(-\omega;\omega,0,0)$, and the anisotropy $\Delta\eta(\omega)=\eta_{zzzz}(-\omega;\omega,0,0)-\eta_{zzxx}(-\omega;\omega,0,0)$ obtained for

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TABLE III. Neon. The hypermagnetizabilities $\eta_{zzzz}(-\omega;\omega,0,0)$, $\eta_{zzxx}(-\omega;\omega,0,0)$, and the anisotropy $\Delta\eta(\omega)=\eta_{zzzz}(-\omega;\omega,0,0)-\eta_{zzxx}(-\omega;\omega,0,0)$ computed at HF-SCF, CCS, CC2, CCSD, and CC3 levels using analytic response functions and unrelaxed orbitals for the static limit.

| | HF-SCF | | | CCS | | | CC2 | | | CCSD | | | CC3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −1.1802 | −1.6165 | 0.4363 | −1.3600 | −1.7965 | 0.4365 | −1.8656 | −2.4152 | 0.5496 | −1.6809 | −2.1826 | 0.5017 | −1.6119 | −2.1154 | 0.5035 |
| aug-cc-pVTZ | −1.5597 | −2.3680 | 0.8083 | −1.8282 | −2.6655 | 0.8373 | −2.4936 | −3.5278 | 1.0342 | −2.1980 | −3.1509 | 0.9529 | −2.1268 | −3.0835 | 0.9567 |
| aug-cc-pVQZ | −1.8880 | −3.1024 | 1.2144 | −2.2041 | −3.4716 | 1.2674 | −3.0716 | −4.6704 | 1.5987 | −2.6632 | −4.1286 | 1.4653 | −2.5982 | −4.0719 | 1.4737 |
| aug-cc-pV5Z | −2.0502 | −3.6890 | 1.6388 | −2.3793 | −4.0926 | 1.7134 | −3.4114 | −5.6338 | 2.2224 | −2.9197 | −4.9413 | 2.0216 | −2.8663 | −4.9031 | 2.0369 |
| d-aug-cc-pVDZ | −2.5047 | −3.7148 | 1.2101 | −2.8647 | −4.0978 | 1.2331 | −4.4049 | −6.2002 | 1.7952 | −3.8065 | −5.4201 | 1.6136 | −3.6733 | −5.2745 | 1.6012 |
| d-aug-cc-pVTZ | −2.2813 | −3.9771 | 1.6958 | −2.6145 | −4.3833 | 1.7687 | −4.1113 | −6.5749 | 2.4635 | −3.4496 | −5.6540 | 2.2044 | −3.3841 | −5.5967 | 2.2127 |
| d-aug-cc-pVQZ | −2.1433 | −4.0929 | 1.9496 | −2.4740 | −4.5075 | 2.0335 | −3.8574 | −6.6937 | 2.8363 | −3.1994 | −5.7172 | 2.5178 | −3.1513 | −5.6915 | 2.5402 |
| d-aug-cc-pV5Z | −2.0427 | −4.2186 | 2.1758 | −2.3731 | −4.6376 | 2.2645 | −3.6164 | −6.8202 | 3.2038 | −3.0093 | −5.8343 | 2.8250 | −2.9643 | −5.8220 | 2.8577 |
| t-aug-cc-pVDZ | −2.6324 | −3.8953 | 1.2629 | −2.9929 | −4.2770 | 1.2841 | −4.7559 | −6.7233 | 1.9674 | −4.0607 | −5.7962 | 1.7356 | −3.9207 | −5.6409 | 1.7202 |
| t-aug-cc-pVTZ | −2.0450 | −4.1437 | 2.0986 | −2.3673 | −4.5544 | 2.1870 | −3.7730 | −6.9630 | 3.1901 | −3.1345 | −5.9482 | 2.8137 | −3.0692 | −5.8973 | 2.8280 |
| t-aug-cc-pVQZ | −2.0079 | −4.1626 | 2.1547 | −2.3351 | −4.5787 | 2.2435 | −3.6050 | −6.8469 | 3.2418 | −2.9929 | −5.8341 | 2.8412 | −2.9404 | −5.8118 | 2.8715 |
| t-aug-cc-pV5Z | −2.0240 | −4.2230 | 2.1990 | −2.3543 | −4.6421 | 2.2878 | −3.5656 | −6.8392 | 3.2736 | −2.9735 | −5.8456 | 2.8721 | −2.9268 | −5.8341 | 2.9072 |
| t-aug-cc-pCVTZ | −2.0380 | −4.1348 | 2.0968 | −2.3602 | −4.5457 | 2.1855 | −3.7340 | −6.8985 | 3.1645 | −3.1022 | −5.8943 | 2.7921 | −3.0529 | −5.8703 | 2.8174 |
| t-aug-cc-pCVQZ | −2.0072 | −4.1614 | 2.1543 | −2.3344 | −4.5775 | 2.2430 | −3.5866 | −6.8141 | 3.2275 | −2.9785 | −5.8076 | 2.8292 | −2.9356 | −5.8022 | 2.8667 |

TABLE IV. Neon. The hypermagnetizabilities $\eta_{zzzz}(-\omega;\omega,0,0)$, $\eta_{zzxx}(-\omega;\omega,0,0)$, and the anisotropy $\Delta\eta(\omega)=\eta_{zzzz}(-\omega;\omega,0,0)-\eta_{zzxx}(-\omega;\omega,0,0)$ computed at HF-SCF, CCS, CC2, CCSD, and CC3 levels using analytic response functions, unrelaxed orbitals, and $\lambda=632.8$ nm ($\omega=7.200\,28\times10^{-2}$ a.u.).

| | HF-SCF | | | CCS | | | CC2 | | | CCSD | | | CC3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −1.2029 | −1.6203 | 0.4174 | −1.3852 | −1.8024 | 0.4172 | −1.9102 | −2.4204 | 0.5102 | −1.7200 | −2.1868 | 0.4668 | −1.6487 | −2.1196 | 0.4709 |
| aug-cc-pVTZ | −1.5850 | −2.3765 | 0.7915 | −1.8567 | −2.6770 | 0.8203 | −2.5447 | −3.5417 | 0.9971 | −2.2411 | −3.1625 | 0.9214 | −2.1685 | −3.0945 | 0.9261 |
| aug-cc-pVQZ | −1.9154 | −3.1173 | 1.2018 | −2.2355 | −3.4903 | 1.2548 | −3.1279 | −4.6966 | 1.5686 | −2.7096 | −4.1503 | 1.4407 | −2.6435 | −4.0929 | 1.4494 |
| aug-cc-pV5Z | −2.0812 | −3.7116 | 1.6305 | −2.4146 | −4.1197 | 1.7052 | −3.4757 | −5.6752 | 2.1995 | −2.9719 | −4.9755 | 2.0036 | −2.9175 | −4.9366 | 2.0191 |
| d-aug-cc-pVDZ | −2.5390 | −3.7418 | 1.2027 | −2.9036 | −4.1291 | 1.2256 | −4.4908 | −6.2603 | 1.7696 | −3.8745 | −5.4677 | 1.5932 | −3.7373 | −5.3201 | 1.5828 |
| d-aug-cc-pVTZ | −2.3179 | −4.0100 | 1.6921 | −2.6559 | −4.4210 | 1.7651 | −4.1974 | −6.6459 | 2.4485 | −3.5171 | −5.7098 | 2.1927 | −3.4498 | −5.6515 | 2.2017 |
| d-aug-cc-pVQZ | −2.1807 | −4.1289 | 1.9482 | −2.5162 | −4.5485 | 2.0323 | −3.9434 | −6.7717 | 2.8283 | −3.2663 | −5.7777 | 2.5114 | −3.2170 | −5.7514 | 2.5344 |
| d-aug-cc-pV5Z | −2.0795 | −4.2560 | 2.1765 | −2.4147 | −4.6801 | 2.2654 | −3.6999 | −6.9008 | 3.2009 | −3.0742 | −5.8966 | 2.8224 | −3.0283 | −5.8840 | 2.8557 |
| t-aug-cc-pVDZ | −2.6715 | −3.9308 | 1.2593 | −3.0368 | −4.3171 | 1.2803 | −4.8549 | −6.8092 | 1.9543 | −4.1385 | −5.8624 | 1.7240 | −3.9938 | −5.7040 | 1.7102 |
| t-aug-cc-pVTZ | −2.0818 | −4.1807 | 2.0989 | −2.4088 | −4.5964 | 2.1876 | −3.8616 | −7.0471 | 3.1856 | −3.2033 | −6.0130 | 2.8097 | −3.1362 | −5.9610 | 2.8249 |
| t-aug-cc-pVQZ | −2.0444 | −4.1999 | 2.1555 | −2.3765 | −4.6211 | 2.2446 | −3.6897 | −6.9289 | 3.2393 | −3.0585 | −5.8973 | 2.8388 | −3.0048 | −5.8745 | 2.8697 |
| t-aug-cc-pV5Z | −2.0604 | −4.2605 | 2.2001 | −2.3956 | −4.6847 | 2.2891 | −3.6483 | −6.9201 | 3.2718 | −3.0378 | −5.9081 | 2.8703 | −2.9902 | −5.8962 | 2.9060 |
| t-aug-cc-pCVTZ | −2.0748 | −4.1718 | 2.0971 | −2.4017 | −4.5877 | 2.1860 | −3.8215 | −6.9817 | 3.1602 | −3.1702 | −5.9585 | 2.7884 | −3.1197 | −5.9337 | 2.8141 |
| t-aug-cc-pCVQZ | −2.0437 | −4.1988 | 2.1551 | −2.3758 | −4.6199 | 2.2441 | −3.6706 | −6.8956 | 3.2250 | −3.0436 | −5.8704 | 2.8268 | −2.9999 | −5.8646 | 2.8647 |

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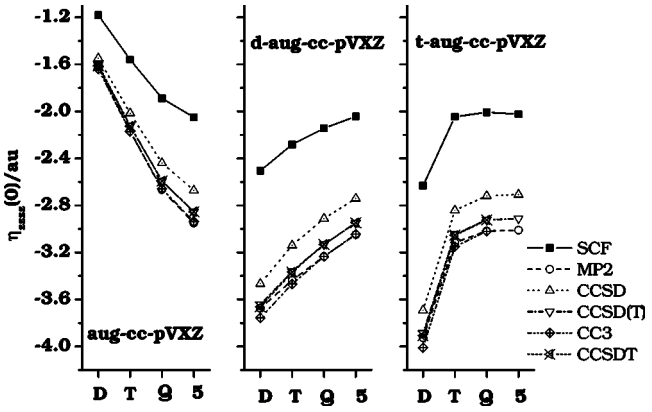



FIG. 1. Neon. The dependence of the hypermagnetizability tensor component $\eta_{zzzz}(0)$ (in a.u.) on the basis set. Cardinal number on the abscissa.

the HF-SCF, CCS, CC2, CCSD, and CC3 hierarchy of analytic response functions in the static case and at a wavelength of 632.8 nm, respectively. As for neon, the results presented in Table V are obtained in an orbital-relaxed approximation, whereas those of Tables VI and VII (except at the HF-SCF level) are obtained using an orbital-unrelaxed approach.

### 1. Basis-set and correlation convergence

The basis-set convergence is similar though somewhat less regular for argon than for neon, see Table V and Figs. 3 and 4 for $\eta_{zzzz}(0)$ and $\eta_{zzxx}(0)$, respectively. The convergence is rather smooth already with doubly augmented basis sets of triple-$\zeta$ quality for $\eta_{zzzz}(0)$, whereas small oscillations can be seen for $\eta_{zzxx}(0)$ as the size of the basis increases. The differences between CCSDT/t-aug-cc-pVQZ and CCSDT/t-aug-cc-pVTZ results are $\approx$0.6 a.u. for $\eta_{zzzz}(0)$, $\approx$1.0 a.u. for $\eta_{zzxx}(0)$, and $\approx$0.4 a.u. for $\Delta\eta(0)$, corresponding to changes in the order of 1%–2% upon increasing the cardinal number at this level.

The basis-set convergence is very similar for all the correlated wave function models. As for neon, absolute values of both tensor components and the anisotropy increase by $\approx$3%–4.5% when going from CCSD to CCSDT. For the t-aug-cc-pVQZ basis set, the increase is of $\approx$0.8 a.u. For argon we have no estimates for the effect of excitations be-

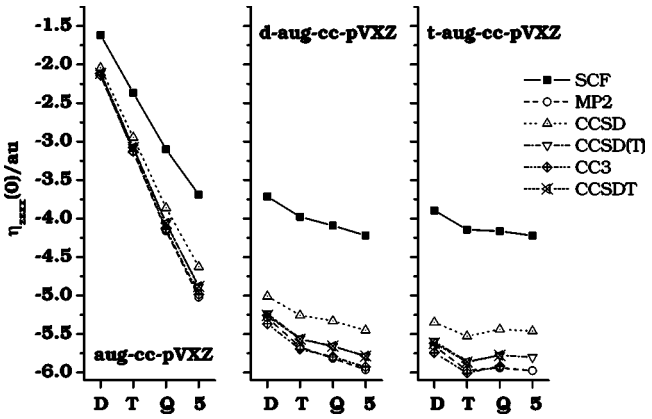



FIG. 2. Neon. The dependence of the hypermagnetizability tensor component $\eta_{zzxx}(0)$ (in a.u.) on the basis set. Cardinal number on the abscissa.

TABLE V. Argon. The static hypermagnetizabilities $\eta_{zzzz}(0;0,0,0)$ and $\eta_{zzxx}(0;0,0,0)$, and the anisotropy $\Delta\eta(0)=\eta_{zzzz}(0;0,0,0)-\eta_{zzxx}(0;0,0,0)$ obtained using a finite electric field approach, analytically evaluated magnetizabilities, and orbital-relaxation included.

| Basis | MP2 | | | CCSD | | | CCSD(T) | | | CC3 | | | CCSDT | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −16.442 | −21.569 | 5.127 | −16.379 | −21.509 | 5.130 | −16.736 | −21.937 | 5.200 | −16.805 | −22.011 | 5.206 | −16.776 | −21.979 | 5.203 |
| aug-cc-pVTZ | −20.619 | −32.058 | 11.439 | −20.011 | −31.420 | 11.409 | −20.662 | −32.279 | 11.617 | −20.780 | −32.423 | 11.642 | −20.689 | −32.315 | 11.626 |
| aug-cc-pVQZ | −24.249 | −41.524 | 17.275 | −22.974 | −39.807 | 16.833 | −23.869 | −41.116 | 17.247 | −24.043 | −41.351 | 17.308 | −23.876 | −41.130 | 17.254 |
| aug-cc-pV5Z | −22.007 | −41.905 | 19.898 | | | | | | | | | | | | |
| d-aug-cc-pVDZ | −31.583 | −44.871 | 13.288 | −30.969 | −44.151 | 13.182 | −32.076 | −45.623 | 13.548 | −32.319 | −45.925 | 13.605 | −32.173 | −45.748 | 13.575 |
| d-aug-cc-pVTZ | −24.088 | −46.466 | 22.378 | −22.904 | −44.801 | 21.896 | −23.931 | −46.439 | 22.509 | −24.141 | −46.746 | 22.605 | −23.959 | −46.482 | 22.524 |
| d-aug-cc-pVQZ | −23.076 | −46.758 | 23.682 | −21.602 | −44.363 | 22.761 | −22.553 | −46.008 | 23.455 | −22.747 | −46.314 | 23.567 | −22.553 | −46.009 | 23.456 |
| t-aug-cc-pVDZ | −31.394 | −44.523 | 13.129 | −30.753 | −43.765 | 13.012 | −31.864 | −45.247 | 13.383 | −32.110 | −45.552 | 13.442 | −31.962 | −45.373 | 13.411 |
| t-aug-cc-pVTZ | −22.239 | −47.575 | 25.336 | −21.166 | −45.813 | 24.647 | −22.119 | −47.522 | 25.404 | −22.317 | −47.845 | 25.528 | −22.147 | −47.567 | 25.420 |
| t-aug-cc-pVQZ | −21.990 | −47.307 | 25.316 | −20.618 | −44.849 | 24.231 | −21.523 | −46.528 | 25.005 | −21.708 | −46.840 | 25.133 | −21.524 | −46.529 | 25.005 |

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TABLE VI. Argon. The hypermagnetizabilities $\eta_{zzzz}(-\omega;\omega,0,0)$, $\eta_{zzxx}(-\omega;\omega,0,0)$, and the anisotropy $\Delta\eta(\omega)=\eta_{zzzz}(-\omega;\omega,0,0)-\eta_{zzxx}(-\omega;\omega,0,0)$ computed at HF-SCF, CCS, CC2, CCSD, and CC3 levels using analytic response functions and unrelaxed orbitals for the static limit.

| | HF-SCF | | | CCS | | | CC2 | | | CCSD | | | CC3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −14.285 | −18.763 | 4.478 | −17.110 | −22.209 | 5.098 | −17.479 | −22.885 | 5.406 | −17.117 | −22.360 | 5.243 | −16.807 | −22.024 | 5.217 |
| aug-cc-pVTZ | −17.736 | −28.082 | 10.346 | −21.152 | −33.142 | 11.990 | −21.841 | −33.676 | 11.835 | −21.078 | −32.759 | 11.682 | −20.770 | −32.426 | 11.656 |
| aug-cc-pVQZ | −20.818 | −36.313 | 15.495 | −24.506 | −42.120 | 17.615 | −25.312 | −43.000 | 17.688 | −24.157 | −41.433 | 17.277 | −23.993 | −41.298 | 17.305 |
| aug-cc-pV5Z | −18.920 | −36.793 | 17.872 | −22.398 | −42.661 | 20.264 | −22.843 | −43.105 | 20.262 | −21.759 | −41.529 | 19.770 | −21.690 | −41.569 | 19.879 |
| d-aug-cc-pVDZ | −26.232 | −37.280 | 11.048 | −30.623 | −42.549 | 11.926 | −33.640 | −47.539 | 13.900 | −32.550 | −46.085 | 13.535 | −32.284 | −45.900 | 13.615 |
| d-aug-cc-pVTZ | −19.858 | −39.384 | 19.527 | −23.354 | −45.311 | 21.957 | −25.418 | −48.390 | 22.972 | −24.184 | −46.663 | 22.479 | −24.090 | −46.685 | 22.595 |
| d-aug-cc-pVQZ | −19.433 | −40.237 | 20.805 | −22.940 | −46.239 | 23.298 | −24.077 | −48.173 | 24.096 | −22.771 | −46.144 | 23.373 | −22.681 | −46.220 | 23.539 |
| d-aug-cc-pV5Z | −18.839 | −40.783 | 21.944 | −22.311 | −46.808 | 24.497 | −22.943 | −47.998 | 25.056 | −21.747 | −46.054 | 24.307 | −21.722 | −46.298 | 24.576 |
| t-aug-cc-pVDZ | −26.013 | −36.887 | 10.874 | −30.380 | −42.123 | 11.742 | −33.452 | −47.192 | 13.740 | −32.328 | −45.691 | 13.362 | −32.074 | −45.526 | 13.451 |
| t-aug-cc-pVTZ | −18.309 | −40.203 | 21.894 | −21.737 | −46.161 | 24.424 | −23.567 | −49.504 | 25.937 | −22.399 | −47.705 | 25.306 | −22.271 | −47.778 | 25.507 |
| t-aug-cc-pVQZ | −18.532 | −40.668 | 22.136 | −22.005 | −46.685 | 24.680 | −23.011 | −48.710 | 25.699 | −21.762 | −46.643 | 24.881 | −21.647 | −46.744 | 25.097 |
| t-aug-cc-pV5Z | −18.655 | −40.840 | 22.185 | −22.125 | −46.867 | 24.742 | −22.727 | −48.098 | 25.371 | −21.542 | −46.128 | 24.587 | | | |
| t-aug-cc-pCVDZ | −26.041 | −36.882 | 10.841 | −30.410 | −42.120 | 11.710 | −33.273 | −46.920 | 13.647 | −32.114 | −45.370 | 13.256 | −32.018 | −45.421 | 13.402 |
| t-aug-cc-pCVTZ | −18.266 | −39.950 | 21.684 | −21.678 | −45.918 | 24.239 | −23.106 | −48.416 | 25.310 | −21.960 | −46.673 | 24.713 | −22.058 | −47.184 | 25.126 |
| t-aug-cc-pCVQZ | −18.541 | −40.547 | 22.005 | −22.005 | −46.571 | 24.566 | −22.622 | −47.776 | 25.154 | −21.399 | −45.762 | 24.363 | −21.494 | −46.270 | 24.776 |

TABLE VII. Argon. The hypermagnetizabilities $\eta_{zzzz}(-\omega;\omega,0,0)$, $\eta_{zzxx}(-\omega;\omega,0,0)$, and the anisotropy $\Delta\eta(\omega)=\eta_{zzzz}(-\omega;\omega,0,0)-\eta_{zzxx}(-\omega;\omega,0,0)$ computed at HF-SCF, CCS, CC2, CCSD, and CC3 levels using analytic response functions, unrelaxed orbitals, and $\lambda=632.8$ nm ($\omega=7.200\,28\times10^{-2}$ a.u.).

| | HF-SCF | | | CCS | | | CC2 | | | CCSD | | | CC3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ | $\eta_{zzzz}$ | $\eta_{zzxx}$ | $\Delta\eta$ |
| aug-cc-pVDZ | −14.825 | −18.872 | 4.048 | −17.731 | −22.406 | 4.676 | −18.241 | −23.053 | 4.811 | −17.870 | −22.511 | 4.641 | −17.549 | −22.164 | 4.615 |
| aug-cc-pVTZ | −18.338 | −28.340 | 10.001 | −21.861 | −33.536 | 11.674 | −22.664 | −34.038 | 11.374 | −21.876 | −33.099 | 11.224 | −21.567 | −32.749 | 11.183 |
| aug-cc-pVQZ | −21.562 | −36.854 | 15.293 | −25.378 | −42.833 | 17.455 | −26.294 | −43.715 | 17.421 | −25.090 | −42.107 | 17.016 | −24.930 | −41.960 | 17.030 |
| aug-cc-pV5Z | −19.674 | −37.357 | 17.683 | −23.276 | −43.399 | 20.123 | −23.817 | −43.843 | 20.026 | −22.682 | −42.222 | 19.540 | −22.626 | −42.257 | 19.631 |
| d-aug-cc-pVDZ | −27.152 | −38.093 | 10.941 | −31.686 | −43.528 | 11.842 | −34.988 | −48.720 | 13.732 | −33.846 | −47.202 | 13.356 | −33.571 | −47.009 | 13.437 |
| d-aug-cc-pVTZ | −20.717 | −40.196 | 19.479 | −24.347 | −46.305 | 21.958 | −26.621 | −49.515 | 22.894 | −25.327 | −47.720 | 22.393 | −25.241 | −47.743 | 22.502 |
| d-aug-cc-pVQZ | −20.300 | −41.081 | 20.780 | −23.944 | −47.270 | 23.326 | −25.238 | −49.296 | 24.058 | −23.860 | −47.188 | 23.328 | −23.781 | −47.269 | 23.488 |
| d-aug-cc-pV5Z | −19.695 | −41.641 | 21.946 | −23.302 | −47.856 | 24.554 | −24.054 | −49.108 | 25.054 | −22.793 | −47.090 | 24.297 | −22.785 | −47.346 | 24.560 |
| t-aug-cc-pVDZ | −26.954 | −37.726 | 10.772 | −31.465 | −43.128 | 11.663 | −34.839 | −48.426 | 13.586 | −33.659 | −46.853 | 13.194 | −33.396 | −46.681 | 13.284 |
| t-aug-cc-pVTZ | −19.149 | −41.060 | 21.911 | −22.709 | −47.201 | 24.492 | −24.749 | −50.698 | 25.950 | −23.520 | −48.826 | 25.306 | −23.400 | −48.903 | 25.503 |
| t-aug-cc-pVQZ | −19.377 | −41.525 | 22.149 | −22.985 | −47.731 | 24.746 | −24.143 | −49.852 | 25.709 | −22.824 | −47.705 | 24.881 | −22.719 | −47.812 | 25.092 |
| t-aug-cc-pV5Z | −19.503 | −41.700 | 22.197 | −23.108 | −47.917 | 24.809 | −23.829 | −49.211 | 25.381 | −22.578 | −47.167 | 24.588 | | | |
| t-aug-cc-pCVDZ | −26.984 | −37.719 | 10.735 | −31.497 | −43.124 | 11.627 | −34.647 | −48.140 | 13.493 | −33.427 | −46.517 | 13.090 | −33.336 | −46.569 | 13.234 |
| t-aug-cc-pCVTZ | −19.016 | −40.838 | 21.823 | −22.652 | −46.949 | 24.297 | −24.256 | −49.568 | 25.311 | −23.050 | −47.754 | 24.704 | −23.178 | −48.286 | 25.108 |
| t-aug-cc-pCVQZ | −19.387 | −41.395 | 22.008 | −22.986 | −47.610 | 24.624 | −23.723 | −48.879 | 25.156 | −22.431 | −46.788 | 24.357 | −22.556 | −47.316 | 24.761 |

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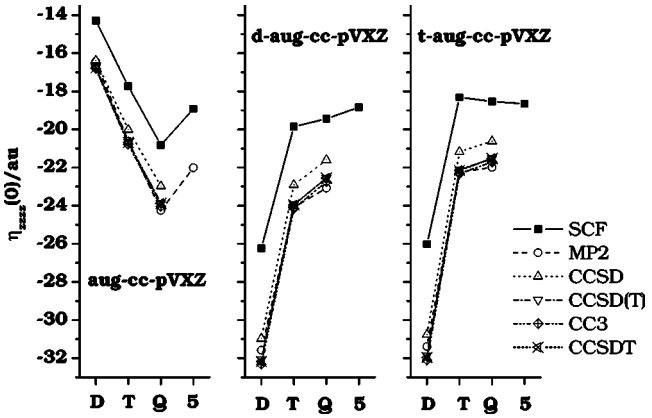



FIG. 3. Argon. The dependence of the hypermagnetizability tensor component $\eta_{zzzz}(0)$ (in a.u.) on the basis set. Cardinal number on the abscissa.

yond triple excitations. As the effect of triple excitations for the anisotropy of the hypermagnetizability is of the same relative size for argon and neon, it is probably justified to assume that for argon the effect of excitations higher than triples is also small and may be neglected.

#### 2. Orbital-relaxed vs orbital-unrelaxed results

As for neon, an analysis can be made for argon concerning the relationships between orbital-relaxed and orbital-unrelaxed results by comparing the CCSD and CC3 columns of Tables V and VI. CCSD orbital-unrelaxed results for the tensor components are on the average 4% to 5% larger than their orbital-relaxed results. Negligible differences, at most 0.2%–0.3%, appear for the CC3 values corresponding to absolute differences not greater than 0.02–0.03 a.u. These are far smaller than the uncertainties resulting from the basis set and correlation treatment. It is thus reasonable to expect that for all practical purposes, CCSDT orbital-relaxed and orbital-unrelaxed results are essentially identical.

#### 3. All-electron calculation in valence basis sets

For argon we have, as for neon, performed all-electron calculations with triply augmented valence and core-valence sets, see Tables VI and VII. The differences between the results in core-valence and valence basis sets decrease when increasing the cardinal number from T to Q. At the CC3 level, the difference between the t-aug-cc-pCVTZ results and t-aug-cc-pVTZ is $\approx 0.38$ a.u. for $\Delta\eta$. For the corresponding quadruple-$\zeta$ basis sets the difference lowers slightly to $\approx 0.32$ a.u. For all wave function models, the use of core-valence correlation consistent sets leads to a decrease in the absolute value of the hypermagnetizability anisotropy.

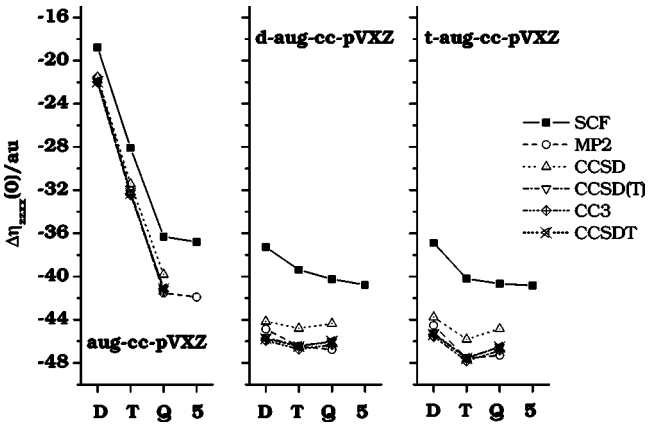



FIG. 4. Argon. The dependence of the hypermagnetizability tensor component $\eta_{zzxx}(0)$ (in a.u.) on the basis set. Cardinal number on the abscissa.

#### 4. Dispersion

The frequency dispersion of the hypermagnetizability tensor components and of the anisotropy can be discussed by comparing the analytic response data of Table VII, computed at a wavelength of 632.8 nm, with those of Table VI. The parallel component changes by at most $\approx 5\%$, and the perpendicular component by $\approx 2.5\%$ for basis sets of reasonable good quality and are rather independent of the electronic structure model. Once again, the anisotropy, due to a cancellation of the contributions to dispersion, is basically unaffected. Thus for the d-aug-cc-pV5Z basis set, at the CC3 level, the increase of the anisotropy of the hypermagnetizability when going from $\lambda = \infty$ to $\lambda = 632.8$ nm is only 0.016 a.u., corresponding to about 0.065%.

For argon, as for neon, two measurements have been reported for the CME, one at 514.5 nm (Ref. 12) and one at 790 nm.[14] Using the same arguments as for neon, the frequency dispersion can be neglected when comparing the present results with experiment.

#### 5. Best estimates

Our best estimate for the static hypermagnetizability anisotropy is obtained by adding to the CCSDT/t-aug-cc-pVQZ result (25.005 a.u.) the difference between the CC3/t-aug-cc-pCVQZ (24.776 a.u.) and CC3/t-aug-cc-pVQZ (25.097 a.u.) values, thus considering explicitly the correction due to the use of core-valence sets in all-electron calculations. The ''best static estimate'' thus obtained is $\Delta\eta(0) \approx 24.7$ a.u. The frequency dispersion can be neglected. In the case of argon we do not specify an absolute error, as done for neon, since above we could only speculate on the quantitative effect of the limitations in our approximations. For example and in particular, we miss in this case information on the effect of excitations beyond triples in the cluster expansions, which we can only expect as being small. A precise value for the absolute error cannot in our view be substantiated.

### C. Comparison with previous calculations and with experiment

Table VIII contains our best estimates for the hypermagnetizability anisotropy $\Delta\eta$ and, for comparison, previous theoretical results and experimental results.

#### 1. Ne

The CME of neon has been studied by Jaszuński and co-workers using MCSCF response methods,[11] and their estimate, for a wavelength of 514.5 nm, is of 2.670 $\pm 0.145$ a.u. Bishop and Cybulski, using MP2 perturbation theory, determined a value of 3.029 a.u. at $\lambda = 632.8$ nm, which becomes 3.034 a.u. at 514.5 nm.[10] Their static limit

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TABLE VIII. Comparison of present results for the hypermagnetizability anisotropy $\Delta\eta$ with previous *ab initio* estimates and with experiment.

| | $\lambda$ | This work[a] | Other *ab initio* | Expt. |
|---|---|---|---|---|
| Neon | $\infty$ | 2.89(10) | 2.841,[b] 2.869,[c] 2.687,[d] 3.017[e] | |
| | 790 nm | | | $3.2\pm1.2$[f] |
| | 632.8 nm | | 2.838,[b] 2.868,[c] 3.029[e] | |
| | 514.5 nm | | 2.836,[b] 2.866,[c] $2.670\pm0.145$,[d] 3.034[e] | $1.25\pm0.07$[g] |
| Argon | $\infty$ | 24.7 | 24.40[h] | |
| | 790 nm | | | $27\pm5$,[f] |
| | 632.8 nm | | 24.39,[h] 25.68[e] | |
| | 514.5 nm | | 24.36,[h] 25.70,[e] 24.14[i] | $30.0\pm4.5$[j] |

[a]The number in parentheses, when present, indicates the estimated absolute error on the last digit. Frequency dependence negligible, see text.
[b]Reference 80, orbital-unrelaxed CCSD/d-aug-cc-pV5Z with frozen 1*s* orbital.
[c]Reference 79, orbital-unrelaxed CCSD/q-aug-cc-pV5Z with all electrons correlated.
[d]Reference 11, MCSCF response.
[e]Reference 10, pseudoenergy MP2.
[f]Reference 14, pressure of $1.52\times10^5$ Pa, temperatures in the range 285–293 K. The value is estimated for an average of 289 K.
[g]Reference 9, temperature of 298.15 K and extrapolated at a pressure of 1 atm.
[h]Reference 80, orbital-unrelaxed CCSD/d-aug-cc-pV5Z with frozen core.
[i]Reference 13. MCSCF response.
[j]Reference 12.

estimate was $\Delta\eta(0)=3.017$ a.u.[10] Hättig and co-workers,[79] using CCSD with a q-aug-cc-pV5Z basis set and with all electrons correlated obtained values of $\Delta\eta$ of 2.869 a.u. ($\lambda=\infty$), 2.868 a.u. ($\lambda=632.8$ nm) and 2.866 a.u. ($\lambda=514.5$ nm). Coriani, Hättig, and Rizzo[80] have published values of $\Delta\eta=2.841$ a.u. ($\lambda=\infty$), $\Delta\eta=2.838$ a.u. ($\lambda=632.8$ nm), and $\Delta\eta=2.836$ a.u. ($\lambda=514.5$ nm), obtained again using a CCSD response approach and a d-aug-cc-pV5Z basis set with the 1*s* electrons frozen.

The analysis of the results of measurements of the CME of neon at $\lambda=514.5$ nm, a temperature of 298.15 K, and extrapolated at a pressure of 1 atm leads to an experimental estimate of $\Delta\eta=1.25\pm0.07$ a.u.[9] Very recent measurements, employing different experimental conditions ($\lambda=790$ nm, a pressure of $1.52\times10^5$ Pa and temperatures in the range 285–293 K) yield an estimate of $\Delta\eta$ of $3.2\pm1.2$ a.u., see Ref. 14, as a value estimated for an average of 289 K.

Our current *ab initio* result, $\Delta\eta=2.89(10)$ a.u., confirms and sets a precise and reliable interval of confidence for the previous CCSD estimates of Refs. 79 and 80. The MCSCF response result of Ref. 11 underestimate $\Delta\eta$, whereas MP2 theory[10] overestimates it. Concerning comparison with experiment, the current benchmark *ab initio* value is quite close to the center of the distribution of the measurements of Ref. 14. Agreement with experiment is on the other hand guaranteed by the huge error bars in the experimental results. As far as the experimental results in Ref. 9 is concerned, the current study confirms that the estimate these authors obtain is probably flawed due to some undetected systematic error.

#### 2. Ar

Previous theoretical values for $\Delta\eta$ of argon were computed by Bishop and Cybulski, using a pseudoenergy MP2 approach ($\Delta\eta=25.68$ a.u. at $\lambda=632.8$ nm, $\Delta\eta=25.70$ a.u. at $\lambda=514.5$ nm),[10] by Jaszuński and co-workers, who employed MCSCF response ($\Delta\eta=24.15$ a.u., at $\lambda=514.5$ nm) (Ref. 13) and by Coriani, Hättig, and Rizzo ($\Delta\eta=24.40$ a.u., $\lambda=\infty$, $\Delta\eta=24.39$ a.u., $\lambda=632.8$ nm, $\Delta\eta=24.36$ a.u., $\lambda=514.5$ nm).[80]

Carusotto and co-workers have measured a $\Delta\eta=30.0\pm4.5$ a.u., for $\lambda=514.5$ nm.[12] Muroo and co-workers very recently measured a value of $\Delta\eta=27\pm5$ a.u., at a wavelength $\lambda=790$ nm, a pressure of $1.52\times10^5$ Pa, and temperatures in the range 285–293 K.[14] As for neon, the value is estimated for an average of 289 K.

The present *ab initio* estimate, 24.7 a.u., including the effect of triple excitations, corrects upward by a fraction of an atomic unit the previous CCSD values of Ref. 80, thus placing the CC value in between the MCSCF response[13] and the pseudoenergy MP2 (Ref. 10) estimates. Agreement between theory and experiment for the CME of argon has never been apparently a problem, and this study is no exception.

### D. Digression. Change of the origin of the magnetic induction field

When the origin of the gauge for the magnetic induction field is changed, the anisotropy of the hypermagnetizability changes as discussed in the Appendix, see Eq. (A6). The dependence on the vector describing the change of origin can be written explicitly as a function of the coordinates of the displacement and of two response functions, i.e., $\Gamma_i=\langle\langle\mu_z^e;\mu_z^e,\mu_i^p,\mu_i^p\rangle\rangle$ with $i=z$ and $i=x$. These response functions vanish for complete one-electron basis sets, when the hypervirial relationship holds. The extent to which these responses are different from zero and approach zero as the quality of the basis set improves can be used as an indicator of the degree of completeness of the one-electron basis set. In Table IX these response functions are listed for the range of correlation-consistent basis sets employed throughout this study.

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TABLE IX. Dependence of the hypermagnetizability anisotropy (response functions $\Gamma_i = \langle\langle \mu_z^e ; \mu_z^e, \mu_i^p, \mu_i^p \rangle\rangle$ with $i=z$ and $i=x$; see the Appendix) on the change of origin of the magnetic gauge.

| | Neon | | | | Argon | | | |
|---|---|---|---|---|---|---|---|---|
| | CCSD | | CC3 | | CCSD | | CC3 | |
| Basis set | $\Gamma_x$ | $\Gamma_z$ | $\Gamma_x$ | $\Gamma_z$ | $\Gamma_x$ | $\Gamma_z$ | $\Gamma_x$ | $\Gamma_z$ |
| aug-cc-pVDZ | −1.5760 | −0.9420 | −1.6207 | −0.9313 | −25.9216 | −6.0506 | −26.4575 | −6.0407 |
| aug-cc-pVTZ | −3.3526 | −1.4104 | −3.4932 | −1.5137 | −23.9340 | −10.7063 | −25.3344 | −11.5164 |
| aug-cc-pVQZ | −3.4075 | −1.1984 | −3.6684 | −1.4128 | −16.3580 | −2.6349 | −18.0929 | −3.6218 |
| aug-cc-pV5Z | −1.9414 | −0.4680 | −2.2667 | −0.7428 | −6.5109 | −1.7477 | −8.0154 | −2.6843 |
| d-aug-cc-pVDZ | −7.0890 | −0.8201 | −7.2565 | −1.1331 | −45.2861 | −10.3237 | −46.5400 | −10.9706 |
| d-aug-cc-pVTZ | −2.7177 | −0.4982 | −3.0566 | −0.8250 | −6.7734 | −0.9979 | −8.3438 | −2.1474 |
| d-aug-cc-pVQZ | −1.0103 | −0.1421 | −1.3545 | −0.4540 | −2.0054 | 0.8912 | −3.3642 | −0.6462 |
| d-aug-cc-pV5Z | 0.1565 | 0.1941 | −0.1820 | −0.1100 | 0.6643 | 1.0434 | −0.5482 | 0.1477 |
| t-aug-cc-pVDZ | −7.4263 | −1.6757 | −7.5861 | −1.9632 | −45.5828 | −11.4102 | −46.8420 | −12.0695 |
| t-aug-cc-pVTZ | −0.6398 | 0.4388 | −0.3681 | 0.9686 | 0.5231 | 2.2251 | −0.8064 | 1.1726 |
| t-aug-cc-pVQZ | 0.2764 | 0.3902 | −0.6241 | 0.7809 | 1.5871 | 2.2980 | 0.3834 | 1.4106 |
| t-aug-cc-pV5Z | 0.2671 | 0.2431 | −0.6864 | −0.5967 | 1.2159 | 1.2554 | | |

From the data in the table it can be seen that the $\Gamma_x$ and $\Gamma_z$ response functions do indeed become smaller and smaller as the basis-set quality increases. The observed trend is slow but quite smooth.

## V. CONCLUSIONS

We have performed a detailed study of the hypermagnetizability anisotropy of neon and argon. To this end we have used the most recent state-of-the-art wave functions and property models, and a wide range of correlation-consistent basis sets. The static hypermagnetizability has been calculated, using a finite (electric) field procedure from analytically obtained magnetizabilities using approaches ranging from HF-SCF, MP2, CCSD, CCSD(T), CC3, CCSDT, CCSDTQ, CCSDTQP up to FCI. Frequency dependence has been analyzed through analytical response-function calculations by employing a hierarchy of coupled-cluster models ranging from CCS to CC2, CCSD, and CC3.

We have established the convergence toward FCI results for Ne and have shown that excitations beyond triples yield negligible contributions to the hypermagnetizability tensor components. For both neon and argon, a comparison of CCSDT and CCSD results shows that inclusion of triple excitations increases the anisotropy by roughly 3%–5%. As for neon, the effect of excitations beyond triples is expected to have only a rather small effect on the CME of argon.

Basis-set completeness has been studied in depth, and the use of core-valence sets in all-electron calculations has allowed to determine the effect of core correlation which has been found to be small. An interesting part of this study has been the comparison of results obtained at correlated level with and without relaxation of the orbitals to the externally applied electric field. The differences of the two approaches, which go to zero at the FCI limit, are still sizable at CCSD level, but the difference reduces quite rapidly as soon as higher excitations are considered. The frequency dispersion was analyzed, and it was found to be negligible. The only foreseeable source of uncertainty left out of our analysis is the effect of relativity, which has so far not been studied for mixed electric and magnetic birefringences.

The best estimates obtained, $\Delta\eta(0) = 2.89(10)$ a.u. for neon and $\Delta\eta(0) = 24.7$ a.u. for argon, with negligible frequency dependence, allow to set precise, benchmark quality references for the CME for these two gases. The accuracy exceeds that of experiment, and the results may be used as reference values in further measurements of the CME. The current estimates confirm that the value measured in Ref. 9 probably is flawed due to an undetected systematic error.

## ACKNOWLEDGMENTS

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## APPENDIX: MAGNETIC GAUGE DEPENDENCE

For a change of magnetic origin described by the vector $O_G$, the following changes apply to the expressions in Eqs. (4) and (5)—$\Delta^G P$ below indicates $[P(R_G') - P(R_G)]$—

$$\Delta^G \eta^p_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0) = +\tfrac{1}{2}\epsilon_{\gamma\sigma\eta} O_{G,\sigma} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^p_\eta, \mu^m_\delta \rangle\rangle_{\omega,0,0} + \tfrac{1}{2}\epsilon_{\delta\tau\rho} O_{G,\tau} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^m_\gamma, \mu^p_\rho \rangle\rangle_{\omega,0,0} - \tfrac{1}{4}\epsilon_{\gamma\sigma\nu}\epsilon_{\delta\tau\rho} O_{G,\sigma} O_{G,\tau} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^p_\nu, \mu^p_\rho \rangle\rangle_{\omega,0,0}, \quad \text{(A1)}$$

$$\Delta^G \eta^d_{\alpha\beta\gamma\delta}(-\omega;\omega,0) = +\tfrac{1}{4} O_{G,\gamma} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^e_\delta \rangle\rangle_{\omega,0} + \tfrac{1}{4} O_{G,\delta} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^e_\gamma \rangle\rangle_{\omega,0} - \tfrac{1}{2} O_{G,\epsilon}\delta_{\gamma\delta} \langle\langle \mu^e_\alpha ; \mu^e_\beta, \mu^e_\epsilon \rangle\rangle_{\omega,0}, \quad \text{(A2)}$$

where we have introduced the operator

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$$\mu_\alpha^p = -\sum_i p_{i,\alpha}^G. \tag{A3}$$

See Eqs. (42) and (43) in Ref. 54. For atoms, see detailed discussion in Ref. 54, symmetry considerations simplify the above equations to

$$\Delta^G \eta^p_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0) = -\tfrac{1}{4}\epsilon_{\gamma\sigma\nu}\epsilon_{\delta\tau\rho}O_{G,\sigma}O_{G,\tau} \times \langle\langle \mu_\alpha^e;\mu_\beta^e,\mu_\nu^p,\mu_\rho^p\rangle\rangle_{\omega,0,0}, \tag{A4}$$

$$\Delta^G \eta^d_{\alpha\beta\gamma\delta}(-\omega;\omega,0) = 0, \tag{A5}$$

and the effect of a change of magnetic gauge on the anisotropy of the hypermagnetizability for spherical systems can be written explicitly as

$$\Delta^G \Delta\eta(\omega) = \frac{(O_{G,z}^2 - O_{G,x}^2 - O_{G,y}^2)}{4}\langle\langle \mu_z^e;\mu_z^e,\mu_x^p,\mu_x^p\rangle\rangle_{\omega,0,0} + \frac{O_{G,y}^2}{4}\langle\langle \mu_z^e;\mu_z^e,\mu_z^p,\mu_z^p\rangle\rangle_{\omega,0,0}. \tag{A6}$$

This equation expresses the exact dependence on the choice of magnetic gauge in approximate calculations. When a complete one-electron basis set is employed, and thus the commutation relationships

$$[\mu_\alpha^e,\mathcal{H}] = i\mu_\alpha^p \tag{A7}$$

apply ($\mathcal{H}$ is here the Hamiltonian), the response function $\langle\langle \mu_\alpha^e;\mu_\beta^e,\mu_\gamma^p,\mu_\delta^p\rangle\rangle_{\omega,0,0}$ vanishes exactly,[54] and, as expected, the observable (the birefringence) becomes magnetic gauge invariant. To prove that we make use of the symmetry of the response functions upon a simultaneous interchange of both the indices and the associated frequencies, and write

$$\langle\langle \mu_\alpha^e;\mu_\beta^e,\mu_\gamma^p,\mu_\delta^p\rangle\rangle_{\omega,0,0} = \langle\langle \mu_\gamma^p;\mu_\beta^e,\mu_\alpha^e,\mu_\delta^p\rangle\rangle_{\omega,-\omega,0}. \tag{A8}$$

Then we apply the relationship holding for cubic response functions[51,54]

$$\langle\langle [V^{\omega_0},\mathcal{H}];V^{\omega_1},V^{\omega_2},V^{\omega_3}\rangle\rangle_{\omega,-\omega,0} = -\tfrac{1}{2}\mathcal{P}_{123}\langle\langle [V^{\omega_0},V^{\omega_1}];V^{\omega_2},V^{\omega_3}\rangle\rangle_{-\omega,0}, \tag{A9}$$

where $V^\omega$ denotes a perturbation associated to frequency $\omega$, and $\mathcal{P}(i,j,\ldots)$ generates the sum of responses with the indices $i,j,\ldots$ permuted. We then recognize that in the limit of a complete one-electron basis set, besides Eq. (A7), also the following relationships hold ($N_e$ is the total number of electrons)

$$[\mu_\alpha^e,\mu_\beta^e] = 0, \tag{A10}$$

$$[\mu_\alpha^e,\mu_\beta^p] = iN_e\delta_{\alpha\beta}, \tag{A11}$$

and end up proving trivially that the response function in Eq. (A8) vanishes in the limit of a complete one-electron basis set.


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