

Paper IV

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Analytic calculations of frequency-dependent hypermagnetizabilities and Cotton–Mouton constants using London atomic orbitals

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Abstract

We present the first gauge-origin independent, frequency-dependent calculations of the hypermagnetizability anisotropy, which determines the temperature-independent contribution to magnetic field-induced linear birefringence, the so-called Cotton–Mouton effect. A density matrix-based scheme for analytic calculations of frequency-dependent molecular properties for self-consistent field models has recently been developed, which is valid also with frequency- and field-dependent basis sets. Applying this scheme to Hartree–Fock wave functions, and using London atomic orbitals in order to obtain gauge-origin independent results, we have calculated the hypermagnetizability anisotropy. Our results show that the use of London orbitals lead to somewhat better basis set convergence for the hypermagnetizability compared to conventional basis sets, and that London orbitals are mandatory in order to obtain reliable magnetizability anisotropies.

I. INTRODUCTION

When linearly polarized light passes through a fluid in a direction perpendicular to an externally applied magnetic field, a linear birefringence, determined by the Cotton–Mouton constant ${}_mC$ ^{1–5} arises

$$\Delta n = n_{\parallel} - n_{\perp} = {}_mC\lambda B^2, \quad (1)$$

where n is the refractive index of the medium and Δn the anisotropy arising from the differences in its value for the components of the polarization vector aligned parallel (n_{\parallel}) and perpendicular (n_{\perp}) with respect to the direction of the external field, respectively. λ is the wavelength of the incident light, and B is the external magnetic field induction. The ellipticity⁶ resulting from the effect is in general small, but the subject has gained renewed experimental interest^{7–10} due to the possibility of measuring the birefringence of vacuum in the presence of strong magnetic fields as a means of verifying the theory of quantum electrodynamics.^{11,12} The state of experimental (and theoretical) work on the Cotton–Mouton effect has been reviewed by Rizzo, Rizzo and Bishop.⁵

Experiment, however, still faces many technical difficulties, and the ability to calibrate experimental observations against accurate theoretical calculations of the quantities that determine the Cotton–Mouton effect¹³—the electric dipole polarizability, the magnetizability and the hypermagnetizability anisotropies—has proven to be an important means of improving the quality of experimental data, as clearly demonstrated for instance in the case of the Cotton–Mouton effect of the neon atom.^{8,10,14–17}

From a computational point of view, the hypermagnetizability anisotropy poses several challenges. First of all, it is a frequency-dependent, fourth-order molecular property which requires the use of cubic response theory in order for the dispersion of the tensor to be properly taken into account.^{18–20} Analytic implementations of cubic response functions have been presented for Hartree–Fock,²¹ multiconfigurational self-consistent field (MCSCF)²² and coupled-cluster wave functions,²³ as well as for Kohn–Sham density functional theory.^{24,25} Several studies of the hypermagnetizability anisotropy and the Cotton–Mouton effect have been presented in the literature in recent years.^{17,26–34,36} For an account of theoretical calculations of the Cotton–Mouton effect, we refer to Refs. 5,37–39.

A further complication in the calculation of the hypermagnetizability anisotropy arises from the fact that the hypermagnetizability involves the second-order response of the frequency-dependent polarizability to a static, external magnetic field induction. The presence of the magnetic field perturbation implies that the calculated hypermagnetizability will be in general gauge-origin dependent, and that gauge invariant results will only be obtained for variational wave functions in the limit of a complete basis set.

Origin-independent hypermagnetizabilities can be obtained for variational wave functions also in finite basis sets if London atomic orbitals are used.^{41,42} In addition to providing origin-independent results, the London orbitals also ensure rapid basis set convergence for static magnetic properties, as perhaps most clearly illustrated for the magnetizability of PF₃.⁴³ However, by introducing London atomic orbitals, an explicit dependence of the atomic and molecular orbitals on the external magnetic field perturbation is introduced, leading to additional complications in the response formalism and the subsequent implementation of the theory. Indeed, there exists to date no analytical implementation of hypermagnetizabilities using London atomic orbitals, neither in the static electric field limit or for a frequency-dependent electric field. The original scheme devised for calculating origin-independent hypermagnetizabilities using London atomic orbitals⁴² obtained the hypermagnetizability

tensor by finite electric-field differentiation of the analytically calculated magnetizability, the latter calculated using London atomic orbitals. This required taking proper account of the correction terms arising because of the coupling between the electric dipole operator and the London orbitals.

In this work we unite the two approaches for calculating the hypermagnetizability tensor, presenting the first frequency-dependent, origin-independent calculations of the hypermagnetizability tensor using London atomic orbitals to obtain gauge-origin independent results. The calculations are performed using a new, general scheme for calculating frequency-dependent molecular properties for self-consistent field states,^{44,45} including also corrections arising from the explicit dependence in the atomic basis set on the applied perturbations (such as geometry perturbations or external magnetic field inductions). The theory is formulated in the atomic orbital (AO) basis, and uses the elements of the density matrix as the basic variables. The code is a stand-alone code that only requires as input the (perturbed) density matrices as well as the necessary one- and two-electron integrals. As such, it can also be easily extended to two- and four-component SCF models.⁴⁶

We apply our origin-independent hypermagnetizability implementation to the calculation of the Cotton–Mouton effect in a series of fluorobenzenes as well as of benzene. For many of these molecules there exist experiment data^{47–51} to which we can compare our results, as well as some earlier theoretical calculations using density-functional (DFT) and coupled cluster theory.^{33,34} By choosing a series of molecules with an increasing number of fluorine atoms, we can explore the importance of London atomic orbitals for obtaining basis-set limit results for the magnetizability and hypermagnetizability, a task which has been demonstrated to be challenging in the case of the magnetizability of fluorine-rich molecules.^{34,43}

The rest of the paper is organized as follows: In Section II we present the theory for analytic, frequency-dependent calculations of the hypermagnetizability using London atomic orbitals. In Section III we summarize the details of our calculations and define the quantities of interest for the Cotton–Mouton effect. In Section IV we present and discuss our results, with particular emphasis on the comparison between data obtained with and without London orbitals, and in Section V we summarize our results.

II. THEORY

In this section we will describe our formalism for the calculation of the analytic, frequency-dependent polarizabilities, magnetizabilities and hypermagnetizabilities using London atomic orbitals. The formalism is valid for a general time- and perturbation-dependent basis set,³⁵ and it is formulated using the density matrix in the atomic orbital basis as the basic variable. The general framework for the calculation of frequency-dependent properties is described elsewhere,⁴⁴ and here we will only give the main features of the approach for the specific case of the polarizability, magnetizability and hypermagnetizability.

A. The quasi-energy magnetic-field derivative

The magnetic moment $\mathbf{m}=\{m_x, m_y, m_z\}$ of a molecule in an applied static, homogeneous magnetic field $\mathbf{B}=\{B_x, B_y, B_z\}$ is the sum of the expectation values of the magnetic moment operator $\hat{\mathbf{m}}=\{\hat{m}_x, \hat{m}_y, \hat{m}_z\}$ and the field-contracted diamagnetic susceptibility operator $\hat{\xi}\mathbf{B}$, where $\hat{\xi}$ is a 3×3 matrix of operators. According to the Hellmann-Feynman theorem, for a

variational wavefunction, \mathbf{m} is also the negative first derivative of the energy E with respect to an applied homogeneous magnetic field $\mathbf{B}=\{B_x, B_y, B_z\}$

$$\mathbf{m} = \langle \psi | \hat{\mathbf{m}} + \hat{\boldsymbol{\xi}} \mathbf{B} | \psi \rangle = -\frac{d}{d\mathbf{B}} E(\psi), \quad (2)$$

$$E(\psi) = \langle \psi | \hat{H} + \hat{V} | \psi \rangle, \quad (3)$$

$$\hat{V} = -\mathbf{B} \cdot \hat{\mathbf{m}} - \frac{1}{2} \mathbf{B} \cdot \hat{\boldsymbol{\xi}} \mathbf{B}, \quad (4)$$

where \hat{V} is the external potential operator arising from the homogeneous magnetic field \mathbf{B} , and \hat{H} is the molecular Hamiltonian describing the unperturbed molecular system.

Assuming a closed-shell molecule, the magnetic moment operator $\hat{\mathbf{m}}$ is given by

$$\hat{m}_\alpha = -\frac{1}{2} \hat{l}_{\alpha,O} = -\frac{1}{2} \sum_{\beta,\gamma=x,y,z} \epsilon_{\alpha\beta\gamma} \hat{r}_{\beta,O} \hat{p}_\gamma, \quad \alpha = x, y, z, \quad (5)$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita antisymmetric tensor, and \hat{l}_α , \hat{r}_β and \hat{p}_γ are components of the electronic angular momentum, position and linear momentum operators, respectively. The diamagnetic susceptibility operator $\hat{\boldsymbol{\xi}}$ is given by

$$\hat{\xi}_{\alpha\beta} = \frac{1}{4} \left(\hat{r}_{\alpha,O} \hat{r}_{\beta,O} - \delta_{\alpha\beta} \sum_{\gamma} \hat{r}_{\gamma,O} \hat{r}_{\gamma,O} \right), \quad (6)$$

where the summation runs over the Cartesian directions x, y, z .

In Eq. 5, we have explicitly indicated that the magnetic moment operator depends on an arbitrarily chosen gauge origin O . Computed observable magnetic properties will only be independent of this gauge origin in the limit of complete basis sets.⁵⁶ In order to ensure that our calculated results are independent of the choice of gauge origin also for finite basis sets, we will utilize London Atomic orbitals (LAOs, also known as Gauge-Including Atomic Orbitals, GIAOs) defined as⁴¹

$$\chi_\mu = \exp(-i \mathbf{A}_{MO} \cdot \mathbf{r}) \omega_\mu, \quad (7)$$

where ω_μ is an ordinary perturbation-independent cartesian or spherical Gaussian basis function, and where the effect of the magnetic vector potential \mathbf{A}_{MO} appearing in the complex phase factor

$$\mathbf{A}_{MO} = \frac{1}{2} \mathbf{B} \times \mathbf{R}_{MO}, \quad (8)$$

is to move the global gauge origin O to the “best” local gauge origin for each individual basis function, which is chosen to be the center to which the basis function is attached. In the case of static external magnetic fields, which is the case for the magnetizability and hypermagnetizability, all references to the global gauge origin O vanish in the integrals contributing to the properties, and therefore the calculation is independent of the choice of global gauge origin.^{42,56,57}

Analogous to the energy of a time-independent molecular system, the quasi-energy of a time-dependent system $Q(\psi)$ is defined as⁵²⁻⁵⁵

$$Q(\psi) = \left\{ \left\langle \psi \left| \hat{H} + \hat{V}^t - i \frac{d}{dt} \right| \psi \right\rangle \right\}_t, \quad (9)$$

where the brace denotes a time average, defined as

$$\{ \dots \}_t = \lim_{r,s \rightarrow \infty} \frac{1}{r+s} \int_{-r}^{+s} \dots dt, \quad (10)$$

and the normalized wavefunction ψ is required to have the same fundamental frequency(ies) as the (generally) time-dependent external potential operator \hat{V}^t , and are thus Fourier series over the same infinite but *discrete* frequency set

$$\hat{V}^t = \sum_{k=-\infty}^{\infty} e^{i\omega_k t} \hat{V}_{\omega_k}, \quad \hat{V}_{-\omega_k} = \hat{V}_{\omega_k}^\dagger, \quad (11)$$

$$\psi(t) = \sum_{k=-\infty}^{\infty} e^{i\omega_k t} \psi_{\omega_k}, \quad \langle \psi | \psi \rangle = 1. \quad (12)$$

Although this relation does not uniquely determine the variational wavefunctions ψ , as $e^{-i\omega_k t} \psi$ (for any k) is also variational, differing in quasi-energy by ω_k , it restricts the variational wavefunctions to a discrete set, and ensures that the time average in Eq. 10 is well-defined.

If ψ is a variational wavefunction—that is, if the quasi-energy $Q(\psi)$ is stationary with respect to variations in ψ , the *time-dependent* Hellmann-Feynman theorem applies to the frequency-dependent magnetic moment \mathbf{m}_ω

$$\mathbf{m}_\omega = \{e^{-i\omega t} \langle \psi | \hat{\mathbf{m}} + \hat{\boldsymbol{\xi}} \mathbf{B} | \psi \rangle\}_t = -\frac{d}{dB_\omega} Q(\psi), \quad (13)$$

$$\hat{V}^t = \mathbf{B} \cdot \hat{\mathbf{m}} + \frac{1}{2} \mathbf{B} \cdot \hat{\boldsymbol{\xi}} \mathbf{B}, \quad \mathbf{B}(t) = \sum_\omega e^{-i\omega t} \mathbf{B}_\omega, \quad (14)$$

where \mathbf{B}_ω is the ω -frequency strength (complex-valued, defining field direction, amplitude and phase) of the applied oscillating magnetic field. Note that although the quasi-energy Q is real-valued, its derivative $\frac{d}{dB_\omega} Q$ will in general be complex, satisfying $(\frac{d}{dB_\omega} Q)^* = \frac{d}{dB_\omega^*} Q = \frac{d}{dB_{-\omega}} Q$.

Notice in Eq. 9 that time-differentiation is applied to the ket $|\psi\rangle$, but not to the bra $\langle\psi|$. This asymmetry makes it difficult to parameterize Q in terms of density operators derived from $|\psi\rangle\langle\psi|$, such as the atomic orbital density matrix \mathbf{D} in self-consistent field (SCF) models, since these are symmetric in bra and ket. However, as we have demonstrated in Ref. 44, SCF quasi-energy derivatives $\frac{d}{da} Q$ are readily expressible in terms of \mathbf{D} , also in the case of a time-dependent basis set explicitly dependent on the parameter a .

The SCF quasi-energy derivative with respect to an external magnetic field strength $\mathbf{a} = \mathbf{B}_{\omega_a}$ expressed in terms of the density matrix in the atomic orbital basis can be written as⁴⁴

$$\frac{d}{da} Q = Q^a(\mathbf{D}) = \left\{ \frac{\partial}{\partial a} E(\mathbf{D}) - \text{Tr} \left(\frac{d}{da} \mathbf{S} \right) \mathbf{W} \right\}_t \stackrel{\text{Tr}_t}{=} \frac{\partial}{\partial a} E(\mathbf{D}) - \mathbf{S}^a \mathbf{W}, \quad (15)$$

where we have introduced a superscript notation Q^a , \mathbf{S}^a for (total) derivatives, and $\stackrel{\text{Tr}_t}{=}$ denotes that we will take the trace of the matrix products involved as well as perform time averaging.

In this work we study the Hartree-Fock model, for which the generalized energy $E(\mathbf{D})$ is the sum of the Hartree-Fock energy, the interaction energy between the molecule and the external field (v_{nuc} denoting the nuclear contribution), and an additional term $-\frac{i}{2} \text{Tr} \mathbf{T} \mathbf{D}$ arising from the time-dependence of the AOs

$$E(\mathbf{D}) = h_{\text{nuc}} + \text{Tr} \mathbf{h} \mathbf{D} + \text{Tr} \frac{1}{2} \mathbf{G}(\mathbf{D}) \mathbf{D} \quad (16)$$

$$+ v_{\text{nuc}} + \text{Tr} \mathbf{V} \mathbf{D} - \frac{i}{2} \text{Tr} \mathbf{T} \mathbf{D},$$

$$\mathbf{F} = \frac{\partial}{\partial \mathbf{D}^T} E(\mathbf{D}) = \mathbf{h} + \mathbf{V} + \mathbf{G}(\mathbf{D}) - \frac{i}{2} \mathbf{T}, \quad (17)$$

where the generalized Fock matrix \mathbf{F} also has been introduced. The density matrix \mathbf{D} , the generalized “energy-weighted density matrix” \mathbf{W} , the overlap matrix \mathbf{S} , the one-electron Hamiltonian matrix \mathbf{h} , the time-differentiation matrix \mathbf{T} , the external potential matrix \mathbf{V} and the two-electron matrix $\mathbf{G}(\mathbf{D})$ in the atomic orbital basis, are given by

$$\mathbf{D} = \mathbf{C}\mathbf{C}^\dagger, \quad (18)$$

$$\mathbf{W} = \mathbf{D}\mathbf{F}\mathbf{D} + \frac{i}{2}\dot{\mathbf{D}}\mathbf{S}\mathbf{D} - \frac{i}{2}\mathbf{D}\mathbf{S}\dot{\mathbf{D}}, \quad \dot{\mathbf{D}} = \frac{d}{dt}\mathbf{D}, \quad (19)$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle, \quad (20)$$

$$h_{\mu\nu} = \left\langle \chi_\mu \left| -\frac{1}{2}\nabla^2 - \sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|} \right| \chi_\nu \right\rangle, \quad (21)$$

$$T_{\mu\nu} = \langle \chi_\mu | \dot{\chi}_\nu \rangle - \langle \dot{\chi}_\mu | \chi_\nu \rangle, \quad \dot{\chi}_\nu = \frac{d}{dt}\chi_\nu, \quad (22)$$

$$V_{\mu\nu} = \langle \chi_\mu | \hat{V}^t | \chi_\nu \rangle = \langle \chi_\mu | \mathbf{B} \cdot \hat{\mathbf{m}} + \frac{1}{2}\mathbf{B} \cdot \hat{\boldsymbol{\xi}}\mathbf{B} | \chi_\nu \rangle, \quad (23)$$

$$G_{\mu\nu}(\mathbf{D}) = \sum_{\rho\sigma} (g_{\mu\nu\rho\sigma} - g_{\mu\sigma\rho\nu})D_{\sigma\rho}, \quad (24)$$

where \mathbf{C} is the molecular orbital coefficient matrix, \mathbf{C}^\dagger its adjoint (conjugate transpose), and $g_{\mu\nu\rho\sigma}$ the two-electron integrals

$$g_{\mu\nu\rho\sigma} = \int \int \chi_\mu^*(\mathbf{x}_1)\chi_\nu(\mathbf{x}_1)\frac{1}{r_{12}}\chi_\rho^*(\mathbf{x}_2)\chi_\sigma(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2. \quad (25)$$

We note the close similarity in structure between the expression for the quasi-energy gradient in Eq. 15 and the expression introduced by Pulay for the molecular gradient.⁵⁸ The form of the expression is the same, but our definition involves time-dependent generalized matrices that also allow for frequency dependence in the atomic-orbital basis set.

Inserting Eq. 16 for $E(\mathbf{D})$ into Eq. 15 and evaluating the partial derivative, we obtain the expression for the (negative) Hartree-Fock magnetic moment

$$-\mathbf{m}_{\omega_a} = Q^a \stackrel{\text{Tr}_t}{=} \mathbf{h}^a\mathbf{D} + \frac{1}{2}\mathbf{G}^a(\mathbf{D})\mathbf{D} + \mathbf{V}^a\mathbf{D} - \frac{i}{2}\mathbf{T}^a\mathbf{D} - \mathbf{S}^a\mathbf{W}, \quad (26)$$

where we have used the fact that the nuclei do not interact with the magnetic field and that thus h_{nuc}^a and v_{nuc}^a are zero, and that the integrals \mathbf{h} , \mathbf{G} , \mathbf{T} and \mathbf{S} also depend on the magnetic field strength \mathbf{a} through the LAOs χ_μ .

B. Magnetizability

The frequency-dependent magnetizability $\boldsymbol{\xi}(\omega, \nu)$ is a 3×3 matrix depending on two frequencies, and is the derivative of the magnetic moment \mathbf{m}_ω with respect to \mathbf{B}_ν , or equivalently by Eq. 13, the negative second derivative of the quasi-energy

$$\boldsymbol{\xi}(\omega, \nu) = \frac{d}{d\mathbf{B}_\nu}\mathbf{m}_\omega = -\frac{d^2}{d\mathbf{B}_\nu d\mathbf{B}_\omega}Q(\psi). \quad (27)$$

In order to obtain the formula for the Hartree-Fock magnetizability, we differentiate the magnetic moment Eq. 15 with respect to $\mathbf{b}=\mathbf{B}_{\omega_b}$, and use the chain rule on the first term $\frac{\partial}{\partial \mathbf{a}}E(\mathbf{D})$

$$-\boldsymbol{\xi}(\omega_a, \omega_b) = Q^{ab} \stackrel{\text{Tr}_t}{=} \frac{\partial^2}{\partial \mathbf{a} \partial \mathbf{b}}E(\mathbf{D}) + \left(\frac{\partial}{\partial \mathbf{a}}\mathbf{F}\right)\mathbf{D}^b + \mathbf{S}^{ab}\mathbf{W} + \mathbf{S}^a\mathbf{W}^b, \quad (28)$$

where \mathbf{D}^b is the perturbed density matrix (*vide infra*), and \mathbf{W}^b is defined in terms of \mathbf{D}^b through differentiation of Eq. 19

$$\begin{aligned}\mathbf{W}^b &= \mathbf{D}^b \mathbf{F} \mathbf{D} + \frac{i}{2} \dot{\mathbf{D}}^b \mathbf{S} \mathbf{D} - \frac{i}{2} \mathbf{D}^b \mathbf{S} \dot{\mathbf{D}} \\ &+ \mathbf{D} \mathbf{F}^b \mathbf{D} + \frac{i}{2} \dot{\mathbf{D}} \mathbf{S}^b \mathbf{D} - \frac{i}{2} \mathbf{D} \mathbf{S}^b \dot{\mathbf{D}} \\ &+ \mathbf{D} \mathbf{F} \mathbf{D}^b + \frac{i}{2} \dot{\mathbf{D}} \mathbf{S} \mathbf{D}^b - \frac{i}{2} \mathbf{D} \mathbf{S} \dot{\mathbf{D}}^b.\end{aligned}\quad (29)$$

Since the unperturbed system is time-independent, $\dot{\mathbf{D}}$ is zero while \mathbf{D}^b is on the form $e^{-i\omega_b t} \mathbf{M}$, with \mathbf{M} being time independent, and thus the expression above reduces to

$$\mathbf{W}^b = \mathbf{D}^b \mathbf{F} \mathbf{D} + \mathbf{D} \mathbf{F}^b \mathbf{D} + \mathbf{D} \mathbf{F} \mathbf{D}^b + \frac{\omega_b}{2} \mathbf{D}^b \mathbf{S} \mathbf{D} - \frac{\omega_b}{2} \mathbf{D} \mathbf{S} \mathbf{D}^b. \quad (30)$$

C. Perturbed density matrices

Eq. 28 involves the 3 first-order perturbed density matrices \mathbf{D}^b (corresponding to the three cartesian components of the magnetic field strength \mathbf{b}), which must be determined in order to calculate the magnetizability. The details of the derivation of the equations that can be used to determine the perturbed density matrices to arbitrary order were given in Ref. 44, but for completeness, we will give the highlights of the derivation in this section.

The set of equations that can be used to determine the perturbed densities are obtained by differentiating the time-dependent self-consistent field equation (TDSCF) and the idempotency condition for the density matrix

$$\mathbf{0} = \mathbf{F} \mathbf{D} \mathbf{S} - \mathbf{S} \mathbf{D} \mathbf{F} - \frac{i}{2} \mathbf{S} (\mathbf{D} \mathbf{S}) \dot{} - \frac{i}{2} (\mathbf{S} \mathbf{D}) \dot{} \mathbf{S} = \mathbf{Y}, \quad (31)$$

$$\mathbf{0} = \mathbf{D} \mathbf{S} \mathbf{D} - \mathbf{D} = \mathbf{P}, \quad (32)$$

with respect to \mathbf{b} . A dot over the parenthesis here indicates that time differentiation is to be applied to the product inside the parenthesis, and the TDSCF matrix \mathbf{Y} and idempotency matrix \mathbf{P} are introduced for future reference when determining the hypermagnetizability from the variational Lagrangian for the magnetic moment (*vide infra*). From Eqs. 31 and 32 we get two equations for \mathbf{D}^b

$$\mathbf{0} = \mathbf{F}^b \mathbf{D} \mathbf{S} - \mathbf{S} \mathbf{D} \mathbf{F}^b - \frac{i}{2} \mathbf{S}^b (\mathbf{D} \mathbf{S}) \dot{} - \frac{i}{2} (\mathbf{S} \mathbf{D}) \dot{} \mathbf{S}^b \quad (33)$$

$$\begin{aligned}&+ \mathbf{F} \mathbf{D}^b \mathbf{S} - \mathbf{S} \mathbf{D}^b \mathbf{F} - \frac{i}{2} \mathbf{S} (\mathbf{D}^b \mathbf{S}) \dot{} - \frac{i}{2} (\mathbf{S} \mathbf{D}^b) \dot{} \mathbf{S} \\ &+ \mathbf{F} \mathbf{D} \mathbf{S}^b - \mathbf{S}^b \mathbf{D} \mathbf{F} - \frac{i}{2} \mathbf{S} (\mathbf{D} \mathbf{S}^b) \dot{} - \frac{i}{2} (\mathbf{S}^b \mathbf{D}) \dot{} \mathbf{S},\end{aligned}$$

$$\mathbf{0} = \mathbf{D}^b \mathbf{S} \mathbf{D} + \mathbf{D} \mathbf{S}^b \mathbf{D} + \mathbf{D} \mathbf{S} \mathbf{D}^b - \mathbf{D}^b. \quad (34)$$

The perturbed Fock matrix \mathbf{F}^b in Eq. 33 has two contributions, namely the field-perturbed integrals $\frac{\partial}{\partial \mathbf{b}} \mathbf{F}$, and the unperturbed two-electron matrix operator $\frac{\partial}{\partial \mathbf{D}^T} \mathbf{F} = \mathbf{G}$ contracted with the perturbed density matrix \mathbf{D}^b (relaxation contribution)

$$\mathbf{F}^b = \frac{d}{d\mathbf{b}} \mathbf{F} = \frac{\partial}{\partial \mathbf{b}} \mathbf{F} + \mathbf{G}(\mathbf{D}^b). \quad (35)$$

In order to decouple Eqs. 33 and 34, we recall that the unperturbed matrix $\mathbf{D} \mathbf{S}$ is a projector,⁴⁰ and thus split \mathbf{D}^b into four ‘‘blocks’’

$$\begin{aligned}\mathbf{D}^b &= [\mathbf{D} \mathbf{S} \mathbf{D}^b \mathbf{S} \mathbf{D} + (\mathbf{1} - \mathbf{D} \mathbf{S}) \mathbf{D}^b (\mathbf{1} - \mathbf{S} \mathbf{D})] \\ &+ [\mathbf{D} \mathbf{S} \mathbf{D}^b (\mathbf{1} - \mathbf{S} \mathbf{D}) + (\mathbf{1} - \mathbf{D} \mathbf{S}) \mathbf{D}^b \mathbf{S} \mathbf{D}] = \mathbf{D}_p^b + \mathbf{D}_h^b\end{aligned}\quad (36)$$

which correspond to the occupied-occupied, unoccupied-unoccupied, occupied-unoccupied, and unoccupied-occupied blocks, respectively. We denote the two first blocks the *particular* component \mathbf{D}_p^b , and the last two the *homogeneous* component \mathbf{D}_h^b . Inserting the partitioning of \mathbf{D}^b defined in Eq. 36 into Eq. 34, keeping the full expansion for \mathbf{D}_h^b and then using the idempotency condition to eliminate many of the terms, we find that the contribution from \mathbf{D}_h^b to the perturbed idempotency condition vanishes

$$\begin{aligned}
-\mathbf{DS}^b\mathbf{D} &= (\mathbf{D}_p^b + \mathbf{D}_h^b)\mathbf{SD} + \mathbf{DS}(\mathbf{D}_p^b + \mathbf{D}_h^b) - (\mathbf{D}_p^b + \mathbf{D}_h^b) \\
&= [\mathbf{D}_p^b + \mathbf{DSD}^b(1-\mathbf{SD}) + (1-\mathbf{DS})\mathbf{D}^b\mathbf{SD}] \mathbf{SD} \\
&\quad + \mathbf{DS} [\mathbf{D}_p^b + \mathbf{DSD}^b(1-\mathbf{SD}) + (1-\mathbf{DS})\mathbf{D}^b\mathbf{SD}] \\
&\quad - [\mathbf{D}_p^b + \mathbf{DSD}^b(1-\mathbf{SD}) + (1-\mathbf{DS})\mathbf{D}^b\mathbf{SD}] \\
&= \mathbf{D}_p^b\mathbf{SD} + \mathbf{DSD}_p^b - \mathbf{D}_p^b.
\end{aligned} \tag{37}$$

\mathbf{D}_p^b is therefore a particular solution to the linear set of equations in Eq. 34, whereas \mathbf{D}_h^b solves the corresponding homogeneous equation

$$\mathbf{0} = \mathbf{D}_h^b\mathbf{SD} + \mathbf{DSD}_h^b - \mathbf{D}_h^b. \tag{38}$$

By manipulating \mathbf{D}_p^b we find that it can be written in terms of a Hermitian matrix \mathbf{N}

$$\begin{aligned}
\mathbf{D}_p^b &= \mathbf{DSD}^b\mathbf{SD} + (1-\mathbf{DS})\mathbf{D}^b(1-\mathbf{SD}) \\
&= (\mathbf{D}^b\mathbf{SD} + \mathbf{DSD}^b - \mathbf{D}^b)\mathbf{SD} \\
&\quad + \mathbf{DS}(\mathbf{D}^b\mathbf{SD} + \mathbf{DSD}^b - \mathbf{D}^b) - (\mathbf{D}^b\mathbf{SD} + \mathbf{DSD}^b - \mathbf{D}^b) \\
&= \mathbf{NSD} + \mathbf{DSN} - \mathbf{N},
\end{aligned} \tag{39}$$

which we recognize as $-\mathbf{DS}^b\mathbf{D}$ from Eq. 34

$$\mathbf{N} = \mathbf{D}^b\mathbf{SD} + \mathbf{DSD}^b - \mathbf{D}^b = -\mathbf{DS}^b\mathbf{D}. \tag{40}$$

Similarly, manipulating \mathbf{D}_h^b , we find that it can be written in terms of an anti-Hermitian matrix \mathbf{X}

$$\begin{aligned}
\mathbf{D}_h^b &= \mathbf{DSD}^b(1-\mathbf{SD}) + (1-\mathbf{DS})\mathbf{D}^b\mathbf{SD} \\
&= (\mathbf{D}^b\mathbf{SD} - \mathbf{DSD}^b)\mathbf{SD} - \mathbf{DS}(\mathbf{D}^b\mathbf{SD} - \mathbf{DSD}^b) \\
&= \mathbf{XSD} - \mathbf{DSX},
\end{aligned} \tag{41}$$

which gives

$$\mathbf{X} = \mathbf{D}^b\mathbf{SD} - \mathbf{DSD}^b, \tag{42}$$

which must be determined from Eq. 33. Inserting for \mathbf{D}^b and \mathbf{F}^b in Eq. 33 and separating the terms involving the unknown \mathbf{D}_h^b , we obtain the equation

$$\begin{aligned}
\mathbf{G}(\mathbf{D}_h^b)\mathbf{DS} - \mathbf{SDG}(\mathbf{D}_h^b) + \mathbf{FD}_h^b\mathbf{S} - \mathbf{SD}_h^b\mathbf{F} - \frac{i}{2}\mathbf{S}(\mathbf{D}_h^b\mathbf{S})\dot{} - \frac{i}{2}(\mathbf{SD}_h^b)\dot{}\mathbf{S} \\
&= -\{\mathbf{G}(\mathbf{D}_p^b)\mathbf{DS} - \mathbf{SDG}(\mathbf{D}_p^b) \\
&\quad + (\frac{\partial}{\partial b}\mathbf{F})\mathbf{DS} - \mathbf{SD}(\frac{\partial}{\partial b}\mathbf{F}) - \frac{i}{2}\mathbf{S}^b(\mathbf{DS})\dot{} - \frac{i}{2}(\mathbf{SD})\dot{}\mathbf{S}^b \\
&\quad + \mathbf{FD}_p^b\mathbf{S} - \mathbf{SD}_p^b\mathbf{F} - \frac{i}{2}\mathbf{S}(\mathbf{D}_p^b\mathbf{S})\dot{} - \frac{i}{2}(\mathbf{SD}_p^b)\dot{}\mathbf{S} \\
&\quad + \mathbf{FDS}^b - \mathbf{S}^b\mathbf{DF} - \frac{i}{2}\mathbf{S}(\mathbf{DS}^b)\dot{} - \frac{i}{2}(\mathbf{S}^b\mathbf{D})\dot{}\mathbf{S}\}
\end{aligned} \tag{43}$$

At $\mathbf{b} = \mathbf{0}$, the unperturbed system is time independent, and the perturbed integrals are products of a time-dependent phase factor and a time-independent matrix: $\frac{\partial}{\partial b}\mathbf{F}=e^{-i\omega_b t}\mathbf{M}$, $\mathbf{S}^b=e^{-i\omega_b t}\mathbf{M}$. This means that the matrices \mathbf{D}_h^b and \mathbf{D}_p^b are also of this form, and we may evaluate the time-derivatives in Eq. 43, which then reduces to

$$\begin{aligned} & \mathbf{G}(\mathbf{D}_h^b)\mathbf{D}\mathbf{S} - \mathbf{S}\mathbf{D}\mathbf{G}(\mathbf{D}_h^b) + \mathbf{F}\mathbf{D}_h^b\mathbf{S} - \mathbf{S}\mathbf{D}_h^b\mathbf{F} - \omega_b\mathbf{S}\mathbf{D}_h^b\mathbf{S} \\ &= -\left\{ \mathbf{G}(\mathbf{D}_p^b)\mathbf{D}\mathbf{S} - \mathbf{S}\mathbf{D}\mathbf{G}(\mathbf{D}_p^b) + \left(\frac{\partial}{\partial b}\mathbf{F}\right)\mathbf{D}\mathbf{S} - \mathbf{S}\mathbf{D}\left(\frac{\partial}{\partial b}\mathbf{F}\right) \right. \\ &+ \mathbf{F}\mathbf{D}_p^b\mathbf{S} - \mathbf{S}\mathbf{D}_p^b\mathbf{F} - \omega_b\mathbf{S}\mathbf{D}_p^b\mathbf{S} \\ &\left. + \mathbf{F}\mathbf{D}\mathbf{S}^b - \mathbf{S}^b\mathbf{D}\mathbf{F} - \frac{\omega_b}{2}\mathbf{S}\mathbf{D}\mathbf{S}^b - \frac{\omega_b}{2}\mathbf{S}^b\mathbf{D}\mathbf{S} \right\}, \end{aligned} \quad (44)$$

in which the only time-dependence is a net phase factor $e^{-i\omega_b t}$ on both sides, which may be canceled.

In the case of perturbation-independent basis sets, all terms on the right-hand side of Eq. 44 involving \mathbf{S}^b and \mathbf{D}_p^b vanish, the latter because \mathbf{D}_p^b is defined in terms of \mathbf{S}^b , see Eqs. 39 and 40, and the right-hand side is further reduced to

$$-\left\{ \left(\frac{\partial}{\partial b}\mathbf{F}\right)\mathbf{D}\mathbf{S} - \mathbf{S}\mathbf{D}\left(\frac{\partial}{\partial b}\mathbf{F}\right) \right\} = \mathbf{B}^{[1]}. \quad (45)$$

Introducing the notation

$$\mathbf{E}^{[2]}\mathbf{D}_h^b = \mathbf{G}(\mathbf{D}_h^b)\mathbf{D}\mathbf{S} - \mathbf{S}\mathbf{D}\mathbf{G}(\mathbf{D}_h^b) + \mathbf{F}\mathbf{D}_h^b\mathbf{S} - \mathbf{S}\mathbf{D}_h^b\mathbf{F}, \quad (46)$$

$$\mathbf{S}^{[2]}\mathbf{D}_h^b = \mathbf{S}\mathbf{D}_h^b\mathbf{S}, \quad (47)$$

we note that we for the case of perturbation-independent basis sets can write Eq. 44 compactly as

$$(\mathbf{E}^{[2]} - \omega_b\mathbf{S}^{[2]})\mathbf{D}_h^b = \mathbf{B}^{[1]}, \quad (48)$$

which is identical to the result of Ref. 59. Eq. 44 is therefore a generalization to perturbation-dependent basis sets of the linear sets of equations for which a linearly-scaling, density matrix-based response solver has been developed by Coriani *et al.*,⁵⁹ and this is the solver we will use in this work.

Although we will not go through the details, second and higher-order equations (corresponding to Eqs. 33 and 34) are solved in an analogous manner (see also Ref. 44). There are then more terms entering on the right-hand side of Eq. 40, in \mathbf{N} (and thus \mathbf{D}_p^{ab}), and more terms on the right-hand side of Eq. 44. However, the structure will in all be cases be of the form of Eq. 48 (see again Ref. 44 for an exhaustive discussion).

D. Dipole moment and polarizability

It is at this point useful to briefly consider the electric-field analogues of the (frequency-dependent) magnetic moment and magnetizability, namely the (electric) dipole moment $\boldsymbol{\mu}_\omega$ and polarizability $\boldsymbol{\alpha}(\omega, \nu)$, which are defined as

$$\boldsymbol{\mu}_\omega = \left\{ e^{-i\omega t} \langle \psi | \hat{\boldsymbol{\mu}} | \psi \rangle \right\}_t = -\frac{d}{dF_\omega} Q(\psi), \quad (49)$$

$$\boldsymbol{\alpha}(\omega, \nu) = \frac{d}{dF_\nu} \boldsymbol{\mu}_\omega = -\frac{d^2}{dF_\omega dF_\nu} Q(\psi), \quad \mathbf{F}(t) = \sum_\omega e^{-i\omega t} \mathbf{F}_\omega, \quad (50)$$

$$\hat{V}^t = -\mathbf{F} \cdot \hat{\boldsymbol{\mu}} - \mathbf{B} \cdot \hat{\mathbf{m}} - \frac{1}{2} \mathbf{B} \cdot \hat{\boldsymbol{\xi}} \mathbf{B}, \quad (51)$$

where $\hat{\boldsymbol{\mu}}=\{\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z\}$ is the electric dipole moment operator, and \mathbf{F}_ω are the complex frequency strengths of the applied external electric field \mathbf{F} , which enters the external potential operator \hat{V}^t together with the magnetic field. Whereas the LAOs depended on the magnetic field strengths \mathbf{B}_ω , they are independent of the electric field strengths $\mathbf{f}=\mathbf{F}_{\omega_f}$, and hence $\mathbf{S}^f, \mathbf{h}^f, \mathbf{G}^f, \mathbf{T}^f$ are all zero. Moreover, as opposed to the magnetic-field, which appeared quadratically in Eq. 27, the electric field appears only linearly in \hat{V}^t . The formulas for the (negative) dipole moment and polarizability, analogous to Eqs. 15 and 28, are therefore much simpler

$$Q^f(\mathbf{D}) \stackrel{\text{Tr}_t}{=} \frac{\partial}{\partial f} E(\mathbf{D}) \stackrel{\text{Tr}_t}{=} \mathbf{V}^f \mathbf{D}, \quad (52)$$

$$Q^{fg}(\mathbf{D}) \stackrel{\text{Tr}_t}{=} \left(\frac{\partial}{\partial f} \mathbf{F} \right) \mathbf{D}^g \stackrel{\text{Tr}_t}{=} \mathbf{V}^f \mathbf{D}^g, \quad (53)$$

with $\mathbf{g}=\mathbf{F}_{\omega_g}$ another electric field strength, and where the perturbed density matrix \mathbf{D}^g can be obtained using the solver of Ref. 59 for solving Eq. 48 using the right-hand side for perturbation-independent basis set defined in Eq. 45 in terms of the dipole moment integrals.

E. Hypermagnetizability

The hypermagnetizability $\boldsymbol{\eta}$ is a $3 \times 3 \times 3 \times 3$ tensor and a fourth-order property, and is the negative fourth derivative of the quasi-energy

$$\boldsymbol{\eta}(\omega_a, \omega_b, \omega_f, \omega_g) = -\frac{d^4}{dadbdfdg} Q(\mathbf{D}) = -Q^{abfg}(\mathbf{D}). \quad (54)$$

A formula for Q^{abfg} can be obtained by differentiating the negative magnetizability Eq. 28 twice, with respect electric field strengths \mathbf{f} and \mathbf{g} . This formula will contain the third-order perturbed density matrix \mathbf{D}^{bfg} . However, according to the $2n+1$ rule, alternative formulas exist involving only first- and second-order perturbed density matrices. These can be derived by first constructing a *Lagrangian* from the (negative) magnetic moment⁴⁴ $Q^a(\mathbf{D})$ (the first-order quasi-energy derivative), which is stationary with respect to variations in \mathbf{D} (*i.e.* variational)

$$\begin{aligned} Q^a(\mathbf{D}, \mathbf{X}_a, \mathbf{L}_a) &\stackrel{\text{Tr}_t}{=} \frac{\partial}{\partial a} E(\mathbf{D}) - \mathbf{S}^a \mathbf{W} - \mathbf{L}_a (\mathbf{DSD} - \mathbf{D}) \\ &\quad - \mathbf{X}_a (\mathbf{FDS} - \mathbf{SDF} - \frac{i}{2} \mathbf{S}(\mathbf{DS}) - \frac{i}{2} (\mathbf{SD})\mathbf{S}) \\ &\stackrel{\text{Tr}_t}{=} \frac{\partial}{\partial a} E(\mathbf{D}) - \mathbf{S}^a \mathbf{W} - \mathbf{X}_a \mathbf{Y} - \mathbf{L}_a \mathbf{P}, \end{aligned} \quad (55)$$

where the first two terms are the $Q^a(\mathbf{D})$ from Eq. 15, and the anti-Hermitian Lagrange multiplier \mathbf{X}_a multiplies the TDSCF matrix (or equation residual) \mathbf{Y} , introduced in Eq. 31, while the Hermitian Lagrange multiplier \mathbf{L}_a multiplies the idempotency matrix \mathbf{P} , introduced in Eq. 32. Starting from the equation $\frac{\partial}{\partial \mathbf{D}^T} Q^a(\mathbf{D}, \mathbf{X}_a, \mathbf{L}_a) = \mathbf{0}$ it can be shown (see Ref. 44) that the multipliers can be expressed in terms of the corresponding perturbed density matrix \mathbf{D}^a as

$$\mathbf{X}_a = \mathbf{D}^a \mathbf{SD} - \mathbf{DSD}^a, \quad (56)$$

$$\begin{aligned} \mathbf{L}_a &= \mathbf{F}^a \mathbf{DS} - (\mathbf{FD} - \frac{i}{2} \dot{\mathbf{S}}\mathbf{D} - i\mathbf{S}\dot{\mathbf{D}})\mathbf{S}^a \\ &\quad + \mathbf{SDF}^a - \mathbf{S}^a (\mathbf{DF} + \frac{i}{2} \mathbf{D}\dot{\mathbf{S}} + i\dot{\mathbf{D}}\mathbf{S}) - \mathbf{F}^a. \end{aligned} \quad (57)$$

According to the $2n+1$ rule, since $Q^a(\mathbf{D}, \mathbf{X}_a, \mathbf{L}_a)$ in Eq. 55 is variational, we can differentiate it three times, and simply omit the third-order perturbed arguments \mathbf{D}^{bfg} , \mathbf{X}_a^{bfg} , \mathbf{L}_a^{bfg} from the resulting formula (alternatively, we could omit both second- and third-order arguments, but in that case the first-order multipliers can *not* be omitted (*vide infra*), which means second-order equations need to be solved anyway)

$$Q_{1,2}^{abfg} \stackrel{\text{Trt}}{=} \left(\frac{\partial}{\partial a} E(\mathbf{D}) \right)_2^{bfg} - \mathbf{S}^{ab} \mathbf{W}^{fg} - \mathbf{S}^a \mathbf{W}_2^{bfg} - \mathbf{X}_a \mathbf{Y}_2^{bfg} - \mathbf{L}_a \mathbf{P}_2^{bfg}, \quad (58)$$

where the subscripts on $Q_{1,2}^{abfg}$ indicate that perturbed density matrices to 1st order in the first field \mathbf{a} and 2nd order in the other fields \mathbf{b} , \mathbf{f} and \mathbf{g} are involved, while the subscripts on $\left(\frac{\partial}{\partial a} E(\mathbf{D}) \right)_2^{bfg}$, \mathbf{W}_2^{bfg} , \mathbf{Y}_2^{bfg} and \mathbf{L}_2^{bfg} indicate that perturbed density matrices to 2nd order are included. Since the LAOs (and overlap matrix) are independent of the electric field, the following vanishing terms have been omitted from Eq. 58

$$-\mathbf{S}^{af} \mathbf{W}^{bg} - \mathbf{S}^{ag} \mathbf{W}^{bf} - \mathbf{S}^{abf} \mathbf{W}^g - \mathbf{S}^{abg} \mathbf{W}^f - \mathbf{S}^{afg} \mathbf{W}^b - \mathbf{S}^{abfg} \mathbf{W} = \mathbf{0}. \quad (59)$$

Moreover, the first- and second-order perturbed multipliers have also been omitted from Eq. 58, as they multiply first- and second-order perturbed \mathbf{Y} and \mathbf{P} , which are zero when density matrices to second order are included

$$\begin{aligned} & -\mathbf{X}_a^{fg} \mathbf{Y}^b - \mathbf{X}_a^{bg} \mathbf{Y}^f - \mathbf{X}_a^{bf} \mathbf{Y}^g - \mathbf{X}_a^g \mathbf{Y}^{bf} - \mathbf{X}_a^f \mathbf{Y}^{bg} - \mathbf{X}_a^b \mathbf{Y}^{fg} \\ & -\mathbf{L}_a^{fg} \mathbf{P}^b - \mathbf{L}_a^{bg} \mathbf{P}^f - \mathbf{L}_a^{bf} \mathbf{P}^g - \mathbf{L}_a^g \mathbf{P}^{bf} - \mathbf{L}_a^f \mathbf{P}^{bg} - \mathbf{L}_a^b \mathbf{P}^{fg} = \mathbf{0}. \end{aligned} \quad (60)$$

After some further manipulations of Eq. 58 (see Ref. 44), by which the third-order *partial derivative* Fock matrices and overlap matrices are moved out of \mathbf{W}_2^{bfg} , \mathbf{Y}_2^{bfg} and \mathbf{L}_2^{bfg} , and become new terms in $\left(\frac{\partial}{\partial a} E(\mathbf{D}) \right)_2^{bfg}$, it can be simplified to

$$Q_{1,2}^{abfg} \stackrel{\text{Trt}}{=} E_{1,2}^{abfg} - \mathbf{S}^{ab} \mathbf{W}^{fg} - \mathbf{S}^a \mathbf{W}_{2'}^{bfg} - \mathbf{X}_a \mathbf{Y}_{2'}^{bfg} - \mathbf{L}_a \mathbf{P}_{2'}^{bfg}, \quad (61)$$

where the added prime in the subscripts indicates that no third-order partial derivatives of Fock matrices or overlap matrices are included.

Differentiating Eq. 16 four times, keeping only terms involving the designated set of perturbed density matrices, and taking into account that the LAOs are independent of \mathbf{f} and \mathbf{g} , the following expression for $E_{1,2}^{abfg}$ is found

$$\begin{aligned} E_{1,2}^{abfg} \stackrel{\text{Trt}}{=} & \left(\frac{\partial^3}{\partial a \partial b \partial g} \mathbf{F} \right) \mathbf{D}^f + \left(\frac{\partial^3}{\partial a \partial b \partial f} \mathbf{F} \right) \mathbf{D}^g + \mathbf{G}^{ab} (\mathbf{D}^f) \mathbf{D}^g \\ & + \left(\frac{\partial^2}{\partial a \partial b} \mathbf{F} \right) \mathbf{D}^{fg} + \left(\frac{\partial^2}{\partial a \partial f} \mathbf{F} \right) \mathbf{D}^{bg} + \left(\frac{\partial^2}{\partial a \partial g} \mathbf{F} \right) \mathbf{D}^{bf} \\ & + \mathbf{G}^b (\mathbf{D}^a) \mathbf{D}^{fg} + \mathbf{G}^a (\mathbf{D}^b) \mathbf{D}^{fg} + \mathbf{G}^a (\mathbf{D}^f) \mathbf{D}^{bg} + \mathbf{G}^a (\mathbf{D}^g) \mathbf{D}^{bf}. \end{aligned} \quad (62)$$

Analogously, differentiating Eqs. 19, 31 and 32 three times, keeping terms involving perturbed matrices to second order, and utilizing that the unperturbed matrices are time-independent, while the perturbed matrices carry time-dependent phase factors with the respective frequencies, the following compact expressions for $\mathbf{W}_{2'}^{bfg}$, $\mathbf{Y}_{2'}^{bfg}$ and $\mathbf{P}_{2'}^{bfg}$ can be

derived

$$\mathbf{W}_{2'}^{bfg} = \mathbf{D}^b [\mathbf{F}^f \mathbf{D} + \mathbf{F}^g \mathbf{D}^f + \mathbf{F}^f \mathbf{D}^g + (\mathbf{F} + \frac{\omega_b - \omega_f - \omega_g}{2} \mathbf{S}) \mathbf{D}^{fg}] \quad (63)$$

$$\begin{aligned} &+ \mathbf{D}^f [\mathbf{F}^{bg} \mathbf{D} + \mathbf{F}^g \mathbf{D}^b + (\mathbf{F}^b + \frac{\omega_f - \omega_g}{2} \mathbf{S}^b) \mathbf{D}^g] \\ &+ \mathbf{D}^g (\mathbf{F}^{bf} \mathbf{D} + \mathbf{F}^f \mathbf{D}^b) + \mathbf{D}^{bf} [\mathbf{F}^g \mathbf{D} + (\mathbf{F} + \frac{\omega_b + \omega_f - \omega_g}{2} \mathbf{S}) \mathbf{D}^g] \\ &+ \mathbf{D}^{bg} [\mathbf{F}^f \mathbf{D} + (\mathbf{F} + \frac{\omega_b + \omega_g - \omega_f}{2} \mathbf{S}) \mathbf{D}^f] + \mathbf{D}^{fg} (\mathbf{F}^b - \frac{\omega_f + \omega_g}{2} \mathbf{S}^b) \mathbf{D} + \text{h.c.} \end{aligned}$$

$$\mathbf{Y}_{2'}^{bfg} = [\mathbf{F}^f \mathbf{D} + \mathbf{F}^g \mathbf{D}^f + \mathbf{F}^f \mathbf{D}^g + (\mathbf{F} - \frac{\omega_b + 2\omega_f + 2\omega_g}{2} \mathbf{S}) \mathbf{D}^{fg}] \mathbf{S}^b \quad (64)$$

$$+ (\mathbf{F}^f \mathbf{D}^b + \mathbf{F}^{bg} \mathbf{D}^f + \mathbf{F}^{bf} \mathbf{D}^g + \mathbf{F}^g \mathbf{D}^{bf} + \mathbf{F}^f \mathbf{D}^{bg} + \mathbf{F}^b \mathbf{D}^{fg}) \mathbf{S} - \text{h.c.}$$

$$\mathbf{P}_{2'}^{bfg} = (\mathbf{D}^b \mathbf{S} + \mathbf{D} \mathbf{S}^b) \mathbf{D}^{fg} + \mathbf{D}^f (\mathbf{S}^b \mathbf{D}^g + \mathbf{S} \mathbf{D}^{bg}) + \mathbf{D}^g \mathbf{S} \mathbf{D}^{fb} + \text{h.c.}, \quad (65)$$

where ‘‘h.c.’’ is a short-hand notation for all the preceding terms with the matrix products in reverse order and opposite sign on the frequencies. We note that these formulæ become slightly simpler for the Cotton-Mouton hypermagnetizability, for which the frequencies are $\omega_a = \omega_b = 0$, $\omega_f = -\omega_g = \omega$.

The above equations form the necessary components to calculate the hypermagnetizability tensor, using London atomic orbitals to ensure gauge-origin independence of the calculated result, as well as employing frequency-dependent electric fields. This formalism has been implemented in a local version of the Dalton quantum chemistry program.⁶⁰

III. COMPUTATIONAL DETAILS

We have calculated the frequency-dependent polarizability, the magnetizability and the hypermagnetizability for the series of molecules C_6H_6 , $\text{C}_6\text{H}_5\text{F}$, $o\text{-C}_6\text{H}_4\text{F}_2$, $m\text{-C}_6\text{H}_4\text{F}_2$, $p\text{-C}_6\text{H}_4\text{F}_2$, $1,3,5\text{-C}_6\text{H}_3\text{F}_3$ and C_6F_6 , using both London atomic orbitals and conventional basis sets. In the latter case, the center of mass of the molecule has in all cases been chosen as gauge origin.

For isotropic diamagnetic fluids composed of ‘‘non-spherical’’ molecules, the Cotton-Mouton constant has two contributions, one temperature-independent term determined by the hypermagnetizability anisotropy $\Delta\eta$ and a temperature-dependent contribution $\Delta[\alpha\xi]$ ^{13,42}

$${}_m C = \frac{2\pi N_A}{27} \left(\Delta\eta + \frac{2}{15kT} \Delta[\alpha\xi] \right), \quad (66)$$

where N_A is Avogadro’s number, k is the Boltzmann constant and T the temperature in Kelvin.

The hypermagnetizability anisotropy is defined as

$$\Delta\eta = \frac{1}{5} \left(\eta_{\alpha\beta, \alpha\beta} - \frac{1}{3} \eta_{\alpha\alpha, \beta\beta} \right), \quad (67)$$

where summation over repeated indices is implied. The anisotropy appearing in the temperature-dependent term is defined as

$$\Delta[\alpha\xi] = \alpha_{\alpha\beta} \xi_{\alpha\beta} - \alpha_{\alpha\alpha} \xi_{\beta\beta}, \quad (68)$$

which for axial molecules reduces to $\Delta\alpha\Delta\xi$, where the polarizability ($\mathcal{P} = \alpha$) and magnetizability ($\mathcal{P} = \xi$) anisotropies are defined as

$$\Delta\mathcal{P} = \mathcal{P}_{\parallel} - \mathcal{P}_{\perp}. \quad (69)$$

For completeness, we also report the polarizability and magnetizability anisotropies defined in the case of a general planar molecule

$$\Delta\mathcal{P} = \mathcal{P}_{zz} - \frac{1}{2}(\mathcal{P}_{xx} + \mathcal{P}_{yy}), \quad (70)$$

where z denotes the axis perpendicular to the molecular plane.

The geometries of all molecules have been optimized employing the cc-pVTZ basis set of Dunning⁶¹ while using Becke’s 3-parameter exchange functional⁶² together with the Lee–Yang–Parr correlation functional⁶³ (B3LYP).⁶⁴ We note that in previous theoretical work,^{33,34} experimental geometries have been employed. Therefore small differences will appear between our results and earlier theoretical calculations, due to the small differences in the choice of molecular geometries.

For the calculation of the properties, we have used the augmented correlation-consistent basis sets of Woon and Dunning,^{61,65} as diffuse functions are known to be important in order to obtain accurate results both for electric polarizabilities and magnetizabilities, and because these basis sets have been demonstrated to be well suited for the calculation of polarizabilities, magnetizabilities and hypermagnetizabilities.^{43,65,66} In order to explore the basis set convergence, we have utilized basis sets of double-, triple-, and quadruple-zeta quality. All calculations have employed a wavelength of 632.8 nm, as also used by Rizzo *et al.*^{33,34} For fluorobenzene we have also studied the dispersion of the hypermagnetizability anisotropy in more detail, using a larger number of wavelengths. Since our analytic implementation of the frequency-dependent hypermagnetizability using London atomic orbitals is currently restricted to Hartree–Fock wave functions, electron correlation effects will be missing in our results for the polarizabilities, magnetizabilities, hypermagnetizabilities and Cotton–Mouton constants.

The geometry optimizations have been done using the Dalton quantum chemistry program,⁶⁰ whereas the molecular properties have been calculated using a local version of the Dalton program in which the scheme described in Section II has been implemented. The code is interfaced to the density matrix-based Hartree–Fock energy⁶⁷ and response⁵⁹ code of Jørgensen, Coriani and coworkers. All calculations have been run in parallel on 40-90 processors on the local supercomputer at the University of Tromsø, using the parallel implementation described in Ref. 68.

IV. RESULTS

We have collected our results for the investigated molecules in Table I. In the Table, we report the polarizability anisotropy, the magnetizability anisotropy, the hypermagnetizability anisotropy, the product $\Delta[\alpha\xi]$ as well as the Cotton–Mouton constant for a temperature of 304.1 K, as also chosen previously by Rizzo *et al.*^{33,34} Since the electric dipole polarizability does not depend on whether London orbitals are used or not, we only report these results once in the tables.

We emphasize already at this point that the Cotton–Mouton effect is more or less entirely determined by the Langevin-type orientational temperature-dependent part, in all cases studied here. The large changes observed between London and no-London results for the Cotton–Mouton constant are thus entirely due to differences in the magnetizability rather than in the hypermagnetizability anisotropy. At the same time, the smallness of the electronic rearrangement effect, essentially represented by the hypermagnetizability

anisotropy, makes it very hard to extract it from experimental measurements of the magnetic field-induced linear birefringence, since the results of these measurements, made at different temperatures, must be extrapolated to the infinite-temperature limit. These difficulties are reflected in the very generous error bars at times associated with the experimental datum (*vide infra*).

Looking at the general trends for the molecules investigated, we note the very small differences in the polarizability anisotropies across the set of molecules. Indeed, the addition of an extra fluorine atom increases the polarizability anisotropy by less than 2%. There is furthermore hardly any difference in the polarizability anisotropy of the *ortho*-, *meta*- and *para*-difluorobenzenes (-37.10 a.u., -37.03 a.u., and -37.11 a.u., respectively, for the aug-cc-pVQZ basis set). The differences between aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ results are in general very small, the latter being for instance -40.81 , -40.56 and -40.43 a.u. in the case of hexafluorobenzene.

The situation is somewhat similar for the magnetizability anisotropy, though the changes induced by the addition of an extra fluorine atom is in this case larger. In general, the addition of a fluorine atom reduces the magnetizability anisotropy by a little bit less than 8%. We also observe a rather large basis set effect on the magnetizability anisotropy compared to the trend in the basis set convergence most often observed for magnetizabilities. It is on the other hand known that magnetizability anisotropies are in general somewhat harder to converge with respect to both basis set size⁴³ and, in particular, electron correlation⁶⁹ effects than the isotropic magnetizability. However, we note that the differences between the aug-cc-pVTZ and the aug-cc-pVQZ basis set results are in general small, and that the aug-cc-pVTZ basis set results can be considered essentially converged, except in the case of hexafluorobenzene. We also note that the no-London results show a very slow basis set convergence, and that even the aug-cc-pVQZ basis set results cannot be considered fully converged when conventional basis sets are used.

The most spectacular example of the challenges of calculating magnetizability anisotropies can be seen for C_6F_6 . Without London orbitals, the magnetizability anisotropy is reduced almost by a factor of two going from the aug-cc-pVDZ to the aug-cc-pVTZ basis set (from -57.16 a.u. to -31.85 a.u.), and an equally dramatic change can be observed going from the aug-cc-pVTZ to the aug-cc-pVQZ basis set, the result for the aug-cc-pVQZ basis set being -17.39 a.u. In relative terms, the changes are however even more dramatic for the London atomic orbital calculations, for which the magnetizability anisotropy increases (in absolute value) by a factor of eight going from the aug-cc-pVDZ basis set to the aug-cc-pVTZ basis set (from -0.88 a.u. to -6.65 a.u.). However, it is somewhat rewarding to note that the additional changes induced by going to the aug-cc-VQZ basis are much smaller, though still increasing the magnetizability anisotropy by almost 50%, the result for the aug-cc-pVQZ basis being -9.01 a.u.. In terms of the absolute magnitude of the changes, these are fairly small. However, the magnetizability anisotropy does not appear to be fully converged even with the aug-cc-pVQZ basis set (containing as many as 960 basis functions) and London orbitals, though we would estimate the basis set limit results to be around -10.5 au to -11.0 a.u. based on the basis-set convergence observed for the other fluorobenzenes. Hexafluorobenzene thus confirms previous observations of slow basis-set convergence for the magnetizability of fluorine-containing molecules,^{34,43} though the basis-set convergence observed here also when using London atomic orbitals is exceptionally poor.

Turning our attention to the results for the hypermagnetizabilities in Table I, we note that the very poor basis set convergence trend of the magnetizability anisotropy is not inherited by

the hypermagnetizability anisotropy. In particular, even though the absolute values of both the magnetizability and its anisotropy are strongly dependent on the use of London atomic orbitals, as well as on the size of the basis set when London orbitals are not employed, this is not the case for the hypermagnetizability. Indeed, even for the fluorine-rich hexafluorobenzene, there is very little difference between London and conventional results ($-59.1/-60.6$ a.u., $-106.5/-96.2$ a.u., and $-103.4/-108.2$ a.u. for the London/NoLondon results obtained using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively). The basis-set dependence of the hypermagnetizability compared to the magnetizability thus appears to behave in much the same manner as most first-order properties calculated using *ab initio* methods: even though the absolute energy is in general very poorly predicted, the variation of the energy with respect to externally applied perturbations is well reproduced, even for modest-sized basis sets in the case of electric perturbations, often leading to excellent convergence for the molecular properties with the size and quality of the basis set.

Considering in more detail the convergence of the hypermagnetizability anisotropy with respect to the size of the basis set, we note that it is difficult to detect clear convergence trends. In some cases, such as for benzene, the no-London results are very stable (156.0, 155.4, and 154.8 a.u. for the DZ, TZ and QZ basis sets, respectively), converged already at the aug-cc-pVDZ level, whereas the London orbital result changes by $\approx 23\%$ and $\approx 9\%$ in passing from aug-cc-pVDZ to aug-cc-pVTZ to aug-cc-pVQZ (202.5, 155.7 and 137.7 a.u.), respectively, being in apparently accidental agreement with the no-London results when using the triple-zeta basis set. As the number of fluorine atoms in the molecules increases, the London atomic orbital results appear in general to converge faster than the no-London results, whereas the opposite trend is observed in case of the hydrogen-rich molecules.

Part of the somewhat unsystematic convergence behavior of the hypermagnetizability anisotropy with the size of the basis set is due to the fact that the anisotropy is a sum of several contributions of different signs (see Eq. 67), partially cancelling each other. Systematic trends in the convergence of the components of the hypermagnetizability may thus be hidden in accidental cancellations of hypermagnetizability component contributions, leading to artificially poor (or good) basis set convergence. A more relevant criterion for evaluating the basis set convergence of the hypermagnetizability may therefore be found by inspecting the individual tensor components.

In Table II and III, we have collected the symmetry-unique, non-vanishing tensor components of the hypermagnetizability for C_6H_6 and $C_6H_3F_3$, respectively. The most striking feature of these results is perhaps that in the case of C_6H_6 , many of the components appear to be far from converged, even when using the aug-cc-pVQZ basis set, in particular when London orbitals are employed. The η_{xxxx} component, for instance, shows no indication of being close to the basis set limit: the London orbital results change from 256 a.u. for the aug-cc-pVDZ basis, to 123 a.u. for aug-cc-pVTZ, to 64 a.u. for the aug-cc-VQZ basis. A similar slow basis set convergence is observed for the no-London results for this hypermagnetizability component, although the convergence is faster than for the London orbital results. Assuming the London and no-London results to converge to the same basis limit, it would appear that the basis-set limit result for η_{xxxx} is approximately 40 a.u. Another striking indication coming from the results in Table II, is that the extremely fast basis set convergence observed in the case of the no-London results for the hypermagnetizability anisotropy of benzene is purely accidental and the result of a fortunate cancellation of slowly converging hypermagnetizability tensor components. Still, the basis set convergence appears in general to be better in the case of conventional basis sets than when London orbitals are used for

the majority of the hypermagnetizability components of benzene.

The situation changes as we add fluorine atoms to the benzene framework, and in the case of 1,3,5-trifluorobenzene (see Table III), the London orbital results converge nicely for all components. Only small changes are in general observed going from the aug-cc-pVTZ to the aug-cc-pVQZ basis set, whereas the aug-cc-pVDZ basis in general appears to be too small to be reliable. We note that there are still differences between the London and no-London results using the aug-cc-pVQZ basis set, but the better basis set convergence of the London orbital results would indicate that the basis-set limit should be close to the results of the London orbital calculations.

For fluorobenzene we have also carried out calculations to investigate the frequency dependence of the hypermagnetizability anisotropy, and the results obtained at the aug-cc-pVTZ level of theory are collected in Table IV. We note that the dispersion of the hypermagnetizability anisotropy is as usual very small, and noticeable dispersion effects are seen only as the region of very short wavelengths is approached. In contrast, the temperature-dependent contribution of the Cotton–Mouton constant shows a rather noticeable dispersion effect. Any experimentally observed dispersion in the Cotton–Mouton constant of benzene and the fluorobenzenes is therefore dominated by the temperature-dependent contribution.

Benzene and hexafluorobenzene have previously been studied theoretically by Rizzo *et al.*,^{33,34} both at the Hartree–Fock and density-functional levels of theory, as well also by coupled-cluster methods in the case of benzene. After correcting for an error in the sign of the paramagnetic contribution in Refs. 33,34 (see Ref. 73), a very good agreement between our no-London results and the results of Rizzo *et al.* is observed. The small residual differences are due to differences in the molecular geometry, as we use optimized geometries whereas experimental structures were used in Ref. 34. Rizzo *et al.* reached the conclusion that correlation effects on the hypermagnetizability anisotropy were moderate (about 20–25%). Actually, once the sign of the paramagnetic contribution is corrected, the correlation effects are seen to be very minor, with the Hartree–Fock, BLYP, B3LYP and CCSD results all differing by only a few percent in the case of benzene (159.5 a.u., 158.6 a.u., 157.2 a.u. and 165 a.u., respectively).⁷³ This small electron correlation effect may once again be accidental, due to a fortunate cancellation of errors in the individual components. These results do however lend hope that Hartree–Fock and density-functional theory may be able to provide reliable estimates for the hypermagnetizability anisotropies. As expected, correlation effects on the polarizability and magnetizability anisotropies were found to be larger.^{33,34}

There exist experimental results for the Cotton–Mouton effect in benzene,^{47–49} fluorobenzene,⁵⁰ 1,3,5-trifluorobenzene and hexafluorobenzene,^{47,48} and these results are collected in Table V together with our results. Experimentally, the hypermagnetizability anisotropy is obtained by extrapolating the Cotton–Mouton constant measured for different temperatures to the infinite-temperature limit. As already noted from our results above, the contribution of the hypermagnetizability anisotropy to the Cotton–Mouton effect is very small, making the experimental estimation of the effect difficult, often giving rise to very large experimental error bars for the hypermagnetizability anisotropies.

From Table V we note a in general rather good agreement between theory and experiment for the polarizability and magnetizability anisotropies, with a clear preference for the more recent experimental results of Ritchie and Watson⁷¹ in the case of the polarizability anisotropies of benzene and hexafluorobenzene. Note that Rizzo *et al.*^{33,34} demonstrated that electron correlation effects lead in general to an increase in the polarizability anisotropy, yielding very good agreement with the polarizability anisotropies measured by Ritchie and

Watson.³⁴ Note also that the polarizability anisotropies reported in an earlier study by Lukins, Buckingham and Ritchie⁴⁷ appear in general to be too large. Since these polarizabilities were used by Lukins *et al.* to derive the magnetizability anisotropies, we would expect these magnetizability anisotropies to be too small, which seems indeed to be the case in comparison to the theoretical data in the case of benzene and 1,3,5-trifluorobenzene. However, electron correlation effects can at the same time be expected to increase the magnetizability anisotropy slightly.³⁴

Due to the difficulties in extrapolating the temperature dependence of the Cotton–Mouton effect to the infinite-temperature limit, the error bars on the experimental data for the hypermagnetizability anisotropies are very generous, and this makes it easy for our calculated hypermagnetizability anisotropy to be within the experimental error bars. We note the stunning agreement with experiment in the case of hexafluorobenzene (our result is -103.4 a.u., to be compared with the experimental result of -100 ± 880), and that the calculated hypermagnetizability anisotropy of benzene has the wrong sign (137.7 a.u.) compared to the center of the distribution of the experimental observations (-2700 ± 2000 a.u.). However, Lukins *et al.* were cautious about the sign of the hypermagnetizability anisotropy of benzene in view of the estimated error bars, as well as the fact that a study by Geschka *et al.*⁴⁹ indicated a positive sign for the hypermagnetizability anisotropy ($\Delta\eta=700\pm1400$ au, interestingly enough having been neglected in the determination of the temperature dependence of the birefringence by the authors of Ref. 49), in agreement with our calculations.

Despite the differences in the calculated and experimental magnetizability and polarizability anisotropies, the agreement between the experimental and theoretical values for ${}_mC$ is quite satisfactory, and in all cases only slightly outside the experimental errors bars. The reason for this perhaps somewhat surprisingly good agreement is due to the fact that whereas the calculated polarizability anisotropy is somewhat too small, the calculated magnetizability anisotropy is somewhat too large, leaving the total temperature-dependent contribution to the Cotton–Mouton constant in good agreement with experiment. The inclusion of electron correlation effects would improve the agreement between theory and experiment further.^{33,34}

V. SUMMARY

We have presented the first analytic, frequency-dependent calculations of the hypermagnetizability anisotropy using London atomic orbitals to ensure gauge-origin independent results. The implementation is based on a general framework for the calculation of higher-order, frequency-dependent molecular properties including corrections arising from perturbation-dependent basis functions, and it is currently limited to Hartree–Fock wave functions. On the other hand, the approach employed here is in principle applicable to any self-consistent field reference state which can be formulated in terms of density matrices.

We have demonstrated that the hypermagnetizability is less sensitive to the use of London orbitals than the magnetizability itself, and the electric-field variation of the magnetizability is thus modelled qualitatively correct, and to a large extent also quantitatively, both by conventional basis sets as well as London orbitals. The hypermagnetizability anisotropy converges fairly rapidly with increasing size of the basis set used, although this seems to a large extent to be due to a fortunate cancellation of errors in the more slowly converging components of the hypermagnetizability tensor. Whereas in the case of benzene the individual components of the hypermagnetizability tensor are actually converging slightly faster using conventional basis functions than using London orbitals, the use of the latter improves

the basis set convergence when one or more fluorine atoms are put in place of the hydrogen atoms in the benzene molecule.

Obtaining basis-set limit results for the hypermagnetizability tensor has been shown to be a challenging task. The introduction of London atomic orbitals leads to somewhat improved basis set convergence in the components of the hypermagnetizability tensor, although these improvements are not always reflected in the convergence of the hypermagnetizability anisotropy. This situation thus partly reflects the observations made for the calculation of optical rotations, involving the mixed electric dipole–magnetic dipole polarizability, where only small improvements in basis set convergence are observed when using London orbitals compared to conventional basis sets.⁷² However, both for the optical rotation and the hypermagnetizability tensor, the use of London orbitals ensures gauge-origin independence of the results. The latter, combined with the improvements in the basis set convergence for the individual tensor components, suggests that the scheme proposed here should be used in future calculations of the hypermagnetizability, in particular for larger molecules.

Agreement between our calculated results and available experimental data is in general satisfactory, in particular considering the fact that our results have been obtained at the Hartree–Fock level of theory. For the polarizability and magnetizability anisotropies, our data are in general within the error bars of the most recent experimental data, whereas our predictions for ${}_mC$ is just outside the experimental error bars. For the hypermagnetizability anisotropies, our calculated results are within the very generous experimental error bars. Our results support the evidence for a positive value for the hypermagnetizability anisotropy of benzene.

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Table I: Calculated results for the electric dipole polarizability anisotropy $\Delta\alpha$ (see Eq. 70), magnetizability anisotropy $\Delta\xi$ (see Eq. 70), the product $\Delta[\alpha\xi]$ (see Eq. 68), the hypermagnetizability anisotropy $\Delta\eta$ (see Eq. 67) and the corresponding Cotton–Mouton constants (see Eq. 66). A wavelength of 632.8 nm is employed in the calculations. ${}_mC$ is given in units of $10^{-16} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1} (4\pi\epsilon_0)$ for a temperature of 304.1 K, whereas all other quantities are given in atomic units. “Lon” and “NoLon” indicate the use of perturbation-dependent London Orbitals or conventional basis sets, respectively.

Basis	$\Delta\alpha$	$\Delta\xi$	$\Delta[\alpha\xi]$	$\Delta\eta$	${}_mC$
C₆H₆					
aug-cc-pVDZ (Lon)	-35.34	-13.50	318.1	202.5	2.49
aug-cc-pVTZ (Lon)	-35.71	-14.21	338.5	155.7	2.65
aug-cc-pVQZ (Lon)	-35.82	-14.43	344.5	137.7	2.69
aug-cc-pVDZ (NoLon)	-20.40	480.5	156.0	3.76	
aug-cc-pVTZ (NoLon)	-17.51	416.8	155.4	3.26	
aug-cc-pVQZ (NoLon)	-15.47	369.5	154.8	2.89	
C₆H₅F					
aug-cc-pVDZ (Lon)	-36.03	-12.64	303.4	111.8	2.37
aug-cc-pVTZ (Lon)	-36.34	-13.09	317.1	88.9	2.48
aug-cc-pVQZ (Lon)	-36.41	-13.28	322.2	82.8	2.53
aug-cc-pVDZ (NoLon)	-24.70	596.7	106.2	4.66	
aug-cc-pVTZ (NoLon)	-18.91	459.3	101.2	3.59	
aug-cc-pVQZ (NoLon)	-15.22	369.8	97.1	2.89	
<i>o</i>-C₆H₄F₂					
aug-cc-pVDZ (Lon)	-36.85	-11.42	280.2	54.3	2.19
aug-cc-pVTZ (Lon)	-37.07	-12.19	300.8	38.0	2.35
aug-cc-pVQZ (Lon)	-37.10	-12.44	307.3	43.0	2.40
aug-cc-pVDZ (NoLon)	-28.49	703.5	56.9	5.50	
aug-cc-pVTZ (NoLon)	-20.29	502.7	52.1	3.93	
aug-cc-pVQZ (NoLon)	-15.17	375.4	47.6	2.93	
<i>m</i>-C₆H₄F₂					
aug-cc-pVDZ (Lon)	-36.76	-11.58	283.5	43.1	2.21
aug-cc-pVTZ (Lon)	-37.00	-11.79	290.4	28.7	2.27
aug-cc-pVQZ (Lon)	-37.03	-11.94	294.4	25.4	2.30
aug-cc-pVDZ (NoLon)	-30.52	757.0	60.7	5.91	
aug-cc-pVTZ (NoLon)	-20.87	518.1	48.2	4.05	
aug-cc-pVQZ (NoLon)	-15.07	373.1	41.0	2.91	
<i>p</i>-C₆H₄F₂					
aug-cc-pVDZ (Lon)	-36.82	-11.40	279.4	41.8	2.18
aug-cc-pVTZ (Lon)	-37.06	-11.81	291.6	26.1	2.28
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Basis	$\Delta\alpha$	$\Delta\xi$	$\Delta[\alpha\xi]$	$\Delta\eta$	mC
aug-cc-pVQZ (Lon)	-37.11	-12.00	296.5	16.1	2.32
aug-cc-pVDZ (NoLon)		-31.99	796.7	65.0	6.22
aug-cc-pVTZ (NoLon)		-21.56	535.6	47.4	4.18
aug-cc-pVQZ (NoLon)		-15.38	381.3	37.3	2.98
C ₆ H ₃ F ₃					
aug-cc-pVDZ (Lon)	-37.53	-10.26	256.8	-14.3	2.00
aug-cc-pVTZ (Lon)	-37.69	-10.29	258.6	-24.1	2.02
aug-cc-pVQZ (Lon)	-37.69	-10.45	262.5	-21.0	2.05
aug-cc-pVDZ (NoLon)		-37.28	932.7	24.3	7.28
aug-cc-pVTZ (NoLon)		-23.15	581.6	1.6	4.54
aug-cc-pVQZ (NoLon)		-14.94	375.3	-7.5	2.93
C ₆ F ₆					
aug-cc-pVDZ (Lon)	-40.81	-0.88	24.02	-59.1	0.185
aug-cc-pVTZ (Lon)	-40.56	-6.65	179.8	-106.5	1.40
aug-cc-pVQZ (Lon)	-40.43	-9.01	242.7	-103.4	1.89
aug-cc-pVDZ (NoLon)		-57.16	1555	-60.6	12.14
aug-cc-pVTZ (NoLon)		-31.85	861.2	-96.2	6.72
aug-cc-pVQZ (NoLon)		-17.39	468.8	-108.2	3.66

Table II: The symmetry-unique non vanishing tensor components of the hypermagnetizability of C_6H_6 . The molecule is located in the xy plane, with long axis of the molecule along the x axis. All results reported in atomic units.

	no-London			London		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
η_{xxxx}	-20.54	12.13	23.51	255.72	122.56	63.89
η_{xxyy}	-133.96	-38.04	-5.65	181.58	89.43	41.02
η_{xxzz}	272.02	264.23	251.68	328.13	268.53	285.70
η_{xyxy}	56.70	25.07	14.56	37.03	17.07	11.43
η_{xzxz}	270.06	291.97	296.29	301.73	278.60	288.19
η_{zzxx}	97.65	141.99	161.98	188.28	188.40	196.58
η_{zzzz}	-343.59	-317.35	-299.49	-216.49	-254.71	-335.14
$\Delta\eta$	156.0	155.4	154.8	202.5	157.7	137.7

Table III: The symmetry-unique non vanishing tensor components of the hypermagnetizability of $C_6F_3H_3$. The molecule is located in the xy plane, with long axis of the molecule along the x axis. All results reported in atomic units.

	no-London			London		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
η_{xxxx}	42.95	76.47	95.15	175.31	129.80	116.48
η_{xxyy}	67.58	166.40	208.78	311.47	251.39	234.29
η_{xxzz}	-28.59	90.71	151.78	223.67	224.95	225.80
η_{xyxy}	-12.32	-45.05	-56.81	-68.05	-60.75	-58.91
η_{xzxz}	79.68	87.46	90.20	86.83	85.91	89.72
η_{zzxx}	210.18	219.63	235.90	271.47	272.76	264.50
η_{zzzz}	-95.43	-53.79	-21.10	32.02	-24.55	-27.14
$\Delta\eta$	24.3	1.6	-7.5	-14.3	-24.1	-21.0

Table IV: Calculated dispersion of fluorobenzene using the aug-cc-pVTZ basis set and London atomic orbitals. All results reported in atomic units.

λ (nm)	∞	633	550	442	350
Δ [$\alpha\xi$]	301.22	317.09	322.72	336.45	363.19
$\Delta\eta$	88.16	88.42	88.27	87.29	82.30

Table V: Comparison of theoretical and experimental results for the polarizability, magnetizability and hypermagnetizability anisotropies for C_6H_6 , C_6H_5F , $C_6H_3F_3$ and C_6F_6 . All theoretical data are calculated using London atomic orbitals. ${}_mC$ is given in CGS units of $10^{-16} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$ ($4\pi\epsilon_0$), $\Delta[\alpha\xi]$ in units of $10^{-15} \text{ cm}^3 \text{ G}^{-2} \text{ mol}^{-1}$ ($4\pi\epsilon_0$) K, whereas all other data are reported in atomic units. The theoretical data have been obtained at the Hartree-Fock/aug-cc-pVQZ, using a wavelength of 632.8 nm and assuming a temperature of 304.1 K.

	C_6H_6		C_6H_5F		$C_6H_3F_3$		C_6F_6	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
$\Delta\alpha$	-35.82	-40.9 ± 0.8^a	-36.41	-39 ± 3^b	-37.69	-42.9 ± 1.3^a	-40.43	-45.2 ± 1.3^a
		-37.79 ± 1.15^c						-42.82 ± 1.27^c
$\Delta\xi$	-14.43	-13.13 ± 0.51^d	-13.28	-11.9 ± 0.2^e	-10.45	-9.19 ± 0.66^d	-9.01	-7.95 ± 0.29^d
		-11 ± 1^f				-8.2 ± 0.4^f		-6.7 ± 0.3^f
		-13.15 ± 0.42^g						
$\Delta[\alpha\xi]$	81.8	84.9 ± 2.8	76.5		62.3	62.3 ± 4.0	57.6	56.9 ± 1.2
$\Delta\eta$	137.7	-2700 ± 2000^h	82.8	0 ± 1700^i	-21.0	-500 ± 3000^h	-103.4	-100 ± 880^h
${}_mC$	2.69	2.74 ± 0.07^j	2.53	1.84 ± 0.04^k	2.05	2.00 ± 0.05^l	1.89	1.87 ± 0.03^m
		2.22 ± 0.10^n				1.72 ± 0.07^n		1.51 ± 0.07^n
		2.59 ± 0.07^o						

^aReported in Ref. 47, based on the data reported in Ref. 70.

^bRef. 50, $\lambda=632.8$ nm.

^cRef. 71.

^dRef. 47.

^eRef. 50. $\xi_{xx}=-8.65\pm 0.13$; $\xi_{yy}=-7.93\pm 0.13$; $\xi_{zz}=-20.2\pm 0.17$ with x along the C_2 axis and z perpendicular to the plane.

^fRef. 48.

^gRef. 49.

^hRef. 47, $\lambda=441.6$ nm.

ⁱRef. 50, *assumed*.

^jRef. 47 for a wavelength of 441.6 nm and $T=300.1$ K.

^kRef. 50, $\lambda=632.8$ nm, $T=405.6\pm 0.8$ K.

^lRef. 47 for a wavelength of 441.6 nm and $T=303.8$ K.

^mRef. 47 for a wavelength of 441.6 nm and $T=304.1$ K.

ⁿRef. 48, $\lambda=632.8$ nm.

^oRef. 49, $\lambda=632.8$ nm, $T=304.1$ K

