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We present the first gauge-origin independent formulation of Jones birefringence at the Hartree–Fock level of theory. Gauge-origin independence is achieved through the use of London atomic orbitals. The implementation is based on a recently proposed atomic orbital-based response theory formulation that allows for the use of both time- and perturbation-dependent basis sets [Thorvaldsen, Ruud, Kristensen, Jørgensen, and Coriani, J. Chem. Phys. **129**, 214108 (2008)]. We present the detailed expressions for the response functions entering the Jones birefringence when London atomic orbitals are used. The implementation is tested on a set of polar and dipolar molecules at the Hartree–Fock level of theory. It is demonstrated that London orbitals lead to much improved basis-set convergence, and that the use of small, conventional basis sets may lead to the wrong sign for the calculated birefringence. For large basis sets, London orbitals and conventional basis sets converge to the same results. © *2011 American Institute of Physics*. [doi:10.1063/1.3645182]

I. INTRODUCTION

When linearly polarized monochromatic light passes through a sample exposed to external uniform electric and magnetic induction fields that are applied parallel to each other and perpendicular to the direction of propagation of the light beam, an anisotropy of the refractive index of the sample is observed. This anisotropy in the refractive index was first theoretically predicted in 1948 by Jones,[1] from which the anisotropy now bears its name, Jones birefringence. The first experimental observations of Jones birefringence in liquids was made by Rikken and co-workers more than 50 years later, at the start of this century.[2–5]

The theory of Jones birefringence was developed by Graham and Raab.[6] The birefringence is bilinear in the electric and magnetic induction field strengths, but with the pairs of axes for these induction field strengths bisecting those used in the more common Kerr[7,8] and Cotton–Mouton[9,10] birefringences. We note that the so-called "Magneto-electric birefringence"[11,12] from a theoretical point of view is equivalent to Jones birefringence,[13] even though the experimental setup differs in the two experiments. As such, the results we obtain here will be applicable to both these birefringences.

The first *ab initio* studies of Jones birefringence was presented by Rizzo and Coriani, who also identified the relevant response functions entering the expression for the birefringence.[14] In their first study, Rizzo and Coriani calculated the observable quantity of Jones birefringence, the anisotropy of the refractive index for the light polarized at $+45°$ and $-45°$ with respect to the direction of polarization of the light in Jones birefringence, in the atomic systems He, Ne, Ar, Kr as well as the linear non-dipolar molecules H_2, N_2, C_2H_2, and the dipolar molecule CO. These calculations were performed at the coupled-cluster level of theory including single and double excitations[15–17] using the

Hartree–Fock and coupled-cluster implementations of the quadratic and cubic response theories.[18–26] The authors more recently extended their study of Jones birefringence to larger molecules[27,28] using density functional response theory.[29,30] We recently explored the effects of a solvent, modeled by a polarizable dielectric continuum model (PCM),[31–33] on the Jones birefringence,[34] building on the extensions of the PCM to quadratic and cubic response functions.[35–37] The field of *ab initio* calculations of Jones birefringence (as well as other birefringences) has been reviewed several times by Rizzo and co-workers.[38–40]

In this paper, we present the extension of our analytic scheme for the calculation of derivatives of the electronic quasienergy for time- and perturbation-dependent basis sets[41] to the study of Jones birefringence using London atomic orbitals. The use of London atomic orbitals[42] ensures that the calculated birefringence is origin independent, in contrast to earlier theoretical calculations of Jones birefringence, and particular attention will here be given to investigate the convergence of the numerical results with and without London orbitals. Results will be presented for two non-dipolar molecules, carbon tetrachloride and naphthalene, and the dipolar molecule chlorobenzene.

The remainder of the paper is organized as follows: In Sec. II, we will briefly summarize the theory for Jones birefringence and the relationship between the observable anisotropy in the refractive index to the molecular response functions and quasienergy derivatives. In Sec. III, we will describe our quasienergy derivative theory for calculating the relevant energy derivatives using time-dependent London atomic orbitals[43] to ensure gauge-origin independence of the observable Jones birefringence. This derivation will follow very closely our previous implementation of the relevant tensors determining the Cotton–Mouton effect.[44] In Sec. IV, we will briefly summarize the computational details, before we present and discuss our results in Sec. V, with an emphasis on demonstrating the gauge-origin independence of our

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formalism and the improvements observed in basis-set convergence when LAOs are used. Finally, in Sec. VI we give some concluding remarks.

II. THEORY

When linearly polarized monochromatic light interacts with a molecule in the presence of both an external electric field and a magnetic induction field applied parallel to each other and perpendicular to the direction of the propagating light beam, an anisotropy of the refractive index will be observed.[1] The specific birefringence $[\Delta n]$ observed for a gas with molar volume V_m and unit electric and unit magnetic fields may be written as

$$[\Delta n] = \frac{(n_{-45°} - n_{+45°})V_m}{M E_x B_x} = \frac{N_A}{30\epsilon_0 c_0 M} \times \left\{ J_0 + \frac{J_T}{T} \right\}$$

$$= [\Delta n^{(0)}] + \frac{[\Delta n^{(T)}]}{T}, \tag{1}$$

where N_A is Avogadro's number, M is the molar mass, ϵ_0 is the electric constant, c_0 is the speed of light in vacuo, and T is the temperature. We have, here, assumed that the radiation field is propagating in the z direction, and that the electric and magnetic fields have been applied in the x direction, using E_x and B_x to represent the x components of the electric $\boldsymbol{E}$ and magnetic $\boldsymbol{B}$ fields, respectively. If the molar mass is given in g mol^{-1}, and the quantity inside the curly brackets is computed in atomic units, $[\Delta n]$ is obtained in units of cm^4 g^{-1} V^{-1} T^{-1} from

$$[\Delta n] \approx 2.25681 \times 10^{-19} \times \frac{1}{M[\text{g mol}^{-1}]} \times \left\{ J_0 + \frac{J_T}{T} \right\}[\text{a.u.}]. \tag{2}$$

This equation is valid for a gas with molar volume V_m, for which the density of the gas ρ is given by M/V_m.

It is customary to report the Jones birefringence in terms of a Jones constant k_J, defined through the relation[3]

$$\Delta n = n_{-45°} - n_{+45°} = k_J \lambda \, \boldsymbol{E} \cdot \boldsymbol{B} \tag{3}$$

and involving explicitly the wavelength of the radiation, λ. Here, k_J is given as

$$k_J = \frac{N_A \rho}{30\epsilon_0 c_0 M \lambda} \times \left\{ J_0 + \frac{J_T}{T} \right\}$$

$$\approx 2.25681 \times 10^{-12} \times \frac{\rho[\text{g cm}^{-3}]}{\lambda[\text{nm}] \times M[\text{g mol}^{-1}]}$$

$$\times \left\{ J_0 + \frac{J_T}{T} \right\}[\text{a.u.}], \tag{4}$$

with the resulting value of the Jones constant being given in units of V^{-1} T^{-1} when the density of the gas ρ, molar mass, and wavelength is given in the SI units specified above in square parentheses, with the quantity in graph parentheses computed in atomic units.

Rizzo and co-workers[14,34] showed that the quantities J_0 and J_T can be related to a set of the cubic and quadratic response functions, respectively,

$$J_0 = \mathcal{G}_{\text{para}}^{(3)} + \mathcal{G}_{\text{dia}}^{(3)} + \mathcal{A}'^{,(3)}, \tag{5}$$

$$J_T = \frac{1}{k_B} \left[\mathcal{G}_{\text{para}}^{(2)} + \mathcal{G}_{\text{dia}}^{(2)} + \mathcal{A}'^{,(2)} \right], \tag{6}$$

where k_B is the Boltzmann constant.

The quantities appearing in Eqs. (5) and (6) are defined as (using Einstein's summation convention over repeated Greek indices)

$$\mathcal{G}_{\text{para}}^{(3)} = 3G_{\alpha\beta\alpha\beta}^{\text{para}} + 3G_{\alpha\beta\beta\alpha}^{\text{para}} - 2G_{\alpha\alpha\beta\beta}^{\text{para}}, \tag{7}$$

$$\mathcal{G}_{\text{dia}}^{(3)} = 3G_{\alpha\beta\alpha\beta}^{\text{dia}} + 3G_{\alpha\beta\beta\alpha}^{\text{dia}} - 2G_{\alpha\alpha\beta\beta}^{\text{dia}}, \tag{8}$$

$$\mathcal{A}'^{,(3)} = -\frac{\omega}{2}\varepsilon_{\alpha\beta\gamma}(a'_{\alpha\beta\delta\delta\gamma} + a'_{\alpha\beta\delta\gamma\delta}), \tag{9}$$

$$\mathcal{G}_{\text{para}}^{(2)} = \mu_\alpha \left(3G_{\alpha\beta\beta}^{\text{para}} + 3G_{\beta\alpha\beta}^{\text{para}} - 2G_{\beta\beta\alpha}^{\text{para}} \right), \tag{10}$$

$$\mathcal{G}_{\text{dia}}^{(2)} = \mu_\alpha \left(3G_{\alpha\beta\beta}^{\text{dia}} + 3G_{\beta\alpha\beta}^{\text{dia}} - 2G_{\beta\beta\alpha}^{\text{dia}} \right), \tag{11}$$

$$\mathcal{A}'^{,(2)} = -\frac{\omega}{2}\varepsilon_{\alpha\beta\gamma}(\mu_\gamma a'_{\alpha\beta\delta\delta} + \mu_\delta a'_{\alpha\beta\delta\gamma}), \tag{12}$$

where ω is the circular frequency of the radiation, and μ_α is the α component of the permanent electric dipole moment. We have also introduced the Levi-Civita alternating tensor $\varepsilon_{\alpha\beta\gamma}$. We note that from Eqs. (6) and (10)–(12) that J_T vanishes for a non-dipolar molecule and $G_{\alpha\beta\gamma}^{\text{para}}$, $G_{\alpha\beta\gamma}^{\text{dia}}$, and $a'_{\alpha\beta\gamma\delta}$ do, therefore, not have to be computed in this case.

The tensors defined in Eqs. (7)–(12) correspond to a set of general frequency-dependent hyperpolarizabilties, see Refs. 14 and 34,

$$a'_{\alpha\beta\gamma\delta}(-\omega;\omega,0) = a'_{\alpha\gamma\beta\delta}(-\omega;\omega,0)$$
$$= -\Im \langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta \rangle\rangle_{\omega,0}$$
$$= i \langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta \rangle\rangle_{\omega,0}, \tag{13}$$

$$a'_{\alpha\beta\gamma\delta\epsilon}(-\omega;\omega,0,0) = a'_{\alpha\gamma\beta\delta\epsilon}(-\omega;\omega,0,0)$$
$$= \Im \langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta, \hat{\mu}_\epsilon \rangle\rangle_{\omega,0,0}$$
$$= -i \langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta, \hat{\mu}_\epsilon \rangle\rangle_{\omega,0,0}, \tag{14}$$

$$G_{\alpha\beta\gamma}^{\text{para}}(-\omega;\omega,0) = \Re \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma \rangle\rangle_{\omega,0}$$
$$= \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma \rangle\rangle_{\omega,0}, \tag{15}$$

$$G_{\alpha\beta\gamma\delta}^{\text{para}}(-\omega;\omega,0,0) = -\Re \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma, \hat{\mu}_\delta \rangle\rangle_{\omega,0,0}$$
$$= -\langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma, \hat{\mu}_\delta \rangle\rangle_{\omega,0,0}, \tag{16}$$

$$G_{\alpha\beta\gamma}^{\text{dia}}(-\omega;\omega) = -\Re \langle\langle \hat{\mu}_\alpha; \hat{\xi}_{\beta\gamma}^{\text{dia}} \rangle\rangle_\omega = -\langle\langle \hat{\mu}_\alpha; \hat{\xi}_{\beta\gamma}^{\text{dia}} \rangle\rangle_\omega, \tag{17}$$

$$G^{\mathrm{dia}}_{\alpha\beta\gamma\delta}(-\omega;\omega,0) = \Re\langle\langle\hat{\mu}_\alpha; \hat{\xi}^{\mathrm{dia}}_{\beta\gamma}, \hat{\mu}_\delta\rangle\rangle_{\omega,0} = \langle\langle\hat{\mu}_\alpha; \hat{\xi}^{\mathrm{dia}}_{\beta\gamma}, \hat{\mu}_\delta\rangle\rangle_{\omega,0},$$
(18)

where the last equalities hold for real electronic reference wavefunctions. In these equations, we have in addition to the electric dipole operator $\hat{\boldsymbol{\mu}}$ also introduced the magnetic dipole ($\hat{\boldsymbol{m}}$) and, in order to follow the derivation of Graham and Raab,[6] the traced electric quadrupole ($\hat{\boldsymbol{q}}$) operators, defined as, respectively,

$$\hat{\mu}_\alpha = -\sum_i r_{i\alpha},$$
(19)

$$\hat{q}_{\alpha\beta} = -\sum_i r_{i\alpha} r_{i\beta},$$
(20)

$$\hat{m}_\alpha = -\frac{1}{2}\sum_i ((\boldsymbol{r}_i - \boldsymbol{O}) \times \boldsymbol{p}_i)_\alpha,$$

$$= -\frac{1}{2}\sum_i \varepsilon_{\alpha\beta\gamma}(r_{i\beta} - O_\beta)p_{i\gamma} = -\frac{1}{2}\sum_i l_{i\alpha,O}, \quad (21)$$

$$\hat{\xi}^{\mathrm{dia}}_{\alpha\beta} = \frac{1}{4}\sum_i ((r_{i\alpha} - O_\alpha)(r_{i\beta} - O_\beta) - |\boldsymbol{r}_i - \boldsymbol{O}|^2 \delta_{\alpha\beta}), \quad (22)$$

where the summations run over the electrons, and the standard notation for Cartesian components of the position ($r_{i\alpha}$), linear momentum ($\hat{p}_{i\alpha}$), and angular momentum (about the origin $\boldsymbol{O}$, $\hat{l}_{i\alpha,O}$) operators of electron i is used. In Eqs. (21) and (22), we have explicitly indicated that the magnetic moment and diamagnetic susceptibility operators depend on a gauge-origin $\boldsymbol{O}$. In the limit of a complete basis, for variational wavefunctions, calculated molecular magnetic properties will be independent of this choice of gauge origin, whereas calculations using finite basis sets in general display a dependence on the choice of gauge origin.[45,46] Note that we have omitted nuclear contributions to these operators, which do not contribute to the quadratic and cubic response functions.

Equations (13)–(18) have previously been used to calculate Jones birefringence at the density-functional level of theory,[27,28] including also the effects of a dielectric medium,[34] as well as at the coupled-cluster level of theory.[14] However, these studies have only used conventional basis sets, and the results were, therefore, not formally gauge-origin independent, although fairly large basis sets were used in these studies in order to reduce the gauge-origin dependence of the results and to achieve near basis-set limit results.

Before proceeding, let us first consider the relation of the tensors in Eqs. (13)–(18) to tensors that appear in other birefringences, as these will give us valuable guidelines for the evaluation of the various hyperpolarizability tensors when London orbitals are used in the calculation. We first note that Eqs. (15)–(18) correspond to the same tensors that appear in the calculation of the first and second electric-field derivatives of the magnetizability, the latter appearing in the calculation of the Cotton–Mouton effect,[44,47] the main difference being that whereas all magnetic fields appearing in the Cotton–Mouton effect are static, one of the magnetic field components will be frequency-dependent in the case of Jones birefringence, with also the introduction of a static electric field. We may, therefore, build on our previous analytic

implementation of the Cotton–Mouton constants[44] when deriving an expression for Jones birefringence in which also time-periodic London atomic orbitals are used.[43]

The polarizabilities in Eqs. (13) and (14) can be considered as the magnetic-field derivatives of the electric dipole–electric quadrupole polarizability and the electric dipole–electric quadrupole–electric dipole hyperpolarizability. These undifferentiated polarizabilities appear in the calculation of Buckingham birefringence.[48,49] We previously presented a gauge-origin independent approach for calculating Buckingham birefringence using London atomic orbitals[50] and we will also build on this derivation in order to derive computable expressions for the tensors in Eqs. (13) and (14).

In Sec. III, we will derive the working equations for the Jones birefringence building on our open-ended scheme for the calculation of quasienergy derivatives using both time- and perturbation-dependent basis sets.[41] The derivation will follow very closely the derivations already presented for the Cotton–Mouton[44] and Buckingham birefringences.[50]

III. METHODOLOGY

In order to derive variational formulas for the response functions in Eqs. (13)–(18), we employ the quasienergy derivative method.[24,41,51] Given a time-independent Hamiltonian $\hat{H}$, a (time-)periodic external potential operator $\hat{V}^t$, and a periodic wavefunction $\psi(t)$, both with period $T = 2\pi/\omega$, the quasienergy is determined by the time-averaged expectation value

$$Q(\psi) = \frac{1}{T}\int_{t_0}^{t_0+T} \langle\psi|\hat{H} + \hat{V}^t - i\frac{\partial}{\partial t}|\psi\rangle dt, \quad (23)$$

where t_0 is arbitrary since the integrand is periodic. It follows from the Hermiticity of $\hat{H}$ and $\hat{V}^t$ and the normalization of ψ, that Q is real valued. In our case, the external potential consists of (dipole- and quadrupole-) interactions with an inhomogeneous electric field and (dipole-) interaction with a homogeneous magnetic field,[52]

$$V^t = -\sum_\alpha F_\alpha \hat{\mu}_\alpha - \frac{1}{2}\sum_{\alpha\beta} G_{\alpha\beta}\,\hat{q}_{\alpha\beta}$$

$$-\sum_\alpha B_\alpha \hat{m}_\alpha - \frac{1}{2}\sum_{\alpha\beta} B_\alpha B_\beta\,\hat{\xi}^{\mathrm{dia}}_{\alpha\beta}. \quad (24)$$

The fields $\boldsymbol{F}(t)$, $\boldsymbol{G}(t)$, and $\boldsymbol{B}(t)$ are parameterized as having a static- and a frequency-dependent component

$$F_\alpha(t) = F_{0\alpha} + F_{\omega\alpha}e^{-i\omega t} + F^*_{\omega\alpha}e^{+i\omega t}, \quad (25)$$

$$G_{\alpha\beta}(t) = G_{0\alpha\beta} + G_{\omega\alpha\beta}e^{-i\omega t} + G^*_{\omega\alpha\beta}e^{+i\omega t}, \quad (26)$$

$$B_\alpha(t) = B_{0\alpha} + B_{\omega\alpha}e^{-i\omega t} + B^*_{\omega\alpha}e^{+i\omega t}, \quad (27)$$

in which the coefficients will serve as perturbation parameters. Here, $\boldsymbol{F}_0$ and $\boldsymbol{B}_0$ are the applied static electric and magnetic fields, while $\boldsymbol{F}_\omega$, $\boldsymbol{G}_\omega$, and $\boldsymbol{B}_\omega$ are determined by the polarization, phase, and amplitude of the light beam. No static electric field gradient is applied in the Jones experiment, and $\boldsymbol{G}_0$ is only included here for generality.

In order to ensure gauge-origin independence of our calculated results also in the case of finite basis sets, we will employ London atomic orbitals (LAOs, also known as gauge-including atomic orbitals, GIAOs). The LAOs are magnetic-field dependent, and in this case also time-dependent, and are defined as[42,43]

$$\chi_\mu(\mathbf{r}; \mathbf{B}) = \exp\left(-\frac{i}{2}\mathbf{B}(t) \times (\mathbf{R}_{K(\mu)} - \mathbf{O}) \cdot \mathbf{r}\right) X_\mu(\mathbf{r} - \mathbf{R}_{K(\mu)}),$$
(28)

where X_μ is an ordinary Cartesian or spherical Gaussian- or Slater-type orbital, and $K(\mu)$ denotes the atom at which χ_μ is centered.

The advantage of the quasienergy in Eq. (23) is that variations in ψ (differentiation with respect to ψ) gives the time-dependent Schrödinger equation as a variational condition. Therefore (for variational ψ), perturbation by (differentiation with respect to) any field strength gives the corresponding observable of the time-dependent system

$$\frac{dQ}{dF_{\omega\alpha}^*} = \frac{\partial Q}{\partial F_{\omega\alpha}^*} = \{\langle\psi| - e^{+i\omega t}\hat{\mu}_\alpha|\psi\rangle\}_T = -\langle\mu_\alpha\rangle_{-\omega},$$
(29)

where we have introduced the short-hand notation $\{\ldots\}_T = 1/T\int_{t_0}^{t_0+T}\ldots dt$ for time-averaging. This expression, thus, corresponds to the time-averaged Hellmann–Feynman theorem. Moreover, additional differentiations with respect to field strengths give derivatives of these observables, i.e., response functions, when evaluated at $\hat{V}^t = 0$,

$$\frac{d^2Q}{dF_{\omega\alpha}^* dF_{\omega\beta}} = -\frac{d}{dF_{\omega\beta}}\langle\mu_\alpha\rangle_{-\omega} = +\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta\rangle\rangle_\omega.$$
(30)

Note that the sign changes due to the opposite sign conventions for potential and moment operators.

Equation (23) is not readily applied to the Hartree–Fock model, for which the energy is given in terms of atomic-orbital density matrix coefficients $D_{\mu\nu}$, one-electron integrals $h_{\mu\nu}$ and two-electron integrals $g_{\mu\nu\rho\delta}$,

$$E_{\text{HF}}(\mathbf{D}) = \text{Tr}\,\mathbf{hD} + \frac{1}{2}\text{Tr}\,\mathbf{G(D)D} + h_{\text{nuc}},$$
(31)

$$h_{\mu\nu} = \langle\chi_\mu| - \frac{1}{2}\nabla^2 - \sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|}|\chi_\nu\rangle,$$
(32)

$$G_{\mu\nu}(\mathbf{D}) = \sum_{\rho\sigma}(g_{\mu\nu\rho\sigma} - g_{\mu\sigma\rho\nu})D_{\sigma\rho},$$
(33)

$$g_{\mu\nu\rho\sigma} = \iint \chi_\mu^*(\mathbf{x}_1)\chi_\nu(\mathbf{x}_1)\frac{1}{r_{12}}\chi_\rho^*(\mathbf{x}_2)\chi_\sigma(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2,$$
(34)

where h_{nuc} is the nuclear repulsion energy, which does not contribute to the response functions studied in this paper.

Fortunately, however, observables such as Eq. (29) can be conveniently formulated in terms of $\mathbf{D}$, the external potential integrals $V_{\mu\nu} = \langle\chi_\mu|\hat{V}^t|\chi_\nu\rangle$, the external potential of the nuclei v_{nuc} (which will not concern us), the anti-symmetric time-differentiation integrals $T_{\mu\nu} = \langle\chi_\mu|\partial\chi_\nu/\partial t\rangle - \langle\partial\chi_\mu/dt|\chi_\nu\rangle$,

and the overlap integrals $S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle$ (see Ref. 41),

$$\frac{dQ}{d\mathbf{B}_\omega} = \left\{\frac{\partial E_{\text{HF}}(\mathbf{D})}{\partial\mathbf{B}_\omega} + \text{Tr}\frac{\partial\mathbf{V}}{\partial\mathbf{B}_\omega}\mathbf{D} + \frac{\partial v_{\text{nuc}}}{\partial\mathbf{B}_\omega}\right.$$
$$\left. - \frac{i}{2}\text{Tr}\frac{\partial\mathbf{T}}{\partial\mathbf{B}_\omega}\mathbf{D} - \text{Tr}\frac{\partial\mathbf{S}}{\partial\mathbf{B}_\omega}\mathbf{W}\right\}_T,$$
(35)

$$\mathbf{W} = \mathbf{DFD} + \frac{i}{2}\frac{\partial\mathbf{D}}{\partial t}\mathbf{SD} - \frac{i}{2}\mathbf{DS}\frac{\partial\mathbf{D}}{\partial t},$$
(36)

$$\mathbf{F} = \mathbf{h} + \mathbf{G(D)} + \mathbf{V} - \frac{i}{2}\mathbf{T},$$
(37)

$$\frac{dQ}{d\mathbf{G}_\omega} = \left\{\text{Tr}\frac{\partial\mathbf{V}}{\partial\mathbf{G}_\omega}\mathbf{D} + \frac{\partial v_{\text{nuc}}}{\partial\mathbf{G}_\omega}\right\}_T,$$
(38)

where we have introduced the so-called energy-weighted density matrix $\mathbf{W}$ and the Fock matrix $\mathbf{F}$. We note the close similarity in structure between the expression for the quasienergy derivative in Eq. (35), and the expression introduced by Pulay for the molecular (geometrical) gradient for the Hartree–Fock model in the AO basis.[53] The form of the expression is the same, but Eq. (35) is generalized to account for externally applied fields ($\mathbf{V}$, v_{nuc}), time-dependence of the density matrix ($\partial\mathbf{D}/\partial t$), as well as time-dependence of the basis set $\chi_\mu(\mathbf{T})$. Notice also in Eq. (38) that for fields which do not enter the basis functions, Eq. (35) takes the simpler form of an electronic expectation value plus a nuclear contribution.

From Eqs. (35) and (38), we may now derive formulas for the linear, quadratic, and cubic response functions by further differentiation, while taking into account the dependence of $\mathbf{D}$ on the fields, and using the idempotency and self-consistency conditions which apply to $\mathbf{D}$,

$$0 = \mathbf{DSD} - \mathbf{D},$$
(39)

$$0 = \mathbf{FDS} - \mathbf{SDF} - \frac{i}{2}\mathbf{S}\frac{\partial\mathbf{DS}}{\partial t} - \frac{i}{2}\frac{\partial\mathbf{SD}}{\partial t}\mathbf{S}.$$
(40)

Repeated differentiation of Eq. (35) produces a large number of terms. We will therefore adopt the following more concise superscript notation to denote perturbed quantities (field-strength derivatives), evaluated at zero fields ($\hat{V}^t = 0$), and stripped of their time dependence (e.g., $1/e^{-i\omega t}$),

$$\mathbf{D}^{B_\omega} = \frac{1}{e^{-i\omega t}}\left.\frac{d\mathbf{D}}{d\mathbf{B}_\omega}\right|_{\hat{V}^t=0},$$
(41)

$$\mathbf{V}^{GB} = \frac{1}{e^{-i\omega t}}\frac{1}{1}\left.\frac{\partial^2\mathbf{V}}{\partial\mathbf{G}_\omega\partial\mathbf{B}_0}\right|_{\hat{V}^t=0},$$
(42)

$$\mathbf{G}^{BB} = \frac{1}{e^{-i\omega t}}\frac{1}{1}\left.\frac{\partial^2\mathbf{G}}{\partial\mathbf{B}_\omega\partial\mathbf{B}_0}\right|_{\hat{V}^t=0},$$
(43)

$$\mathbf{W}^{F_\omega^* F_0} = \frac{1}{e^{+i\omega t}}\frac{1}{1}\left.\frac{d^2\mathbf{W}}{d\mathbf{F}_\omega^* d\mathbf{F}_0}\right|_{\hat{V}^t=0},$$
(44)

where (1/1) indicates that the second derivative applies to a static perturbing field. Note here that frequencies are omitted in the notation for perturbed integrals which are independent of frequencies (all except $\mathbf{T}$). Comparing with

Eqs. (13)–(18) and (24), we make the following identification of the quadratic response functions:

$$G^{\text{para}}_{\alpha\beta\gamma} + G^{\text{dia}}_{\alpha\beta\gamma} = \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma \rangle\rangle_{\omega,0}$$
$$- \langle\langle \hat{\mu}_\alpha; \hat{\xi}^{\text{dia}}_{\beta\gamma} \rangle\rangle_\omega = Q^{B_{\omega\beta} F^*_{\omega\alpha} B_{0\gamma}}, \quad (45)$$

$$a'_{\alpha\beta\gamma\delta} = i\langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta \rangle\rangle_{\omega,0} = -i\, Q^{G_{\omega\beta\gamma} F^*_{\omega\alpha} B_{0\delta}} \quad (46)$$

and obtain the corresponding formulas by differentiating Eqs. (35) and (38),

$$Q^{B_\omega F^*_\omega B_0} \overset{\text{Tr}}{=} \mathbf{V}^{BBF}\mathbf{D} + \mathbf{V}^{BF}\mathbf{D}^{B_0}$$
$$+ \left(\mathbf{h}^{BB} + \mathbf{V}^{BB} - \frac{i}{2}\mathbf{T}^{B_\omega B_0} + \mathbf{G}^{BB}(\mathbf{D}) \right)\mathbf{D}^{F^*_\omega}$$
$$+ \left(\mathbf{h}^{B} + \mathbf{V}^{B} - \frac{i}{2}\mathbf{T}^{B_\omega} + \mathbf{G}^{B}(\mathbf{D}) \right)\mathbf{D}^{F^*_\omega B_0}$$
$$+ \mathbf{G}^{B}(\mathbf{D}^{F^*_\omega})\mathbf{D}^{B_0} - \mathbf{S}^{BB}\mathbf{W}^{F^*_\omega} - \mathbf{S}^{B}\mathbf{W}^{F^*_\omega B_0}, \quad (47)$$

$$Q^{G_\omega F^*_\omega B_0} \overset{\text{Tr}}{=} \mathbf{V}^{GB}\mathbf{D}^{F^*_\omega} + \mathbf{V}^{G}\mathbf{D}^{F^*_\omega B_0}, \quad (48)$$

where by $\overset{\text{Tr}}{=}$ we indicate that a trace is to be taken of the matrix products on the right-hand side. Explicit formulas for matrices $\mathbf{W}^{F^*_\omega}$ and $\mathbf{W}^{F^*_\omega B_0}$ are obtained from Eq. (36),

$$\mathbf{W}^{F^*_\omega} = \mathbf{D}^{F^*_\omega}\left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D} + \mathbf{D}\mathbf{F}^{F^*_\omega}\mathbf{D} + \mathbf{D}\left(\mathbf{F} + \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{F^*_\omega}, \quad (49)$$

$$\mathbf{W}^{F^*_\omega B_0} = \mathbf{D}^{F^*_\omega B_0}\left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D} + \frac{1}{2}\mathbf{D}\mathbf{F}^{F^*_\omega B_0}\mathbf{D} + \mathbf{D}^{B_0}\mathbf{F}^{F^*_\omega}\mathbf{D}$$
$$+ \mathbf{D}^{F^*_\omega}\left(\left(\mathbf{F}^{B_0} - \frac{\omega}{2}\mathbf{S}^B\right)\mathbf{D} + \left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{B_0} \right) + \text{h.c.}, \quad (50)$$

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 frequency factors $\omega/2$. The six first-order and nine second-order perturbed density matrices are determined by solving a set of linear response equations, either in the atomic or the molecular orbital basis.[19,54–57] The specific case of determining perturbed densities for external frequency-dependent magnetic fields, when using London atomic orbitals, have been described in detail in our previous work on the Cotton–Mouton effect,[44] and the interested reader is referred to this paper for more information about the details of the approach.

For the two cubic response functions, the identifications are

$$G^{\text{para}}_{\alpha\beta\gamma\delta} + G^{\text{dia}}_{\alpha\beta\gamma\delta} = -\langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma, \hat{\mu}_\delta \rangle\rangle_{\omega,0,0}$$
$$+ \langle\langle \hat{\mu}_\alpha; \hat{\xi}^{\text{dia}}_{\beta\gamma}, \hat{\mu}_\delta \rangle\rangle_{\omega,0} = Q^{B_{\omega\beta} F^*_{\omega\alpha} B_{0\gamma} F_{0\delta}}, \quad (51)$$

$$a'_{\alpha\beta\gamma\delta\epsilon} = -i\langle\langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta, \hat{\mu}_\epsilon \rangle\rangle_{\omega,0,0} = -i\, Q^{G_{\omega\beta\gamma} F^*_{\omega\alpha} B_{0\delta} F_{0\epsilon}}. \quad (52)$$

In principle, these fourth-order quasienergy derivatives can be obtained by differentiating Eqs. (35) and (38) three times, and this is the approach used for instance in the open-ended

scheme for higher-order electric polarizabilities,[41,58–61] as well as in the calculation of geometrical derivatives of electric (hyper)polarizabilities. This approach, often referred to as the $n+1$ rule,[62,63] is advantageous when one of the applied perturbations has many more components than the other perturbations, for instance, the number of geometrical distortions in a large molecule versus the three components of the electric field, since one can avoid having to solve any perturbed equations for the perturbation with a large number of components.

However, when the number of components is fairly similar for the different applied perturbations as is the case for Jones birefringence where the fields have either three or six independent components each, it is in general much more advantageous to use the so-called $2n+1$ rule, which for Jones birefringence implies that only first- and second-order perturbed densities need to be determined.

Although the quasienergy Q is variational, its derivative $dQ/d\mathbf{B}_\omega$ is by itself not variational (in $\mathbf{D}$), and we may, therefore, not apply the $2n+1$ rule directly (by omitting higher order terms). However, as presented in Ref. 41, Eq. (35) can be made variational by adding Lagrange multipliers ($\mathbf{L}$, $\mathbf{X}$) for the two equations $\mathbf{D}$ must satisfy

$$\frac{dQ}{d\mathbf{B}_\omega} \to \frac{dQ}{d\mathbf{B}_\omega} - \{\text{Tr}\,\mathbf{LP}\}_T - \{\text{Tr}\,\mathbf{XY}\}_T, \quad (53)$$

where $\mathbf{P}$ denotes the idempotency expression in Eq. (39) and $\mathbf{Y}$ denotes the self-consistency expression in Eq. (40). The Lagrange multipliers can be expressed in terms of the solution of the corresponding first-order equation for $d\mathbf{D}/d\mathbf{B}_\omega$,[41]

$$\mathbf{L} = \frac{d\mathbf{F}}{d\mathbf{B}_\omega}\mathbf{DS} - \left(\mathbf{FD} - \frac{i}{2}\frac{\partial\mathbf{S}}{\partial t}\mathbf{D} - i\mathbf{S}\frac{\partial\mathbf{D}}{\partial t} \right)\frac{\partial\mathbf{S}}{\partial\mathbf{B}_\omega}$$
$$+ \mathbf{SD}\frac{d\mathbf{F}}{d\mathbf{B}_\omega} - \frac{\partial\mathbf{S}}{\partial\mathbf{B}_\omega}\left(\mathbf{DF} + \frac{i}{2}\mathbf{D}\frac{\partial\mathbf{S}}{\partial t} + i\frac{\partial\mathbf{D}}{\partial t}\mathbf{S} \right) - \frac{d\mathbf{F}}{d\mathbf{B}_\omega}, \quad (54)$$

$$\mathbf{X} = \frac{d\mathbf{D}}{d\mathbf{B}_\omega}\mathbf{SD} - \mathbf{DS}\frac{d\mathbf{D}}{d\mathbf{B}_\omega}. \quad (55)$$

Differentiating the variational Lagrangian expression in Eq. (53) three times, and omitting terms containing third-order matrices, we obtain

$$Q^{B_\omega F^*_\omega B_0 F_0} \overset{\text{Tr}}{=} \mathbf{V}^{BBF}\mathbf{D}^{F_0} + \mathbf{V}^{BBF}\mathbf{D}^{F^*_\omega}$$
$$+ \left(\mathbf{h}^{BB} + \mathbf{V}^{BB} - \frac{i}{2}\mathbf{T}^{B_\omega B_0} + \mathbf{G}^{BB}(\mathbf{D}) \right)\mathbf{D}^{F^*_\omega F_0}$$
$$+ \mathbf{G}^{BB}(\mathbf{D}^{F^*_\omega})\mathbf{D}^{F_0} + \mathbf{V}^{BF}\mathbf{D}^{B_0 F_0} + \mathbf{V}^{BF}\mathbf{D}^{F^*_\omega B_0}$$
$$+ \mathbf{G}^{B}(\mathbf{D}^{F^*_\omega})\mathbf{D}^{B_0 F_0} + \mathbf{G}^{B}(\mathbf{D}^{B_0})\mathbf{D}^{F^*_\omega F_0}$$
$$+ \mathbf{G}^{B}(\mathbf{D}^{B_\omega})\mathbf{D}^{F^*_\omega F_0} + \mathbf{G}^{B}(\mathbf{D}^{F^*_\omega B_0})\mathbf{D}^{F_0}$$
$$- \mathbf{S}^{BB}\mathbf{W}^{F^*_\omega F_0} - \mathbf{S}^{B}\mathbf{W}^{F^*_\omega B_0 F_0}_{2'}$$
$$- \mathbf{L}_{B_\omega}\mathbf{P}^{F^*_\omega B_0 F_0}_{2'} - \mathbf{X}_{B_\omega}\mathbf{Y}^{F^*_\omega B_0 F_0}_{2'}, \quad (56)$$

$$Q^{G_\omega F^*_\omega B_0 F_0} \overset{\text{Tr}}{=} \mathbf{V}^{GB}\mathbf{D}^{F^*_\omega F_0} + \mathbf{G}^{B}(\mathbf{D}^{G_\omega})\mathbf{D}^{F^*_\omega F_0}$$
$$- \mathbf{L}_{G_\omega}\mathbf{P}^{F^*_\omega B_0 F_0}_{2'} - \mathbf{X}_{G_\omega}\mathbf{Y}^{F^*_\omega B_0 F_0}_{2'}, \quad (57)$$

where the subscript $2'$ denotes that only contributions up to second order are included in those matrices, in accordance with the $2n+1$ rule. As before, the matrices $\mathbf{W}^{F_\omega^* F_0}$ and $\mathbf{W}_{2'}^{F_\omega^* B_0 F_0}$ are determined from Eq. (36),

$$
\begin{aligned}
\mathbf{W}^{F_\omega^* F_0} = {} & \mathbf{D}^{F_\omega^* F_0}\left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D} \\
& + \frac{1}{2}\mathbf{D}\mathbf{F}^{F_\omega^* F_0}\mathbf{D} + \mathbf{D}^{F_0}\mathbf{F}_\omega^{F_\omega^*}\mathbf{D} \\
& + \mathbf{D}^{F_\omega^*}\left(\mathbf{F}^{F_0}\mathbf{D} + \left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{F_0}\right) + \text{h.c.}, \quad (58)
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{W}_{2'}^{F_\omega^* B_0 F_0} = {} & \mathbf{D}^{F_\omega^* B_0}\left(\mathbf{F}^{F_0}\mathbf{D} + \left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{F_0}\right) + \mathbf{D}^{F_0}\mathbf{F}_\omega^{F_\omega^* B_0}\mathbf{D} \\
& + \mathbf{D}^{F_\omega^* F_0}\left(\left(\mathbf{F}^{B_0} - \frac{\omega}{2}\mathbf{S}^B\right)\mathbf{D} + \left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{B_0}\right) \\
& + \mathbf{D}\mathbf{F}_\omega^{F_\omega^*}\mathbf{D}^{B_0 F_0} \\
& + \mathbf{D}^{F_\omega^*}\bigg(\mathbf{F}^{B_0 F_0}\mathbf{D} + \mathbf{F}^{F_0}\mathbf{D}^{B_0} + \left(\mathbf{F}^{B_0} - \frac{\omega}{2}\mathbf{S}^B\right)\mathbf{D}^{F_0} \\
& \quad + \left(\mathbf{F} - \frac{\omega}{2}\mathbf{S}\right)\mathbf{D}^{B_0 F_0}\bigg) \\
& + \mathbf{D}^{B_0}(\mathbf{F}^{F_\omega^* F_0}\mathbf{D} + \mathbf{F}_\omega^{F_\omega^*}\mathbf{D}^{F_0}) + \text{h.c.} \quad (59)
\end{aligned}
$$

The Lagrange multipliers $\mathbf{L}_{B_\omega}$, $\mathbf{X}_{B_\omega}$, $\mathbf{L}_{G_\omega}$, and $\mathbf{X}_{G_\omega}$ are determined by evaluating Eqs. (54) and (55) for $\hat{V}^t = 0$,

$$
\mathbf{L}_{B_\omega} = \mathbf{F}^{B_\omega}\mathbf{DS} + \mathbf{SDF}^{B_\omega} - \mathbf{F}^{B_\omega} - \mathbf{FDS}^B - \mathbf{S}^B\mathbf{DF},
$$

$$
\mathbf{X}_{B_\omega} = \mathbf{D}^{B_\omega}\mathbf{SD} - \mathbf{DSD}^{B_\omega}, \quad (60)
$$

$$
\mathbf{L}_{G_\omega} = \mathbf{F}^{G_\omega}\mathbf{DS} + \mathbf{SDF}^{G_\omega} - \mathbf{F}^{G_\omega}, \quad (61)
$$

$$
\mathbf{X}_{G_\omega} = \mathbf{D}^{G_\omega}\mathbf{SD} - \mathbf{DSD}^{G_\omega}. \quad (62)
$$

Finally, the residuals of the third-order equations with up to second-order contributions, $\mathbf{P}_{2'}^{F_\omega^* B_0 F_0}$ and $\mathbf{Y}_{2'}^{F_\omega^* B_0 F_0}$, are obtained from Eqs. (39) and (40),

$$
\begin{aligned}
\mathbf{P}_{2'}^{F_\omega^* B_0 F_0} = {} & \left(\mathbf{D}^{B_0}\mathbf{S} + \mathbf{DS}^B\right)\mathbf{D}^{F_\omega^* F_0} + \mathbf{D}^{F_0}\mathbf{SD}^{F_\omega^* B_0} \\
& + \mathbf{D}^{F_\omega^*}(\mathbf{S}^B\mathbf{D}^{F_0} + \mathbf{SD}^{B_0 F_0}) + \text{h.c.}, \quad (63)
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{Y}_{2'}^{F_\omega^* B_0 F_0} = {} & (\mathbf{F}^{F_\omega^* F_0}\mathbf{D}^{B_0} + \mathbf{F}^{B_0 F_0}\mathbf{D}^{F_\omega^*} + \mathbf{F}^{B_0 F_\omega^*}\mathbf{D}^{F_0} \\
& + \mathbf{F}^{F_0}\mathbf{D}^{B_0 F_\omega^*} + \mathbf{F}_\omega^{F_\omega^*}\mathbf{D}^{B_0 F_0} + \mathbf{F}^{B_0}\mathbf{D}^{F_\omega^* F_0})\mathbf{S} \\
& + (\mathbf{F}^{F_\omega^* F_0}\mathbf{D} + \mathbf{F}^{F_0}\mathbf{D}^{F_\omega^*} + \mathbf{F}_\omega^{F_\omega^*}\mathbf{D}^{F_0} \\
& + (\mathbf{F} - \omega\mathbf{S})\mathbf{D}^{F_\omega^* F_0})\mathbf{S}^B - \text{h.c.} \quad (64)
\end{aligned}
$$

IV. COMPUTATIONAL DETAILS

Calculations have been carried out for carbon tetrachloride (CCl_4), chlorobenzene (C_6H_5Cl), and naphthalene ($C_{10}H_8$).

All geometries were optimized at the density-functional level of theory, using the three-parameter exchange functional of Becke[64] in combination with the Lee–Yang–Parr

correlation functional,[65] commonly referred to as the B3LYP functional,[66] and using Dunning's correlation-consistent basis set of triple-zeta quality (cc-pVTZ).[67,68] For a higher order molecular property such as Jones birefringence, the choice of basis set is important in order to obtain reliable results. In many of our earlier studies of nonlinear birefringences, the strength of the augmented correlation-consistent basis sets have been demonstrated.

Here, we present a study of the effects of using London orbitals on the basis-set convergence of the property. The dependence of the different cubic response function contributions to the temperature-independent contribution of the Jones birefringence is illustrated for CCl_4 using the aug- and daug-cc-pVXZ basis sets. For naphthalene, we also test the origin independence of the results with respect to a shift of the coordinate system. Results are presented for two choices of gauge origin, the first one with the origin at the molecule center-of-mass and the second with the origin at the center of one of the aromatic rings.

The wavelength $\lambda = 632.8$ nm, as used in experiment, was selected. The calculations were carried out using a parallel version[69,70] of the DALTON 2.0 program.[71]

V. RESULTS AND DISCUSSIONS

We have collected the results for the two temperature-independent contributions to the Jones birefringence of carbon tetrachloride in Table I. In the table, we report the results obtained both with conventional basis sets and with London atomic orbitals. We note from the table the very strong basis-set dependence of the calculated results, in particular for the conventional basis set, where two sets of diffuse basis functions appear to be mandatory (the daug-cc-pVXZ basis set) in order to get results that are reasonably close to the apparent basis-set limit. Only the results obtained with the daug-

TABLE I. Results for the Jones birefringence of CCl_4 as obtained with and without London atomic orbitals for different correlation-consistent basis sets. For the calculations using a conventional basis set, the carbon atom has been selected as gauge origin. All results reported in atomic units for a wavelength of 632.8 nm.

Basis set	$\mathcal{G}_{\text{para}}^{(3)} + \mathcal{G}_{\text{dia}}^{(3)}$	$\mathcal{A}'^{,(3)}$	J_0
London atomic orbitals			
aug-cc-pVDZ	6979.6	−296.3	6683.3
aug-cc-pVTZ	5306.9	−314.7	4992.2
aug-cc-pVQZ	4220.3	−315.9	3904.4
daug-cc-pVDZ	4307.6	−292.8	4014.8
daug-cc-pVTZ	4102.8	−319.2	3783.6
daug-cc-pVQZ	4014.4	−320.6	3693.8
Conventional basis set			
aug-cc-pVDZ	−4198.9	−107.3	−4306.2
aug-cc-pVTZ	−650.3	−162.6	−812.9
aug-cc-pVQZ	2605.6	−223.1	2382.4
daug-cc-pVDZ	−483.7	−210.9	−694.6
daug-cc-pVTZ	3728.1	−295.5	3432.6
daug-cc-pVQZ	4001.8	−310.4	3691.4

cc-pVQZ basis are in reasonably good agreement for both London atomic orbitals and conventional basis functions.

The basis-set convergence is fairly slow also when London atomic orbitals are used, the results obtained with the aug-cc-pVQZ basis set still being about 5% too large compared to the estimated basis-set limit for J_0 of ~3700 a.u. The results in Table I suggest that even when London atomic orbitals are used, two sets of diffuse functions are desirable in order to ensure that the results are close to the basis-set limit. To some extent, this result is not too surprising, as it is well known that the improvements in basis-set convergence obtained when London atomic orbitals are used to calculate the magnetic dipole operator for frequency-dependent perturbations is limited.[72] As the $\mathcal{G}^{(3)}$ tensor involves a frequency-dependent magnetic dipole operator, this may reflect this expected slow basis-set convergence.

At the same time, the very strong basis-set dependence of the Jones birefringence contrasts with our observation for the Cotton–Mouton effect,[44] where only a limited improvement in basis-set convergence was observed. It is particularly interesting to note that the slow basis-set convergence of the Jones birefringence is dominated by the $\mathcal{G}^{(3)}$ contribution which, except for the introduction of a frequency on the magnetic-field component, bears very strong resemblance to the second hypermagnetizability tensor that determines the Cotton–Mouton effect, for which the importance of London atomic orbitals were found to be negligible. In the case of our results for $\mathcal{G}^{(3)}$ in Table I, we in particular, note that a wrong sign is obtained for this contribution when small conventional basis sets are used. Due to the dominance of this contribution to the overall anisotropy of the refractive index, an incorrectly predicted sign of the observable Jones birefringence is also obtained, a result which very clearly demonstrates the need for London orbitals in the calculation of Jones birefringence. Independently of the choice of basis set, a correctly predicted sign is obtained for the Jones birefringence of CCl_4 when London atomic orbitals are used.

The origin of the variation in basis-set dependence of calculated linear and nonlinear molecular properties involving external or internal sources of electric or magnetic fields remains unclear,[44,50,72–74] and it appears that only numerical investigations will be able to reveal the basis-set improvements that can be expected from the use of London atomic orbitals in the calculation of properties involving static or frequency-dependent magnetic field perturbations.

A problem with the use of basis sets with very diffuse basis functions is that one often experience problems with linear dependencies in the basis sets. As such, the much improved basis-set convergence for the Jones birefringence when LAOs are used gives us confidence that we may be able to attack also larger molecules using only the augmented correlation-consistent basis sets. In Table II, we report our results obtained using these basis sets for the naphthalene molecule. For the conventional basis sets, we report the calculated Jones birefringence using both the centre of mass and the centre of one of the aromatic rings in the molecule as gauge origin.

We note from Table II that the difference in basis-set convergence for the London and no-London orbital results is smaller than was the case for CCl_4, and in general slightly

TABLE II. Results for the Jones birefringence of naphthalene ($C_{10}H_8$) as obtained with and without London atomic orbitals for different augmented correlation-consistent basis sets. For the calculations using a conventional basis set, results are reported both using the center of mass and the center of one of the aromatic rings as gauge origin. All results reported in atomic units for a wavelength of 632.8 nm.

Basis set	$\mathcal{G}_{para}^{(3)} + \mathcal{G}_{dia}^{(3)}$	$\mathcal{A}'^{,(3)}$	J_0
London atomic orbitals			
aug-cc-pVDZ	16538.1	−1030.7	15507.4
aug-cc-pVTZ	12693.2	−1068.3	11624.9
aug-cc-pVQZ	11556.9	−1046.8	10510.0
Conventional basis set, center of mass gauge origin			
aug-cc-pVDZ	4995.2	−528.8	4466.4
aug-cc-pVTZ	9360.3	−750.5	8609.8
aug-cc-pVQZ	10598.8	−878.1	9720.7
Conventional basis set, center of aromatic ring as gauge origin			
aug-cc-pVDZ	3053.0	−480.6	2572.4
aug-cc-pVTZ	8731.0	−724.4	8006.6
aug-cc-pVQZ	10393.2	−864.2	9529.0

better, in particular with respect to the quality of the results obtained without London orbitals. Part of the reason for this improved basis-set convergence can be traced to the fact that basis functions on neighbouring atoms act as diffuse polarizing functions in the basis describing the electron density of a particular nucleus, making it less critical to use a very diffuse basis set for larger molecules.

Although the basis-set convergence of the conventional basis set is improved in naphthalene compared to tetrachloromethane, the basis-set convergence of the $\mathcal{A}'^{,(3)}$ contribution remains very poor. In contrast, as was also the case for CCl_4, the London atomic orbital results for this term shows very little basis-set dependence, making the basis-set dependence entirely due to the $\mathcal{G}^{(3)}$ term when London atomic orbitals are used.

In Table II, we report the results for two different gauge origins, the center of mass and the center of one of the aromatic rings, in the calculations using conventional basis sets. We do not report the numbers for the London atomic orbital calculations, even though in general the $\mathcal{G}^{(3)}$ and $\mathcal{A}'^{,(3)}$ contributions are origin dependent even when using LAOs, although the final observable birefringence is not. However, for a nonpolar molecule with inversion symmetry, the origin dependence of the individual contributing terms vanish for exact states, as discussed by Rizzo and Coriani,[14] and thus also when London atomic orbitals are used.

The dependence of the results obtained with conventional basis sets on the choice of gauge origin is quite strong for the aug-cc-pVDZ basis set, reducing quickly as the quality of the basis set is improved. In accordance with the observed basis-set convergence, the $\mathcal{G}^{(3)}$ term displays a much stronger basis-set dependence than the $\mathcal{A}'^{,(3)}$ term, and thus the observed origin dependence of J_0 is thus largely dependent on $\mathcal{G}^{(3)}$ only.

Let us now turn our attention to a dipolar molecule, chlorobenzene, for which we will then also have contributions

TABLE III. Results for the Jones birefringence of chlorobenzene as obtained with and without London atomic orbitals for different augmented correlation-consistent basis sets. All results reported in atomic units for a wavelength of 632.8 nm.

Basis set	$\mathcal{G}^{(3)}_{\text{para}}+\mathcal{G}^{(3)}_{\text{dia}}$	$\mathcal{A}'^{,(3)}$	J_0	$\mathcal{G}^{(2)}_{\text{para}}+\mathcal{G}^{(2)}_{\text{dia}}$	$\mathcal{A}'^{,(2)}$	J_T
London atomic orbitals						
aug-cc-pVDZ	10908.5	–555.4	10353.1	–49.7	8.4	–41.3
aug-cc-pVTZ	7057.6	–595.9	6461.7	–51.3	8.1	–43.2
aug-cc-pVQZ	5655.2	–607.9	5047.3	–51.6	8.0	–43.6
Conventional basis sets						
aug-cc-pVDZ	–800.3	–313.3	–1113.6	–77.3	9.3	–68.0
aug-cc-pVTZ	2660.1	–422.6	2237.5	–59.6	8.5	–51.1
aug-cc-pVQZ	4399.9	–503.2	3896.7	–48.2	8.1	–40.1

from the temperature-dependent contribution to the Jones birefringence. The results obtained both with and without London atomic orbitals for the temperature-dependent and temperature-independent contributions for this molecule, using the augmented correlation-consistent basis sets, are collected in Table III.

As was the case for tetrachloromethane, the use of London atomic orbitals is important in order to ensure a correct sign for the Jones birefringence, as we note that the contribution from $\mathcal{G}^{(3)}$ to the temperature-independent contribution of the observable birefringence has the wrong sign when the aug-cc-pVDZ basis set is used with conventional basis sets. The trends observed for carbon tetrachloride and naphthalene prevail for this molecule, with a fairly strong basis-set dependence being observed also for the $\mathcal{G}^{(3)}$ contribution when LAOs are used, whereas LAOs largely remove any basis-set dependence of the $\mathcal{A}'^{,(3)}$ contribution. As such, the temperature-independent contribution displays a fairly strong basis-set dependence when using London orbitals, and an aug-cc-pVQZ basis set is recommended in order to get results close to the basis-set limit when using London orbitals. For conventional basis sets, the aug-cc-pVQZ basis still gives a temperature-independent contribution to the Jones birefringence which is too small by about 20% if we assume that the LAO aug-cc-pVQZ results are close to the basis-set limit.

Considering the temperature-dependent contribution to the Jones birefringence, we note that London atomic orbitals give results that are largely independent of the size of the basis set, whereas the conventional basis displays a rather slow basis-set convergence. As is the case for the temperature-independent contribution, the $\mathcal{G}^{(2)}$ contribution dominates the temperature-dependent contribution to the Jones birefringence and shows the largest basis-set dependence. Indeed, the $\mathcal{A}'^{,(2)}$ contribution to J_T is largely independent of basis set

quality and good agreement is obtained for this contribution both with and without the use of London atomic orbitals, the difference being about 15% for the aug-cc-pVDZ basis set, and negligible for the larger basis sets.

When LAOs are employed, the $\mathcal{G}^{(2)}$ contribution is largely basis set independent, with a small difference with respect to the estimated basis-set limit results of about 5% observed for the aug-cc-pVDZ basis set. In contrast, the results obtained for this contribution are reduced by more than 30% when going from the aug-cc-pVDZ basis set to the aug-cc-pVQZ basis set when conventional basis functions are used. Because of the dominance of the $\mathcal{G}^{(2)}$ contribution to the temperature-dependent part of the Jones constant, and the partial cancellation of the $\mathcal{G}^{(2)}$ and $\mathcal{A}'^{,(2)}$ terms, an even stronger basis-set dependence is observed for the total temperature-dependent contribution when conventional basis sets are used, from –68.0 a.u. to –40.1 a.u. when going from the aug-cc-pVDZ to the aug-cc-pVQZ basis set. We finally note that the results in Table II indicate that the LAO and conventional basis set results do not appear to converge to the basis-set limit. We believe this is due to basis set artifacts, the aug-cc-pVQZ basis set not being fully saturated, in particular in the out-of-plane direction, to allow for basis-set limit results to be obtained when conventional basis sets are used.

In Table IV, we have collected the results obtained for the observable birefringence in terms of the Jones constant k_J. The Jones birefringence of tetrachloromethane and chlorobenzene have been measured by Roth and Rikken,[3,5] although only upper bounds could be experimentally obtained. Our results are within the upper bound of the experimental observation. We note, however, that solvent effects, as modeled by a dielectric continuum model, can be substantial, as demonstrated in an earlier work,[34] and thus our estimates given in Table IV can be expected to be too small. For the Jones birefringence of naphthalene, we are not aware of any experimental observations. Our results suggest that naphthalene has a too small Jones birefringence to allow it to be experimentally measurable within the current experimental detection limits.

VI. SUMMARY

We have presented the first gauge-origin independent implementation of Jones birefringence. The birefringence involves several third- and fourth-order mixed electric dipole, magnetic dipole and electric quadrupole polarizabilities, and gauge-origin independence has been ensured through the use of time-periodic London atomic orbitals.[42,43] The nonlinear response functions that appear in the expression for Jones birefringence show many similarities to the response

TABLE IV. Jones constants for the molecules investigated in this work calculated at the aug-cc-pVQZ level of theory using London atomic orbitals. A wavelength of 632.8 nm has been used. For chlorobenzene, a temperature of 294.15 K has been used. Experimental data taken from Ref. 3.

Molecule	M	ρ	$J_0 \times 10^{-3}$	$k_B \times J_T \times 10^{-6}$	$\Delta n^{(0)} \times 10^{18}$	$\Delta n^{(T)} \times 10^{13}$	$\Delta n \times 10^{18}$	k_J	k_J exp
CCl_4	153.82	1.594	3.904		5.728		5.728	0.144	< 3
C_6H_5Cl	112.56	1.106	5.047	–13.769	10.120	–0.276	–83.7348	–1.4635	< 2
$C_{10}H_8$	128.17	1.145	10.51		18.506		18.506	0.335	

functions appearing in the calculation of the Cotton–Mouton effect, which has facilitated the extension of our recent implementation of the gauge-origin independent calculation of the Cotton–Mouton effect[44] to the calculation of Jones birefringence using the general framework for higher order derivatives using time- and perturbation-dependent basis sets.[41]

In contrast to our study of basis-set dependence of the Cotton–Mouton effect, we find that London atomic orbitals are necessary in order to obtain results that are close to the basis-set limit. For small molecules, a basis set of daug-cc-pVDZ is sufficient to ensure basis-set limit results when London atomic orbitals are used. However, as this basis set in general can be expected to give problems with linear dependence, a fairly good result can also be obtained using the aug-cc-pVTZ basis set. In order to reach results of a similar quality when using conventional basis sets, a basis set of at least aug-cc-pVQZ quality appears to be needed.

There are not many reports of experimental observations of Jones birefringence in the literature,[3,5] and for the molecules so far studied theoretically in the literature,[27,28,34] only experimental upper bounds could be established. With the formalism presented here, we are in a position to attack much larger molecules for which the Jones constant has been experimentally measured. Such a study will lend confidence not only to the theoretical calculations, but also to the experimental observations. However, we have previously noted that solvent effects appear to be significant for the Jones birefringence,[34] and further work is needed in order to establish the importance of electron correlation for the Jones birefringence.[27,28] We expect in the future to build on our recently proposed scheme for calculating the necessary derivatives of exchange–correlation functionals using automatic differentiation techniques[60] to address the question of electron correlation effects on the Jones birefringence.

ACKNOWLEDGMENTS

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