Analytic calculations of nonlinear mixed electric and magnetic frequency-dependent molecular properties using London atomic orbitals: Buckingham birefringence

Dmitry Shcherbin,[a] **Andreas J. Thorvaldsen,**[a] **Kenneth Ruud,***[a] **Sonia Coriani**[b] **and Antonio Rizzo**[c]

We present the results of the first gauge-origin independent calculations, carried out at Hartree–Fock level, of the molecular parameters that describe the electric-field-induced linear birefringence, also known as Buckingham birefringence. Focus is in particular on the temperature-independent contribution to the observable. We employ a recently developed analytical scheme for calculating frequency-dependent molecular properties of arbitrary order for self-consistent field methods using basis sets that depend explicitly on the frequency and on the external perturbations. The method is applied to naphthalene, fluorobenzene and furan, three systems for which the Buckingham birefringence has been studied experimentally. It is demonstrated that LAOs lead to significant improvements in the basis set convergence of the temperature-independent contribution to the Buckingham birefringence, and that the results obtained on the basis of aug-cc-pVDZ quality London atomic orbital calculations are closer to the basis set limit than the results obtained on the basis of conventional aug-cc-pVQZ quality calculations. The computed values can be used to correct for the neglect of the temperature-independent higher-order contribution often implied in the derivation of the effective quadrupole moments from experimental measurements of the induced birefringence at a single temperature.

I. Introduction

Birefringences are gaining increasing interest, theoretically as well as experimentally, see for instance ref. 1–3 for recent accounts. A common element of many kinds of birefringences is the occurrence of linear and nonlinear polarizabilities involving mixed electric and magnetic fields. From a theoretical point of view, the presence of time-dependent magnetic fields creates additional computational complications, as the calculated results will in general be dependent on an artificially chosen gauge origin for calculations performed in incomplete basis sets.[4–6] Furthermore, origin-independent results can only be obtained for variational methods.[7]

A solution to the problem of the origin dependence of approximate calculations involving magnetic fields is offered by the use of London atomic orbitals (LAOs).[8–12] LAOs move the global gauge origin to a local gauge origin that is optimal for each individual basis function, namely the centre to which it is attached. London orbitals have been successfully applied to the calculation of a large number of magnetic and mixed electric and magnetic properties.[13–17] However, with a few

exceptions, with optical rotation[18] and electronic circular dichroism[19,20] as the prime examples, the magnetic fields have in most cases been static.

Krykunov and Autschbach derived a formalism for the calculation of linear response properties using time-periodic magnetic-field-dependent atomic orbitals based on a quasi-energy ansatz,[21] and applied it to the calculation of optical rotations[22] and frequency-dependent magnetizabilities.[23] Since Krykunov and Autschbach took as a starting point an expression of the quasienergy itself, the molecular orbitals had to be used as the basic variables due to the asymmetry of the bra and ket states with respect to time differentiation. We note that an alternative formulation for calculating linear response properties using LAOs for time-dependent electromagnetic fields has been presented in the literature, introducing a natural connection between the unperturbed and magnetic-field perturbed molecular orbitals.[24,25] In this way, when using LAOs the magnetic moment operator behaves exactly as the exact one-electron operator also for finite basis sets. However, all these implementations have been restricted to the linear response case—that is, to the study of frequency-dependent second-order magnetic properties or second-order mixed electric and magnetic properties. LAOs have been utilized also for third-order[26–29] and fourth-order[30] molecular properties involving an external magnetic field. However, in these applications of LAOs to higher-order molecular properties, the magnetic field has been static.

We recently presented a generalization of the approach of Krykunov and Autschbach for calculating molecular

[a] *Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway*
[b] *Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, via L. Giorgieri 1, I-34127 Trieste, Italy and Centre for Theoretical and Computational Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*
[c] *Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche (IPCF-CNR), Area della Ricerca, via G. Moruzzi 1, I-56124 Pisa, Italy*

properties of arbitrary order with basis sets that could in general be both time and perturbation dependent.[26] In addition to being open-ended with respect to the order of the applied perturbations, the implementation was developed fully in the atomic orbital basis. It was demonstrated that in order to develop a theory based on a quasienergy formalism using the elements of the density matrix in the atomic orbital basis as free parameters, the basic starting point has to be the quasienergy gradient and not the quasienergy itself. The formalism has been implemented in a general manner and has been applied to the study of properties as diverse as coherent anti-Stokes Raman scattering,[31] pure vibrational contributions to nonlinear optical properties,[32] hypermagnetizabilities[30] and Raman optical activity.[33] However, in all these applications, the basis functions either depended on the time dependence of the applied perturbations or on the perturbation itself, and never on both effects simultaneously. The present application to electric field gradient-induced birefringence (EFGB) is therefore the first where our methodology is applied to a property in which the basis functions are simultaneously time and perturbation dependent, and it can also be considered an extension of the work of Krykunov and Autschbach[21] to nonlinear properties formulated in the atomic orbital basis.

The systems which are under analysis here, and for which we study the response to a static external electric-field-gradient at the Hartree–Fock level of theory, are a relatively large non-dipolar system (naphthalene) and two smaller dipolar molecules (fluorobenzene and furan). The relevance of the polarity of the system will be made evident in the following section. All three systems studied here have been the subject of experimental investigations. A combination of Kerr,[34,35] Cotton–Mouton[36–38] and Buckingham[39,40] linear birefringence measurements were employed in the group of Ritchie to determine the quadrupole moment of these molecules. Measurements were carried out at the infinite dilution limit for naphthalene[41] (λ = 632.8 nm) and fluorobenzene[42] (λ = 441.6 and 632.8 nm, respectively) dissolved in carbon tetrachloride at 298 K. The Buckingham birefringence of furan, thiophene and selenophene at infinite dilution was measured in cyclohexane at 298 K and at a wavelength of 632.8 nm.[43] In the case of the two molecules with a permanent dipole moment, the study was aimed at determining the so-called *effective quadrupole centre* (EQC),[44,45] the frequency-dependent location in space which can be considered as the origin of the molecular quadrupole in dipolar molecules.

The rest of the paper is organized as follows. In section II we briefly outline the main elements of the theory of Buckingham birefringence. We then present our formalism for atomic orbital-based response theory for time- and perturbation-dependent basis sets in order to calculate the nonlinear polarizabilities that determine the Buckingham birefringence in section III. In section IV we summarize the details of the calculations whose results are presented and discussed in section V. Finally, in section VI we give some concluding remarks and an outlook.

II. Buckingham birefringence

The EFGB,[39,46] also known as the "Buckingham effect" or "Buckingham birefringence", is the anisotropy of the refractive index n observed when plane-polarized light passes through a fluid in a direction perpendicular to an external electric field gradient. For an (ideal) gas it is given by the expression (in SI units, constant pressure)

$$\Delta n = n_X - n_Y = \frac{N_A \nabla E}{15 V_m \varepsilon_0} s = \frac{3 \nabla E}{2 V_m} {}_m Q(\omega, T), \qquad (1)$$

$$ {}_m Q(\omega, T) = \frac{2 N_A}{45 \varepsilon_0} s, \qquad (2)$$

where N_A is Avogadro's number, V_m is the molar volume, ∇E is the field gradient—with $\nabla E = \nabla E_{XX} = -\nabla E_{YY}$; $\nabla E_{ZZ} = 0$, ε_0 is the vacuum permittivity, and eqn (2) defines the so-called Buckingham constant, a function of the circular frequency ω and of the temperature T. In this expression, the light is assumed to propagate along the Z direction. The function s will be defined below. The measurement of EFGB is one of the standard routes to experimentally determine the molecular quadrupole moment,[47–49] as suggested by Buckingham in 1959,[39] and first realized by Buckingham and Disch in 1963.[40]

The original theory of the EFGB was formulated for non-dipolar systems—that is, systems where the quadrupole moment does not depend on the choice of origin.[39,50,51] In this case the molecular function s, a function of ω and T, is given simply as

$$s = b(\omega) + \frac{1}{kT} \Theta_{\alpha\beta} \alpha_{\alpha\beta}(-\omega; \omega), \qquad (3)$$

where $\boldsymbol{\Theta}$ and $\boldsymbol{\alpha}(-\omega;\omega)$ are the second-rank cartesian tensors representing the molecular (traceless) quadrupole moment and frequency-dependent electric dipole polarizability, respectively, whereas the temperature-independent contribution is

$$b(\omega) = B_{\alpha\beta,\alpha\beta}(-\omega; \omega, 0) - \mathscr{B}_{\alpha,\alpha\beta,\beta}(-\omega; \omega, 0)$$
$$- \frac{5}{\omega} \varepsilon_{\alpha\beta\gamma} J'_{\alpha,\beta,\gamma}(-\omega; \omega, 0). \qquad (4)$$

In this equation, $\varepsilon_{\alpha\beta\gamma}$ is the Levi–Civita antisymmetric tensor and implicit summation over repeated indices is implied. In the expression for $b(\omega)$ we have introduced the mixed polarizabilities

$$B_{\alpha\beta,\gamma\delta}(-\omega;\omega,0) = B_{\alpha\beta,\gamma\delta}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\Theta}_{\gamma\delta} \rangle\rangle_{\omega,0}, \qquad (5)$$

$$\mathscr{B}_{\alpha,\beta\gamma,\delta}(-\omega;\omega,0) = \mathscr{B}_{\alpha,\beta\gamma,\delta}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{\Theta}_{\beta\gamma}, \hat{\mu}_\delta \rangle\rangle_{\omega,0}, \qquad (6)$$

$$J'_{\alpha,\beta,\gamma}(-\omega;\omega,0) = J'_{\alpha,\beta,\gamma}(\omega) = i\langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{\mu}_\gamma \rangle\rangle_{\omega,0}, \qquad (7)$$

involving the electric dipole, electric quadrupole and magnetic dipole operators

$$\hat{\mu}_\alpha = - \sum_i \hat{r}_{i,\alpha O}, \qquad (8)$$

$$\hat{\Theta}_{\alpha\beta} = -\frac{1}{2} \sum_i [\hat{r}_{i,\alpha O} \hat{r}_{i,\beta O} - \delta_{\alpha\beta} \hat{r}_{i,\gamma O} \hat{r}_{i,\gamma O}], \qquad (9)$$

$$\hat{m}_\alpha = - \sum_i \frac{1}{2} \hat{l}_{i,\alpha O} = -\frac{1}{2} \varepsilon_{\alpha\beta\gamma} \sum_i \hat{r}_{i,\beta O} \hat{p}_{i,\gamma}, \qquad (10)$$

In eqns (8)–(10) the explicit summations run over the electrons in the molecule, and we have introduced $r_{i,\alpha}$, $p_{i,\alpha}$ and $l_{i,\alpha}$ as the

α-components of the operators for electron i, respectively. The explicit dependence of the operators on an arbitrarily chosen gauge origin O is also indicated.

In 1968 Buckingham and Longuet-Higgins[44] extended the theory of EFGB to dipolar fluids, where the quadrupole moment becomes origin dependent. The expression for s, eqn (3), remains valid, but then only for a specific choice of (frequency dependent) origin for the quadrupole operator, namely the EQC, defined as the point in coordinate space where the expression

$$A_{\beta,\alpha\beta}(-\omega;\omega) + \frac{5}{\omega}\varepsilon_{\alpha\beta\gamma}G'_{\beta,\gamma}(-\omega;\omega) \qquad (11)$$

vanishes. The term in eqn (11), multiplied by $1/kT$ and by the cartesian component of the molecular dipole moment μ_α, should otherwise be subtracted from the right-hand side of eqn (3) for a choice of origin different than the EQC

$$s = b(\omega) + \frac{1}{kT}\left\{ \Theta_{\alpha\beta}\alpha_{\alpha\beta}(-\omega;\omega) \right. \\ \left. -\mu_\alpha\left[A_{\beta,\alpha\beta}(-\omega;\omega) + \frac{5}{\omega}\varepsilon_{\alpha\beta\gamma}\,G'_{\beta,\gamma}(-\omega;\omega)\right]\right\}, \qquad (12)$$

In eqn (11), we have also introduced the mixed polarizabilities

$$A_{\alpha,\beta\gamma}(-\omega;\omega) = -\langle\langle\hat{\mu}_\alpha;\hat{\Theta}_{\beta\gamma}\rangle\rangle_\omega, \qquad (13)$$

$$G'_{\alpha\beta}(-\omega;\omega) = -i\langle\langle\hat{\mu}_\alpha;\hat{m}_\beta\rangle\rangle_\omega, \qquad (14)$$

which also enter the theory of optical rotation for oriented systems.[18,50,51] For exact operators, as well as when LAOs are used, and for planar molecules, as those studied in this paper—laying in the y,z plane, and with the dipole moment along the z-axis—the EQC, placed along the z-axis, is defined by its distance $R_z^{(EQC)}$ from a given reference origin (the one chosen for the calculation of the molecular properties, most usually the center of nuclear masses)[52]

$$R_z^{(EQC)} = \frac{\frac{5}{\omega}(G'_{x,y} - G'_{y,x}) + A_{x,zx} + A_{y,zy} + A_{z,zz}}{2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}}$$
$$= \frac{\frac{5}{\omega}(G'_{x,y} - G'_{y,x}) + A_{x,zx} + A_{y,zy} + A_{z,zz}}{2\Delta\alpha}, \qquad (15)$$

where we have also introduced the polarizability anisotropy $\Delta\alpha$.

The molecular theory for EFGB was a matter of debate for some years, as two different expressions for the effect were shown to lead to very different estimates for both the quadrupole moment and the location of the EQC.[44,53–55] The puzzle was however resolved in 2003,[56,57] and there is now complete agreement between the existing molecular theories for Buckingham birefringence.

As other birefringences, the EFGB contains at constant pressure two contributions—a temperature-dependent and a temperature-independent one, see eqns (3) and (12). For non-dipolar species, the former involves the electric-dipole polarizability and the molecular quadrupole moment (eqn (3)), whereas for dipolar molecules an additional contribution comes from a term mixing the molecular dipole moment, the dipole–quadrupole and the dipole–magnetic dipole polarizabilities (eqn (12)). The temperature-independent contribution $b(\omega)$—which basically describes the changes in the effective

polarizability induced by the electric field gradient—has the same form for both types of systems and involves a combination of three hyperpolarizabilities, namely two dipole–dipole–quadrupole electric hyperpolarizabilities—where the frequency argument is either associated with the dipole or with the quadrupole operator—and an electric dipole–electric dipole–magnetic dipole term.

Irrespective of whether the system is dipolar or not, the temperature-independent contribution to the EFGB is a well-defined property, as it can be obtained from a linear regression on birefringence values measured at different temperatures. However, in carrying out the experimental measurements aimed at finding the quadrupole moment, it is often assumed that this contribution can be neglected since it is expected to be much smaller than the temperature-dependent one.[40,48,58] This clearly introduces an additional source of error in the experimental value.[1,59]

When temperature-dependent measurements are not feasible, computational values of the $b(\omega)$ contribution could in principle be used to extract a value for the molecular quadrupole moment from the experimental value of the birefringence. For quadrupolar systems, the accuracy of the computed values will only depend on the accuracy of the method of choice—i.e. on the limitations in the one- and N-electron representations (basis set size and wavefunction/potential parametrizations).[1,59] For dipolar species, however, an additional source of error would in general be present, as the hyperpolarizability contribution becomes origin dependent.

Again for planar molecules, by employing the usual expressions for the effect of a change of origin on the property tensors,[50,51] say from O to $O + R^{(EQC)}$, the exact origin dependence of the temperature-independent term can be shown to be given by[52,54,59]

$$b^{O + R^{(EQC)}}(\omega) = b^O(\omega) + \tfrac{5}{2}R_z^{(EQC)}b'(\omega) \qquad (16)$$

where

$$b'(\omega) = (\beta_{xxz} - \beta_{x,x,z}^{Mixed}) + (\beta_{yyz} - \beta_{y,y,z}^{Mixed}) \\ - (\beta_{zxx} - \beta_{z,x,x}^{Mixed}) - (\beta_{zyy} - \beta_{z,y,y}^{Mixed}), \qquad (17)$$

measures the difference between the first electric dipole hyperpolarizability β and the mixed hyperpolarizability β^{Mixed}—i.e. the first electric dipole hyperpolarizability in the mixed length-velocity representation

$$\beta_{\alpha\beta\gamma}(-\omega;\omega,0) = \langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega,0}, \qquad (18)$$

$$\beta_{\alpha,\beta,\gamma}^{Mixed}(-\omega;\omega,0) = -\frac{i}{\omega}\langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta^p,\hat{\mu}_\gamma\rangle\rangle_{\omega,0}, \qquad (19)$$

with $\hat{\mu}_\beta^p$ being the dipole operator in the velocity gauge[52,54,59]

$$\hat{\mu}_\alpha^p = -\sum_i \hat{p}_{i,\alpha}. \qquad (20)$$

For quadrupolar systems, both quantities in eqns (18) and (19) are zero due to molecular symmetry, whereas this does not apply for dipolar molecules. However, if the hyper-virial condition is satisfied and the basis set is complete, the mixed and regular hyperpolarizabilities coincide irrespective of molecular symmetry, and the origin dependence disappears. For variational approximate methods, the use of LAOs[8–12]

ensures that the calculated $b(\omega)$ is origin independent also for a finite basis set, since the LAO basis (in the natural connection[24,25]) guarantees that the approximate magnetic dipole operator, defined as the magnetic field derivative of the Hamiltonian in LAOs, behaves as the exact magnetic dipole operator for any basis set.[60]

In the next section we present an atomic orbital-based response theory, where the time and perturbation dependence of the LAOs can be properly taken into account, deriving the necessary expressions for the quadratic response functions that determine the temperature-independent contribution to the EFGB, *i.e.* to $b(\omega)$.

III. AO density based quasienergy derivative formulae for the tensors $J'(\omega)$, $B(\omega)$ and $\mathscr{B}(\omega)$

Here the main elements of our formalism for the calculation of response functions of arbitrary order for time- and perturbation-dependent basis sets will be briefly summarized. Full details have been presented elsewhere.[26] Therefore we limit the discussion to those features of the approach that are relevant for the calculation of the $b(\omega)$ contribution to the EFGB.

Let's consider an external field consisting of monochromatic electromagnetic radiation combined with a static inhomogeneous electric field. In the electric quadrupole–magnetic dipole approximation, the external potential is then given by (atomic units used throughout unless where specified)

$$
\begin{aligned}
\hat{V}(t) = {} & [f \exp(i\omega t) + f^* \exp(-i\omega t) + e]\cdot(-\hat{\mu}) \\
& + [q \exp(-i\omega t) + q^*\exp(i\omega t) + g]\cdot(-\hat{\Theta}) \\
& + [-i(b + a) \exp(-i\omega t) \\
& + i(b^* + a^*) \exp(i\omega t)]\cdot(-\hat{m}),
\end{aligned} \tag{21}
$$

where $f = \{f_x, f_y, f_z\}$ is the complex electric field, or Jones vector, defining the intensity, polarization and phase of the radiation. q is the complex electric field gradient tensor arising from the radiation. e and g are the static electric field and field gradient, respectively. The magnetic field contribution has for convenience been split into two parts: $-ib$ (b not to be confused with $b(\omega)$) is the complex magnetic field strength which in addition to entering the external potential has also an explicit dependence in the time-dependent basis set. $-ia$ represents the same complex magnetic field strength, but the time-dependent basis set does not depend on this magnetic field strength. The factor $-i$ has been given explicitly, in order to get real-valued derivative integrals, which avoids the use of imaginary algebra in the implementation. In our formalism, the complex magnetic field strengths $-ib$ and $-ia$ will therefore correspond to using and not using, respectively, the time-dependent LAOs defined as[8,21]

$$
\xi_\mu(\boldsymbol{x}) = \exp\left\{-\frac{i}{2}[(-ib \exp(-i\omega t) + ib^* \exp(i\omega t))\times\boldsymbol{R}_\mu]\cdot\boldsymbol{r}\right\}\chi_\nu(\boldsymbol{x}), \tag{22}
$$

where χ_ν represents a conventional Cartesian or spherical Gaussian basis function. In the limit of a complete one-particle basis set, $-ib$ and $-ia$ mimic the same external magnetic field. Their representation will be different in finite basis sets.

From the Maxwell equations, q, b and a are related to f by

$$
b = a = \tfrac{i}{c}\boldsymbol{k} \times f, \quad q = -\tfrac{i\omega}{2c}(\boldsymbol{k}f^T + f\boldsymbol{k}^T), \tag{23}
$$

where $\boldsymbol{k}$ is a normalized vector directed along the direction of propagation and perpendicular to f, whereas c is the speed of light.

Let now w be any of the field strengths appearing in the Hamiltonian or in the external potential, where it is associated with the operator corresponding to some observable, and potentially it is also included in the basis set. The Hartree–Fock quasienergy derivative $\frac{\mathrm{d}}{\mathrm{d}w}Q$ is then defined by the equation[26]

$$
\frac{\mathrm{d}}{\mathrm{d}w}Q = Q^w \stackrel{\mathrm{Tr}_t}{=} \frac{\partial}{\partial w}E(\boldsymbol{D}) - \boldsymbol{S}^w \boldsymbol{W}, \tag{24}
$$

which by the (time-dependent) Hellmann-Feynman theorem is also the value of the observable. With the notation $\stackrel{\mathrm{Tr}_t}{=}$ here we indicate the trace of the matrix expressions and the time average of all terms. We have used superscripts as short-hand notation for derivatives, thus $\boldsymbol{S}^w = \frac{\mathrm{d}}{\mathrm{d}w}\boldsymbol{S}$. In eqn (24) we have introduced a generalized expression for the Hartree–Fock energy as a function of the electron density $\boldsymbol{D}$ as

$$
E(\boldsymbol{D}) \stackrel{\mathrm{Tr}}{=} h_{\mathrm{nuc}} + v_{\mathrm{nuc}} + (\boldsymbol{h} + \boldsymbol{V}(t) - \tfrac{i}{2}\boldsymbol{T})\boldsymbol{D} + \tfrac{1}{2}\boldsymbol{G}(\boldsymbol{D})\boldsymbol{D}, \tag{25}
$$

where h_{nuc} and v_{nuc} are the nuclear repulsion energy and the interaction between the external fields and the nuclei, respectively. $\boldsymbol{h}$ and $\boldsymbol{G}(\boldsymbol{D})$ are the conventional one- and two-electron matrices in the field-free case, defined in terms of our LAO basis

$$
h_{\mu\nu} = \left\langle \xi_\mu \left| -\frac{1}{2}\nabla^2 - \sum_K \frac{Z_K}{r_K} \right| \xi_\nu \right\rangle, \tag{26}
$$

$$
G(\boldsymbol{D})_{\mu\nu} = \sum_{\sigma\rho} D_{\sigma\rho}(g_{\mu\nu\rho\sigma} - g_{\mu\sigma\rho\nu}). \tag{27}
$$

The summation over K runs over all the nuclei in the molecule and it involves the nuclear charges Z_K and the positions of the electrons relative to nucleus K, r_K. $g_{\mu\nu\rho\sigma}$ is a two-electron integral

$$
g_{\mu\nu\rho\sigma} = \int\int \xi_\mu^*(\boldsymbol{x}_1)\xi_\nu(\boldsymbol{x}_1)\frac{1}{r_{12}}\xi_\rho^*(\boldsymbol{x}_2)\xi_\sigma(\boldsymbol{x}_2)\mathrm{d}\boldsymbol{x}_1\mathrm{d}\boldsymbol{x}_2. \tag{28}
$$

In the expression for the quasienergy derivative, eqn (24), we have introduced the derivative of the overlap matrix with respect to the field strength

$$
S_{\mu\nu}^w = \frac{\mathrm{d}}{\mathrm{d}w}\langle \xi_\mu | \xi_\nu \rangle, \tag{29}
$$

as well as the generalized time-and-energy-weighted density matrix defined as

$$
\boldsymbol{W} = \boldsymbol{DFD} + \tfrac{i}{2}\boldsymbol{DS}\dot{\boldsymbol{D}} - \tfrac{i}{2}\boldsymbol{DS}\dot{\boldsymbol{D}} \tag{30}
$$

where $\dot{\boldsymbol{D}}$ indicates the time-differentiated density matrix. In this last equation, the generalized Fock matrix $\boldsymbol{F}$ appears, defined as the partial derivative of the energy functional in eqn (25) with respect to the density matrix transposed

$$
\boldsymbol{F} = \frac{\partial}{\partial \boldsymbol{D}^T}E(\boldsymbol{D}) = \boldsymbol{h} + \boldsymbol{V}(t) - \tfrac{i}{2}\boldsymbol{T} + \boldsymbol{G}(\boldsymbol{D}). \tag{31}
$$

Both eqns (25) and (31) involve the anti-symmetric time derivative of the overlap matrix

$$T_{\mu\nu} = \langle \dot{\xi}_\mu | \xi_\nu \rangle - \langle \xi_\mu | \dot{\xi}_\nu \rangle. \tag{32}$$

The above equations are all formulated using only the density matrix in the atomic orbital basis, a basis which may be both time and field dependent. Higher-order response properties can now be obtained by differentiation of the expression for the quasienergy derivative eqn (24), taking into account the implicit dependence of the density matrix on the applied fields.[26]

Inserting eqn (25) into eqn (24), choosing $w = b$, and differentiating the quasienergy derivative in eqn (24) twice, once with respect to the electric fields e (associated to the frequency ω) and once with respect to (static) f, respectively, we obtain a formula for the quadratic response $Q^{bfe}_{-\omega,\omega,0}$[26,31]

$$Q^{bfe}_{-\omega,\omega,0} \overset{\mathrm{Tr}_t}{=} V^{bf}_{-\omega,\omega} D^e_0 + V^{be}_{-\omega,0} D^f_\omega + (h^b_{-\omega} + V^b_{-\omega} - \tfrac{i}{2} T^b_{-\omega}) D^{fe}_{\omega,0}$$
$$+ G^b_{-\omega}(D) D^{fe}_{\omega,0} + G^b_{-\omega}(D^e_0) D^f_\omega - S^b_{-\omega} W^{fe}_{\omega,0}, \tag{33}$$

$$Q^{b_\beta f_\alpha e_\gamma}_{-\omega,\omega,0} = J'_{\alpha,\beta,\gamma}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{\mu}_\gamma \rangle\rangle_{\omega,0}, \tag{34}$$

where we have used the fact that f only enters v_{nuc} and V, and only linearly. We have also exploited the fact that when we take the trace of the resulting matrices

$$\mathrm{Tr}[G(D^A) D^B] = \mathrm{Tr}[G(D^B) D^A]. \tag{35}$$

Taking advantage of the fact that the basis set does not depend on f or e, $W^{fe}_{\omega,0}$ can be shown to be given by the expression

$$W^{fe}_{\omega,0} = D^e_0 F^f_\omega D + D^e_0 F D^f_\omega + D F^f_\omega D^e_\omega - \tfrac{\omega}{2} D^e_0 S D^f_\omega$$
$$+ D F^f_\omega D^e_0 + D^f_\omega F D^e_0 + D^f_\omega F^e_0 D + \tfrac{\omega}{2} D^f_\omega S D^e_0$$
$$+ D^{fe}_{\omega,0} F D + D F^{fe}_{\omega,0} D + D F D^{fe}_{\omega,0} + \tfrac{\omega}{2} D^{fe}_{\omega,0} S D - \tfrac{\omega}{2} D S D^{fe}_{\omega,0}, \tag{36}$$

where we have taken into account that D^f_ω carries the phase factor $exp(i\omega t)$, thus $i\dot{D}^f = -\omega D^f_\omega$, which also applies to $D^{fe}_{\omega,0}$, while D^e_0 is static, and therefore $\dot{D}^e = 0$. We note that although all matrices in eqn (33) carry time-dependent exponential phase factors, these cancel each other, thus making the time average redundant. The integrals appearing in $V^{bf}_{-\omega,\omega}$ are the same as those that were introduced when calculating Cotton–Mouton constants using finite difference techniques in combination with LAOs[17]

$$V^{b_\beta f_\alpha}_{\mu\nu} = Q_{MN} \langle \chi_\mu | r_\beta r_\alpha | \chi_\nu \rangle, \tag{37}$$

where r_β refers to the β component of the electron position operator appearing in the phase of the London orbital, whereas r_α is the α component of the position operator appearing in the electric dipole moment operator. Q_{MN} is an antisymmetric matrix containing the differences between the centers of expansion of orbitals χ_μ and χ_ν

$$Q_{MN} = \frac{1}{2} \begin{bmatrix} 0 & -Z_{MN} & Y_{MN} \\ Z_{MN} & 0 & -X_{MN} \\ -Y_{MN} & X_{MN} & 0 \end{bmatrix} \tag{38}$$

Replacing b with a in eqn (33), we obtain the corresponding quadratic response function, $Q^{afe}_{-\omega,\omega,0}$, for the case when LAOs are *not* employed

$$Q^{afe}_{-\omega,\omega,0} \overset{\mathrm{Tr}_t}{=} V^a_{-\omega} D^{fe}_{\omega,0},$$
$$Q^{a_\beta f_\alpha e_\gamma}_{-\omega,\omega,0} = J'_{\alpha,\beta,\gamma}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{\mu}_\gamma \rangle\rangle_{\omega,0}, \tag{39}$$

where we have used the fact that the fields only enter V (and v_{nuc}), and only linearly.

The tensor $\mathscr{B}_{\alpha\beta,\gamma\delta}$ is obtained from eqn (39) by replacing a with q

$$Q^{qfe}_{-\omega,\omega,0} \overset{\mathrm{Tr}_t}{=} V^q_{-\omega} D^{fe}_{\omega,0},$$
$$Q^{q_{\beta\gamma} f_\alpha e_\delta}_{-\omega,\omega,0} = \mathscr{B}_{\alpha,\beta\gamma,\delta}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{\Theta}_{\beta\gamma}, \hat{\mu}_\delta \rangle\rangle_{\omega,0}, \tag{40}$$

while $B_{\alpha\beta,\gamma\delta}$ is obtained by replacing a with g and e with f^*, respectively

$$Q^{gff^*}_{0,\omega,-\omega} \overset{\mathrm{Tr}_t}{=} V^g_0 D^{ff^*}_{\omega,-\omega},$$
$$Q^{g_{\gamma\delta} f_\alpha f^*_\beta}_{0,\omega,-\omega} = B_{\alpha\beta,\gamma\delta}(\omega) = \langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\Theta}_{\gamma\delta} \rangle\rangle_{\omega,0}. \tag{41}$$

The linear response tensors that determine the temperature-dependent part are obtained as intermediates in the determination of the quadratic response functions needed for $b(\omega)$

$$Q^{f^*f}_{-\omega,\omega} = V^{f^*}_{-\omega} D^f_\omega; \quad Q^{f^*_\alpha f_\beta}_{-\omega,\omega} = \langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle\rangle_\omega \tag{42}$$

$$Q^{qf}_{-\omega,\omega} = V^q_{-\omega} D^f_\omega; \quad Q^{q_{\alpha\beta} f_\gamma}_{-\omega,\omega} = \langle\langle \hat{\Theta}_{\alpha\beta}; \hat{\mu}_\gamma \rangle\rangle_\omega \tag{43}$$

$$Q^{bf}_{-\omega,\omega} = V^b_{-\omega} D^f_\omega; \quad Q^{b_\alpha f_\beta}_{-\omega,\omega} = -i\langle\langle \hat{m}_\alpha; \hat{\mu}_\beta \rangle\rangle_\omega \tag{44}$$

We have derived the above formulae using the $n + 1$ rule—that is, we determine the quasienergy corrections to order $2 + 1 = 3$ (quadratic response) from the perturbed density matrix up to an order of 2 ($D^f_\omega, D^e_0, D^{fe}_{\omega,0}, D^{ff^*}_{\omega,-\omega}$). In this manner, the full temperature-independent contribution to the EFGB, $b(\omega)$, can be determined by solving a total of 21 perturbed density matrices. Alternative formulae were derived in which in many cases the stronger $2n + 1$ rule is used to determine the third-order energy corrections.[26] In the case of the EFGB, this would lead to a total of 24 perturbed densities to be determined if both the London and no-London results are of interest in a given calculation ($D^f_\omega, D^e_0, D^b_{-\omega}, D^a_{-\omega}, D^q_\omega, D^g_0$). This makes the $n + 1$ rule approach slightly more advantageous in this case.

The calculation of the tensors that determine the temperature-dependent and temperature-independent contributions to the Buckingham birefringence thus requires the determination of first- and second-order perturbed density matrices. These perturbed density matrices can be determined entirely in the atomic-orbital basis,[26] using for instance the linear-scaling response equation solver of Coriani et al.[61] as done in the present work. For details about the determination of the perturbed density matrices, we refer to ref. 26 and 30.

IV. Computational details

We have calculated all first-order properties (dipole and quadrupole moments), frequency-dependent polarizabilities and hyperpolarizabilities entering the molecular expression of the EFGB for the quadrupolar system naphthalene, and for the dipolar systems fluorobenzene (C_6H_5F) and furan (C_4H_4O), using both LAOs and conventional basis sets at the Hartree–Fock level of theory. Results at two different origins are presented for the dipolar systems, in order to illustrate the gauge-origin dependence of the temperature-independent term for conventional basis sets, and the effect of introducing the LAO basis. In one case the origin was placed at the center of nuclear masses of the molecule (labelled CM), in the other case either on the F (fluorobenzene) or the O (furan) atoms. All molecules were placed in the yz plane, with the z axis aligned along the C_2 symmetry axis. For naphthalene the z axis coincides with the CC bond that fuses the two benzene rings (see Fig. 1).

The geometries of fluorobenzene and naphthalene were optimized at the DFT level employing the cc-pVTZ basis set[62] and Becke's 3-parameter exchange functional[63] together with the Lee–Yang–Parr correlation functional[64] (B3LYP).[65] This geometry for fluorobenzene was also used in a recent study of the Cotton-Mouton effect.[30] The structure used for furan is the gas-phase optimized geometry at the B3LYP/aug-cc-pVTZ level employed in ref. 52.

For the calculations of the properties, we have used the augmented correlation-consistent basis sets of Woon and Dunning,[66] as diffuse functions are known to be important to obtain accurate results for all properties of interest for EFGB. In order to explore the basis set convergence, we have chosen basis sets of double-, triple-, and quadrupole-zeta quality. We have employed the wavelength of 632.8 nm, the one used in the experiment for all three molecules,[41–43] in all calculations. For fluorobenzene, the linear response calculations needed to determine the position of the EQC were also performed for $\lambda = 441.6$ nm, since the experimental study of ref. 42 was carried out also at this wavelength. Values of the Buckingham constant, eqn (2), are reported for the temperature used in the experiments, 298 K. Since our analytical implementation of the frequency-dependent mixed electric and magnetic hyperpolarizability using LAOs is currently restricted to Hartree–Fock wave functions, electron correlation effects will be missing in our results.

The geometry optimizations have been performed using the distributed version of the Dalton quantum chemistry program,[67] whereas the molecular properties have been calculated using a local version of Dalton, in which the scheme described in section 3 has been implemented.[26] The code is interfaced to the linearly-scaling Hartree–Fock energy[68] and response[61] code of Jørgensen, Coriani and coworkers. All calculations have been run in parallel using the parallel implementation described in ref. 69 at the local HP supercomputer installed at the University of Tromsø.

V. Results

The following discussion will be split into two parts. We will focus first on the results obtained with and without the use of LAOs for the hyperpolarizabilities that determine the temperature-independent contribution to the Buckingham birefringence. The origin and basis set dependence of the results will be illustrated. Following this, we will collect our results for the EQC, quadrupole moment and other experimentally observable quantities as derived from our calculations and compare them to available experimental data.

In Table 1 we have collected the results for the different hyperpolarizability tensors that contribute to the temperature-independent $b(\omega)$ term for naphthalene. Since the quadrupole hyperpolarizabilities do not depend on whether LAOs are used or not, we only report one set of results for them, whereas both LAO and conventional basis set (NoLAO) results are reported for $J'(\omega)$ and $b(\omega)$.

We start by considering the $J'(\omega)$ average, for which we observe that the LAO results converge very rapidly, being more or less fully converged already at the aug-cc-pVDZ basis set level. This fast basis set convergence is somewhat surprising. Even though LAOs have been shown to give basis-set limit results already at the aug-cc-pVDZ level for static magnetic properties involving only the magnetic field as a perturbation, the magnetizability,[70,71] they were shown to be somewhat less effective when the applied electromagnetic field is time dependent, as is for instance the case for optical rotation[15,72,73] and electronic circular dichroism.[60,73] A similar
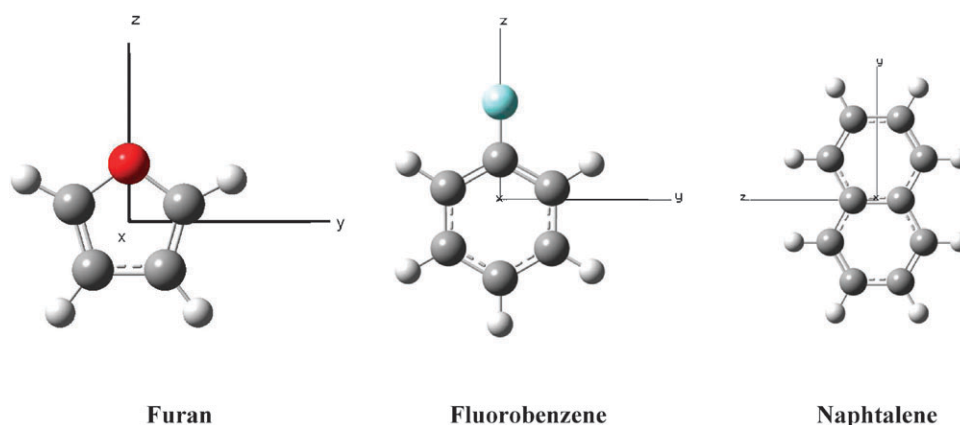

Fig. 1 The structures and geometrical arrangement of the three molecules studied here.

Table 1 Naphthalene. Calculated results for the hyperpolarizability tensor averages and for the temperature independent contribution $b(\omega)$ to Buckingham birefringence. A wavelength of 632.8 nm is employed in the calculations. All quantities are given in atomic units. "LAO" and "NoLAO" indicate the use of perturbation dependent London Orbitals or conventional basis sets, respectively

Basis	B	$\mathscr{B}$	J'		b	
			NoLAO	LAO	NoLAO	LAO
aug-cc-pVDZ	−28058.0	−27343.3	124.76	132.63	−1250.33	−1323.13
aug-cc-pVTZ	−29565.9	−28803.9	129.54	132.69	−1300.89	−1329.97
aug-cc-pVQZ	−29924.4	−29144.5	131.05	132.25	−1317.24	−1328.30

Table 2 Furan. Calculated results for the hyperpolarizability tensor averages and for the temperature independent contribution $b(\omega)$ to Buckingham birefringence. A wavelength of 632.8 nm is employed in the calculations. All quantities are given in atomic units. "LAO" and "NoLAO" indicate the use of perturbation dependent London Orbitals or conventional basis sets, respectively

Basis	Origin	B	$\mathscr{B}$	J'		b	
				NoLAO	LAO	NoLAO	LAO
aug-cc-pVDZ	CM	−9472.5	−9378.1	25.52	31.26	−248.80	−301.97
	O	−9655.9	−9541.9	24.92	30.98	−245.93	−301.97
aug-cc-pVTZ	CM	−10188.3	−10059.6	28.95	31.16	−285.20	−305.60
	O	−10405.5	−10258.5	28.54	30.89	−283.79	−305.60
aug-cc-pVQZ	CM	−10500.3	−10354.5	30.26	31.17	−299.56	−307.99
	O	−10726.7	−10563.6	29.93	30.92	−298.86	−307.99

Table 3 Fluorobenzene. Calculated results for the hyperpolarizability tensor averages and for the temperature independent contribution $b(\omega)$ to Buckingham birefringence. A wavelength of 632.8 nm is employed in the calculations. All quantities are given in atomic units. "LAO" and "NoLAO" indicate the use of perturbation dependent London Orbitals or conventional basis sets, respectively

Basis	Origin	B	$\mathscr{B}$	J'		b	
				NoLAO	LAO	NoLAO	LAO
aug-cc-pVDZ	CM	−12322.4	−12075.0	53.79	57.51	−531.00	−565.42
	F	−13858.7	−13605.8	53.42	57.43	−528.26	−565.42
aug-cc-pVTZ	CM	−13180.7	−12915.5	55.97	57.56	−553.55	−568.28
	F	−14797.7	−14525.5	55.73	57.46	−552.27	−568.28
aug-cc-pVQZ	CM	−13450.3	−13179.2	56.76	57.39	−561.60	−567.45
	F	−15090.0	−14811.4	56.58	57.28	−560.91	−567.45

fast basis set convergence of the $J'(\omega)$ term is also observed for furan in Table 2 and for fluorobenzene, see Table 3. This excellent basis set convergence is to a large extent also reflected in the individual tensor components of $J'(\omega)$, though additional improvements arise due to the averaging procedure, the LAO and NoLAO results being more similar in terms of basis set convergence for the individual tensor components. LAOs thus seem to give a more uniform description of the different components of the $J'(\omega)$ tensor than if only conventional basis sets were used. Still, even for the average of $J'(\omega)$, the basis set convergence with conventional basis sets is quite good.

As can be seen from Table 1, the basis set convergence for the $B(\omega)$ and $\mathscr{B}(\omega)$ terms is much slower than for $J'(\omega)$. Even with the aug-cc-pVQZ basis set (1168 basis functions) the changes in the tensor averages are still substantial, with an increase of about 1.2% going from the aug-cc-pVTZ to the aug-cc-pVQZ basis set. However, we also note from eqn (4) that the two quadrupole hyperpolarizabilities largely cancel each other (exactly in the infinite wavelength limit) and they contribute only approximately half of the final value for $b(\omega)$. The two tensors have approximately the same basis set convergence, yielding a much smaller basis set dependence when their difference is taken. As such, the slower basis set convergence of the NoLAO compared to the LAO results for $b(\omega)$

arises from the magnification of the basis set convergence of $J'(\omega)$ due to the prefactor of $5/\omega$. The improved basis set convergence obtained with the use of LAOs is particularly evident in the observable, the temperature-independent contribution $b(\omega)$.

Turning our attention now to the results reported in Table 2 for the dipolar molecule furan, we note first of all that the temperature-independent contribution $b(\omega)$ is indeed origin independent when calculated using LAOs. It is worth noting, however, that the origin dependence of the calculations using conventional basis sets is rather small, reflecting the fact that the shift in $J'(\omega)$ is small, both with and without LAOs, when shifting the origin. Therefore the NoLAO calculations yield results that are only moderately origin dependent.

As for naphthalene, the tensor averages of $B(\omega)$ and $\mathscr{B}(\omega)$ are very slowly convergent, but with a parallel basis set dependence. Therefore the dependence of their difference on the extension of the basis set does not contribute significantly to the overall basis set dependence of the temperature-independent contribution to the Buckingham birefringence. As such, the aug-cc-pVDZ results obtained with LAOs for $b(\omega)$ are within 2–3% of the basis set limit, whereas the aug-cc-pVDZ results with conventional basis sets are off by

almost 20%. Even with the aug-cc-pVQZ basis set, the NoLAO results for $b(\omega)$ are further away from the basis-set limit than those obtained with LAOs using the aug-cc-pVDZ basis set.

The results obtained for fluorobenzene are reported in Table 3. They display the same trends as already observed for naphthalene and furan. We note, however, the very strong dependence of the quadrupole operator on the choice of origin, which is reflected in the strong origin dependence of the $B(\omega)$ and $\mathscr{B}(\omega)$ contributions. However, the origin dependence in the two quadrupolar hyperpolarizabilities is very similar. This, in combination with the very modest origin dependence of the $J'(\omega)$ tensor average, leads to a very minor origin dependence of the temperature-independent $b(\omega)$ term for conventional basis sets.

In Table 4, a comparison between our *ab initio* results and experiment, in particular with the data obtained in the EFGB studies by Calvert and Ritchie for naphthalene,[41] and by Dennis *et al.* for furan[43] and fluorobenzene,[42] is made. The table gathers all the results obtained in this study using our best basis set (aug-cc-pVQZ) at the Hartree–Fock level of theory and with the use of LAOs for the mixed electric-magnetic response tensors, $J'(\omega)$ and $G'(\omega)$.

Since we are resorting to an approach where electron correlation effects are neglected, we refrain from going into a detailed discussion of the comparison of the first-order (the molecular dipole and quadrupole moments) and of the linear response properties—$\alpha(\omega)$, $A(\omega)$ and $G'(\omega)$—with other computational results or experiment. *Ab initio* studies of the

electric dipole polarizability[74] and quadrupole moment[75] of naphthalene can be found in the literature. The Buckingham birefringence of furan was the subject of ref. 52, and readers are referred to that paper for further analysis of the response of this polar molecule to radiation and to an external electric field gradient. Fluorobenzene was one of the systems selected for the recent *ab initio* study, closely related to the present, of the hypersusceptibilities rationalizing the temperature-independent contribution to the Cotton–Mouton effect, where LAOs were employed.[30] For a study of the molecular quadrupole moment of fluorobenzene, see ref. 76. The quadrupole moment of furan is discussed in ref. 77. We only note here that for both the electric dipole polarizability and the quadrupole moment (the latter computed and measured at the center of nuclear masses), our Hartree–Fock values are in satisfactory agreement with experiment, with the exception of the $\alpha_{xx}(-\omega;\omega)$ component of fluorobenzene, which appears to be somewhat underestimated. It is also apparent that the independent particle approximation cannot provide estimates of the electric dipole moments of furan or fluorobenzene of a quality which can compete with the accuracy achieved in experiment.

As for the CME or Kerr effects,[1–3] the EFGB is dominated by the Langevin-type, orientational temperature-dependent part. Therefore neglecting the hyperpolarizability contribution changes the observable—$_mQ(\omega, T = 298 \text{ K})$—by $\approx 1.6\%$ for naphthalene, $\approx 1.8\%$ for furan and $\approx 2.3\%$ for fluorobenzene. At the same time, the smallness of the electronic rearrangement effect, represented by the hyperpolarizability contribution

Table 4 Results for the observable quantities for naphthalene, furan and fluorobenzene as obtained in this work using the aug-cc-pVQZ basis set and London atomic orbitals at the Hartree–Fock level of theory. $\lambda = 632.8$ nm, corresponding to $\omega \approx 0.072$ au (except where explicitly given). Comparison with available experimental data. Atomic units

	Naphthalene		Furan		Fluorobenzene	
	This work	Expt.[a]	This work[b]	Expt.[c]	This work[d]	Expt.[e]
μ_z			−0.3094	−0.2601 ± 0.0024	−0.7014	−0.586 ± 0.012
$\alpha_{xx}(\omega)$	67.965	77.0	35.425	39.00 ± 1.80	44.898	52.10 ± 1.82
$\alpha_{yy}(\omega)$	124.995	134 (147)	57.278	55.13 ± 3.28	81.103	77.09 ± 2.85
$\alpha_{zz}(\omega)$	172.410	146 (132)	53.584	53.31 ± 1.46	81.517	78.18 ± 1.21
$\alpha_{\text{ani}}(\omega)$	75.930		7.233	6.25 ± 2.57	18.517	13.60 ± 2.37
$\alpha_{\text{ave}}(\omega)$	121.790		48.762	49.15 ± 1.34	69.173	
$\Theta_{xx}^{(\text{CM})f}$	−10.149	−10.03 ± 1.11	−4.726	−4.53 ± 0.29	−4.717	−4.68 ± 0.22
$\Theta_{yy}^{(\text{CM})f}$	4.955	5.04 ± 1.11	4.569		6.103	5.01 ± 0.60
$\Theta_{zz}^{(\text{CM})f}$	5.194	5.04 ± 1.11	0.157		−1.386	−0.33 ± 0.65
$A(\omega) + \frac{5}{\omega}G'(\omega)$			60.027	70 ± 70	10.218	−15 ± 22
$R_z^{(\text{EQC})}(\omega)^g$			4.150	6 ± 6	0.276	−0.57 ± 0.83
$\Theta_{xx}^{(\text{EQC})}(\omega)$			−6.010	−6.06 ± 1.20	−4.911	−4.35 ± 0.45
$\Theta_{yy}^{(\text{EQC})}(\omega)$			3.285		5.909	
$\Theta_{zz}^{(\text{EQC})}(\omega)$			2.725		−0.999	
$\frac{1}{kT}\Theta_{\alpha\beta}\alpha_{\alpha\beta} \times 10^{-5}$	8.743		1.088		1.804	
$b(\omega)$	−9962.3		−2309.9		−4255.9	
$_mQ(\omega,T) \times 10^{-28}$	29.07	26.3 ± 1.6	4.24	3.88 ± 0.40	6.18	4.63 ± 0.30

[a] Ref. 41. The authors obtain the tensor elements of the electric dipole polarizability and quadrupole moment from combined measurements of Cotton–Mouton and Kerr birefringences and molar refraction. In this process they obtain two sets of results for the polarizability tensor (second set in parentheses for the xx and yy components), and they assume axial symmetry for the quadrupole. The study is carried out in CCl$_4$. [b] B3LYP/aug-cc-pVTZ results in the gas phase from ref. 52: $\mu_z = -0.2626$, $\alpha_{xx} = 35.982$, $\alpha_{yy} = 60.838$, $\alpha_{zz} = 54.986$, $\Theta_{xx}^{(\text{CM})} = -4.146$, $(A + \frac{5}{\omega}G') = 38.949$, $R_z^{(\text{EQC})} = 2.853$, $\Theta_{xx}^{(\text{EQC})} = -4.896$, $b(\omega) = -2115.2$. [c] Ref. 43. Electric dipole moment value taken from the literature, see ref. 43. [d] Results obtained with a wavelength $\lambda = 441.6$ nm: $\alpha_{xx} = 45.966$, $\alpha_{yy} = 84.517$, $\alpha_{zz} = 84.669$, $(A + \frac{5}{\omega}G') = 18.605$, $R_z^{(\text{EQC})} = 0.502$. [e] Ref. 42. Results measured for a wavelength of $\lambda = 441.6$ nm: $\alpha_{xx} = 53.01 \pm 1.52$, $\alpha_{yy} = 80.67 \pm 2.18$, $\alpha_{zz} = 81.39 \pm 0.85$, $(A + \frac{5}{\omega}G') = -15 \pm 18$, $R_z^{(\text{EQC})} = -1.0 \pm 0.7$. [f] Center of nuclear masses as origin. [g] Distance in the direction of the dipole moment from the EQC to CM.

$b(\omega)$, makes it very hard to extract it from experimental measurements of the electric field gradient induced linear birefringence, since to this end the results of these measurements, made at different temperatures, must be extrapolated to the infinite-temperate limit. These difficulties are reflected in the very generous error bars generally associated with the experimental data when available. Also, in view of both the large error bars of experiment and the good performance of Hartree–Fock in determining the electric dipole dynamic polarizability and the quadrupole moment, the computed values of $_mQ(\omega, T = 298\ \text{K})$ of naphthalene and furan reproduce quite satisfactorily the experimental data. The same does not happen for fluorobenzene, where we compute $_mQ(\omega, T = 298\ \text{K}) = 6.18 \times 10^{28}$ au, whereas Dennis and co-workers measured (albeit in a carbon tetrachloride solution) a weaker effect, $_mQ(\omega, T = 298\ \text{K}) = (4.63 \pm 0.30) \times 10^{28} =$ au.[42] The reason for this discrepancy appears to be in the overestimation of the electric dipole polarizability anisotropy by the Hartree–Fock model, as well as the neglect of solvent effects.

A final word on the computational estimates of the EQC, i.e. of $R_z^{(\text{EQC})}$. This is placed ≈ 4.1 au away from the center of nuclear masses (along the dipole axis, in the direction of the dipole moment) for furan, and only ≈ 0.3 au in the same direction for fluorobenzene. Both for the combination of linear response tensors involved in the theoretical expression of $R_z^{(\text{EQC})}$ and for the resulting displacement itself, agreement with experiment is once again reasonable, especially considering the large error bars of the latter.

VI. Summary and outlook

We have presented a scheme for the analytical calculation of quadratic response functions involving time-dependent electromagnetic fields in combination with the use of LAOs to obtain origin-independent results for the temperature-independent contribution to the Buckingham birefringence. This work can thus either be considered an extension of the use of time-dependent LAOs in connection with a quasienergy formalism from second-order molecular properties[21] to third-order molecular properties, or alternatively an extension of the use of LAOs in third-order molecular properties involving a static magnetic field[78] to a frequency-dependent magnetic field. The formalism has been developed fully in the atomic orbital basis, making it directly applicable to the use in linearly scaling SCF schemes.

In contrast to what has been observed both for second-order properties involving frequency-dependent electromagnetic fields, such as optical rotation[15,72,73] as well as recently also observed in the case of the second-order static magnetic field perturbed frequency-dependent polarizability—the hyper-magnetizability involved in the determination of the Cotton–Mouton effect[30]—the LAOs lead to significantly improved basis set convergence of the temperature-independent contribution to the Buckingham birefringence. Indeed, even with an aug-cc-pVDZ basis set, the results obtained using LAOs are closer to the estimated basis-set limits than those yielded by the aug-cc-pVQZ conventional basis set.

While furan[43] was already studied computationally in our group recently,[52] this study is the first one analyzing Buckingham birefringence of naphthalene and fluorobenzene, two species for which measurements were performed in the group of Ritchie in the eighties.[41,42] In all cases, the contribution of the temperature-independent contribution $b(\omega)$ is negligible, influencing the value of the overall observable, the Buckingham constant $_mQ(\omega, T)$, by 2.3% at the most. While experiment and theory easily agree on the estimate of the effect measured at 298 K—with the computed $_mQ(\omega, T = 298\ \text{K})$ being always a bit overestimated with respect to the center of the distribution of experimental data—some disagreement remains for fluorobenzene, apparently due both to our over-estimate of the electric dipole dynamic polarizability computed at the Hartree–Fock level and to the neglect of solvent effects, which should be included for a comparison with an experiment performed in carbon tetrachloride solution.[42] Estimates for the location of the EQC were given for both furan and fluorobenzene, the two polar molecules investigated in this work. The shift with respect to the center of nuclear masses leading to the so-called effective quadrupolar center is rather large for furan (≈ 4.2 au) and much smaller for fluorobenzene (≈ 0.28 au) for $\lambda = 632.8$ nm, and these values easily fit the large error bars of the indirect experimental determination.[42,43] The same can be said for the combination of linear response tensor, $A(\omega) + 5/\omega G'(\omega)$, also estimated from experiment.

The importance of London orbitals in order to achieve basis-set limit results shows that these may be useful in the study of other birefringences involving higher-order contributions from the magnetic field, such as magnetochirality[50,79] and Jones or magnetoelectric birefringences.[50,80,81] As the formalism used in this work is open-ended with respect to the order of the applied perturbations, assuming the necessary one- and two-electron derivative integrals are available, we plan to extend our work to these birefringences in the future, as well as add the possibility to include electron correlation effects in the form of density functional theory.

Acknowledgements

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