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Gauge-origin independent calculations of electric-field-induced second-harmonic generation circular intensity difference using London atomic orbitals

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We present the first gauge-origin independent calculations of the circular intensity difference (CID) in electric-field-induced second-harmonic generation (EFISHG), including all contributions up to the electric-quadrupole–magnetic-dipole level. A recursive, open-ended response theory framework in combination with the use of London atomic orbitals allows us to ensure gauge-origin independent results. We apply this approach to study EFISHG-CID in a collection of chiral amino acids. We demonstrate that diffuse polarizing basis functions are critical in order to obtain accurate CIDs, and that a basis set of at least aug-cc-pVTZ quality is needed in order to obtain results close to the basis-set limit. The use of London orbitals does not lead to significantly faster basis set convergence, although the improved basis set convergence allows the aug-cc-pVDZ basis set to be used with some confidence for larger molecules.

1. Introduction

Second-harmonic generation (SHG) is a non-linear process that generates frequency doubling at non-resonant conditions. In this process, two photons are absorbed from the incident light, and one photon is emitted with twice the frequency of the incident photons [1]–[2]. In the electric dipole approximation, in its most naive form, SHG is only observed for non-centrosymmetric systems, and it would therefore in general not be observed in isotropic samples. However, utilizing scattering processes such as hyper-Rayleigh scattering [3] or multiphoton processes [4–6], SHG can be observed in isotropic media. An alternative approach is to remove the isotropy and break the symmetry, for instance by applying an external static electric field can be applied, as done in the case of electric-field-induced second harmonic generation (EFISHG) experiments [7]–[8].

A benefit of multiphoton spectroscopy is that it allows for the use of longer wavelengths, allowing for deeper penetration into living tissue while also improving focality, and second-harmonic generation and its absorptive counterpart, two-photon absorption, are today gaining increasing importance for biological imaging. [9–13] The circular intensity difference (CID) describes the difference in absorption of left and right circularly polarized light. For isotropic media, this phenomenon can only occur in chiral molecules, which by definition have non-superimposable enantiomeric structures [14]. Since many biological molecules are chiral, the combined effect of CID and SHG might provide additional information beyond that which

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can be obtained from SHG alone, and thus potentially be an important tool for studying the structure of biological systems (see e.g. Refs. [15, 16]).

There are in the literature only two computational studies of EFISHG-CID, [17, 18] but circular dichroism has been observed in SHG experiments when the experimental setup as a whole is chiral. [19–23] In order to describe the EFISHG-CID phenomenon, it is necessary to leave the electric dipole approximation and consider contributions up to the electric-quadrupole–magnetic-dipole order [14, 24]. When going beyond the electric dipole approximation, the problem of origin dependence has to be taken into account, since the magnetic dipole and the electric quadrupole moments are origin-dependent quantities. However, as the circular intensity difference is an observable, it will by necessity have to be an origin-independent quantity [14, 24].

The problem of origin dependence appears at two levels: Firstly, the observable quantity have to be defined in an origin-independent manner. Although rather obvious, we note that the problem of origin independence remains challenging for the frequency-dependent magnetizabilities as well as the material constants. [25–28] Secondly, at the computational level, origin-independent properties involving magnetic-field perturbations can only be achieved for variational wave functions in the complete basis set limit, as can for instance be achieved through the use of multiwavelets, [29] or using local gauge-origin approaches (*vide infra*). List *et al.* have proposed to avoid the multipole expansion altogether to achieve origin independence, [30] but this approach has not yet been applied to the study of non-dominant contributions to the induced dipole moment, as for instance is the case in optical rotation where it is not the total induced dipole moment that is needed, but rather that arising from the magnetic component of the electromagnetic wave. For approximate calculations in finite basis sets, the results will in general depend on the placement of the origin of the system. In the recent study by Rizzo and Ågren, fairly large basis sets were used in order to obtain results close to the basis-set limit, and thus reduce the dependence of their calculated results on the choice of gauge origin. [18] Nevertheless, for many magnetic properties, even fairly large basis sets may not suffice in order to reach the basis-set limit, [29, 31] making it highly desirable to develop methods that improve basis set convergence and ensure gauge-origin independent results.

London atomic orbitals [32] have been shown to be a versatile tool for providing origin-independent results of magnetic properties also for finite basis sets [33–37] by introducing a fixed, local gauge origin for each individual atomic orbital. In this work, we present the first implementation of London atomic orbitals for the calculation of EFISHG-CID at the Hartree–Fock level of theory and investigate the importance of using London atomic orbitals for improving basis set convergence and to obtain gauge-origin independent results. We also discuss the magnitude of the contributions beyond the electric dipole approximation (magnetic dipole and electric quadrupole) to the EFISHG-CID signal.

The molecular properties that must be calculated, and subsequently combined to form the observable EFISHG-CID signal, are various fourth-order derivatives of the molecular energy. The collections of perturbations that define these properties consist of combinations of the electric dipole, electric quadrupole and magnetic dipole operators in different cubic response functions. [17, 18] The use of London atomic orbitals increases the complexity of the response theory compared to the case when such orbitals are not used (*i.e.* when using conventional Gaussian basis sets). Our group has recently developed an atomic density-matrix-based formulation of response theory that also includes the effects of perturbation-dependent basis sets. [38] The method has been shown to be amendable to the use of recursive

programming routines, thereby making it fully open-ended with respect to the order of the applied perturbations, [39] as long as the perturbation ansatz remains valid for the interaction of the electronic density with the applied perturbations. We have recently used this program to calculate various high-order properties, such as anharmonic force fields [40], anharmonic infrared and Raman spectra [41], hyper-Raman spectra [42] as well as a variety of multiphoton absorption processes. [43, 44]. We have also used a pilot implementation of the open-ended response-theory code to calculate fourth-order birefringences using London atomic orbitals, such as the Cotton–Mouton effect [45] and Jones birefringence. [46] However, this is the first study of EFISHG-CID using London atomic orbitals, and also one of the first applications of the recursive implementation [39] to higher-order magnetic responses using London atomic orbitals, noting that this general framework has been used to calculate both two- and three-photon circular dichroism using LAOs. [47, 48]

Here we perform a basis-set convergence study on (L)-Alanine, (L)-Arginine, (L)-Aspartic acid, (L)-Cysteine and (L)-Tryptophan at the Hartree-Fock level of theory, comparing the basis-set convergence of the London and conventional basis set results. A comparison with previous studies [18] on these molecules is also made. We restrict ourselves to a discussion of the theory of EFISHG-CID in the non-resonant case.

The rest of the paper is organized as follows: In Section 2, we present the theory, starting in Section 2.1 with a recapitulation of the EFISHG-CID phenomenon, moving on to present various aspects related to basis sets and gauge-origin independence in Section 2.2. In Section 2.3, we briefly recapitulate the open-ended response theory framework and the recursive implementation used to calculate the properties that enter into the expressions for the EFISHG-CID observable. We summarize our computational details in Section 3 and present and discuss our results in Section 4. Finally, we give some concluding remarks and an outlook in Section 5.

2. Theory

2.1. EFISHG-CID

EFISHG-CID is a process where two photons of equal circular frequency ω are absorbed, and one photon of frequency 2ω is emitted [49]. If μ is the polarization of the incident photons and μ' is the polarization of the emitted photon, the general expression for the radiant intensity, defined as the energy radiated in a given direction with polarization μ' , given per unit time and unit solid angle, is [17, 18]

$$I(\mu, \mu') = \frac{8E^2\omega^4 I_0^2 N^2}{(4\pi\epsilon_0)^3 c_0^5} [I^d(\mu, \mu') + \frac{1}{c_0} I^m(\mu, \mu') + \frac{\omega}{c_0} I^q(\mu, \mu')], \quad (1)$$

where \mathbf{E} is the static electric field intensity, I_0 is the incident light intensity, and N is the number of absorbers in the sample. The quantities $I^d(\mu, \mu')$, $\frac{1}{c_0} I^m(\mu, \mu')$ and $\frac{\omega}{c_0} I^q(\mu, \mu')$ combine different cubic response functions involving interactions of the different multipole moments appearing in the multipolar expansion of the propagating light wave. Truncating the multipolar expansion at the electric quadrupole–magnetic dipole level, the relevant cubic response functions are

$$\gamma_{\alpha,\beta,\gamma,\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = -\langle\langle \mu_\alpha; \mu_\beta, \mu_\gamma, \mu_\delta \rangle\rangle_{\omega_1, \omega_2, \omega_3}, \quad (2)$$

$$G_{\alpha,\beta,\gamma,\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = -i\langle\langle \mu_\alpha; \mu_\beta, m_\gamma, \mu_\delta \rangle\rangle_{\omega_1, \omega_2, \omega_3}, \quad (3)$$

$$A_{\alpha,\beta,\gamma\epsilon,\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = -\langle\langle \mu_\alpha; \mu_\beta, q_{\gamma\epsilon}, \mu_\delta \rangle\rangle_{\omega_1, \omega_2, \omega_3}, \quad (4)$$

where we have introduced the electric dipole operator $\boldsymbol{\mu}$, the electric quadrupole operator in its traced form \mathbf{q} and the magnetic dipole operator \mathbf{m} , defined in atomic units respectively as

$$\boldsymbol{\mu} = \sum_j q_j \mathbf{r}_j, \quad (5)$$

$$\mathbf{q} = \frac{1}{2} \sum_j q_j \mathbf{r}_j \mathbf{r}_j^T, \quad (6)$$

$$\mathbf{m} = \frac{1}{2} \sum_j \frac{q_j}{m_j} \mathbf{l}_j = \frac{1}{2} \sum_j \frac{q_j}{m_j} \mathbf{r}_j \times \mathbf{p}_j, \quad (7)$$

where q_j and m_j are the charge and mass of the electrons, and where \mathbf{r}_j and \mathbf{p}_j are the position and linear momentum of electron j , respectively.

The exact expressions for the intensities $I^d(\mu, \mu')$, $I^m(\mu, \mu')$ and $I^q(\mu, \mu')$ in eq. 1 will depend on the polarization of the incident photons as well as the polarization of the scattered photons and this will be defined by the experimental set-up. For a more detailed discussion of the different polarization set-ups for EFISHG-CID, we refer to Ref. [49] and Ref. [18]. We here limit ourselves to noting that there are only three independent experimental set-ups that will lead to circular intensity differences in the scattered light for chiral molecules. Indicating the different experimental set-ups by the subscript i , the final expression for the circular intensity difference of all three experiments has been shown to be given by the equation [18, 49]

$$CID_i = \frac{1}{c_0} \frac{[M_i(\omega) + \omega Q_i(\omega)]}{D_i(\omega)} \quad i = 1, 2, 3, \quad (8)$$

where $M_i(\omega)$, $\omega Q_i(\omega)$, and $D_i(\omega)$ are linear combinations of the cubic response functions in eqs 2–4. D_i is defined in terms of cubic response functions involving the electric dipole-only second hyperpolarizability tensor and is given by (using here and in the following the Einstein summation convention for repeated indices)

$$D_i(\omega) = \frac{A_{i,1}}{225} |R_i(\omega)|^2, \quad (9)$$

$$R_i(\omega) = A_{i,2} \gamma_{\lambda,\lambda,\mu,\mu}^{\omega,\omega,0} + A_{i,3} \gamma_{\lambda,\mu,\mu,\lambda}^{\omega,\omega,0}, \quad (10)$$

where $A_{i,j}$ are elements of a matrix containing information about polarization and rotational averaging for the different unique experiments. The matrix A is given by

$$A = \begin{pmatrix} +1/2 & +2 & +1 \\ +1/2 & +1 & -2 \\ +1/4 & +3 & -1 \end{pmatrix}. \quad (11)$$

In a similar manner, we can write M_i , which involves products of the second hyperpolarizability tensor and cubic response functions with one magnetic dipole operator replacing one of the electric dipole operators, as

$$M_i(\omega) = \frac{B_{1,i}}{225} R_i(\omega) (B_{i,2} G_{\nu,\nu,\tau,\tau}^{\omega,\omega,0} + B_{i,3} G_{\nu,\tau,\nu,\tau}^{\omega,\omega,0} + B_{i,4} G_{\nu,\tau,\tau,\nu}^{\omega,\omega,0} + B_{i,5} G_{\tau,\nu,\nu,\tau}^{\omega,\omega,0} + B_{i,6} G_{\nu,\nu,\tau,\tau}^{\omega,\omega,0}), \quad (12)$$

$$B = \begin{pmatrix} -1 & +1 & -4 & +1 & -2 & -1 \\ +1 & +4 & -1 & -1 & +1 & -2 \\ +1/2 & +3 & +3 & -2 & +3 & -1 \end{pmatrix}. \quad (13)$$

Finally, the Q_i contribution involves products of the second hyperpolarizability tensor with cubic response functions in which the electric quadrupole operator replaces one of the electric dipole operators, and is defined by

$$Q_i(\omega) = \frac{C_{i,1}}{225} R_i(\omega) [W_{i,1}^{\nu\tau\pi\rho\sigma} A_{\nu,\tau,\pi\rho,\sigma}^{\omega,\omega,0} + W_{i,2}^{\nu\tau\pi\rho\sigma} A_{\pi,\tau,\nu\sigma,\rho}^{\omega,-2\omega,0}] \quad (14)$$

$$W_{i,1}^{\alpha\beta\gamma\delta\epsilon} = C_{i,2} \epsilon_{\alpha\beta\gamma} \delta_{\delta\epsilon} + C_{i,3} \epsilon_{\alpha\beta\delta} \delta_{\gamma\epsilon} + C_{i,4} \epsilon_{\alpha\gamma\delta} \delta_{\beta\epsilon} \quad (15)$$

$$W_{i,2}^{\alpha\beta\gamma\delta\epsilon} = C_{i,5} \epsilon_{\alpha\beta\delta} \delta_{\gamma\epsilon} \quad (16)$$

$$C = \begin{pmatrix} -1 & +1 & 0 & -1 & 0 \\ -1 & +1 & -1 & +2 & +2 \\ -1/2 & +2 & -1 & +1 & +2 \end{pmatrix}. \quad (17)$$

The electric quadrupole and magnetic dipole moments entering in the response functions defining the CID_i in Eq. 8 are origin dependent: Indeed, even the individual terms appearing in Eq. 8 are origin dependent, as a shift in gauge origin will lead to changes in both $M_i(\omega)$ and $Q_i(\omega)$ —that is, $\Delta M_i(\omega) \neq 0$ and $\Delta Q_i(\omega) \neq 0$. However, as shown by Rizzo and Ågren, [18] $\Delta M_i(\omega) + \omega \Delta Q_i(\omega) = 0$, and thus the observable, is origin independent, as is also the case for the electric-dipole-only function $D_i(\omega)$. We will in the next section discuss this in somewhat more detail, with emphasis on how the use of London orbitals may ensure gauge-origin independence also for finite basis sets.

2.2. Basis sets and gauge origin-independence

As shown in Ref. [49], to correctly describe chiroptical properties it is necessary to include contributions involving the electric-quadrupole and magnetic-dipole operators. In order to demonstrate gauge-origin independence, we now discuss the origin dependence of the different cubic response functions in eqs. 2–4.

Let us consider a displacement \mathbf{R} of the origin of the coordinate of the multipolar expansion defined as $\mathbf{r}' = \mathbf{r} - \mathbf{R}$. The cubic response functions introduced in Eqs. (2)–(4) then change as [18]

$$\Delta\gamma_{i,j,k,l}^{\omega_1,\omega_2,\omega_3} = 0, \quad (18)$$

$$\Delta G_{i,j,k,l}^{\omega_1,\omega_2,\omega_3} = -\frac{1}{2}\epsilon_{k\lambda\rho}R_{\lambda}^{\omega_1,\omega_2,\omega_3}\Lambda_{i,j,\rho,l}^{\omega_1,\omega_2,\omega_3}, \quad (19)$$

$$\Delta A_{i,j,km,l}^{\omega_1,\omega_2,\omega_3} = -\frac{1}{2}R_k^{\omega_1,\omega_2,\omega_3}\gamma_{i,j,m,l}^{\omega_1,\omega_2,\omega_3} - \frac{1}{2}R_m^{\omega_1,\omega_2,\omega_3}\gamma_{i,j,k,l}^{\omega_1,\omega_2,\omega_3}, \quad (20)$$

where

$$\begin{aligned} \Lambda_{\alpha,\beta,\gamma,\delta}^{\omega_1,\omega_2,\omega_3} &= \Lambda_{\alpha,\beta,\gamma,\delta}(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) \\ &= -i\langle\langle \mu_{\alpha}; \mu_{\beta}, \mu_{\gamma}^p, \mu_{\delta} \rangle\rangle_{\omega_1,\omega_2,\omega_3}, \end{aligned} \quad (21)$$

and $\mu^p = \sum_j \frac{q_j}{m_j} \mathbf{p}_j$ is the dipole velocity operator.

In these expressions, the electric dipole operator appears both in its length- and its velocity-gauge representations, the latter arising from the magnetic dipole operator upon shifting the gauge origin. It is possible to rewrite the response function Eq. (21) in the length gauge, using the equation of motions and the commutator relations [50, 51]

$$\hbar\omega\langle\langle A; B \rangle\rangle_{\omega} = \langle\langle [A, H_0]; B \rangle\rangle_{\omega} + \langle\langle [A, B] | 0 \rangle\rangle, \quad (22)$$

$$p_j = \frac{im_e}{\hbar e} [\mu_j, H_0], \quad (23)$$

where H is the electronic Hamiltonian.

These relations need to be satisfied in order to prove that the EFISHG-CID_{*i*} are origin invariant. In practical calculations, these relations will only be fulfilled for variational wave functions in the limit of a complete basis set. [52] Using the response functions of an exact state [50], inserting the shift of the cubic response function in the definition of the tensors D_i , M_i , and Q_i in Eqs. 10, 13 and 17 and after some algebraic manipulation, it can be shown that

$$\Delta M_i(\omega) + \omega\Delta Q_i(\omega) = 0, \quad (24)$$

proving the origin independence of CID_{*i*}(ω). The use of a finite basis set implies that operators are represented in a matrix representation, therefore the commutator relations are no longer fulfilled. As the basis set quality is increased, the commutators converge to their respective basis-set limits.

Gauge-origin independent magnetic properties can be ensured through the use of London Atomic Orbitals (LAOs), also known as Gauge Including Atomic Orbitals (GIAOs) [32]. The LAOs are defined as:

$$\zeta_j(\mathbf{r}_M, \mathbf{A}_M^e) = \chi_j(\mathbf{r}_M) e^{-i\mathbf{A}_M^e \cdot \mathbf{r}}, \quad (25)$$

where χ_j is a spatial component of an atomic orbital centered on nucleus M located at \mathbf{R}_M and $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M$ is the position of the electron relative to the nucleus M . \mathbf{A}_M^e is the potential that defines the dependence of the atomic orbital on the

external magnetic field strength. Thus, LAOs are obtained by multiplying each basis function with a complex phase factor that depends explicitly on the uniform external static magnetic field. Upon a shift in the gauge origin, the magnetic dipole operator changes as $\mathbf{m} \rightarrow \mathbf{m} - \frac{i}{2\hbar}[\mu, H_0] \times \mathbf{R}$, ensuring origin independence. It has been shown that a magnetic dipole operator satisfying this origin dependence also for finite basis sets can be defined when LAOs are used, see eqn. 36 in Ref. [53], and this form of the magnetic dipole operator is recovered in our Lagrangian approach. [38]

2.3. Analytic calculation of response functions

In order to determine the different CID_i from eqn. (8), it is necessary to calculate the properties $\gamma_{\alpha\beta\gamma\delta}$, $G_{\alpha\beta\gamma\delta}$ and $A_{\alpha\beta\epsilon\gamma\delta}$ defined in eqns. (2)-(4). In a recent work, we presented a recursive implementation [39] for the analytic calculation of response properties based on theoretical work in our group [38]. The recursive nature of the approach ensures that any quantities needed (*e.g.* one- or two-electron integrals) can be obtained from connected modules and programs, and the calculation of $\gamma_{\alpha\beta\gamma\delta}$, $G_{\alpha\beta\gamma\delta}$ and $A_{\alpha\beta\epsilon\gamma\delta}$ therefore becomes a straightforward application of our program. We will here present a brief summary of the approach, limited to the aspects that are relevant for the properties considered in this work. In this section, we will use a tilde to denote quantities evaluated at general perturbation strengths, while the absence of a tilde denotes evaluation at zero perturbation strengths.

Response properties defined by operators A, B, \dots can be written as perturbation-strength ε_i derivatives of a time-averaged quasienergy Lagrangian $\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T$ evaluated at zero perturbation strength, where $\{\cdot\}_T$ denotes time averaging. For a linear response function, this can be exemplified by

$$\langle\langle A; B \rangle\rangle_{\omega_b} = \left. \frac{d\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T}{d\varepsilon_b} \right|_{\{\varepsilon\}=0} = L^{ab}; \quad \omega_a = -\omega_b, \quad (26)$$

where

$$\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T \stackrel{\{\text{Tr}\}_T}{=} \tilde{\mathcal{E}}^{0,a} - \tilde{\mathbf{S}}^a \tilde{\mathbf{W}}, \quad (27)$$

where $\stackrel{\{\text{Tr}\}_T}{=}$ symbolizes that tracing and time-averaging is carried out for the terms on the right-hand side. In eqn. (27), the overlap matrix \mathbf{S} and the frequency-weighted Fock matrix \mathbf{W} were introduced, where the latter is given by

$$\tilde{\mathbf{W}} = \tilde{\mathbf{D}} \tilde{\mathcal{F}} \tilde{\mathbf{D}} + \frac{i}{2} (\dot{\tilde{\mathbf{D}}} \tilde{\mathbf{S}} \tilde{\mathbf{D}} - \tilde{\mathbf{D}} \tilde{\mathbf{S}} \dot{\tilde{\mathbf{D}}}), \quad (28)$$

where the generalized Fock matrix \mathbf{F} is (restricting ourself to Hartree–Fock wave functions)

$$\tilde{\mathcal{F}} = \tilde{\mathbf{F}} - \frac{i}{2} \tilde{\mathbf{T}} = \tilde{\mathbf{h}} + \tilde{\mathbf{G}}(\tilde{\mathbf{D}}) + \tilde{\mathbf{V}}^t - \frac{i}{2} \tilde{\mathbf{T}}, \quad (29)$$

and the generalized Hartree–Fock energy is

$$\tilde{\mathcal{E}} \stackrel{\{\text{Tr}\}_T}{=} \tilde{E}(\tilde{\mathbf{D}}, t) - \frac{i}{2} \tilde{\mathbf{T}} \tilde{\mathbf{D}} \quad (30)$$

$$\stackrel{\{\text{Tr}\}_T}{=} (\tilde{\mathbf{h}} + \tilde{\mathbf{V}}^t + \frac{1}{2} \tilde{\mathbf{G}}(\tilde{\mathbf{D}}) - \frac{i}{2} \tilde{\mathbf{T}}) \tilde{\mathbf{D}} + \tilde{h}_{nuc}. \quad (31)$$

Eqs. (29) and (31) contain several contributions: the half-differentiated overlap matrix \mathbf{T} , the one-electron integral matrix \mathbf{h} , the interaction operator for the external field \mathbf{V}^t and the two-electron matrix \mathbf{G} . We refer to previous work[38] for definitions of these quantities, but note that the \hat{a} in

$$\tilde{V}_{\mu\nu}^t = \sum_a \exp(-i\omega_a t) \varepsilon_{\hat{a}} \langle \tilde{\chi}_\mu | \hat{a} | \tilde{\chi}_\nu \rangle \quad (32)$$

will involve the electric dipole, electric quadrupole and magnetic dipole operators defined in Eqs. 5–7. By differentiating eqn. (27) using the desired perturbations and evaluating the expression at zero perturbation strength, expressions for the linear and quadratic response functions L^{ab} and L^{abc} can be obtained as

$$L^{ab} \stackrel{\{\text{Tr}\}_T}{=} \mathcal{E}^{0,ab} + \mathcal{E}^{1,a} \mathbf{D}^b - \mathbf{S}^{ab} \mathbf{W} - \mathbf{S}^a \mathbf{W}^b, \quad (33)$$

$$\begin{aligned} L^{abc} \stackrel{\{\text{Tr}\}_T}{=} & \mathcal{E}^{0,abc} + \mathcal{E}^{1,ac} \mathbf{D}^b + \mathcal{E}^{1,ab} \mathbf{D}^c + \mathcal{E}^{2,a} \mathbf{D}^b \mathbf{D}^c \\ & + \mathcal{E}^{1,a} \mathbf{D}^{bc} - \mathbf{S}^{abc} \mathbf{W} - \mathbf{S}^{ab} \mathbf{W}^c - \mathbf{S}^{ac} \mathbf{W}^b - \mathbf{S}^a \mathbf{W}^{bc}, \end{aligned} \quad (34)$$

where we have used the fact that there will at most be a linear dependence in the basis set on the applied perturbations (from the magnetic-field component of the light). We have in the above expressions introduced the notation

$$\mathcal{E}^{m,abc} = \frac{\partial^{m+3} \mathcal{E}}{(\partial \mathbf{D}^T)^m \partial \varepsilon_a \partial \varepsilon_b \partial \varepsilon_c}, \quad (35)$$

where tracing is carried out as in the example

$$\text{Tr} \mathcal{E}^{2,a} \mathbf{D}^b \mathbf{D}^c = \sum_{\alpha\beta\mu\nu} \frac{\partial^3 \mathcal{E}}{\partial D_{\alpha\beta}^T \partial D_{\mu\nu}^T \partial \varepsilon_a} D_{\alpha\beta}^b D_{\mu\nu}^c. \quad (36)$$

Eqs. (33) and (34) are expressions that adhere to the so-called $(n+1)$ rule [54]. It is in general possible to express response properties according to other rules between this rule and the so-called $(2n+1)$ rules through the method of Lagrange multipliers [54]. We begin by defining as matrices $\tilde{\mathbf{Y}}$ and $\tilde{\mathbf{Z}}$ the idempotency condition

$$\tilde{\mathbf{Y}} = \tilde{\mathbf{D}} \tilde{\mathbf{S}} \tilde{\mathbf{D}} - \tilde{\mathbf{D}}, \quad (37)$$

and the time-dependent self-consistent field (SCF) condition

$$\tilde{\mathbf{Z}} = [(\tilde{\mathcal{F}} - \frac{i}{2} \tilde{\mathbf{S}} \frac{d}{dt}) \tilde{\mathbf{D}} \tilde{\mathbf{S}}]^\ominus, \quad (38)$$

respectively, where the notation

$$\left[\tilde{\mathbf{M}} \right]^{\ominus} = \tilde{\mathbf{M}} - \tilde{\mathbf{M}}^{\dagger}, \quad (39)$$

was introduced, and where, correspondingly,

$$\left[\tilde{\mathbf{M}} \right]^{\oplus} = \tilde{\mathbf{M}} + \tilde{\mathbf{M}}^{\dagger}, \quad (40)$$

can be defined. In eqs. (39) and (40), we consider any time differentiation to take place before adjungation. Using the ansatz

$$\tilde{\lambda}_a = [\tilde{\mathbf{D}}^a \tilde{\mathbf{S}} \tilde{\mathbf{D}}]^{\ominus}, \quad (41)$$

for the Lagrange multiplier λ_a to $\tilde{\mathbf{Y}}$ leads to the determination of the multiplier $\tilde{\zeta}$ to $\tilde{\mathbf{Z}}$ as

$$\tilde{\zeta}_a = [\tilde{\mathcal{F}}^a (\tilde{\mathbf{D}} \tilde{\mathbf{S}} - \frac{1}{2}) - (\tilde{\mathcal{F}} \tilde{\mathbf{D}} - \frac{i}{2} \dot{\tilde{\mathbf{S}}} \tilde{\mathbf{D}} - i \tilde{\mathbf{S}} \dot{\tilde{\mathbf{D}}}) \tilde{\mathbf{S}}^a]^{\oplus}, \quad (42)$$

and it is now possible to write the expression for an arbitrary response property compactly as

$$\begin{aligned} \langle \langle A; B, C, \dots \rangle \rangle_{\omega_{bc\dots}} &= \mathcal{L}_{k,n}^{abc\dots} \stackrel{\{\text{Tr}\}_T}{=} \mathcal{E}_{k,n}^{abc\dots} - (\mathbf{S}\mathbf{W})_{n_W}^{abc\dots} - (\mathbf{S}^a \mathbf{W})_{k_S, n'_W}^{bc\dots} \\ &\quad - (\boldsymbol{\lambda}^a \mathbf{Y})_{k_\lambda, n'_Y}^{bc\dots} - (\boldsymbol{\zeta}^a \mathbf{Z})_{k_\zeta, n'_Z}^{bc\dots}, \end{aligned} \quad (43)$$

where the subscripts on k and n define the choice of rule for including or excluding terms involving various perturbed arguments such as perturbed density matrices, constituting a generalization that allows truncation rule choices between and including the so-called $(n+1)$ and $(2n+1)$ rules. We refer to previous work[38],[39] for a more detailed presentation of this and other aspects of the theory and implementation, including a description of how the perturbed density and Fock matrices that enter into eqn. (43) can be calculated.

The relevant response functions for the present work are all cubic response functions and the contributions that must be calculated can be identified from eqn. (43). Making the rule choice $(k, n) = (1, 2)$ for the calculation of $\gamma_{\alpha, \beta, \gamma, \delta}^{\omega_1, \omega_2, \omega_3}$ and $(k, n) = (0, 3)$ for $A_{\gamma \epsilon, \beta, \alpha, \delta}^{\omega_1, -\omega_\sigma, \omega_3}$ and $G_{\alpha, \beta, \gamma, \delta}^{\omega_1, -\omega_\sigma, \omega_3}$ —rearranging the expression so that any non-electric dipole perturbations are defined to be perturbation a , and omitting contributions that must be zero upon differentiation because of lack of dependence on the perturbing operators—the expressions for the various properties take the relatively simple forms

$$\gamma_{\alpha, \beta, \gamma, \delta}^{\omega_1, \omega_2, \omega_3} \stackrel{\{\text{Tr}\}_T}{=} -\boldsymbol{\lambda}^{\mu_\alpha} \mathbf{Y}_{2'}^{\mu_\beta \mu_\gamma \mu_\delta} - \boldsymbol{\zeta}^{\mu_\alpha} \mathbf{Z}_{2'}^{\mu_\beta \mu_\gamma \mu_\delta}, \quad (44)$$

$$A_{\gamma\epsilon,\beta,\alpha,\delta}^{\omega_1,-\omega_\sigma,\omega_3} \stackrel{\{\text{Tr}\}_T}{=} \mathcal{E}^{1,\mu_\gamma\epsilon} \mathbf{D}^{\mu_\alpha\mu_\beta\mu_\delta}, \quad (45)$$

and

$$G_{\alpha,\beta,\gamma,\delta}^{\omega_1,-\omega_\sigma,\omega_3} \stackrel{\{\text{Tr}\}_T}{=} \mathcal{E}^{1,m_\gamma} \mathbf{D}^{\mu_\alpha\mu_\beta\mu_\delta} + \mathcal{E}^{2,m_\gamma} \mathbf{D}^{\mu_\beta} \mathbf{D}^{\mu_\alpha\mu_\delta} + \mathcal{E}^{2,m_\gamma} \mathbf{D}^{\mu_\alpha} \mathbf{D}^{\mu_\beta\mu_\delta} + \mathcal{E}^{2,m_\gamma} \mathbf{D}^{\mu_\delta} \mathbf{D}^{\mu_\alpha\mu_\beta} - \mathbf{S}^{m_\gamma} \mathbf{W}^{\mu_\beta\mu_\alpha\mu_\delta}, \quad (46)$$

where the subscript in $\mathbf{Y}_{2'}^{\mu_\beta\mu_\gamma\mu_\delta}$ indicates that only terms involving density and overlap matrices perturbed at most to second order are kept, so that

$$\begin{aligned} \mathbf{Y}_{2'}^{\mu_\beta\mu_\gamma\mu_\delta} = & [\mathbf{D}^{\mu_\gamma\mu_\delta} \mathbf{S}^{\mu_\beta} \mathbf{D} + \mathbf{D}^{\mu_\gamma\mu_\delta} \mathbf{S} \mathbf{D}^{\mu_\beta} + \mathbf{D}^{\mu_\beta\mu_\delta} \mathbf{S}^{\mu_\gamma} \mathbf{D} + \mathbf{D}^{\mu_\delta} \mathbf{S}^{\mu_\beta\mu_\gamma} \mathbf{D} + \\ & \mathbf{D}^{\mu_\delta} \mathbf{S}^{\mu_\gamma} \mathbf{D}^{\mu_\beta} + \mathbf{D}^{\mu_\beta\mu_\delta} \mathbf{S} \mathbf{D}^{\mu_\gamma} + \mathbf{D}^{\mu_\delta} \mathbf{S}^{\mu_\beta} \mathbf{D}^{\mu_\gamma} + \mathbf{D}^{\mu_\delta} \mathbf{S} \mathbf{D}^{\mu_\beta\mu_\gamma} + \\ & \mathbf{D}^{\mu_\beta\mu_\gamma} \mathbf{S}^{\mu_\delta} \mathbf{D} + \mathbf{D}^{\mu_\gamma} \mathbf{S}^{\mu_\beta\mu_\delta} \mathbf{D} + \mathbf{D}^{\mu_\gamma} \mathbf{S}^{\mu_\delta} \mathbf{D}^{\mu_\beta} + \mathbf{D}^{\mu_\beta} \mathbf{S}^{\mu_\gamma\mu_\delta} \mathbf{D}]^\oplus, \end{aligned} \quad (47)$$

and where $\mathbf{Z}_{2'}^{\mu_\beta\mu_\gamma\mu_\delta}$ and $\mathbf{W}^{\mu_\beta\mu_\alpha\mu_\delta}$ are constructed in a similar manner, the latter term without the order restriction that is imposed on $\mathbf{Y}_{2'}^{\mu_\beta\mu_\gamma\mu_\delta}$ and $\mathbf{Z}_{2'}^{\mu_\beta\mu_\gamma\mu_\delta}$.

3. Computational details

The EFISHG-CID observables have been calculated for the five different chiral systems studied by Rizzo and Ågren, namely (L)-Alanine, (L)-Arginine, (L)-Aspartic acid, (L)-Cysteine and (L)-Tryptophan, using the same geometries as in Ref.[18]. All calculations have been carried out at the HF level of theory, and have been performed using the augmented and non-augmented Dunning-style basis sets [55, 56] aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ. For (L)-Alanine, we have performed a more extensive basis sets analysis using a series of cc-pVXZ, aug-cc-pVXZ and daug-cc-pVXZ(X=D,T,Q) basis sets.

The response properties needed to determine these properties have been calculated using the recursive response code presented earlier. In this work, the code has been run as a locally modified version of the DALTON [57, 58] quantum chemistry program. The library GEN1INT[59][60] was used to calculate the differentiated one-electron integral contributions. The response equations that arise as part of the process of determining the perturbed density and Fock matrices were solved using the linear response solver of Jørgensen, Jensen and Olsen.[61]

The calculations of the EFISHG-CIDs have been performed for different gauge origins in order to test the dependence of the calculated CIDs on a shift in the gauge origin and to verify the correctness of the London atomic orbital implementation. We have used four different gauge origins: at the center of mass, shifting the gauge origin of the molecules along the x-axis by 1 Å and 5 Å, respectively, and finally placing the gauge origin on one of the hydrogen atoms.

All CIDs have been calculated using the formula reported in eq. (8) at a frequency $\omega = 0.072$ a.u. corresponding to a wavelength of $\lambda = 632.5$ nm.

4. Results and discussion

We start our discussion by commenting on the individual contributions $D_i(\omega)$, $M_i(\omega)$ and $Q_i(\omega)$ contributing to the final EFISHG-CID values as expressed in Eq.(8). In Table 1, we report $D_i(\omega)$, $M_i(\omega)$ and $Q_i(\omega)$ for (L)-alanine using both a conventional basis set and using LAOs for the cc-pVDZ and aug-cc-pVDZ basis sets. For the conventional basis set, the center of mass has been used as gauge origin. The general observations made for this molecule also hold for the other molecules considered in this work.

Contribution	cc-pVDZ			aug-cc-pVDZ		
	i=1	i=2	i=3	i=1	i=2	i=3
$M(\omega)$	-6.92	-0.13	-2.19	-24.96	-0.98	-7.36
	<i>-4.35</i>	<i>-0.10</i>	<i>-1.36</i>	<i>-26.19</i>	<i>-0.91</i>	<i>-7.84</i>
$Q(\omega)$	0.13	0.06	0.02	5.47	0.96	0.86
$D(\omega)$	209.90	22.56	47.41	2691.60	294.44	602.78

Table 1. $D_i(\omega)$, $M_i(\omega)$ and $Q_i(\omega)$ contributions for (L)-alanine. LAO results for $M_i(\omega)$ in italics, and the center of mass has been used as gauge origin for the conventional basis set. Results are reported in 10^4 atomic units.

As noted by Rizzo and Ågren [18], $D_i(\omega)$, which involves the second electric-dipole hyperpolarizability tensor, is 2-3 orders of magnitude larger in absolute value than the other parameters. We note that in eq.(8), the function $Q_i(\omega)$ which depends on the cubic response function involving the electric-quadrupole term is multiplied by the frequency of the incoming light $\omega = 0.072$ a.u., and as a consequence we expect that the CIDs will be dominated by $D_i(\omega)$ and $M_i(\omega)$. In general, we find that the use of LAOs does not significantly change $M_i(\omega)$. Similar observations have also been reported for other nonlinear birefringences. [62–66] In contrast, the inclusion of diffuse polarizing functions can be seen to be very important for all the molecular parameters, increasing the different contributions by about an order of magnitude. Interestingly, the smallest effect of augmentation is for the contribution involving the magnetic dipole operator, $M_i(\omega)$, which is surprising as diffuse polarizing functions have been shown to be important for magnetic and chiroptical properties. [67, 68]

Atom	x	y	z
H	0.6845690	-1.9830120	-0.0479770
H	2.1338560	-1.4180460	0.4993280
H	0.6849940	0.1253820	1.4683160
H	0.9446230	2.1875190	0.1462130
H	2.4000320	1.2247000	-0.0400780
H	1.2086440	1.2356500	-1.3440700
H	-0.9909530	1.7706270	0.2420230
O	-1.3628200	-1.1845700	-0.2086840
O	-1.5631430	1.0095400	0.0701730
C	0.6641370	0.0022810	0.3669710
C	-0.8299270	-0.1284830	0.0300720
C	1.3286690	1.2413750	-0.2578120
N	1.3378080	-1.2048030	-0.0930080

Table 2. Optimized structure for L-alanine reported in Å.

We have collected our results without using London atomic orbitals for the

EFISHG-CID of (L)-Alanine for different gauge choices of gauge origins in Table 3. These results are also plotted in Figure 1 together with the London atomic orbital results. In all calculations, we have used the cc-pVDZ basis set and placed the gauge origin at the center of mass, on the hydrogen atom furthest away from the center of mass, and at a position in which the x-component of the gauge origin have been shifted by 1 Å and 5 Å with respect to the initial gauge origin, respectively. The geometry of (L)-alanine is reported in the Table 2.

Gauge Origin	CID(1)	CID(2)	CID(3)
CM	-240.5	-41.4	-337.6
Hydrogen	-240.5	-41.4	-337.6
1 Å	-333.7	-41.4	-476.2
5 Å	-745.3	-40.1	-1089.3

Table 3. Results for the EFISHG-CID of (L)-alanine for the different unique experimental setups calculated using different gauge origins and without using London atomic orbitals. Results reported in 10^6 atomic units.

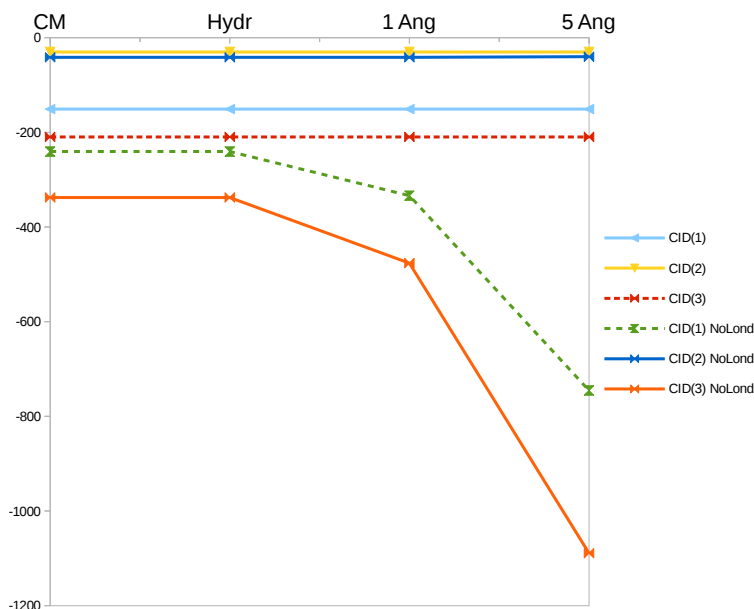


Figure 1. Comparison of the EFISHG-CID values of (L)-alanine obtained with and without LAOs for different gauge origins. Results reported in 10^6 atomic units.

The results show the importance of addressing the lack of origin independence in calculations of properties that depend on an external magnetic field using conventional basis sets, as all CIDs in this case depend strongly on the choice of gauge origin. As expected, our calculations using LAOs give the same results for all CIDs (polarization set-ups), independent of the choice of gauge origin. The effect of changing the gauge origin increases significantly when increasing the distance between the gauge origin and the center of mass of the molecule, and in particular when the gauge origin is located outside the molecule (5 Å).

We have calculated the EFISHG-CIDs for (L)-alanine using different basis sets, with and without London atomic orbitals. The results obtained with the cc-pVXZ, aug-cc-pVXZ, daug-cc-pVXZ (X=D,T,Q) families of basis sets are shown in Figure 2. We see how LAOs gives a smooth and fast convergence of the CIDs with increasing basis set size, although convergence is slow when there are no diffuse functions in the basis set (cc-pVXZ). Diffuse functions are therefore always needed to get reliable results both with and without LAOs. Once diffuse basis sets of triple zeta quality is used, LAOs are not very important. However, LAOs allow us to also use the aug-cc-pVDZ basis and still get reasonably converged results. For larger systems, where large basis sets cannot be used and where the gauge origin can be expected to be rather far away from certain parts of the molecule, the use of LAOs will be important in order to obtain results close to the basis-set limit. Nevertheless, whenever possible, the aug-cc-pVTZ basis set is recommended for EFISHG-CID calculations even when LAOs are used.

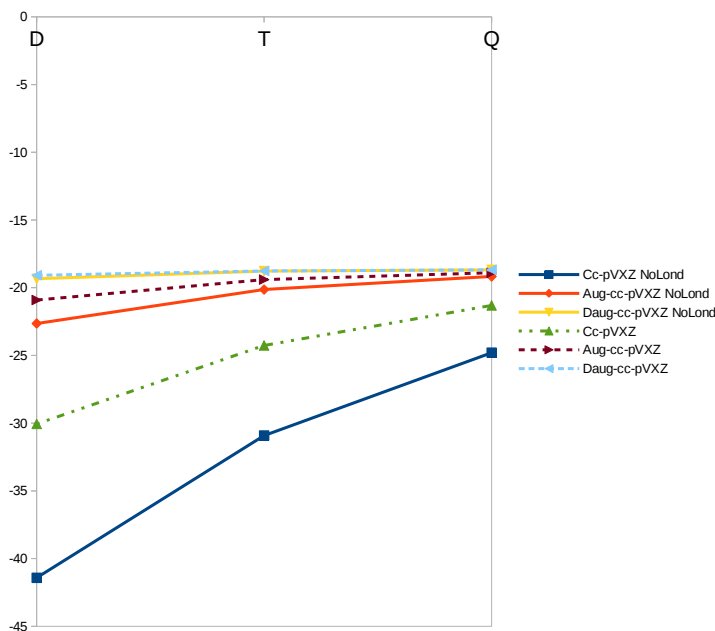


Figure 2. Comparison of the EFISHG-CID₃ values obtained with LAO and without LAO for (L)-Alanine, for different basis sets. Results reported in 10^6 atomic units.

In Tables 4–6, we have collected the results obtained for the EFISHG-CID for five different amino acids, following previous work [18], namely (L)-Alanine, (L)-Arginine, (L)-Aspartic acid, (L)-Cysteine and (L)-Tryptophan. We have used both conventional basis sets as well as London atomic orbitals, and results are reported for the three basis sets that can be expected to provide qualitatively correct results—that is, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ. To better illustrate the basis set dependence, we have in Figure 3 plotted the results for the three basis sets in the case of (L)-aspartic acid, as a representative case for our results.

As already observed in the case of alanine, CID(2) shows very little difference between the LAO and non-LAO results, and in general displays a very modest basis

set dependence, cysteine being the only exception to this. In contrast, CID(1) and CID(3) still display fairly large basis set dependence, and it is only with the aug-cc-pVTZ basis set that the LAO and non-LAO results agree well. Cysteine remains a problematic case, where the difference observed between the LAO and non-LAO results with the aug-cc-pVTZ basis set still remains fairly large. Considering the change in the basis set going from aug-cc-pVTZ to aug-cc-pVQZ as observed for alanine, we expect the LAO results obtained with the aug-cc-pVTZ basis set to be close to the basis set limit. The cc-pVDZ basis set, as well as the cc-pVTZ basis

Molecule/Basis	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
(L)-Alanine	-150.8	-123.7	-69.9	-66.1
	<i>-240.5</i>	<i>-177.9</i>	<i>-66.6</i>	<i>-66.9</i>
(L)-Arginine	-54.2	-51.0	-85.2	-83.4
	<i>11.7</i>	<i>-20.6</i>	<i>-84.7</i>	<i>-81.2</i>
(L)-Asparticacid	-68.6	-64.3	-48.1	-53.6
	<i>-21.3</i>	<i>-31.7</i>	<i>-43.4</i>	<i>-31.7</i>
(L)-Cysteine	-39.5	229.5	-60.3	-62.4
	<i>-131.2</i>	<i>-457.7</i>	<i>-387.2</i>	<i>-53.9</i>
(L)-Tryptophan	-46.1	-53.8	-143.5	-131.4
	<i>-55.2</i>	<i>-53.5</i>	<i>-151.0</i>	<i>-131.9</i>

Table 4. CID(1) calculated for different basis sets and amino acids using London atomic orbitals (results without London atomic orbitals reported in italics). Results reported in 10^6 atomic units.

Molecule/Basis	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
(L)-Alanine	-30.1	-24.2	-20.9	-19.4
	<i>-41.4</i>	<i>-30.9</i>	<i>-22.6</i>	<i>-20.1</i>
(L)-Arginine	28.4	24.9	15.6	14.4
	<i>30.18</i>	<i>22.9</i>	<i>13.2</i>	<i>13.2</i>
(L)-Asparticacid	12.7	10.3	-0.7	0.4
	<i>13.0</i>	<i>8.9</i>	<i>0.8</i>	<i>0.6</i>
(L)-Cysteine	-2786.2	2846.8	2.9	7.2
	<i>-4657.9</i>	<i>3620.5</i>	<i>-10.4</i>	<i>1.9</i>
(L)-Tryptophan	-16.5	0.7	51.2	43.8
	<i>-35.3</i>	<i>-12.4</i>	<i>49.2</i>	<i>41.6</i>

Table 5. CID(2) calculated for different basis sets and amino acids using London atomic orbitals (results without London atomic orbitals reported in italics). Results reported in 10^6 atomic units.

CID(3)	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
(L)-Alanine	-209.6	-172.7	-94.2	-89.3
	<i>-337.6</i>	<i>-250.1</i>	<i>-88.3</i>	<i>-90.1</i>
(L)-Arginine	-94.4	-88.0	-134.3	-131.2
	<i>2.7</i>	<i>-41.8</i>	<i>-132.3</i>	<i>-127.4</i>
(L)-Asparticacid	-108.1	-100.8	-71.6	-71.6
	<i>-37.9</i>	<i>-51.5</i>	<i>-65.3</i>	<i>-76.6</i>
(L)-Cysteine	-599.3	-77.3	-93.6	-99.5
	<i>-844.8</i>	<i>-86.9</i>	<i>-53.6</i>	<i>-83.7</i>
(L)-Tryptophan	-58.0	-76.3	-229.0	-210.2
	<i>-63.3</i>	<i>-70.3</i>	<i>-238.9</i>	<i>-209.9</i>

Table 6. CID(3) calculated for different basis sets and amino acids using London atomic orbitals (results without London atomic orbitals reported in italics). Results reported in 10^6 atomic units.

set in some cases, is in general not able to give results that can be considered even qualitatively correct.

We do not speculate, on the basis of the results presented here, on the accuracy of our results compared to possible future experimental observations. Comparisons with experiment and the check of the method should include the inclusion of solvent effects in the calculations. Furthermore, Rizzo and Ågren showed that electron correlation, as described by density-functional theory, can be substantial. [18] However, although their results were obtained without the use of LAOs, our results give support to the quality of their results considering that they used the aug-cc-pVTZ basis set, which we have demonstrated in general is in good agreement with the corresponding LAO results and close to the expected basis-set limit.

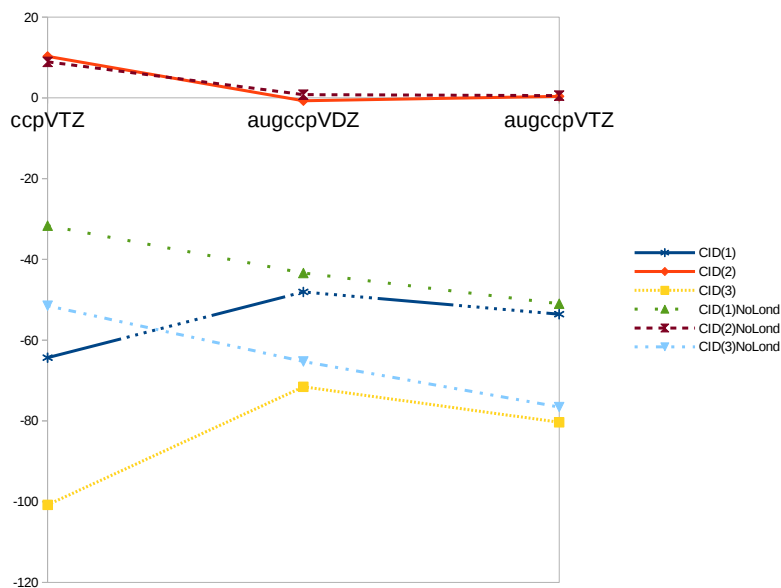


Figure 3. Results of the EFISHG-CID for (L)-Aspartic acid with LAO and without LAO. Results reported in 10^6 atomic units.

5. Concluding remarks

We have calculated the EFISHG-CID of five natural chiral amino acids, including effects of the electric dipole, electric quadrupole and magnetic dipole operators, at the Hartree–Fock level of theory. Gauge-origin independence has been achieved using London atomic orbitals, and these are the first gauge-origin independent results presented to date. We have demonstrated that although the LAOs lead to gauge-origin independent results, the improvement in basis set convergence is only moderate, and large basis sets of aug-cc-pVTZ quality must be used to ensure results close to the basis-set limit. This observation has also been made for other linear and nonlinear birefringences. [62, 65, 66]

We have shown that the CIDs calculated without LAOs display a rather strong dependence on the choice of gauge origin, in particular when the gauge origin is placed outside of the molecular framework. Consequently, although our study has shown that LAOs only lead to moderate improvements in basis set convergence for the five simple amino acids studied here, we can expect LAOs to be much more important for larger systems where a single global gauge origin is expected to be less adequate for larger parts of the molecule. Our results suggest that the non-LAO results obtained previously at the density-functional theory level by Rizzo and Ågren, [18] are reliable as far as basis set convergence is concerned, and that they give an accurate prediction of the magnitude of future experimental observations EFISHG-CIDs, assuming that electron correlation functionals are reliably described by the B3LYP functional for this property. However, to confirm this assumption, the use of LAOs in calculations of EFISHG-CID should be extended to the level of density functional theory.

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