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ABSTRACT

We present a method for obtaining origin-independent electronic circular dichroism (ECD) in the length-gauge representation LG(OI) without the usage of London atomic orbitals. This approach builds upon the work by Caricato [J. Chem. Phys. **153**, 151101 (2020)] and is applied to rotatory strengths and ECD spectra from damped response theory. Numerical results are presented for time-dependent Hartree–Fock and density-functional theory, the second-order algebraic diagrammatic construction method, and linear-response coupled-cluster theory with singles and approximate doubles. We can support the finding that the common choice of placing the gauge origin in the center of mass of a molecule in conventional length-gauge calculations involving chiroptical properties might not be optimal and show that LG(OI) is a valuable alternative for the origin-independent calculation of ECD spectra. We show that, for a limited test set, the convergence of the rotatory strengths calculated with the LG(OI) approach toward the basis-set limit tends to be faster than for the established velocity gauge representation. Relationships between the sum-over-states expression of the optical rotation in the LG(OI) framework and its representation in terms of response functions are analyzed.

I. INTRODUCTION

Electronic circular dichroism (ECD) is the differential absorption of left- and right-circularly polarized light.[1] A molecule must be chiral in order to exhibit ECD, where the signals of two enantiomers are identical in magnitude but opposite in sign.[2] From an experimentalist's perspective, ECD is primarily interesting because it can be helpful in assigning the absolute configuration of chiral compounds by comparing experimental spectra with reference spectra provided by calculations.[3,4] To give an example, ECD can aid the elucidation of the secondary and tertiary structure of proteins.[5] Modern experimental applications include time-resolved monitoring of the conformational dynamics of the backbone of peptides and proteins[6] as well as polymers during the aggregation process.[7] Likewise from a theoretical point of view, ECD is a fascinating molecular property, because, among other intricacies, it is much more sensitive to structural perturbations or solvent effects than regular electronic absorption spectra.[8] Reliable theoretical methods are highly useful for these applications, and developments toward accurate computational schemes for calculating ECD are thus indispensable.

Over the past decades, numerous computational methods have emerged to predict and describe ECD,[9–20] and most of them rely on response theory of some sort. As arguably the most prominent examples, time-dependent density-functional theory[11,12,14] (TDDFT) and members of the hierarchy of coupled cluster methods, such as coupled cluster with singles and doubles[16,21] (CCSD), are particularly worth mentioning. In calculations, ECD as a response property can be determined by considering the real part of the complex electric dipole–magnetic dipole polarizability tensor describing a molecule's electric dipole response to a perturbing external magnetic field.[22,23] ECD is, thus, closely related to optical rotatory dispersion (ORD), which depends on the imaginary part of this tensor. In the context of exact response theory, the concept of *gauge* *invariance* implies that the choice of the quantum-mechanical operator to describe the interaction of a molecule with an external field is not unique.[24] To give an example, there exist different representations of the electric-dipole operator, which in turn also makes the description of ECD ambiguous. In this regard, discussions of the representation of the electric-dipole operator are typically confined to its two most popular choices, namely, the length and the velocity gauge.[12,14,15,25]

All computational response methods rely on approximate solutions of the Schrödinger equation and additionally make use of incomplete basis sets. As a result, the principles of exact response theory do not necessarily apply anymore and numerical results of ECD calculations may highly depend on the choice of the electric-dipole operator (and potentially the coordinate origin).[14,26] The fact that there is no apparent reason to prefer one representation to another is, thus, a large problem of using approximate methods for the calculation of ECD (and ORD for that matter). However, while properties described in the length gauge may converge faster with the size of the basis set,[14,27] approximate ECD calculations in the length gauge depend on the origin of the molecule's reference Cartesian coordinate system and are, without further tools such as London orbitals thus generally impractical.[14,25,28] Conversely, calculations using the velocity gauge are invariant with respect to the choice of the (gauge) origin and have, therefore, become the *de facto* standard.[29,30]

In this work, we extend a computational scheme for calculating origin-independent optical rotation parameters in the length-gauge representation [LG(OI)] proposed by one of us[31] to electronic circular dichroism (ECD). In the original approach, the diagonal elements of the optical-rotation tensor (and thus its isotropic part) are made origin-independent. To this end, the electric-dipole polarizability in mixed dipole representation, where one of the electric dipole operators follows the length and the other one the velocity representation, is decomposed via a singular-value decomposition and the left and right singular vectors are applied to the optical-rotation tensor. Here, we develop two strategies in order to transfer this concept to calculations of ECD spectra: On the one hand, we start from rotatory strengths that are commonly obtained along with excitation energies. On the other hand, we consider ECD directly as the real part of the electric dipole–magnetic dipole polarizability tensor as it can be calculated using damped response theory.[23,32–36] To the best of our knowledge, we report the first application of origin-independent ECD in the length-gauge representation not relying on London atomic orbitals.[37,38]

This article is structured as follows: First, we provide a concise derivation of the working equations. Second, we present some proof-of-principle calculations for time-dependent Hartree–Fock (TDHF)[39] and density functional theory,[40] the second-order algebraic diagrammatic construction method [ADC(2)],[41] and linear-response coupled-cluster theory with singles and approximate doubles (LR-CC2)[42,43] demonstrating the efficacy of this ansatz for both ECD approaches. We then compare the basis-set convergence behavior of the LG(OI) and the established velocity gauge rotator strengths. Differences for both methods for a larger test case with a delocalized π-system are discussed. The relationship between the origin-independent length-gauge optical rotation introduced in Ref. 31 and the rotatory strengths presented here is analyzed. Finally, we conclude from our results.

II. THEORY

To obtain a compact notation, we first introduce the following property operators:

$$\hat{\boldsymbol{\mu}} = -\sum_i^{n_e} \boldsymbol{r}_i, \tag{1}$$

$$\hat{\boldsymbol{m}} = -\frac{\mathrm{i}}{2}\sum_i^{n_e} (\boldsymbol{r} \times \nabla)_i, \tag{2}$$

$$\hat{\boldsymbol{p}} = -\mathrm{i}\sum_i^{n_e} \nabla_i \tag{3}$$

as the electronic-dipole operator [Eq. (1)], the magnetic-dipole operator [Eq. (2)], and the electronic momentum operator [Eq. (3)], respectively. All operators include a sum over all n_e electrons. Similarly to Ref. 31, linear response properties will contain a superscript (X, Y), indicating the representation of its underlying operators, for example, the electric-dipole polarizability tensor in mixed-gauge representation would be denoted $\boldsymbol{\alpha}^{(\mu,p)}$. Furthermore, Hartree atomic units will be used throughout this article unless stated otherwise.

In response theory, it is especially convenient to express molecular properties in terms of the linear response function $\langle\langle \mathcal{A}; \mathcal{B}\rangle\rangle_\omega$, which, in very general terms, describes the response of some property described by operator $\mathcal{A}$ to an induced, possibly frequency (ω)-dependent perturbation that can be represented by operator $\mathcal{B}$.[44] For exact wave functions, the sum-over-states linear response function reads[45]

$$\langle\langle \mathcal{A}; \mathcal{B}\rangle\rangle_\omega = \sum_{n\neq 0}\left(\frac{\langle 0|\mathcal{A}|n\rangle\langle n|\mathcal{B}|0\rangle}{\omega + \mathrm{i}\gamma - \omega_{0n}} - \frac{\langle 0|\mathcal{B}|n\rangle\langle n|\mathcal{A}|0\rangle}{\omega + \mathrm{i}\gamma + \omega_{0n}}\right), \tag{4}$$

which sums over all excited states n with excitation energies ω_{0n} and transition moments $\langle 0|\mathcal{A}|n\rangle$. If not explicitly specified otherwise, we take the limit $\gamma \to 0^+$ in the following. Any electronic-structure theory with which the time-dependent expectation value $\langle\mathcal{A}\rangle$ can be described provides such a response function, including Hartree–Fock (HF), density-functional theory (DFT), or various coupled cluster (CC) approximations, such as coupled cluster with singles and (approximate) doubles (CC2, CCSD). In this work, we only consider the general concept of response functions to make use of their compact notation, which, besides exact response theory, is commonly used across all approximate methods. Explicit expressions and technical details concerning response functions in the CC context can be found elsewhere.[45,46] Remarks for HF/DFT linear response functions can be found in the Implementation section of the supplementary material or in Refs. 47–50.

Generally, isotropic chiroptical properties are related to the electric dipole–magnetic dipole polarizability tensor $\boldsymbol{G}'$ that describes a magnetic-dipole perturbation on the electric dipole of a molecule. Using the response-function notation from above, it can be expressed as

$$\boldsymbol{G}'(\omega) = -\langle\langle \boldsymbol{\mu}; \boldsymbol{m}\rangle\rangle_\omega, \tag{5}$$

where the bold-type notation implies that this linear response function can be evaluated for three Cartesian components of the observable and the perturbation, respectively, and linear response functions for two dipole operators are, thus, generally 3 × 3 tensors. The $\boldsymbol{G}'$ tensor is related to the optical-rotation tensor $\boldsymbol{\beta}$ following[30]

$$\boldsymbol{\beta}(\omega) = -\omega^{-1}\mathrm{Im}\big[\boldsymbol{G}'(\omega)\big]. \tag{6}$$

Note that, in this article, we restrict ourselves to isotropic samples and hence do not consider contributions of the electric dipole-electric quadrupole tensor to the optical rotation. The isotropic average of $\boldsymbol{\beta}$

$$\beta(\omega) = \frac{1}{3}\,\mathrm{Tr}[\boldsymbol{\beta}(\omega)] \tag{7}$$

is then directly related to the specific rotation $[\alpha]$ in deg/[dm (g/ml)] conventionally reported in experimental studies[29]

$$[\alpha]_\omega = 1.343\times 10^{-4}\frac{\tilde{\nu}^2}{M}\beta(\omega), \tag{8}$$

where M is the molecular mass and $\tilde{\nu}$ is the frequency of the incident light in cm^{-1}.

In practical calculations, the coordinate system a molecule is placed in is arbitrary, and the results should be independent of this choice. Using the dipole-length (LG) representation of the electric-dipole operator, the optical rotation, as given in Eq. (6), is inherently origin dependent, which, adopting the notation of Lazzaretti *et al.*,[31,51,52] can be expressed as a function of some displaced origin of this coordinate system $\boldsymbol{O}' = \boldsymbol{O} + \boldsymbol{d}$ as

$$\beta_{ij}^{(\mu,m)}(\boldsymbol{O}') = \beta_{ij}^{(\mu,m)}(\boldsymbol{O}) - \frac{1}{2}\alpha_{ik}^{(\mu,p)}\epsilon_{jkl}d_l. \tag{9}$$

Here, the Einstein summation convention is used, the frequency dependency is omitted for brevity, and $\boldsymbol{\epsilon}$ and $\boldsymbol{\alpha}^{(\mu,p)}$ denote the Levi–Civita tensor and the electric-dipole polarizability in mixed gauge representation, respectively. In response theory for exact wave functions, the second summand in Eq. (9) vanishes for the trace of $\boldsymbol{\beta}$ on the grounds of symmetry properties of $\boldsymbol{\epsilon}$ and $\boldsymbol{\alpha}$.[31] For calculations involving approximate methods and finite basis sets, however, this is not necessarily true for the LG optical rotation. This is related to the fact that $\boldsymbol{\alpha}^{(\mu,p)}$, in particular, is not a symmetric tensor.[52]

In Ref. 31, it was shown that a singular-value decomposition (SVD) of the mixed-gauge polarizability,

$$\boldsymbol{\alpha}^{(\mu,p)}(\omega) = -\omega^{-1}\,\mathrm{Im}\langle\langle\boldsymbol{\mu};\boldsymbol{p}\rangle\rangle_\omega, \tag{10}$$

yields the diagonal matrix $\boldsymbol{\alpha}_D^{(\mu,p)}(\omega)$ containing the singular values as well as the frequency-specific unitary matrices $\boldsymbol{U}_\omega$ and $\boldsymbol{V}_\omega$,

$$\boldsymbol{\alpha}_D^{(\mu,p)}(\omega) = \Big\langle \boldsymbol{U}_\omega|\boldsymbol{\alpha}^{(\mu,p)}(\omega)|\boldsymbol{V}_\omega\Big\rangle, \tag{11}$$

which can be used to make the trace of the LG optical rotation tensor origin independent[31] [cf. Eq. (9)],

$$\tilde{\boldsymbol{\beta}}^{(\mu,m)}(\omega) = \Big\langle \boldsymbol{U}_\omega|\boldsymbol{\beta}^{(\mu,m)}(\omega)|\boldsymbol{V}_\omega\Big\rangle, \tag{12}$$

$$\tilde{\beta}^{(\mu,m)}(\boldsymbol{O},\omega) = \tilde{\beta}^{(\mu,m)}(\boldsymbol{O}',\omega). \tag{13}$$

Here and in the following, the purpose of a tilde above a tensor is to denote an origin independency of its trace. We note that this transformation can equally well be applied to $\boldsymbol{G}'$ and the optical-rotation tensor, since these are related by a simple scalar multiplication for a specific frequency [see Eq. (6)]. This origin-independent length-gauge representation is denoted as LG(OI).[31]

A. Electronic circular dichroism

In practice, the inherently complex linear response function in Eq. (4) is routinely approximated by taking the limit $\gamma \to 0^+$. This is a well-justified approximation in off-resonant spectral regions. However, it renders the response function either purely real or imaginary and leads to singularities for $\omega \to \omega_{0n}$. By contrast, damped response theory employs a finite value for γ such that the linear response function remains complex and these singularities do not appear. From the imaginary part of the electric-dipole polarizability and the real part of the electric dipole–magnetic dipole polarizability (both in length-gauge representation), the linear absorption and electronic circular dichroism can be obtained directly as a function of the frequency, respectively.

Conversely, the real part (as indicated by a bar) of the mixed-gauge electric-dipole polarizability $\bar{\boldsymbol{\alpha}}^{(\mu,p)}$,

$$\bar{\boldsymbol{\alpha}}^{(\mu,p)}(\varpi) = -\omega^{-1}\,\mathrm{Re}\langle\langle\boldsymbol{\mu};\boldsymbol{p}\rangle\rangle_\varpi, \tag{14}$$

is related to linear absorption, where $\varpi = \omega + \mathrm{i}\gamma$. This is due to the fact that the response function $\langle\langle\boldsymbol{\mu};\boldsymbol{p}\rangle\rangle$ is purely imaginary for real frequencies. The real part of the mixed-gauge polarizability can, similarly to Eq. (11), be decomposed via SVD

$$\bar{\boldsymbol{\alpha}}_D^{(\mu,p)}(\varpi) = \Big\langle \boldsymbol{U}_\varpi|\bar{\boldsymbol{\alpha}}^{(\mu,p)}(\varpi)|\boldsymbol{V}_\varpi\Big\rangle, \tag{15}$$

again yielding frequency- and damping-specific unitary matrices $\boldsymbol{U}_\varpi$ and $\boldsymbol{V}_\varpi$ and singular-value matrix $\bar{\boldsymbol{\alpha}}_D^{(\mu,p)}(\varpi)$. Analogously, $\boldsymbol{G}'$ becomes complex if a complex frequency is employed in the evaluation of the response function. While the optical rotation is related to its imaginary part, ECD is related to its real part that can be expressed as

$$\bar{\boldsymbol{G}}'^{(\mu,p)}(\varpi) = -\mathrm{Re}\langle\langle\boldsymbol{\mu};\boldsymbol{m}\rangle\rangle_\varpi. \tag{16}$$

The trace of $\bar{\boldsymbol{G}}'$ can be made origin independent by virtue of a transformation using the $\boldsymbol{U}_\varpi$ and $\boldsymbol{V}_\varpi$ matrices obtained from an SVD of the real mixed-gauge polarizability (see above),

$$\tilde{\bar{\boldsymbol{G}}}'^{(\mu,m)}(\varpi) = \Big\langle \boldsymbol{U}_\varpi|\bar{\boldsymbol{G}}'^{(\mu,m)}(\varpi)|\boldsymbol{V}_\varpi\Big\rangle. \tag{17}$$

The isotropic ECD is then obtained as[22,23]

$$\Delta\tilde{\varepsilon}(\varpi) = -6.334\omega\ \mathrm{Tr}\Big[\tilde{\bar{\boldsymbol{G}}}'^{(\mu,m)}(\varpi)\Big]. \tag{18}$$

B. Rotatory strengths

The isotropic optical rotation $\beta(\omega)$ can be formulated via a sum-over-states expression in terms of the rotatory strengths of all transitions[12,53]

$$\beta(\omega) = \frac{2c}{3}\sum_{n\neq 0}\frac{R^{0n}}{\omega_{0n}^2 - \omega^2}, \tag{19}$$

where c is the speed of light. In case of the LG(OI) optical rotation, the left-hand side is origin independent. Therefore, it seems plausible to assume that there exists an LG representation of the rotatory strengths that is equally origin independent. In general terms, rotatory strengths can be expressed as[54,11]

$$R^{(\mu,m),0n} = \frac{1}{2}\mathrm{Im}\Big[\langle 0|\hat{\boldsymbol{\mu}}|n\rangle \cdot \langle n|\hat{\boldsymbol{m}}|0\rangle + \big(\langle 0|\hat{\boldsymbol{m}}|n\rangle \cdot \langle n|\hat{\boldsymbol{\mu}}|0\rangle\big)^{*}\Big], \tag{20}$$

an expression that turns out to be nothing but the trace of the electric dipole–magnetic dipole transition-strength tensor $\boldsymbol{T}^{(\mu,m),0n}$ for transition $0 \rightarrow n$[45]

$$\boldsymbol{T}^{(\mu,m),0n} = \frac{1}{2}\mathrm{Im}\Big[\big(\langle 0|\hat{\boldsymbol{\mu}}|n\rangle \otimes \langle n|\hat{\boldsymbol{m}}|0\rangle\big) + \big(\langle 0|\hat{\boldsymbol{m}}|n\rangle \otimes \langle n|\hat{\boldsymbol{\mu}}|0\rangle\big)^{\dagger}\Big], \tag{21}$$

where ⊗ denotes the outer product and † the conjugate transpose. Furthermore, we have used a symmetrized formulation for the sake of generality across the approximate computational methods used in this article.

A comparison to the sum-over-states representation of the origin dependence of the optical rotation tensor

$$\beta_{ij}^{(\mu,m)}(\boldsymbol{O}') = \beta_{ij}^{(\mu,m)}(\boldsymbol{O}) - \frac{1}{2}\alpha_{ik}^{(\mu,p)}\epsilon_{jkl}d_l, \tag{22}$$

$$\Leftrightarrow\; 2c\sum_{n\neq 0}\frac{T_{ij}^{(\mu,m),0n}(\boldsymbol{O}')}{\omega_{0n}^2-\omega^2} = 2c\sum_{n\neq 0}\frac{T_{ij}^{(\mu,m),0n}(\boldsymbol{O})}{\omega_{0n}^2-\omega^2} - \frac{1}{2}2\sum_{n\neq 0}\frac{T_{ik}^{(\mu,p),0n}}{\omega_{0n}^2-\omega^2}\epsilon_{jkl}d_l, \tag{23}$$

$$= 2c\sum_{n\neq 0}\frac{T_{ij}^{(\mu,m),0n}(\boldsymbol{O}) - \frac{1}{2c}T_{ik}^{(\mu,p),0n}\epsilon_{jkl}d_l}{\omega_{0n}^2-\omega^2} \tag{24}$$

allows us to identify the origin dependence of the electric dipole–magnetic dipole transition-strength tensor $\boldsymbol{T}^{(\mu,m),0n}$, similarly to Eq. (9), as

$$T_{ij}^{(\mu,m),0n}(\boldsymbol{O}') = T_{ij}^{(\mu,m),0n}(\boldsymbol{O}) - \frac{1}{2c}T_{ik}^{(\mu,p),0n}\epsilon_{jkl}d_l, \tag{25}$$

which holds for each transition separately. In Eq. (25), we use the same definitions as in Eq. (9) and $\boldsymbol{T}^{(\mu,p),0n}$ is the mixed-gauge electric-dipole transition-strength tensor defined in Eq. (26). Corresponding to the real or imaginary part of $\boldsymbol{G}'$, the tensor in Eq. (25) needs to be transformed via a transformation as is proposed in Eq. (11) to make its trace origin independent. Here, the transformation is obtained from an SVD of the mixed-gauge electric-dipole transition-strength tensor

$$\boldsymbol{T}^{(\mu,p),0n} = \frac{1}{2}\mathrm{Im}\Big[\big(\langle 0|\hat{\boldsymbol{\mu}}|n\rangle \otimes \langle n|\hat{\boldsymbol{p}}|0\rangle\big) + \big(\langle 0|\hat{\boldsymbol{p}}|n\rangle \otimes \langle n|\hat{\boldsymbol{\mu}}|0\rangle\big)^{\dagger}\Big], \tag{26}$$

yielding the transition-specific unitary matrices $|\boldsymbol{U}_{0n}\rangle$ and $|\boldsymbol{V}_{0n}\rangle$ and singular-value matrix $\boldsymbol{T}_D^{(\mu,p),0n}$,

$$\boldsymbol{T}_D^{(\mu,p),0n} = \Big\langle \boldsymbol{U}_{0n}\big|\boldsymbol{T}^{(\mu,p),0n}\big|\boldsymbol{V}_{0n}\Big\rangle. \tag{27}$$

Already at this point it becomes apparent that the rotation matrices that diagonalize individual transition-strength tensors [as given in Eq. (26)] will, in general, be different from those matrices that diagonalize the sum of the tensors in the last term of Eq. (24). As a result, one has to choose between reference coordinate systems that make the optical rotation origin independent and those that make individual transition-strength tensors origin independent. More details on this point are given in Sec. IV E. Applied to the electric dipole–magnetic dipole transition-strength tensor, one finds

$$\tilde{\boldsymbol{T}}^{(\mu,m),0n} = \Big\langle \boldsymbol{U}_{0n}\big|\boldsymbol{T}^{(\mu,m),0n}\big|\boldsymbol{V}_{0n}\Big\rangle, \tag{28}$$

$$\tilde{R}^{0n} = \mathrm{Tr}\Big(\tilde{\boldsymbol{T}}^{(\mu,m),0n}\Big), \tag{29}$$

where $\widetilde{R}^{0n}$ is the origin-independent LG(OI) rotatory strength. Note that as for the frequency-dependent case, this transformation must be performed for each transition separately so that the $|\boldsymbol{U}_{0n}\rangle$ and $|\boldsymbol{V}_{0n}\rangle$ matrices will generally be different for different transitions.

III. COMPUTATIONAL DETAILS

The LG(OI) approach for ECD has been implemented in a development version of the quantum-chemistry code Serenity[55,56] and will be a part of an upcoming release of that program. All calculations presented in the following were performed with this software. To avoid numerical noise, we use very tight (convergence) thresholds, i.e., (i) an integral neglect and Schwarz prescreening threshold of 10^{-14} a.u., (ii) a HF-energy threshold of 10^{-9} a.u., (iii) a maximum RMSD of density matrix of 10^{-9} a.u., (iv) a maximum residual norm of the ground-state CC vector function of 10^{-9} a.u. (only relevant for CC2), (v) a maximum residual norm of excitation vectors (rotatory strengths) of 10^{-9} a.u., and (vi) a maximum residual norm of response vectors (damped ECD) of 10^{-9} a.u. is employed. An aug-cc-pVDZ[57,58] basis set is used throughout. The (LR-)CC2/ADC(2) calculations make full use of the resolution-of-the-identity (RI) approximation,[43,59] and the correlation-consistent auxiliary basis set corresponding to aug-cc-pVDZ[60] was used. To be consistent with Ref. 31, we used the same three prototypical chiral molecules as employed in that study. These include (−)-hydrogen peroxide (**1**), (*S*)-(*P*)-2,3-pentadiene (**2**), and (*S*)-(−)-norbornenone (**3**) (see Fig. 1). Structures of molecules **2** and **3** were taken from Ref. 61. All geometries were optimized using DFT employing B3LYP[62,63] as an approximation for the exchange–correlation functional and an aug-cc-pVTZ[57,58] basis set. The center of mass of all molecules was set to $\boldsymbol{O} = (0, 0, 0)^T$. To demonstrate the origin (in)dependence of the LG(OI)-ECD spectra, we employ the displacement vector $\boldsymbol{d} = -(10^3, 10^3, 10^3)^T$ Å, by which the molecule is to be translated so that its origin is moved to $\boldsymbol{O}' = \boldsymbol{O} + \boldsymbol{d}$. Instead of displacing the molecule, however, we set the gauge-origin of the dipole operators to $\boldsymbol{O} - \boldsymbol{d}$ effectively having the same effect.

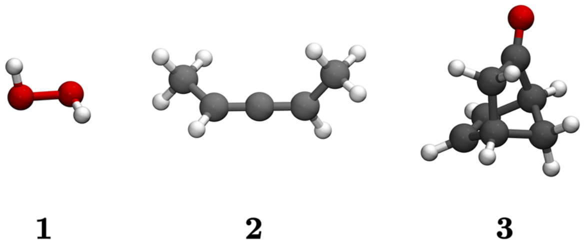

FIG. 1. Structures of the molecules employed in Ref. 31 and in this study.

IV. RESULTS AND DISCUSSION

A. Rotatory strengths

In Table I, we show a comparison of rotatory strengths of the four lowest-lying transitions of molecule **1** in dipole-velocity representation (VG), in dipole-length representation (LG), and in origin-independent dipole-length representation [LG(OI)]. Results for the approximate methods TDHF, ADC(2), and LR-CC2 are shown. Across all three methods, we find an origin dependence of the R^{02} (rotatory strength belonging to the $|0\rangle \rightarrow |2\rangle$ transition) and R^{03} rotatory strengths, while none is found for R^{01} and R^{04}, or is negligible at most. The LG(OI) approach leads to rotatory strengths that are origin independent regardless of its dipole-length representation for all methods and considered transitions. In some cases, see, e.g., $R^{03}(\boldsymbol{O})$ computed with ADC(2), a large deviation between the LG(OI) approach with respect to the LG one of the order of 25% can be observed. This agrees with one of the findings in Ref. 31 stating that the center of mass need not necessarily be an optimal choice for the gauge origin in optical-rotation calculations.[31] This result is not surprising given the close relationship of these two properties [see Eq. (19)].

B. ECD from damped response theory

In Fig. 2, we show a comparison of ECD as a function of the frequency from damped TDHF response theory calculated with the conventional LG and the modified LG(OI) approach. Here, instead

TABLE I. Excitation energies and rotatory strengths of the four lowest-lying transitions of molecule **1** for the approximate methods TDHF, ADC(2), and LR-CC2 in dipole-velocity representation (VG), in dipole-length representation (LG), and in origin-independent dipole-length representation [LG(OI)]. For one set of results, the gauge origin was set to the center of mass of the molecule $(\boldsymbol{O})$, and for the other one, it was set to $\boldsymbol{O}' = \boldsymbol{O} - \boldsymbol{d}$. Excitation energies ω_{0n} and rotatory strengths R^{0n} are given in eV and 10^{-40} esu^2 cm^2, respectively. Note that in the VG case, we have $R^{0n}(\boldsymbol{O}') = R^{0n}(\boldsymbol{O})$ throughout, and the expression in Eq. (29) was used in the LG(OI) case. An aug-cc-pVDZ basis was used.

	TDHF					
	VG		LG		LG(OI)	
n	ω_{0n}	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$
1	6.53	−5.8810	−4.6650	−4.6651	−4.6650	−4.6650
2	7.82	8.2826	6.9391	520.8796	7.7895	7.7895
3	8.71	−16.7286	−16.5477	−21.8373	−16.5241	−16.5241
4	9.37	26.9990	26.7123	26.7123	26.7123	26.7123
	ADC(2)					
	VG		LG		LG(OI)	
n	ω_{0n}	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$
1	5.99	−17.6547	−10.2772	−10.2769	−10.2772	−10.2772
2	6.33	−22.4459	−14.7681	676.6863	−17.4712	−17.4712
3	7.20	25.6568	16.8182	2494.9335	20.6852	20.6852
4	7.38	36.0989	27.9774	27.9759	27.9774	27.9774
	LR-CC2					
	VG		LG		LG(OI)	
n	ω_{0n}	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$	$R^{0n}(\boldsymbol{O})$	$R^{0n}(\boldsymbol{O}')$
1	6.01	−13.2386	−12.3090	−12.3090	−12.3090	−12.3090
2	6.44	−19.0926	−18.7460	194.1181	−19.6258	−19.6258
3	7.22	20.0030	18.6443	760.1031	20.1136	20.1136
4	7.49	34.4190	35.3473	35.3471	35.3473	35.3473

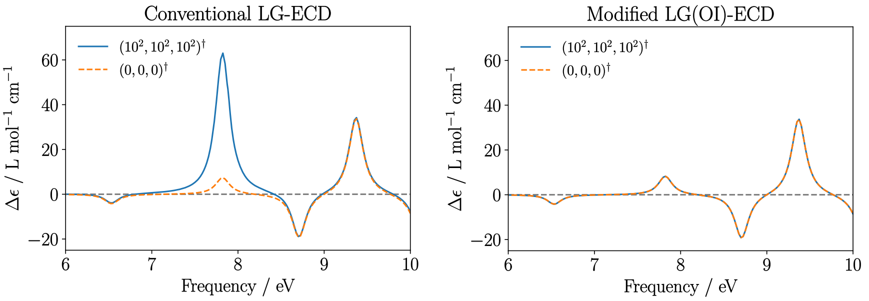

FIG. 2. Comparison of the conventional and modified LG-ECD as a function of the frequency (for molecule **1**). For each method, the ECD is shown with the gauge origin placed in either the center of mass of the molecule $[(0,0,0)^T]$ or translated to $(10^2, 10^2, 10^2)^T$ Å. A damping parameter of 0.1 eV was used for all calculations. The damped TDHF response equations were solved for 201 equidistant frequencies in the 6–10 eV frequency window.

of $\boldsymbol{O}'$, we chose to employ $-(10^2, 10^2, 10^2)^T$ as a displacement vector (or, more precisely, $(10^2, 10^2, 10^2)^T$ as the gauge origin) because $\boldsymbol{O}'$ led to very large absorption maxima making the interpretation of the spectra difficult. We find that the LG(OI) approach leads to a spectrum that is independent of the employed gauge origin. In contrast, clear differences are found for the conventional LG approach, especially for the second-lowest absorption maximum. This is consistent with what was found for the rotatory strengths for which an origin dependence could only be identified for the second- and third-lowest transition (where it was only significant for the former of the two) while the lowest and fourth-lowest ones were largely unaffected by the gauge-origin displacement. We would like to point out that the LG(OI) approach also yields origin-independent rotatory strengths and damped-response ECD from TDDFT (see Table S2 and Fig. S1, respectively, in the supplementary material). This was to be expected since TDHF and TDDFT

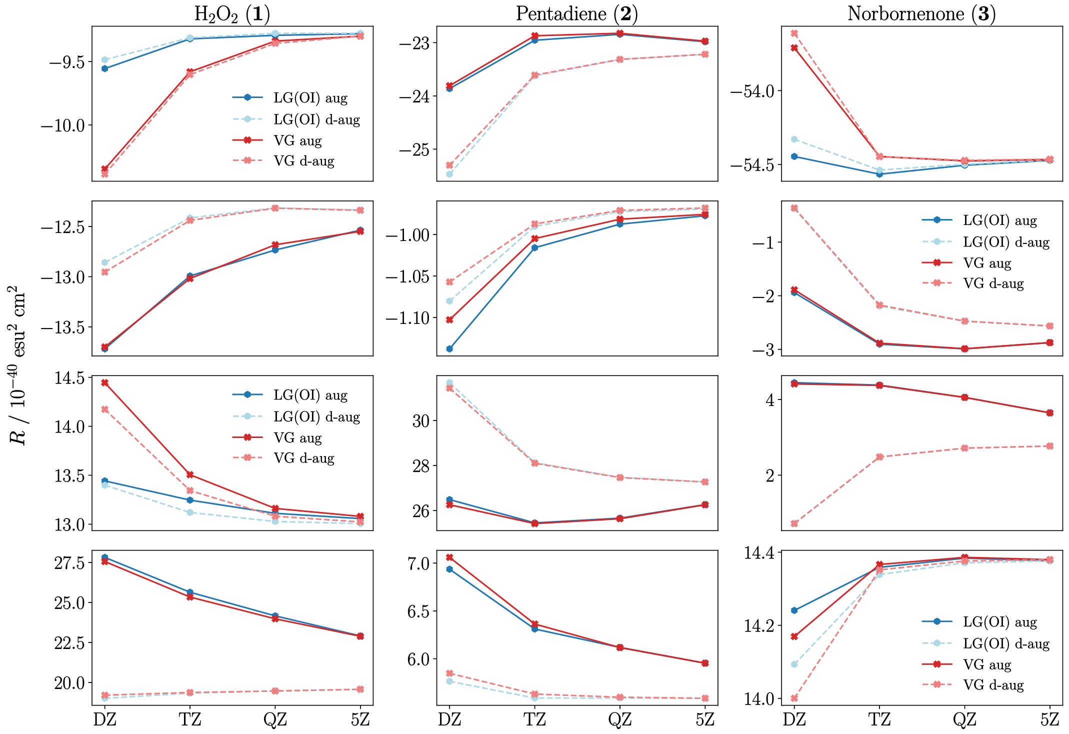

FIG. 3. Basis-set dependence of the LG(OI) and VG rotatory strengths for all three molecules (columns) and the four lowest-lying transitions (starting at the top row with the lowest transition). (TD-)DFT was used in combination with PBE0[64,65] as an approximation for the exchange–correlation functional as well as the singly and doubly augmented correlation-consistent basis sets aug-cc-pv$X$ and d-aug-cc-pv$X$.

share the general structure of their respective linear response function.

C. Basis-set convergence

In Fig. 3, we display the basis-set dependence of the LG(OI) and VG rotatory strengths of the four lowest-lying transitions of all three molecules to discuss possible advantages and disadvantages of the LG(OI) approach with respect to convergence with the size of the basis set.

For most of the transitions and molecules shown, we find a smooth convergence toward the basis-set limit, to which the doubly augmented basis sets are on average closer than the singly augmented ones. In general, the LG(OI) and VG rotatory strengths give very similar results, which are almost indistinguishable for some transitions and basis sets, especially for $\zeta = 4$ or 5. The most interesting question in this context is however, whether the LG(OI) rotatory strengths converge faster to the basis set limit than the VG ones or vice versa. To answer this question, those rotatory strengths for which the behavior of LG(OI) and VG differs significantly are considered in detail. The first and third transition of molecule **1** and the first transition of molecule **3** stand out in this respect. For these three rotatory strengths, the LG(OI) results are close to the basis set limit already for $\zeta = 2$ or 3, regardless of the augmentation level, while the VG ones are still far from convergence. Apart from these clear cases, there are some excitations where one of the two approaches has a slight advantage in terms of basis-set convergence. For molecule **2**, the rotatory strength of the second-lowest transition shows a different behavior. Here, the VG results are a little closer to the basis set limit than the LG(OI) results. However, the fourth-lowest transitions of both molecule **2** and **3** represent cases for which the LG(OI) results are moderately closer to the basis-set limit than the VG ones. For all other rotatory strengths, no significant difference between LG(OI) and VG is found. Overall, we find a clear advantage of the LG(OI) approach for three of the 12 transitions, as well as two transitions for which the LG(OI) approach and one transition for which the VG approach exhibits a slightly faster basis-set convergence. In the other cases, the basis-set convergence is very similar for both approaches.

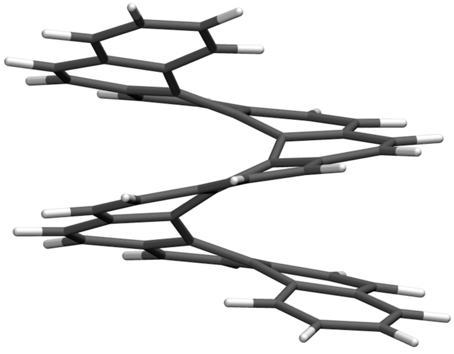

FIG. 4. Structure of (*P*)-[11]helicene as taken from Ref. 66.

D. (*P*)-[11]helicene

As a larger test case with a delocalized π-system, we consider (*P*)-[11]helicene that, as a member of the helicene family, has been studied previously in the literature.[67,66] The geometry was taken from the supplementary material of Ref. 66 and is displayed in Fig. 4. We employ the SOS[68,69]-ADC(2)[70] method in combination with an opposite-spin scaling of 1.3[69] as well as a Laplace transformation of the orbital-energy denominator[71] and a threshold of 10^{-5} for the numerical integration resulting in six quadrature points. The Laplace grid points were generated with the open-source library `laplace-minimax`.[72,73] Furthermore, we use natural auxiliary functions[74,75] neglecting the virt–virt block of the three-index MO integrals and discard those with an eigenvalue below 10^{-2}. We freeze all 1s orbitals of second-row atoms and employ an aug-cc-pVDZ basis set.

In Fig. 5, we compare the LG, LG(OI) and VG ECD spectra of (*P*)-[11]helicene for two choices of gauge-origin $\boldsymbol{O}$. The 50 lowest-lying excitation energies and corresponding rotatory strengths were determined for these spectra with the methodology described earlier. The experimental ECD spectrum was taken from Ref. 76, and the computed spectra were red-shifted by 0.2 eV. In the frequency window between 3 and 5 eV, there are four main bands of the

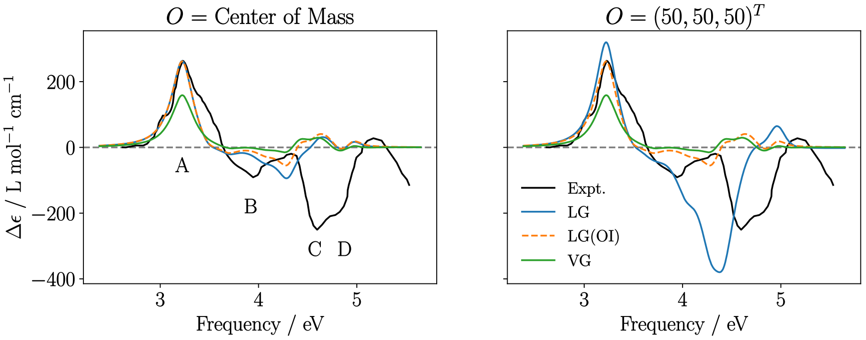

FIG. 5. Comparison of LG, LG(OI), and VG ECD spectra of (*P*)-[11]helicene obtained with a Laplace-transformed variant of SOS-ADC(2) and an opposite-spin scaling of 1.3. An aug-cc-pVDZ basis was used. The rotatory strengths were broadened with Lorentzian functions with a full width at half maximum of 0.2 eV. The experimental spectrum was taken from Ref. 76 and digitized. The computed spectra are red-shifted by 0.2 eV and scaled so that the first band of the LG(OI) spectrum matches the first experimental one.

experimental spectrum, namely, a large positive one at about 3.2 eV (A), a small negative one at about 3.9 eV (B), and two large, overlapping negatives ones at about 4.6 and 4.8 eV (C, D). The general shape of the computed spectra reproduces the experimental one fairly well. However, the transition energies of the upper three bands (B, C, and D) seem to be underestimated by several tenths of eV, and the magnitude of the rotatory strengths is far too small. While the regular LG approach yields origin-dependent ECD spectra, the spectra computed with the LG(OI) and VG approaches are as expected, origin independent. Placing the gauge origin in the center of mass of the molecule, the LG and LG(OI) spectra are visibly different as evidenced by the negative band at about 4.3 eV. Displacing the gauge origin to $\boldsymbol{O} = (50, 50, 50)^T$, we find a strong origin-dependence of the rotatory strength of this particular transition in the LG case. The LG ECD spectrum for the strongly displaced gauge origin appears to be in better agreement with the experiment, but this is obviously due to error cancellation between method-inherent errors and the (arbitrary) choice of gauge origin. When comparing the LG(OI) and VG results, only small differences are found for the values of the rotatory strengths where the VG ones are generally somewhat smaller.

E. Sum-over-states representability

As already mentioned earlier, the derivation of the LG(OI)-ECD scheme seemingly suggests that the LG(OI) optical rotation might be representable via a sum-over-states expression of the LG(OI) rotatory strengths. In the following, we will first demonstrate in detail why this is generally not the case and proceed by rationalizing the actual relationship between the two expressions.

The regular LG optical rotation tensor reads

$$\boldsymbol{\beta}^{(\mu,m)}(\omega) = 2c \sum_{n \neq 0} \frac{\boldsymbol{T}^{(\mu,m),0n}}{\omega_{0n}^2 - \omega^2}. \tag{30}$$

Performing a SVD for the mixed-gauge polarizability for the same frequency and multiplying both sides of the equation from the left with $\langle \boldsymbol{U}_\omega|$ and from the right with $|\boldsymbol{V}_\omega\rangle$ yields

$$\tilde{\boldsymbol{\beta}}^{(\mu,m)}(\omega) = 2c \sum_{n \neq 0} \frac{\left\langle \boldsymbol{U}_\omega | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_\omega \right\rangle}{\omega_{0n}^2 - \omega^2}. \tag{31}$$

Comparing the origin dependence of the optical rotation tensor [Eq. (9)] to that of the electric dipole–magnetic dipole transition strength tensor [Eq. (25)], it becomes clear that, in general,

$$\left\langle \boldsymbol{U}_\omega | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_\omega \right\rangle \neq \tilde{\boldsymbol{T}}^{(\mu,m),0n} = \left\langle \boldsymbol{U}_{0n} | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_{0n} \right\rangle \tag{32}$$

since obviously the frequency-specific rotation matrices $|\boldsymbol{U}_\omega\rangle$ and $|\boldsymbol{V}_\omega\rangle$ are not necessarily identical to the transition-specific rotation matrices $|\boldsymbol{U}_{0n}\rangle$ and $|\boldsymbol{V}_{0n}\rangle$, respectively. This, in particular, implies that the frequency-specific reference coordinate system [which is obtained from an SVD of the mixed-gauge polarizability and in which the LG(OI) optical rotation tensor is evaluated] is not necessarily identical to each of the transition-specific ones [which are obtained from an SVD of the mixed-gauge electric dipole–electric dipole transition strength tensors and in which the LG(OI) rotatory strength is evaluated]. As a result, simply summing up the LG(OI) rotatory strengths leads to a mismatch of reference coordinate systems and will, thus, generally not yield the LG(OI) optical rotation without further considerations. We note in passing that this implies that the trace of $\left\langle \boldsymbol{U}_\omega | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_\omega \right\rangle$ is not necessarily origin independent while its sum over states n of course is.

Before turning to the general case, we would first like to stress that specific rotations from LG(OI), either evaluated directly

$$\tilde{\beta}^{(\mu,m)}(\omega) = \frac{1}{3} \mathrm{Tr} \left\langle \boldsymbol{U}_\omega | \boldsymbol{\beta}^{(\mu,m)}(\omega) | \boldsymbol{V}_\omega \right\rangle \tag{33}$$

or via a sum-over-states expression using the origin-independent LG(OI) rotatory strengths [cf. Eq. (19)]

$$\tilde{R}^{0n} = \mathrm{Tr} \left\langle \boldsymbol{U}_{0n} | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_{0n} \right\rangle \tag{34}$$

are necessarily identical in two different limits. First, they converge to the same value in the limit of a complete basis set (at least for TDHF/TDDFT) that eliminates any origin dependency and, thus, trivially makes the LG(OI) optical rotation sum-over-states representable by the LG(OI) rotatory strengths. An illustration for specific rotations from TDDFT for molecule **1** is shown in Fig. 6. In the second limiting case, we assume a (model) response problem consisting of only one transition. This may approximately be the case if there is an energetically well-separated transition in resonance with the external field of frequency ω so that one term in the sum dominates the entire expression. Under these circumstances, the sum-over-states expression in Eq. (30) relates the optical rotation and the electric dipole–magnetic dipole transition-strength tensor by merely a scalar multiplication. Therefore, the $|\boldsymbol{U}_\omega\rangle$ and $|\boldsymbol{V}_\omega\rangle$ matrices (regardless of ω) are identical to $|\boldsymbol{U}_{01}\rangle$ and $|\boldsymbol{V}_{01}\rangle$, respectively, of that specific transition $|0\rangle \rightarrow |1\rangle$. We have numerically verified this using molecule **1** (TDHF, aug-cc-pVDZ), restricting the reference orbitals to the highest-occupied and lowest-unoccupied molecular orbitals. Here, we find for both approaches the following specific rotations (in deg/[dm (g/ml)]): (i) −52.7689 for $\lambda = 633$ nm, (ii) −61.3416 for $\lambda = 589$ nm, and (iii) −184.4429 for $\lambda = 355$ nm.

In the general case, however, it is also possible to express the LG(OI) optical rotation tensor in a sum-over-states fashion, including the LG(OI) electric dipole–magnetic dipole transition-strength tensors [which are used to calculate the LG(OI) rotatory strengths]. To do so, we recall that, for each transition and frequency, the $|\boldsymbol{U}\rangle$ and $|\boldsymbol{V}\rangle$ matrices are always orthogonal because they consist of the singular vectors of a singular-value decomposition, i.e.,

$$\langle \boldsymbol{U}|\boldsymbol{U}\rangle = |\boldsymbol{U}\rangle\langle \boldsymbol{U}| = \langle \boldsymbol{V}|\boldsymbol{V}\rangle = |\boldsymbol{V}\rangle\langle \boldsymbol{V}| = \mathbf{1}. \tag{35}$$

Inserting the outer-product identities of transition $|0\rangle \rightarrow |n\rangle$ into Eq. (31), one obtains

$$\tilde{\boldsymbol{\beta}}^{(\mu,m)}(\omega) = 2c \sum_{n \neq 0} \frac{\langle \boldsymbol{U}_\omega | \boldsymbol{U}_{0n} \rangle \langle \boldsymbol{U}_{0n} | \boldsymbol{T}^{(\mu,m),0n} | \boldsymbol{V}_{0n} \rangle \langle \boldsymbol{V}_{0n} | \boldsymbol{V}_\omega \rangle}{\omega_{0n}^2 - \omega^2}, \tag{36}$$

$$= 2c \sum_{n \neq 0} \frac{\left\langle \boldsymbol{U}_{0n \rightarrow \omega} | \tilde{\boldsymbol{T}}^{(\mu,m),0n} | \boldsymbol{V}_{0n \rightarrow \omega} \right\rangle}{\omega_{0n}^2 - \omega^2}, \tag{37}$$

with the definitions

$$|\boldsymbol{U}_{0n \rightarrow \omega}\rangle = \langle \boldsymbol{U}_{0n} | \boldsymbol{U}_\omega \rangle, \tag{38}$$

$$|\boldsymbol{V}_{0n \rightarrow \omega}\rangle = \langle \boldsymbol{V}_{0n} | \boldsymbol{V}_\omega \rangle. \tag{39}$$

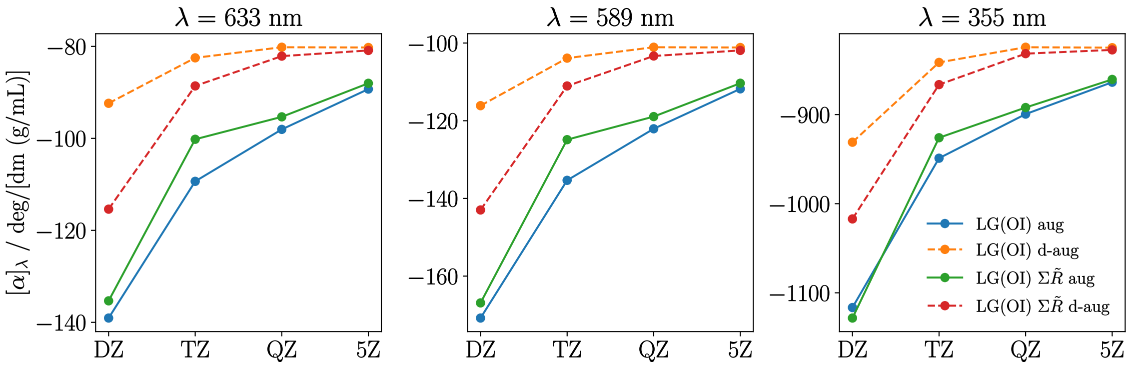

FIG. 6. Basis-set dependence of the specific rotation evaluated directly [LG(OI)] and obtained as a sum-over-states expression using the LG(OI) rotatory strengths [LG(OI)($\Sigma\tilde{R}$)] for molecule **1** and three wavelengths. The gauge origin was set in the center of mass of the molecule. The aug-cc-pV*X* and d-aug-cc-pV*X* basis sets were employed, and PBE[64] was used as an approximation for the exchange–correlation functional.

The product of two orthogonal matrices is always orthogonal; hence, the matrices $\lvert \boldsymbol{U}_{0n\rightarrow\omega}\rangle$ and $\lvert \boldsymbol{V}_{0n\rightarrow\omega}\rangle$ must also be orthogonal. A multiplication with one of these matrices can, thus, be understood as yet another rotation that, in this context, can be identified as the rotation from the LG(OI) reference coordinate system for the transition 0*n* (in which the trace of $\boldsymbol{T}^{(\mu,m),0n}$ is origin-independent and corresponds to the rotatory strength) to that of the frequency ω (in which the trace of $\tilde{\boldsymbol{\beta}}^{(\mu,m)}(\omega)$ is origin-independent and a third of which corresponds to the isotropic optical rotation). A numerical verification can be found in Table II where the specific rotations corresponding to the right-hand side of Eq. (37) [LG(OI)($\Sigma\tilde{R}'$)] are compared to regular length gauge [LG], regular length gauge calculated via a sum-over-states expression [LG(ΣR)] and origin-independent length gauge evaluated directly [LG(OI)].

We note again that the LG(OI) optical rotation [Eq. (12)] is *not* necessarily sum-over-states representable by the LG(OI) rotatory strengths [Eq. (29)]. However, rewriting Eq. (31) the way done in Eq. (37) clearly demonstrates that the reason for this is simply a mismatch of the frequency-specific and transition-specific LG(OI) coordinate systems: Diagonalizing a sum of tensors simply requires different rotation matrices than diagonalizing each term in the sum separately. As such, this mismatch is straightforwardly eliminated by simple additional rotations via the orthogonal transformations performed by $\lvert \boldsymbol{U}_{0n\rightarrow\omega}\rangle$ and $\lvert \boldsymbol{V}_{0n\rightarrow\omega}\rangle$. It is important to mention that this mismatch is merely a result of the different origin dependencies as evidenced by comparing Eqs. (9) and (25) and thus clearly does not imply unphysical behavior of the LG(OI) approach. Similar arguments can be given in the case of damped LG(OI) ECD when using complex frequencies, and we refer to Sec. 2 of the supplementary material for a more detailed discussion.

TABLE II. Comparison of the Hartree–Fock specific rotations {in deg/[dm (g/ml)]} for molecule **1** in regular length gauge [LG], regular length gauge calculated via a sum-over-states expression [LG(ΣR)], origin-independent length gauge [LG(OI)], and origin-independent length gauge calculated via a sum-over-states expression, where the additional rotations as discussed in Eq. (37) were performed [LG(OI)($\Sigma\tilde{R}'$)]. An aug-cc-pVDZ basis set was used.

λ/nm	LG	LG(ΣR)	LG(OI)	LG(OI)($\Sigma\tilde{R}'$)
		$[\alpha]_\lambda(\boldsymbol{O})$		
633	11.506 3	11.506 3	11.1409	11.1409
589	12.497 3	12.497 3	12.0680	12.0680
355	−8.970 1	−8.970 1	−10.4569	−10.4569
		$[\alpha]_\lambda(\boldsymbol{O}')$		
633	7 131.891 8	7131.891 8	11.1409	11.1409
589	8 359.961 5	8359.961 5	12.0680	12.0680
355	28 156.490 1	28 156.490 1	−10.4569	−10.4569

V. CONCLUSION

In this article, we have presented a simple extension of the LG(OI) approach for calculating origin-independent optical rotation in the length gauge proposed in Ref. 31 to electronic circular dichroism. Using this method, origin-independent ECD in the dipole-length representation can be obtained from both conventional rotatory strengths and damped response theory, regardless of the approximate computational method used. Similarly to the transformation of the optical-rotation tensor shown in Ref. 31, we consider the mixed representation of the electric dipole transition-strength tensor and the real part of the electric-dipole polarizability tensor in mixed dipole representation (length, velocity), respectively. A singular-value decomposition of these tensors yields the unitary matrices making the traces of the electric dipole–magnetic dipole transition strength (whose isotropic average gives the rotatory strength) and the real part of the electric dipole–magnetic dipole polarizability tensor (being proportional to the frequency-dependent ECD) origin independent.

We implemented the LG(OI) method for ADC(2) and LR-CC2 as well as TDHF and TDDFT. The spin-scaled variants of the former [explicitly demonstrated for the spin-opposite scaled ADC(2) case in this article] and the Tamm–Dancoff approximation of the latter two approaches is also included. Tamm–Dancoff results can be found in the supplementary material. For (−)-hydrogen peroxide, we have shown rotatory strengths for some transitions of three flavors: velocity gauge (VG), length gauge (LG), and modified length gauge [LG(OI)]. We could verify that the LG(OI) rotatory strengths are origin independent, regardless of the employed electronic-structure method, variational or not. Furthermore, we could, similarly to Ref. 31, observe that the center of mass might not always be the best choice for a gauge origin if one is forced to use the conventional LG approach. Additionally, we also considered ECD computed using damped response theory. Here, we have presented results consistent with the rotatory strengths investigated in the preceding step, and the efficacy of the LG(OI) approach was shown. Based on the three small test molecules and the four lowest-lying transitions each, we have performed a basis-set convergence study comparing the performance of the LG(OI) and VG rotatory strengths. For three of the 12 transitions, we have found a clear advantage of the LG(OI) approach, two with a small advantage for LG(OI) approach and one with a small advantage for the VG approach. This indicates that the basis-set convergence in the length gauge may actually be faster on average, which is in line with a recent work by Parsons *et al.*,[77] which found LG(OI) to have a slight advantage over the modified velocity gauge representation of optical rotation in this respect. We have successfully applied the LG(OI)-ECD approach to (P)-[11]helicene as a larger molecule with a delocalized π-system. We have discussed the relationship between the LG(OI) optical rotation presented in Ref. 31 and LG(OI) rotatory strengths. By virtue of simple mathematical arguments, we have shown that the former is not simply sum-over-states representable by the latter. However, we have presented a way to reconcile the expressions for the LG(OI) optical rotation and rotatory strengths via a sum-over-states expression. Here, we have shown that an additional rotation of the corresponding electric dipole–magnetic dipole transition tensor from the transition-specific coordinate system (as it is used for the rotatory strengths) to the frequency-specific one (as it is used for the optical rotation) is necessary.

Given the fact the VG rotatory strengths are also origin independent, it is still of great interest to systematically assess whether the convergence toward the basis-set limit (in the TDHF/TDDFT case) using the dipole-length representation is, in fact, faster than in the dipole-velocity one.[15,31,78,79] Moreover, one could use LG(OI) rotatory strengths as an additional indicator for determining a generally better *standard choice* gauge origin in chiroptical-property calculations than the center of mass of a molecule.[31]

SUPPLEMENTARY MATERIAL

Discussion of the implementation within the TDHF and TDDFT as well as ADC(2) and CC2 framework, discussions of the sum-over-states representability of the damped ECD, excitation energies and rotatory strengths (for CIS and TDDFT), and damped ECD spectra (TDDFT) of molecule **1** as well as excitation energies and rotatory strengths [TDHF, ADC(2), and LR-CC2] and damped ECD spectra (TDHF) of molecules **2** and **3** can be found in the supplementary material.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data supporting the findings of this study are available either within the supplementary material or upon reasonable request from the authors.

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