

On the Choice of Coordinate Origin in Length Gauge Optical Rotation Calculations

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In this work, we explore the issue of origin dependence in optical rotation (OR) calculations in the length dipole gauge (LG) using standard approximate methods belonging to density functional theory (DFT) and coupled cluster (CC) theory. We use the origin-invariant LG approach, LG(OI), that we recently proposed as reference for the calculations, and we study whether a proper choice of coordinate origin and molecular orientation can be made such that diagonal elements of the LG-OR tensor match those of the LG(OI) tensor. Using a numerical search algorithm, we show that multiple spatial orientations can be found where the LG and LG(OI) results match. However, a simple analytical procedure provides a spatial orientation where the origin of the coordinate system is close to the center of mass of the molecule. At the same time, we also show that putting the origin at the center of mass is not an ideal choice for every molecule (relative errors in the OR up to 70% can be obtained in our test set). Finally, we show that the choice of coordinate origin based on the analytical procedure is transferable across different methods and it is superior to putting the origin in the center of mass or center of nuclear charge. This is important because the LG(OI) approach is trivial to implement for DFT, but not necessarily for non-variational methods in the CC family. Therefore, one can determine an optimal coordinate origin at DFT level and use it for standard LG-CC response calculations.

Keywords: Optical Rotation, Origin Dependence, Length Gauge, CCSD, DFT.

I. INTRODUCTION

Optical rotation (OR) is the angle by which plane polarized light is rotated as it passes through an optically active medium.¹ Two enantiomers will generate OR of same magnitude but opposite sign, so this property can be used to assign the absolute configuration of chiral molecules in a sample. Although the OR value can be determined experimentally, calculations are needed to match the OR sign to a specific enantiomer.^{2–19} Efforts have also been made to provide a more chemically intuitive picture of this structure-property relationship.^{20–27} Therefore, it is desirable to continue to pursue more accurate and efficient methods for performing OR simulations, and to better understand the limitations of practical approximate methods.

These limitations revolve around a few key factors: the incompleteness of the basis set and of the treatment of electron correlation in practical calculations, the inability of treating quantum effects in electrons and nuclei on the same footing, and the inability to treat the environment around a chiral molecule at the quantum level. Although these limitations are common to simulations of many molecular properties, they are particularly important for OR due to its sensitivity to molecular structure and intermolecular interactions. Typically, vibrational contributions to OR are treated with perturbative formulas, but it is hard to determine the accuracy of this approach.^{28–31} For solvation the situation is even worse, as there is no standard recipe to accurately reproduce its effect, and the anomalous shift in OR going from gas to solution

phase is largely not understood.^{32–43} For OR in the solid phase, a few efforts have begun to appear but simulations are not at a mature state.^{44–46} Electron correlation incompleteness is also difficult to overcome, because chiral molecules tend to be too large for high-level methods. Among the systematically improvable methods, the most accurate and yet affordable one is coupled cluster with single and double excitations (CCSD),^{15–19,47,48} but we have recently shown that CCSD may not be as close to convergence in terms of electron correlation treatment as one would hope.^{48,49} On the other hand, density functional theory (DFT) methods dominate the field of OR simulations because of their favorable cost to accuracy ratio.^{11–15,41,50} However, although it has been shown that the accuracy can be improved with range-tuning,⁵¹ the typical DFT issue of system dependent-accuracy is also present for this property. The basis set dependence in OR calculations has been well studied,^{52–58} and basis sets have been formulated specifically for OR calculations in an attempt to decrease computational cost while maintaining accuracy.^{59–62}

A consequence of basis set and electron correlation incompleteness is that different choices of gauge for the external field representation provide different numerical values of the OR, contrary to exact calculations. Two common choices are the length gauge (LG) and the velocity gauge (VG), which differ in the representation of the electric dipole operator.^{63,64} VG calculations include an unphysical static limit, which must be calculated and subtracted out explicitly; a procedure called modified VG (MVG).⁷ Approximate LG-OR calculations are origin dependent, which is also unphysical. The issue can be solved using London orbitals^{65,66}, where a magnetic field dependent phase factor is included on each atomic basis function. This is a general approach

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that can be useful for many magnetic properties, but at the cost of significantly more complicated equations and implementations.^{9,10,12,67} Additionally, this approach requires the inclusion of the orbital response, which is standard in DFT but not in CCSD (unless complicated orbital optimization procedures are used^{68,69}). We proposed a different approach, called origin-invariant LG or LG(OI), where the origin dependence of the OR is removed with a clever transformation of the OR tensor.^{47,48} The LG(OI) approach is considerably simpler to implement than London orbitals and it works equally well for variational and non-variational methods, but it is specific to OR calculations. In a recent work, we showed that LG(OI) converges to the complete basis set limit slightly faster than MVG.⁴⁹

In this work, we investigate whether a meaningful choice of coordinate origin and molecular orientation can be made for a standard LG calculation so that it matches the LG(OI) result. In previous work, we have proposed an analytical approach to determine the spatial orientation of a molecule so that the diagonal elements of the OR tensor match between LG and LG(OI) calculations.⁴⁸ Here we try to understand if that choice has any general physical characteristic and how the OR results compare with more common choices of coordinate origin (e.g., the center of mass or the center of nuclear charge). We also determine whether the choice of molecular orientation where the LG and LG(OI) OR match is unique, by using a numerical procedure that iteratively performs rigid rotations and translations of the molecule until the diagonal elements and the trace of the LG and LG(OI) OR tensors agree within a given threshold. Finally, we explore whether this choice of molecular orientation is transferable between different methods (for instance, from a specific functional to another one or to CCSD). This is important because while LG(OI) is trivial to implement for DFT and has no impact on the computational cost, it does require some effort for CCSD (both in terms of initial implementation and for the computational cost, if the symmetric version of the response function is used). Therefore, it may be useful to find a special LG origin for DFT and use it for a standard LG-OR CCSD calculation.

This paper is organized as follows. Section II reviews the equations relevant to this work. Section III lists the computational details for the calculations. Section IV reports the results for the test calculations, and Section V discusses and summarizes the results.

II. THEORY

This section reviews the most important equations for the calculation of optical rotation that are useful for the discussion of the simulations. The OR in isotropic media is commonly reported as a spatially averaged quantity normalized for the path length of the sample and its concentration, called specific rotation $[\alpha]_\omega$, in units of

$\text{deg} [\text{dm}(\text{g/mL})]^{-1}$:

$$[\alpha]_\omega = \frac{(72 \times 10^{-6}) \hbar^2 N_A \omega^2 \text{Tr}(\beta)}{c^2 m_e^2 M} \frac{1}{3} \quad (1)$$

where \hbar is the reduced Planck's constant (J s), N_A is Avogadro's number, c is the speed of light (m/s), m_e is the mass of an electron (kg), and M is the molar mass (amu). β (a.u.) is the electric dipole-magnetic dipole polarizability tensor¹⁷:

$$\beta_{\alpha\beta} = 2 \sum_{j \neq 0} \text{Im} \frac{\langle \psi_0 | \mu_\alpha | \psi_j \rangle \langle \psi_j | m_\beta | \psi_0 \rangle}{\omega_{j0}^2 - \omega^2} \quad (2)$$

where ψ_0 and ψ_j represent the ground and j th excited state wavefunctions, μ_α is the electric dipole operator, m_β is the magnetic dipole operator, ω_{j0} is the j th excitation frequency, and ω is the frequency of the impinging radiation. Greek letter indexes represent Cartesian coordinates. This sum-over-state (SOS) formulation of β is not convenient for fast calculations, which are commonly performed using linear response (LR) theory^{7,9,17,70,71}. In brief, LR replaces the evaluation of the excited states in Eq. 2 with the solution of response equations for one of the multipole perturbations; this produces a perturbed density in the molecular orbital (MO) or atomic orbital (AO) basis, which is then contracted with the MO or AO integrals for the other multipole operator. For variational methods like Hartree-Fock (HF) or DFT, the choice of perturbation for the response equation is immaterial as either choice leads to the same tensor values.⁹ For non-variational methods like CC theory, the symmetric formulation of the response function requires the solution of the response equations for both perturbations while the non-symmetric formulation requires only one perturbation but two sets of perturbed amplitudes.^{72,73} Therefore, both CC-LR formulations are computationally equivalent for the evaluation of β .

For exact calculations, $\text{Tr}(\beta)$ is an origin and gauge independent quantity. However, practical calculations are based on approximate methods where typically both the basis set and the treatment of electron correlation are incomplete. Therefore, the choice of gauge matters and the two most common choices are the length and velocity gauges (LG and VG), where the electronic part of the electric dipole operator (in a.u.) is represented as:^{63,64}

$$\boldsymbol{\mu}^R = -\mathbf{r} \quad (3)$$

$$\boldsymbol{\mu}^P = -\mathbf{p} \quad (4)$$

where \mathbf{r} is the position operator and \mathbf{p} is the momentum operator. The LG formulation suffers from origin dependence, which can be addressed by using London orbitals for variational methods^{9,10,12,65-67} or with our origin-invariant formulation [LG(OI)] for any method, discussed below.^{47,48} The VG suffers from an unphysical static limit that needs to be evaluated and subtracted out explicitly

(called the modified VG or MVG approach)⁷. In previous work, we studied how the evaluation of $[\alpha]_\omega$ converges towards basis set and electron correlation completeness.⁴⁹

In this work, we investigate how the choice of origin affects standard LG-OR calculations. Therefore, we need to discuss the expressions that quantify this dependence. Considering an origin displacement:

$$\mathbf{O}' = \mathbf{O} + \mathbf{d} \quad (5)$$

the β tensor elements vary as^{7,63,64}

$$\beta_{\alpha\beta}(\mathbf{O}') = \beta_{\alpha\beta}(\mathbf{O}) + \frac{1}{2}\epsilon_{\beta\gamma\delta}\alpha_{\alpha\gamma}^{(R,P)}d_\delta \quad (6)$$

where ϵ is the Levi-Civita operator and α is the electric dipole-electric dipole polarizability tensor. The superscript (R, P) indicates a mixed-gauge representation of the electric dipole operator according to Eqs. 3-4.

Although in exact calculations α is symmetric no matter the electric dipole operator representation, this is not the case anymore for $\alpha^{(R,P)}$ in approximate calculations, which leads to the origin dependence of the LG-OR:

$$\begin{aligned} \text{Tr}[\beta(\mathbf{O}')] = & \text{Tr}[\beta(\mathbf{O})] + \frac{1}{2}[d_x(\alpha_{yz} - \alpha_{zy}) \\ & + d_y(\alpha_{zx} - \alpha_{xz}) + d_z(\alpha_{xy} - \alpha_{yx})] \end{aligned} \quad (7)$$

where we neglected the (R, P) superscript for clarity.

In LG(OI), one performs a singular value decomposition (SVD) of $\alpha^{(R,P)}$

$$\alpha^{(R,P)} = \mathbf{U}\alpha_D^{(R,P)}\mathbf{V}^\dagger \quad (8)$$

where $\alpha_D^{(R,P)}$ is diagonal and \mathbf{U} and \mathbf{V}^\dagger are unitary transformations^{47,48}. Applying the inverse transformation to β

$$\tilde{\beta} = \mathbf{U}^\dagger\beta\mathbf{V} \quad (9)$$

leads to diagonal elements of the transformed $\tilde{\beta}$ tensor that are now origin invariant, so that the corresponding $[\alpha]_\omega^{LG(OI)}$ is also origin invariant. The LG(OI) transformation is a post-processing treatment of the β tensor that is trivial to implement and apply. In HF or DFT, one needs only to calculate the perturbed density for the μ^R operator and then contract it with the appropriate multipole integrals to obtain all relevant tensors: the standard electric dipole-electric dipole polarizability in the length and mixed gauges, the electric dipole-magnetic dipole polarizability β , and even the electric dipole-electric quadrupole polarizability necessary to calculate the full OR tensor for oriented systems.^{44,48} In this sense, the LG(OI)-OR is a free subproduct of a standard electric polarizability calculation. For CC methods, our current implementation with the symmetric form of the LR function requires an explicit evaluation of the μ^P perturbed densities. However, a non-symmetric formulation of the LR function would only require the evaluation of the μ^R perturbed amplitudes, similar to the DFT case.

In Ref. 48, we showed that the molecule can be reoriented and translated analytically so that the diagonal elements of β match those of $\tilde{\beta}$. This can be accomplished by first orienting the molecule along the principal axes of the symmetric part of $\alpha^{(R,P)}$. This is followed by a rigid translation according to Eq. 6 such that:

$$\begin{cases} \tilde{\beta}_{xx} = \beta_{xx}(\mathbf{O}') = \beta_{xx}(\mathbf{O}) + \frac{1}{2}(d_z\alpha_{xy} - d_y\alpha_{xz}) \\ \tilde{\beta}_{yy} = \beta_{yy}(\mathbf{O}') = \beta_{yy}(\mathbf{O}) + \frac{1}{2}(d_x\alpha_{yz} - d_z\alpha_{yx}) \\ \tilde{\beta}_{zz} = \beta_{zz}(\mathbf{O}') = \beta_{zz}(\mathbf{O}) + \frac{1}{2}(d_y\alpha_{zx} - d_x\alpha_{zy}) \end{cases} \quad (10)$$

In the next section, we will call this choice of origin (and orientation) \mathbf{O}^{An} .

From an analysis of Eq. 7, it is easy to realize that there is an infinite number of choices of origin that give $[\alpha]_\omega^{LG} = [\alpha]_\omega^{LG(OI)}$. For a given orientation, the elements of the $\alpha^{(R,P)}$ are origin invariant. Introducing the notation $\gamma_\alpha = (\alpha_{\beta\gamma} - \alpha_{\gamma\beta})$, the last term in Eq. 7 can be set to zero by choosing a non-nil γ_α , say γ_z , and set the corresponding origin displacement to:

$$d_z = -\frac{d_x\gamma_x + d_y\gamma_y}{\gamma_z} \quad (11)$$

Therefore, starting from \mathbf{O}^{An} , one can choose any pair of values for d_x and d_y and find the value of d_z that maintains $[\alpha]_\omega^{LG} = [\alpha]_\omega^{LG(OI)}$.

However, the question remains whether there are alternative choices of origin and molecular orientation where $\beta_{\alpha\alpha} = \tilde{\beta}_{\alpha\alpha}$ for all diagonal elements. This would require that the second terms in each equation in Eq. 10 are simultaneously zero, which is a problem with six unknowns and three equations. To seek out these alternative spatial orientations of the molecules, we wrote a Python script that attempts the search numerically. The script uses a Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimization module in SciPy⁷⁴ to determine the necessary shift and rotation. This algorithm seeks to minimize the root mean squared difference (RMSD) between the diagonal elements and the trace of the LG and LG(OI) β tensors by performing consecutive rotations and shifts of the coordinate system. Gradients of the RMSD are calculated with numerical differentiation of the four target variables (i.e., the tensor diagonal elements and trace) with respect to rigid translations and rotations. After some initial testing, the displacement for the numerical derivative was set to 10^{-4} Å for translations and 10^{-4} rad for rotations. The trust radius for the displacements during the optimization was set to 10^{-1} Å and 10^{-1} rad at the beginning of the procedure, and incrementally decreased close to convergence. Convergence was reached when the RMSD for each variable was below 10^{-8} . We performed two sets of orientation optimization, one starting from the origin at the center of mass (COM) and orientation equivalent to that at \mathbf{O}^{An} , and a second one starting from the same orientation but arbitrarily translating the COM by 10 Å in each Cartesian direction. In the following, we

call the origin found by the numerical procedure with the two starting points \mathbf{O}^{Num} and \mathbf{O}^{Far} , respectively.

III. METHODS

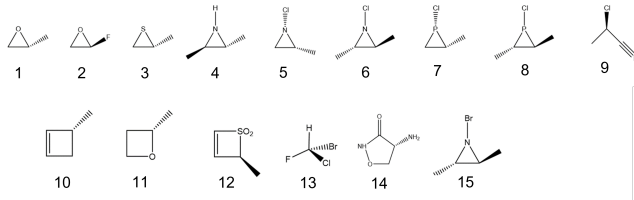


FIG. 1: The test set of molecules used for OR calculations.

OR values are computed in the LG and LG(OI) for a set of 15 rigid, organic molecules (see Figure 1) using CAM-B3LYP⁷⁵ and the aug-cc-pVDZ basis set.⁷⁶ The initial geometries were obtained from Refs. 55,56,58. All calculations are performed in the gas-phase. The OR is calculated with different choices of origin: \mathbf{O}^{An} , \mathbf{O}^{Num} , \mathbf{O}^{Far} , \mathbf{O}^{COM} , and \mathbf{O}^{COC} . The first three are described in Section II. \mathbf{O}^{COM} indicates that the COM is placed at the origin and the molecular orientation is obtained from the analytical procedure; \mathbf{O}^{COC} indicates that the center of nuclear charge (which is obtained as the COM but using the nuclear charges rather than masses) is placed at the origin and the orientation is the same as for \mathbf{O}^{COM} .

Calculations are also performed at B3LYP and CCSD levels (with the same basis set) with the LG(OI) approach and with LG at three different origins: \mathbf{O}^{COM} , \mathbf{O}^{COC} , and the CAM-B3LYP analytical origin ($\mathbf{O}_{\text{CAM}}^{\text{An}}$). All calculations were performed at the sodium D line, 589.3 nm, to avoid any issue with resonance,^{1,50,67} using a development version of the Gaussian suite of programs⁷⁷.

The results in Section IV are primarily represented using the unsigned percent relative error:

$$\Delta_i = \left| \frac{\lambda_i^{\text{LG}} - \lambda_i^{\text{LG(OI)}}}{\lambda_i^{\text{LG(OI)}}} \right| \times 100 \quad (12)$$

where the subscript i denotes the molecule number from Figure 1 and λ is the quantity under study (e.g., individual diagonal elements of the β tensor or the specific rotation).

IV. RESULTS

We start the analysis by comparing the collective LG and LG(OI) OR results for the four choices of origin: \mathbf{O}^{An} , \mathbf{O}^{Num} , \mathbf{O}^{COM} , and \mathbf{O}^{COC} , shown in Table I. The table reports the mean unsigned relative error (MURE), maximum and minimum relative errors (MAX and MIN),

	\mathbf{O}^{An}	\mathbf{O}^{Num}	\mathbf{O}^{COM}	\mathbf{O}^{COC}
MURE	0.00	0.00	4.16	3.37
MAX	0.00	0.00	21.31	21.94
MIN	0.00	0.00	0.07	0.02
STDV	0.00	0.00	5.81	5.54

TABLE I: Statistical analysis for CAM-B3LYP OR values.

and the standard deviation of the relative error (STDV) over the set of 15 molecules in Figure 1, where the relative error is calculated for the specific rotation ($\lambda_i \equiv [\alpha]_D(i)$ in Eq. 12). The analytical and the numerical procedure for the translation of the molecules leads to an essentially perfect match of the LG(OI) results. On the other hand, setting the origin at either the COM or COC may result in significant errors: although the average error for each is not necessarily large (about 4% and 3%, respectively), there is significant deviation (STDV = 6%) with a maximum error of 21-22% in the test set for both. The individual LG errors for both the \mathbf{O}^{COM} and \mathbf{O}^{COC} choices are reported in Figure S1 of the supporting information (SI).

	\mathbf{O}^{An}	\mathbf{O}^{Num}	\mathbf{O}^{COM}	\mathbf{O}^{COC}	\mathbf{O}^{Far}
xx	0.00	0.00	0.68	0.52	0.02
yy	0.01	0.01	1.94	1.84	0.01
zz	0.00	0.00	1.47	1.09	0.05

TABLE II: Mean Unsigned Relative Error (%) for CAM-B3LYP β diagonal elements.

The matching of the LG and LG(OI) specific rotation with \mathbf{O}^{An} and \mathbf{O}^{Num} is not due to cancellation of error, but to the matching of the individual diagonal elements of the β tensor, as shown by the % MURE results in Table II. The errors for the individual molecules are shown in Figure S2 of the SI, and the raw data are collected in Tables S1-S4 of the SI. Furthermore, the analytical and numerical procedures lead to the same position and orientation of the molecules: this is shown in Figure 2, which reports the distance of \mathbf{O}^{An} and \mathbf{O}^{Num} from the COM, and in Figure S3 in the SI, which reports the overlaid geometry of each molecule obtained with the two procedures. Even for molecule 15, Figure S3 in the SI shows that the two structures are essentially overlapped. The difference is likely due to a small origin dependence of the OR along the x axis direction, which the numerical procedure is unable to fully capture. In principle, an exact matching could be obtained by improving the numerical algorithm by implementing analytical gradients and further tightening the thresholds for convergence, but this is beyond the scope of this work. In general, these results show that the convergence of the β tensor towards the LG(OI) values is faster than the convergence of the position and orientation of the molecule in space. Note that \mathbf{O}^{An} is rather close to the COM (within 1 Å for each molecule), but the latter is not necessarily a good choice

of origin for every molecule, as shown in Table I and Figure S1 of the SI. Interestingly, the average errors for the individual diagonal elements of β with the COM/COC origins are each smaller than the average error for the specific rotation (compare both the \mathcal{O}^{COM} and \mathcal{O}^{COC} results in Table I with those in Table II). This is because the elements of the β tensor are signed quantities and a small error in the diagonal elements may lead to a larger error in the trace.

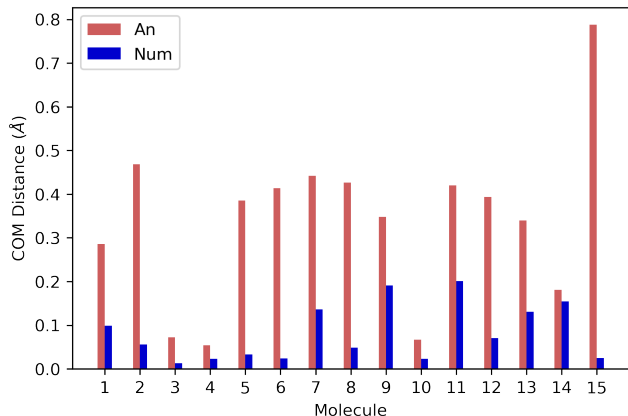


FIG. 2: Distance (\AA) between the center of mass (COM) and the coordinate origin at \mathcal{O}^{An} and \mathcal{O}^{Num} for each molecule.

Although the numerical procedure starting from the COM consistently leads to an orientation of the molecules that matches that obtained with the analytical procedure, other choices of origin and orientation can also lead to perfect matching of the diagonal elements of the LG β tensor with the corresponding LG(OI) values. These geometries were found by starting the numerical procedure with each molecule far away from the origin of the coordinate system (as explained in Section II, the COM was arbitrarily shifted by 10 \AA in every Cartesian direction). The numerical procedure found a new origin and orientation for all 15 molecules with negligible errors in the diagonal β elements, as shown in Table II (\mathcal{O}^{Far} column) and Figure S2 of the SI. The distance of the COM from the origin of this coordinate system (\mathcal{O}^{Far}) is shown in Figure 3, with values that vary from 7 \AA to almost 25 \AA (a comparison of the orientation between \mathcal{O}^{An} and \mathcal{O}^{Far} is shown in Figure S4 of the SI). These results show that the orientation associated with \mathcal{O}^{An} is not unique, although it is the closest to the COM.

Lastly, the \mathcal{O}^{An} obtained from a CAM-B3LYP calculation ($\mathcal{O}_{\text{CAM}}^{\text{An}}$) is used to perform a length gauge OR calculation using B3LYP and CCSD. The same calculation is performed using \mathcal{O}^{COM} and \mathcal{O}^{COC} , and both are compared to the LG(OI) calculation at the corresponding level of theory. The results are displayed in Figure 4 and the raw data are reported in Tables S5-S6 of the SI. It is evident that $\mathcal{O}_{\text{CAM}}^{\text{An}}$ is in general a drastically better choice than either \mathcal{O}^{COM} or \mathcal{O}^{COC} for both levels

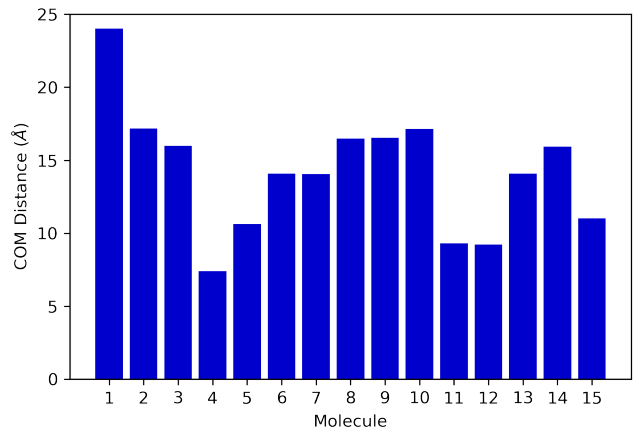


FIG. 3: Distance (\AA) between the center of mass (COM) and the coordinate origin at \mathcal{O}^{Far} for each molecule.

of theory. There are few cases where all choices of origin have small errors: Molecules 3, 4, 10, and 14. However, in other cases the difference is stark. For instance, for B3LYP the relative error for Molecule 13 falls from 25% to 1% passing from $\mathcal{O}^{\text{COM}}/\mathcal{O}^{\text{COC}}$ to $\mathcal{O}_{\text{CAM}}^{\text{An}}$. For CCSD, the change is even more dramatic for molecules 9 (the errors goes from 72% to 1%) and 13 (from 50% with \mathcal{O}^{COM} to 47% with \mathcal{O}^{COC} to 1% with $\mathcal{O}_{\text{CAM}}^{\text{An}}$). Therefore, the choice of position and orientation obtained with the analytical procedure at one level of theory seems transferable to other levels of theory.

V. DISCUSSION AND CONCLUSIONS

Origin dependence is an unfortunate byproduct of approximations for standard LG calculations, but LG(OI) can remedy this for variational and nonvariational methods. In this work we have discussed two methods for locating the position and orientation of a molecule in space for which a standard LG-OR calculation is equivalent to LG(OI) in both the trace of the β tensor and its diagonal elements (within 1% relative error). While calculations with the coordinate origin at the COM or COC did not yield poor results for all cases, both the analytical and numerical procedure consistently showed substantial improvement over those choices of origin. When the COM was used as the starting point for the optimization routine, the resulting \mathcal{O}^{Num} proved to be essentially the same to \mathcal{O}^{An} (the agreement would improve if tighter thresholds were employed for the numerical procedure).

It was also shown that an infinite number of origins can be chosen such that $\text{Tr}(\tilde{\beta}) = \text{Tr}(\beta)$ (see Eqs. 7 and 11). The numerical procedure also located an alternative origin (\mathcal{O}^{Far}) for all molecules where the individual diagonal elements of the LG and LG(OI) OR tensors matched each other to within 1% (and not just the trace). For each case, the newly found \mathcal{O}^{Far} proved to be at a fairly

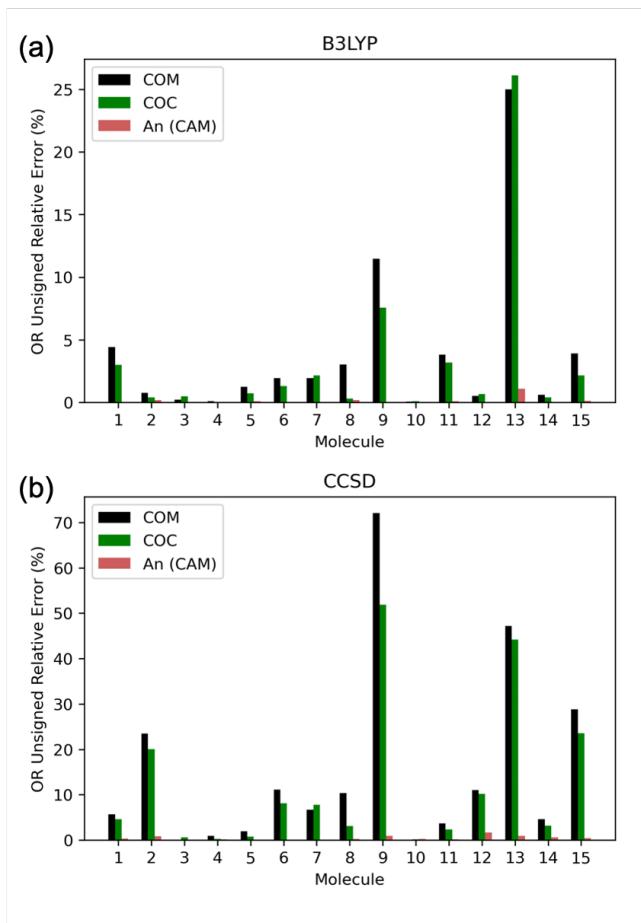


FIG. 4: Unsigned relative error in OR values calculated using B3LYP (a) and CCSD (b) with the coordinate origin at O^{COM} , O^{COC} , and O^{CAM} .

large distance from the initial point $O^{\text{An}}/O^{\text{Num}}$ (for instance, the COM is nearly 25 Å away from the origin of the coordinate system for Molecule 25), indicating that O^{Far} is in fact distinct from O^{An} and not only different due to numerical precision.

We also showed that O^{An} is transferable to other levels of theory. In fact, this choice of molecular orientation calculated at CAM-B3LYP level was consistently better than putting the origin at the COM or COC for both B3LYP and CCSD. In extreme cases like molecule 9 for CCSD, the relative error decreased from 70% with the origin at the COM to 1%. Overall, using O^{An} for B3LYP and CCSD produced errors $<2\%$.

In summary, we demonstrated that the molecular orientation with O^{An} as the coordinate origin provides the most faithful representation of the LG(OI) OR tensor using a standard LG approach. Although other choices of origin and orientation are possible, O^{An} is more natural because it is close to the COM of the molecule and it can be obtained with a simple analytical procedure. Furthermore, this choice of orientation is transferable across methods so it can be computed at a lower level where

the implementation of LG(OI) is simple, and used for standard LG calculations at higher levels of theory.

SUPPORTING INFORMATION

The Supporting Information includes the $[\alpha]_D$ unsigned relative error for each molecule when the coordinate origin is in O^{COM} and O^{COC} (Figure S1); the unsigned relative error for $\beta_{\alpha\alpha}$ for each molecule with the coordinate origin in O^{An} , O^{Num} , O^{COM} , O^{COC} , and O^{Far} (Figure S2); the overlaid structure of each molecule obtained with the analytical and numerical procedures: O^{An} vs. O^{Num} and O^{An} vs. O^{Far} (Figures S3-S4); the $\beta_{\alpha\alpha}$ and $[\alpha]_D$ values computed at CAM-B3LYP/aug-cc-pVDZ level for each molecule with LG(OI) and with LG at every applicable origin: O^{An} , O^{Num} , O^{COM} , O^{COC} , and O^{Far} (Tables S1-S4); $[\alpha]_D$ values computed at B3LYP and CCSD/aug-cc-pVDZ levels with LG(OI) and LG at O^{CAM} , O^{COM} , and O^{COC} origins (Tables S5-S6); the geometry of each molecule obtained with the analytical procedure and the numerical procedure starting with the COM far from the coordinate origin (O^{An} in Tables S7-S21 and O^{Far} in Tables S22-S36, respectively).

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the National Science Foundation through Grant No. CHE-2154452.

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