Derivation and Implementation of the Optical Rotation Tensor for Chiral Crystals

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This work reports the derivation and implementation of the electric dipole-magnetic dipole and electric dipole-electric quadrupole polarizability tensors at density functional theory level with periodic boundary conditions (DFT-PBC). These tensors are combined to evaluate the Buckingham/Dunn tensor that describes the optical rotation (OR) in oriented chiral systems. We detail several aspects of the derivation of the equations, and present test calculations that verify the correctness of the tensors formulation and of their implementation. The results show that the full OR tensor is completely origin invariant as for molecules and that PBC calculations match molecular cluster calculations on 1D chains. A preliminary investigation on the choice of density functional, basis set, and gauge indicates a similar dependence as for molecules: the functional is the primary factor that determines the OR magnitude, followed by the basis set and to a much smaller extent the choice of gauge. However, diffuse functions may be problematic for PBC calculations even if they are necessary for the molecular case. A comparison with experimental data of OR for the tartaric acid crystal shows reasonable agreement given the level of theory employed. The development presented in this work offers the opportunity to simulate the OR of chiral crystalline materials with general purpose DFT-PBC methods, which in turn may help to understand the role of intermolecular interactions on this sensitive electronic property.

Keywords: Optical Rotation, Gauge Dependence, Response Theory, Periodic Boundary Conditions

I. INTRODUCTION

Measurements of optical rotation (OR) have long been used to characterize chiral systems, but it was only relatively recently that the first Hartree-Fock level simulations were performed to compute this property\textsuperscript{1}. Great strides have been made towards more accurate, efficient, and predictive OR simulations since these initial calculations: extensions to post-Hartree-Fock levels of theory\textsuperscript{2–5}, development of OR-optimized basis sets\textsuperscript{6–9}, improved understanding of the role of solvation\textsuperscript{10–14}, and approaches for decomposing the OR into more chemically intuitive contributions\textsuperscript{15–19}. In spite of these efforts, OR remains a very challenging property to compute accurately and a clear structure-property relationship remains unknown.

Many of the current difficulties related to computing OR stem from comparisons made with solution phase experiments.\textsuperscript{20} Accurately replicating experimental OR in solution is not as simple as just determining the OR for the minimum energy structure; multiple configurations of the molecule can exist in solution, requiring a conformational search and subsequent Boltzmann averaging of the OR from each conformer. Not only does this require an extensive, costly search to ensure that all relevant conformers are found, but the energies of each conformer must also be determined to a high accuracy, as any errors in the exponential energy-weighting could greatly distort the conformer populations and thus the average OR.\textsuperscript{21} Compounding these issues is the need to model the surrounding solvent, which can influence the conformer populations and contribute to the OR itself through the formation of a chiral shell around a given conformer. Implicit electrostatic models of solvation account for some of these effects, but neglect specific solvent-solute interactions and the induced chirality of the solvation shell.\textsuperscript{14} Incorporating some explicit solvent molecules has mixed results, as the decision of how many solvent molecules to include and where to place them is typically made in an ad hoc fashion. Including a full solvation shell would be less arbitrary, but requires molecular dynamics (MD) simulations to determine reasonable solvation shell configurations and the levels of theory that can be used for these system sizes may not be sufficiently accurate\textsuperscript{11–13,22–24}. Larger solvation shells currently preclude the use of quantum mechanical (QM) calculations altogether, and there is no general approach that provides accurate results.

Comparisons with crystalline solids, particularly molecular crystals, would eliminate or greatly simplify a number of these issues. The rigidity and regularity of a crystal would simplify the “solvant” environment by eliminating the need for conformational averaging. The extended structure around a molecule can be determined from the crystal structure and can be readily simulated through the use of periodic boundary conditions (PBC). In principle, solid state experiments allow the entire OR tensor to be resolved, unlike solution or gas phase where only the isotropic OR can be measured. However, linear birefringence is 2-3 orders of magnitude larger than circular birefringence. Therefore, OR measurements are typically performed along special axes (called optic axes) where linear birefringence is zero, although the experi-

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mental determination of the directions corresponding to these axes is difficult. Nonetheless, a direct comparison with experimental data for solids would provide complimentary information about this property that is not easily accessible for solvated systems.

Despite early attempts to determine the optical activity of periodic systems, no general purpose approach is available. Rerat and Kirtman recently presented an implementation of the electric dipole-magnetic dipole polarizability with PBC, which is one of the tensors necessary to evaluate the OR in solids. Here, we present the first derivation of the full OR tensor at density functional theory with PBC (DFT-PBC) level, including both the electric dipole-magnetic dipole and electric dipole-electric quadrupole contributions. This implementation is based on the approach of Scuseria and coworkers to compute the PBC electric dipole-electric dipole polarizability tensor using an atomic orbital (AO) basis. This work reports numerical tests that confirm the correct physical properties of the OR tensor (i.e., its origin invariance), a preliminary analysis of the dependence of the choice of approximate density functional, basis set, and choice of gauge, and a direct comparison with experimental data for the tartaric acid chiral crystal, (2R,3R)–Ca.

The paper is organized as follows. In section II, expressions for the electric dipole-magnetic dipole and electric dipole-electric quadrupole polarizabilities are derived that satisfy periodic boundary conditions. Section III describes the computational procedure for the simulations. In section IV, simulations on cluster models and crystalline systems are presented. Section V concludes the discussion.

II. THEORY

Optical activity is governed by the rank-2 Buckingham/Dunn B tensor:

\[ B_{\alpha\beta} = \frac{1}{2} \left[ \beta_{\alpha\beta} + \beta_{\beta\alpha} + \sum_{\gamma,\delta} (\epsilon_{\alpha\gamma\delta} A_{\gamma,\delta\beta} + \epsilon_{\beta\gamma\delta} A_{\gamma,\delta\alpha}) \right] \]  

where \( \epsilon \) is the Levi-Civita operator, \( \beta \) is the electric dipole-magnetic dipole polarizability tensor, and \( A \) is the electric dipole-electric quadrupole polarizability tensor. In the length gauge,

\[ \beta_{\alpha\beta} = 2 \sum_{j=0} \text{Im} \frac{\langle \psi_0 | \mu^L_\alpha | \psi_j \rangle \langle \psi_j | m_\beta | \psi_0 \rangle}{\omega_j^2 - \omega^2} = \text{Im} \langle \mu^L_\alpha : m_\beta \rangle_{\omega} \]  

while in the velocity gauge

\[ \beta_{\alpha\beta} = \frac{2}{\omega} \sum_{j=0} \text{Re} \frac{\langle \psi_0 | \mu^V_\alpha | \psi_j \rangle \langle \psi_j | m_\beta | \psi_0 \rangle}{\omega_j^2 - \omega^2} = \text{Re} \langle \mu^V_\alpha : m_\beta \rangle_{\omega} \]  

where \( \langle \cdot : \cdot \rangle \) is the response function of the enclosed operators.

Throughout, we use atomic units unless otherwise specified and denote tensors over Cartesian indices using bold font and matrices over an orbital basis with an underline. Since there has been some confusion in the literature regarding the use of the \( G' \) symbol to indicate the electric dipole-magnetic dipole polarizability with or without the \( \omega^2 \) factor, we use the notation \( \beta = -\omega^{-2} G' \). Greek indices denote Cartesian coordinates, \( \omega \) is the frequency of the incident electromagnetic radiation while \( |\psi_j\rangle \) and \( \omega_j \) are the \( j \)th excited state wave function and excitation frequency, respectively. These definitions for \( \beta \) and \( A \) are valid for non-resonant optical activity (\( \omega \neq \omega \)) calculations; resonant optical activity is discussed in greater detail elsewhere.

For isotropic media, the observed optical rotation is commonly reported as a normalized quantity in units of \( \text{deg} \ [\text{mL}/\text{g}]^{-1} \), known as specific rotation:

\[ [\alpha]_\omega = \frac{(72 \times 10^6) h^2 N_A \omega^2}{3 c^2 m_e^2 M} \text{Tr}(B) \]

where \( h \) 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 electron rest mass (kg), and \( M \) is the molecular mass (amu). Another common set of units for isotropic OR is deg L dm⁻¹ mol⁻¹, which can be obtained by multiplying the specific rotation in Eq. 6 by a factor of \( M/1000 \). Note that Eq. 6 depends on \( \omega \) both through the constant prefactor on the right hand side as well through \( B \). For an oriented system, the \( \frac{1}{2} \text{Tr}(B) \) factor should be replaced by \( \beta_n \), the average of the components of the \( B \) tensor that are perpendicular to the direction of the beam.

By defining a chiroptical response tensor \( B \),

\[ B_{\alpha\beta} = \frac{1}{2} [\text{Tr}(B) \delta_{\alpha\beta} - B_{\alpha\beta}] \]

the OR parameter for a light beam in the direction of the unit vector \( \mathbf{n} \) is

\[ \beta_n = \mathbf{n}^T B \mathbf{n} \]

By defining this alternative chiroptical response tensor, one can easily compute the specific rotation for light traveling in an arbitrary direction relative to the oriented material. The evaluation of polarizability tensors using the sum-over-states formulas in Eqs. 2-5 is impractical, and linear response theory is used instead. This requires...
the evaluation of a perturbed density as the solution of coupled-perturbed Kohn-Sham (CPKS) equations for one of the multipole moments, which is then contracted with the integrals of the paired perturbation for a specific tensor. For PBC calculations, we use the CPKS implementation for the length gauge electric dipole $\mu^L$ from Scuseria and coworkers.\textsuperscript{39} Therefore, extending $\beta$ and $\Theta$ (and consequently $\beta$) to periodic systems reduces to the problem of defining $\mu^V$, $m$, and $\Theta$ operators that are translation invariant (i.e., consistent with periodic boundary conditions) that can be evaluated over an AO basis. The evaluation of $\mu^L$ is trivial, as it amounts to a Fourier transform to $k$-space of the real-space $\nabla_r$ integrals over the central and replicated cells, which already have the proper translational symmetry. The only complication is the extension of the periodic CPKS algorithm to handle anti-Hermitian matrices that are stored in lower-triangular form. For the derivation of the equations for $m$, and $\Theta^V$, we follow the approach used for $\mu^L$.\textsuperscript{39,52} This is a different approach than that used in Ref. 37 for $m$, although the final expression is the same. Once the PBC dipole integrals are available, it is sufficient to evaluate the perturbed density for the dipole operator $D^\mu$ (with either choice of gauge) and contract it with the magnetic dipole integrals to form $\beta$ and with the electric quadrupole integrals to form $A$.

### A. Periodic Magnetic Dipole

In real space, the matrix elements of the magnetic dipole for a periodic system can be written as

$$m^0_{\mu \nu} = -\langle \mu | r \times p | \nu \rangle = -\langle \mu | (r \times p) e^{-iDl \cdot r} | \nu \rangle$$

(9)

where $\mu, \nu$ are atomic orbital indices, $D$ is a matrix with (in general) three translation vectors as columns, $l$ is a vector indexing the cells along each translation vector, with $0$ the center cell, and $e^{-iDl \cdot r}$ is the translation operator. Due to the presence of the translation operator, the magnetic dipole matrix is not Hermitian, i.e. $m^0_{\mu \nu} = m^0_{\nu \mu}$.

$$m^0_{\mu \nu} = -\langle \mu | (r \times p) e^{-iDl \cdot r} | \nu \rangle$$

(10)

The second step is the result of $re^{-iDl \cdot p} = e^{-iDl \cdot p} r + [r, e^{-iDl \cdot p}]$ where $[\cdot, \cdot]$ is the commutator. The third step evaluates the commutator in the second term using the relationship $[r, f(p)] = if'(p)$ which holds for any function of momentum $f(p)$ expressed in atomic units.\textsuperscript{53} The last step uses that the magnetic dipole and momentum matrix elements are pure imaginary, so taking their complex conjugates is equivalent to negating them.

Expressing the magnetic dipole matrix in a Hermitian form will help us to collect terms that arise during the derivation and is convenient for storing/manipulating the matrix in our implementation. Defining

$$\tilde{m}^{0t}_{\mu \nu} = \frac{1}{2}(m^0_{\mu \nu} - m^0_{\nu \mu}) = m^0_{\mu \nu} + \frac{1}{2} Dl \times p^0_{\mu \nu} = (\tilde{m}^0_{\mu \nu})^*$$

(11)

produces a Hermitian matrix by splitting the origin dependent momentum term between the given matrix element and the corresponding adjoint matrix element.

We can now proceed to transforming the magnetic dipole operator to a translation invariant form. This involves substituting the length operator $r$ with a translation invariant form\textsuperscript{38,39,52}

$$r \equiv i \exp (ik \cdot r) \nabla_k \exp (-ik \cdot r).$$

(12)

Applying this transformation to the magnetic dipole operator yields

$$-r \times p = -i e^{ik \cdot r} \nabla_k e^{-ik \cdot r} \times p$$

$$= e^{ik \cdot r} (-i \nabla_k \times p) e^{-ik \cdot r} + e^{ik \cdot r} (-i \nabla_k \times [e^{-ik \cdot r}, p])$$

$$= e^{ik \cdot r} (-i \nabla_k \times p) e^{-ik \cdot r} + e^{ik \cdot r} (-i \nabla_k \times k) e^{-ik \cdot r}$$

$$= -i e^{ik \cdot r} \left[ (\nabla_k \times p) + (\nabla_k \times k) \right] e^{-ik \cdot r}$$

(13)

The second step uses the identity $\exp (ik \cdot r) p = p \exp (ik \cdot r) + [\exp (ik \cdot r), p]$. The commutator is then evaluated in the third step using $[f(r), p] = i f'(r)$.\textsuperscript{53}

Using the transformed operator, we can now derive magnetic dipole matrix elements between Bloch functions

$$\tilde{m}_{\mu k, \nu q} = -i \langle \nu | e^{ik \cdot r} ((\nabla_k \times p) + (\nabla_k \times k)) e^{-ik \cdot r} | \mu \rangle$$

$$= -i \langle u_{\nu k} | \nabla_k \times p | u_{\nu k} \rangle - i \langle u_{\mu k} | \nabla_k \times k | u_{\mu k} \rangle$$

(14)

with

$$|q \rangle = \sum_{l_1=-L_1}^{L_1} \sum_{l_2=-L_2}^{L_2} \sum_{l_3=-L_3}^{L_3} e^{i k (\Omega l \cdot r)} \sum_{\nu=1}^{\Omega} C_{\nu q} (k) \chi^\dagger_{\nu} (r)$$

(15)

and

$$u_{\nu k} (r) = e^{-i k \cdot r} |q \rangle$$

(16)

$|q \rangle$ is the $q$th Bloch function at point $k$ in reciprocal space, $u_{\nu k} (r)$ is the cell periodic part of that Bloch function, and $C$ is the matrix of crystal orbital (CO) coefficients for that $k$ point.\textsuperscript{38,39,54} To simplify the notation, we write the triple sum over cell indices as a single sum over the multi-index $l$

$$\sum_{l=-L}^{L} = \sum_{l_1=-L_1}^{L_1} \sum_{l_2=-L_2}^{L_2} \sum_{l_3=-L_3}^{L_3}$$

(17)

The crystal orbital PBC magnetic dipole matrix is indicated as $\tilde{m}$ to distinguish it with from the AO matrix $m$ and the Hermitian AO matrix $\tilde{m}$. We now must express these reciprocal-space, CO matrix elements in terms of real-space, AO matrix elements so they can be evaluated.
We can start to evaluate the first term on the right hand side Eq. 14 by applying the operators sequentially to the cell periodic ket

\[ -i \mathbf{p} | u_{qk} \rangle = \left[ - \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \frac{\partial \chi_{\nu}^{l} (r)}{\partial \mathbf{r}} + i k \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \chi_{\nu}^{l} (r) \right] \tag{18} \]

where \( \Xi \) is simply a collection of the terms produced by applying the momentum operator to the ket. Continuing to apply \( \nabla_k \times \) yields

\[ \nabla_k \times \Xi = \left[ i \mathbf{r} \times \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \frac{\partial \chi_{\nu}^{l} (r)}{\partial \mathbf{r}} \right] \tag{19a} \]

\[ -i \sum_{l=-L}^{L} Dl \times e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \frac{\partial \chi_{\nu}^{l} (r)}{\partial \mathbf{r}} \tag{19b} \]

\[ \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} \frac{\partial C_{\nu} (k)}{\partial k} \chi_{\nu}^{l} (r) + ik \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} \frac{\partial C_{\nu} (k)}{\partial k} \chi_{\nu}^{l} (r) \tag{19c} \]

We can evaluate the ket of the second term of Eq 14 in the same way

\[ -i \nabla_k \times k | u_{qk} \rangle = \left[ - \mathbf{r} \times e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \chi_{\nu}^{l} (r) \right] \tag{20d} \]

\[ + \sum_{l=-L}^{L} (Dl) \times k e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} C_{\nu} (k) \chi_{\nu}^{l} (r) \tag{20e} \]

\[ -ik \sum_{l=-L}^{L} e^{ik(Dl-r)} \sum_{\nu=1}^{\Omega} \frac{\partial C_{\nu} (k)}{\partial k} \chi_{\nu}^{l} (r) \tag{20f} \]

Notice, Eqs. 19d-f and 20d-f are identical except for their sign, so these contributions will cancel out. Projecting on the cell periodic bra in Eq. 19, we obtain an expression for the periodic magnetic dipole matrix

\[ \mathbf{m} = \begin{bmatrix} C^{\dagger} \mathbf{m} \mathbf{C} \tag{21a} \\
- i C^{\dagger} (\nabla_k \times \mathbf{p}) \mathbf{C} \tag{21b} \\
- i C^{\dagger} \mathbf{p} \mathbf{C} \times \mathbf{U} \tag{21c} \end{bmatrix} \]

where 21a-c are the corresponding terms to 19a-c. \( \mathbf{U} \) is the vector of matrices that transforms the CO coefficients \( \mathbf{C} \) to their gradient with respect to \( \mathbf{k} \), \( \nabla_k \mathbf{C} = \mathbf{C} \mathbf{U} \), as defined in Ref. 38. We can make one further simplification by noting that

\[ -i \nabla_k \times \mathbf{p} \mu_{\nu} = -i \nabla_k \times \sum_{l=-L}^{L} e^{ik(Dl-r)} \mathbf{p}_{\mu \nu}^{ot} \]

\[ = \sum_{l=-L}^{L} e^{ik(Dl-r)} \times \mathbf{p}_{\mu \nu}^{ot} \tag{22} \]

which we can utilize to transform the real-space magnetic dipole matrix \( \mathbf{m} \) to the Hermitian matrix \( \tilde{\mathbf{m}} \) in Eq. 11.

The resulting expression for the periodic magnetic dipole is

\[ \tilde{\mathbf{m}} = C^{\dagger} \mathbf{m} \mathbf{C} - \frac{i}{2} C^{\dagger} (\nabla_k \times \mathbf{p}) \mathbf{C} - i C^{\dagger} \mathbf{p} \mathbf{C} \times \mathbf{U} \tag{23} \]

Recently, Rérat and Kirtman independently published a derivation of the PBC magnetic dipole, along with some proof of concept calculations of the \( \beta \) tensor\(^{37} \). As Rérat and Kirtman note, ensuring that \( \beta \) has all real elements is equivalent to the constraint that \( \tilde{\mathbf{m}} \) is Hermitian. However, the second term in Eq. 23 is anti-Hermitian and the third term in non-Hermitian. To ensure that the OR tensor is real, we explicitly symmetrize the magnetic dipole matrix. In practice, we only need to symmetrize the third term of Eq. 23, as the first term is already Hermitian and the second term, being anti-Hermitian, is canceled out by the symmetrization.

**B. Periodic Electric Quadrupole**

The derivation of electric quadrupole for a periodic system proceeds in much the same way as for the magnetic dipole. The following will focus on the velocity form of the electric quadrupole operator, as this is the form used in both the modified velocity gauge (MVG)\(^{35} \) and origin-independent length gauge [LG(OI)].\(^{5} \) In the velocity gauge, the real space matrix elements of the electric quadrupole are written as

\[ Q_{\mu \nu}^{ot} = \langle \mu | \frac{1}{2} (r \otimes \mathbf{p} + \mathbf{p} \otimes r) | \nu \rangle \]

\[ = \langle \mu | r \otimes \mathbf{p} | \nu \rangle = \langle \mu | r \otimes \mathbf{p} e^{-i Dl \mathbf{p}} | \nu \rangle \tag{24} \]

where \( \otimes \) is the outer product and \( \mathbf{C} \) is the symmetric outer product. Again, the presence of the translation operator leads to a non-Hermitian matrix, which we can correct by reallocating the deviation from Hermiticity for a given matrix element evenly between itself and its corresponding adjoint element. We first determine the form of this deviation by moving the translation operator from
where $\Gamma$ just collects the intermediate terms produced by applying the momentum operator. Continuing to apply

$$Q_{\mu\nu}^{0l} = \langle \mu_0| r \circ p e^{-iD_l p} | \nu_0 \rangle$$
$$= \langle \mu_0| r \circ p | \nu_0 \rangle + \langle \mu_0| [r, e^{-iD_l p}] \circ p | \nu_0 \rangle$$
$$= \langle \mu_0| r \circ p | \nu_0 \rangle + D_l \circ (\langle \mu_0| r | \nu_0 \rangle)$$
$$= -Q_{\nu\mu}^{0l} - D_l \circ p^{0l}_{\nu\mu}$$ (25)

Knowing the form of the deviation, we can define a Hermitian quadrupole in the same manner as for the magnetic and electric dipoles

$$\hat{Q}_{\mu\nu}^{0l} = \frac{1}{2} (Q_{\mu\nu}^{0l} - Q_{\nu\mu}^{0l}) = Q_{\mu\nu}^{0l} - \frac{1}{2} D_l \circ p^{0l}_{\mu\nu} = (Q_{\nu\mu}^{0l})^*$$ (26)

We can now proceed to apply the transformation of Eq. 12 to the quadrupole operator in order to make it translation invariant.

$$r \circ p = (i e^{i k \cdot p} \nabla_k e^{-i k \cdot p}) \circ p$$
$$= e^{i k \cdot r} (i \nabla_k \circ p) e^{-i k \cdot r} + e^{i k \cdot r} (i \nabla_k \circ [e^{-i k \cdot r}, p])$$
$$= e^{i k \cdot r} (-i \nabla_k \times p) e^{i k \cdot r} + e^{i k \cdot r} (i \nabla_k \circ k) e^{-i k \cdot r}$$
$$= i e^{i k \cdot r} ([\nabla_k \circ p] + (\nabla_k \circ k)) e^{-i k \cdot r}$$ (27)

The expression for the PBC quadrupole operator in Eq. 13 is very similar in form to that of the PBC magnetic dipole in Eq. 13, with the only difference being a change of sign and the substitution $\times \rightarrow \circ$. Consequently, applying the PBC quadrupole operator to the cell periodic ket leads to similar contributions. Applying the first term of the transformed operator to the cell periodic ket, we obtain

$$i \nabla_k \circ r \circ p = \left[ \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \sum_{\nu=1}^{L} C_{q\nu}(k) \frac{\partial \chi_{\nu}(r)}{\partial r} \right] r \circ p_{\mu\nu}$$
$$= \Gamma$$ (28)

The remaining terms simplify to

$$\nabla_k \circ r \circ p_{\mu\nu} = i \nabla_k \circ \left[ \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \frac{\partial \chi_{\nu}(r)}{\partial r} \right] r \circ p_{\mu\nu}$$
$$= -\sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \frac{\partial \chi_{\nu}(r)}{\partial r}$$ (30a)

where $\delta$ is the Kronecker delta. The "extra" term 29g (compare to Eq. 19) appears since the outer product allows $\nabla_k$ to act on the $\hat{k}$ in the second term of Eq. 28. Applying to the ket of the second term proceeds similarly

$$\left[ \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \sum_{\nu=1}^{L} C_{q\nu}(k) \chi_{\nu}(r) \right]$$
$$= \left[ \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \sum_{\nu=1}^{L} C_{q\nu}(k) \chi_{\nu}(r) \right]$$
$$= \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \sum_{\nu=1}^{L} C_{q\nu}(k) \chi_{\nu}(r)$$ (30f)

where these terms are equal and opposite in sign to Eq. 29d-g and thus cancel out of the final expression. After applying the bra, the remaining terms simplify to

$$\hat{Q} = \left[ C^\dagger Q C \right]$$ (31a)
$$+ i C^\dagger (\nabla_k \circ p) C$$ (31b)
$$+ i C^\dagger p C \circ U$$ (31c)

It is convenient to re-express the AO basis quadrupole $\hat{Q}$ as the Hermitian matrix $\hat{Q}$. Noting that

$$i \nabla_k \circ p_{\mu\nu} = i \nabla_k \circ \left[ \sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \frac{\partial \chi_{\nu}(r)}{\partial r} \right] r \circ p_{\mu\nu}$$
$$= -\sum_{l=L}^{L} e^{i k \cdot (D_l - r)} \frac{\partial \chi_{\nu}(r)}{\partial r}$$
the PBC electric quadrupole can be rewritten as
\[
\mathbf{Q} = \mathbf{C}^\dagger \hat{\mathbf{Q}} \mathbf{C} + \frac{i}{2} \mathbf{C}^\dagger \left( \nabla_k \otimes \mathbf{p} \right) \mathbf{C} + i \mathbf{C}^\dagger \mathbf{p} \mathbf{C} \otimes \mathbf{U}
\]  
(33)
to incorporate \( \hat{\mathbf{Q}} \). To the best of our knowledge, this is the first derivation of the PBC electric quadrupole. Notice the resemblance in form with Eq. 23, where the main difference is the use of a symmetric direct product rather than a cross product, along with a change of sign in each term. As was the case with the Eq. 23, we need to ensure that \( \hat{\mathbf{Q}} \) is Hermitian and we again achieve this via explicit symmetrization, with the second term in Eq. 33 canceling out due to being anti-Hermitian.

Once the perturbed density \( \mathbf{P}^\mu \) is evaluated from the periodic CPKS equations, the \( \beta \) and \( \mathbf{A} \) tensors are computed as:
\[
\beta_{\alpha\beta} = \sum_k \sum_{ai} \hat{m}_{\alpha,ai}(k) \mathbf{P}^\mu_{\beta,ai}(k)
\]
(34) 
\[
A_{\alpha,\beta\gamma} = \sum_k \sum_{ai} \hat{Q}_{\beta\gamma,ai}(k) \mathbf{P}^\mu_{\alpha,ai}(k)
\]
(35) 
and then combined as in Eqs. 1 and 7 to obtain the \( \mathbf{B} \) tensor. Note that both expressions in Eqs. 34-35 are missing a term that depends on the \( k \)-derivative of the perturbed density,\(^{56}\) but we will show in section IV that this is numerically small for practical calculations. Although the tensors calculated within the MVG approach are origin invariant,\(^{55}\) this is not directly the case with the LG approach. However, this issue is resolved by applying the LG(OI) transformation,\(^{2,3}\) which avoids the need to employ gauge-including atomic orbitals.\(^{49,57-59}\)

C. Chiral Crystal OR

The optical rotation of chiral crystals can only be measured accurately along the optic axis, because in any other direction the circular birefringence is obscured by the much larger linear birefringence.\(^{25,60}\) The optic axis is defined as the direction perpendicular to the central circular section(s) of the ellipsoid called the indicatrix. The semi-axes of this ellipsoid are oriented along the principal axes of the dielectric tensor \( \varepsilon_r \). For low-polar media, the dielectric tensor is related to the electric dipole-electric dipole polarizability tensor \( \mathbf{A} \) (all in a.u.) as\(^{25,60}\)
\[
\mathbf{A} = \mathbf{R}_{\alpha}(\theta) \mathbf{B} \mathbf{R}_{\alpha}(\theta)^\dagger
\]
(39)
where \( \mathbf{R}_{\alpha}(\theta) \) is the rotation matrix. Finally, the \( z \) diagonal component of the transformed tensor, \( B_{zz}^{33} \), corresponds to the measured OR of the crystal along the optic axis. The OR for chiral crystals is usually expressed in deg/mm; the conversion from deg L dm\(^{-1}\) mol\(^{-1}\) to deg/mm is obtained by multiplying the OR by \( 100N_AV_{dm}^{-1} \) when \( N_A \) is Avogadro’s number and \( V_{dm} \) is the unit cell volume in dm\(^3\). We emphasize two important details: i) in approximate (i.e., virtually all) calculations, the optic axes are different for different choices of gauge, because the numerical values of the \( \alpha \) tensor depend on this choice; ii) for LG(OI), the \( \mathbf{B} \) tensor is already oriented along the principal axis of the corresponding \( \alpha \) tensor,\(^{2,3}\) therefore only the second transformation (in Eq. 39) is necessary.

III. COMPUTATIONAL DETAILS

All calculations were performed with a development version of the GAUSSIAN suite of programs.\(^{61}\) Two functionals were used: the pure functional SVWN5 (called LDA in Ref. 37) and the range-separated hybrid HSE06,\(^{62}\) which has exact exchange only in the short range. Both functionals allow faster simulations for periodic systems because exact exchange is absent in the
A pruned (99,590) grid was used for both the energy and linear response part of the calculations for all systems. Several basis sets and k-point grids were used for different test systems, as detailed in section IV. The OR tensors were computed with the MVG and LG(OI) schemes.

IV. RESULTS

A. Origin Dependence

The first system we consider is a chain of H₂O₂ molecules with a 1D periodicity along the direction of the O–O bond, with a single molecule in the unit cell and a lattice vector a = 4 Å, as in Ref. 37. The geometry of the unit cell is reported in Table S1 of the supporting information (SI). This is almost the same setup as in Ref. 37: the lattice vector is along the x axis, but now the origin is located at the center of the O–O bond, so that the C₂ rotation axis coincides with the y axis. A grid of 500 k points was used.

The results in Tables I-II demonstrate that the full OR tensor B is origin invariant as for molecules. The results in the tables are obtained with the guess density (the SOS approach in Ref. 37) at the SVWN5/STO-3G level with two choices of gauge, MVG and LG(OI), respectively, at the original geometry and at one translated geometry (O − d origin, with d = (100, 100, 100) Å). B(β) and B(A) represent the contributions of β and A to B, respectively, see Eqs. 1 and 7.

<table>
<thead>
<tr>
<th>O</th>
<th>O − d</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>0.7108</td>
<td>0.0000</td>
</tr>
<tr>
<td>y</td>
<td>0.0000</td>
</tr>
<tr>
<td>z</td>
<td>-1.7993</td>
</tr>
<tr>
<td>B(β)</td>
<td>B(β)</td>
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<tr>
<td>x</td>
<td>y</td>
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<tr>
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<td>y</td>
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<tr>
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<td>0.0000</td>
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<tr>
<td>y</td>
<td>0.0000</td>
</tr>
<tr>
<td>z</td>
<td>-0.9162</td>
</tr>
<tr>
<td>B(A)</td>
<td>B(A)</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>0.2214</td>
<td>0.0000</td>
</tr>
<tr>
<td>y</td>
<td>0.0000</td>
</tr>
<tr>
<td>z</td>
<td>-0.8831</td>
</tr>
</tbody>
</table>

The results in Tables I-II demonstrate that the full OR tensor B is origin invariant as for molecules. The results in the tables are obtained with the guess density (the SOS approach in Ref. 37) at the SVWN5/STO-3G level with two choices of gauge, MVG and LG(OI), respectively, at the original geometry and at one translated geometry by -100 Å in every Cartesian direction. The tables also report the β and A tensor contributions to B, see Eqs. 2-5, which are individually origin dependent but in opposite directions, such that these effects cancel out in B. More specifically, for MVG in Table I, only the trace of β is origin invariant, but the individual tensor elements are not; the yy element is origin invariant because of the symmetry of this specific system, but it would not be in general. For LG(OI) in Table II, the diagonal elements of the β and A tensors are fixed by the LG(OI) transformation and only the off-diagonal elements are origin dependent. It is important to note that the elements of the β and A tensors are comparable in magnitude. Furthermore, each diagonal element of B depends on the other two diagonal elements of β and A, see Eq. (7); for instance, Bzz ∝ βxx + βyy. These details are not relevant for the isotropic OR of systems in gas and solution phase because this is proportional to Tr(B) and the A tensor is traceless, but they are fundamental for oriented systems. Therefore, only the B tensor can be compared with experimental data.

B. Comparison with Cluster Models

The same model system is used to compare PBC and large molecular cluster calculations, which helps to verify that the implementation is correct. The SVWN5/cc-pVQZ model chemistry was employed as in Ref. 37, and the PBC calculation used a 1000 k-point mesh. We consider two molecular cluster sizes with 39 and 37 H₂O₂ units. The “unit cell” tensors are then obtained as the average of the 39-unit calculation and as the averaged difference between the 39 and 37-unit calculations. For this comparison, using a geometry with the origin in the center of the O–O bond is convenient because the unit cell in the PBC calculation matches the central unit in the cluster calculations. The results for the fully relaxed density with MVG and LG(OI) are shown in Figures 1.
and 2, respectively. The figures include the tensor elements and the spatially averaged trace (all in a.u.) for the full $\mathbf{B}$ tensor as well as for the $\beta$ and $A$ contributions. The isotropic OR values (in units of deg L dm$^{-1}$ mol$^{-1}$) are reported in Table III and all the tensor elements are reported in Tables S2-S4 of the SI.

The data in Figures 1-2 show very good agreement between the molecular cluster and PBC calculations for all the elements of the $\mathbf{B}$ tensor, irrespective of the choice of gauge. The largest difference is found for the $xz$ element: 9-11% for MVG and 15-17% for LG(OI). The discrepancy is likely due simultaneously to the limited size of the cluster models and the lack of the $\nabla_k P^\mu$ terms.

**TABLE III.** Isotropic OR (deg L dm$^{-1}$ mol$^{-1}$) at 300 nm for H$_2$O$_2$ calculated with MVG and LG(OI) at the SVWN5/cc-pVQZ level for the periodic chain (PBC), for the average of the 39-unit molecular cluster (39/39), and for the averaged difference between the 39 and 37-unit molecular clusters [(39-37)/2].

<table>
<thead>
<tr>
<th></th>
<th>MVG</th>
<th>LG(OI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39/39</td>
<td>32.2</td>
<td>34.0</td>
</tr>
<tr>
<td>(39-37)/2</td>
<td>31.0</td>
<td>32.5</td>
</tr>
<tr>
<td>PBC</td>
<td>35.4</td>
<td>35.4</td>
</tr>
</tbody>
</table>
in the PBC expressions in Eqs. 34 and 35, respectively. However, these effects are small and they are likely considerably less significant than the approximations in the level of theory and basis set size that are necessary for the simulation of real systems. The MVG and LG(OI) results also match each other for the isotropic OR (see the Trace values in the figures and the results in Table III). This indicates that this basis set is close to completeness for this system and the calculations approach gauge invariance.\textsuperscript{54} The PBC-MVG value in Table III is in very good agreement with the value reported in Ref. 37: 36.1 deg L dm\textsuperscript{-1} mol\textsuperscript{-1} (the small discrepancy is due to the extreme sensitivity of this property to unavoidable differences in numerical thresholds between different implementations). The differences in the individual elements of the $\mathbf{B}$ tensor between MVG and LG(OI) is due to the fact the SVD transformation in the latter corresponds to a rotation of the system;\textsuperscript{3} repeating the MVG calculation at this rotated geometry would lead to matching elements. More importantly, the molecular cluster and PBC calculations do not match each other for the $\mathbf{B}$ and $\mathbf{A}$ contributions to $\mathbf{B}$, as shown in panels b) and c) of Figures 1-2. The $yy$ and $zz$ elements of the $\mathbf{B}$ contribution are much smaller in the PBC case compared to the molecular cluster case; simultaneously, the corresponding elements of the $\mathbf{A}$ contribution have the opposite sign. It is only in the full $\mathbf{B}$ tensor that these contributions combine properly to provide the same picture.

### C. Choice of Functional and Basis Set

We provide a preliminary comparison of the basis set function and functional dependence of OR calculations between isolate molecules and periodic systems. Specifically, we compare the isolated $\text{H}_2\text{O}_2$ molecule at the geometry of the unit cell with 1D-periodic calculations as in the previous examples for two functionals: SVWN5 and HSE06, and three basis sets: aug-cc-pVTZ, cc-pVQZ, and aug-cc-pVQZ (in the following shortened to aTZ, QZ, and aQZ, respectively). A grid of 500 $k$ points was used in the PBC calculations. To simplify the comparison, we focus on the isotropic OR (i.e., $\text{Tr}(\mathbf{B})$) rather than the whole tensor. The specific rotation values for all calculations are reported in Table S5 of the SI. Here, we report relative $\%$ changes in OR calculated as:

$$
\Delta QZ = 100 \times \left( \frac{[\alpha]^{X,Y}_{QZ} - [\alpha]^{LG(OI)}_{QZ}}{[\alpha]^{LG(OI)}_{QZ}} \right)_{W}^{Z} \tag{40}
$$

$$
\Delta_{HSE06} = 100 \times \left( \frac{[\alpha]^{SVWN5,Y}_{Y} - [\alpha]^{HSE06}_{Y}}{[\alpha]^{HSE06}_{Y}} \right)_{Z}^{X} \tag{41}
$$

where $X = \text{MVG}, \text{LG(OI)}$; $Y = \text{aTZ, QZ, aQZ}$; $W = \text{SVWN5, HSE06}$; and $Z = \text{Mol, PBC}$. In other words, $\Delta QZ$ in Eq. 40 tests the change in basis set and choice of gauge within the same method ($W$) and system ($Z$), while $\Delta_{HSE06}$ in Eq. 41 tests the change in functional within the same choice of gauge ($X$), basis set ($Y$), and system ($Z$).

#### FIG. 3. Relative changes ($\%$) of isotropic OR at 300 nm for isolated (Mol) and 1D-periodic (PBC) $\text{H}_2\text{O}_2$: a) $\Delta QZ$ for SVWN5, b) $\Delta QZ$ for HSE06, c) $\Delta_{HSE06}$, see text for the definitions.

The calculated values of $\Delta QZ$ are plotted in Figure 3a-b. These results show that, for the molecular case, both functionals are close to basis set completeness and gauge invariance. However, the differences between aTZ and aQZ for any choice of gauge are considerably smaller than with QZ. For instance, the aTZ-aQZ difference within the same gauge is 2-3% and $< 10\%$ between choices of gauge; on the other hand, the difference with either basis set and QZ is 15-25% within the same gauge, and the MVG-LG(OI) difference for QZ is 16-21%. This indicates that the use of diffuse functions is more important than increasing the basis set size from $T\zeta$ to $Q\zeta$. However, the situation is very different for the PBC calculations. Fig-
ure 3a-b shows that QZ results are 2-2.5 times smaller than the aTZ ones, and 3-4 times smaller than the aQZ ones. The $\Delta QZ$ values are smaller for HSE06/aTZ than for SVWN5, but the opposite trend manifests for aQZ. The difference between choices of gauge is most significant for the aTZ basis set. The change in trend with respect to the molecular case is likely due to the spatial extension of diffuse functions, which may lead to strong interactions between repeated units in adjacent cells.

The difference between functionals ($\Delta_{HSE06}$) is shown in Figure 3c. The SVWN5 results are significantly larger than those obtained with HSE06. For the molecular case, QZ values are twice as large with the pure functional than with the hybrid, and thrice as large with aTZ and aQZ. For the periodic calculations, this difference increases to a factor of three and four for QZ and aTZ, respectively, but it decreases to a factor of two for aQZ. The change from molecular to periodic cases is likely due to intermolecular interactions. However, the different behavior across basis sets may be another indication that diffuse functions may be problematic for PBC calculations. In any case, the choice of functional seems to have the largest impact on the calculated values, followed by the choice of basis set, and to a much smaller degree by the choice of gauge.

**D. Tartaric Acid Crystal**

The last system that we consider is tartaric acid, (2R,3R)–C$_4$H$_6$O$_6$, for which experimental data are available. We used the same geometry as in Rérat et al., but the calculations were performed with HSE06 rather than PBE0 because the former is computationally more efficient. The $k$ point grid is $6 \times 8 \times 8$. The geometry was also rotated so that the coordinate axes coincide with the principal axes of the symmetric part of the mixed-gauge electric dipole–electric dipole polarizability, which is the best representation of the coordinate system for the LG(OI) approach as explained in Ref. 3. The unit cell geometry is reported in Table S6 of the SI.

<table>
<thead>
<tr>
<th>$\beta$ (deg/mm)</th>
<th>LG(OI)</th>
<th>Exp$^{26}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{xx}$</td>
<td>0.1206</td>
<td>0.1184</td>
</tr>
<tr>
<td>$\delta_{yy}$</td>
<td>0.0332</td>
<td>0.0312</td>
</tr>
<tr>
<td>$\varepsilon_{zz}$</td>
<td>−5.6</td>
<td>−4.6</td>
</tr>
<tr>
<td>$\theta_{zz}$</td>
<td>0.0480</td>
<td>0.0504</td>
</tr>
<tr>
<td>$\theta_{yy}$</td>
<td>−0.0041</td>
<td>−0.0038</td>
</tr>
<tr>
<td>$\varepsilon_{xx}$</td>
<td>−5.1</td>
<td>−4.6</td>
</tr>
</tbody>
</table>

Table IV reports a comparison of experimental and calculated data for the angle $2\theta$, the birefringence $\delta_{\alpha\beta} = n_{\alpha} - n_{\beta}$, and the optical rotation along the z axis, all of which are defined in Section II C. We report these values calculated along the $\varepsilon_r$, principal axes (denoted by the superscript $\varepsilon$) and with the coordinate system rotated to have the z axis along the optic axis (denoted by the $\alpha$ superscript), see discussion in section II C. The full tensors and other intermediate quantities that were used to evaluate the data in the table are reported in Tables S7–S10 of the SI. The agreement between theoretical and experimental values in Table IV is very good, considering the basis set utilized in the calculations. The error is 14-16% for the angle $2\theta$ and 19-29% for the birefringence $\delta$, indicating that the electric dipole-electric dipole polarizability is reasonably accurate. The error for the OR is larger (about 50% if the latest experimental value of $−12.5 \pm 1.0$ deg/mm is considered), but it is consistent with the error for the isotropic OR of molecules at this level of theory. The choice of gauge is less important than that of the level of theory as the MVG and LG(OI) results are very close to each other. This is also confirmed by the polar plots representation of the OR tensors in Figure 4–5. In these plots, the unit cell was rotated such that the coordinate system matches the orientation of the tensor, and $z$ coincides with the optic axis. The difference in geometrical orientation between MVG and LG(OI) is small, barely detectable in the figures. The polar plots are also virtually indistinguishable between figures. It is interesting to emphasize that the plots of the $\beta$ and $A$ contributions to $B$ were scaled down by a factor of 10 compared to the full $B$ plot, to fit within the same picture frame.

These results are also in reasonable agreement with those reported in Rérat et al., which were obtained with the same basis set but a different functional (PBE0). A direct comparison is only possible with the MVG birefringence ($\delta_{xx} = 0.0916$, $\delta_{yy} = 0.0256$): the better agreement with experiment suggests that long-range exact exchange (absent in HSE06) may play an important role in OR calculations of solids. The angle $2\theta$ is only reported in Ref. 37 as an average value across multiple calculations with different choices of gauge and with/without orbital relaxation ($70^\circ \pm 10^\circ$), but it is in the same range as the values we report in Table IV. However, it is unclear how the OR is evaluated in Ref. 37, since only the diagonal elements of the $\beta$ tensor were calculated. If we build a partial tensor $\beta(MVG)$ with only the diagonal components of $\beta$ and we subject this to the transformations in Eqs. 38–39, we obtain $\beta_{zz}^{\alpha\alpha} = −8.8$ deg/mm, which is in good agreement with the $−6.6$ deg/mm reported in Ref. 37 (note that the levels of theory in this work and in Ref. 37 are different, thus all the numerical values used in Eqs. 38–39 are also different). On the other hand, if we repeat the procedure utilizing the full $\beta(MVG)$ tensor, the OR along the optic axis is nonsensical: $\beta_{zz}^{\alpha\alpha} = +103.1$ deg/mm, because it is in general origin dependent. Furthermore, it is stated in Ref. 37 that the contribution of
FIG. 4. Polar plots of the LG(OI) OR tensors (deg/mm) at 680 nm for tartaric acid: (a) $B$, (b) $\beta$ contribution to $B$, and (c) $A$ contribution to $B$. The $z$ axis is oriented along the optic axis, the axes and tensors are centered at the center of mass of the unit cell for clarity. The blue color corresponds to positive values of the tensor and the orange to negative values. The $B$ tensor is scaled by a factor of 2, the $\beta$ and $A$ tensors are scaled by a factor of 20 for clarity. Polar plots were made using Pymol\textsuperscript{66}.

The $A$ tensor along the optic axis is zero. This is not the case, because the contributions of $A$ to the diagonal of $B$ are of the type $A_{\alpha,\beta,\gamma}$, with $\alpha \neq \beta \neq \gamma$ (see Eq. 7), and the operators $\hat{\mu}_\alpha$ and $\hat{\Theta}_{\beta,\gamma}$ can belong to the same irrep. This is also confirmed visually in Figures 4-5 and numerically in Tables S9-S10 of the SI. Therefore, the good agreement with the measured OR reported in Ref. 37 may be fortuitous, and only the full $B$ tensor should be compared directly to experiment.

A final comment is warranted for the $yx$ birefringence when the $z$ and optic axes are aligned, which is not as close to zero as it should be even accounting for the numerical precision of the calculations ($\delta_{yx} = -0.0038$ for MVG in Table IV). The discrepancy is due to the
fact the linear relationship between the dielectric tensor and the $\alpha$ tensor in Eq. 36 is only approximate. The Clausius-Mossotti equation would be more accurate, but it is non-linear and more difficult to evaluate. By trial and error we found that the angle that sets $\delta_{\alpha\beta} = 0$ for MVG is $2\theta = 62.2^\circ$, rather than 66.5$^\circ$ as in the table. However, with this optimal angle the OR along the optic axis is only changed by 0.1 deg/mm (from -5.1 to -5.2 deg/mm). Therefore, this error is negligible compared to other approximations.

V. CONCLUSIONS

In this work, we report the derivation and implementation at DFT level of the magnetic dipole and electric quadrupole integrals for PBC calculations. These integrals are used to evaluate the mixed polarizability tensors $\beta$ and $\alpha$ that form the full OR tensor $B$ for oriented systems. The implementation is tested in section IV, where we show that the $B$ tensor is origin invariant, see Tables I-II. We also show that the PBC calculations match the results for model cluster calculations for all tensor elements, see Figures 1-2. A preliminary analysis indicates that the choice of density functional, basis set, and gauge integrals are used to evaluate the mixed polarizability tensors $\beta$.

The Supporting Information includes: the geometry of the unit cell of the 1D $H_2O_2$ chain; the MVG and LG(OI) tensors for the 39 and 37-unit molecular chains of $H_2O_2$ molecules as well as the tensors for the PBC calculations; the specific rotation for the periodic 1D $H_2O_2$ chain computed with the SVWN5 and HSE06 functionals and the aTZ, QZ, and aQZ basis sets; the geometry of the unit cell of tartaric acid; the MVG and LG(OI) $\alpha$ tensors, refractive indices along the $\alpha$ principal axes, and OR tensors for the tartaric acid crystal.

ACKNOWLEDGMENTS

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56 Private communication from M. Rérat and B. Kirtman.