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First-principles calculation of the optical rotatory power of periodic systems: Modern theory with modern functionals

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An analysis of orbital magnetization in insulators is provided. It is shown that a previously proposed electronic orbital angular-momentum operator generalizes the "modern theory of orbital magnetization" to include nonlocal Hamiltonians. Expressions for magnetic transition dipole moments needed for the calculation of optical rotation and other properties are developed. A variety of issues that arise in this context are critically analyzed. These issues include periodicity of the operators, previously proposed band dispersion terms, and, if and where needed, evaluation of reciprocal space derivatives of orbital coefficients. Our treatment is used to determine the optical rotatory power of insulators employing a formulation that accounts for electric dipole–electric quadrupole (DQ), as well as electric dipole–magnetic dipole, contributions. An implementation in the public CRYSTAL program is validated against a model finite system and applied to the α-quartz mineral through linear-response time-dependent density functional theory with a hybrid functional. The latter calculations confirmed the importance of DQ terms. Agreement against experiment was only possible with (i) use of a high-quality basis set, (ii) inclusion of a fraction of nonlocal Fock exchange, and (iii) account of orbital-relaxation terms in the calculation of response functions.

I. INTRODUCTION

The rotatory power of an optically active material refers to its capacity to rotate the plane of polarization of plane-polarized light. For a nonmagnetic medium, the angle of rotation per unit distance Φ_u of light of wavelength λ, propagating along the direction u, may be expressed in terms of diagonal elements of the optical rotation (OR) tensor β_u [1],

$$\Phi_u(\omega) = \left(\frac{2\pi}{\lambda}\right)^2 \frac{4\pi \beta_u(\omega)}{V}, \qquad (1)$$

where V is the volume per unit cell of the optically active medium and ω is the frequency of the electromagnetic radiation. At variance with the notation of a previous article [2], here u is the direction of the light beam.

For finite systems, the theory is well established, based on a multipole expansion of the interaction Hamiltonian $\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}$ [3,4]. This results in a formula for the OR angle about the u direction that is proportional to the sum of a dynamic magnetic dipole–electric dipole (DD) and an electric dipole–electric quadrupole (DQ) term [3–5]. For samples in solution, orientational averaging then leads to a sum over all directions given by the trace of the DD tensor (the DQ tensor being traceless) [3–6].

For infinite periodic systems (e.g., crystalline solids), the theory of OR or, for that matter, the orbital response to electromagnetic fields in general is not as straightforward. In the case

of electric fields, it was noticed as early as 1962 that integrals of the simple operator $-\mathbf{r}$ over crystalline orbitals (COs) $\psi_{n,\mathbf{k}}$,

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}+i\phi_n(\mathbf{k})} u_{n,\mathbf{k}}(\mathbf{r}), \qquad (2)$$

are undefined since their value depends on the (arbitrary) choice of the unit cell [7]. In Eq. (2), $|u_{n,\mathbf{k}}\rangle$ are the cell-periodic Bloch functions (BF) and $\phi(\mathbf{k})$ is the arbitrary (apart from the constraints provided by periodic boundary conditions) phase of the COs.

In the same 1962 paper, Blount noted that this problem can be avoided by replacing $-\mathbf{r}$ for $-ie^{i\mathbf{k}\cdot\mathbf{r}}\nabla_k e^{-i\mathbf{k}\cdot\mathbf{r}}$, leading to the replacement $-\mathbf{r} \rightarrow -(\mathbf{r} + i\nabla_k)$ for periodic systems. The same operator was applied by Otto (1992) as well as Kirtman *et al.* (2000), then extended to two dimensions (2D) and 3D by Ferrero *et al.* (2008), and subsequently utilized by many others for the calculation of linear as well as nonlinear optical properties, vibrational spectra, and piezoelectricity, for instance [8–18]. This treatment also coincides with King-Smith, Vanderbilt, and Resta's "modern theory of polarization" [19–22].

As for magnetic fields in periodic systems, a suitable theoretical framework was first suggested around the same time by Brown and by Zak (1964) based on group-theoretic considerations [23–25]. However, their approach was not formulated in terms of conventional Bloch functions, as used in practical Kohn-Sham density functional theory (KS-DFT) calculations. Nonetheless, Brown and Zak's analysis provided the starting point for an understanding of the quantum Hall effect (and eventually topological insulators and other topological states of matter) in the work of Thouless and co-workers [26–28].

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A practical formulation for calculating the orbital magnetization of an insulator did not occur until much later with Ceresoli, Thonhauser, Vanderbilt, and Resta's (CTVR) "modern theory of orbital magnetization" [29,30]. This approach was soon after extended to Chern insulators and metals by Shi, Vignale, Xiao, and Niu (SVXN) [31]. SVXN also showed that their treatment was valid in the presence of electron-electron interactions, through a theoretical framework known as spin-current DFT (SC-DFT).

Applications of the CTVR theory have mostly been limited to tight-binding calculations or calculations with local or generalized gradient approximations, but not the hybrid functionals of generalized Kohn-Sham (GKS) theory, and without orbital relaxation effects [30,32–41]. Indeed, some of our recent work has shown that hybrid functionals may be particularly important within the framework of SC-DFT by providing a nonlocal dependence of the exchange-correlation (xc) functional on current densities, as practically demonstrated in the case of Weyl semimetals and $\mathbb{Z}_2$ topological insulators [42–50]. Here we show that a generalization of CTVR to include nonlocal functionals coincides with a previous treatment of the orbital response to magnetic fields by Springborg, Molayem, and Kirtman (SMK) [51].

The CTVR theory pertains to expectation values for calculation of the orbital magnetization (a first-order property). For higher orders (e.g., OR, a second-order property), we require transition moments between the ground and excited states. In this paper, we resolve a variety of issues that remain concerning the theory of OR.

Remaining issues include (i) the agreement (or lack thereof) versus large finite systems, (ii) the possibility of missing terms proportional to the derivative in reciprocal space of coefficients of the perturbed wave function, (iii) the possibility of missing "band dispersion" terms, (iv) a strategy for the effective treatment of quasidegeneracies, and (v) the importance of DQ terms for calculations in the solid state. Questions concerning items (i), (ii), and (v) are explicitly raised in Ref. [52]; item (iii) occurs as a result of the treatment in Ref. [53]; and item (iv) is a key computational issue that occurs in evaluating the matrix elements of ∇_k.

The paper is organized as follows: In Sec. II, we develop the formalism for the orbital magnetization from a Wannier function perspective. This analysis shows how the SMK "angular momentum" generalizes CTVR's "modern theory" to nonlocal functionals. In Sec. IV, we show how the same formalism for orbital magnetization may alternatively be developed from a perturbation theory perspective. This provides a convenient route for developing expressions for transition moments (and, thus, higher-order properties) and provides answers regarding items (i), (ii), and (v). Technical aspects of the formal developments are discussed in the appendices, including, particularly, Appendix C regarding (iii).

II. FORMALISM: WANNIER FUNCTION PERSPECTIVE

A. Review of modern theory for insulators

With infinite periodic systems, the eigenfunctions $|\psi_{n,\mathbf{k}}\rangle$ of the single-particle Hamiltonian,

$$\hat{H}|\psi_{n,\mathbf{k}}\rangle = \epsilon_{n,\mathbf{k}}|\psi_{n,\mathbf{k}}\rangle, \tag{3}$$

are crystalline orbitals (COs), which may be written in Bloch form as in Eq. (2). In the following, we use Dirac's notation for the abstract states $|\psi_{n,\mathbf{k}}\rangle$ [54]. Specific representations, e.g., in direct space, are obtained as $\langle\mathbf{r}|\psi_{n,\mathbf{k}}\rangle = \psi_{n,\mathbf{k}}(\mathbf{r})$.

A key quantity in the discussion of magnetic properties of periodic systems is the Chern (vector) invariant $\mathbf{C}$ [26],

$$\mathbf{C} = \frac{i}{2\pi}\int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} \langle\nabla_k u_{n,\mathbf{k}}| \wedge |\nabla_k u_{n,\mathbf{k}}\rangle. \tag{4}$$

In Eq. (4) and elsewhere, the superscript occ refers to the occupied manifold, while the subscript BZ indicates integration over the first Brillouin zone (FBZ). As will be discussed below, we are concerned here with systems where $\mathbf{C}$ vanishes in the absence of a magnetic field,

$$\mathbf{C} = \mathbf{0}, \tag{5}$$

thus excluding condensed-matter realizations of the anomalous quantum-Hall effect (Chern insulators) which are left for future work [55,56].

In the case of insulating systems with a vanishing $\mathbf{C}$, a unitary transformation of the BFs provides localized Wannier functions (WFs) $|n\mathbf{R}\rangle$,

$$|n\mathbf{R}\rangle = \Omega \int_{\text{BZ}} d\mathbf{k}\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}|u_{n,\mathbf{k}}\rangle, \tag{6a}$$

with the inverse transform given by

$$|u_{n,\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}|n\mathbf{R}\rangle, \tag{6b}$$

where Ω is the volume of the FBZ and $\mathbf{R}$ is a direct lattice vector (with the corresponding sum running over the infinite set). The transformation of Eq. (6) is of course, like the orbitals themselves, only determined up to an arbitrary phase $e^{i\phi'_n(\mathbf{k})}$. For the moment, we set $\phi'_n(\mathbf{k}) = 0$, its effect being discussed further on.

In the case of band insulators, the density matrix has exponential decay in direct space [57] and it is possible to represent the orbitals in well-localized form, as per Eq. (6a). This procedure is also applicable to $\mathbb{Z}_2$ topological insulators [58]. On the other hand, for metals, the power-law decay of the density matrix means that the localization procedure diverges [59]. A similar behavior occurs for Chern insulators due to the existence of conducting chiral edge states [60].

For "Wannier representable" band (or $\mathbb{Z}_2$ topological) insulators, CTVR write the orbital magnetization of a large, finite sample of N_c cells cut from the bulk as [30]

$$\mathbf{M} = -\frac{1}{2c\Omega N_c}\sum_{\mathbf{R}}^{N_c}\sum_n^{\text{occ}} \langle n\mathbf{R}|\mathbf{r}\wedge i[H,\mathbf{r}]|n\mathbf{R}\rangle, \tag{7}$$

where c is the speed of light. Equation (7) is justified and computationally convenient for local Hamiltonians, with matrix elements of the velocity operator $\hat{\mathbf{v}}$ that read

$$\langle n\mathbf{R}|\nabla_r/i|n\mathbf{R}\rangle = \langle n\mathbf{R}|i[H,\mathbf{r}]|n\mathbf{R}\rangle. \tag{8}$$

Indeed, substituting Eq. (8) into Eq. (7), $\mathbf{M}$ reduces to the standard first-order perturbation theory expression, in terms of a matrix elements of the electronic angular-momentum operator $\hat{\mathbf{L}} = \mathbf{r}\wedge\nabla_r/i$. At this point, we note that the situation

is different for calculations with a nonlocal GKS Hamiltonian since the replacement

$$\nabla_r \to -[H, \mathbf{r}] \tag{9}$$

fails to account for the fact that $\mathbf{r}$ does not commute with the nonlocal terms.

Let us stress that no multipole theory of the magnetic field can be written directly from $-[H, \mathbf{r}]$, other than through the replacement proposed by Eq. (9). In this sense, the ∇_r operator is the "fundamental quantity" (and not $-[H, \mathbf{r}]$).

In the thermodynamic limit (i.e., $N_s/N_b \to 0$, with N_b the number of WFs $|n\mathbf{R}\rangle$ centered in the interior of the sample and N_s the number centered at the surface), using translational symmetry, the contribution to Eq. (7) from the bulk WFs becomes [30]

$$\mathbf{M}_{\text{LC}} = -\frac{1}{2c\Omega} \sum_n^{\text{occ}} \langle n\mathbf{0}|\mathbf{r} \wedge i[H, \mathbf{r}]|n\mathbf{0}\rangle. \tag{10}$$

On the other hand, the contribution to Eq. (7) from the N_s surface localized orbitals w_s reads [30]

$$\mathbf{M}_{\text{IC}} = -\frac{1}{2c\Omega N_c} \left\{ \sum_s^{N_s} \langle w_s|(\mathbf{r} - \mathbf{r}_s) \wedge i[H, \mathbf{r}]|w_s\rangle \right. $$
$$\left. + \mathbf{r}_s \wedge \langle w_s|i[H, \mathbf{r}]|w_s\rangle \right\}, \tag{11}$$

where we have used the shorthand notation $\mathbf{r}_s = \langle w_s|\mathbf{r}|w_s\rangle$ to denote the centers of the surface orbitals. Indeed, in the thermodynamic limit, even though the first term vanishes, $\mathbf{r}_s$ is large and a nonvanishing contribution from the second term in Eq. (11) remains [30]. Then, Eq. (10) is related to currents circulating in the bulk of the solid [the so-called local-circulation (LC) term], while Eq. (11) originates from current circulating at the surface of the solid [the itinerant-circulation (IC) term]. Remarkably, however, both contributions may be rewritten solely in terms of WFs centered in the bulk.

In reciprocal space, the final expressions for the LC term are [30]

$$\mathbf{M}_{\text{LC}} = \frac{1}{2c}\Re \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} \langle \nabla_k u_{n,\mathbf{k}}| \wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle, \tag{12a}$$

and for the IC term [30],

$$\mathbf{M}_{\text{IC}} = \frac{1}{2c}\Re \int_{\text{BZ}} d\mathbf{k} \sum_{m,n}^{\text{occ}} \delta_{m,n}/i \, \epsilon_{n,\mathbf{k}} \langle \nabla_k u_{n,\mathbf{k}}| \wedge |\nabla_k u_{m,\mathbf{k}}\rangle, \tag{12b}$$

where

$$H_{\mathbf{k}} = e^{-i\mathbf{k}\cdot\mathbf{r}} H e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{12c}$$

The total orbital magnetization is the sum of the LC and IC contributions [30],

$$\mathbf{M} = \mathbf{M}_{\text{LC}} + \mathbf{M}_{\text{IC}}. \tag{12d}$$

In deriving Eq. (16), CTVR inserted $\mathbb{1} = \sum_l^{\text{all}} |w_l\rangle\langle w_l|$ into Eq. (11), yielding the relation

$$\langle w_s|i[H, \mathbf{r}]|w_s\rangle = 2\Re \sum_l^{\text{all}} \langle w_s|\mathbf{r}|w_l\rangle\langle w_l|H/i|w_s\rangle. \tag{13}$$

Here we note that for calculations in a finite basis set, it is then necessary to remove the identity from the resulting expressions. In other words, for finite basis set calculations, it is necessary to make the replacement

$$\sum_l^{\text{all}} |w_l\rangle\langle w_l| \to \mathbb{1} \tag{14}$$

in Eq. (12b) for $\mathbf{M}_{\text{IC}}$.

To make the presence of the identity more explicit in Eq. (12b), we use

$$\sum_m^{\text{occ}} \delta_{m,n}\epsilon_{n,\mathbf{k}} = \sum_l^{\text{all}} \delta_{l,n}\epsilon_{n,\mathbf{k}} = \sum_l^{\text{all}} \langle u_{l,\mathbf{k}}|H_{\mathbf{k}}|u_{n,\mathbf{k}}\rangle \tag{15}$$

to write Eq. (12b) as

$$\mathbf{M}_{\text{IC}} = \frac{1}{2c}\Re \int_{\text{BZ}} d\mathbf{k} \sum_l^{\text{all}} \sum_n^{\text{occ}} \langle \nabla_k u_{n,\mathbf{k}}| \wedge |\nabla_k u_{l,\mathbf{k}}\rangle$$
$$\times \langle u_{l,\mathbf{k}}|H_{\mathbf{k}}/i|u_{n,\mathbf{k}}\rangle. \tag{16}$$

In the following, we develop expressions that are generally valid for nonlocal Hamiltonians and a finite basis set, in a manner that achieves the replacements warranted by Eqs. (9) and (14). The result shows a connection with a previously proposed treatment by SMK [51].

B. Expressions for nonlocal Hamiltonians and a finite basis

1. Local circulation term

For further development, it proves useful to develop the derivatives of Eq. (6b),

$$\nabla_k |u_{n,\mathbf{k}}\rangle = -i \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}(\mathbf{r} - \mathbf{R})|n\mathbf{R}\rangle \tag{17a}$$

and

$$\nabla_r |u_{n,\mathbf{k}}\rangle = -i\mathbf{k}|u_{n,\mathbf{k}}\rangle + \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle. \tag{17b}$$

Furthermore, multiplying Eq. (17a) by $H_{\mathbf{k}}$, while making use of Eq. (12c), provides

$$H_{\mathbf{k}}\nabla_k |u_{n,\mathbf{k}}\rangle = -i \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}H(\mathbf{r} - \mathbf{R})|n\mathbf{R}\rangle. \tag{18}$$

In Appendix A, we use Eqs. (17a)–(18), and the replacement of Eq. (9), required for nonlocal Hamiltonians to develop the following relation:

$$\wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle \to \wedge \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle$$
$$= \wedge \nabla_r|u_{n,\mathbf{k}}\rangle + \wedge i\mathbf{k}|u_{n,\mathbf{k}}\rangle. \tag{19}$$

Equation (19) starts with a vector multiplication, as the relation is only defined up to a gauge $\mathbf{A} \wedge \mathbf{B} = \mathbf{A} \wedge \mathbf{C} \to \mathbf{C} = \mathbf{B} + a\mathbf{A}$ (see Appendix A). Finally, inserting Eq. (19) into Eq. (12a) yields

$$\mathbf{M}_{\text{LC}} = \frac{1}{2c}\Re \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} [\langle \nabla_k u_{n,\mathbf{k}}| \wedge \nabla_r|u_{n,\mathbf{k}}\rangle$$
$$+ \langle \nabla_k u_{n,\mathbf{k}}| \wedge i\mathbf{k}|u_{n,\mathbf{k}}\rangle]. \tag{20}$$

Then, applying ∇_k to Eq. (2), we obtain a representation of the position operator for a periodic system due to Blount [7],

$$\mathbf{r}\psi_{n,\mathbf{k}}(\mathbf{r}) = ie^{i\mathbf{k}\cdot\mathbf{r}}\nabla_k u_{n,\mathbf{k}}(\mathbf{r}) - i\nabla_k\psi_{n,\mathbf{k}}(\mathbf{r}). \quad (21)$$

Inserting Eq. (21) into Eq. (20) provides

$$\mathbf{M}_{\text{LC}} = -\frac{1}{2c}\Re\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\langle\psi_{n,\mathbf{k}}|(\mathbf{r}+i\nabla_k)^\dagger\wedge\nabla_r/i|\psi_{n,\mathbf{k}}\rangle. \quad (22)$$

2. Itinerant circulation term

Returning to Eq. (16) and using the Hermiticity of $H_{\mathbf{k}}$, we obtain

$$\mathbf{M}_{\text{IC}} = \frac{1}{2c}\Re\int_{\text{BZ}}d\mathbf{k}\sum_l^{\text{all}}\sum_n^{\text{occ}}\langle\nabla_k u_{n,\mathbf{k}}|\wedge|\nabla_k u_{l,\mathbf{k}}\rangle$$
$$\times\langle u_{l,\mathbf{k}}|H_{\mathbf{k}}/i|u_{n,\mathbf{k}}\rangle$$
$$= \frac{1}{2c}\Re\int_{\text{BZ}}d\mathbf{k}\sum_l^{\text{all}}\sum_n^{\text{occ}}\langle u_{n,\mathbf{k}}|H_{\mathbf{k}}/i|u_{l,\mathbf{k}}\rangle$$
$$\times\langle\nabla_k u_{l,\mathbf{k}}|\wedge|\nabla_k u_{n,\mathbf{k}}\rangle. \quad (23)$$

The combination of Eq. (14) with Eq. (23) gives

$$\mathbf{M}_{\text{IC}} = \frac{1}{2c}\Re\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\langle u_{n,\mathbf{k}}|H_{\mathbf{k}}/i\nabla_k^\dagger\wedge\nabla_k|u_{n,\mathbf{k}}\rangle. \quad (24)$$

By utilizing the conjugate transpose of Eq. (19) along with Eq. (21), Eq. (24) leads to

$$\mathbf{M}_{\text{IC}} = \frac{1}{2c}\Re\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\langle\psi_{n,\mathbf{k}}|\nabla_r^\dagger/i\wedge(\mathbf{r}+i\nabla_k)|\psi_{n,\mathbf{k}}\rangle. \quad (25)$$

3. SMK "angular-momentum" operator

From the combination of Eqs. (12d), (22), and (25), we obtain an expression for the orbital magnetization in terms of the SMK "Hermitized angular-momentum" operator,

$$\mathbf{M} = -\frac{1}{2c}\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\langle\psi_{n,\mathbf{k}}|\frac{\hat{\mathbf{\Lambda}}+\hat{\mathbf{\Lambda}}^\dagger}{2}|\psi_{n,\mathbf{k}}\rangle, \quad (26a)$$

where

$$\hat{\mathbf{\Lambda}} = (\mathbf{r}+i\nabla_k)\wedge\nabla_r/i. \quad (26b)$$

The SMK theory thus corresponds to a generalization of CTVR's modern theory of orbital magnetization to calculations with (generally) nonlocal Hamiltonians in a finite basis set.

III. EFFECT OF THE ORBITAL PHASES AND GAUGE-ORIGIN INVARIANCE

It was mentioned in Sec. II A that the complex Bloch orbitals and WFs are only determined up to an arbitrary phase $e^{i\phi_n(\mathbf{k})}$. From Eq. (26b), the effect on the orbital magnetization of changing the phase of the Bloch orbitals is to make the replacement

$$\mathbf{r} \to \mathbf{r} - \nabla_k\phi_n(\mathbf{k}) \quad (27)$$

in matrix elements of $\hat{\mathbf{\Lambda}}$. Therefore, changing the phase of $|\psi_{n,\mathbf{k}}\rangle$ has exactly the same effect as changing the gauge origin by an amount $-\nabla_k\phi_n(\mathbf{k})$ for the matrix element involving orbital $|\psi_{n,\mathbf{k}}\rangle$. Equation (27) has already been pointed out by SMK. The particular choice of the phase, then, becomes irrelevant for gauge-origin invariant calculations [for instance, at the complete basis set (CBS) limit; see Eq. (30) below]. In our calculations, we set the term $-\nabla_k\phi_n(\mathbf{k})$ to zero. Generally speaking, an approximate calculation may depend on the gauge origin and, by extension, on the choice of the phase [61]. Another criterion of relevance for Eq. (26) is the behavior of the "angular-momentum" operator under a lattice translation from $\hat{\mathbf{\Lambda}}(\mathbf{r})$ to $\hat{\mathbf{\Lambda}}(\mathbf{r}+\mathbf{R})$. A periodic operator $\hat{O}$ satisfies $\hat{O}(\mathbf{r}) = \hat{O}(\mathbf{r}+\mathbf{R})$. We can work out the effect of translation by a lattice vector $\mathbf{R}$ by returning to Eq. (26), from which we find

$$-\frac{1}{4c}\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\langle\psi_{n,\mathbf{k}}|(\mathbf{r}+\mathbf{R}+i\nabla_k)\wedge\nabla_r/i|\psi_{n,\mathbf{k}}\rangle + \text{H.c.} \quad (28)$$

The translation therefore leads to the (generally) nonvanishing contribution,

$$-\frac{1}{4c}\int_{\text{BZ}}d\mathbf{k}\sum_n^{\text{occ}}\mathbf{R}\wedge\langle\psi_{n,\mathbf{k}}|\nabla_r/i|\psi_{n,\mathbf{k}}\rangle + \text{H.c.}, \quad (29)$$

and, in the general case, we obtain $\hat{\mathbf{\Lambda}}(\mathbf{r}) \neq \hat{\mathbf{\Lambda}}(\mathbf{r}+\mathbf{R})$. Of course, the translation is equivalent to changing the gauge origin by $\mathbf{R}$. Then, just like in the case of gauge origin, $\hat{\mathbf{\Lambda}}$ becomes periodic if the orbitals are exact (i.e., at the CBS limit). Indeed, at the CBS limit, we may insert Eq. (14) as well as Eq. (9) into Eq. (26), yielding

$$\mathbf{M} = -\frac{1}{4c}\int_{\text{BZ}}d\mathbf{k}\sum_l^{\text{all}}\sum_n^{\text{occ}}\langle\psi_{n,\mathbf{k}}|(\mathbf{r}+i\nabla_k)|\psi_{l,\mathbf{k}}\rangle$$
$$\wedge\langle\psi_{l,\mathbf{k}}|\nabla_r/i|\psi_{n,\mathbf{k}}\rangle + \text{H.c.}$$
$$= \frac{1}{4c}\int_{\text{BZ}}d\mathbf{k}\sum_l^{\text{all}}\sum_n^{\text{occ}}\frac{\langle\psi_{n,\mathbf{k}}|\nabla_r|\psi_{l,\mathbf{k}}\rangle}{\epsilon_{n,\mathbf{k}}-\epsilon_{l,\mathbf{k}}}$$
$$\wedge\langle\psi_{l,\mathbf{k}}|\nabla_r/i|\psi_{n,\mathbf{k}}\rangle + \text{H.c.}, \quad (30)$$

which is obviously both periodic and gauge-origin invariant, and is also independent of the choice of $-\nabla_k\phi_n(\mathbf{k})$.

Because $\hat{\mathbf{\Lambda}}$ is only periodic at the CBS limit (or in any other basis that ensures gauge-origin invariance), in practice, exact comparison against large finite systems can only be expected with a large basis set. Moreover, the usual reciprocity between sampling of reciprocal space (i.e., number of $\mathbf{k}$ points to sample the FBZ) and direct space (i.e., size of the supercell expansion) is only verified at the CBS limit. In Sec. VII, we present numerical results that explicitly demonstrate this behavior.

In the case of finite systems, it has very recently been shown that a finite basis set of London atomic orbitals yields the same translational behavior as the exact orbitals [62]. Whether a similar relationship can be developed for infinite, periodic systems remains to be demonstrated.

IV. FORMALISM: PERTURBATION THEORY PERSPECTIVE

The result obtained in Sec. II (for the magnetization in terms of a "Hermitized angular-momentum" operator) that was derived using Wannier functions may alternatively be developed through perturbation theory (PT). The latter approach is similar to the derivation presented by SVXN in generalizing the CTVR treatment to metals and Chern insulators [31]. This approach is also more convenient for extension to higher-order properties.

We begin by considering a transition matrix element of the first-order interaction Hamiltonian for the orbital response to a magnetic field which, in the CO basis, is

$$-\frac{i}{c}\langle\psi_{n,\mathbf{k}}|\nabla_r\cdot\mathbf{A}+\mathbf{A}\cdot\nabla_r|\psi_{a,\mathbf{k}'}\rangle. \tag{31}$$

In Eq. (31), $\mathbf{A}$ is the magnetic vector potential. In the Coulomb gauge (for which $\nabla_r\cdot\mathbf{A}=\mathbf{0}$),

$$\mathbf{A}=i\mathbf{B}_0\wedge\frac{\mathbf{q}}{q^2}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}, \tag{32}$$

where $\mathbf{B}_0$ is the (constant) amplitude of the magnetic field with wave vector $\mathbf{q}$ and frequency ω ($q=|\mathbf{q}|$). Then, for a spatially oscillating magnetostatic field $\mathbf{B}=[B_x,0,0]^T$ propagating in a direction orthogonal to x (i.e., transversal wave, $q_x=0$),

$$\mathbf{A}(\mathbf{r})=iB_{0x}\begin{pmatrix}0\\-q_z\,e^{i(q_yr_y+q_zr_z)}/q^2\\q_y\,e^{i(q_yr_y+q_zr_z)}/q^2\end{pmatrix} \tag{33}$$

and $q^2=q_y^2+q_z^2$.

Inserting Eq. (33) into Eq. (31) provides

$$\frac{B_{0x}}{cq^2}\langle\psi_{n,\mathbf{k}}|e^{i(q_yr_y+q_zr_z)}(q_y\nabla_z-q_z\nabla_y)|\psi_{a,\mathbf{k}'}\rangle. \tag{34}$$

In Appendix B, we show that this integral is null, except when

$$\mathbf{k}-\mathbf{k}'=\mathbf{q}. \tag{35}$$

We now expand $e^{i(q_yr_y+q_zr_z)}$, $|\psi_{n,\mathbf{k}}\rangle$, and $|\psi_{m,\mathbf{k}'}\rangle$ to first order in $\mathbf{q}$, around the midpoint $\bar{\mathbf{k}}=(\mathbf{k}+\mathbf{k}')/2$, also using Eq. (35), yielding

$$\frac{B_{0x}}{cq^2}\left\langle\psi_{n,\bar{\mathbf{k}}}+\left(\frac{q_y}{2}\nabla_{\bar{k}_y}+\frac{q_z}{2}\nabla_{\bar{k}_z}\right)\psi_{n,\bar{\mathbf{k}}}\right|$$
$$\times[1+i(q_yr_y+q_zr_z)](q_y\nabla_z-q_z\nabla_y)$$
$$\times\left|\psi_{a,\bar{\mathbf{k}}}-\left(\frac{q_y}{2}\nabla_{\bar{k}_y}+\frac{q_z}{2}\nabla_{\bar{k}_z}\right)\psi_{a,\bar{\mathbf{k}}}\right\rangle. \tag{36}$$

For a spatially homogeneous field, we take the limit $\mathbf{q}\to\mathbf{0}$ of Eq. (36). Then, we write $q_y=q\cos\theta$ and $q_z=q\sin\theta$, and average over θ, which gives

$$\frac{B_{0x}}{2c}\langle\psi_{n,\bar{\mathbf{k}}}|ir_y\nabla_z-ir_z\nabla_y+\frac{1}{2}\nabla_{\bar{k}_y}^\dagger\nabla_z-\frac{1}{2}\nabla_{\bar{k}_z}^\dagger\nabla_y$$
$$-\frac{1}{2}\nabla_{\bar{k}_y}\nabla_z+\frac{1}{2}\nabla_{\bar{k}_z}\nabla_y|\psi_{a,\bar{\mathbf{k}}}\rangle, \tag{37}$$

where we have used $\langle\cos^2\theta\rangle=\langle\sin^2\theta\rangle=\frac{1}{2}$, as well as $\langle\cos\theta\rangle=\langle\sin\theta\rangle=0$. Repeating the process for y- and

z-directed fields, we get

$$-\frac{\mathbf{B}_0}{2c}\cdot\langle\psi_{n,\mathbf{k}}|\left[\mathbf{r}+\frac{i}{2}(\nabla_{\mathbf{k}}-\nabla_{\mathbf{k}}^\dagger)\right]\wedge\frac{\nabla_r}{i}|\psi_{a,\mathbf{k}}\rangle. \tag{38}$$

Finally, employing the Hermiticity of $\mathbf{r}$ and the anti-Hermiticity of ∇_r, Eq. (38) may be written in terms of the Hermitized SMK operator of Eq. (26b),

$$-\frac{\mathbf{B}_0}{2c}\cdot\langle\psi_{n,\mathbf{k}}|\frac{\hat{\mathbf{\Lambda}}+\hat{\mathbf{\Lambda}}^\dagger}{2}|\psi_{a,\mathbf{k}}\rangle. \tag{39}$$

Equation (39) is the analog (for transition moments) of Eq. (26) of Sec. II for the orbital magnetization.

V. EXTENSION TO OPTICAL ROTATION

A. Operators for the rotatory strengths

For OR, following Stephen [63], Tinoco [4], Snir and Schellman [64], Hansen and Avery [3], and subsequent work [65,66], it is convenient to describe the interaction of the system with circularly polarized light using the electromagnetic $\mathbf{A}$ gauge (vanishing scalar potential) leading to the interaction Hamiltonian,

$$\{\exp[i\mathbf{q}\cdot\mathbf{r}]\mathbf{A}_0(\mathbf{q})+\text{c.c.}\}\cdot\mathbf{p}+\mathbf{p}\cdot\{\mathbf{A}_0(\mathbf{q})\exp[i\mathbf{q}\cdot\mathbf{r}]+\text{c.c.}\}. \tag{40}$$

In the following, we generalize the theory of Stephen and co-workers to periodic systems. This allows us to extend a previous treatment [2], to include not only DD, but also DQ contributions to the OR tensor.

We assume here that $\mathbf{A}_0(\mathbf{q})$ is sufficiently slowly varying so that only the leading terms in $\exp[\pm i\mathbf{q}\cdot\mathbf{r}]\approx 1\pm i\mathbf{q}\cdot\mathbf{r}$ will contribute to the response. Choosing $\mathbf{q}=\hat{\mathbf{z}}q$, differences in the absorption of left- and right-circularly polarized light lead to rotatory strengths proportional to [3,63]

$$\hat{\mathbf{z}}\cdot\langle\psi_{n,\mathbf{k}}|\exp[-i\mathbf{q}\cdot\mathbf{r}]\mathbf{p}|\psi_{a,\mathbf{k}'}\rangle\wedge\langle\psi_{a,\mathbf{k}'}|\exp[i\mathbf{q}\cdot\mathbf{r}]\mathbf{p}|\psi_{n,\mathbf{k}}\rangle, \tag{41}$$

including effects from multipoles of all orders. Expansion of Eq. (41) to first order in $\mathbf{q}$, following the developments in Eqs. (31)–(39), leads to the simplified formula

$$\langle\psi_{n,\mathbf{k}}|p_x|\psi_{a,\mathbf{k}}\rangle\langle\psi_{a,\mathbf{k}}|\frac{\hat{\Omega}_z+\hat{\Omega}_z^\dagger}{2}p_y|\psi_{n,\mathbf{k}}\rangle$$
$$-\langle\psi_{n,\mathbf{k}}|p_y|\psi_{a,\mathbf{k}}\rangle\langle\psi_{a,\mathbf{k}}|\frac{\hat{\Omega}_z+\hat{\Omega}_z^\dagger}{2}p_x|\psi_{n,\mathbf{k}}\rangle, \tag{42}$$

where we have introduced the shorthand notation

$$\hat{\mathbf{\Omega}}=\mathbf{r}+i\nabla_k. \tag{43}$$

Repeating the procedure for arbitrary orientations u of the light beam provides

$$\left[\langle\psi_{n,\mathbf{k}}|\mathbf{p}|\psi_{a,\mathbf{k}}\rangle\wedge\langle\psi_{a,\mathbf{k}}|\frac{\hat{\mathbf{\Omega}}+\hat{\mathbf{\Omega}}^\dagger}{2}\vee\mathbf{p}|\psi_{n,\mathbf{k}}\rangle\right]_u$$
$$\equiv\sum_{v,w}\epsilon_{u,v,w}\langle\psi_{n,\mathbf{k}}|p_v|\psi_{a,\mathbf{k}}\rangle\langle\psi_{a,\mathbf{k}}|\frac{\hat{\Omega}_u+\hat{\Omega}_u^\dagger}{2}p_w|\psi_{n,\mathbf{k}}\rangle \tag{44}$$

for the rotatory strengths, where $\epsilon_{u,v,w}$ is the Levi-Civita symbol and we have introduced a compact notation for the product

∨. Equation (44) includes both DD and DQ contributions, as can be seen by adding and subtracting appropriate matrix elements including $p_u \frac{\hat{\Omega}_w + \hat{\Omega}_w^\dagger}{2}$:

$$
\begin{aligned}
\text{DQ} + \text{DD} &= \left[\langle \psi_{n,\mathbf{k}} | \mathbf{p} | \psi_{a,\mathbf{k}} \rangle \wedge \langle \psi_{a,\mathbf{k}} | \frac{\hat{\boldsymbol{\Omega}} + \hat{\boldsymbol{\Omega}}^\dagger}{2} \vee \mathbf{p} | \psi_{n,\mathbf{k}} \rangle \right]_u \\
&= \frac{1}{2} \sum_{v,w} \epsilon_{u,v,w} \langle \psi_{n,\mathbf{k}} | p_v | \psi_{a,\mathbf{k}} \rangle \left[\langle \psi_{a,\mathbf{k}} | \frac{\hat{\Omega}_u + \hat{\Omega}_u^\dagger}{2} p_w \right. \\
&\quad + p_u \frac{\hat{\Omega}_w + \hat{\Omega}_w^\dagger}{2} | \psi_{n,\mathbf{k}} \rangle + \langle \psi_{a,\mathbf{k}} | \frac{\hat{\Omega}_u + \hat{\Omega}_u^\dagger}{2} p_w \\
&\quad \left. - p_u \frac{\hat{\Omega}_w + \hat{\Omega}_w^\dagger}{2} | \psi_{n,\mathbf{k}} \rangle \right].
\end{aligned}
\tag{45}
$$

With the DQ term (i.e., the first term in square brackets) being traceless, orientational averaging (summing over $u = x, y, z$) leads to an expression involving only the DD contribution,

$$
\langle \psi_{n,\mathbf{k}} | \mathbf{p} | \psi_{a,\mathbf{k}} \rangle \cdot \langle \psi_{a,\mathbf{k}} | \frac{\hat{\boldsymbol{\Lambda}} + \hat{\boldsymbol{\Lambda}}^\dagger}{2} | \psi_{n,\mathbf{k}} \rangle.
\tag{46}
$$

We note that Eqs. (44)–(46) contain no terms from the action of $\nabla_{\mathbf{k}}$ on the first-order electric field matrix elements $\langle \psi_{n,\mathbf{k}} | \mathbf{p} | \psi_{a,\mathbf{k}} \rangle$. Just like for the magnetization from Eq. (30), the rotatory strengths become independent of the gauge origin and orbital phase at the CBS limit (or in another basis that ensures gauge-origin invariance). This may be seen by inserting Eq. (14) as well as Eq. (9) into Eq. (45), yielding

$$
\begin{aligned}
\text{DQ} + \text{DD} &= \sum_l^{\text{all}} \left[-\langle \psi_{n,\mathbf{k}} | \mathbf{p} | \psi_{a,\mathbf{k}} \rangle \wedge \frac{\langle \psi_{a,\mathbf{k}} | \nabla_r | \psi_{l,\mathbf{k}} \rangle}{\epsilon_{n,\mathbf{k}} - \epsilon_{l,\mathbf{k}}} \right. \\
&\quad \left. \vee \langle \psi_{l,\mathbf{k}} | \mathbf{p} | \psi_{n,\mathbf{k}} \rangle \right]_u + \text{H.c.},
\end{aligned}
\tag{47}
$$

which is periodic and does not depend on the gauge origin or the gradient of the orbital phases $-\nabla_{\mathbf{k}} \phi_n(\mathbf{k})$.

Finally, in recent work on OR, Wang and Yan found a new "band dispersion" contribution to the rotatory strengths. In Appendix C, we show how this band dispersion term is an alternate formulation of the magnetic dipole term in Eq. (45) for semilocal functionals. As a consequence, band dispersion contributions are not included in our formulation.

B. Optical rotation tensor

In the Supplemental Material (SM) [67], we develop a formula for the diagonal elements of the OR tensor β_u, being related to the OR angle through Eq. (1) (including both magnetic-dipole as well as electric-quadrupole contributions) based on the operators of Eq. (44) and time-dependent double-perturbation theory.

$\boldsymbol{\beta}$ relates the components of the magnetic-dipole plus electric-quadrupole moments induced by the electric field $\boldsymbol{\eta}$ to the time derivative of the electric field $\boldsymbol{\mathcal{E}}$ (see SM for more details) [1,67],

$$
\boldsymbol{\eta}(\omega) = \frac{\boldsymbol{\beta}(\omega)}{c} \frac{\partial}{\partial t} \boldsymbol{\mathcal{E}}(t, \omega).
\tag{48}
$$

For practical calculations, we expand the COs in a finite set of functions $\varphi_{\mu,\mathbf{k}}$ labeled by the index μ,

$$
|\psi_{l,\mathbf{k}}\rangle = \sum_\mu C_{\mu,l}(\mathbf{k}) |\varphi_{\mu,\mathbf{k}}\rangle,
\tag{49}
$$

with the CO coefficients $C_{\mu,l}(\mathbf{k})$ being determined from the solution of the field-free GKS-DFT equations. To write a compact expression for β_u, it is convenient to use an analytical expression for the derivatives of the coefficients $C_{\mu,l}(\mathbf{k})$ in terms of a matrix $\mathbf{Q}$ [68],

$$
\nabla_{\mathbf{k}} C_{\mu,l}(\mathbf{k}) = \sum_{l'}^{\text{all}} \mathbf{Q}_{l',l}(\mathbf{k}) C_{\mu,l'}(\mathbf{k}).
\tag{50}
$$

Similarly, the u-component electric-field perturbed coefficients $C_{\mu,n}^{(u),\pm}(\mathbf{k})$ are written in terms of a matrix $\mathbf{U}$ (in the noncanonical treatment, only anti-Hermitian virt-occ inter-bank elements $U_{an}^{(u),\pm}$ are nonvanishing) [69],

$$
C_{\mu,n}^{(u),\pm}(\mathbf{k}) = \sum_a^{\text{virt}} U_{an}^{(u),\pm}(\mathbf{k}) C_{\mu,a}(\mathbf{k}).
\tag{51}
$$

In Eq. (50), $\mathbf{Q}$ is determined from the derivative of the GKS equation and orthonormality condition [68],

$$
\mathbf{Q}_{l,l'}(\mathbf{k}) = \frac{\mathbf{K}_{l,l'}(\mathbf{k}) - \epsilon_{l',\mathbf{k}} \mathbf{D}_{l,l'}(\mathbf{k})}{\epsilon_{l',\mathbf{k}} - \epsilon_{l,\mathbf{k}}},
\tag{52a}
$$

for off-diagonal $l \neq l'$ elements and

$$
\Re[\mathbf{Q}_{l,l}(\mathbf{k})] = -\frac{1}{2} \mathbf{D}_{l,l}(\mathbf{k})
\tag{52b}
$$

for diagonal elements. Here, $\mathbf{K}_{l,l'}(\mathbf{k})$ and $\mathbf{D}_{l,l'}(\mathbf{k})$ are the $\mathbf{k}$ derivatives of the GKS-DFT Hamiltonian and overlap matrices, respectively, for fixed CO coefficients. The imaginary part of $\mathbf{Q}_{l,l}(\mathbf{k})$, on the other hand, is determined by integers associated with the phase function $\phi(\mathbf{k})$ of Eq. (2) [10], which we set to zero, as discussed in Sec. III.

In our implementation, we work with the Hermitian quantity

$$
\tilde{\mathbf{Q}}_{l,l'}(\mathbf{k}) = \mathbf{Q}_{l,l'}(\mathbf{k}) + \frac{1}{2} \mathbf{D}_{l,l'}(\mathbf{k}).
\tag{53}
$$

In terms of these coefficients, the final formula for β_u reported in Eq. (S44) is given by

$$
\begin{aligned}
\beta_u(\omega) &= \frac{1}{\omega} \text{P.V.} \int' d\mathbf{k} \sum_n^{\text{occ}} \sum_a^{\text{virt}} \text{Im}\{ [U_{an}^+(\mathbf{k}) - U_{an}^-(\mathbf{k})] \\
&\quad \wedge [\tilde{\mathbf{v}}_{na}(\mathbf{k}) + \mathbf{q}_{na}(\mathbf{k})] \}_u,
\end{aligned}
\tag{54}
$$

where

$$
\begin{aligned}
\mathbf{q}_{na}(\mathbf{k}) &= \frac{1}{2} \sum_l^{\text{all}} \left\{ \left[\tilde{\mathbf{Q}}_{l,n}(\mathbf{k}) - \frac{1}{2} \mathbf{D}_{l,n}(\mathbf{k}) \right] \vee \langle \psi_{a,\mathbf{k}} | \nabla_r | \psi_{l,\mathbf{k}} \rangle \right. \\
&\quad \left. - \left[\tilde{\mathbf{Q}}_{l,a}^*(\mathbf{k}) - \frac{1}{2} \mathbf{D}_{l,a}^*(\mathbf{k}) \right] \vee \langle \psi_{l,\mathbf{k}} | \nabla_r | \psi_{n,\mathbf{k}} \rangle \right\},
\end{aligned}
\tag{55}
$$

and $\mathbf{v}_{na}$ is defined below in Eq. (57).

In Eq. (54), the prime indicates that integration is restricted to the portion of the FBZ with positive coordinates [we have made use of the fact that the operators of Eq. (44) are odd

under inversion $\mathbf{k} \to -\mathbf{k}$] and P.V. indicates that the integral must be interpreted in terms of its Cauchy principal value (or, equivalently, its finite part). Thus, the elements of $\tilde{\mathbf{Q}}$ are calculated as

$$\tilde{\mathbf{Q}}_{l,l'}(\mathbf{k}) = \lim_{\eta \to 0^+} \frac{\mathbf{K}_{l,l'}(\mathbf{k}) - \frac{1}{2}(\epsilon_{l,\mathbf{k}} + \epsilon_{l',\mathbf{k}})\mathbf{D}_{l,l'}(\mathbf{k})}{\epsilon_{l',\mathbf{k}} - \epsilon_{l,\mathbf{k}} + i\eta}, \quad (56)$$

for $l \neq l'$ with η being a small positive number. The parameter η provides an effective means to deal with quasidegeneracies for occ-occ or virt-virt blocks of $\tilde{\mathbf{Q}}$, wherein the denominator in Eq. (56) vanishes in the limit $\eta \to 0$. In Sec. VII, we demonstrate that accurate calculations are not sensitive to the value of η, provided that it is sufficiently small. Finally, in Eq. (54), $\tilde{\mathbf{v}}_{na} = \frac{\mathbf{v}_{na} + \mathbf{v}_{an}^*}{2}$, where $\mathbf{v}_{na}$ reads

$$\mathbf{v}_{na} = \langle \psi_{n,\mathbf{k}} | (\mathbf{r} + \mathbf{R}_O) \vee \mathbf{p} | \psi_{a,\mathbf{k}} \rangle, \quad (57)$$

and $\mathbf{R}_O$ is the gauge origin.

The $U_{an}^{(u),\pm}(\mathbf{k})$ matrix elements of Eq. (51) for the u-component of the electric dipole moment, which are used in sum-over-states (SOS) calculations, are

$$U_{an}^{(u),\pm}(\mathbf{k}) = \frac{\langle \psi_{a,\mathbf{k}} | \Omega_u | \psi_{n,\mathbf{k}} \rangle}{\epsilon_{a,\mathbf{k}} - \epsilon_{n,\mathbf{k}} \pm \omega}$$
$$\simeq -\frac{\langle \psi_{a,\mathbf{k}} | \nabla_u | \psi_{n,\mathbf{k}} \rangle}{(\epsilon_{a,\mathbf{k}} - \epsilon_{n,\mathbf{k}} \pm \omega)(\epsilon_{a,\mathbf{k}} - \epsilon_{n,\mathbf{k}})}. \quad (58)$$

For time-dependent (TD)-DFT calculations, these must be augmented with orbital-relaxation contributions, calculated here through a self-consistent solution of the coupled-perturbed generalized Kohn-Sham (CPKS) equations (sometimes also called density functional perturbation theory, DFPT) [2,70]. In Eq. (58), the last equality implies the validity of the off-diagonal hypervirial relation, which holds only for calculations employing semilocal Hamiltonians (or a complete basis). We denote calculations with the operator Ω_u on the left of the last equality as the length (or L) formulation, and those with the ∇_u operator as the nabla (or V) formulation.

As discussed in Rérat and Kirtman [2], the OR tensor is independent of $\mathbf{R}_O$ by construction if the nabla operator is used in Eq. (58). In that case, we set $\mathbf{R}_O = \mathbf{0}$ (V0 formulation). On the other hand, calculations with the length operator are generally gauge-origin dependent, and, then, we use the electronic centroid $\mathbf{R}_O = \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} \langle \psi_{n,\mathbf{k}} | \mathbf{r} | \psi_{n,\mathbf{k}} \rangle$ as the gauge origin (LC formulation).

VI. COMPUTATIONAL DETAILS

Unless explicitly stated otherwise, all calculations were performed with a developer's version of the CRYSTAL23 code [71], employing all-electron Gaussian atomic-orbital (AO) basis sets. The field-free calculations were converged down to a criterium of 1×10^{-10} Hartree a.u. (E_h) on the total energy.

The xc contribution was calculated by numerical quadrature using Gauss-Legendre radial and Lebedev angular point distributions [72–74], with the quadrature weights proposed by Becke [75]. We used a pruned grid consisting of 99 radial points and 1454 angular points (keyword XXLGRID in the CRYSTAL23 manual) [76]. The XCFUN library [77] was employed to take the Slater Vosko-Wilk-Nusair (SVWN5) [local density approximation (LDA)], Perdew Burke Ernzerhof

(PBE) [generalized gradient approximation (GGA)], and PBE0 (hybrid approximation) xc functional derivatives required for the first-order CPKS procedure [78–81]. More specific details are available in the SM, where the full input decks are provided [67].

VII. RESULTS AND DISCUSSION

The implementation is validated in several respects on chains of H_2O_2, which has served as a model system in previous work [2,52]. In detail, we discuss the following:

(1) the effect of the parameter η of Eq. (56) for dealing with quasidegeneracies in the calculation of $\mathbf{k}$ derivatives of the unperturbed orbital coefficients;

(2) comparisons of infinite against finite chains, where matching results against the large finite system is obtained as the CBS limit is approached; and

(3) the equivalence of sampling reciprocal space (number of $\mathbf{k}$ points in the FBZ) and direct space (size of the supercell) being verified as the CBS limit is approached.

Points (2) and (3) here were anticipated from the discussion in Sec. III. After validation of our approach, we present applications to the calculation of OR from linear-response (LR) TD-DFT in the adiabatic approximation with hybrid functionals in α-quartz, where the importance of (i) DQ terms, (ii) orbital relaxation, (iii) nonlocal Fock exchange, and (iv) completeness of the basis set expansion is discussed.

A. Validation on finite and infinite chains of H_2O_2

The calculations on H_2O_2 chains were performed with geometries reported in Ref. [2] and available from the input decks in the SM [67]. The correlation-consistent polarized valence family of basis sets of Dunning was employed, with double, triple, and quadruple ζ (cc-pv$X$z, with $X = $ D, T, Q) [82]. We do not report on calculations beyond quadruple ζ because we obtained quasilinear dependencies with quintuple ζ and larger basis sets, and the corresponding results, then, heavily depended on the overlap eigenvalue threshold for canonical orthonormalization. The comparison of finite vs infinite H_2O_2 chains was done with the SVWN5 functional of the LDA, and SOS-V0 formulation, being the computationally simplest case that allows us to discuss all relevant aspects. We report calculations of the mean OR, which is calculated from the DD, but not DQ term, as per Eq. (46), so as to discuss the calculation of matrix elements of the Hermitized angular-momentum $\hat{\mathbf{\Lambda}} + \hat{\mathbf{\Lambda}}^\dagger$ operator.

Figure 1 provides values of the mean OR of H_2O_2 chains as a function of chain length and size of the single-particle basis expansion. The solid lines represent fits to polynomials of the form $c_4/x^4 + c_3/x^3 + c_2/x^2 + c_1/x + c_0$. The value of the fitted c_0 coefficients (representing the reference finite oligomer value, extrapolated to infinite chain length) is plotted in the dashed lines, i.e., 38.50, 45.67, and 54.72 °/mm for $X = $ D, T, Q.

To confirm the quality of the single-particle basis set expansion, in Table I we provide length and nabla results on finite oligomers with AO, as well as gauge-including AO (GIAO) basis sets. The GIAO results were obtained with the implementation in the GAUSSIAN program [83]. Of course,

TABLE I. Mean OR as calculated with the V0 and LC formulations and an atomic-orbital (AO) and gauge-including atomic-orbital (GIAO) basis on the isolated H_2O_2 molecule and 10-unit and 20-unit oligomer. Calculations on the isolated molecule included orbital relaxation to allow comparison against the GIAO implementation.

cc-pv$X$z	$1 \times H_2O_2$			$10 \times H_2O_2$		$20 \times H_2O_2$	
	LC-AO	V0-AO	L-GIAO	LC-AO	V0-AO	LC-AO	V0-AO
D	70.45	75.61	59.24	21.56	42.20	27.56	40.34
T	65.99	59.67	54.53	32.08	47.98	29.43	46.82
Q	66.83	54.66	55.32	56.67	55.99	55.35	55.24

all values for a given system should coincide at the CBS limit. The good agreement with the cc-pvQz basis set (last row of the table) is indicative that the calculations are nearly converged to the CBS limit. Although length and nabla gauge cc-pvQz results still show considerable disparity on the isolated H_2O_2 molecule (66.83 vs 54.66), the differences become much smaller for longer chain lengths (e.g., 55.35 vs 55.24 for the 20-unit oligomer).

Next, we turn to periodic calculations on the infinite H_2O_2 chain. As per Eqs. (54)–(56), the periodic formulation requires a careful treatment of quasidegeneracies in the calculation of $\nabla_k C_{\mu,l}(\mathbf{k})$. Of course, for an exact solution of the GKS-DFT equations, the $C_{\mu,l}(\mathbf{k})$ are differentiable [7] and, then, $\tilde{\mathbf{Q}}$ in Eq. (56) must be finite, even at quasidegeneracies. Practical calculations, on the other hand, are approximate solutions of the GKS-DFT equations and, therefore, require a judicious choice of the η parameter of Eq. (56) for systems that contain quasidegeneracies in the occupied and/or virtual band structure. As a test for systems with quasidegeneracies, we construct supercells of the H_2O_2 polymer (the supercell introduces quasidegeneracies in the FBZ) and report values of the mean OR for $\times 7$, $\times 9$, and $\times 11$ supercell Γ-point calculations in Table II. The table confirms that the mean OR is not sensitive to the precise value of η, as long as it is sufficiently small (at least 10^{-14} E_h a.u. in this case). Based on the results of Table II, we employ the value $\eta = 10^{-14}$ E_h a.u. in all subsequent calculations. With this value of η, the Γ-point results match the infinite oligomer value of $38.50 °/mm$ for the sufficiently large $\times 9$ and $\times 11$ supercells. Although this choice of η allows us to achieve the necessary level of numerical accuracy, convergence of the calculated values with respect to, e.g., the number of $\mathbf{k}$ points and other numerical tolerances, is relatively slow. To improve the implementation, a more elaborate scheme for a treatment of quasidegeneracies in the calculations of derivatives of the CO coefficients $\nabla_k C_{\mu,l}(\mathbf{k})$ will be presented in a forthcoming paper, in conjunction with different applications.

With the choice of η being established, we perform calculations on the small cell of H_2O_2 with many $\mathbf{k}$ points and compare sampling of reciprocal (number of $\mathbf{k}$ points in the FBZ) and direct (size of the supercell expansion) spaces in Table III. For the small cell, results are fully converged with 500 $\mathbf{k}$ points. A calculation with a $\times 3$ supercell expansion and 3 $\mathbf{k}$ points was performed to compare with the 9/1 calculation. With periodic operators, we expect these two calculations to be exactly equivalent because of the equivalence of sampling reciprocal and direct spaces. Calculations with $\times 7$ and $\times 11$ supercell expansions are also provided to study the convergence of the result with respect to supercell size.

Table III confirms the analysis of Sec. III. Generally, in a finite basis, $\hat{\mathbf{\Lambda}} + \hat{\mathbf{\Lambda}}^\dagger$ is not periodic and only becomes periodic at the CBS limit. As a consequence, significant differences between the small cell vs infinite oligomer results (first and last columns of the table, i.e., 47.90 vs $38.50 °/mm$) are obtained with the double-ζ basis set. The difference is greatly improved at the triple-ζ level to 47.88 vs $45.67 °/mm$. Finally, essentially matching results (53.55 vs $54.72 °/mm$) are gotten with the quadruple-ζ basis set.

Again, because of the nonperiodicity of $\hat{\mathbf{\Lambda}} + \hat{\mathbf{\Lambda}}^\dagger$, disparities can be observed for sampling of reciprocal vs direct space, especially with a small basis set. Concentrating on the 3/3 vs 9/1 calculations (second and fourth columns of the table), significant differences (44.07 vs $38.50 °/mm$) are obtained with a double-ζ basis set, which is improved to 46.14 vs $45.67 °/mm$ at the triple-ζ level, and, finally, almost matching results of 54.25 vs $54.72 °/mm$ are obtained at the quadruple-ζ level. As mentioned in Sec. III, the nonperiodicity of $\hat{\mathbf{\Lambda}} + \hat{\mathbf{\Lambda}}^\dagger$ is associated with its gauge-origin dependence. In the case of finite systems, the problem may be solved by including field-dependent phase factors in the basis functions (GIAOs) [62,84]. Whether a related, or alternative, approach to the problem can be developed for infinite, periodic systems remains to be demonstrated.
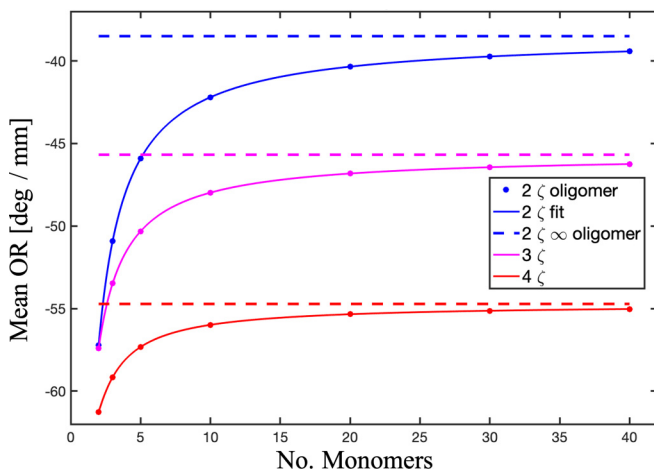

FIG. 1. Mean OR of finite H_2O_2 oligomers (dots), employing the cc-pv$X$z (X = D, T, Q) basis sets (blue, magenta, red), polynomial fits (solid lines), and values extrapolated to infinite chain length (dashed lines).

TABLE II. Γ-point calculation of the mean OR (in $°/mm$) on supercells of an H_2O_2 polymer with the cc-pvDz basis set. The ∞-oligomer reference value is $38.499\,°/mm$.

η	10^{-8}	10^{-10}	10^{-12}	10^{-14}	10^{-16}	10^{-75}	10^{-150}
$\times 7$	49.986	44.537	38.654	38.506	38.506	38.506	38.506
$\times 9$	50.584	45.504	38.502	38.499	38.499	38.499	38.499
$\times 11$	50.530	44.557	35.315	38.499	38.499	38.499	38.499

B. Application to α-quartz

Quartz is the dominant mineral composing the Earth's outer crust. The low-temperature α-quartz phase crystallizes in a trigonal space group, in either right- or left-handed helix (space groups $P3_121$ and $P3_221$) polymorphs, which may be distinguished experimentally on the basis of their optical rotatory power [85].

Here, we report first-principles calculations of the OR in right α-quartz (i.e., $P3_221$ dextrorotatory α-quartz with clockwise rotation of the plane of polarization when facing the source of light). Indeed, this sign convention for the OR angle about direction u provides [5]

$$\Phi_u(\omega) = \frac{[n_L(\omega) - n_R(\omega)]\pi}{\lambda}, \tag{59}$$

where n_L (n_R) is the refractive index for left (right) circularly polarized light in the (v, w) plane. Then, Φ_u is negative if $n_R > n_L$, i.e., the rotation of the plane of polarization is towards the right (dextro-rotatory) for light coming towards the observer.

We obtain converged results with a dense $24 \times 24 \times 24$ Monkhorst-Pack net for sampling of reciprocal space (see SM [67] for full input decks). To assess the effect of the quality of the single-particle basis set, we performed calculations with the double- and triple-ζ valence polarization basis sets of Peintinger, Oliveira, and Bredow (POB-DZVP and POB-TZVP) [86], as well as the 6-311G(d) basis set of Heyd and co-workers [87], and quasirelativistic effective-core potentials and valence basis sets, from adjustment to the multiconfigurational Wood-Boring Hamiltonian (ECP-MWB) [88]. Crystal structures were fully optimized, under constraints provided by the trigonal space group, with the PBE0 functional. The optimized lattice parameters and GKS indirect band gaps are reported in Table IV, as compared with values from high-resolution powder x-ray diffraction and electron energy loss spectroscopy experiments and photoconductivity measurements [89–92]. Calculations with all four basis sets provide GKS gaps (7.639 to 9.220 eV) that are somewhat underestimated, compared to the experimental value of 8.9

to 11.5 eV [89–92]. This may be expected, as the calculated gaps from GKS eigenvalue differences are largely dependent on the fraction of Fock exchange and neglect exciton effects [70]. For the lattice parameters, a good agreement against the experiment is obtained with the Heyd basis sets. It is also noteworthy that the total energy is lowest with the Heyd basis set.

At the previously optimized PBE0 geometries, we then calculated the OR tensor, employing the SOS and LR-TD-DFT approaches (i.e., without and with account of orbital relaxation contributions), using the PBE and PBE0 functionals. Since α-quartz, is a uniaxial positive mineral, the optic axis lies parallel to the c crystallographic axis and experimental measurements are available at a wavelength of $\lambda = 589.44$ nm, yielding a value $\Phi_c = -21.7\,°/mm$ [85].

Calculated values with the length (LC) and nabla (V0) gauges for the electric dipole operator are reported in Table V. The table shows that an inclusion of both Fock exchange and orbital relaxation is crucial in the calculation of the OR tensor. As far as orbital relaxation is concerned, a comparison of SOS vs LR-TD-DFT values shows a large difference, e.g., 9.01 to -2.23 for PBE and 3.49 to 0.10, for PBE0 with V0 and the DZVP basis set. The most extreme case occurs with the Heyd basis set, where orbital relaxation results in a change of Φ_c from 4.39 to -63.22 for PBE and 0.97 to -26.14 for PBE0. The importance of orbital relaxation has also been stressed in a concurrent work [93]. The effect of including 25% Fock exchange in the functional is also quite important; in the V0 case, the LR-TD-DFT values go from -2.23 to 0.10 for DZVP, -2.31 to -0.042 for TZVP, and -63.22 to -26.14 for the Heyd G-311G(d) basis.

One way to assess the quality of the single-particle basis is by comparing relative LR-TD-DFT values in the length and nabla gauges. In principle, the LC and V0 values should match at the CBS limit. A small variation, therefore, indicates a good

TABLE III. Mean OR in $(°/mm)$ for different supercell expansions, number of **k** points, and basis sets, as compared to the reference infinite oligomer values.

Cells/**k** points	1/500	3/3	7/1	9/1	11/1	∞-oligo.
cc-pvDz	47.90	44.07	38.51	38.50	38.50	38.50
cc-pvTz	47.88	46.14	45.68	45.67	45.67	45.67
cc-pvQz	53.55	54.25	54.75	54.72	54.72	54.72

TABLE IV. Optimized lattice parameters (Angstrom), indirect band gaps (eV) of α-quartz with the PBE0 functional and different basis sets, as compared to experimental values [89–92]. Total energy differences ΔE_{Heyd} are also reported with respect to the Heyd 6-311G(d) value.

	a	c	Gap	ΔE_{Heyd}
ECP-MWB	5.209	5.735	7.639	–
POB-DZVP	5.019	5.546	9.220	0.749
POB-TZVP	4.998	5.481	8.837	0.011
Heyd 6-311G(d)	4.927	5.431	8.431	0.000
Experiment	4.913	5.405	8.9–11.5	–

TABLE V. PBE and PBE0 calculation of Φ_c (in $°/\text{mm}$) on α-quartz at wavelength $\lambda = 589.44$ nm with the SOS and LR-TD-DFT approaches (i.e., without and with account of orbital-relaxation contributions) for different basis sets. The experimental value is $\Phi_c = -21.7\,°/\text{mm}$ [85].

	PBE			
	SOS		LR-TD-DFT	
Basis set	LC	V0	LC	V0
ECP-MWB	-20.98	21.20	-43.61	-5.53
POB-DZVP	10.35	9.01	3.24	-2.23
POB-TZVP	7.90	6.64	1.12	-2.31
Heyd 6-311G(d)	-6.96	4.39	-56.29	-63.22
	PBE0			
	SOS		LR-TD-DFT	
Basis set	LC	V0	LC	V0
ECP-MWB	-13.43	7.73	-31.48	-1.96
POB-DZVP	4.81	3.49	0.80	0.10
POB-TZVP	2.42	4.27	3.37	-0.042
Heyd 6-311G(d)	-1.72	0.97	-36.05	-26.14

quality basis. The relative variation is much smaller for the Heyd basis set than for the ECP-MWB, POB-DZVP, or POB-TZVP ones. This result agrees with the preceding calculations of total energies and lattice parameters, but not the indirect gaps.

For our best calculation (PBE0 functional, Heyd basis set, LR-TD-DFT treatment, gauge-origin invariant V0 formulation), we obtain $\Phi_c = -26.14\,°/\text{mm}$, in good agreement with the experimental value of $\Phi_c = -21.7\,°/\text{mm}$. For this particular calculation, the individual contributions from the DD and DQ terms to the total Φ_c are $DD = -14.62\,°/\text{mm}$ and $DQ = -11.52\,°/\text{mm}$, thereby confirming the importance of DQ terms for calculations in the solid state, as also stressed in two other recent studies [52,53]. The DQ term also cannot be ignored for other crystal systems and appears to be generally necessary for OR calculations in the solid state.

Although the Heyd basis set yields reasonably good agreement with experiment, Table V displays a large dependence on the gauge (LC vs V0), as well as the basis set. To improve this dependence, in the future we will consider the possibility of modifying the single-particle orbitals by field-dependent phase factors. Indeed, the OR values are very sensitive to the presence and exact nature of diffuse functions in the basis set. Removal of the most diffuse s and p functions in the Heyd basis set changes the PBE0 LR-TD-DFT values obtained with the V0 (LC) formulation from $\Phi_c = -26.14(-36.05)\,°/\text{mm}$ to $\Phi_c = 252.02\,(-4.17)\,°/\text{mm}$. Finally, preliminary analysis indicates that the effect of the basis set is influenced in a major way by its capacity to yield accurate geometries. For instance, the PBE0 LR-TD-DFT values obtained with the POB-TZVP basis set of $3.37\,(-0.042)\,°/\text{mm}$ with the V0 (LC) formulation are much improved to $-4.98(-5.01)°/\text{mm}$ by using the optimized geometry from the Heyd basis set. The same values are further improved to $-8.54(-8.84)°/\text{mm}$ by the addition of a p function with exponent of 0.12 bohr^{-2} on the O

atoms. Good agreement with the experiment on OR, therefore, requires good agreement on optimized geometries.

VIII. CONCLUSIONS

A previously proposed electronic "angular-momentum" operator is shown to generalize the "modern theory of orbital magnetization" to nonlocal Hamiltonians (e.g., hybrid exchange-correlation functionals of generalized Kohn-Sham theory). A rigorous development of the theory demonstrates that previously suggested "band dispersion" terms, as well as terms involving reciprocal space derivatives of the perturbed wave function, can be avoided. Finally, it is shown that while the angular momentum operator is (in principle) periodic at the complete basis set limit (or in another basis that ensures gauge-origin invariance), it is not so in the general case.

The formalism is applied to calculating the optical rotatory power (OR) of insulators in the public CRYSTAL program, where expressions are developed in terms of the electric dipole–electric quadrupole (DQ) as well as the electric dipole–magnetic dipole (DD) contributions. For effective calculations, a strategy is developed to deal with quasidegeneracies in obtaining derivatives of the orbital coefficients with respect to the wave vector. Our implementation is validated by comparison with a model finite system and we report on an application to the α-quartz mineral, with linear-response time-dependent density functional theory calculations, that employ a hybrid as well as a nonhybrid functional. This application confirms the importance of DQ terms for OR calculations in the solid state. In the case of α-quartz, agreement versus experiment was only possible with an explicit account of (i) use of a high-quality basis set, (ii) inclusion of a fraction of nonlocal exact exchange in the exchange-correlation functional, and (iii) taking account of orbital relaxation.

For an implementation that is less dependent on the number of **k** points used to sample reciprocal space, as well as other numerical parameters, we will present in the future an improved scheme for the treatment of quasidegeneracies in determining derivatives of the orbital coefficients with respect to the wave vector. This will be done in conjunction with different applications for periodic systems of interest.

APPENDIX A: DERIVATION OF EQ. (19)

Expanding the matrix element of Eq. (12a) in WFs using Eqs. (17a) and (18) gives

$$
\begin{aligned}
\mathbf{M}_{\text{LC}} &= \frac{1}{2c}\Re \sum_n^{\text{occ}} \int_{\text{BZ}} d\mathbf{k} \sum_{\mathbf{R}\mathbf{R}'} e^{-i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \\
&\quad \times \langle n\mathbf{R}'|(\mathbf{r}-\mathbf{R}') \wedge H/i(\mathbf{r}-\mathbf{R})|n\mathbf{R}\rangle \\
&= \frac{1}{2c\Omega}\Re \sum_n^{\text{occ}} \sum_{\mathbf{R}\mathbf{R}'} \delta_{\mathbf{R}\mathbf{R}'}\langle n\mathbf{R}'|(\mathbf{r}-\mathbf{R}') \wedge H/i(\mathbf{r}-\mathbf{R})|n\mathbf{R}\rangle \\
&= -\frac{1}{2c\Omega}\Re \sum_n^{\text{occ}} \sum_{\mathbf{R}} \langle n\mathbf{R}|(\mathbf{r}-\mathbf{R}) \wedge iH(\mathbf{r}-\mathbf{R})|n\mathbf{R}\rangle.
\end{aligned}
$$
(A1)

Then, inserting Eq. (9) into Eq. (A1) provides

$$
\begin{aligned}
\mathbf{M}_{\mathrm{LC}} &= -\frac{1}{2c\Omega}\Re \sum_n^{\mathrm{occ}} \sum_{\mathbf{R}} \langle n\mathbf{R}|(\mathbf{r}-\mathbf{R}) \\
&\quad \wedge [\nabla_r/i + i(\mathbf{r}-\mathbf{R})H]|n\mathbf{R}\rangle \\
&= -\frac{1}{2c\Omega}\Re \sum_n^{\mathrm{occ}} \sum_{\mathbf{R}} \langle n\mathbf{R}|(\mathbf{r}-\mathbf{R}) \wedge \nabla_r/i|n\mathbf{R}\rangle, \quad (\text{A2})
\end{aligned}
$$

where we have used $(\mathbf{r}-\mathbf{R}) \wedge (\mathbf{r}-\mathbf{R}) = \mathbf{0}$.

Inserting Eq. (17a) into Eq. (A2) gives

$$
\begin{aligned}
\mathbf{M}_{\mathrm{LC}} &= -\frac{1}{2c}\Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \sum_{\mathbf{R}\mathbf{R}'} \langle n\mathbf{R}'|(\mathbf{r}-\mathbf{R}') \\
&\quad \wedge e^{-i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R}-\mathbf{r}+\mathbf{r})}\nabla_r/i|n\mathbf{R}\rangle \\
&= -\frac{1}{2c}\Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \left(-i\sum_{\mathbf{R}} \langle \nabla_{\mathbf{k}}u_{n,\mathbf{k}}| \right. \\
&\quad \left. \wedge e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r/i|n\mathbf{R}\rangle \right) \\
&= \frac{1}{2c}\Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \sum_{\mathbf{R}} \langle \nabla_{\mathbf{k}}u_{n,\mathbf{k}}| \wedge e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle.
\end{aligned}
\tag{A3}
$$

Comparing Eq. (A3) with Eq. (12a), we conclude

$$
\wedge H_{\mathbf{k}}/i|\nabla_{\mathbf{k}}u_{n,\mathbf{k}}\rangle = \wedge \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle + a|\nabla_{\mathbf{k}}u_{n,\mathbf{k}}\rangle,
\tag{A4}
$$

where we have used, for arbitrary vectors $\mathbf{A}$ $\mathbf{B}$, $\mathbf{C}$ and scalar a, $\mathbf{A} \wedge \mathbf{B} = \mathbf{A} \wedge \mathbf{C} \rightarrow \mathbf{C} = \mathbf{B} + a\mathbf{A}$. Inserting Eq. (A4) into Eq. (A3), we find

$$
\begin{aligned}
\mathbf{M}_{\mathrm{LC}} &= \Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \langle \nabla_{\mathbf{k}}u_{n,\mathbf{k}}| \wedge \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle \\
&\quad + a \times \mathbf{0},
\end{aligned}
\tag{A5}
$$

which shows that $\mathbf{M}_{\mathrm{LC}}$ is invariant to the particular choice of a. We make the simplest possible choice $a = 0$, and obtain, by comparing Eq. (A5) with Eq. (12a),

$$
\begin{aligned}
&\Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \langle \nabla_{\mathbf{k}}u_{n,\mathbf{k}}| \wedge \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle \\
&\quad = \Re \sum_n^{\mathrm{occ}} \int_{\mathrm{BZ}} d\mathbf{k} \langle \nabla_k u_{n,\mathbf{k}}| \wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle. \quad (\text{A6})
\end{aligned}
$$

Hence,

$$
\wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle \rightarrow \wedge \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\nabla_r|n\mathbf{R}\rangle,
\tag{A7}
$$

which is simply the first statement in Eq. (19). The second equality in Eq. (19) is then directly obtained from Eq. (17b).

APPENDIX B: MOMENTUM CONSERVATION

The matrix elements in Eq. (34) have the form

$$
\int_{-\infty}^{\infty} d\mathbf{r}\, \psi_{n,\mathbf{k}}^*(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\hat{O}(\mathbf{r})\psi_{m,\mathbf{k}'}(\mathbf{r}),
\tag{B1}
$$

where $\hat{O}(\mathbf{r})$ is a periodic operator $\hat{O}(\mathbf{r}) = \hat{O}(\mathbf{r}-\mathbf{R})$, and $\mathbf{R} = l\mathbf{a}$ for some integer l and lattice parameter $\mathbf{a}$. Writing the COs in terms of Bloch functions, we have

$$
\begin{aligned}
&\int_{-\infty}^{\infty} d\mathbf{r}\, e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}u_{n,\mathbf{k}}^*(\mathbf{r})\hat{O}(\mathbf{r})u_{m,\mathbf{k}'}(\mathbf{r}) \\
&= \sum_{l\in\mathbb{Z}} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot l\mathbf{a}} \int_0^{\mathbf{a}} d\mathbf{r}\, e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}u_{n,\mathbf{k}}^*(\mathbf{r})\hat{O}(\mathbf{r})u_{m,\mathbf{k}'}(\mathbf{r}),
\end{aligned}
\tag{B2}
$$

where we have used the lattice periodicity of $\hat{O}$ and u. Using the identity

$$
\sum_{l\in\mathbb{Z}} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot l\mathbf{a}} = \frac{2\pi}{\mathbf{a}} \cdot \delta(\mathbf{k}'-\mathbf{k}+\mathbf{q}),
\tag{B3}
$$

the integral gives zero unless $\mathbf{k}'-\mathbf{k} = -\mathbf{q}$.

APPENDIX C: MAGNETIZATION WITH SEMILOCAL FUNCTIONALS IN TERMS OF A "BAND DISPERSION" FORMULA

Following Eqs. (12a), (16), (22), and (25), we may write the orbital magnetization as

$$
\begin{aligned}
\mathbf{M} &= \frac{1}{c}\Re \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^{\mathrm{occ}} \langle \nabla_k u_{n,\mathbf{k}}| \wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle \\
&= \frac{1}{c}\Re \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^{\mathrm{occ}} [\langle \nabla_k u_{n,\mathbf{k}}| \wedge H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle \\
&\quad + \langle \nabla_k u_{n,\mathbf{k}}| \wedge (\nabla_k H_{\mathbf{k}})/i|u_{n,\mathbf{k}}\rangle \\
&\quad - \langle \nabla_k u_{n,\mathbf{k}}| \wedge (\nabla_k H_{\mathbf{k}})/i|u_{n,\mathbf{k}}\rangle].
\end{aligned}
\tag{C1}
$$

Then, using $\nabla_k(H_{\mathbf{k}}|u_{n,\mathbf{k}}\rangle) = (\nabla_k H_{\mathbf{k}})|u_{n,\mathbf{k}}\rangle + H_{\mathbf{k}}|\nabla_k u_{n,\mathbf{k}}\rangle$, Eq. (12d) may be rewritten as

$$
\begin{aligned}
\mathbf{M} &= \frac{1}{c}\Re \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^{\mathrm{occ}} [\langle \nabla_k u_{n,\mathbf{k}}| \wedge \nabla_k(H_{\mathbf{k}}/i|u_{n,\mathbf{k}}\rangle) \\
&\quad - \langle \nabla_k u_{n,\mathbf{k}}| \wedge (\nabla_k H_{\mathbf{k}})/i|u_{n,\mathbf{k}}\rangle].
\end{aligned}
\tag{C2}
$$

For arbitrary scalar fields ϑ and φ, by inserting $\nabla\vartheta \wedge \nabla\varphi = -\nabla \wedge ([\nabla\vartheta]\varphi)$ into Eq. (C2), we get

$$
\begin{aligned}
\mathbf{M} &= \frac{1}{c}\Re \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^{\mathrm{occ}} [-\nabla_k \wedge \langle \nabla_k u_{n,\mathbf{k}}|H_{\mathbf{k}}/i|u_{n,\mathbf{k}}\rangle \\
&\quad - \langle \nabla_k u_{n,\mathbf{k}}| \wedge (\nabla_k H_{\mathbf{k}}/i)|u_{n,\mathbf{k}}\rangle] \\
&= \frac{1}{c}\Re \int_{\mathrm{BZ}} d\mathbf{k} \sum_n^{\mathrm{occ}} [\nabla_k \wedge \langle u_{n,\mathbf{k}}|H_{\mathbf{k}}/i|\nabla_k u_{n,\mathbf{k}}\rangle^* \\
&\quad - \langle \nabla_k u_{n,\mathbf{k}}| \wedge (\nabla_k H_{\mathbf{k}}/i)|u_{n,\mathbf{k}}\rangle]
\end{aligned}
$$

$$= \frac{1}{c} \Re \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} [\boldsymbol{\nabla}_k \wedge \langle u_{n,\mathbf{k}} | H_{\mathbf{k}} / i | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle$$
$$- \langle \boldsymbol{\nabla}_k u_{n,\mathbf{k}} | \wedge (\boldsymbol{\nabla}_k H_{\mathbf{k}} / i) | u_{n,\mathbf{k}} \rangle]. \tag{C3}$$

We now use the following identity obtained as a corollary to the divergence theorem:

$$\iiint_V dV \, \boldsymbol{\nabla} \wedge \mathbf{F} = \oiint_S d\mathcal{S} \, \mathbf{n}_k \wedge \mathbf{F}, \tag{C4}$$

for some vector field $\mathbf{F}$ over the volume V bounded by the closed surface $\mathcal{S}$ with vector normal $\mathbf{n}_k$. Inserting Eq. (C4) into Eq. (C3), we get

$$\mathbf{M} = \frac{1}{c} \Re \sum_n^{\text{occ}} \left[\oiint_S d\mathcal{S} \, \mathbf{n}_k \wedge \langle u_{n,\mathbf{k}} | H_{\mathbf{k}} / i | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle \right.$$
$$\left. - \int_{\text{BZ}} d\mathbf{k} \, \langle \boldsymbol{\nabla}_k u_{n,\mathbf{k}} | \wedge (\boldsymbol{\nabla}_k H_{\mathbf{k}} / i) | u_{n,\mathbf{k}} \rangle \right]. \tag{C5}$$

Over $\mathcal{S}$ (the edge of the Brillouin zone, where $e^{i\mathbf{k}\cdot\mathbf{R}}$ for lattice vector $\mathbf{R}$ is pure real), the real part of the integrand in the first

term vanishes because $\psi_{n,\mathbf{k}}$ is pure real. We now use

$$(\boldsymbol{\nabla}_k H_{\mathbf{k}}) | u_{n,\mathbf{k}} \rangle = \boldsymbol{\nabla}_k | H_{\mathbf{k}} u_{n,\mathbf{k}} \rangle - H_{\mathbf{k}} | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle$$
$$= (\boldsymbol{\nabla}_k \epsilon_{n,\mathbf{k}}) | u_{n,\mathbf{k}} \rangle + \epsilon_{n,\mathbf{k}} | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle - H_{\mathbf{k}} | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle. \tag{C6}$$

Inserting Eq. (C6), as well as the identity $\sum_l^{\text{all}} | u_{l,\mathbf{k}} \rangle \langle u_{l,\mathbf{k}} | = \mathbb{1}$ into Eq. (C5) gives

$$\mathbf{M} = -\frac{1}{c} \Re \sum_n^{\text{occ}} \sum_l^{\text{all}} \int_{\text{BZ}} d\mathbf{k} \, \{ \langle \boldsymbol{\nabla}_k u_{n,\mathbf{k}} | u_{l,\mathbf{k}} \rangle$$
$$\wedge [\langle u_{l,\mathbf{k}} | (\boldsymbol{\nabla}_k \epsilon_{n,\mathbf{k}} / i) | u_{n,\mathbf{k}} \rangle + (\epsilon_{n,\mathbf{k}} - \epsilon_{l,\mathbf{k}}) / i \langle u_{l,\mathbf{k}} | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle] \}. \tag{C7}$$

Now, using the fact that the real part of the term with $\langle \boldsymbol{\nabla}_k u_{n,\mathbf{k}} | u_{l,\mathbf{k}} \rangle \wedge \langle u_{l,\mathbf{k}} | \boldsymbol{\nabla}_k u_{n,\mathbf{k}} \rangle$, being the cross product of a vector with itself vanishes, we get

$$\mathbf{M} = \frac{1}{c} \Re \int_{\text{BZ}} d\mathbf{k} \sum_n^{\text{occ}} \langle \boldsymbol{\nabla}_k u_{n,\mathbf{k}} | u_{n,\mathbf{k}} \rangle \wedge (\boldsymbol{\nabla}_k \epsilon_{n,\mathbf{k}} / i), \tag{C8}$$

which is Wang and Yan's "band dispersion" term [53].

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