Natural Optical Activity from Density-Functional Perturbation Theory

Asier Zabalo[1] and Massimiliano Stengel[1,2]
[1]*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain*
[2]*ICREA-Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain*

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We present an accurate and computationally efficient first-principles methodology to calculate natural optical activity. Our approach is based on the long-wave density-functional perturbation theory and includes self-consistent field terms naturally in the formalism, which are found to be of crucial importance. The final result is expressed exclusively in terms of response functions to uniform field perturbations and avoids troublesome summations over empty states. Our strategy is validated by computing the natural optical activity tensor in representative chiral crystals (trigonal Se, α-HgS, and α-SiO$_2$) and molecules (C$_4$H$_4$O$_2$), finding excellent agreement with experiment and previous theoretical calculations.

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Natural optical activity (NOA) refers to the first-order spatial dispersion of the macroscopic dielectric tensor [1]. Empirically, it manifests as optical rotation (OR), which is a property of certain structures to rotate the plane of the polarization of light that travels through them [2,3]; at difference with the Faraday effect, NOA is reciprocal and doesn't require magnetism to be present [4]. It was first measured in quartz crystals back in 1811 by Arago, and historically, most of the studied optically active materials turned out to be chiral. In fact, chirality is a sufficient but not necessary condition for NOA to be present, as optically active achiral systems also exist [5]. Since its discovery, natural optical activity has been attracting increasing research interest, and reliable experimental measurements now exist for many materials, both in molecular [6–10] and crystalline form [11–17].

Parallel to the experiments, there have been considerable advances in the theoretical understanding of optical rotation as well [2,11,18–20]. *Ab initio* methods like Hartee-Fock (HF), [9] coupled-cluster (CC) [21], and density functional theory (DFT) [6,7,22] have recently become popular in the context of NOA. While most of the available literature is about small molecules, notable attempts at calculating optical activity in solids do exist. It is worth mentioning, for example, the pioneering works by Zhong, Levine, Allan, and Wilkins, [19,20] based on a numerical long-wavelength expansion of the electromagnetic response function. Later, Malashevich and Souza [23] and Pozo and Souza [24] derived analytical expressions for the NOA, thus reviving the interest in the field; their formalism has been implemented very recently within an *ab initio* context [25]. The agreement between theory and experiment achieved in these works is quite good, e.g., for trigonal Se [23,24], α quartz [19,20], and trigonal Te [26].

In spite of the remarkable progress, however, a systematic, first-principles-based and computationally efficient methodology to compute the NOA has not been established yet. The first issue concerns the treatment of the self-consistent fields (SCFs). These were accounted for in Ref. [27] and found to be of crucial importance, but the numerical differentiations with respect to the wave vector **q** that were used therein have limited a widespread application of their method. The existing analytical expressions [23,24] for the NOA are, in principle, better suited to an *ab initio* implementation [25], but the SCF contributions are systematically neglected therein. Another disadvantage with the existing techniques lies in that they require cumbersome sums over empty states; this introduces an additional potential source of error, as the convergence with respect to the number of bands tends to be slow. There are additional technical subtleties that have not been considered in the context of the NOA, for example, regarding the correct treatment of the current-density response in the presence of nonlocal pseudopotentials [28]. It is unquestionable that the current limitations rule out the study of many systems of outstanding interest (e.g., electrotoroidic compounds [29,30]), which are hardly accessible to the currently available schemes.

Here we present, within the framework of first-principles long-wave density functional perturbation theory (DFPT), a method to calculate the natural optical activity that overcomes the aforementioned limitations and is equally valid for molecules and extended solids. Building on Ref. [31], we express the natural optical activity tensor as the first-order spatial dispersion (i.e., derivative with respect to the wave vector **q**) of the macroscopic dielectric function. Crucially, the capabilities of the recently implemented long-wave module [32] of ABINIT [33,34] allow for an efficient calculation by combining response functions that are already available in the code (e.g., **k** derivatives, electric and orbital magnetic field perturbations). This way, summations over excited states are entirely avoided, and the effect of local fields is automatically included without the need for an *ad hoc* treatment. We validate our methodology by computing the NOA tensor for well-known chiral structures, including trigonal crystals (Se, α-HgS, and α-SiO$_2$) and the C$_4$H$_4$O$_2$ molecule. Our numerical results show fast convergence with respect to the main computational parameters, and are in excellent agreement with experiment and earlier theoretical calculations.

Our starting point is the double Fourier transform in frequency ω and wave vector $\mathbf{q}$ of the permittivity function, $\epsilon_{\alpha\beta}(\omega, \mathbf{q})$. By expanding $\epsilon_{\alpha\beta}(\omega, \mathbf{q})$ in powers of the wave vector $\mathbf{q}$, around $\mathbf{q} = \mathbf{0}$, we obtain

$$\epsilon_{\alpha\beta}(\omega, \mathbf{q}) = \epsilon_{\alpha\beta}(\omega, \mathbf{q} = \mathbf{0}) + iq_\gamma \eta_{\alpha\beta\gamma}(\omega) + \ldots, \quad (1)$$

where $\eta_{\alpha\beta\gamma}(\omega)$ is the natural optical activity tensor [1]. (From now on, we adopt Einstein summation conventions for the Cartesian indices $\alpha\beta\gamma$.) In absence of dissipation (i.e., in the transparent regime), $\epsilon_{\alpha\beta}(\omega, \mathbf{q})$ is a 3×3 Hermitian matrix, which at $\mathbf{q} = \mathbf{0}$ becomes real symmetric in crystals with time-reversal (TR) symmetry. The frequency-dependent natural optical activity tensor is then also real and satisfies $\eta_{\alpha\beta\gamma}(\omega) = -\eta_{\beta\alpha\gamma}(\omega)$, which means that only 9 of the 27 components of $\eta_{\alpha\beta\gamma}$ are independent. As a consequence, $\eta_{\alpha\beta\gamma}$ is often rearranged into the second-rank *gyration* or *gyrotropic* tensor, $g_{\alpha\beta}$, [1]

$$g_{\alpha\beta}(\omega) = \frac{1}{2}\epsilon_{\gamma\delta\alpha}\eta_{\gamma\delta\beta}(\omega), \quad (2)$$

where $\epsilon_{\gamma\alpha\delta}$ is the Levi-Civita symbol. Assuming a crystal structure with the point group 32 (trigonal Se, α-HgS, and α-SiO$_2$ belong to this crystal class), and considering that the optical axis is oriented along the z Cartesian direction [19],

$$\boldsymbol{g}(\omega) = \begin{pmatrix} g_{11}(\omega) & 0 & 0 \\ 0 & g_{11}(\omega) & 0 \\ 0 & 0 & g_{33}(\omega) \end{pmatrix}, \quad (3)$$

where $g_{11} = \eta_{231}$ and $g_{33} = \eta_{123}$. The optical rotatory power ρ is then given by [19]

$$\rho(\omega) = \frac{\omega^2}{2c^2} g_{33}(\omega), \quad (4)$$

where c is the speed of light. In this work, we shall focus on the $\omega \to 0$ limit, where the components of both $\boldsymbol{g}$ and $\boldsymbol{\eta}$ tend to a finite constant,

$$\eta_{\alpha\beta\gamma} = \eta_{\alpha\beta\gamma}(\omega \to 0), \qquad g_{\alpha\beta} = g_{\alpha\beta}(\omega \to 0). \quad (5)$$

At leading order in the frequency, this yields a rotatory power of

$$\rho(\omega) \simeq (\hbar\omega)^2 \bar{\rho}, \qquad \bar{\rho} = \frac{g_{33}}{2(\hbar c)^2}, \quad (6)$$

where $\hbar$ is the reduced Planck constant. The constant $\bar{\rho}$ is usually expressed in the units of deg $/[\mathrm{mm}\,(\mathrm{eV})^2]$] and can be directly compared to experimental measurements.

To make further progress, we shall express the dielectric function in the low-frequency limit as a second derivative of the ground state energy with respect to two spatially modulated electric fields ($\boldsymbol{\mathcal{E}}$) [35]

$$\epsilon_{\alpha\beta}(\mathbf{q}) = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathbf{q}}. \quad (7)$$

This allows us to write the natural optical activity tensor as the first derivative of $\epsilon_{\alpha\beta}(\mathbf{q})$ with respect to q_γ,

$$\eta_{\alpha\beta\gamma} = -\frac{4\pi}{\Omega}\mathrm{Im}E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\gamma}, \qquad E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\gamma} = \left.\frac{\partial E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathbf{q}}}{\partial q_\gamma}\right|_{\mathbf{q}=\mathbf{0}}, \quad (8)$$

where Ω is the volume of the unit cell. By virtue of the "$2n+1$" theorem [31], $E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\gamma}$ can be written in terms of uniform-field response functions, which are already available in public first-principles packages like ABINIT. More specifically, we find

$$E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\gamma} = E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathrm{elst},\gamma} + 2s\int_{\mathrm{BZ}}[d^3k]E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathbf{k},\gamma}, \quad (9)$$

where $s = 2$ is the spin multiplicity, and the shorthand notation $[d^3k] = \Omega/(2\pi)^3 d^3k$ is used for the Brillouin-zone (BZ) integral. [We assume that the system under study is a TR symmetric insulator.] The electrostatic (elst) term is defined as

$$E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathrm{elst},\gamma} = \int_\Omega\int n^{\mathcal{E}_\alpha}(\mathbf{r})K_\gamma(\mathbf{r},\mathbf{r}')n^{\mathcal{E}_\beta}d^3r d^3r', \quad (10)$$

where $n^{\mathcal{E}_\beta}$ is the first-order charge density response to $\mathcal{E}_\beta$, and $K_\gamma(\mathbf{r},\mathbf{r}')$ is the first $\mathbf{q}$ derivative of the Hartree exchange and correlation kernel. The wave function term of Eq. (9), in turn, can be written as

$$\begin{aligned} E^{\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathbf{k},\gamma} = {} & \mathcal{X}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta}_{\mathbf{k}} + \mathcal{Y}^{\mathcal{E}_\alpha\mathcal{E}_\beta k_\gamma}_{\mathbf{k}} + \mathcal{Y}^{k_\gamma\mathcal{E}_\alpha\mathcal{E}_\beta}_{\mathbf{k}} \\ & + \mathcal{W}^{\alpha,\beta\gamma}_{\mathbf{k}} + (\mathcal{W}^{\beta,\alpha\gamma}_{\mathbf{k}})^*. \end{aligned} \quad (11)$$

We shall explain Eq. (11) term by term in the following.

For three generic perturbations, λ_1, λ_2, and λ_3, the calligraphic symbols in the first line are defined as

$$\mathcal{X}^{\lambda_1\lambda_2\lambda_3}_{\mathbf{k}} = \sum_m \langle u^{\lambda_1}_{m\mathbf{k}}|\hat{\mathcal{H}}^{\lambda_2}_{\mathbf{k}}|u^{\lambda_3}_{m\mathbf{k}}\rangle \quad (12)$$

and

$$\mathcal{Y}_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3} = -\sum_{mn} \langle u_{m\mathbf{k}}^{\lambda_1} | u_{n\mathbf{k}}^{\lambda_3} \rangle \langle u_{n\mathbf{k}}^{(0)} | \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle. \tag{13}$$

(The band indices m, n run over the occupied states only.) Here, $|u_{m\mathbf{k}}^{\lambda}\rangle$ are the first-order wave functions and the first-order calligraphic Hamiltonian is given by $\hat{\mathcal{H}}_{\mathbf{k}}^{\lambda} = \hat{H}_{\mathbf{k}}^{\lambda} + \hat{V}^{\lambda}$, where $\hat{H}_{\mathbf{k}}^{\lambda}$ is the external perturbation and $\hat{V}^{\lambda}$ is the SCF potential response. Note that $\hat{\mathcal{H}}_{\mathbf{k}}^{k_\gamma} = \hat{H}_{\mathbf{k}}^{k_\gamma}$ as there is no SCF contribution to the derivative in $\mathbf{k}$ space, and $\hat{\mathcal{H}}_{\mathbf{k}}^{\mathcal{E}_\alpha} = \hat{V}^{\mathcal{E}_\alpha}$ in the above equations since the "external potential" is a purely cross-gap operator in the electric-field case [31].

The third line is defined as

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \sum_m i \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | u_{m\mathbf{k},\gamma}^{A_\beta} \rangle, \tag{14}$$

where $|u_{m\mathbf{k},\gamma}^{A_\beta}\rangle$ indicates the wave function response to an electromagnetic vector potential at first order in the modulation vector $\mathbf{q}$. (See Sec. V of Ref. [36] for more details.) We can write $\mathcal{W}$ as a sum of two contributions that are, respectively, symmetric ($\mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma}$) and antisymmetric ($\mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma}$) with respect to $\beta \leftrightarrow \gamma$ exchange,

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} + \mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma}. \tag{15}$$

These objects are given by

$$\mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} = \frac{i}{2} \sum_m \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | \partial_{\beta\gamma}^2 u_{m\mathbf{k}}^{(0)} \rangle \tag{16}$$

and

$$\mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma} = \frac{1}{2} \sum_m \epsilon_{\delta\beta\gamma} \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | u_{m\mathbf{k}}^{B_\delta} \rangle. \tag{17}$$

In Eq. (16), $\partial_{\beta\gamma}^2$ represents a second derivative in $\mathbf{k}$ space. The $|\partial_{\beta\gamma}^2 u_{m\mathbf{k}}^{(0)}\rangle$ functions in $\mathcal{S}$ are the well known $d^2/dk_\beta dk_\gamma$ wave functions [31,45,46]; whereas in Eq. (17), $|u_{m\mathbf{k}}^{B_\delta}\rangle$ is the wave function response to a uniform orbital magnetic field, B_δ, as defined in Refs. [47,48].

For finite systems, the above theory nicely recovers the established formulas that are used in quantum chemistry calculations (more details can be found in Sec. VII of Ref. [36]). Our formulation, however, presents many crucial advantages. First, Eq. (9) has been derived within a DFPT framework, and hence avoids the cumbersome summations over unoccupied states that are required by other methods. Second, all contributions to Eq. (11) are individually independent of the choice of the origin, and equally valid for both molecules and extended crystals; this implies that our formulas are free of cancellation errors due to incomplete basis sets. Third, all the aforementioned terms are independent of the choice of the wave function gauge by construction, as they are all expressed as parametric derivatives (with respect to $\mathbf{q}$) of multiband gauge-invariant quantities. Fourth, the treatment of the current-density response in the presence of nonlocal pseudopotentials complies with the prescriptions of Ref. [28]. Finally, and most importantly, SCF terms naturally appear in our formalism, both directly in E_{elst} and $\mathcal{Y}$ (both terms vanish if local fields are neglected), and indirectly in the other terms via the first-order wave functions $|u_{m\mathbf{k}}^{\mathcal{E}_\alpha}\rangle$ (see Sec. VI of Ref. [36]).

A natural question to ask at this point is whether Eq. (11) is unique, or whether there are other combinations of the same ingredients that yield the same result. Two inequivalent definitions of $E_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha^* \mathcal{E}_\beta}$ can, at most, differ by a vanishing Brillouin-zone integral; so the question boils down to asking whether we can combine the individual pieces in Eq. (11) in such a way that the result is the total $\mathbf{k}$ derivative of some function $f(\mathbf{k})$. An obvious choice for $f(\mathbf{k})$ consists in identifying it with the $\mathbf{k}$ derivative of the macroscopic dielectric tensor. Indeed, by applying the $2n+1$ theorem to the stationary expression [35,49,50] for $E_{\mathbf{k},\mathbf{q}=\mathbf{0}}^{\mathcal{E}_\alpha^* \mathcal{E}_\beta}$, we find

$$\begin{aligned} \left.\frac{\partial E_{\mathbf{k},\mathbf{q}}^{\mathcal{E}_\alpha^* \mathcal{E}_\beta}}{\partial k_\gamma}\right|_{\mathbf{q}=\mathbf{0}} = {} & \mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{X}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} + \mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta} \\ & + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta} + \mathcal{Y}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} \\ & + 2\mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} + 2(\mathcal{S}_{\mathbf{k}}^{\beta,\alpha\gamma})^*. \end{aligned} \tag{18}$$

Then, by subtracting the latter expression from Eq. (11), we obtain another equally valid formula for the NOA,

$$\begin{aligned} [E_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha \mathcal{E}_\beta}]' = {} & -(\mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{X}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta}) \\ & - \mathcal{W}_{\mathbf{k}}^{\alpha,\gamma\beta} - (\mathcal{W}_{\mathbf{k}}^{\beta,\gamma\alpha})^*. \end{aligned} \tag{19}$$

Numerical tests confirm the consistency of Eqs. (11) and (19) to a very high degree of accuracy. We therefore conclude that Eq. (9) is not unique; on the contrary, there are infinite possible definitions of the gyrotropy tensor, differing from our Eq. (9) by a dimensionless constant times Eq. (18).

This arbitrariness can be regarded a direct consequence of the *electromagnetic* (EM) gauge freedom. Indeed, the last lines in both Eqs. (11) and (19) have the physical meaning of Berry curvatures in the parameter space spanned by a uniform magnetic field ($\mathbf{B}$) and an electric field. Such curvatures are, as we said, insensitive to the choice of the coordinate origin and the wave function gauge. This result was achieved by expressing the $\mathbf{B}$-field response function in a cell-periodic form, consistent with the density-operator theory of Essin *et al.* [47]. Notwithstanding these undeniable advantages, the aforementioned Berry curvatures retain an inherent dependence

TABLE I. Calculated independent components of the gyration tensor (in bohr) and the optical rotatory power $\bar{\rho}$ defined in Eq. (6) (in deg$/[\mathrm{mm}\,(\mathrm{eV})^2]$ units). Values in brackets are computed neglecting the SCF terms.

	g_{11}	g_{33}	$\bar{\rho}$
Se	−1.307 (−1.547)	−1.913 (−0.458)	−74.5 (−17.8)
α-HgS	0.775 (0.554)	−1.861 (−1.274)	−72.5 (−49.6)
α-SiO$_2$	−0.071 (−0.001)	0.125 (0.019)	4.9 (0.7)

on the EM gauge [51]. More specifically, the symbol $\mathcal{W}^{\alpha,\beta\gamma}$ is expressed in a Landau gauge where the β component of the $\mathbf{A}$ field increases linearly along γ; so when going from Eqs. (11)–(19) we have essentially switched between two Landau gauges in the last term, and collected the leftovers in the form of $\mathcal{X}$ and $\mathcal{Y}$. [It is, of course, possible to define a third variant of Eq. (11), where the contribution of $\mathcal{S}$ cancels out, at the expense of having a slightly longer list of $\mathcal{X}$ and $\mathcal{Y}$ symbols.] Ideally, one would like to exploit this freedom to obtain a physically intuitive separation between well-defined (and possibly individually measurable) physical effects; whether such a choice exists is an interesting open question, which we shall defer to a later work.

Our first principles calculations are performed with the open-source ABINIT [33,34] package. (Details of the computational parameters are provided in Sec. I of Ref. [36].) Overall, our approach displays a remarkably fast convergence with respect to the main computational parameters (plane-wave energy cutoff and number of $\mathbf{k}$ points, see Ref. [36], Sec. III). In Table I we show the converged numerical values for the independent components of the gyration tensor and the optical rotatory power in our test set of trigonal crystals: trigonal Se, α-HgS, and α-SiO$_2$ (numerical values in brackets are obtained neglecting SCF terms). Our results are in fairly good agreement with literature values, even if a scissor operator was applied in Ref. [27] to correct the local-density approximation (LDA) band gap. (More details can be found in Ref. [36], Sec. IV.) Trigonal Se is an interesting exception, in that Ref. [27] reports an opposite sign to ours for the non-SCF value of the g_{33} component; although the reason for this discrepancy is unclear, we remain confident in the accuracy of our results, as other values nicely agree with ours in both magnitude and sign. Overall, our results confirm the crucial importance of local-field SCF contributions, consistent with the conclusions of Ref. [27].

Given the large impact of SCF fields on the results, we decided to repeat our calculations within the Perdew-Burke-Ernzerhof (PBE) [52] parametrization of the generalized gradient approximation (GGA). The corresponding values are reported in Table II. (Further details can be found in Ref. [36], Sec. II.) Interestingly, for a given crystal structure the choice between the LDA and GGA seems to have a relatively small influence on the calculated coefficients, except for the g_{33} component of Se where such deviation reaches ~50%. Conversely, the structural parameters do appear to have a significant impact on the final result. To account for this fact, we have tested various models for the crystal structure, either using the experimental (exp) one, or relaxed to mechanical equilibrium (either within the LDA or GGA). Our analysis shows that the fundamental gap depends on the volume of the unit cell, and such a dependence has a strong impact on the calculated $\boldsymbol{g}$-tensor components. For example, in the LDA equilibrium structure of Se the electronic band gap is so small that we were unable to converge g_{11} and g_{33} to meaningful values. Conversely, even if the PBE parametrization of the GGA displays a significant overcorrection of the equilibrium volume, it yields results that are in much closer agreement with the experiment. To rationalize this outcome, note that the PBE parametrization yields an aspect ratio ($c/a = 1.13$) that almost perfectly matches the experimental value ($c/a = 1.14$), while the relaxed LDA value ($c/a = 1.30$) is clearly incorrect. It is also interesting to note that the NOA, unlike other linear-response properties (e.g., the dielectric tensor), has a nontrivial dependence on the structure (and hence on the amplitude of the gap). The final result originates from the mutual cancellation of several terms, not all of which are expected to diverge in the metallic limit. This means that some components of $\boldsymbol{g}$ may change rather dramatically with structure, while others remain essentially unaltered (see Sec. II of Ref. [36] for more details).

TABLE II. Comparison between the LDA and GGA for the independent components of the gyration tensor for Se, α-HgS, and α-SiO$_2$, for different structures. In the Structure column, “exp” refers to the experimental structure, while Se (LDA) means that the structure was relaxed with the LDA, for example.

	g_{11} (bohr)		g_{33} (bohr)	
Structure	LDA	GGA	LDA	GGA
Se(exp)	−1.306	−1.301	−1.910	−1.329
Se(GGA)	−1.408	−1.431	−1.802	−1.216
α-HgS (LDA)	0.775	0.663	−1.861	−1.645
α-HgS (GGA)	−0.716	−0.692	−0.065	−0.065
α-SiO$_2$ (LDA)	−0.071	−0.071	0.125	0.125
α-SiO$_2$ (GGA)	−0.085	−0.085	0.168	0.167

We now focus on the isolated molecule C$_4$H$_4$O$_2$. Table III shows our computed gyration tensor (multiplied by the volume of the simulation cell Ω), with and without SCF terms; as in crystals, the latter have a huge impact on some components. We also report the optical rotatory parameter β, which in molecular systems relates to the rotatory power $\alpha(\omega)$ via [53,54]

$$\alpha(\omega) = \frac{N_A \omega^2}{Mc^2}\beta, \qquad \beta = \frac{\Omega}{4\pi}\frac{1}{2}\sum_a \frac{1}{3} g_{aa}. \tag{20}$$

TABLE III. Calculated independent components of the gyration tensor times the volume of the simulation cell (Ω) for $C_4H_4O_2$. Values are given in Hartree atomic units.

	Ωg_{11}	Ωg_{22}	Ωg_{33}	$(\Omega/2)(g_{12}+g_{21})$	β
With SCF	−69.69	−68.12	−33.98	−267.32	−2.28
Without SCF	−72.52	−56.18	144.90	−629.35	0.21

Here N_A is the Avogadro number and M is the molar mass of the molecule. Our computed value of β almost exactly matches the value of $\beta = -2.29$ that was reported in Ref. [55]. Although such a level of agreement gives us confidence in the correctness of our implementation, it may be to some extent coincidental, given the differences in our respective approximations and computational schemes.

In summary, we have presented a formulation of optical dispersion within the framework of density-functional perturbation theory. Our methodology brings the first-principles calculation of the gyration tensor to the same level of accuracy and computational ease as standard linear-response properties, e.g., the dielectric tensor. We have also discussed some formal aspects of the theory, e.g., the nonuniqueness of Eq. (9), which we relate to the gauge freedom of electromagnetism. As an outlook, a natural step forward consists in generalizing our method to finite frequencies, and to magnetic materials with broken time-reversal symmetry; progress along these lines will be presented in a forthcoming publication.

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