

# Reversality of optical interactions in noncentrosymmetric media

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The interaction of an electromagnetic wave with a noncentrosymmetric crystal is not necessarily time reversible, and the departure from reversality may be seen in nonlocal (wave-vector linear) phenomena. However, relativistic symmetry with respect to simultaneous time and space inversion is always preserved in optics.

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We revise the widely accepted belief that linear optical interactions obey time reversality. We have come to the conclusion that the analysis of light-matter interaction should be based on the validity of relativistic reversality, i.e.,  $PT$  invariance (where  $T$  and  $P$  are time and space inversion operators), rather than on simple  $T$  invariance.<sup>1</sup> Examples of the violation of microscopic reversality for scattering of electrons in a noncentrosymmetric potential were given by Belinicher and Sturman,<sup>2</sup> and here we address the consequences of the lack of space-inversion symmetry on the reversality of optical interactions. All the results presented below are consequences of the propagating electromagnetic wave's not having a defined parity with respect to space inversion or a defined symmetry with respect to time reversal (see, for example, Ref. 3). We found that the difference between  $T$  and  $PT$  invariance is significant when relativistic terms in light-matter interaction are taken into account in crystals lacking inversion centers. We show that  $T$ -odd interactions may emerge only in first-order spatial dispersion, i.e., wave-vector proportional phenomena, and that in some crystal structures they may be probed optically. This research has been stimulated by recent observations of the time-nonreversible optical phenomenon in noncentrosymmetric cubic crystals<sup>4,5</sup> that was explained by use of a specific model for a direct-gap zinc blende semiconductor.<sup>5</sup> Here we show that nonreversality is a general feature of nonlocal light-matter interactions in crystals that lack inversion centers and may be predicted without recourse to any particular material.

Transformations of the molecular characteristics and electromagnetic fields under space and time inversion have been discussed by numerous sources.<sup>6-8</sup> To summarize these results, under the parity operator  $P$  molecular characteristics transform as follows: coordinates of the elements of molecular structure  $\mathbf{r} \Rightarrow -\mathbf{r}$ , gradients of internal molecular characteristics  $\nabla \Rightarrow -\nabla$ ; kinetic momenta of particles  $\mathbf{p} = -i\hbar(\partial/\partial\mathbf{r}) \Rightarrow -\mathbf{p}$ ; internal molecular electrostatic potential  $V(\mathbf{r}) \Rightarrow V(\mathbf{r})$ ; angular and spin momenta of electrons  $\mathbf{L} \Rightarrow \mathbf{L}$ ;  $\boldsymbol{\sigma} \Rightarrow \boldsymbol{\sigma}$ ; electric field strength  $\mathbf{E}(\mathbf{r}, t) \Rightarrow -\mathbf{E}(-\mathbf{r}, t)$ ; magnetic induction  $\mathbf{B}(\mathbf{r}, t) \Rightarrow \mathbf{B}(-\mathbf{r}, t)$ ; and vector potential  $\mathbf{A}(\mathbf{r}, t) \Rightarrow -\mathbf{A}(-\mathbf{r}, t)$  [for example, for an electromag-

netic wave  $\mathbf{A}^{(0)} \cos(\omega t - \mathbf{kr}) \Rightarrow -\mathbf{A}^{(0)} \cos(\omega t + \mathbf{kr})$ ]. Under the time-reversality operator  $T$  these characteristics transform as follows:  $\mathbf{r} \Rightarrow \mathbf{r}$ ;  $\nabla \Rightarrow \nabla$ ;  $\mathbf{p} \Rightarrow -\mathbf{p}$ ;  $V(\mathbf{r}) \Rightarrow V(\mathbf{r})$ ;  $\mathbf{L} \Rightarrow -\mathbf{L}$ ;  $\boldsymbol{\sigma} \Rightarrow -\boldsymbol{\sigma}$ ;  $\mathbf{E}(\mathbf{r}, t) \Rightarrow \mathbf{E}(\mathbf{r}, -t)$ ;  $\mathbf{B}(\mathbf{r}, t) \Rightarrow -\mathbf{B}(\mathbf{r}, -t)$ ; and  $\mathbf{A}(\mathbf{r}, t) \Rightarrow -\mathbf{A}(\mathbf{r}, -t)$  [for example, for an electromagnetic wave  $\mathbf{A}^{(0)} \cos(\omega t - \mathbf{kr}) \Rightarrow -\mathbf{A}^{(0)} \cos(\omega t + \mathbf{kr})$ ]. Within the scope of electromagnetic forces any molecular or crystal Hamiltonian obeys time ( $T$ ) and space ( $P$ ) inversion symmetry separately.<sup>9</sup> For instance, separate  $P$  and  $T$  reversality is obvious for the relativistic Hamiltonian of an optical electron of mass  $m$  and electric charge  $e$  (Ref. 6):

$$H = \frac{\mathbf{p}^2}{2m} + eV - \frac{e\hbar^2}{8m^2c^2} \nabla^2 V + \frac{e\hbar}{4m^2c^2} [\nabla V \times \mathbf{p}] \cdot \boldsymbol{\sigma}. \quad (1)$$

Here  $\mathbf{p}$  and  $\boldsymbol{\sigma}$  are the momentum and the spin of the particle, respectively, and  $V$  is the internal crystal electrostatic potential, which may be expressed as  $V(\mathbf{r}) = \sum e_p/|\mathbf{r} - \mathbf{r}_p|$  (the summation is performed over  $p$  labeling charges different from the optical electron).  $V(\mathbf{r})$  may be presented as a sum of even and odd functions of coordinate  $V(\mathbf{r}) = V_{\text{odd}}(\mathbf{r}) + V_{\text{even}}(\mathbf{r})$ , where  $V_{\text{even}}(\mathbf{r}) = V_{\text{even}}(-\mathbf{r}) = 1/2 \sum (e_p/|\mathbf{r} - \mathbf{r}_p| + e_p/|\mathbf{r} + \mathbf{r}_p|)$  and  $V_{\text{odd}}(\mathbf{r}) = -V_{\text{odd}}(-\mathbf{r}) = 1/2 \sum (e_p/|\mathbf{r} - \mathbf{r}_p| - e_p/|\mathbf{r} + \mathbf{r}_p|)$ . Note that not only  $V(\mathbf{r})$  but also  $V_{\text{odd}}(\mathbf{r})$  and  $V_{\text{even}}(\mathbf{r})$  are simultaneously  $P$  invariant: from  $P\{\mathbf{r}\} = -\mathbf{r}$ ,  $P\{\mathbf{r}_p\} = -\mathbf{r}_p$  it follows that  $P\{V_{\text{odd}}(\mathbf{r})\} = V_{\text{odd}}(\mathbf{r})$  and  $P\{V_{\text{even}}(\mathbf{r})\} = V_{\text{even}}(\mathbf{r})$ .

However, reversality of the molecular or crystal Hamiltonian itself is not equivalent to reversality of its interaction with an external electromagnetic wave; i.e., from  $T\{H\} = H$  it does not necessarily follow that  $T\{H_{\text{int}}\} = H_{\text{int}}$ . Indeed, in Coulomb gauge the light-matter interaction Hamiltonian corresponding to Eq. (1) is<sup>6</sup>

$$H_{\text{int}} = -\frac{e}{mc} \mathbf{p} \cdot \mathbf{A}(\mathbf{r}, t) + \frac{e^2}{2mc^2} \mathbf{A}^2(\mathbf{r}, t) - \frac{e^2\hbar}{4m^2c^3} [\nabla V \times \mathbf{A}(\mathbf{r}, t)] \cdot \boldsymbol{\sigma} - \boldsymbol{\mu} \cdot \mathbf{B}(\mathbf{r}, t). \quad (2)$$

Here  $\mathbf{A}(\mathbf{r}, t)$  is the vector potential of the wave,  $\mathbf{B}(\mathbf{r}, t)$  is its magnetic induction, and  $\boldsymbol{\mu} = (e\hbar/2mc)\boldsymbol{\sigma}$ . Let us consider a linearly polarized light wave of frequency  $\omega$  and wave vector  $\mathbf{k}$ :  $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}^{(0)} \cos(\omega t - \mathbf{k}\mathbf{r})$ . Using the transformation rules described above, one can see that  $H_{\text{int}}$  is  $PT$  but not  $T$  invariant.<sup>10</sup> To demonstrate clearly the implications of this nonreversality we limit consideration to the first-order spatial dispersion effects; i.e., we expand the vector potential of the wave in proximity to the optical electron  $A_\alpha(\mathbf{r}, t) = A_\alpha(0, t) + r_\beta[\nabla_\beta A_\alpha(\mathbf{r}, t)]_{\mathbf{r}=0} + \dots$ <sup>11</sup> If we introduce the electric-dipole, electric-quadrupole, and magnetic-dipole moment operators  $\mathbf{d} = e\mathbf{r}$ ,  $q_{\alpha\beta} = 1/2(3r_\alpha r_\beta - \mathbf{r}^2 \delta_{\alpha\beta})e$ , and  $\mathbf{m} = (e/2mc)[\mathbf{r} \times \mathbf{p}] + \boldsymbol{\mu}$ , respectively, the time-nonreversible effects of light-matter interaction are due to the difference between  $H_{\text{int}}$  and  $T\{H_{\text{int}}\}$ :

$$\begin{aligned} \Delta H_{\text{int}} = H_{\text{int}} - T\{H_{\text{int}}\} = & -\frac{2}{3c} k_\alpha \frac{\partial q_{\alpha\beta}}{\partial t} A_\beta^{(0)} \sin(\omega t) \\ & - 2\mathbf{m} \cdot [\mathbf{k} \times \mathbf{A}^{(0)}] \sin(\omega t) \\ & - \frac{e^2 \hbar}{2m^2 c^3} \{(\mathbf{r} \cdot \nabla V)(\boldsymbol{\sigma} \cdot [\mathbf{k} \times \mathbf{A}^{(0)}]) \\ & - (\mathbf{r} \cdot \boldsymbol{\sigma})(\nabla V \cdot [\mathbf{k} \times \mathbf{A}^{(0)}])\} \sin(\omega t). \end{aligned} \quad (3)$$

Equation (3) does not contain electric-dipole terms  $\{H_{\text{int,ED}} = (d/c)[\partial \mathbf{A}(0, t)/\partial t]\}$ , i.e., the electric-dipole interactions are time reversible. The  $T$ -odd part [Eq. (3)] of the interaction Hamiltonian will contribute to macroscopic observables, such as the absorption and refractive coefficients, if at least some of the matrix elements  $\langle a | \Delta H_{\text{int}} | b \rangle$  are nonzero. Here  $\langle a |$  and  $\langle b |$  are wave functions of the total Hamiltonian  $H$ . Calculation of these matrix elements in the general case is rather complicated. However, the analysis may be significantly simplified if we consider the departure from centrosymmetry and spin-orbit coupling to be small perturbations:  $|V_{\text{odd}}(\mathbf{r})| \ll |V_{\text{even}}(\mathbf{r})|$  and  $|(e\hbar/4m^2c^2)[\nabla V \times \mathbf{p}]| \ll |\mathbf{p}^2/2m + eV|$  [see Eq. (1)]. The centrosymmetric spinless Hamiltonian  $H_0 = \mathbf{p}^2/2m + eV_{\text{even}}(\mathbf{r})$  is an even function of  $\mathbf{r}$ , and correspondingly all its nondegenerate states are either even or odd functions of  $\mathbf{r}$  (see, for example, Ref. 3). Let us consider two states of  $H_0$  with wave functions  $\langle a_0 |$  and  $\langle b_0 |$  of opposite parity. The wave functions  $\langle a |$  and  $\langle b |$  of the total Hamiltonian  $H$  differ from  $\langle a_0 |$  and  $\langle b_0 |$  by small corrections  $\langle \delta a_0 |$  and  $\langle \delta b_0 |$  that are due to lack of a center of inversion and to spin-related contributions. These corrections may have parities different from the parity of undisturbed wave functions. Within the scope of the perturbation approach,  $\langle a | \Delta H_{\text{int}} | b \rangle = \langle a_0 | \Delta H_{\text{int}} | b_0 \rangle + \langle \delta a_0 | \Delta H_{\text{int}} | b_0 \rangle + \langle a_0 | \Delta H_{\text{int}} | \delta b_0 \rangle + \dots$

The first two terms on the right-hand side of Eq. (3) are coordinate-even functions, and the major first term of their matrix elements  $\langle a_0 | \Delta H_{\text{int}}^{1,2} | b_0 \rangle$  vanishes as the result of integration over all space. Therefore quadrupole and magnetic-dipole terms may give rise to time-nonreversible absorption or refraction only if distortion of the wave functions as the result of non-centrosymmetry and/or spin-orbit coupling is taken

into account. This eventuality was discussed in our earlier paper.<sup>4</sup> However, the spatial symmetry of the third term in Eq. (3) is not necessarily coordinate even. This term originates from the spin-orbit coupling, and its spatial symmetry is determined by the internal crystal potential  $V(\mathbf{r})$ . It gives rise to the coordinate-odd part of  $\Delta H_{\text{int}}$ , which is

$$\begin{aligned} \Delta H_{\text{int,odd}} = & -\frac{e^2 \hbar}{2m^2 c^3} \{(\mathbf{r} \cdot \nabla V_{\text{odd}})(\boldsymbol{\sigma} \cdot [\mathbf{k} \times \mathbf{A}^{(0)}]) \\ & - (\mathbf{r} \cdot \boldsymbol{\sigma})(\nabla V_{\text{odd}} \cdot [\mathbf{k} \times \mathbf{A}^{(0)}])\} \sin(\omega t). \end{aligned} \quad (4)$$

The major component of the matrix element of  $\Delta H_{\text{int,odd}}$  i.e.,  $\langle a_0 | \Delta H_{\text{int,odd}} | b_0 \rangle$ , does not vanish and may make a significant contribution to  $T$ -odd light-matter interactions. As far as we are aware, this term was not previously considered.

Therefore we see that the absorption-refraction process associated with interaction Hamiltonian equation (2) it is not necessary invariant with respect to  $T$ . The  $T$ -noninvariant contributions to the interaction Hamiltonian are linear in the wave vector  $\mathbf{k}$  of the light wave [see Eq. (3)]. Correspondingly, small corrections to the absorption-refraction coefficients that appear in the background of conventional  $T$ -even absorption-refraction are first-order terms in the wave vector of light. This means that  $T$ -odd interactions may emerge only in first-order spatial dispersion phenomena in crystals that lack an inversion center.

In conclusion, we need to recall that the assumption of microscopic reversality<sup>12</sup> leads to restraints on optical susceptibilities in the constitutive equation describing a medium  $D_i = \varepsilon_{ij} E_j + \nabla_m \gamma_{ijm} E_j$ . These restraints are  $\varepsilon_{ij} = \varepsilon_{ji}$  for the dielectric tensor and  $\gamma_{ijm} = -\gamma_{jim}$  for the nonlocality tensor.<sup>13,14</sup> If time microscopic reversality is broken, these restraints do not necessarily hold. Because terms violating time reversality appear as  $\mathbf{k}$ -linear terms in Eq. (3), they affect only the last term in the constitutive equation, and antisymmetry with respect to permutation of the first two indices in this susceptibility is not generally required by the Onsager principle.<sup>12</sup>

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