Analytic and geometric properties of photoinduced effects in noncentrosymmetric crystals: Photovoltaic current and optical rectification

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Abstract – An original dispersion relation between the stationary coherent nonlinear optical responses by current and polarisation is obtained. The dispersion relation provides a new complementary tool that can be employed to study light-induced charge transport models and facilitate experimental data analysis. It is shown that the origin of the coherent current and the dc-polarisation induced in a noncentrosymmetric crystal under illumination is related to the theory of the Berry phase and can be represented in terms of the renormalised geometric potentials. This renormalisation originates from the extra phase difference acquired by a carrier in the light field on the quantum transition between the electronic bands. The gauge invariance of the corresponding expressions for the current and the polarisation is demonstrated.

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Introduction. – Investigations of the interaction of an incident light with the electronic subsystem of a noncentrosymmetric crystal have exposed a number of time-independent effects of the second order in the amplitude of the external field. One of these effects is the anomalous bulk photovoltaic effect (APE), which consists of the generation of a directional macroscopic current in the closed circuit of a spatially homogeneous semiconductor [1–3]. Another related phenomenon is the optical rectification effect (ORE), which implies that the crystal becomes polarised [4]. Both of these effects are stationary second-order responses to light perturbation on the summarised zero frequency — the APE along the current and the ORE along the polarisation. The mechanism of the APE consists of two channels of different origin: a ballistic channel [2] and a coherent channel [5–9]. The latter channel is independent of the carriers’ scattering relaxation times and is determined by the interference of quantum transition amplitudes [6], which is related to the effective shift of the carrier wave packet in real space [10].

In the late 1980s, we ascertained for the first time a special relationship between the current and the dc-polarisation. This relationship is given by the duality transformation [11–13]

\[ P(\omega) = \eta^{-1} j(\omega), \]

which, before passing to the limit \( \eta \to 0 \), allows us to express the ORE polarisation \( P \) through the coherent current \( j \) of the APE for a given frequency \( \omega \) of the incident light. Here, the parameter \( \eta \), which is a reciprocal averaged relaxation time, mathematically plays the role of an intermediate variable that would usually be taken to zero in the final calculations in nonlinear optics. Equation (1) has been obtained within the framework of the density matrix by considering the equation of motion for the coordinate operator. In theoretical practice, the expression has allowed us to calculate the ORE polarisation by using the result of the summation over the intermediate electronic states [11–13].

In general, eq. (1) reflects the relationship between dissipative and non-dissipative processes in the system. The product \( \eta P(\omega) \) can be interpreted as the unique source of coherent APE current; in the limit \( \eta \to 0 \), the product creates selection rules for electron-hole generation induced by the absorption of photons with optical transition energies. It thereby provides steady-state
charge transport in a noncentrosymmetric semiconductor. Because the processes of energy exchange between the light wave and the crystalline medium depend also on the frequency of the electromagnetic field, one can expect that the duality transformation in eq. (1) corresponds to a wider dispersion relation that connects spectral distributions of the APE and ORE. In the present work, we derive such a generalised relation. As a practical tool, the relation will be especially useful for experimentalists because it provides a simple procedure for relating the spectral representations of the relevant polarisation and current to one another.

On the other hand, an interconnection between the coherent APE current and geometrical features [14] of the Bloch states [15,16] has not been completely realised. Moreover, the key issue of the gauge invariance of the Bloch states [15,16] has not been completely realised. Further insight into the geometrical features of the coherent APE current and the ORE polarisation is fundamental in the theory of nonlinear media. It was shown in a number of previous works [5–11,17] that this quantity: i) determines the physical structure of the macroscopic APE current and the ORE polarisation; ii) establishes the existence of both effects in noncentrosymmetric crystals. The last point is due to the relevant symmetric properties of the matrix elements involving in \( F_{\alpha \beta}^{\omega \eta}(k) \).

The quantity \( F_{\alpha \beta}^{\omega \eta}(k) \) is fundamental in the theory since directly depends on the microscopic properties of a nonlinear medium. It was shown in a number of previous works [5–11,17] that this quantity: i) determines the physical structure of the macroscopic APE current and the ORE polarisation; ii) establishes the existence of both effects in noncentrosymmetric crystals. The last point is due to the relevant symmetric properties of the matrix elements involving in \( F_{\alpha \beta}^{\omega \eta}(k) \).

The dispersion relation between the coherent APE current and the ORE polarisation. – Second-order interaction processes between light and matter have been investigated in a number of our works [8,12,13,17]; the results from these works will be used in our present theoretical analysis. In the context of the duality of eq. (1), the functional formulation of the coherent APE current can be written as a sum of Lorentzian functions:

\[
J_\alpha(\omega) = \frac{C}{\omega^2} \sum_{\epsilon=\pm} \sum_{\beta=x,y} I_\beta \sum_{n,l} \int d^3k \mathcal{L}_{n\ell}(k, \epsilon, \omega, \eta) \Phi_{n\ell}^{\alpha \beta}(k),
\]

where

\[
\mathcal{L}_{n\ell}(k, \epsilon, \omega, \eta) = \frac{\eta}{(E_n(k) - E_\ell(k) + \omega)^2 + \eta^2},
\]

\[
\Phi_{n\ell}^{\alpha \beta}(k) = |p_{n\ell}^\beta(k)|^2 [f_n(k) - f_\ell(k)] \text{Re} \left[ F_{n\ell}^{\alpha \beta}(k) \right],
\]

\[
F_{n\ell}^{\alpha \beta}(k) = -[R_n^\alpha(k) - R_\ell^\beta(k)] + \frac{1}{i} \partial \ln |p_{n\ell}^\beta(k)|. \quad (5)
\]

Here \( I_3 \) is the intensity of an elliptically polarised light wave, \( C \) is a distinct constant, \( p_{n\ell}^\beta(k) \) with \( n \neq l \) and \( R_n^\alpha(k) \) are the matrix elements of the momentum \( \mathbf{p} = -i \partial/\partial \mathbf{r} \) and coordinate \( (i \partial/\partial k) \) operators on the periodic Bloch amplitudes \( u_{n\ell}(r) \), the indices \( \alpha \) and \( \beta \) denote the Cartesian components, and \( f_n(k) \equiv f(E_n(k)) \) are the Fermi occupation factors of the electronic states with band energies \( E_n(k) \). The response by the coherent APE current is represented by \( j(\omega) = \lim_{\eta \rightarrow 0} J_\alpha(\omega) \); correspondingly, the ORE polarisation is \( P(\omega) = \lim_{\eta \rightarrow 0} \eta^{-1} J_\alpha(\omega) \).

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representation of (7) which is related to a Cauchy principal-value integral by

\[ P(\omega) = \frac{1}{\pi} \frac{d}{d\omega} \mathcal{P} \int_{-\infty}^{+\infty} \frac{dx}{x-\omega} j(x). \quad (8) \]

If one defines the Hilbert transform of a real function of the real variable \( j(\omega) \) as \((e.g., \ [24, 25])\)

\[ \mathcal{H}\{j(\omega)\} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{dx}{x-\omega} j(x), \quad (9) \]

it is seen from eq. (8) that the ORE polarisation is a derivative with respect to \( \omega \) of the Hilbert transform of the coherent APE current. By using the property \( d\mathcal{H}\{j(\omega)\}/d\omega = \mathcal{H}\{dj(\omega)/d\omega\}, \) eq. (8) can be rewritten as

\[ P(\omega) = \frac{1}{\pi} \frac{d}{d\omega} \int_{-\infty}^{+\infty} \frac{dx}{x-\omega} \frac{dj(x)}{dx}. \quad (10) \]

With the help of eqs. (9) and (10) the ORE polarisation can be regarded as the convolution of the frequency derivative of the coherent APE current with a power function of the form \( 1/(x-\omega). \)

The above results (eqs. (7), (8), and (10)) constitute our desired dispersion relation, which connects the frequency dependencies of the coherent APE current and the ORE polarisation. Therefore, once we know a spectral representation of one quantity the above equations give the relevant representation of the other. In fact, this provides a new complementary tool for the study of steady-state nonlinear optical effects. A more practical motivation for these studies lies in their technological importance.

Because \( P(\omega) = P(-\omega), \) relation (7) can be also written as

\[ P(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} dx \frac{\omega^2 + \omega^2}{(x^2 - \omega^2)^2} j(x) = \frac{1}{\pi} \frac{d}{d\omega} \int_{-\infty}^{+\infty} dx \frac{\omega}{x^2 - \omega} j(x). \quad (11) \]

As a simple illustration of eq. (11), the spectral frequency profile of \( P(\omega) \) for a \( \delta \)-shaped coherent APE current \( j(\omega) = j_0 [\delta(\omega - \omega_0) + \delta(\omega + \omega_0)] \) is given (for \( \omega \neq \omega_0 \)) by

\[ P(\omega) = \frac{2j_0}{\pi} \frac{\omega_0^2 + \omega^2}{(\omega_0^2 - \omega^2)^2}. \quad (12) \]

**The geometric properties.** – In this section, we shall show that the quantity \( F_{ln}^\beta \) carries information about the geometric structure of the APE current and the ORE polarization that is directly associated with the properties of a noncentrosymmetric medium. Let \( \Theta_{ln}^\beta(k) \) be the phase of the interband matrix element of the momentum operator: \( p_{ln}^\beta(k) = |p_{ln}^\beta(k)| e^{i\Theta_{ln}^\beta(k)}. \) For reasons given above, the first derivative of the amplitude \( \partial |p_{ln}^\beta(k)|/\partial k_n \) does not contribute to the integral in eq. (2) and, correspondingly, eq. (5) can be written as

\[ F_{ln}^{\alpha\beta}(k) = -[R_{ln}^{\alpha\beta}(k) - R_{ln}^{\beta\alpha}(k)] + \frac{\partial \Theta_{ln}^\beta(k)}{\partial k_n} \quad (13) \]

Equation (13) contains two terms, the first of which (in the square brackets) describes the difference in the positions of the electron charge for the initial and final states. The second is more specific since it is directly connected with the \( k \)-dependences of the phase \( \Theta_{ln}^\beta(k) \). Note that the general information about the \( k \)-structure of \( \Theta_{ln}^\beta(k) \) is contained in the relation (modulo \( 2\pi \)):

\[ \Theta_{ln}^\beta(k) + \Theta_{ln}^\beta(-k) = -\pi, \]

which is readily apparent from the symmetry property \( p_{ln}^\beta(-k) = -p_{ln}^\beta(k) \) \((e.g., \ [6]\)). Thus, we can represent the phase angle as

\[ \Theta_{ln}^\beta(k) = -\pi/2 + 2\Xi_{ln}^\beta(k), \quad (14) \]

where the second term (odd with respect to \( k \)), \( 2\Xi_{ln}^\beta(k) \), belongs only to a noncentrosymmetric medium. In particular, with linear-\( k \) corrections it may be written as (\( e.g., \ [27]\)):

\[ 2\Xi_{ln}^\beta = \sum \gamma_{ln}^\beta k^r, \]

where \( B \) is system-dependent coefficients. It is easy to verify that eq. (14) along with eq. (13) provide the corresponding nonzero contribution to the Brillouin-zone integral in eq. (2).

By using the definition of a gauge potential (a Berry connection) in the \( k \)-space for the band \( n \) as \( A_n \equiv R_{nn} \), one has

\[ F_{ln}^\beta = A_n - A_1 + \text{grad}\Theta_{ln}^\beta. \quad (15) \]

As seen from eqs. (2)–(5) and (15), the expression for the current in the geometrical sense is formulated in terms of vector potentials and not fields, and so the relevant gauge invariance must be verified. Clearly, the current is an observable physical quantity and should be independent of the freedom to change the phase of the Bloch wave function arbitrarily at each point in \( k \)-space.

The gauge symmetry of the current is simply stated from eq. (5) by considering the quantity \( F_{ln}^\beta \) to be invariant under a local gauge transformation: \( u_{nk}(r) \rightarrow e^{i\varphi_n(k)} u_{nk}(r) \) where the quantity \( \varphi_n(k) \) is an arbitrary phase of the Bloch amplitude. According to the sense of the Berry potential, we can call such a gauge geometric. As a direct consequence, we reveal the physical role played by the gradient term in eqs. (5) and (15) as follows: the term maintains the geometric gauge invariance of the coherent APE current and the ORE polarisation, and hence eliminates the arbitrary non-gauge contributions caused by phases of the Bloch amplitudes. In view of eq. (15), this allows us to conceptually treat the phases of the matrix elements of the momentum operator as compensating fields.

Now that we have described the roles of both components in eq. (15), it is possible to gain better insight into the basic properties of the quantity \( F_{ln}^\beta \). First, with the
use of the phase angle $\Xi^\beta_{ln}$ from eq. (14) we can rewrite eq. (15) as

$$F^\beta_{ln} = A^\beta_n - A^\beta_l,$$

(16)

where $A^\beta_n = A_n + \nabla \Xi^\beta_{ln}$ and $A^\beta_l = A_l + \nabla \Xi^\beta_{nl}$, respectively. Furthermore, we call attention to the point that, due to the Stokes theorem, the calculation of the difference between the Berry phases $\Phi_n$ and $\Phi_l$, which are acquired by the wave functions of the Bloch initial $\psi_{nk}(r)$ and final $\psi_{lk}(r)$ states, does not involve the gradient terms

$$\Phi_n - \Phi_l = \oint \nabla \cdot [A_n - A_l] = \oint \nabla \cdot [A^\beta_n - A^\beta_l].$$

(17)

A key observation that directly follows from eq. (17) is that there is a simple way to rewrite the quantities $A^\beta_n$ by employing the definition of the Berry connection

$$A^\beta_n = (u^\beta_{nk}(r) / i \partial / \partial k | u^\beta_{nk}(r)),$$

(18)

where the matrix elements are calculated on the Bloch amplitudes renormalised by multiplying by the phase factor: $u^\beta_{nk}(r) = u^\beta_{nk}(r)e^{-i \Xi^\beta_{nk}}$.

Such a representation of the phase-renormalised Bloch states, in which the relevant gradient terms move into the phases of the Bloch amplitudes, leads to a new understanding of the role played by the phases of the interband matrix elements of the momentum operator in noncentrosymmetric crystals and, therefore, allows us to draw several conclusions: i) From eqs. (16) and (18), one sees the geometrical meaning of $F^\beta_{ln}$ as the quantity representing a difference of the renormalised potentials of the $n$ and $l$ electronic bands. ii) The phase factor $e^{-i \Xi^\beta_{nk}}$ provides a direct argument that an extra nontriviality appears in the geometry of the Bloch states of the perturbed noncentrosymmetric system, a nontriviality that is of geometric phase origin (a similar extra phase, often called “statistical”, takes place in studies of the statistics of quasiparticles entering the quantum Hall effect [28]). Geometrically, the allocated phase factor is what incorporates the effect of the other band in the Bloch amplitude of the given band through half of the additional phase of the momentum matrix element, $\Xi^\beta_{ln}$, between these bands. This, in turn, implies that it is also possible to consider the quantity $\Xi^\beta_{ln}$ in the sense of phenomena such as the Aharonov-Bohm effect [29] as the phase difference adiabatically acquired by the electron on the transition between the $n$ and $l$ bands. iii) These phase differences cannot be ignored because they are employed as compensating fields to ensure that equations for the coherent APE current and the ORE polarisation are independent of the choice of the Bloch amplitude phase. Thus, the geometric gauge invariance of both physical quantities is provided by a nontrivial superposition of the difference between the “bare” Berry connections and the interband phase difference acquired in the electron transitions. iv) In addition to item i), it is interesting to note that if one chooses the parallel-transport gauge for both $n$ and $l$, then $A_n$ and $A_l$ are both zero and all of the effect is pushed into the grad $\Theta^\beta_{ln}$ term. Therefore $\Theta^\beta_{ln}$ may be considered as the phase difference between the $n$ and $l$ bands when both are parallel-transported.

We must emphasise that the coherent photoinduced current of the APE and the dc-polarisation of the ORE are completely defined by the gauge-invariant contributions of the renormalised Berry connections in the space of the Bloch states’ quasimomenta. Because they are determined by the geometry of this space and not by the particular dynamics of the Bloch electrons, neither effect naturally depends on the specific scattering mechanisms of the carriers. For the present case, the characteristic geometric features are associated with the interference of quantum transitions between the intermediate electronic states. Therefore, using the terminology of the anomalous Hall effect [30], such contributions can be called intrinsic contributions.

In this situation, the meaning of the relaxation parameter $\eta$, which, like the Berry phase, is strictly related to the adiabatic evolution of the system, can also be deepened. One may say that the parameter limits the time to collect the necessary Berry phase change during the light period.

**Discussion.** – The final question on which our study can shed light concerns the interrelation of the analytical and geometrical properties of the coherent APE current and the ORE polarisation. Following a causal formulation of the coherent nonlinear photoinduced effects [17], consider the evolution of the electronic subsystem of a crystal in the external light field. According to the concept of time ordering in the dynamic quantum multi-electron system [31–33] and by using the results of ref. [17], an expression giving the stationary second-order response for an arbitrary operator $\hat{D}$ can be rewritten in terms of the Heaviside step functions $\Theta(t)$ as follows:

$$\delta^{(2)}(\hat{D}) = i^{-2}e^{-\eta t} \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2 e^{\eta t_2}$$

$$\times \Theta(t - t_1) \Theta(t_1 - t_2) \left< \left[ \hat{D}(t), \hat{V}(t_1), \hat{V}(t_2) \right] \right|_0.$$

(19)

Causal-like sequencing of interactions (time ordering) in the time evolution of the system is imposed here in an explicit form through the products of the Heaviside step functions. In eq. (19), $\hat{V}(t)$ is the perturbation caused by illumination, the tilde means the interaction representation and index “$0$” selects the stationary part of $\delta^{(2)}(\hat{D})$.

A valuable property of a representation like eq. (19) is the possibility to employ a time sharing scheme [32,33] in which the time ordering is separated into two terms —the uncorrelated ($T_{unc}$) and correlated ($T_{corr}$) parts— by using the following representation of the function.
\[ \Theta(t_1 - t_2) : \]
\[ \Theta(t_1 - t_2) = \frac{1}{2} \left( \frac{1}{T_{unc}} + \text{sign}(t_1 - t_2) \right). \tag{20} \]

Clearly, the two contributions tend to complement each other. The first contribution, \( T_{unc} \), corresponds to an independent time approximation where the \( \tilde{V}(t_j) \) interactions are disconnected among themselves in time. The second contribution, \( T_{corr} \), connects the \( \tilde{V}(t_j) \) at different times [32]. By employing the Fourier transform of \( \Theta(t_1 - t_2) \), the given scheme (20) can be supplemented with two parallelisms [31,33]

\[ T_{unc} \rightarrow \lim_{\eta \to 0} \frac{\eta}{(E_0 - E + \omega)^2 + \eta^2} = \pi \delta(E_0 - E \pm \omega), \tag{21} \]

\[ T_{corr} \rightarrow \lim_{\eta \to 0} \frac{E_0 - E \pm \omega}{(E_0 - E + \omega)^2 + \eta^2} = \frac{\mathcal{P}}{E_0 - E \pm \omega}, \tag{22} \]

where \( E \) is an excited state in the electronic subsystem.

In order to see whether the coherent APE charge transport and the ORE polarisation can be categorised according to their time-ordering properties, we shall consider separately each contribution prescribed by eqs. (20)–(22). As a first case, we discuss the situation driven by \( T_{unc} \) (i.e., the time-independent part of \( \Theta(t) \)) in which the sequence of the interactions \( \tilde{V}(t_j) \) is unimportant. As mentioned in ref. [32], the second-order process can be represented in this approximation by two independent one-step processes, which correspond in eq. (21) to the delta function. At the same time, as seen from eq. (3) at \( \eta \to 0 \), the one-photon interband absorption processes are responsible for the generation of free carriers. Because they are dependent on the relevant amplitudes, these processes maintain no phase information inside the area occupied by electrons. This implies that we need to invoke the system’s other degrees of freedom in order to discover the asymmetry responsible for the rise of the coherent APE current \( j(\omega) \). In quantum-mechanical systems, one available degree of freedom belongs to the macroscopic geometric properties in the k-space of the Bloch states [15]. As we have seen above, the microscopic origin of a macroscopic coherent current is related to an interplay of the Berry geometric potentials and the interband phase differences. In a medium without a centre of inversion, the sum of these quantities provides gauge-invariant polar distributions in individual electron transitions between the Bloch states in momentum space.

Therefore, one can conclude that the light-induced stationary coherent APE charge transport, being of geometric origin, does not need any special time correlations between electrons. This result is not surprising because one should expect that time-correlating processes cannot be involved in the case under consideration due to the absence of the time-reversal invariance associated with the bulk macroscopic current. Moreover, from the quantum-mechanical point of view correlation in time, which is initially an attribute of the incident photons due to Bose statistics, is destroyed along with the photons themselves, which are absorbed in order to generate the electron transitions.

A diametrically opposite situation takes place in the second case when the time-dependent part of \( \Theta(t) \) in eq. (20) is considered. This case includes the time-correlating processes in the time evolution of the electron subsystem excited by the external electromagnetic field. In a mathematical context, the case is given by the principal value contribution in eq. (22) and driven by \( T_{corr} \). From eqs. (2), (3), (1), and (22), one sees that the light-induced ORE polarisation \( P(\omega) \) can be associated with the effect of the time correlation term, \( T_{corr} \). This result implies that the interactions of a light wave with the electron subsystem at various times must interfere to polarise a nonlinear medium. The need for such interference can be described in a more pictorial way. The external perturbations affecting the electron subsystem lead to local changes of the electron density distribution that, in turn, create imbalances with respect to the corresponding density of the positive background. In the case of the time correlations, these imbalances will be accumulated in a sequential and dependent manner in order to involve a sufficiently large number of valence electrons in virtual transitions. The induced polarisation is, thus, a result of a new macroscopic redistribution of the electronic charge.

Following from the above discussion, time ordering is the result of a nonlinear effect due to the specific correlations caused by the interactions of a light wave with the electronic subsystem. This leads to interesting consequences with respect to the two physical quantities related by the duality transformation in eq. (1): one turns out to be connected with the time correlation while the other is not (at least in the second-order approximation). Simultaneously, both of them are caused by the geometric features in the k-space of the Bloch states. In addition to the explanation given in the introduction, this observation allows us to treat the factor \( \eta \) as a driving parameter, which shifts the time correlated and uncorrelated contributions amongst themselves at \( \eta \to 0 \). Next, analogously to the above treatment of (1), the physical meaning of the dispersion relation in eq. (7) can also be completed. One can say that this relation interconnects the time correlated contributions with the uncorrelated contributions with respect to \( \omega \). Obviously, such an add-on to the explanation of (7) should have greater generality because, for example, a similar treatment exists for a much different situation (i.e., fast collisions of atoms with matter and light) [32].

In summary, we focused our attention on the analytical properties and the geometric meaning of the second-order photoinduced effects in noncentrosymmetric crystals. We established an original dispersion relation, which connects the spectral representations of
the coherent APE current and the ORE polarisation. It was shown that both phenomena are encoded by the renormalised Berry connections (potentials). The renormalisation of the Berry connections is determined by the interband phase differences in the quantum transitions between the Bloch states and provides the underlying gauge symmetry in the $k$-space. We compared properties of the coherent APE current and the ORE polarisation with respect to a physical picture in which the electron subsystem is considered to be correlated in two different ways. It was determined that one way takes into account the time-correlating processes created by the light wave while the other way includes the correlations related to intrinsic geometrical features of the Bloch states. As a result, we observed that the ORE polarisation appears to be the combined result of both ways. Conversely, the coherent APE current is solely associated with the second way.

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