Pyroelectric vector and related polarization effects

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The principal fact that the pyroelectric vector $\mathbf{P}^0$ typical of polar crystals is invisible in equilibrium has been verified. Nevertheless, the general formula for $\mathbf{P}^0$ as a definite bulk quantity associated only with the inversion properties of a given charge distribution in the bulk has been obtained. Its application to ferroelectric perovskites BaTiO$_3$, PbTiO$_3$, and KNbO$_3$ is discussed.

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For many years the pyroelectric vector stays to be one of the most mysterious objects in solid state physics, though the phenomena of pyro- and ferroelectricity are classical [1, 2]. The attempts to grasp it result in the concept that this value can be described within an adiabatic evolution between characteristic states [3]. The elegant realization of this approach for electron subsystems [4] is based on the formalism of the Berry phase [5] in which case the integration over a closed contour in a parametric space arises and is reduced to a quantized flow through that contour. Many important results are obtained within this approach [5, 6, 7, 8, 11]. However, an evolution route over equilibrium states [8, 9] is a subtle problem characteristic of thermodynamic charge systems [10], as discussed below. One more problem is that the pyroelectricity is a structural property of polar crystals [1, 10] and so must be typical of every crystal structure without inversion, notwithstanding is the description classical or quantum. It implies that apart from the quantum Berry-phase approach [11, 12], other more classical treatments should exist.

Here we propose a novel approach to this subject and represent the pyroelectric vector $\mathbf{P}^0$ in the form of a general invariant specifying polar crystals. Expressed in terms of characteristic length parameters and effective charges in the bulk, $\mathbf{P}^0$ is defined as a function of state, without recourse to any evolution. As a result, it can be estimated with making use of classical charge distributions, though a quantum-mechanical calculation of effective charges is eventually assumed.

Interested in periodic charge distributions in the bulk, we first point out that any local polarization $\mathbf{P}$ as a bulk property associated with the crystal symmetry [13, 14, 15] and so independent of a small external field $\mathbf{E}$ should give the field contribution $-\mathbf{PE}$ to the specific energy, but this contribution is absent in equilibrium. To visualize this fact, we note that the projection $P_z$ along any principal axis $z$ is determined by the effective one-dimensional charge distribution $\bar{\rho}(z) = \bar{\rho}(z+c)$, with the period $c$ appropriate to the case, which arises after integrating the initial charge distribution over normal cross-sections of a unit cell. The value of $P_z$ can then be written down as

$$ P_z = \frac{1}{c} \int_0^c dg \left[ \int_0^c z\bar{\rho}(z)dz + \int_0^c (z+c)\bar{\rho}(z)dz \right] = 0. \quad (1) $$

Here the fact that the uniform field component $E_z$ does not distinguish any fixed choice of the unit cell boundaries in the bulk is taken into account. So, the expression in square brackets describes the polarization of the unit-cell portion of $\bar{\rho}(z)$ shifted by $g$ from any initial one, while the outer integral with the factor $1/c$ accounts for the averaging over all shifts as equiprobable. After interchanging the order of integration in (1), the final result follows from charge neutrality of a unit cell.

This issue follows the statement by Larmor [13, 14] that any bulk dipolar properties are not typical of crystals in equilibrium. Such states are associated with the thermodynamic limit [14, 15], with sample surfaces adjusted so as to exclude depolarization effects [16, 17]. Notwithstanding, if a finite sample is metastable because of unstable charged surface [15], the surface charges always form a macroscopic dipole which interacts with an external field and, being proportional to a sample volume, can be formally represented as an additive composition of dipoles in the bulk. Such dipoles have, without doubt, the bulk nature at the first moment of forming a steady-state surface [14, 15]. But due to the disturbance of a bulk symmetry near the surface, initial polarization effects do not recognize polar crystals [13, 15]. To single out true bulk effects, the scheme of a sample placed between shorted condenser plates normal to the polar axis is usually applied [1, 2]. But the effect of $\mathbf{P}^0$ is then also removed in accord with [1], so that only increments in $\mathbf{P}^0$ caused by changes in temperature or stresses are actually recorded via transient signals [1].

Since $\mathbf{P}^0$ is evanescent for observation on polar crystals in equilibrium [14, 15, 16] and the polarity reversal is impossible as an equilibrium physical process in pure pyroelectrics, the definition of $\mathbf{P}^0$ as a bulk measure of polarity associated with the inversion symmetry of a given state alone should be addressed. To gain insight into this subject, we first consider a simple Bravais lattice composed of point charges $q$. We assume that this lattice is immersed in a uniform neutralizing charge background and are interested in a dipolar moment $\mathbf{p}$ of the volume of a unit-cell parallelepiped specified by elementary translations $a_1$, $a_2$, and $a_3$ and situated anyhow in the bulk. If the inner point charge is displaced by $r$ from the parallelepiped center initially, then it is easy to show that
upon any displacement \( \mathbf{R} \) of that parallelepiped through the bulk, with casting \( \mathbf{r} - \mathbf{R} \) in terms of \( \{ \mathbf{a}_k \} \), \( \mathbf{p}(\mathbf{R}) \) takes the form
\[
\mathbf{p}(\mathbf{R}) = q \mathbf{R}_0, \quad q(\mathbf{r} - \mathbf{R}) = q \mathbf{R}_0 (\text{mod} \{ q \mathbf{a}_k \}),
\]
provided that \( \mathbf{R}_0 \) belongs to the parallelepiped volume. This result is evident, for when a recurrent point charge leaves the unit-cell volume, the inner portion of background begins to neutralize the next point charge entering. So, \( \mathbf{p}(\mathbf{R}) \) is a periodic saw-tooth function of \( \mathbf{R} \) with vertical jumps and with zero mean value in agreement with \( \mathbf{1} \). Sites of this Bravais lattice and midpoints in between are its inversion points. Thus, a unit cell centered on any of those inversion points is described by \( \mathbf{p} = 0 \). In the cases of midpoints it implies that any of \( q \) on the unit-cell boundaries is to be evenly shared between adjacent unit cells \( \mathbf{2} \), \( \mathbf{2} \), in accord with \( \mathbf{2} \).

Every regular structure of point charges of different species may be cast in terms of simple Bravais sublattices introduced. To describe their polarization, the one-dimensional treatment is expedient along directions normal to each couple of parallel faces of the foregoing elementary parallelepiped so as to exclude multiple projections of every particular Bravais sublattice on the axis under examination. These directions are defined by the unit vectors \( \mathbf{e}_k \) and by the periods \( d_k = (\mathbf{a}_k \mathbf{e}_k) \), where
\[
\mathbf{e}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{||\mathbf{a}_2||\mathbf{a}_3||^2 - (\mathbf{a}_2 \mathbf{a}_3)^2||^2} ^{1/2}
\]
and the transformation \( \mathbf{e}_1 \rightarrow \mathbf{e}_2 \rightarrow \mathbf{e}_3 \) is cyclic.

We begin with a combination of two Bravais sublattices, which is then specified by their projections per normal section of an elementary parallelepiped on a given \( k \)-direction, as shown in Fig. \( \mathbf{1a} \), where the label \( k \) on all the parameters is omitted for brevity. The foregoing four symmetrical choices of the unit cell lead to four different values of the dipolar moment:
\[
p_1 = \frac{(l_{12} - l_{21}) q_2}{2}, \quad p_2 = -\frac{(l_{12} - l_{21}) q_1}{2},
\]
\[
\begin{aligned}
  p_3 &= l_{12} q_2, \quad p_4 = -l_{12} q_1 \text{ at } l_{12} < l_{21}, \\
  p_5 &= -l_{21} q_2, \quad p_6 = l_{21} q_1 \text{ at } l_{12} > l_{21}.
\end{aligned}
\]
Also keeping in mind the following combination
\[
\frac{p_1 + p_2}{2} = -\frac{(l_{12} - l_{21})(q_1 - q_2)}{4}
\]
antisymmetric to inversion, we conclude that the general antisymmetric invariant containing all the motifs typical of \( \mathbf{1} - \mathbf{3} \) takes the form
\[
\mathcal{I}(q_1, q_2; l_{12}, l_{21}) = l_{12}l_{21}(l_{12} - l_{21})q_1q_2(q_1 - q_2).
\]
Each of six zeros of \( \mathbf{3} \) excludes any polarization and this set of zeros is complete. The symmetry of \( \mathbf{3} \) also implies that in the case at hand the inversion can be defined in the four equivalent manners: (i) \( l_{12} \rightarrow -l_{12} \) and \( l_{21} \rightarrow -l_{21} \); (ii) \( q_1 \rightarrow -q_1 \) and \( q_2 \rightarrow -q_2 \); (iii) \( l_{12} \leftrightarrow l_{21} \); (iv) \( q_1 \leftrightarrow q_2 \). Note that the transformation \( (q_1; l_{12}) \leftrightarrow (q_2; l_{21}) \), that is the combination of (iii) and (iv), results in \( p_1 \leftrightarrow p_2 \), but \( p_3 \rightarrow p_4 \) takes place after the additional shift \( +q_1 l_{12} + l_{21} \), where \( l_{12} + l_{21} = d_k \) in agreement with \( \mathbf{2} \). Hence, those couples of cells are not mixed by operations related to inversion and so may be discussed separately.

To create \( \mathbf{4} \) normalized per unit cell, we start from unit cell '1', where the antisymmetric charge combination arises as a result of inversion relative to the unit-cell midpoint, as shown in Fig. \( \mathbf{1b} \). The end charges and a background then disappear, so that the constraint of neutrality becomes explicit, with conserving \( p_1 \) in form \( \mathbf{4} \). Next we decompose each charge above into fractions \( A_1, A_2, \) and \( A_3 \), which are then inverted relative to the ends of the unit cell in an antisymmetric fashion shown in Fig. \( \mathbf{1c} \). Taking into account the relation \( A_1 + A_2 + A_3 = 1 \) normalizing the result per actual charges, the dipolar moment \( \mathbf{p}_1 \) of modified cell '1' can be written as
\[
\tilde{p}_1 = q_2 \left[ \frac{l_{12} - l_{21}}{2} + d_k B_1 \right] = p_1 + q_2 d_k B_1,
\]
where \( B_1 = A_2 - A_3 \) is a new parameter. Thus the effect of inversion is realized in form \( \mathbf{5} \) as a shift of the \( q_2 \)-sublattice relative to the \( q_1 \)-one.

The value of \( \tilde{p}_2 \) is defined in the same way, but with \( B_2 = -B_1 \) that supports the above treatment in terms of shifts and follows from the transformation \( \mathbf{p}_1 \leftrightarrow \tilde{p}_2 \) associated with \( (q_1; l_{12}) \leftrightarrow (q_2; l_{21}) \). Next we assume a functional form \( B_j = D_j / D_0 \), so as to satisfy \( \mathbf{6} \), where \( D_j \) are polynomials bilinear in \( q_j \) and \( l_{jj'} \), provided that \( D_1 = -D_2 \) is antisymmetric upon \( (q_1; l_{12}) \leftrightarrow (q_2; l_{21}) \), whereas \( D_0 \) is symmetric upon both \( q_1 \leftrightarrow q_2 \) and \( l_{12} \leftrightarrow
to the formal splitting of any nonzero same sign and so homogeneous. In this case form (7) instead of \( q \)
result, we arrive at the normalized value small perturbation. Note that the other three choices of \( t \)
is also antisymmetric with respect to the replacement: \( q_1 \to l_1, l_2 \to q_2, q_2 \to l_{21}, \) and \( l_{21} \to q_1. \) In the event of (9) and (10) this fact results in \( t_1 = 2. \)
If \( (q_1 q_2) < 0, \) a similar consideration, but with \( |q_1 q_2| \)
instead of \( q_1 q_2 \) in \( D_t \), gives rise to (9), where
\[
D = d_k^2(q_1^2 + q_2^2 + t_1|q_1 q_2|) + 2tl_{12}l_{21}q_1 q_2.
\]
In this case there is an additional limiting condition
\[
\mathcal{P}_2\{q,-q; a, b\} \to b \to \infty -aq
\]
corresponding to a Bravais lattice of point dipoles with a period \( b \) and leading to \( t_2 = 2 - t. \)
The parameter \( t \) is common to (9) and (10) from the continuity of (9). On comparing the limit of (9)
as \( q_1 \to \infty \) and \( l_{21} \to \infty \) to (9), we obtain \( t = 2, \) because \( q_2 \) and \( l_{21} \) then describe a small perturbation. Note that the other three choices of limiting couples of parameters are also admissible. As a result, we arrive at the normalized value
\[
\mathcal{P}_2(q_1, q_2; l_{12}, l_{21}) = \begin{cases} 
-\mathcal{I}(q_1, q_2; l_{12}, l_{21}) & \text{at } (q_1 q_2) > 0, \\
\frac{d^2_k(q_1^2 + q_2^2 + 4l_{12}l_{21}q_1 q_2)}{d^2_k(q_1^2 + q_2^2) - 4l_{12}l_{21}q_1 q_2} & \text{at } (q_1 q_2) < 0.
\end{cases}
\]
The treatment above can be generalized to \( n \) sublattices described by an ordered set \( \{q_j\} = \{q_1, \ldots, q_n\} \) and by a complementary set \( \{l_{jj+1}\} = \{l_{12}, l_{23}, \ldots, l_{n1}\} \) of nearest-neighbor distances. Keeping in mind that every couple of charges gives the independent contribution described by (10), we readily reach
\[
\mathcal{P}_n(\{q_j\}; \{l_{jj+1}\}) = \frac{1}{n} \sum_{j=1}^{n} \sum_{j' \neq j} \mathcal{P}_2(q_j, q_{j'}; l_{jj'}, l_{j'j}),
\]
where \( l_{jj'} + l_{j'j} = d_k \) for every \( j \) and \( j'. \) Every particular \( \mathcal{P}_2(q_j, q_{j'}; l_{jj'}, l_{j'j}) \) is counted twice in (14), so that its own normalization is neutralized there.

It is important that \( \mathcal{P}_n(\{q_j\}; \{l_{jj+1}\}) \) is not additive to the formal splitting of any nonzero \( q_j \) into fractions, of which number would multiply the contribution of \( \tilde{p}_j \) to \( \mathcal{P}_n(\{q_j\}; \{l_{jj+1}\}), \) with destroying the symmetry effect.

Thus, every set of coinciding projections of point lattices must be reckoned once.

To describe a real structure composed of \( m \) sublattices of point nuclei \( q_j^{\text{nucl}} \) with a compensating electron density in the above manner, we map \( q_j^{\text{nucl}} \) onto the sets \( \{q_{k,j}\} \) of \( n_k \) point charges, with retrieving the label \( k \) associated with \( e_k, \) whereas the three electron charge projections \( \rho_k(z) \) on these \( k\)-directions are defined like \( \rho(z) \) in (1). Since any of \( \rho_k(z) \) is consistent with the structural parameters \( \{l_{kk+1}\} \) connected with \( \{q_{k,j}\} \) in equilibrium, its effect on (1) is reduced to the replacement of \( q_{k,j} \) by effective charges:
\[
\tilde{q}_{k,j} = q_{k,j} + q_{k,j}^{\text{el}}, \quad Q = \sum_{j=1}^{n_k} q_{k,j}^{\text{el}} = -\sum_{j=1}^{m} q_j^{\text{nucl}},
\]
where \( Q, \) the sum of \( q_{k,j}^{\text{el}} \), is determined by the last equality allowing for the total electrical neutrality.

To determine \( q_{k,j}^{\text{el}} \), a new set of unit cells based on the set \( \{l_{jj+1}\} \) is to be introduced so as to avoid the degeneracy associated with symmetric charge positions used above. To this end, we note that any of the intervals \( l_{jj+1} \) is topologically equivalent, notwithstanding is it large or small relative to the others, and so must contain the boundary points of just one unit-cell species \( j \) of length \( d_k. \) By homogeneity, the boundaries of the \( j \)-th unit cells are assumed to be shifted by \( \xi_k l_{jj+1} \) from the centers of the intervals \( l_{jj+1} \) at a given \( j, \) with \(-1/2 < \xi_k < 1/2\) common to all \( j. \) The values of \( q_{k,j}^{\text{el}} \) are then determined by the set of \( n_k \) linear equations which, at different \( j, \) describe the dipolar moments \( F_j^{(k)}(\xi_k) \) of the electron charge distributions within the \( j \)-th unit cells in terms of the contributions of point charges \( q_{k,j}^{\text{el}} \) located properly:
\[
\sum_{j'=1}^{n_k} q_{k,j'}^{\text{el}} r_{jj'}^{(k)} = F_j^{(k)}(\xi_k),
\]
\[
F_j^{(k)}(\xi_k) = \int_{-d_k/2}^{d_k/2} z \rho_k^{(j)}(\xi_k, z') d z' = Q R_j^{(k)}(\xi_k).
\]
Here the center of the \( j \)-th unit cell is the origin common to the position \( r_{jj'}^{(k)} \) of the \( j \)-th charge, to the variable \( z' \) specifying \( \rho_k^{(j)}(\xi_k, z') \) from \( \rho_k^{(j)}(z) \), and to \( R_j^{(k)}(\xi_k) \), the center of gravity of the electron charge in that unit cell. On substituting the right equality of (17) into (16), with taking (15) into account, the equations (16) become homogeneous, so that their nontrivial solution exists at
\[
\det \left[ r_{jj'}^{(k)} - R_j^{(k)}(\xi_k) \right] = 0.
\]
This is quite natural, because \( Q \) furnishes one more constraint on \( q_{k,j}^{\text{el}}. \) On casting \( r_{jj'}^{(k)} \) in terms of \( l_{jj+1} \), one can prove by induction that relation (18) is converted into
\[
\sum_{j=1}^{n_k} l_{jj+1} \left[ F_j^{(k)}(\xi_k) + \xi_k Q l_{jj+1}^{(k)} \right] = 0.
\]
TABLE I: Pyroelectric vector and concomitant parameters of some ABO$_3$ perovskites which are ferroelectric in a tetragonal phase, with model uniform spherical electron distributions employed. Experimental and Berry-phase-approach (BPA) results are also given for comparison.

|            | BaTiO$_3$ | PbTiO$_3$ | KNbO$_3$ |
|------------|-----------|-----------|-----------|
| $a$ (nm)$^a$ | 0.39947   | 0.3904    | 0.3997    |
| $c$ (nm)$^a$ | 0.40336   | 0.4150    | 0.4063    |
| $\eta_a$   | 0.012     | 0.041     | 0.019     |
| $\eta_\alpha$ | -0.023   | 0.112     | -0.025    |
| $\eta_\beta$ | -0.014   | 0.112     | -0.021    |
| $\xi$      | -0.00999  | 0.0558    | -0.0320   |
| $\tilde{q}_A/e$ | 26.843 | 31.093    | 4.961     |
| $\tilde{q}_B/e$ | 0.944    | 0.385     | 14.774    |
| $\tilde{q}_{\eta}/e$ | -22.416 | -24.280   | -5.434    |
| $\tilde{q}_{\eta}/e$ | -5.371   | -7.198    | -14.301   |
| $P^0$ (C m$^{-2}$) | 0.306    | -0.727    | 0.358     |
| $|P_{\eta 0}^0| (C m^{-2})^b$ | 0.26     | 0.75      | 0.37      |
| $|P_{\eta 0}^0| (C m^{-2})^c$ | 0.30; 0.28 | 0.74; 1.04 | 0.35; 0.40 |

$^a$BaTiO$_3$ and PbTiO$_3$ in Ref. [23], KNbO$_3$ in Ref. [24].

$^b$BaTiO$_3$ in Ref. [22], PbTiO$_3$ in Ref. [21], KNbO$_3$ in Ref. [25].

$^c$Ref. [6] and Ref. [8], respectively.

$^d$Ref. [7], calculations at 700 K and at 295 K, respectively!

$^e$Ref. [4] and Ref. [8], respectively.

With making use of the left equality of (17), equation (19) specifies a self-consistent value of $\xi_k$, while set (16) gives rise to $\tilde{q}_{k,j}$, so that $\tilde{q}_{k,j}$ in (15) has been definite.

On joining all the results obtained together, the pyroelectric density vector is well-defined by the form

$$P^0 = \frac{1}{v} \sum_{k=1}^{3} \mathbf{e}_k P_{mk} \{ \tilde{q}_{k,j} \}; \{ \tilde{q}_{j,j+1}^{(k)} \},$$

(20)

where $v$ is the unit-cell volume. Deduced from pristine charges by linear operations, (20) agrees with (11).

Note that in the phase-transition problem relation (20) implies that a sole nonzero component of $P^0$ can arise without jumps, with treating $P^0$ as an order parameter small near the transition point [10, 19]. Furthermore, different nonzero projections of $P^0$ in (20) can arise separately, as it happens in BaTiO$_3$ and KNbO$_3$ [2, 21, 22].

Concentrating on regular states, here we estimate the polarization of BaTiO$_3$, PbTiO$_3$, and KNbO$_3$ in a tetragonal phase. In general terms of ABO$_3$ perovskite, such a ferroelectric phase is determined by the lattice constants $a$ and $c$ and by extra displacements $c_B$, $c_\eta$, and $c_{\eta 1}$ of the B, O$_1$, and two O$_1$ sublattices relative to the A one, provided that O$_1$ and O$_{\eta 1}$ ions surround B along $c$ and in lateral directions, respectively, and positive $\eta_\alpha$ defines the polar direction. The simple model of uniform electron distributions within ionic spheres of Ba$^{2+}$, Pb$^{2+}$, Ti$^{4+}$, K$^+$, Nb$^{5+}$, and O$^{2-}$ ions, with O$_{\eta 1}$ anions in contact, is employed. With making use of the structural parameters listed in Table I and with account of the atomic numbers $Z_{Ba} = 56$, $Z_{Ti} = 22$, $Z_{O} = 8$, $Z_{Pb} = 82$, $Z_{K} = 19$, and $Z_{Nb} = 41$, the effective charges $\tilde{q}$ are obtained as a solution of equations (15)-(19) and are listed in Table I in units of the elementary charge $e$. Then the values of $P^0$ are obtained with the help of (13), (14), and (20) and agree with the experimental data, as shown in Table I. On comparing with the results of the Berry-phase approach shown in Table I as well, our estimate is much closer to the experimental data on PbTiO$_3$ at room temperature [26], but is comparable in other cases.

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