

Modern Polarization Theory

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This note is a complementary material on contemporary polarization theory that unfortunately all standard textbooks like [1] and [2] omitted.

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I. CLASSICAL DEFINITION OF POLARIZATION

Let me recapitulate the classical definition of dielectric polarization in standard textbooks. Both Aschcroft&Mermin and Jackson **define \mathbf{P} as the dipole moment per primitive cell** (maybe with different term like “averaging all kinds of molecules in a small volume”), or mathematically,

$$\mathbf{P} := \frac{\sum_{i \in \text{cell}} \mathbf{p}_i}{V}. \quad (1)$$

To ensure that equation (1) is well-defined, *dipole moment* for the i -th molecule/atom should be calculated before

$$\mathbf{p}_i := \sum_{j \in i} e \mathbf{r}_{ij}, \quad (2)$$

where the sum runs over all electrons for molecule/atoms i .

One may discovered that both definitions for dipole moment and electric polarization above depends on the naive picture of treating electrons as classical charged spheres. This fallacy seems to be stupid, since we all know that quantum effect (wave function) should be considered when discussing the distribution of electrons in a molecule or atom. So at least (1) and (2) should be generalized to continuum form by introducing the spatial average, which is done by Russakoff [3] and subsequently be widely adopted in standard textbooks of electrodynamics [1] and solid state physics [2]

$$\mathbf{P} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} \, \mathbf{r} \rho(\mathbf{r}). \quad (3)$$

But they just stop here, believing themselves that the above definition grab the *macroscopic* level of physics without diving into the *microscopic* understanding. In the following paper, we will show that (3) **is actually neither experimental meaningful nor theoretically well-defined**.

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II. FALLACIES ON CLASSICAL DEFINITION

A. Theoretical Aspects

The microscopic understanding of electric polarization has long been evaded, not only at the first-principle level, but even at some models that sounds to be microscopic. In a typical real insulator, for example, ferroelectric (FE) oxides, the bonding has a mixed ionic and covalent character [4], as is shown in FIG. 1. So sizable fraction of electrons

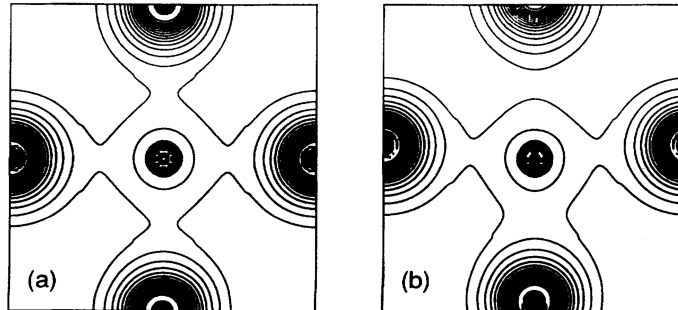


FIG. 1: **Electronic Charge Density for 2p State of Oxygen in KNbO₃.** (a) is an ideal centrosymmetric structure displayed for comparison, while (b) is experimental result observed in ferroelectric structure in the vertical plane passing through Nb atom (at figure center). Figure is extrated from [4].

will be shared among ions in rather a *delocalized* manner. This fact breaks down the physical picture of (3) because a *canonical* choice of primitive cell is demanded before performing the volume integral, whose boundary naturally situates at the region with charge density zero, as is illustrated in the venerable Clausius-Mossotti (CM) model [5] in FIG. 2.

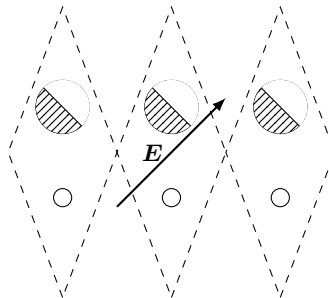


FIG. 2: **CM Model of Polarization:** A sketch of 2D polarized crystal within CM model. External electric fields E are applied in the direction as the arrow does, and shaded areas are the deformed charge density of polarizable anions (big circles), while the cations (small circles) are (assume to be) not.

However, such choice becomes frustrated for delocalized distribution of electrons because integral (3) has to truncate at the region where electron density is nonzero. So any other choice of the primitive cell will result in a different value of electric polarization. To put it more clear, let us take crystalline silicon as an example. *Ab-initio* calculation is performed under pseudopotential implementation of density-functional theory in a series of paper of Hybertsen and Louie in [6, 7], as is shown in FIG. 3. Even though the induced charge displays some dipole-like shapes, one CANNOT find a canonical choice of primitive cell.

To eliminate this, one may tempt to define the polarization as intergral over the entire sample

$$\mathbf{P} = \frac{1}{V_{\text{sample}}} \int_{\text{sample}} d\mathbf{r} \, \mathbf{r} \rho(\mathbf{r}). \quad (4)$$

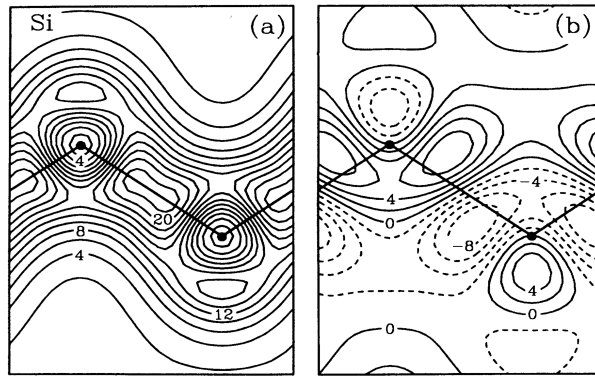


FIG. 3: **Induced Charge Density in the $(\bar{1}\bar{1}0)$ Plane:** In part (a) the pseudo valence charge from a self-consistent local density functional calculation for crystalline silicon is plotted in the $[1\bar{1}0]$ plane. In part (b) the induced charge due to a constant applied electric field in the vertical direction. The contour interval is 2 electrons per unit cell in both panels. Negative contours are indicated by dashed lines. The bond chain is indicated schematically. Figure is extracted from [5, 7].

But due to periodicity of our lattice, to ensure the convergence of integral¹ in (4), one must assume a macroscopic but *finite* crystal. And this confinement will inevitably introduce the contribution from boundary, which cannot be easily disentangled from the bulk's, while we are only interested in *bulk* properties².

Therefore, though counterintuitive, the only conclusion we can draw is that, **a periodic electronic charge distribution in a polarized crystalline solid cannot, even in principle, be used to construct a meaningful definition of *bulk* polarization.**

B. Experimental Aspects

One may be disturbing for the conclusion we've drawn above. Because bulk properties is natural to be determined by bulk quantities. But if you stand on the experimental point of view, all counterintuitive parts seem to become acceptable.

In fact, no matter what kind of polarization we are interested in, in experiments certainly no one relies on the microscopic dipoles for one cell (even if we can and even we successfully obtained, this quantity is still microscopic, rather than macroscopic). Instead, ditto for the spirits of linear-response theory and transport measurement, **we always put the entire macroscopic sample in a close circuit, imposing some stimulus like external electric field, pressure, or temperature gradient, and then read the macroscopic response $\mathbf{j}(\mathbf{r}, t)$ from Ampere meter.** Thus what we are measuring is actually the *change* of polarization $\Delta\mathbf{P}$ under stimulus, given by

$$\Delta\mathbf{P} = \int dt \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} \mathbf{j}(\mathbf{r}, t). \quad (5)$$

Equation (5) compares the difference of electric polarization at time $t = 0$ and $t = T$. We can safely generalize it to any other *adiabatic evolution* parameterized by λ going from $\lambda = 0$ to $\lambda = 1$ (after re-parameterization)

$$\Delta\mathbf{P} = \int_0^1 d\lambda \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} \mathbf{j}(\mathbf{r}, \lambda). \quad (6)$$

Despite the elaborate argument we've shown above, equation (5) or (6) can also be derived from the microscopic definition of polarization (up to some divergence-free part, which is given by *magnetization*. For an in-depth discussion, see [10, 11] and [12])

$$\nabla \cdot \mathbf{P}(\mathbf{r}) = -\rho(\mathbf{r})$$

¹ Otherwise we will encounter a divergent and meaningless summation of alternating series.

² In fact the debate whether piezoelectricity or ferroelectricity is a bulk or a surface effect lasted in literature until about 1990s [5, 8]. Nowadays we know that they are both bulk properties [9].

and the continuity relation of charge current

$$\frac{\partial \rho(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j} = 0.$$

Equation (6) is indeed a perfect definition because first it avoid the discussion on the bulk charge distribtion so there is no longer problems in canonically selecting primitive cells. Second the boundary contribution polarization is also substracted from the difference. Lastly we do use macroscopic current to define the macroscopic polarization so there is no hierarchy conflict on the philosophy of emergentism in CMP.

III. BERRY PHASE FOR BULK POLARIZATION

In this section, we will re-written (6) by Berry phases with the many-body argument of Niu, Thouless, and Wu [13] without involvement of non-interacting bloch wave function (TKNN theory) like Resta or Vanderbilt's original paper [5, 14] does. Similar discussion can also be found from [11] or recent paper of Watanabe and Oshikawa [15]. Ortiz and Martin first constructed the many-body formulation of bulk polarization in [11]. Here we try to generalize their work, release the confinement of dimensionality to (d+1)D and focus on the hypercube sample of the volume $V = L_1 \times \cdots L_d$.

Suppose eletrons in the bulk insulator subject to a general two-body interaction $V(|\mathbf{r}_i - \mathbf{r}_j|)$ from Coulomb scattering, impurity scattering etc., then *many-body* Hamiltonian takes the form of

$$H(\lambda) = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_i U(\mathbf{r}_i, \lambda) + \frac{1}{2} \sum_{i \neq j} V(|\mathbf{r}_i - \mathbf{r}_j|), \quad (7)$$

where adiabatic single-body potential $U(\mathbf{r}_i, \lambda)$ is included as well.

Continuously deforming our setup of close circuit such that multiple faces of our hypercube will connects with others. Similar to [13], under so-called magnetic translation [16] (which is a *large* gauge transformation) our *many-body* wave function allows a particle-indice-indepdent phase shift [17]

$$\mathcal{T}_i(L_\mu, \hat{x}_\mu) \psi(\mathbf{r}_i, \lambda) = e^{i\alpha_\mu L_\mu} \psi(\mathbf{r}_i, \lambda) \quad (8)$$

because of the total antisymmetry of many-body wave function. Each group of $\{\alpha_\mu\}$ determines one kind of twisted boundary condition of our system.

Eigen problem of $\{\psi(\mathbf{r}_i, \lambda), H(\lambda)\}$ is equivalent to those differing by just a many-body unitary transformation $\{\phi(\mathbf{r}_i, \boldsymbol{\alpha}, \lambda), \tilde{H}(\boldsymbol{\alpha}, \lambda)\}$, where

$$\phi(\mathbf{r}_i, \boldsymbol{\alpha}, \lambda) \equiv U \psi(\mathbf{r}_i, \lambda) = \left(\prod_\mu e^{-i\alpha_\mu (x_1 + \cdots + x_N)} \right) \psi(\mathbf{r}_i, \lambda),$$

and

$$\tilde{H}(\boldsymbol{\alpha}, \lambda) \equiv U H(\lambda) U^\dagger = - \sum_i \frac{1}{2m_i} \left[\sum_\mu (-i\hbar \partial_{i\mu} + i\alpha_\mu)^2 \right] + \sum_i U(\mathbf{r}_i, \lambda) + \frac{1}{2} \sum_{i \neq j} V(|\mathbf{r}_i - \mathbf{r}_j|). \quad (9)$$

Kinetic part of (9) is a reminiscent of the minimal coupling of electromagnetic field. So mathematically $\boldsymbol{\alpha}$ can be interpreted as factitious magnetic vector potential $\mathbf{A} \propto \boldsymbol{\alpha}$. Thus for specific boundary condition $\{a_\mu\}$, by definition the current density operator is

$$\hat{j}_\alpha^\mu \equiv \frac{\delta \hat{H}}{\delta A_\mu} = \frac{\partial \hat{H}(\boldsymbol{\alpha}, \lambda)}{\partial \alpha_\mu}. \quad (10)$$

Macroscopic current density at “time” λ is given by the thermal and quantum average of many-body ground states

$$j_\alpha^\mu(\lambda) \equiv \langle \phi(\mathbf{r}_i, \boldsymbol{\alpha}, \lambda) | \hat{j}_\alpha^\mu | \phi(\mathbf{r}_i, \boldsymbol{\alpha}, \lambda) \rangle,$$

then adabatic evalution (parameterized by λ) theory can be applied, giving [10, 18]

$$j_\alpha^\mu(\lambda) = \partial_{\alpha_\mu} \varepsilon_\alpha + \Omega_{\alpha, \lambda}^\mu, \quad (11)$$

where Berry curvature

$$\Omega_{\alpha,\lambda}^{\mu} \equiv i \left[\partial_{\lambda} \langle \phi | \partial_{\alpha_{\mu}} \phi \rangle - \partial_{\alpha_{\mu}} \langle \phi | \partial_{\lambda} \phi \rangle \right]. \quad (12)$$

Since we are working with bulk insulator, where a finite gap always exists during the adiabatic evolution, **the bulk quantity should be insensitive to the deformation of boundary conditions under thermodynamic limit** [13, 17]. Therefore we can average over an ensemble of many-body system with different boundary condition $0 < \alpha_{\mu} < 2\pi/L_{\mu}$, obtaining

$$j^{\mu}(\lambda) = \prod_{\mu} \left(L_{\mu} \int_0^{2\pi/L_{\mu}} \frac{d\alpha_{\mu}}{2\pi} \right) j_{\alpha}^{\mu}(\lambda). \quad (13)$$

Substituting (13) to the modern definition of polarization (6), and re-writting $\theta_{\mu} \equiv \alpha_{\mu}/L_{\mu}$, we finally have

$$\Delta P^{\mu} = \int_0^1 d\lambda \int \frac{d\theta}{(2\pi)^d} \Omega_{\theta,\lambda}^{\mu}. \quad (14)$$

Equation (14) is now the modern definition of macroscopic electric polarization. And its validity has already been proved in experiments, like [14].

IV. APPENDIX

A. Insensitivity of Boundary Condition for Gapped System

In this section, we will proof that

Claim 1. The difference for the measured macroscopic current for one *fixed* boundary condition j_{α}^{μ} and the one under average of boundary condition $j^{\mu}(\lambda)$ drops like $1/L$ and vanishes at thermodynamic limit.

▷ The dependence of the macroscopic current on twisted boundary condition $\{\alpha_{\mu}\}$ enters through the many-body Hamiltonian. And since there is a non-vanishing gap Δ_g in our system (as a characteristic length), any small changes in parameters of α (whose dimension is $[L]^{-1}$) must lead to changes on $\tilde{H}(\alpha)$ of order $\mathcal{O}(\Delta_g)$. Hence

$$\frac{\partial j^{\mu}(\lambda, \alpha)}{\partial \alpha_{\mu}} \equiv \frac{1}{L_{\mu}} \frac{\partial j^{\mu}(\lambda, \theta)}{\partial \theta_{\mu}} \propto \frac{\Delta_g}{L_{\mu}} \times \text{constant}$$

for asymptotically large systems, which vanishes at thermodynamic limit. □

Another proof of the insensitivity of boundary condition can also be found in the appendix of [13].

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