The structure of electronic polarization and its strain dependence

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Abstract

The $\phi(\vec{k}_\perp) \sim \vec{k}_\perp$ relation is called polarization structure. By density functional calculations, we study the polarization structure in ferroelectric perovskite PbTiO$_3$, revealing (1) the $\vec{k}_\perp$ point that contributes most to the electronic polarization, (2) the magnitude of bandwidth, and (3) subtle curvature of polarization dispersion. We also investigate how polarization structure in PbTiO$_3$ is modified by compressive inplane strains. The bandwidth of polarization dispersion in PbTiO$_3$ is shown to exhibit an unusual decline, though the total polarization is enhanced. As another outcome of this study, we formulate an analytical scheme for the purpose of identifying what determine the polarization structure at arbitrary $\vec{k}_\perp$ points by means of Wannier functions. We find that $\phi(\vec{k}_\perp)$ is determined by two competing factors: one is the overlaps between neighboring Wannier functions within the plane perpendicular to the polarization direction, and the other is the localization length parallel to the polarization direction. Inplane strain increases the former while decreases the latter, causing interesting non-monotonous effects on polarization structure. Finally, polarization dispersion in another paradigm ferroelectric BaTiO$_3$ is discussed and compared with that of PbTiO$_3$.

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I. INTRODUCTION

Electric polarization is a key quantity for computing and understanding technologically-relevant effective charges, dielectric and piezoelectric responses that are the derivatives of polarization with respect to atomic displacement, electric field, and strain, respectively.\[1\] Polarization also plays an important role in the methodology development of the theory dealing with finite electric fields in infinite solids, by minimization of the free energy $F = U - \vec{E} \cdot \vec{P}$ \[2, 3, 4, 5\]. Total electric polarization consists of electronic contribution ($\vec{P}_{el}$) and ionic component ($\vec{P}_{ion}$). Computing the latter component is straightforward using point charges, while calculating the electronic polarization is not. Today $\vec{P}_{el}$ is calculated using the sophisticated modern theory of polarization \[6, 7\]. According to the theory, $\vec{P}_{el}$ corresponds to a geometrical phase of the valence electron states,

$$\vec{P}_{el} = \frac{2e}{(2\pi)^3} \int d\vec{k}_\perp \phi(\vec{k}_\perp) \ ,$$  

(1)

where

$$\phi(\vec{k}_\perp) = i \sum_{n=1}^{M} \int_{0}^{G_\parallel} d\vec{k}_\parallel \langle u_{n\vec{k}} | \frac{\partial}{\partial \vec{k}_\parallel} | u_{n\vec{k}} \rangle$$  

(2)

is the Berry phase of occupied Bloch wave functions $u_{n\vec{k}}$. Subscripts $\parallel$ and $\perp$ mean parallel and perpendicular to the polarization direction, respectively. Practically, to carry out the $\vec{P}_{el}$ calculations, the integral in Eq.(1) is replaced by a weighted summation of the phases at sampled discrete $\vec{k}$-points (Monkhorst-Pack scheme[8], for example) in the 2D $\vec{k}_\perp$ plane, namely, $\vec{P}_{el} = \sum_{\vec{k}_\bot} \omega(\vec{k}_\bot) \phi(\vec{k}_\bot)$ with weight $\sum_{\vec{k}_\bot} \omega(\vec{k}_\bot) = 1$. The polarization at individual $\vec{k}_\bot$, $\phi(\vec{k}_\bot)$, is calculated as the phase of the determinant formed by valence states at two neighboring $\vec{k}$s on the $\vec{k}_\parallel$ string as \[6, 7\]

$$\phi(\vec{k}_\bot) = \text{Im}\{\ln \prod_{j=0}^{J-1} \det(\langle u_{k_{j,m}} | u_{k_{j+1,n}} \rangle)\} \ .$$  

(3)

Defined as such, the total polarization $\vec{P} = \vec{P}_{ion} + \vec{P}_{el}$ could be uniquely determined and gauge independent up to a modulus constant. In Eq.(1) one sees that, it is the $\phi(\vec{k}_\bot)$ phases at different $\vec{k}_\bot$ that determine the electronic polarization. The purpose of this work is to study the properties of $\phi(\vec{k}_\bot)$.

The physical significance of the $\phi(\vec{k}_\bot)$ quantity can be understood by analogy. It is well known that band structure, which describes the relation between single-particle orbital energy and electron wave vector $\vec{k}$, is very useful for understanding electronic, photo-excitation,
and photoemission properties in solids[9]. The $\phi(\vec{k}_{\perp}) \sim \vec{k}_{\perp}$ relation may be similarly termed as “polarization structure”, or “polarization-phase structure”. Electron states in band structure can be changed by photo-excitation or emission. The $\vec{k}_{\perp}$-point polarization phase can be altered by electric fields, which act as a possible excitation source for electrical polarization. Note that electrical fields do not alter the electron wave vector ($\vec{k}_{\perp}$) perpendicular to the direction of the field, and thus $\vec{k}_{\perp}$ remains a conserved quantity. The field-induced variation of $\phi(\vec{k}_{\perp})$ in fact manifests the $\vec{k}_{\perp}$-dependent polarization current. As a result, the relevance of polarization structure to electronic polarization is like the band structure to electronic properties.

Furthermore, understanding the $\phi(\vec{k}_{\perp})$ quantity is of useful value from both fundamental and computational points of view. Fundamentally, this quantity is determined by the Bloch wave functions, not in the ordinary sense of spatial distribution, but through the interesting aspects of the Berry’s phase of occupied manifold of electron states. Studying how $\phi(\vec{k}_{\perp})$ depends on $\vec{k}_{\perp}$ may yield better understanding of electron states, as well as the rather intriguing connection between these states and their contributions to polarization in insulator solids. Computationally, we first recognize that the $\phi(\vec{k}_{\perp})$ phase computed from Eq.(3) always produces a value within the principal range $[0, 2\pi]$. In reality, depending on the dispersion of $\phi(\vec{k}_{\perp})$ as a function of $\vec{k}_{\perp}$, it is possible that the phases for different $\vec{k}$ points fall in different branches. In other words, the true $\phi(\vec{k}_{\perp})$ values may fall in the principal range for some $\vec{k}_{\perp}$ points (Let us denote this set of $\vec{k}_{\perp}$ points as $\vec{k}_{\perp}(I)$), while falling out of the principal range for other $\vec{k}_{\perp}$ (to be denoted as $\vec{k}_{\perp}(II)$). We find numerically that this indeed happens for real materials particularly when polarization is large; a specific example is given in section II. When this occurs, one must not artificially shift the phases of the $\vec{k}_{\perp}(II)$ into the principal range, as computers do according to Eq.(3). Though this shift makes no difference to the polarization phase of individual $\vec{k}_{\perp}$ points, it will alter the total $\vec{P}_{el}$ polarization, yielding spurious magnitude of polarization. Only when the phase of every $\vec{k}_{\perp}$ is shifted by a constant $2\pi$ will the total $\vec{P}_{el}$ polarization remain equivalent. To find out which $\vec{k}_{\perp}$ may generate a phase not in the principal range, one in principle should compute the whole dispersion structure of polarization and then map out the $\phi(\vec{k}_{\perp})$ for all $\vec{k}_{\perp}$ points based on the assumption that the $\phi(\vec{k}_{\perp})$ phase is a continuous function of wave vector $\vec{k}_{\perp}$, which makes it important to study the properties of the $\phi(\vec{k}_{\perp})$ phase as a function of $\vec{k}_{\perp}$.

Despite the relevance, the dispersion structure of polarization is nevertheless not com-
pletely understood. More specifically, (1) little is known about what determine the $\phi(\vec{k}_\perp)$ phase at individual $\vec{k}_\perp$. In Eq.(3), $\phi(\vec{k}_\perp)$ is determined by the wave functions of a string of $\vec{k}_\parallel$ points, not just a single $\vec{k}$. As a result, the answer to the question is highly non-trivial. (2) For a given ferroelectric substance (say, the prototypical PbTiO$_3$), it is not clear which $\vec{k}_\perp$ exhibits the largest polarization contribution. Does the $\Gamma$ point always contribute most or least? (3) We do not know if the Berry’s phases at different $\vec{k}_\perp$s share a similar value or are very different from each other, that is, a problem concerning the dispersion width of the polarization structure. Slightly more intriguing, one may wonder along which direction the $\phi \sim \vec{k}_\perp$ curve shows the largest dispersion? (4) Even for two commonly studied ferroelectrics, BaTiO$_3$ and PbTiO$_3$, we do not know how different or similar their polarization structures are.

Recently, there is another active field in the study of polarization, which concerns the use of in-plane strain to tune the ferroelectric polarization [10, 11, 12, 13]. This tunability stems from the fundamental interest in the strain-polarization coupling. Imposed under in-plane strain ferroelectrics subject to modifications of chemical bonds and/or charge transfer, thereby the interaction between atoms is altered. It has been known that a compressive in-plane strain tends to enhance the total polarization. But the amplitude of enhancement was found to be highly material dependent. [12, 13] Considering the importance of the strain effects, one might want to know how the $\phi(\vec{k}_\perp)$ phase from each $\vec{k}_\perp$ can be influenced by strain. Strain effects on the polarization dispersion remain largely unknown, however. It would be of interest to examine how the strain may tune and modify the dispersion of polarization structure. Specific questions on this aspect are: in what manner would the in-plane strain change the relative contributions and curvatures at different $\vec{k}_\perp$, and how the band width of the dispersion curve is to be altered.

With these questions in mind, we here study the dispersion structure of the polarization in ferroelectric perovskites, as well as its dependence on in-plane strains. Two complementary approaches (first-principles density functional calculations and analytical formulations) are used. By means of analytical formulation, we aim at a better understanding on what specific quantities and/or interactions determine the polarization at individual $\vec{k}_\perp$ point. Our calculations reveal some useful knowledge on the polarization structure in perovskite ferroelectrics. For example, the largest $\phi(\vec{k}_\perp)$ contribution is shown not to come from the zone center, but from the zone boundary. We also find that the polarization curve in PbTiO$_3$
is notably flat along the Π − X₁ direction, and exhibits, however, a strong dispersion along the Π − X₂ axis. Our theoretical analysis further reveals that the flat dispersion along the Π − X₁ direction is caused by a small amount of participation from the nearest-neighbor interaction between the Wannier functions. Finally, the present study also demonstrates some rather interesting differences in PbTiO₃ and BaTiO₃, in terms of the polarization structures as well as their strain dependences.

II. THE POLARIZATION STRUCTURE OF LEAD TITANATE

We first present the density functional calculations on the polarization structure in PbTiO₃. In its ferroelectric phase PbTiO₃ is tetragonal (|a₁| = |a₂| = a, |a₃| = c) and possesses a large spontaneous polarization. The polarization is along the c-axis direction, perpendicular to the ⃗k⊥ plane. Calculations are performed within the local density approximation (LDA) [14]. We use pseudopotential method with mixed basis set [15]. The Troullier-Martins type of pseudopotentials are employed [16]. Details for generating pseudopotentials, including atomic configurations, pseudo/all-electron matching radii, and accuracy checking, were described elsewhere [17]. The energy cutoff is 100 Ryd, which is sufficient for convergence. The calculations are performed in two steps: the optimized cell structure and atomic positions are first determined by minimizing the total energy and Hellmann-Feynman forces, and after the structural optimization, the polarization dispersion of φ(⃗k⊥) is calculated using the modern theory of polarization [6, 7]. Our LDA-calculated inplane lattice constant for unstrained PT is a=3.88Å, with c/a = 1.04, both agreeing well with other existing calculations.

Figure II(a) shows the reduced 2D Brillouin zone that the⃗k⊥ points sample over. The calculated φ phases at individual ⃗k⊥ points along the Π → X₁ → X₂ → Π path are given in Fig.II(b). Reciprocal-space coordinates of X₁ and X₂ are ⃗k⊥ = (π/a, 0) and (π/a, π/a), respectively. The dispersion curve is rigidly shifted such that the phase at Π is taken as the zero reference.

Before we discuss the specific results in Fig.II we need to point out that the shape of this ⃗k⊥-dependent phase curve is translation invariant. As is known, the electronic polarization alone can be an arbitrary value, if the solid is uniformly translated with respect to a fixed origin of coordinates. Though different translations will change the absolute location of the
polarization-dispersion curve, the shape of the curve remains unaffected, however. This can be easily illustrated by analyzing the change in the $\phi(\vec{k}_\perp)$ phase when one displaces the solid arbitrarily. Let the wave function of the original system be $\psi_{nk}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{nk}(\vec{r})$, where $u_{nk}(\vec{r}) = u_{nk}(\vec{r} + \vec{R})$. Now, we displace the solid by an arbitrary vector $\vec{r}_0$ while the origin of coordinates is fixed. Let us denote the original system using script A and the displaced system using script B, so $\vec{r}_B = \vec{r}_A + \vec{r}_0$. The wave functions of the displaced system satisfy

$$\psi_{nk}^B(\vec{r}_B) = \psi_{nk}^A(\vec{r}_A) = \psi_{nk}^A(\vec{r}_B - \vec{r}_0).$$

Thus we have $u_{nk}^B(\vec{r}_B) = e^{-i\vec{k} \cdot \vec{r}_0} u_{nk}^A(\vec{r}_B - \vec{r}_0)$. Substituting this relation into Eq.(2) or Eq.(3), one can obtain that the $\phi(\vec{k}_\perp)$ of the displaced system is

$$\phi^B(\vec{k}_\perp) = \phi^A(\vec{k}_\perp) + \vec{r}_0 \cdot \vec{G}_{\parallel N_{occ}^{\text{band}}},$$

where $N_{occ}^{\text{band}} = M$ is the number of bands occupied by electrons. The phase differences between the A and B systems are thus a constant, independent of $\vec{k}_\perp$.

Several observations are ready in Fig.1(b): (1) The largest $\phi(\vec{k}_\perp)$ polarization does not come from the zone-center $\Gamma$ point. Rather surprisingly, the largest $\phi(\vec{k}_\perp)$ phase is from the $X_2$ point which lies at the far end of the BZ. (2) The polarization curve is flat along the $\Gamma - X_1$ line, showing only a small dispersion. On the other hand, the dispersion becomes very large along the $\Gamma - X_2$ direction. (3) At $\vec{k}_\perp$ points of high symmetry (such as $\Gamma$, $X_1$, or $X_2$), the curve in Fig.1(b) has zero slope, similar to the electron band structure. (4) The dispersion of polarization also shows subtle details which could not be easily understood. For example, there is a local (though not very pronounced) maximum along the $\Delta_1$ line, making the $X_1$ point a local minimum in both $\Gamma - X_1$ and $X_1 - X_2$ directions.

Our calculations further reveal that, despite the fact that the polarization in Fig.1(b) exhibits substantial $\vec{k}_\perp$ dependency, the dispersion width ($\sim 0.6$) is much smaller than $2\pi$. This finding is important for the following reason. As described in the introduction, if the differences of the $\phi(\vec{k}_\perp)$ phases at different $\vec{k}_\perp$ points are greater than $2\pi$, one would encounter a difficulty in determining which branch of phase a specific $\vec{k}_\perp$ point should be assigned. This difficulty can be avoided only after the phases of all $\vec{k}_\perp$ points are mapped out. Fortunately, the result in Fig.1(b) tells us that the phase contributions from different $\vec{k}_\perp$ points are fairly close, and the differences are far less than the critical value of $2\pi$ that may
cause the above difficulty. Nevertheless, we should point out that even a small polarization dispersion as in Fig.1(b) may still give rise to spurious results on total polarization. To illustrate this, we displace all five atoms in PbTiO$_3$ along the polar $c$-axis by a distance $z_0$. Fig.2(a) shows the total (electronic + ionic) polarization, computed from the geometric phase, as a function of the displacement $z_0$ (in unit of $c$). Intuition tells us that the total polarization should be uniquely determined and translationally invariant. However, we see in Fig.2(a) that unphysical discontinuity happens for some $z_0$ points, and this discontinuity shows up periodically. To understand what causes the discontinuity, we examine the phase contributions from individual $\vec{k}_\perp$ (sampled according to the Monkhorst-Pack scheme[8]), depicted in Fig.2(b). Figure 2(b) shows that the individual-$\vec{k}_\perp$ phases indeed are a periodic function of $z_0$, explaining why the discontinuity in Fig.2(a) is periodic. Here it may be useful to comment briefly on the length of the periodicity. One might think that by displacing the solid by a distance of $c$ in the $c$-axis direction, the $\phi(\vec{k}_\perp)$ phase would change by a value of $2\pi$. However, the periodicity in Fig.2 is much smaller than $c$. The explanation is simple. As a matter of fact, in real space the individual $\phi(\vec{k}_\perp)$ has a periodicity of $\frac{1}{N_{\text{band}}\parallel}c$ (instead of $c$), which for PbTiO$_3$ the periodicity is $0.0455c$ because $N_{\text{band}}^{\text{occ}} = 22$. This is indeed consistent with the numerical calculation in PT (Fig.2b). The length of periodicity can be seen from Eq.\ref{eq:5}, showing that, whenever $\vec{r}_0 = \frac{n}{N_{\text{band}}}\vec{R}_\parallel$ ($n$ is an arbitrary integer and $\vec{R}_\parallel$ is the lattice vector along the $\vec{G}_\parallel$ direction), the $\phi^B(\vec{k}_\perp)$ and $\phi^A(\vec{k}_\perp)$ differ by $\phi^B(\vec{k}_\perp) = \phi^A(\vec{k}_\perp) + 2\pi n$. Fig.2(b) also reveals the reason responsible for the discontinuity of the total polarization. Spurious discontinuity occurs when the $\phi(\vec{k}_\perp)$ phases of some (but not all) individual $\vec{k}_\perp$ exceed $2\pi$ [Fig.2(b)]. Under this situation, computers incorrectly shift the phases of these $\vec{k}_\perp$ points back to the principle range, yielding spurious total polarization. According to our experience, spurious polarization often takes place in two circumstances: one is for materials of very large polarization, such as tetragonal BiScO$_3$, and another is when atoms in the unit cell are translationally shifted. Given the small bandwidth of the $\phi(\vec{k}_\perp)$ dispersion, it is now straightforward that, by using different $\vec{r}_0$s, we can avoid the spurious polarization. However for some materials, if the dispersion width from different $\vec{k}_\perp$ points is larger than $2\pi$, one may have to rely on the continuity of the $\phi(\vec{k}_\perp)$ phases, and map out the phases of individual $\vec{k}_\perp$ points over the whole two-dimensional $\vec{k}_\perp$ plane in order to find the correct phase branch.
III. STRAIN DEPENDENCE OF POLARIZATION STRUCTURE

An important property of ferroelectrics is that the polarization is strongly dependent on strain. While strain can change the total polarization, response of the polarization dispersion structure to strain could also be an interesting problem. Here we investigate the response of the polarization structure under in-plane strain in PbTiO$_3$. For each in-plane ($a$) lattice constant, the out-of-plane $c$ lattice constant and atomic positions are fully relaxed, by minimizing the DFT total energy. The polarization structure is then determined using the optimal structure.

Figure 3 shows the phase dispersion curves for PbTiO$_3$ at different in-plane lattice constants. All curves are shifted so that the phase at Γ point is zero, in order to conduct direct comparison. Three conclusions can be drawn from Fig.3 (1) The relative phase, $\phi(\vec{k}_\perp) - \phi(\Gamma)$, changes drastically for $X_2$, but not so significantly for $X_1$. (2) At increasing strain, (or smaller in-plane $a$ constant), the bandwidth of the dispersion initially changes very little when $a = 3.84\text{Å}$, and then starts to decrease upon further increasing strain to $a = 3.80\text{Å}$. The decline of the dispersion bandwidth is rather surprising, since a compressive inplane strain is known to enhance the total polarization in PT. The decline is also counterintuitive when one considers that the decreasing inplane lattice constant makes the atom-atom coupling stronger within the inplane directions, and should therefore have increased the bandwidth. One possible reason that may cause the decrease of the bandwidth is given in the next section. As a result of the declining dispersion, the polarization curve becomes notably “flat” at small $a = 3.65\text{Å}$. (3) The curvature of the dispersion also shows subtle changes, featured by the fact that a new dispersion minimum appears along the $X_2-\Gamma$ line at large strain. As a consequence, the dispersion curvature [i.e., the second derivative $\nabla^2_{\vec{k}_\perp} P(\vec{k}_\perp)$] at Γ point alters its sign from being positive (at large $a$) to negative (at small $a$). Furthermore, the local maximum between Γ – $X_1$ for unstrained PT turns into a new minimum at large inplane strains. Meanwhile, the $X_1$ point changes from a minimum into a saddle point, when strain increases.

The calculations thus reveal that, while inplane strain has been previously known to introduce interesting modifications (sometimes markedly enlarged [12] and sometimes remarkably small [13]) to the total $c$-axis polarization, its effects on the polarization dispersion at individual $\vec{k}_\perp$ points appear to be even richer, showing that the polarization structure
indeed worths studying. The subtle response of the polarization structure, as predicted above, indicate that there is new and rather complex physics behind the results in Fig.3.

While we know that the strain-induced changes in the polarization dispersion must be associated with the fundamental modification of electron wave functions, we also have to admit that the DFT results obtained in our numerical calculations are puzzling, and an intuitive understanding of the results is difficult for two reasons. First, this is an early attempt to investigate the polarization structure, and there is not much previous understanding in the literature. Second, although Eq.(2) and Eq.(3) allow us to compute precisely the polarization of individual \( \vec{k}_\perp \), a direct and more intuitive connection between \( \phi(\vec{k}_\perp) \) and Bloch wave functions is hard to capture from these equations. As a result, it would be very helpful if one could find an alternative way to understand the polarization structure and the computation results. For instance, what determines the polarization at individual \( \vec{k}_\perp \) point, and why \( \phi(\vec{k}_\perp) \) maximizes at the \( X_2 \) point? In the next section, we attempt a scheme which we wish to be able to offer a more intuitive understanding of the polarization structure.

IV. WANNIER FUNCTION FORMULATION OF POLARIZATION STRUCTURE

As mentioned above, Eq.(2) and Eq.(3) give us little intuitive sense on the direct \( \vec{k}_\perp \) dependence of the Berry’s phase. In order to get more insight, we use Wannier functions to analyze the polarization structure. Previously, Wannier functions have been found very useful in analyzing real-space local polarization\[18, 19\]. Here we employ the Wannier-function approach for a different purpose, namely to understand the \( \vec{k}_\perp \)-dependence of the polarization structure. The Wannier functions are defined as

\[
W_n(\vec{r} - \vec{R}) = \frac{\sqrt{N\Omega}}{(2\pi)^3} \int_{BZ} d\vec{k} e^{i\vec{k} \cdot (\vec{r} - \vec{R})} u_{nk}(\vec{r})
\]

or

\[
u_{nk}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{-i\vec{k} \cdot (\vec{r} - \vec{R})} W_n(\vec{r} - \vec{R})
\]

where \( \vec{R} \) runs over the whole real-space lattice vectors. By substituting Eq.(7) into Eq.(2) and carrying out analytically the integral over \( \vec{k}_\parallel \), it is straightforward to derive, for tetrag-
onal perovskites, the polarization at individual $\vec{k}_\perp$ as

$$
\phi(\vec{k}_\perp) = \frac{2\pi}{c} \sum_{\vec{R}_\perp} \sum_{n=1}^{M} \int \vec{r}_\parallel W_n^*(\vec{r}) W_n(\vec{r} - \vec{R}_\perp) e^{i\vec{k}_\perp \cdot \vec{R}_\perp} d\vec{r}
$$

(8)

where $\vec{r}_\parallel$ is the projection of vector $\vec{r}$ along the polarization direction, $\vec{R}_\perp$ is the projection of lattice vector $\vec{R}$ onto the plane perpendicular to the polarization direction. For convenience of discussion, we separate the sum over $\vec{R}_\perp$ into the $\vec{R}_\perp = 0$ term and the rests,

$$
\phi(\vec{k}_\perp) = \phi_0 + \frac{2\pi}{c} \sum_{\vec{R}_\perp \neq 0} \sum_{n=1}^{M} \int \vec{r}_\parallel W_n^*(\vec{r}) W_n(\vec{r} - \vec{R}_\perp) e^{i\vec{k}_\perp \cdot \vec{R}_\perp} d\vec{r}
$$

(9)

where for $\vec{R}_\perp = 0$, $\phi_0 = \sum_{n=1}^{M} \int (\vec{r}_\parallel) W_n^*(\vec{r}) W_n(\vec{r}) d\vec{r}$ is the phase contribution from the same unit cell. Eq.(9) is the basis for understanding the polarization structure. From this equation, we observe the following.

First, it is now clear that the $\vec{k}_\perp$-dependent part of $\phi(\vec{k}_\perp)$ comes only from the $\vec{R}_\perp \neq 0$ terms, which correspond to the overlap of the Wannier functions in neighboring cells. In other words, the $\vec{k}_\perp$ dependence of the $\phi(\vec{k}_\perp)$ phase results from the overlap of the Wannier functions of different cells that are displaced by $\vec{R}_\perp$ from each other within the plane that is perpendicular to the direction of polarization. While the choice of the Wannier function is known to be non-unique due to the gauge uncertainty, the sum of the Wannier-function overlap over occupied bands is a uniquely defined quality which does not depend on the gauge. It is this quantity that determines the shape of the polarization structure.

Second, Eq.(9) explains why the bandwidth of polarization dispersion is often much smaller than $2\pi$. Since only the second term in this equation is $\vec{k}_\perp$ dependent, and since the Wannier functions are generally well localized compared to the size of unit cell, one expects the overlap $W_n^*(\vec{r}) W_n(\vec{r} - \vec{R}_\perp)$ to be much smaller than unity for $\vec{R}_\perp \neq 0$. This is consistent with our numerical results in Fig.11, namely, $\phi(\vec{k}_\perp) - \phi_0 \approx 0.6 \ll 2\pi$.

Third, since the dispersion in $\phi(\vec{k}_\perp)$ comes from the overlap of the Wannier functions between cells of different $\vec{R}_\perp$s in the $xy$-inplane directions, it explains why the polarization structure is very sensitive to inplane strain, where by changing inplane lattice constant, the distances between neighboring cells are effectively altered. Meanwhile, we recognize that a precise understanding of how the bandwidth depends on the inplane strain is not as simple as one might think. Naively one tends to think that, with the decline of inplane lattice constant, the dispersion is to increase, since the overlap $W_n^*(\vec{r}) W_n(\vec{r} - \vec{R}_\perp)$ increases when
$\vec{R}_\perp$ decreases. This will lead to the widening of the polarization dispersion width, which is opposite to what we found in Fig.3. This puzzling contradiction can be resolved by noticing that, in addition to being dependent on the overlap strength between $W_n(\vec{r})$ and $W_n(\vec{r} - \vec{R}_\perp)$ within the perpendicular plane, the dispersion width also hinges on the localization length ($l_{\|WF}$) of the Wannier functions along the direction parallel to the polarization, as a result of the $\vec{r}_{\|}$ operator in Eq.(9). With the increasing inplane strain, the $l_{\|WF}$ is to shrink. We thus see that the bandwidth of polarization is determined by the balance of two competing factors between the increasing Wannier-function overlap and the decreasing $l_{\|WF}$ localization length. When the latter dominates, the bandwidth declines as we have seen in Fig.3 from numerical calculations.

V. CURVE ANALYSIS

With the general understanding of the polarization structure in the above section, we next attempt to determine analytically the polarization dispersion specifically for PbTiO$_3$, aimed to obtain further insight into the important details of the polarization structure. As will become clear later, our analysis in the following also explains what determines the $\phi(\vec{k}_\perp)$ polarization at special points of $\Gamma$, $X_1$ and $X_2$. We begin by defining parameters

$$t(\vec{R}_\perp) = \frac{2\pi}{c} \sum_{n=1}^{M} \int \vec{r}_\| W_n^*(\vec{r}) W_n(\vec{r} - \vec{R}_\perp) d\vec{r},$$  \hspace{1cm} (10)

and then,

$$\phi(\vec{k}_\perp) = \sum_{\vec{R}_\perp} t(\vec{R}_\perp) e^{i \vec{k}_\perp \cdot \vec{R}_\perp}.$$  \hspace{1cm} (11)

For dielectrics of insulating nature, Wannier functions are highly localized, and decay exponentially with the distance [20, 21]. As a result, $t(\vec{R}_\perp)$ also decay quickly with the increase of $|\vec{R}_\perp|$, so we can adopt the tight-binding like approach and consider only several $\vec{R}_\perp$s that correspond to some nearest neighbors (NN). We consider up to the 2$^{nd}$ NNs, where

$$\vec{R}_\perp = \begin{cases} 
(0 \ 0) & \text{on site} \\
(\pm a \ 0) & \text{1NNs} \\
(0 \ \pm a) & \text{1NNs} \\
(\pm a \ \pm a) & \text{2NNs} 
\end{cases}$$
Taking advantage of tetragonal symmetry, we can rewrite Eq. (11) as

\[
\phi(\vec{k}_\perp) = t_0 + 2t_1[\cos(k_1a) + \cos(k_2a)] + 2t_2[\cos(k_1 + k_2)a + \cos(k_1 - k_2)a],
\]

where \(t_i\) is the \(i^{th}\) NNs contribution defined in Eq. (10), and \(\vec{k}_\perp = (k_1, k_2)\). This expression gives us a more direct sense of the \(\phi(\vec{k}_\perp)\) polarization dispersion, approximated to the second nearest neighbors. At special \(\vec{k}_\perp\) points of \(\Gamma\), \(X_1\), and \(X_2\), the phases are \(\phi(\Gamma) = t_0 + 4t_1 + 4t_2\), \(\phi(X_1) = t_0 - 4t_2\), and \(\phi(X_2) = t_0 - 4t_1 + 4t_2\), respectively. We could thus clearly see that the \(t_0\) term, corresponding to \(\vec{R}_\perp = 0\), acts to rigidly shift the polarization curve as a whole. Meanwhile, the phase relative to the \(\Gamma\) (i.e., the dispersion) is determined by the \(t_1\) and \(t_2\) quantities, and more specifically,

\[
\begin{align*}
\phi(X_1) - \phi(\Gamma) &= -4t_1 - 8t_2, \\
\phi(X_2) - \phi(\Gamma) &= -8t_1.
\end{align*}
\]

These equations are useful, since they tell us that (1) the relative height at \(X_2\) (which contributes most to the polarization in PT), \(\phi(X_2) - \phi(\Gamma)\), is determined by \(t_1\), associated with the overlap of the Wannier function in the 1\(^{st}\) NNs. \(t_1 < 0\) for PbTiO\(_3\) in equilibrium. (2) Under the assumption that \(t_2\) is negligible, \(\phi(X_2) - \phi(\Gamma)\) will be larger than \(\phi(X_1) - \phi(\Gamma)\) by a factor of 2.

Within the second nearest-neighbor approximation, one can further determine analytically the dispersion along the \(\Gamma \rightarrow X_1 \rightarrow X_2 \rightarrow \Gamma\) line in the 2D Brillouin zone as

\[
\phi(\vec{k}_\perp) = \begin{cases} 
  t_0 + 2t_1 + (2t_1 + 4t_2)\cos(k_1a), & \text{for } \Gamma \rightarrow X_1 \text{ with } k_2 = 0 \\
  t_0 - 2t_1 + (2t_1 - 4t_2)\cos(k_2a), & \text{for } X_1 \rightarrow X_2 \text{ with } k_1 = \pi/a \\
  t_0 + 2t_2 + 4t_1\cos(k_1a) + 2t_2\cos(2k_1a), & \text{for } X_2 \rightarrow \Gamma \text{ with } k_1 = k_2.
\end{cases}
\]

The polarization structure could thus be expressed as a simple combination of cosine functions.

To examine whether the second-NN approximation is sufficient, we fit the analytical results to the numerical DFT calculations to determine the \(t_i\) (\(i = 0, 1, 2\)) parameters. Note that only \(\phi(\vec{k}_\perp)\)s at three points (i.e., \(\Gamma\), \(X_1\) and \(X_2\)) are fitted. The obtained \(t_i\) values are given in Table I. These values are then used to determine the whole dispersion curve,
TABLE I: The fitting $t_1$ and $t_2$ parameters for PbTiO$_3$ at different lattice constants. $t_0$ is not shown here since it does not affect dispersion.

| $a$(Å) | $t_1$   | $t_2$   |
|--------|---------|---------|
| 3.88   | -0.072  | 0.031   |
| 3.84   | -0.072  | 0.032   |
| 3.80   | -0.064  | 0.031   |
| 3.72   | -0.031  | 0.023   |
| 3.65   | -0.010  | 0.016   |

Shown in Fig.1(b) for PbTiO$_3$ in equilibrium structure of $a = 3.88\text{Å}$. We could see that the analytical curve agrees well with the DFT result, implying that the 2nd NN approximation works. On the other hand, some fine structure of the curve (such as the small local maximum along the $\Gamma - X_1$) can not be reproduced, where for a better fitting, approximation beyond the 2nd NNs would be necessary.

From Table I one can also see how the $t_i$ quantities are influenced by inplane strain. $t_1$ declines substantially as $a$ decreases below 3.80Å, while $t_2$ shows a less dependence on inplane strain. This makes sense since, by varying the inplane strain, the main effect lies in altering the nearest-neighbor interaction among Wannier functions. For $a > 3.80\text{Å}$, $|t_1|$ approximately equals 2$|t_2|$, confirming the importance of the nearest neighbor interaction. For large strains of $a < 3.72\text{Å}$, $|t_1|$ and $|t_2|$ become comparable, for which it is likely that higher orders of NNs are also needed.

VI. COMPARISON WITH BARIUM TITANATE

It is of interest to compare the polarization dispersions between BaTiO$_3$ (BT) and PbTiO$_3$ (PT), since these two substances have rather different tetragonality, magnitude of polarization, and sizes of A-site atoms. For this purpose, we have studied the polarization structure in BT, for which a tetragonal symmetry is enforced so that a direct comparison with PT can be made. Following the same procedure as for PT, we optimize the cell structure and atomic positions of BT at different inplane lattice constants, and calculate the corresponding polarization structures.
Fig. 4 displays the polarization structure for BaTiO$_3$ at different inplane lattice constants. Let us first focus on the dispersion of the equilibrium BaTiO$_3$. The LDA-calculated equilibrium inplane lattice constant of BT is $a = 3.95\,\text{Å}$. Apart from similarities to PT (e.g., $\phi$ maximizes at $X_2$), our calculations reveal some interesting differences between PT and BT under zero strain: (1) The BT dispersion curve has a significantly smaller bandwidth ($\sim 0.42$) than that of PT ($\sim 0.57$). Since the bandwidth is determined by the difference $\phi(X_2) - \phi(\Gamma)$, i.e., by $t_1$, a smaller bandwidth indicates less overlapping Wannier’s functions between nearest neighbors in BaTiO$_3$, which could be explained by the larger inplane lattice constant $a$ for BT at equilibrium. (2) Unlike PT, the polarization in BT is not small at $X_1$. This again can be attributed to the large inplane lattice constant in BT, which leads to a negligible contribution from the 2nd NNs, i.e., $t_2$ is small in BT. Indeed, we numerically found that $t_2$ is -0.007 in BT, compared to 0.031 in PT. By Eq. (13), $\phi(X_1)$ is about half of the $\phi(X_2)$ value if $t_2$ is small, which is indeed born out in Fig. 4. (3) As a consequence of observation (2), the dispersions of BT and PT along the $\Gamma \rightarrow X_1$ are not quite similar. There is a local maximum between $\Gamma - X_1$ for PT, whereas for BT, no local maximum exists and $X_1$ becomes a saddle point.

Upon strain, BaTiO$_3$ and PbTiO$_3$ exhibit sharp difference in their strain dependence of dispersion bandwidth. As we saw previously in Fig. 3, inplane strain causes the bandwidth declining for PbTiO$_3$. However, for BaTiO$_3$, a dramatic *enlargement* in bandwidth occurs, when $a$ decreases from 3.95Å to 3.85Å. The bandwidth maintains a large value at $a=3.75\,\text{Å}$, after which it starts to drop. In BaTiO$_3$ the polarization dispersion bandwidth thus shows an interesting non-monotonous dependence on inplane strain. This characteristic non-monotonous dependence strongly supports our conjecture that the two competing factors determine the bandwidth, as described above in Section IV. When strain is small in BT, the overlapping of Wannier functions located at the nearest neighboring $\vec{R}_{\perp}s$ plays a dominant role, and the increasing overlap leads to a larger $|t_1|$ and thus larger bandwidth. As inplane strain becomes large ($a < 3.85\,\text{Å}$), the atom-atom interaction along the $c$-axis is considerably weakened due to elongated $c$-lattice length. As a consequence, the shrinking $l_{\parallel}^{WF}$ localization length of Wannier functions along the $\vec{r}_{\parallel}$ direction takes over and becomes dominant, giving rise to the declining bandwidth. This, once again, reveals that the polarization dispersion contains rich information. To make more quantitative comparison, we replot in Fig. 5 the strain dependence of the $\phi(\vec{k}_{\perp})$ phases at $X_1$ and $X_2$, relative to the $\Gamma$
point. Fig. 5 is of some useful value since it allows us to contrast the $\vec{k}_\perp$-specific polarizations in two materials at the same fixed in-plane lattice constant. The difference between BT and PT is thus not related in a significant sense to atom-atom distance, but largely due to the overlap of respective Wannier functions. In Fig. 5, both $\phi(X_1)$ and $\phi(X_2)$ are seen to be far greater in BaTiO$_3$ than in PbTiO$_3$, for a fixed $a$ constant. The greater values of $\phi(\vec{k}_\perp)$ in BT could possibly originate from the fact that the Wannier functions in this material is more spreading due to the larger size of Ba atom.

From the comparison between PT and BT, we could see that the polarization structure has some common features for materials with similar structure, and meanwhile, some distinctions revealing the identities of materials. The common features allow us to understand the polarization structure in general, just as for band structure, most III-V semiconductors have direct band gaps. Differences in polarization structure manifest the electron wave functions and interatomic interactions on microscopic scale.

VII. SUMMARY

Two different approaches are employed to study the polarization structure in perovskite ferroelectrics. Numerically we use the density functional total-energy calculations and the modern theory of polarization. Analytically we formulate a scheme to describe the $\vec{k}_\perp$ dependence of the polarization phase using Wannier functions. By parameterizing the Wannier-function overlapping, we further identify the quantities that determine the $\phi(\vec{k}_\perp)$ phases at special $\vec{k}_\perp$ points of interest. Our specific findings are summarized in the following.

For PbTiO$_3$ at equilibrium, (i) the $\phi(\vec{k}_\perp)$ phase maximizes at the Brillouin zone boundary of the 2D $\vec{k}_\perp$ plane, not the zone center. (ii) The polarization structure shows little dispersion along the $\Gamma - X_1$ line. However, the dispersion is large along the $\Gamma - X_2$. (iii) The bandwidth of the dispersion curve is far below $2\pi$. The small dispersion considerably eases the difficulty in assigning the correct branch of individual $\vec{k}_\perp$ phase, but caution still needs to be taken when the $\phi(\vec{k}_\perp)$ phase is approaching $2\pi$.

Analytically, (iv) the expression, Eq. (9), is given as the basis for understanding the polarization structure. It also explains why the polarization bandwidth is small compared to $2\pi$. (v) The polarization phase at individual $\vec{k}_\perp$ is revealed to depend on the competition of two factors, namely the overlapping strength of Wannier functions within the perpendicular
plane and the localization length $l_{\parallel}^{WF}$ of these Wannier functions. (vi) Within the 2NN approximation, the $\phi(X_1)$ and $\phi(X_2)$ values in ferroelectric perovskite are found to be $\phi(X_1) - \phi(\Gamma) = -4t_1 - 8t_2$, $\phi(X_2) - \phi(\Gamma) = -8t_1$. If $t_2$ is negligible, the latter is 2 times of the former. (vii) When PbTiO$_3$ is under compressive inplane strain, the polarization bandwidth is found to decrease, whereas the total polarization increases. The declining bandwidth implies that the localization length $l_{\parallel}^{WF}$ of Wannier functions plays a dominating role in PbTiO$_3$.

By comparing BaTiO$_3$ with PbTiO$_3$, we show (viii) the equilibrium BT exhibits a smaller bandwidth of 0.42, as compared to the bandwidth of 0.57 in PT. (ix) $\phi(X_1)$ in BaTiO$_3$ is not small, unlike PT. The difference comes from the fact that $t_2$ is negligible in BT, leading to the result that $\phi(X_1)$ is about half of the value of $\phi(X_2)$. But in PT, $t_2$ can not be neglected, and acts to offset the $t_1$ contribution, giving rise to smaller $\phi(X_1)$ and flat dispersion along the $\Gamma - X_1$ line. (x) As BaTiO$_3$ is under increasing inplane strains, its polarization bandwidth displays a characteristic non-monotonic variation by first increasing dramatically and then declining. The finding lends a support to the qualitative understanding that two competing factors determine the $\phi(\vec{k}_{\perp})$ phase. (xi) When BaTiO$_3$ and PbTiO$_3$ are constrained to the same inplane lattice constant, the $\phi(X_1)$ and $\phi(X_2)$ are shown to be significantly larger in BT than in PT, unlike the case when two materials are in equilibrium.

We conclude by pointing out that there are still many aspects of polarization structure we do not yet understand. For example, we have not pursued beyond the 2nd nearest neighbors to explain the local maximum between $\Gamma$ and $X_1$ in unstrained PT. We also do not know the physical significance when $\phi(X_1)$ changes from a local minimum to a saddle point as displayed in Fig.3 for PbTiO$_3$ under strains. We believe that further analysis of the polarization structure could yield better knowledge on the physics of dielectrics. Like band structure of solids, we hope that the polarization structure can provide us a new tool of studying ferroelectric materials and properties.

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FIG. 1: (a) The 2D Brillouin zone for the $\vec{k}_\perp$ plane; (b) Berry’s phase at different $\vec{k}_\perp$ points for PbTiO$_3$ at equilibrium (symbols: direct calculation results; curve: analytical results). The $\phi(\vec{k}_\perp)$ phase is in units of radian.

FIG. 2: (Color online) (a) Total polarization in strained PbTiO$_3$ of inplane lattice constant $a = 3.72\text{Å}$ as a function of the uniform displacement $z_0$ of five atoms; (b) the $\phi(\vec{k}_\perp)$ phases at six Monhorst-Pack sampling $\vec{k}_\perp$ points as a function of $z_0$. For each $c/N_{\text{occ}}$ change in $z_0$, the $\phi(\vec{k}_\perp)$ phases change by $2\pi$. In (b), the $\phi(\vec{k}_\perp)$ phase curves are enlarged in the right side of the figure for $z_0$ between 0.044 and 0.048.
FIG. 3: (Color online) The $\phi$ phases of different $\vec{k}_\perp$-points, for PbTiO$_3$ under different inplane lattice constants. Symbols are direct calculation results; curves are guides for eyes.

FIG. 4: (Color online) Polarization dispersions for BaTiO$_3$ at different inplane lattice constants. Symbols are direct calculation results; lines are guide for eyes.

FIG. 5: Dependencies of the $\phi(\vec{k}_\perp)$ phases at $X_1$ point (left) and at $X_2$ point (right) as a function of inplane lattice constant, for PT and BT.