Theoretical estimation of longitudinal flexoelectric response in polar perovskite oxides

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1 Reference planes and directions

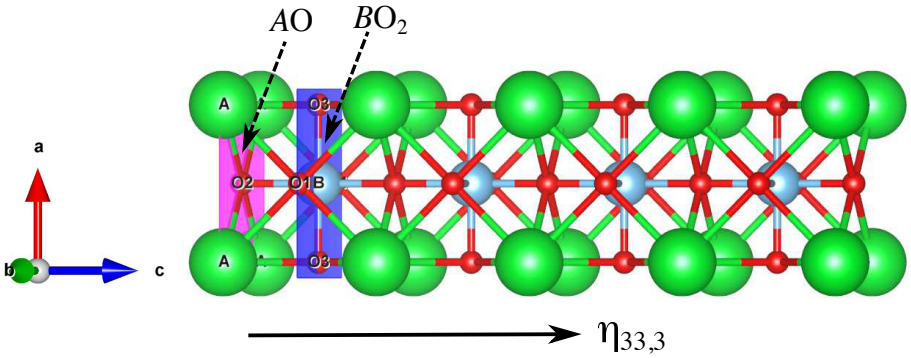

Figure S1: The normal direction of the AO plane in pink and the BO_2 plane in blue is along the c axis, and the strain gradient is also applied along the c axis. Since the two oxygen atoms (O1 and O3), occupying each BO_2 plane, are fully relaxed, the lattice parameter along the c axis can be different depending on whether we use the fixed Ti atoms (clamped-atom lattice constant, c_{clamped}) or the relaxed O atoms (relaxed-atom lattice constant, c_{relaxed}). We found that the flexoelectric coefficients obtained from the different definitions of lattice parameters with the clamped or the relaxed atoms show close agreement, and they also give similar results to the ones obtained with the A-site atoms as in the Refs. [1, 2].

2 Optimization

2.1 Born effective charges (BECs)

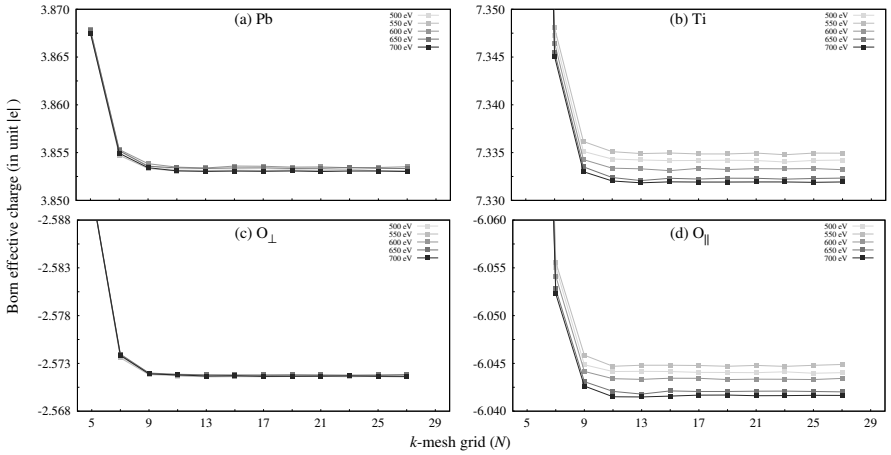

Figure S2: The convergence of BECs of $PbTiO_3$ ($Pm\bar{3}m$), calculated using DFPT as a function of the k-mesh density and the number of plane wave bases. The subdivisions of k-mesh along the reciprocal lattice vectors are $(N \times N \times N)$ denoted here by single N, which varies in the range of $(5{\times}5{\times}5 \sim 27{\times}27{\times}27)$, and the ENCUT energies vary in the range of (500∼700 eV). The variation in BECs of Pb, Ti, $O_\perp$, and $O_\parallel$ are shown in a, b, c, and d, respectively. Here $O_\perp$ and $O_\parallel$ represent the BEC of oxygen atom perpendicular and parallel to the Ti-O bond.

2.2 Supercell size

The percentage difference in displacements of clamped- and relaxed-atoms is denoted by Δ, which drops from 7.9% to 2.5% with the increase of supercell size from 1×1×8 to 1×1×16 (See Fig. S3).

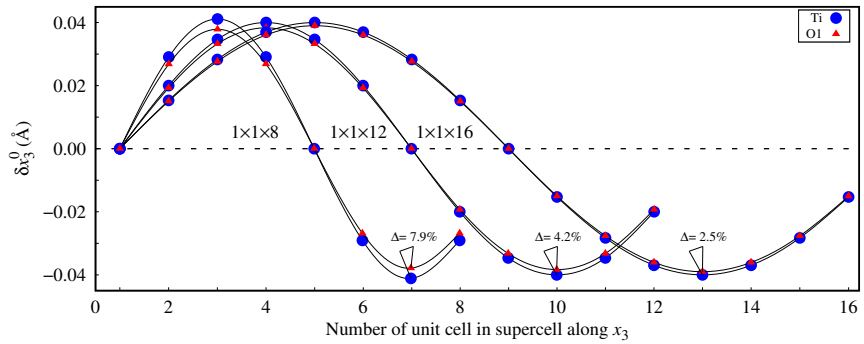

Figure S3: The displacements of clamped Ti and relaxed O1 atoms from their equilibrium (unstrained) positions along the x_3-axis in the deformed supercells of $SrTiO_3$. Here O1 represents one of the oxygen atoms in the TiO_2 plane. The percentage difference in Ti and O1 displacements (Δ) varies with the increase of supercell size (i.e., from 1×1×8 to 1×1×16).

3 Local polarization

Fig. S4 shows the effect of precisely determined BECs and high-quality relaxation of atomic positions in a deformed supercell on the resultant local polarization in low strain gradient regimes. In both cases of Figs. S4(a) and S4(b), the structures are under the same sinusoidal strain gradient. However, in Fig. S4(a), relaxation is done with the forces and energy convergence criteria as in Ref. [1], and BECs are taken from Ref. [3], while Fig. S4(b) is the result of this work (i.e., using accurate BECs and high-quality atomic positions relaxation), which clearly shows the inadequacy of the previous works to determine the correct local polarization, especially in low strain gradient regimes.

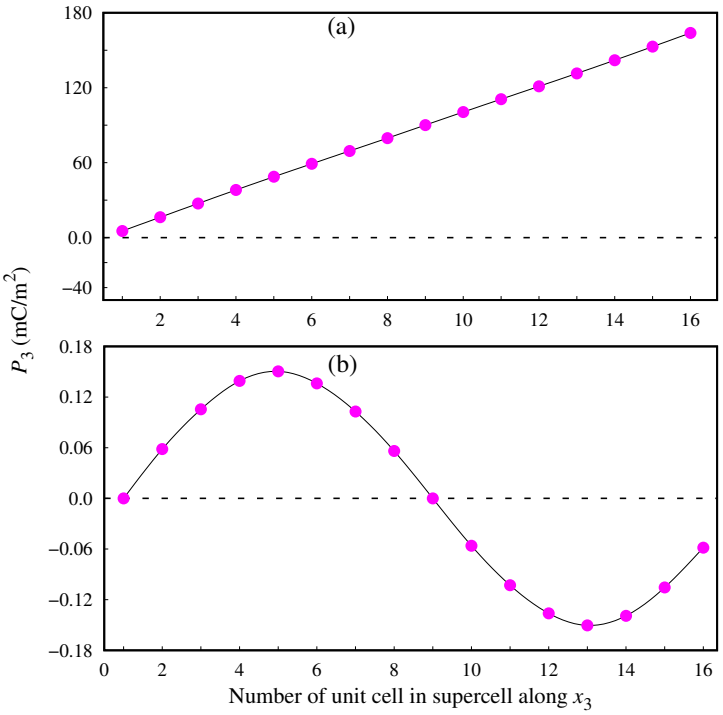

Figure S4: The calculated local polarization along x_3 of $PbTiO_3$ ($Pm\bar{3}m$), induced by sinusoidal strain gradient considering (a) BECs from Ref. [3] and relaxed supercell with LDA functional and relaxation criteria given in Ref. [1] (b) BECs and relaxed supercells with GGA functional and relaxation criteria given in this work.

4 Displacements of atoms

To analyze the polarization responses in Fig. S4, the displacements of all the atoms from their mean positions after relaxation are determined and plotted in Fig. S5, which clearly shows the fact that the coarse relaxation criteria prevent the atoms in Fig. S5(a) from relaxing to the well-converged positions as in Fig. S5(b).

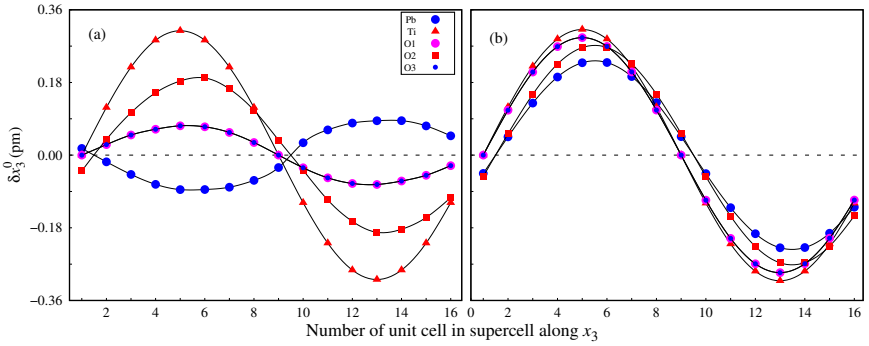

Figure S5: The displacements of all atoms (i.e., fixed along x_3 (Ti) and fully relaxed (i.e., Pb and O)) along the x_3 direction from mean positions in $PbTiO_3$ ($Pm\overline{3}m$) using the relaxation criteria of (a) Ref. [1] and (b) this work. O1 and O3 represent the two oxygens in the TiO_2 plane, and O2 represents the oxygen in the PbO plane.

5 Structure and BECs of tetragonal $BaTiO_3$

Table S1: Lattice parameters (a, c in Å) and diagonal components of BEC tensors (Z^*, in $\mid e \mid$) of $BaTiO_3$ in the $P4mm$ phase. The symbols O1 and O2 represent the oxygen atoms in TiO_2 and BaO planes, respectively.

		This study	Refs. [4, 5]
a (Å)		4.0009	3.9970
c (Å)		4.2245	4.0314
Z^*_{Ba}	xx	2.6892	2.72
	yy	2.6892	2.72
	zz	2.8894	2.83
Z^*_{Ti}	xx	6.9135	6.94
	yy	6.9135	6.94
	zz	4.8712	5.84
Z^*_{O1}	xx	−2.0986	−2.14
	yy	−5.5959	−5.53
	zz	−1.8487	−1.95
Z^*_{O2}	xx	−1.9082	−1.99
	yy	−1.9082	−1.99
	zz	−4.0632	−4.73

6 Strain gradient vs. polarization

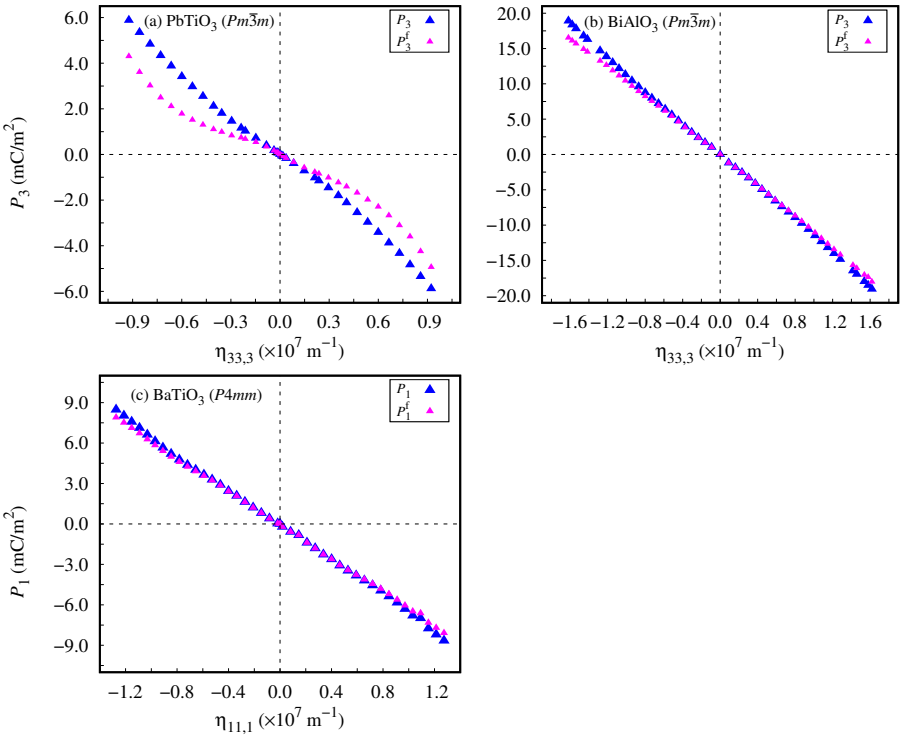

Figure S6: Strain gradient $\eta_{33,3}$ vs. polarization along x_3 for (a) $PbTiO_3$ and (b) $BiAlO_3$ in their $Pm\bar{3}m$ phase. (c) Strain gradient $\eta_{11,1}$ vs. polarization along x_1 (the non-polar crystallographic direction [100]) for $BaTiO_3$ in the $P4mm$ phase. The sampling points with blue triangles indicate the total local polarization P_3 (i.e., piezoelectric + flexoelectric), whereas the magenta triangles represent the only flexoelectric polarization P_3^{f} or P_1^{f}.

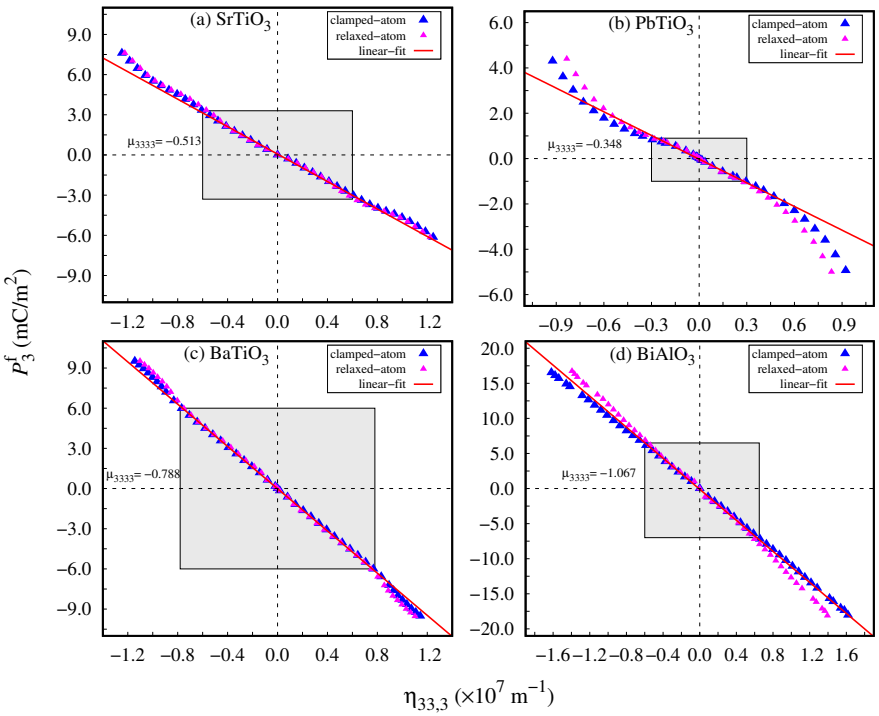

Figure S7: The flexoelectric polarization vs. strain gradients $\eta_{33,3}$ for cubic perovskite oxides. The shaded rectangles show the linear regions (where flexoelectric responses with the lattice parameters defined from clamped and relaxed atoms are nearly the same) that are used for fitting (red solid line) to find the flexoelectric coefficients.

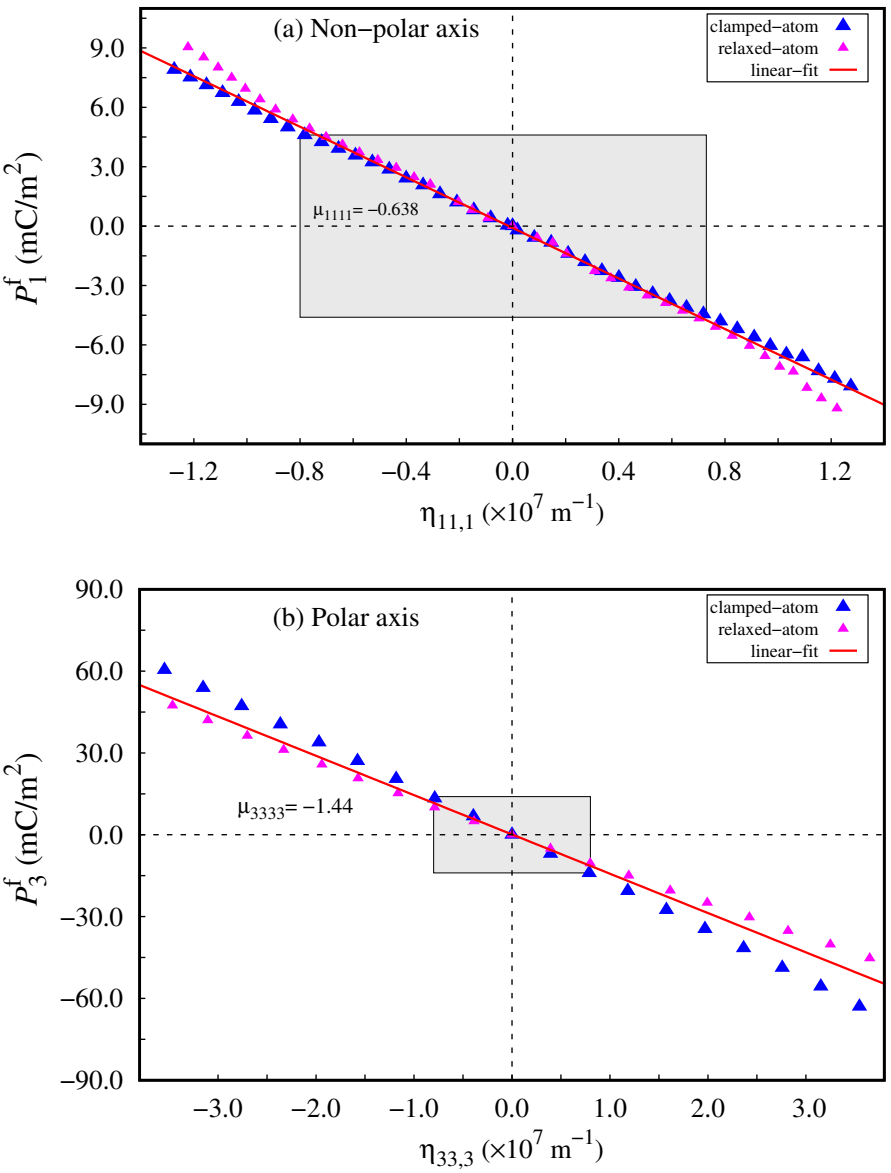

Figure S8: Flexoelectric polarization vs. (a) strain gradient $\eta_{11,1}$ along the non-polar axis and (b) strain gradient $\eta_{33,3}$ along the polar axis for $BaTiO_3$ ($P4mm$). The shaded rectangles show the linear regions considered for fitting (red solid line).

7 Flexoelectric Coefficients

The flexoelectric coefficients are determined by considering the strain gradient of clamped-atom and relaxed-atom and are tabulated in Table S2.

Table S2: Flexoelectric coefficient μ_{3333} and μ_{1111}, considering the strain gradients of clamped and relaxed atoms

	Phase	μ_{3333} (nC/m)		μ_{1111} (nC/m)	
		Clamped	Relaxed	Clamped	Relaxed
$SrTiO_3$	$Pm\bar{3}m$	-0.505	-0.519	....	....
$BaTiO_3$		-0.778	-0.799	....	....
$PbTiO_3$		-0.334	-0.364	....	....
$BiAlO_3$		-1.068	-1.149	....	....
$BaTiO_3$	$P4mm$	-1.716	-1.291	-0.617	-0.668

References

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