Towards a full first-principles theory of flexoelectricity

Jiawang Hong[1], Olivier Delaire[1], Gustau Catalan[2,3], Emilio Artacho[4,5] and David Vanderbilt[6]

[1] Materials Science and Technology Division Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA
[2]ICN2–Institut Catala de Nanociencia i Nanotecnologia, Campus UAB, 08193 Bellaterra (Barcelona), Spain
[3]ICREA - Institucio Catalana de Recerca i Estudis Avanc ̧ats, 08010 Barcelona, Spain
[4]Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK
[5]Nanogune and DIPC, Tolosa Hiribidea 76, 20018 San Sebastia ́n, Spain
[6]Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA

Flexoelectricity is the electromechanical coupling effect between strain gradient and electronic polarization. It is always allowed by symmetry because a strain gradient automatically breaks inversion symmetry. This is unlike the case of piezoelectricity, which can only occur in noncentrosymmetric materials. Flexoelectricity can have a significant effect on the functional properties of dielectric nanostructures due to the much larger strain gradient at the nanoscale than at macroscopic scales. The possibility of large effects at the nanoscale, with application to functional nanodevices, has triggered a recent increase of interest in flexoelectricity. [1-12] The development of nanoscience and nanotechnology requires a better understanding of flexoelectricity, and a better ability to utilize flexoelectric effects for a variety of purposes. Despite growing experimental interest, there have been relatively few theoretical studies of flexoelectricity, especially in the context of first-principles calculations. This is in part due to challenges in treating strain gradients in the calculations.

Direct first-principles calculations of flexoelectricity require the use of supercells with periodic boundary conditions, whereas a strain gradient, by definition, results in an inhomogeneous distribution of lattice parameters and thus a breaking of the lattice periodicity. We introduce an "accordion" supercell in which the strain gradient is itself periodic, thus allowing the recovery of the periodic boundary condition (Fig.1). We calculate the longitudinal flexoelectric response in rhombohedral $BaTiO_3$ and tetragonal $SrTiO_3$ perovskites at constant electric displacement boundary condition. [4] Based on this approach, the calculation of the transverse flexoelectric response was recently developed. [7, 12] This method is applicable even to low-symmetry systems. It offers a promising approach to determine the full flexoelectric tensor components for dielectric materials from first principles. However, the origin of the flexoelectrity and the surface role is unclear from this direct first-principles method.

In order to understand the origin of the flexoelectricity, we developed a complete first-principles theory of flexoelectric tensors, formulated in such a way that the tensor elements can be computed directly in the context of density-functional calculations. [6, 10] We reveal that the origin of flexoelectricity is from the electronic contribution due to octupoles ($Q^{(3)}$) and the lattice contribution due to the interaction between effective charges ($Q^{(1)}$) and the atomic displacements induced by the strain gradient (N), as well as the interaction between quadrupoles ($Q^{(2)}$) and the displacements induced by the strain (Γ), as can be seen in Eq. (1). We find that surfaces have contributions to the total flexoelectric response, which is related to dependence of the surface work function on local strain. We propose a method to calculate the flexoelectric coefficients in supercells with different orientations by using first-principles methods (Fig.2), including lattice and electronic contributions, under fixed E or fixed D electric boundary conditions in different parts of the procedure.

$$\mu_{\alpha\beta\gamma\delta} = V_c^{-1}\sum_{I\tau} Q^{(1)}_{I\alpha\tau} N_{I\tau\beta\gamma\delta} - \frac{1}{4} V_c^{-1}\sum_{I\tau}\left(Q^{(2)}_{I\alpha\tau\delta}\Gamma_{I\tau\beta\gamma} + Q^{(2)}_{I\alpha\tau\gamma}\Gamma_{I\tau\beta\delta}\right) + \frac{1}{6} V_c^{-1}\sum_{I} Q^{(3)}_{I\alpha\beta\gamma\delta} \qquad (1)$$

For the time being, it is still challenging for both theory and experiment to obtain the full flexoelectric tensor components for even the simplest cubic crystal. Combining the first-principles calculations and experiment to obtain the full flexoelectric tensor will be discussed.

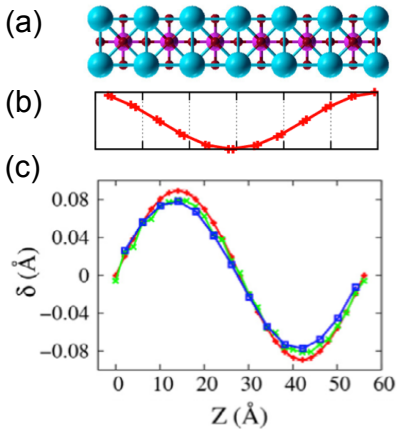

Fig.1 (a) Supercells for direct first-principles calculations without strain gradient; (b) strain gradient profile in the supercells; (c) the atomic displacement after relaxation (atom Ba is fixed, red) in $BaTiO_3$ (green:O, blue:Ti).

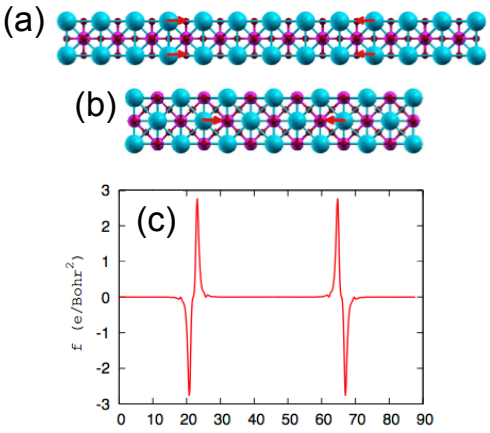

Fig.2 Original (a) and 45o-rotated (b) supercell for first-principles calculation; (c) change of charge-density distribution (a) in SrTiO3 supercell (original frame) at fixed *D*.

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