Berry-phase theory of polar discontinuities at oxide-oxide interfaces

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In the framework of the modern theory of polarization, we rigorously establish the microscopic nature of the electric displacement field **D**. In particular, we show that the longitudinal component of **D** is preserved at a coherent and insulating interface. To motivate and elucidate our derivation, we use the example of LAO/STO interfaces and superlattices, where the validity of the above conservation law is not immediately obvious. Our results generalize the "locality principle" of constrained-**D** density functional theory to the first-principles modeling of charge-mismatched systems.

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In classical electrostatics, the normal component of the electric displacement field **D** is preserved,

$$(\mathbf{D}_1 - \mathbf{D}_2) \cdot \hat{\mathbf{n}} = 0\,, \qquad (1)$$

at an insulating (charge-carrier-free) planar interface between two homogeneous insulators. Here $\mathbf{D}_1$ and $\mathbf{D}_2$ are the values of the macroscopic electric displacement in material 1 and 2 and $\hat{\mathbf{n}}$ is the plane orientation. While this is in principle a macroscopic law, recent first-principles calculations (e.g., on multicomponent perovskite superlattices)[1] have shown that it is applicable even at the *microscopic* level. Given this success, one would be tempted to adopt Eq. (1) in full generality for the description of insulating interfaces at the nanoscale, where the conservation of $D = \mathbf{D} \cdot \hat{\mathbf{n}}$ facilitates the interpretation and modeling of many phenomena.

There are, however, a number of cases which have emerged recently where the applicability of Eq. (1) is not immediately obvious. The prototypical example is that of a charge-mismatched interface between two crystalline insulators. Polar interfaces have been the object of intense research in the past few years, motivated by the recent observation of two-dimensional metallicity at interfaces between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO).[2,3] Interestingly, first-principles calculations have recently demonstrated that the LAO/STO interface can remain *insulating* under certain conditions, and in such a regime the oxide lattice undergoes rather unusual relaxation patterns. For example, in the case of a thin film of LAO deposited on the (001) surface of STO, strong "ferroelectric-like" polar distortions were reported in the LAO overlayer while the substrate remains essentially unperturbed.[4] Conversely, in periodic LAO/STO superlattices it was shown that the LAO and STO components spontaneously polarize in *opposite* directions, the largest distortions occurring now in STO.[5] The source of this polarization discontinuity ΔP is understood: it is induced by electric fields arising from extra interface charges $\pm e/2$ (for IV-III and II-III interfaces respectively) resulting from the "polar discontinuity" between the II-IV (STO) and III-III (LAO) perovskites. Similar issues arise for the case of II-IV/I-V (e.g., STO/$KNbO_3$) superlattices.[6] In these examples one is seemingly forced to conclude that Eq. (1) is violated, since the ΔP gives rise to a corresponding discontinuity in D that is inconsistent with Eq. (1).

One way to resolve this issue is to accept a definition of "free charge" as including *everything* other than bound charge, as suggested by some authors (e.g., Ref. 7, Sec. 4.3.1). Then Eq. (1) is fixed by adding a "free charge" term on the right to represent the polar-discontinuity charge, even though this is anything but "free." Another possibility, proposed by Murray and Vanderbilt,[6] is to introduce a *compositional* charge density $\rho_{\rm comp}$, which is distinct both from bound charge ($\rho_{\rm bound} = -\nabla \cdot \mathbf{P}$) and from truly free charge (associated with charge carriers), and write

$$\rho_{\rm tot} = \rho_{\rm free} + \rho_{\rm bound} + \rho_{\rm comp}. \qquad (2)$$

With $\nabla \cdot \mathbf{D} = 4\pi(\rho_{\rm free} + \rho_{\rm comp})$, Eq. (1) becomes, for an insulating interface,

$$(\mathbf{D}_1 - \mathbf{D}_2) \cdot \hat{\mathbf{n}} = 4\pi\sigma_{\rm comp}. \qquad (3)$$

While these approaches already provide a satisfactory account of the phenomena described in Refs. 4,5,6, there are good reasons to seek an alternative description. First, both of the above approaches are somewhat awkward, either introducing a third kind of charge, or describing as "free" a form of charge that is fixed. Second, it is necessary to assess the range of applicability of Eq. (1), i.e. to identify a general criterion for deciding in what cases it should be replaced by Eq. (3). Third, one would like to establish a true microscopic definition of all quantities appearing in Eq. (2), particularly $\rho_{\rm comp}(\mathbf{r})$ and $\rho_{\rm bound}(\mathbf{r})$. Given the ever-increasing interest in perovskite thin films and superlattices, such an analysis is particularly urgent in order to provide timely support for the experimental work with appropriate modeling tools.

Here we show that the incompatibility between Eq. (1) and the "polar discontinuity" can instead be elegantly resolved in the framework of the Berry-phase modern theory of polarization. In particular, we show that Eq. (1)

is exact without the need for extensions, once D is expressed in terms of the formal (rather than the effective) macroscopic polarization, and is a direct consequence of the interface theorem.[8] This result puts the "locality principle" of constrained-**D** density functional theory[1] on a firm theoretical basis, and generalizes its scope to the case of charge-mismatched superlattices and heterostructures. In the following, we will first introduce some basic properties of the formal polarization in periodic insulators. Based on these properties, we will then establish the link between Eq. (1) and the interface theorem. Finally, we will demonstrate these ideas in practice by performing calculations of a model LAO/STO superlattice.

In an independent-electron (or mean-field) picture, the total charge density of an insulator can be expressed as a sum of contributions from ion cores and Wannier functions. Let $\mathbf{r}_\alpha$ and $\mathbf{r}_i$ represent the ion core and Wannier center locations, respectively, for a choice of "basis" that tiles the crystal under primitive translations $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. The dipole moment of this discrete set of charged objects divided by the cell volume defines the macroscopic polarization $\mathbf{P}$.[9,10] We shall be concerned with a single component of the polarization, i.e., its projection in the direction $\hat{\mathbf{n}}$ parallel to $\mathbf{a}_2 \times \mathbf{a}_3$; let this be direction x. Then we have an essentially one-dimensional problem with $P = P_x$ given by

$$P = \frac{1}{\Omega}\Big(\sum Q_\alpha x_\alpha - e\sum x_i\Big)\,, \tag{4}$$

where Q_α and $-e$ are the charges of a given ionic core and Wannier function, respectively, and Ω is the cell volume. While this is rigorous, it has a degree of arbitrariness in that one may choose to include in the crystal basis any of the infinitely repeated images of each Wannier function or ion core. As shown schematically in Fig. 1(a), this implies that P is a multi-valued function; it is only defined modulo a "quantum of polarization" $\Delta P = e/S$, where $S = |\mathbf{a}_2 \times \mathbf{a}_3|$ is the cell surface area.

The polarization in Eq. (4) is the *formal* polarization corresponding to the raw result of a Berry-phase calculation (in contrast to the *effective* polarization, defined relative to a centrosymmetric reference).[11] It is essential to understand that the formal polarization does *not* necessarily vanish in a centrosymmetric material (i.e., $\mathbf{P}$=0 is not contained in the lattice of allowed values). Practical realizations of this situation are III-III perovskites like LAO in their cubic five-atom reference structure. With x along the (100) direction, the lattice of allowed values is $P = \pm e/2S$, $\pm 3e/2S$, ..., as shown schematically in Fig. 1(b). This occurs essentially because the individual LaO and AlO$_2$ layers have formal charges of $\pm e$. In contrast, II-IV perovskites like STO, which have formally neutral AO and BO$_2$ layers, have $P = 0$, $\pm e/S$, ..., as illustrated in Fig. 1(a). We now show that this fundamental difference in the respective P-lattices of LAO and STO is the key to reconciling Eq. (1) and the "misbehavior" of charge-mismatched interfaces.

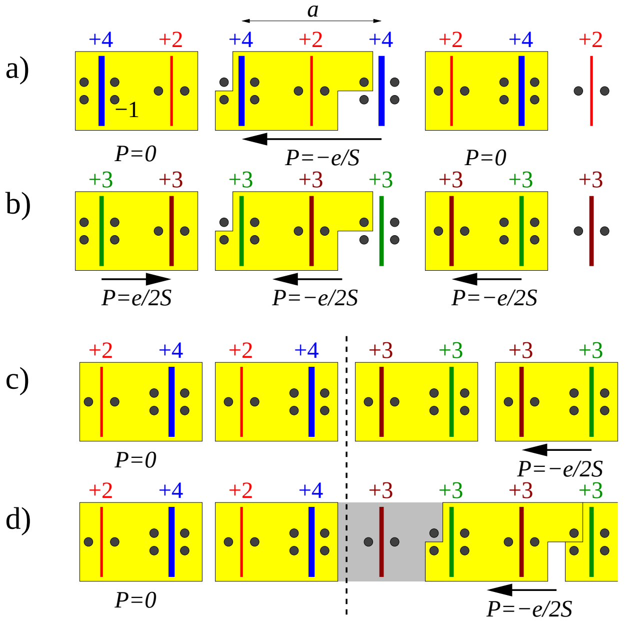

FIG. 1: (Color online) Schematic representation of formal polarization in the bulk (a-b) and at interfaces (c-d). Blue and red vertical lines represent BO$_2$ and AO layers in a II-IV perovskite (a); green and brown are the same but in a III-III perovskite (b). Black circles represent electronic Wannier centers (not all are explicitly shown). Different choices of basis (grouping) lead to values of P differing by $\Delta P = e/S$. (c) Choice of basis such that no charges are left in the interface region. (d) Choice of bias leaving net-neutral interface region (grey).

Consider a coherent insulating[12] interface between LAO and STO with perfect (1×1) periodicity, i.e. $\mathbf{a}_2$ and $\mathbf{a}_3$ are common to both crystals and lie on the interface plane. Fig. 1(c-d) shows an example with a TiO$_2$:LaO interface termination, but similar considerations apply for other terminations. Then it is always possible to group ions and Wannier functions into a basis for STO and one for LAO (yellow areas in the figure) such that the leftover interface region (grey shaded area) is overall charge neutral; two examples are provided in the figure. We use these basis conventions to define the bulk polarization in STO (P_1) and LAO (P_2) via Eq. (4). Because of the neutrality of the interface region, it follows that the macroscopic density of *bound* charge at the interface is

$$\sigma_{\rm bound} = P_1 - P_2. \tag{5}$$

This is essentially the "interface theorem" of Ref. 8, a central result of the modern theory of polarization.

Eq. (5) implies that the bound charge at the interface is determined by the discontinuity of *formal* bulk polarizations of the two participating materials, removing the need to complement the theory with $\rho_{\rm comp}$.[13] At the TiO$_2$:LaO interface sketched in Fig. 1(c-d), for example, Eq. (5) would yield a $\sigma_{\rm bound}$ of exactly half an electron per unit cell if both bulks were centrosymmetric, consistent with the heuristic arguments of the "polar catastrophe"[3] model. However, macroscopic electric fields $\mathcal{E}_1$ and $\mathcal{E}_2$ will typically be present in materials 1 and 2, since

Gauss's theorem implies that

$$4\pi\sigma_{\rm bound} = -\mathcal{E}_1 + \mathcal{E}_2\,, \tag{6}$$

and the self-consistent solution is the one in which the polarizations P_1 and P_2 are the equilibrium values in the corresponding fields $\mathcal{E}_1$ and $\mathcal{E}_2$. These polar distortions, in turn, screen the discontinuity in P. Introducing the electric displacement[14]

$$\mathbf{D} = \boldsymbol{\mathcal{E}} + 4\pi\mathbf{P}\,, \tag{7}$$

it follows from Eq. (6) that $D_1 - D_2 = 0$, which is exactly Eq. (1). [Note that the multivalued character of P propagates to the D through Eq. (7); D is lattice-valued with a "quantum" $\Delta D = e/4\pi S$.] Thus, the phenomena discussed in the introduction emerge as a *consequence* to Eq. (1), rather than as an exception to it.

To substantiate this interpretation, where all charge not associated with free carriers is counted as bound charge, $\rho_{\rm bound}(\mathbf{r}) = \rho_{\rm tot}(\mathbf{r})$, it is useful to look back at the theory developed in Ref. 15. The authors defined a "local" polarization through[16]

$$\frac{d\bar{P}(x)}{dx} = -\bar{\rho}_{\rm bound}(x), \tag{8}$$

where the bar indicates planar averaging over the yz planes and "macroscopic" averaging[17] along the heterostructure stacking direction x. This leads to a microscopic definition of the displacement field, $\bar{D}(x) = \bar{\mathcal{E}}(x) + 4\pi\bar{P}(x)$, where the local electric field is given by the *microscopic* Maxwell equations,

$$\frac{d\bar{\mathcal{E}}(x)}{dx} = \frac{1}{4\pi}\bar{\rho}_{\rm tot}(x). \tag{9}$$

Combining Eqs. (8) and (9) we obtain that $\bar{D}(x)$ must be constant throughout the superlattice, consistent with Eq. (1). It is also straightforward to show that $\bar{P}(x)$ converges to P_1 or P_2 sufficiently far from the interface.

These arguments, therefore, generalize both the "locality principle" of constrained-D theory[1] and the theory of local dielectric response[15] to the case of charge-mismatched systems. However, this result comes at a price: One must accept that the formal polarization in a centrosymmetric perovskite like LAO does not vanish (and might even be non-zero in centrosymmetric STO, depending on the branch choice). While this may be counterintuitive, it is an established aspect of the modern theory of polarization,[11] and has been already crucial for answering important questions in the physics of complex oxides such as BiFeO$_3$.[18] Here we show that the "half-quantum" nature of a III-III (or I-V) perovskite is not merely a technical annoyance; rather, it acquires a well-defined physical meaning through Eq. (5).

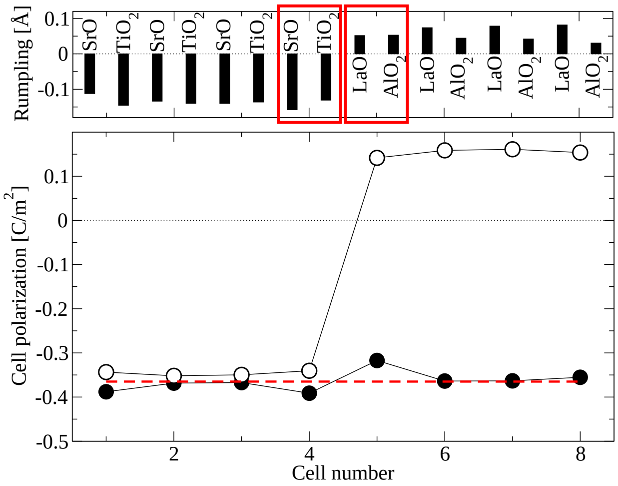

FIG. 2: (Color online) Top panel: cation-oxygen rumplings, $\delta_{\rm AO}$ and $\delta_{\rm BO2}$, in a given layer of the (LAO)$_4$/(STO)$_4$ superlattice. The red boxes indicate the grouping of the layers adopted for defining P_j and $\tilde{P}_j$. Bottom panel: cell polarizations $\tilde{P}_j$ (open symbols), P_j (filled symbols) and macroscopic value $P_{\rm Berry}$ (dashed horizontal line).

To elucidate in practice the continuity of the formal polarization at a polar interface, we now consider explicitly a periodic superlattice composed of four layers each of STO and LAO in a tetragonal 1×1 supercell with the in-plane lattice parameter set to the theoretical equilibrium value of $a_0 = 7.274$ a.u. for cubic STO. Our calculations are performed within the local-density approximation of density-functional theory and the projector-augmented-wave method,[19] with a plane-wave cutoff of 60 Ry. The Brillouin zone is sampled with a $(6\times6\times1)$ Monkhorst-Pack grid. We relax the ionic forces and the out-of-plane stress to a tolerance of 10^{-5} Ha/bohr and 10^{-7} Ha/bohr^2, respectively. After relaxation the system remains insulating with a large gap of ∼1.5 eV, in qualitative agreement with Ref. 5. We then inspect the local polarization profile using two contrasting approaches as follows.

First, we define a local *formal* polarization P_j for each of the eight cells j by inserting the coordinates of the ionic positions and Wannier centers of the cell in question into Eq. (4).[20] The definition of a "cell" is fixed by the previous choice of basis for each bulk material. The calculated P_j values are shown as the filled circles in Fig. 2, where it is assumed that the chosen basis was the one sketched in the top panel of Fig. 2, also corresponding to Fig. 1(c). The total Berry-phase polarization of the supercell, $P_{\rm Berry} = 1/8\sum_j P_j$, is then simply the average of the local P_j values. (Our definition of P_j is closely related to the prescription of Ref. 21, except that a further subdivision into contributions from AO and BO$_2$ layers was introduced there.)

Second, by using the same grouping convention, we define the local *effective* polarization $\tilde{P}_j$ of cell j as

$$\tilde{P}_j = \frac{e}{\Omega}\sum_{\alpha\in j} Z^*_\alpha \Delta x_\alpha\,, \tag{10}$$

where Z^*_α and Δx_α are the Born effective charge and atomic displacement of atom α respectively. (Displacements are defined relative to a stack of ideal centrosymmetric cells.) The resulting $\tilde{P}_j$ values are plotted as the open symbols in Fig 2.

Strikingly, the Wannier-based formal polarization P_j is rather uniform, with little departure from the average value $P_{\rm Berry} = -0.365$ C/m^2 shown as the dashed line in Fig. 2. This confirms the validity of our arguments: At electrostatic equilibrium the system tries to minimize the macroscopic electric fields present on either side of the interface by making the discontinuity in the "formal" P as small as possible. Interestingly, in our heterostructure, the LAO and STO components acquire oppositely oriented structural distortions (upper panel of Fig. 2) in order to achieve this goal. This is reflected by the abrupt discontinuity in the "effective" local polarization pattern $\tilde{P}_j$. Note that in the STO region $\tilde{P}_j$ and P_j almost coincide, since our branch choice for the formal polarizations implies $P = \tilde{P} = 0$ for bulk STO in its centrosymmetric ground state. The difference between $\tilde{P}_j$ and P_j in the LAO region of the plot (Fig. 2) corresponds to half a quantum of polarization, as expected.

To corroborate our conclusions, we now show that the local properties deep in the LAO and STO regions are determined by the macroscopic D, and do not directly depend on the specific details of the interface. To that end, we calculate (within the same computational parameters and symmetry constraints) the equilibrium structure of bulk LAO and bulk STO with D constrained[14] to take the value D=-0.365 C/m^2 extracted from the heterostructure in electrostatic equilibrium. The average bucklings $\delta_{\rm LaO}$=0.078 Å and $\delta_{\rm AlO2}$=0.044 Å extracted from cells 6-7 are in excellent agreement with bulk LAO values of 0.078 Å and 0.043 Å respectively, while $\delta_{\rm SrO}$=-0.140 Å and $\delta_{\rm TiO2}$=-0.140 Å (coincidentally the same for both layers) extracted from cells 2-3 similarly match the bulk STO values of -0.137 Å and -0.140 Å. The largest discrepancy is ∼3 mÅ, confirming the soundness of our arguments. A similar reasoning can be used to interpret the results of Refs. 4 and 22: when D=0 is enforced by symmetry, an electric field[22] of $\mathcal{E}$=0.24 V/Å and significant ferroelectric-like rumplings[4] ($\delta_{\rm LaO}$=0.26 Å, $\delta_{\rm AlO2}$=0.15 Å) were reported in the LAO layer. To check whether these results are consistent with our arguments, we repeated our *bulk* LAO calculations at D=0 and found $\mathcal{E}$=0.238 V/Å, $\delta_{\rm LaO}$=0.241 Å and $\delta_{\rm AlO2}$=0.143 Å, in excellent agreement with the literature values.

In conclusion, we have demonstrated that the conservation of the longitudinal component of D expressed in Eq. (1) is a *microscopic* law that explains and predicts the behavior of insulating interfaces and superlattices in a variety of electrical boundary conditions. This fundamental principle, together with state-of-the art finite field approaches,[1,14] is a powerful theoretical tool to complement and guide experiments in the emerging field of interface nanoengineering. Our ideas are very general, and can readily be applied to a wide range of physical systems such as, e.g., nitride superlattices where the issue of interface polarity poses important technological challenges.[23]

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