First-principles modeling of electrostatically doped perovskite systems

Massimiliano Stengel

1Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

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The unusual behavior of the (001) LaAlO$_3$/SrTiO$_3$ interface is commonly understood in terms of the “polar catastrophe” (PC) model. By stacking charged (LaO)$^+$ and (AlO)$_2^-$ layers on top of the charge-neutral TiO$_2$ and SrO layers, one obtains a net interface charge density of $\sigma_{PC} = +e/2S$, where $S$ is the unit-cell cross section. This produces a diverging electrostatic energy, unless $\sigma_{PC}$ is neutralized by an external free charge, which would explain the appearance of confined mobile carriers at this interface.

This model, while appealing, misses many important effects, that are crucial for a realistic description of the interface. For example, it was shown that strong polar distortions in LaAlO$_3$ and/or in SrTiO$_3$ partially screen the excess charge, delaying the onset of metalliclicity far beyond what the PC arguments would predict. Next, it was shown that H adsorbrates or oxygen vacancies at the open LAO surface can profoundly alter the sheet density of free carriers. Moreover, reversible metal-insulator transitions can also be induced upon application of an external bias. Both effects go clearly beyond the oversimplified PC description. Finally, the PC model cannot predict truly microscopic properties of the system, such as the spatial decay and confinement of the free electrons near the interface. In an attempt to answer these latter crucial questions, various quantum-mechanical explanations were proposed, but their relative importance, especially in relationship to the macroscopic electrostatics arguments, is unclear.

A route towards bridging the gap between classical electrostatics and quantum theory in LAO/STO and related systems was proposed in Ref. 3. The strategy is based on the “formal” definition of the polarization, $P$, in quantum-mechanical systems, which has a simple classical interpretation in terms of a point-charge model (see Fig. 1). The dipole moment of an individual (LaO)-(AlO)$_2$ unit is $d = -ea/2$ [black arrows in Fig. 1(b)], where $a$ is the out-of-plane lattice parameter and $e$ is the (positive) electronic charge. This corresponds to a “built-in” polarization $P_{LAO}^0 = -e/2S$, where $S$ is the cell surface. Conversely, $P_{STO}^0 = 0$ because the STO layers are formally charge-neutral. Note that there is no left-over ionic charge at the interface – we have reinterpreted $\sigma_{PC}$, as a surface density of bound charge, that arises because of a discontinuity in $P$.

Depending on the electrical boundary conditions, macroscopic electric fields, respectively $\mathcal{E}_{LAO}$ and $\mathcal{E}_{STO}$, will be present on one or either side of the junction. The electric fields will in turn perturb the individual LAO and STO layers, producing an “induced” polarization that we call $\Delta P_{LAO}$ and $\Delta P_{STO}$. If we now define the total polarization as $P = P_{LAO}^0 + \Delta P$, and the electric displacement as $D = \varepsilon_0 \mathcal{E} + P$, an exact relationship follows,

$$D_{LAO} - D_{STO} = \sigma_{free}, \quad (1)$$

where $\sigma_{free}$ is a surface density of “free” charge confined to the interface region. Eq. 1 generalizes the PC model by taking rigorously into account the effect of polar distortions ($\Delta P$ is implicitly contained in $D$), external biases ($\mathcal{E}(D)$ is a bulk property of either material, and is a unique function of $D$, see Fig. 1(c)] and
charged species adsorbed on the far-away surfaces (the flux of \( D \) corresponds to the surface charge density). By appropriately choosing the two independent parameters \( D_{\text{LAO}} \) and \( D_{\text{STO}} \) one can therefore describe the local properties of an ideal interface within arbitrary boundary conditions, encompassing virtually all theoretical approaches (stoichiometric or non-stoichiometric superlattices and various flavors of slab geometries) that were used so far in the literature.\(^1\) \(^2\) One does not need to worry about the specific mechanisms and/or supercell geometries that determine a certain equilibrium value of \( D_{\text{LAO}} \) and \( D_{\text{STO}} \), as long as the interface can be thought as isolated (say, separated by at least two or three unit cells of LAO and STO on either side).

To work our way towards the microscopics, it is now tempting to take the analogy to macroscopic Maxwell equations one step further, and write

\[
\frac{dD(z)}{dz} = \rho_{\text{free}}(z), \tag{2}
\]

Here \( \rho_{\text{free}}(z) \) is the spatially resolved planar average of free carriers, whose integral along \( z \) yields \( \sigma_{\text{free}} \). It is easy to verify that Eq. \( \text{2} \) is consistent with Eq. \( \text{1} \). Here one runs into trouble, however, as one needs to establish a truly microscopic definition of both \( D(z) \) and \( \rho_{\text{free}} \). (Note that this is not necessary at the level of Eq. \( \text{1} \) which deals only with macroscopic quantities.) This is a nontrivial issue in a typical metal, where the polarization (and hence \( D \)) is ill-defined. Furthermore, \( \rho_{\text{free}} \) is microscopically difficult to identify, as the bands corresponding to the conduction electrons are generally entangled with lower-lying bound states. In a doped oxide or semiconductor, however, the valence and conduction bands usually preserve their identity, i.e. a well-defined energy gap persists between conduction-band and valence-band states. This naturally leads to a definition of \( \rho_{\text{free}} \) based on the overall density of the partially occupied states near the Fermi level. The remainder is an integer number of electrons that we identify as bound charges. We use these latter orbitals to define a layer-resolved electric displacement based on a Wannier decomposition of the polarization,\(^3\) \(^4\) in analogy with standard insulators.

We are now ready to verify Eq. \( \text{2} \) directly on our first-principles calculations. To provide a representative number of test cases, we study three combinations of \( D_{\text{STO}} \) and \( D_{\text{LAO}} \), which are summarized in the insets of Figure \( \text{a-d} \). Case (a) corresponds to full compensation, e.g. that of a thick LAO overlayer on a thick STO substrate. Case (b) corresponds to partial compensation, which can occur at intermediate LAO thicknesses\(^5\), or in the case of an electrical bias applied between the electron gas and an electrode deposited on the free surface. Case (c) physically corresponds to a “back-gating” regime, where an electrical bias is applied between the electron gas and an electrode placed at the other end of the STO substrate. In practice, we use slab geometries of the type vacuum/(SrTiO\(_3\))\(_n\)/LaAlO\(_3\)/vacuum (we use \( n = 16 \) and \( m = 3 \) in our calculations), where the boundary conditions on \( D \) are enforced as explained in the Supplementary Information. (All the other relevant computational parameters are also described there.) In Fig. \( \text{a-d} \) we show the relaxed \( \rho_{\text{free}}(z) \) (a-c) and the layer-by-layer (locally averaged) electric displacement \( D_l \) (d) for each combination. In Fig. \( \text{d} \) we also plot three curves that we constructed by numerically integrating the nanosmoothed charge densities, \( \rho_{\text{free}}(z) \). We are therefore verifying the integral version of Eq. \( \text{2} \)

\[
D(z) = \int_{-\infty}^{z} \rho_{\text{free}}(t) \, dt + D(-\infty). \tag{2}
\]

The matching is excellent in all cases, demonstrating the high accuracy of Eq. \( \text{2} \). Note that in one of the examples (case c) \( \rho_{\text{free}} \) decays to zero relatively fast when moving away from the interface, while it spreads over the whole volume of the SrTiO\(_3\) film in the other two cases. This is due to the fact that in c the asymptotic electric field in STO is not zero, but equal to \( E(D = -0.2) \sim -12 \text{ MV/m} \) [see Fig. \( \text{c} \)]

This produces a confining wedge potential, that limits the spread of \( \rho_{\text{free}} \). Conversely, in (a) and (b), \( E \) vanishes at \( z \to -\infty \), and the outermost electrons are only loosely bound.

Eq. \( \text{2} \) is an important result, in that it establishes a direct, virtually exact relationship between the density of compensating carriers and the local polarization in LAO and STO. This answers pressing experimental questions concerning precisely this point, as polar distortions in SrTiO\(_3\) were recently observed.\(^6\) This also has profound implications over the theoretical understanding of electron confinement in this system, as we shall demonstrate in the following.

Essentially, the equilibrium distribution of the conduction charge is determined by two competing effects. One is the electrostatic energy, that tends to localize the electrons as close to the interface as possible. The
performed calculations of bulk SrTiO

FIG. 3. Bulk properties of SrTiO3 used in the tight-binding model. Upper panels: internal potential (a) and dielectric constant (b) as a function of $D$. Lower panels: $t_{2g}$ conduction band structure for $D = 0$ (c) and $D = -\varepsilon/2S$ (d).

strength of the attraction will depend on the static dielectric constant of the underlying insulator. The other is the quantum-mechanical kinetic energy of the electrons. This will tend to spread the electrons in space, with a strength that depends on the band dispersion. To see whether, and to what extent, the large polar distortions in STO affect these competing driving forces, we performed calculations of bulk SrTiO3 as a function of the electric displacement $D$, by covering the range of $D_{\text{STO}}$ values that are relevant for the LAO/STO system. For each value of $D$ we extract the built-in electric field, the total internal energy and the relevant parameters of the lower part of the conduction band. These are the tight-binding hopping integrals between Ti-derived orbitals with $t_{2g}$ symmetry $(d_{xy}, d_{xz}$ and $d_{yz})$. As the $t_{2g}$ orbitals are fairly well localized in space, it is sufficient for the present study to consider only the first three shells of nearest-neighbors Ti sites.

In Fig. 3(a) we show the electric field as a function of the displacement field $D$. Note the strong nonlinearity, which is evident in the plot of the dielectric constant as a function of $D$ [Fig. 3(b)]. In Fig. 3(c) we show the band structure as it results from the third-neighbor Hamiltonian, for the centrosymmetric cubic state at $D = 0$. Note the symmetry of the bands, which are characterized by a three-fold degeneracy at $\Gamma$. A polarization [the extreme case $D = -\varepsilon/2S$ is shown in Fig. 3(d)] lifts this degeneracy, by producing a strong splitting at $\Gamma$ between the degenerate $d_{xz}/d_{yz}$ orbitals and the $d_{xy}$ orbital. This splitting is dominated by the strong reduction in the $d_{xz}/d_{yz}$ bandwidth along the $\Gamma \to X$ and $\Gamma \to Z$ directions – the corresponding hopping terms are reduced by as much as 30% and 25%, respectively. Polarization-related changes in other matrix elements appear to be less pronounced.

We shall now use these data to develop a quantitative model of the equilibrium distribution $\rho_{\text{free}}(z)$. We make a rather bold assumption here, and state that the role played by the LaAlO3 overlayer in determining $\rho_{\text{free}}(z)$ is marginal, except for two crucial effects: i) it confines the conduction electrons to the STO side, and ii) it defines the electrical boundary conditions through the value of $D_{\text{LAO}}$. Based on this Ansatz, we represent the LAO/STO interface systems discussed in the previous paragraphs as pure STO slabs, periodic in plane and $n$-layer thick, where the boundary values of the electric displacement field at the two surfaces are set to $D_{\text{STO}}$ and $D_{\text{LAO}}$. To each Ti site $l$ we assign three orbitals of $t_{2g}$ symmetry, and a charge density $\rho_l$. The charge density defines the local value of the electric displacement $D_l$ through Eq. 2. The Hamiltonian matrix elements are defined by the electrostatic potential $V_l$ [calculated from $D_l$ using the bulk $V_{\text{STO}}(D)$ of Fig. 3(a)], which rigidly shifts the on-site terms, and by the $D_l$-dependent hopping parameters that we interpolate from the bulk SrTiO3 data. Upon diagonalization we obtain the wavefunctions, that self-consistently determine $\rho_l$ within the constraint Eq. 1.

In Fig. 4 we compare the results of the model to the first-principles simulations discussed earlier. We include in the comparison a fourth simulation that we did for case $D_{\text{STO}} = 0, D_{\text{LAO}} = -\varepsilon/2S$, but with a thicker STO layer ($n = 24$). The agreement is remarkably good. This indicates that the polarization-dependent bulk properties of SrTiO3, together with the boundary values of $D$, are sufficient to explain the distribution of conduction charge in this system. This suggests that the interaction
between Ti- and La-derived orbitals is not an essential factor in determining electron confinement, contrary to the conclusions of Ref. [4]. Binding of the electrons to the interface is indeed guaranteed by Eq. [2].

Now that we have a reliable model we can directly quantify the impact of each specific STO bulk property on the distribution of $\rho_{\text{rec}}$. First, if we neglect the non-linearity in the dielectric permittivity $\varepsilon_{\text{STO}}(D)$, and instead use a constant $\varepsilon_{\text{STO}}(D) = \varepsilon_{\text{STO}}(0) \approx 500$ we obtain a much broader distribution [blue curve in Fig. 3(d)]. This indicates that the carrier distribution is strongly sensitive to the dielectric properties of bulk STO; this seems to be an accepted fact in the experimental community, [13] but has received surprisingly little attention in earlier ab-initio studies. Second, if we suppress the $D$-dependence of the STO band structure, and use the $D=0$ $t_{2g}$ Hamiltonian throughout the film, we obtain [green curve in Fig. 3(d)] an excessive accumulation of charge in the near-interface region. This effect can be understood by comparing the self-consistent bandstructures of the original [Fig. 4(d)] and the “$t_{2g}(D=0)$” [Fig. 4(d1)] tight-binding models. In both cases there is a strong splitting at $\Gamma$ between the $d_{xz}$ and $d_{yz}/d_{yz}$ bands, in agreement with the findings of Refs. [13, 15, and 19]. In Fig. 4(d1), however, this splitting is only induced by confinement effects due to the wedge-like electrostatic potential near the interface [20]. The polarization-induced perturbations in the STO $t_{2g}$ bands [Fig. 4(d)] significantly enhance such a splitting [Fig. 4(d2)] and shift the $d_{xz}/d_{yz}$ bands further up in energy. (The effect is strongest on the lowest $d_{xz}/d_{yz}$ band, marked with a red arrow in the figure). This upshift, in turn, pushes the weight of the $d_{xz}/d_{yz}$ electrons away from the LAO interface, which explains the difference between the respective electron distributions [green and black curves in Fig. 4(d)]. Note that an analogous $t_{2g}$ splitting was experimentally observed in LAO/STO, [21] and theoretically also discussed in the context of the closely related LaTiO$_3$/SrTiO$_3$ system. [22]

The tight-binding method used here has clear points of contact with the strategy of Refs. [22] and [23]. However, in our approach there is a crucial innovation. Here, at difference with Ref. [22] we extract all the ingredients of the model from bulk calculation of pure insulating SrTiO$_3$, without including any adjustable parameter. This forces us to build a universal and transferable model, which can be readily applied to essentially any situation involving electrostatic doping of SrTiO$_3$, and is not restricted to the specifics of the LaAlO$_3$/SrTiO$_3$ interface. For example, our strategy could be readily used, with little modifications, to interpret the recent findings of electron gases at the bare SrTiO$_3$ surface. [20]. More importantly, our model could be readily extended to account for other physical ingredients not considered here, e.g. strong correlations [12] and strain effects: [24] all we need to do is to refine the theoretical description of bulk STO that we take as input. This is an enormous advantage, both conceptually (the model is based on few parameters that are easy to interpret) and practically (the tight-binding model is several orders of magnitude more efficient than a full first-principles calculation). More generally, our results open exciting new avenues for the study of confined electron gases in oxide systems, with optimal accuracy and dramatically reduced computational cost.

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[1] A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004).
[2] R. Pentcheva and W. E. Pickett, Phys. Rev. Lett. 102, 107602 (2009).
[3] M. Stengel and D. Vanderbilt, Phys. Rev B 80, 241103 (2009).
[4] N. C. Bristowe, E. Artacho, and P. B. Littlewood, Phys. Rev. B 80, 045425 (2009).
[5] W.-J. Son, E. Cho, J. Lee, and S. Han, Journal of Physics: Condensed Matter 22, 315501 (2010).
[6] C. Cen, S. Thiel, J. Mannhart, and J. Levy, Science 323, 1026 (2009).
[7] C. Cen, et al., Nature Materials 7, 298 (2008).
[8] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneide, and J. Mannhart, Science 313, 1942 (2006).
[9] H. Chen, A. Kolpak, and S. Ismail-Beigi, Phys. Rev. B 82, 085430 (2010).
[10] K. Janicka, J. P. Velev, and E. Y. Tsybals, Phys. Rev. Lett. 102, 106803 (2009).
[11] R. Resta and D. Vanderbilt, in Physics of Ferroelectrics: A Modern Perspective, edited by K. M. Rabe, C. H. Ahn, and J.-M. Triscone (Springer-Verlag, Berlin Heidelberg, 2007).
[12] R. Pentcheva and W. E. Pickett, J. Phys.: Condens. Matter 22, 043001 (2010).
[13] H. Chen, A. M. Kolpak, and S. Ismail-Beigi, Advanced Materials 22, 28812899 (2010).
[14] X. Wu, O. Diéguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. 97, 107602 (2006).
[15] W.-J. Son, E. Cho, B. Lee, J. Lee, and S. Han, Phys. Rev. B 79, 245411 (2009).
[16] G. Singh-Bhalla, et al., Nature Physics (2010).
[17] M. Stengel, N. A. Spaldin, and D. Vanderbilt, Nature Physics 5, 304 (2009).
[18] O. Copie, et al., Phys. Rev. Lett. 102, 216804 (2009).
[19] Z. S. Popović, S. Satpathy, and R. M. Martin, Phys. Rev. Lett. 101, 256801 (2008).
[20] A. F. Santander-Syro, et al., arXiv:1009.3412 (2010).
[21] M. Salluzzo, et al., Phys. Rev. Lett. 102, 166804 (2009).
[22] S. Okamoto, A. J. Millis, and N. A. Spaldin, Phys. Rev. Lett. 97, 056802 (2006).
[23] S. Okamoto and A. J. Millis, Nature 428, 630 (2004).
[24] C. W. Bark, et al., arXiv:1011.4082 (2010).