Ab initio calculations of BaTiO$_3$ and PbTiO$_3$ (001) and (011) surface structures

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We present and discuss the results of calculations of surface relaxations and rumplings for the (001) and (011) surfaces of BaTiO$_3$ and PbTiO$_3$, using a hybrid B3PW description of exchange and correlation. On the (001) surfaces, we consider both AO (A = Ba or Pb) and TiO$_2$ terminations. In the former case, the surface AO layer is found to relax inward for both materials, while outward relaxations of all atoms in the second layer are found at both kinds of (001) terminations and for both materials. The surface relaxation energies of BaO and TiO$_2$ terminations on BaTiO$_3$ (001) are found to be comparable, as are those of PbO and TiO$_2$ on PbTiO$_3$ (001), although in both cases the relaxation energy is slightly larger for the TiO$_2$ termination. As for the (011) surfaces, we consider three types of surfaces, terminating on a TiO layer, a Ba or Pb layer, or an O layer. Here, the relaxation energies are much larger for the TiO-terminated than for the Ba or Pb-terminated surfaces. The relaxed surface energy for the O-terminated surface is about the same as the corresponding average of the TiO and Pb-terminated surfaces on PbTiO$_3$, but much less than the average of the TiO and Ba-terminated surfaces on BaTiO$_3$. We predict a considerable increase of the Ti-O chemical bond covalency near the BaTiO$_3$ and PbTiO$_3$ (011) surface as compared to both the bulk and the (001) surface.

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I. INTRODUCTION

Thin films of ABO$_3$ perovskite ferroelectrics play an important role in numerous microelectronic, catalytic, and other high-technology applications, and are frequently used as substrates for growth of other materials such as cuprate superconductors. Therefore, it is not surprising that a large number of ab initio quantum mechanical calculations have dealt with the atomic and electronic structure of the (001) surface of BaTiO$_3$, PbTiO$_3$, and SrTiO$_3$ crystals. In order to study the dependence of the surface relaxation properties on the exchange-correlation functionals and the type of basis (localized vs. plane-wave) used in the calculations, a detailed comparative study of SrTiO$_3$ (001) surfaces based on ten different quantum-mechanical techniques was recently performed.

Due to intensive development and progressive miniaturization of electronic devices, the surface structure as well as the electronic properties of the ABO$_3$ perovskite thin films have been extensively studied experimentally during the last years. The SrTiO$_3$ (001) surface structure has been analyzed by means of low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS), ultraviolet electron spectroscopy (UPS), medium-energy ion scattering (MEIS), and surface X-ray diffraction (SXRD). Nevertheless it is important to note that the LEED and RHEED experiments contradict each other in the sign (contraction or expansion) of the interplanar distance between top metal atom and the second crystal layer for the SrO-terminated SrTiO$_3$ (001) surface. The most recent experimental studies on the SrTiO$_3$ surfaces include a combination of XPS, LEED, and time-of-flight scattering and recoil spectrometry (TOF-SARS) as well as metastable impact electron spectroscopy (MIES). In these recent studies, well-resolved 1x1 LEED patterns were obtained for the TiO$_2$-terminated SrTiO$_3$ (001) surface. Simulations of the TOF-SARS azimuthal scans indicate that the O atoms are situated 0.1 Å above the Ti layer (surface plane) in the case of the TiO$_2$-terminated SrTiO$_3$ (001) surface.

While the (001) surfaces of SrTiO$_3$, BaTiO$_3$ and PbTiO$_3$ have been extensively studied, much less is known about the (011) surfaces. The scarcity of information about these surfaces is likely due to the polar character of the (011) orientation. (011) terminations of SrTiO$_3$ have frequently been observed, but efforts towards the precise characterization of their atomic-scale structure and corresponding electronic properties has only begun in the last decade, specifically using atomic-force microscopy (STM), Auger spectroscopy, and low-energy electron-diffraction (LEED) methods.

To the best of our knowledge, very few ab initio studies of perovskite (011) surfaces exist. The first ab initio study of the electronic and atomic structures of several (1x1) terminations of the (011) polar orientation of the SrTiO$_3$ surface was performed by Bottin et al. One year later Heifets et al. performed very comprehensive ab initio Hartree-Fock calculations for four possible terminations (TiO, Sr, and two kinds of O terminations) of the SrTiO$_3$ (011) surface. Recently Heifets et al. performed ab initio density-functional calculations of the atomic structure and charge redistribution for different terminations of the BaZrO$_3$ (011) surfaces. However, despite the high technological potential of BaTiO$_3$ and PbTiO$_3$, we are unaware of any previous ab initio cal-
calculations performed for the BaTiO$_3$ and PbTiO$_3$ (011) surfaces. In this study, therefore, we have investigated the (011) as well as the (001) surfaces of BaTiO$_3$ and PbTiO$_3$, with an emphasis on the effect of the surface relaxation and rumpling, surface energies, and the charge redistributions and changes in bond strength that occur at the surface.

II. PRELIMINARIES

A. Computational method

We carry out first-principles calculations in the framework of density-functional theory (DFT) using the CRYS$\mathrm{TAL}$ computer code.$^{38}$ Unlike the plane-wave codes employed in many previous studies,$^{31,32}$ CRYS$\mathrm{TAL}$ uses localized Gaussian-type basis sets. In our calculations, we adopted the basis sets developed for BaTiO$_3$ and PbTiO$_3$ in Ref. [35]. Our calculations were performed using the hybrid exchange-correlation B3PW functional involving a mixture of non-local Fock exact exchange, LDA exchange, and Becke’s gradient corrected exchange functional combined with the non-local gradient corrected correlation potential of Perdew and Wang.$^{35,36,37}$ We chose the hybrid B3PW functional for our current study because it yields excellent results for the SrTiO$_3$, BaTiO$_3$, and PbTiO$_3$ bulk lattice constant and bulk modulus.$^{17,33}$

The reciprocal-space integration was performed by sampling the Brillouin zone with an $8 \times 8 \times 8$ Pack-Monkhorst mesh,$^{38}$ which provides a balanced summation in direct and reciprocal spaces. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, and 14 were chosen for the dimensionless Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap, and second exchange pseudo-overlap parameters, respectively.$^{24}$

An advantage of the CRYS$\mathrm{TAL}$ code is that it treats isolated 2D slabs, without any artificial periodicity in the $z$ direction perpendicular to the surface, as commonly employed in most previous surface band-structure calculations (e.g., Ref. [3]). In the present $ab$ initio investigation, we have studied several isolated periodic two-dimensional slabs of cubic BaTiO$_3$ and PbTiO$_3$ crystals containing 7 planes of atoms.

B. Surface geometries

The BaTiO$_3$ and PbTiO$_3$ (001) surfaces were modeled using symmetric (with respect to the mirror plane) slabs consisting of seven alternating TiO$_2$ and BaO or PbO layers, respectively. One of these slabs was terminated by BaO planes for the BaTiO$_3$ crystal (or PbO planes for PbTiO$_3$) and consisted of a supercell containing 17 atoms. The second slab was terminated by TiO$_2$ planes for both materials and consisted of a supercell containing 18 atoms. These slabs are non-stoichiometric, with unit cell formulae Ba$_{4}$Ti$_3$O$_{10}$ or Pb$_{2}$Ti$_3$O$_{10}$, and Ba$_{5}$Ti$_4$O$_{11}$ or Pb$_{5}$Ti$_4$O$_{11}$ for BaTiO$_3$ and PbTiO$_3$ perovskites, respectively. These two (BaO or PbO and TiO$_2$) terminations are the only two possible flat and dense (001) surfaces for the BaTiO$_3$ or PbTiO$_3$ perovskite lattice structure. The sequence of layers at the TiO$_2$-terminated (001) surface of BaTiO$_3$ is illustrated in Fig. 1.

Unlike the (001) cleavage of BaTiO$_3$ or PbTiO$_3$, which naturally gives rise to non-polar BaO (or PbO) and TiO$_2$ terminations, a naive cleavage of BaTiO$_3$ or PbTiO$_3$ to create (011) surfaces leads to the formation of polar surfaces. For example, the stacking of the BaTiO$_3$ crystal along the (011) direction consists of alternating planes of $O_2$ and BaTiO units having nominal charges of $−4e$ and $+4e$ respectively, assuming $O^{2−}$, $Ti^{4+}$, and $Ba^{2+}$ constituents. (Henceforth we shall use BaTiO$_3$ for presentation purposes, but everything that is said will apply equally to the PtTiO$_3$ case.) Thus, a simple cleavage leads to $O_2$-terminated and BaTiO-terminated (011) surfaces that are polar and have nominal surface charges of $−2e$ and $+2e$ per surface cell respectively. These are shown as the top and bottom surfaces in Fig. 2(a) respectively. If uncompensated, the surface charge would lead to an infinite electrostatic cleavage energy. In reality, the polar surfaces would probably become metallic in order to remain neutral, but in view of the large electronic gaps in the perovskites, such metallic surfaces would presumably be unfavorable. Thus, we may expect rather generally that such polar crystal terminations are relatively unstable in this class of materials.$^{3}$

On the other hand, if the cleavage occurs in such a way as to leave a half layer of $O_2$ units on each surface, we obtain the non-polar surface structure shown in Fig. 2(b). Every other surface O atom has been removed, and the remaining O atoms occupy the same sites as in the bulk structure. We shall refer to this as the “O-terminated” (011) surface, in distinction to the “$O_2$-terminated” polar surface already discussed in Fig. 2(a). The non-polar nature of the O-terminated surface can be confirmed by noting that the 7-layer 15-atom Ba$_5$Ti$_3$O$_9$ slab shown in Fig. 2(b), which has two O-terminated surfaces, is neutral. It is also possible to make non-polar TiO-terminated and Ba-terminated surfaces, as shown in Figs. 2(c) and
FIG. 2: (Color online.) Side views of slab geometries used to study BaTiO$_3$ (011) surfaces. (a) Stoichiometric 8-layer slab with O$_2$-terminated and BaTiO-terminated surfaces at top and bottom respectively. (b) 7-layer slab with O-terminated surfaces. (c) 7-layer slab with TiO-terminated surfaces. (d) 7-layer slab with Ba-terminated surfaces. (d), respectively. This is accomplished by splitting a BaTiO layer during cleavage, instead of splitting an O$_2$ layer. For the TiO and Ba-terminated surfaces, we use 7-layer slabs having composition Ba$_2$Ti$_4$O$_{10}$ (16 atoms) and Ba$_4$Ti$_2$O$_8$ (14 atoms) as shown in Fig. 2(c-d), respectively. These are again neutral, showing that the surfaces are non-polar (even though they no longer have precisely the bulk BaTiO$_3$ stoichiometry).

III. RESULTS OF CALCULATIONS

A. BaTiO$_3$ and PbTiO$_3$ (001) surface structure

In the present calculations of the BaTiO$_3$ and PbTiO$_3$ (001) surface atomic structure, we allowed the atoms located in the two outermost surface layers to relax along the z-axis (the forces along the x and y-axes are zero by symmetry). Here we use the term “layer” to refer to a BaO, PbO, or TiO$_2$ plane, so that there are two layers per stacked unit cell. For example, on the BaO or PbO-terminated surfaces, the top layer is BaO or PbO and the second layer is TiO$_2$; displacements of the third-layer atoms were found to be negligibly small in our calculations and thus were neglected.

The calculated atomic displacements for the TiO$_2$ and BaO-terminated (001) surfaces of BaTiO$_3$, and for the TiO$_2$ and PbO-terminated (001) surfaces of PbTiO$_3$, are presented in Table I. For BaTiO$_3$ (001), comparisons are also provided with the surface atomic displacements obtained by Padilla and Vanderbilt, using plane-wave DFT methods in the local-density approximation (LDA), and by Heifets et al. using a classical shell-model (SM) approach. Similarly, for PbTiO$_3$ (001), Table I shows comparisons with the plane-wave LDA calculations of Meyer and Vanderbilt. The relaxation of the surface metal atoms in both the BaTiO$_3$ and PbTiO$_3$ surfaces is much larger than that of the oxygen ions, leading to a considerable surface rumpling, which we quantify via a parameter $s$ defined as the relative displacement of the oxygen with respect to the metal atom in a given layer.

The surface rumpling and relative displacements of three near-surface planes are presented in Table II. According to our calculations, atoms of the first surface layer relax inwards (i.e., towards the bulk) for BaO and PbO terminations of both materials. Our calculations are in a qualitative agreement with the ab initio calculations performed by Padilla and Vanderbilt, for BaTiO$_3$, and by Meyer and Vanderbilt for PbTiO$_3$. However, the predictions of the SM calculation disagree with the first-principles calculations: the SM predicts that the first-layer oxygen ions relax outward on the BaO-terminated BaTiO$_3$ (001) surface, rather than inwards. However, the magnitudes of the displacements are relatively small ($\approx 0.63\%$ of the lattice constant $a_0$ in this study and $1.00\%$ of $a_0$ in the SM calculations, which may be close to the error bar of the classical shell model. Outward relaxations of all atoms in the second layer are found at both (001) terminations of the BaTiO$_3$ and PbTiO$_3$ surfaces. From Table I, we can conclude that the magnitudes of the atomic displacements calculated using different ab initio methods and using the classical shell model are in a reasonable agreement.

In order to compare the calculated surface structures further with experimental results, the surface rumpling $s$ and the changes in interlayer distances $\Delta d_{12}$ and $\Delta d_{23}$, as defined in Fig. 1, are presented in Table II. Our calculations of the interlayer distances are based on the positions of relaxed metal ions, which are known to be much stronger electron scatterers that the oxygen ions.

For BaTiO$_3$ (001), the rumpling of TiO$_2$-terminated surface is predicted to exceed that of BaO-terminated surface by a factor of two. This finding is in line with the values of surface rumpling reported by Padilla and Vanderbilt. In contrast, PbTiO$_3$ demonstrates practically the same rumpling for both terminations. From Table II one can see that qualitative agreement between all theoretical methods is obtained. In particular, the relaxed (001) surface structure shows a reduction of interlayer distance $\Delta d_{12}$ and an expansion of $\Delta d_{23}$ according to all ab initio and shell-model results.

As for experimental confirmation of these results, we are unfortunately unaware of experimental measurements of $\Delta d_{12}$ and $\Delta d_{23}$ for the BaTiO$_3$ and PbTiO$_3$ (001) surfaces. Moreover, for the case of the SrO-terminated SrTiO$_3$ (001) surface, existing LEED and RHEED experiments actually contradict each other regarding the sign of $\Delta d_{12}$. In view of the absence of clear experimental determinations of these parameters, therefore, the first-principles calculations are a particularly important tool for understanding the surface properties.
TABLE I: Vertical atomic relaxations (in percent of bulk lattice constant) for BaTiO$_3$ and PbTiO$_3$ (001) surfaces. Positive sign corresponds to outward atomic displacement. ‘SM’ indicates shell-model calculation of Ref. [16]; ‘LDA’ are previous calculations of Ref. [5] and [9] for BaTiO$_3$ and PbTiO$_3$ respectively.

| BaTiO$_3$ (001) surface relaxations | BaTiO$_3$ (001) surface relaxations | PbTiO$_3$ (001) surface relaxations |
|-------------------------------------|-------------------------------------|-------------------------------------|
| Termination                        | Layer | Ion | This study | SM       | LDA       | Layer | Ion | This study | LDA       |
| BaO                                | 1     | Ba  | -1.99      | -3.72    | -2.79     | 1     | Pb  | -3.82      | -4.36     |
|                                    |       | O   | -0.63      | 1.00     | -1.40     |       | O   | -0.31      | -0.46     |
|                                    |       | Ti  | 1.74       | 1.25     | 0.92      |       | Ti  | 3.07       | 2.39      |
|                                    |       | O   | 1.40       | 0.76     | 0.48      |       | O   | 2.30       | 1.21      |
| TiO$_2$                            | 1     | Ti  | -3.08      | -2.72    | -3.89     | TiO$_2$| Ti  | -2.81      | -3.40     |
|                                    |       | O   | -0.35      | -0.94    | -1.63     |       | O   | 0.31       | -0.34     |
|                                    |       | Ba  | 2.51       | 2.19     | 1.31      |       | Pb  | 5.32       | 4.53      |
|                                    |       | O   | 0.38       | -0.17    | -0.62     |       | O   | 1.28       | 0.43      |
|                                    |       | Ti  | -0.33      | -0.75    |           |       | Ti  | -0.92      |           |
|                                    |       | O   | -0.01      | -0.35    |           |       | O   | -0.27      |           |

B. BaTiO$_3$ and PbTiO$_3$ (011) surface structure

To our knowledge, we have performed the first ab initio calculations for BaTiO$_3$ and PbTiO$_3$ (011) surfaces. We have studied the TiO$_2$-terminated, BaO or PbO-terminated, and O-terminated surfaces illustrated in Fig. 2(c), (d), and (b), respectively. The computed surface atomic relaxations are reported in Table III.

Focusing first on the BaTiO$_3$ surfaces, we find that the Ti ions in the outermost layer of the TiO-terminated surface move inwards (towards the bulk) by 0.0786$a_0$, whereas the O ions in the outermost layer move outwards by 0.0261$a_0$. The Ba atoms in the top layer of the Ba-terminated surface of Fig. 2(d) move inwards by 0.0867$a_0$ and 0.0540$a_0$, respectively. The agreement between our ab initio B3PW and the classical SM calculations is satisfactory for all three of these surface terminations. In particular, the directions of the displacements of first and second-layer atoms coincide for all three terminations. This indicates that classical SM calculations with a proper parameterization can serve as a useful initial approximation for modeling the atomic structure in perovskite thin films.

Turning now to our results for the PbTiO$_3$ (011) surfaces, we find that all metal atoms in the outermost layer move inwards irrespective of the termination. Surface oxygen atoms are displaced outwards for the TiO-terminated surface, while oxygen atoms move inwards in the O-terminated surface. The displacement patterns of atoms in the outermost surface layers are similar to those of the BaTiO$_3$ (011) surfaces, as well as classical shell model results for BaTiO$_3$. For example, the atomic displacement magnitudes of Ti and oxygen atoms in the TiO-terminated PbTiO$_3$ (011) surface are -0.0813$a_0$ and 0.033$a_0$ respectively. The Pb atom is displaced inwards by 0.1194$a_0$ for the PbO-terminated surface, similar to the corresponding BaTiO$_3$ case. Overall, Table III shows similar displacement patterns for the BaTiO$_3$ and PbTiO$_3$ (011) surfaces, as well as qualitatively similar results for both ab initio and classical shell-model descriptions.

C. BaTiO$_3$ and PbTiO$_3$ (001) and (011) surface energies

In the present work, we define the unrelaxed surface energy of a given surface termination X to be one half of the energy needed to cleave the crystal rigidly into an unrelaxed surface X and an unrelaxed surface with the complementary termination X'. For BaTiO$_3$, for example, the unrelaxed surface energies of the complementary BaO and TiO$_2$-terminated (001) surfaces are equal, as are those of the TiO and Ba-terminated (011) surfaces (and similarly for PbTiO$_3$). The relaxed surface energy is defined to be the energy of the unrelaxed surface plus the (negative) surface relaxation energy. These definitions are chosen for consistency with Refs. [17,28]. Unlike the authors of Refs. [21,29], we have made no effort to introduce chemical potentials here, so the results must be used with caution when addressing questions of the
Similarly, for the BaTiO$_3$ respectivly. Thus, and Ba-terminated surfaces shown in Fig. 2(c) and (d)

The relaxed surface energy is then

$$E_{\text{surf}}(X) = \frac{1}{4} [E_{\text{surf}}(\text{Ba}) + E_{\text{surf}}(\text{TiO}) - 7E_{\text{bulk}}],$$

where $X = \text{BaO}$ or TiO$_2$ specifies the termination, $E_{\text{surf}}(\text{Ba})$ and $E_{\text{surf}}(\text{TiO})$ are the unrelaxed BaO and TiO$_2$-terminated slab energies, $E_{\text{bulk}}$ is energy per bulk BaTiO$_3$ unit cell, and the factor of four comes from the fact that four surfaces are created by the two cleavages needed to make the two slabs. The relaxation energy for each termination can be computed from the corresponding slab alone using

$$\Delta E_{\text{rel}}^\text{surf}(X) = \frac{1}{2} [E_{\text{surf}}(X) - E_{\text{surf}}^\text{unr}(X)],$$

where $E_{\text{surf}}(X)$ is a slab energy after relaxation. The relaxed surface energy is then

$$E_{\text{surf}}(X) = E_{\text{surf}}^\text{unr}(X) + \Delta E_{\text{rel}}^\text{surf}(X).$$

Similarly, for the BaTiO$_3$ (011) case, a cleavage on a bulk BaTiO plane gives rise to the complementary TiO and Ba-terminated surfaces shown in Fig. 2(c) and (d) respectively. Thus,

$$E_{\text{surf}}^\text{unr}(X) = \frac{1}{4} [E_{\text{surf}}^\text{unr}(\text{Ba}) + E_{\text{surf}}^\text{unr}(\text{TiO}) - 6E_{\text{bulk}}],$$

where the energy is the same for $X = \text{TiO}$ or Ba, $E_{\text{surf}}^\text{unr}(\text{Ba})$ and $E_{\text{surf}}^\text{unr}(\text{TiO})$ are energies of the unrelaxed slabs. Relaxation energies can again be computed independently for each slab in a manner similar to Eq. (2).

Finally, the (011) surface can also be cleaved to give two identical self-complementary O-terminated surfaces of the kind shown in Fig. 2(b). In this case the 7-layer slab has the stoichiometry of three bulk unit cells, so the relaxed surface energy of the O-terminated (011) surface is

$$E_{\text{surf}}(O) = \frac{1}{2} [E_{\text{surf}}(O) - 3E_{\text{bulk}}],$$

where $E_{\text{surf}}(O)$ is the relaxed energy of the slab having two O-terminated surfaces. Everything said here about BaTiO$_3$ surfaces applies in exactly the same way to the corresponding PbTiO$_3$ surfaces.

The calculated surface energies of the relaxed BaTiO$_3$ (001) and (011) surfaces are presented in Table IV. In BaTiO$_3$, the relaxation energies of the TiO$_2$ and BaO-terminated surfaces applies in exactly the same way to the corresponding PbTiO$_3$ surfaces.

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**TABLE III: Calculated surface relaxations of BaTiO$_3$ and PbTiO$_3$ (011) surfaces (in percent of the lattice constant) for the three surface terminations. ‘SM’ indicates comparative results from the shell-model calculation of Ref. [10].**

| Layer | Ion | $\Delta z$ | $\Delta y$ | $\Delta z$ (SM) | $\Delta y$ (SM) |
|-------|-----|------------|------------|-----------------|---------------|
| TiO-terminated | 1   | 7.86       | -6.93      | -6.93           | -6.93         |
|       | 1   | 2.61       | 6.45       | 6.45            | 6.45          |
|       | 2   | -1.02      | -1.66      | -1.66           | -1.66         |
|       | 3   | -0.88      | -3.85      | -3.85           | -3.85         |
|       | 3   | 0          | -2.40      | -2.40           | -2.40         |
|       | 3   | Ti         | 1.59       | 1.59            | 1.59          |
| Ba-terminated | 1   | -8.67      | -13.49     | -13.49          | -13.49        |
|       | 2   | 0.80       | 2.80       | 2.80            | 2.80          |
|       | 3   | 0.16       | -1.20      | -1.20           | -1.20         |
|       | 3   | -0.43      | -2.94      | -2.94           | -2.94         |
|       | 3   | Ba         | 2.52       | 2.52            | 2.52          |
| O-terminated | 1   | -5.40      | -1.67      | -11.16          | -11.16        |
|       | 2   | -0.15      | -6.38      | -1.83           | -1.83         |
|       | 2   | 1.54       | 4.84       | 4.84            | 4.84          |
|       | 2   | 1.95       | 2.97       | 4.54            | 4.54          |
|       | 3   | 0.90       | 4.49       | 6.52            | 6.52          |

**TABLE IV: Calculated surface energies for BaTiO$_3$ and PbTiO$_3$ (001) and (011) surfaces (in eV per surface cell). ‘SM’ indicates comparative results from the shell-model calculation of Ref. [10].**

| Surface | Termination | $E_{\text{surf}}$ | $E_{\text{surf}}$ (SM) |
|---------|-------------|-------------------|------------------------|
| BaTiO$_3$ (001) | TiO | 1.07 | 1.40 |
|         | BaO | 1.19 | 1.45 |
| BaTiO$_3$ (011) | TiO | 2.04 | 2.35 |
|         | Ba  | 3.24 | 4.14 |
|         | O   | 1.72 | 1.81 |
| PbTiO$_3$ (001) | TiO | 0.74 | 0.83 |
|         | PbO | 0.83 | 0.83 |
| PbTiO$_3$ (011) | TiO | 1.36 | 1.36 |
|         | Pb  | 2.03 | 2.03 |
|         | O   | 1.72 | 1.72 |
terminated surfaces (−0.23 and −0.11 eV respectively) are comparable, leading to rather similar surface energies. On the (011) surfaces, however, the relaxation energies vary more strongly with termination. For example, we find a relaxation energy of −2.13 eV for the TiO-terminated surface, much larger than −0.93 eV for the Ba-terminated surface. The relaxation energy of −1.15 eV for O-terminated surface gives rise to a relaxed energy of the O-terminated surface (1.72 eV) that is much lower than the average of the TiO and Ba-terminated surfaces (2.64 eV), indicating that it takes much less energy to cleave on an O$_2$ plane than on a BaTiO$_3$ plane. The shell-model results of Ref. [16] for the BaTiO$_3$ surfaces are given shown for comparison; the results are qualitatively similar, but there are some significant quantitative differences, especially for the Ba-terminated (011) surface.

The corresponding results are also given for the (001) and (011) surfaces of PbTiO$_3$ in Table IV. The results for the (001) surfaces are similar to those for BaTiO$_3$, although the relaxed surface energies are somewhat lower. For the case of the (011) surfaces, however, we find a different pattern than for BaTiO$_3$. We find a very large relaxation energy of −1.75 eV for the TiO-terminated surface, compared with −1.08 eV for the Pb-terminated surface and −1.12 eV for the O-terminated surface. The average energy of the TiO and Pb-terminated surfaces is now 1.69 eV, to be compared with 1.72 eV for the O-terminated surface, indicating that the cleavage on a PbTiO or an O$_2$ plane has almost exactly the same energy cost.

### D. BaTiO$_3$ and PbTiO$_3$ (001) and (011) surface charge distribution and chemical bonding

To characterize the chemical bonding and covalency effects, we used a standard Mulliken population analysis for the effective static atomic charges $Q$ and other local properties of the electronic structure as described, for example, in Ref. [39,40]. The results are presented in Table V. Our calculated effective charges for bulk PbTiO$_3$ are $+1.354 e$ for the Pb atom, $+2.341 e$ for the Ti atom, and $−1.232 e$ for the O atom. The bond population describing the chemical bonding is $+98 me$ between Ti and O atoms, $+16 me$ between Pb and O atoms, and $+2 me$ between Pb and Ti atoms. Our calculated effective charges for bulk BaTiO$_3$ are $+1.797 e$ for the Ba atom, $+2.367 e$ for the Ti atom, and $−1.388 e$ for the O atom indicate a high degree of BaTiO$_3$ chemical bond covalency. The bond population between Ti and O atoms in BaTiO$_3$ bulk is exactly the same as in PbTiO$_3$, while that between Ba and Ti is slightly negative, suggesting a repulsive interaction between these atoms in the bulk of the BaTiO$_3$ crystal.

For the TiO$_2$-terminated BaTiO$_3$ and PbTiO$_3$ (001) surfaces, the major effect observed here is a strengthening of the Ti-O chemical bond near the BaTiO$_3$ and PbTiO$_3$ (001) surfaces, which was already pronounced for the both materials in the bulk. Note that the Ti and O effective charges for bulk BaTiO$_3$ and PbTiO$_3$ are much smaller than those expected in an ionic model ($+4 e$, and $−2 e$), and that the Ti-O chemical bonds in bulk BaTiO$_3$ and PbTiO$_3$ are fairly heavily populated.

| Layer | Property | Ion | $Q$ | $P$ | $Q$ | $P$ | $Q$ | $P$ |
|-------|----------|-----|-----|-----|-----|-----|-----|-----|
| 1     | $D$      | Ti  | −0.124 | Ba | −0.080 | Ti | −0.111 | Pb | −0.150 |
|       | $P$      |     | 126 | −30 | 2.752 | 114 | 1.279 | 54 |
| 2     | $D$      | O   | −0.014 | O | −0.025 | O | −0.012 | O | −0.012 |
|       | $P$      |     | −80 | 80  | 1.473 | 44  | 1.184 | 106|
| 3     | $Q$      | Ti  | 1.767 | Ba | 2.379 | Ti | 1.275 | Pb | 2.331 |
|       | $P$      |     | −30 | 88  | −1.343 | 8 | −1.167 | 6 |
|       | $Q$      | O   | −1.371 | O | −1.417 | O | −1.207 | O | −1.259 |
|       | $P$      |     | 98  | −34 | −34  | 18  | −34  | 96 |
| Bulk  | $Q$      | Ba  | 1.797 | Ba | 1.797 | Pb | 1.354 | Pb | 1.354 |
|       | $P$      |     | −34 | −34 | −34  | 16  | −34  | 16 |
|       | $Q$      | O   | −1.388 | O | −1.388 | O | −1.232 | O | −1.232 |
|       | $P$      |     | 98  | 98  | 98   | 98  | 98   |

**TABLE V:** Calculated magnitudes of atomic displacements $D$ (in Å), effective atomic charges $Q$ (in e), and bond populations $P$ between metal-oxygen nearest neighbors (in $10^{-3}$ e) for the BaTiO$_3$ and PbTiO$_3$ (001) surfaces.
for both materials.

The Ti-O bond population for the TiO$_2$-terminated BaTiO$_3$ and PbTiO$_3$ (011) surfaces are $+126\,\text{me}$ and $+114\,\text{me}$ respectively, which is about 20% larger than the relevant value in the bulk. In contrast, the Pb-O bond population of $-30\,\text{me}$ is small for the PbO-terminated PbTiO$_3$ (001) surface, and the Ba-O bond population of $-30\,\text{me}$ is even negative for the BaO-terminated BaTiO$_3$ (001) surface, indicating a repulsive character. The effect of the difference in the chemical bonding is also well seen from the Pb and Ba effective charges in the first surface layer, which are close to the formal ionic charge of $+2\,\text{e}$ only in the case of the BaTiO$_3$ crystal.

The interatomic bond populations for three possible BaTiO$_3$ (011) surface

| Atom A | Atom B | $P$ | $Q$ | $\Delta Q$ |
|--------|--------|-----|-----|------------|
| Ti(I)  | O(I)   | 130 | 3.97 | 0.186 |
| O(II)  | Ti(II) | 72  | 1.22 | 0.092 |
| Ba(III)O(III) | Ti(III) | 112 | 2.09 | 0.072 |
| Ba(IV) | Ti(IV) | 72  | 1.22 | 0.092 |

The major effect observed here is a strong increase of the Ti-O chemical bonding near the BaTiO$_3$ and PbTiO$_3$ (011) surface as compared to already large bonding near the (001) surface $+126\,\text{me}$ and $+114\,\text{me}$, respectively, and in the bulk $+98\,\text{me}$. For the O-terminated (011) surface the O(I)-Ti(II) bond population is as large as $+168\,\text{me}$ for BaTiO$_3$ and $+128\,\text{me}$ for PbTiO$_3$, i.e., considerably larger than in the bulk and on the (001) surface.

Our calculations demonstrate that for the TiO-terminated BaTiO$_3$ and PbTiO$_3$ (011) surfaces, the Ti-O bond populations are larger in the direction perpendicular to the surface $+198\,\text{me}$ for BaTiO$_3$ and $+196\,\text{me}$ for PbTiO$_3$) than in plane $+130\,\text{me}$ for BaTiO$_3$ and $+132\,\text{me}$ for PbTiO$_3$. The Ti-O bond populations for the TiO-terminated PbTiO$_3$ (011) surface in the direction perpendicular to the surface is twice as large as the Ti-O bond population in PbTiO$_3$ bulk.

In Table VII we present the calculated Mulliken effective charges $Q$, and their changes $\Delta Q$ with respect to the bulk values, near the surface. We analyzed the charge redistribution between different layers in slabs with all three BaTiO$_3$ and PbTiO$_3$ (011) surface terminations. The charge of the surface Ti atoms in the TiO-terminated BaTiO$_3$ and PbTiO$_3$ (011) surface terminations are given in Table VI. The major effect observed here is a strong increase of the Ti-O chemical bonding near the BaTiO$_3$ and PbTiO$_3$ (011) surface as compared to already large bonding near the (001) surface $+126\,\text{me}$ and $+114\,\text{me}$, respectively, and in the bulk $+98\,\text{me}$. For the O-terminated (011) surface the O(I)-Ti(II) bond population is as large as $+168\,\text{me}$ for BaTiO$_3$ and $+128\,\text{me}$ for PbTiO$_3$, i.e., considerably larger than in the bulk and on the (001) surface.

For both materials.

The Ti-O bond population for the TiO$_2$-terminated BaTiO$_3$ and PbTiO$_3$ (001) surfaces are $+126\,\text{me}$ and $+114\,\text{me}$ respectively, which is about 20% larger than the relevant value in the bulk. In contrast, the Pb-O bond population of $+54\,\text{me}$ is small for the PbO-terminated PbTiO$_3$ (001) surface, and the Ba-O bond population of $-30\,\text{me}$ is even negative for the BaO-terminated BaTiO$_3$ (001) surface, indicating a repulsive character. The effect of the difference in the chemical bonding is also well seen from the Pb and Ba effective charges in the first surface layer, which are close to the formal ionic charge of $+2\,\text{e}$ only in the case of the BaTiO$_3$ crystal.

The interatomic bond populations for three possible

for BaTiO$_3$ and PbTiO$_3$ (011) surface terminations are given in Table VI. The major effect observed here is a strong increase of the Ti-O chemical bonding near the BaTiO$_3$ and PbTiO$_3$ (011) surface as compared to already large bonding near the (001) surface $+126\,\text{me}$ and $+114\,\text{me}$, respectively, and in the bulk $+98\,\text{me}$. For the O-terminated (011) surface the O(I)-Ti(II) bond population is as large as $+168\,\text{me}$ for BaTiO$_3$ and $+128\,\text{me}$ for PbTiO$_3$, i.e., considerably larger than in the bulk and on the (001) surface.

Our calculations demonstrate that for the TiO-terminated BaTiO$_3$ and PbTiO$_3$ (011) surfaces, the Ti-O bond populations are larger in the direction perpendicular to the surface $+198\,\text{me}$ for BaTiO$_3$ and $+196\,\text{me}$ for PbTiO$_3$) than in plane $+130\,\text{me}$ for BaTiO$_3$ and $+132\,\text{me}$ for PbTiO$_3$. The Ti-O bond populations for the TiO-terminated PbTiO$_3$ (011) surface in the direction perpendicular to the surface is twice as large as the Ti-O bond population in PbTiO$_3$ bulk.

In Table VII we present the calculated Mulliken effective charges $Q$, and their changes $\Delta Q$ with respect to the bulk values, near the surface. We analyzed the charge redistribution between different layers in slabs with all three BaTiO$_3$ and PbTiO$_3$ (011) surface terminations. The charge of the surface Ti atoms in the TiO-terminated BaTiO$_3$ and PbTiO$_3$ (011) surface terminations are given in Table VI. The major effect observed here is a strong increase of the Ti-O chemical bonding near the BaTiO$_3$ and PbTiO$_3$ (011) surface as compared to already large bonding near the (001) surface $+126\,\text{me}$ and $+114\,\text{me}$, respectively, and in the bulk $+98\,\text{me}$. For the O-terminated (011) surface the O(I)-Ti(II) bond population is as large as $+168\,\text{me}$ for BaTiO$_3$ and $+128\,\text{me}$ for PbTiO$_3$, i.e., considerably larger than in the bulk and on the (001) surface.
BaTiO$_3$ and PbTiO$_3$ (001) surface is reduced by 0.151 e and 0.129 e, respectively. Metal atoms in the third layer lose much less charge. Except in the central layer (and, in the case of PbTiO$_3$, in the subsurface layer), the O ions also reduce their charges, becoming less negative. The largest charge change is observed for BaTiO$_3$ and PbTiO$_3$ subsurface O atoms (+0.233 e and +0.175 e, respectively). This gives a large positive change of +0.466 e and +0.350 e in the charge for each BaTiO$_3$ and PbTiO$_3$ subsurface layer.

On the Ba-terminated and Pb-terminated BaTiO$_3$ and PbTiO$_3$ (011) surface, negative changes in the charge are observed for all atoms except for Ba and Ti in the BaTiO$_3$ third layer, Ti atom in the PbTiO$_3$ third layer, and subsurface oxygen atom in PbTiO$_3$. The largest charge changes are at the surface Ba and Pb ions. It is interesting to notice that, due to the tiny difference in the chemical bonding between BaTiO$_3$ and PbTiO$_3$ perovskites, the charge change for the BaTiO$_3$ subsurface O ion (−0.095 e) and PbTiO$_3$ subsurface O ion (+0.092 e) have practically the same magnitude, but opposite signs.

For the O-terminated BaTiO$_3$ and PbTiO$_3$ (011) surfaces, the largest calculated changes in the charge are observed for the BaTiO$_3$ and PbTiO$_3$ surface O atom (+0.230 e and +0.221 e, respectively). The change of the total charge in the second layer is negative and almost equal for both materials. For the TiO$_2$ crystal, this reduction by 0.249 e comes mostly from Ti atom (−0.154 e). In the PbTiO$_3$ crystal, the reduction by 0.230 e appears mostly due to a decrease of the Ti atom charge by 0.104 e, as well as a reduction of the Pb atom charge by 0.097 e.

### IV. CONCLUSIONS

In summary, motivated by the scarcity of experimental investigations of the BaTiO$_3$ and PbTiO$_3$ surfaces and the contradictory experimental results obtained for the related SrTiO$_3$ surface, we have carried out predictive electronic structure calculations to investigate the surface atomic and electronic structure of the BaTiO$_3$ and PbTiO$_3$ (001) and (011) surfaces. Using a hybrid B3PW approach, we have calculated the surface relaxation of the two possible terminations (TiO$_2$ and BaO or PbO) of the BaTiO$_3$ and PbTiO$_3$ (001) surfaces, and three possible terminations (TiO, Ba or Pb, and O) of the BaTiO$_3$ and PbTiO$_3$ (011) surfaces. The data obtained for the surface structures are in a good agreement with previous LDA calculations of Padilla and Vanderbilt, the LDA plane-wave calculations of Meyer et al., and in fair agreement with the shell-model calculations of Heifets et al.

According to our calculations, atoms of the first surface layer relax inwards for BaO and PbO terminated (001) surfaces of both materials. Outward relaxations of all atoms in the second layer are found at both terminations of BaTiO$_3$ and PbTiO$_3$ (001) surfaces. In BaTiO$_3$, the rumpling of the TiO$_2$-terminated (001) surface is predicted to exceed that of the BaO-terminated (001) surface by a factor of two. In contrast, PbTiO$_3$ exhibits practically the same rumplings for both (TiO$_2$ and PbO) terminations. Our calculated surface energies show that the TiO$_2$-terminated (001) surface is slightly more stable for both materials than the BaO or PbO-terminated (001) surface. The O-terminated BaTiO$_3$ and TiO-terminated PbTiO$_3$ (011) surfaces have surface energies close to that of the (001) surface. Our calculations suggest that the most unfavorable (011) surfaces are the Ba or Pb-terminated ones for both the BaTiO$_3$ and PbTiO$_3$ cases. We found that relaxation of the BaTiO$_3$ and PbTiO$_3$ surfaces for is considerably stronger for all three (011) terminations than for the (001) surfaces. The atomic displacements in the third plane from the surface for the three terminations of BaTiO$_3$ and PbTiO$_3$ (011) surfaces are still large. Finally, our ab initio calculations indicate a considerable increase of Ti-O bond covalency near the BaTiO$_3$ and PbTiO$_3$ (011) surface relative to BaTiO$_3$ and PbTiO$_3$ bulk, much larger than for the (001) surface.

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