Ab initio modeling of surface structure for SrTiO$_3$ perovskite crystals

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We present and discuss the results of calculations of SrTiO$_3$ (100) surface relaxation and rumpling with two different terminations (SrO and TiO$_2$). These are based on *ab initio* Hartree-Fock method with electron correlation corrections and density functional theory calculations with different exchange-correlation functionals, including hybrid exchange techniques. Both approaches use the localized Gaussian-type basis set. All methods agree well on surface energies and on atomic displacements, as well as on considerable increase of covalency effects nearby the surface. More detailed experiments on surface rumpling and relaxation are necessary for further testing theoretical predictions.

Thin films of ABO_3 perovskite ferroelectrics are important for many high-tech applications including high capacity memory cells, catalysis, optical wave guides, integrated optics applications, substrates for high-T_c cuprate superconductor growth, etc.,[1-4] for which surface structure and quality are of primary importance. In this study, we calculated the relaxed atomic structure of the SrTiO$_3$ (100) surface for the cubic phase. The SrTiO$_3$ (100) surface relaxation has been experimentally studied by means of low energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), medium energy ion scattering (MEIS), and surface x-ray diffraction (SXRD) measurements.[5-9] Recently, several *ab initio*[10-16] and shell model (SM) (Refs. 17–20) theoretical studies were published for the (100) surface of BaTiO$_3$ and SrTiO$_3$ crystals. In order to check how sensitive surface relaxation properties are to details of the *ab initio* methods used in calculations, i.e., exchange-correlation functionals, pseudopotentials, and localized/plane wave basis set, in this report we performed a detailed comparative study based on a number of different techniques. We employed several methods: HF with different DFT-type *a posteriori* electron correlation corrections to the total energy[21] such as generalized gradient approximation (HFGGA), Perdew-91 (HFPer91), Lee, Yang, Parr (HFLYP) and full-scale DFT calculations based on the Kohn-Sham equation with a number of exchange-correlation functionals, including local density approximation (LDA), generalized gradient approximations (GGA) by Perdew and Wang (PW), Perdew, Burke, and Ernzerhof (PBE), as well as Becke exchange functional with Lee-Yang-Parr correlation functional (BLYP). We also included a comparison with *hybrid* HF-DFT exchange functionals, in which Hartree-Fock exchange was mixed with DFT exchange functionals using Becke's three parameter method, combined with the non-local correlation functionals by Perdew and Wang (B3PW), as those by Lee, Yang, and Parr (B3LYP). For all calculations, we used the CRYSTAL-98 computer code (see Ref. 22, and references therein for all mentioned techniques), in which both (HF/DFT) types of calculations are implemented on equal grounds. Unlike previous plane-wave calculations, this code uses the localized Gaussian-type basis set. In our simulations we applied the standard basis set recommended for SrTiO$_3$.[22] Another advantage of the CRYSTAL-98 code is its treatment of purely two-dimensional slabs, without artificial periodicity in the direction perpendicular to the surface, commonly employed in most other surface calculations (e.g., Refs. 10 and 16).

For optimization of atomic coordinates through minimization of the total energy per unit cell, we wrote a small code that implements conjugated gradients optimization technique[25] with numerical computation of derivatives. Using this code, we optimized the atomic positions in several top layers of a SrTiO$_3$ slab consisting of seven planes terminated by TiO$_2$, or by SrO on both sides of symmetrical a slab.

Before starting the surface calculations, we tested these methods on the bulk properties, the lattice constant a_0 and the bulk modulus B (Table I). LDA calculations are found to underestimate a_0 by 0.8% and overestimate B by 20%. The

TABLE I. The optimized lattice constant a_0 and bulk modulus B for the bulk SrTiO$_3$ as calculated using DFT and HF approaches. Experimental values: a_0 (extrapolated to 0 K) $= 3.89$ Å, $B = 179$ GPa (Ref. 23). Bulk modulus is calculated using fourth order polynomials, numbers in brackets are results of the fit to the standard Murnaghan equation of the state (Ref. 24).

Method	a_0, Å	B, GPa
DFT: LDA	3.86	215 (210)
BLYP	3.98	165 (157)
PWGGA	3.93	195 (176)
PBE	3.93	195 (171)
Hybrid: B3LYP	3.94	187 (184)
B3PW	3.91	186 (191)
HF: HF	3.93	211 (208)
HF GGA	3.83	253 (245)
HF P91	3.83	252 (245)
HFLYP	3.86	244 (237)

TABLE II. Atomic relaxation of uppermost three layers (in percent of lattice constant) for $SrTiO_3$ (100) found for the *ab initio* HF and DFT calculations (see text). Positive (negative) values refer to displacements in the direction outwards (inwards) the surface. Note that in DFT calculations only atomic positions in the two outermost planes were optimized. References 10 and 16 refer to LDA-plane wave calculations with Caperley-Alder exchange-correlation functionals using ultrasoft pseudopotentials and norm-conserving semilocal (Ref. 26) pseudopotentials.

| | | | | (a) TiO_2-terminated $SrTiO_3$ surface | | | | | | | | | |
| | | | | DFT (Kohn Sham) | | | | | | Hartree-Fock with *a posteriori* corrections | | | |
N	Ion	(Ref. 10)	(Ref. 16)	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
1.	Ti^{4+}	−3.4	−1.79	−2.12	−2.03	−2.19	−2.28	−1.88	−2.31	−2.74	−3.20	−3.19	−3.05
	O^{2-}	−1.6	−0.26	−1.11	−0.72	−0.93	−0.90	−0.57	−1.19	−1.38	−2.20	−2.20	−1.87
2.	Sr^{2+}	2.5	4.61	2.21	2.38	2.18	2.64	2.75	2.04	1.91	1.81	1.93	1.87
	O^{2-}	−0.5	0.77	0.07	0.21	0.01	0.12	0.45	0.0	−0.13	−0.15	−0.17	−0.17
3.	Ti^{4+}	−0.7	−0.26							−0.26	−0.28	−0.28	−0.28
	O^{2-}	−0.5	0.26							−0.05	−0.13	−0.14	−0.14

| | | | | (b) SrO-terminated $SrTiO_3$ surface | | | | | | | | | |
| | | | | DFT (Kohn Sham) | | | | | | Hartree-Fock with *a posteriori* corrections | | | |
N	Ion	(Ref. 11)	(Ref. 17)	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
1.	Sr^{2+}	−5.7	−6.66	−4.91	−4.28	−4.29	−4.57	−4.60	−4.30	−2.61	−4.16	−4.13	−3.74
	O^{2-}	0.1	0.02	0.92	0.64	0.61	0.78	1.00	1.03	1.56	0.41	0.35	0.10
2.	Ti^{4+}	1.2	1.79	1.20	1.16	1.25	1.34	1.30	1.20	0.79	0.48	0.48	0.56
	O^{2-}	0.0	0.26	0.48	0.86	0.85	0.86	0.67	0.55	0.51	0.23	0.17	0.27
3.	Sr^{2+}	−1.2	−1.54							−0.49	−0.69	−0.69	−0.70
	O^{2-}	−0.1	0.26							0.01	−0.25	−0.02	−0.14

HF method without any correlation corrections overestimates both a_0 (by 1%) and B (by 16%). HF with GGA corrections makes a_0 too small (by −1.5%) but B even larger (by 41%). The hybrid B3PW method gives much better result for B (a discrepancy by 4%) and by only 1% overestimates a_0. In other words, it is quite difficult to choose the optimal method reproducing all properties equally well, but the hybrid B3PW method looks the best.

The atomic displacements in the outmost $SrTiO_3$ planes obtained here using various *ab initio* methods (see Table II) are in qualitative agreement with previous plane wave calculations.[11,16] Both DFT and HF with correlation effects predict Sr displacement on the SrO-terminated surface to be larger than that for Ti atom on the TiO_2-terminated surface, also in agreement with previous *ab initio* calculations. All theoretical methods predict surface O atom inward relaxation for the TiO_2 termination, in contrast to the SrO termination. Relaxation of atoms in the third plane is already quite small.

Atomic displacements, the effective static charges (obtained using the Mulliken population analysis), and bond populations between nearest metal and oxygen atoms are given in Table III. For the analysis we use the B3PW results. The major effect observed here is strengthening of the Ti-O chemical bond near the surface, which is already pronounced in the bulk. Note that Ti and O effective charges (2.3e and −1.4e, respectively) are much smaller than those expected in an ionic model; furthermore the Ti-O bond is considerably populated (82me, m = milli). The Ti-O bond population for the TiO_2-terminated surface is 128me, which is about 50% larger than the relevant values in the bulk. The Ti-O populations in the direction perpendicular to the surface, i.e., between Ti and O atoms in the first and second, the second and third plane, and lastly, the third and fourth planes (124me, 92me, and 84me) also exceed the bulk value. In contrast, the Sr-O populations are very small and even negative which indicates the repulsion. This effect is also well seen from the Sr effective charges, which is close to the formal ionic charge of $+2e$.

Figures 1(a) and 1(c) (total electron densities) confirm the Ti-O covalency effects discussed above, whereas the difference electron density maps [Figs. 1(b) and 1(d)] (calculated with respect to Sr^{2+}, Ti^{4+}, and C^{2-} ions) demonstrate considerable charge density redistribution for both $SrTiO_3$ surface terminations. These maps show that there is no trace of covalent bonding between Sr and O atoms. The Sr atoms nearest to the surface are polarized. Their electronic density is shifted inwards the bulk on TiO_2-terminated surface and outwards on the SrO-terminated surface. For both terminations the nearest to the surface Ti-O bond becomes stronger, but the next nearest bond becomes weaker. All these observations, made from the electronic density maps, are entirely consistent with Mulliken charges and bond population analysis in the Table III.

In order to calculate the surface energy, we start with the cleavage energy for unrelaxed SrO- and TiO_2-terminated sur-

TABLE III. Calculated absolute magnitudes of atomic displacements d (in Å), the effective atomic charges Q (in e) and bond populations P between nearest Me-O atoms (in *me*) for the TiO$_2$ and SrO terminations.

(a) TiO$_2$-terminated SrTiO$_3$ surface

No.	Ion		DFT B3PW	DFT B3LYP	Hartree-Fock HF	Hartree-Fock HFGG A
1.	Ti^{4+}	D	−0.086	−0.079	−0.107	−0.1245
		Q	2.165	2.197	2.507	2.502
		P	128	124	146	142
	O^{2-}	D	−0.037	−0.028	−0.054	−0.0856
		Q	−1.241	−1.257	−1.395	−1.400
		P	−10	−10	−28	−30
2.	Sr^{2+}	D	0.085	0.094	0.074	0.0705
		Q	1.833	1.834	1.890	1.888
		P	−10	−8	−20	−20
	O^{2-}	D	0.0004	0.008	−0.005	−0.006
		Q	−1.297	1.307	−1.418	−1.401
		P	92	92	104	104
3.	Ti^{4+}	D			−0.010	−0.011
		Q	2.269	2.313	2.553	2.552
		P	86	86	114	114
	O^{2-}	D			−0.002	−0.005
		Q	−1.363	−1.376	−1.476	−1.476
		P	−10	−8	−22	−22
Bulk	Ti^{4+}	Q	2.272	2.325	2.584	2.50
		P	82	74	112	100
	O^{2-}	Q	−1.375	−1.392	−1.497	−1.466
		P	−10	−8	−20	−28
	Sr^{2+}	Q	1.852	1.852	1.909	1.898

(b) SrO-terminated SrTiO$_3$ surface

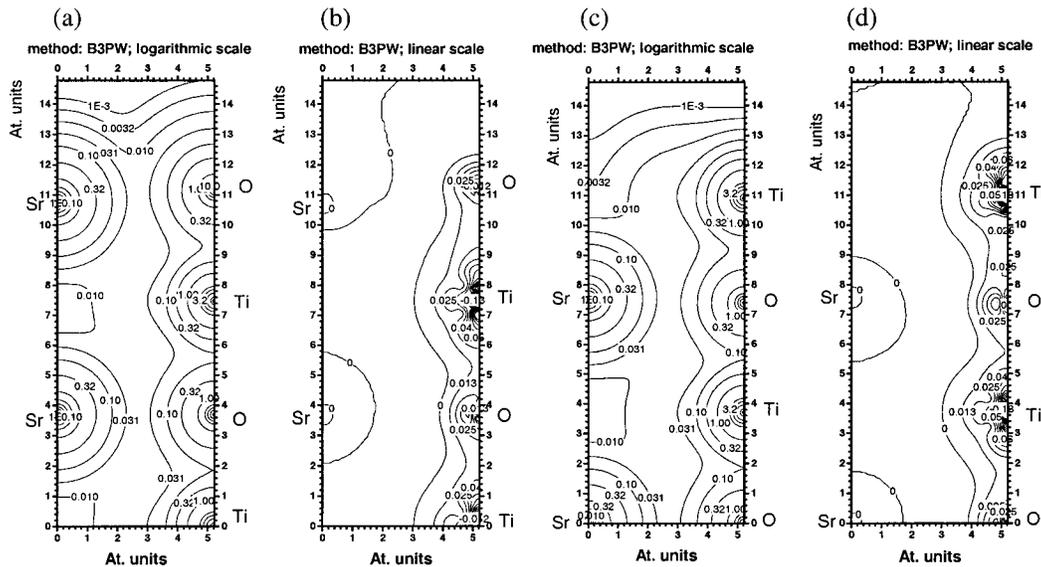| No.	Ion		DFT B3PW	DFT B3LYP	Hartree-Fock HF	Hartree-Fock HFGG A
1	Sr^{2+}	d	−0.168	−0.168	−0.102	−0.162
		Q	1.829	1.833	1.897	1.894
		P	−4	−2	−20	−20
	O^{2-}	d	0.024	0.025	0.061	0.016
		Q	−1.44	−1.459	−1.581	−1.555
		P	166	160	198	208
2	Ti^{4+}	d	0.049	0.046	0.031	0.019
		Q	2.24	2.282	2.536	2.524
		P	56	58	90	84
	O^{-2}	d	0.32	0.033	0.020	0.009
		Q	−1.423	−1.434	−1.517	−1.523
		P	−10	−8	−20	−20
3	Sr^{2+}	d			−0.019	−0.027
		Q	1.857	1.855	1.907	1.906
		P	−10	−8	−22	−22
	O^{2-}	d			0.0	−0.01
		Q	−1.398	−1.409	−1.508	−1.503
		P	80	80	108	108
Bulk	Ti^{4+}	Q	2.272	2.325	2.584	2.50
		P	82	74	112	100
	O^{2-}	Q	−1.375	−1.392	−1.497	−1.466
		P	−10	−8	−10	−28
	Sr^{2+}	Q	1.852	1.852	1.909	1.898

FIG. 1. The total (a and c) and difference (b and d) electron density maps in the cross section perpendicular to the (100) surface with SrO (a,b) and TiO$_2$ (c,d) terminations.

TABLE IV. Calculated surface energies (in eV per surface cell). Results for Refs. 10 and 16 are averaged over both surfaces.

	(Ref. 10)	(Ref. 16)	DFT (Kohn Sham)						Hartree-Fock with *posteriori* corrections			
			LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
SrO	1.26	1.21	1.19	1.19	1.18	1.17	1.20	1.16	1.38	1.25	1.26	1.28
TrO$_2$			1.23	1.24	1.22	1.22	1.25	1.21	1.42	1.28	1.30	1.33

faces. In our calculations the two seven layer SrO- and TiO$_2$-terminated slabs represent together seven bulk unit cells. Surfaces with both terminations arise simultaneously under cleavage of the crystal and the relevant cleavage energy is distributed equally between created surfaces. Therefore, we assume that the cleavage energy is the same for both terminations:

$$E_s^{(\text{unrel})} = \tfrac{1}{4}\left[E_{\text{slab}}^{(\text{unrel})}(\text{SrO}) + E_{\text{slab}}^{\text{unrel}}(\text{TiO}_2) - 7E_{\text{bulk}}\right],$$

where $E_{\text{slab}}^{(\text{unrel})}(\text{SrO})$ and $E_{\text{slab}}^{(\text{unrel})}(\text{TiO}_2)$ are unrelaxed SrO- and TiO$_2$-terminated slab energies, E_{bulk} energy per a bulk unit cell, and a factor of four comes from the fact that we create four surfaces upon cleavage procedure. Next, we can calculate the (negative) relaxation energies for each of SrO and TiO$_2$ terminations, when both sides of slabs relax:

$$E_{\text{rel}}(A) = \tfrac{1}{2}\left[E_{\text{slab}}(A) - E_{\text{slab}}^{(\text{unrel})}(A)\right],$$

$E_{\text{slab}}(A)$ is a slab energy after relaxation, $A = \text{SrO}$ or TiO_2. Lastly, the surface energy sought for is just a sum of the cleavage and relaxation energies

$$E_s(A) = E_s^{(\text{unrel})} + E_{\text{rel}}(A).$$

The results of calculations for the surface energy of relaxed surfaces E_s are presented in Table IV. In all calculations the E_s values for SrO termination are slightly smaller than for the TiO$_2$ termination. However, the energy difference is small and both surfaces are stable and energetically equally favorable, in agreement with the experimental observation.[5] Note that the surface energy of 1.37 eV/cell, which was calculated for TiO$_2$-terminated surface by the SM approach,[20] is also slightly larger than the surface energy for SrO termination (1.33 eV/cell). The *ab initio* LAPW calculations[14] gave similar average surface energies of 1.27 eV/cell.

For both SrO and TiO$_2$ terminations, surface relaxation is characterized by the surface rumpling (s) (the relative displacement of O with respect to a metal atom in the first plane), interplane distances between top metal and the second crystal layers (Δd_{12}), and between the second and the third crystal layers (Δd_{23}). Our calculations of the interplane distances are based on the metal ion (Ti or Sr) displacements from unrelaxed planes, which are known to be much stronger electron scatters than O ions.[5]

A comparison of a series of our HF and DFT calculations with the two previous *ab initio* plane-wave studies[10,16] and

TABLE V. Surface rumpling s, and relative displacements of the three near-surface planes for the Sr- and Ti-terminated SrTiO$_3$ (100) surfaces (in percent of the bulk lattice parameters).

Method	SrO-terminated			TiO$_2$-terminated		
	S	Δd_{12}	Δd_{23}	s	Δd_{12}	Δd_{23}
DFT LDA	5.8	−6.1		1.0	−4.3	
BLYP	5.4	−5.9		1.3	−4.9	
PBE	5.6	−5.9		1.3	−4.6	
PWGGA	5.3	−5.5		1.1	−4.4	
B3LYP	4.9	−5.4		1.3	−4.4	
B3PY	4.9	−5.5		1.3	−4.4	
HF	4.2	−3.4	1.3	1.4	−4.7	2.2
HF-GGA	4.6	−4.6	1.2	1.0	−5.0	2.1
HF-P91	4.5	−4.6	1.2	1.0	−5.0	2.1
HF-LYP	3.8	−4.3	1.3	1.2	−4.9	2.2
Ab initio (Ref. 10)	5.8	−6.9	2.4	1.8	−5.9	3.2
Ab initio (Ref. 16)	7.7	−8.6	3.3	1.5	−6.4	4.9
Shell model (Ref. 18)	4.5	−4.8	1.5	1.1	−4.0	1.2
Shell model (Ref. 20)	8.2	−8.6	3.0	1.2	−6.4	4.0
LEED expt. (Ref. 5)	4.1±2	−5±1	2±1	2.1±2	1±1	−1±1
RHEED expt. (Refs. 6,7)	4.1	2.6	1.3	2.6	1.8	1.3

SM calculations[20] is presented in Table V. The agreement is quite good for all applied functionals. All theoretical methods (both quantum mechanical, irrespective on particular exchange-correlation functional and basis set type, and SM) give the same signs for both the rumpling and change of the interplanar distances. They predict much larger rumpling for the SrO surface in comparison to that for the TiO_2 surface, compression of the distance between the first and second planes, and its expansion for the second and third planes.

In general, the results of the LEED experiments[5] agree quite well with our B3PW calculations (except for the compression of the distance between second and third planes in the SrO termination case). It was also found in recent MEIS experiments[8] that on the Ti-terminated $SrTiO_3$ surface $s \approx 1.5\%$ which again is in agreement with our results. Note, however, that the LEED and RHEED experiments contradict each other in the sign of the Δd_{12} for SrO-terminated surface. Another problem is that LEED, RHEED, and MEIS experiments argue that the topmost O atoms always move outwards from the surface whereas all calculations predict for the TiO_2 terminated surface that O atoms go *inwards*. The reason for this is not clear and discussed in Refs. 9 and 10. Even more important is a clear contradiction between three abovementioned experiments and recent SXRD (Ref. 9)

where oxygen atoms are predicted to move inwards for *both* surface terminations, reaching 12.5% for the TiO_2 surface. It is obvious that conflicting experimental results should be resolved before further comparison with theoretical calculations.

Summing up, a comparison of *ab initio* HF and DFT calculations employing different exchange-correlation functionals and localized/plane wave basis clearly demonstrates their good agreement for the *rumpling* and the relative displacements of the second and third planes nearby the $SrTiO_3$ surface. In contrast, four types of electron diffraction experiments used so far clearly contradict each other. Our *ab initio* calculations indicate considerable increase of the Ti-O bond covalency near the surface. This could be important for the electronic structure of surface defects, as well as for adsorption and surface diffusion of atoms and small molecules relevant for catalysis.

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