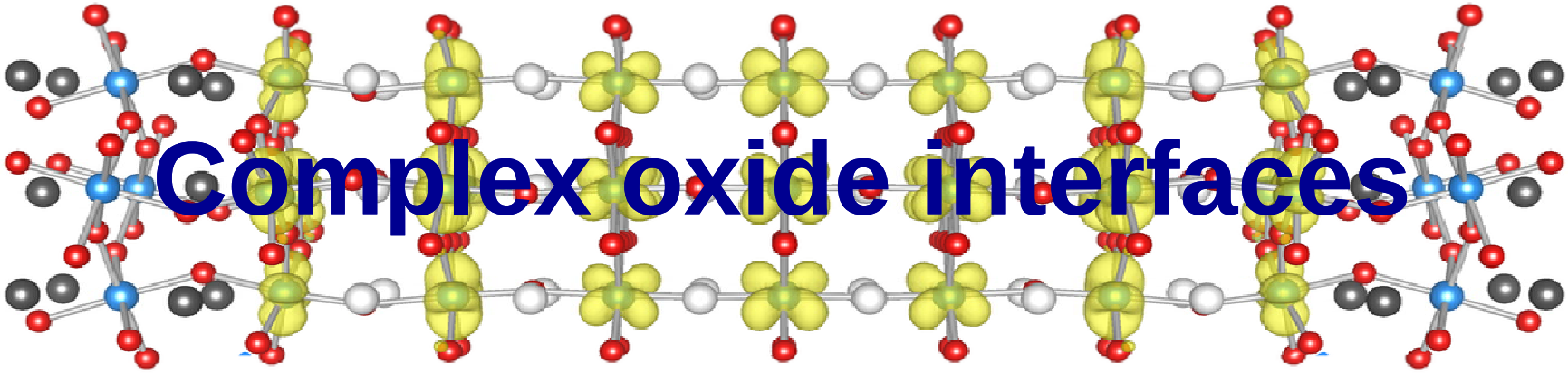


Complex oxide interfaces

Chris G. Van de Walle

Anderson Janotti, Lars Bjaalie, Luke Gordon,

Burak Himmetoglu, K. Krishnaswamy

Materials Department, University of California, Santa Barbara

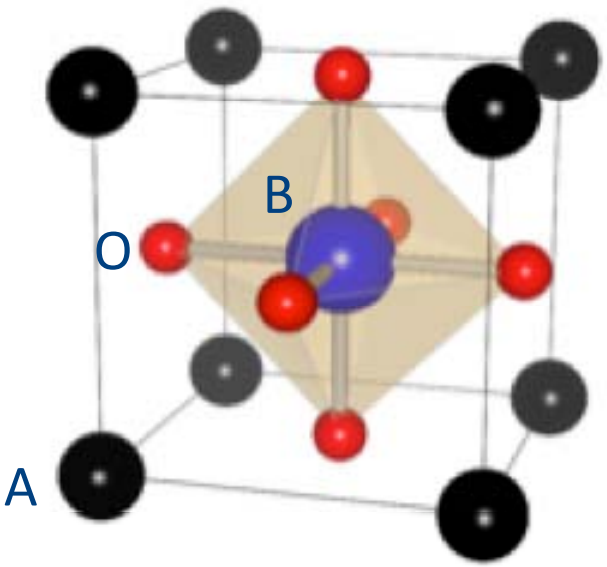
Acknowledgments: NSF, ARO, ONR; XSEDE

ES2013
June 11-14, 2013
Williamsburg, Virginia

http://www.mrl.ucsb.edu/~vandewalle

UCSB

Complex oxides: ABO_3 perovskites



$SrTiO_3$: A = Sr, B= Ti

$LaAlO_3$: A = La, B= Al

Complex oxides interfaces

Many interesting properties:

- High-k dielectrics
- Colossal magnetoresistance
- Ferroelectricity
- Superconductivity
- Charge ordering
- Spin dependent transport

Interplay of structural, electronic and transport properties

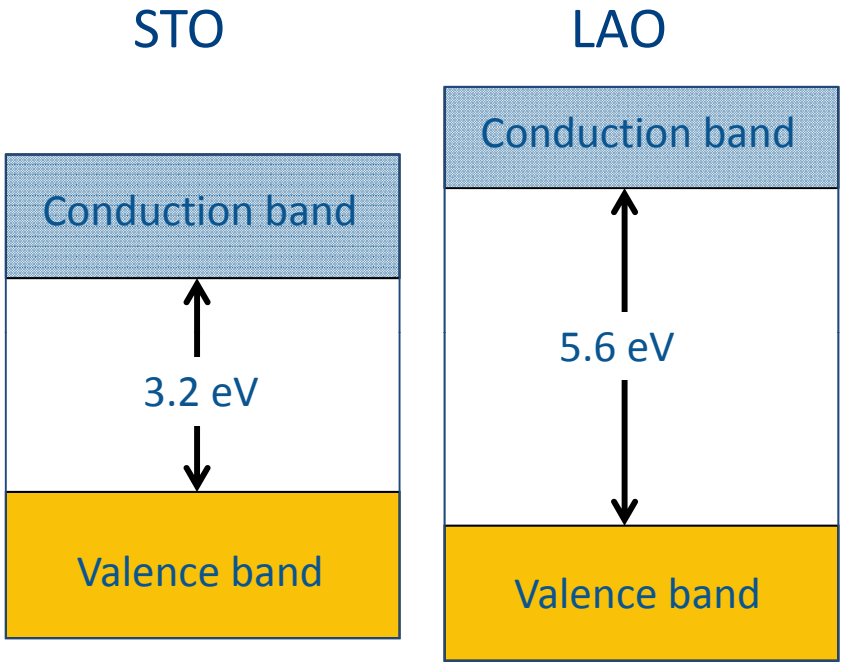
Applications:

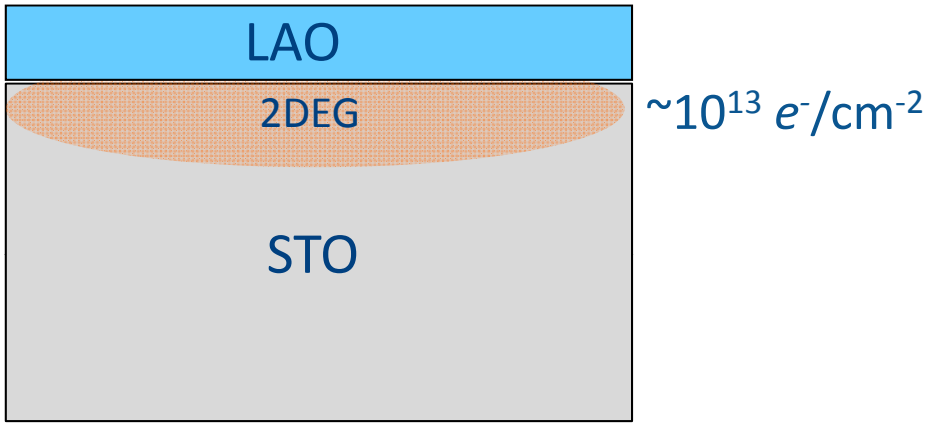
- Sensors
- Electrodes in fuel cells
- Memory devices (memristors)

UCSB

$SrTiO_3$ and $LaAlO_3$: Wide-band-gap oxides

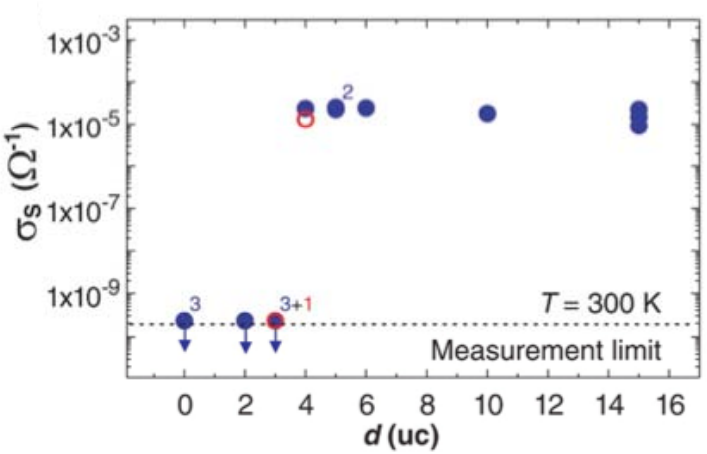
A two-dimensional electron gas (2DEG) forms at the STO/LAO interface





A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).

- 2DEG appears only for LAO layers thicker than 4 unit cells



S. Thiel *et al*. Science **313**, 1942-1945 (2006).

UCSB

The two-dimensional electron gas at the STO/LAO interface

"Where do the carriers come from?"

1. Polar catastrophe/ surface

Ohtomo & Hwang, Nature **427**, 423 (2004).
Mannhart et al., MRS Bull. Nov. 2008.
Mannhart et al., MRS Bull. Nov. 2008.

2. Oxygen vacancies (near the interface or in STO bulk)

Brinkman *et al*., Nat. Matter. **6**, 493 (2007).
Kalabukhov *et al*., Phys. Rev. B **75,** 121404(R) (2007).
Siemons *et al*., Phys. Rev. Lett. **98**, 196802 (2007).
Bristowe *et al*., Phys. Rev. B **83**, 205405 (2011).
Li *et al*, Phys. Rev. B **84**, 245307 (2011).

3. Atomic intermixing (STO substrate, LAO surface, …)

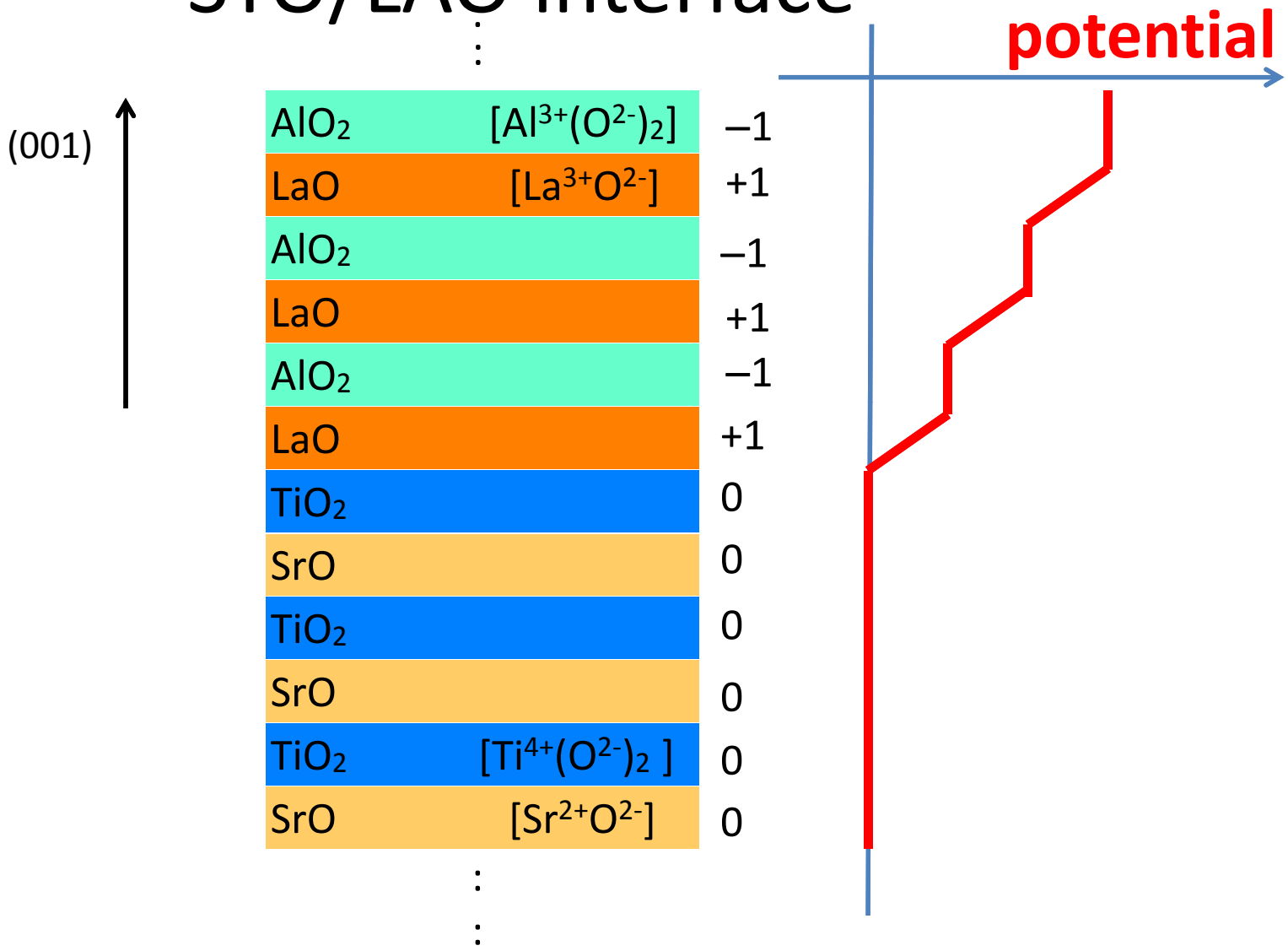
Nakagawa *et a*l., Nat. Matter. **5**, 204 (2006).
Qiao *et al*., Surf. Sci. **605**, 1381 (2011)

3. Electronic reconstructions

Pentcheva and Pickett, Phys. Rev. B **74**, 035112 (2006)
Popovic et al, Phys. Rev. Lett. **101**, 256801 (2008)

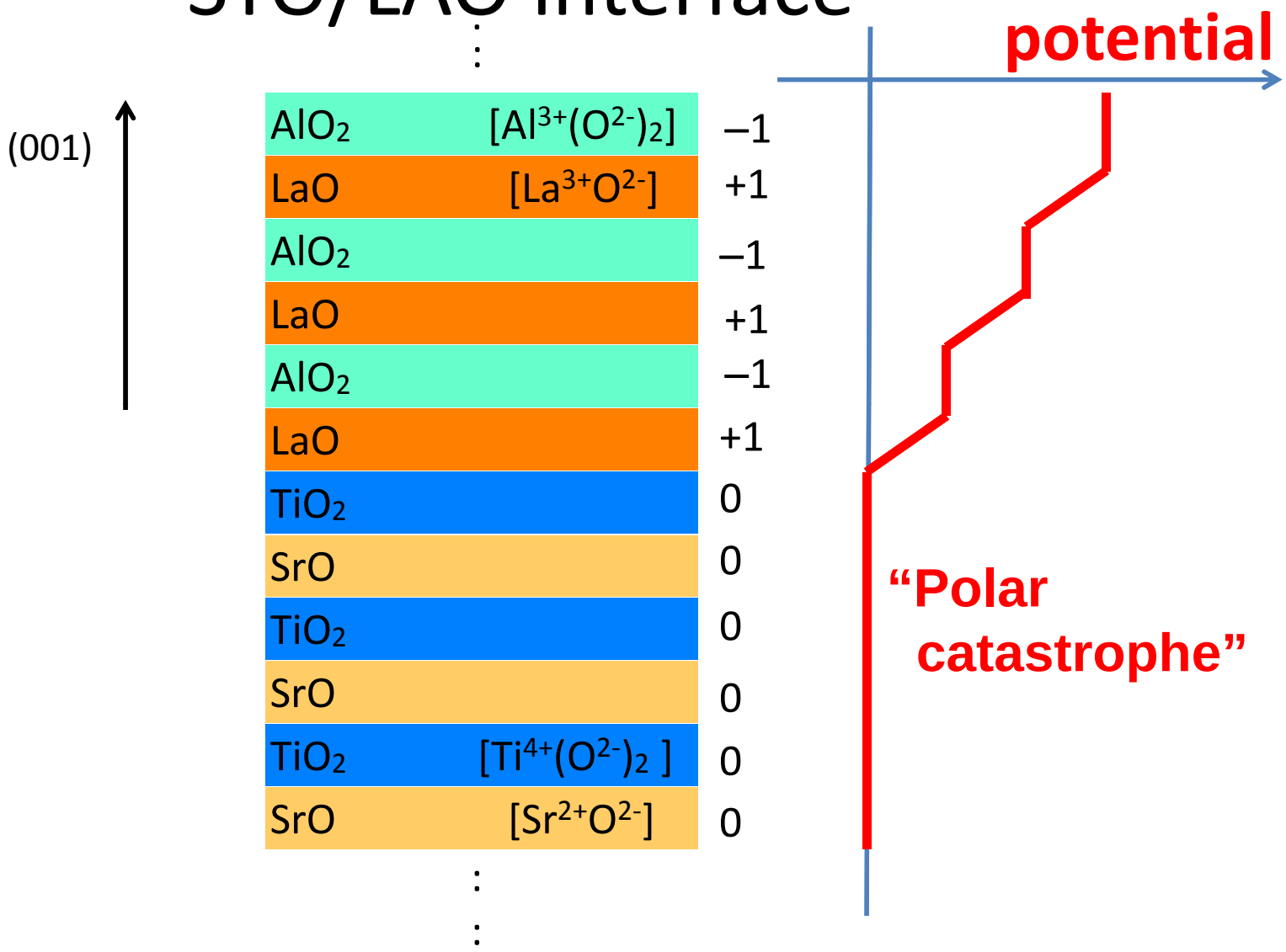
UCSB

STO/LAO interface



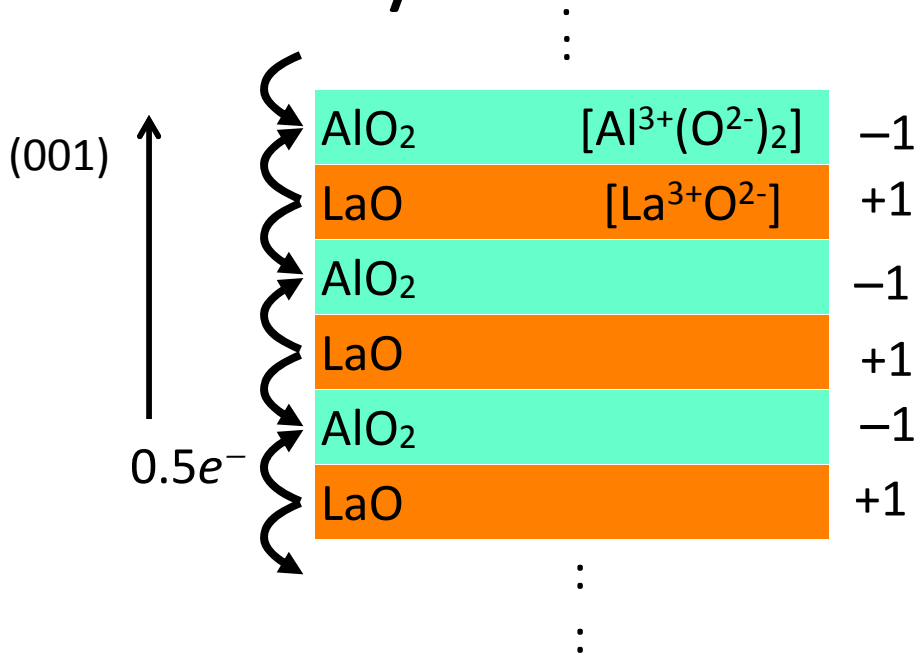
UCSB

STO/LAO interface



UCSB

STO/LAO interface



"Problem" arises from ionic picture

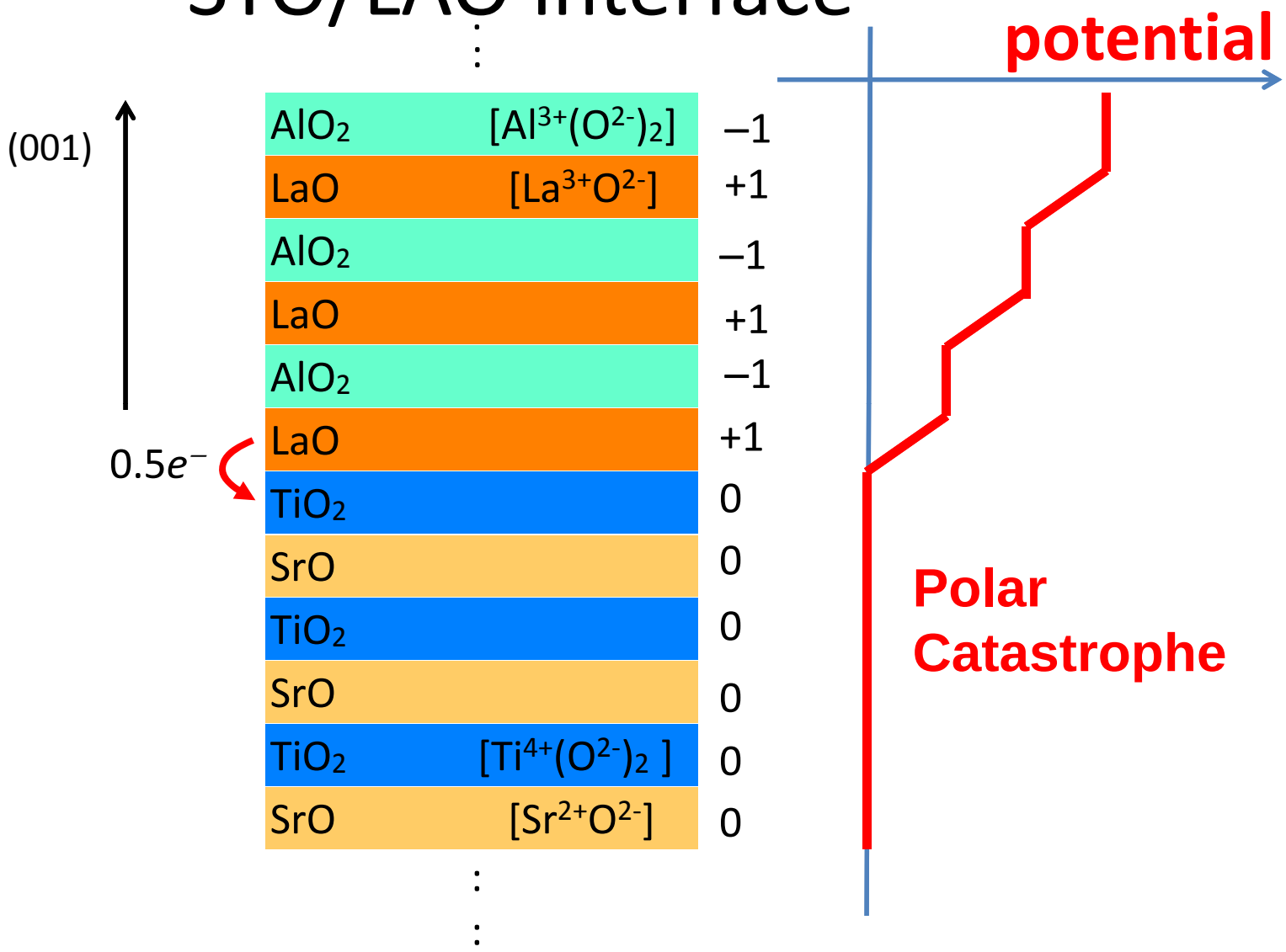
All layers originally neutral

LaO ("donor") layer donates 0.5 e^- to AlO_2 on either side

At the interface: "extra" 0.5 e^- !...

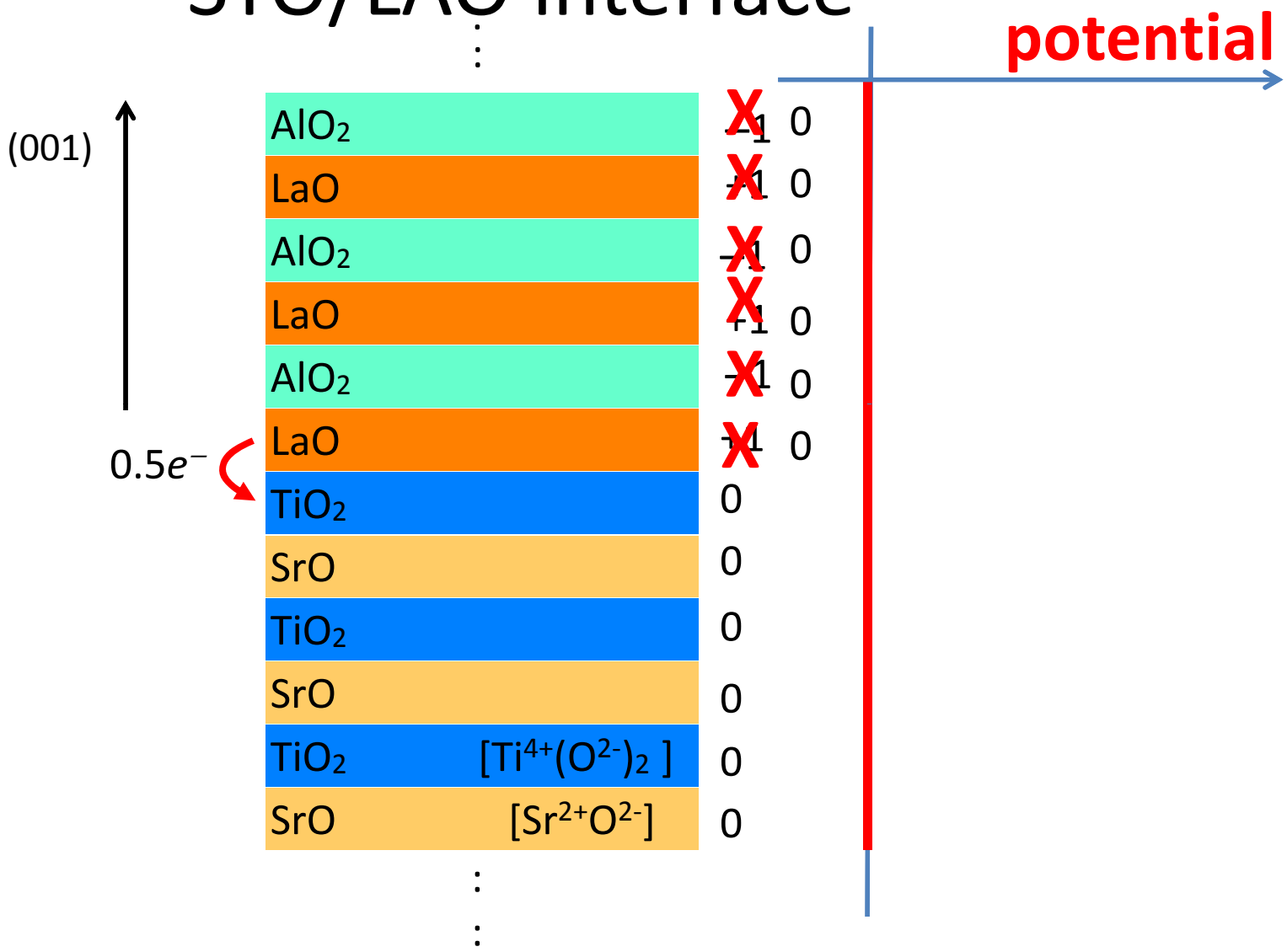
UCSB

STO/LAO interface



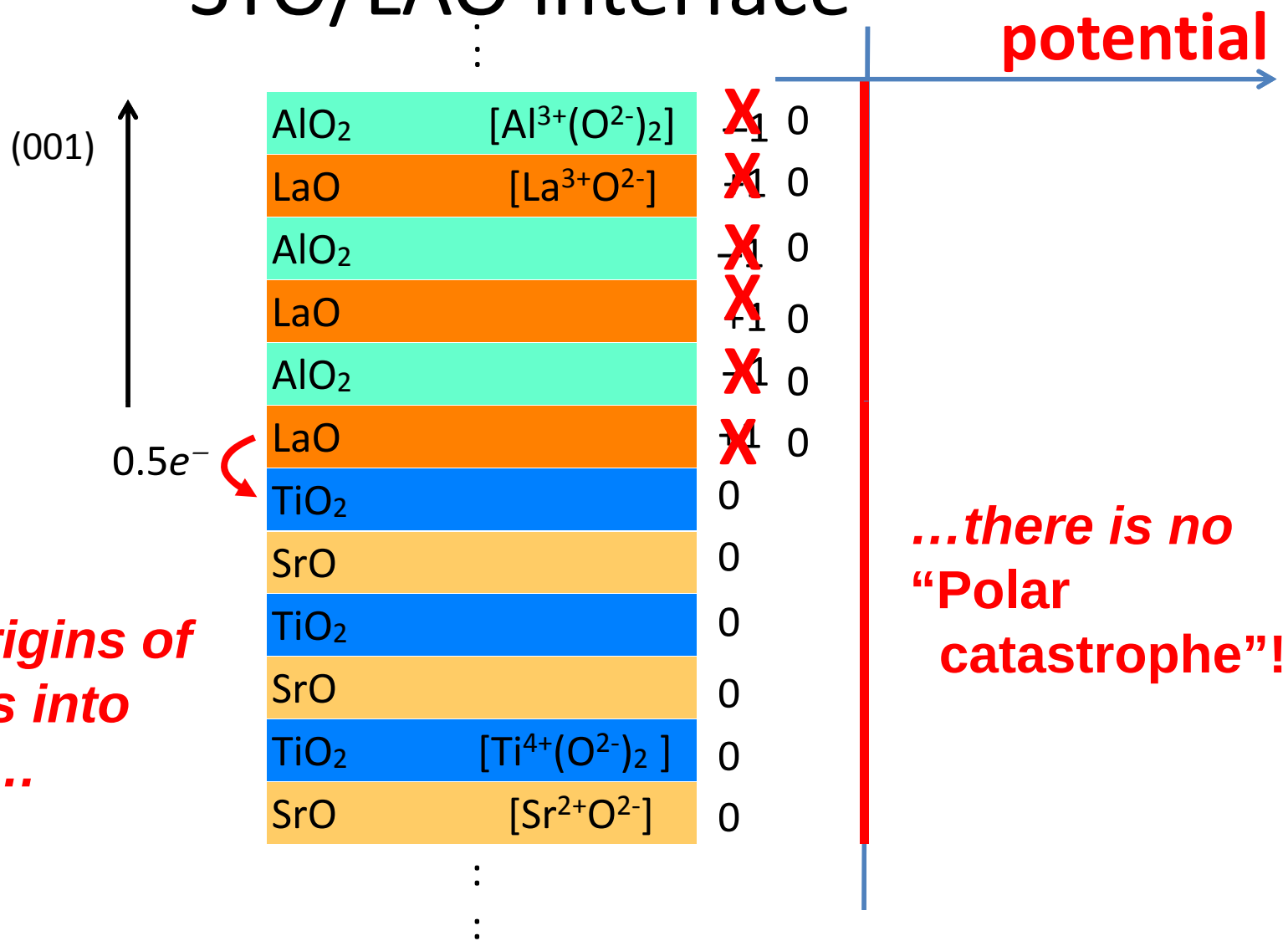
UCSB

STO/LAO interface



UCSB

STO/LAO interface

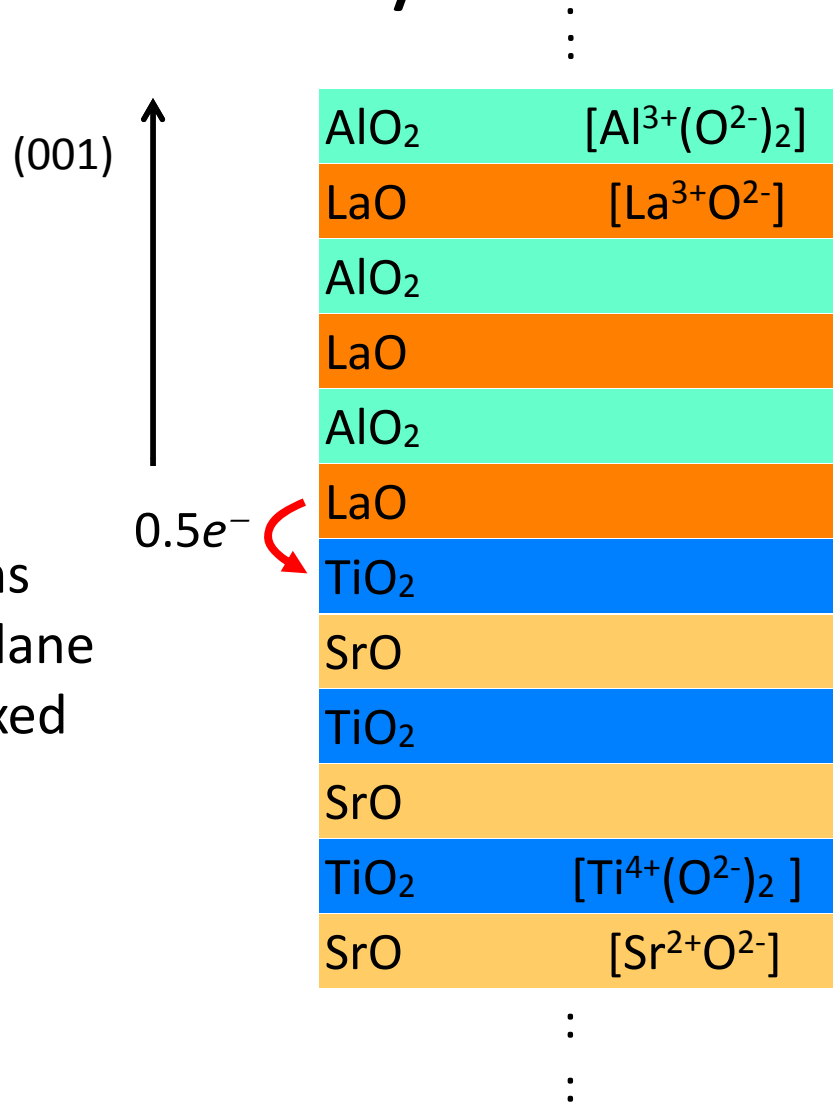


If take origins of electrons into account…

…there is no "Polar catastrophe"!

UCSB

STO/LAO interface



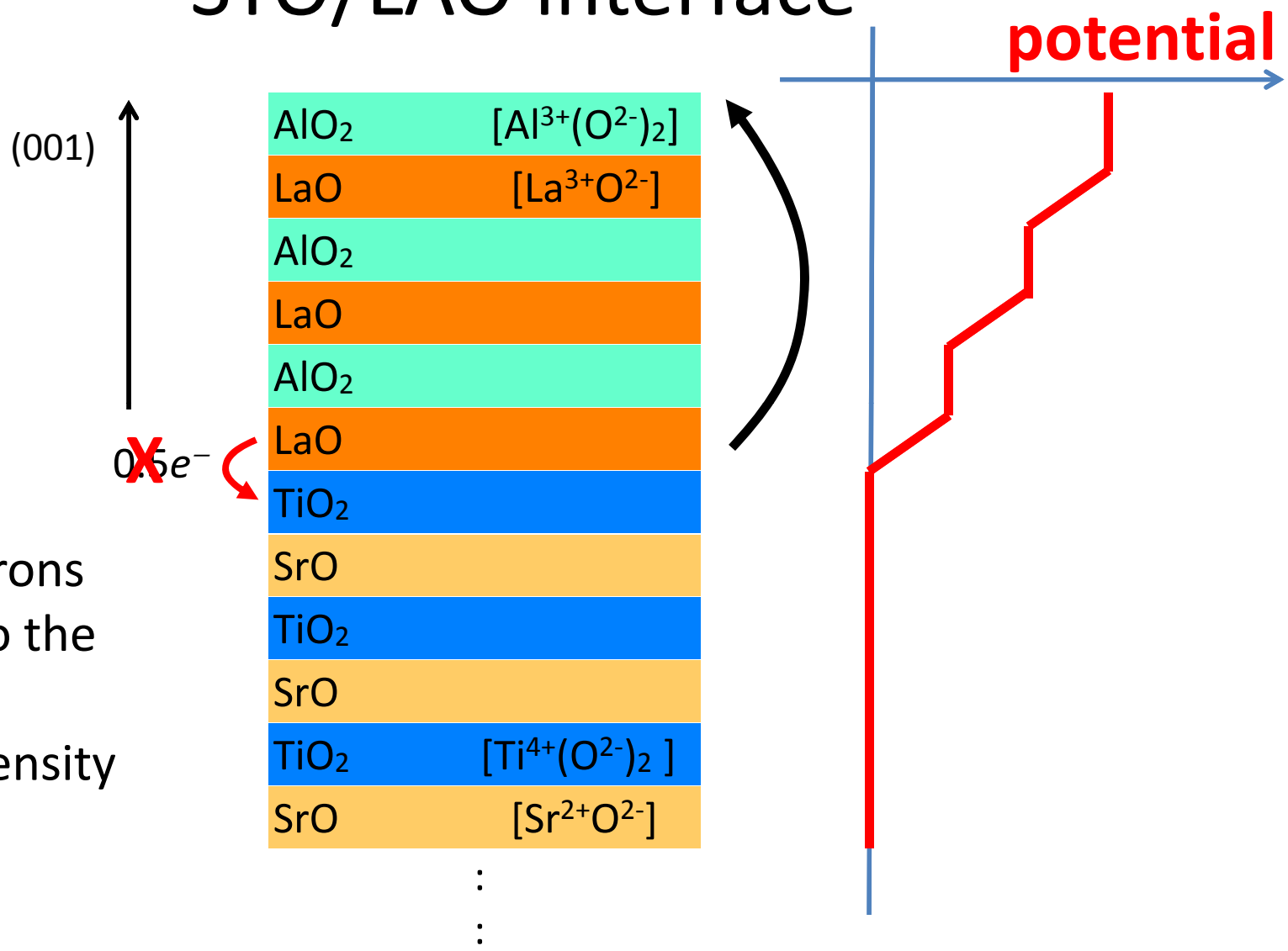
Free electrons bound to a plane of positive fixed charges

Ideal interface: $0.5e^-$ per unit cell area

$$n = 3 \times 10^{14}\ \text{cm}^{-2}$$

UCSB

STO/LAO interface



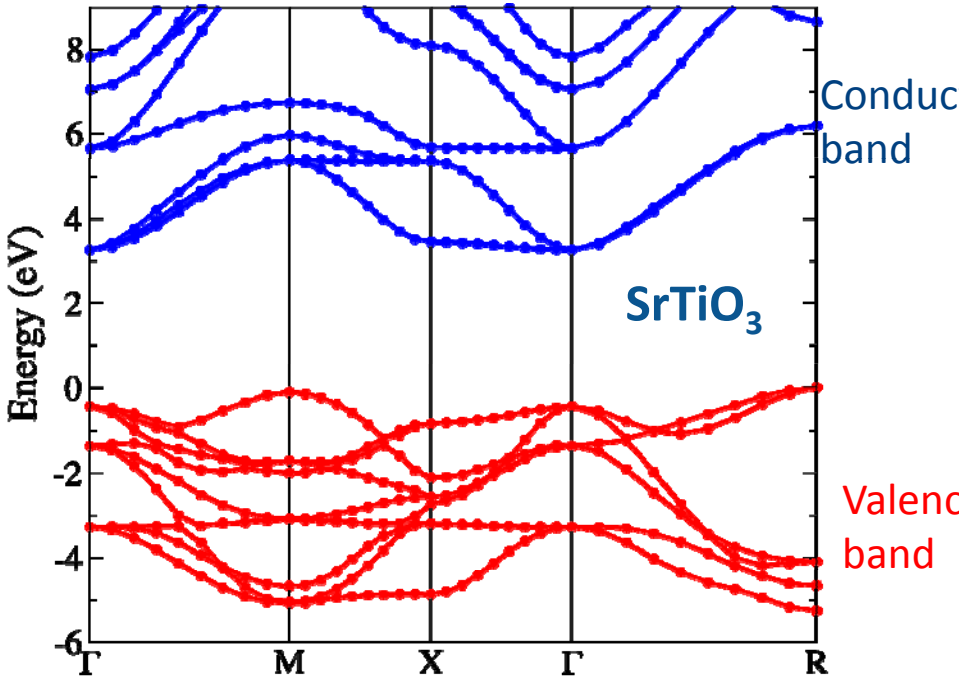
If free electrons leak away to the top surface, the 2DEG density decreases

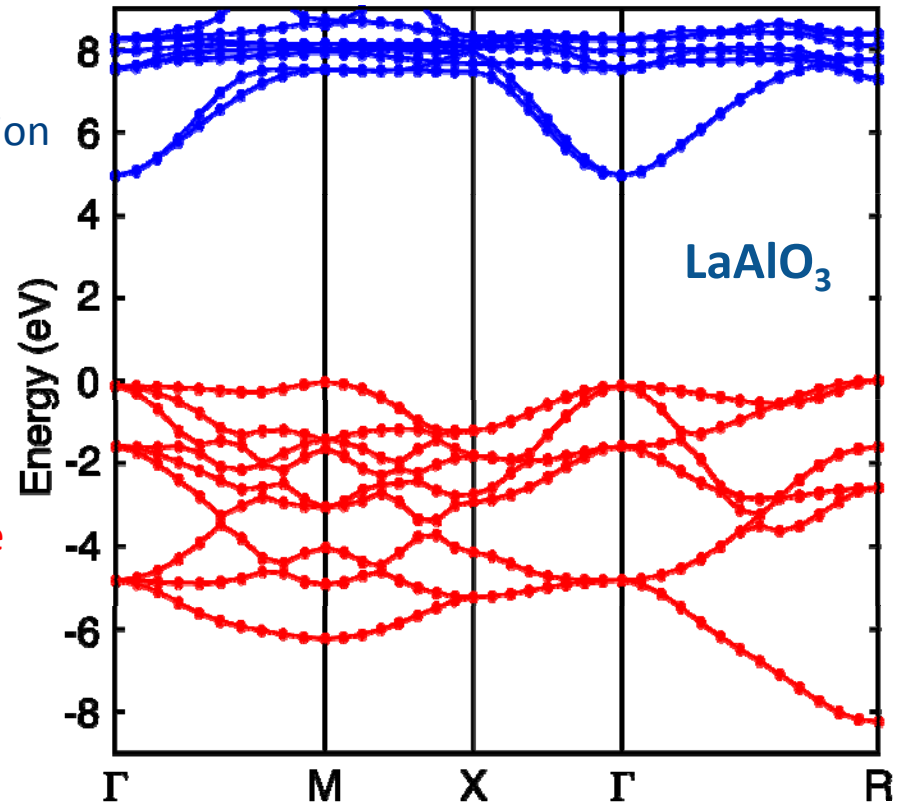
UCSB

$SrTiO_3$, $LaAlO_3$, and STO/LAO from first principles

-Density functional theory, hybrid functional (HSE)

J. Heyd, G.E. Scuseria and M. Ernzerhof,
J. Chem. Phys.**118,** 8207 (2003); **124**, 219906(E) (2006).

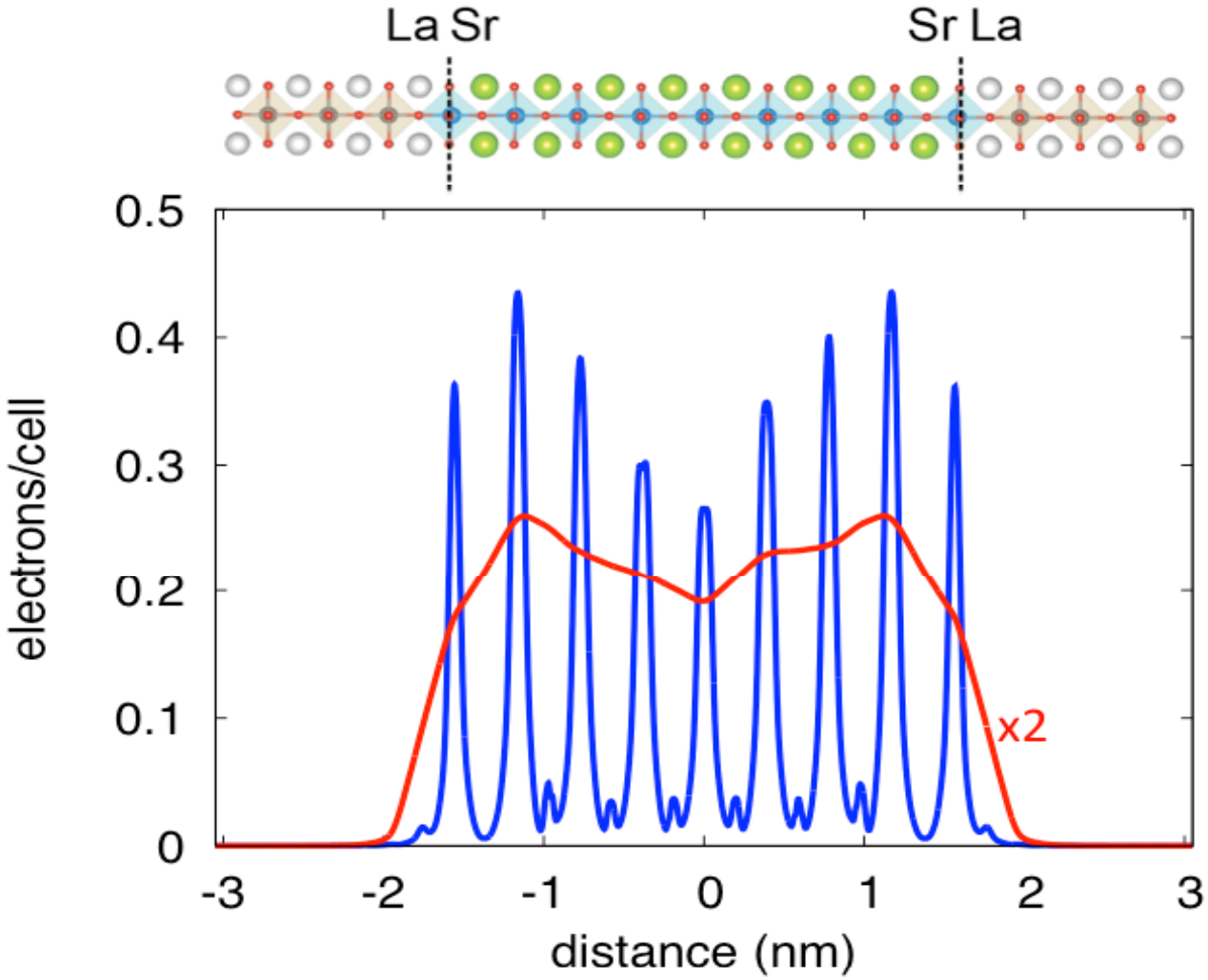




Conduction band: Ti d (t_{2g} < e_g)
Valence band: O 2p bands

Conduction band: Al 3s, La 5d
Valence band: O 2p bands

First-principles calculations



Total charge:
0.5 e^- per interface!

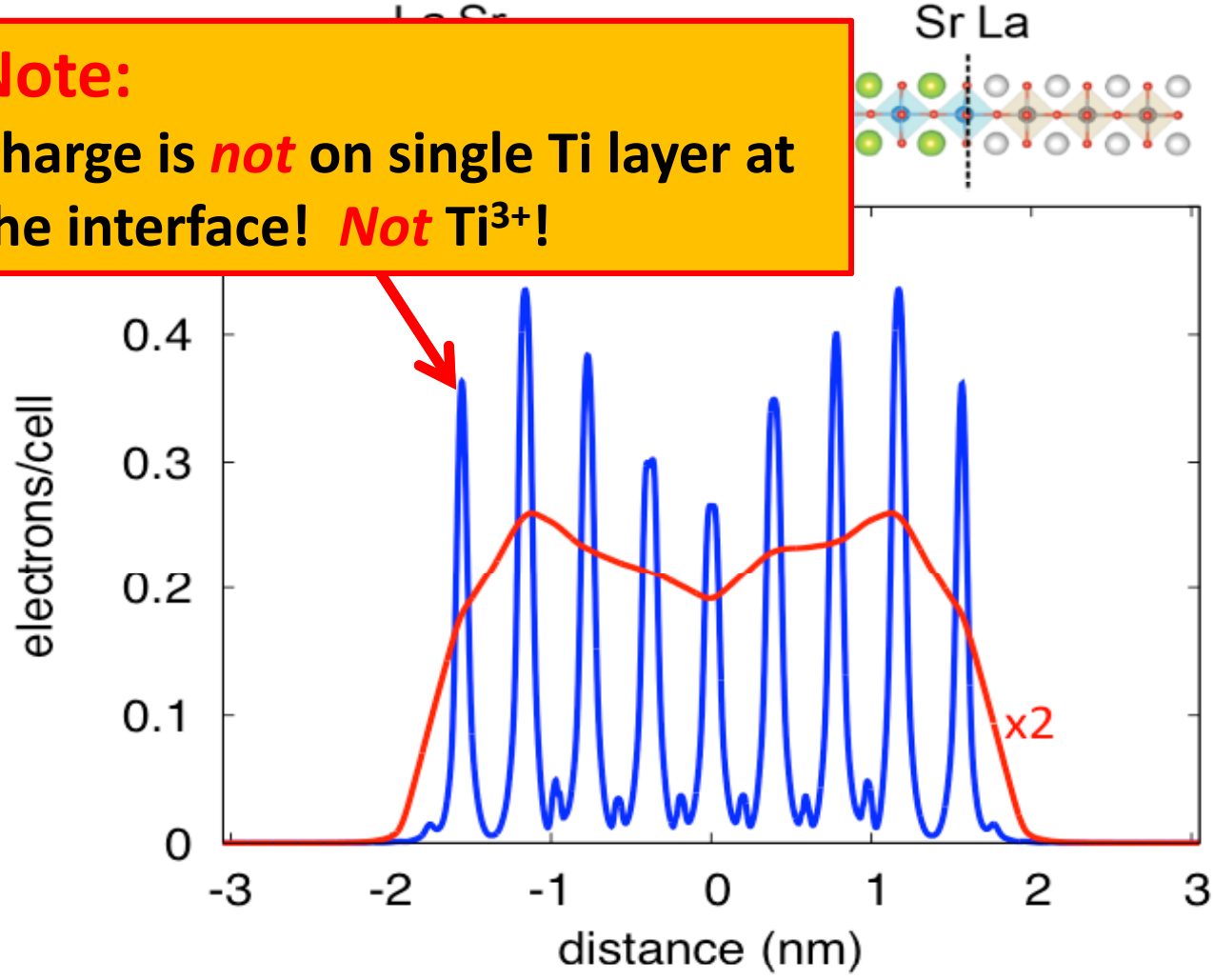
n=3x10^{14} cm^{-2}

A. Janotti, L. Bjaalie, L. Gordon, C. G. Van de Walle, Phys. Rev. B **86**, 241108(R) (2012).

UCSB

First-principles calculations

Note:
Charge is *not* on single Ti layer at the interface! *Not* Ti^{3+}!



Total charge:
0.5 e^- per interface!

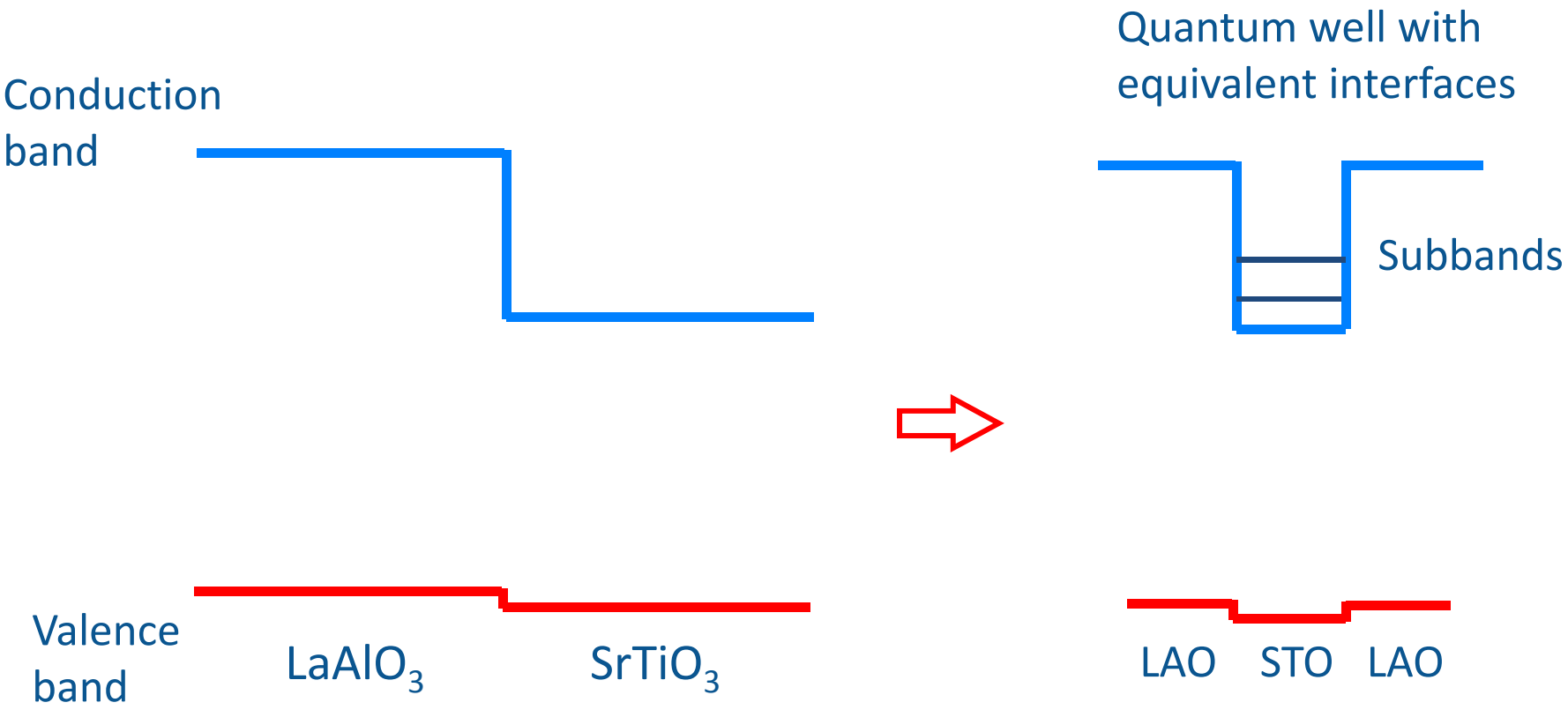
n=3x10^{14} cm^{-2}

A. Janotti, L. Bjaalie, L. Gordon, C. G. Van de Walle, Phys. Rev. B **86**, 241108(R) (2012).

UCSB

Band alignments

Density functional theory, hybrid functional

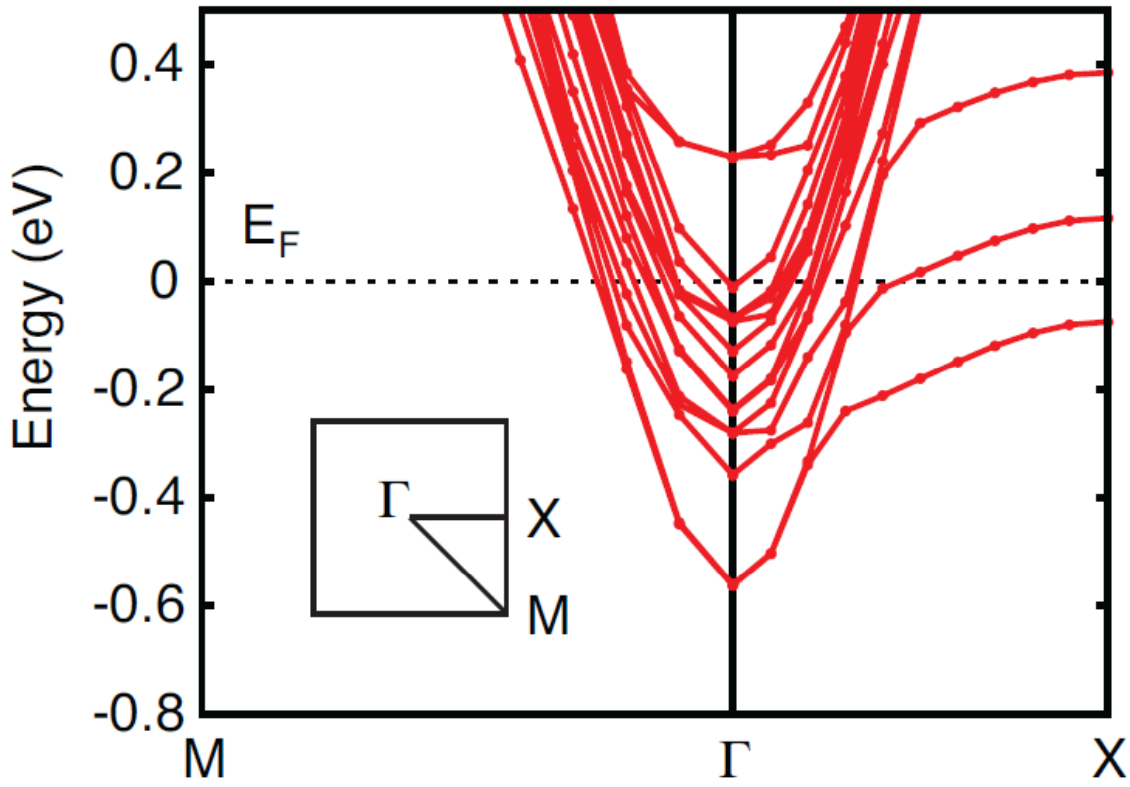


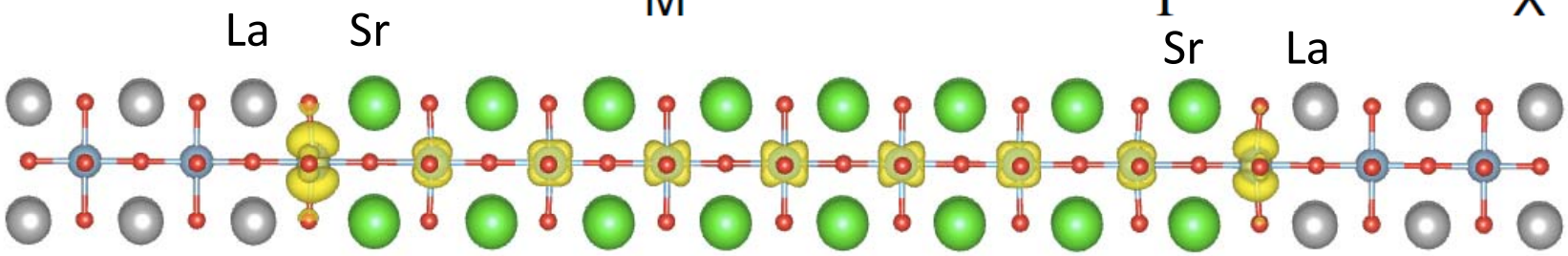
In agreement with experimental results of
Chambers *et al.*, Surface Science Reports (2010).

UCSB

First-principles calculations

Subbands from $(STO)_{8.5}/(LAO)_{7.5}$ superlattice



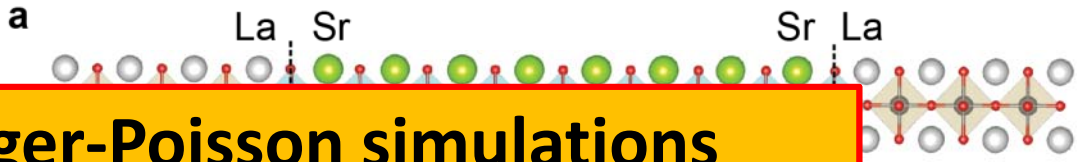


Popovic *et al.*, Phys. Rev. Lett. **101**, 256801 (2008).

Chen *et al.*, Adv. Matter. **22**, 2881 (2010).

UCSB

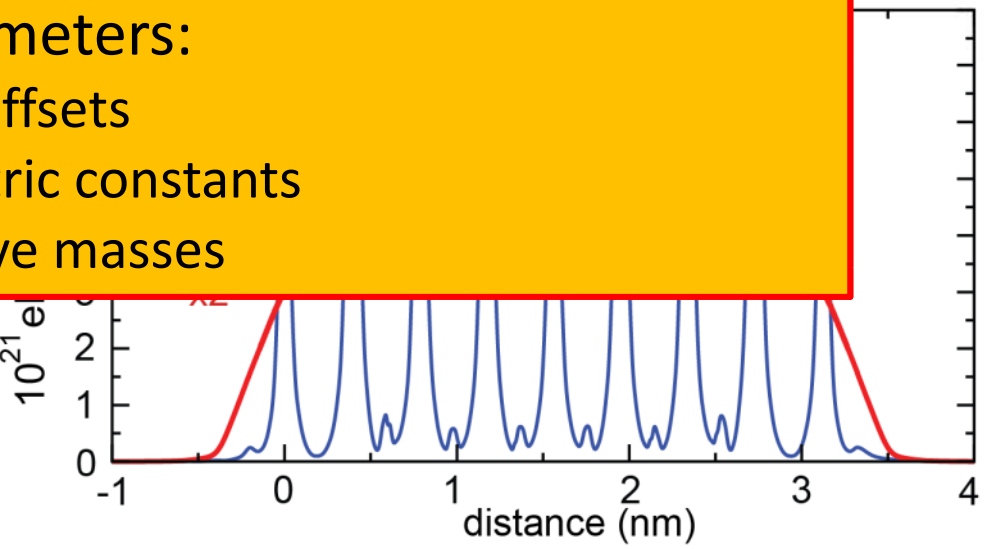
First principles *versus* Schrödinger-Poisson

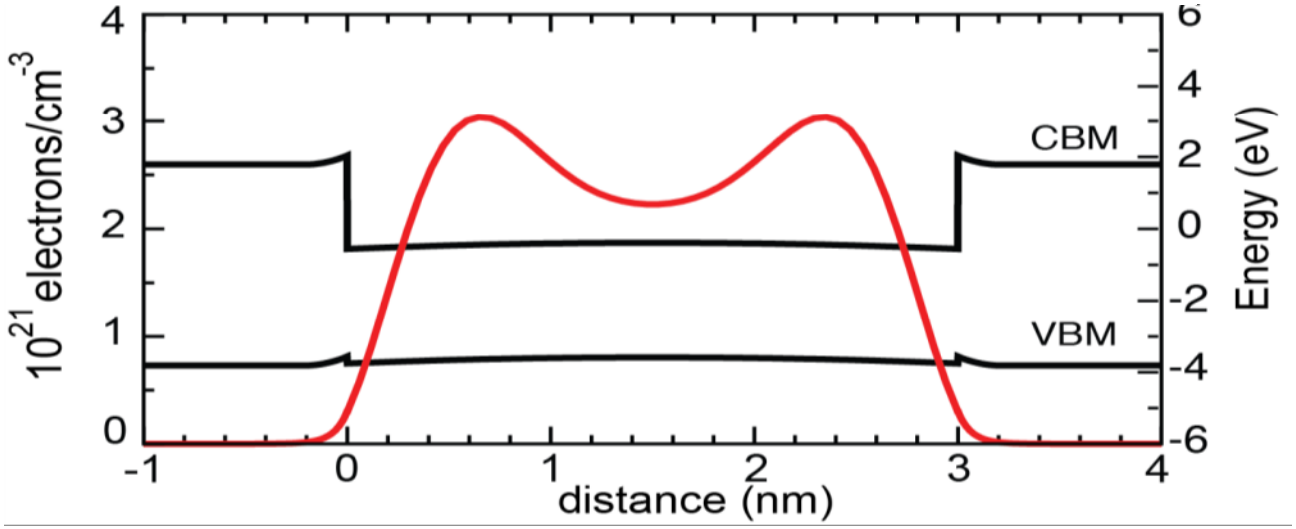


Schrödinger-Poisson simulations

Input parameters:

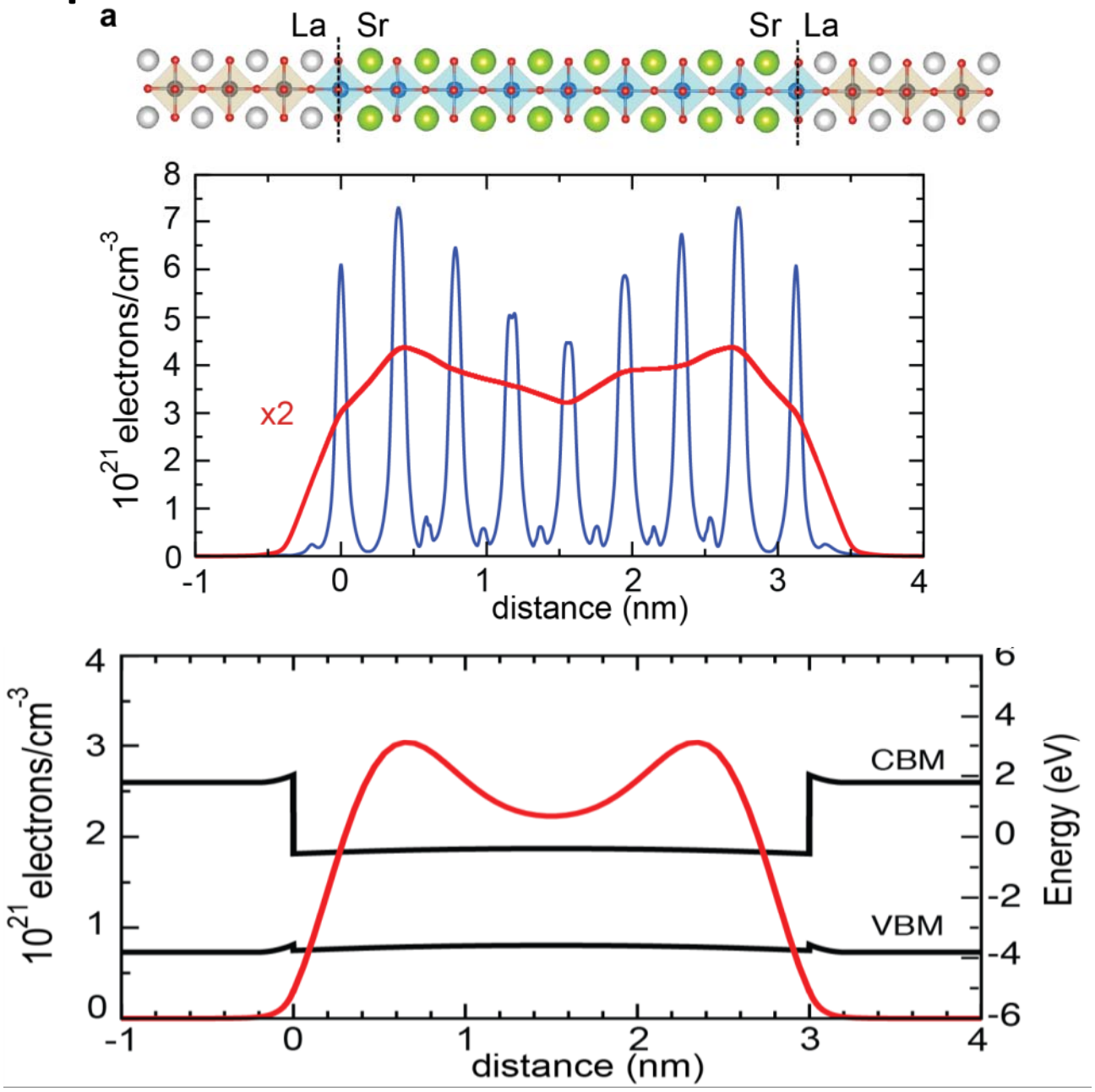
- Band offsets
- Dielectric constants
- Effective masses





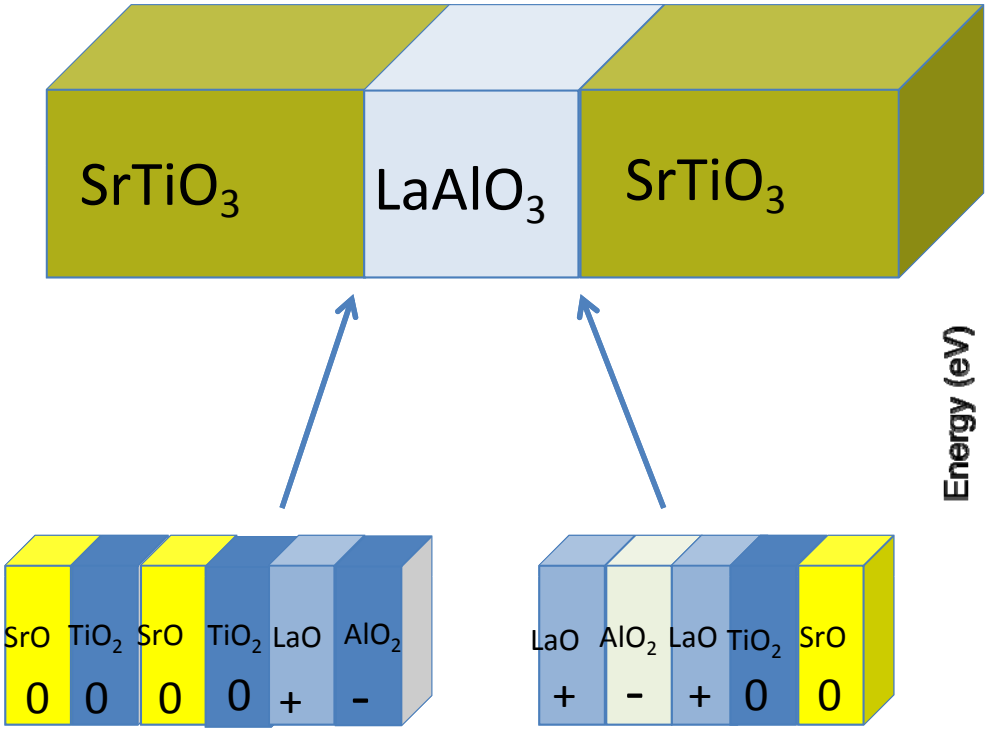
UCSB

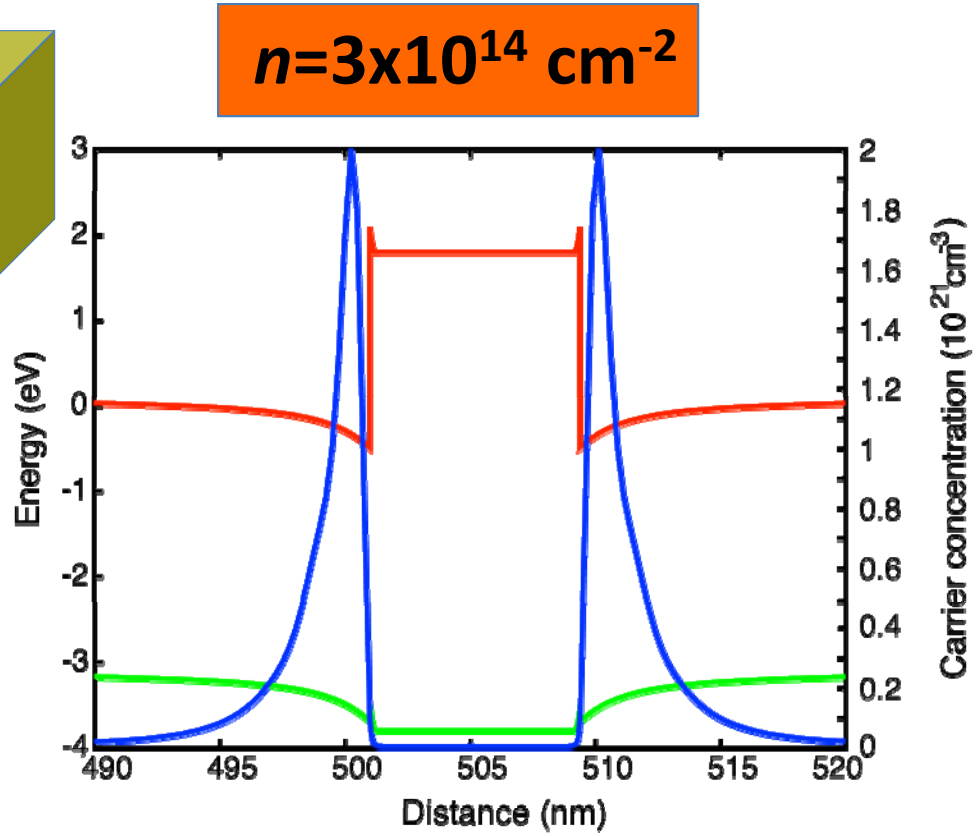
First principles *versus* Schrödinger-Poisson



UCSB

STO/LAO/STO : Symmetric heterostructure



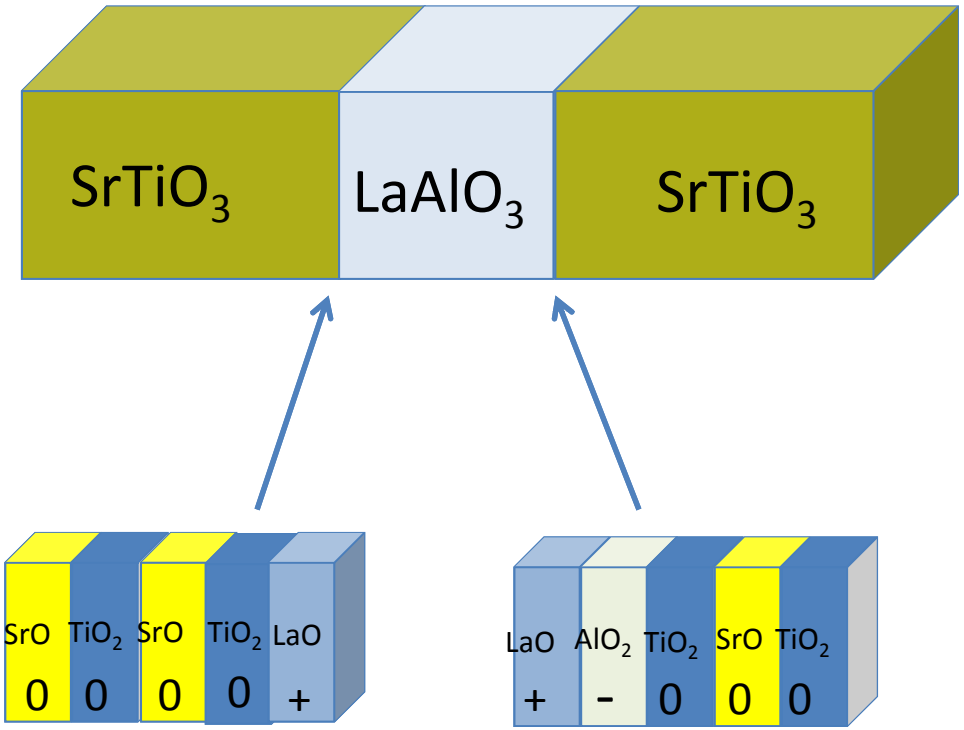


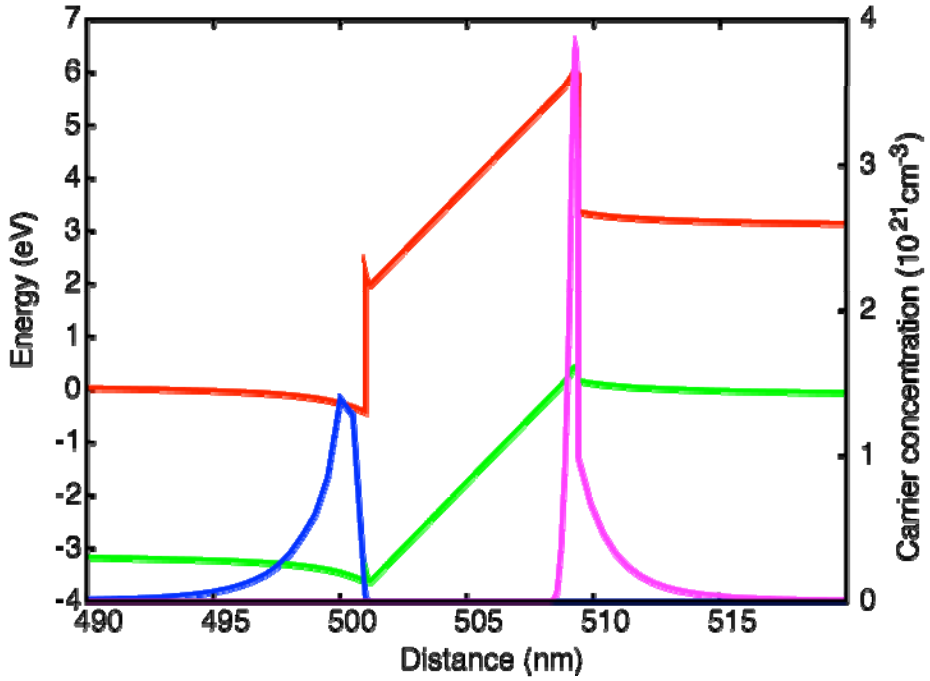
- Flat potential across LAO
- 0.5e^- per unit cell per interface

UCSB

STO/LAO/STO – Asymmetric heterostructure

LaO-terminated on the left, AlO_2-terminated on the right





- Potential increase across the LAO layer
- Low 2DEG density
  - – electrons leak to other interface

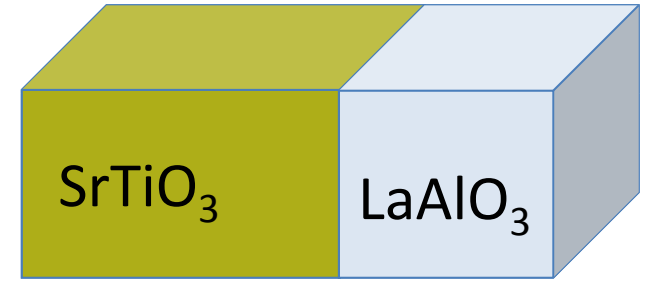
charge density
conduction band
valence band

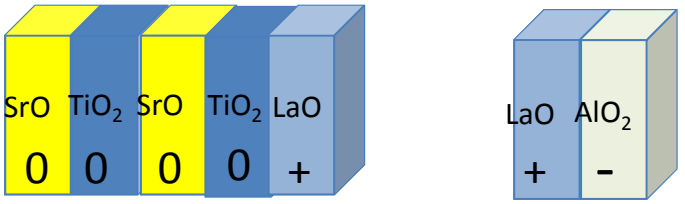
UCSB

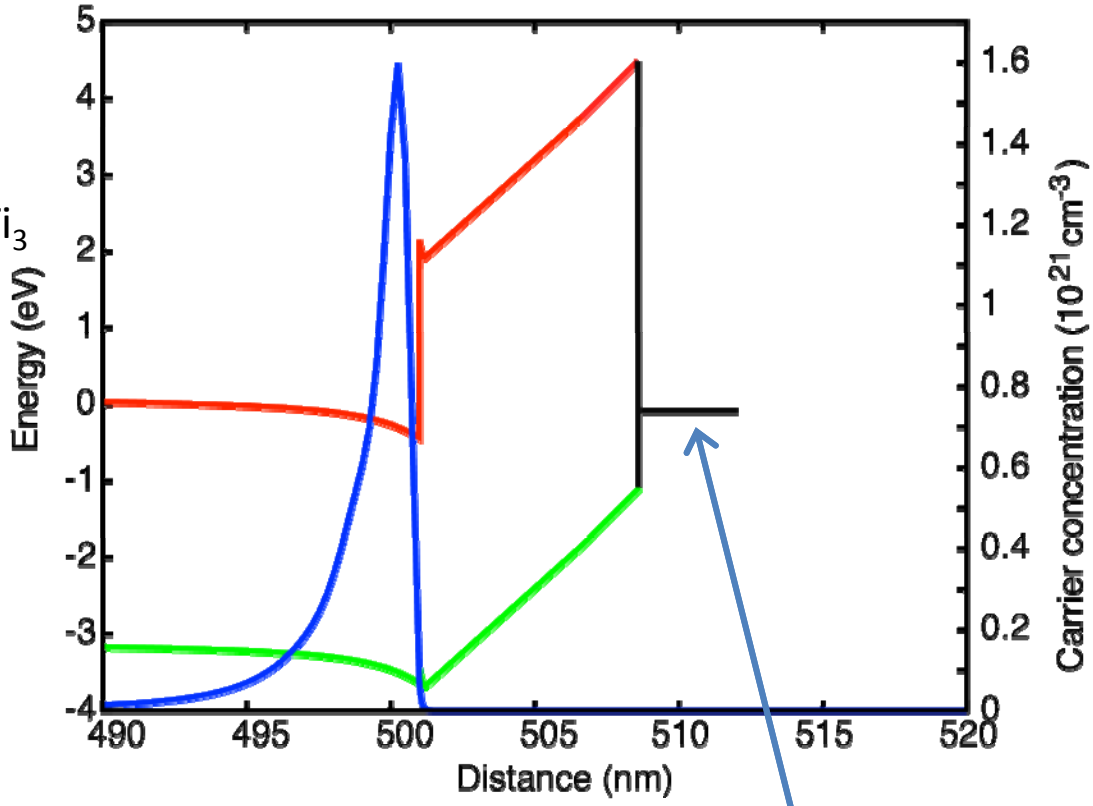
STO/LAO: Surface

LAO surface AlO_2-terminated

$n \approx 10^{13}$ cm^{-2}





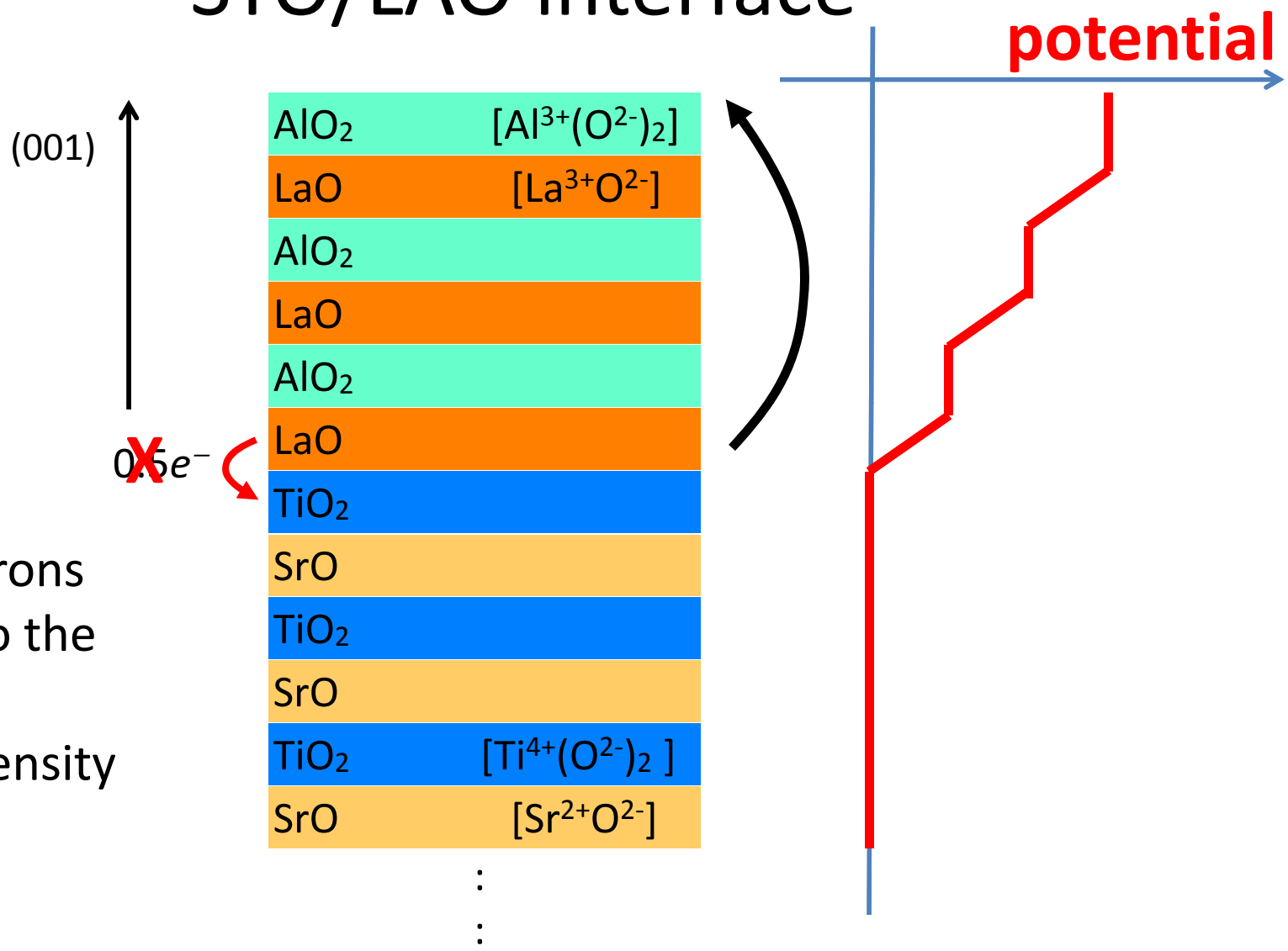


- potential increase across the LAO layer
- lower 2DEG density
  - – electrons leak to surface

electrons go into surface states on LAO surface

UCSB

STO/LAO interface

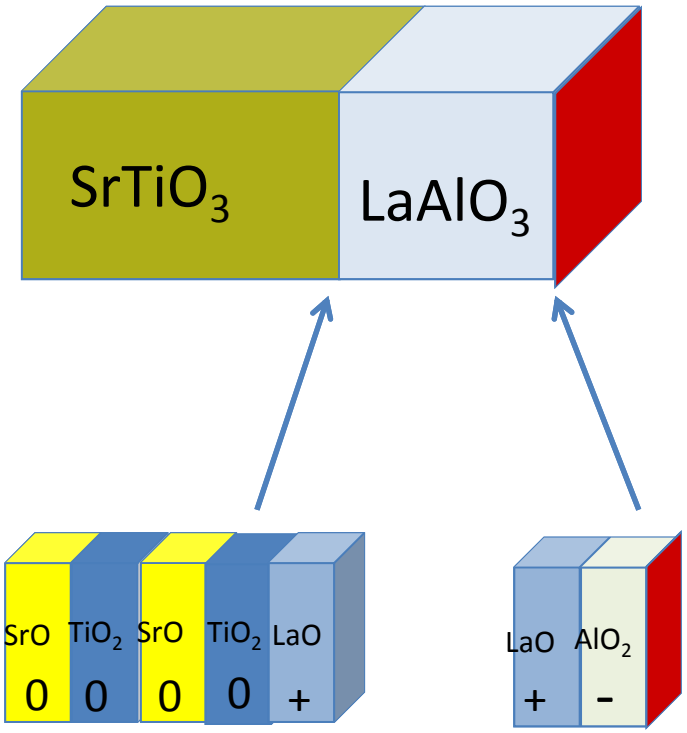


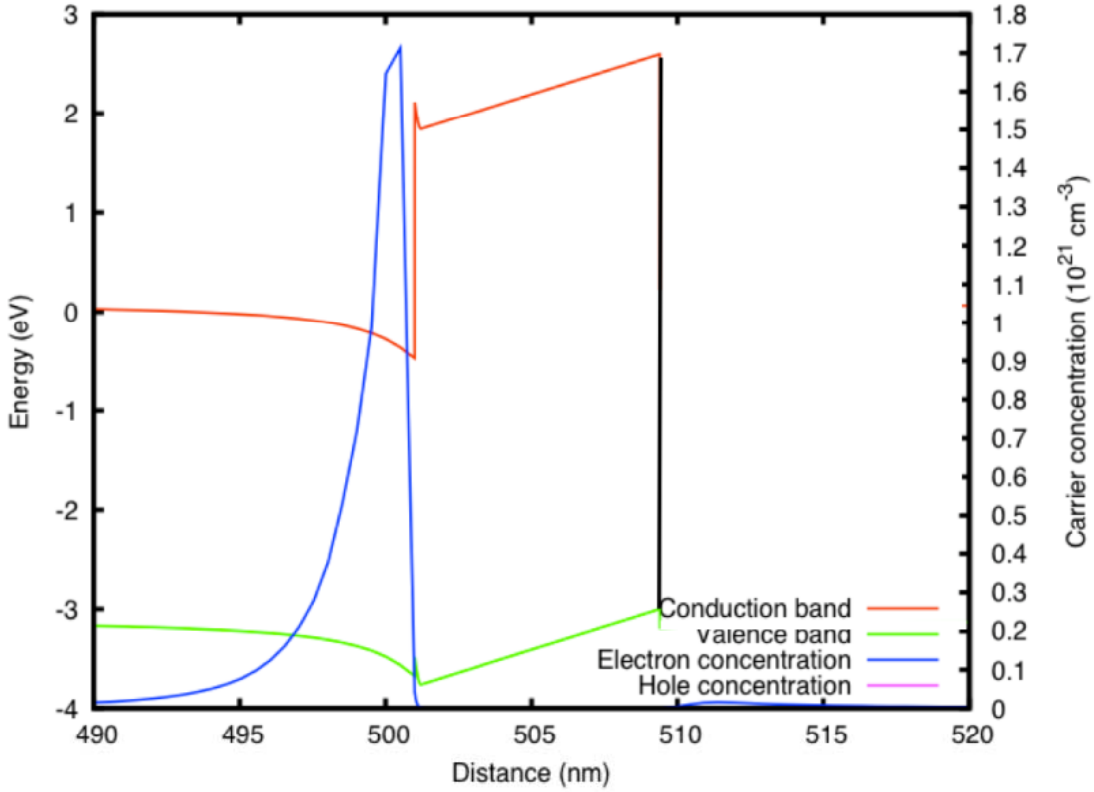
If free electrons leak away to the top surface, the 2DEG density decreases

UCSB

STO/LAO: Surface

LAO surface passivated



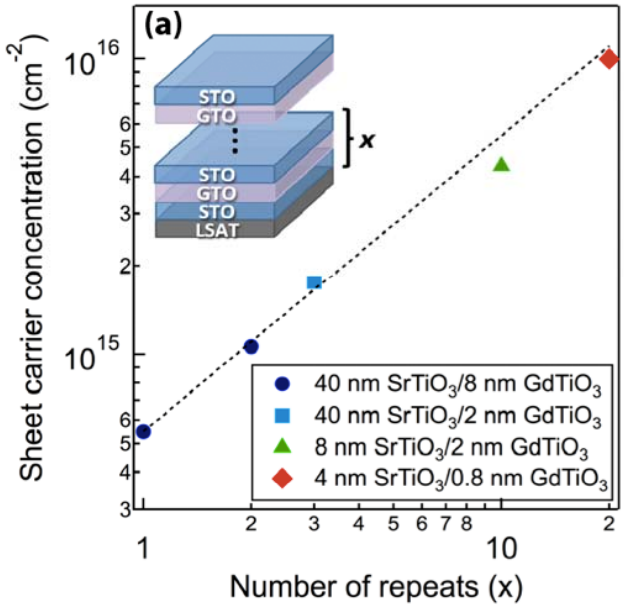


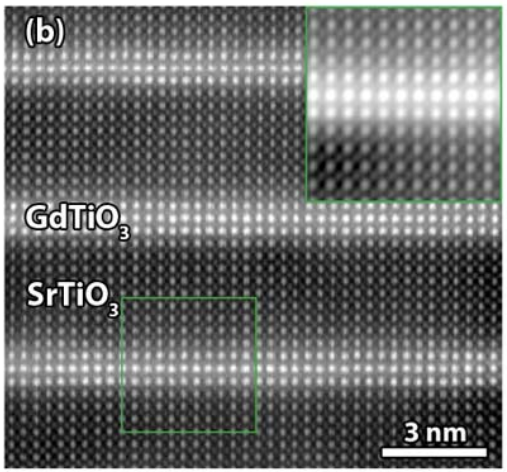
- Potential almost flat across the LAO layer
- High 2DEG density
  - hydrogen passivation, or metal cap layer (work function!)

R. Arras *et al.*, Phys. Rev. B 85, 125404 (2012).

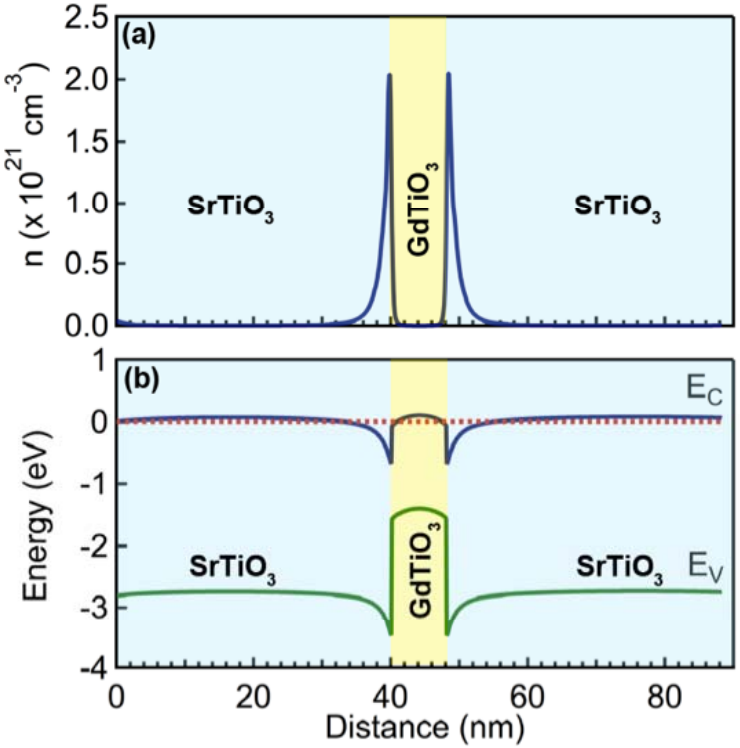
UCSB

Other materials combinations? $SrTiO_3/GdTiO_3$ superlattices





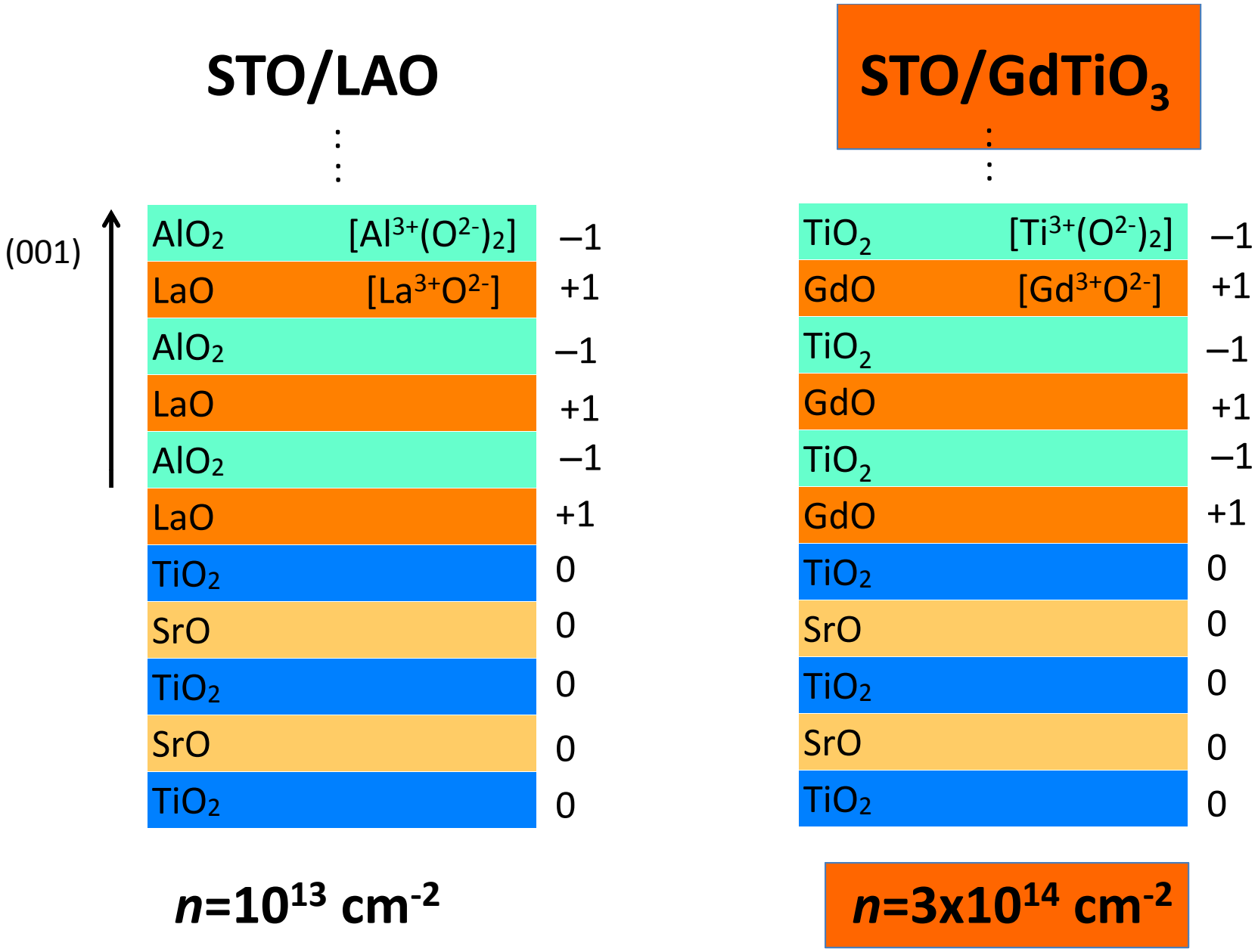
Schrödinger-Poisson simulations



STO/GTO: 0.5 *e*- per unit cell per interface

P. Moetakef *et al.*,
Appl. Phys. Lett. **99**, 232116 (2011).

UCSB

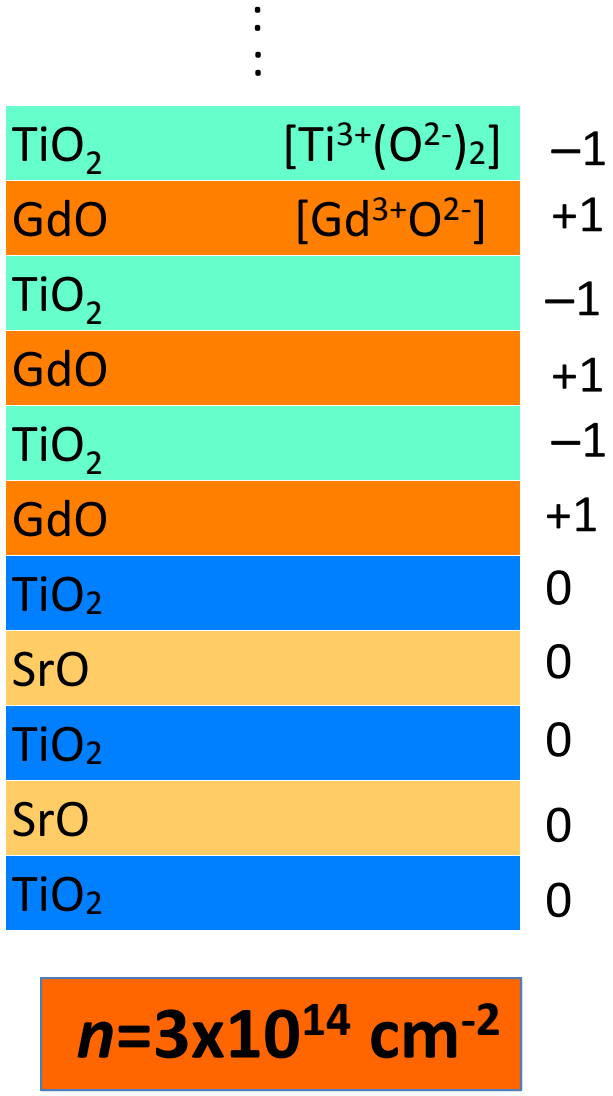


P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, Appl. Phys. Lett. **99**, 232116 (2011).

UCSB

Why is STO/GTO different from STO/LAO?

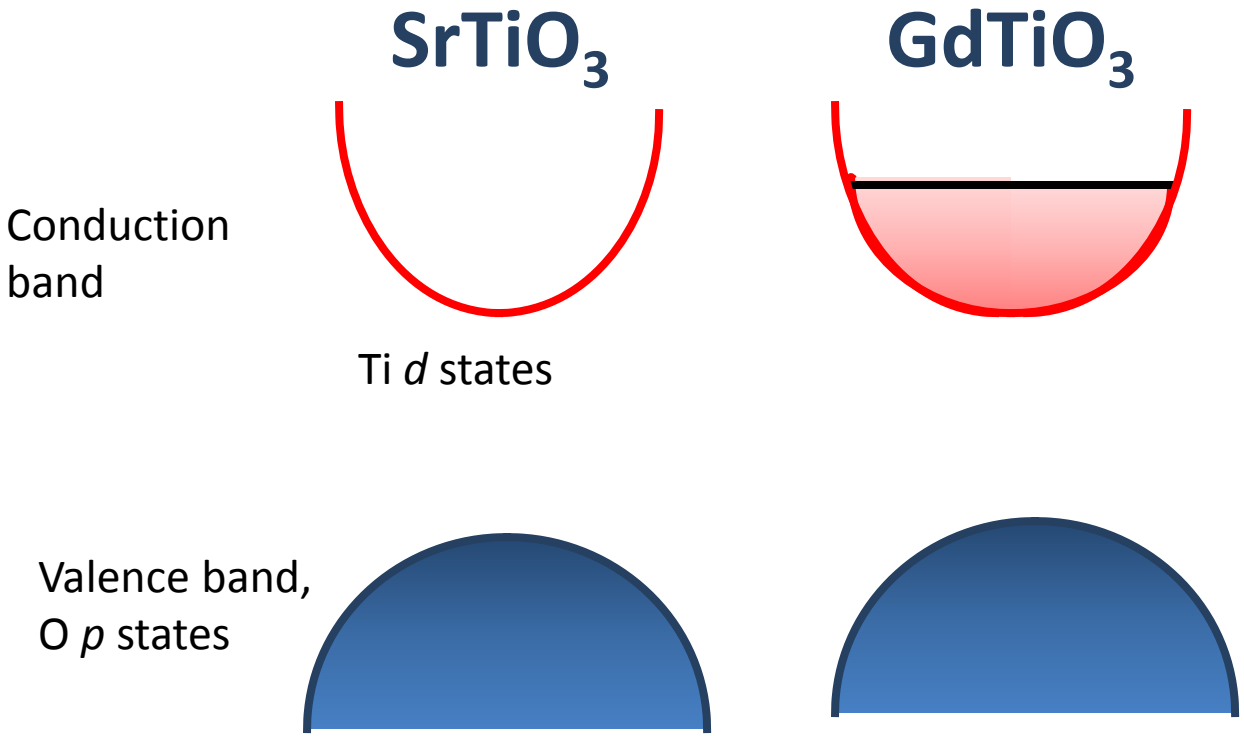
- Interface is *not* different
  - Confirmed by first-principles calculations
- But: STO can be grown with high quality on top of GTO!
  - ➔ symmetric interfaces
  - Superlattices
  - Full 2DEG density
- GTO surfaces: "auto-passivated"



P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, Appl. Phys. Lett. **99**, 232116 (2011).

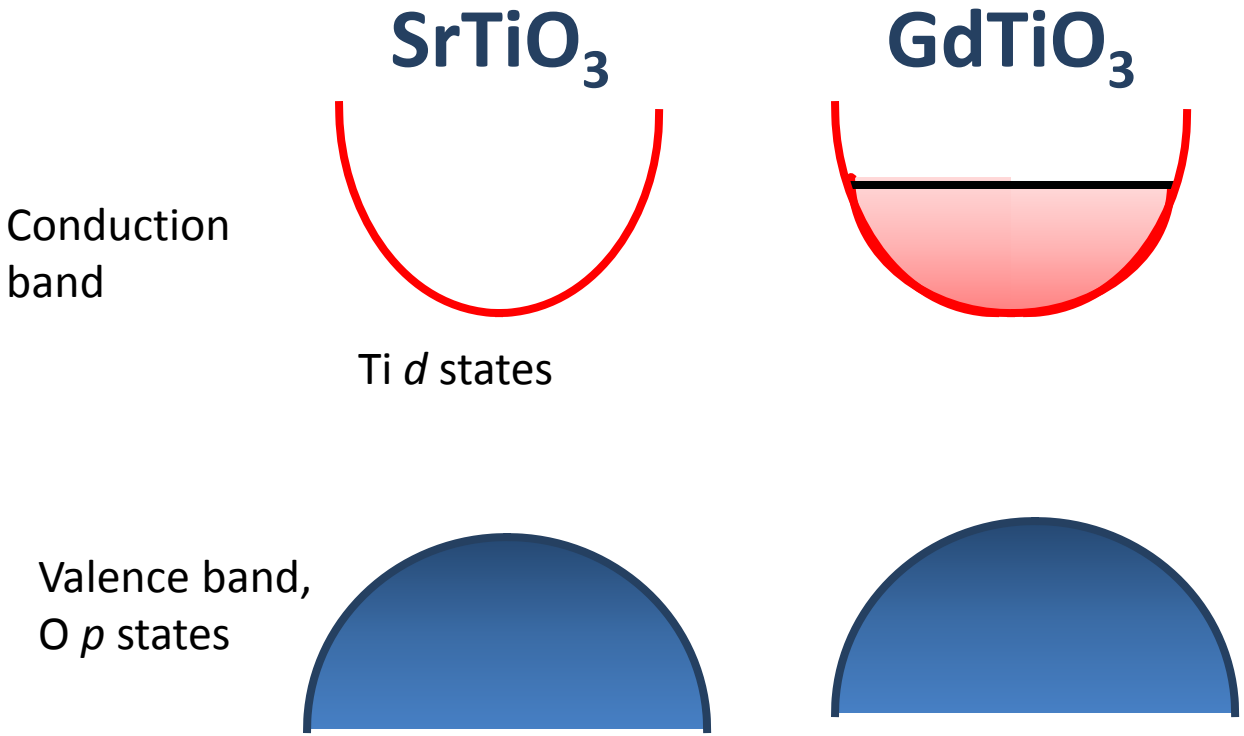
UCSB

Mott physics: $SrTiO_3$ versus $GdTiO_3$



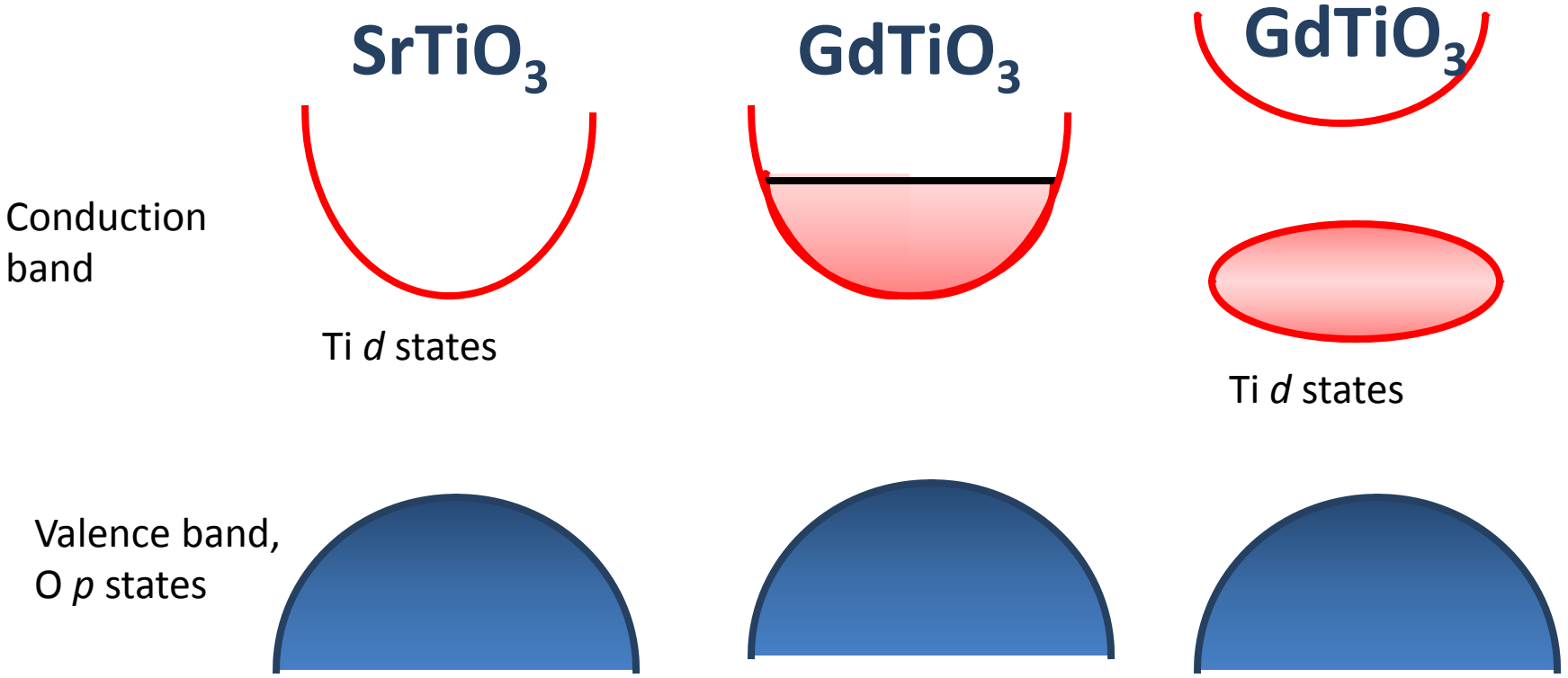
UCSB

Mott physics: $Sr^{2+}TiO_3$ versus $Gd^{3+}TiO_3$



UCSB

Mott physics: $SrTiO_3$ versus $GdTiO_3$

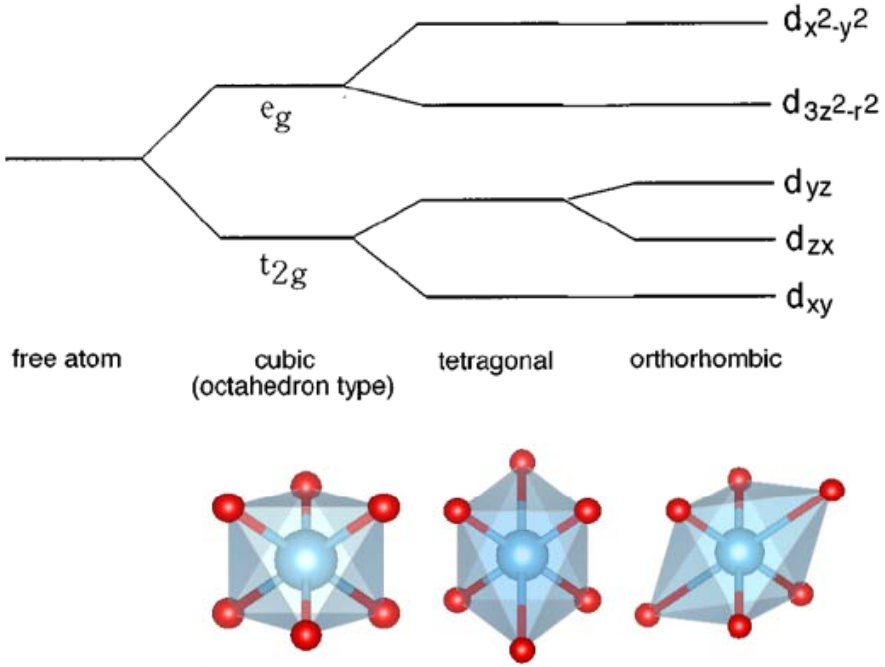


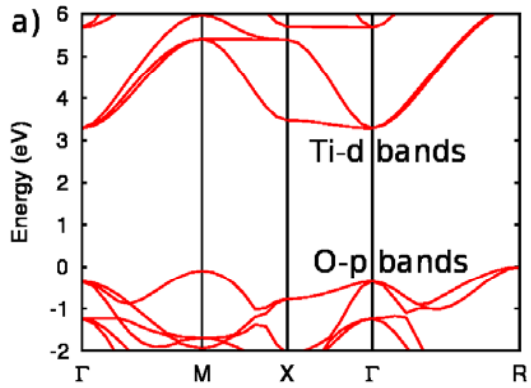
UCSB

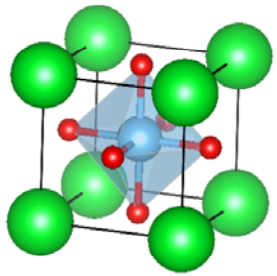
$GdTiO_3$ properties

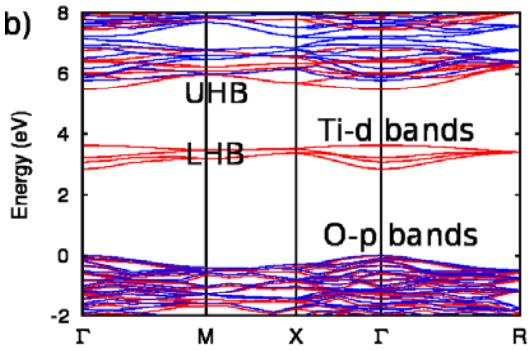
GTO a $3d^1$ Mott insulator: Mott/band insulator interface

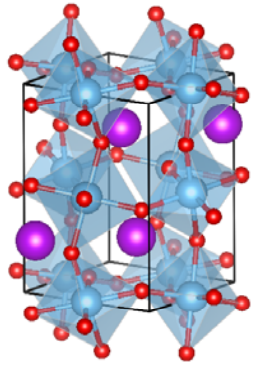
GTO unit cell: 20-atom orthorhombic, *Pnma* space group







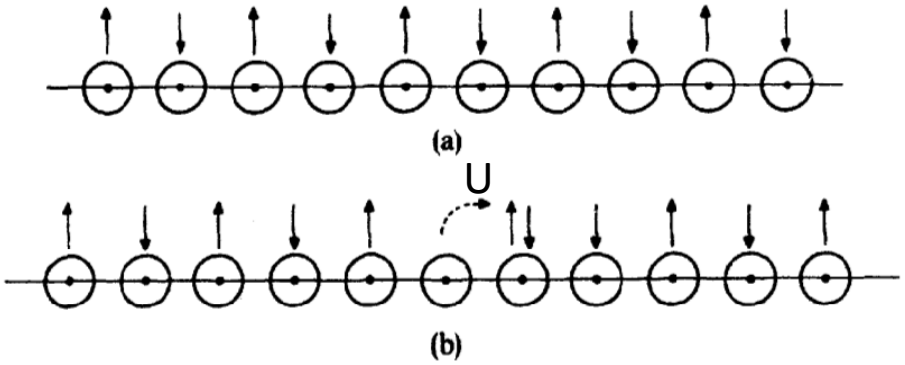


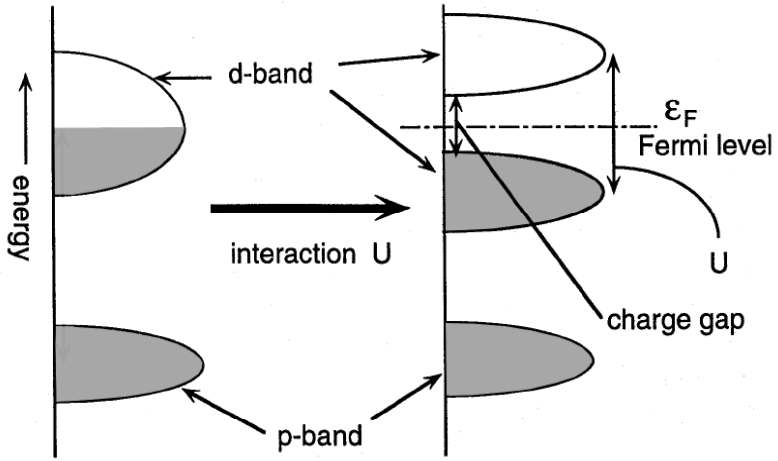


$GdTiO_3$ properties

Ti $3d^1$ electrons highly localized:

From strong intra-atomic electron-electron repulsion





First principles approaches:

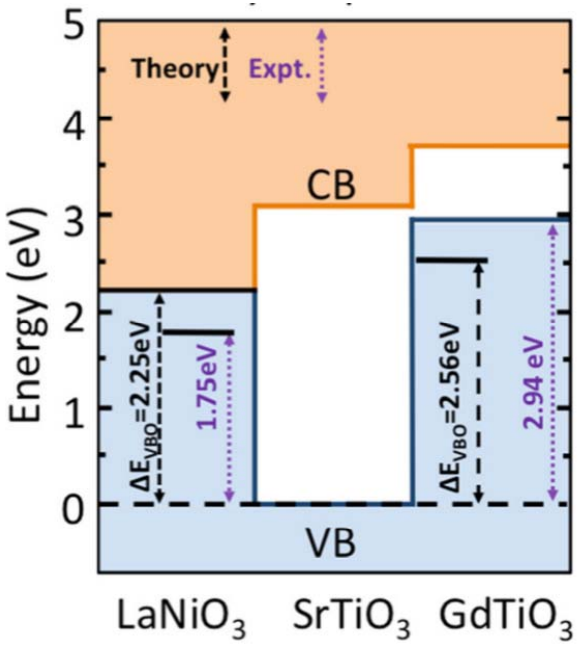
DFT+U: static correlations, $^{U}/_{W} \gg 1, \mathrm{T} = 0$

Hybrid functionals: Inclusion of exact Hartree-Fock exchange (self-interaction partially cancelled)

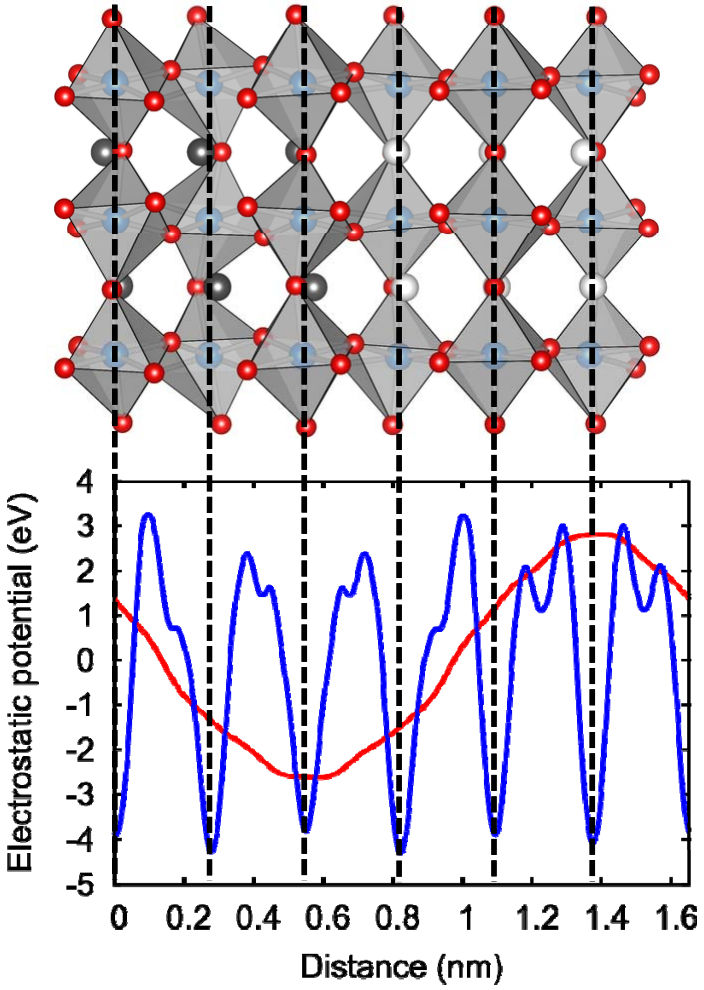
UCSB

$SrTiO_3/GdTiO_3$ superlattices: band offsets

Calculating band offsets by using the (110) interface: no electron transfer



G. Conti *et al. J. Appl. Phys.* 113, 143704 (2013).



Macroscopic average x10

UCSB

Summary

- First-principles calculations
- Schrödinger-Poisson modeling
- Hybrid functional capable of capturing the physics of Mott insulators and the STO/GTO system
- Electrons in the 2DEG at STO/LAO and STO/GTO are *intrinsic* to the interface
  - Asymmetry of interfaces (or interface+surface) causes electrons to leak away in the STO/LAO case
- "And so, my fellow theorists: ask not where the electrons *come from*—ask where the electrons *disappear to*."

Reference:
A. Janotti, L. Bjaalie, L. Gordon, and C. G. Van de Walle, Phys. Rev. B 86, 241108(R) (2012).

UCSB