

# Quantum chemistry simulations of $\text{LaAlO}_3/\text{SrTiO}_3$ interface electronic structure

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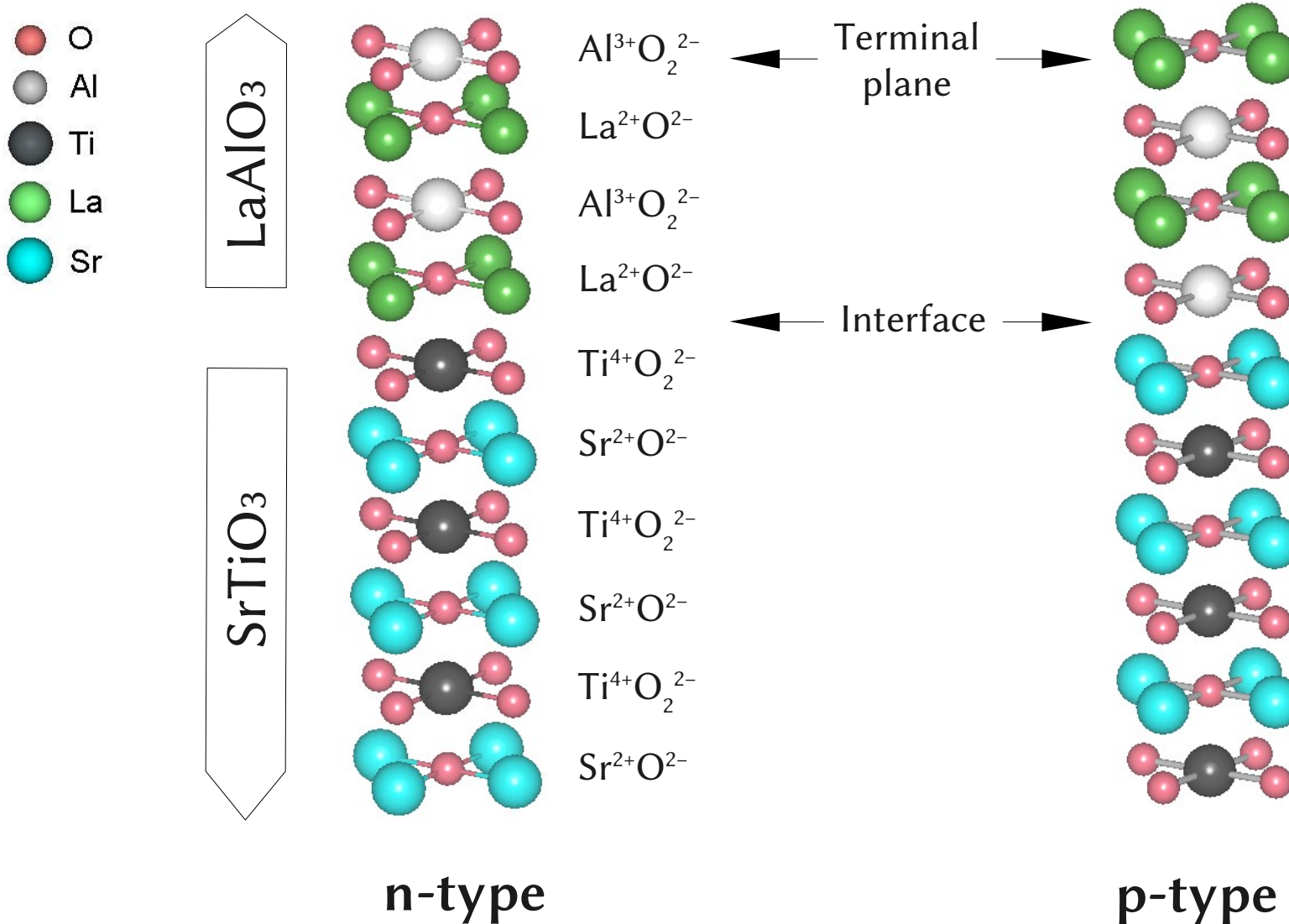
# Outline

- Introduction and motivation.
- Thermodynamic stability of  $\text{LaAlO}_3$  (001) surfaces.
- $\text{LaAlO}_3/\text{SrTiO}_3$ : Electronic structure and charge redistribution.
- Summary and conclusions.

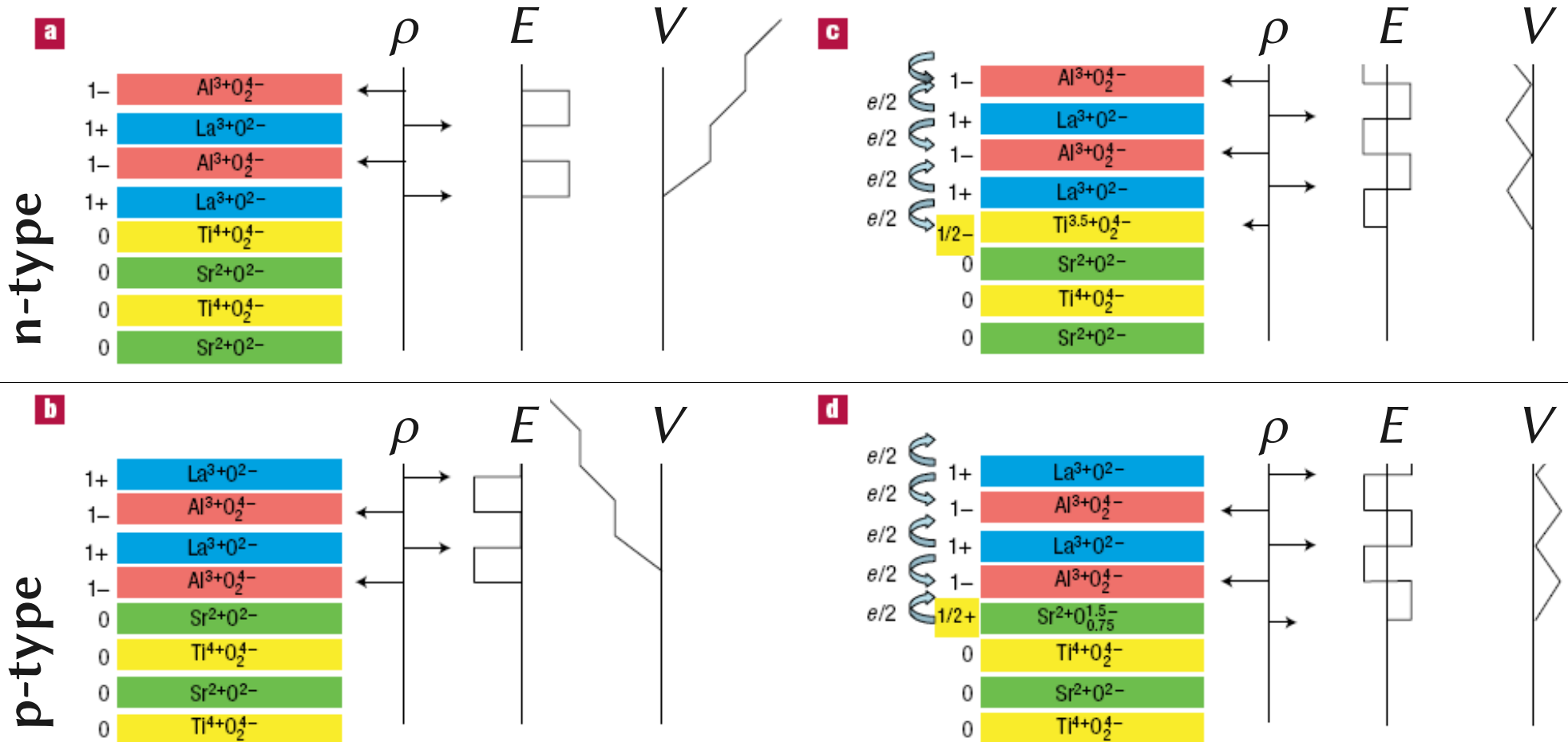
# Introduction and Motivation

- Depending on the preparation conditions, the system may be either **insulating** or **highly conducting**!
- In this study we simulated **plane-by-plane** epitaxial **growth** of  $\text{LaAlO}_3$  (001) films atop  $\text{SrTiO}_3$  (001) substrate. Calculated charge redistribution in the studied structures allows us to provide deeper insight into the origin of their conductivity.
- Calculated thermodynamic stability of  $\text{LaAlO}_3$  (001) surfaces offers a possible explanation of insulating behaviour for p-type interfaces.

# Structure and types of the interface



# The polar catastrophe



Nakagawa, N., *et al.* Why some interfaces cannot be sharp. *Nature Mat.* 5, 25

$\rho$  – charge density in each layer  
 $E$  – electric field projection on z-axis  
 $V$  – plane potential with respect to the first LAO plane

# Used approaches

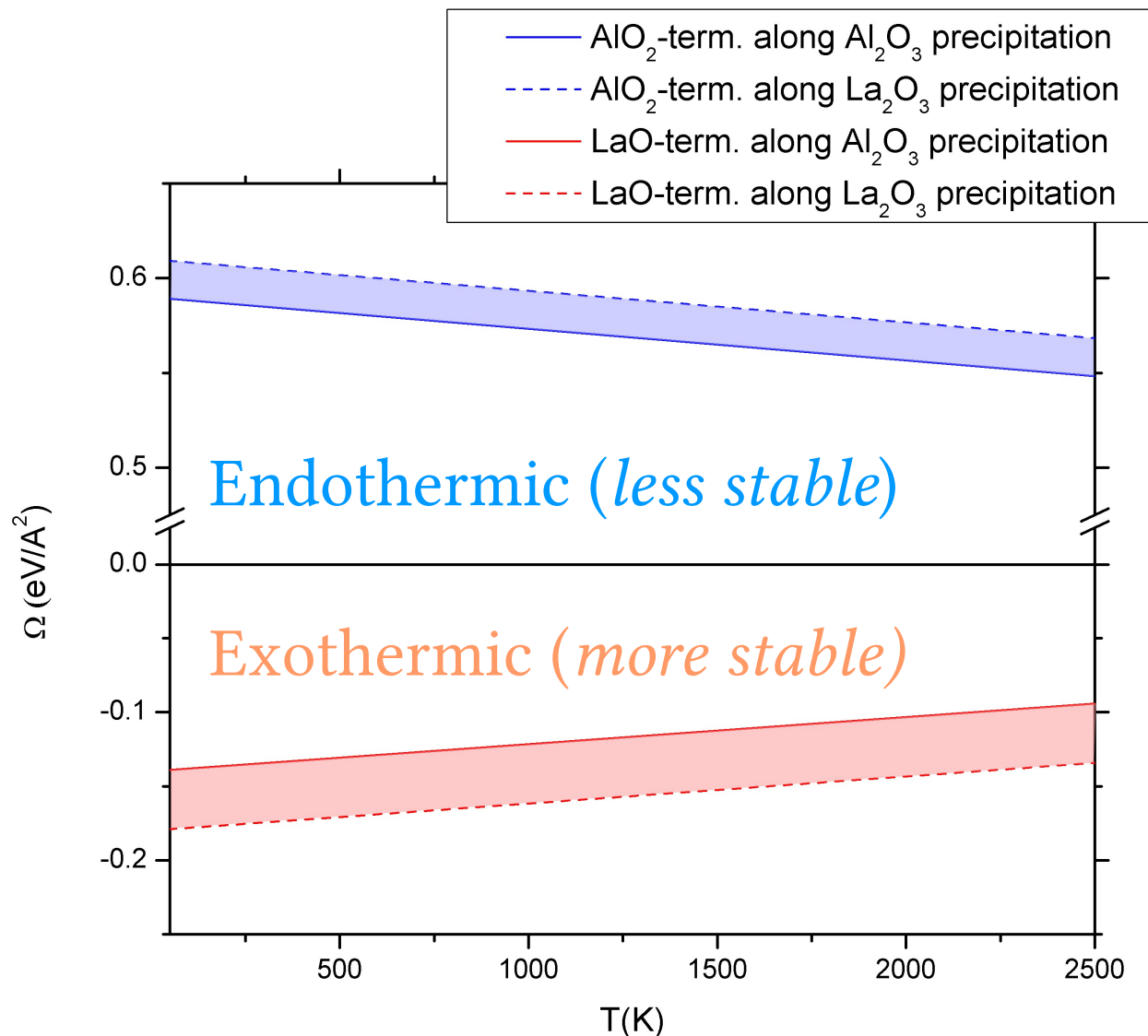
<b>Approach</b>	DFT LCAO	DFT Plane Waves
<b>Functional</b>	Hybrid B3PW	GGA PW91
<b>Comp. code</b>	CRYSTAL09	VASP5

# Pre-calculations

*Optical band gap as calculated by different Hamiltonians*

	LDA	PW GGA	B3PW	HF	Exp
SrTiO <sub>3</sub>	2.04	1.77	3.63	11.97	3.25
LaAlO <sub>3</sub>		3.18	6.15		6.5
BaTiO <sub>3</sub>	1.92	1.84	3.50	11.73	3.2
PbTiO <sub>3</sub>	1.40	1.56	2.87	10.01	3.4

# Thermodynamics of LAO (001) surfaces

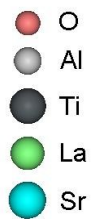


Thermodynamic grand potential as calculated by means of B3PW.

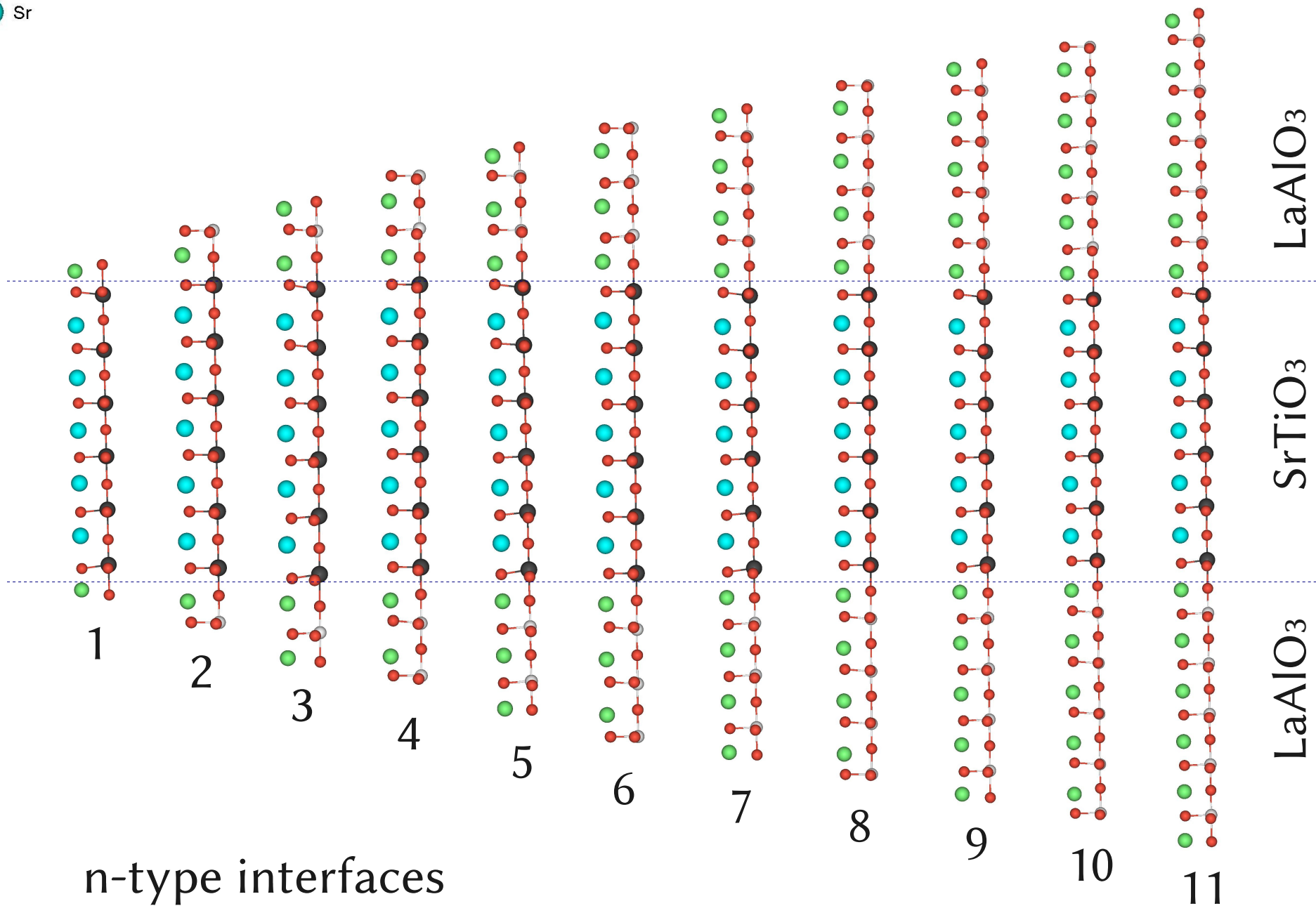
Picture is qualitatively the same for PW91-GGA functional

**LaO termination is more favourable.**





# Interfaces studied

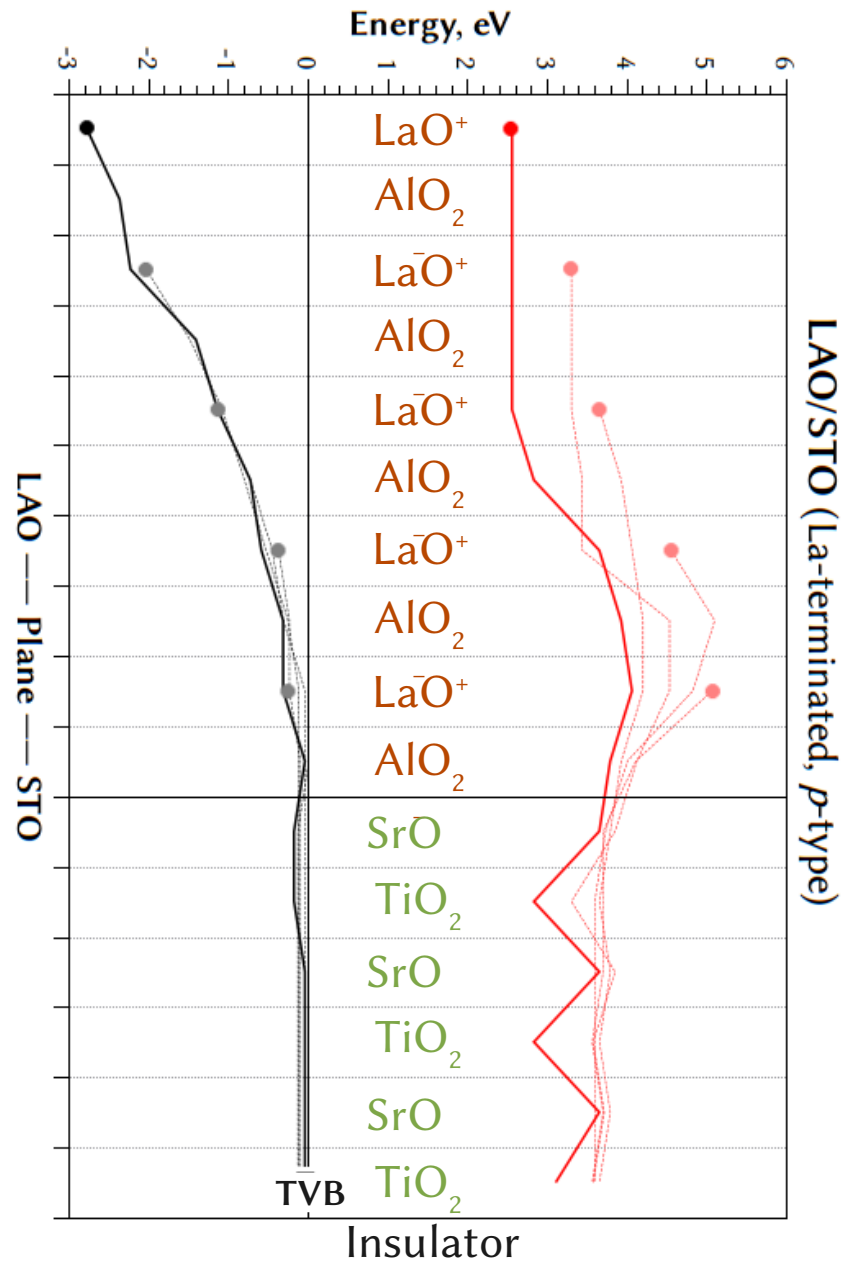
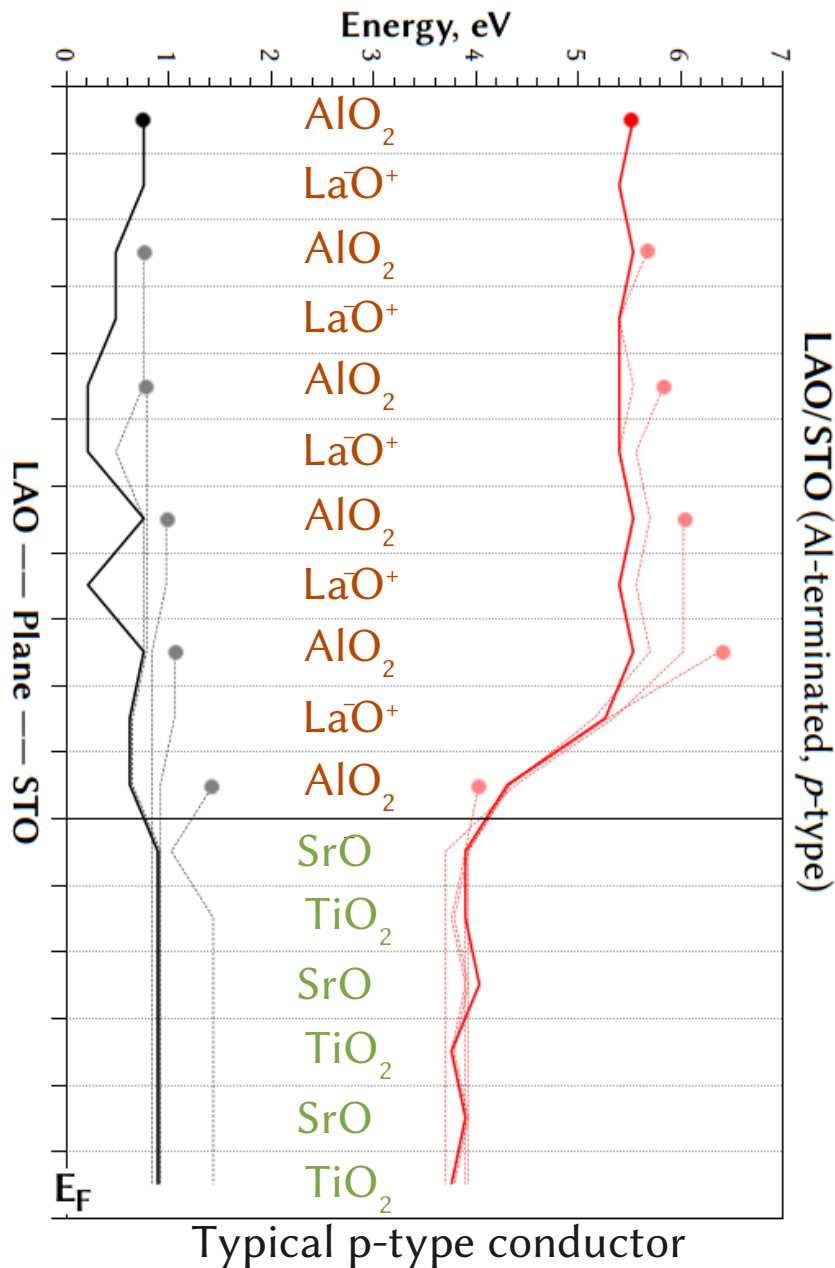


# Conductance of the system vs. termination

No. of planes	n-type	CRYSTAL	VASP	p-type	CRYSTAL	VASP
	Termination	Gap, eV	Gap, eV	Termination	Gap, eV	Gap, eV
1	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.
2	AlO <sub>2</sub> <sup>-</sup>	3.65	1.41	LaO <sup>+</sup>	4.00	1.60
3	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.
4	AlO <sub>2</sub> <sup>-</sup>	2.91	1.03	LaO <sup>+</sup>	4.05	1.69
5	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.
6	AlO <sub>2</sub> <sup>-</sup>	1.96	0.40	LaO <sup>+</sup>	4.05	1.51
7	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.
8	AlO <sub>2</sub> <sup>-</sup>	1.07	0.03	LaO <sup>+</sup>	3.80	0.48
9	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.
10	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.	LaO <sup>+</sup>	2.92	0.25
11	LaO <sup>+</sup>	Cond.	Cond.	AlO <sub>2</sub> <sup>-</sup>	Cond.	Cond.



# p-Type interfaces: band edges



# Electronic charge redistribution

n-Type			p-Type		
LaO <sup>+</sup>		<b>0.19</b>	AlO <sub>2</sub> <sup>-</sup>		<b>-0.28</b>
AlO <sub>2</sub> <sup>-</sup>	<b>0.26</b>	-0.50	LaO <sup>+</sup>	<b>0.08</b>	0.45
LaO <sup>+</sup>	-0.44	0.45	AlO <sub>2</sub> <sup>-</sup>	-0.38	-0.38
AlO <sub>2</sub> <sup>-</sup>	0.44	-0.48	LaO <sup>+</sup>	0.43	0.42
LaO <sup>+</sup>	0.47	0.48	AlO <sub>2</sub> <sup>-</sup>	-0.39	-0.38
AlO <sub>2</sub> <sup>-</sup>	-0.46	-0.48	LaO <sup>+</sup>	0.39	0.41
LaO <sup>+</sup>	0.47	0.49	AlO <sub>2</sub> <sup>-</sup>	-0.38	-0.38
AlO <sub>2</sub> <sup>-</sup>	-0.46	-0.47	LaO <sup>+</sup>	0.38	0.42
LaO <sup>+</sup>	0.48	0.49	AlO <sub>2</sub> <sup>-</sup>	-0.38	-0.38
AlO <sub>2</sub> <sup>-</sup>	-0.47	-0.46	LaO <sup>+</sup>	0.38	0.46
LaO <sup>+</sup>	0.52	0.44	AlO <sub>2</sub> <sup>-</sup>	-0.42	-0.38
TiO <sub>2</sub>	0.04	0.06	SrO	-0.02	-0.01
SrO	-0.05	-0.05	TiO <sub>2</sub>	0.02	0.02
	Cond.	Cond.		Insul.	Cond.

Calculated Mulliken effective net charge with respect to bulk for the thickest interfaces explored

# Summary and conclusion

- n-Type interfaces exhibit n-type conductance if terminated by LaO plane. If the structure is  $\text{AlO}_2$ -terminated, conductance appears only if the film is thicker than 5 u.c. in agreement with earlier studies.
- p-Type interfaces are insulators if LaO-terminated and p-type conductors otherwise.
- According to experiment p-Type interfaces are always insulating. This may occur due to the fact that LaO-terminated  $\text{LaAlO}_3$  (001) surfaces are thermodynamically more stable.
- Charge redistribution shows that an excess of electrons or holes, giving rise to conductivity, is concentrated in the topmost surface layer.