Pusvadītāju heterostruktūru kvantu mehāniskie aprēķini: $LaAlO_3$ plānās kārtiņas uz $SrTiO_3$ pamatnes – kā rodas vadāmība?

D. Bočarovs, A. Sorokins, V. Kaščejevs un S. Piskunovs

Eiropas Sociālā fonda projekts
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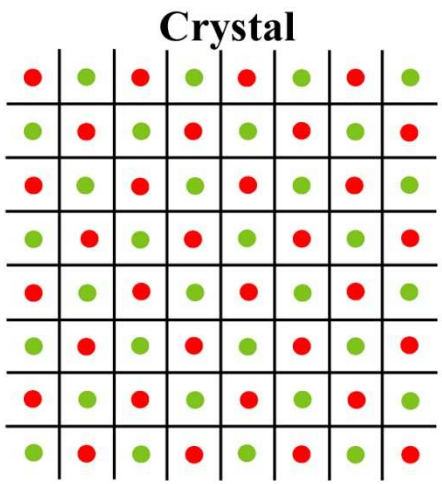
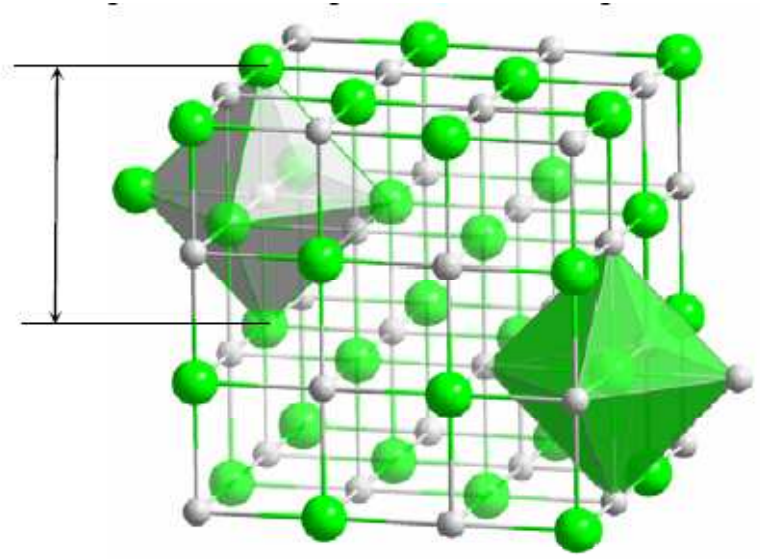
Outline of presentation

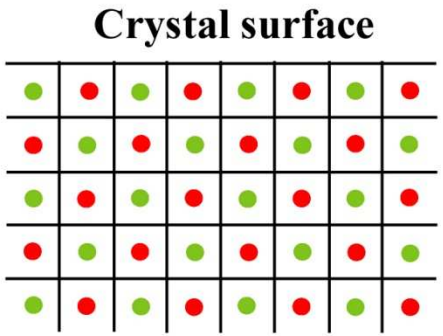
- Why $LaAlO_3/SrTiO_3$? An introduction.
- Modeling from first principles. Theoretical background in short.
- Stability of $LaAlO_3$(001) surfaces.
- $LaAlO_3/SrTiO_3$: Electronic structure and charge redistribution.
- Summary and conclusions.

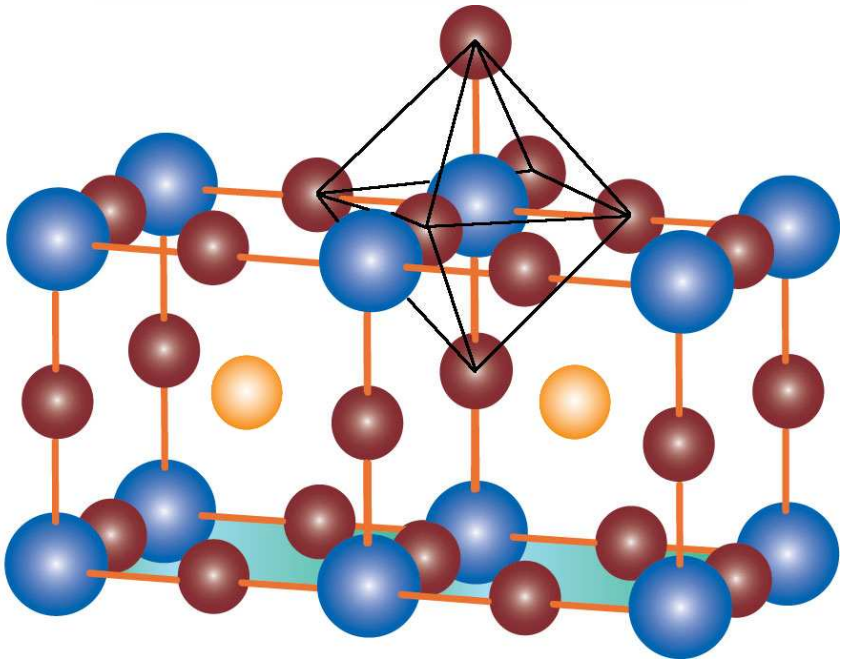
Crystals: $LaAlO_3$ and $SrTiO_3$





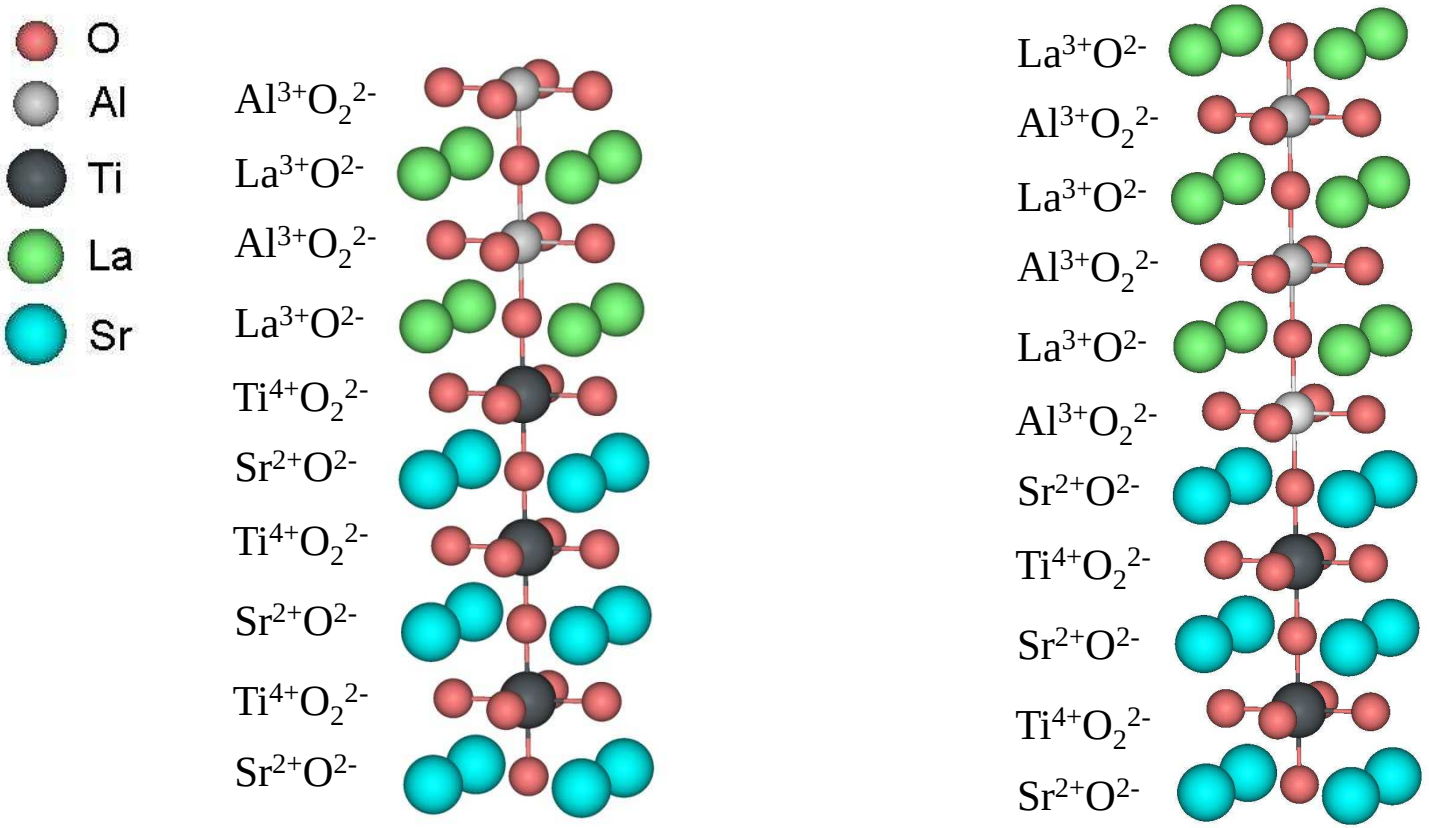
NaCl





ABO_3

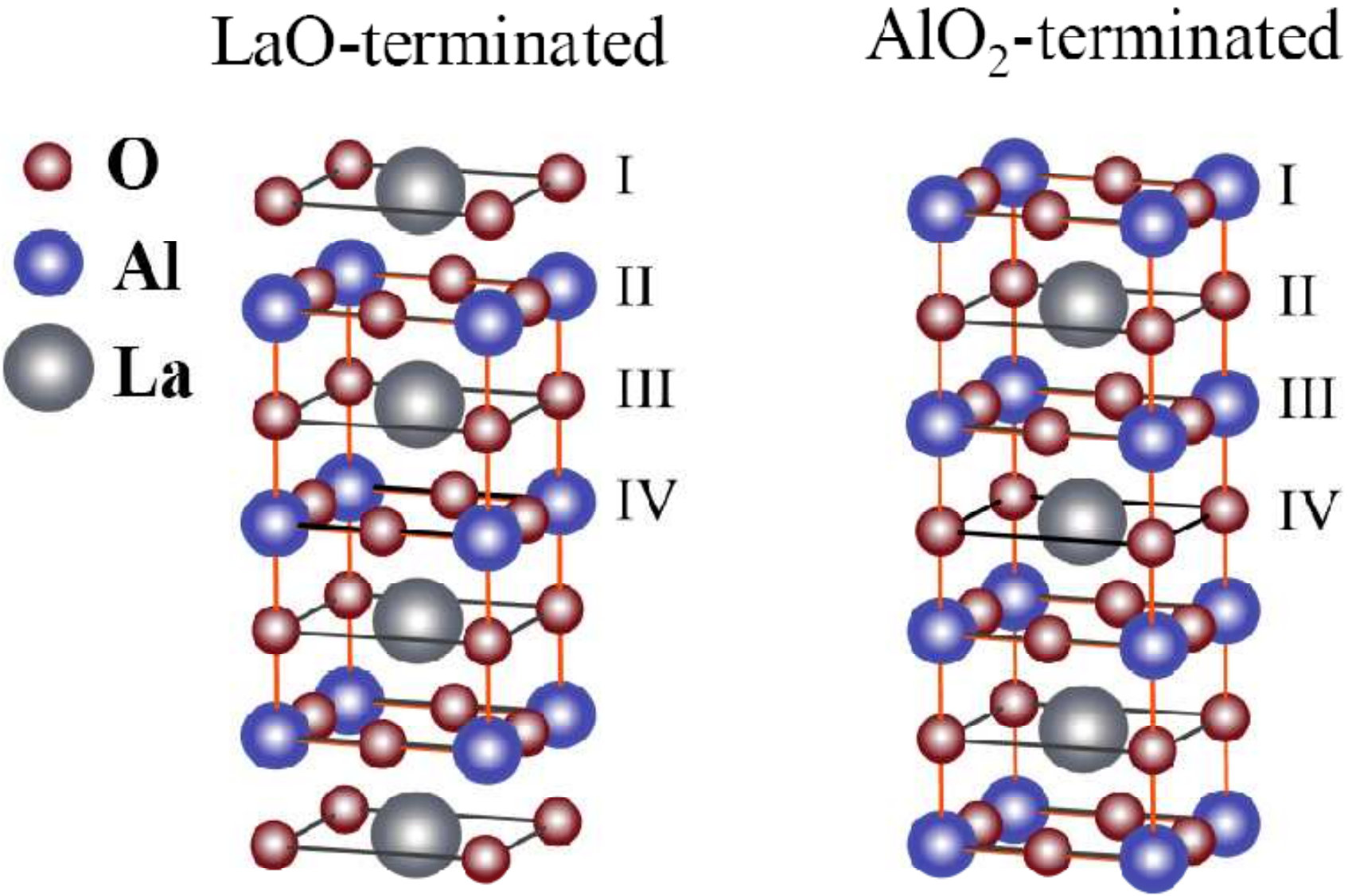
Why $LaAlO_3/SrTiO_3$? Motivation



The interface between the two band insulators $LaAlO_3$ and $SrTiO_3$ can be highly conducting...

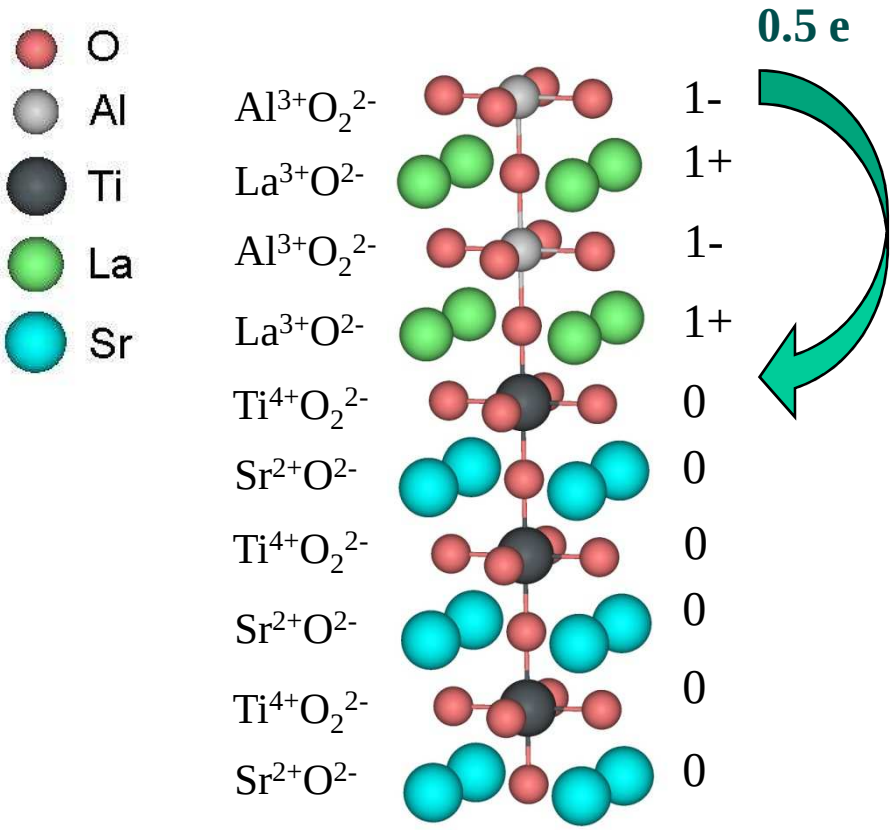
Ohtomo and Hwang, *Nature* **427** (2004) 423

Perfect $LaAlO_3$(001) surfaces: terminations

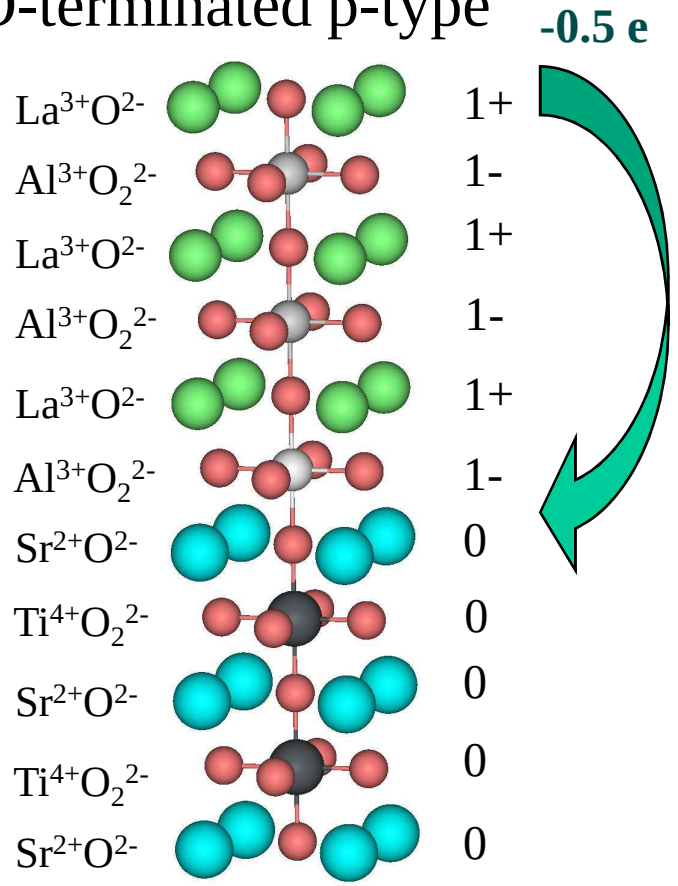


$LaAlO_3/SrTiO_3$?

AlO_2-terminated. n-type



LaO-terminated p-type



Why $LaAlO_3/SrTiO_3$? Motivation

- Depending on film thickness and preparation method $LaAlO_3/SrTiO_3$ interface can be **insulating** or exhibit high carrier mobility exceeding 10^4 cm^2 V^{-1} s^{-1} (O vacancies, La/Sr intermixing?)

- Hole-doped interface (p-type) is found to be insulating!

- Electronic structure calculations have contributed significantly, but the physical nature of the polar discontinuity at interface is still unclear.

- In this contribution we simulate plane-by-plane epitaxial growth of $LaAlO_3$ thin film atop $SrTiO_3$. Calculated electron charge redistribution at the interface allows us to provide deeper insight into the origin of its conductivity.

Theoretical background: Hartree-Fock method

Wave functions as Slater determinants:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1)\\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N)\end{vmatrix}$$

Hartree-Fock equation ($\hbar = m = e = 1$):

$$\left[-\frac{1}{2}\nabla_i^2+\sum_\alpha\frac{-Z_\alpha}{|\mathbf{R}_\alpha-\mathbf{r}|}+\int\frac{\sum_j^N\phi_j(\mathbf{r}')\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right]\phi_i(\mathbf{r})-\int\frac{\sum_j^N\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}')d\mathbf{r}'=\varepsilon_i\phi_i(\mathbf{r})$$

$$\hat{H}^{HF}=\hat{T}(\mathbf{r};\mathbf{k})+\hat{V}(\mathbf{r};\mathbf{k})+\hat{J}(\mathbf{r};\mathbf{k})+\hat{K}(\mathbf{r};\mathbf{k})$$

$\hat{T}$, $\hat{V}$, $\hat{J}$ and $\hat{K}$ are kinetic, electron-nuclei, Coulomb and non-local exchange operators

Electron correlation problem!!!

Theoretical background: Density Functional Theory

The expectation value of a Hamiltonian, i.e. the total energy *in the ground state*, is a functional of the *electronic density*.

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})]$$

The Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_\alpha \frac{-Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$\text{with} \quad \rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

Approximations for E_{xc}:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))d\mathbf{r} \;;\; E_{xc}^{GGA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r}$$

Theoretical background: Hybrid exchange-correlation functionals

$$E_{XC}^{Hybrid}(\rho) = a_{HF} E_X^{HF}(\rho) + a_{DFT} E_{XC}^{DFT}(\rho)$$

$$E_{XC} = E_{XC}^{LSDA} + a_0\left(E_X^{Fock} - E_X^{LSDA}\right) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{GGA}$$

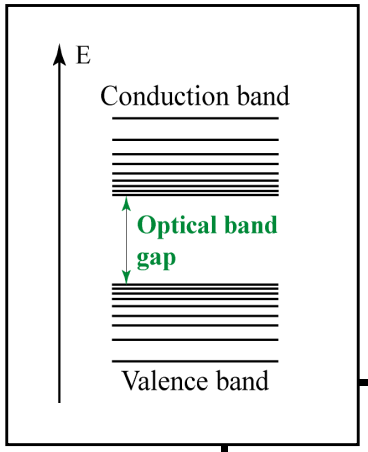
Semiempirical coefficients $a_0 = 0.20, \quad a_X = 0.72, \quad a_C = 0.81$

GGA correlation ⇒ Lee, Yang, and Parr = B3LYP

Perdew and Wang = B3PW

- A.D.Becke, *J.Chem.Phys.* **98** (7), 5648 (1993)
- C.Lee, W.Yang, R.G.Parr, *Phys. Rev. B* 37 (2), 785 (1988)
- J.P.Perdew, Y.Wang, *Phys. Rev. B* 45 (23), 13244 (1992)

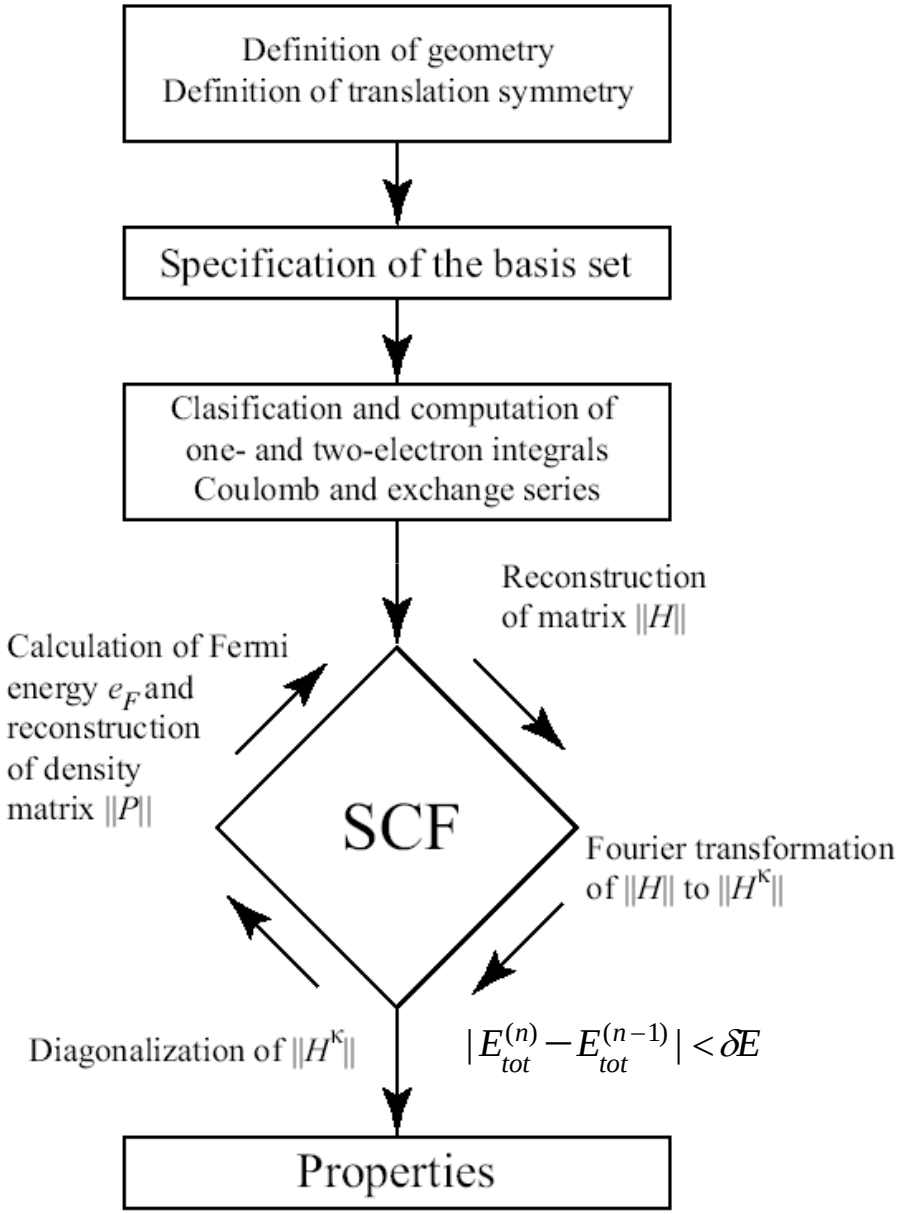
Results on bulk perovskites: Optical band gap



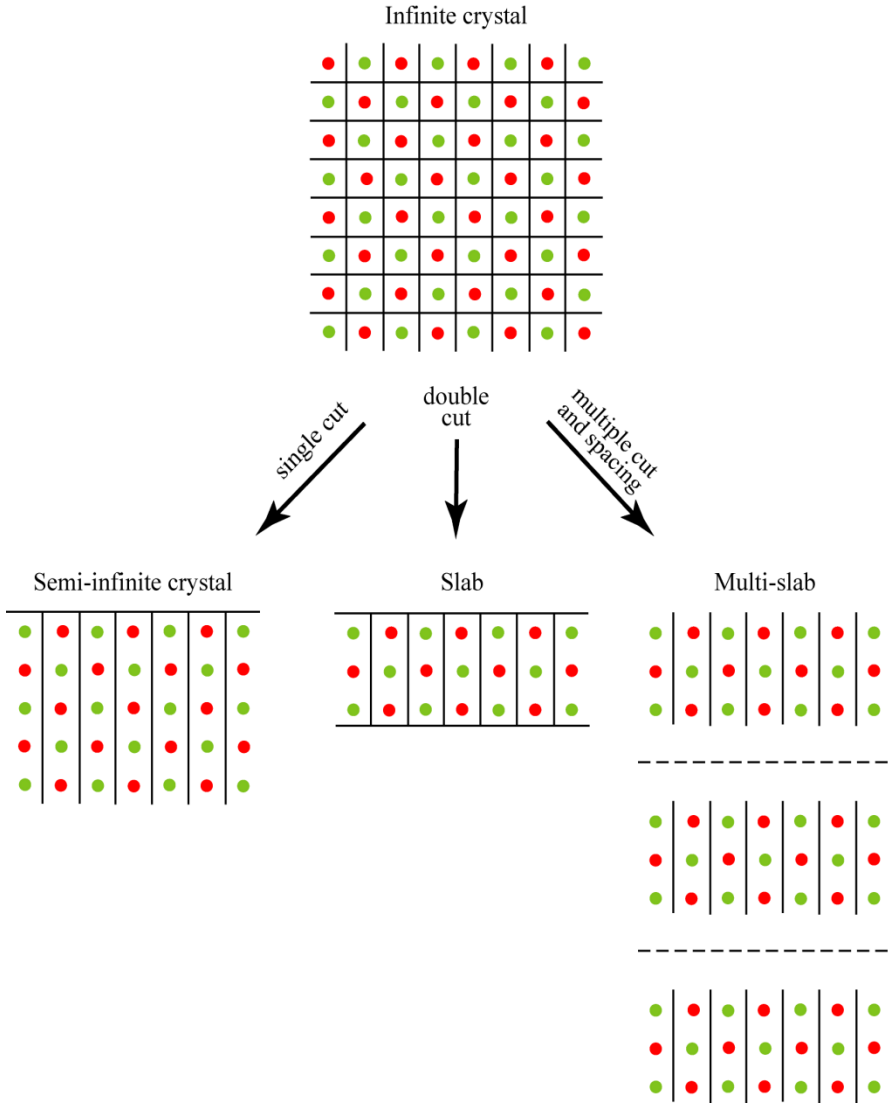
The calculated optical band gap (eV) by means of different Hamiltonians.

	LDA	GGA	B3PW	B3LYP	HF	Exp.
$SrTiO_3$	2.04	1.97	**3.63**	**3.57**	11.97	**3.25**
$LaAlO_3$			**6.15**			**6.5**
$BaTiO_3$	1.92	1.84	**3.50**	**3.42**	11.73	**3.2**
$PbTiO_3$	1.40	1.56	**2.87**	**2.92**	10.01	**3.4**

Flow chart of the CRYSTAL code



Perfect $LaAlO_3$(001) surfaces: Choosing of model



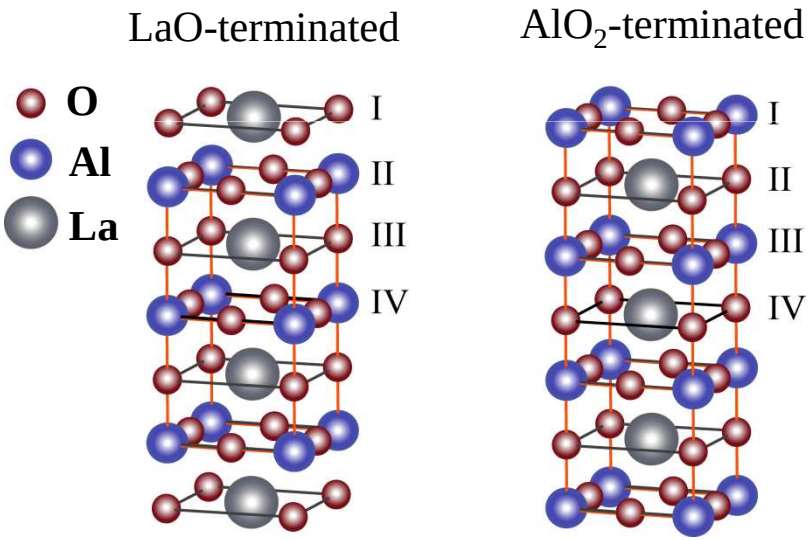
Models for simulating surfaces starting from a perfect 3D crystal.

Slab model:

Less computationally demanding

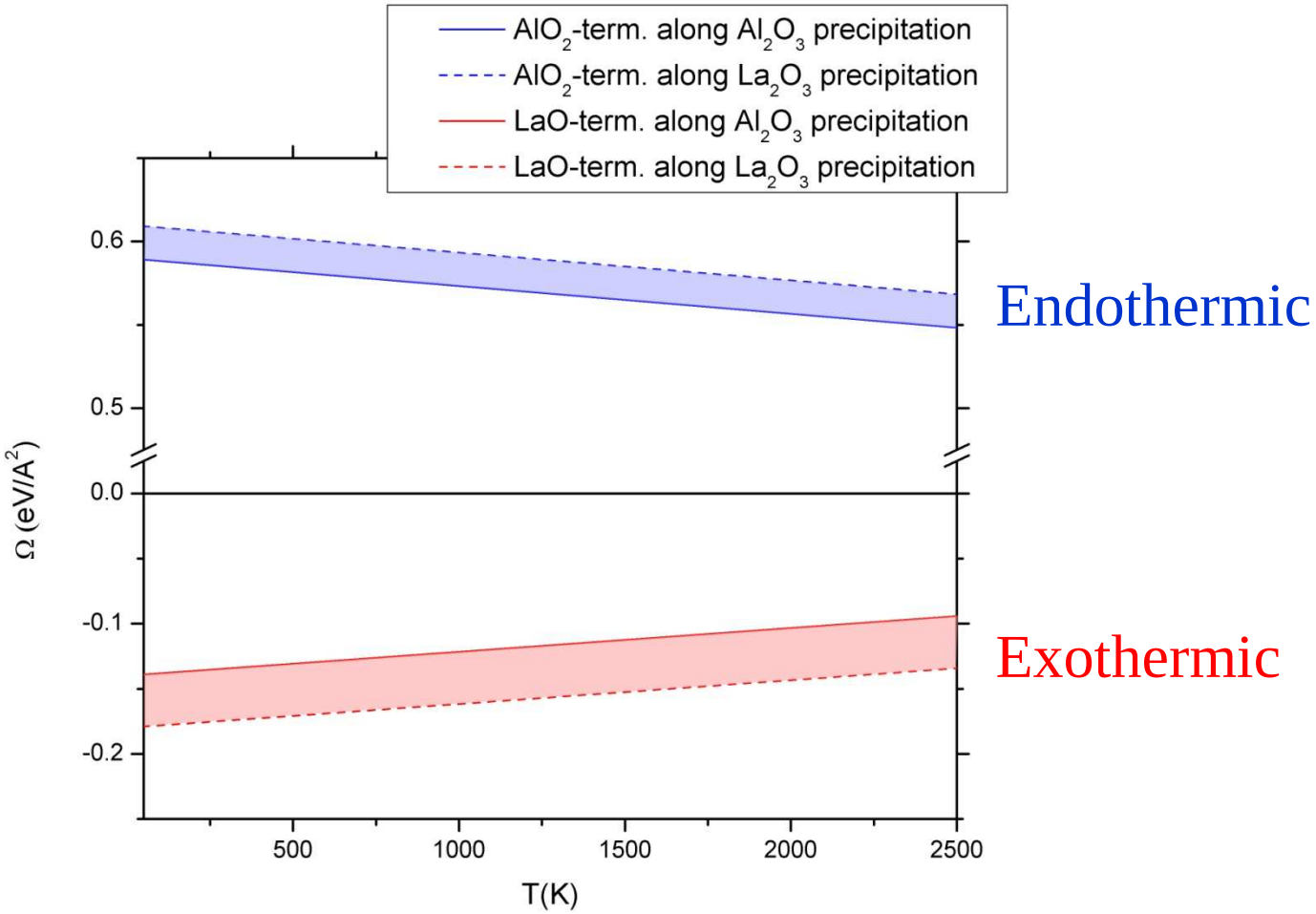
No spurious interactions

Proper boundary conditions



(001) slab unit cells periodicaly repeated in *x-y* plane as adopted in present calculations.

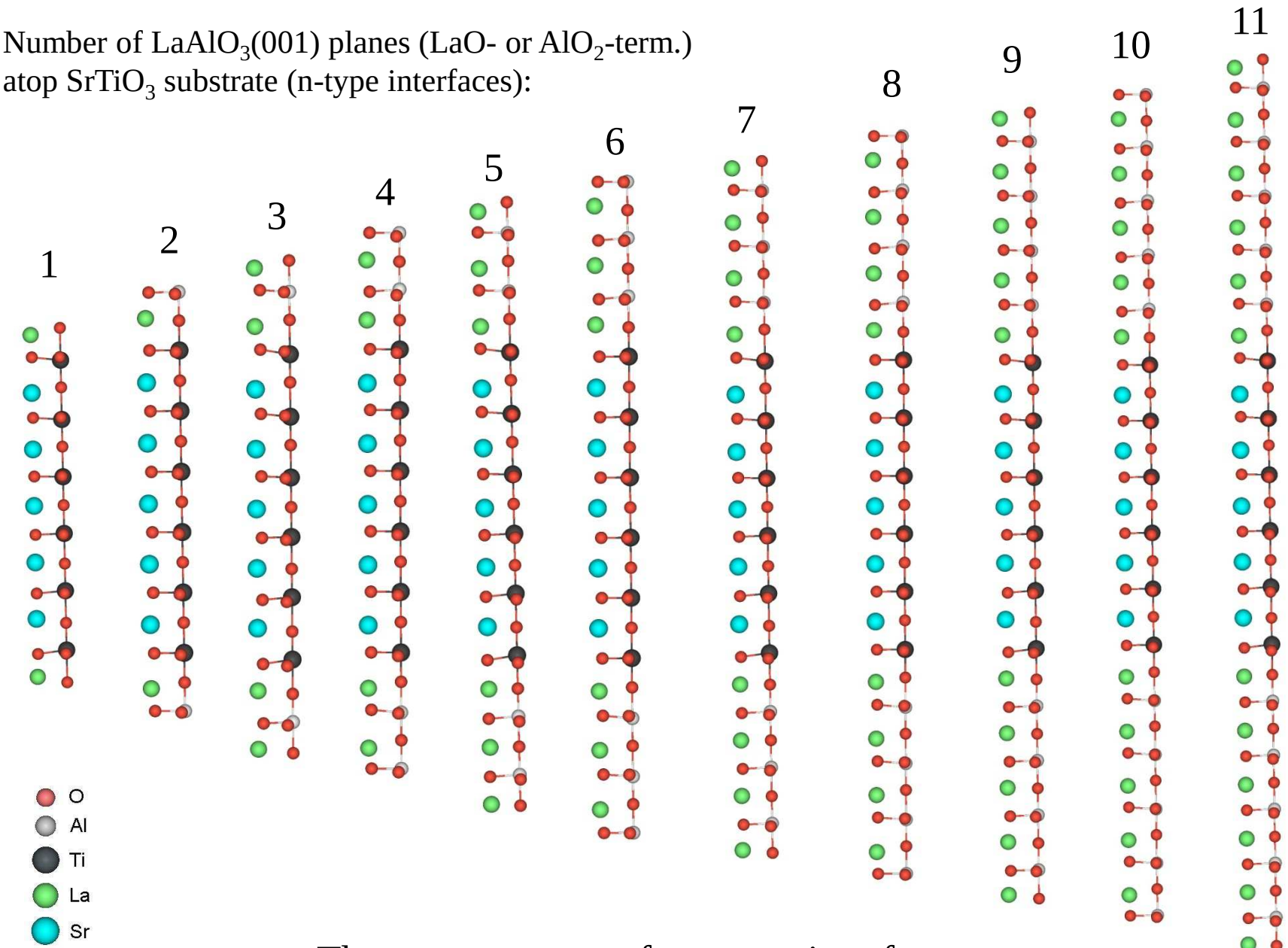
Thermodynamic stability of perfect $LaAlO_3(001)$ surfaces



Thermodynamic grand potential for $LaAlO_3(001)$ as calculated by means of B3PW. Formation of LaO-terminated surface is **exothermic** reaction.

$LaAlO_3/SrTiO_3(001)$ surfaces structures we study

Number of $LaAlO_3(001)$ planes (LaO- or AlO_2-term.) atop $SrTiO_3$ substrate (n-type interfaces):

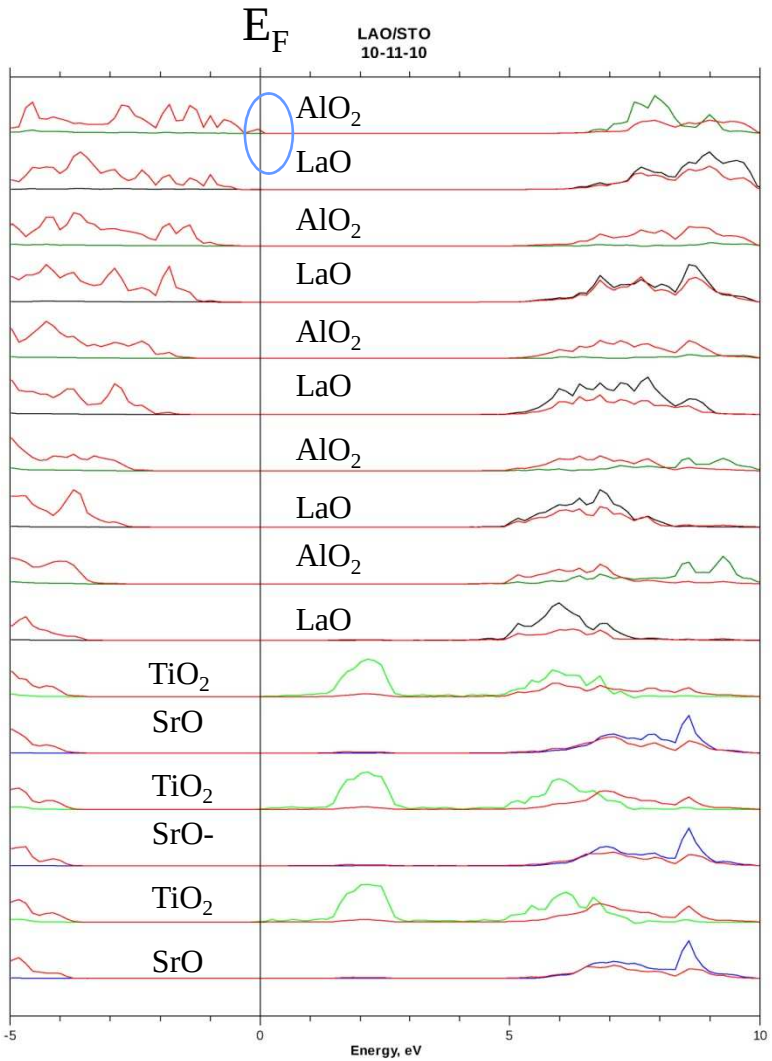


The same sequence for p-type interfaces.

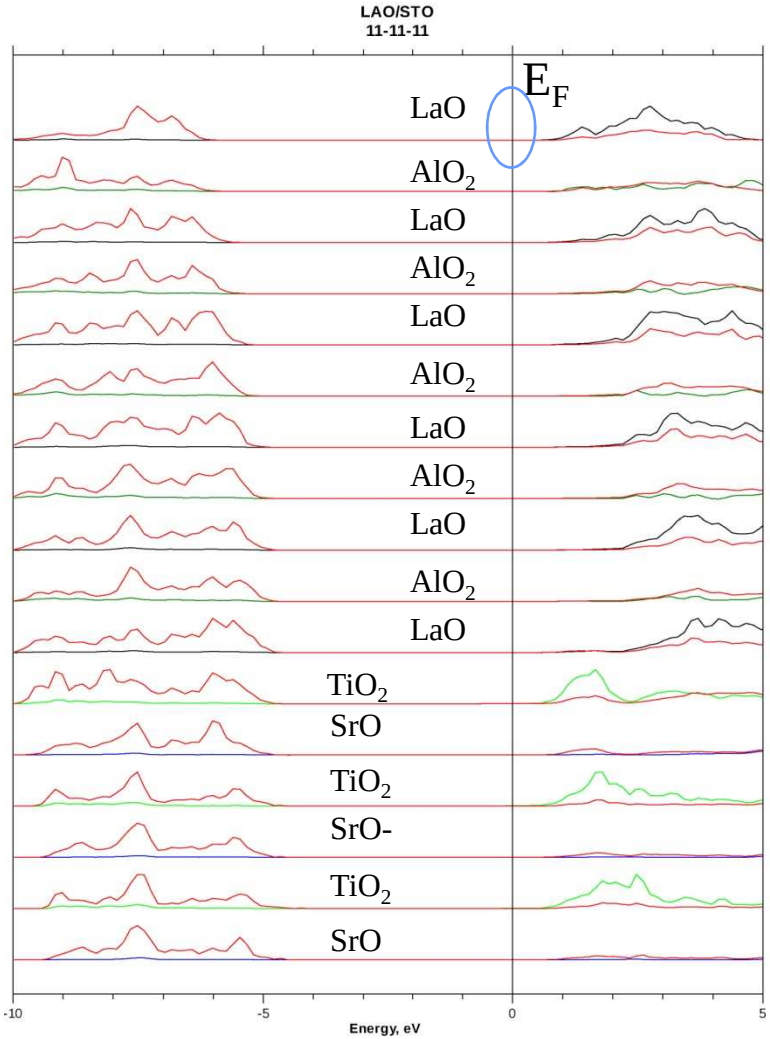
$LaAlO_3/SrTiO_3(001)$: Conductance *vs.* termination

	n-type		p-type	
Nr. of planes	Termination	Gap, eV	Termination	Gap, eV
1	LaO-	Cond.	AlO_2-	Cond.
2	AlO_2-	3.65	LaO-	4.00
3	LaO-	Cond.	AlO_2-	Cond.
4	AlO_2-	2.91	LaO-	4.05
5	LaO-	Cond.	AlO_2-	Cond.
6	AlO_2-	1.96	LaO-	4.05
7	LaO-	Cond.	AlO_2-	Cond.
8	AlO_2-	1.07	LaO-	3.80
9	LaO-	Cond.	AlO_2-	Cond.
10	AlO_2-	**Cond.**	LaO-	2.92
11	LaO-	Cond.	AlO_2-	Cond.

$LaAlO_3/SrTiO_3(001)$ of n-type: PDOS

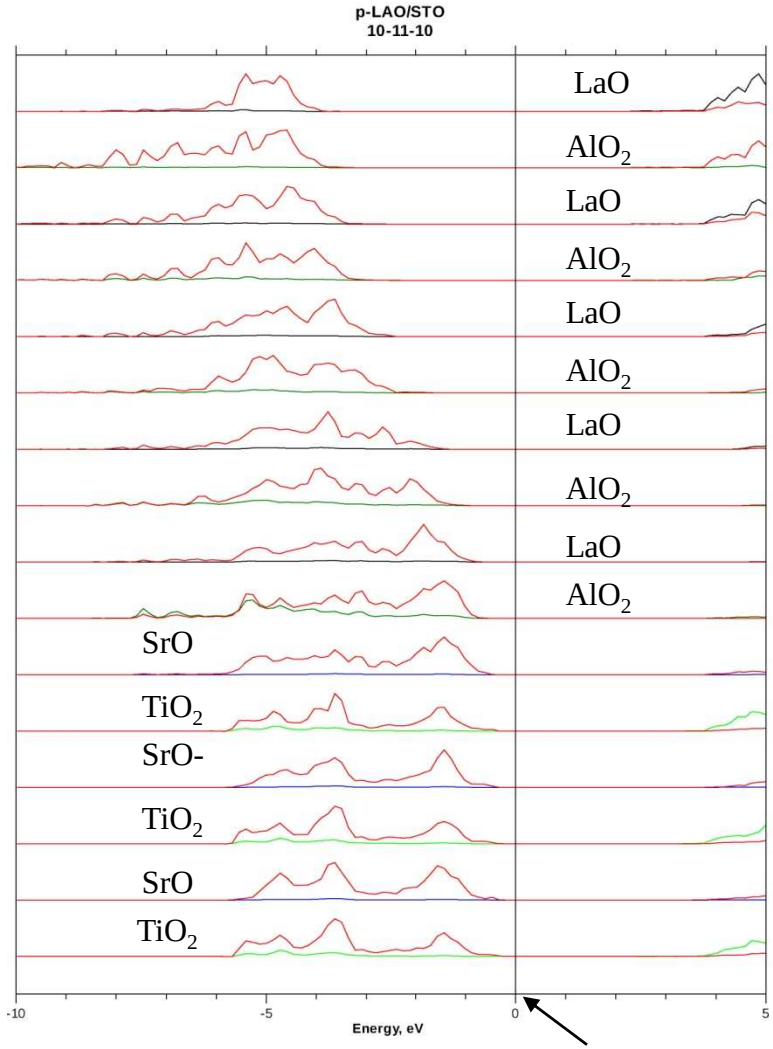


Conductance due to closing the gap.

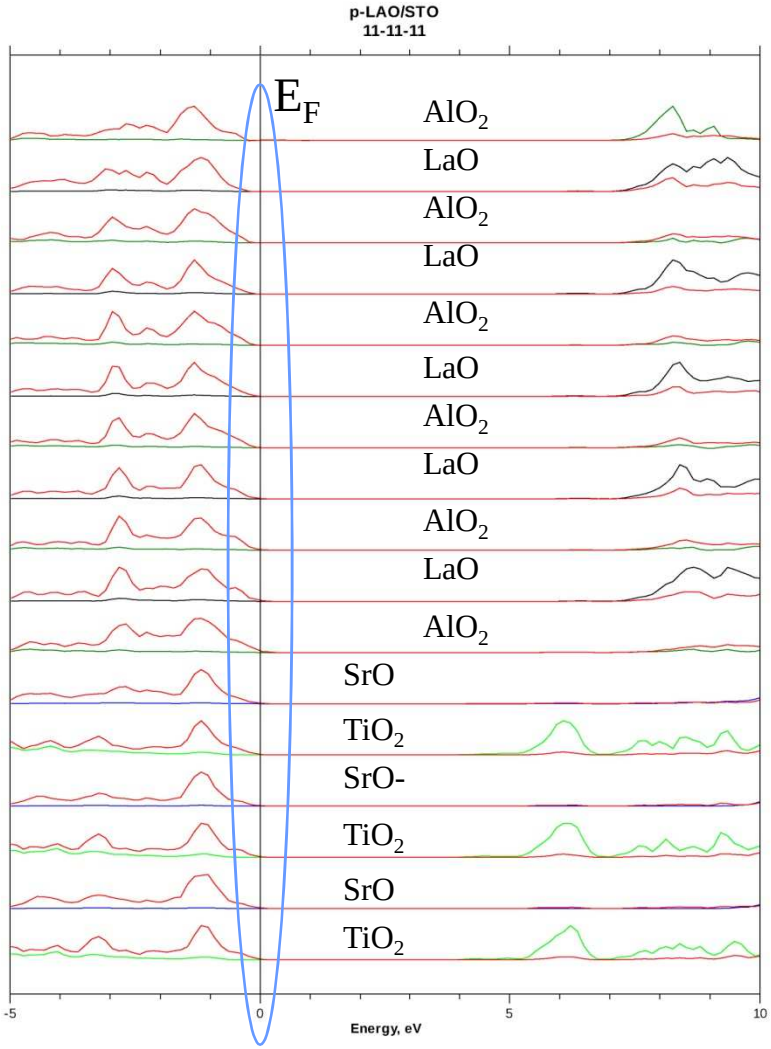


Typical n-type conductor

$LaAlO_3/SrTiO_3$(001) of p-type: PDOS



Top of VB
(insulator)



Typical p-type conductor

$LaAlO_3/SrTiO_3(001)$: electron charge redistribution

	n-type	Cond.		p-type	Cond.
LaO	**Cond.**	**0.19**	AlO_2	**Ins.**	**-0.28**
AlO_2	-0.26	-0.50	LaO	0.08	0.45
LaO	0.44	0.45	AlO_2	-0.38	-0.38
AlO_2	-0.44	-0.48	LaO	0.43	0.42
LaO	0.47	0.48	AlO_2	-0.39	-0.38
AlO_2	-0.46	-0.48	LaO	0.39	0.41
LaO	0.47	0.49	AlO_2	-0.38	-0.38
AlO_2	-0.46	-0.47	LaO	0.38	0.42
LaO	0.48	0.49	AlO_2	-0.38	-0.38
AlO_2	-0.47	-0.46	LaO	0.38	0.46
LaO	0.52	0.44	AlO_2	-0.42	-0.38
TiO_2	0.04	0.06	SrO	-0.12	-0.01
SrO	-0.05	-0.05	TiO_2	0.02	0.02

Calculated Mulliken effective net charge with respect to bulk.

Summary and conclusions

- **Quantum chemistry accompanied with *ab initio* thermodynamics is a reliable tool to predict stability and electronic properties of a complex surface structures such as $LaAlO_3/SrTiO_3$ heterointerface.**
- **LaO-terminated $LaAlO_3$(001) is the most stable surface at elevated temperatures.**
- **Our calculations predict the conductance for AlO_2-term. n-type interface due to closing of the band gap if the $LaAlO_3$(001) film is thicker than 5 u.c., while LaO-term n-type interface is typical n-type conductor. LaO-term. p-type interface is always insulator. However AlO_2-term. p-type heterostructure is predicted to be a p-type conductor.**

Many Thanks For Your Attention!