FIRST-PRINCIPLES MODELING OF OXYGEN INTERACTION WITH ABO_3-TYPE PEROVSKITE SURFACES

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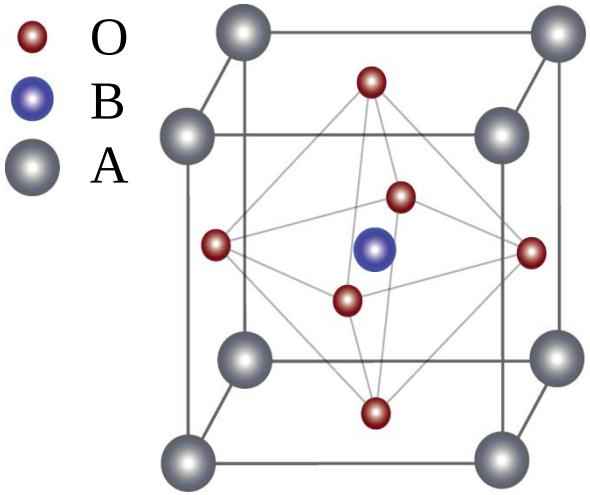
Motivation:

- Oxygen adsorption on ABO_3 surfaces:
  - gas sensors,
  - photocatalysis,
  - fuel cells,
  - ...

- Excellent model materials for simulations on more complex perovskite solid solutions.

ABO_3 perovskites we study:



A = Sr^{2+}, La^{3+}

B = Ti^{4+}, Mn^{3+}

O = O^{2-}

Oxygen adsorption at (001) surface of:

- $SrTiO_3$
- $LaMnO_3$
- $La_{0.875}Sr_{0.125}MnO_3$ (LSM)

Computational details

Hybrid exchange-correlation functional within DFT

$$E_{XC} = E_{XC}^{LSDA} + 0.2\left(E_X^{Fock} - E_X^{LSDA}\right) + 0.72\Delta E_X^{B88} + 0.81\Delta E_C^{PWGGA,LYP}$$

B3PW, B3LYP → A.D. Becke, *J. Chem. Phys.* **98** (1993) 1372, 5648.

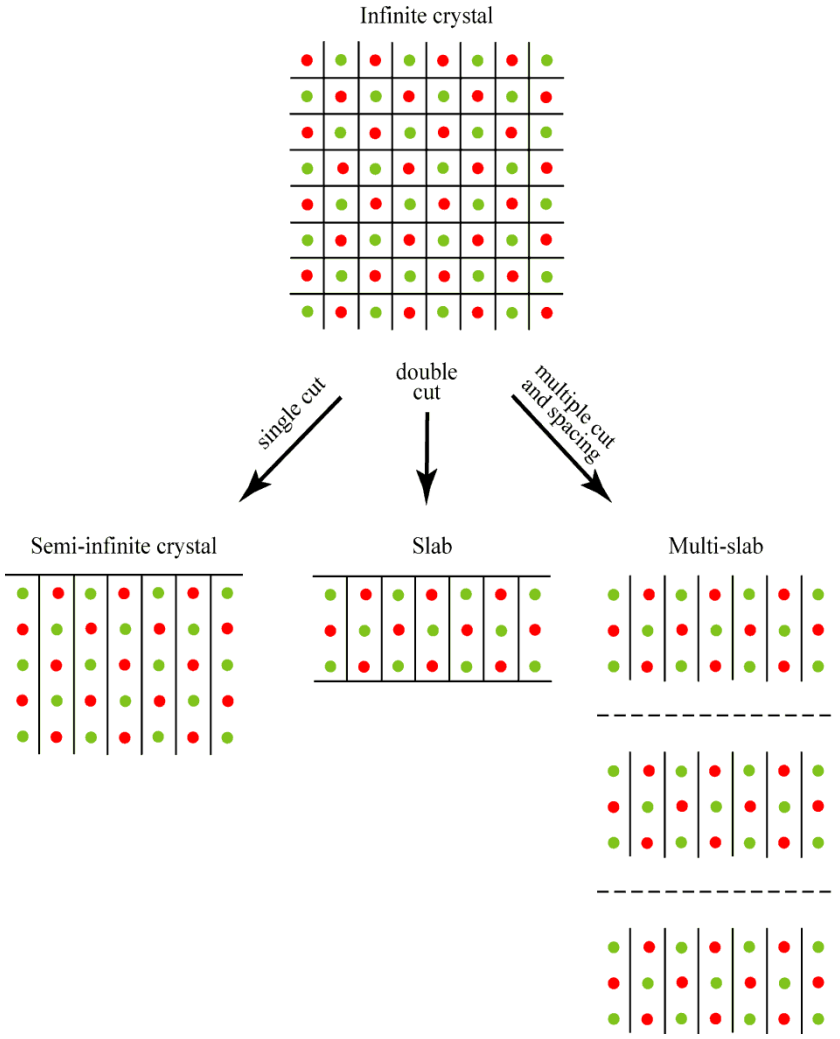
- Computer code: CRYSTAL (http://www.crystal.unito.it/).
- Method: LCAO(CO)-GTF.
- Basis sets adopted:

$SrTiO_3$: S. Piskunov *et al.*, *Comp. Mat. Sci.* **29** (2004) 165,

$LaMnO_3$, LSM: S. Piskunov *et al.*, *Phys. Rev. B* **76** (2007) 012410.

LCAO results have been critically compared with those obtained by means of PBE-GGA PW method (VASP code)

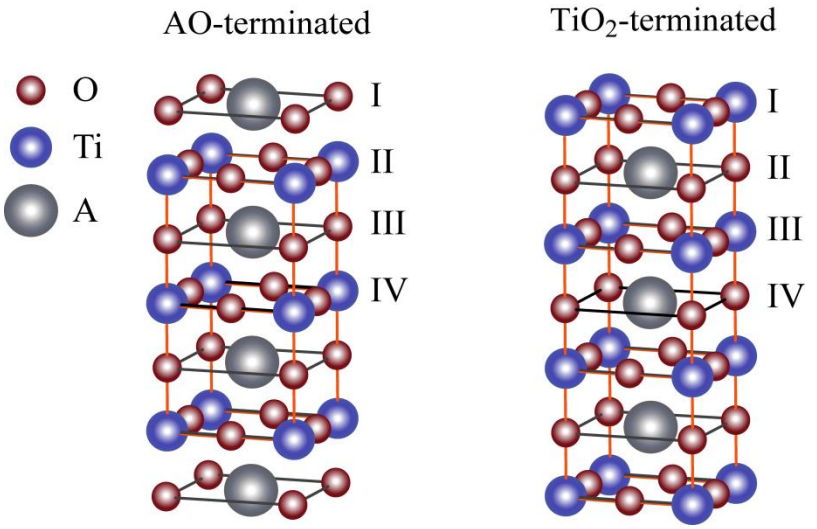
Modeling



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

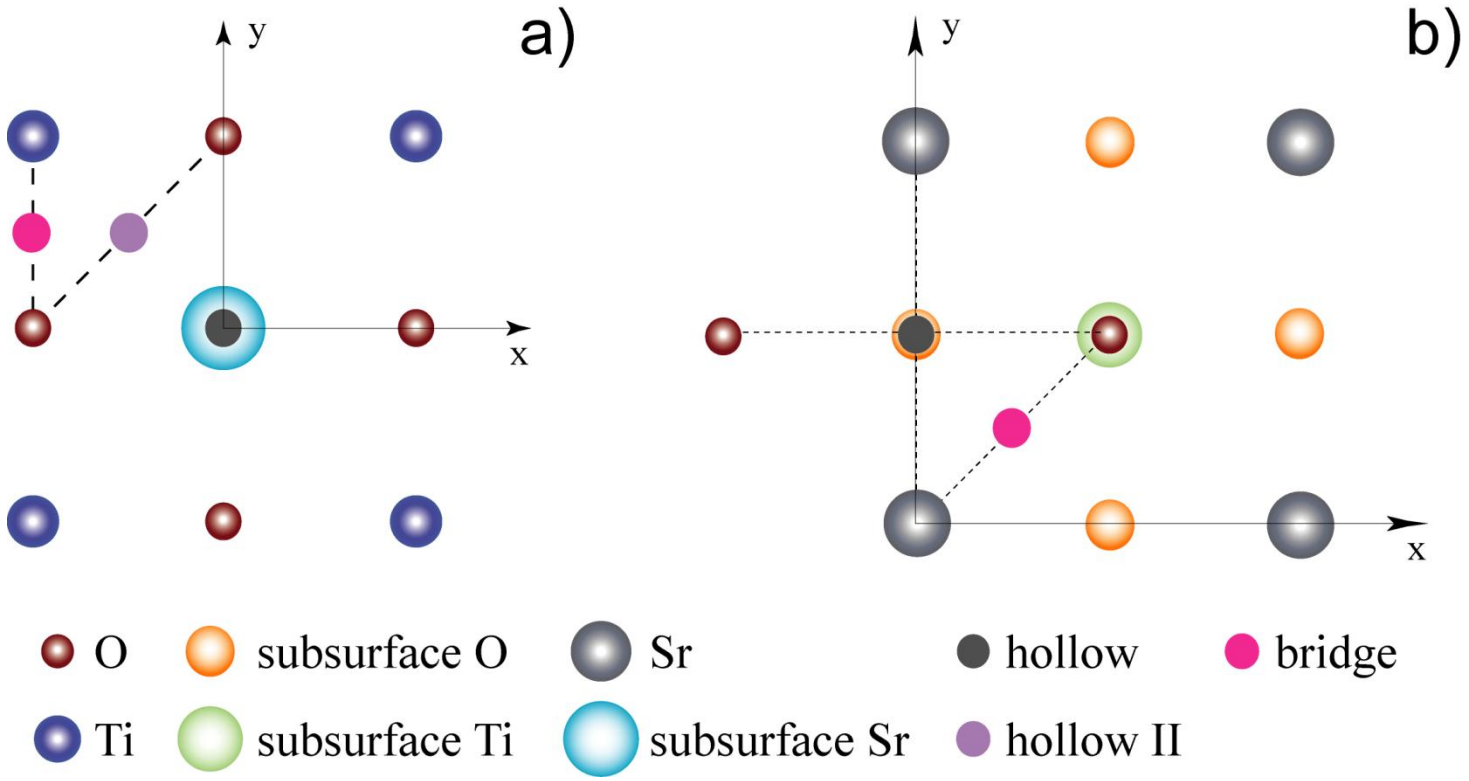
Slab model:

- **Less computationally demanding**
- **No spurious interactions**
- **Proper boundary conditions**
- **For adsorption Super Cell approach have been used**



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

Examined adsorption sites ($SrTiO_3$ (001), top view)



Top views of a) TiO_2- and b) SrO-terminated surfaces with the possible positions for oxygen adsorption.

Atomic oxygen adsorption over $SrTiO_3$(001): Energy of adsorption

$$E_{ads} = \frac{1}{2}\left(E_{tot}^{system} - E_{tot}^{slab} - 2E_{tot}^{O_{triplet}}\right)$$

Site	PW PBE	LCAO B3PW	Site	PW PBE	LCAO B3PW
TiO_2-termination			SrO-termination		
Ti	**2.13**	**0.70**	Sr	0.57	0.37
O	2.51	1.76	O	2.44	1.54
bridge	2.96	2.03	bridge	3.06	2.43
hollow II	0.12	0.93	hollow	1.73	1.08

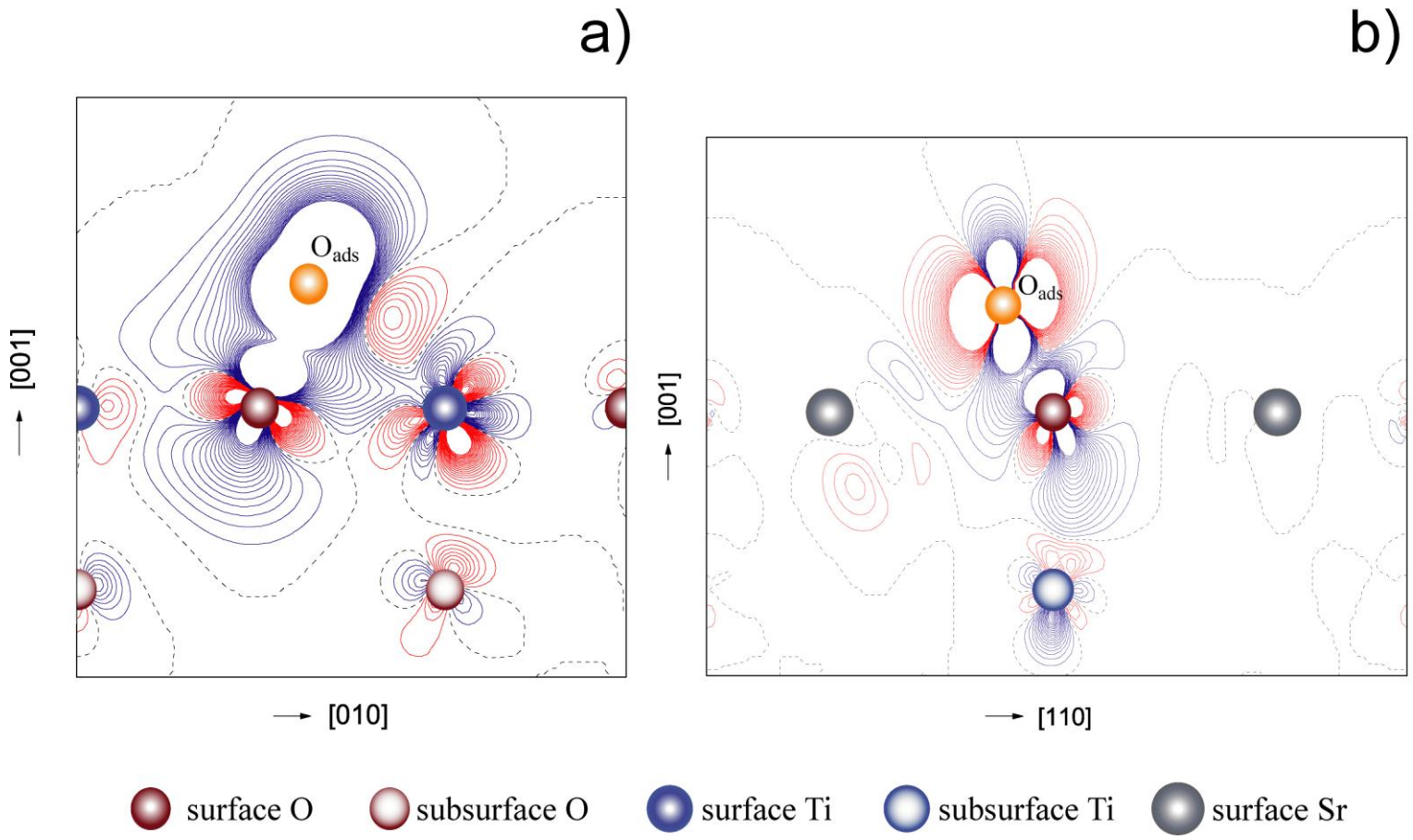
Calculated adsorption energies (in eV) in pure DFT plane wave method with the PBE functional (PW-PBE, VASP code) and in the hybrid HF-DFT LCAO method with the B3PW functional (LCAO-B3PW, CRYSTAL code). The adsorbed oxygen atom was considered in the ground (triplet) state.

Atomic oxygen adsorption over $SrTiO_3$(001): Atomic charge

Site	PW PBE			LCAO B3PW		
	O_{ads}	O_{surf}	$Ti(Sr)_{surf}$	O_{ads}	O_{surf}	$Ti(Sr)_{surf}$
TiO_2-termination						
O	-1.39	-1.31	2.05	-0.62	-0.77	2.29
bridge	-1.51	-1.29	2.13	-0.52	-0.79	2.28
SrO-termination						
O	-1.24	-0.89	2.03	-0.71	-0.90	1.86
bridge	-1.29	-1.18	1.56	-0.84	-0.88	1.85

Effective atomic charges in *e* (Bader analysis in PW-PBE and Mulliken analysis in LCAO-B3PW) for the adsorbed oxygen atom and the nearest surface O and Ti (or Sr) atoms for optimized adsorption structures of $SrTiO_3$ (001) substrates. Atomic charges at the pristine surface layer -- PW-PBE: **Ti 2.03**, **O -0.84** (TiO_2 termination); **Sr 1.56**, **O -0.72** (SrO termination); LCAO-B3PW: **Ti 2.31**, **O -1.32**; **Sr 1.84**, **O -1.52**.

Electronic charge redistribution for atomic oxygen atop bridge sites of $SrTiO_3(001)$



Two-dimensional difference electron density maps for O_{ads} over bridge site at a) TiO_2- and b) SrO-terminated surfaces. Black, red and blue isolines correspond to the zero, positive and negative values of electron density, respectively.

Adsorption of molecular oxygen

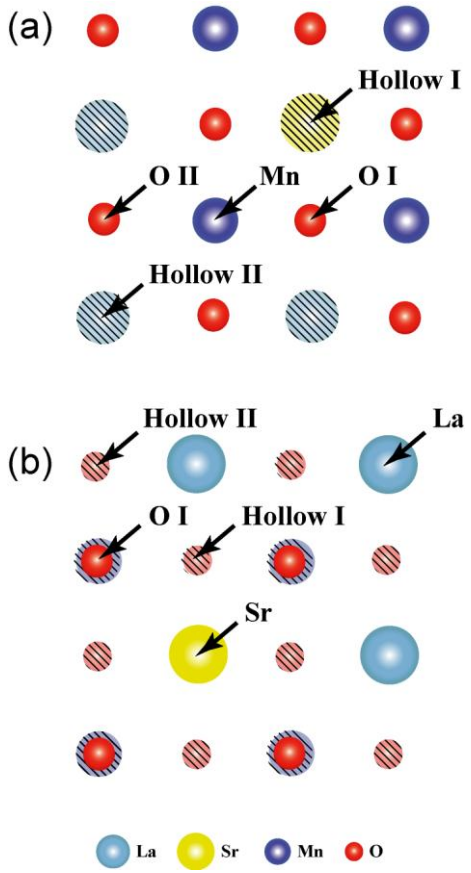
- O_2 in triplet state adsorbs on **hollow** sites. E_{ads} = 0.02 eV for adsorption on SrO-term. surface, and 0.09 eV if TiO_2 termination is considered. **VASP yields 0.25 eV for bridge position.**
- **No** charge transfer between adsorbate and surface.
- Distance between surface and adsorbate ~ 3 Å.
- Invariance of the O_2 bond length.
- **Weak physisorption.**

ABO_3 adsorption: atomic oxygen

Calculated by means of LCAO E_{ads} (in eV) with respect to atomic O

Adsorption site "atop":	$SrTiO_3$	$LaMnO_3$	LSM
MnO_2-terminated (001)			
Mn/Ti	-0.70	-4.11*	-3.90
OI	-1.76	-1.96	-1.81
OII	--	--	-2.17
Hollow I	-0.93	-1.78	-1.72
Hollow II	--	--	-1.91
La(Sr)O-terminated (001)			
La	--	-3.51	-2.98
Sr	-0.37	--	-2.64
O	-1.54	-2.22	-2.33
Hollow I	-1.08	-4.43	-3.91
Hollow II	--	--	-4.14

- **VASP GGA calculations yield -4.02 eV (Kotomin *et al.*, PCCP 2008, 10, 4644)**



Adsorption sites: (a) MnO_2- and (b) La(Sr)O-term. Hatched atoms are from subsurface atomic plane.

ABO_3 adsorption: molecular oxygen

Energy of adsorption (in eV):

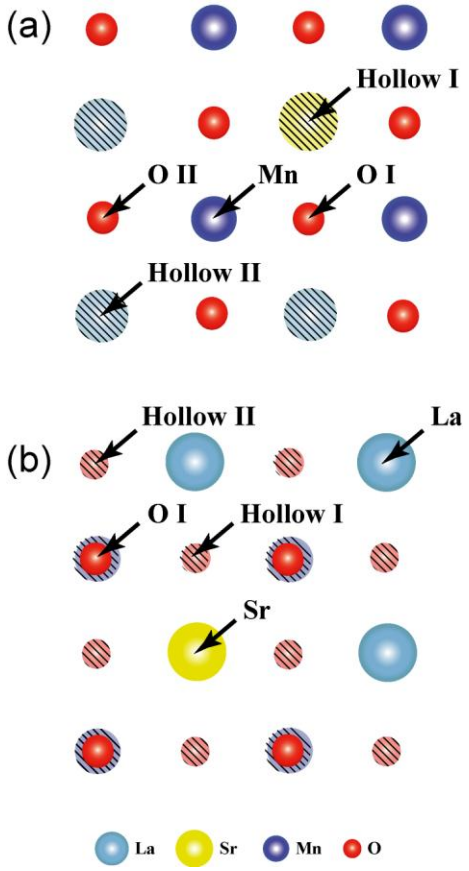
$$2E_{ads} = E_{tot}^{slab+adsorbate} - E_{tot}^{slab} - 2E_{tot}^{O_2}$$

Calculated E_{ads} (in eV)

Adsorption site "atop":	O_2/LSM
MnO_2-terminated (001)	
Mn	-1.41*
Vacancy I	-2.53 (E_{vac} = 2.21)
La(Sr)O-terminated (001)	
Hollow II	-2.67
Vacancy I	-3.93 (E_{vac} = 3.79)

*** VASP GGA calculations yield -1.13 eV for O_2/$LaMnO_3$(001) atop Mn (Kotomin *et al.*, PCCP 2008, 10, 4644)**

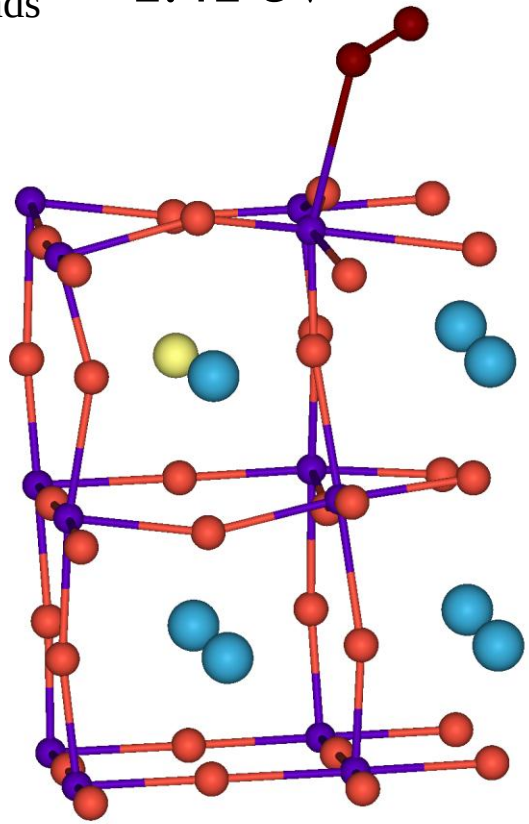
$E^{O_2}_{diss}$ = 5.30 eV vs. 5.12 eV in exp.



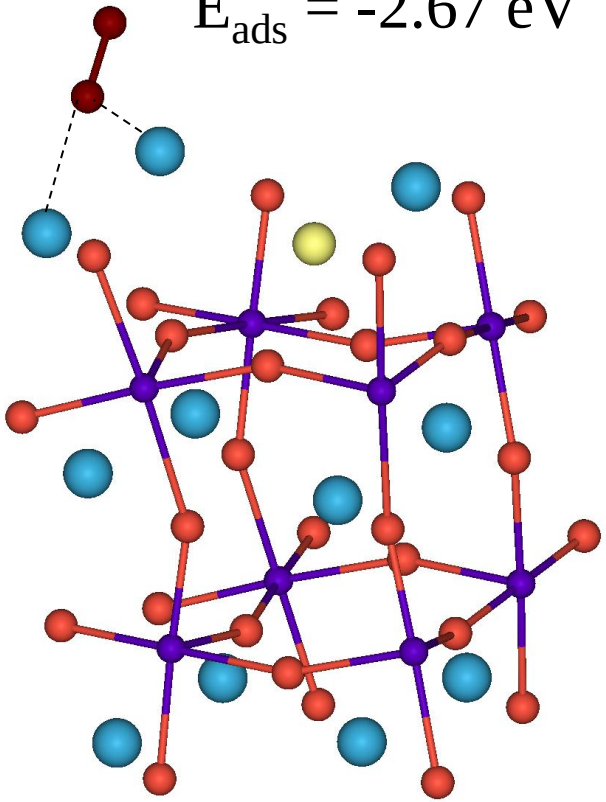
Adsorption sites: (a) MnO_2- and (b) La(Sr)O-term. Hatched atoms are from subsurface atomic plane.

Energetically favorable O_2 adsorption on LSM(001)

Δq_{O2} = -0.22 e
E_{ads} = -1.41 eV



Δq_{O2} = -0.90 e
E_{ads} = -2.67 eV



La
Sr
Mn
O

Summary and conclusions

- ✓ The most favorable oxygen adsorption sites are **bridge** positions for $SrTiO_3$(001) and **Mn** and "**hollow**" sites for MnO_2- and La(Sr)O-terminated $LaMnO_3$/LSM(001), respectively.

- ✓ O_{ads} tends to form peroxide ion with surface oxygen for $SrTiO_3$(001), while Mn dangling bond is saturated by O_{ads} for LaMnO3/LSM(001).

- ✓ Only weak physisorption is predicted for O_2 in case of $SrTiO_3$(001). O_2 is chemisorbed atop $LaMnO_3$/LSM(001).

- ✓ Much more mobile surface oxygen vacancies (activation energy 0.14 eV *vs*. ~1 eV for O_{ads} diffusion along (001)) are responsible for ionic transport along surface.

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