Structure of CoO(001) surface from DFT+U calculations

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Motivation

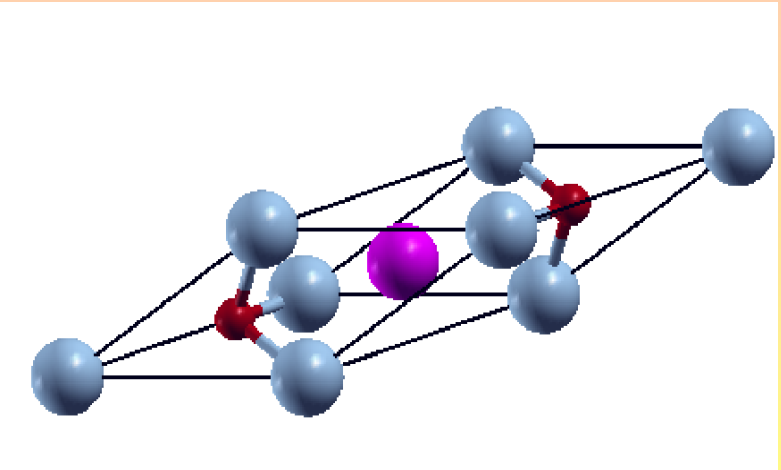
- Transition-metal oxides(TMOs) exhibit outstanding photo-catalytic activities which are generally surface-dependent.
- basic DFT calculations :
  1. insulating behaviour : NiO
  2. metallic or semi-metallic behaviour: CoO
- lattice distorsions might induce :
  - symmetry breaking
  - unquenched orbital magnetic moment.
- existence of a multideterminant ground state ?
- interaction between electrons of the unfilled 3d shell
- DFT+U method
- CoO(001) surface

Summary

- Introduction
- calculation of the Hubbard parameter U for CoO
- CoO bulk and surface relaxation
- Multiple-Quantum well behavior

CoO

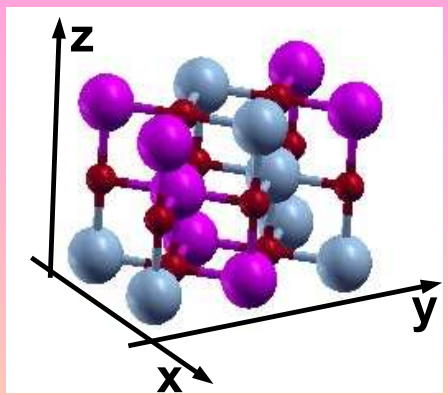
- NaCl cubic type structure of the $Fm\bar{3}m$ space group
- Tomiyasu : more complex monoclinic magnetic structure below the Neel temperature T_N .
- AF-I structure: ferromagnetic (001) planes stacked along the [001] direction
- Here : AF-II structure : alternatively packed ferromagnetic (111) planes along the [111] direction
- $R\bar{3}m$ space group.

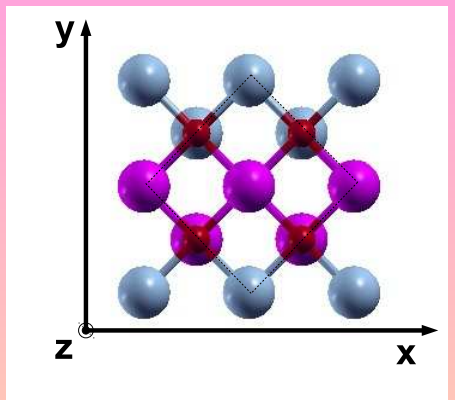


Theoretical details

- Generalized Gradient Approximation-Perdew Burke Ernzerhof(GGA-PBE)
- Ultrasoft pseudopotentials with Rappe Rabe Kaxiras Joannopoulos(RRKJ)
- 9 valence electrons for Cobalt and 6 for Oxygen atoms.
- 40 Ry cutoff for energy
- 320 Ry cutoff for density
- Monkhorst-Pack k-points for integrations
- $12 \times 12 \times 12$ for bulk calculations,
- $12 \times 6 \times 1$ for 1×2 on xy plane slabs
- $6 \times 6 \times 1$ for 2×2 slabs

Slabs used in the calculation





1×2 three layers slab . Top view of a 2×2 slab.

- CoO(001) is experimentally a non polar surface.
- vacuum of 17.06 Å in the direction perpendicular to the surface.
- no need to apply a dipole correction
- Quantum ESPRESSO suite of codes on K20 GPU

Computation of U

- M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005)

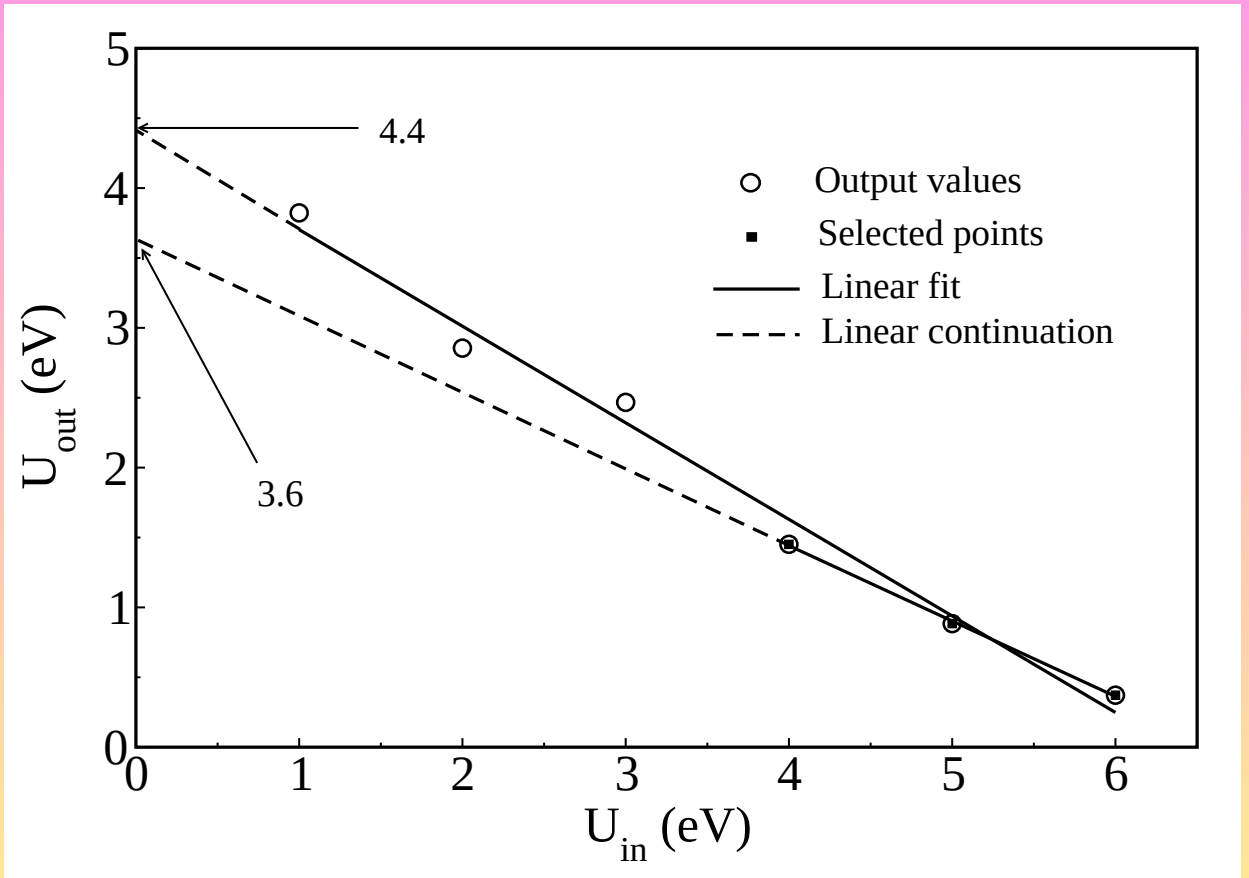
$$U = \frac{\partial \alpha_I^{KS}}{\partial n_I} - \frac{\partial \alpha_I}{\partial n_I} = (\chi_0^{-1} - \chi^{-1})_{II}. \quad (1)$$

  - α : perturbation imposed on site atom I
  - n_I : occupations numbers
  - χ : response matrices
- H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Phys. Rev. Lett. 97, 103001 (2006)
  - converged value of U by a linear fit
  - U_0 for one unit cell of 4 atoms, zero Hubbard potential.
  - U_{in} is provided U_{out} can be computed from linear response.

$$U_{out} = U_{scf} - \frac{U_{in}}{m} \quad (2)$$

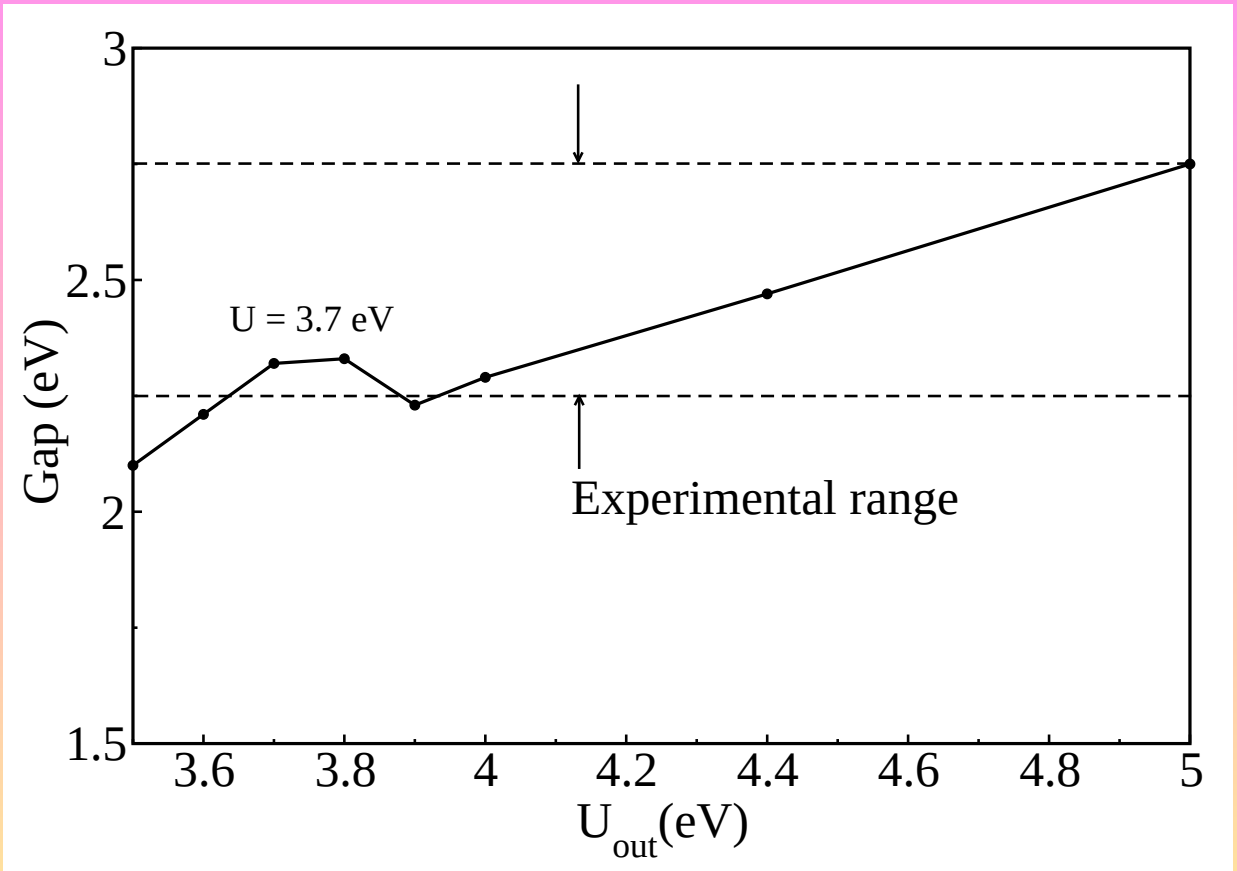
  - m is a degeneracy parameter

Computation of U



- U=3.7 eV gives a gap of 2.3 eV

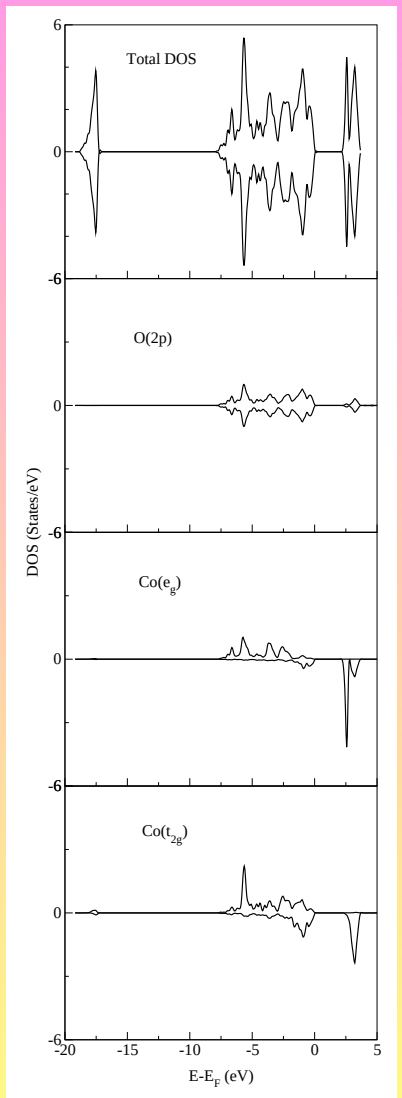
Band gap



CoO band gap as a function of U around U_{scf}.

- exact ground state.
- Meredig et al. failed to locate the ground state
- they used the value U_{eff} = 6.1 eV previously reported for CoO

DOS



- doubled peak in the conduction band from unoccupied t_{2g} and e_g states.
- weak separation between the two states : Co^{2+} is in a weak field or high spin configuration.
- top of the valence band is mainly dominated by oxygen p states
- bottom of the conduction band has its major contribution from t_{2g} state.
- CoO is a charge transfer insulator instead of Mott-Hubbard kind.

Magnetic moment

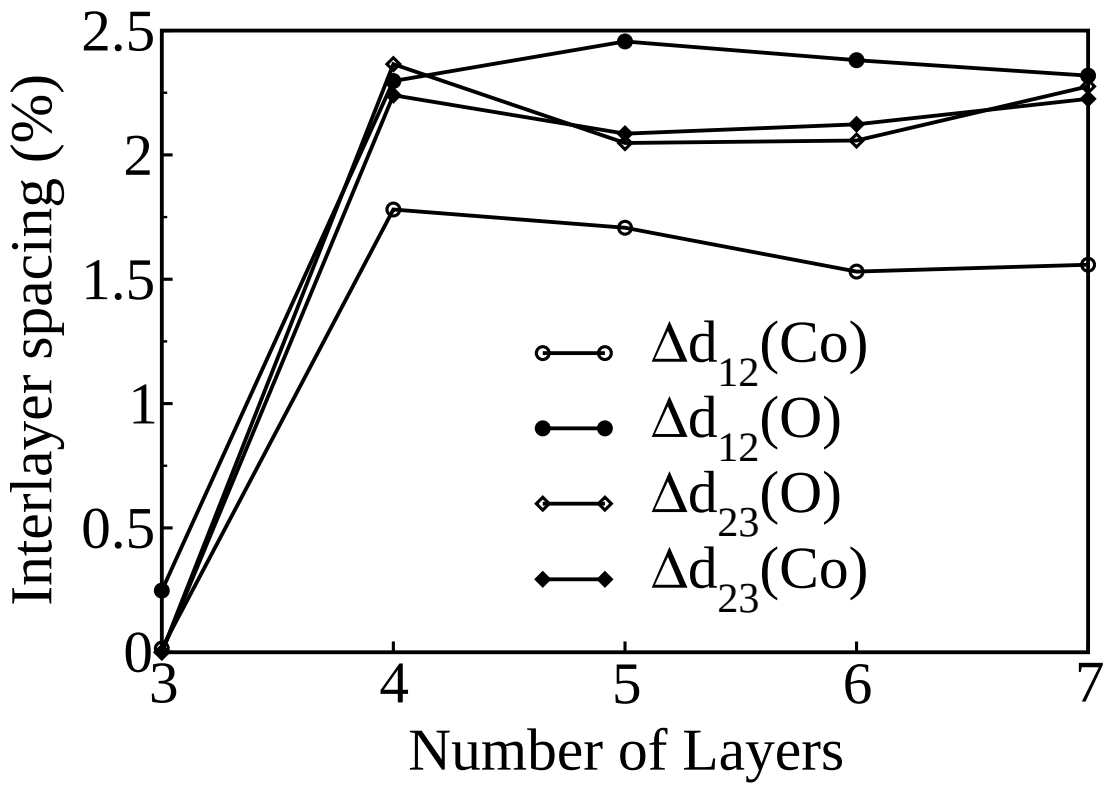
- Co^{2+} ions : 2.9μ_B.
- Rödl et al. in 2009 reported GGA and GGA+U total spin moment of 2.4-2.6μ_B,
- Co^{2+} magnetic moment (μ_B) in CoO. Orbital contribution is about 0.8μ_B

Magnetic moment	Method	Component
3.8±0.1 Herrmann et al. 1978	exp.	total
3.98(6) Jauch et al. 2001	exp.	total
2.80-2.84 Imada et al. 2001	exp.	spin component only
2.74 Wdowik et al. 2007	GGA+U	spin component only
2.90 This work	GGA+U	spin component only

CoO surface

- bulk NiO has similar properties than CoO
- (001) surfaces STM images are different.
- CoO(001) appears to exhibit a small rumpling.
- At topmost surface layer, the relaxation height of Co ions is different from O ions
- Surface relaxation of O ions is almost 2.3%
- Cobalt ions $\Delta d_{12} = 1.5\%$.
- $\Delta d_{23} = 2.1\%$ from the second surface layer.
- Relaxations are outwards : exp. results from Felton et al . 1979
- Surface atoms in CoO relax by less than $\pm 3\%$ with respect to bulk spacing.

CoO surface structure



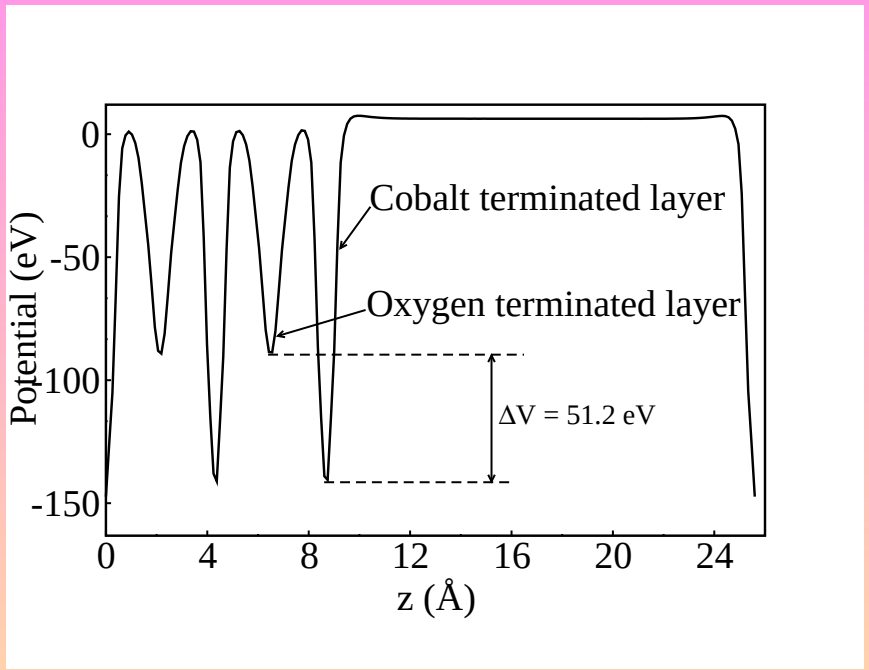
Surface energy

- Surface energy was calculated according to

$$\sigma = \frac{1}{2A}(E_{slab} - nE_{bulk}) \tag{3}$$

- E_{slab} total energy of the relaxed slabs
- E_{bulk} the optimized bulk energy per formula unit
- n the number of formula units in a slab
- $2A$ the total area of the surface.
- Surface energy of CoO(001) of $0.8 J/m^2$.
- Low surface energy indicates CoO(001) surface is energetically very favorable for catalytic applications.

Quantum well



- Multiple Quantum Wells (MQWs)
- Difference between O-terminated and the Co-terminated
- Potential difference $\Delta V = 51.2eV$ is somewhat high.
- CoO surface could be useful for optoelectronic devices

Conclusion

- Two effective Hubbard parameters U: 7.1 eV and 3.7 eV could be used.
- Self consistency determination ?
- Property under investigation ?
- We argued that the value U=3.7 eV is the most suitable.
- CoO(001) surface atoms relax outwards
- Rumpling from discrepancy between O ions and Co ions relaxation
- Band gap and surface energy : CoO(001) is favorable for catalysis
- Optoelectronic applications based on Multiple Quantum Well devices
- Perspectives : study other TM oxides and more complicated systems
- Model catalytic effects
- Thanks : ANR MINAFC, Souad Ammar-Merah