New Perspectives in *ab initio* Calculations for Semiconducting Oxides

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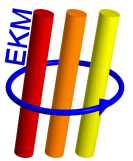
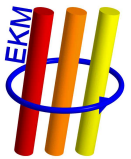
Institute of Physics, University of Augsburg

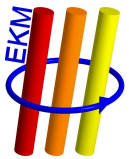
October 28, 2010



Outline

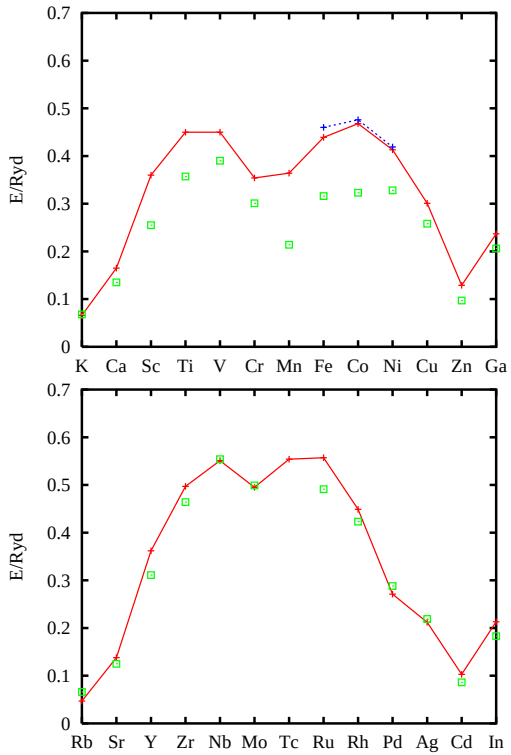


Outline

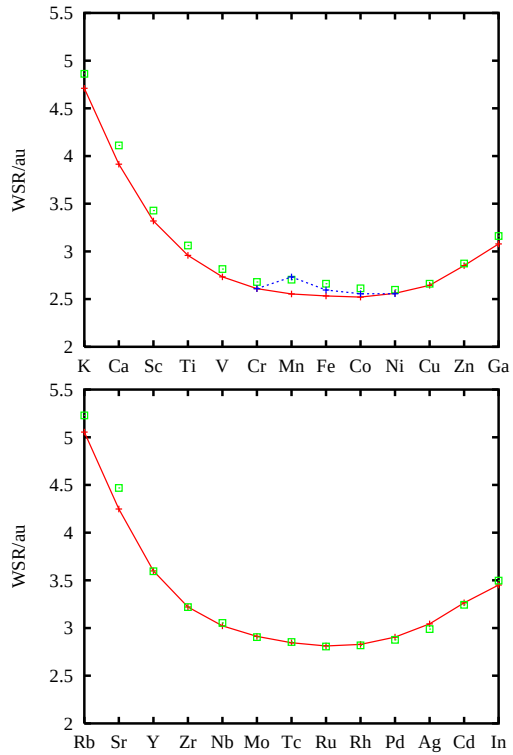


Calculated Electronic Properties

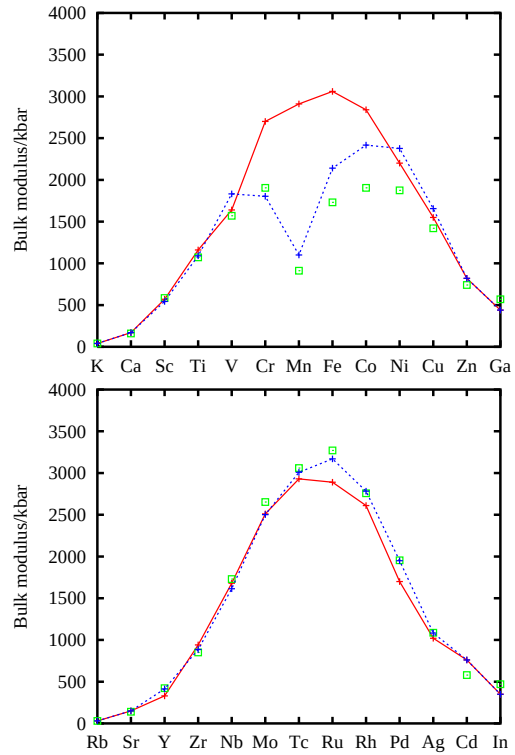
Moruzzi, Janak, Williams (IBM, 1978)



Cohesive Energies
≙ Stability



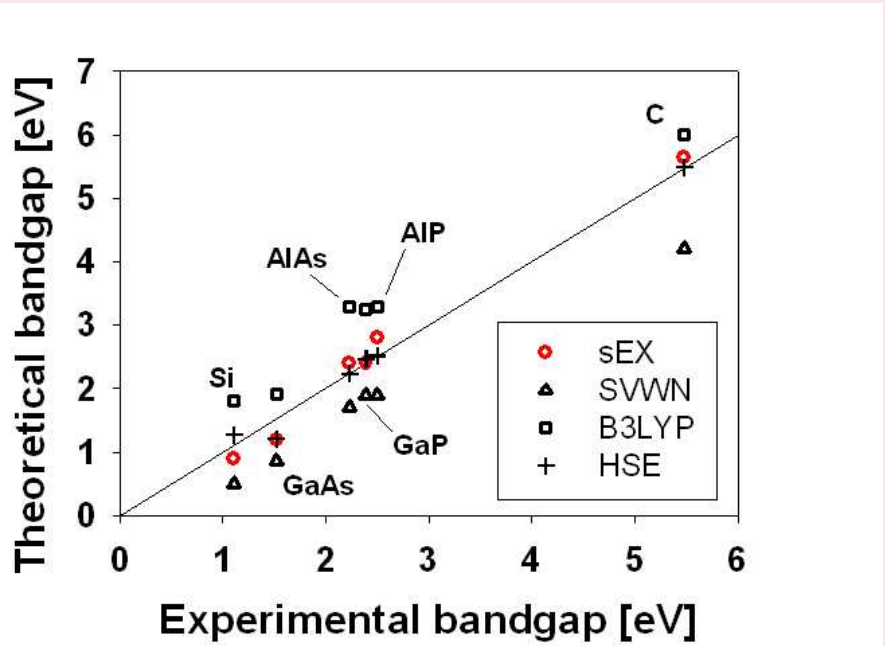
Wigner-Seitz-Rad.
≙ Volume



Compressibility
≙ Hardness

Energy band structures from screened HF exchange

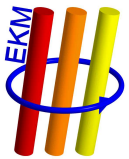
Si, AlP, AlAs, GaP, and GaAs



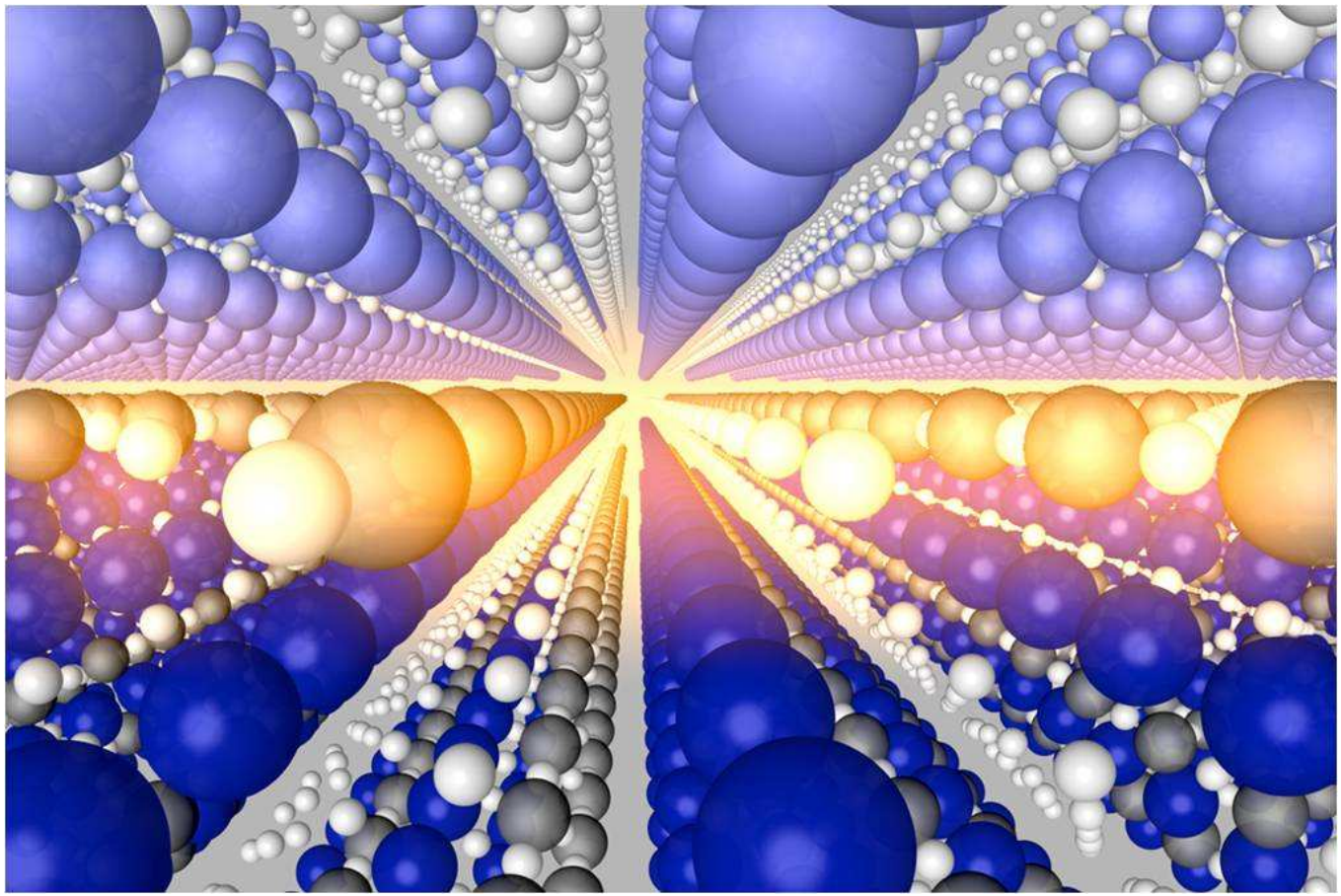
Experimental and theoretical bandgap properties

Shimazaki, Asai
JCP **132**, 224105 (2010)

Outline



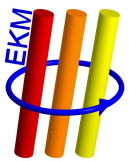
2D Electron Gas at $LaAlO_3$-$SrTiO_3$ Interface



2D Electron Gas at $LaAlO_3$-$SrTiO_3$ Interface

Issues

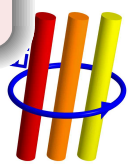
- Role of electronic correlations?
  - $SrTiO_3$, $LaAlO_3$: band insulators
  - $SrTiO_3/LaAlO_3$ interface: MIT (# $LaAlO_3$ layers)
  - magnetic properties of the interface
  - superconductivity below $\approx 200\,\mathrm{mK}$
- What is the origin of the 2-DEG?
  - intrinsic mechanism?
  - defect-doping?



Slab Calculations for the $LaAlO_3$-$SrTiO_3$ Interface

Structural setup of calculations

- central region: 5 layers $SrTiO_3$, TiO_2-terminated
- sandwiches: 2 to 5 layers $LaAlO_3$, AlO_2 surface
- vacuum region $\approx$ 20 Å
- inversion symmetry
- lattice constant of $SrTiO_3$ from GGA (3.944 Å)



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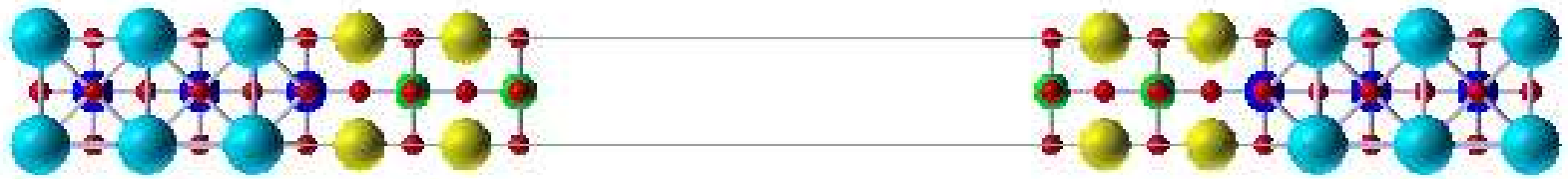
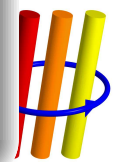


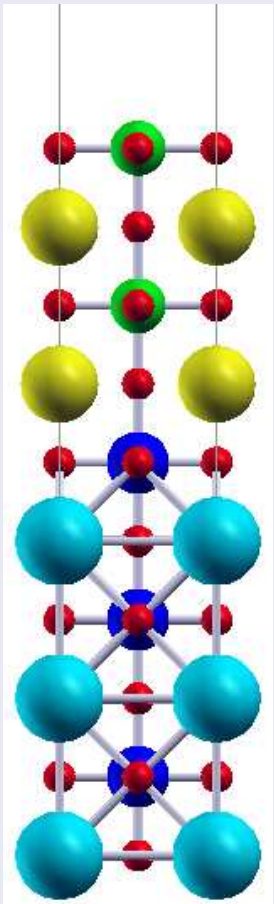
Calculational method

- Vienna Ab Initio Simulation Package (VASP)
- GGA-PBE
- Steps:
  1. optimization of $SrTiO_3$ lattice constant
  2. slab calculations
     - full relaxation of all atomic positions
     - $5 \times 5 \times 1$ **k**-points
     - Γ-centered **k**-mesh
     - Methfessel-Paxton BZ-integration



Slab Calculations for the $LaAlO_3$-$SrTiO_3$ Interface

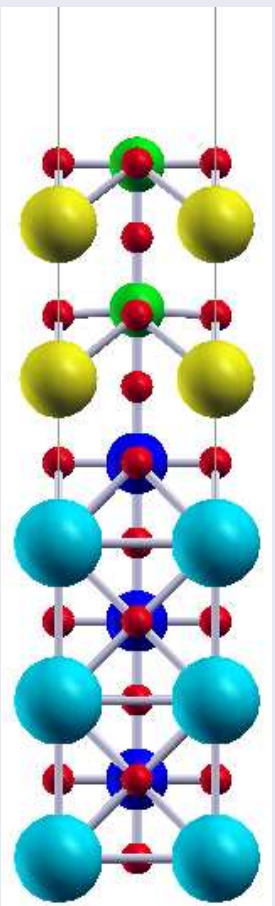
Ideal



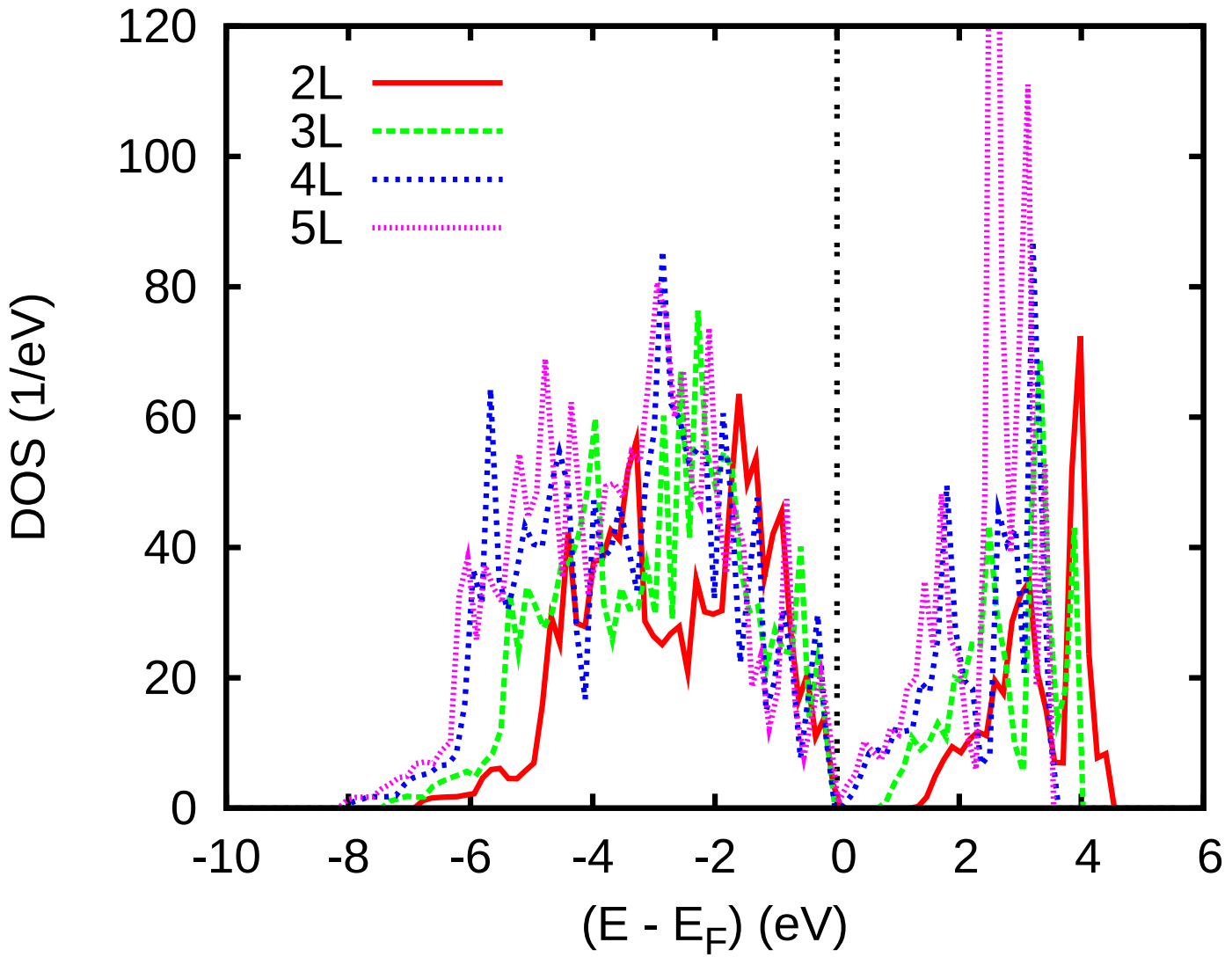
Structural relaxation

- AlO_2 surface layers
  - strong inward relaxation
  - weak buckling
- LaO layers
  - strong buckling
- AlO_2 subsurface layers
  - buckling
- TiO_2 interface layers
  - small outward relaxation

Optimized

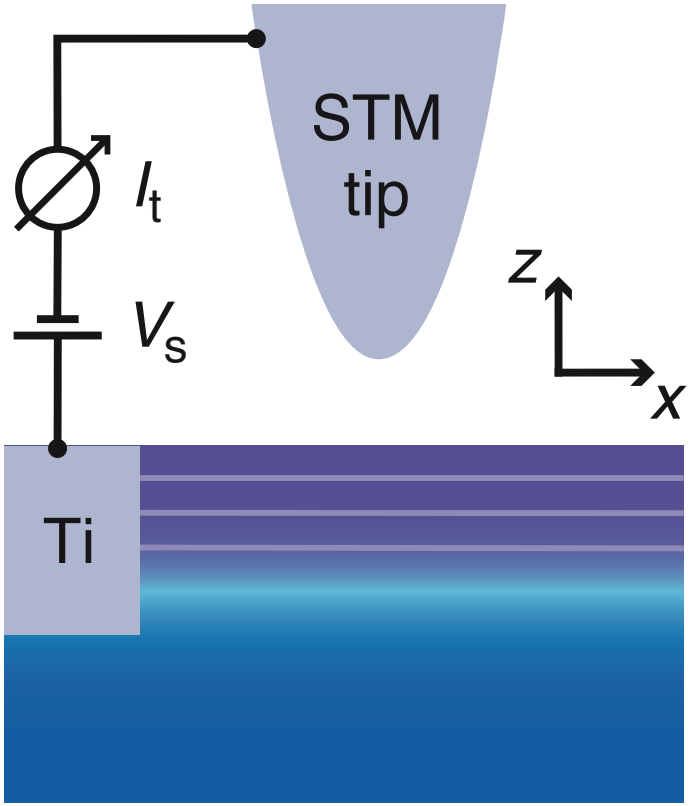


Slab Calculations for the $LaAlO_3$-$SrTiO_3$ Interface



Tunneling Spectroscopy of $LaAlO_3$-$SrTiO_3$ Interface

What is the origin of the 2-DEG?
Intrinsic mechanism or defect-doping?

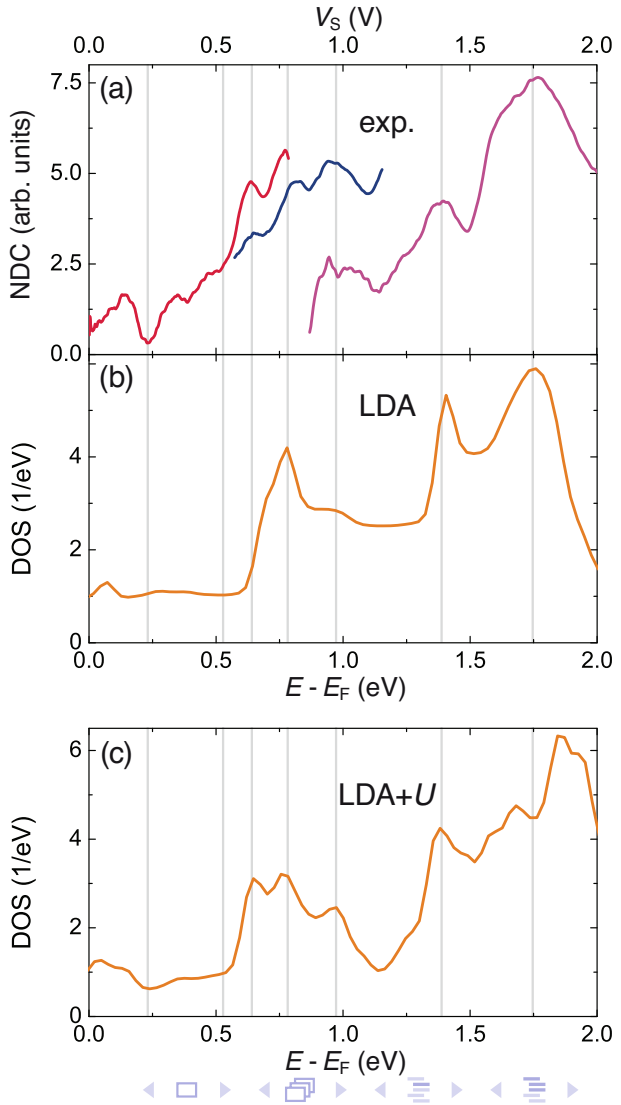


4 unit cells $LaAlO_3$
interface electron system
$SrTiO_3$

M. Breitschaft *et al.*, PRB **81**, 153414 (2010)

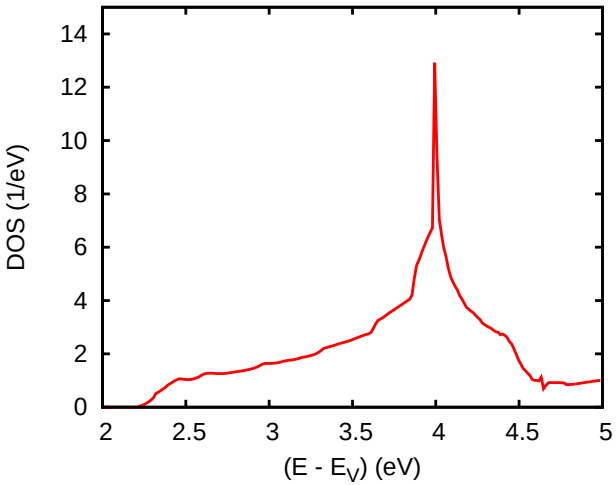
Tunneling Spectroscopy of $LaAlO_3$-$SrTiO_3$ Interface

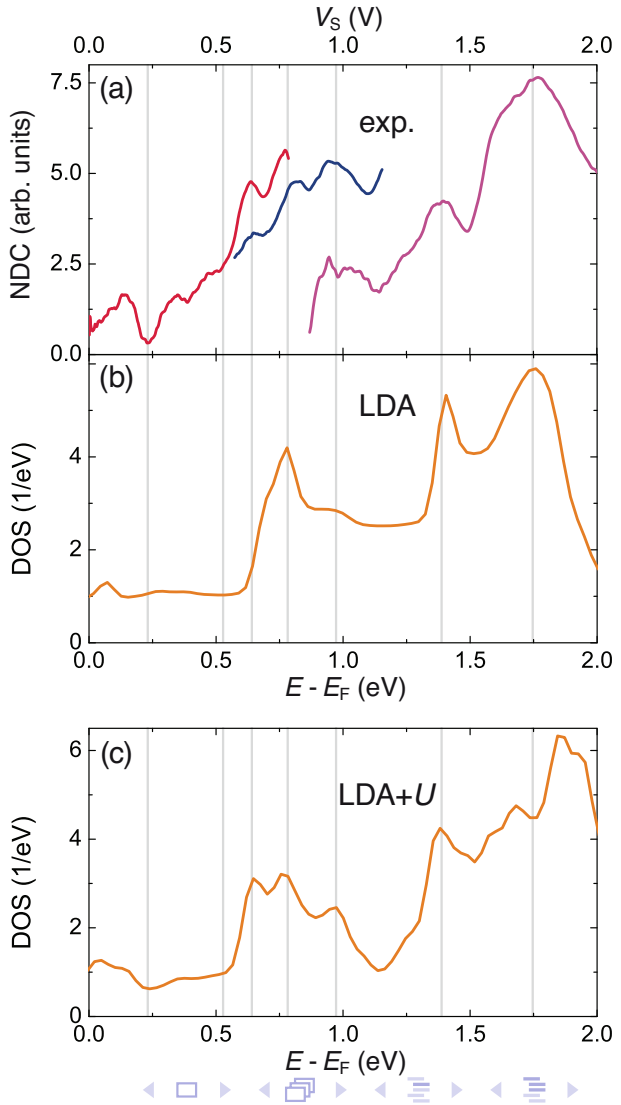
- 4uc $LaAlO_3$ on $SrTiO_3$, tunneling data
- 4uc $LaAlO_3$ on $SrTiO_3$, LDA calculations, DOS of interface Ti
- 4uc $LaAlO_3$ on $SrTiO_3$, LDA+*U* calculations, DOS of interface Ti



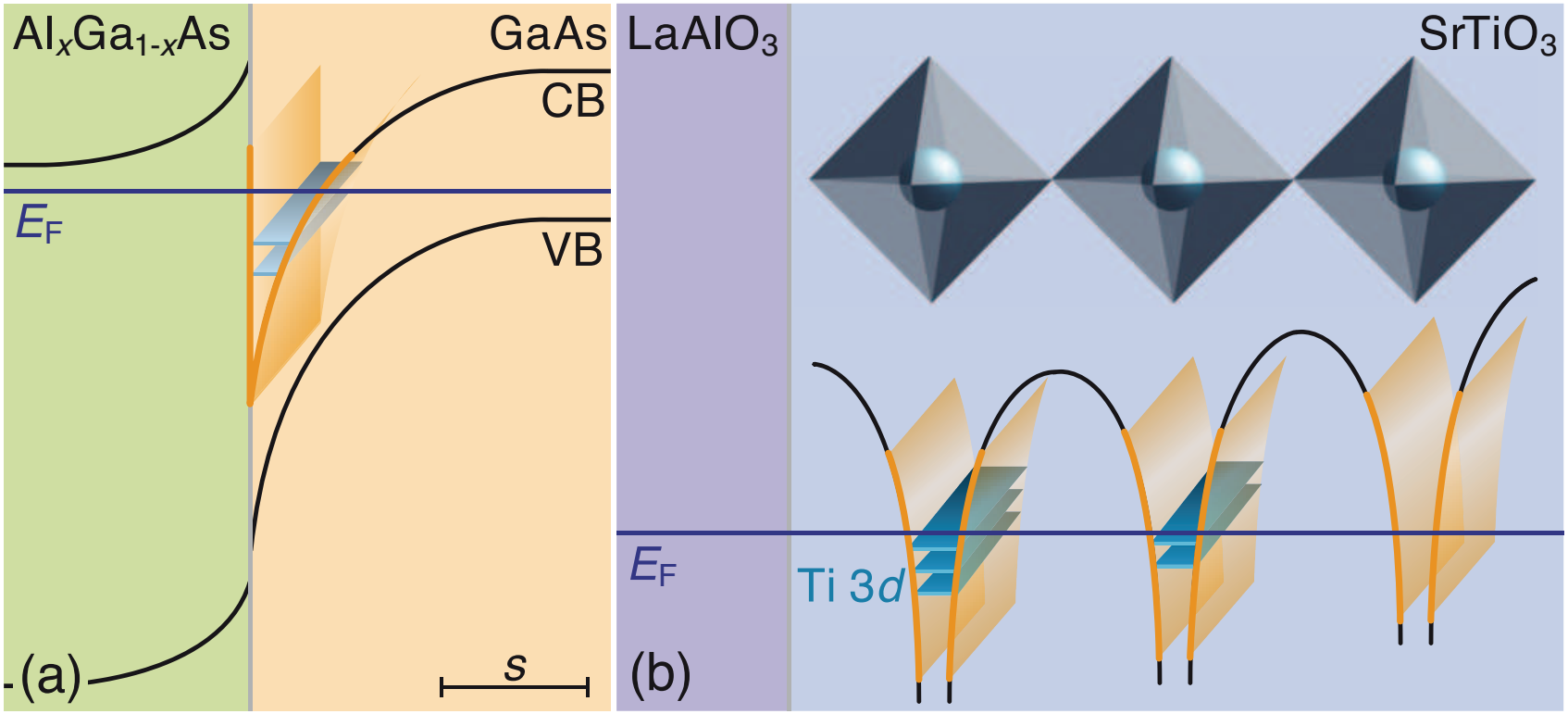
Tunneling Spectroscopy of $LaAlO_3$-$SrTiO_3$ Interface

- bulk $SrTiO_3$,
  LDA calculations,
  conduction band DOS





"2D Electron Liquid State" at $LaAlO_3$-$SrTiO_3$ Interface

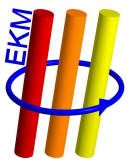


M. Breitschaft *et al.*, PRB **81**, 153414 (2010)

Critical review of the Local Density Approximation

Limitations and Beyond

- LDA exact for homogeneous electron gas (within QMC)
- Spatial variation of ρ ignored
  - $\rightarrow$ include $\nabla\rho(\mathbf{r}), \ldots$
  - $\rightarrow$ Generalized Gradient Approximation (GGA)
- Self-interaction cancellation in $v_{Hartree} + v_x$ violated
  - $\rightarrow$ repair using exact Hartree-Fock exchange functional
  - $\rightarrow$ hybrid functionals (PBE0, HSE03, HSE06)



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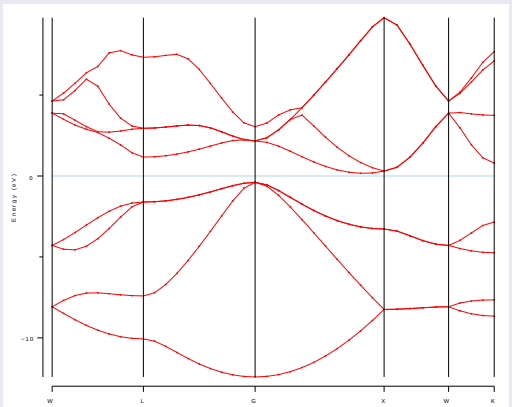
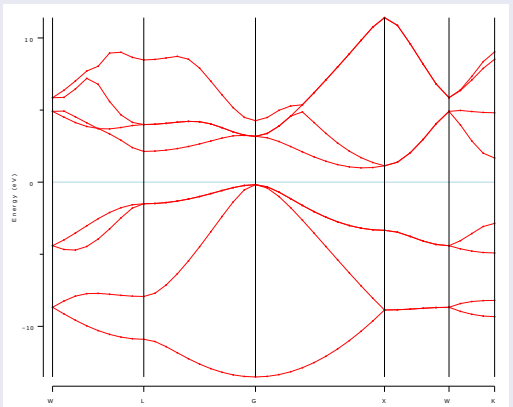
GGA



Si bandgap

- exp: 1.11 eV
- GGA: 0.57 eV
- HSE: 1.15 eV

HSE



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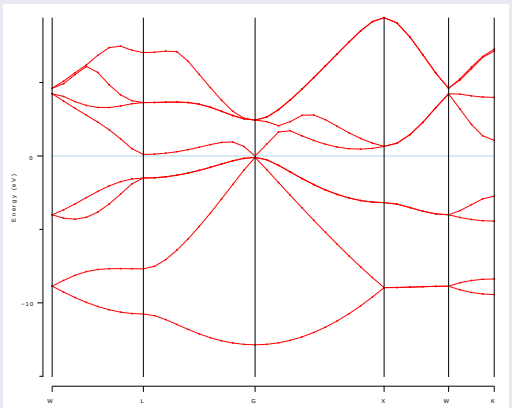
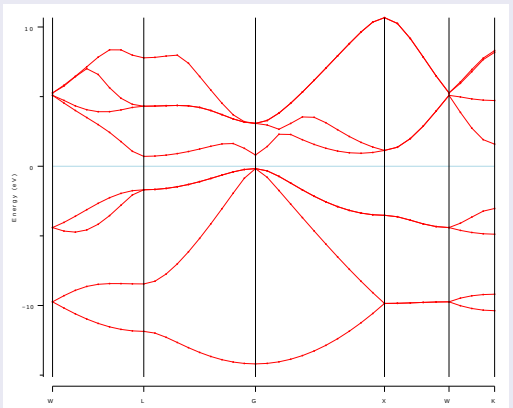
GGA



Ge bandgap

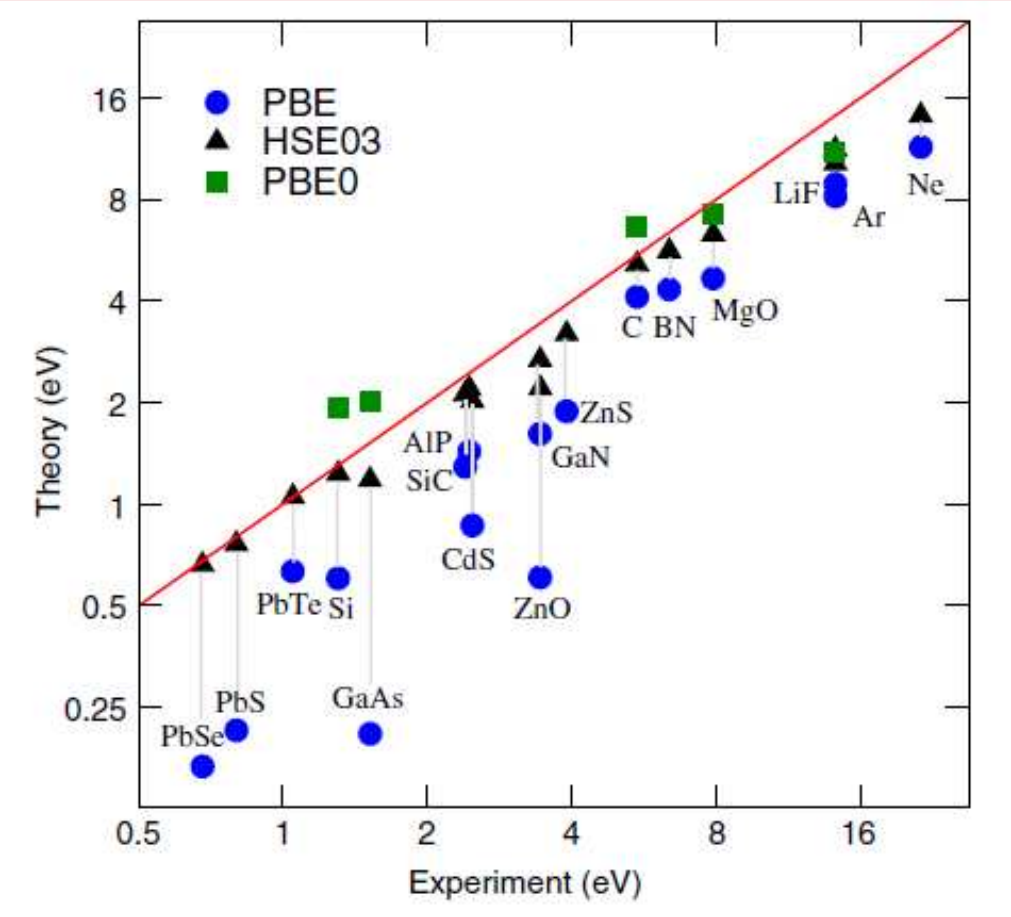
- exp: 0.67 eV
- GGA: 0.09 eV
- HSE: 0.66 eV

HSE



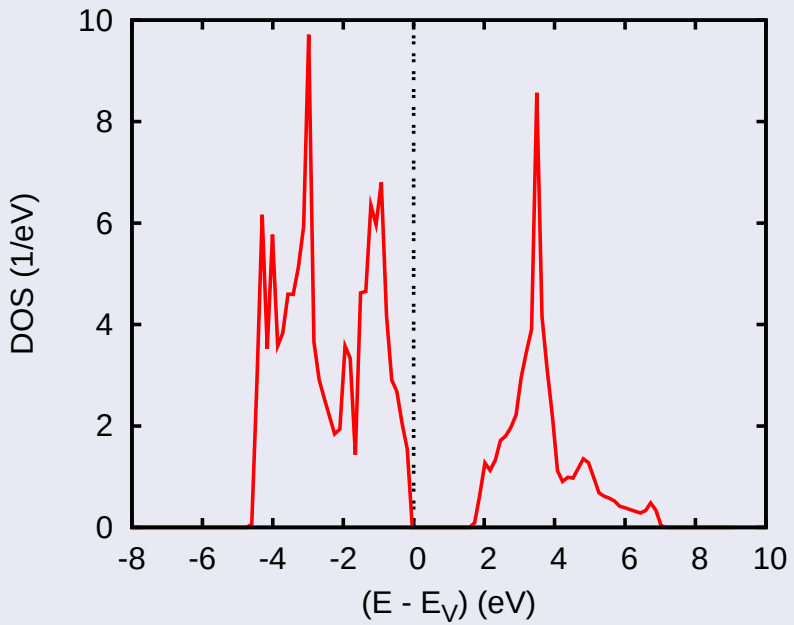
Critical review of the Local Density Approximation

Calculated vs. experimental bandgaps



$SrTiO_3$

GGA

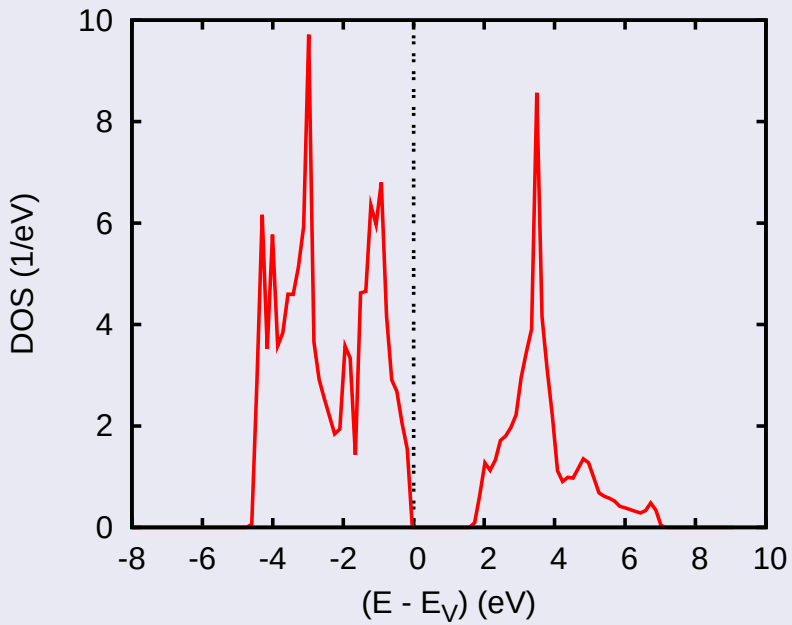


Bandgap

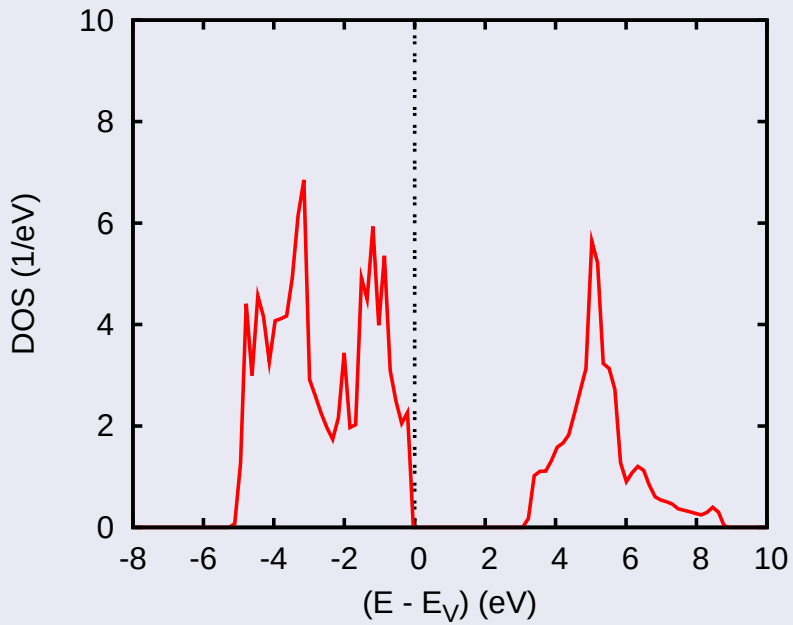
GGA: $\approx 1.6\,eV$, exp.: $3.2\,eV$

$SrTiO_3$

GGA



HSE

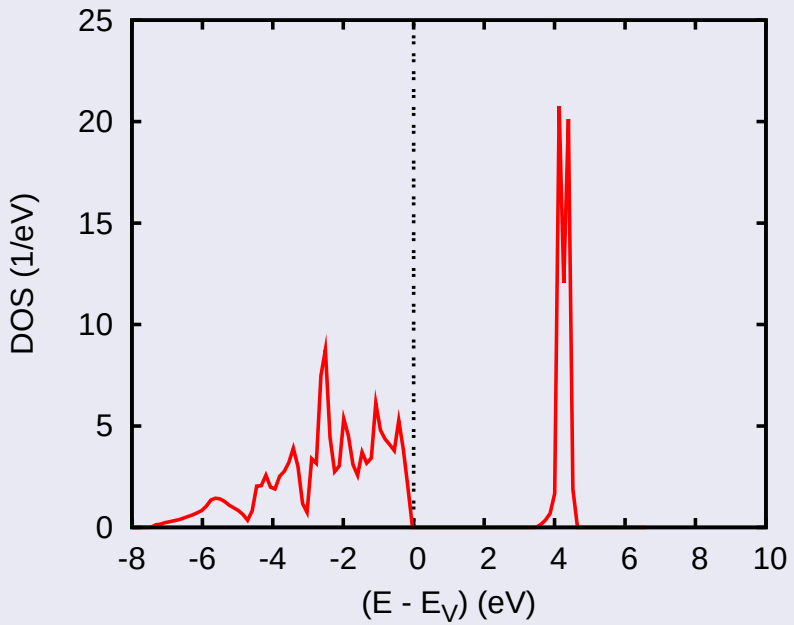


Bandgap

GGA: $\approx 1.6\,eV$, HSE: $\approx 3.1\,eV$, exp.: $3.2\,eV$

$LaAlO_3$

GGA

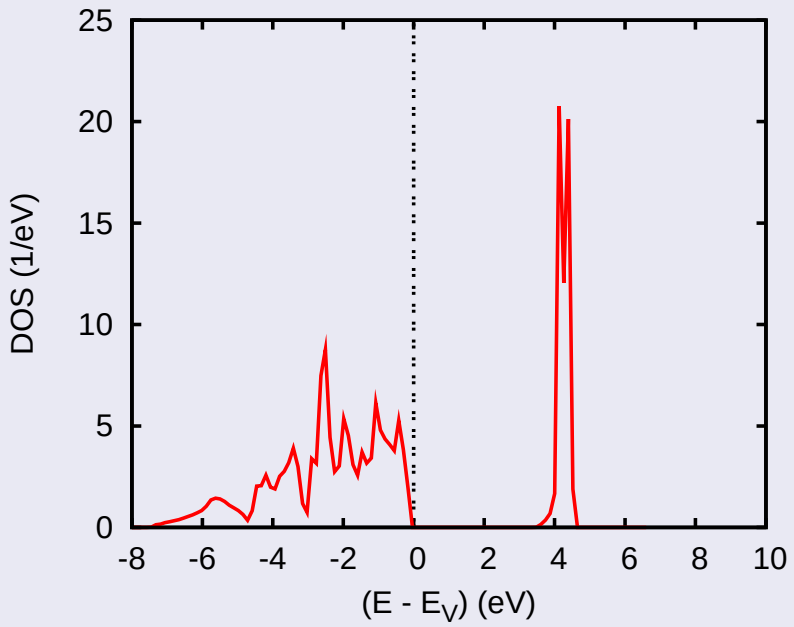


Bandgap

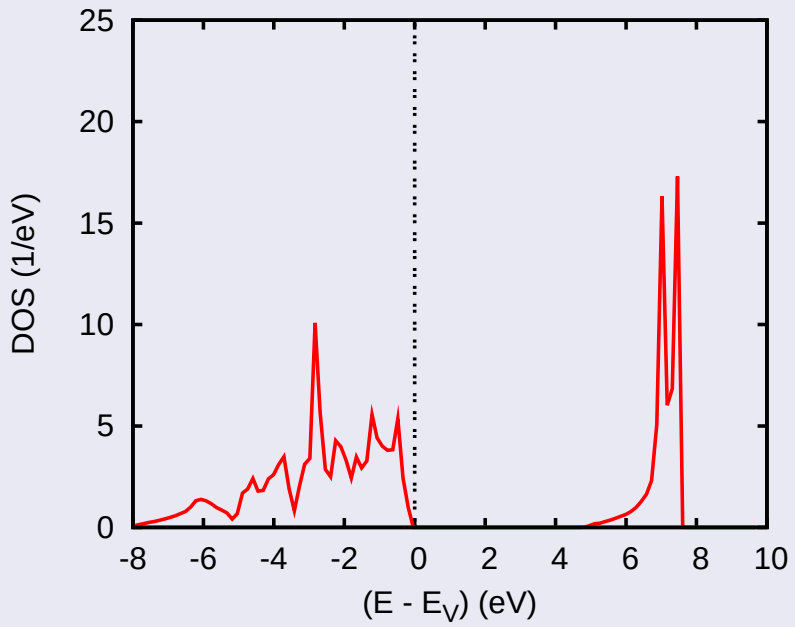
GGA: $\approx 3.5\,eV$, exp.: $5.6\,eV$

$LaAlO_3$

GGA



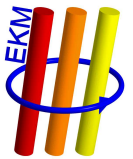
HSE



Bandgap

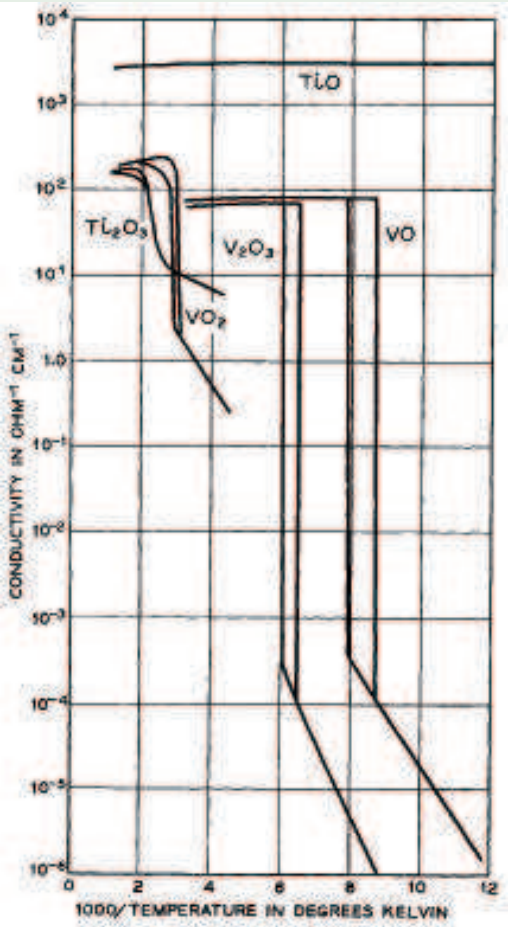
GGA: $\approx 3.5\,eV$, HSE: $\approx 5.0\,eV$, exp.: $5.6\,eV$

Outline



Metal-Insulator Transition of VO_2

Morin, PRL 1959

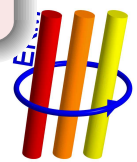


Metal-Insulator Transitions (MIT)

- VO_2 (d^1)
  - 1st order, 340 K, $\Delta\sigma \approx 10^4$
  - rutile $\longrightarrow$ M_1 (monoclinic)
- V_2O_3 (d^2)
  - 1st order, 170 K, $\Delta\sigma \approx 10^6$
  - corundum $\longrightarrow$ monoclinic
  - paramagn. $\longrightarrow$ AF order

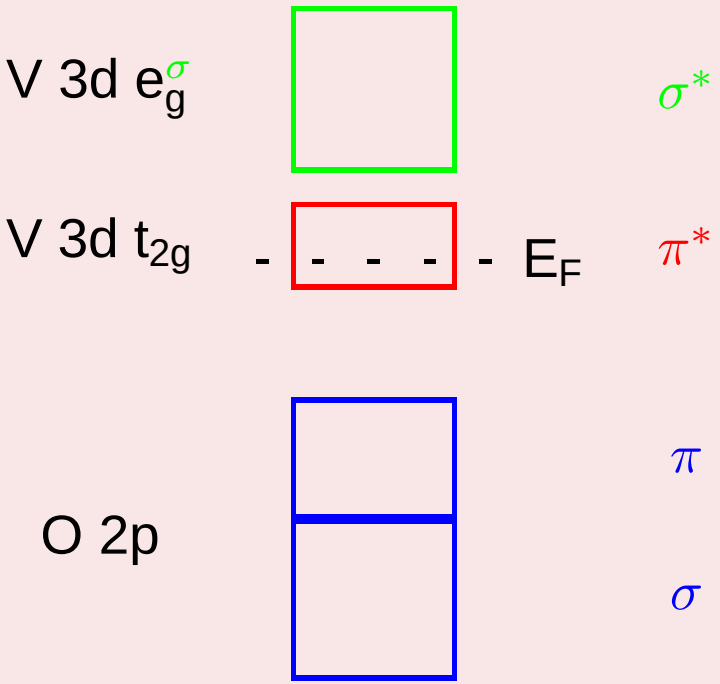
Origin of the MIT???

- Structural Changes?
- Electron Correlations?



Metal-Insulator Transition of VO_2

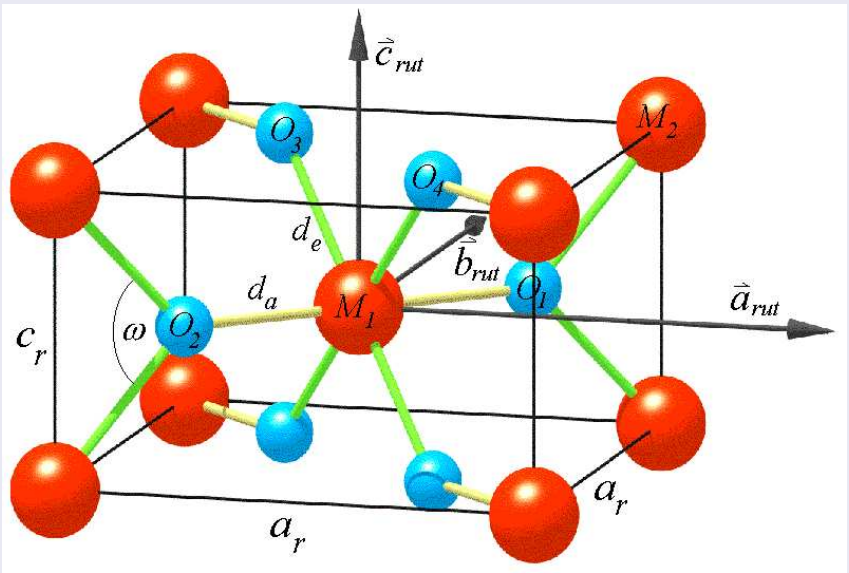
Octahedral Coordination



- V 3*d*-O 2*p* hybridization
  - σ, σ^* (p-de_g^σ)
  - π, π^* (p-dt_{2g})

Rutile Structure

- simple tetragonal
- $P4_2/mnm$ (D_{4h}^{14})



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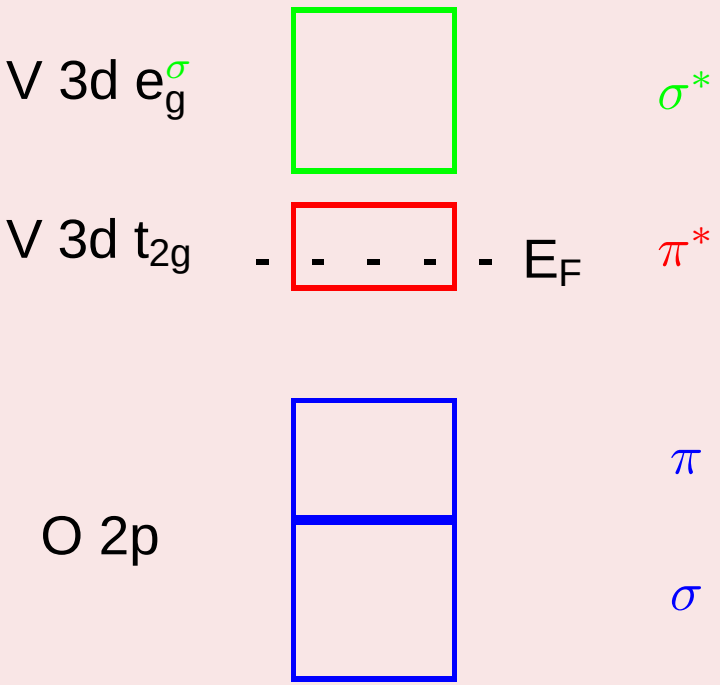
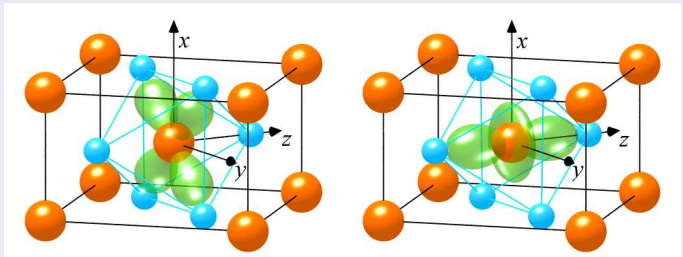
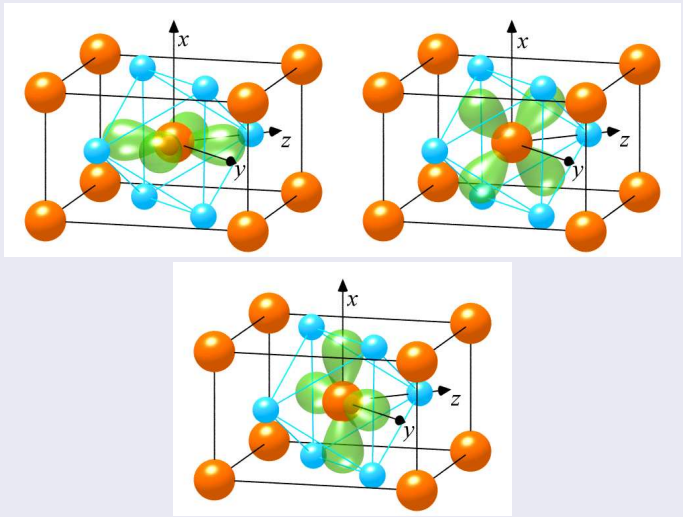


- V 3*d*-O 2*p* hybridization
  - σ, σ^* (p-de_g^σ)
  - π, π^* (p-dt_{2g})

e_g^σ Orbitals

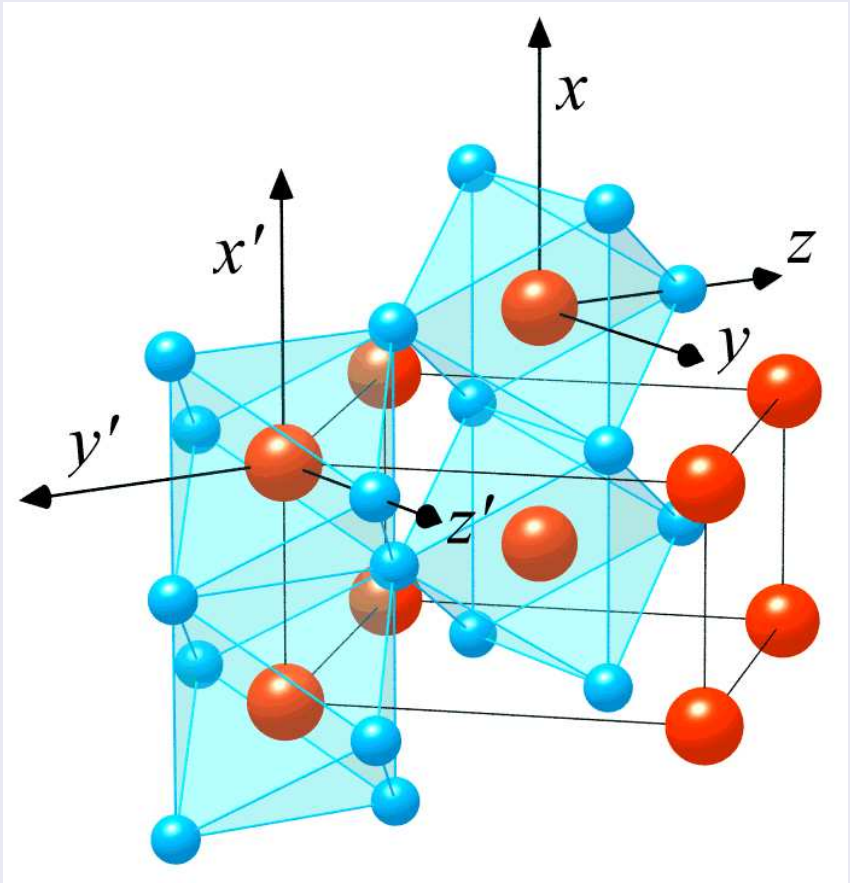


t_{2g} Orbitals



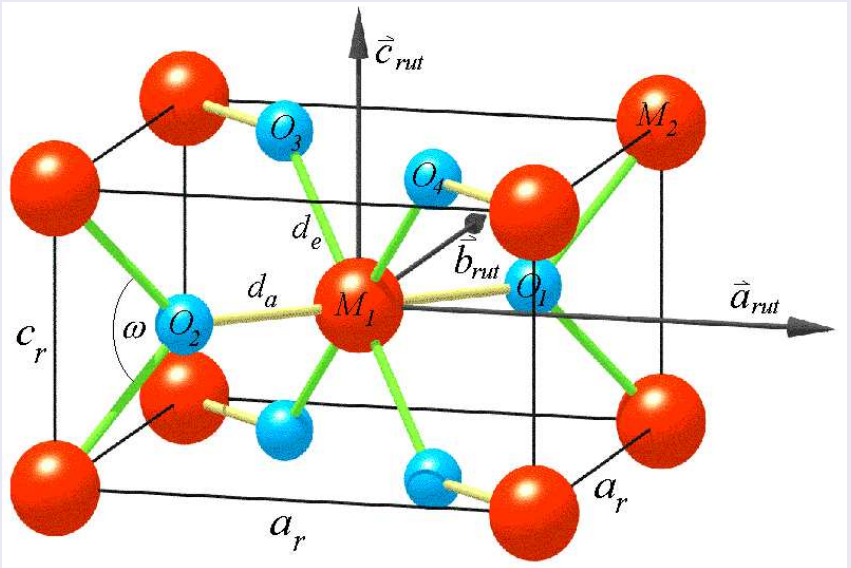
Metal-Insulator Transition of VO_2

Octahedral Chains



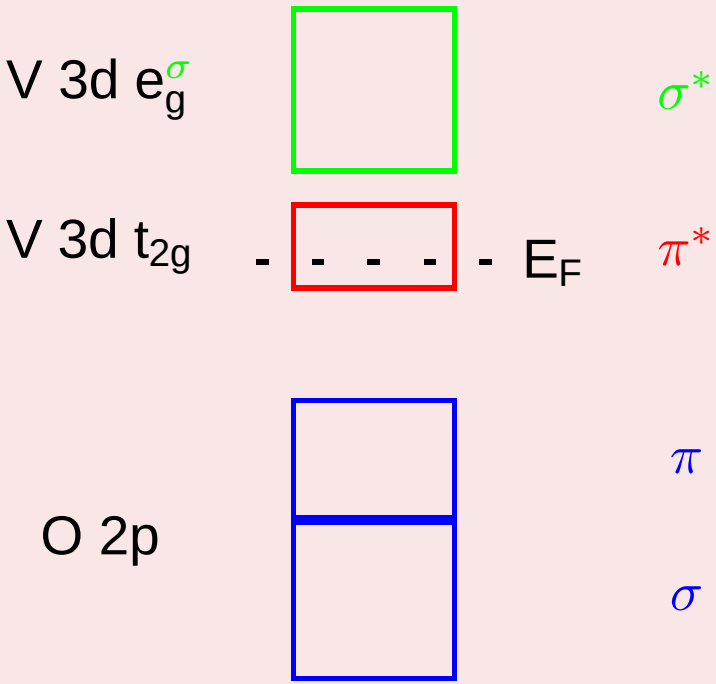
Rutile Structure

- simple tetragonal
- $P4_2/mnm\ (D_{4h}^{14})$

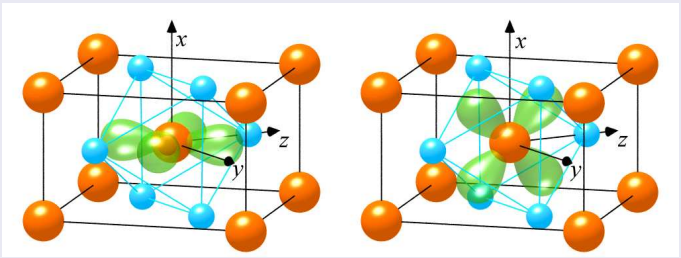


Metal-Insulator Transition of VO_2

Octahedral Coordination

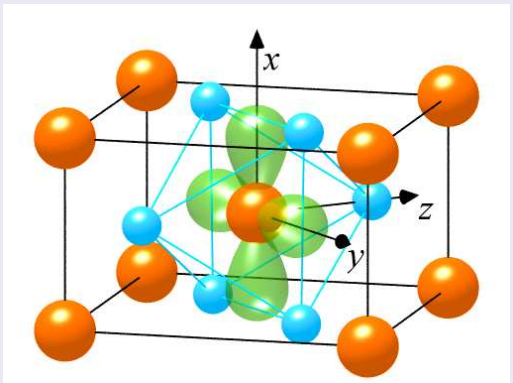


t_{2g} Orbitals



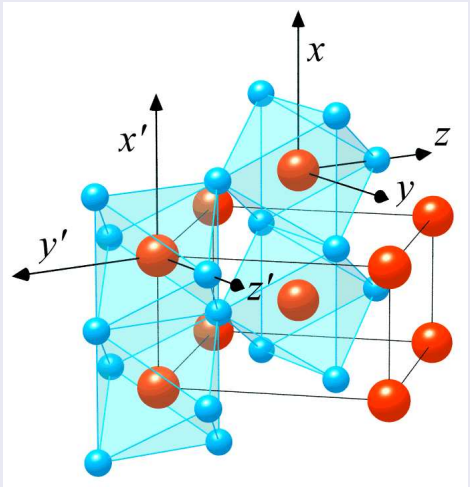
$e_g^\pi = \text{“}\pi^*\text{”}$

$a_{1g} = \text{“}d_{\|}\text{”}$



Metal-Insulator Transition of VO_2

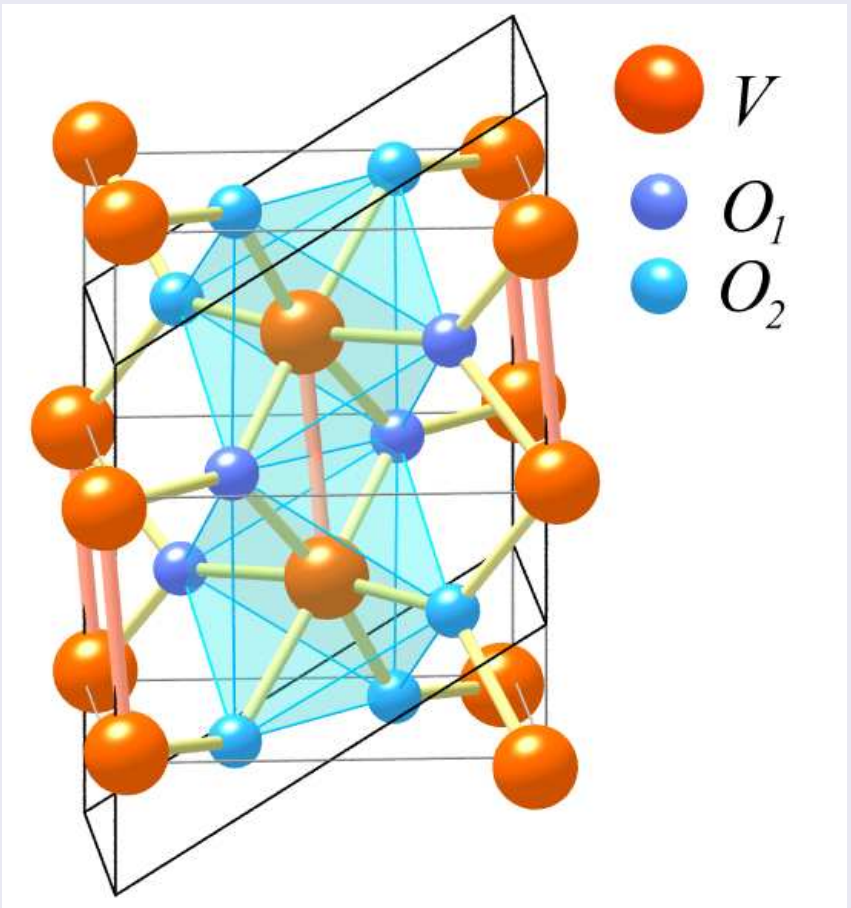
Rutile Structure



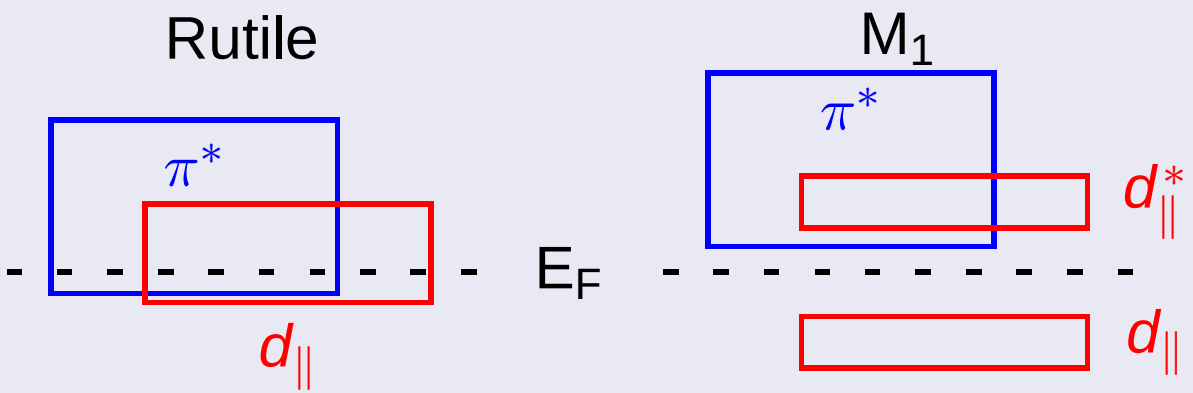
Structural Changes

- V-V dimerization $\parallel c_R$
- antiferroelectric displacement $\perp c_R$

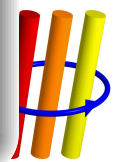
M_1-Structure



Metal-Insulator Transition of VO_2



- Goodenough, 1960-1972
  - metal-metal dimerization $\| c_R \rightarrow$ splitting into $d_{||}, d_{||}^*$
  - antiferroelectric displacement $\perp c_R \rightarrow$ upshift of π^*
- Zylbersztejn and Mott, 1975
  - splitting of $d_{||}$ by electronic correlations
  - upshift of π^* unscreenes $d_{||}$ electrons

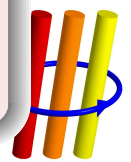


Metal-Insulator Transition of VO_2

Other Compounds

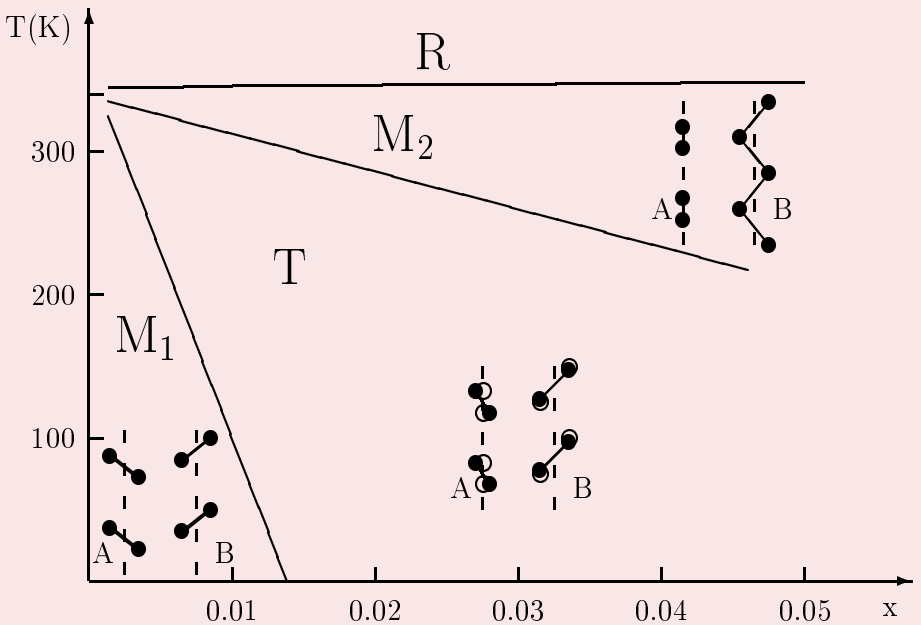
	d^0	d^1	d^2	d^3	d^4	d^5	d^6
3d	TiO_2 (S)	VO_2^* (M–S)	CrO_2 (F–M)	MnO_2 (AF–S)			
4d		NbO_2^* (M–S)	MoO_2^* (M)	TcO_2^* (M)	RuO_2 (M)	RhO_2 (M)	
5d		TaO_2 (?)	WO_2^* (M)	ReO_2^* (M)	OsO_2 (M)	IrO_2 (M)	PtO_2^* (M)

* deviations from rutile, M = metal, S = semiconductor
F/AF = ferro-/antiferromagnet



Metal-Insulator Transition of VO_2

Other Phases



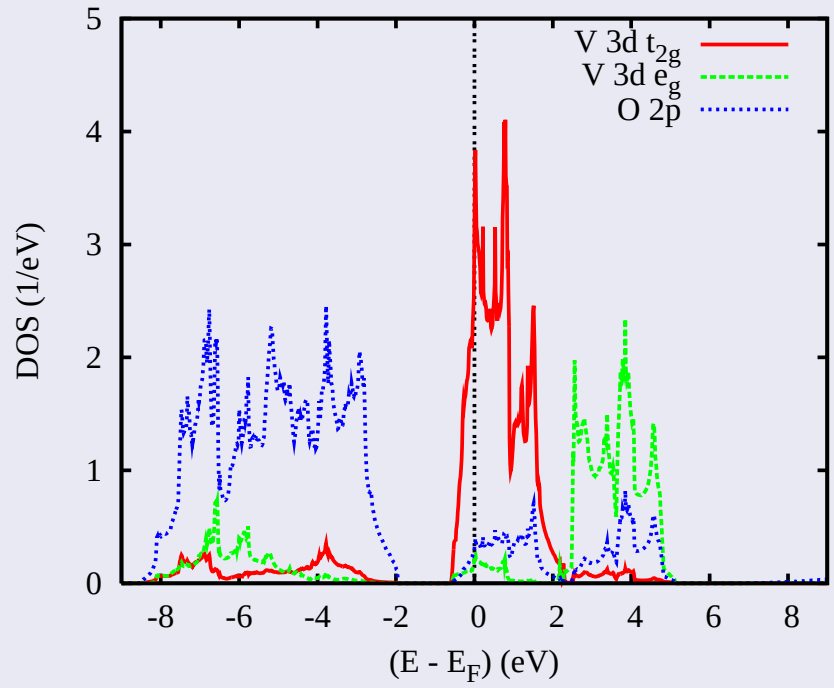
- doping with Cr, Al, Fe, Ga
- uniaxial pressure $\parallel \langle 110 \rangle$

$Cr_xV_{1-x}O_2$
Pouget, Launois, 1976

Electronic Structure in Detail

Rutile Structure

- molecular-orbital picture ✓
- octahedral crystal field
  $\Longrightarrow$ V 3*d* t_{2g}/e_g
- V 3*d*–O 2*p* hybridization

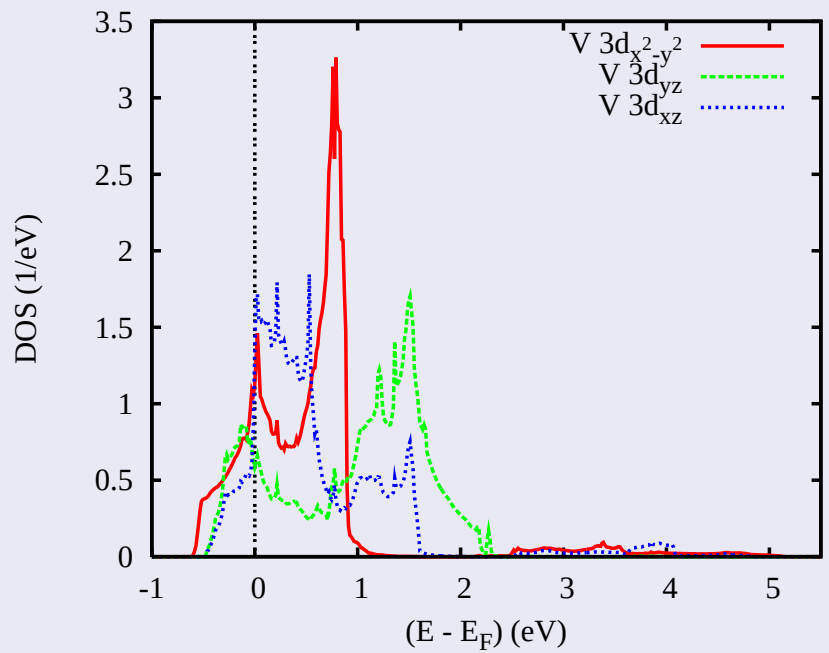


VE, Ann. Phys. (Leipzig) **11**, 650 (2002)

Electronic Structure in Detail

Rutile Structure

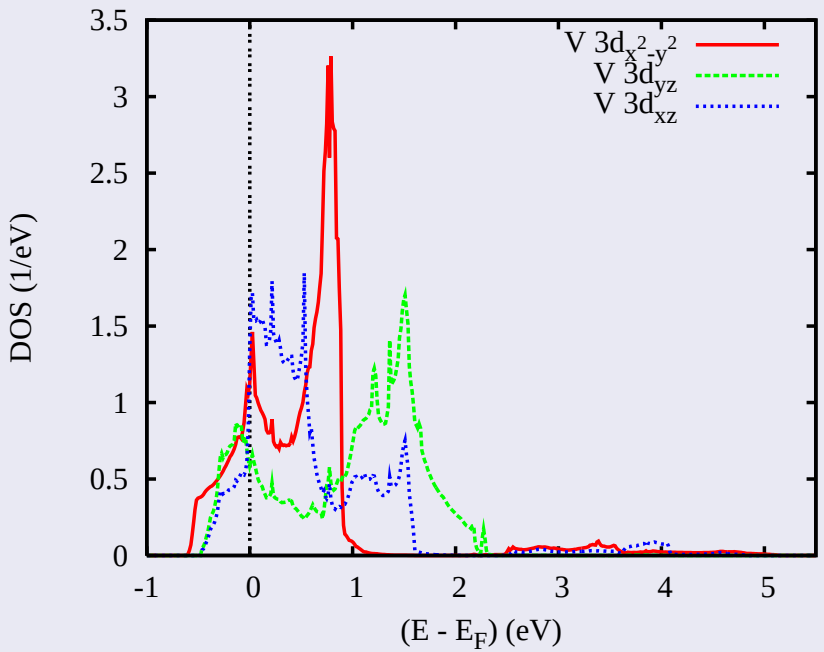
- molecular-orbital picture ✓
- octahedral crystal field
  $\Longrightarrow$ V 3d t_{2g}/e_g
- V 3d–O 2p hybridization
- t_{2g} at E_F: $d_{x^2-y^2}$, d_{yz}, d_{xz}
- $n(d_{x^2-y^2}) \approx n(d_{yz}) \approx n(d_{xz})$



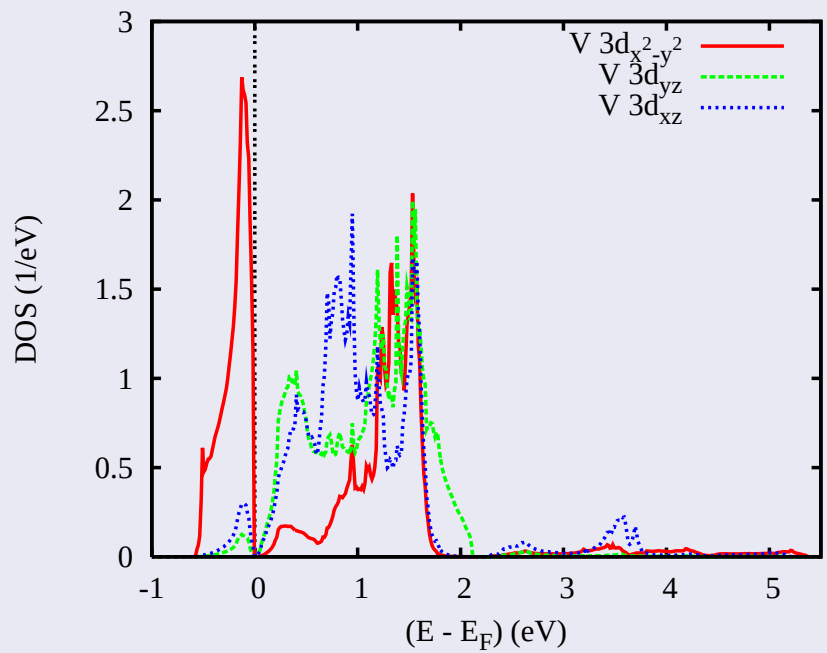
VE, Ann. Phys. (Leipzig) **11**, 650 (2002)

Electronic Structure in Detail

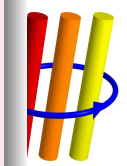
Rutile Structure



M_1 Structure



- bonding-antibonding splitting of $d_{||}$ bands
- energetical upshift of π^* bands $\Longrightarrow$ orbital ordering
- optical band gap on the verge of opening



Further investigations

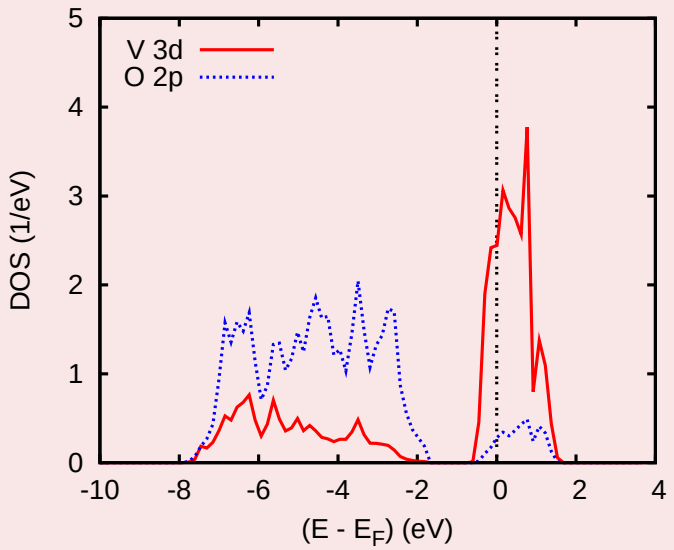
Cluster-DMFT Calculations

- Rutile-VO_2
  - moderately correlated metal
- M_1-VO_2
  - correlations strong/weak on $d_{||}/\pi^*$
  - optical band gap of 0.6 eV
- Phase Transition
  - “correlation-assisted Peierls transition”

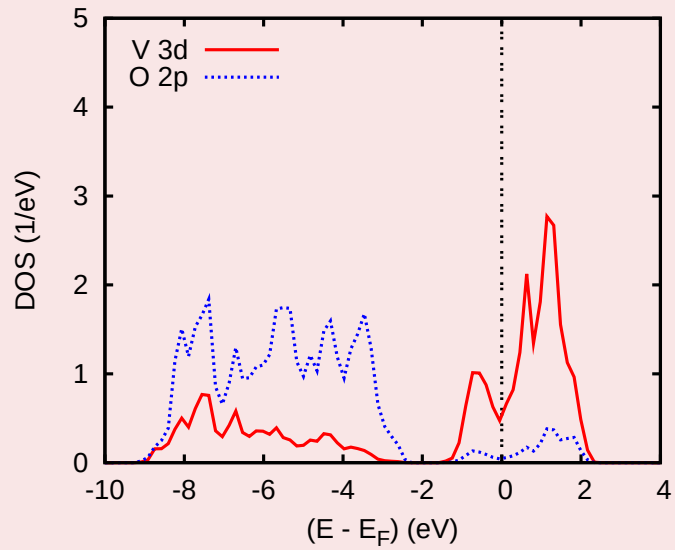
S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges
PRL **94**, 026404 (2005)

New Calculations: GGA vs. HSE

Rutile Structure GGA

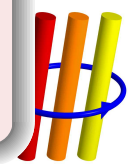


Rutile Structure HSE



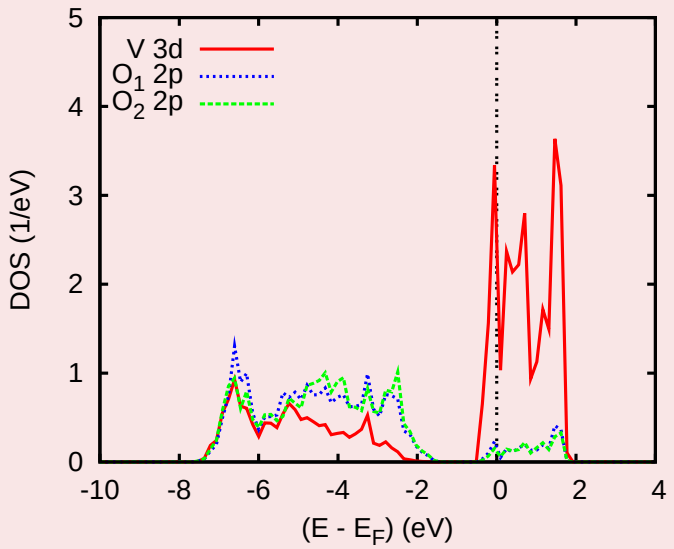
Rutile Structure: GGA $\Longrightarrow$ HSE

- broadening of O $2p$ and V $3d$ t_{2g}(!) bands
- splitting within V $3d$ t_{2g} bands

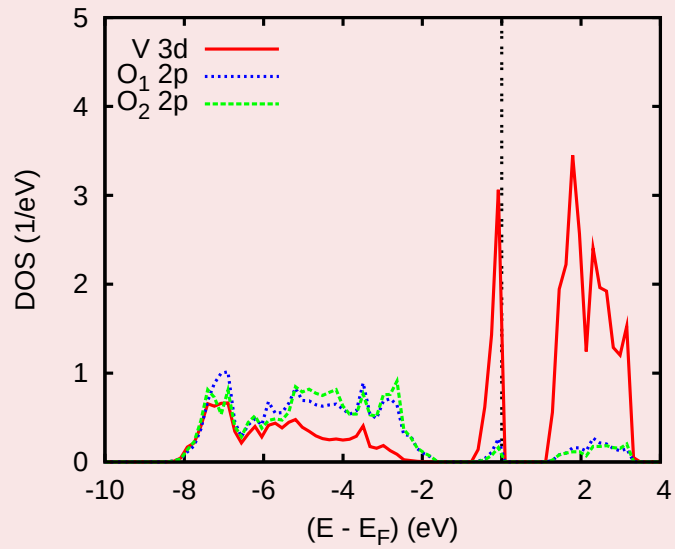


New Calculations: GGA vs. HSE

M_1 Structure GGA



M_1 Structure HSE

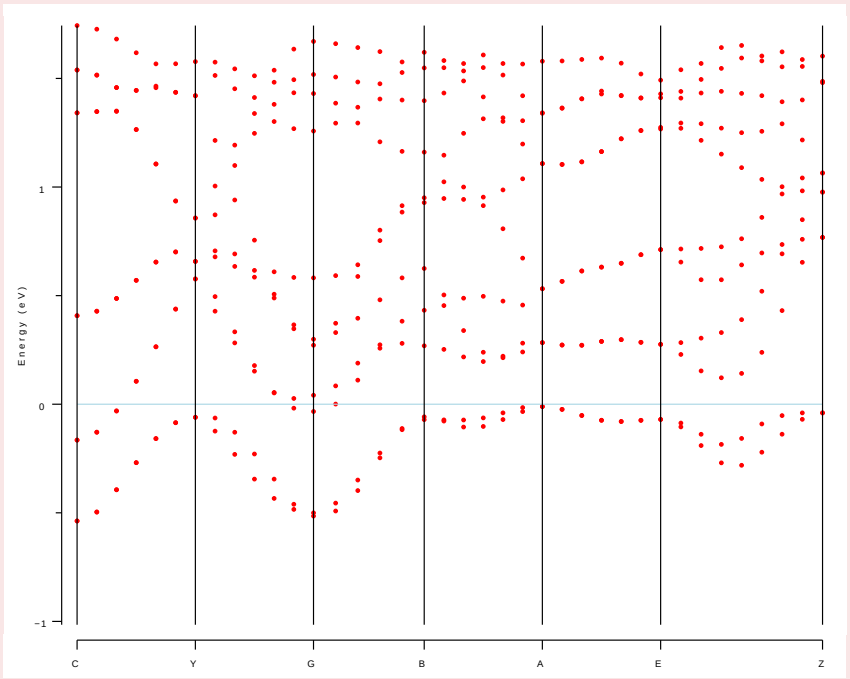


M_1 Structure: GGA $\Longrightarrow$ HSE

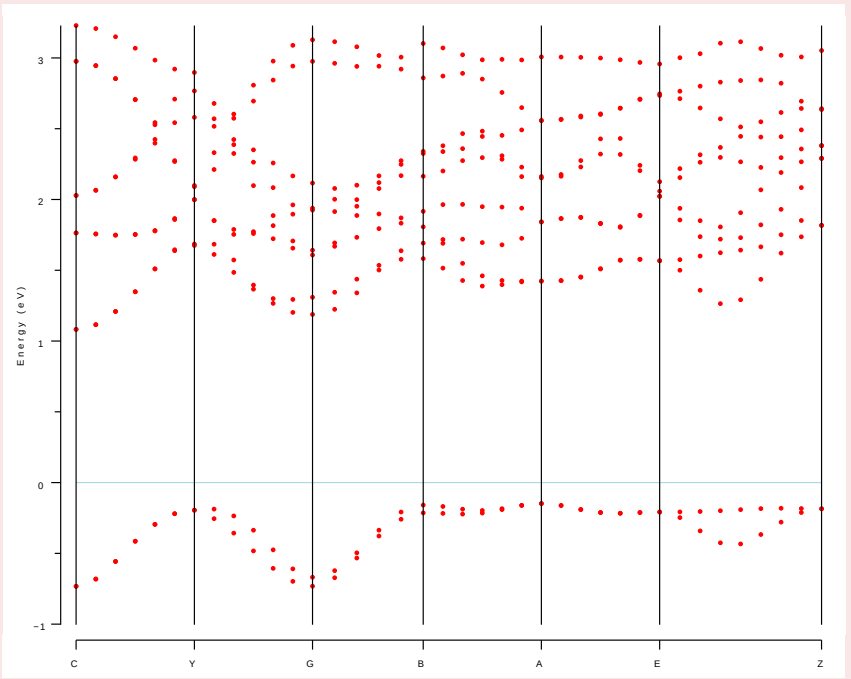
- splitting of $d_{||}$ bands, upshift of π^* bands
- optical bandgap of ≈ 1 eV

New Calculations: GGA vs. HSE

M_1 Structure GGA

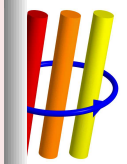


M_1 Structure HSE



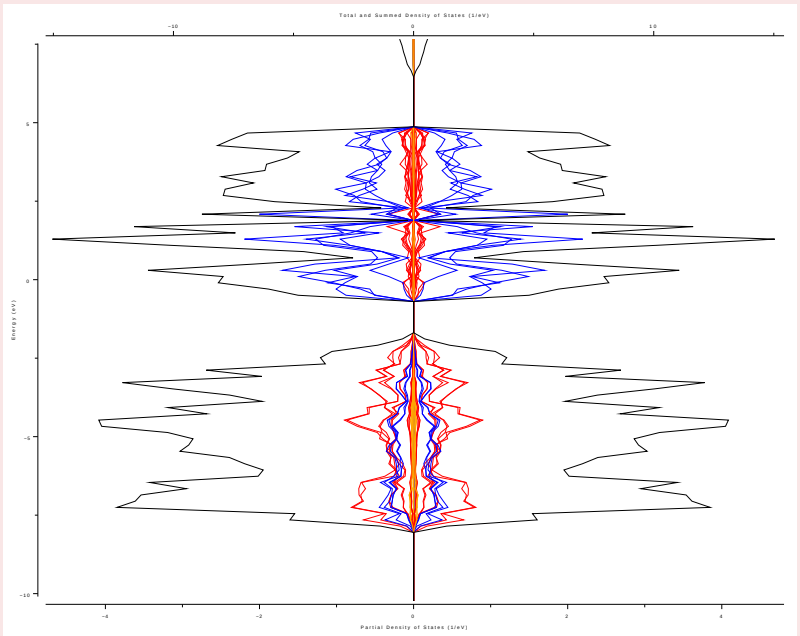
M_1 Structure: GGA $\Longrightarrow$ HSE

- splitting of $d_{\|}$ bands, upshift of π^* bands
- optical bandgap of ≈ 1 eV

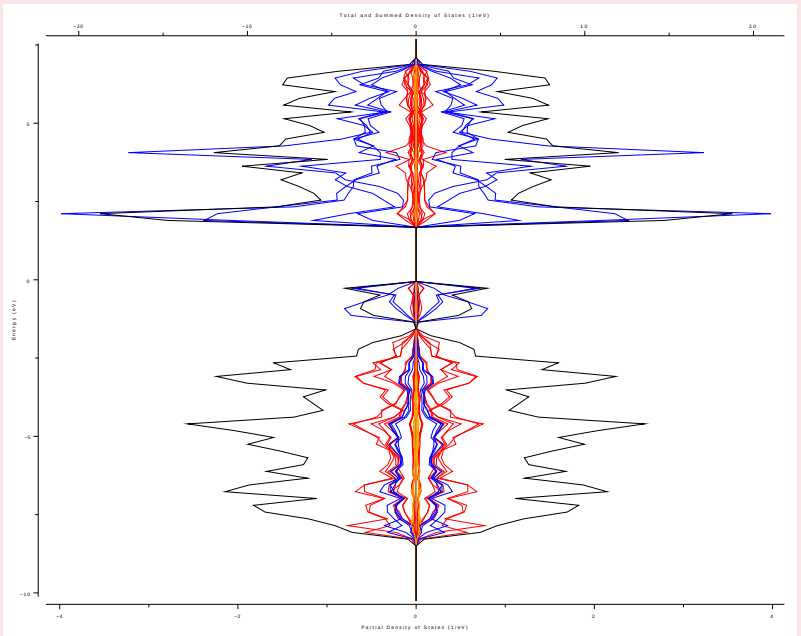


New Calculations: GGA vs. HSE

M_2 Structure GGA



M_2 Structure HSE



M_2 Structure: GGA $\Longrightarrow$ HSE

- localized magnetic moment of 1 μ_B
- optical bandgap of $\approx$ 1.6 eV

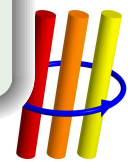
Unified Picture

Rutile-Related Transition-Metal Dioxides

VO_2 ($3d^1$), NbO_2 ($4d^1$), MoO_2 ($4d^2$)
(WO_2 ($5d^2$), TcO_2 ($4d^3$), ReO_2 ($5d^3$))

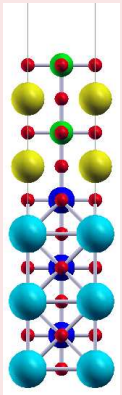
- instability against similar local distortions
  - metal-metal dimerization $\parallel c_R$
  - antiferroelectric displacement $\perp c_R$
- („accidental“) metal-insulator transition of the d^1-members

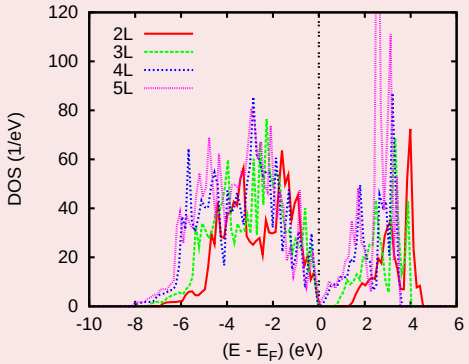
VE *et al.*, J. Phys.: CM **12**, 4923 (2000)
VE, Ann. Phys. **11**, 650 (2002)
VE, EPL **58**, 851 (2002)
J. Moosburger-Will *et al.*, PRB **79**, 115113 (2009)

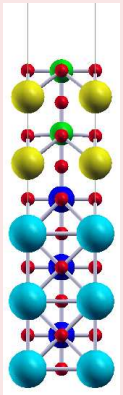


Success Stories

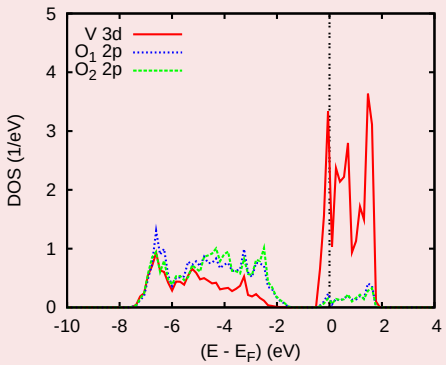
$LaAlO_3/SrTiO_3$

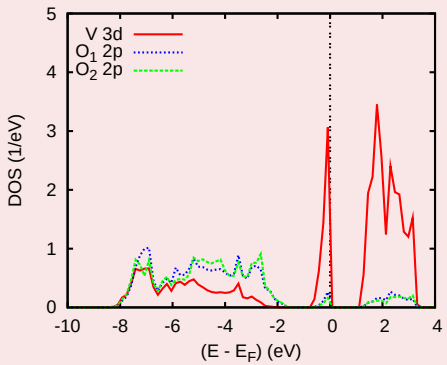


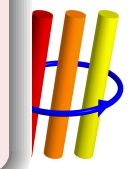




Metal-Insulator Transitions in VO_2







Acknowledgments

Augsburg

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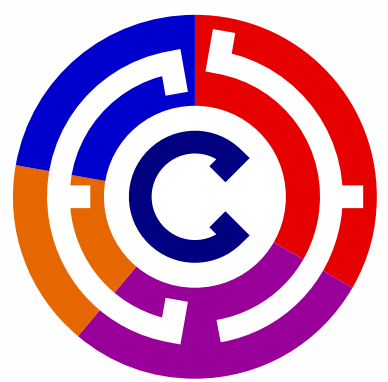

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