Understanding Oxygen on LSM Surfaces

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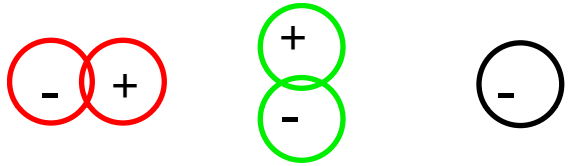
We will see how an O atom can be captured on a $SrMnO_3$ surface

(surprisingly difficult)

Electronic Structure by Tight Binding

Start at beginning, oxygen atom



Important level: $\varepsilon_p = -13.5eV$

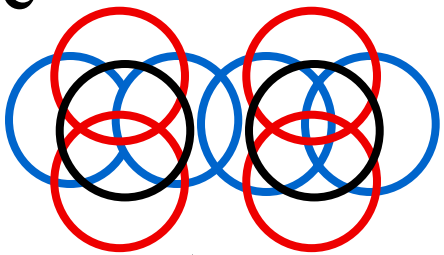
Three orientations, two spins

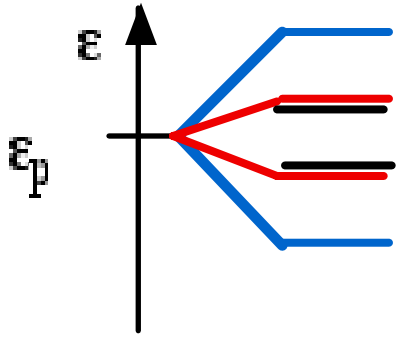
Four electrons, Hund's Rule

Electron affinity:

$$\varepsilon_p^* = \varepsilon_p + U = -1.47eV$$

Oxygen Molecule



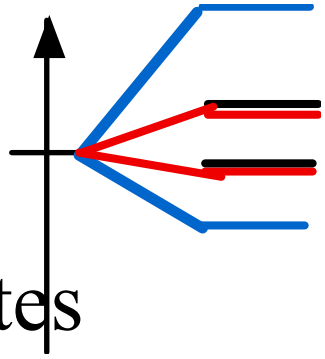


$V_{pp\sigma} = 2.22 \frac{\hbar^2}{md^2}$ $\qquad V_{pp\pi} \approx -1/3 V_{pp\sigma}$ (but use exponential)

Eight Electrons, half-filled antibond π

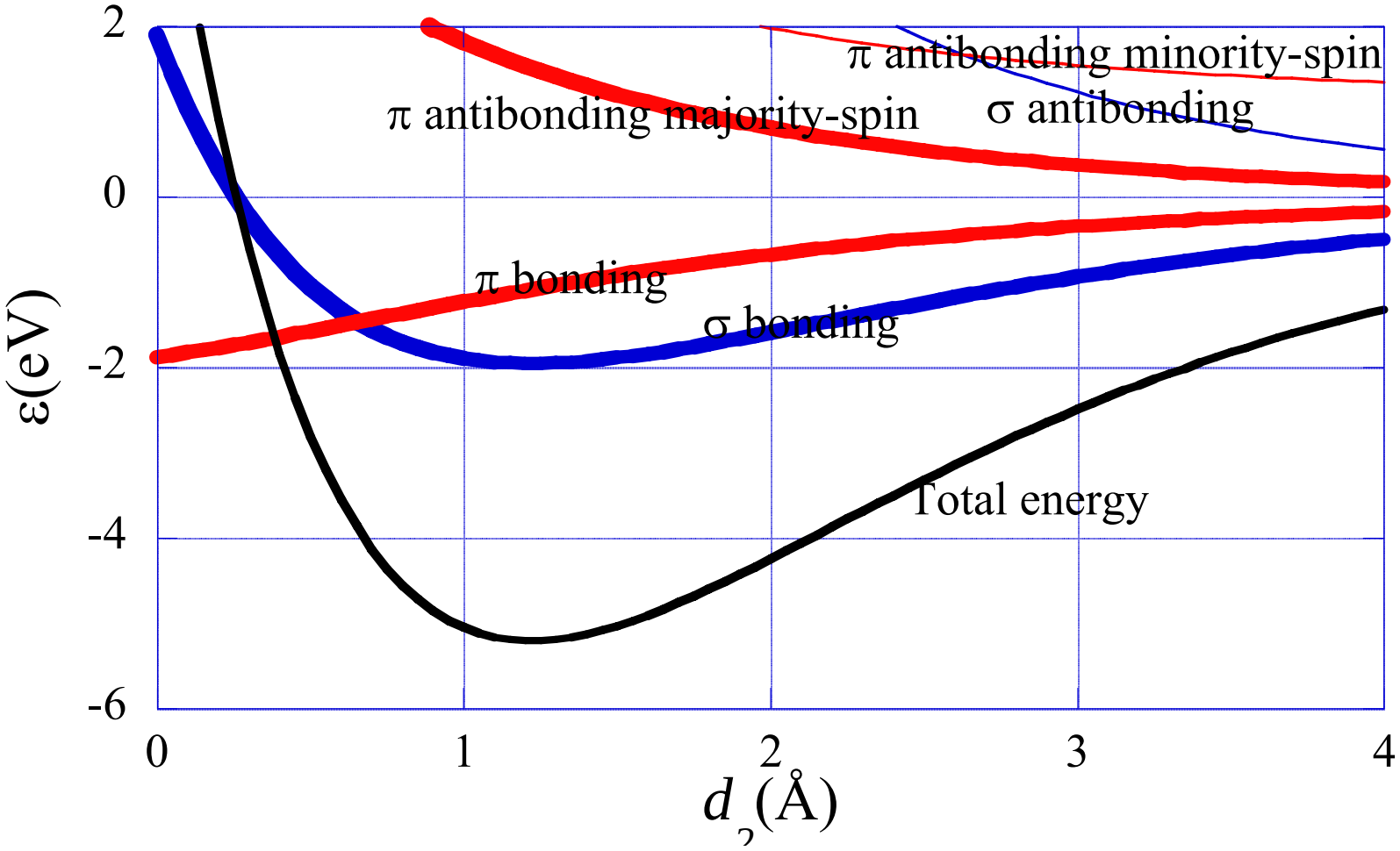
Hund's Rule: Again spin one.

Also repulsion $\delta\varepsilon_p \propto \frac{V_{pp\sigma}^2}{\varepsilon_p}$



Total energy ≈ sum for occupied states

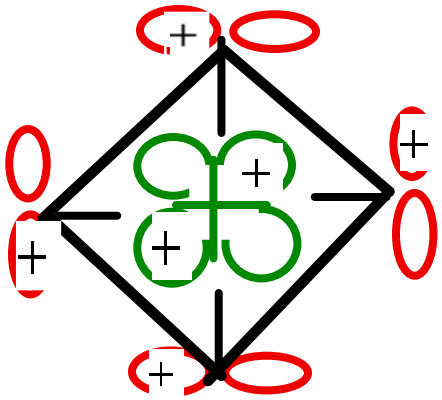
- Bring two oxygen atoms together:



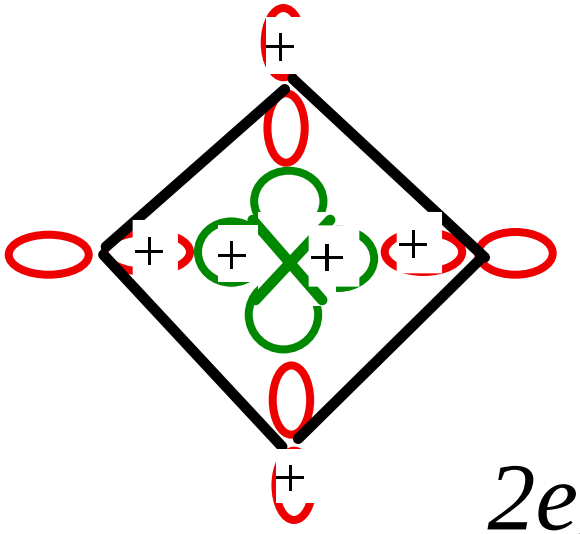
LSM arXiv:0807.2248

Essential Electronic Structure:

Cluster States (Coupled $|p\rangle$ and $|d\rangle$)



$3t_g$

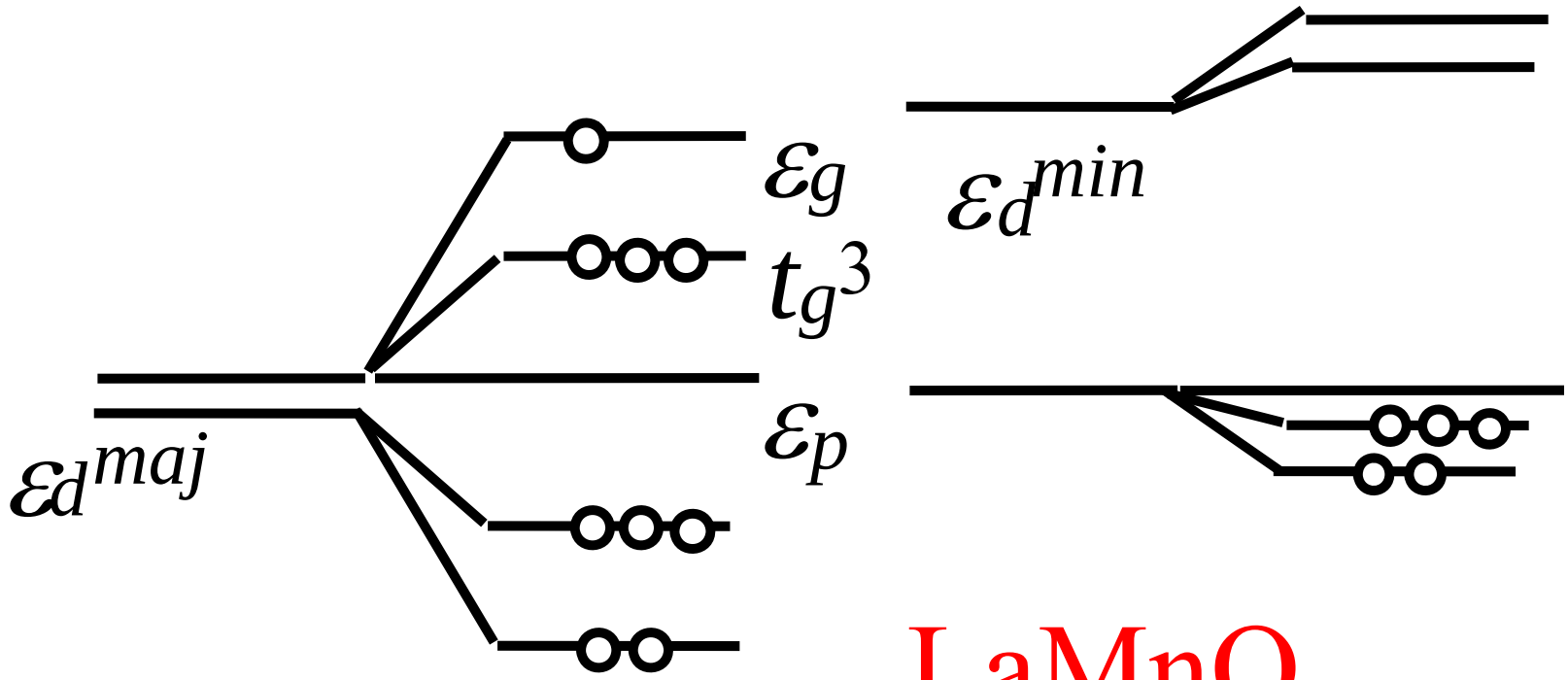


$2e_g$

$2V_{pd\pi} = 1.25$ eV

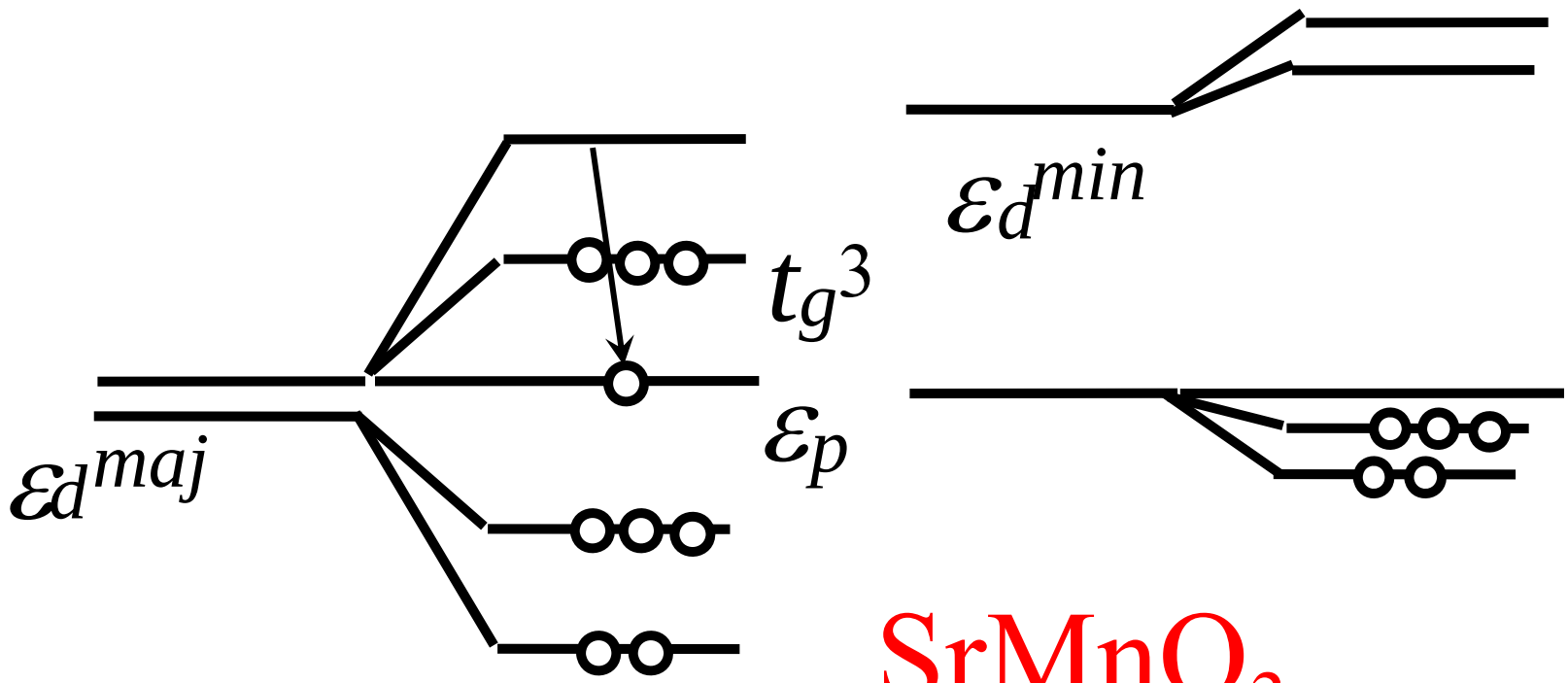
$\sqrt{3}\ V_{pd\sigma} = -1.88$ eV

Cluster Levels
e_g levels are most important



$LaMnO_3$

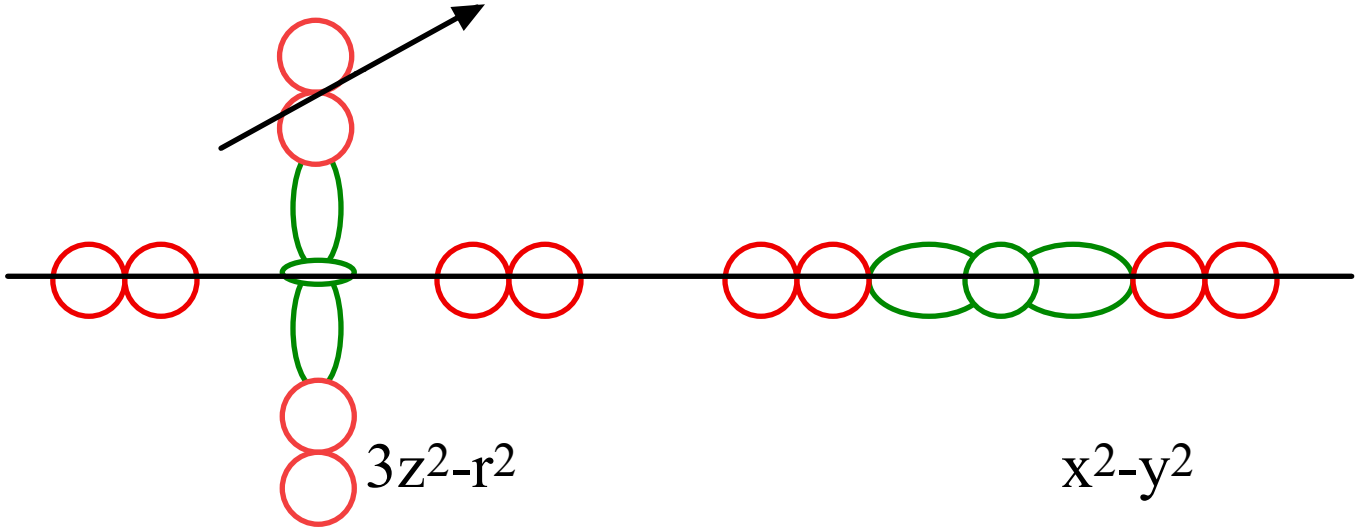
Drop 2nd e_g majority-spin el'n



$SrMnO_3$

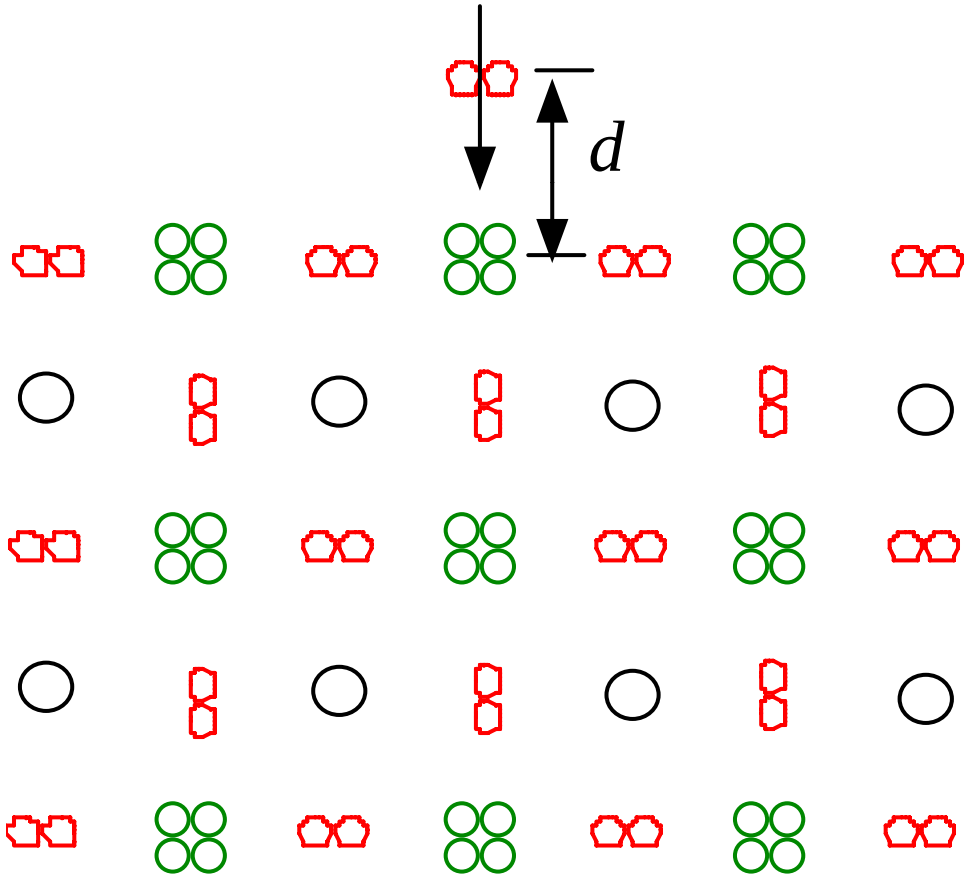
- Surfaces of LSM

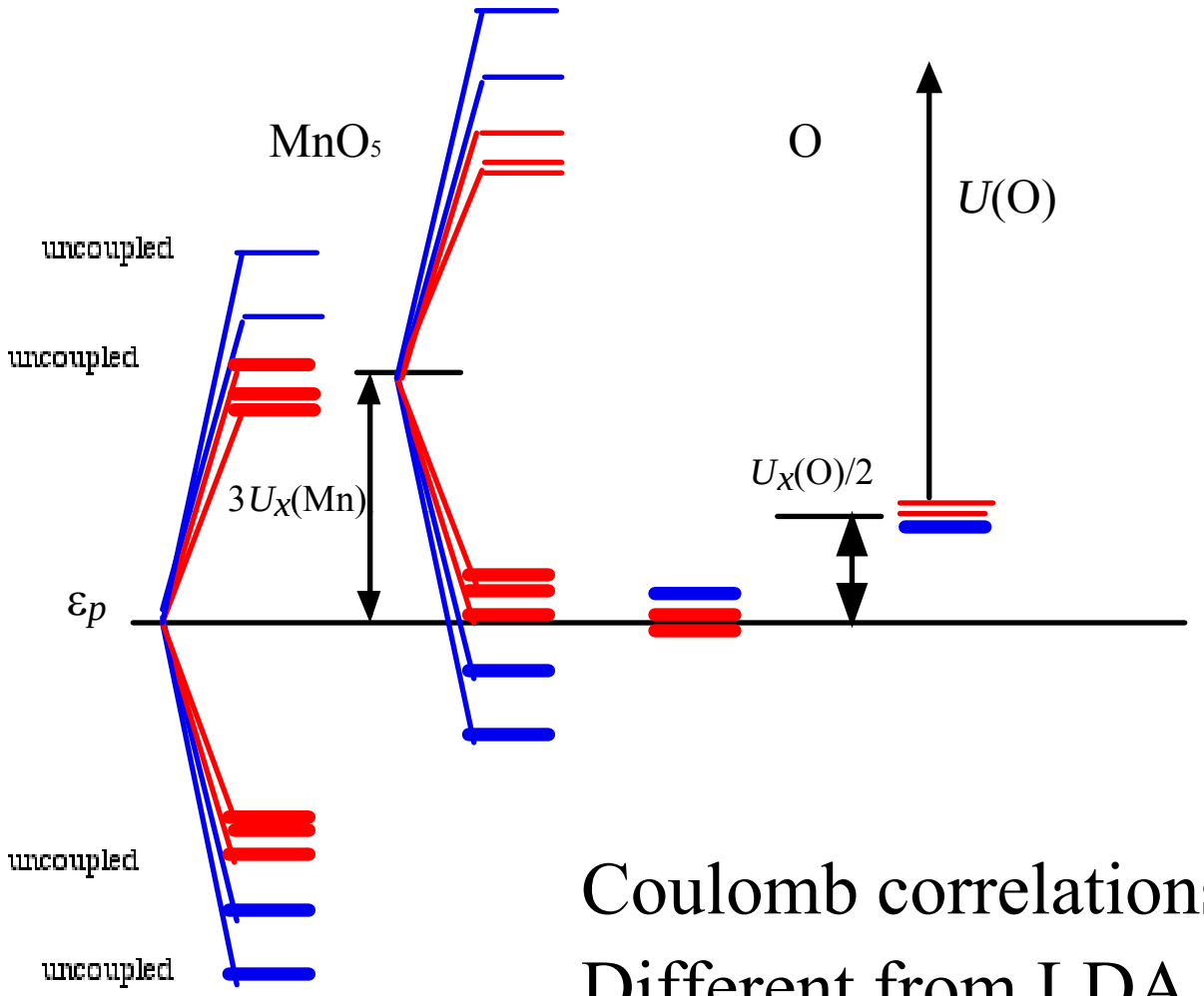
Modified clusters



Treated surface energy and relaxation

First an oxygen *atom* on $SrMnO_3$





Coulomb correlations
Different from LDA

The interesting case is when antiparallel.

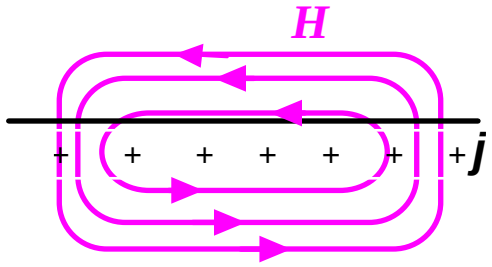
Interesting side issue

Antiparallel alignment for attachment

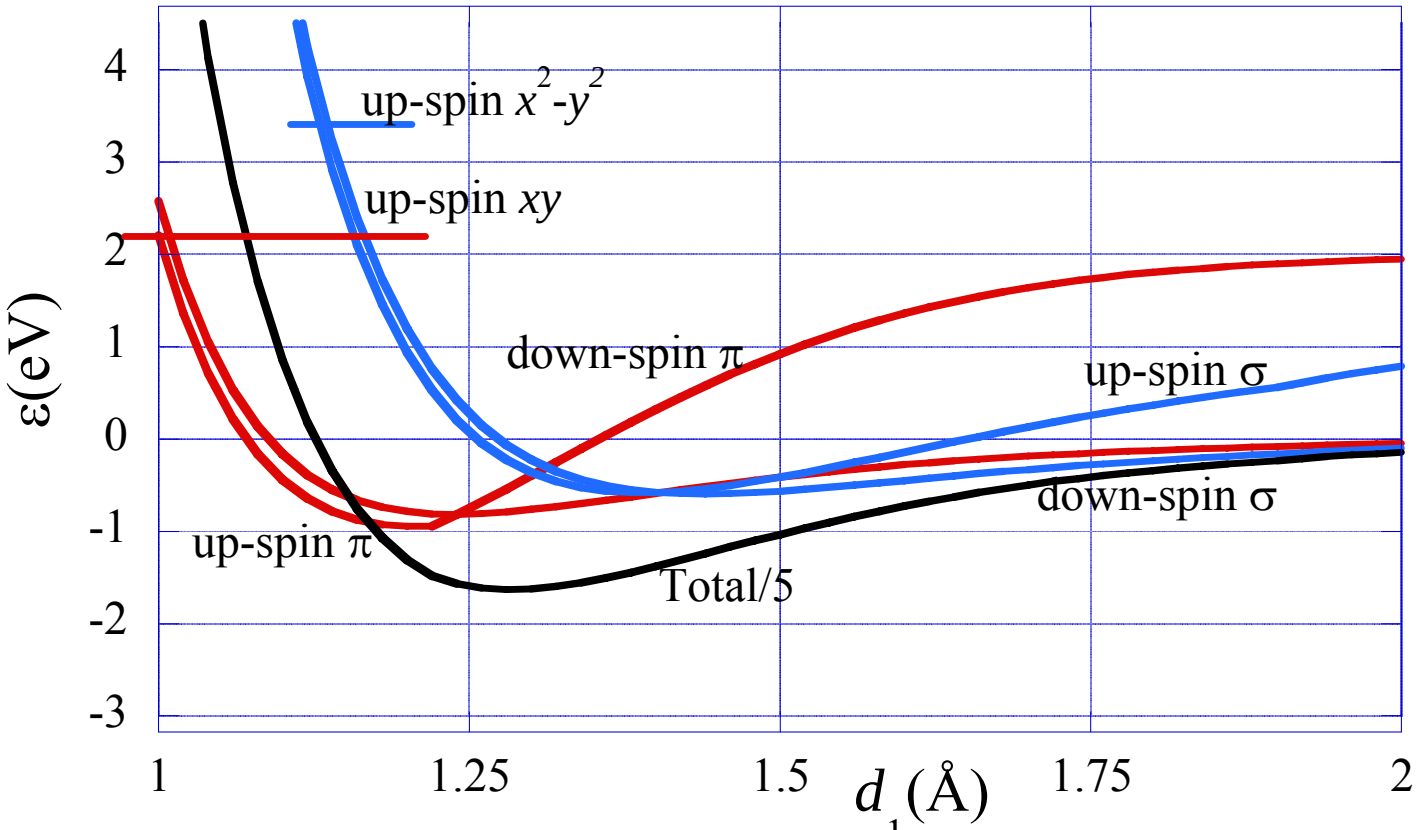
Applied magnetic field favors parallel

Suppresses attachment (in principle)

Surface current favors attachment

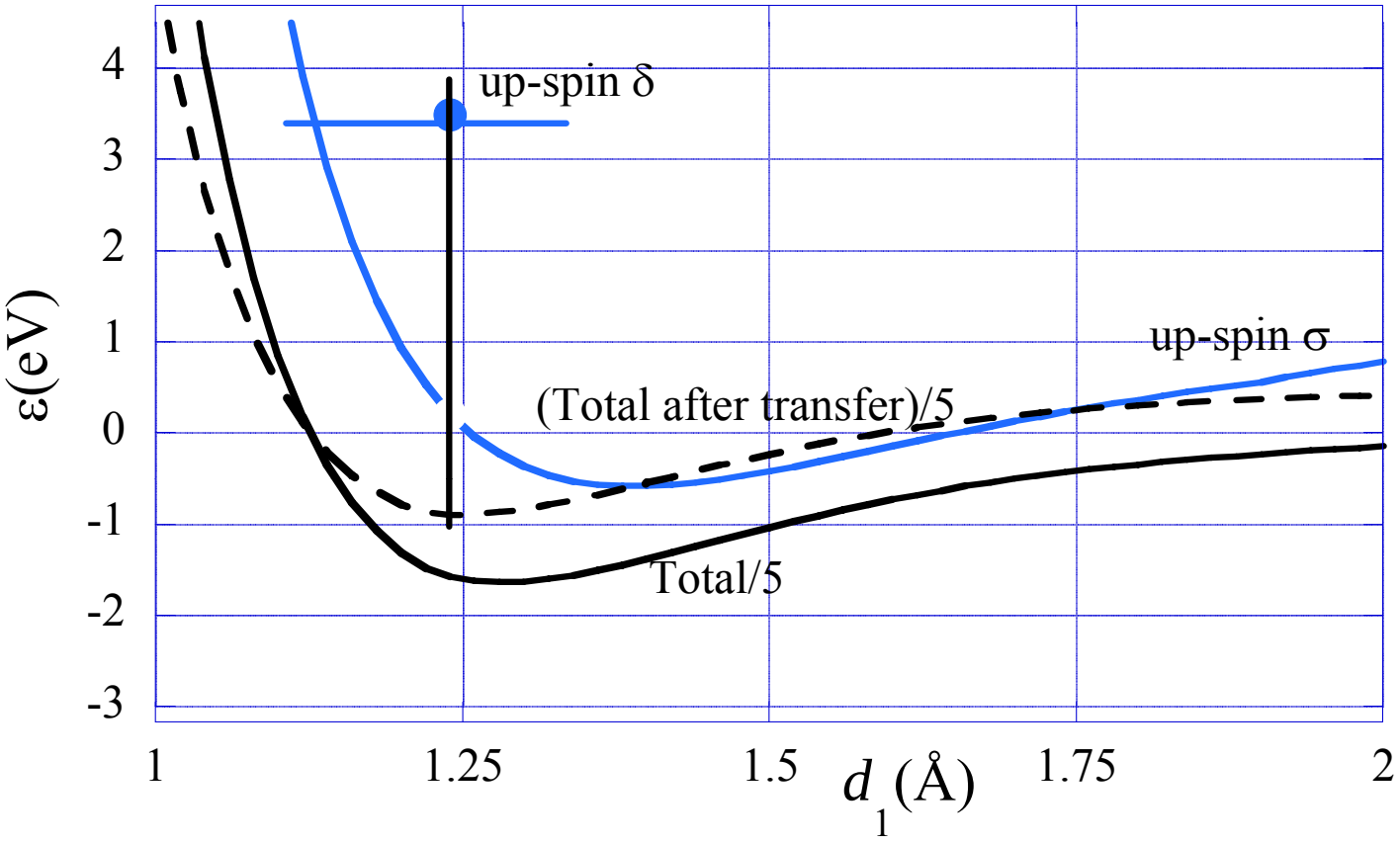


- But $2\mu H = 1.16\times10^{-6}$ eV at 1000 gauss



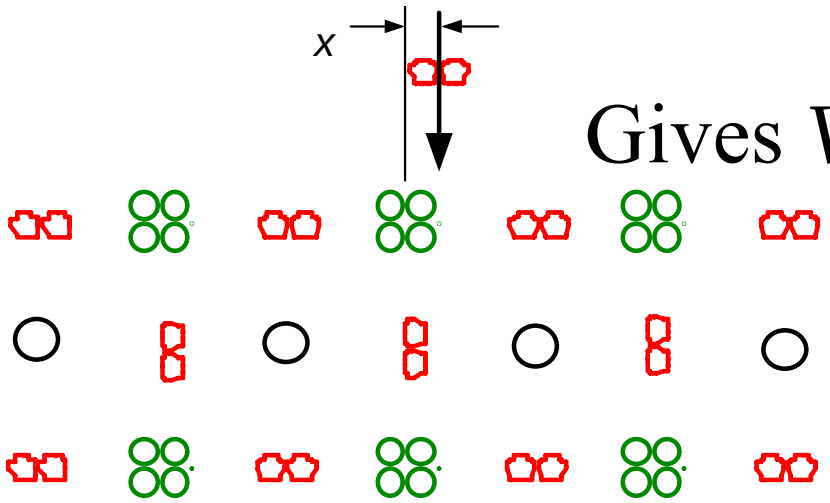
- Must bounce off unless something *happens*

Something can! Level crossing.

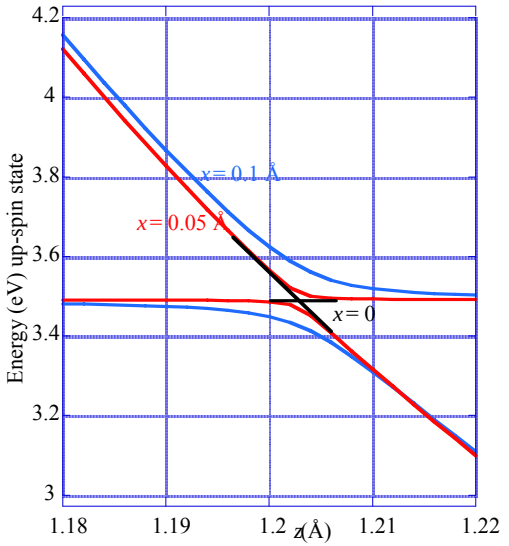


- System left vibrating, and with an electron in an excited state.

Levels only cross at one point



Gives $V' \propto x^2$

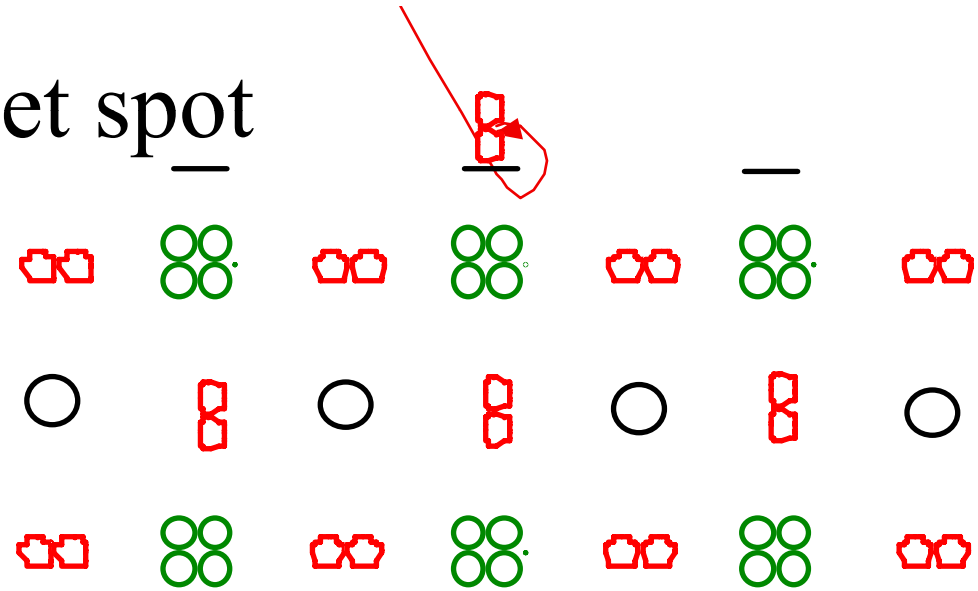


- No help,

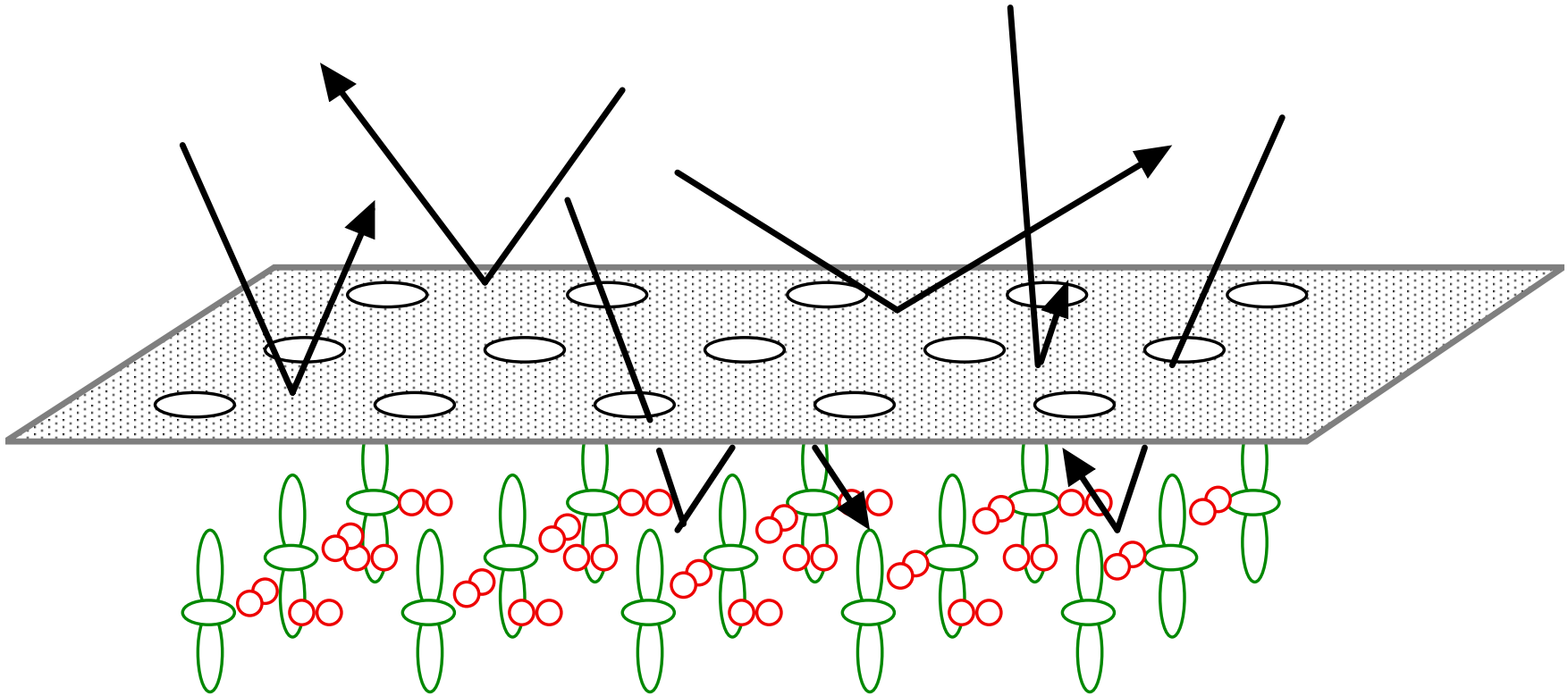
  But can jump

$$P_{12}=2\pi V'^2/(\hbar\partial(\varepsilon_1-\varepsilon_2)/\partial t)\propto x^4$$

Sweet spot



Some 7% of surface area



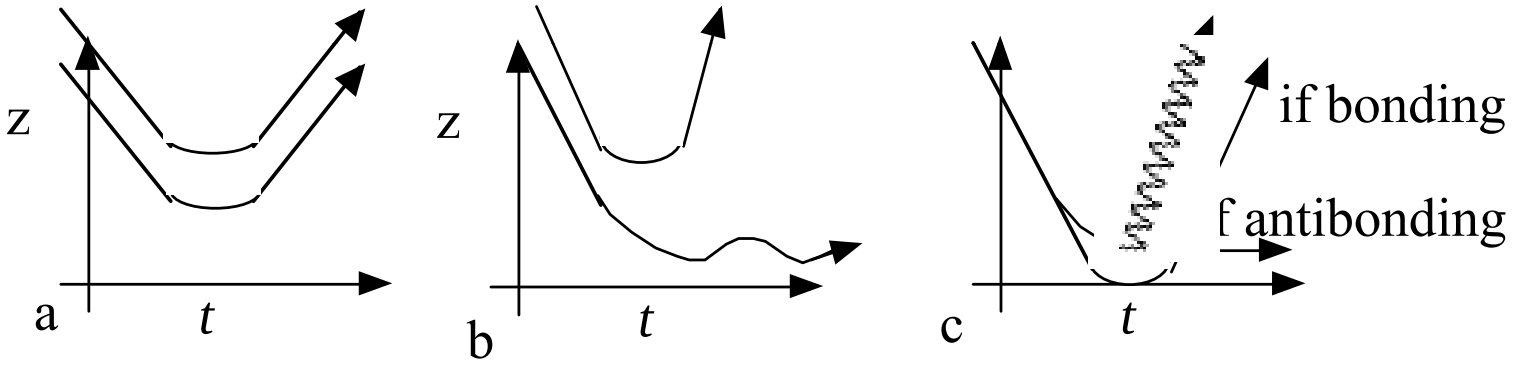
- No sweet spot over O-site
- Not so favorable in $LaMnO_3$

  but Mn^{4+} sites OK in LSM

Next on agenda: O_2

Same formulation

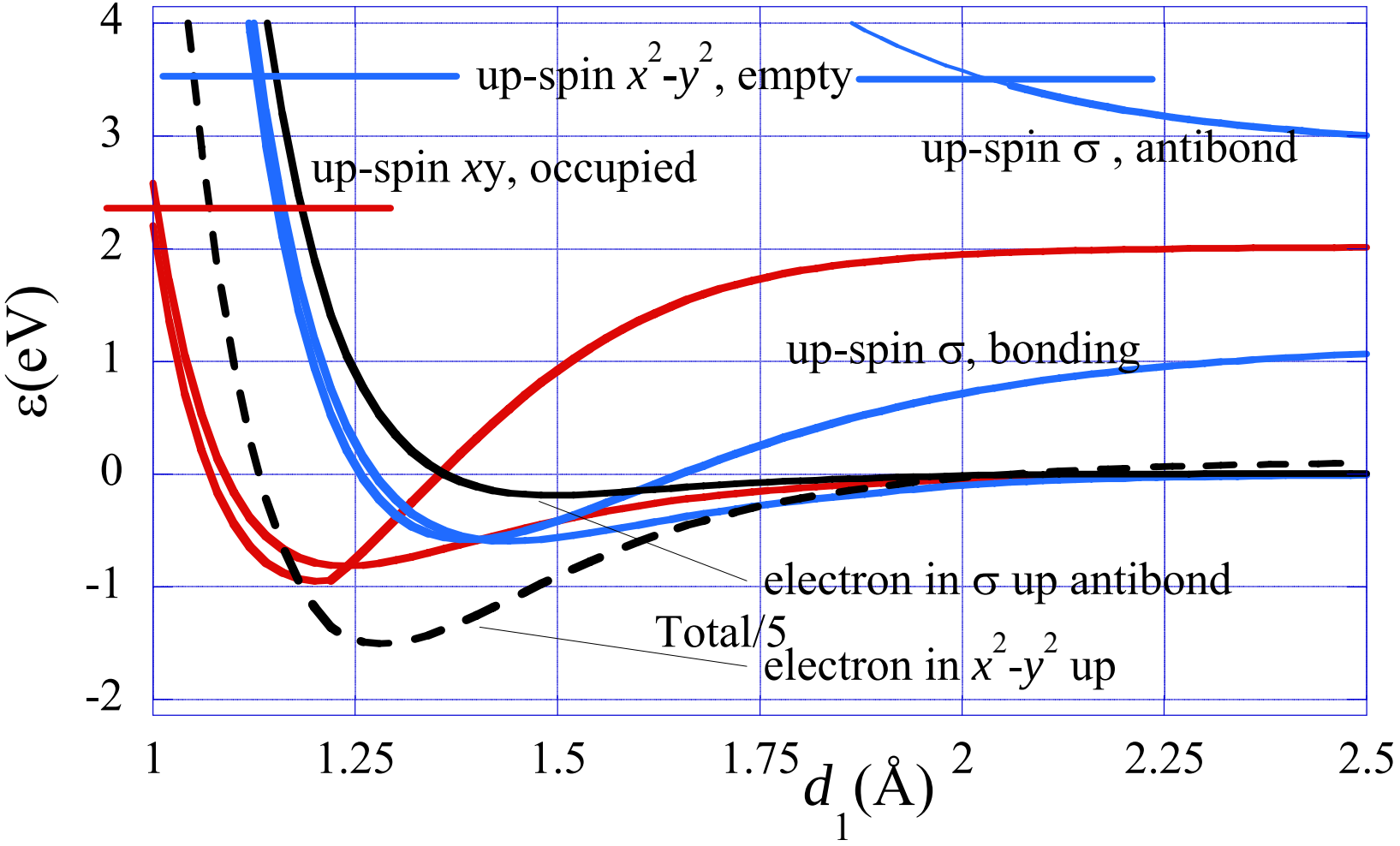
O_2 vertical, over Mn:



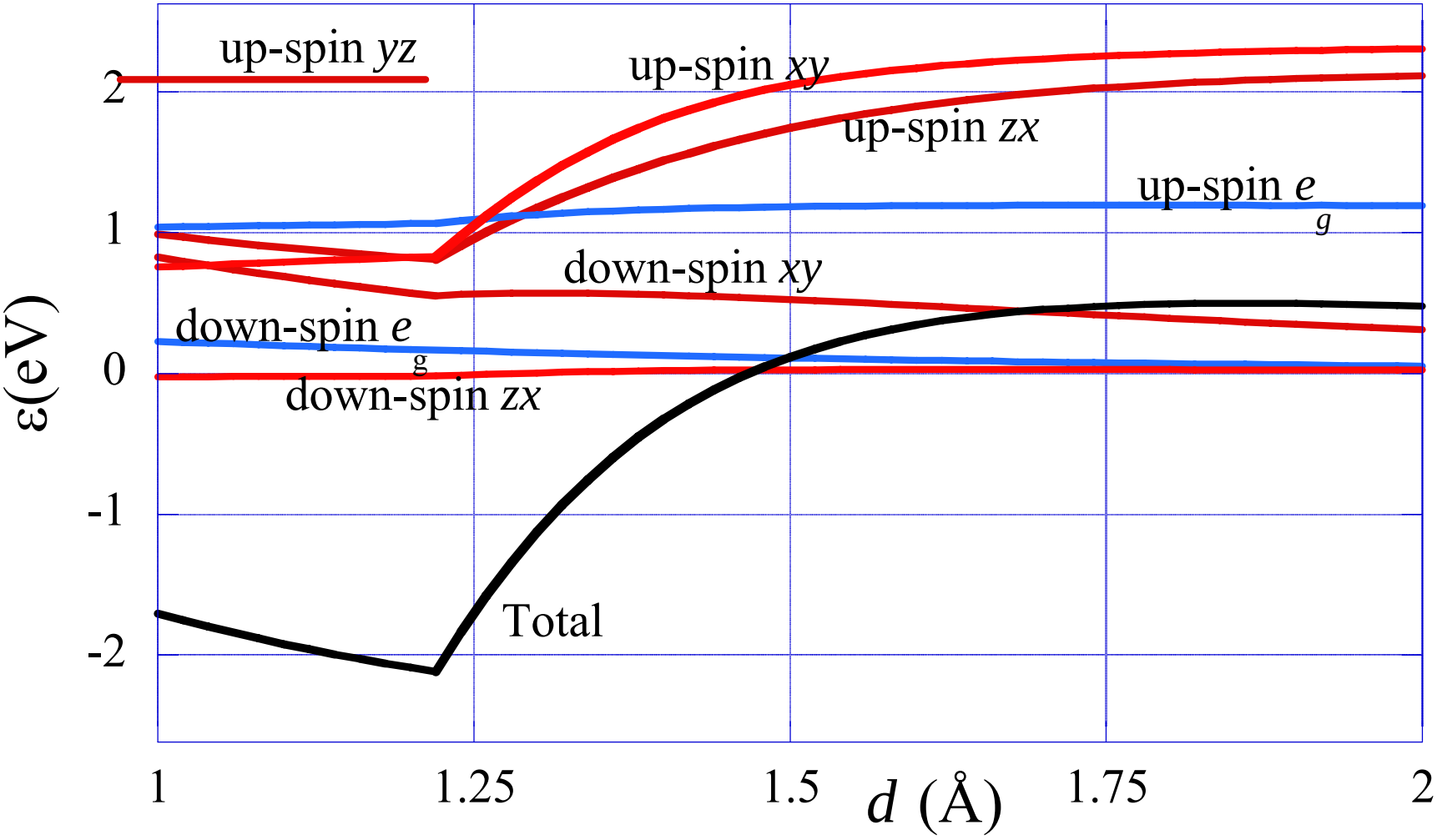
Many possibilities.

Need include vacant site.

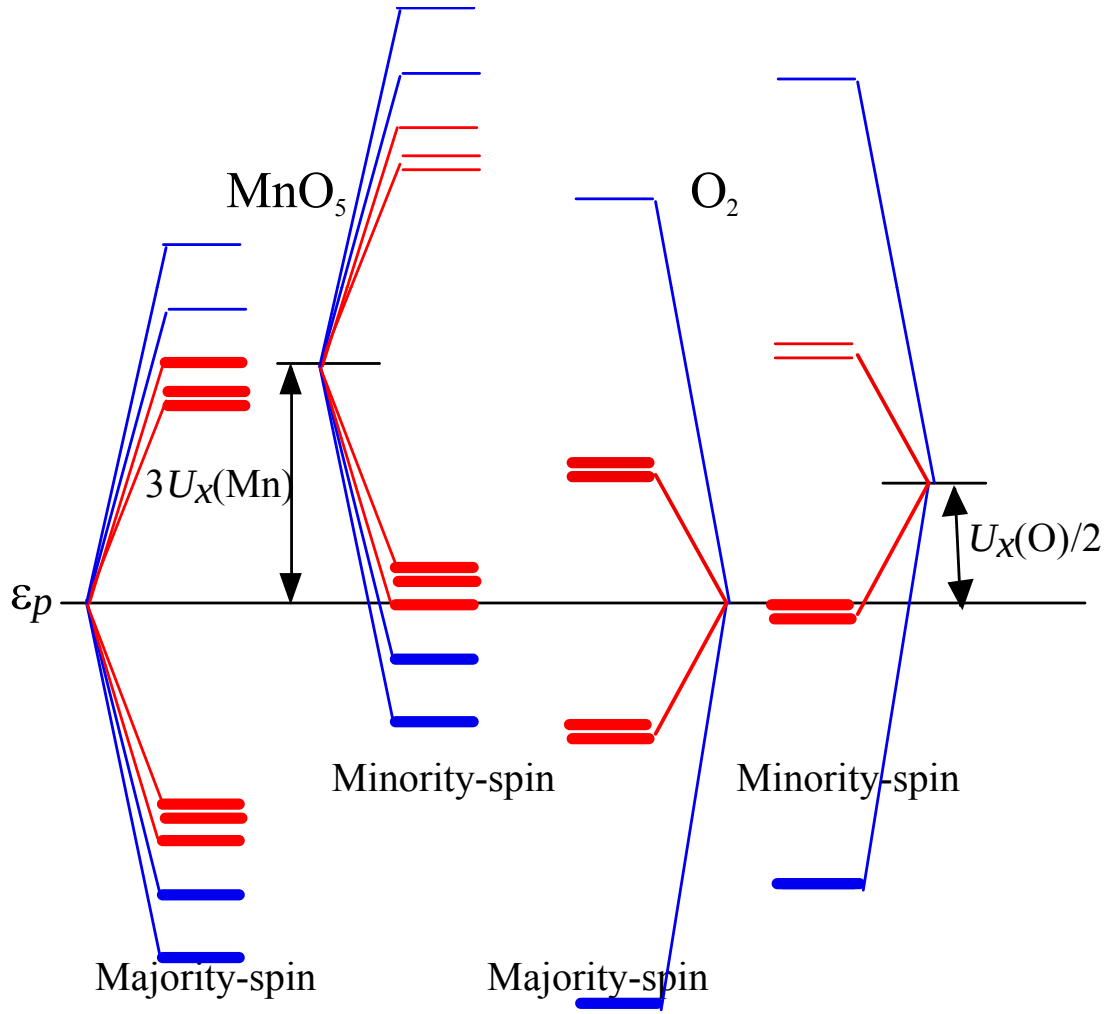
O on $LaMnO_3$


4
3
2
1
0
-1
-2
ε(eV)
up-spin x^2-y^2, empty
up-spin xy, occupied
up-spin σ , antibond
up-spin σ, bonding
electron in σ up antibond
Total/5
electron in x^2-y^2 up
1
1.25
1.5
1.75
2
2.25
2.5
d_1 (Å)

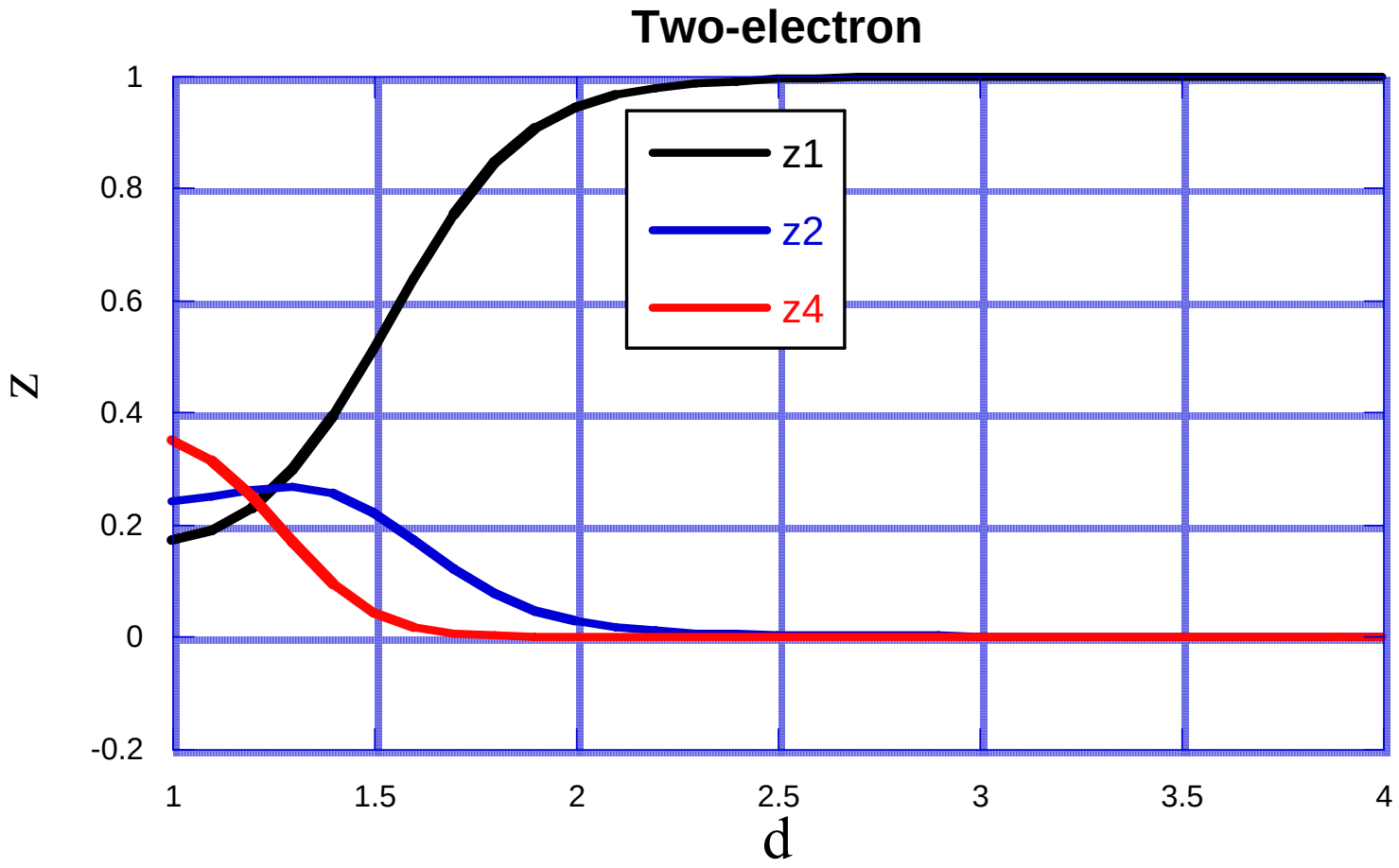
Oxygen over O site



O_2 on $SrMnO_3$


MnO5
O2
3UX(Mn)
UX(O)/2
εp
Minority-spin
Minority-spin
Majority-spin
Majority-spin

Charges from two-electron calc.



O on MnO_5, charge on O