Electronic Structure of Cathode Materials

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- Electronic structure is basis for all properties of condensed matter.

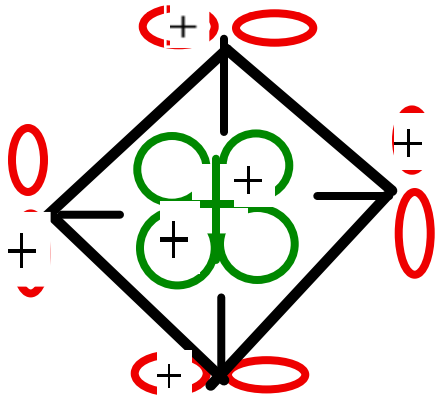
  Will discuss basic electronic structure
  Then summarize consequences

- Usual to build on earlier understanding
  Chemist: chemical bond
  Physicist: energy bands
  Both inappropriate for cathode materials
  e. g., $La_{1-x}Sr_xMnO_3$

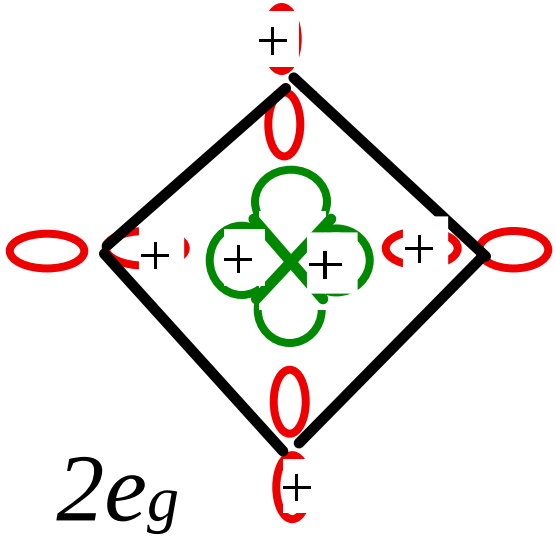
- Bonding in manganites (also Fe,Co,Ni)

  Dominated by *s* to *p* transfer

  Tiny part from MnO_6 cluster states



$3t_g$



$2e_g$

But they dominate all other properties!

- MnO, Mn^{2+}, all 5 majority-spin occupied
  All 5 minority-spin empty. Moment 5μ
  Heisenberg coupling, antiferro.

- Mn_2O_3, $LaMnO_3$, Mn^{3+} (one e_g empty)
- MnO_2, $SrMnO_3$, Mn^{4+} (both e_g's empty)

- $La_{1-x}Sr_xMnO_3$, Some each

- Like bond orbitals in semiconductors

  But in semiconductors

  they combine to form energy bands.

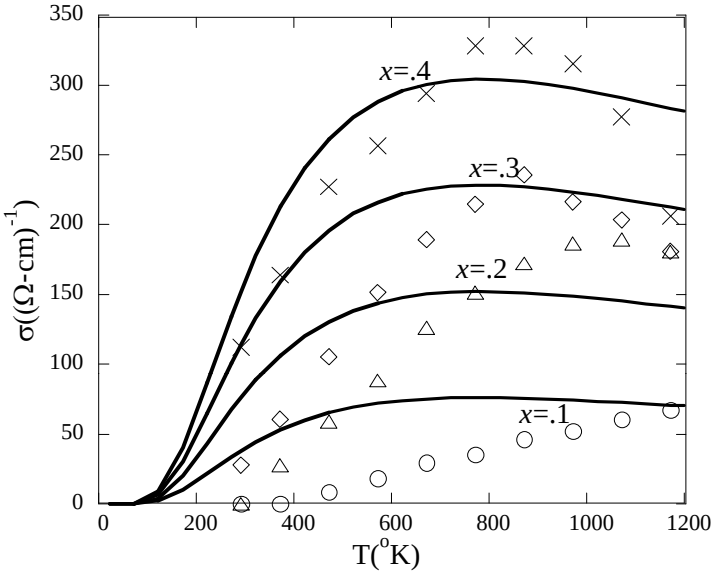
  Electrons flow as if free;

  In $La_{1-x}Sr_xMnO_3$, $Mn^{3+} \rightarrow Mn^{4+}$

  Move mainly by thermal excitation

  (Small polaron hopping, not flow)

LSCF



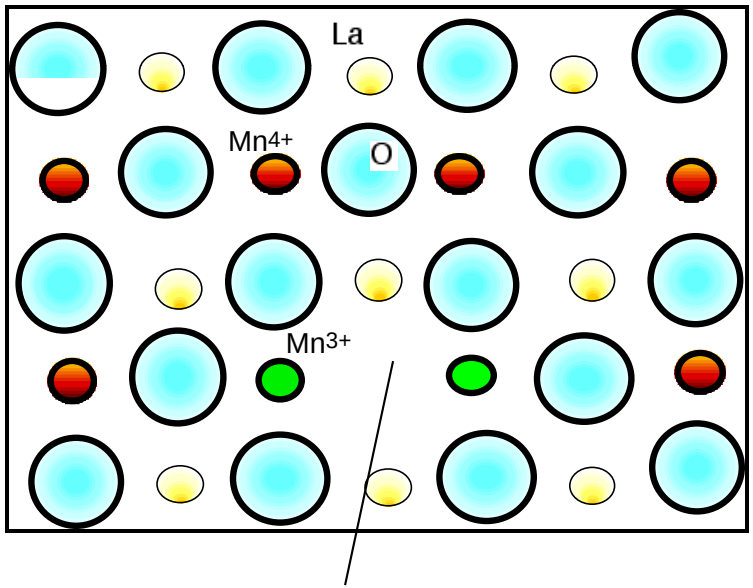
- Incontrovertible evidence, I think
- Must analyze systems in terms of local cluster orbitals

Consequences, Doping

- Semiconductors P(Si): (alchemy)
  Carriers in conduction band, conduct
- Different in NaCl, local state at impurity
  Special case, Cl vacancy, F-center
- Zirconia $Y(ZrO_2)$
  Neutrality by oxygen vacancies, V^{2+}
- Manganites La in $SrMnO_3$
  Convert Mn^{4+} clusters to Mn^{3+}

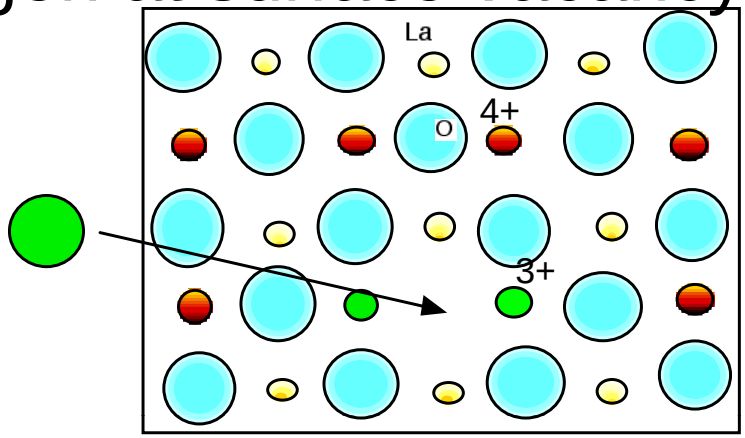
- Another Consequence
- O Vacancy^{2+} in YZO *because of* neutrality
- OV^{2+} in $SrMnO_3$ causes $2Mn^{4+} \rightarrow 2Mn^{3+}$

  Will want to be adjacent to vacancy

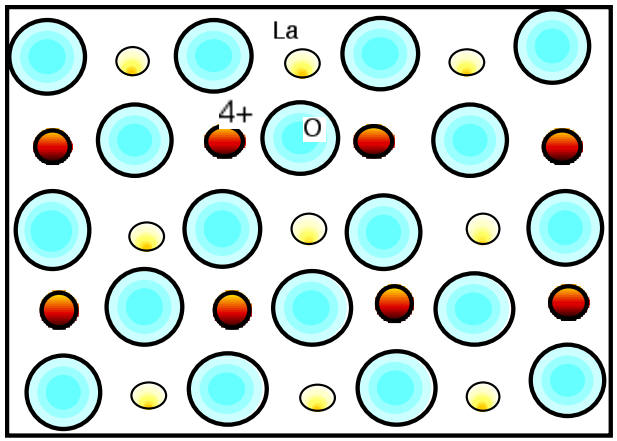


- Neutral Oxygen vacancy, like F-center

- Oxygen at surface vacancy



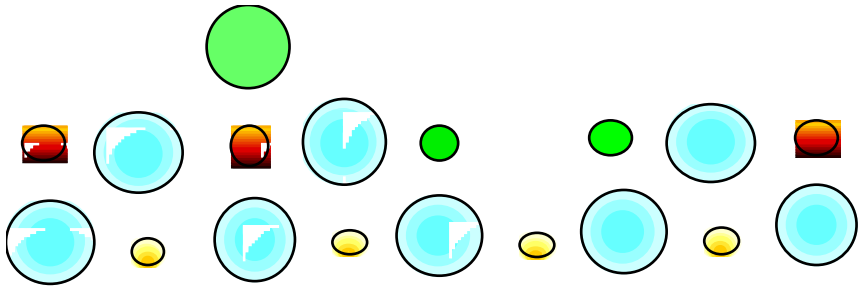
- Neutral atom fills neutral vacancy



No ionization!

Electron transfer at YZO-LSM interface!

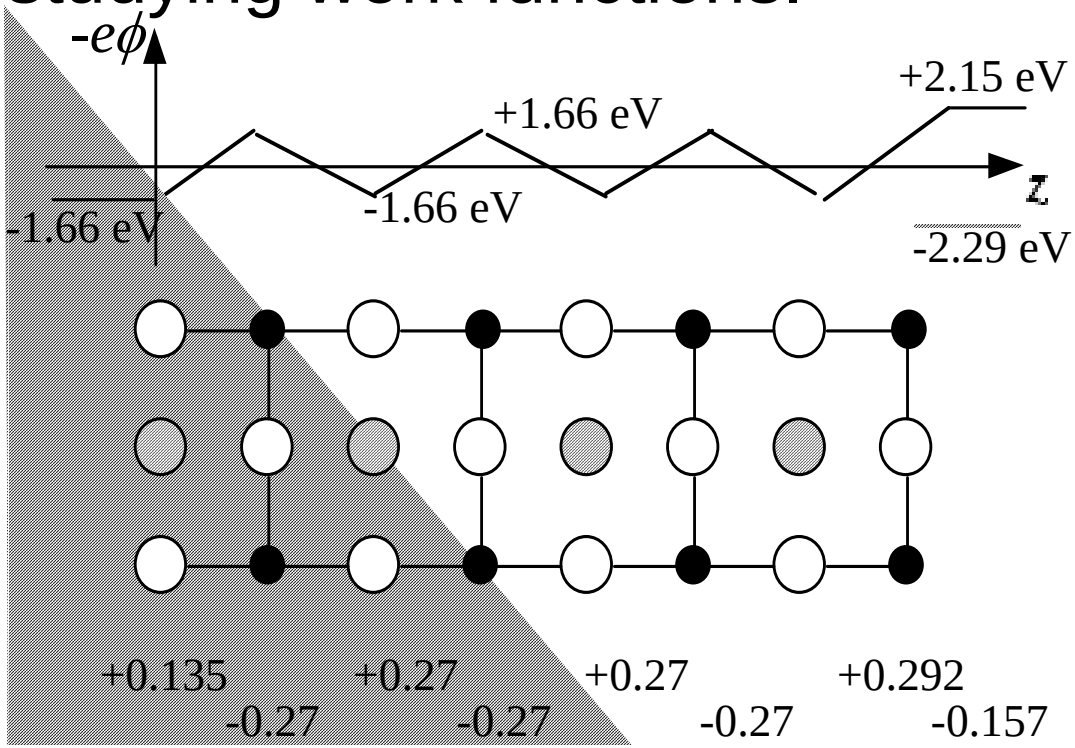
- Problem: Adatom bond is stronger on Mn^{4+}



Slows incorporation.

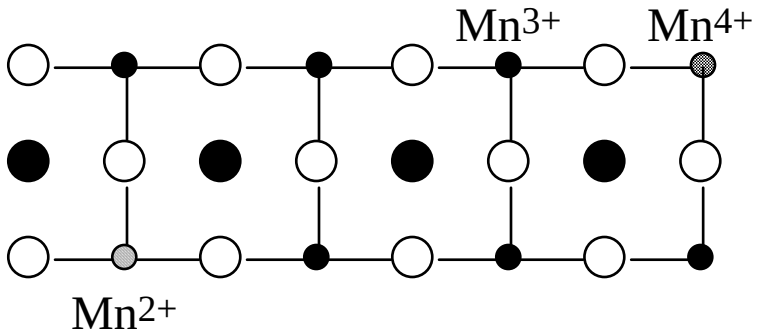
Maybe there's a way around?

- To better understand surfaces,
  studying work functions.



$SrMnO_3$, Layers formally neutral, SrO, MnO_2

- $LaMnO_3$. Planes formally charged
  So surface has net charge
  Total energy would diverge
  But neutralize with half planes



Leaves too large dipole. We'll see!

- Walter A. Harrison, *Tight-Binding Theory of Lanthanum Strontium Manganate*, arXiv:0807.2248. (2009).

- Walter A. Harrison, *Oxygen atoms and molecules at $La_{1-x}Sr_xMnO_3$ surfaces*, Phys. Rev. B **81**, 045433 (2010) (arXiv:0911.2268).

- Walter A. Harrison, *Theoretical Alchemy,* World Scientific Publishing Company, (Singapore, 2010).

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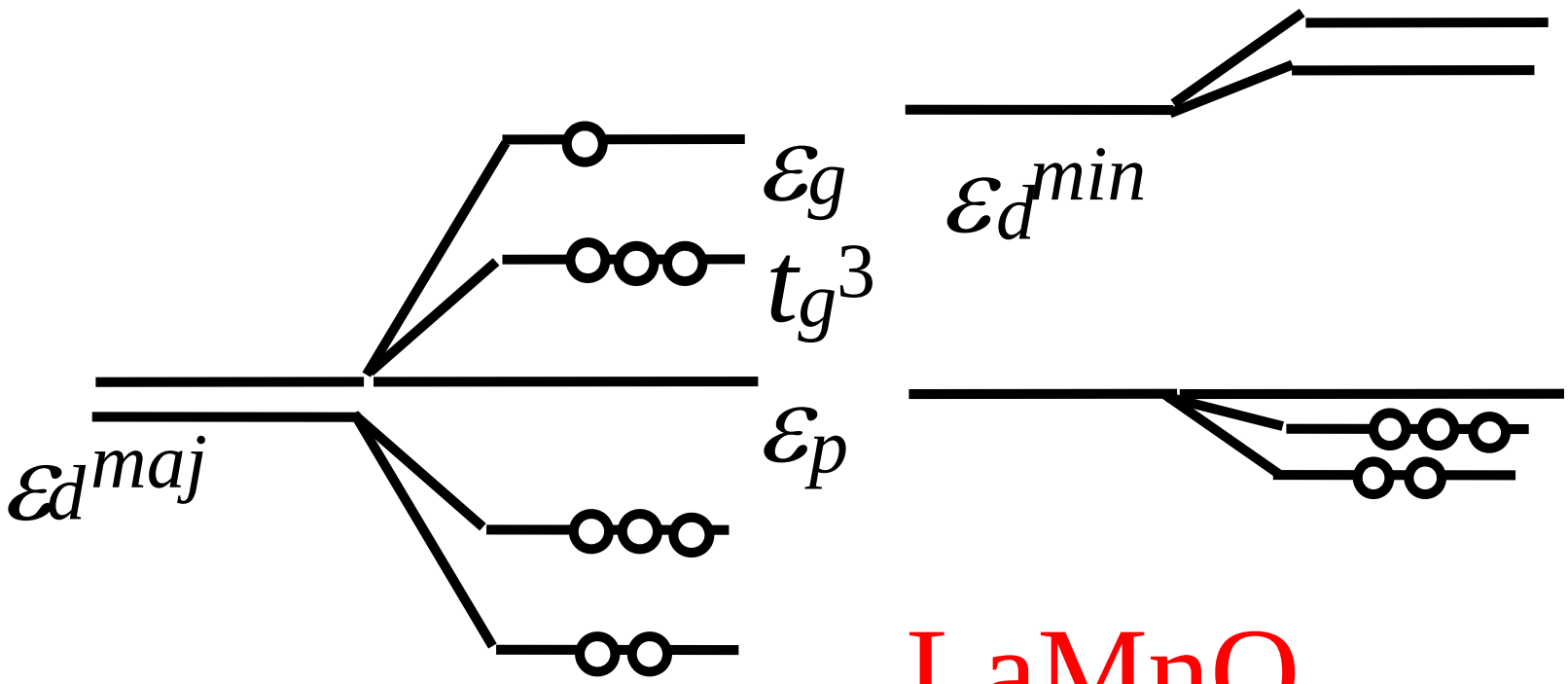
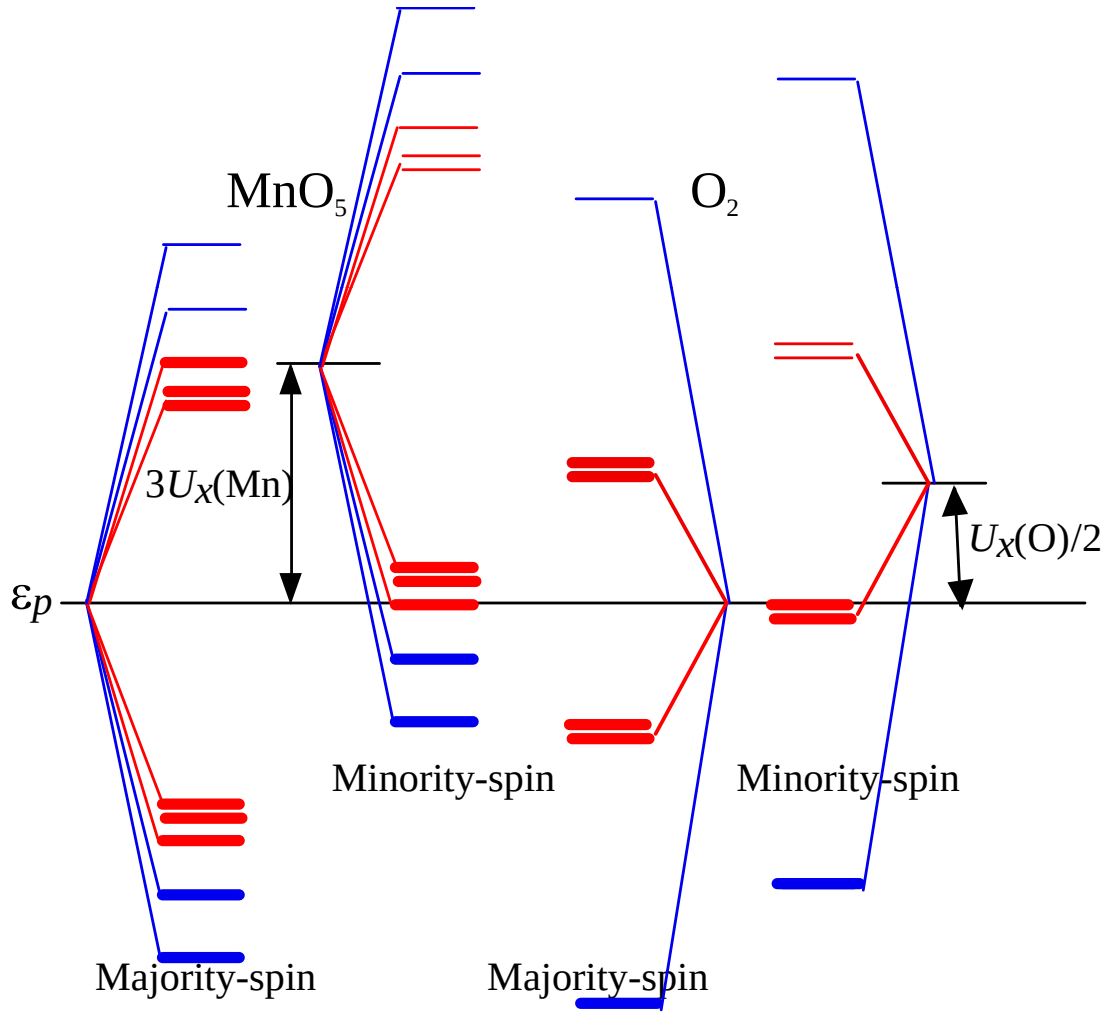
Cluster Levels

e_g levels are most important



$LaMnO_3$

O_2 on $SrMnO_3$


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