Density Functional Theory and Applications to Transition Metal Oxides

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Blueberry Muffins

The blueberries change the taste, but the muffin is still basically a muffin.

The taste does not depend much on the distribution of berries.

Pre-History

Westminster Abbey, London

"*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations that are much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.*"

P.A.M. Dirac, *Proc. Roy. Soc. (Lond)* **123**, 714 (1929).

$H\psi = E\psi$: Many Body Problem, with correlated many-body wavefunctions ➔ Too hard.

Wigner and Seitz (1955)

"If one had a great calculating machine, one might apply it to the problem of solving the Schrodinger equation for each metal and obtain thereby the interesting physical quantities, such as cohesive energy, the lattice constant, and similar parameters. Presumably, the results would agree with experimentally determined quantities and nothing vastly new would be gained from the calculation. **It would be preferable, instead, to have a vivid picture of the behavior of the wave functions, a simple description of the essence of the factors which determine cohesion, and an understanding of the origins** *..."*

E.P. Wigner and F. Seitz, Solid State Physics, Vol. 1 (1955).

The Electron Gas

D. Ceperley, Nature **397**, 386 (1999).
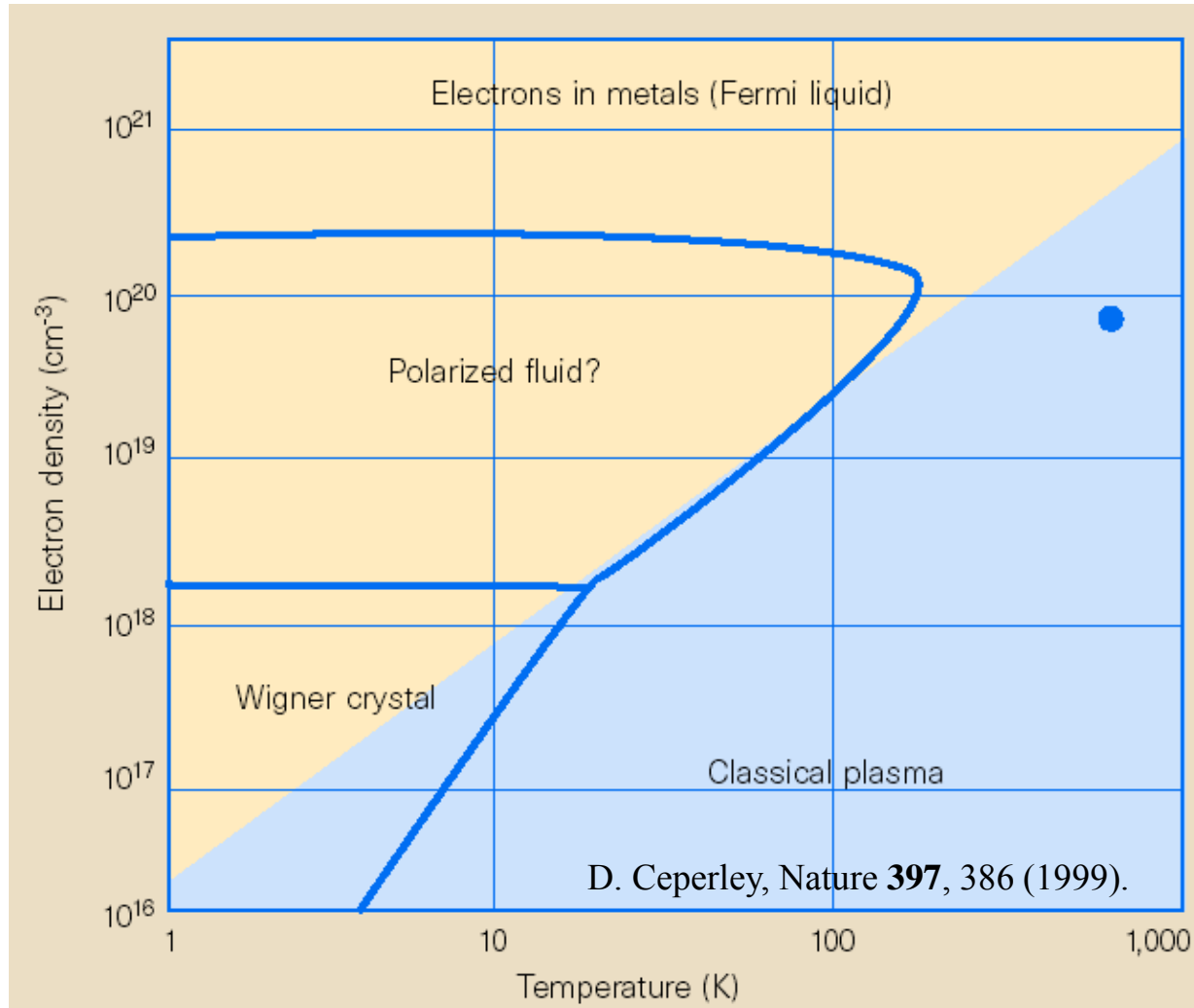
bcc **Fe:** n_{av} =2.2x10^{24} e/cm³ (total); n_{av}= 6.8x10^{23} e/cm³ (valence)

Nothing Interesting Happens in the Uniform Electron Gas at Densities of Solids

The Electron Gas Now With Nuclei

He: liquid at 0 K
W: melts at 3695 K

WARNING

If you do not ask questions, I will.

(corollary) If you do not contradict me, I will.

Property Prediction and Surprises

Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

M. T. Yin* and Marvin L. Cohen

*Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720*

(Received 29 March 1982)

TABLE II. Comparison of calculated and measured static properties of Si and Ge.

	Lattice constant (Å)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
Si			
Calculation	5.451	4.84	0.98
Experiment	5.429[a]	4.63[b]	0.99[c]
Ge			
Calculation	5.655	4.26	0.73
Experiment	5.652[a]	3.85[b]	0.77[c]
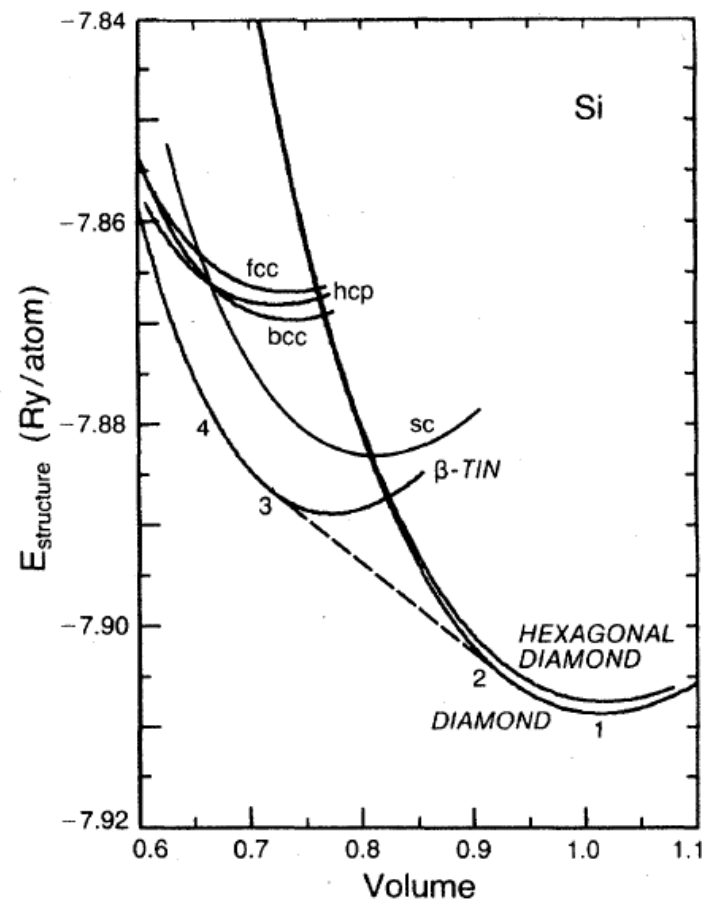
One of many early works of this type.
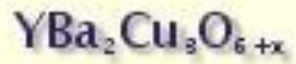
$YBa_2Cu_3O_{6+x}$
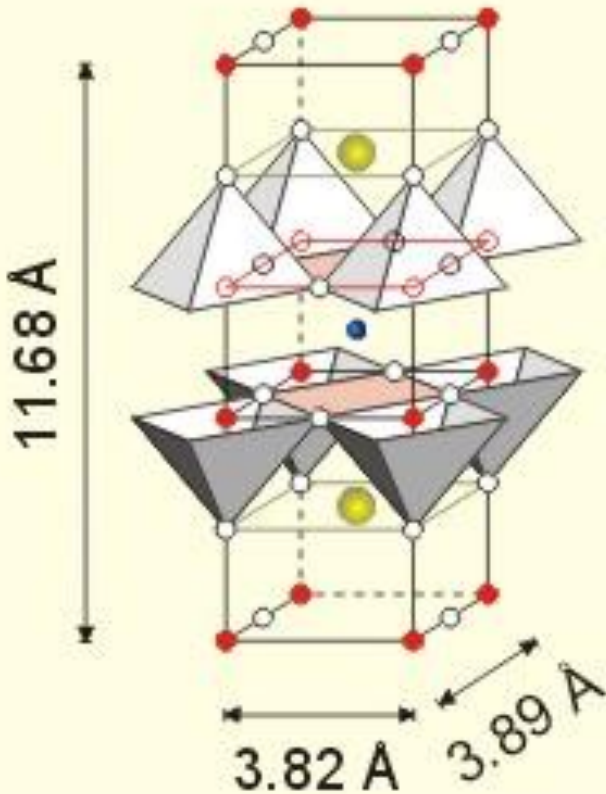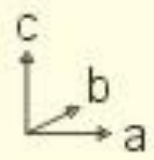
- Y
- Ba
- Cu
- O

Cu(1), O(4)

Ba, O(1)

Cu(2), O(2), O(3)

Y

Cu(2), O(2), O(3)

Ba, O(1)

Cu(1), O(4)

11.68 Å

3.82 Å   3.89 Å

M. Opel

High-T_c Electronic Structures are 2D

Pickett, Cohen, Krakauer, Singh

Bi$_2$Sr$_2$(Ca$_x$Y$_{1-x}$)Cu$_2$O$_{8+\delta}$

Ca /Y
Cu, O(2,3)
Sr, O(1)
Bi, O(4)
Bi, O(4)
Sr, O(1)
Cu, O(2,3)
Ca /Y
Cu, O(2,3)
Sr, O(1)
Bi, O(4)
Bi, O(4)
Sr, O(1)
Cu, O(2,3)
Ca /Y

29 Å

5.5 Å

M. Opel

La$_3$Ni$_2$B$_2$N$_3$ (12K SC)
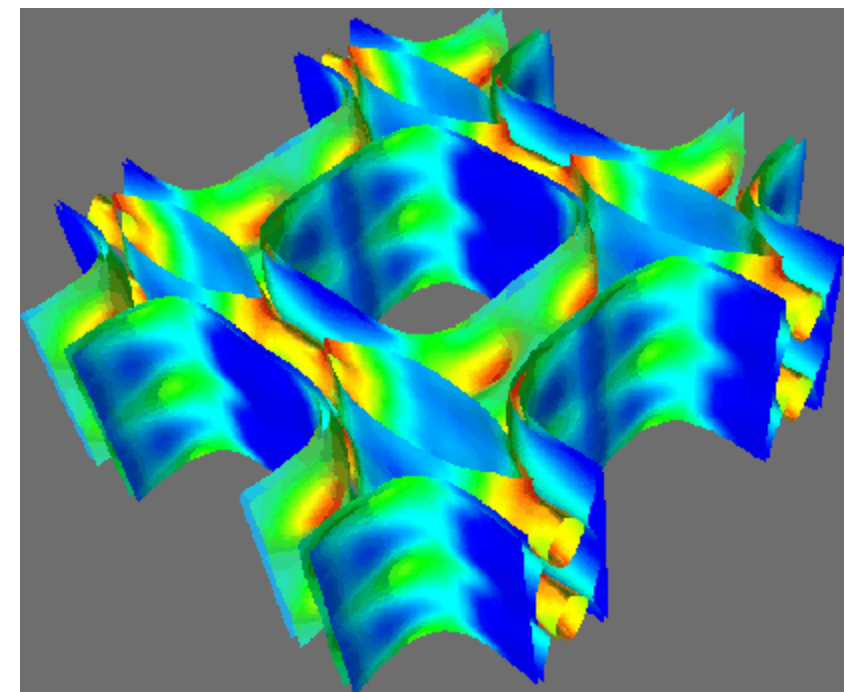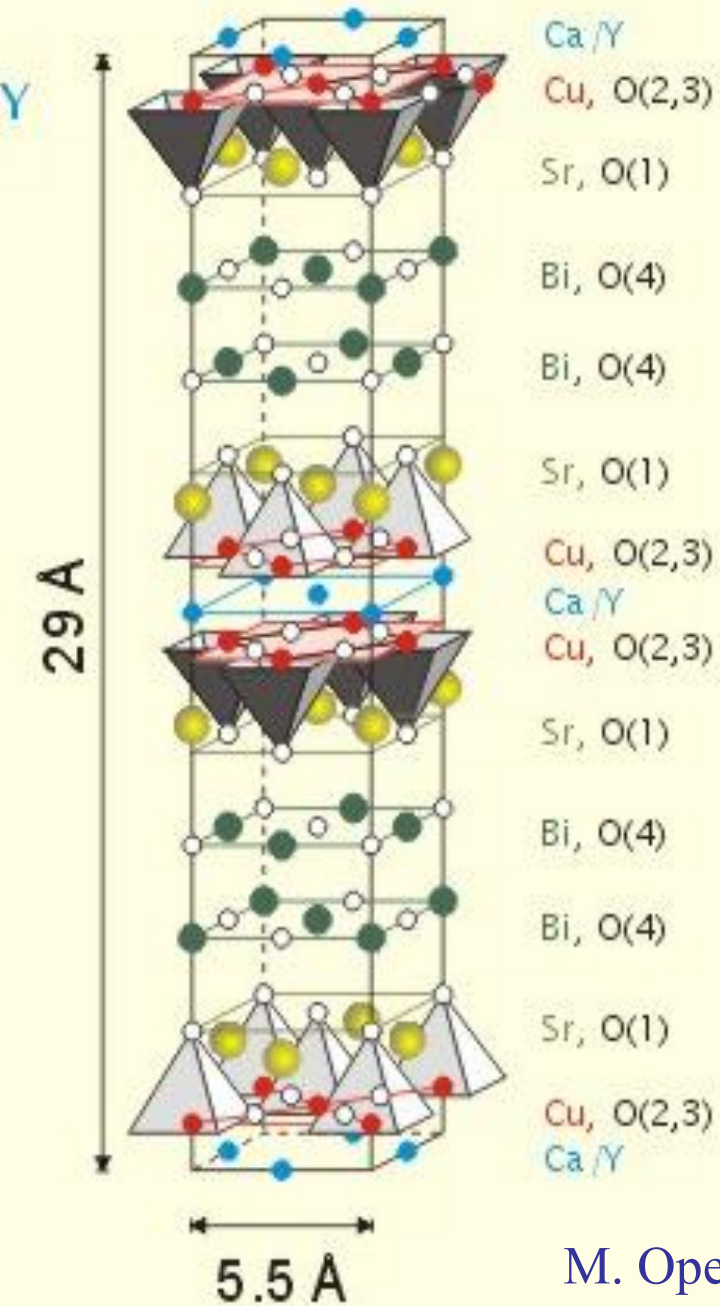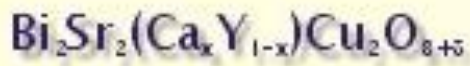
NEWS: 1994
(Nagarajan, PRL;
 Cava, Nature)

A new family of
superconductors
with T$_c$ up to 23K

*Is 23K the tip of
the iceberg?*

LaN

Ni$_2$B$_2$

(Fig. by Huang et al.)
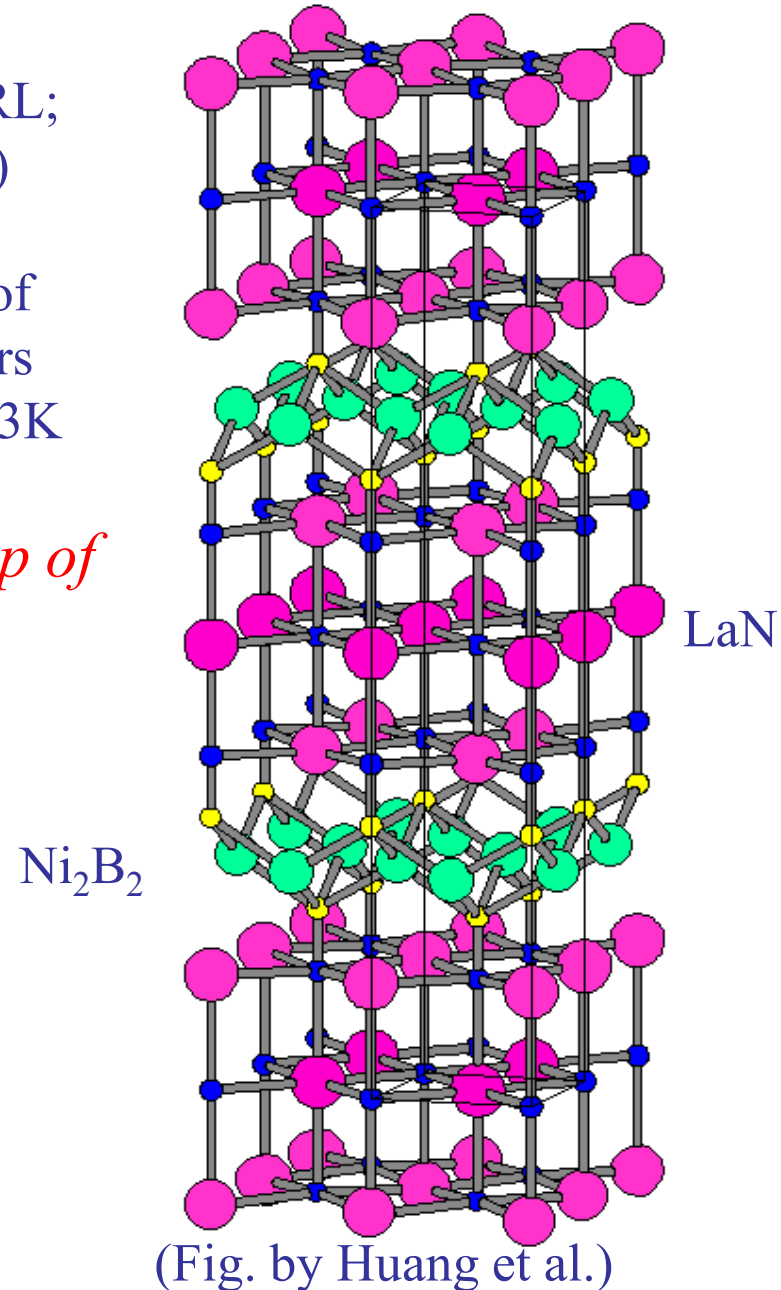
ANSWER: 1994 (Pickett and Singh, PRL) NO!

Fermi Surface of YNi_2B_2C (T_c=16K)
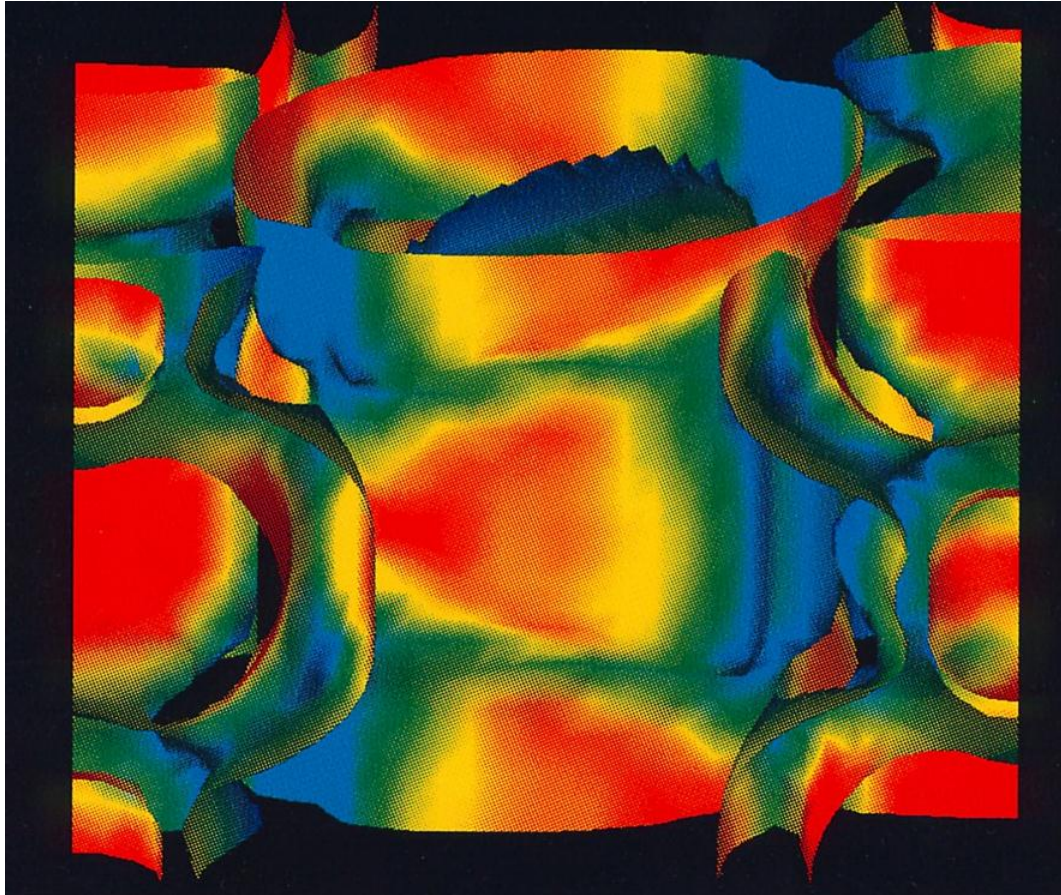
- Electronic structures are very three dimensional

- Due to strong B-C bonds

- Large electron phonon coupling is responsible for superconductivity (conventional mechanism).

- **NOT THE BASIS OF A NEW FAMILY OF HIGH TEMPERATURE SUPERCONDUCTORS**

Density Functional Theory

Standard approach: properties are governed by a wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \; ; \; H\Psi = E\Psi$$

Given the Hamiltonian, we focus on solving for the wavefunction and extract observables as expectation values of operators with this wavefunction – for N electrons this is a $3N$ dimensional problem.

Density Functional Theory: Hohenberg-Kohn theorem tells us

- Energy and other observables of the ground state are given as functionals of the density $\rho(\mathbf{r})$ which exists in 3 dimensions only.
- The ground state density is unique and is the density that minimizes this functional.

$$E = E[\rho] \; ; \; \rho = \min_{E[\rho]} \{\rho\}$$

The functional E is proven to exist, but is not given by the theorem.

Kohn-Sham Approach

Any density N electron density can be written as the density corresponding to an N electron Slater determinant (never mind that the true wavefunction cannot).

$$\rho(\mathbf{r}) = \Sigma \; \varphi_i(\mathbf{r})^* \varphi_i(\mathbf{r}) \; ; \; i=1,2, \ldots, N$$

Where the $\varphi_i(\mathbf{r})$ are the Kohn-Sham orbitals
➔ variational principle for ρ yields a variational principle for the $\varphi_i(\mathbf{r})$.

Kohn and Sham then separated terms that should be large in the functional leaving a (hopefully) small remainder as the unknown functional.

$$E[\rho] = T_s[\rho] + E_{ext}[\rho] + U_{Hartree}[\rho] + E_{xc}[\rho]$$

where, like E, E_{xc} is unknown. E_{xc} is defined by this equation.

Kohn-Sham Equations

Use the variational principle to write single particle equations for the Kohn-Sham orbitals.

$$\{T_s + V_{ext} + V_{Hartree} + V_{xc}\}\varphi_i = \varepsilon_i \varphi_i$$

$$\rho(\mathbf{r}) = \Sigma \; \varphi_i(\mathbf{r})^*\varphi_i(\mathbf{r}) \;\; ; \; i=1,2, \dots , N$$

Here, V_{hartree} and V_{xc} are functionals of the density (functional derivatives of the energy terms with respect to density), so generally these equations must be solved self-consistently.

This is straightforwardly generalizable to magnetic systems via spin-density functional theory where instead of a single function one has spin-densities, $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ for the collinear case and a four component spinor for non-collinear.

The Local Density Approximation

Generally one may write

$$E[\rho] = \int \rho(\mathbf{r}) \, \varepsilon_{xc}[\rho](\mathbf{r}) \, \mathrm{d}^3\mathbf{r}$$

The local (spin) density approximation consists of taking $\varepsilon_{xc}[\rho]$ at each point $\mathbf{r}$ as the value for the uniform electron gas at the density for this $\mathbf{r}$.

This exceedingly simple approximation works remarkably well, especially considering that the electron gasses of solids are nothing close to the uniform electron gas.

Hartree-Fock vs. Approximate DFT

- Hartree-Fock is a controlled approximation. Approximate DFT is not.

  ➢ We can systematically improve Hartree-Fock, but with DFT we always have to "guess" about what is / is not already included. LDA+x need not be better than LDA (but it may very well be). **Be Judicious.**

- Hartree-Fock gives poor results for materials. Modern approximate DFT is typically excellent for structures, energies etc.

- There are no metals, no stable Fermi surfaces and no Fermi liquids in Hartree-Fock. There are in DFT, perhaps too many.

Never equate DFT calculations with Hartree-Fock.

Modern Density Functionals

$$E[\rho] = \int \rho(\mathbf{r})\, \varepsilon_{xc}[\rho](\mathbf{r})\, d^3\mathbf{r}$$

(1) Local (spin) density approximation: $\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{local}(\rho(\mathbf{r}))$

- Widely used, especially for metals.

(2) Generalized gradient approximations (GGA, Langreth, Perdew):
$$\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{gga}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)$$

- Much improved binding energies compared to LDA (chemical accuracy).

- Not gradient expansions, but sophisticated functionals based on exact scaling relations for the inhomogeneous electron gas (electron gas in solids is very non-uniform – can't use gradient expansions).

- New versions, e.g. PBE-SOL, Wu-Cohen, give almost uniform improvement over LDA in structural properties.

# Modern Density Functionals

(3) Hybrid functionals (Becke and others):

- Mixture of GGA and Hartree-Fock exchange on the Kohn-Sham orbitals.

- Common in chemistry and semiconductor physics (band gaps are better than standard LDA or GGA's).

(4) Van der Waal's Functionals (Langreth, Lundqvist):

- Non-local functionals that incorporate dispersion interactions.

- Surface science, molecular systems, water, DNA, carbon materials, etc.

Fermi Surfaces
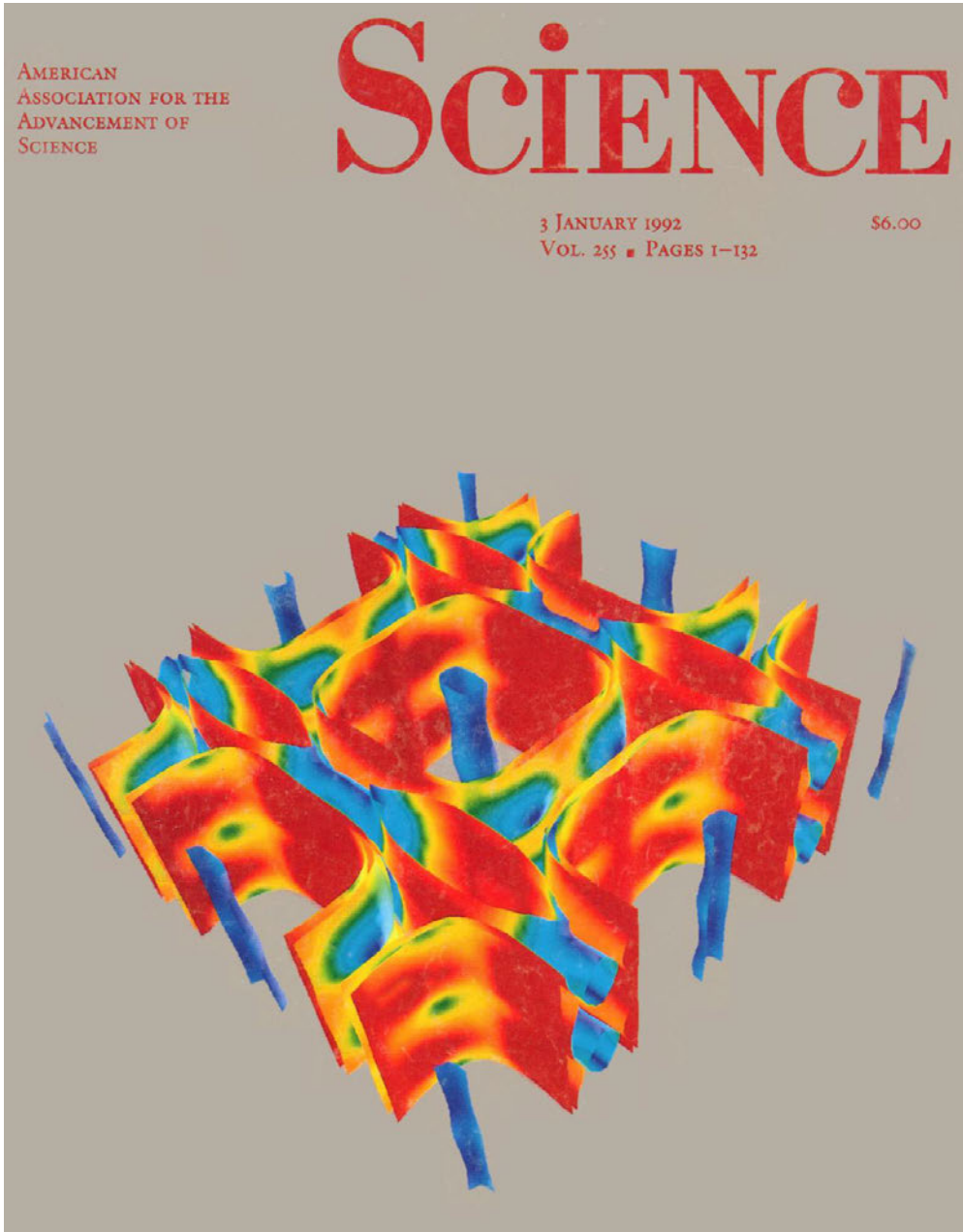
Based on Kohn-Sham eigenvalues, which are not fundamentally related to excitation energies in exact DFT – but this is known to be predictive and useful based on experience.

Band Structures
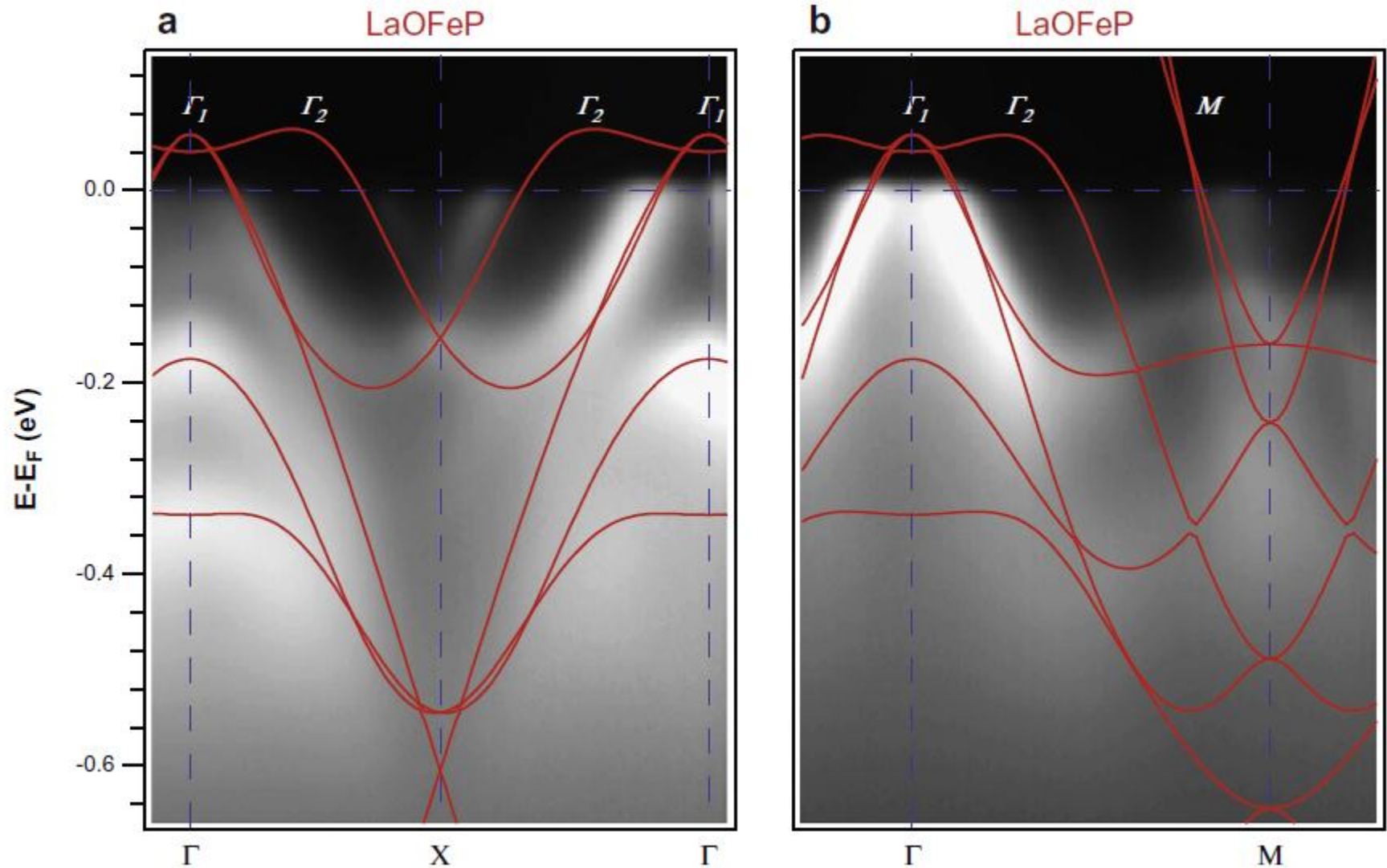
D.H Lu (2009)

Band Structure Related Quantities

- Optical properties.

- Excitation energies.

- Electronic transport.
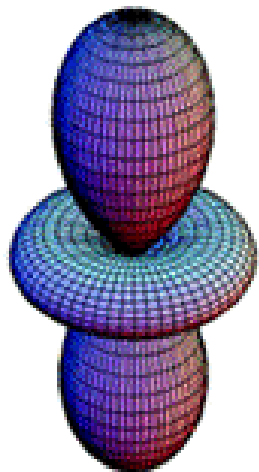
- Electron-Phonon interactions.

- etc.

None of these are fundamental in DFT, but they are often quite accurate, and the inaccuracies are well established from much experience.

This is very useful because DFT is tractable, microscopic and predictive.

CRYSTAL FIELD AND

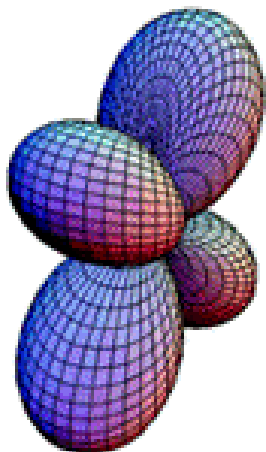# JAHN-TELLER DISTORTIONS

The d Orbitals

e_g orbitals

$3z^2$-r^2

x^2-y^2

t_{2g} orbitals

zx

yz

xy
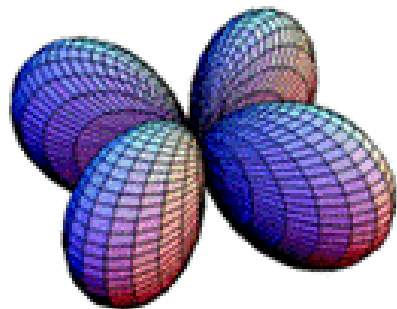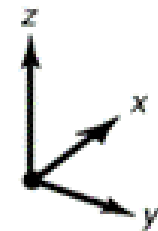
e_g orbitals point at the corners of the octahedron
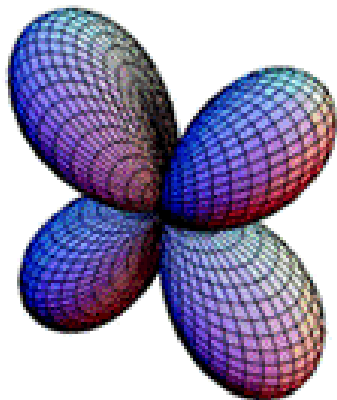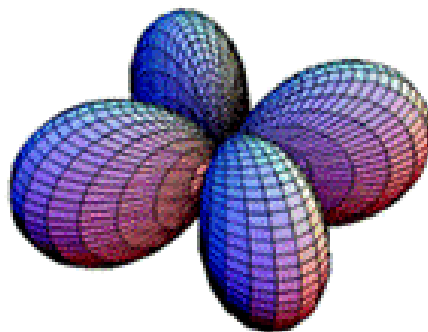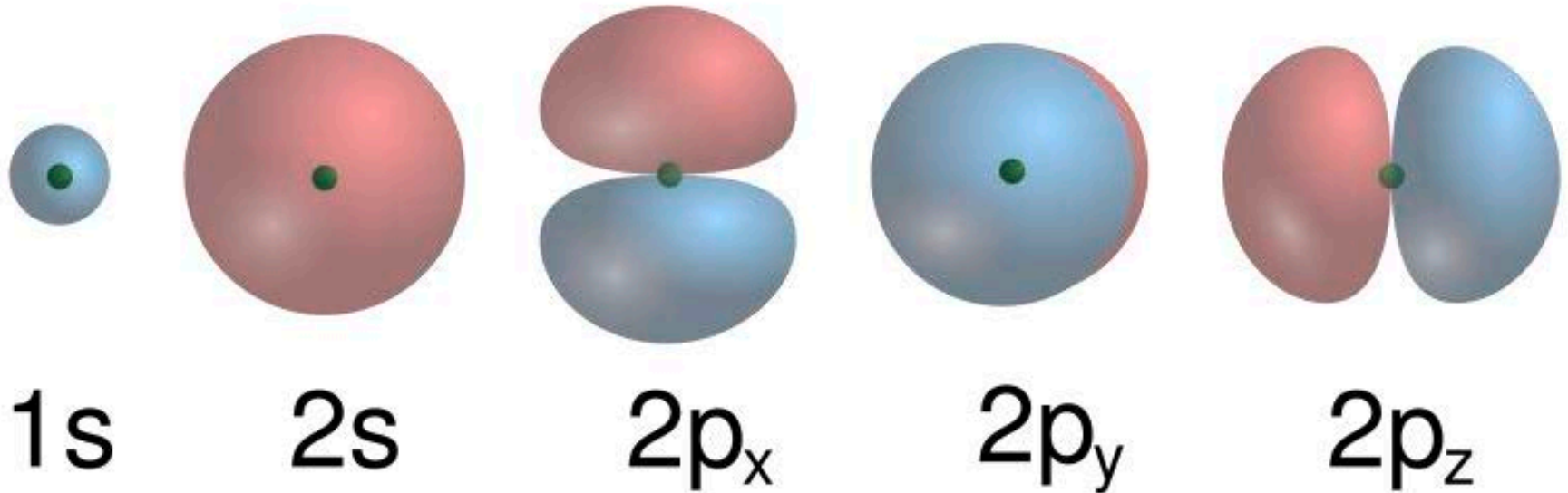
t_{2g} orbitals do not.

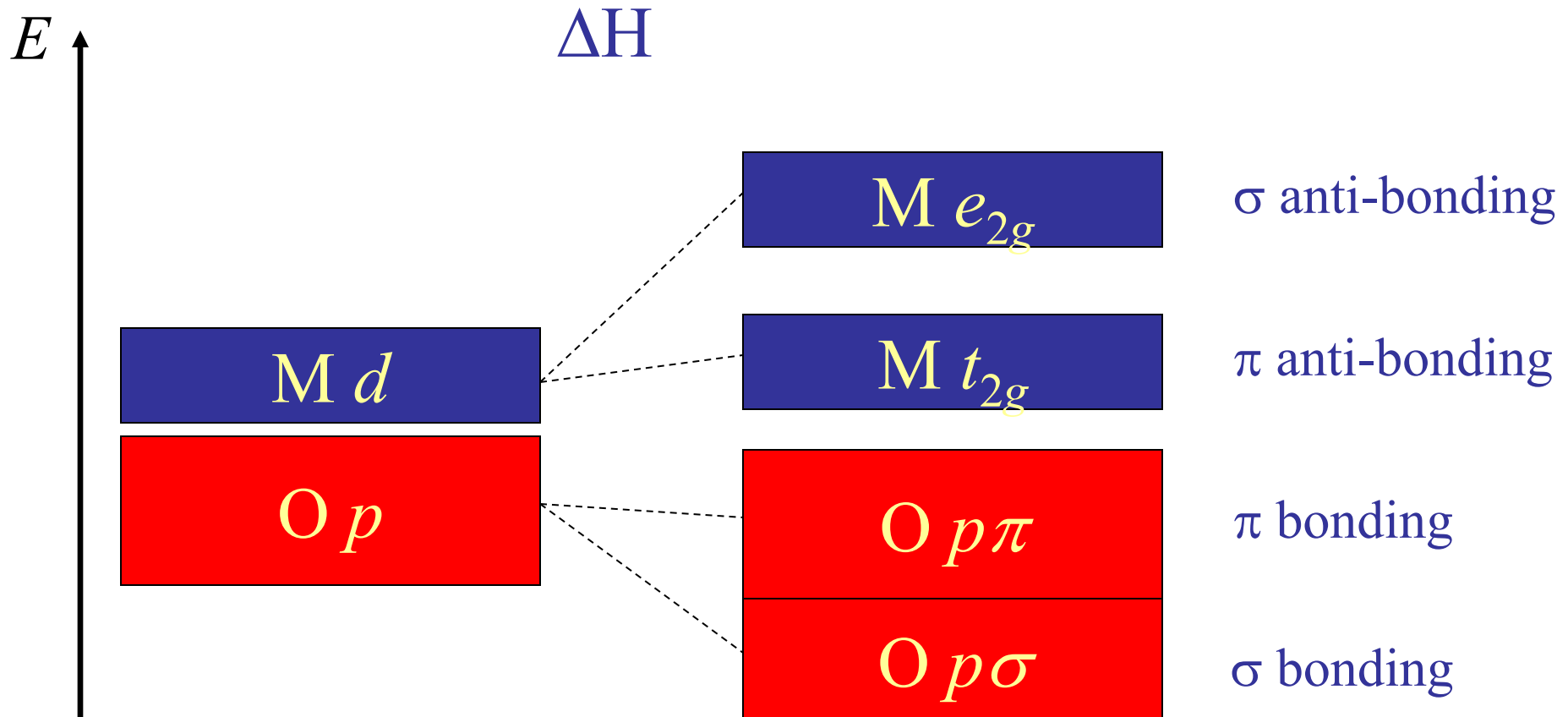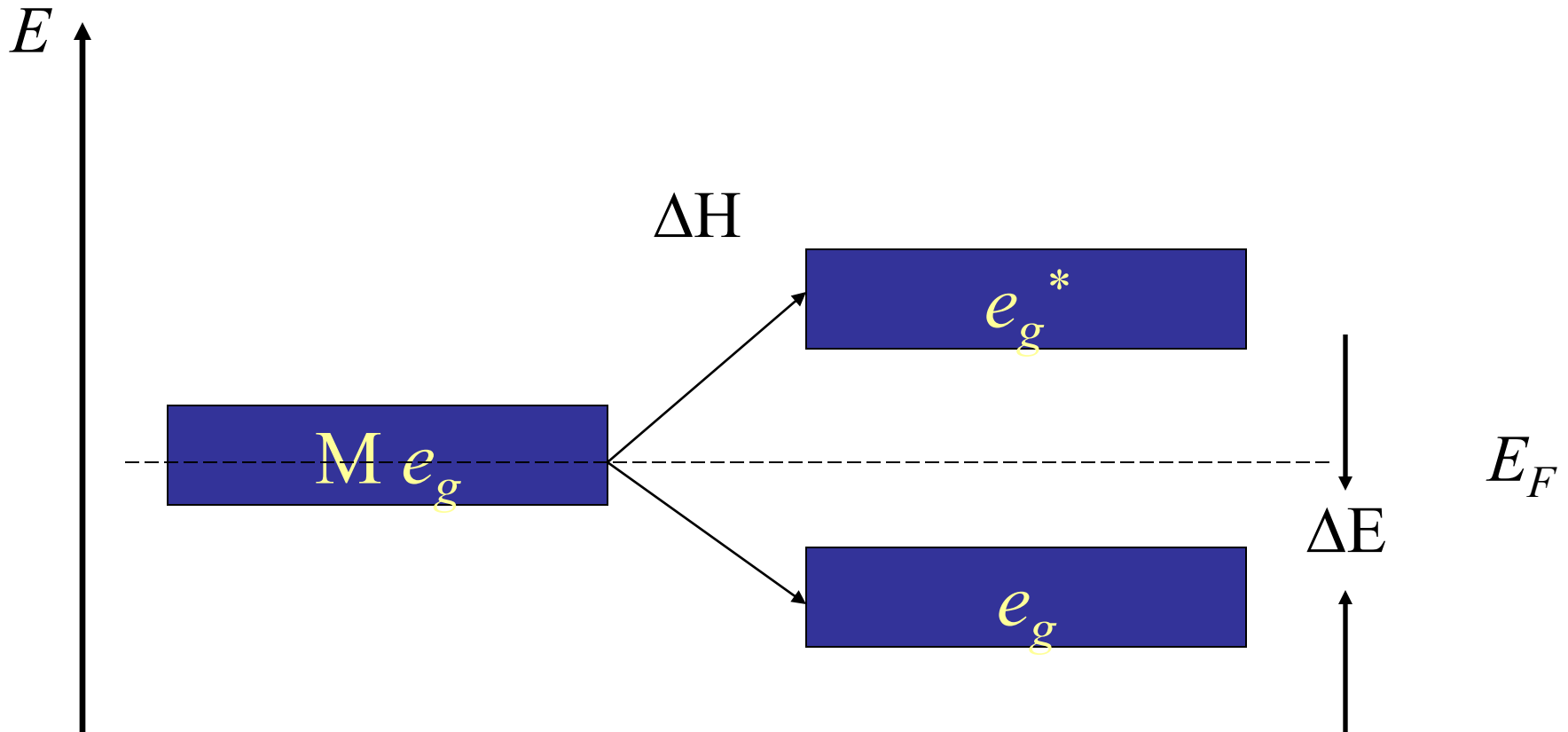From Vinobalan Durairaj web site

The O p Orbitals

From wikipedia

- One of these (p_σ) points at the center of the octahedron.
- The other two (p_π) are perpendicular.

The Octahedral Crystal Field

ΔH

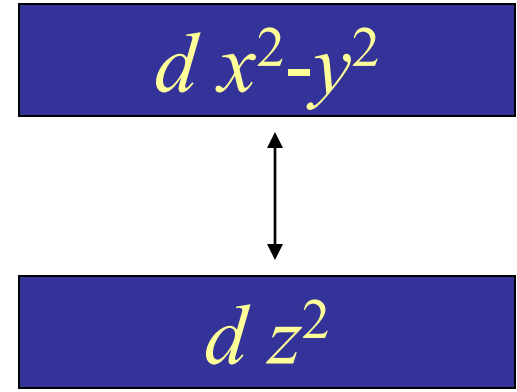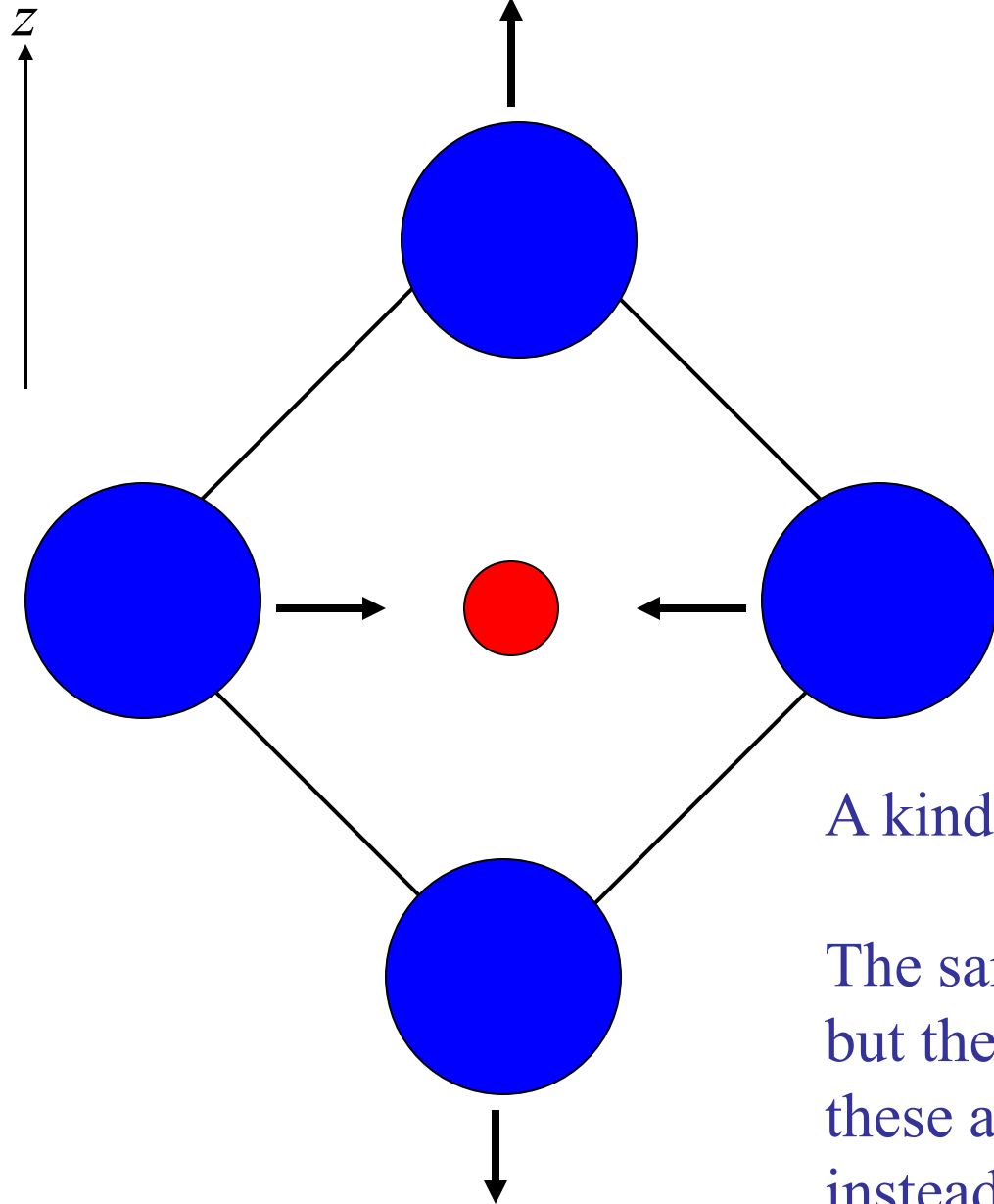In transition metal oxides crystal field is due (mostly) to hybridization

Jahn-Teller Effect

For a sufficiently narrow level with partial occupation, we expect a splitting to lower the energy. How does this happen (i.e. what is ΔH)?
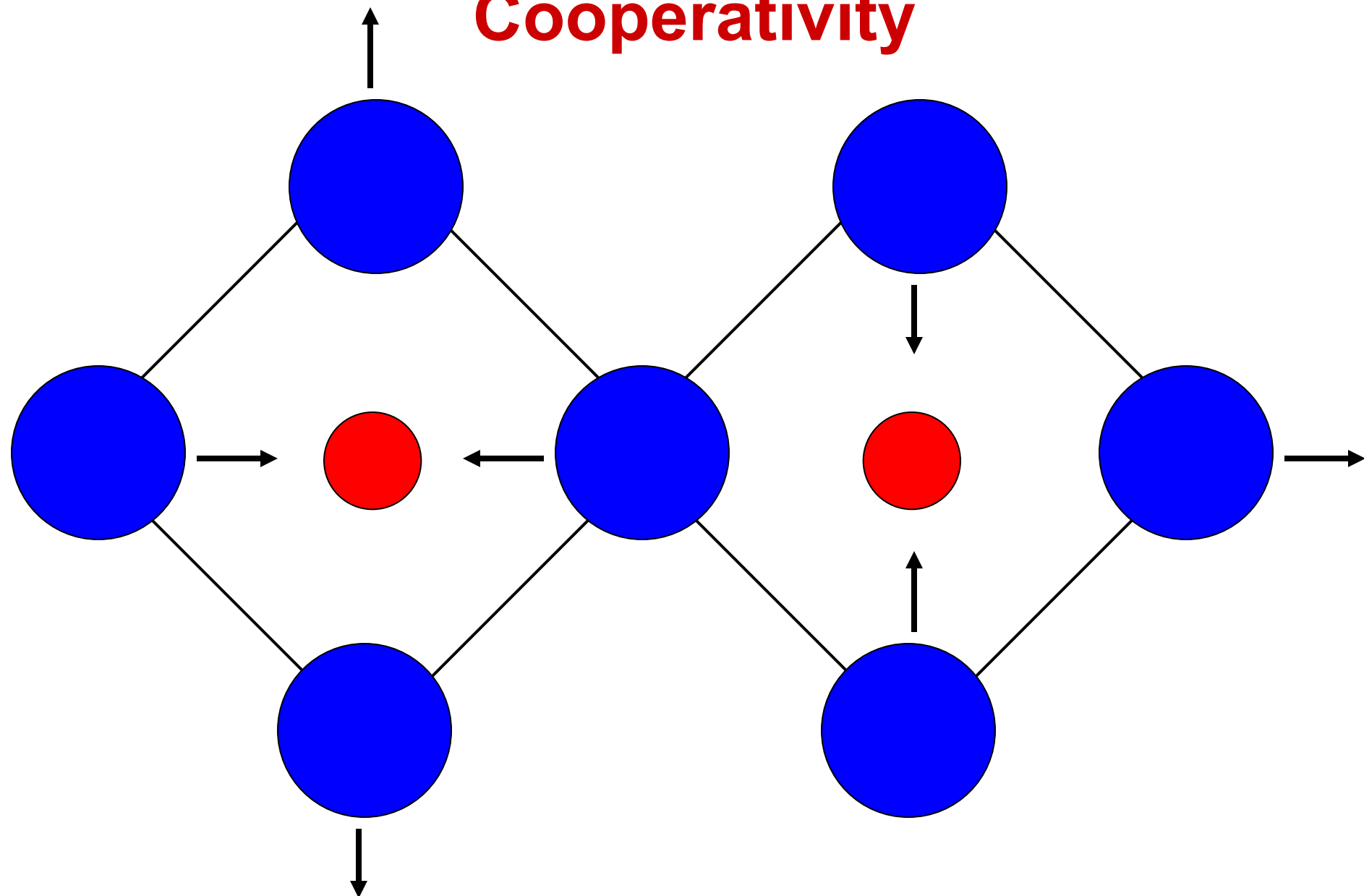
Large band-width works against this.

Jahn-Teller Effect

z

$d\ x^2-y^2$

$d\ z^2$

A kind of orbital ordering.
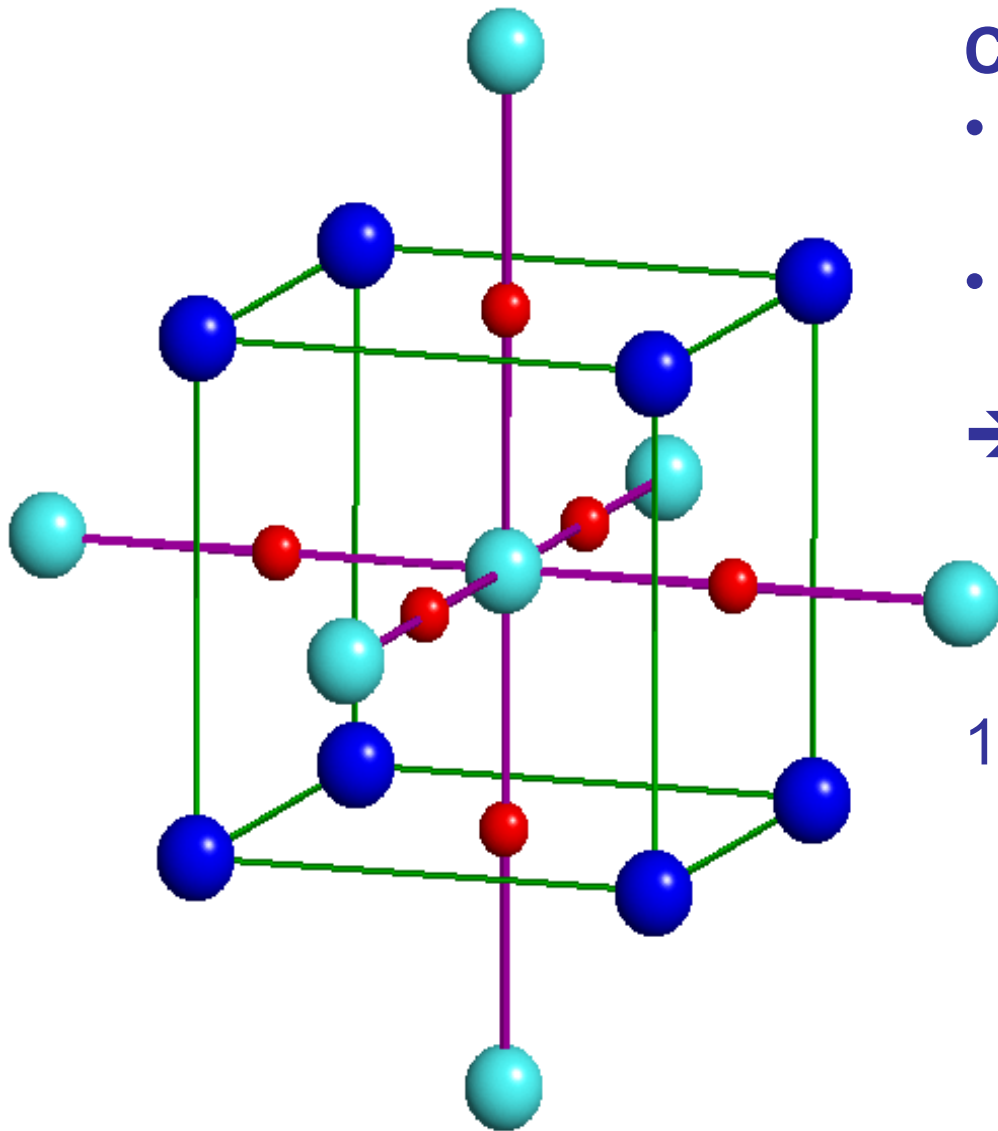
The same thing works for t_{2g} orbitals but the effect is (much) smaller because these are involved in weak π bonds instead of strong σ bonds

Cooperativity

Jahn-Teller is long range – corresponding zone boundary modes have long coherence length (zone center also possible – ferroelastic)
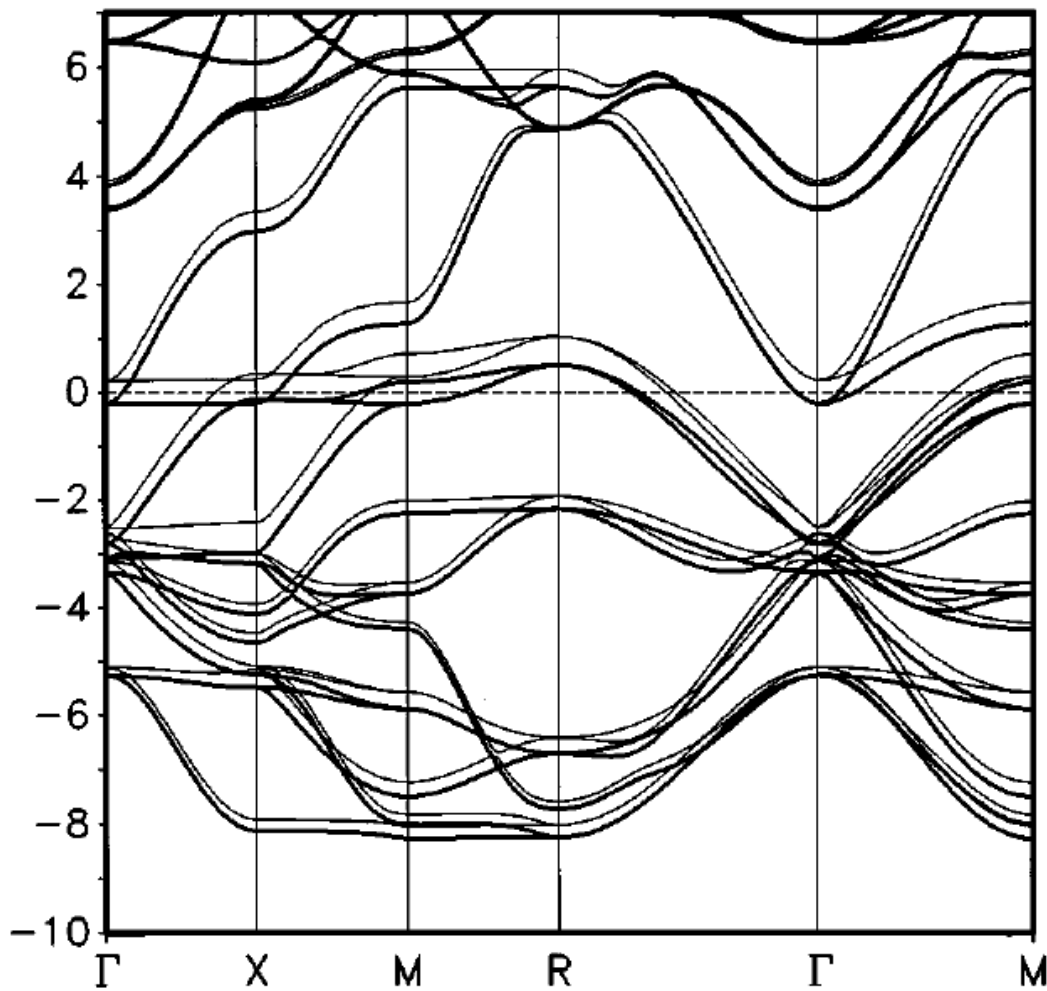
Geometric Considerations (O and B-site)

Cubic structure:
- O – O distance is $a/\sqrt{2}$ (can have direct hopping)
- B – B distance is a (too far for much direct hopping).

➜ Metal bands are formed via hopping through O.

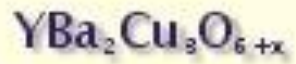1D linear chains along Cartesian directions ➜ 1D and 2D bands.
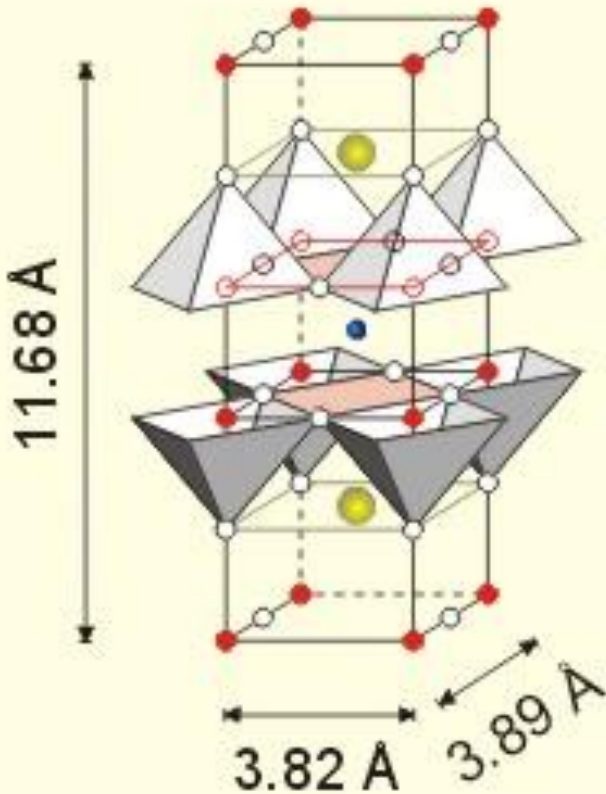
Geometric Considerations (O and B-site)

Cubic SrRuO$_3$

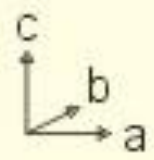Flat bands

Planar Fermi surfaces (e.g. cubes rather than spheres).

$YBa_2Cu_3O_{6+x}$

- Y
- Ba
- Cu
- O

Cu(1), O(4)

Ba, O(1)

Cu(2), O(2), O(3)

Y

Cu(2), O(2), O(3)

Ba, O(1)

Cu(1), O(4)

11.68 Å
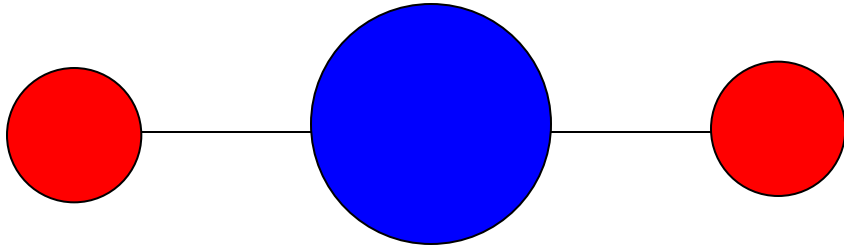
3.82 Å   3.89 Å

M. Opel

High-T_c Electronic Structures are 2D
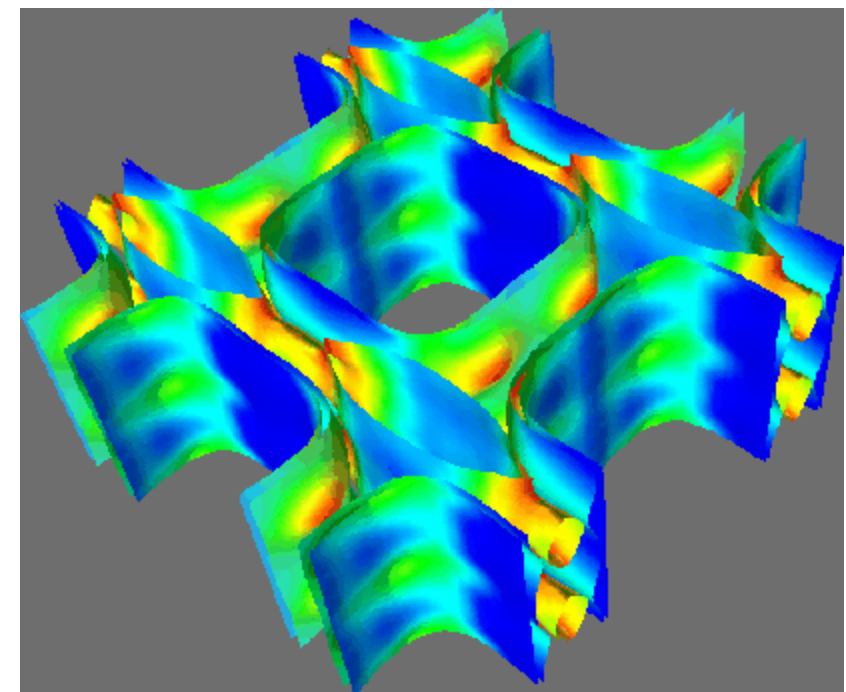
Pickett, Cohen, Krakauer, Singh

Hopping Through O

O p_x, p_y, p_z point along Cartesian directions (90 degrees apart):

Cubic:

Tilted:

- Reduced $pd\sigma$ hopping.

- Narrower e_g bands.

- Additional splittings due to symmetry lowering.

- Maximum $pd\sigma$ hopping.

- Wide e_g bands.

- Can broaden t_{2g} bands depending on details.

Tilts reduce band width but do not reduce hybridization (i.e. crystal field).

- Direct m-m hopping.

Tilts and Hopping Through O


(Sr,Ca)$_2$RuO$_4$ (Nakatsuji)
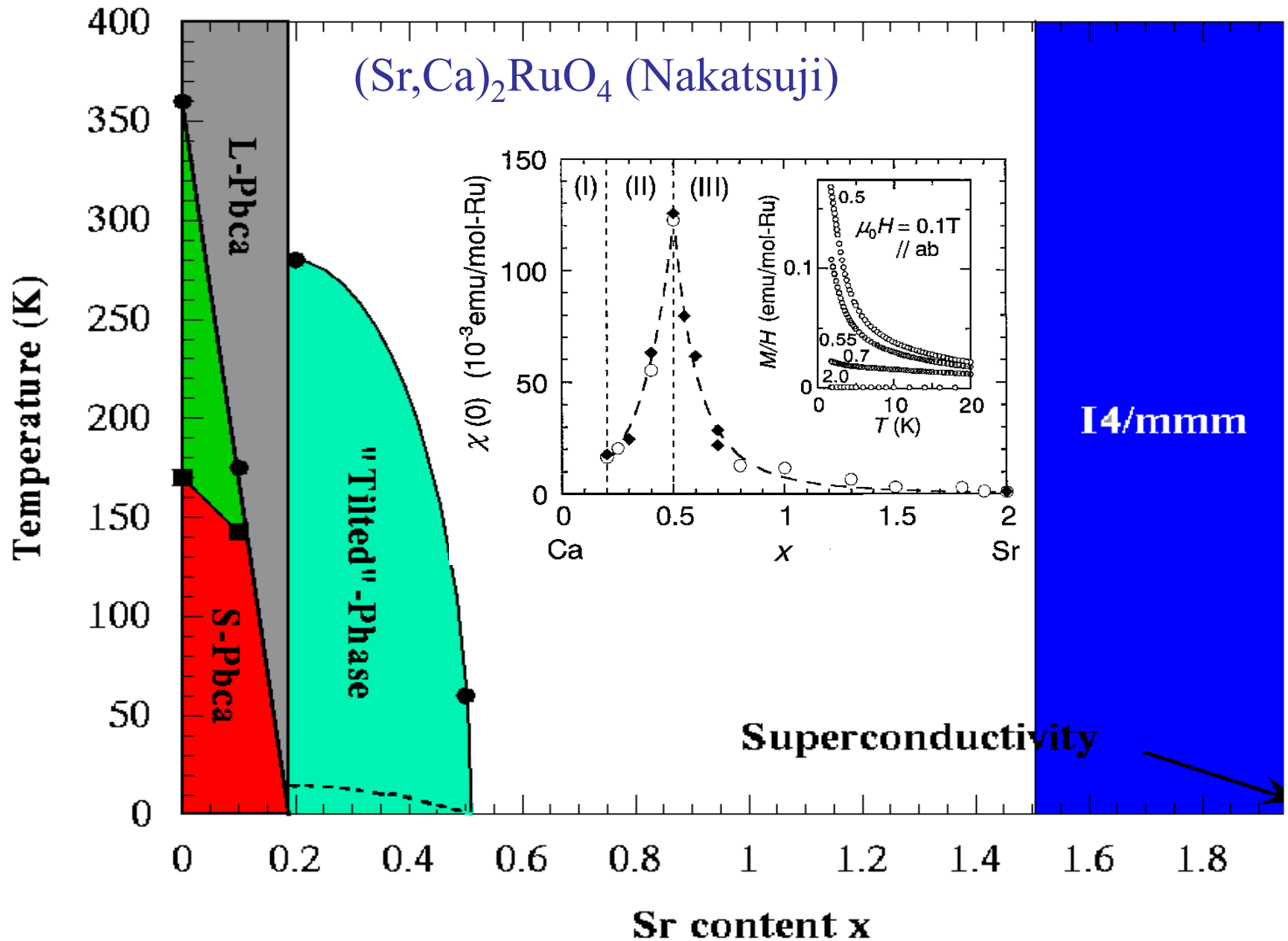
MAGNETISM: Moment Formation

Local Atomic Moments (Hund's Rules)

1. For a given electron configuration, the term with maximum multiplicity (maximum S) has the lowest energy (exchange / Coulomb correlation).
2. For a given multiplicity, the term with the largest value of L has the lowest energy (Coulomb correlation).
3. For a given term, in an atom with outermost sub-shell half-filled or less, the level with the lowest value of J lies lowest in energy. If the outermost shell is more than half-filled, the level with highest value of J is lowest in energy (spin-orbit).
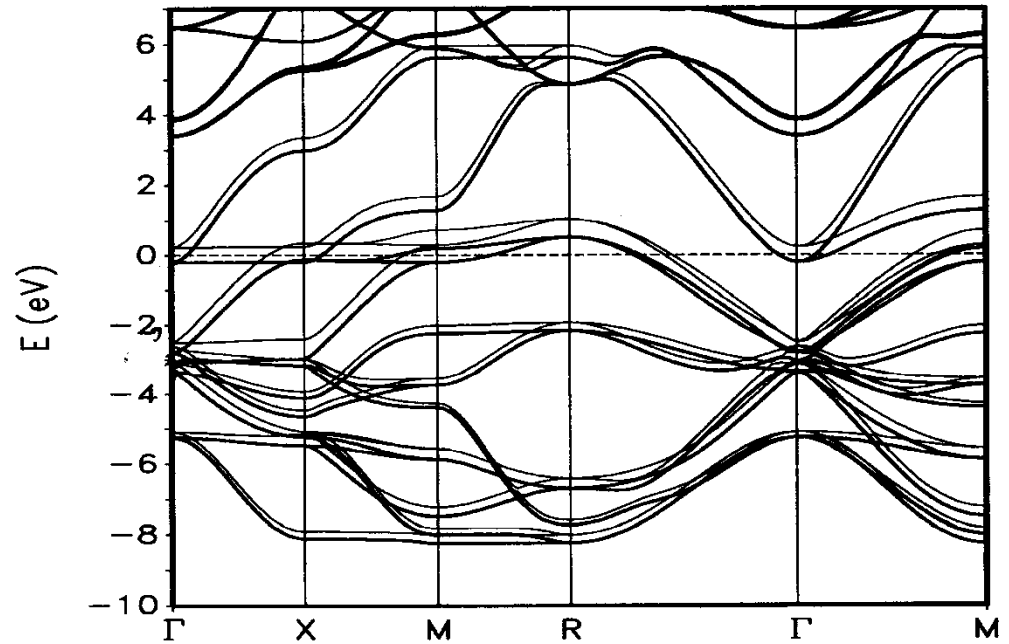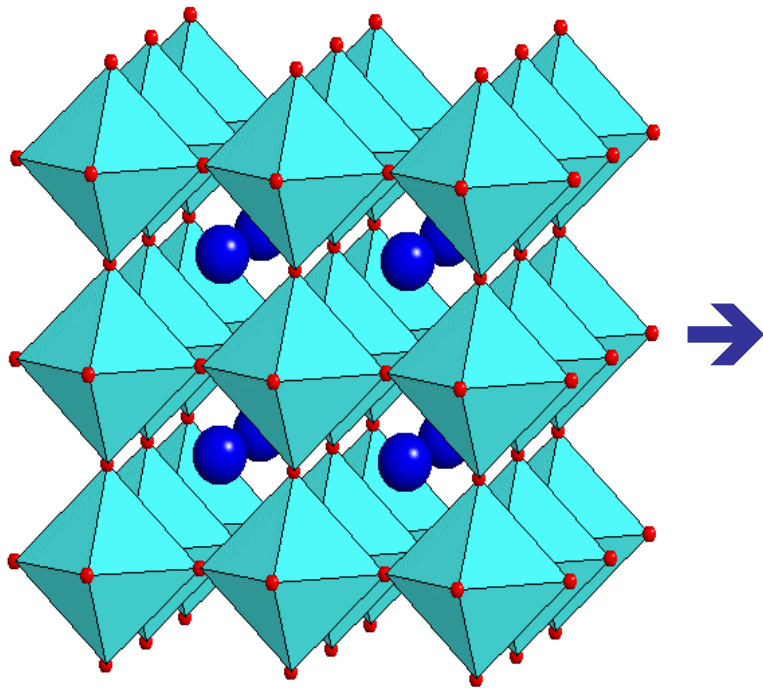
1st Rule:
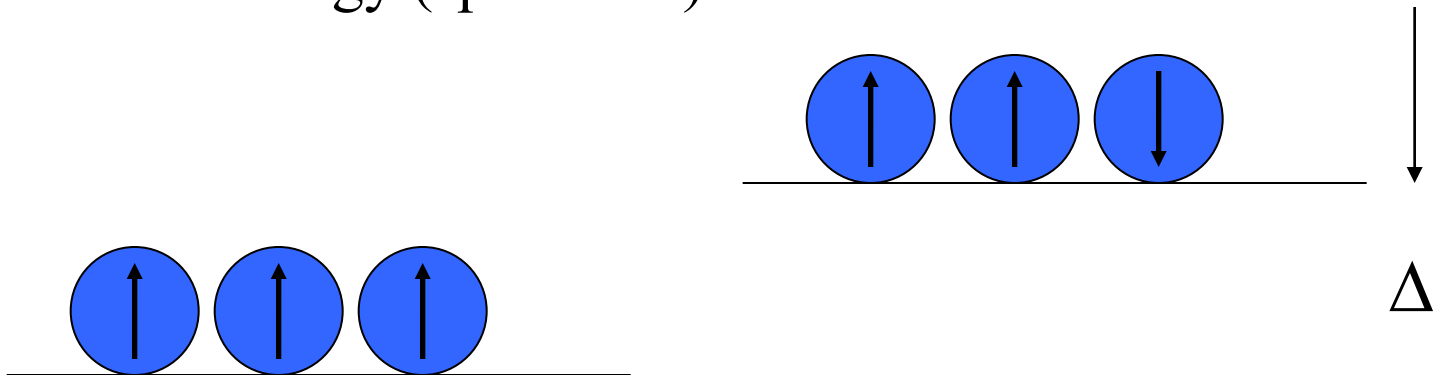
In solids levels broaden into bands.
If band width, W $> \Delta$ this may not work (➔ low spin).

Stoner Model (Itinerant Magnets)
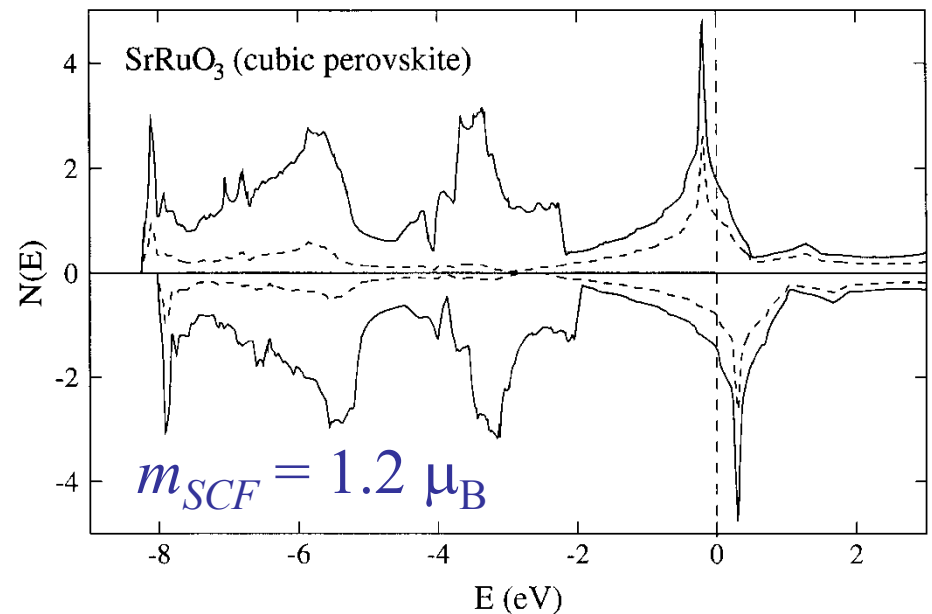

SrRuO$_3$ (cubic perovskite)

m_{SCF} = 1.2 μ_B

Band structure effects can lead to high degeneracy near E_F ➔ magnetic instability and energy lowering.

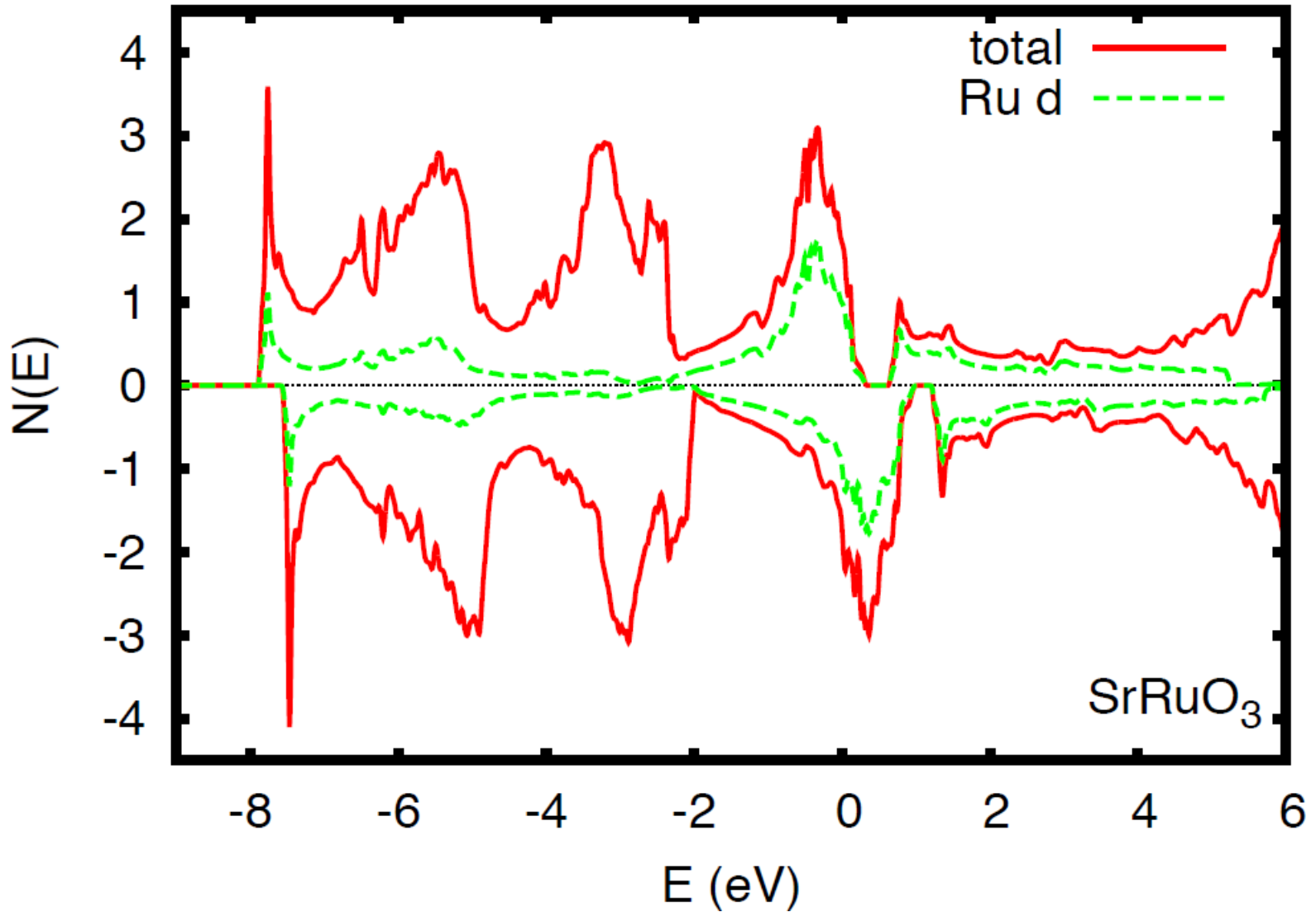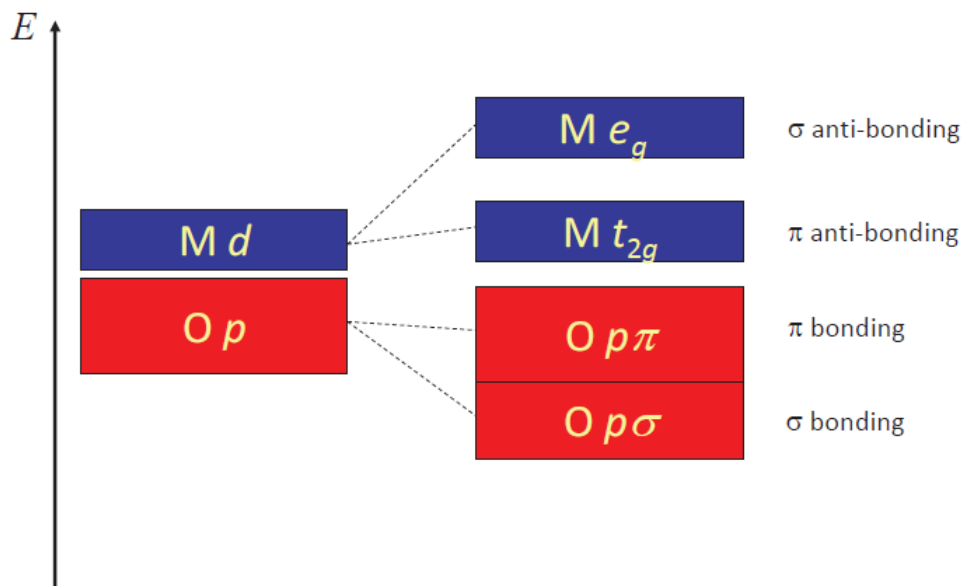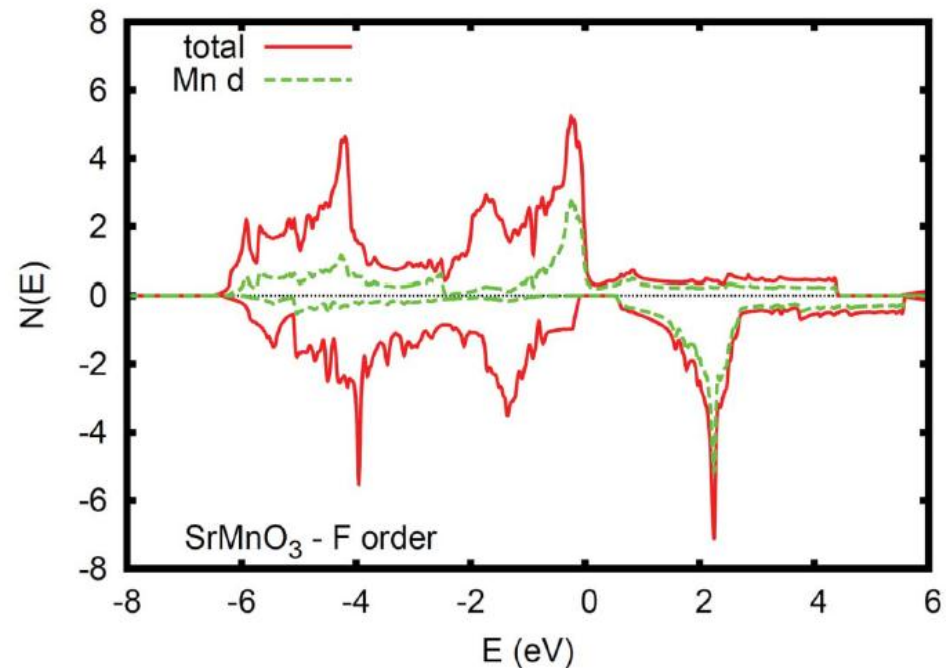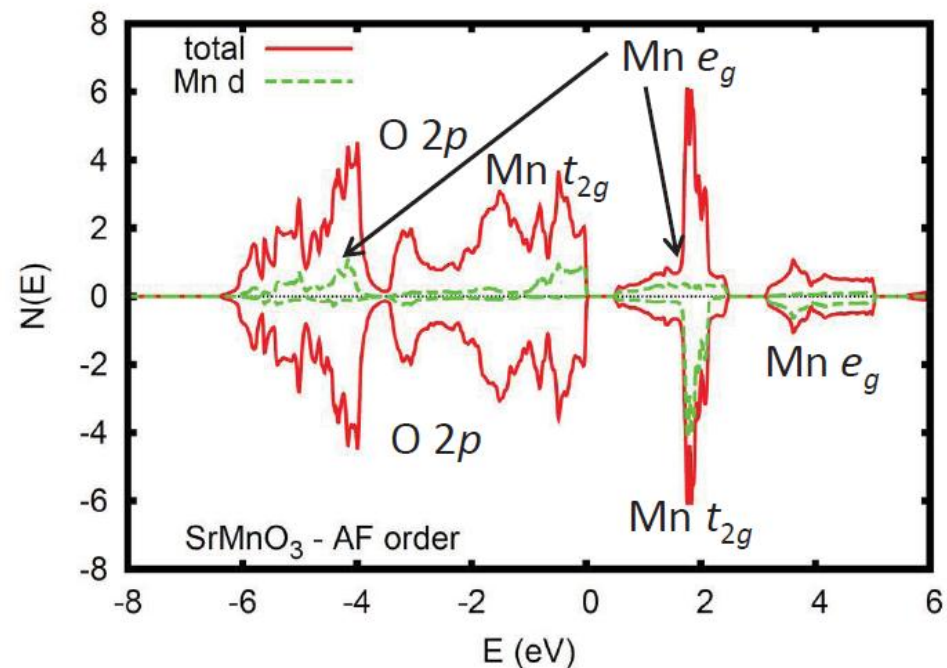Stoner Criterion:

$N(E_F)I > 1$

$I \sim 0.7 - 0.9$ eV for d elements.

Perovskite (orthorhombic) SrRuO₃

Perovskite SrMnO₃

Question:

How Does the Spectrum (DOS) Look Above the Ordering Temperature?

Interaction Between Moments (Exchange)

- Moment formation by itself is not magnetism. Ordering is required, and therefore interactions between moments on different sites are what underlie magnetism.

- Some Mechanisms:

  - Direct exchange – two atoms are touching (or very close) so that their wavefunctions overlap. The interaction is like that which gives rise to Hund's first rule. It can be positive or negative depending on the separation of the atoms, but it falls off very strongly with distance.

  - Super Exchange – coupling of spins through spin dependent overlap typically involving other atoms.

  - Conduction electron mediated exchange: e.g. RKKY, magnetic semiconductors … Moments interact with conduction electrons which mediate the coupling.

Conduction Electron Mediated Exchange

In weak interacting limit medium has some response, $\chi(\mathbf{q})$, which defines the interaction through $\chi(\mathbf{r}_i\text{-}\mathbf{r}_j)$. More generally the response may differ for strong interactions at short range but at long distance would still take RKKY type form in a metal.
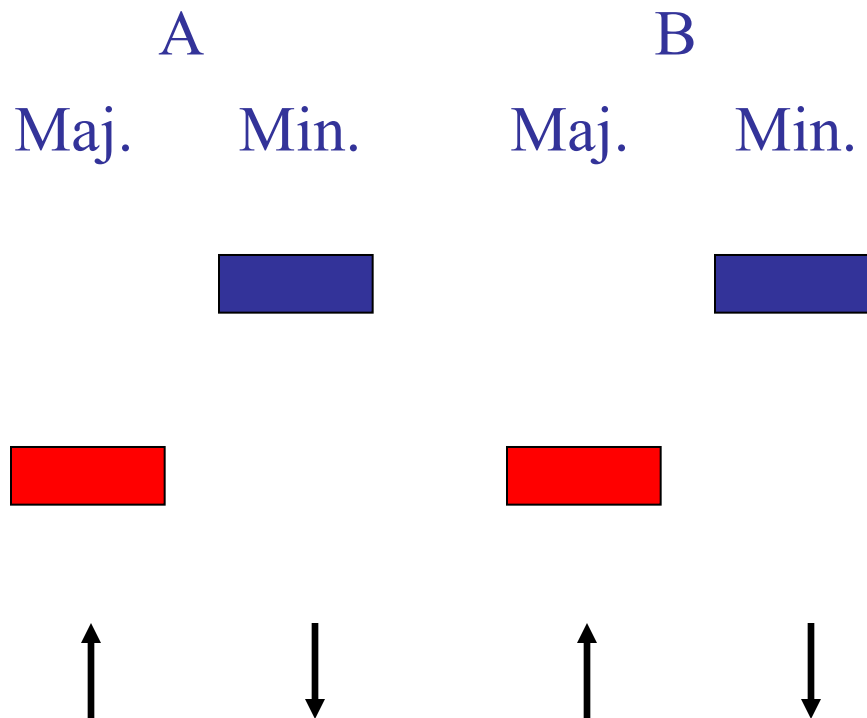
Super Exchange and Related

Consider two magnetic ions which interact via O and consider parallel and anti-parallel alignments of the moments:
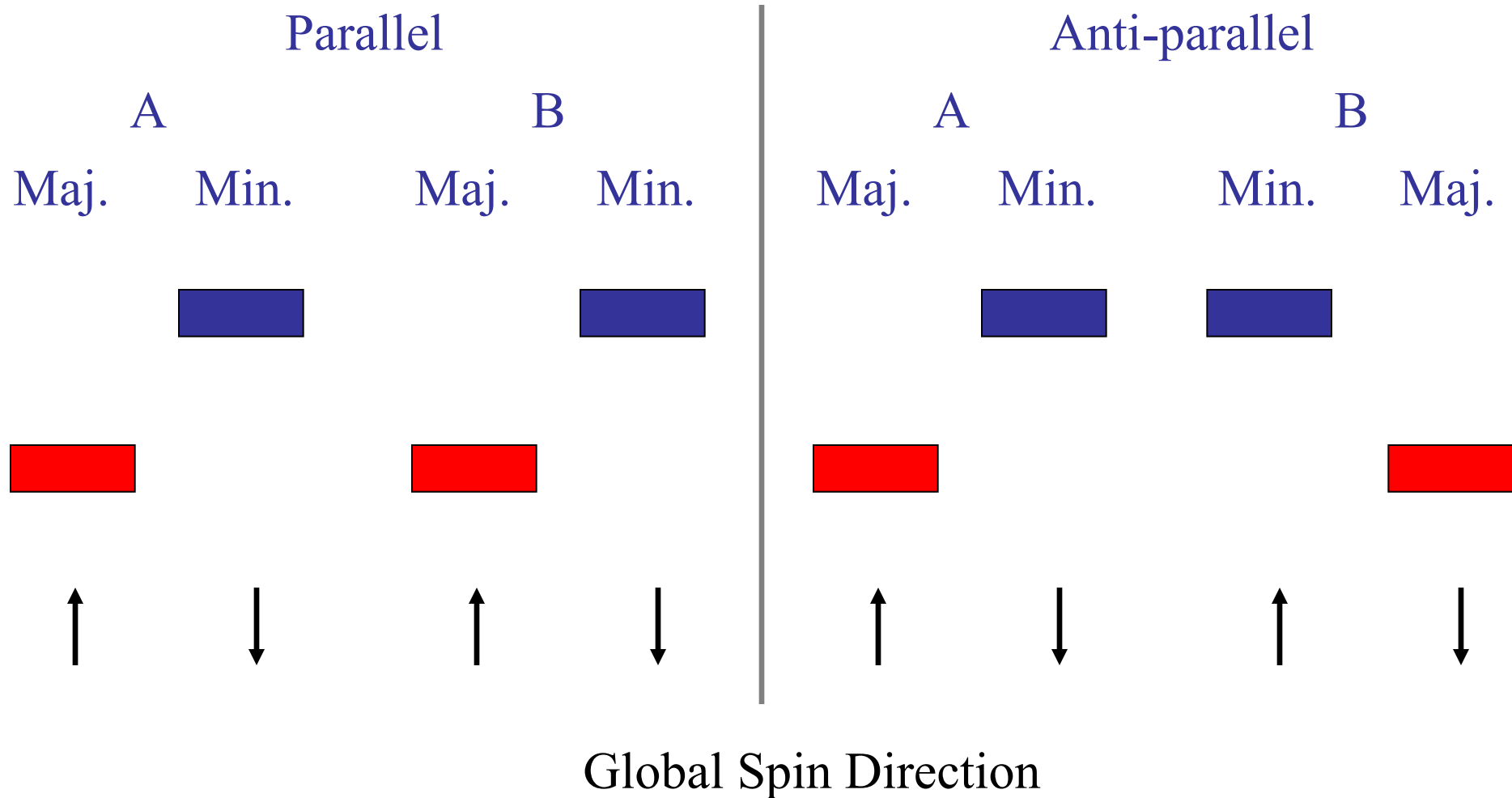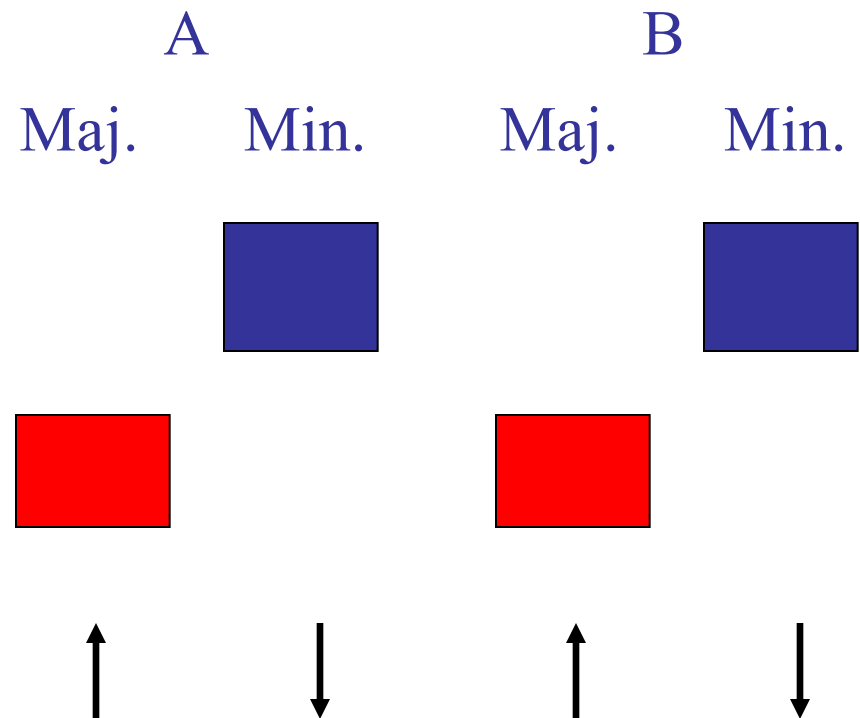

Global Spin Direction

Band Formation

In the absence of spin orbit and non-collinear structures hopping is separate for spin up and spin down.
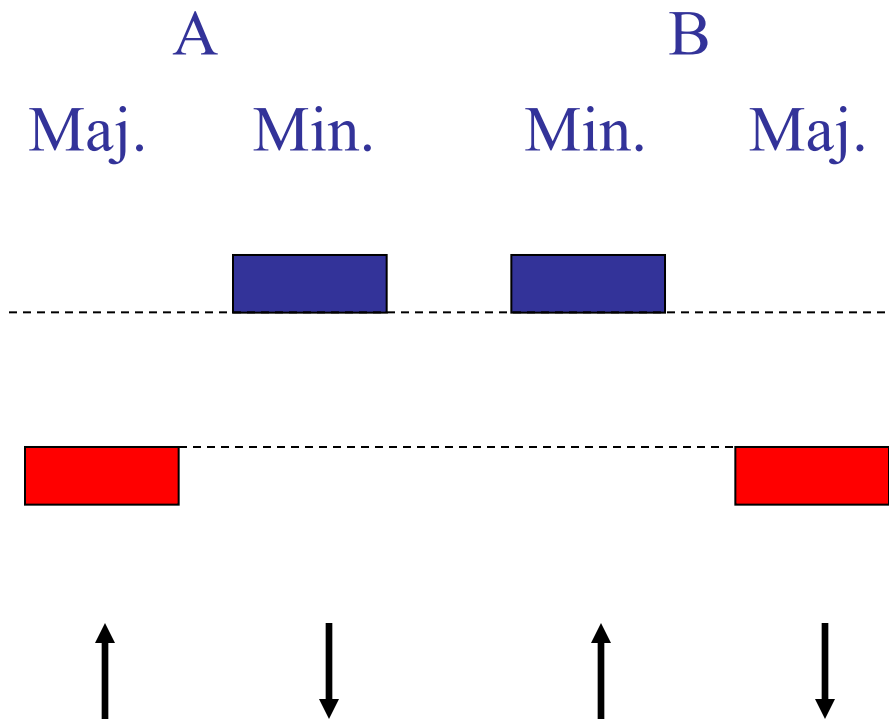
Parallel Case:

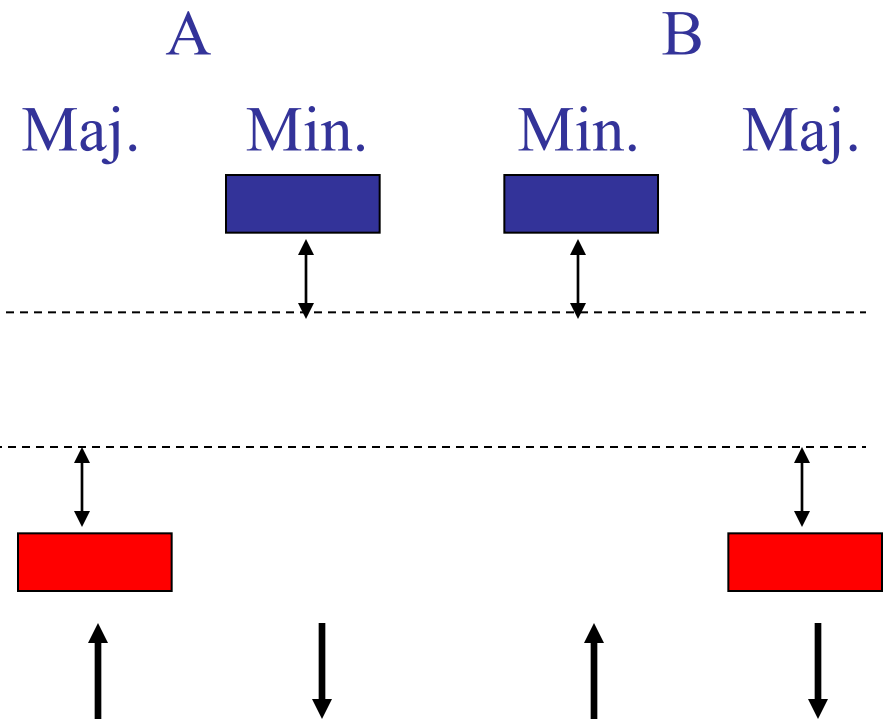Parallel Case with hopping:

Global Spin Direction

Band Formation

In the absence of spin orbit and non-collinear structures hopping is separate for spin up and spin down.

Anti-parallel Case:

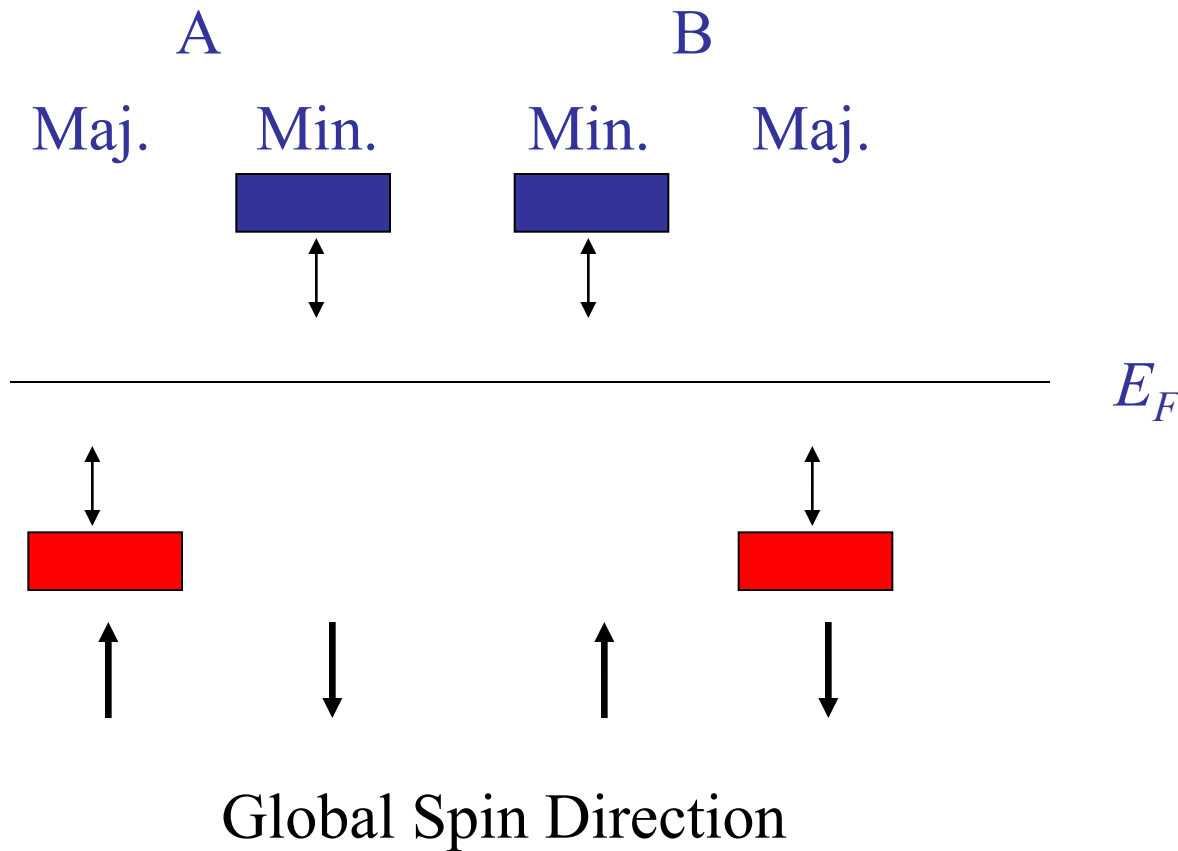Anti-parallel with hopping:

Global Spin Direction

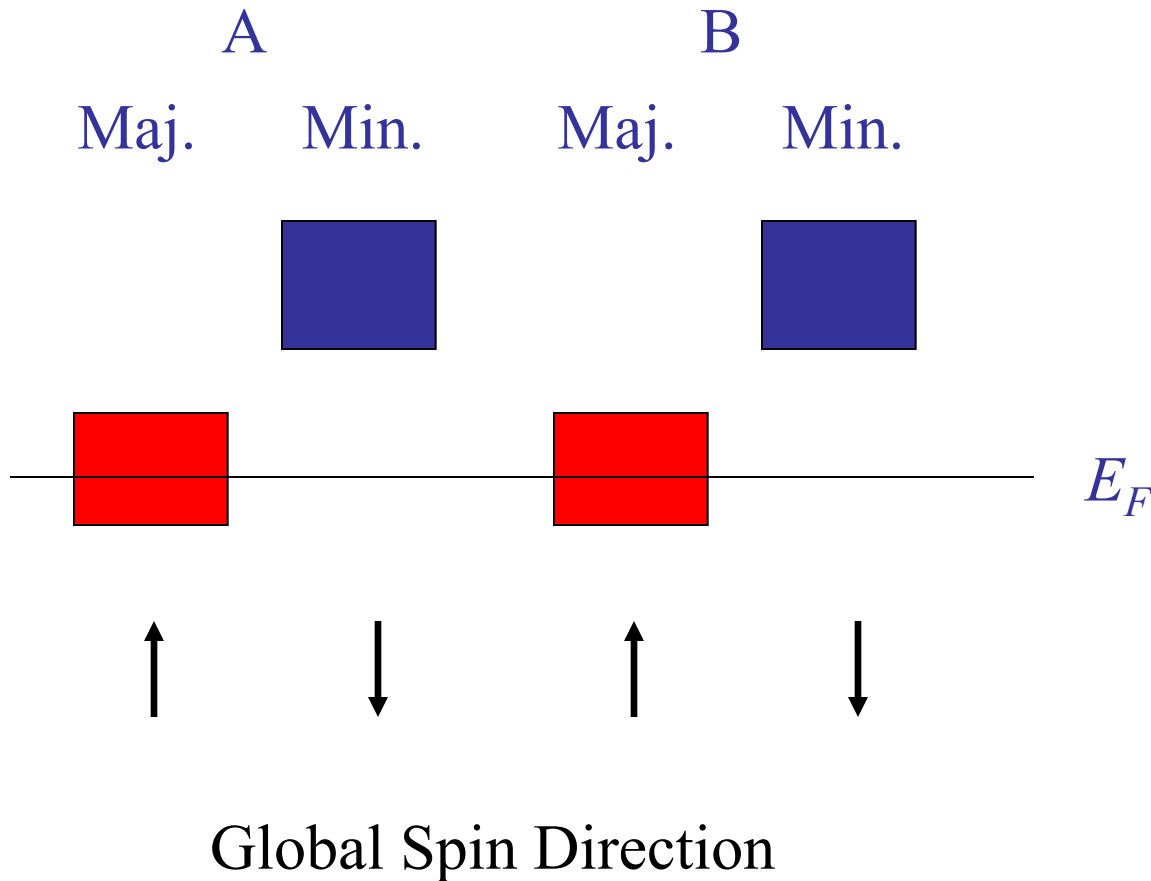# Antiferromagnetic Super Exchange

Anti-parallel with hopping:

A   B

Maj.   Min.   Min.   Maj.

Average energy of ***occupied states*** is lowered. Favors antiferromagnetic alignment (super exchange)

E_F

Global Spin Direction

Ferromagnetic Exchange

A   B

Maj.   Min.   Maj.   Min.

E_F

Global Spin Direction

Average energy of *occupied states* is lowered. Favors ferromagnetic alignment (super exchange).

This is the nature of the double exchange in manganites: It competes with Jahn-Teller, which would split the e_g level.

What Favors Strong Super Exchange?

1. High spin state.

2. Bond angles that favor M – O – M hopping (i.e. 180° for e_g).

3. Strong hybridization with O.

   - Large orbitals that overlap strongly with O (e_g much better than t_{2g}).

   - Short M-O neighbor distances.

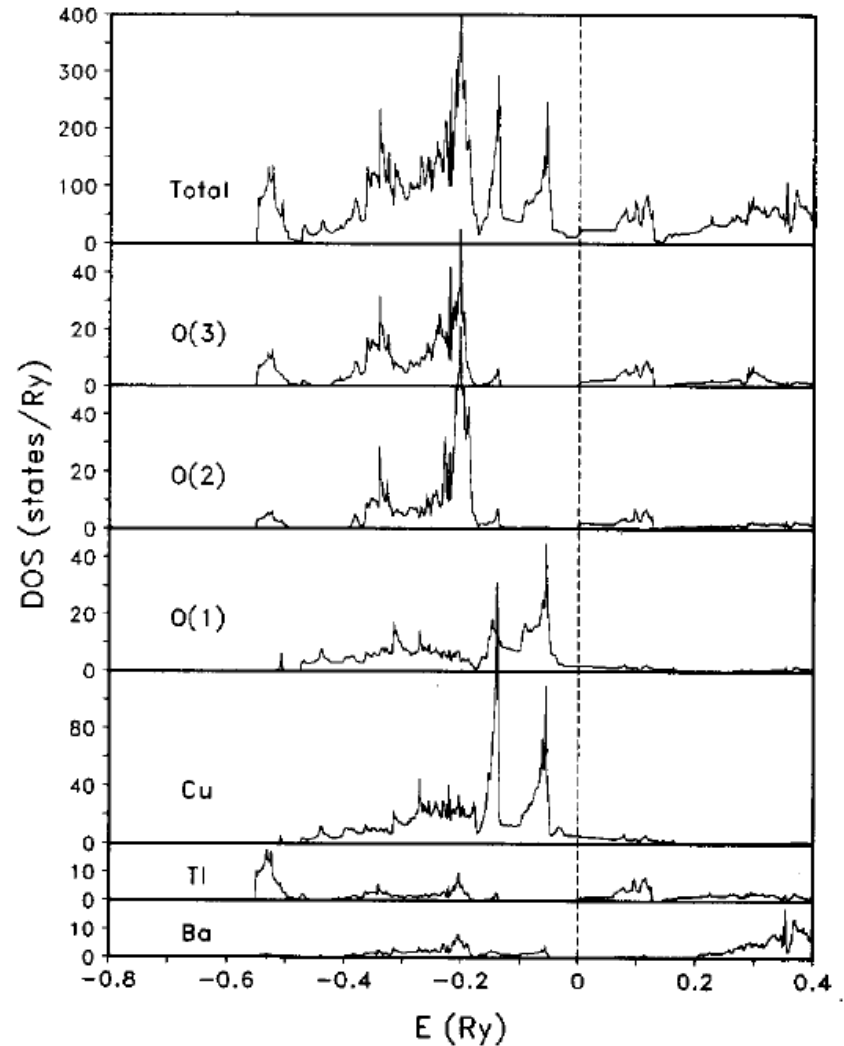   - d-states that are close in energy to the O p states (e.g. high metal valence states like Cu^{2+}).

A   B

Maj.   Min.   Min.   Maj.
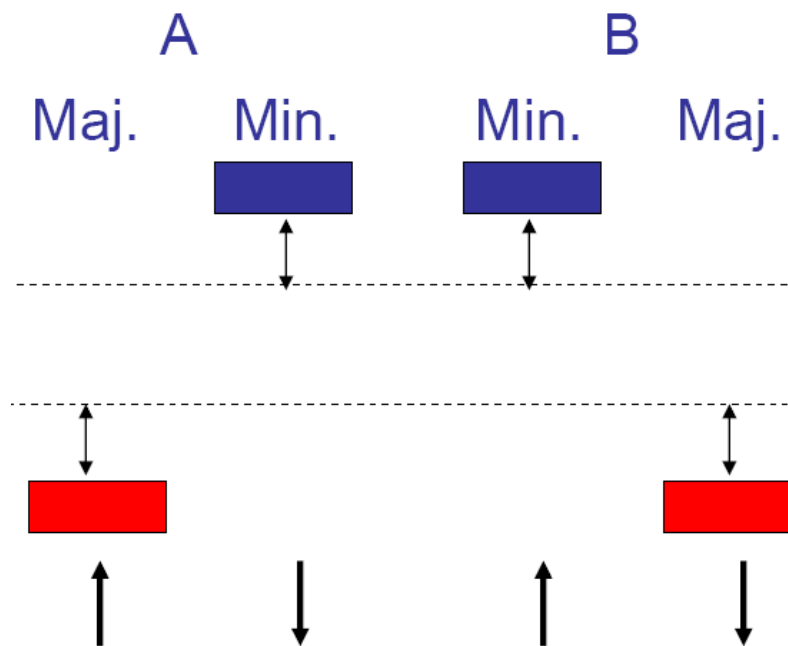
- In perovskites the interaction proceeds through O.

Example: Cuprate Superconductors (Spin ½)

$Tl_2Ba_2CuO_6$ Note hybridization of Cu and in-plane O(1)
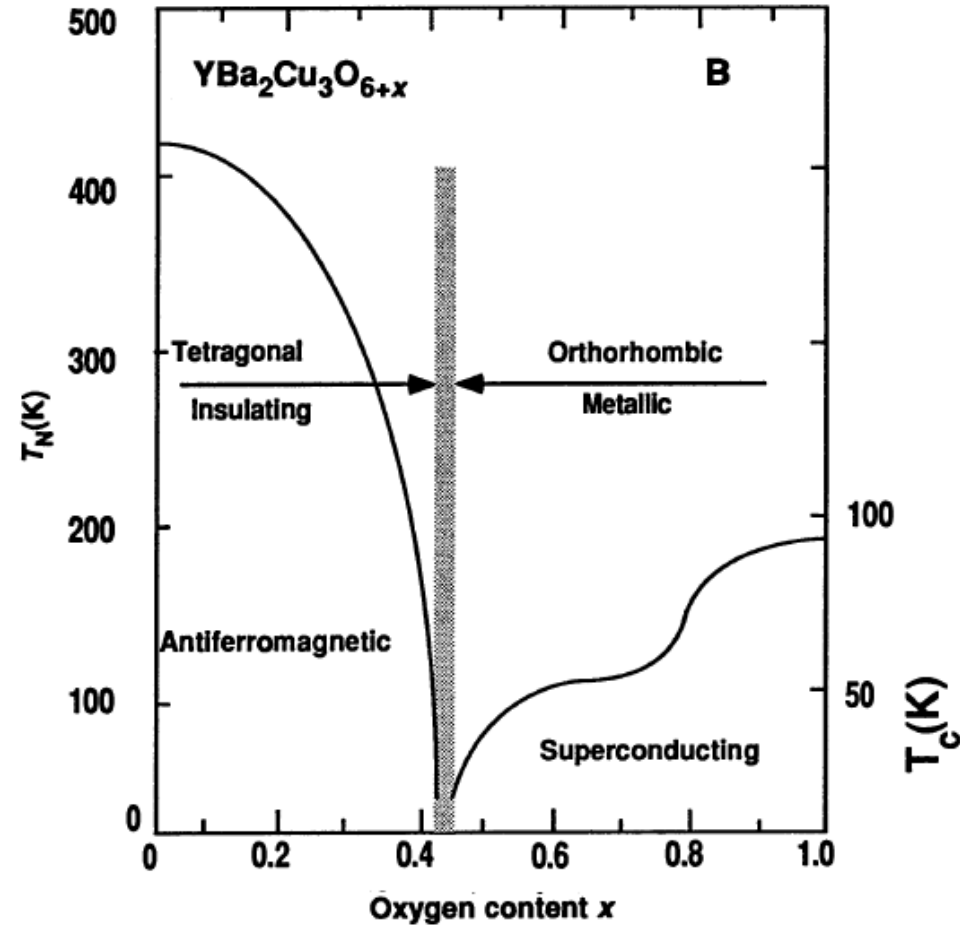
Highest T_c cuprates have long apical O bond (and short in plane bonds), are hole doped and have flat CuO_2 planes (straight bonds).

SrTcO$_3$

High Temperature Magnetic Ordering in the 4d Perovskite SrTcO$_3$

Efrain E. Rodriguez,[1] Frédéric Poineau,[2] Anna Llobet,[3] Brendan J. Kennedy,[4] Maxim Avdeev,[5] Gordon J. Thorogood,[6] Melody L. Carter,[6] Ram Seshadri,[7] David J. Singh,[8] and Anthony K. Cheetham[9]
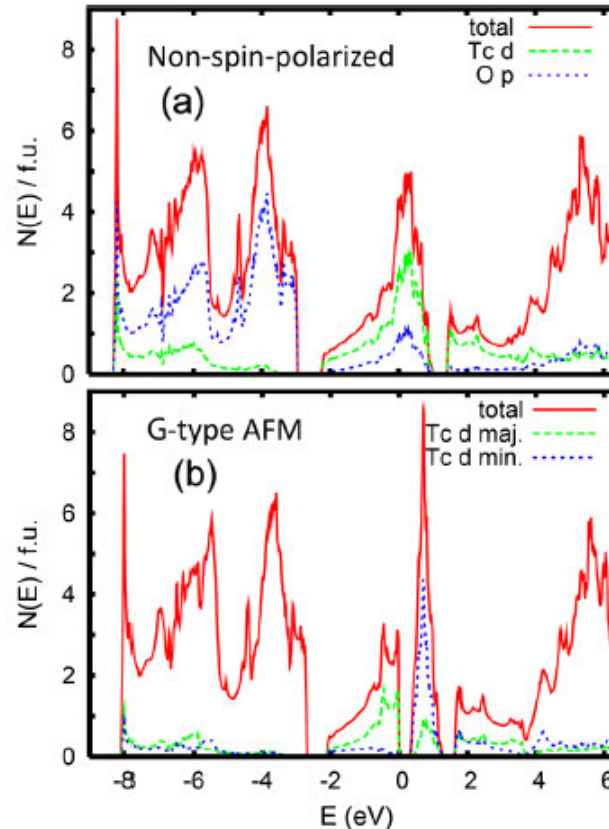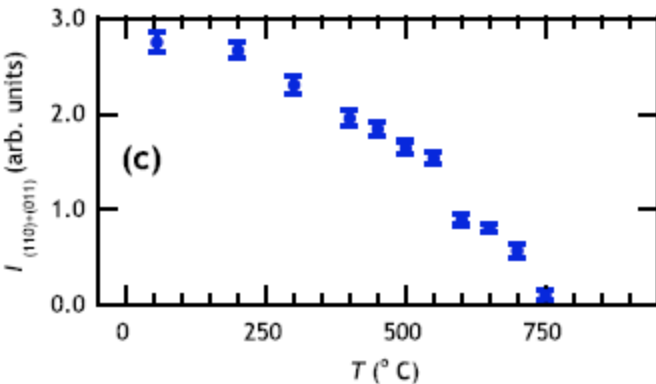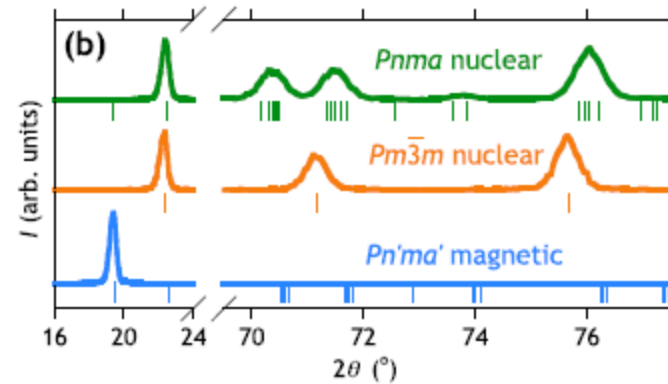
SrTcO$_3$ and CaTcO$_3$

- CaTiO$_3$ structure.
- No 3d-elements.
- High temperature magnetic ordering.

Explanation:

(1) Narrow t_{2g} bands ➔ magnetic instability.

(2) Strong covalency through O yields high inter-site coupling (high T_N).

(3) Half full t_{2g} favors G-type AFM.

SrRuO$_3$ (4 t_{2g} electrons): ferromagnetic and has high anisotropy even though it is almost cubic.
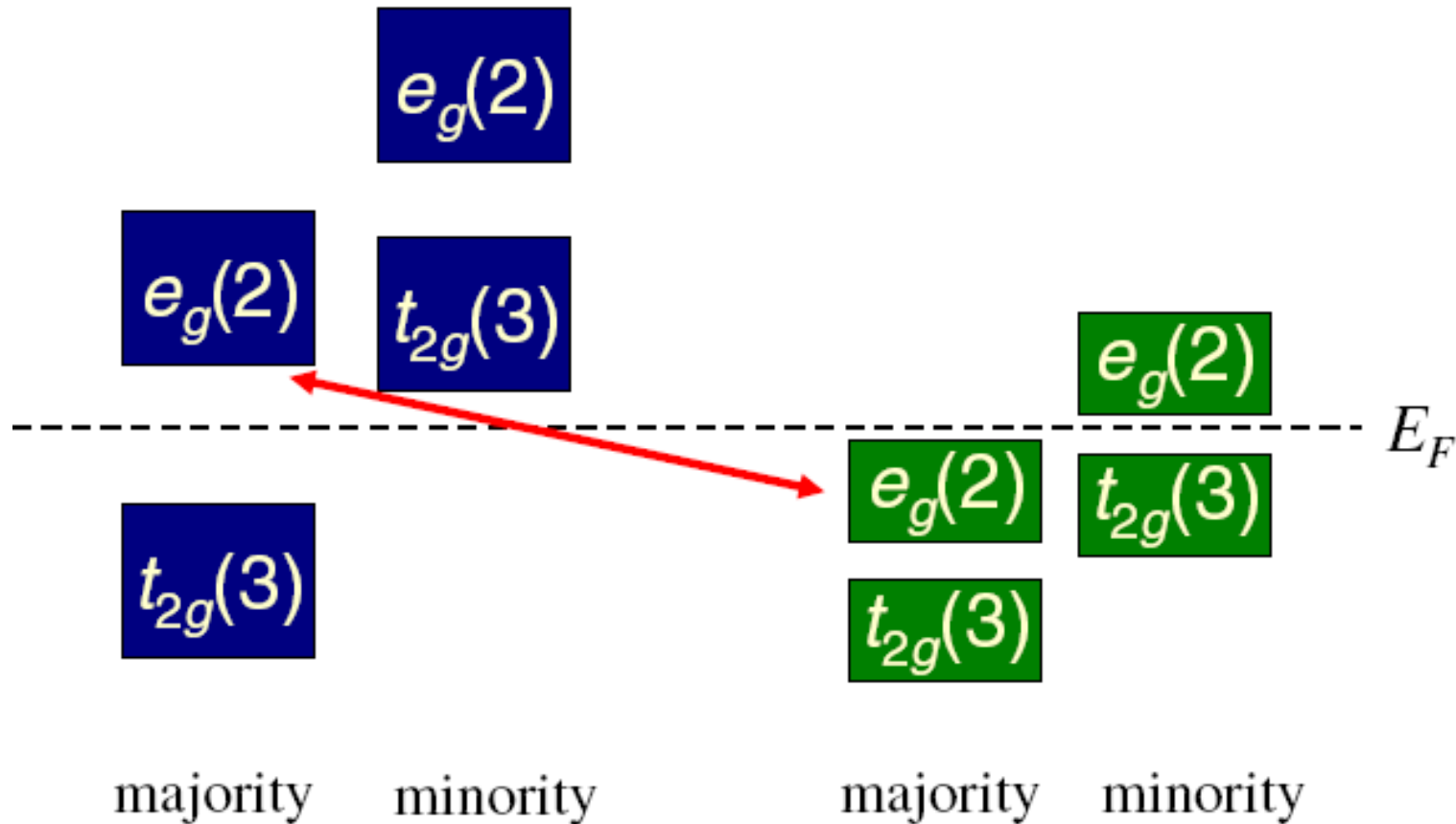
Covalency favors strong superexchange.
Disfavors moment formation.
High T_N >1000 K from a balance.

An Example (R_2NiMnO$_6$) Double Perovskite

Azuma et al., Oratani et al., Mater et al., DJS et al.

Mn^{4+} (d^3 r=0.67Å) Ni^{2+} (d^8 r=0.83Å)

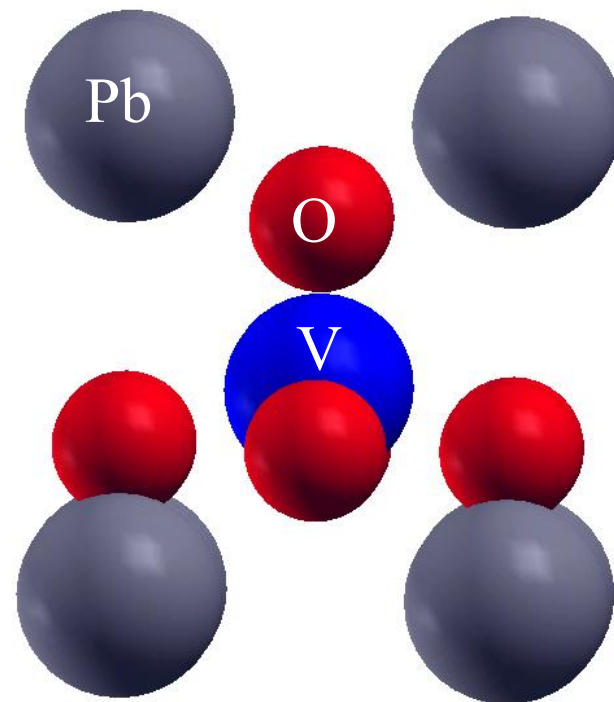A ferromagnet via standard Anderson super exchange.

Another Example PbVO$_3$

Perovskite, polar tetragonal structure $P4mm$; extreme $c/a \sim 1.23$.

Shpanchenko (2004), Belik (2005), Uratani (2005), DJS (2006).

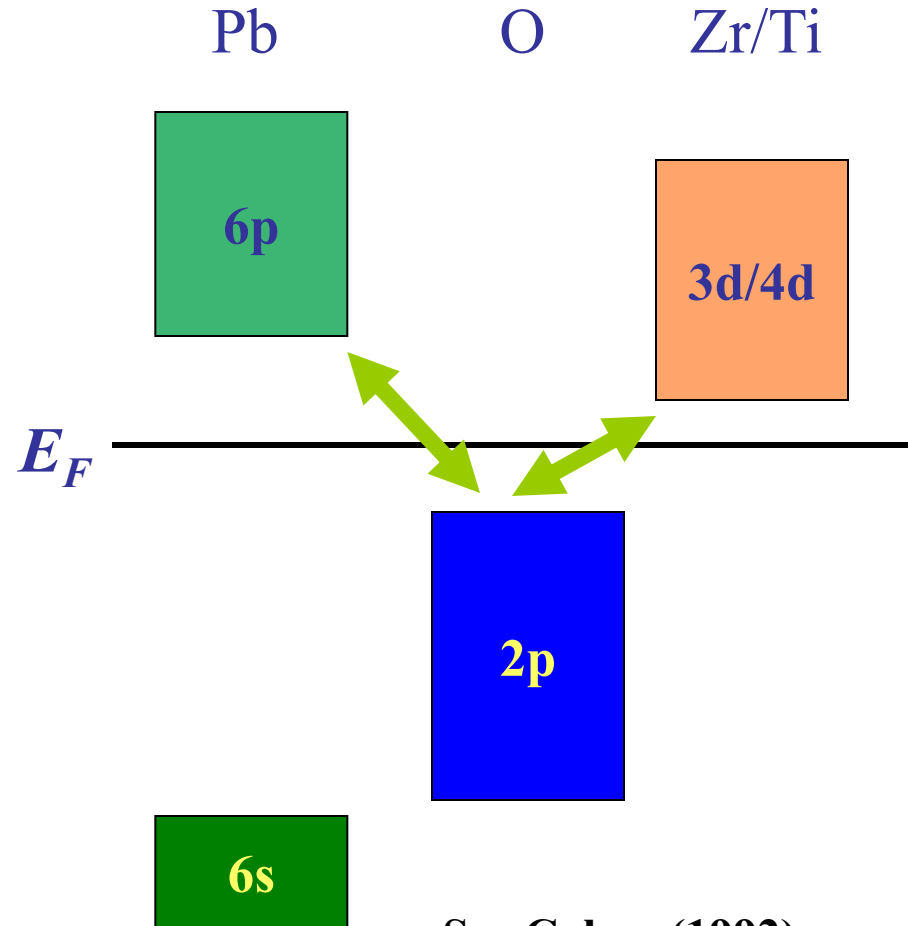Ionic model: $Pb^{2+}V^{4+}(O^{2-})_3$

- Two stereochemically active ions:

- Pb^{2+} on A-site

- V^{4+} on B-site (also magnetic)

- No transition with T up to 570K

- Tetragonal to Cubic transition at $P\sim$2 GPa.
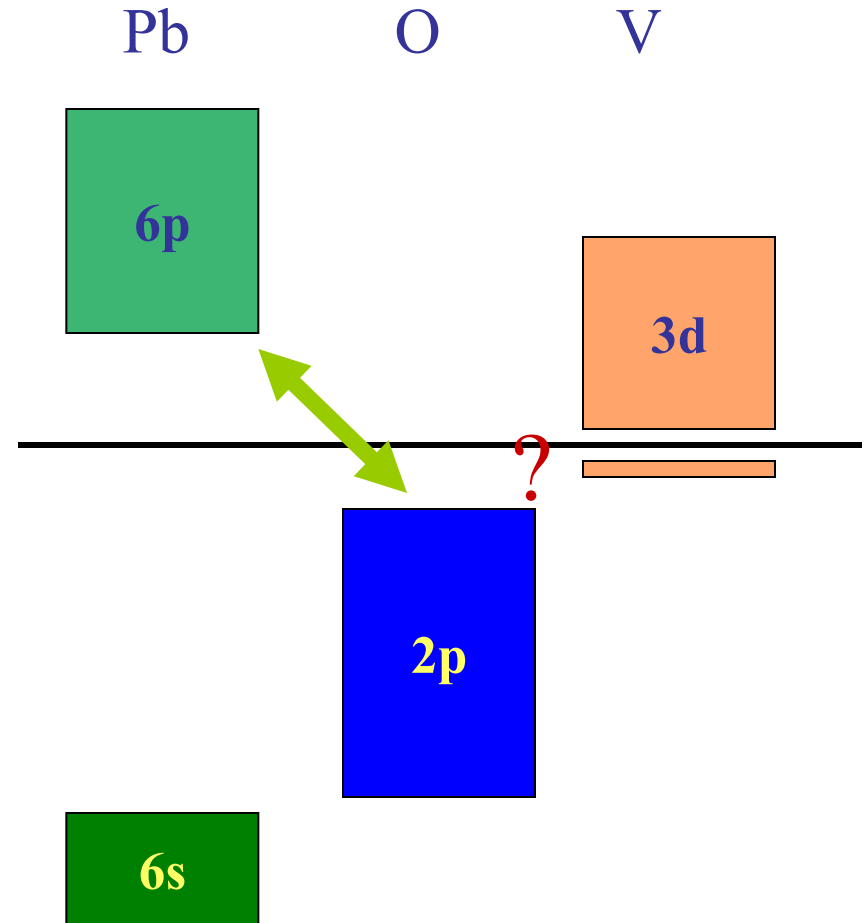
Hybridization Schemes

PZT

$c/a \sim 1.015 - 1.06$, $T_C \sim 250 - 450$ °C

Pb   O   Zr/Ti

6p   3d/4d

E_F

2p

6s

See Cohen (1992).

PbVO$_3$

$c/a \sim 1.23$, T_C *unknown*

Pb   O   V

6p   3d

?

2p

6s

V^{4+} in Oxides

Two normal configurations:

CaVO$_3$, SrVO$_3$

Sr$_2$VO$_4$ ….
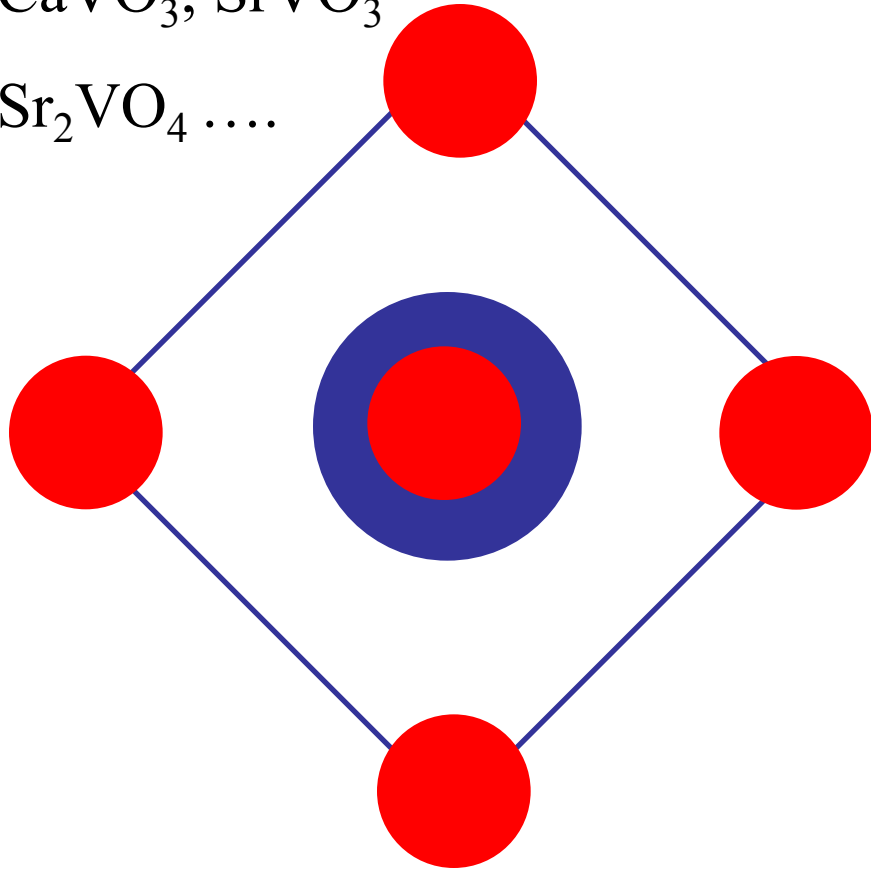
K$_2$V$_3$O$_8$ ….

PbVO$_3$
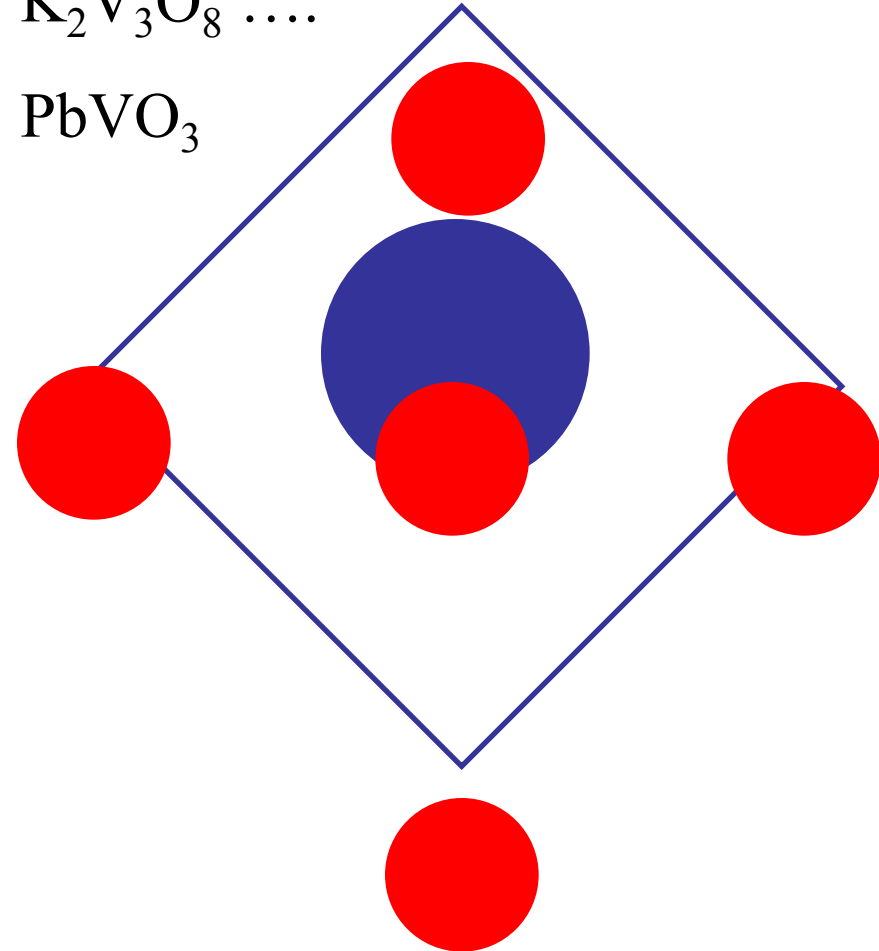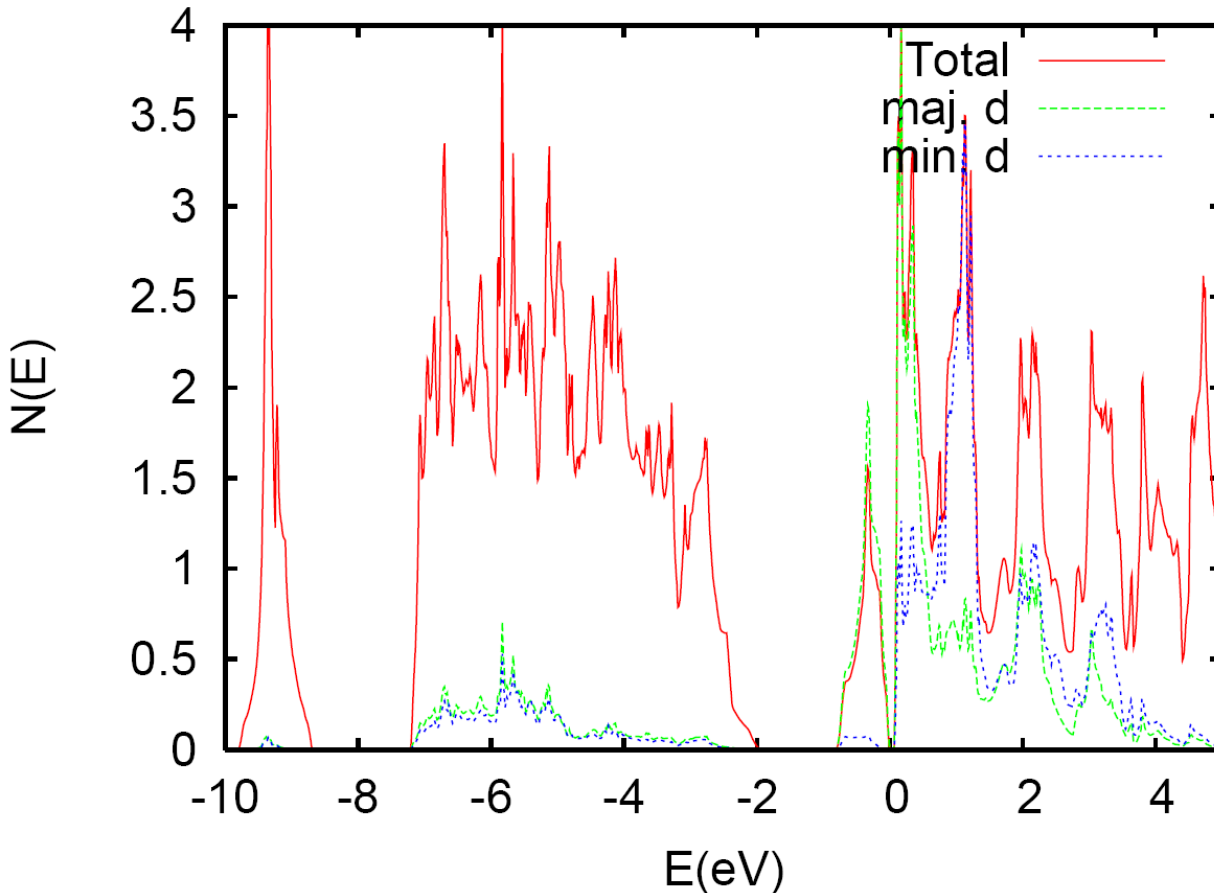

Metal or Mott Insulator.

Magnetic insulator.
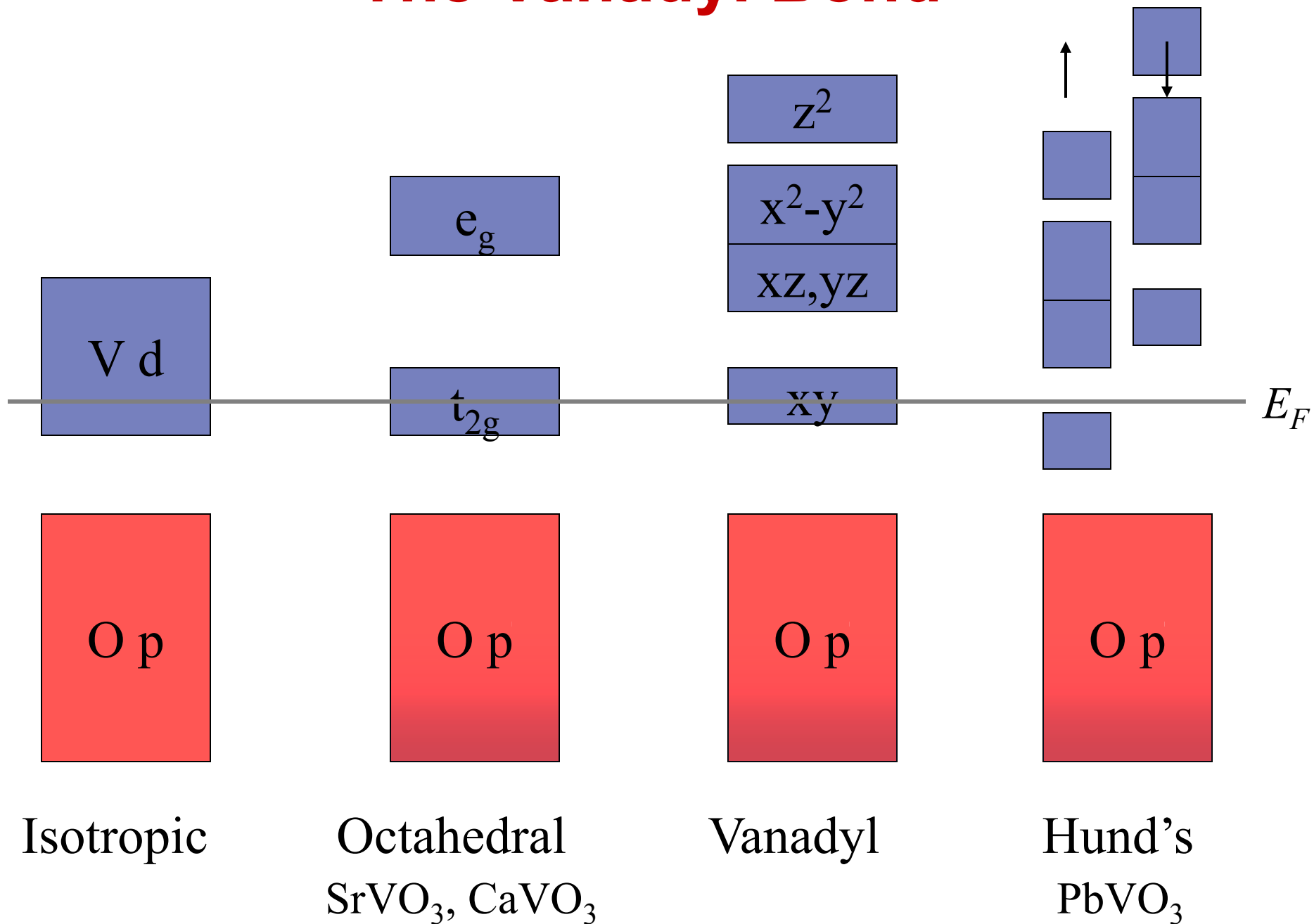
Short bond (1.55 – 1.60 Å)

Moment Formation in PbVO₃

- LDA Calculations with LAPW method, *c.f.* Shpanchenko, Uratani.

- Stable local moments on V ($m_s = 1\mu_B$).

- Ground state is AF C-type.

Conf.	*E*(meV)
NSP	0
F	-111.2
G	-127.3
A	-91.8
C	**-127.8**

The Vanadyl Bond

MAGNETOELASTIC COUPLINGS

Why is Magnetism Coupled to the Lattice?

1. Moment formation affects bonding.

   - Difference in size of high spin and low spin ions (Shannon).

   - Moment formation competes with bonding (bonds have paired electrons in normal cases) -- Invar

2. Exchange interactions depend on structure through hopping integrals and on-site terms (relative shifts in levels).

3. Relativistic effects (spin orbit and Dzyaloshinsky-Moria) couple spin directions to the lattice – magnetostriction, moment canting.
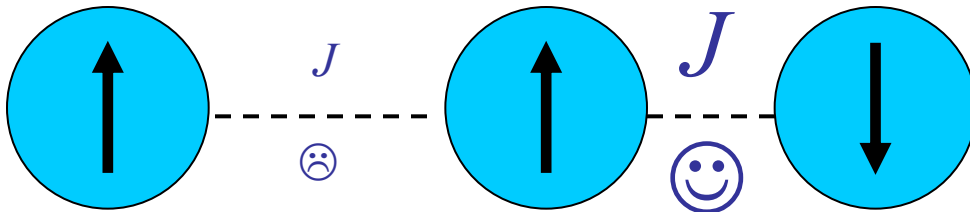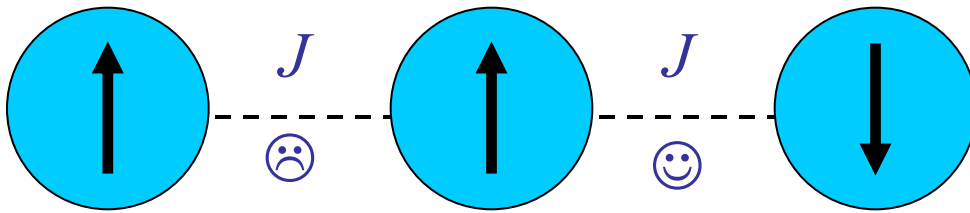
How Does It Work?

Heisenberg Model $J \sim t^2/\Delta E$

$$\mathcal{H} = -\sum_{i,j} \mathcal{J}_{ij}\vec{s_i} \cdot \vec{s_j}$$

But both ΔE and t depend on position – The hopping t is from wave function overlap, which is very strongly dependent on distance (exponential) and bond angles. $J \rightarrow J(\mathbf{r}_i\text{-}\mathbf{r}_j,\theta)$
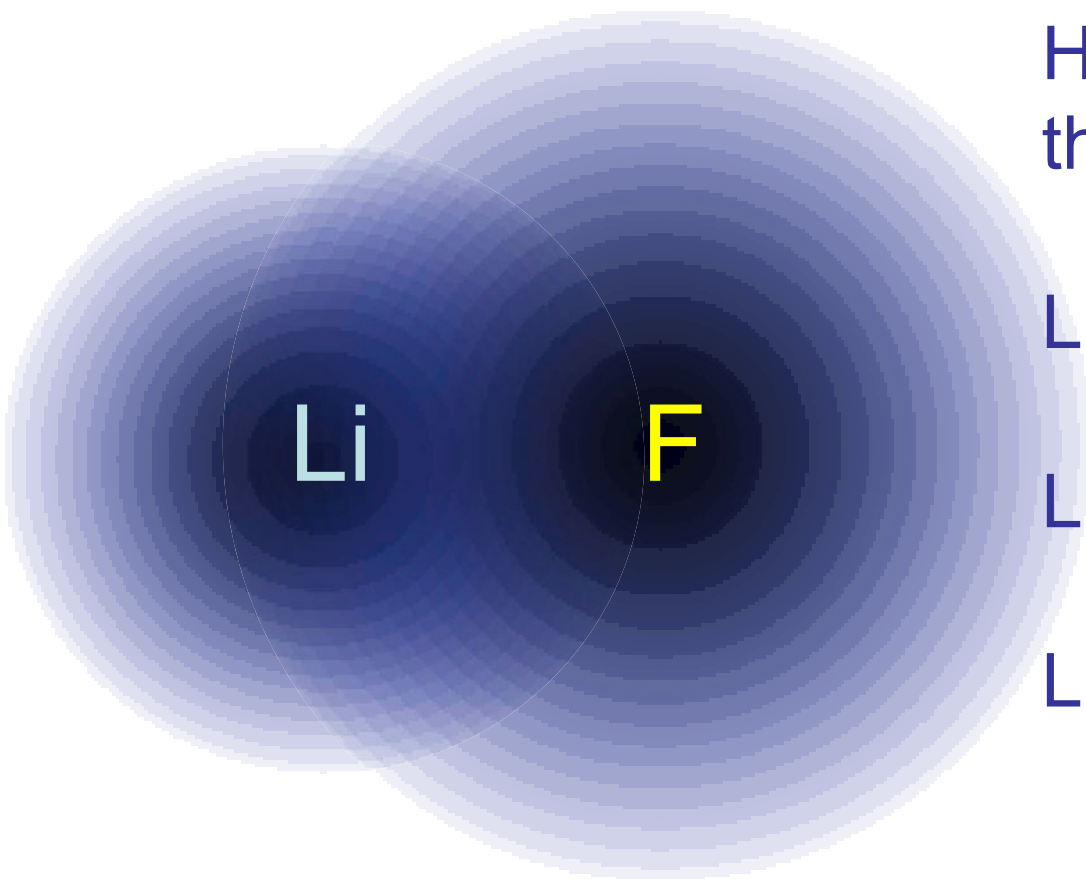

"Spin-Dimer"

A kind of bonding

Can accomplish the same thing with M – O – M bond angles in perovskites or by lattice strain (e.g. MnO).

How Do We Know What is What
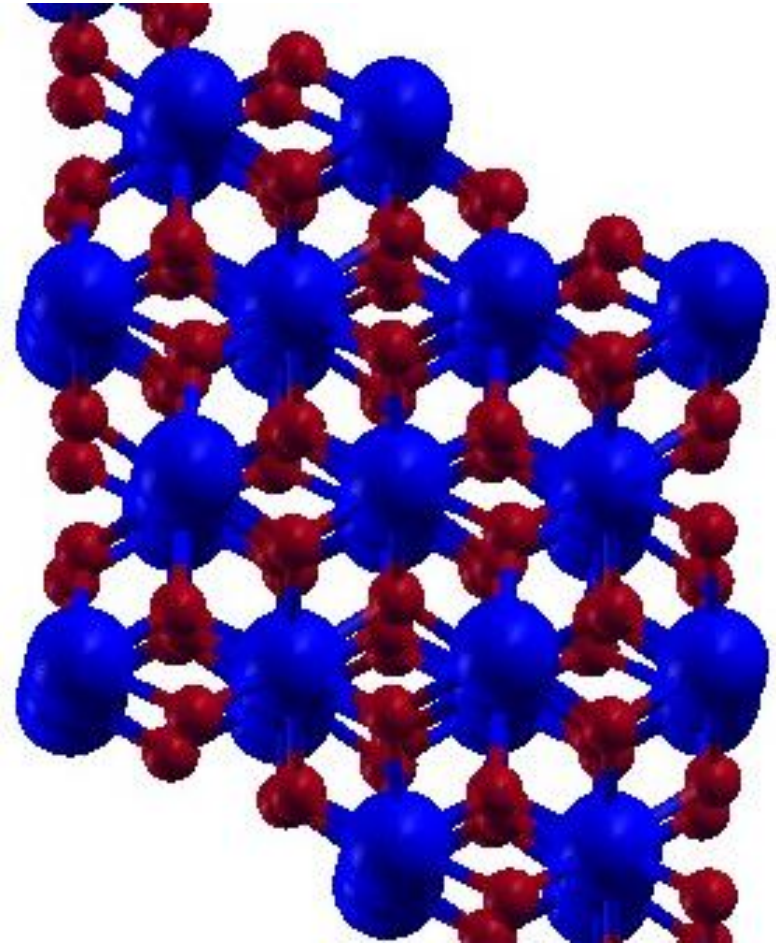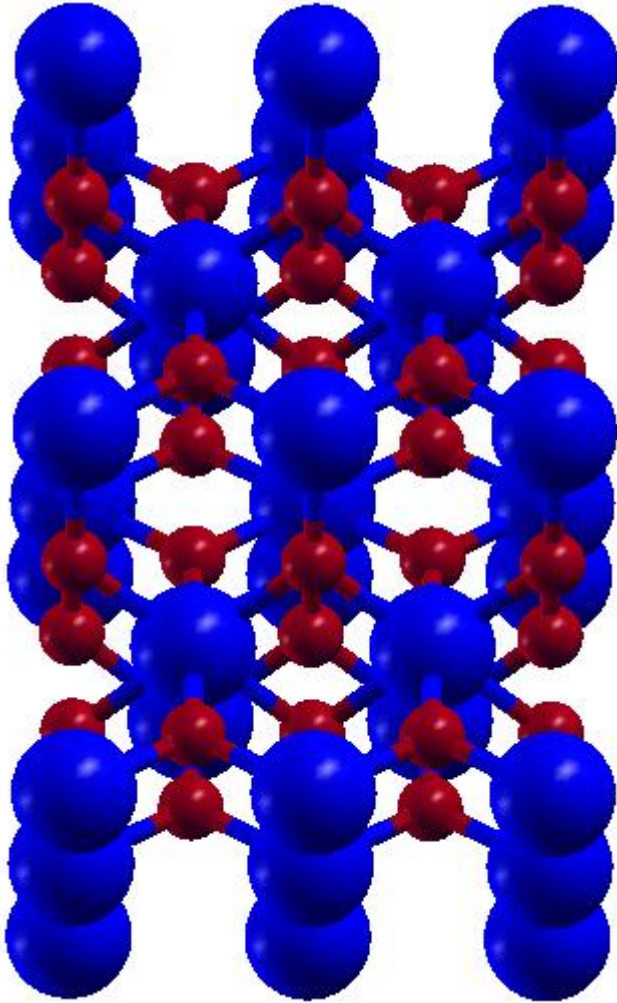
Li   F

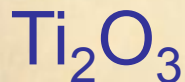How do we understand this in useful terms:

$Li^+ F^-$?

LiF (covalent)?

$Li^- F^+$?

Note: An expansion in radial functions times spherical harmonics is complete ➜ Expansion about more than one site is over-complete (ambiguous).

An Example: Two Titanium Oxides

TiO_2 Ti_2O_3

Both have Ti octahedrally coordinated by O.

A Chemist's View

TiO$_2$

Ti$_2$O$_3$

Electronegativity:

Ti: 1.54   O: 3.44

Large difference means O is O^{2-} and therefore we have Ti^{4+} and Ti^{3+} respectively. These are known common valence states of Ti.
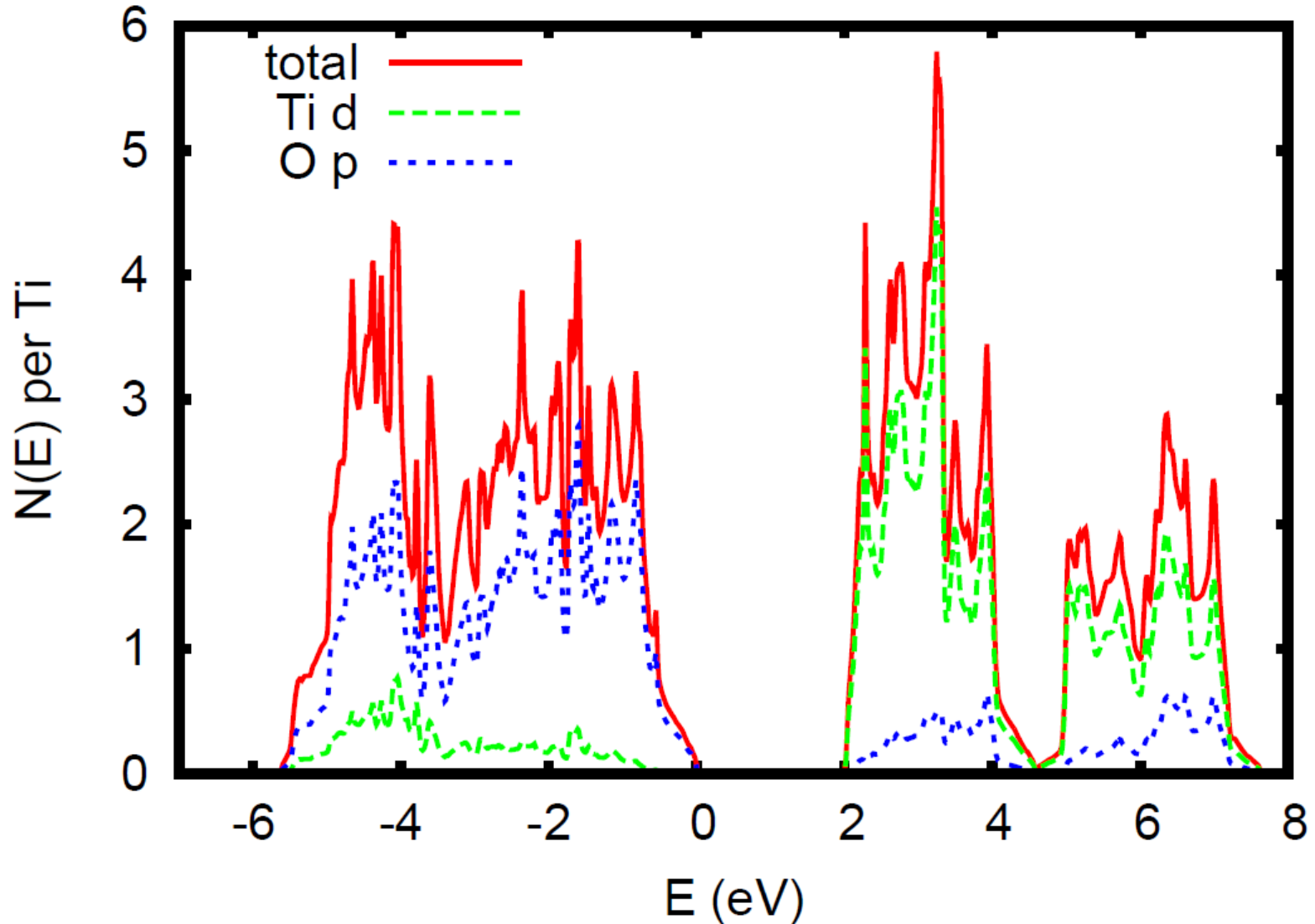
22	47.88
3560	4,3
1935	Ti
4.54	
[Ar]3d^{2}4s^2	
Titanium	

Things are not always so simple:
- Smaller electronegativity differences (e.g. BaFe$_2$As$_2$).
- Metals (e.g. PdCoO$_2$).
- Multiple mixed valence ions (e.g. MnFe$_2$O$_4$ – Mn^{2+}Fe^{3+}; Mn^{4+}Fe^{2+} etc.).

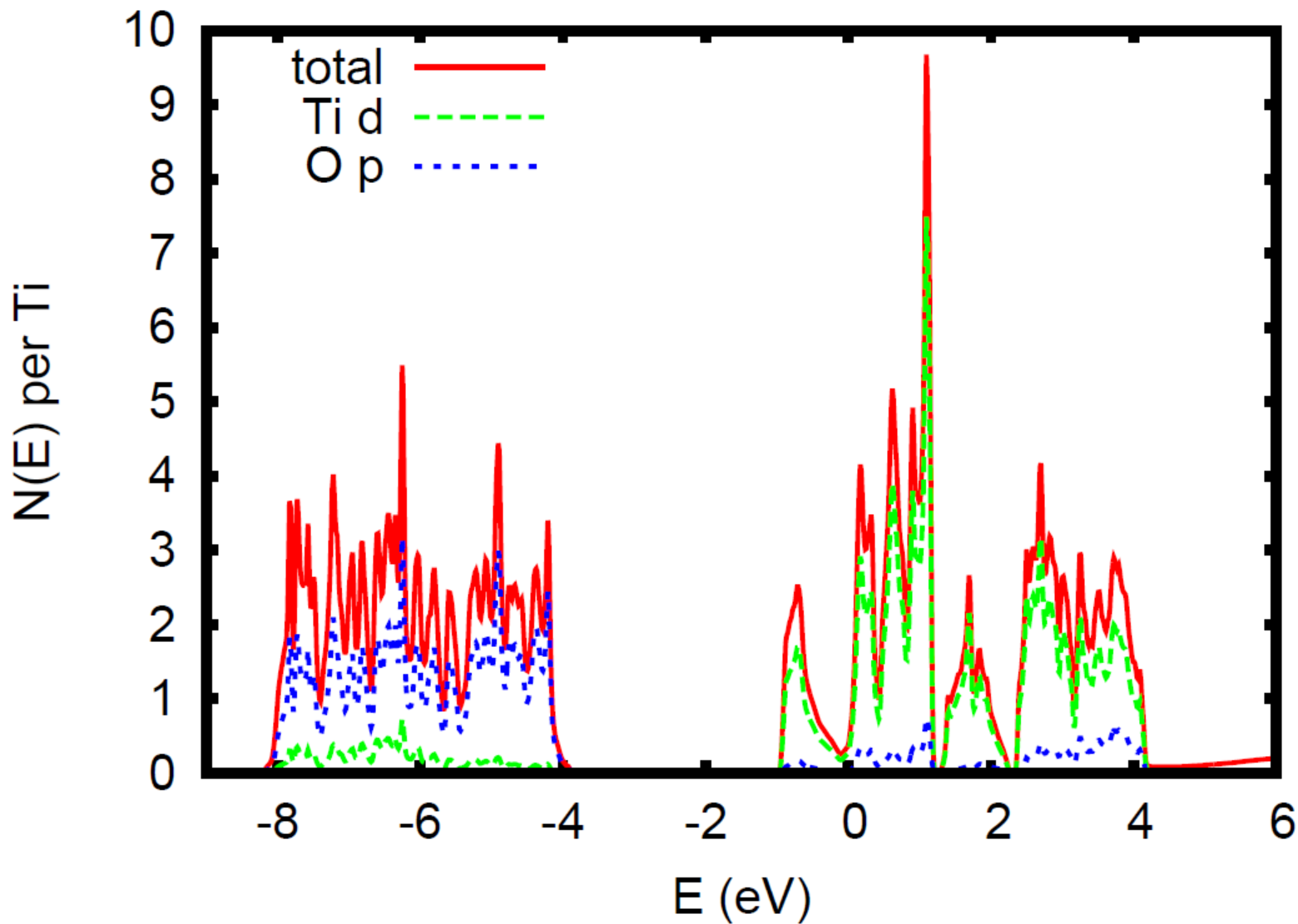# Density of States for TiO₂
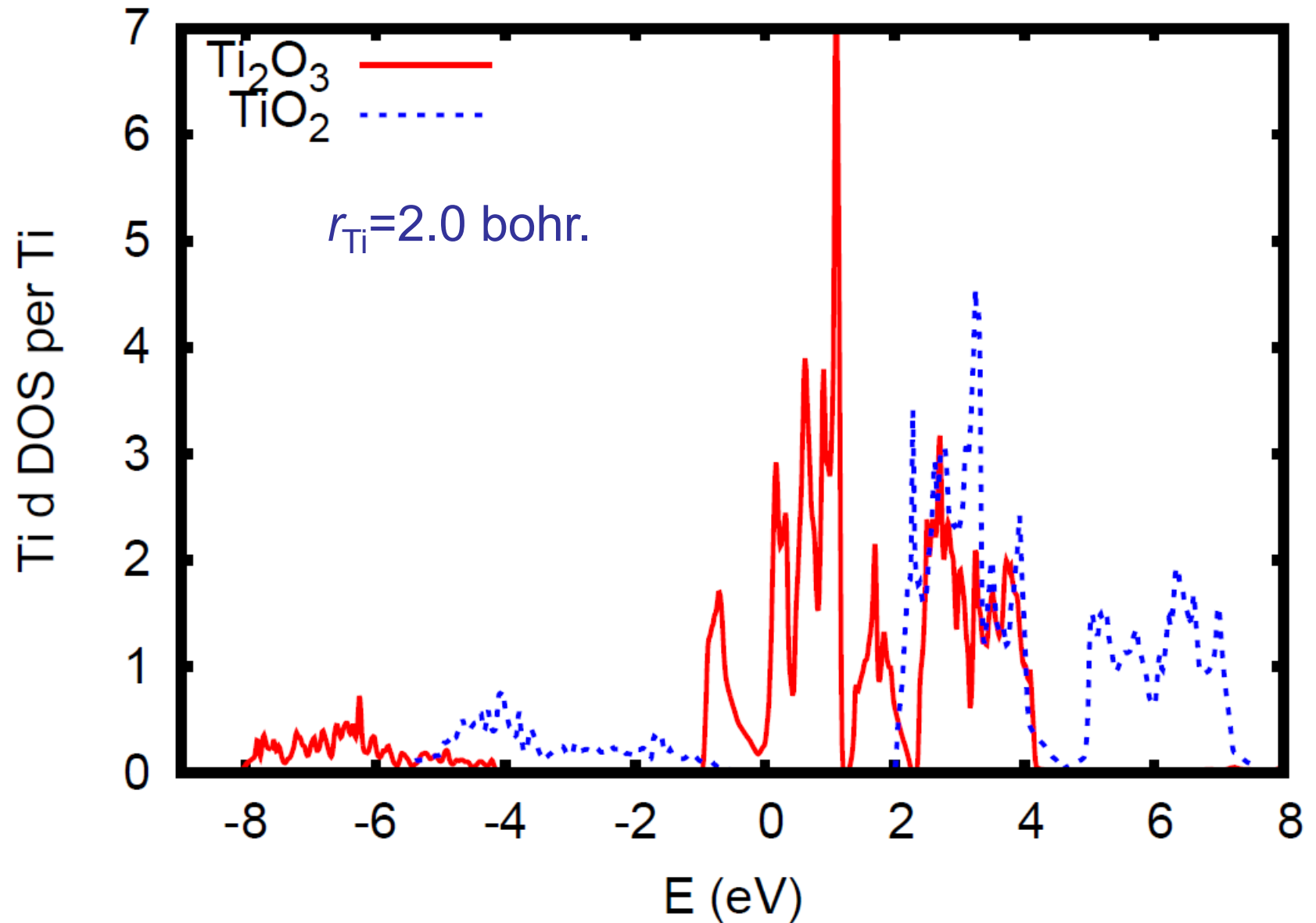
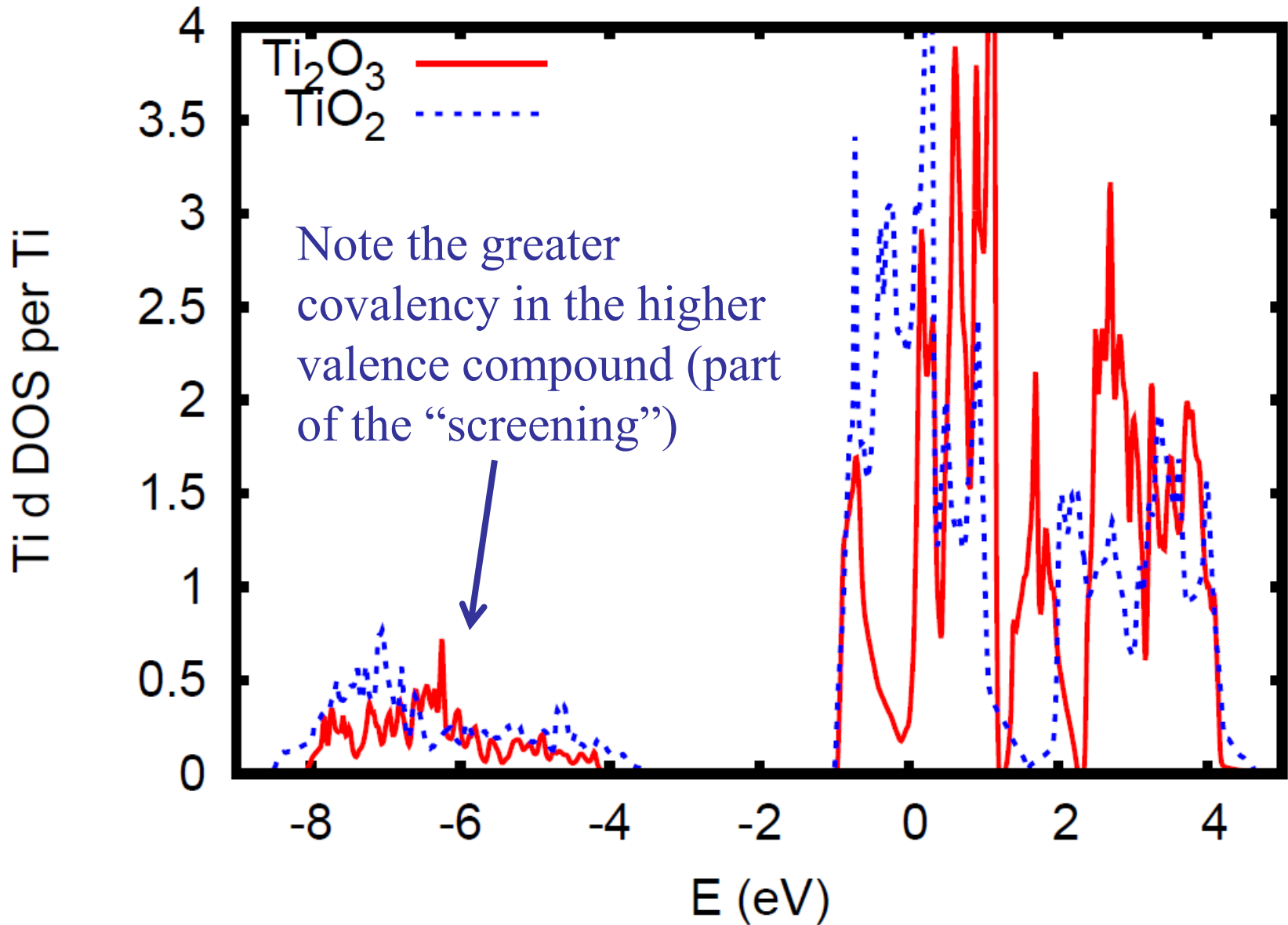LAPW calculation with r_{Ti}=2.0 bohr, r_O=1.6 bohr

Density of States for Ti_2O_3

LAPW calculation with r_{Ti}=2.0 bohr, r_O=1.6 bohr

Comparison of Ti d Projections

Ti d Projections with 3 eV Shift

Deep Core Level Positions

- Reflect the Coulomb potential, which should vary with valence.

- Experimentally accessible quantities.

- Absolute position is arbitrary in a solid state calculation: Need to look either at differences or relative to some physical reference, e.g. Fermi level.

$O\ 1s - Ti\ 1s$ (PBE GGA).

TiO_2: 4357.73 eV

Ti_2O_3: 4356.09 eV

- Difference is > 1 eV and can be used to characterize valence. However, the differences in non-oxides/halides are smaller, and this is indirect (relies on reference compounds).

- Higher binding energy for metal ion means higher valence.

- Can be misleading for hypothetical crystal structures.
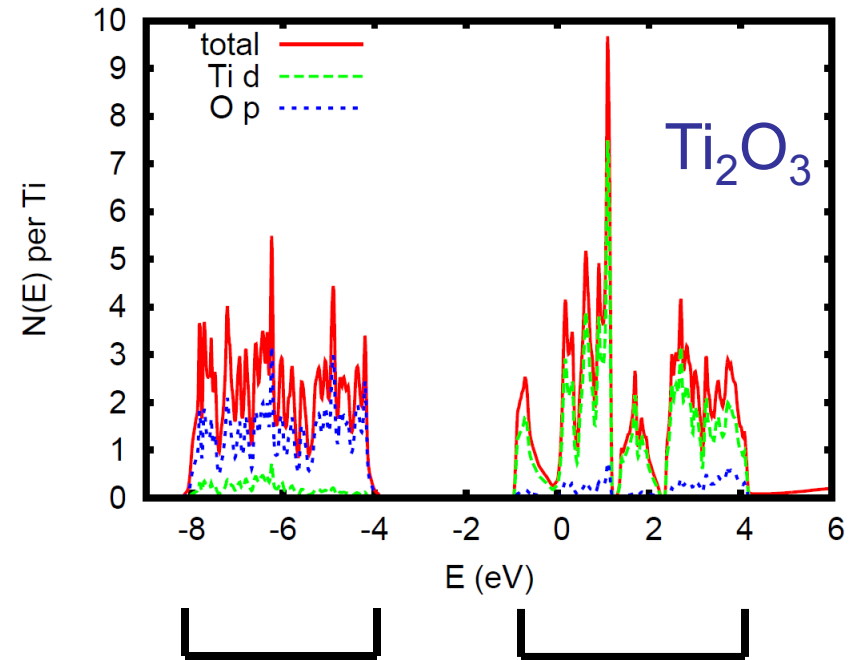
What Can Be Done for TiO₂ / Ti₂O₃

- Do DFT calculations; find band characters and then count.
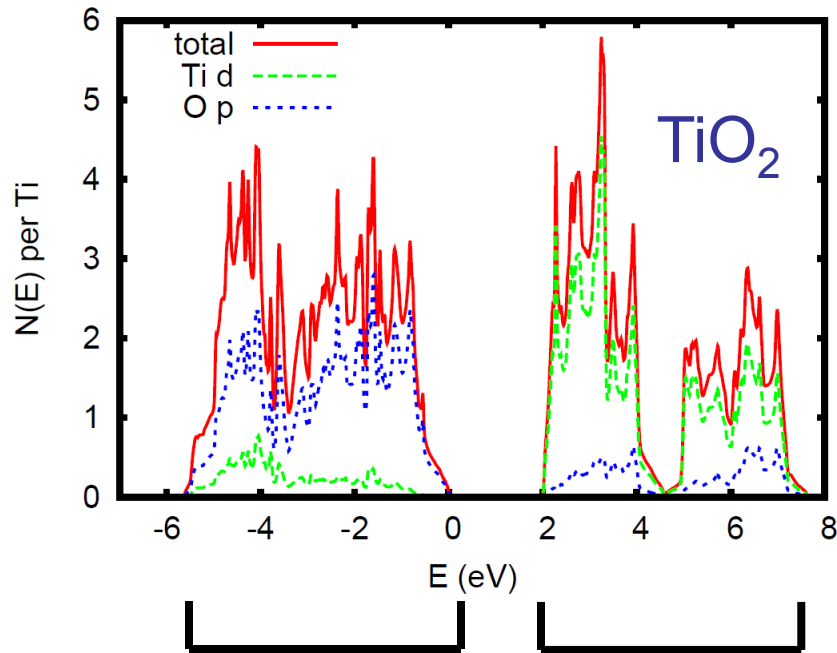
O p Ti d

O p Ti d

12 O p bands occupied (24 e) per cell (Ti_2O_4), no occupied d bands ➔ Ti^{4+}

18 O p bands occupied (36 e) per cell (Ti_4O_6), 2 occupied d bands ➔ Ti^{3+}

Questions?