3.320/SMA5107: Lecture 9b (3/3/05)

Applications and Performance of DFT methods

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

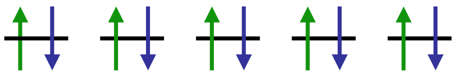
Spin Polarization: The Local Spin Density Approximation (LSDA)

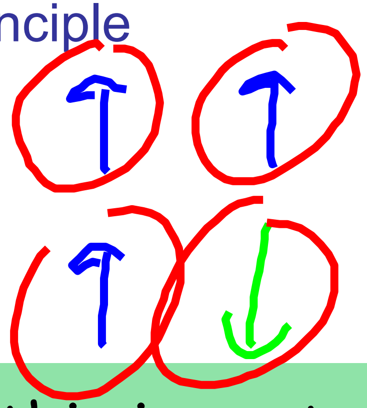
- Electrons have spin +(-) 1/2 μ_B
- Spin is treated as a scalar quantity (this is approximate, as relation to angular momentum makes it a vector quantity)
- Two spin states often referred to as "up"↑ and "down"↓
- Up-Up interaction is different from Up-Down

Exchange Effects: *Refresher*

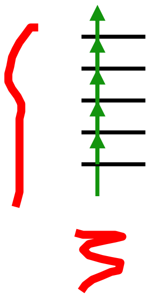
Hund's rule: A consequence of Pauling exclusion principle

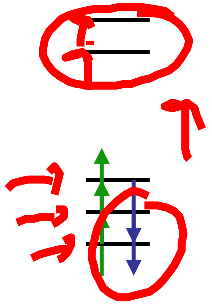
e.g. for atomic d-levels





Even in solids where energy levels are split, can get parallel filling if splitting is not too large





Why is this important ?

Filling of different orbitals may give the atom different chemical properties

Materials can carry a magnetic moment

$$\rho_\uparrow \neq \rho_\downarrow$$

Spins in Density Functional Theory

In principle $E_{xc}[\rho]$ "knows" about this effect, but in practice it is poorly approximated since only total charge density is variable

But in practice, need to help LDA along …

Solution: Treat up and down densities separately

Local Spin Density (LSD) = LDA with different charge density for up and down electrons

$\rho_\uparrow \quad \rho_\downarrow$.

$$v_{eff}^{\uparrow} = v(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\partial E_{xc}\left[\rho^{\uparrow},\rho^{\downarrow}\right]}{\partial \rho^{\uparrow}}$$

$$v_{eff}^{\downarrow} = v(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\partial E_{xc}\left[\rho^{\uparrow},\rho^{\downarrow}\right]}{\partial \rho^{\downarrow}}$$

Up and down charge density can be different $\rho_\uparrow \neq \rho_\updownarrow$

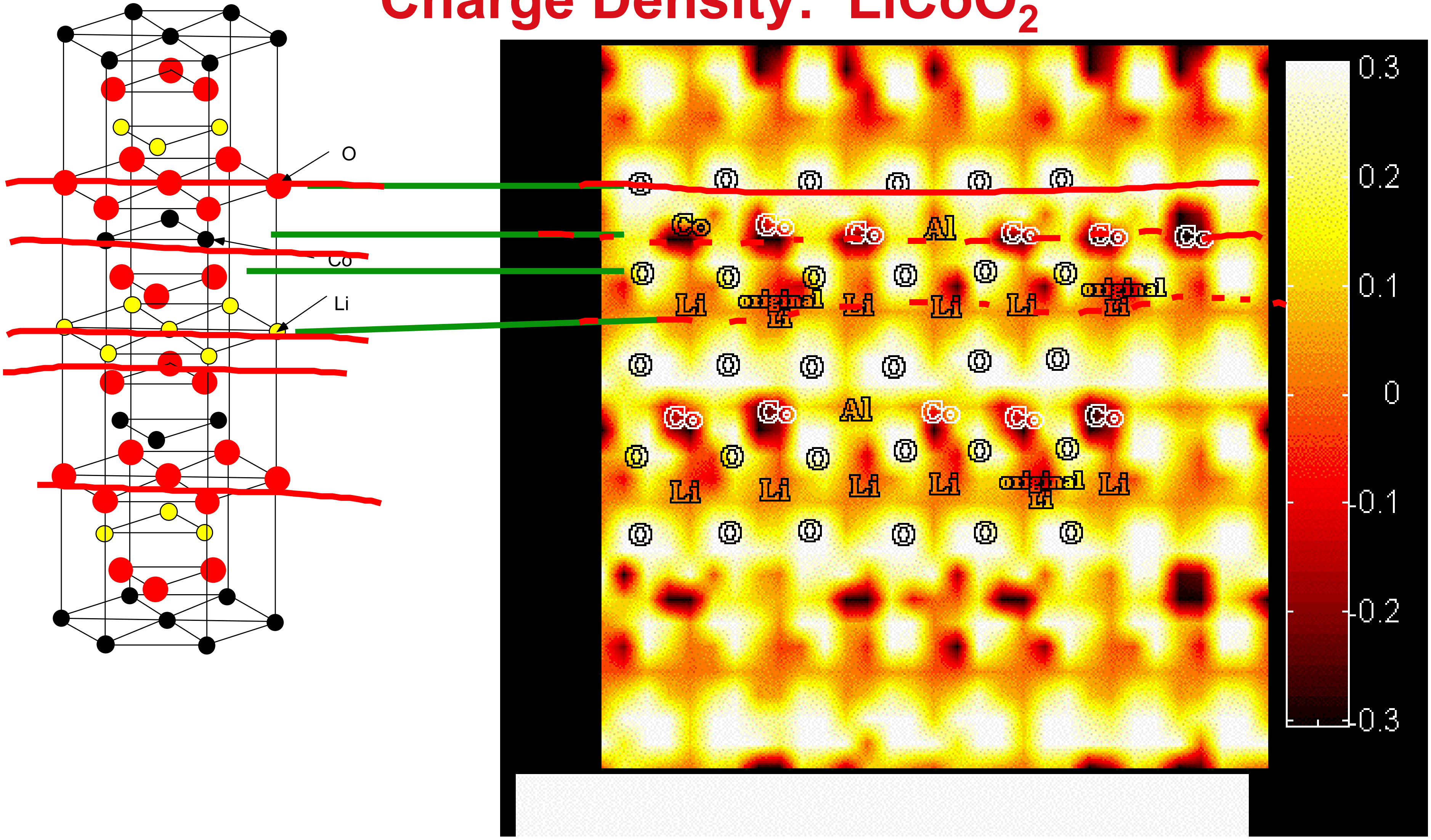
Similar to restricted and unrestricted Hartree Fock

Regular LDA can not capture exchange effect well since it is non-local

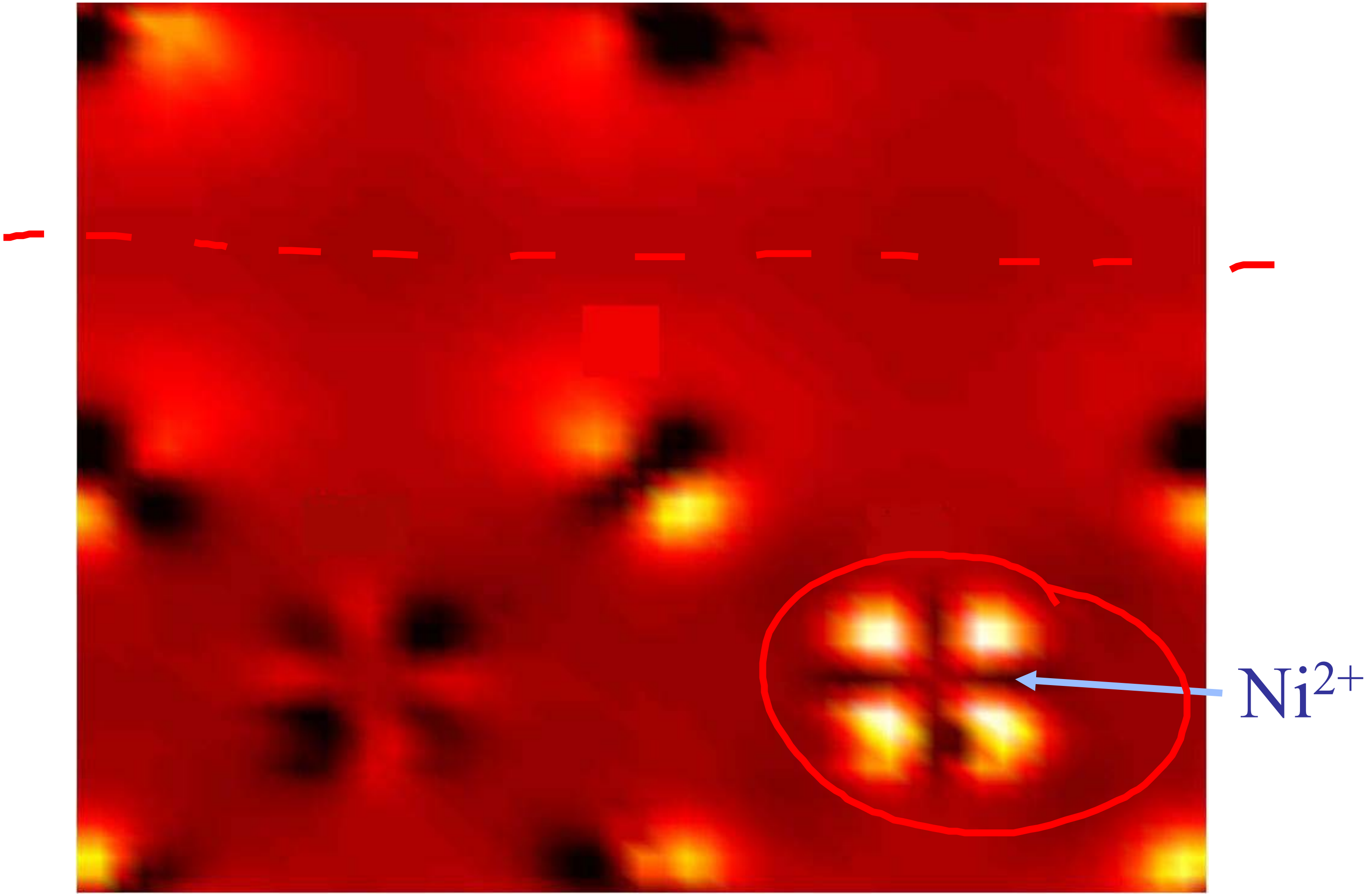
A spin-polarized version of GGA exists as well

Cr

Charge Density: $LiCoO_2$



Spin Density: filters out unpolarized ions (e.g. O^{2-})



How good is the output from LDA/GGA ?

Computational quantum mechanics provides very basic information: Energy, charge density, band structure, optimized atomic positions, etc.

How do I make a faster car from this ?

Photo of sports car removed
for copyright reasons.

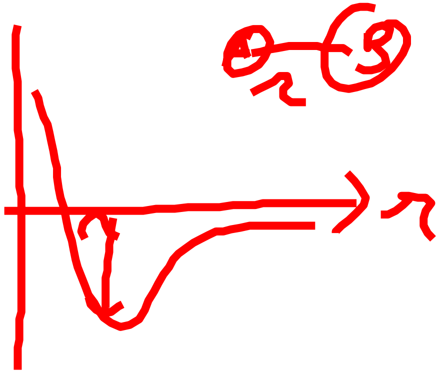
First evaluate accuracy of basic information
-> then understands how that propagates
into higher order models

Energies of Atoms

energy in Ry	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
GGA: PW91	214.928	229.296	249.24	275.564	2108.926	2149.997	2199.433	2257.893
LDA	214.668	228.892	248.686	274.849	2108.045	2148.939	2198.189	2256.455
Expt.	214.958	229.334	249.308	275.088	2109.174	2150.126	2199.45	2257.856
energy in Ry	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
GGA: PW91	2324.514	2400.12	2484.686	2578.669	2682.386	2796.152	2920.278	21055.077
LDA	2322.867	2398.265	2482.618	2576.384	2679.88	2793.419	2917.313	21051.876
Expt.	2324.49	2400.086	2484.672	2578.696	2682.764	2796.2	2920.298	21055.098
energy in Ry	**K**	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
GGA: PW91	21199.825	21355.144	23850.018	24154.2	24471.917	24803.334	25148.619	25507.943
LDA	21196.383	21351.466	23843.66	24147.583	24465.038	24796.191	25141.209	25500.263

LDA underestimates stability of atom, GGA is closer

Small Molecules



Binding Energy

	exp (ev)	LDA	GGA	HF
H2	-4.753	-4.913	-4.540	-3.64
LiH	-2.509	-2.648	-2.322	
O2	-5.230	-7.595	-6.237	-1.28
H20	-10.078	-11.567	-10.165	
F2	-1.66	-3.32		1.37

Binding energy too high in LDA, GGA is closer but sometimes bound to weak. Pure Hartree Fock without corrections is terrible.

Lattice Parameters in Solids

	exp	LDA	Δ	GGA	Δ
Si	5.427	5.4	-0.50%	5.49	1.16%
Ge	5.65	5.62	-0.53%	5.74	1.59%
GaAs	5.65	5.62	-0.53%	5.73	1.42%
Al	4.03	3.98	-1.31%	4.09	1.57%
Cu	3.60	3.52	-2.35%	3.62	0.44%
Ag	4.07	4.00	-1.69%	4.17	2.47%
Ta	3.30	3.26	-1.12%	3.32	0.80%
W	3.16	3.14	-0.67%	3.18	0.67%
Pt	3.91	3.90	-0.41%	3.97	1.49%
Au	4.06	4.05	-0.13%	4.16	2.48%

LDA tends to “overbind”, GGA “underbinds” GGA error more variable

Bulk Modulus in Solids (in GPA)

	exp	LDA	Δ	GGA	Δ
Si	99	96	-3.03%	83	-16.16%
Ge	77	78	1.30%	61	-20.78%
GaAs	76	74	-2.63%	65	-14.47%
Al	77	84	9.09%	73	-5.19%
Cu	138	192	39.13%	151	9.42%
Ag	102	139	36.27%	85	-16.67%
Ta	193	224	16.06%	197	2.07%
W	310	337	8.71%	307	-0.97%
Pt	283	307	8.48%	246	-13.07%
Au	172	198	15.12%	142	-17.44%

LDA tends to be too stiff. GGA too soft

Oxides

	exp	LDA	Δ	GGA	Δ
MgO	4.21	4.17	-0.95%		
TiO2 (a)	4.59	4.548	-0.92%	4.623	0.72%
TiO2 (c)	2.958	2.944	-0.47%	2.987	0.98%
Al2O2	5.128	5.091	-0.72%	5.185	1.11%
BaTiO3	4	3.94	-1.50%		
PbTiO3	3.9	3.833	-1.72%	3.891	-0.23%
SnO2	4.737	4.637	-2.11%		
β-MnO2 (a)	4.404	4.346	-1.32%	4.444	0.91%
b-MnO2 (c)	2.876	2.81	-2.29%	2.891	0.52%

Summary of Geometry Prediction

LDA under-predicts bond lengths (always ?)

GGA error is less systematic though over-prediction is common.

errors are in many cases < 1%, for transition metal oxides < 5%

Predicting Structure: The Energy Scales

Accuracy required to predict physical behavior is astonishing

V

Atomic energy: -1894.074 Ry

Fcc V : -1894.7325 Ry

Bcc V : -1894.7125 Ry

Cohesive energy is 0.638 Ry (0.03% of total E)

Fcc/bcc difference is 0.02 Ry (0.001% of total E)

Mixing energies are also order 10^{-6} fraction of total E

How can we ever get physical behavior correct ?

Large cancellation of errors !

Elemental Crystal Structures: GGA pseudopotential method

🟥 experimentally found to be fcc

🟩 experimentally found to be bcc

$E_{bcc} - E_{fcc}$

(kJ/mole)

H -0.12																
Li 0.13 0.11 0.11	**Be** 2.19 0.04 0.50											**B** 34.77	**C** -19.71 -6.00	**N** -21.12	**O** 10.24	**F** -4.53
Na 0.12 0.05 0.05	**Mg** 1.37 0.50 0.50	←	←	←		VASP-PAW SGTE data Saunders *et al.*		→	→	→		🟥 **Al** 9.21 10.08 10.08	**Si** -1.89 -4.00 -4.00	**P** -16.04 7.95	**S** -17.65	**Cl** -4.46
K 0.04 -0.05 -0.05	🟥 **Ca** 1.64 1.41 0.93	**Sc** 5.80 -3.02	**Ti** 4.79 0.48	🟩 **V** -23.95 -7.50 -15.30	🟩 **Cr** -30.76 -6.12 -9.19	**Mn** 7.41 0.78 1.80	🟩 **Fe** -8.45 -7.97	**Co** 8.36 1.71 4.20	🟥 **Ni** 9.23 7.99 7.49	🟥 **Cu** 2.84 4.02 4.02	**Zn** 5.94 -0.08 6.03	**Ga** 1.48 0.70 0.70	**Ge** 0.70 -1.90 -1.90	**As** -10.71	**Se** -14.67	**Br** -2.85
Rb 0.08 -0.20 -0.20	🟥 **Sr** 0.43 1.33 0.75	**Y** 10.02 1.19	**Zr** 3.61 -0.29	🟩 **Nb** -31.20 -13.50 -22.00	🟩 **Mo** -38.74 -15.20 -28.00	**Tc** 19.04 8.00 8.00	**Ru** 48.93 9.00 14.00	🟥 **Rh** 32.39 19.00 19.00	🟥 **Pd** 3.74 10.50 10.50	🟥 **Ag** 2.27 3.40 3.40	**Cd** 4.90	**In** 1.02 0.64 0.65	**Sn** 0.99 -1.11 0.25	**Sb** -8.96	**Te** -11.19	**I** -1.26
Cs 0.10 -0.50 -0.50	🟩 **Ba** -1.62 -1.80 -1.80		**Hf** 10.14 2.38 -4.14	🟩 **Ta** -23.75 -16.00 -26.50	🟩 **W** -45.03 -19.30 -33.00	**Re** 24.87 6.00 18.20	**Os** 70.92 14.50 30.50	🟥 **Ir** 59.39 32.00 32.00	🟥 **Pt** 7.85 15.00 15.00	🟥 **Au** 1.90 4.25 4.25	**Hg** -1.02	**Tl** -1.40 -0.09 0.07	**Pb** 4.06 2.40 2.40	**Bi** -4.53 1.40	**Po**	**At**
		La 12.22	**Ce** 22.40	**Pr** 11.55	**Nd** 11.99	**Pm** 12.55	**Sm** 12.88	**Eu** -1.61	**Gd** 13.11	**Tb** 12.97	**Dy** 12.73	**Ho** 12.36	**Er** 11.86	**Tm**	**Yb**	**Lu** 9.91
Fr	**Ra**	**Ac** 12.56	**Th** 13.95	**Pa** 17.09	**U** -10.36	**Np** -23.17	**Pu** 11.73	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

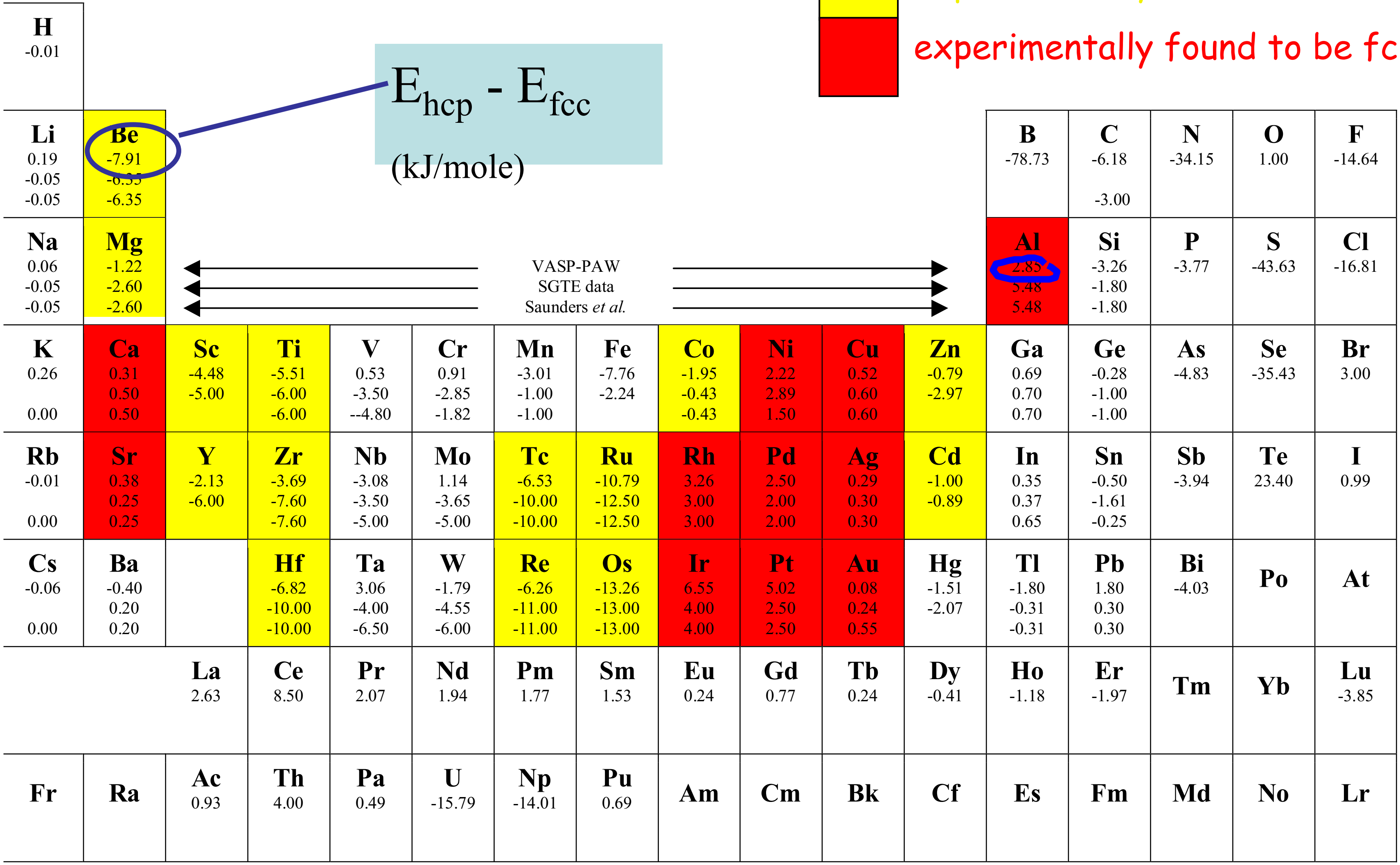
data taken from:

Y. Wang,[*a] S. Curtarolo, [et al.] *Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability*, Computer Coupling of Phase Diagrams and Thermochemistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90.

Elemental Crystal Structures: GGA pseudopotential method

🟨 experimentally found to be hcp

🟥 experimentally found to be fcc



$E_{hcp} - E_{fcc}$ (kJ/mole)

VASP-PAW
SGTE data
Saunders *et al.*

H -0.01																
Li 0.19 -0.05 -0.05	🟨 **Be** -7.91 -6.35 -6.35											**B** -78.73	**C** -6.18 -3.00	**N** -34.15	**O** 1.00	**F** -14.64
Na 0.06 -0.05 -0.05	🟨 **Mg** -1.22 -2.60 -2.60											🟥 **Al** 2.85 5.48 5.48	**Si** -3.26 -1.80 -1.80	**P** -3.77	**S** -43.63	**Cl** -16.81
K 0.26 0.00	🟥 **Ca** 0.31 0.50 0.50	🟨 **Sc** -4.48 -5.00	🟨 **Ti** -5.51 -6.00 -6.00	**V** 0.53 -3.50 --4.80	**Cr** 0.91 -2.85 -1.82	**Mn** -3.01 -1.00 -1.00	**Fe** -7.76 -2.24	🟨 **Co** -1.95 -0.43 -0.43	🟥 **Ni** 2.22 2.89 1.50	🟥 **Cu** 0.52 0.60 0.60	🟨 **Zn** -0.79 -2.97	**Ga** 0.69 0.70 0.70	**Ge** -0.28 -1.00 -1.00	**As** -4.83	**Se** -35.43	**Br** 3.00
Rb -0.01 0.00	🟥 **Sr** 0.38 0.25 0.25	🟨 **Y** -2.13 -6.00	🟨 **Zr** -3.69 -7.60 -7.60	**Nb** -3.08 -3.50 -5.00	**Mo** 1.14 -3.65 -5.00	🟨 **Tc** -6.53 -10.00 -10.00	🟨 **Ru** -10.79 -12.50 -12.50	🟥 **Rh** 3.26 3.00 3.00	🟥 **Pd** 2.50 2.00 2.00	🟥 **Ag** 0.29 0.30 0.30	🟨 **Cd** -1.00 -0.89	**In** 0.35 0.37 0.65	**Sn** -0.50 -1.61 -0.25	**Sb** -3.94	**Te** 23.40	**I** 0.99
Cs -0.06 0.00	**Ba** -0.40 0.20 0.20		🟨 **Hf** -6.82 -10.00 -10.00	**Ta** 3.06 -4.00 -6.50	**W** -1.79 -4.55 -6.00	🟨 **Re** -6.26 -11.00 -11.00	🟨 **Os** -13.26 -13.00 -13.00	🟥 **Ir** 6.55 4.00 4.00	🟥 **Pt** 5.02 2.50 2.50	🟥 **Au** 0.08 0.24 0.55	**Hg** -1.51 -2.07	**Tl** -1.80 -0.31 -0.31	**Pb** 1.80 0.30 0.30	**Bi** -4.03	**Po**	**At**
		La 2.63	**Ce** 8.50	**Pr** 2.07	**Nd** 1.94	**Pm** 1.77	**Sm** 1.53	**Eu** 0.24	**Gd** 0.77	**Tb** 0.24	**Dy** -0.41	**Ho** -1.18	**Er** -1.97	**Tm**	**Yb**	**Lu** -3.85
Fr	**Ra**	**Ac** 0.93	**Th** 4.00	**Pa** 0.49	**U** -15.79	**Np** -14.01	**Pu** 0.69	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

data taken from:

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Summary: Comparing Energy of Structures

For most elements, both LDA and GGA predict the correct structure for a material (as far as we know)

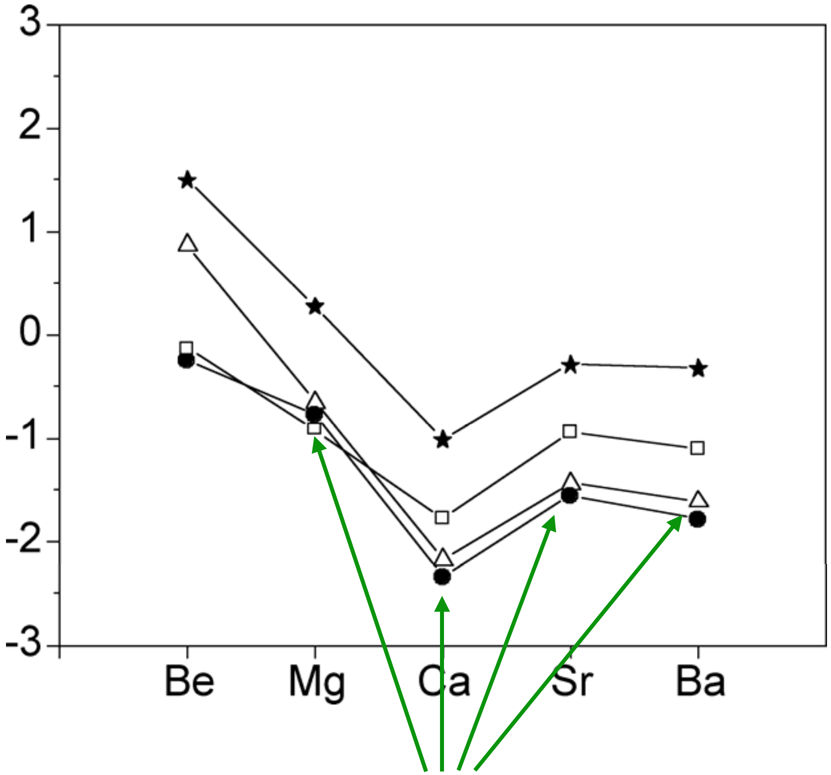
Notable exceptions: Fe in LDA; materials with substantial electron correlation effects (e.g. Pu)

High Throughput studies are now possible.

Metal Hydrides

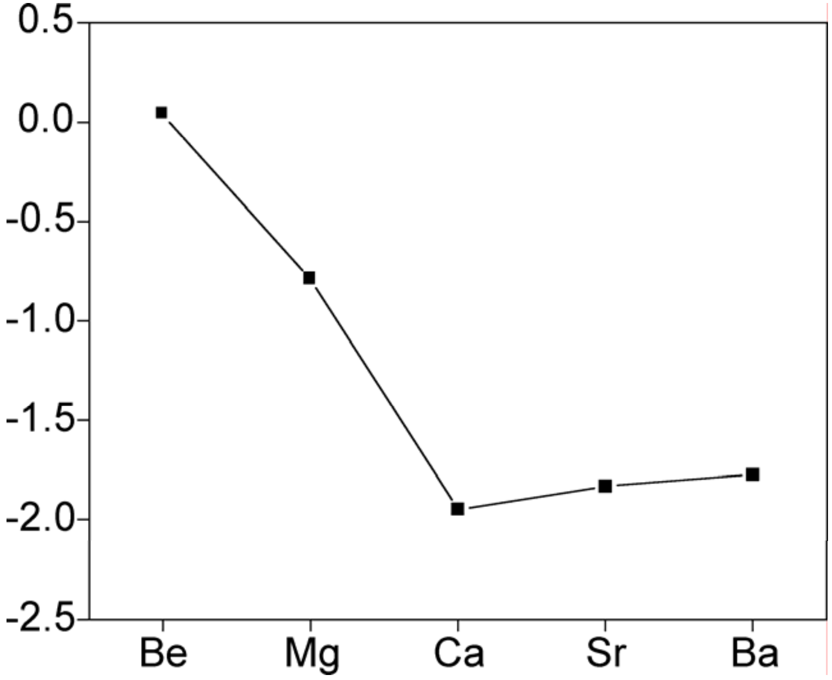
Hydride formation energy: $M + H_2 \rightarrow MH_2$

LDA Calculation



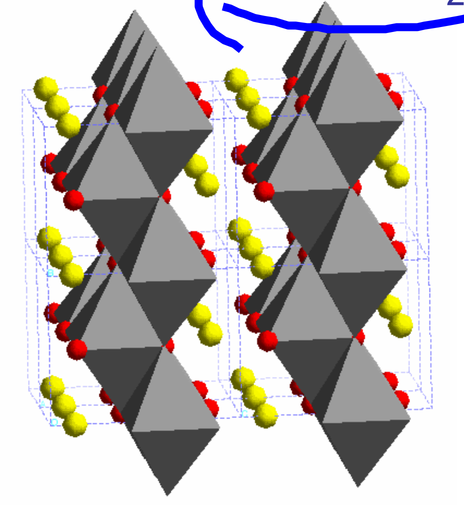
Correct structure !

Experiment

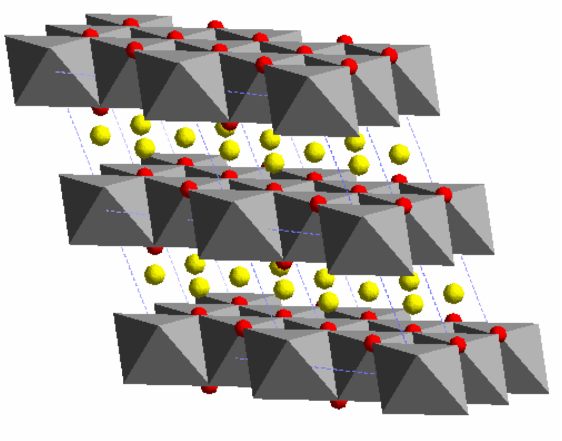


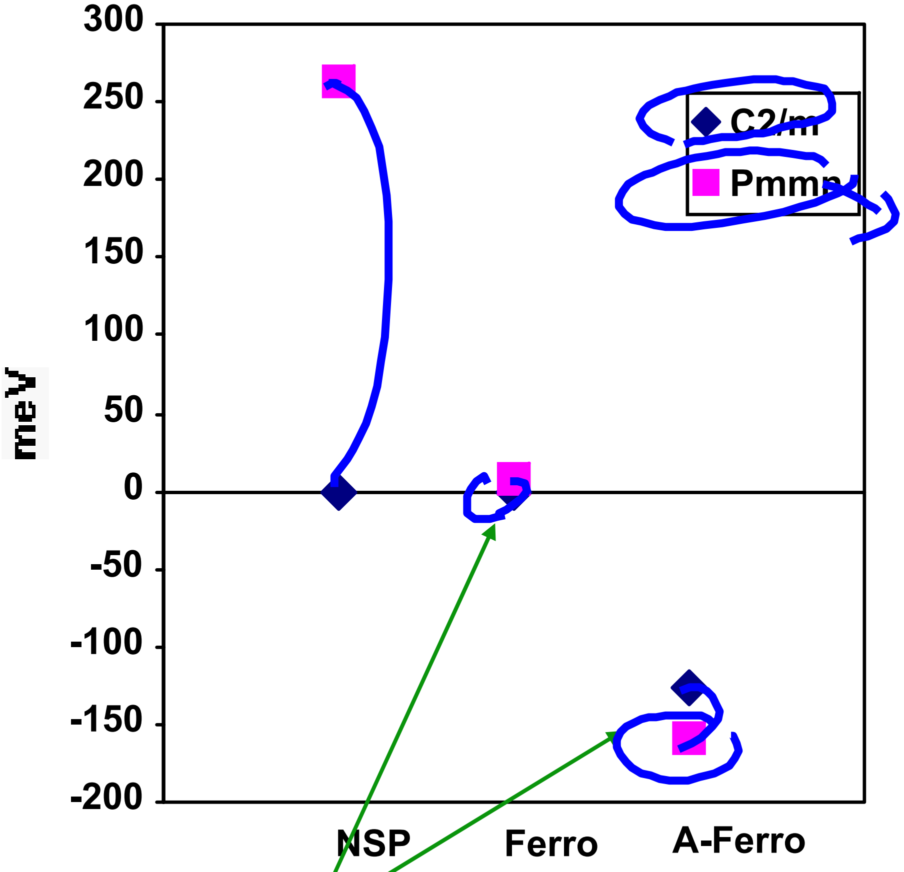
Spin Polarization can be Important (in particular for transition metal compounds

Pmmn: structure of $LiMnO_2$



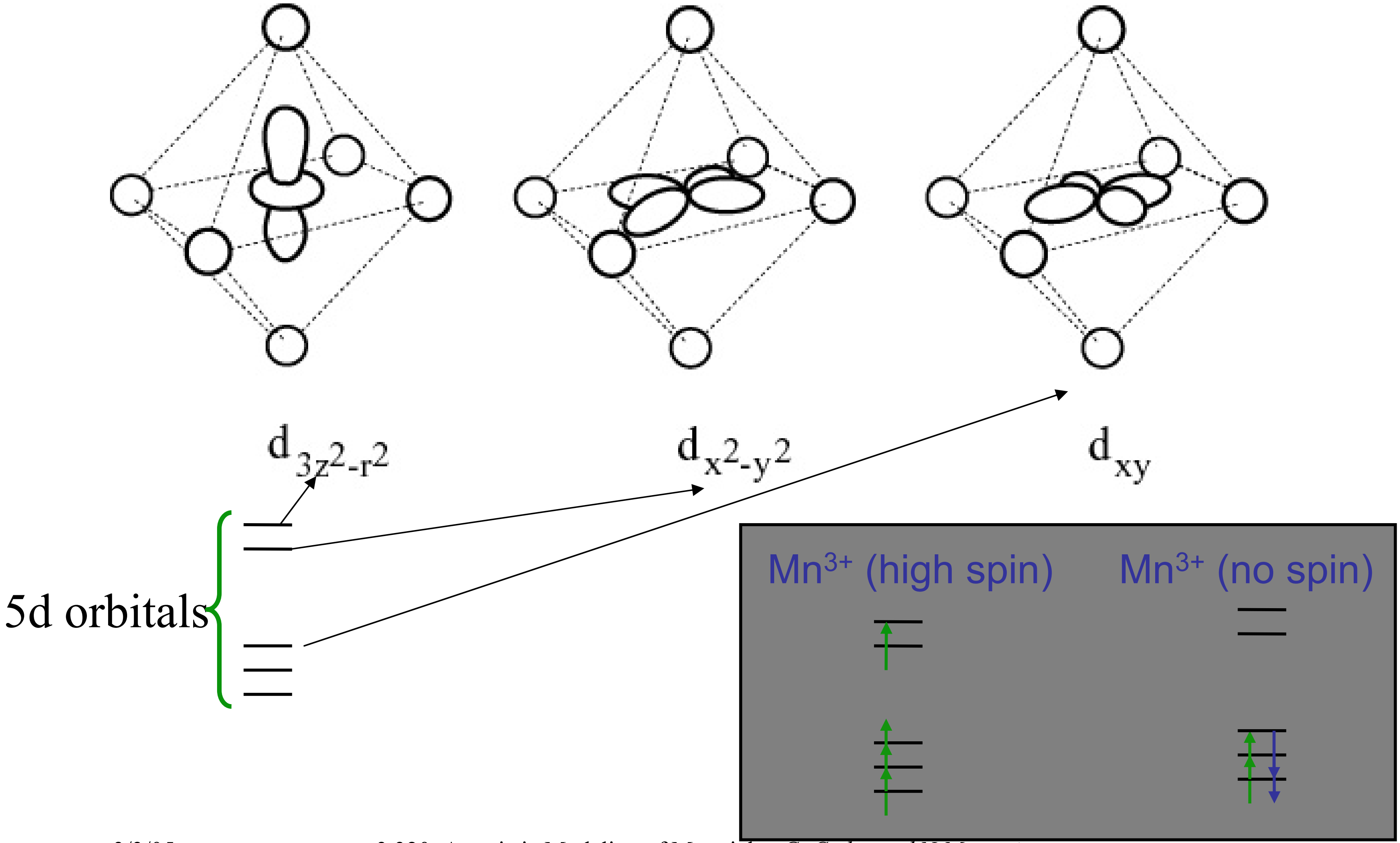
C2/m: other common structure





Spin polarized calculations

Orbital filling depends on spin polarization



Reaction Energies

Reaction	**Exp (eV)**	**LDA (eV)**	Δ
Li (bcc) + Al (fcc) -> LiAl (compound)	-0.2457	-0.2234	9.08%
0.5 Cu(fcc) + 0.5 Au(fcc) -> CuAu	-0.053	-0.0193	63.58%
Li(bcc) + CoO2 -> LiCoO2	-4.25	-3.75	11.76%

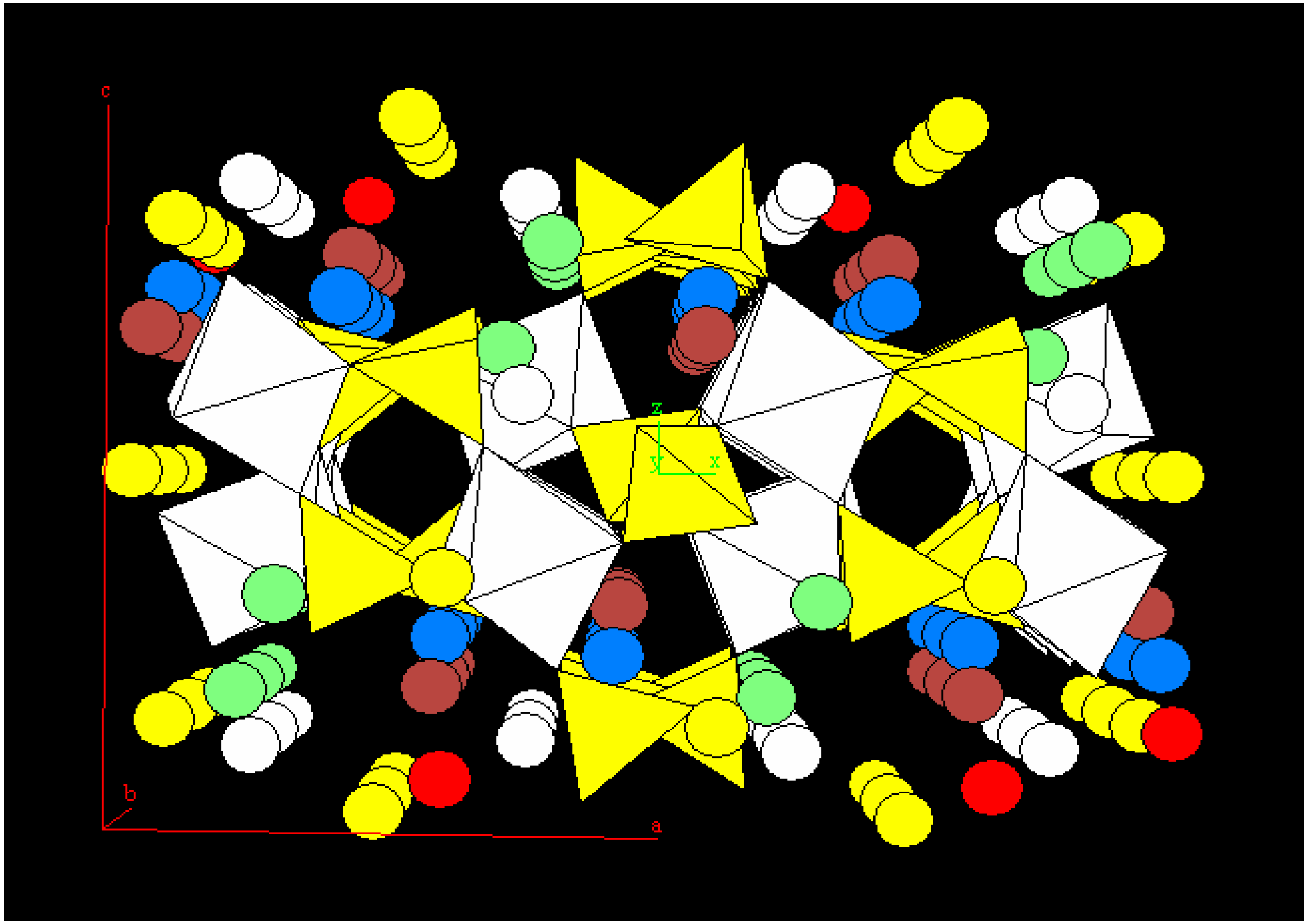
Redox Reactions can be more Problematic

Fe^{3+} $2+$

	GGA	Exp
$FePO_4 + Li \rightarrow LiFePO_4$	2.8 eV	3.5 eV
$MnO_2 + Li \rightarrow LiMn_2O_4$	3.6 eV	4.1 eV
$V_2(PO_4)_3 + Li \rightarrow LiV_2(PO_4)_3$	3.3 eV	4.6 eV

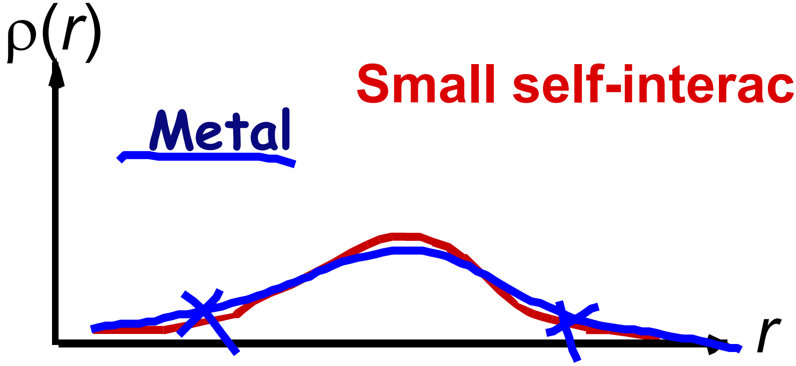
All these reactions involve the transfer of an electron from a delocalized state in Li metal to a localized state in the transition metal oxide (phosphate)

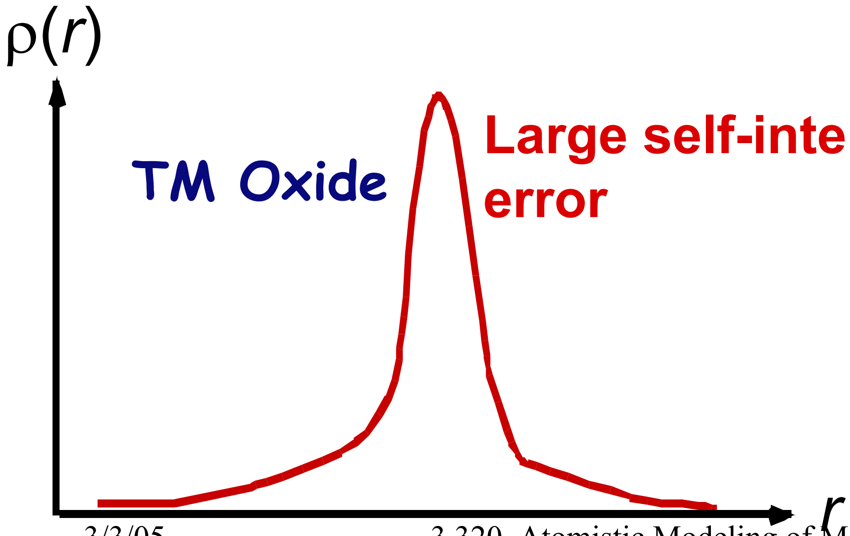
Structure of $LiV_2(PO_4)_3$



In standard DFT an electron interacts with the effective potential generated by all the electrons (including itself)

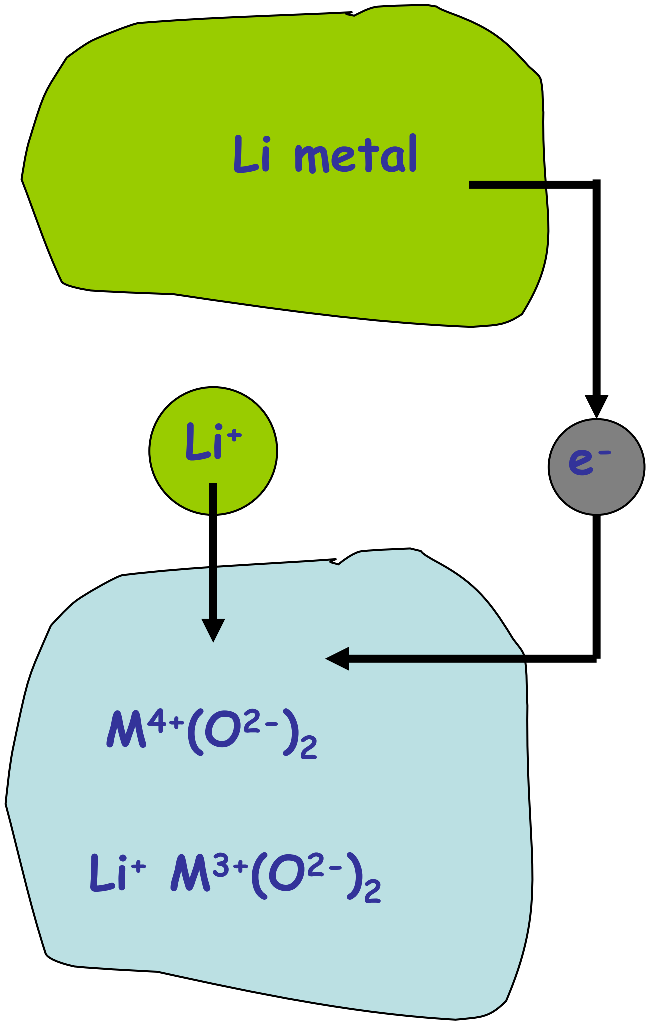
$$H = \sum_i H_i = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \sum_{i=1}^{N_e} V_{effective}(r_i)$$

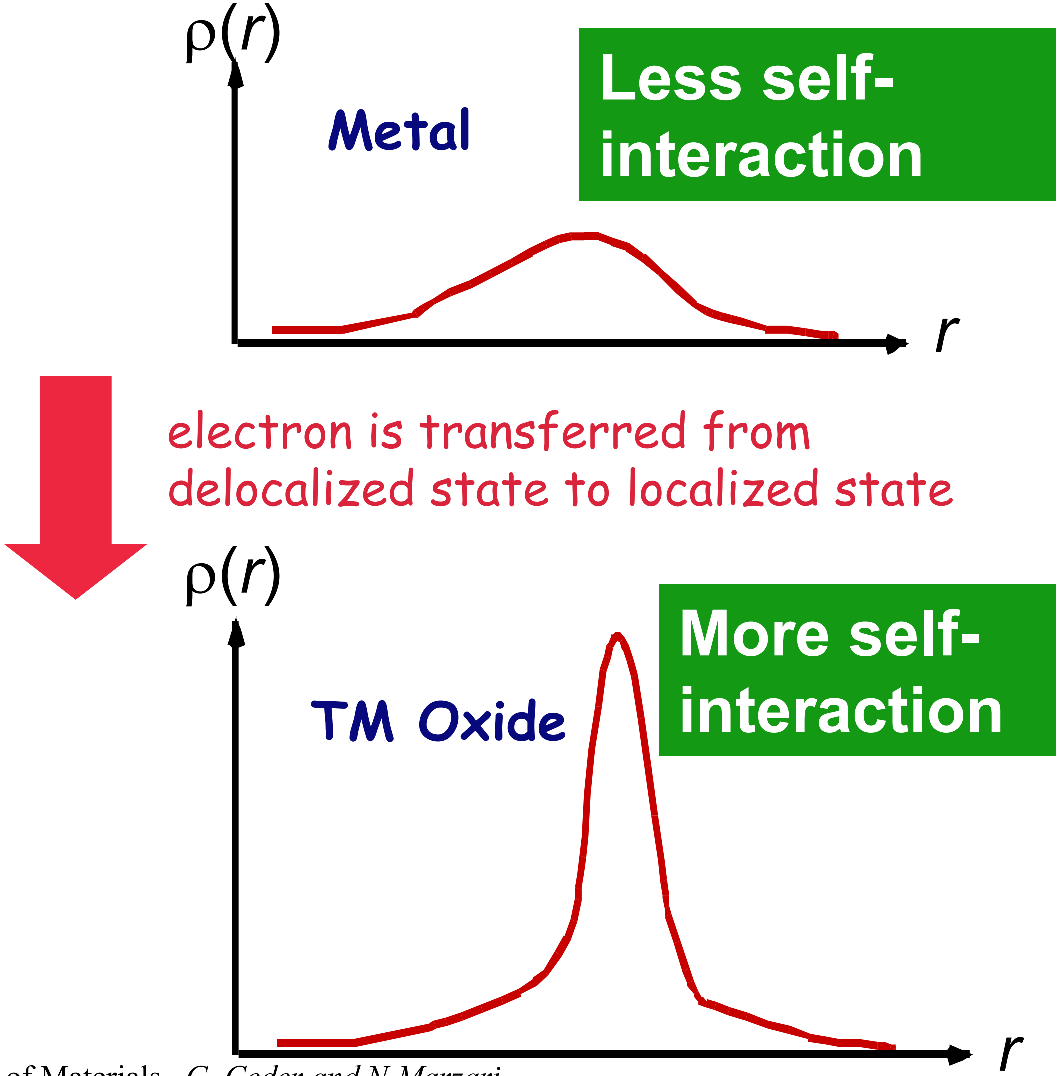




Self interaction in DFT is key problem in transition metal oxides

Li insertion into cathode transfers electron from a delocalized to a localized state





Less self-interaction

electron is transferred from delocalized state to localized state

More self-interaction

Summary (LDA)

Lattice constants: 1-3% too small

Cohesive Energies: 5-20% too strongly bound

Bulk Modulus: 5-20% (largest errors for late TM)

Bandgaps: too small

GGA gives better cohesive energies. Effect on lattice parameters is more random. GGA important for magnetic systems.