Electronic Structure of Correlated Materials: LDA+U, DMFT, and Others

Purpose:

Understanding the limitation of standard local approximations to describe the correlated electron systems

Understanding the basic idea of LDA+U and related methods

Suggested Reading:

R. G. Parr and W. Yang, "Density functional theory of atoms and molecules (OUP 1989)"

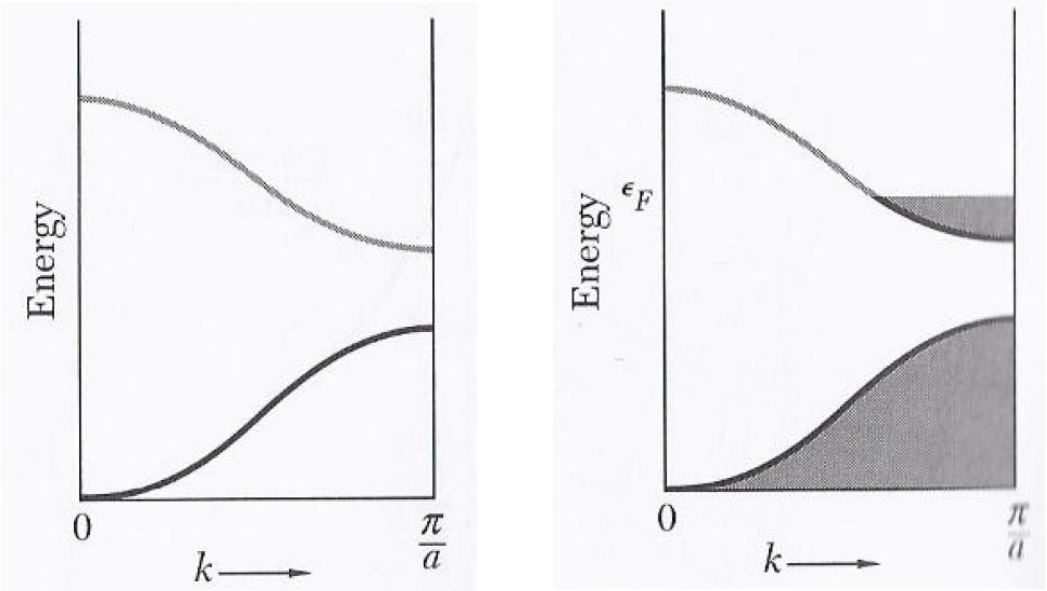
R. M. Martin, "Electronic structure: Basic theory and practical methods (CUP 2004)"

V. I. Anisimov et al., "Strong Coulomb correlations in electronic structure calculations: Beyond the local density approximation (Gordon & Breach 2000)"

Myung Joon Han (KAIST-Physics, mj.han@kaist.ac.kr)

Very Basic of Band Theory

Insulator **Metal**

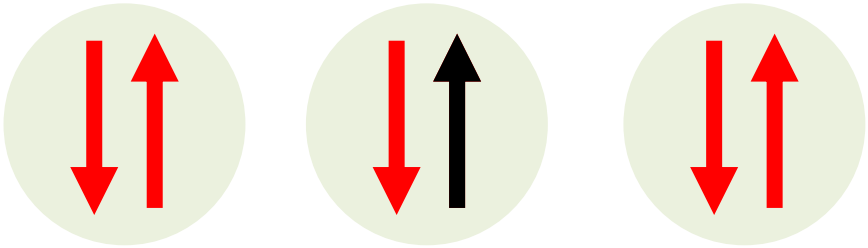


Kittel, Introduction to Solid State Physics

✓ **A material with partially-filled band(s) should be a metal**

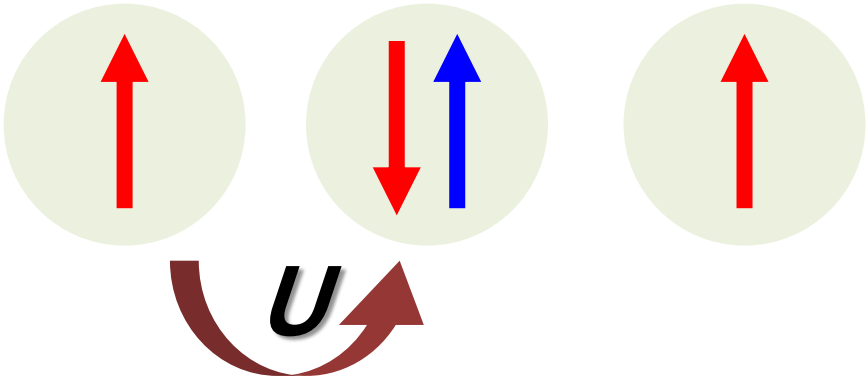
Insulator: Pauli and Mott

Pauli exclusion: band insulator



W. E. Pauli

Coulomb repulsion: Mott (-Hubbard) insulator

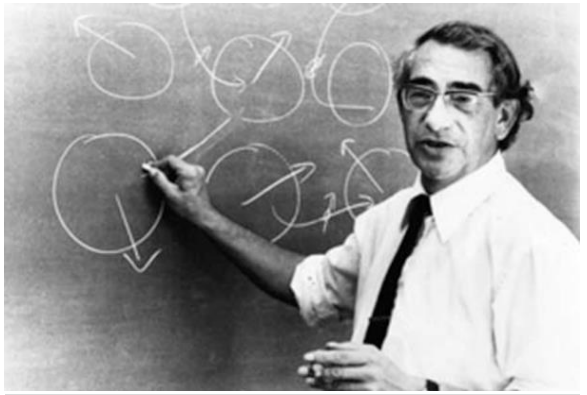


N. F. Mott
Proc. Phys. Soc. London (1949)

Localized Orbital and Hubbard Model

Hubbard Model (1964)

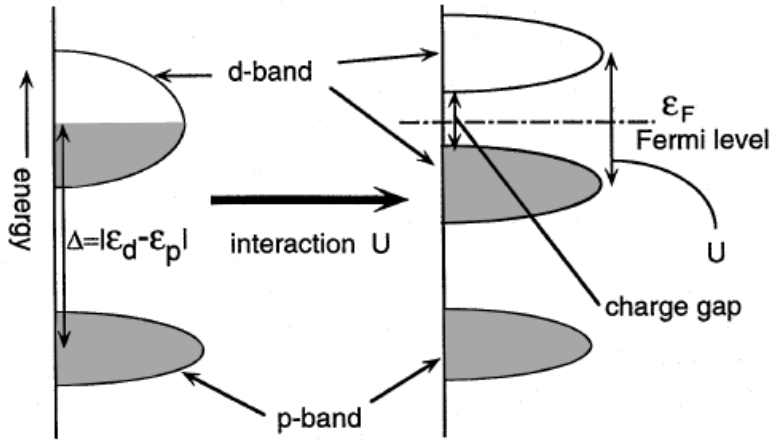
$$H = -\sum_{i,j,\sigma} t_{ij}(c^{\dagger}_{i\sigma}c_{j\sigma} + \text{H.c.}) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$



http://theor.jinr.ru/~kuzemsky/jhbio.html

'Hopping' term between the sites

On-site Coulomb repulsion in the correlated orbitals



Additional electron occupation requires the energy cost :

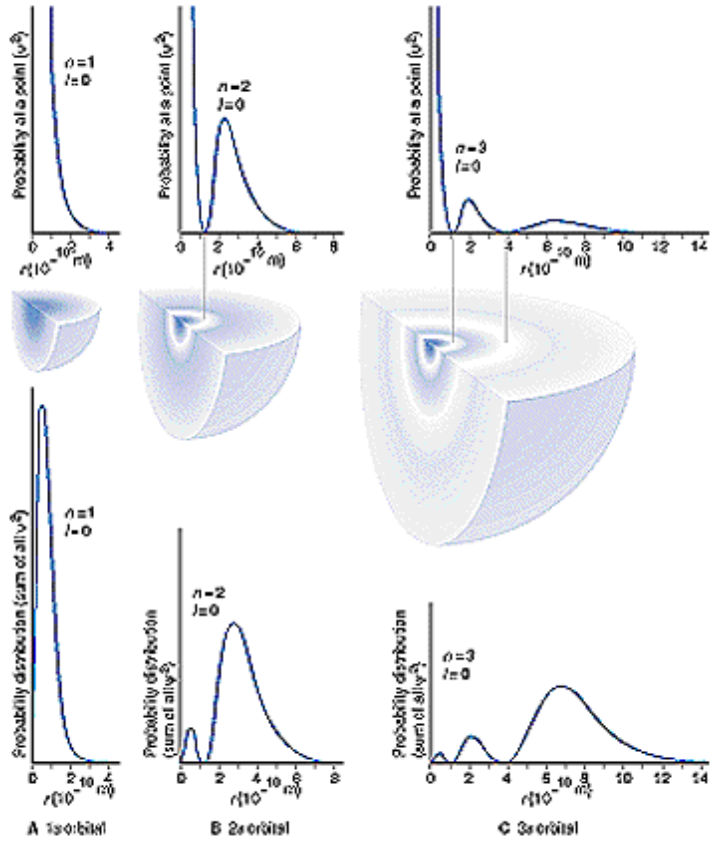
$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^{n})$$

Imada, Fujimori, Tokura, Rev. Mod. Phys. (1998)

Actually Happening Quite Often

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine	xenon
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ✶	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 [209]	
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ✶ ✶	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]			

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]



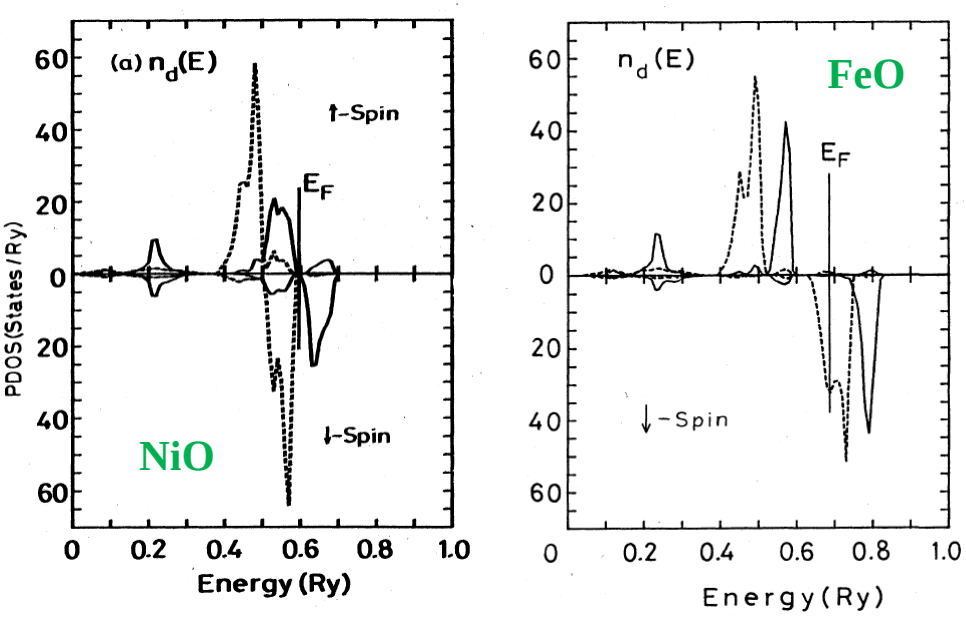
Localized valence wavefunctions

Partially filled 3d, 4f, 5f orbitals

→ magnetism and others

Applying LDA to Mott Insulators

Oguchi et al., PRB (1983)
Terakura et al., PRB (1984)



- ✓ Too small or zero band gap
- ✓ Magnetic moment underestimated
- ✓ Too large exchange coupling (Tc)

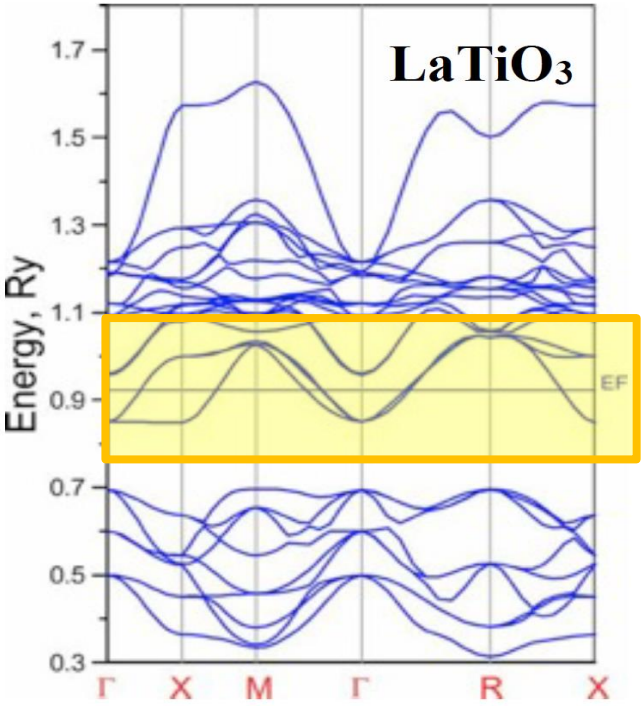


TABLE III. Experimental and theoretical exchange parameters (in K) of the first and the second neighbors.

MnO		MnS		NiO		
J_1	J_2	J_1	J_2	J_1	J_2	Reference
−14.4	−7.0	−8.0	−9.0	−50	−85	22
−9.0	−10.4					25
				16	−222	26
−10.0	−11.0					23
−28	−28					24
−30.3	−29.8	−10	−27	61	−1230	present paper

Combining LDA with Hubbard Model

PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

Band theory and Mott insulators: Hubbard U instead of Stoner I

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(Received 4 September 1990; revised manuscript received 5 March 1991)

We propose a form for the exchange-correlation potential in local-density band theory, appropriate for Mott insulators. The idea is to use the "constrained-local-density-approximation" Hubbard parameter U as the quantity relating the single-particle potentials to the magnetic- (and orbital-) order parameters. Our energy functional is that of the local-density approximation plus the mean-field approximation to the remaining part of the U term. We argue that such a method should make sense, if one accepts the Hubbard model and the success of constrained-local-density-approximation parameter calculations. Using this *ab initio* scheme, we find that all late-3d-transition-metal monoxides, as well as the parent compounds of the high-T_c compounds, are large-gap magnetic insulators of the charge-transfer type. Further, the method predicts that $LiNiO_2$ is a low-spin ferromagnet and NiS a local-moment p-type metal. The present version of the scheme fails for the early-3d-transition-metal monoxides and for the late 3d transition metals.

Basic idea: Introduce Hubbard-like term into the energy functional (and subtract the equivalent LDA term to avoid the double counting)

$$E_{LDA+U} = E_{LDA} + E_U - E_{dc} \qquad \text{where } E_U = \frac{1}{2}\sum_{ilm\sigma} U n^{\sigma}_{ilm} n^{\sigma'}_{ilm'}$$

LDA+U Functional

The original functional form (Anisimov et al. 1991)

$$E = E^{\mathrm{LDA}} + \tfrac{1}{2} \sum_{m,m',\sigma} U(n_{im\sigma} - n^0)(n_{im'-\sigma} - n^0) + \tfrac{1}{2} \sum_{\substack{m,m',\sigma \\ (m \neq m')}} (U - J)(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0) \, .$$

i : site index (orbitals)

$\mathbf{n^0}$: average d-orbital occupation (no double counting correction)

J: Hund coupling constant

Orbital-dependent potential

$$V_{m\sigma} = U \sum_{m'} (n_{m'-\sigma} - n^0) + (U - J) \sum_{m'(\neq m)} (n_{m'\sigma} - n^0) + V^{\mathrm{LDA}}$$

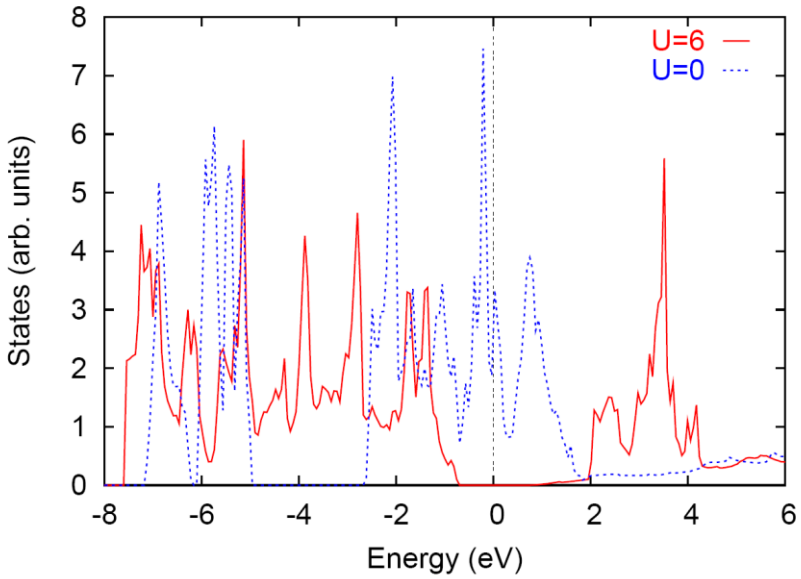
LDA+U Result

TABLE I. Calculated band gaps of MnO, FeO, CoO, and NiO as a function of $\bar{U}$ values. Here we use the dual representation for the description of the on-site density matrix.

$\bar{U}$ (eV)	MnO	FeO	CoO	NiO
0	0.04	0.00	0.00	0.36
2	1.68	0.76	1.20	1.56
4	2.12	1.96	2.20	2.53
6	4.21	2.77	3.01	3.89
Calc. (LSDA)	0.8[a]	0.0[a]	0.0[a]	0.2[a]
Calc. (LDA+U)	3.5[b]	3.2[c]	3.2[d]	3.1[e]
Expt.	3.6-3.8[f]	2.4[g]	2.4[h]	4.0[i], 4.3[j]

Wurtzite-structured CoO :

MJH and Yu, JKPS (2006); JACS (2006)



	Mulliken			Voronoi			
$\bar{U}$ (eV)	Full	Dual	On-site	Full	Dual	On-site	Other group results
0	1.30	1.30	1.30	1.28	1.28	1.28	1.0 ($\bar{U}$=0.0)[a]
2	1.48	1.54	1.59	1.46	1.51	1.55	
4	1.59	1.66	1.71	1.55	1.61	1.66	
6	1.66	1.74	1.79	1.62	1.69	1.72	1.59 ($\bar{U}$=6.9)[b]
Expt.							1.77[c], 1.64[d], 1.90[e]

MJH, Ozaki and Yu PRB (2006)

Further Issues

- ✓ **Rotational invariance and several different functional forms**

$$E^{U}[\{n\}] = \tfrac{1}{2}\sum_{\{m\},\sigma} \{\langle m,m''|V_{ee}|m',m'''\rangle n^{\sigma}_{mm'} n^{-\sigma}_{m''m'''} + (\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle) n^{\sigma}_{mm'} n^{\sigma}_{m''m'''}\},$$

$$E_{\mathrm{dc}}[\{n^{\sigma}\}] = \tfrac{1}{2}Un(n-1) - \tfrac{1}{2}J[n^{\uparrow}(n^{\uparrow}-1) + n^{\downarrow}(n^{\downarrow}-1)]$$

(So-called) fully localized limit:
Liechtenstein et al. PRB (1995)

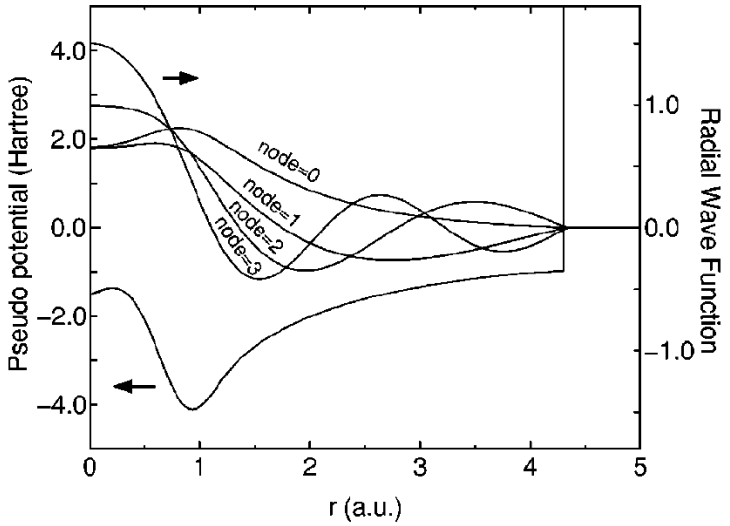
(So-called) around the mean field limit:
Czyzyk et al. PRB (1994)

$$E^{\mathrm{LSDA+AMF}} = E^{\mathrm{LSDA}} + \frac{1}{2}\sum_{m,m',\sigma} U_{mm'}(n_{m\sigma} - n^{0}_{\sigma}) \times (n_{m'-\sigma} - n^{0}_{-\sigma}) + \frac{1}{2}\sum_{m,m',m\neq m',\sigma} (U_{mm'} - J_{mm'})(n_{m\sigma} - n^{0}_{\sigma}) \times (n_{m'\sigma} - n^{0}_{\sigma})\,. \qquad (3)$$

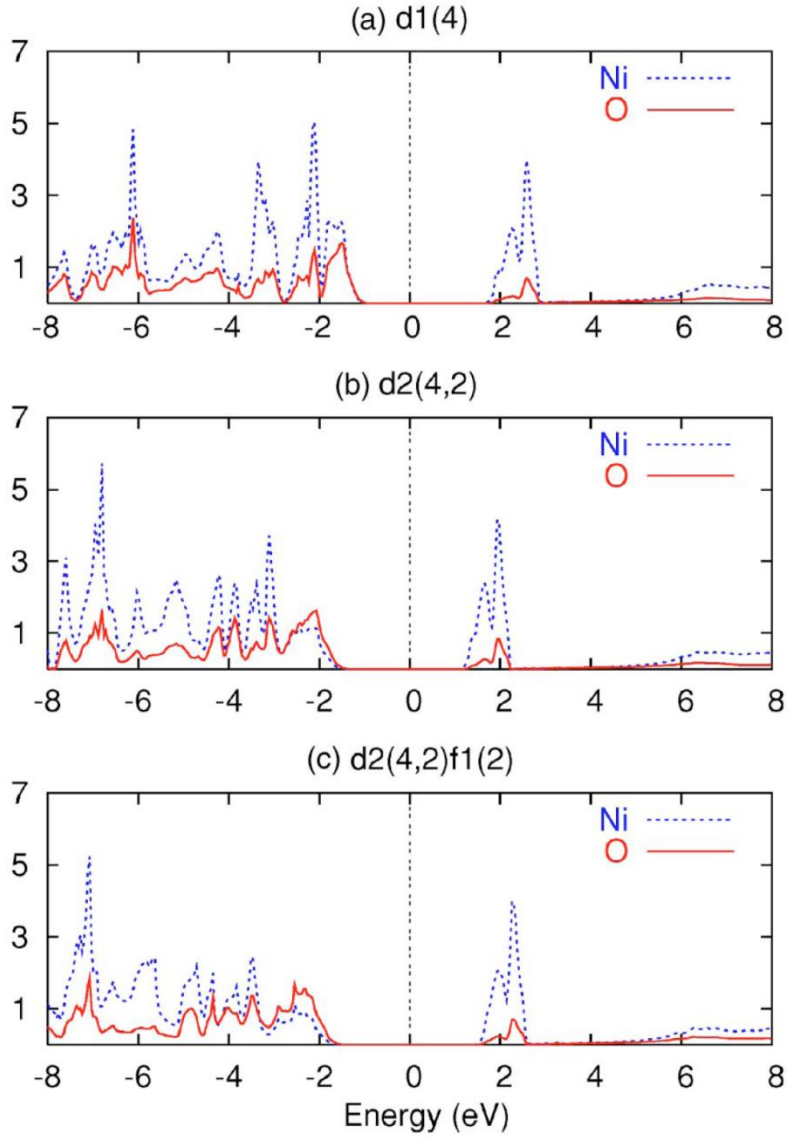
LDA+U based on LCPAO (1)

- ✓ **Numerically generated (pseudo-) atomic orbital basis set:**

  Non-orthogonal multiple d-/f-orbitals with arbitrarily-chosen cutoff radii



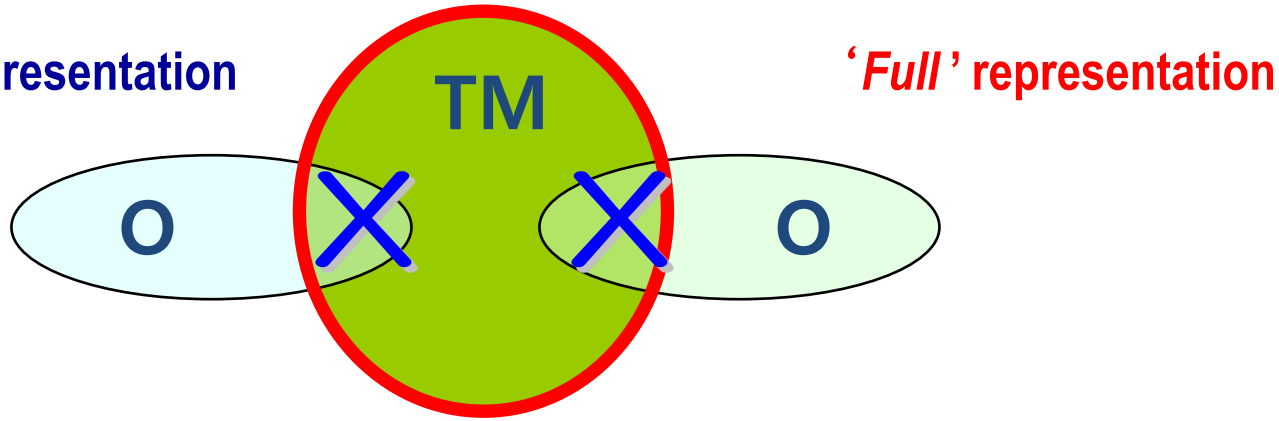
T. Ozaki, Phys. Rev. B (2003)
MJH, Ozaki, Yu, Phys. Rev. B (2006)



LDA+U based on LCPAO (2)

✓ **Non-orthogonality and no guarantee for the sum rule**

See, for example, Pickett et al., (1998)



Proposed '*dual*' representation:

$$\hat{\rho}^{\sigma}_{smm'} = \frac{1}{2}(|s\tilde{m}\sigma\rangle\langle sm'\sigma| + |sm\sigma\rangle\langle s\tilde{m}'\sigma|)$$

Sum rule satisfied:

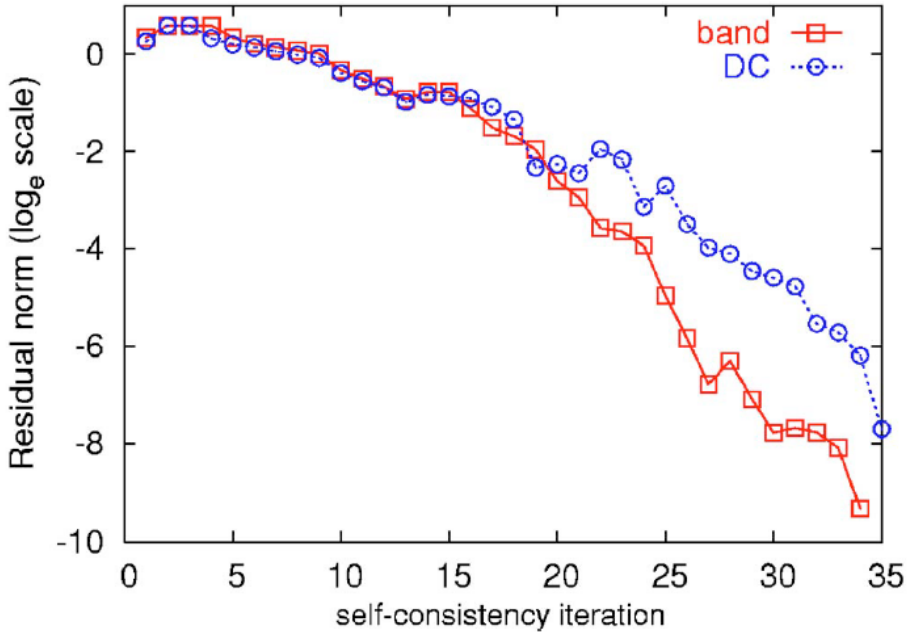
$$\sum_{\sigma} Tr(n^{\sigma}) = \sum_{\sigma} \frac{1}{2}[Tr(S\rho^{\sigma}) + Tr(\rho^{\sigma}S)] = N_{ele}$$

where n^{σ} is the density matrix.

LDA+U based on LCPAO (3)

- ✓ **LMTO: Anisimov et al. Phys. Rev. B (1991)**
- ✓ **FLAPW: Shick et al. Phys. Rev. B (1999)**
- ✓ **PAW: Bengone et al. Phys. Rev. B (2000)**
- ✓ **PP-PW: Sawada et al., (1997); Cococcioni et al., (2005)**

- ✓ **LCPAO and O(N) LDA+U: Large-scale correlated electron systems**



MJH, Ozaki, Yu,
Phys. Rev. B (2006)

Limitations

- ✓ **How to determine the U and J values?**

  No fully satisfactory way to determine the key parameters

- ✓ **How to define the double-counting energy functional?**

  Rotationally invariant versions, fully-local form, around the mean-field form, etc

  See, Anisimov et al. (1991); Czyzyk and Sawatzky (1994); Dudarev et al. (1998)

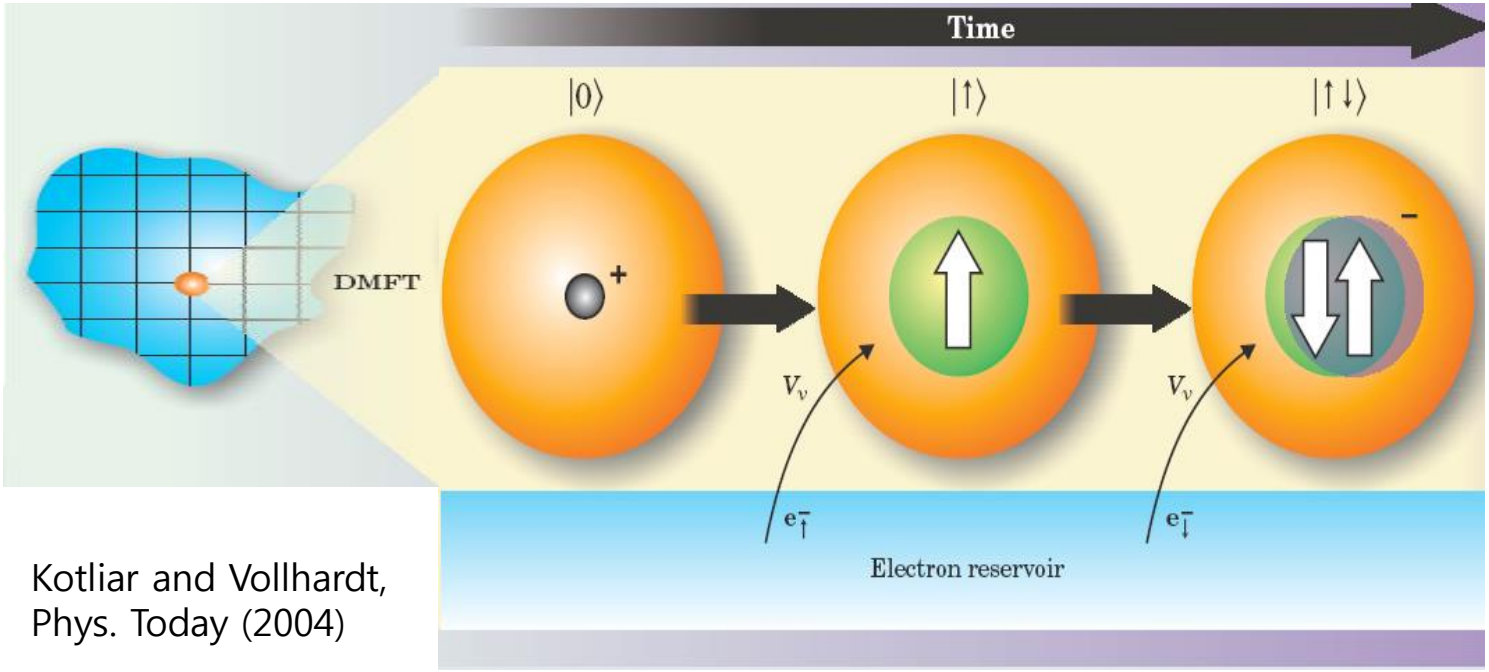
- ✓ **It is a static Hartree-Fock method**

  The correlation effect beyond this static limit cannot be captured

  → **Dynamical mean-field theory**

Dynamical Correlation and DMFT

✓ **Dynamical mean-field theory**



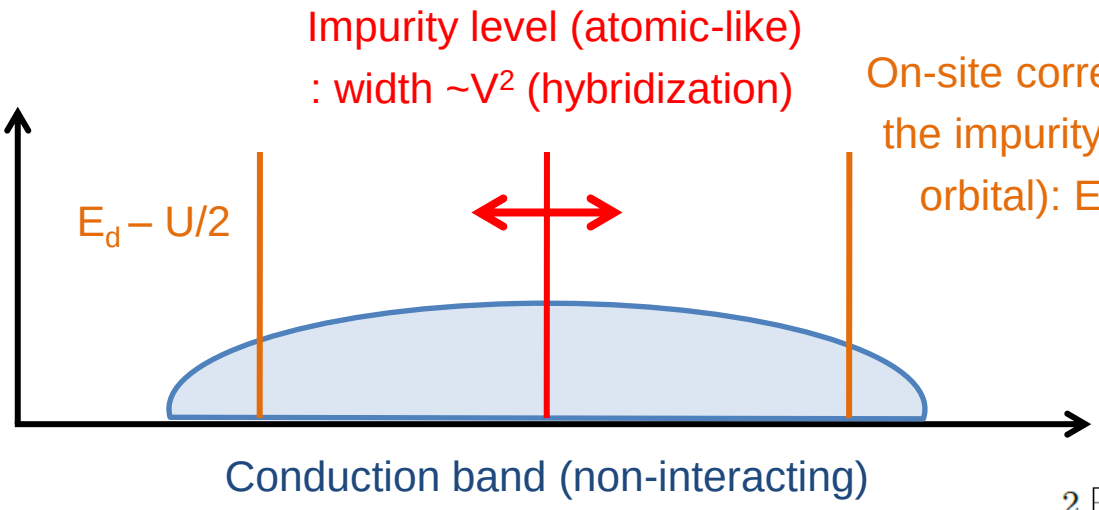
Kotliar and Vollhardt, Phys. Today (2004)

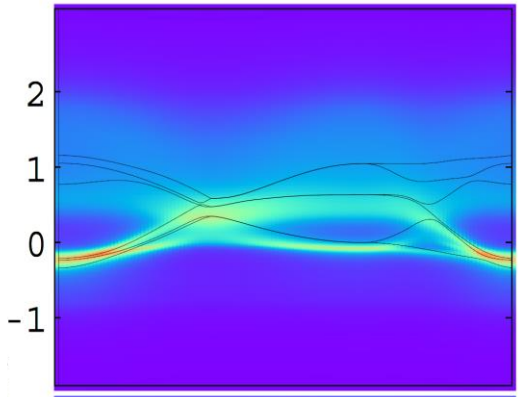
Mapping '**Hubbard Hamilnoian**' into '**Anderson Impurity Hamiltonian**' plus '**self-consistent equation**'

Georges and Kotliar Phys. Rev. B (1992)

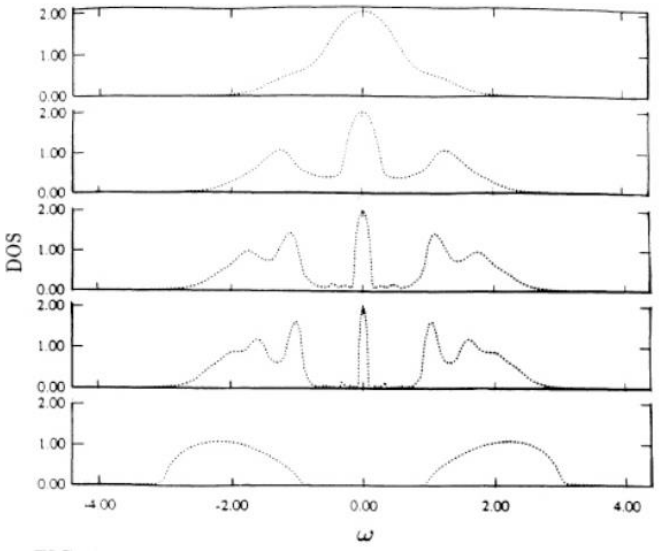
Georges et al., Rev. Mod. Phys.(1996); Kotliar et al., Rev. Mod. Phys.(2006);

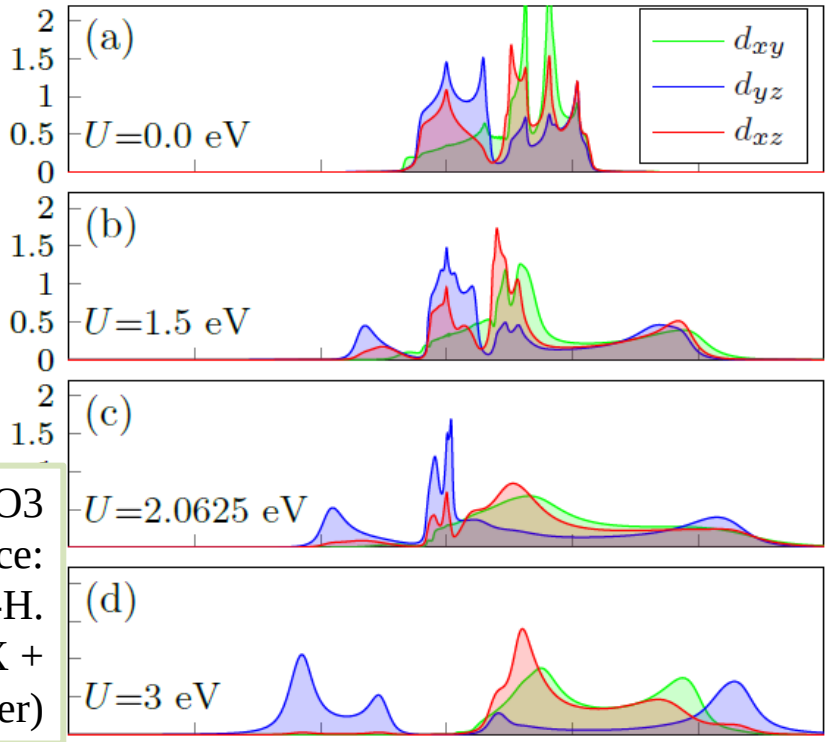
DMFT Result





Zhang et al., PRL (1993)





LaTiO3/LaAlO3 superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)

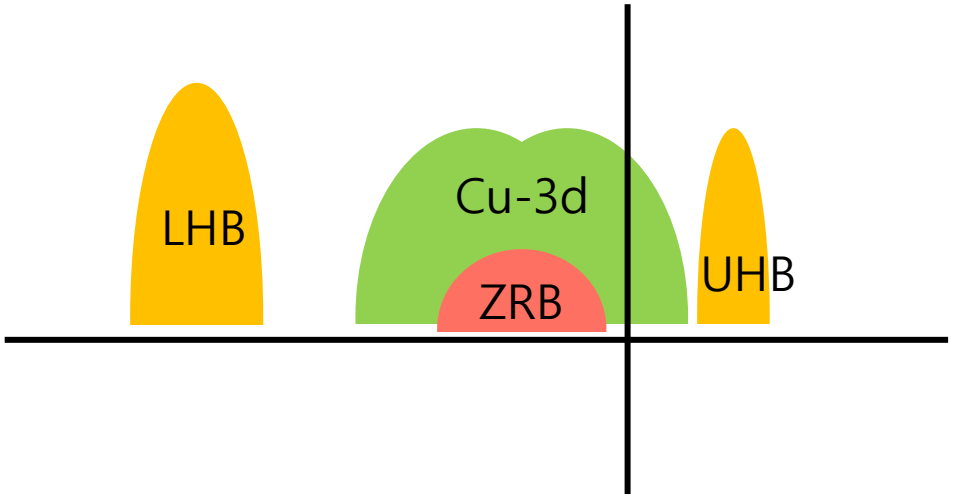
Comparison

LDA
No on-site correlation
(homogeneous electron gas)

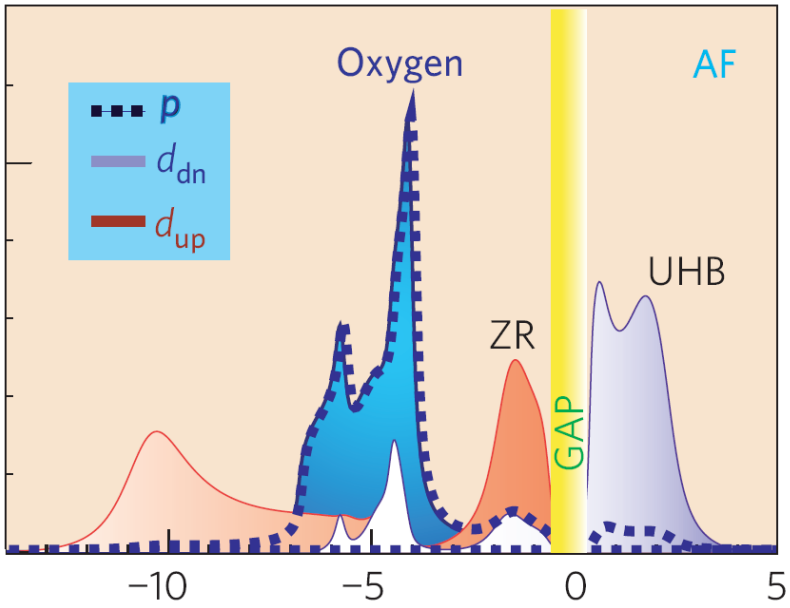
LDA+U
Hubbard-U correlation
Static approximation

LDA+DMFT
Hubbard-U correlation
Dynamic correlation

Application to high-T_c cuprate



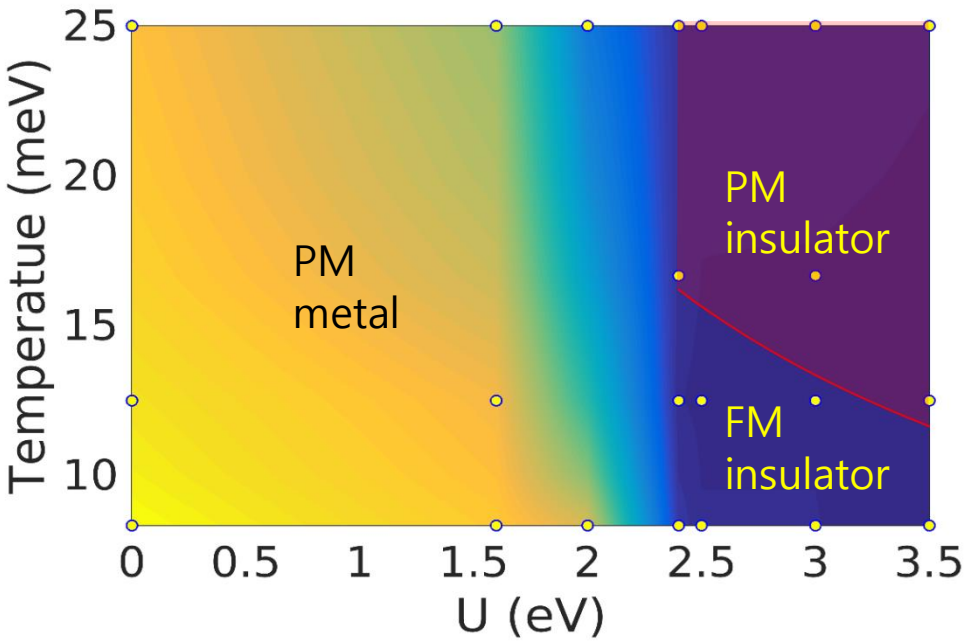
Weber et al., Nature Phys. (2010)

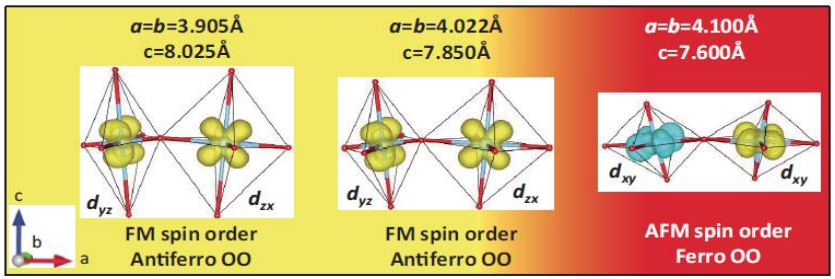


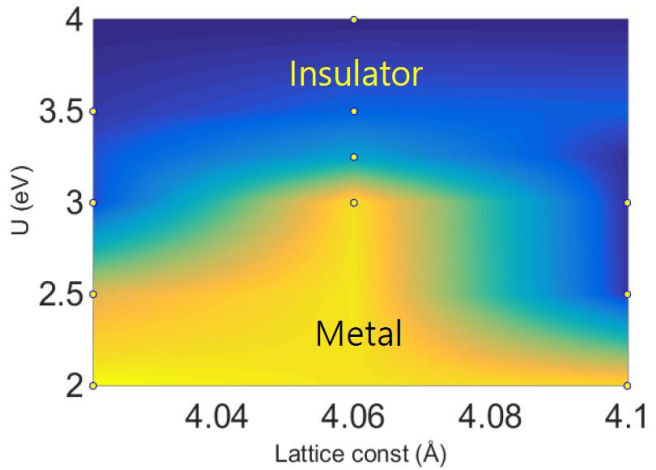
LDA+U and DMFT

- ✓ **LDA+U is static (Hartree) approximation of DMFT →**
- ✓ **Temperature dependency**
- ✓ **Electronic property near the phase boundary**
- ✓ **Paramagnetic insulating and correlated metallic phase**

LaTiO3/LaAlO3 superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)







Other Methods

- ✓ **Hybrid functionals, self-interaction correction, etc**
  - Inclusion of atomic nature can always be helpful
  - ‘Controllability’ versus ‘parameter-free’-ness
  - Hidden parameters (or factors)
  - Computation cost (→ relaxation etc)

- ✓ **(Self-consistent) GW**
  - Parameter-free way to include the well-defined self energy
  - No way to calculate total energy, force,…etc
  - Fermi liquid limit

Tran and Blaha, PRL (2009)