ISS-2018 Summer School (Kashiwa, 07/04/2018)

First-principles description of correlated electron materials: LDA+U and beyond

Purpose:

- ✓ *Understanding the limitation of standard local approximations to describe correlated electron systems*
- ✓ *Understanding the basic idea of LDA+U and other related methods*
- ✓ *Understanding recent progress on LDA+U functionals*

Myung Joon Han (KAIST, Physics)

PART 1

Contents:

- ✓ *Failure of LDA and similar approximations to describe correlated electron physics*
- ✓ *Basics of LDA+U : Idea, technical and physical issues…*
- ✓ *DMFT (dynamical mean field theory) and others*

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)"

Georges et al., "dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions" Rev. Mod. Phys. (1996)

Kotliar et al., "Electronic structure calculations with dynamical mean-field theory" Rev. Mod. Phys. (2006)

Local Density Approximation

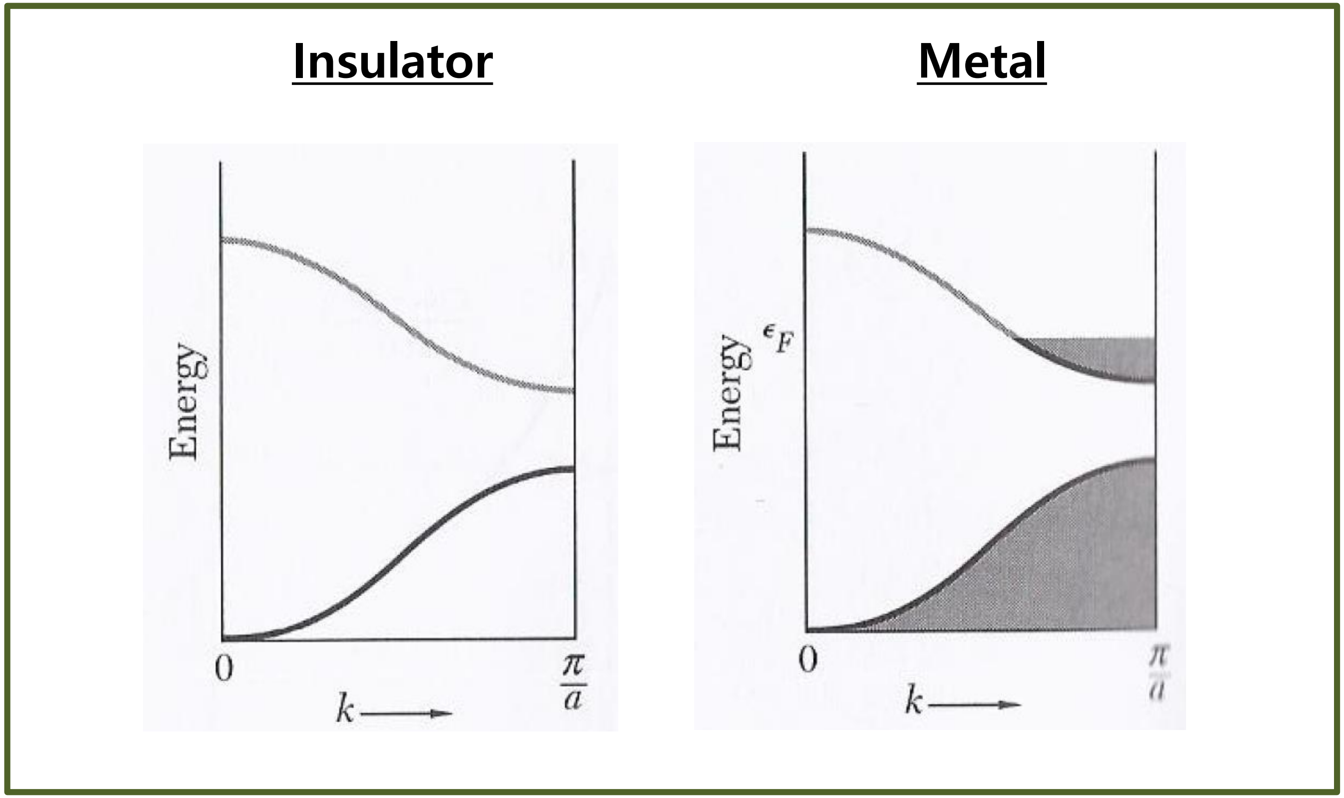
- ✓ ‘Local’ approximation based on the solution of ‘homogeneous’ electron gas

- ✓ Get in trouble whenever these approximations become invalidated: For examples,

  (Weak) van der Waals interaction originating from the fluctuating dipole moments

  (Strong) On-site Coulomb repulsion which is originated from the atomic nature of localized d- or f- electrons in solids

Very Basic of Band Theory

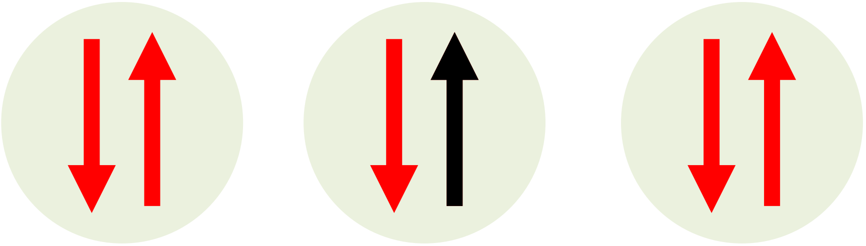


Kittel, Introduction to Solid State Physics

A material with partially-filled band(s) should be metallic

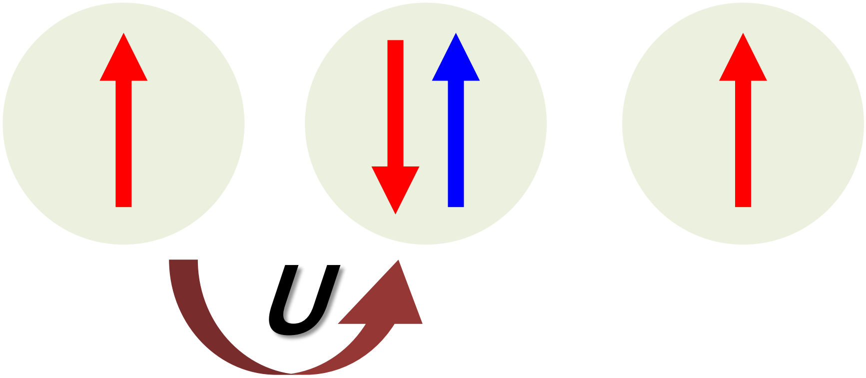
Insulator: Pauli and Mott

Pauli exclusion: band insulator



W. E. Pauli

Coulomb repulsion: Mott (-Hubbard) insulator



N. F. Mott

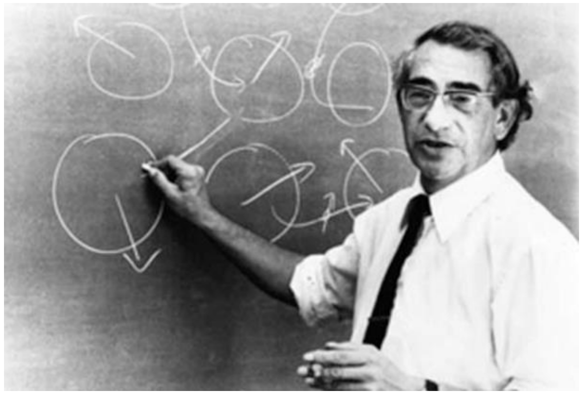
Localized Orbital and Hubbard Model

Hubbard Model (1964)

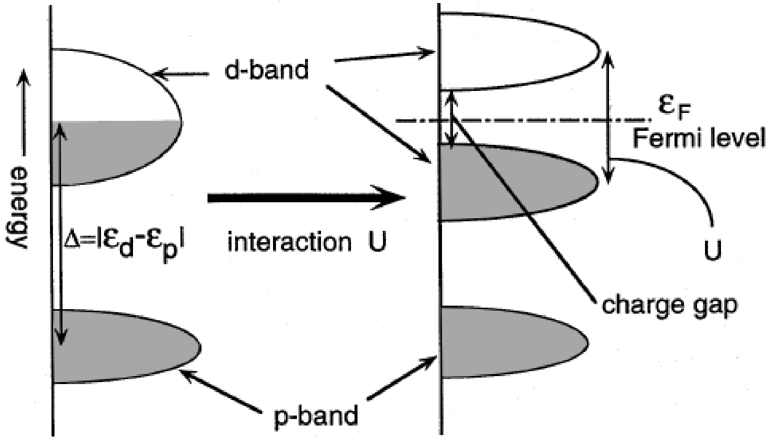
$$H = -\sum_{i,j,\sigma} t_{ij}(c^{\dagger}_{i\sigma} c_{j\sigma} + \text{H.c.}) + U\sum_{i} n_{i\uparrow} n_{i\downarrow}$$

‘Hopping’ term between the sites

On-site Coulomb repulsion in the correlated orbitals



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

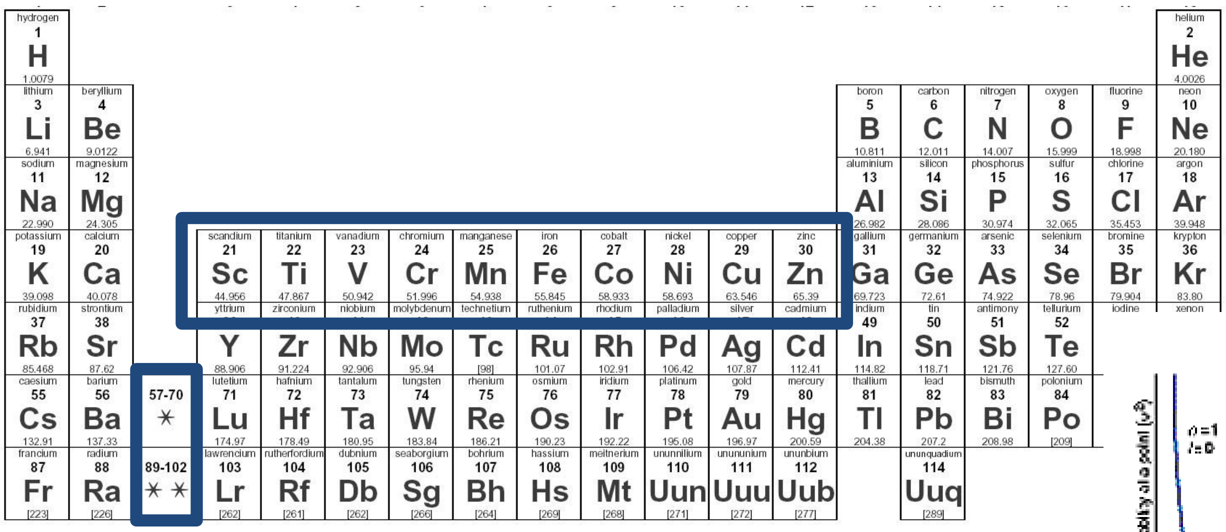


Additional electron occupation requires the energy cost :

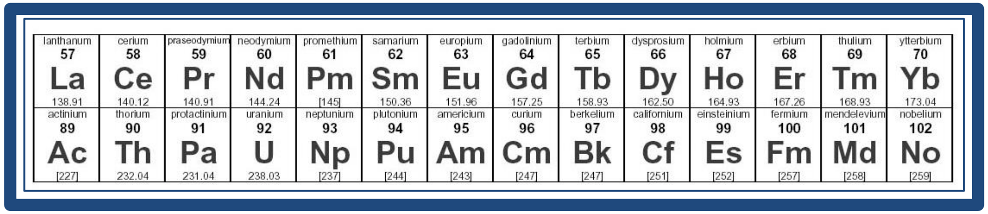
$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^{n})$$

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

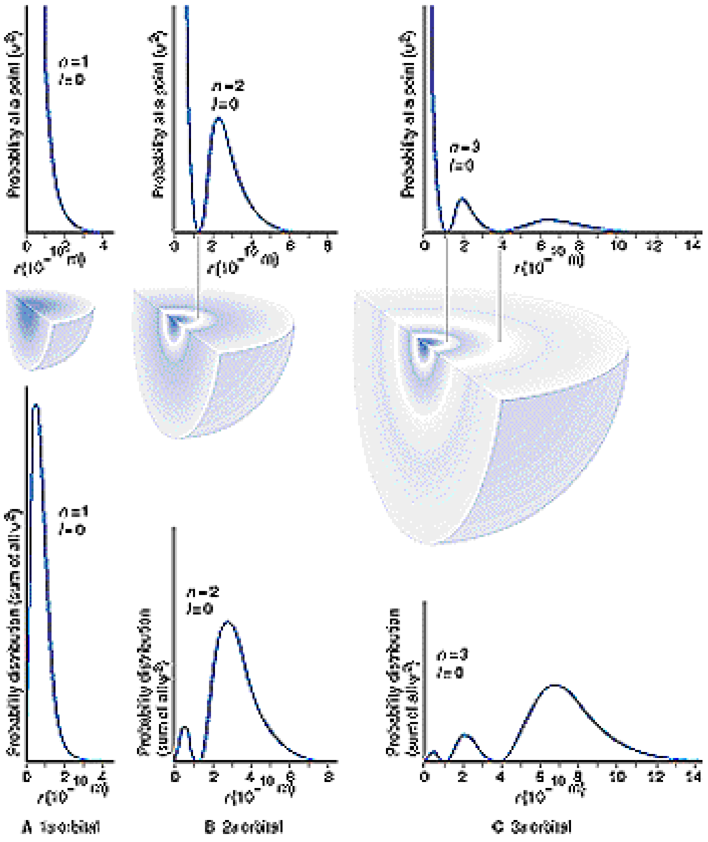
Actually Happening Quite Often



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 Y 88.906	zirconium Zr 91.224	niobium Nb 92.906	molybdenum Mo 95.94	technetium Tc [98]	ruthenium Ru 101.07	rhodium Rh 102.91	palladium Pd 106.42	silver Ag 107.87	cadmium 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 Po [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

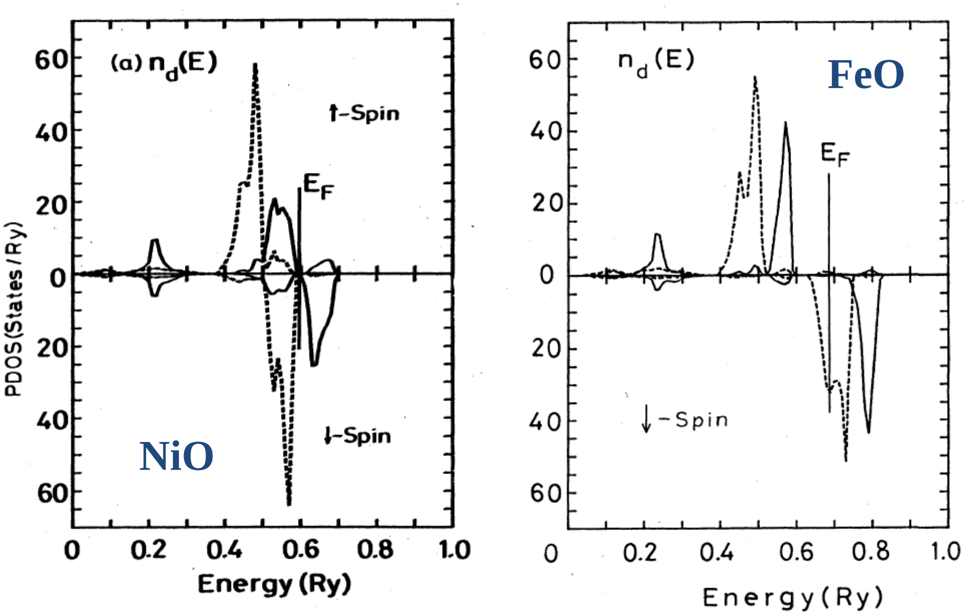
Partially filled 3d, 4f, 5f orbitals

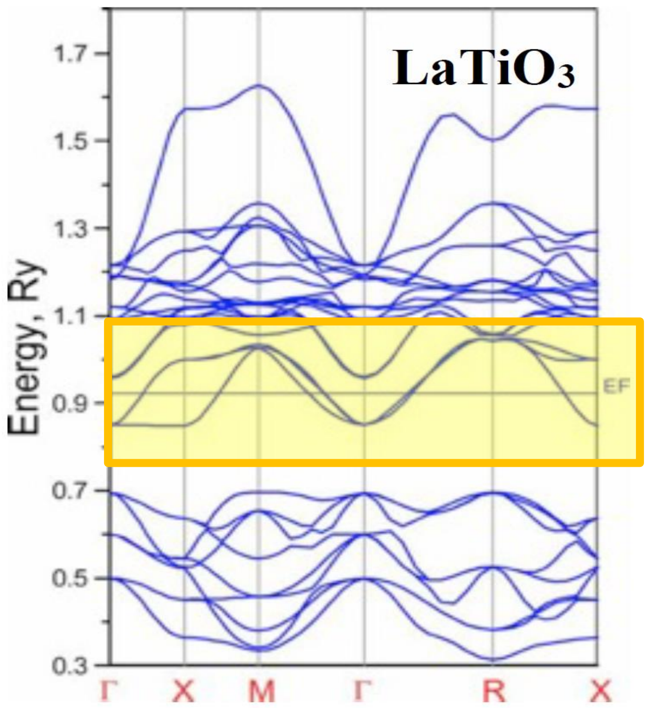
→ magnetism and others

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)





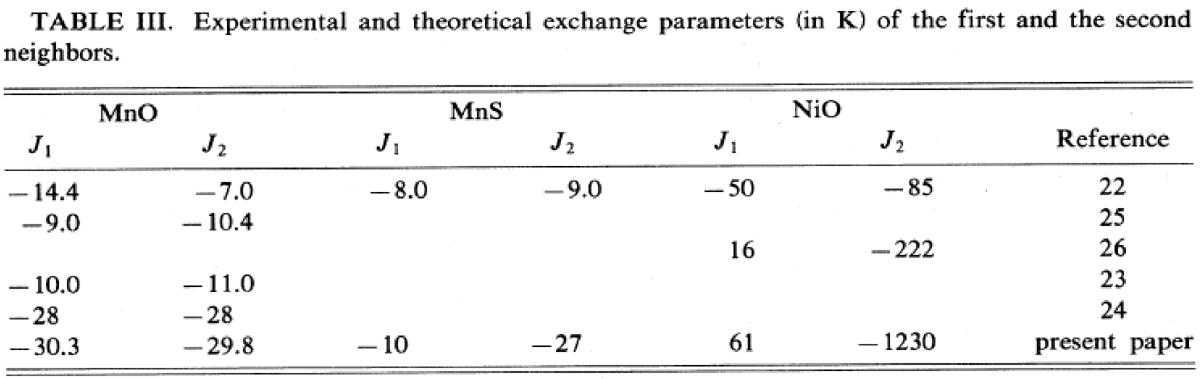
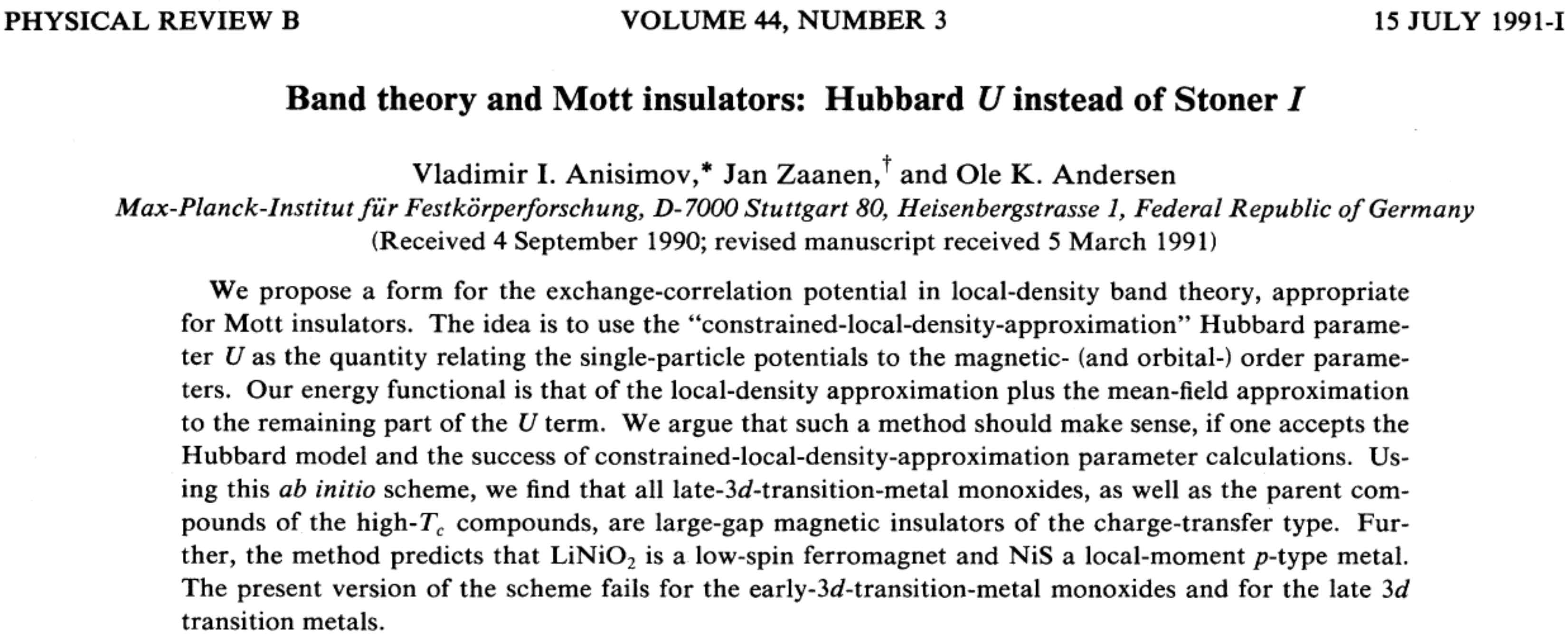


TABLE III. Experimental and theoretical exchange parameters (in K) of the first and the second neighbors.

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

Vladimir I. Anisimov,* Jan Zaanen,† and Ole K. Andersen
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Heisenbergstrasse 1, Federal Republic of Germany

(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-3*d*-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-3*d*-transition-metal monoxides and for the late 3*d* transition metals.

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

$$E_{LDA+U} = E_{LDA} + E_U - E_{dc}$$

where $E_U = \frac{1}{2} \sum_{ilm\sigma} U n^{\sigma}_{ilm} n^{\sigma'}_{ilm'}$

LDA+U Functional

The (original) form of energy functional (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)

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

J: Hund coupling constant

Orbital-dependent potential

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

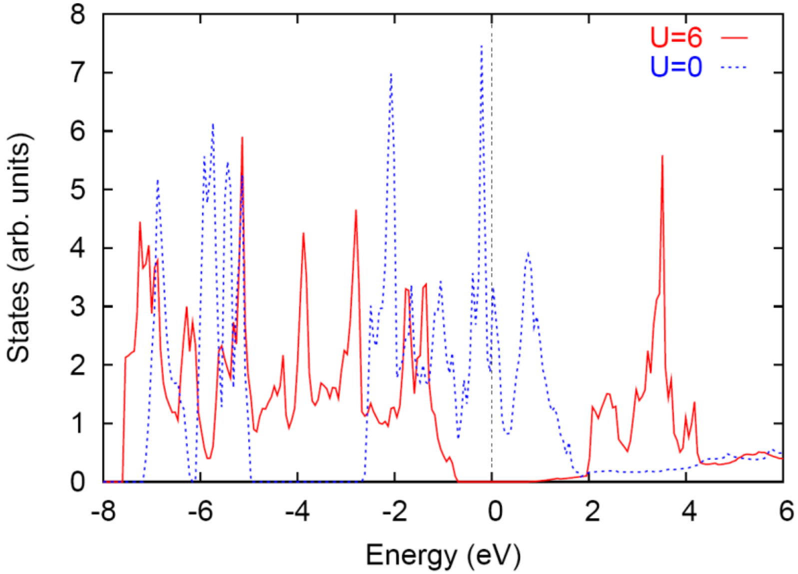
LDA+U Result

- **Band gap (in eV) :**

$\bar{U}$ (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 et al., JKPS (2006); JACS (2006)



- **Magnetic moment of NiO (in μ_B) :**

	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**

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

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

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

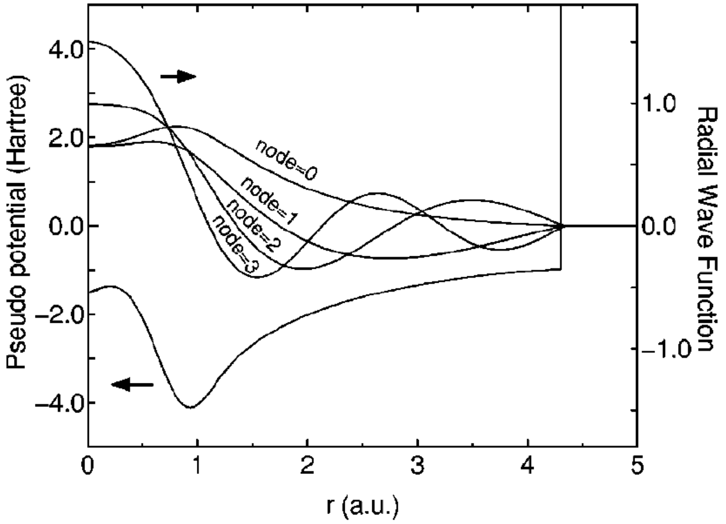
(So-called) around the mean field limit:
Czyzyk et al. PRB (1994)

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

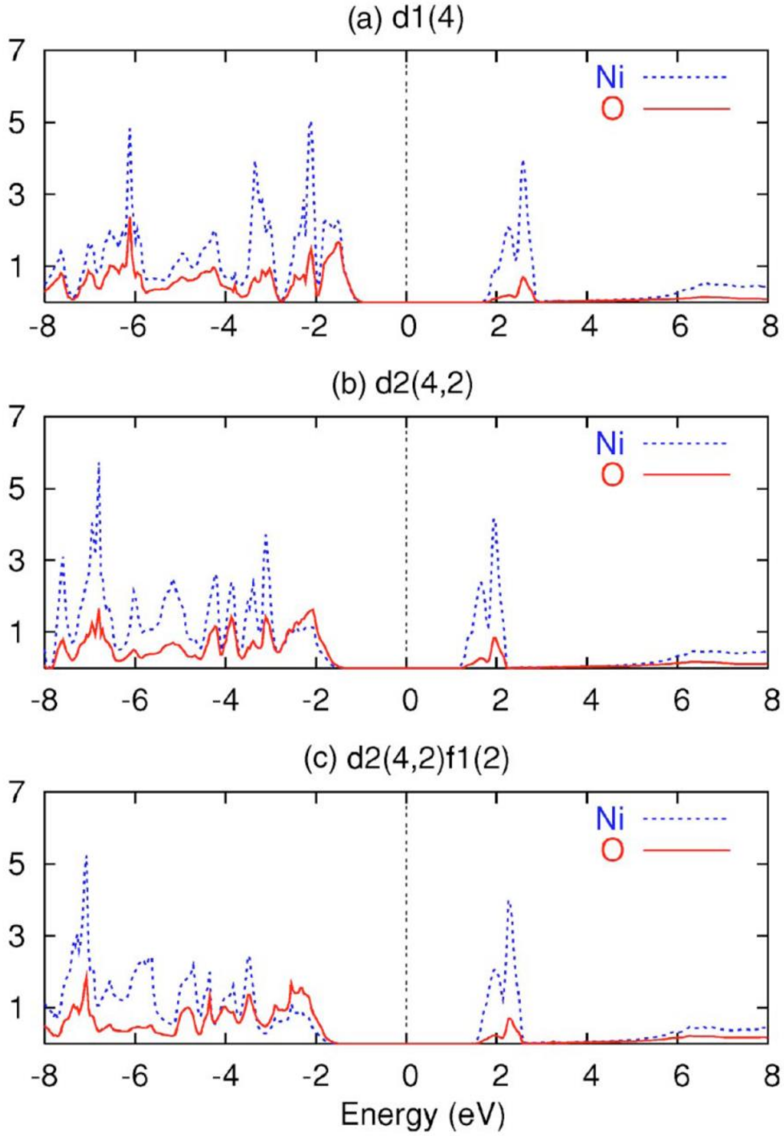
LDA+U based on LCPAO (1)

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

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



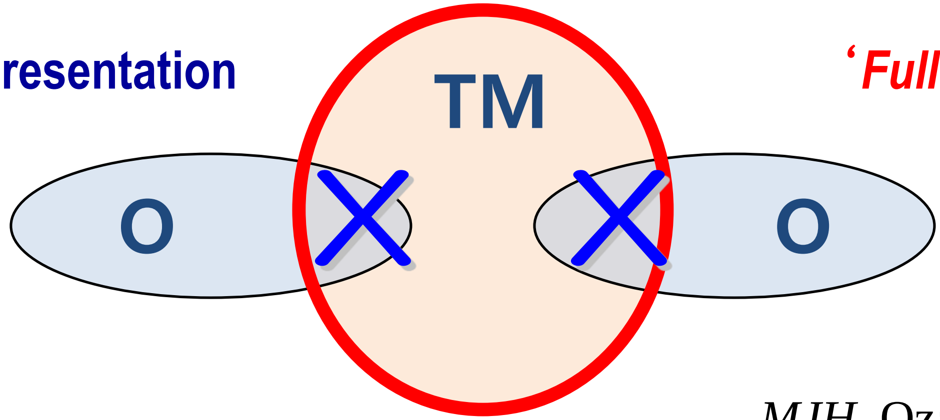
T. Ozaki, Phys. Rev. B (2003)
MJH, Ozaki, Yu, Phys. Rev. B (2006)



LDA+U based on LCPAO (2)

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

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



'*On-site*' representation

'*Full*' representation

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

Proposed '*dual*' representation:

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

Sum rule satisfied:

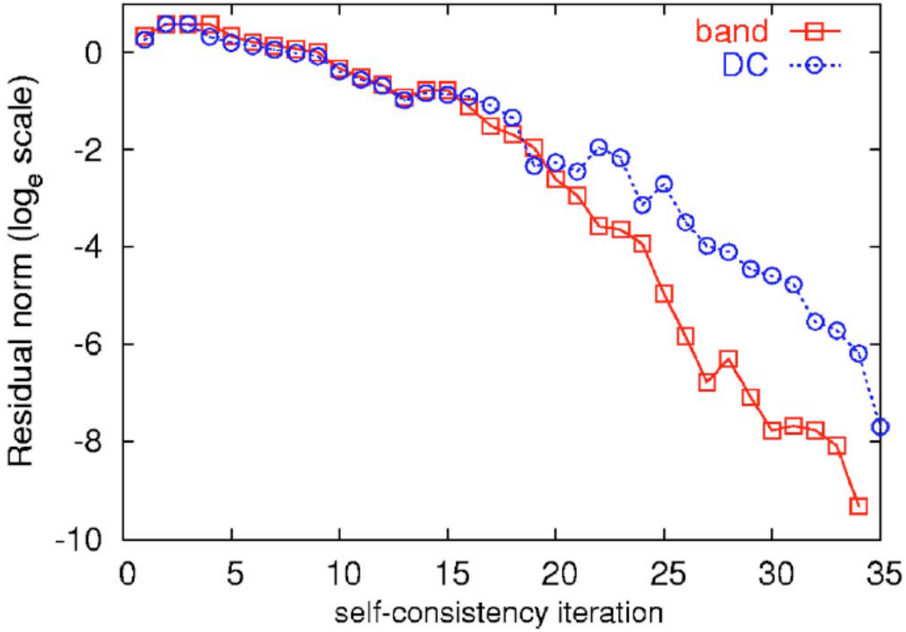
$$\sum_{\sigma} Tr(n^{\sigma}) = \sum_{\sigma} \frac{1}{2}[Tr(S\rho^{\sigma}) + Tr(\rho^{\sigma} S)] = N_{ele}$$

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

  c-LDA (e.g., Hybersen, Andersen, Anisimov et al 1980s, Cococcioni et al. 2005), c-RPA (Aryasetiawan, et al. 2004, 2006, 2008, Sasioglu 2011), m-RPA (Sakakibara, *MJH* et al. 2016)

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

  Fully-localized limit, Around-the-mean-field form, Simplified rotationally invariant from, etc

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

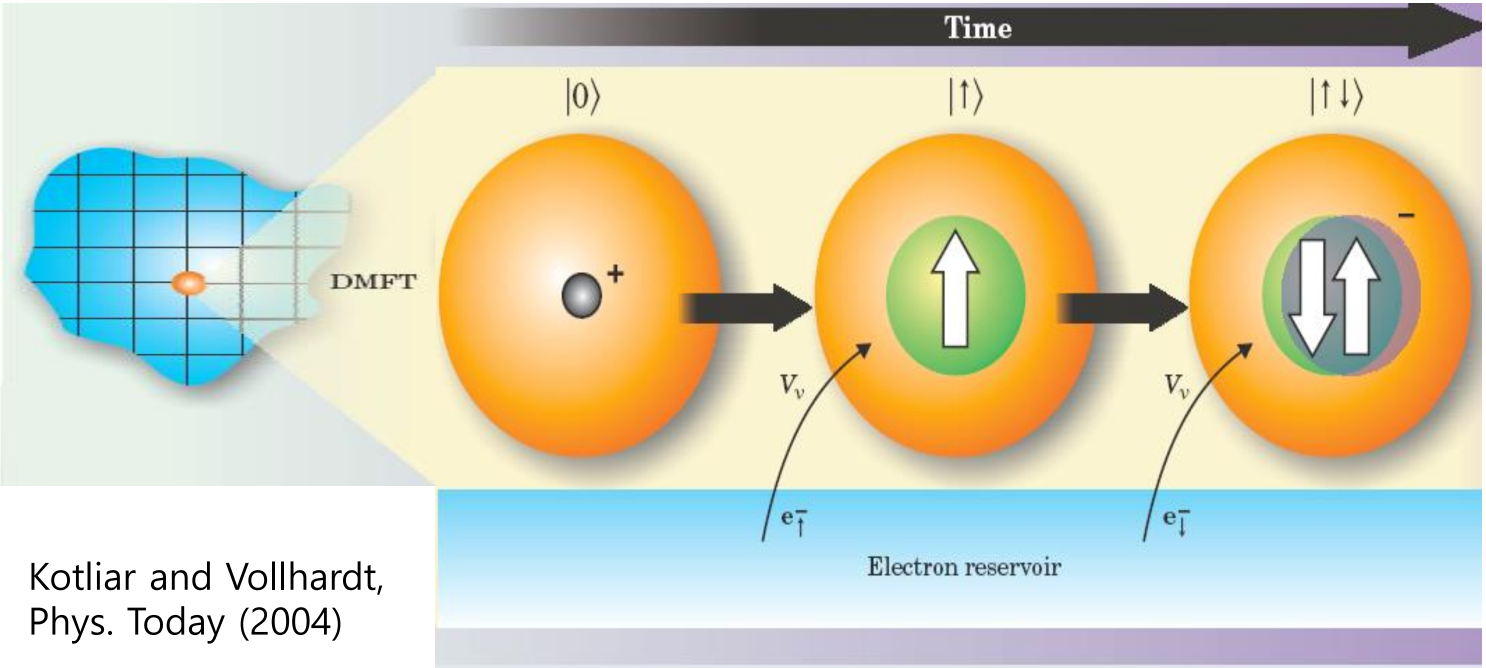
- ✓ **It is a static Hartree-Fock method**

  The correlation effect beyond this static limit cannot be captured

  → **Dynamical mean-field theory**

Dynamical Correlation and DMFT

- ✓ **Dynamical mean-field theory**



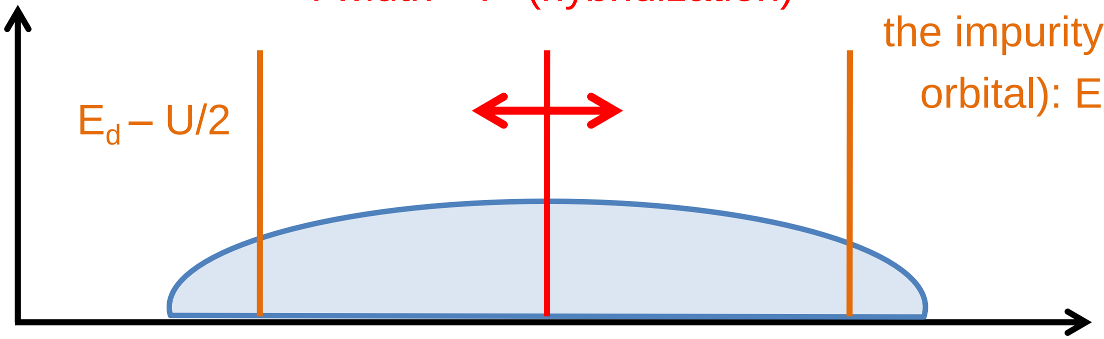
Kotliar and Vollhardt,
Phys. Today (2004)

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

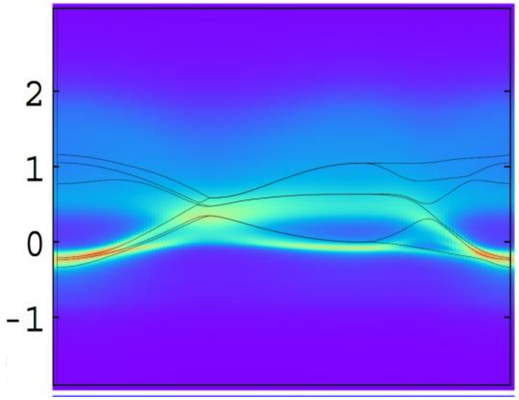


Impurity level (atomic-like)
: width ~V^2 (hybridization)

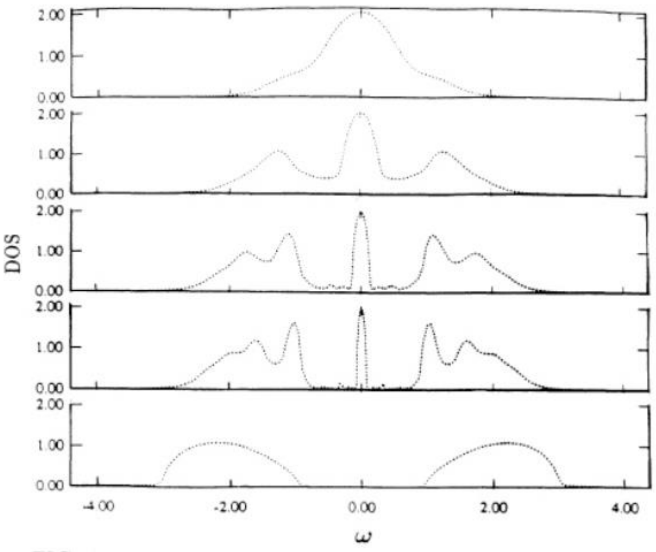
$E_d - U/2$

On-site correlation at the impurity site (or orbital): $E_d + U/2$

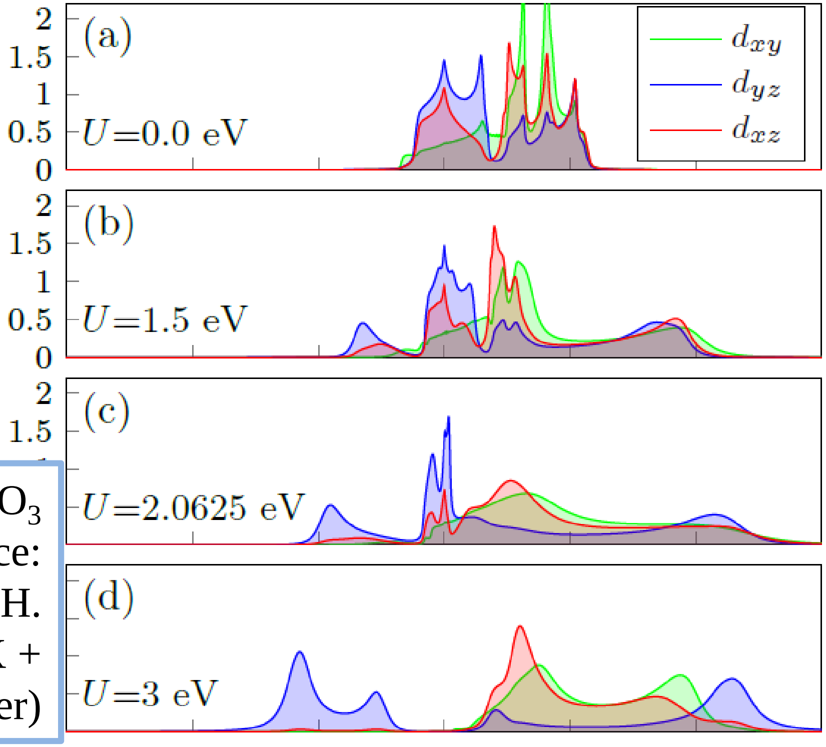
Conduction band (non-interacting)



Zhang et al., PRL (1993)



LaTiO$_3$/LaAlO$_3$ superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)



Comparison

LDA

No on-site correlation
(homogeneous electron gas)

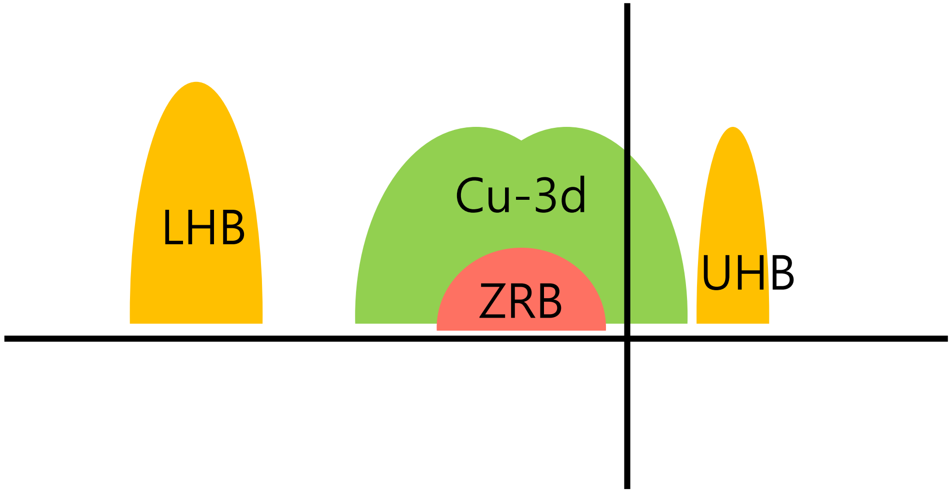
LDA+U

Hubbard-U correlation
Static approximation

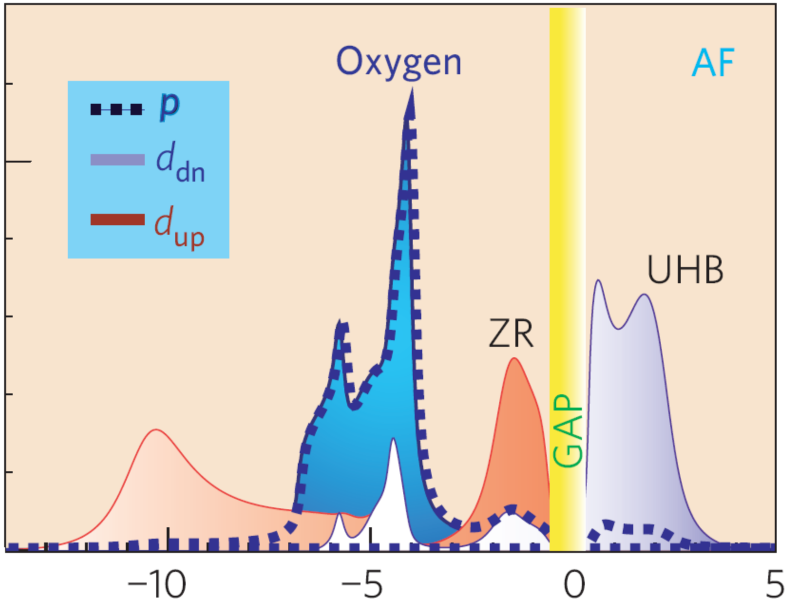
LDA+DMFT

Hubbard-U correlation
Dynamic correlation

Application to high-T_c cuprate



Weber et al., Nature Phys. (2010)

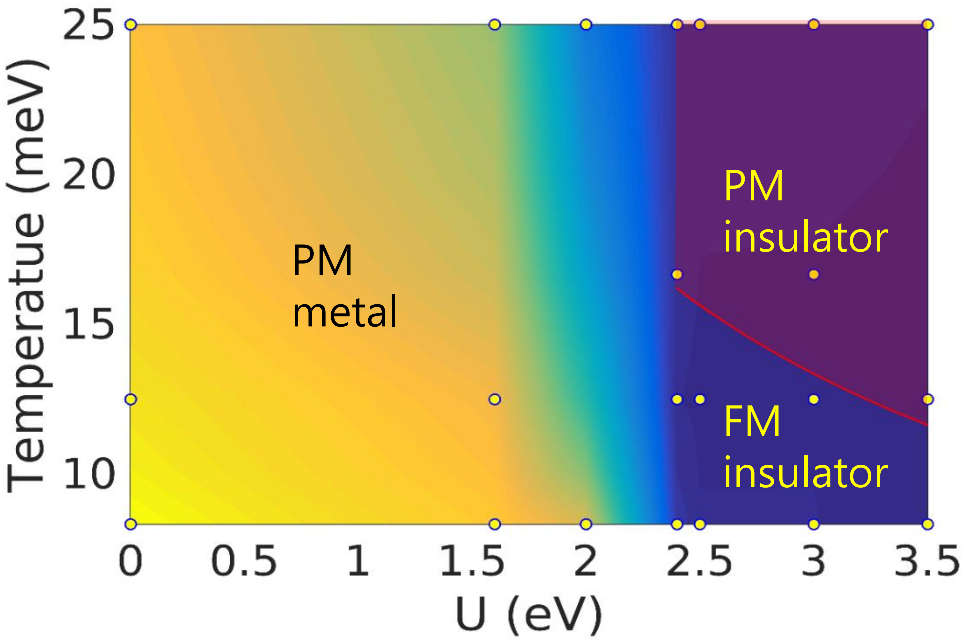


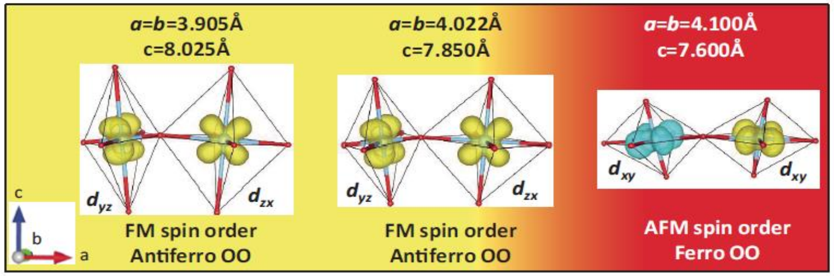
LDA+U and DMFT

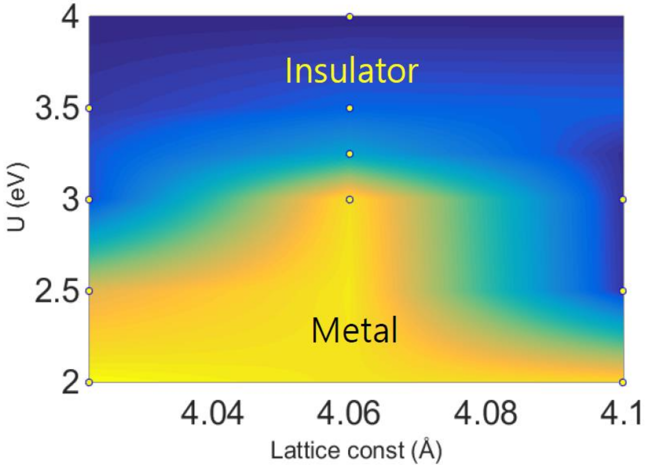
✓ **LDA+U is the static (Hartree) approximation of DMFT :**

- **Temperature dependency**
- **Electronic property near the phase boundary**
- **Paramagnetic insulating and correlated metallic phase**

$LaTiO_3/LaAlO_3$ superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)







Other Methods

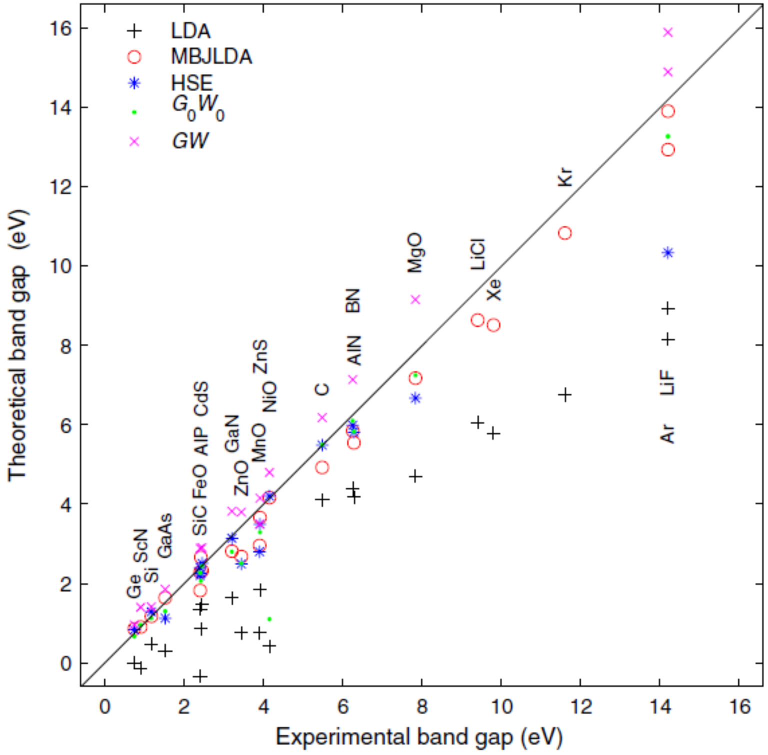
✓ **Hybrid functionals, self-interaction correction, etc**

- 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)



PART 2

Purpose:

- ✓ *Introducing recent progress on understanding LDA+U functionals*

Contents:

- ✓ *LDA+U functionals reformulated*
- ✓ *Comparison of LDA+U with LSDA+U*
- ✓ *Case studies and Perspective*

Suggested Reading:

S. Ryee and MJH, Sci. Rep. (2018)
S. Ryee and MJH, J. Phys.: Condens. Matter. (2018)
S. W. Jang et al., arXiv:1803.00213

J. Chen et al., Phys. Rev. B (2015)
H. Park et al., Phys. Rev. B (2015)
H. Chen et al., Phys. Rev. B (2016)

DFT+U (or +DMFT) Formalism: Basic Idea

$$E^{\text{DFT+U}}[\rho^\sigma, \mathbf{n}^\sigma] = E^{\text{DFT}}[\rho^\sigma] + E^{\text{int}}[\mathbf{n}^\sigma] - E^{\text{dc}}$$

where $E^{\text{int}}[\mathbf{n}^\sigma]$: Hubbard-type on-site interaction term

E^{dc} : (conceptually) the same interaction energy in LDA/GGA

DFT+U (or +DMFT) Formalism: The Issue (1)

$$E^{\mathrm{DFT+U}}[\rho^\sigma, \mathbf{n}^\sigma] = E^{\mathrm{DFT}}[\rho^\sigma] + \boxed{E^{\mathrm{int}}[\mathbf{n}^\sigma]} - \boxed{E^{\mathrm{dc}}}$$

where $E^{\mathrm{int}}[\mathbf{n}^\sigma]$: Hubbard-type on-site interaction term

E^{dc} : (conceptually) the same interaction energy in LDA/GGA

- E^{int} **:** Expression, basis-set dependence, rotational invariance,… etc
- E^{dc} **:** No well-established prescription

→ **FLL** (fully localized limit) vs **AMF** (around the mean field)

Anisimov, Solovyev *et al.*, PRB (1993)
Czyzyk & Sawatzky, PRB (1994)
Liechtenstein *et al.*, PRB (1995)
Petukhov, Mazin *et al.*, PRB (2003)
Pourovskii, Amadon *et al.*, PRB (2007)
Amadon, Lechermann *et al.*, PRB (2008)
Karolak et al., J. Electron Spectrosc. Relat. Phenom. (2010)
X. Wang, ***MJH*** *et al.*, PRB (2012)
H. Park, Millis, Marianetii, PRB (2014)
Haule, PRL (2015)
…

DFT+U (or +DMFT) Formalism: The Issue (2)

$$E^{\mathrm{DFT+U}}[\rho^\sigma, \mathbf{n}^\sigma] = \boxed{E^{\mathrm{DFT}}[\rho^\sigma]} + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}$$

where $E^{\mathrm{int}}[\mathbf{n}^\sigma]$: Hubbard-type on-site interaction term

E^{dc} : (conceptually) the same interaction energy in LDA/GGA

- E^{int} **:** Expression, basis-set dependence, rotational invariance,… etc
- E^{dc} **:** No well-established prescription

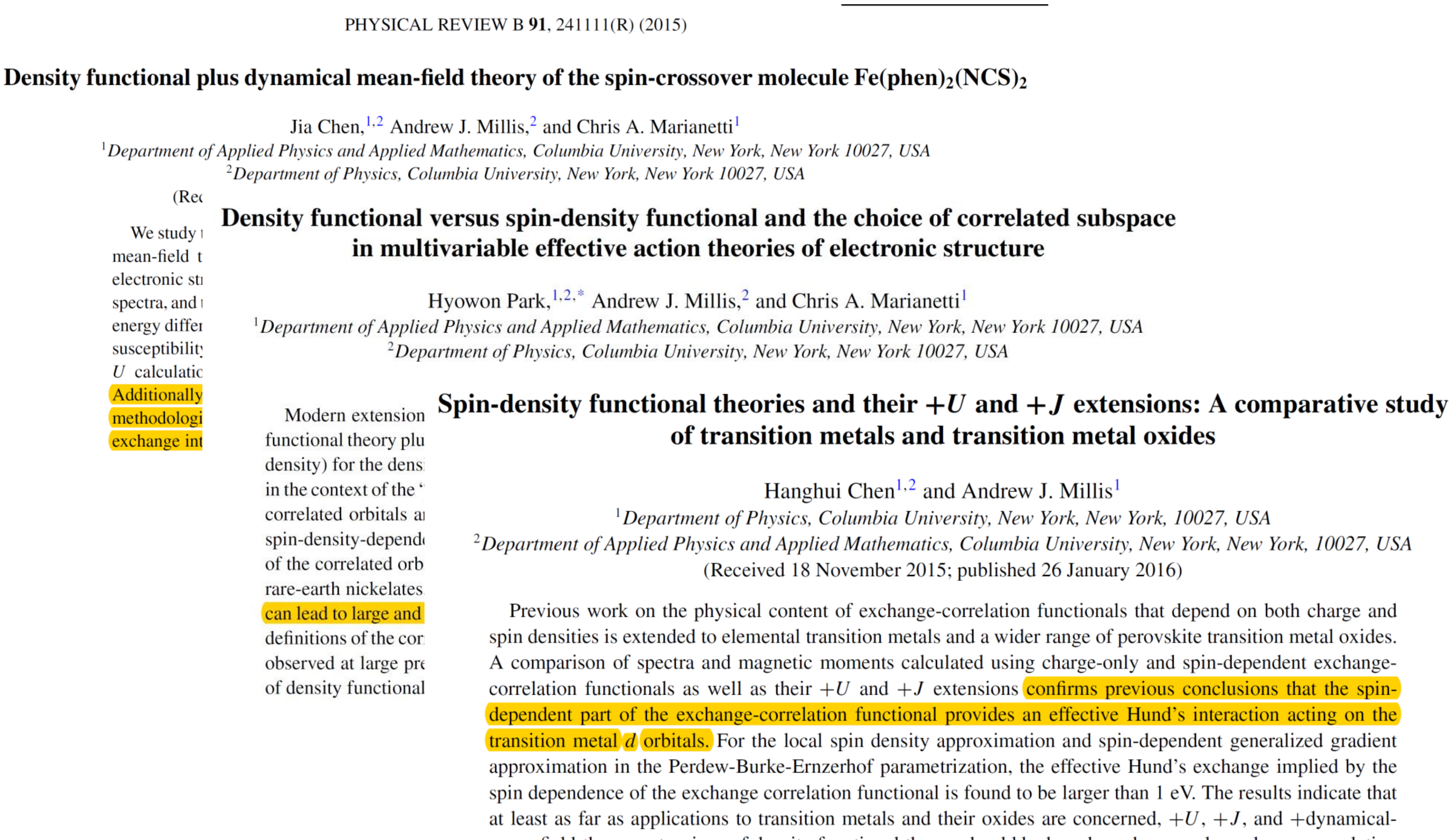
→ **FLL** (fully localized limit) vs **AMF** (around the mean field)

- E^{DFT} **:** *charge-only-density* XC (**LDA**) or *spin-density* XC (**LSDA**) ??

CDFT+U	**SDFT+U**
Anisimov et al., PRB (1991) Anisimov et al., PRB (1993) Solovyev et al., PRB (1994)	Czyzyk et al., PRB (1994) Liechtenstein et al., PRB (1995) Dudarev et al., PRB (1998)

Recent Case Studies

No systematic formal analysis on this fundamental issue
(Some case studies and internal agreement in DMFT community)



PHYSICAL REVIEW B **91**, 241111(R) (2015)

Density functional plus dynamical mean-field theory of the spin-crossover molecule Fe(phen)$_2$(NCS)$_2$

Jia Chen,[1,2] Andrew J. Millis,[2] and Chris A. Marianetti[1]
[1] Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA
[2] Department of Physics, Columbia University, New York, New York 10027, USA

(Rec

We study t
mean-field t
electronic st
spectra, and t
energy differ
susceptibility
U calculatio
Additionally
methodologi
exchange int

Density functional versus spin-density functional and the choice of correlated subspace in multivariable effective action theories of electronic structure

Hyowon Park,[1,2,*] Andrew J. Millis,[2] and Chris A. Marianetti[1]
[1] Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA
[2] Department of Physics, Columbia University, New York, New York 10027, USA

Modern extension
functional theory plu
density) for the dens
in the context of the "
correlated orbitals a
spin-density-depend
of the correlated orb
rare-earth nickelates
can lead to large and
definitions of the cor
observed at large pre
of density functional

Spin-density functional theories and their $+U$ and $+J$ extensions: A comparative study of transition metals and transition metal oxides

Hanghui Chen[1,2] and Andrew J. Millis[1]
[1] Department of Physics, Columbia University, New York, New York, 10027, USA
[2] Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York, 10027, USA

(Received 18 November 2015; published 26 January 2016)

Previous work on the physical content of exchange-correlation functionals that depend on both charge and spin densities is extended to elemental transition metals and a wider range of perovskite transition metal oxides. A comparison of spectra and magnetic moments calculated using charge-only and spin-dependent exchange-correlation functionals as well as their $+U$ and $+J$ extensions confirms previous conclusions that the spin-dependent part of the exchange-correlation functional provides an effective Hund's interaction acting on the transition metal d orbitals. For the local spin density approximation and spin-dependent generalized gradient approximation in the Perdew-Burke-Ernzerhof parametrization, the effective Hund's exchange implied by the spin dependence of the exchange correlation functional is found to be larger than 1 eV. The results indicate that at least as far as applications to transition metals and their oxides are concerned, $+U$, $+J$, and +dynamical-

The Issue Formulated

- **Total energy; CDFT+U and SDFT+U**

$$E^{\mathrm{CDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N]$$

$$E^{\mathrm{SDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho^\sigma] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N^\sigma]$$

where $$E^{\mathrm{int}} = \frac{1}{2}\sum_{\{m_i\},\sigma,\sigma'} n^\sigma_{m_1m_2}\{\underline{\langle m_1, m_3|V_{ee}|m_2, m_4\rangle} - \underline{\langle m_1, m_3|V_{ee}|m_4, m_2\rangle}\delta_{\sigma\sigma'}\}n^{\sigma'}_{m_3m_4}$$

Coulomb interaction tensor using two input parameters; ***U*** and ***J***

The choice of XC functional: charge-only (LDA/GGA) or spin (LSDA/SGGA)

The expression of interactions (including double counting)

CDFT(LDA) +U

SDFT(LSDA) +U

×

FLL (fully localized limit)

AMF (around mean-field)

Liechtenstein et al., PRB (1995)
Dudarev et al., PRB (1998)

Anisimov et al., PRB (1991)

‘FLL (fully localized limit)’ Formalism

S. Ryee and MJH,
Sci. Rep. (2018)

- **Total energy; CDFT+U and SDFT+U**

$$E^{\mathrm{CDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N]$$

$$E^{\mathrm{SDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho^\sigma] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N^\sigma]$$

- **Potential**

$$V^{U,\sigma}_{m_1m_2} = \delta E^U/\delta n^\sigma_{m_1m_2} = \delta(E^{\mathrm{int}} - E^{\mathrm{dc}})/\delta n^\sigma_{m_1m_2} = V^{\mathrm{int},\sigma}_{m_1m_2} - V^{\mathrm{dc},\sigma}_{m_1m_2}$$

- **FLL formulations: cFLL (CDFT+U version) and sFLL (SDFT+U version)**

$$E^{\mathrm{int}} = \frac{1}{2}\sum_{\{m_i\},\sigma,\sigma'} n^\sigma_{m_1}\{\underbrace{\langle m_1,m_2|V_{ee}|m_1,m_2\rangle}_{\text{direct interaction}} - \underbrace{\langle m_1,m_2|V_{ee}|m_2,m_1\rangle\delta_{\sigma\sigma'}}_{\text{exchange interaction}}\}n^{\sigma'}_{m_2}$$

cFLL

$$E^{\mathrm{dc}}_{\mathrm{cFLL}} = \frac{1}{2}UN(N-1) - J\frac{N}{2}\left(\frac{N}{2}-1\right)$$

$$V^{\mathrm{dc},\sigma}_{\mathrm{cFLL},m_1m_2} = \left\{U\left(N-\frac{1}{2}\right) - J\left(\frac{N}{2}-\frac{1}{2}\right)\right\}\delta_{m_1m_2}$$

sFLL

$$E^{\mathrm{dc}}_{\mathrm{sFLL}} = \frac{1}{2}UN(N-1) - J\frac{N}{2}\left(\frac{N}{2}-1\right) - \frac{1}{4}JM^2$$

$$V^{\mathrm{dc},\sigma}_{\mathrm{sFLL},m_1m_2} = \left\{U\left(N-\frac{1}{2}\right) - J\left(N^\sigma-\frac{1}{2}\right)\right\}\delta_{m_1m_2}$$

✓ sFLL double counting with $-\frac{1}{4}JM^2$: in competition with spin-density XC energy

✓ Double counting potential: cFLL (spin-independent) vs sFLL (spin-dependent)

‘AMF (around mean-field)’ Formalism

S. Ryee and MJH,
Sci. Rep. (2018)

- **Total energy; CDFT+U and SDFT+U**

$$E^{\mathrm{CDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N]$$

$$E^{\mathrm{SDFT}+U} = T_s[\rho^\sigma] + \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r})\rho + E_{HXC}[\rho^\sigma] + E^{\mathrm{int}}[\mathbf{n}^\sigma] - E^{\mathrm{dc}}[N^\sigma]$$

- **Potential**

$$V^{U,\sigma}_{m_1m_2} = \delta E^U/\delta n^\sigma_{m_1m_2} = \delta(E^{\mathrm{int}} - E^{\mathrm{dc}})/\delta n^\sigma_{m_1m_2} = V^{\mathrm{int},\sigma}_{m_1m_2} - V^{\mathrm{dc},\sigma}_{m_1m_2}$$

- **AMF formulations: cAMF (CDFT+U version) and sAMF (SDFT+U version)**

$$E^U_{\mathrm{AMF}} = E^{\mathrm{int}}_{\mathrm{AMF}} - E^{\mathrm{dc}}_{\mathrm{AMF}} = \frac{1}{2}\sum_{\{m_i\},\sigma,\sigma'} \widetilde{n}^\sigma_{m_1m_2}\{\underbrace{\langle m_1,m_3|V_{ee}|m_2,m_4\rangle}_{\text{direct interaction}} - \underbrace{\langle m_1,m_3|V_{ee}|m_4,m_2\rangle\delta_{\sigma\sigma'}}_{\text{exchange interaction}}\}\widetilde{n}^{\sigma'}_{m_3m_4}$$

cAMF

$$\widetilde{n}^\sigma_{m_1m_2} = n^\sigma_{m_1m_2} - \frac{1}{2(2l+1)}(N\delta_{m_1m_2})$$

sAMF

$$\widetilde{n}^\sigma_{m_1m_2} = n^\sigma_{m_1m_2} - \frac{1}{2(2l+1)}(N + \mathrm{sgn}(\sigma)M)\delta_{m_1m_2}$$

✓ In cAMF/sAMF, the interaction is described by the fluctuation w.r.t. the average *charge/spin* occupation (double counting implicit).

Analysis (1): Energetics

✓ cFLL: $E^{U+\mathrm{XC}} \equiv E^{\mathrm{int}}[\mathbf{n}^{\sigma}] - \underline{\left[\frac{1}{2}UN(N-1) - J\frac{N}{2}\left(\frac{N}{2}-1\right)\right]}$ **cFLL dc**

N: # of electrons in correlated subspace

M: mag. mom.

✓ sFLL: $E^{U+\mathrm{XC}} \equiv E^{\mathrm{int}}[\mathbf{n}^{\sigma}] - \underline{\left[\frac{1}{2}UN(N-1) - \frac{J}{2}\sum_{\sigma} N^{\sigma}(N^{\sigma}-1)\right]} - IM^2/4$ **sFLL dc**

- **Spin-polarization energy of LDA/GGA** is also present in SDFT+U (but not in CDFT+U)

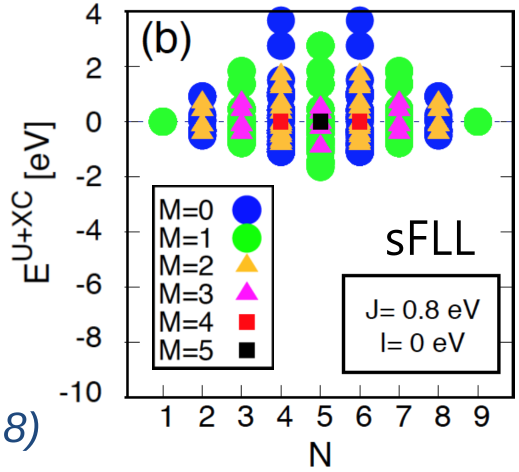
  ✓ Represented by **Stoner *I*** (in general material dependent)

  (cf) In general, for real materials, $I_{\mathrm{SGGA}} > I_{\mathrm{LSDA}}$. See, for example, S. Ryee and **MJH**, Sci. Rep. (2017)

- **“Model” *d*-shell electronic configurations**

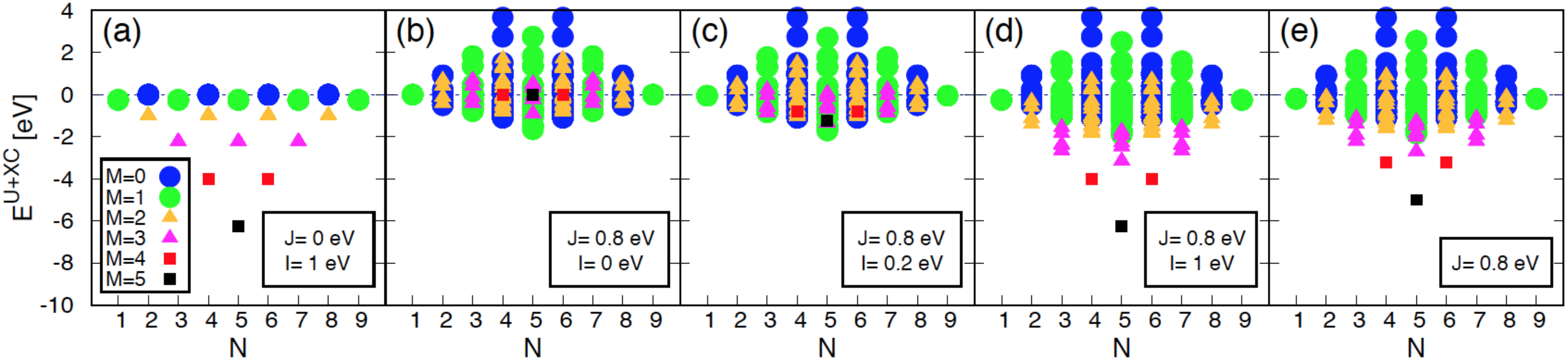
  ✓ All possible integer-occupancy configurations
  e.g.) ${}_{10}C_5 = 252$ configurations for 5 electrons

  ✓ Hund *J* and Stoner *I* used as the control parameters



S. Ryee and MJH, Sci. Rep. (2018)

Analysis (1): Energetics (FLL)



* U = 5 eV   * (a) – (d): sFLL   (e): cFLL

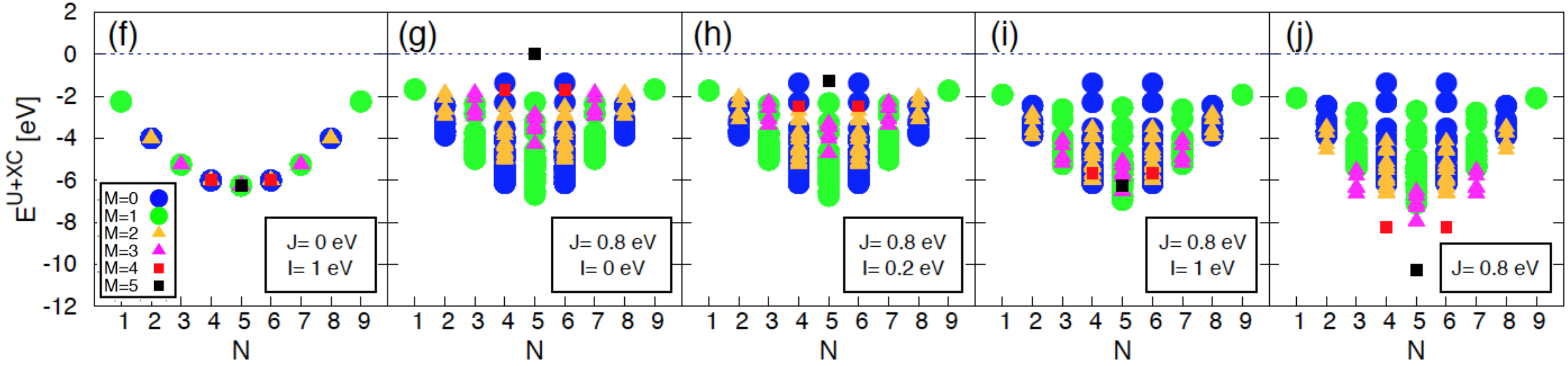
✓ **cFLL (charge-only density functional formulation)**

→ **The moment formation is favored as J increases.**

✓ **sFLL (spin-density functional formulation)**

→ **J in competition with I_{Stoner} : even for sufficiently large J, high-spin state can be unfavored.**

Analysis (1): Energetics (AMF)



* U = 5 eV   * (f) – (i): sAMF   (j): cAMF

cAMF → The moment formation is favored as J increases.

sFLL → J in competition with I_{Stoner} : high-spin state is hardly favored.

sDFT+U (based on spin-density XC) can easily give *unphysical* electronic and magnetic solutions…! (consistent with the previous case studies)

Analysis (2): Potentials

- **J-only contribution of DFT+U potential:**

$$\widetilde{V}^{\mathrm{int},\sigma}_{J,m_1} = \sum_{m_2,\sigma'} \{\langle m_1, m_2|V_{J,ee}|m_1, m_2\rangle - \langle m_1, m_2|V_{J,ee}|m_2, m_1\rangle \delta_{\sigma\sigma'}\} n^{\sigma'}_{m_2}$$

J-only (excluding *U*-related terms) contribution to the Coulomb interaction tensor:

$$\langle m_1, m_2|V_{J,ee}|m_1, m_2\rangle = \sum_{\{m_i'\}} \left[S_{m_1 m_1'} S_{m_2 m_3'} \left\{ \sum_{k\neq 0} \alpha_k(m_1', m_3', m_2', m_4') F^k \right\} S^{-1}_{m_2' m_1} S^{-1}_{m_4' m_2} \right]$$

α_k: Racah-Wigner numbers
F^k: Slater integrals

CDFT+U

$$\widetilde{V}^{U,\sigma}_{\mathrm{cFLL},m} = \widetilde{V}^{\mathrm{int},\sigma}_{J,m} + J\left(\frac{N}{2} - \frac{1}{2}\right)$$

$$\widetilde{V}^{U,\sigma}_{\mathrm{cAMF},m} = \widetilde{V}^{\mathrm{int},\sigma}_{J,m} + J\left(\frac{2l}{2l+1}\frac{N}{2}\right)$$

spin-*in*dependent ‘d-c’ potentials

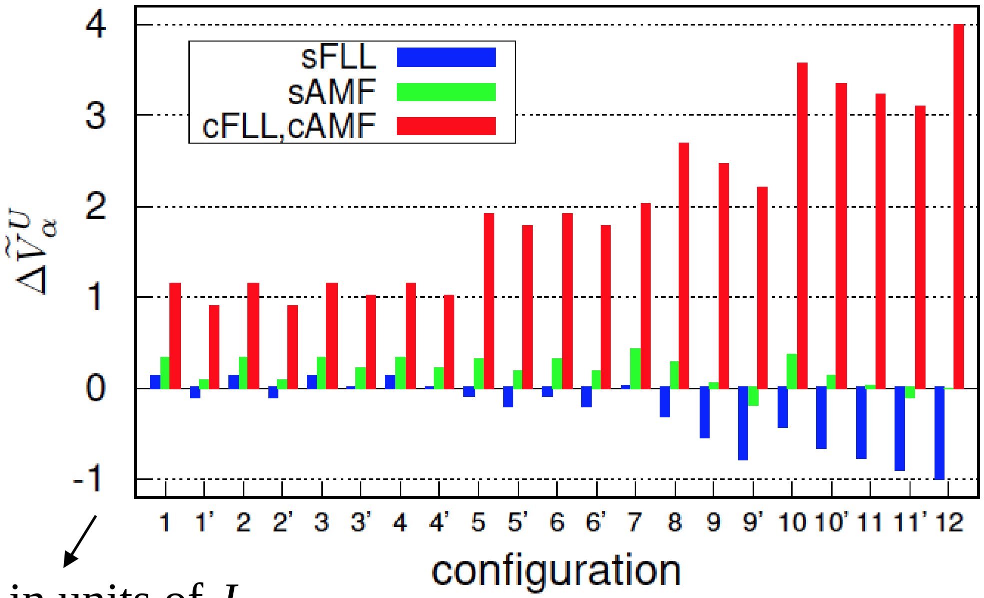
SDFT+U

$$\widetilde{V}^{U,\sigma}_{\mathrm{sFLL},m} = \widetilde{V}^{\mathrm{int},\sigma}_{J,m} + J\left(N^\sigma - \frac{1}{2}\right)$$

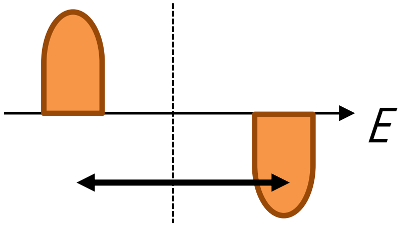
$$\widetilde{V}^{U,\sigma}_{\mathrm{sAMF},m} = \widetilde{V}^{\mathrm{int},\sigma}_{J,m} + J\left(\frac{2l}{2l+1}N^\sigma\right)$$

spin-dependent ‘d-c’ potentials

Analysis (2): Potentials

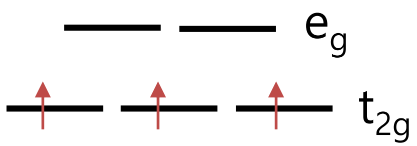


in units of J

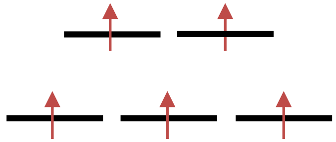


$\Delta\widetilde{V}^U_\alpha \equiv \widetilde{V}^{U,\downarrow}_\alpha - \widetilde{V}^{U,\uparrow}_\alpha$: ***J-induced*** spin-splitting

No. 8 :



No. 12 :



$$V^{\mathrm{dc},\sigma}_{\mathrm{cFLL},m_1m_2} = \left\{U\left(N-\frac{1}{2}\right) - J\left(\frac{N}{2}-\frac{1}{2}\right)\right\}\delta_{m_1m_2}$$

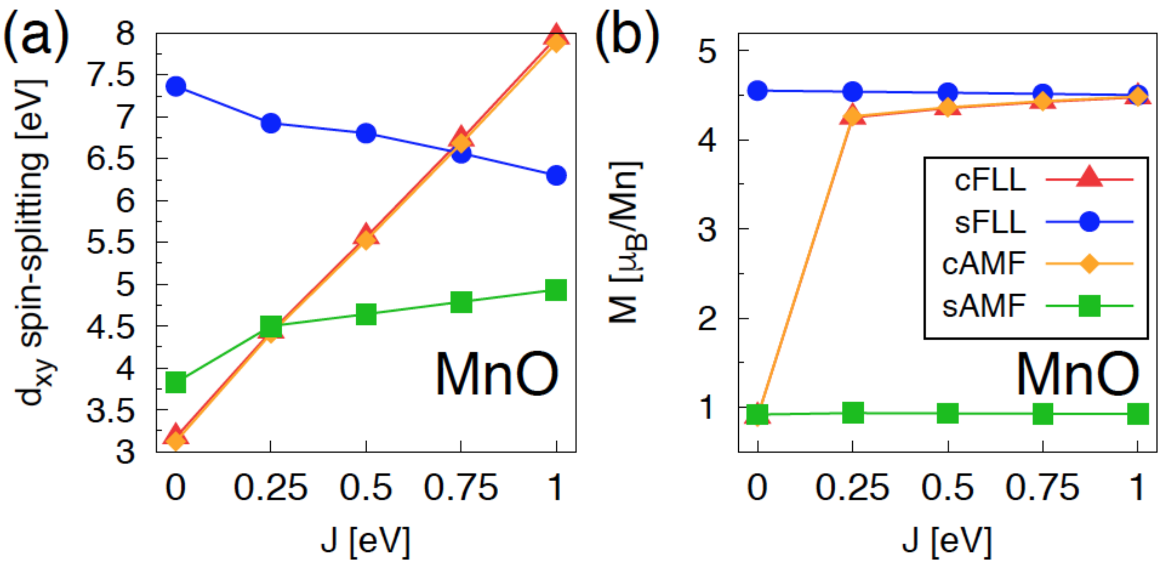
$$V^{\mathrm{dc},\sigma}_{\mathrm{sFLL},m_1m_2} = \left\{U\left(N-\frac{1}{2}\right) - J\left(N^\sigma-\frac{1}{2}\right)\right\}\delta_{m_1m_2}$$

: competes with XC spin splitting ~ *IM*

In CDFT+U, the spin splitting is nothing to do with double counting.

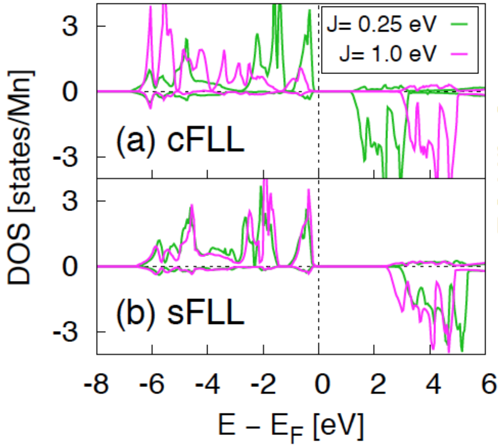
In SDFT+U, the double-counting potential is not cancelled out by SDFT contribution (~ *IM*): Ambiguity in describing spectral property.

Application to real materials: MnO and NiO

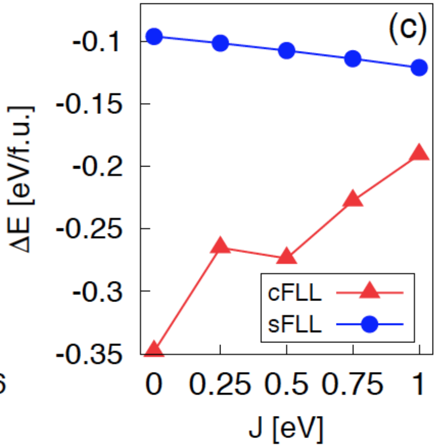


- **cFLL and cAMF : Low-spin to high-spin transition is well described as a function of J, which is not the case for sFLL and sAMF.**

MnO



$$\Delta E = E_{AF} - E_{FM}$$



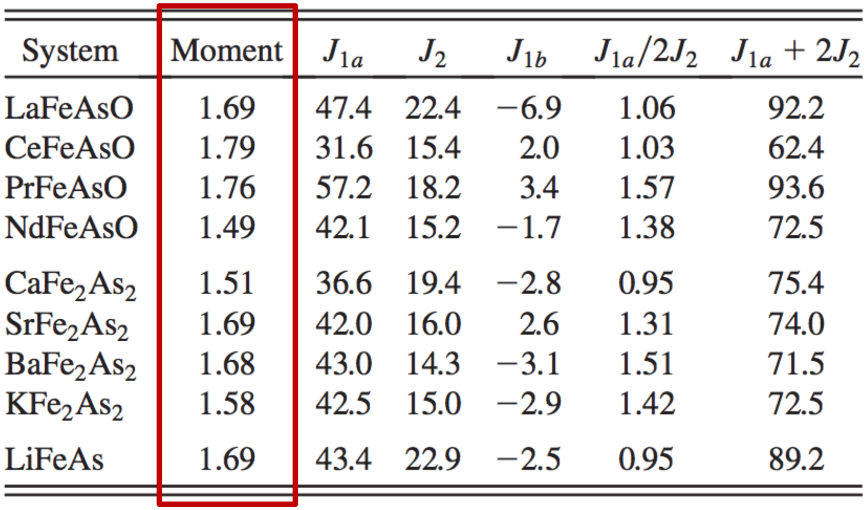
(cf) For half-filled *d*-shell,

$$J_{ex} \sim -\frac{t^2}{U+4J}$$

S. Ryee and MJH, Sci. Rep. (2018)

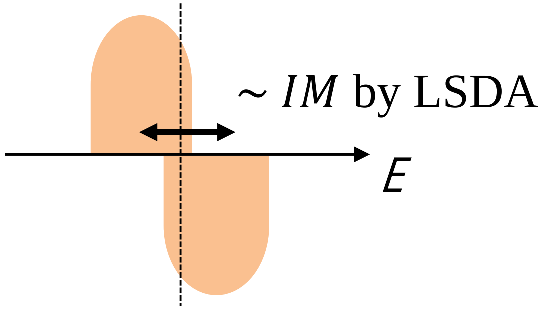
Application to real materials: $BaFe_2As_2$ (AF metal)

- **LSDA overestimates the moments of Fe-pnictides (Exp. ~ 1 μ_B)**



System	Moment	J_{1a}	J_2	J_{1b}	$J_{1a}/2J_2$	$J_{1a}+2J_2$
LaFeAsO	1.69	47.4	22.4	−6.9	1.06	92.2
CeFeAsO	1.79	31.6	15.4	2.0	1.03	62.4
PrFeAsO	1.76	57.2	18.2	3.4	1.57	93.6
NdFeAsO	1.49	42.1	15.2	−1.7	1.38	72.5
$CaFe_2As_2$	1.51	36.6	19.4	−2.8	0.95	75.4
$SrFe_2As_2$	1.69	42.0	16.0	2.6	1.31	74.0
$BaFe_2As_2$	1.68	43.0	14.3	−3.1	1.51	71.5
KFe_2As_2	1.58	42.5	15.0	−2.9	1.42	72.5
LiFeAs	1.69	43.4	22.9	−2.5	0.95	89.2

M. J. Han et al., PRL (2009)



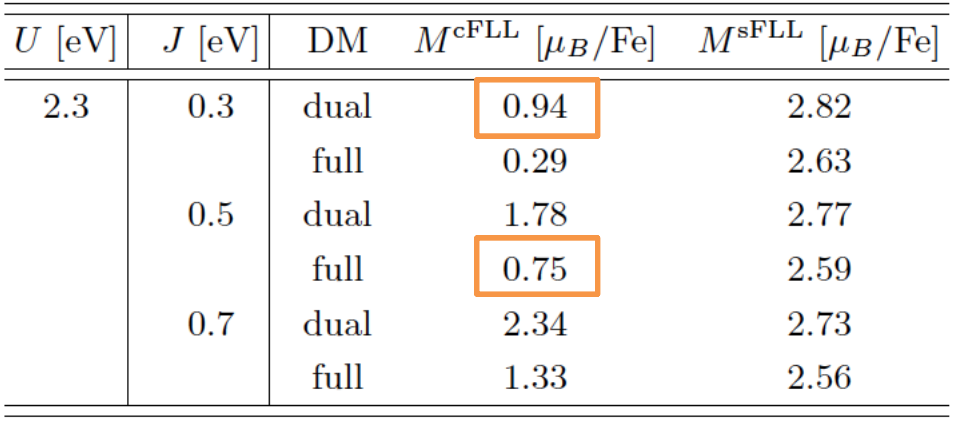
large I in LSDA → large moment

1) Empirical way of accounting for spin-fluctuations; $I_R \sim sI$

L. Ortenzi et al., PRL (2015)
J. Lischner et al., PRB (2015)
…

S. Ryee and MJH, arXiv:1709.03214

$BaFe_2As_2$



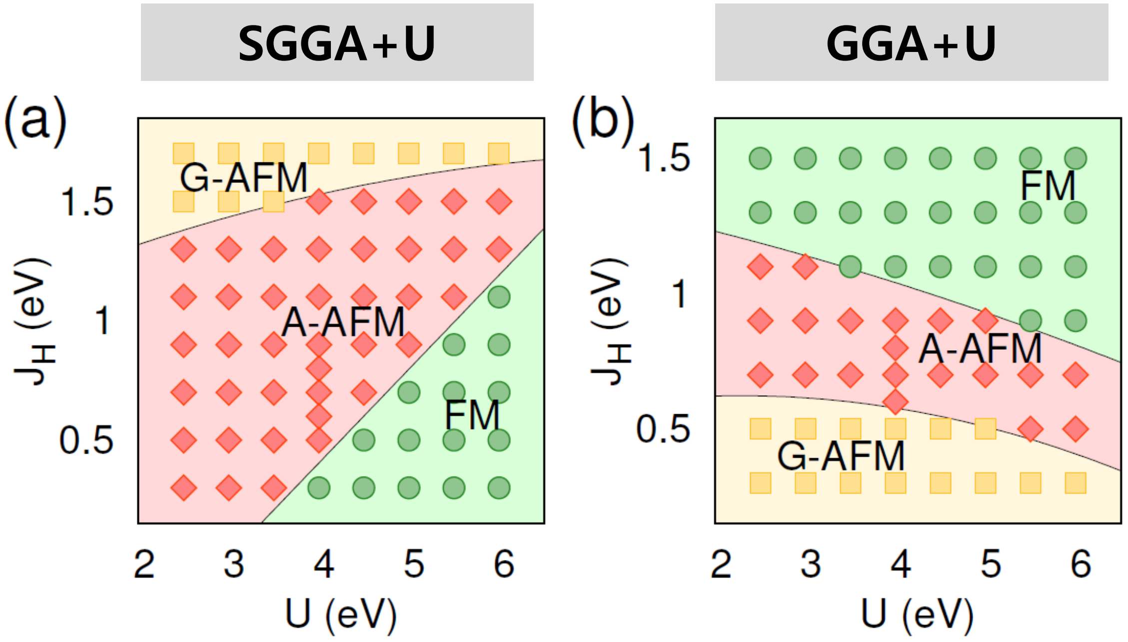
U [eV]	J [eV]	DM	M^{cFLL} [μ_B/Fe]	M^{sFLL} [μ_B/Fe]
2.3	0.3	dual	0.94	2.82
		full	0.29	2.63
	0.5	dual	1.78	2.77
		full	0.75	2.59
	0.7	dual	2.34	2.73
		full	1.33	2.56

2) Using *negative* U in sFLL

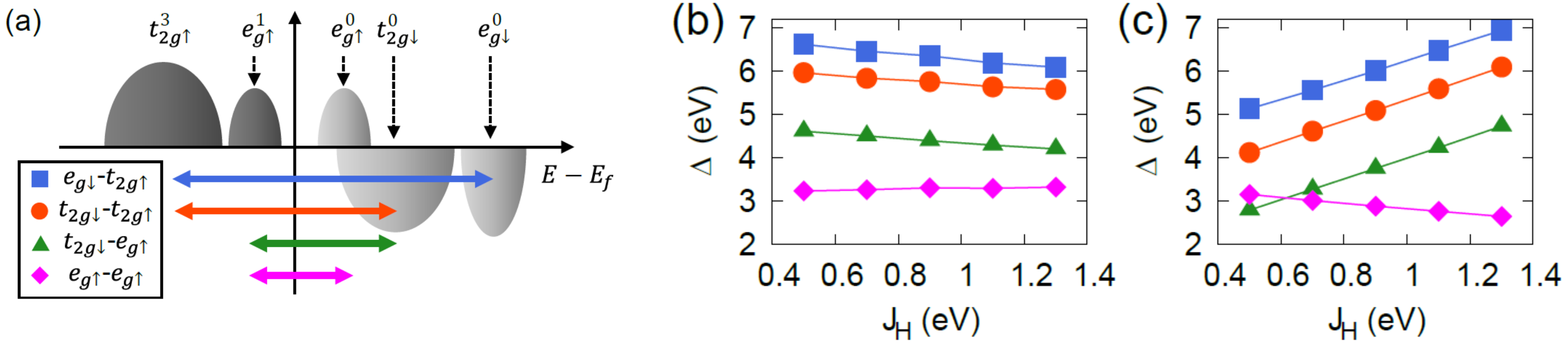
M. Yi et al., PRB (2009)
H. Nakamura et al., Physica C (2009)
…

Application to real materials: $LaMnO_3$

S. W. Jang et al, arXiv:1803.00213

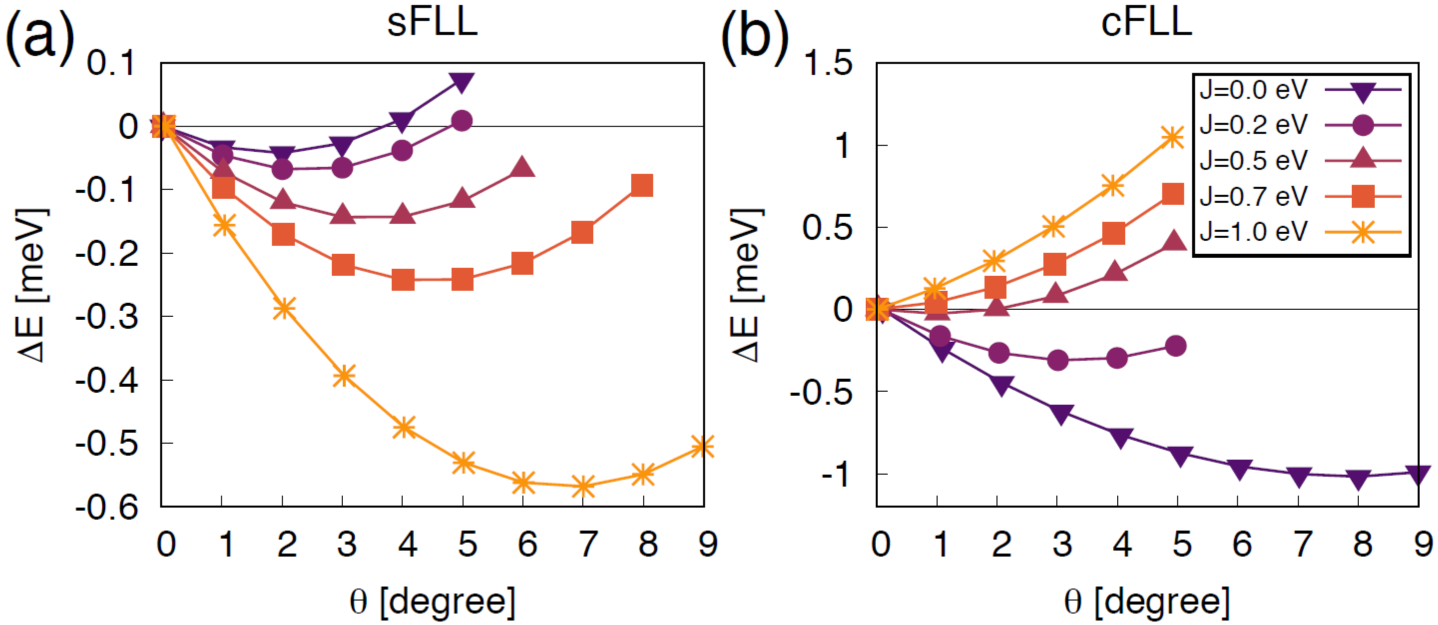


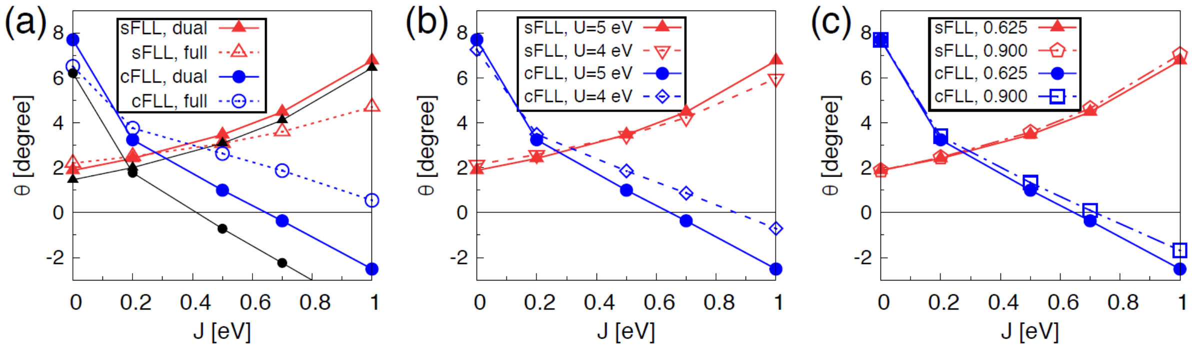
The first CDFT+U calculation for this classical material. The detailed electronic structure and orbital-dependent magnetic interaction analyzed.



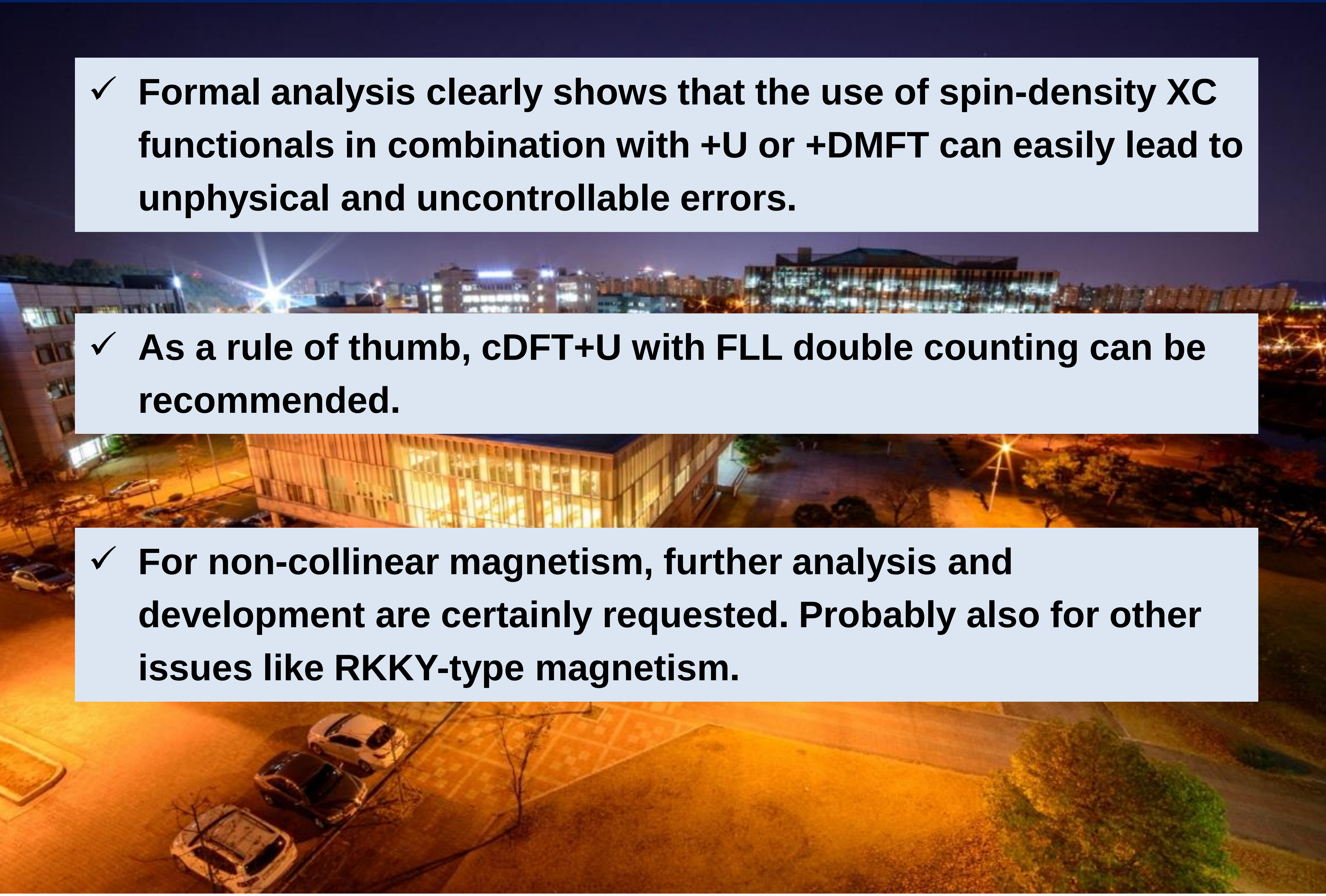
The Case for Non-collinear Orders

S. Ryee and MJH, J. Phys. CM (2018)





Summary and Perspective (Part 2)



- ✓ Formal analysis clearly shows that the use of spin-density XC functionals in combination with +U or +DMFT can easily lead to unphysical and uncontrollable errors.
- ✓ As a rule of thumb, cDFT+U with FLL double counting can be recommended.
- ✓ For non-collinear magnetism, further analysis and development are certainly requested. Probably also for other issues like RKKY-type magnetism.