New Frontiers in QMC Materials Science

Jaron T. Krogel

OLCF Users Meeting

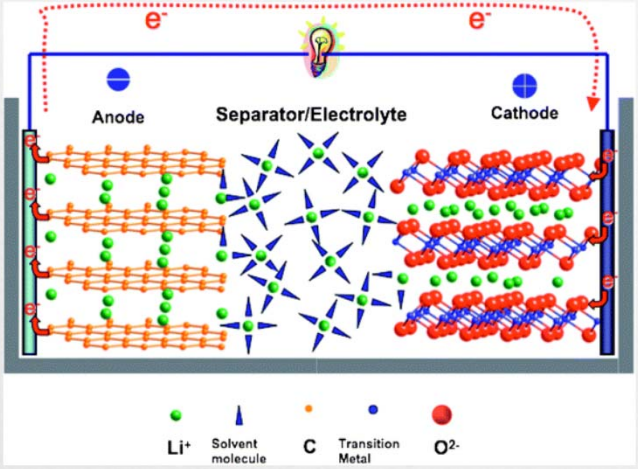
23 July 2014

Outline

- Motivation
  - Predictive theory for transition metal oxide systems
- Quantum Monte Carlo
  - Sketch of QMC methodology: what is QMC?
  - Overview of capabilities and problem domain
- Frontiers in QMC Materials Science
  - Efficiency: High throughput/accessibility
  - Materials: Transition metal oxides

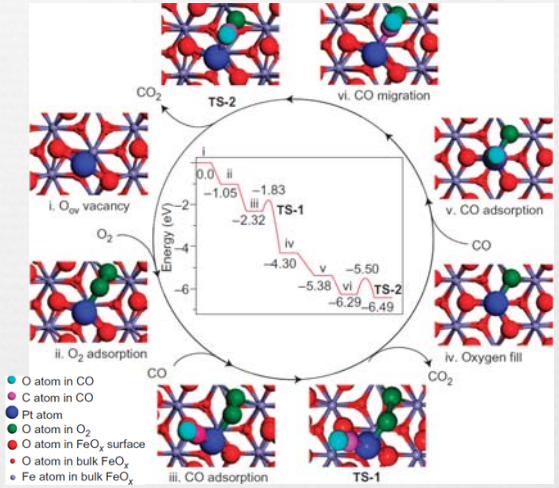
Energy Applications of TM Oxides

Li-Ion Batteries



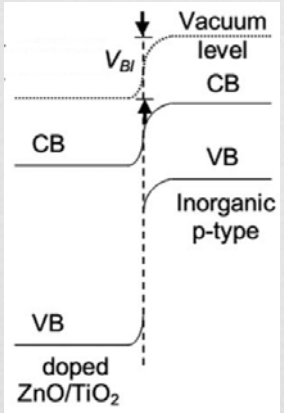
Meng et al. EES **2** 589 (2009)

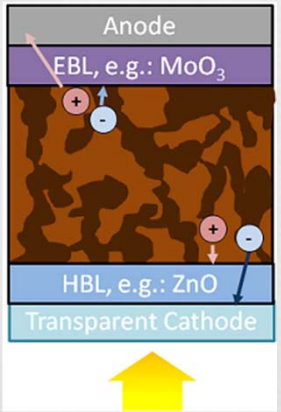
Catalysis



Qiao et al. NC **3** 634 (2011)

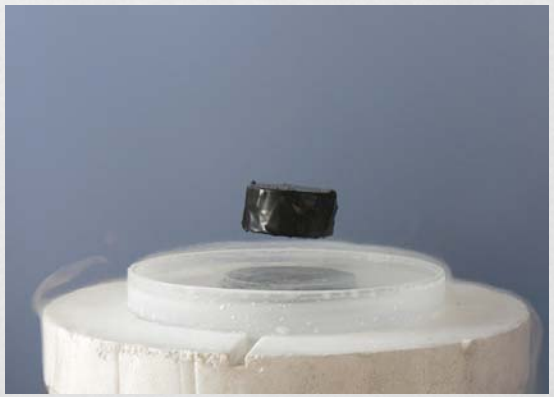
Photovoltaics





Hoye et al. APLM **1** 060701 (2013)

Superconductivity



Predictive Theory for Materials Science

- Transition metal oxide materials are essential to energy applications: catalysis, Li-ion batteries, superconductivity, etc.
- Materials Genome Initiative: faster, more accurate predictions

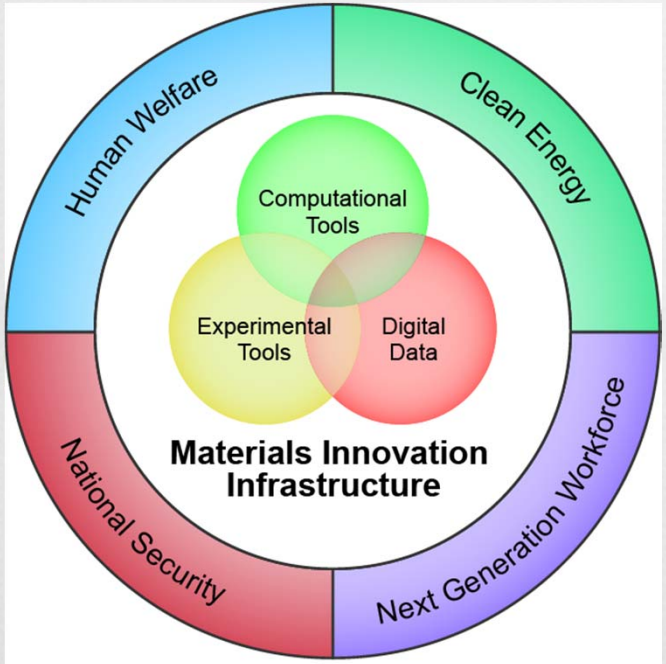


Figure 3: Initiative overview

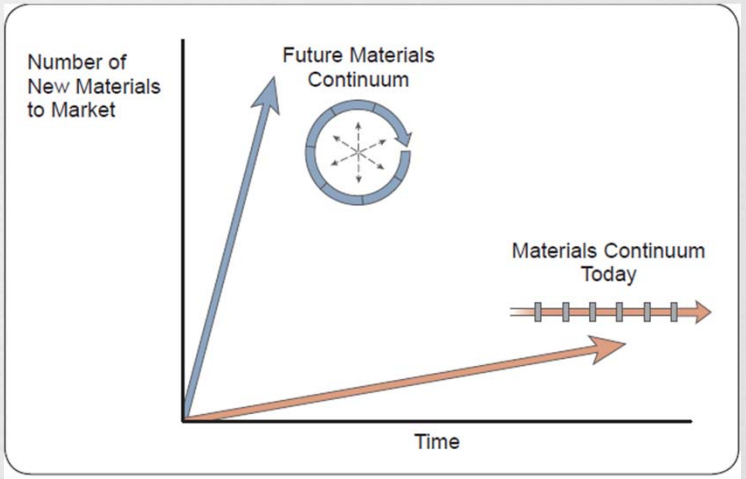


Figure 2: Initiative acceleration of the materials continuum

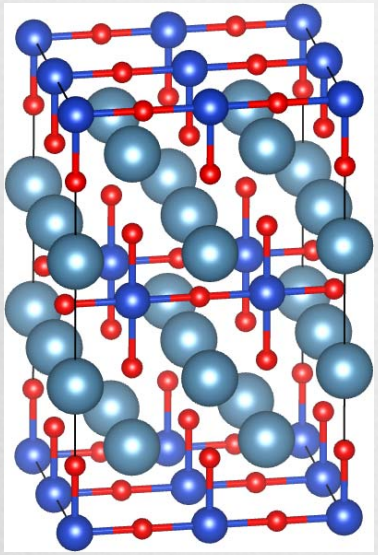
http://www.whitehouse.gov/mgi

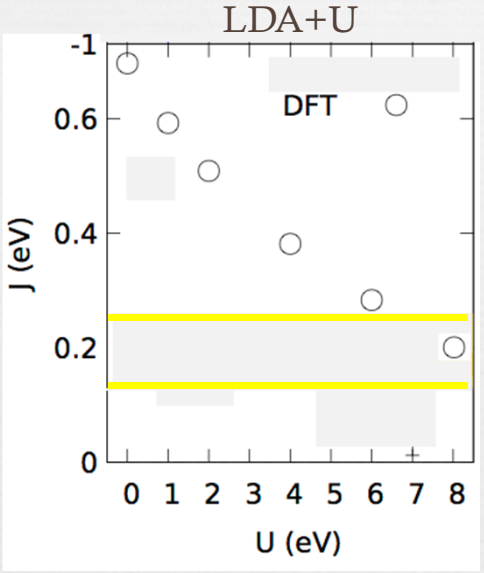
Predictive Theory for Materials Science

- Transition metal oxide materials are essential to energy applications: catalysis, Li-ion batteries, superconductivity, etc.
- Accurate description is challenging for elec. structure methods
  - Strong electron correlation
  - Open shell d-states w/ near degeneracy
- Density Functional Theory (DFT) may not give the desired level of accuracy, in some cases, w/o empirical adjustment
  - Hubbard U parameter in LDA/GGA+U
  - Fraction of exact exchange in hybrid functionals (e.g. HSE)
- There is a need to go beyond DFT for certain, important cases

Examples of Empiricism

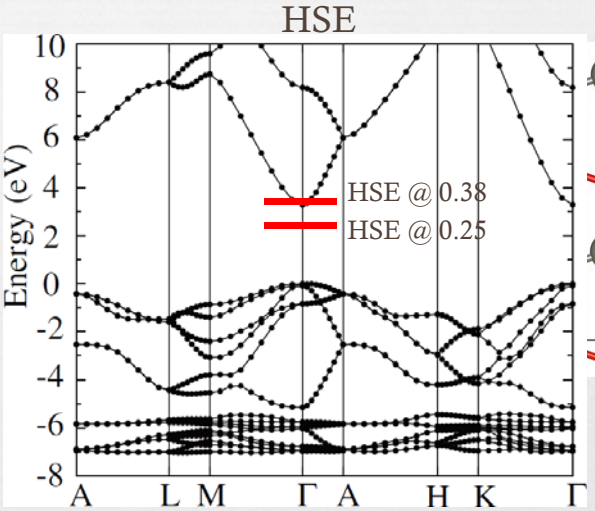
- 1D cuprate Ca_2CuO_3

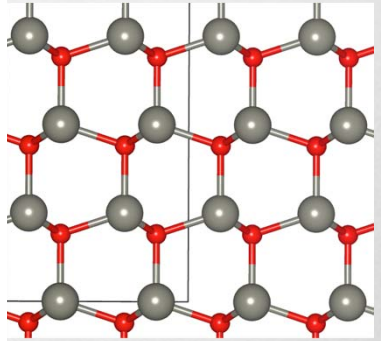




- Results sensitive to choice of U
- Hubbard U adjusted to match experimental J

- Band gap of zinc oxide





- Gap depends on exch. fraction
- Adjusted to match exp. gap, 3.4 eV

Beyond DFT: Quantum Monte Carlo

- Quantum Monte Carlo (QMC) provides an alternative to DFT for target systems
- QMC has recently been successfully applied to transition metal oxide systems
  - Cohesive energies of MnO[1], FeO[2], NiO[3]
  - Band gaps of MnO[4], FeO[2]
- Can we obtain predictive accuracy other properties?
  - spin states in cuprates
  - defects in semiconducting oxides

[1]Kolorenc et al. PRB **82** 115108 (2010)
[2]Kolorenc et al. PRL **101** 185502 (2008)
[3]Needs et al. IJMPB **17** 5425 (2003)
[4]Mitas et al. RMG **71** 137 (2010)

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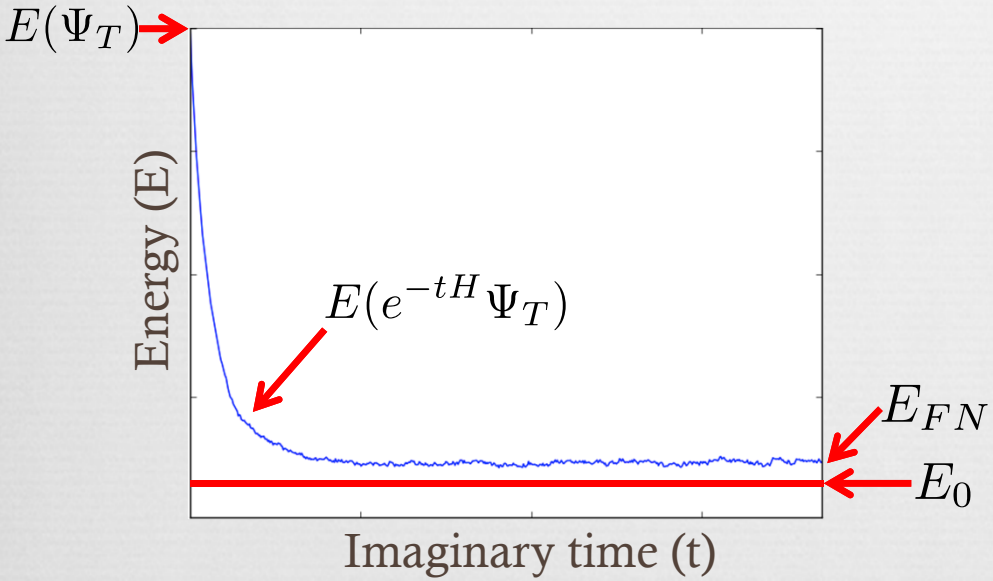
- Motivation
  - Predictive theory for transition metal oxide systems
- Quantum Monte Carlo
  - Sketch of QMC methodology: what is QMC?
  - Overview of capabilities and problem domain
- Frontiers in QMC Materials Science
  - Efficiency: High throughput/accessibility
  - Materials: Transition metal oxides
  - Measurement: Quantities beyond the total energy
  - Analysis: Big data

Sketch of QMC Methodology

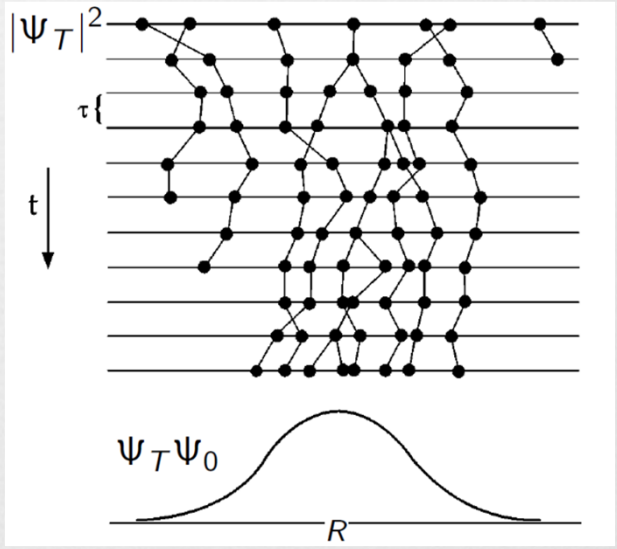
- QMC directly attacks the many body Schrödinger equation

$$H\Psi_n = E_n\Psi_n, \quad H = \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_i v_{r_i}^{eI} + \sum_{i<j} v_{r_i - r_j}^{ee}$$

Constrained projection onto ground state



Projection $\rightarrow$ branching random walk



- Essential approximations: Fixed nodes, pseudopotentials

$$\Psi_T = 0$$
$$e^{-tH}\Psi_T = 0$$

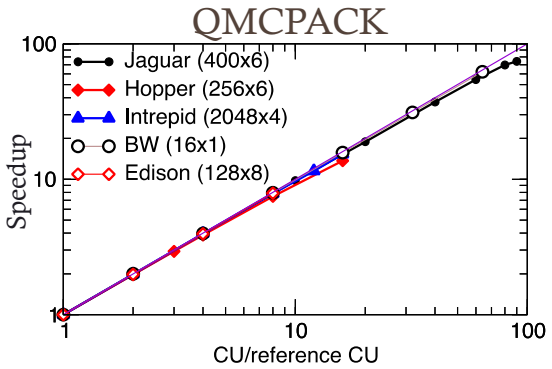
$$v^{eI} \approx \sum_\ell |Y_{\ell m}\rangle v_\ell^{PP} \langle Y_{\ell m}|$$

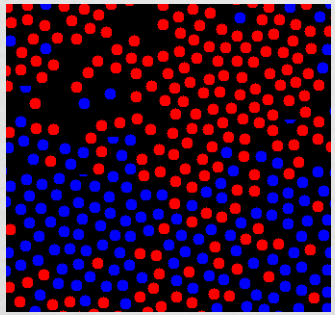
Scope of QMC Calculations

- General physics
  - Can be applied to solids, molecules, van der Waals & strongly correlated materials on equal footing
- High accuracy
  - Provide predictive accuracy on important systems
  - Provide data to parameterize models for larger systems
- High human time
  - Controllable approx. take time to minimize for quality
- High computational cost
  - Small systems (100's of atoms), scales like $O(N^3)$

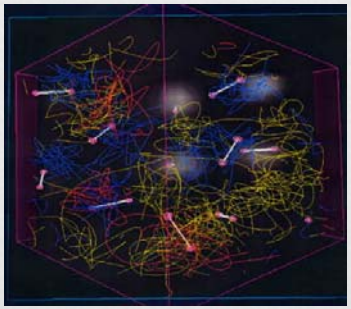
Expanding Domain of Application

- High cost moderated by near perfect scaling
- QMC typically performed on light elements
- Advances in computing power have expanded QMC's domain to include challenging materials
- With Titan, QMC can now be applied to transition metal oxides, such as the cuprates

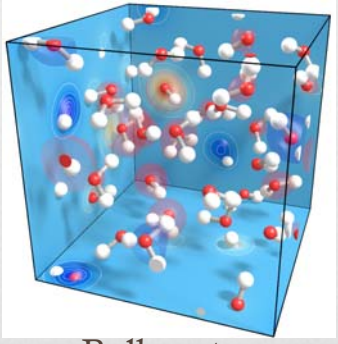




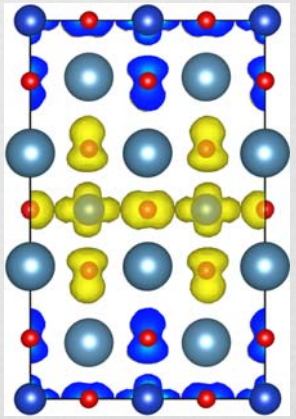
Hard-core bosons, CDC 6600 (1974)



Dense Hydrogen, Origin (2000)



Bulk water, XT5 (2009)



Cuprate: Ca_2CuO_3, XE6/XK7 (2013)

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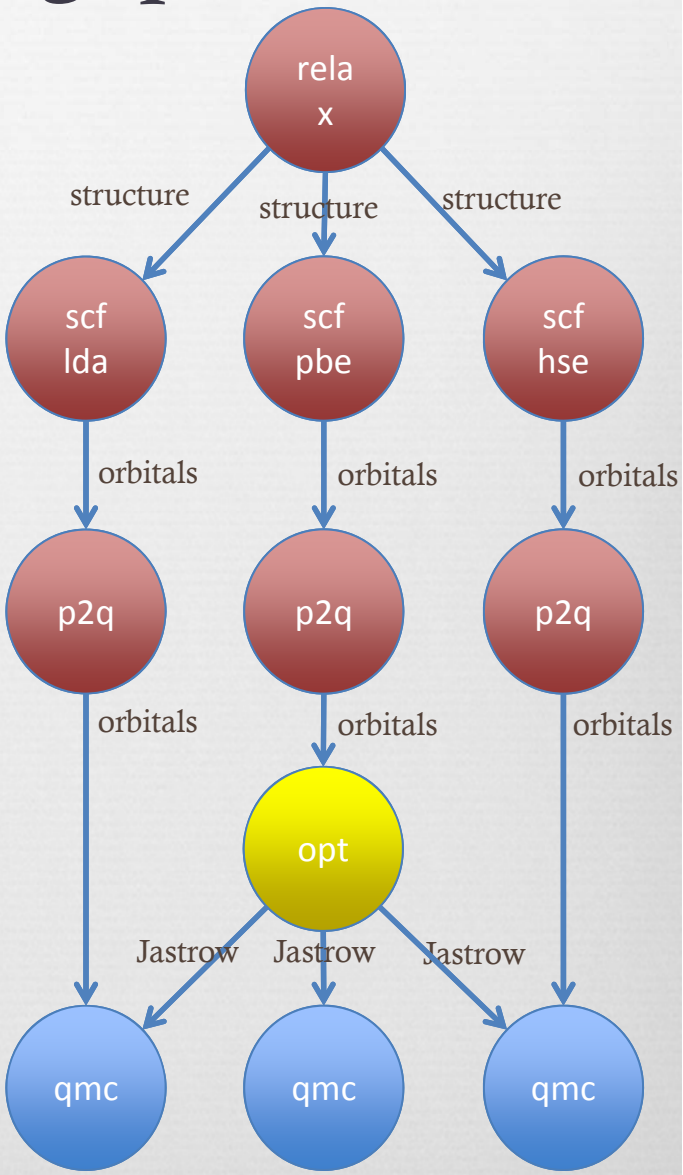
Frontier: High-Throughput

- QMC calc.'s have many stages, time consuming
- Created a user system that combines expert knowledge with automation: the Project Suite
- Enables high-throughput, complex workflows
- Reduces errors, increases productivity
- Provides natural documentation of exact work performed: greater reproducibility
- Three researchers w/o prior QMC expertise used the Project Suite to produce quality work quickly


Kateryna Foyevtsova


Juan Santana-Palacio


Chandrima Mitra



QMC Glue Collaboration

- QMC Training Program (ANL, summer 2014) used the Project Suite
- QMC Glue is in line with the Materials Genome Initiative

How Accurate is QMC?

- Bulk modulus for ionic, covalent, metallic, & vdW solids

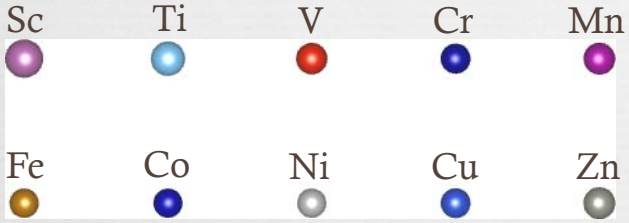
Material	DMC	Statistical error	LDA	PBE	AM05	HSEsol	vdW-DF2	vdW-optB86b	Experiment
Al	83.35	0.58	81.40	76.50	83.90	85.60	60.10	77.00	82.00
Ar	3.80	0.10	7.10	0.74		0.41	4.90	3.62	3.38
Be	119.28	2.42	136.26	136.30	128.50	130.60	126.50	119.70	121.65
BN	399.34	1.92	394.00	373.00	378.00	413.30	343.80	374.70	410.20
BP	172.85	2.08	171.00	161.70	165.00	178.90	146.32	163.30	168.00
C	450.86	3.54	456.00	433.10	442.00	480.40	395.00	431.00	454.70
Kr	3.90	0.10	6.78	0.63		0.50	4.72	3.71	3.66
LiCl	35.53	0.48	40.40	31.80	30.30	36.30	32.30	34.30	38.70
Li	12.64	0.26	13.70	13.90	13.00	13.30	14.70	13.40	13.90
LiF	74.40	1.47	66.70	67.70	65.80	77.20	68.90	70.20	76.30
SiC	239.61	0.48	224.00	211.50	217.00	237.30	191.00	215.00	229.10
Si	105.95	0.44	93.60	88.30	90.20	101.30	79.60	91.20	100.80
Xe	3.60	0.10	6.17	0.53		0.77	4.22	3.65	3.87
ME	−0.15	0.54	−1.83	−10.16	−8.17	5.89	−23.71	−10.56	
MAE	4.53	0.54	5.95	13.09	9.92	6.49	24.84	10.56	
MRE (%)	−1.10	0.40	−0.96	−6.15	−6.22	1.94	−12.31	−6.30	
MARE (%)	3.94	0.40	4.65	8.55	7.81	4.04	14.26	6.30	
ME (all)	−0.09	0.42	−0.70	−8.54		3.82	−18.01	−8.11	
MAE (all)	3.55	0.42	5.28	10.76		5.70	19.34	8.16	
MRE (all) (%)	0.08	0.48	18.86	−23.73		−18.09	−3.08	−4.63	
MARE (all) (%)	5.03	0.48	23.18	25.58		22.69	17.35	5.94	

Shulenburger & Mattsson PRB **88** 245117 (2013)

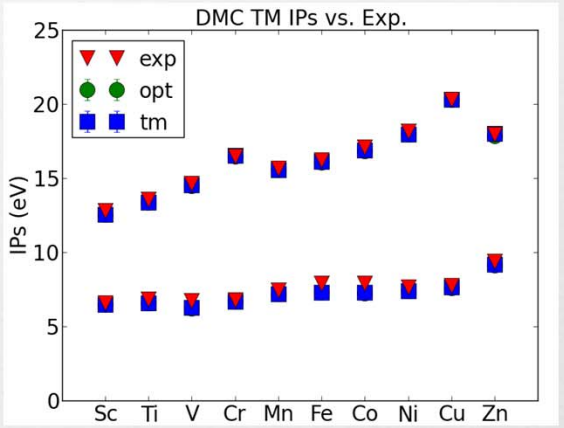
Accurate Pseudopotentials

- Small (Ne) core PP's* tested for TM's. Expensive, but accurate.

Atoms



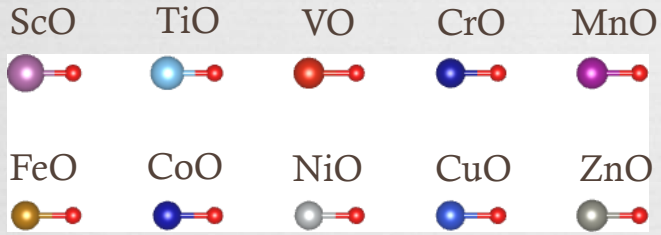
Ionization Potentials



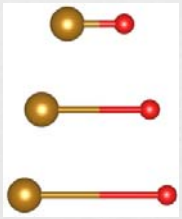
2nd IP

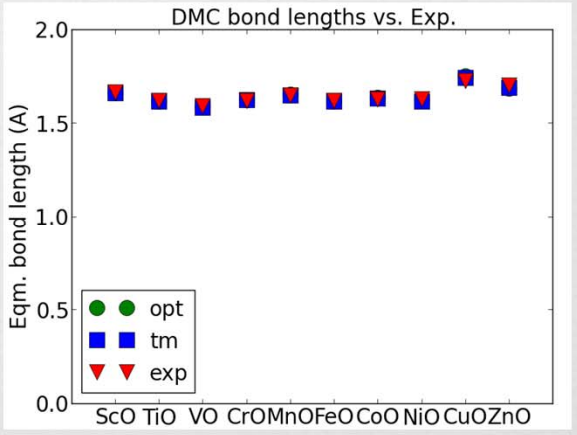
1st IP

Dimers



Binding Curves





Krogel, Santana, Foyevtsova, Reboredo (in progress)

*Special thanks to H. Dixit for approach to PP generation.

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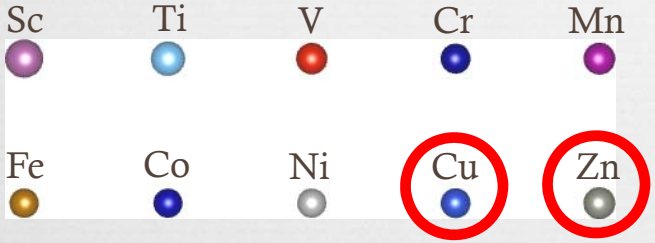

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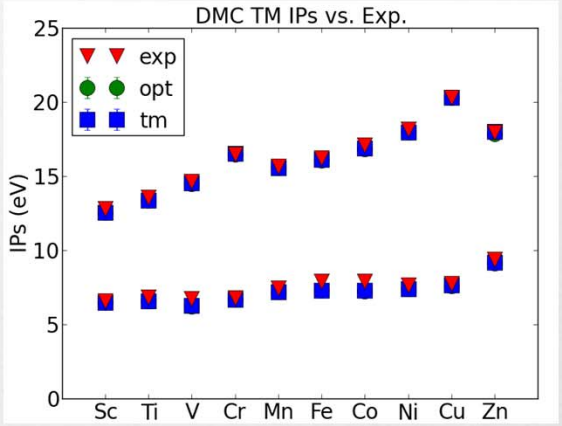

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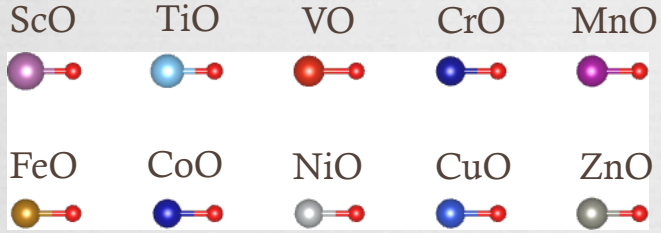

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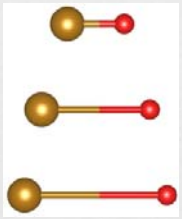

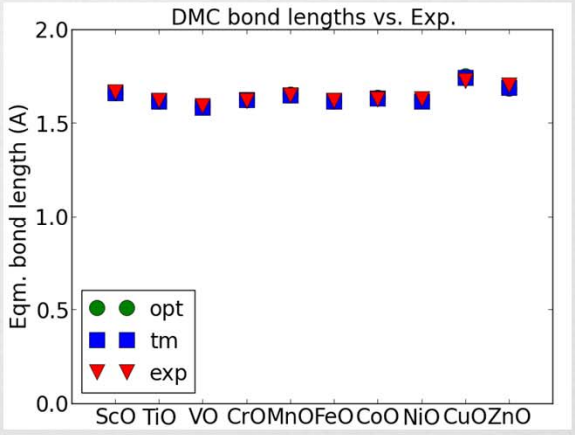

Krogel, Santana, Foyevtsova, Reboredo (in progress)

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Frontier: Transition Metal Oxides

- Challenges
  - strongly correlated d-electrons
  - valence space must contain many electrons for high-accuracy
- Materials studied
  - Ca_2CuO_3: 1-dimensional cuprate, spin states
  - $Ca_2CuO_2Cl_2$: 2-dimensional cuprate, charge excitations
  - ZnO: semiconductor, O vacancy ionization levels

Representative Cuprates

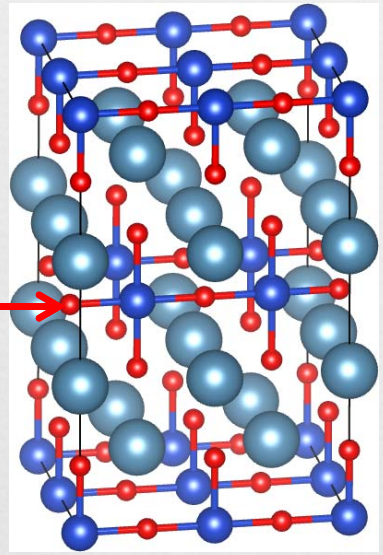
- Important target for accurate calculations are the host materials of high-T_c superconductivity: the cuprates
- Spin d.o.f. may cause attraction between charge carriers
- Need an accurate description of:
  - Spin excitation spectra
  - Hole quasiparticle energies
  - Spin-hole interactions

Representative Cuprates

- Two representative systems:
  - Ca_2CuO_3: effectively 1-dimensional, does not superconduct
  - $Ca_2CuO_2Cl_2$: effectively 2-dimensional, superconducting

Ca_2CuO_3

CuO_3 1D chains

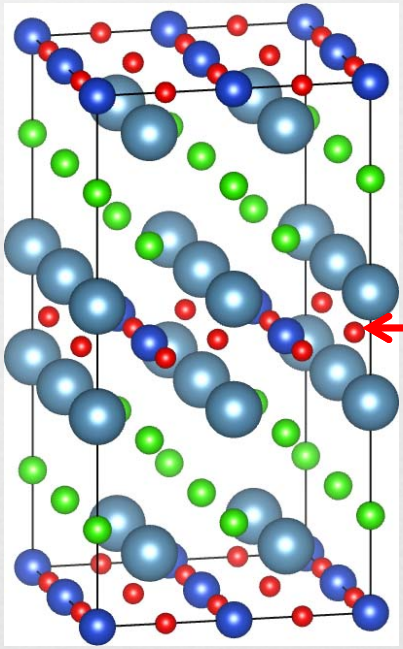


Ca
Cu
O
Cl

Fovevtsova, **Krogel**, Kim, Kent, Dagotto, Reboredo PRX **4** 031003 (2014)

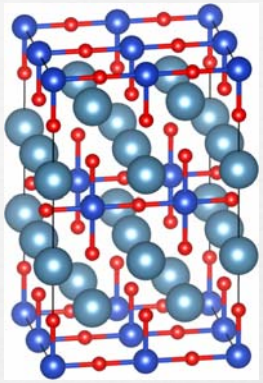
$Ca_2CuO_2Cl_2$

CuO_2 2D plane



Krogel et al. (in progress)

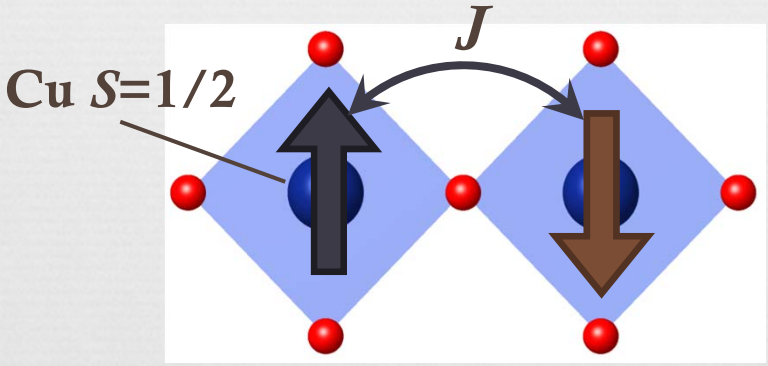
1D Cuprate: $(Sr/Ca)_2CuO_3$



- Simple structure modeled well by 1D spin chain system
- Nearest neighbor Heisenberg Hamiltonian

$$H = \sum_{<ij>} J \vec{S}_i \vec{S}_j$$

- Single parameter: superexchange coupling constant *J*



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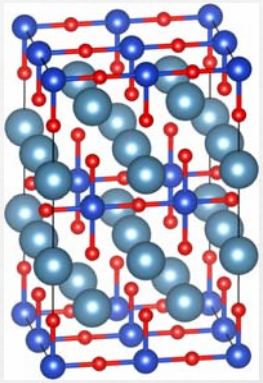
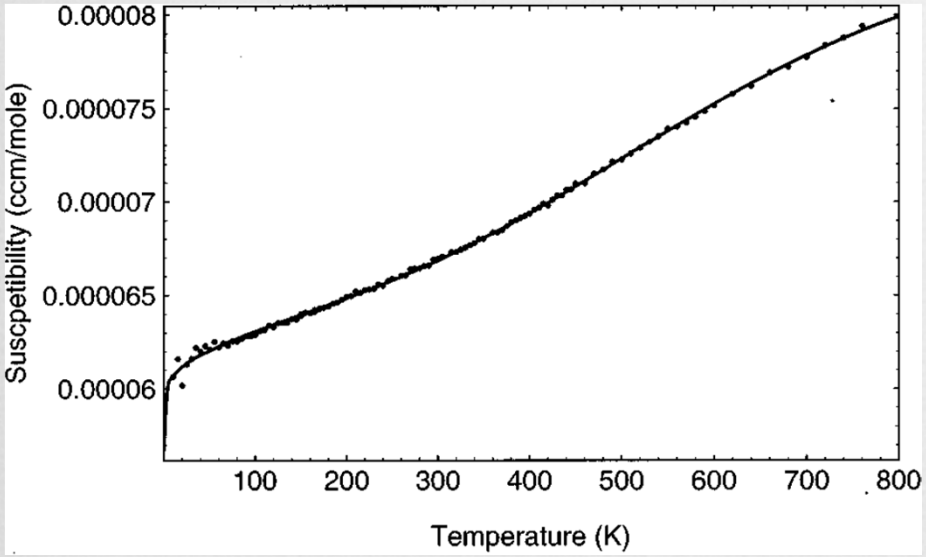


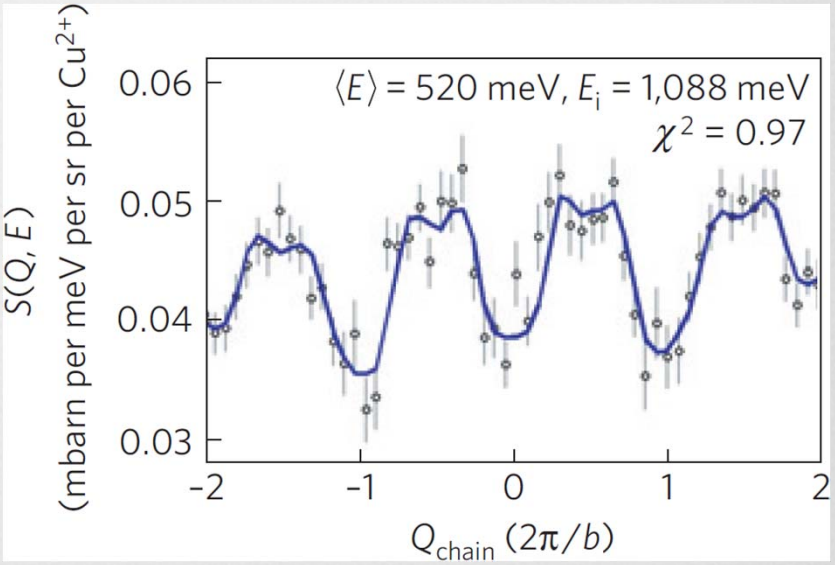
- Can obtain J from a variety of experimental probes:
  $\chi(T)$, ARPES, INS, NMR (Sr_2CuO_3)

Magnetic Susceptibility $\chi(T)$



S. Eggert PRB **53** 5116 (1996)

Inelastic Neutron Scattering (INS)



A. C. Walters et al. Nat. Phys. **5** 867 (2009)

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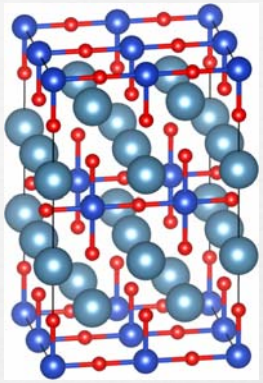

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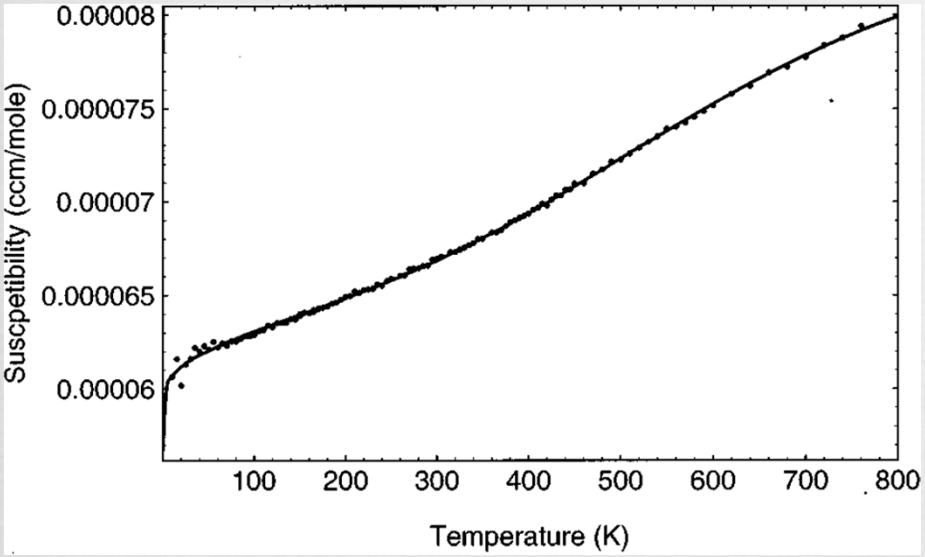
  $\chi(T)$, ARPES, INS, NMR (Sr_2CuO_3)

Magnetic Susceptibility $\chi(T)$

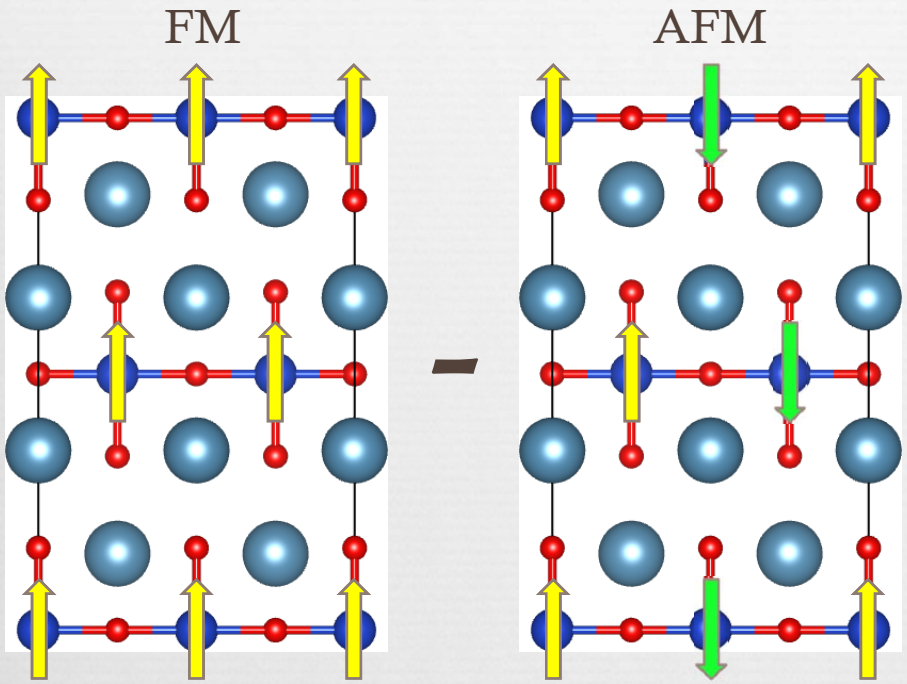


S. Eggert PRB **53** 5116 (1996)

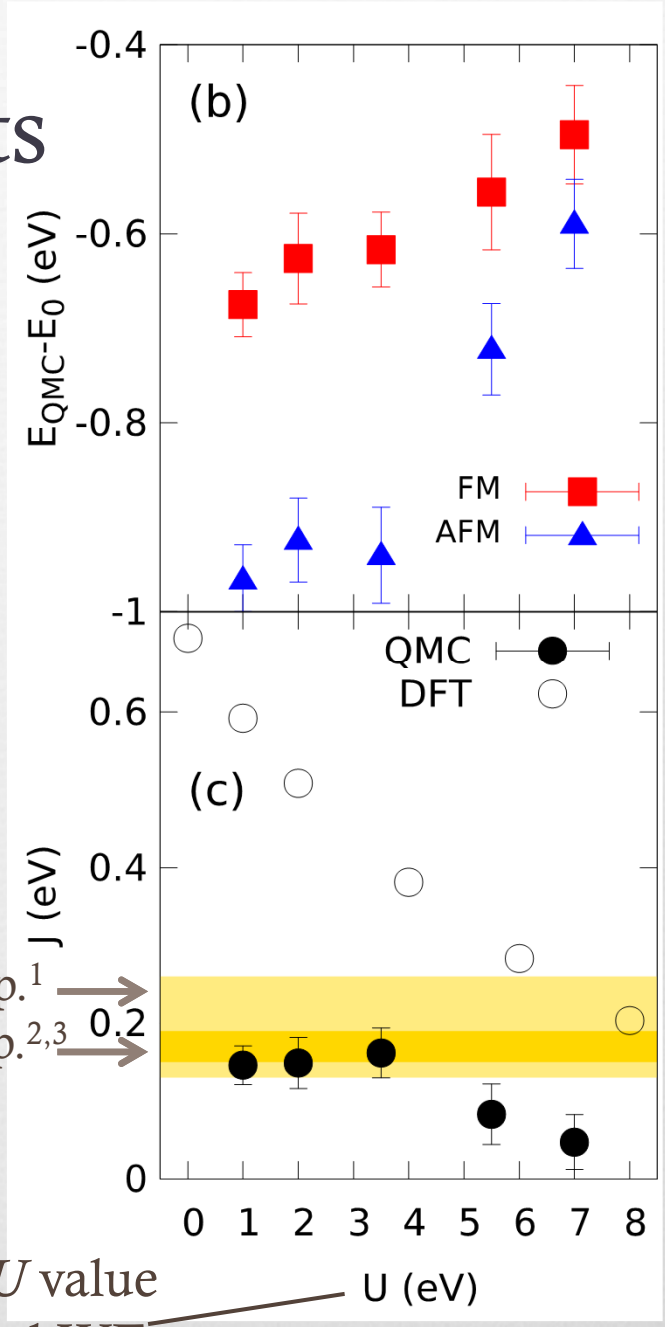
Inelastic Neutron Scattering (INS)

Spallation Neutron Source

QMC Results



$$J \propto E^{FM} - E^{AFM}$$



INS Exp.[1]
$\chi(T)$ Exp.[2,3]

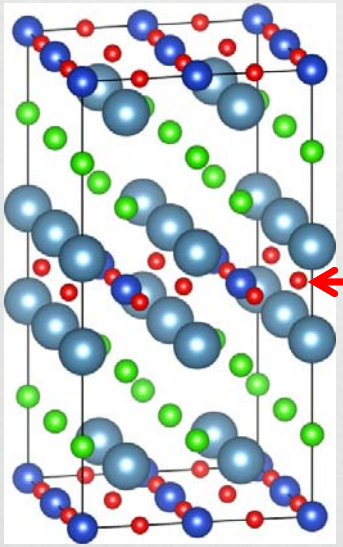
LDA+U *U* value of the trial WF

1 A. C. Walters et al. Nat. Phys. **5** 867 (2009)
2 S. Eggert PRB **53** 5116 (1996)
3 N. Motoyama et al. PRL **76** 3212 (1996)

2D Cuprate: $Ca_2CuO_2Cl_2$

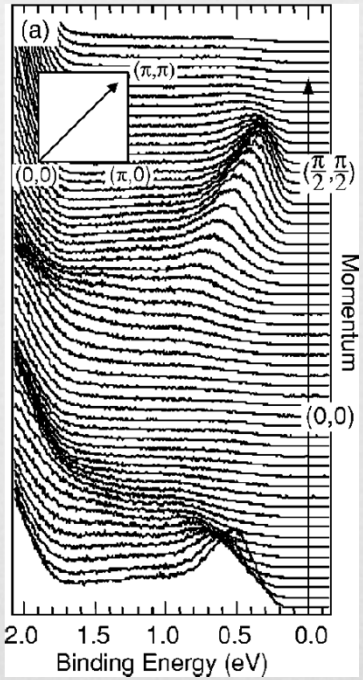
- CCOC ($Ca_2CuO_2Cl_2$) superconducts w/ hole doping
- Study hole addition/electron removal in AFM ground state
- ARPES experiments directly probe electron removal energies

$Ca_2CuO_2Cl_2$



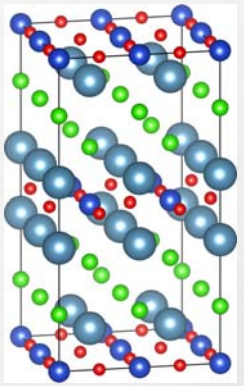
add h^+ / remove e^-

ARPES

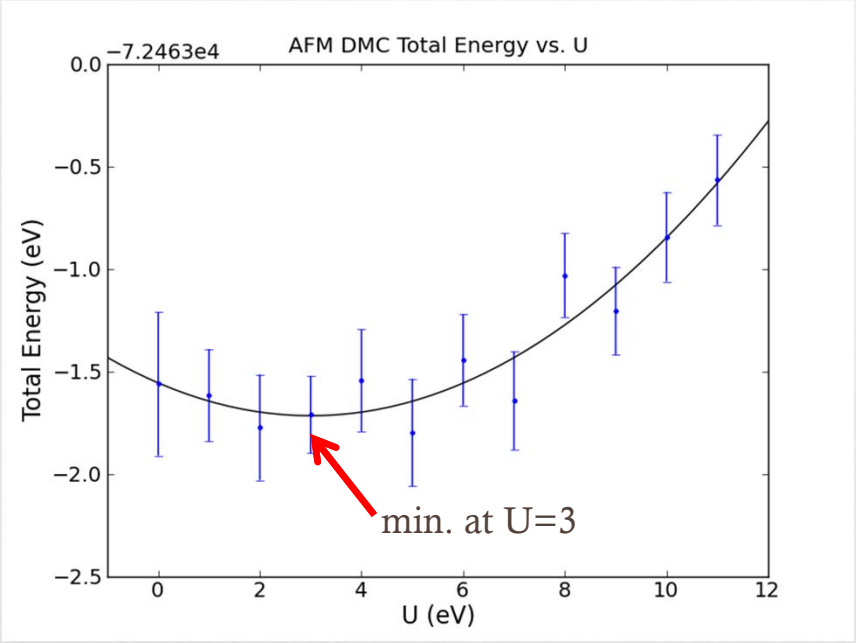


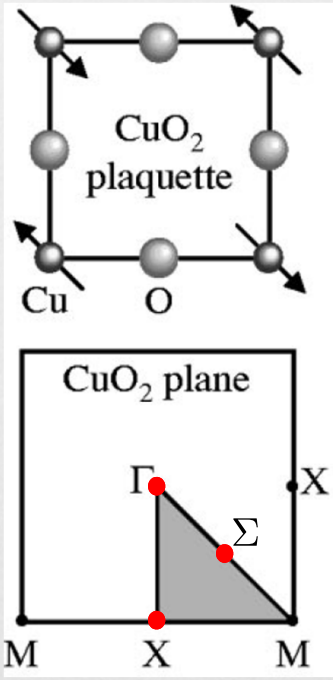
Ronning et al. PRB **71** 094518 (2005)

2D Cuprate: $Ca_2CuO_2Cl_2$



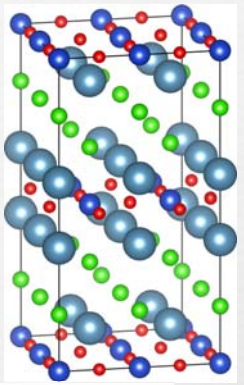
- Minimize AFM energy in QMC w.r.t. U from LDA+U
- Obtain hole-doped CCOC energies at high symm. k-points



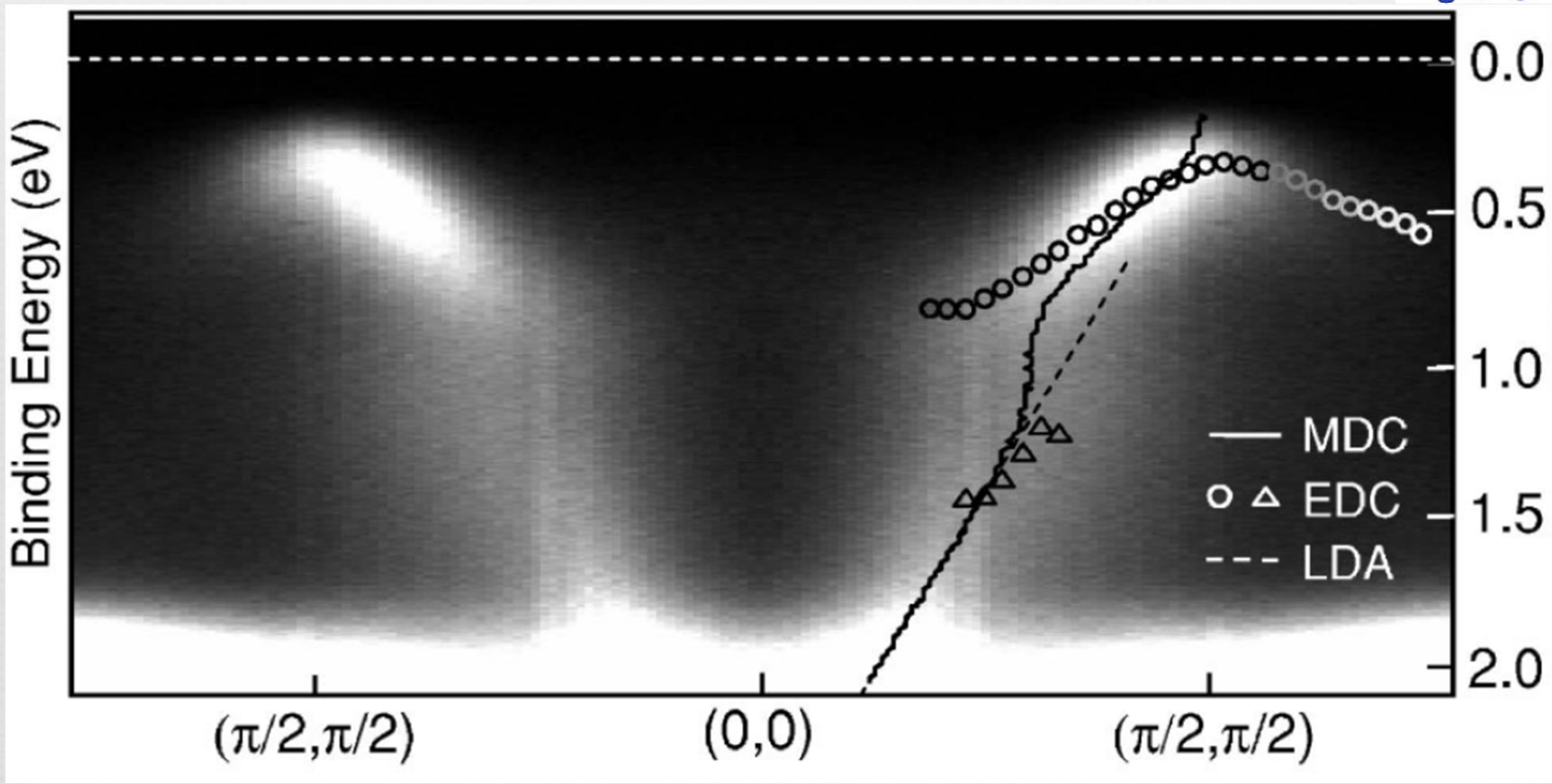


QMC for CCOC+h^+ at Γ, Σ, X

Comparison of QMC & ARPES



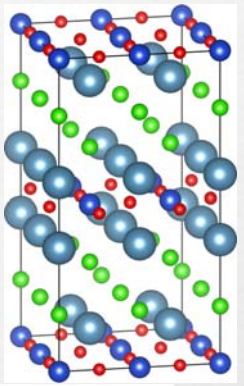
- ARPES data along (110) including Γ & Σ



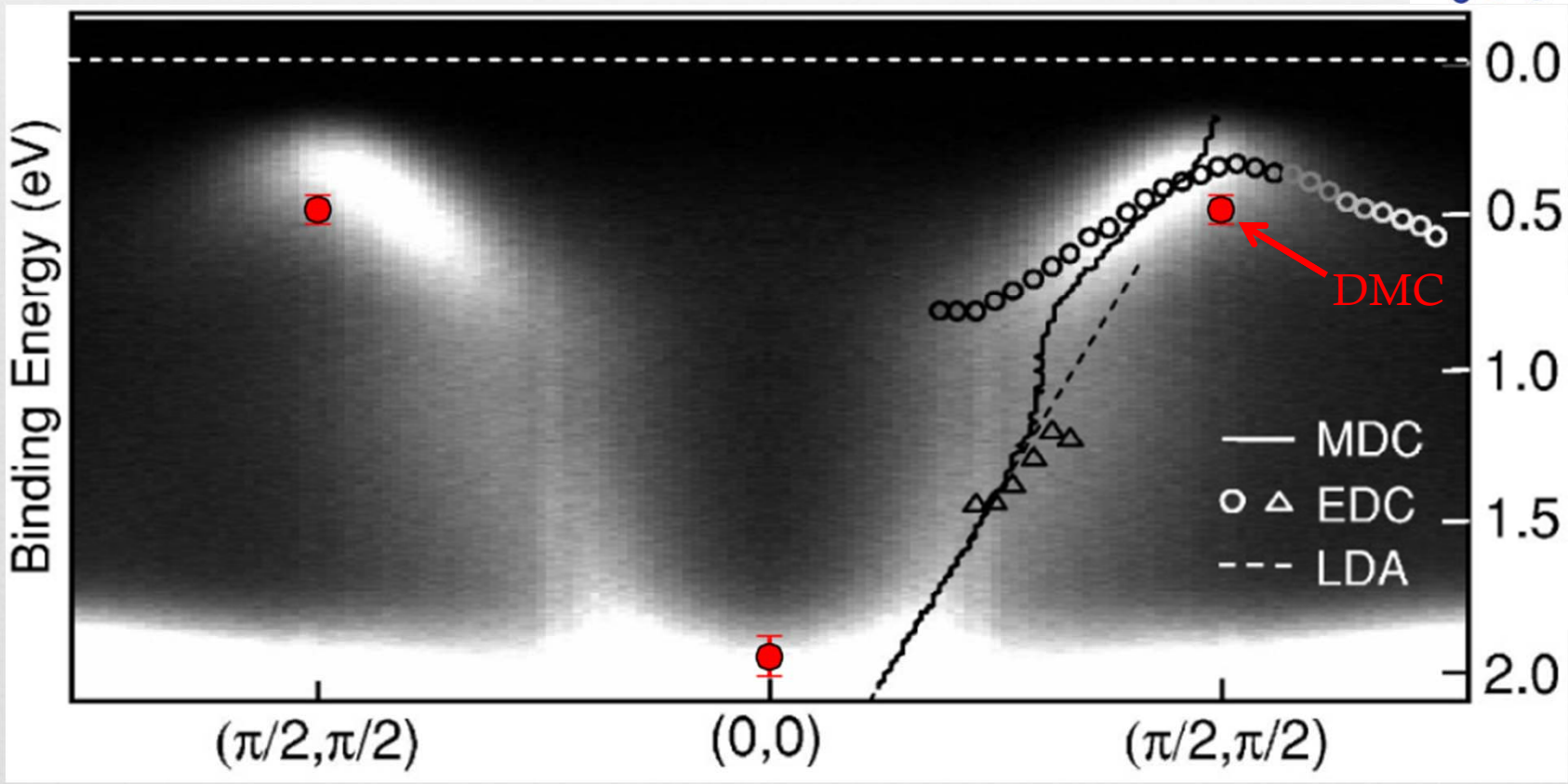
Σ Γ Σ

Ronning et al. PRB **71** 094518 (2005)

Comparison of QMC & ARPES

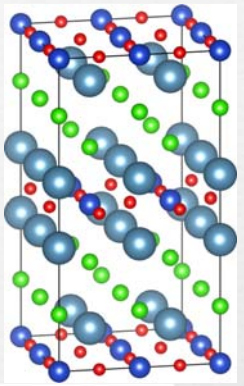


- QMC results for $E_{\Sigma}^{+} - E_{\Gamma}^{+}$ agree w/ ARPES

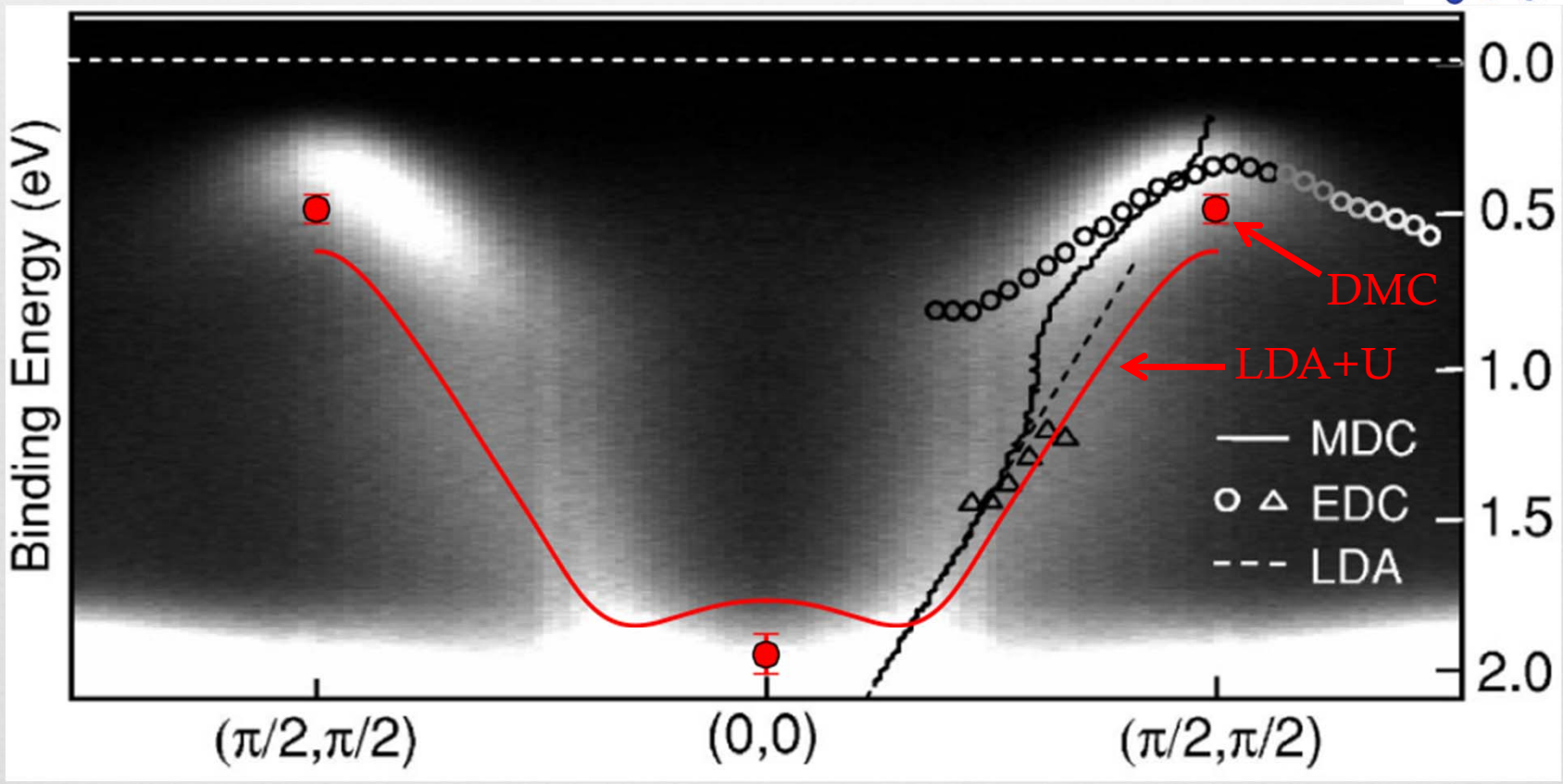


Ronning et al. PRB **71** 094518 (2005)

Comparison of QMC & ARPES



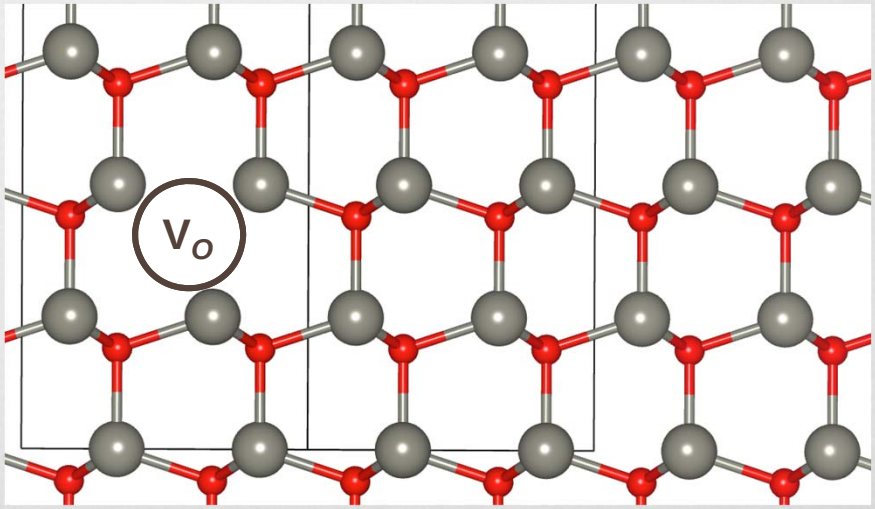
- LDA+U fitted to QMC gives qualitative band shape



Ronning et al. PRB **71** 094518 (2005)

Defects in ZnO

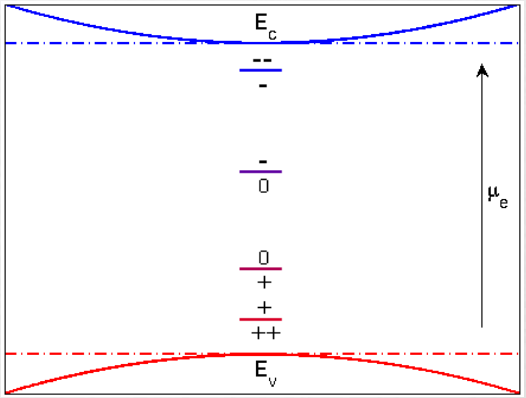
- ZnO is a transparent semiconductor w/ a wide range of potential applications
- Development of applications has been hindered by undesirable n-type conductivity
- Precise identity of shallow donor is unknown, many candidates: O vacancy, Zn interstitial, H impurity, …
- Begin w/ QMC study of O vacancy



Santana, **Krogel**, Kim, Kent, Reboredo (submitted to PRL)

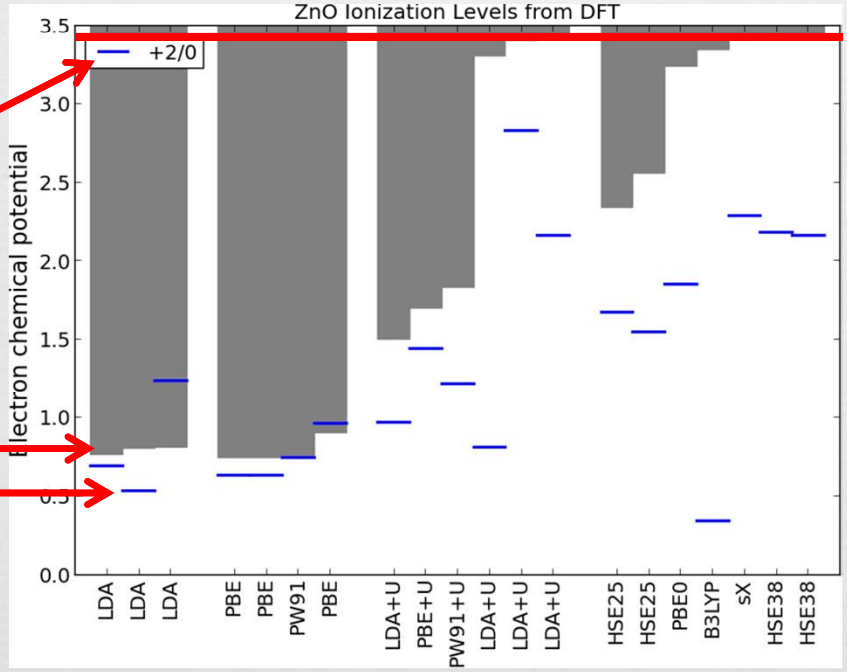
Defect Identification: Ionization Levels

- Ionization level: μ_e where defect changes charge state
- IL's probed experimentally by, e.g., DLTS
- Identification is strongly aided by theory



DFT's agree:
+2/0 is the only observable level

DFT's disagree:
- Band gap
- Loc. of +2/0 in the gap



LDA GGA's LDA/GGA+U Hybrids

$$\mathcal{E}(q'/q) = -\frac{E_f(q') - E_f(q)}{q' - q}$$

$\mathcal{E}(q'/q)$: Ionization level, q to q'

$E_f(q)$: Defect formation energy

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- Band gap
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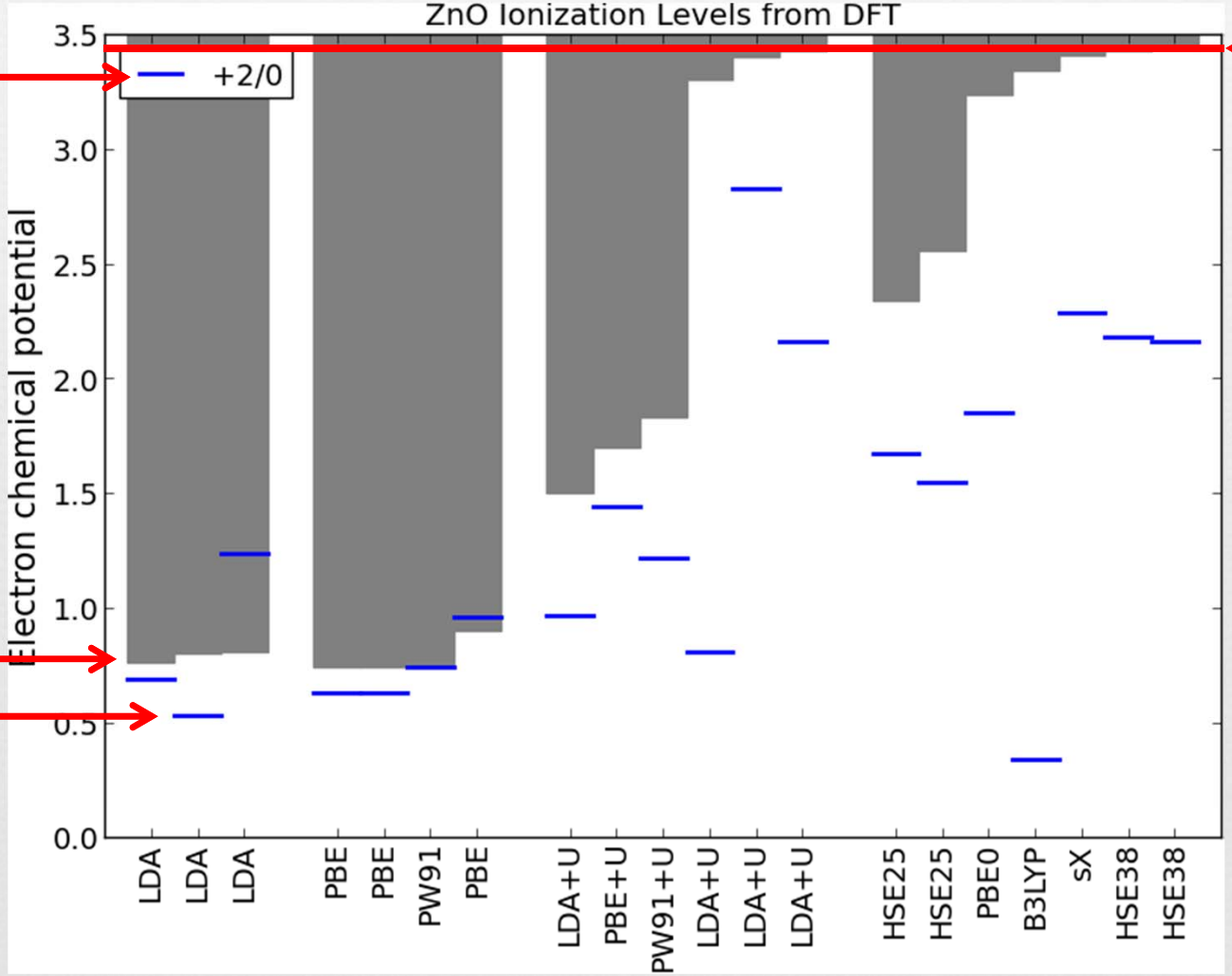
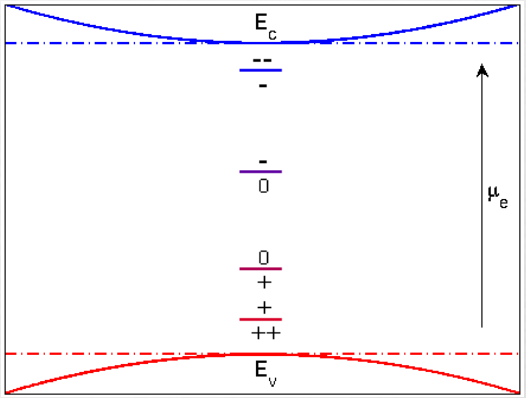


Experimental band gap

LDA GGA's LDA/GGA+U Hybrids

Defect Identification: Ionization Levels

- Ionization level: μ_e where defect changes charge state
- IL's probed experimentally by, e.g., DLTS
- Identification is strongly aided by theory



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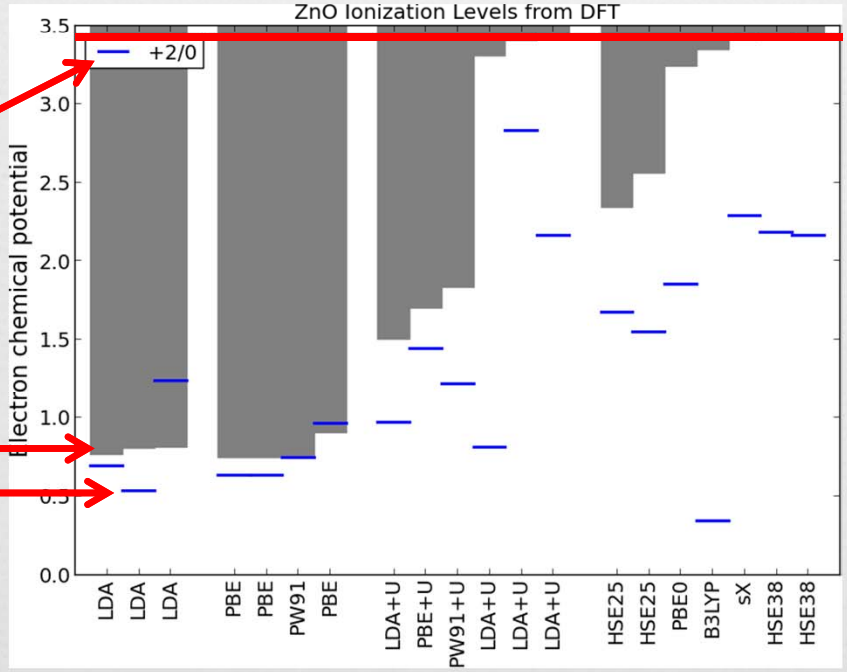

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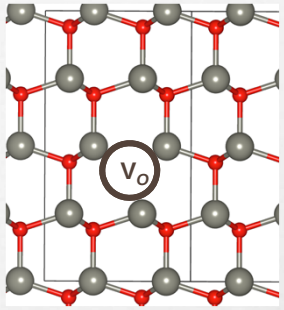
$\mathcal{E}(q'/q)$: Ionization level, q to q'

$E_f(q)$: Defect formation energy

QMC Formation Energies

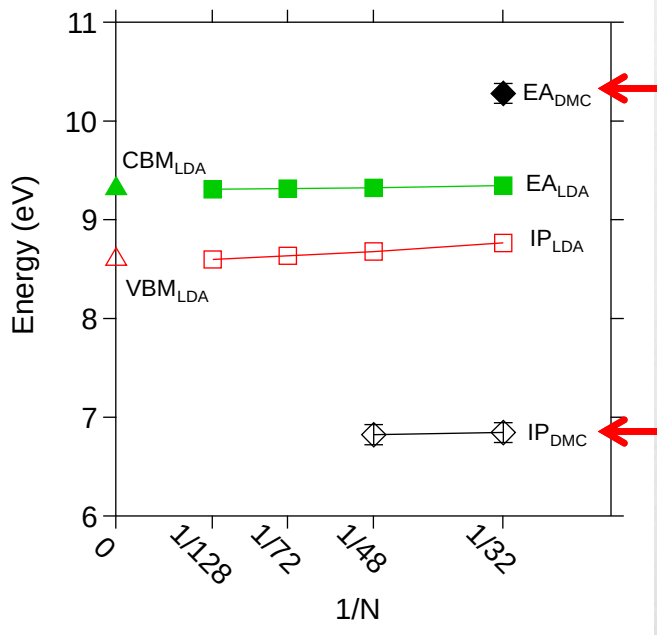


- Formation energy ingredients

$$E_f[V_O^q] = E[V_O^q] - E[ZnO] + \mu_O + q\mu_e + E_{corr}[V_O^q]$$

supercell total energies (QMC)	chemical potentials (QMC)	strain/polarization finite size correction (DFT/Exp.)

- QMC band gap & chemical potential (μ_e)



CBM: electron addition

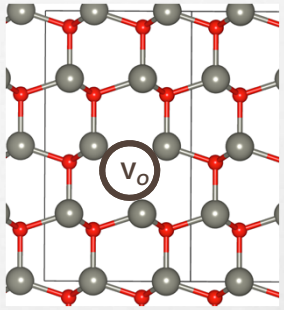
Band gap
- QMC: 3.43(9) eV
- Exp.[1]: 3.44 eV

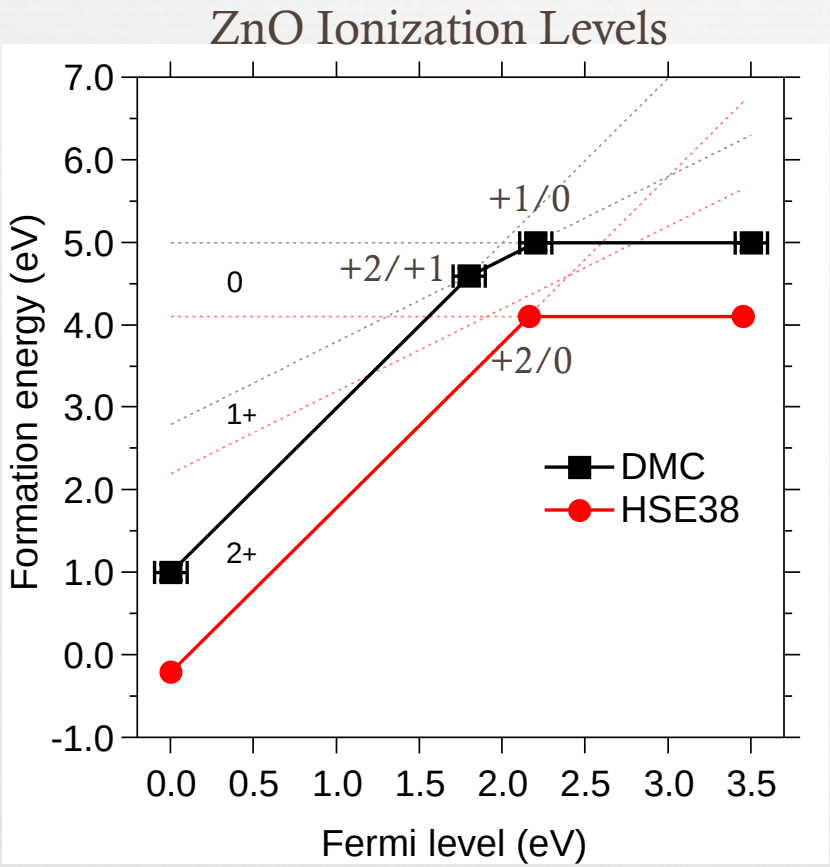
VBM: electron removal

μ_e

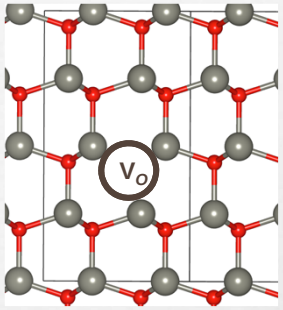
[1]Reynolds et al. PRB **60** 2340 (1999)

QMC Ionization Levels

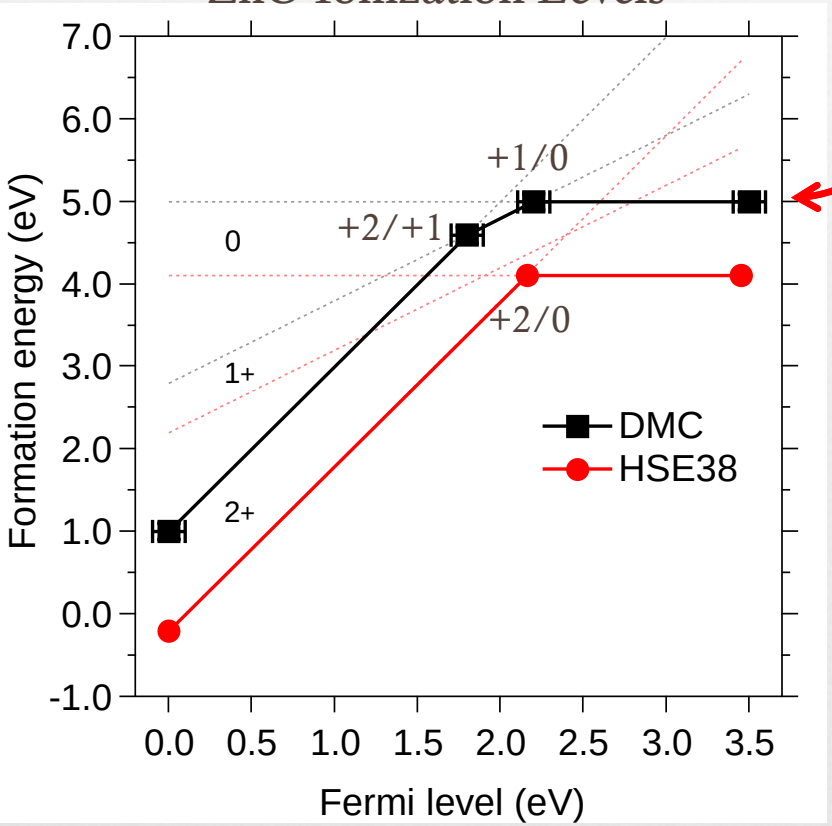




QMC Ionization Levels



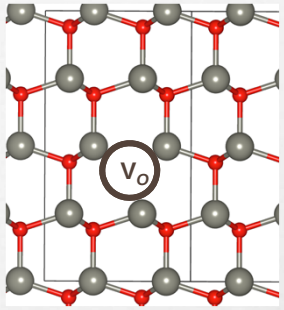
ZnO Ionization Levels

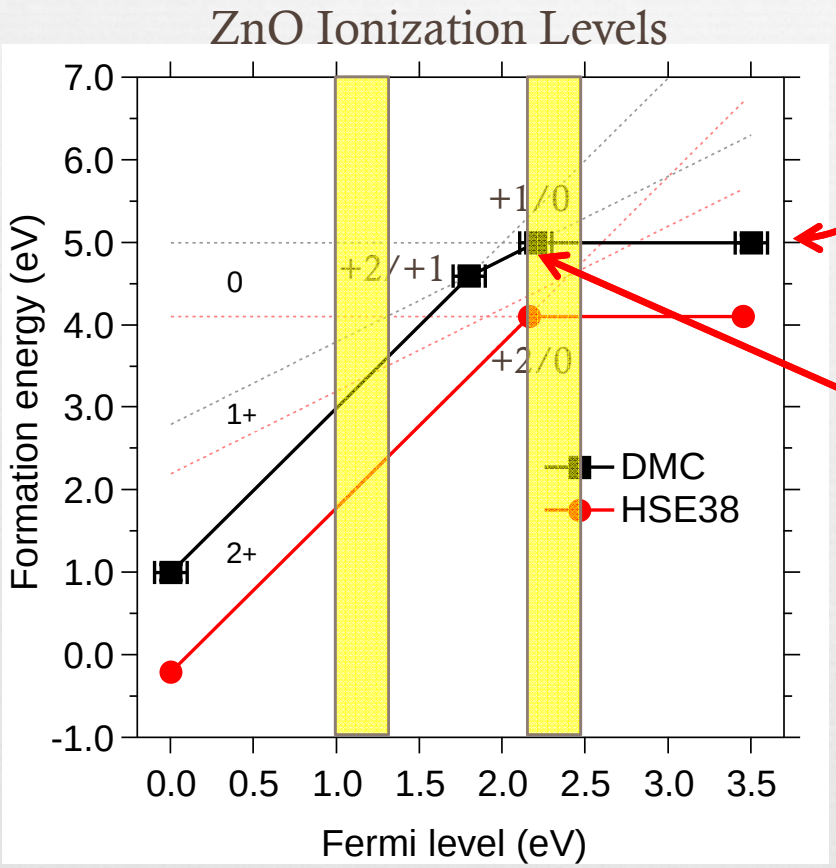


V^0 formation energy:
- QMC: 5.0, 5.2 eV
- Exp.: 5.5[1], 6 eV[2]

[1]Kim et al. JPCB **114** 7874 (2010)
[2]Quemener et al. APL **100** 112108 (2012)

QMC Ionization Levels





<u>V^0 formation energy:</u>
- QMC: 5.0, 5.2 eV
- Exp.: 5.5[1], 6 eV[2]

<u>$V^{+/0}$ ionization level:</u>
- QMC: 2.2, 2.5 eV
- DLTS: 2.4 eV[3]
- EPR: 2.5 eV[4]

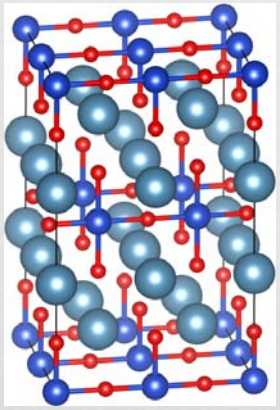
<u>Unassigned V levels</u>
- DLTS: 2.2, 2.4 eV[5]

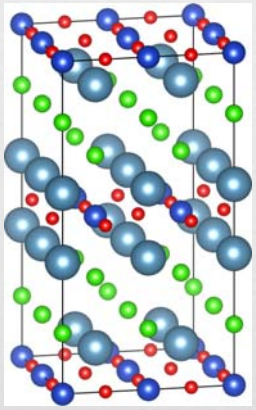
[1]Quemener et al. APL **100** 112108 (2012)
[2]Kim et al. JPCB **114** 7874 (2010)
[3]Chicot et al. arXiv 1401.6851 (2014)
[4]Vlasenko et al. PRB **71** 125210 (2005)
[5]Quemener et al. APL **99** 112112 (2011)

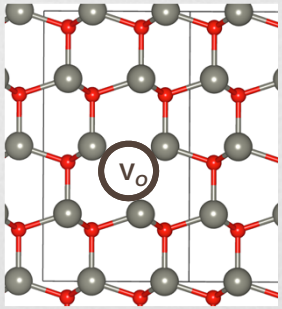
Computing Resources: Titan at OLCF

Millions of hours

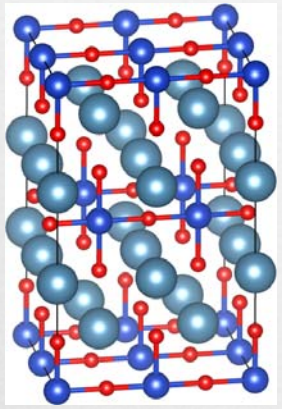
OLCF
Oak Ridge Leadership Computing Facility







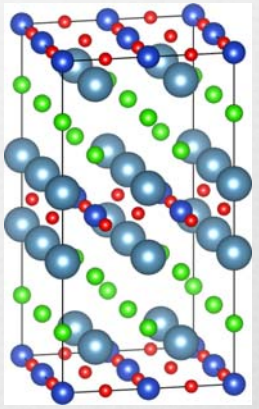
Collaborators for TMO Systems



Kateryna Foyevtsova

Elbio Dagotto

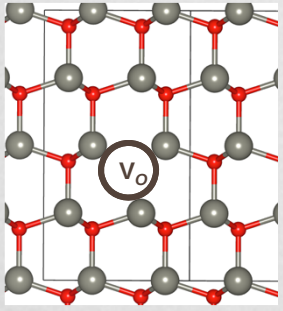
Fernando Reboredo



Jeongnim Kim

Paul Kent

Fernando Reboredo



Juan Santana-Palacio

U.S. DEPARTMENT OF ENERGY

Summary

- There is a need for predictive electronic structure theory of transition metal oxide systems
  - With world-class computing resources (Titan), QMC can meet this need
- Tools now exist for high-throughput comp. with QMC
- Predictive accuracy can be reached with QMC
  - Superexchange coupling constant, J, for Ca_2CuO_3
  - Charged excitations (holes) in $Ca_2CuO_2Cl_2$
  - O vacancy in ZnO: band gap, form. energy, ion. levels

Fixed Phase Diffusion Monte Carlo

A many body method with controllable approximations

- Many body Hamiltonian

$$H = \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_i v_{r_i}^{eI} + \sum_{i<j} v_{r_i - r_j}^{ee}$$

- Trial wave function, best variational approximation

$$\Psi_T = e^{-J} D^{\uparrow} D^{\downarrow} = |\Psi_T| e^{i\phi_T}$$

- Projection via diffusion integral w/ fixed phase constraint

$$\Psi_{FP} = \lim_{t\to\infty} \int dR' \langle R|e^{-tH}|R'\rangle \Psi_T(R') = |\Psi_{FP}| e^{i\phi_T}$$

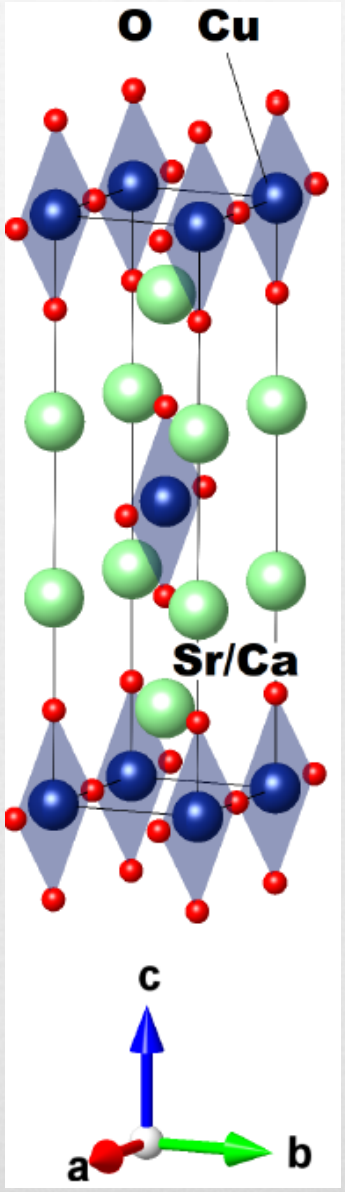
- Total energy within fixed phase approximation

$$E_{FP} = \frac{\langle \Psi_{FP}|H|\Psi_T\rangle}{\langle \Psi_{FP}|\Psi_T\rangle} \geq E_0$$

$$\text{if } \phi_T = \phi_0, \text{ then } \Psi_{FP} = \Psi_0 \ \& \ E_{FP} = E_0$$

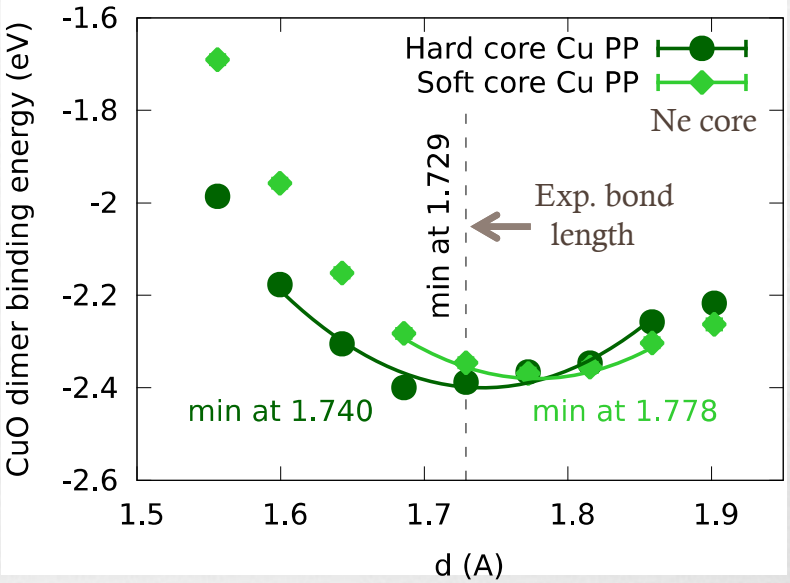
Computational Details

- PW code Quantum Espresso
  - LDA+U Slater determinant
- Supercell
  - 2x1x1 $4x[Ca_2CuO_3]$ 228 e^-
  - 2x2x1 $8x[Ca_2CuO_3]$ 456 e^-
- K-points
  - 4x4x1 prim cell Monkhorst-Pack
- Pseudopotentials
  - Ne-core Cu & Ca
  - He-core O



Pseudopotential Validation

Cu PP core	Ionization Energy
Ar 11 e- valence	Poor DOS
Mg 17 e- valence	8.302(36) eV
Ne 19 e- valence	7.724(37) eV
Experiment	7.72638(1) eV



- Accurate description of Cu semicore states is crucial
- But expensive… 500 Ry PW Ecut needed for hard Cu