

Quantum Monte Carlo from Benchmarking to Understanding Nanoscale Materials

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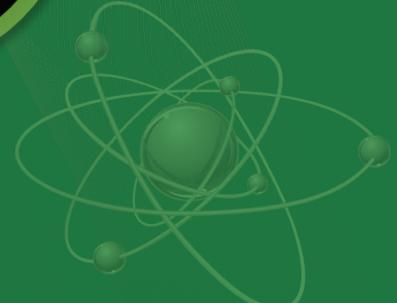
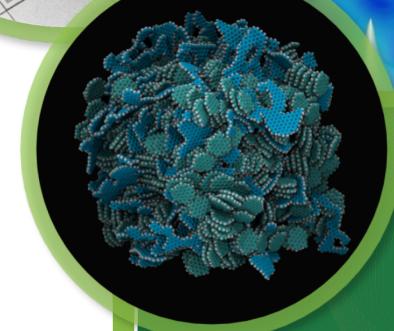
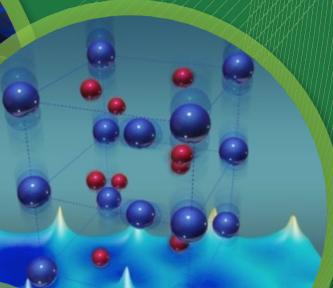


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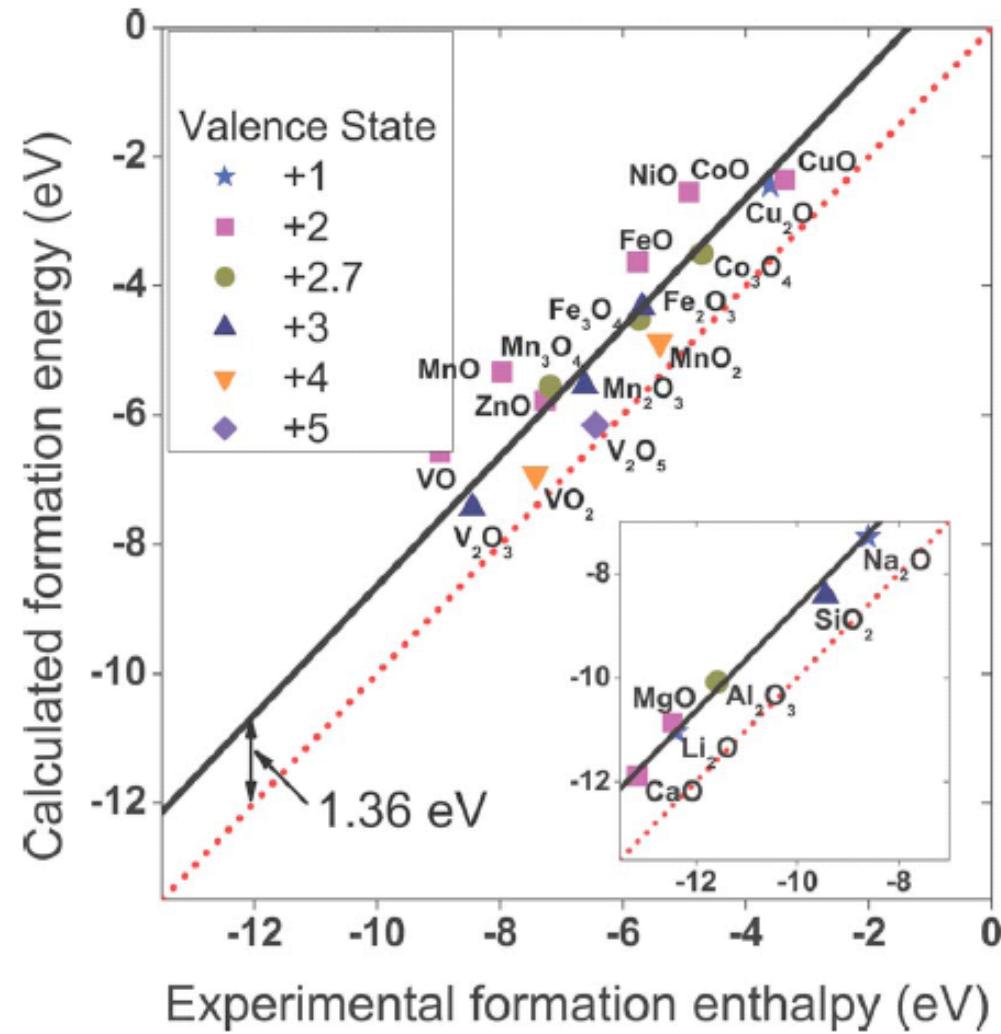
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Outline

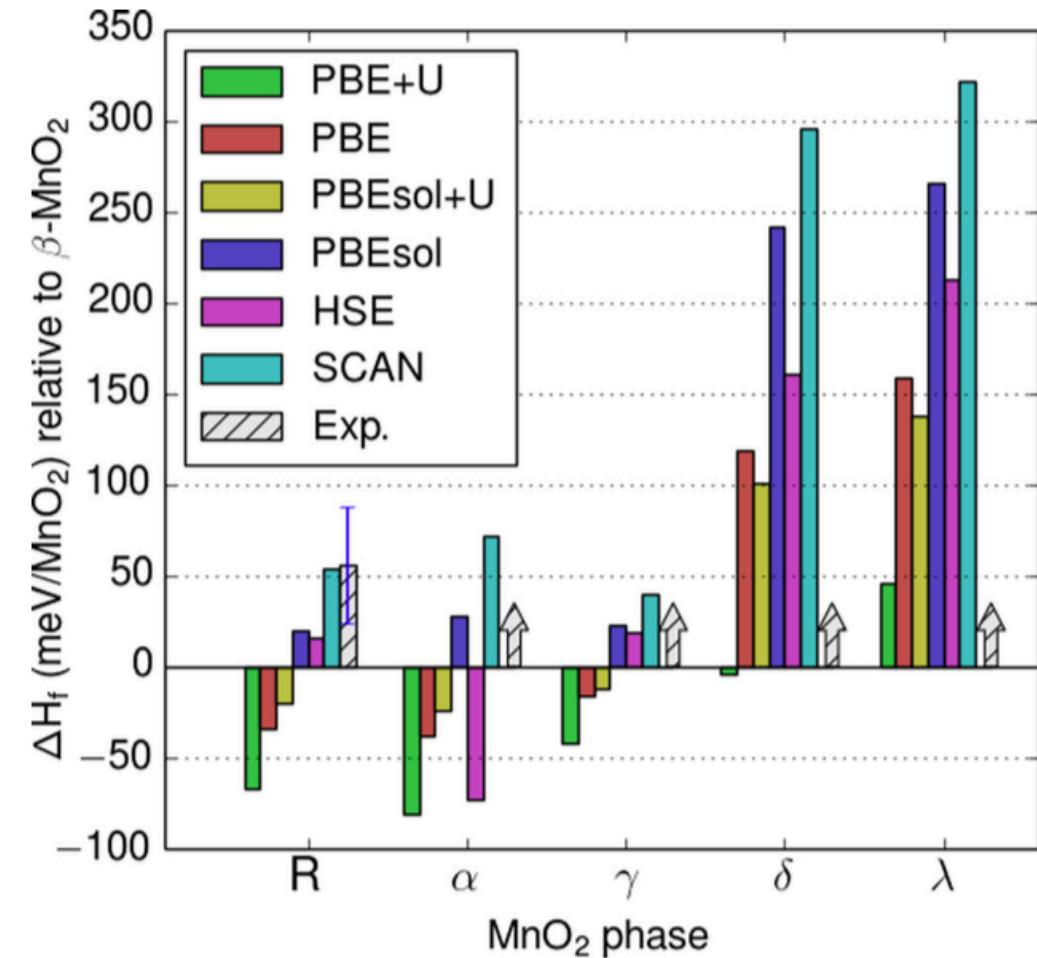
- Benchmarking with DMC:
 - High throughput formation energies with DMC
 - Transition metal oxides: CoO example
- Nanoscale materials with DMC:
 - Excited states of Mn⁴⁺ doped insulators
 - Lattice modulation in epitaxial LaCoO₃
- Enabling larger simulations: Hybrid representation of many-body wavefunction

High Throughput Materials Simulations with Diffusion Monte Carlo (DMC)

DFT has low computational cost but accuracy shortcomings

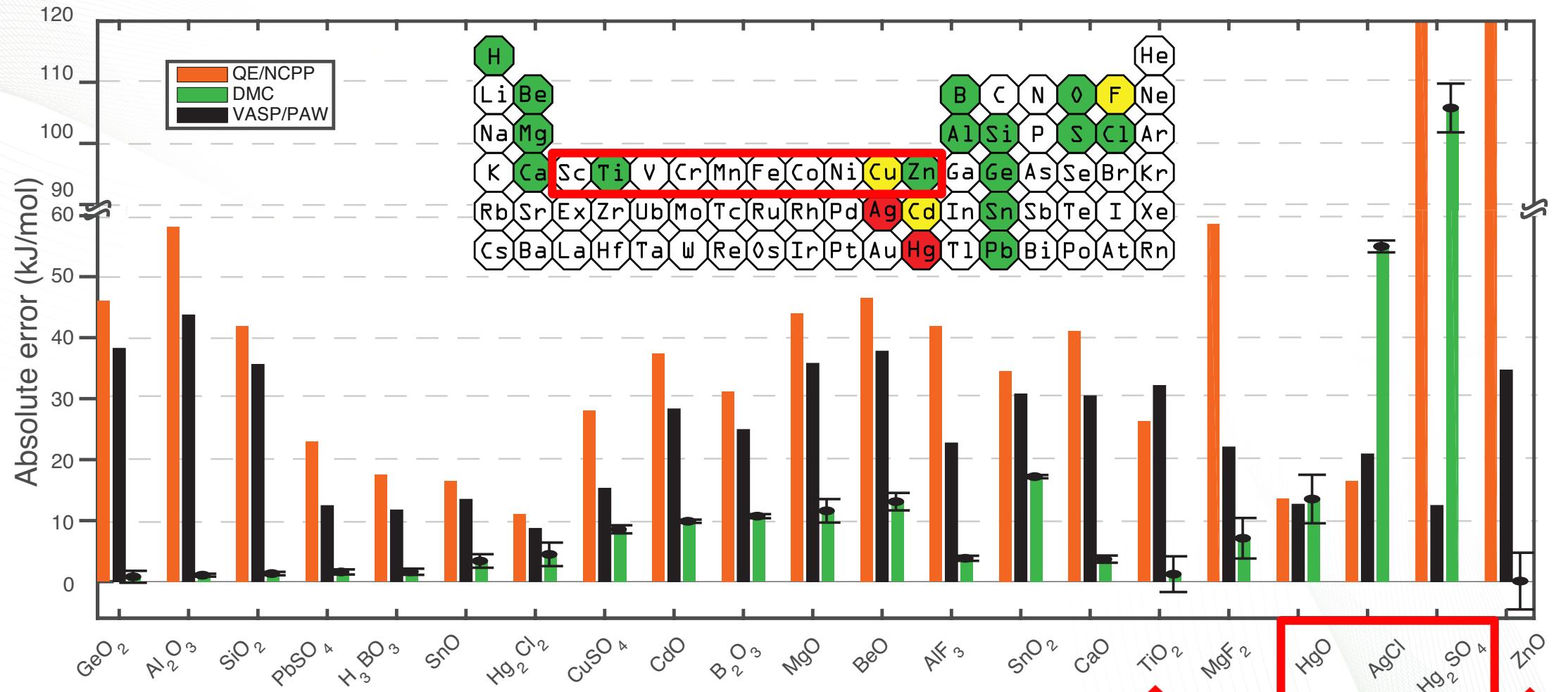


L. Wang et al., *PRB*. 73 (2006) 195107



D. Kitchaev et al., *PRB*. 93 (2016) 045132

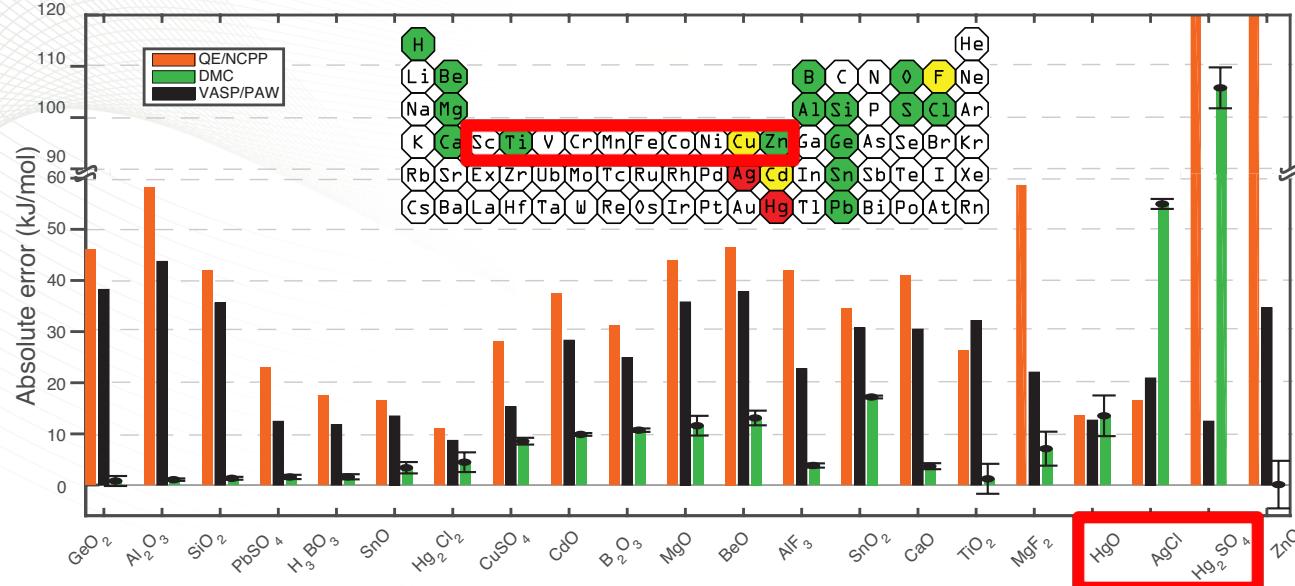
Diffusion Monte Carlo (DMC) is a practical alternative to DFT



Saritas, K., Mueller, T., Wagner, L., & Grossman, J. C. (2017). *JCTC*, 13(5), 1943–1951.

On-going effort is to simulate all first row transition metal oxides

User effort can be reduced with an automated scheme



Literature	# of compounds	MAE (eV/atom)
MP	1386	0.133
OQMD (on MP structures)	1386	0.108
This work		
CODATA, VASP	21	0.276
CODATA, DMC	21	0.058(6)
CODATA-{Ag, Hg}, VASP	17	0.257
CODATA-{Ag, Hg}, DMC	17	0.028(5)

MP: Materials project

OQMD: Open quantum materials database

- Due to large computational/human time required, it was rare to see multiple materials studied with DMC in the same work.
- DMC accuracy often exceeds DFT, a DMC database can be realized in near future

- DMC is well suited for parallel programming
- Compared to other correlated methods, DMC has favorable scaling, $O(N^3)$, with the system size
- ≈30-60 secs per material with Titan (9th in TOP 500)
- 200K materials in ICSD: > 6 months

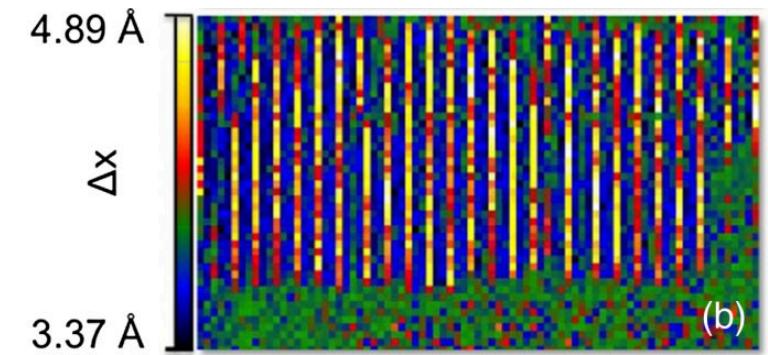
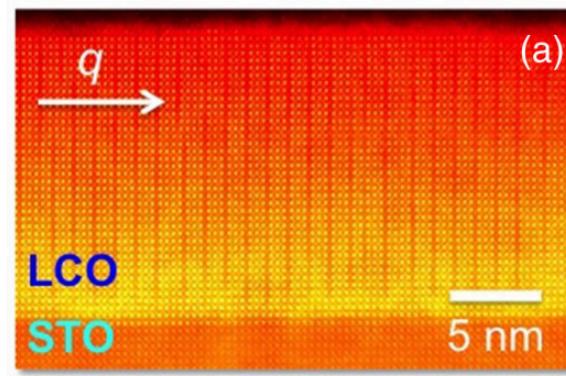
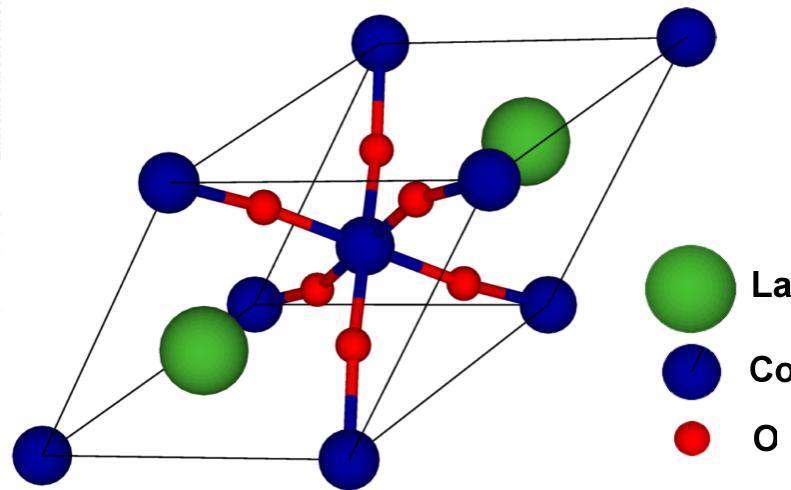


Saritas, K., Mueller, T., Wagner, L., & Grossman, J. C. (2017). *JCTC*, 13(5), 1943–1951.

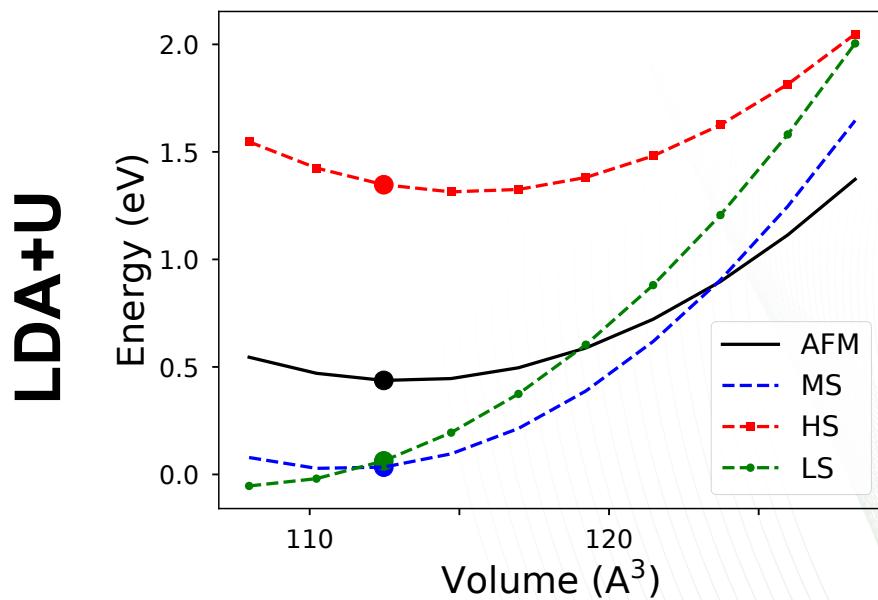
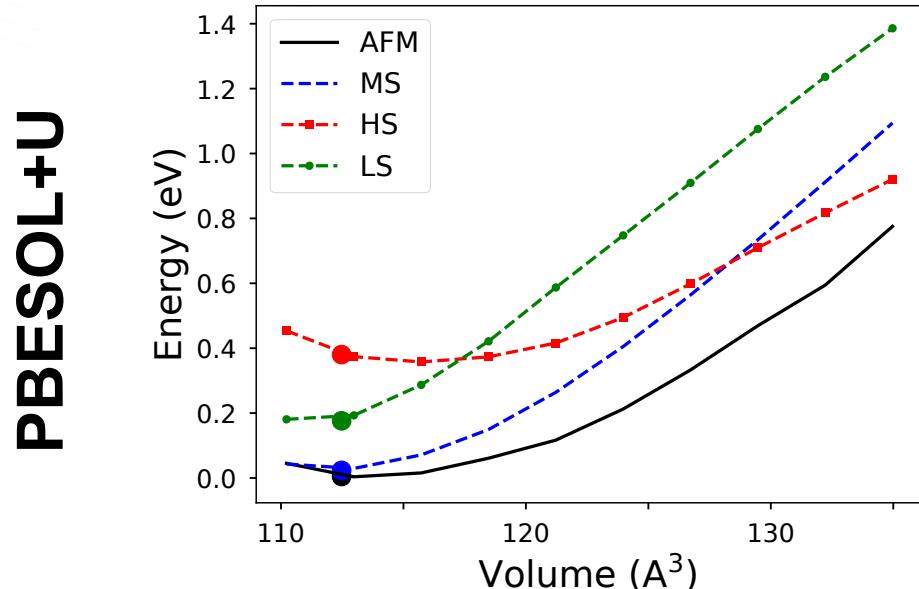
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Transition metal oxides with DMC: CoO example

CoO as a stepping stone towards cobaltites

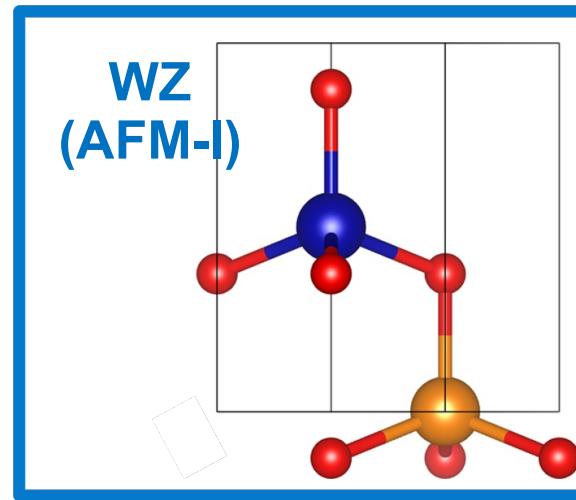
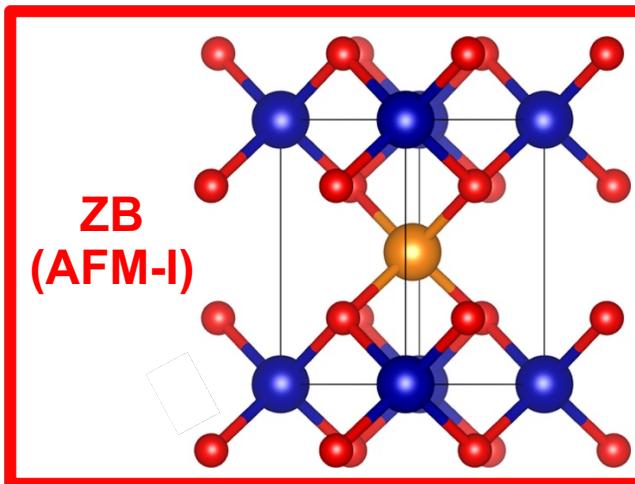
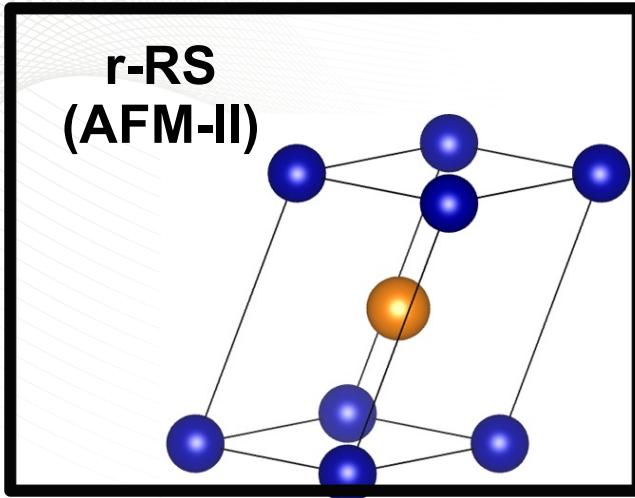


Biškup, N., Salafranca, J., Mehta, V., Oxley, M. P., Suzuki, Y., Pennycook, S. J., ... Varela, M. (2014). *PRL*, 112(8), 087202.

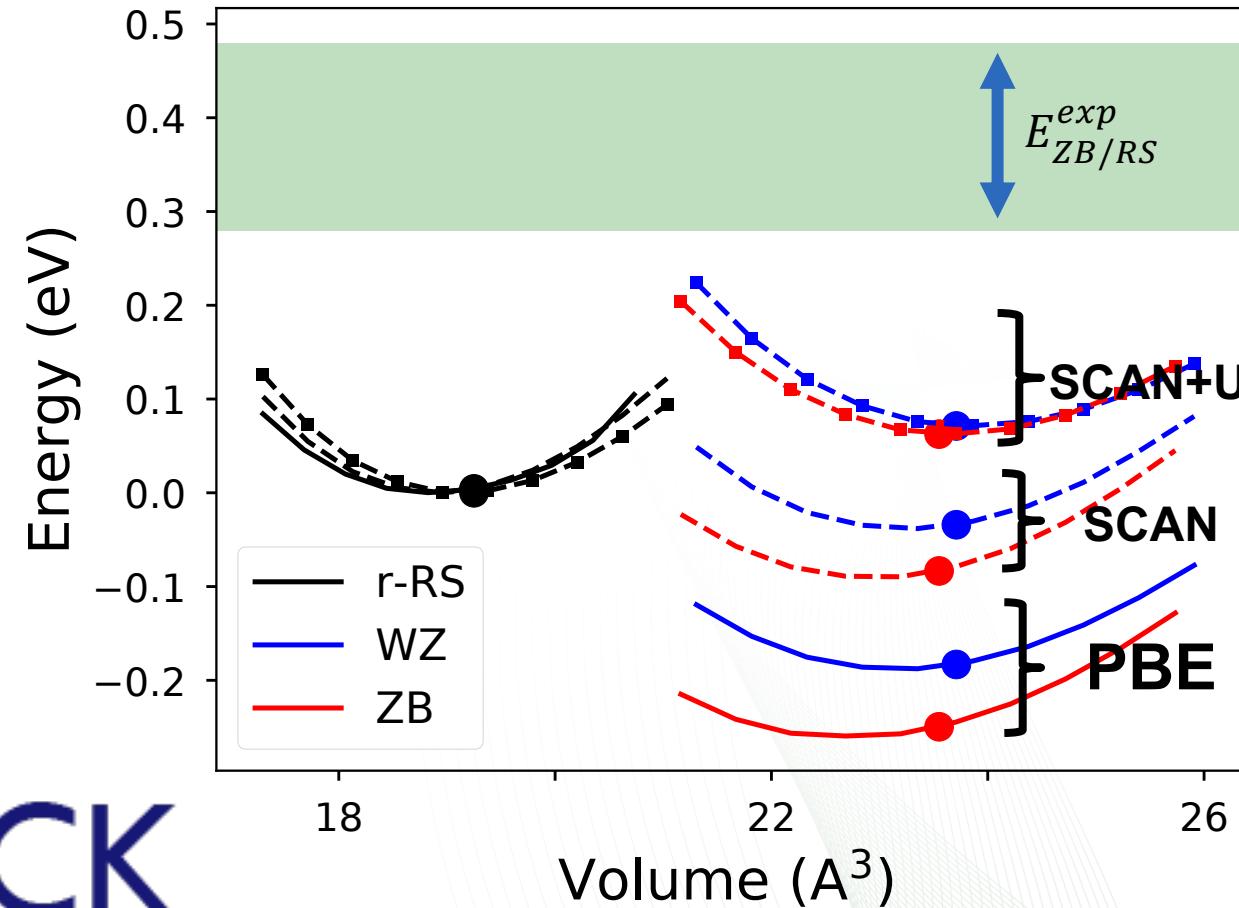


Magnetic configuration of LaCoO_3 (LCO) can be tuned under strain

Rhombohedrally distorted rocksalt (r-RS) CoO is the most stable polymorph

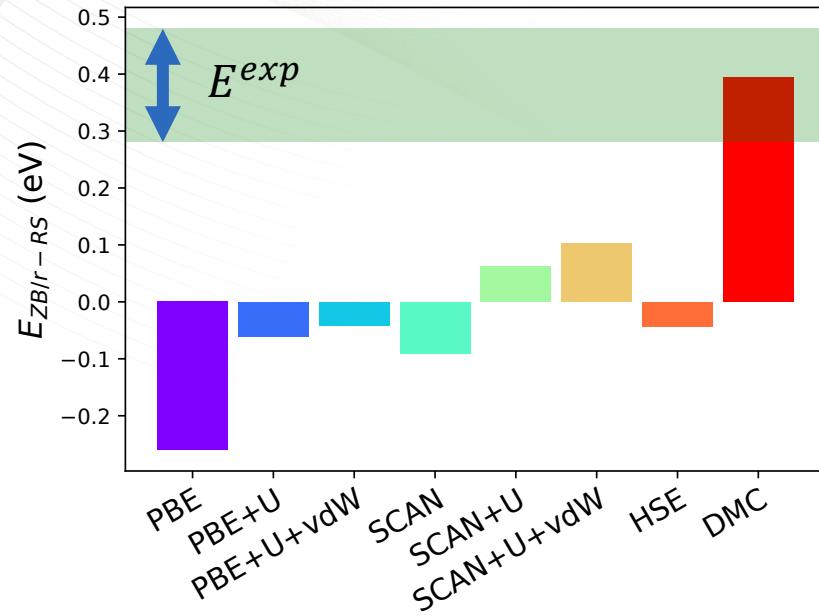


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Bulk CoO stabilities: theory vs. experiment

ZB/r-RS

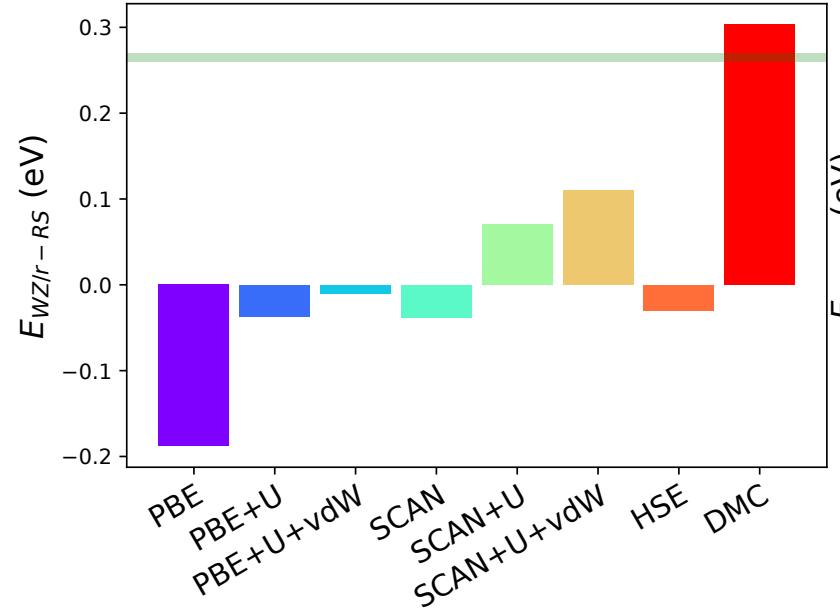


Peng, H., & Perdew, J. P. (2017). *PRB*, 96(10).

Exp. (0.38 \pm 0.1 eV):

DiCarlo, J., & Navrotsky, A. (1993). *J. Am. Cer. Soc.*, 76(10), 2465–2467.

WZ/r-RS



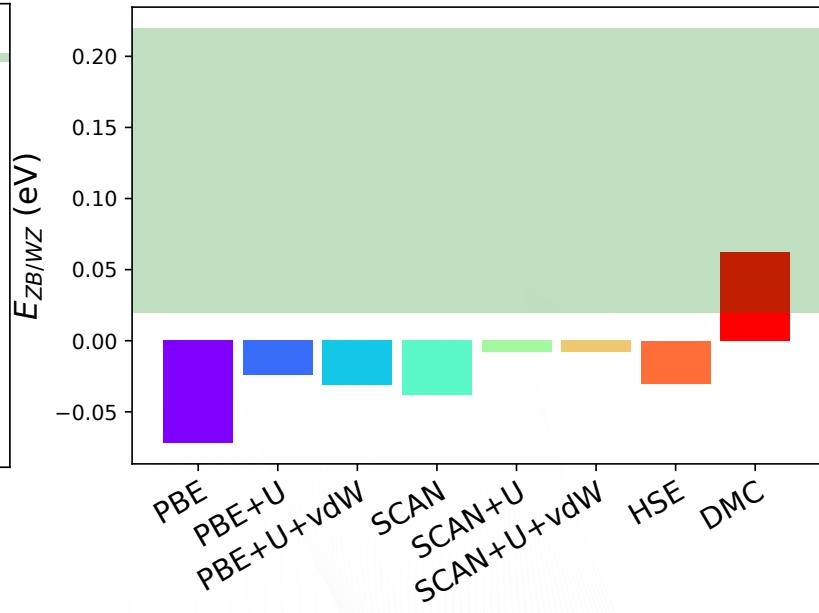
Semi-empirical (0.26 eV):

Grimes, R. W., & Lagerlof, K. P. D. (1991). *J. Am. Cer. Soc* 74(2), 270–273.

Exp. (0.27 eV):

Navrotsky, A., & Muan, A. (1971). *J. Inorg. and Nuc. Chem.*, 33(1), 35–47.

ZB/WZ



Exp. (0.12 \pm 0.1 eV):

$$E_{ZB/WZ}^{exp} = E_{ZB/RS}^{exp} - E_{WZ/RS}^{exp}$$

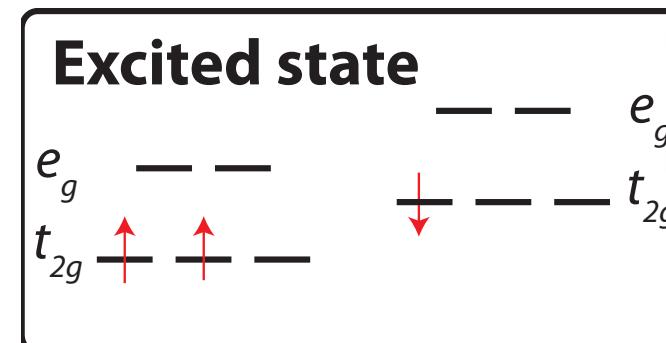
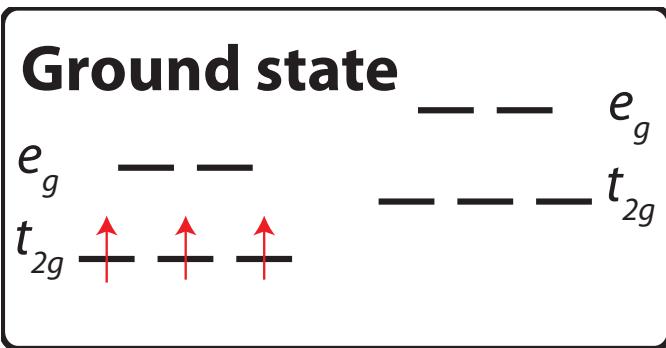
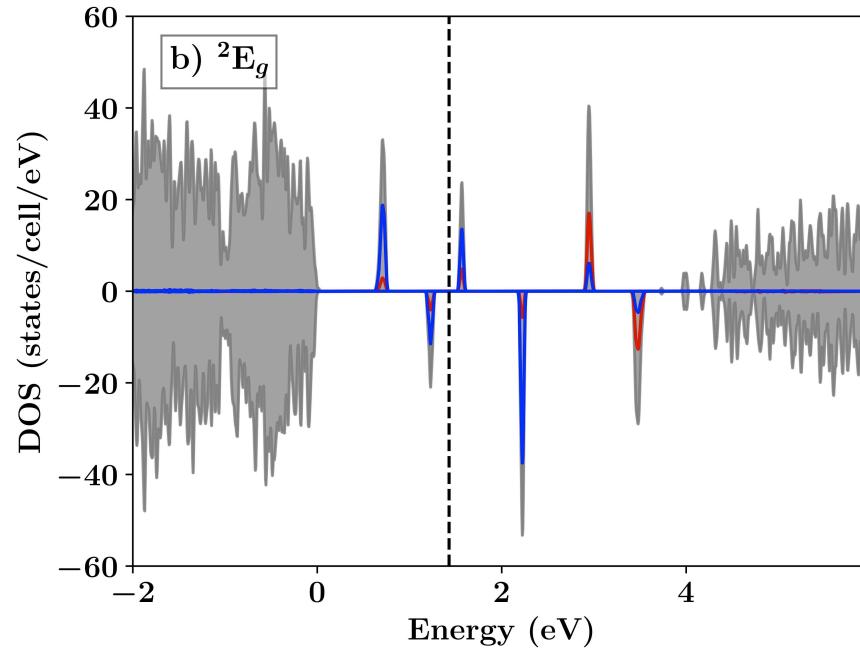
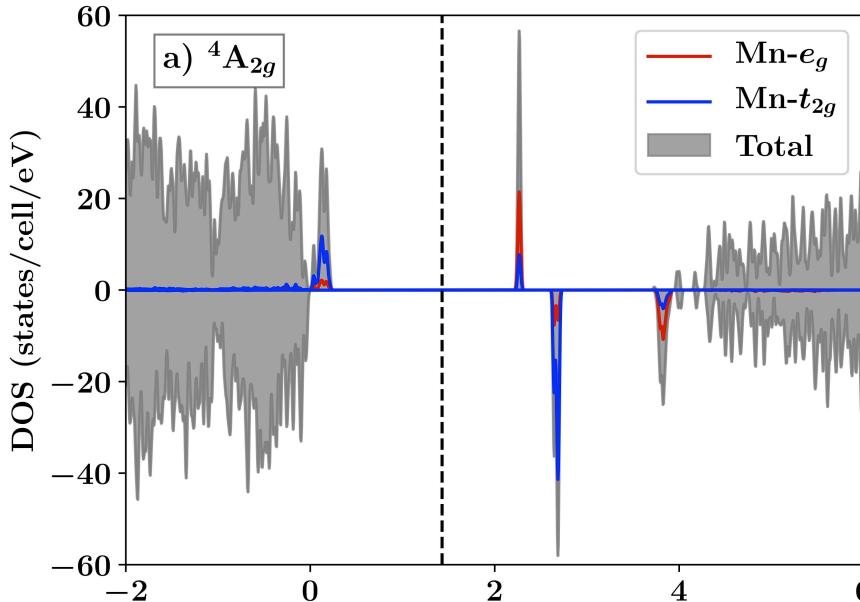
SCAN+U is able to reproduce $E_{ZB/r-RS}$ and $E_{WZ/r-RS}$ qualitatively, but not $E_{ZB/WZ}$

Similar research recently performed in ORNL

- **Mn-oxides:** Saritas, K., Krogel, J. T., Kent, P. R. C., & Reboredo, F. A. *Physical Review Materials*, 2(8), 085801, (2018).
- **VO₂:** Kylänpää, I., Balachandran, J., Ganesh, P., Heinonen, O., Kent, P. R. C., & Krogel, J. T. *Physical Review Materials*, 1(6), 065408, (2017).
- **MnNiO₃:** Dzubak, A. L., Mitra, C., Chance, M., Kuhn, S., Jellison, G. E., Sefat, A. S., Krogel, J. T., Reboredo, F. A. *Journal of Chemical Physics*, 147(17), 174703, (2017).
- **IIA and IIIB oxides:** Santana, J. A., Krogel, J. T., Kent, P. R. C., & Reboredo, F. A. (2016). *Journal of Chemical Physics*, 144, 174707, (2016).
- **NiO:** Mitra, C., Krogel, J. T., Santana, J. A., Reboredo, F. A. *The Journal of Chemical Physics*, 143(143), 164710–164705, (2015).

Optical emission energies of transition metal doped insulators

DFT largely underestimates emission energies of Mn⁴⁺ doped insulators



Motivation

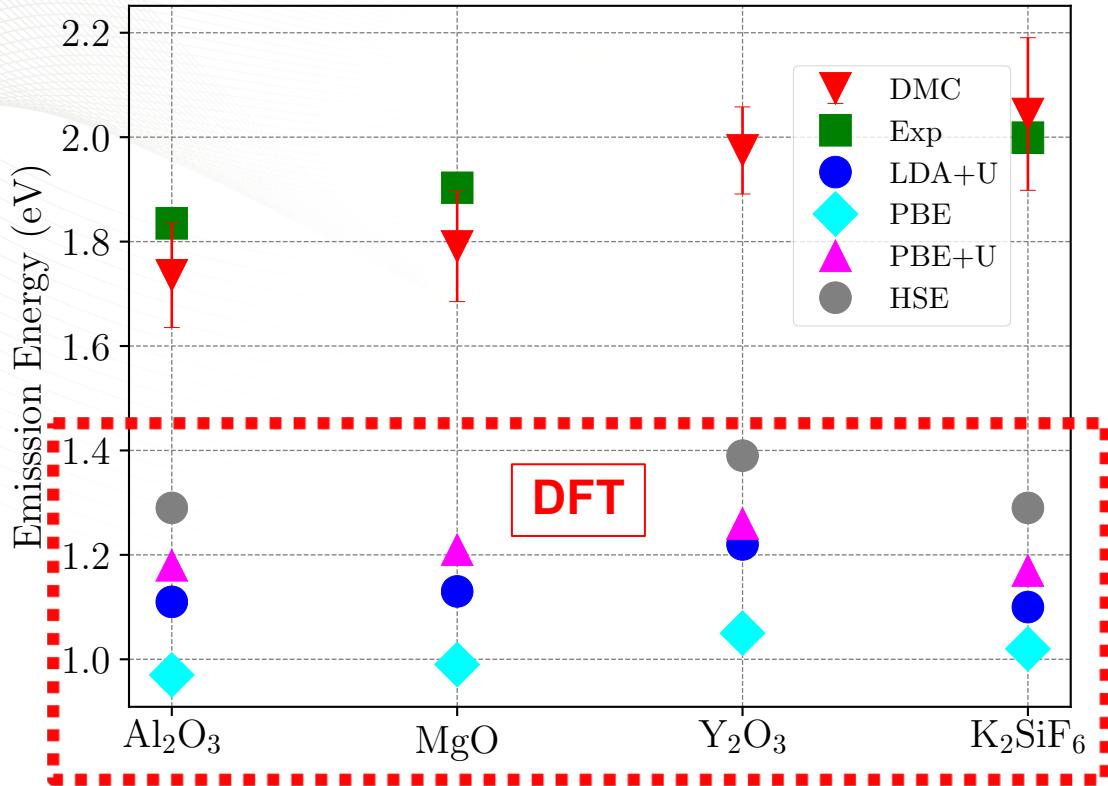
- Eu³⁺ doped Y₂O₃ is used as red phosphor in LEDs
- It is of interest to substitute Eu³⁺ with other impurities due to materials scarcity

Scope

- Density Functional Theory (DFT) underestimates emission energies and the trends are wrong between different insulator host families
- Interesting problem for DMC, which is essentially a ground state method

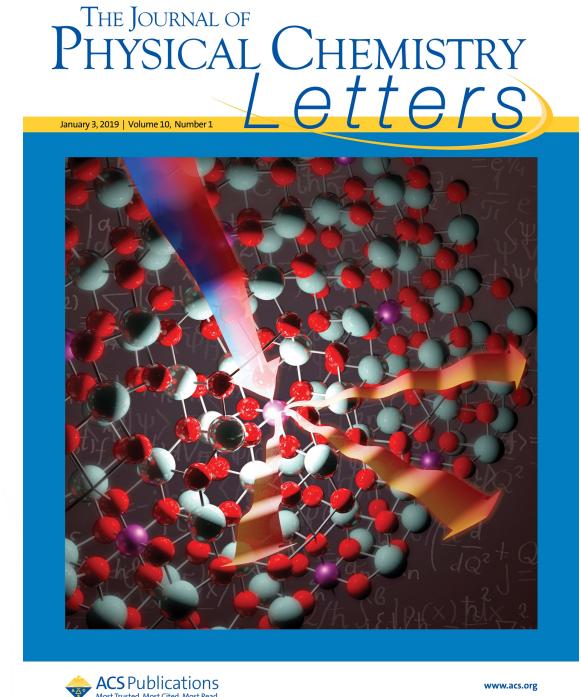
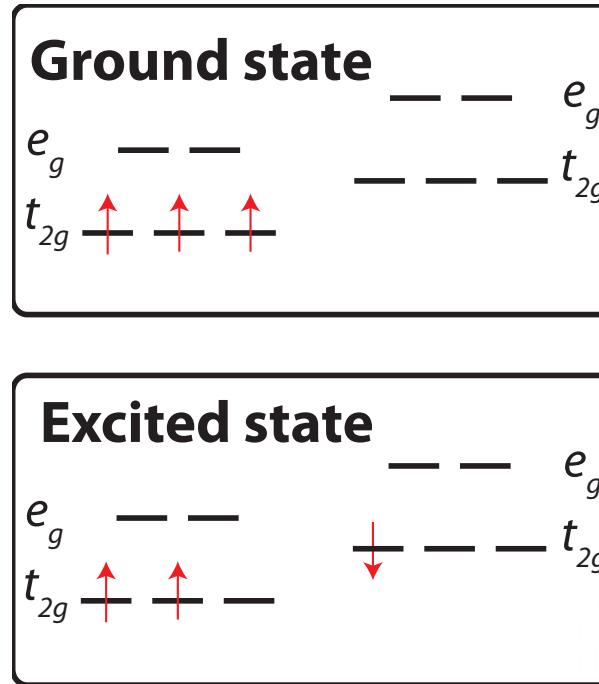
Saritas, K., Ming, W., Du, M.-H., & Reboreda, F. A. *The Journal of Physical Chemistry Letters*, 10(1), 67–74, (2019).

DFT largely underestimates emission energies of Mn⁴⁺ doped insulators



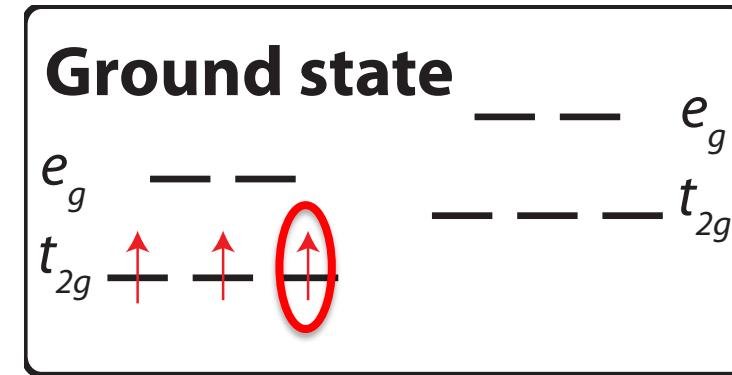
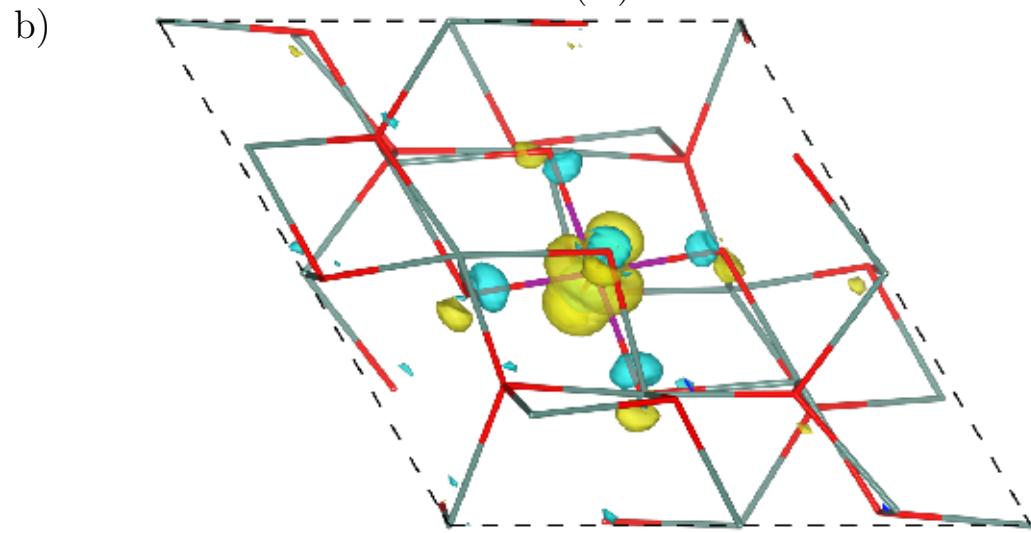
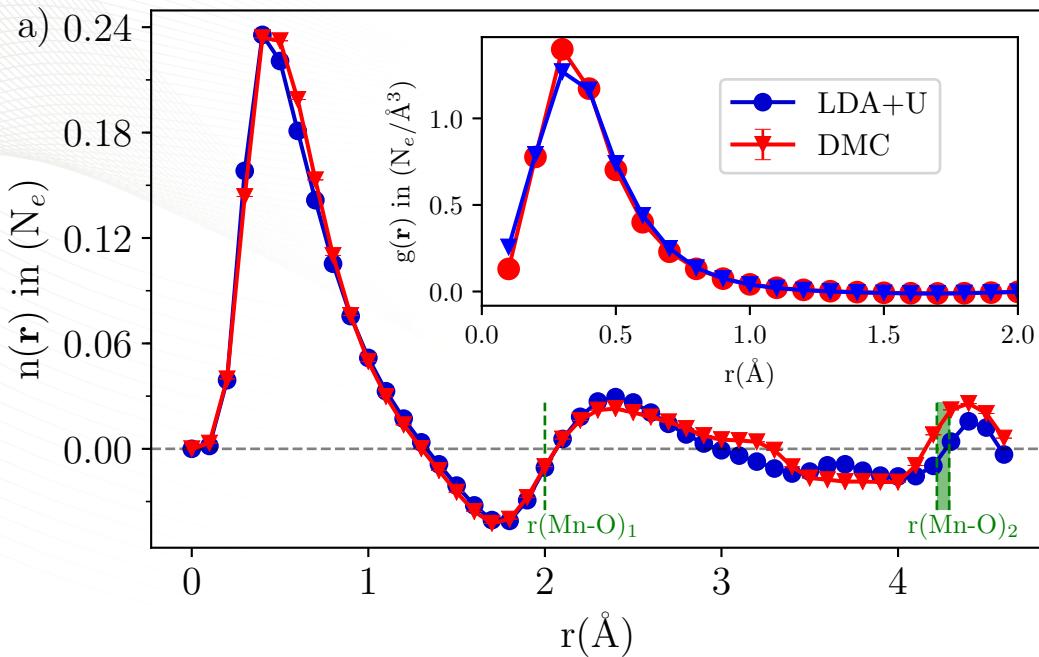
$$\Delta E_{\text{emission}} = E(\text{excited}) - E(\text{ground})$$

- All DFT functionals fail quantitatively
- Trends between oxide hosts are reproduced in DFT, but trends between oxide and fluoride hosts are not.



Saritas, K. et. al., JPCL,
10(1), 67-74, (2019).

Localization of the excited charge density



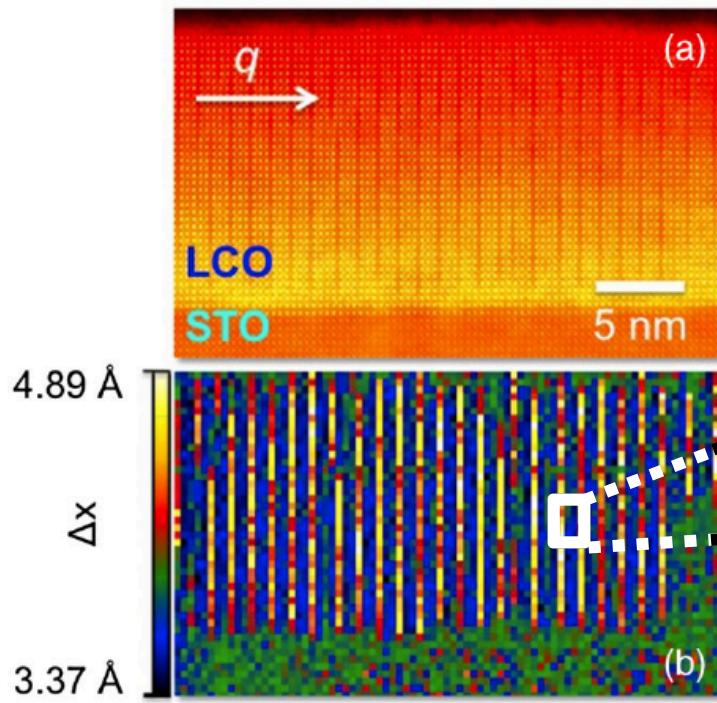
- Excitation must be localized within the simulation cell, otherwise image interactions may plague the final energies
- We would like to see if DFT and DMC methods predict different densities since energies predicted are considerably different

Saritas, K. et. al., **JPCL**, 10(1), 67-74, (2019).

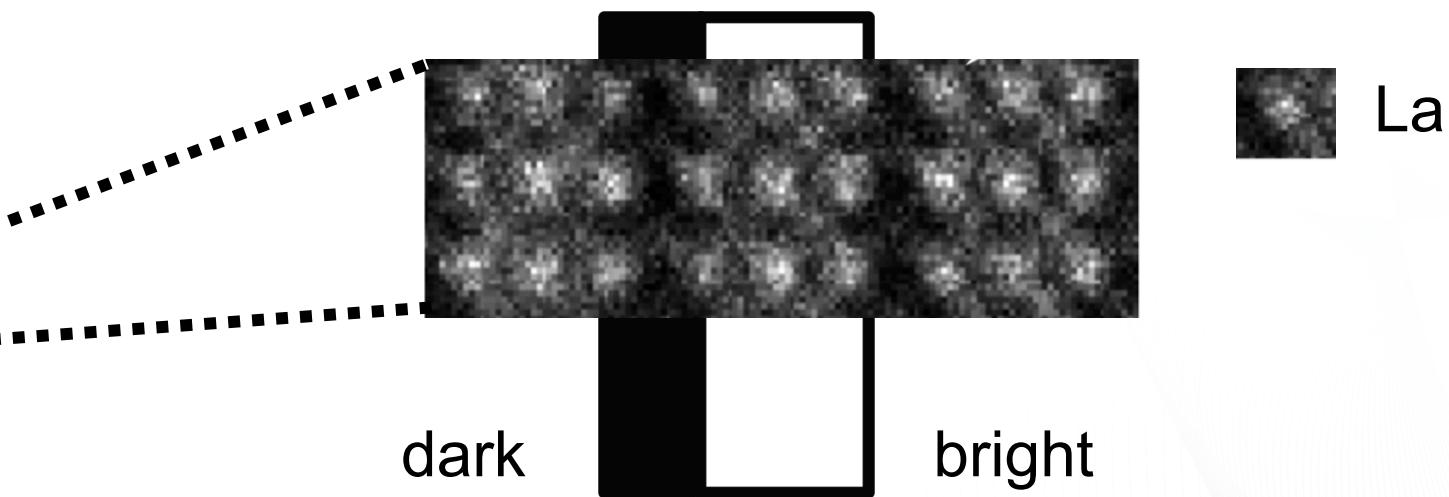
Magnetic properties of epitaxial and bulk LaCoO₃

Motivation

- Why epitaxial LaCoO_3 on SrTiO_3 (LCO on STO) is FM?
- LCO on STO has interesting strain relaxation: ($a_{\text{STO}} > a_{\text{LCO}}$), La-La separation is modulated

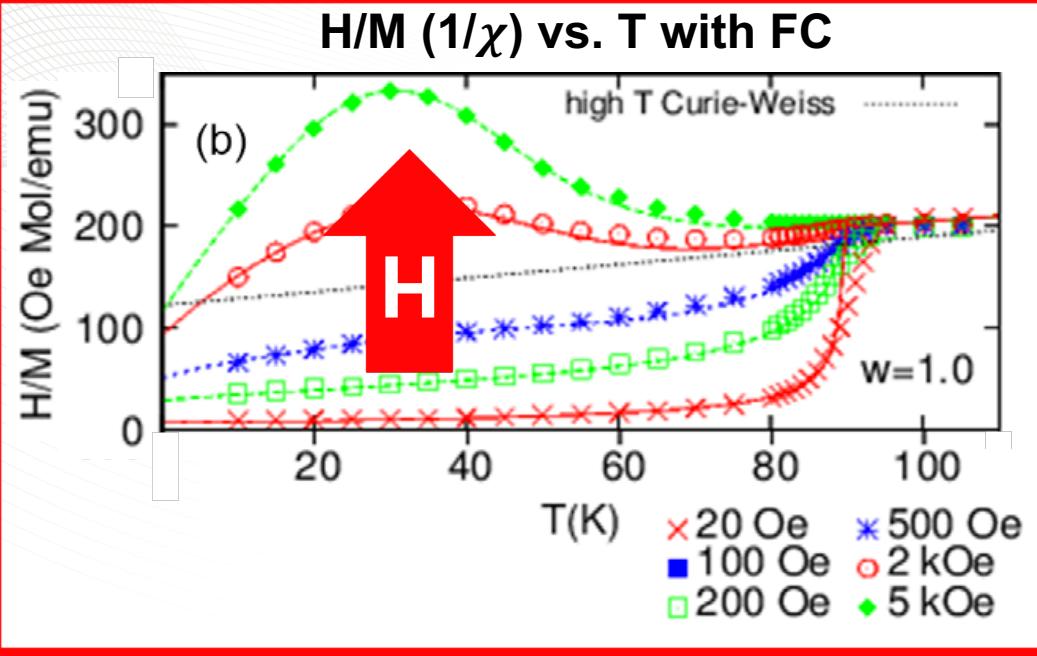


Biskup, et. al., PRL, 112, 087202, (2014).
Choi et. al., Nano Letters, 12(9), 4966–4970, (2012).
Kwon et. al., Chem. Mater., 26(8), 2496–2501, (2014).



- **What drives the lattice modulation and FM?**
 1. Magnetic moment of Co atoms in the dark layer
 2. Defects (V_O etc.) yield net magnetization on Co atoms

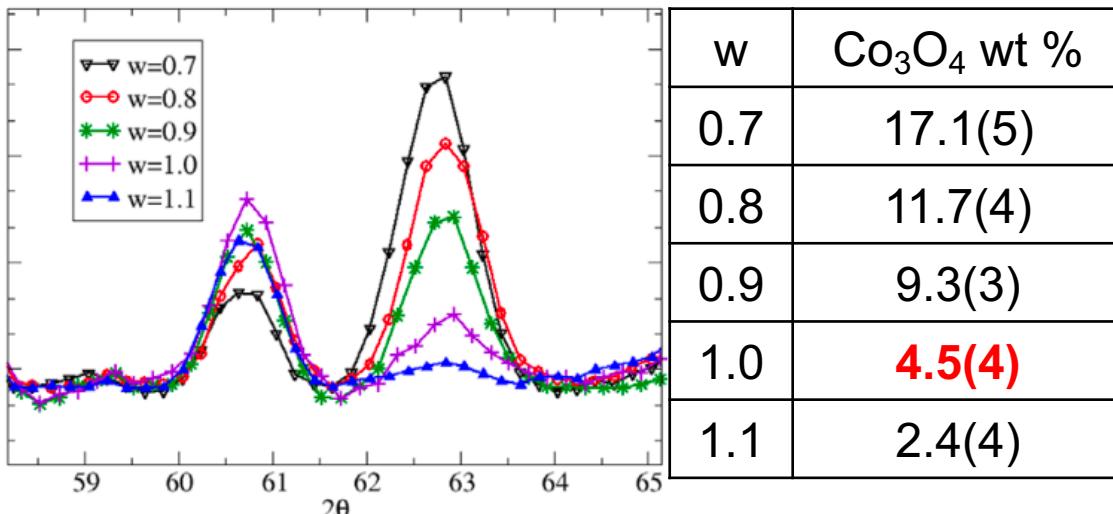
Bulk LaCoO₃ magnetic ground state is still under debate



- Model 1:
 - Diamagnetic ground state at 0 K
- Raccah P.M. and Goodenough. J.B.
Phys. Rev., 155(3), 932, (1967)

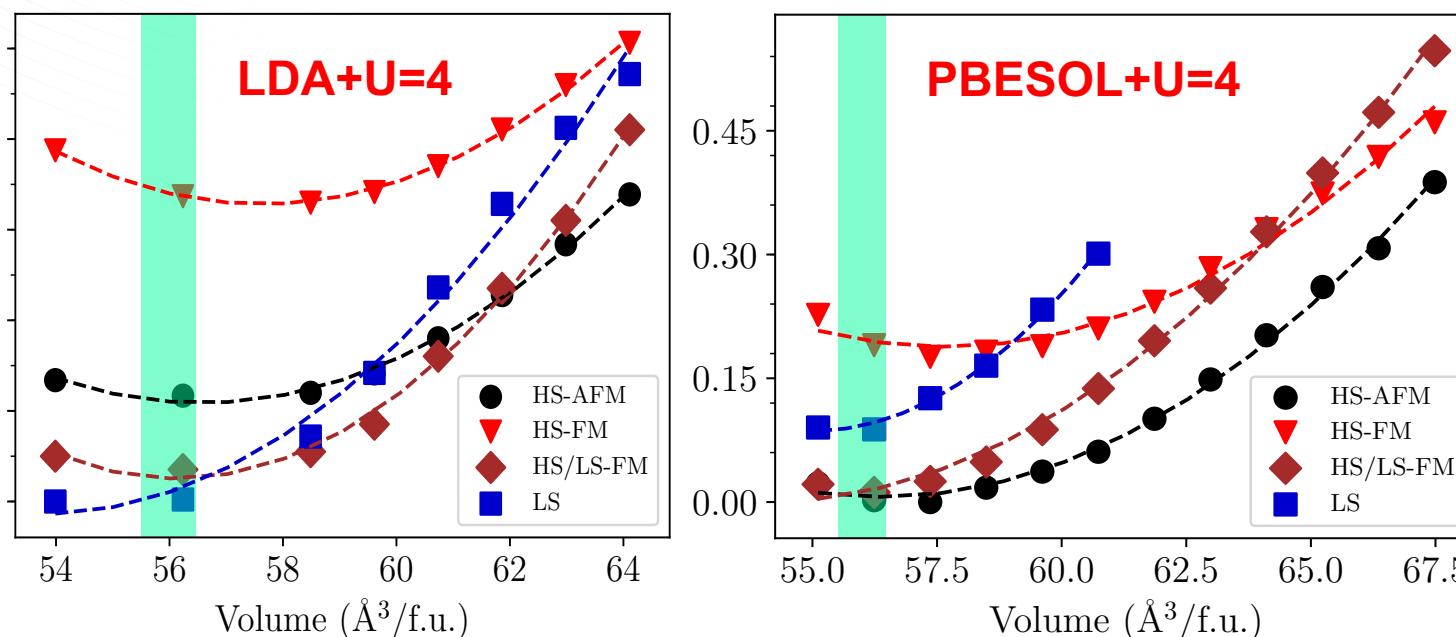
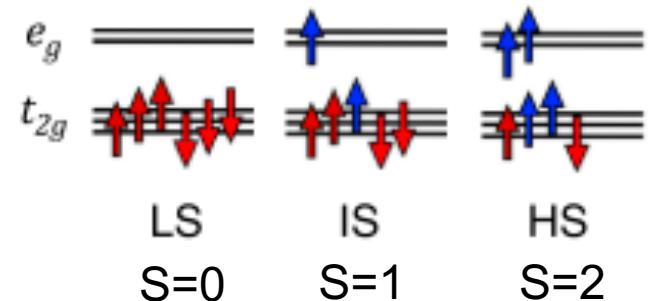
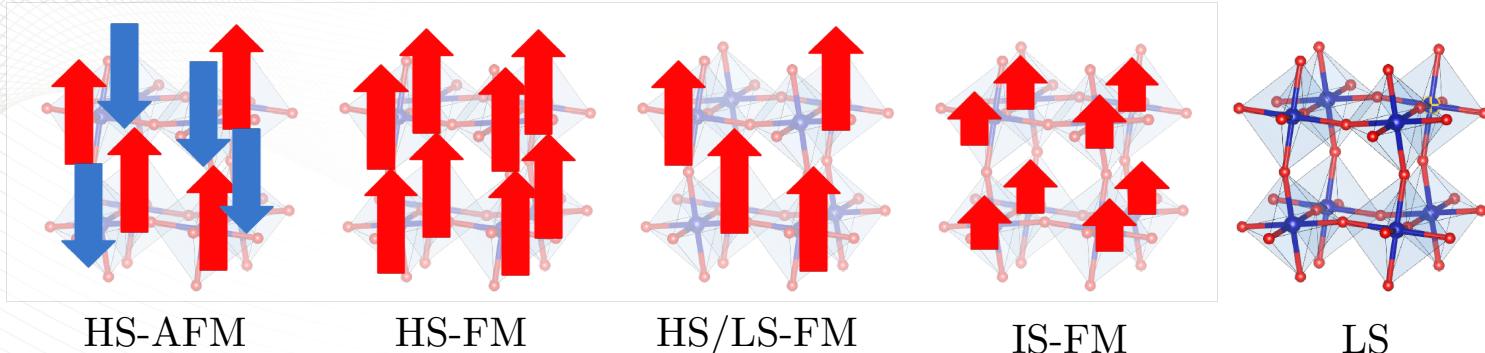
- Model 2:
 - LaCoO₃ is paramagnetic AFM > 100K , but long range ordering is never observed at lower T.
- Durand et. al., JCP Condens. Matt.,
27(12), 126001–126013, (2015).

Neutron diffraction on bulk La_wCoO₃



- LCO may coexist with Co₃O₄ and CoO
- Precipitates complicate the single phase analysis
- Accurate theoretical calculations are key

The accuracy of density functional theory (DFT) is not enough to resolve the magnetic states

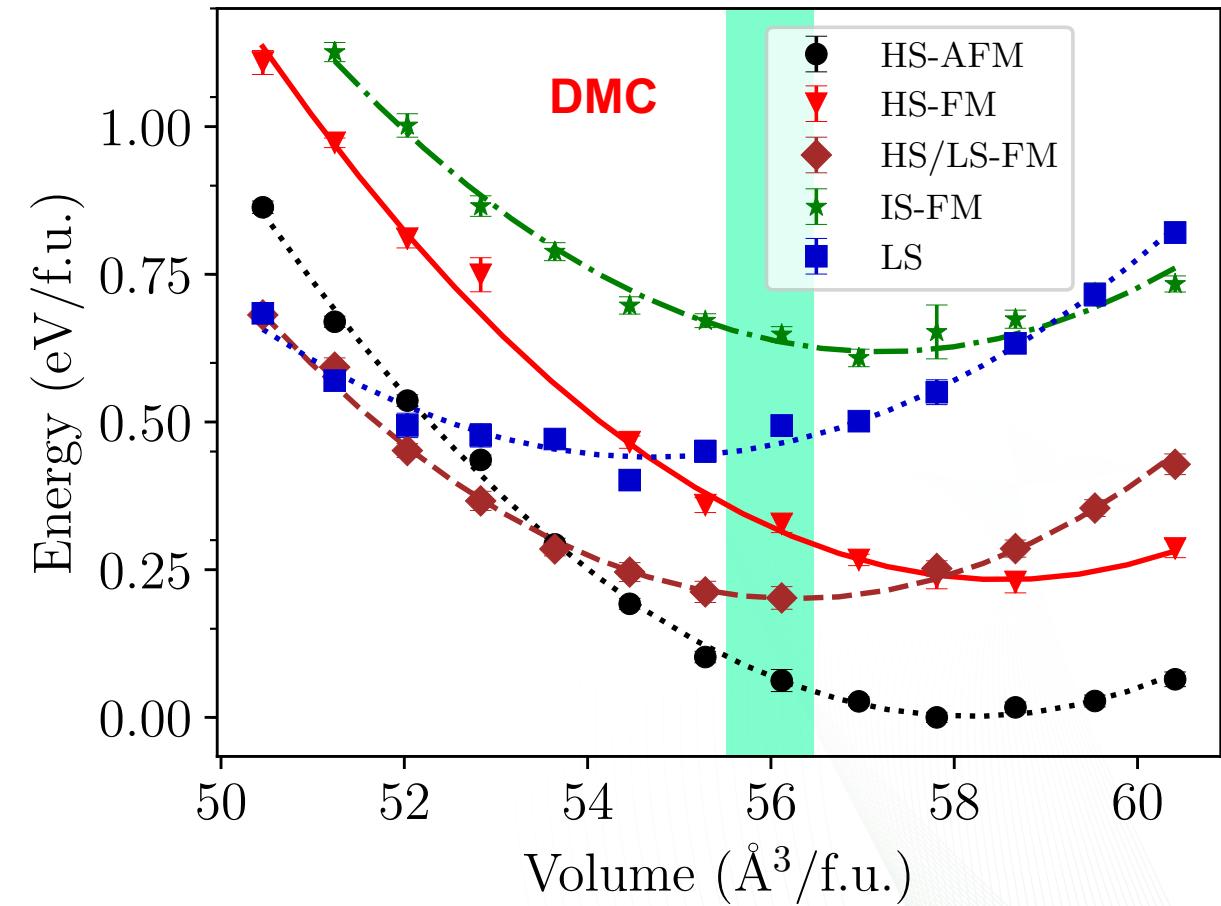
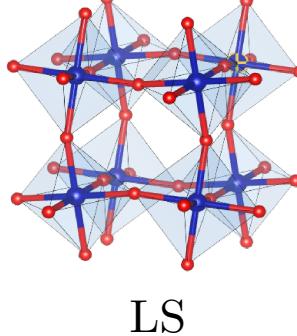
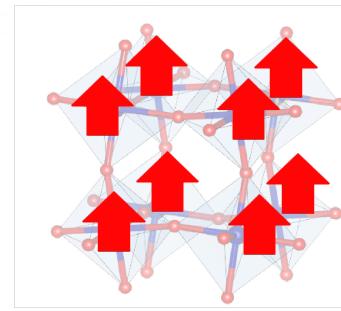
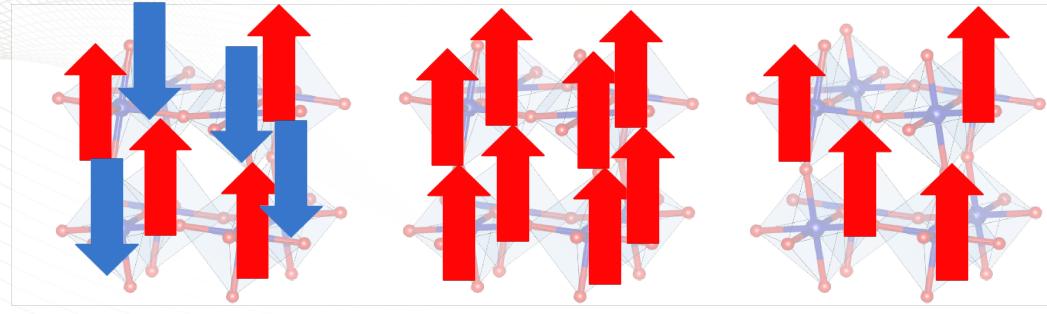


Sterbinsky et. al., **PRL**, 120(19), 197201, (2018).

- **Different XC functionals are used for different properties**
- **A theoretical method which performs well across multiple properties is needed**

Saritas, K. Krogel, J.T., Okamoto, S., Ho-Nyung, L. Reboreda, F.A., submitted to Physical Review Materials

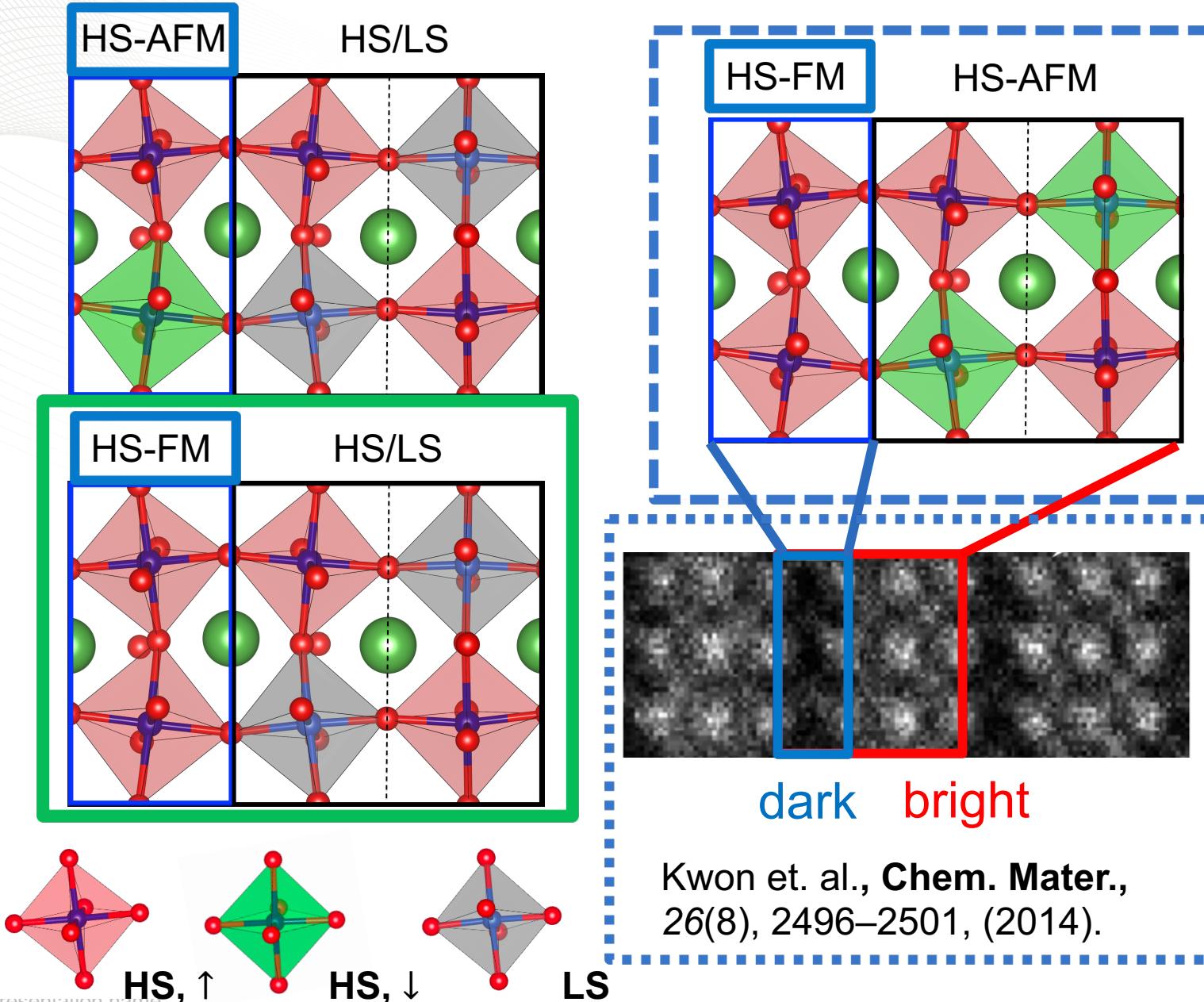
Back to epitaxial LaCoO₃: DMC predicts HS-AFM ground state for bulk LaCoO₃



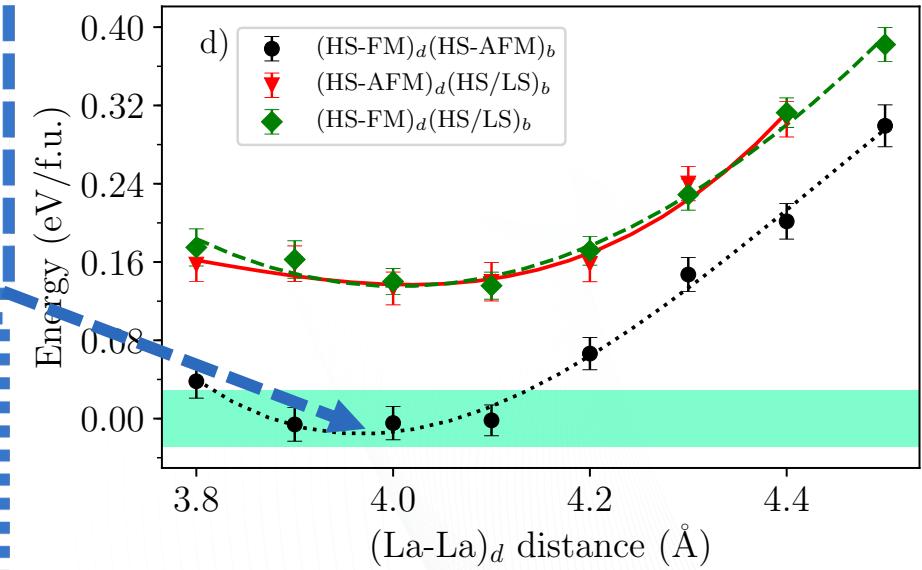
Saritas, K. Krogel, J.T., Okamoto, S., Ho-Nyung, L. Reboreda, F.A., submitted to *Physical Review Materials*

**HS-AFM (G-type) structure is predicted as DMC ground state
DMC agrees with the recent experiments**

Inhomogeneous lattice modulation of LaCoO_3 on STO under uniaxial strain



Energy relative to bulk
strained LaCoO_3



Saritas, K. Krogel, J.T., Okamoto,
S., Ho-Nyung, L. Reboredo,
F.A., submitted to *Physical
Review Materials*

LaCoO_3 summary

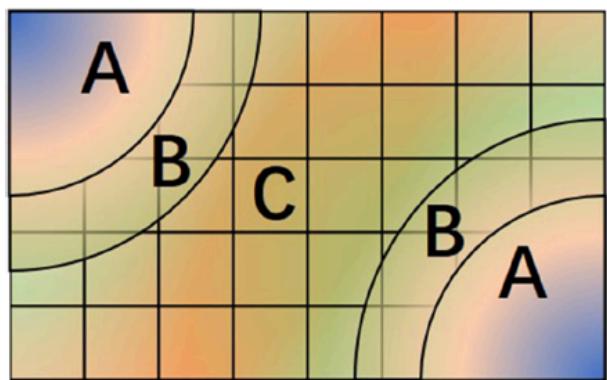
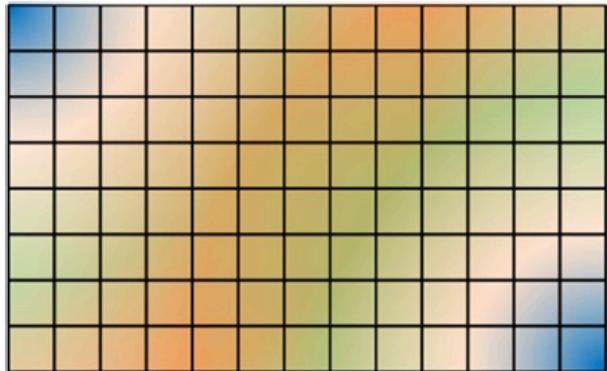
- DMC predicts an antiferromagnetic ground state for bulk LaCoO_3
- DMC explains ferromagnetism on uniaxial strained LaCoO_3
- The origin of lateral modulation remains unclear
- A La-La separation of 4.5 Å in epitaxial LaCoO_3 suggest non-stoichiometric samples or other extrinsic effects
- Defects under uniaxial strain will be studied

Similar research recently performed in ORNL

- **SrFeO₃-LaFeO₃ defects:** Santana, J. A., Krogel, J. T. , Kent, P. R. C., and Reboredo, F. A., *J. Chem. Phys.*, 147(3), p. 034701, (2017).
- **Perovskite superlattices:** Santana, J. A. *et al.*, *J. Chem. Theory Comput.*, 13(11), pp. 5604–5609, (2017).
- **ZnO defects:** Santana, J. A., Krogel, J. T., Kim, J., Kent, P. R. C., & Reboredo, F. A. *Journal of Chemical Physics*, 142(16), (2015).

Hybrid orbital representation for QMC

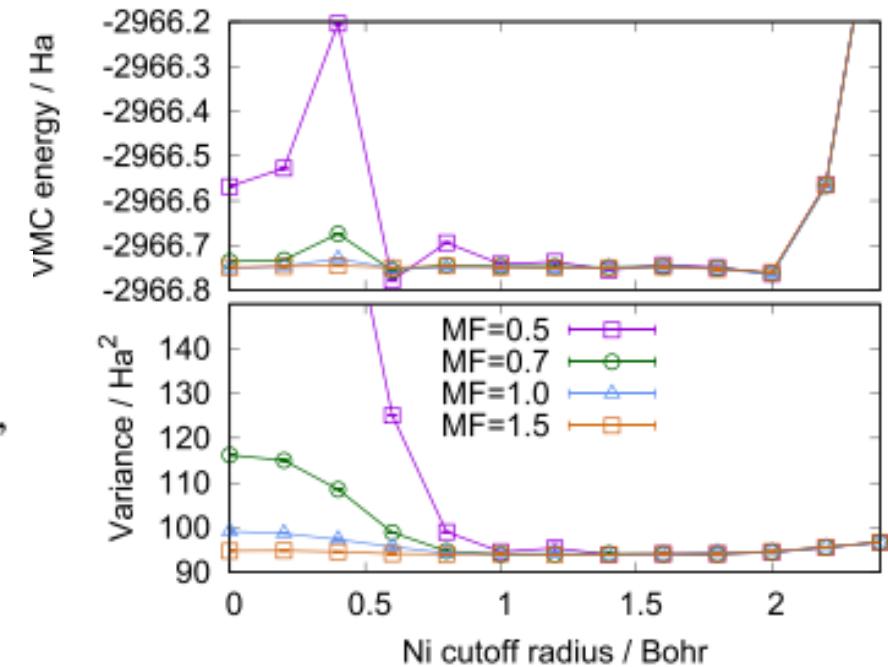
New hybrid representation largely extends memory limitations



$$\phi_n^A(\mathbf{r}) = R_{n,l,m}(r)Y_{l,m}(\hat{r}),$$

$$\phi_n^B(\mathbf{r}) = S(r)\phi_n^A(\mathbf{r}) + (1 - S(r))\phi_n^C(\mathbf{r}),$$

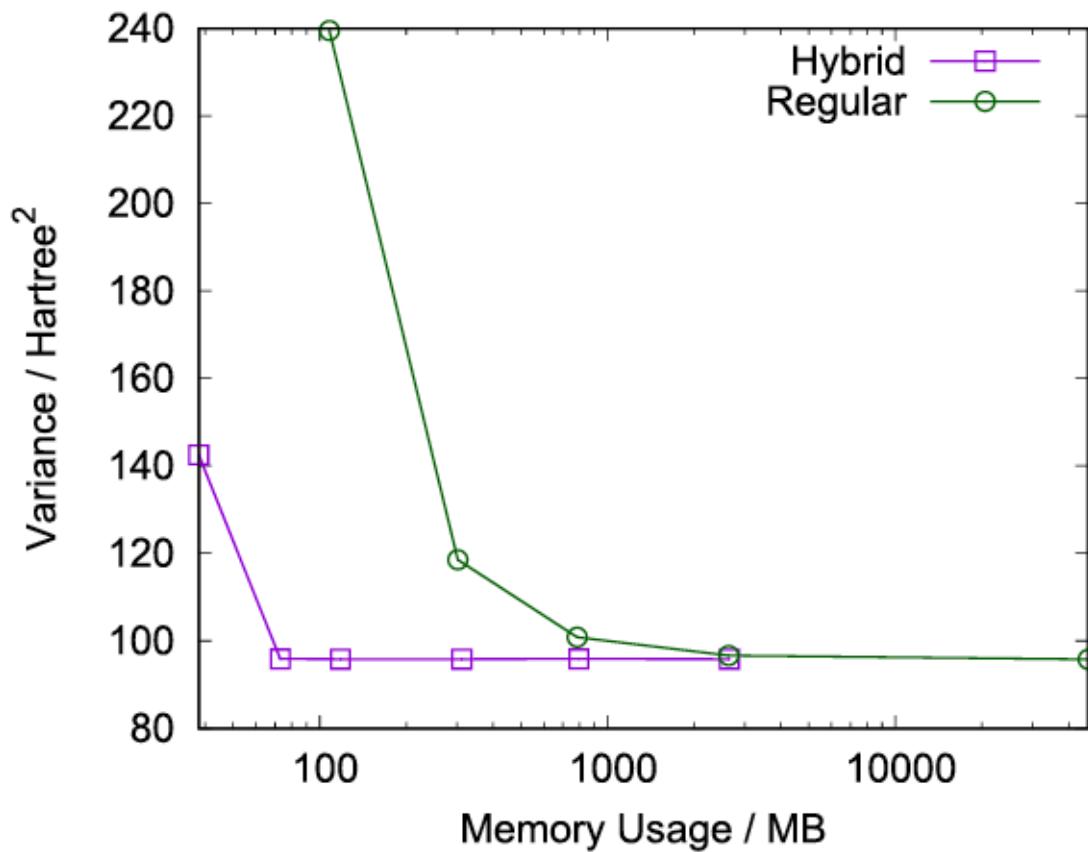
$$S(r) = \frac{1}{2} - \frac{1}{2} \tanh \left[\alpha \left(\frac{r - r_{A/B}}{r_{B/C} - r_{A/B}} - \frac{1}{2} \right) \right],$$



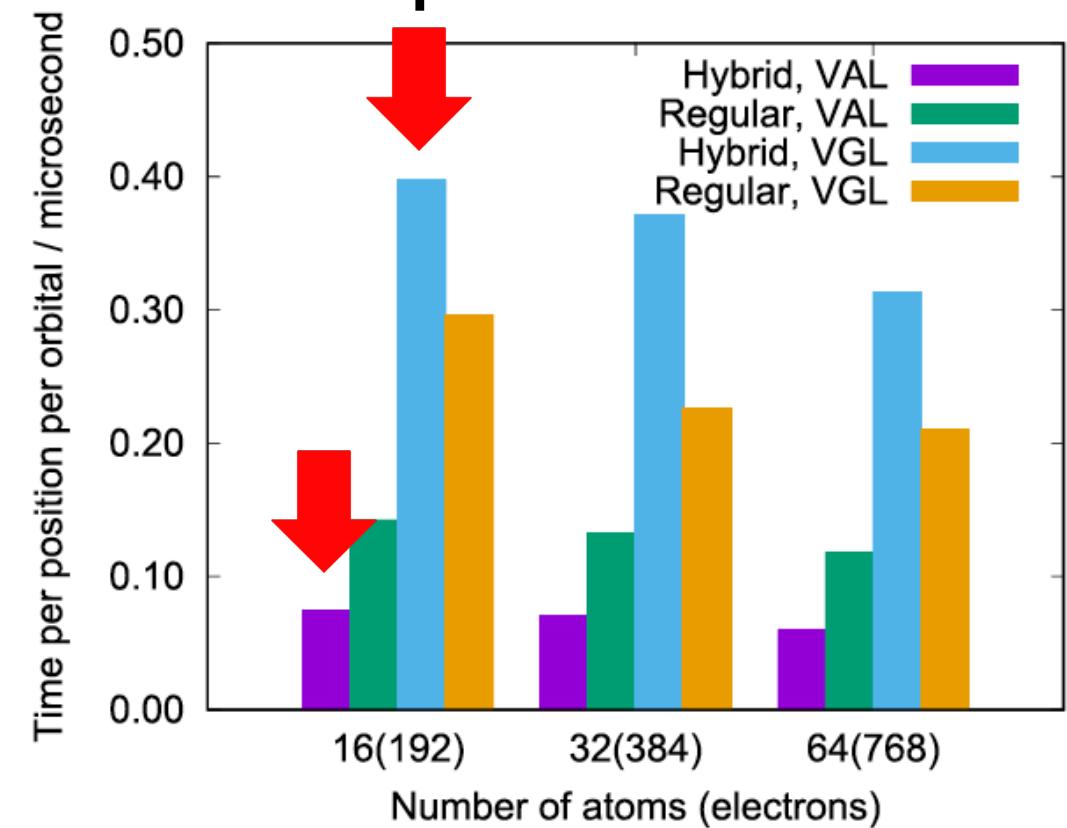
Luo, Y., Esler, K. P., Kent, P. R. C., & Shulenburger, L.
Journal of Chemical Physics, 149(8), 84107, (2018).

Hybrid representation computational performance

Memory performance



Evaluation of single particle orbitals



Luo, Y., Esler, K. P., Kent, P. R. C., & Shulenburger, L.
Journal of Chemical Physics, 149(8), 84107, (2018).

Summary

- DMC benchmarks for perfect crystalline systems can be performed routinely in modest computers
- Most benchmarking effort is towards studying more ambitious systems
- Larger simulations are enabled with efficient algorithms

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<http://qmcpack.org>



Thank you!