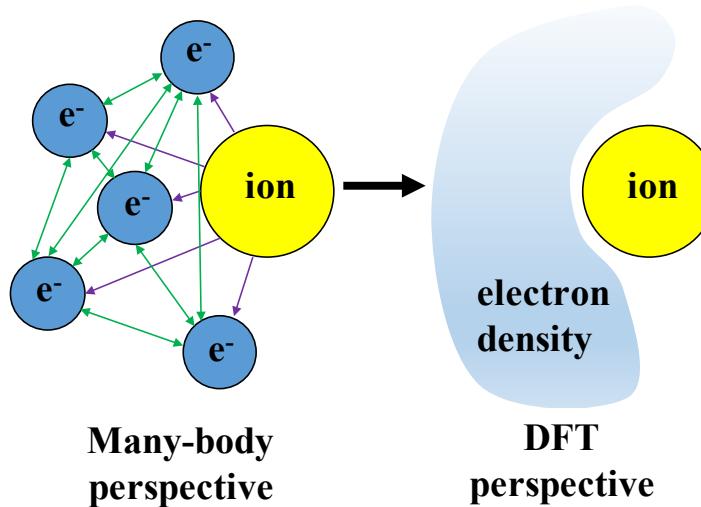


Modeling at Chemical Accuracy For Energy Applications

Dr. Can Ataca

UMBC – Department of Physics

- **VERY VERY BRIEF!!!** – Computational Methodologies
- Materials Applications of Modeling at Chemical Accuracy
 - 1. 2D GaSe (QMC)
 - “A first principles Quantum Monte Carlo study of two-dimensional (2D) GaSe”, D. Wines, K. Saritas, C. Ataca, *J. Chem. Phys.*, 153, 154704 (2020)
 - 2. 2D $\text{GaS}_x\text{Se}_{1-x}$ alloys (QMC)
 - “A pathway towards high throughput Quantum Monte Carlo simulations for alloys: A case study of two-dimensional (2D) $\text{GaS}_x\text{Se}_{1-x}$ ”, D. Wines, K. Saritas, C. Ataca, *J. Chem. Phys.*, 155, <https://doi.org/10.1063/5.0070423>
 - 3. 2D MnO_2 (QMC)
 - “Many-body Quantum Monte Carlo treatment of ferromagnetism in monolayer MnO_2 ”, D. Wines, K. Saritas, C. Ataca, under review at ACS Applied Materials&Interfaces
 - 4. Li-Air Battery Cathodes
 - “Investigation of Li-air Battery Discharge Products with QMC”, G. Chaney, K. Saritas, C. Ataca, In Preparation
 - Summary and Future Perspectives



DFT Successes

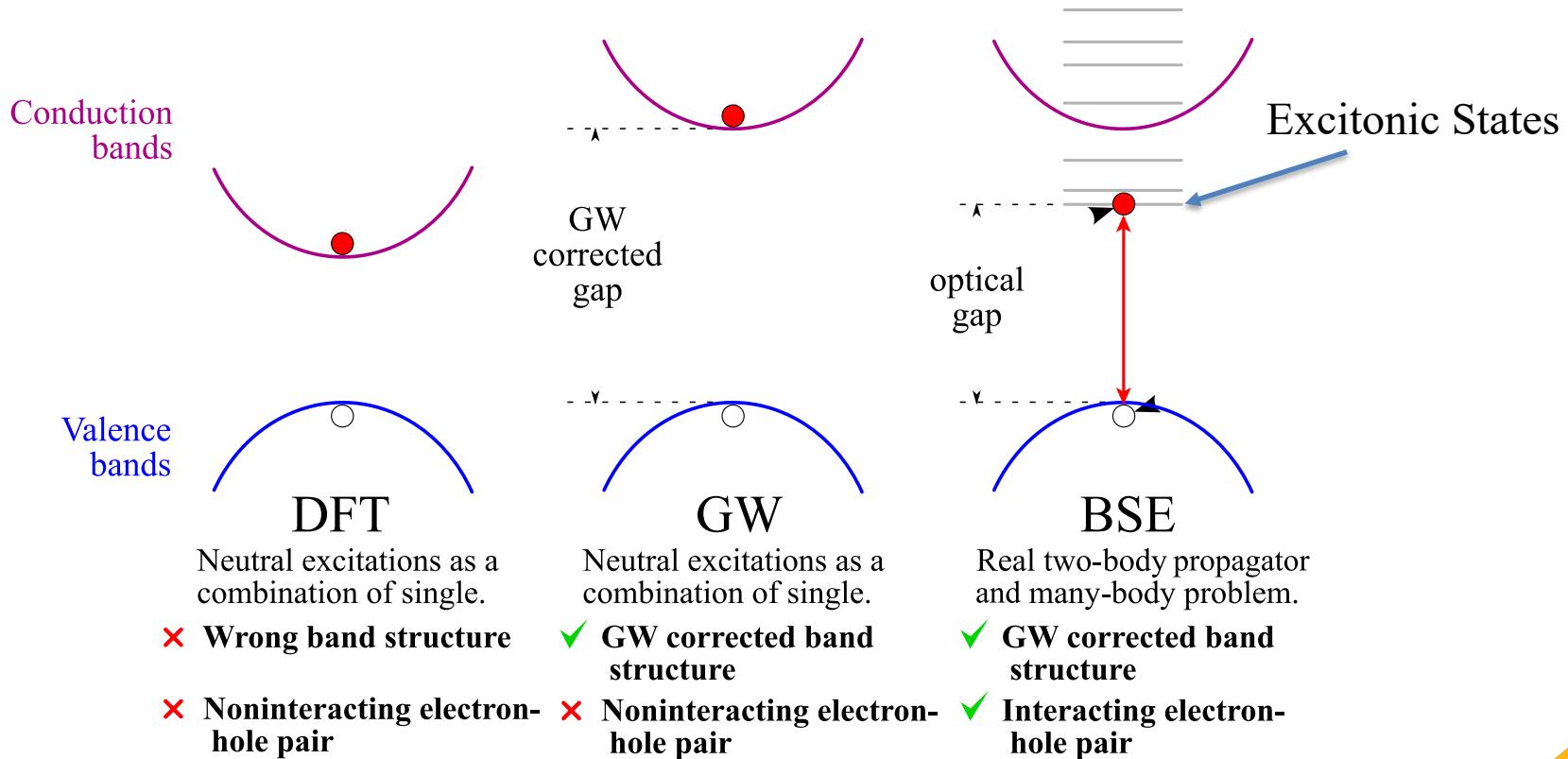
- Reduces 3N-dimensional problem to 3
- Good balance between **computational efficiency** and **accuracy**

DFT Shortcomings

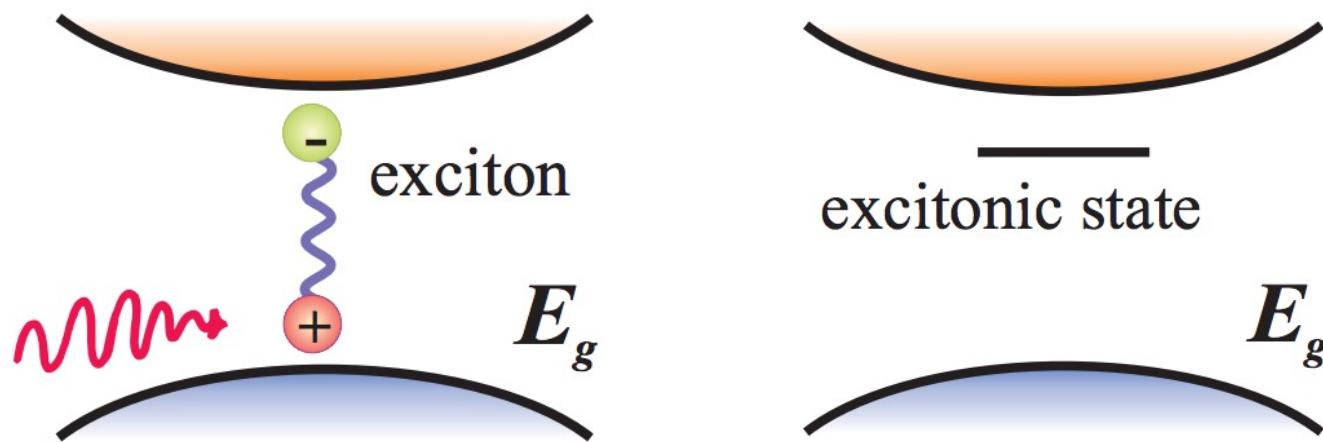
- **Results depend directly on which XC functional is used**
- van der Waals interactions (vdW corrections)
- Systems with strongly localized and correlated electrons (DFT+U)
- Band gaps

Proposed Solutions

- Post DFT methods (many-body perturbation theory)
- Stochastic methods (Quantum Monte Carlo)



- Quasiparticle gaps obtained with GW
- Optical gaps obtained from first peak in dielectric function (with BSE)
- Exciton binding energy, $E_b = E_{GW} - E_{opt}$

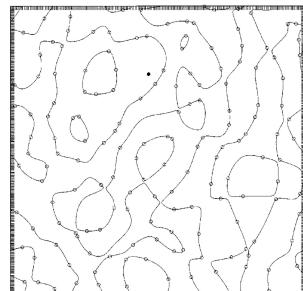


Diffusion Monte Carlo (DMC)

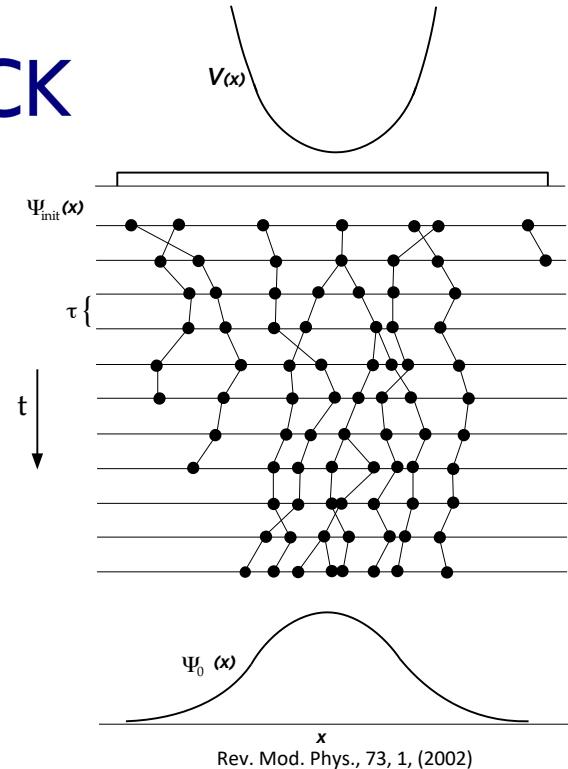
$$-\frac{\partial_t \Phi(\mathbf{R}, t)}{\partial t} = (\hat{H} - E_T) \Phi(\mathbf{R}, t),$$

Imaginary-time Schrödinger Eq.

- DMC: Simulate **diffusion** of walkers in **imaginary-time** until you reach **steady state**
- Equation is solved by a **Green's function** that propagates each walker
- **Fixed-node approximation**
- Timestep **errors**
- Finite size **effects**

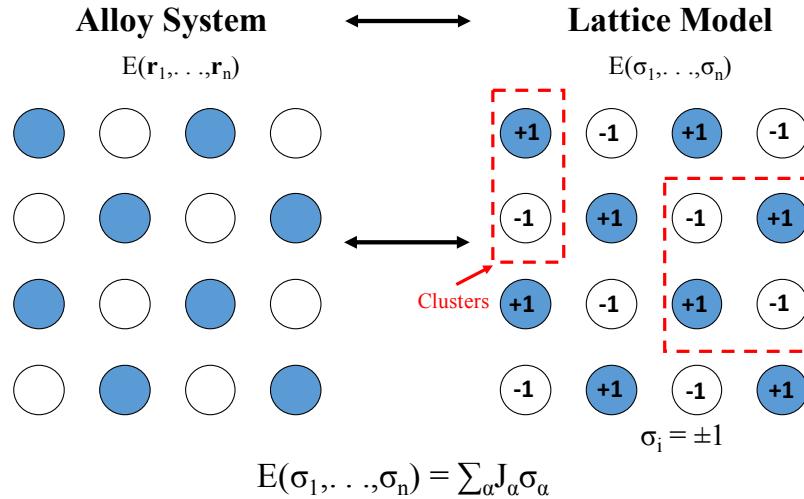
QMCPACK

Fixed-nodal surface

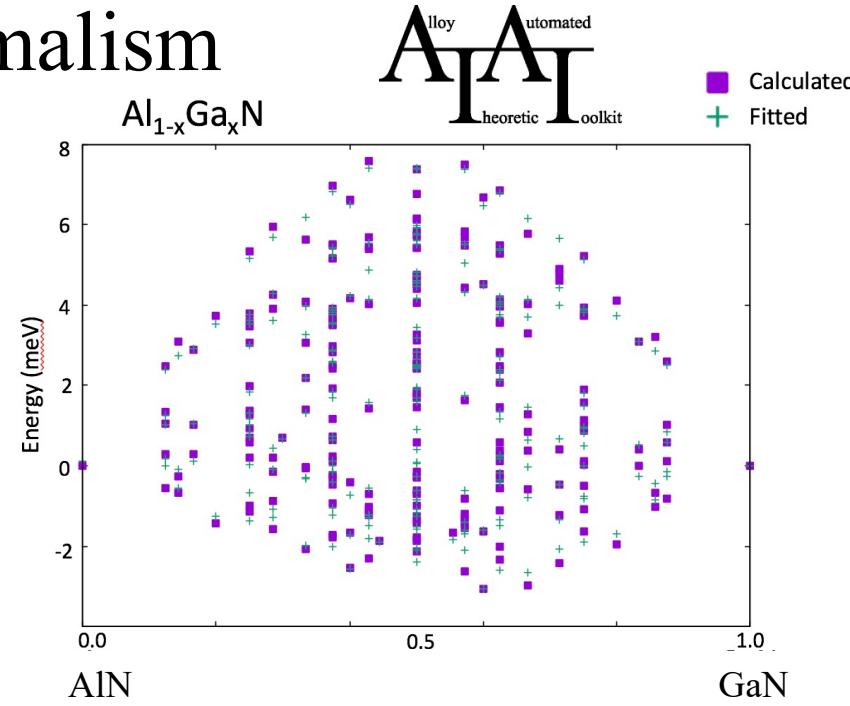


Diffusion of walkers in imaginary time

Cluster Expansion (CE) Formalism



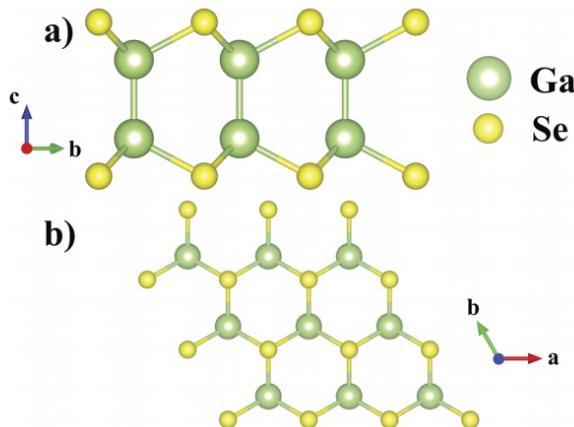
- CE formalism allows us to study **energetics of alloy system**
- **DFT energies** are generally used as **training set**
- **Fitted energies** are determined from statistical methods (quantified by **cross validation**)



Cross Validation Score Calculated Fitted

$$CV = \frac{1}{n} \sum_{i=1}^n (E_i - \hat{E}_{(i)})^2$$

Materials Applications of Modeling at Chemical Accuracy

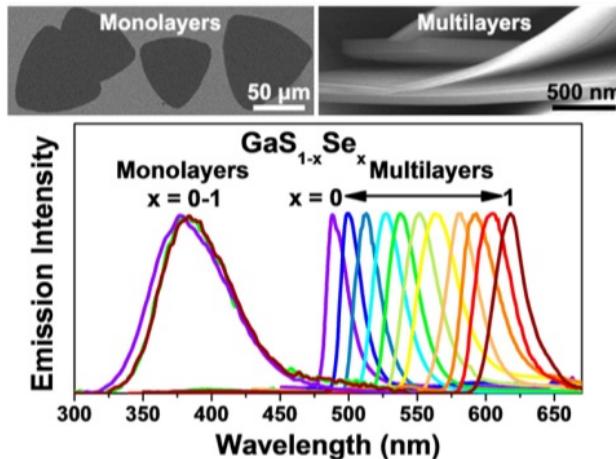


J. Chem. Phys., 153, 154704 (2020)

QMCPACK

Motivation

- **2D GaSe** is a semiconductor suitable for photovoltaics, transistors, water-splitting, adatoms also binds strongly to surface (energy applications)
- Post transition metal chalcogenides predicted to have **lower exciton binding energy** than transition metal dichalcogenides
- DFT functionals **disagree** and results are **off from experiment**



ACS Nano 9, 9585–9593 (2015).

[1] Sci. Rep. 4, 5497 (2014).

[2] Phys. Rev. B 96, 035407 (2017).

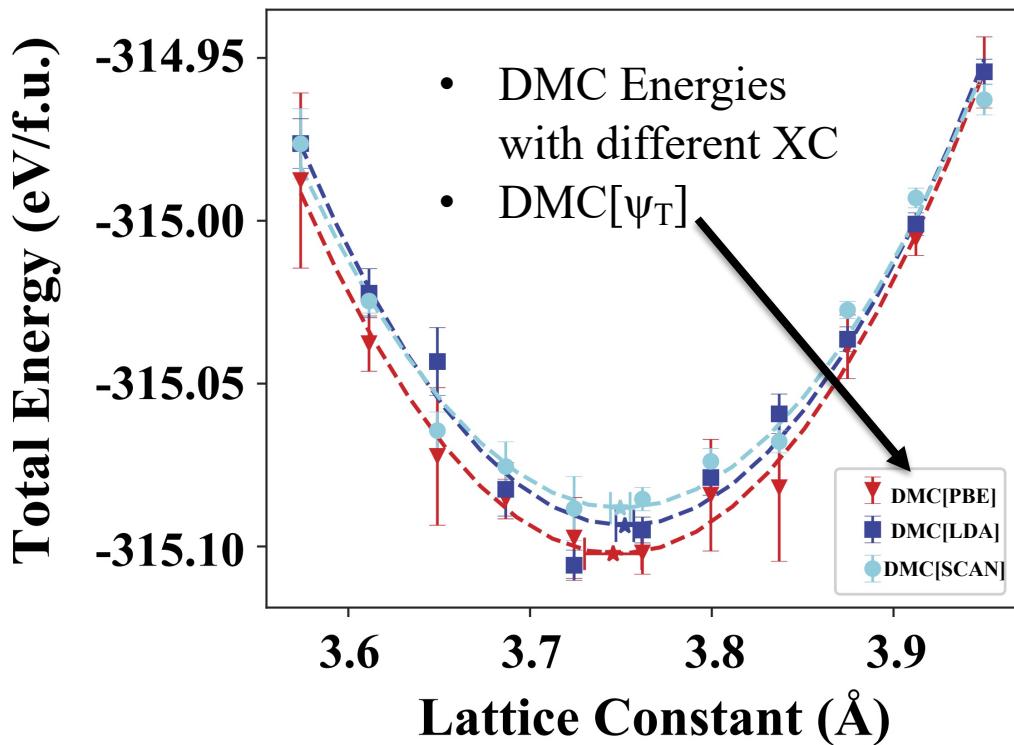
[3] ACS Nano 9, 9585 (2015).

2D GaSe in Experiment

- $a = b = 3.74 \text{ \AA}$ [1]
- $E_{QP} = 3.5 \text{ eV}$ (on graphene) [2]
- $E_{opt} = 3.3 \text{ eV}$ (on SiO_x/Si) [3]
- **Alloys have been synthesized in few-layer form, band gap is tunable** [3]

Goal: Use QMC for 2D GaSe

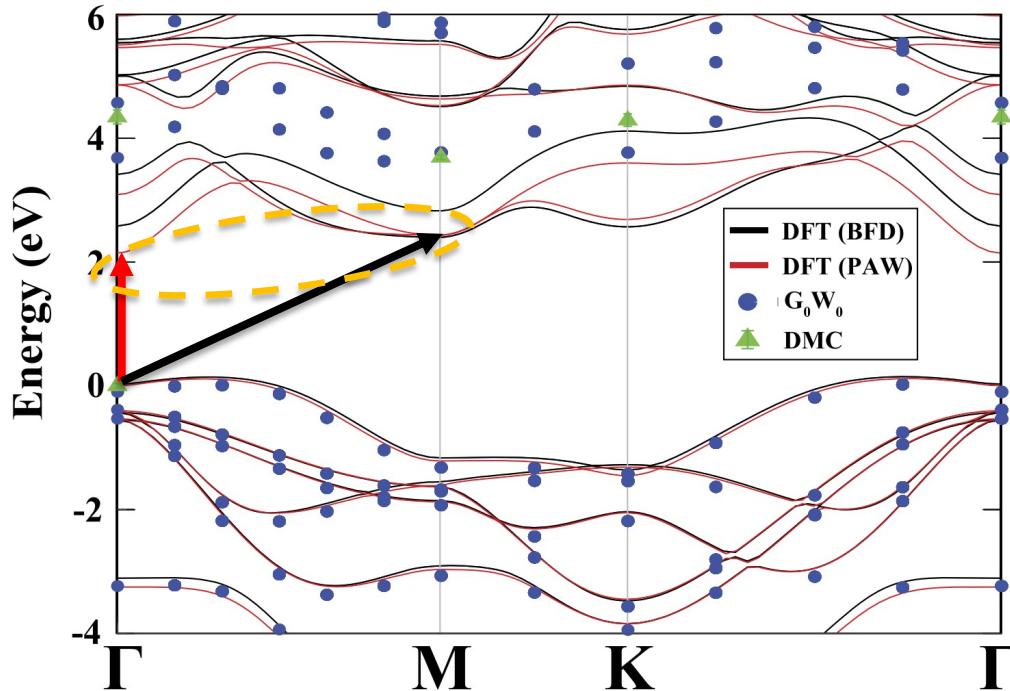
- Obtain “chemically accurate” **results for GaSe** from diffusion Monte Carlo (**DMC**) since DMC has weak dependence on starting wavefunction (WF)
- Calculate lattice parameters, band gap, cohesive energy
- **Benchmark** with DFT and GW results (**multiple functionals**) and **experiment**



J. Chem. Phys., 153, 154704 (2020)

PBE: 3.81 Å
LDA: 3.71 Å
SCAN: 3.76 Å
Exp: 3.74 Å

- Lattice scaled isotropically
Using a trial wavefunction (ψ_T)
from PBE, LDA, and SCAN
yields in similar results at the
DMC level
- DMC[PBE]: 3.74(2) Å
- DMC[LDA]: 3.75(1) Å
- DMC[SCAN]: 3.75(1) Å



J. Chem. Phys., 153, 154704 (2020)

- Energy difference between each high symmetry point at the conduction band edge is small
- Results in **incorrect band gap prediction** and **direct/indirect discrepancy**
- DFT and GW band gaps are **heavily dependent** on **functional** and **pseudopotential choice**
- Benchmarked with PBE, SCAN, HSE06, G_0W_0 and QMC pseudopotentials (BFD and ccECP)

*PBE functional used for DFT, G_0W_0 and DMC (above)

Functional	Kohn-Sham Gap	Direct (D) or Indirect (I)
PBE (PAW)	2.14	D
PBE (BFD)	2.37	I
SCAN (PAW)	2.53	D
SCAN (BFD)	2.78	I
HSE (PAW)	3.11	D

Method	Quasiparticle Gap	D or I
G_0W_0 -PBE (PAW)	3.81	D
G_0W_0 -SCAN (PAW)	3.14	D
DMC (BFD)	3.69(5)	I

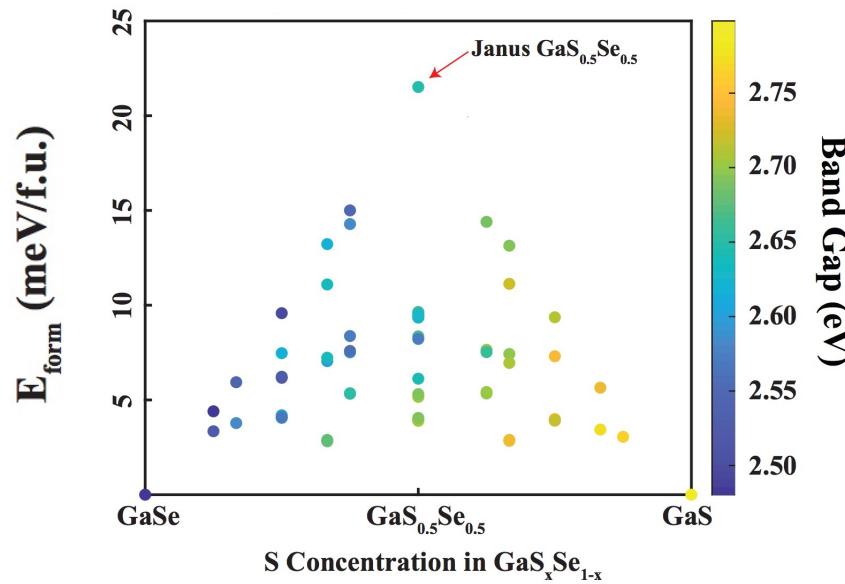
- 2D GaSe is an **indirect** semiconductor, QP gap and in **good agreement** with experiment (3.5 eV)
- Upper bound of 80 meV for exciton binding energy (from 3.70(4) eV optical gap)
- Have in depth **theoretical benchmarks** for this material, which will aid future studies involving DMC and 2D materials

Motivation

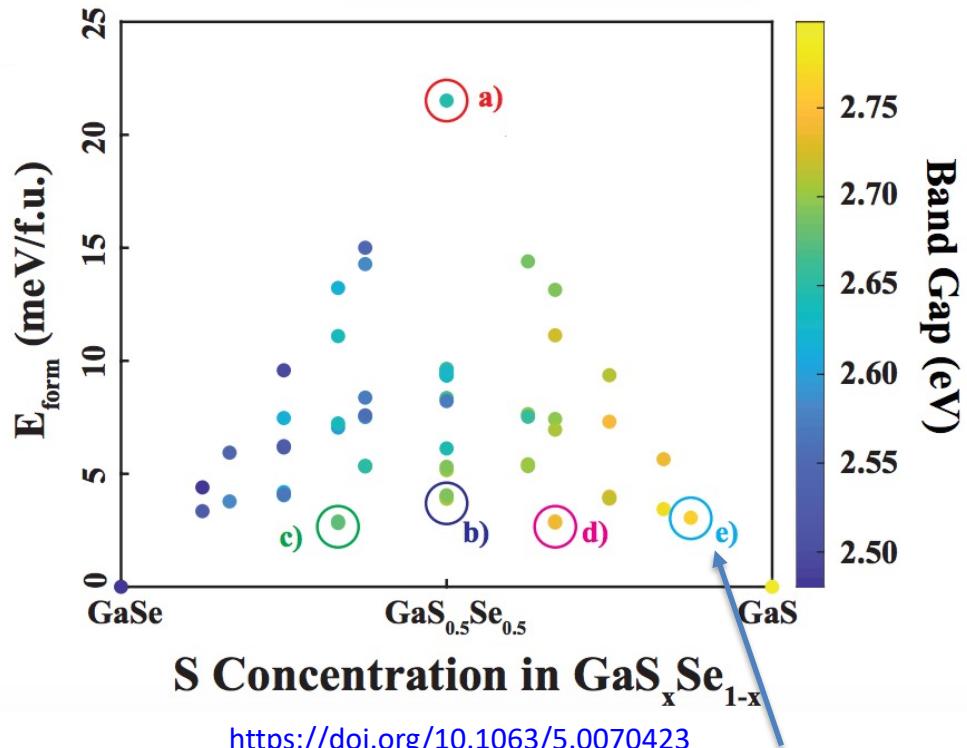
- **Alloying** is an effective way to **engineer** 2D material properties
- 2D Janus $\text{GaS}_x\text{Se}_{1-x}$ and $\text{GaS}_x\text{Se}_{1-x}$ have been studied at the DFT level

Goal

- Develop a procedure to study properties of 2D alloys with similar atomic environments using DMC
- Study the effect of different Jastrow parameters on the VMC and DMC energies to minimize the number of simulations needed (*Jastrow sharing*) while still reducing localization error

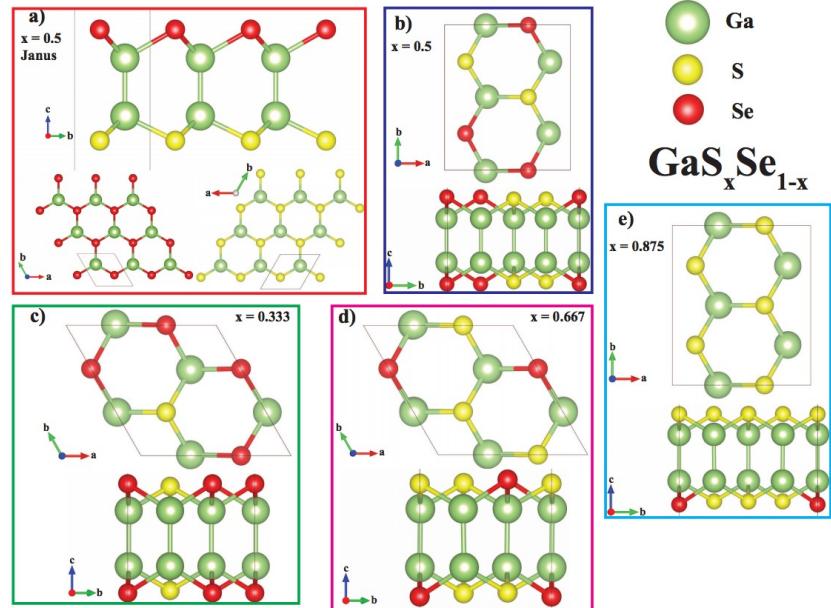


UMBC 2D $\text{GaS}_x\text{Se}_{1-x}$ Alloys: DFT



*Structures optimized and energy hull obtained with SCAN+rvv10

<https://doi.org/10.1063/5.0070423>



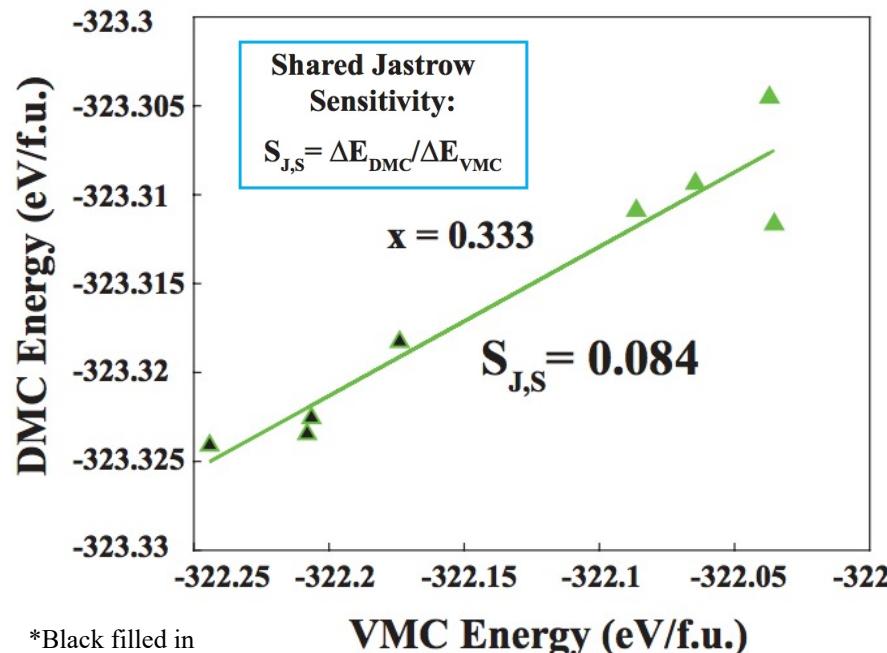
- Energy hull diagram calculated with DFT
- Screen most stable structures from hull

$$E_{\text{form}} = E_{\text{GaSSe}} - x^* E_{\text{GaSe}} - (1 - x)^* E_{\text{GaS}}$$

DMC-J2	Janus	x = 0.5	x = 0.333	x = 0.667
Janus Jastrow	0	-3(7)	-9(7)	-6(7)
x = 0.5 Jastrow	3(4)	0	5(7)	-9(8)
x = 0.333 Jastrow	-7(5)	4(9)	0	6(9)
x = 0.667 Jastrow	-9(7)	-2(8)	-2(6)	0
x = 0.875 Jastrow	-8(4)	-5(8)	-2(6)	-3(7)

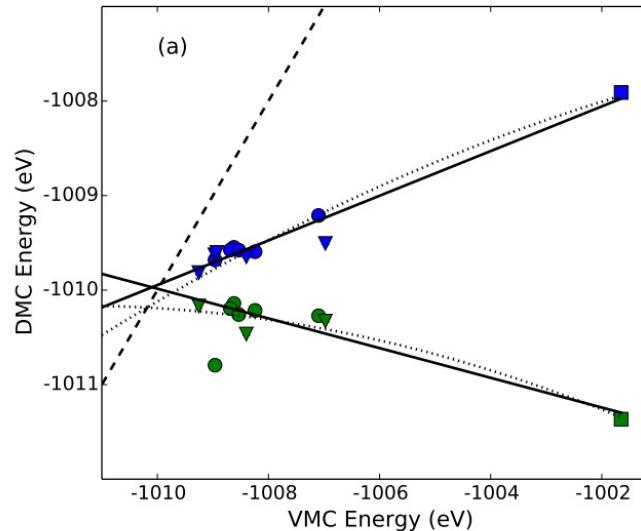
*Energy differences
(in meV) between
DMC with self
Jastrows and shared
Jastrows (J_2, J_3 not
depicted)

- Sharing Jastrows nearly **identical** at the DMC level (same number of steps and walkers)
- Localization error is still decreased no matter which Jastrows are used
- Most convenient to **reuse** Jastrows from cell with **smallest Wigner-Seitz radius**



*Black filled in shapes J2, others J3

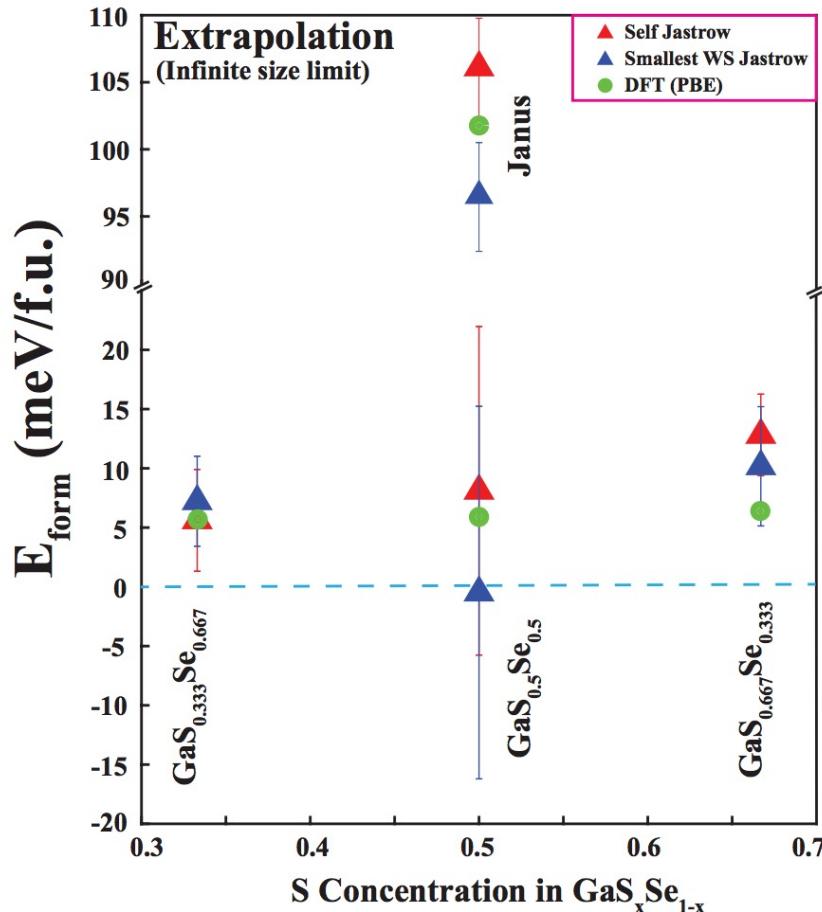
- **Shared Jastrow Sensitivity:** DMC energy decrease per unit decrease in VMC energy calculated with *self-Jastrows* and *shared-Jastrows* (per f.u.)
- Analogous to *Jastrow Sensitivity* [1, 2] for atoms
- Sensitivity values are comparable to those tabulated for atoms in [1, 2]



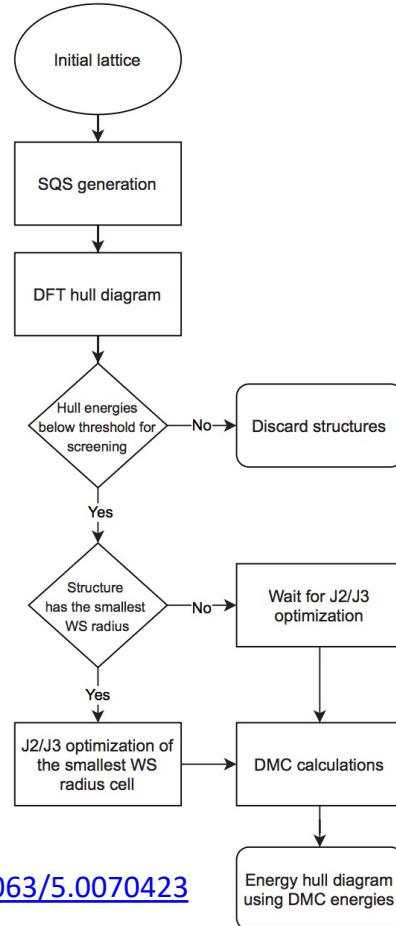
J. Chem. Phys. **146**, 244101 (2017)

[1] Dzubak, Krogel, Reboredo, J. Chem. Phys. **147**, 024102 (2017)

[2] Krogel, Kent, J. Chem. Phys. **146**, 244101 (2017)



- DMC calculated energy **hull diagram**
- Extrapolated to **infinite size limit**
- Comparison of DMC energies calculated with alloy's **self Jastrows** versus **Jastrows** of the **smallest WS cell, nearly identical**
- DFT and DMC are in close agreement, beneficial for benchmarking our hull diagram for low and high E_{form} structures

**VMC Computational Time (seconds)**

	1 Supercell	Extrapolation	Energy Hull
Self Jastrow	755	7,124	24,043
WS Jastrow	134	134	134

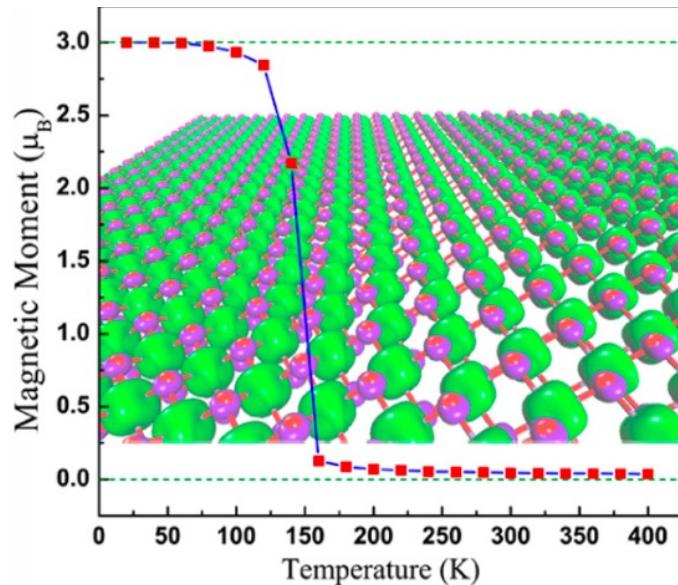
DMC Computational Time (seconds)

	1 Supercell	Extrapolation	Energy Hull
Self Jastrow	2,143	32,899	93,066
WS Jastrow	2,109	33,259	93,170

- By using WS Jastrow, extra VMC is avoided (other supercell sizes, other stoichiometries)
- When self Jastrows are used, VMC accounts for substantial amount of total cost (~1/4), cannot be neglected
- Jastrow does not change the DMC time needed to achieve target error bar



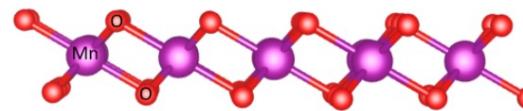
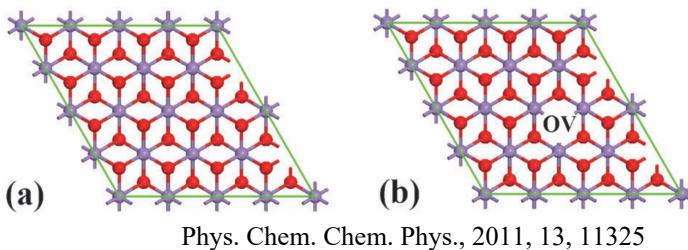
Motivation: 2D MnO₂ with QMC



J. Phys. Chem. Lett. 2013, 4, 3382

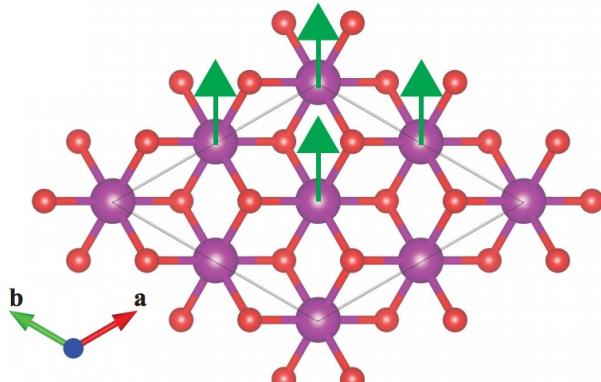
Motivation

- 2D MnO₂ has been reliably synthesized
- Semiconducting
- **Predicted ferromagnetic**
- Catalytic applications
- T and H phase predicted stable
(C. Ataca *et al.*, J. Phys. Chem. C. 116, 8983 (2012))

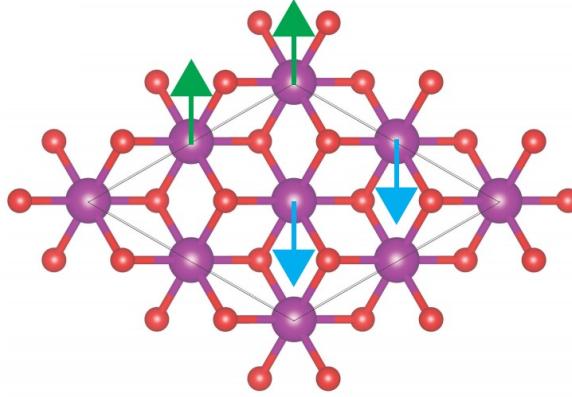


https://www.2dsemiconductors.com/2D_mno2/

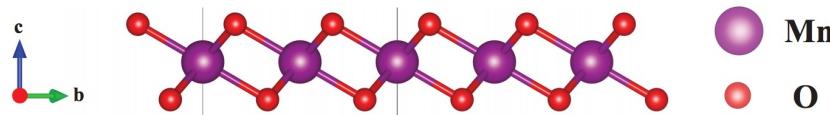




Ferromagnetic (FM)



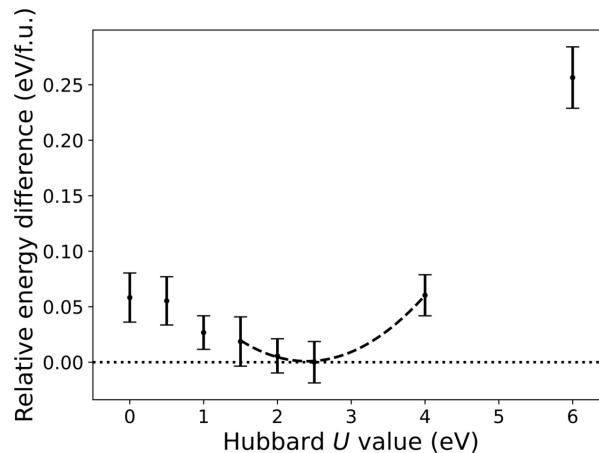
Antiferromagnetic (AFM)



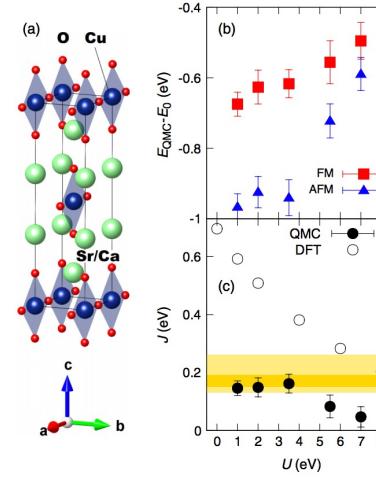
DFT Functional	$E_{\text{FM}} - E_{\text{AFM}}$ (meV/fu)
PBE	-8
PBE+U=2	-37
PBE+U=3.5	-55
SCAN	-3
SCAN+U=2	-16
SCAN+U=3.5	-29
LDA	18
LDA+U=2	-25
LDA+U=3.5	-44

Goal: QMC

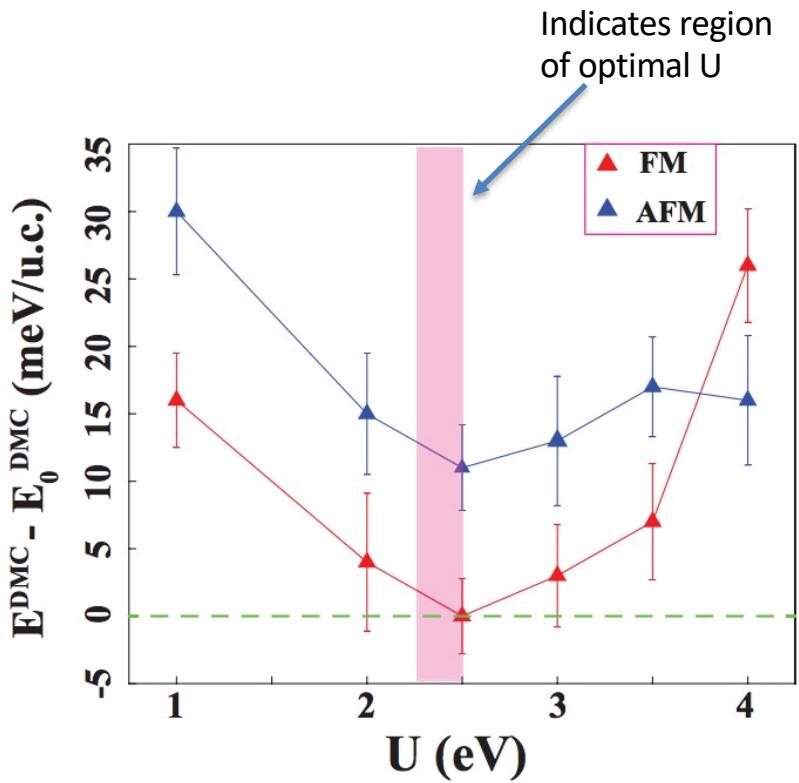
- An additional higher level of confirmation of FM in 2D MnO₂ to incentivize experimentalists to explore this further, estimate T_C
- Incorporation of using U to variationally determine the optimal trial WF for a 2D material
- Lose strong dependence on functional and U value, demonstrate this method is effective for 2D transition metal oxides



Phys. Rev. Materials 5, 064006



Phys. Rev. X 4, 031003



*Relative energy with respect to 0 eV

*Hard RRKJ (OPT) norm conserving potentials

*Trial WF created with PBE. 36 atom cell

Easy axis single ion anisotropy Heisenberg isotropic exchange Anisotropic symmetric exchange

$$\mathcal{H} = - \left(\sum_i D(S_i^z)^2 + \frac{J}{2} \sum_{i,i'} \vec{S}_i \cdot \vec{S}_{i'} + \frac{\lambda}{2} \sum_{i,i'} S_i^z S_{i'}^z \right)$$

Mn Atoms

$E_{\text{FM},z} = -4S^2D - 12S^2(J + \lambda)$

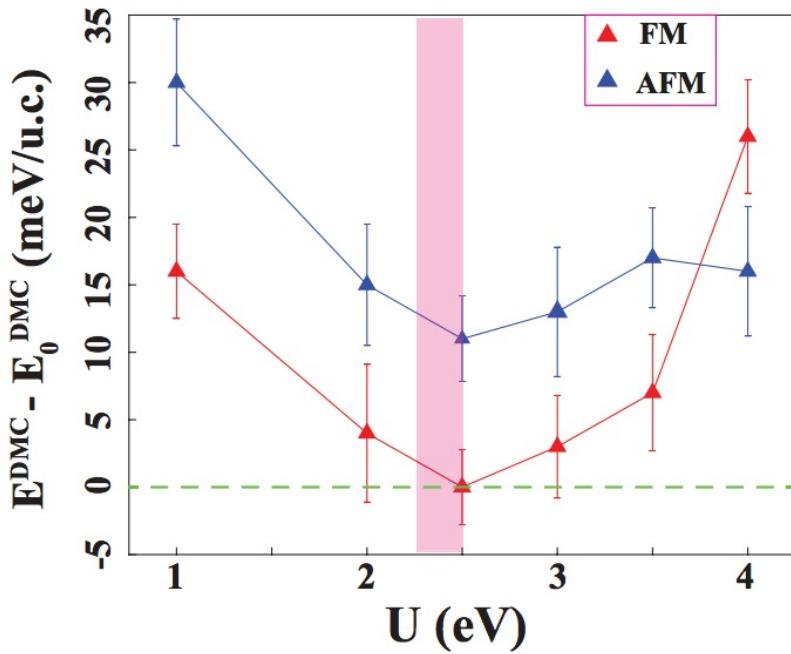
$E_{\text{AFM},z} = -4S^2D + 4S^2(J + \lambda)$

$E_{\text{FM},x} = -12S^2J$

$E_{\text{AFM},x} = +4S^2J$

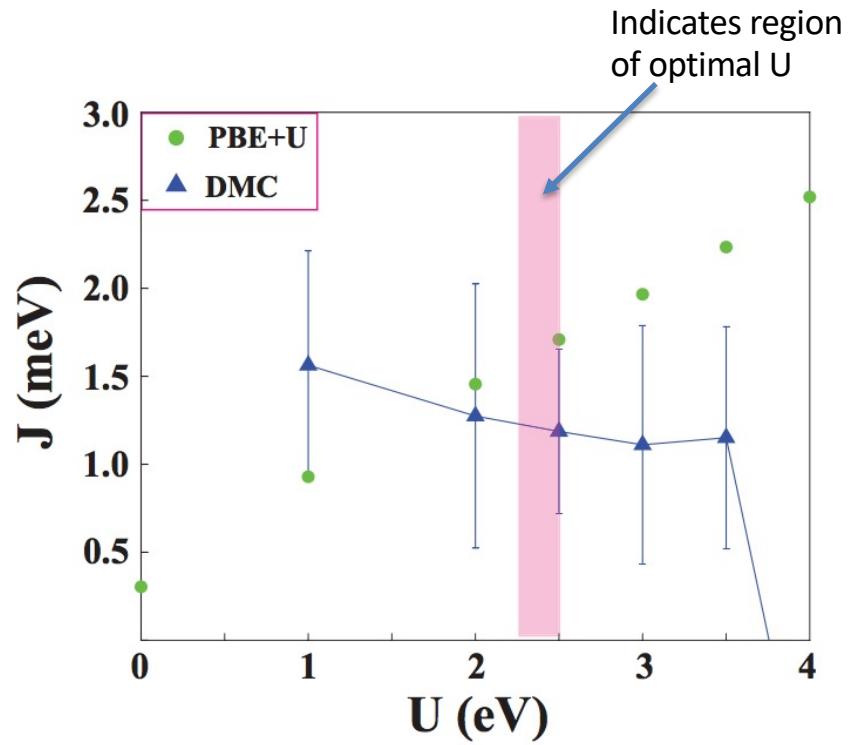
Determining J from QMC ($\lambda=0$)

D and λ are determined by running PBE+U (PAW)



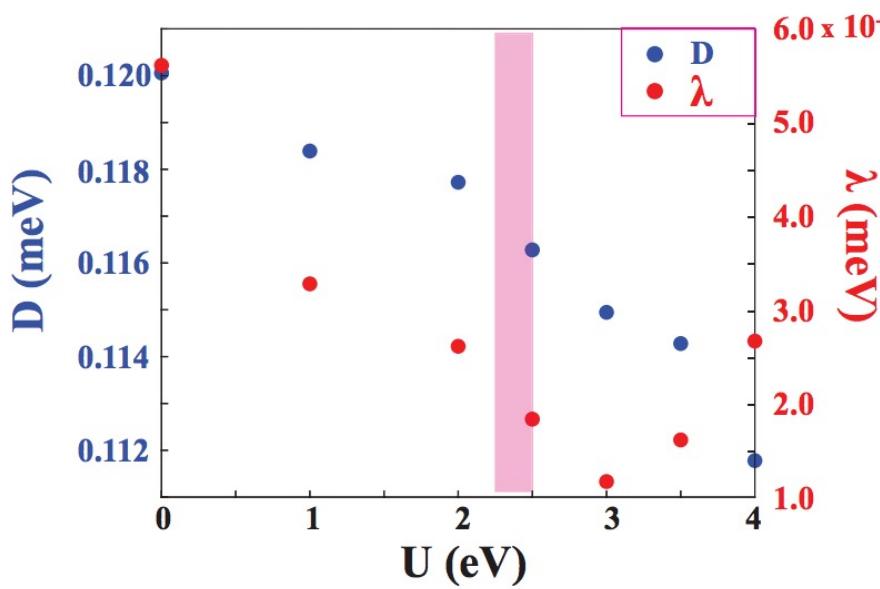
*Relative
energy with
respect to 0 eV

*Hard RRKJ (OPT) norm
converging potentials

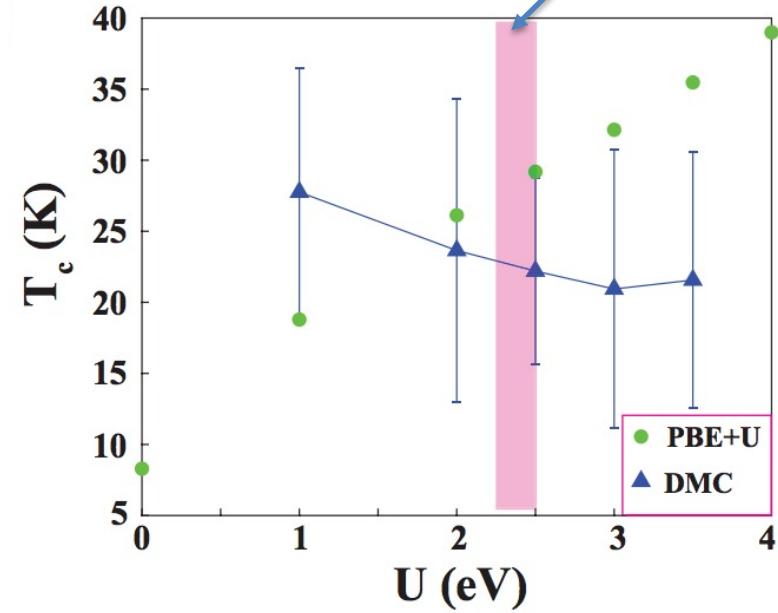


*Trial WF
created with
PBE. 36 atom cell

$$\mathcal{H} = - \left(\sum_i D(S_i^z)^2 + \frac{J}{2} \sum_{i,i'} \vec{S}_i \cdot \vec{S}_{i'} + \frac{\lambda}{2} \sum_{i,i'} S_i^z S_{i'}^z \right)$$

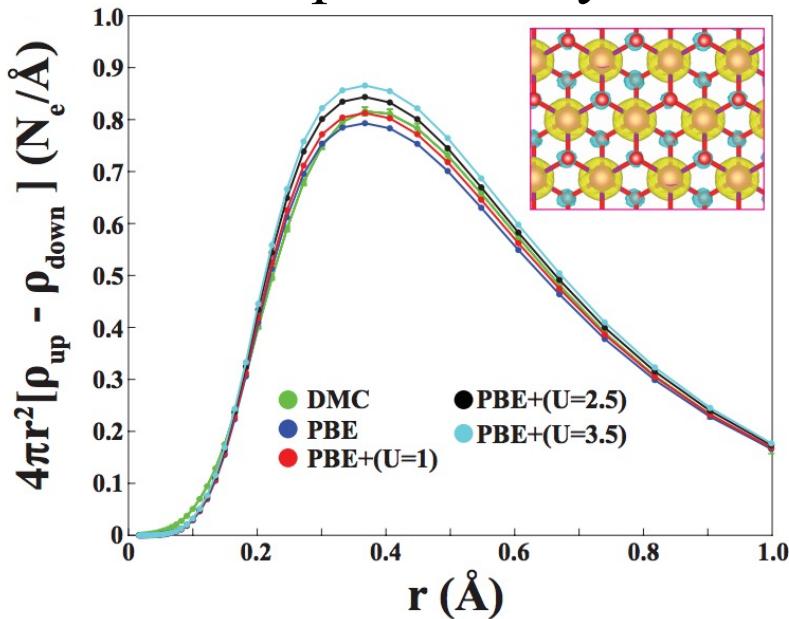


*Obtained from spin-orbit PBE (PAW) DFT calculations

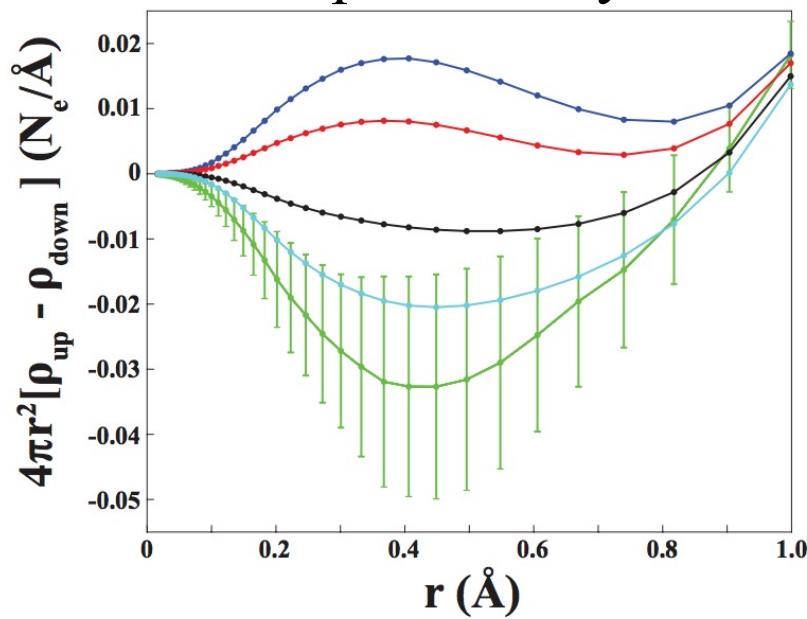


* T_c estimated from method of Torelli and Olsen

Mn Spin Density

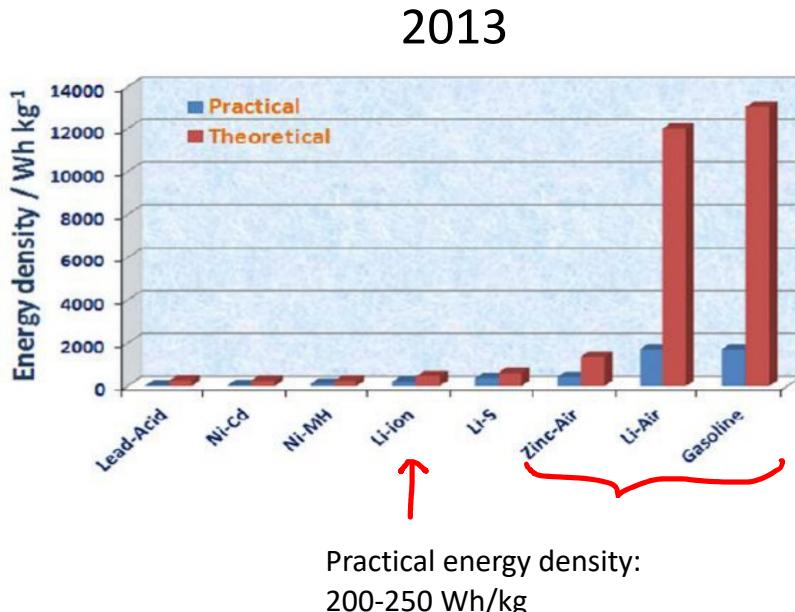


O Spin Density



$$\rho_1 = 2\rho_{\text{DMC}} - \rho_{\text{VMC}} + \mathcal{O}[(\Phi - \Psi_T)^2]$$

Metal-air batteries have benefits compared to intercalation chemistries.



Li-ion Batteries

- Are reaching their performance limit
- Are not predicted to be able to power EVs over long trips.

Metal-Air batteries

- Have **greater capacity and energy** than Li-ion batteries
- Are light and compact
- Low cost
- Are **environmentally friendly**

Metal-air batteries use oxygen as cathode

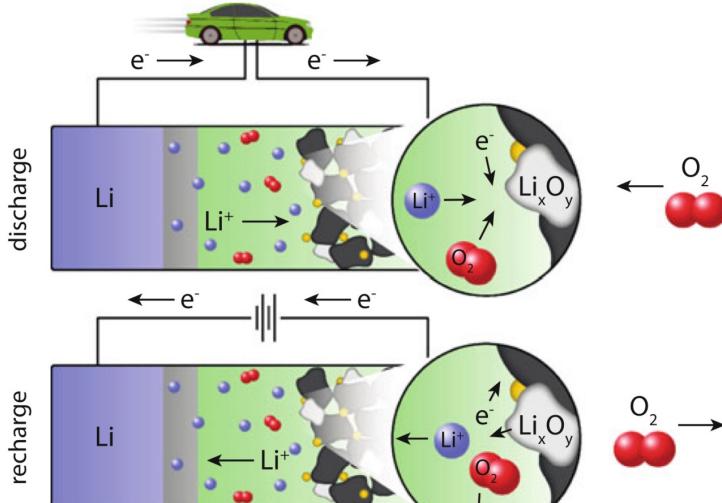
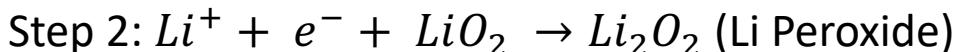
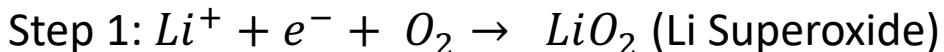
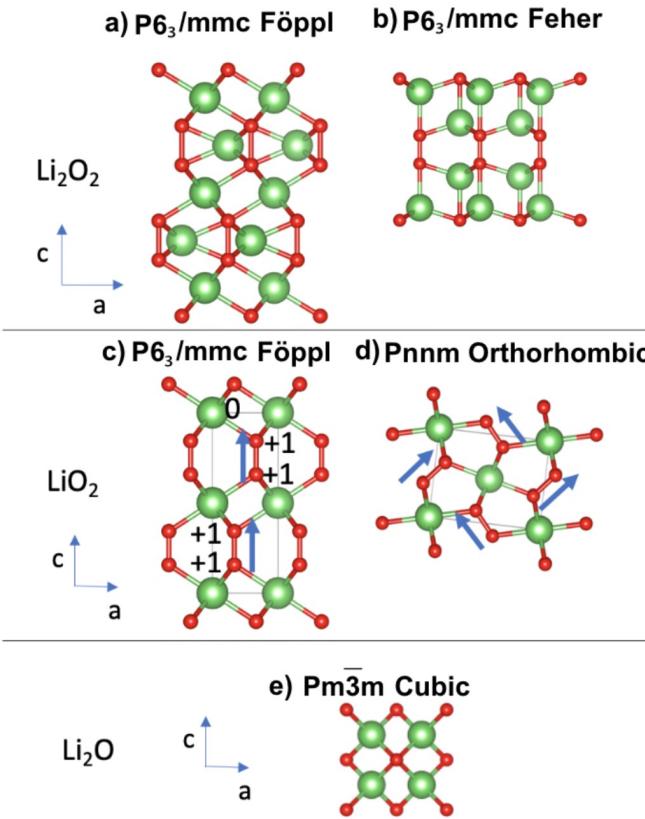


Image from University of Michigan Engineering Dept

Discharging

- Porous cathode material allow O_2 to flow in.
- metal ions oxidized at anode travel to cathode
- Oxygen reduction reaction (ORR) at cathode





Experimental results of Li_2O_2 suggests two phases

Formation Enthalpy (ΔH_{form}) of Li_2O_2

(A)	ΔH (eV/O ₂)	
experimental	$-6.57(9)^a$	-6.557^b
(B)		
	ΔH (eV/O ₂)	
	Féher	Föppl
PBE	-5.69	-6.24
HSE06	-5.90	-6.52

J. Phys. Chem. Lett. 2011, 2, 2483–2486

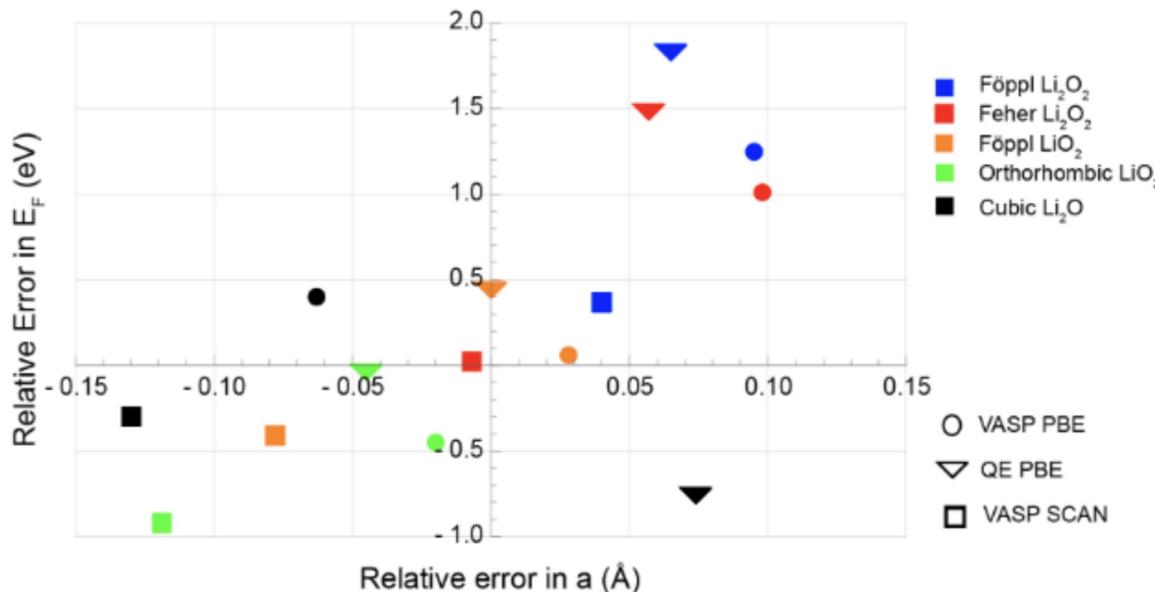
- Sample not from Li-air cell, but commercial powder
- Feher structure changes significantly during PBE relax
- DFT struggles with O₂ bonds

DFT underestimates band gap of Li_2O_2

Method type	This work	Prior work
DFT	1.99 (PBE)	1.98 (LDA) [54] 1.88 (RPBE) [24] 1.94 (PBE) [28]
Hybrid functional	4.19 (HSE)	4.2 (HSE) [26] 4.5 (HSE) [27] 4.44 (B3LYP) [55]
GWA	6.37 (scGW) 5.15 (G_0W_0)	4.91 (G_0W_0) [24] 4.81 (G_0W_0) [28]

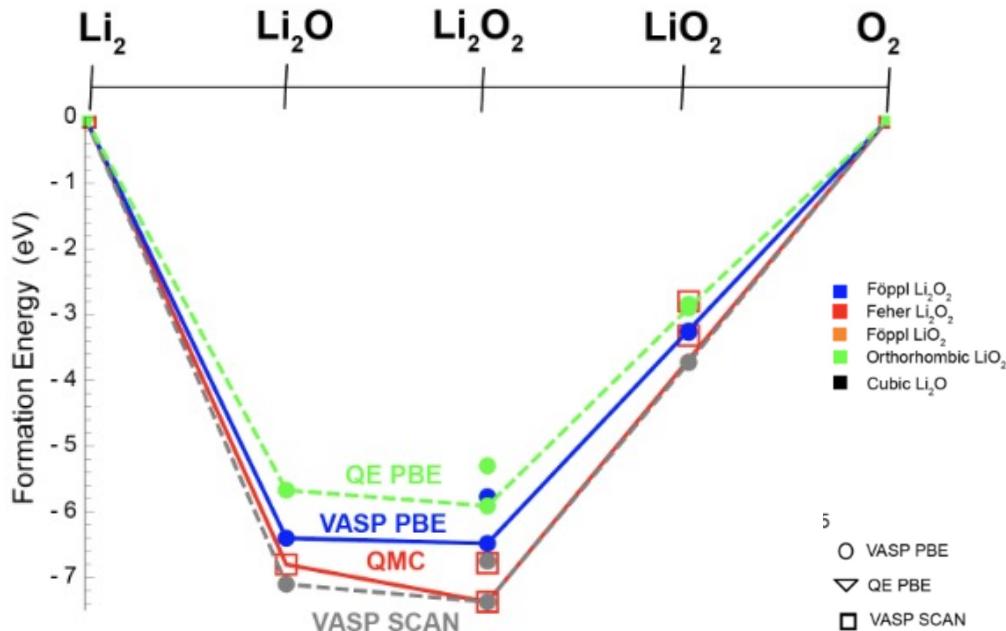
- DFT and HSE underestimate gap
- GW does not scale well with supercell size, and relies on DFT orbitals
- We want a method that scales well and isn't as reliant on DFT orbitals!

Relative errors of “a” parameter and formation energy compared to QMC values



- QE-PBE and VASP-PBE values are within 0.05 Å and 0.5 eV of each other.
- For both Li_2O_2 structures and Li_2O , **SCAN** predicts formation energy close to the QMC value (within 0.05 Å and 0.5 eV)
- SCAN **shrinks** lattice constants of all structures, except for Föppl Li_2O_2

Convex Hulls for QMC and each DFT functional



- For Föppel Li_2O_2 and Li_2O , **SCAN** predicts formation energy close to the QMC value
- For the rest of the structures, PBE gives a more accurate prediction



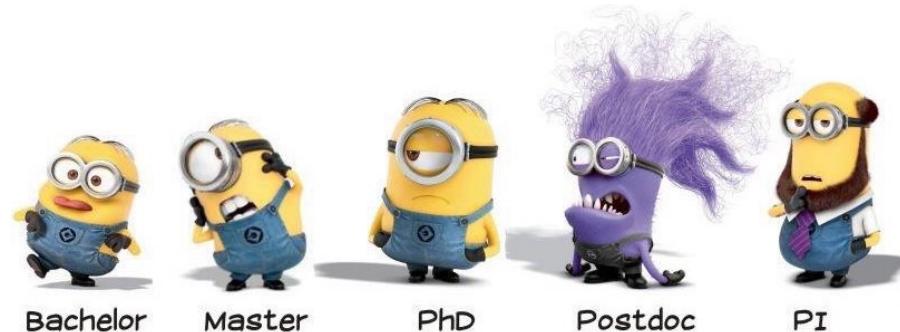
UMBC Summary and Future Perspectives

- QMC methods can be used to obtain chemically accurate properties of exotic 2D materials, correlated battery electrodes, results can be directly compared to measured values
- QMC methods can be extended to “non-ideal” systems (alloys, doping, defects) in a computationally efficient way, opening up pathway to tune properties and guide experimentalists
- Advancements in QMCPACK and pseudopotential development (spin-orbit) will open the door to study more interesting phenomena with QMC (2D TMDs, topological materials, materials for quantum computing)

Daniel Wines, Gracie Chaney



Dr. Kayahan Saritas



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E-mail: ataca@umbc.edu

