Breakthrough Petascale Quantum Monte Carlo Calculations

Shiwei Zhang, PI
Department of Physics, College of William and Mary

co-Pis: David Ceperley and Lucas Wagner, Department of Physics, University of Illinois
Elif Ertekin, Department of Mechanical Science & Engineering, University of Illinois

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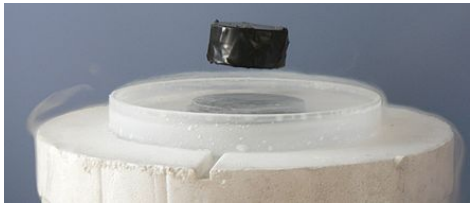
our challenge

Question: what do the following have in common?

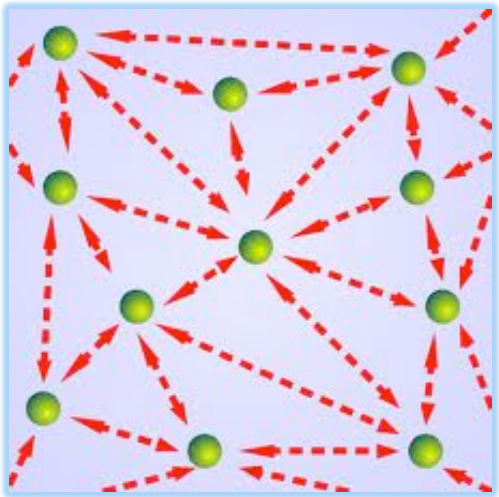


Answer: their properties can be described by the solution of an interacting quantum mechanical problem.

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle$$

$$H = \underbrace{-\sum_i \frac{1}{2}\nabla_i^2 - \sum_{\alpha i}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{\alpha\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}}_{\text{Separable (non-interacting) part}} + \underbrace{\sum_{ij}\frac{1}{r_{ij}}}_{\text{Electron-electron}}$$

Kinetic energy | **Electron-nucleus** | **Nucleus-nucleus**

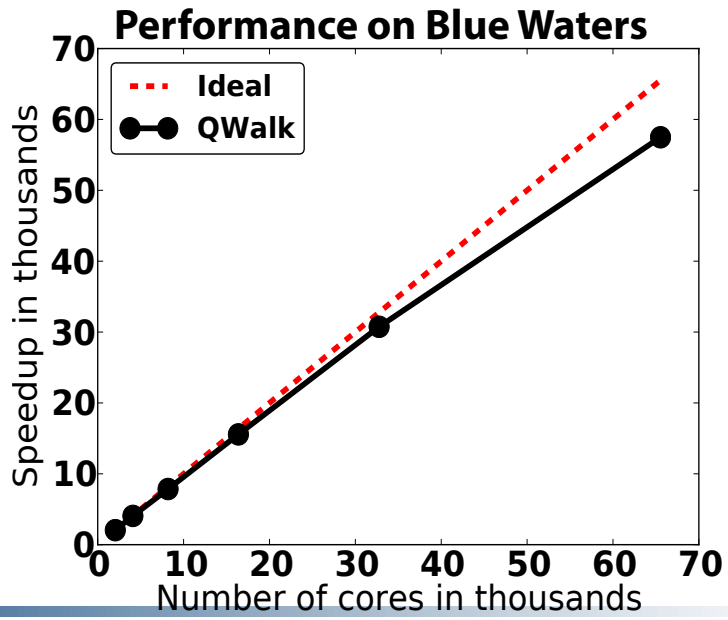


a brief history of our problem

- Sommerfeld model: just ignore the interactions altogether
- Hartree, Hartree-Fock: mean-field description of the interactions
- density functional theory: an effective mean field description of the interactions
- coupled cluster, quantum chemistry methods: interactions through expansion in one particle states
- quantum Monte Carlo: statistical approach to explicit many-particle interactions

Why quantum Monte Carlo?

Method	Computational Scaling	Directly based on Schrödinger Equation?	Accurate Band Gap?	Accurate Total Energy?
DFT	~ CN_e^3	No	No	Sometimes
Hybrid DFT	~ $5*CN_e^{3-4}$	No	Often	Often
DFT+U	~ CN_e^3	No	When Fitted	Sometimes
GW	~ CN_e^4	Yes	Often	No
QMC	~ $100*CN_e^3$	Yes	Yes	Yes

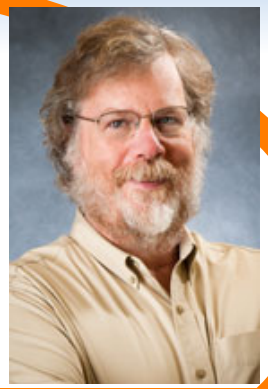


our team

Shiwei Zhang

New methods for quantum simulation

Materials at extreme pressures, planetary interiors, hydrogen



David Ceperley

Goal: quantitative simulation of interesting many body systems

Lucas Wagner

Correlated electron matter, transition metal systems

Application to materials for engineering, semiconductors, point defects

Elif Ertekin

our approach

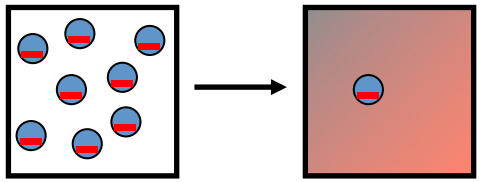
Density Functional Theory

Energy ⟷ Electron density

$$E_0 = E[n_0]$$

Hohenberg & Kohn, 1964

Interacting → Non-interacting



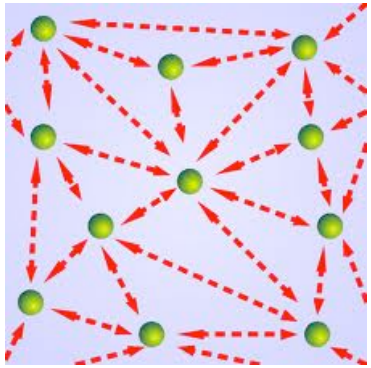
Kohn & Sham, 1965

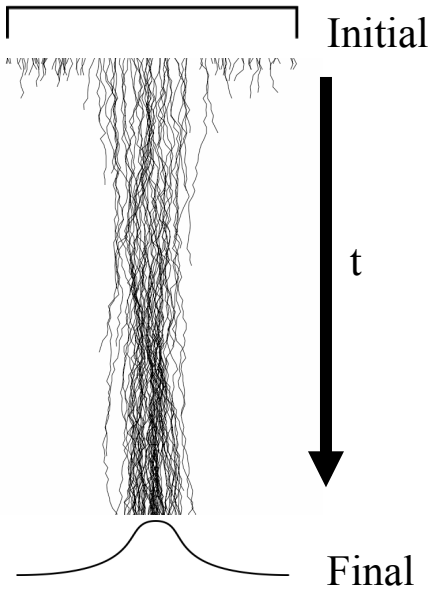
Walter Kohn (left), receiving the Nobel prize in chemistry in 1998.

Quantum Monte Carlo

Statistical Approach to Solving the Interacting, Many Body Problem

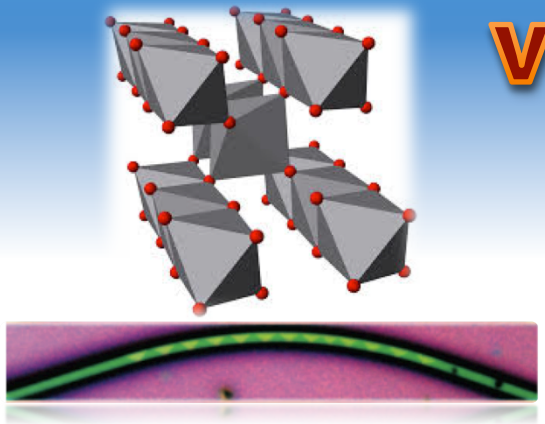
$$H\psi(r_1, r_2, r_3 r_4 \ldots) = E\psi(r_1, r_2, r_3 r_4 \ldots)$$

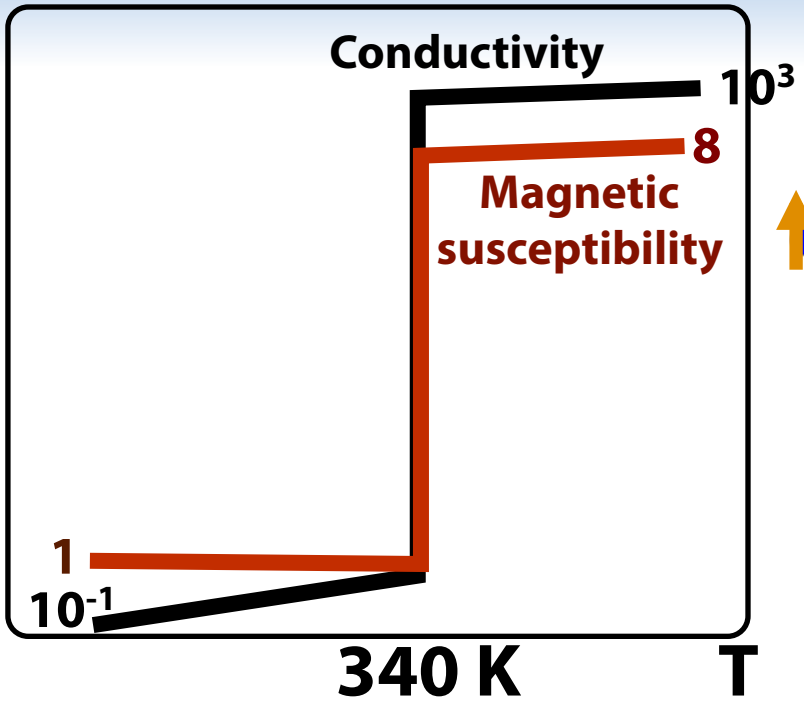




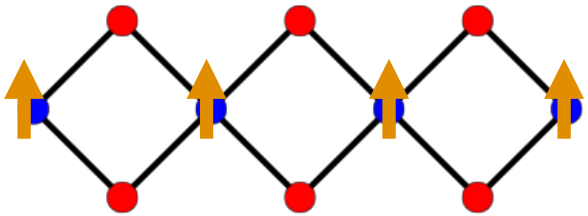
some examples from our work

vanadium dioxide

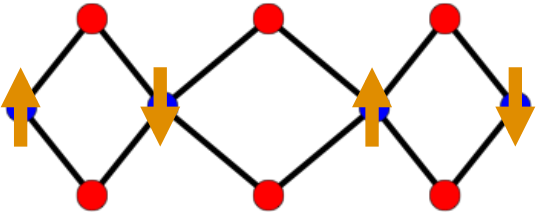


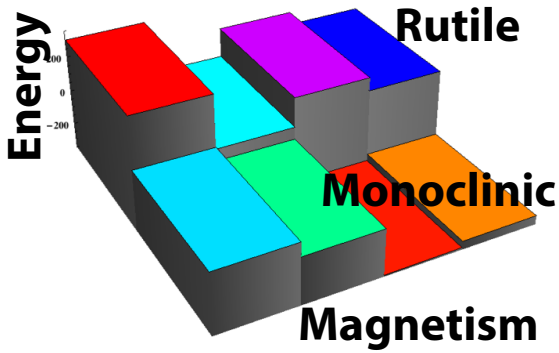


Rutile



Monoclinic

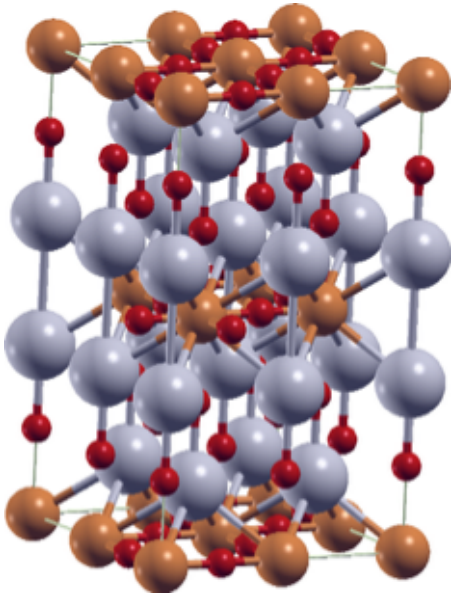


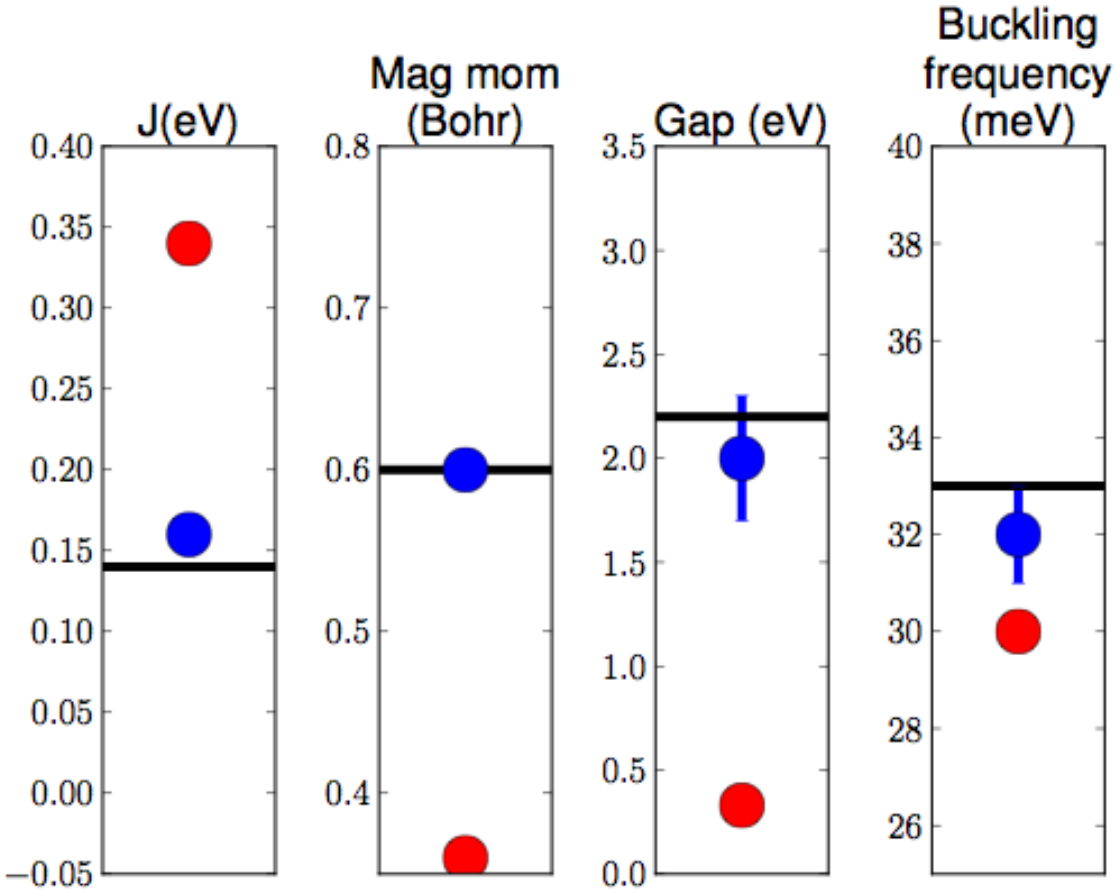


- No spins: structural transition would happen, but no MIT
- No structure: possible low-temperature FM ordering, but no MIT
- The MIT is a cooperative transition; the Goodenough model was good enough (… almost)

Zheng, Wagner (submitted 2014)

the cuprates : high T_c superconductivity





Experiment

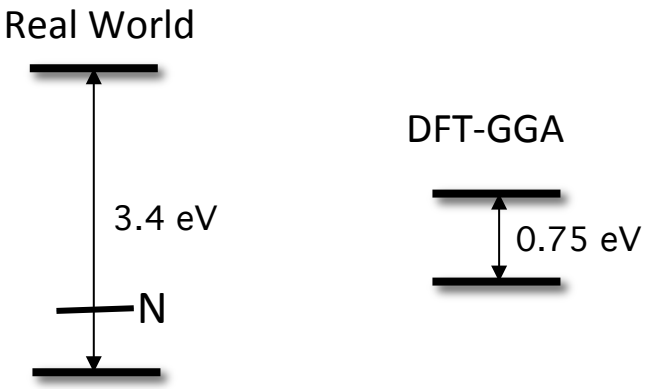
FN-DMC

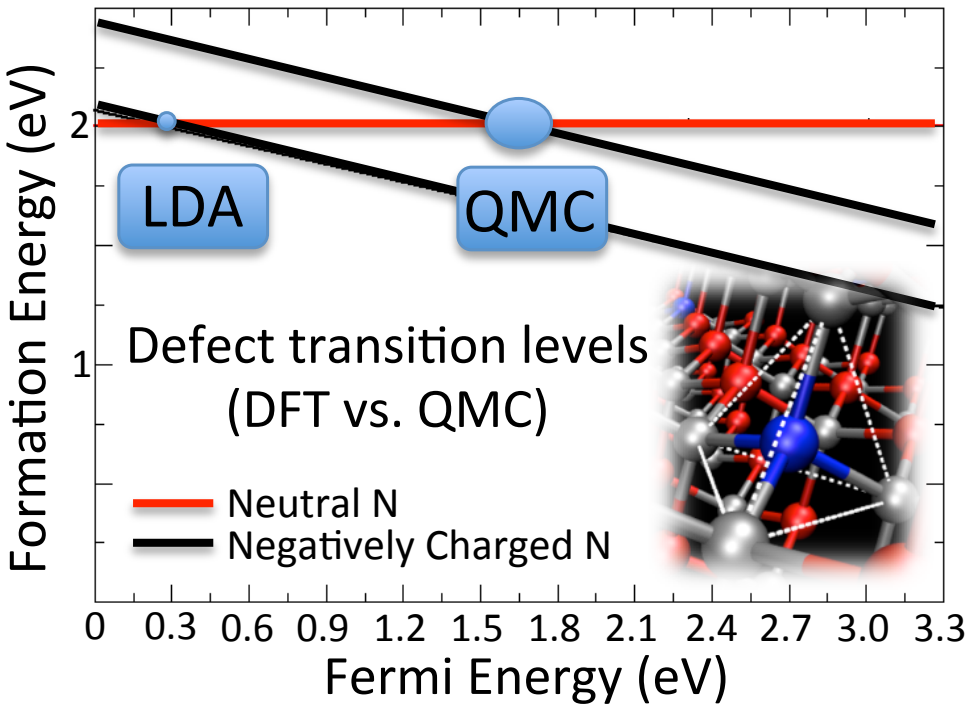
DFT(PBE)

L.K. Wagner and P. Abbamonte arXiv:1402.4680

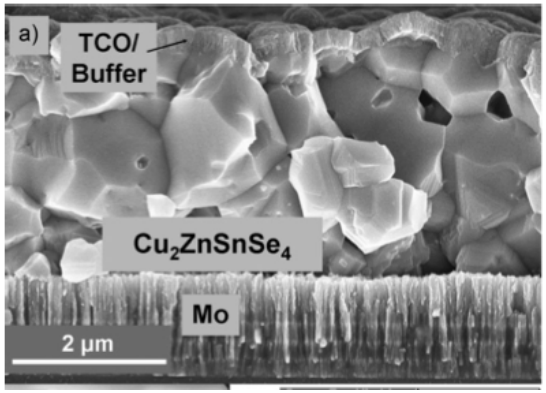
doping in zinc oxide

- accurate prediction of point defect properties – especially thermal and optical ionization energies – would be very useful for point defect engineering
- but defect properties have proven challenging to model via first principles, *e.g.* band gap problem
- question of historical significance: can N doping lead to p-type conductivity in zinc oxide?
- QMC : quantitative agreement with most recent experimental data

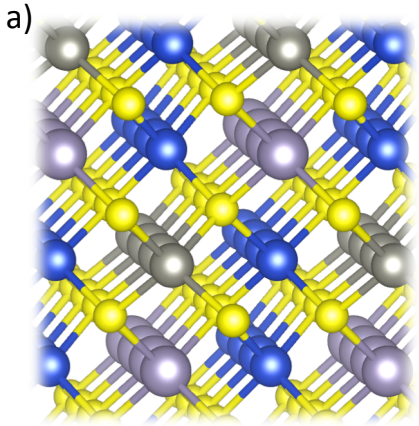


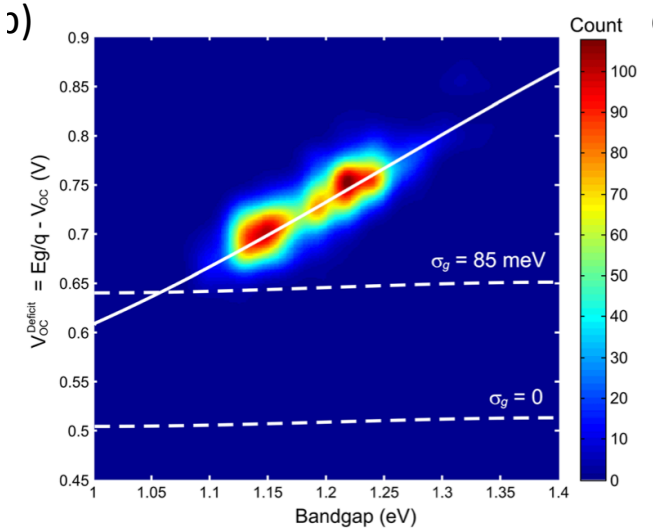


new materials for photovoltaics: kesterite CZTS/Se

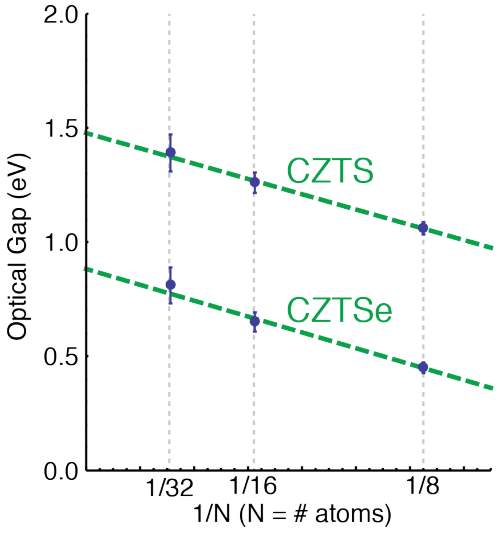


Todorov et al., *Adv. Mater.* **22** E156-E159, 2010. conversion efficiency : ~11%





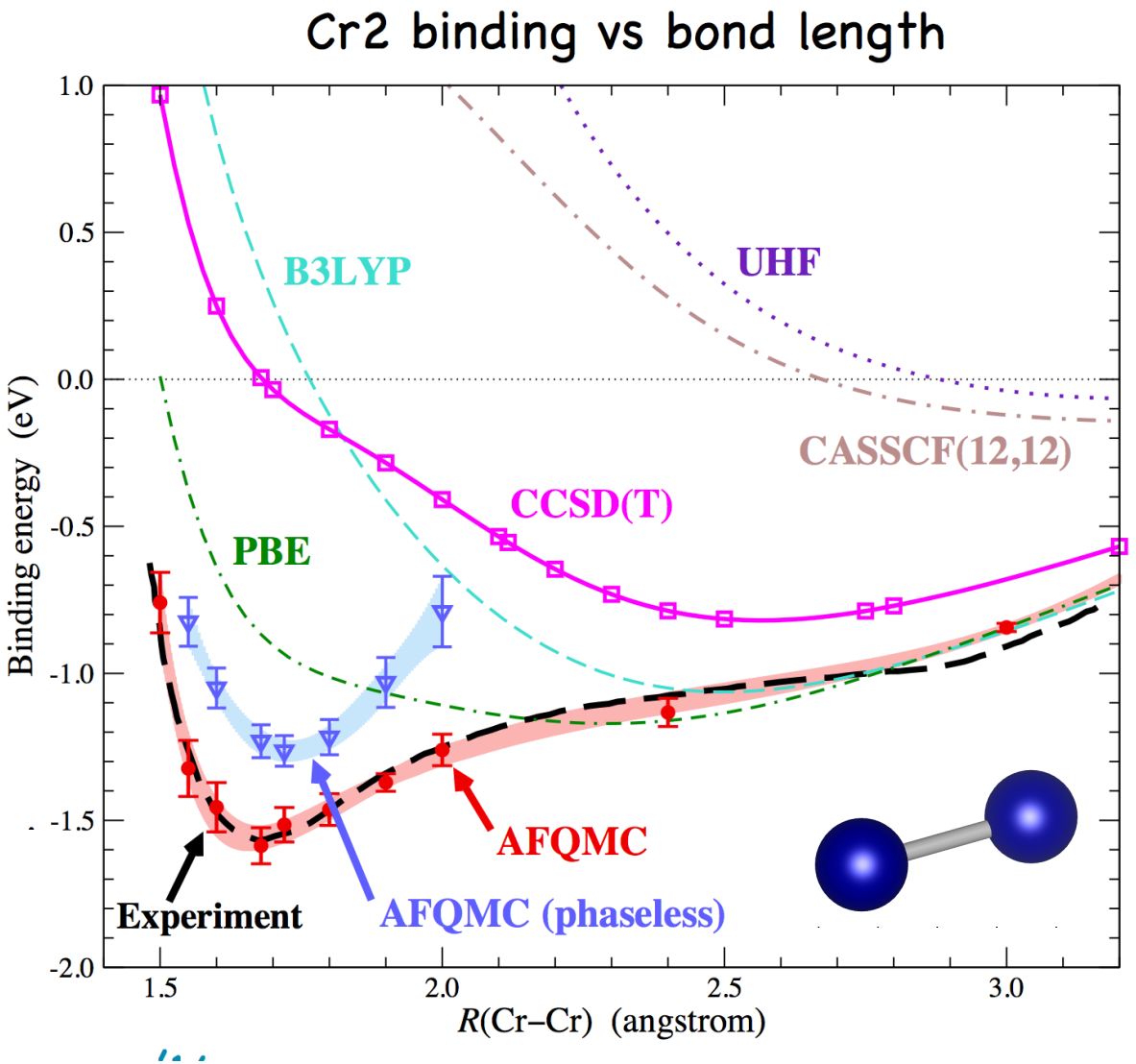
Gokmen, Gunawen, Todorov, and Mitzi, Appl. Phys. Lett. 2013.



- CZTS/CZTSe: relatively new thin-film photovoltaic converter
- Despite rapid early progress, recently performance improvements have flattened out
- Challenge: identify the defect or defect cluster that is responsible for the low open-circuit voltages in devices
  - Cu_{Zn}, Zn_{Cu}, or $|Cu_{Zn}+V_{Zn}|$
- QMC results give quantitative calculations of band gap, defect calculations underway

chromium dimer

- Cr_2 dissociation : landmark example of an interacting electron system
- Best quantum chemistry methods fall short in capturing the physics, which includes:
  - sextuple bond
  - structural sensitivity
  - antiferromagnetic correlations
  - shoulder
- Near exact calculation on BW using AFQMC is the most accurate theoretical result to date

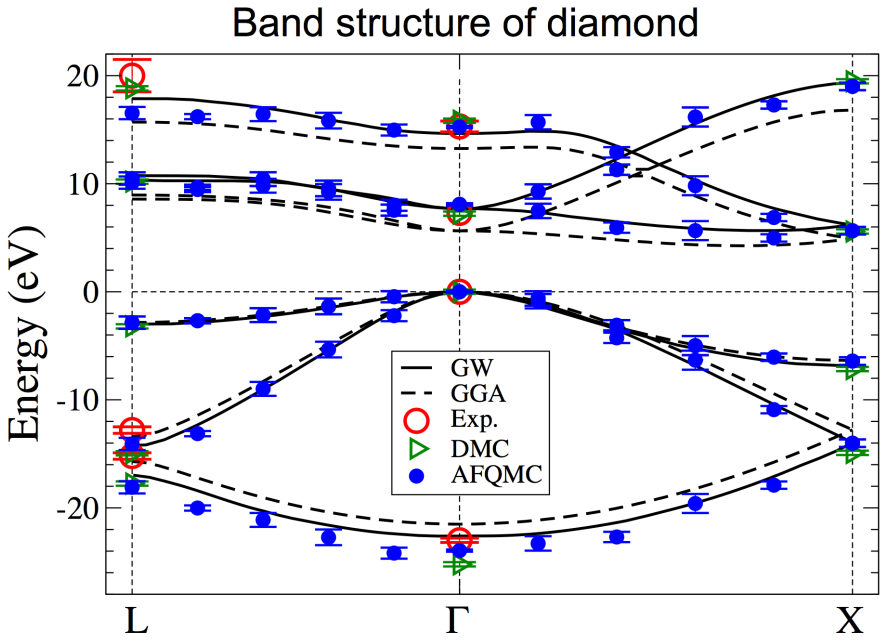


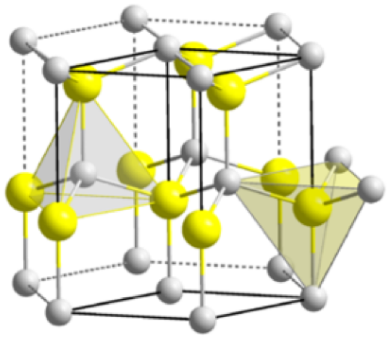
Purwanto, Zhang, Krakauer, in prep 2014

excited states in solids

application to diamond and zinc oxide

- Accurate excited states is a notorious problem for conventional electronic structure methods
- AFQMC methodology developed; benchmarked on two materials: diamond carbon and wurtzite zinc oxide
- Preliminary assessment: quantitative agreement with experiment





method	***Band gap*** (eV)
GGA	0.77
LDA+*U*	1.0
Hybrid functionals	3.3; 2.9
GW	2.4, 2.8, 2.6
AFQMC	**3.26(16)**
experiment	**3.3-3.57**

Ma, Zhang, Krakauer, New J. of Phys (2013).

conclusions/what next?

- Thanks to Blue Waters, we have been able to choose ambitious problems in many-body interacting electron systems.

- hydrogen under pressure: unveiling the states of matter at the interior of Jupiter
- understanding magnetism-doping-phonon relationships in high T_c superconductors
- magnesium oxide under pressure: what is the thermal conductivity of the earth's crust?
- getting rid of unwelcome defects - polarons and DX centers - in thin-film photovoltaic materials
- continued efforts at methodology development (AFQMC), esp. for excited states in solids