New applications of Diffusion Quantum Monte Carlo

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Platinum: W. Parker, A. Benali, N. Romero (ANL),
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Computational Support: INCITE, Oak Ridge & Argonne LCF

Outline

1. Introduction
   - Methods: Fixed node diffusion Quantum Monte Carlo
   - Current limitations and approximations

2. Recent Applications of QMC

3. Graphite and Lithium intercalated graphite
   - A near model system where we can diagnose DFT errors

4. Platinum surface energy

5. Summary

Quantum Monte Carlo

- In this talk, focus on applications of fixed node diffusion Quantum Monte Carlo. Solve the full atomistic & electronic Schrodinger equation at zero temperature

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Other QMC methods are highly complementary
  - AFQMC, FCIQMC,….

Fixed-node Diffusion Monte Carlo

- DMC is a many-body wavefunction projection method
- We solve the time dependent Schrodinger equation in imaginary time

$$\frac{\partial|\psi\rangle}{\partial\tau} = -\hat{H}|\psi\rangle \qquad |\psi(\delta\tau)\rangle = \sum_{i=0}^{\infty} c_i e^{-\epsilon_i \delta\tau}|\phi_i\rangle$$

- Ground state is projected out in long time limit using importance sampling
- Electrons are Fermions!
  - Enforce a fermionic solution via the “fixed-node approximation”. Force solution to have same nodes (zeros) as trial wavefunction.
  - Introduces a variational error: use an approximate nodal surface, usually from another method, e.g. DFT, limited CI, FCIQMC
- Gives a robust method with good properties: variational (testable choices), nominally N^2-N^4 scaling, readily parallelized...

Systematic errors in DMC

1. The fixed-node approximation used to control the **Fermion sign problem**
   - Improvements require optimizing the nodes of trial wavefunctions with many parameters.
   - State of art is ~10000 parameters
2. If **pseudopotentials** are used, they must be sufficiently accurate.
   - DMC contains an additional approximation when used with PPs and inexact trial wavefunctions
3. Convergable technical errors
   - **Finite size error** in periodic calculations
     - In common with other many-body methods
   - **Time step error** in DMC calculations

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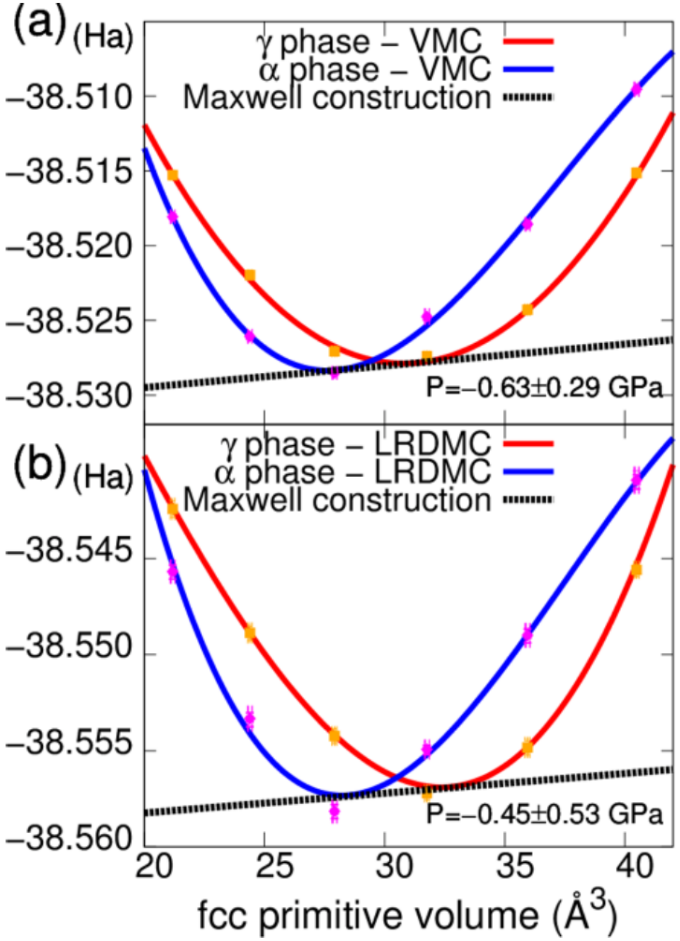
Cerium alpha-gamma phase transition

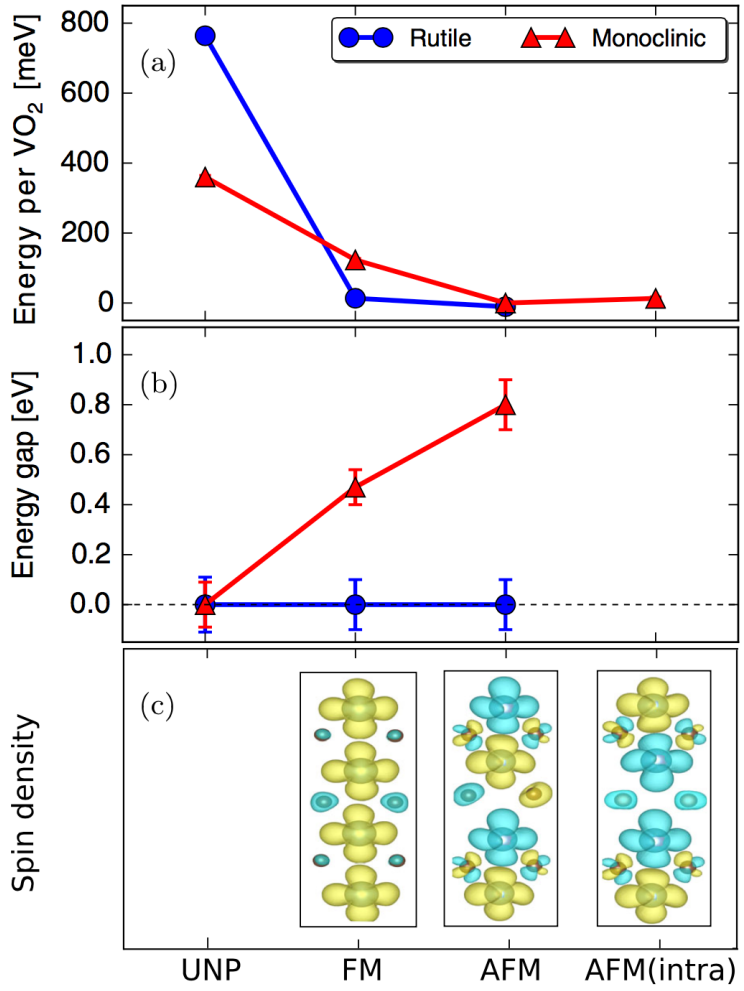


N. Devaux, M. Casula, F. Decremps, S. Sorella
PRB **91** 0811019(R) (2015)

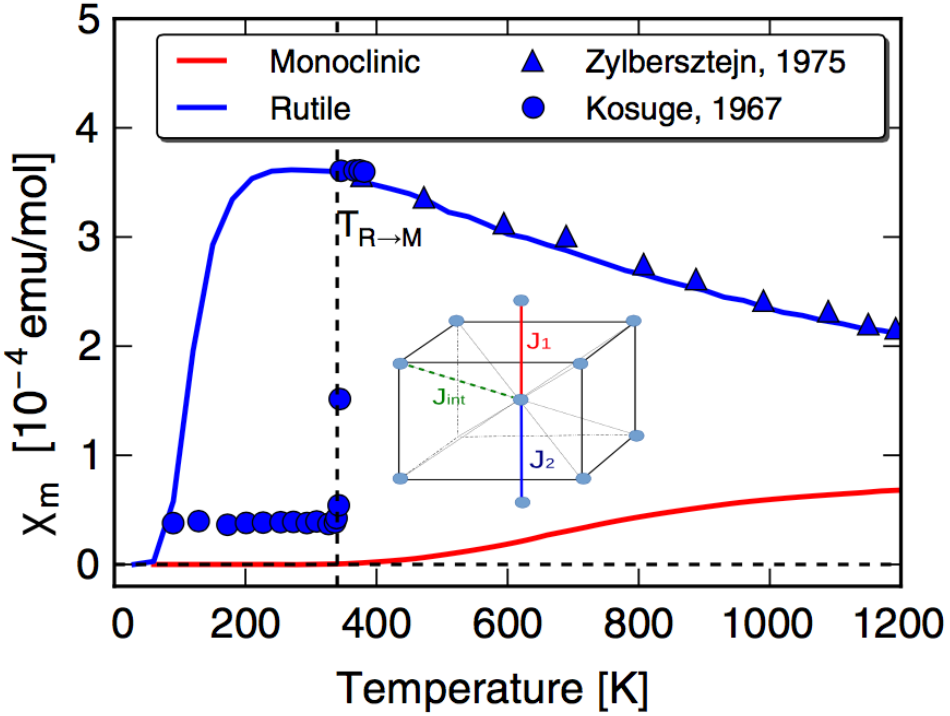
- Electronic origins of phase transition via VMC and DMC, extensive analysis.
- 10^4 parameter optimization of wavefunction! Accuracy determined by trial wavefunction flexibility, not starting point.

VO_2 metal-insulator transition

- "…structural transition directly causes M-I transition and change in coupling of vanadium spins"



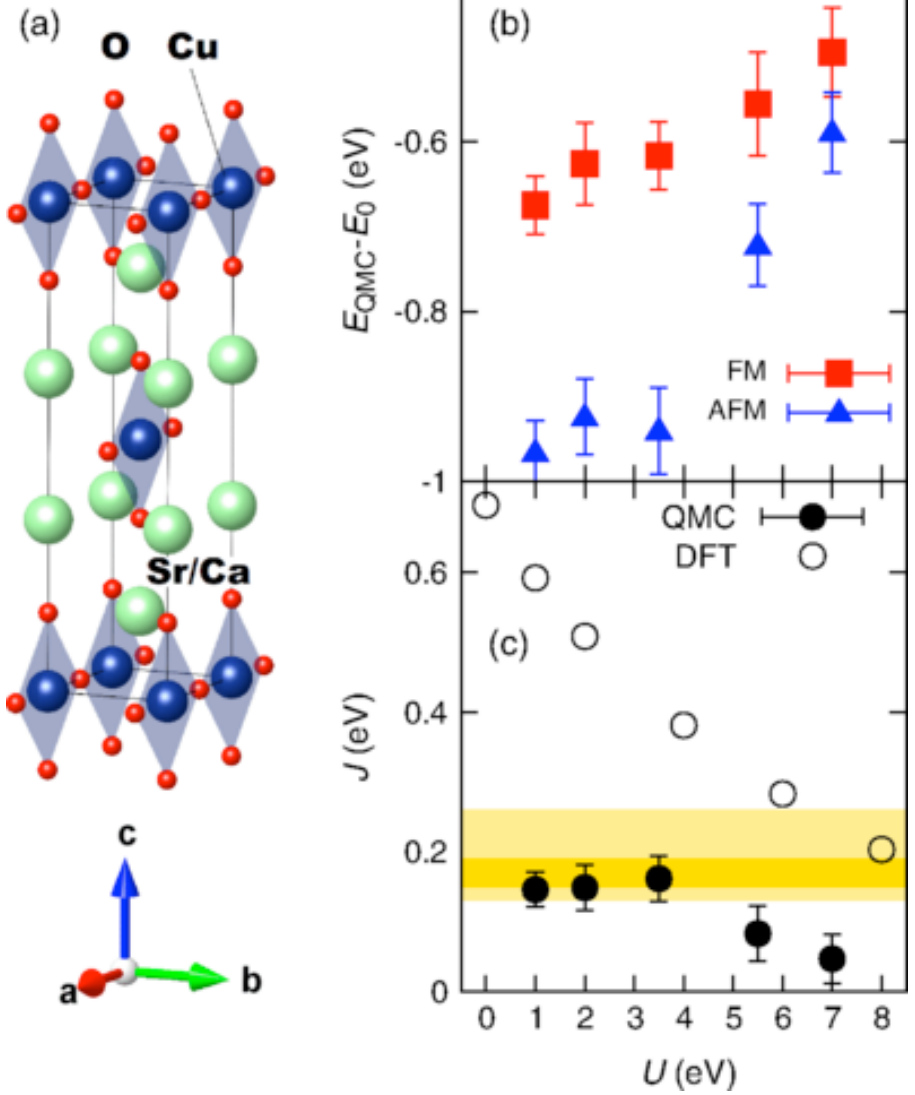
H. Zheng and L. K Wagner
PRL **114** 176401 (2015)



Copper oxides

K. Foyevtsova et al. PRX 4 031003 (2014)

Ab initio prediction of magnetic exchange coupling in Ca_2CuO_3



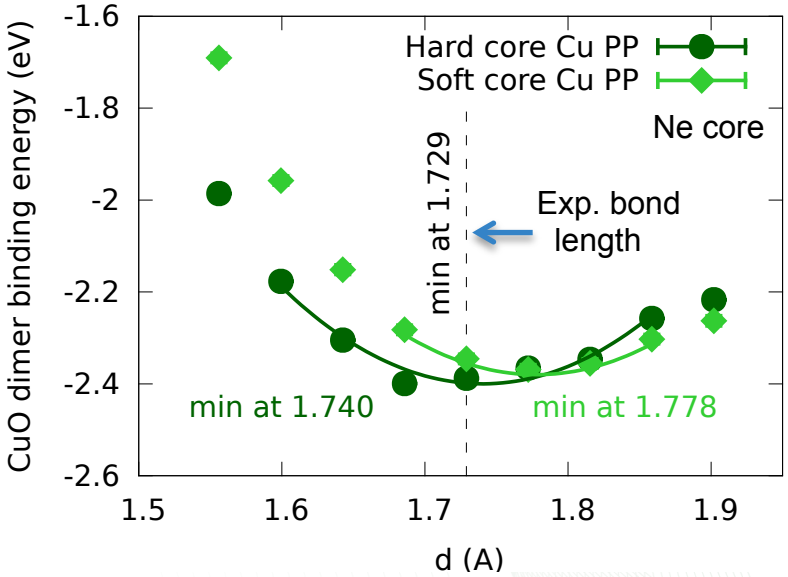
Variationally find the best nodal surface. Here given by U~1-3 eV

Best nodal surface predicts exchange coupling in agreement with experiment.

Pseudopotential Validation: Cu

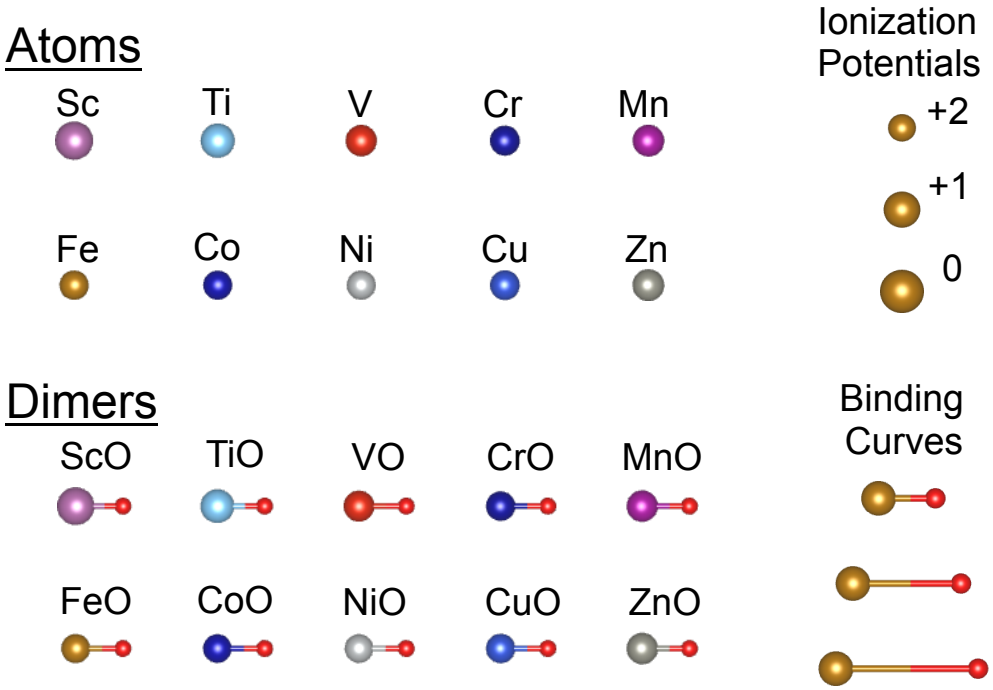
- Accurate description of Cu semicore states is crucial
- Today QMC PPs are norm conserving and without non-linear core corrections. Requires conservative choices.
- 500 Ry plane-wave E_{cut} needed for 19 valence electron Cu. Expensive in memory, but not more costly to evaluate in QMC.
- Cu-O dimer within 0.01A of experiment

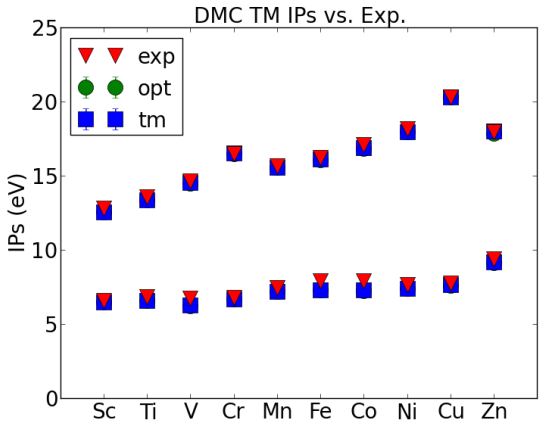
Cu PP core	1st Ionization Energy
Ar 11 e^- valence	Poor DOS
Mg 17 e^- valence	8.302(36) eV
Ne 19 e^- valence	7.724(37) eV
Experiment	7.72638(1) eV

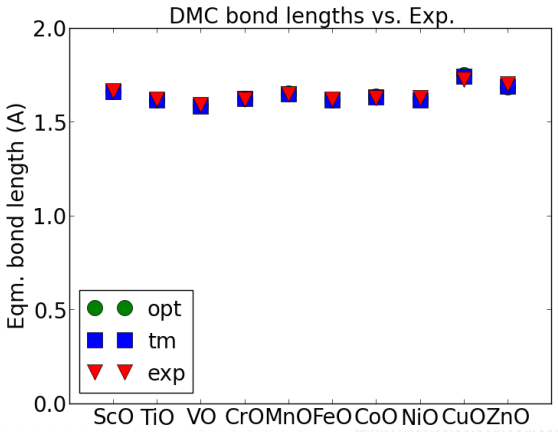


Accurate Pseudopotentials

- Small (Ne) core PP's tested for transition metal atoms.
- Expensive in electron count and memory, but accurate.
- An accurate "larger core" scheme is highly desirable.







Krogel, Santana, Reboredo (Submitted, PRB 2015)

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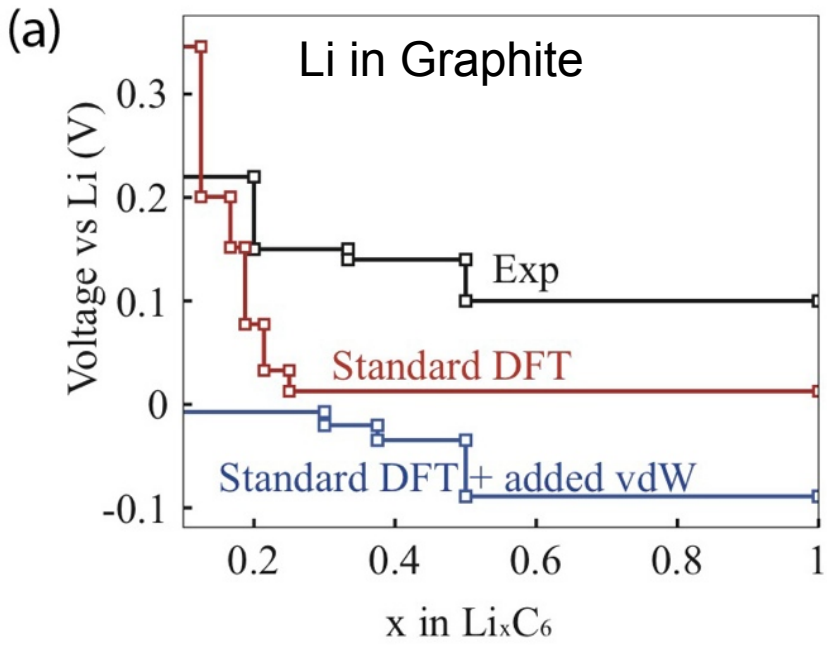
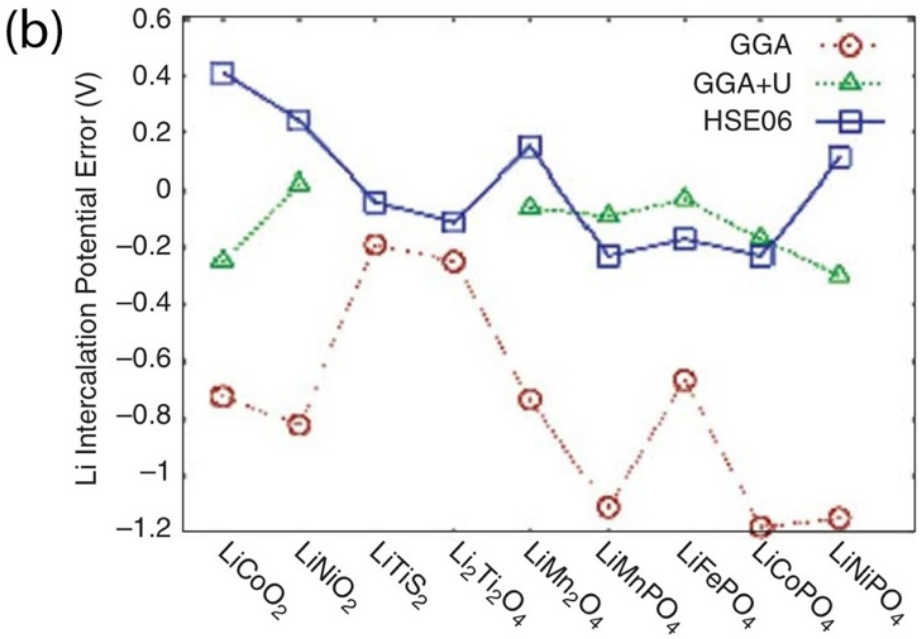
DFT for Li in graphite is suspect

DFT errors for standard Li ion electrodes can be large



Persson PRB 82 125416 (2010)



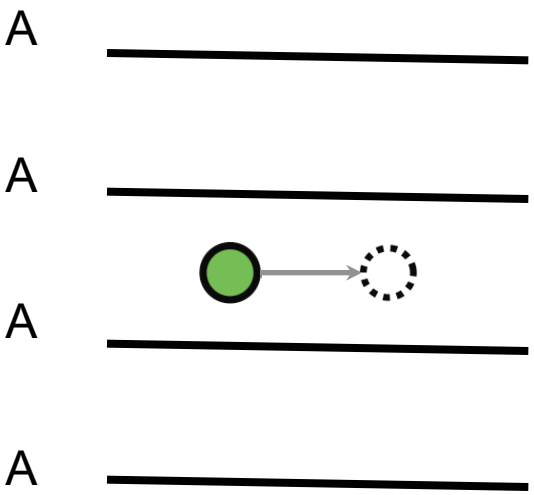
Ceder MRS Bull 35 693 (2010)
For TMOs, even DFT+U is a compromise, HSE worse.

We can fit the voltage (macroscopic) to a trusted value but how can, e.g., we be certain of the dynamics?

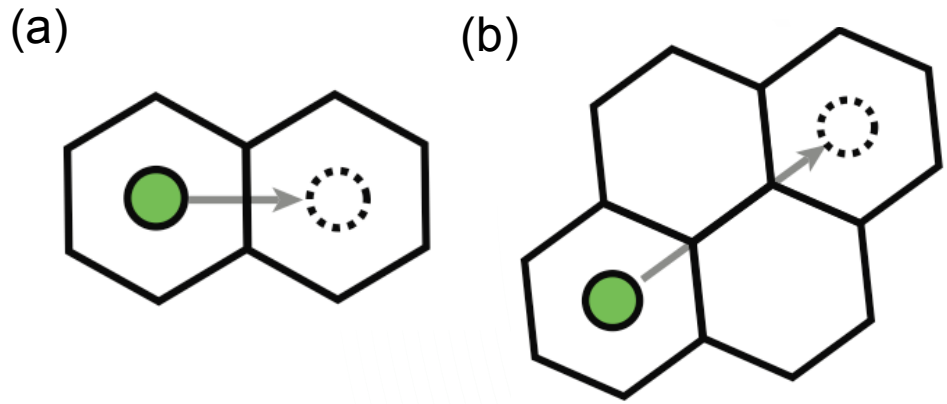
- Grimme & vdw-DFT. Lee Nano Letters 12 4624 (2012)

Model system: Dilute Li in A-A Graphite

- We adopt the simplest model graphite system that captures the essential physics
- We vary planar separation to test accuracy of Van der Waals and charge transfer
- We compute diffusion barriers and binding energies for one Li in A-A graphite: removes ambiguity of Li location



Side view



Top view
Two diffusion paths studied

Computational methodology

- Better than chemical accuracy (<1kcal/mol) has been demonstrated for molecular interactions with standard Slater-Jastrow wavefunctions and fixed node DMC
  - c.f. Papers of Dubecky & Mitas, e.g. PCCP 16 20915 (2014)
- We used fixed node DMC as implemented in QMCPACK http://qmcpack.org
  - O(200) atom unit cells, four graphene planes+Li atoms
  - Single determinant nodes from underlying DFT
  - Well tested pseudopotentials
  - Twist averaging (“k-points”)
- DFT: Quantum Espresso, FHI-AIMS, VASP.

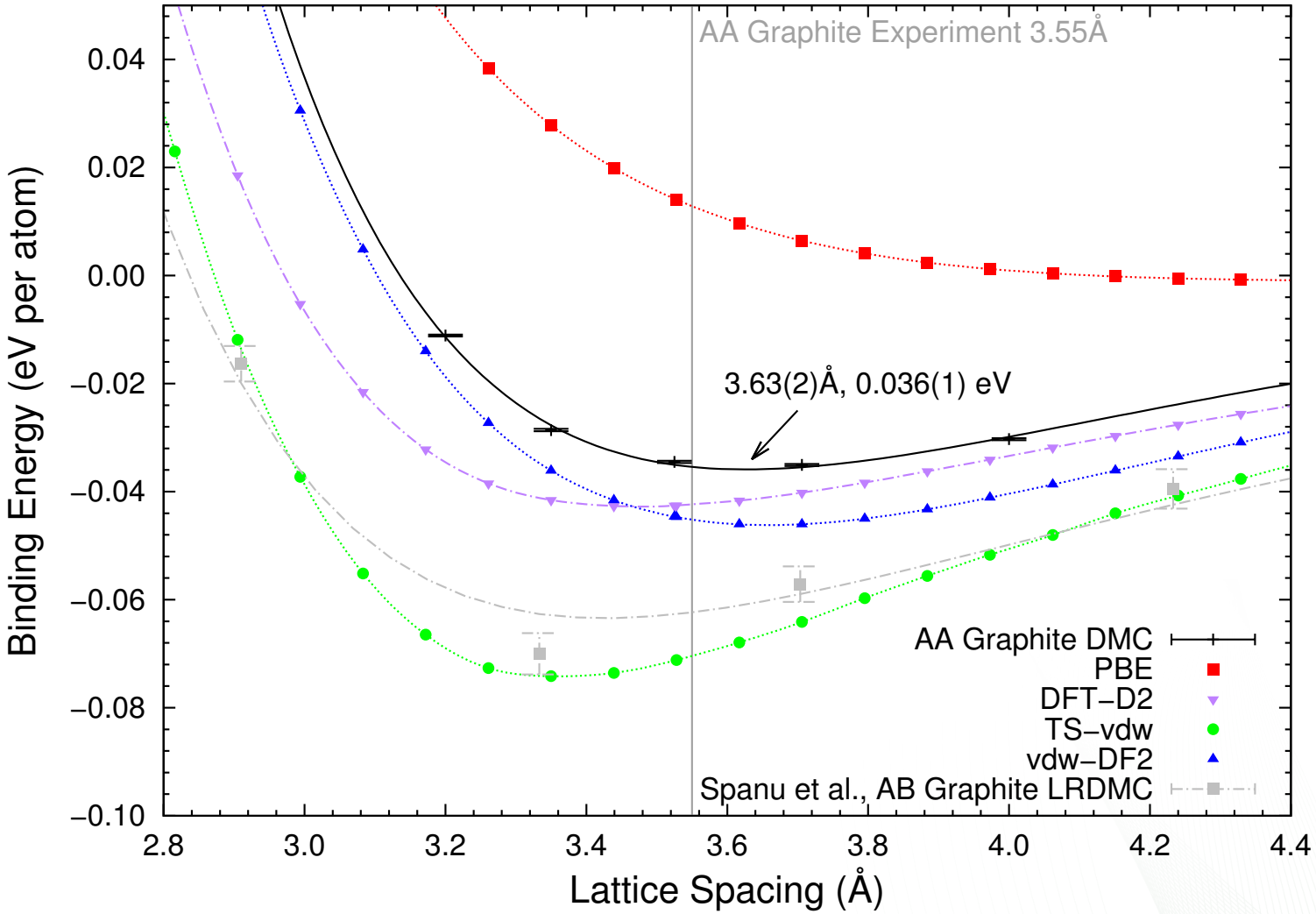
We test four flavours of DFT of increasing sophistication

- PBE
  - Local GGA, no vdw contribution
- DFT-D2 / "Grimme's method"
  - Electrostatically motivated additive term in ionic Hamiltonian
  - Very popular due to cheapness

$$E = E_{DFT} - \frac{s_6}{2} \sum_{i<j} \frac{C_6^{ij}}{|r_{ij}|^6} f(r_{ij})$$

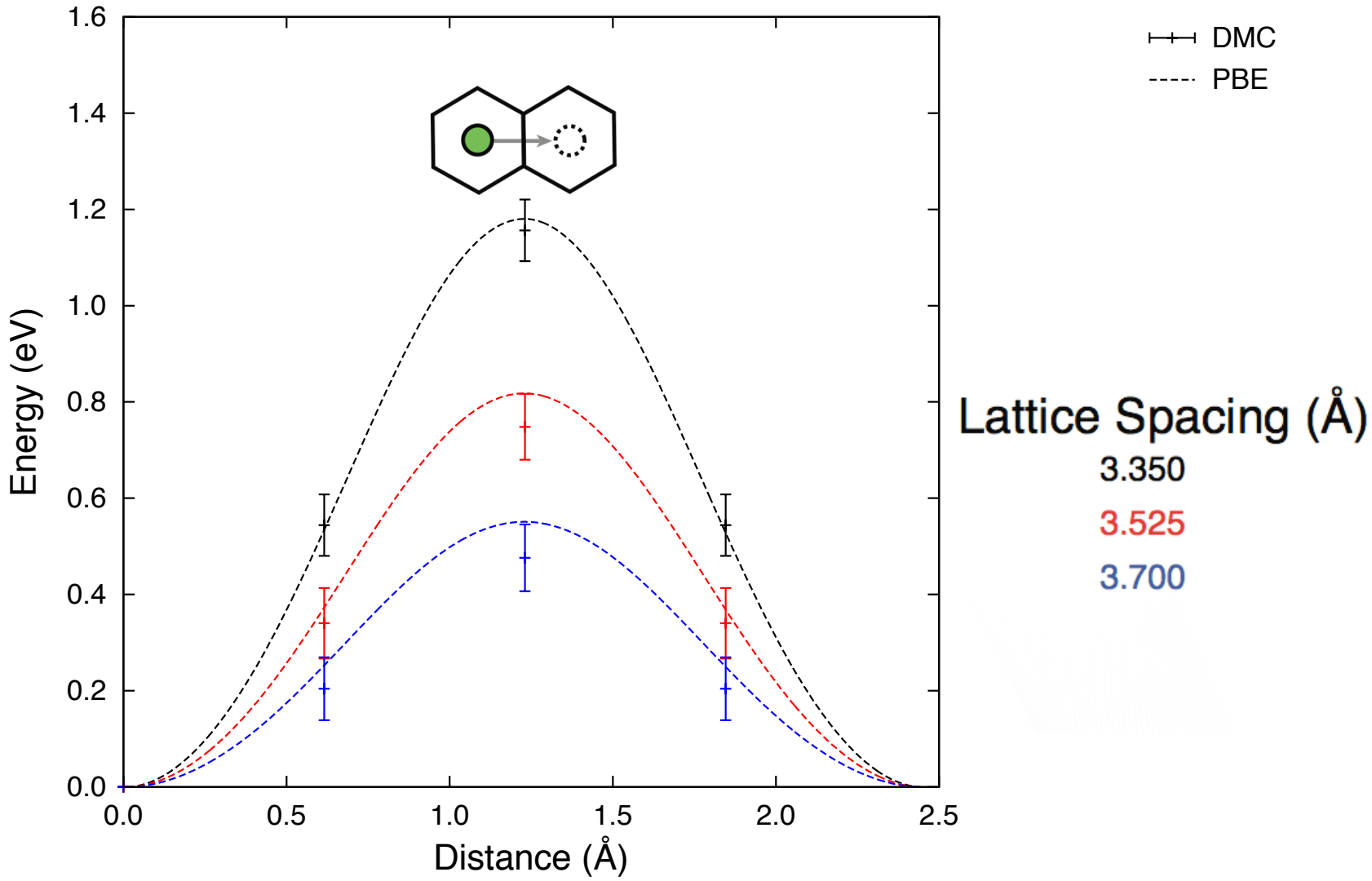
- Tkatchenko-Scheffler vdw
  - Environment dependent screening of C_6 in Grimme's scheme
- vdw-DF2 self-consistent DFT and earlier versions.
  - vdw-DF2 Lee et al. PRB 2010, vdw-DF Dion PRL 2004
  - Fully non-local functionals should respond to charge transfer missed by other methods

A-A Graphite



- DMC is within 0.1A of experiment. A-A graphite sensibly higher in energy than A-B structure.

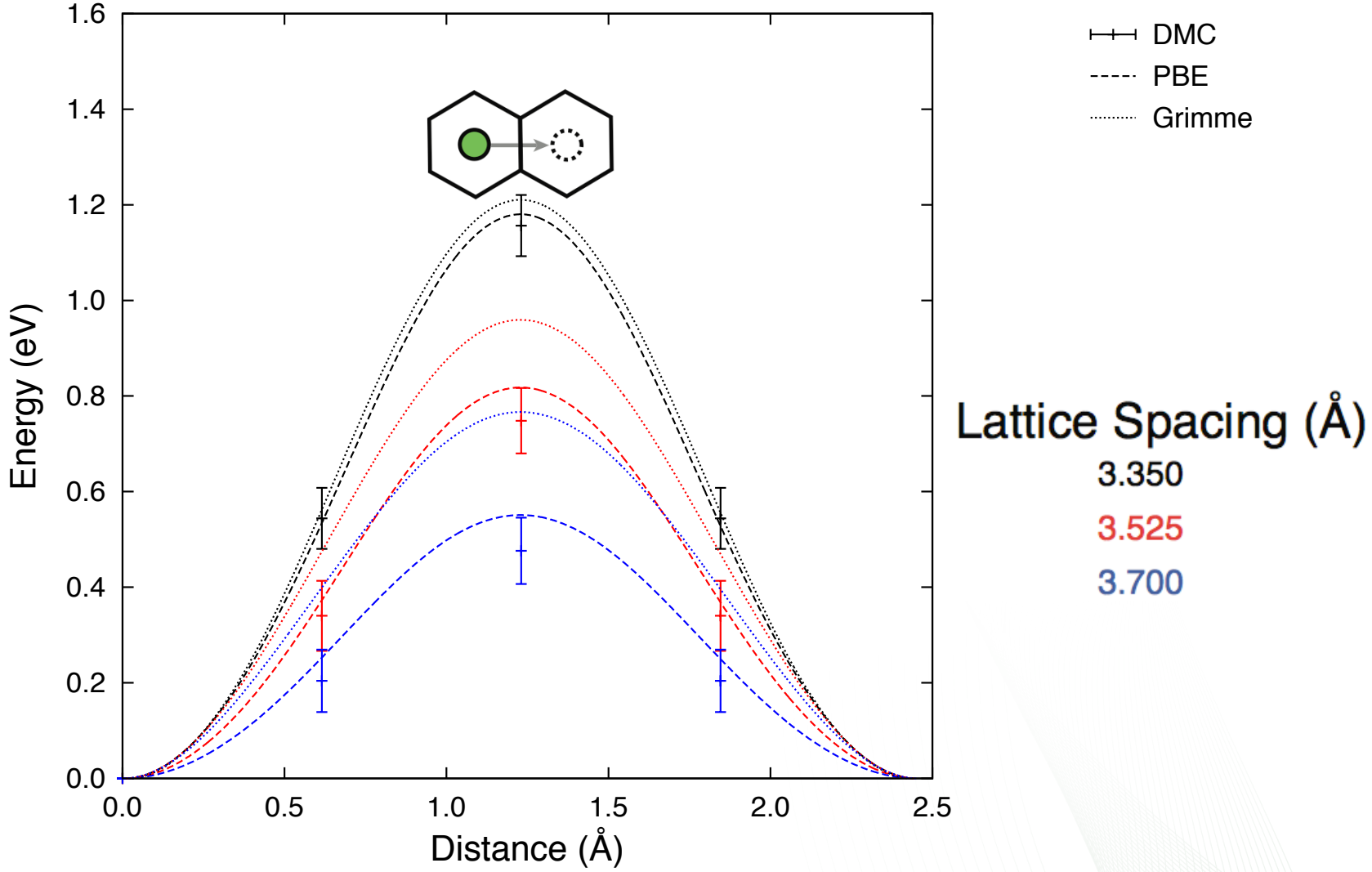
Results: Diffusion



PBE very accurate at fixed lattice constant!

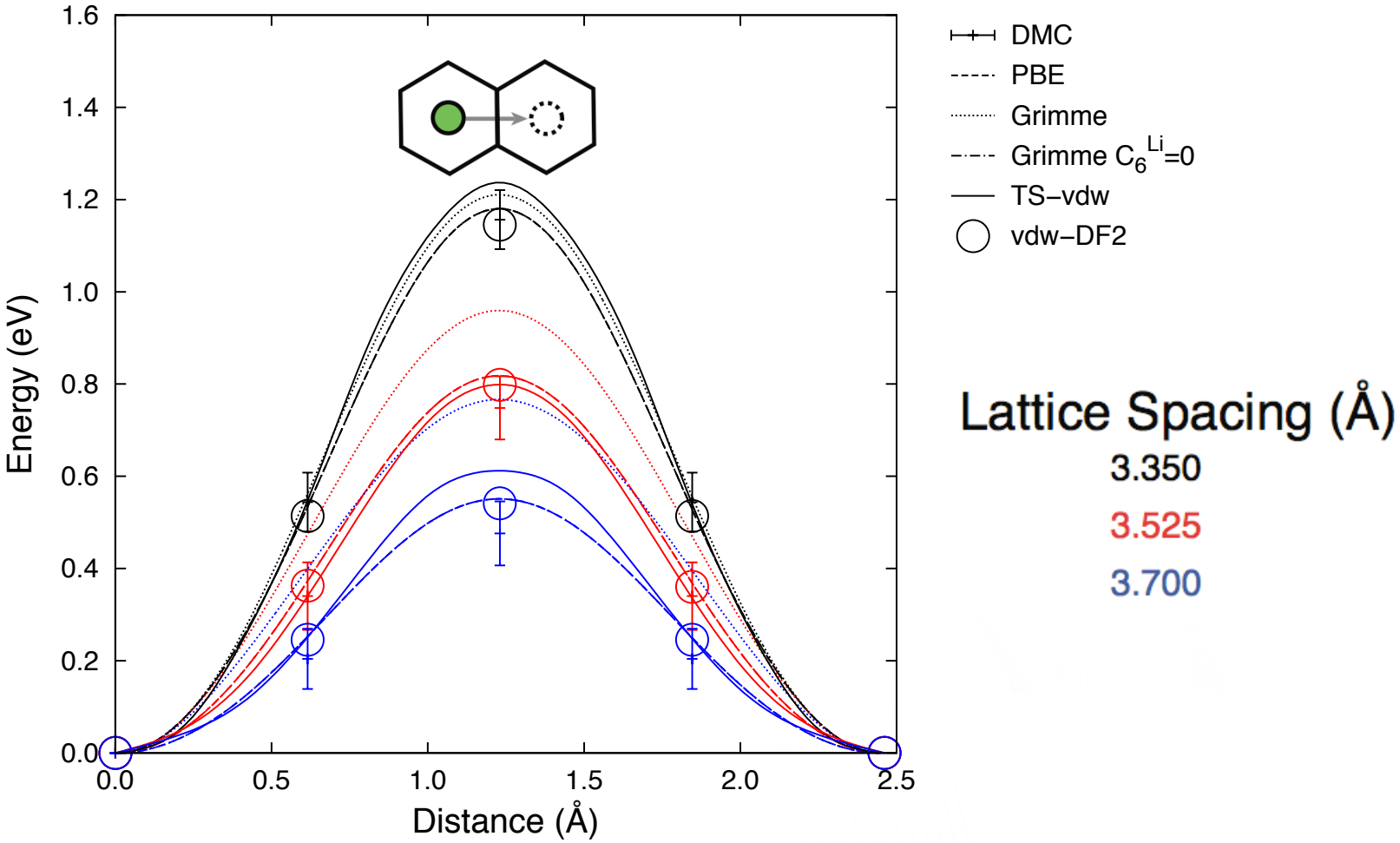
- Charge transfer is well captured

Results: Diffusion



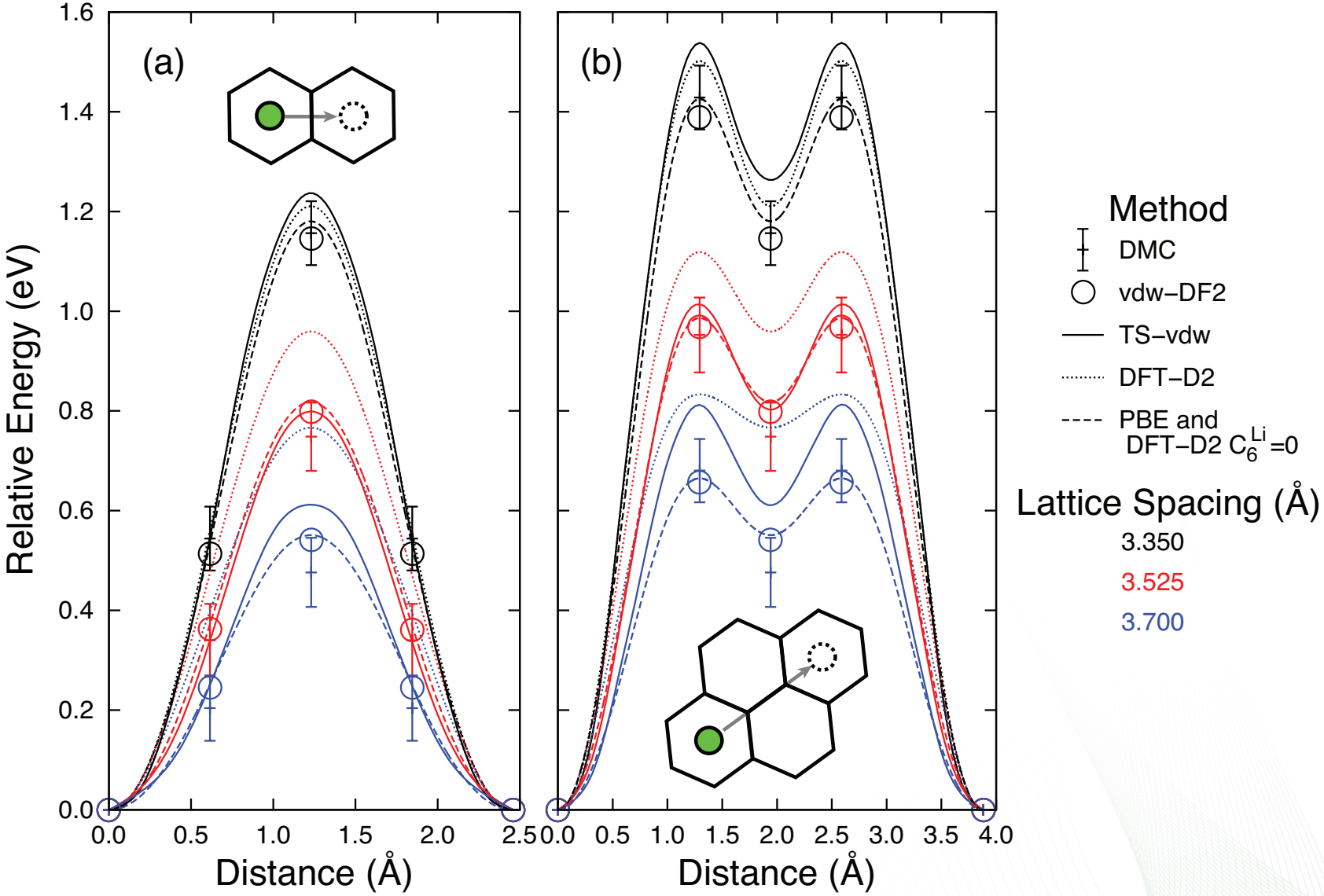
Grimme DFT-D2 worse than PBE! By attempting to improve results we have worsened them!

Results: Diffusion



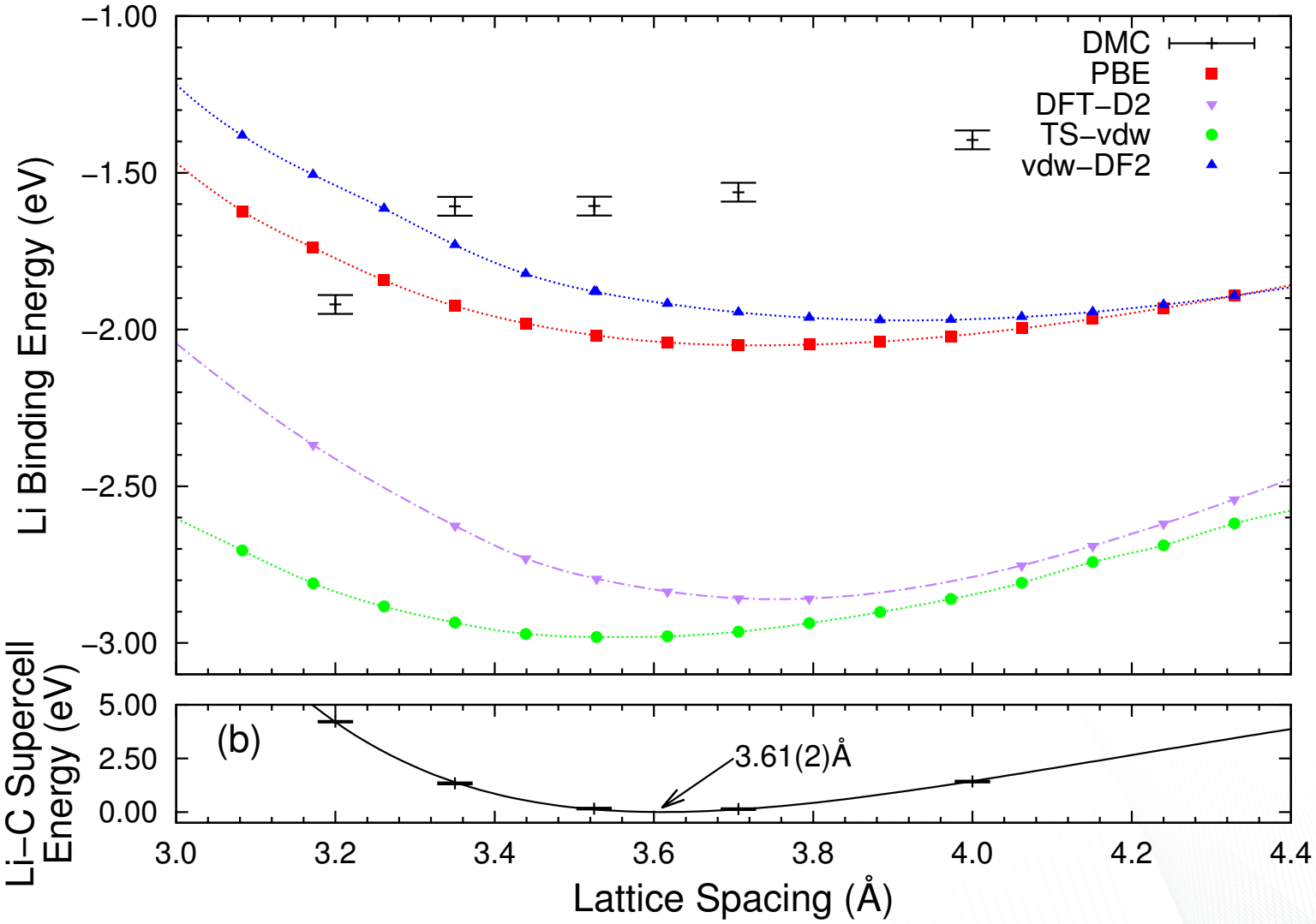
- TS-vdw is quite accurate. Refit Grimme C_6^{Li}=0 DFT-D2 excellent
- vdw-DF2 is best overall. Dion (not shown) similar

Results: Diffusion



- Identical conclusions found for second path

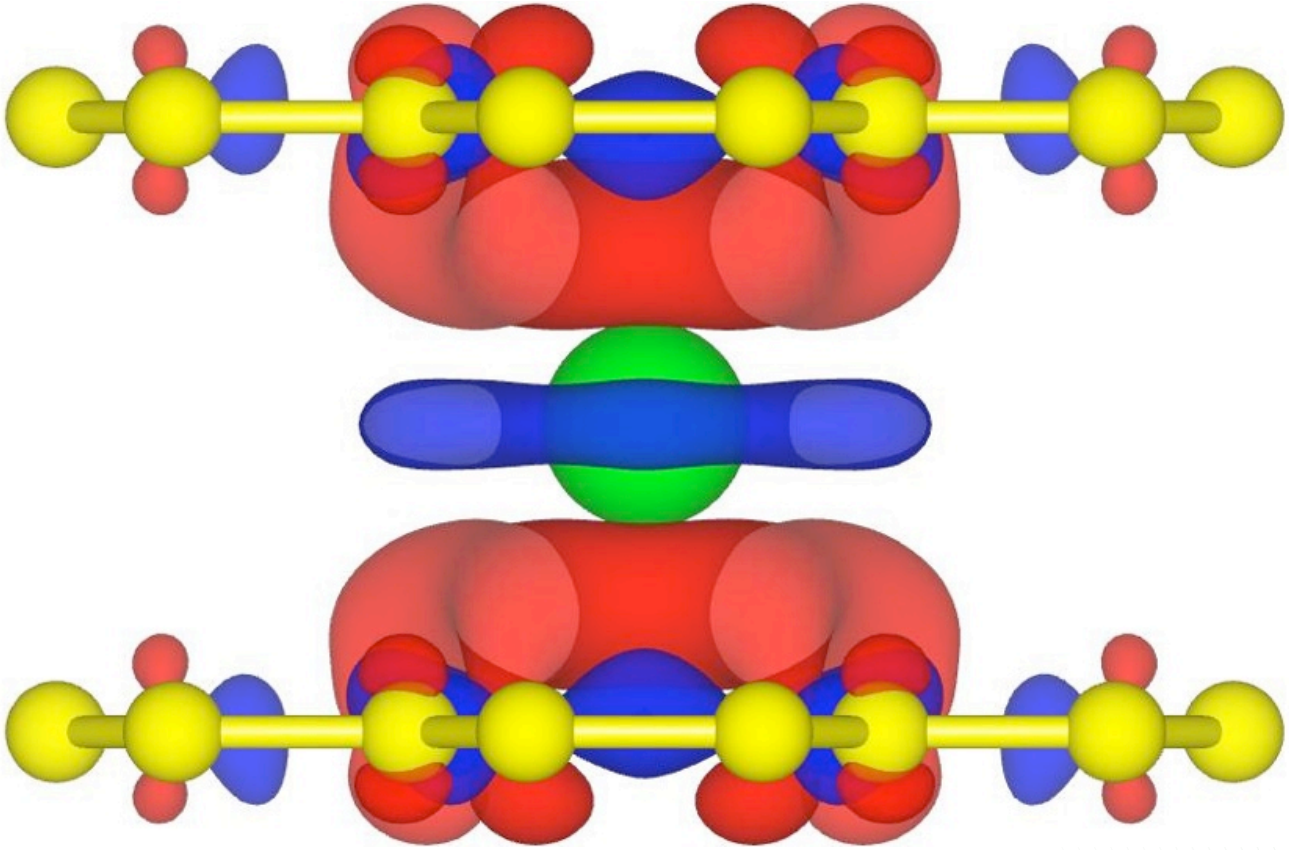
Results: Li Binding



No “perfect” DFT, but for pure DFTs, errors typical of a local GGA

Charge density differences $\rho_{(Li-C)} - \rho_C$

- Li atom donates charge to nearby carbon atoms
  - Li polarizability must change in local environment
  - Self-consistent vdw-DFTs are closer to QMC data



Increased charge (**RED**) Decreased charge (**BLUE**)

Summary

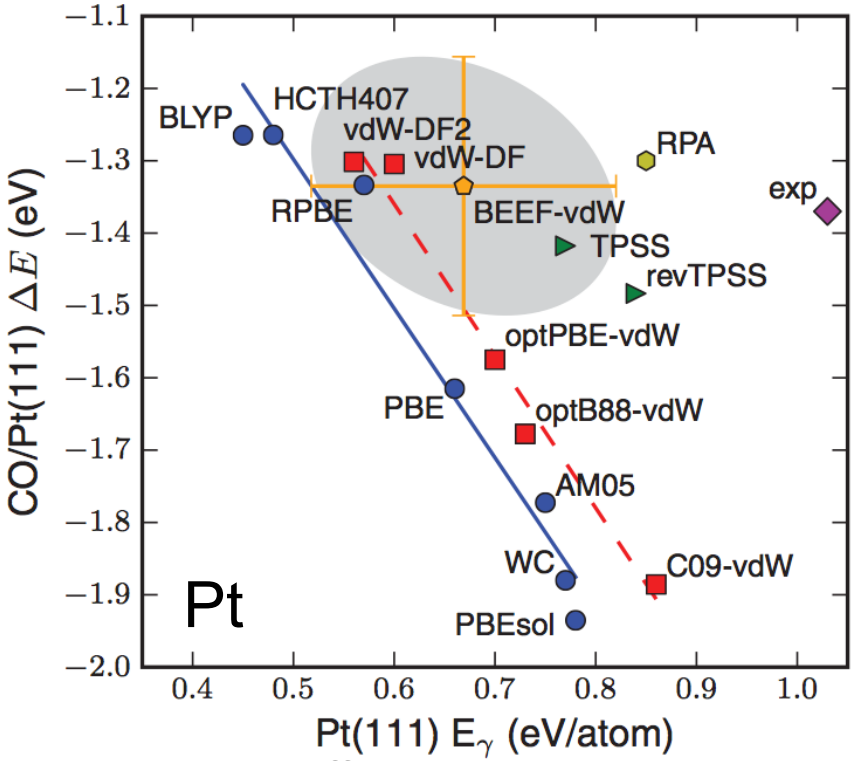
Ganesh et al. JCTC **10** 5318 (2014)

- Self-consistent van der Waals schemes capture (small) additional charge transfer/polarization missed by PBE and are more accurate. Li binding energies not perfect, but should be good for dynamics.
- Methods that modify the ionic Hamiltonian must be carefully parameterized according to the actual charge transfer.

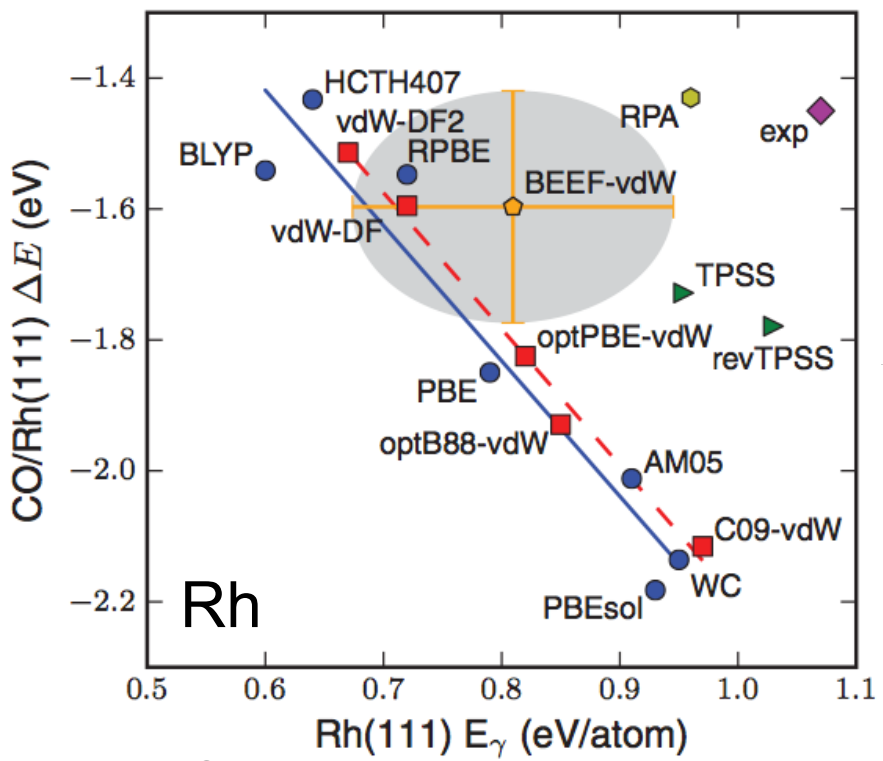
- Based on these QMC results we have performed reactive force-field studies fit to self-consistent vdw DFT data. Raju et al. JCTC **11** 2156 (2015)

QMC for catalytic surfaces

- Accurate adsorption and reaction barrier energies for typical catalytic species remain a grand challenge.
- The variation between different electronic structure predictions is physically consequential. No clear “failure” as per vdw systems.



Wellendorff PRB **85** 245149 (2012)



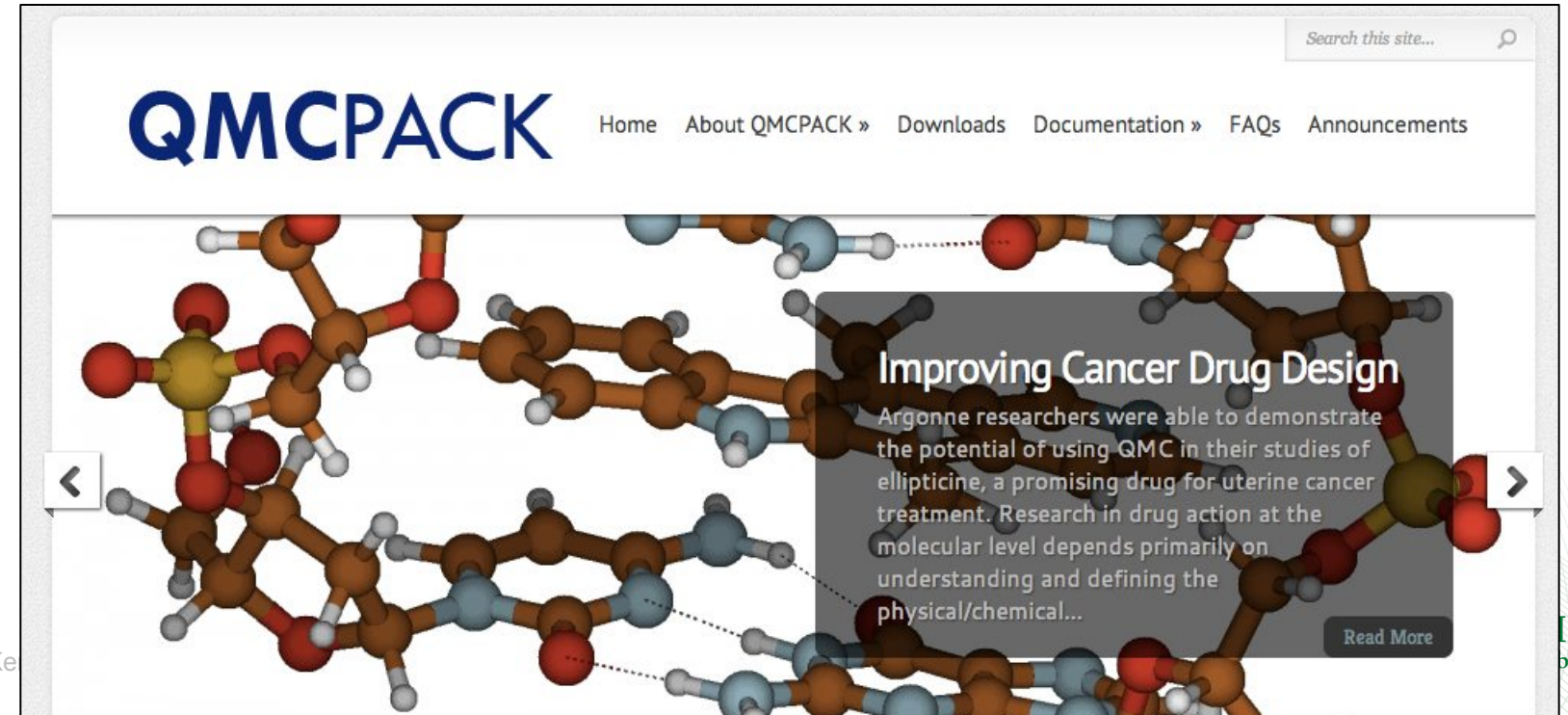
RPA: Schimka Nat. Mat **9** 741 (2010)

Colors: Different classes of DFT/methodology.

No functional or information theoretic combination of functionals reproduces the experimental surface energy and CO adsorption energy for Pt or Rh.

QMCPACK http://www.qmcpack.org

- QMCPACK is a fully open-source production level QMC code. Entire toolchain is non-proprietary.
- We are transitioning to a user-focused package, with documentation, build instructions, training, videos.
- Suggestions, questions are welcome on google group or by email



Summary

- Quantum Monte Carlo methods are now being applied across the periodic table.
- QMC is being applied to systems where established electronic structure methods are not predictive.
- While significant improvements are desirable, the predictive power of standard QMC approaches is very good and will continue to improve.

Postdoctoral positions available at ORNL and other DOE labs

Email: kentpr@ornl.gov

Defects in ZnO

J. Santana, J. Krogel, J. Kim, P. R. C. Kent, and F. A. Reboredo JCP **142** 164705 (2015)

- Application of well-established charged defects & chemical potentials formalism to DMC
- 0.5eV+ differences in defect formation energies between DMC and tuned hybrid DFT.