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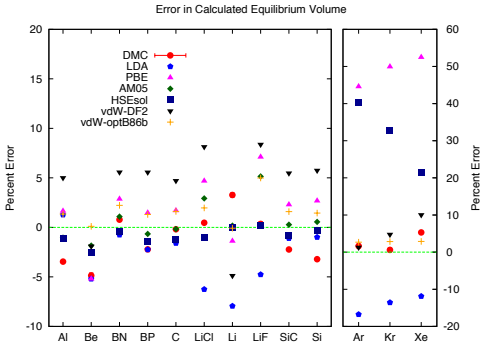

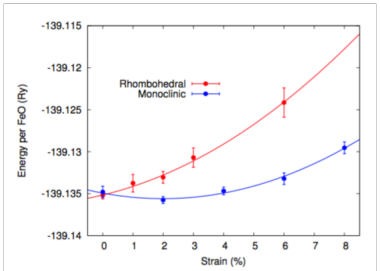

Benchmarking Failure: Exposing Limitations in DMC Applied to Materials

L. Shulenburger

Sandia National Laboratories

Exceptional service in the national interest

Center for Predictive Simulation of Functional Materials (http://cpsfm.ornl.gov)

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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What is the aim?

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- Integrate ourselves into the materials design conversation
  - DFT is already doing this to an extent – What do we bring to the table?
    - Accurate results!
- Need also to treat the complexity of real materials
- Need to convince others of our accuracy

If predictive accuracy is the goal, how do we build confidence?

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- Avoid approximations where possible

If predictive accuracy is the goal, how do we build confidence?

Sandia National Laboratories

- Avoid approximations where possible
- Systematic improvability!

If predictive accuracy is the goal, how do we build confidence?

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- Avoid approximations where possible
- Systematic improvability!
- Comparison to “higher level theory”

If predictive accuracy is the goal, how do we build confidence?

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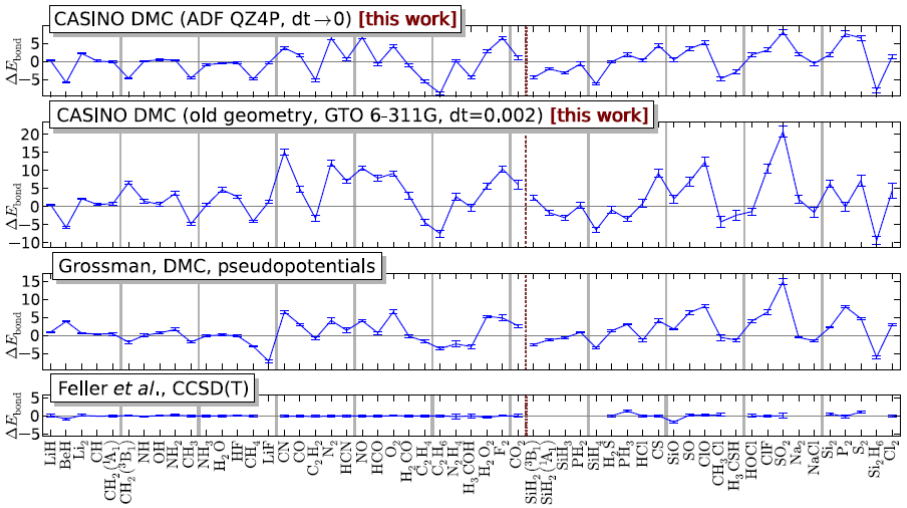
- Avoid approximations where possible
- Systematic improvability!
- Comparison to “higher level theory”
- Comparison to experiment

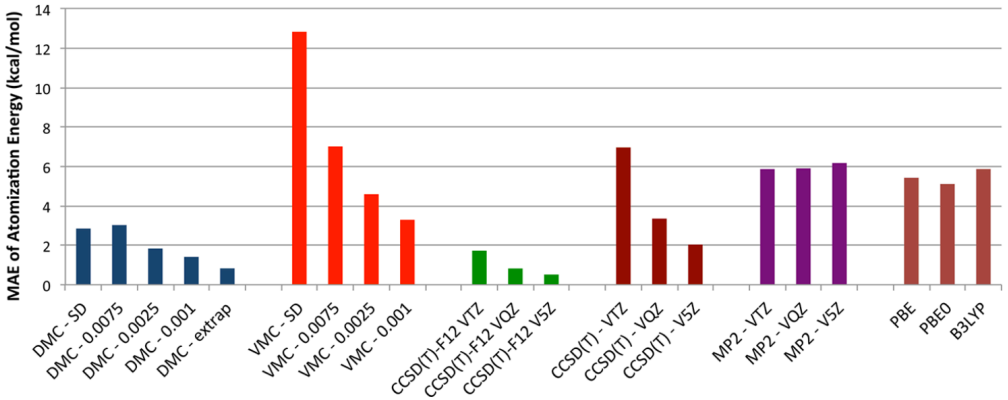
Relatively long tradition of test sets for DMC

- For molecules…



Nemec et al, JCP. **132**, 034111 (2010)

Morales et al. JCTC. **8**, 2181 (2012)



Solids / Condensed matter poses other challenges

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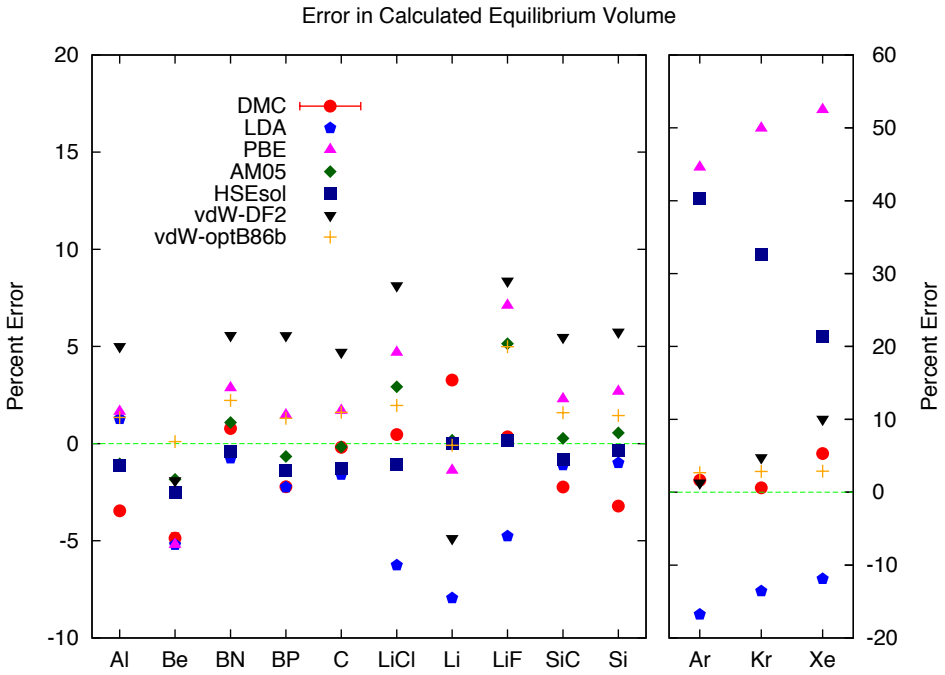
- Reference data is not known as precisely
- Finite Size effects!
- Lack of “practical” systematically improvable trial wavefunctions
- Computational cost

An initial test pointed to possible improvements, but was not focused

- Calculate energy vs lattice constant for a wide range of molecules
- This pointed to areas where the methodology could be improved
- Pseudopotentials…



LNS and TRM, PRB 88, 245117 (2013)

New test targeted at specific issues

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- Pseudopotentials for heavier elements
- Problems with simplistic nodal surface in solids
- Band gaps for strongly correlated materials
- Difficult to optimize geometry in solids
- Spin-orbit coupling / relativity is not currently treated
- How to sample spin degrees of freedom with current methods?

Tests to exercise these

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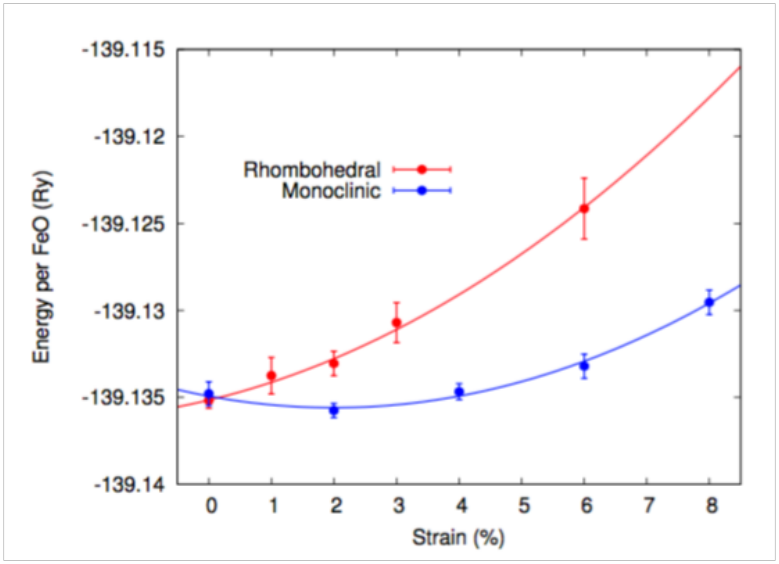
Tests to exercise these

- Equilibrium properties of Ce (lattice constant / bulk modulus)
  - Inspired by Devaux et al PRB 91, 081101(R)
  - Excellent physical insights, but absolute EOS did not match experiment
  - Probes PP problem, but also potentially nodes and relativity

	VMC ($T = 0$ K)	LRDMC ($T = 0$ K)	Expt.
V_{eq}^{α} (Å^3)	27.4 ± 0.1	28.4 ± 0.2	28.52 [18]
V_{eq}^{γ} (Å^3)	30.8 ± 0.2	32.3 ± 0.3	34.35 [21]
B^{α} (GPa)	48 ± 1	50 ± 3	35 [22]
B^{γ} (GPa)	38 ± 1	45 ± 3	21–24 [23,24]
V_{min} (Å^3)	28.0 ± 0.2	28.5 ± 0.3	28.2 [13]
V_{max} (Å^3)	31.3 ± 0.3	32.7 ± 0.4	32.8 [13]
δV (%)	11.7 ± 0.6	13.8 ± 1.1	15.1 [13]
p_t (GPa)	−0.63 ± 0.29	−0.45 ± 0.53	0.7 [13]
ΔU (meV)	13 ± 1	12 ± 3	25 [13]

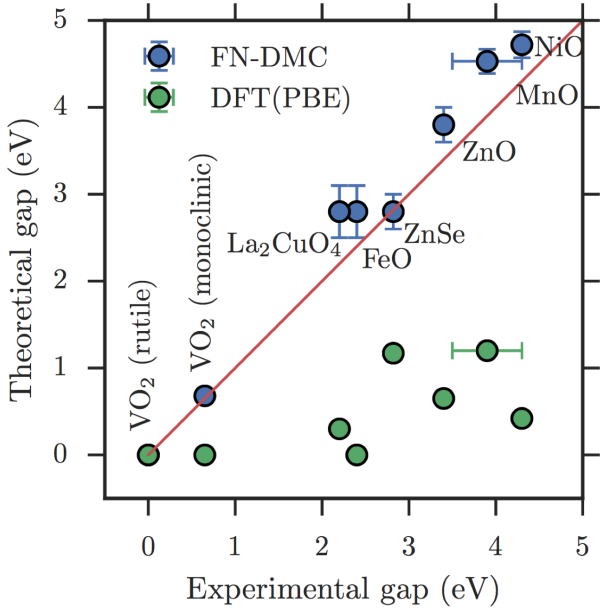
Tests to exercise these

- Equilibrium properties of Ce (lattice constant / bulk modulus)
- Equilibrium strain of FeO
  - EOS and phase transition previously studied by Kolorenc and Mitas Phys. Rev. Lett. **101**, 185502 (2008)
  - AFM coupling along 111 direction, but sign of strain varies depending on trial wavefunction
  - Easy to imagine optimization within d manifold will yield improvements
  - Primarily probes nodal surface but also PP



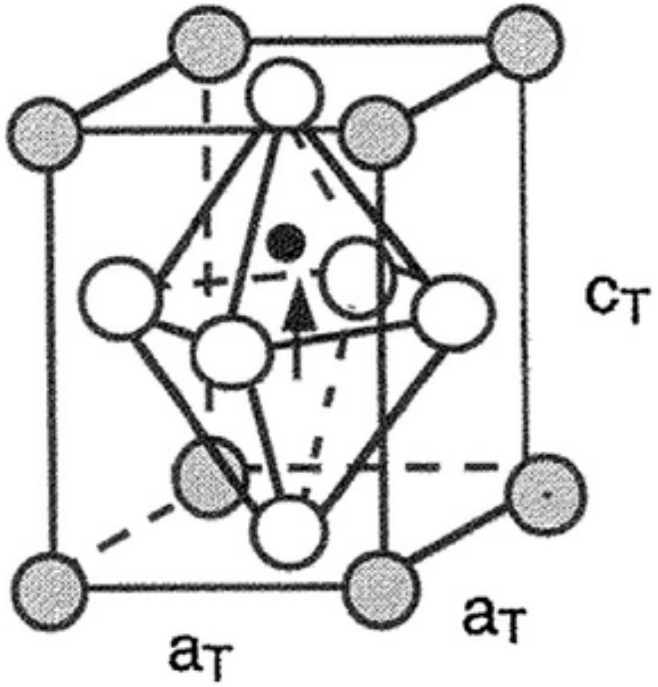
Tests to exercise these

- Equilibrium properties of Ce (lattice constant / bulk modulus)
- Equilibrium strain of FeO
- Band gap of CoO
  - Indirect gap semiconductor
  - Band gaps in transition metal oxides are good but not great
    - See for example
      Wagner and Ceperey, Rep. Prog. Phys. **79**, 094501 (2016)
  - Very difficult to even open a gap in mean field methods
  - Similar problems to FeO, but need excitaitons



Tests to exercise these

- Equilibrium properties of Ce (lattice constant / bulk modulus)
- Equilibrium strain of FeO
- Band gap of CoO
- Soft mode of $PbTiO_3$
  - Ferroelectric distortion of material
  - Direction is known but methods get amplitude incorrect
  - Potentially involves geometry optimization, PP, nodes and relativity



Tests to exercise these

- Equilibrium properties of Ce (lattice constant / bulk modulus)
- Equilibrium strain of FeO
- Band gap of CoO
- Soft mode of $PbTiO_3$
- Magnetic moment of Fe
  - Ferromagnetic metal
  - How to find the location of the fermi surface / chemical potential
  - Mainly tests spin degrees of freedom, some PP

What is missing?

- This room contains the world's experts on QMC applied to solids
  - What else breaks?

Outlook

- By carefully designing “hard” tests, can directly stress potential deficiencies in approximations
- Much work is already underway to mitigate these challenges
  - Nodal surface in solids may be the last to fall