Quantum Monte Carlo for Transition Metal Oxides

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and
Computational Nanosciences Group
University of California, Berkeley

QMC in the Apuan Alps III

In collaboration with Lubos Mitas (NCSU)
and Jeff Grossman (UCB)

Before the feature presentation
An advertisement

- www.qwalk.org : open-source QMC code
- C++, nice, very extensible
- Long list of features

- www.nanohub.org : pays part of my salary
- Lots of useful tools and learning material, including QMC!

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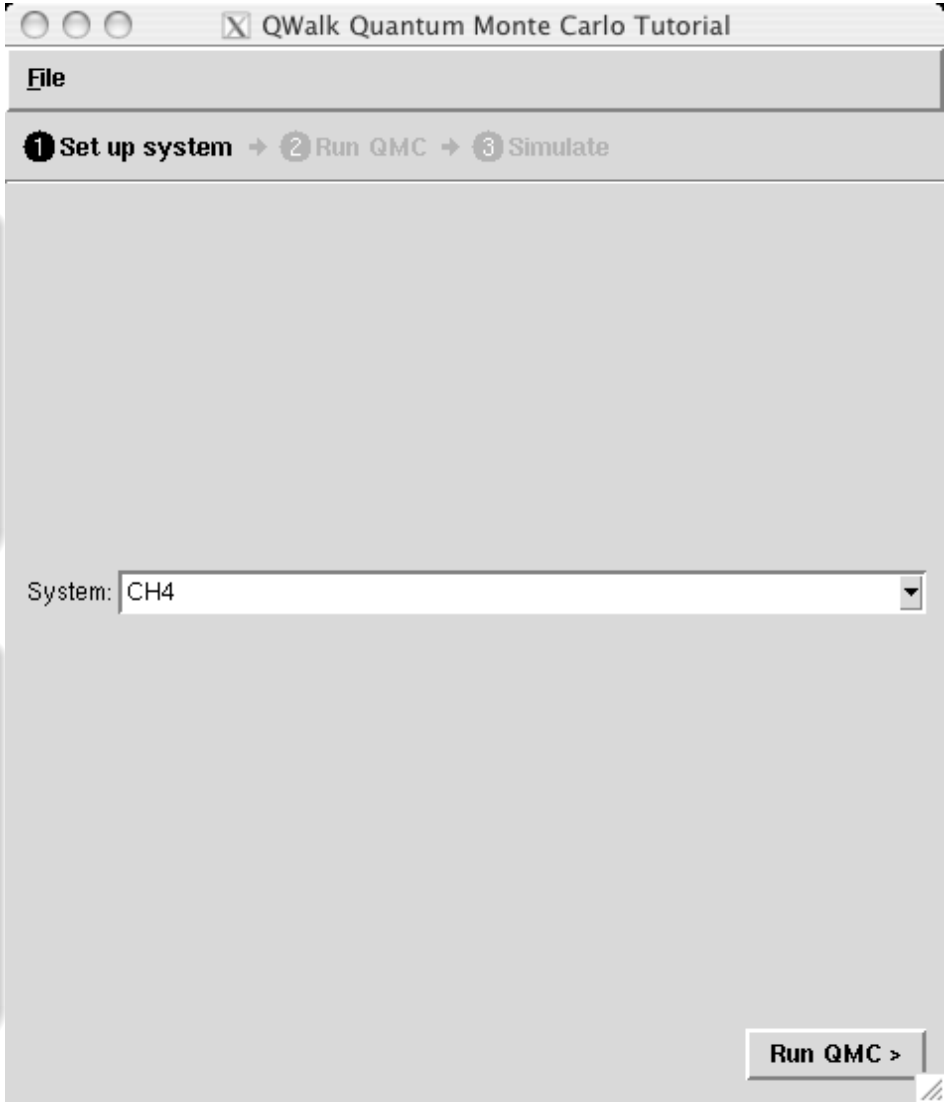

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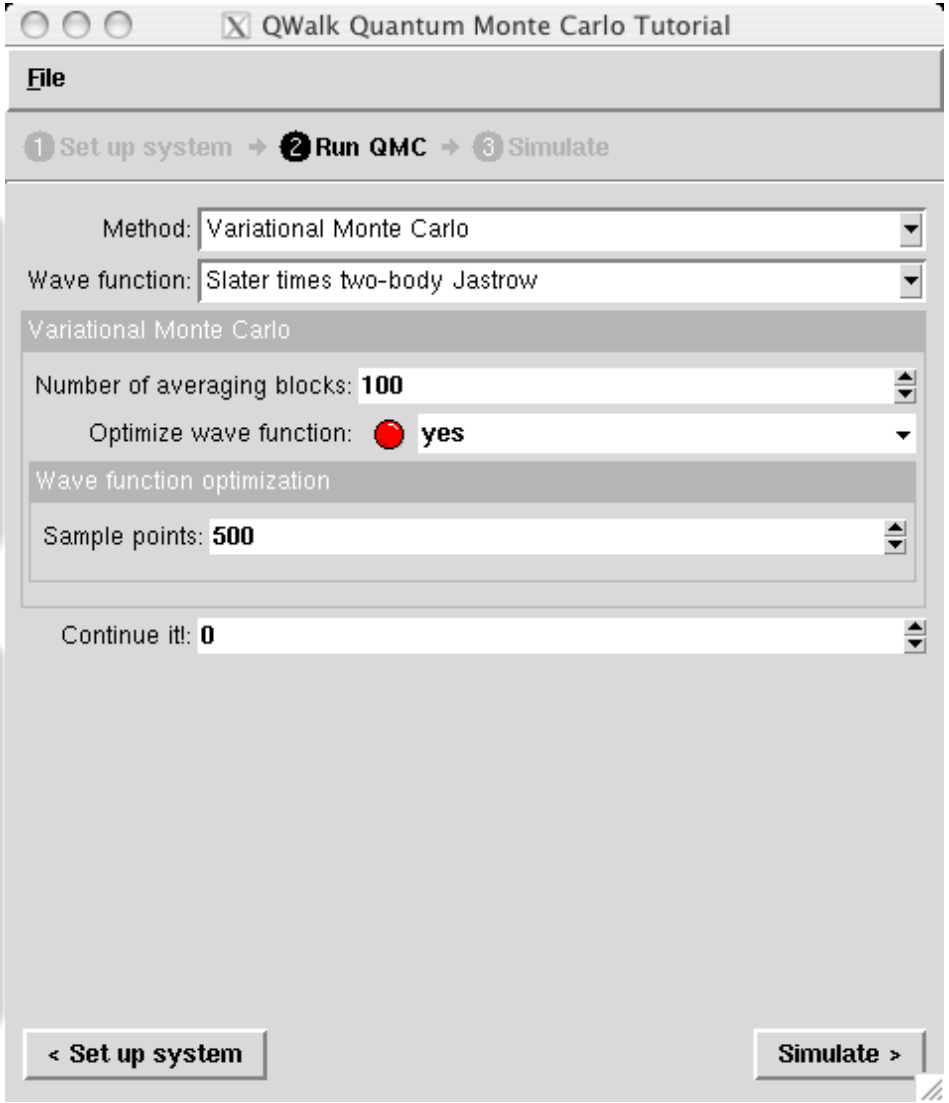

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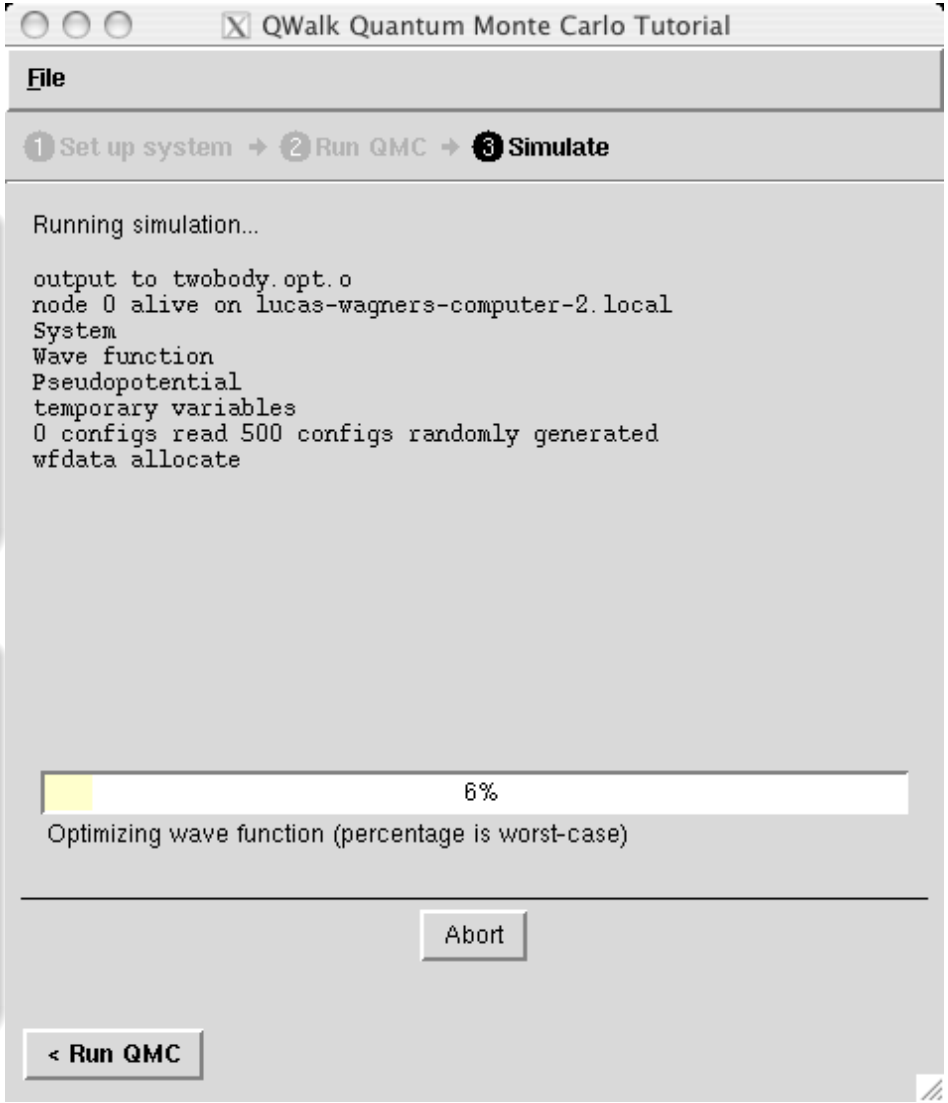

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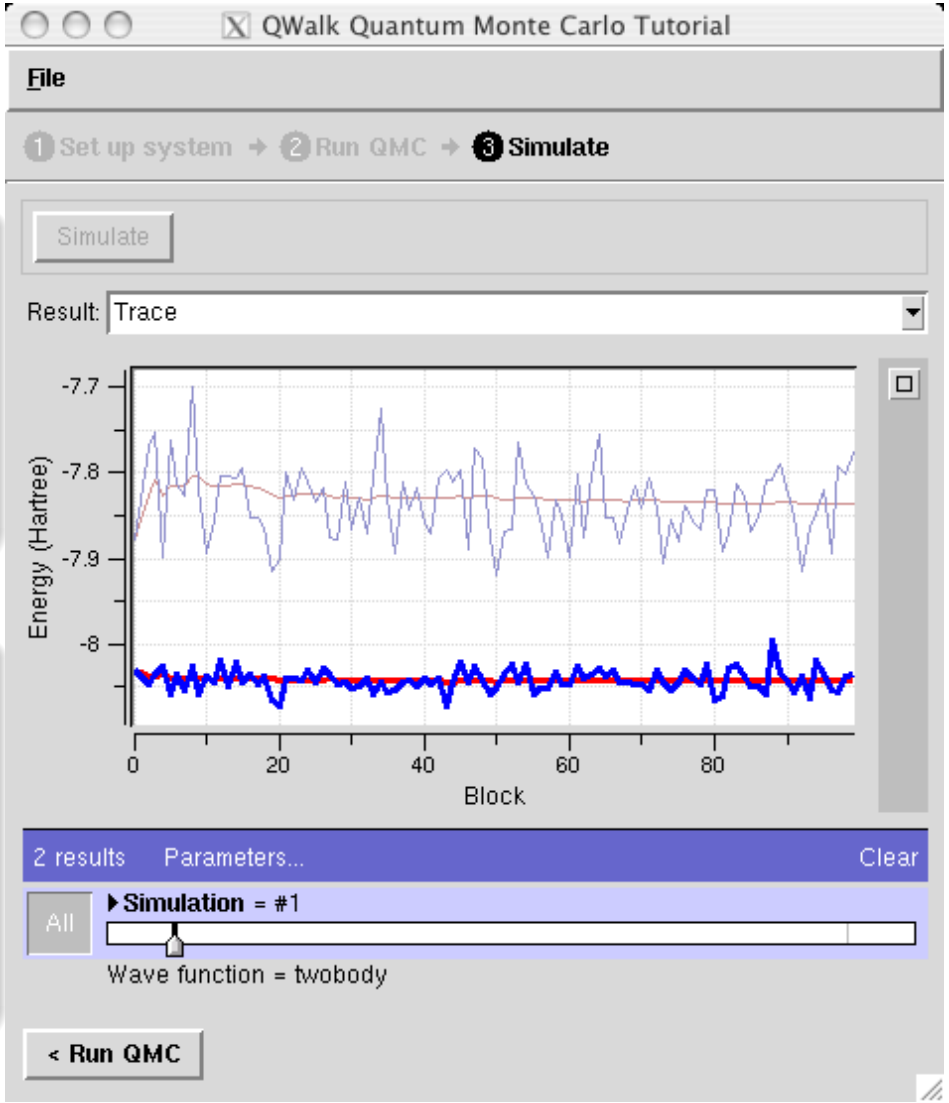

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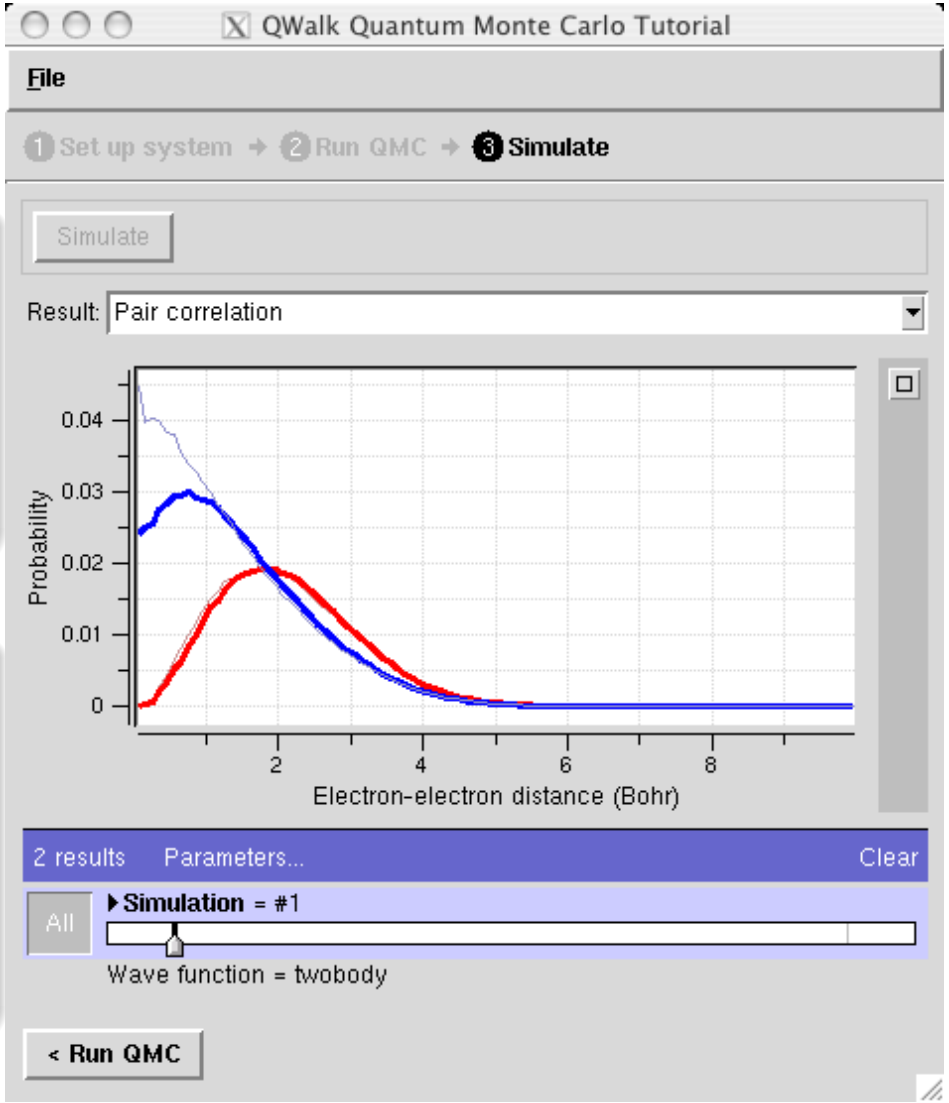


In this talk

Goal

- Method to calculate the properties of transition metal (TM) materials.
- D-orbitals behave very differently from S and P–how?
- References:
  - JCP **126** 034105 (2007)
  - J. Phys: Condensed Matter topical review coming very soon

Methods

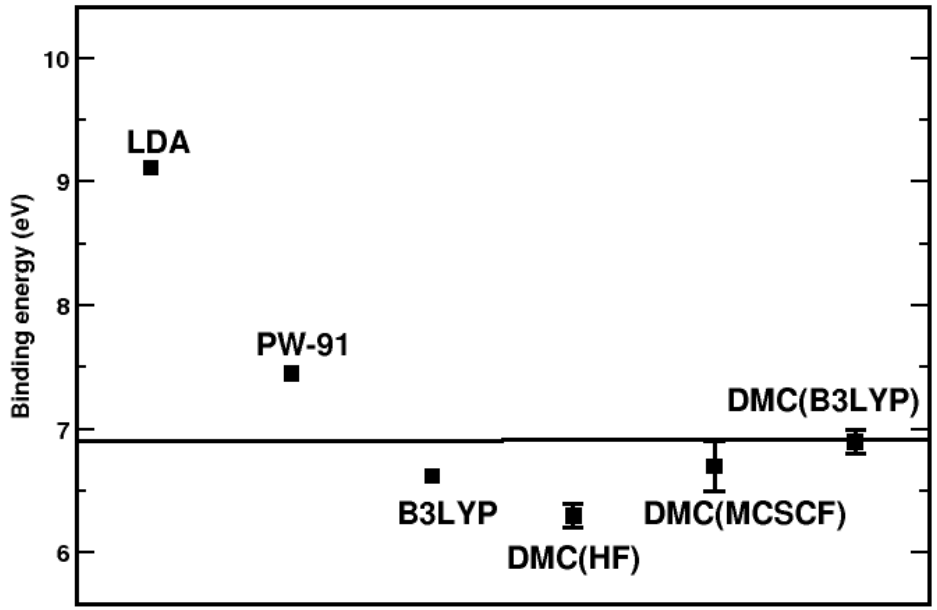
- DFT and DMC, mostly
- Small core (Ne) ECP on TM
- TZ basis set
- QWalk (www.qwalk.org) for all QMC calculations
- GAMESS and CRYSTAL for mean-field
- Will decribe newish methods as we go.

TMO molecules

- Two atom molecules: small, good for benchmarks
- TM-O bond is present from ferroelectrics to supernova remnants
- DFT and HF describe them poorly..

Want a scalable, accurate method on these materials.

Energetics: Binding energy of TiO



Results depend on the nodes

- Hartree-Fock nodes are poor
- B3LYP nodes are good
- d-p hybridization is important

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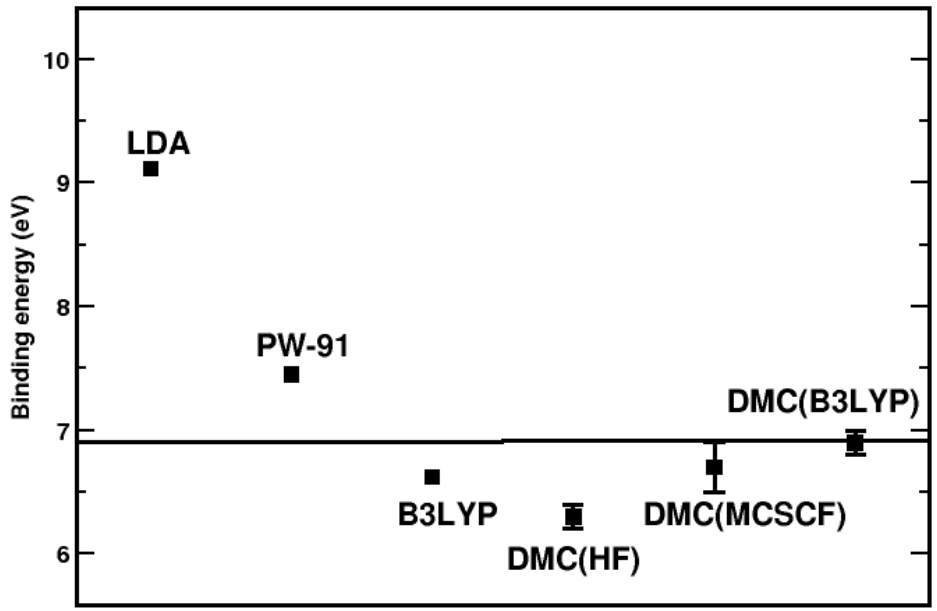
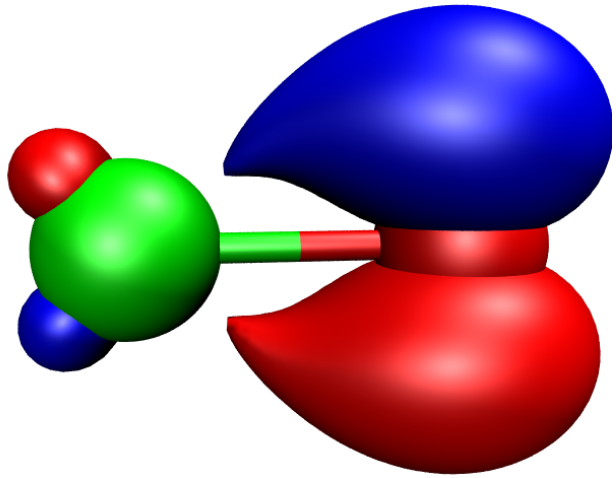
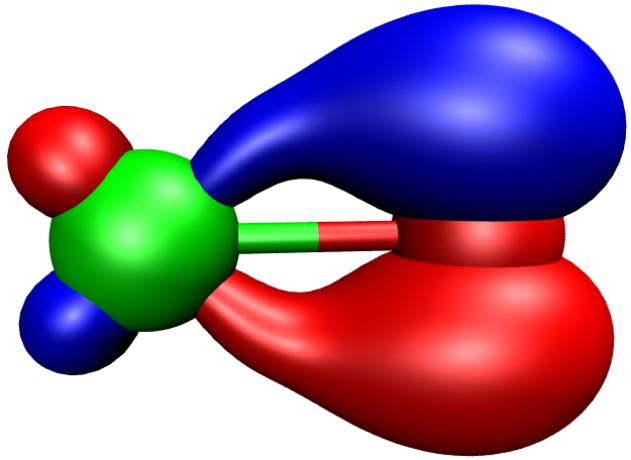


Hartree-Fock orbital



B3LYP orbital



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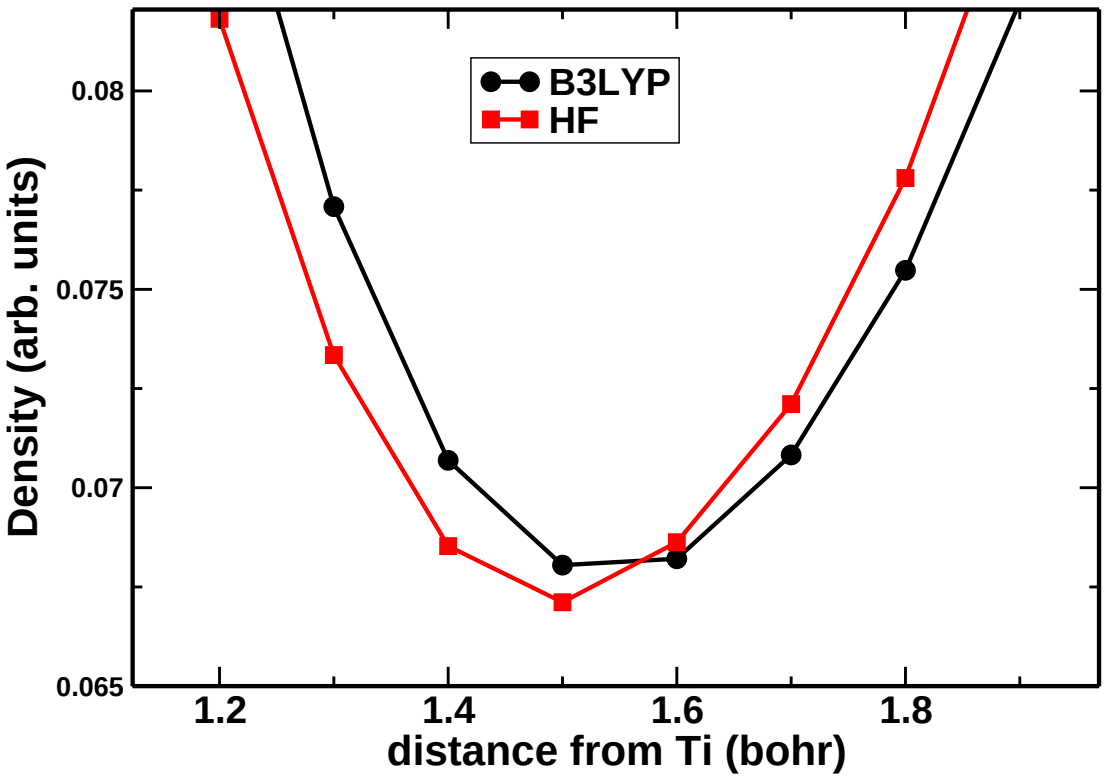
How's the density in QMC?



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- QMC(HF) also enhances hybridization
- QMC(B3LYP) enhances hybridization even more
- HF nodes limit hybridization in QMC

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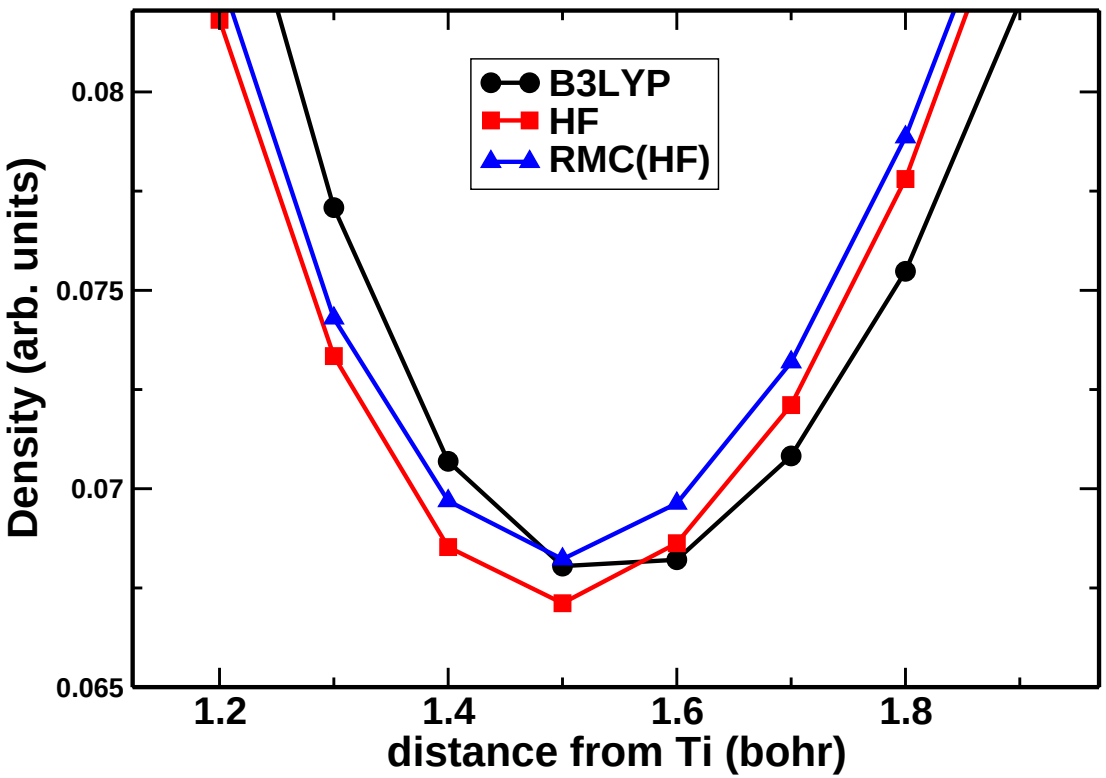

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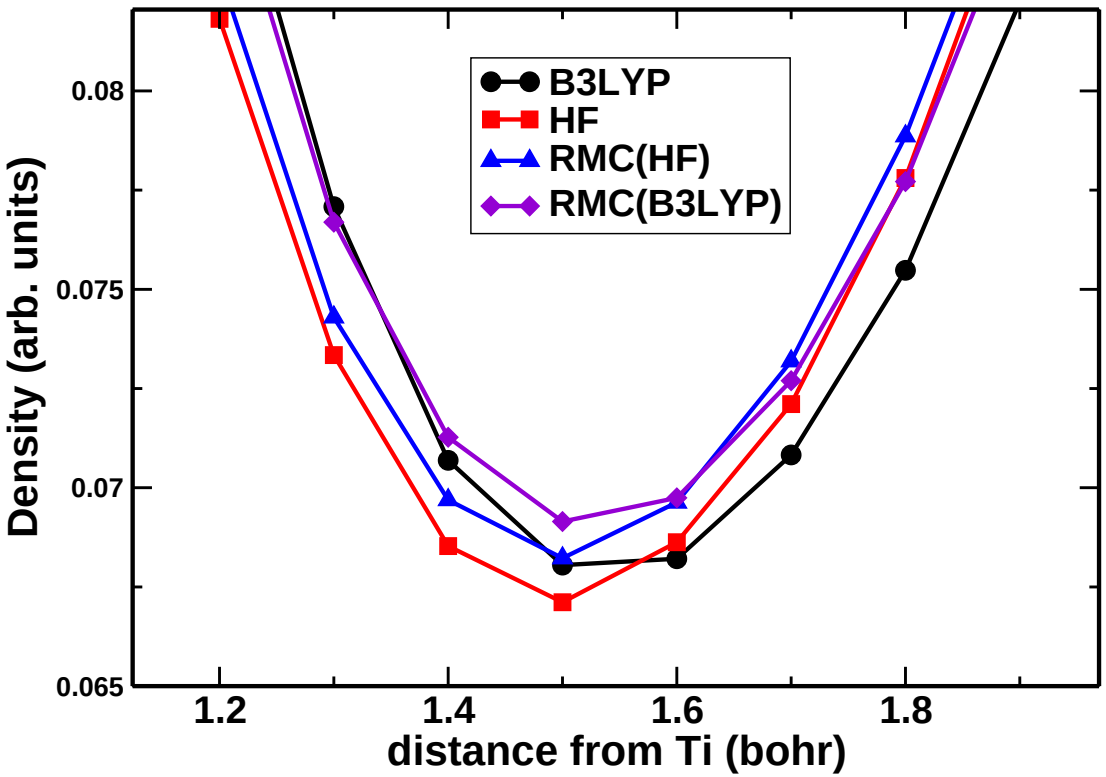

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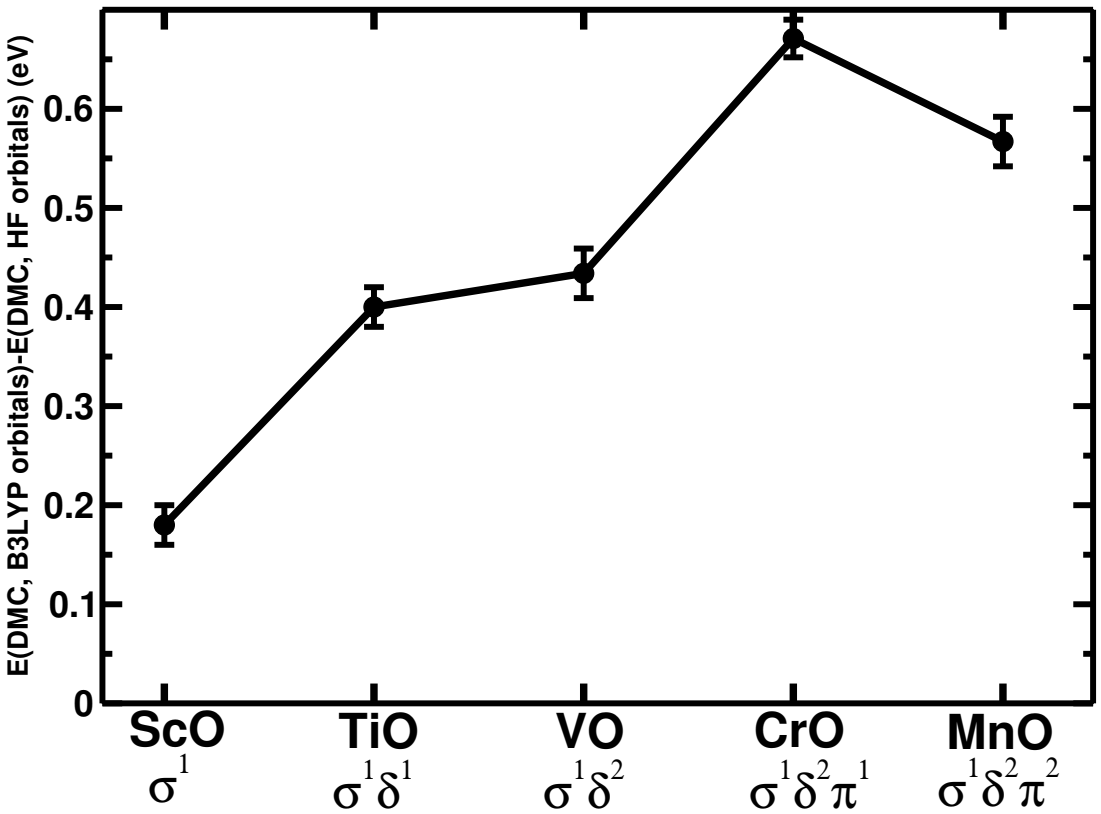
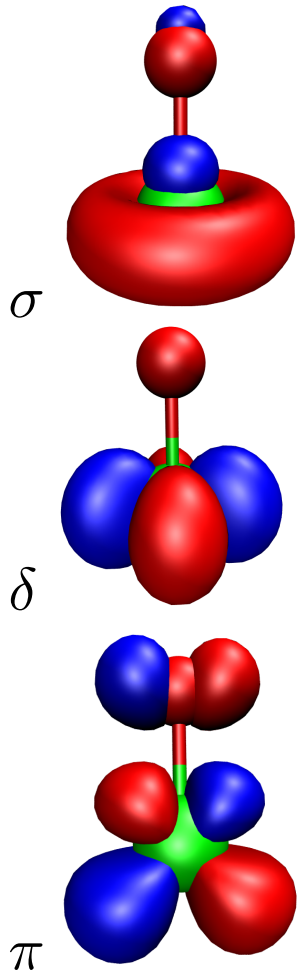
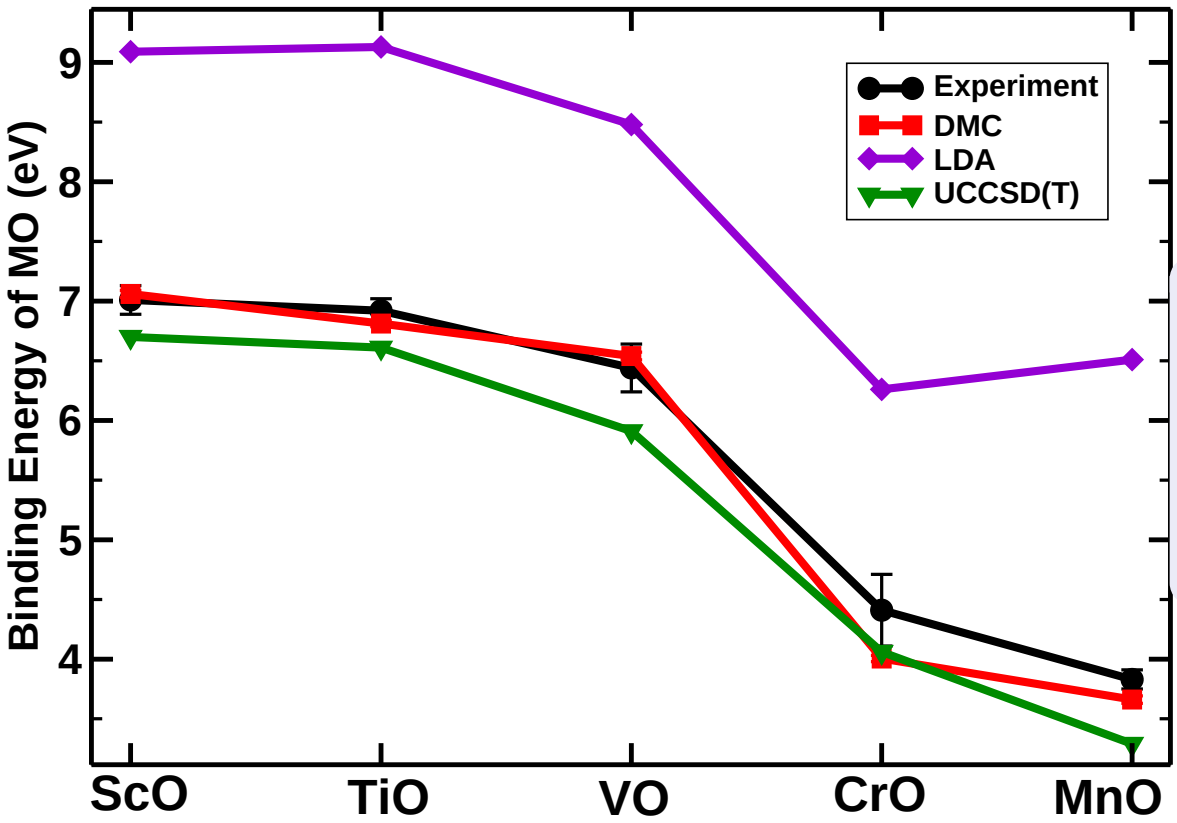
Orbital dependence of the fixed-node approximation





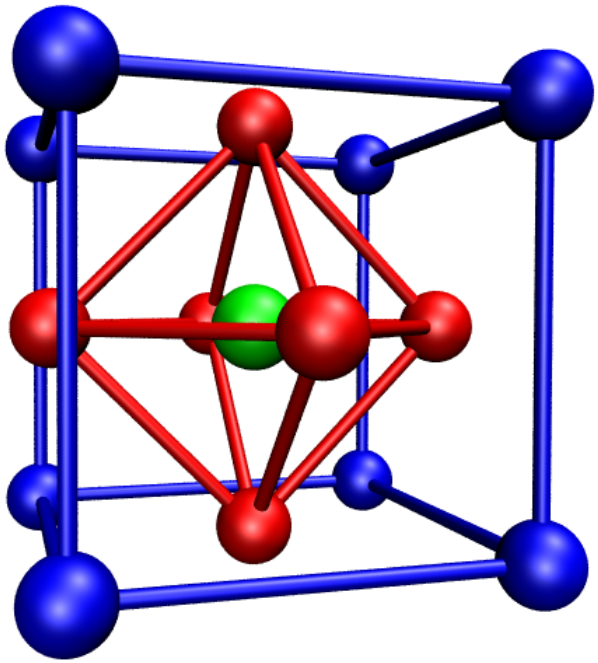
Each type of symmetry increases the importance of correlation in the orbitals.

Binding Energies of TMO Molecules

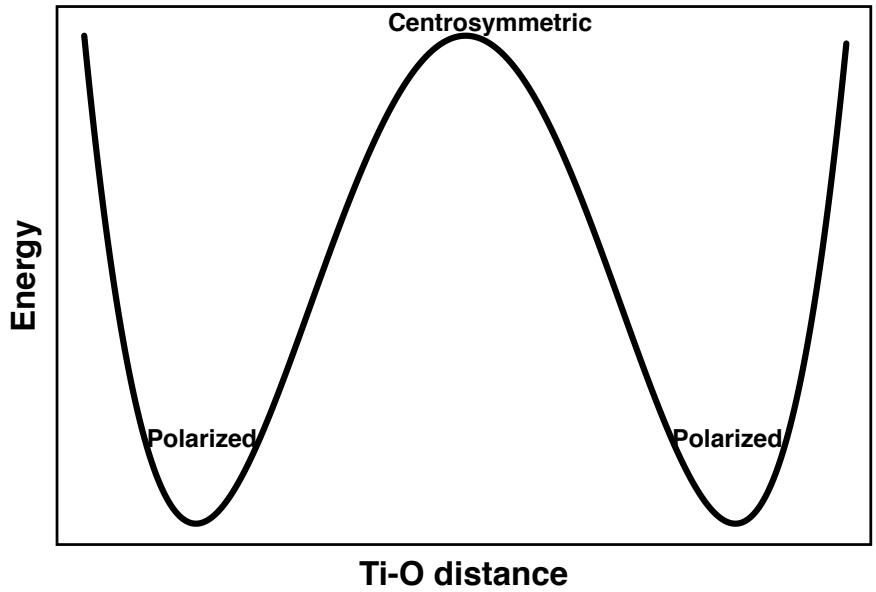


Method	RMS deviation
LDA	2.19
UCCSD(T)	0.31
DMC	0.21

$BaTiO_3$: Ferroelectric



Ba
Ti
O

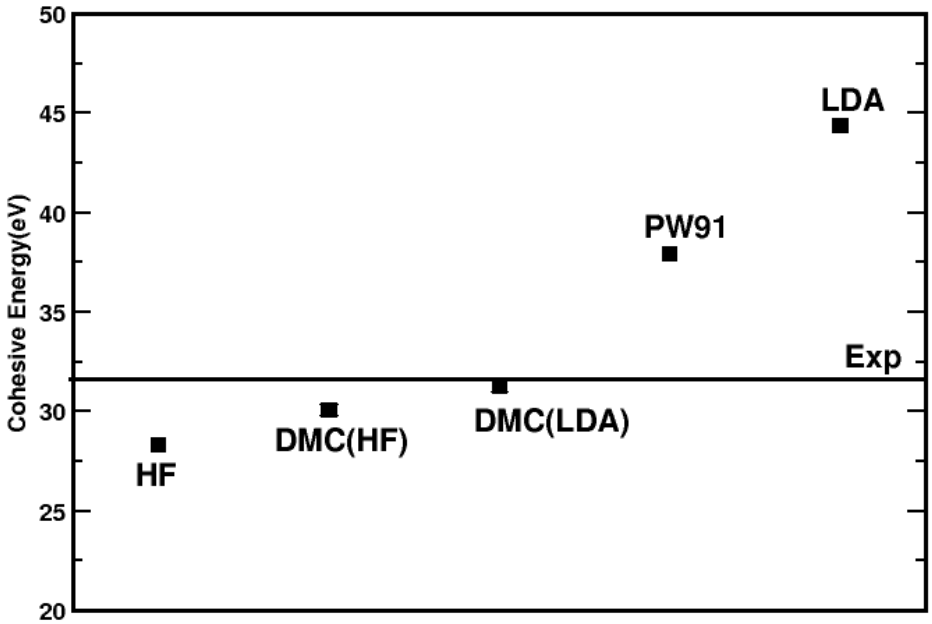


Cubic phase

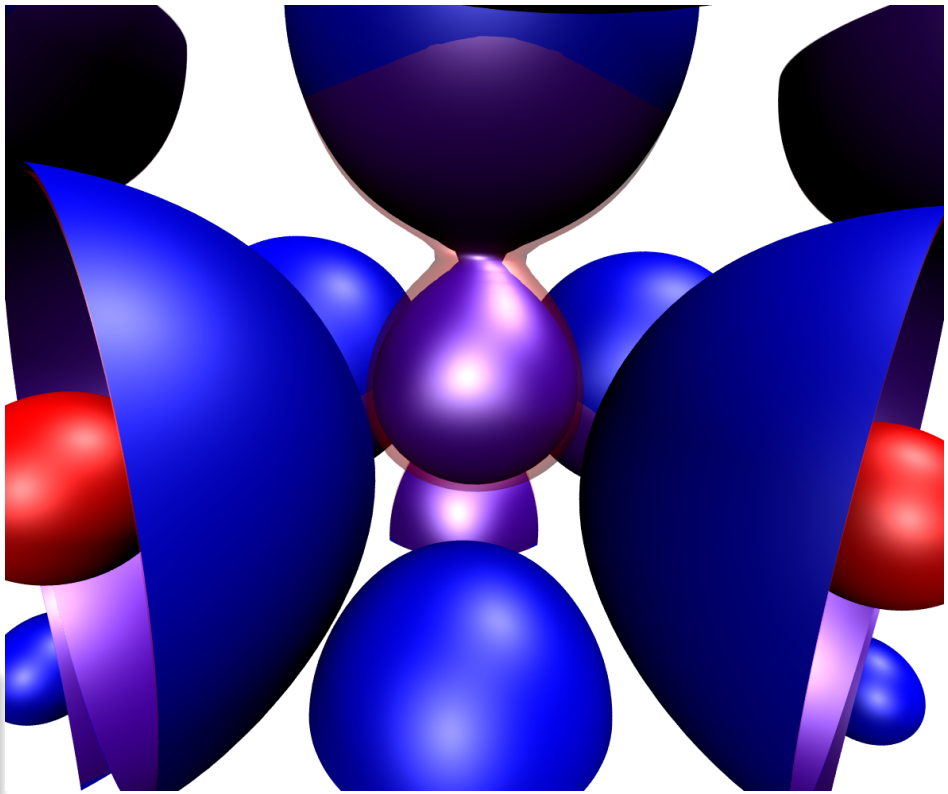
$BaTiO_3$ challenges

- Ferroelectric effect driven by the Ti-O interaction which is very sensitive to the lattice constant
- LDA underestimates volume by 1%, suppresses polarization by 50%
- GGA overestimates volume more
- Distortions, etc are ok in DFT if the volume is set to experimental

$BaTiO_3$: cohesive energy



- Orbitals matter. More d-p hybridization than Hartree-Fock.
- Lattice constant?



LDA density versus Hartree-fock density

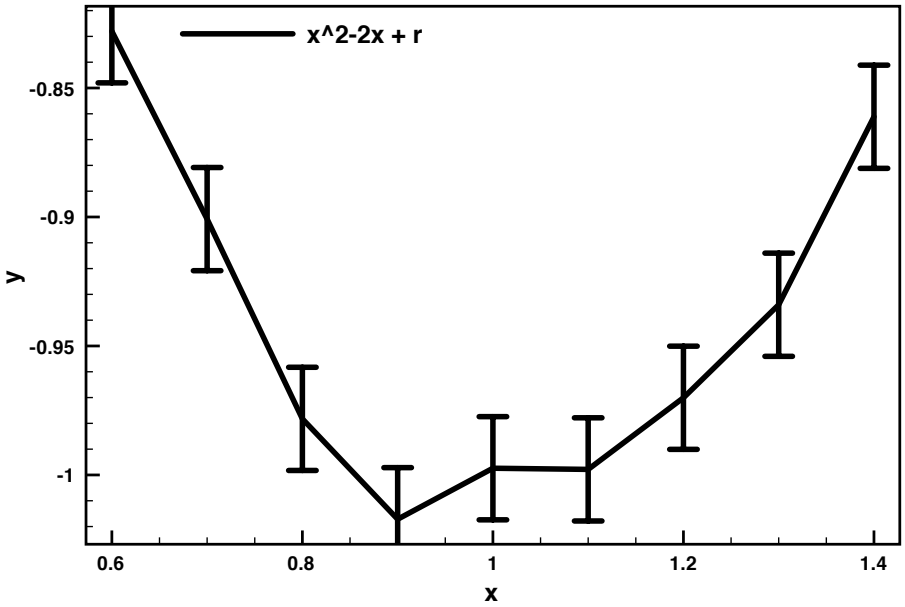
Minimum Energy Geometry
A Bayesian Approach

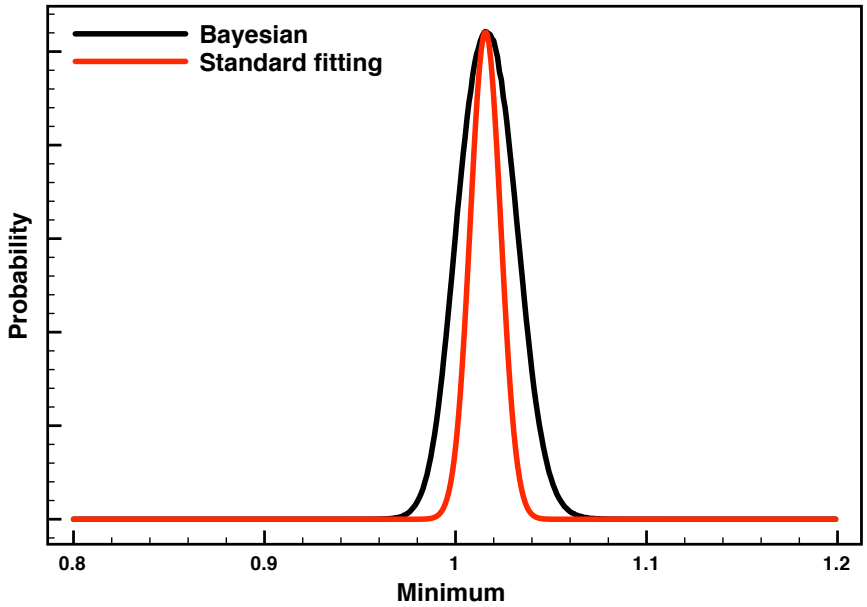
Idea: Use accurate (but noisy) QMC energies to find equilibrium geometry.

Theory

- Given data D and model M: $P(M|D) = \frac{P(D|M)P(M)}{P(D)}$
- $P(M)$: Prior distribution
- $P(D)$: Normalization
- $P(D|M) \propto \prod_i exp(\frac{-(M(x_i)-D(x_i))^2}{(2\sigma(x_i)_D^2)})$

An example
Standard fitting versus Bayesian



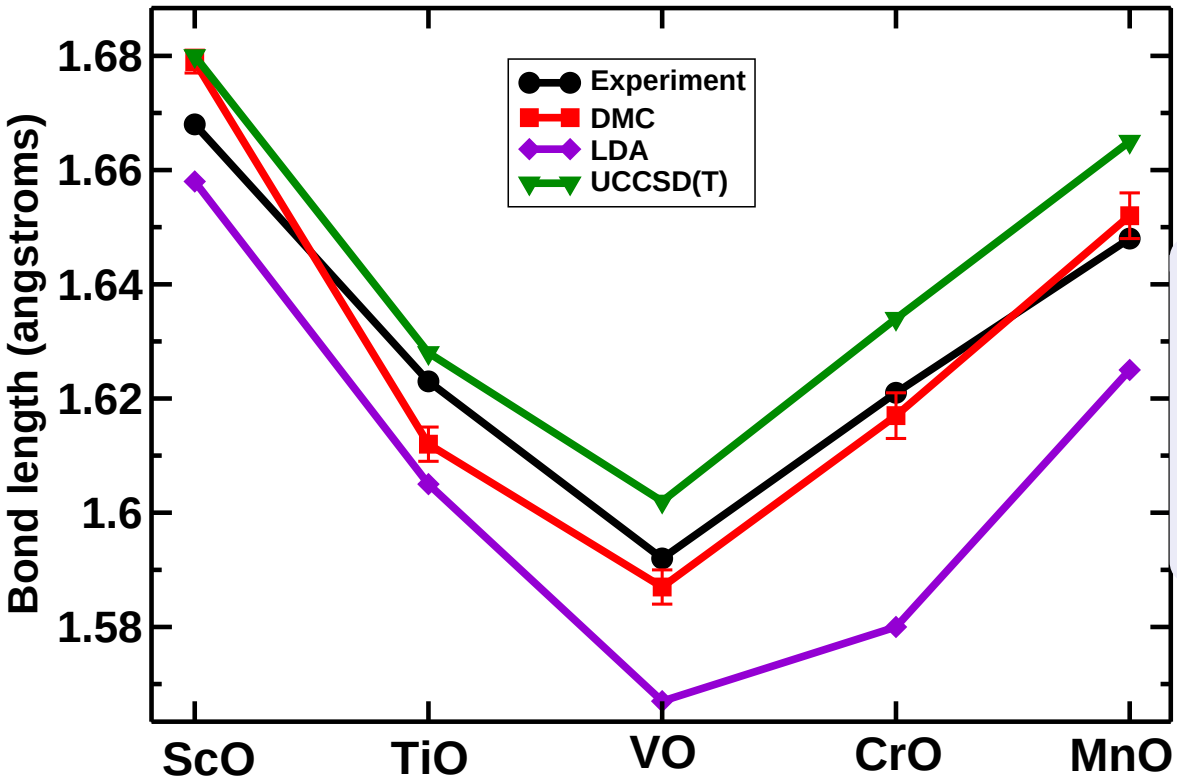


- $M(x) = a + bx + cx^2$
- $\text{pdf}(\min) = \int\int\int P(M|D)\delta(\min - \frac{-b}{2c})da\ db\ dc$
- Standard fitting underestimates the uncertainty!

Other uses for Bayesian analysis

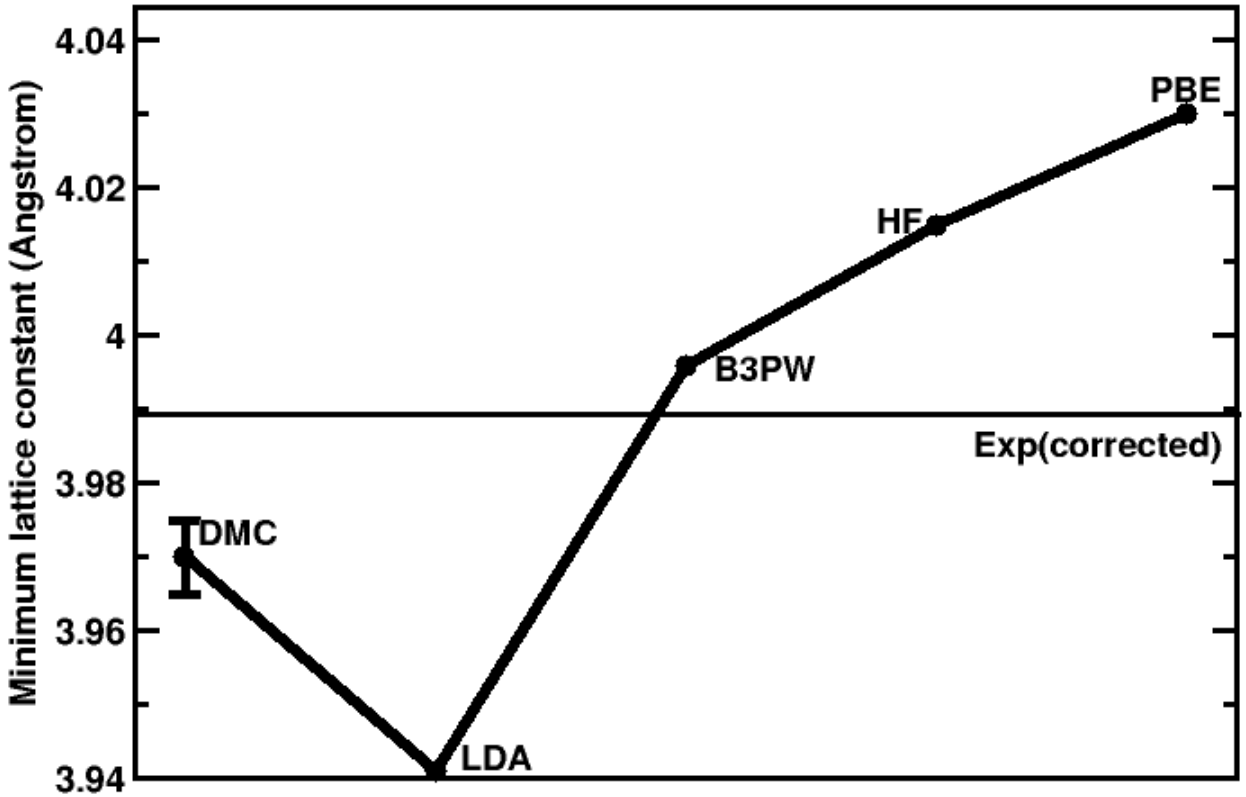
- Predicting best next point
- Model comparison
- What is the probability that E_{min} of phase A is larger than E_{min} of phase B?

TMO Molecules: Minimum Bond Lengths



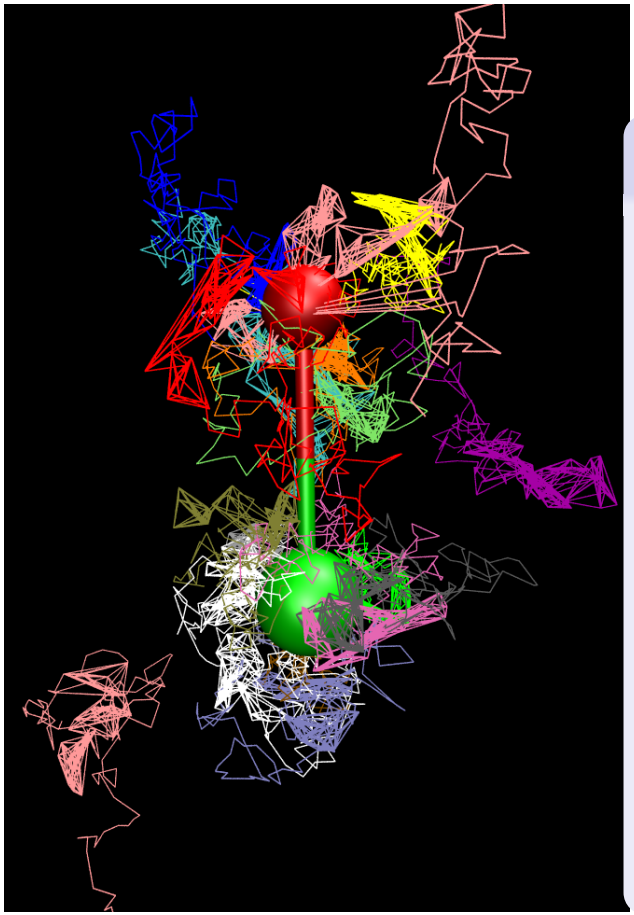
Method	RMS deviation
LDA	0.033
UCCSD(T)	0.011
DMC	0.008

$BaTiO_3$: Cubic Volume



- Same method as used on TMO molecules
- 320 electrons, 960 dimensional integrals

Reptation Monte Carlo



RMC walker on TiO

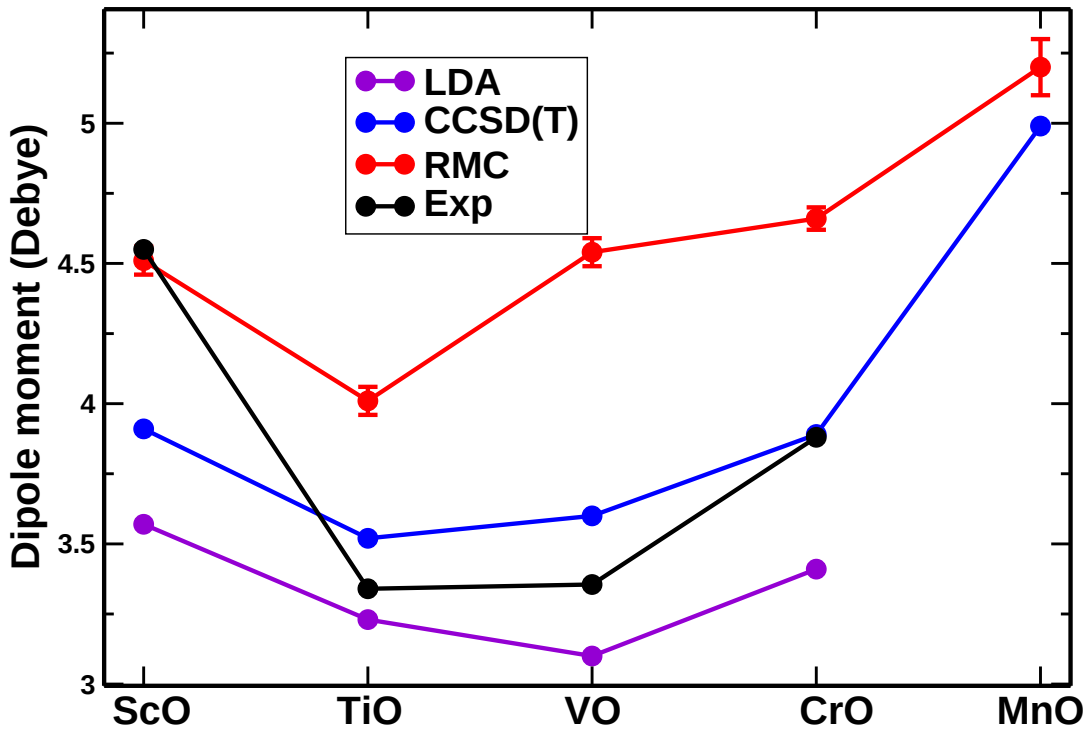
Algorithm sketch

- Need the pure distribution $\Phi_0\Phi_0$
- Walkers are paths:
  $s = \{X_0, X_1, \ldots, X_{n-1}, X_n\}$
- Sample the path distribution
  $\Psi_T(X_0)G(X_0, X_1, \tau)\ldots G(X_{n-1}, X_n, \tau)\Psi_T(X_n)$

$$\mathrm{pdf}(X_0) = \mathrm{pdf}(X_n) = \Psi_T\Phi_0$$

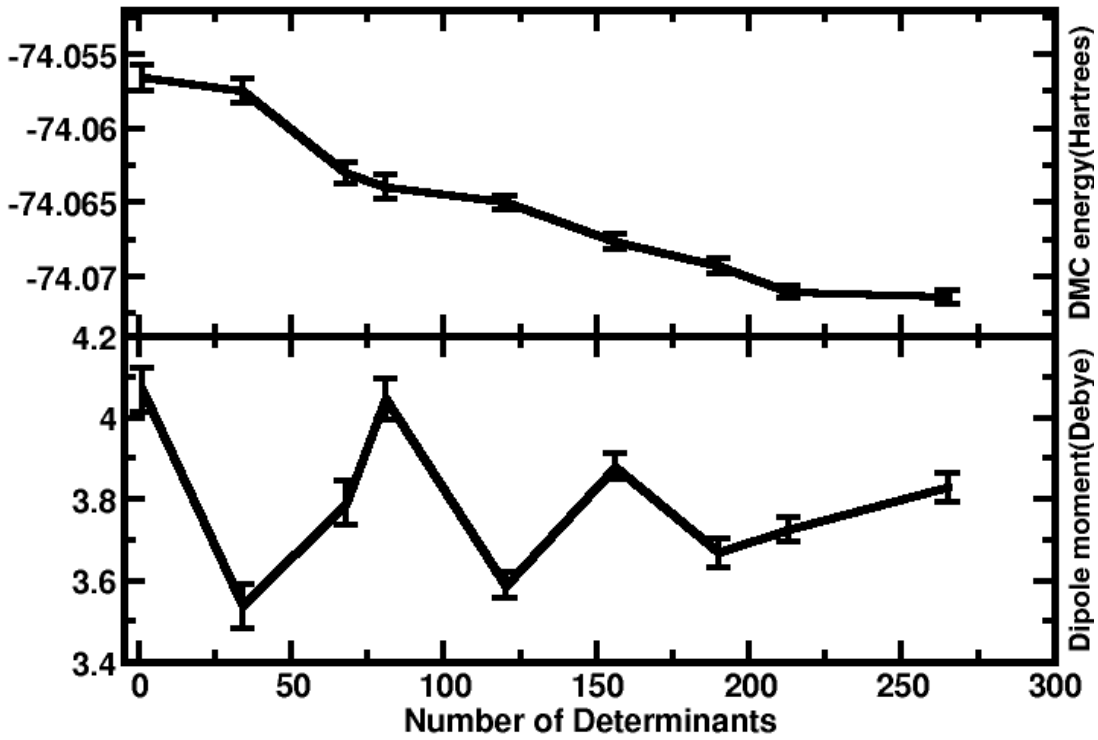
$$\mathrm{pdf}(X_{\frac{n}{2}}) = \Phi_0^2$$

Performance of Slater-Jastrow wave function



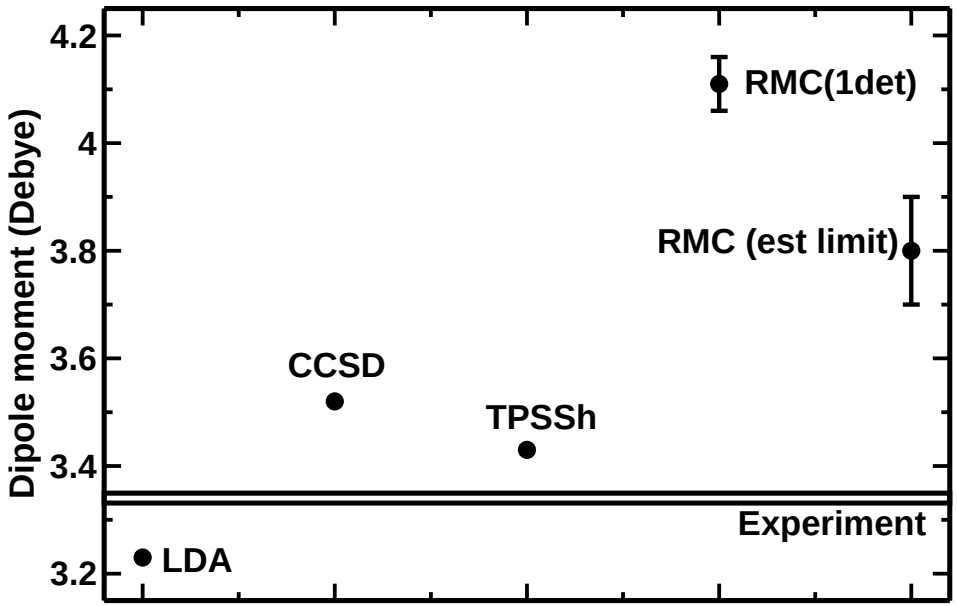
RMC mostly overestimates the dipole moment..why?

Case study: TiO



- Determinant weights optimized in VMC
- Significant energy gain, change in dipole moment
- Close to CC number, but still higher than experiment.

TiO dipole moment in detail



- Seems closer, but quite far away
- PSP error $\sim$ 0.1 Debye..

Conclusion

New Methods:

- First application of RMC to heavy atoms
- Bayesian fitting is versatile and correct

Performance on TMO's:

- Energetics, with a good trial function, are wonderful
- For dipole moments, it looks more challenging. More calculations would be interesting.

Physics about correlation:

- Enters heavily in the d-p hybridization of TMO's
- Is fundamentally important: it affects the one-particle density significantly

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