Efficient, pseudopotential-free auxiliary-field quantum Monte Carlo calculations in solids

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ABSTRACT

We present an approach for efficient, pseudopotential-free many-body calculations in periodic solids using the phaseless auxiliary-field quantum Monte Carlo (AFQMC) method. We employ the frozen core (FC) technique to obviate the need for pseudopotentials. In parallel to many-body quantum chemistry methods, tightly-bound inner electrons occupy frozen canonical orbitals, which are determined from a lower level of theory, such as Hartree-Fock or CASSCF. Since AFQMC random walks take place in a many-electron Hilbert space spanned by a one-particle basis, FC can be realized without introducing additional approximations. The same formalism also allows a basis transformation (downfolding) to an effective one-particle orbital basis using, for example, a truncated set of Kohn-Sham DFT orbitals. Both FC and downfolding provide significant computational savings over fully correlating all the electrons in full plane-wave basis, while retaining excellent transferability and accuracy. We demonstrate the approach by calculating the equation of state and energy gap of bulk MnO in antiferromagnetic and nonmagnetic phases.

Auxiliary-Field Quantum Monte Carlo

AFQMC is a many-body wave function method for quantum chemistry and condensed matter physics

- High accuracy demonstrated for ~ 100 molecular and solid systems
- Low polynomial scaling: $\mathcal{O}(M^3 - M^4)$
  $\Rightarrow$ promising for large systems
- Orbital-based QMC method
  $\Rightarrow$ flexible choice of basis

Basic method: ground state projection

$$e^{-\tau\hat{H}} e^{-\tau\hat{H}} \cdots e^{-\tau\hat{H}} |\Psi_T\rangle \rightarrow |\Phi_0\rangle$$

via Hubbard-Stratonovich (HS) transformation

$$e^{-\tau\hat{H}} \underset{\tau\to 0}{=} \int d\boldsymbol{\sigma} P(\boldsymbol{\sigma}) e^{-\tau\hat{h}(\boldsymbol{\sigma})}$$

Implemented as importance-sampled random walks in Slater-determinant space with phaseless approximation [Zhang & Krakauer, PRL **90**, 136401 (2003)]

AFQMC for Extended Systems

Two issues in accurate calculations for solids:

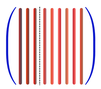
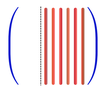
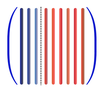
- Core electrons present an outstanding issue for all many-body methods
  - Negligible effects in chemical bondings, reactions, or properties
  - Often eliminated using pseudopotentials (PPs)
  - But PPs can introduce uncontrollable systematic errors
  - Most PPs were intended for HF or DFT
- Sheer number of plane waves ($> 10^4$) makes AFQMC calculations formidable

Two-part solution to these issues:

- Use **frozen core (FC)** approach
- Transformation to a **compact basis set**

Frozen-core approximation in AFQMC

AFQMC Random Walker $|\phi\rangle$ (Slater Determinant)

All-electron	Pseudopotential	Frozen core
		
Expensive: core electrons fully correlated	Core replaced by PP: issues with accuracy	Core electrons frozen at HF or DFT level of theory

Advantages of frozen core:

- Eliminates the need of pseudopotential
- Significantly reduces the number of electrons *and* basis functions
- Reduces statistical error
- Maintains high accuracy

After freezing core orbitals, we obtain

$$\hat{H}_{\rm fc} = \sum_{ij\in{\rm val}} K_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl\in{\rm val}} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l + \sum_{ij\in{\rm val}} V_{ij}^{c\text{-}v} c_i^\dagger c_j + E_{\rm core} + E_{\rm n-n}$$

- Contains only valence degrees of freedom ($E_{\rm core}$ = constant)
- Fully nonlocal $\hat{V}^{c\text{-}v}$ describes the effects of core on valence electrons
- Identical to $\hat{H}_{\rm fc}$ in quantum chemistry if Gaussian basis is used in AFQMC
- $\hat{H}_{\rm fc}$ is imported to AFQMC with no further approximation

Basis Transformation (Downfolding) for Extended Systems

Challenge: Plane-wave basis in solids converges systematically, but is inefficient for many-body AFQMC calculations.

Need to devise more compact, effective basis for AFQMC:

- localized orbitals (e.g. Wannier functions)
- various downfolding methods
- Gaussian-type (GTO), Slater-type (STO), or other numerical basis sets

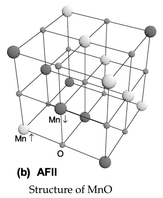
Proof-of-concept work — "Poor-man downfolding"

- First, perform DFT in unbiased plane wave (PW) basis
- Pick KS orbitals within a specified energy range above the core states
- Then perform AFQMC with much smaller subset of KS orbitals ("KS basis")

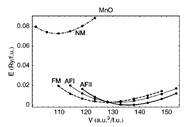
→ Core orbitals can be frozen with the FC approach

Application: Phases of Bulk MnO

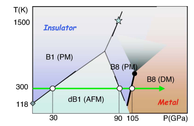
Purpose: Study the effect of a typical norm-conserving Neon-core PP for transition metals



Structure of MnO
(From: Pask et al, PRB 2001)

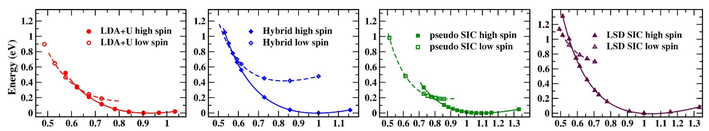


LDA equation of state



Schematic phase diagraom of MnO
(From: Yoo et al, PRL 2005)

- MnO: Rocksalt crystalline structure
- Various electronic phases: AFM I, AFM II, FM, NM
- At high pressures: high-to-low spin moment and volume collapse
- Various flavors of DFT predicts different transition pressure



(From: Kasinathan et al, PRB 2006)

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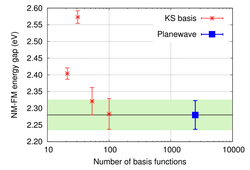
MnO low–high-spin energy gap

"NM"–FM gap: $\Delta E \equiv E_{S=1/2} - E_{S=5/2}$

- MnO primitive unit cell, $a = 8.4$ Å
- Norm-conserving, single-projector PPs generated with OPIUM
- He-core PP → approximating AE calculation
- Plane-wave or truncated KS basis
- KS band energy cutoff $\sim \epsilon_{3p} + 4.7$ Ha
- L point only

Basis convergence check



Comparing DFT (all-electron and PPs) and AFQMC

			ΔE (eV)	
Mn PP	Basis	Nbasis	DFT (GGA)	AFQMC
Ne-core	PW 50 Ha	2488	1.51	2.28(4)
	KS	53		2.32(4)
He-core	PW 800 Ha	160046	1.14	
	KS	59		1.76(3)
He-core + FC	KS	55		1.77(2)
AE	LAPW		1.13	
AE	PAW*		1.11	

PAW: * Ne core frozen at atomic level

Results:

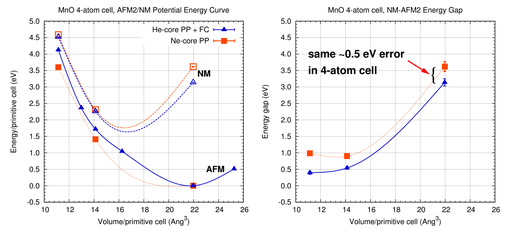
- Gap is converged at ~ 50 KS basis functions (1/40 of the original PW basis)
- He-core PP (with/without FC): excellent approximation to AE
- Ne-core PP: > 0.5 eV error → issues with single-projector PP

MnO NM–AFM energy gap

Gap between NM and AFM II phases: $\Delta E \equiv E_{\rm NM} - E_{\rm AFM}$

- MnO rhombohedral 4-atom unit cell, L point only
- Comparing: Ne-core PP to He-core PP + FC
  QMC cost is *identical* in both cases.

Preliminary Results



Summary & Outlook

Frozen core AFQMC succesfully implemented in solid systems with basis downfolding:

- Calculation cost is significantly reduced
- FC avoids issues with pseudopotentials

Further development:

- Basis downfolding/frozen core at arbitrary Bloch vector **k** (already implemented)
- What is the most appropriate downfolded basis representation for solids?

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Computing provided by:

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