



Quantum Monte Carlo Simulations of a Single Iron Impurity in MgO



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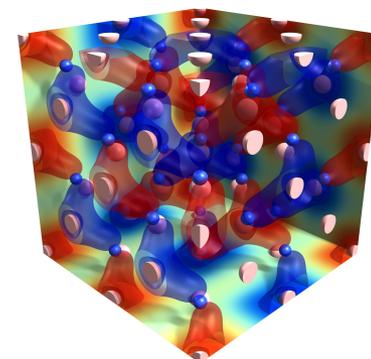
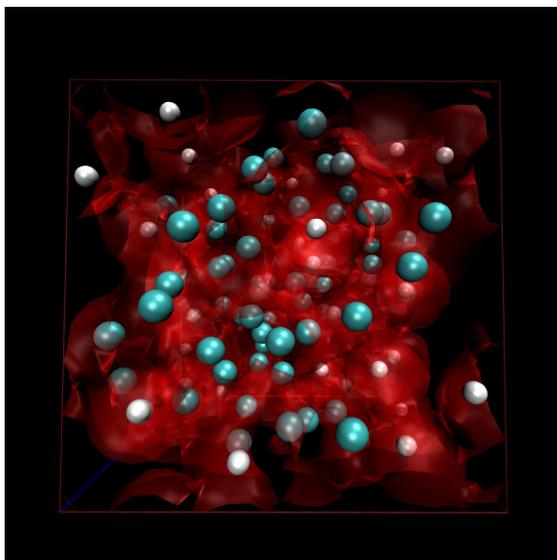


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1) Introduction to Methods

- Standard DFT: often good for standard band theory; fails for strong correlation.
- DFT+U: corrects DFT for strong correlation using Hubbard U parameter.
- QMC: best many-body method ground state properties for given nodal surface

2) Results of QMC (Mg,Fe)O Calculations

- Determine U with QMC:
 - Optimized energy with respect to U in trial wave function from DFT+U
- Equations of State for 1 Fe impurity in MgO



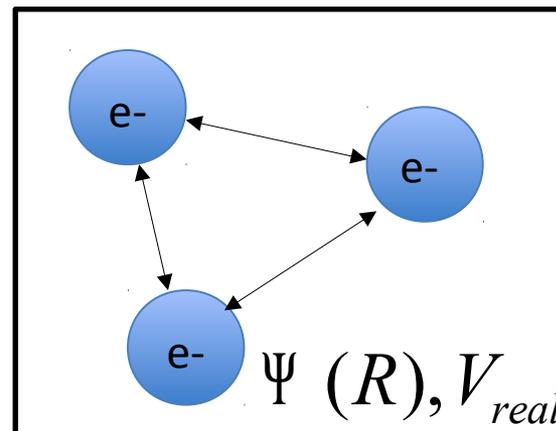
Nobel Prize Chemistry, 1998 (Kohn and Pople)
Often successful; computationally efficient

$$\hat{H}\Psi = E\Psi \quad (\text{many-body Schrödinger Equation})$$

One-to-one mapping

Hohenberg-Kohn Theorems

Minimize $E_{TOT}[n]$ wrt density variation

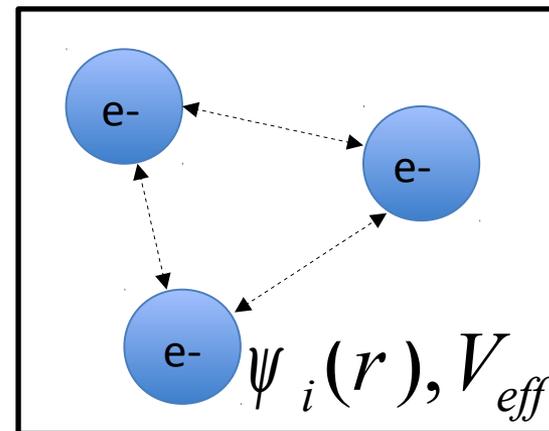


$$E_{TOT}[n] = T[n] + E_{ion}[n] + E_H[n] + E_{XC}[n]$$

One-particle Kohn-Sham equations:

$$H\Psi_i = \left[\frac{1}{2} \nabla^2 + V_{eff}(r) \right] \Psi_i = \varepsilon_i(r)$$

$$V_{eff}(r) = V_{ion} + V_H + V_{XC}$$



XC fit to electron gas computed by QMC; Many different flavors to choose from:
LDAs, GGAs, metaGGAs, Hybrids



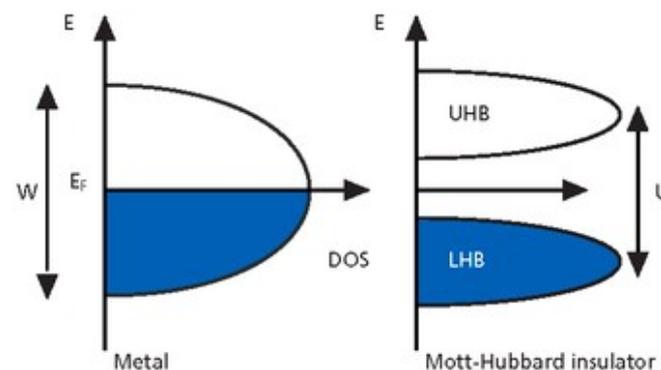
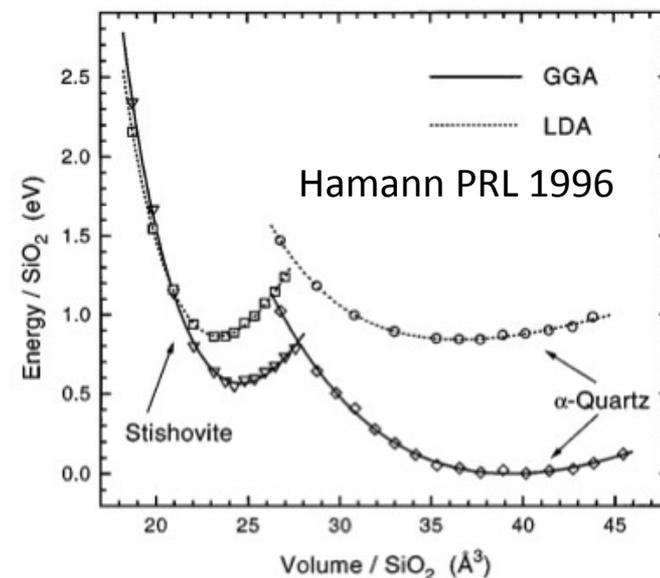
Shortcomings of Standard DFT



- **Perfect XC functional does not exist**
 - Structural properties with 3%.
 - Bulk Moduli accurate within 10-15%
 - GGA: better at energy differences between systems.
 - Example: Silica quartz-stishovite transition.

- **Band gaps severely underestimated (30% or more)**
 - XC functionals are continuous functions.

- **Fails for strong electron correlation/localization**
 - Transition metal oxides: MnO, FeO, CoO, NiO
 - Mott insulators
 - d-shell oxides, strong electron correlations
 - Standard DFT predicts metallic ground state
 - Correct antiferromagnetic ground state
 - Magnetic moments too low.



Standard DFT models standard band theory.
Otherwise, electron correlation is insufficient.

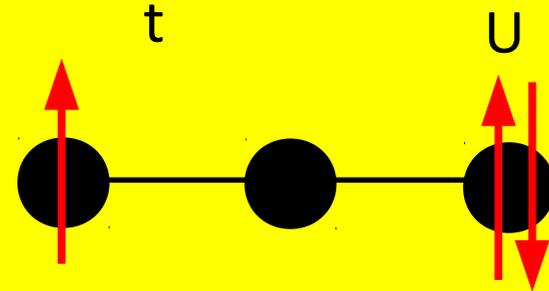


DFT correlation corrected in the spirit of the Hubbard U model:

$$H = -t \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Kinetic energy

On-site
Potential energy



KE and U competition models
strong, localized electron correlation
(mott insulators, magnetism, high T SC)

DFT+U: Add Hubbard-like, localization term to the standard functional.

$$E_{TOT}[n(r)] = E[n(r)]_{DFT} + E_{Hub}[\{n_m^{i\sigma}\}] - E_{DC}[\{n_m^{i\sigma}\}] \quad \begin{array}{l} \text{(Anisimov, JPCM 1997)} \\ \text{(Cococcioni, PRB 2005)} \end{array}$$

E_{Hub} depends on U (Coulomb and J (exchange)); Acts on localized d and f electrons.

Allows for large Coulombic repulsion between localized electrons

Allows DFT to predict highly correlated, localized materials properties.



How to choose U and J?



Several methods of computing U have been developed:

- 1) Linear response (internally consistent, basis-set independent) (Cococcioni 2005)
- 2) Constrained DFT calculations based on localized (LMTO) basis set (Anisimov 1991)
- 3) Calculate U from augmented plane-wave methods (Madsen 2005)
- 4) Other methods: cellular (Cox 1974) method, supercell methods (Norman 1988, Anisimov 1997, Pickett 1998, Solovyev 2005), and solid atom method (Yoon 2005).

...

Each theory group tends to use their own method and criteria for choosing a U.

Computing U with methods beyond DFT?

Determine U with Quantum Monte Carlo



Many methods go beyond standard DFT; each has its strength and weaknesses...

Diagrammatic Many-body extensions to DFT:

- DMFT: non-perturbative treatment of local interactions; Maps many-body lattice to local impurity model. Includes local correlations and full freq. dependence of self energy.
- GW: includes k-dependent correlations; no freq. dependence.

Many-body Quantum Chemistry Methods

Wave function-based; multi-determinant CI, MP2, CCSD (Impractical for solid calculations)

Quantum Monte Carlo (QMC)

- Direct, stochastic many-body method
- Correlation explicitly included via Jastrow function.
- Massively, and embarrassingly parallel
- Highest accuracy method for finding ground state

All of these methods are currently computationally expensive and cumbersome. As computational power evolves, QMC will become more routine.



Monte Carlo

- Solves many-dimensional integrals efficiently
- Statistical error is independent of dimension

$$\sigma \sim \frac{1}{\sqrt{N_{MCsamples}}}$$

Variational Monte Carlo

Solve variational principle for **fixed form** many-body wave function.

Pick a form for the wave function: Slater-Jastrow

$$\Psi(R) = e^{J(R)} [D^\uparrow(R) D^\downarrow(R)]$$

$J(R)$ is parameterized Jastrow Correlation factor: polynomial expansion in particle separation

$D(R)$ is a Slater Determinant comprised of single-particle DFT orbitals.

$$E_{vmc} = \int dR |\Psi|^2 \left[\frac{H\Psi}{\Psi} \right] \approx \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} E_L(R_i) \pm \sqrt{\frac{1}{N_{MC}} (\langle E_L^2 \rangle - \langle E_L \rangle^2)}$$

Jastrow parameters (polynomial coefficients) are optimized by minimizing

- 1) Variance of the energy.
- 2) The energy itself.
- 3) Combinations of both in practice.

VMC gives best energy for a fixed wave function form.

QMC methods reviews:

Needs, J Cond. Mat. 2010

Foulkes, Rev. Mod. Phys. 2001



Diffusion Monte Carlo

Schrodinger's equation is transformed to an imaginary time diffusion/rate equation:

$$\tau \rightarrow it$$

$$i \frac{\partial \Psi}{\partial t} = H\Psi = \left[-\frac{1}{2} \nabla^2 + V(R) \right] \Psi$$

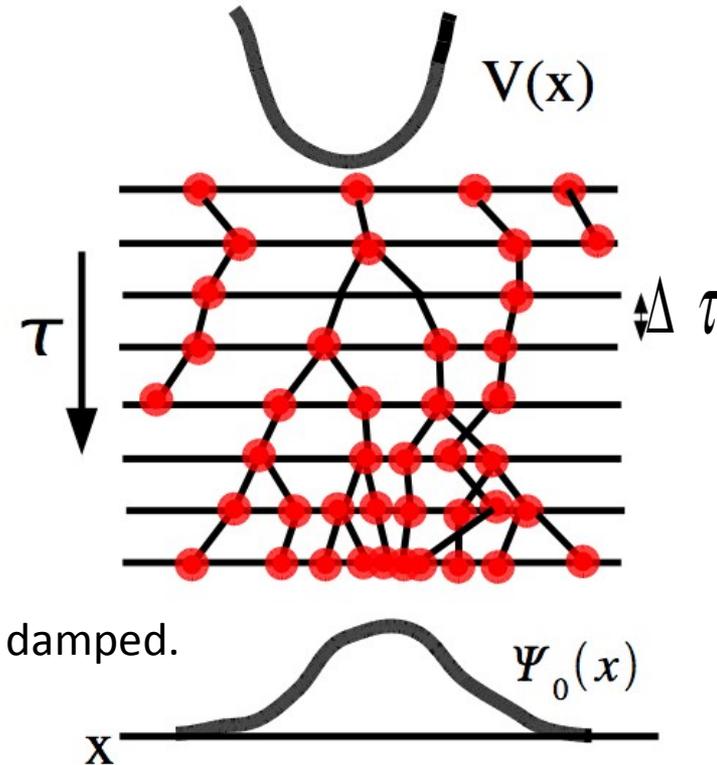
Solved formally via a Green's function projector:

$$\Psi_{GroundState} = \lim_{\Delta t \rightarrow 0} \prod_{j=1}^{N \rightarrow \infty} e^{(-H\Delta t)} \Psi_{VMC}$$

Projects out ground state; excited states exponentially damped.

Wave function is no longer a fixed form.

Ψ is represented statistically by a population of e- configurations. Each time-step, the population undergoes a random diffusion and potential-dependent birth/death process.



DMC is exact within the *fixed node approximation*:

Nodes of the wave function are fixed to ensure a positive probability density function.



Controlled approximations:

- 1) Statistical error:** Increase number of samples to achieve desired accuracy
- 2) Numerical determinant orbitals** (orbitals on a grid gains factor of N speed up)
Reduce grid spacing until energy converges
- 3) DMC time-step:** determines accuracy at which wave function is sampled.
Reduce time-step until energy converges
- 4) Finite-size simulation cell**
Twist averaging; larger simulation cells; KZK or MPC corrections correlations
- 5) Finite population** size causes a bias in DMC energy
Increase population to minimize bias

Uncontrolled Approximations:

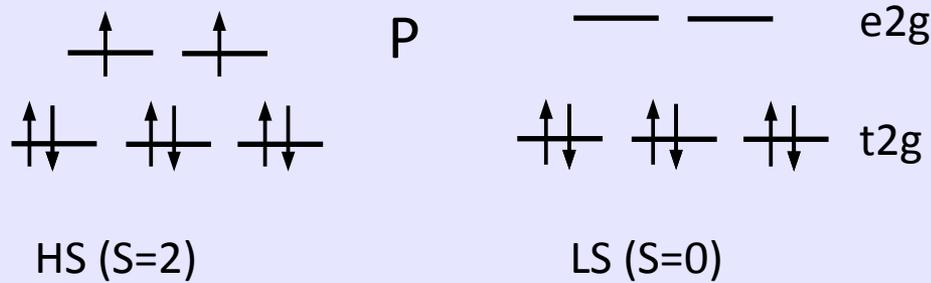
- 1) Pseudopotentials:** replace atomic core with an effective potential.
- 2) Pseudopotential locality:** trial wave function is used to project the nonlocal angular momentum components of the pseudopotential (because an analytic DMC wave function does not exist)
Lattice methods can provide upper bound on the approximation
- 3) Fixed node**
Backflow transformation of orbital coordinates estimates the size of this error.



QMC Calculations of (Mg,Fe)O



(Mg,Fe)O: abundant mineral in Earth's lower mantle.
 Experiments and DFT+U have identified a
 pressure-induced high-spin to low-spin transition:



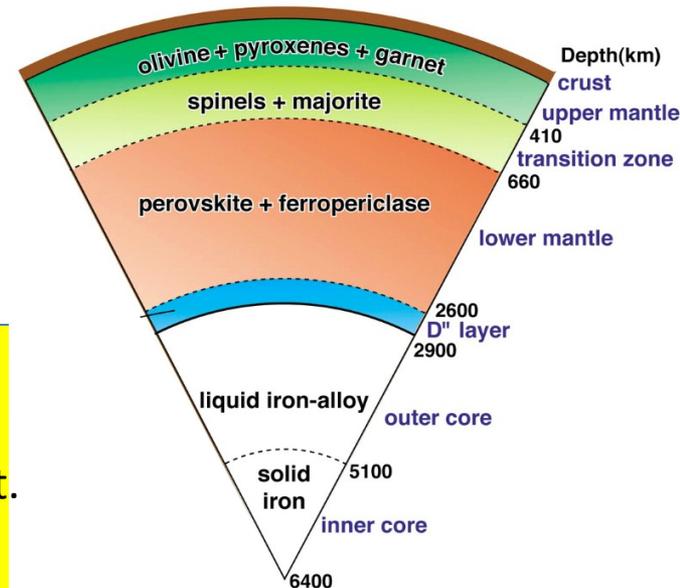
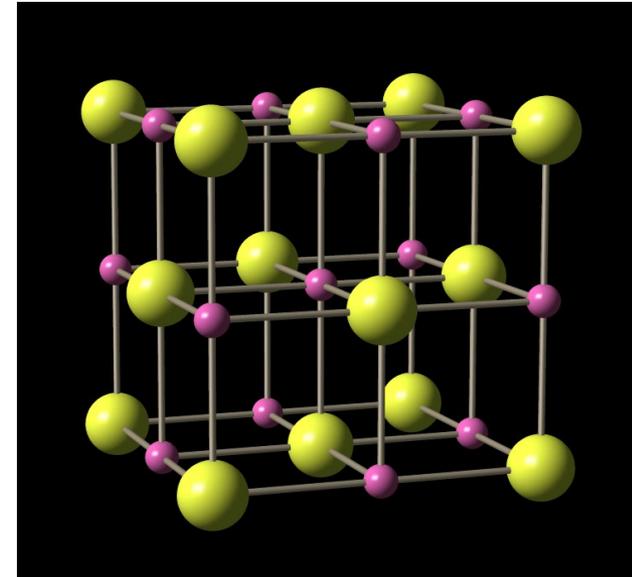
Strongly correlated electrons in Fe-3d orbitals

Spin transition has important geophysical implications:

- partition coefficient of Fe between MgO and pv/ppv
- radiative conductivities
- material hardening

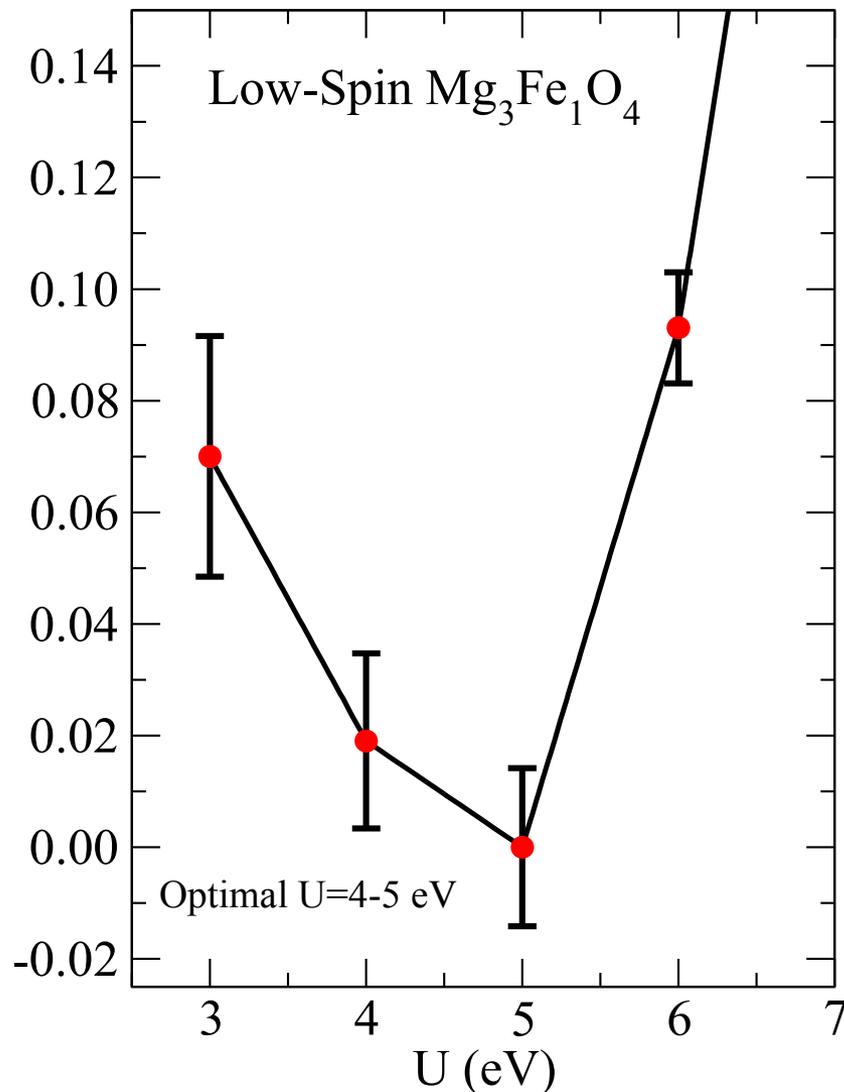
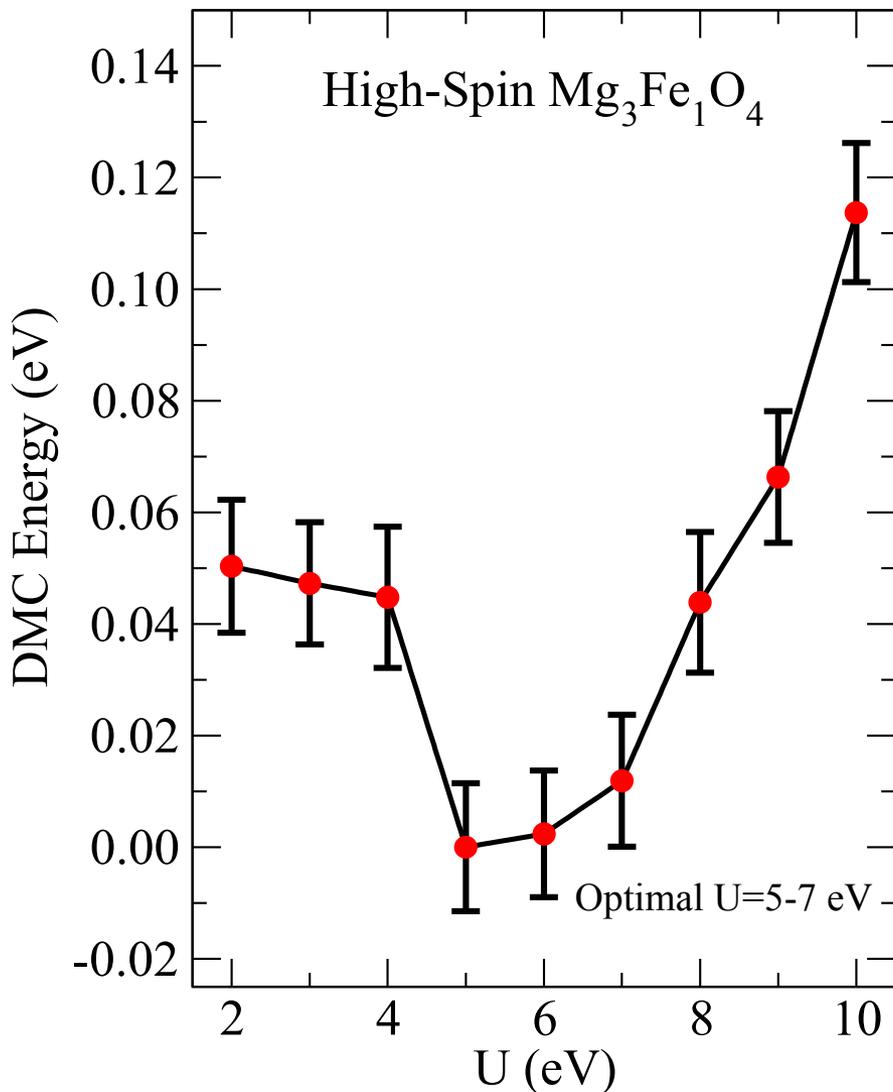
Goals for our initial QMC study:

- Access the feasibility of studying (Mg,Fe)O.
- Study 1 Fe compressed in otherwise iron free environment.
- Compare with LDA+U and DMFT (tbd) approaches.





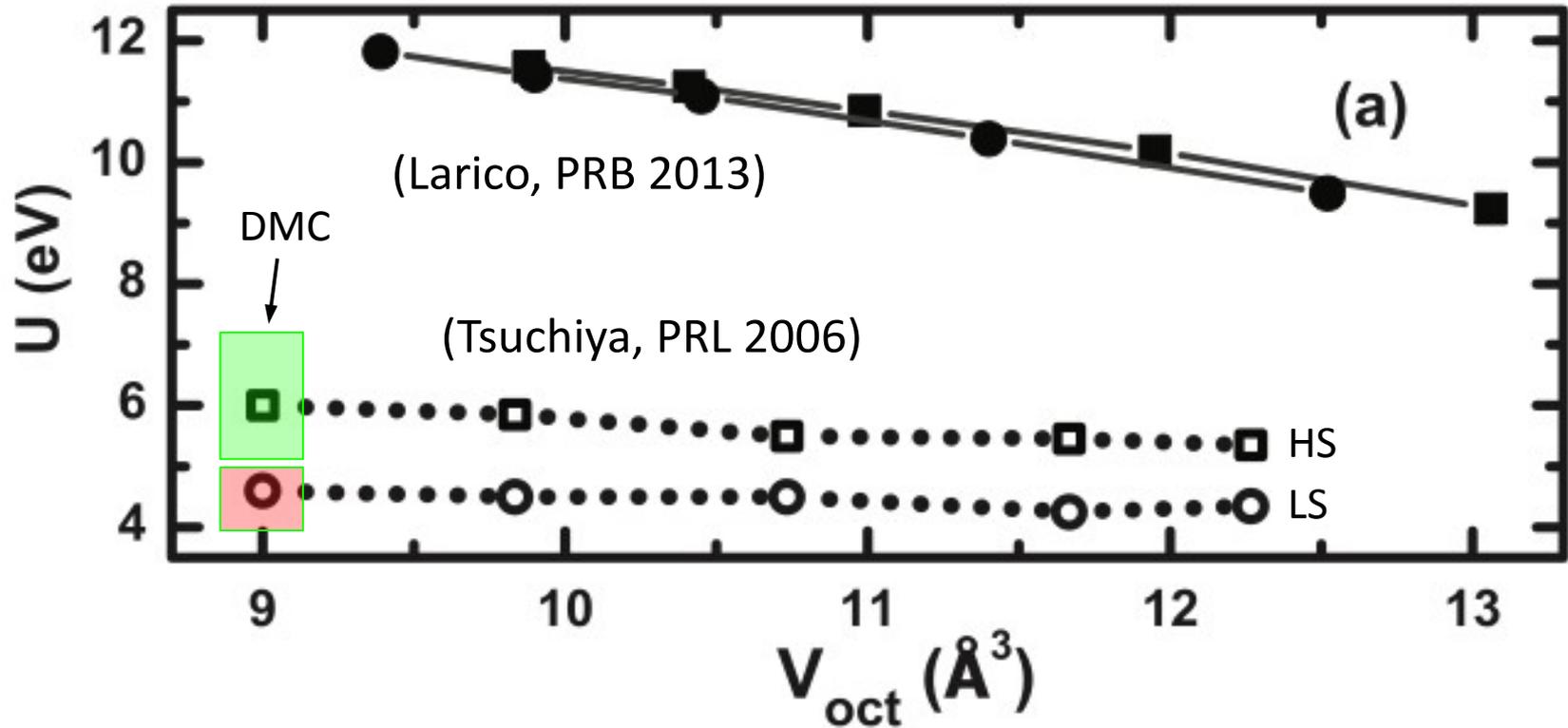
DMC Determines Optimal (Mg,Fe)O U parameter



DMC energy versus U from trial wave functions with a range of DFT+ U inputs. DMC is variational; Lower energy is always a better estimate of the ground state.



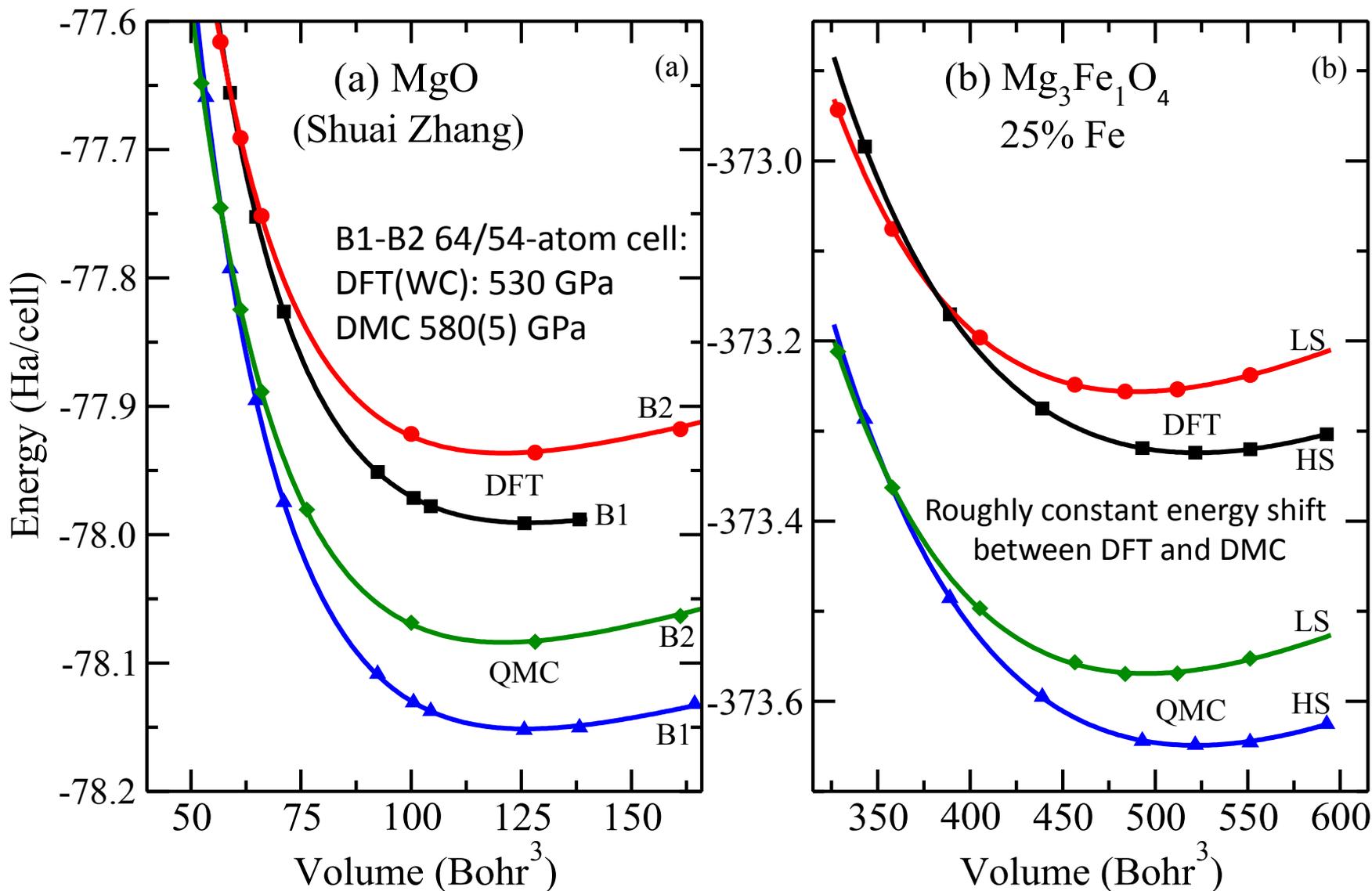
Comparison of computed U parameters for (Mg,Fe)O



DMC prediction of best U using DFT+U trial wave function agrees with Cococcioni's linear response method.



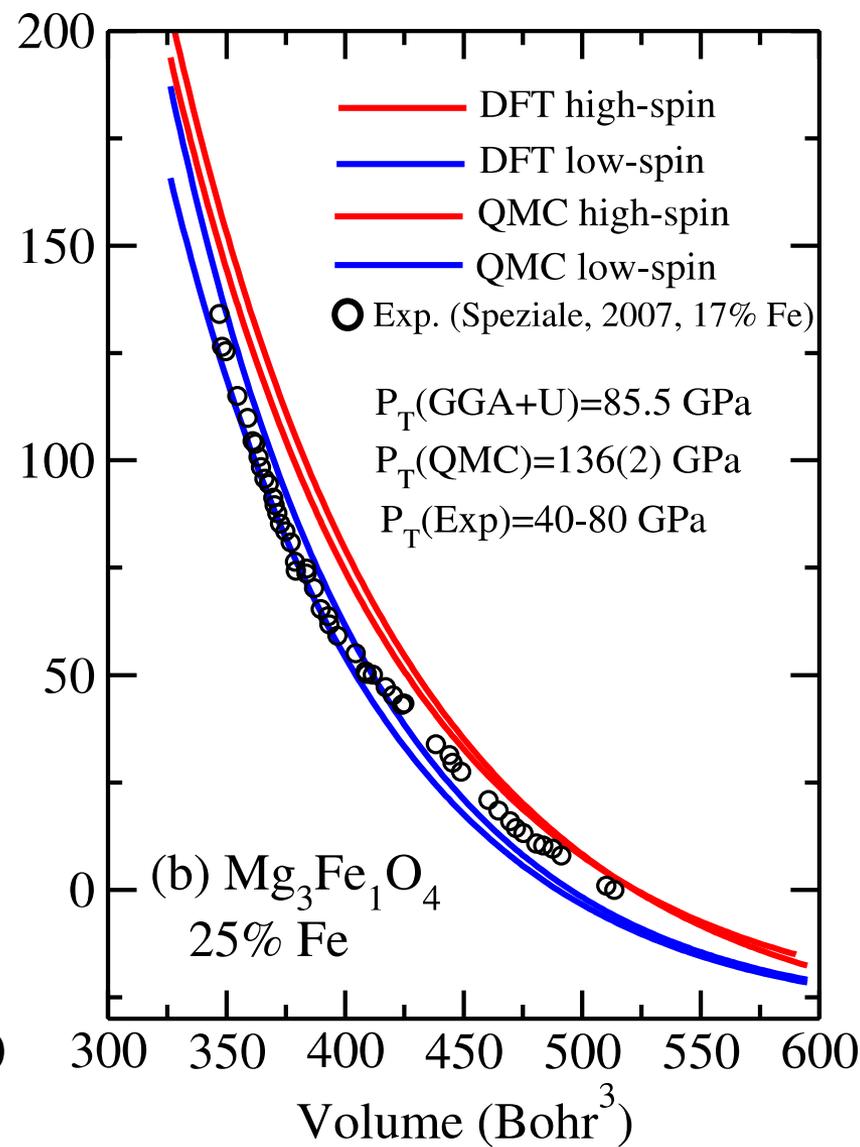
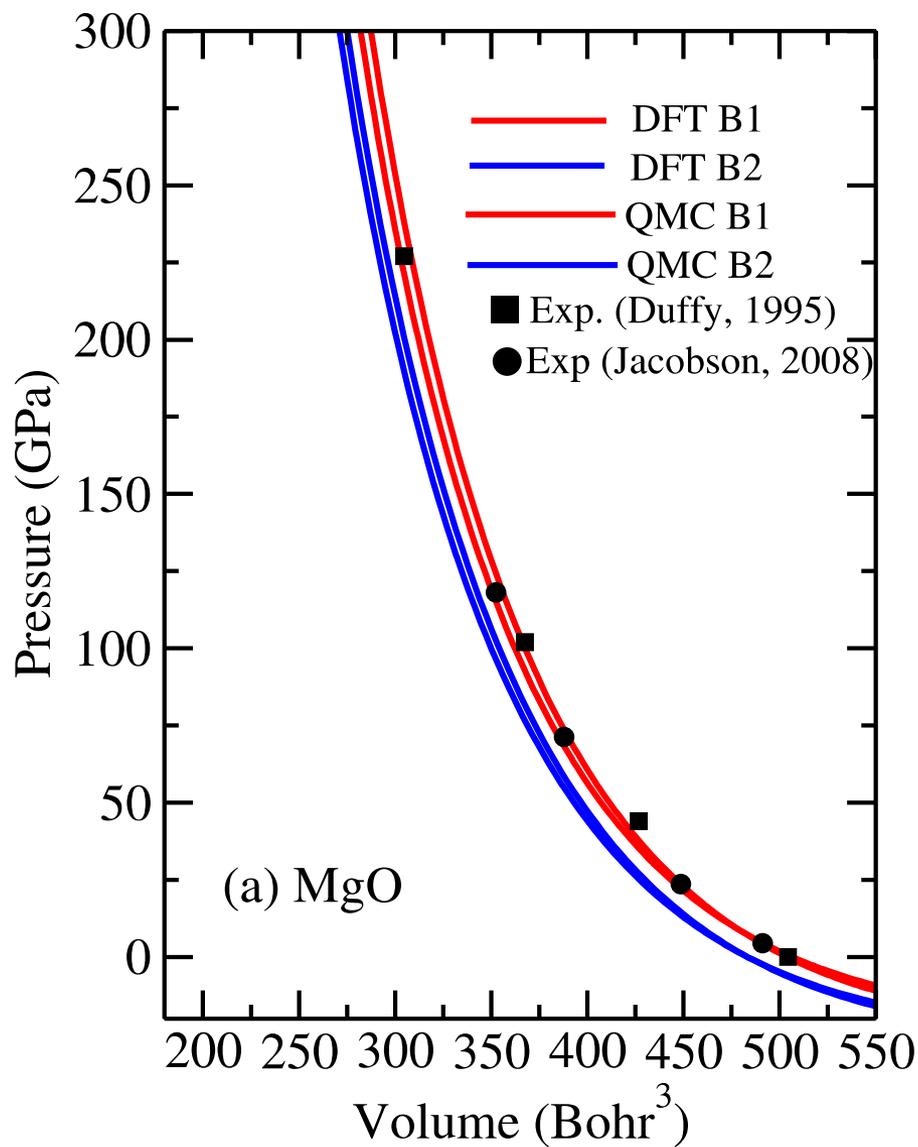
1 Fe impurity in MgO: 8-atom cell E(V)



DFT(WC) and DMC E(V) curves for MgO and Mg₃Fe₁O₄.
Data fit with Vinet equation of state.



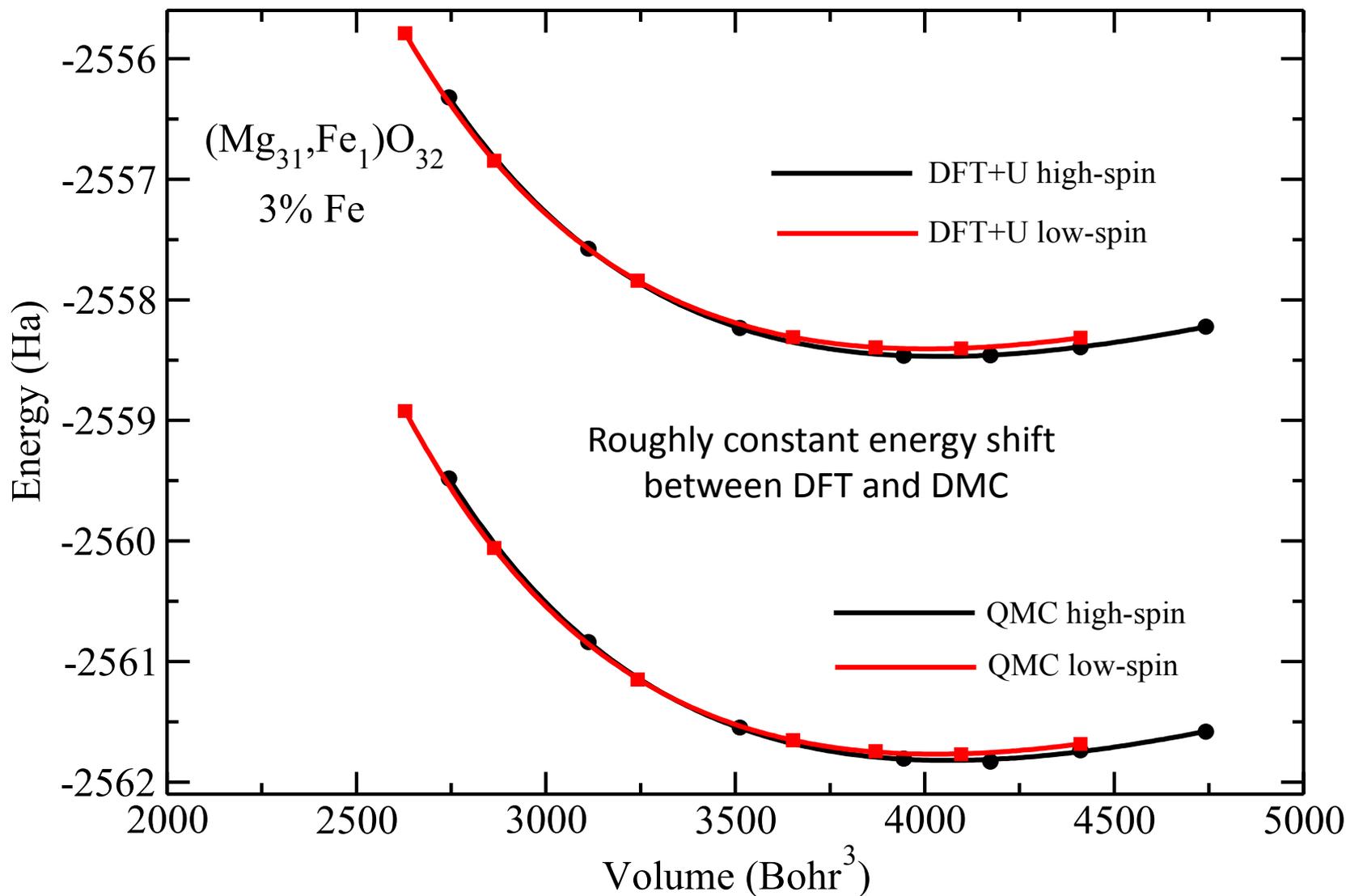
1 Fe impurity in MgO: 8-atom cell P(V)



DMC and DFT P(V) 25% Fe curves agree well with experimental data at 17% Fe. Small (8-atom) cell causes significant finite size errors in the DMC transition pressure.



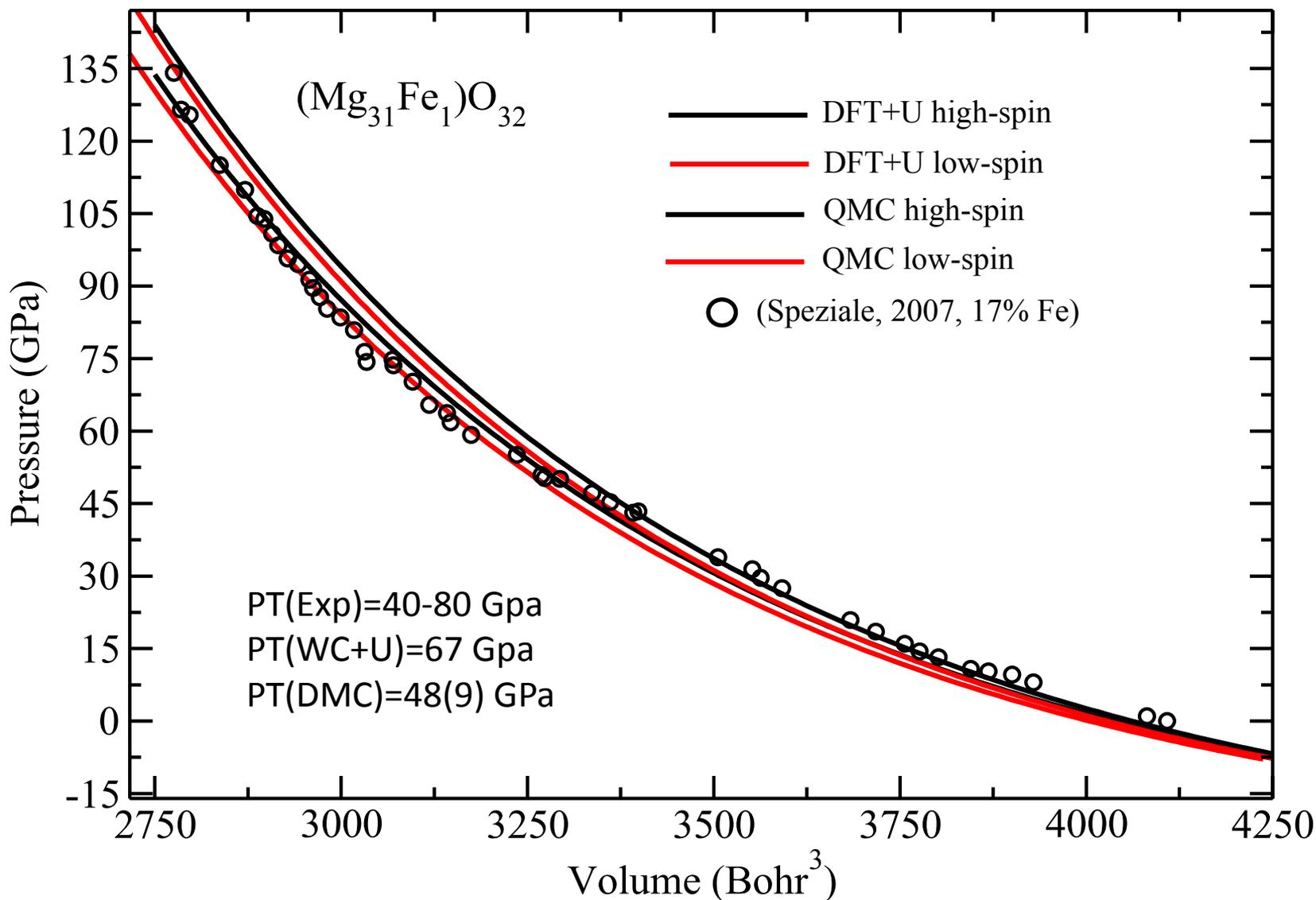
1 Fe impurity in MgO: 64-atom cell E(V)



DFT(WC) and DMC E(V) curves for Mg₃₁Fe₁O₃₂.
Data fit with Vinet equation of state.



1 Fe impurity in MgO: 64-atom cell P(V)



DMC and DFT P(V) 3% Fe curves compared with 17% Fe experimental data. DMC transition pressure is significantly improved in the larger, 64-atom cell.



Conclusions



System	V0 (Bohr ³)	K0 (GPa)	K'0	Notes
HS DMC (64)	507.8(9)	165	4.3(2)	3 % Fe
LS DMC (64)	503(2)	163	4.5(3)	3% Fe
HS DFT-WC(64)	504.8	158	4.3	3% Fe
LS DFT-WC(64)	500.5	158	4.4	3% Fe
HS DMC (8)	521.5(5)	177(3)	4.1(1)	25% Fe
LS DMC (8)	495.1(5)	176(3)	4.7(1)	25% Fe
HS DFT-WC(8)	522.6	161	4.2	25% Fe
LS DFT-WC(8)	489.7	173	4.5	25% Fe
HS Experiment	515.38	160	4.2	25% Fe (Matsui, 2012)
LS Experiment	452-513	136-246	4	17% Fe (Speziale, 2007)

- DFT+U offers accurate solutions for strongly correlated systems; Dependence on unknown U parameter and XC-functional is not ideal.
- QMC is offers a more generally applicable and formal solution for materials. The method is expensive, but shown to be feasible for hand full of systems. Popularity will grow with access to high performance computational resources.
- QMC is a good way to determine the value of U for DFT+U calculations.
- DFT+U and (preliminary) QMC both work well for (Mg,Fe)O equations of state.