Effect of nodal surface on the geometry of antiferromagnetic FeO

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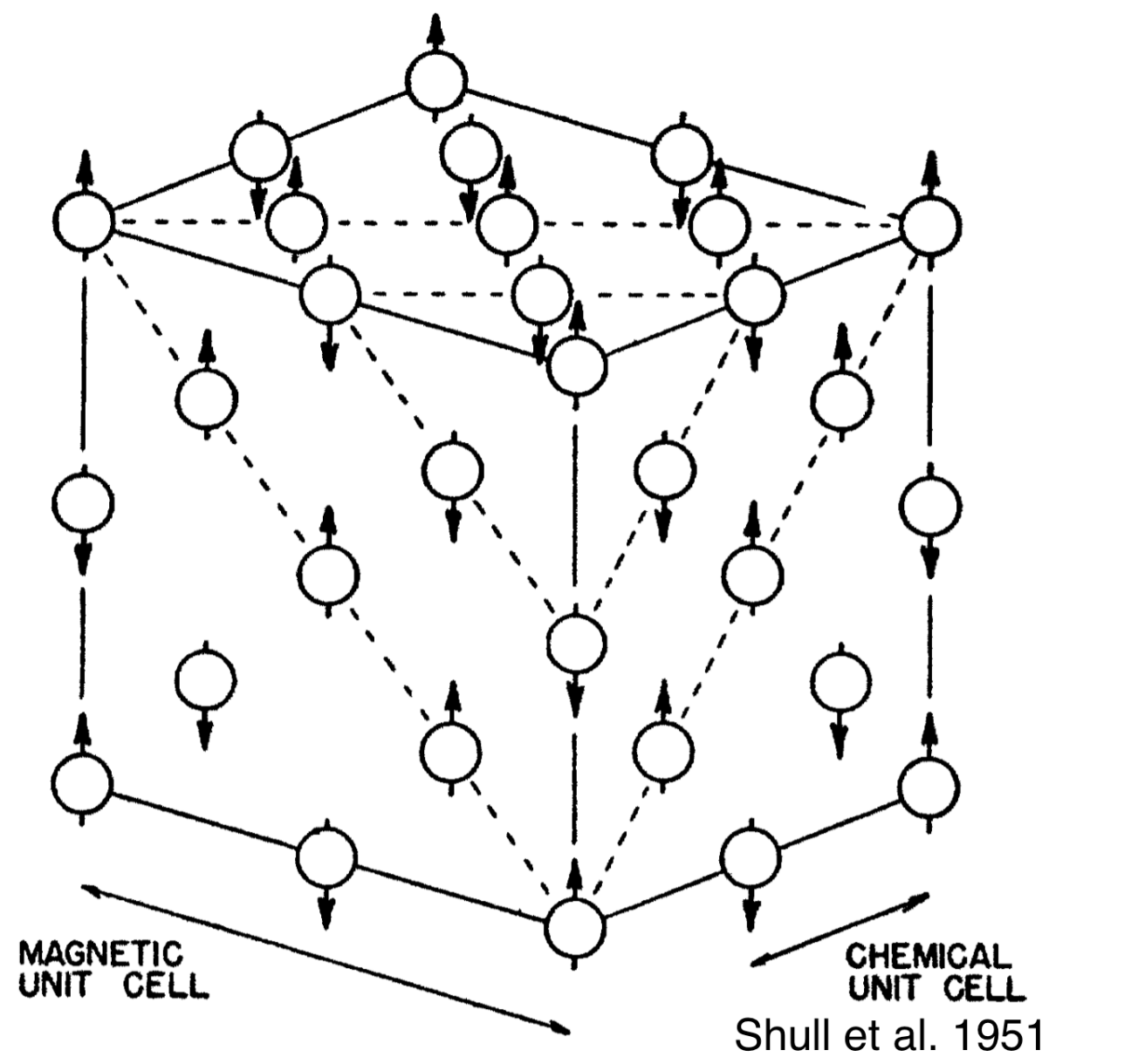
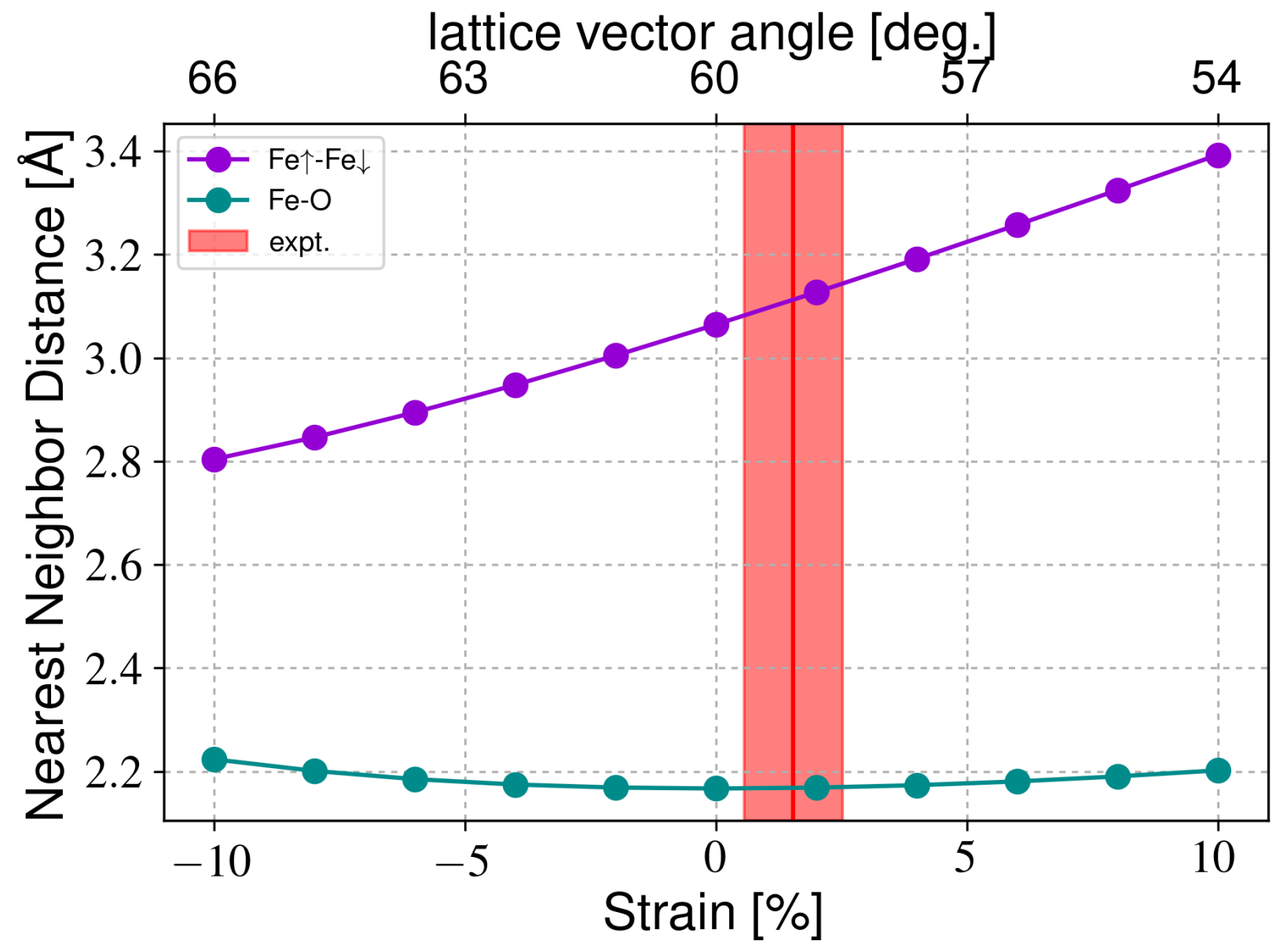
0 - Plain language summary

We tested some of the approximations made when solving the many-body quantum mechanical equations for an interacting system of atoms and electrons. We used iron oxide (FeO) as a test system because it is famously difficult to accurately describe from a theoretical standpoint. That's because the d-electrons in the iron atoms violate assumptions made in many common methods of solving the Shrödinger equation. To do this, we combined two methods called density functional theory (DFT), and quantum Monte Carlo (QMC). DFT describes many-body interactions in an average way, while QMC treats them explicitly. However, QMC requires as input the results of a DFT calculation. We find that QMC solutions are highly sensitive to the initial DFT wave functions. The results imply that more advanced descriptions of the many body wave function may be needed to obtain highly accurate properties of so called "correlated" systems within QMC.

1 - A challenge for theory and experiment

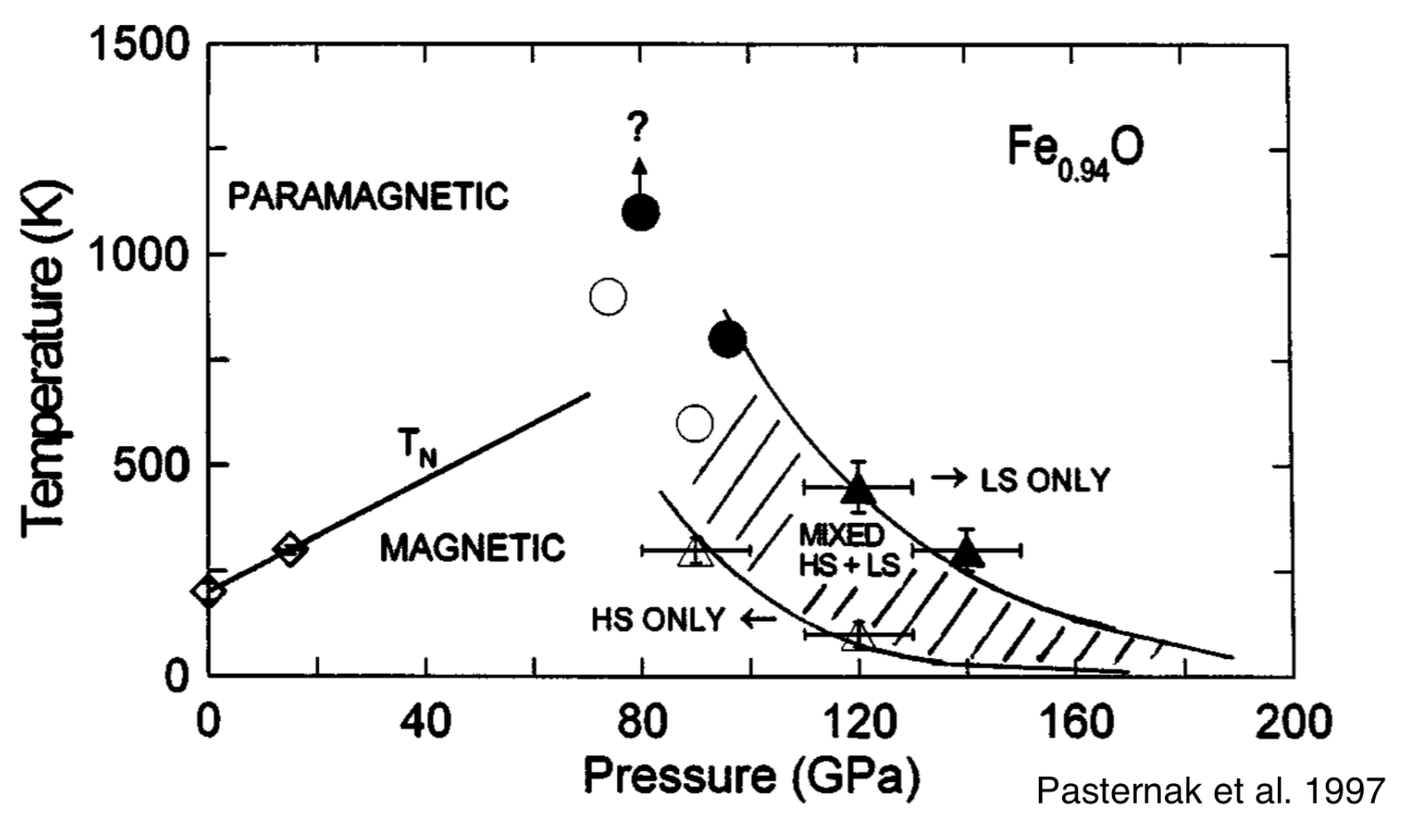


Shull et al. 1951



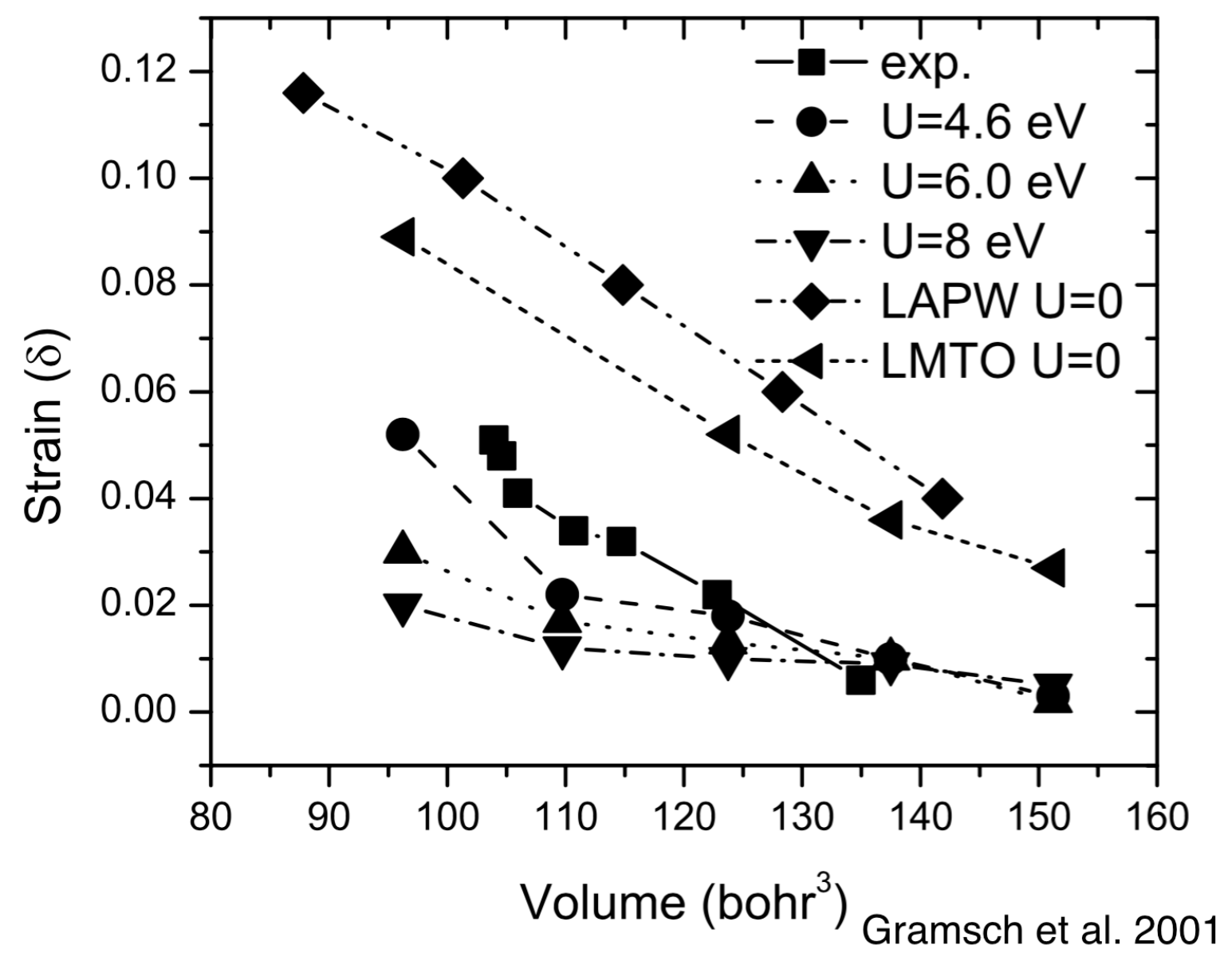
- Ground-state FeO has antiferromagnetic (AFM) ordering of ferromagnetic planes of iron atoms parallel to [111].
- Magnetoelastic coupling leads to rhombohedral distortion of cubic B1 lattice.
- Due to open shell *d*-electrons FeO is a prototypical Mott insulator [1].

2 - Magnetic and structural phase diagrams of FeO

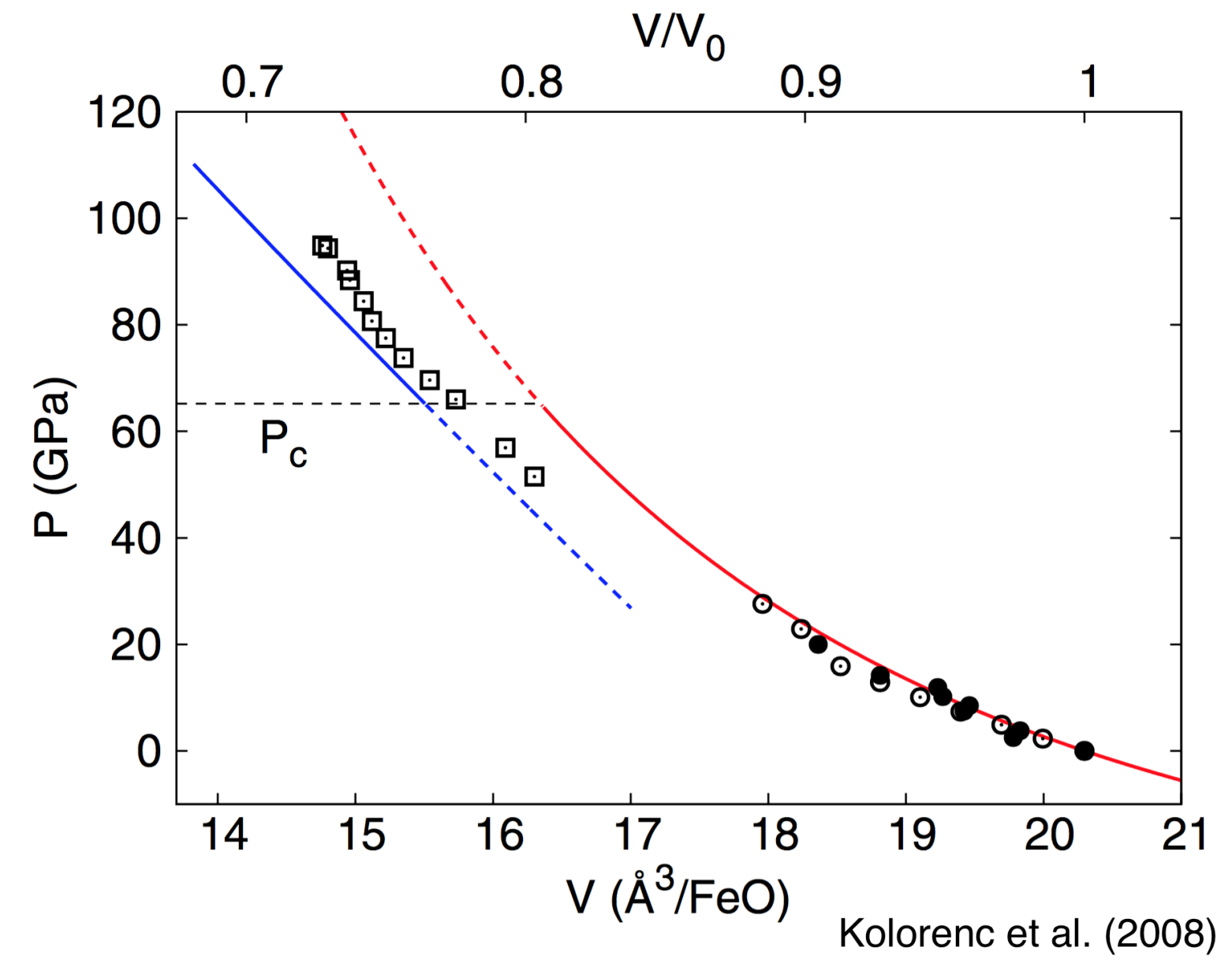


Pasternak et al. 1997

- Magnetic phase diagram of FeO remains uncertain
- Experiments indicate AFM to possible NM transition at high pressure
- Possible spin collapse in ground state at high pressure



Gramsch et al. 2001



Kolorenc et al. (2008)

- DFT fails to capture strain evolution - highly XC dependant
- QMC ignores magnetoelastic coupling completely. Underestimates phase transition pressures.

4 - Density functional theory & electronic exchange and correlation

Main idea: *The many-body wave function is constructed from single particle wave functions.*

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{1}$$

The exchange correlation functional ($E_{XC}[\rho]$) captures the correlation energy missed in the single particle approximation. The "true" functional is not known, so approximate forms are used in practice:

LDA & GGA

$$E_X^{GGA} = \int d\mathbf{r}\rho(\mathbf{r})F_X^{GGA}(s)\epsilon_X^{hom}(\rho(\mathbf{r})) \tag{2}$$

Where $s = |\nabla\rho|/2k_f\rho$, and $k_f = (3\pi^2\rho)^{1/3}$.

DFT+U

Includes additional on-site coulomb interaction for d- and f-electrons.

Hybrid

Some fraction of Hartree-Fock "exact" exchange is added.

5 - Quantum Monte Carlo calculations

Main idea: *The interacting many-body problem can be solved stochastically.*

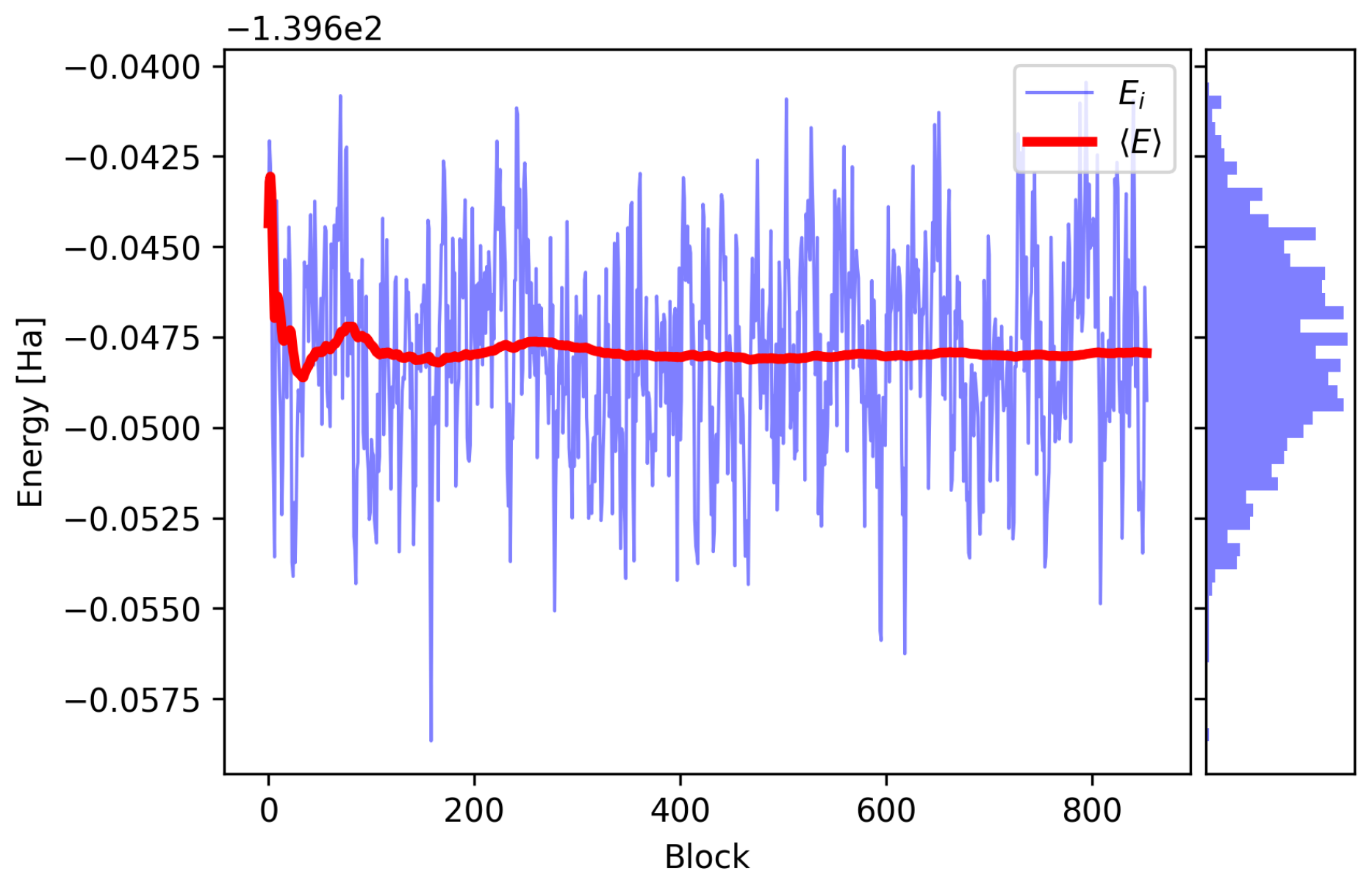


Figure: QMC ground state energy of FeO.

Diffusion Monte Carlo (DMC) solves the imaginary time Schrödinger Equation:

$$\frac{\partial\Psi}{\partial\beta} = -\hat{H}\Psi = \left(\lambda\nabla^2 - V(\mathbf{r})\right)\Psi(\mathbf{r},\beta) \tag{3}$$

by stochastically applying the projector: $G(\beta) = e^{-\beta\hat{H}}$

$$|\Phi_0\rangle \propto \lim_{\beta\to\infty} e^{-\beta\hat{H}}|\Psi\rangle \tag{4}$$

where the many-body wave function is represented in a Slater-Jastrow form:

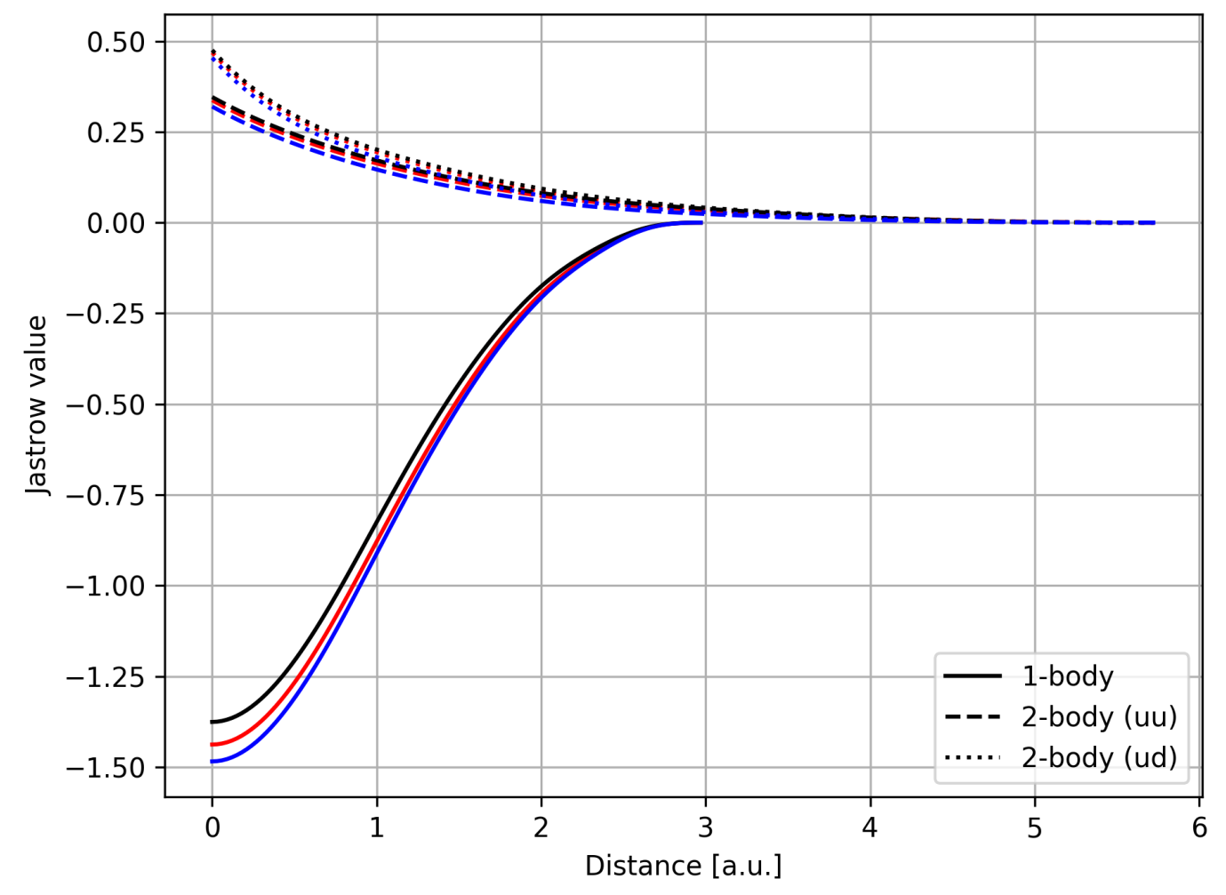
$$\Psi = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix} e^{J(\{\mathbf{r},\mathbf{R}\})}$$

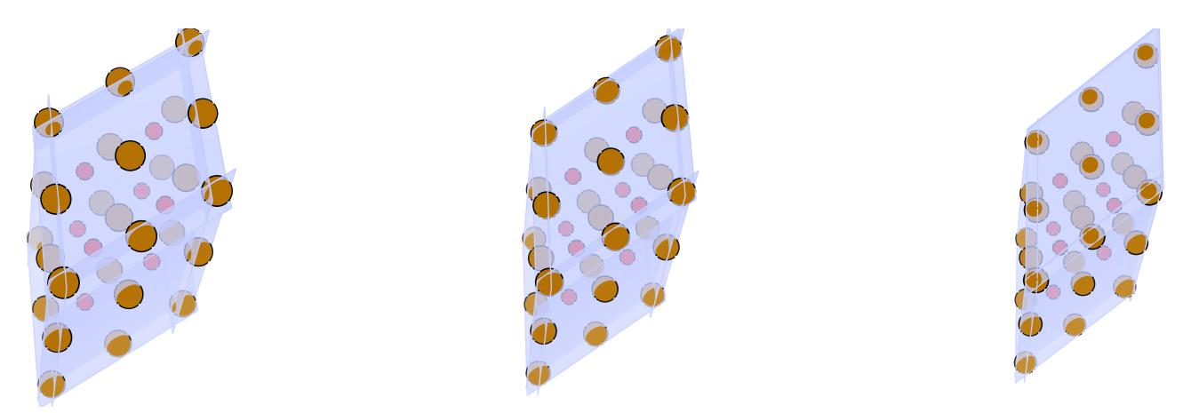
However, the DMC algorithm fails for electrons without one further restriction, called the "fixed node approximation", which requires that particles cannot cross regions of the wave function with opposite sign.

Procedure

1. Generate trial wave functions with DFT for strained AFM FeO.
2. Use VMC to optimize 1- and 2-body Jastrow factors.
3. Compute ground state DMC energies for various strains and XC functionals.
4. Evaluate the effectiveness of commonly used XCs for describing equilibrium geometry of AFM FeO.

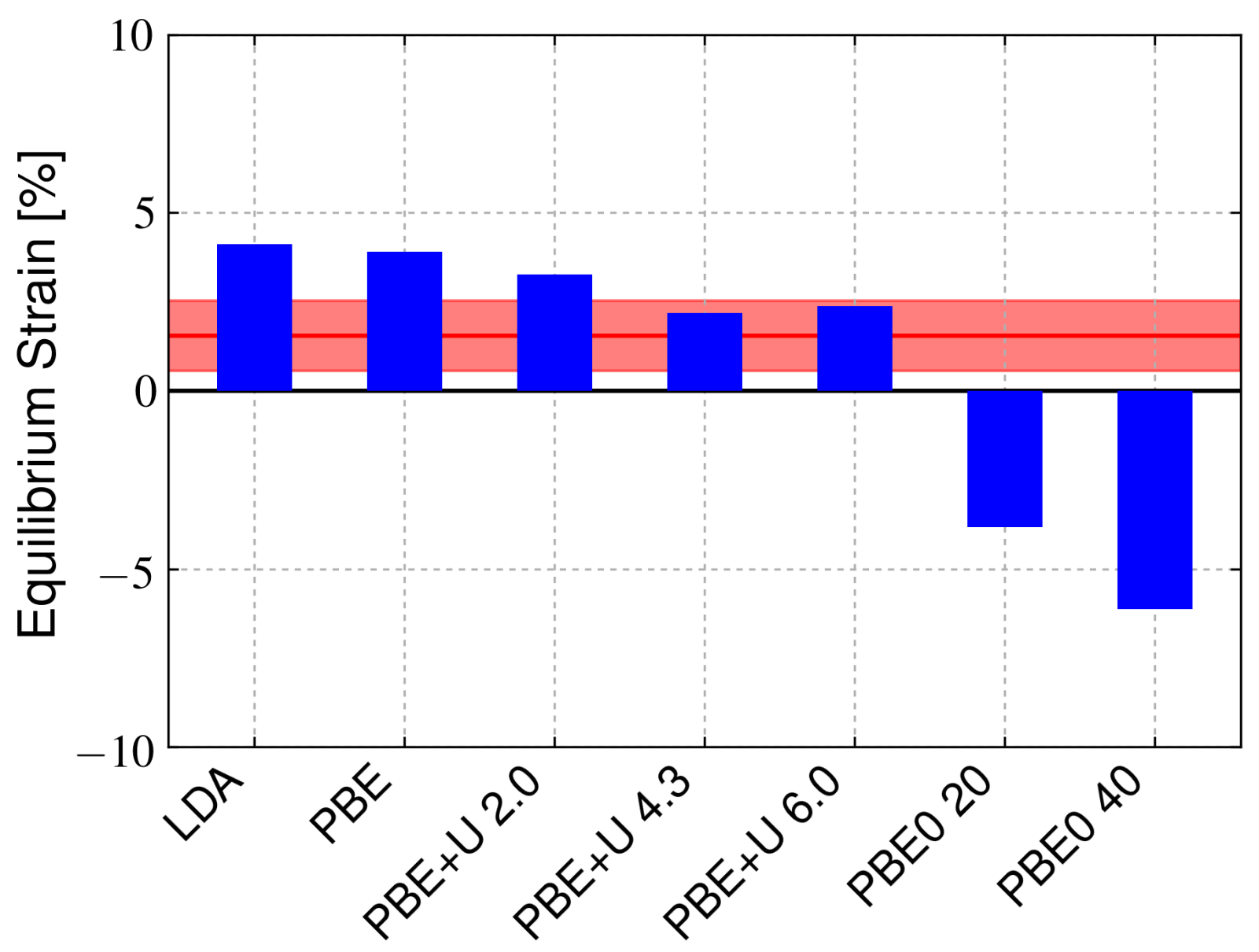
6 - Jastrow factors





Left: Jastrow factors for PBE functional as a function of strain. Optimized jastrows for -8%, 0%, and 8% strain are shown in red, black, and blue, respectively. **Above:** Corresponding strained crystal structures. From left to right: -8% strain, 0% strain, +8% strain.

7 - Results - DFT equilibrium geometry



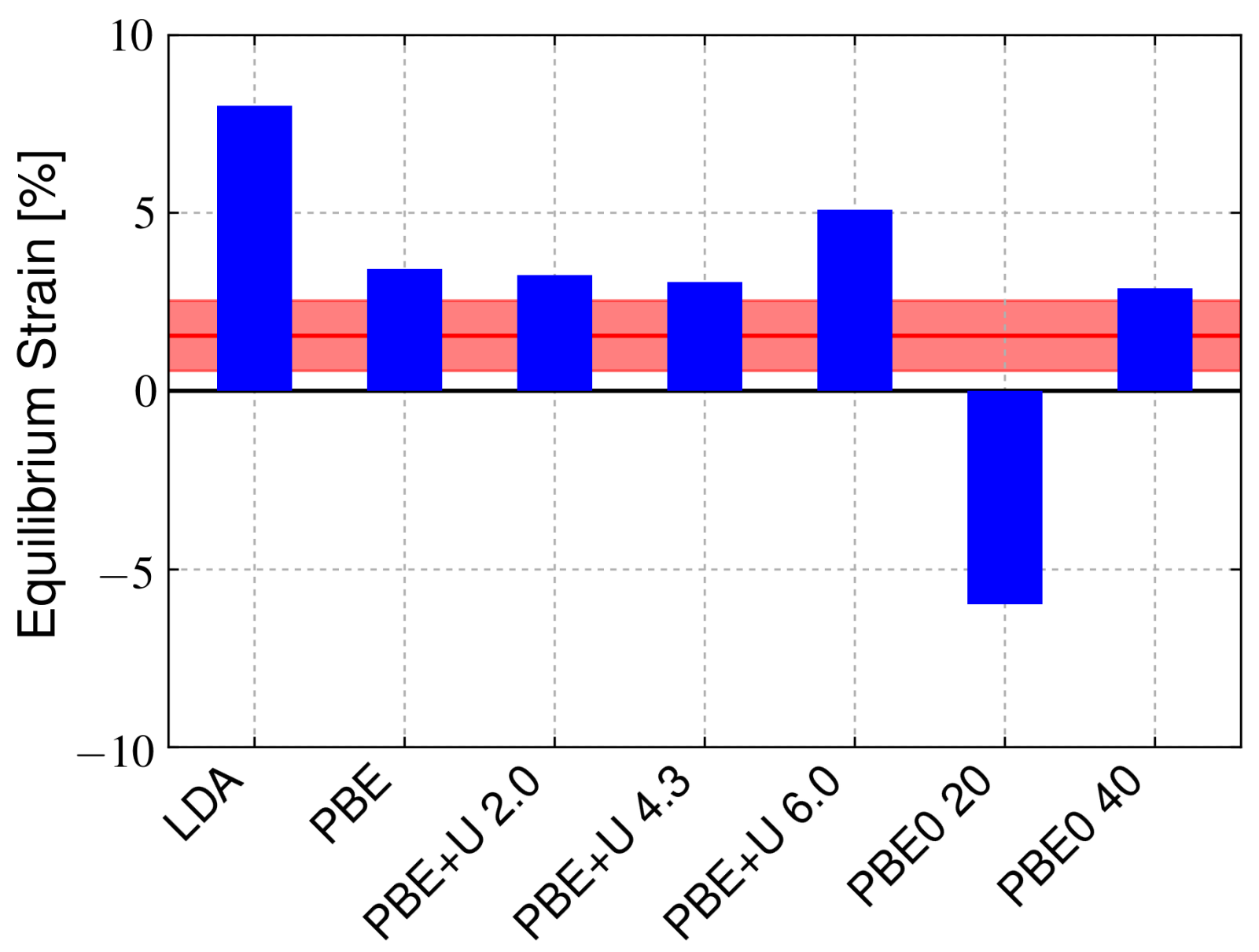
DFT calculations

- Used `Quantum ESPRESSO`
- Pseudopotentials from [2]
- 5x5x5 k-point grid on magnetic primitive cell
- Energy cut off of 4080 eV

DFT Results

- LDA and PBE overestimate strain
- Increasing Hubbard *U* reduces strain
- Exact exchange predicts wrong sign of strain

8 - Results - DMC equilibrium geometry

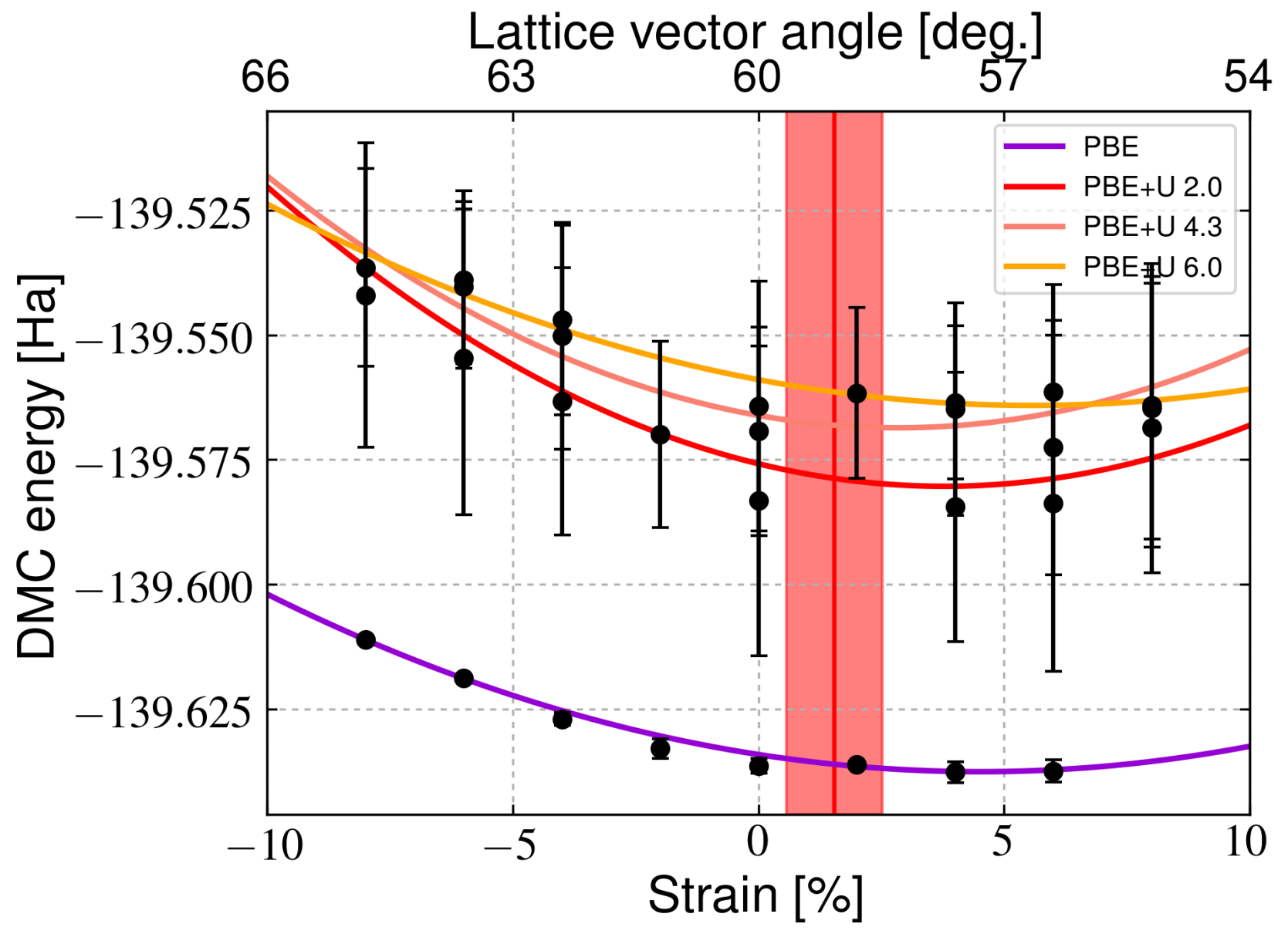


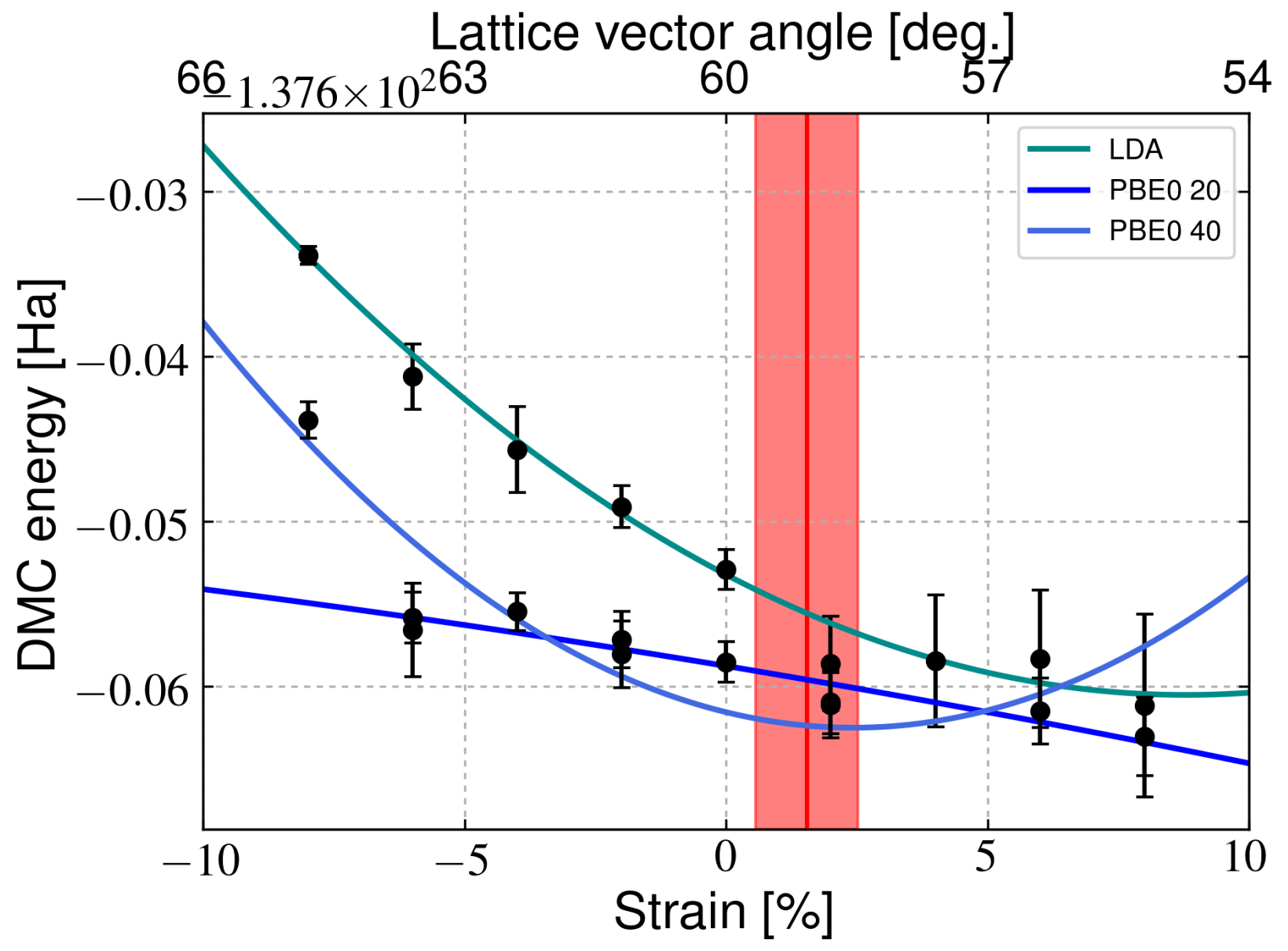
QMC calculations

- Used `QMCPACK`
- Pseudopotentials from [2]
- 64 atom supercell
- 1- and 2-body jastrow factors for each strain and XC.

QMC Results

- Equilibrium strain very sensitive to nodal surface.
- Nonlinear effect of *U* and exact echange at DMC level.





9 - Conclusions

1. Both 1- and 2-body jastrow factors are insensitive to strain and trial wave function.
2. PBE has the lowest ground-state energy within DMC.
3. Equilibrium geometry of AFM FeO is very sensitive to the nodal surface.
4. Finite size analysis *in progress* also important to constrain [3].

Acknowledgments & References

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1. N. Mott, Metal-Insulator Transitions (Taylor & Francis Ltd, 1974).
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3. M. Holzmann et al. Phys. Rev. B 94, 035126 (2016).

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