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Towards a systematically improvable many-body description of antiferromagnetic iron oxide

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National Nuclear Security Administration

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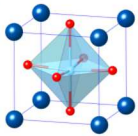
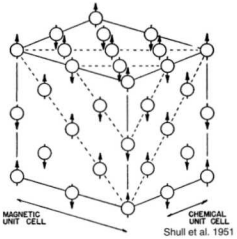
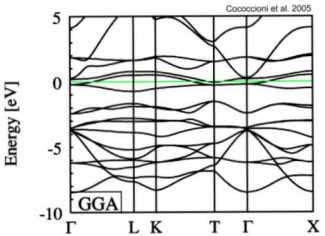
CPSFM | Center for Predictive Simulation of Functional Materials

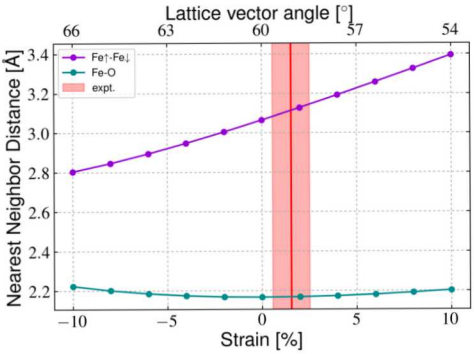


Thanks to the Center for Predictive Simulation of Functional Materials, DOE BES Computational Materials Sciences program. http://cpsfm.ornl.gov/

FeO is an interesting system for theory

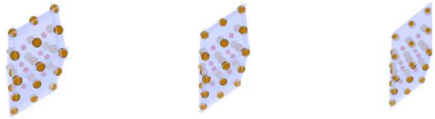






Groundstate properties:

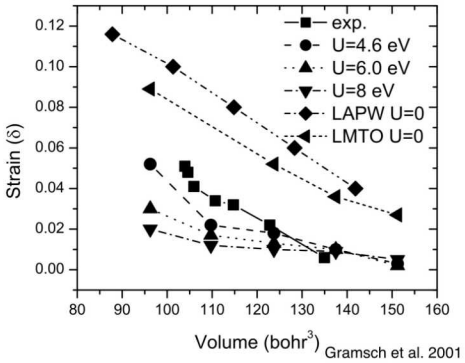
- Antiferromagnetic structure
- Rhombohedral lattice distortion
- Prototypical Mott insulator



Previous work on the ground state

Equilibrium lattice distortion within one-body methods:[1]

- Experiments suggest $\sim 2\%$ distortion
- Distortion sensitive to Fe $3d$ treatment
- Naïve approach with e.g. $+U$ can fail
- Care is required! *ab-initio*?



Gramsch et al. 2001

[1] Gramsch et al. (2003) 10.2138/am-2003-2-301

How to do better than DFT

Let's work with the non-relativistic electronic hamiltonian:

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Many approaches to solving the above:

DFT

$$\hat{H}^{DFT} = \sum_i h_i + V_{xc}$$

- Mapping onto non-interacting system
- Parameterized V_{xc}
- Can solve exactly

QMC

- Stochastically sample $\hat{H}$
- Statistical (variational) estimate of E_0
- **Input wave function**
- Suffers from "sign problem"
- Solve approximately (but controllably)

In real space QMC we construct a trial many body wave function of the form:

$$\Phi^T(\mathbf{r}) = D^{\uparrow}(\mathbf{r})D^{\downarrow}(\mathbf{r})e^{J(\mathbf{r})}$$

with

$$D \equiv \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

where
$\{\phi_i\}$ from DFT $\leftarrow$ This is the hard part
and $J = f(|\mathbf{r}_i - \mathbf{r}_j|)$ picks up correlation

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and $J = f(|\mathbf{r}_i - \mathbf{r}_j|)$ picks up correlation

VMC is conceptually straightforward:

$$E_{VMC} = \frac{\langle \Phi^T(\mathbf{r}) | \hat{H}(\mathbf{r}) | \Phi^T(\mathbf{r}) \rangle}{\langle \Phi^T(\mathbf{r}) | \Phi^T(\mathbf{r}) \rangle} \geq E_0$$

MCMC sample the distribution:

$$\Pi(\mathbf{r}) = \frac{|\Phi^T(\mathbf{r})|^2}{\int d\mathbf{r} |\Phi^T(\mathbf{r})|^2}$$

To evaluate energy:

$$E_{VMC} = \int d\mathbf{r} \Pi(\mathbf{r}) E_L(\mathbf{r}) = \frac{1}{N} \sum_n^N E_L(\mathbf{r}^{(n)})$$

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DMC is more sophisticated, $it \to \tau$:

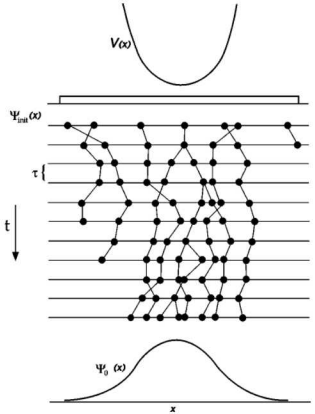
$$-\frac{\partial \Phi^T}{\partial \tau}(\mathbf{r}, \tau) =$$

$$-\frac{1}{2}\sum_i^N \nabla_i^2 \Phi^T(\mathbf{r}) \quad \text{diffusion}$$

$$+(V(\mathbf{r}) - E_T)\Phi^T(\mathbf{r}) \quad \text{branching}$$

For long projection times:

$$\lim_{\tau\to\infty} \Phi^T e^{\tau(\hat{H}-E_T)} \propto \Psi_0$$



Foulkes et al. *RMP*, 2001

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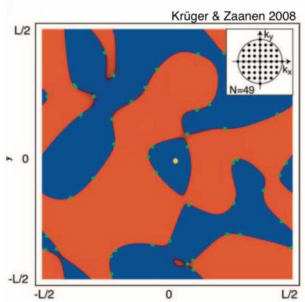
$$\lim_{\tau\to\infty} \Phi^T e^{\tau(\hat{H}-E_T)} \propto \Psi_0$$

But, DMC is subject to "sign problem" because $\Pi(\mathbf{r}) = \frac{\Phi^{T*}(\mathbf{r})\Psi_0(\mathbf{r})}{\int d\mathbf{r}\ \Phi^{T*}(\mathbf{r})^*\Psi_0(\mathbf{r})} \notin [0,1]$

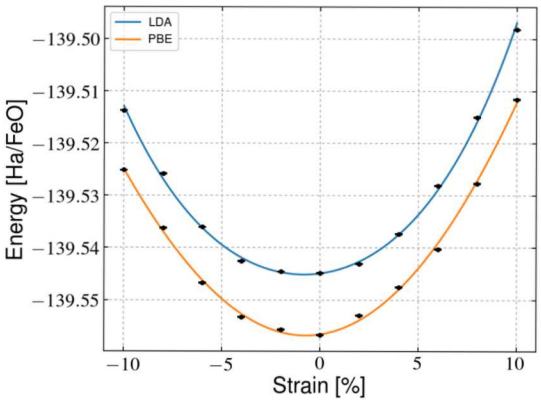


Requires the "fixed-node" approximation

Simple wave functions

Idea #1: Use PBE orbitals to construct wfn. Hope Jastrow fixes it.

- VMC predicts 0 distortion



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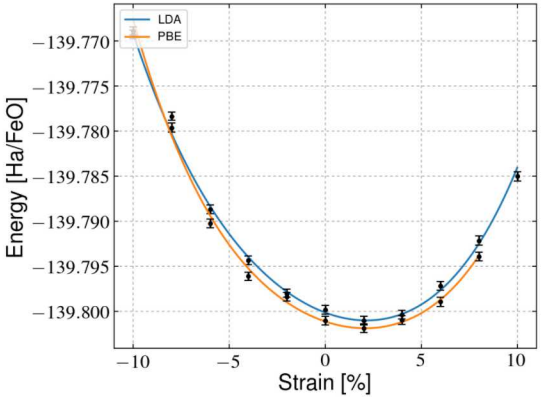

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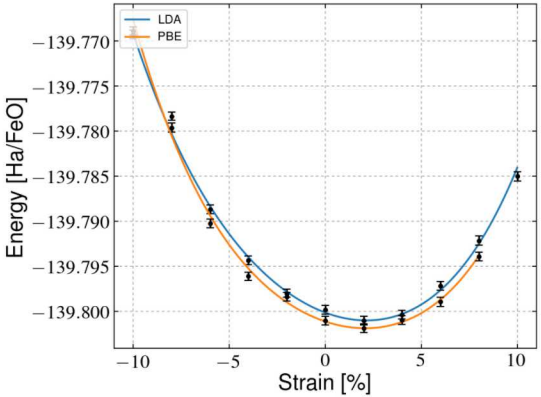
- $\sigma^2(E) \approx 4$



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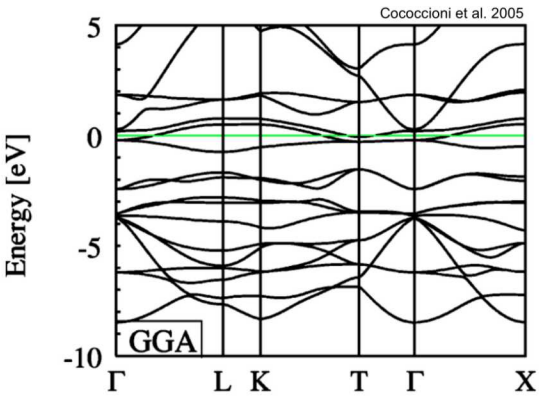
- $\sigma^2(E) \approx 4$
- But, these orbitals are crummy!

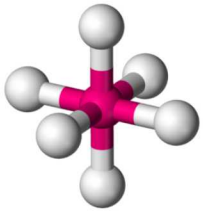


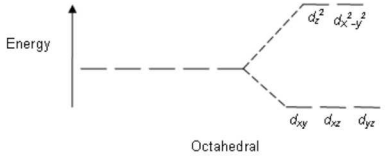
Wave function generation example: DFT+U

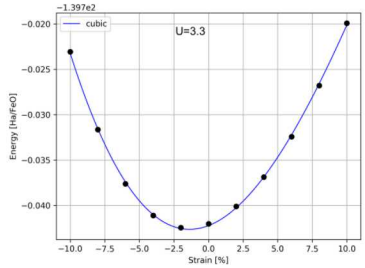
Idea #2: Use PBE+U orbitals to construct wfn.

Summary of $+U$ calculations:

- d-matrix predicted equilibrium strain
- Not obvious (to me) which is best
- Metal/insulator both possible







spin config:

$$\uparrow \quad 1\,1\,1\,1\,1$$
$$\downarrow \quad 0\,0\,0\,0\,1$$

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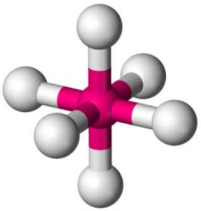

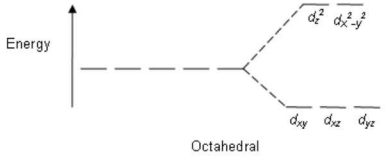

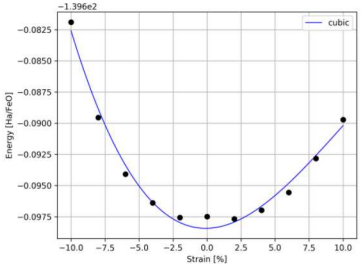

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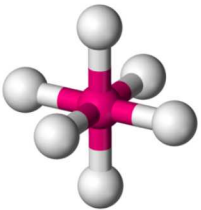

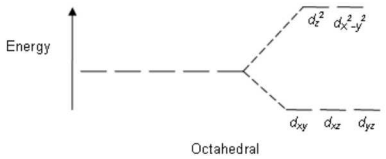

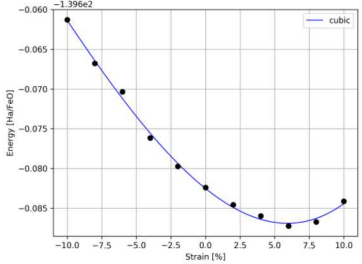

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Effect of U_{eff} on trial wave function

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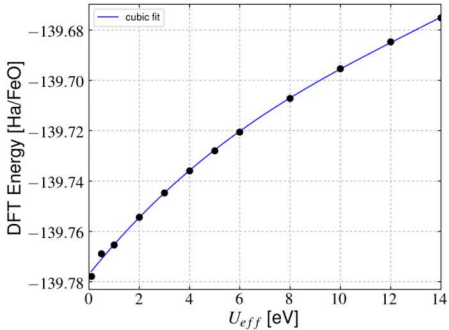
DFT

QMC



As expected, DFT energy monotonically increases with U_{eff}

Effect of U_{eff} on trial wave function

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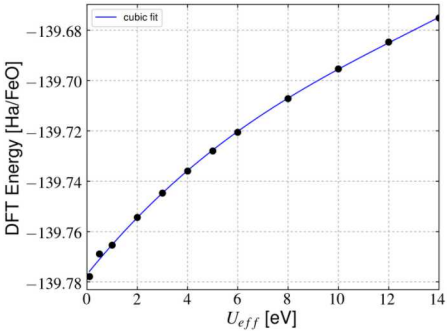
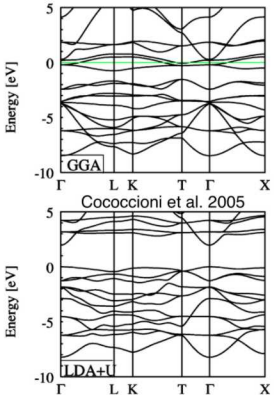
DFT



QMC



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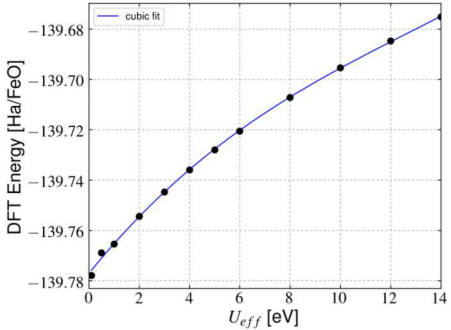
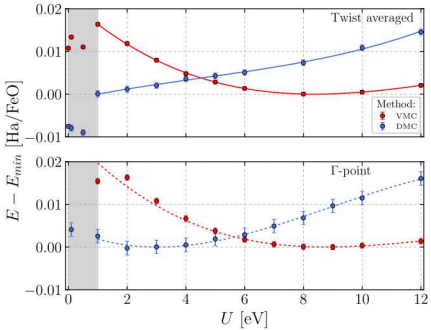


QMC

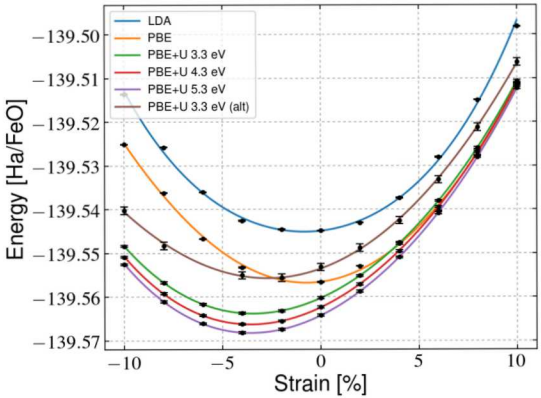


DMC energy also monotonically increases with U_{eff} after twist-averaging

Simple wave functions

Idea #2: Use PBE+U orbitals to construct wfn.

- VMC predicts - distortion



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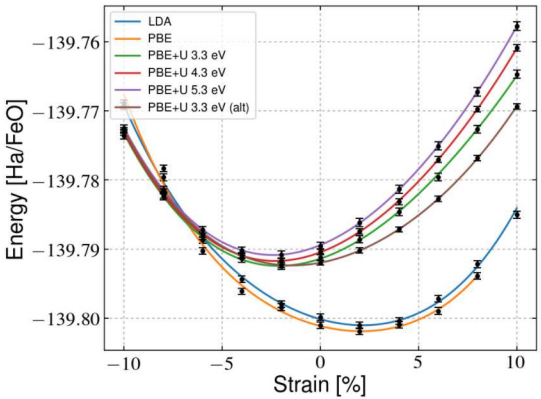

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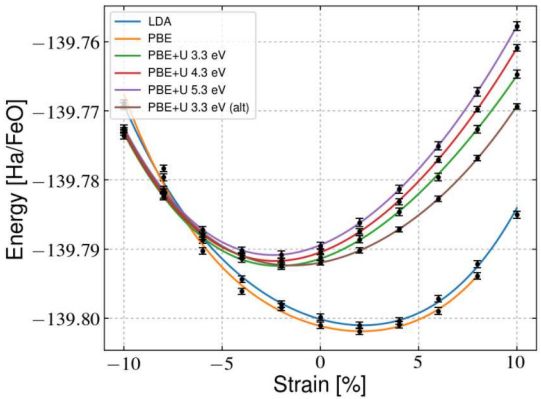

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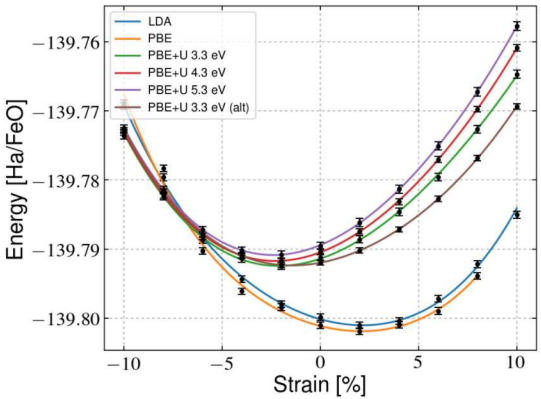
- $\sigma^2(E) \approx 4$
- orbitals still crummy!



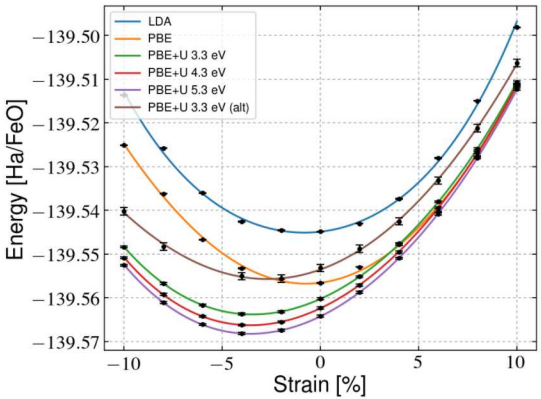
Idea #3: Use crappy orbitals to construct wfn., patch up with fancy techniques

In principle:

$$\Phi^T(\mathbf{r}) = \sum D^{\uparrow}(\mathbf{r}) D^{\downarrow}(\mathbf{r}) e^{J(\mathbf{r})}$$

Or, can use "backflow" transformation to introduce correlation into orbitals:

$$\Phi^T(\mathbf{r}) \to \Phi^T(\xi); \qquad \xi = \sum_{i,j} c_{ij} |\mathbf{r}_i - \mathbf{r}_j|$$



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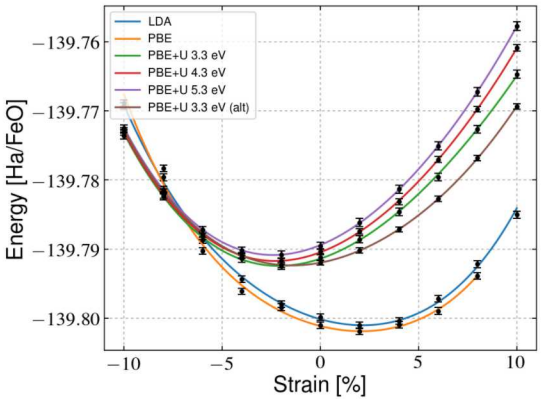
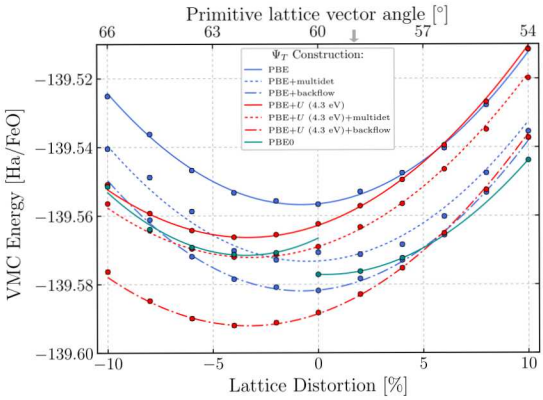


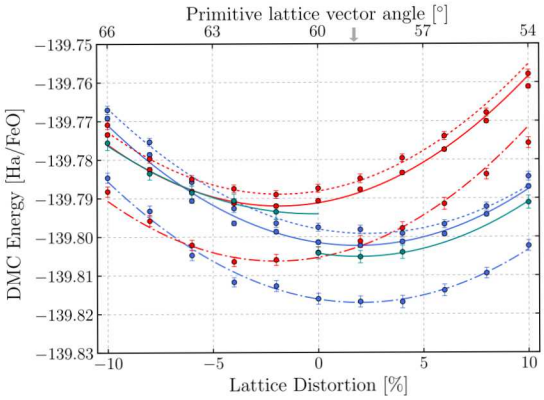
Putting it all together:

- LDA/PBE (-) strain



Putting it all together:

- LDA/PBE (-) strain
- PBE+U (-) strain lower E
- Increasing U lowers energy further



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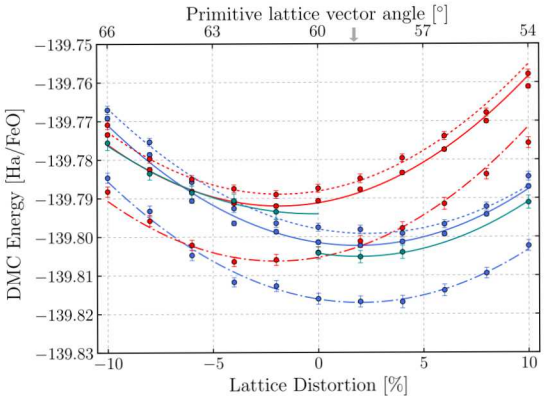
- PBE+bf much lower energy
- PBE+md can beat bf



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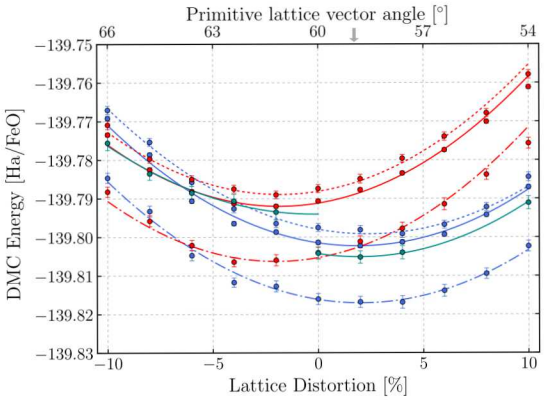
- LDA/PBE (-) strain
- PBE+U (-) strain lower E
- Increasing U lowers energy further
- PBE+bf much lower energy
- PBE+md can beat bf
- No Φ^T predicts (+) strain



Summary and outlook

- Need more advanced wave functions to accurately describe complex materials
- Backflow and multi-determinant expansions show promise, but don't scale
- Future work: Magnetic transitions at high P

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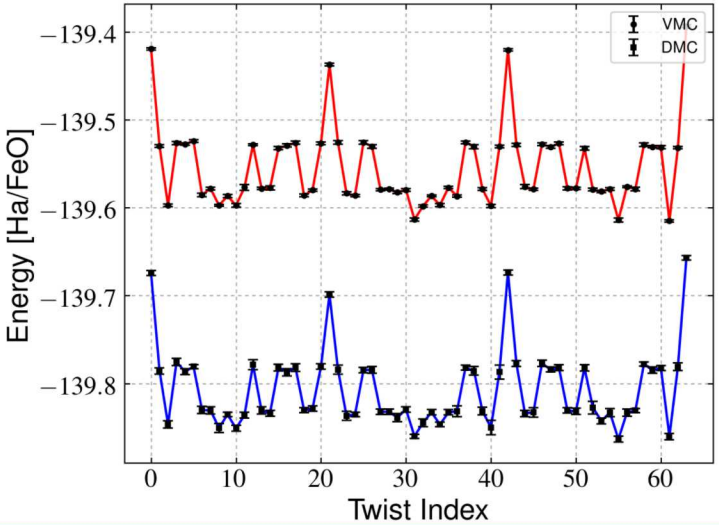
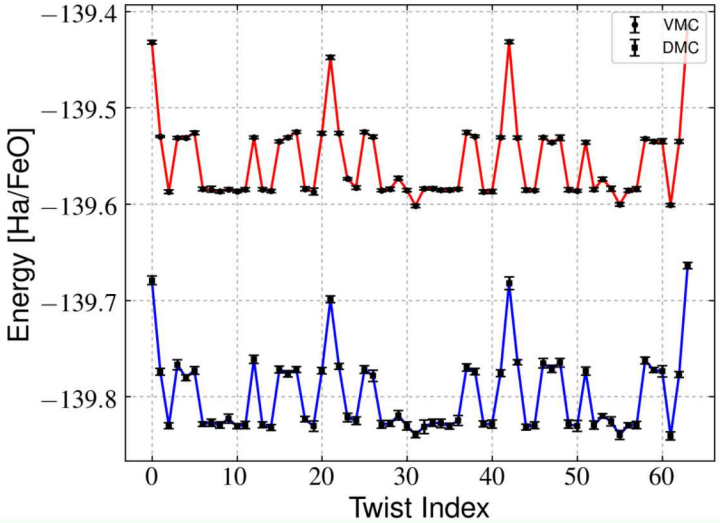
Thank you!

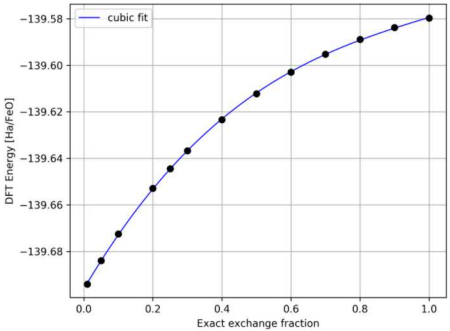
why is $+U$ higher?

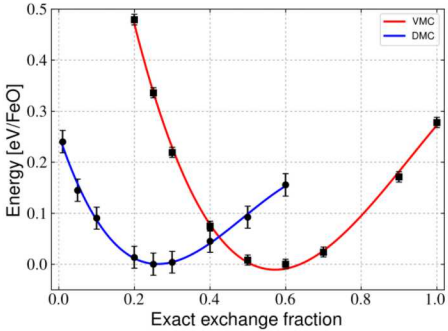


why is $+U$ higher?



Effect of hybrid exchange on trial wave function





Results in progress:

DMC suggests exx approx. 4 mHa/FeO lower energy than $+U$