SAND2018-9498PE

CMS Thrust 1: SNL Site Update

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U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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Objectives

- To improve the accuracy of state of the art QMC calculations.
  - Deployment of advanced wave functions **for solids**.
  - Matrix element engine for .
- To increase the number and fidelity of observables available in current QMC calculations.
  - Forces
  - Deployment/development of RMC and forward walking.

Starting point independence and systematic improvability

Completed Work

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Multi-Slater Determinant Jastrow

$$\Psi_{MSD} = e^{-J} \sum_{i=0}^{N_{CSF}} \alpha_k \Phi_k \quad (1)$$

$$\Phi_k = \sum_i c_k^i \det(M_i^{\uparrow}) \det(M_i^{\downarrow}) \quad (2)$$

- MSD wave functions are in principle "systematically improvable".
- Goal: "spend more computer time, get a better answer".

Systematic Improvability: An Example

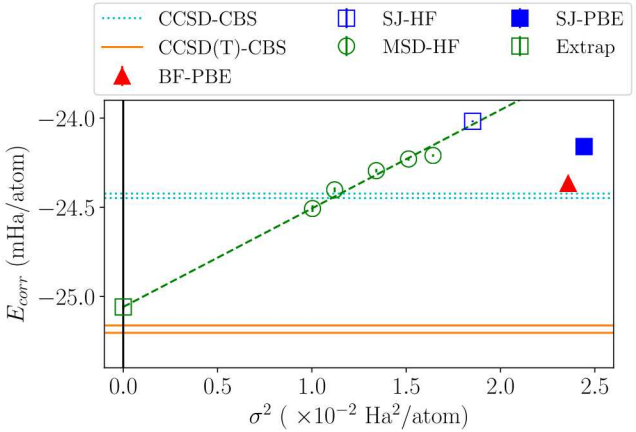
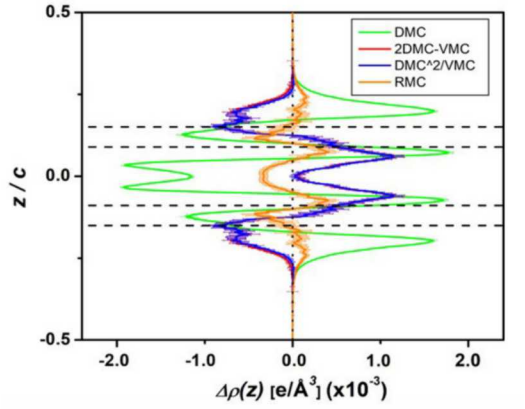


Figure: Systematic improvement for a $\rho/\rho_0 = 3.75$ snapshot of 4 D_2 molecules

Pure Sampling with Reptation MC: Blue Phosphorus



- Implemented collection of density observable over pure distribution.
- Noticeable differences between "mixed" and "extrapolated" estimates. Good agreement with DFT.

In Progress

Towards Advanced Materials: FeO

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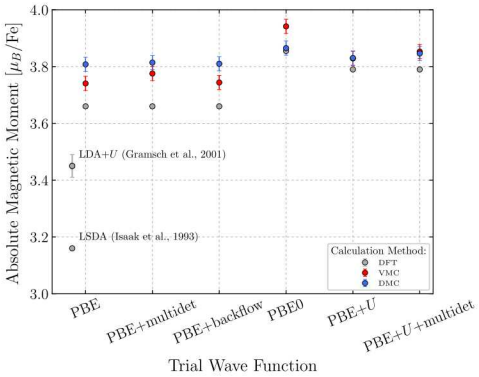
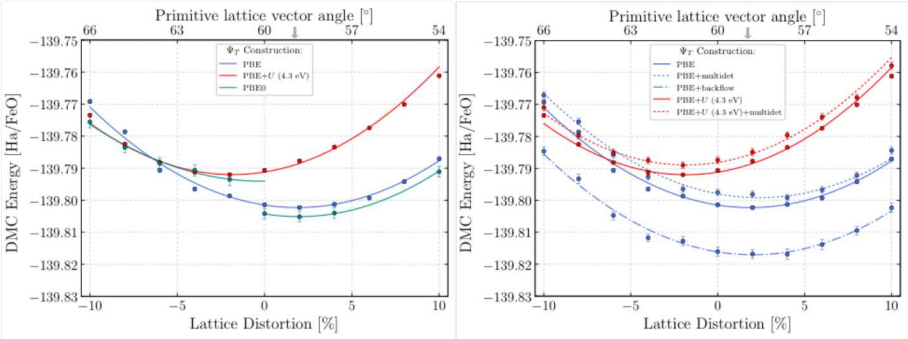
- FeO is an important material in geophysics.
- Transition metal oxide. Close analogue with functional materials.
- Attempt to ascertain whether systematic improvability is possible using advanced wave functions.

FeO: Magnetic Moment



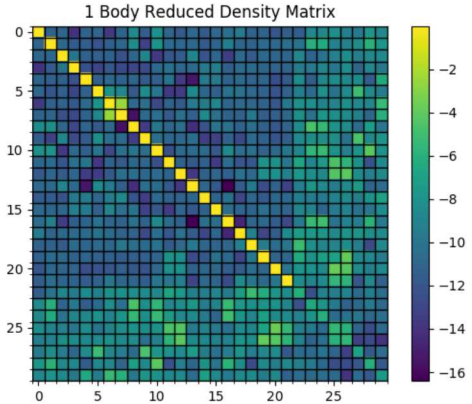
- Robust prediction of magnetic moment using a slew of trial wave functions.
- Not sensitive to the starting point or flavor of trial wave function.

FeO: Magneto-elastic Coupling



- Strain vs. energy curves for several types of trial wave functions.
- Not able to achieve starting point independent answers using existing methods.

Advanced Wave Functions: FeO



- Currently working on diagonalizing 1-RDM to obtain natural orbitals from DMC.

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Need

- Compute Hamiltonian matrix elements for the same Hamiltonian and orbitals as used in DMC.
- Use with selected CI methods for generating multi-determinant expansions.
- Direct comparison between DMC and AFQMC.

Progress

- $\langle \mathbf{k}\nu | \nabla^2 | \mathbf{k}'\nu' \rangle$ – Implemented
- $\langle \mathbf{k}\nu | \hat{v}^{\ell} | \mathbf{k}'\nu' \rangle$ – Implemented
- $\langle \mathbf{k}\nu | \hat{v}^{nl} | \mathbf{k}'\nu' \rangle$ – Implemented, but debugging.
- $\langle \mathbf{k}\nu, \mathbf{k}'\nu' | \hat{v}^{ee} | \mathbf{k}''\nu'', \mathbf{k}'''\nu''' \rangle$ – Partial implementation

$$\mathbf{F}_{ZVZB} = \left(-\nabla_I \hat{H}\right) + \frac{(\hat{H} - E_L)(-\nabla_I \Psi_T)}{\Psi_T} + 2(E_L - \langle E_L \rangle)\frac{(-\nabla_I \Psi_T)}{\Psi_T} \quad (3)$$

Issues

- Handling periodic boundary conditions. Long range breakups.
- Handling the non-local piece.

$$\frac{\partial}{\partial R_{J,\gamma}}\frac{\hat{V}_{NL}\Psi_T}{\Psi_T} = -\sum_i\sum_\ell(2\ell+1)\underbrace{v_l'(r_{iJ})\frac{r_{iJ,\gamma}}{r_{iJ}}}\sum_\alpha\left[w_\alpha P_\ell\left(\cos\theta_{iJ}^\alpha\right)\frac{\Psi_T(\ldots\mathbf{q}_{iJ}^\alpha\ldots)}{\Psi_T(\ldots\mathbf{r}_i\ldots)}\right] \quad (4)$$

$$- \sum_i\sum_\ell(2\ell+1)v_l(r_{iJ})\sum_\alpha\left[w_\alpha\underbrace{P_\ell'(\cos\theta_{iJ}^\alpha)r_{iJ}^{-1}\left(u_\gamma^\alpha-\cos\theta_{iJ}^\alpha\frac{r_{iJ,\gamma}}{r_{iJ}}\right)}\frac{\Psi_T(\ldots\mathbf{q}_{iJ}^\alpha\ldots)}{\Psi_T(\ldots\mathbf{r}_i\ldots)}\right] \quad (5)$$

$$+ \sum_i\sum_\ell(2\ell+1)v_l(r_{iJ})\sum_\alpha\left[w_\alpha P_\ell\left(\cos\theta_{iJ}^\alpha\right)\underbrace{\frac{\partial_{i,\mu}\Psi_T(\ldots\mathbf{q}_{iJ}^\alpha\ldots)}{\Psi_T(\ldots\mathbf{r}_i\ldots)}\left(\delta_{\gamma\mu}-\frac{r_{iJ,\gamma}u_\mu^\alpha}{r_{iJ}}\right)}\right] \quad (6)$$

$$+ \frac{\hat{V}_{NL}\frac{\partial\Psi_T}{\partial R_{J,\gamma}}}{\Psi_T}-\left(\frac{\hat{V}_{NL}\Psi_T}{\Psi_T}\right)\frac{\frac{\partial\Psi_T}{\partial R_{J,\gamma}}}{\Psi_T} \quad (7)$$

	QMC	HF	Δ	Z
$F^{l}_{0,x}$	0.02472(3)	0.02464	0.00009	2.882
$F^{l}_{0,y}$	0.01943(3)	0.01936	0.00007	2.384
$F^{l}_{0,z}$	0.00773(3)	0.00779	-0.00006	-2.069
$F^{nl}_{0,x}$	-0.01382(5)	-0.01384	0.00003	0.471
$F^{nl}_{0,y}$	-0.00927(5)	-0.00935	0.00008	1.552
$F^{nl}_{0,z}$	-0.00028(5)	-0.00030	-0.00002	0.373

Table: Perturbed BCC unit cell in PBC. 8 Na atoms, BFD 1 electron pseudopotential with s, p, and d channels.

Future Work

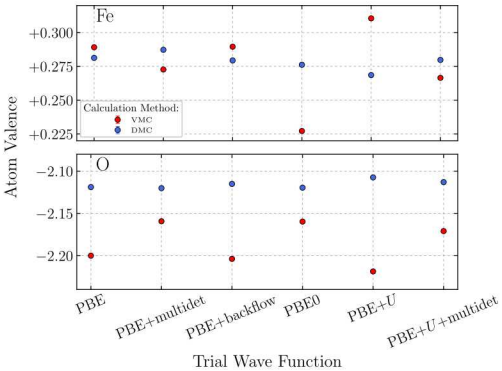
$$\mathbf{F}_{ZVZB} = \left(-\nabla_I \hat{H}\right) + \frac{(\hat{H} - E_L)(-\nabla_I \Psi_T)}{\Psi_T} + 2(E_L - \langle E_L \rangle)\frac{(-\nabla_I \Psi_T)}{\Psi_T} \qquad (8)$$

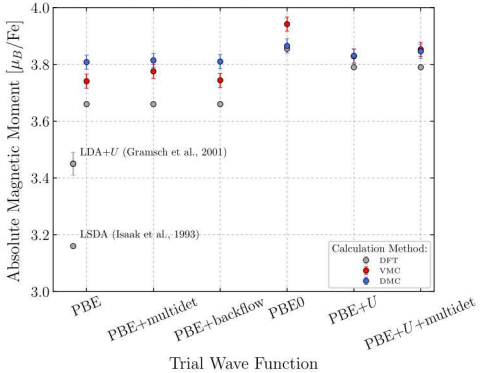
- Implement and test zero-variance and zero-bias terms.
- Build ZVZB friendly VMC and DMC drivers.
- Use forces! Geometry optimization, phonons, etc.
- Stresses require $\frac{\partial}{\partial R_{J,\mu}} \frac{\partial}{\partial R_{J,\gamma}} \frac{\hat{V}_{NL}\Psi_T}{\Psi_T}$

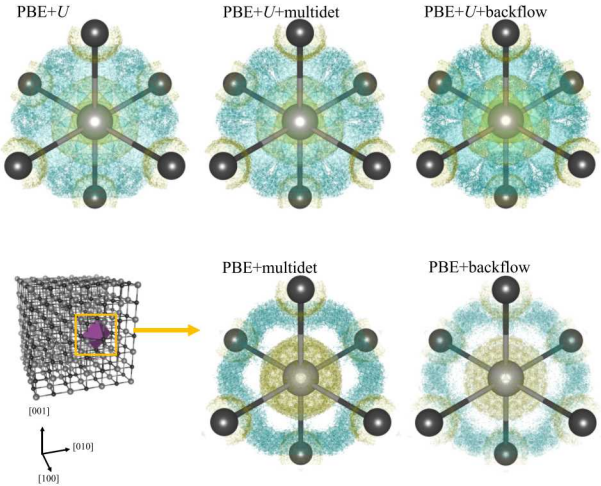
- Look into using selected CI methods for multi-determinant expansions.
- Investigate advanced wave functions like iterative backflow.

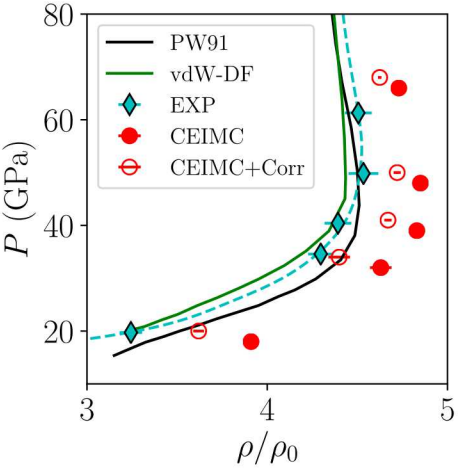
Future Work

Extra Figs 1


Fe
O
Atom Valence
+0.300
+0.275
+0.250
+0.225
−2.10
−2.15
−2.20
Calculation Method:
VMC
DMC
PBE
PBE+multidet
PBE+backflow
PBE0
PBE+U
PBE+U+multidet
Trial Wave Function


Absolute Magnetic Moment [μ_B/Fe]
4.0
3.8
3.6
3.4
3.2
3.0
LDA+U (Gramsch et al., 2001)
LSDA (Isaak et al., 1993)
Calculation Method:
DFT
VMC
DMC
PBE
PBE+multidet
PBE+backflow
PBE0
PBE+U
PBE+U+multidet
Trial Wave Function


PBE+U
PBE+U+multidet
PBE+U+backflow
PBE+multidet
PBE+backflow
[001]
[010]
[100]


80
60
40
20
3
4
5
P (GPa)
ρ/ρ_0
PW91
vdW-DF
EXP
CEIMC
CEIMC+Corr