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VALIDATING SPIN-ORBIT QMC FOR EQUATION OF STATE CALCULATIONS OF HEAVY ELEMENTS

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OUTLINE

- Overview of the system
- DFT Cold curves.
  - Magnetic state, equation of state, etc.
- QMC Cold Curves
- Compare/Contrast
- Future Work

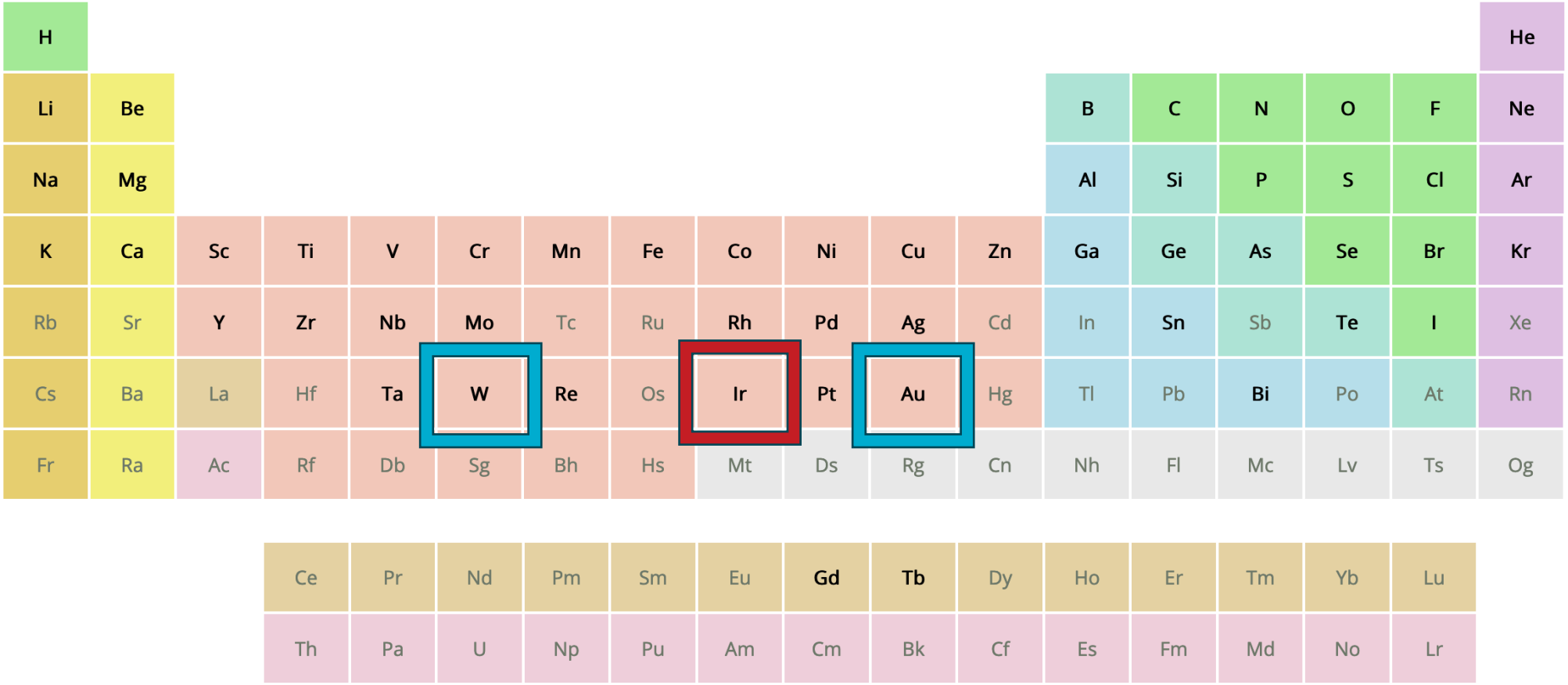
PURPOSE

- Diffusion Monte Carlo has been used extensively for constructing accurate equations of state, specifically cold curves.
- Spin-Orbit Diffusion Monte Carlo is a generalization of the method to systems with non-collinear wave functions. Most important use case is for systems with spin-orbit coupling, but non-collinear magnetism is also important.
- Implemented in QMCPACK. Compatible with molecules and solids.
- Goal is to understand the systematic biases, practical strengths and limitations of this method.

COLD CURVES FOR SPIN-ORBIT SYSTEMS

Pseudopotential Library

A community website for pseudopotentials/effective core potentials developed for high accuracy correlated many-body methods such as quantum Monte Carlo and quantum chemistry.

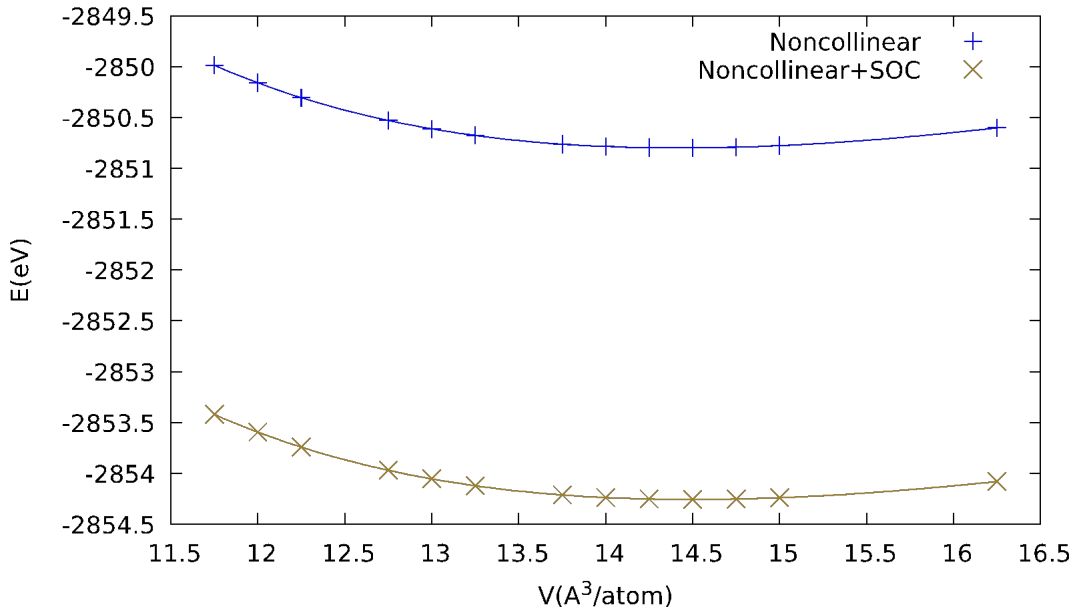


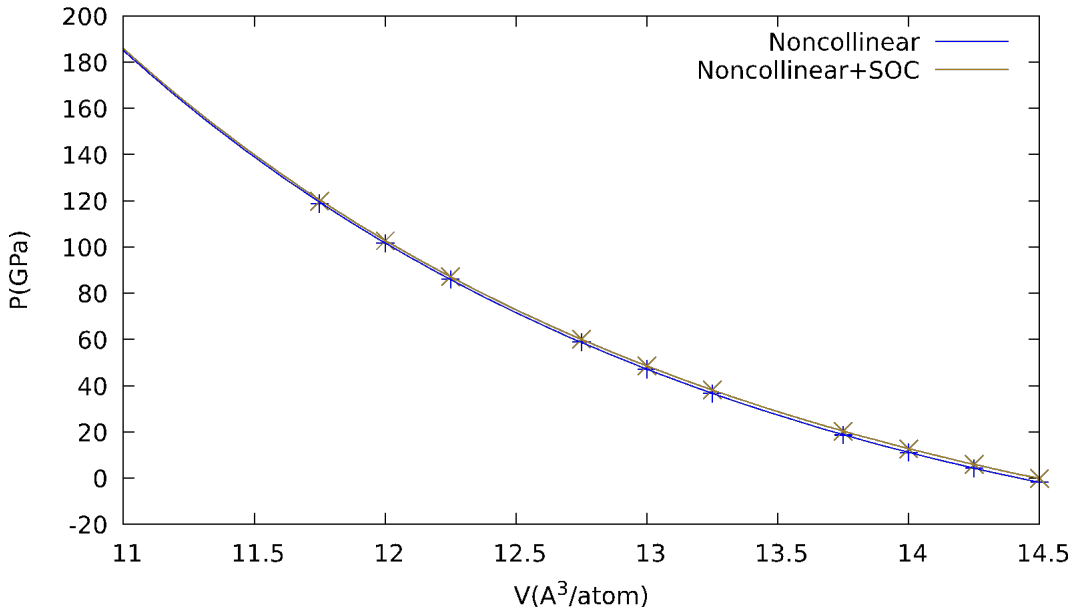
From https://pseudopotentiallibrary.org

DFT SIMULATIONS

- PBE functional.
- Ir ccECP pseudopotentials for scalar relativistic and spin-orbit.
- No evidence of ghost-states.
- Does NOT support a magnetic ground state (even in supercells).
- 28x28x28 gamma-shifted Monkhorst-Pack grid.
- 800Ry planewave cutoff.
- Cross-checked against ELK and VASP. Some differences in lattice constant, but very consistent results.

DFT RESULTS





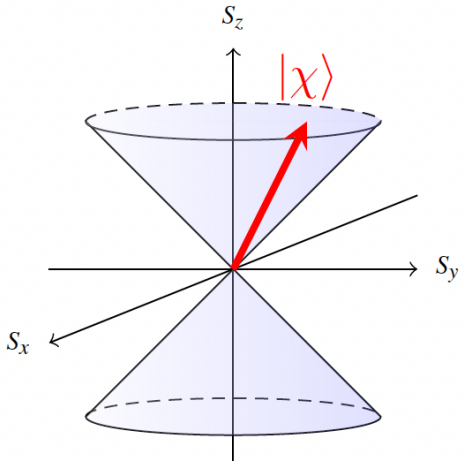
Quantity	No-SOC	SOC	Δ
E_0(eV)	-2850.799	-2854.255	-3.456
V_0(Å^3)	14.420	14.492	0.071
B_0(GPa)	349.590	338.254	-11.336

SPIN SAMPLING

Rather than sample discrete spin-flips, we shift to an overcomplete continuous representation of spin degrees of freedom.

$$\langle \mathbf{x}|\psi\rangle = \phi^{\uparrow}(\mathbf{r})\chi^{\uparrow}(s) + \phi^{\downarrow}(\mathbf{r})\chi^{\downarrow}(s)$$

$$|\mathbf{x}\rangle = |\mathbf{r}\rangle|s\rangle$$



New continuous representation

$$\begin{aligned} \langle s|\chi^{\uparrow}\rangle &= \chi^{\uparrow}(s) = e^{is} \\ \langle s|\chi^{\downarrow}\rangle &= \chi^{\downarrow}(s) = e^{-is} \end{aligned} \qquad s \in [0, 2\pi)$$

$$\langle \chi^{\beta}|\chi^{\alpha}\rangle = \int_0^{2\pi} \frac{ds}{2\pi} \langle \chi^{\beta}|s\rangle\langle s|\chi^{\alpha}\rangle = \delta_{\beta,\alpha}$$

With a continuous representation, the spin variable can be sampled in the same way the spatial variables are. Monte Carlo sampling is efficient, simply changes $\mathbf{R} \in \mathbb{R}^{3N} \Rightarrow \mathbf{X} \in \mathbb{R}^{4N}$

DIFFUSION MONTE CARLO WITH DYNAMIC SPINS

$$|\Psi_0\rangle \propto \lim_{\tau\to\infty} \exp\left[-\tau\mathcal{H}\right]|\Psi_T\rangle \qquad E_0 = \lim_{\tau\to\infty} \frac{\langle\Psi(\tau)|\mathcal{H}|\Psi_T\rangle}{\langle\Psi(\tau)|\Psi_T\rangle}$$

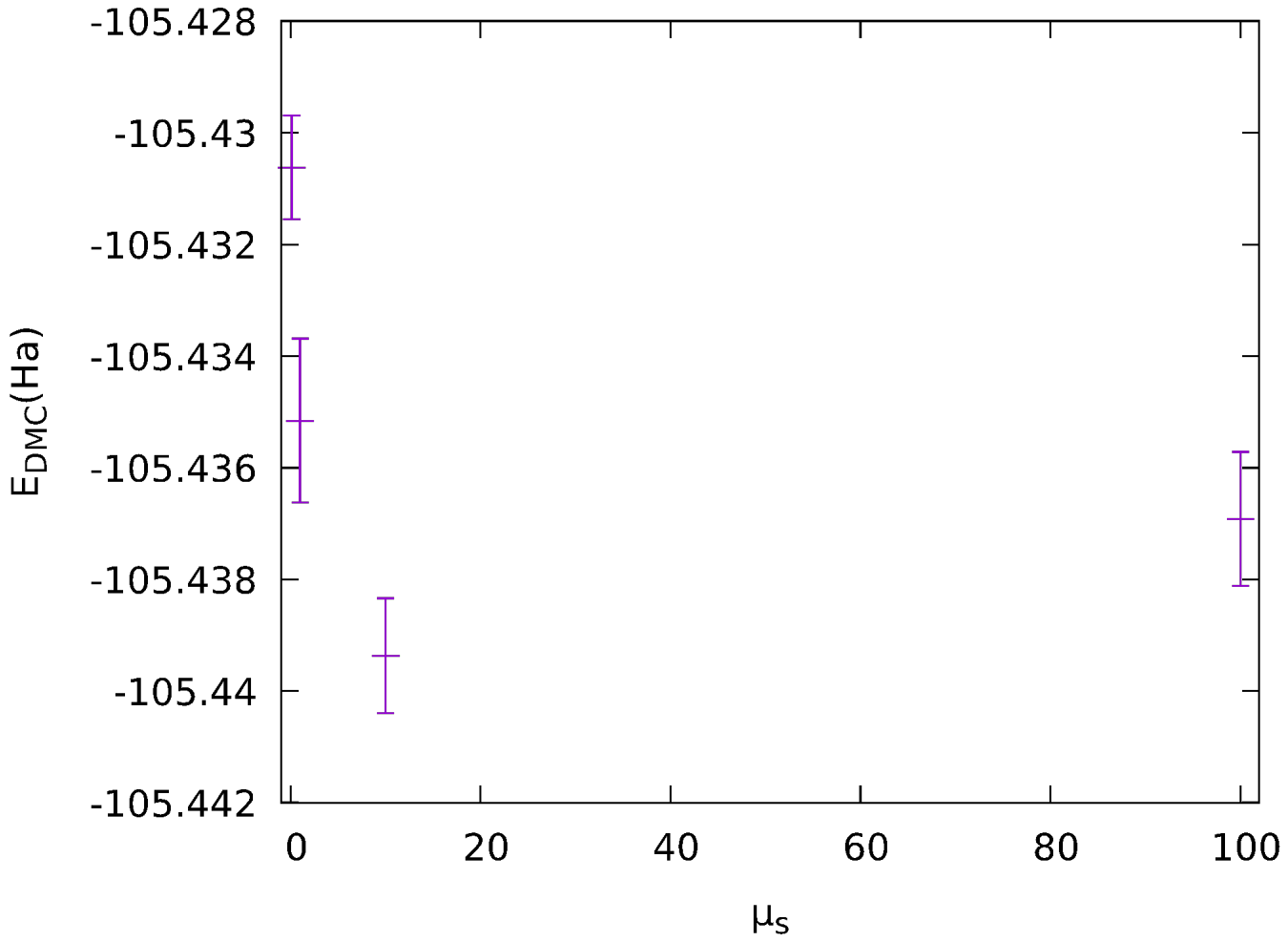
$$\langle \mathbf{X}' = (\mathbf{R}', \mathbf{S}')|\Psi^{(n+1)}\rangle = \int d\mathbf{X} G(\mathbf{X}\to\mathbf{X}';\tau)\langle\mathbf{X}|\Psi^{(n)}\rangle$$

$$G(\mathbf{X}\to\mathbf{X}';\tau) \propto G(\mathbf{R}\to\mathbf{R}';\tau)\exp\left(-|\mathbf{S}'-\mathbf{S}-\tau_s\mathbf{v}_s(\mathbf{S})|^2/2\tau_s\right)$$

$$H_{\mathrm{DMC}} \to H_{\mathrm{DMC}} + \sum_i T_i^s \qquad T_i^s = -\frac{1}{2\mu_s}\left[\frac{\partial^2}{\partial s_i^2} + 1\right]$$

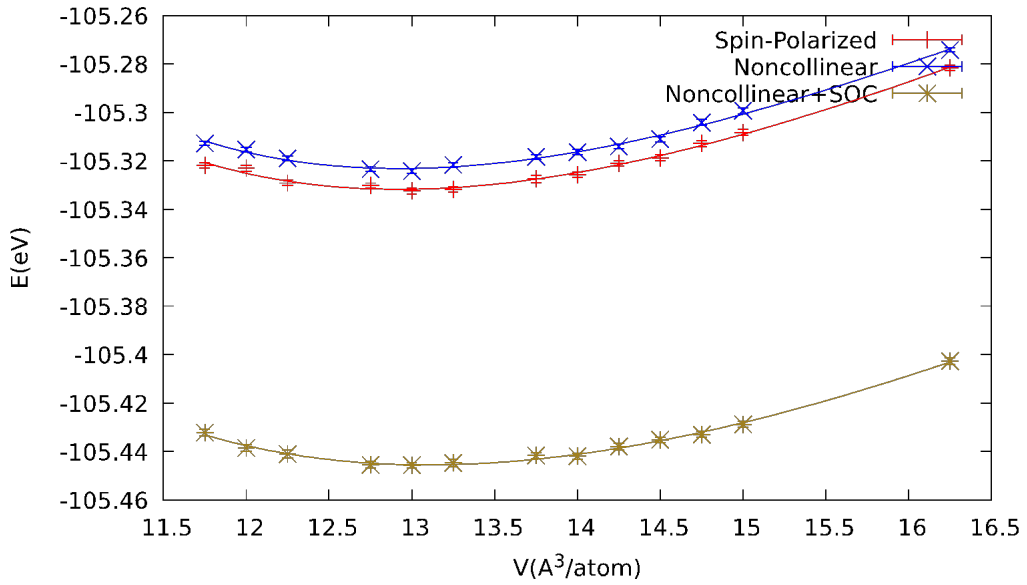
$$\sum_i T_i^s \prod_j \psi_j(\mathbf{r}_i, s_i) = 0$$

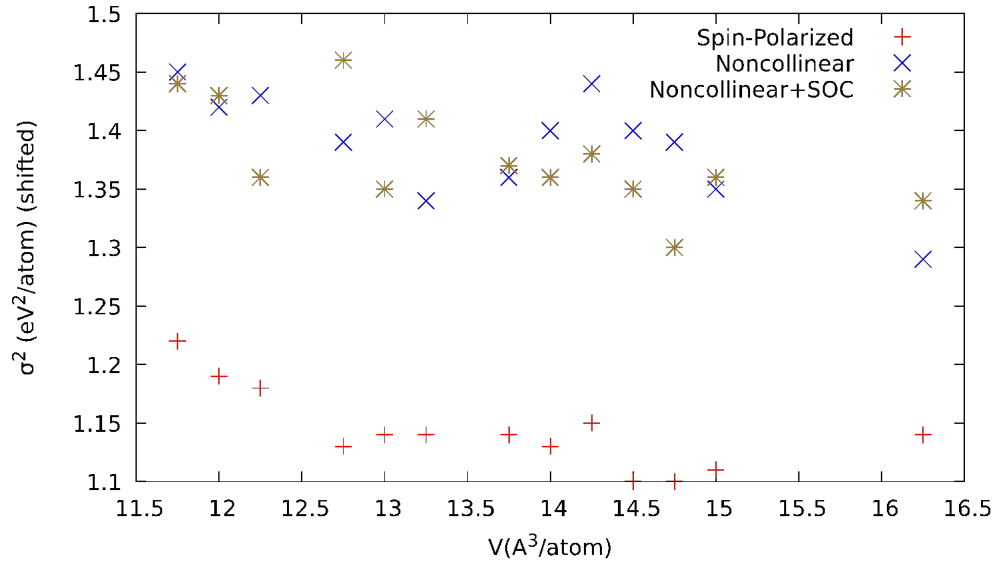
SPIN MASS CONVERGENCE

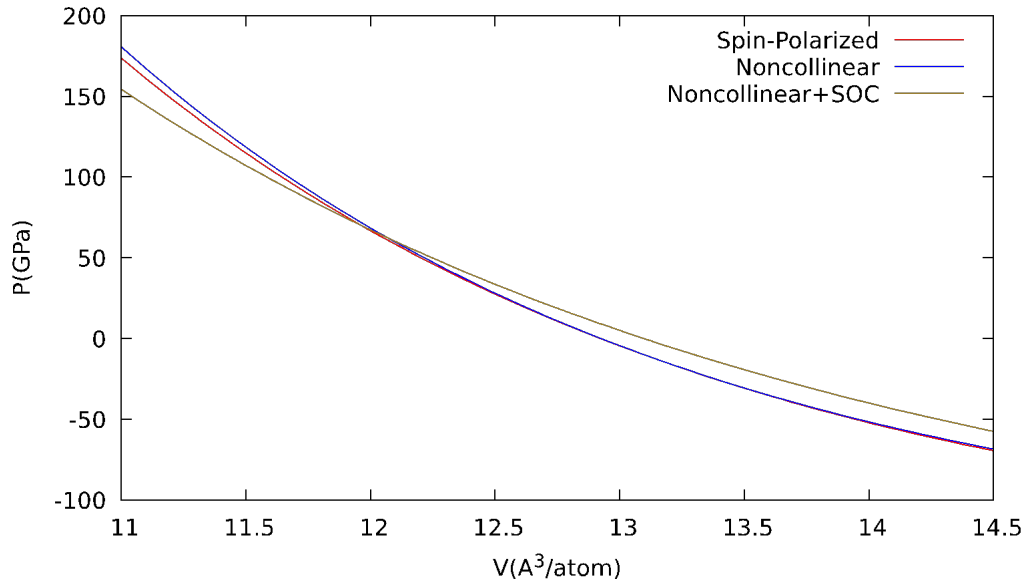


- Spin mass of 10 represents convergence.
- All calculations will use this value.

COMPARISON OF QMC COLD CURVES







(Top Left) DMC Energy vs. volume for a normal Spin-Polarized (no SOC) calculation, versus a noncollinear calculation with and without spin-orbit coupling.

(Top Right) Pressure vs. volume. No noticeable differences between Spin-Polarized and non-collinear DMC, except at higher pressures. Big difference from Noncollinear+SOC.

(Left) Variance vs. volume for all three types of wave functions. Non-collinear calculations have noticeably higher variance.

EFFECT OF SPIN-ORBIT COUPLING IN QMC

Quantity	Value (+SOC)	Value+SOC - Value-NOSOC
E_0(eV)	-2869.319	-3.329
V_0(Å^3)	13.096	0.171
B_0(GPa)	669	-110

DFT predicts ~3.45eV

- All these quantities correspond to the ambient values, obtained from Vinet EOS fits.
- Spin-Orbit energy difference is comparable to DFT (3.45eV), but detectably different.
- Very little change in ambient volume: 1.3%
- Bulk modulus shows a huge difference: 16%
- These are **very different** from DFT, but these are non-twist-averaged, single atom cell results. Important thing is that it gives “sensible” answers right now.

CONCLUSIONS & FUTURE WORK

- Initial stress tests of the method show expected behavior. Orders of magnitudes are correct, numerically stable.
- All results were using a naiive algorithm for performing spin integrals. New code 12x faster. Will allow us to hit system sizes comparable to normal DMC calculations.

<u>For the future</u>

- Finish twist-averaging calculations for 8 atom units cells.
- Do finite size extrapolations to get a cold curve in the thermodynamic limit.
- Finish Au and W.
- Perform orbital optimization.
  - Non magnetic ground state with PBE. Its customary to do exact exchange and “+U” scans to improve the starting orbitals, but this might not be necessary with new QMC orbital optimization capability.

ACKNOWLEDGEMENTS

CPSFM | Center for Predictive Simulation of Functional Materials

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https://cpsfm.ornl.gov

QMCPACK

https://qmcpack.org