# Towards a diffusion Monte Carlo study of Mott transition in MnO under pressure

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## Outline

1. **Brief introduction to diffusion Monte Carlo**
2. **Improving trial wave functions:**
   - **Long range periodic Jastrow**
     - **silicon interstitials**
   - **backflow transformations:**
     - **First row atoms**
     - **Quantum dots**
3. **Towards MnO . . .**
   - **Pseudopotential validation**

# Collaborations

Cyrus Umrigar

- MnO
  - Richard Hennig
  - Kevin Driver
  - John Wilkins
- Quantum dots
  - Devrim Güçlu
  - Harold Baranger
- Atomic systems
  - Frank Petruzielo
  - Julien Toulouse

# Introduction to DMC

- Ground state is obtained by projection from trial wavefunction $\Psi_T(\mathbf{R})$:

$$\Psi_{GS}(\mathbf{R}) = \lim_{t \longrightarrow \infty} e^{-t\mathcal{H}} \Psi_T(\mathbf{R}) = e^{-\tau\mathcal{H}}\, e^{-\tau\mathcal{H}} \ldots e^{-\tau\mathcal{H}} \Psi_T(\mathbf{R})$$

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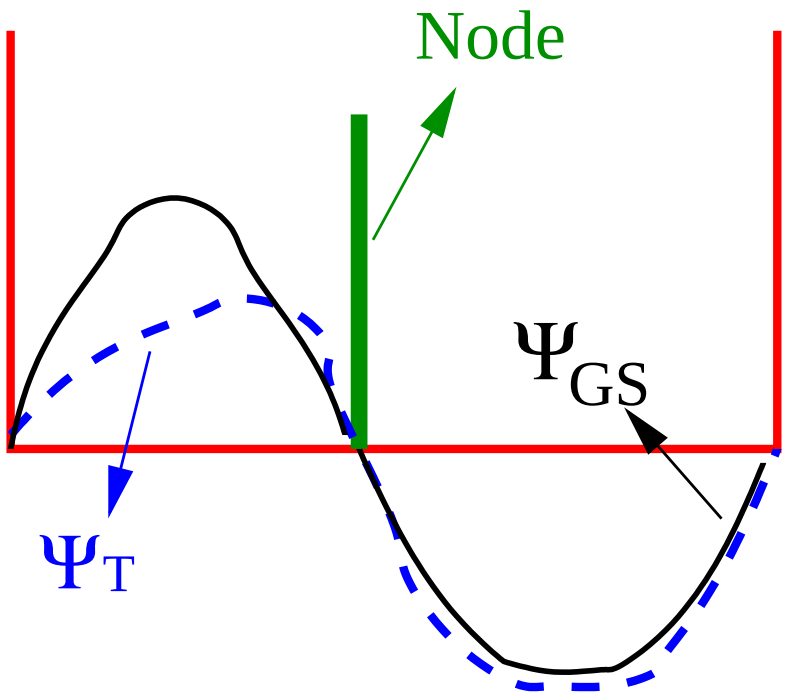


Stable solution:

- ✔ exact if nodes are exact
- ✔ variational if nodes are approximate

Find the best trial WF! VMC optimization

# Trial wavefunctions in DMC

- Slater type:

$$\Psi_T(\mathbf{R}) = \sum_{i}^{\mathrm{ndet}} c_i \, D_i^{\uparrow} \, D_i^{\downarrow}$$

$c_i$ are CI coefficients, and $D_i^{\uparrow}$ and $D_i^{\downarrow}$ are spin-up and spin-down determinants

$\mathbf{R} = (\vec{\mathbf{r}}_\mathbf{1}, \vec{\mathbf{r}}_\mathbf{2}, \ldots, \vec{\mathbf{r}}_\mathbf{N})$ 3N-dimensional vector.

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- Slater-Jastrow type:

$$\begin{aligned} \Psi_T(\mathbf{R}) &= e^{J(\mathbf{R})} \sum c_i \, D_i^{\uparrow} \, D_i^{\downarrow} \\ J(\mathbf{R}) &= J_{ee} + J_{en} + J_{een} + \ldots \end{aligned}$$

  $J(\mathbf{R})$ introduces 1-body, 2-body, 3-body, . . . correlations. Forces $\Psi_T(\mathbf{R})$ to satisfy cusp conditions.

- $J(\mathbf{R}, \{\alpha\})$ is parametrized. $\{\alpha\} = \{\alpha_{ee}, \alpha_{en}, \alpha_{een}\}$ and CI coefficients are optimized with VMC

- Slater-Jastrow type works well for molecular systems and solids.

# Trial wavefunctions in DMC (periodic systems)

- Jastrow factors suitable for isolated systems are short ranged!
- long-range Jastrow correlations: Prendergast, Bevan, Fahy PRB '02

$$
\begin{aligned}
J_{LR}(\mathbf{R}) &= J_{LR}^{(1)} + J_{LR}^{(2)} \\
J_{LR}^{(1)} &= \sum_{\text{stars}} \sum_{i}^{\text{nelec}} p_s \cos\left(\vec{k}\cdot\vec{r}_i\right) + q_s \sin\left(\vec{k}\cdot\vec{r}_i\right) \\
J_{LR}^{(2)} &= \sum_{\text{stars}} \sum_{i,j}^{\text{nelec}} r_s \cos\left[\vec{k}\cdot(\vec{r}_i - \vec{r}_j)\right]
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$r_s$, $p_s$, and $q_s$ are variational parameters optimized with VMC.

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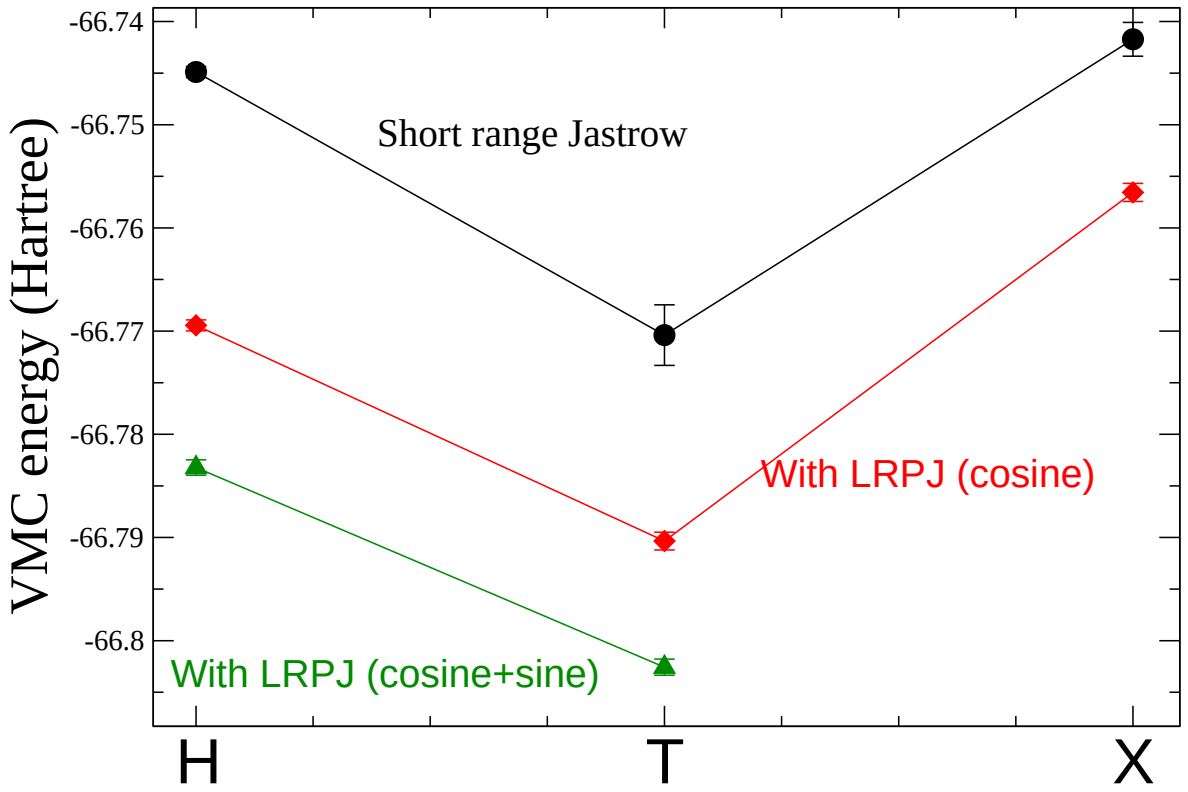
- For one-body $J_{LR}^{(1)}$ all stars consistent with the point group of the crystal are included:
  - ✔ non-inversion symmetry case
  - ✔ symmorphic and non-symmorphic cases

# Silicon interstitials (preliminary)




- ✔ DMC study using CHAMP by Batista and coworkers PRB ’06
- ✔ (16 +1) atom supercell- $(64 + 4)$ electrons. Three kinds of interstitials **H**, **T** and **X**
- ✔ variance reduction: From $\sigma^2 = 0.8$ to $\sigma^2 = 0.6$ Hartree$^2$
- ✔ smaller locality error, efficient simulation, . . .

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- For solids, Slater-Jastrow with periodic long-range correlations:

$$J_{LR}(\mathbf{R}) = \sum_{s} \sum_{i}^{\mathrm{nelec}} \left[ p_s \, \cos\left(\vec{k} \cdot \vec{r}_i\right) + q_s \, \sin\left(\vec{k} \cdot \vec{r}_i\right) \right] + \sum_{s} \sum_{i,j}^{\mathrm{nelec}} r_s \cos\left[\vec{k} \cdot (\vec{r}_i - \vec{r}_j)\right]$$

- With a single determinant, all these WFs have same nodes!

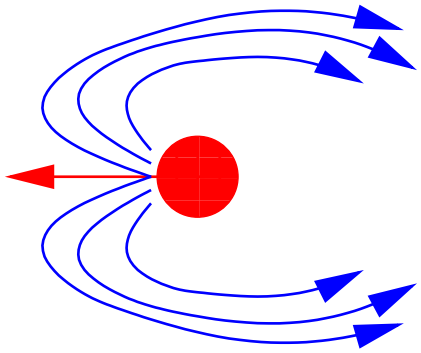
  all DMC energies should be the same

# backflow transformations

Feynman-Cohen backflow (liquid He II): Phs. Rev. '56

excited-state WF with an excitation of momentum $\vec{q}$:

$$\prod_i e^{i\vec{q}\cdot\vec{r}_i}\phi_0 \longrightarrow \prod_i e^{i\vec{q}\cdot\vec{x}_i}\phi_0$$



where $\vec{x}_i = \vec{r}_i + \sum_{j\neq i}\eta(r_{ij})\vec{r}_{ij}$

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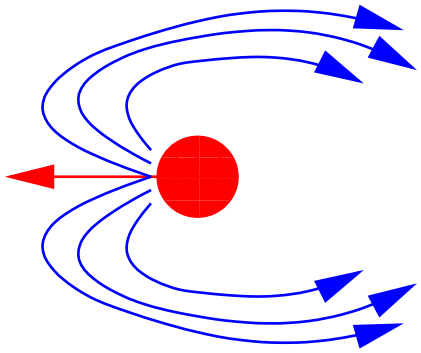

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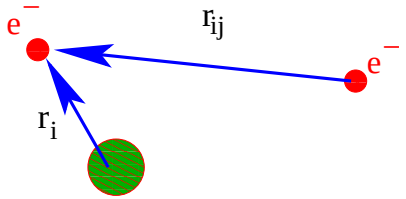
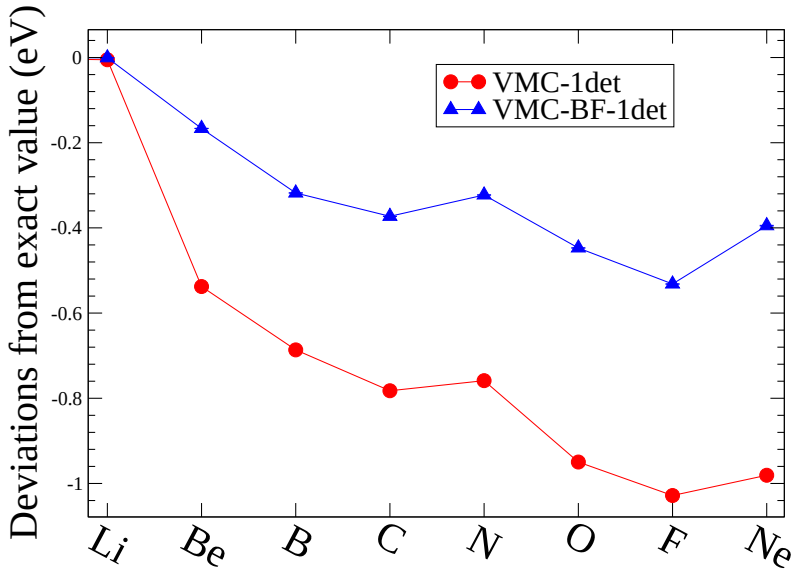
- In Fermionic systems, backflow transformations modify the nodes
- Applied to the Fermionic homogeneous electron gas [Schmidt PRL '81]
- Generalized to inhomogeneous systems [Rios PRE '06]

$$\vec{x}_i = \vec{r}_i + \sum_{j\neq i}\eta(r_i, r_j, r_{ij})\vec{r}_{ij} + \sum_{j\neq i}\xi(r_i, r_j, r_{ij})\vec{r}_i$$

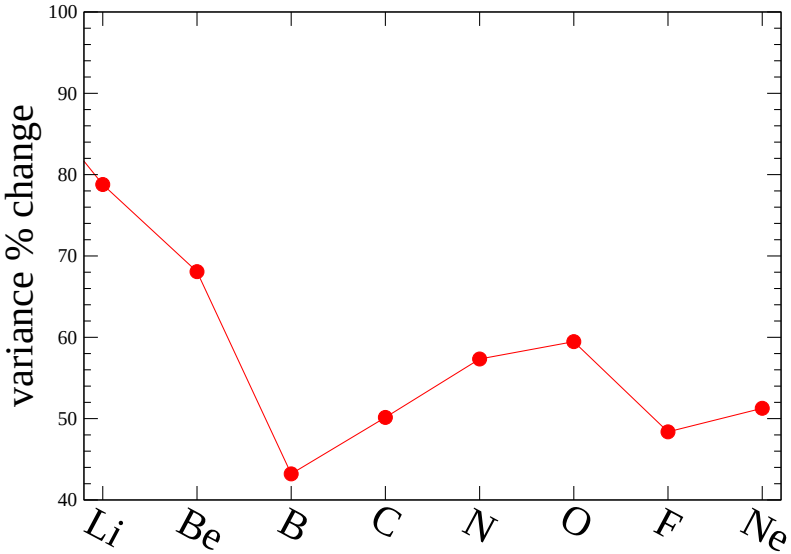



- backflow is highly desirable in solids
- implemented in champ and applied to molecular systems and quantum dots

# VMC energies of first row atoms (preliminary)




- only VMC with 1-det




- Large reduction in variance

# Quantum dots

- Quantum dots are very similar to atoms (artificial atoms)

$$\mathcal{H} = \sum_i \left( -\frac{1}{2}\nabla_{\mathbf{i}}{}^2 + \frac{1}{2}\omega^2 r_i^2 \right) + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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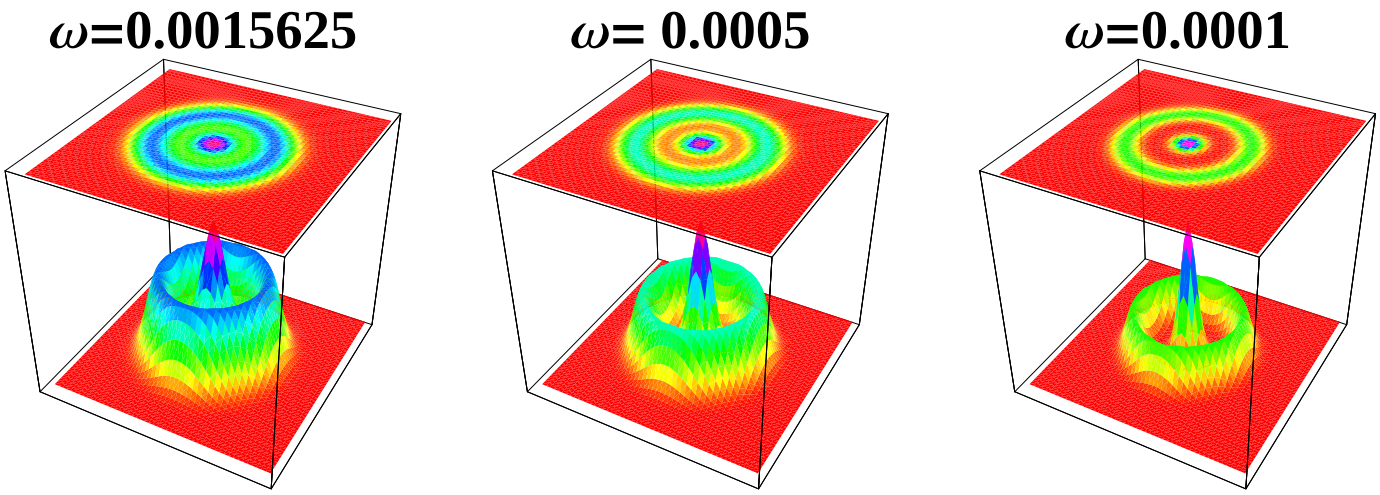
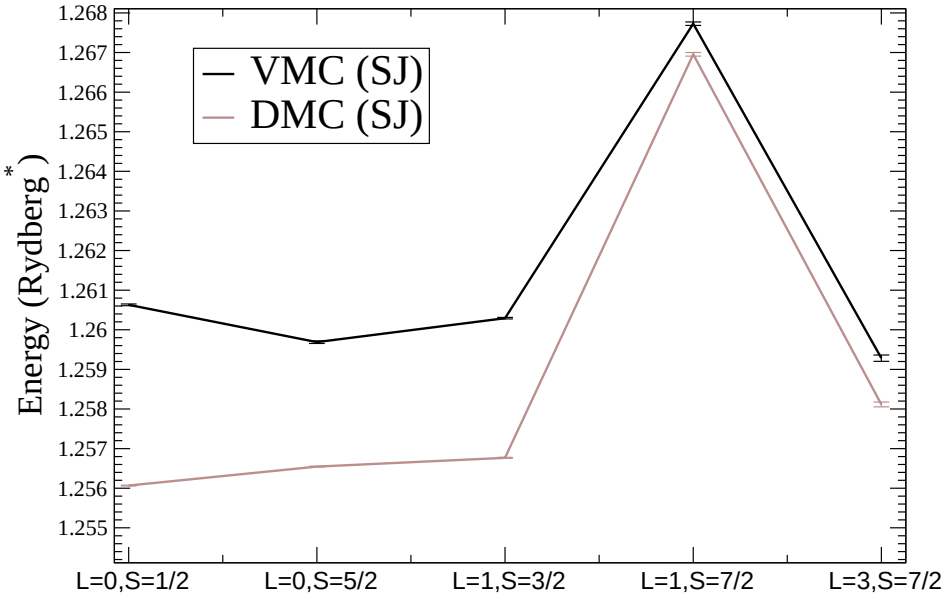
Electron density:



# qdots with backflow

$N = 7$ and $w = 0.0015625$



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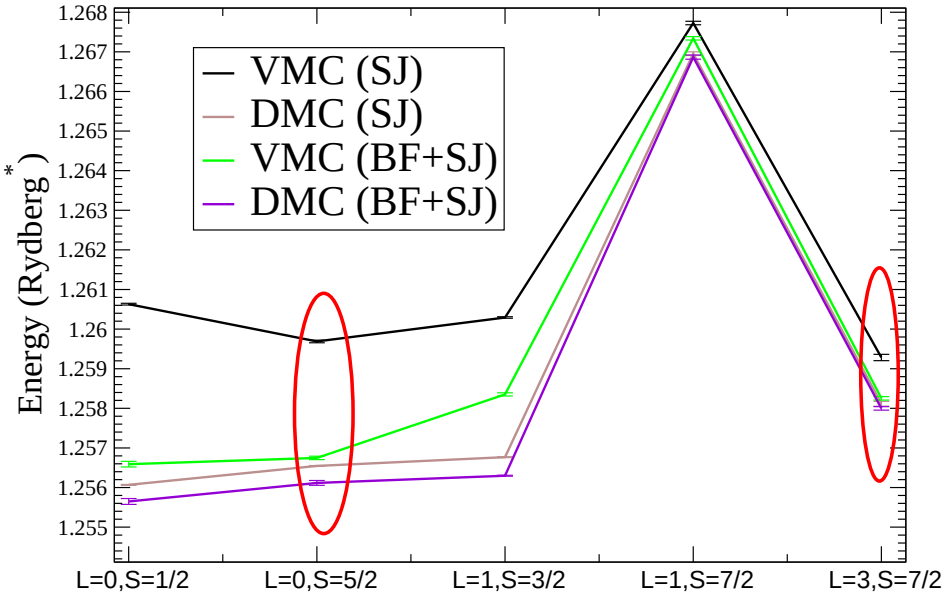

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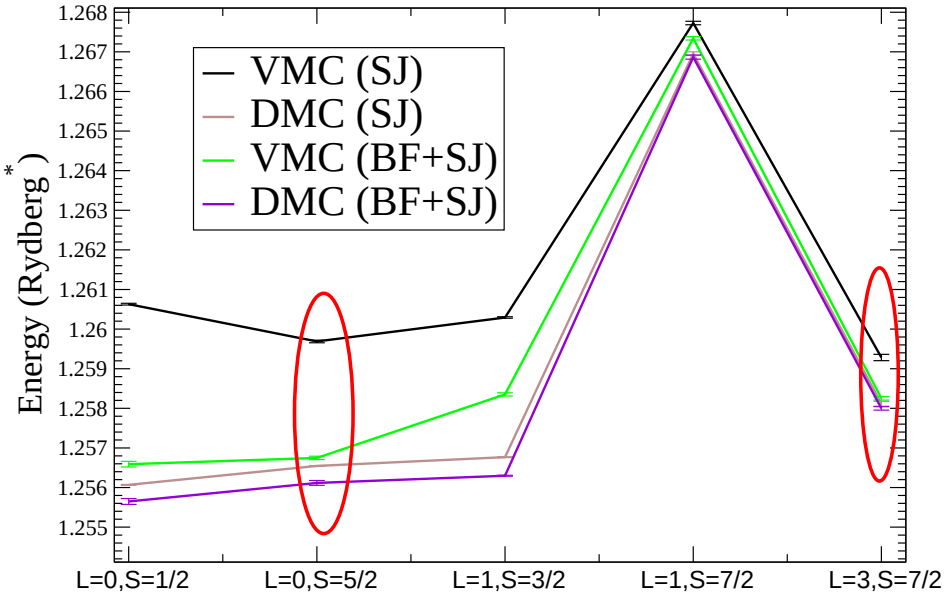
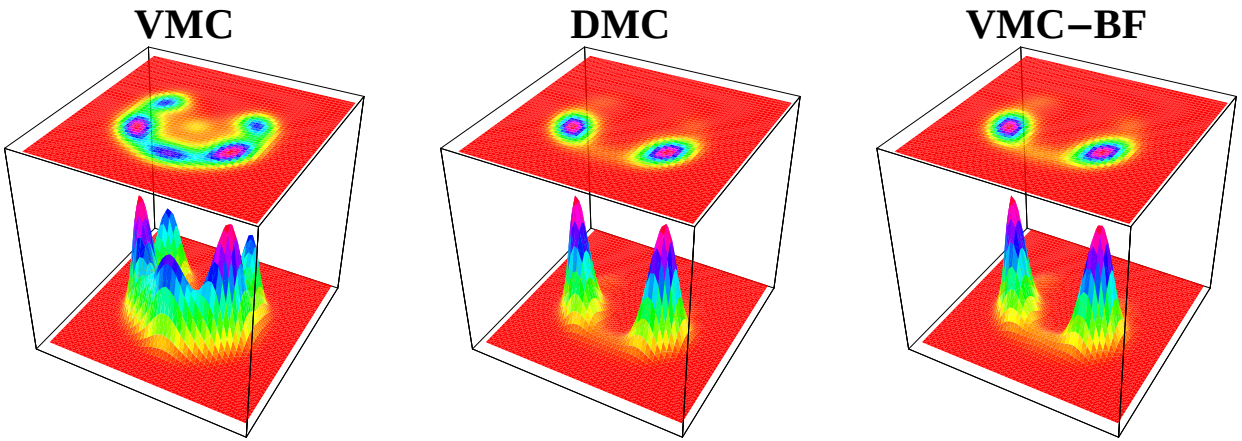



pair density $g_{\downarrow,\downarrow}$ (N=7, $w = 0.0005$)

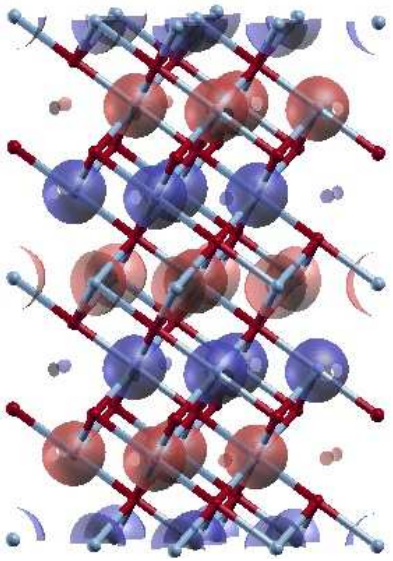


# Where are we?

1. Brief review of diffusion Monte Carlo
2. Trial wave functions?
3. Long range periodic Jastrow
   - ☞ silicon intersteials
4. backflow transformations:
   - ☞ First row atoms
   - ☞ Quantum dots
5. Towards MnO . . .
   - ☞ Pseudopotentials validation
   - ☞ HF or GGA pseudopotentials

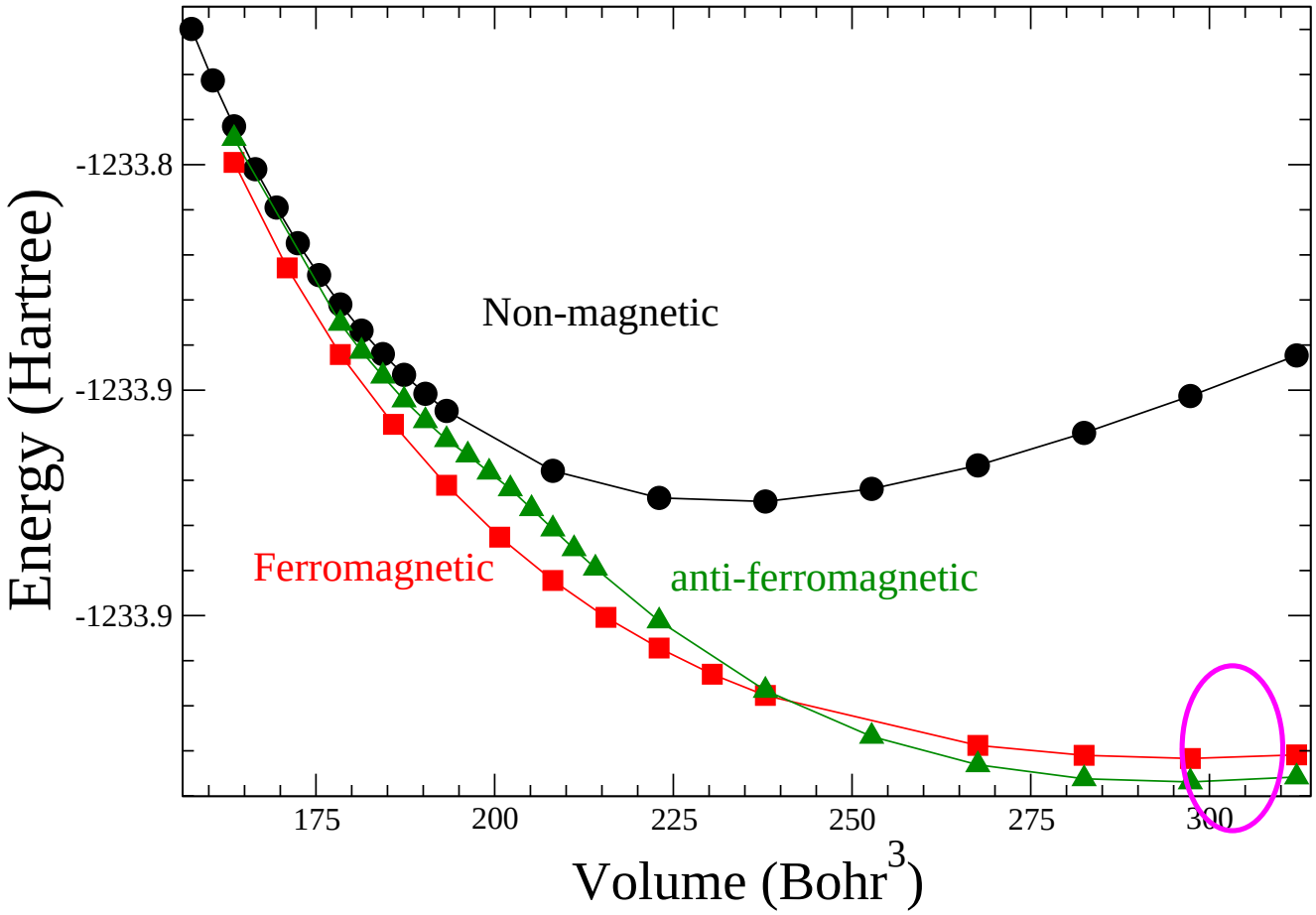
# Study of anti-ferromagnetic MnO (preliminary)

- ✔ AF FCC structure: Mn moments anti-parallel along adjacent sheets in the [111] plane
- ✔ Experimentally:
  - First-order insulator-metal transition near 100 GPa
  - volume collapse by $\approx 5\%$ equilbrium volume
  - moment collapse: 5 $\longrightarrow$ 1 bohr magneton
- ✔ Rich physics  Cohen Science '97, Kasinathan PRB '06, Kunes Nature materials '08



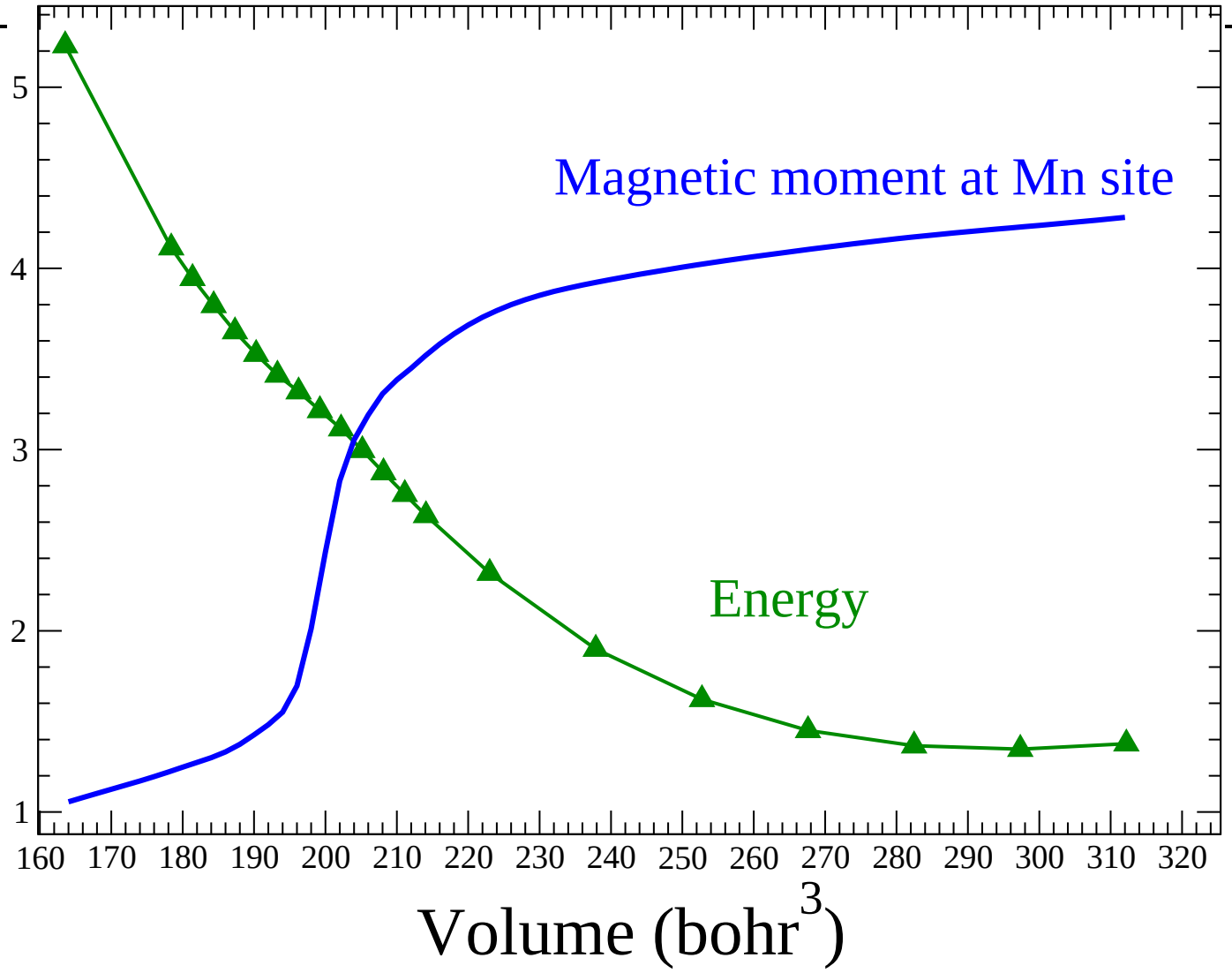
# All-electron equation of state (preliminary)

Calculations done with GGA/PBE using WIEN2k




- ✔ Three different phases of MnO (FCC structure)
- ✔ AFM phase is the ground state under ambient pressures
- ✔ volume collapse in AFM phase for high pressures

# Magnetic and volume collapse (all-electron) (preliminary)




high-spin to low-spin transition ($5/2 \longrightarrow 1/2$) Kasinathan PRB '06,

# Towards a DMC of MnO

- ✔ Which pseudopotentials to use?
  - X Wide spread belief that HF pseudopotentials are better than DFT ones in QMC
  - X HF pseudopotentials are cleaner in descreening step (DFT fixed by NLCC)
  - X Limited experience shows that HF and GGA PsP are okay but not LDA one
  - X OPIUM can generate HF and DFT pseudopotentials Al-Saidi, Walter and Rappe PRB'08
  - X small core pseudopotentials

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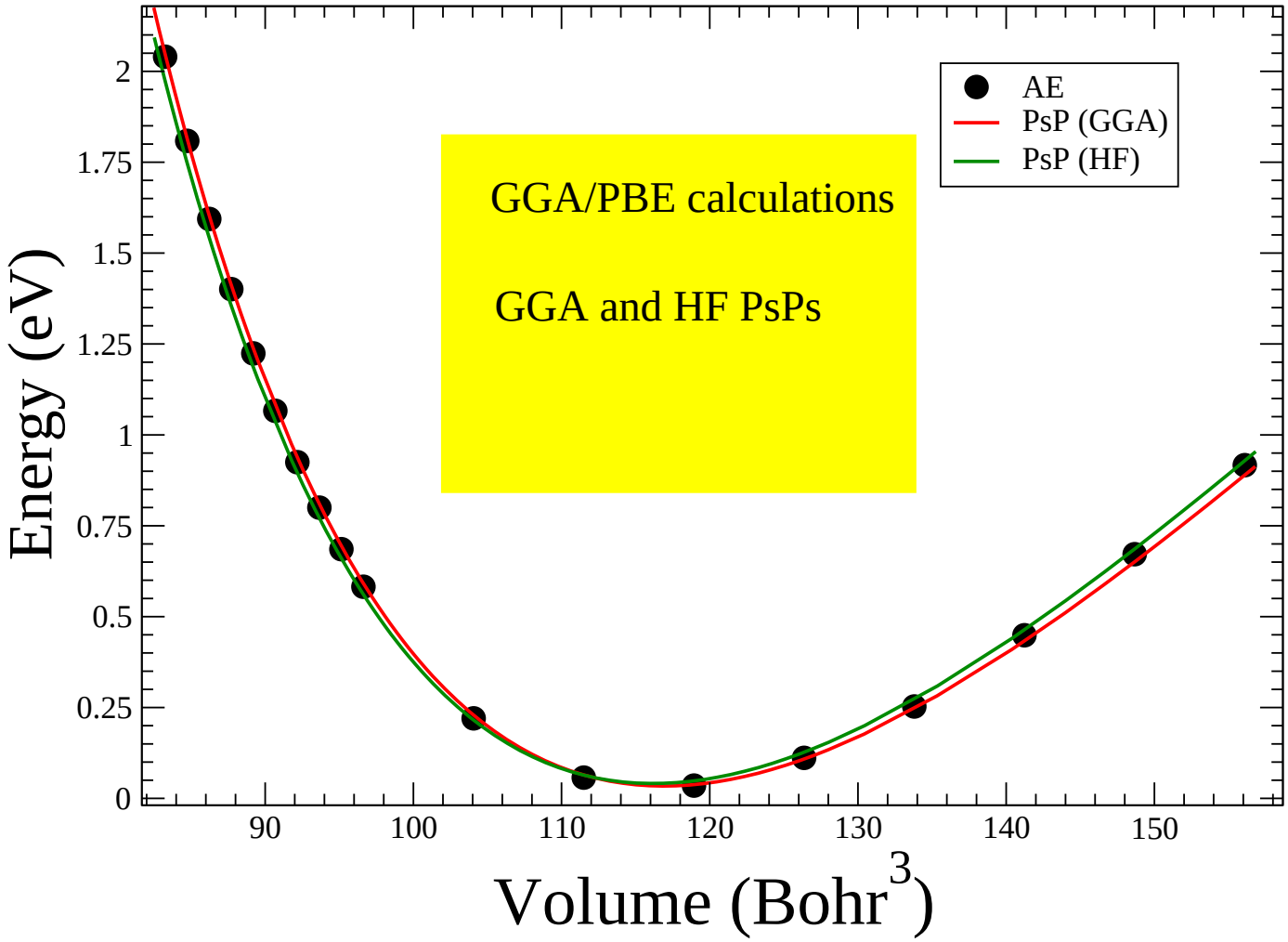
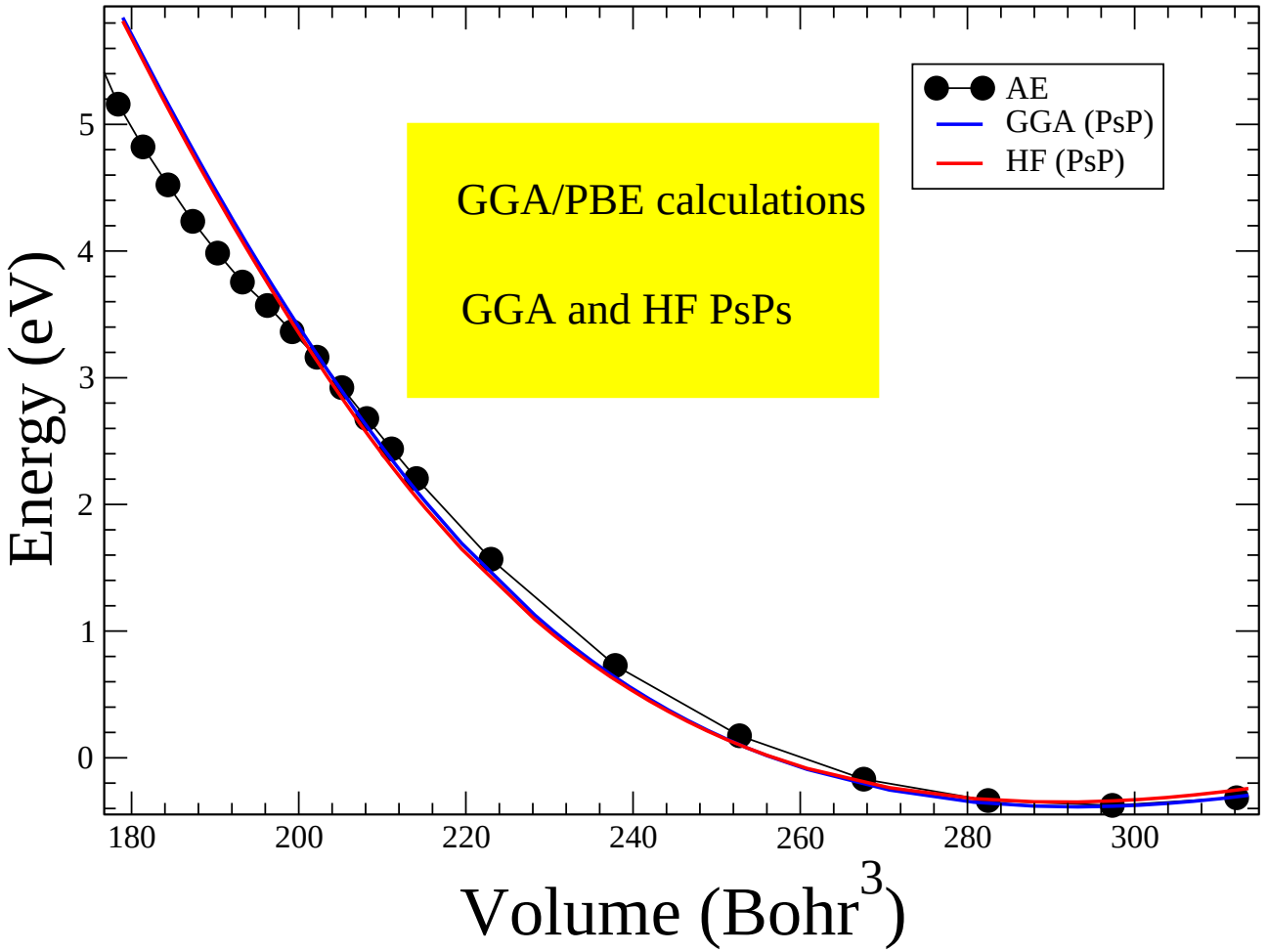
- ✔ What kind of trial WF?
  - X We want to optimize the orbitals
  - X For high pressures, GGA trial wavefunctions will be okay
  - X Near the equilibrium geometry, LDA+U (or HF) might be best

# Non magnetic phase (preliminary)



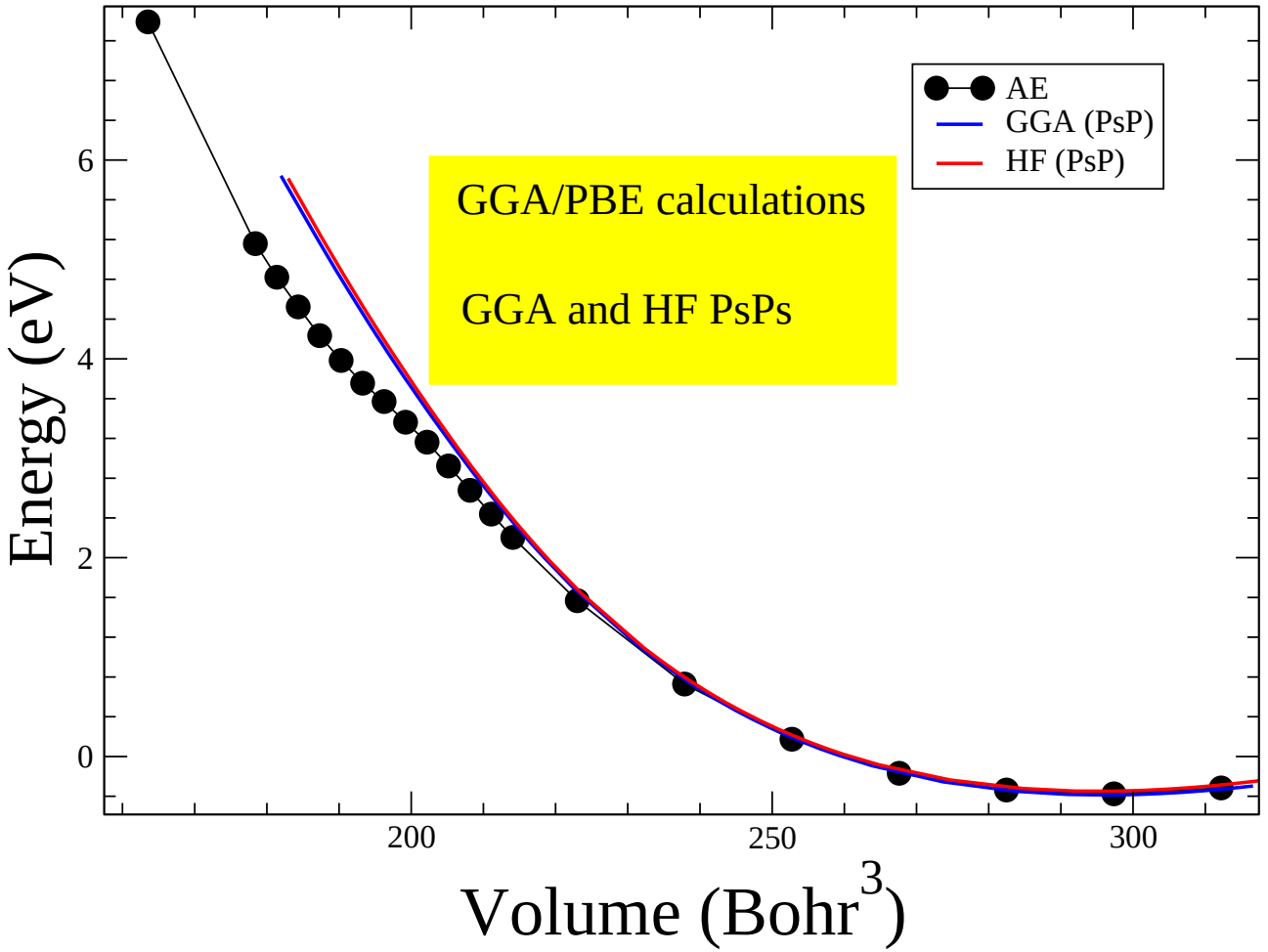

✔ Excellent agreement between all-electron and pseudopotential results

# AFM magnetic phase (preliminary)




- ✔ pseudopotential equilibrium volume is $\approx 1$ % smaller than all-electron one
- ✔ Birch-Murnaghan $B0$ and $B0'$ are also in excellent agreement
- ✔ pseudopotentials do not seem to give a volume collapse????

# AFM magnetic phase (aligning equilb. positions)




- ✔ High pressures, larger deviations between pseudopotential and all-electron
- ✔ change in magnetic properties of system
- ✔ similar behavior has been seen by Kolorenc and Mitas PRB ’07

# Summary

- ✔ Most general long-range periodic Jastrow factor for solids
- ✔ Backflow transformations:
  - atoms and molecules
  - quantum dots
  - solids . . . easily implemented
- ✔ Investigating different pseudopotentials for our MnO study
- ✔ Future work
  - orbital optimization for solids
  - finite-size correction scheme

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