

# Progress Report on Auxiliary-Field QMC for Strongly Correlated Systems

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- **Part 1** Accurate  $C_2$  potential energy curve (PEC) with truncated CASSCF trial WF: ground & excited states
  - $C_2$  ground state is magnetic and nontrivial due to low-lying excited states (Abrams & Sherrill, JCP 2004; Umrigar et al., PRL 2007)
  - Much interest in developing methods for accurate excited states.
  - Magnetic systems such as MnO requires accurate treatment of spin.
  - Removing spin contamination in trial WFs:  $F_2$  molecule
  - Realistic basis results for  $C_2$ .
- **Part 2** MnO calculation with AFQMC: preliminaries

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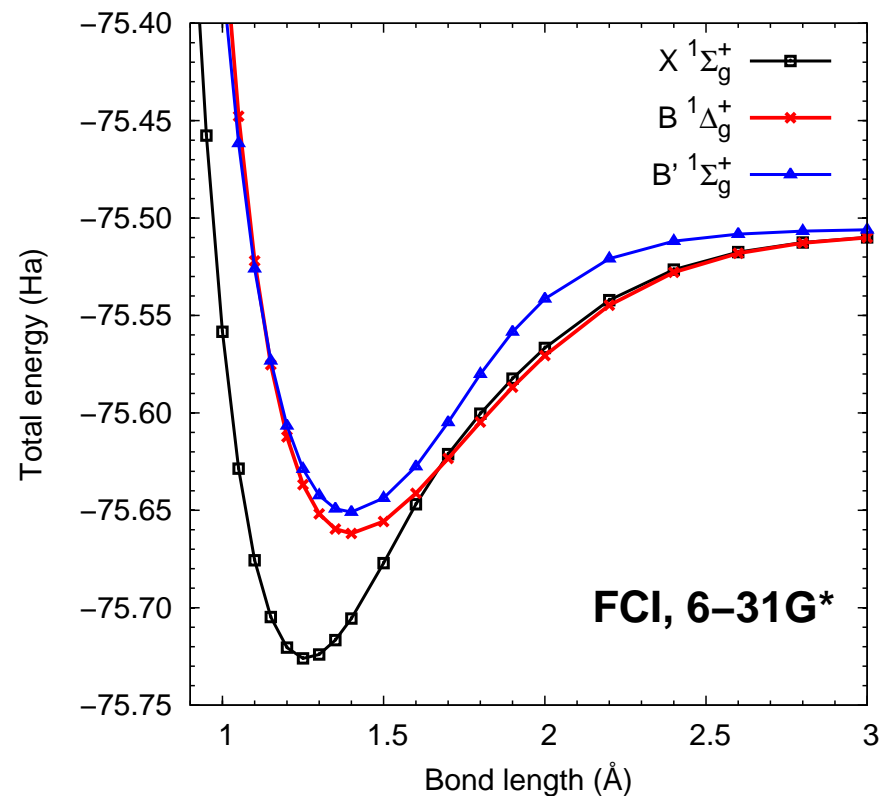
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## PART 1—C<sub>2</sub> Molecule: Challenge for Accurate PECs

C<sub>2</sub> is a complicated molecule:

- strongly correlated
- ground state is antiferromagnetic
- low-lying excited states
- level crossings
- C<sub>2</sub> electronic states show strong multireference character (g.s. contains only  $\sim 70\%$  RHF).



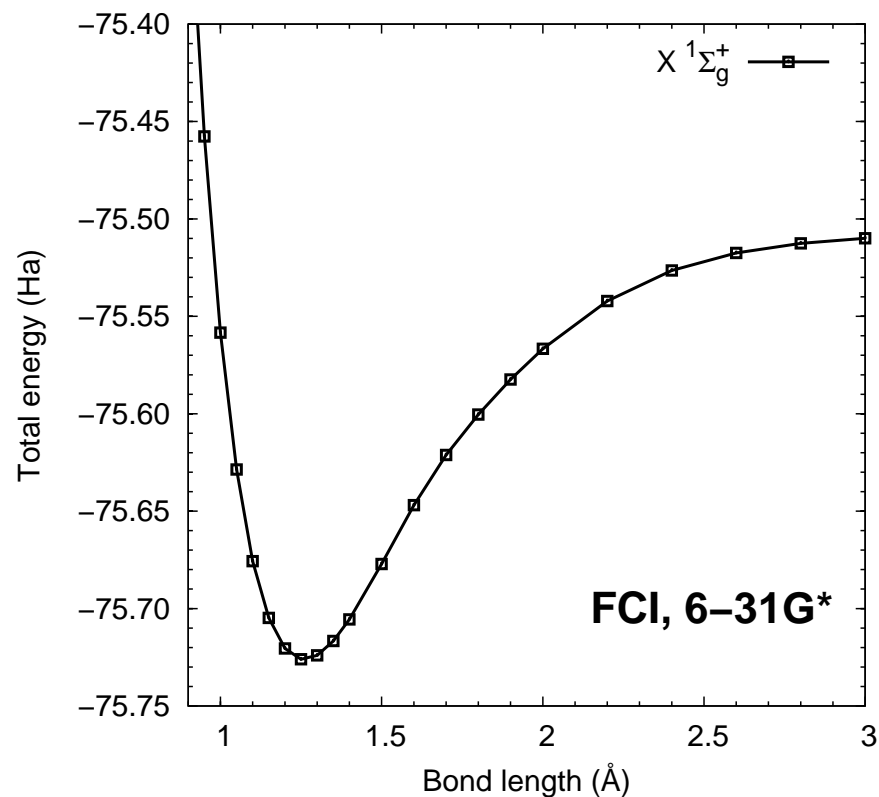
Source: Abrams & Sherrill, JCP 121, 9211 (2004)

## Difficulty of Ground State Calculations

Nonparallelity error (NPE) of ground state

PECs,  $r = 0.9 - 3.0 \text{ \AA}$ .

Method	NPE (mHa)
RHF	212
UHF	78
MP2	130
RCCSD(T)	98
UCCSD(T)	34
CISD	116
CISDT	51
CISDTQ	26



Source: Abrams & Sherrill, JCP 121, 9211 (2004)

- NPE is worse for excited states.
- Accurate PEC calculation requires method that works in strong correlation regime.

## Auxiliary-Field Quantum Monte Carlo

Task: find the ground state of a many-body Hamiltonian in second-quantized form

$$\hat{H} = \hat{K} + \hat{V}$$

Use iterative projection from a trial solution  $|\Psi_T\rangle$

$$e^{-\tau\hat{H}} e^{-\tau\hat{H}} \dots e^{-\tau\hat{H}} |\Psi_T\rangle = |\Phi_0\rangle;$$

$$e^{-\tau\hat{H}} \approx e^{-\tau\hat{K}} e^{-\tau\hat{V}} \quad (\tau \rightarrow 0^+)$$

One-body term:  $e^{-\tau\hat{K}} |\phi\rangle \rightarrow |\phi'\rangle$   $|\phi\rangle = \text{Slater determinant}$

Two-body term  $\rightarrow$  sum of the square of one-body operators:

$$\hat{V} = \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l = \frac{1}{2} \sum_{\alpha} \lambda_{\alpha} (\hat{v}_{\alpha})^2$$

$$e^{-\frac{1}{2}\tau\lambda\hat{v}^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\sigma e^{-\frac{1}{2}\sigma^2} e^{\sigma\sqrt{-\tau\lambda}\hat{v}}$$

Ground-state projection  $\rightarrow$  a high-dimensional integral  $\rightarrow$  random walk in  $|\phi\rangle$ :

$$|\phi'\rangle = \int d\sigma P(\sigma) e^{-\tau\hat{h}(\sigma)} |\phi\rangle$$

## Phaseless AFQMC

- **Reason:** Complex-valued  $e^{-\tau\hat{h}(\sigma)}$  leads to severe fluctuations in the phase of  $|\phi\rangle$ .
- **Phaseless approximation:** Constrain the random walk with the trial wave function:<sup>1</sup>
  - Importance sampling:  $|\Phi_0\rangle = \sum_{\phi} w_{\phi} \frac{|\phi\rangle}{\langle\Psi_T|\phi\rangle}$ .
  - Weight  $w_{\phi}$  be real all the time.
  - Restrict phase rotation in  $\langle\Psi_T|\phi\rangle$  to avoid circling around complex-phase origin:

$$\theta \equiv \arg\left(\frac{\langle\Psi_T|\phi'\rangle}{\langle\Psi_T|\phi\rangle}\right)$$

$$w_{\phi'} \propto w_{\phi} \max(\cos(\theta), 0)$$

- Method is not variational, but gives excellent approximation of the ground state.

<sup>1</sup> S. Zhang and H. Krakauer, PRL (2003)

## Getting the Spin Right: Spin Contamination Problem

We typically deal with spin-independent electronic Hamiltonian:

$$[\hat{H}, \hat{S}^2] = 0$$

Nondegenerate eigenstates must have definite spin states, i.e. they are also eigenstates of the total electronic spin  $\hat{S}^2$ .

Wave functions that are not eigenstates of  $\hat{S}^2$  are said to be *spin contaminated*.

## Getting the Spin Right: Spin Contamination Problem

Some “singlet” WFs are not spin pure  
(most notably, UHF):

$$|\text{UHF}\rangle = c_s |\Psi^s\rangle + c_t |\Psi^t\rangle + \dots$$

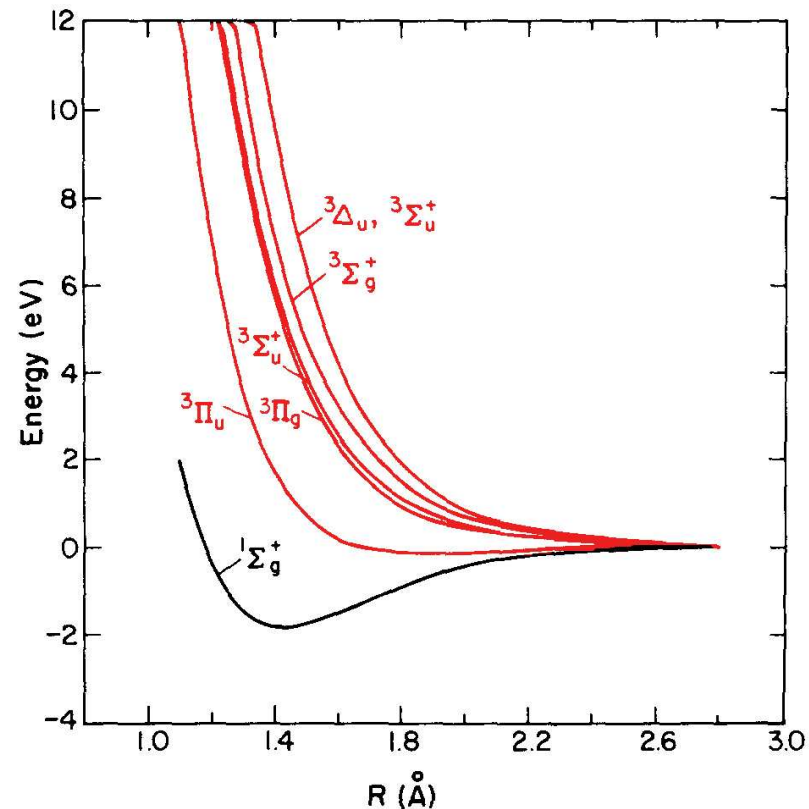
Ideal AFQMC projection of  $|\text{UHF}\rangle$   
would lead to exact ground state:

$$\left(e^{-\tau\hat{H}}\right)^n |\text{UHF}\rangle \rightarrow C |\Phi_0^s\rangle + O(e^{-n\tau(E_0^t - E_0^s)}) |\Phi_0^t\rangle$$

Phaseless AFQMC modifies the  
projection; this  
can lead to spin-contaminated solution:

$$\left(e^{-\tau\hat{H}}\right)^{n \rightarrow \infty} |\text{UHF}\rangle \rightarrow C_s |\Phi_0^s\rangle + C_t |\Phi_0^t\rangle + \dots$$

especially if there are nearby triplets!



[F<sub>2</sub> triplet PEC: Cartwright and Hay, JCP (1979)]

## Removing Spin Contamination in AFQMC

**Idea:** Start the projection with a singlet-spin-pure population  $\{ |\phi_s\rangle \}$

- Each AFQMC walker is a Slater determinant
- AFQMC projection does not alter  $\hat{S}^2$  of spin-pure determinants:

$$\left( e^{-\tau \hat{H}} \right)^{n \rightarrow \infty} |\phi_s\rangle \rightarrow |\phi'_s\rangle$$

- Triplet and higher-spin states in  $\langle \text{UHF} |$  drop out automatically!

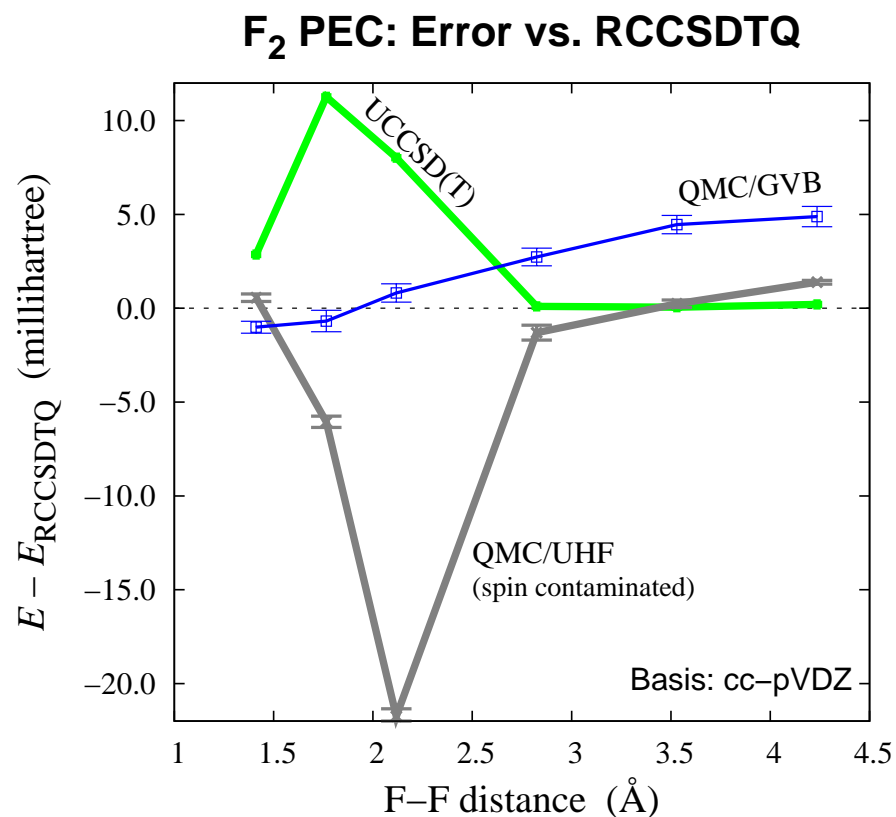
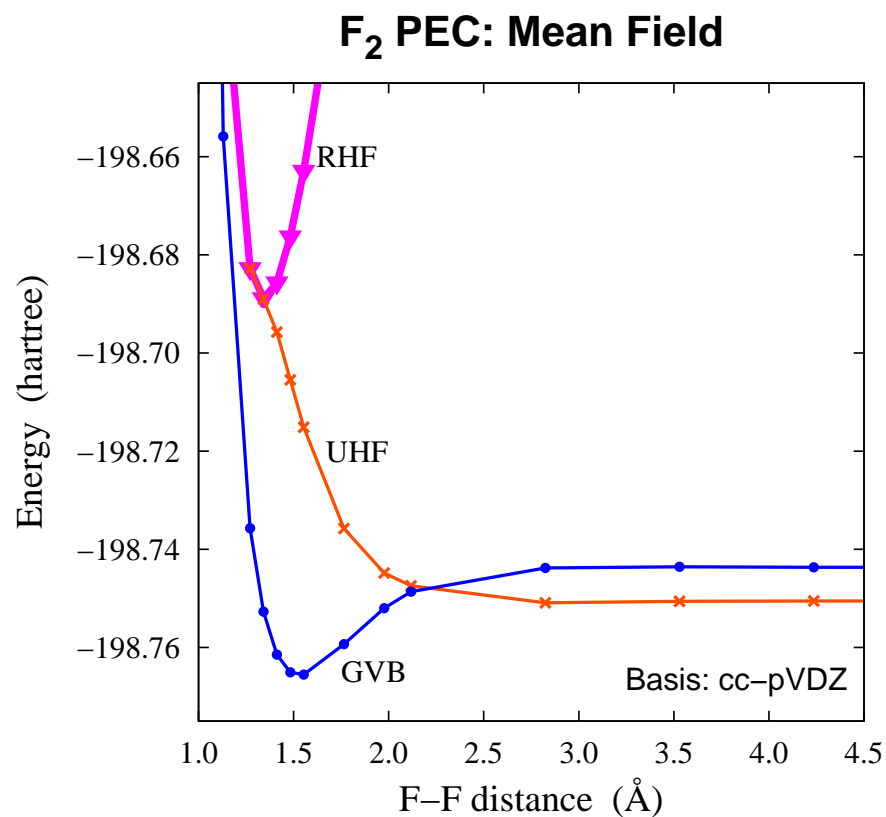
$$\langle \text{UHF} | e^{-\tau \hat{H}} | \phi_s \rangle = c_s \langle \Psi^s | e^{-\tau \hat{H}} | \phi_s \rangle \quad (\text{exact by symmetry})$$

- Energy mixed estimator  $\frac{\langle \text{UHF} | \hat{H} e^{-\tau \hat{H}} | \phi_s \rangle}{\langle \text{UHF} | e^{-\tau \hat{H}} | \phi_s \rangle}$  is also free from spin contamination.
- Typical starting point:  $|\phi_s\rangle = |\text{RHF}\rangle$ .



## Test Case of Spin Projection Method: F<sub>2</sub> Molecule\*

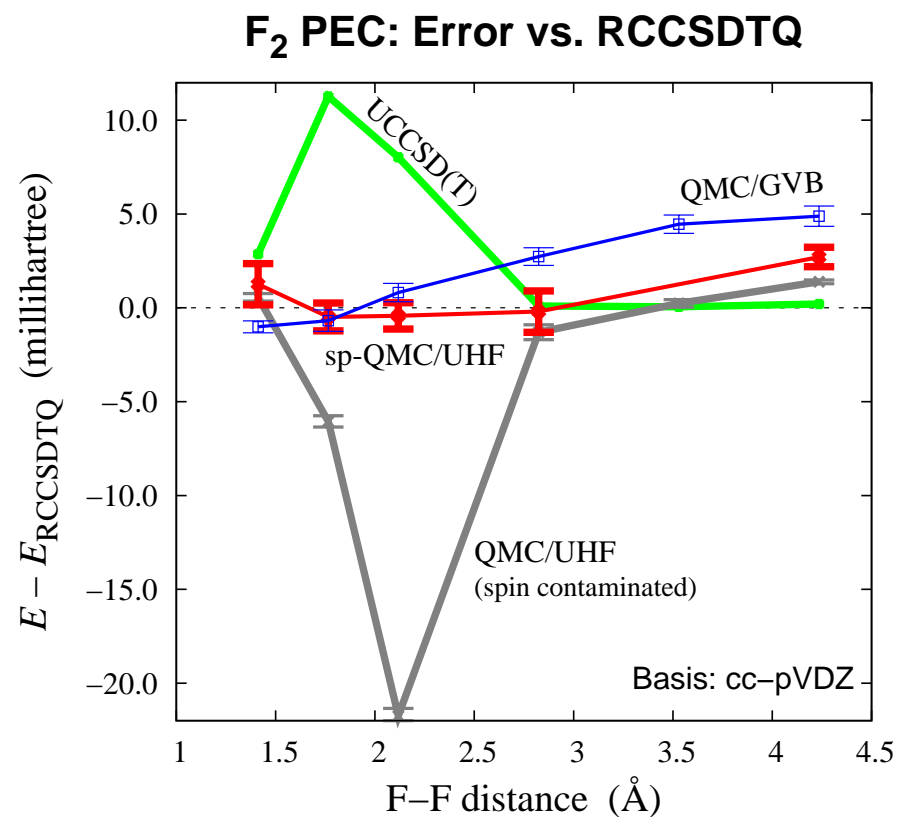
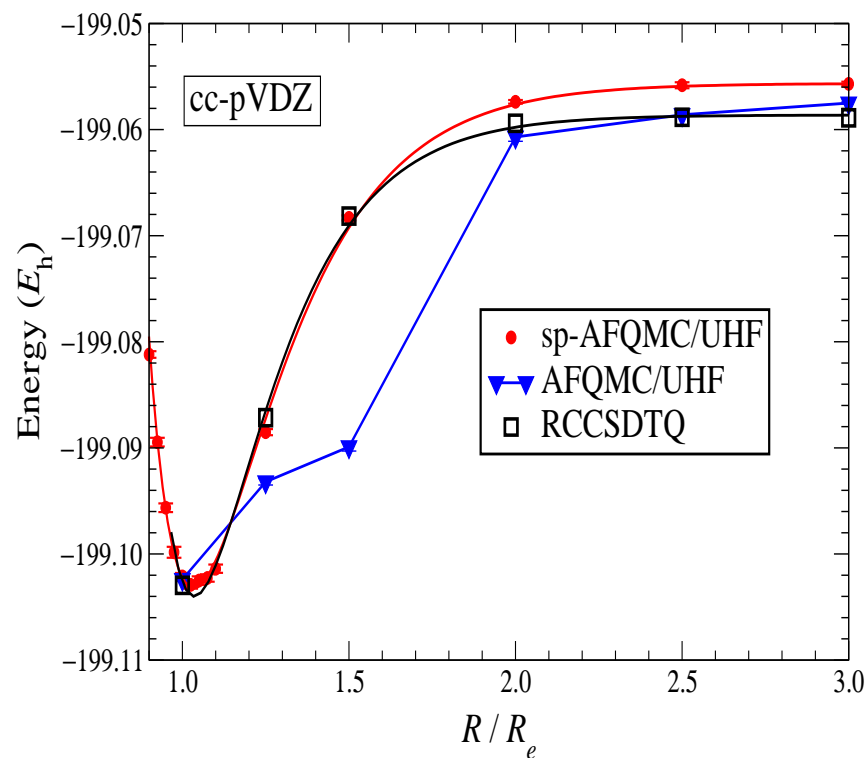
- UHF predicts that F<sub>2</sub> is unbound.
- **Spin contamination:** AFQMC/UHF yields large error around  $R_{F-F} \sim 2$ .



RCCSDTQ: Musial & Bartlett, JCP (2005)

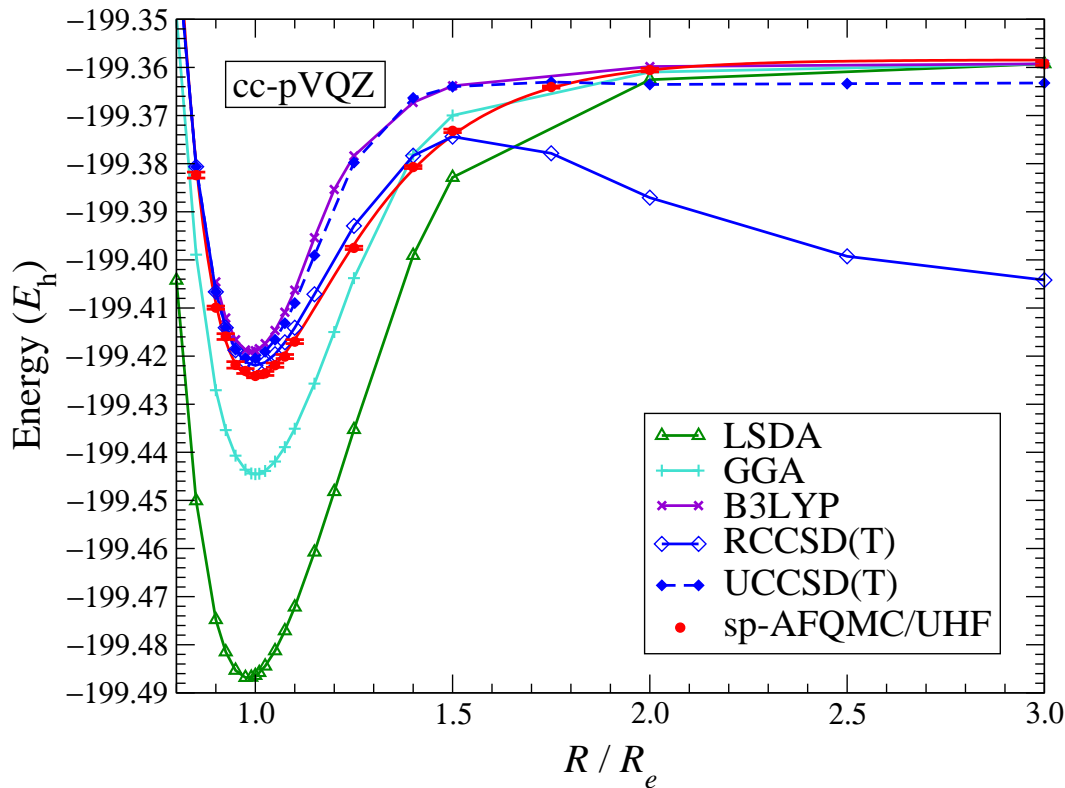
\*Work done in collaboration with Wissam Al-Saidi.

## F<sub>2</sub> PEC with spin-projected QMC/UHF



**Spin-projected QMC/UHF yields accurate results over the entire range, from equilibrium to dissociation.**

## Application: F<sub>2</sub> Realistic PEC and Spectroscopic Constants



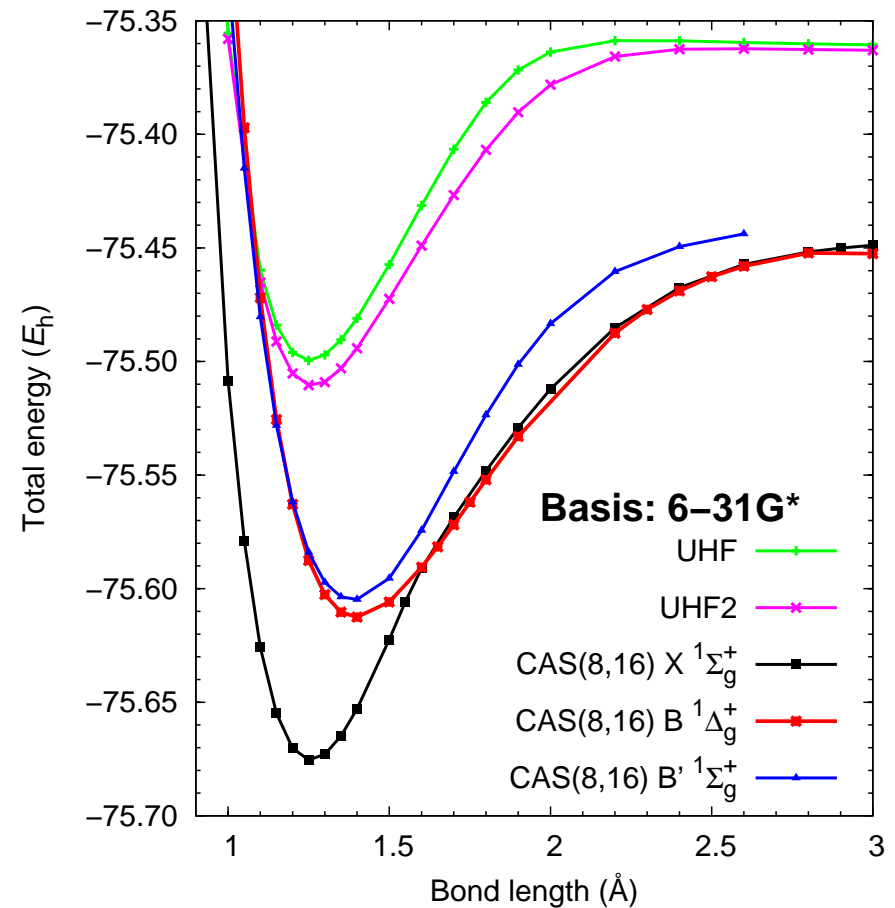
- RCCSD(T) diverges at geometries away from equilibrium
- DFT methods and UCCSD(T) yield wells that are too narrow → vibrational frequencies too high
- LDA and GGA overestimates the well depth

	Units	B3LYP	RCCSD(T)	sp-QMC/UHF	Expt.
Equilibrium distance ( $r_e$ )	Å	1.394	1.411	1.411(2)	1.4131(8)
Vibrational frequency ( $\omega_e$ )	cm <sup>-1</sup>	1109	929	912(11)	917
Dissociation energy ( $D_e$ )	eV	1.62	1.59 <sup>a</sup>	1.70(1) <sup>a</sup>	1.693(5)

<sup>a</sup>Estimated using converged atom calculation.

## $C_2$ PEC: AFQMC with CASSCF Trial WF

- $C_2$  electronic states show strong multireference character.
- RHF determinant has only  $\sim 70\%$  weight in the FCI ground state.
- Multireference CASSCF WF:  
8 active electrons, 16 active orbitals.

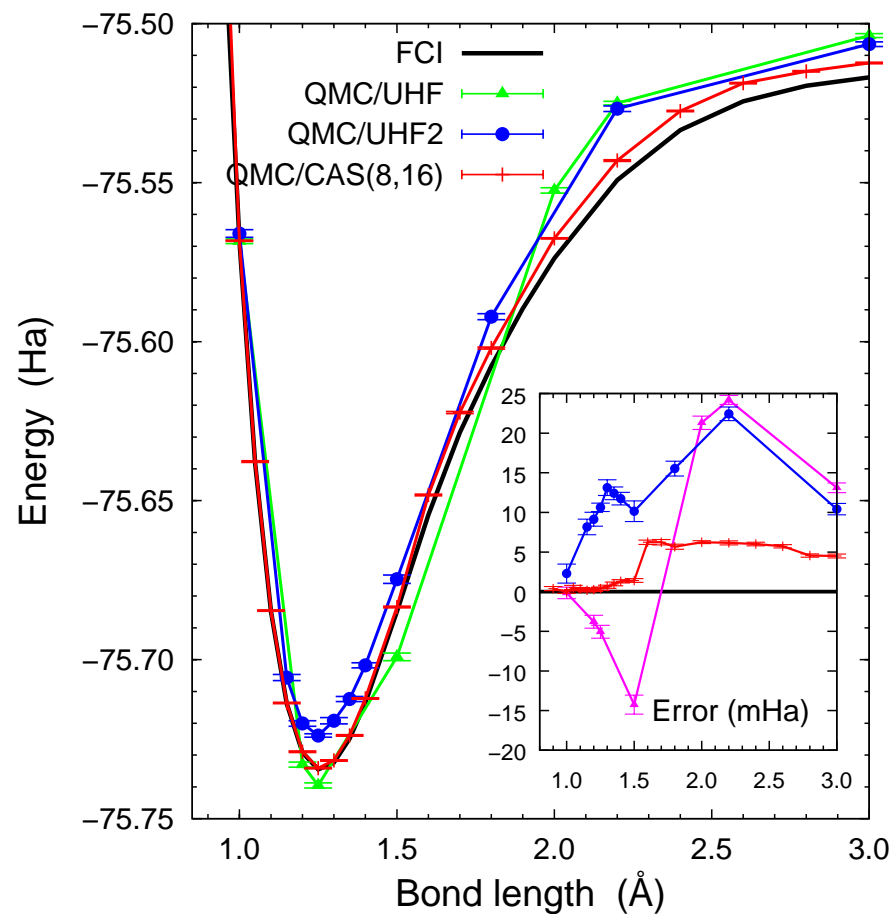


## C<sub>2</sub> PEC: AFQMC with CASSCF Trial WF

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CISDTQ	26
QMC/UHF	38
QMC/UHF2	20
QMC/CAS(8,16)	6



Truncated CASSCF  $\Psi_T$ : 40 – 270 determinants.

## How CASSCF WF Allows Excited State Calculation in AFQMC

Three lowest singlet states in  $C_2$  molecule:

- $X^1\Sigma_g^+$  : ground state
- $B^1\Delta_g^+$  :  $L_z = 2$ , different spatial symmetry
- $B'^1\Sigma_g^+$  : same spatial symmetry as the ground state

Theoretically, unconstrained AFQMC projection will always lead to ground state:

$$\left(e^{-\tau\hat{H}}\right)^n |\Psi_T\rangle \rightarrow |\Phi_0\rangle$$

## How CASSCF WF Allows Excited State Calculation in AFQMC

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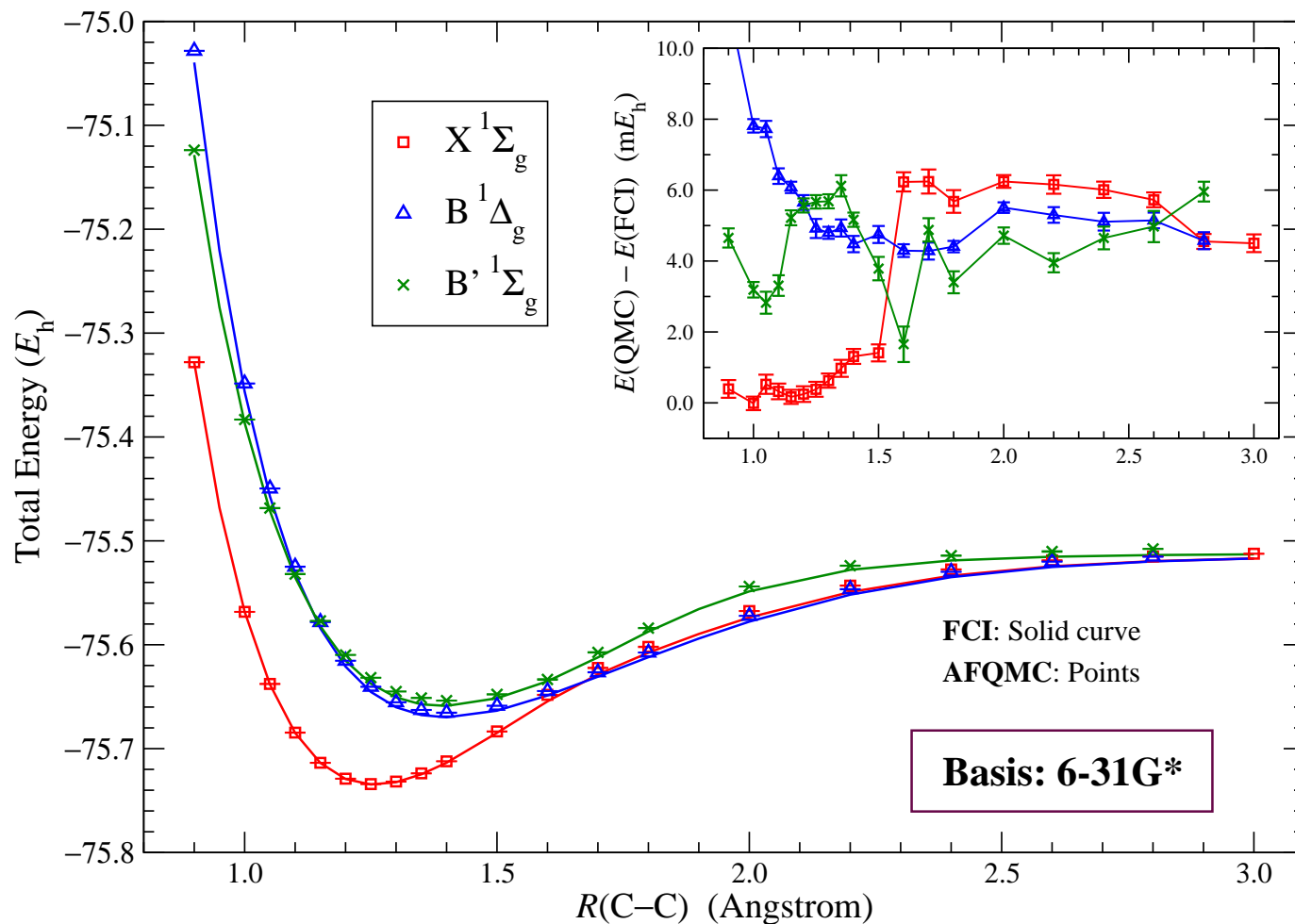
In the phaseless AFQMC,  $|\Psi_T\rangle$  guides and constrains the random walk:

- $|\Psi_T\rangle$  “filters” out the unwanted spatial symmetry:

$$\langle \Psi_T^\Sigma | e^{-\beta \hat{H}} | \phi \rangle = c_\Sigma \langle \Psi_T^\Sigma | e^{-\beta \hat{H}} | \phi^\Sigma \rangle \quad (\text{by symmetry})$$

- CAS trial WFs  $|\Psi_T^X\rangle$ ,  $|\Psi_T^B\rangle$ ,  $|\Psi_T^{B'}\rangle$  are orthogonal to each other. Each contains the right mixture of determinants for a particular state.
- $|\Psi_T\rangle$  together with the phaseless constraint prevents the “collapse” of the excited state.
- For the  $B'$  state:  $\langle \Psi_T^{B'} | X \rangle \approx 0$ .

# AFQMC PECs with Truncated CASSCF(8,16) $\Psi_T$

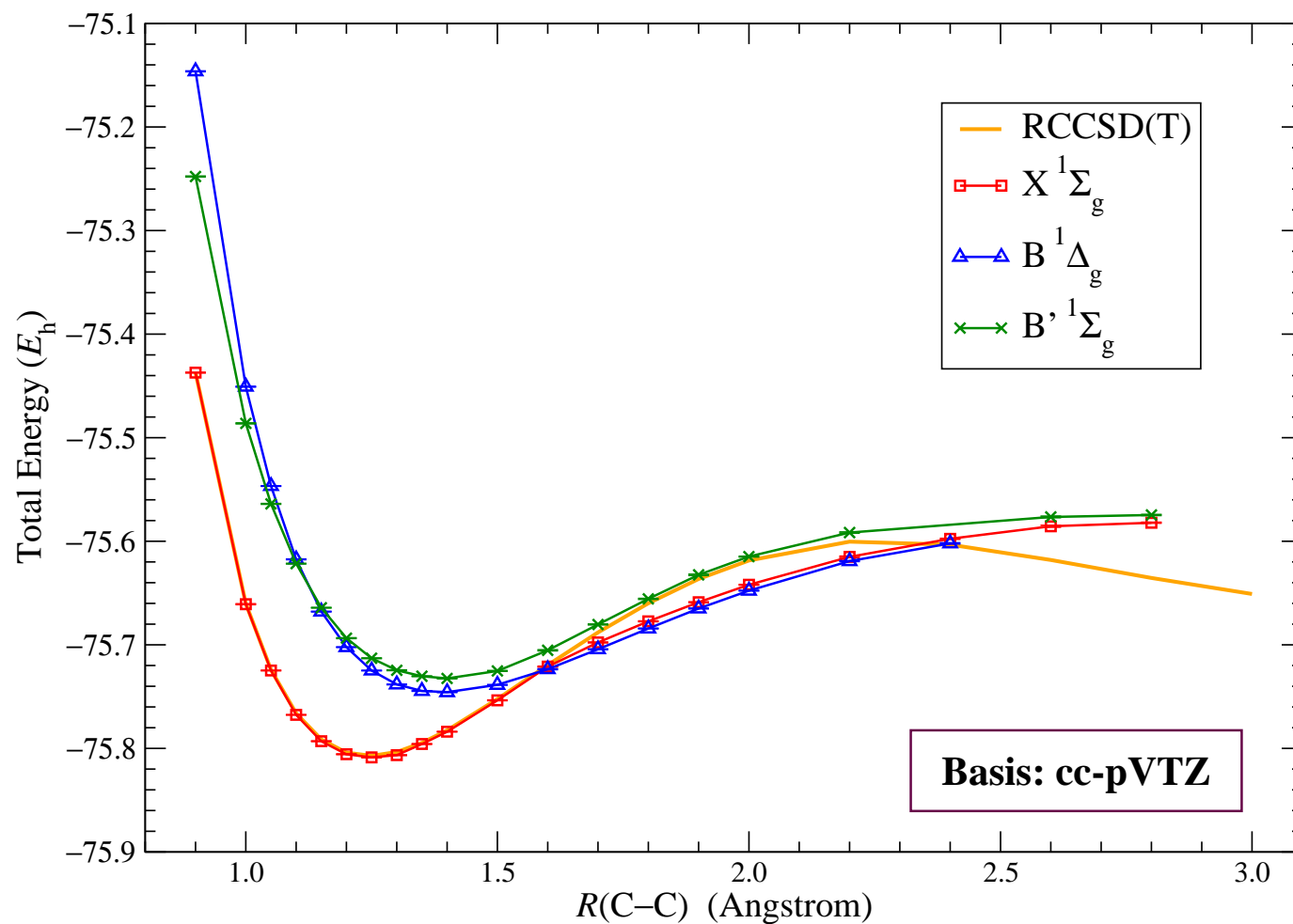


**With CASSCF(8,16) WF we can obtain both the ground and excited states of  $C_2$ .**

Note: the  $X$  and  $B'$  states are of the same symmetry.



## Realistic Basis Set Results: AFQMC PECs with Truncated CASSCF(8,16)



## Realistic Basis Set Results: Spectroscopic Constants

	CASSCF(8,16)	CCSD(T)	QMC	Expt.	
<b>Ground State</b>					
$r_e$	1.2479	1.2508	1.2462(9)	1.2425	Å
$\omega_e$	1862	1842	1884(17)	1855	cm <sup>-1</sup>
$D_e$	6.53	6.03	6.32(1)	6.33	eV
<b><i>B</i> Excited State</b>					
$r_e$	1.3966		1.391(1)	1.3855	Å
$\omega_e$	1395		1376(23)	1407	cm <sup>-1</sup>
$T_e$	1.511		1.723(7)	1.498	eV
<b><i>B'</i> Excited State</b>					
$r_e$	1.3814		1.393(1)	1.3774	Å
$\omega_e$	1489		1441(12)	1424	cm <sup>-1</sup>
$T_e$	1.779		2.082(8)	1.910	eV

## **PART 3—Prelude to MnO Calculation with AFQMC**

- Calculation done in planewave basis with pseudopotentials.
- Must obtain good quality pseudopotentials that can yield the correct magnetism.
- Check code scaling for large number of CPUs.

### **Designing Correct Pseudopotentials**

- Mn and O psp rarely used in magnetic calculations in literature (Gopal et al., PRB 2004; Koloenc & Mitas, PRB 2007).
- Benchmark psp calculations against existing results (LDA, GGA).
- Our initial tests seem to indicate sensitivity to the Mn psp quality.

## Determining Pseudopotential Quality

PSP	LDA	HF	AF QMC	CCSD(t)
IP ( $X \rightarrow X^+$ )				expt = 10.49
OPIUM	10.57	9.97	10.74(6)	
GL-ECP	10.41	9.94	10.61(3)	10.48
AE	10.53	9.91		10.50
IP ( $X \rightarrow X^{++}$ )				expt = 30.26
OPIUM	30.42	29.41	30.79(6)	
GL-ECP	29.97	29.11	30.28(6)	30.13
AE	30.37	29.08		30.23
$D_e (X_2 \rightarrow 2X)$				expt = 5.08
OPIUM	5.96	1.74	5.18(15)	
GL-ECP	5.29	0.98	3.88(8)	4.39
AE	6.18	1.65		4.98

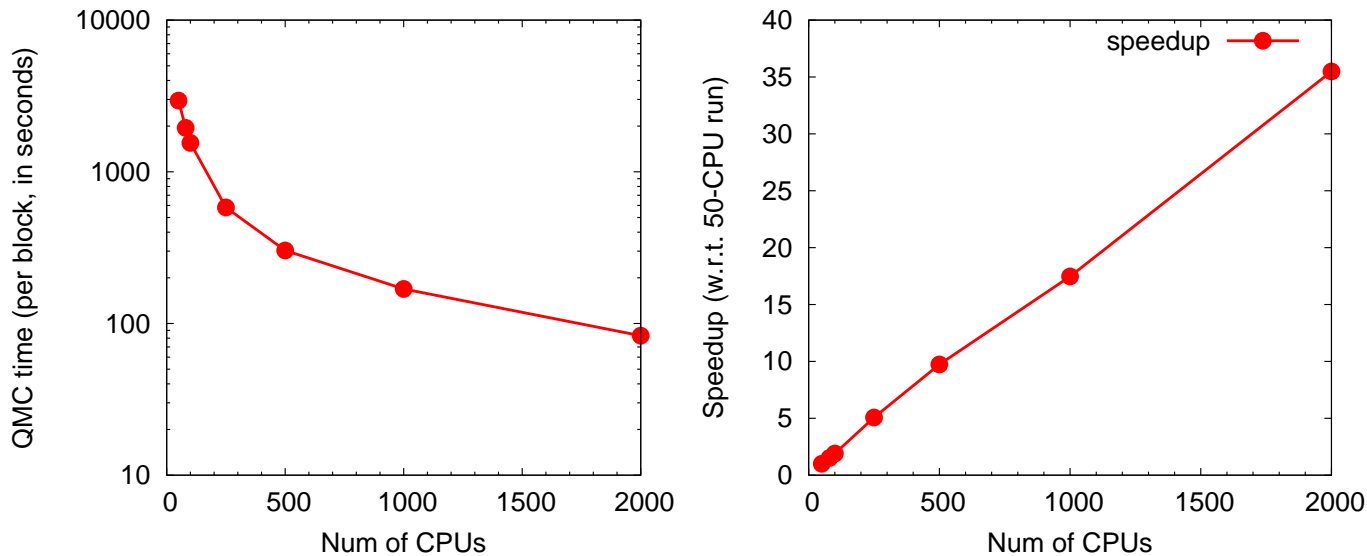
AE = all-electron. All energies are in eV.

*NOTE:* GL-ECP is not suitable for dissociation energy due to lack of  $d$ -channel.

- AF QMC shows a greater sensitivity to the quality of pseudopotential compared to mean-field methods
- Hartree-Fock seems to give a better indication of the quality of pseudopotentials for use in many-body calculations

## AFQMC Scaling on to 1000+ CPUs

(preliminary)



- Each QMC walker steps forward independently of others.
- Each step is a very expensive operation, scaling as  $N^2 M \log M$ .
- Communication among CPUs only happen at population control stage (every 5 steps or so).
- Exchanging walker only done from slave to slave nodes. Walker size in MnO (2x2x2 supercell) is relatively modest,  $O(1\text{MB})$ .
- We expect the code scales nicely well into thousands of CPUs.

## SUMMARY

- Accurate AFQMC PEC for strongly correlated systems such as  $C_2$  is obtained using multireference trial WFs.
- Molecular excited states can be reliably computed by virtue of (near) orthogonality of the multireference trial WFs.
- Spin-projected AFQMC allows us to employ an otherwise effective but spin-contaminated trial WF.
- MnO crystal calculation: in preparation stage. Code scaling looks promising.