Progress Report on Auxiliary-Field QMC for Strongly Correlated Systems

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• **Part 1** Accurate C₂ potential energy curve (PEC) with truncated CASSCF trial WF: ground & excited states
  
  – C₂ 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: F₂ molecule
  
  – Realistic basis results for C₂.

• **Part 2** MnO calculation with AFQMC: preliminaries

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PART 1—C₂ Molecule: Challenge for Accurate PECs

C₂ is a complicated molecule:

- strongly correlated
- ground state is antiferromagnetic
- low-lying excited states
- level crossings
- C₂ 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, \( r = 0.9 - 3.0 \, \text{Å}. \)

<table>
<thead>
<tr>
<th>Method</th>
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<td>CISDTQ</td>
<td>26</td>
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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 \( |\Psi_T\rangle \)

\[ e^{-\tau \hat{H}} e^{-\tau \hat{H}} \cdots e^{-\tau \hat{H}} |\Psi_T\rangle = |\Phi_0\rangle ; \]

\[ e^{-\tau \hat{H}} \approx e^{-\tau \hat{K}} e^{-\tau \hat{V}} \quad (\tau \to 0^+) \]

One-body term:

\[ e^{-\tau \hat{K}} |\phi\rangle \rightarrow |\phi'\rangle \quad |\phi\rangle = \text{Slater determinant} \]

Two-body term → 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 → a high-dimensional integral → 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:\textsuperscript{1}
  
  - 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.

\textsuperscript{1} 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):

$$|\text{UHF}\rangle = c_s |\Psi_s\rangle + c_t |\Psi_t\rangle + \ldots$$

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

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

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

$$\left(e^{-\tau \hat{H}}\right)^{n\rightarrow\infty} |\text{UHF}\rangle \rightarrow C_s |\Phi_0^s\rangle + C_t |\Phi_0^t\rangle + \ldots$$
especially if there are nearby triplets!

[F₂ 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:
  \[
  \left( e^{-\tau \hat{H}} \right)^{n \to \infty} |\phi_s\rangle \to |\phi'_s\rangle
  \]
- 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: F₂ Molecule*

- UHF predicts that F₂ 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.
Spin-projected QMC/UHF yields accurate results over the entire range, from equilibrium to dissociation.
Application: F$_2$ 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

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

$^a$Estimated using converged atom calculation.
C₂ PEC: AFQMC with CASSCF Trial WF

- C₂ 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$_2$ PEC: AFQMC with CASSCF Trial WF

Nonparallelity error (NPE) of ground state PECs, $r = 0.9 - 3.0$ Å.

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<tr>
<td>QMC/UHF</td>
<td>38</td>
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<tr>
<td>QMC/UHF2</td>
<td>20</td>
</tr>
<tr>
<td>QMC/CAS(8,16)</td>
<td>6</td>
</tr>
</tbody>
</table>

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

Three lowest singlet states in C\textsubscript{2} molecule:

- $X \Sigma^+_g$: ground state
- $B \Delta^+_g$: $L_z = 2$, different spatial symmetry
- $B' \Sigma^+_g$: same spatial symmetry as the ground state

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

- $|\Psi_T\rangle$ “filters” out the unwanted spatial symmetry:
  \[
  \langle \Psi^\Sigma_T \vert e^{-\beta \hat{H}} \vert \phi \rangle = c_\Sigma \langle \Psi^\Sigma_T \vert e^{-\beta \hat{H}} \vert \phi^\Sigma \rangle \quad \text{(by symmetry)}
  \]

- CAS trial WFs $|\Psi^X_T\rangle$, $|\Psi^B_T\rangle$, $|\Psi^{B'}_T\rangle$ 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: $\langle \Psi^{B'}_T \vert X \rangle \approx 0$. 
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

<table>
<thead>
<tr>
<th></th>
<th>CASSCF(8,16)</th>
<th>CCSD(T)</th>
<th>QMC</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ground State</strong></td>
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<td></td>
</tr>
<tr>
<td>$r_e$</td>
<td>1.2479</td>
<td>1.2508</td>
<td>1.2462(9)</td>
<td>1.2425 Å</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>1862</td>
<td>1842</td>
<td>1884(17)</td>
<td>1855 cm$^{-1}$</td>
</tr>
<tr>
<td>$D_e$</td>
<td>6.53</td>
<td>6.03</td>
<td>6.32(1)</td>
<td>6.33 eV</td>
</tr>
<tr>
<td><strong>B Excited State</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_e$</td>
<td>1.3966</td>
<td></td>
<td>1.391(1)</td>
<td>1.3855 Å</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>1395</td>
<td></td>
<td>1376(23)</td>
<td>1407 cm$^{-1}$</td>
</tr>
<tr>
<td>$T_e$</td>
<td>1.511</td>
<td></td>
<td>1.723(7)</td>
<td>1.498 eV</td>
</tr>
<tr>
<td><strong>B’ Excited State</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_e$</td>
<td>1.3814</td>
<td></td>
<td>1.393(1)</td>
<td>1.3774 Å</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>1489</td>
<td></td>
<td>1441(12)</td>
<td>1424 cm$^{-1}$</td>
</tr>
<tr>
<td>$T_e$</td>
<td>1.779</td>
<td></td>
<td>2.082(8)</td>
<td>1.910 eV</td>
</tr>
</tbody>
</table>
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 psps rarely used in magnetic calculations in literature (Gopal et al., PRB 2004; Kolorenc & 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

<table>
<thead>
<tr>
<th></th>
<th>PSP</th>
<th>LDA</th>
<th>HF</th>
<th>AF QMC</th>
<th>CCSD(t)</th>
</tr>
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<tbody>
<tr>
<td><strong>IP (X → X⁺)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>expt = 10.49</td>
</tr>
<tr>
<td>OPIUM</td>
<td>10.57</td>
<td>9.97</td>
<td></td>
<td>10.74(6)</td>
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<tr>
<td>GL-ECP</td>
<td>10.41</td>
<td>9.94</td>
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<td>10.61(3)</td>
<td>10.48</td>
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<tr>
<td>AE</td>
<td>10.53</td>
<td>9.91</td>
<td></td>
<td></td>
<td>10.50</td>
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<tr>
<td><strong>IP (X → X⁺⁺)</strong></td>
<td></td>
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<td>expt = 30.26</td>
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<tr>
<td>OPIUM</td>
<td>30.42</td>
<td>29.41</td>
<td>29.79(6)</td>
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<tr>
<td>GL-ECP</td>
<td>29.97</td>
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<td>30.28(6)</td>
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<tr>
<td>AE</td>
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<td>29.08</td>
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<tbody>
<tr>
<td><strong>Dₑ (X₂ → 2X)</strong></td>
<td></td>
<td></td>
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<td>expt = 5.08</td>
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<tr>
<td>OPIUM</td>
<td>5.96</td>
<td>1.74</td>
<td>5.18(15)</td>
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<tr>
<td>GL-ECP</td>
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<td>0.98</td>
<td>3.88(8)</td>
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<td>4.39</td>
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<tr>
<td>AE</td>
<td>6.18</td>
<td>1.65</td>
<td></td>
<td></td>
<td>4.98</td>
</tr>
</tbody>
</table>

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

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

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