A Full Configuration Interaction
QMC Perspective on the
Homogeneous Electron Gas

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Quantum Monte Carlo in the Apuan Alps
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Why?

• A real challenge for FCI(QMC)
• ...a new method in fully-periodic calculations
• Model systems can give physical insight without added complexity of real systems
• ...an application with development in mind
• Exact (finite/complete basis) energy benchmarks
• What does the wavefunction look like?
70 years of history...

- 1934 Wigner crystal
- 1956 Landau theory of Fermi liquids
- 1957 Gell-Mann & Brueckner RPA
- 1962 Overhauser spin/charge density waves
- 1980 Ceperley-Alder QMC

...and so much more.
DMC: very successful

Phase transitions, spectral functions, effective mass, QP renomalization factor

(Ceperley, Needs, Holzmann, Drummond, Foulkes, Ballone, Gurturbay etc. etc.)

Post-HF quantum chemistry: new studies of the solid state (e.g. LiH)

(Schutz, Manby, Kresse, Stoll, Fulde etc. etc.)

Open question: what does $|\Psi\rangle = \sum_i c_i |D_i\rangle$ look like?
$$\hat{H} = \sum_{\alpha} -\frac{1}{2} \nabla^{2}_{\alpha} + \sum_{\alpha \neq \beta} \frac{1}{2} \hat{v}_{\alpha \beta} + \text{const.}$$

$$\psi_{k} = \sqrt{\frac{1}{L^{3}}} \ e^{ik \cdot r} \ \delta_{s \sigma}$$

Finite particle number: $N$

Uniform density: $r_{s}$

(I am discussing 3D but will show 2D schematics)
Using \( |\Psi\rangle = \sum_i c_i |D_i\rangle \) to solve \( \hat{H}\Psi = E\Psi \)
The problem with determinantal expansions...

... simulation-cell HEG has large amounts of dynamic correlation at real metal $r_s$-values

figure due to George Booth
Perturbative approaches (MP2, CCD(T)) diverge...

- Simulate $M$ with consistent $N$
- Measure band gap (closes in TDL)
- Take difference w.r.t RPA
Measure band gap
(closes in TDL)

Take difference w.r.t RPA

RPA $E_{\text{corr}} \approx 0.9\text{eV/el}$

14–1030 electrons $r_s=1.0$
(sc, bcc, fcc lattices)

Measure band gap (closes in TDL)
MP2 diverges...

RPA due to Andreas Grueneis, VASP
CCD converges...

RPA/CCD due to Andreas Grueneis, VASP
CID goes to zero (C.E./elec)...
...and CCD(T) diverges.

RPA/CCD(T) due to Andreas Grueneis, VASP
\[ |\Psi\rangle = \sum_i c_i |D_i\rangle \]

\[ \Psi_0 = \lim_{\tau \to \infty} e^{-\tau(\hat{H}-\hat{S})}\Psi_{\tau=0} \]

\[ -\frac{dc_i}{d\tau} = (H_{ii} - S)c_i + \sum_{j\neq i} H_{ij}c_j \]

FCIQMC: GH Booth, AJW Thom, A Alavi, JCP 131 5, 054106 (2009)
\[ -\frac{dc_i}{d\tau} = (H_{ii} - S)c_i + \sum_{j\neq i} H_{ij}c_j \]

Walker population

\[ \Psi(\tau), H_{ij}(\tau) \]

Spawning

Death/cloning

FCIQMC: GH Booth, AJW Thom, A Alavi, JCP 131 5, 054106 (2009)
Initiator FCIQMC ($i$-FCIQMC)

Coupling of $\Psi(\tau), H_{ij}(\tau)$

Only consider $H_{ij}$ over those determinants with a certain population

$$-\frac{dc_i}{d\tau} = (H_{ii} - S)c_i + \sum_{j \neq i} H_{ij}c_j$$

Stabilises $S$ over a much larger range of walker populations

$N_w \rightarrow \infty$ limit must be found

i-FCIQMC: D Cleland, GH Booth, A Alavi, JCP 132 4, 041103 (2010)
Initiator FCIQMC ($i$-FCIQMC)

$N_w \to \infty$ limit must be found
Overview

- Introduction
- **Plane wave basis set incompleteness error**
- **Comparison with DMC and finite size effects**
- **Insights from the FCIQMC wavefunction**
Plane wave basis sets

Finite $N$

Finite $M$
CBS limit is recovered as $1/M$...

Complete basis set (CBS) limit

Largest space treated

Finite $M$ variational w.r.t. CBS limit

Spin-polarization/dimension dependent…

e.g. 1D spin-polarized, $1/M^3$

25 electrons, 1D ferromagnetic

5 electrons, 1D ferromagnetic

due to Jennifer Mohr
CBS limit is recovered as $\frac{1}{M}$...

Complete basis set (CBS) limit

Finite $M$ variational w.r.t. CBS limit

Largest space treated

\[ E_{\text{corr}} = \sum_{j \in \{\text{doubles}\}} \langle D_j \mid H \mid D_0 \rangle \frac{C_j}{C_0} \]

\[ E_{\text{corr}} = \sum_{ij} \sum_{ab} \delta_{k_i-k_a, k_j-k_b} \left( v_{k_i-k_a} - v_{k_j-k_a} \right) \frac{C_{k_i,k_j}^{k_a,k_b}}{C_0} \]

Pairwise addition of virtual contributions

Consider a different definition of basis set

- It is possible to define two momentum transfer vectors for an excitation.
- Show there are three sensible choices for basis sets based on this.
- Originates from basis set convergence work in solid state systems.

Consider a different definition of basis set

\[ E_{\text{corr}} = \sum_{j \in \{\text{doubles}\}} \langle D_j \mid H \mid D_0 \rangle \frac{C_j}{C_0} \]

\[ E_{\text{corr}} = \sum_{\text{occ}} \sum_{\text{virt}} \delta_{k_i-k_a,k_j-k_b} \left( \nu_{k_i-k_a} - \nu_{k_j-k_a} \right) \frac{C_{k_i,k_j}^{k_a,k_b}}{C_0} \]

Pairwise addition of virtual contributions

Assume fixed

Consider a different definition of basis set

\[
E_{\text{corr}} = \sum_{j \in \{\text{doubles}\}} \langle D_j \mid H \mid D_0 \rangle \frac{c_j}{c_0}
\]

\[
E_{\text{corr}} = \sum_{ij} \sum_{ab} \delta_{k_i - k_a \cdot k_j - k_b} \left( v_{k_i - k_a} - v_{k_j - k_a} \right) \frac{c_{k_a k_b}^{k_c}}{c_0}
\]

\[
\sum_{ab}^k F(k) \rightarrow \sum_{ab}^g F(g)
\]

For multi-reference calculations, there is a trade-off...

\[
E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{k_i - k_a \cdot k_j - k_b} \left( v_{k_i - k_a} - v_{k_j - k_a} \right) \frac{C_{k_a k_b}^{k_i k_j}}{C_0}
\]

\[
\sum_{ab}^{k_c} F(k)
\]

\[
\sum_{ab}^{g_c} F(g)
\]

Slower/less accurate extrapolation

Neglects coefficient relaxation

<table>
<thead>
<tr>
<th>$r_s$</th>
<th>$M$</th>
<th>k extrapolation</th>
<th>g extrapolation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1850</td>
<td>-0.5969(3)</td>
<td>-0.5959(7)</td>
</tr>
<tr>
<td>1.0</td>
<td>1850</td>
<td>-0.5325(4)</td>
<td>-0.5316(4)</td>
</tr>
<tr>
<td>2.0</td>
<td>1850</td>
<td>-0.4447(4)</td>
<td>-0.444(1)</td>
</tr>
<tr>
<td>5.0</td>
<td>778</td>
<td>-0.306(1)</td>
<td>-0.307(1)</td>
</tr>
</tbody>
</table>
For multi-reference calculations, there is a trade-off...

\[ E_{\text{corr}} = \sum_{ij} \sum_{ab} \delta_{k_i-k_a, k_j-k_b} \left( v_{k_i-k_a} - v_{k_j-k_a} \right) \frac{C_{k_ia}^{k_i} k_{ib}^{k_j}}{C_0} \]

- Single (multi-reference) calculation
- Immediate CBS estimate
- Systematically improvable

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- Comparison with DMC and finite size effects
- Insights from the FCIQMC wavefunction
How good are the HF nodes?

- Single-determinant Slater-Jastrow wavefunction
- Real-space propagation using a Green's function propagator
- Makes the Schrödinger equation diffusive
- Must enforce anti-symmetry explicitly:

\[ f(x, \tau) = \Psi(x, \tau) \phi_T(x) \]

- How good are the trial wavefunction’s nodes? (infer from energy)
\textit{i-FCIQMC}, exact except for:

\begin{itemize}
  \item Basis set incompleteness error
  \item Initiator error
\end{itemize}

\textbf{DMC}, exact except for:

\begin{itemize}
  \item Fixed-node error (after backflow)
  \item (Time-step error)
\end{itemize}


Consistent with:
DMC results due to Pablo López-Ríos
The correlation energy undulates with changing $N$...

**Diagram:**

- **Correlation energy (a.u. per elec.)**
- **$N$**
- **VMC**

*Shell-filling effects*

$(r_s=1.0$ a.u.$)$

*Non-zero twist angle*

VMC results due to Pablo López-Ríos
...but so does the gap.

What happens at the TDL?

VMC results due to Pablo López-Ríos

(r_s=1.0 a.u.)

0.1-2mHa/el
Simulation cell HEG systems can resemble clusters of electrons in $k$-space more than the continuum picture of a sphere.

Offset can cause ‘repopulation’

C Lin, F-H Zong, D M Ceperley, Phys Rev E 64, 016702 (2001)
These now have different correlation energies…

(HF changes regardless)
54 electron system
$\Gamma$ -point different from average

20 electron system

DMC/VMC results due to Pablo López-Ríos
Twist-averaging yields a smooth pattern with $N$...

Correlation energy (a.u. $\times 10^{-3}$ per elec.)

- VMC
- DMC
- FCIQMC

Thermodynamic limit (TDL)

$r_s = 1.0$ a.u.

DMC/VMC results due to Pablo López-Ríos
With an underlying relationship

\[ E_0 = E_{\text{corr, DMC}} + \lambda (E_{\text{corr, DMC}} - E_{\text{corr, VMC}}) \]

DMC/VMC results due to Pablo López-Ríos
Using this relationship...

DMC/VMC results due to Pablo López-Ríos

$r_s = 1.0$ a.u.
Ratios are hopefully fairly constant with $N$, so return to 14 electrons...

DMC/VMC results due to Pablo López-Ríos
How well does DMC do in retrieving the missing correlation energy in VMC?

DMC/VMC results due to Pablo López-Ríos
Overview

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What about the wavefunction?

$i$-FCIQMC directly simulates a representation of the wavefunction (walkers)

- Is the wavefunction recognisably multi-reference?
- What are the most important excitations?
- How does this compare with molecules?
- ...or other theories?

(Speculative/preliminary)
A remarkably simple ‘sign structure’?

1st order PT has the correct coefficient signs*

14 electrons, \( r_s = 1.0 \) (high density)
14 electrons, $r_s=0.5$

Rescale by $10^{-4}$ if using intermediate normalization.
14 electrons, $r_s = 1.0$

Emergence of higher excitations earlier

Leading coefficient goes down
14 electrons, $r_s=2.0$

Emergence of higher excitations earlier

Leading coefficient goes down
How does this relate to molecules?

Stretched N$_2$ RHF

$N_{ex} = 2$

$N_{ex} = 3$

$N_{ex} = 4$

$N_{ex} = 5$

$N_{ex} = 6$

$N_{ex} = 7$

$N_{ex} = 8$
How does this relate to molecules?

Stretched N\(_2\) UHF

- All walkers
- \(N_{ex} = 2\)
- \(N_{ex} = 3\)
- \(N_{ex} = 4\)
- \(N_{ex} = 5\)
- \(N_{ex} = 6\)
- \(N_{ex} = 7\)
- \(N_{ex} = 8\)
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References

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• HEG/cusps: A Grueneis et al. in preparation
• HEG/diverences: JJS et al. in preparation