Quantum Monte Carlo approach to the Full CI problem

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- Introductory remarks
- FCIQMC
- i-FCIQMC
- Demonstrations I
  - Some technicalities: occupation number representation and annihilation
  - Spin-flip and time-reversal symmetry
  - Semi-Stochastic adaptation
- Demonstrations II
  - Non-uniform excitation generation
  - Density matrices and property calculations
- Applications
  - Excited States
  - CASSCF
  - Anions, and diatomic molecules
  - Uniform electron gas
  - Solids
  - F12
Many-Electron Schrödinger equation

\[ H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{i} v(r_i) \]

\[ H \Psi_0 = E_0 \Psi_0 \]
\[ \Psi_0 = \Psi_0(x_1, \ldots, x_N) \quad x = (r, \sigma) \]

Electrons are Fermions:

\[ \Psi_0(\ldots x_i, \ldots, x_j \ldots) = -\Psi_0(\ldots x_j, \ldots, x_i \ldots) \]

Atomic units \( \hbar = m_e = |e| = 1 \quad E_h = 27.211 \text{ eV} \)
**Ab initio strategies to get $E_0$**

**Quantum Chemical**
- Finite basis sets
- Many-body approximations
  - Hartree-Fock (mean-field theory)
  - Many Body Perturbation theory, Coupled cluster methods
  - **Full Configuration Interaction.**
- **Systematically improvable.**
- **Expensive**

**Density Functional Theory**
- Exchange Correlation functional ⇒
- *Uncontrolled approximation*, not systematically improvable.
- **Widely used.**

**Quantum Monte Carlo**
- Stochastic exploration of the configuration space
- No basis sets
- Fixed Node approximation (in diffusion QMC) due to Fermion sign problem ⇒*Uncontrolled error.*
Slater determinant space: the Hilbert space for fermions

Suppose we have in hand a set of \(2M\) spin-orbitals [e.g. RHF, UHF, pw]

\[
\left| D_i \right> = \left| D_{n_1n_2..n_N} \right> = \frac{1}{\sqrt{N!}} \det[u_{n_1} u_{n_2} ... u_{n_N}]
\]

Antisymmetric \(N\)-electron basis

\[
N_{FCI} = \binom{M}{N_{\alpha}} \binom{M}{N_{\beta}}
\]

\(N_{\alpha} = 5, N_{\beta} = 5, M = 100\)

\(\rightarrow N_{FCI} \approx 10^{16}\)

HF determinant \(D_0\) (Fermi Vacuum)

2\(h\), 2\(p\)

4\(h\), 4\(p\)
Full configuration interaction

\[ H = \sum_{i}^N \frac{1}{2} \nabla_i^2 + \sum_{i<j} \frac{1}{|r_i - r_j|} + \sum_{i} v(r_i) \]

\[ H\Psi_0 = E_0\Psi_0 \]

\[ \Psi_0 = \sum_{i} C_i |D_i\rangle \quad \text{Include all (symmetry-allowed) determinants within basis} \]

Variationally minimise wrt \( C_i \)  

\[ \Rightarrow \sum_{i} \langle D_j | H | D_i \rangle C_i = E_0 C_j \]

Ground-state eigenvalue problem in an exponentially large space

\[ \langle D_i | H | D_j \rangle \] can be positive or negative: this is a source of sign problem, but is NOT the Fermion sign problem!

Largest FCI calculation to date \( \sim 10^{10} \) determinants (\( N_2 \) molecule)  


Hubbard model: \( 159 \times 10^9 \) determinants  

[Yamada, Imamura, Machida, on the Earth Simulator]
Properties of FCI wavefunctions and energies

- Variationally the minimum energy achievable within the given one-electron basis

- Total energy $E_0$ is invariant to orthonormal transformations of the orbitals

- Pure spin eigenfunctions

- Size consistent

- Do not satisfy electron-electron cusp conditions

- Slow convergence of energy wrt basis set
  - Need to use large basis sets, and extrapolate to CBS
Hamiltonian matrix elements (Slater-Condon rules)

Since $H$ contains at most 2-body interactions:

$$\langle D_i \mid H \mid D_j \rangle = 0 \text{ if } D_i \text{ and } D_j \text{ differ by more than 2 spin-orbitals}$$

Hamiltonian connects only single and double excitations:

$$\langle D_i \mid U \mid D_j \rangle = \langle ij \mid r_{12}^{-1} \mid ab \rangle - \langle ij \mid r_{12}^{-1} \mid ba \rangle$$

Spin selection rule:

$$\langle D_i \mid H \mid D_j \rangle = 0 \text{ if } S_z[D_i] \neq S_z[D_j]$$

$$\langle D_i \mid H \mid D_i \rangle = \sum_{i<j} \left[ \langle ij \mid ij \rangle - \langle ij \mid ji \rangle \right]$$

$$\langle D_i \mid H \mid D_j \rangle = \sum_{k} \left[ \langle ik \mid ak \rangle - \langle ik \mid ka \rangle \right]$$

$$\langle D_i \mid H \mid D_j \rangle = \langle ij \mid ab \rangle - \langle ij \mid ba \rangle$$

Maximum connectivity

$$N(N-1)(2M-N)(2M-N-1)/4 \approx N^2 M^2$$

Other symmetries may also exist:

- Translational invariance;
- Molecules: point group symmetry

For $D_i, D_j$ differing by one spin-orbital

For $D_i, D_j$ differing by two spin-orbitals
Slater determinant space is a giant network with “small world” character

Number of nodes (determinants) grows exponentially in $N$ and $M$

Connectivity around each node is roughly uniform: $N^2M^2$

→ The network is close to “infinite dimensional”, i.e. connectivity around each node is very high.

The number of steps from any node to any other node takes (at most) $N/2$ steps

There are very few “ergodic” bottlenecks, i.e. non-stationary distributions are rapidly mixed.

The FCI problem is a linear problem, with only one minimum, other stationary points being saddles.
Our Strategy

Quantum Monte Carlo

Quantum Chemistry (Full CI)

“Darwinian Game of Life” (i-FCI/QMC)

Emergent many-electron wavefunctions

Reduced Density Matrices

Nodal structure is emergent

\[ \gamma_q^p = \langle \Psi | a_p \dagger a_q | \Psi \rangle \]
\[ \Gamma_{pq}^{rs} = \langle \Psi | a_r \dagger a_s a_q a_p | \Psi \rangle \]

Properties (forces, dipole moments, …)

R12/F12 [Correcting for the Coulomb cusp]

CASSCF, DMET…
From “amplitudes” to “walkers”

Consider a population of $N_w$ “walkers” which inhabit Slater determinant space

$$\{i_1, i_2, \ldots, i_{N_w}\}$$

Each with an associated sign $s_i = +1$ or $-1$

$$\{s_1, s_2, \ldots, s_{N_w}\}$$

We will define the amplitude on $i$ to be the signed sum of walkers on $D_i$:

$$C_i \propto \sum_{j=1}^{N_w} s_j \delta_{i,i_j} = N_i$$
Pictorial example

\[ N_w = \sum_i |N_i| = 11 \]

Normalisation = \[ \frac{1}{\sqrt{\sum_i N_i^2}} = \frac{1}{\sqrt{19}} \]
FCIQMC is a stochastic means to solve the imaginary-time Schrödinger equation for the FCI coefficients by means of a population dynamics of a set of positive and negative walkers, such that

\[
\frac{dC_i}{d\beta} = - \sum_j (H_{ij} - S\delta_{ij})C_i
\]

by means of a "shift" (population control parameter)

\[
\lim_{\beta \to \infty} \langle N_i \rangle \propto C_i
\]
A differential formulation for the CI coefficients

Let: \[ K_{ij} = H_{ij} - E_0^{(0)} \delta_{ij} \]

Consider the set of coupled first-order equations:

\[ -\frac{dC_i}{dt} = \sum_j (K_{ij} - S \delta_{ij}) C_j \]

If \( \sum_j K_{ij} C_j = S C_i \Rightarrow \frac{dC_i}{dt} = 0 \Rightarrow \) The distribution is stationary and is an eigenstate of \( K \) (and hence \( H \))

If \( S = E_0 - E_0^{(0)} \) The stationary distribution is the exact ground-state

Any arbitrary initial distribution \( \{C_j\} \) will tend to the exact ground-state

However: this is not very useful, as we need the complete of \( \{C_j\} \) to complete the force calculation \( \Rightarrow \) the MEMORY BOTTLENECK OF FCI
We want to generate a population dynamics for our set of walkers so that the rate of change of walkers on a given determinant satisfies the imaginary-time Schrödinger equation:

\[
K_{ij} = H_{ij} - E_{HF} \delta_{ij}
\]

\[
-\frac{dC_i}{dt} = \sum_j (K_{ij} - S \delta_{ij})C_j = (K_{ii} - S)C_i + \sum_{j \neq i} K_{ij}C_j
\]

- **Reduce/enhance population on** \(i\), proportional to \((K_{ii} - S)\) and \(C_i\)
- **Diagonal Death (or cloning) processes**
  - Reduce if \(K_{ij}C_j > 0\)
  - Enhance if \(K_{ij}C_j < 0\)
- **Annihilation processes**
- **Spawning processes (child of** \(j\) **on** \(i\))**
  - The sign of the child depends on the sign of \(K_{ij}\)
Overview of FCIQMC algorithm:
a random Game of Life, death and annihilation

Start with $N$ (positive) walkers on $D_0$, an initial value of $S$, and time-step $\tau$

- Spawning (birth) processes
- (Diagonal) death/cloning processes
- Annihilation step
- Adjust Shift (in constant $N$ mode)

$$S \rightarrow S - \frac{1}{A\tau} \ln \frac{N_{current}}{N_{old}}$$

Pictorial example

\[ N_w = \sum_{i} |N_i| = 11 \]

Normalisation = \[ \frac{1}{\sqrt{\sum_{i} N_i^2}} = \frac{1}{\sqrt{19}} \]
Spawning

spawning event

configuration space
Death
Death

configuration space

\[ i \]
Annihilation
Annihilation

configuration space

\( i \)
The rules of the “Game of Life”
(derived from the underlying imaginary-time S.E.)

Probability of death

\[ p_d = \tau |H_{ii} - E_{HF} - S| \]

Probability to spawn new walker

\[ p_s = \tau \frac{|H_{ij}|}{p_{gen}(j|i)} \]

\[ \sum_j p_{gen}(j|i) = 1 \]

\[ p_{gen}(j|i) \sim (N^2M^2 + NM)^{-1} \]

If \( H_{ij} < 0 \), child has same sign as parent.
If \( H_{ij} > 0 \) child has opposite sign of parent.
The projected energy
(non-variational)

\[ E = \frac{\langle D_0 | H | \Psi \rangle}{\langle D_0 | \Psi \rangle} \]
\[ = \sum_j \langle D_0 | H | D_j \rangle \langle D_j | \Psi \rangle \]
\[ = E_{HF} + \sum_{j \in \text{doubles}} \langle D_0 | H | D_j \rangle \frac{C_j}{C_0} \]

where \( \frac{C_j}{C_0} = \frac{N_j}{N_0} \)
$\text{Be}_2$ (cc-pVTZ). $N_{\text{FCI}} = 346,485$ determinants

Graph showing the evolution of wavefunction and energy over iterations. The figure includes lines for Exact $\Psi$, $\langle \Psi \rangle$, $\Psi(\tau)$, Shift, $E(\tau)$, and FCI, with iterations ranging from 0 to 100,000.
$\text{Be}_2$ (cc-pVTZ). $N_{\text{FCI}} = 346,485$ determinants

![Graph showing iterations vs. energy shifts for $\text{Be}_2$ (cc-pVTZ)]
H2O (all electron, cc-pVDZ, $452 \times 10^6$ determinants)

- **Variable shift mode**
- **Coherent exponential growth**
- **Incoherent exponential growth**

**“Annihilation plateau”**
Comparison with existing FCI

TABLE I. Results for systems with FCI comparisons. The geometries for the N$_2$ molecule were eqm: 2.068\,\textit{a}_0, stretched: 4.2\,\textit{a}_0, and C$_2$: 1.272 73 Å. The geometry for the water molecule was taken from Ref. 35. The working space includes all point group symmetry of the molecule from $D_{2h}$ or the largest available subset thereof. All systems had core electrons frozen apart from H$_2$O. $N_{\text{FCI}}$ is the size of the FCI space in the $D_{2h}$ point group ($C_{2v}$ for H$_2$O. The digit in italics for $E_{\text{total}}$, represents the first uncertain digit. $N_c$ is the number of walkers required to achieve the plateau. $f_c = N_c / N_{\text{FCI}}$.

<table>
<thead>
<tr>
<th>System</th>
<th>$(N,M)$</th>
<th>$N_{\text{FCI}} / 10^6$</th>
<th>$N_c / 10^6$</th>
<th>$f_c$</th>
<th>$E_{\text{total}}$</th>
<th>$E_{\text{FCI}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne: aug-cc-pVDZ</td>
<td>(8,22)</td>
<td>6.69</td>
<td>0.21</td>
<td>0.031</td>
<td>$-128.70949$</td>
<td>$-128.709476$</td>
<td>33</td>
</tr>
<tr>
<td>C$_2$: cc-pVDZ</td>
<td>(8,26)</td>
<td>27.9</td>
<td>15.0</td>
<td>0.538</td>
<td>$-75.7299$</td>
<td>$-75.729853$</td>
<td>34</td>
</tr>
<tr>
<td>H$_2$O: cc-pVDZ</td>
<td>(10,24)</td>
<td>451</td>
<td>26</td>
<td>0.058</td>
<td>$-76.24186$</td>
<td>$-76.241860$</td>
<td>35</td>
</tr>
<tr>
<td>N$_2$-eqm: cc-pVDZ</td>
<td>(10,26)</td>
<td>541</td>
<td>270</td>
<td>0.499</td>
<td>$-109.27649$</td>
<td>$-109.276527$</td>
<td>33</td>
</tr>
<tr>
<td>N$_2$-stretched: cc-pVDZ</td>
<td>(10,26)</td>
<td>541</td>
<td>345</td>
<td>0.637</td>
<td>$-108.9669$</td>
<td>$-108.96695$</td>
<td>36</td>
</tr>
</tbody>
</table>
New systems

TABLE II. Predicted FCI results. The geometries of the molecules were (in Å): CN (1.1941), HF (0.91622), CH₄ (rCH₁ = 1.087728), CO (1.1448), H₂O (rOH = 0.975512, θ = 110.565°) (Ref. 35), O₂ (1.2074), and NaH (1.885977). CN and O₂ orbitals were constructed from a restricted open-shell HF calculation with a spin multiplicity of two and three, respectively. CN, CH₄, CO, and O₂ had frozen core electrons. The number in brackets represents the error in the previous digit, obtained through a Flyvbjerg–Petersen blocking analysis (Ref. 37) of E(τ).

<table>
<thead>
<tr>
<th>System</th>
<th>(N,M)</th>
<th>N₉CI/10⁶</th>
<th>Nₖ/10⁶</th>
<th>fₖ</th>
<th>Eₜotal</th>
<th>E_CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be: cc-V5Z</td>
<td>(4,91)</td>
<td>2.11</td>
<td>0</td>
<td>0</td>
<td>-14.64638(2)</td>
<td>-14.64629</td>
</tr>
<tr>
<td>CN: cc-pVDZ</td>
<td>(9,26)</td>
<td>246</td>
<td>173</td>
<td>0.704</td>
<td>-92.4938(3)</td>
<td>-92.49164</td>
</tr>
<tr>
<td>HF: cc-pCVDZ</td>
<td>(10,23)</td>
<td>283</td>
<td>0.998</td>
<td>0.0035</td>
<td>-100.27098(3)</td>
<td>-100.27044</td>
</tr>
<tr>
<td>CH₄: cc-pVDZ</td>
<td>(8,33)</td>
<td>419</td>
<td>377</td>
<td>0.898</td>
<td>-40.38752(1)</td>
<td>-40.38974</td>
</tr>
<tr>
<td>CO: cc-pVDZ</td>
<td>(10,26)</td>
<td>1080</td>
<td>777</td>
<td>0.719</td>
<td>-113.05644(4)</td>
<td>-113.05497</td>
</tr>
<tr>
<td>H₂O: cc-pCVDZ</td>
<td>(10,28)</td>
<td>2410</td>
<td>47.4</td>
<td>0.0196</td>
<td>-76.28091(3)</td>
<td>-76.28028</td>
</tr>
<tr>
<td>O₂: cc-pVDZ</td>
<td>(12,26)</td>
<td>5409</td>
<td>2651</td>
<td>0.490</td>
<td>-149.9875(2)</td>
<td>-149.98562</td>
</tr>
<tr>
<td>NaH: cc-pCVDZ</td>
<td>(12,32)</td>
<td>205300</td>
<td>63.8</td>
<td>0.00031</td>
<td>-162.6090(1)</td>
<td>-162.60901</td>
</tr>
</tbody>
</table>
How to reduce $N_w$ while maintaining FCI accuracy?
Overview of initiator-FCIQMC

Start with $N$ (positive) walkers on $D_0$, an initial value of $S$, and time-step $\tau$

- Spawning (birth) processes
- Survival of the fittest
  [Cleland, Booth, Alavi, J Chem Phys, 132, 041103, (2010)]
- (Diagonal) death/cloning processes
- Annihilation step
- Adjust Shift (in constant $N$ mode)
Survival of the fittest and “initiators”

If $D$ is empty, child of $P$ spawned onto $D$ survives only if $P$ is an initiator ($N_P > n_{add}$)

The value of $n_{add}$ is not crucial, as long as it is sensibly chosen. We typically use $n_{add} = 2$ or 3.

Initiators can bring to life new determinants
Convergence of energy of $N_2$ with i-FCIQMC
Is the initiator method exact?

• In the limit of large walker number, all determinants acquire an occupation, and therefore all newly spawned walkers survive the test of “survival of the fittest”.
• Therefore the large walker number limit of “i-FCIQMC” is FCIQMC.
• Since the large walker limit of FCIQMC is FCI, we have that the large walker limit of i-FCIQMC is FCI.
Convergence of i-FCIQMC with walker number.

$N_2$ in cc-pVDZ

$N_{\text{FCI}} = 5.4 \times 10^8$
The effect of varying $n_{\text{add}}$

CO in cc-pVQZ

$N_{\text{FCI}} = 4.7 \times 10^{14}$

![Graph showing the number of walkers at the reference vs. error in total energy/millihartrees. The graph includes data for various $n_a$ values: $n_a = 1$, $n_a = 2$, $n_a = 3$, $n_a = 4$, $n_a = 6$, and $n_a = 10$. The x-axis represents the total number of walkers, $N_{\text{tot}} / 10^6$, and the y-axis represents the error in total energy/millihartrees.]}
The Be$_2$ (VTZ) with i-FCIQMC: a simulation with 2,000 walkers
Energy, compared with subspace diagonalisations (c.f. Stochastic CI)
The instantaneous $i$-FCIQMC wavefunction is very coarse-grained representation of the exact wavefunction (Be$_2$-VTZ, $N_{FCI}=346,485$, $N_w=2,000$)
But the **time-averaged** $i$-FCIQMC wavefunction with 2,000 walkers (Be$_2$, VTZ, $N_{\text{FCI}} = 346485$) is essentially perfect.
Scaling: $N_w$ versus $N_{\text{FCI}}$


\[ N_w \sim N_{\text{FCI}}^{0.157} \]

i-FCIQMC, $N_w$ required to achieve 50,000 walkers on the HF determinant.
The set of initiators is dynamic and self-selecting

• Black-box method - no knowledge of the wavefunction is assumed.
• **Key parameter is the number of walkers**
  • Increase until convergence is achieved.
  • We usually aim for enough walkers so that about ~50,000 have accumulated on the HF. (This is a conservative criterion)
• CPU time is proportional to walker number
• On the downside: it is difficult to know *a priori* how many walkers are needed to achieve desired accuracy.
• In practice, ~200M walkers is sufficient for systems we have so far looked at (first row dimers in VQZ basis sets, Cr2, 54-electron UEG)
Parallel scaling

![Graph showing parallel scaling with lines for Ideal Scaling and FCIQMC Scaling.](image-url)
Occupation number representation

A determinant is uniquely specified by a binary-string of length $2M$

$$i = [1, 1, 0, 0, 1, 1, 0, \ldots, 0, 1]$$

$N1's$, $2M-N0s$

A bit string has a unique and invertible index, $I$, associated with it

$$I = \sum_{i=0}^{2M-1} n_i 2^i \quad (n_i = 0, 1)$$

$I \leftrightarrow i$
Implications

(1) **Compact storage.** Given a machine with 64-bit integers [INTEGER*8] the number of integers required to specify the index of a determinant is:

\[ \left\lfloor \frac{2M}{64} \right\rfloor \]

(2) A list of a **random** selection of determinants can always be uniquely ordered.

\[ I_1 < I_2 < I_3 \ldots \]

Such ordered lists are easy to search: crucial for the annihilation step!
Two further uses of bit-string representation of determinants

**Excitation generation**: select a pair of 1’s and a pair of 0’s to interchange. The basic step of FCIQMC is very fast (~$10^8$ per core per second)

**Parallelisation**: using Hash functions. List of occupied determinants are distributed over a multi-processor machine via

$$H(I) \mod N_{\text{proc}}$$

which returns a **unique but uniformly distributed** integer $[0,N_{\text{proc}}-1]$. *All walkers on a given determinant are located on the same core, which facilitates the annihilation step.*
What we store is an ordered list of instantaneously occupied determinants, together with the signed number of walkers on each

\[ I_1 < I_2 < \ldots < I_{N_d} \]

\[ N[I_1] \quad N[I_2] \quad \ldots N[I_{N_d}] \]

\[ N[I_i] = \text{signed number of walkers on } I_i \]

\[ \sum_{i}^{N_d} |N[I_i]| = N_w \]
Annihilation is the crucial “fermionic” step

The newly spawned walkers are inserted into the main list of walkers at the points

List of parent determinants

\[ I_1 < I_2 < \ldots < I_{Nd} \]

Sorted List of newly spawned walkers

\[ J_1 < J_2 < \ldots J_{Ns} \]

Loop over the J-list

For each \( J_i \), see if there is a member of the I-list equal to it.
If so, update

\[ N[I_i] \rightarrow N[I_i] + N[J_i] \]

This takes care of the annihilation step. If \( N[I_i] = 0 \) as a result, \( I_i \) is removed from the I-list
Otherwise, locate the position for which

\[ I_i < J_j < I_{i+1} \]
This produces a merged list with updated occupations

\[ I_1 < I_2 < J_1 < \ldots \]
\[ N[I_1] \quad N[I_2] \quad N[J_1] \ldots \]

Merging and annihilations takes

\[ \mathcal{O}[N_s \log N_d] \]

Typically, this step costs only a few percent of the overall CPU time
Electron affinities with i–FCIQMC: \[ \text{A} + e^- \rightarrow \text{A}^- \]

Comparison with Expt* (relativistically corrected)

\[ \text{aug-VDZ} = [4s3p2d] \sim 23, \text{aug-VTZ} = [5s4p3d2f] \sim 46, \text{aug-VQZ} = [6s5p4d3f2g] \sim 80, \]

\[ \text{aug-VXZ} \sim (1/3)(X+1)(X+3/2)(X+2) + (X+1)^2 \]


First-row Diatomics

Size of spaces and required Nw’s to accumulate 50,000 walkers on the HF det.

<table>
<thead>
<tr>
<th>Diatomic</th>
<th>Basis</th>
<th>N, 2M</th>
<th>N_FCI</th>
<th>N_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>VQZ</td>
<td>8, 216</td>
<td>6.1 x 10^11</td>
<td>2.6 x 10^6</td>
</tr>
<tr>
<td>CN</td>
<td>VQZ</td>
<td>9, 216</td>
<td>4.8 x 10^13</td>
<td>7.6 x 10^7</td>
</tr>
<tr>
<td>N2</td>
<td>VQZ</td>
<td>10, 216</td>
<td>2.4 x 10^14</td>
<td>3.0 x 10^7</td>
</tr>
<tr>
<td>CO</td>
<td>VQZ</td>
<td>10, 216</td>
<td>4.7 x 10^14</td>
<td>6.0 x 10^7</td>
</tr>
<tr>
<td>NO</td>
<td>VQZ</td>
<td>11, 216</td>
<td>1.5 x 10^16</td>
<td>1.1 x 10^8</td>
</tr>
<tr>
<td>O2</td>
<td>VQZ</td>
<td>12, 216</td>
<td>6.4 x 10^16</td>
<td>5.9 x 10^7</td>
</tr>
<tr>
<td>F2</td>
<td>VQZ</td>
<td>14, 216</td>
<td>1.3 x 10^19</td>
<td>5.0 x 10^7</td>
</tr>
</tbody>
</table>

eg. note that the 14-electron F$_2$ is ~20% cheaper than the 10-electron CO, despite the fact that the space is 5 orders of magnitude larger!
### i-FCIQMC Diatomic dissociation energies in kcal mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Basis</th>
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<td>VQZ</td>
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<td>143.44(5)</td>
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<tr>
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Dissociation energies of some strongly correlated first-row molecules

(F12 correction added to VQZ)

Errors (kcal mol\(^{-1}\)) in the De and comparison to other methods

<table>
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<tr>
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<tr>
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<td>-1.1</td>
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<tr>
<td>CCSD(T)(^a)</td>
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<td>-1.5</td>
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<td>-0.6</td>
<td>-0.3</td>
<td>-1.0</td>
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<tr>
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<td>-0.3</td>
<td>-0.4</td>
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<td>0.5</td>
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(a) D. Feller and J. Sordo, J Chem Phys 2000, 113, 485
(b) L. Bytautas and K. Ruedenberg, J Chem Phys 2005, 122, 154110
(c) J.C. Grossman, J Chem Phys, 2002, 117, 1434
MO diagrams: the two leading determinants

Be$_2$

\begin{align*}
3\sigma & \quad 3\sigma \\
2\sigma^* & \quad 2\sigma^* \quad \circ \quad \circ \\
2\sigma & \quad 2\sigma
\end{align*}

C$_2$

\begin{align*}
3\sigma & \quad 3\sigma \\
2\pi & \quad 2\pi \\
2\sigma^* & \quad 2\sigma^* \quad \circ \\
2\sigma & \quad 2\sigma
\end{align*}

CN

\begin{align*}
3\sigma & \quad 3\sigma \\
2\pi & \quad 2\pi \\
2\sigma^* & \quad 2\sigma^* \quad \circ \\
2\sigma & \quad 2\sigma
\end{align*}

NO

\begin{align*}
2\pi^* & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\pi & \quad \uparrow \quad \uparrow \\
3\sigma & \quad \uparrow \\
2\sigma^* & \quad \uparrow \\
2\sigma & \quad \uparrow
\end{align*}

O$_2$

\begin{align*}
2\pi^* & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\pi & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
3\sigma & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\sigma^* & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\sigma & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow
\end{align*}

F$_2$

\begin{align*}
3\sigma^* & \quad \uparrow \quad \uparrow \\
2\pi^* & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
3\sigma & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\pi & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\sigma^* & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
2\sigma & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow
\end{align*}
Slip-flip and time-reversal symmetry

In the absence of a magnetic field, and for systems with even numbers of electrons, it is always permissible to take

\[ I = I_\alpha I_\beta \quad \quad N_\alpha = N_\beta \]

\[ \bar{I} = I_\beta I_\alpha \]

\[ |D_{I_\beta I_\alpha}\rangle = U_T |D_{I_\alpha I_\beta}\rangle \]

Form the linear combination

\[ |D_I\rangle \leftarrow \frac{1}{\sqrt{2}} [ |D_I\rangle \pm |D_{\bar{I}}\rangle ] \]

\[ S = \text{even} \]

\[ S' = \text{odd} \]
Semi-Stochastic i-FCIQMC

Select a small subset of determinants $\mathcal{D}$ (called the **deterministic** space)
Do part of the force update deterministically

$$-rac{dN_i}{d\tau} = (H_{ii} - S)N_i + \sum_{j\in\mathcal{D}}' H_{ij} N_j + \sum_{j\in\mathcal{D}'}' H_{ij} N_j$$

Death step as per FCIQMC
Spawning step as per i-FCIQMC

Sum computed exactly for given $N_j$ in $\mathcal{D}$

Nick Blunt has a **parallel** implementation of the SS method in the NECI code
Projected energy via a multi-determinant trial wavefunction

Select a subset of determinants $\mathcal{T}$ (need not be the same as $\mathcal{D}$)

$$
\psi_T = \sum_{i \in \mathcal{T}} c_i |D_i\rangle
$$

$c_i$ are a set of fixed coefficients obtained by diagonalising $H \in \mathcal{T}$

$$
E = \frac{\langle \Psi | H | \Psi_T \rangle}{\langle \Psi | \Psi_T \rangle} = \frac{\sum_{i \in \mathcal{CT}, j \in \mathcal{T}} C_i c_j H_{ij}}{\sum_{i \in \mathcal{T}} C_i c_i} = \sum_{i \in \mathcal{CT}} C_i h_i
$$

$h_i = \sum_{j \in \mathcal{T}} H_{ij} c_j, \quad i \in \mathcal{CT}$

$\mathcal{CT}$ is space of determinants connected to $\mathcal{T}$
FIG. 3 (color online). Relative efficiency of SQMC vs dimension |\mathcal{D}| of the deterministic space for the carbon dimer with a cc-pVTZ basis. Results are shown for trial wave functions of increasing size. The top two curves are for \mathcal{D} and \mathcal{T} generated with two applications of our iterative scheme. The 165 and 1766 determinant wave functions with some quadruple excitations have much higher efficiency than the 4282 determinant wave function without any. For this system, \(N \approx 10^9\).
Time-step in a.u. for $N_2$ in cc-pVXZ basis sets

\[ \tau (N_2) \]

\[ M \sim X^3 \]

\[ \tau \sim (N^2 M^2)^{-1} \]
Uniform Generation Scheme

\[ p_{\text{gen}}(A|I) = p_{\text{gen}}(B|I) = \ldots = \frac{1}{4} \]

\[ p_s(A|I) = \tau \frac{0.1}{\frac{1}{4}} = 0.4\tau \]

\[ p_s(B|I) = \tau \frac{0.001}{\frac{1}{4}} = 0.004\tau \]

The largest allowable \( \tau \) is set by \( p_s \leq 1 \)

\[ \rightarrow \tau = \frac{1}{0.4} = 2.5 \]

\[ \rightarrow p_s(A|I) = 1 \]

\[ p_s(B|I) = 0.01, \text{ etc} \]

\[ p(\text{to spawn}) = (3/4) \times .01 + (1/4) \times 1 = 0.2575 \]

Rejection ratio is high
Hamiltonian-Weighted Excitation Generation

Construct an algorithm to select $j$ from $i$ so that

$$P_{gen}(j|i) \propto |H_{ij}|$$

In the ideal case (where proportionality is exact), the spawning rate is constant:

$$p_s = \tau \ast const$$

$\tau$ can then be maximised with the condition $p_s \leq 1$ (and $p_d \leq 1$)

To do this exactly costs $O(N^2M^2)$
**Weighted Generation Scheme**

\[
\sum_{A} |H_{AI}| = 0.103
\]

\[
p_{gen}(A|I) = \frac{0.1}{0.103} = 0.971
\]

\[
p_{gen}(B|I) = \frac{0.001}{0.103} = 0.00971
\]

\[
p_{s}(A|I) = p_{s}(B|I) = 0.103\tau
\]

largest allowable \( \tau = 1/0.103 = 9.71 \)

\[
p_{s}(A|I) = p_{s}(B|I) = p_{s}(C|I) = p_{s}(D|I) = 1
\]

\[
p(to\ \text{spawn}) = 1
\]

Two advantages: allows larger timesteps, and minimises rejections
However, it is possible to devise a determinant selection algorithm based on a **Cauchy-Schwarz** decomposition of $H_{ij}$ which costs only $O(M)$ to compute!

In practice this allows $\tau$ to scale substantially better with system size, as well as lead to significant overall efficiency.
For opposite-spin excitations

\[ \sigma_i = \sigma_a \neq \sigma_j = \sigma_b \]

\[
\begin{array}{cc}
D_i & i & j \\
D_j & a & b
\end{array}
\]

\[ \langle ij|ab\rangle \leq \sqrt{\langle ia|ia\rangle \langle jb|jb\rangle} \]

\[ p(ij|ab) = p(ab|ij)p(ij) \]

\[ p(ab|ij) = p(a|i)p(b|j) \;
\text{[For same-spin, include exchange term]}\]

Select hole \( a \) according to:

\[ p(a|i) \propto \sqrt{\langle ai|ai\rangle} \]

\[ p(a|i) = \frac{\sqrt{\langle ai|ai\rangle}}{\sum_i \sqrt{\langle ai|ai\rangle}} \quad \leftarrow O(M) \]
tau for N2 with VXZ basis-sets

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Standard</th>
<th>Newexcitgen</th>
</tr>
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<tr>
<td>VDZ</td>
<td>1E-05</td>
<td>1E-04</td>
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<tr>
<td>VTZ</td>
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<td>1E-02</td>
</tr>
<tr>
<td>VQZ</td>
<td>1E-01</td>
<td>1E-00</td>
</tr>
</tbody>
</table>

Cost per walker per successful spawn per unit time

- VDZ: 0.0001, 0.0001, 0.0001
- VTZ: 0.0010, 0.0100, 0.1000
- VQZ: 0.0100, 0.1000, 1.0000

- Standard: Circles
- Newexcitgen: Squares
Reduced density matrices

The 1- and 2-electron RDMs are defined in the orbital basis as:

\[ \gamma_{q}^{p} = \langle \Psi | a_{p}^{\dagger} a_{q} | \Psi \rangle \]

\[ \Gamma_{pq}^{rs} = \langle \Psi | a_{r}^{\dagger} a_{s}^{\dagger} a_{q} a_{p} | \Psi \rangle \]

The 1-RDM can be obtained from the 2-RDM by tracing out an electron

\[ \gamma_{p}^{q} = \frac{1}{N - 1} \sum_{r} \Gamma_{pr}^{qr} \]

Normalisation conditions:

\[ \sum_{pq} \Gamma_{pq}^{pq} = \binom{N}{2} \]

\[ \sum_{p} \gamma_{p}^{p} = N \]
Properties such as $E$, $S^2$, electron density, forces, etc can be calculated via the 1 and 2-RDMs

$$\hat{O} = \sum_{ij} \hat{O}_{ij}$$

$$\langle \Psi | \hat{O} | \Psi \rangle = \Gamma_{rs}^{pq} \hat{O}_{rs}^{pq}$$

Energy

$$E = h_p^q \gamma_q^p + \frac{1}{2} g_{pq}^{rs} \Gamma_{rs}^{pq}$$

Nuclear gradients

Hellmann-Feynman+Pulay

$$\frac{\partial E}{\partial \mathbf{R}} = \gamma_q^p \frac{\partial h_p^q}{\partial \mathbf{R}} + \frac{1}{2} \Gamma_{pq}^{rs} \frac{\partial g_{pq}^{rs}}{\partial \mathbf{R}}$$

Spin

$$\langle S^2 \rangle = \frac{3}{4} N + \frac{1}{4} \sum_{ij} \sum_{\sigma} \Gamma_{i\sigma j\sigma}^{i\sigma j\sigma} - \frac{1}{2} \sum_{ij} \Gamma_{i\alpha j\beta}^{i\alpha j\beta} - \sum_{ij} \Gamma_{i\alpha j\beta}^{i\alpha j\beta}$$
Calculation of the RDMs

\[ \Gamma_{pq}^{rs} = \sum_i C_i^* C_j \text{ where } |j\rangle = a_r^\dagger a_s^\dagger a_q a_p |i\rangle \]

This is very expensive, because for each occupied determinant, i, need to search over all its double excitations.

Instead, use the fact that in FCIQMC, we **sample** all double-excitations according to the Hamiltonian matrix elements.

Therefore, we can use the **spawning step to stochastically sample** the contributions to the 2-RDM!

\[ \Gamma_{pq}^{rs} = \sum_{i \in pq} \frac{C_i C_j}{p[j|i]} \times p[j|i] \quad \text{Spawning probability} \]
In practice, replace the product of the $C_i$ coefficients with the time-average of the products of the walker populations

$$\Gamma_{pq}^{rs} \propto \sum_{i \in pq} \frac{\langle N_i N_j \rangle_\tau}{p[j|i]} \times p[j|i]$$

Normalisation is fixed by:

$$\sum_{pq} \Gamma_{pq} = \binom{N}{2}$$
When we do this, the result is not good!

Figure 6.1 – This data, corresponding to simulations on C\textsubscript{2} cc-pVTZ, is taken directly from Ref. [25], showing the very slow convergence of $E_{RDM}$ and significant error at large $N_w$, even once $E_P$ is well-converged.
Figure 7.1 – The diagonal elements of the 2-RDM are systematically overestimated in the uncorrected stochastic RDM method. This data corresponds to i-FCIQMC calculations run on $N_2$ cc-pVDZ, $r = 1.094 \text{Å}$ with 8 frozen core electrons and $N_w = 25000$. The 2-RDM was accumulated stochastically according to the method described in Section 6.1 for $\sim 5 \times 10^6$ iterations. The reals calculation uses $\gamma = 4$, $N_{occ} = 1$. 
What is wrong?

The diagonal matrix elements have a bias

\[ \Gamma_{pq}^{pq} \propto \sum_{i \in pq} \langle N_i^2 \rangle_\tau \]

The instantaneous populations fluctuate about their exact value:

\[ N_i = N_i^{ex} + \delta N_i \]

\[ \langle \delta N_i \rangle_\tau = 0 \]

But the time-average of the square shows a positive bias:

\[ \langle N_i^2 \rangle_\tau = (N_i^{ex})^2 + \langle (\delta N_i)^2 \rangle_\tau \]
The solution: replica trick

Run two independent simulations in parallel and use the instantaneous populations on the two replicas to compute the RDM!

\[
\Gamma_{pq}^p \propto \sum_{i \in \{pq\}} \langle N_i^{(1)} N_i^{(2)} \rangle_{\tau}
\]

Since the two populations are \textit{strictly uncorrelated}, it is easy to show

\[
\langle \delta N_i^{(1)} \delta N_i^{(2)} \rangle_{\tau} = 0
\]

Therefore:

\[
\Gamma_{pq}^p \propto \sum_{i \in \{pq\}} \langle N_i^{(1)} \rangle_{\tau} \langle N_i^{(2)} \rangle_{\tau}
\]
Figure 8.1 – The systematic sampling bias affecting the diagonal elements of the 2-RDM is removed when using the replica sampling method described in Section 8.1. This data corresponds to i-FCIQMC calculations run on $\text{N}_2$ cc-pVDZ, $r = 1.094 \text{ Å}$ with 8 frozen core electrons and $N_w = 25000$. The 2-RDMs are well-converged with respect to simulation time, accumulated stochastically for $\sim 5 \times 10^6$ iterations. The reals calculations use $\gamma = 4$, $N_{\text{occ}} = 1$. Section 7.1 details how these errors are calculated. Different bin widths are used for diagonal and off-diagonal elements to allow the features of each distribution to be clearly seen.

Overy, Booth, Blunt, Shepherd, Cleland, Alavi, JCP, 141, 244117 (2014)
Figure 8.17 – Comparing the uncorrected and replica-sampled RDMs through values of $E_{\text{RDM}}$ for $C_2$ cc-pVTZ. This refers directly back to Figure 6.1, though all values have been newly generated for this plot. Uncorrected RDMs were calculated with the integer i-FCIQMC algorithm (consistent with Ref. [25]), whilst replica-sampled RDMs use the real coefficients algorithm with $\chi = 4$, $N_{\text{occ}} = 1$, to represent the best quality RDM available with the techniques presented in this chapter.
Figure 9.1 – Energies and internuclear forces in the H₂ cc-pVTZ binding curve. The inset of the upper panel shows the i-FCIQMC gradients plotted as tangent lines on the
**FIG. 1.** Top: Potential energy profile for the N-N bond dissociation of N$_2$ relative to the energy of two isolated nitrogen atoms in the electronic ground state. Bottom: corresponding forces at one nitrogen atom computed using analytic gradients from i-FCIQMC reduced density matrices, compared to FCI with numerical differentiation. Results are identical within the accuracy of the numerical differentiation. The respective minimum energy ($E_{\text{min}} = -0.2685$ a.u.) and force ($F_{\text{min}} = 0.0$ a.u.) at an internuclear distance of 2.144 a.u. is indicated by the blue symbols. All results were obtained with a 6-31G basis set.

**FIG. 2.** Absolute forces acting on the oxygen and hydrogen atoms in a H$_2$O molecule computed using i-FCIQMC and FCI with a 6-31G and cc-pVTZ basis set (the sign corresponds to the z-component of the force vector). The data were acquired for symmetric displacements of the hydrogen atoms from the equilibrium geometry. The abscissa indicates the OH bond length of the respective molecular geometry.
# Dipole moment of CO

Thomas et al, JCP, 143, 054108 (2015)

## Table

<table>
<thead>
<tr>
<th>Method</th>
<th>( \mu_z/ea_0 ) (aug-cc-pVXZ-DK)</th>
<th>( \mu_z/ea_0 ) (CBS (DT))</th>
<th>( \mu_z/ea_0 ) (CBS (TQ))</th>
</tr>
</thead>
</table>
| HF         | \(-0.10135\)                     | \(-0.10369\)                | ...                         | ...
| MRCI       | \(0.07175\)                      | \(0.07066\)                 | \(0.07419\) \(0.06929\)    | ...
| CCSD       | \(0.06829\)                      | \(0.05087\)                 | \(0.05278\) \(0.04681\)    | ...
| \(i\)-FCIQMC | \(0.05893(3)\)                 | \(0.0474(4)\)               | \(0.05112\) \(0.0437\)      | ...

Expt \(0.044-0.048\)
FIG. 3. Calculated dipole moments for CO in an aug-cc-pVDZ-DK basis as a function of the number of walkers. Increasing the walker population is beneficial in reducing the stochastic error in the final result, but a qualitative description of the system is achieved at rather modest $N_w$, as indicated by the fineness of the scale presented here.
Dipole moment of CO: comparison with CCSD

TABLE II. Comparison of obtained dipole moments of CO in a small cc-pVDZ basis to the deterministic FCI result. As in Table I, at all levels of theory, the two core orbitals were held frozen and neither relaxed nor optimised for the response of an electric field. The $i$-FCIQMC result being in error by less than 0.1%, the density matrices derived therefrom are thus shown to be of near-FCI quality. The coupled-cluster results—obtained by finite differentiation ($\pm 2 \times 10^{-5} \, E_h \, e^{-1} \, a_0^{-1}$) using the MOLPRO$^{46, 66}$ and MRCC$^{67}$ codes—are slow to converge to the FCI limit, with quadruple excitations needed for high accuracy.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\mu_z/e\alpha_0$</th>
<th>Absolute relative error (%)</th>
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</tr>
<tr>
<td>MRCI</td>
<td>0.0973</td>
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<tr>
<td>CCSD</td>
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<td>9.94</td>
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<tr>
<td>CCSDT</td>
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<td>CCSDTQP</td>
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</tr>
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</tr>
<tr>
<td>FCI</td>
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</table>
Polarisabilities: finite fields

FIG. 4. Calculated dipole polarisabilities for the Ne atom in an aug-cc-pVTZ-DK basis with different applied field strengths, $\xi_z$. As in the section on the dipole moment of CO, the i-FCIQMC calculations were performed using $6(10^8)$ walkers, a dynamic time step, and the adjustable parameters $N_{\text{occ}} = 1$, $\chi = 4$, $\kappa = 0.01$, and $n_a = 3.0$. Sufficiently small fields establish the required pseudo-linear relationship between the polarisability and the applied field, but too small a field gives rise to large stochastic errors. This initial
Polarisabilities of rare-gas atoms

TABLE IV. $i$-FCIQMC polarisabilities of the noble gases Ne, Ar, and Kr, obtained in aug-cc-pVTZ-DK and aug-cc-pVQZ-DK basis sets, along with the extrapolated complete-basis-set limit results. The number in brackets indicates the error in the preceding digit, obtained as the standard deviation of the results of three independent calculations. The experimental results are shown for comparison.\textsuperscript{71,72} The $i$-FCIQMC calculations were performed using $\Theta \left(10^8\right)$ walkers, with the adjustable parameters $N_{\text{occ}} = 1$, $\chi = 4$, $\kappa = 0.01$, and $n_a = 3.0$, and run for 48 hours on 320 cores.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_{zz}/e^2a_0^2E_h^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aug-cc-pVTZ-DK</td>
</tr>
<tr>
<td>Ne</td>
<td>2.42(1)</td>
</tr>
<tr>
<td>Ar</td>
<td>10.855(5)</td>
</tr>
<tr>
<td>Kr</td>
<td>16.81(4)</td>
</tr>
</tbody>
</table>
Excited States: Gram-Schmidt Projection

\[ H_1 = H \]
\[ H_2 = H - |\Psi_1\rangle \frac{\langle \Psi_1 | \Psi_2 \rangle}{\langle \Psi_1 | \Psi_1 \rangle} \]

\[ H_k = H - \sum_{j}^{k-1} |\Psi_j\rangle \frac{\langle \Psi_j | \Psi_k \rangle}{\langle \Psi_j | \Psi_j \rangle} \]

Population 1
C2 molecule (6-31G*)
Eqn geometry
Excited States: Hubbard Model

<table>
<thead>
<tr>
<th>FCI</th>
<th>FCIQMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14.7147075</td>
<td>-14.7147079(2)</td>
</tr>
<tr>
<td>-13.1868974</td>
<td>-13.1868931(74)</td>
</tr>
<tr>
<td>-13.1265762</td>
<td>-13.1265734(63)</td>
</tr>
<tr>
<td>-12.9714039</td>
<td>-12.9714105(12)</td>
</tr>
<tr>
<td>-12.9519154</td>
<td>-12.952030(264)</td>
</tr>
<tr>
<td>-12.9252960</td>
<td>-12.925266(28)</td>
</tr>
</tbody>
</table>

TABLE I. Energy/t for the lowest-energy eigenstates for the 14-site, 1D periodic Hubbard model, at $U/t = 1$. Only the $K = 0$, $M_s = 0$ sector was used. The FCI values are always within 2 standard errors, which are of size $\sim 10^{-4} - 10^{-6}E_h$ for excited states. $1.8 \times 10^7$ iterations were performed, with approximately $2 \times 10^4$ walkers used per state. A CISD space was used to form both the deterministic and trial spaces$^{18,23}$. The initiator adaptation was not used, in order to remove initiator error to assess other potential biases instead.
Excited States of C$_2$: comparison with DMRG

![Graphs showing energy levels for different states at two different distances, R = 1.24253 Å and R = 2.0 Å.]

**FIG. 5.** Left: $R = 1.24253$ Å. Right: $R = 2.0$ Å for C$_2$ in a cc-pVQZ basis. Initiator error convergence for four low-energy states obtained from simulations with $M_s = 0$, $S = \text{even}$ and restricted to $\Sigma_g$. Energies are plotted relative to the energy obtained at the largest walker population, $3.2 \times 10^7$ walkers for $R = 1.25$ Å and $1.6 \times 10^7$ walkers for $R = 2.0$ Å. Simulations used a deterministic space of size $D = 10^4$ and a trial space of size $T = 2 \times 10^8$. Error bars are plotted but are too small to be visible. As for the equivalent cc-pVTZ plot, the initiator error is larger for excited states than for the ground state. The initiator error is larger in the stretched regime for all states. The dashed line shows 1m$E_h$, from which it is seen that 1m$E_h$ accuracy is achieved with less than $2 \times 10^6$ walkers in the most challenging case.
Excited States of C2: Binding Curves in VQZ basis

FIG. 6. Four low-energy states of C2 in a cc-pVQZ basis, obtained from simulations with $M_s = 0$, $S =$ even and restricted to $\Sigma_g$. Simulations used $1.6 \times 10^7$ walkers per state, with a deterministic space of size $D = 10^4$ and a trial space of size $T = 2 \times 10^3$. Error bars are plotted but are too small to be visible, typically of order $10^{-6} - 10^{-5}E_h$, whereas initiator error is expected to be of order $10^{-4}E_h$. 
FCIQMC as the CI solver in CASSCF

\[ \Psi = e^{-\kappa} \sum_{i \in A} C_i |D_i\rangle \]

\[ \kappa = \sum_{p>q} \kappa_{pq} [E_{pq} - E_{qp}], \quad E_{pq} = \sum_\sigma a_{p\sigma}^* a_{q\sigma} \]

\[ \frac{\partial E}{\partial \kappa_{pq}} = \langle \Psi | [H, E^{-}_{pq}] | \Psi \rangle \]

\[ \tilde{\phi}_p = \cos(\kappa_{pq}) \phi_p + \sin(\kappa_{pq}) \phi_q \]
\[ \tilde{\phi}_q = \cos(\kappa_{pq}) \phi_q - \sin(\kappa_{pq}) \phi_p \]

Core

Virtual

Active
\( n \) electrons
\( m \) orbitals

Core
Figure 7.7: The convergences of (6, 6) and (10, 10) CASSCF calculations for benzene (upper panel) and naphthalene (lower panel) respectively, illustrating the close agreement between the deterministic and stochastic formulations. The energy of each stochastic macroiteration is given as the average of those of three independent calculations, and the error bars by the corresponding standard deviation. In both the (6, 6) and the (10, 10) examples, the convergence was achieved with $\Theta(10^5)$ walkers.
Phenanthrene, (14,14)

$E/E_h = -5.3609 \times 10^2$

Independent runs
Average

[Graph showing the relationship between $E/E_h$ and a range of values from 0 to 10, with the graph indicating a downward trend and labels for independent runs and average.]
Triphenylene, (18,18)

\begin{align*}
E/E_h &= -6.887 \times 10^2 \\
\end{align*}
Coronene, \((24,24)\)
F12: capturing the e-e cusp

\[
\left( \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \Psi(r_{12} = 0)
\]
F12 methodology: perturbative correction employing a geminal basis

[Torheyden, Valeev JCP 131, 171103 (2009), Kong, Valeev, JCP, 135, 214105, (2011)]

\[
E = E_{FCI} + E_{[2]}S + E_{[2]}R_{12}
\]

\[
E_{[2]}S = f^a_t^q \gamma^p_q
\]

\[
E_{[2]}R_{12} = \frac{1}{2} V_{xy}^{pq} + \frac{1}{16} t_{rs}^{vw} (B_{vw}^{xy} \Gamma_{pq}^{rs} - X_{vw}^{xy} \Phi_{pq}^{rs}) t_{xy}^{pq}
\]

\[
V_{pq}^{xy} = \frac{1}{2} \left[ \nu_{pq}^{rs} - g_{rs}^{ta} \gamma^u_t r_{ua}^{xy} - \frac{1}{2} g_{rs}^{tu} r_{tu}^{rs} \right] \Gamma_{pq}^{rs}
\]

\[
r_{pq}^{xy} = \hat{S}_{xy} \langle p' q' | f(r_{12}) | xy \rangle
\]
F12-corrections with plane-wave basis sets are extremely effective

Valeev-Torheyden-Kong [2]_{R12}+[2]_2 corrections for the C_2 binding curve, based on i-FCIQMC calculated density matrices

What is the “best” basis to get a maximally sparse description

Löwdin (1956): The **natural orbital** basis

The one-particle basis that diagonalises the reduced one-particle density matrix

\[ \gamma_{pq} = \langle \Psi | a_p^\dagger a_q | \Psi \rangle \]

\[ \sum_q \gamma_{pq} \nu_{qi} = n_i \nu_{pi} \]

i-th natural orbital

natural orbital occupation number

\[ 0 \leq n_i \leq 1 \]
Stretched N$_2$ molecule
STO-3G
FCI wavefunction in UHF and UNO basis
**Uniform electron gas**

\[
u_k = \frac{1}{\sqrt{\Omega}} e^{i \mathbf{k} \cdot \mathbf{r}} \quad \mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z)
\]

\[
L = \Omega^{1/3} = \left( \frac{4\pi N}{3} \right)^{1/3} \times r_s
\]

\[
\frac{1}{2} k_{\text{max}}^2 \leq E_c \quad k_{\text{max}}^2 = \left( \frac{2\pi}{L} \right)^2 n_{\text{max}}^2
\]

\[
\langle k_1 k_2 | r_{12}^{-1} | k_3 k_4 \rangle = \frac{4\pi}{\Delta k^2} \delta_{k_1 + k_2, k_3 + k_4}
\]

\[
\Delta k = k_3 - k_1
\]
UEG cutoffs and size of space

N=54 electrons, $r_s=1$

<table>
<thead>
<tr>
<th>$n_{\text{max}}^2$</th>
<th>$E_c$(Ry)</th>
<th>#spin-orbitals</th>
<th>size of space</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.63</td>
<td>294</td>
<td>3.70E+054</td>
</tr>
<tr>
<td>13</td>
<td>13.82</td>
<td>406</td>
<td>4.00E+062</td>
</tr>
<tr>
<td>16</td>
<td>17.01</td>
<td>514</td>
<td>2.33E+068</td>
</tr>
<tr>
<td>49</td>
<td>52.11</td>
<td>2838</td>
<td>2.10E+108</td>
</tr>
</tbody>
</table>
UEG $r_s = 0.5$ au

Uniform electron gas for N=14 system: FN-DMC(bf) vs i-FCIQMC

Correlation energy (a.u. per elec.) vs $r_s$ (a.u.)

-0.045 -0.040 -0.035 -0.030 -0.025 -0.020

DMC

FCIQMC

i-FCIQMC: James Shepherd
DMC calculations be P. Rios-Lopez and R. Needs
Uniform electron gas: fixed node error in DMC

![Graph showing fixed node error vs. $r_s$]
Real Solids: complex wavefunctions

LiH
(3x3x3 cell, 54 electrons, 54 bands) $N_{\text{FCI}} \sim 10^{30}$
Equation of State
comparison with MP2, CCSD, CCSD(T) computed using VASP
<table>
<thead>
<tr>
<th></th>
<th>LiH</th>
<th>C</th>
<th>BN</th>
<th>AlP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>-2.386</td>
<td>-8.039</td>
<td>-7.149</td>
<td>-4.629</td>
</tr>
<tr>
<td>CCSD</td>
<td>-2.454</td>
<td>-7.295</td>
<td>-6.572</td>
<td>-4.107</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-2.483</td>
<td>-7.545</td>
<td>-6.782</td>
<td>-4.347</td>
</tr>
<tr>
<td>Expt.</td>
<td>-2.487</td>
<td>-7.545</td>
<td>-6.758</td>
<td>-4.322</td>
</tr>
</tbody>
</table>

**TABLE I:** Cohesive energies (eV/atom) evaluated within the quantum chemical hierarchy. Experimental values have been corrected for zero point vibration energies.
Finite-size convergence of the cohesive energy
Spin gap of NiO

(2x1x1 cell, 32 electrons, 38 bands)
3-Band Hubbard Model of a Cuprate

10 (Cu) sites with 10 holes (half-filling)

\[ \hat{H} = \sum_{i,\sigma} (\varepsilon_d - \mu) d_{i,\sigma}^\dagger d_{i,\sigma} + \sum_{i,\nu,\sigma} (\varepsilon_{p,\nu} - \mu) p_{i,\nu,\sigma}^\dagger p_{i,\nu,\sigma} \\
+ \sum_{i,j,\nu,\sigma} (t_{i,j,\nu} d_{i,\sigma}^\dagger p_{j,\nu,\sigma} + \text{h.c.}) + \sum_{i,\nu,j,\kappa,\sigma \neq i,j} t'_{i,j,\nu} p_{i,\kappa,\sigma}^\dagger p_{j,\nu,\sigma} \\
+ \sum_{i} U_d d_{i,\uparrow}^\dagger d_{i,\uparrow} d_{i,\downarrow}^\dagger d_{i,\downarrow}. \]

(1)

Table 1. Parameters for a three-band model (in eV) calculated with a constrained first principles calculation for La$_2$CuO$_4$ done by Hybertsen et al. [12].

<table>
<thead>
<tr>
<th>$\Delta$</th>
<th>$t'$</th>
<th>$t''$</th>
<th>$U_d$</th>
<th>$U_p$</th>
<th>$U_{pd}$</th>
<th>$U_{pp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>1.3</td>
<td>0.65</td>
<td>10.5</td>
<td>4</td>
<td>1.2</td>
<td>0</td>
</tr>
</tbody>
</table>
3-Band Hubbard model energies

\[ N_{FCI} = \left( \binom{30}{5} \right)^2 \approx 20 \times 10^9 \]

RHF: \(-9.5206318541964\)

UHF: \(-15.2905361816484\)

Exact: \(-15.817 (5)\)

\[ N_w \approx 10^9 (\text{UHF basis}) \]

\[ N_w \approx 10^8 (\text{RHF basis}) \]
Which orbitals to use: RHF or UHF?

RHF

Coefficient $C_i$ in $\psi = \sum_i C_i \cdot D_i$

Energy of Determinant $E_i$ / a.u.
Which orbitals to use: RHF or UHF?

UHF

Coefficient $C_i$ in $\psi = \sum C_i \psi_i$

Energy of Determinant $E_i / \text{a.u.}$
Natural Orbitals: RNO or UNO?
Natural Orbitals: RNO or UNO?

UNO

Coefficient $C_i$ in $\psi = \sum C_i D_i$

Energy of Determinant $E_i$ / a.u.
Conclusions and outlook

- FCIQMC is a very promising QMC approach to the quantum chemical FCI problem.
- It allows for the exact treat of sizeable electronic systems.
- As a new technique, it has significant development potential.
- A vast range of interesting physical systems, including strongly correlated solids, are now within realistic computational range.
- Implemented in MOLPRO
- Interfaced to VASP, QChem, Dalton, …
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Olle Gunnarsson