QMC: What are the odds of that?

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What are the questions?

- What are the statistics of estimates in QMC?
- Is the statistical error kept under control?
- Can better estimates be made?
- What influence does the nodal surface have on all this?

Here VMC and variance minimisation is examined analytically, and numerically for an isolated C atom.

Answered in three sections:

1 - Statistical analysis of 'standard sampling' VMC

2 - A new 'residual sampling' strategy, and an analysis of its statistics

3 - Statistical analysis of variance minimisation for both standard sampling and residual sampling
1 - Standard VMC

Basic equation of MC:

\[ \int_V f \, d\mathbf{R} \approx V \bar{f} \pm V \epsilon[f], \quad P(\mathbf{R}) = 1/V \]  \hspace{1cm} (1)

For estimate of operator \( \hat{f} \) \( f = \hat{f}_\psi \psi \) using unnormalised many-body trial wavefunction \( \psi^2(\mathbf{R}) \)

\[ \langle f \rangle \approx \frac{\psi^2 \bar{f}}{\psi^2} \pm \epsilon \left[ \psi^2 f, \psi^2 \right], \quad P(\mathbf{R}) = 1/V \]  \hspace{1cm} (2)

Using importance sampling and assuming the CLT is valid:

\[ \langle f \rangle \approx \bar{f} \pm \epsilon [f], \quad P(\mathbf{R}) = \lambda \psi^2 \]  \hspace{1cm} (3)

\[ \approx \bar{f} \pm \sqrt{\text{Var}[f]} \]  \hspace{1cm} (4)

- Importance sampling with \( \psi^2 \) makes the equations simple. Is it the best choice?
- Does the CLT hold? For \( r \) finite samples what replaces it?
- At the nodal surface \( \psi^2 \rightarrow 0 \) and \( E_L \rightarrow \pm \infty \). This may be bad sampling for \( f = f(E_L) \)
3N-d distribution → 1-d distribution

Why?: Easier to deal with the general case analytically.

A change of the random variable from spatial to energy:

\[
\langle E_L \rangle = \int_V \psi^2 E_L d\mathbf{R} \quad (5)
\]
\[
= \int_{-\infty}^{\infty} P_{\psi^2}(E) E dE \quad (6)
\]

with

\[
P_{\psi^2}(E') = \int_{E=E_L} \frac{P(\mathbf{R})}{|\nabla_{\mathbf{R}} E_L|} d^{3N-1}\mathbf{R} \quad (7)
\]

- A histogram of \( E_L \) approximates the ‘seed’ distribution \( P_{\psi^2} \)
- \( |\nabla_{\mathbf{R}} E_L| \) results from curvilinear co-ordinates and change of variables.
- Useless numerically, but useful analytically.
Form of $P_{\psi^2}$ and singularities in $E_L = T_L + V_L$

3 types for electron+atomic nuclei problems:

1 - singularity in nuclear potential part of $V_L$ not cancelled by singularity in $T_L$

2 - singularity in e-e potential not cancelled by singularity in $T_L$

3 - singularity in $T_L$ due to zeroes in $\psi(R)$

1&2 can be prevented by enforcing correct cusp conditions on $\psi^2$, 3 cannot.

**Type 3 only**

Introduce new co-ordinates $\mathbf{R} = \mathbf{X} + S_{\perp} \hat{n}$ for expansion about nodal surface:

- $\mathbf{X}$ vector to nodal surface, $S_{\perp}$ distance $\perp$ to nodal surface

$$\psi^2(\mathbf{R}) = a_2(\mathbf{X}) S_{\perp}^2 + a_3(\mathbf{X}) S_{\perp}^3 + \ldots$$  \hspace{1cm} (8)

$$E_L(\mathbf{R} + S_{\perp} \hat{n}) - E_0 = b_{-1}(\mathbf{X}) S_{\perp}^{-1} + b_0(\mathbf{X}) + b_1(\mathbf{X}) S_{\perp} + \ldots$$  \hspace{1cm} (9)

$$\Rightarrow$$

$$P_{\psi^2}(E) = \frac{1}{(E - E_0)^4} \left( e_0 + \frac{e_1}{(E - E_0)} + \ldots \right)$$  \hspace{1cm} (10)

$E^{-4}$ (‘leptokurtotic’ or ‘fat’) tails are general to any trial wavefunction with Type 3 singularities only.
Type 3 singularities only

All-electron Carbon. Trial wavefunction is multideterminant+jastrow+backflow.

Estimated seed probability distribution

General asymptotic form is:

$$\lim_{|E| \to \infty} P_{\psi^2}(E) = c_3 E^{-4} \quad E \to \pm \infty$$  \hspace{1cm} (11)

Also shown are $P_{\psi^2} = \frac{\sqrt{\sigma}}{\pi} \frac{\sigma^3}{\sigma^4 + (E - E_0)^4}$, and Gaussian with $E_0$ and $\sigma$ the mean and standard deviation of sampled $E_L$. 
Type 2 singularities only

All-electron C. Trial wavefunction is HF determinant.

Estimated seed probability distribution

General asymptotic form is:

$$\lim_{|E| \to \infty} P_{\psi^2}(E) = \begin{cases} 
   c_2 E^{-4} & E \to +\infty \\
   0 & E \to -\infty 
\end{cases}$$

(12)
Type 1 & Type 2 singularities

All-electron C. Trial wavefunction is HF determinant with Gaussian basis.

Estimated seed probability distribution

General asymptotic form is:

\[
\lim_{|E| \to \infty} P_{\psi^2}(E) = \begin{cases} 
  c_2 E^{-4} & E \to +\infty \\
  c_1 E^{-4} & E \to -\infty 
\end{cases}
\]  

(13)
The Central Limit theorem - summary

Consider a distribution, $p(x)$, mean 0

CLT is derived by finding the distribution of the sum of $r$ $x$'s sampled from $p(x)$:

$$s_r = x_1 + \ldots + x_r$$  \hspace{1cm} (14)

The distribution of $s_r$ is given by the convolution relations

$$P_r(s_r) = p(x) * P_{r-1}(s_{r-1})$$  \hspace{1cm} (15)

Taking the fourier transform of this gives

$$P_r(k) = p(k)^r = e^{r \ln p(k)}$$  \hspace{1cm} (16)
**IF** $p(k)$ is continuous at $k = 0$ **THEN**

- Taylor expansion of $\ln p(k)$ (cumulant expansion)
- Factor out largest term in $P_r(k)$
- Expand the smaller factor as series, and FT back:

$$P_r(\rho) = \frac{1}{\sqrt{2\pi}} e^{-\rho^2/2} \left[ 1 + \frac{p_1(\rho)}{\sqrt{r}} + \ldots \right]$$

(17)

with each $p_n(\rho)$ a polynomial in $\rho$ - a Gram-Charlier expansion.*

- As $r \to \infty$ $P_r(\rho)$ approaches a Normal distribution.
- Deviations from the normal distribution for finite $r$ decay away exponentially in $\rho$
- Deviations from the normal distribution for finite $r$ decay away as $1/r^{1/2}$

* $\rho = \frac{\sqrt{r}}{\sigma}(E - \mu)$
**BUT**, a general property of Fourier transforms is

\[
\text{FT}\quad p(x)|_{x \to \pm \infty} \sim \frac{1}{|x|^q} \quad \rightarrow \quad p(k)|_{k \to \pm 0} \sim |k|^{q-1}
\]  

For our trial wavefunctions the seed distribution \(P_{\psi^2}(E) \sim 1/E^4\)

This means there is \(|k|^3\) discontinuity in the FT of \(P_{\psi^2}(E)\), so no cumulant or Gram-Charlier expansion is possible.
CLT for total energy estimate

Rescale energy variables so ‘seed’ distribution has mean 0 and variance 1, $P_{\psi^2}(E) \rightarrow p(x)$.

$$s_r = x_1 + \ldots + x_r$$

(20)

distribution given by convolution

$$P_r(s_r) = p(x) * P_{r-1}(s_{r-1}) \quad , \quad P_r(k) = p(k)^r = e^{r \ln p(k)}$$

(21)

$p(k)$ can be expanded about $k = 0$ as

$$P_r(k) = \exp \left[ -r \frac{1}{2} k^2 + r \frac{\lambda}{3\sqrt{2}} |k|^3 + \ldots \right]$$

(22)

with $\lambda$ a measure of the magnitude of the $E^{-4}$ tails, and not related to the mean or average of $P_{\psi^2}(E)$. 
Factoring, series expansion of smaller factor, and inverse transformation gives

\[ P_r(\rho) = \phi_0(\rho) + \frac{\lambda}{3\sqrt{2r}} \phi_1(\rho) + \ldots \]  \hspace{1cm} (23)

- \( \phi_0(\rho) = \frac{1}{\sqrt{2\pi} \rho^2} e^{-\rho^2/2} \), with mean and variance as before
- \( \lim_{\rho \to \pm \infty} P_r(\rho) = \sqrt{\frac{2}{\pi}} \frac{1}{\rho} \frac{\lambda}{r} \)
- CLT is valid.
- Deviations from the normal distribution for finite \( r \) decay away as \( 1/\rho^4 \).

* \( \rho = \frac{\sqrt{r}}{\sigma} (E - E_0) \)
Total energy estimate for finite $r$?

Distribution of errors in the total energy estimate - $r = 10^5$

- Crossover between Gaussian and $1/\rho^4$ occurs at $\rho_c^2 \approx \ln \frac{\pi r}{4\lambda^2}$
- For $\lambda = 1, r > 10^3$ then confidence of $< 99.99\%$ is CLT
- For $\lambda > 10, r > 10^3$ then finite $r$ effects lower confidence
- Depends weakly on $r/\lambda^2$, with $\lambda$ an unknown property of the trial wavefunction.
- For all cases probability of an outlier does not decrease exponentially, but much slower.
CLT for variance of the local energy

Same strategy as before, but sum of $x^2 - 1$:

Rescale energy variables to $u = x^2 - 1$ and $p(u) \to 1/u^{5/2}$ as $u \to \infty$

Find the distribution of the sum of $r$ $u$'s sampled from $p(u)$:

$$s_r = x_1^2 + \ldots + x_r^2 - r = u_1 + \ldots + u_r$$  \hspace{1cm} (24)

distribution given by convolution

$$P_r(s_r) = p(u) \ast P_{r-1}(s_{r-1}), \quad P_r(k) = p(k)^r = e^{r \ln p(k)}$$  \hspace{1cm} (25)

and expansion about $k = 0$

$$P_r(k) = \exp \left[ -r \frac{4\lambda}{3\pi^{1/2}} (1 \mp i)|k|^{3/2} + rk^2 + \ldots \right]$$  \hspace{1cm} (26)
Factoring, series expansion of smaller factor, and inverse transformation gives:

\[ P_r(\bar{v}) = \frac{\sqrt{3}}{\pi} \frac{1}{2\gamma} \left[ \frac{\bar{v} - \sigma^2}{2\gamma} \right]^2 \exp \left( \left[ \frac{\bar{v} - \sigma^2}{2\gamma} \right]^3 \right) \]

\[ \times \left[ -\text{sgn} \left[ \frac{\bar{v} - \sigma^2}{2\gamma} \right] K_{1/3} \left( \left| \frac{\bar{v} - \sigma^2}{2\gamma} \right|^3 \right) + K_{2/3} \left( \left| \frac{\bar{v} - \sigma^2}{2\gamma} \right|^3 \right) \right] \]

with the ‘width’ of the distribution decided by the magnitude of the tails

\[ \gamma = \left[ \frac{6\lambda^2}{\pi r} \right]^{1/3} \sigma^2 \]

- Not a normal distribution in the limit \( r \to \infty \)
- \( \gamma \) is not related to moments of seed distribution

\[ \bar{v} = \text{Var}[E_L] \]
• CLT is not valid (variance is infinite). Law of large number (LLN).

• A sample is most likely to be below mean, and outliers are very likely.

• Outlier probability falls as $1/r^{5/2}$, and not exponentially.

• Confidence limits defined via CLT are not valid. A new definition needs $\lambda$, and will scale as $r^{-1/3}$.
$4^{th}$ moment, $\mu_4$?

Same strategy as before, but sum of $x^4$

Obtain distribution of $u = x^4 - 1$

- $P_r(k) \sim \exp[-a r k^{3/4} + \ldots]$
- $P_r(\mu_4) \asymp r^{1/4} / \mu_4^{7/4}$
- $P_r(\mu_4)$ gets wider as $r$ increases
- $P_r(\mu_4)$ has infinite mean and variance
- neither CLT or LLN are valid $\rightarrow$ no statistical convergence
Conclusion

• CLT applies to energy estimate for large enough $r$.

• Outliers are not exponentially unlikely for $r < \infty$.

• CLT does not apply to variance estimates as $r$ increases. LLN does.

• Neither LLN or CLT apply to higher moments than the variance.

• Error in the variance estimate are unknown (unless we stop being rigorous), but does go to zero.
2. ‘Residual Sampling’ - can the CLT be reinstated?

Use importance sampling with a different sampling distribution - not $\psi^2$

\[
\langle f(E_L) \rangle \approx \frac{w(E_L)f(E_L)}{w(E_L)} \pm \epsilon [w f, w], \quad P(R) = \lambda \psi^2 / w(E_L)
\]

choose

\[
w = \frac{\epsilon^2}{(E_L - E_0)^2 + \epsilon^2}
\]

Why?:

- $P(R)$ is now non-zero and smooth over the nodal surface.
- $\epsilon \to \infty$ gives standard sampling.
- Estimate of error is different - ratio of two random variables.
- Sample from $P(R)$ with Metropolis
Error from the Bivariate CLT

Define $\overline{\mu}_2 = \overline{wf}$ and $\overline{\mu}_1 = \overline{w}$

The pair $\overline{\mu}_2, \overline{\mu}_1$ from $r$ samples is a 2d random vector sampled from the distribution

$$P_r(\overline{\mu}_2, \overline{\mu}_1) = \frac{1}{2\pi} \frac{1}{\sqrt{c_{11}c_{22} - c_{12}^2}} e^{-q^2/2} \tag{31}$$

$$q^2 = \frac{1}{c_{11}c_{22} - c_{12}^2} \left[ c_{22} (\overline{\mu}_1 - \mu_1)^2 - 2c_{12} (\overline{\mu}_1 - \mu_1) (\overline{\mu}_2 - \mu_2) + c_{11} (\overline{\mu}_2 - \mu_2)^2 \right] \tag{32}$$

and

$$c_{22} = \frac{1}{r} (wf - \mu_2)^2$$

$$c_{12} = \frac{1}{r} (wf - \mu_2)(w - \mu_1)$$

$$c_{11} = \frac{1}{r} (w - \mu_1)^2 \tag{33}$$

$f = E_L$ gives distribution of numerator/denominator for total energy estimate $\overline{wE_L}/\overline{w}$

$f = (E_L - \mu_2/\mu_1)^2$ gives distribution of numerator/denominator for residual variance estimate.

All co-moments exist $\rightarrow$ CLT is valid, and tails are exponential
Get confidence limits using Fieller’s theorem. Confidence range of $\frac{\mu_2}{\mu_1}$ is $(l_l, l_u)$ with

$$l_u/l_l = \frac{(\mu_1 \cdot \mu_2 - q_0^2 c_{12}) \pm \sqrt{(\mu_1 \cdot \mu_2 - q_0^2 c_{12})^2 - (\mu_1^2 - q_0^2 c_{11}) (\mu_2^2 - q_0^2 c_{22})}}{\mu_1^2 - q_0^2 c_{11}}$$

(34)

and $q_0 = \sqrt{2} \text{erf}^{-1}(c)$ defining confidence of $c$ in the estimate of $\mu_2/\mu_1$.

- The CLT is now valid for any $f(E_L)$
Estimate of total energy

Histogram of $10^3$ total energy estimates, each total energy estimate from $10^3$ configurations.

- Residual sampling and standard sampling are not significantly different
Size of confidence interval estimated using CLT for standard, Fieller’s theorem for residual sampling.

- Residual sampling and standard sampling are not significantly different
- For both error $\sim 1/r^{1/2}$
Estimate of variance of local energy

Histogram of $10^3$ variance estimates, each variance estimate from $10^3$ configurations.

- Residual sampling and standard sampling are very different
- Standard sampling shows the $[\text{Var}]^{-5/2}$ tails and outliers expected
- Residual sampling gives well defined confidence limits from the co-moments and bivariate CLT.
- Standard sampling does not.
Estimate error in variance of local energy

Size of confidence interval estimated using CLT expression for standard, and Fieller's theorem for residual sampling.

- Residual sampling and standard sampling are very different
- Standard sampling error $\sim 1/r^{1/3}$ and random noise. Error estimate is not valid.
- Residual sampling error $\sim 1/r^{1/2}$. Error is valid.
- Residual sampling gives well defined confidence limits from the co-moments and bivariate CLT.
- Standard sampling does not.

The difference is near the nodal hypersurface
Conclusions

- If we want to reintroduce the CLT, and remove the persistent $x^{-q}$ tails in the distribution of estimates, then we can, using residual sampling.

- For the variance this interpolates between sampling the numerator perfectly, and sampling the denominator perfectly.

- Residual sampling gives us well defined confidence limits for the variance in terms of the moments, while standard sampling does not.

- Residual sampling adds 2 new parameters ($E_0$ and $\epsilon$) but is not sensitive to them. They can be optimised.
3. Variance minimisation and Correlated sampling

- Sample using distribution $P(\alpha_0)$, with $\alpha_0$ a parameters of the trial wavefunction.

- Choose a quantity whose minimum we wish to find, eg total energy:

$$O(\alpha) = \left\langle \frac{P(\alpha)}{P(\alpha_0)} E_L(\alpha) \right\rangle_{P_{\alpha_0}} / \left\langle \frac{P(\alpha)}{P(\alpha_0)} \right\rangle_{P_{\alpha_0}} = \langle f_2(\alpha, \alpha_0) \rangle / \langle f_1(\alpha, \alpha_0) \rangle$$ (35)

Expand the averaged quantity in the numerator and denominator as a taylor series, and taking numerical averages gives

$$\overline{O(\alpha)} = \frac{f_2(\alpha, \alpha_0)}{f_1(\alpha, \alpha_0)} = \frac{f_2(\alpha_0) + f'_2(\alpha_0)(\alpha - \alpha_0) + \ldots}{f_1(\alpha_0) + f'_1(\alpha_0)(\alpha - \alpha_0) + \ldots}$$ (36)

- What is the statistical error in this estimate of $O(\alpha)$?

  Analyse statistics of each coefficient seperately:

  - Does it converge to a constant as $r \to \infty$?

  - Does it obey the CLT?
Example: $O(\alpha) = \text{total energy, standard sampling}$

$X = \text{vector to nodal surface, } \hat{n} = \text{vector } \perp \text{ nodal surface at } X, S_\perp = \text{distance } \perp \text{ to nodal surface}$

\begin{align*}
P(R; \alpha) &= a_2(X; \alpha)(S_\perp - S_0(X; \alpha))^2 + \ldots \\
E_L(R; \alpha) - E_0(\alpha) &= b_{-1}(X; \alpha)(S_\perp - S_0(X; \alpha))^{-1} + \ldots \\
f_2^{(n)}(R) &= \frac{1}{P(R; \alpha_0)} \frac{d^n}{d\alpha^n} \left[ P(R; \alpha) E_L(R; \alpha) \right]_{\alpha_0} \\
f_1^{(n)}(R) &= \frac{1}{P(R; \alpha_0)} \frac{d^n}{d\alpha^n} \left[ P(R; \alpha) \right]_{\alpha_0}
\end{align*}

- For each coefficient $f_{1/2}^{(n)}$ transform to a 1-D distribution, with the new random variable $x = f_{1/2}^{(n)}(R)$
- This is done by integrating over $f_{1/2}^{(n)}(R) = x$ hypersurface, as for VMC analysis.
- We get the asymptotic tails of the distribution $p(x)$ whose average is $\tilde{f}_{1/2}^{(n)}$
Limit theorems for sample average of $p(x) \asymp |x|^{-q}$

<table>
<thead>
<tr>
<th>$q$</th>
<th>Limit theorem</th>
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</thead>
<tbody>
<tr>
<td>$3 &lt; q$</td>
<td>CLT</td>
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<tr>
<td>$2 &lt; q \leq 3$</td>
<td>LLN</td>
</tr>
<tr>
<td>$1 &lt; q \leq 2$</td>
<td>No statistical limit</td>
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<tr>
<td>$q \leq 1$</td>
<td>Not a PDF</td>
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</tbody>
</table>

- The distribution of the numerator or denominator is the fattest distribution of all the coefficients (for $\alpha \neq \alpha_0$)
- The distribution of the num./den. is bivariate CLT if all coefficients are CLT.
- The distribution of the num./den. is bivariate LLN if all coefficients are CLT or LLN
- The distribution of the num./den. does not converge if any coefficient is not CLT or LLN.
**Standard sampling -** \( P = \lambda \psi_\alpha^2 \)

<table>
<thead>
<tr>
<th></th>
<th>Numerator</th>
<th>Denominator</th>
<th>Stat. of ( O(\alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optimate</strong></td>
<td>( n = 0 )</td>
<td>( n = 1 )</td>
<td>( n &gt; 1 )</td>
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<tr>
<td>Energy reweighted</td>
<td>CLT</td>
<td>LLN</td>
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<tr>
<td>Variance reweighted</td>
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<tr>
<td>limited reweight</td>
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<tr>
<td>artificial weight</td>
<td>CLT</td>
<td>CLT</td>
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رعيَتىَ: \( O(\alpha) = \left\langle \frac{\psi^2}{\psi^2_{\alpha_0}}(E_L - \langle E_L \rangle)^2 \right\rangle / \left\langle \frac{\psi^2}{\psi^2_{\alpha_0}} \right\rangle \)

رعىَتىَ: \( O(\alpha, \alpha_0) = \langle (E_L - \langle E_L \rangle)^2 \rangle \)

ريعَتىَ: As reweighting, with a maximum \( P/P(\alpha_0) \) enforced

ريعَتىَ: \( O(\alpha, \alpha_0) = \langle h(E_L)(E_L - \langle E_L \rangle)^2 \rangle / \langle h(E_L) \rangle \) with \( h(E_L) \asymp \) Gaussian in \( E_L \)
## Residual sampling - $P = \lambda \psi^2_{\alpha_0}/w(\alpha_0)$

<table>
<thead>
<tr>
<th>Optimate</th>
<th>Numerator</th>
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<th>Denominator</th>
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<th>Stat. of $O(\alpha)$</th>
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<tr>
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<td>Res. Variance</td>
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<td>bivariate CLT</td>
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</table>

- reweighted: $O(\alpha) = \left\langle \frac{\psi^2}{\psi^2_{\alpha_0}} w(\alpha_0)(E_L - \langle E_L \rangle)^2 \right\rangle / \left\langle \frac{\psi^2}{\psi^2_{\alpha_0}} w(\alpha_0) \right\rangle$
- unweighted: $O(\alpha, \alpha_0) = \langle (E_L - \langle E_L \rangle)^2 \rangle$
- limited reweight: As reweighting, with a maximum $P/P(\alpha_0)$ enforced
- artificial weight: $O(\alpha, \alpha_0) = \langle h(E_L)(E_L - \langle E_L \rangle)^2 \rangle / \langle h(E_L) \rangle$ with $h(E_L) \simeq$ Gaussian in $E_L$
Estimated $O(\alpha)$

$r = 10^5$ configurations for each of 8 $O(\alpha)$'s

Estimate of variance using reweighting

- Standard sampling to generate $\overline{O(\alpha)}$ is distributed via LLN
- Residual sampling to generate $\overline{O(\alpha)}$ is distributed via CLT
- Residual sampling provides the best estimate to $\overline{O(\alpha)}$
Optimisation

\[ r = 10^5 \text{ configurations.} \]

Total energy

\[
\begin{array}{cccccc}
\text{no. cycle.} & 1 & 2 & 3 & 4 & 5 \\
E_{tot} (\text{a.u.}) & -37.84 & -37.83 & -37.82 & & \\
\end{array}
\]

Residual variance

\[
\begin{array}{cccccc}
\text{no. cycle.} & 1 & 2 & 3 & 4 & 5 \\
\text{Var}^2 & 0.05 & 0.05 & 0.05 & & \\
\end{array}
\]

Std. - artificial weights and samples using \( \psi(\alpha_0)^2 \)

Res. - reweighting and samples using \( \psi(\alpha_0)^2 / w(\alpha_0) \)

- The standard method starts with jastrow/multidet. optimised, backflow parameters set to zero
- The residual method starts with jastrow/backflow/multideterminant parameters set to zero
- Optimisation using reweighting and residual sampling provides a lower energy and variance than standard sampling with artificial weights.
Conclusions

• For standard VMC we cannot assume that CLT and ‘\( r \) is large enough’ apply. Many of the estimates are not distributed as CLT for \( r \rightarrow \infty \).

• A new sampling ‘Residual Sampling’ with a distribution that is non-zero at the nodal hypersurface reintroduces the CLT for all estimates.

• Optimisation for standard sampling finds the minimum of \( O(\alpha) \). This is not distributed as CLT, unless the nodal surface is removed from sampling (using artificial weights).

• Optimisation for residual sampling finds the minimum of \( O(\alpha) \). This is distributed as CLT, with sampling taking place at the nodal surface.

• Optimisation with residual sampling gives the lowest total energy and variance of the local energy, and the lowest statistical error.
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