Optimization on Random Surfaces

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Numerical Integration

- To solve a Many-Body Quantum mechanics problem we need to integrate in a lot of dimensions

Estimates of integrals of unknown functions for r sample points in D dimensions:

- Standard 'evenly spaced grid' gives $\epsilon \propto \left(\frac{1}{r}\right)^{p/D}$
- Monte Carlo gives $\epsilon \propto \left(\frac{1}{r}\right)^{1/2}$

Both assume sampled function is 'well behaved':

- Standard 'evenly spaced grid' assumes function is smooth
- Monte Carlo assumes CLT is valid

Quantum Monte Carlo (VMC)

Sample 3N dimensional space with PDF $P(\mathbf{R})$

$$\text{Est}\left[E_{tot}\right] = \frac{\sum \psi^2 E_L / P}{\sum \psi^2 / P} \quad = \quad \frac{\langle \psi | \hat{H} | \psi \rangle + \text{Y}}{\langle \psi | \psi \rangle + \text{X}}$$

where $E_L = \psi^{-1} \hat{H} \psi$.

Simplest case is ‘Standard Sampling’: Choose $P(\mathbf{R}) = A\psi(\mathbf{R})^2$, then

$$\text{Est}\left[E_{tot}\right] = \frac{1}{r} \sum E_L \quad = \quad \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} + \text{W}$$

- W is the random error in a sum of random variables, so what is its distribution?
- **IF** the CLT is valid then it is Gaussian with mean 0, and variance $\sigma / r^{1/2}$.

3N $\longrightarrow$ 1 dimension

Why?: Easier to deal with the general case analytically

A change of the random variable from spatial to energy:

$$\begin{aligned} E_{tot} &= \int_V \psi^2 E_L d^{3N}\mathbf{R} / \int_V \psi^2 d^{3N}\mathbf{R} \\ &= \int_{-\infty}^{\infty} P_{\psi^2}(E) E dE \end{aligned}$$

with

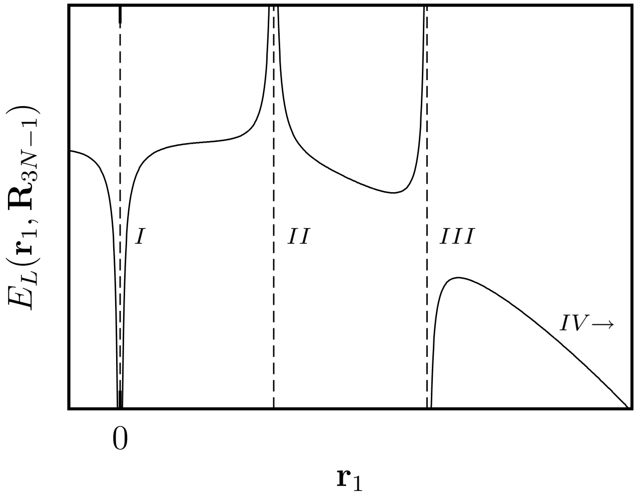
$$P_{\psi^2}(E) = \int_{E=E_L} \frac{P(\mathbf{R})}{|\nabla_{\mathbf{R}} E_L|} d^{3N-1}\mathbf{R}$$

- A histogram of E_L approximates the 'seed' PDF P_{ψ^2}
- $|\nabla_{\mathbf{R}} E_L|$ results from curvilinear co-ordinates and change of variables.
- Useless numerically, but useful analytically.

What can we say about P_{ψ^2}?

Singularities in the local energy:

$$E_L(\mathbf{R}) \;=\; -\frac{1}{2}\frac{\nabla^2_{\mathbf{R}}\psi}{\psi} + \sum_{i<j}\frac{1}{r_{ij}} - \sum_i \frac{Z}{r_i}$$

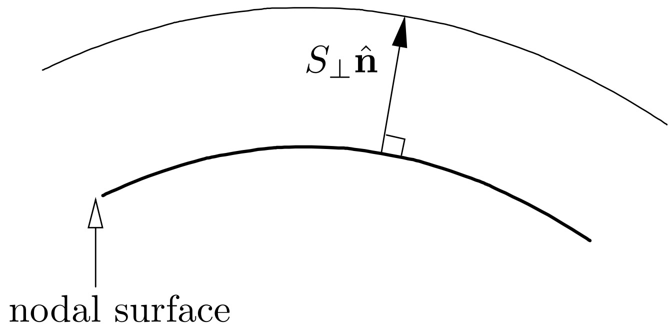


- $E_L(\mathbf{R}) = E_{tot}$ if the trial wavefunction, ψ, is exact
- Enforce Kato cusp conditions $\longrightarrow$ no Coulomb singularities
- Nodal surface is $\psi = 0$, and is $3N-1$ dimensional
- Kinetic energy part gives singularity on a $3N-1$ dimensional surface

$\longrightarrow$ Type III singularities provide information about P_{ψ^2} for large $|E|$

What can we say about P_{ψ^2}?

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



$$\begin{aligned} \psi &= a_1 S_\perp + \ldots \\ E_L &= b_{-1} S_\perp^{-1} + \ldots \\ P(\mathbf{R})/|\nabla E_L| &= c_4 S_\perp^4 + \ldots \\ P_{\psi^2}(E) &= d_{-4} E^{-4} + \ldots \end{aligned}$$

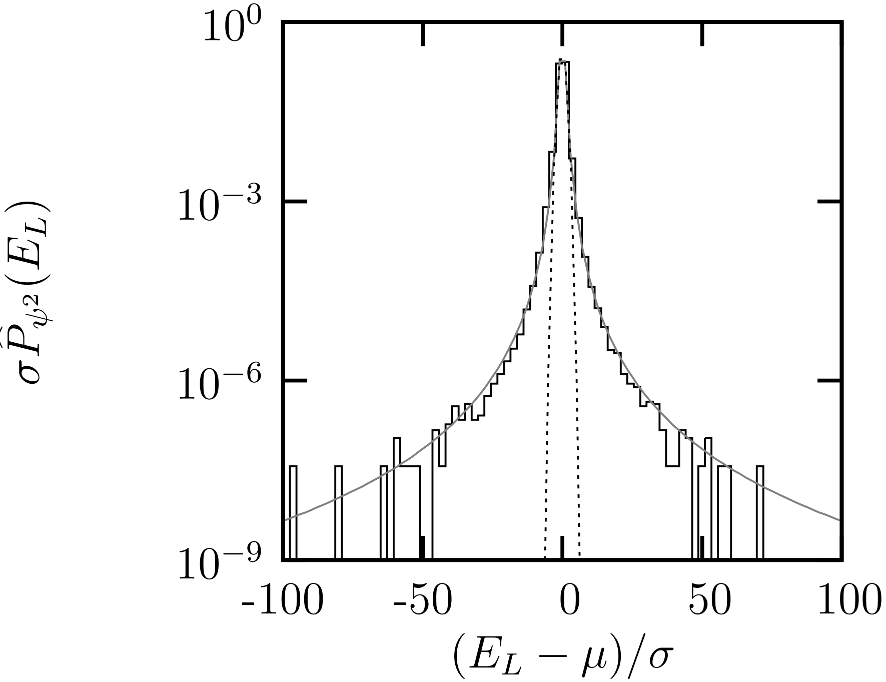
or more completely

$$P_{\psi^2}(E) = (E - E_0)^{-4} \left(e_0 + \frac{e_1}{(E - E_0)} + \ldots \right) \quad |E| \gg E_0$$

Example: All-electron isolated Carbon atom

- Jastrow + 48 determinants + backflow:

$$\psi = e^{J(\mathbf{R})} \sum_m a_m D_m^{\uparrow}(\mathbf{R}') D_m^{\downarrow}(\mathbf{R}') \quad with \quad \mathbf{R}' = \mathbf{R}'(\mathbf{R})$$



Estimated seed probability density function

- 93% correlation energy at VMC level

Also shown is $\frac{\sqrt{2}}{\pi} \frac{\sigma^3}{\sigma^4 + (E-\mu)^4}$, and a Normal distribution

Random error in total energy estimate

$$\text{Est}\left[E_{tot}\right] = \frac{1}{r}\left(E_1 + \ldots + E_r\right)$$

Product of probability of r samples energies that add up to $rE_{tot} \rightarrow$ convolution integrals

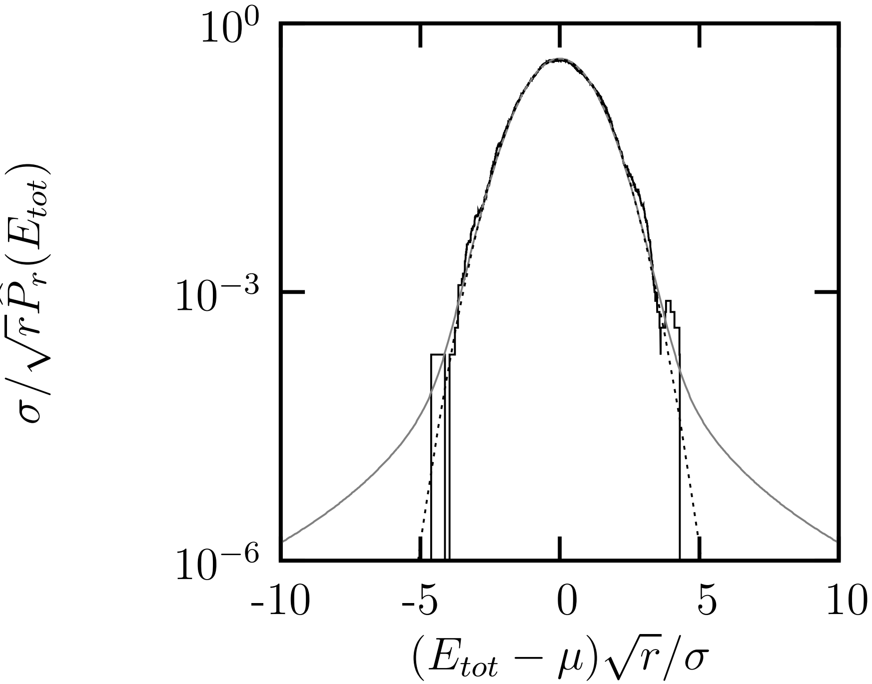
$$\begin{aligned} P_{r=2}(2E_{tot}) &= \int P_{\psi^2}(E_1)P_{\psi^2}(E_2)\delta(E_1+E_2-2E_{tot})dE_1dE_2 = P_{\psi^2}\star P_{\psi^2} \\ P_r(rE_{tot}) &= P_{\psi^2}\star P_{\psi^2}\star\ldots\star P_{\psi^2} \end{aligned}$$

- Take Fourier transform of $P_{\psi^2}(E)$
- Take the r^{th} power
- Take the inverse Fourier transform
- Rescale some variables to get the PDF of averages instead of sum

$$P_r(y) = \frac{1}{\sqrt{2\pi}}\left[1+\frac{\eta}{\sqrt{r}}\frac{d^3}{dy^3}+\mathcal{O}\left(\frac{1}{r}\right)\right]e^{-y^2/2}+\left[\frac{\lambda}{3\pi}\frac{1}{\sqrt{r}}\frac{d^3}{dy^3}D\left(\frac{y}{\sqrt{2}}\right)+\mathcal{O}\left(\frac{1}{r}\right)\right]$$

$$y = (E_{tot}-\mu)/\sigma$$

PDF of estimate of Total energy



- Approximate PDF from 10^4 estimates of total energy, with $r = 10^3$
- For small $|E|$, PDF is dominated by $\frac{1}{\sqrt{2\pi}} e^{-x^2/2}$
- For large $|E|$, PDF is dominated by $\frac{\sqrt{2}}{\pi} \frac{\lambda}{\sqrt{r}} 1/x^4$ ($\lambda \approx 1$ for Carbon trial wavefunction)
- CLT is true in its weakest form

PDF of estimate of the ‘Residual Variance’, v

Optimisation of wavefunctions using the ‘residual variance’, v

$$\left(\hat{H} - E_{tot}\right)\psi = \delta = \left(E_L - E_{tot}\right)\psi$$

$v = \int \delta^2 d\mathbf{R} \geq 0$, and zero for exact ψ

- To optimise the wavefunction v is often minimised
- Analyse effect of tails, as before:

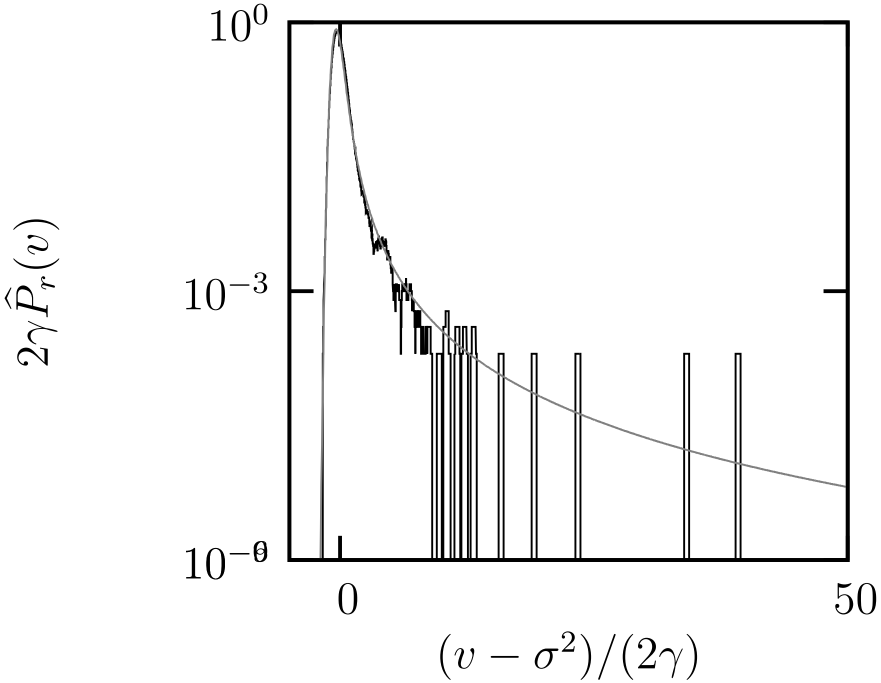
$$\begin{aligned} P_r(\overline{v}) &= \frac{\sqrt{3}}{\pi}\frac{1}{2\gamma}\left[\frac{\overline{v}-\sigma^2}{2\gamma}\right]^2 \exp\left(\left[\frac{\overline{v}-\sigma^2}{2\gamma}\right]^3\right) \\ &\times \left[-\text{sgn}\left[\overline{v}-\sigma^2\right] K_{1/3}\left(\left|\frac{\overline{v}-\sigma^2}{2\gamma}\right|^3\right) + K_{2/3}\left(\left|\frac{\overline{v}-\sigma^2}{2\gamma}\right|^3\right)\right] \end{aligned}$$

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

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

- This limit theorem is a case of a gives ‘Levy skew alpha-stable distribution’
- ‘CLT’ is a special case of the Levy skew alpha-stable distribution

PDF of estimate of the 'Residual Variance', v



- Approximate PDF from 10^4 estimates of residual variance, with $r = 10^3$
- Small v, $\propto e^{x^3}$. Large $v \propto 1/x^{5/2}$
- PDF has no variance, γ has no vigorous statistical estimate and is $\propto r^{-1/3}$

- CLT is valid in its weakest form for the total energy
- CLT not valid for residual variance
- CLT is likely to be invalid for estimates of other physical quantites
- **Because**: ψ^2 samples E_L rarely where it is largest, at the nodal surface

What about other estimates? Generally given by

$$\text{Est}_r\left[X\right] = \frac{1}{r}\sum_{n=1}^{r} x_L(\mathbf{R}_n),$$

for some x_L

e.g.

- Non-local pseudopotentials $\longrightarrow$ weak CLT (x^{-4} tails decay with r)
- Kinetic energy $\longrightarrow$ 'Stable Law' with $x^{-5/2}$ tails
- Hellmann-Feynman forces $\longrightarrow$ 'Stable Law' with $x^{-5/2}$ tails on LHS and RHS
- Relativistic corrections $\longrightarrow$ 'Stable Law' with $x^{-5/2}$ tails
- Linearised basis optimisation $\longrightarrow$ 'Stable Law' with $x^{-5/2}$ tails

Can the CLT be reinstated ?

Residual sampling

Instead of sampling with $P = A\psi^2$, sample with $P = A\psi^2/w$, then

$$\text{Est}\left[E_{tot}\right] = \frac{\sum wE_L}{\sum w} = \frac{\langle\psi|\hat{H}|\psi\rangle + \mathsf{Y}}{\langle\psi|\psi\rangle + \mathsf{X}}$$

and the residual variance,

$$\text{Est}\left[\int \delta^2 d\mathbf{R}\right] \quad = \quad \frac{\sum w(E_L - E_{tot})^2}{\sum w} = \frac{\int \psi^2 (E_L - E_{tot})^2 d\mathbf{R} + \mathsf{Y}}{\int \psi^2 d\mathbf{R} + \mathsf{X}}$$

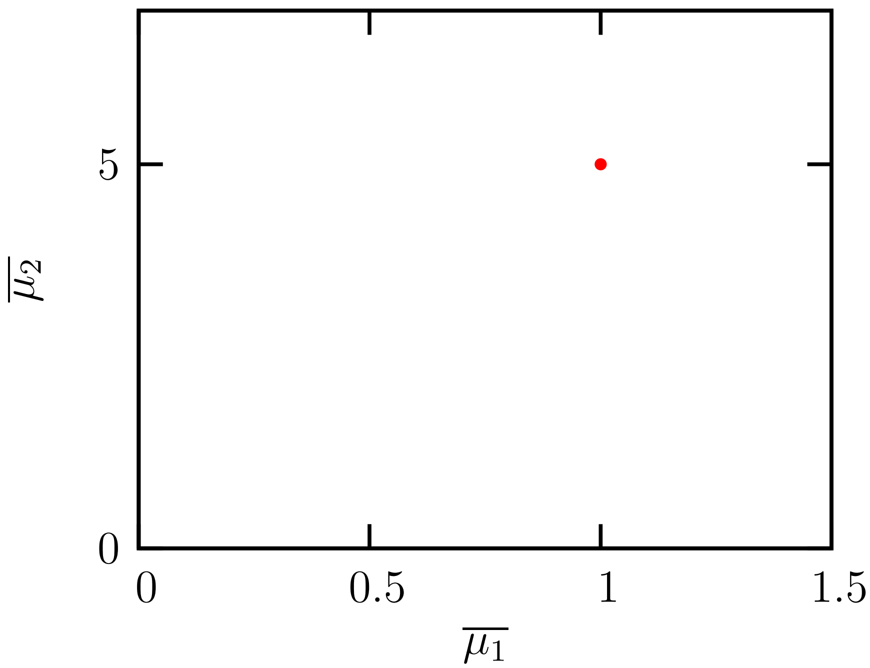
Choose the weighting function

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

to ‘interpolate’ beween sampling the numerator and denominator perfectly.

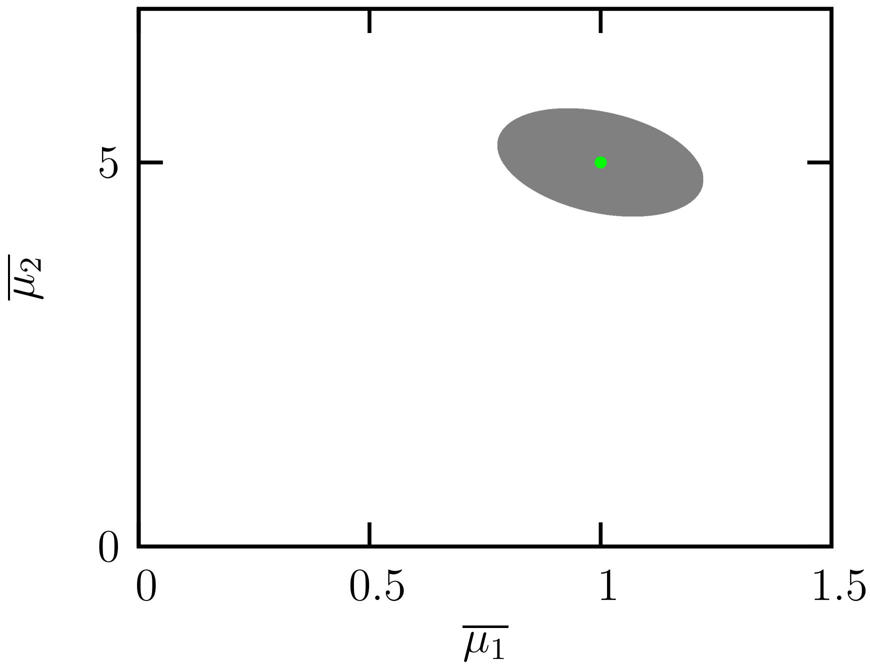
- No singularities, and no power law tails
- Quotient of two correlated random variables, each a sum of random variables

Fieller's Theorem



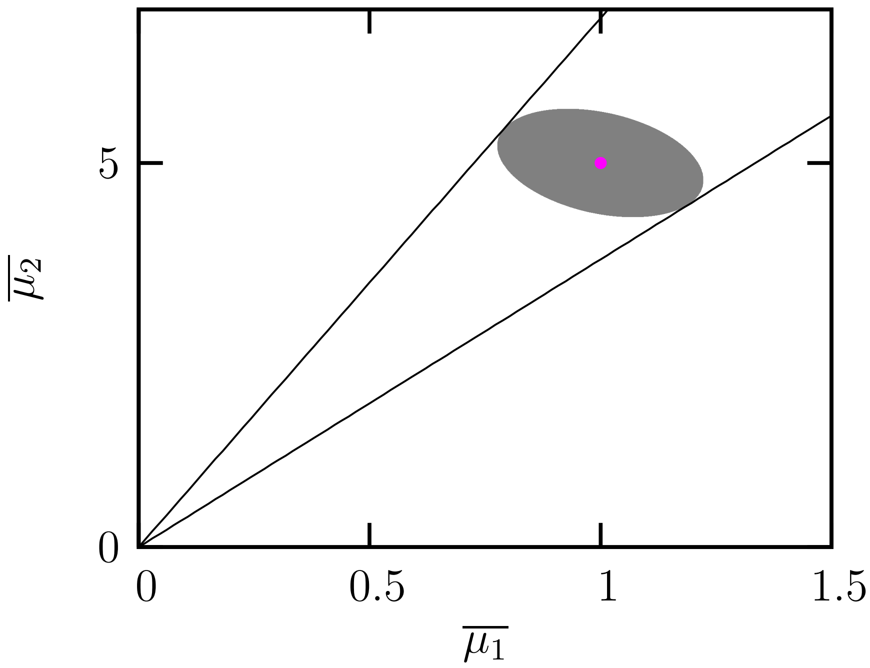
- (μ_2, μ_1) that give Est $= \mu_2/\mu_1$

Fieller's Theorem



- (μ_2, μ_1) that give Est $= \mu_2/\mu_1$
- Ellipse containing 39% of probability from covariance matrix and bivariate CLT

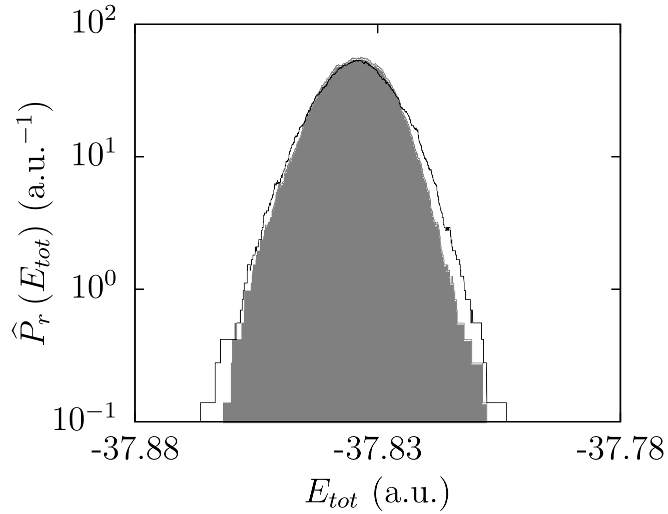
Fieller's Theorem



- (μ_2, μ_1) that give Est $= \mu_2/\mu_1$
- Ellipse containing 39% of probability from covariance matrix
- Wedge that contains 68.3% of probability

$\Rightarrow m_1 < \mu_2/\mu_1 < m_2$ with confidence 68.3%

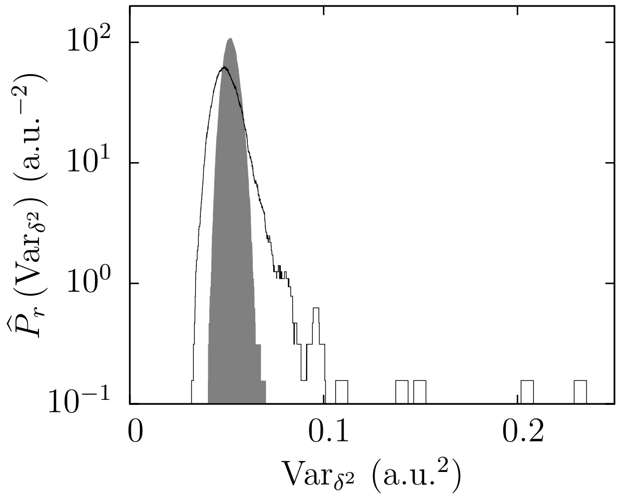
Estimate of total energy



Estimated PDF from 10^3 total energy estimates.

- Residual sampling (filled) and standard sampling (unfilled) are not significantly different
- Residual sampling reduces error by $\sim 30\%$
- For other systems standard sampling may give 'power law' outliers (depending on λ)
- For all systems residual sampling does not give 'power law' outliers

Estimate of residual variance

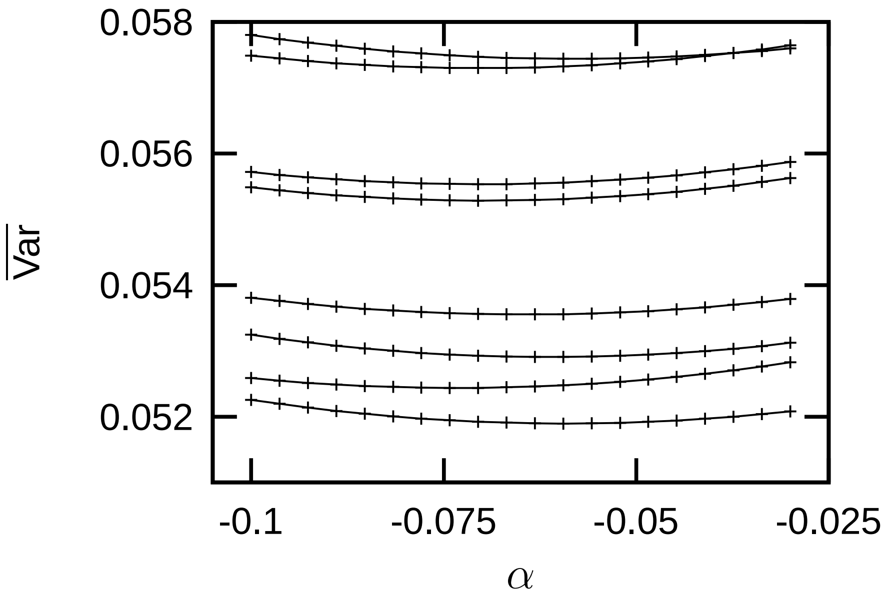


Estimated PDF from 10^3 residual variance estimates.

- Residual sampling and standard sampling are very different
- Standard sampling shows the $v^{-5/2}$ tails and outliers expected
- Residual sampling gives well defined confidence limits for estimate via the bivariate CLT
- Standard sampling does not

Trial function optimization

- Choose an variational principle $\longrightarrow$ 'Optimate function' of parameters $\{\alpha\}$
- Estimate this function using Monte Carlo sampling $\longrightarrow$ 'Correlated sampling'
- Find minimum of this function, for example



So, what is the 'random error' in the estimated 'Optimate function', $O(\{\alpha\})$?

- What is the PDF of the estimated $O(\{\alpha\})$ at a given $\{\alpha\}$?
- Does the estimated $O(\{\alpha\})$ statistically converge for large r?

Estimate of Optimate

Many 'optimates' are possible,

Example 1: Total energy variational principle, $O(\{\alpha\} = \langle\psi|\hat{H}|\psi\rangle/\langle\psi|\psi\rangle$

$$\mathsf{Est}_r\left[O(\{\alpha\})\right] \;=\; \frac{\mathsf{Est}_r\left[\int \psi_\alpha^2 . E_{L,\alpha} d\mathbf{R}\right]}{\mathsf{Est}_r\left[\int \psi_\alpha^2 d\mathbf{R}\right]}$$

Standard sampling: samples distributed as $P_{std} = \psi_{\alpha_0}^2$

$$\mathsf{Est}_r\left[O(\{\alpha\})\right] \;=\; \frac{\langle \psi_\alpha^2/\psi_{\alpha_0}^2 . E_{L,\alpha}\rangle}{\langle \psi_\alpha^2/\psi_{\alpha_0}^2\rangle}$$

For $\alpha = \alpha_0$ nodal singularity in the averaged variable is $S_\perp^{-1}$:

- twosided x^{-4} tails in the 'seed' distribution
- weak CLT is valid

For $\alpha \neq \alpha_0$ nodal singularity in the averaged variables is $S_\perp^{-2}$

- twosided $x^{-5/2}$ tails in the 'seed' distribution
- 'Mean function' exists in limit $r \rightarrow \infty$
- CLT is invalid, Stable distribution with $|x|^{-5/2}$ tails results

More completely, for the total energy as the optimate $\mathsf{O}(\alpha)$ and standard sampling the estimated function takes the form

$$\mathsf{Est}_r\left[\mathsf{O}(\alpha)\right] = \frac{\mathsf{a}_0 + \mathsf{a}_1(\alpha - \alpha_0) + \mathsf{a}_1(\alpha - \alpha_0)^2 + \ldots}{\mathsf{b}_0 + \mathsf{b}_1(\alpha - \alpha_0) + \mathsf{b}_1(\alpha - \alpha_0)^2 + \ldots}$$

where $(\mathsf{a}_n, \mathsf{b}_n)$ are random variables, and the CLT does not hold for $n > 0$

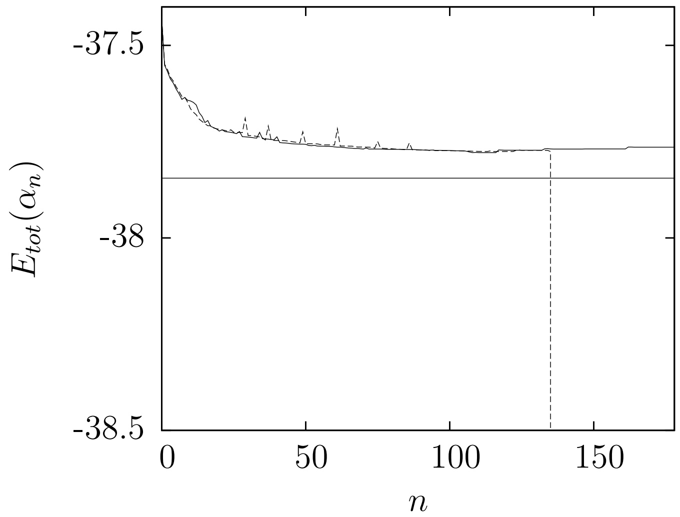
Residual sampling: samples distributed as $P_{res} = \psi_{\alpha 0}^2 / w_{\alpha 0}$

$$\mathsf{Est}_r\left[O(\{\alpha\})\right] = \frac{\langle \psi_\alpha^2 / \psi_{\alpha_0}^2 . w_{\alpha_0} E_{L,\alpha} \rangle}{\langle \psi_\alpha^2 / \psi_{\alpha_0}^2 . w_{\alpha_0} \rangle}$$

No singularity in averaged variables, so

- No power law tails
- CLT valid for all α
- $(\mathsf{a}_n, \mathsf{b}_n)$ are normally distributed for all n

Example: All-electron isolated Carbon atom



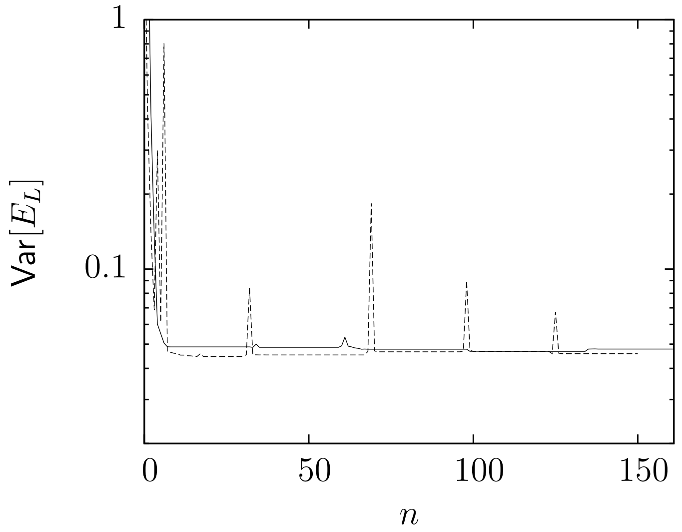
Example 2: Variance minimisation $O(\{\alpha\}) = \langle\psi| \left(\hat{H} - E_0\right) \cdot \left(\hat{H} - E_0\right) |\psi\rangle / \langle\psi|\psi\rangle$

Standard sampling: For all α, $S_\perp^{-2}$ singularity at $\psi_{\alpha_0} = 0$

- One sided power law tail, $x^{-5/2}$
- No CLT is valid, replaced by 'Stable law'

Residual sampling: No singularities

- CLT valid in its strongest form

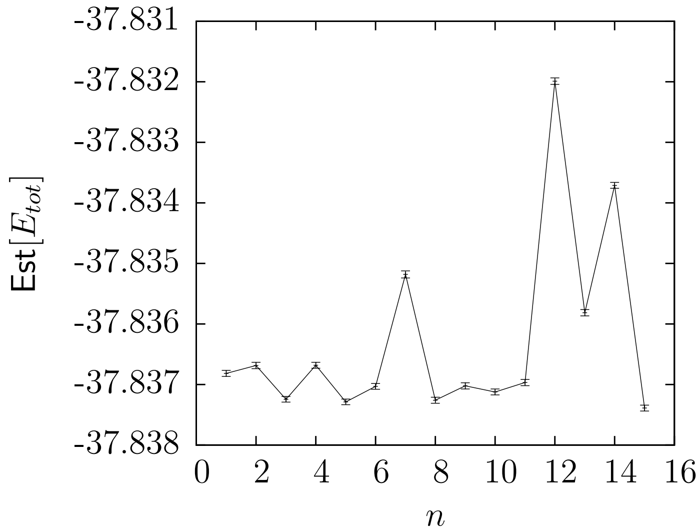


A more general optimate with residual sampling - samples distributed as $P_{res} = \psi^2_{\alpha_0}/w_{\alpha_0}$

$$\text{Est}_r\left[O(\{\alpha\})\right] = \frac{\langle \psi^2_\alpha/\psi^2_{\alpha_0}.w_{\alpha_0} f_n(E_{L,\alpha} - E_0)\rangle}{\langle \psi^2_\alpha/\psi^2_{\alpha_0}.w_{\alpha_0}\rangle}$$

for different choices of f_n

Total energy after optimisation



‘Residual Variance’, and magnitude of tails after optimisation

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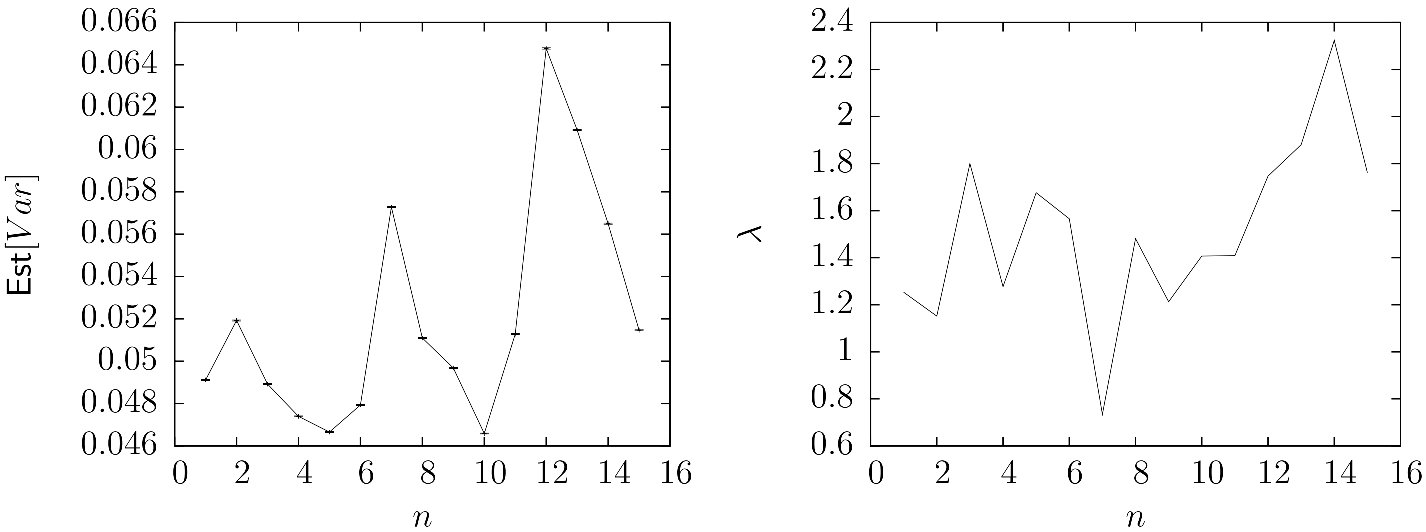

Conclusions

- We cannot assume the CLT is true for estimates in ‘standard sampling QMC’
- ‘r large’ enough must be shown to be true for each estimate in ‘standard sampling QMC’
- The CLT can be reinstated by using an alternative sampling strategy
- Random functions whose minimum gives ‘optimum’ wavefunctions are not generally normally distributed
- The residual sampling strategy can guarantee that the CLT is valid for estimates and optimisation functions, as long as they exist
- With residual sampling optimisation functions can be chosen on physical grounds - to give a good wavefunction at the nodal surface and small *fixed node error* in DMC

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