Energy minimisation in variational quantum Monte Carlo

M.D. Brown

J.R. Trail, P. López Ríos, and R.J. Needs

09/05/07

Quantum Monte Carlo - VMC

- Variational quantum Monte Carlo (VMC)
  - evaluation of high-dimensional integrals using stochastic integration
  - doesn't change input trial wavefunction $\Psi_T(\mathbf{R})$

$$\begin{aligned}
\frac{\langle \Psi_T(\mathbf{R})|\hat{H}|\Psi_T(\mathbf{R})\rangle}{\langle \Psi_T(\mathbf{R})|\Psi_T(\mathbf{R})\rangle} &= \frac{\int \Psi_T \hat{H} \Psi_T \, \mathrm{d}\mathbf{R}}{\int \Psi_T^2 \, \mathrm{d}\mathbf{R}} \\
&= \frac{\int \Psi_T^2 \, \Psi_T^{-1} \hat{H} \Psi_T \, \mathrm{d}\mathbf{R}}{\int \Psi_T^2 \, \mathrm{d}\mathbf{R}} \\
&\simeq \frac{1}{N} \sum_{i=1}^{N} E_L(\mathbf{R}_i)
\end{aligned}$$

Quantum Monte Carlo - DMC

- Diffusion quantum Monte Carlo (DMC)
  - evolves input trial wavefunction stochastically in imaginary time ($\tau = it$)
  - changes Ψ_T: enhances ground-state component
  - energy is variational (cannot go below ground-state energy)
  - fixed-node approximation: nodal surface of Ψ_T doesn't change

$$\begin{aligned} \Psi_T(\mathbf{R}, t) &= \sum_{i=0}^{M} a_i \Phi_i(\mathbf{R}) e^{-iE_i t} \\ &= \sum_{i=0}^{M} a_i \Phi_i(\mathbf{R}) e^{-E_i \tau} \end{aligned}$$

The importance of optimisation

- Steps of a QMC calculation:

  1. Optimise Ψ_T: adjust variable parameters using information from VMC
  2. Use Ψ_T as input for DMC

- Fundamental accuracy of DMC only limited by fixed-node approximation
  $\Rightarrow$ DMC returns the lowest possible energy for the input nodal surface

- Optimisation must make Ψ_T's nodal surface as close as possible to ground state's

Variance minimisation

- Established ‘standard’ method
  - minimise the variance of the energy, evaluated in VMC
  - use Newton-Raphson-style algorithm on the approximation to σ^2 over a fixed set of sampled configurations

$$\begin{aligned}\sigma^2 &= \frac{\langle\Psi_T|\hat{H}^2|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} - \left[\frac{\langle\Psi_T|\hat{H}|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle}\right]^2 \\ &\simeq \frac{1}{N}\sum_{i=1}^{N}\left[E_L(\mathbf{R}_i) - \langle E_L\rangle\right]^2\end{aligned}$$

- Fixed-sampling technique only stable for variance (not energy) minimisation

- Energy minimisation may give a better nodal surface

Diagonalisation in QMC

$$\Psi_T \quad = \quad \sum_{i=1}^{n} c_i \phi_i$$

- Minimise energy over linear basis $\{\phi_i\} \Rightarrow$ standard eigenproblem

$$\frac{\partial E}{\partial c_i} = 0 \quad \forall\, i \quad \Rightarrow \quad (\mathbf{H} - E\mathbf{S})\mathbf{c} = 0$$

$$H_{ij} = \frac{\langle \phi_i | \hat{H} | \phi_j \rangle}{\langle \Psi_T | \Psi_T \rangle} \quad ; \quad S_{ij} = \frac{\langle \phi_i | \phi_j \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

- Evaluate $\{H_{ij}\}$, $\{S_{ij}\}$ in VMC
  Exact H_{ij} is symmetric $\Rightarrow$ explicitly symmetrise inexact VMC estimates

- Symmetric H_{ij} estimator has prohibitively large noise, e.g. requires 15×10^9 VMC configurations for good $\{H_{ij}\}$ estimates for Be atom Slater determinants [1]

[1] K.E. Riley and J.B. Anderson, Molecular Physics **101**(20), 3129 (2003)

A better H_{ij} estimator

- 'Traditional' eigenproblem derivation makes E stationary with respect to coefficients $\{c_i\}$

- Nightingale and Melik-Alaverdian[2] reformulated derivation assuming instead that $\{\phi_i\}$ span an invariant subspace of H
  $\Rightarrow$ suggests we should use unsymmetrised VMC H_{ij} estimator

- Both estimators converge to exact H_{ij} as no. of VMC configurations increases, but unsymmetric does so *much* more quickly
  $\Rightarrow$ many orders of magnitude lower noise

- Unsymmetric estimator makes optimisation of linear wavefunction parameters with respect to energy easy and accurate in VMC

[2] M.P. Nightingale and V. Melik-Alaverdian, Phys. Rev. Lett. **87**, 043401 (2001)

Extension to non-linear parameters

- An advantage of QMC is explicitly-correlated many-body trial wavefunctions with many non-linear variable parameters

- Optimise all parameters $\mathbf{p}$ using diagonalisation, by first-order Taylor expansion

$$\begin{aligned} \Psi_T(\mathbf{p}+\delta\mathbf{p}) &= \Psi_T(\mathbf{p}) + \sum_{i=1}^{n} \delta p_i \left.\frac{\partial \Psi_T}{\partial p_i}\right|_{\mathbf{p}} + \mathrm{O}(\delta p^2) \\ &= \sum_{i=0}^{n} c_i \phi_i + \mathrm{O}(\delta p^2) \end{aligned}$$

- Neglect $\mathrm{O}(\delta p^2)$ and iterate to convergence

- Neglecting $\mathrm{O}(\delta p^2)$ is an uncontrolled approximation, relying on small $\delta\mathbf{p}$
  $\Rightarrow$ optimisation can diverge
  $\Rightarrow$ several techniques used to prevent divergence[3]

[3] e.g. C.J. Umrigar *et al.*, Phys. Rev. Lett. **98**, 110201 (2007)

Energy minimisation in action: the first row atoms

- Early investigations showed energy minimisation generally outperforming variance minimisation, especially for linear parameters
  $\Rightarrow$ test on a system where linear parameters are important

- (All-electron) first row atoms (Li to Ne) require multi-determinant expansions to describe nodal surface well

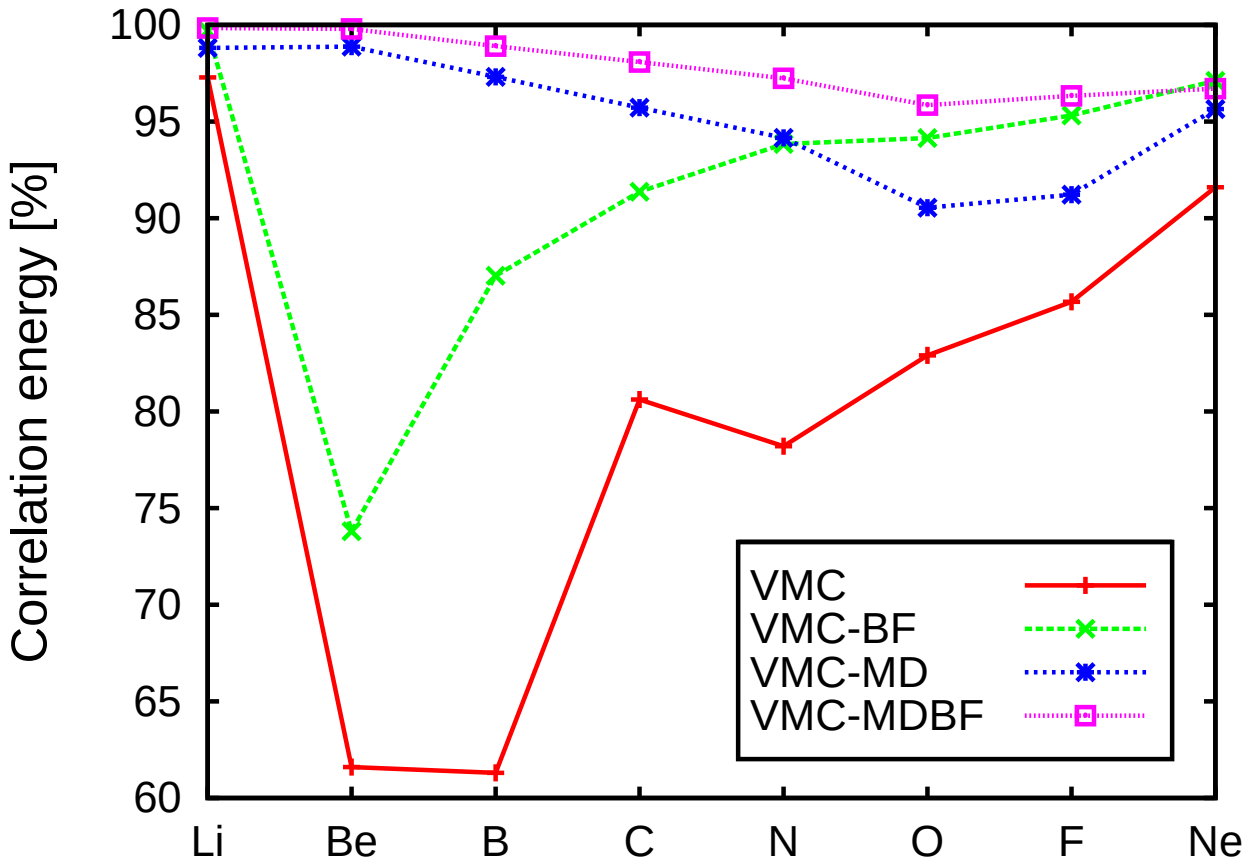
- Use multi-determinant Slater-Jastrow wavefunctions with backflow[4]
  20 CSFs (= 83 determinants for Li, 499 for Ne)

$$\Psi_T(\{\mathbf{r}_i\}) \quad = \quad e^{J(\{\mathbf{r}_i\})} \sum_{j=1}^{n} c_j \Phi_j(\{\mathbf{x}_i\})$$

- Coefficients $\{c_j\}$ of Slater determinants $\{\Phi_j\}$ are linear
  Jastrow and backflow parameters are non-linear
  Optimise all parameters using energy minimisation

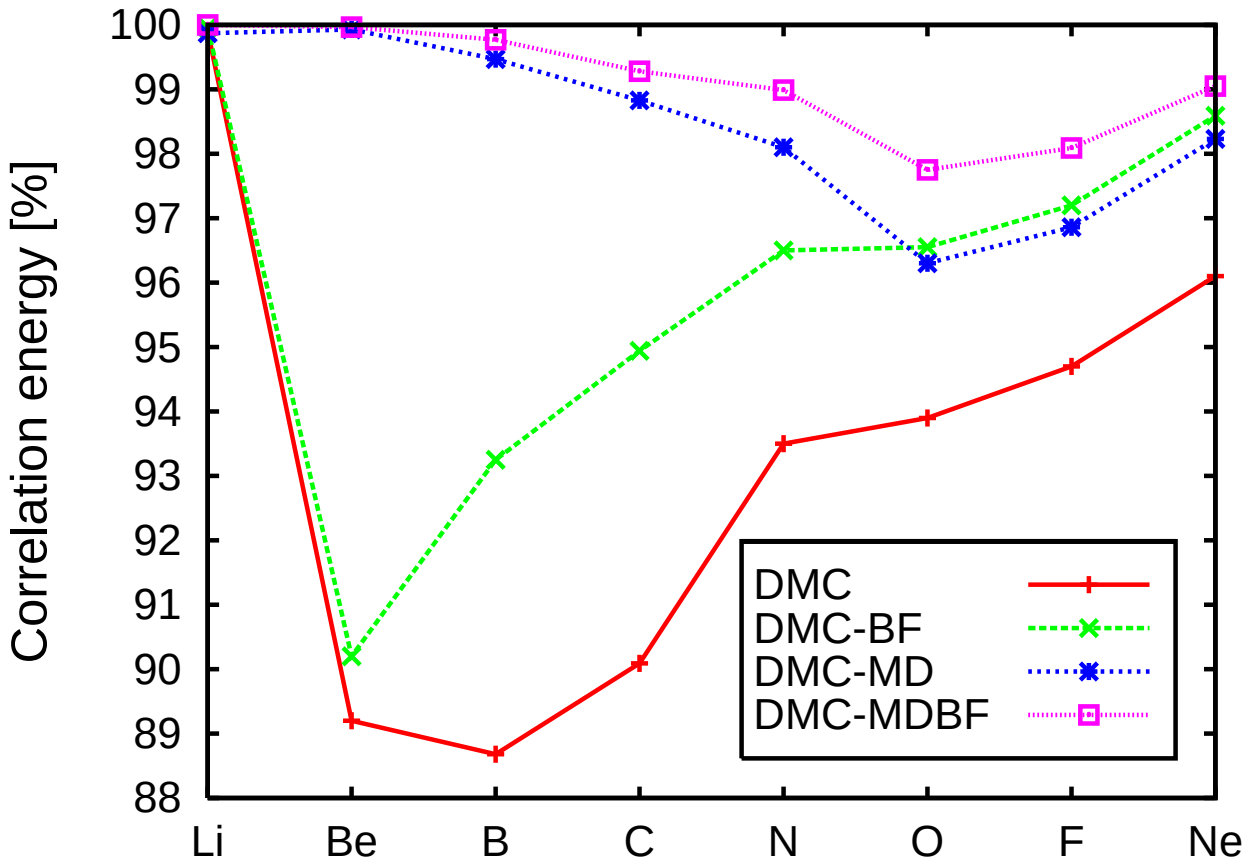
[4] P. López Ríos *et al.*, Phys. Rev. E **74**, 066701 (2006)

Energy minimisation in action: VMC



- Optimisation successful for all atoms and wavefunctions
- Multiple determinants are essential

Energy minimisation in action: DMC



- Recover 99%+ of correlation energy for Li-N and Ne, 97% for O and 98% for F
- Multiple determinants and backflow both needed for best energies

Conclusions

- Energy minimisation
  - can be done reliably and efficiently in VMC
  - can be superior to variance minimisation
- First row atoms
  - DMC accuracy now comparable to quantum chemistry methods, and could be further improved (orbital optimisation, more CSFs) (plus DMC scales well with system size, and is variational)
  - adds to evidence that backflow is effective in a wide range of systems
- Further work
  - apply energy minimisation to a wider variety of systems
  - continue improvements to algorithm's stability

MCHF energies