Wave Function Optimization and VMC

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Outline

- Motivation
- History of Wave Function Optimization
- Optimization in QMCPACK
- Multideterminant Example

Motivation: Variational Quantum Monte Carlo

VMC Computes observables over a trial wave function

$$\left\langle \hat{O} \right\rangle_{\psi^2} = \frac{\int dR \ \psi_T^\dagger(R)\, \hat{O}\, \psi_T(R)}{\int dR \ |\psi_T(R)|^2}$$

The trial wave function is *everything*. It determines all observables!

What are the errors in observables due to the trial wave function?

Motivation: Trial Wave Function Error

VMC Energy:

$$E_v = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} = \left\langle \frac{\hat{H}\psi_T}{\psi_T} \right\rangle_{\psi_T^2} = \langle E_L \rangle_{\psi_T^2}$$

Trial Wave Function Error:

$$\psi_T = \psi_0 + \delta\psi$$

VMC Energy Error:

$$\begin{aligned} \Delta_E &= \langle E_L - E_0 \rangle_{\psi_T^2} \\ &= \frac{\langle \delta\psi | \hat{H} - E_0 | \delta\psi \rangle}{\langle \psi_T | \psi_T \rangle} = \mathcal{O}[\delta\psi^2] \end{aligned}$$

VMC Energy Variance:

$$\begin{aligned} \sigma_E &= \left\langle (E_L - E_0)^2 \right\rangle_{\psi_T^2} \\ &= \frac{\langle \delta\psi | (\hat{H} - E_0)^2 | \delta\psi \rangle}{\langle \psi_T | \psi_T \rangle} = \mathcal{O}[\delta\psi^2] \end{aligned}$$

Motivation: Trial Wave Function Error

VMC Observables:

$$O_v = \frac{\langle \psi_T | \hat{O} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} = \left\langle \frac{\hat{O}\psi_T}{\psi_T} \right\rangle_{\psi_T^2} = \langle O_L \rangle_{\psi_T^2}$$

VMC Observable Error:

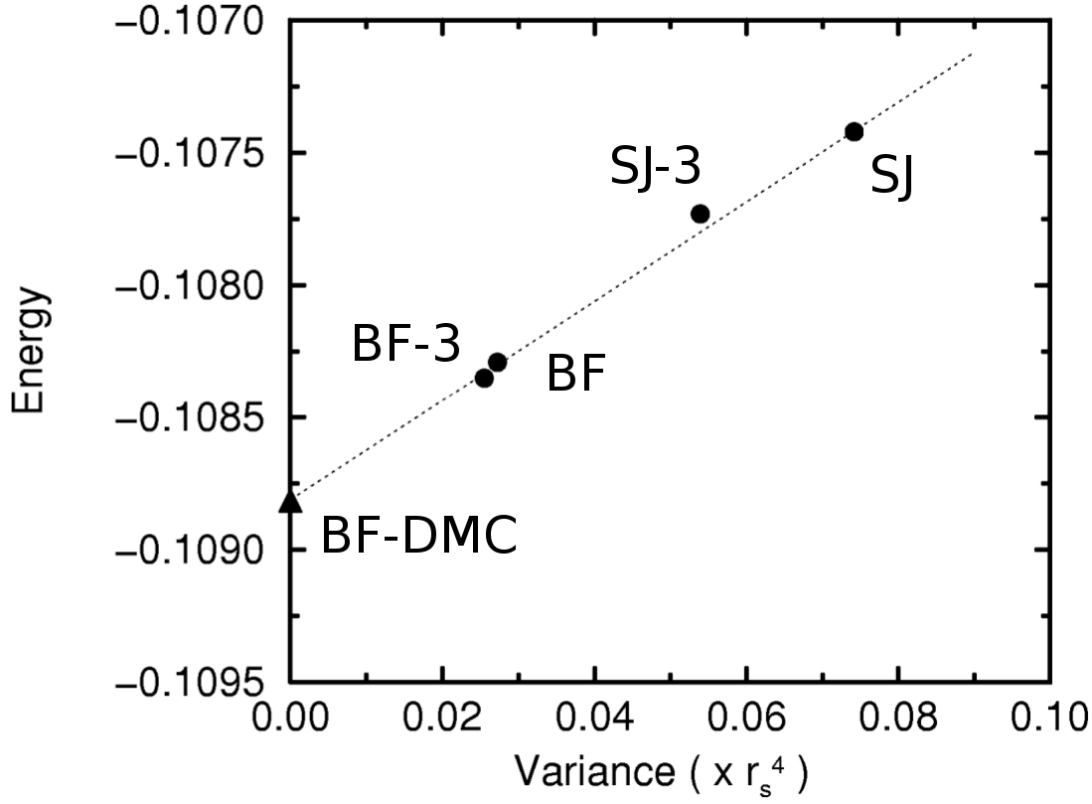
$$\begin{aligned} \Delta_O &= \langle O_L - O_0 \rangle_{\psi_T^2} \\ &= \frac{\langle \psi_0 | 2(\hat{O} - O_0) | \delta\psi \rangle}{\langle \psi_T | \psi_T \rangle} = \mathcal{O}[\delta\psi] \end{aligned}$$

VMC Observable Variance:

$$\begin{aligned} \sigma_O &= \left\langle (O_L - O_0)^2 \right\rangle_{\psi_T^2} \\ &= \frac{\langle \psi_0 | 2(\hat{O} - O_0)^2 | \delta\psi \rangle}{\langle \psi_T | \psi_T \rangle} = \mathcal{O}[1] \end{aligned}$$

Improve estimators and trial function!

Motivation: Energy and Variance



$$\sigma_E = \mathcal{O}[\delta\psi^2], \qquad \Delta_E = \mathcal{O}[\delta\psi^2]$$

Kwon, Ceperley, Martin. Phys. Rev. B 48, 12037 (1993)

History

Historical Tour of Wave Function Optimization

- "By hand"
- Variance Minimization: Conjugate Gradient
- Energy Minimization: Linear Method

History: First VMC Calculation

PHYSICAL REVIEW VOLUME 138, NUMBER 2A

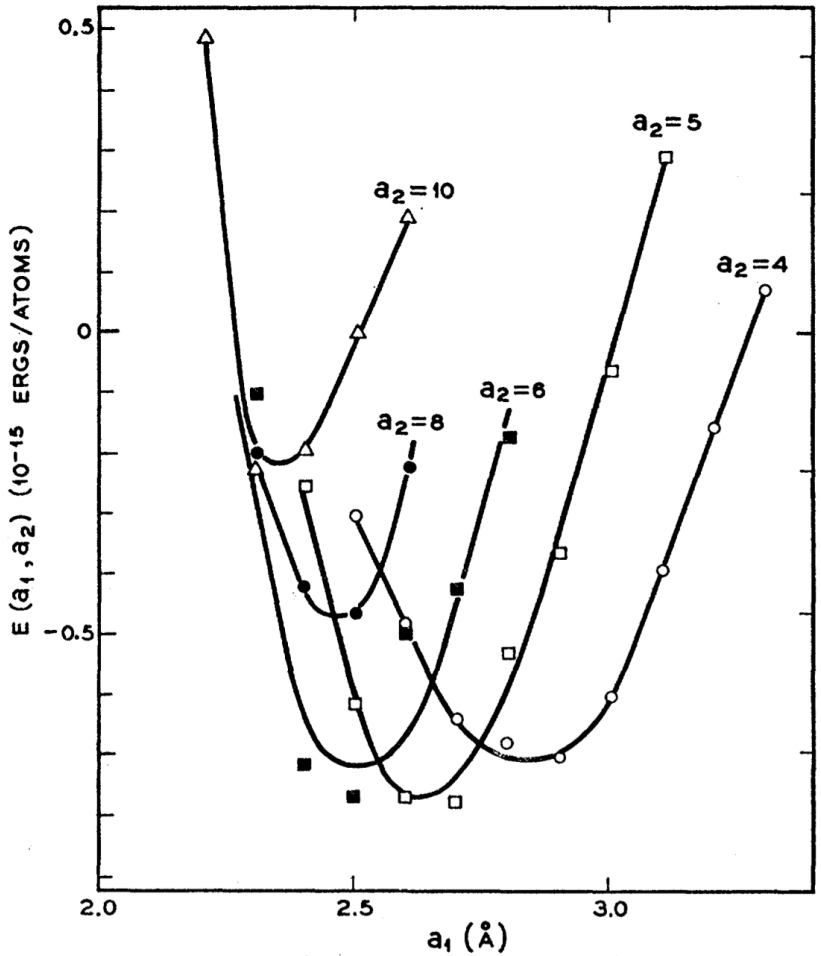
Ground State of Liquid He^4†

W. L. McMillan*
Department of Physics, University of Illinois, Urbana, Illinois
(Received 16 November 1964)

The properties of the ground state of liquid He^4 are studied using a variational wave function of the form $\Pi_{i<j} f(r_{ij})$. The Lennard-Jones 12-6 potential is used with parameters determined from the gas data by deBoer and Michiels. The configuration space integrals are performed by a Monte Carlo technique for 32 and 108 atoms in a cube with periodic boundary conditions. With $f(r)=\exp[-(2.6\,\text{Å}/r)^5]$, the ground-state energy is found to be -0.78×10^{-15} ergs/atom, which is 20% above the experimental value. The liquid structure factor and the two-particle correlation function are in reasonably good agreement with the x-ray and neutron scattering experiments.

McMillan. Phys. Rev. 138, A442–A451 (1965)

History: First Wave Function Optimization



McMillan. Phys. Rev. 138, A442–A451 (1965)

Lennard-Jones Potential

$$V(r) = 4\epsilon\left((\sigma/r)^{12} - (\sigma/r)^{6}\right)$$
$$r = r_{ij} = |r_i - r_j|$$

Wave function

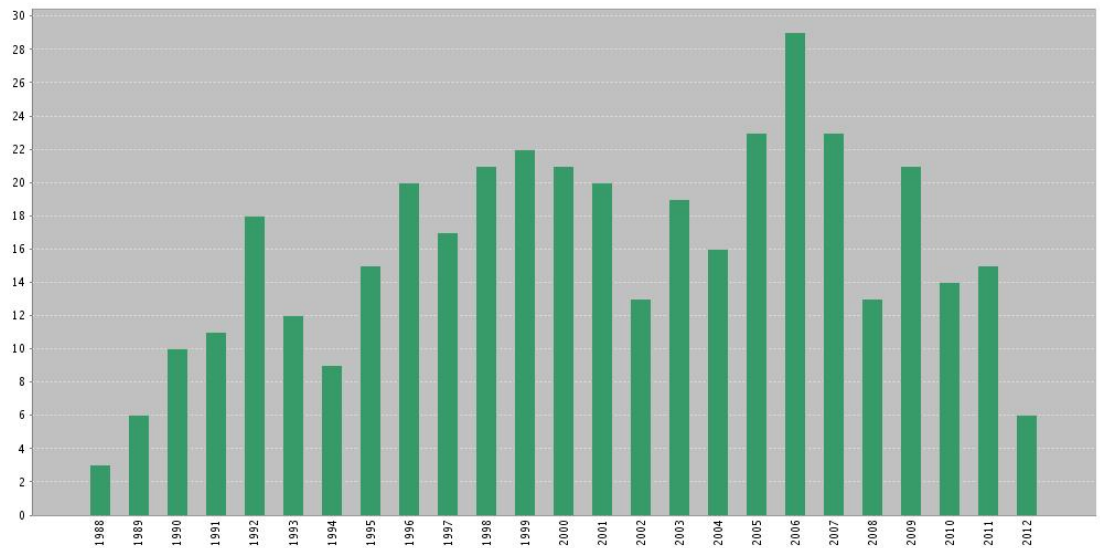
$$\psi_T(R) = \prod_{i<j} f(r_{ij})$$
$$f(r) = \exp(-(a_1/r)^{a_2})$$

History: Variance Minimization

Optimized Trial Wave Functions for Quantum Monte Carlo Calculations

C. J. Umrigar, K. G. Wilson, and J. W. Wilkins
Theory Center and Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, New York 14853
(Received 24 December 1987)

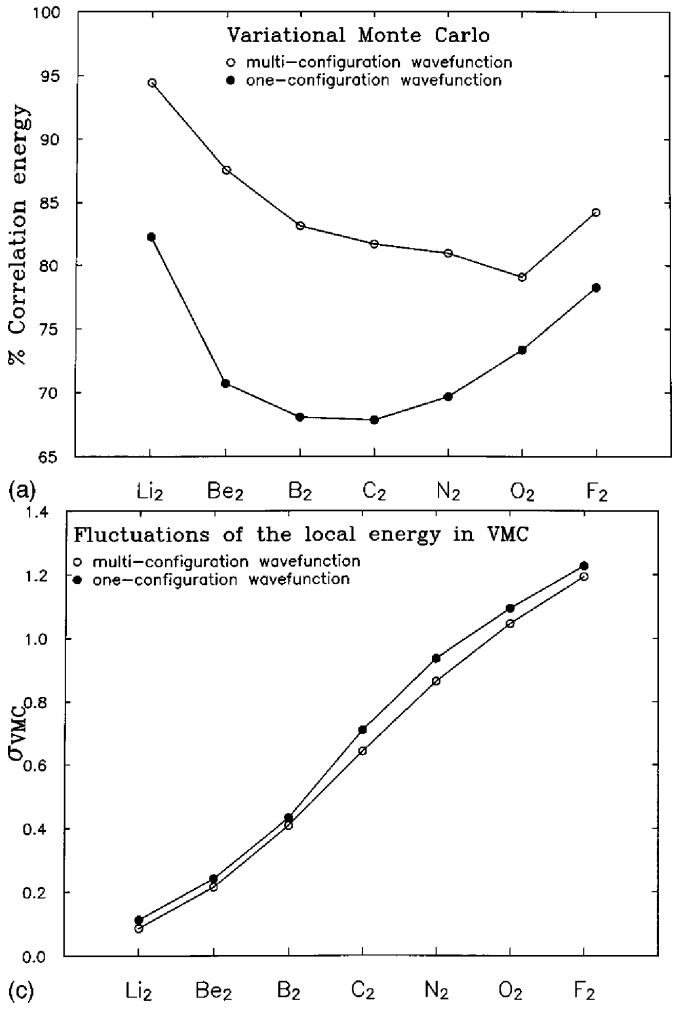
We present a procedure for obtaining optimized trial wave functions for use in quantum Monte Carlo calculations that have both smaller statistical errors and improved expectation values, compared to commonly used functions. Results are presented for several two-electron atoms and ions (including some excited states) and for the Be atom.



Umrigar, Wilson,Wilkins. Phys. Rev. Lett. 60, 1719–1722 (1988)

http://apps.webofknowledge.com/full_record.do?product=UA&qid=2&SID=2DIOelIj7c5jdPIAAi9

History: Variance Minimization



Filippi, Umrigar. J. Chem. Phys. 105, 213 (1996)

Parameterized trial wave function,

$$\begin{aligned} \psi_T(p) &= \mathcal{J}(p_j) \sum p_{kl} D_k^{\uparrow} D_l^{\downarrow}, \\ p &= \{p_j, p_{kl}\} \end{aligned}$$

The Cost function, $C(p)$:

$$C(p,c) = c_1 \left\langle (E_L(p) - \langle E_L(p) \rangle)^2 \right\rangle_{\psi_T^2(p)} + c_2 \left\langle |E_L(p) - E_{target}| \right\rangle_{\psi_T^2(p)} + \ldots$$

Minimize $C(p)$ using anything (e.g. Levenberg-Marquardt)

$\mathcal{O}[10^1] - \mathcal{O}[10^2]$ parameters

History: Variance Minimization Limits

Complete basis set limit: σ and E_L Minimization are the same.
Finite Sample: Variance bound from below, Energy is not

$$\begin{aligned} \left\langle (E_L(p) - \langle E_L(p) \rangle)^2 \right\rangle_{\psi_T^2(p)} &\geq 0 \\ \left\langle |E_L(p) - E_{target}| \right\rangle_{\psi_T^2(p)} &\geq 0 \\ \left\langle E_L(p) - E_0 \right\rangle_{\psi_T^2(p)} &> -\infty \end{aligned}$$

Simple example, H atom, 1 sample:

$$\psi_T(p, r) = exp(-pr), \qquad r = \epsilon$$
$$E_L(p, \epsilon) - E_0 = \frac{-p^2}{2} + \frac{p-1}{\epsilon} + \frac{1}{2}$$
$$p_{opt} = 1/\epsilon$$
$$E_L(1/\epsilon, \epsilon) - E_0 = \frac{1}{\epsilon}\left(\frac{1}{2\epsilon} - 1\right) + \frac{1}{2}$$

History: Variance Minimization Problems

TABLE V. Ground-state properties of H_2 from VMC calculated using Ψ_3.[a,b]

	EOEG	EOVG	VOEG	VOVG
r_{12}	2.1629(3)	2.1598(3)	2.1504(3)	2.2666(3)
r_{12}^2	5.609(2)	5.594(2)	5.571(2)	6.170(2)
r_{12}^3	16.885(8)	16.820(8)	16.94(1)	19.67(2)
r_{12}^{-1}	0.589 94(7)	0.590 94(7)	0.594 12(7)	0.561 12(7)
r_{12}^{-2}	0.5244(8)	0.5257(6)	0.5305(7)	0.4696(5)
r_{1a}	1.5520(2)	1.5488(2)	1.5530(3)	1.6532(3)
r_{1a}^2	3.040(1)	3.028(1)	3.048(1)	3.445(2)
r_{1a}^3	7.158(5)	7.116(5)	7.276(8)	8.70(1)
r_{1a}^{-1}	0.9106(2)	0.9125(2)	0.9045(2)	0.8526(2)
r_{1a}^{-2}	1.608(5)	1.617(7)	1.554(5)	1.408(5)
$r_{1a}r_{1b}$	2.709(1)	2.700(1)	2.722(1)	3.021(1)
$r_{1a}r_{2a}$	2.3524(5)	2.3424(5)	2.3620(5)	2.6720(6)
$r_{1a}r_{2b}$	2.4010(5)	2.3914(5)	2.4051(5)	2.7327(6)
z_1z_2	−0.1226(2)	−0.1225(2)	−0.1065(2)	−0.1336(2)
x_1x_2	−0.0663(2)	−0.0661(2)	−0.0606(2)	−0.0674(2)
$(z_1^2+z_2^2)/2$	1.0175(3)	1.0152(3)	1.0050(4)	1.1398(5)
$(x_1^2+x_2^2)/2$	0.7661(3)	0.7633(3)	0.7769(4)	0.8382(4)
$(r_1^2+r_2^2)/2$	2.5495(6)	2.5424(7)	2.5583(8)	2.8165(9)
Q_2	0.4787(7)	0.4678(7)	0.5252(8)	0.651(1)
Q_4	0.34(1)	0.32(1)	0.40(2)	0.65(3)
u_z^2	2.2802(9)	2.2754(6)	2.2245(7)	2.547(1)
u_z	1.2150(2)	1.2134(2)	1.1961(2)	1.2863(2)
u_c^2	3.330(1)	3.3184(8)	3.349(1)	3.623(1)
u_c	1.5884(2)	1.5854(2)	1.5894(2)	1.6524(3)
u_c^{-1}	1.0218(2)	1.0241(2)	1.0199(2)	0.9821(2)
$\Sigma_i\lvert\Delta_i^{\mathrm{rel}}\rvert$	0.857	0.764	1.313	3.737

[a]All entries are in atomic units. R_{exp}=1.401 bohr (Ref. 22).
[b]EO and VO are energy-and variance-optimizations, respectively. VG is optimization performed with the bond distance free to vary. EG is optimization with the bond distance fixed equal to the experimental value.

Snajdr, Rothstein. J. Chem. Phys. 112, 4935 (2000)

History: Linear Method

Alleviation of the Fermion-Sign Problem by Optimization of Many-Body Wave Functions

C. J. Umrigar,[1] Julien Toulouse,[1] Claudia Filippi,[2] S. Sorella,[3] and R. G. Hennig[4]

[1]*Theory Center and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA*

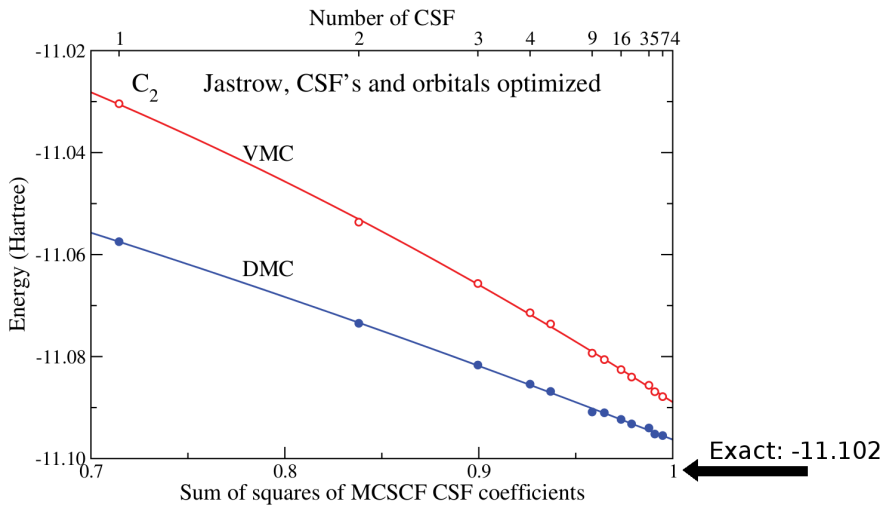
[2]*Instituut Lorentz, Universiteit Leiden, Niels Bohrweg 2, Leiden, NL-2333 CA, The Netherlands*

[3]*INFM-Democritos National Simulation Centre, and SISSA, Trieste, Italy*

[4]*Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*

(Received 3 November 2006; published 15 March 2007)

We present a simple, robust, and highly efficient method for optimizing all parameters of many-body wave functions in quantum Monte Carlo calculations, applicable to continuum systems and lattice models. Based on a strong zero-variance principle, diagonalization of the Hamiltonian matrix in the space spanned by the wave function and its derivatives determines the optimal parameters. It systematically reduces the fixed-node error, as demonstrated by the calculation of the binding energy of the small but challenging C_2 molecule to the experimental accuracy of 0.02 eV.



Umrigar, Toulouse, Filippi, Sorella, Hennig. Phys. Rev. Lett. 98, 110201 (2007)

Linear Method

Using orthogonalized first order Taylor series expansion:

$$\begin{aligned}
\psi_i(p^0, R) &= \frac{\partial}{\partial p_i}\psi(p, R)\big|_{p=p^0} \\
\overline{\psi}_i(p^0, R) &= \psi_i(p^0, R) - \langle\psi_i|\psi\rangle\,\psi(p^0, R) \\
\psi_{\mathrm{lin}}(p, R) &= \psi(p^0, R) + \sum_{i=1}^{N_p} \Delta p_i \overline{\psi}_i(p^0, R)
\end{aligned}$$

Build a generalized eigenvalue problem:

$$\overline{\mathbf{H}}\mathbf{\Delta p} = E_{\mathrm{lin}}\overline{\mathbf{S}}\mathbf{\Delta p}$$

$$H_{ij} = \left\langle \frac{\overline{\psi}_i}{\psi}\frac{\hat{H}\overline{\psi}_j}{\psi} \right\rangle_{\psi^2}, \qquad S_{ij} = \left\langle \frac{\overline{\psi}_i}{\psi}\frac{\overline{\psi}_j}{\psi} \right\rangle_{\psi^2}$$

Algorithm stabilized by $H_{ii} = H_{ii} + (1 - \delta_{i0})\exp\lambda$

Linear Method

For linear parameters (e.g. determinant coefficients)

1. Solve generalized eigenvalue problem:

$$\overline{\mathbf{H}}\mathbf{\Delta p} \quad = \quad E_{\mathrm{lin}}\overline{\mathbf{S}}\mathbf{\Delta p}$$

2. New parameters are $p' = p^0 + \Delta p$.

Linear Method

For *non-linear* parameters (e.g. Jastrow, backflow, orbital, etc. coefficients) unknown normalization for wave function.

$$\begin{aligned} \psi_i(p^0, R) &= \frac{\partial}{\partial p_i}\mathcal{N}(p)\psi(p, R)\big|_{p=p^0} \\ \psi_{\rm lin}(p, R) &= \psi(p^0, R) + \mathcal{N}(p)\sum_{i=1}^{N_p}\Delta p_i\overline{\psi}_i(p^0, R) \end{aligned}$$

Once Δp is found, rescaling is admitted.

$$p' = p^0 + \alpha\Delta p$$

α set by $||\psi_{\rm lin}|| = ||\psi||$ or line minimization.

QMCPACK Linear Algorithm

$C(c,p) = c_E \langle\ E_L(p)\ \rangle\ +\ c_\sigma \langle\ (E_L(p) -\ \langle\ E_L(p)\ \rangle)^2 \rangle$

While $|C_{new}(c,p) - C_{old}(c,p)| > \epsilon$

Run VMC

Fill $\bar{H}$, $\bar{S}$

Generate $\{w_i\}$

Invert S

$\bar{H} \rightarrow \bar{S}^{-1}\ \bar{H}$

While $\max(|\Delta\ p_i|) > p_{max}$

$H_{ii} = H_{ii} + (1 - \delta_{i0})e^{\lambda}$

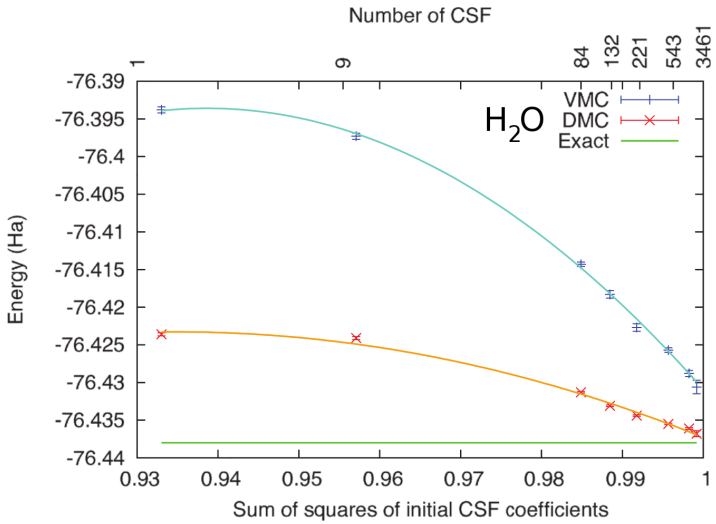
Solve $\bar{H}\Delta\ p = E_{lin}\bar{S}\Delta\ p$

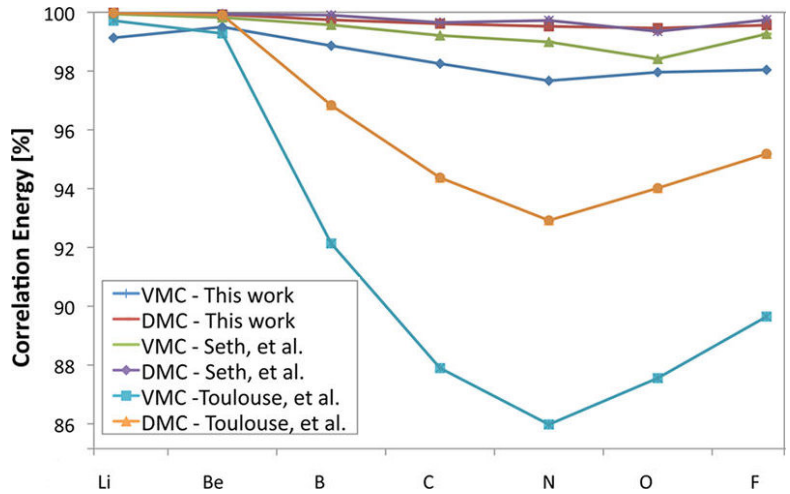
Quartic fit minimize, $C(c, p + \alpha\ \Delta\ p)$

Over $\{w_i\}$, for α_{opt}

$C_{new} = C(c, p + \alpha_{opt}\ \Delta\ p)$

Multideterminant Example





Massive Multideterminant Expansion:

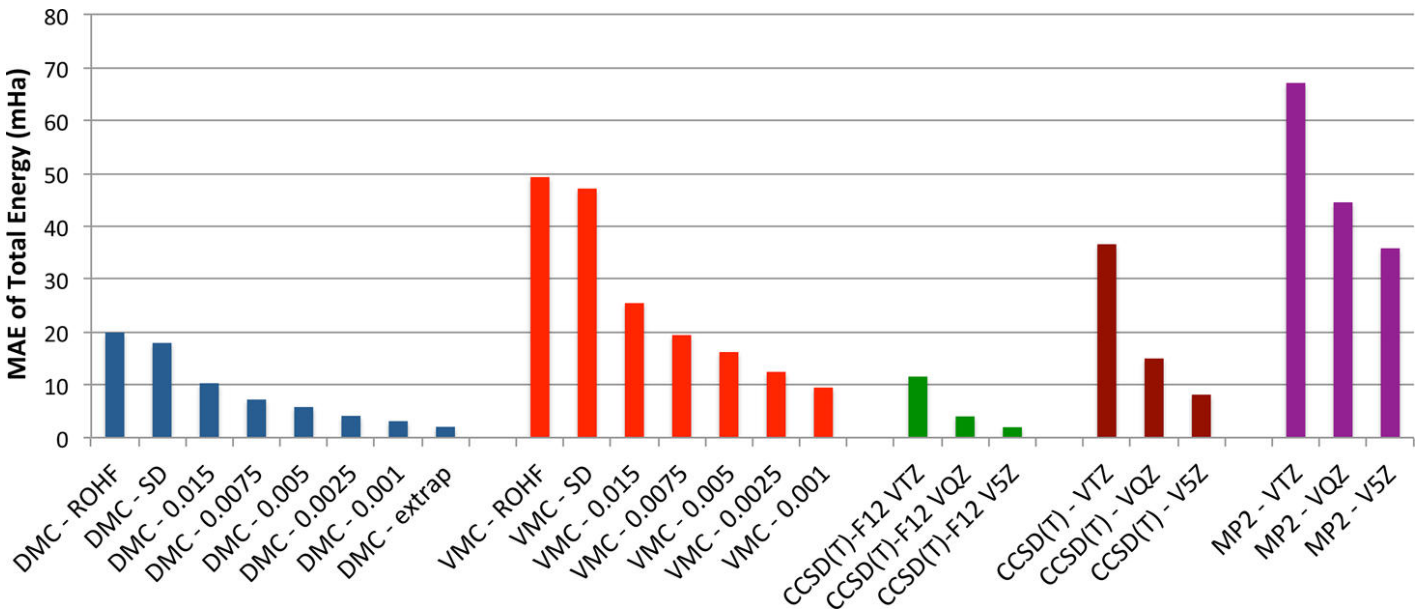
$$\psi(p) = \mathcal{J}(p_j) \sum p_{kl} D_k^{\uparrow} D_l^{\downarrow}, \quad p = \{p_j, p_{kl}\}$$

Number of CSF: 3461, Number of Determinants: 18427

Clark, Morales, JM, Kim, Scuseria. J. Chem. Phys. 135, 244105 (2011)

Morales, JM, Clark, Kim, Scuseria. J. Chem. Theory Comput., 2012, 8 (7), pp 2181–2188

Multideterminant Example



Morales, JM, Clark, Kim, Scuseria. J. Chem. Theory Comput., 2012, 8 (7), pp 2181–2188

Conclusions

What we've learned:

- How errors in the wave function effect observables
- Some history of wave function optimization
- Current state of the art: Linear method
- Optimization in QMCPACK and multideterminant expansions give excellent results

Beyond VMC Wave Function Optimization

Problems:

- Fixed Node Error
- Must VMC and DMC energy minimum coincide? No!
- Usually if VMC energy is better, so is DMC.

Methods:

- Overlap Maximization / Self Healing
- Energy minimization in DMC
- Direct nodal optimization
- Released Node