QMCPACK Training Program

Argonne National Laboratory

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Quantum Monte Carlo Methods

Wave-function Optimization

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Outline

- Basics
- Cost Functions
- Optimization Algorithms
  - Algorithms
  - Estimators
- QMCPACK specifics

VMC Review

VMC: Calculate matrix elements with a given wave-function using MC integration

Energy

$$E_V[\Psi_T,\{a_i\}] = \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \frac{\int d\vec{r}\ \Psi_T^* \hat{H} \Psi_T}{\int d\vec{r}\ \Psi_T^* \Psi_T} = \int d\vec{r}\ \pi(\vec{r}) E_L(\vec{r})$$

Variance

$$\sigma^2 = \frac{\langle \Psi_T | (\hat{H} - E_V)^2 | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \langle \hat{H}^2 \rangle - E_V^2$$

VMC Distribution

$$\pi(\vec{r}) = \frac{|\Psi_T(\vec{r})|^2}{\int d\vec{r}\,' |\Psi_T|^2}$$

Local Energy

$$E_L(\vec{r}) = \frac{\langle \vec{r} | \hat{H} | \Psi_T \rangle}{\langle \vec{r} | \Psi_T \rangle}$$

- Variational Principle: Rigorous upper bound to the energy (= only for exact wfn)

$$E_V[\Psi_T] >= E_{exact}$$

- Zero-Variance Principle: (Only!!!) Exact solution has zero variance

$$E_V \xrightarrow[\sigma^2 \to 0]{} E_{exact}$$

Wave-function Optimization

- Wave-function optimization used to be a complicated and time consuming task. Recent developments led to robust and efficient methods, e.g. linear method.
- QMC can use complicated wave-functions!
  - Include terms which depend on inter-electron distances, three-body terms, etc.
    - Very hard in deterministic methods, leads to high-dimensional integrals!
- Typical strategy:
  - Add variational freedom to the trial wave-function.
  - Optimize with VMC.
  - If result is not accurate enough, increase flexibility of your trial wave-function.

Type of variational parameters

Standard wave-function form: $\Psi_T(\vec{r}) = A(\vec{r})e^{J(\vec{r})}$

Anti-symmetric term

- Typically a linear combination of Slater Determinants of single particle orbitals
- Anti-symmetric under particle exchange
- Variational parameters can include:
  - Linear coefficients
  - Parameters in the single particle orbitals
  - Parameters in the basis set
    - gaussian exponents

Multi-Particle Correlation

- Best known as the Jastrow
- Symmetric under particle exchange
  - Does not affect the nodes!
  - In principle, only affects efficiency in DMC! (Very important nonetheless)

$$J(\vec{r}) = \sum_i u^{e-I}(\vec{r}_i) + \sum_{i>j} u^{e-e}(\vec{r}_i, \vec{r}_j) + \ldots$$

- Many forms of variational parameters!

More on trial wave-functions tomorrow!

Cost Functions – What to optimize?

- 2 main alternatives: **Energy** and **variance** minimization
  - For a given wave-function form, both conditions can lead to different wave-functions.
    - Parameters that lead to energy minimum do not lead to variance minimum.
  - Energy minimization is typically preferred, but it is more challenging.
  - Variance minimization is usually faster and more stable.
  - Other conditions can be used, e.g. maximize overlap with exact wave-function, minimize mean absolute difference of local energy, etc.
- Most codes (including QMCPACK) can optimize a mixture of energy and variance.

$$Cost = \alpha E + \beta\sigma^2$$

Optimization Methods

Gradient and hessian of the cost function

$$g_i^t = \left(\frac{\partial C(\vec{a})}{\partial a_i} \right) \Bigg|_{\vec{a}=\vec{a}_t} \qquad h_{ij}(\vec{a}_t) = \left(\frac{\partial^2 C(\vec{a})}{\partial a_i \partial a_j} \right) \Bigg|_{\vec{a}=\vec{a}_t}$$

Derivatives of the wave-function

$$\Psi_i(\vec{a}) = \left(\frac{\partial \Psi(\vec{a})}{\partial a_i} \right) \Bigg|_{\vec{a}=\vec{a}_t} \qquad \Psi_{ij}(\vec{a}) = \left(\frac{\partial^2 \Psi(\vec{a})}{\partial a_i \partial a_j} \right) \Bigg|_{\vec{a}=\vec{a}_t}$$

Steepest Descents

$$\vec{a}^{t+1} = \vec{a}^t - \gamma \vec{g}^t$$

- Will converge to the minimum, but slowly.
- Different type of parameters vary on very different length scales
  - linear parameters in the determinant expansion vs parameters in the exponent
- Small values of γ are typically required for smooth convergence.
- No need for hessians!

Optimization Methods

Newton's Method

$$C(\vec{a}) = C(\vec{a}_0) + \vec{g}^{\,t} \bullet \Delta\vec{a} + \frac{1}{2}\Delta\vec{a} \bullet \overleftrightarrow{h} \bullet \Delta\vec{a}$$

$$\vec{a}^{\,t+1} = \vec{a}^{\,t} - \overleftrightarrow{h} \bullet \vec{g}^{\,t}$$

- Efficient method, typically requires less iterations than SD.
- Needs second derivatives!
  - These can be hard to implement, many potential cross terms!

Linear Method

1. Expand the wave-function to first order around the current set of parameters

$$\overline{\Psi}_{lin}(\vec{a}) = \Psi_0 + \sum_{i=1}^{N_{opt}} \Delta a_i \overline{\Psi}_i$$

Orthogonalized Derivatives

$$\overline{\Psi}(\vec{a}) = \frac{\Psi(\vec{a})}{\sqrt{\langle \Psi(\vec{a}) | \Psi(\vec{a}) \rangle}}$$

$$\overline{\Psi}_i = \left(\frac{\partial \overline{\Psi}(\vec{a})}{\partial a_i} \right)\Bigg|_{\vec{a}=\vec{a}_0} = \Psi_i - \langle \Psi_0 | \Psi_i \rangle \Psi_0 = \Psi_i - S_{0,i}\Psi_0$$

2. Minimization of the linear energy leads to a generalized eigenvalue problem:

$$\min E_{lin}(\vec{a}) = \min \frac{\langle \overline{\Psi}_{\min}(\vec{a}) | \hat{H} | \overline{\Psi}_{\min}(\vec{a}) \rangle}{\langle \overline{\Psi}_{\min}(\vec{a}) | \overline{\Psi}_{\min}(\vec{a}) \rangle}$$

$$\overline{H} \bullet \Delta\vec{a} = E_{lin} \overline{S} \bullet \Delta\vec{a}$$

$$\overline{H}_{i,j} = \langle \overline{\Psi}_i | \hat{H} | \overline{\Psi}_j \rangle$$

$$\overline{S}_{i,j} = \langle \overline{\Psi}_i | \overline{\Psi}_j \rangle$$

Hamiltonian and overlap matrix over N_{opt}+1 basis functions $\{\Psi_0, \overline{\Psi}_1, \ldots, \overline{\Psi}_{N_{opt}}\}$

J. Toulouse and C. Umrigar, "*Optimization of quantum Monte Carlo wave functions by energy minimization* ",J. Chem. Phys. **126**, 084102 (2007).

Gradients and Hessian of the VMC Energy

$$\frac{dE}{da_i} = \frac{d}{da_i}\left[\frac{\int d\vec{R}\,\pi(\vec{R})E_L(\vec{R})}{\int d\vec{R}\,\pi(\vec{R})}\right] = 2\left\langle \frac{\Psi_i}{\Psi}\left(E_L - \langle E_L\rangle\right)\right\rangle$$

$$\frac{d^2E}{da_i da_j} = 2\left\langle\left(\frac{\Psi_{ij}}{\Psi} - \frac{\Psi_i}{\Psi}\frac{\Psi_j}{\Psi}\right)\left(E_L - \langle E_L\rangle\right)\right\rangle + 4\left\langle\left(\frac{\Psi_i}{\Psi} - \left\langle\frac{\Psi_i}{\Psi}\right\rangle\right)\left(\frac{\Psi_j}{\Psi} - \left\langle\frac{\Psi_j}{\Psi}\right\rangle\right)\left(E_L - \langle E_L\rangle\right)\right\rangle$$
$$+\left\langle\frac{\Psi_i}{\Psi}\left(E_{L,j} - \langle E_{L,j}\rangle\right) + \frac{\Psi_j}{\Psi}\left(E_{L,i} - \langle E_{L,i}\rangle\right)\right\rangle$$

Gradient of the local energy

$$E_{L,i}(\vec{R}) = \frac{\partial E_L(\vec{R})}{\partial a_i}$$

Notice that $\left\langle E_{L,i}(\vec{R})\right\rangle = 0$

All quantities necessary to construct the hessian and gradients can be easily calculated from a standard VMC calculation.

J. Toulouse and C. Umrigar, "*Optimization of quantum Monte Carlo wave functions by energy minimization* ",J. Chem. Phys. **126**, 084102 (2007).

Hamiltonian and Overlap Matrices

$$\bar{S}_{00} = 1 \qquad \bar{S}_{i0} = \bar{S}_{0j} = 0$$

$$\bar{S}_{i,j} = \left\langle \frac{\Psi_i}{\Psi}\frac{\Psi_j}{\Psi} \right\rangle - \left\langle \frac{\Psi_i}{\Psi} \right\rangle \left\langle \frac{\Psi_j}{\Psi} \right\rangle$$

$$\bar{H}_{0,0} = \langle E_L \rangle$$

$$\bar{H}_{0,j} = \left\langle \frac{\Psi_j}{\Psi}\left(E_L - \langle E_L \rangle\right) \right\rangle + \langle E_{L,j} \rangle$$

$$\bar{H}_{i,0} = \left\langle \frac{\Psi_i}{\Psi}\left(E_L - \langle E_L \rangle\right) \right\rangle$$

$$\bar{H}_{i,j} = \left\langle \frac{\Psi_i}{\Psi}\frac{\Psi_j}{\Psi}E_L \right\rangle - \left\langle \frac{\Psi_i}{\Psi} \right\rangle \left\langle \frac{\Psi_j}{\Psi}E_L \right\rangle - \left\langle \frac{\Psi_j}{\Psi} \right\rangle \left\langle \frac{\Psi_i}{\Psi}E_L \right\rangle + \left\langle \frac{\Psi_i}{\Psi} \right\rangle \left\langle \frac{\Psi_j}{\Psi} \right\rangle \langle E_L \rangle - \left\langle \frac{\Psi_i}{\Psi}\left(E_{L,j} - \langle E_{L,j} \rangle\right) \right\rangle$$

Non-symmetric H matrix leads to lower variance!

J. Toulouse and C. Umrigar, "*Optimization of quantum Monte Carlo wave functions by energy minimization* ",J. Chem. Phys. **126**, 084102 (2007).

Solving 1-D Minimization Problem

- Due to the strong non-linearity of many parameter types, it is usually necessary to perform a 1-D minimization along the direction produced by the previous methods. Some options:
  - Use a fixed (and small) time-step.
    - Leads to very slow convergence.
  - Evaluate the cost function at various points along the chosen direction and fit a polynomial
    - Cost function can be evaluated with a short VMC calculation, with correlated sampling or using reweighting.
  - Perform a direct line-minimization using reweighting.
    - Careful with wave-function overlap (reweighting efficiency) when parameters get far.
- C. Umrigar, et al. suggest various rescaling procedures to obtain reasonable step lengths, thus avoiding the line minimization step.
  - C.Umrigar, et al., "*Alleviation of the Fermion-Sign Problem by Optimization of Many-Body Wave Functions*" PRL 98, 110201 (2007).

Reweighting

Monte Carlo Integration

$$Q = \int f(x)\, g(x)\, dx \;=\; \frac{1}{N}\sum_i f(x_i) + O\left[\sqrt{\frac{\sigma_f^2}{N}}\right]$$

The points in the set $\{x_i\}$ are distributed according to g(x).

What happens when we want to perform the integral with respect to a different distribution g'(x), but we already have a set of points sampled from g(x).
Can we estimate the new integral using the old set? **YES, use reweighting!!!**

$$Q' = \int f(x)\, g'(x)\, dx \;= \int \left[f(x)\frac{g'(x)}{g(x)} \right] g(x)\, dx \;= \frac{1}{N}\sum_i \left[f(x_i)\frac{g'(x_i)}{g(x_i)} \right] + O\left[\sqrt{\frac{\sigma^2_{f\frac{g'}{g}}}{N}}\right]$$

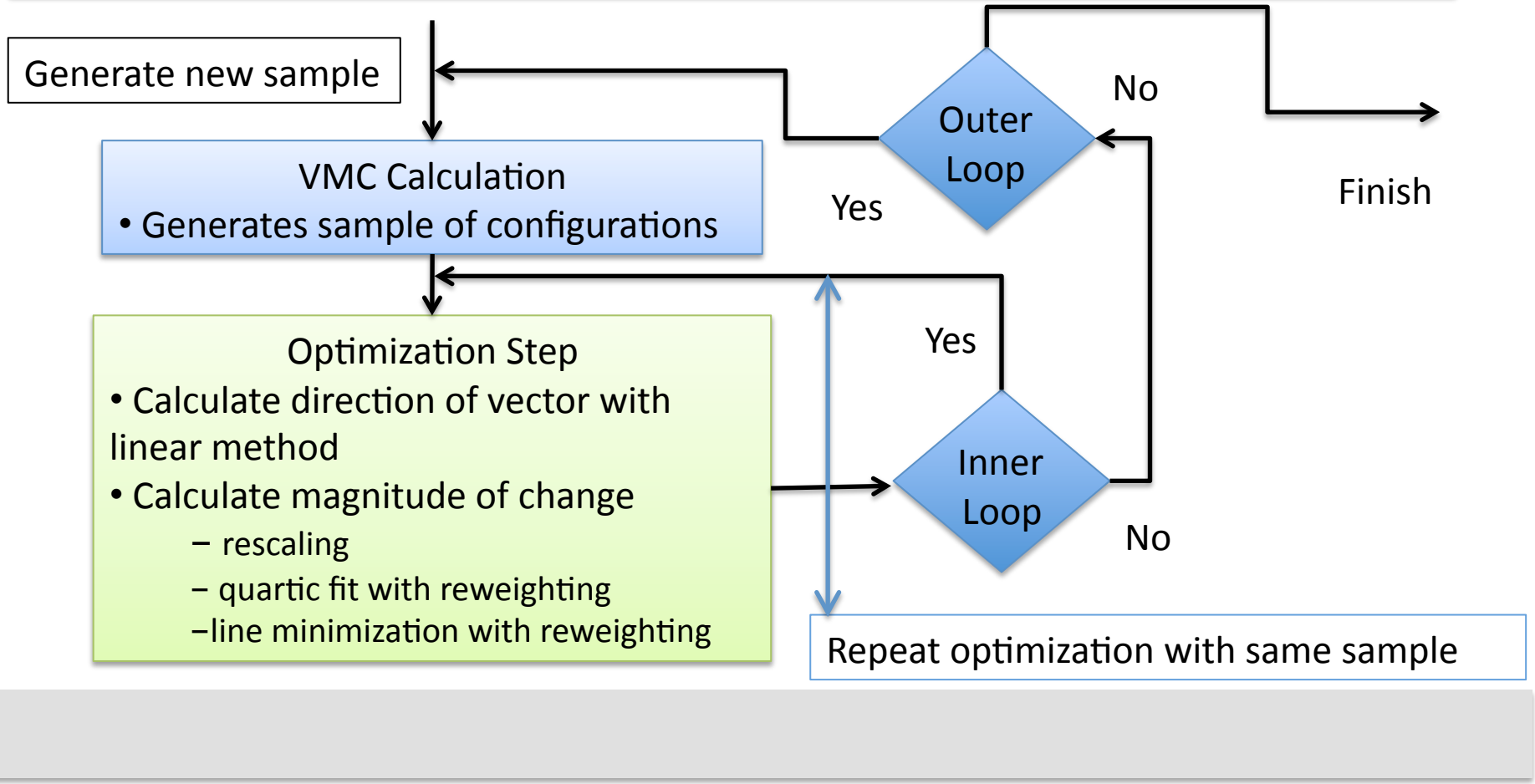
The efficiency of the procedure will depend on how close g and g' are.

Effective number of samples: $\dfrac{N_{eff}}{N} = \dfrac{< w >^2}{< w^2 >}$, where $\mathrm{w(x)} = \dfrac{\mathrm{g'(x)}}{\mathrm{g(x)}}$

QMCPACK Specifics - I

The linear method is the recommended optimization algorithm in QMCPACK.

- Robust: Can handle all type of parameters efficiently.
- Fast and simple: Only first derivatives of the wave-function and local energy are needed.



QMCPACK Specifics – Sample XML Block

Outer loop: Redo optimization with new sample

```
<loop max="10">
 <qmc method="linear" move="pbyp" checkpoint="-1" gpu="no">
   <parameter name="blocks">     10  </parameter>
   <parameter name="warmupsteps"> 25 </parameter>
   <parameter name="steps"> 1 </parameter>
   <parameter name="substeps"> 20 </parameter>
   <parameter name="timestep"> 0.5 </parameter>
   <parameter name="samples"> 10240  </parameter>
   <cost name="energy">                    0.95 </cost>
   <cost name="unreweightedvariance">      0.0 </cost>
   <cost name="reweightedvariance">        0.05 </cost>
   <parameter name="useDrift">  yes </parameter>
   <parameter name="bigchange">10.0</parameter>
   <estimator name="LocalEnergy" hdf5="no"/>
   <parameter name="usebuffer"> yes </parameter>
   <parameter name="nonlocalpp"> yes </parameter>
   <parameter name="MinMethod">quartic</parameter>
   <parameter name="exp0">-6</parameter>
   <parameter name="alloweddifference"> 1.0e-5 </parameter>
   <parameter name="stepsize">  0.15 </parameter>
   <parameter name="nstabilizers"> 1 </parameter>
 </qmc>
</loop>
```

VMC parameters

Cost function

Optimization parameters

QMCPACK Specifics

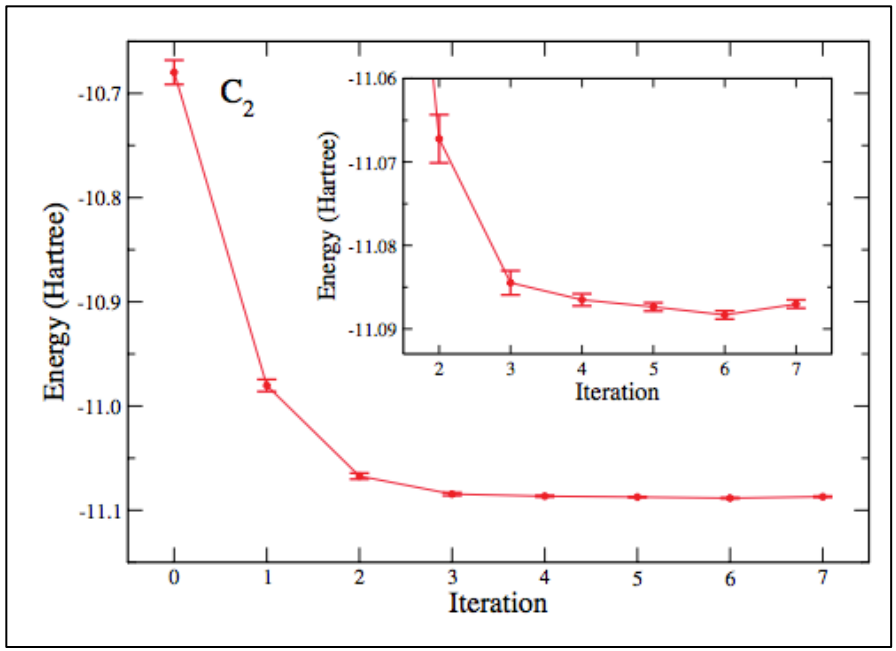
- Important parameters:
  - ***bigchange***: (default 50.0) largest parameter change allowed
  - ***usebuffer***: (default "no") Save useful information during VMC
  - ***nonlocalpp***: (default "no") Include non-local energy on 1-D min
  - ***MinMethod***: (default "quartic") Method to calculate magnitude of parameter change
    - quartic: fit quartic polynomial to 4 values of the cost function obtained using reweighting along chosen direction
    - linemin: direct line minimization using reweighting
    - rescale: no 1-D minimization. Uses Umrigar's suggestions.
  - ***stepsize***: (default 0.25) step size in either quartic or linemin methods.
  - ***alloweddifference***: (default 1e-4) Allowed increased in energy
  - ***exp0***: (default -16.0) Initial value for stabilizer (shift to diagonal of H)
    - Actual value of stabilizer is 10^exp0
  - ***nstabilizers***: (default 3) Number of stabilizers to try
  - ***stabilizaterScale***: (default 2.0) Increase in value of exp0 between iterations.
  - ***max_its***: (default 1) number of inner loops with same sample

QMCPACK Specifics

- Important parameters:
  - ***minwalkers***: (default 0.3) minimum value allowed for the ratio of effective samples to actual number of walkers in a reweighting step. The optimization will stop if the effective number of walkers in any reweighting calculation drops below this value. Last set of acceptable parameters are kept.
  - **maxWeight:** (defaul 1e6) Maximum weight allowed in reweighting. Any weight above this value will be reset to this value.

- Recommendations:
  - Set ***samples*** to equal to (#***threads***)*****blocks***.
  - Set ***steps*** to 1. Use ***substeps*** to control correlation between samples.
  - For cases where equilibration is slow, increase both **substeps** and **warmupsteps**.
  - For hard cases (e.g. simultaneous optimization of long MSD and 3-Body J), set ***exp0*** to 0 and do a single inner iteration (***max_its***=1) per sample of configurations.

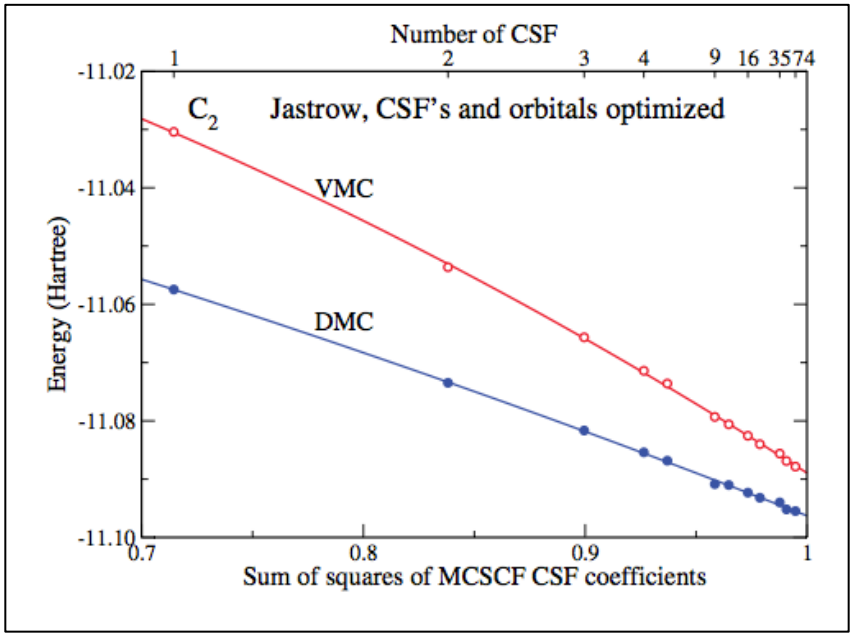
Examples from literature



Simultaneous optimization of Jastrow, CSF and orbital parameters.

- Robust and automatic
- Little need for human intervention

- Convergence to mHa accuracy with less than 10 iterations
- Can recover energy in large MSD expansions!



C.Umrigar, et al., "*Alleviation of the Fermion-Sign Problem by Optimization of Many-Body Wave Functions*" PRL **98**, 110201 (2007).

Important References

- X. Lin, et al., "*Optimization of quantum Monte Carlo wave functions using analytical energy derivatives*", J. Chem. Phys. **112**, 2650 (2000).
- C. Umrigar and C. Filippi, "*Energy and Variance Optimization of Many-Body Wave Functions",* PRL **94**, 150201 (2005).
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- A. Scemama, et al., "*Simple and efficient approach to the optimization of correlated wave functions*", J. Chem. Phys. **73**, 241101 (R) (2006).
-J. Toulouse and C. Umrigar, "*Optimization of quantum Monte Carlo wave functions by energy minimization* ",J. Chem. Phys. **126**, 084102 (2007).
- C.Umrigar, et al., "*Alleviation of the Fermion-Sign Problem by Optimization of Many-Body Wave Functions*" PRL **98**, 110201 (2007).
- J. Toulouse and C. Umrigar, "*Full optimization of Slater-Jastrow wavefunctions with application to the first-row atoms and homonuclear dimers*", J. Chem. Phys. **128**, 174101 (2008).