# Worksheet 1: Optimisation of a Jastrow factor for LiH (90 minutes)

Neil D. Drummond

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## 1 Introduction

### 1.1 Overview

In yesterday's practical session you learned how to run basic QMC calculations using CASINO and how to analyse the data generated in those calculations using the REBLOCK utility. In this session you will learn how to optimise trial wave functions using CASINO, which is not only a crucial step in any QMC project, but also (probably) the most difficult aspect of using QMC.

It is hoped that by the end of this worksheet users will be able to (i) choose suitable Jastrow factors for real systems, (ii) run variance- and energy-minimisation calculations to optimise Jastrow factors.

### 1.2 Trial wave functions: the basics

Most QMC calculations use trial wave functions consisting of a product of Slater determinants for spin-up and spin-down electrons and a *Jastrow factor*, which is an explicit function of interparticle distances. The Slater determinants contain orbitals generated using either Hartree–Fock theory or density-functional theory, while the Jastrow factor contains parameters to be optimised within QMC.

The CASINO manual can be found in `~/CASINO/manual/casino_manual.pdf`. The form of the Jastrow factor is described in Sec. 22 of the CASINO manual, and the format of the JASTROW block in `correlation.data` is described in Sec. 7.4.2. Only $u$, $\chi$ and $f$ terms are used in this worksheet. If necessary, please refer to these sections of the manual as you proceed through this worksheet.

### 1.3 Variance minimisation: the basics

Optimisation of a wave function by variance minimisation proceeds as follows: (i) a VMC calculation is performed in order to generate a set of electron configurations distributed according to the square of the initial trial wave function; (ii) the local energy of each configuration, and hence the variance of the local energies, can be evaluated as a function of the wave-function parameters; this variance is minimised with respect to the parameters; (iii) CASINO returns to step (i) and generates a new set of configurations distributed according to the new wave function; and so on. So the optimisation process consists of alternating cycles of VMC *configuration generation* and *variance minimisation*.

The user simply needs to set up the `input` file with the parameters required to drive the initial VMC calculation and to specify the parameters required for the variance-minimisation stage, and CASINO will carry out the alternating sequence of configuration-generation and variance-minimisation calculations.

### 1.4 Energy minimisation: the basics

This is almost the same as described above for variance minimisation, except that in step (ii) above the linear-least-squares energy-minimisation algorithm is used.

# 2 Variance minimisation

Let's start by optimising a Jastrow factor for a lithium hydride molecule.

- Go to the `LiH` directory. This directory contains CASINO input files for a LiH molecule. Hartree–Fock orbitals represented in a Gaussian basis set are held in `gwfn.data`, the Jastrow factor is specified in `correlation.data` and the input parameters required to drive the CASINO calculation are held in `input`.
- Open the `correlation.data` file using your favourite text editor:
  - The *truncation order* $C$ determines how smooth the Jastrow factor is: the $C$th derivative of the Jastrow factor is discontinuous at the cutoff length. A truncation order of $C = 2$ is the lowest value allowed by quantum mechanics. In practice the truncation order is usually set to $C = 3$, as this makes the local energy continuous at the cutoff lengths, which is helpful if the cutoff lengths are to be optimised by variance minimisation.
  - Note that all parameters (including the cutoff lengths) are followed by either "0" or "1", indicating whether the parameter value is fixed or optimisable.
  - The Jastrow factor contains $u$ (electron–electron), $\chi$ (electron–nucleus) and $f$ (electron–electron–nucleus) terms. There are separate $\chi$ and $f$ functions (sets of data) for the lithium and hydrogen nuclei. Each of these terms are of polynomial form.
  - The number of terms in the polynomials is controlled by the "expansion orders" $N_u$, $N_\chi$, $N_f^{\rm ee}$ and $N_f^{\rm eN}$.
  - Note the *spin-dependence* flags. LiH is not spin-polarised, so the spin dependence of the electron–nucleus terms $\chi$ is $S_\chi = 0$, meaning that the same $\chi$ functions are used for spin-up and spin-down electrons. On the other hand, the spin dependence of $u$ is $S_u = 1$, meaning that different $u$ functions are used for pairs of electrons with parallel and antiparallel spins. *What would the best value for the spin dependence of $f$ be in principle?*
- Please delete the lines containing the polynomial expansion coefficients *between* (but not including!) "Parameter values ; Optimizable (0=NO; 1=YES)" and "END SET . . ." for each type of term and each type of atom in order to create a "blank" Jastrow factor.[1] (There are five such sets of parameters.) When CASINO runs with a "blank" Jastrow factor for a molecule, the trial wave function is simply the Slater wave function.[2]
- Now examine the `input` file. Observe that:
  - **runtype** is set to "vmc_opt", meaning "perform VMC configuration generation then variance minimisation (repeatedly)".
  - **opt_cycles** is set to 3, meaning "perform three configuration-generation / optimisation cycles". (Typically **opt_cycles** should be set to 4 or more.)
  - The number of configurations to be used in the optimisation (**vmc_nconfig_write**=10000) is less than the number of configuration moves on which energies are written out during the VMC calculation (**vmc_nstep**=50000). Typically, one should use **vmc_nconfig_write**=10000 configurations or more for unreweighted variance minimisation. Using a larger value of **vmc_nstep** ensures that the configurations used in the optimisation are independent.
  - **vmc_equil_nstep** (number of equilibration steps) is set to 5000; this should be more than adequate in most cases. Equilibration is relatively cheap, so there is rarely any need to economise here.
  - **opt_method** is "varmin", meaning "use the standard variance-minimisation method to optimise the wave function".

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[1] Warning: a blank Jastrow factor is not the same as the Jastrow factor with all the parameters set to 0.

[2] A VMC calculation in which the trial wave function is a Slater wave function is called a *Hartree–Fock VMC* (HFVMC) calculation. If the orbitals were generated using a Hartree–Fock code then all HFVMC-calculated energy components should agree with the energy components calculated by the code used to generate the orbitals; if the orbitals were generated using DFT then the HFVMC kinetic energy should be in agreement with the kinetic energy calculated by the generating code. One should always check for this when studying a new system.

- Type e.g. *casinohelp opt_method* to obtain information about the **opt_method** keyword. Try this for a few other keywords in the `input` file. Remeber to use CASINOHELP when you encounter any other keywords you are unsure about in subsequent activities and worksheets.

- Type *runqmc -B* to start the CASINO calculation.

- Every now and again, while the optimisation is proceeding, type *envmc*. The output should look a bit like this:

```
ENVMC v0.80: Script to extract VMC energies from CASINO output files.
Usage: envmc [-kei] [-ti] [-fisq] [-pe] [-vee] [-vei] [-vnl] [-nc]
         [-vr] [-rel] [-ct] [-nf <no. of figures in error bars>] [files]

File: ./out
Block averages recomputed for current run.
Corrected for serial correlation using correlation time method.
Energies in au, sample variances in au^2.

VMC #1: E     = -7.997(9) ; var  = 1.7(4) (correlation.out.0)
VMC #2: E     = -8.056(2) ; var  = 0.064(1) (correlation.out.1)
VMC #3: E     = -8.056(2) ; var  = 0.0622(9) (correlation.out.2)
VMC #4: E     = -8.060(2) ; var  = 0.064(1) (correlation.out.3)
        Total CASINO CPU time  ::: 145.5700 seconds
```

  This shows the VMC energy at each configuration-generation stage. The set of wave-function parameters that led to, for example, the VMC energy at the fourth cycle are contained in `correlation.out.3`, as indicated. Optimising the parameters has lowered both the total energy and the variance significantly. Essentially all of the improvement occurred in the first iteration.

- For more detailed information about the calculation, examine the contents of the `out` file. It is always a good idea to check this file, to verify that the QMC calculation proceeded as expected.

- Use ENVMC to identify the `correlation.out.`$x$ file that gives the lowest VMC energy, then rename that file as `correlation.data`.

- Type *clearup* to remove the other output files.

- Now perform a final, more accurate VMC calculation with your new wave function, to obtain the VMC energy. Set **runtype** to "vmc", **vmc_nconfig_write** to 0 and increase **vmc_nstep** to 500000 in the `input` file. Type *runqmc -B*, and when the run has finished use REBLOCK to analyse the data. You should obtain an energy of about $-8.0559(6)$ a.u.

- You can also obtain the energy and energy variance by typing *envmc*.

Congratulations, you have successfully carried out a QMC wave-function optimisation! Please take a note of the VMC energy (and error bar) and energy variance that you obtained, then type *clearup* to remove the output files.

## 3 Accelerated variance minimisation for linear parameters

If one only wants to optimise linear Jastrow parameters (so all cutoff lengths are fixed) then the unreweighted variance of the local energies is a quartic function of the free parameters, and the optimisation process can be greatly accelerated. Let's reoptimise the linear Jastrow parameters for the lithium hydride molecule.

- In directory `LiH`, open the `correlation.data` file and delete all the lines with linear Jastrow parameters to create a "blank" Jastrow factor, as you did before. Set the optimisable flag of each of the five cutoff lengths to "0".

- Open the `input` file and set the **opt_method** keyword to “varmin_linjas”.
- The other `input` parameters should be as they were when you performed “standard” variance minimisation (you will need to reduce **vmc_nstep** to 50000, and set **vmc_nconfig_write** to 10000 and **runtype** to “vmc_opt”).
- Type *runqmc -B*. As before, you can monitor the progress of the calculation using ENVMC.
- The total time for the optimisation process should be rather less this time.

Again, choose the `correlation.out.`$x$ file that gives the lowest energy, then perform a more accurate evaluation of its VMC energy (follow the instructions in Sec. 2). The result should be essentially the same as you got before, although the energies may differ by more than the VMC error bars. *What is the additional source of variance?*

Note that the accelerated optimisation scheme scales better with system size than the standard version; hence it becomes more useful in large systems.

## 4 Energy minimisation

Now let’s reoptimise the linear Jastrow parameters for the lithium hydride molecule using energy minimisation. Since we are usually interested in the energy it is generally preferable to optimise wave functions by energy minimisation, although it is often necessary to perform a preliminary optimisation by variance minimisation, to generate a good starting point for energy minimisation.

- Delete the five sets of linear parameters to create a “blank” Jastrow factor, as you have done before. Make sure that all five cutoff lengths are fixed (optimisable flags are set to “0”).
- Open the `input` file and set the **opt_method** keyword to “emin”.
- The other input parameters should be as they were when you performed “standard” variance minimisation (set **vmc_nstep** to 50000, **vmc_nconfig_write** to 10000 and **runtype** to “vmc_opt”).
- Type *runqmc -B*. As before, you can monitor the progress of the calculation using ENVMC.

Again, choose the wave function that gives the lowest energy, then perform a more accurate evaluation of its VMC energy and variance (follow the instructions in Sec. 2). Varmin and emin should give similar results when used to optimise a Jastrow factor for a small molecule like LiH—do you find this to be the case?

## 5 Changing the number of parameters

Choosing how to parametrise a wave function is the most difficult aspect of wave-function optimisation. The variational principle implies that adding more parameters can only improve the wave function; in practice, however, the wave function is optimised using a finite sampling of configuration space, and attempting to optimise too many parameters results in instabilities in the optimisation procedure.

Let’s study the effect of changing the number of optimisable parameters for our LiH molecule.

- Open the `correlation.data` file. Try increasing the expansion orders $N_u$ and $N_\chi$ from 2 to 4. (Remember that there are two $\chi$ functions; you should increase the expansion orders for both.)
- Delete all the linear parameters to create a “blank” Jastrow factor.
- Use **opt_method**= “varmin_linjas” to optimise the parameters. (Remember to adjust **vmc_nstep**, **vmc_nconfig_write** and **runtype**.)
- Use ENVMC to choose the best `correlation.out.`$x$ file and perform a long VMC calculation using this file. How does the energy compare with what you got before? What about the variance? Has the wave function improved?

If you have time, carry out some further investigations:

- What happens if you increase the expansion orders $N_f^{\rm ee}$ and $N_f^{\rm eN}$ to 3?
- What happens if you increase the spin dependence of $f$ from 0 to 1?
- What happens if you use **opt_method**=“emin” instead of “varmin_linjas”?

At the end of this investigation, you should be able to choose (and optimise) a good Jastrow factor for use in a QMC study of LiH.

It is essentially never necessary to have $N_u > 8$, $N_\chi > 6$ or $N_f^{\rm ee,eN} > 3$. In fact $N_u = 8$, $N_\chi = 6$ and $N_f^{\rm ee,eN} = 3$ are fairly typical in studies of real systems.

# 6 Putting it all together (homework activity)

(Please complete Worksheet 2 before starting this activity.)

In order to test that you have understood everything that has been covered, carry out a study of Jastrow-factor optimisation for an all-electron Ne atom:

- Go to the `Ne_atom` directory.
- Study the effect of using different numbers of $u$, $\chi$ and $f$ parameters, different spin dependences and starting with different cutoff lengths.
- Determine a reasonable number of configurations to use in the optimisation: this must represent a trade-off between the limited time and computer resources at your disposal and the desire to use as many configurations as possible.

The DMC energy of the neon atom is $-128.9233(2)$ a.u.: you may use this result to evaluate the fraction of correlation energy that you retrieve in each case.

This is the sort of preliminary investigation that one has to carry out before starting a QMC project.