Project 2;
Variational Monte Carlo studies of electronic systems

Github repository:

https://github.com/filiphl/FYS4411.git

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Abstract

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2.1 Preliminary derivations

While performing VMC it is of course favourable to use analytical expressions, should they not demand a significant increase in CPU time. We will therefore need to calculate the local energy $E_L = \frac{1}{\Psi_T} H \Psi_T$ and the quantum force $F = \frac{2}{\Psi_T} \nabla \Psi_T$. The Hamiltonian H used will be:

$$H = H_0 + H_I = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right) + \sum_{i<j} \frac{1}{r_{ij}} \tag{1}$$

The Laplacian will be the most demanding quantity to calculate.

2.1.1 Singlet electron state

For an electron in a harmonic oscillator potential, the energy is given by $\epsilon_n = \omega(n+1)$, where we have used natural units and $n = n_x + n_y + \ldots$. For two non-interacting electrons, the energy is $\epsilon_{n_1,n_2} = \omega(n_{x,1} + n_{y,1} + \ldots + n_{x,2} + n_{y,2} + \ldots + 2)$. Obviously the energy is lowest for $n_1 = n_2 = 0$, giving $\epsilon_{0,0} = 2\omega$.
Since $n_1 = n_2 = 0$ means the two electron are in the same spatial wavefunction, they must have different spins. Since electrons are spin-$\frac{1}{2}$ particles, they combine to give total spin zero, i.e. they form the singlet state.

For the singlet electron state we will use the trial wavefunction:

$$\Psi_T(\mathbf{r}_1, \mathbf{r}_2) = C e^{-\frac{\alpha\omega}{2}(r_1^2+r_2^2)} e^{\frac{ar_{12}}{1+\beta r_{12}}} \tag{2}$$

The Laplacian of which (for particle i) is:

$$\nabla_i^2 \Psi_T = \nabla_i(\nabla_i \Psi_T) \tag{3}$$

We will use the following change of coordinates when it simplifies calculations.

$$\begin{aligned}
\frac{\partial}{\partial r_{i,j}} &= \frac{\partial r_{12}}{\partial r_{i,j}}\frac{\partial}{\partial r_{12}} \\
\rightarrow \nabla_i &= \frac{(-1)^i}{r_{12}}(x_1 - x_2, y_1 - y_2)\frac{\partial}{\partial r_{12}} \\
&= \frac{(-1)^i}{r_{12}}\mathbf{r}_{12}\frac{\partial}{\partial r_{12}}
\end{aligned} \tag{4}$$

Where $r_{i,j}$ is element j of $\mathbf{r}_i$. The gradient, which is also needed for the quantum force, is then:

$$\begin{aligned}
\nabla_i \Psi_T &= -\alpha\omega\mathbf{r}_i\Psi_T + \frac{(-1)^i}{r_{12}}\mathbf{r}_{12}\left[\frac{\partial}{\partial r_{12}}\left(\frac{ar_{12}}{1+\beta r_{12}} \right) \right]\Psi_T \\
&= \left[-\alpha\omega\mathbf{r}_i + \frac{(-1)^i}{r_{12}}\mathbf{r}_{12}\frac{a}{(1+\beta r_{12})^2} \right]\Psi_T
\end{aligned} \tag{5}$$

which means the Laplacian is:

$$\begin{aligned}
\nabla_i^2 \Psi_T &= [\nabla_i[\ldots]]\,\Psi_T + [\ldots]\nabla_i\Psi_T \\
&= [\nabla_i[\ldots]]\,\Psi_T + [\ldots]^2\Psi_T
\end{aligned} \tag{6}$$

where $[\ldots]$ is the last parenthesis in equation 5. The parenthesis in the first term above is:

$$\begin{aligned}
\nabla_i\left[-\alpha\omega\mathbf{r}_i + \frac{(-1)^i}{r_{12}}\mathbf{r}_{12}\frac{a}{(1+\beta r_{12})^2} \right] &= -2\alpha\omega + \frac{(-1)^i}{r_{12}}\left(\frac{(-1)^i 2ar_{12}}{(1+\beta r_{12})^2} - \frac{(-1)^i 2a\beta r_{12}}{(1+\beta r_{12})^3} - \frac{(-1)^i a}{r_{12}(1+\beta r_{12})^2} \right) \\
&= -2\alpha\omega - \frac{a}{(1+\beta r_{12})^2}\left(\frac{1}{r_{12}} - \frac{2}{r_{12}} + \frac{2\beta}{1+\beta r_{12}} \right) \\
&= -2\alpha\omega + \frac{a}{r_{12}(1+\beta r_{12})^2} - \frac{2a\beta}{(1+\beta r_{12})^3}
\end{aligned} \tag{7}$$

Which gives:

$$\nabla_i^2 \Psi_T = \left[-2\alpha\omega + \frac{a}{r_{12}(1+\beta r_{12})^2} - \frac{2a\beta}{(1+\beta r_{12})^3} + \alpha^2\omega^2 r_i^2 + \frac{a^2}{(1+\beta r_{12})^4} - \frac{2\alpha\omega a(-1)^i}{r_{12}(1+\beta r_{12})^2}\mathbf{r}_i \cdot \mathbf{r}_{12} \right] \Psi_T \qquad (8)$$

We therefore have:

$$\sum_{i=1}^2 \frac{1}{\Psi_T}\nabla_i^2 \Psi_T = -4\alpha\omega + \frac{2a}{r_{12}(1+\beta r_{12})^2} - \frac{4a\beta}{(1+\beta r_{12})^3} + \alpha^2\omega^2(r_1^2 + r_2^2) + \frac{2a^2}{(1+\beta r_{12})^4} - \frac{2\alpha\omega a}{(1+\beta r_{12})^2}r_{12} \qquad (9)$$

2.1.2   Filled, 2-dimensional shell states

If we again consider the non-interacting, harmonic oscillator confined electron system, we can increase the number of electrons beyond 2. If, in some wondrous universe, we had fermions with three different spins states (like a spin-1 boson), then for three electrons we could again set $n_1 = n_2 = n_3 = 0$ and have an anti-symmetric spin state. However, in our world, we must go up in energy for more than two electrons.
The $n = 0$ state was the ground state. The next state has degeneracy 2; $(n_1, n_2) = (1,0),(0,1)$. After that we have degeneracy 3;$(n_1, n_2) = (2,0),(1,1),(0,2)$. Each of these states are doubly degenerate due to spin.

The reason in explaining this is because, assuming we have a so-called "full shell" problem[1], we can do some manipulations that greatly reduce the number of calculations necessary to perform VMC. Firstly, we need to rewrite the total wavefunction.
As is already known, the true wavefunction is approximated by an analytical solution to some simpler problem, and a Jastrow factor. The analytical part can be written as a Slater determinant:

$$\Psi_D = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \dots & \phi_{N-1}(\mathbf{r}_1) & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \dots & \phi_{N-1}(\mathbf{r}_2) & \phi_N(\mathbf{r}_2) \\ & & \vdots & & \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \dots & \phi_{N-1}(\mathbf{r}_N) & \phi_N(\mathbf{r}_N) \end{vmatrix} \qquad (10)$$

and therefore our trial wavefunction will be:

$$\Psi_T = \Psi_D \Psi_C \;, \;\; \Psi_C = \prod_{i<j}^N e^{f_{ij}} \;\;, \;\; f_{ij} \equiv \frac{ar_{ij}}{1 + \beta r_{ij}} \qquad (11)$$

where α, β are the variational parameters, a is connected to particle spins, and N is the total number of particles. Obviously, Ψ_D is a time consuming object to calculate at every Metropolis step. We will therefore do some neat tricks that reduce the number of calculations.
The first is to rewrite Ψ_D by using that the Hamiltonian is spin-independent. Firstly, we move all spin-up particles to the "first" $\frac{N}{2}$-positions, and the spin-down particles the remainder of positions.

2.1.3   The Metropolis ratio test

At each Metropolis step, we need the ratio of probabilities. We first define $R \equiv \frac{\Psi_T^n}{\Psi_T^o}$, where "$n$" means the new wavefunction and "o" means the old (or the current, but "c" could be confused with "correlation"). Written out, this is:

$$R = \frac{|D_+^n|}{|D_+^o|}\frac{|D_-^n|}{|D_-^o|}\frac{\Psi_C^n}{\Psi_C^o} \qquad (12)$$

If we only move one position at a time, then only one row in either D_+ or D_- will change. This means if we move a spin-up position, then $|D_-^n| = |D_-^o|$, so we need only consider one of the determinant fractions for each R.
Through some simple steps, one can show the determinant fraction (R_D) reduces to:

$$R_D = \sum_{j=1}^{N/2} D_{ij}(\mathbf{r}^n)D_{ji}^{-1}(\mathbf{r}^o) \qquad (13)$$

---

[1]For every new tier in energy, we fill it up with electrons. So all considered tiers, or "shells", are full.

where D_{ij}^{-1} is element ij of the inverse of D, D is either the spin-up or spin-down determinant, and $\mathbf{r}_i$ is the moved position. Since $D_{ij}(\mathbf{r}) = \phi_j(\mathbf{r}_i)$, the only difficulty remaining is to find the elements of the inverse matrix.

The elements of an inverse matrix are given by the Sherman-Morrison formula, which, when applied to the current case, gives:

$$D_{kj}^{-1}(\mathbf{r}^n) = \begin{cases} D_{kj}^{-1}(\mathbf{r}^o) - \frac{D_{ki}^{-1}(\mathbf{r}^o)}{R_D} \sum_{l=1}^{N/2} D_{il}(\mathbf{r}^n) D_{lj}^{-1}(\mathbf{r}^o) & \text{if } j \neq i \\[2em] \frac{D_{ki}^{-1}(\mathbf{r}^o)}{R_D} & \text{if } j = i \end{cases} \tag{14}$$

The ratio for the correlation function has a rather nice expression:

$$\begin{aligned} \frac{\Psi_C^n}{\Psi_C^o} &= \prod_{i<j}^{N/2} e^{(f_{ij}^n - f_{ij}^o)} \\ &= \exp\left(\sum_{i<j}^{N/2} f_{ij}^n - f_{ij}^o \right) \\ &= \exp\left(\sum_{i=0}^{k-1} (f_{ik}^n - f_{ik}^o) + \sum_{j=k+1}^{N/2} (f_{kj}^n - f_{kj}^o) \right) \end{aligned} \tag{15}$$

were we used $f_{ij}^n - f_{ij}^o = 0 \; \forall \, i,j \neq k$, and k is the moved position. The first sum is then for $j = k$ and the second sum is for $i = k$, with the restriction $i < j$.

The only step that remains is to square and multiply the two ratios[2].

2.1.4   Importance sampling

In importance sampling, each suggested move requires the calculation of the quantum force:

$$x_{new} = x_{old} + DF(x_{old})\Delta t + \xi\sqrt{\Delta t} \tag{16}$$

Solutions to the Fokker-Planck equation gives the transition probability, which must be multiplied with the probability density. The transition probability is therefore given by:

$$G(y, x, \Delta t) = \frac{1}{(4\pi D\Delta t)^{3N/2}} \exp\left\{ -\frac{(y - x - D\Delta t F(x))^2}{4D\Delta t} \right\} \tag{17}$$

where y is the new position and x the old, and the acceptance test becomes:

$$q(y, x) = \frac{G(x, y, \Delta t)|\Psi_T(y)|^2}{G(y, x, \Delta t)|\Psi_T(x)|^2} \tag{18}$$

The quantum force, given by $F = 2\frac{\nabla\Psi_T}{\Psi_T}$, requires the gradient of Ψ_T. Obviously, the quantum force can be written[3]:

$$F = 2\left(\frac{\nabla|D_+|}{|D_+|} + \frac{\nabla|D_-|}{|D_-|} + \frac{\nabla\Psi_C}{\Psi_C} \right) \tag{19}$$

Of course, when only position k is altered, only the k'th gradient in ∇ changes, and needs to be re-evaluated. We know the determinant can written:

$$|D| = \sum_{j=1}^{N/2} D_{kj} C_{jk} \tag{20}$$

where C_{jk} are the cofactors of D, and is independent of the i'th row in D, i.e. changing k does not change C_{jk}. It is therefore independent of the position change. Changing row i means all the other gradients in $\nabla|D|$ are the same as before, and we only need to re-evaluate $\nabla_k|D|$. This means:

---

[2]Or multiply and then square. Really, it's up to you.

[3]The superscript "o" has been dropped since there will be no "mix" of new and old coordinates for the rest of this subsection.

$$
\begin{aligned}
\frac{\nabla_k |D|}{|D|} &= \frac{\nabla_k \sum_{j=1}^{N/2} D_{kj} C_{jk}}{|D|} \\
&= \sum_{j=1}^{N/2} \frac{(\nabla_k D_{kj}) C_{jk}}{|D|} \\
&= \sum_{j=1}^{N/2} (\nabla_k D_{kj}) D_{jk}^{-1}
\end{aligned}
\tag{21}
$$

which, from equation 14, means:

$$
\frac{\nabla_k |D^n|}{|D^n|} = \frac{1}{R_D} \sum_{j=1}^{N/2} (\nabla_k D_{kj}^n)(D_{jk}^o)^{-1}
\tag{22}
$$

The correlation function gradient can be expressed:

$$
\begin{aligned}
\frac{\nabla_k \Psi_C}{\Psi_C} &= \frac{1}{\Psi_C} \nabla_k e^{\sum_{i<j}^{N} f_{ij}} \\
&= \sum_{i=1}^{k-1} \nabla_k f_{ik} + \sum_{j=k+1}^{N} \nabla_k f_{kj}
\end{aligned}
\tag{23}
$$

but since f_{ij} only depends on r_{ij}, it would preferable to express ∇_k in terms of r_{ij}. In equation 4, we showed this change for a simpler system. Applied to this problem, we can derive:

$$
\begin{aligned}
\nabla_k &= \frac{1}{r_{ik}} \mathbf{r}_{ik} \frac{\partial}{\partial r_{ik}} \\
&\text{or} \\
\nabla_k &= -\frac{1}{r_{jk}} \mathbf{r}_{jk} \frac{\partial}{\partial r_{jk}}
\end{aligned}
\tag{24}
$$

which gives:

$$
\frac{\nabla_k \Psi_C}{\Psi_C} = \sum_{i=1}^{k-1} \frac{\mathbf{r}_{ik}}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{j=k+1}^{N} \frac{\mathbf{r}_{kj}}{r_{kj}} \frac{\partial f_{kj}}{\partial r_{kj}}
\tag{25}
$$

We now have all the necessary tools to perform importance sampling.

2.1.5   Local energy

Lastly, the local energy needs to be calculated. As usual, the Laplacian fraction $\frac{\nabla^2 \Psi_T}{\Psi_T}$ is the most demanding object to calculate. the starting point is:

$$
\frac{\nabla^2 \Psi_T}{\Psi_T} = \frac{\nabla^2 |D_+|}{|D_+|} + \frac{\nabla^2 |D_-|}{|D_-|} + \frac{\nabla^2 \Psi_C}{\Psi_C} + 2\left(\frac{\nabla |D_+|}{|D_+|} + \frac{\nabla |D_-|}{|D_-|} \right) \cdot \frac{\nabla \Psi_C}{\Psi_C}
\tag{26}
$$

which looks easy enough. The last term contain vectors already known, while the first two are derived in the exact same manner as for the gradients, i.e.

$$
\frac{\nabla_k^2 |D|}{|D|} = \sum_{j=1}^{N/2} (\nabla_k^2 D_{kj}) D_{jk}^{-1}
\tag{27}
$$

Unfortunately, the middle term is not so nice to find. However, the middle steps are omitted here, and the final result is:

$$
\frac{\nabla_k^2 \Psi_C}{\Psi_C} = \left(\frac{\nabla_k \Psi_C}{\Psi_C} \right)^2 + \sum_{i=1}^{k-1} \left[\frac{d-1}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} + \frac{\partial^2 f_{ik}}{\partial r_{ik}^2} \right] + \sum_{j=k+1}^{N} \left[\frac{d-1}{r_{kj}} \frac{\partial f_{kj}}{\partial r_{kj}} + \frac{\partial^2 f_{kj}}{\partial r_{kj}^2} \right]
\tag{28}
$$

where d is the dimension we consider and:

$$\frac{\partial f_{ij}}{\partial r_{ij}} = \frac{a_{ij}}{(1 + \beta r_{ij})^2} \tag{29}$$

$$\frac{\partial^2 f_{ij}}{\partial r_{ij}^2} = -\frac{2a_{ij}\beta}{(1 + \beta r_{ij})^3} \tag{30}$$

The reason a_{ij} is indexed is because it equals 1 for anti-parallel spins and $\frac{1}{3}$ for parallel.

3   Results

4   Comments

$$\frac{\partial f_{ij}}{\partial r_{ij}} = \frac{a_{ij}}{(1 + \beta r_{ij})^2}$$

$$\frac{\partial^2 f_{ij}}{\partial r_{ij}^2}$$

$$\frac{2a_{ij}\beta}{1 + \beta r_{ij})^3}$$