Report FYS4411 - Project 1

Filip Sund
filipsu@fys.uio.no

Spring 2013

Theory

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V},$$

where

$$\hat{T} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right)$$

and

$$\hat{V} = \sum_{i=1}^{N} u(\mathbf{r}_i) + \sum_{j,i=1}^{N} v(\mathbf{r}_i, r_j) + \sum_{i,j,k=1}^{N} u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots$$

The expectation value of the hamiltonian H

$$E[H] = \langle H \rangle \approx \frac{\int \mathrm{d}\mathbf{R} \psi_T^*(\mathbf{R}) H(\mathbf{R}) \psi_T(\mathbf{R})}{\int \mathrm{d}\mathbf{R} \psi_T^*(\mathbf{R}) \psi_T(\mathbf{R})}$$

Probability distribution function

$$P(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int |\psi_T(\mathbf{R})|^2 \mathrm{d}\mathbf{R}}$$

Local energy

$$E_{LR} = \frac{1}{\psi_T(\mathbf{R})} H \psi_T(\mathbf{R}),$$

where $\psi_T(\mathbf{R})$ is our trial wavefunction. This gives

$$E[H] = \langle H \rangle \approx \int P(\mathbf{R}) E_{LR}(\mathbf{R}) \mathrm{d}\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^{N} P(\mathbf{R}_) E_{LR}(\mathbf{R}_i),$$

where N is the number of Monte Carlo samples.

Metropolis acceptance check

$$\omega = \frac{P(\mathbf{R}_p)}{P(\mathbf{R})}.$$

Importance sampling

Quantum force

$$\mathbf{F} = 2\frac{1}{\Psi_T}\nabla\Psi_T.$$

This term is responsible for pushing the walker towards regions of configuration space where the trial wave function is large, increasing the efficiency of the simulation in contrast to the Metropolis algorithm where the walker has the same probability of moving in every direction.

New Metropolis test

$$q(\mathbf{R}_p, \mathbf{R}) = \frac{G(\mathbf{R}, \mathbf{R}_p, \Delta t)|\Psi_T(\mathbf{R}_p)|^2}{G(\mathbf{R}_p, \mathbf{R}, \Delta t)|\Psi_T(\mathbf{R})|^2}$$

Efficient calculation of wave function ratios

Ratio of trial wave functions

$$R = \frac{\Psi_T^{\text{new}}}{\Psi_T^{\text{curr}}} = \frac{\Psi_D^{\text{new}}}{\Psi_D^{\text{curr}}} \cdot \frac{\Psi_C^{\text{new}}}{\Psi_C^{\text{curr}}} = R_D \cdot R_C,$$

where Ψ_D is our Slater determinant, and Ψ_C is the correlation function.

For the quantun force we need

$$\frac{\nabla\Psi_T}{\Psi_T},$$

which can be rewritten as

$$\frac{\nabla\Psi_T}{\Psi_T} = \frac{\nabla(\Psi_D\Psi_C)}{\Psi_D\Psi_C} = \frac{\Psi_C\nabla\Psi_D + \Psi_D\nabla\Psi_C}{\Psi_D\Psi_C} = \frac{\nabla\Psi_D}{\Psi_D} + \frac{\nabla\Psi_C}{\Psi_C}.$$

For the kinetic energy term of the local energy we need

$$\frac{\nabla^2\Psi_T}{\Psi_T},$$

which can be rewritten as

$$\begin{aligned}
\frac{\nabla^2\Psi_T}{\Psi_T} &= \frac{\nabla^2(\Psi_D\Psi_C)}{\Psi_D\Psi_C} = \frac{\nabla\cdot[\nabla(\Psi_D\Psi_C)]}{\Psi_D\Psi_C} \\
&= \frac{\nabla\cdot[\Psi_C\nabla\Psi_D + \Psi_D\nabla\Psi_C]}{\Psi_D\Psi_C} \\
&= \frac{\nabla\Psi_C\cdot\nabla\Psi_D + \Psi_C\nabla^2\Psi_D + \nabla\Psi_C\cdot\nabla\Psi_C + \Psi_D\nabla^2\Psi_C}{\Psi_D\Psi_C} \\
&= 2\frac{\nabla\Psi_C\cdot\nabla\Psi_D}{\Psi_D\Psi_C} + \frac{\nabla^2\Psi_D}{\Psi_D} + \frac{\nabla^2\Psi_C}{\Psi_D}.
\end{aligned}$$

The correlation function

We define the correlation function as

$$\Psi_C = \prod_{i<j}^{N} g(r_{ij}) = \prod_{i=1}^{N}\prod_{j=i+1}^{N} g(r_{ij}),$$

where $r_{ij} = \sqrt{(x_i - x_j)^2 + \ldots}$. For the Padé-Jastrow form we have

$$g(r_{ij}) = \exp\left(\frac{\alpha r_{ij}}{1+\beta r_{ij}}\right) = \exp(f_{ij}),$$

so we can write

$$\Psi_C = \prod_{i=1}^{N}\prod_{j=i+1}^{N} \exp(f_{ij}) = \exp\left(\sum_{i=1}^{N}\sum_{j=i+1}^{N} f_{ij}\right).$$

The total number of different relative distances r_{ij} is $N(N-1)/2$, and they can be stored in a upper diagonal matrix:

$$\begin{pmatrix} 0 & r_{1,2} & r_{1,3} & \cdots & r_{1,N} \\ 0 & 0 & r_{2,3} & \cdots & r_{2,N} \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \ddots & r_{N-1,N} \\ 0 & 0 & 0 & \cdots & 0 \end{pmatrix}.$$

We see that we can also store $g(r_{ij})$ in the same way. We now see that if we only move one particle at the time, say the kth particle, we only change row and column k of the r_{ij}- and g_{ij}-matrices. Since the diagonal and the lower diagonal parts are all zero, this means we only change $N-1$ elements of the $N \times N$ matrices.

We then see that we get the following expression for the correlation part of the ratios of wave functions

$$R_C = \frac{\Psi_C^{\text{new}}}{\Psi_C^{\text{curr}}} = \prod_{i=1}^{k-1}\frac{g_{ik}^{\text{new}}}{g_{ik}^{\text{curr}}}\prod_{i=k+1}^{N}\frac{g_{ki}^{\text{new}}}{g_{ki}^{\text{curr}}},$$

which, we for the Padé-Jastrow form can write as

$$R_C = \frac{\Psi_C^{\text{new}}}{\Psi_C^{\text{curr}}} = \frac{e^{U_{\text{new}}}}{e^{U_{\text{curr}}}} = e^{\Delta U},$$

where

$$\Delta U = \sum_{i=1}^{k-1}(f_{ik}^{\text{new}} - f_{ik}^{\text{curr}}) + \sum_{i=k+1}^{N}(f_{ki}^{\text{new}} - f_{ki}^{\text{curr}}).$$

Derivatives of the correlation

For the quantom force and the kinetic energy part of the local energy we need the following derivative

$$\frac{\nabla_i \Psi_C}{\Psi_C} = \frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_i},$$

for all dimensions and for all particles i.

[BLACK MAGIC, slides page 82-85]

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{\mathbf{r}_{ik}}{r_{ik}}\frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N}\frac{\mathbf{r}_{ki}}{r_{ki}}\frac{\partial f_{ki}}{\partial r_{ki}},$$

where $\mathbf{r}_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. For the *linear Padé-Jastrow* we have

$$f_{ij} = \frac{\alpha r_{ij}}{1+\beta r_{ij}},$$

which yields the close form expression

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

Derivatives

$$\begin{aligned}
E_{L2} &= \frac{1}{\Psi_T}\hat{\mathbf{H}}\Psi_T \\
&= \frac{1}{\Psi_T}\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\exp\left(-\alpha(r_1+r_2) + \frac{r_{12}}{2(1+\beta r_{12})}\right)
\end{aligned}$$

We see that the most work-intensive parts will be the ones with the Laplacian, so we start with those. We then get

$$\begin{aligned}
\nabla_1^2 \exp\Big(-\alpha(r_1+r_2)\Big)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) &= \nabla_1^2 AB \\
&= (\nabla_1^2 A)B + A(\nabla_1^2 B) + 2(\vec{\nabla}_1 A)(\vec{\nabla}_1 B).
\end{aligned}$$

We will now focus on the Laplacian of A and B. For $\nabla_1^2 B$ we get

$$\begin{aligned}
\nabla_1^2 B &= \nabla_1^2 \exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) \\
&= \left(\frac{\partial^2}{\partial x_1^2} + \dots\right)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) \\
&= \left(\frac{\partial}{\partial x_1} + \dots\right)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right)\left(\frac{\partial}{\partial x_1} + \dots\right)\frac{r_{12}}{2(1+\beta r_{12})}, \qquad (1)
\end{aligned}$$

which we see gets pretty messy pretty fast. So we do some intermediate steps

$$\begin{aligned}
\left(\frac{\partial}{\partial x_1}\right)\frac{r_{12}}{2(1+\beta r_{12})} &= \frac{\left(\frac{\partial}{\partial x_1}r_{12}\right)\cdot 2(1+\beta r_{12}) - r_{12}\cdot 2\beta\left(\frac{\partial}{\partial x_1}r_{12}\right)}{4(1+\beta r_{12})^2} \\
&= \frac{\frac{\partial}{\partial x_1}r_{12}}{2(1+\beta r_{12})^2}. \qquad (2)
\end{aligned}$$

Now we're getting somewhere. We then find the needed derivative separately

$$\begin{aligned}\frac{\partial}{\partial x_1} r_{12} &= \frac{\partial}{\partial x_1}\sqrt{(x_1-x_2)^2+\dots} \\ &= \frac{1}{2r_{12}}\frac{\partial}{\partial x_1}\Big((x_1-x_2)^2+\dots\Big) \\ &= \frac{1}{r_{12}}(x_1-x_2).\end{aligned}$$

We then insert this into equation (2), and get

$$\left(\frac{\partial}{\partial x_1}\right)\frac{r_{12}}{2(1+\beta r_{12})} = \frac{x_1-x_2}{2r_{12}(1+\beta r_{12})^2}$$

If we insert this into equation (1) we get

$$\begin{aligned}\nabla_1^2 \exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) &= \left(\frac{\partial}{\partial x_1}+\dots\right)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right)\frac{(x_1-x_2)+\dots(y,z)}{2r_{12}(1+\beta r_{12})^2} \\ &= \left[\left(\frac{\partial}{\partial x_1}+\dots\right)\frac{r_{12}}{2(1+\beta r_{12})}\right]\cdot\exp(\dots) \\ &\quad + \exp(\dots)\cdot\left[\left(\frac{\partial}{\partial x_1}+\dots\right)\frac{(x_1-x_2)+\dots(y,z)}{2r_{12}(1+\beta r_{12})^2}\right].\end{aligned}$$

The derivative in the first part we have already seen and solved in equation (2), but the derivative in the second part needs some work:

$$\left(\frac{\partial}{\partial x_1}+\dots\right)\frac{(x_1-x_2)+\dots(y,z)}{2r_{12}(1+\beta r_{12})^2}.$$

For coordinate x_1 we get

$$\begin{aligned}\left(\frac{\partial}{\partial x_1}\right)\left[\frac{\frac{1}{r_{12}}(x_1-x_2)}{2(1+\beta r_{12})^2}+\dots\right] &= \frac{\left(\frac{\partial}{\partial x_1}\frac{x_1}{r_{12}}\right)\cdot 2(1+\beta r_{12})^2 - \frac{1}{r_{12}}(x_1-x_2)\cdot 4(1+\beta r_{12})\beta\left(\frac{\partial}{\partial x_1}r_{12}\right)}{4(1+\beta r_{12})^4}+\dots \\ &= \frac{\left(\frac{\partial}{\partial x_1}\frac{x_1}{r_{12}}\right)(1+\beta r_{12}) - \frac{2\beta}{r_{12}}(x_1-x_2)\left(\frac{\partial}{\partial x_1}r_{12}\right)}{2(1+\beta r_{12})^3}+\dots\end{aligned}$$

For $\nabla_1^2 A$ we get

$$\begin{aligned}\nabla_1^2 A &= \nabla_1^2 \exp\Big(-\alpha(r_1+r_2)\Big) \\ &= \left(\frac{\partial^2}{\partial x_1^2}+\cdots\right)\exp\Big(-\alpha(r_1+r_2)\Big) \\ &=\end{aligned}$$

NEW STUFF

$$\frac{\partial}{\partial x_1}r_{12} = \frac{1}{r_{12}}(x_1-x_2)$$

$$
\begin{aligned}
\frac{\partial^2}{\partial x_1^2} r_{12} &= \frac{\partial}{\partial x_1} \frac{1}{r_{12}} (x_1 - x_2) \\
&= \frac{1}{r_{12}} - \frac{(x_1 - x_2)^2}{r_{12}^3}
\end{aligned}
$$

$$
\frac{\partial}{\partial x_1} \frac{1}{r_{12}} = -\frac{x_1 - x_2}{r_{12}^3}
$$