FYS4411 - Computational quantum mechanics

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Project 2;
Variational Monte Carlo studies of electronic systems

Github repository:

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

Sean Bruce Sangolt Miller
s.b.s.miller@fys.uio.no

Filip Henrik Larsen
filiphenriklarsen@gmail.com

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Abstract

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2 Theory and Methods

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 the singlet electron state we will use the trial wavefunction:

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

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 greatly simplifies calculations.

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

Where $r_{i,j}$ is element j of 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:

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

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

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

Which gives:

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

We therefore have:

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

2.2

3 Results

4 Comments