Variational Monte-Carlo Simulations of Atomic Systems

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https://github.com/lastis/FYS4411

Abstract

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I. INTRODUCTION

To evaluate the results of the numerical methods, we investigated the possibility of finding a closed-form solution of the ground-state energy using the Variational Principle.

II. METHODS

A. Trial Wavefunctions

The trial wavefunction of Beryllium can be written as a product of a Slater determinant part and a correlation part on the form

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \psi_D \psi_C \tag{1}$$

where the Slater determinant is

$$\begin{aligned}\psi_D &= Det\left(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \phi_3(\mathbf{r}_3), \phi_4(\mathbf{r}_4)\right) \\ &= \left(\phi_{1s}^1\phi_{2s}^2 - \phi_{1s}^2\phi_{2s}^1\right)\left(\phi_{1s}^3\phi_{2s}^4 - \phi_{1s}^4\phi_{2s}^3\right)\end{aligned} \tag{2}$$

and the correlation part is

$$\psi_C = \prod_{i<j}^{4} g_{ij} = \prod_{i<j}^{4} \exp\left(\frac{a r_{ij}}{1+\beta r_{ij}}\right) \tag{3}$$

Here $\phi_i(\mathbf{r}_i)$ are the hydrogen-like wavefunctions. They are given by the $1s$ and $2s$ orbital parts

$$\begin{aligned}\phi_{1s}^i &= e^{-\alpha r_i} \\ \phi_{2s}^i &= (1 - \alpha r_i/2)\, e^{-\alpha r_i/2}\end{aligned}$$

which are dependent on the cartesian positions $\mathbf{r}_i = (x_i, y_i, z_i)$. The relative distance between two particles is

$$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}$$

and obviously $r_{ij} = r_{ji}$.

We want to determine the local energy E_L to approximate the ground state energy of the atom. The general expression for the local energy is

$$E_L = \frac{1}{\psi_T(\mathbf{R})}\widehat{\mathbf{H}}\psi_T(\mathbf{R})$$

and the Hamiltonian can generally be described as a sum of the contributions to the potential energy by the electron-electron repulsion and the nucleus-electron interaction, as well as the kinetic energy. This gives us a Hamiltonian for N particles on the form

$$\begin{aligned}\widehat{\mathbf{H}} &= \widehat{\mathbf{K}} + \widehat{\mathbf{V}} \\ &= \sum_i (\hat{k}_i + \hat{v}_i) + \sum_{i<j} \hat{v}_{ij} \\ &= -\sum_{i=1}^{N}\left[\frac{\hat{\nabla}_i^2}{2} + \frac{Z}{r_i}\right] + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{r_{ij}}\end{aligned}$$

Where Z is the atomic number.

From this expression, it's clear that $\widehat{\mathbf{K}}$ is the only operator that changes the trial wavefunction when we calculate the local energy. Therefore, we must calculate the following quantities

$$\frac{1}{\psi_T}\hat{k}_i\psi_T = -\frac{1}{2}\frac{\hat{\nabla}_i^2\psi_T}{\psi_T}$$

For Beryllium, the trial wavefunction is a product of the Slater determinant part and the correlation part, namely $\psi_T = \psi_D\psi_C$.

The product rule of differentiation gives us

$$\frac{\hat{\nabla}^2\psi_T}{\psi_T} = \frac{\hat{\nabla}^2\psi_D}{\psi_D} + 2\frac{\hat{\nabla}\psi_D}{\psi_D}\cdot\frac{\hat{\nabla}\psi_C}{\psi_C} + \frac{\hat{\nabla}^2\psi_C}{\psi_C}$$

B. Efficient Computation of the Slater Determinant

For larger atoms, the evaluation of the gradient and the Laplacian of the Slater determinant becomes increasingly numerically demanding to compute. Computing these quantities with brute force, leads to $N \cdot d$ operations to find the determinant and thus multiplying this with our $O(N^3)$ operations. In the following, we derive a method that deals with this issue, and achieves a lower number of operations.

We can approximate the Slater determinant as

$$\Phi(\mathbf{r}_1, ..., \mathbf{r}_N) \propto \det\uparrow \cdot \det\downarrow$$

where the spin determinants are the determinants which only depend on spin up and spin down respectively. The determinants are 2×2 for Berylllium and 5×5 for Neon. This is true only if $\widehat{\mathbf{H}}$ is spin independent.

Then, $\det\hat{D} = |\hat{D}| = |\hat{D}|_\uparrow \cdot |\hat{D}|_\downarrow$, where the Slater matrices are dependent on the positions of the electrons. Each time we update the positions and differentiate the Slater determinant, the Slater matrix is changed, but by calculating the determinant from scratch each time, we will certainly do unnecessary computations.

This is solved by the following algorithm, that instead of calculating the determinant, updates the *inverse* of the Slater matrix suitably.

We first express (i,j) elements of the inverse of $\hat{D}$ as

$$d_{ij}^{-1} = \frac{C_{ji}}{|\hat{D}|}$$

where C_{ji} is the transposed cofactor-matrix element of $\hat{D}$.

This motivates the ratio

$$R \equiv \frac{|\hat{D}(\mathbf{r}^{new})|_\uparrow}{|\hat{D}(\mathbf{r}^{old})|_\uparrow} = \frac{\sum_{j=1}^N d_{ij}^{new} C_{ij}^{new}}{\sum_{j=1}^N d_{ij}^{old} C_{ij}^{old}}$$

Every time we move particle i, the i-th row of $\hat{D}$ changes, and we have to update the inverse. However, the i-th row of $\hat{C}$ is independent[1] of the i-th row of $\hat{D}$, which means that we must have

$$\hat{C}_{ij}^{new} = \hat{C}_{ij}^{old} = (d_{ji}^{-1})^{old} \cdot |\hat{D}| \text{ for } j = 1, ..., N$$

and using

$$\sum_{k=1}^N d_{ik}\, d_{kj}^{-1} = \delta_{ij}$$

The result is

$$R = \sum_{j=1}^N d_{ij}^{new} (d_{ji}^{-1})^{old} = \sum_{j=1}^N \phi_j(\mathbf{r}_i^{new})\, d_{ji}^{-1}(\mathbf{r}_i^{old})$$

The algorithm for updating the inverse of the matrix when a new position is accepted is then

Algorithm 1 Inverse of Slater Matrix

```
1: procedure UPDATE COLUMNS j ≠ i
2:     for each column i ≠ j do
3:         S_j = Σ_{l=1}^N d_il(r^new) d_lj^{-1}(r^old)
4:         (d_kj^{-1})^new = (d_kj^{-1})^old − (S_j/R)(d_ki^{-1})^old
5: procedure UPDATE COLUMN i
6:     (d_ki^{-1})^new = (1/R)(d_ki^{-1})^old
```

We can then calculate the gradient and laplacian as

$$\frac{\hat{\nabla}_k |\hat{D}|}{|\hat{D}|} = \sum_{j=1}^N \nabla_k \phi_j(\mathbf{r}_i^{new})\, d_{ji}^{-1}(\mathbf{r}_i^{old})$$

$$\frac{\hat{\nabla}_k^2 |\hat{D}|}{|\hat{D}|} = \sum_{j=1}^N \nabla_k^2 \phi_j(\mathbf{r}_i^{new})\, d_{ji}^{-1}(\mathbf{r}_i^{old})$$

[1] Since the cofactor-matrix elements c_{ij} is defined by removing i-th row and j-th column from a matrix $\hat{A}$, and then taking the determinant of the remaining matrix.

REMEMBER TO SAY SOMETHING ABOUT NUMBER OF OPERATIONS.

III. RESULTS

Appendix A: Mathematical Derivations

1. The wavefunction of Beryllium

We start by finding the first and second derivative of the determinant part, which are only dependent on the radii of the particles. This means that the gradient can be written

$$\hat{\nabla} f = \hat{\mathbf{r}} \frac{\partial f}{\partial r} \text{ and } \hat{\nabla}^2 f = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}$$

where $\mathbf{r} = r\hat{\mathbf{r}}$.

We define the functions

$$\begin{aligned} f_i &\equiv -\frac{\alpha \mathbf{r}_i}{2} \\ g_i &\equiv \exp(f_i) \\ F_{ij} &\equiv \phi_{1s}(\mathbf{r}_i)\phi_{2s}(\mathbf{r}_j) - \phi_{1s}(\mathbf{r}_j)\phi_{2s}(\mathbf{r}_i) \end{aligned}$$

and use them to simplify derivatives of the Hydrogen-like wavefunctions in the following way

$$\begin{aligned} \phi_{1s}^i &= g_i^2 \\ \frac{\partial \phi_{1s}^i}{\partial r_i} &= -\alpha g_i^2 \\ \frac{\partial^2 \phi_{1s}^i}{\partial r_i^2} &= \alpha^2 g_i^2 \\ \phi_{2s}^i &= g_i(1+f_i) \\ \frac{\partial \phi_{2s}^i}{\partial r_i} &= -\alpha g_i (1 + f_i/2) \\ \frac{\partial^2 \phi_{2s}^i}{\partial r_i^2} &= \frac{3\alpha^2}{4} g_i (1 + f_i/3) \\ \phi_{2p_k}^i &= \alpha k_i g_i \text{ for } k_i = x_i, y_i, z_i \\ \frac{\partial \phi_{2p_k}^i}{\partial r_i} &= \left(\frac{1}{r_i} - \frac{\alpha}{2}\right) \alpha k_i g_i \\ \frac{\partial^2 \phi_{2p_k}^i}{\partial r_i^2} &= \left(\left[\frac{1}{r_i} - \frac{\alpha}{2}\right]^2 - \frac{1}{r_i}\right) \alpha k_i g_i \end{aligned}$$

and then the terms required to calculate the Slater determinant

$$\begin{aligned} F_{ij} &= g_i^2(1+f_j)g_j - g_j^2(1+f_i)g_i \\ \frac{\partial F_{ij}}{\partial r_i} &= -\alpha g_i g_j (g_i(1+f_j) - g_j(1+f_i/2)) \\ \frac{\partial^2 F_{ij}}{\partial r_i^2} &= \alpha^2 g_i g_j (g_i(1+f_j) - \frac{3}{4} g_j (1+f_i/3)) \\ \frac{\partial F_{ij}}{\partial r_j} &= \alpha g_i g_j (g_j(1+f_i) - g_i(1+f_j/2)) \\ \frac{\partial^2 F_{ij}}{\partial r_j^2} &= -\alpha^2 g_i g_j (g_j(1+f_i) - \frac{3}{4} g_i (1+f_j/3)) \end{aligned}$$

The determinant part is

$$\psi_D = F_{12}F_{34}$$

where the first is only affected by differentiation with respect to particle 1 or 2, and opposite for the second part

$$\frac{\hat{\nabla}_1\psi_D}{\psi_D} = \frac{\hat{\nabla}_1 F_{12}}{F_{12}} \qquad \frac{\hat{\nabla}_2\psi_D}{\psi_D} = \frac{\hat{\nabla}_2 F_{12}}{F_{12}}$$

$$\frac{\hat{\nabla}_3\psi_D}{\psi_D} = \frac{\hat{\nabla}_3 F_{34}}{F_{34}} \qquad \frac{\hat{\nabla}_4\psi_D}{\psi_D} = \frac{\hat{\nabla}_4 F_{34}}{F_{34}}$$

The result is two different quantities

$$\frac{\hat{\nabla}_k\psi_D}{\psi_D} = \begin{cases} \frac{\hat{\nabla}_i F_{ij}}{F_{ij}} & = -\alpha\frac{\mathbf{r}_i}{r_i}\frac{(g_i(1+f_j)-g_j(1+f_i/2))}{g_i(1+f_j)-g_j(1+f_i)}, \text{ if } k=i=j-1 \\ \frac{\hat{\nabla}_j F_{ij}}{F_{ij}} & = -\alpha\frac{\mathbf{r}_j}{r_j}\frac{(g_i(1+f_j/2)-g_j(1+f_i))}{g_i(1+f_j)-g_j(1+f_i)}, \text{ if } k=j=i+1 \end{cases}$$

one for particles 1 and 3, and one for 2 and 4, where $i \in 1,3$ and $j \in 2,4$.

For the second derivative part, we have

$$\frac{\hat{\nabla}_k^2\psi_D}{\psi_D} = \begin{cases} \frac{\hat{\nabla}_i^2 F_{ij}}{F_{ij}} & = \frac{\alpha^2(g_i(1+f_j)-\frac{3}{4}g_j(1+f_i/3))-\frac{2\alpha}{r}(g_i(1+f_j)-g_j(1+f_i/2))}{g_i(1+f_j)-g_j(1+f_i)} \\ \frac{\hat{\nabla}_j^2 F_{ij}}{F_{ij}} & = \frac{\alpha^2(\frac{3}{4}g_i(1+f_j/3)-g_j(1+f_i))-\frac{2\alpha}{r}(g_i(1+f_j/2)-g_j(1+f_i))}{g_i(1+f_j)-g_j(1+f_i)} \end{cases}$$

with the same conditions as above. Now we move on to the calculation of the correlation parts, given by the function in (3).

First off, we define

$$f_{ij} \equiv \frac{ar_{ij}}{1+\beta r_{ij}}$$

with the corresponding derivatives (with respect to r_{ij})

$$f'_{ij} = \frac{a}{(1+\beta r_{ij})^2}$$
$$f''_{ij} = \frac{-2a\beta}{(1+\beta r_{ij})^3}$$

The gradient of the wavefunction, divided by the wavefunction, for particle k in the x-direction is then

$$\left[\frac{\hat{\nabla}_k\psi_C}{\psi_C}\right]_x = \frac{1}{\psi_C}\frac{\partial\psi_C}{\partial x_k}$$

If we look at the first derivative in the x-direction, we see that the parts of the wavefunction that is not dependent on k, will remain unaffected by the differentiation. When we split the expression for $i<k$ and $k>i$, we get that

$$\begin{aligned}
\frac{\partial\psi_C}{\partial x_k} &= \prod_{i,j\neq k} g_{ij}\frac{\partial}{\partial x_k}\left[\prod_{i<k} g_{ik}\cdot\prod_{i>k} g_{ki}\right] \\
&= \prod_{i,j\neq k} g_{ij}\left[\prod_{i>k} g_{ki}\frac{\partial}{\partial x_k}\prod_{i<k} g_{ik} + \prod_{i<k} g_{ik}\frac{\partial}{\partial x_k}\prod_{i>k} g_{ki}\right] \\
&= \prod_{i,j\neq k} g_{ij}\left[\prod_{i>k} g_{ki}\sum_{i<k}\frac{\partial g_{ik}}{\partial x_k}\prod_{p\neq i} g_{pi} + \prod_{i<k} g_{ik}\sum_{i>k}\frac{\partial g_{ki}}{\partial x_k}\prod_{q\neq i} g_{iq}\right. \\
&= \prod_{i<j} g_{ij}\left[\frac{1}{\prod_{i<k} g_{ik}}\sum_{i<k}\frac{\partial g_{ik}}{\partial x_k}\prod_{p\neq i} g_{pi} + \frac{1}{\prod_{i>k} g_{ki}}\sum_{i>k}\frac{\partial g_{ki}}{\partial x_k}\prod_{p\neq i}\right. \\
&= \psi_C\left[\sum_{i<k}\frac{1}{g_{ik}}\frac{\partial g_{ik}}{\partial x_k} + \sum_{i>k}\frac{1}{g_{ki}}\frac{\partial g_{ki}}{\partial x_k}\right] \qquad (4)
\end{aligned}$$

Here we factorized the wavefunction outside the expression, and noticed that the only part that doesn't cancel is the ik-th and ki-th in the sums.

Dividing by the wavefunction, we get

$$\begin{aligned}
\left[\frac{\hat{\nabla}_k\psi_C}{\psi_C}\right]_x &= \sum_{i=1}^{k-1}\frac{1}{g_{ik}}\frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N}\frac{1}{g_{ki}}\frac{\partial g_{ki}}{\partial x_k} \\
&= \sum_{i=1}^{k-1}\frac{\partial f_{ik}}{\partial x_k} - \sum_{i=k+1}^{N}\frac{\partial f_{ki}}{\partial x_i} \\
&= \sum_{i=1}^{k-1}\frac{x_k-x_i}{r_{ik}}\frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N}\frac{x_i-x_k}{r_{ki}}\frac{\partial f_{ki}}{\partial r_{ki}}
\end{aligned}$$

since g_{ij} is an exponential function, so $\partial g_{ij}/\partial x_i = g_{ij}\partial f_{ij}/\partial x_j$. We also used the fact that $\partial g_{ij}/\partial x_i = -\partial g_{ij}/\partial x_j$ to differentiate with respect to the second index in both of the sums. Finally, we have used the chain rule to attain an expression that is dependent on the distance between the two particles

$$\frac{\partial f_{ij}}{\partial x_j} = \frac{\partial f_{ij}}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial x_j} = \frac{x_j-x_i}{r_{ij}}\frac{\partial f_{ij}}{\partial r_{ij}}$$

Thus

$$\begin{aligned}
\frac{\hat{\nabla}_k\psi_C}{\psi_C} &= \sum_{i=1}^{k-1}\frac{\mathbf{r}_{ik}}{r_{ik}}\frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N}\frac{\mathbf{r}_{ki}}{r_{ki}}\frac{\partial f_{ki}}{\partial r_{ki}} \\
&= \sum_{i=1}^{k-1}\frac{\mathbf{r}_{ik}}{r_{ik}}\frac{a}{(1+\beta r_{ik})^2} - \sum_{i=k+1}^{N}\frac{\mathbf{r}_{ki}}{r_{ki}}\frac{a}{(1+\beta r_{ki})^2} \\
&= \sum_{i\neq k}\frac{\mathbf{r}_{ik}}{r_{ik}}\frac{a}{(1+\beta r_{ik})^2}
\end{aligned}$$

From (4), we can gather that the double derivative part is described by

$$
\begin{aligned}
\left[\frac{\hat{\nabla}^2\psi_C}{\psi_C}\right]_x &= \frac{1}{\psi_C}\frac{\partial}{\partial x_k}\left(\psi_C\left[\sum_{i<k}\frac{\partial f_{ik}}{\partial x_k}+\sum_{i>k}\frac{\partial f_{ki}}{\partial x_k}\right]\right) \\
&= \left[\sum_{i<k}\frac{\partial^2 f_{ik}}{\partial x_k^2}+\sum_{i>k}\frac{\partial^2 f_{ki}}{\partial x_k^2}\right]+\frac{1}{\psi_C}\frac{\partial\psi_C}{\partial x_k}\left[\sum_{i<k}\frac{\partial f_{ik}}{\partial x_k}+\sum_{i>k}\frac{\partial f_{ki}}{\partial x_k}\right] \\
&= \sum_{i\neq k}\frac{\partial^2 f_{ik}}{\partial x_k^2}+\left[\sum_{i=1}^{k-1}\frac{\partial f_{ik}}{\partial x_k}-\sum_{i=k+1}^{N}\frac{\partial f_{ki}}{\partial x_i}\right]^2 \\
&= \sum_{i\neq k}\frac{\partial}{\partial x_k}\left(\frac{\partial f_{ik}}{\partial r_{ik}}\frac{\partial r_{ik}}{\partial x_k}\right)+\left[\sum_{i\neq k}\frac{\partial r_{ik}}{\partial x_k}\frac{\partial f_{ik}}{\partial r_{ik}}\right]^2 \\
&= \sum_{i\neq k}\left[\frac{\partial r_{ik}}{\partial x_k}\frac{\partial}{\partial x_k}\frac{\partial f_{ik}}{\partial r_{ik}}+\frac{\partial f_{ik}}{\partial r_{ik}}\frac{\partial^2 r_{ik}}{\partial x_k^2}\right]+\left[\sum_{i\neq k}\frac{\partial r_{ik}}{\partial x_k}f'_{ik}\right]\left[\sum_{j\neq k}\frac{\partial r_{jk}}{\partial x_k}f'_{jk}\right] \\
\left[\frac{\hat{\nabla}^2\psi_C}{\psi_C}\right]_x &= \sum_{i\neq k}\left[\left(\frac{\partial r_{ik}}{\partial x_k}\right)^2 f''_{ik}+f'_{ik}\frac{r_{ik}^2-(x_k-x_i)^2}{r_{ik}^3}\right] \\
&\quad+\sum_{j\neq k}\left[\frac{\partial r_{ik}}{\partial x_k}f'_{ik}\left(\frac{\partial r_{ik}}{\partial x_k}f'_{ik}+\sum_{j\neq k,i}\frac{\partial r_{jk}}{\partial x_k}f'_{jk}\right)\right] \\
\left[\frac{\hat{\nabla}^2\psi_C}{\psi_C}\right]_x &= \sum_{i\neq k}\left[\left(\frac{\partial r_{ik}}{\partial x_k}\right)^2 f''_{ik}+f'_{ik}\frac{r_{ik}^2-(x_k-x_i)^2}{r_{ik}^3}\right] \\
&\quad+\sum_{j\neq k}\left[\left(\frac{\partial r_{ik}}{\partial x_k}f'_{ik}\right)^2+\sum_{j\neq k,i}\frac{\partial r_{ik}}{\partial x_k}f'_{ik}\frac{\partial r_{jk}}{\partial x_k}f'_{jk}\right] \\
\left[\frac{\hat{\nabla}^2\psi_C}{\psi_C}\right]_x &= \sum_{i\neq k}\left[\left(\frac{x_k-x_i}{r_{ik}}\right)^2 f''_{ik}+f'_{ik}\frac{r_{ik}^2-(x_k-x_i)^2}{r_{ik}^3}\right] \\
&\quad+\sum_{j\neq k}\left[\left(\frac{x_k-x_i}{r_{ik}}f'_{ik}\right)^2+\sum_{j\neq k,i}\frac{(x_k-x_i)(x_k-x_j)}{r_{ik}r_{jk}}f'_{ik}f'_{jk}\right] \\
\left[\frac{\hat{\nabla}^2\psi_C}{\psi_C}\right]_x &= \sum_{i\neq k}\left[\left(\frac{x_k-x_i}{r_{ik}}\right)^2 f''_{ik}+f'_{ik}\frac{r_{ik}^2-(x_k-x_i)^2}{r_{ik}^3}\right] \\
&\quad+\sum_{i,j\neq k}\frac{(x_k-x_i)(x_k-x_j)}{r_{ik}r_{jk}}f'_{ik}f'_{jk}
\end{aligned}
$$

If we now sum up for all dimensions, we get

$$
\begin{aligned}
\frac{\hat{\nabla}^2\psi_C}{\psi_C} &= \sum_{i\neq k}\left[\frac{r_{ik}^2}{r_{ik}^2}f''_{ik}+f'_{ik}\frac{3r_{ik}^2-r_{ik}^2}{r_{ik}^3}\right]+\sum_{i,j\neq k}\frac{(x_k-x_i)(x_k-x_j)}{r_{ik}r_{jk}}f'_{ik}f'_{jk} \\
&= \sum_{i\neq k}\left[f''_{ik}+\frac{2}{r_{ik}}f'_{ik}\right]+\sum_{i,j\neq k}\frac{(x_k-x_i)(x_k-x_j)}{r_{ik}r_{jk}}f'_{ik}f'_{jk}
\end{aligned}
$$