Ground state of Helium atom

This problem combines what we have learned about the technique of Monte-Carlo simulation with atomic physics. In particular, we will use Monte-Carlo techniques to estimate the ground-state wave function and energy of a helium atom. Remember a He atom has two electrons, two protons, and two neutrons. While the nucleus we can regard as a single particle for our purposes, the three body problem (nucleus and two electrons) does not allow for an exact analytical solution.

The Hamiltonian for the problem in a set of units with $|e| = 1$ (i.e. the electron and proton charge), $m = 1$ and $\hbar = 1$ is,

$$\hat{H} = -\frac{1}{2} \nabla^2_{\vec{r}_1} - \frac{1}{2} \nabla^2_{\vec{r}_2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

where $r_1 = |\vec{r}_1|$, $r_2 = |\vec{r}_2|$, and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. The ground-state solution satisfies

$$\hat{H} \Psi_0(\vec{r}_1, \vec{r}_2) = E_0 \Psi_0(\vec{r}_1, \vec{r}_2)$$

where $E_0$ is the ground-state energy. For any trial wave function $\Phi_T(\vec{r}_1, \vec{r}_2)$ different from the ground-state wave function $\Psi_0(\vec{r}_1, \vec{r}_2)$, the energy expectation value given by

$$E = \frac{\int \cdots \int \Phi_T^*(\vec{r}_1, \vec{r}_2) \hat{H} \Phi_T(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2}{\int \cdots \int \Phi_T^*(\vec{r}_1, \vec{r}_2) \Phi_T(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2}$$

satisfies $E > E_0$. We can approach the problem of obtaining the ground-state wave function by considering different trial wave functions with the goal of minimizing $E$. The integrals required to compute $E$ are difficult to do analytically and lend themselves well to being approximated by Monte-Carlo.

Consider a trial wave function of the form,

$$\Phi_T(\vec{r}_1, \vec{r}_2) = e^{-\alpha r_1} e^{-\alpha r_2} e^{\beta r_{12}}$$

where $\alpha$ and $\beta$ are free parameters we can vary to minimize the energy $E$. Notice that this wave function is not normalized in any way. That is usually not adequate, but the Monte-Carlo integration will automatically take care of the normalization issue by correctly computing the relative probability of finding the electrons at two different points $\vec{r}_1$ and $\vec{r}_2$. 


First rewrite the energy expectation value as (omitting the coordinates in the wave functions for brevity)

\[
E = \frac{\int ... \int \Phi_T^{-1} \hat{H} \Phi_T (\Phi_T^* \Phi_T) \, d^3 r_1 d^3 r_2}{\int ... \int \Phi_T^* \Phi_T \, d^3 r_1 d^3 r_2}
\]

This suggests that if we sample states randomly with probability \( \Phi_T^* (\vec{r}_1, \vec{r}_2) \Phi_T (\vec{r}_1, \vec{r}_2) \) we can approximate the integral. Note that the denominator in the expression for the energy expectation value does not need to be evaluated, because we are only required to choose states on the basis of their relative probability density.

Using the expression for the trial wave function above, evaluate the “local energy” term

\[
\Phi_T^{-1} \hat{H} \Phi_T
\]

Your answer will involve only the coordinates and the parameters \( \alpha \) and \( \beta \)

In your code, you need to define six coordinates to define the locations of the two electrons, \((x_1, y_1, z_1, x_2, y_2, z_2)\). Choose a parameter \( \alpha \) that is reasonable (Hint: Think about the length scales involved in the Helium atom). Begin with a random set of coordinates and evaluate \( \Phi_T^* (\vec{r}_1, \vec{r}_2) \Phi_T (\vec{r}_1, \vec{r}_2) \). Now make a random move in each of the six coordinates. You can use any step size in principle, but I suggest you keep it something smaller than the size of the atom. For the new set of coordinates, again evaluate \( \Phi_T^* (\vec{r}_1, \vec{r}_2) \Phi_T (\vec{r}_1, \vec{r}_2) \). If this quantity increases, then accept the step. If it is smaller, then draw a random number between zero and one and accept the step if the random number is less than the ration of the probability density between the two states. Repeat the process. You will find that after many steps the system should settle down to where about as many steps are rejected as accepted. At this point you can evaluate the “local energy” term above to begin to approximate the integral for \( E \). How does the result depend on the number of random moves accepted \( N \)?

Repeat for a few different values of \( \alpha \) and \( \beta \). Can you find values for \( \alpha \) and \( \beta \) that result in a minimum \( E \)?