

Format for delivery of report and programs

The format of the project is that of a printed file or hand-written report. The programs should also be included with the report. Write **only your candidate number** on the first page of the report and state clearly that this is your report for project 5 of FYS3150/FYS4150, fall 2013. There will be a box marked 'FYS3150/FYS4150' at the reception of the Department of Physics (room FV128).

Project 5, Numerical integration and variational Monte Carlo methods, deadline Monday December 9, 12pm (noon)

The first part of this project deals with numerical integration of a six-dimensional integral. This integral represents the expectation value of the Coulomb interaction between two electrons in a harmonic oscillator well. The integral appears in many quantum mechanical applications. We will employ both Gauss-Legendre and Gauss-Hermite quadrature and Monte-Carlo integration. Furthermore, you will need to parallelize your codes.

The second part extends these calculations to a variational Monte Carlo (VMC) calculation of the energy for two interacting electrons in a three-dimensional quantum dot well. You can then use project 2 to benchmark your VMC calculations against numerically exact diagonalization results.

The task of the first part is to integrate first in a brute force manner a six-dimensional integral which is used to determine the ground state correlation energy between two electrons confined to a three-dimensional harmonic oscillator potential.

We assume that the wave function of each electron can be modelled like the single-particle wave function of an electron in a three-dimensional harmonic oscillator. The single-particle wave function for an electron i in the lowest harmonic oscillator state $n_x = n_y = n_z = 0$ is given in terms of a dimensionless position variable (the wave function is not properly normalized)

$$\mathbf{r}_i = x_i \mathbf{e}_x + y_i \mathbf{e}_y + z_i \mathbf{e}_z,$$

as

$$\psi_0(\mathbf{r}_i) = \exp(-(\alpha^2 r_i^2/2)),$$

where $\alpha = \sqrt{m\omega/\hbar}$ is a parameter related to the mass of the particle m and the oscillator frequency ω and

$$r_i^2 = x_i^2 + y_i^2 + z_i^2.$$

We will simply fix $\alpha = 1$ in the first part. We will also stay with cartesian coordinates for all exercises. It is fully possible to switch to spherical coordinates. One would then need to replace the Hermite polynomials with Laguerre polynomials.

The ansatz for the wave function for two electrons is then given by the product of two harmonic oscillator wave functions in their lowest oscillator energy

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \exp(-(\alpha^2(r_1^2 + r_2^2))/2).$$

This function is not properly normalized. Note that it is not possible to find a closed-form solution to Schrödinger's equation for two interacting electrons in a three-dimensional harmonic oscillator well.

The integral we need to solve is the quantum mechanical expectation value of the correlation energy between two electrons which repel each other via the classical Coulomb interaction, namely

$$\left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \int_{-\infty}^{\infty} d\mathbf{r}_1 d\mathbf{r}_2 \exp(-(\alpha^2(r_1^2 + r_2^2))) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (1)$$

Note again that our wave function is not normalized. There is a normalization factor missing, but for this project we don't need to worry about that.

- a) Use Gauss-Legendre quadrature and compute the integral by integrating for each variable x_1, y_1, z_1, x_2, y_2 and z_2 from $-\infty$ to ∞ . How many mesh points do you need before the results converges at the level of the third leading digit? Hint: the single-particle wave function $\exp(-\alpha^2 r_i^2)/2$ is more or less zero at $r_i \approx ?$ (find the appropriate limit). You can therefore replace the integration limits $-\infty$ and ∞ with $-?$ and $?$, respectively. You need to check that this approximation is satisfactory, that is, make a plot of the function and check if the abovementioned limits are appropriate.
- b) The Legendre polynomials are defined for $x \in [-1, 1]$. The previous exercise gave a very unsatisfactory ad hoc procedure. We wish to improve our results. It can therefore be useful to change to another type of polynomials and employ the Hermite polynomials. The Hermite polynomials are defined for $x \in (-\infty, \infty)$ and carry a weight function $\exp(-ar_i^2)$, with a being a constant. Replace the Gauss-Legendre approach in a) with Hermite polynomials. The function GaussHermite.cpp can be found at the webpage of the course, see under the project link. Do your results improve? Compare with the results from a).

Important notice for c++ programmers:, the function which computes the Gauss-Hermite integration points and weights returns arrays which start at 1 and end n instead of the default values 0 and $n - 1$. You need to declare an array of length $n + 1$.

- c) Compute the same integral but now with brute force Monte Carlo integration and compare your results with those from the previous points. Discuss the differences. With brute force we mean that you should use the uniform distribution.
- d) Improve your brute force Monte Carlo calculation by using importance sampling. Hint: use a gaussian distribution. Chapter 11.5 of the lecture notes has an example for a six-dimensional integral with a Gaussian distribution. The function GaussianDeviate.cpp included with this project can be used. Does the variance decrease? Does the CPU time used compared with the brute force Monte Carlo decrease in order to achieve the same accuracy? Comment your results and make a list over the time each method uses. Compare the results also.
- e) Finally, for the last exercise you should parallelize your code using MPI or openMP and run either on your laptop or the machines at the computer laboratory. Comment these results as well. In particular, we want to see whether you achieve an optimal speed-up or not.

Our next step is to perform a VMC calculation of the ground state energy of two interacting electrons confined to a three-dimensional harmonic oscillator well. We label r_1 the position of electron 1 and similarly r_2 the position of electron 2. We will set the mass of the electrons $m = 1$, the oscillator frequency $\omega = 1$, and $\hbar = c = 1$. We will thus use so-called atomic units. The contribution to the potential energy from the harmonic oscillator potential for the two electrons is

$$\frac{1}{2} (r_1^2 + r_2^2). \quad (2)$$

Adding the electron-electron repulsion with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, the total potential energy $V(r_1, r_2)$ is

$$V(r_1, r_2) = \frac{1}{2} (r_1^2 + r_2^2) + \frac{1}{r_{12}}, \quad (3)$$

yielding the total Hamiltonian

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{2} (r_1^2 + r_2^2) + \frac{1}{r_{12}}, \quad (4)$$

and Schrödinger's equation reads

$$\hat{H}\psi = E\psi. \quad (5)$$

All equations are in so-called atomic units. The distances r_i and r_{12} are dimensionless.

The basic wave functions we will employ in this part are

$$\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \exp(-\alpha^2(r_1^2 + r_2^2)/2), \quad (6)$$

and

$$\psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \exp(-\alpha^2(r_1^2 + r_2^2)/2) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right), \quad (7)$$

with β as a new variational parameter. Your task is to perform a Variational Monte Carlo calculation using the Metropolis algorithm to compute the integral

$$\langle H \rangle = \frac{\int d\mathbf{R} \psi_T^*(\mathbf{R}) H(\mathbf{R}) \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^*(\mathbf{R}) \psi_T(\mathbf{R})}, \quad (8)$$

with the above trial wave functions.

f) Compute

$$\langle H \rangle = \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) H(\mathbf{R}) \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}, \quad (9)$$

for the two electrons in a three-dimensional Harmonic oscillator well using a variational Monte Carlo method employing the Metropolis algorithm to sample over different states. You will have to calculate

$$\langle H \rangle = \int P(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R}, \quad (10)$$

where E_L is the local energy. Here all calculations are performed with the trial wave function $\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})$ only. Study the stability of your calculation as function of the number of Monte Carlo samples and compare these results with the numerically exact calculations from project 2. In order to compare the numbers you need to figure out the relation between α and the frequencies you used in project 2. Another useful test is to compare the results without the Coulomb repulsion between two electrons. Then you have simple closed form expressions for the total energy. The energy is then simply the sum of two non-interacting electrons trapped in a three-dimensional harmonic oscillator well.

Your Monte Carlo moves are determined by

$$\mathbf{R}' = \mathbf{R} + \delta \times r, \quad (11)$$

where r is a random number from the uniform distribution and δ a chosen step length. In solving this exercise you need to devise an algorithm which finds an optimal value of δ for each variational parameter α , resulting in roughly 50% accepted moves. For which values of α should you perform the variations? Plot the variational energy as a function of α and localize the variational minimum.

Make a plot of the variance as a function of the number of Monte Carlo cycles. You should parallelize your code.

g) Use thereafter the optimal value for α as a starting point for computing the ground state energy of the helium atom using the trial wave functions $\psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})$. In this case you need to vary both α and β . The strategy here is to use α from the previous exercise, [1f)] and then vary β in order to find the lowest energy as function of β . Thereafter you change α in order to see whether you find an even lower energy and so forth.

Which one of the wave functions $\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})$ and $\psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})$ would you prefer? Give arguments for your choices.

h) This part is optional but gives you an additional 30% on the final score! Find closed form expressions for the local energy for the above two trial wave functions. Implement the closed-form expressions for the local energy and compare the speed-up in CPU time with respect to the numerical derivation involved in the calculation of kinetic energy. How a large a speed-up do you obtain?

Variational Monte Carlo methods will be discussed during week 47.

References

- [1] B. L. Hammond, W. A. Lester and P. J. Reynolds, Monte Carlo methods in Ab Initio Quantum Chemistry, World Scientific, Singapore, 1994, chapters 2-5 and appendix B.