Project 1 FYS4411 Spring 2011: Variational Monte Carlo studies and density functional theory of quantum dots

The aim of this project is to use the Variational Monte Carlo (VMC) method and density functional theory to evaluate the ground state energy, onebody densities, expectation values of the kinetic and potential energies and single-particle energies of quantum dots with $N = 2$, $N = 6$ and $N = 12$ electrons, so-called closed shell systems.

Part 1: Variational Monte Carlo calculations of quantum dots

Theoretical background and description of the physical system

We consider a system of electrons confined in a pure two-dimensional isotropic harmonic oscillator potential, with an idealized total Hamiltonian given by

$$\widehat{\mathbf{H}} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right) + \sum_{i<j} \frac{1}{r_{ij}}, \tag{1}$$

where natural units ($\hbar = c = e = m_e = 1$) are used and all energies are in so-called atomic units a.u. We will study systems of many electrons N as functions of the oscillator frequency ω using the above Hamiltonian. The Hamiltonian includes a standard harmonic oscillator part

$$\widehat{\mathbf{H}}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right),$$

and the repulsive interaction between two electrons given by

$$\widehat{\mathbf{H}}_1 = \sum_{i<j} \frac{1}{r_{ij}},$$

with the distance between electrons given by $r_{ij} = \sqrt{\mathbf{r}_1 - \mathbf{r}_2}$. We define the modulus of the positions of the electrons (for a given electron i) as $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2}$.

1a) In exercises 1a-1e we will deal only with a system of two electrons in a quantum dot with a frequency of $\hbar\omega = 1$. The reason for this is that we have exact closed form expressions for the ground state energy from Taut's work for selected values of ω, see M. Taut, Phys. Rev. A **48**, 3561 (1993). The energy is given by 3 a.u. (atomic units) when the interaction between the electrons is included. If only the harmonic oscillator part of the Hamiltonian, the so-called unperturbed part,

$$\widehat{\mathbf{H}}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right),$$

the energy is 2 a.u. The wave function for one electron in an oscillator potential in two dimensions is

$$\phi_{n_x, n_y}(x, y) = A H_{n_x}(\sqrt{\omega} x) H_{n_y}(\sqrt{\omega} y) \exp\left(-\omega(x^2 + y^2)/2\right).$$

The functions $H_{n_x}(\sqrt{\omega} x)$ are so-called Hermite polynomials, discussed in appendix while A is a normalization constant. For the lowest-lying state we have $n_x = n_y = 0$ and an energy $\epsilon_{n_x, n_y} = \omega(n_x + n_y + 1) = \omega$. Convince yourself that the lowest-lying energy for the two-electron system is simply 2ω.

The unperturbed wave function for the ground state of the two-electron system is given by

$$\Phi(\mathbf{r_1}, \mathbf{r_2}) = C \exp\left(-\omega(r_1^2 + r_2^2)/2\right),$$

with C being a normalization constant and $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2}$. Note that the vector $\mathbf{r_i}$ refers to the x and y position for a given particle. What is the total spin of this wave function? Find arguments for why the ground state should have this specific total spin.

1b) We want to perform a Variational Monte Carlo calculation of the ground state of two electrons in a quantum dot well with different oscillator energies, assuming total spin $S = 0$ using the Hamiltonian of Eq. (1). In our first attempt we will use a brute force Metropolis sampling with a trial wave function which has the following form

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}) = C \exp\left(-\alpha\omega(r_1^2 + r_2^2)/2\right) \exp\left(\frac{a r_{12}}{2(1 + \beta r_{12})}\right), \tag{2}$$

where a is equal to one when the two electrons have anti-parallel spins and $1/3$ when the spins are parallel. Finally, α and β are our variational parameters.

Your task is to perform a Variational Monte Carlo calculation using the Metropolis algorithm to compute the integral

$$\langle E \rangle = \frac{\int d\mathbf{r_1} d\mathbf{r_2} \psi_T^*(\mathbf{r_1}, \mathbf{r_2}) \widehat{\mathbf{H}}(\mathbf{r_1}, \mathbf{r_2}) \psi_T(\mathbf{r_1}, \mathbf{r_2})}{\int d\mathbf{r_1} d\mathbf{r_2} \psi_T^*(\mathbf{r_1}, \mathbf{r_2}) \psi_T(\mathbf{r_1}, \mathbf{r_2})}. \tag{3}$$

You should parallelize your program. As an optional possibility, to program GPUs can be used instead of standard parallelization with MPI throughout the project.

Find the energy minimum and compute also the mean distance $r_{12} = \sqrt{\mathbf{r_1} - \mathbf{r_2}}$ (with $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2}$) between the two electrons for the optimal set of the variational parameters. A code for doing a VMC calculation for a two-electron system (the three-dimensional helium atom) can be found on the webpage of the course, see under programs.

You should also find a closed-form expression for the local energy. Compare the results of this calculation (in terms of CPU time) compared with a calculation which performs a brute force numerical derivation.

1c) Introduce now importance sampling and study the dependence of the results as a function of the time step δt. Compare the results with those obtained under 1a) and comment eventual differences. In performing the Monte Carlo analysis you should use blocking as a technique to make the statistical analysis of the numerical data. The code has to run in parallel.

1d) With the optimal parameters for the ground state wave function, compute the one-body density. Discuss your results and compare the results with those obtained with a pure harmonic oscillator wave functions. Run a Monte Carlo calculations without the Jastrow factor as well and compute the same quantities. How important are the correlations induced by the Jastrow factor? Compute also the expectation value of the kinetic energy and potential energy using $\omega = 0.01$, $\omega = 0.28$ and $\omega = 1.0$. Comment your results.

1e) Repeat step 1c) by varying the energy using the conjugate gradient method to obtain the best possible set of parameters α and β. Discuss the results.

The previous exercises have prepared you for extending your calculational machinery to other systems. Here we will focus on quantum dots with $N = 6$ and $N = 12$ electrons. It is convenient to make modules or classes of trial wave functions, both many-body wave functions and single-particle wave functions and the quantum numbers involved, such as spin, value of n_x and n_y quantum numbers.

The new item you need to pay attention to is the calculation of the Slater Determinant. This is an additional complication to your VMC calculations. If we stick to harmonic oscillator like wave functions, the trial wave function for say an $N = 6$ electron quantum dot can be written as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_6}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \ldots, \phi_6(\mathbf{r_6})\right) \prod_{i<j}^{6} \exp\left(\frac{ar_{ij}}{(1 + \beta r_{ij})}\right), \qquad (4)$$

where Det is a Slater determinant and the single-particle wave functions are the harmonic oscillator wave functions for the $n_x = 0, 1$ and $n_y = 0, 1$ orbitals. For the $N = 12$ quantum dot, the trial wave function can take the form

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_{12}}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \ldots, \phi_{12}(\mathbf{r_{12}})\right) \prod_{i<j}^{12} \exp\left(\frac{ar_{ij}}{2(1 + \beta r_{ij})}\right), \qquad (5)$$

In this case you need to include the $n_x = 2$ and $n_y = 2$ wave functions as well. Observe that $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2}$. Use the Hermite polynomials defined in the appendix.

(1f) Write a function which sets up the Slater determinant handle larger systems as well. Find the Hermite polynomials which are needed for $n_x = 0, 1, 2$ and obviously n_y as well. Compute the ground state energies of quantum dots for $N = 6$ and $N = 12$ electrons, following the same set up as in exercise 1e) for $\omega = 0.01$, $\omega = 0.28$

and $\omega = 1.0$. The calculations should include parallelization, blocking, importance sampling and energy minimization using the conjugate gradient approach. To test your Slater determinant code, you should reproduce the unperturbed single-particle energies when the electron-electron repulsion is switched off. Convince yourself that the unperturbed ground state energies for $N = 6$ is 10ω and for $N = 12$ we obtain 28ω. What is the expected total spin of the ground states?

1g) With the optimal parameters for the ground state wave function, compute again the onebody density. Discuss your results and compare the results with those obtained with a pure harmonic oscillator wave functions. Run a Monte Carlo calculations without the Jastrow factor as well and compute the same quantities. How important are the correlations induced by the Jastrow factor? Compute also the expectation value of the kinetic energy and potential energy using $\omega = 0.01$, $\omega = 0.28$ and $\omega = 1.0$. Comment your results.

Part 2; Density Functional theory for quantum dots

The second part involves the solution of the so-called Kohn-Sham equations for quantum dots. Eventually, if time allows, we will try to construct an optimal density functional for quantum dots using our optimal VMC calculations.

(2a) We limit ourselves to quantum dots with $N = 2$ and $N = 6$ electrons only. The first step is to develop a code that solves the Kohn-Sham equations for $N = 2$ and $N = 6$ quantum dot systems with frequencies $\omega = 0.01$, $\omega = 0.28$ and $\omega = 1.0$ ignoring the exchange contribution. This corresponds to solving the Hartree equations. Solve the Kohn-Sham equations with this approximation for these quantum dot systems and find the total density determined in terms of the single-particle wave functions ψ_i as

$$\rho^H(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2,$$

where the single-particle functions ψ_i are the solutions of the approximated Kohn-Sham equations. Check that the density is normalised to

$$\int d^3 r \rho^H(\mathbf{r}) = N.$$

Compare this density with the corresponding density you get by solving the VMC calculations. Discuss your results.

(2b) A popular approximation to the exchange potential in the density functional is to approximate the contribution to this term by the corresponding result from the infinite electron gas model in two dimensions. For the exchange interaction $V_x(\mathbf{r})$ we will use the local-density approximation of Rajagopal and Kimball, see Phys. Rev. B **15**,

2819 (1977). Use the Kohn-Sham equations to compute the total ground state energy of the same ground states as in 2a) with the above approximation to the exchange potential. Compare the resulting energy with that obtained from your Monte Carlo calculation with and without the Jastrow factor.

(2c) *Optional:* The final step is to construct the exchange energy by using the density from the best VMC result. Compare the exchange energy with the one obtained by the local density approximation from the previous point. Comment your results.

Additional material on Hermite polynomials

The Hermite polynomials are the solutions of the following differential equation

$$\frac{d^2H(x)}{dx^2} - 2x\frac{dH(x)}{dx} + (\lambda - 1)H(x) = 0. \tag{6}$$

The first few polynomials are

$$H_0(x) = 1,$$
$$H_1(x) = 2x,$$
$$H_2(x) = 4x^2 - 2,$$
$$H_3(x) = 8x^3 - 12,$$

and

$$H_4(x) = 16x^4 - 48x^2 + 12.$$

They fulfil the orthogonality relation

$$\int_{-\infty}^{\infty} e^{-x^2} H_n(x)^2 dx = 2^n n! \sqrt{\pi},$$

and the recursion relation

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x).$$

Recipe for writing project reports

Here follows a brief recipe and recommendation on how to write a report for each project.

- Give a short description of the nature of the problem and the eventual numerical methods you have used.

- Describe the algorithm you have used and/or developed. Here you may find it convenient to use pseudocoding. In many cases you can describe the algorithm in the program itself.

- Include the source code of your program. Comment your program properly.

- If possible, try to find analytic solutions, or known limits in order to test your program when developing the code.

- Include your results either in figure form or in a table. Remember to label your results. All tables and figures should have relevant captions and labels on the axes.

- Try to evaluate the reliabilty and numerical stability/precision of your results. If possible, include a qualitative and/or quantitative discussion of the numerical stability, eventual loss of precision etc.

- Try to give an interpretation of you results in your answers to the problems.

- Critique: if possible include your comments and reflections about the exercise, whether you felt you learnt something, ideas for improvements and other thoughts you've made when solving the exercise. We wish to keep this course at the interactive level and your comments can help us improve it. We do appreciate your comments.

- Try to establish a practice where you log your work at the computerlab. You may find such a logbook very handy at later stages in your work, especially when you don't properly remember what a previous test version of your program did. Here you could also record the time spent on solving the exercise, various algorithms you may have tested or other topics which you feel worthy of mentioning.

Format for electronic delivery of report and programs

The preferred format for the report is a PDF file. You can also use DOC or postscript formats. As programming language we prefer that you choose between C++, Fortran95 or Python. Finally, we recommend that you work together. Optimal working groups consist of 2-3 students, but more people can collaborate. You can then hand in a common report.

Literature

1. M. Taut, Phys. Rev. A **48**, 3561 - 3566 (1993).

2. 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.

3. B.H. Bransden and C.J. Joachain, Physics of Atoms and molecules, Longman, 1986. Chapters 6, 7 and 9.

4. A. K. Rajagopal and J. C. Kimball, see Phys. Rev. B **15**, 2819 (1977).