

Assignment 3: The Quantum Monte Carlo method

deadline Tuesday April 12 2022

In this Assignment you will use the *Variational Monte Carlo* method to solve the Schrödinger equation and find the ground state energy for a few quantum systems. You can read more about Variational Quantum Monte Carlo for example in Chapter 12 of Jos Thijssens's book *Computational Physics*. This book is available as e-book from Stockholm University Library. If you are logged in at your University account you can read the book or download chapters (as PDF). You can try to follow this link: <http://ebooks.cambridge.org/chapter.jsf?bid=CB09781139171397&cid=CB09781139171397A114&tabName=Chapter> Alternatively, go to the library homepage <https://www.su.se/stockholm-university-library/>, login to your SU-account (if you are not already logged in) press E-book and search for the book in the box. Easiest is to use the ISBN number: 9781139171397.

Background

The wave function describing a N -particle quantum system in three-dimensions is a $3N$ -dimensional object, or even larger if the spin degree of freedom is considered. Because of this only true few-particle systems (i.e. with two or three particles) can really be solved without approximations concerning the many-body aspects. The traditional approach on larger systems is to use mean-field methods (e.g. Hartree-Fock or Density Functional Theory) and then different strategies to pick the most important effects beyond that (e.g. configuration interaction). Quantum Monte Carlo uses a completely different approach. With it, it is possible to get hold of the ground state for a true many-body system without constructing the full $3N$ -dimensional wave function. Instead the wave function is evaluated at local points in space chosen statistically through *random walks*, e.g. guided by the *Metropolis* algorithm, Metropolis et al., J. Chem. Phys. 21, 1087 (1953), <http://link.aip.org/link/?JCPSA6/21/1087/1>.

Short description

The starting point for the method is a trial wave function $\Psi(x_1, x_2, \dots)$, where x_1, x_2, \dots refer to the coordinates of the particles in the system. The relative probability to be in a specific point in space is $|\Psi(x_1, x_2, \dots)|^2$. We now walk around randomly and find new positions guided by the probability:

0. Start with choosing arbitrary positions for the particles. Then go through the following steps many, many times.
1. Choose a new position for particle i
2. Calculate $p = |\Psi(x_1, x_2, \dots, x_i^{new}, \dots)|^2 / |\Psi(x_1, x_2, \dots, x_i^{old}, \dots)|^2$.
3. If $p \geq 1$ keep the new position. If $p < 1$, keep the new position with probability p .
4. Choose a new position for particle j (and so on).
5. Calculate $p = \dots$

It is the process of accepting or rejecting the new state of the system with probability p that is the essence of the Metropolis algorithm. Very similar steps are gone through in the numerical solutions of the Ising model for example. After walking around for quite a while (to minimize starting point dependences) you start to calculate the *local energy*, $E_L(x_1, x_2, \dots)$.

$$E_L(x_1, x_2, \dots) = \frac{H\Psi(x_1, x_2, \dots)}{\Psi(x_1, x_2, \dots)} \quad (1)$$

at every new accepted position. Again, do this many, many times and calculate the average of the local energy, $\langle E_L \rangle$, and its variance, $\langle E_L^2 \rangle - \langle E_L \rangle^2$. Then start all over again from 0 above. Do this many times and calculate now also the average of the results you get for $\langle E_L \rangle$ (i.e. the average of the average), and the average of the variance. In this way you get an approximation of the expectation

value of the Hamiltonian with your trial wave function. The approximation gets closer and closer to the real expectation value, the more you go through your loops above.

The next step is to vary the trial wave function in order to minimize the average of the local energy. For this one can write the wave function in terms of parameters that can be varied in a systematic way. We will only use trial wave functions with one parameter to vary, but in more elaborate calculations one may have more than one.

The weak point of Quantum Monte Carlo methods is the choice of trial wave function. To choose it is in the general case an art in itself. For a problem where we do not know the answer it is often not obvious what form to use, and it might be hard to know that the true wave function really lies in the space that is covered by the variations.

Your tasks

- Start with the one-dimensional one-particle Harmonic oscillator to understand the method. Some instructions follow below. Check also the book by Thijssen which goes through this example in some detail.
- Write also a minimizing routine. Use for example *Golden Section Search in One Dimension* from Numerical Recipes Chapter 10.1.
- To get a taste of the real power of the method solve for two electrons confined by a two-dimensional harmonic oscillator. This is a model for a two-dimensional quantum dot, an object that can be created at the interfaces between layers of semiconductors. A dot is a type of a man-made atom. See more below.

One particle in a one-dimensional Harmonic oscillator

Remember that the Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega^2 x^2}{2} \quad (2)$$

which can be rewritten with $z = x\sqrt{m\omega/\hbar}$ (making z dimensionless), giving the Schrödinger equation in the following form:

$$-\frac{1}{2} \frac{\partial^2}{\partial z^2} \Psi(z) + \frac{z^2}{2} \Psi(z) = \frac{E}{\hbar\omega} \Psi(z) \quad (3)$$

Use now a trial wave function $\Psi(z) = e^{-\alpha z^2}$. Here we know that the exact solution has $\alpha = 1/2$, and we expect to find this through the minimization-procedure. The local energy is, cf. Eq.(1),

$$\frac{E_L}{\hbar\omega} = \alpha + z^2 \left(\frac{1}{2} - 2\alpha^2 \right). \quad (4)$$

Through the random walk procedure you access, with a uniform distribution of the random numbers, random points between some reasonable points z_{min} and z_{max} , large enough that your result does not depend on them, but not much larger than necessary to be efficient. It is also possible to use exponentially distributed random numbers. Plot the local energies, $\langle E_L^\alpha \rangle$, as well as the variance as a function of α . You can easily calculate the analytical expectation value of H :

$$\langle H_\alpha \rangle = \frac{\int \Psi_\alpha(z) H \Psi_\alpha(z) dz}{\int \Psi_\alpha(z) \Psi_\alpha(z) dz} \quad (5)$$

and compare. Write a routine that varies α to find the minimum. What happens to the variance when you approach $\alpha = 1/2$? Plot also a histogram over the points you visit through the random walk and compare with the probability density of the trial wave function. When you are ready with this part of the Assignment you should have got a grasp of the method and can start with an interesting case; one that is not solved easily with other methods.

Two electrons in a two-dimensional Harmonic oscillator

Here the Hamiltonian is

$$H = \left(\sum_{i=1}^2 -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} + \frac{mx_i^2\omega^2}{2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y_i^2} + \frac{my_i^2\omega^2}{2} \right) + \frac{e^2}{4\pi\epsilon_0\epsilon_r} \frac{1}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}}. \quad (6)$$

We will use Cartesian coordinates in order to keep it simple, although polar coordinates might be more efficient. The mass m here is not the bare electron mass, but an effective mass in the semiconductor material, and ϵ_r is the relative permittivity of the material. Depending on these material-dependent parameters, and on ω , the Coulomb repulsion (the last term) can be of smaller or lesser importance. Again we change to the reduced units above $\bar{x} = x\sqrt{m\omega/\hbar}$, $\bar{y} = y\sqrt{m\omega/\hbar}$, giving the equation

$$\left(\left(\sum_{i=1}^2 -\frac{1}{2} \frac{\partial^2}{\partial \bar{x}_i^2} + \frac{\bar{x}_i^2}{2} - \frac{1}{2} \frac{\partial^2}{\partial \bar{y}_i^2} + \frac{\bar{y}_i^2}{2} \right) + \frac{me^2}{4\pi\epsilon_0\epsilon_r\hbar^2} \sqrt{\frac{\hbar}{m\omega}} \frac{1}{\sqrt{(\bar{x}_1 - \bar{x}_2)^2 + (\bar{y}_1 - \bar{y}_2)^2}} \right) \Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2) = \frac{E}{\hbar\omega} \Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2) \quad (7)$$

Let us also introduce the dimensionless parameter

$$\lambda = \frac{me^2}{4\pi\epsilon_0\epsilon_r\hbar^2} \sqrt{\frac{\hbar}{m\omega}} \quad (8)$$

which gives

$$\left(\left(\sum_{i=1}^2 -\frac{1}{2} \frac{\partial^2}{\partial \bar{x}_i^2} + \frac{\bar{x}_i^2}{2} - \frac{1}{2} \frac{\partial^2}{\partial \bar{y}_i^2} + \frac{\bar{y}_i^2}{2} \right) + \frac{\lambda}{\sqrt{(\bar{x}_1 - \bar{x}_2)^2 + (\bar{y}_1 - \bar{y}_2)^2}} \right) \Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2) = \frac{E}{\hbar\omega} \Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2) \quad (9)$$

where λ is the ratio between the typical length in the harmonic oscillator and that of the Coulomb interaction. A large λ value corresponds to a weaker confinement and an increased relative importance of the electron-electron interaction.

The trial wave function can now be chosen to be

$$\Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2) = e^{-(\bar{x}_1^2 + \bar{y}_1^2 + \bar{x}_2^2 + \bar{y}_2^2)/2} e^{\frac{\lambda\sqrt{(\bar{x}_1 - \bar{x}_2)^2 + (\bar{y}_1 - \bar{y}_2)^2}}{1 + \alpha\sqrt{(\bar{x}_1 - \bar{x}_2)^2 + (\bar{y}_1 - \bar{y}_2)^2}}}. \quad (10)$$

The first exponential is just the product of the ground-state wave functions for non-interacting harmonic oscillators, one in \bar{x} and one in \bar{y} for each particle. The ground state energy of the non-interacting system is $4 \times \hbar\omega/2 = 2\hbar\omega$. The second exponential is a so called Jastrow function. Different versions of it is commonly used for Quantum Monte Carlo calculations. The form here is chosen to be able to reproduce the so called cusp in the wave function for two-particles of opposite spin, in 2D, when $x_1 = x_2$ and $y_1 = y_2$. You can read more e.g. here <http://dx.doi.org/10.1103/PhysRevB.67.235307>. The variational parameter is here α .

To get the local energy we need (among other things) the second derivative of $\Psi(\bar{x}_1, \bar{y}_1, \bar{x}_2, \bar{y}_2)$, for each coordinate. After some algebra one can show that:

$$\begin{aligned} & \frac{\partial^2}{\partial \bar{x}_i^2} e^{-(\bar{x}_i^2 + \bar{y}_i^2 + \bar{x}_j^2 + \bar{y}_j^2)/2} e^{\frac{\lambda r_{ij}}{1 + \alpha r_{ij}}} = e^{-(\bar{x}_i^2 + \bar{y}_i^2 + \bar{x}_j^2 + \bar{y}_j^2)/2} e^{\frac{\lambda r_{ij}}{1 + \alpha r_{ij}}} \\ & \times \left(-1 + \frac{\lambda}{(1 + \alpha r_{ij})^2 r_{ij}} - \frac{\lambda(\bar{x}_i - \bar{x}_j)^2}{(1 + \alpha r_{ij})^3 r_{ij}^3} (1 + 3\alpha r_{ij}) + \left(-x_i + \frac{\lambda(x_i - x_j)}{(1 + \alpha r_{ij})^2 r_{ij}} \right)^2 \right) \\ & \text{where } r_{ij} = \sqrt{(\bar{x}_i - \bar{x}_j)^2 + (\bar{y}_i - \bar{y}_j)^2} \end{aligned}$$

A very first check of your routine is to ensure that with $\lambda = 0$ you get the correct result for two particles in a two-dimensional harmonic oscillator, i.e. $E/\hbar\omega = 2$. The next step is to check against results from the literature. It has been shown that for $\lambda = 1$ the results is $E/\hbar\omega = 3$. You should get a value close to that. After you have checked your method in this way you should try some larger λ -values where the electron-electron interaction is more important. It is an interesting aspect of quantum dots that the relative importance of the electron-electron interaction can be varied.

Some final comments:

- Random numbers The built-in functions in C/C++ and Fortran that generates random numbers do actually generate the same series of random number every time! In order to get a true random number you need a *seed* for the sequence of random numbers that is different for each run. For this you can e.g. use the current time. Check for some of the first runs that you really manage to get a series of random numbers. You will find many suggestion on the internet.
- Random walk There is a vast literature on random numbers and random number generators (you can start with numerical recipes if you want to learn more). It is probably possible to find elaborate routines for the random walk, but this is not necessary. You can write a simple routine yourself that uses the built-in random number generators.
- In these type of calculations some loops will be executed over and over again, and you will soon realize that it takes some time. So be careful what you put inside the loops! You might want to time parts of the program to understand where most of the time is spent and of what you can do to speed up the calculation.