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Variational Monte Carlo methods in Quantum Mechanics. Two electrons confined in a three dimensional isotropic harmonic oscillator potential.

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To get an upper bound for the ground state energy of two electrons confined in a three dimensional isotropic harmonic oscillator potential a code was developed using variational quantum Monte Carlo methods. When the electrons are treated as non-interacting an analytic solution exists. This was compared to the numerical solution which was the same. For calculations of the full Hamiltonian including the repulsive Coulomb term two trial wave functions were used. Measurements were taken for value of oscillator frequency $\omega \in \{0.01, 0.05, 0.25, 0.75, 1.0\}$. For $\omega = 1$ the exact ground state energy is 3.558 a.u.[3] and was measured here to be 3.7362 a.u.. The relation between total expectation value of the total kinetic and potential energy was found to follow a power relation when the Coulomb term was included but was a constant without it. By introducing a Jastrow factor to fulfil the cusp condition for the two electrons the expectation value of the distance between them increased and the trial energy decreased.

Introduction and theory:

One way to confine electrons is in a harmonic potential and these systems often referred to as quantum dots. They are an important concept in condensed matter and material physics with appearances in e.g. solar sells, nano medicine and televisions[3]. In quantum mechanics there are a handful of exactly solvable systems and two electrons in a three dimensional isotropic harmonic oscillator potential for certain frequencies is one[4]. This gives a good benchmark, as other methods and algorithms are developed to solve problems that have to be solved numerically. One of such methods is variational calculations based on the variational principle. Therefore, here we developed a code using Monte Carlo methods for variational calculations with known analytical expressions for benchmarks.

A. Variational Principle

The variational principle in quantum mechanics states that if we have a wave function anzats for the ground state called a trial wave function, ψ_T, then the expectation value of the Hamiltonian or the energy of the system[2],

$$\langle H \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})H\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})} \tag{1}$$

is an upper bound to the true ground state energy E_0,

$$E_0 \leq \langle H \rangle \tag{2}$$

The equality only holds if the trial wave function is the same as the true ground state wave function.

For the variational calculations the trial wave function then depends on one or more variational parameters. The expectation value of the Hamiltonian, $\langle H \rangle$, is calculated for this trial wave function. The final step is then minimizing the expectation value with regards to the variational parameters and this gives an upper bound to the ground state energy. As this can involve evaluating many multidimensional integral it motivates the use of Monte Carlo methods.

B. Variational Monte Carlo

When calculating multidimensional integrals using MC methods we need a probability distribution. Here the trial wave function defines a quantum-mechanical probability distribution[2],

$$P(\mathbf{R};\alpha) = \frac{|\Psi_T(\mathbf{R};\alpha)|^2}{\int |\Psi_T(\mathbf{R};\alpha)|^2} \tag{3}$$

where the denominator is a normalization factor. For the exact ground state wave function, Ψ_{GS}, the ground state energy is given by,

$$\langle H \rangle = \frac{\int d\mathbf{R}\Psi_{GS}^*(\mathbf{R})H\Psi_{GS}(\mathbf{R})}{\int d\mathbf{R}\Psi_{GS}^*(\mathbf{R})\Psi_{GS}(\mathbf{R})} \tag{4}$$

To find the upper bound to this value using variational calculations we define a new operator called the local energy operator, $\hat{E}_L(\mathbf{R};\alpha)$,

$$\hat{E}_L(\mathbf{R};\alpha) = \frac{1}{\Psi_T(\mathbf{R};\alpha)}\hat{H}\Psi_T(\mathbf{R};\alpha) \tag{5}$$

Using this local energy operator and the probability distribution, eq. 3, we calculate the expectation value of the local energy

$$\langle E_L(\alpha) \rangle = \int P(\mathbf{R};\alpha)\hat{E}_L(\mathbf{R};\alpha)d\mathbf{R} \tag{6}$$

This equation relates the expectation value to Monte Carlo methods. Then finally to find an upper bound to the ground state energy we minimize the value with respect to the variational parameters, essentially calculating this integral many times for different values of variational parameters and finding the lowest value. For an in depth explanation of Monte Carlo methods see page 337 and onwards in lectures by Morten Hjorth-Jensen[2].

C. Implementation and Metropolis test

When evaluation the integral, eq. 6, we need to use the Metropolis algorithm when we propose new steps in the N-dimensional space. This then involves the use of the quantum mechanical probability distribution, eq. 3. The following two tests encapsulate how we accept or decline a move from a position $\mathbf{R}$ to a new position $\mathbf{R}'$[2].
1. If

$$\frac{P(\mathbf{R}';\alpha)}{P(\mathbf{R};\alpha)} > 1$$

then the move is accepted.
2. If

$$r \leq \frac{P(\mathbf{R}';\alpha)}{P(\mathbf{R};\alpha)}$$

we accept, where r is a randomly generated number from a uniform distribution on $[0,1]$.

If these two condition are not met we decline the move. The advantage of the Metropolis algorithm in conjunction with MC calculations is that we never have to evaluate the normalization factor due to the fact that we evaluate the ratio of probabilities. We now turn our attention to an example where we apply these methods.

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D. Two electrons in an isotropic harmonic oscillator potential.

Let's now take a look at the ground state of two electrons situated in a three dimensional isotropic harmonic oscillator potential characterized by a frequency, ω. The total Hamiltonian for both electrons is[3],

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right) + \sum_{i<j} \frac{1}{r_{ij}} \qquad (7)$$

Where constants $\hbar = c = e = m_e = 1$ are in natural units and the unit of energy is atomic units, a.u. All distances are also dimensionless. The standard harmonic oscillator for two non-interacting electrons is

$$\hat{H}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right) \qquad (8)$$

with the repulsive Coulomb term being

$$\hat{H}_1 = \sum_{i<j} \frac{1}{r_{ij}} \qquad (9)$$

where $r_{ij} = \sqrt{\mathbf{r}_1 - \mathbf{r}_2}$ is the distance between the electrons.

For the standard harmonic oscillator, eq. 8, an analytic solution exists and for certain values of the frequency, ω, a known analytic solution exists for the full Hamiltonian[4].

In this article we take a look a two different trial wave functions[3],

$$\Psi_{T1}(\mathbf{r}_1, \mathbf{r}_2) = C \exp\left(\frac{-\alpha\omega(r_1^2 + r_2^2)}{2} \right) \qquad (10)$$

which is the exact analytical ground state wave function for the unperturbed Hamiltonian and has total spin zero as we are dealing with two electrons which cannot be in in the same quantum state due to symmetry[1]. The other trial wave function is,

$$\Psi_{T2}(\mathbf{r}_1, \mathbf{r}_2) = C \exp\left(\frac{-\alpha\omega(r_1^2 + r_2^2)}{2} \right) \qquad (11)$$
$$\times \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})} \right)$$

with variational parameters α and β and the normalization factor C. The second trial wave function satisfies a so called cusp condition by including a Jastrow factor, which is the add-on to the first trial wave function. In short this factor takes into account the behaviour of the two electron system as they get close to one another, that is as $r_{12} \to 0$[2].

When the the Coulomb interaction is disregarded the analytical value for the local energy for the first trial function, eq. 10, is the following,

$$E_{L1} = \frac{1}{2}\omega^2 \left(r_1^2 + r_2^2 \right) \left(1 - \alpha^2 \right) + 3\alpha\omega \qquad (12)$$

with the exact result for the ground state energy being 3ω. With the Coulomb repulsive term this becomes,

$$E_{L1} = \frac{1}{2}\omega^2 \left(r_1^2 + r_2^2 \right) \left(1 - \alpha^2 \right) + 3\alpha\omega + \frac{1}{r_{12}} \qquad (13)$$

To obtain this expression we use eq. 5 and for the first trial wave function it is the following,

$$E_{L1} = \frac{1}{\Psi_{T1}} \hat{H} \Psi_{T1} \qquad (14)$$

Let's first consider the kinetic energy term for the first electron and as the wave function is only dependent on the radial coordinate in spherical coordinates this reduces down to,

$$\nabla_1^2 \Psi_{T_1} = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial \Psi_{T1}}{\partial r_1} \right)$$
$$= 2r_1 \frac{\partial \Psi_{T1}}{\partial r_1} + r_1^2 \frac{\partial^2 \Psi_{T1}}{\partial r_1^2}$$
$$= (-3\alpha\omega + (\alpha\omega r_1)^2)\Psi_{T1}$$

similarly for the contribution to the kinetic energy from the other electron

$$\nabla_2^2 \Psi_{T_1} = (-3\alpha\omega + (\alpha\omega r_2)^2)\Psi_{T1}$$

The potential term reads,

$$\left(\frac{1}{2}\omega^2(r_1^2 + r_2^2) + \frac{1}{r_{12}} \right)\Psi_{T1}$$

and when both parts are taken together,

$$
\begin{aligned}
E_{L1} &= \frac{1}{\Psi_{T1}}\hat{H}\Psi_{T1} \\
&= \frac{1}{\Psi_{T1}}\left(-\frac{1}{2}(-3\alpha\omega + (\alpha\omega r_1)^2) \right. \\
&\quad - \frac{1}{2}(-3\alpha\omega + (\alpha\omega r_2)^2) \\
&\quad \left. + \frac{1}{2}\omega^2(r_1^2 + r_2^2) + \frac{1}{r_{12}} \right)\Psi_{T1} \\
&= \frac{1}{2}\omega^2 \left(r_1^2 + r_2^2 \right)\left(1 - \alpha^2 \right) + 3\alpha\omega + \frac{1}{r_{12}}
\end{aligned}
$$

In similar way the analytical expression for the second trial wave function can be found, and it is[3]

$$
\begin{aligned}
E_{L2} = E_{L1} &+ \frac{1}{2(1 + \beta r_{12})^2} \\
&\left\{ \alpha\omega r_{12} - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}} \right\}
\end{aligned}
\tag{15}
$$

where E_{L1} now includes the Coulomb repulsive term.

E. Virial Theorem

There is proportionality between the total expectation value of the total kinetic energy, $\langle T \rangle$, and the expectation value of the total potential energy, $\langle V \rangle$. This is known as the virial theorem. In the case of the simple harmonic oscillator with no coulomb interaction this ratio is[3],

$$\langle T \rangle = \langle V \rangle \tag{16}$$

For the case where we include the Coulomb interaction this becomes dependant on the oscillator

frequency. Here a power model was used to characterize this behaviour,

$$\frac{\langle T \rangle}{\langle V \rangle} = A \cdot \omega^\gamma \tag{17}$$

where A and γ are constants.

F. Implementation, code and data

All code and data for this article can be found on `https://github.com/bjornaki/CompPhysics/tree/master/Project5`. At first we look at a simple case for two non-interacting electrons and compare to analytic answer. Then we measure the upper bound to the ground state energy for several different frequencies, $\omega \in \{0.01, 0.05, 0.25, 0.5, 0.75, 1\}$. For each value the first local energy, eq. 12, is minimized with regards to α and used as a starting point for the minimization for the second trial wave function with regards to β. Using this we again minimize the seconds trial wave function energy with regards to α and then once again for β. These results are then represented and used as optimal parameters.

Results

A. Two non-interacting electrons in a simple harmonic oscillator

For reference we start by calculating the expectation value of energy for two non-interacting electrons in the quantum harmonic oscillator. This case has an analytical solution and the first trial wave-function is the analytical solution. Thus when minimized with regards to α we obtain the exact ground state energy and the exact ground state wave function. This can be seen in figure 1. This case is measured for $\omega = 1$ and the energy is $E = 3$ with $\alpha = 1$. Furthermore, the variance is zero indicating this is the exact solution. Figure 1 serves as an example as how measurements were

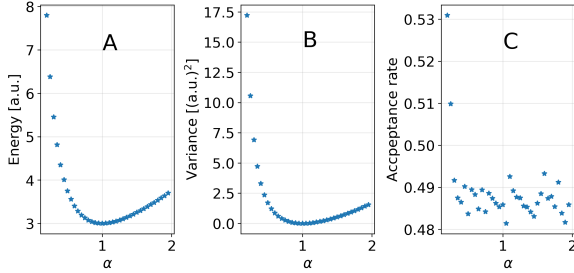carried out with around 50% acceptance rate for proposed moves.

Figure 1: MC measurement for two non-interacting electrons in a isotropic harmonic oscillator as a function of the variational parameter α. 10^6 MC cycles with $\omega = 1$. **A.** Energy. **B.** Variance. **C.** Ratio of accepted moves.

B. Two trial wave functions for two electrons

We now extend our calculations using the method developed but now including the Coulomb interaction when calculating the expectation value of the total energy. We start by minimizing the first trial wave function with regards to α. This minimum is then used as a starting point to minimize the the expectation value of the total energy for the second trial wavefunction, eq. 11. This was done two times for each parameter, α and β, to obtain an upper bound to the ground state energy. These minimal values for α and β along with the upper bound to the ground state energy and the respective variance, σ^2, are found in table 1.

Table 1: Minimal value for the expectation value of the total energy for the second trial wave function. The optimal values for parameters α and β with the respective variance, σ^2.

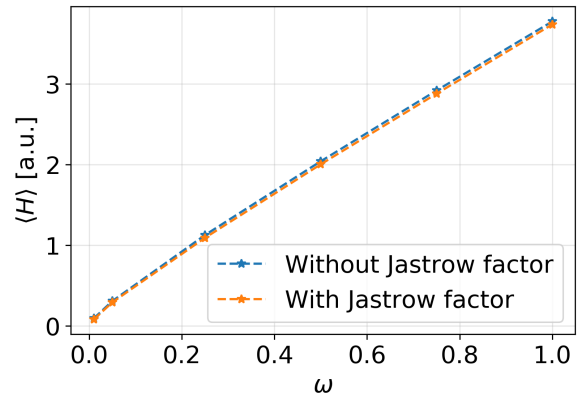| ω	$\langle H \rangle$ [a.u.]	α	β	σ^2 [(a.u.)^2]
0.01	0.0806	0.670	0.067	$3.0569 \cdot 10^{-5}$
0.05	0.2916	0.660	0.180	$1.0986 \cdot 10^{-3}$
0.25	1.0909	0.910	0.205	$9.3021 \cdot 10^{-4}$
0.5	2.0027	0.920	0.290	$2.9856 \cdot 10^{-3}$
0.75	2.8777	0.930	0.340	$5.0684 \cdot 10^{-3}$
1	3.7362	0.945	0.6075	$1.6786 \cdot 10^{-2}$

Figure 2: Total expectation value of energy as a function of the harmonic oscillator frequency.

C. Virial Theorem

The virial theorem states that the expectation value for the total expectation value of the total kinetic energy and potential energy are the same for the simple harmonic oscillator with non-interacting electrons. This behaviour is observed here and can be seen in figure 3. We then investigate this proportionality for ratio of the kinetic and potential energy for the second trial wave function. This is also seen in figure 3. By taking the natural logarithm of equation 17 we obtain a linear fit to this proportionality as a function of ω. A and γ are constants found to be $A = -0.56389$ and $\gamma = 0.34132$. This fit is also
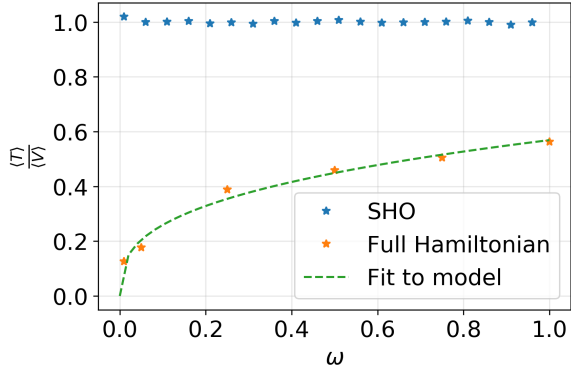
shown in figure 2.

Figure 3: Ratio of expectation value of the total kinetic energy and total potential energy for both two non-interacting electrons and where the repulsive Coulomb term is included. The dotted line represents a fit according to model, eq. 17.

D. Distance between electrons

As the strength of the oscillator potential is increased the distance between electrons decreases. For the optimal parameters obtained and the minimum in energy we measured the expectation value of the distance between electrons at that minimum with and without the Jastrow factor. We see when the Jastrow factor is included the distance between electrons increases, see fig. 4, and the upper bound to the ground state energy decreases as can be seen in fig 2.
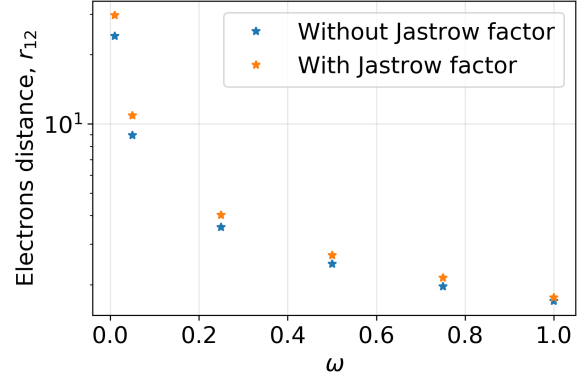

Figure 4: The average distance between the two electrons on logarithmic scale as a function of potential frequency, ω.

Discussion

Two non-interacting electrons in a simple harmonic oscillator

In the case of the two non-interacting electrons in the simple harmonic oscillator potential the analytical ground state energy and ground state wave function was obtained. Obtaining this results motivates further use of the code developed on a case where an analytical result cannot be obtained.

B. Two trial wave functions for two electrons

When we include the Jastrow factor in the second trial wave function we better encapsulate the two electrons behaviour when they approach each other and thus get lower trial energy for all measured values of ω.

C. Virial Theorem

The virial theorem states for a simple harmonic oscillator the ratio between the kinetic and potential energy is equal to one independent of the oscillator frequency. This is however not the case for when we include the Coulomb term as then

the potential energy is also dependent on the relative distance of the electrons. We quantify this behaviour with a power-relation. As the oscillator potential is increased the expectation value of the kinetic energy grows larger relative to the potential energy.

D. Distance between electrons

As mentioned as the oscillator potential is increased the distance between electrons decreases. As the Coulomb force is relatively short range most of the system energy is in the kinetic energy for low ω but as the electrons move closer to one another the Coulomb term contributes more and more to the potential energy. By introducing a Jastrow factor as was done for the second trial wave function the expectation value of the distance between electrons increases and the energy decreases.

Conclusions and next steps

We have now developed a code that measures and evaluates an upper bound to the ground state energy for two electrons in an isotropic three dimensional harmonic oscillator using quantum variational Monte Carlo methods. For the case where the electrons are treated as non-interacting an analytical solution exists and we obtained this exact value numerically. When one finds the exact ground state wave function the variance is zero. Based on these calculations two trial wave functions were used to do variational calculations with repulsive Coulomb term included in the full Hamiltonian. When a Jastrow factor is included like in the second trial wave function the upper bound to the ground state energy is lowered even further compared to when it is left out like for the first trial wave function. This is because by introducing a Jastrow factor the wave function satisfies the so called cusp condition when the two electrons are close to one another.

As the oscillator frequency, ω, is increased the potential energy becomes relatively larger than the kinetic energy, as opposed to the case where the Coulomb term is excluded and the ratio stays a constant. This was quantified with a power relation, eq.17.

Further work would be to investigate more closely the relation between the kinetic and potential energy for more values of the oscillator potential. In addition further variational parameters and new trial wave functions could be introduced to try to give a better estimate for the ground state energy.

References

[1] David J. Griffiths and Darrel F. Schroeter. *Introduction to Quantum Mechanics*. Cambridge University Press, 2018.

[2] Morten Hjorth-Jensen. Computational Physics, Lecture Notes Fall 2015.

[3] Morten Hjorth-Jensen. Project 5, Quantum Monte Carlo of confined electrons. https://github.com/CompPhysics/ComputationalPhysics/blob/master/doc/Projects/2019/Project5/QuantumMonteCarlo/pdf/QuantumMonteCarlo.pdf, 2019.

[4] M. Taut. Two electrons in an external oscillator potential: Particular analytic solutions of a coulomb correlation problem. *PHYSICAL REVIEW A*, 1993.