

Project 5

Quantum Monte Carlo of Confined Electrons

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The motivation for the project is in exploring the system of 2 electrons in a harmonic oscillator potential, taking greater care with the interaction between the electrons as well as the separable case of a pure harmonic oscillator potential. The system is explored through the variational Monte Carlo method using a uniform sampling and the Metropolis sampling rule. Benchmarking the program is done with the non-interacting case and gradually disturbing the system by introducing first interactions between the electrons and later by making the wave function more complex. Initially, the wavefunction is optimized through minimizing the energy and comparing over varying frequencies. Later, the optimizations also include the second variational parameter and the optimization now goes sequentially over the 2 parameters. Several issues remain with the results, and the plan to study the system with the Virial theorem fell through.

I. INTRODUCTION

The project aims to evaluate the ground state energy per particle of the system with 2 electrons in a harmonic oscillator potential. The system is represented in the 3 dimensional cartesian coordinate system.

The method chosen is a stochastic approach with the variational principle, variational Monte Carlo simulation. Most such simulations are done in a 2 dimensional system, but in order to compare with other studies approaching the system as an eigen value problem and utilizing matrix representations of the discretized equations and linear algebra to reduce and solve the problem, the project maintains a 3 dimensional representation.

Section I, theory, explores the system and it's description as well as the relevant observables and their description. Followed by a discussion of the stochastic interpretation of the integral and a presentation of the algorithm used to represent the system.

Section II, results, presents the information obtained by the calculations. The energetic reliance on α as well as the variance of the system under over these changes is plotted. There is also a brief representation of the missing and erroneous data from the more complex system.

Section III, conclusion, attempts to make some sense of the information gathered and to point towards weak points in the solution as well as steps which could improve further examinations.

II. THEORY AND METHODS

A. system

Quantum dots are a lively research area for condensed matter physics and material science with wide reaching applications from quantum computing to solar cells.

The main aim is to study these systems with a focus on understanding the repulsive forces between the electrons. The advantage of the VMC approach is the ability to use cartesian coordinates over polar, such as with the eigenvalue approach. The sparse matrix reduction greatly simplifies the calculations, but the direct readability is less clear.

Our system is of electrons confined in a pure 3D isotropic harmonic oscillator potential with an idealized total Hamiltonian

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

having set the natural units $\hbar = c = e = m_e = 1$, as well as denoting energies in atomic units $a.u.$

Thus all results will be scaled. The first sum is the standard harmonic oscillator, whilst the latter part of the Hamiltonian is the repulsive forces between the electrons.

$$\hat{H}^0 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 r_i^2 \right) \quad (2)$$

$$\hat{H}' = \sum_{i<j} \frac{1}{r_{ij}} \quad (3)$$

The distance $r_{ij} = \sqrt{\vec{r}_1 - \vec{r}_2}$ is between the 2 particles, each position given as $r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}$.

The first step will be the unperturbed harmonic oscillator Hamiltonian mentioned above (2). Setting $\hbar\omega = 1$ gives the energy $3a.u.$ This will serve as a benchmark during development of the code.

In 3 dimensions, the wave equation is

$$\psi_{\vec{n}}(\vec{r}) = A H_{n_x}(\sqrt{\omega} x) H_{n_y}(\sqrt{\omega} y) H_{n_z}(\sqrt{\omega} z) e^{-\omega r^2/2} \quad (4)$$

The $H_{n_i}(\omega i)$ are the Hermite polynomials and A is a normalization constant. for the ground state, and assuming opposing spins, the energy becomes $\epsilon_{\vec{n}} = \frac{3}{2}$ per electron. This brings the total energy up to $3a.u$ as stated previously. The unperturbed ground state eigenfunction for the 2 electron system then becomes

$$\bar{\Psi}(\vec{r}_1, \vec{r}_2) = C e^{-\frac{1}{2}\omega(r_1^2 + r_2^2)} \quad (5)$$

with C as a normalization constant.

Since the electrons are fermions, they obey the Pauli exclusion principle. This means that the ground state is non-degenerate with each having opposing spin. This could also be likened to the singlet state in the nlm style Dirac notation. The total spin of this system must therefore be 0.

B. approximation

Our first two trial wave functions will be

$$\Psi_{T_1}(\vec{r}_1, \vec{r}_2) = Ce^{-\frac{1}{2}\alpha\omega(r_1^2+r_2^2)} \quad (6)$$

$$\Psi_{T_2}(\vec{r}_1, \vec{r}_2) = Ce^{-\frac{1}{2}\alpha\omega(r_1^2+r_2^2)} e^{\frac{r_{12}}{2(1+\beta r_{12})}} \quad (7)$$

With α and β as variational parameters.

The energy at a given distance, r_1, r_2 is our local energy

$$\begin{aligned} E_{L_1} &= \frac{H\Psi_{T_1}(\vec{r}_1, \vec{r}_2, \alpha)}{\Psi_{T_1}(\vec{r}_1, \vec{r}_2, \alpha)} \\ &= \frac{1}{2}\omega^2(r_1^2 + r_2^2)(1 - \alpha^2) + 3\alpha\omega \end{aligned} \quad (8)$$

The road there is found in (14). As this has a well defined and simple energy function, it is a good target for benchmarking. As the repulsive Coloumb interaction is purely dependent on positions and works between particles, adding it to our simple 2-particle state results in

$$E_{L_1} = \frac{1}{2}\omega^2(r_1^2 + r_2^2)(1 - \alpha^2) + 3\alpha\omega + \frac{1}{r_{12}} \quad (9)$$

which is eschewed somewhat by the electron interaction. We can approach a best estimate by varying α . The results of this can also be used to compare the second trial function once total energy has been found for both.

The second trial wavefunction, (7) gives a few extra products, but thanks to the product rule, they separate into

$$E_{L_2} = E_{L_1} + \frac{1}{2(1+\beta r_{12})^2} \left[\alpha\omega r_{12} - \frac{1}{2(1+\beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1+\beta r_{12}} \right] \quad (10)$$

and have an exact energy for $\omega = 1$ of $3.558a.u.$ this can be correlated to the eigenvalue approach to the quantum dot[1].

C. simulation

The chosen integrator over these quantum states is the variational Monte Carlo method. We want to apply the variational principle for approaching the ground state of a pair of electrons in a harmonic oscillator potential, assuming a singlet spin state. This means the spatial equations need to be symmetric to accomodate the Pauli exclusion principle. this fits well with the chosen trial wave functions, as they are symmetric under spatial parity. For the variational method, we need to find the trial energy,

$$\begin{aligned} \langle H \rangle &= \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \quad \text{see appendix (V B)} \\ &= \int d\vec{r} E_L(\vec{r}) P(\vec{r}) \quad \text{which discretizes to} \\ &= \frac{1}{N_{MC}} \sum_i^{N_{MC}} P(\vec{r}) E_L(\vec{r}) \quad \text{with possibly extra variational parameters.} \end{aligned} \quad (11)$$

For the MC sample, there needs to be an acceptance rule as well as a method for sampling each step. The Metropolis sampling equation is a decent way of deciding, considering the possibility of finding ratios between probabilities from the wavefunction. As a sampling rule, the basic uniform distribution works. Though this means discarding values outside the acceptance, it gives an acceptable result.

The step length is found by running through a shorter sequence, minimizing the variance during runtime and stopping once the acceptance rate is acceptably close to 50%.

The program setup is of a base wavefunction class and more specific inheritors, depending on the system as well as a VMC class for Monte Carlo simulations of various types. The two types are managed by the main class, which reads input from the command line and decides which parts of the program to run. To allow for pure virtual functions in the base, the parameters are sent in with a vector of vectors, each of which is then iterated through as needed.

```

for each particle do
  for each dimension do
    Take a random step of length  $rnd \cdot \delta$ ,  $rnd \in [-1,1]$ 
    check the energetic gain in taking the step.
    compare probability ratio between the 2 positions to a stochastic number  $a \in 0.0,1.0$ 
    if  $a \leq \Pr\{\Delta E\}$  then
      apply change
      update positions and count as an accepted configuration
    end
  else
    Keep old positions
  end
end
end
| Calculate forces.

```

Algorithm 1: The algorithm for 1 MC cycle.

III. RESULTS

Initial outline of the program was taken from Mathias Vege's online example code (??). The base wavefunction class is a pure virtual base and will throw an exception if the derived classes do not contain at least a method for calculating the power, or the local energy. Running through the various α and ω values saw no change in which α 's gave the minimum energy over different ω . These records are unfortunately missing.

though later runs with $\omega = 1$ have produced good results, where the pure harmonic oscillator Hamiltonian produces a minimal energy at $\alpha = 1$ with a variance σ^2 of 0 at this minima. The relationship between energy per particle and α can be observed in figure (1). The data file is represented in table (II). Figure 1 shows how $\langle E \rangle \rightarrow 3a.u$ as $\alpha \rightarrow 1$. Here we can also see, that the variance disappears.

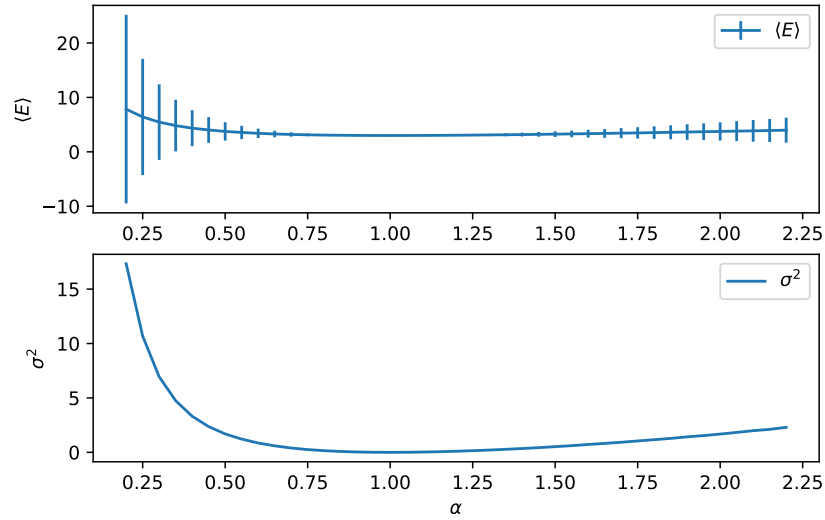


FIG. 1.

As one can see in the appendix table, the distance between the electrons was not updated.

Adding in the second trial wave function, makes the system more complicated, as there are now 2 variables affecting the energy. To find the optimal ones, the best fit for α with the first trial function was used to find a best fit for the new β . These 2 values are found by running an MC integration over an array of length 40 between 0.2 and 2.3, with a stepsize of 0.05. This is to ensure that a global rather than a local minimum is found. Next, these values are used to successively update the other through running a while loop optimization. Whenever the next step has a greater energy than the last, the algorithm reverses direction and halves the step size. This continues until neither a step forward nor backwards produces a lower energy.

TABLE I. Table of first run

ω	α	β	$\langle E \rangle$	σ^2	$ r_{12} $	acceptance
$1 \cdot 10^{-2}$	$9.5 \cdot 10^{-3}$	$9.03 \cdot 10^{-3}$	$1.81 \cdot 10^1$	$3 \cdot 10^1$	$0 \cdot 10^0$	$5.29 \cdot 10^{-1}$
$5 \cdot 10^{-1}$	$4.75 \cdot 10^{-1}$	$4.51 \cdot 10^{-1}$	$6.46 \cdot 10^0$	$1.13 \cdot 10^1$	$0 \cdot 10^0$	$5.29 \cdot 10^{-1}$
$1 \cdot 10^0$	$9.51 \cdot 10^{-1}$	$9.03 \cdot 10^{-1}$	$5.47 \cdot 10^0$	$6.87 \cdot 10^0$	$0 \cdot 10^0$	$5.26 \cdot 10^{-1}$

IV. CONCLUSION

The simulation with the first trial energy produces results that mimic what one would expect, minimizing around the $3a.u.$ mark. This is in very good agreement to the HO hamiltonian. The fit is, perhaps, too good for the full expression including the interaction between the electrons. The interaction should shift the energy. Looking at the results for the average distance there seems to be an error in my calculation of this distance. If the distance is always cast to 0, or similar, then the interaction it would have on the environment might be poor as well. This error should result in the cusp condition, or the greatest effect, seeing as how the interaction is inversely proportional to the distance between the 2 electrons.

Looking at the results from I, also shows that the energy fluctuates with ω . A high angular frequency in the potential means that the system has a large amount of energy. A higher potential also forces the electrons to stay at a closer distance which leads to a greater influence from the interactions between them. As the surrounding field weakens, the electron repulsion pushes the electrons further away, and the Jastrow effect lessens. Comparing this to the results in project 2, regarding the eigenvalue approach to the system, we see this relationship. This is in stark contrast to the results produced here. This is likely due to an error in the evaluation of the local energies for the more complex system, as it did not show up on the early simulations with the non-interacting electrons. A guess here, is in the splitting of the energy to allow for extracting kinetic and potential energy for later simulations of the virial theorem. i

As mentioned previously, the measured distance is also cast to 0 at all points. This might point towards something wrong in the storage of the variables, or in the calculation itself.

This project has gone quite a bit over the given time limit, largely due to various bugs with the program, as well as problems implementing the various tests. Points of improvement are clearly in the derived wave function classes, which are both cluttered and likely faulty. My next move would probably be to make a cleaner version and gather all energy into 1 result. Next, I would look into the implementation of the sum of the squares of positions and the distance between the electrons. Once these have been verified to produce the correct results, I could either modify the energy or make the kinetic and potential energies by extracting the opposite from the local energy.

Furthermore, I would like to generalize the "finder" objects in the vmc system to be more general, so as to not have one for each variable. During the process in the week leading up to and the weekend following after the deadline, the VMC class in particular grew quite clustered. Tidying this up by consistently applying the appropriate private variables and extracting via getters and setters would likely make further work easier.

A clear improvement could also be made using importance sampling. Currently half of all changes suggested are rejected, which wastes several cpu cycles.

V. APPENDIX

A. First trial wavefunction local energy

using $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ and that

$$\begin{aligned} \frac{\partial^2}{\partial x_1^2} \Psi T_1 &= \frac{\partial}{\partial x_1} \left(-\alpha \omega x_1 e^{-\frac{1}{2}(r_1^2 + r_2^2)} \right) \\ &= -\alpha \omega + (\alpha \omega x_1^2) e^{-\frac{1}{2}(r_1^2 + r_2^2)} \end{aligned} \quad (12)$$

Which is the same for y and z . Summing up each contribution and halving from the fraction in the hamiltonian and for each particle leads to

$$\frac{\partial^2}{\partial x_1^2} \Psi T_1 = -3\alpha \omega + \alpha \omega (r_1^2 - r_2^2) e^{-\frac{1}{2}(r_1^2 + r_2^2)} \quad (13)$$

and the last $\omega^2(r_1^2 + r_2^2)$ is from the positional potential element of the Hamiltonian.

$$\begin{aligned}
E_{L_1} &= \frac{H\Psi_{T_1}(\vec{r}_1, \vec{r}_2, \alpha)}{\Psi_{T_1}(\vec{r}_1, \vec{r}_2, \alpha)} \\
&= C^{-1} e^{\frac{1}{2}\alpha\omega(r_1^2 + r_2^2)} \frac{1}{2} \left(-\nabla_1^2 - \nabla_2^2 + \omega^2(r_1^2 + r_2^2) \right) C e^{-\frac{1}{2}\alpha\omega(r_1^2 + r_2^2)} \\
&= e^{\frac{1}{2}\alpha\omega(r_1^2 + r_2^2)} \frac{1}{2} \left(-\alpha^2\omega^2(r_1^2 + r_2^2) + 6\alpha\omega + \omega^2(r_1^2 + r_2^2) \right) e^{-\frac{1}{2}\alpha\omega(r_1^2 + r_2^2)} \\
&= \frac{1}{2}\omega^2(r_1^2 + r_2^2) (1 - \alpha^2) + 3\alpha\omega
\end{aligned} \tag{14}$$

B. Trial energy transformation

$$\begin{aligned}
\langle H \rangle &= \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \\
&= \frac{\int d\vec{r} \Psi_T^*(\vec{r}) H(\vec{r}) \Psi_T(\vec{r})}{\int d\vec{r} \Psi_T^*(\vec{r}) \Psi_T(\vec{r})}
\end{aligned} \tag{15}$$

$$\begin{aligned}
&= \frac{\int d\vec{r} \Psi_T^* E_L \Psi_T}{A} \quad \text{rewriting } H\Psi_T = E_L\Psi_T \quad \text{and} \quad \int d\vec{r} \Psi_T^* \Psi_T = A \\
&= \frac{1}{A} \int d\vec{r} E_L(\vec{r}) P(\vec{r}) A \quad \text{using } P(\vec{r}) \equiv \frac{\Psi_T^* \Psi_T}{A} \\
&= \int d\vec{r} E_L(\vec{r}) P(\vec{r})
\end{aligned} \tag{16}$$

C. Ψ_{T_1} with electron electron interaction

[1] M. Hjorth-Jensen, <http://compphysics.github.io/ComputationalPhysics/doc/Projects/2018/Project2/html/Project2.html> (2018).

TABLE II. Table of first run

α	$\langle E \rangle$	σ^2	$ r_{12} $	acceptance
$2 \cdot 10^{-1}$	$7.85 \cdot 10^0$	$1.73 \cdot 10^1$	$0 \cdot 10^0$	$7.76 \cdot 10^{-1}$
$2.5 \cdot 10^{-1}$	$6.41 \cdot 10^0$	$1.07 \cdot 10^1$	$0 \cdot 10^0$	$7.5 \cdot 10^{-1}$
$3 \cdot 10^{-1}$	$5.46 \cdot 10^0$	$6.94 \cdot 10^0$	$0 \cdot 10^0$	$7.27 \cdot 10^{-1}$
$3.5 \cdot 10^{-1}$	$4.82 \cdot 10^0$	$4.74 \cdot 10^0$	$0 \cdot 10^0$	$7.07 \cdot 10^{-1}$
$4 \cdot 10^{-1}$	$4.35 \cdot 10^0$	$3.32 \cdot 10^0$	$0 \cdot 10^0$	$6.89 \cdot 10^{-1}$
$4.5 \cdot 10^{-1}$	$4.02 \cdot 10^0$	$2.36 \cdot 10^0$	$0 \cdot 10^0$	$6.71 \cdot 10^{-1}$
$5 \cdot 10^{-1}$	$3.75 \cdot 10^0$	$1.69 \cdot 10^0$	$0 \cdot 10^0$	$6.53 \cdot 10^{-1}$
$5.5 \cdot 10^{-1}$	$3.56 \cdot 10^0$	$1.22 \cdot 10^0$	$0 \cdot 10^0$	$6.39 \cdot 10^{-1}$
$6 \cdot 10^{-1}$	$3.4 \cdot 10^0$	$8.6 \cdot 10^{-1}$	$0 \cdot 10^0$	$6.25 \cdot 10^{-1}$
$6.5 \cdot 10^{-1}$	$3.28 \cdot 10^0$	$5.96 \cdot 10^{-1}$	$0 \cdot 10^0$	$6.11 \cdot 10^{-1}$
$7 \cdot 10^{-1}$	$3.19 \cdot 10^0$	$3.98 \cdot 10^{-1}$	$0 \cdot 10^0$	$5.98 \cdot 10^{-1}$
$7.5 \cdot 10^{-1}$	$3.13 \cdot 10^0$	$2.54 \cdot 10^{-1}$	$0 \cdot 10^0$	$5.85 \cdot 10^{-1}$
$8 \cdot 10^{-1}$	$3.08 \cdot 10^0$	$1.53 \cdot 10^{-1}$	$0 \cdot 10^0$	$5.73 \cdot 10^{-1}$
$8.5 \cdot 10^{-1}$	$3.04 \cdot 10^0$	$8 \cdot 10^{-2}$	$0 \cdot 10^0$	$5.62 \cdot 10^{-1}$
$9 \cdot 10^{-1}$	$3.02 \cdot 10^0$	$3.32 \cdot 10^{-2}$	$0 \cdot 10^0$	$5.51 \cdot 10^{-1}$
$9.5 \cdot 10^{-1}$	$3 \cdot 10^0$	$7.93 \cdot 10^{-3}$	$0 \cdot 10^0$	$5.4 \cdot 10^{-1}$
$1 \cdot 10^0$	$3 \cdot 10^0$	$0 \cdot 10^0$	$0 \cdot 10^0$	$5.3 \cdot 10^{-1}$
$1.05 \cdot 10^0$	$3 \cdot 10^0$	$7.2 \cdot 10^{-3}$	$0 \cdot 10^0$	$5.21 \cdot 10^{-1}$
$1.1 \cdot 10^0$	$3.01 \cdot 10^0$	$2.77 \cdot 10^{-2}$	$0 \cdot 10^0$	$5.11 \cdot 10^{-1}$
$1.15 \cdot 10^0$	$3.03 \cdot 10^0$	$5.85 \cdot 10^{-2}$	$0 \cdot 10^0$	$5.01 \cdot 10^{-1}$
$1.2 \cdot 10^0$	$3.05 \cdot 10^0$	$1.01 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.93 \cdot 10^{-1}$
$1.25 \cdot 10^0$	$3.07 \cdot 10^0$	$1.52 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.84 \cdot 10^{-1}$
$1.3 \cdot 10^0$	$3.11 \cdot 10^0$	$2.1 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.76 \cdot 10^{-1}$
$1.35 \cdot 10^0$	$3.14 \cdot 10^0$	$2.78 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.68 \cdot 10^{-1}$
$1.4 \cdot 10^0$	$3.17 \cdot 10^0$	$3.52 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.59 \cdot 10^{-1}$
$1.45 \cdot 10^0$	$3.21 \cdot 10^0$	$4.32 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.53 \cdot 10^{-1}$
$1.5 \cdot 10^0$	$3.25 \cdot 10^0$	$5.22 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.46 \cdot 10^{-1}$
$1.55 \cdot 10^0$	$3.29 \cdot 10^0$	$6.13 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.39 \cdot 10^{-1}$
$1.6 \cdot 10^0$	$3.33 \cdot 10^0$	$7.24 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.32 \cdot 10^{-1}$
$1.65 \cdot 10^0$	$3.39 \cdot 10^0$	$8.21 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.24 \cdot 10^{-1}$
$1.7 \cdot 10^0$	$3.43 \cdot 10^0$	$9.28 \cdot 10^{-1}$	$0 \cdot 10^0$	$4.18 \cdot 10^{-1}$
$1.75 \cdot 10^0$	$3.48 \cdot 10^0$	$1.05 \cdot 10^0$	$0 \cdot 10^0$	$4.12 \cdot 10^{-1}$
$1.8 \cdot 10^0$	$3.53 \cdot 10^0$	$1.16 \cdot 10^0$	$0 \cdot 10^0$	$4.06 \cdot 10^{-1}$
$1.85 \cdot 10^0$	$3.59 \cdot 10^0$	$1.28 \cdot 10^0$	$0 \cdot 10^0$	$3.99 \cdot 10^{-1}$
$1.9 \cdot 10^0$	$3.64 \cdot 10^0$	$1.42 \cdot 10^0$	$0 \cdot 10^0$	$3.94 \cdot 10^{-1}$
$1.95 \cdot 10^0$	$3.7 \cdot 10^0$	$1.54 \cdot 10^0$	$0 \cdot 10^0$	$3.88 \cdot 10^{-1}$
$2 \cdot 10^0$	$3.75 \cdot 10^0$	$1.68 \cdot 10^0$	$0 \cdot 10^0$	$3.82 \cdot 10^{-1}$
$2.05 \cdot 10^0$	$3.81 \cdot 10^0$	$1.83 \cdot 10^0$	$0 \cdot 10^0$	$3.77 \cdot 10^{-1}$
$2.1 \cdot 10^0$	$3.86 \cdot 10^0$	$1.99 \cdot 10^0$	$0 \cdot 10^0$	$3.72 \cdot 10^{-1}$
$2.15 \cdot 10^0$	$3.92 \cdot 10^0$	$2.11 \cdot 10^0$	$0 \cdot 10^0$	$3.67 \cdot 10^{-1}$
$2.2 \cdot 10^0$	$3.98 \cdot 10^0$	$2.3 \cdot 10^0$	$0 \cdot 10^0$	$3.61 \cdot 10^{-1}$