

Project 2

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Chapter 1

Introduction

Chapter 2

Theory

We consider a system of electrons situated in an isotropic harmonic oscillator potential. We will use Hartree's atomic units¹ in order to get the idealized Hamiltonian presented below:

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 |\mathbf{r}_i|^2 \right) + \sum_{i<j} \frac{1}{r_{ij}}. \quad (2.1)$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two electrons. The first term of the hamiltonian is a simple harmonic oscillator potential affecting a single particle. Because electrons repel each other, we also get a repulsive term as part of the Hamiltonian - the so-called perturbation of the system.

2.1 Wavefunction

The two-dimensional solution for a single particle in a harmonic oscillator potential (consider equation (2.1) for a single particle) is the following wave function:

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

where H_i are Hermite polynomials (see A.1), and A is the normalization constant. For the lowest lying state, we have $n_x = n_y = 0$ and hence the energy $\epsilon_{n_x, n_y} = \omega(n_x + n_y + 1) = \omega$. For the closed shell configurations, $N = 2, 6, 12$ and 20 the exact ground state energy is given in Table 1.

¹ $\hbar = c = e = m_e = 1$, see [1].

N	E (a.u)
2	2ω
6	10ω
12	28ω
20	60ω

Table 1: Given exact ground state energy (a.u) (without perturbation) for closed-shell number of electrons. ω is the oscillator frequency.

The total wave function for a non-interacting two-electron system is therefore given as:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = C \exp \left[-\frac{\omega}{2} (|\mathbf{r}_1|^2 + |\mathbf{r}_2|^2) \right],$$

with an energy of 2ω . The total spin in the ground state is simply zero as the two electrons living in the state is paired with opposite spins (eg. $\pm 1/2$).

The ground state energy is given by the unperturbed system. Adding a perturbation/interaction will rise the energy. For the simplest system with two electrons, this perturbation can be found through perturbation theory, whilst for a higher number of particles, other measurements or actions must be taken to find the energy(?).

2.2 Local energy

By definition, the local energy is given by

$$E_l = \frac{1}{\Psi_T} \hat{H} \Psi_T$$

Ψ_T is the trial wavefunction of the system. The Hamiltonian is given by equation (2.1) and the trial wavefunction is

$$\Psi_T(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1 * \Psi_2 = C \exp(-\alpha\omega(r_1^2 + r_2^2)/2) \exp\left(\frac{ar_{12}}{1 + \beta r_{12}}\right)$$

Where $a = 1$ when the two electrons in question have anti-parallel spins and $a = 1/3$ when the spins are parallel. α, β are the variational parameters.

Hence, the local energy is shown to be (see appendix)

$$E_L = 2\alpha\omega + \frac{1}{2} + \omega^2(1 - \alpha^2)(r_1^2 + r_2^2) - \frac{a}{(1 + \beta r_{12})^2} \left(-\alpha\omega r_{12} + \frac{a}{(1 + \beta r_{12})^2} + \frac{1 - \beta r_{12}}{r_{12}(1 + \beta r_{12})} \right) + \frac{1}{r_{12}}. \quad (2.2)$$

Equation (2.2) is our analytic expression for the local energy of the two electron system.

The numerical local (kinetic) energy is calculated using the derivative of the velocity utilizing the two point approximation of the first derivative

$$\frac{dg(x)}{dx} \approx \frac{g(x + \Delta x) - g(x - \Delta x)}{2\Delta x}$$

Second derivative by three point approximation

$$\frac{d^2g(x)}{dx^2} \approx \frac{g(x + \Delta x) - 2g(x) + g(x - \Delta x)}{\Delta x^2}$$

Δx is the stepsize which we let run towards zero. The error is proportional to (Δx^2) .

Chapter 3

Method

3.1 Testing

Testing in Rust is normally divided in two categories: *unit tests* and *integration tests*. Unit tests are small codes to test specific functions inside the code. These tests are normally written in the same file as the functions themselves, but inside a module annotated with `cfg(test)`.

On the other hand, integration tests are written externally to the library, and is made to test the integration of the functions in the program. These tests are often much larger than unit tests, and are made to make sure that the internal functions work well with each other, from the standpoint of an external user. Therefore, integration tests are normally written in a separate `tests` directory at the same level as the `src` directory.

We will write mainly unit tests in our program, to ensure that our functions return the expected values, and to reduce the mental overhead of debugging when making larger changes to the codebase.

More on testing can be found in the official documentation of the Rust programming language [2].

3.2 Parallelization

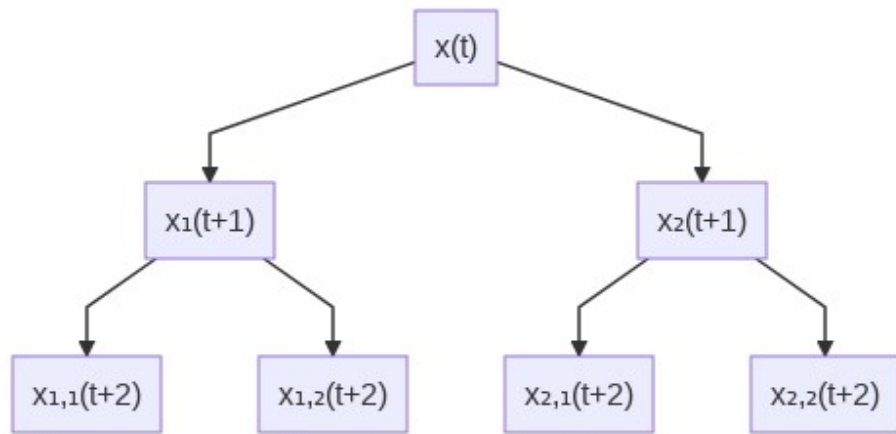


Figure 3.1: Temporary diagram for visualization

Chapter 4

Results

Chapter 5

Discussion

Chapter 6

Conclusion

Appendix A

Appendix

A.1 Hermite polynomials

The Hermite polynomials are given by the following sequence

$$H_n(x) = c_{n+m}x^n + c_{n-1+m}x^{n-1} \dots + c_mx^0, \quad m = \sum_{i=1}^n i$$

where the coefficients c_n are given by the triangle sequence shown below [3]:

$$c_i = 1, 0, 2, -2, 0, 4, 0, -12, 0, 8, 12, 0, -48, \dots$$

A.2 Analytical Laplace of the Trial wavefunction

The trial wavefunction of a two-particle system is

$$\Psi_T(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1 * \Psi_2 = C \exp(-\alpha\omega(r_1^2 + r_2^2)/2) \exp\left(\frac{ar_{12}}{1 + \beta r_{12}}\right)$$

as defined in theory section {2.2}.

The Laplacian is the double derivative in all dimensions, defined as:

$$\Delta f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

The calculations:

Calculate all the shit

boop

References

- [1] D. R. Hartree, “The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods,” *Mathematical Proceedings of the Cambridge Philosophical Society*, vol. 24, no. 1, pp. 89–110, Jan. 1928, doi: 10.1017/S0305004100011919.
- [2] Rust-Docs, “Test organization,” 2021. <https://doc.rust-lang.org/book/ch11-03-test-organization.html> (accessed Apr. 27, 2021).
- [3] V. Jovovic, “A060821 - triangle $t(n,k)$ read by rows giving coefficients of hermite polynomial of order n ($n \geq 0$, $0 \leq k \leq n$).” *The On-Line Encyclopedia of Integer Sequences*. Apr. 2001, Accessed: Apr. 27, 2021. [Online]. Available: <https://oeis.org/A060821>.