

FYS4411 - Computational Physics II: Quantum Mechanical Systems

Project 1

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<https://www.github.com/Oo1Insane1oO/FYS4411>

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Abstract

In this project we have used Hartree-Fock theory to estimate single particle energies in a quantum-dot system using a harmonic oscillator (in two dimensions) as basis and analyzed the convergence rate for the Hartree-Fock method. The convergence was seemingly good for most parameters, however some was seen to converge quite slowly. The Hartree-Fock limit was not reached for all calculations where the oscillator frequency was low. The degeneracies were not preserved. Tables of calculated ground state energies are given.

I INTRODUCTION

In this project we will look at properties of confined interacting systems of electrons in 2 dimension, called quantum dots. The systems will be closed shell systems. The main basis used will be the harmonic oscillator(in two dimensions) and the method to be examined is the Hartree-Fock method. We use the Hartree-Fock method to modify the harmonic oscillator potential to account for the Coulomb interaction between the electrons.

Motivation for using Hartree-Fock theory is the desire to find the ground state energy for a given Hamiltonian. Hartree-Fock methods gives an estimation for this energy. The method also introduces a so-called Hartree-Fock potential(in reality just an operator) which can be thought of as introducing an explicit medium dependence for the two-body interaction between the fermions. This effectively creates a mean field in which the fermions move, meaning no apparent external potential is present in the calculations. Therefore Hartree-Fock theory does not care about external one-body potentials which would be present in a non-approximate nuclear system, making it possible to find an expression for the expectation value of the Hamiltonian(as will be shown).

II THEORY

II.A HERMITE POLYNOMIALS

Hermite polynomials $H(x)$ are solutions to the differential equation

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

The polynomials fulfill the orthogonality relation

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

with the recurrence relation

$$H_{n+1} = H_n - 2nH_{n-1} \quad (3)$$

II.B ASSOCIATED LAGUERRE POLYNOMIALS

The associated Laguerre polynomials are solutions to the differential equation

$$x \frac{d^2L}{dx^2} + (\alpha + 1 - x) \frac{dL}{dx} + nL = 0 \quad (4)$$

with α and n being real numbers.

The polynomials are orthogonal with respect to the inner product and follow the recurrence relation

$$L_{k+1}^{(\alpha)} = \frac{(2k+1+\alpha-x)L_k^{(\alpha)} - (k+\alpha)L_{k-1}^{(\alpha)}}{k+1} \quad (5)$$

II.C HARMONIC OSCILLATOR

II.C.1 Cartesian Coordinates

The harmonic oscillator system in 2 dimensions and in natural units is given by the following Hamiltonian

$$\hat{H}_0 = \frac{1}{2} \sum_{i=1}^N (-\nabla_i^2 + \omega^2 r_i^2) \quad (6)$$

The wave functions in this case is then:

$$\phi_{n_x, n_y}(x, y) = A H_{n_x}(\sqrt{\omega}x) H_{n_y}(\sqrt{\omega}y) e^{-\frac{\omega}{2}(x^2+y^2)} \quad (7)$$

where H_n is a hermite polynomial of order n and A is a normalization constant. The quantum numbers n_x and n_y go as $n_x, n_y = 0, 1, 2, \dots$. While ω is the oscillator frequency.

The energies is

$$E = \hbar\omega(n_x + n_y + 1) \quad (8)$$

II.C.2 Polar Coordinates

In order to change to polar coordinates (r, θ) we introduce the usual transformations for Cartesian

$$\begin{aligned} x &= r \cos \theta \\ y &= r \sin \theta \\ r &= \sqrt{x^2 + y^2} \end{aligned} \quad (9)$$

Introducing a separable solution in the radial and angular coordinates as an ansatz ($\psi(r, \theta) = R(r)Y(\theta)$) gives

$$\begin{aligned} R_{nm}(r) &= \sqrt{\frac{2n!}{(n+|m|)!}} \left(\frac{m_q \omega}{\hbar}\right)^{\frac{1}{2}(|m|+1)} r^{|m|} e^{-\frac{m_q \omega}{2\hbar} r^2} L_n^{|m|} \left(\frac{m_q \omega}{\hbar} r^2\right) \quad n = 0, 1, 2, \dots \\ Y_m(\theta) &= \frac{1}{\sqrt{2\pi}} e^{im\theta} \quad m = 0, \pm 1, \pm 2, \dots \end{aligned} \quad (10)$$

where m_q is the particle mass, $L_n^{|m|}$ is the associated Laguerre polynomials.

The eigenfunction is thus

$$\psi_{nm}(r, \theta) = \sqrt{\frac{n!}{\pi(n+|m|)!}} \left(\frac{m_q \omega}{\hbar}\right)^{\frac{1}{2}(|m|+1)} r^{|m|} e^{-\frac{m_q \omega}{2\hbar} r^2} L_n^{|m|} \left(\frac{m_q \omega}{\hbar} r^2\right) e^{im\theta} \quad (11)$$

with eigenenergies

$$E = \hbar\omega(2n + |m| + 1) \quad (12)$$

II.D LAGRANGE MULTIPLIERS

See [3, 4]. The optimization method of Lagrange multipliers maximizes(or minimizes) a function $f : \mathbb{R}^N \rightarrow \mathbb{R}$ with a constraint $g : \mathbb{R}^N \rightarrow \mathbb{R}$. We assume that f and g have continuous first derivatives in all variables(continuous first partial derivatives).

Given the above we can define a so-called Lagrangian \mathcal{L}

$$\mathcal{L}[x_1, \dots, x_N, \lambda_1, \dots, \lambda_M] = f(x_1, \dots, x_N) - \lambda g(x_1, \dots, x_N) \quad (13)$$

where the λ is called a Lagrange-multiplier. We now state that if $f(x_1^0, \dots, x_N^0)$ is a maxima of $f(x_1, \dots, x_N)$ then there exists a Lagrange-multiplier λ_0 such that $(x_1^0, \dots, x_N^0, \lambda_0)$ is a stationary point for the Lagrangian. This then yields the $N + 1$ Lagrange-equations

$$\sum_{i=1}^N \frac{\partial \mathcal{L}}{\partial x_i} + \frac{\partial \mathcal{L}}{\partial \lambda} = 0 \quad (14)$$

to be solved for x_1, \dots, x_N and λ .

II.E LEIBNIZ FORMULA

See[5]. Given a square $N \times N$ matrix M with elements m_{ij} being the entry of i 'th row and j 'th column of M . The Leibniz formula states that the determinant of M is

$$\det(M) = \sum_{\sigma \in S_n} \text{sgn}(\sigma) \prod_{j=1}^N m_{\sigma(j), j} \quad (15)$$

where S_n is $+1$ for even permutations and -1 for odd.

Defining the n -fold Levi-Civita symbol $\varepsilon_{\{i_N\}}$ (gives $+1$ for even permutations and -1 for odd and 0 if no permutation exists) with $\{i_N\}$ being the row(or column) indices of M , we may rewrite Leibniz formula as

$$\det\{M\} = \sum_{i \in \{i_N\}} \varepsilon_{\{i_N\}} \prod_{j=1}^N m_{ji_j} \quad (16)$$

II.F DETERMINANT OF UNITARY MATRICES

Assume we have a square unitary matrix U of size N meaning

$$U^\dagger = U^{-1} \Leftrightarrow U^\dagger U = I \quad (17)$$

According to the spectral theorem[1], matrix U can be decomposed as

$$U = V D V^{-1} = V D V^\dagger \quad (18)$$

where V is a unitary matrix and D is a diagonal unitary matrix, both of size N . Taking the determinant of equation 18 gives

$$\begin{aligned} \det\{U\} &= \det\{V D V^{-1}\} \\ &= \det\{V\} \det\{D\} \det\{V^{-1}\} \\ &= \det\{V V^{-1}\} \det\{D\} \\ &= \det\{I\} \det\{D\} \\ \det\{U\} &= \det\{D\} \end{aligned} \quad (19)$$

where we have used that $\det\{AB\} = \det\{A\} \det\{B\}$ and the fact that V is unitary. Since D is unitary we have

$$D D^\dagger = \mathbb{1} \Rightarrow D^2 = \mathbb{1} \Rightarrow D = \text{diag}(e^{i\theta}, e^{i\theta}, \dots, e^{i\theta}) \quad (20)$$

that is the elements along the diagonal of D are all equal to a complex number of absolute value 1. The determinant of U is thus

$$\det\{U\} = \prod_{k=1}^N d_{kk} = e^{i\theta N} \quad (21)$$

this new complex number also has absolute value unity

$$|e^{i\theta N}| = e^{i\theta N} e^{-i\theta N} = e^0 = 1 \quad (22)$$

II.G HARTREE-FOCK THEORY

With Hartree-Fock theory one tries to find an estimation for the single particle energy, that is solving Schrödinger's equation for the many-body Hamiltonian given by the Born-Oppenheimer approximation for N electrons and assuming the wave-function is given by a single Slater determinant.

II.G.1 Energy Functional

In order to find the Hartree-Fock equations we first need an expression for energy functional (which will be minimized). The variational principle gives us the following restriction on the ground state energy

$$E_0 \leq E[\phi] = \int \phi^* \hat{H} \phi d\tau = \langle \phi | \hat{H} | \phi \rangle \quad (23)$$

here τ is a short-hand notation for the N -dimensional differentials dr_1, \dots, dr_N , ϕ is a normalized trial wave-function and \hat{H} is the Hamiltonian defined as

$$\hat{H} = \hat{H}_0 + \hat{H}_I \quad (24)$$

where \hat{H}_0 is a Hamiltonian with some known solution (i.e. harmonic oscillator) and \hat{H}_I is the Hamiltonian describing particle interactions (i.e. Coulomb interaction). We also assume that the interaction Hamiltonian only depends on the relative particle distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$.

Introducing a permutation operator \hat{P} (interchange two particles) we can define an antisymmetrization operator \hat{A}

$$\hat{A} = \frac{1}{N!} \sum_p (-1)^p \hat{P} \quad (25)$$

Since \hat{H} is invariant under permutations, \hat{H} and \hat{A} commute. We also observe that $\hat{A}^2 = \hat{A}$ since permutations of the Slater determinant (applying \hat{A} twice to a state) reproduces \hat{A} again.

The wave-function ansatz can be expressed in terms of a linear combination

$$\psi_\mu = \sum_j C_{j\mu} \phi_j(r_\mu) \quad (26)$$

We now have that the single Slater determinant for the wave-function ϕ can be rewritten as

$$\phi(\vec{r}_1, \dots, \vec{r}_N, \alpha_1, \dots, \alpha_M) = \sqrt{N!} \hat{A} \prod_{i,\rho} \psi_{\alpha_\rho}(\vec{r}_i) \quad (27)$$

where the α 's are all the quantum numbers needed to describe the wave function. The expectation value for H_0 is now with the rewritten function, equation 27

$$\langle \phi | \hat{H}_0 | \phi \rangle = N! \prod_{i,\rho} \langle \psi_{\alpha_\rho}(\vec{r}_i) | \hat{H}_0 | \psi_{\alpha_\rho}(\vec{r}_i) \rangle \quad (28)$$

We replace \hat{H}_0 by the sum of the one-body operator \hat{h}_0 and use the fact that the single-particle wave-functions ψ_μ are orthogonal to end up with.

$$\langle \phi | \hat{H}_0 | \phi \rangle = \sum_{\mu=1}^N \langle \psi_\mu(\vec{r}) | \hat{h}_0 | \psi_\mu(\vec{r}) \rangle = \sum_{\mu=1}^N \langle \mu | \hat{h}_0 | \mu \rangle \quad (29)$$

For the interaction part we have a similar derivation as with \hat{H}_0 .

$$\langle \phi | \hat{H}_I | \phi \rangle = N! \prod_{i,\rho} \langle \psi_{\alpha_\rho}(\vec{r}_i) | \hat{A} \hat{H}_I \hat{A} | \psi_{\alpha_\rho}(\vec{r}_i) \rangle \quad (30)$$

The interaction Hamiltonian H_I and the antisymmetrization operator \hat{A} commute (since \hat{A} commutes with $\hat{H} = \hat{H}_0 + \hat{H}_I$) giving

$$\hat{A} \hat{H}_I \hat{A} = \frac{1}{N!^2} \sum_{i < j} (-1)^{2p} V(r_{ij}) \hat{P} = \frac{1}{N!^2} \sum_{i < j} V(r_{ij}) (1 - P_{ij}) \quad (31)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and P_{ij} switches particle i and j . The jump to $1 - P_{ij}$ comes from the fact that we only permute once, all other contributions from applying \hat{P} vanishes due to orthogonality between the ψ 's. The expectation value is thus

$$\langle \phi | \hat{H}_I | \phi \rangle = \sum_{i < j} \prod_{k,\rho} \langle \psi_{\alpha_\rho}(\vec{r}_k) | V(r_{ij}) (1 - P_{ij}) | \psi_{\alpha_\rho}(\vec{r}_k) \rangle \quad (32)$$

Changing summations indices to μ and ν and writing out equation 32 we get

$$\begin{aligned} \langle \phi | \hat{H}_I | \phi \rangle &= \sum_{i < j} \prod_{k,\rho} [\langle \psi_{\alpha_\rho}(\vec{r}_k) | V(r_{ij}) | \psi_{\alpha_\rho}(\vec{r}_k) \rangle - \langle \psi_{\alpha_\rho}(\vec{r}_k) | V(r_{ij}) | \psi_{\alpha_k}(\vec{r}_\rho) \rangle] \\ \langle \phi | \hat{H}_I | \phi \rangle &= \frac{1}{2} \sum_{\mu, \nu} [\langle \mu \nu | \hat{v} | \mu \nu \rangle - \langle \mu \nu | \hat{v} | \nu \mu \rangle] \end{aligned} \quad (33)$$

with $\hat{v} = V(r_{ij})$. The factor 1/2 is due to double summations over pairs of states. Defining the antisymmetric matrix element (for a general element (p, q, r, s))

$$\langle pq | \hat{v} | rs \rangle_{AS} = \langle pq | \hat{v} | rs \rangle - \langle pq | \hat{v} | sr \rangle \quad (34)$$

the expectation value is

$$\langle \phi | \hat{H}_I | \phi \rangle = \frac{1}{2} \sum_{\mu, \nu} \langle \mu \nu | \hat{v} | \mu \nu \rangle_{AS} \quad (35)$$

and thus the energy functional is finally

$$E[\phi] = \sum_{\mu} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu \nu} \langle \mu \nu | \hat{v} | \mu \nu \rangle_{AS} \quad (36)$$

II.G.2 Hartree-Fock Equations

We start by expanding the Hartree-Fock wave-function as a linear combination of some known orthonormal basis $\Phi = \{\phi_\lambda(\vec{r})\}$.

$$\psi_p^{\text{HF}} = \sum_{\lambda} C_{p\lambda} \phi_\lambda(\vec{r}) \quad (37)$$

The expanded basis is also orthonormal since we have, due to the orthonormality of the ϕ_λ 's, that

$$\langle \psi_p^{\text{HF}} | \psi_q^{\text{HF}} \rangle = \sum_{\lambda \mu} C_{p\lambda}^* C_{q\mu} \langle \phi_\lambda | \phi_\mu \rangle = 0 \quad (38)$$

Writing the total wave function Ψ^{HF} as a Slater determinant

$$\Psi^{\text{HF}}(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \sum_{\lambda} C_{1\lambda} \phi_{\lambda}(r_1) & \sum_{\lambda} C_{1\lambda} \phi_{\lambda}(r_2) & \cdots & \cdots & \sum_{\lambda} C_{1\lambda} \phi_{\lambda}(r_N) \\ \sum_{\lambda} C_{2\lambda} \phi_{\lambda}(r_1) & \sum_{\lambda} C_{2\lambda} \phi_{\lambda}(r_2) & \cdots & \cdots & \sum_{\lambda} C_{2\lambda} \phi_{\lambda}(r_N) \\ \vdots & \vdots & \cdots & \cdots & \vdots \\ \sum_{\lambda} C_{N\lambda} \phi_{\lambda}(r_1) & \sum_{\lambda} C_{N\lambda} \phi_{\lambda}(r_2) & \cdots & \cdots & \sum_{\lambda} C_{N\lambda} \phi_{\lambda}(r_N) \end{vmatrix}$$

$$\Psi^{\text{HF}}(\vec{r}) = \frac{1}{\sqrt{N!}} \det(\hat{C}) \det(\Phi) \quad (39)$$

with \hat{C} being the collective coefficients matrix and $\det(\Phi)$ being the determinant given by $\phi_{\lambda}(r)$. The latter equality is better seen if we rewrite Ψ^{HF} with Leibniz formula (equation 15)

$$\begin{aligned} \Psi^{\text{HF}}(\vec{r}) &= \frac{1}{\sqrt{A!}} \sum_{\{i_N\}} \varepsilon_{\{i_N\}} \prod_{j=1}^A \sum_{\lambda} C_{i_j \lambda} \phi_{\lambda}(r_{i_j}) \\ &= \frac{1}{\sqrt{A!}} \left(\sum_{\{i_N\}} \varepsilon_{\{i_N\}} \prod_{j=1}^A \sum_{\lambda} C_{i_j \lambda} \right) \left(\sum_{\{i_N\}} \varepsilon_{\{i_N\}} \prod_{j=1}^A \phi_{\lambda}(r_{i_j}) \right) \\ &= \frac{1}{\sqrt{A!}} \det(\hat{C}) \det(\Phi) \end{aligned} \quad (40)$$

where we applied Leibniz formula again in the last equality. We can see that the new Slater determinants only differ by a complex constant since \hat{C} is unitary. The determinant of unitary matrices are always equal to a complex number $e^{i\theta}$ whose absolute value is 1. See section II.F.

Inserting the new basis functions into the expression for the energy functional, equation 36 and using i, j, k, l as indices for states below the Fermi level and $\alpha, \beta, \gamma, \delta$ as all possible single particle states (including the ones below Fermi level) we get.

$$E[\Psi^{\text{HF}}] = \sum_{i\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \quad (41)$$

Introducing the Lagrange multiplier and minimizing according to Lagrange multiplier method described in section II.D and noticing that $\langle \alpha | \beta \rangle = \delta_{\alpha\beta}$ (where $\delta_{\alpha\beta}$ is the Kronecker-delta) we get the constraints

$$\langle p | q \rangle = \sum_{\alpha} C_{p\alpha}^* C_{q\alpha} \quad (42)$$

and the functional to be minimized reads

$$\mathcal{L}[\Psi^{\text{HF}}] = E[\Psi^{\text{HF}}] - \sum_{i\alpha} \varepsilon_i C_{i\alpha}^* C_{i\alpha} \quad (43)$$

where ε_i is the Lagrange multiplier (of units energy).

Minimizing with respect to $C_{p\alpha}^*$ we obtain the Euler-Lagrange equations

$$\frac{\partial}{\partial C_{p\alpha}^*} \left[E[\Psi^{\text{HF}}] - \sum_{j\alpha} \varepsilon_j C_{j\alpha}^* C_{j\alpha} \right] = \frac{\partial \mathcal{L}}{\partial \varepsilon_p} \quad (44)$$

Since the constraints are all leveled functions, that is the functions only scale the energy functional $E[\Psi^{\text{HF}}]$, we can effectively ignore the equation regarding the Lagrange multiplier ε_p meaning the Lagrange equations reduces to

$$\frac{\partial}{\partial C_{p\alpha}^*} \left[E[\Psi^{\text{HF}}] - \sum_{j\alpha} \varepsilon_j C_{j\alpha}^* C_{j\alpha} \right] = 0 \quad (45)$$

We solve the individual parts starting with the functional $E[\Psi^{\text{HF}}]$

$$\begin{aligned} \frac{\partial}{\partial C_{p\alpha}^*} \left[\sum_{i\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \right] &= \sum_{\beta} C_{p\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \\ \frac{\partial}{\partial C_{p\alpha}^*} \left[\frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \right] &= \sum_{ij\beta\gamma\delta} C_{p\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \end{aligned} \quad (46)$$

The latter derivation uses the product-rule giving

$$\frac{\partial}{\partial C_{p\alpha}^*} \left[\sum_{ij\alpha\beta} C_{i\alpha}^* C_{j\beta}^* \right] = \delta_{jp} \delta_{ip} \delta_{\alpha\beta} \sum_{ij\alpha\beta} (C_{p\beta}^* + C_{p\alpha}^*) = 2 \sum_{\beta} C_{p\beta}^* \quad (47)$$

The second term in equation 45 is

$$\frac{\partial}{\partial C_{p\alpha}^*} \left[- \sum_{j\alpha} \varepsilon_j C_{j\alpha}^* C_{j\alpha} \right] = -\varepsilon_p C_{p\alpha} \quad (48)$$

Gathering equation 46 and equation 48 yields in the Hartree-Fock equations

$$\sum_{\beta} C_{p\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_{j\beta\gamma\delta} C_{j\beta}^* C_{j\delta} C_{p\gamma} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} = \varepsilon_p^{\text{HF}} C_{p\alpha} \quad (49)$$

Rewriting by pulling the β sum out and defining the Hartree-Fock matrix element

$$h_{\alpha\beta}^{\text{HF}} \equiv \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_{j\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \quad (50)$$

we get the equation

$$\sum_{\gamma} h_{\alpha\beta}^{\text{HF}} C_{p\beta} = \varepsilon_p^{\text{HF}} C_{p\alpha} \quad (51)$$

Assuming $|\beta\rangle$ forms an eigenbasis for \hat{h}_0 we can set $\langle \alpha | \hat{h}_0 | \beta \rangle = \varepsilon_{\alpha} \delta_{\alpha\beta}$ giving

$$h_{\alpha\beta}^{\text{HF}} = \varepsilon_{\alpha} \delta_{\alpha\beta} + \sum_{j\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \quad (52)$$

Giving the eigenvalue problem

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{p\beta} = \varepsilon_p^{\text{HF}} C_{p\alpha} \quad (53)$$

where the C 's are the orthogonal eigenvectors of h^{HF} and $\varepsilon_p^{\text{HF}}$ are the eigenvalues that represent the single-particle energies.

The task is then to solve the above equation iteratively until the single-particle energies $\varepsilon_p^{\text{HF}}$ have reached a predefined convergence criteria.

II.G.3 Convergence Criteria

The convergence criteria for the iterative process involved in the eigenvalue problem, equation 53 is usually given by a simple brute-force difference criteria

$$\frac{1}{N} \sum_i \left| \varepsilon_i^{\text{HF,new}} - \varepsilon_i^{\text{HF,old}} \right| \leq \lambda \quad (54)$$

with λ being a small positive number.

II.G.4 Rewrite Ground State Energy

We may rewrite the ground state energy by adding and subtracting $\hat{U}^{\text{HF}} = \sum_{\mu\nu} \langle \mu | \hat{u}^{\text{HF}} | \nu \rangle$, that is adding and subtracting the so-called Hartree-Fock potential

$$E[\Psi^{\text{HF}}] = \sum_{i\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \hat{U}^{\text{HF}} + \frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{u}^{\text{HF}} | \gamma\delta \rangle_{AS} - \hat{U}^{\text{HF}} \quad (55)$$

with

$$\hat{u}^{\text{HF}} |pq\rangle = \sum_{pq} (\langle pq | \hat{v} | pq \rangle - \langle pq | \hat{v} | qp \rangle) |pq\rangle = \sum_{pq} \langle pq | \hat{v} | pq \rangle_{AS} |pq\rangle \quad (56)$$

We start by reducing the first two terms in equation 55 giving

$$\begin{aligned} \sum_{i\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \hat{U}^{\text{HF}} &= \sum_{i\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 + \hat{u}^{\text{HF}} | \beta \rangle \\ &= \sum_i \varepsilon_i^{\text{HF}} \end{aligned} \quad (57)$$

and the latter two yield

$$\frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} - \hat{U}^{\text{HF}} = -\frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{i\gamma} C_{j\beta}^* C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \quad (58)$$

where we used equation 56.

The ground state energy estimation is thus by gathering equations 57 and 58

$$E_0^{\text{HF}} = \sum_i \varepsilon_i^{\text{HF}} - \frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \quad (59)$$

II.G.5 Density Matrix

The coefficients (the C 's) involved in the Hartree-Fock equations and the equation for the energy can be rewritten by defining a density matrix ρ . The elements are defined as

$$\rho_{\gamma\delta} \equiv \sum_i C_{i\gamma}^* C_{i\delta} \quad (60)$$

the Hartree-Fock matrix element given in equation 50 is thus

$$h_{\alpha\beta}^{\text{HF}} = \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_{\gamma\delta} \rho_{\gamma\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \quad (61)$$

and the ground state energy given in equation 59 is

$$E_0^{\text{HF}} = \sum_i \varepsilon_i^{\text{HF}} - \frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} \rho_{\alpha\gamma} \rho_{\beta\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \quad (62)$$

The density matrix is useful since one can pre-calculate it in every iteration of the Hartree-Fock algorithm, see section II.G.6.

II.G.6 Hartree-Fock Algorithm

Using the results gained from section II.G, the Hartree-Fock algorithm is as follows

Algorithm 1 Hartree-Fock algorithm

- | | |
|---|--|
| 1: assemble interaction elements | ▷ $\langle pq \hat{v} rs \rangle_{AS}$ |
| 2: Set density matrix | ▷ Use equation 60 |
| 3: while count < maxiteration & difference > λ do | |
| 4: Calculate Hartree-Fock matrix | ▷ As given in equation 61 |
| 5: Find eigenvalues and eigenvectors of Hartree-Fock matrix | ▷ These are the energies and coefficients |
| 6: Calculate new density matrix | |
| 7: Calculate difference | ▷ Given in equation 54 |
| 8: increment count | |
| 9: end while | |
| 10: Calculate ground state energy | ▷ With equation 62 |
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III SETUP

See <https://www.github.com/Oo1Insane1oO/FYS4411> for C++ program for the Hartree-Fock algorithm.

The program sets up a basis in Cartesian coordinates (see class basis.cpp) and converts the quantum numbers when assembling the interaction matrix elements and running the Hartree-Fock algorithm.

Most methods used are given in class Methods(methods.cpp). Only one is used for the Hartree-Fock calculations is the Kronecker-delta delta function, kronk.

List of files

- basis.cpp: Sets up the basis as mentioned, assembles the interaction matrix and runs the Hartree-Fock algorithm.
- methods.cpp: Contains specific functions for different methods.
- tests.cpp: Module for unit tests.
- main.cpp: Main program.

As mentioned the calculations sets up the interaction matrix before running the Hartree-Fock loop. This is done with a dictionary data-structure (hash-table) where the key is a pair of (M, M_s) that is the conserved quntum numbers and the value is a vector of matrix elements for the possible (p, q, r, s) . To extract the values we have another hash-table with the keys being an array of size 4 with the pair (p, q, r, s) and the value being the index in the mentioned vector. In essence the structure is build using the following function

Algorithm 2 Function assemble(run)

```

1: integralmap := map<array<int,4>, int> >                                ▷ Mapping hash with indices
2: sizes := map<array<int,2>, int> >                                       ▷ Hash containing sizes
3: for p=0 to states.size do
4:   for q=p to states.size do
5:     for r=0 to states.size do
6:       for s=r states.size do
7:          $M = m_p + m_q$                                                     ▷ Quantum number conservation
8:          $S = \sigma_p + \sigma_q$ 
9:         if  $M = m_r + m_s$  &  $S = \sigma_r + \sigma_s$  then
10:          if run=first then                                              ▷ Find sizes of vectors
11:            pqrsSize = sizes[(M,S)]
12:            pqsrSize = sizes[(M,S)] + 1
13:            integralmap.insert((p,q,r,s), pqrsSize)                    ▷ Set keys and values in map hash
14:            integralmap.insert((p,q,s,r), pqsrSize)
15:            integralmap.insert((q,p,s,r), pqrsSize)
16:            integralmap.insert((q,p,r,s), pqsrSize)
17:            sizes[(M,S)] += 2                                           ▷ Increment sizes
18:          else if run=second then
19:            interactionMatrix[(M,S)] . setsize(sizes[(M,S)])           ▷ Set size of interaction matrix
20:          else
21:            temporary =  $F(p, q, r, s)$                                     ▷ Function  $F$  finding element
22:            interactionMatrix[(M,S)] [integralmap(p,q,r,s)] = tmp      ▷ Set value
23:            interactionMatrix[(M,S)] [integralmap(p,q,s,r)] = -tmp      ▷ Set symmetric value
24:          end if
25:        end if
26:      end for
27:    end for
28:  end for
29: end for
30: if run=first then
31:   assemble(run=second)                                                 ▷ Call assemble for setting sizes
32: else if run=second then
33:   assemble(run=third)                                                 ▷ Calls assemble for calculating elements
34: else
35:   return
36: end if

```

This gives a memory efficient mapping by only saving non-zero matrix elements. The only con of using this data structure is the overhead introduced in the look-up time (a binary search of complexity $\mathcal{O}(\log(N))$) when extracting the elements.

Notice also that in algorithm 2 we do not calculate the symmetric elements (q, p, s, r) as they just point to (p, q, r, s) in the mapping hash.

The Hartree-Fock calculations use the definition based on the density matrix described in equation 61 and lastly calculates the energy using equation 62.

IV RESULTS

The program was run for $N = 2, 6, 12, 20$ electrons using 5–11 single particle orbitals and $\lambda = 10^{-10}$ as the convergence criterion(as explained in equation 54). The results are given in tables 1, 2, 3, 4, 5 and 6 below,

Energies with $\omega = 0.1$

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	0.52567	16	5	3.96315	21	5	14.05499	620	5	38.03121	18
6	0.52567	16	6	3.87062	28	6	3.42603	51	6	19.60586	32
7	0.52564	16	7	3.86314	30	7	2.02661	43	7	8.89723	60
8	0.52564	16	8	3.85288	32	8	1.73187	46	8	3.50147	53
9	0.52564	16	9	3.85259	32	9	1.84503	47	9	1.07254	63
10	0.52564	16	10	3.85239	32	10	1.97213	64	10	0.22356	71
11	0.52564	16	11	3.85239	32	11	2.01583	75	11	0.12611	66

Table 1: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .**Energies with $\omega = 0.2$**

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	0.88233	14	5	6.38235	19	5	22.04898	19	5	58.16924	17
6	0.88233	14	6	6.29937	26	6	21.41041	480	6	54.70488	19
7	0.88221	14	7	6.29648	27	7	6.60408	67	7	18.68379	65
8	0.88221	14	8	6.29356	27	8	6.56846	74	8	12.03922	52
9	0.88229	14	9	6.29356	27	9	6.73862	80	9	9.61748	58
10	0.88229	14	10	6.29354	27	10	6.80551	83	10	9.11494	60
11	0.88229	14	11	6.29354	27	11	6.81341	84	11	9.31710	90

Table 2: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .**Energies with $\omega = 0.3$**

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	1.20438	13	5	8.50506	19	5	28.91335	48	5	75.28015	17
6	1.20438	13	6	8.43321	24	6	28.36114	516	6	71.02941	19
7	1.20436	13	7	8.43215	24	7	11.52061	96	7	28.69881	66
8	1.20436	13	8	8.43146	24	8	11.62498	123	8	21.38629	42
9	1.20435	13	9	8.43144	24	9	11.77318	108	9	19.08132	62
10	1.20435	13	10	8.43140	24	10	11.80681	106	10	18.87573	92
11	1.20435	13	11	8.43140	24	11	11.80842	110	11	19.18601	110

Table 3: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .**Energies with $\omega = 0.4$**

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	1.50802	13	5	10.46763	19	5	35.19951	17	5	90.79899	18
6	1.50802	13	6	10.40572	23	6	34.71792	154	6	85.87241	19
7	1.50802	13	7	10.40529	23	7	34.30442	229	7	38.84908	75
8	1.50802	12	8	10.40522	22	8	17.58746	186	8	31.12996	60
9	1.50801	12	9	10.40511	22	9	16.89789	161	9	29.00048	81
10	1.50801	12	10	10.40517	22	10	16.91580	153	10	29.02411	108
11	1.50801	12	11	10.40517	22	11	16.91621	148	11	29.33753	125

Table 4: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .

Energies with $\omega = 0.5$

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	1.79975	12	5	12.32513	19	5	41.10885	17	5	104.99587	719
6	1.79975	12	6	12.27141	21	6	40.75051	66	6	99.75460	19
7	1.79975	12	7	12.27138	21	7	40.30272	86	7	49.07933	81
8	1.79975	12	8	12.27136	21	8	40.26375	112	8	41.11926	76
9	1.79974	12	9	12.27134	21	9	40.21669	100	9	39.21778	96
10	1.79974	12	10	12.27133	21	10	40.21625	104	10	39.39971	128
11	1.79974	12	11	12.27132	21	11	40.21611	101	11	39.67842	132

Table 5: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .Energies with $\omega = 1.0$

$N = 2$			$N = 6$			$N = 12$			$N = 20$		
R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I	R	$E_0[au]$	I
5	3.16192	11	5	20.74840	17	5	67.56993	19	5	168.42637	109
6	3.16192	11	6	20.72026	18	6	67.29687	37	6	161.33972	19
7	3.16191	11	7	20.72013	18	7	66.93475	29	7	159.95872	28
8	3.16191	11	8	20.71925	18	8	66.92309	41	8	158.40017	41
9	3.16191	11	9	20.71925	18	9	66.91224	43	9	158.22603	173
10	3.16191	11	10	20.71922	18	10	66.91204	43	10	158.01767	58
11	3.16191	11	11	20.71922	18	11	66.91137	38	11	158.01028	68

Table 6: Table of Hartree-Fock energies with single particle orbitals R , energy E_0 and number of iterations I .

V DISCUSSION

VA ENERGY MINIMA

We see from the results given in section IV, that the energies in some cases increase as we increase the number of single particle states. This behaviour can be traced back to the assumption leading to the Hartree-Fock equations.

Recall that the first ansatz before we acquired the Hartree-Fock equations was from the variational principle. This guarantees only that the expectation value of the total Hamiltonian (estimate for ground state energy) has an extremal, which is not necessarily a minimum.

One may be tempted to only blame the variational condition for the poor estimation, however the instability only reveals when the oscillator frequency (labeled ω in equation 8) is reduced. When the mentioned frequency is reduced, one effectively reduces the gap between the energy of the single particle states, meaning we blur the difference between states. This is crucial when we look at states above the Fermi level since now it is easier for the electron to jump to the states above Fermi level. In order to account for the possible energy level (to an approximate) we need more single particle states when the energy gap is reduced.

VB CONVERGENCE

Looking at the results we see that the number of iterations needed before the Hartree-Fock energies reach the convergence criterion explained in section II.G.3 mostly reach convergence quickly (usually under 100 iterations), but for some.

Observe also that the number of iterations needed before convergence also increases as we increase the number of electrons, this may be due to the fact that we use a brute-force criteria. The brute-force criteria is a simple average over all the eigenenergies of the Hartree-Fock matrix. This means we have more and more contributions as we increase the number of particles giving rise to more variations in the individual eigenvalues which in turn gives more variations in the averages.

The Hartree-Fock limit was not reached for all the calculations, hinting to that we might need more single-particle shells in order for the limit to be reached.

V.C DEGENERACY

As for the degeneracy of states, we had some. Compared to the original basis, the harmonic oscillator, the same degeneracies were present for the Hartree-Fock energies when only 1 and 2 single particle orbitals were set as the cutoff. For more orbitals we had more energy levels present.

VI CONCLUSION

In conclusion, the calculations for the given parameters were likely to scarce since the Hartree-Fock limit was not reached for all. The reason for this was simply time, that is, the runtime of the program. This can be improved by further parallelization and implementing a different data-structure for the interaction matrix.

The results were not too bad for $\omega = 1$ as the Hartree-Fock limit was actually reached for 2 and 6 electrons at least. The degeneracies seen in the Harmonic oscillator case is not always present in the Hartree-Fock energies.

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