

# Time-Dependent Hartree-Fock

## FYS4411 - Project 2

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Abstract

### I. INTRODUCTION

The Hartree-Fock method has for a long time been a very powerful tool for solving many-body problems in quantum mechanics, specifically in the context of solving the electronic Schrödinger equation. Today, it is a central building block for many Post-Hartree-Fock methods such as Configuration Interaction and Coupled Cluster computations. In quantum chemistry, the Hartree-Fock method may be employed to obtain the potential energy surface of molecules from which interesting properties like molecular geometries and vibrational modes may be deduced, while at the same time obtaining the electronic wavefunction revealing information about atomic and molecular dipole behaviour and polarizability in excitation fields [1].

In this report, it will be our business to validate our implementation of a general time dependent Hartree Fock (GTDHF) solver by comparing our results against those produced by Zanghellini et al. in [2]. More to the point, we shall study a 1D quantum dot consisting of two electrons in a harmonic oscillator field, producing the ground state energy  $E_0$  in the stationary state and the time dependent orbital overlap integral  $P(t, t_0)$ .

Going forward, we shall present Hartree Fock theory in both the stationary and time dependent case, before discussing how the GTDHF solver is implemented. Having this in order, we will present the obtained results and discuss them in light of the comparable results produced by Zanghellini et al, before finally making some summary remarks on the presented work and the project in its entirety.

### II. METHODS

Before presenting the Hartree Fock method, we wish to lay a contextual foundation for what we are working with. We are going to analyze a 1D system consisting of two interacting electrons in a harmonic oscillator potential. In accordance with the work in [2], the Hamiltonian in one dimension reads

$$\hat{H} = \sum_{i=1}^n \left( -\frac{1}{2} \frac{d}{dx} + \frac{1}{2} m \omega^2 x^2 \right) + \sum_{i < j}^n \frac{\alpha}{\sqrt{(x_i - x_j)^2 + a^2}} \quad (1)$$

using atomic units. Here,  $n$  represents the number of electrons (2 in our case),  $\alpha = 1$  denotes strength of the Coulomb interaction and  $a = 0.25$  is a shielding

term added in the 1D Coulomb interaction to avoid problems arising from dividing by values close to zero. In addition to confining the system to 1D, this shielding term adds an extra simplification of the system which lets us analyze it more easily. Notice here the pair-wise summation over all electrons in the interaction term.

We will now introduce a set of basis functions. Then we will show how we can combine these basis functions to form anti-symmetric states for our system. Next we will show how to vary this anti-symmetric state in a way which minimizes the energy of an approximate Hamiltonian, and how to calculate various values of interest. Finally we will show how to time-evolve our state with an additional potential acting on the particles.

#### A. The Harmonic Oscillator Basis

Invoking the Schrödinger equation in the non-interacting case for a single particle labeled  $n$

$$\left( -\frac{1}{2} \frac{d}{dx} + \frac{1}{2} \omega^2 x^2 \right) \chi_n(x) = \epsilon_n \chi_n(x) \quad (2)$$

leads to the well known solutions for the harmonic oscillator with eigenenergies  $\epsilon_n = \omega(n + 0.5)$  and corresponding eigenstates

$$\chi_n(x) = \left( \frac{\omega}{\pi} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} \mathcal{H}_n(\sqrt{\omega} x) \quad (3)$$

where  $\mathcal{H}_n$  are Hermite polynomials (See VI).

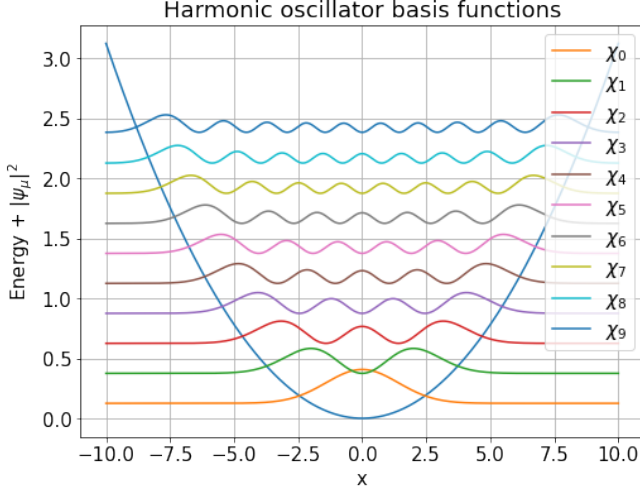


Figure 1. The harmonic oscillator eigenstates. These will be used as a basis.

These harmonic oscillator energy-eigenstates will be used as a basis for constructing the ground state for the interacting system. We use the python library `quantum-systems`[3] to set up this *spatial* single particle basis  $\{\chi_n\}_{n=1}^{l/2}$  spanning our  $(l/2)$ -dimensional model space.

As it is our business to study electrons, or more generally *fermions*, it is important that the single particle descriptions account for not only the spatial dimensions, but the intrinsic spin coordinate of each electron too. In this project, we want to create a general Hartree-Fock solver which in turn implies that we study general spin systems on the form

$$\psi(x, m_s) = \chi_1(x)\alpha(m_s) + \chi_2(x)\beta(m_s) \quad (4)$$

where  $\chi_i(x)$  denotes the spatial functions,  $\sigma \in \{\alpha, \beta\}$  are the spin functions and  $m_s \in \{\uparrow, \downarrow\}$  is the spin quantum number.

We again use the `quantum-systems` python-library to construct a basis, only now with spin being taken into account. We use the spin basis functions

$$\begin{aligned} \alpha(\uparrow) &= 1, & \beta(\uparrow) &= 0 \\ \alpha(\downarrow) &= 0, & \beta(\downarrow) &= 1 \end{aligned} \quad (5)$$

Using the `quantum-systems` python-library we construct a basis of size  $\ell$  where half the functions have the spatial functions  $\{\chi_n\}_{n=1}^{\ell/2}$  and spin up, while the other half have the same spatial functions only with spin down.

$$\begin{aligned} |\psi_{2i-1}\rangle &= \chi_i(x)\alpha(m_s) & \text{for } i = 1, 2, 3, \dots, l \\ |\psi_{2i}\rangle &= \chi_i(x)\beta(m_s) & \text{for } i = 1, 2, 3, \dots, l \end{aligned} \quad (6)$$

This basis will be used extensively in our report and code. It was chosen because the non-interacting system often is

a good approximation to the interacting system for sufficiently small perturbations. It is also orthogonal, since the harmonic oscillator spatial functions are orthogonal, and the spin basis functions are all either spin up or spin down. From here on, spin will be simply assumed in the input to these functions, for compactness.

## B. The Slater Determinant

With the full Hamiltonian in (1) we may invoke the time independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (7)$$

with  $|\Psi\rangle$  representing the many-body wavefunction of the interacting system. In the non-interacting case, the ground state is a single Slater determinant. We therefore choose to approximate the exact ground state of the interacting system with a single Slater determinant.

$$|\Psi\rangle \approx |\Phi\rangle = |\phi_1\phi_2\dots\phi_n\rangle \quad (8)$$

A Slater determinant is an anti-symmetrized product of molecular orbitals. In the two electron case, this takes the form

$$\begin{aligned} |\Phi\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) \\ \phi_2(x_1) & \phi_2(x_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (|\phi_1\rangle \otimes |\phi_2\rangle - |\phi_2\rangle \otimes |\phi_1\rangle) \end{aligned} \quad (9)$$

or more generally for an  $n$ -electron system,

$$|\Phi\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_n) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(x_1) & \phi_n(x_2) & \dots & \phi_n(x_n) \end{vmatrix} \quad (10)$$

The molecular orbitals in  $|\Phi\rangle$  can be expressed as linear combinations of our harmonic oscillator basis functions.

$$|\phi_i\rangle = \sum_{\mu=1}^l C_{\mu i} |\psi_{\mu}\rangle \quad (11)$$

Note that since we only have  $\ell$  basis functions for an infinite dimensional space, how well the  $\phi_i$ 's approximate the actual ground state is limited by the size as well as the quality of our basis.

Our approximation to the ground state of our system then, will be a Slater determinant consisting of the molecular orbitals  $|\phi_i\rangle$  which are decided by the coefficient matrix  $C$ .

### C. The Hartree-Fock eigenvalue equation

We wish to find the coefficient matrix  $C$  which minimizes the energy of the system, to best approximate the ground state of our system. Minimizing the energy to find the ground state follows the variational principle: Since any state can be expressed as a linear combination of the energy-eigenstates of the system, the energy will be the weighted sum of the corresponding eigen-energies, and thus cannot be lower than the ground state energy.

$$E_{gs} \leq \langle \Phi | \hat{H} | \Phi \rangle \quad (12)$$

In addition to minimizing the energy, we want the molecular orbitals to be orthonormal. Together these problems can be expressed as minimizing the following expression:

$$L[\phi_1, \dots, \phi_n, \boldsymbol{\lambda}] = \langle \Phi | \hat{H} | \Phi \rangle - \lambda_{qp} (\langle \phi_p | \phi_q \rangle - \delta_{pq}) \quad (13)$$

where  $\boldsymbol{\lambda}$  are the Lagrange multipliers. Minimizing this expression leads to the Hartree-Fock eigenvalue equation [4]

$$\hat{f} |\phi_p\rangle = \varepsilon_p |\phi_p\rangle \quad (14)$$

where  $\hat{f}$  is the single-particle Fock-operator. It consists of the typical one-body part of the exact Hamiltonian, while the Coulomb interaction is simplified so that each particle only "sees" the mean electric field set up by the other particles. This simplification leads to a direct and exchange term using the operator  $\hat{u} = \frac{1}{r_{ij}}$ , where  $r_{ij}$  is the distance between the two electrons in the integral. The Fock-operator's matrix elements in the harmonic oscillator basis are given by

$$\begin{aligned} \hat{f}_{\mu\nu} &= \langle \psi_\mu | \hat{f} | \psi_\nu \rangle \\ &= \langle \psi_\mu | \hat{h} | \psi_\nu \rangle + \sum_{i=1}^n \langle \psi_\mu \phi_i | \hat{u} | \psi_\nu \phi_i \rangle - \langle \psi_\mu \phi_i | \hat{u} | \phi_i \psi_\nu \rangle \\ &= h_{\mu\nu} + \sum_{i=1}^n \langle \psi_\mu \phi_i | \hat{u} | \psi_\nu \phi_i \rangle_{AS} \\ &= h_{\mu\nu} + \sum_{i=1}^n \sum_{\kappa, \lambda=1}^l C_{\kappa i}^* C_{\lambda i} \langle \psi_\mu \psi_\kappa | \hat{u} | \psi_\nu \psi_\lambda \rangle_{AS} \\ &= h_{\mu\nu} + \sum_{\kappa, \lambda=1}^l D_{\lambda\kappa} \langle \psi_\mu \psi_\kappa | \hat{u} | \psi_\nu \psi_\lambda \rangle_{AS} \\ &= h_{\mu\nu} + \sum_{\kappa, \lambda=1}^l D_{\lambda\kappa} u_{\nu\lambda}^{\mu\kappa} \end{aligned} \quad (15)$$

where we defined the density matrix  $D_{\lambda\kappa} = \sum_{i=1}^n C_{\kappa i}^* C_{\lambda i}$ . The integrals  $h_{\mu\nu}$  and  $u_{\nu\lambda}^{\mu\kappa}$  are calculated and accessed using the `quantum-systems` python-library.

With these matrix elements of  $\hat{f}$ , we can project equation 14 onto an element of our basis and get

$$\begin{aligned} \langle \psi_\mu | \hat{f} | \phi_p \rangle &= \varepsilon_p \langle \psi_\mu | \phi_p \rangle \\ \sum_{\nu=1}^l C_{\nu p} f_{\mu\nu} &= \varepsilon_p \sum_{\nu=1}^l C_{\nu p} \delta_{\mu\nu} \\ \implies \mathbf{F}\mathbf{C} &= \mathbf{C}\boldsymbol{\epsilon} \end{aligned} \quad (16)$$

where the latter eigenvalue equations are known as the Roothan-Hall equations. This looks like a simple eigenvalue problem, the columns of  $\mathbf{C}$  will be the eigenvectors of  $\mathbf{F}$ , and  $\boldsymbol{\epsilon}$  will be the eigenvalues. However,  $\mathbf{F}$  depends on  $\mathbf{C}$ , so solving the equation is not so simple.

One approach to this problem is the self-consistent field method. Make an initial guess for  $\mathbf{C}$ , calculate  $\mathbf{F}$ , and let the eigenvectors of  $\mathbf{F}$  form the new guess for  $\mathbf{C}$ . Repeat until  $\mathbf{C}$  or the energy changes by an amount smaller than some tolerance. Convergence of this method is not guaranteed, but is helped by having a well behaved system and starting close to the ground state.

The method might temporarily converge at a local minimum before continuing toward another minimum or simply getting stuck at the local minimum. Note that the true ground state of the system has a symmetrical spatial part, and thus an anti-symmetrical spin part, since the ground state of such a system in 1D must be non-degenerate [5]. The restricted Hartree-Fock (RHF) method ensures that the state we find has a symmetrical spatial part, and anti-symmetric spin part (the particles are forced in spin up, spin down pairs). The general Hartree-Fock method (GHF) however, which we will use, only ensures that the total state is antisymmetric.

### D. Expectation values

There are some expectation values of interest we wish to calculate. The first is the energy. Note the double sum and fraction  $\frac{1}{2}$  in front of the second term. We wish to calculate the energy from the Coulomb term from all electrons  $i$  to all electrons  $j$ , which is why we sum over all electrons in this manner. Since the interchange of  $i$  and  $j$  gives the same contribution, we divide the sum by 2. The Coulomb terms from particle  $i$  to electron  $j = i$

all equal 0.

$$\begin{aligned}
\langle E \rangle &= \sum_{i=1}^n \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^n \langle \phi_i \phi_j | \hat{u} | \phi_i \phi_j \rangle_{AS} \\
&= \sum_{i=1}^n \sum_{\mu,\nu=1}^l C_{\mu i}^* C_{\nu i} \langle \psi_\mu | \hat{h} | \psi_\nu \rangle \\
&+ \frac{1}{2} \sum_{i,j=1}^n \sum_{\mu,\nu,\kappa,\lambda=1}^l C_{\mu i}^* C_{\kappa j}^* C_{\nu i} C_{\lambda j} \langle \psi_\mu \psi_\kappa | \hat{u} | \psi_\nu \psi_\lambda \rangle_{AS} \\
&= \sum_{\mu,\nu=1}^l D_{\nu\mu} \langle \psi_\mu | \hat{h} | \psi_\nu \rangle \\
&+ \frac{1}{2} \sum_{\mu,\nu,\kappa,\lambda=1}^l D_{\nu\mu} D_{\lambda\kappa} \langle \psi_\mu \psi_\kappa | \hat{u} | \psi_\nu \psi_\lambda \rangle_{AS}
\end{aligned} \tag{17}$$

Next is the expected value of position. As position is a single particle operator it is much more straightforward.

$$\begin{aligned}
\langle x \rangle &= \sum_{i=1}^n \langle \phi_i | \hat{x} | \phi_i \rangle \\
&= \sum_{i=1}^n \sum_{\mu,\nu=1}^l C_{\mu i}^* C_{\nu i} \langle \psi_\mu | \hat{x} | \psi_\nu \rangle \\
&= \sum_{\mu,\nu=1}^l D_{\nu\mu} \langle \psi_\mu | \hat{x} | \psi_\nu \rangle
\end{aligned} \tag{18}$$

Finally we need an expression for the electron density of single particles:

$$\begin{aligned}
\rho_p(x) &= \phi_p(x)^* \phi_p(x) = \sum_{\mu,\nu=1}^l C_{\mu p}^* C_{\nu p} \psi_\mu(x)^* \psi_\nu(x) \\
&= \sum_{\mu=1}^l C_{\mu p}^* C_{\mu p} \psi_\mu(x)^* \psi_\mu(x) = \sum_{\mu=1}^l |C_{\mu p}|^2 |\psi_\mu(x)|^2
\end{aligned} \tag{19}$$

Where we used the orthogonality of the harmonic oscillator basis to remove the double sum.

## E. Time-dependent General Hartree-Fock solver

Going forward, we wish to describe the time dependent behaviour of the system at hand. In our case, we perturb the system by shining a laser  $\hat{L}(t)$  on it. Firstly, we make the same ansatz for the wavefunction as in the stationary case by  $|\Psi(\mathbf{t})\rangle \approx |\Phi(\mathbf{t})\rangle = |\phi_1(t)\phi_2(t)\phi_3(t)\dots\phi_n(t)\rangle$  as to say that the time dependence of the full many-body wavefunction is solely pertained to the time dependence of the molecular orbitals themselves. The molecular orbitals' time evolution is dictated by the time dependent Schrödinger equation on the form [6]

$$i \frac{d}{dt} |\phi_p(t)\rangle = \hat{\mathcal{F}}(t) |\phi_p(t)\rangle \tag{20}$$

where  $\hat{\mathcal{F}}(t)$  now describes a temporally evolving Fock operator due to the laser term  $\hat{L}(t)$  by

$$\begin{aligned}
\hat{\mathcal{F}}(t) &= \hat{f} + \hat{L}(t) \\
\hat{\mathcal{F}}_{\mu\nu}(t) &= \hat{f}_{\mu\nu} - \mathcal{E}_0 \hat{x}_{\mu\nu} \sin(\Omega t)
\end{aligned} \tag{21}$$

where  $\hat{x}_{\mu\nu}$  are the matrix elements of the matrix storing expected positions,  $\mathcal{E}_0$  denotes the electric field strength and  $\Omega$  is the laser frequency. This dipole laser interaction is entirely inspired by the work in [2]. As in the stationary case, we perform a basis transformation into the harmonic oscillator basis by projecting the basis onto equation 20. Under this transformation, we assume that the harmonic oscillator basis functions are temporally invariant, and that the time evolution only occurs in the coefficients. This leads to

$$\begin{aligned}
i \frac{d}{dt} \langle \psi_\mu | \phi_p(t) \rangle &= \langle \psi_\mu | \hat{\mathcal{F}}(t) | \phi_p(t) \rangle \\
i \sum_{\nu=1}^l \frac{d}{dt} C_{\nu p}(t) \langle \psi_\mu | \psi_\nu \rangle &= \sum_{\nu=1}^l C_{\nu p}(t) \langle \psi_\mu | \hat{\mathcal{F}}(t) | \psi_\nu \rangle \\
i \frac{d}{dt} C_{\mu\nu}(t) &= C_{\nu p}(t) \mathcal{F}_{\mu\nu}(t)
\end{aligned} \tag{22}$$

or, more conveniently

$$\begin{aligned}
C'_{\mu\nu}(t) &= -i \mathcal{F}_{\mu\nu}(t) C_{\nu p}(t) \\
\Rightarrow \mathbf{C}'(t) &= -i \mathcal{F}(t) \mathbf{C}(t)
\end{aligned} \tag{23}$$

We set the state at time 0 to be the ground state found by solving the Roothan-Hall equations. The right side of this differential equation is entirely dependent on  $\mathbf{C}(t)$ , and the left side gives us its derivative. Since we know  $\mathbf{C}(0)$ , we can calculate  $\mathbf{C}'(0)$  and use this to approximate  $\mathbf{C}(0 + \Delta t)$ . By repeating this procedure we can approximate  $\mathbf{C}(t)$  for  $t > 0$ . We use an ODE integrator (the "vode" ODE integrator from scipy) to perform the integration.

## F. Overlap

After we have time-evolved our ground state, we wish to analyze the time-evolved state. The first value of interest is the overlap,  $P(t_1, t_0)$ , the probability of being in the state of time  $t_0$  at time  $t_1$ .

We define the matrix elements

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \tag{24}$$

where  $\{\chi_\mu\}_{\mu=1}^l$  is some basis of spin-orbitals which can overlap.

Now let  $\mathbf{C}$  and  $\mathbf{G}$  be two coefficient matrices which describe two Slater determinants  $|\Psi\rangle$  and  $|\Phi\rangle$  using the basis  $\{\chi_\mu\}_{\mu=1}^l$ . We now define the matrix elements

$$\begin{aligned}
T_{ij} &= \langle \psi_i | \phi_j \rangle \\
&= \sum_{\mu\nu} C_{\mu i}^* G_{\nu j} \langle \chi_\mu | \chi_\nu \rangle \\
&= \sum_{\mu\nu} C_{\mu i}^* G_{\nu j} S_{\mu\nu} \\
\Rightarrow \mathbf{T} &= \mathbf{C}^\dagger \mathbf{S} \mathbf{G}
\end{aligned} \tag{25}$$

Now let  $|\Psi\rangle$  and  $|\Phi\rangle$  consist of two molecular orbitals. Their inner product can be written as:

$$\begin{aligned}
\langle \Psi | \Phi \rangle &= \frac{1}{\sqrt{2}} (\langle \psi_1 | \otimes \langle \psi_2 | - \langle \psi_2 | \otimes \langle \psi_1 |) \\
&\quad \frac{1}{\sqrt{2}} (|\phi_1\rangle \otimes |\phi_2\rangle - |\phi_2\rangle \otimes |\phi_1\rangle) \\
&= \frac{1}{2} (\langle \psi_1 | \phi_1 \rangle \langle \psi_2 | \phi_2 \rangle - \langle \psi_2 | \phi_1 \rangle \langle \psi_1 | \phi_2 \rangle \\
&\quad - \langle \psi_1 | \phi_2 \rangle \langle \psi_2 | \phi_1 \rangle + \langle \psi_2 | \phi_2 \rangle \langle \psi_1 | \phi_1 \rangle) \\
&= \langle \psi_1 | \phi_1 \rangle \langle \psi_2 | \phi_2 \rangle - \langle \psi_2 | \phi_1 \rangle \langle \psi_1 | \phi_2 \rangle \\
&= \sum_{\mu, \nu, \kappa, \lambda=1}^l C_{\mu 1}^* C_{\nu 2}^* G_{\kappa 1} G_{\lambda 2} \langle \chi_\mu | \chi_\kappa \rangle \langle \chi_\nu | \chi_\lambda \rangle \\
&\quad - C_{\mu 2}^* C_{\nu 1}^* G_{\kappa 2} G_{\lambda 1} \langle \chi_\nu | \chi_\kappa \rangle \langle \chi_\mu | \chi_\lambda \rangle \\
&= \sum_{\mu, \nu, \kappa, \lambda=1}^l C_{\mu 1}^* C_{\nu 2}^* G_{\kappa 1} G_{\lambda 2} S_{\mu\kappa} S_{\nu\lambda} \\
&\quad - C_{\mu 2}^* C_{\nu 1}^* G_{\kappa 2} G_{\lambda 1} S_{\nu\kappa} S_{\mu\lambda} \\
&= \det(\mathbf{T})
\end{aligned} \tag{26}$$

Notice how at the third equality half the terms and the factor  $\frac{1}{2}$  disappear as the latter half of the terms were identical to the first half. The antisymmetry of  $|\Psi\rangle$  was in a way unneeded as every combination of  $\langle \psi_i |$  and  $|\phi_j\rangle$  is guaranteed by the antisymmetry of  $|\Phi\rangle$ .

Now let  $\sigma, \tau \in S_n$  be all permutations of the molecular orbitals  $|\psi_i\rangle$  and  $|\phi_i\rangle$  respectively. The inner product of two Slater determinants  $|\Psi\rangle$  and  $|\Phi\rangle$  with  $n$  molecular orbitals can be written as

$$\begin{aligned}
\langle \Psi | \Phi \rangle &= \frac{1}{n!} \sum_{\sigma, \tau \in S_n} (-1)^{|\sigma||\tau|} \prod_{i=1}^n \langle \psi_{\sigma(i)} | \phi_{\tau(i)} \rangle \\
&= \frac{1}{n!} \sum_{\sigma, \tau \in S_n} (-1)^{|\sigma||\tau|} \prod_{i=1}^n \mathbf{T}_{\sigma(i)\tau(i)} \\
&= \sum_{\sigma \in S_n} (-1)^{|\sigma|} \prod_{i=1}^n \mathbf{T}_{i\sigma(i)} \\
&= \det(\mathbf{T})
\end{aligned} \tag{27}$$

where we used the observation from earlier that the antisymmetry of  $|\Phi\rangle$  was "unneeded" at the third equality.

Now we can finally return to our harmonic oscillator basis  $\{\psi_\mu\}_{\mu=1}^l$  and time-dependent coefficient matrix  $\mathbf{C}(t)$  and define the overlap, the probability of being in the state of time  $t_0$  at time  $t_1$ , as

$$P(t_1, t_0) = |\langle \Phi(t_1) | \Phi(t_0) \rangle|^2 = |\det(\mathbf{C}^\dagger(t_1) \mathbf{C}(t_0))|^2 \tag{28}$$

We now express the overlap in the basis of orthonormal energy-eigenstates  $\{|\xi_\mu\rangle\}_{\mu=1}^\infty$  with eigenenergies  $E_\mu$ . We consider a time evolution with no external laser field from time  $t_0$  to  $t_1$ , where  $t_1 - t_0 = t$ . We also define coefficients  $c_\mu(t')$  which define the state at a time  $t'$ :  $|\Phi(t')\rangle = \sum_{\mu=1}^\infty c_\mu(t') |\xi_\mu\rangle$ . Note that since the Hamiltonian is time-independent, the energy-eigenstates can be time evolved as follows:

$$c_\mu(t_1) |\xi_\mu\rangle = c_\mu(t_0) |\xi_\mu\rangle e^{-iE_\mu(t_1-t_0)} = c_\mu(t_0) |\xi_\mu\rangle e^{-iE_\mu t} \tag{29}$$

We now get

$$\begin{aligned}
\langle \Phi(t_1) | \Phi(t_0) \rangle &= \sum_{\mu, \nu=1}^\infty c_\mu(t_1)^* c_\nu(t_0) \langle \xi_\mu | \xi_\nu \rangle \\
&= \sum_{\mu=1}^\infty c_\mu(t_0)^* c_\mu(t_0) \langle \xi_\mu | \xi_\mu \rangle e^{-iE_\mu t} \\
&= \sum_{\mu=1}^\infty |c_\mu(t_0)|^2 e^{-iE_\mu t}
\end{aligned} \tag{30}$$

where we used the orthonormality of the basis, in addition to its time evolution at the second equality. This then gives us

$$\begin{aligned}
|\langle \Phi(t_1) | \Phi(t_0) \rangle|^2 &= \langle \Phi(t_1) | \Phi(t_0) \rangle \langle \Phi(t_0) | \Phi(t_1) \rangle \\
&= \sum_{\mu=1}^\infty |c_\mu(t_0)|^2 e^{-iE_\mu t} \sum_{\nu=1}^\infty |c_\nu(t_0)|^2 e^{iE_\nu t} \\
&= \sum_{\mu, \nu=1}^\infty |c_\mu(t_0)|^2 |c_\nu(t_0)|^2 e^{-i(E_\mu - E_\nu)t}
\end{aligned} \tag{31}$$

This result shows us that the overlap of a system can be expressed as some constants which oscillate through time with frequencies equal to differences of energy-eigenvalues of the system. Since we already have a way of calculating the overlap as a function of time, we will use a Fourier transform to find these frequencies, and thus, energy differences.

We can achieve a similar result by analyzing the expectation value of position. We will need to use the harmonic potential theorem discussed in [7], which implies that the whole system will move and be excited as a single-particle trapped in a harmonic oscillator potential. From the theory of the harmonic oscillator[8], we know that the position operator is related to the ladder operators by

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}_+ + \hat{a}_-) \tag{32}$$

Where  $\hat{a}_+$  and  $\hat{a}_-$  raise and lower the energy of a state, respectively. We can now show that the expected value of  $x$  at time  $t_1$ , where  $t_1 - t_0 = t$ , is

$$\begin{aligned}
 \langle \hat{x}(t_1) \rangle &= \langle \Psi(t_1) | \hat{x} | \Psi(t_1) \rangle \\
 &= \sum_{\mu, \nu=1}^{\infty} c_{\mu}(t_1)^* c_{\nu}(t_1) \langle \xi_{\mu} | \hat{x} | \xi_{\nu} \rangle \\
 &= \sum_{\mu, \nu=1}^{\infty} c_{\mu}(t_0)^* c_{\nu}(t_0) \langle \xi_{\mu} | \hat{x} | \xi_{\nu} \rangle e^{-i(E_{\nu} - E_{\mu})t} \\
 &= \sum_{\mu, \nu=1}^{\infty} K_{\mu\nu} (\langle \xi_{\mu} | \xi_{(\nu+1)} \rangle + \langle \xi_{\mu} | \xi_{(\nu-1)} \rangle) e^{-i(E_{\nu} - E_{\mu})t}
 \end{aligned} \tag{33}$$

where  $K_{\mu\nu}$  is only a compact way to hide away uninteresting constants. We see that the only terms in the sum which are non-zero are the ones where  $\mu$  and  $\nu$  differ by 1 (due to the orthogonality of the basis), which means the only frequencies that will show up in the data are the ones given by an energy difference of only 1 level. Since the energy of the harmonic oscillator only increases in steps of  $\omega$ , the only frequency that should appear when Fourier transforming  $\langle \hat{x}(t) \rangle$  is  $\omega$ .

### III. RESULTS

All code used for the results in this report is available at [9] in a Jupyter Notebook. The notebook is quite short, and the calculations are very close to the formulas for the sums and matrix multiplications derived in the previous section, so we urge the reader to skim through it to see in more detail how our results were produced.

#### A. The Ground State

The electron density of the ground state approximations we found with SCF are shown in figure 2.

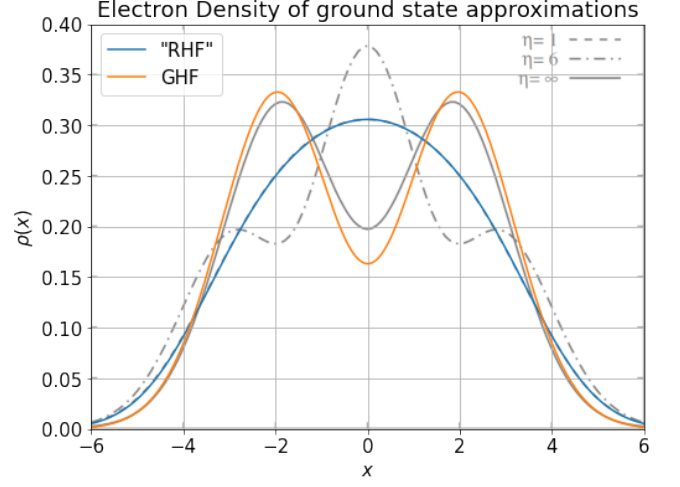


Figure 2. The electron density  $\rho(x)$  for the ground state of the interacting system imposed on the figure presented in [2]. These plots were produced with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations, both with identity as the initial guess. The line for  $\eta = 1$  is entirely covered by the line labeled "RHF".

The expected value of energy for these approximations, together with selected energies from [2] are shown in table

	Energy
"RHF"	1.1796
Zanghellini, $\eta = 1$	1.1795
GHF	0.8450
Zanghellini, $\eta = \infty$	0.8247

Table I. The energies of the ground states we calculated with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations. Selected energies from the calculations of Zanghellini [2] are also shown, for reference.

The energy of the ground state approximation as a function of the number of SCF iterations is shown in figure 3.



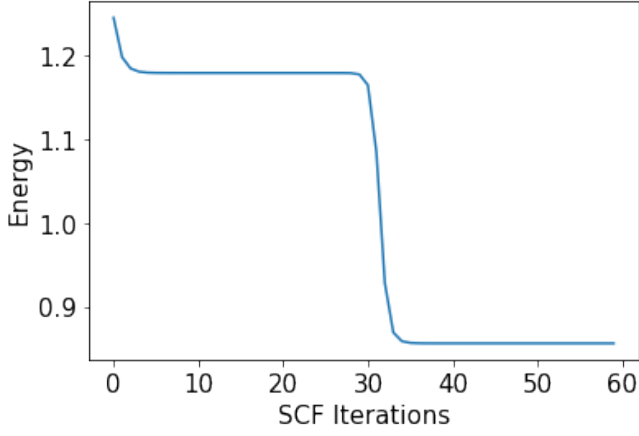


Figure 3. The energy of the ground state approximation as a function of the number of SCF iterations. The starting guess for the coefficient matrix was the identity matrix.

We now wish to analyze the qualitative differences of our "RHF" and GHF approximations. The electron densities of the separate molecular orbitals in our ground state approximations are shown in figure 4.

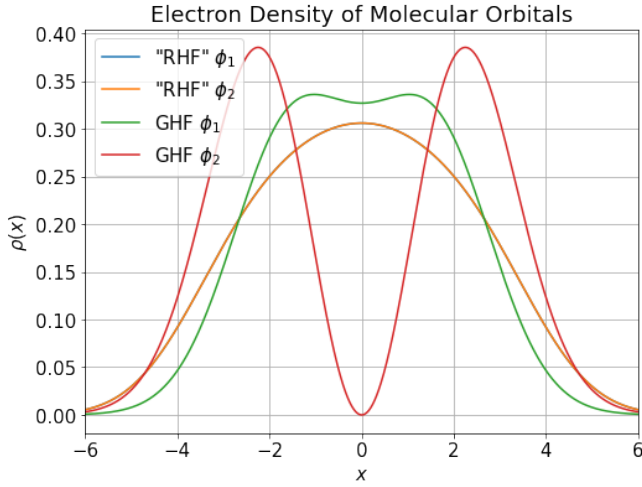


Figure 4. The electron density  $\rho(x)$  for the molecular orbitals of the ground state of the interacting system. These plots were produced with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations, both with identity as the initial guess. The line labeled "RHF"  $\phi_1$  is entirely covered by the line labeled "RHF"  $\phi_2$ .

The coefficients of the molecular orbitals shown in figure 4 (in the harmonic oscillator basis from equation 6) are shown in table II.

$\psi_i$	"RHF" $\phi_1$	"RHF" $\phi_2$	GHF $\phi_1$	GHF $\phi_2$
1	-0.31	0.88	-0.05	-0.00
2	0.88	0.31	0.96	0.00
3	-0.00	-0.00	-0.00	0.05
4	0.00	-0.00	0.00	-0.99
5	0.11	-0.33	0.01	0.00
6	-0.33	-0.11	-0.26	-0.00
7	0.00	0.00	0.00	-0.01
8	-0.00	0.00	-0.00	0.11
9	-0.03	0.08	0.00	0.00
10	0.08	0.03	-0.03	-0.00
11	-0.00	-0.00	0.00	-0.00
12	0.00	-0.00	-0.00	0.01
13	0.00	-0.00	0.00	0.00
14	-0.00	-0.00	-0.01	-0.00
15	-0.00	-0.00	0.00	-0.00
16	0.00	-0.00	-0.00	0.00
17	0.00	-0.00	0.00	0.00
18	-0.00	-0.00	-0.00	-0.00
19	-0.00	-0.00	0.00	-0.00
20	0.00	-0.00	-0.00	0.00

Table II. The coefficients of the molecular orbitals shown in figure 4 (in the harmonic oscillator basis from equation 6). The odd numbered basis functions have spin up, and the even numbered basis function have spin down.

## B. Time Evolution

We time evolved the ground state approximations from figure 2 with a constant oscillating laser field, the resulting overlap between the initial state and the state at time  $t$  is shown in figure 5.

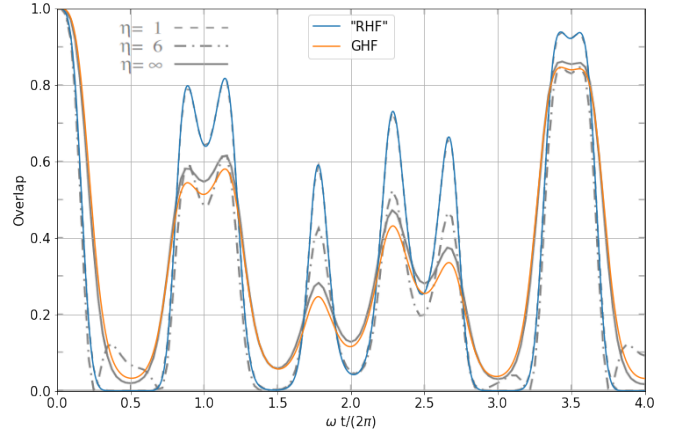


Figure 5. The time dependent overlap  $P(t_0, t)$  between the initial ground state and the time evolution of the state under the influence of a laser with amplitude  $\epsilon_e = 1$  and frequency  $\Omega = 8\omega$ . Our results are imposed on the results from [2]. These plots were produced with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations followed by the solution of equation 23 using an integrator. The line for  $\eta = 1$  is almost entirely covered by the line labeled "RHF".

We now perform the same time evolution as before, only

that we shut off the laser after  $1\omega/(2\pi)$  (the time unit from [2], and in our figures) and let the time evolution run unperturbed until  $201\ 1\omega/(2\pi)$ . The overlap and corresponding Fourier spectrum from after the laser pulse is shown in figure 6.

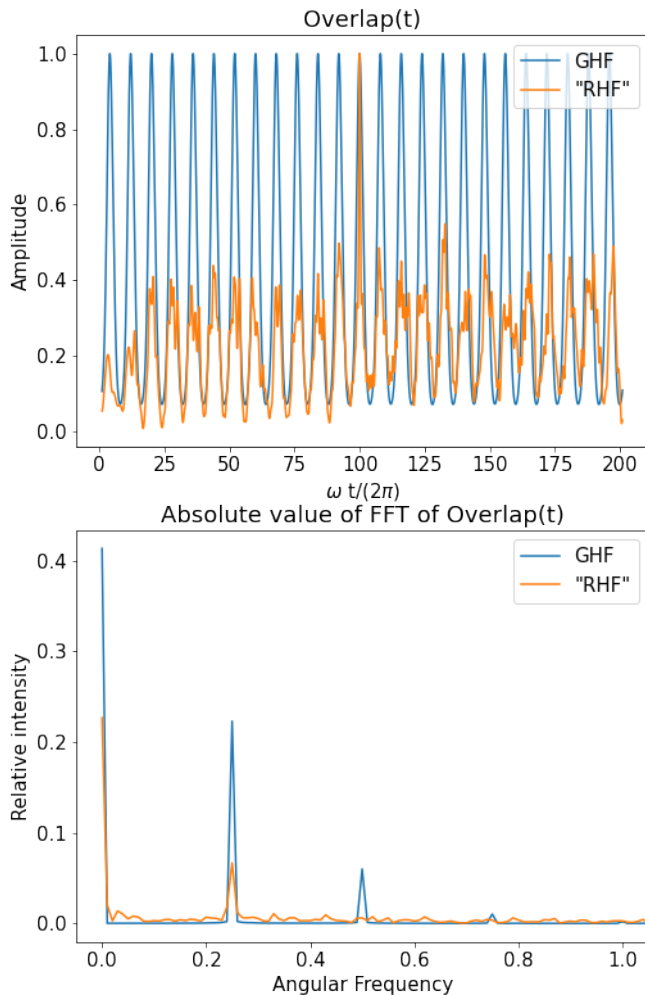


Figure 6. Top figure: The time dependent overlap  $P(t_0, t)$  between the state at time  $t_0$  and the time evolution of the state with no external laser field, after a laser pulse which stopped at time  $t_0$  has excited the system. These plots were produced with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations followed by the solution of equation 23 (with the laser field shutting off at  $t_0 = 1\omega/(2\pi)$ ) using an integrator. Bottom figure: The corresponding Fourier spectra of the overlap.

The expected value of position and corresponding Fourier spectrum from after the laser pulse is over is shown in figure 7.

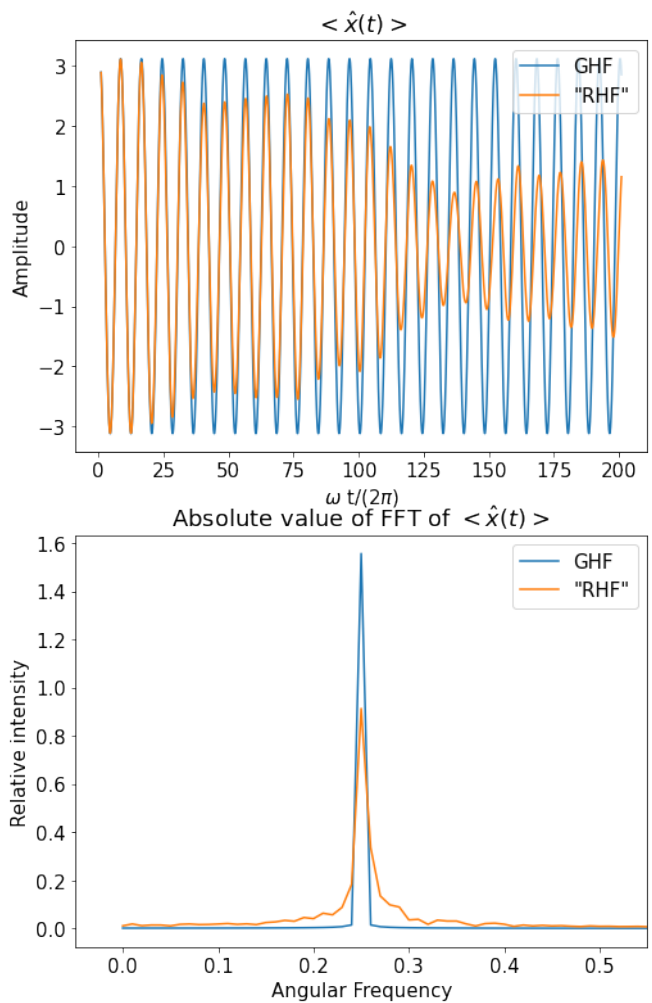


Figure 7. Top figure: The time dependent expected value of position, after a laser pulse (with amplitude  $\epsilon_e = 1$  and frequency  $\Omega = 8\omega$ ) which stopped at time  $t_0$  has excited the system. These plots were produced with 20 ("RHF") and  $2 \cdot 10^4$  (GHF) SCF iterations followed by the solution of equation 23 (with the laser field shutting off at  $t_0 = 1\omega/(2\pi)$ ) using an integrator. Bottom figure: The corresponding Fourier spectra of the expected value of position.

The peaks in the Fourier spectrum in figure 7 are at the angular frequency  $0.25 + -0.01$  for both the GHF and "RHF" state.

## IV. DISCUSSION

### A. The Ground State

Our main goal was reproducing the results from Zanghellini[2], and we were successful in finding a ground state with an electron density and energy which matches their result for the most naive model labeled  $\eta = 1$ . Their solution labeled  $\eta = \infty$  is the exact ground state of the system, which we can't replicate due to the simplicity of



our model. Figure 2 shows that the state we found labeled "RHF" seemingly perfectly matches the one found by Zanghellini, and table I shows that the "RHF" labeled state also has a good match when it comes to the energy, 1.1796 to their 1.1795. We predict the small discrepancy might simply come from a numerical effect from the many integrals and matrix operations that lead to this one number. As we have no access to their code, it is impossible to tell.

In addition to reproducing the result from Zanghellini, we also found that our general Hartree-Fock solver found another approximation to the ground state to the system. This different solution comes as no surprise as Zanghellini implemented the unrestricted Hartree-Fock method, where each molecular orbital must have either spin up or spin down, whereas our general Hartree-Fock implementation allows the orbitals to have any combination of the two.

The first ground state approximation we found was only a local minimum, as shown in figure 3. Its molecular orbitals have the same spatial part, as shown in figure 4 and table II, but opposite and thus orthogonal spin parts as shown in table II. We choose to label this approximation "RHF", as opposed to RHF, since it has the energy, spatial part and opposite spins of the restricted Hartree-Fock approximation, but the molecular orbitals don't have spin strictly up or down.

The other ground state approximation we found, we label GHF. It has an orthogonal spatial part, as shown in table II, while the spin of the molecular orbitals is mixed with no pattern. It comes as a surprise that the state which minimizes the energy has molecular orbitals with orthogonal spatial parts, as the true ground state is non-degenerate and thus is a spin-singlet with matching spatial parts instead. It is however encouraging that the GHF solution gives a much better approximation to the true electron density and energy of the true ground

state, as shown in figure 2 and table I. The electron density now has the two peaks of the exact solution, though their shape is clearly wrong. The energy is 0.8450, which is much closer to the exact result of 0.8247.

## B. Time Evolution

We also had a goal of reproducing the time dependant overlap of Zanghellini. As shown in figure 5, the time evolution of the "RHF" state matches the time evolution of Zanghellini's  $\eta = 1$  state. Again we see that the GHF state is a better, though qualitatively wrong approximation to the true ground state.

In addition to reproducing the time dependant overlap with an oscillating laser field, we calculated the time dependant overlap after a laser pulse had affected the state. This overlap and its Fourier spectrum is shown in figure 6. As expected from equation 31, we extract frequencies equal to the energy transition of system, which equal those of the harmonic oscillator. The results for the "RHF" state include a great deal of noise, which is expected since it is only a local minimum far from the true ground state, and thus should not necessarily obey equation 31.

The time dependant expected value of position also gave results consistent with the theory, in this case equation 33. As expected, only the frequency of the harmonic oscillator appeared in the Fourier spectrum. And again, the "RHF" state had some noise, probably because it is only a local minimum far from the true ground state, and thus should not necessarily obey equation 33.

## V. CONCLUSION

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- [1] C. D. Sherrill, , 1 (2000).
  - [2] J. Zanghellini, M. Kitzler, T. Brabec, and A. Scrinzi, *Journal of Physics B: Atomic, Molecular and Optical Physics* **37**, 763 (2004).
  - [3] "<https://github.com/Schoyen/quantum-systems>," (2021).
  - [4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, 1st ed. (Dover Publications, Inc., Mineola, 1996) pp. 115–122.
  - [5] S. Kar and R. Parwani, *EPL (Europhysics Letters)* **80**, 1 (2007).
  - [6] Øyvind Sigmundson Schøyen, *Real-time quantum many-body dynamics*, *Master's thesis* (2019) pp. 73–74.
  - [7] S. Zanoli, X. Roca-Maza, G. Colò, and S. Shen, *Physical Review Letters* **123** (2019), 10.1103/physrevlett.123.112501.
  - [8] D. J. Griffiths and D. F. Schroeter, *Introduction to Quantum Mechanics*, 3rd ed. (Cambridge University Press, 2018) p. 47.
  - [9] "Github repository with code and results: <https://github.com/KarlHenrik/FYS4411-Gruppe/tree/main/Project2>," (26.4.2021).

## VI. APPENDIX

### A. Appendix A

The physicist's Hermite polynomials are defined as follows

$$\mathcal{H}_n = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$$

and the first few take the form

$$\begin{aligned} H_0 &= 1 \\ H_1 &= 2x \\ H_2 &= 4x^2 - 2 \\ H_3 &= 8x^3 - 12x \end{aligned} \tag{34}$$