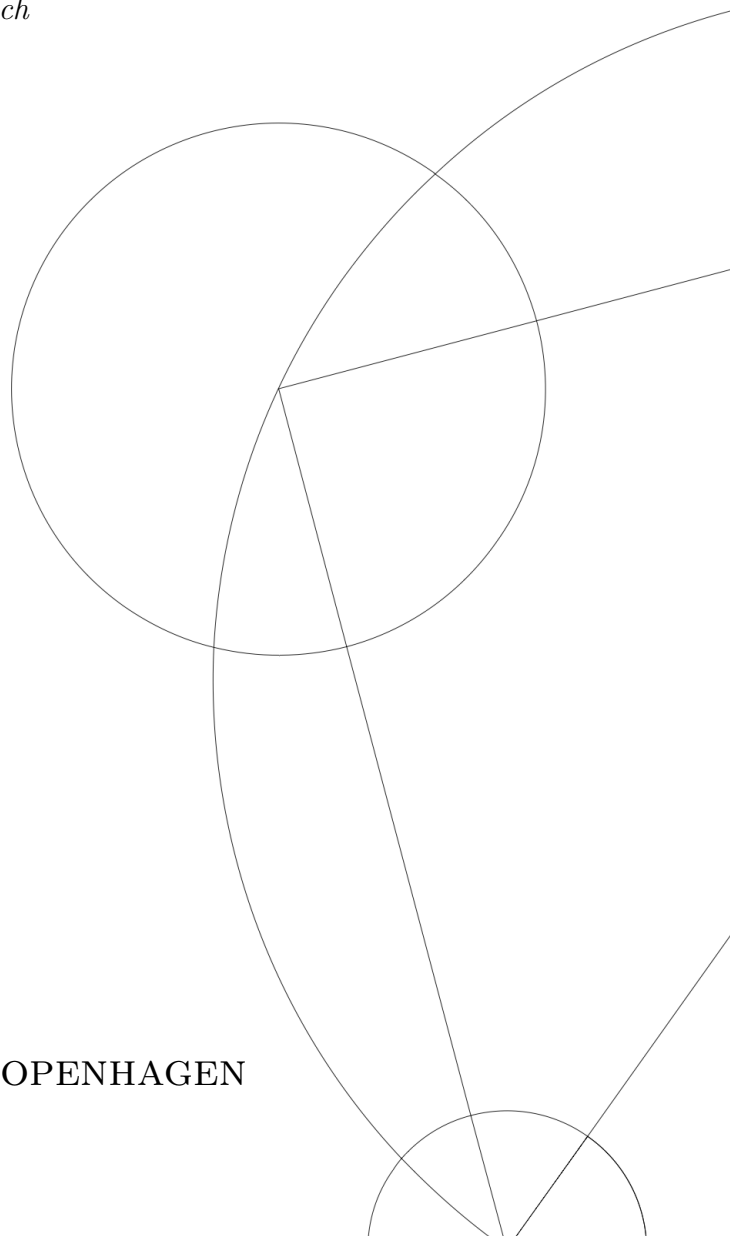# The Hartree-Fock Method

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Abstract

In this thesis we will focus mainly on the Hartree-Fock method where states are approximated using a Slater determinant. The dynamics of many body quantum mechanical systems is a problem that cannot be numerically solved exactly so we instead use computational methods to find self consistent solutions to the HF equation. Both the stationary and time dependent Hartree-Fock (HF) equations are considered analytically and solved numerically. For the derivation of the time dependent HF equation we use the time dependent variational principle to find equations of motion of the single particle states. The developed program uses an iterative approach to solving the Hartree-Fock equation which for a small two particle system lets us understand how well the Hartree-Fock method is. Our results focus on 1 dimension where we have, for example, found self consistent states for 15 protons in a chain and the Xenon atom. By comparing an exact solution to the HF, we find that this approximation method, and therefore the program, works best when applied to systems with low entanglement entropy.

Contents

1 Introduction

The dynamics of many body quantum mechanical systems is a problem that cannot be numerically solved exactly. We therefore turn to approximations of such systems to make them computable. This thesis' concern will be the Hartree-Fock method, which is simply approximating a system using a Slater determinant. One of the goals is to develop a program which can implement this approximation method so we are able work with many body problems.

To apply this approximation method we will use the variational principle and derive the Hartree-Fock equation. This equation describes the condition that the single particle states has to fulfill to extremize (hopefully minimize) its expectation energy. A mean field Hamiltonian can be extracted from this equation, that depends on all the states that constructs the Slater determinant. A set of self consistent states are therefore used to define this mean field Hamiltonian while also being eigenstates that satisfy the Hartree-Fock equation.

To study the dynamics of this approximation we use of the time dependent variational principle, which can be used to derive the time dependent Schödinger equation (TDSE). This method uses the principle of least action, for which we use the Euler-Lagrange equation to extremize. Doing this will give us an approximate TDSE called the Time Dependent Hartree-Fock equation. This equation describes the equations of motion of each single particle state in the Slater determinant.

We wish to gauge when the Hartree-Fock method is a good approximation such that we know when it is a good idea to use it and when it is too far-fetched. To get a general idea of when the method will work we develop the notion of correlation/entanglement entropy as a measure for exactly this.

Lastly we look at different setups that the program has successfully found solutions for. For the two particle system we are able to compare the Hartree-Fock solutions to the exact solutions to get a better idea of how well the approximation scheme works. We display the power of this approximation with more complex systems such as 1D proton chains and large 1D atoms.

1.1 The Inherent Complexity of Many Particle Systems

Systems with many particles are notoriously hard to work with because of the numerous amount of mutual interactions. To capture exactly how complex a system of multiple particles can become, we will look into how they are represented using Hilbert spaces. This will let us directly see how the size of the problem explodes exponentially as more particles are included and how complex the structure of a multi-particle state actually is.

In quantum mechanics any system can be represented by a vector $|\psi\rangle$ in a Hilbert space $\mathcal{H}$. The state is unique up to normalization and a phase factor $e^{i\alpha}$ for some $\alpha \in \mathbb{R}$. If the system consists of two particles, then its Hilbert space can be written as the tensor product of the particles Hilbert spaces, that is $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ [3]. As an example we can consider two fermionic particles, then their collective state, has to be anti-symmetric under particle exchange, for example $|\psi\rangle = (|\psi_1\rangle_1 \otimes |\psi_2\rangle_2 - |\psi_2\rangle_1 \otimes |\psi_1\rangle_2)/\sqrt{2}$. So there is already some complexity for a simple system of two fermionic particles. Continuing onward we will use the shorthand $|\psi_1\rangle_1 \otimes |\psi_2\rangle_2 = |\psi_1\rangle_1 |\psi_2\rangle_2$. If $\{|\psi_i\rangle_1\}$ and $\{|\psi'_j\rangle_2\}$ are bases of $\mathcal{H}_1$ and $\mathcal{H}_2$ respectively, then $\{|\psi_i\rangle_1 |\psi'_j\rangle_2\}$ will be a basis for $\mathcal{H}$ [5]. That means the number of elements in this basis on $\mathcal{H}$ is the number of basis elements on $\mathcal{H}_1$ times that of $\mathcal{H}_2$.

Extending these ideas to systems with N particles, we can construct the systems using $\mathcal{H} = \bigotimes_{i=1}^{N} \mathcal{H}_i$. Following the idea behind the shorthand on two Hilbert spaces, we will begin using the product notation $\prod_{i=1}^{N} |\psi_i\rangle_i$ instead of the symbol $\bigotimes_{i=1}^{N} |\psi_i\rangle_i$. As an example we can consider a set of N spin-1/2 systems. Taking the tensor product of their Hilbert spaces we find that the dimension grows exponentially with N, namely $\dim \mathcal{H} = 2^N$.

Finally we will consider the operators on the composite Hilbert space. On each $\mathcal{H}_i$ there are operators O_i for the system indexed by i. We call O_i a single particle (or system) operator. The single particle operators on the composite space are of the form

$$\tilde{O}_n := \left(\bigotimes_{i=1}^{n-1} I_i \right) \otimes O_n \otimes \left(\bigotimes_{j=n+1}^{N} I_j \right).$$

For example the Hamiltonian $H_1 := \sum_{n=1}^{N} \tilde{H}_n$ describes a system of N non-interacting particles. Operators that represent interacting particles cannot be written using this simple tensor notation. This increases the difficulty of finding its eigenstates, which is what we often want to know, especially if it is the Hamiltonian of the system.

So from all this we can see how complex of a problem many particle systems can easily become. Since the size of the Hilbert space grows exponentially with the amount of particles, so will the operators. Because these operators also can be complex in themselves, it becomes a great computational problem to find the eigenstates.

2   The Hartree-Fock Method

In light of the discussion on the complexity of many body quantum systems, it seems impossible to solve such a system in an exact way. For this reason we turn to approximations. We are in particular interested in systems with identical fermionic particles because most atoms and molecules consist of a lot of identical fermions, namely electrons, protons, and neutrons. The approximation we will use for this is the Hartree-Fock method, for which the underlying assumption is that the state vector of a system is described by a particular state called a Slater determinant. In this section we will find an expression for the expectation energy of such a state. According the the variational principle, we will then have an upper limit for the ground state energy for the system's Hamiltonian.

If we have a Hilbert space $\mathcal{H}_0$ and N orthonormal states $|1\rangle, \ldots, |N\rangle$ in $\mathcal{H}_0$, then we define the Slater determinant as

$$|\Psi\rangle := \frac{1}{\sqrt{N!}} \begin{vmatrix} |1\rangle_1 & \cdots & |N\rangle_1 \\ \vdots & \ddots & \vdots \\ |1\rangle_N & \cdots & |N\rangle_N \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} |\sigma(i)\rangle_i, \tag{2.1}$$

where the subscripts denotes the index used for the particles. The sum is over all permutations σ in the group of N-element permutations, S_N. The Slater determinant is anti-symmetric under particle exchange and is used to describe fermionic states. There is a similar construction for bosons called the Slater permanent which is eq. (2.1) but without the sgn for the permutation.

Any interaction between N particles is characterized by an operator H_{int} on $\mathcal{H} = \mathcal{H}_0^{\otimes N}$. We distinguish this from the single particle operators in that the interaction operator H_{int} cannot necessarily be written as a tensor product of single particle operators. The Hamiltonian we will consider in this thesis consists of a sum of single particle Hamiltonians and a sum of all interactions between two different particles i, j,

$$H = \sum_{i=1}^{N} \tilde{H}_i + \frac{1}{2} \sum_{i \neq j}^{N} H_{ij}.$$

The interaction potential H_{ij} is assumed symmetric in it's two indices and acts as an identity on particles that are not i nor j.

The expectation of the Hamiltonian for a Slater determinant is

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} \langle \Psi | \tilde{H}_i | \Psi \rangle + \frac{1}{2} \sum_{i \neq j}^{N} \langle \Psi | H_{ij} | \Psi \rangle$$

$$= \frac{1}{N!} \sum_{\sigma, \mu \in S_N} \text{sgn}(\sigma) \text{sgn}(\mu) \left[\sum_{i=1}^{N} \left(\prod_{k \neq i}^{N} \delta_{\sigma(k)}^{\mu(k)} \right) {}_i\langle \sigma(i) | H_i | \mu(i) \rangle_i \right.$$

$$\left. + \frac{1}{2} \sum_{i \neq j}^{N} \left(\prod_{k \neq i,j}^{N} \delta_{\sigma(k)}^{\mu(k)} \right) {}_j\langle \sigma(j) |_i \langle \sigma(i) | H_{ij} | \mu(i) \rangle_i \, | \mu(j) \rangle_j \right]. \tag{2.2}$$

Using the derivation in Appendix A this reduces to

$$\langle \Psi | H | \Psi \rangle = \frac{1}{N} \sum_{i=1}^{N} \sum_{k=1}^{N} {}_i\langle k | H_i | k \rangle_i + \frac{1}{2N(N-1)} \sum_{i \neq j}^{N} \sum_{k \neq l}^{N} \left[{}_j\langle l |_i \langle k | H_{ij} | k \rangle_i \, | l \rangle_j - {}_j\langle l |_i \langle k | H_{ij} | l \rangle_i \, | k \rangle_j \right].$$

It is impossible to distinguish between the particles because they are identical. This means that we cannot label the Hamiltonians, because it is physically impossible to know which identical particle it corresponds to. Therefore we will instead use a single particle operator so $H_i = H_1$ for all $i \in [N]$[1] and similarly an interaction potential so $H_{ij} = H_2$ for all $i \neq j$. This lets us write the expectation energy as

$$\langle \Psi | H | \Psi \rangle = \sum_{k=1}^{N} \langle k | H_1 | k \rangle + \frac{1}{2} \sum_{k \neq l}^{N} \left[\langle l | \langle k | H_2 | k \rangle | l \rangle - \langle l | \langle k | H_2 | l \rangle | k \rangle \right]. \tag{2.3}$$

Note that for the Slater permanent the minus sign in the square brackets would have been a plus. We can make eq. (2.3) nicer by letting the sum run over all $k, l \in [N]$, as the $k = l$ terms cancel,

$$\langle \Psi | H | \Psi \rangle = \sum_{k=1}^{N} \langle k | H_1 | k \rangle + \frac{1}{2} \sum_{k,l=1}^{N} \left[\langle l | \langle k | H_2 | k \rangle | l \rangle - \langle l | \langle k | H_2 | l \rangle | k \rangle \right]. \tag{2.4}$$

This is the general expression for the expectation energy of a Slater determinant which gives us an expression for the upper limit of the ground state energy. We see that the expected energy consists of the total single particle energies and a more complex interaction part.

We will in the next section try to minimize the expectation energy using functional derivatives. In preparation for that, we will look at Slater determinants that consists only of spacial and spin parts. This can be done by writing each state the Slater determinant consists of as $|k\rangle = |\alpha_k\rangle \otimes |\sigma_k\rangle$, where α_k is the spacial part and σ_k is the spin part. This lets us pick the position basis for the spacial part of the state by projecting $\psi_k(\mathbf{r}) := \langle \mathbf{r} | \alpha_k \rangle$. We do this to each single state particle in the Slater determinant by writing $\psi_k(\mathbf{r}_i) = \langle \mathbf{r}_i | \alpha_k \rangle$ where $\mathbf{r}_i$ is the coordinates of the i'th particle such that

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \mathrm{sgn}(\sigma) \prod_{i=1}^{N} \psi_{\sigma(i)}(\mathbf{r}_i). \tag{2.5}$$

If we further assume the Hamiltonians H_1 and H_2 are independent of spin so we can restate eq. (2.4) explicitly in this basis:

$$\langle \Psi | H | \Psi \rangle = \sum_{k=1}^{N} \int \psi_k^*(\mathbf{r}') H_1(\mathbf{r}') \psi_k(\mathbf{r}') \, \mathrm{d}\mathbf{r}'$$
$$+ \frac{1}{2} \sum_{k,l=1}^{N} \iint \psi_l^*(\mathbf{r}_2) \psi_k^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r}_2) \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2) \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2$$
$$- \frac{1}{2} \sum_{k,l=1}^{N} \delta_{\sigma_k}^{\sigma_l} \iint \psi_k^*(\mathbf{r}_2) \psi_l^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r}_2) \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2) \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2. \tag{2.6}$$

To get a better idea of what the two interaction terms are in eq. (2.4), we can try using the Coulomb potential $H_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\varepsilon_0} \frac{Q^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$. The first term is then

$$\iint \frac{1}{4\pi\varepsilon_0} \frac{\left[Q |\psi_k(\mathbf{r}_1)|^2 \right] \left[Q |\psi_l(\mathbf{r}_2)|^2 \right]}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2,$$

which looks like a classical Coulomb interaction between the two charge densities $\rho_k(\mathbf{r}) = Q |\psi_k(\mathbf{r})|^2$ and $\rho_l(\mathbf{r}) = Q |\psi_l(\mathbf{r})|^2$. The second term is harder to interpret. Firstly, it does not contribute to the expectation energy when two states have different spin, even for an interaction that only depends on the position and charge of the particles. Secondly, we cannot interpret

$$\iint \frac{1}{4\pi\varepsilon_0} \frac{[Q \psi_l^*(\mathbf{r}_1) \psi_k(\mathbf{r}_1)] [Q \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)]}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2$$

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[1]The shorthand $[N]$ denotes the set $\{1, 2, \ldots, N\}$.

as two distinct charge densities from each state because the states share the same particle positions in the expression. So this term does not have an easy classical counterpart as compared to the first term. Usually this term is called an exchange integral [2] since it is similar to the Coulomb term above, but two indices are exchanged.

2.1 The Hartree-Fock equation

Because we now have a way of getting an upper limit for the ground state energy, it would be in our best interest to find the lowest upper limit we can using the Hartree-Fock method. To do this, we will minimize eq. (2.6) over all possible Slater determinants using functional derivatives. From this we will get a set of N coupled differential equations that can be used to find extrema to the expectation energy and therefore also minima.

To get the coupled differential equations, we will minimize the expectation energy w.r.t. each single particle wave function $\psi_q(\mathbf{r})$ under the condition that they are all normalized. To do this we introduce a set of Lagrange multipliers ε_q and instead minimize $\langle\Psi|H|\Psi\rangle = \langle\Psi|H|\Psi\rangle + \sum_{k=1}^N \varepsilon_k \left[1 - \int |\psi_k(\mathbf{r})|^2 \, d\mathbf{r} \right]$. Because functionals are extremized when their functional derivatives are zero, the condition we want to enforce is

$$0 \overset{!}{=} \frac{\partial \langle\Psi|H|\Psi\rangle}{\partial \psi_q^*(\mathbf{r})} = \frac{\partial}{\partial \psi_q^*(\mathbf{r})} \left(\sum_{k=1}^N \int \psi_k^*(\mathbf{r}')(H_1(\mathbf{r}') - \varepsilon_q)\psi_k(\mathbf{r}') \, d\mathbf{r}' + \varepsilon_k \right. \tag{2.7a}$$

$$+ \frac{1}{2} \sum_{k,l=1}^N \iint \psi_l^*(\mathbf{r}_2)\psi_k^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r}_2)\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{2.7b}$$

$$\left. - \frac{1}{2} \sum_{k,l=1}^N \delta_{\sigma_k}^{\sigma_l} \iint \psi_k^*(\mathbf{r}_2)\psi_l^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r}_2)\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \right). \tag{2.7c}$$

Functional derivatives are considered in [4], but we will give a brief introduction on how to use them. The general rule for this kind of functional derivative is to move $\partial/\partial\psi_q^*(\mathbf{r})$ inside the integral and use $\frac{\partial \psi_k^*(\mathbf{r}')}{\partial \psi_{k'}^*(\mathbf{r})} = \delta_k^{k'}\delta(\mathbf{r} - \mathbf{r}')$. We further note the product rule works as expected with functional derivatives. The reason we use the complex conjugate of $\psi_q(\mathbf{r})$ is because it spares us from doing a complex conjugation at the end of the calculations.

First we see that line (2.7a) is just $(H_1(\mathbf{r}) - \varepsilon_q)\psi_q(\mathbf{r})$. The second line is

$$(2.7b) = \frac{1}{2} \sum_{k=1}^N \int \psi_k^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r})\psi_k(\mathbf{r}_1)\psi_q(\mathbf{r}) \, d\mathbf{r}_1 + \frac{1}{2} \sum_{l=1}^N \int \psi_l^*(\mathbf{r}_2) H_2(\mathbf{r}, \mathbf{r}_2)\psi_q(\mathbf{r})\psi_l(\mathbf{r}_2) \, d\mathbf{r}_2 \,,$$

and finally the third line gives

$$(2.7c) = -\frac{1}{2} \sum_{l=1}^N \delta_{\sigma_q}^{\sigma_l} \int \psi_l^*(\mathbf{r}_1) H_2(\mathbf{r}_1, \mathbf{r})\psi_q(\mathbf{r}_1)\psi_l(\mathbf{r}) \, d\mathbf{r}_1 - \frac{1}{2} \sum_{k=1}^N \delta_{\sigma_k}^{\sigma_q} \int \psi_k^*(\mathbf{r}_2) H_2(\mathbf{r}, \mathbf{r}_2)\psi_k(\mathbf{r})\psi_q(\mathbf{r}_2) \, d\mathbf{r}_2 \,.$$

By changing the labelling in the sum $l \to k$, we can simplify eq. (2.7) to

$$\varepsilon_q \psi_q(\mathbf{r}) = H_1(\mathbf{r})\psi_q(\mathbf{r}) + \left[\sum_{k=1}^N \int \psi_k^*(\mathbf{r}') H_2(\mathbf{r}, \mathbf{r}')\psi_k(\mathbf{r}') \, d\mathbf{r}' \right] \psi_q(\mathbf{r})$$

$$- \int \left[\sum_{k=1}^N \delta_{\sigma_k}^{\sigma_q} \psi_k^*(\mathbf{r}') H_2(\mathbf{r}, \mathbf{r}')\psi_k(\mathbf{r}) \right] \psi_q(\mathbf{r}') \, d\mathbf{r}' \,. \tag{2.8}$$

The terms in the square brackets defines the Hartree and Fock potentials, respectively:

$$V_H(\mathbf{r}) := \sum_{k=1}^N \int \psi_k^*(\mathbf{r}') H_2(\mathbf{r}, \mathbf{r}')\psi_k(\mathbf{r}') \, d\mathbf{r}' \quad \text{and} \quad V_F^q(\mathbf{r}, \mathbf{r}') := -\sum_{k=1}^N \delta_{\sigma_k}^{\sigma_q} \psi_k^*(\mathbf{r}') H_2(\mathbf{r}, \mathbf{r}')\psi_k(\mathbf{r}),$$

and thereby we establish the Hartree-Fock (HF) equation

$$\varepsilon_q \psi_q(\mathbf{r}) = \left(H_1(\mathbf{r}) + V_H(\mathbf{r})\right) \psi_q(\mathbf{r}) + \int V_F^q(\mathbf{r}, \mathbf{r}') \psi_q(\mathbf{r}') \, \mathrm{d}\mathbf{r}' \,. \tag{2.9}$$

This is the coupled differential equations we talked about at the start of this section, but since they are of the same form, we use the same name for all of them. So if we find a set of N orthonormal states that all fulfill these equations, they will extemize the expectation energy. It it important to notice that there may exist a set of states that are not orthogonal, but still fulfill eq. 2.9, so it is crucial to ensure that they are all orthogonal when trying to find minima of the expectation energy using the Hartree-Fock equation. For a bosonic state, using the Slater permanent, the sums in V_H and V_F would be over $k \in [N] \setminus \{q\}$ and the minus sign in V_F would not be there.

Looking back to the Coulomb interaction, the Hartree potential is akin to an electric potential with charge distribution $Q \sum_{k=1}^{N} |\psi_k(\mathbf{r}')|^2$,

$$V_H(\mathbf{r}) = \frac{Q}{4\pi\varepsilon_0} \int \frac{Q \sum_{k=1}^{N} |\psi_k(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \,.$$

This would suggest the Hartree potential accounts for a Coulomb interaction between the particles. The interpretation of the Fock potential is more complicated, firstly the terms in the sum are zero for states which have non-equal spin and secondly it acts on the state $\psi_q(\mathbf{r}')$ non-locally by integrating over $\mathbf{r}'$.

The right hand side of the HF equation can be interpreted as a mean field Hamiltonian H_{MF} that acts on the wave function ψ by

$$H_{\mathrm{MF}}(\psi) := \left(H_1(\mathbf{r}) + V_H(\mathbf{r})\right) \psi(\mathbf{r}) + \int V_F^q(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \, \mathrm{d}\mathbf{r}' \,. \tag{2.10}$$

A particular collection of subsets of the eigenstates of this mean field Hamiltonian is of great interest; namely the subsets of states that can be put into the definitions of the Hartree and Fock potentials and give the same mean field Hamiltonian. We shall call such a collection of states *self consistent* states. Each state in a self consistent collection $\{\psi_q(\mathbf{r})\}$ satisfies the HF equation, and therefore comprise a Slater determinant, if they are orthogonal, that extremizes its expectation energy. Finally note that because of the construction of the Fock potential, the mean field Hamiltonian might act differently on states with different spin even though we assumed the interaction to be independent of spin. An interesting special case is when there are N particles, with N being a multiple of $2s + 1$, from which a spacial degeneracy can arise between states of different spin.

2.2 Relation Between Energy and Lagrange Multipliers

Usually when Lagrange multipliers are introduced in some physical system they have some relation to something physically measurable (for example in statistical mechanics β is related to temperature). As we will show, there is a physical relation between the Lagrange multipliers ε_q and the expectation energy of the Slater determinant.

Using (2.8), we can simply multiply by $\psi_q^*(\mathbf{r})$, integrate over $\mathbf{r}$, and sum over all $q \in [N]$, from which we then find

$$\sum_{q=1}^{N} \varepsilon_q \int |\psi_q(\mathbf{r})|^2 \, \mathrm{d}\mathbf{r} = \sum_{q=1}^{N} \int \psi_q \left(H_1(\mathbf{r}) + V_H(\mathbf{r})\right) \psi_q(\mathbf{r}) \, \mathrm{d}\mathbf{r} + \iint \psi_q(\mathbf{r}) V_F^q(\mathbf{r}, \mathbf{r}') \psi_q(\mathbf{r}') \, \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r}$$

$$= \sum_{q=1}^{N} \int \psi_q^*(\mathbf{r}) H_1(\mathbf{r}) \psi_q(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$

$$+ \sum_{k,q=1}^{N} \iint \psi_q^*(\mathbf{r}) \psi_k^*(\mathbf{r}') H_2(\mathbf{r}', \mathbf{r}) \psi_k(\mathbf{r}') \psi_q(\mathbf{r}) \, \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r}$$

$$- \sum_{k,q=1}^{N} \delta_{\sigma_q}^{\sigma_k} \iint \psi_k^*(\mathbf{r}) \psi_k^*(\mathbf{r}') H_2(\mathbf{r}', \mathbf{r}) \psi_k(\mathbf{r}) \psi_q(\mathbf{r}') \, \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r} \,.$$

Under the imposed normalization condition $\int |\psi_q(\mathbf{r})|^2 \, d\mathbf{r} = 1$ and by defining the single particle energies $E_q := \int \psi_q^*(\mathbf{r}) H_1(\mathbf{r}) \psi_q(\mathbf{r}) \, d\mathbf{r}$ we have the following relation,

$$\langle \Psi | H | \Psi \rangle = \frac{1}{2} \sum_{q=1}^{N} (E_q + \varepsilon_q). \tag{2.11}$$

The terms in the sum, $(E_q + \varepsilon_q)/2$, can be perceived as the *effective single state energy* for a specific state $|q\rangle$.

3   The Time Dependent Variational Principle

We now turn our attention to the dynamics of a system. Usually we would turn to the time dependent Schrödinger equation (TDSE), however we have already established that the Hamiltonian of a big system is incredibly hard to work with. It is the goal of this section to find an approximation to the dynamics for such systems.

The method we will use is called the time dependent variational principle (TDVP), so we will start by giving a brief review of it. This introduction will largely be based on meetings with our supervisors, and [6]. For a system described by a state vector $|\psi\rangle$ we start with the Lagrangian

$$L = \langle \psi | i\hbar \partial_t - H | \psi \rangle.$$

To obtain the equations that govern the dynamics of the system we have to use the principle of least action. This principle states that the action $S = \int_{t_1}^{t_2} L \, dt$ is stationary, that is $\delta S = 0$. To see that this gives the TDSE we let $\psi^*(\mathbf{r})$ vary,

$$\delta S = \int_{t_1}^{t_2} \int \delta \psi^*(\mathbf{r}, t)(i\hbar \partial_t - H)\psi(\mathbf{r}, t) \, d\mathbf{r} \, dt = 0.$$

For this to be zero for all possible variations, we must have $(i\hbar \partial_t - H)\psi(\mathbf{r}, t) = 0$. Formally this is an argument using the fundamental lemma of the Calculus of variations, [9]. In other words, $\psi(\mathbf{r}, t)$ has to satisfy the TDSE, $i\hbar \partial_t \psi(\mathbf{r}, t) = H\psi(\mathbf{r}, t)$. Note that if we had used $\psi(\mathbf{r})$ as a variational parameter we would have gotten the complex conjugate of the TDSE.

A more general way to use this principle is to use wave functions that are parametrized $|\psi(\mathbf{s})\rangle$ by a set of parameters $\mathbf{s} = \begin{pmatrix} s_1 & s_2 & \dots & s_n \end{pmatrix}$. When the Lagrangian depends on these parameters $L(\mathbf{s}, \dot{\mathbf{s}}, t) = \langle \psi(\mathbf{s}) | i\hbar \partial_t - H | \psi(\mathbf{s}) \rangle$, the principle of least action then tells us that the action has to be stationary w.r.t each of these parameters. For this the Euler-Lagrange equations for the parameters is used,

$$\frac{\partial L}{\partial s_i} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{s}_i} = 0.$$

These gives us the effective equations of motion for the parameters $\mathbf{s}$. For an example of how to use this method for a simple spin-1/2 system see Appendix B.

3.1   The Time Dependent Hartree-Fock Equation

We now use the TDVP on the single particle wave functions $\psi_k(\mathbf{r}, t)$ in the Slater determinant as variational parameters. The time dependency of the single particle state $|k\rangle$ at a time t is denoted $|k; t\rangle$. The Slater determinant is then

$$|\Psi; t\rangle := \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} |\sigma(i); t\rangle_i.$$

In position basis the individual wave functions are $\psi_k(\mathbf{r}_i, t) := \langle \mathbf{r}_i | k; t\rangle$ such that the Slater determinant wave function is

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} \psi_{\sigma(i)}(\mathbf{r}_i, t). \tag{3.1}$$

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The methodology is to minimize the action w.r.t. each single particle wave function $\psi_k(\mathbf{r}, t)$ and thereby find an 'equation of motion' for this state. We will therefore consider each wave function as a variable parameter and collect these in a vector $\boldsymbol{\psi}(\mathbf{r}, t) := \begin{pmatrix} \psi_1(\mathbf{r}, t) & \psi_2(\mathbf{r}, t) & \dots & \psi_N(\mathbf{r}, t) \end{pmatrix}$. In general, consider a state $|\Psi; t\rangle$ which depend on each element in the vector $\boldsymbol{\psi}$, then the Lagrangian of this state is

$$L(\boldsymbol{\psi}, \dot{\boldsymbol{\psi}}, t) = \langle \Psi; t | i\hbar\partial_t - H | \Psi; t \rangle = \langle \Psi; t | i\hbar\partial_t | \Psi; t \rangle - \langle \Psi; t | H | \Psi; t \rangle. \tag{3.2}$$

We shall now calculate each term for the state $|\Psi; t\rangle$ being the Slater determinant, starting with $\langle \Psi; t | H | \Psi; t \rangle$. This term is equivalent to eq. (2.4), however as these earlier calculations were time independent we may change the notation in the equation; $|k\rangle \to |k; t\rangle$, $H_1 \to H_1(t)$ and $H_2 \to H_2(t)$ to indicate their time dependency. The second term $\langle \Psi; t | i\hbar\partial_t | \Psi; t \rangle$ is

$$\langle \Psi(t) | i\hbar\partial_t | \Psi(t) \rangle = \frac{1}{N!} \sum_{\sigma, \mu \in S_N} \mathrm{sgn}(\sigma)\mathrm{sgn}(\mu) \left[\prod_{i=1}^{N} {}_i\langle \sigma(i); t | \right] i\hbar\partial_t \left[\prod_{j=1}^{N} |\mu(j); t\rangle_j \right]$$

$$= \frac{1}{N!} \sum_{\sigma, \mu \in S_N} \mathrm{sgn}(\sigma)\mathrm{sgn}(\mu) \sum_{k=1}^{N} \left[\prod_{i \neq k}^{N} {}_i\langle \sigma(i); t | \right] {}_k\langle \sigma(k); t | i\hbar\partial_t | \mu(k); t\rangle_k \left[\prod_{j \neq k}^{N} |\mu(j); t\rangle_j \right]$$

$$= \frac{1}{N!} \sum_{\sigma, \mu \in S_N} \mathrm{sgn}(\sigma)\mathrm{sgn}(\mu) \sum_{k=1}^{N} \prod_{i \neq k}^{N} \delta_{\sigma(i) k}^{\mu(i)} {}_k\langle \sigma(k); t | i\hbar\partial_t | \mu(k); t\rangle_k. \tag{3.3}$$

The last equality has a similar structure to eq. (2.2) which we have already reduced, therefore establishing

$$\langle \Psi(t) | i\hbar\partial_t | \Psi(t) \rangle = \sum_{k=1}^{N} \langle k; t | i\hbar\partial_t | k; t \rangle. \tag{3.4}$$

Substituting eq. (2.4) with its notational change and eq. (3.4) into their respective terms of eq. (3.2), we obtain the Lagrangian

$$L(\boldsymbol{\psi}, \dot{\boldsymbol{\psi}}, t) = \sum_{k=1}^{N} \langle k; t | i\hbar\frac{\partial}{\partial t} - H_1 | k; t \rangle - \frac{1}{2} \sum_{k \neq l}^{N} \left[\langle l; t | \langle k; t | H_2 | k; t \rangle | l; t \rangle - \langle l; t | \langle k; t | H_2 | l; t \rangle | k; t \rangle \right].$$

The next step is to minimize the action $S := \int_{t_1}^{t_2} L(\boldsymbol{\psi}, \dot{\boldsymbol{\psi}}, t) \, \mathrm{d}t$ w.r.t the vector $\boldsymbol{\psi}$. That is, varying the parameters of $\boldsymbol{\psi}$ such that $\frac{\partial S}{\partial \boldsymbol{\psi}} = 0$. This condition is equivalent to the Lagrangian satisfying the Euler-Lagrange equations for each $\psi_q^*(\mathbf{r}, t)$. For simplicity we will define the operator

$$T_q := \frac{\partial}{\partial \psi_q^*(\mathbf{r}, t)} - \frac{\partial}{\partial t} \frac{\partial}{\partial \dot{\psi}_q^*(\mathbf{r}, t)},$$

such that the Euler-Lagrange equation for $\psi_q^*(\mathbf{r}, t)$ is $T_q L = 0$. We will now let this operator act on each term of (3.2) separately, starting with $\langle \Psi; t | i\hbar\partial_t | \Psi; t \rangle$

$$T_q \left(\sum_{k=1}^{N} \int \psi_k^*(\mathbf{r}', t) i\hbar\frac{\partial}{\partial t} \psi_k(\mathbf{r}', t) \, \mathrm{d}\mathbf{r}' \right) = i\hbar\frac{\partial}{\partial t} \psi_q(\mathbf{r}, t). \tag{3.5}$$

The second term, $\langle \Psi; t | H | \Psi; t \rangle$, is independent of $\dot{\psi}_q$ such that it reduces to $T_q \langle \Psi; t | H | \Psi; t \rangle = \frac{\partial}{\partial \psi_q(\mathbf{r}, t)} \langle \Psi; t | H | \Psi; t \rangle$. This expression is similar to the one used to find the HF equation in Section 2.1. In fact, it is just the right hand side of eq. (2.9), except all terms are now time-dependent with respect to the wave functions

$$T_q \langle \Psi; t | H | \Psi; t \rangle = \left[H_1(\mathbf{r}, t) + V_H(\mathbf{r}, t) \right] \psi_q(\mathbf{r}) + \int V_F^q(\mathbf{r}, \mathbf{r}', t) \psi_q(\mathbf{r}') \, \mathrm{d}\mathbf{r}'. \tag{3.6}$$

Rearranging $T_q L$ by setting eq. (3.5) equal to (3.6) we then obtain the the Time Dependent Hartree Fock (TDHF) equation

$$i\hbar\frac{\partial\psi_q(\mathbf{r},t)}{\partial t} = [H_1(\mathbf{r},t) + V_H(\mathbf{r},t)]\,\psi_q(\mathbf{r},t) + \int V_F^q(\mathbf{r},\mathbf{r}',t)\psi_q(\mathbf{r}',t)\,\mathrm{d}\mathbf{r}'\,. \tag{3.7}$$

The result is the equations of motion of the parameters which in this case is ψ_q. The TDHF equation is similar to time dependent Schödinger equation, which can be seen if we write it using our (time-dependent) mean field Hamiltonian H_{MF}

$$i\hbar\frac{\partial\psi(t)}{\partial t} = H_{\mathrm{MF}}(\psi(t)). \tag{3.8}$$

This equation simply tells us how the single particle states that comprise a Slater determinant have to change in time. In the case when H_1 and H_2 are time independent, a set of self consistent wave functions $\{\psi_q\}_{q\in[N]}$ are stationary for the TDHF equation. By this we mean that $\psi_q(\mathbf{r},t) = \psi_q(\mathbf{r})e^{-i\varepsilon_q t/\hbar}$ solves eq. (3.8). This can be seen by first noting that all the phases cancel in $H_{\mathrm{MF}}(t)$ by definition of the Hartree-Fock potentials, which means it will be constant in time. From this, it is easy to see that the phase changing set of self consistent wave functions solves the TDHF equation.

To ensure that a collection of states $\{\psi_i\}_{i\in[N]}$ that solve the TDHF equation remain normalized over time, we check that $\int|\psi_q(\mathbf{r},t)|^2\,\mathrm{d}\mathbf{r}$ is constant in time. This can be shown by first using the following expansion:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int|\psi_q(\mathbf{r},t)|^2\,\mathrm{d}\mathbf{r} = \int\frac{\partial|\psi_q(\mathbf{r},t)|^2}{\partial t}\,\mathrm{d}\mathbf{r} = \int\psi_q^*(\mathbf{r},t)\frac{\partial\psi_q(\mathbf{r},t)}{\partial t} + \frac{\partial\psi_q^*(\mathbf{r},t)}{\partial t}\psi_q(\mathbf{r},t)\,\mathrm{d}\mathbf{r}\,,$$

and then secondly substituting eq. 3.7 into it. From this we get that the normalization is constant in time because its derivative is zero.

4   Setup of Numerical Calculations

The Hartree-Fock equation is a system of coupled differential equations, which can be hard at best, and impossible at worst, to solve analytically. Therefore we will try to find solutions to it numerically instead by developing an algorithm that can be implemented in a program. To do this however, we have to construct the necessary operators, so we are able to calculate all the quantities we want. This includes basic operators, the mean field Hamiltonian, and the expectation energy.

To start off with we will introduce our discrete space, so let $X = \{x_i\}_{i\in[n]} \subset \mathbb{R}$ be a set of n points with $\Delta x_i = x_{i+1} - x_i$. In this discrete space the state vectors are considered functions $f : X \to \mathbb{C}$.

4.1   Construction of The Discrete Operators

Now we will construct the functions we need on the discrete space, which can then be turned into matrices that can be used in a program. Let $f : X \to \mathbb{C}$ and we will immediately assume that $\Delta x = \Delta x_i$ for all $i \in [n]$ for the sake of simplicity–although not strictly required. The central difference quotient of f is defined as

$$\frac{\Delta f}{\Delta x} = \frac{f(x + \Delta x/2) - f(x - \Delta x/2)}{\Delta x},$$

and is useful, because $\Delta f/\Delta x \to \frac{\mathrm{d}f}{\mathrm{d}x}$ in the limit where $n \to \infty$. The second difference quotient is similarly defined by

$$\frac{\Delta^2 f}{\Delta x^2} = \frac{\Delta\left(\frac{\Delta f}{\Delta x}\right)}{\Delta x} = \frac{f(x + \Delta x) + f(x - \Delta x) - 2f(x)}{\Delta x^2}, \tag{4.1}$$

with the same property of converging to the second order differential. Integrals can be made discrete too just like differentials. This can be done by using middle sums. In this construction, we can pick

a $\xi_i \in [x_i, x_{i+1}]$ for each $i \in [n]$, but the simple $\xi_i = x_i$ is easier to work with. From this we have the correspondence

$$\int f(x)\,\mathrm{d}x \sim \sum_{i=1}^{n} f(x_i)\Delta x.$$

Using these operators on discritized wave functions $\psi : X \to \mathbb{C}$, we can write the expectation of the Hartree and Fock potentials discreetly. Firstly, the expectation energy becomes

$$E = \sum_{k=1}^{N}\sum_{i=1}^{n} \psi_k^*(x_i)H_1(x_i)\psi_k(x_i)\Delta x \tag{4.2a}$$

$$+ \frac{1}{2}\sum_{i,j=1}^{n}\sum_{k,l=1}^{N} \psi_l^*(x_j)\psi_k^*(x_i)H_2(x_i,x_j)\psi_k(x_i)\psi_l(x_j)\Delta x^2 \tag{4.2b}$$

$$- \frac{1}{2}\sum_{i,j=1}^{n}\sum_{\sigma\in\Sigma}\sum_{k_\sigma,l_\sigma=1}^{N_\sigma} \psi_{k_\sigma}^*(x_j)\psi_{l_\sigma}^*(x_i)H_2(x_i,x_j)\psi_{k_\sigma}(x_i)\psi_{l_\sigma}(x_j)\Delta x^2. \tag{4.2c}$$

Here Σ is the set of possible spins and $\sum_{k_\sigma}^{N_\sigma}$ is a sum over the states with spin σ. The Hartree and Fock potentials are

$$V_H(x) = \sum_{k=1}^{N}\sum_{i=1}^{n} \psi_k^*(x_i)H_2(x,x_i)\psi_k^*(x_i)\Delta x \quad\text{and}\quad V_F^q(x,x') = -\sum_{k=1}^{N}\delta_{\sigma_k}^{\sigma_q}\psi_k^*(x')H_2(x,x')\psi_k(x). \tag{4.3}$$

Considering the Fock potential, we can rewrite the integral of the Fock potential acting on the q'th state as following

$$\int V_F^q(\mathbf{r},\mathbf{r}')\psi_q(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \sim -\sum_{i=1}^{n}\sum_{k=1}^{N}\delta_{\sigma_k}^{\sigma_q}\psi_k^*(x_i)H_2(x,x_i)\psi_k(x)\psi_q(x_i)\Delta x. \tag{4.4}$$

4.2 Basis of Finite Vector Space

To implement the above functions, we will now rewrite them as matrices that can act on vectors or other matrices. To do this we start with our wave functions $\psi : X \to \mathbb{C}$ which can be represented by the column vector $\psi = \begin{pmatrix}\psi(x_1) & \ldots & \psi(x_n)\end{pmatrix}^T$. With this, we can write the kinetic operator $T = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$ as a matrix that can act on ψ by using eq. (4.1)

$$T = -\frac{\hbar^2}{2m\Delta x^2}\begin{pmatrix} -2 & 1 & & \\ 1 & -2 & \ddots & \\ & \ddots & \ddots & 1 \\ & & 1 & -2 \end{pmatrix}.$$

Similarly the way V_0 and V_H acts on the vector ψ motivates the following definitions

$$V_0 := \mathrm{diag}(V(x_1),\ldots,V(x_n)) \quad\text{and}\quad V_H := \mathrm{diag}(V_H(x_1),\ldots,V_H(x_n)). \tag{4.5}$$

To tackle the Fock potential and the energy, it is worthwhile to store all our wave functions in one matrix, so let $\{\psi_q\}_{q\in[N]}$ be a collection of column vectors. By putting the vectors together into a n-by-N matrix $\Phi := \begin{pmatrix}\psi_1 & \psi_2 & \ldots & \psi_N\end{pmatrix}$ such that $\Phi_{ij} = \psi_j(x_i)$, we see as a first result that

$$(\Phi\Phi^\dagger)_{ij} = \sum_{k=1}^{N}\Phi_{ik}(\Phi^\dagger)_{kj} = \sum_{k=1}^{N}\Phi_{ik}\Phi_{jk}^* = \sum_{k=1}^{N}\psi_k(x_i)\psi_k^*(x_j).$$

To simplify the notation for the interaction potential, we will introduce the matrix $(H_2)_{ij} = H_2(x_i, x_j)$. By multiplying $(H_2)_{ij} = (H_2)_{ji}$ onto each index in $(\Phi\Phi^\dagger)_{ij}$ we may define the matrix of the Fock potential, that acts on states with specific spin σ, by its indices

$$(V_F^\sigma)_{ij} := -(\Phi\Phi^\dagger)_{ij}(H_2)_{ji}\Delta x = -\sum_{k=1}^N \psi_k(x_i)\psi_k^*(x_j)H_2(x_j, x_i)\Delta x. \qquad (4.6)$$

To justify this definition we check that this matrix acts on a state ψ_q with spin σ in similar way as eq. (4.4) evaluated at $x = x_i$

$$(V_F^\sigma\psi_q)_i = \sum_{j=1}^n (V_F)_{ij}(\psi_q)_j = -\sum_{j=1}^n\sum_{k=1}^N \psi_k(x_i)\psi_k^*(x_j)H_2(x_j, x_i)\psi_q(x_j)\Delta x.$$

From this we can construct the previously discussed mean field Hamiltonian

$$H_{\text{MF}}^\sigma := T + V + V_H + V_F^\sigma.$$

The problem is then to find a set of self consistent eigenstates $(\psi_q)_{q\in[N]}$ to H_{MF}^σ such that $H_{\text{MF}}^\sigma\psi_q = \varepsilon_q\psi_q$ for some constants ε_q using the mean field Hamiltonian that matches the spin of the wave function.

If we naively implemented the expectation energy using eq. (4.2) where it still uses the sums over the wave functions, then it scales badly with the amount of particles in the system. Therefore we will simplify each line of eq. (4.2) to get a expression that only requires some matrix multiplications after a sum over the different spins. For Equation (4.2a), we define $\Theta := \Phi\Phi^\dagger$ and see that

$$(4.2a) = \sum_{k=1}^N\sum_{i=1}^n \Phi_{ik}^* \left[\sum_{j=1}^n (H_1)_{ij}\Phi_{jk}\right]\Delta x = \sum_{k=1}^N\sum_{i=1}^n (\Phi^\dagger)_{ki}(H_1\Phi)_{ik}\Delta x$$

$$= \sum_{k=1}^N (\Phi^\dagger H_1\Phi)_{kk}\Delta x = \text{Tr}[\Phi^\dagger H_1\Phi]\Delta x = \text{Tr}[H_1\Theta]\Delta x.$$

For Equation (4.2b), let us introduce the vector $\Omega_i := \sum_{k=1}^N |\Phi_{ik}|^2$ and the matrix $\Gamma_H := \Omega\Omega^\dagger$. In this notation the term becomes

$$(4.2b) = \frac{1}{2}\sum_{i,j=1}^n\sum_{k,l=1}^N |\Phi_{ik}|^2(H_2)_{ij}|\Phi_{jl}|^2\Delta x^2 = \frac{1}{2}\sum_{i,j=1}^n \Omega_i(H_2)_{ij}\Omega_j\Delta x^2 = \frac{1}{2}\Omega^T H_2\Omega\Delta x^2$$

$$= \frac{1}{2}\text{Tr}\left[\Omega^T H_2\Omega\right]\Delta x^2 = \frac{1}{2}\text{Tr}\left[H_2\Omega\Omega^T\right]\Delta x^2 = \frac{1}{2}\text{Tr}[H_2\Gamma_H]\Delta x^2.$$

For Equation (4.2c) we define the matrices $(\Theta_\sigma)_{ij} := \sum_{k_\sigma=1}^{N_\sigma} \Phi_{ik_\sigma}\Phi_{jk_\sigma}^*$ and $(\Gamma_F)_{ij} := \sum_{\sigma\in\Sigma} |(\Theta_\sigma)_{ij}|^2$ and then get

$$(4.2c) = \frac{1}{2}\sum_{i,j=1}^n\sum_{\sigma\in\Sigma}\sum_{k_\sigma,l_\sigma=1}^{N_\sigma} \Phi_{jk_\sigma}^*\Phi_{il_\sigma}^*(H_2)_{ij}\Phi_{ik_\sigma}\Phi_{jl_\sigma}\Delta x^2$$

$$= \frac{1}{2}\sum_{i,j=1}^n\sum_{\sigma\in\Sigma}(H_2)_{ij}(\Theta_\sigma)_{ij}(\Theta_\sigma)_{ij}^*\Delta x^2 = \frac{1}{2}\sum_{i,j=1}^n (H_2)_{ji}(\Gamma_F)_{ij}\Delta x^2 = \frac{1}{2}\text{Tr}[H_2\Gamma_F]\Delta x^2,$$

where it was used that H_2 is symmetric. It can be useful to introduce the notation Φ_σ, which is a version of Φ where only states with spin σ are included, because it lets us write $\Theta_\sigma = \Phi_\sigma\Phi_\sigma^\dagger$. Putting all this together, the expectation energy is

$$E = \text{Tr}[H_1\Theta]\Delta x + \frac{1}{2}\left(\text{Tr}[H_2\Gamma_H] - \text{Tr}[H_2\Gamma_F]\right)\Delta x^2 = \text{Tr}[H_1\Theta]\Delta x + \frac{1}{2}\text{Tr}[H_2\Gamma]\Delta x^2, \qquad (4.7)$$

where $\Gamma := \Gamma_H - \Gamma_F$.

Now that our mean field operator is constructed and the expectation energy can be calculated, we can implement them in a program that can solve the Hartree-Fock equation numerically without using matrices with dimensions larger than $n \times n$, compared to the exact solution that would require us to compute the eigenstates of a $n^N \times n^N$ Hamiltonian matrix.

4.3   The Algorithm

Oftentimes finding an analytic solution to the Hartree-Fock equation is difficult. It is therefore natural to turn to numeric simulation to find an approximate solution. In this section we will describe our attempt at writing a program that finds the Stater determinant with the least energy numerically.

The program uses a finite set of n discrete points on a section of length L with separation Δx and with the Hamiltonians set up as described in the previous section. To keep track of which wave functions in Φ have what spin, we also use an array that contains the spin of the wave functions using the same state indexing as Φ does.

To start off with, the program uses a set of initial guesses for the wave functions and stores them in Φ. Then an iterative approach is used, where in each iteration it calculates H_{MF} for each spin using the current Φ. It will then change Φ using one of three algorithms we have implemented that are used to find a Slater determinant with lower energy than the previous iteration. The three algorithms are described below.

The first algorithm is called the "lowest state energy" algorithm. It uses a value $0 \le \eta_{\mathrm{it}} \le 1$ as an parameter for defining $H_{\mathrm{MF}}^{\mathrm{it}} := \eta_{\mathrm{it}} H_{\mathrm{MF}} + (1 - \eta_{\mathrm{it}}) H_{\mathrm{MF}}^{\mathrm{old}}$, where $H_{\mathrm{MF}}^{\mathrm{old}}$ is the mean field Hamiltonian from the previous iteration. Here η_{it} is used to control how big a percentage of H_{MF} is used to change $H_{\mathrm{MF}}^{\mathrm{it}}$ between iterations. The algorithm then chooses the eigenfunctions of $H_{\mathrm{MF}}^{\mathrm{it}}$ with lowest effective single state energy and stores them as the new states in Φ. The idea behind using the lowest effective single state energies comes from eq. (2.11), where such a set can give a lower expectation energy.

The second "closest state energy" algorithm also uses the effective single state energies of $H_{\mathrm{MF}}^{\mathrm{it}}$, but instead of choosing the lowest ones, it compares them with the ones from the previous iteration. The comparison is done by finding which new energies are closest to the old energies. The eigenstates for these new energies are then chosen as the new states. This causes conflict when two or more old states (with the same spin) wish to become the same new state. To resolve this we instead let the old energy that is the closest to one of the new energies "choose" the state it wants first. Then that state becomes unavailable for the other old energies and the process is repeated for the one with the next closest energy and so on.

The third "gradient" algorithm calculates the energy gradient of eq. (2.6). This is done by taking the functional derivative with respect to each state, meaning it is calculated using $\nabla E = H_{\mathrm{MF}} \Phi$ (separated by spin) for all states at once. Since the negative of the gradient points towards a set of functions with lower energy, we can get new states using $\Phi^{\mathrm{new}} = \Phi - \eta_{\mathrm{gr}} \nabla E$ where η_{gr} is a variable parameter that controls the step size. The new states might not be normalized nor orthonormal with respect to states with the same spin. So the new states are normalized and then the Gram-Schmidt procedure is applied. It then checks if the energy is lower than before, and if not, it tries again with a lower η_{gr} until a certain threshold where it is reset to a default value, which lets it take larger steps.

The first algorithm to be used in the program is the lowest state energy algorithm. It will then continue to use it each iteration until the new expectation energy is greater than the previous expectation energy. When this happens, the old states will be restored and the program will switch to the closest state energy algorithm. Now the same thing happens if the expectation energy is greater, except it will begin using the gradient algorithm until it is unable to find an η_{gr} that lowers the expectation energy within a set amount of iterations. When this happens, it will go back to using the lowest eigenvalue algorithm.

The program will continue to run like this until it reaches a convergence criterion which is a value between 0, which is zero convergence, and 1, which is perfect convergence. The convergence itself is calculated by first finding $\Phi_{\mathrm{HF}} := H_{\mathrm{MF}} \Phi$ (separated by spin). We would expect a perfect convergence if all the states were eigenfunctions to H_{MF}, since it would then fulfill eq. (2.9). To capture this, we first normalize each function in Φ_{HF} so they become $\Phi_{\mathrm{HF}}^{\mathrm{norm}}$ and then define the convergence as $C := \langle \Phi_{\mathrm{HF}}^{\mathrm{norm}} | \Phi \rangle$ which is just the product over all the inner products of the states in Φ and $\Phi_{\mathrm{HF}}^{\mathrm{norm}}$.

4.4   Time Evolution

In this section we want to write about a possible implementation of time evolution in a program. For this use the matrix H_{MF} as a generator of translations in time. We now consider wave functions

which are time dependent, i.e. ψ is a map $\psi : \mathbb{R} \to \mathbb{C}^n$ defined by $\psi_q(t) = \begin{pmatrix} \psi_q(x_1, t) & \dots & \psi_q(x_n, t) \end{pmatrix}^T$, where $\psi_q(x, t)$ is the usual wave function on continuous space. The TDHF equation on a discrete set of points $\{x_i\}_{i \in [n]}$ is then

$$i\hbar \frac{\partial}{\partial t} \psi_q(t) = H_{MF}(t) \psi_q(t). \tag{4.8}$$

For a $H_{\text{MF}}(t)$ which is constant in time the solution to eq. (4.8) is

$$\psi_q(t + dt) = e^{-iH_{MF}(t)dt/\hbar} \psi_q(t). \tag{4.9}$$

However, by definition H_{MF} is time dependent. We counter this by expanding $H_{\text{MF}}(t + dt) = \sum_{j=0}^{\infty} \frac{1}{j!} H_{\text{MF}}^{(j)}(t) dt^j$ for some small dt. Particularly in the limit $dt \to 0$, truncating to zeroth order, we have $H_{MF}(t + dt) \approx H_{MF}(t)$.

To include this in the algorithm we use discrete time steps, $t \in \{\dots, -2dt, -dt, 0, dt, 2dt, \dots\}$, and given a state vector $\psi(t)$ at some time t, we can find the state at some later time $\psi(t + dt)$ by eq. (4.9). To give an outline: start with some states Ψ at a time $t = 0$ and then step it forward in time using a small time step dt using the method above. The time step used for this is proportional to $\hbar/E$, just setting $dt = \hbar/E$ does not guarantee stability, and it is usually needed to be scale it down by some factor. Each iteration we then calculate H_{MF} again to be used for the next time step.

Using this implementation, even with a high grid resolution and low time steps, it would always begin to fail. The measure for failure in this context is that the wave functions retain their overall structure, but with significant ripple effects, which grows worse over additional time steps. This implementation is ill suited for an extended number of time steps, although a more complex algorithm might be able to do this.

5 Simulating Using The 1D Electrostatic Potential

To work with electrostatic potentials in one dimension, we will generalize three dimensional electrostatics using Gauss law $\boldsymbol{\nabla} \cdot \mathbf{E} = \rho(\mathbf{r})/\varepsilon_0$. If we assume that the electric field is rotationally symmetric then we get

$$\frac{Q_{\text{enc}}}{\varepsilon_0} = \frac{1}{\varepsilon_0} \int_V \rho(\mathbf{r}) \, \mathrm{d}^n \mathbf{r} = \int_V \boldsymbol{\nabla} \cdot E(\mathbf{r}) \, \mathrm{d}^n \mathbf{r} = \int_A E(\mathbf{r}) \cdot \mathrm{d}^n \mathbf{a} = \sigma_{n-1} r^{n-1} E(r),$$

where σ_{n-1} is the surface area of a n-dimensional unit sphere, which can be calculated using Corollary 16.21 in [8], from which we get

$$E(r) = \frac{Q_{\text{enc}}}{[2\pi^{n/2}/\Gamma(n/2)]\varepsilon_0} \frac{1}{r^{n-1}} \overset{\text{1D}}{\equiv} \frac{Q_{\text{enc}}}{2\varepsilon_0}.$$

If $\rho(\mathbf{r})$ is just a point charge at some point x_0, then Q_{enc} will just be a constant Q for all radii. Describing the direction of the electric field using the sgn function

$$E(x) = \frac{Q}{2\varepsilon_0} \text{sgn}(x - x_0)$$

means the potential[2] for a particle with charge q is

$$\begin{aligned} V(x) &= -q \int_{\mathcal{O}}^x E(x') \, \mathrm{d}x = -\frac{Qq}{\varepsilon_0} \int_{\mathcal{O}}^x \text{sgn}(x' - x_0) \, \mathrm{d}x' \\ &= -\frac{Qq}{2\varepsilon_0} \left[\int_{\mathcal{O}}^{x_0} \text{sgn}(x' - x_0) \, \mathrm{d}x' + \int_{x_0}^x \text{sgn}(x' - x_0) \, \mathrm{d}x' \right] \\ &= -\frac{Qq}{2\varepsilon_0} \left[\begin{cases} \mathcal{O} - x_0 & \text{if } \mathcal{O} < x_0 \\ x_0 - \mathcal{O} & \text{if } \mathcal{O} > x_0 \end{cases} + \begin{cases} x_0 - x & \text{if } x < x_0 \\ x - x_0 & \text{if } x > x_0 \end{cases} \right] \\ &= \frac{Qq}{2\varepsilon_0} \left[|\mathcal{O} - x_0| - |x_0 - x| \right]. \end{aligned}$$

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[2]Not the electric potential.

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In practice the $|\mathcal{O} - x_0|$ term just adds a constant to the Hamiltonian and therefore we disregard it.

To mimic the lengths of objects in three dimensions in one dimension, we have to adjust ε_0. To do this, we find the ground state of the 1D hydrogen atom and then define ε_0 so $\langle x^2 \rangle = a_0^2$, where $a_0 = 0.052\,91$ nm is the 3D Bohr radius. The motivation behind this definition is that it also holds for the 3D ground state. The derivation of the hydrogen solutions in 1D is written in Appendix D. Since $\langle x^2 \rangle$ is hard to calculate analytically, we instead evaluated it numerically for different choices of ε_0 and choose the one that matched the criterion $\langle x^2 \rangle = a_0^2$ best, which gave us the value $\varepsilon_0 = 11.835 \times 10^6$ F m.

5.1 Correlation and Entropy

The question of when a Slater determinant is a good approximation to the ground state quickly arises. We will try to answer this question presently.

We have found an upper limit on the ground state energy in eq. (2.6). To get an idea of how good the Slater determinant is at estimating the ground state energy, we will try to look at the correlation of states. A composite state is correlated if it cannot be written as a simple tensor, which means the state of each subsystem cannot be described independently. Since entropy is a measure of how much information can be gathered from a system, it can be used to get a rough idea of "how much" a state is correlated. But to do this, we first need to define entropy on a quantum system.

We define the density operator of a state $|\Psi\rangle$ to be the operator ρ given by

$$\rho := |\Psi\rangle\langle\Psi|. \tag{5.1}$$

By itself the density operator yields no new information compared to the state $|\psi\rangle$. However it becomes meaningful from the definition of the entanglement entropy. Consider an N particle composite system from which we can define the n-particle reduced density operator as

$$\rho_n := \mathrm{Tr}_{n+1} \ldots \mathrm{Tr}_N \, \rho,$$

where Tr_i is the partial trace on the i'th Hilbert space. This operation is generalized from the familiar trace on matrices, to the following: let Q be a set of orthonormal basis vectors, then the partial trace over the i'th system is (See for example [3] Chapter 5)

$$\mathrm{Tr}_i \, \rho = \sum_{q \in Q} {}_i\langle q|\rho|q\rangle_i \, .$$

The entanglement entropy of n particles is defined by

$$S(\rho_n) := \mathrm{Tr}\left[\rho_n \log \rho_n\right]. \tag{5.2}$$

We will use this to find the single particle entanglement entropy of the Slater determinant. First we find the density operator of a Slater determinant

$$\rho = \frac{1}{N!} \sum_{\mu,\sigma \in S_N} \mathrm{sgn}(\mu)\mathrm{sgn}(\sigma) \prod_{i,j=1}^{N} |\mu(j)\rangle_j \,_i\langle\sigma(i)| \tag{5.3}$$

The next step is to trace out $N-1$ of the particles in the system. This is done in Section C.1, which gives us

$$\rho_1 = \frac{1}{N!} \sum_{\sigma \in S_N} |\sigma(N)\rangle_N \,_N\langle\sigma(N)| = \frac{1}{N} \sum_{q=1}^{N} |q\rangle_N \,_N\langle q| = \frac{1}{N} \mathbb{1}_N. \tag{5.4}$$

The entropy is then

$$S = -\mathrm{Tr}[\rho_1 \log \rho_1] = \log N. \tag{5.5}$$

This result is in fact the lowest single particle entanglement entropy for any fermionic state (Coleman's theorem, see for example [7]). From this we can gather that a Slater determinant is the least correlated fermionic state there is. As a result, we would expect that a Slater determinant would become worse at approximating a fermionic state as the entropy increases. This would also mean that we would expect the upper limit of the energy gotten from the Slater determinant to diverge from the ground state energy together with the entanglement entropy.

5.2 Born Oppenheimer Approximation and The Stability of H_2 in 1D

The simplest multi-atom system is the Hydrogen molecule. This is a special case of interest since we can test by exact numerical calculation how well the Hartree-Fock approximation is at finding the true ground state energy. To make it explicit, the exact numerical calculation finds eigenstates to $H_H \otimes I + I \otimes H_H + H_2$, where $\otimes$ is the Kronecker product and H_H is the hydrogen Hamiltonian defined in Appendix D, eq. (D.1). Here H_2 is constructed by $\text{diag}(-\frac{q^2}{2\varepsilon_0}|\mathbf{x} \otimes \mathbf{1} - \mathbf{1} \otimes \mathbf{x}|)$ where $\mathbf{x}$ and $\mathbf{1}$ are a column vectors consisting the grid points $\{x_n\}$ and ones respectively, while $|-|$ is applied element wise on the vector. We have assumed that the ground state will be a spin singlet, so the total ground state can be written as $\psi(x_1, x_2) \otimes (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. We will then use that the entropy of this state can be written as a sum of spacial and spin parts, $S = S_{\text{spacial}} + S_{\text{spin}}$ which can be shown by explicit calculation.

To understand the stability of the four body system of the hydrogen molecule we use the Born-Oppenheimer approximation method, which can be summarized in two steps. In the first step we find the energy of the system–ignoring protons kinetic energy–for a set of separations. The energy of the system in this case is the electron energy and the protons potential energy. The second step is to use the energy curve as a potential for the protons, and simulate their wave function and energy. This is done with the Hamiltonian using the protons relative coordinates which is described in detail in Appendix E, eq. (E.6). The results are seen in Figure 1, below.
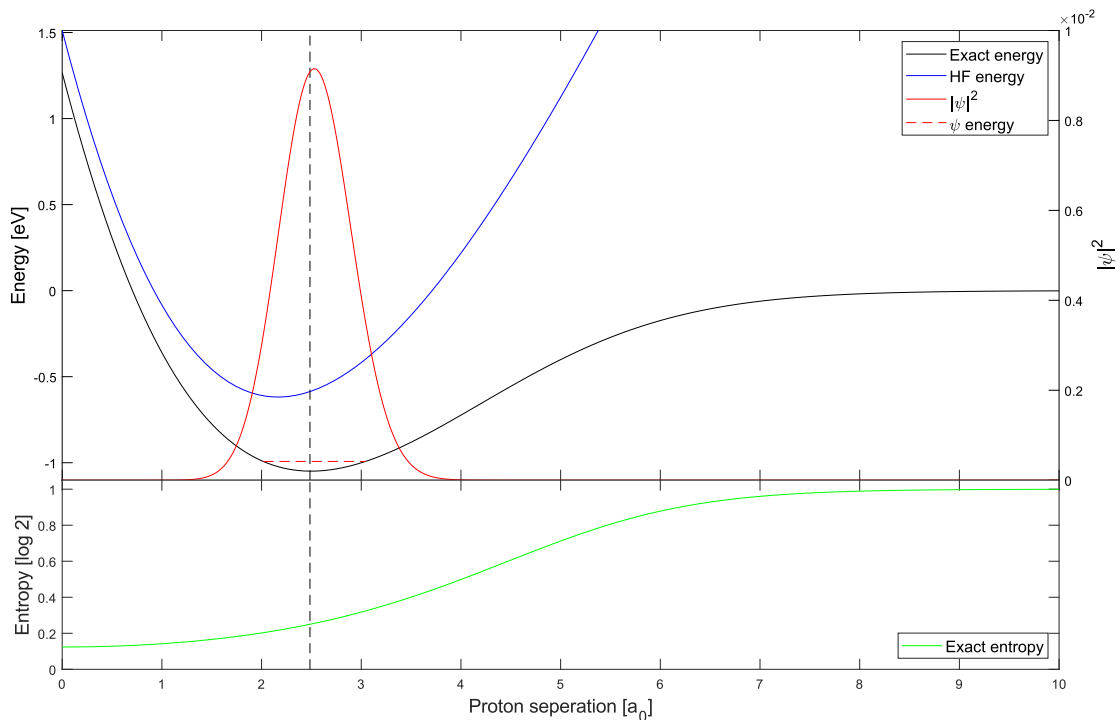

Figure 1: Plot of the ground state energy (black line) and the corresponding HF energy (blue line) for the hydrogen molecule as a function of the proton separation. The plotted energies are the electron system energies adjusted using the Born Oppenheimer method and offset by two times the hydrogen ground state energy. The red curve is the proton interaction ground state that has the black curve as potential, while the dashed red line is its energy. The black dashed line represents the proton separation for which the exact energy is the lowest. The green curve is the single particle entanglement entropy for the spacial part of the ground state found by the exact numerical simulation.

The minimum of the exact energy curve is $-1.049\,\text{eV}$ which happens at a proton separation of $a \approx 0.132\,\text{nm} = 2.485a_0$ and using the Hamiltonian from Appendix E, eq. (E.6), the lowest energy of the protons is $-0.993\,\text{eV}$. Let us consider how the energy curves behave at the extremes of the protons separation. For a large proton separation the energy of the exact simulation goes to zero on the plot which is, by the offset, equal to two times the single hydrogen ground state. The reason for this can be explained by writing the total Hamiltonian as $H = T_{e_1} + T_{e_2} + H_{e_1 e_2} + H_{e_1 p_1} + H_{e_1 p_2} + H_{e_2 p_1} + H_{e_2 p_2} + H_{p_1 p_2}$ where it is assumed that the protons have negligible kinetic energy. At long separations, $H_{e_1 e_2} \approx -H_{e_1 p_2}$ and $H_{p_1 p_2} \approx -H_{e_2 p_1}$ because of the opposite signs of the charges, so the Hamiltonian becomes $H \approx T_{e_1} + H_{e_1 p_1} + T_{e_2} + H_{e_2 p_2}$, which is just two non-interacting hydrogen atoms. We have confirmed that the energy goes to zero within $1\,\text{meV}$ with simulations going up to $100a_0$. This was done by checking a few separations from $10a_0$ to $100a_0$, but still using the same number of grid points (meaning lower grid resolution) as in Figure 1. We expect any outliers from this to be numerical errors as the grid resolution is low at these extreme distances. For short proton separations the energy curve increases untill it reaches its maximum at zero distance, i.e. the Helium atom, because of the charge repulsion. So in this simple model Helium is not stable compared to the hydrogen molecule. For it to be stable we would need to include additional interactions, e.g. the strong nuclear force.

Since we have neglected the protons kinetic energy, it is not certain that the exact ground state we found is actually bounded (less energy than two non-interacting hydrogen atoms). To get an idea if it is, we will look at the protons relative momentum, while they lay in the Born-Oppenheimer potential that we have just looked at. The Hamiltonian for this is derived in Appendix E. Solving this numerically, we get the probability distribution of the protons separation and the energy, which is denoted as ψ in Figure 1. From this we get that the relative movement between the protons still lets the system be bounded. From the probability distribution we also get that the expected proton separation is $\langle x_{\text{rel}} \rangle = 2.548a_0$ with a standard deviation $\sigma_{x_{\text{rel}}} = 0.365a_0$.

The energy curve obtained from the Hartree-Fock method also uses the Born-Oppenheimer approximation. For large proton separations, at above about $8a_0$, the energy curve increases linearly. Similar to the exact method, we confirmed this via checking at 10 different separations from $10a_0$ to $100a_0$ from which we found a slope of $1.123\,\text{eV}/\text{a}_0$ with a standard deviation of $0.019\,\text{eV}/\text{a}_0$. For protons close to each other it is similar to the exact energy curve. These two extremes are neatly explained by the notion developed in Section 5.1 that entropy is a measure of how good the HF approximation is. The entropy curve is lowest when the protons are on top of each other, i.e. Helium, where we also see that the two energy curves are closest, while the opposite is true for large separations where it goes to $\log 2$.

As a comparison to the proton wave function we found using the energy curve obtained from the exact simulation we have done the same using the energy curve found by the Hartree-Fock method. The minimum this energy curve is $-0.618\,\text{eV}$ and is found at a proton separation of $a \approx 2.194a_0$. The wave function is similar although slightly shifted to the left. The expectation of the proton separation using this wave function then becomes $\langle x_{\text{rel}} \rangle = 2.191a_0$ with a standard deviation of $\sigma_{x_{\text{rel}}} = 0.327a_0$. So in the HF approximation we would expect that the proton separation would be closer than it actually is, as seen with the exact calculation, but not by much.

5.3 HF on Larger Systems

Simulating with the HF approximation is computationally easier than finding exact solutions for many particle systems. Exact solutions require matrices that are $n^N \times n^N$ while the HF program uses $n \times n$, but a more complex algorithm. The two-particle system discussed in the previous section is handled well by both methods. We will now analyze systems with more particles, which cannot feasibly be done exactly, using the HF algorithm and look at the results.

As a first example we will consider 15 electrons in a equidistant chain of 15 protons with separation $a = 0.1315\,\text{nm}$. The potential from proton chain is constructed using a sum of single hydrogen Hamiltonians H_H with the protons as the potential centers. The results are shown in Figure 2.
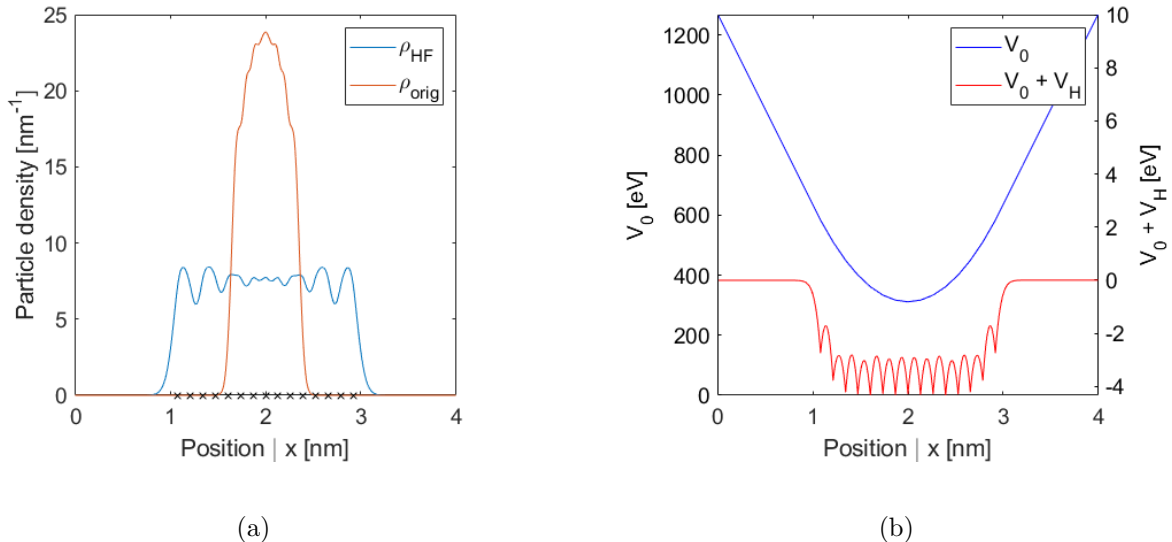
(a)   (b)

Figure 2: Results from HF simulation for 15 electrons and 15 protons separated by equal distance $a = 0.1315\,\mathrm{nm}$ and using 1001 grid points. Figure (a) shows the particle density of the Slater determinant with lowest effective single state energy (blue line), found by the HF algorithm, plotted together with the particle density of the initial guess (orange curve), which is the ground state solution for H_1. Figure (b) shows the proton chain potential V_0 and its sum with the Hartree potential V_H.

To calculate the particle density, we introduce the particle density operator which for a point x is represented by the operator on N particles by $\sum_{i=1}^{N} \delta(x_i - x)$. The particle density in Figure 2 is found by

$$\rho(x) = \int \ldots \int \Psi^*(x_1, \ldots, x_N) \left[\sum_{i=1}^{N} \delta(x_i - x) \right] \Psi(x_1, \ldots, x_N) \, \mathrm{d}x_1 \ldots \mathrm{d}x_N \,.$$

In both the cases for the Slater determinant and the initial guess, this is equal to the sum of the individual particles' probability distributions, i.e. $\rho(x) = \sum_{i=1}^{N} |\psi_i(x)|^2$.

In Figure 2 (a) we see that the particle density of the states found using Hartree-Fock method is considerably wider than the original guess. Keep in mind the original guess is the true ground state for non interacting fermions. This clearly shows that the electrons try to spread out because of their mutual repulsion. Interestingly the density of electrons is more uniformly distributed over the whole chain. This is a trend we found for different numbers of protons on the proton chains. For shorter chains, e.g. 5 or 10 protons, there is still some 'pointyness' to the particle density, similar to the initial guess. So increasing the number of protons results in a more uniform distribution, and one could imagine this trend continuing for more than 15 protons. However the convergence becomes poorer for systems with more particles and we are therefore unable to check this properly.

In Figure 2 (b), the bottoms of the saw tooth formation made by $V_0 + V_H$ aligns with the locations of the protons. Furthermore we see that $V_0 + V_H$ cancel at the the edges where the wave functions go to zero. At low grid resolutions this cancellation is not exact, however this problem can be resolved by increasing the grid resolution and letting the program run for longer.

Finally we turn to single atoms. The HF algorithm works better for these compared to the proton chains. The two large atoms we will look at are P (15 protons) and Xe (54 protons), which are shown in Figure 3 below.
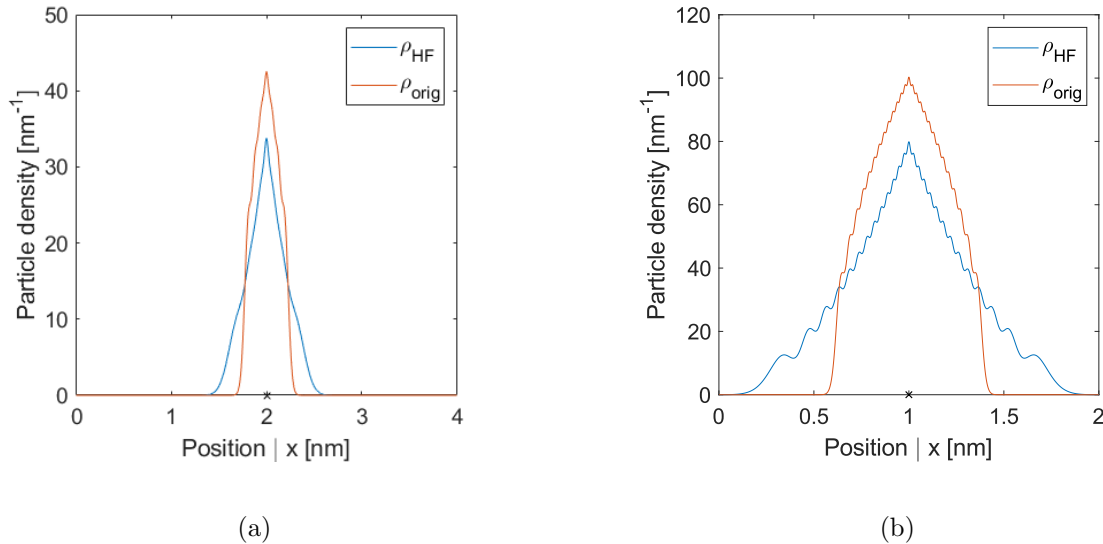
Figure 3: Results from HF simulation of large atoms. Figure (a) shows the particle density of the initial guess (orange line) with the particle density of the self consistent states (blue line) for the Phosphorus system. Similarly Figure (b) shows the particle density of the initial guess (orange line) with the particle density of the self consistent states (blue line) for the Xenon system.

In both (a) and (b) of Figure 3 the particle densities are oscillating for both the initial guess and the self consistent states, though it is not so notisable in (a). Furthermore the self consistent states produce a particle density which is considerably wider than the non interacting guess, but they are also of a fundamentally different shape compared to the densities of the proton chain.

To check these states of Xenon are not dominated by the particle in a box eigenstates, we have done a similar simulation with the length $L = 3\,\text{nm}$. We found that the particle densities are almost identical which leads us to believe that the length scale of the simulation did not have a significant role in the outcome.

To get a better understanding of the complicated Fock potential, we have plotted the Fock matrix from eq. (4.4) for two cases, one being a 15 proton chain and the other being a Phosphorus atom. The result is shown on Figure 4 below.
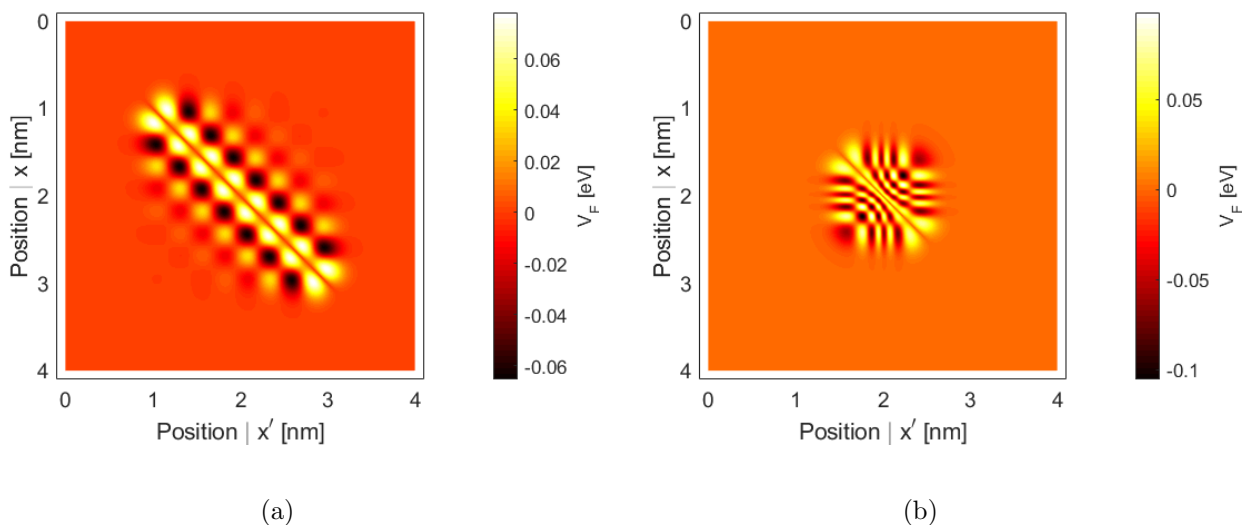

Figure 4: Nonlocal Fock potential matrix from HF simulation calculated using eq. (4.4). Figure (a) shows the Fock potential for 15 proton chain while Figure (b) shows the Fock potential for a Phosphorus atom.

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Graphically Figure 4 is very nice, but it is also hard to interpret. For the proton chain the Fock potential appears more spread out along the diagonal. In comparison, the Fock potential from the Phosphorus system is more centered. Furthermore, by the heat-map axis we see slightly higher peaks and lower troughs for the Phosphorus atom compared to the proton chain.

We note that there is no guarantee that the program finds a set of states that converges, i.e. a set of self consistent wave functions. The requirement that the energy has to reduce at each step in the iteration is a strict one which, for some systems, may slow down single iterations. This is particularly a problem for many particles where in extreme cases it might stop converging entirely because it is unable to find a set of states that lowers the energy more. In such a scenario the best one can hope for is that it is already in a somewhat converged state. This is especially apparent for chains with a large number of protons and electrons, where we have found the program unable to converge several times. Since it seems to work well for single atoms as seen above, it might suggest that the exact solution for proton chains have higher correlation which could make it hard to represent using a Slater determinant. As an example of this we can consider the proton chain of more than 20 protons. Our testing leads us to believe that such systems get stuck at some low convergence, specifically the 20 proton chain is stuck at about 0.9677 convergence. With higher grid resolution this number is reduced further.

6   Discussion and Conclusion

To lessen the inherent complexity of many particle quantum systems we have used the Hartree-Fock method that works on the assumption that states can be approximated by a Slater determinant/permanent. In the first sections we have found an effective mean field Hamiltonian on a system described by a Slater determinant. We did this by first calculating the expectation energy of a Slater determinant, eq. (2.6). By then requiring the single particle wave functions to be normalized (by means of Lagrange multipliers ε_q) and taking the functional derivative with respect to each state the Slater determinant was constructed by, we derived the Hartree-Fock (HF) equation, (2.9),

$$\varepsilon_q \psi_q(\mathbf{r}) = [H_1(\mathbf{r}) + V_H(\mathbf{r})] \psi_q(\mathbf{r}) + \int V_F^q(\mathbf{r}, \mathbf{r}') \psi_q(\mathbf{r}') \, \mathrm{d}\mathbf{r}' .$$

Finally we found a relation between the Lagrange multipliers introduced and the expectation energy, (2.11).

We have used the time dependent variational principle (TDVP) to study the dynamics of the Slater determinant. In doing so we apply the principle of least action and use the Euler Lagrange equations to obtain effective equations of motion of each single particle state ψ_q. The equation of motion is the time dependent Hartree-Fock equation, (3.7),

$$i\hbar \frac{\partial \psi_q(\mathbf{r}, t)}{\partial t} = [H_1(\mathbf{r}, t) + V_H(\mathbf{r}, t)] \psi_q(\mathbf{r}, t) + \int V_F^q(\mathbf{r}, \mathbf{r}', t) \psi_q(\mathbf{r}', t) \, \mathrm{d}\mathbf{r}' .$$

The interpretation is that this equation restricts the nature of the single particle wave functions in time and space. This has the form of a mean field Hamiltonian: $i\hbar \partial_t \psi(t) = H_{\mathrm{MF}}(\psi(t))$. Additionally we found that a set of self consistent states $\{\psi_q\}$ that solve the HF equation are stationary states, i.e. $\psi_q(\mathbf{r}, t) = \psi_q(\mathbf{r}) e^{-i\varepsilon_q t/\hbar}$ solves the TDHF equation.

We then developed wave functions on discrete spaces and the common operators used in quantum mechanics. To make it possible to find solutions to the HF equation numerically, we had to simplify at computationally optimize the expression for the expectation energy. We used this in a program we made that iteratively searched for a solution that fulfilled the HF equation. The program had different algorithms for finding a solution that it switched between. To ensure we got a good upper bound for the actual ground state energy, we used the criterion that each iteration should give a lower energy Slater determinant.

To get an idea of how good a Slater determinant is a approximating the ground state of a system, we turned to the correlation and entanglement entropy. As a result, we developed the idea that the

Hartree-Fock method would give better results for states with low entanglement entropy since Slater determinants have the lowest possible entropy of all fermionic states (Coleman's theorem).

One of the results of this program is the comparison of the Hartree-Fock method and an exact simulation on a 1D hydrogen molecule. A comparison obtained from Born-Oppenheimer energy curves of these two methods shows that the Hartree-Fock method works best for systems of low correlation. We then tested the program for systems with more particles, particularly using potentials from a varying number of protons in a chain with fixed separation. The HF method works well up to 15 protons on a chain, whereas the exact simulation is computationally unfeasible to complete because it is limited by the problems size. For single atom systems the HF algorithm successfully finds a set of self consistent states, likely because of its comparatively low correlation.

References

[1]   Irene A. Abramowitz Milton & Stegun. *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*. Dover, ISBN: 9780486612720.

[2]   Stephen Blundell. *Magnetism in Condensed Matter*. Oxford University Press, 2014. ISBN: 9780198505914.

[3]   Matthias Christandl. "Quantum Information Theory lecture notes". 2018.

[4]   Eberhard Dreizler Reiner M. & Engel. *Density Functional Theory: An Advanced Course*. Springer, 2011. ISBN: 9783642140907.

[5]   David S. Dummit & Richard M. Foote. *Abstract Algebra, 3rd Edition*. Wiley, July 2003. ISBN: 9780471433347.

[6]   Donald H. Kobe. "Lagrangian Densities and Principle of Least Action in Nonrelativistic Quantum Mechanics". In: *arXiv:0712.1608v1* (2007).

[7]   Marius Lemm. "On the entropy of fermionic reduced density matrices". In: *arXiv:1702.02360v1* (2017), p. 3.

[8]   René L. Schilling. *Measures, Integrals and Martingales, 2nd Edition*. Cambridge University Press, April 2017. ISBN: 9781316620243.

[9]   Berfinnur Durhuus & Jan P. Solovej. *Mathematical Physics*. Department of Mathematical Sciences, University of Copenhagen, October 2014. ISBN: 9788770784528.

We include a link to a folder inlcuding most of the algorithms we have used to produce the results in this thesis: `https://www.dropbox.com/sh/tlzz0lymr8xlmww/AADMJXxg7v8froZaJPJKRFQLa?dl=0`.

A Permutations in Detail

The expectation of the Hamiltonian for a Slater determinant is

$$\langle\Psi|H|\Psi\rangle = \sum_{i=1}^{N}\langle\Psi|\tilde{H}_i|\Psi\rangle + \frac{1}{2}\sum_{i\neq j}^{N}\langle\Psi|H_{ij}|\Psi\rangle$$

$$= \sum_{i=1}^{N}\sum_{\sigma,\mu\in S_N}\mathrm{sgn}(\sigma)\mathrm{sgn}(\mu)\left(\prod_{k\neq i}^{N}\delta_{\sigma(k)}^{\mu(k)}\right){}_i\langle\sigma(i)|H_i|\mu(i)\rangle_i \tag{A.1a}$$

$$+ \frac{1}{2}\sum_{i\neq j}^{N}\sum_{\sigma,\mu\in S_N}\mathrm{sgn}(\sigma)\mathrm{sgn}(\mu)\left(\prod_{k\neq i,j}^{N}\delta_{\sigma(k)}^{\mu(k)}\right){}_j\langle\sigma(j)|{}_i\langle\sigma(i)|H_{ij}|\mu(i)\rangle_i\,|\mu(j)\rangle_j . \tag{A.1b}$$

To work with this, we introduce the notation $[N] := \{1,2,\ldots,N\}$. On the first line, (A.1a): for the Kronecker delta to be non-zero, the two permutations σ and μ must be equal on the set $[N]\setminus\{i\}$. However, a permutation is a bijection, meaning $\sigma(i)=\mu(i)$ also, and therefore $\sigma=\mu$. As a consequence we have $\mathrm{sgn}(\sigma)\mathrm{sgn}(\mu)=1$. Furthermore, for each pair $i,k\in[N]$ there are $(N-1)!$ possible permutations σ with the property $\sigma(i)=k$. This means we can replace the sum of $\sigma,\mu\in S_N$ with a sum over k. Putting this all together the first line reads

$$(\text{A.1a}) = (N-1)!\sum_{i=1}^{N}\sum_{k=1}^{N}{}_i\langle k|H_i|k\rangle_i .$$

On the second line, (A.1b): for the Kronecker delta to be non-zero, the two permutations σ and μ must be equal on the set $[N]\setminus\{i,j\}$. Again using the bijective property of the permutations, one can deduce there are only two possibilities which are $\sigma(i)=\mu(i)\wedge\sigma(j)=\mu(j)$ or $\sigma(i)=\mu(j)\wedge\sigma(j)=\mu(i)$, with $\mathrm{sgn}(\sigma)\mathrm{sgn}(\mu)$ equal to 1 and -1 respectively. For each of the two cases one can apply the same sum replacing method as before. Note that μ can be uniquely determined from σ in both cases. For each $i,j\in[N]$ with $i\neq j$ and some $k,l\in[N]$ with $k\neq l$, there are $(N-2)!$ permutations with the properties $\sigma(i)=k$ and $\sigma(j)=l$. Replacing the sum of $\sigma,\mu\in S_N$ with a sum over k,l satisfying $k\neq l$ then gives

$$(\text{A.1b}) = \frac{(N-2)!}{2}\sum_{i\neq j}^{N}\sum_{k\neq l}^{N}\left[{}_j\langle l|{}_i\langle k|H_{ij}|k\rangle_i\,|l\rangle_j - {}_j\langle l|{}_i\langle k|H_{ij}|l\rangle_i\,|k\rangle_j\right] .$$

The expectation energy is then

$$\langle\Psi|H|\Psi\rangle = \frac{1}{N}\sum_{i=1}^{N}\sum_{k=1}^{N}{}_i\langle k|H_i|k\rangle_i + \frac{1}{2N(N-1)}\sum_{i\neq j}^{N}\sum_{k\neq l}^{N}\left[{}_j\langle l|{}_i\langle k|H_{ij}|k\rangle_i\,|l\rangle_j - {}_j\langle l|{}_i\langle k|H_{ij}|l\rangle_i\,|k\rangle_j\right] . \tag{A.2}$$

B   Example of TDVP on a Spin State

Here we will give an example of how the time dependent variational principle can give us the equations of motion for a simple system that consists only of spin. Suppose we are given a Hamiltonian $H = -\gamma B S_z$–that is a magnetic field of strength B pointing in the z direction. The general idea is to parameterize the spin states, in this case we do this via the polar, θ, and azimuthal, ϕ, angles in the following manner

$$\psi(\theta, \phi) = \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}.$$

Say we put θ and ϕ into a vector of parameters $\mathbf{s} = \begin{pmatrix} \theta & \phi \end{pmatrix}$ then the Lagrangian is

$$L(\mathbf{s}, \dot{\mathbf{s}}, t) = \langle \psi(\mathbf{s})|i\hbar \frac{\mathrm{d}}{\mathrm{d}t} - H|\psi(\mathbf{s})\rangle = \langle \psi(\mathbf{s})|i\hbar \frac{\mathrm{d}}{\mathrm{d}t}|\psi(\mathbf{s})\rangle - \langle \psi(\mathbf{s})|H|\psi(\mathbf{s})\rangle .$$

We calculate these two terms separately:

$$\langle \psi(\mathbf{s})|H|\psi(\mathbf{s})\rangle = -\frac{\gamma B\hbar}{2} \begin{pmatrix} \cos(\theta/2) & e^{-i\phi} \sin(\theta/2) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}$$

$$= -\frac{\gamma B\hbar}{2} \left(\cos^2(\theta/2) - \sin^2(\theta/2) \right) = -\frac{\gamma B}{2} \cos(\theta).$$

And then

$$\langle \psi(\mathbf{s})|i\hbar \frac{\mathrm{d}}{\mathrm{d}t}|\psi(\mathbf{s})\rangle = i\hbar \begin{pmatrix} \cos(\theta/2) & e^{-i\phi} \sin(\theta/2) \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}$$

$$= i\hbar \begin{pmatrix} \cos(\theta/2) & e^{-i\phi} \sin(\theta/2) \end{pmatrix} \begin{pmatrix} -\frac{\dot\theta}{2} sin(\theta/2) \\ i\dot\phi e^{i\phi} \sin(\theta/2) + e^{i\phi} \frac{\dot\theta}{2} cos(\theta/2) \end{pmatrix}$$

$$= i\hbar \left[-\frac{\dot\theta}{2} \cos(\theta/2) \sin(\theta/2) + i\dot\phi \sin^2(\theta/2) + \frac{\dot\theta}{2} \sin(\theta/2) \cos(\theta/2) \right]$$

$$= -\hbar\dot\phi \sin^2(\theta/2).$$

Putting these together,

$$L(\mathbf{s}, \dot{\mathbf{s}}, t) = -\hbar\dot\phi \sin^2(\theta/2) + \frac{\gamma B\hbar}{2} \cos(\theta).$$

The underlying principle is that of least action. That is equivalent to the parameters θ and ϕ satisfying the Euler-Lagrange equations. Firstly for θ or s_1 we find

$$0 = \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{s}_1} \right) - \frac{\partial L}{\partial s_1} = \frac{\mathrm{d}}{\mathrm{d}t} (0) - \left(-\hbar\dot\phi \sin(\theta/2) \cos(\theta/2) + \frac{\gamma B\hbar}{2} \sin(\theta) \right)$$

$$= \frac{\hbar\dot\phi}{2} \sin(\theta) - \frac{\gamma B\hbar}{2} \sin(\theta)$$

$$= \frac{\hbar\dot\phi - \gamma B\hbar}{2} \sin(\theta). \tag{B.1}$$

Similarly we find for ϕ or s_2,

$$0 = \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{s}_2} \right) - \frac{\partial L}{\partial s_2} = \frac{\mathrm{d}}{\mathrm{d}t} \left(-\hbar \sin^2(\theta/2) \right) - 0$$

$$= -\frac{\hbar\dot\theta}{2} \sin(\theta/2) \cos(\theta/2)$$

$$= -\frac{\hbar\dot\theta}{4} \sin(\theta).$$

The functions $\theta(t)$ that solve this differential equation are either a piecewise continuous function whose values are multiple of π, such that the sin is zero. Or are constant in time at any value $[0, \pi]$. This

restricts the movement of the spin to at most rotate about the z axis. By letting $\theta(t) \in (0, \pi)$ be constant in time, such that $\sin(\theta(t))$ is nonzero we solve for $\dot{\phi}$

$$\dot{\phi} = \gamma B.$$

This of course implies that the polar angle increases linearly with time, $\phi = \gamma B + \phi_0$, giving rise to a constant rotation about the z-axis. The frequency of rotation is $\omega = \gamma B$.

This result should come as no surprise as it coincides with what the time dependent Schödinger equation predicts. If the reader is not familiar with this, look up Lamor precession, e.g. D.J. Griffiths' introduction to quantum mechanics 2nd edition, p. 179.

C Partial Trace

Let Q be a countable orthonormal basis on each $\mathcal{H}_i$, for all $i \in [N]$. Then the $N - n$'th successive partial trace on an operator O is given by

$$\text{Tr}_{n+1} \ldots \text{Tr}_N O = \prod_{k=n+1}^{N} \left(\sum_{q_k \in Q} {}_k\langle q_k|[O] \prod_{l=n+1}^{N} |q_l\rangle_l \right). \tag{C.1}$$

Proof. The proof will be done by induction. Let $n = N - 1$, then the statement says

$$\text{Tr}_N \rho = \sum_{q_N \in Q} {}_N\langle q_N|\rho|q_N\rangle_N,$$

which is true per definition of the partial trace. Now assume the statement is true for $N - n$'th successive partial trace, then by applying the partial trace over system n we find

$$\text{Tr}_n \text{Tr}_{n+1} \ldots \text{Tr}_N O = \text{Tr}_n[\text{Tr}_{n+1} \ldots \text{Tr}_N O]$$

$$= \text{Tr}_n \prod_{k=n+1}^{N} \left(\sum_{q_k \in Q} {}_k\langle q_k|O \prod_{l=n+1}^{N} |q_l\rangle_l \right)$$

$$= \sum_{q_n \in Q} {}_n\langle q_n| \prod_{k=n+1}^{N} \left(\sum_{q_k \in Q} {}_k\langle q_k|O \prod_{l=n+1}^{N} |q_l\rangle_l \right) |q_n\rangle_n$$

$$= \prod_{k=n+1}^{N} \left(\sum_{q_n \in Q} {}_n\langle q_n| \right) \left(\sum_{q_k \in Q} {}_k\langle q_k| \right) O \prod_{l=n+1}^{N} |q_l\rangle_l \, |q_n\rangle_n$$

$$= \prod_{k=n}^{N} \sum_{q_k \in Q} {}_k\langle q_k|O \prod_{l=n}^{N} |q_l\rangle_l = \prod_{k=n}^{N} \left(\sum_{q_k \in Q} {}_k\langle q_k|O \prod_{l=n}^{N} |q_l\rangle_l \right).$$

The statement is then true for all $n \in [N - 1]$ by the method of induction. $\qquad\square$

C.1 Trace of Density Operator for Slater Determinant

We start by noting that the density operator for the Slater determinant can be rewritten as

$$\rho = \sum_{\mu,\sigma \in S_N} \text{sgn}(\mu)\text{sgn}(\sigma) |\mu(1)\rangle_1 {}_1\langle\sigma(1)| \prod_{i,j\neq1}^{N} |\mu(j)\rangle_j {}_i\langle\sigma(i)|. \tag{C.2}$$

where the product in (C.2) is over all i, j except when both equals 1. We then pick an orthonormal basis which includes the single particle states that are used to construct the Slater determinant so $\{|1\rangle_i, \ldots, |N\rangle_i\} \subset Q$. Furthermore the product in eq. (C.2) is labelled by $\tilde{\rho} := \prod_{i,j\neq1}^{N} |\mu(j)\rangle_j {}_i\langle\sigma(i)|$ and note that the partial trace only acts on the terms in this product. Reducing this operator by tracing out $N - 1$ systems gives $\tilde{\rho}_1 := \text{Tr}_2 \ldots \text{Tr}_N \tilde{\rho}$:

$$\tilde{\rho}_1 = \prod_{k=2}^{N} \sum_{q_k \in Q} {}_k\langle q_k| \left[\prod_{i,j\neq1}^{N} |\mu(j)\rangle_j {}_i\langle\sigma(i)| \right] \prod_{l=2}^{N} |q_l\rangle_l = \prod_{k=2}^{N} \sum_{q_k \in Q} \prod_{i,j\neq1}^{N} {}_k\langle q_k|\mu(j)\rangle_j \prod_{l=2}^{N} {}_i\langle\sigma(i)|q_l\rangle_l$$

$$= \prod_{k=2}^{N} \sum_{q_k \in Q} \prod_{i,j\neq1}^{N} \delta_k^j \delta_{q_k}^{\mu(j)} \prod_{l=2}^{N} \delta_i^l \delta_{\sigma(i)}^{q_l} = \prod_{k=2}^{N} \sum_{q_k \in Q} \prod_{i=2}^{N} \delta_{q_k}^{\mu(k)} \delta_{\sigma(i)}^{q_i} = \sum_{q_2,\ldots,q_N \in Q} \prod_{i,j=2}^{N} \delta_{q_j}^{\mu(j)} \delta_{\sigma(i)}^{q_i}$$

$$= \prod_{i=2}^{N} \delta_{\sigma(i)}^{\mu(i)}. \tag{C.3}$$

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The last equality implies that the permutations σ and μ must be the same for the sums in eq. (5.3) to be non-zero. We therefore replace the double sum by a single sum over σ and find

$$\rho_1 = \frac{1}{N!} \sum_{\mu,\sigma \in S_N} \text{sgn}(\mu)\text{sgn}(\sigma)\, |\mu(N)\rangle_N \,_N\langle \sigma(N)| \prod_{i=2}^{N} \delta^{\mu(i)}_{\sigma(i)} = \frac{1}{N!} \sum_{\sigma \in S_N} |\sigma(N)\rangle_N \,_N\langle \sigma(N)|.$$

D Hydrogen Atom in 1D

With the 1D hydrogen potential the Schrödinger equation reads

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}(x) - \frac{Qq}{2\varepsilon_0}|x_0 - x|\psi(x) = H_{\mathrm{H}}\psi(x). \tag{D.1}$$

To solve this we split the potential up into two parts and find two sets of solutions. This can be done by rewriting and changing the absolute value to a sign:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}(x) = a(b - |x_0 - x|)\psi(x), \quad a := \frac{2mQq}{2\hbar^2\varepsilon_0}, \quad b := -\frac{2\varepsilon_0}{Qq}E \tag{D.2}$$

Changing variables to $z(x) = a^{1/3}(-|x_0 - x| + b)$ and changing the differential operator by expanding $\mathrm{d}/\mathrm{d}x = \mathrm{d}z/\mathrm{d}x\,\mathrm{d}/\mathrm{d}z$ such that by the product rule we have

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}(z) = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}z}{\mathrm{d}x}\cdot\frac{\mathrm{d}\psi}{\mathrm{d}z}(z)\right) = \frac{\mathrm{d}^2z}{\mathrm{d}x^2} + \left(\frac{\mathrm{d}z}{\mathrm{d}x}\right)^2\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2}(z) = \left(\frac{\mathrm{d}z}{\mathrm{d}x}\right)^2\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2}(z) \tag{D.3}$$

The last equality is obtained by realizing that $\mathrm{d}^2y/\mathrm{d}x^2 = 0$. Note that $\mathrm{d}z/\mathrm{d}x = \mathrm{sgn}(x_0 - x)a^{1/3}$; then by putting (D.3) into (D.2)

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2}(z) = z(x)\psi(z). \tag{D.4}$$

This is the Airy equation. The solutions to this equation are spanned by two linearly independent functions called the Airy functions, namely Ai and Bi. So any wave function solving this equation is of the form $\psi(z) = A\mathrm{Ai}(z) + B\mathrm{Bi}(z)$.

Assuming q and Q are opposite charges $a^{1/3}$ is a negative number then $z(x) \to +\infty$ for $x \to \pm\infty$ and therefore the constant B must be zero for the wave function to be normalizable. For simplicity we distinguish between when $x > x_0$ and $x < x_0$ and by labeling z as z_+ and z_- respectively:

$$\psi(z) = \begin{cases} A\mathrm{Ai}(z_+) & x > x_0 \\ B\mathrm{Ai}(z_-) & x < x_0 \end{cases} \quad \text{with} \quad z_\pm(x) = a^{1/3}(\pm(x_0 - x) + b).$$

Using the notation $z_0 = z(x_0) = z_\pm(x_0)$. The continuity condition requires that the wave function is continuous, especially x_0 for which

$$A\mathrm{Ai}(z_0) = \lim_{x \to x_0^+}\psi(z) \stackrel{!}{=} \lim_{x \to x_0^-}\psi(z) = B\mathrm{Ai}(z_0). \tag{D.5}$$

This can only hold if either $A = B$, or $\mathrm{Ai}(z_0) = 0$–or both. Firstly we consider $A = B$ such that $\psi(z) = A\mathrm{Ai}(z)$ for some normalization constant A—[1]. A similar condition says that the derivative of a wave function must also be continuous. Especially in x_0 the derivative of the wave function gives

$$\frac{\mathrm{d}\psi}{\mathrm{d}x}(z) = \begin{cases} Az_+'\mathrm{Ai}'(z_+) & x > x_0 \\ Az_-'\mathrm{Ai}'(z_-) & x < x_0 \end{cases} = \begin{cases} Aa^{1/3}\mathrm{Ai}'(z_+) & x > x_0 \\ Aa^{1/3}\mathrm{Ai}'(z_-) & x < x_0 \end{cases}.$$

Then by requiring that the derivative is continuous:

$$Aa^{1/3}\mathrm{Ai}'(z_0) = \lim_{x \to x_0^+}\frac{\mathrm{d}\psi}{\mathrm{d}x}(z) \stackrel{!}{=} \lim_{x \to x_0^-}\frac{\mathrm{d}\psi}{\mathrm{d}x}(z) = -Aa^{1/3}\mathrm{Ai}'(z_0).$$

For this equality to hold we must restrict the energy E such that $\mathrm{Ai}'(z_0) = 0$. The solutions to the equation is a set of real numbers $\{a_n'\}_{n\in\mathbb{N}}$–which can be found numerically. Then for any n by solving $z_0 = a_n'$ the energy is found to be

$$E_n' = -\left(\frac{\hbar^2 Q^2 q^2}{8m\varepsilon_0^2}\right)^{1/3}a_n'. \tag{D.6}$$

If, in the other case for (D.5), $\mathrm{Ai}(z_0) = 0$, requiring that the derivative is continuous:

$$A a^{1/3} \mathrm{Ai}'(z_0) = \lim_{x \to x_0^+} \frac{\mathrm{d}\psi}{\mathrm{d}x}(z) \stackrel{!}{=} \lim_{x \to x_0^-} \frac{\mathrm{d}\psi}{\mathrm{d}x}(z) = -B a^{1/3} \mathrm{Ai}'(z_0).$$

Then z_0 has to equal one of the set of numbers $\{a_n\}_{n \in \mathbb{N}}$ which consists of roots to the Ai function. Solving $z_0 = a_n$ we find, similar to (D.6)

$$E_n = - \left(\frac{\hbar^2 Q^2 q^2}{8m\varepsilon_0^2} \right)^{1/3} a_n. \tag{D.7}$$

Picking an energy in this spectrum we propose $\mathrm{Ai}'(z_0) \neq 0$, and therefore the requirement from (D) implies that $A = -B$. We see the energy spectrum must be the union of E_n' and E_n. For the first few solutions we have $E_1' < E_1 < E_2' < E_2 < \dots$ this motivates the following conjecture.

Conjecture 1. *For 1D hydrogen the wave functions are alternating even and odd*

$$\psi(z) = \begin{cases} A \mathrm{Ai}(z) & \text{if } n \text{ is odd} \\ A \mathrm{sgn}(x - x_0) \mathrm{Ai}(z) & \text{if } n \text{ is even} \end{cases}. \tag{D.8}$$

And the energy spectrum are given by the energies in (D.6) and (D.7) in the following manner

$$E_n = - \left(\frac{\hbar^2 Q^2 q^2}{8m\varepsilon_0^2} \right)^{1/3} \begin{cases} a_{\lceil n/2 \rceil}' & \text{if } n \text{ is odd} \\ a_{n/2} & \text{if } n \text{ is even} \end{cases}. \tag{D.9}$$

E   Reduced mass

E.1   Newtons Equations

Consider two interacting particles 1 and 2 with masses m_1, m_2, momenta $\mathbf{p}_1, \mathbf{p}_2$ and spacial coordinates $\mathbf{r}_1, \mathbf{r}_2$, respectively. Given an interaction potential V which only depends on relative distance $\mathbf{r}_{\text{rel}} := \mathbf{r}_1 - \mathbf{r}_2$ newtons equations for each particle is

$$\mathbf{F}_{12} = m_1 \ddot{\mathbf{r}}_1 \quad \text{and} \quad \mathbf{F}_{21} = m_2 \ddot{\mathbf{r}}_2. \tag{E.1}$$

We wish to find the dynamics of the center of mass of the system, and of the relative coordinates of the particles.

Adding the two equations of (E.1) we find

$$\mathbf{F}_{\text{cm}} := \mathbf{F}_{12} + \mathbf{F}_{21} = m_1 \ddot{\mathbf{r}}_1 + m_2 \ddot{\mathbf{r}}_2 = (m_1 + m_2) \ddot{\mathbf{r}}_{\text{cm}}$$

where $\mathbf{r}_{cm}$ is the center of mass of the system, as usually defined by

$$\mathbf{r}_{\text{cm}} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}.$$

Multiplying the first equation of (E.1) by m_2 and the second one by m_1 and subtracting the two, we find

$$m_2 \mathbf{F}_{12} - m_1 \mathbf{F}_{21} = m_1 m_2 \ddot{\mathbf{r}}_1 - m_1 m_2 \ddot{\mathbf{r}}_2 = m_1 m_2 \ddot{\mathbf{r}}_{\text{rel}}$$

Noting that $\mathbf{F}_{12} = -\mathbf{F}_{21}$ we conclude

$$\mathbf{F}_{\text{rel}} := \mathbf{F}_{12} = \frac{m_1 m_2}{m_1 + m_2} \ddot{\mathbf{r}}_{\text{rel}} = \mu \ddot{\mathbf{r}}_{\text{rel}},$$

where $\mu := \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

This motivates the definitions of the center of mass momentum as

$$\mathbf{p}_{\text{cm}} := (m_1 + m_2) \dot{\mathbf{r}}_{\text{cm}} = \mathbf{p}_1 + \mathbf{p}_2. \tag{E.2}$$

Such that $\mathbf{F}_{\text{cm}} = \dot{\mathbf{p}}_{\text{cm}}$. Furthermore defining the relative momentum by

$$\mathbf{p}_{\text{rel}} = \mu \dot{\mathbf{r}}_{\text{rel}} = \frac{\mathbf{p}_1}{1 + m_1/m_2} - \frac{\mathbf{p}_2}{1 + m_2/m_1}. \tag{E.3}$$

Now we can rewrite $\mathbf{p}_1$ and $\mathbf{p}_2$ using $\mathbf{p}_{\text{cm}}$ and $\mathbf{p}_{\text{rel}}$. First we use $\mathbf{p}_2 = \mathbf{p}_{\text{cm}} - \mathbf{p}_1$ to get

$$\mathbf{p}_{\text{rel}} = \frac{\mathbf{p}_1}{1 + m_1/m_2} - \frac{\mathbf{p}_{\text{cm}} - \mathbf{p}_1}{1 + m_2/m_1} = \mathbf{p}_1 - \frac{\mathbf{p}_{\text{cm}}}{1 + m_2/m_1} = \mathbf{p}_1 - \frac{m_1}{m_1 + m_2} \mathbf{p}_{\text{cm}}.$$

From here we can write $\mathbf{p}_1$ and–using that to find–$\mathbf{p}_2$ as

$$\mathbf{p}_1 = \frac{m_1}{m_1 + m_2} \mathbf{p}_{\text{cm}} + \mathbf{p}_{\text{rel}} \quad \text{and} \quad \mathbf{p}_2 = \frac{m_1}{m_1 + m_2} \mathbf{p}_{\text{cm}} - \mathbf{p}_{\text{rel}}. \tag{E.4}$$

E.2   Hamiltonian in Center of Mass and Relative Coordinates

We will now consider the results of the previous subsection and its relation to the Hamlitonian of the two particle system. First we introduce a potential which depends only on the distance between the two particles $V(\mathbf{r}_1 - \mathbf{r}_2)$. Then by using the relation established in (E.4) the Hamiltonian is

$$\begin{aligned}
H &= \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\mathbf{r}_1 - \mathbf{r}_2) \\
&= \frac{\left(\frac{m_1}{m_1+m_2} \mathbf{p}_{\text{cm}} + \mathbf{p}_{\text{rel}}\right)^2}{2m_1} + \frac{\left(\frac{m_2}{m_1+m_2} \mathbf{p}_{\text{cm}} - \mathbf{p}_{\text{rel}}\right)^2}{2m_2} + V(\mathbf{r}_{\text{rel}}) \\
&= \left(\frac{m_1 \mathbf{p}_{\text{cm}}^2}{2(m_1+m_2)^2} + \frac{\mathbf{p}_{\text{cm}} \cdot \mathbf{p}_{\text{rel}} + \mathbf{p}_{\text{rel}} \cdot \mathbf{p}_{\text{cm}}}{2(m_1+m_2)} + \frac{\mathbf{p}_{\text{rel}}^2}{2m_1}\right) \\
&\quad + \left(\frac{m_2 \mathbf{p}_{\text{cm}}^2}{2(m_1+m_2)^2} - \frac{\mathbf{p}_{\text{cm}} \cdot \mathbf{p}_{\text{rel}} + \mathbf{p}_{\text{rel}} \cdot \mathbf{p}_{\text{cm}}}{2(m_1+m_2)} + \frac{\mathbf{p}_{\text{rel}}^2}{2m_2}\right) + V(\mathbf{r}_{\text{rel}}) \\
&= \frac{\mathbf{p}_{\text{cm}}^2}{2(m_1+m_2)} + \frac{\mathbf{p}_{\text{rel}}^2}{2\mu} + V(\mathbf{r}_{\text{rel}}). \tag{E.5}
\end{aligned}$$

If there is no external potential on the system the center of mass momentum is constant. This way we can remove it from our expression as it just gives an energy shift.

In the case when the two particles have equal mass m, the reduced mass is $\mu = m/2$ and therefore the Hamiltonian is

$$H = \frac{\mathbf{p}_{\text{rel}}^2}{2(m/2)} + V(\mathbf{r}_{\text{rel}}). \tag{E.6}$$

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