

# The Coupled Cluster Method

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## Abstract

The Coupled Cluster method is a Post-Hartree-Fock method for solving the electronic many-body problem. Its combination of speed and accuracy has made it the gold standard of such methods. In this report we will present a summary of the theory and our implementation of the coupled cluster doubles and singles doubles equations. Selected results will also be shown for simple electronic systems to verify the implementation, and to see how the theory matches the numerical results. We find that the CCSD method indeed is exact in the space spanned by its basis for systems of two electrons. We also find that the CCD method is indeed very dependant on being given a Hartree-Fock basis, having an error in the energy of  $0.0130a.u.$  with a Hartree-Fock basis, but  $0.2270a.u.$  without. We also see that the particle density is far from exact, as is expected from a non-variation method, and that convergence is helped greatly by a sophisticated convergence acceleration scheme.

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# 1 Introduction

The coupled cluster method is one of the best methods for finding approximate solutions to the electronic Schrödinger equation. It is one of many post Hartree-Fock methods which improve upon the single Slater determinant from the Hartree-Fock method. The coupled cluster method uses the exponential cluster operator to describe a large number number of Slater determinants, which together can accurately account for electron correlations. This approach uses only using a small number of parameters, leading to fast computations. The method was introduced into quantum chemistry in the 1960s by Čížek and Paldus [4] [2, 3, 1], and has since become one of the most used methods for solving many-electron systems. Many variants of the method have been developed, including variational formulations as well as a formulation using perturbation theory to efficiently include an estimate for triple excitations (CCSD(T)) [4]. We will focus on the simple variants of coupled cluster doubles (CCD) and coupled cluster singles doubles (CCSD).

Our goals with this work has been to learn about a state of the art method for many-body quantum physics calculations, as well as producing code which can be used as both a benchmark and a building block for a masters thesis. This report therefore serves mostly as a short summary of the Couple Cluster theory and the way we chose to implement it. Despite not including any new contributions to the field, we still feel that the work put into this report and code has been very valuable.

We will begin by summarizing the parts of Hartree-Fock theory that we deem relevant, including spin-orbitals, the Slater determinant, and the solution to the Hartree-Fock equation.

In the theory section, we begin by presenting the equation we wish to solve, the Schrödinger equation. The rest of the theory will describe one of the many methods used to solve this equation, the Coupled Cluster(CC) method. The solution given by CC is a linear combination of so called Slater determinants.

We describe how to construct such a Slater determinant, and how the Hartree-Fock method can make it into a decent approximation to the ground state of a system. The subsection regarding second quantization describes how to construct new determinants from the Hartree-Fock determinant, and we present cluster operators, which is a system used to create very many determinants. After that, the Coupled Cluster wavefunction and central equations are finally presented. We then present some of the techniques required to simplify the equations into a workable form. Finally, we present two simple physical systems we will attempt to solve using the CC method.

In the implementation section, we summarize the central algorithms we implemented for this report. These include an implementation of Wick's Theorem contraction rules for simplifying parts of the CC equations. Evaluating the one- and two-body matrix elements, as well as finding a Hartree-Fock basis and transforming the matrix elements. Finally, details of evaluating the amplitude equations, and methods to improve convergence of the iterative scheme are presented. One of these methods is the direct inversion of the iterative

subspace(DIIS), which we explain in some detail.

The results section includes the energy of the two systems found with different methods. We also show results regarding convergence of the coupled cluster methods and finally the particle density. The discussion of the results are included as the results are presented. Finally, we summarize the report and discuss further areas of interest in the conclusion.

## 2 Theory

### 2.1 The Schrödinger Equation

The problem we are solving is the electronic Schrödinger Equation.

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (1)$$

where  $\hat{H}$  is the Hamiltonian operator.  $|\Psi\rangle$  is the eigenstate of the Hamiltonian, and  $E$  is its eigenvalue, the energy of the state. The Hamiltonian acts as a description of a physical system, and it is our goal to find the state  $|\Psi\rangle$  which describes how particles will behave in this system, and the energy of this state,  $E$ .

We limit ourselves to time-independent electronic systems of  $N$  electrons where the Hamiltonian contains the kinetic energy of the electrons, the energy from one-body potentials  $V_i$ , and the Coulomb repulsion between electrons.

$$\hat{H} = \sum_i -\frac{1}{2} \nabla_i^2 + V(\mathbf{x}_i) + \sum_{i < j} \frac{1}{r_{ij}} \quad (2)$$

where the sums over  $i$  and  $j$  go over all  $N$  electrons. The restricted double sum  $i < j$  ensures that we don't double count the repulsion between electrons.

The one-body potential  $V(\mathbf{x}_i)$  will typically be a harmonic oscillator potential or the Coulomb repulsion from protons, but can be any one-body potential. If we include atomic nuclei in our systems of interest we will assume that they are stationary, since they generally move much slower than electrons (the Born-Oppenheimer approximation).

### 2.2 The Hartree-Fock Approximation

Imagine that you are looking at two electrons that are trapped together in some well potential. If one electron is observed in the center of the well, you know that the other electron is unlikely to be observed near the center, as the electrons repel each other and "tend to avoid each other". This example shows that you cannot give each electron its own one-electron function that ignores the other electrons, since the movement of electrons are correlated.

The electronic Hamiltonian of equation 2 has a two-body term, which means that one cannot separate equation 1 into one equation for each electron. If this

was possible, we could solve the one-electron equations separately and then combine the resultant one-electron functions into a solution to the whole problem.

Despite this not being a good solution, as we have just discussed, we now choose to approximate our wavefunction as the product of one-electron functions  $\phi_i$ .

$$\Psi^{HP} = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots\phi_n(\mathbf{x}_n) \quad (3)$$

where the numbers 1...n indicate which electron goes with each function. This type of wavefunction is called a Hartree-Product.

The one-electron functions are called spin-orbitals, and contain a spatial and spin component.

$$|\phi\rangle = \phi(\mathbf{x}) = \phi_1(x)a(m_s) + \phi_2(x)\beta(m_s) \quad (4)$$

where

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

The Hartree-Product wavefunction has the problem that it is not-antisymmetric: Swapping electron 1 and 2 does not change the sign of the wavefunction. This can be solved by adding together all possible orderings of the one-electron functions with altering signs depending on the number of permutations. One must also normalize the function depending on the number of terms in the sum. For two electrons this will look like:

$$\begin{aligned} |\Phi_0\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (|\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\rangle - |\phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\rangle) \\ &= |\phi_1\phi_2\rangle \end{aligned} \quad (6)$$

Where the final notation implies both the anti-symmetrization,  $\mathbf{x}$ -ordering and normalization. This type of wavefunction is called a Slater determinant, and for  $n$  electrons it can be written as

$$\begin{aligned} |\Phi_0\rangle &= \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_n(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_n) & \phi_2(\mathbf{x}_n) & \dots & \phi_n(\mathbf{x}_n) \end{vmatrix} \\ &= |\phi_1\phi_2\dots\phi_n\rangle \end{aligned} \quad (7)$$

Minimizing the energy of equation 1 with a single Slater determinant wavefunction is the same as solving the Hartree-Fock equation [10]

$$\begin{aligned} (-\frac{1}{2}\nabla_1^2 + V(\mathbf{x}_1))\phi_i(\mathbf{x}_1) + \sum_{j \neq i} \left[ \int d\mathbf{x}_2 |\phi_j(\mathbf{x}_2)|^2 \frac{1}{r_{12}} \right] \phi_i(\mathbf{x}_1) \\ - \sum_{j \neq i} \left[ \int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \phi_i(\mathbf{x}_2) \right] \phi_j(\mathbf{x}_1) = \epsilon_i \phi_i(\mathbf{x}_1) \end{aligned} \quad (8)$$

The first term in equation 8 is the kinetic energy and one-body potential from the electronic Hamiltonian of equation 2. We define

$$h(1) = -\frac{1}{2}\nabla_1^2 + V(\mathbf{x}_1) \quad (9)$$

The second term is the mean-field coulomb interaction between electron 1 and all others. By taking the average interaction from all other particles, weighted by their probability density, we have simplified the Coulomb interaction into a one-body potential. This is an approximation, as there is no "average-field" in the actual Coulomb interaction, each pair of positions has a single interaction strength. The third term is an exchange term which appears due to the wavefunction being a Slater determinant. It has no simple physical interpretation.

We can combine the second and third terms using the permutation operator  $P(ij)$  which has the effect

$$P(ij)f(i, j) = f(i, j) - f(j, i) \quad (10)$$

We can also remove the restrictions on both sums, as the two extra terms will cancel out. We define the Hartree-Fock potential

$$v^{HF}(1) = \sum_j \int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} P(1, 2) \phi_j(\mathbf{x}_2) \quad (11)$$

and the Fock operator

$$f(1) = h(1) + v^{HF}(1) \quad (12)$$

the Hartree-Fock equations can now be written as

$$f|\phi_i\rangle = \epsilon_i |\phi_i\rangle \quad (13)$$

Now we need to find the molecular orbitals  $|\phi_i\rangle$  that satisfy equation 13. This is a quite complicated problem as the operator  $f$  depends on the orbitals  $|\phi_i\rangle$ , making this a non-linear equation.

The equation is solved by writing the orbitals as a linear combination of basis functions

$$|\phi_i\rangle = \sum_{\mu}^L C_{\mu i} |\psi_i\rangle \quad (14)$$

The equation can be solved exactly with a complete basis, but in practice one has to choose a limited set of  $L$  basis function which hopefully fits the system at hand well. The choice and number of basis functions are central to both the speed of the calculation and the accuracy of the result.

An iterative scheme is then employed to optimize the coefficients  $C$ . The result is  $L$  orbitals  $|\phi_i\rangle$  that satisfy equation 13. The  $N$  orbitals with the lowest energies  $\epsilon_i$  form the Slater determinant which is the solution, the Hartree-Fock wavefunction.

A summary of the limitations of the Hartree-Fock solution (not including the simplifications of the electronic hamiltonian of equation 2)

1. A single Slater determinant of one-electron functions is used
2. The Coulomb interaction is treated as a mean field
3. The incomplete basis means that the space of solutions is limited

Some useful integrals for both the Hartree-Fock procedure and Coupled Cluster are the one-electron integrals

$$h_{ai} \equiv \langle \psi_a | h | \psi_i \rangle, \quad (15)$$

the two-electron integrals

$$\begin{aligned} \langle ab || ij \rangle &\equiv \langle \psi_a \psi_b || \psi_i \psi_j \rangle \equiv \langle \psi_a \psi_b | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_a \psi_b | \frac{1}{r_{12}} | \psi_j \psi_i \rangle, \\ &= \int \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_a(\mathbf{x}_1) \psi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2), \\ &- \int \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_a(\mathbf{x}_1) \psi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \psi_j(\mathbf{x}_1) \psi_i(\mathbf{x}_2), \end{aligned} \quad (16)$$

which come straight from the Coulomb interaction and exchange term. And finally the Fock-Matrix elements

$$f_{ai} \equiv h_{ai} + \sum_{j=1}^n \langle \psi_a \phi_j || \psi_i \phi_j \rangle, \quad (17)$$

The Coupled Cluster equations we will solve are written in terms of these integrals. There are  $L^2$  one-body integrals and  $L^4$  two-body integrals. The basis vectors used to compute these integrals are chosen to somewhat fit the system of interest, sometimes being the eigenstates of the system when interactions between particles are ignored, other times being Gaussian- or Slater-Type orbitals which have been optimized for the system. When Hartree-Fock has been used to find optimized orbitals from the chosen basis, we transform the integrals to instead use the Hartree-Fock orbitals as a basis.

The Hartree-Fock method has now given us a single optimized Slater determinant of  $N$  spin-orbitals, for a given system and a given basis set of size  $L$ . We also have access to  $L - N$  unused spin-orbitals and integrals between all  $L$  spin-orbitals. The next step is now to produce other Slater-determinants using our starting determinant and our  $L - N$  unused spin-orbitals.

### 2.3 Second Quantization

Given a Slater determinant, we can define a new determinant with an extra electron and orbital using a creation operator

$$a_p^\dagger |\phi_q \dots \phi_s\rangle = |\phi_p \phi_q \dots \phi_s\rangle \quad (18)$$

Likewise we can remove an electron and orbital using an annihilation operator

$$a_p |\phi_p \phi_q \dots \phi_s\rangle = |\phi_q \dots \phi_s\rangle \quad (19)$$

If you add an orbital which is already present, you will get zero. Due to the anti-symmetrization of the determinant

$$a_q^\dagger |\phi_q \dots \phi_s\rangle = 0 \quad (20)$$

If you remove an orbital which is not included in the determinant, you also get zero.

$$a_p |\phi_q \dots \phi_s\rangle = 0 \quad (21)$$

A state with no orbitals or electrons is the true vacuum state  $|\rangle$ . With these rules we can write any Slater determinant as a combination of creation operators acting on the true vacuum state.

$$a_q^\dagger \dots a_s^\dagger |\rangle = |\phi_q \dots \phi_s\rangle \quad (22)$$

As the interchange of two columns in a determinant changes the sign, the interchange of two creation or annihilation operators also changes the sign. They anticommute.

$$\begin{aligned} a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger &= 0 \\ a_p a_q + a_q a_p &= 0 \end{aligned} \quad (23)$$

The anticommutator relation of creation and annihilation operators is

$$a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq} \quad (24)$$

where  $\delta_{pq}$  is the Kronecker delta, which equals 1 when  $p = q$  and 0 when  $p \neq q$ . This means that when we swap two neighbouring creation and annihilation operators we end up with an extra term in our expression.

## 2.4 Cluster Operators

The Hartree-Fock method gave us a single optimized Slater determinant. Since it only contains single-electron functions, it cannot properly describe electron-correlations: Electron-correlations can only be properly described by many-electron functions. All is not lost however, as we can construct many-electron functions using only combinations of products of our single-electron functions. For instance, any 2-variable function can be written as a linear combination of 1-variable function products like this

$$f(\mathbf{x}_1, \mathbf{x}_2) = \sum_{p < q} \phi_p(\mathbf{x}_1) \phi_q(\mathbf{x}_2), \quad (25)$$

where we sum over a complete basis of functions. Using this principle, we can use a linear combination of determinants (each having a different combination of orbitals from a complete basis) to describe any  $N$ -variable function.

These Slater determinants with the different  $\phi_i$ 's can be written as different excitations of the Hartree-Fock wavefunction, our reference determinant. An excitation of the reference determinant is when we replace the occupied orbitals already present in the determinant with unoccupied orbitals from the basis of



orbitals. An example of such a determinant where we replace the occupied orbital  $\phi_i$  with the unoccupied orbital  $\phi_a$  can be written as

$$a_a^\dagger a_i |\phi_i \phi_j \dots \phi_k\rangle = |\phi_a \phi_j \dots \phi_k\rangle \quad (26)$$

We now introduce a naming convention for the orbitals, which will be very important later. Occupied orbitals are called holes, hole states or hole orbitals and are labeled  $i, j, k, \dots$ . Unoccupied orbitals are called particles, particle states or particle orbitals and are labeled  $a, b, c, \dots$ .

Any determinant can be written as excitations of the reference determinant, and it is convenient to do so, since it is the determinant with the lowest energy. There are many possible excited determinants however, so we use cluster operators to create them in a compact and organized way.

We define a single-orbital cluster operator, with its corresponding weights  $t_i^a$

$$\hat{t}_i = \sum_a t_i^a a_a^\dagger a_i, \quad (27)$$

where we loop over all unoccupied orbitals  $a$ . Applying this operator to the reference determinant creates a linear combination of the  $L - N$  singly excited determinants where orbital  $\phi_i$  has been exchanged with each of the  $L - N$  unoccupied orbitals.

$$\hat{t}_i |\phi_i \phi_j \dots\rangle = \sum_a t_i^a |\phi_a \phi_j \dots\rangle \quad (28)$$

Likewise we define a two-orbital cluster operator

$$\hat{t}_{ij} = \sum_{a>b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \quad (29)$$

The one-orbital cluster operator only exchanges the orbital  $\phi_i$  for unoccupied orbitals. It is convenient to define a total one-orbital cluster operator

$$\hat{T}_1 = \sum_i \hat{t}_i \quad (30)$$

Applying the total one-orbital cluster operator to the reference determinant produces a linear combination of all possible single excitations. Not only those where orbital  $\phi_i$  has been exchanged.

The two-orbital cluster operator becomes

$$\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} \quad (31)$$

And in general the n-orbital cluster operator is

$$\hat{T}_n = \sum_{ij\dots ab\dots} t_{ij\dots ab\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i \quad (32)$$

## 2.5 The Coupled Cluster Equations

### 2.5.1 The wavefunction ansatz

Recall that we wish to create new determinants from our reference determinant, and that we wish to find the combination of these that best satisfy the Schrödinger equation. Using the cluster operators we can write the linear combination of all possible excited determinants as

$$|\Psi_{CI}\rangle = (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N) |\Phi_0\rangle = \hat{T} |\Phi_0\rangle, \quad (33)$$

where  $N$  is the number of electrons. This wavefunction ansatz, called the configuration interaction (CI) ansatz, gives the exact solution to the Schrödinger equation, within the space of our basis. It has the problem however, of being too difficult to optimize for large systems. The number of parameters that must be found is simply too large.

A way around this problem is to model higher excitations as combinations of lower excitations. We don't "need"  $\hat{T}_4$  for instance, when we could use  $\hat{T}_2^2$  to give us quadruple excitations. This works surprisingly well in practice, as a quadruple excitation are often just two unrelated double excitations anyway. We will however need to optimize the  $\hat{T}_2$  amplitudes for describing both double excitations and quadruple excitations (through  $\hat{T}_2^2$ ) in order to get the best results. Sextuple and octuple excitations and so on can be modeled in the same way using only  $\hat{T}_2$ . In this way all possible excitations can be modeled with only combinations of  $\hat{T}_1$  and  $\hat{T}_2$ .

A normal approach is therefore to include only single and double excitations,  $\hat{T} = \hat{T}_1 + \hat{T}_2$ . This is called coupled cluster singles and doubles (CCSD). The wavefunction ansatz using this method can be written as

$$|\Psi_{CCSD}\rangle = (1 + \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \hat{T}_2 + \hat{T}_2\hat{T}_1 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4 + \dots) |\Phi_0\rangle, \quad (34)$$

where the terms inside the parentheses can be written as the power series expansion of an exponential function, since  $\hat{T}_1$  and  $\hat{T}_2$  commute:

$$|\Psi_{CCSD}\rangle = e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle = e^{\hat{T}} |\Phi_0\rangle, \quad (35)$$

Another, less common approach is coupled cluster doubles (CCD) which only includes double excitations.

$$|\Psi_{CCD}\rangle = (1 + \hat{T}_2 + \hat{T}_2^2 + \hat{T}_2^3 + \dots) |\Phi_0\rangle = e^{\hat{T}_2} |\Phi_0\rangle = e^{\hat{T}} |\Phi_0\rangle, \quad (36)$$

It might seem strange to only use double excitations instead of only using single excitations, but when using a Hartree-Fock determinant, Brillouin's theorem tells us that we cannot reach a lower energy using only single excitations [10].

Both these approaches both suffer from not being well suited to modeling triple excitations. Including  $\hat{T}_3$  is often not worth the increased computational complexity however, but there are methods which include a triples (T) correction that are very accurate and still quite fast [4].

### 2.5.2 The Equations to be solved

We wish to solve the Schrödinger equation

$$\begin{aligned}\hat{H}|\Psi\rangle &= E|\Psi\rangle, \\ \hat{H}e^{\hat{T}}|\Phi_0\rangle &= Ee^{\hat{T}}|\Phi_0\rangle.\end{aligned}\tag{37}$$

From here we can left multiply with some carefully chosen states to reach an equation which we can solve for the energy:

$$\begin{aligned}\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= \langle\Phi_0|e^{-\hat{T}}Ee^{\hat{T}}|\Phi_0\rangle, \\ \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= E,\end{aligned}\tag{38}$$

where the reader must note that  $e^{-\hat{T}} \neq (e^{\hat{T}})^\dagger$ , making this equation different from the actual expectation value of the energy, which is  $\langle\Psi|\hat{H}|\Psi\rangle$ . This method is therefore not variational, as we are not working with the proper expression for the energy. When  $\hat{T}$  is not truncated however, the equation gives the correct energy, which we can use as a kind of theoretical backing that this will give somewhat good results.

Further, we get an equation we can solve for the  $\hat{T}_1$  amplitudes (only applicable for CCSD):

$$\begin{aligned}\langle\Phi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= \langle\Phi_i^a|e^{-\hat{T}}Ee^{\hat{T}}|\Phi_0\rangle, \\ \langle\Phi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= 0,\end{aligned}\tag{39}$$

and finally an equation we can solve for the  $\hat{T}_2$  amplitudes:

$$\begin{aligned}\langle\Phi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= \langle\Phi_{ij}^{ab}|e^{-\hat{T}}Ee^{\hat{T}}|\Phi_0\rangle, \\ \langle\Phi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle &= 0.\end{aligned}\tag{40}$$

The steps following this are quite involved, and more suited for a textbook. We will therefore present only a short description of the mathematical tools used and the steps taken to simplify the equations further in the next sections.

## 2.6 Simplifying the equations

### 2.6.1 Normal ordering

We have already written the cluster operators  $\hat{T}_1$  and  $\hat{T}_2$  in terms of creation and annihilation operators, and we will later show how  $e^{-\hat{T}}\hat{H}e^{\hat{T}}$  can be written using creation and annihilation operators. We can also write the Hamiltonian in terms of these operators

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle a_p^\dagger a_q - \frac{1}{4} \langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r.\tag{41}$$

This is quite helpful, as we can now work on equation 38, 39, and 40 using only the tools of second quantization.

We can write all of these equations as expectation values of the reference determinant. The  $\hat{T}_1$  equation, for instance, can be written as

$$\langle \Phi_0 | (a_i^\dagger a_a) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0. \quad (42)$$

This will be the key to turn these equations into a workable form, writing them as expectation values of the reference determinant. To evaluate these expectation values, we use normal ordering and Wick's theorem.

A string of creation and annihilation operators is normal ordered if all operators that destroy hole and particle states are to the right of the operators that create them. A reminder:  $a_i^\dagger$  destroys a hole, as it fills it with orbital  $i$ .  $a_i$  creates a hole, as it removes orbital  $i$  and leaves a hole.  $a_a^\dagger$  creates a particle state, as it adds the "particle"  $a$ . And finally,  $a_a$  destroys a particles state, as it removes "particle"  $a$ . The ordering scheme in normal ordering then becomes

$$a_a^\dagger, a_i \text{ left of } a_i^\dagger, a_a. \quad (43)$$

This is called normal ordering with respect to a reference determinant, there also exists normal ordering with respect to vacuum, which we will not use. When a string of operators is normal ordered, we can label it as normal ordered using curly braces as such

$$\{a_i a_a^\dagger a_a a_i^\dagger\}. \quad (44)$$

The expectation value of a normal ordered string of operators with respect to the reference determinant is zero so long as it includes operators that destroy states

$$\langle \Phi_0 | \{a_i a_a^\dagger \dots a_a a_i^\dagger\} | \Phi_0 \rangle = 0. \quad (45)$$

This is because the rightmost operator acting on the reference determinant then always gives zero.

### 2.6.2 Wick's theorem

Wick's theorem is an incredibly useful theorem that can make any string of creation and annihilation operators into a sum of normal ordered operators and easily evaluated Kronecker-deltas. This will come in handy, as the normal ordered operators will disappear when evaluating expectation values, as seen in the previous section. And recall that the equations we wish to solve, equations 38, 39, and 40, can be written in terms of only creation and annihilation operators. Wick's theorem can therefore reduce these equations into only easily evaluated Kronecker-deltas.

The theorem uses something called contractions. A contraction between two operators is given by

$$\overline{AB} \equiv AB - \{AB\}, \quad (46)$$

where one must normal order the operators in the curly brackets and change the sign of the term with the curly brackets for each permutation of neighbouring

operators necessary to do this. If the two contracted operators are not next to each other, the string of operators must be permuted to bring them together, with the sign changing every permutation.

This means that

$$\begin{aligned}\overline{a_i^\dagger a_j} &= a_i^\dagger a_j - \{a_i^\dagger a_j\} = a_i^\dagger a_i + a_j a_i^\dagger = \delta_{ij}, \\ \overline{a_a a_b^\dagger} &= a_a a_b^\dagger - \{a_a a_b^\dagger\} = a_a a_b^\dagger + a_b^\dagger a_a = \delta_{ab}, \\ \overline{a_a^\dagger a_b} &= \overline{a_i^\dagger a_i} = 0.\end{aligned}\tag{47}$$

All other contractions involve Kronecker-deltas between hole and particle indices, which are zero.

We are now ready to present Wick's theorem:

$$\begin{aligned}ABC \cdots XYZ &= \{ABC \cdots XYZ\}_v \\ &+ \sum_{\text{singles}} \{\overline{AB} \cdots XYZ\} \\ &+ \sum_{\text{doubles}} \{\overline{ABC} \cdots XYZ\} \\ &+ \cdots\end{aligned}\tag{48}$$

which gives us a way of turning a string of operators into sums of normal ordered string, with some contractions to be evaluated. And the generalized Wick's theorem:

$$\begin{aligned}\{ABC \cdots\} \{XYZ \cdots\} &= \{ABC \cdots XYZ\} \\ &+ \sum_{\text{singles}} \{\overline{AB} \cdots XYZ\} \\ &+ \sum_{\text{doubles}} \{\overline{ABC} \cdots XYZ\} \\ &+ \cdots\end{aligned}\tag{49}$$

which describes how to normal order the product of two normal ordered strings. When all the terms in a string are contracted, we call the string fully contracted. In this case a convenient trick applies: If the lines describing the contractions cross an even number of times, the result is positive, if not the result is negative. For instance

$$\{\overline{a_i^\dagger a_a} \overline{a_j a_b^\dagger}\} = -\delta_{ij} \delta_{ab},\tag{50}$$

We are now ready to return to the equations at hand.

### 2.6.3 Getting a workable Hamiltonian

Working with a Hamiltonian written in terms of normal-ordered second-quantized operators will make our life much easier. It can be shown that such a normal

ordered Hamiltonian can be defined as

$$\begin{aligned}
\hat{H}_N &= \hat{H} - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \\
&= \sum_{pq} f_{pq} \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \\
&= \hat{F}_N + \hat{V}_N
\end{aligned} \tag{51}$$

We will use this Hamiltonian instead when solving equations 38, 39, and 40. We can now define

$$\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}}. \tag{52}$$

This expression can be simplified via the so-called Campbell-Baker-Hausdorff formula into

$$\begin{aligned}
\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}} &= \hat{H}_N + [\hat{H}_N, \hat{T}] + \frac{1}{2!} [[\hat{H}_N, \hat{T}], \hat{T}] + \frac{1}{3!} [[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}] \\
&\quad + \frac{1}{4!} [[[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}], \hat{T}] + \dots
\end{aligned} \tag{53}$$

Many of these terms will disappear when we insert this expression into equations 38, 39, and 40: Since  $\hat{H}_N$  is a two-particle operator, whenever the left and right hand side of it differ by more than two orbitals, you will get zero.

Many terms will also cancel, and it can be shown that the only non-zero terms are those in which the Hamiltonian  $\hat{H}_N$  has at least one contraction with every cluster operator  $\hat{T}_n$  on its right. If we use these results and insert  $\hat{T} = \hat{T}_1 + \hat{T}_2$  we get

$$\begin{aligned}
\bar{H} &= \left( \hat{H}_N + \hat{H}_N \hat{T}_1 + \hat{H}_N \hat{T}_2 + \frac{1}{2} \hat{H}_N \hat{T}_1^2 + \frac{1}{2} \hat{H}_N \hat{T}_2^2 + \hat{H}_N \hat{T}_1 \hat{T}_2 \right. \\
&\quad + \frac{1}{6} \hat{H}_N \hat{T}_1^3 + \frac{1}{2} \hat{H}_N \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{H}_N \hat{T}_1 \hat{T}_2^2 + \frac{1}{6} \hat{H}_N \hat{T}_2^3 \\
&\quad \left. + \frac{1}{24} \hat{H}_N \hat{T}_1^4 + \frac{1}{6} \hat{H}_N \hat{T}_1^3 \hat{T}_2 + \frac{1}{4} \hat{H}_N \hat{T}_1^2 \hat{T}_2^2 + \frac{1}{6} \hat{H}_N \hat{T}_1 \hat{T}_2^3 + \frac{1}{24} \hat{H}_N \hat{T}_2^4 \right)_c,
\end{aligned} \tag{54}$$

where the  $c$  tells us to only include contractions where  $\hat{H}_N$  has at least one contraction with every cluster operator  $\hat{T}_n$  on its right.

## 2.6.4 Simplifying to matrix-elements

The next step is to use Wick's theorem and the rules of normal ordering to simplify equation 38, 39, and 40, only with  $\hat{H}_N$ , as discussed in the previous section (So that the energy equation becomes  $\langle \Phi_0 | \bar{H} | \Psi_0 \rangle = 0$ , and the amplitude equations become  $\langle \Phi_i^a | \bar{H} | \Psi_0 \rangle = 0$  and  $\langle \Phi_0 | \bar{H} | \Psi_{ij}^{ab} \rangle = 0$ ).

$\bar{H}$  includes the term  $\frac{1}{2} \hat{H}_N \hat{T}_1^2$ , which can be written as  $\frac{1}{2} (\hat{F}_N + \hat{V}_N) \hat{T}_1^2$ . We will now show how to evaluate the term  $\langle \Phi_i^a | \frac{1}{2} \hat{V}_N \hat{T}_1^2 | \Phi_0 \rangle$  from the  $\hat{T}_1$  amplitude equations. We choose this term in particular because when we implemented the Coupled Cluster equations into code, we discovered a discrepancy between the

equations provided by Crawford & Schaefer [4], and Shavitt & Bartlett [9]. It is the evaluation of  $\langle \Phi_i^a | \frac{1}{2} \hat{V}_N \hat{T}_1^2 | \Phi_0 \rangle$  from the  $\hat{T}_1$  amplitude equations that differs in the two books.

In equation 152 of Crawford & Schaefer [4], they get the terms

$$- \sum_{klc} \langle kl || ci \rangle t_k^c t_l^a - \sum_{kcd} \langle ka || cd \rangle t_k^c t_i^d \quad (55)$$

While in equation 10.23 of Shavitt & Bartlett [9], they get the terms

$$- \sum_{klc} \langle kl || ic \rangle t_k^a t_l^c + \sum_{kcd} \langle ak || cd \rangle t_i^c t_k^d \quad (56)$$

By swapping the indices  $k$  and  $l$  in the first sum, and  $c$  and  $d$  in the second, we get

$$\begin{aligned} & - \sum_{klc} \langle lk || ic \rangle t_l^a t_k^c + \sum_{kcd} \langle ak || dc \rangle t_i^d t_k^c, \\ & = - \sum_{klc} \langle kl || ci \rangle t_k^c t_l^a + \sum_{kcd} \langle ka || cd \rangle t_k^c t_i^d, \end{aligned} \quad (57)$$

where we used the fact that we can interchange two indices on one side of the two-body integrals if we also change the sign. We see that the equations from the two books differ in the sign of the second term. We therefore went through the trouble of evaluating these terms ourselves, both to reassure ourselves that the equations from Shavitt & Bartlett were correct, as confirmed by other sources, but also as a good example and exercise.

We start by writing out the expression in terms of annihilation and creation operators

$$\langle \Phi_i^a | (\hat{V}_N \hat{T}_1^2) | \Phi_0 \rangle = \frac{1}{8} \sum_{pqrs} \sum_{ld} \sum_{kc} \langle pq || rs \rangle t_l^d t_k^c \langle \Phi_0 | \{a_i^\dagger a_a\} (\{a_p^\dagger a_q^\dagger a_s a_r\} \{a_d^\dagger a_l\} \{a_c^\dagger a_k\})_c | \Phi_0 \rangle \quad (58)$$

Wick's theorem tells us that we need to evaluate all possible contractions between the strings of operators (and not within the strings), and the  $c$  tells us that the two  $\hat{T}_1$ -s must share at least one contraction with  $\hat{V}_N$ . Furthermore, since we are computing an expectation value between reference determinants, terms from Wick's theorem that contain un-contracted operators will disappear. That is, only fully contracted terms must be included. We also only need to consider contractions that give non-zero results. With this in mind, we write out the possible contractions and the matrix elements that follow:

$$\begin{aligned}
\langle \Phi_i^a | (\hat{V}_N \hat{T}_1^2) | \Phi_0 \rangle &= \frac{1}{8} \sum_{pqrs} \sum_{ld} \sum_{kc} \langle pq|rs \rangle t_l^d t_k^c \langle \Phi_0 | \{a_i^\dagger a_a\} \{a_p^\dagger a_q^\dagger a_s a_r\} \{a_d^\dagger a_l\} \{a_c^\dagger a_k\}_c | \Phi_0 \rangle \\
&= \sum_{pqrs} \sum_{ld} \sum_{kc} \langle pq|rs \rangle t_l^d t_k^c \left( \right. \\
&\quad \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \\
&\quad + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \\
&\quad + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \\
&\quad + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \\
&\quad + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \\
&\quad \left. + \{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_d^\dagger a_l a_c^\dagger a_k\} \right) \\
&= \frac{1}{8} \sum_{pqrs} \sum_{ld} \sum_{kc} \langle pq|rs \rangle t_l^d t_k^c (\delta_{is} \delta_{ad} \delta_{pl} \delta_{qk} \delta_{rc} - \delta_{is} \delta_{ad} \delta_{pk} \delta_{ql} \delta_{rc} - \delta_{is} \delta_{ac} \delta_{pl} \delta_{qk} \delta_{rd} \\
&\quad + \delta_{is} \delta_{ac} \delta_{pk} \delta_{ql} \delta_{rd} - \delta_{ir} \delta_{ad} \delta_{pl} \delta_{qk} \delta_{sc} + \delta_{ir} \delta_{ad} \delta_{pk} \delta_{ql} \delta_{sc} \\
&\quad + \delta_{ir} \delta_{ac} \delta_{pl} \delta_{qk} \delta_{sd} - \delta_{ir} \delta_{ac} \delta_{pk} \delta_{ql} \delta_{sd} - \delta_{il} \delta_{ap} \delta_{qk} \delta_{sd} \delta_{rc} \\
&\quad + \delta_{il} \delta_{ap} \delta_{qk} \delta_{sc} \delta_{rd} + \delta_{il} \delta_{aq} \delta_{pk} \delta_{sd} \delta_{rc} - \delta_{il} \delta_{aq} \delta_{pk} \delta_{sc} \delta_{rd} \\
&\quad + \delta_{ik} \delta_{ap} \delta_{ql} \delta_{sd} \delta_{rc} - \delta_{ik} \delta_{ap} \delta_{ql} \delta_{sc} \delta_{rd} - \delta_{ik} \delta_{aq} \delta_{pl} \delta_{sd} \delta_{rc} \\
&\quad + \delta_{ik} \delta_{aq} \delta_{pl} \delta_{sc} \delta_{rd}) \\
&= \frac{1}{8} \left( \sum_{lkc} \langle lk|ci \rangle t_l^a t_k^c - \sum_{lkc} \langle lk|ci \rangle t_l^a t_k^c - \sum_{ldk} \langle lk|di \rangle t_l^d t_k^a \right. \\
&\quad + \sum_{kld} \langle kl|di \rangle t_l^d t_k^a - \sum_{lkc} \langle lk|ic \rangle t_l^a t_k^c + \sum_{lkc} \langle kl|ic \rangle t_l^a t_k^c \\
&\quad + \sum_{ldk} \langle lk|id \rangle t_l^d t_k^a - \sum_{ldk} \langle kl|id \rangle t_l^d t_k^a - \sum_{dkc} \langle ak|cd \rangle t_i^d t_k^c \\
&\quad + \sum_{dkc} \langle ak|dc \rangle t_i^d t_k^c + \sum_{dkc} \langle ka|cd \rangle t_i^d t_k^c - \sum_{dkc} \langle ka|dc \rangle t_i^d t_k^c \\
&\quad + \sum_{ldc} \langle al|cd \rangle t_l^d t_i^c - \sum_{ldc} \langle al|dc \rangle t_l^d t_i^c - \sum_{ldc} \langle la|cd \rangle t_l^d t_i^c \\
&\quad \left. + \sum_{ldc} \langle la|dc \rangle t_l^d t_i^c \right) \\
&= - \sum_{klc} \langle kl|ci \rangle t_k^c t_l^a + \sum_{kcd} \langle ka|cd \rangle t_k^c t_i^d
\end{aligned}$$



We see that the terms provided from Shavitt & Bartlett were indeed correct. We describe how we used code to help us find the contractions and produce the equations in section 3.1. This is only a very small number of the total number of terms that need to be evaluated for the Coupled Cluster method. Similar calculations need to be performed for every single term in  $\bar{H}$  for both the energy,  $\hat{T}_1$  and  $\hat{T}_2$  equations.

## 2.7 The simplified equations

By using a normal ordered Hamiltonian and employing Wick's theorem to turn equations 38, 39, and 40 into the workable matrix-element form we get the following equations:

### 2.7.1 The Energy Equations

The difference between the energy of the reference determinant and the energy of the coupled cluster wave function is called the correlation energy, since it is the energy difference arising from accounting for electron correlations. The correlation energy for the CCD wave function is:

$$E_{CCD} - E_0 = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \frac{1}{4} \sum_{aibj} \langle ij || ab \rangle t_{ij}^{ab}. \quad (60)$$

The correlation energy for the CCSD wave function is:

$$E_{CCSD} - E_0 = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \sum_{ia} f_{ia} t_i^a + \frac{1}{4} \sum_{aibj} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \langle ij || ab \rangle t_i^a t_j^b. \quad (61)$$

### 2.7.2 The Amplitude Equations

The CCD amplitude equation for the  $\hat{T}_2$  amplitudes is:

$$\begin{aligned} 0 = & \langle ab || ij \rangle + \sum_c (f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc}) - \sum_k (f_{kj} t_{ik}^{ab} - f_{ki} t_{jk}^{ab}) \\ & + \frac{1}{2} \sum_{cd} \langle ab || cd \rangle t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \langle kl || ij \rangle t_{kl}^{ab} + P(ij)P(ab) \sum_{kc} \langle kb || cj \rangle t_{ik}^{ac} \\ & + \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_{ij}^{cd} t_{kl}^{ab} + P(ij) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ac} t_{jl}^{bd} \\ & - P(ij) \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{ik}^{dc} t_{lj}^{ab} - P(ab) \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{lk}^{ac} t_{ij}^{db} \end{aligned} \quad (62)$$

The CCSD amplitude equation for the  $\hat{T}_1$  amplitudes is:

$$\begin{aligned}
0 = & f_{ai} + \sum_c f_{ac} t_i^c - \sum_k f_{ki} t_k^a + \sum_{kc} \langle ka \| ci \rangle t_k^c + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ka \| cd \rangle t_{ki}^{cd} \\
& - \frac{1}{2} \sum_{klc} \langle kl \| ci \rangle t_{kl}^{ca} - \sum_{kc} f_{kc} t_i^c t_k^a - \sum_{klc} \langle kl \| ci \rangle t_k^c t_l^a + \sum_{kcd} \langle ka \| cd \rangle t_k^c t_i^d \\
& - \sum_{klcd} \langle kl \| cd \rangle t_k^c t_i^d t_l^a + \sum_{klcd} \langle kl \| cd \rangle t_k^c t_{li}^{da} - \frac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_{ki}^{cd} t_l^a - \frac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_{kl}^{ca} t_i^d
\end{aligned} \tag{63}$$

where the reader will recognize the last two terms on the second line as the terms we computed ourselves in the previous section.

The CCSD amplitude equation for the  $\hat{T}_2$  amplitudes can be found in appendix A.

### 2.7.3 Solving the $\hat{T}_1$ amplitude equation

The  $\hat{T}_1$  and  $\hat{T}_2$  amplitude equations can be solved with an iterative approach. Given an initial set of amplitudes, we compute a new set of amplitudes which better satisfy the equations. These new amplitudes can then be improved upon once again, and so on, until we (hopefully) have amplitudes which completely satisfy the equations. First, we need to formulate expressions for updating the amplitudes.

We start by manipulating the  $\hat{T}_1$  amplitude equation so that we get an expression for  $t_i^a$ . We start by separating the diagonal terms from the Fock-Matrix summations.

$$\begin{aligned}
0 &= \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle \\
0 &= f_{ai} + f_{aa} t_i^a - f_{ii} t_i^a + \sum_c (1 - \delta_{ca}) f_{ac} t_i^c - \sum_k (1 - \delta_{ik}) f_{ik} t_k^a + \dots
\end{aligned} \tag{64}$$

Defining

$$D_i^a = f_{ii} - f_{aa}, \tag{65}$$

we can write

$$\begin{aligned}
D_i^a t_i^a &= f_{ai} + \sum_c (1 - \delta_{ca}) f_{ac} t_i^c - \sum_k (1 - \delta_{ik}) f_{ik} t_k^a + \dots, \\
t_i^a &= \frac{1}{D_i^a} (f_{ai} + \sum_c (1 - \delta_{ca}) f_{ac} t_i^c - \sum_k (1 - \delta_{ik}) f_{ik} t_k^a + \dots),
\end{aligned} \tag{66}$$

giving us an expression for a new  $t_i^a$ , which should better satisfy the  $\hat{T}_1$  amplitude equation. Using this expression, we can update the  $\hat{T}_1$  amplitudes iteratively by setting the amplitudes  $t_i^a$  equal to the value we compute for the right hand side.

This approach can have trouble converging however. Section 3.4 describes schemes which improve convergence by cleverly combining the old  $t_i^a$  values

with the new ones computed in equation 66. The use of these schemes motivate finding an expression for difference between these  $t_i^a$  values. First, we define

$$\Omega_i^a = \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle. \quad (67)$$

Now, the difference between the old  $t_i^a$  values and the new ones computed from equation 66 can be written as

$$\Delta t_i^a = t_i^a - \frac{1}{D_i^a} (\Omega_i^a - D_i^a t_i^a) = \frac{\Omega_i^a}{D_i^a} \quad (68)$$

To begin the iterative approach, we need to make an initial guess for the amplitudes. We choose to set all amplitudes to 0, and from equation 66 then get the initial guess

$$t_i^a = \frac{f_{ai}}{D_i^a}. \quad (69)$$

### 2.7.4 Solving the $\hat{T}_2$ amplitude equation

The steps for finding an expression for  $t_{ij}^{ab}$  (for both CCD and CCSD) are the same as for  $t_i^a$ . We define

$$\begin{aligned} D_{ij}^{ab} &= f_{ii} + f_{jj} - f_{aa} - f_{bb}, \\ \Omega_{ij}^{ab} &= \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle. \end{aligned} \quad (70)$$

Separating out the diagonal terms from the Fock-Matrix summations we get

$$\begin{aligned} 0 &= \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle, \\ D_{ij}^{ab} t_{ij}^{ab} &= \langle ab || ij \rangle + P(ab) \sum_c (1 - \delta_{bc}) f_{bc} t_{ij}^{ac} - P(ij) \sum_k (1 - \delta_{kj}) f_{kj} t_{ik}^{ab} + \dots, \\ t_{ij}^{ab} &= \frac{1}{D_{ij}^{ab}} (\langle ab || ij \rangle + P(ab) \sum_c (1 - \delta_{bc}) f_{bc} t_{ij}^{ac} - P(ij) \sum_k (1 - \delta_{kj}) f_{kj} t_{ik}^{ab} + \dots). \end{aligned} \quad (71)$$

The difference between the initial values  $t_{ij}^{ab}$  and the ones computed from the right hand side of equation 71 is

$$\Delta t_{ij}^{ab} = t_{ij}^{ab} - \frac{1}{D_{ij}^{ab}} (\Omega_{ij}^{ab} - D_{ij}^{ab} t_{ij}^{ab}) = \frac{\Omega_{ij}^{ab}}{D_{ij}^{ab}} \quad (72)$$

This difference  $\Delta t_{ij}^{ab}$  will be used along with  $\Delta t_i^a$  to update the  $\hat{T}$  amplitudes. Section 3.4 describes schemes that improve upon the crude guesses  $t_i^a \rightarrow t_i^a + \Delta t_i^a$  and  $t_{ij}^{ab} \rightarrow t_{ij}^{ab} + \Delta t_{ij}^{ab}$  for the new amplitudes.

The initial guess for the amplitudes is again found by setting them to zero which leads to equation 71 giving us the initial guess

$$t_{ij}^{ab} = \frac{\langle ab || ij \rangle}{t_{ij}^{ab}}. \quad (73)$$

## 2.8 Expectation values other than energy

The Coupled Cluster method is not variational, which means that it can give energies lower than the exact ground state energy. This might seem like a big problem, but the method is typically very accurate, so it isn't [6]. What is a big problem however, is that other expectation values are not guaranteed to have accurate values. Since the Coupled Cluster method is not variational, it does not satisfy the conditions of the Hellman-Feynman theorem, and it therefore doesn't necessarily give accurate values for other expectation values when we get an accurate value for the energy. We should therefore not interpret other expectation values as physically relevant. This does not stop us from computing these expectation values however.

A useful quantity when computing one- and two-body expectation values are the density matrices [7]. The one-body density matrix is given by

$$\rho_{qp} = \langle \Psi | a_p^\dagger a_q | \Psi \rangle. \quad (74)$$

If we use our CCSD wave function on the right, and  $\langle \Psi_0 | e^{-T}$  on the left, we get

$$\begin{aligned} \rho_{qp} &= \langle \Psi_0 | e^{-T} a_p^\dagger a_q e^T | \Psi_0 \rangle, \\ &= \langle \Psi_0 | e^{-T} (\{a_p^\dagger a_q\} + \{\overline{a_p^\dagger a_q}\}) e^T | \Psi_0 \rangle, \\ &= \langle \Psi_0 | e^{-T} (\{a_p^\dagger a_q\} + \delta_{pq} \delta_{pi}) e^T | \Psi_0 \rangle, \\ &= \langle \Psi_0 | e^{-T} \{a_p^\dagger a_q\} e^T | \Psi_0 \rangle + \delta_{pq} \delta_{pi}, \\ &= \delta_{pi} \delta_{qa} t_i^a + \delta_{pq} \delta_{pi}, \end{aligned} \quad (75)$$

where we used the normal ordering rules discussed earlier to reach the second to last line. To evaluate the final expectation value with the normal ordered  $\{a_p^\dagger a_q\}$ , we simply used the expectation value computed for  $(\hat{F}_N)_{pq} = f_{pq} \{a_p^\dagger a_q\}$  earlier. If we used the CCD wavefunction, we would only get the second term.

One of the quantities of interest we can compute is the particle density, the probability density of finding any electron at a given position  $x$ .

$$\rho(x_1) = N \left( \prod_{i=2}^N \int dx_i \right) |\Psi(x_1, x_2, \dots, x_N)|^2, \quad (76)$$

which we can also express using the one-body density as[6]

$$\rho(x) = \sum_{pq} \phi_p^*(x) \rho_{pq} \phi_q(x). \quad (77)$$

## 2.9 The harmonic quantum dot system

We will test the CCD and CCSD methods on a system of two electrons in a harmonic potential in one dimension. This system acts as a good benchmark as we have ground state energies from other authors using other methods to compare to, as well as the basis vector integrals being relatively simple and

cheap to compute. We will also see the importance of convergence accelerators when analyzing this system.

The Hamiltonian for the system is

$$\hat{H} = \sum_i -\frac{1}{2} \frac{d^2}{dx_i^2} + \frac{1}{2} \omega^2 x_i^2 + \sum_{i < j} \frac{1}{\sqrt{(x_i - x_j)^2 + a^2}}, \quad (78)$$

where  $\omega$  is the strength of the harmonic oscillator potential and  $a$  is a shielding parameter which prevents the Coulomb interaction from becoming too strong when the electrons are close.

If we ignore all interaction, the stationary states for the system are [5] (still using atomic units)

$$\psi_n(x) = \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad (79)$$

where  $\xi = \sqrt{\omega}x$  and  $H_n$  is the Hermite polynomial of order  $n$ . The energy of these state (with no interaction) is

$$E_n = \left(n + \frac{1}{2}\right) \omega. \quad (80)$$

These stationary states form a complete basis in positional space. If we use two copies of each state and pair each with a spin basis vector, we get a complete basis for both the positional and spin space.

$$\begin{aligned} |\psi_{2i-1}\rangle &= \psi_i(x) \alpha(m_x) \quad \text{for } i = 1, 2, 3, \dots, l, \\ |\psi_{2i}\rangle &= \psi_i(x) \beta(m_x) \quad \text{for } i = 1, 2, 3, \dots, l. \end{aligned} \quad (81)$$

This spin-doubled harmonic oscillator basis will be used as the basis for our Hartree-Fock and Coupled Cluster calculations. We will be limited to a truncated basis, using only a limited number  $l$  of the infinite stationary states. The systems with and without interaction are quite similar however, so this truncated basis will hopefully be able to express the ground state well.

## 2.10 The Pairing Model

A nice system for testing the validity of our methods is the pairing model. In it, there are  $p$  levels, each with a degeneracy of 2, due to the two possible spin values  $\sigma = \pm$ . Each level is associated with a one-body energy

$$\hat{H}_0 = \delta \sum_{p\sigma} (p-1) a_{p\sigma}^\dagger a_{p\sigma}, \quad (82)$$

where  $\delta$  is a model parameter we here set to 1. There is also an energy contribution from the two-body interaction

$$\hat{V} = -\frac{1}{2} g \sum_{pq} a_{p+}^\dagger a_{p-}^\dagger a_{q+} a_{q-}, \quad (83)$$

where  $g$  is the interaction strength.

We employ a basis of 8 single-particle states, two for each  $p$  value 1-4, and with alternating spins. We then choose to look at a system of 4 particles. The Hartree-Fock determinant of this system is built up by just the 4 first lowest energy basis states, using them as hole-states with the rest becoming particle-states. The states, with all this in mind, are shown in table

p	$\sigma$	E	Type
1	+	-g/2	Hole
1	-	-g/2	Hole
2	+	1-g/2	Hole
2	-	1-g/2	Hole
3	+	3	Particle
3	-	3	Particle
4	+	3	Particle
4	-	3	Particle

The one- and two-body matrix elements of this basis can be computed directly from equations 82 and 83. With the matrix elements and a Hartree-Fock Slater determinant, we can try to approximate the exact ground state of the system using Coupled Cluster. This model has the quirk that single-excitations give a much higher energy, due to the interaction requiring two pairs of  $p$  values. This makes the number of possible excited determinants quite small, and an analytical exact multi-determinant solution is possible, as shown in [8]. We later compare our CC results to the exact and many-body perturbation theory of second order energies from [8].

### 3 Implementation

#### 3.1 Wick's Theorem Implementation

In equation 59 we showed all the full contractions from the expression

$$\langle \Phi_i^a | (\hat{V}_N \hat{T}_1^2) | \Phi_0 \rangle = \frac{1}{8} \sum_{pqrs} \sum_{ld} \sum_{kc} \langle pq | rs \rangle t_l^d t_k^c \langle \Phi_0 | \{a_i^\dagger a_a\} (\{a_p^\dagger a_q^\dagger a_s a_r\} \{a_d^\dagger a_l\} \{a_c^\dagger a_k\})_c | \Phi_0 \rangle, \quad (84)$$

coming from the CCSD  $\hat{T}_1$  amplitude equations. We quickly realized finding them by hand would be very difficult. There are many of them, and seemingly no straightforward way to find them all. We therefore opted for a programmatic approach which we will outline in this section.

We know from the discussion of normal ordering, that the only single contractions that give non-zero results are  $a_i^\dagger a_j = \delta_{ij}$  where  $i$  and  $j$  are hole states, and  $a_a a_b^\dagger = \delta_{ab}$  where  $a$  and  $b$  are particle states. Wick's theorem also tells us that contractions only need to be evaluated between normal ordered strings, and not within them. These two results lets us greatly limit the total number of "valid" single contractions.

We represent each operator as being particle or hole and dagger or no dagger, and giving it the index of the string of operators it belongs to. For instance  $a_d^\dagger$  is a hole operator, with a dagger and index 3. Strings and dictionaries are employed to represent this in code. By then looping over all possible pairs of operators we can test whether they obey the rules stated above with a couple of if-statements. Of 45 possible, we are left with 16 valid single contractions.

Next we loop over all the combinations of 5 valid single contractions, see which ones have no repeat operators, and that have contractions between  $\hat{V}$  and both  $\hat{T}_1$ -s. Sets are used to check for repeat operators, and a regular expression is used to check for the required single contractions. Of 4368 combinations, 16 are valid full contractions.

Finally we turn these full contractions, along with their corresponding Kronecker delta products into Latex code using string interpolation, writing the resulting Latex code to file. The simple and elegant syntax of the `simpler-wick` Latex package was of great help. The signs of the Kronecker delta products were corrected by hand by simply counting the number of crossings in the fully contracted terms. The remaining operations of turning Kronecker delta products into sums of matrix elements, and then simplifying these sums was done by hand since it took little time.

### 3.2 Basis Vector Integrals and Hartree-Fock

We have implemented code to compute the matrix elements  $h_{ai}$ ,  $\langle ab||ij \rangle$  and  $f_{ai}$ . For the harmonic quantum dots system, we implemented functions to inductively evaluate Hermite polynomials, which are needed to evaluate the harmonic oscillator basis functions in space. The integrals over space are computed using the trapezoidal method, using discrete values over a 1D grid. The pairing system basis and matrix elements are computed directly using simple analytical results straight from the the system description.

We have also implemented finding a Hartree-Fock basis given the initial matrix elements, and then computing the matrix elements again using the Hartree-Fock basis.

### 3.3 Amplitude Equation Evaluation

There are many ways to evaluate the right hand sides of the amplitude equations, but we have chosen a simple one, to save time developing the code.

The right hand side of the  $\hat{T}_1$  amplitude equation (equation 63) must be evaluated for every amplitude  $t_i^a$ , that is,  $n(l-n)$  times. The equation includes a quadruple loop with  $n^2(l-n)^2$  evaluations. The computational complexity of evaluating the  $\hat{T}_1$  amplitude equation is thus  $O(n^3l^3)$ .

The right hand side of the  $\hat{T}_2$  amplitude equation (equation 94) must be evaluated for every amplitude  $t_{ij}^{ab}$ , where  $a < b$  and  $i < j$ . The amplitudes where  $b < a$  and  $j < i$  can be found by interchanging  $a$  with  $b$  and  $i$  with  $j$ , remembering that each interchange flips the sign. Where  $a = b$  and  $i = j$ , the amplitudes are always zero. This means that there are  $n(n-1)/2 \cdot (l-n)(l-n)$

$n - 1)/2$  evaluations (A restricted double loop has first  $n - 1$  evaluations of the inner loop, then  $n - 2$ , and so on.  $(n(n - 1))/2$  in total). The equation includes a quadruple loop with  $n^2(l - n)^2$  evaluations. The computational complexity of evaluating the  $\hat{T}_2$  amplitude equation is thus  $O(n^4l^4)$ .

To speed up evaluation, parallelization is utilized. Since we are only looking at systems with  $n = 2$ , we parallelize over the  $(l - n)$   $a$  values, for both equations, to make use of more CPU threads.

The computational complexity of our CCSD implementation is  $O(n^4l^4)$ . However, factoring the large sums in the  $\hat{T}_2$  amplitude equation into smaller terms, and storing intermediate values can lead to a complexity of only  $O(l^6)$  [4], which is often much faster. This does come at the cost of writing more values to memory, and more time writing the actual code. We opted to implement the equations as written, since more speed was not needed for the small systems we are interested in.

### 3.4 Convergence Acceleration

The iterative scheme to solve the amplitude equations shown in section 2.7.3 is not guaranteed to converge quickly, if at all. In this section we present two schemes that aim to speed up or even allow convergence of the iterative scheme.

From equation 69 and 73 we have initial amplitudes we together now call  $t$ , and from equations 68 and 72 we have the crude updates to  $t$  which we together now call  $\Delta t$ . (Whenever we "combine" tensors of numbers like this in this section, we first unravel them into vectors, and then concatenate them in the corresponding code. After we have computed the new  $t$ , we reshape everything back how it was.) The simplest iterative scheme which we will improve upon is this:

$$t \rightarrow t + \Delta t. \quad (85)$$

#### 3.4.1 Alpha filter

If the iterative scheme does not converge when updating  $t$  by  $\Delta t$ , a natural alternative is to update it by a scaled down  $\Delta t$ , by "taking smaller steps". This is often an improvement upon the crude approach. Introducing a scaling parameter  $\alpha \in [0, 1]$ , we define a new iterative scheme using an Alpha filter

$$t \rightarrow t + \alpha \Delta t. \quad (86)$$

#### 3.4.2 Direct inversion of the iterative subspace

A more sophisticated approach is to look at the  $m$  previous  $t$ -s and  $\Delta t$ -s, and see which combination of them best fulfills the amplitude equations. Recall that the amplitude equations are

$$\begin{aligned} 0 &= \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle, \\ 0 &= \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle, \end{aligned} \quad (87)$$



and that we defined

$$\begin{aligned}\Omega_i^a &= \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle, \\ \Omega_{ij}^{ab} &= \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle.\end{aligned}\tag{88}$$

$\Omega_i^a$  and  $\Omega_{ij}^{ab}$  are clearly good measures of how well the  $t$ -s satisfy the amplitude equations, when they are all zero, the equations are satisfied. We will therefore use them as a direct measure of the error. We will from now on call the combination of these errors  $\Omega$ .

We want to find the coefficients  $c_i$  such that

$$t_{new} = \sum_i^m c_i (t_i + \Delta t_i),\tag{89}$$

is the combination of  $t$ -s and  $\Delta t$ -s that best satisfies the amplitude equations. Combining the  $m$  previous errors  $\Omega_i$  in the same way gives us the error vector.

$$\Omega_{new} = \sum_i^m c_i \Omega_i\tag{90}$$

We want to minimize the norm of the error vector under the constraint of the  $c$ -s adding to 1, so that we get a useful solution, and not the trivial  $c_i = 0$  solution. We introduce a Lagrange multiplier  $\lambda$  to satisfy this demand. We now minimize

$$\begin{aligned}L &= ||\Omega_{new}||^2 - 2\lambda \left( \sum_i c_i - 1 \right), \\ &= \sum_{ij} c_j B_{ij} c_i - 2\lambda \left( \sum_i c_i - 1 \right),\end{aligned}\tag{91}$$

where  $B_{ij} = \langle \Omega_j, \Omega_i \rangle$ .

Taking the derivative wrt.  $c_k$  and equating to 0 gives

$$\begin{aligned}\frac{\partial L}{\partial c_k} &= 0, \\ \sum_j B_{kj} c_j + \sum_i B_{ik} c_i - 2\lambda &= 0, \\ 2 \sum_j B_{kj} c_j - 2\lambda &= 0, \\ \sum_j B_{kj} c_j - \lambda &= 0.\end{aligned}\tag{92}$$

The derivatives of the  $c_k$ -s and  $\lambda$  form a system of  $(m + 1)$  linear equations

which we can solve to find the  $c_k$ -s.

$$\begin{bmatrix} B_{11} & B_{12} & B_{13} & \dots & B_{1m} & -1 \\ B_{21} & B_{22} & B_{23} & \dots & B_{2m} & -1 \\ B_{31} & B_{32} & B_{33} & \dots & B_{3m} & -1 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ B_{m1} & B_{m2} & B_{m3} & \dots & B_{mm} & -1 \\ 1 & 1 & 1 & \dots & 1 & 0 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_m \\ \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \quad (93)$$

Each iteration of solving the Coupled-Cluster amplitude equations using direct inversion of the iterative subspace(DIIS) can be summarized as

1. Compute  $\Omega$  and  $\Delta t$
2. Store the current  $t$ ,  $\Omega$  and  $\Delta t$
3. Collect the last  $m$   $t$ -s,  $\Omega$ -s and  $\Delta t$ -s
4. Set up the matrix of equations
5. Solve the equations to get the coefficients  $c_k$
6. Compute your new  $t$  using equation 89

## 4 Results

### 4.1 Pairing Model

The pairing model acts mostly as a simple test of the validity of our methods. Since we are only looking at two particles, and only double excitations are useful when minimizing the energy, both CCD and CCSD should give the exact ground state energy of the system. Figure 4.1 shows that this is the case for all values of the interaction strength  $g$  in the interval  $[-1, 1]$ .

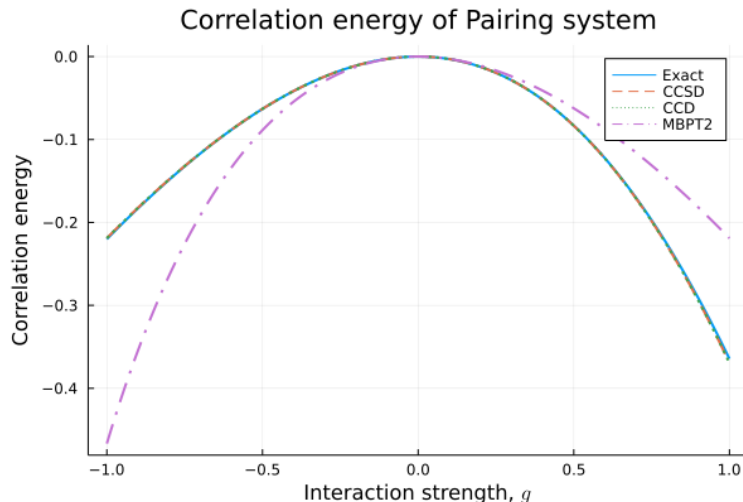


Figure 1: Both the CCD and CCSD method give the exact ground state energy of the Pairing System. Many body perturbation theory of the second order is shown for comparison. See [8] for further discussion on this system and these models, as well as for how the exact energy is computed.

## 4.2 Harmonic Quantum Dots

The parameters used for the computations in this section are as follows: A spin-doubled basis of 10 1D harmonic oscillator functions was used ( $l = 20$ ). The harmonic potential affecting the particles has a strength of  $\omega = 0.25$ . The coulomb interaction has a shielding of  $a = 0.25$ . The system contains  $n = 2$  electrons. A grid of 2001 points from  $x = -10$  to  $x = 10$  was used for computing the integrals.

### 4.2.1 Ground state energy

The harmonic quantum dots system allows us to also test the Hartree-Fock method, and the use of different basis sets when using the Coupled Cluster methods. Table 1 shows the ground state energies reached using different methods. We look at a system of 2 electrons,  $\omega = 0.25$ ,  $a = 0.25$ , using a basis of 10 Harmonic Oscillator functions evaluated on a grid of 2001 points from -10 to 10. Spin is then added to the basis, doubling the number of basis functions. The exact value is provided by Zanghellini [11], who computed the exact energy of the system using an infinite basis. We expect CCSD to give the exact energy in the space spanned by our basis, since it can perfectly include all possible excitations of two electrons, so these values are not expected to be the same.

Method	Energy	Error
HO Functions	1.3837	0.5590
RHF	1.1796	0.3549
HF	0.8450	0.0203
CCD	1.0517	0.2270
RHF+CCD	0.8384	0.0137
HF+CCD	0.8377	0.0130
CCSD	0.8253	0.0006
RHF+CCSD	0.8253	0.0006
HF+CCSD	0.8374	0.0127
Exact	0.8247	0.0000

Table 1: The ground state energies computed for the 1D harmonic quantum dots system with several different methods. The exact value is for an infinite basis.

We see that only using the 2 lowest Harmonic Oscillator basis functions as the ground state solution gives a very high energy compared to the exact solution. This is to be expected, as the harmonic quantum dots system is a highly correlated system. RHF also gives a poor estimate, which is also expected, as electron correlations are the exact thing we need Coupled Cluster to properly account for. HF gives a surprisingly good energy. The exact ground state has anti-symmetric spin, so one could expect that RHF would be able to find the best single-determinant wave function. But under the constraint of only using a single determinant, HF found that the lowest energy is reached using a determinant without anti-symmetric spin, a determinant RHF could not find. The physical interpretation of this solution is shaky, and as seen in the table, it did not work well as the basis for CCSD.

CCD on its own struggles. Double excitations are expected to be the most important when optimizing the energy due to Brillouin’s theorem [10], but that is only when using a Hartree-Fock basis. With the help of the HF and RHF basis however, we see that the Couple-Cluster method comes quite close to the exact ground state.

When only looking at two electrons, CCSD gives the exact solution within the space spanned by the basis function. It therefore does not require a basis optimized by Hartree-Fock in this case. The difference between the energy reached and the exact energy of the system is only due to the limited finite basis. Interestingly, it actually gives a higher energy when using the general Hartree-Fock basis. We have no other explanation for this than that the general Hartree-Fock basis isn’t spin-anti-symmetric, which might add some unexpected

effects when using it for further calculations.

### 4.2.2 Convergence

With the Alpha filter convergence acceleration scheme, convergence was reached after at best 39 iterations for CCD( $\alpha = 0.65$ ) and 55 iterations for CCSD( $\alpha = 0.61$ ). And that is only if you actually know the optimal  $\alpha$ . The number of iterations needed for convergence for other values of  $\alpha$  is shown in figure 4.2.2.

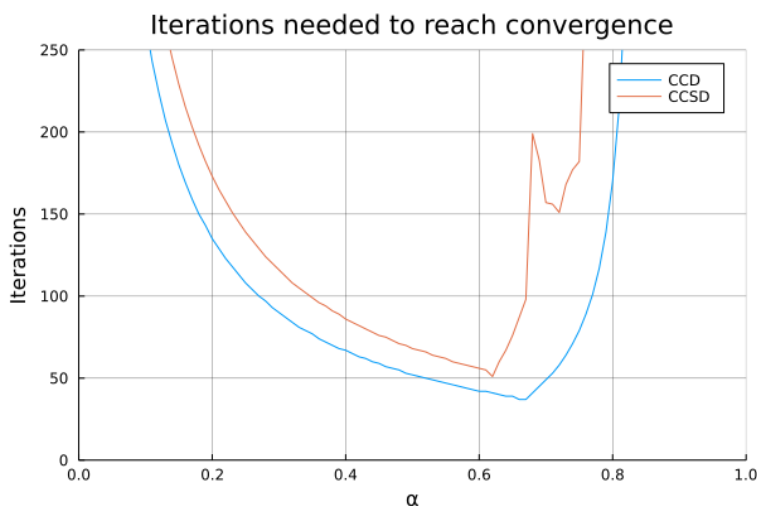


Figure 2: The number of iterations needed to reach convergence for the CCD and CCSD methods when using the alpha mixer with different values of  $\alpha$  to speed up convergence.

We see that the rate of convergence using the alpha filter is heavily dependant on the choice of  $\alpha$ , and that the most straightforward method of  $\alpha = 1$  can converge very slowly, if it even converges at all. Figure 4.2.2 shows the energy per iteration using the alpha mixer with the optimal values for  $\alpha$ .

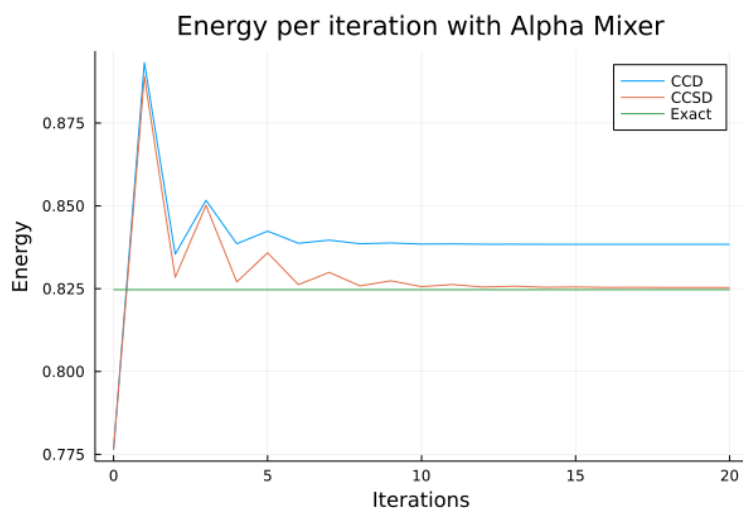


Figure 3: The energy at each iteration when using the alpha mixer with the optimal  $\alpha$  found earlier. The exact energy is shown for reference.

We see that even with the best  $\alpha$ , the Alpha mixer is unable to quickly arrive at the optimal parameters, instead oscillating around slowly improving solutions, converging slowly to the optimal solution.

With DIIS however, the CCD method converged in 15 only iterations, and the CCSD method converged in only 17 iterations. Figure 4.2.2 shows how quickly CCD and CCSD arrive at their optimal energies using DIIS.

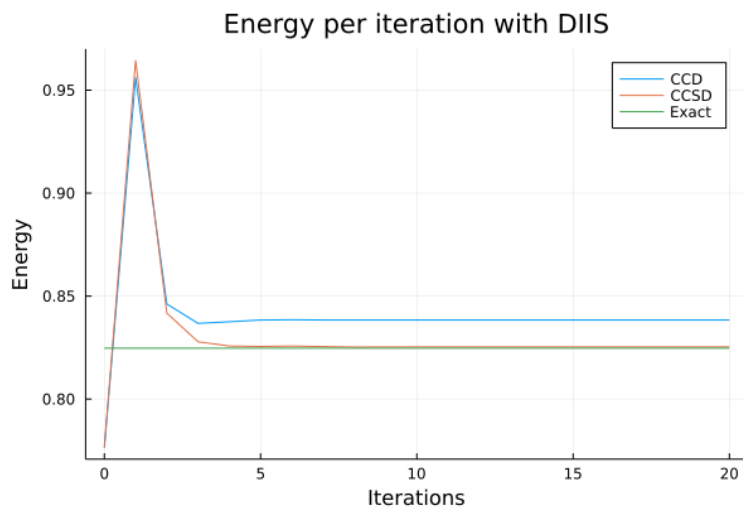


Figure 4: The energy at each iteration when using DIIS to speed up convergence. The exact energy is shown for reference.

CCD and CCSD show similar behaviour, both starting with a too low estimate of the energy before shooting up and then quickly settling around the right energy.

### 4.2.3 Particle Density

The particle density has no guarantees to be sensible at all, as discussed in section 2.8. Nevertheless, we opted to include these results to see how theory and numerical results agree. The particle density of the ground state found with HF and RHF are shown together with the ones found with CCSD using a HF and RHF basis in figure 4.2.3. We do not include results for CCD since it would give the same particle densities as its HF and RHF starting points.

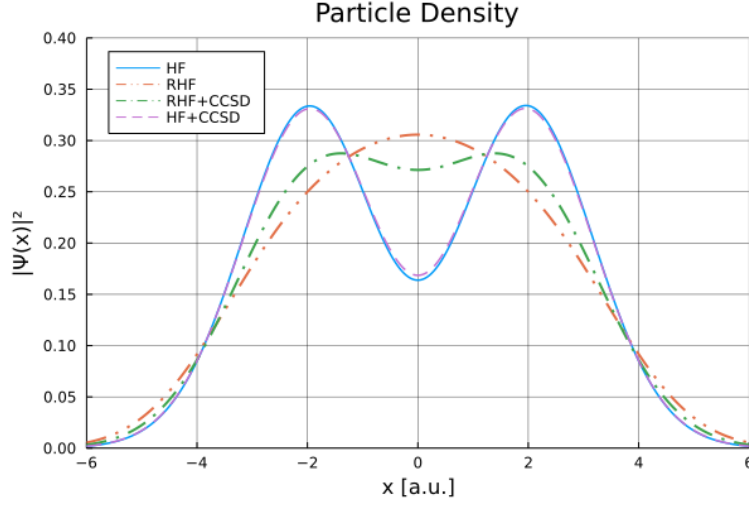


Figure 5: The particle density of the ground state of the harmonic quantum dot system, found using different methods.

From Zanghellini [11] we have the particle density of the exact ground state ( $\eta = \infty$ ), as well as the particle density from a RHF calculation ( $\eta = 1$ ). We overlay our own values over the plot from Zanghellini in figure 4.2.3. We apologize for the messy figure, but hope that the first figure can be helpful for differentiating the lines in the second figure.

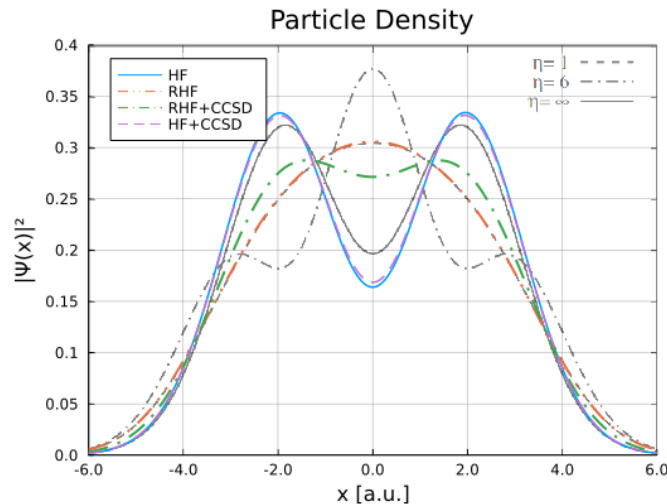


Figure 6: The particle density of the ground state of the harmonic quantum dot system, found using different methods. The new elements not in figure 4.2.3 are the particle densities from a paper by Zanghellini [11] for the same system.

Our particle density for RHF matches the RHF line from Zanghellini. The HF particle density comes much closer to the exact ground state values, but has too low values in the center, and too high values at both of the peaks. We see that the CCSD method actually slightly improves the particle density for both starting bases. The HF+CCSD line is slightly higher in the center, and lower at the peaks. And the RHF+CCD line is also slightly closer to the exact ground state, but only by a little. It is interesting that the CCSD method improves on the particle density, but we see that it is not a suited method for finding a usable value for it. If the particle density is of interest, one would be better suited using a variational formulation of Coupled Cluster.

## 5 Conclusion

Earlier we discussed the details of our implementation of the coupled cluster equations, convergence accelerators, as well as our code to perform the algebraic manipulations needed to even write the equations. Through this work, we have achieved our goal of learning about the coupled cluster method, and writing a useful code for further studies.

We have since shown the validity of our implementation of CCD and CCSD, and have seen confirmation of many theoretical results we expected. The CCSD method is exact in the space spanned by its basis for two electrons, so it did not improve by using a HF basis, reaching an energy only  $0.0006a.u.$  above the exact value in an infinite basis. Interestingly, it actually got a worse energy estimate when using a general Hartree-Fock basis with un-physical spin. Due



to Brillouin’s theorem, we expected double excitations to give the leading correction to the energy when using a Hartree-Fock basis, which was seen with the CCD method having an energy only  $0.0130a.u.$  away from the exact energy, even without single excitations. Without the help of a Hartree-Fock basis, the CCD method had a much larger error of  $0.2270a.u.$ .

We also saw that the DIIS convergence acceleration scheme greatly outperformed the alpha mixer, converging in only 17 iterations for the CCSD method, when the alpha mixer needed 55 at best. Finally, we saw that the particle density was not well optimized, which was expected from a non-variational method.

Further improvements to the method and implementation we presented would be the use of intermediates to speed up the evaluation of the amplitude equations, a more accurate treatment of triple excitations, or the use of a variational formulation to measure properties other than energy. Beyond that, there are a plethora of methods to solve the electronic Schrödinger equation, even within the confines of coupled cluster theory.

# Appendices

## A The CCSD T2 Equation

$$\begin{aligned}
0 = & \langle ab || ij \rangle + \sum_c (f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc}) - \sum_k (f_{kj} t_{ik}^{ab} - f_{ki} t_{jk}^{ab}) + \frac{1}{2} \sum_{kl} \langle kl || ij \rangle t_{kl}^{ab} \\
& + \frac{1}{2} \sum_{cd} \langle ab || cd \rangle t_{ij}^{cd} + P(ij) P(ab) \sum_{kc} \langle kb || cj \rangle t_{ik}^{ac} + P(ij) \sum_c \langle ab || cj \rangle t_i^c \\
& - P(ab) \sum_k \langle kb || ij \rangle t_k^a + \frac{1}{2} P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ac} t_{lj}^{db} + \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_{ij}^{cd} t_{kl}^{ab} \\
& - P(ab) \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{ij}^{ac} t_{kl}^{bd} - P(ij) \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ab} t_{jl}^{cd} + P(ab) \frac{1}{2} \sum_{kl} \langle kl || ij \rangle t_k^a t_l^b \\
& + P(ij) \frac{1}{2} \sum_{cd} \langle ab || cd \rangle t_i^c t_j^d - P(ij) P(ab) \sum_{kc} \langle kb || ic \rangle t_k^a t_j^c + P(ab) \sum_{kc} f_{kc} t_k^a t_{ij}^{bc} \\
& + P(ij) \sum_{kc} f_{kc} t_i^c t_{jk}^{ab} - P(ij) \sum_{klc} \langle kl || ci \rangle t_k^c t_{lj}^{ab} + P(ab) \sum_{kcd} \langle ka || cd \rangle t_k^c t_{ij}^{db} \\
& + P(ij) P(ab) \sum_{kcd} \langle ak || dc \rangle t_i^d t_{jk}^{bc} + P(ij) P(ab) \sum_{klc} \langle kl || ic \rangle t_l^a t_{jk}^{bc} \\
& + P(ij) \frac{1}{2} \sum_{klc} \langle kl || cj \rangle t_i^c t_{kl}^{ab} - P(ab) \frac{1}{2} \sum_{kcd} \langle kb || cd \rangle t_k^a t_{ij}^{cd} \\
& - P(ij) P(ab) \frac{1}{2} \sum_{kcd} \langle kb || cd \rangle t_i^c t_k^a t_j^d + P(ij) P(ab) \frac{1}{2} \sum_{klc} \langle kl || cj \rangle t_i^c t_k^a t_l^b \\
& - P(ij) \sum_{klcd} \langle kl || cd \rangle t_k^c t_i^d t_{lj}^{ab} - P(ab) \sum_{klcd} \langle kl || cd \rangle t_k^c t_l^a t_{ij}^{db} + P(ij) \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_i^c t_j^d t_{kl}^{ab} \\
& + P(ab) \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_k^a t_l^b t_{ij}^{cd} + P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_i^c t_l^b t_{kj}^{ad} \\
& + P(ij) P(ab) \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_i^c t_k^a t_j^d t_l^b
\end{aligned} \tag{94}$$

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