

# Ground state energy of quantum dots using the coupled cluster method

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(Dated: June 5, 2018)

Something about coupled-cluster... Preferably doubles.

## CONTENTS

I. Introduction	1
II. Theory	1
A. Second quantization	1
B. The coupled cluster approximation	2
C. Energy of the coupled cluster approximation	2
1. Coupled cluster doubles energy equation	2
D. Coupled cluster amplitude equations	3
1. The Iterative Scheme	3
2. Intermediate Computations	4
E. Constructing the matrix elements	4
1. Harmonic oscillator basis	4
2. Constructing the Hartree-Fock basis	5
III. Implmentation	5
A. Installation	5
B. Program Structure	6
A. The normal ordered Hamiltonian	6
B. Amplitude Equations	7
C. Finding Amplitude Equation Intermediates	8
D. Coupled cluster doubles diagrams	9
E. Example Script	9
References	11

## I. INTRODUCTION

In this project we will study the ground state energy of quantum dots.

## II. THEORY

In this project we will study a system of  $N$  interacting electrons. We will be looking at a Hamiltonian consisting of a one-body and a two-body part. The one-body part is given by

$$h(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2\mathbf{r}_i^2, \quad (1)$$

where we use natural units  $\hbar = c = e = 1$  and set the mass to unity. The two-body part is the Coulomb interaction potential.

$$u(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2)$$

We thus get the total Hamiltonian

$$H = h + u = \sum_{i=1}^N h(\mathbf{r}_i) + \sum_{i<j}^N u(\mathbf{r}_i, \mathbf{r}_j), \quad (3)$$

where  $h$  is the full one-body operator and  $u$  the full two-body operator, i.e., over the entire system. Working in a basis of  $L$  single particle functions,  $\{|p\rangle\}_{p=1}^L$ . We define the reference Slater determinant as

$$|\Phi_0\rangle \equiv |1, 2, \dots, N\rangle, \quad (4)$$

i.e., a tensorproduct of the  $N$  first single particle functions,  $|i\rangle$ , of the system. We call these single particle functions *occupied* as they are contained in the Slater determinant. We will denote the occupied indices with  $i, j, k, l, \dots \in \{1, \dots, N\}$ , the *virtual* states with  $a, b, c, d, \dots \in \{N+1, \dots, L\}$  and general indices with  $p, q, r, s, \dots \in \{1, \dots, L\}$ . In terms of sets of basis functions we can write this as

$$\{|p\rangle\}_{p=1}^L = \{|i\rangle\}_{i=1}^N \cup \{|a\rangle\}_{a=N+1}^L, \quad (5)$$

i.e., the general indexed states consists of both occupied and virtual states. Note that the single particle functions are orthonormal, i.e.,

$$\langle p|q\rangle = \delta_{pq}. \quad (6)$$

We can construct other Slater determinants in this basis by exciting or relaxing the reference determinant. A general excitation is labeled  $|\Phi_{ij\dots}^{ab\dots}\rangle$  which means that we have removed the single particle functions with indices  $i, j, \dots$  from the reference and added  $a, b, \dots$ . Note that

$$\langle \Phi_{ij\dots}^{ab\dots} | \Phi_0 \rangle = 0, \quad (7)$$

for any excitation.

### A. Second quantization

Employing the creation operators,  $a_p^\dagger$ , and the destruction operators,  $a_p$ , we can write the Hamiltonian as

$$H = \sum_{pq} h_q^p a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \quad (8)$$

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\* Project code: <https://github.com/Schoyen/FYS4411>

where the sums are general indices over all  $L$  basis states and the matrix elements are defined as

$$h_q^p \equiv \langle p|h|q\rangle, \quad (9)$$

$$\langle pq||rs\rangle \equiv \langle pq|u|rs\rangle - \langle pq|u|sr\rangle. \quad (10)$$

Note that we use the chemists notation to label the antisymmetric matrix elements.

## B. The coupled cluster approximation

We approximate the true wavefunction,  $|\Psi\rangle$ , of the system by the coupled cluster wavefunction,  $|\Psi_{CC}\rangle$ , defined by

$$|\Psi_{CC}\rangle \equiv e^T |\Phi_0\rangle = \left( \sum_{i=0}^n \frac{1}{n!} T^n \right) |\Phi_0\rangle, \quad (11)$$

where the *cluster operator*,  $T$ , is given by a sum of  $p$ -excitation operators labeled  $T_p$ . They consist of *cluster amplitudes*,  $t_{i\cdots}^a$ , and creation and annihilation operators.

$$T = T_1 + T_2 + \cdots + T_p \quad (12)$$

$$= \sum_{ia} t_i^a a_a^\dagger a_i + \left( \frac{1}{2!} \right)^2 \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j + \dots \quad (13)$$

In the doubles approximation we limit the cluster operator to

$$T \equiv T_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j. \quad (14)$$

The first part of the coupled cluster method consists of constructing the cluster amplitudes using the *amplitude equations*. After we have found the amplitudes we can compute the energy.

## C. Energy of the coupled cluster approximation

When we're going to compute the energy of a system using the coupled cluster approximation we would ideally want to find the expectation value of the energy using the coupled cluster wavefunction.

$$E_{CC} = \langle \Psi_{CC} | H | \Psi_{CC} \rangle. \quad (15)$$

As it turns out, this is an uncomfortable way of finding the energy as  $T \neq T^\dagger$ . Instead we will define what we call the *similarity transformed Hamiltonian*. We plug the coupled cluster wavefunction into the Schrödinger equation.

$$H|\Psi_{CC}\rangle = E_{CC}|\Psi_{CC}\rangle. \quad (16)$$

Next, we left multiply with the inverse of the cluster expansion, i.e.,

$$e^{-T} H |\Psi_{CC}\rangle = e^{-T} E_{CC} |\Psi_{CC}\rangle = E_{CC} |\Phi_0\rangle. \quad (17)$$

Projecting this equation on the reference state we get

$$E_{CC} = \langle \Phi_0 | e^{-T} H | \Psi_{CC} \rangle = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle, \quad (18)$$

where in the latter inner-product we have located the similarity transformed Hamiltonian defined by

$$\bar{H} \equiv e^{-T} H e^T. \quad (19)$$

To simplify the energy equation and the amplitude equations we use the normal ordered Hamiltonian.

$$H = H_N + \langle \Phi_0 | H | \Phi_0 \rangle. \quad (20)$$

The energy equation thus becomes

$$E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E_0 + \langle \Phi_0 | e^{-T} H_N e^T | \Phi_0 \rangle, \quad (21)$$

where the reference energy is given by

$$E_0 = \langle \Phi_0 | H | \Phi_0 \rangle. \quad (22)$$

We now define the normal ordered similarity transformed Hamiltonian as

$$\bar{H}_N \equiv e^{-T} H_N e^T. \quad (23)$$

By expanding the exponentials of this Hamiltonian and recognizing the commutators we get the Baker-Campbell-Hausdorff expansion.

$$\bar{H}_N = H_N + [H_N, T] + \frac{1}{2!} [[H_N, T], T] + \dots \quad (24)$$

From the connected cluster theorem we know that the only nonzero terms in the Baker-Campbell-Hausdorff expansion will be the terms where the normal ordered Hamiltonian has at least one contraction<sup>1</sup> with every cluster operator on its right. This lets us write the expansion as

$$\bar{H}_N = H_N + (H_N T)_c + \frac{1}{2!} (H_N T^2)_c + \dots, \quad (25)$$

where the subscript  $c$  signifies that only contributions where at least one contraction between  $H_N$  and  $T$  has been performed will be included.

### 1. Coupled cluster doubles energy equation

Using the doubles approximation with the cluster operator  $T_2$  defined in Equation 14 the energy equation becomes

$$E_{CCD} = E_0 + \langle \Phi_0 | e^{-T_2} H_N e^{T_2} | \Phi_0 \rangle. \quad (26)$$

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<sup>1</sup> In the Wick's theorem sense.

As the doubles cluster operator doubly excites the reference and using the expansion in Equation 25 we see that we can write the energy equation as

$$E_{\text{CCD}} = E_0 + \langle \Phi_0 | H_N | \Phi_0 \rangle + \langle \Phi_0 | (H_N T_2)_c | \Phi_0 \rangle, \quad (27)$$

as the Hamiltonian is only able to relax one pair of single particle functions. By construction we have that

$$\langle \Phi_0 | H_N | \Phi_0 \rangle = 0. \quad (28)$$

In the second term only the normal ordered two-body operator can contribute as the cluster operator gives a total excitation of +2. As we are projecting onto the reference we have to relax to zero again. The normal ordered Fock operator is at most able to excite and relax by 1 and does therefore not contribute to the overall expression.

$$\langle \Phi_0 | (W_N T_2)_c | \Phi_0 \rangle = \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}. \quad (29)$$

In total the energy equation reduces to

$$E_{\text{CCD}} = \sum_i h_i^i + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}, \quad (30)$$

where the first two terms come from the reference energy as shown in Equation A10.

#### D. Coupled cluster amplitude equations

In order for us to solve the energy equation using the coupled cluster approximation we need to figure out what the cluster amplitudes,  $t_{ij,\dots}^{ab,\dots}$ , are. This is done by projecting Equation 17 onto an excited Slater determinant, i.e.,

$$\langle \Phi_{ij,\dots}^{ab,\dots} | e^{-T} H e^T | \Phi_0 \rangle = 0. \quad (31)$$

Note that in the amplitude equations we can use both the regular and the normal ordered Hamiltonian. They are equal as the reference energy term disappears due to Equation 7. The order of the excitation in the projection determines the order of the amplitudes you will find. In our case we are only interested in the second order amplitudes found in the doubles approximation, hence we will solve the equation

$$\langle \Phi_{ij}^{ab} | e^{-T} H_N e^T | \Phi_0 \rangle = 0, \quad (32)$$

to find an expression that can be used to solve for  $t_{ij}^{ab}$ . By employing the Baker-Campbell-Hausdorff (BCH) expansion, while setting  $T = T_2$ , we find

$$\bar{H} = \left( H_N + H_N T_2 + \frac{1}{2} H_N T_2^2 \right)_C. \quad (33)$$

The subscript  $c$  indicates that only those terms in which the Hamiltonian is connected<sup>2</sup> to every cluster operator

on its right should be included. Since the Hamiltonian contains at most four annihilation and creation operators,  $H_N$  can connect to at most four cluster operators at once. Therefore, the BCH expansion must truncate at the fourth-order terms.

Now comes the rather tedious task of evaluating all the terms that arises from inserting Equation 33 into Equation 32. This can be done by applying Wick's generalised theorem, but the task is a daunting and strenuous one. A few example computations of how this can be done is included in section B. Instead of doing it in this manner, we employ the second quantisation library from SymPy instead<sup>3</sup>. The CCD amplitude equation, from SymPy computation, is

$$\begin{aligned} 0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & + \frac{1}{4} t_{ij}^{cd} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} t_{ij}^{cd} u_{cd}^{ab} \\ & + \frac{1}{2} t_{jm}^{cd} t_{in}^{ab} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{nm}^{ac} t_{ij}^{bd} u_{cd}^{nm} P(ab) \\ & + t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\ & - \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}. \end{aligned} \quad (34)$$

##### 1. The Iterative Scheme

At first, we pick only diagonal elements of  $f$  to be part of the unperturbed Hamiltonian and consider the rest of the terms a perturbation. The second and third terms in Equation 34 can now be rewritten,

$$\begin{aligned} & f_c^b t_{ij}^{ab} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & \rightarrow f_b^b t_{ij}^{ab} - f_a^a t_{ij}^{ba} - f_j^j t_{ij}^{ab} + f_i^i t_{ji}^{ab} \\ & = (f_a^a + f_b^b - f_i^i - f_j^j) t_{ij}^{ab} \\ & = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab} \\ & = -(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) t_{ij}^{ab} \\ & = -D_{ij}^{ab} t_{ij}^{ab}. \end{aligned} \quad (35)$$

The we can define a new function consisting of all of Equation 34 except term number two and three,

$$\begin{aligned} g(u, \tau) = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & + \frac{1}{4} t_{ij}^{cd} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} t_{ij}^{cd} u_{cd}^{ab} \\ & + \frac{1}{2} t_{jm}^{cd} t_{in}^{ab} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{nm}^{ac} t_{ij}^{bd} u_{cd}^{nm} P(ab) \\ & + t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\ & - \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}. \end{aligned} \quad (36)$$

<sup>2</sup> In a Wick's theorem sense

<sup>3</sup> This is also more in the spirit of this project, as it is within the realm of *Computational Physics*.

where  $\tilde{f}$  are the non-diagonal parts of the Fock matrix.

Now we have  $D_{ij}^{ab}t_{ij}^{ab} = g(u, \tau)$ . This allows us to define an iterative scheme,

$$\tau^{(k+1)} = \frac{g(u, \tau^{(k)})}{D_{ij}^{ab}}, \quad (37)$$

with the initial guess

$$\tau^{(0)} = \frac{u_{ij}^{ab}}{D_{ij}^{ab}}. \quad (38)$$

## 2. Intermediate Computations

Looking closely at the amplitude equation in (34) one might come to realize that it contains that this equation contains many of the same structures in several of the terms. This warrants the search for an algebraic transformation of the CCD amplitude equation that has the potential to reduce the amount of floating point operations needed to compute it. As it turns out, such terms exist and they will decrease the computing time necessary by an order of magnitude. We will define the following "intermediates",

$$\chi_{cd}^{ab} = \frac{1}{4}t_{mn}^{ab}u_{cd}^{mn} + \frac{1}{2}u_{cd}^{ab} \quad (39)$$

$$\chi_j^n = \frac{1}{2}t_{jm}^{cd}u_{cd}^{mn} \quad (40)$$

$$\chi_d^a = \frac{1}{2}t_{nm}^{ac}u_{cd}^{nm} \quad (41)$$

$$\chi_{jc}^{bm} = u_{jc}^{bm} + \frac{1}{2}t_{jn}^{bd}u_{cd}^{mn} \quad (42)$$

These intermediate structures will allow us to rewrite Equation 34 to,

$$\begin{aligned} 0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & + t_{ij}^{cd} \chi_{cd}^{ab} + t_{in}^{ab} \chi_j^n P(ij) - t_{ij}^{bd} \chi_d^a P(ab) \\ & + t_{im}^{ac} \chi_{jc}^{bm} P(ab) P(ij) + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}. \end{aligned} \quad (43)$$

The importance of this "trick" will become apparent in due time.

## E. Constructing the matrix elements

Having found the equations needed in order to find an estimate to the ground state energy using the coupled cluster doubles approximation is a well and dandy. But, we need basis functions to create the matrix elements needed to feed into the coupled cluster code. Often these basis functions are not known and we have to use an approximation or utilize Hartree-Fock to create more optimized basis functions.

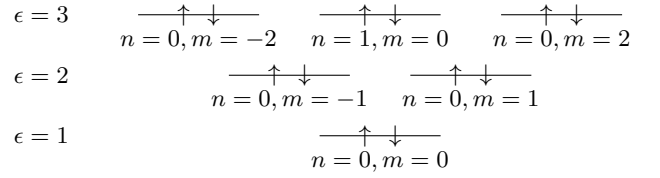


FIG. 1: In this plot we can see the energy degeneracy of the lowest three energy levels in the two-dimensional quantum dot. Each arrow represents a spin up or a spin down state with the quantum numbers  $n$  and  $m$  as listed below.

### 1. Harmonic oscillator basis

We will be looking at a system of two-dimensional quantum dots with a Coulomb repulsion. If we assume, or make it so, that the repulsive two-body part is small we can use eigenfunctions of the one-body part our basis. In this case we have two-dimensional harmonic oscillator functions as eigenfunctions. We can then compute the matrix elements,  $h_q^p$  and  $u_{rs}^{pq}$ , before feeding these into the coupled cluster code.

In polar coordinates we can write the harmonic oscillator wavefunction for a single particle in two dimensions as<sup>4</sup>.

$$\phi_{nm}(r, \theta) = N_{nm}(ar)^{|m|} L_n^{|m|}(a^2 r^2) e^{-a^2 r^2/2} e^{im\theta}, \quad (44)$$

where  $a = \sqrt{m\omega/\hbar}$  is the Bohr radius,  $L_n^{|m|}$  is the associated Laguerre polynomials,  $n$  and  $m$  are the principal and azimuthal quantum numbers respectively and  $N_{nm}$  is a normalization constant given by

$$N_{nm} = a \sqrt{\frac{n!}{\pi(n+|m|)!}}. \quad (45)$$

Included is also the spin,  $\sigma$ , of the wavefunction, which can be either up or down. This means each level,  $(n, m)$ , is doubly occupied. We also have that the wavefunctions are orthonormal

$$\langle n_1 m_1 \sigma_1 | n_2 m_2 \sigma_2 \rangle = \delta_{n_1 n_2} \delta_{m_1 m_2} \delta_{\sigma_1 \sigma_2}. \quad (46)$$

The eigenenergy of a single harmonic oscillator is given by

$$\epsilon_{nm} = \hbar\omega(2n + |m| + 1). \quad (47)$$

Our next job is now to create a mapping from the three quantum numbers  $n$ ,  $m$  and  $\sigma$  to a single quantum number  $\alpha$  as the matrices  $h$  and  $u$  use single indices for each

<sup>4</sup> Note that this is without spin. As we are looking at fermions this means that each mode of the harmonic oscillator functions will be repeated twice.

wavefunction. In Figure 1 we can see the energy levels that needs to be mapped.

Starting from the bottom and working our way upwards from left to right we can label each line from 0 to  $n$  in increasing order. This enumeration will serve as our common quantum number  $\alpha^5$ . We will only work with full *shells*, i.e., we restrict our views to systems of  $N$  particles where  $N$  will be a magic number which we get by counting all spin states for each energy level and the energy levels below. In Figure 1 we can see the magic number  $N \in [2, 6, 12]$ .

The normalization condition now reads

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta} \delta_{\sigma_\alpha \sigma_\beta}, \quad (48)$$

The one-body matrix will be a diagonal matrix with the eigenenergies of the single particle harmonic oscillator functions as elements.

$$\langle \alpha | h | \beta \rangle = \epsilon_\beta \delta_{\alpha\beta} \delta_{\sigma_\alpha \sigma_\beta}. \quad (49)$$

The two-body matrix elements are a little harder to work out as the harmonic oscillator wavefunctions are not eigenfunctions to the correlation operator. Luckily, from E. Anisimovas and A. Matulis (Equation A2)[1] we can get an analytical expression for the two-body matrix elements. We can then construct the antisymmetric two-body matrix elements in the harmonic oscillator basis.

$$\langle \alpha\beta || \gamma\delta \rangle = \langle \alpha\beta | \gamma\delta \rangle - \langle \alpha\beta | \delta\gamma \rangle. \quad (50)$$

As we only need to compute these once it is a good idea to save all non-zero values of  $\langle \alpha\beta || \gamma\delta \rangle$  to a file.

## 2. Constructing the Hartree-Fock basis

Having found the matrix elements of  $h$  and  $u$  we can now use the *self-consistent field iteration* method to construct  $h$  and  $u$  in a *restricted Hartree-Fock* basis. This will yield a better estimate to the actual, unknown basis functions of the system.

The neatest, yet arguably the most abstract, way to write the Hartree-Fock equations for electron  $i^6$  is

$$f_i \varphi_i = \varepsilon_i \varphi_i, \quad (51)$$

where  $f_i$  is the Fock operator,  $\varphi_i$  are eigenstates of the Fock operator consisting of a set of one-electron wavefunctions, called the Hartree-Fock molecular orbitals, and  $\varepsilon_i$  are the eigenenergies of the Fock operator. The fock operator, in matrix notation, is given by

$$F_{pa} = H_{pq} + J(D)_{pq} - \frac{1}{2} K(D)_{pq}, \quad (52)$$

where  $h_i$  is the one-body operator, while the two-body operator is divided into what we call a direct part,

$$J(D)_{pq} = \langle pq | rs \rangle D_{sr}, \quad (53)$$

and an exchange part,

$$K(D)_{pq} = \langle ps | rq \rangle D_{sr}. \quad (54)$$

The direct part of the two-body operator is comparable to classical Coloumb repulsion, while the exchange does not have a classical analog as it arises from the anti-symmetry requirement of the wavefunction.  $D_{sr}$  is the density matrix of the system.

Introducing a basis set transforms the Hartree-Fock equations into the Rothaan equations

$$FC = SC\varepsilon. \quad (55)$$

This is a generalised eigenvalue problem where  $S$  serves as an overlap matrix that must be there in case of non-orthogonal basis. Since the Fock matrix  $F$  depends on its own solution through the orbitals, the eigenvalue problem must be solved iteratively<sup>7</sup>.

## III. IMPLMENTATION

We have costructed a flexible framework for making performing CCD computations, consisting of package for python that is easy to install globally on any computer.

### A. Installation

The software is easy to install by first cloning the GitHub repository,

```
git clone git@github.com:Schoyen/FYS4411.git
```

Then all you need to do is change directory to the project code folder where a MakeFile is included so you only need to build and install,

```
cd FYS4411/project_2/coupled-cluster
make build
make install
```

Now everything should be able to run from anywhere on your computer. To ensure that all requirements of the program are satisfied you can install with `make installr` instead.

<sup>5</sup> Note that we use greek letters  $\alpha, \beta, \dots$  for the harmonic oscillator wavefunctions as opposed to latin letters for the general indices.

<sup>6</sup> This is weird, as electron should be indistinguishable and therefore impossible to label.

<sup>7</sup> This is also the reason why the Hartree-Fock-Roothaan equations are often called the self-consistent-field procedure.

## B. Program Structure

There are three main subsections within our program structure, given in the directory tree below.

```

coupled_cluster
├── matrix_elements
│   ├── generate_matrices
│   └── index_map
├── hartree_fock
│   ├── scf_rhf
│   └── basis_transformation
└── schemes
    ├── ccd
    ├── ccd_sparse
    └── ccd_optimized

```

The first subsection, `matrix_elements`, contains methods for computing matrix elements in harmonic oscillator basis from an analytical expression[1]. Computing the matrix elements is a very intensive task, and the central functions are therefore implemented in C++ with a Cython interface to enable use in Python.

The `hartree_fock` subsection contains methods for changing from harmonic oscillator basis to Hartree-Fock basis as well as an implementation of the self-consistent-field algorithm to make this transaction possible.

The `schemes` subsection is arguably the most important part of this project. The subsection has three different classes that perform the exact same computations, but in different and increasingly intelligent ways. First, `CoupledClusterDoubles` is the most straightforward and naïve way to solve the CCD amplitude equations. Second, because an overbearing amount of the elements in the operator matrices in this problem are zero, we have implemented a sparse matrix CDD solver in `CoupledClusterDoublesSparse`. Third, `CoupledClusterDoublesOptimized` takes advantage of sparse matrices as well, but is also parallelized and optimized with memory use and number of floating point operations in mind.

## Appendix A: The normal ordered Hamiltonian

When constructing the normal ordered Hamiltonian we use Wick's theorem to write the one-body,  $h$ , and the two-body,  $u$ , operators onto a normal ordered form. Specifically we define the normal ordered form in terms of the *Fermi vacuum*<sup>8</sup>. That is, an operator on normal ordered form destroys the reference Slater determinant.

We start by writing the one-body operator,  $h$ , to its

normal-ordered form.

$$h = \sum_{pq} h_q^p a_p^\dagger a_q = \sum_{pq} h_q^p \left( \{a_p^\dagger a_q\} + \{a_p^\dagger \overline{a_q}\} \right) \quad (\text{A1})$$

$$= \sum_{pq} h_q^p \{a_p^\dagger a_q\} + \sum_{pq} h_q^p \delta_{p \in i} \delta_{pq} \quad (\text{A2})$$

$$= h_N + \sum_i h_i^i, \quad (\text{A3})$$

where we have used  $\delta_{p \in i}$  to mean that  $p$  must be an occupied index. Doing the same for the two-body operator is a slightly more tedious endeavor. For brevity we will only write out the operator strings and only keep the non-zero contributions.

$$\begin{aligned} a_p^\dagger a_q^\dagger a_s a_r &= \{a_p^\dagger a_q^\dagger a_s a_r\} + \{a_p^\dagger a_q^\dagger \overline{a_s a_r}\} + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} \\ &\quad + \{a_p^\dagger a_q^\dagger \overline{a_s} a_r\} + \{\overline{a_p^\dagger a_q^\dagger} a_s \overline{a_r}\} \\ &\quad + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{\overline{a_p^\dagger a_q^\dagger} \overline{a_s} a_r\} \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} &= \{a_p^\dagger a_q^\dagger a_s a_r\} - \delta_{p \in i} \delta_{ps} \{a_q^\dagger a_r\} + \delta_{p \in i} \delta_{pr} \{a_q^\dagger a_s\} \\ &\quad + \delta_{q \in i} \delta_{qs} \{a_p^\dagger a_r\} - \delta_{q \in i} \delta_{qr} \{a_p^\dagger a_s\} \\ &\quad - \delta_{p \in i} \delta_{ps} \delta_{q \in j} \delta_{qr} + \delta_{p \in i} \delta_{pr} \delta_{q \in j} \delta_{qs}. \end{aligned} \quad (\text{A5})$$

Inserted into the full two-body operator and sorting out the sums we get

$$\begin{aligned} u &= \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} - \frac{1}{4} \sum_{iqr} \langle iq || ri \rangle \{a_q^\dagger a_r\} \\ &\quad + \frac{1}{4} \sum_{iqs} \langle iq || is \rangle \{a_q^\dagger a_s\} + \frac{1}{4} \sum_{pir} \langle pi || ri \rangle \{a_p^\dagger a_r\} \\ &\quad - \frac{1}{4} \sum_{pis} \langle pi || is \rangle \{a_p^\dagger a_s\} - \frac{1}{4} \sum_{ij} \langle ij || ji \rangle \\ &\quad + \frac{1}{4} \sum_{ij} \langle ij || ij \rangle. \end{aligned} \quad (\text{A6})$$

Using the antisymmetric properties of the two-body matrix elements,

$$\langle pq || rs \rangle = -\langle pq || sr \rangle = -\langle qp || rs \rangle = \langle qp || sr \rangle, \quad (\text{A7})$$

and relabeling of the indices we can rearrange and collect some terms.

$$u = W_N + \sum_{pir} \langle pi || ri \rangle \{a_p^\dagger a_r\} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle, \quad (\text{A8})$$

where the normal ordered two-body operator is

$$W_N = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}. \quad (\text{A9})$$

When we now construct the full Hamiltonian we can collect some terms. The constants in both the one-body

<sup>8</sup> Fermi vacuum defines the reference state, i.e.,  $|\Phi_0\rangle$ , as the vacuum.

and the two-body operator in total constitutes the reference energy.

$$E_0 \equiv \langle \Phi_0 | H | \Phi_0 \rangle = \sum_i h_i^i + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle. \quad (\text{A10})$$

Combining the normal ordered one-body operator and the second term in the two-body operator, i.e., the term with a single creation and annihilation operator pair, we get the normal ordered Fock-operator.

$$F_N = \sum_{pq} h_q^p \{a_p^\dagger a_q\} + \sum_{pq i} \langle pi || qi \rangle \{a_p^\dagger a_q\} \quad (\text{A11})$$

$$= \sum_{pq} f_q^p \{a_p^\dagger a_q\}, \quad (\text{A12})$$

where we have defined the Fock matrix elements as

$$f_q^p = h_q^p + \sum_i \langle pi || qi \rangle. \quad (\text{A13})$$

In total we get the full Hamiltonian

$$H = F_N + W_N + \langle \Phi_0 | H | \Phi_0 \rangle \quad (\text{A14})$$

$$= H_N + \langle \Phi_0 | H | \Phi_0 \rangle, \quad (\text{A15})$$

which is what we wanted to show.[2]

## Appendix B: Amplitude Equations

In this section we have provided a few sample computations of how one would evaluate the amplitude equations using wicks theorem. Starting with the simplest term including only the normal-ordered Hamiltonian,

$$\begin{aligned} & \langle \Phi_{ij}^{ab} | (F_N + V_N) | \Phi_0 \rangle \\ &= \sum_{pq} f_{pq} \langle \Phi_0 | \{a_i^\dagger a_j^\dagger a_b a_a\} \{a_p^\dagger a_q\} | \Phi_0 \rangle \\ &+ \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi_0 | \{a_i^\dagger a_j^\dagger a_b a_a\} \{a_p^\dagger a_q^\dagger a_s a_r\} | \Phi_0 \rangle. \end{aligned} \quad (\text{B1})$$

The one-electron component does not have any full contractions, while the two-electron component produces

one contributing integral,

$$\begin{aligned} & \langle \Phi_{ij}^{ab} | (V_N) | \Phi_0 \rangle \\ &= \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi_0 | \{a_i^\dagger a_j^\dagger a_b a_a\} \{a_p^\dagger a_q^\dagger a_s a_r\} | \Phi_0 \rangle \\ &= \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \\ &\quad \times \left( \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} \right. \\ &\quad \left. + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} \right) \\ &= \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle (\delta_{ap} \delta_{bq} \delta_{js} \delta_{ir} - \delta_{aq} \delta_{bp} \delta_{js} \delta_{ir} \\ &\quad - \delta_{ap} \delta_{bq} \delta_{jr} \delta_{is} + \delta_{aq} \delta_{bp} \delta_{jr} \delta_{is}) \\ &= \langle ab || ij \rangle = u_{ij}^{ab}. \end{aligned} \quad (\text{B2})$$

Next we would like to evaluate  $\langle \Phi_{ij}^{ab} | (F_N + V_N) T_2 | \Phi_0 \rangle$ .

Starting with the term involving the Fock operator  $F_N$ , them,

$$\begin{aligned}
& \langle \Phi_{ij}^{ab} | F_N T_2 | \Phi_0 \rangle \\
&= \frac{1}{4} \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \langle \Phi_0 | \{ a_i^\dagger a_j^\dagger a_b a_a \} \{ \{ a_p^\dagger a_q \} \{ a_c^\dagger a_d^\dagger a_l a_k \} \}_c | \Phi_0 \rangle \\
&= \frac{1}{4} \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \\
&\times \left( \begin{array}{c} \text{Diagram 1: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 2: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 3: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 4: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 5: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 6: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 7: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 8: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 9: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \\ \text{Diagram 10: } \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_c^\dagger a_d^\dagger a_l a_k \} \end{array} \right) \\
&= \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \\
&\times \left( -\delta_{ac} \delta_{bd} \delta_{ik} \delta_{jq} \delta_{lp} + \delta_{ac} \delta_{bd} \delta_{il} \delta_{jq} \delta_{kp} \right. \\
&\quad + \delta_{ac} \delta_{bd} \delta_{iq} \delta_{jk} \delta_{lp} - \delta_{ac} \delta_{bd} \delta_{iq} \delta_{jl} \delta_{kp} \\
&\quad + \delta_{ac} \delta_{bp} \delta_{dq} \delta_{ik} \delta_{jl} - \delta_{ac} \delta_{bp} \delta_{dq} \delta_{il} \delta_{jk} \\
&\quad + \delta_{ad} \delta_{bc} \delta_{ik} \delta_{jq} \delta_{lp} - \delta_{ad} \delta_{bc} \delta_{il} \delta_{jq} \delta_{kp} \\
&\quad - \delta_{ad} \delta_{bc} \delta_{iq} \delta_{jk} \delta_{lp} + \delta_{ad} \delta_{bc} \delta_{iq} \delta_{jl} \delta_{kp} \\
&\quad - \delta_{ad} \delta_{bp} \delta_{cq} \delta_{ik} \delta_{jl} + \delta_{ad} \delta_{bp} \delta_{cq} \delta_{il} \delta_{jk} \\
&\quad - \delta_{ap} \delta_{bc} \delta_{dq} \delta_{ik} \delta_{jl} + \delta_{ap} \delta_{bc} \delta_{dq} \delta_{il} \delta_{jk} \\
&\quad \left. + \delta_{ap} \delta_{bd} \delta_{cq} \delta_{ik} \delta_{jl} - \delta_{ap} \delta_{bd} \delta_{cq} \delta_{il} \delta_{jk} \right) \\
&= (f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc}) - (f_{jk} t_{ik}^{ab} - f_{ik} t_{jk}^{ab}) \\
&= f_{bc} t_{ij}^{ac} P(ab) - f_{kj} t_{ik}^{ab} P(ij) \tag{B3}
\end{aligned}$$

Where in the last steps we have consigned the sums by Einstein summation notation.

### Appendix C: Finding Amplitude Equation Intermediates

Starting from the CCD amplitude equation we factor out terms that will have the same indices if we contract

$$\begin{aligned}
0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
& + \frac{1}{4} t_{ij}^{cd} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} t_{ij}^{cd} u_{cd}^{ab} \\
& + \frac{1}{2} t_{jm}^{cd} t_{in}^{ab} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{nm}^{ac} t_{ij}^{bd} u_{cd}^{nm} P(ab) \tag{C1} \\
& + t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
& + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn},
\end{aligned}$$

$$\begin{aligned}
0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
& + t_{ij}^{cd} \left( \frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
& + t_{in}^{ab} \left( \frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
& - t_{ij}^{bd} \left( \frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \tag{C2}
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{im}^{bc} t_{jn}^{ad} u_{cd}^{mn} P(ij) \\
& + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
& + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn} \\
0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
& + t_{ij}^{cd} \left( \frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
& + t_{in}^{ab} \left( \frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
& - t_{ij}^{bd} \left( \frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \tag{C3}
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ab) P(ij) \\
& + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
& + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn} \\
0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
& + t_{ij}^{cd} \left( \frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
& + t_{in}^{ab} \left( \frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
& - t_{ij}^{bd} \left( \frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \tag{C4} \\
& + t_{im}^{ac} \left( \frac{1}{2} t_{jn}^{bd} u_{cd}^{mn} + u_{jc}^{bm} \right) P(ab) P(ij) \\
& + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}.
\end{aligned}$$



Now we can introduce the intermediate  $\chi$ -terms,

this gives us,

$$\begin{aligned}
 0 = & u_{ij}^{ab} + \tilde{f}_c^b t_{ij}^{ac} P(ab) - \tilde{f}_j^k t_{ik}^{ab} P(ij) \\
 & + t_{ij}^{cd} \chi_{cd}^{ab} + t_{in}^{ab} \chi_j^n P(ij) - t_{ij}^{bd} \chi_d^a P(ab) \\
 & + t_{im}^{ac} \chi_{jc}^{bm} P(ab) P(ij) + \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}.
 \end{aligned} \tag{C9}$$

#### Appendix D: Coupled cluster doubles diagrams

In order to get an expression for the energy equation and the amplitude equations we use a diagrammatic approach.

#### Appendix E: Example Script

$$\chi_{cd}^{ab} = \frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \tag{C5}$$

$$\chi_j^n = \frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \tag{C6}$$

$$\chi_d^a = \frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \tag{C7}$$

$$\chi_{jc}^{bm} = \frac{1}{2} t_{jn}^{bd} u_{cd}^{mn} + u_{jc}^{bm}, \tag{C8}$$

---

```

from coupled_cluster.schemes.ccd_sparse import CoupledClusterDoublesSparse
from coupled_cluster.schemes.ccd_optimized import CoupledClusterDoublesOptimized
from coupled_cluster.hartree_fock.scf_rhf import scf_rhf
from coupled_cluster.matrix_elements.generate_matrices import (
    get_one_body_elements, get_coulomb_elements,
    get_antisymmetrized_elements, add_spin_to_one_body_elements,
    get_one_body_elements_spin
)
from coupled_cluster.matrix_elements.index_map import (
    generate_index_map, IndexMap
)
from coupled_cluster.hartree_fock.basis_transformation import (
    transform_one_body_elements, transform_two_body_elements
)

import numpy as np
import time
import os

file_path = os.path.join("../", "dat")
filename = os.path.join(file_path, "coulomb_{0}.pkl")

num_shells = 12
generate_index_map(num_shells)

omega = 1.0
l = IndexMap.shell_arr[-1]
n = 6
theta = 0.3

filename = filename.format(l)

print ("""
w = {0},
num_shells = {1},
l = {2},
n = {3},

```

```

theta = {4},
filename = {5}
"".format(omega, num_shells, l, n, theta, filename))

h = omega * get_one_body_elements(l)
t0 = time.time()
u = np.sqrt(omega) * get_coulomb_elements(l, filename=filename, tol=1e-12)
t1 = time.time()
print ("Time spent creating Coulomb elements: {0} sec".format(t1 - t0))

t0 = time.time()
c, energy = scf_rhf(h.todense(), u, np.eye(l//2), n//2)
t1 = time.time()
print ("Time spent in SCF RHF: {0} sec".format(t1 - t0))

print ("\tRHF Energy: {0}".format(energy))

hi = transform_one_body_elements(h, c)
t0 = time.time()
oi = transform_two_body_elements(u, c)
t1 = time.time()
print ("Time spent transforming two body elements: {0} sec".format(t1 - t0))

_h = add_spin_to_one_body_elements(hi, l)
t0 = time.time()
_u = get_antisymmetrized_elements(l, oi=oi, tol=1e-12)
t1 = time.time()
print ("Time spent antisymmetrizing two body elements: {0} sec".format(t1 - t0))

t0 = time.time()
ccd_hf_sparse = CoupledClusterDoublesSparse(_h, _u, n)
t1 = time.time()
print ("Time spent setting up CCD code with HF basis: {0} sec".format(t1 - t0))

t0 = time.time()
energy, iterations = ccd_hf_sparse.compute_energy(tol=1e-4, theta=theta)
t1 = time.time()
print ("Time spent computing CCD energy with HF basis: {0} sec".format(t1 - t0))
print ("\tCCD (HF) Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}"
        .format(energy, iterations, (t1 - t0)/iterations))

t0 = time.time()
ccd_hf = CoupledClusterDoublesOptimized(
    _h.todense(), _u.todense(), n, parallel=True)
t1 = time.time()
print ("Time spent setting up CCD (opt, parallel) code with HF basis: {0} sec"
        .format(t1 - t0))

t0 = time.time()
energy, iterations = ccd_hf.compute_energy(tol=1e-4, theta=theta)
t1 = time.time()
print ("Time spent computing CCD (opt, parallel) energy with HF basis: {0} sec"
        .format(t1 - t0))
print ("\tCCD (HF) Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}"
        .format(energy, iterations, (t1 - t0)/iterations))

__h = omega * get_one_body_elements_spin(l)
t0 = time.time()

```

```

__u = np.sqrt(omega) * get_antisymmetrized_elements(l, filename=filename)
t1 = time.time()
print ("Time spent getting antisymmetric two body elements: {0} sec".format(t1 - t0))

t0 = time.time()
ccd = CoupledClusterDoublesSparse(__h, __u, n)
t1 = time.time()
print ("Time spent setting up CCD code with H0 basis: {0} sec".format(t1 - t0))
t0 = time.time()
energy, iterations = ccd.compute_energy(theta=theta)
t1 = time.time()
print ("Time spent computing CCD energy with H0 basis: {0} sec".format(t1 - t0))
print ("\tCCD Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}"
      .format(energy, iterations, (t1 - t0)/iterations))

print (h.density)
print (u.density)
print (_u.density)
print (_h.density)
print (__u.density)
print (__h.density)

```

---

[1] E. Anisimovas and A. Matulis, Journal of Physics: Condensed Matter **10**, 601 (1998).

[2] T. D. Crawford and H. F. Schaefer, Reviews in Computational Chemistry, Volume 14 , 33 (2007).