

# Hello hello

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## Abstract

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## 1 Introduction

## 2 Theory

### 2.1 Mathematical framework and notation

In the following we will use the occupation representation, making use of creation  $a_p^\dagger$  and annihilation  $a_p$  operators. As a shorthand, we will write  $\hat{p}^\dagger \equiv a_p^\dagger$  and  $\hat{p} \equiv a_p$  when no confusion can be made.  $N$  represents the number of occupied states while  $L$  the total number of states in our calculations. The indices  $p, q, \dots$  are reserved for the  $L$  general states, the  $N$  occupied states are indexed by  $i, j, \dots$ , while the  $L - N$  unoccupied (virtual) states by  $a, b, \dots$  indices.

Since we are treating fermionic systems, the canonical anticommutation relations are used

$$\{\hat{p}^\dagger, \hat{q}^\dagger\} = \{\hat{p}, \hat{q}\} = 0 \quad \{\hat{p}^\dagger, \hat{q}\} = \delta_{pq}.$$

One and two body matrix elements are calculated using a computational basis, with explicit expressions for one body Hamiltonians  $h(\mathbf{x})$  and two body interaction  $v(\mathbf{x}, \mathbf{x}')$  here presented in position space

$$\langle p | \hat{h} | q \rangle = \int d\mathbf{x} \psi_p^*(x) \hat{h}(\mathbf{x}) \psi_q(x)$$

$$\langle pq | \hat{v} | rs \rangle = \int d\mathbf{x} d\mathbf{x}' \psi_p^*(\mathbf{x}) \psi_q^*(\mathbf{x}') \hat{v}(\mathbf{x}, \mathbf{x}') \psi_r(\mathbf{x}) \psi_s(\mathbf{x}')$$

with  $\psi_p$  being a single particle wave function, often chosen to be the eigenfunction of  $\hat{h}$ . Note that  $p$  also contain the spin quantum number, meaning that  $d\mathbf{x}$  implicitly contains a spin component. If  $\hat{h}$  or  $\hat{v}$  is spin *independent*, this simply reduces to Kronecker deltas for the spin component. It is often convenient to use antisymmetrized matrix elements, defined as

$$\langle pq || rs \rangle = \langle pq | \hat{v} | rs \rangle - \langle pq | \hat{v} | sr \rangle$$

The shorthands  $h_{pq} \equiv \langle p | \hat{h} | q \rangle$ ,  $v_{rs}^{pq} \equiv \langle pq | \hat{v} | rs \rangle$  and  $\bar{v}_{rs}^{pq} \equiv \langle pq || rs \rangle$  will often be used. Using this formulation, a general two-body operator can be constructed

$$\hat{H} = \sum_{pq} h_{pq} \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{pqrs} \bar{v}_{rs}^{pq} \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \quad (1)$$

The simplest ground state ansatz

$$|\Phi_0\rangle = \hat{i}^\dagger \hat{j}^\dagger \dots |0\rangle,$$

can be evaluated to calculate the simplest energy estimate using Wicks Theorem [6]

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \bar{v}_{ij}^{ij} \equiv E_{\text{ref}}, \quad (2)$$

named the *reference energy*. Commonly wicks theorem is applied to Eq. 1 to pick out the Eq. 2 contribution, defining the *normal ordered* Hamiltonian

$$\hat{H} = \hat{H}_N + E_{\text{ref}} = \hat{F}_N + \hat{V}_N + E_{\text{ref}}$$

where  $\hat{F}_N$  and  $\hat{V}_N$  is the normal ordered *Fock operator* and two body interaction respectively.

$$\hat{F}_N = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\}, \quad (3)$$

$$\hat{V}_N = \frac{1}{4} \sum_{pqrs} \bar{v}_{rs}^{pq} \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} \quad (4)$$

The operators inside the curly brackets denotes *normal ordering*. In constructing the Fock operator, the matrix elements  $f_{pq}$  are given as

$$f_{pq} = h_{pq} + \sum_i \bar{v}_{qi}^{pi}$$

One major reason for doing this is the applicability of the *Generalized Wicks Theorem* (GWT), such that we only need to consider contractions between different normal ordered strings [3].

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (5)$$

## 2.2 Hartree-Fock

The Hartree-Fock method is one of the cheapest and most commonly applied many-body methods. Using the reference energy equation Eq. 2, we perform a basis change to the Hartree-Fock basis, based on minimizing the ansatz expectation value. Using Greek letters to index the computational basis  $\alpha, \beta \dots$ , going over all states  $L$  we can change to the Hartree-Fock basis using

$$|i\rangle = \sum_{\alpha} C_{\alpha i} |\alpha\rangle$$

where  $C_{\alpha i}$  are the basis coefficients. These are the objects used for the parameter search in configuration space. We are however not free to choose an arbitrary transformation, since we require the Hartree-Fock states to be orthogonal  $\langle i|j\rangle = \delta_{ij}$ . We formulate this constraint as a function of the coefficients  $C$

$$\begin{aligned} \mathcal{G}(C) &= \sum_{ij} \epsilon_{ij} (\delta_{ij} - \langle i|j\rangle) \\ &= \sum_{ij} \sum_{\alpha\beta} \epsilon_{ij} (\delta_{ij} - C_{\alpha i}^* C_{\beta j} \langle \alpha|\beta\rangle) = 0 \end{aligned}$$

Where  $\epsilon_{ij}$  as the Lagrange multipliers. The goal is minimizing

$$\begin{aligned} \mathcal{E}(C) &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \sum_{\alpha\beta} C_{\alpha i}^* C_{\beta i} h_{\alpha\beta} \\ &+ \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{\alpha i}^* C_{\beta j}^* C_{\gamma i} C_{\delta j} \bar{v}_{\gamma\delta}^{\alpha\beta} \end{aligned}$$

and thus the relevant Lagrangian then becomes

$$\mathcal{L}(C) = \mathcal{E}(C) + \mathcal{G}(C).$$

The equation to solve are then found by considering a stationary point of the Lagrangian  $\delta\mathcal{L} = 0$  wrt. the coefficients  $C$ . Performing this minimization, we achieve an eigenvalue problem with the matrix

$$h_{\alpha\beta}^{\text{HF}} = h_{\alpha\beta} + \sum_{\gamma\delta} \rho_{\gamma\delta} \bar{v}_{\beta\delta}^{\alpha\gamma}, \quad \rho_{\gamma\delta} = \sum_i C_{\gamma i}^* C_{\delta i} \quad (6)$$

having the coefficients as eigenvectors and the Lagrange multipliers as eigenvalues

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{i\beta} = \epsilon_i C_{i\alpha}. \quad (7)$$

Where the Lagrange multipliers are diagonal since by their Hermiticity we can perform a unitary transformation to a basis where they are diagonal  $\epsilon = U\epsilon'U^\dagger$ . In addition, the matrix  $\rho_{\gamma\delta}$  can be interpreted as the density matrix.

## 2.3 Coupled Cluster

The exact solution  $|\Psi\rangle$  is approximated by an exponential ansatz  $|\Psi_{\text{CC}}\rangle$

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle. \quad (8)$$

The operators  $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$  acting on the ground state ansatz  $|\Phi_0\rangle$  are the so-called *cluster operators* defined as

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\dots \\ ij\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \dots\} \quad (9)$$

where  $m \leq N$ . The scalars  $t_{ij\dots}^{ab\dots}$  are unknown expansion coefficients called *amplitudes*, which we need to solve for. All the creation and annihilation operators of Eq. 9 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\dots)}^{\hat{P}(ab\dots)} = (-1)^{\sigma(\hat{P}) + \sigma(\hat{P}')} t_{ij\dots}^{ab\dots}. \quad (10)$$

Here  $P$  and  $P'$  permutes  $\sigma(P)$  and  $\sigma(P')$  indices respectively. This is the reason for the prefactor of Eq. 9, since we have  $m!$  ways to independently permute particle and hole indices. Instead of having  $(L-N)^m N^m$  independent unknowns, we reduce this number by a factor of  $(m!)^2$ .

## 2.4 Doubles truncation

Considering  $N$  cluster operators in the exponential ansatz of Eq. 8 is not computationally feasible for realistic systems. The common practice is to include one or more  $\hat{T}_m$  operators, making a truncation on  $|\Psi_{\text{CC}}\rangle$  as well. In the following we will include only the double excitation operator  $\hat{T}_2$ , know as the CCD approximation. This gives us

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \approx |\Psi_{\text{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle, \quad (11)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\}, \quad (12)$$

with the four-fold amplitude permutation symmetry<sup>1</sup>,

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \quad (13)$$

Incorporating the CCD approximation in the Schrödinger equation (Eq. 5), we see that

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle, \\ \hat{H}_N e^{\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} e^{\hat{T}_2} |\Phi_0\rangle, \end{aligned} \quad (14)$$

where  $\Delta E_{\text{CCD}} = E - E_{\text{ref}}$ . Expanding both sides and taking the inner product with  $\langle \Phi_0|$ , we in principle get an equation for the energy. However, this approach is

<sup>1</sup>For double amplitudes, the index permutation symmetry is equal to that of antisymmetrized two-body matrix elements  $\langle pq||rs\rangle$ .

not amenable to practical computer implementation [2] since the amplitude equation will be coupled with the energy equation. Therefor, we rather apply a similarity transform to Eq. 14 by multiplying by the inverse of  $e^{\hat{T}_2}$ ,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_N e^{-\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \\ \bar{H} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \end{aligned} \quad (15)$$

where  $\bar{H} = e^{-\hat{T}_2} \hat{H}_N e^{-\hat{T}_2}$  is the similarity transformed Hamiltonian. Using this reformulated eigenvalue problem, we can perform the inner product with different states to calculate both  $\Delta E_{\text{CCD}}$  and  $t_{ij}^{ab}$ . Considering  $\langle \Phi_0 |$  we get

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \Delta E_{\text{CCD}}, \quad (16)$$

named the *energy equation*. Considering excited states, we arrive at the *amplitude equations*

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle, \quad (17)$$

used for finding the unknown amplitudes  $t_{ij}^{ab}$ . To find explicit expressions for Eq. 16 and Eq. 17, we expand  $\bar{H}$  using the Hausdorff expansion

$$\bar{H} = \hat{H}_N + [\hat{H}_N, \hat{T}_2] + \frac{1}{2!} [[\hat{H}_N, \hat{T}_2], \hat{T}_2]. \quad (18)$$

The truncation at the two-fold commutator comes from the fact that we have a two-body interaction combined with  $\hat{T}_2$  only performing double excitations. When evaluated with a doubly excited state, at least one creation or annihilation operator from each of the cluster operators has to be contracted with  $\hat{H}_N$ . Therefor having eight creation and annihilation operators in two  $\hat{T}_2$ , four of them can be contracted with the four from  $\hat{H}_N$ , while the other four with the operators from  $\langle \Phi_{ij}^{ab} |$ . This gives the CCD amplitude equation calculated from

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0 \quad (19)$$

The calculations can be further simplified from Eq. 18, noting that any creation operator  $\hat{a}^\dagger$  or annihilation operator  $\hat{a}$  to the left of  $\hat{H}_N$  can not give any non-zero contractions due to the lack of a  $\hat{a}$  or  $\hat{a}^\dagger$  to its left. Therefor we only get contribution from fully contracted  $\hat{H}_N$ ,  $\hat{H}_N \hat{T}_2$  and  $\hat{H}_N \hat{T}_2 \hat{T}_2$  terms, where each  $\hat{T}_2$  has at least one leg in  $\hat{H}_N$ .

To make practical use of Eq. 16 and Eq. 19, a chain of contractions applying the GWT has to be performed. This is a tedious task, thus all amplitude and energy equations here has been calculated using **Drudge**<sup>2</sup>. The energy equation becomes

<sup>2</sup>Drudge / Gristmill, Symbolic tensor and non-commutative algebra with powerful automatic code generation and optimization, written by Jinmo Zhao and Gustavo E Scuseria, <https://tschijnmo.github.io/drudge/>

$$\Delta E_{\text{CCD}} = \frac{1}{4} \sum_{abij} \bar{v}_{ab}^{ij} t_{ij}^{ab}, \quad (20)$$

with the amplitude equation in its pure glory (using Einstein summation convention)

$$\begin{aligned} &\bar{v}_{ij}^{ab} + \hat{P}(ab) f_{bct} t_{ij}^{ac} - \hat{P}(ij) f_{kjt} t_{ik}^{ab} \\ &+ \frac{1}{2} \bar{v}_{cd}^{ab} t_{ij}^{cd} + \frac{1}{2} \bar{v}_{ij}^{kl} t_{kl}^{ab} + \hat{P}(ab) \hat{P}(ij) \bar{v}_{cj}^{kb} t_{ik}^{ac} \\ &+ \frac{1}{4} \bar{v}_{cd}^{kl} t_{ij}^{cd} t_{kl}^{ab} + \hat{P}(ij) \bar{v}_{cd}^{kl} t_{ik}^{ac} t_{jl}^{bd} \\ &- \frac{1}{2} \hat{P}(ij) \bar{v}_{cd}^{kl} t_{ik}^{dc} t_{lj}^{ab} - \frac{1}{2} \hat{P}(ab) \bar{v}_{cd}^{kl} t_{lk}^{ac} t_{lj}^{db} = 0. \end{aligned} \quad (21)$$

Here we have defined permutation operators  $\hat{P}(pq) = 1 - \hat{P}_{pq}$ , where  $\hat{P}_{pq}$  interchanges the two indices  $p$  and  $q$ .

## 2.5 Spin restriction

Both the HF and CCD frameworks presented here treats matrix elements including spin. If the Hamiltonian is spin-independent, both storing and summation over matrix elements can be significantly reduced. Separating relevant quantum numbers and spin, explicitly  $p = (P, \sigma_P)$  with  $P$  as relevant numbers and  $\sigma_P$  as spin, we see that a general matrix element

$$\langle pq | \hat{v} | rs \rangle = \langle PQ | \hat{v} | RS \rangle \delta_{\sigma_P \sigma_R} \delta_{\sigma_Q \sigma_S},$$

only gives non-zero contributions when both the spins of  $p, r$  and  $q, s$  align. This reduces 16 equal (or vanishing) elements to a single element, improving both storage and computation time. To make use of this however, we must explicitly expand matrix elements and perform spin summations.

## 3 Method

### 3.1 Computational Considerations

The methods used to solve both the HF and CCD equations will be outlined in the following section.

#### 3.1.1 Hartree-Fock

Solving Eq. (7) is as stated simply an eigenvalue problem, with  $\epsilon$  and  $C$  as eigenvalues and vectors respectively. However, we see from Eq. 6 that the construction of  $h_{\alpha\beta}^{\text{HF}}$  requires the density matrix  $\rho$  which again is dependent on the coefficients. To find the correct minimization coefficients an iterative scheme was applied. The initial guess was always chosen to be  $C_{ii}^{(0)} = 1$ <sup>3</sup>. As a stopping criterion, the sum of Lagrange multipliers per occupied states

<sup>3</sup>Note that this is over occupied states only

between iterations  $\Delta$  was used. The iterations stop when  $\Delta$  is below a predetermined tolerance  $\Delta_0$ . This approach is outlined in Algo. 1.

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**Algorithm 1** Outline of Hartree-Fock iterative scheme.

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```

 $C_{ii}^{(0)} \leftarrow 1$ 
while  $\Delta > \Delta_0$  do
   $h^{\text{HF}} \leftarrow f(C^{(n-1)})$  Eq. 6
   $C^{(n)} \leftarrow \text{Eigenvectors}(h^{\text{HF}})$ 
   $\epsilon^{(n)} \leftarrow \text{Eigenvalues}(h^{\text{HF}})$ 
   $\Delta \leftarrow \sum |\epsilon^{(n)} - \epsilon^{(n-1)}|/N$ 
end while

```

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### 3.1.2 Coupled Cluster

The approach for solving the amplitudes in Eq. 19 follow much the same methodology as the HF iterative scheme. Fixed point iterations are a common solution to solving non-linear sets of coupled equations, and is relatively easy to formulate.

Going back to the amplitude equation Eq. 21 we separate the diagonal and off-diagonal part of  $f_{pq}$  as  $f_p^D$  and  $f_{pq}^O$  respectively

$$f_{pq} = \delta_{pq} f_{pp} + (1 - \delta_{pq}) f_{pq} = f_p^D + f_{pq}^O.$$

Considering the  $\hat{P}(ab)$  term with the Fock matrix

$$\hat{P}(ab) f_{bc} t_{ij}^{ac} = f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc},$$

we can insert the diagonal and off-diagonal partition of the Fock matrix giving

$$\begin{aligned} t_{bc} t_{ij}^{ac} &= \delta_{bc} f_{bb} t_{ij}^{ac} + (1 - \delta_{bc}) f_{bc} t_{ij}^{bc} \\ &= f_b^D t_{ij}^{ab} + f_{bc}^O t_{ij}^{ac} \end{aligned}$$

Similarly

$$f_{ac} t_{ij}^{bc} = -f_a^D t_{ij}^{ab} + f_{ac}^O t_{ij}^{bc}$$

Meaning that the  $\hat{P}(ab)$  Fock matrix term can be expressed as the sum over the off-diagonal part, in addition to a no-sum  $f_a^D + f_b^D$  term.

$$\hat{P}(ab) f_{bc} t_{ij}^{ac} = (f_a^D + f_b^D) t_{ij}^{ab} + \hat{P}(ab) f_{bc} t_{ij}^{ac}$$

Performing the same decomposition for the  $\hat{P}_{ij}$  yields the same decomposition. If we go back to Eq. 21 and call every term except the pure diagonal term  $R_{ij}^{ab}(t)$ <sup>4</sup> we get

$$\begin{aligned} \mathcal{F}_{ij}^{ab} t_{ij}^{ab} + R_{ij}^{ab}(t) &= 0, \\ t_{ij}^{ab} &= -\frac{R_{ij}^{ab}(t)}{\mathcal{F}_{ij}^{ab}}, \end{aligned}$$

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<sup>4</sup>Note that this is a function of the amplitudes *resulting* in the four-index term after the sums has been performed.

where we have defined

$$\mathcal{F}_{ij}^{ab} = f_a^D + f_b^D - f_i^D - f_j^D.$$

Note that  $\mathcal{F}_{ij}^{ab}$  is iteration independent and can be pre-computed. This gives a function suitable for fixed point iterations. It is also possible to calculate the new amplitudes using some percentage of the old amplitudes, *slowly mixing* in the new iterations. Parameterized by the mixing parameter  $p \in [0, 1]$ , we update the amplitudes following

$$t_{ij}^{ab,(n+1)} = p t_{ij}^{ab,(n)} + (1 - p) \frac{R_{ij}^{ab}(t^{(n)})}{\mathcal{F}_{ij}^{ab}} \quad (22)$$

Convergence is determined by finding stable solutions to  $t_{ij}^{ab}$  thus we evaluate the CCD contribution Eq. 20 each iteration and stop when the difference between iterations is lower than some predetermined tolerance. The procedure is outlined in Algo. 2

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**Algorithm 2** Outline of Hartree-Fock iterative scheme.

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```

 $t_{ij}^{ab(0)} \leftarrow 0$ 
while  $\Delta > \Delta_0$  do
   $h^{\text{HF}} \leftarrow f(C^{(n-1)})$  Eq. 6
   $C^{(n)} \leftarrow \text{Eigenvectors}(h^{\text{HF}})$ 
   $\epsilon^{(n)} \leftarrow \text{Eigenvalues}(h^{\text{HF}})$ 
   $\Delta \leftarrow \sum |\epsilon^{(n)} - \epsilon^{(n-1)}|/N$ 
end while

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## 3.2 Quantum Mechanical System

### 3.2.1 Helium and Beryllium

The initial testing during development of the CCD and RCCD implementations was performed using Hydrogen wave functions. As a choice of basis sets, these functions are ‘physically motivated’ in the sense of being solutions to the one body electron case. The well-know relevant quantum numbers determining the form of the spatial wave functions are  $n$  as the principal quantum number, with  $l$  and  $m$  as orbital angular momentum and projection respectively. Due to the spherically symmetric potential, the wave function  $\psi_{nlm}$  can be separated in a radial function  $R_{nl}(r)$  and a spherical harmonic  $Y_l^m$ ,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi). \quad (23)$$

The radial part  $R_{nl}(r)$  has the form

$$\begin{aligned} R_{nl}(r) &= A_{nl} e^{-r/na_0} \left( \frac{2r}{na_0} \right)^l [L_{n-l-1}^{2l+1}(2r/na_0)] \\ A_{nl} &= \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \end{aligned}$$

With  $L$  as the associated Laguerre polynomials and  $a_0$  the Bohr radius. For  $l > 0$  the Coulomb interaction integral of Eq. 23 can not be easily evaluated due to  $Y_l^m$  having a non-trivial  $\theta$  and  $\phi$  dependence. Therefor for simplicity we only consider  $s$  orbital ( $l = 0$  states), when calculating  $\langle pq | \hat{v} | rs \rangle$ . This is briefly sketched in Sec. A. The one-body term  $h_{pq}$  are diagonal with

$$h_{nm} = -\frac{Z}{2n^2} \delta_{nm} \quad (24)$$

We will be interested in calculating the ground state energy for Helium and Beryllium, with two and four electrons respectively. In addition to Hartree-Fock and CCD calculations, a comparison to configuration interaction using singles (CIS) will be performed for both Helium and Beryllium. The results will also be benchmarked against the famous work done by Egil A. Hylleraas [4].

### 3.2.2 Two-Dimensional Harmonic Oscillator

To test the HF and CCD implementations on larger basis sets, the two-dimensional harmonic oscillator was chosen.  $N$  electrons are confined in a potential characterized by the oscillation frequency  $\omega$ , with a repulsive Coulomb term

$$H = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 r_i^2 \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (25)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . The natural single particle basis for this problem is the solutions to the non-interactive harmonic oscillator case. Characterized by two quantum numbers  $n_x$  and  $n_y$ , the position space wave function in Cartesian coordinates are expressed as

$$\psi_{n_x n_y}(x, y) = A_{n_x n_y} H_{n_x}(\sqrt{\omega} x) H_{n_y}(\sqrt{\omega} y) e^{-\omega(x^2 + y^2)/2}$$

$$A_{n_x n_y} = \sqrt{\frac{\omega}{\pi 2^{(n_x + n_y)} n_x! n_y!}}$$

The one-body Hamiltonian is diagonal, with the well known energies

$$E_{n_x, n_y} = \hbar\omega(n_x + n_y + 1) \quad (26)$$

for two dimensions. For the Coulomb integral from Eq. 25 a more nuanced consideration is in order. The simplest approach is to solve the Coulomb integrals numerically, however even though we just work in two dimensions, the integral will be two-dimensional with a quite complex integrand. For larger basis sets where  $L \sim 100$ , this approach can not be performed without any clever performance tricks. Luckily this problem has

been solved analytically in spherical coordinates [1], giving a much cheaper way to incorporate the Coulomb integrals. The implementation co-authored by Ø. Schøyen has been used <sup>5</sup>.

We will consider closed shell systems, that is the particle number  $N$  will always correspond to all sets of  $(n_x, n_y)$  which gives the same single particle energy from Eq. 26 and every energy below this. These shell closures are tabulated in Tab. 1.

$R$	$(n_x, n_y)$	$d$	$N$
1	(0, 0)	2	2
2	(1, 0) <sub>1</sub>	4	6
3	(2, 0) <sub>1</sub> , (1, 1)	6	12
4	(3, 0) <sub>1</sub> , (2, 1) <sub>1</sub>	8	20
5	(4, 0) <sub>1</sub> , (3, 1) <sub>1</sub> , (2, 2)	10	30
6	(5, 0) <sub>1</sub> , (4, 1) <sub>1</sub> , (3, 2) <sub>1</sub>	12	42
7	(6, 0) <sub>1</sub> , (5, 1) <sub>1</sub> , (4, 2) <sub>1</sub> , (3, 3)	14	56
8	(7, 0) <sub>1</sub> , (6, 1) <sub>1</sub> , (5, 2) <sub>1</sub> , (4, 3) <sub>1</sub>	16	72
9	(8, 0) <sub>1</sub> , (7, 1) <sub>1</sub> , (6, 2) <sub>1</sub> , (5, 3) <sub>1</sub> , (4, 4)	18	90

**Table 1:** Showing shell closure for first 9 shells. Degeneracy follows  $d = 2R$  with energy per particle  $R\hbar\omega$ . The subscript 1 means the set on  $n$  can be permuted once,  $(x, y)_1 = (x, y), (y, x)$ .

The interactive  $N = 2$  case for  $\omega = 1$  has been solved analytically, giving a ground state energy of 3 a.u.[8]. In addition, [7] have tabulated multiple  $\omega$  frequencies with up to  $N = 20$  electrons, calculated for a variety of CC truncation and schemes.

### 3.2.3 Doubly Magic Nuclei

Define

$$R \quad (27)$$

## 4 Results

### 4.1 Helium and Beryllium

The closed shell Helium and Beryllium calculations are presented in Tab. 2, with relative errors compared to FCI in Tab. 3. For both HF add CCD in both restricted and unrestricted schemes, no problems of convergence was encountered. Adding a mixing parameter  $p > 0$  for CCD only resulted in slower convergence.

<sup>5</sup>Implementation is present at <https://github.com/HyQD/quantum-systems/tree/master>

Atom	$E_{\text{ref}}$	CI	FCI	HF	RHF
He	-2.7500	-2.8385	-2.9037	-2.8311	-2.8311
Be	-13.7160	-14.3621	-14.6674	-14.5083	-14.5083

Atom	CCD	RCCD	CCD(HF)	RCCD(HF)
He	-2.7516	-2.7516	-2.8391	-2.8391
Be	-13.7195	-13.7195	-14.5129	-14.5129

**Table 2:** Ground state energies for Helium and Beryllium in a.u. Calculations done with configuration interaction with both singles and no constraints (full), in addition to HF and CCD in both restricted and unrestricted schemes.

Atom	$E_{\text{ref}}$	CI	HF	RHF
He	5.29	2.25	2.50	2.50
Be	6.49	2.08	1.09	1.09

Atom	CCD	RCCD	CCD(HF)	RCCD(HF)
He	5.24	5.24	2.22	2.22
Be	6.46	6.46	1.05	1.05

**Table 3:** Relative error in % for Helium and Beryllium from Tab. 2, using the FCI results as the exact energies.

## 4.2 Harmonic Oscillator

## 5 Discussion

## 6 Concluding remarks

## References

- [1] E. Anisimovas and A. Matulis. Energy spectra of few-electron quantum dots. *Journal of Physics: Condensed Matter*, 10(3):601, January 1998.
- [2] Rodney J. Bartlett, Clifford E. Dykstra, and Josef Paldus. Coupled-Cluster Methods for Molecular Calculations. In Clifford E. Dykstra, editor, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, NATO ASI Series, pages 127–159. Springer Netherlands, Dordrecht, 1984.
- [3] L. Ferialdi and L. Diósi. General Wick’s Theorem for bosonic and fermionic operators. *Physical Review A*, 104(5):052209, November 2021. arXiv:2110.02920 [hep-th, physics:math-ph, physics:quant-ph].
- [4] Egil A. Hylleraas and Bjarne Undheim. Numerische Berechnung der 2S-Terme von Ortho- und Par-Helium. *Zeitschrift für Physik*, 65(11):759–772, November 1930.
- [5] Aaron Meurer, Christopher P. Smith, Mateusz Paprocki, Ondřej Čertík, Sergey B. Kirpichev, Matthew Rocklin, AMiT Kumar, Sergiu Ivanov, Jason K. Moore, Sartaj Singh, Thilina Rathnayake, Sean Vig, Brian E. Granger, Richard P. Muller, Francesco Bonazzi, Harsh Gupta, Shivam Vats, Fredrik Johansson, Fabian Pedregosa, Matthew J. Curry, Andy R. Terrel, Štěpán Roučka, Ashutosh Saboo, Isuru Fernando, Sumith Kulal, Robert Cimrman, and Anthony Scopatz. Sympy: symbolic computing in python. *PeerJ Computer Science*, 3:e103, January 2017.
- [6] Luca Guido Molinari. Notes on Wick’s theorem in many-body theory, October 2017. arXiv:1710.09248 [cond-mat, physics:math-ph].
- [7] M. Pedersen Lohne, G. Hagen, M. Hjorth-Jensen, S. Kvaal, and F. Pederiva. *Ab initio* computation of the energies of circular quantum dots. *Physical Review B*, 84(11):115302, September 2011.
- [8] M. Taut. Two electrons in a homogeneous magnetic field: particular analytical solutions. *Journal of Physics A: Mathematical and General*, 27(3):1045, February 1994.

## A Hydrogen Coulomb integrals

Considering states without orbital angular momentum, we remove the dependence on the two quantum numbers  $l$  and  $m$ , giving

$$\begin{aligned}\psi_{nlm}(r, \theta, \phi) &\longrightarrow \psi_n(r, \theta, \phi) \\ &= \sqrt{\left(\frac{4}{n^5}\right)} e^{-r/n} L_{n-1}^1(2r/n) Y_0^0.\end{aligned}$$

Where we work in distances of the Bohr radius  $r/a_0 \longrightarrow r$ . Since the Coulomb integral is over two  $\mathbf{r}_1, \mathbf{r}_2 \in \mathbb{R}^3$  spaces, we align  $\mathbf{r}_1$  along the  $y$ -axis and perform the  $\mathbf{r}_2$  integral first. In spherical coordinates, the Coulomb interaction then becomes

$$\hat{v}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{Z}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} \quad (\text{A.1})$$

With these preparations, the integrals can be solved for all  $p, q, r, s$  combinations. The integrals were solved using SymPy [5]