

# 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

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

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

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  $u_{rs}^{pq} \equiv \langle pq || rs \rangle$  will often be used. Using this formulation, a general two-body operator can be constructed

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

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 [Molinari, 2017]

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

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.

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

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

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

$$f_{pq} = h_{pq} + \sum_i u_{qi}^{pi}$$

One major reason for doing this is the applicability of the *Generalized Wicks Theorem*, such that we only need to consider contractions between different normal ordered strings [Ferialdi and Diósi, 2021].

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

## 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

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

where  $C_{\alpha p}$  are the basis coefficients. Assuming the

We are however not free to choose an arbitrary transformation, since we re

$$\mathcal{L} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_i \epsilon_{i\alpha} (\delta_{ij} - \langle i | j \rangle) \quad (6)$$

$$\delta \mathcal{L} = 0$$

Performing this minimization, we achieve an eigenvalue problem with the matrix

$$h_{\alpha\beta}^{\text{HF}} = h_{\alpha\beta} + \sum_{\gamma\delta} \rho_{\gamma\delta} u_{\beta\delta}^{\alpha\gamma}, \quad \rho_{\gamma\delta} = \sum_i C_{\gamma i}^* C_{\delta i} \quad (7)$$

having the coefficients as eigenvectors and the Lagrange multipliers as eigenvalues

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{i\beta} = \epsilon_i C_{i\alpha}. \quad (8)$$

**method?** This is solved iteratively, starting with  $C_{ii} = 1$ <sup>1</sup>, repeatedly diagonalizing  $C$ . As a stopping criteria, the sum of Lagrange multipliers per occupied states between iterations is used.

## 2.3 Coupled Cluster

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

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle. \quad (9)$$

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

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\dots \\ ij\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \dots\} \quad (10)$$

where  $m \leq N$ . The scalars  $t_{ij\dots}^{ab\dots}$  are unknown expansion coefficients called *amplitudes*, which we need to solve for.

<sup>1</sup>Note that this is over occupied states

All the creation and annihilation operators of Eq. 10 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\dots)}^{\hat{P}(ab\dots)} = (-1)^{\sigma(\hat{P}) + \sigma(\hat{P}')} t_{ij\dots}^{ab\dots}. \quad (11)$$

Here  $P$  and  $P'$  permutes  $\sigma(P)$  and  $\sigma(P')$  indices respectively. This is the reason for the prefactor of Eq. 10, 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. 9 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

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \approx |\Psi_{\text{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle, \quad (12)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\}, \quad (13)$$

with the four-fold amplitude permutation symmetry<sup>2</sup>,

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \quad (14)$$

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

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle, \\ \hat{H}_{\text{N}} e^{\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} e^{\hat{T}_2} |\Phi_0\rangle, \end{aligned} \quad (15)$$

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 not amenable to practical computer implementation [Bartlett et al., 1984] since the amplitude equation will be coupled with the energy equation. Therefore, we rather apply a similarity transform to Eq. 15 by multiplying by the inverse of  $e^{\hat{T}_2}$ ,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_{\text{N}} e^{-\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \\ \bar{H} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \end{aligned} \quad (16)$$

where  $\bar{H} = e^{-\hat{T}_2} \hat{H}_{\text{N}} e^{-\hat{T}_2}$  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

<sup>2</sup>For double amplitudes, the index permutation symmetry is equal to that of antisymmetrized two-body matrix elements  $\langle pq || rs \rangle$ .

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \Delta E_{\text{CCD}}, \quad (17)$$

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

$$\langle \Phi_{ij\dots}^{ab\dots} | \bar{H} | \Phi_0 \rangle, \quad (18)$$

used for finding the unknown amplitudes  $t_{ij}^{ab}$ . To find explicit expressions for Eq. 17 and Eq. 18, we expand  $\bar{H}$  using the Hausdorff expansion

$$\bar{H} = \hat{H}_N + \left[ \hat{H}_N, \hat{T}_2 \right] + \frac{1}{2!} \left[ \left[ \hat{H}_N, \hat{T}_2 \right], \hat{T}_2 \right].$$

The truncation at the two-fold commutator comes from the fact that we have a two-body interaction. 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

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

To make practical use of Eq. 17 and Eq. 19

## 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 Quantum Mechanical System

#### 3.1.1 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  $Y_l^m$ ,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi). \quad (20)$$

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

$$R_{nl}(r) = A_{nl} e^{-r/na_0} \left( \frac{2r}{na_0} \right)^l [L_{n-l-1}^{2l+1}(2r/na_0)]$$

$$A_{nl} = \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

With  $L$  as the associated Laguerre polynomials and  $a_0$  the Bohr radius. For  $l > 0$  the Coulomb interaction integral of Eq. 20 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

$$h_{nm} = -\frac{Z}{2n^2} \delta_{nm} \quad (21)$$

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 [Hylleraas and Undheim, 1930].

#### 3.1.2 Two-Dimensional Harmonic Oscillator

#### 3.1.3 Doubly Magic Nuclei

Define

$$R \quad (22)$$

## 4 Results

## 5 Discussion

## 6 Concluding remarks

## References

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## 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

$$\hat{v}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{Z}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} \quad (\text{A.1})$$

With these preparations, the integrals can be solved for all  $p, q, r, s$  combinations. The integrals were solved using SymPy [Meurer et al., 2017]