Master thesis Wilhelm Coupled Cluster

by

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Thesis

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Abstract

This is an abstract text.

To someone

This is a dedication to my cat.

Acknowledgements

I acknowledge my acknowledgements.

Contents

Chapter 1

Introduction

This is a very nice introduction to my myster thesis. or .. lol

Chapter 2

Quantum Mechanics

2.1 Postulates

Quantum

2.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation lies at the heart of many-body quantum mechanics.

2.3 Pauli's Exclusion Principle

Pauli exclusion principle, also called the antisymmetry principle [3]

2.4 The Variational Principle

2.5 Slater Determinant

A system composed of a nuclei and electrons moving in accordance to the forces of electromagnetic attraction can be described by assigning each electron a wave function

$$\phi_i(\mathbf{x}_i) \tag{2.1}$$

Where $\mathbf{x}_i$ is the position vector for the electron i. Describing a system of many electrons can be done writing a Slater Determinant

$$|\Phi_0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & ... & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & ... & \phi_N(\mathbf{x}_2) \\ ... \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & ... & \phi_N(\mathbf{x}_N) \end{vmatrix} \tag{2.2}$$

This way of writing the many-body wave function will represent linear a combination of products of the one-body wave functions ϕ_i's and all the electronic coordinates $\mathbf{x}_i$ distributed among them in all possible ways. Exchanging two lines will change the sign such that the Slater Determinant will respect the antisymmetry requirement.

We can choose the one-body wave functions that is most rewarding the specified system. When calculating on electrons moving with respect to a nuclei, one can choose the wave functions to be the 1s, 2s, 2p, .. orbitals. This representation will not, however, take into account the Colombic repulsion between two electrons and will only be an approximation to the true wavefunction, $|\Psi\rangle$.

2.6 Matrix Elements

Chapter 3

Second Quantization

Second quantization is a new method of representing states and operators.

3.1 Annihilation and Creation operators

We introduce a new way of writing states using the mathematical technique known as second quantization. The main goal is to treat states without paying attention to individual particle coordinates. We represent the empty space with the symbol for vacuum

$$|0\rangle \tag{3.1}$$

To represent a state, we use a creation operator to add the state to the vacuum.

$$\hat{a}_i^\dagger |0\rangle = |\phi_i\rangle \tag{3.2}$$

And the annihilation operator will remove the particle again.

$$\hat{a}_i |\phi_i\rangle = |0\rangle \tag{3.3}$$

Trying to add a new particle to an already filled state and removing an unoccupied state results in zero.

$$\hat{a}_i^\dagger |\phi_i\rangle = 0 \qquad \hat{a}_i |0\rangle = 0 \tag{3.4}$$

Bra states are needed, and by looking at the adjoint of a ket state, we get

$$(|\phi_i\rangle)^\dagger = \langle\phi_i| \tag{3.5}$$

Which results in

$$\left(\hat{a}_i^\dagger |0\rangle\right)^\dagger = \langle 0| \hat{a}_i = \langle \phi_i| \tag{3.6}$$

We see that the creation and annihilator operatorare each other's adjoint operator. We can define the counting operator, $\hat{N}$, which will count how many states are occupied in a Slater determinant

$$\hat{N} = \sum_p \hat{a}_p^\dagger \hat{a}_p = \sum_p \hat{n}_p \tag{3.7}$$

3.2 Strings of Operators

We can now construct the Slater determinant by working on vacuum with a string of creation operators

$$\hat{a}_1^\dagger \hat{a}_2^\dagger ... \hat{a}_N^\dagger |0\rangle = |\phi_1 \phi_2 ... \phi_N\rangle \tag{3.8}$$

Permutations of the operators introduces a sign-change, which is equivalent to interchanging rows in the determinant. We need second quantization to respect the anisymmetrization condition, so a permutation of two states should introduce a change of sign

$$\hat{a}_1^\dagger \hat{a}_2^\dagger |0\rangle = |\phi_1 \phi_2\rangle = - |\phi_2 \phi_1\rangle = -\hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle \tag{3.9}$$

We introduce the permutation operator, $\hat{P}$, which permutes two states in the Slater determinant

$$\hat{P} |\Phi\rangle = (-1)^{\sigma(P)} |\Phi\rangle \tag{3.10}$$

Where $\sigma(P)$ counts how many times the states are interchanged. Demonstrated with creation operators

$$\hat{a}_1^\dagger \hat{a}_2^\dagger ... \hat{a}_i^\dagger \hat{a}_j^\dagger ... \hat{a}_n^\dagger = -\hat{a}_1^\dagger \hat{a}_2^\dagger ... \hat{a}_j^\dagger \hat{a}_i^\dagger ... \hat{a}_n^\dagger \tag{3.11}$$

3.3 Anticommutator Relations

When working on strings of operators, it is very convenient to introduce anti-commutator relations. We define the relation as

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} \tag{3.12}$$

By inserting the annihilation and creation operator, we can compute the relations and look at how they work on the vacuum state

$$\{\hat{a}_i^\dagger \hat{a}_j\} |0\rangle = \hat{a}_i^\dagger \hat{a}_j |0\rangle + \hat{a}_j \hat{a}_i^\dagger |0\rangle = 0 + \delta_{ij} |0\rangle \tag{3.13}$$

Where we have introduced the kroenecker-delta function

$$\delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{ij } i \neq j \end{cases} \tag{3.14}$$

The second case

$$\{\hat{a}_i \hat{a}_j^\dagger\} |0\rangle = \hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i |0\rangle = \delta_{ij} |0\rangle + 0 \tag{3.15}$$

And the two last cases

$$\{\hat{a}_i \hat{a}_j\} |0\rangle = \hat{a}_i \hat{a}_j |0\rangle + \hat{a}_j \hat{a}_i |0\rangle = \hat{a}_i \hat{a}_j |0\rangle - \hat{a}_i \hat{a}_j |0\rangle = 0 \tag{3.16}$$

$$\{\hat{a}_i^\dagger \hat{a}_j^\dagger\} |0\rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger |0\rangle + \hat{a}_j^\dagger \hat{a}_i^\dagger |0\rangle = \hat{a}_i^\dagger \hat{a}_j^\dagger |0\rangle - \hat{a}_i^\dagger \hat{a}_j^\dagger |0\rangle = 0 \tag{3.17}$$

Ending up with our relations

$$\{\hat{a}_i \hat{a}_j\} = 0 \tag{3.18}$$

$$\{\hat{a}_i^\dagger \hat{a}_j^\dagger\} = 0 \tag{3.19}$$

$$\{\hat{a}_i^\dagger \hat{a}_j\} = \{\hat{a}_i \hat{a}_j^\dagger\} = \delta_{ij} \tag{3.20}$$

The last result is very useful for rewriting strings of operators, since it allows us to rewrite a set of two operators as

$$\hat{a}_i^\dagger \hat{a}_j = \{\hat{a}_i^\dagger \hat{a}_j\} - \hat{a}_j \hat{a}_i^\dagger = \delta_{ij} - \hat{a}_j \hat{a}_i^\dagger \tag{3.21}$$

Which will be at the center of Wick's theorem.

3.4 Expectation values

Doing calculations in many-body quantum mechanics, we are primerely interested in expectation values. It is therefore crucial that we develop a solid scheme for calculating these values. We assume all states are orthonormal, giving

$$\langle i|j\rangle = \delta_{ij} \tag{3.22}$$

And for consistency, the vacuum state must be normalized

$$\langle 0||0\rangle = 1 \tag{3.23}$$

because

$$1 = \langle i|i\rangle = \left\langle 0|\hat{a}_i\hat{a}_i^\dagger|0\right\rangle \tag{3.24}$$
$$= \left\langle 0|(\{\hat{a}_i, \hat{a}_i^\dagger\} - \hat{a}_i^\dagger\hat{a}_i)|0\right\rangle \tag{3.25}$$
$$= \langle 0|0\rangle - 0 = \langle 0|0\rangle \tag{3.26}$$

3.5 Representation of Operators

Consider a symmetric one-body operator represented by

$$\hat{F} = \sum_{\mu=1}^{N} \hat{f}_\mu \tag{3.27}$$

The number μ tells us on which particle $\hat{F}$ works on. In this case, we are looking at a symmetric operator because it works identically on all particles. Looking at a matrix element of $\hat{F}$ put petween two Slater determinants.

$$\langle a_1a_2...a_N|\,\hat{F}\,|b_1b_2...b_N\rangle \tag{3.28}$$

$$\sum_\mu \langle a_1a_2...a_N|\,\hat{f}_\mu\,|b_1b_2...b_N\rangle \tag{3.29}$$

3.6 Fermi Vacuum

3.7 Normal Ordering and Wick's Theorem

3.8 Partitioning the Hamiltonian

Chapter 4

Many-Body Methods

We have already justified the use of a Slater Determinant to describe the first approximation of the full wave function, $|\Psi\rangle$. Where

$$|\Psi\rangle \approx |\Phi_0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & ... & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & ... & \phi_N(\mathbf{x}_2) \\ ... \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & ... & \phi_N(\mathbf{x}_N) \end{vmatrix} \tag{4.1}$$

This first representation fails to account for the Coulombic interrraction between the electrons, and we need higher-order approximations on top of the Slater Determinant to improve our results.

This chapter will look at three methods, namely the Configuration interraction, Many-body Perturbation theory and Hartree-Fock approximations. The Master thesis is on Coupled Cluster theory, and that will be more elaborately explained in it's own chapter. It is useful to benchmark Coupled Cluster with similar many-body method.

4.1 Configuration Interraction

We can write the configuration interaction wavefunction as

$$|\Psi_{CI}\rangle = (1 + \hat{C}) |\Phi_0\rangle \tag{4.2}$$

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + ... = \sum_{ia} c_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + ... \tag{4.3}$$

4.2 Many-body Perturbation Theory

4.3 Hartree-Fock approximations

Chapter 5

Coupled-Cluster Theory

In Coupled Cluster theory, the ansatz we make is to make an expansion in the wave function

$$|\Psi\rangle \approx e^{\hat{T}} |\Psi_0\rangle \tag{5.1}$$

The operator $\hat{T}$ is a linear combination of the cluster operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... + \hat{T}_N \tag{5.2}$$

Where the operators represent

$$T_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i \tag{5.3}$$

$$T_2 = \frac{1}{2} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \tag{5.4}$$

$$T_2 = \left(\frac{1}{n!}\right)^2 \sum_{ij..ab..}^{n} t_{ij..n}^{ab..n} \hat{a}_a^\dagger \hat{a}_b^\dagger ... \hat{a}_n^\dagger \hat{a}_n ... \hat{a}_j \hat{a}_i \tag{5.5}$$

$$\tag{5.6}$$

We can write the configuration interaction wavefunction as

$$|\Psi_{CI}\rangle = (1 + \hat{C}) |\Phi_0\rangle \tag{5.7}$$

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + ... = \sum_{ia} c_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + ... \tag{5.8}$$

Comparing this linear expansion to the exponential expansion from Coupled Cluster, we can see that

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}T_1^2 \tag{5.9}$$

Where we can see that even if we truncate Configuration Interaction and Coupled Cluster at the same level, there are more *disconnected* wave function contributions (REFERENCE page 17 IN C&S) in the Coupled Cluster theory. Both the Coupled Cluster and Configuration Interaction theory provides the exact energy by including the operators to infinite order, i.e. no truncation.

5.1 Size Extensivity

It can be important to have a wave function that scales with size. Imagine a two particles, X and Y with infinity separation, they do not interact. This means we should be able to write the total energy as

$$E = E_X + E_Y \tag{5.10}$$

Doing Coupled Cluster

$$\hat{T} = \hat{T}_X + \hat{T}_Y \tag{5.11}$$

$$|\Psi\rangle_{CC} = e^{\hat{T}_X + \hat{T}_Y} |\Phi_0\rangle = e^{\hat{T}_X} e^{\hat{T}_Y} |\Psi_0\rangle \tag{5.12}$$

Since we can write the reference state as a product of the two seperated parts, we are able to write

$$E_{CC} = E_{CC}^X + E_{CC}^Y \tag{5.13}$$

This means Coupled Cluster is size extensive, contrary to the Configuration Interaction.

5.2 The CCD Equations

The Coupled Cluster Doubles equations can be finalized as

$$E_{CCD} = E_{ref} + \Delta E_{CCD} \tag{5.14}$$

With the reference energy defined as

$$E_{ref} = \sum_i \left\langle i \middle| \hat{h}_0 \middle| j \right\rangle + \sum_{ij} \langle ij|\hat{v}|ij\rangle + \frac{1}{2}Av_0 \tag{5.15}$$

and the corrolation energy given by

$$\Delta E_{CCD} = \frac{1}{4}\sum_{ijab} \langle ij|\hat{v}|ab\rangle\, t_{ij}^{ab} \tag{5.16}$$

v_0 is a constant, nonzero for the finite electron gas. After several applications of Wick's theorem, the amplitude equations can be reduced to

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)t_{ij}^{ab} = \langle ab|\hat{v}|ij\rangle + \frac{1}{2}\sum_{cd} \langle ab|\hat{v}|cd\rangle\, t_{ij}^{cd} \tag{5.17}$$

$$+\frac{1}{2}\sum_{kl} \langle kl|\hat{v}|ij\rangle\, t_{kl}^{ab} + \hat{P}\,(ij|ab)\sum_{kc} \langle kb|\hat{v}|cj\rangle\, t_{ik}^{ac} \tag{5.18}$$

$$+\frac{1}{4}\sum_{klcd} \langle kl|\hat{v}|cd\rangle\, t_{ij}^{cd}t_{kl}^{ab} + \frac{1}{2}\hat{P}\,(ij|ab)\sum_{klcd} \langle kl|\hat{v}|cd\rangle\, t_{ik}^{ac}t_{lj}^{db} \tag{5.19}$$

$$-\frac{1}{2}\hat{P}(ij)\sum_{klcd} \langle kl|\hat{v}|cd\rangle\, t_{ik}^{ab}t_{jl}^{cd} - \frac{1}{2}\hat{P}(ab)\sum_{klcd} \langle kl|\hat{v}|cd\rangle\, t_{kl}^{bd}t_{ij}^{ac} \tag{5.20}$$

Where we have defined

$$\hat{P}(ij) = 1 - \hat{P}_{ij} \tag{5.21}$$

Where $\hat{P}_{ij}$ interchanges the two particles occupying the quantum states i and j. Furthermore, we define the operator

$$\hat{P}\,(ij|ab) = (1 - \hat{P}_{ij})(1 - \hat{P}_{ab}) \tag{5.22}$$

We notice that some parts are linear in the amplitude, while some are quadradic. Sorting them into the linear and quadradic parts, L and Q respectably, I get

$$L(t_{ij}^{ab}) = \frac{1}{2}\sum_{cd} \langle ab|\hat{v}|cd\rangle\, t_{ij}^{cd} + \frac{1}{2}\sum_{kl} \langle kl|\hat{v}|ij\rangle\, t_{kl}^{ab} + \hat{P}\,(ij|ab)\sum_{kc} \langle kb|\hat{v}|cj\rangle\, t_{ik}^{ac} \tag{5.23}$$

and

$$Q(t_{ij}^{ab}t_{ij}^{ab}) = \frac{1}{4}\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ij}^{cd}t_{kl}^{ab} + \frac{1}{2}\hat{P}\,(ij|ab)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ik}^{ac}t_{lj}^{db} \tag{5.24}$$

$$-\frac{1}{2}\hat{P}(ij)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ik}^{ab}t_{jl}^{cd} - \frac{1}{2}\hat{P}(ab)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{kl}^{bd}t_{ij}^{ac} \tag{5.25}$$

Labeling each term for practical reasons

$$L_a = \frac{1}{2}\sum_{cd}\langle ab|\hat{v}|cd\rangle\, t_{ij}^{cd} \tag{5.26}$$

$$L_b = \frac{1}{2}\sum_{kl}\langle kl|\hat{v}|ij\rangle\, t_{kl}^{ab} \tag{5.27}$$

$$L_c = \hat{P}\,(ij|ab)\sum_{kc}\langle kb|\hat{v}|cj\rangle\, t_{ik}^{ac} \tag{5.28}$$

$$Q_a = \frac{1}{4}\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ij}^{cd}t_{kl}^{ab} \tag{5.29}$$

$$Q_b = \frac{1}{2}\hat{P}\,(ij|ab)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ik}^{ac}t_{lj}^{db} \tag{5.30}$$

$$Q_c = -\frac{1}{2}\hat{P}(ij)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{ik}^{ab}t_{jl}^{cd} \tag{5.31}$$

$$Q_d = -\frac{1}{2}\hat{P}(ab)\sum_{klcd}\langle kl|\hat{v}|cd\rangle\, t_{kl}^{bd}t_{ij}^{ac} \tag{5.32}$$

5.3 Intermediates

As Coupled Cluster computations are consume large amounts of computational power, researchers are spending much effort trying to reduce computational cost. One way of reducing the cost is by refactoring the amplitude equations such that we can perform an intermediate computation first and use the result to compute various diagrams later.

Rewriting the equation, (5.20) for CCD amplitudes (Source: Gustav Baardsen

/ Audun):

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)t_{ij}^{ab} = \langle ab|\hat{v}|ij\rangle + \frac{1}{2}\sum_{cd} \langle ab|\hat{v}|cd\rangle\, t_{ij}^{cd} \tag{5.33}$$

$$+\frac{1}{2}\sum_{kl} t_{kl}^{ab} \left[\langle kl|\hat{v}|ij\rangle + \frac{1}{2}\sum_{cd} \langle kl|\hat{v}|cd\rangle\, t_{ij}^{cd}\right] \tag{5.34}$$

$$+\hat{P}\,(ij|ab)\sum_{kc} t_{ik}^{ac} \left[\langle kb|\hat{v}|cj\rangle + \frac{1}{2}\sum_{ld} \langle kl|\hat{v}|cd\rangle\, t_{lj}^{db}\right] \tag{5.35}$$

$$-\frac{1}{2}\hat{P}(ij)\sum_{k} t_{ik}^{ab} \left[\sum_{lcd} \langle kl|\hat{v}|cd\rangle\, t_{jl}^{cd}\right] \tag{5.36}$$

$$-\frac{1}{2}\hat{P}(ab)\sum_{c} t_{ij}^{ac} \left[\sum_{kld} \langle kl|\hat{v}|cd\rangle\, t_{kl}^{bd}\right] \tag{5.37}$$

We can now define, and precompute the following values

$$I_1 = \langle kl|\hat{v}|ij\rangle + \frac{1}{2}\sum_{cd} \langle kl|\hat{v}|cd\rangle\, t_{ij}^{cd} \tag{5.38}$$

$$I_2 = \langle kb|\hat{v}|cj\rangle + \frac{1}{2}\sum_{ld} \langle kl|\hat{v}|cd\rangle\, t_{lj}^{db} \tag{5.39}$$

$$I_3 = \sum_{lcd} \langle kl|\hat{v}|cd\rangle\, t_{jl}^{cd} \tag{5.40}$$

$$I_4 = \sum_{kld} \langle kl|\hat{v}|cd\rangle\, t_{kl}^{bd} \tag{5.41}$$

We can now redefine the CCD equation

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)t_{ij}^{ab} = \langle ab|\hat{v}|ij\rangle + \frac{1}{2}\sum_{cd} \langle ab|\hat{v}|cd\rangle\, t_{ij}^{cd} + \frac{1}{2}\sum_{kl} t_{kl}^{ab} I_1 \tag{5.42}$$

$$+\hat{P}\,(ij|ab)\sum_{kc} t_{ik}^{ac} I_2 - \frac{1}{2}\hat{P}(ij)\sum_{k} t_{ik}^{ab} I_3 - \frac{1}{2}\hat{P}(ab)\sum_{c} t_{ij}^{ac} I_4 \tag{5.43}$$

Leading to a reduction of computational cost from $\mathcal{O}(h^4p^4)$ to $\mathcal{O}(h^4p^2)$

Chapter 6

The Pairing Model

The first system I look at is the pairing model. The pairing model has four energy levels with degeneracy two, one for positive and negative spins. I have used a system consisting of four electrons filling up the four lower-most states up to the Fermi level.

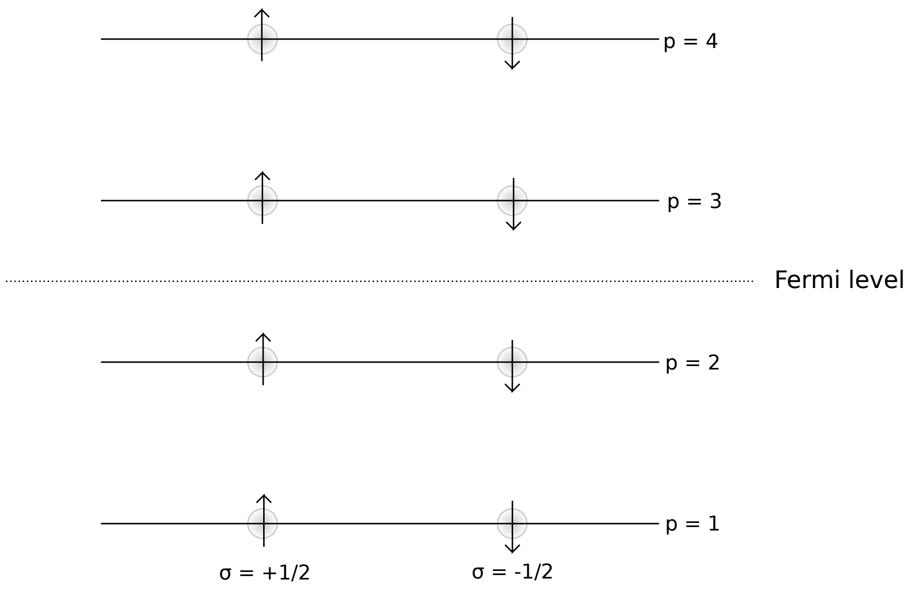


Figure 6.1: A figure depicting a 4 particles-4 holes state. The system consists of occupied particle states below the Fermi level and unoccupied hole states above Fermi level.

6.1 The Hamiltonian

We limit ourselves to a two-body interaction, writing the Hamiltonian as

$$\hat{H} = \sum_{\alpha\beta} \langle\alpha| \hat{h}_0 |\beta\rangle \hat{a}^\dagger_\alpha \hat{a}_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|\hat{v}_0|\gamma\delta\rangle \hat{a}^\dagger_\alpha \hat{a}^\dagger_\beta \hat{a}_\delta \hat{a}_\gamma \tag{6.1}$$

We use the complete basis $|\alpha\rangle$ and define the set as eigenvalues of the one-body operator, $\hat{h}_0$.

The system does require that the total spin is equal to 0. In addition we will not allow spin pairs to be broken, i.e. singly excitated states are not allowed.

$$|\Psi^a_i\rangle = 0 \tag{6.2}$$

We introduce the double creation and annihilation operator.

$$\hat{P}^\dagger_{pq} = \hat{a}^\dagger_{p\sigma} \hat{a}^\dagger_{p-\sigma} \tag{6.3}$$

$$\hat{P}_{pq} = a_{q\sigma} a_{q-\sigma} \tag{6.4}$$

We can rewrite the Hamiltonian as an unperterturbed part and a perturbation

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{6.5}$$

$$\hat{H}_0 = \xi \sum_{p\sigma} (p-1) \hat{a}^\dagger_{p\sigma} \hat{a}_{p\sigma} \tag{6.6}$$

$$\hat{V} = -\frac{1}{2} g \sum_{pq} \hat{a}^\dagger_{p+} \hat{a}^\dagger_{p-} \hat{a}_{q-} \hat{a}_{q+} \tag{6.7}$$

The value of ξ determines the spacing between the energy levels, which I have set to 1. This will not impact the insight attained solving this system. p and q determines the energy level. σ is the spin, with value either $+\frac{1}{2}$ or $-\frac{1}{2}$. Both the unperturbed and perturbed Hamiltonian keeps total spin at 0

We can normal order the Hamiltonian by Wicks general theorem.

$$a^\dagger_p a_q = \left\{a^\dagger_p a_q\right\} + \delta_{pq\in i} \tag{6.8}$$

$$\begin{aligned} a^\dagger_p a^\dagger_q a_s a_r = \left\{a^\dagger_p a^\dagger_q a_s a_r\right\} + \left\{a^\dagger_p a_r\right\} \delta_{qs\in i} - \left\{a^\dagger_p a_s\right\} \delta_{qr\in i} \qquad (6.9)\\ + \left\{a^\dagger_q a_s\right\} \delta_{pr\in i} - \left\{a^\dagger_q a_r\right\} \delta_{ps\in i} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i} \qquad (6.10) \end{aligned}$$

Which gives the Normal-ordered Hamiltonian

$$\hat{H} = \hat{H}_N + E_{ref} \tag{6.11}$$

$$\hat{H}_N = \hat{F}_N + \hat{W} \tag{6.12}$$

$$\hat{F}_N = \sum_{pq} h_{pq} \left\{ \hat{a}^\dagger_{p\sigma} \hat{a}_{p\sigma} \right\} - \sum_{pqi} \langle pi||qi \rangle \left\{ \hat{a}^\dagger_{p+} \hat{a}_{q-} \right\} \tag{6.13}$$

$$\hat{W} = -\frac{1}{2} \sum_{pqrs} \langle pq||rs \rangle \left\{ \hat{a}^\dagger_{p+} \hat{a}^\dagger_{p-} \hat{a}_{q-} \hat{a}_{q+} \right\} \tag{6.14}$$

$$E_{ref} = \sum_{i} h_{ii} + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle \tag{6.15}$$

6.2 Configuration Interaction theory

This system is a good way to benchmark various methods as we can compute the exact solution using Full Configuration Interaction.

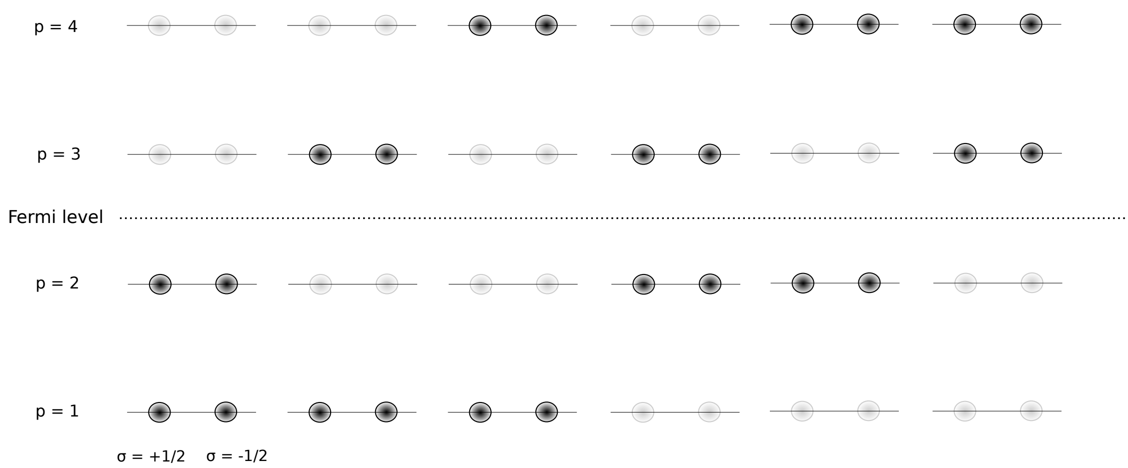


Figure 6.2: Configuration space for given pairing model showing all possible distributions of electrons

We need to diagonalize the Hamiltonian matrix looking at the linear combination of all different compinations of

$$\hat{\mathcal{H}} = \begin{array}{c|cccccc} & |\Phi_0\rangle & |\Phi_{12}^{56}\rangle & |\Phi_{12}^{78}\rangle & |\Phi_{34}^{56}\rangle & |\Phi_{34}^{78}\rangle & |\Phi_{1234}^{5678}\rangle \\ \hline \langle\Phi_0| & & & & & & \\ \langle\Phi_{12}^{56}| & & & & & & \\ \langle\Phi_{12}^{78}| & & & & & & \\ \langle\Phi_{34}^{56}| & & & & & & \\ \langle\Phi_{34}^{78}| & & & & & & \\ \langle\Phi_{1234}^{5678}| & & & & & & \end{array} \tag{6.16}$$

Excluding the 4p-4h excitations one does not diagonalize the exact matrix, but rather the approximated matrix known from Configuration Interaction.

The diagonal elements are calculated using Wick's theorem. Looking first at the ground state calculation with the unperturbed Hamiltonian part

$$\left\langle \Phi_0 \middle| \hat{\mathbf{H}}_\mathbf{0} \middle| \Phi_0 \right\rangle \tag{6.17}$$

$$\langle | \, a_{2\downarrow}a_{2\uparrow}a_{1\downarrow}a_{1\uparrow} \sum_{p\sigma} \delta(p-1) a^\dagger_{p\sigma} a_{p\sigma} a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} a^\dagger_{2\uparrow} a^\dagger_{2\downarrow} \, | \rangle \tag{6.18}$$

Which we see can contract in four different ways, resulting in

$$2\delta(1-1) + 2\delta(2-1) = 2\delta \tag{6.19}$$

And the perturbation part

$$\left\langle \Phi_0 \middle| \hat{\mathbf{V}} \middle| \Phi_0 \right\rangle \tag{6.20}$$

$$\langle | \, a_{2\downarrow}a_{2\uparrow}a_{1\downarrow}a_{1\uparrow} \left(-g/2 \sum_{pq} a^\dagger_{p\uparrow} a^\dagger_{q\downarrow} a_{q\downarrow} a_{p\uparrow} \right) a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} a^\dagger_{2\uparrow} a^\dagger_{2\downarrow} \, | \rangle \tag{6.21}$$

As we can see, there are two ways this can contract, each contributing with the constant factor, $-g/2$ Resulting in the final Hamiltonian matrix

$$\hat{\mathcal{H}} = \begin{pmatrix} 2\delta - g & -g/2 & -g/2 & -g/2 & -g/2 & 0 \\ -g/2 & 4\delta - g & -g/2 & -g/2 & 0 & -g/2 \\ -g/2 & -g/2 & 6\delta - g & 0 & -g/2 & -g/2 \\ -g/2 & -g/2 & 0 & 6\delta - g & -g/2 & -g/2 \\ -g/2 & 0 & -g/2 & -g/2 & 8\delta - g & -g/2 \\ 0 & -g/2 & -g/2 & -g/2 & -g/2 & 10\delta - g \end{pmatrix} \tag{6.22}$$

6.3 Diagrammatic Rules

One can visualize many-body quantum physics by using diagrams.

6.4 Many-Body Perturbation Theory

The Perturbation theory presents a non-iterative approach to approximating the ground state energy. The approach is similar to previous methods. We start by splitting the Hamiltonian into a solvable part and a perturbation.

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{6.23}$$

Where we have chosen our basis such that

$$\hat{H}_0 |\Psi_0\rangle = W_0 |\Psi_0\rangle \tag{6.24}$$

We split the basis aswell

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_i^{\infty} c_i |\phi_i\rangle \tag{6.25}$$

Assuming intermediate normalization

$$\langle\Phi_0|\Psi_0\rangle = 1 \tag{6.26}$$

We can calculate the total exact energy

$$E = \langle\Phi_0| \hat{H}_0 |\Psi_0\rangle + \langle\Phi_0| \hat{V} |\Psi_0\rangle \tag{6.27}$$

Where we know that

$$\langle\Phi_0| \hat{H}_0 |\Psi_0\rangle = W_0 \tag{6.28}$$

And we get the corrolation energy

$$E - W_0 = \Delta E = \langle\Phi_0| \hat{V} |\Psi_0\rangle \tag{6.29}$$

We will usually aim to compute this energy when doing MBPT.

6.4.1 General derivation of Many Body Particle Theory equations

Looking at the equation

$$\hat{V}|\Psi_0\rangle = \hat{H}|\Psi_0\rangle + \hat{H}_0|\Psi_0\rangle \tag{6.30}$$

We reorganize and add the term $\omega|\Psi_0\rangle$ on both sides

$$\hat{V}|\Psi_0\rangle + \omega|\Psi_0\rangle - \hat{H}|\Psi_0\rangle = \omega|\Psi_0\rangle - \hat{H}_0|\Psi_0\rangle \tag{6.31}$$

Remembering that $\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle$, we get

$$|\Psi_0\rangle = \frac{\hat{V} + \omega - E}{\omega - \hat{H}_0}|\Psi_0\rangle \tag{6.32}$$

Before continuing, we introduce the operators $\hat{P}$ and $\hat{Q}$, such that

$$|\Psi_0\rangle = \hat{P}|\Psi_0\rangle + \hat{Q}|\Psi_0\rangle = |\Phi_0\rangle\langle\Phi_0|\Psi_0\rangle + \sum_i |\Phi_i\rangle\langle\Phi_i|\Psi_0\rangle \tag{6.33}$$

$$= |\Phi_0\rangle + \chi \tag{6.34}$$

Giving

$$|\Phi_0\rangle = \hat{P}|\Psi_0\rangle \qquad \chi = \hat{Q}|\Psi_0\rangle \tag{6.35}$$

Using $\hat{R}(\omega) = \frac{\hat{Q}}{(\omega - \hat{H}_0)}$ and multiplying both sides with $\hat{Q}$ from the left in equation (6.32) we attain

$$\hat{Q}|\Psi_0\rangle = \hat{R}(\omega)\left(\hat{V} + \omega - E\right)|\Psi_0\rangle \tag{6.36}$$

Using equations (6.33) and (6.35), we get

$$|\Psi_0\rangle = |\Phi_0\rangle + \hat{R}(\omega)\left(\hat{V} + \omega - E\right)|\Psi_0\rangle \tag{6.37}$$

This is an iterative scheme. We can substitute $|\Psi_0\rangle$ on the right hand side with the entire right hand side. This results in an infinite sum provided the series converges

$$|\Psi_0\rangle = \sum_0^\infty \left\{\hat{R}(\omega)(\hat{V} + \omega - E)\right\}^m |\Phi_0\rangle \tag{6.38}$$

The right hand side does include the energy, E, which must be computed using $E = W_0 + \Delta E$, and

$$\Delta E = \langle \Phi_0 | \hat{V} | \Psi_0 \rangle = \sum_0^{\infty} \langle \Phi_0 | \hat{V} \left[\hat{R}(\omega)(\hat{V} - E + \omega) \right]^m | \Phi_0 \rangle \tag{6.39}$$

6.4.2 Equations for Reileigh-Schrodinger Perturbation Theory

We can interpret ω different ways. I here present the Reileigh-Schrodinger Perturbation Theory which postulates that

$$\omega = W_0 \tag{6.40}$$

Such that

$$|\Psi_0\rangle = \frac{\hat{V} - \Delta E}{\omega - \hat{H}_0} |\Psi_0\rangle \tag{6.41}$$

and we get the final equations

$$|\Psi_0\rangle = \sum_0^{\infty} \left\{ \hat{R}(\omega)(\hat{V} + -\Delta E) \right\}^m |\Phi_0\rangle \tag{6.42}$$

and

$$\Delta E = \sum_0^{\infty} \langle \Phi_0 | \hat{V} \left[\hat{R}(\omega)(\hat{V} - \Delta E) \right]^m | \Phi_0 \rangle \tag{6.43}$$

Taking a closer look at the energy-equations, we find that we can write the first orders as

$$\begin{aligned}
E^{(1)} &= \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = V_{00} \\
E^{(2)} &= \langle \Phi_0 | \hat{V} \hat{R}_0 \hat{V} | \Phi_0 \rangle \\
E^{(3)} &= \langle \Phi_0 | \hat{V} \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} | \Phi_0 \rangle \\
E^{(4)} &= \langle \Phi_0 | \hat{V} \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} | \Phi_0 \rangle - E^{(2)} \langle \Phi_0 | \hat{V} \hat{R}_0^2 \hat{V} | \Phi_0 \rangle
\end{aligned}$$

Because of the frequent appearance, we can rewrite $\hat{V} - E^{(1)}$ as

$$\hat{\Omega} = \hat{V} - E^{(1)} \tag{6.44}$$

We name this new variable the wave operator

6.4.3 Canonical Hartree-Fock

In the pairing model, we work with the Normal-ordered Hamiltonian

$$\hat{H}_N = \hat{F}_N^d + \hat{F}_N^0 + \hat{W} \tag{6.45}$$

Which is part of the total Hamiltonian by

$$\hat{H} = \hat{H}_N + E_{\text{ref}} \tag{6.46}$$

Where

$$\hat{H}_N |\Psi\rangle = \Delta E |\Psi\rangle \tag{6.47}$$

If we use a Canonical Hartree-Fock basis, the Fock matrix will be diagonal, meaning

$$\hat{F}_N^o = 0 \quad \text{and} \quad f_{pq} = \epsilon_p \delta_{pq} \tag{6.48}$$

A noncanonical Hartree-Fock will be block diagonal with

$$f_{ia} = \langle i| \hat{f} |a\rangle = 0 \tag{6.49}$$

6.4.4 Hartree-Fock calculations

When doing Hartree-Fock calculation, we do a change of basis and instead of expanding our Hamiltonian, we vary the wavefunction to minimize the energy. We name the original basis by greek letters and the new basis by latin letters. The original basis should be chosen such that we can calculate the its expectation value.

$$\langle \Phi_0| \hat{H} |\Phi_0\rangle = E^{\text{HF}} \tag{6.50}$$

Variational principle ensures that

$$E^{\text{HF}} > 0 \tag{6.51}$$

We now introduce a change of basis

$$|\psi_a\rangle = \sum_\lambda C_{a\lambda} |\psi_\lambda\rangle \tag{6.52}$$

Varying $C_{p\lambda}$, we can look for the basis providing the lowest energy. We start by rewriting E^{HF} as a functional

$$E\left[\psi\right] = \sum_{a=1}^{N} \langle a| h |a\rangle + \frac{1}{2}\sum_{ab}^{N} \langle ab| v |ab\rangle \tag{6.53}$$

In terms of the original greek basis

$$E\left[\psi\right] = \sum_{a=1}^{N}\sum_{\alpha\beta} C^*_{a\alpha}C_{a\beta} \langle \alpha| h |\beta\rangle + \frac{1}{2}\sum_{ab}^{N}\sum_{\alpha\beta\gamma\delta} C^*_{a\alpha}C^*_{b\beta}C_{a\gamma}C_{b\delta} \langle \alpha\beta| v |\gamma\delta\rangle \tag{6.54}$$

To find the minima, we introduce a Lagrange multiplier before differentiating with respect to $C^*_{a\alpha}$. This will give N equations, one for each state, a. The equations are given by

$$\sum_{\beta} C_{a\beta} \langle \alpha| h |\beta\rangle + \sum_{b}^{N}\sum_{\beta\gamma\delta} C^*_{b\beta}C_{b\delta}C_{a\gamma} \langle \alpha\beta| v |\gamma\delta\rangle = \epsilon_a C_{a\alpha} \tag{6.55}$$

Defining

$$h^{\mathrm{HF}}_{\alpha\gamma} = \langle \alpha| h |\gamma\rangle + \sum_{b=1}^{N}\sum_{\beta\delta} C^*_{b\beta}C_{b\delta} \langle \alpha\beta| v |\gamma\delta\rangle \tag{6.56}$$

We get the short hand iterative equations to be solved

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{a\gamma} = \epsilon_a C_{a\alpha} \tag{6.57}$$

6.4.5 RSPT to for Pairing model

Given that our Hartree-Fock basis is canonical, $\hat{F}^0_N = 0$, and $f_{pq} = \epsilon_p\delta_{pq}$, we can

Chapter 7

Infinite Matter

A study of infinite matter is the most comprehensible way of studying nuclear material. This thesis will study the infinite electron gas before the final study of nuclear material. This is done because of pedagogical reasons and because the electron gas has closed form solutions that provide important benchmarking for the code.

7.1 The Infinate Electron Gas

The infinite electron gas gives a good approximation to valence electrons in metal. The gas consist only of interacting electrons with a uniform background of charged ions. The whole system is charge neutral. We assume a cubic box, length L and volume $\Omega = L^3$, with N_e as the number of electrons with a charge density $\rho = N_e/\Omega$.

We regard the system as homogenic, using the free particle normalized wave function

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{kr}} \xi_\sigma \tag{7.1}$$

Where $\mathbf{k}$ is the wave number and ξ_σ is a spin function.

$$\xi_{+\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \xi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{7.2}$$

Assuming periodic boundary conditions, we acquire the following wave numbers

$$k_i = \frac{2\pi n_i}{L} \quad i = x, y, z \quad n_i = 0, \pm 1, \pm 2, ... \tag{7.3}$$

The electrons interact with the sentral symmetric Colomb potential, $\hat{V}(\mathbf{r}_1, \mathbf{r}_2)$ depending only on the distance $|\mathbf{r}_1 - \mathbf{r}_2|$.

The Hamiltonian for infinite electron gas is

$$\hat{H} = \hat{T} + \hat{V} \tag{7.4}$$

Where we have the kinetic energy, $\hat{T}$ as

$$\hat{T} = \sum_{p} \frac{\hbar^2 k^2}{2m} a^{\dagger}_{k\sigma} a_{k\sigma} \tag{7.5}$$

7.2 Infinite Nuclear Matter

Central to my thesis, is the study of infinite nuclear matter. I look at baryonic matter similar to the dense baryonic matter found in neutron stars. I limit the study to temperatures far below Fermi level. The matter is mostly made up of an equilibrium of baryons and leptons. In neutron star matter, we assume the equilibrium consist of protons, neutrons, electrons and muons with densities larger than 0.1fm^-3. The equilibrium conditions are specified by weak interactions

$$b_1 \rightarrow b_2 + l + \bar{\nu}_l \qquad b_2 + l \rightarrow b_1 + \nu_l \tag{7.6}$$

Where b represent either neutron or proton and $l$is either an electron or muon. ν_l is the corresponding neutrino.

Nuclear matter is a hypothetical system filling all of space at a uniform density. Symmetric nuclear matter (SNM) consist of equal numbers of protons of neutrons, while pure nuclear matter (PNM) consist only of neutrons. For finite-nucleus systems, the most difficult part is calculating the single particle wave function. For nuclear matter we can use plane wave basis and similar to electron gas, the difficult part is calculating the energy and the effective interaction between particles [8]. In my calculations, I have looked at pure nuclear matter.

7.3 Nuclear Interaction

Nuclear matter is composed of baryons, which interacts through the strong force.

7.3.1 The Minnesota Potential

The Minnesota Potential is given as

$$v(r) = (v_R + (1 + P^{\sigma}_{12})v_T/2 + (1 - P^{\sigma}_{12})v_S/2) \tag{7.7}$$

$$\cdot \left(\alpha + (2-\alpha)P^{r}_{12}\right)/2 + (1 + m_{t,1})(1 + m_{t,2})\frac{e^2}{4r} \tag{7.8}$$

where r is given as $|\mathbf{r_1} - \mathbf{r_2}|$ and m_t is the isospin projection of particle 1 or 2. $m_t = \pm 1$. P_{12}^{σ} and P_{12}^{r} are exchange operators for spin and position, respectively [1]. Furthermore, we have used

$$v_R = v_{0R} e^{-k_R r^2}, \quad v_T = -v_{0T} e^{-k_T r^2}, \quad v_S = -v_{0S} e^{-k_s r^2} \tag{7.9}$$

Where the constants v_{0R}, v_{0T}, v_{0S}, k_R, k_T and k_S are given by [9]

1. $v_{0R} = 200\text{MeV}$, $k_R = 0.1487\text{fm}^{-2}$
2. $v_{0T} = 178\text{MeV}$, $k_T = 0.649\text{fm}^{-2}$
3. $v_{0S} = 91.85\text{MeV}$, $k_S = 0.465\text{fm}^{-2}$

Written by second quantisation, we want to calculate the two-body interaction

$$\langle k_p k_q | v | k_r k_s \rangle = \frac{V_0}{L^3} \left(\frac{\pi}{\alpha} \right)^{3/2} e^{-q^2/4\alpha} \delta_{\mathbf{k}_p + \mathbf{k}_q, \mathbf{k}_r + \mathbf{k}_s} \tag{7.10}$$

Where q is the relative momentum transfer

$$\mathbf{q} = \mathbf{p} - \mathbf{p}' \tag{7.11}$$

$$\mathbf{p} = \frac{1}{2}(\mathbf{k}_p - \mathbf{k}_q) \quad \mathbf{p}' = \frac{1}{2}(\mathbf{k}_r - \mathbf{k}_s) \tag{7.12}$$

We can now set up the two-body Matrix-elements for the Minnesota Potential

$$\langle \mathbf{k}_p \mathbf{k}_q | v | \mathbf{k}_r \mathbf{k}_s \rangle = \langle \mathbf{k}_p \mathbf{k}_q | \frac{1}{2} \left(V_R + \frac{1}{2} V_T + \frac{1}{2} V_S \right) | \mathbf{k}_r \mathbf{k}_s \rangle \tag{7.13}$$

$$+ \langle \mathbf{k}_p \mathbf{k}_q | \frac{1}{4} (V_T - V_S) P_{12}^{\sigma} | \mathbf{k}_r \mathbf{k}_s \rangle \tag{7.14}$$

$$- \langle \mathbf{k}_p \mathbf{k}_q | \frac{1}{2} \left(V_R + \frac{1}{2} V_T + \frac{1}{2} V_S \right) P_{12}^{\sigma} P_{12}^{\tau} | \mathbf{k}_r \mathbf{k}_s \rangle \tag{7.15}$$

$$- \langle \mathbf{k}_p \mathbf{k}_q | \frac{1}{4} (V_T - V_S) P_{12}^{\tau} | \mathbf{k}_r \mathbf{k}_s \rangle \tag{7.16}$$

Matrix elements for the spin and isospin exchange operators are

$$\langle \sigma_p \sigma_q | P_{12}^{\sigma} | \sigma_r \sigma_s \rangle = \delta_{\sigma_p, \sigma_s} \delta_{\sigma_q, \sigma_r} \tag{7.17}$$

One can see that these matrix elements come at a far greater computational cost than for electron-electron interaction in the electron gas. Therefore it is necessary to compute and store all elements instead of computing them "on the fly". Source: Lecture 1-2 infinite matter.

Chapter 8

Implementation

In this thesis I have created three different solvers for Coupled Cluster Doubles equations.

1. A naive brute force implementation of the equations summing over all variables.

2. A naive brute force implementation of intermediate equations summing over all variables.

3. Rewriting summations as matrix-matrix multiplications and exploiting various symmetry arguments one can set up a block implementation.

There is a significant performance leap between each method, but I have included the first two solvers for both educational and benchmarking purposes. The Pairing model with 4 particles and 4 holes is a small system that one can easily solve using the naive approach. After producing expected results with the naive solver, I have compared the more complicated solvers to the naive solver for all systems.

8.1 Implementing the CCD equations

The basic steps of all implemented CCD algorithms can be explained through these steps

1. Initialize amplitudes $t^{(0)} = 0$and $\Delta E^{(0)}_{CCD} = 0$

2. Update the amplitudes and calculate $\Delta E^{(1)}_{CCD}$

3. If $|\Delta E^{(1)}_{CCD} - \Delta E^{(0)}_{CCD}| \geq \epsilon$, update amplitudes and compute ΔE^{2}_{CCD}

4. Repeat until $|\Delta E^{(n+1)}_{CCD} - \Delta E^{(n)}_{CCD}| \leq \epsilon$

The difference between the three solvers I have implemented is the way I update amplitudes. The naive brute force solver loops over all indices when computing. An example of diagram L_a is shown below

```
for i in 0, ..., Nholes:
  for j in 0, ..., Nholes:
    for a in Nholes, ..., Nparticles:
      for b in Nholes, ..., Nparticles:
        for c in Nholes, ..., Nparticles:
          for d in Nholes, ..., Nparticles:
            tnew(a,b,i,j) = 0.5  v(a,b,c,d)  told(c,d,i,j)
```

A significant cost reduction can be obtained by factorizing the diagrams as shown in equation (5.43). By calculating the four intermediate diagrams, I_1, I_2, I_3 and I_4 beforehand and storing the results reduce the cost of calculation from $\mathcal{O}(h^4p^4)$ to $\mathcal{O}(h^4p^2)$. The second solver applies this method.

8.2 Matrix Representation of Contractions

Diagrams can be viewed as contractions of tensors of varying degree. An example is the matrix-matrix multiplication product

$$(MN)^{\alpha}_{\gamma} = \sum_{\beta} M^{\alpha}_{\beta} N^{\beta}_{\gamma} \tag{8.1}$$

As our goal is to rewrite the Coupled Cluster equations as matrix-matrix products. We will need to map tensors of rank ≥ 2 onto matrices. One mapping that provides systematic and unique matrix elements can be

$$\langle pq|\hat{v}|rs\rangle = V_{\alpha(p,q),\beta(r,s)} \tag{8.2}$$

Where

$$\alpha(p,q) = p + qN_p \quad \beta(r,s) = r + sN_r \tag{8.3}$$

We need to be careful when mapping tensors this way. Consider first the calculation of the perfectly aligned L_a term

$$L_a = \sum_{cd} \langle ab|\hat{v}|cd\rangle \, t^{cd}_{ij} \tag{8.4}$$

Mapping this equation using equation (8.3)

$$\langle ab|\hat{v}|cd\rangle = v^{cd}_{ab} \rightarrow V^{\alpha(a,b)}_{\beta(c,d)} \tag{8.5}$$

and

$$t_{ij}^{cd} \rightarrow T_{\delta(i,j)}^{\beta(c,d)} \tag{8.6}$$

As we are mapping to unique elements

$$\beta(c, d) = \beta(c, d) \tag{8.7}$$

We can now rewrite the equation

$$(L_a)_\delta^\alpha = \sum_\beta V_\beta^\alpha T_\delta^\beta \tag{8.8}$$

Implying by regarding equation (8.1) that we can rewrite the product as matrix-matrix multiplication

$$L_a = VT \tag{8.9}$$

8.2.1 Aligning elements

Unfortunately, not all product are perfectly aligned like L_a. Consider, for example, the term, L_c

$$L_c = -P\left(ij|ab\right) \sum_{kc} \langle kb|\hat{v}|cj\rangle\, t_{ik}^{ac} \tag{8.10}$$

Using the same mapping scheme

$$\langle kb|\hat{v}|cj\rangle = v_{cj}^{kb} \rightarrow V_{\beta(cj)}^{\alpha(kb)} \tag{8.11}$$

and

$$t_{ik}^{ac} \rightarrow T_{\delta(ik)}^{\gamma(ac)} \tag{8.12}$$

This matrix multiplication is misaligned, and if the number of particles is unequal to the number of holes, the matrices' size will uncompatible.

$$(L_c)_\delta^\alpha \neq -P\left(ij|ab\right) \sum_\beta V_{\beta(cj)}^{\alpha(kb)} T_{\delta(ik)}^{\gamma(ac)} \tag{8.13}$$

We need to find another mapping, such that

$$v_{cj}^{kb} \rightarrow \tilde{V}_{\beta(ck)}^{\alpha(bj)} \tag{8.14}$$

and

$$t_{ik}^{ac} \rightarrow \tilde{T}_{\delta(ia)}^{\gamma(ck)} \tag{8.15}$$

Now, the matrix multiplication is aligned

$$(\tilde{L}_c)_{\delta}^{\alpha} = -P\left(ij|ab\right) \sum_{\beta} \tilde{V}_{\beta(ck)}^{\alpha(bj)} \tilde{T}_{\delta(ia)}^{\gamma(ck)} \tag{8.16}$$

Note, however, that

$$L_c \neq \tilde{L}_c \tag{8.17}$$

We must "realign" $\tilde{L}_c$ to match the correct diagram

$$(\tilde{L}_c)_{\delta(i,a)}^{\alpha(b,j)} \rightarrow (L_c)_{\delta(i,k)}^{\alpha(k,b)} \tag{8.18}$$

Another example is the Qc term

$$Q_c = -\frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle kl|v|cd\rangle\, t_{ik}^{ab} t_{jl}^{cd} \tag{8.19}$$

We can rewrite this as a matrix-matrix multiplication with the matrix elements given by

$$\langle kl|v|cd\rangle = v_{cd}^{kl} \rightarrow V_{\beta(kl)}^{\alpha(cd)} \tag{8.20}$$

$$t_{ik}^{ab} \rightarrow (T_1)_{\gamma(ik)}^{\delta(ab)} \tag{8.21}$$

$$t_{jl}^{cd} \rightarrow (T_2)_{\omega(jl)}^{\eta(cd)} \tag{8.22}$$

Because we sum over the coefficients $klcd$, we must make sure that they belong to the "inner" indexes. This can only be done by creating a hole, particle-particle-hole configuration. We must also change the order of multiplication

$$V_{\beta(kl)}^{\alpha(cd)} \rightarrow \tilde{V}_{\gamma(cdl)}^{\delta(k)} \tag{8.23}$$

$$(T_1)_{\gamma(ik)}^{\delta(ab)} \rightarrow \tilde{(}T_1)_{\delta(k)}^{\alpha(abi)} \tag{8.24}$$

$$(T_2)_{\omega(jl)}^{\eta(cd)} \rightarrow \tilde{(}T_2)_{\beta(j)}^{\gamma(cdl)} \tag{8.25}$$

This gives us

$$(\tilde{Q}_c)_{\beta(j)}^{\alpha(abi)} = -\frac{1}{2}\hat{P}(ij) \sum_{klcd} (\tilde{T}_1)_{\delta(k)}^{\alpha(abi)} \tilde{V}_{\gamma(cdl)}^{\delta(k)} (\tilde{T}_2)_{\beta(j)}^{\gamma(cdl)} \tag{8.26}$$

Which must be realigned back to the properly aligned Q_c before it can be added to the amplitude equations.

$$(\tilde{Q}_c)^{\alpha(abi)}_{\beta(j)} \rightarrow (Q_c)^{\alpha(ab)}_{\beta(ij)} \tag{8.27}$$

We will need a general mapping function that can be used regardless of the amount of states used. It turns out that we can use the same mapping as before, just generalized to N states.

$$\alpha(p_1, p_2, p_3, ..., p_N) = p_1 + p_2 N_1 + p_3 N_1 N_2 + ... + p_N N_1 N_2 ... N_{N-1} \tag{8.28}$$

Where N_n determines the maximum number of states for p_n. If for example $p_n \in i$, i.e. p_n is a hole-state, $N_n = N_{holes}$.

Writing the diagrams as matrix-matrix multiplications serves as a significant reduction of computational time, due to the efficient algortithms in the BLAS-packages for matrix-matrix multiplications. However, since one has to save all the matrices, memory usage will be a problem for large basises.

8.3 Block Implementation

One can both greatly reducing memory usage and improve computational speed by exploiting symmetries for infinite matter . Due to kroenecker delta's in the interaction, one such symmetry is the conservation of momentum

$$\delta_{\mathbf{k}_p+\mathbf{k}_q,\mathbf{k}_r+\mathbf{k}_s} \rightarrow \mathbf{k}_p + \mathbf{k}_q = \mathbf{k}_r + \mathbf{k}_s \tag{8.29}$$

We also conserve spin

$$m_{s_p} + m_{s_q} = m_{s_r} + m_{s_s} \tag{8.30}$$

and for nuclear matter, we will conserve isospin aswell

$$m_{t_p} + m_{t_q} = m_{t_r} + m_{t_s} \tag{8.31}$$

The amplitudes will be subject to the same restrictions, vizualised by the first order amplitude generated by perturbation theory

$$(t_{ij}^{ab})^{t=0} = \frac{\langle ab|\hat{v}|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{8.32}$$

Looking at the L_a term

$$L_a = \sum_{cd} \langle ab|\hat{v}|cd\rangle\, t_{ij}^{ab} \tag{8.33}$$

We see that

$$\mathbf{k}_a + \mathbf{k}_b = \mathbf{k}_c + \mathbf{k}_d = \mathbf{k}_i + \mathbf{k}_j \tag{8.34}$$

And the same for spin

$$m_{s_a} + m_{s_b} = m_{s_c} + m_{s_d} = m_{s_i} + m_{s_j} \tag{8.35}$$

When summing over all variations of contractions, only the quantum numbers preserving the symmetry requirements are nonzero. When storing the interactions in a matrix, most of it will have zero-elements. The blocking method will store the nonzero parts in blocks inside the matrix. By keeping track of the blocks, we can reduce the full matrix-matrix multiplication to a series of multiplications of the blocks. We will hereby refer to the series of blocks as *channels*.

8.3.1 Two-state configurations

As we can see from the L_a diagram, the conservation laws apply for a combination of two states. The next step is then to set up all two-state configurations that will be needed. We start by setting up the direct two-state channels, T, which consist of all two-hole and two-particle configurations. A unique identifier must be set up for the combination of quantum numbers. The identifier is used to aligning the non-zero combinations of two-body states to the same channel. Without this identifier, we will have to loop over all channels for each two-body state. I have used the following function

$$\begin{aligned} \text{Index}(N_x, N_y, N_z, S_z, T_z) =& 2(N_x + m)M^3 + 2(N_y + m)M^2 + \qquad (8.36) \\ & 2(N_z + m)M + 2(S_z + 1) + (T_z + 1) \qquad (8.37) \end{aligned}$$

Using the same logic as in equation (8.3) to get a unique identifier for every combination of N_x, N_y, N_z, S_z and T_z. Which imply that the two-body states have the same momentum, spin and isospin projection, which satisfies our conservation laws. We need m and M to be sufficiently large. I have used

$$m = 2\lfloor\sqrt{N_{\max}}\rfloor \qquad M = 2m + 1 \tag{8.38}$$

Because of the Pauli-exclusion, two particles cannot occupy the same state, so we can further reduce the amount of two-body states by excluding equal one-body states from the channels. An algorithm for setting up the direct channels can be portraied as

for one-body state 1 $\in$ STATES :
  for one-body state 2 $\in$ STATES :
    if one-body state 1 $\neq$ one-body state 2 :
      $N_x = n_{x,1} + n_{x,2}$
      $N_y = n_{y,1} + n_{y,2}$
      $N_z = n_{z,1} + n_{z,2}$
      $S_z = m_{s,1} + m_{s,2}$
      $T_z = m_{t,1} + m_{t,2}$
      $\mathrm{Id} = \mathrm{Index}(N_x, N_y, N_z, S_z, T_z)$
      $T \leftarrow (\text{ one-body state 1, one-body state 2, Id})$

8.3.2 Unaligned channels

Diagram L_a, L_b and Q_a have conservation requirements as shown previously for L_a

$$\mathbf{k}_a + \mathbf{k}_b = \mathbf{k}_c + \mathbf{k}_d = \mathbf{k}_i + \mathbf{k}_j \tag{8.39}$$

Which are implemented using the direct channels. We will however run into some trouble when computing the unaligned diagrams L_c, Q_b, Q_c and Q_d. The L_c diagram is given by

$$L_c = -\hat{P}(ij|ab) \sum_{kc} \langle kb|\hat{v}|cj\rangle \, t_{ik}^{ac} \tag{8.40}$$

Looking at the conservation requirement for L_c

$$\mathbf{k}_k + \mathbf{k}_b = \mathbf{k}_c + \mathbf{k}_j = \mathbf{k}_a + \mathbf{k}_c = \mathbf{k}_i + \mathbf{k}_k \tag{8.41}$$

and

$$m_{s,k} + m_{s,b} = m_{s,c} + m_{s,j} \qquad m_{t,k} + m_{t,b} = m_{t,c} + m_{t,j} \tag{8.42}$$

When realigning the equation, we want it to be

$$\tilde{L}c = -\hat{P}(ij|ab) \sum_{kc} \langle bj|\tilde{v}|ck\rangle \, \langle ck|\, \tilde{t}\, |ai\rangle \tag{8.43}$$

We reorganize the conservation requirements as well to make sure we only calculate the non-zero terms

$$\mathbf{k}_b - \mathbf{k}_j = \mathbf{k}_c - \mathbf{k}_k = \mathbf{k}_c - \mathbf{k}_k = \mathbf{k}_i - \mathbf{k}_a \tag{8.44}$$

Spin and isospin will be subject to the same reorganizing. We see that the direct channels do not represent the right conservation requirement and we must set up the cross channels, X, that consist of particle-hole or hole-particle two-body configurations. An algorithm can be set up as

$$
\begin{aligned}
&\textbf{for} \text{ one-body state } 1 \in \text{STATES} :\\
&\;\textbf{for} \text{ one-body state } 2 \in \text{STATES} :\\
&\;\;\textbf{if} \text{ one-body state } 1 \neq \text{ one-body state } 2 :\\
&\;\;\; N_x = n_{x,1} - n_{x,2}\\
&\;\;\; N_y = n_{y,1} - n_{y,2}\\
&\;\;\; N_z = n_{z,1} - n_{z,2}\\
&\;\;\; S_z = m_{s,1} - m_{s,2}\\
&\;\;\; T_z = m_{t,1} - m_{t,2}\\
&\;\;\; \text{Id} = \text{Index}(N_x, N_y, N_z, S_z, T_z)\\
&\;\;\; X \leftarrow (\text{ one-body state 1, one-body state 2, Id})\\
&\;\;\; \text{Id}' = \text{Index}(-N_x, -N_y, -N_z, -S_z, -T_z)\\
&\;\;\; X' \leftarrow (\text{ one-body state 2, one-body state 1, Id'})
\end{aligned}
$$

Where X' is the cross channel compliment, $X(pq) = X'(qp)$. The coss-channels are used for calculating Q_b and L_c.

Looking at the diagram Q_c

$$Q_c = -\frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd\rangle\, t_{ik}^{ab} t_{jl}^{cd} \tag{8.45}$$

With the momentum conservation requirement

$$\mathbf{k}_k + \mathbf{k}_l = \mathbf{k}_c \mathbf{k}_d = \mathbf{k}_i + \mathbf{k}_k = \mathbf{k}_a + \mathbf{k}_b = \mathbf{k}_j + \mathbf{k}_l = \mathbf{k}_c + \mathbf{k}_d \tag{8.46}$$

We see that we must realign the diagram as

$$\tilde{Q}_c = -\frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle abi|\, \tilde{t}\, |k\rangle \langle k|\, \tilde{v}\, |cdl\rangle \langle cdl|\, \tilde{t}\, |j\rangle \tag{8.47}$$

Which set the conservation requirement as

$$\mathbf{k}_a + \mathbf{k}_b - \mathbf{k}_i = \mathbf{k}_k = \mathbf{k}_k = \mathbf{k}_c + \mathbf{k}_d - \mathbf{k}_l = \mathbf{k}_c + \mathbf{k}_d - \mathbf{k}_l = \mathbf{k}_j \tag{8.48}$$

We set up three-body and corresponding one-body channels to calculate Q_c and Q_d. An example algorithm for the K_h and $K_{p,p,h}$ channels can be outlined as

for one-body state 1 $\in$ HOLES :
$N_x = n_{x,1}$
$N_y = n_{y,1}$
$N_z = n_{z,1}$
$S_z = m_{s,1}$
$T_z = m_{t,1}$
$\mathrm{Id} = \mathrm{Index}(N_x, N_y, N_z, S_z, T_z)$
$K_h \leftarrow$ (one-body state 1, Id)

for one-body state 1 $\in$ PARTICLES :
for one-body state 2 $\in$ PARTICLES :
for one-body state 3 $\in$ HOLES :
if one-body state 1 $\neq$ one-body state 2 :
$N_x = n_{x,1} + n_{x,2} - n_{x,3}$
$N_y = n_{y,1} + n_{y,2} - n_{y,3}$
$N_z = n_{z,1} + n_{z,2} - n_{z,3}$
$S_z = m_{s,1} + m_{s,2} - n_{s,3}$
$T_z = m_{t,1} + m_{t,2} - n_{t,3}$
$\mathrm{Id} = \mathrm{Index}(N_x, N_y, N_z, S_z, T_z)$
$K_{p,p,h} \leftarrow$ (one-body state 1, one-body state 2, one-body state 3, Id)

8.3.3 Permutations

Some diagrams come with permutations. These are easy to handle by simply interchanging indexes when adding the diagram to $t^{(n+1)}$.

for i $\in$ Holes :
 for j $\in$ Holes :
  for a $\in$ Particles :
   for b $\in$ Particles :

$$t^{(n+1)}(a,b,i,j) = t^{(n+1)} - \frac{1}{2}\left(Q_c(a,b,i,j) - Q_c(a,b,j,i)\right)$$

8.4 Setting Up Basis

Before doing coupled cluster calculations, the basis must be set up. An important property of this basis, is the occupied and virtual states. For infinite nuclear matter, the following algorithm can be used to set up the states. This algorithm should reproduce the magic numbers presented.

for shell $\in$ All Shells :
 for $n_x, n_y, n_z \in [-\text{shell}, \text{shell}]$:
  $n = n_x^2 + n_y^2 + n_z^2$
  if $n =$ shell :
   for $m_s \in \{-1, 1\}$
    for $m_t \in \{-1, 1\}$
     States $\leftarrow (e, n_x, n_y, n_z, m_s, m_t)$
     $N_s = N_s + 1$
     if shell $<$ Fermi level :
      $N_h = N_h + 1$

8.5 Parallellization

An important part of optimizing the code, is by setting up a parallell code. By doing this, we can fully utilize the capacity of computers with many processing cores. I have, in this project, used the Super Computer Smaug located at Institute of Physics at the University of Oslo.

Chapter 9

Results

9.1 The Pairing Model

The Pairing Model serve as a valuable benchmark for implemented solvers. As I have looked at a 4p4h configuration, a full configuration interaction solver can be implemented giving the exact solution. One can also calculate the exact solution for second order perturbation theory by hand [6].

$$\Delta E_{MBPT2} = \frac{1}{4}\sum_{abij} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{\epsilon_{ij}^{ab}} = \sum_{a<b,i<j} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{\epsilon_{ij}^{ab}} \tag{9.1}$$

Where

$$\epsilon_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \tag{9.2}$$

and

$$\epsilon_p = h_{pp} + \sum_i \langle pi||pi\rangle \tag{9.3}$$

This results in

$$\Delta E_{MBPT2} = \frac{\langle 01||45\rangle^2}{\epsilon_{01}^{45}} + \frac{\langle 01||67\rangle^2}{\epsilon_{01}^{67}} + \frac{\langle 23||45\rangle^2}{\epsilon_{23}^{45}} \frac{\langle 23||67\rangle^2}{\epsilon_{23}^{67}} \tag{9.4}$$

$$\Delta E_{MBPT2} = -\frac{g^2}{4}\left(\frac{1}{4+g} + \frac{1}{6+g} + \frac{1}{2+g} + \frac{1}{4+g}\right) \tag{9.5}$$

Where g represents the interaction strength. The table below shows my results for various g's both using the exact mbpt2 calculations and my numerically computed results. All results can be accessed on github [10]

g	E_0	exact ΔE_{MBPT2}	ΔE_{MBPT2}
-1	3	-0.466667	-0.466667
-0.5	2.5	-0.0887446	-0.0887446
0	2	0	0
0.5	1.5	-0.0623932	-0.0623932
1	1	-0.219048	-0.219048

Table 9.1: A table showing corrolation energies for Pairing model with 4 particle-states and 4 hole-states.

g	ΔE_{MBPT2}	$\Delta E_{CCD}^{(1)}$
-1	-0.466667	-0.466667
-0.5	-0.0887446	-0.0887446
0	0	0
0.5	-0.0623932	-0.0623932
1	-0.219048	-0.219048

Table 9.2: A table comparing corrolation energies for Pairing model with 4 particle-states and 4 hole-states. This table show that CCD solver used with only a single iteration produces results exactly equal to mbpt2. This was done with the naive implementation of CCD equations

As one can see, the corrolation energies computed perfectly matches which both tells us that the basis set is set up correctly and that the MBPT2 solver is set up correctly. The results presented also match the results found in [6]

The second order perturbation theory is valuble for benchmarking my implementation of Coupled Cluster Doubles. By initializing the first set of amplitudes, t, as zero, I get

$$t_{ij}^{ab(0)} = 0 \tag{9.6}$$

$$t_{ij}^{ab(1)} = \frac{1}{4}\sum_{ijab} \frac{\langle ab||ij\rangle}{\epsilon_{ij}^{ab}} \tag{9.7}$$

Which is equal to second order pertubation theory.

9.1.1 Comparison of CCD solvers

In this thesis I have created three different solvers for Coupled Cluster Doubles equations.

g	ΔE_{CCD} Naive	ΔE_{CCD} Intermediates
0	x	x
-0.5	-0.0630564	-0.0630562
0	0	0
0.5	-0.0833621	-0.0833623
1	-0.369557	-0.369557

Table 9.3: A table comparing corrolation energies for Pairing model with 4 particle-states and 4 hole-states. This table compare results from Naive and Intermediate implementation of CCD equations. A relaxing factor of $w = 0.3$ has been used because of divergence around $g = -1$

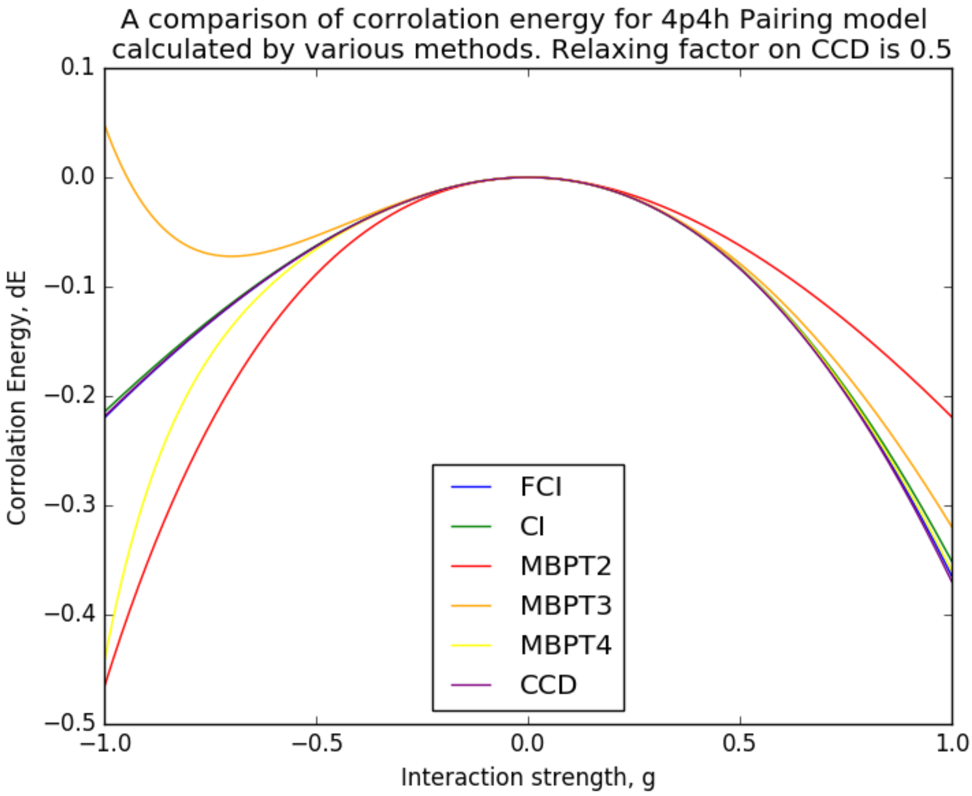
1. A naive brute force implementation of the equations summing over all variables.
2. A naive brute force implementation of intermediate equations summing over all variables.
3. Rewriting summations as matrix-matrix multiplications and exploiting various symmetry arguments one can set up a block implementation.

As shown in table (9.2), the naive implementation reproduces the mbpt2 energies as expected. I have used both the naive and intermediate CCD solver to compute corrolation energies for the Pairing model and again, [6] provides us with a good benchmark for the CCD equations.

As one can see, my solvers reproduce results presented in [6]. For values of g close to -1, one will see a divergence for CCD equations. By introducing a relaxing factor of $w = 0.3$, this problem was solved.

9.1.2 Comparison of various solvers

The full configuration interaction provides us with the exact solution for the 4p4h Pairing model. It can therefore be useful to compare the performance of Perturbation theory to second, third and fourth order with Coupled Cluster Doubles and configuration interaction without the four-particle excitation.



H

Figure 9.1: Comparing

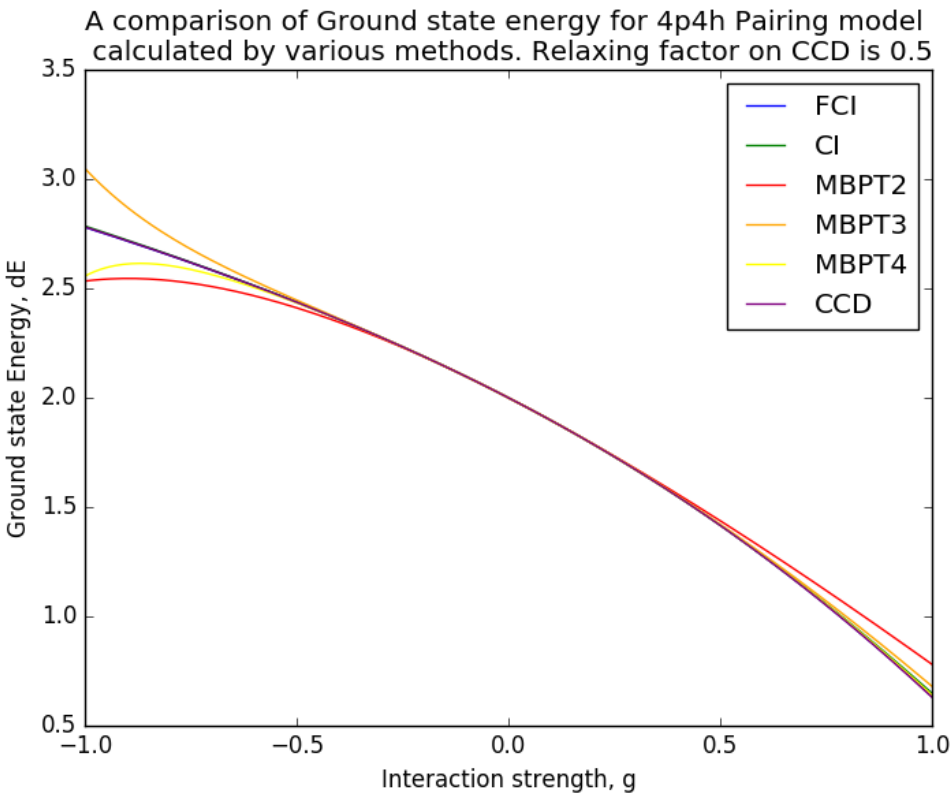

A comparison of Ground state energy for 4p4h Pairing model
calculated by various methods. Relaxing factor on CCD is 0.5
Ground state Energy, dE
Interaction strength, g
FCI
CI
MBPT2
MBPT3
MBPT4
CCD
3.5
3.0
2.5
2.0
1.5
1.0
0.5
−1.0
−0.5
0.0
0.5
1.0

Figure 9.2

Chapter 10

Appendix

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