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.

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

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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 anti-symmetry 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 Coulombic repulsion between two electrons and will only be an approximation to the true wavefunction, $|\Psi\rangle$.

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.

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

We can now write the Slater determinant as a chain of creation operators

$$\hat{a}_1^\dagger \hat{a}_2^\dagger ... \hat{a}_N^\dagger |0\rangle \tag{3.5}$$

Permutations of the operators introduces a sign-change, which is equivalent to interchanging rows in the determinant. This

$$\hat{a}_1^\dagger \hat{a}_2^\dagger |0\rangle = |\phi_1\phi_2\rangle = -|\phi_2\phi_1\rangle = -\hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle \tag{3.6}$$

So we can see that the second quantization respects the antisymmetrization condition. Thus, these operators follow the anti commutation relations

$$\{\hat{a}_i^\dagger \hat{a}_j\} = \delta_{ij} \quad \{\hat{a}_i^\dagger \hat{a}_j^\dagger\} = 0 \quad \{\hat{a}_i \hat{a}_j\} = 0 \tag{3.7}$$

Where δ_{ij} is the Kronecher delta.

3.2 Representation of Operators

3.3 Fermi Vacuum

3.4 Normal Ordering and Wick's Theorem

3.5 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 Clus-

ter, 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.

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.

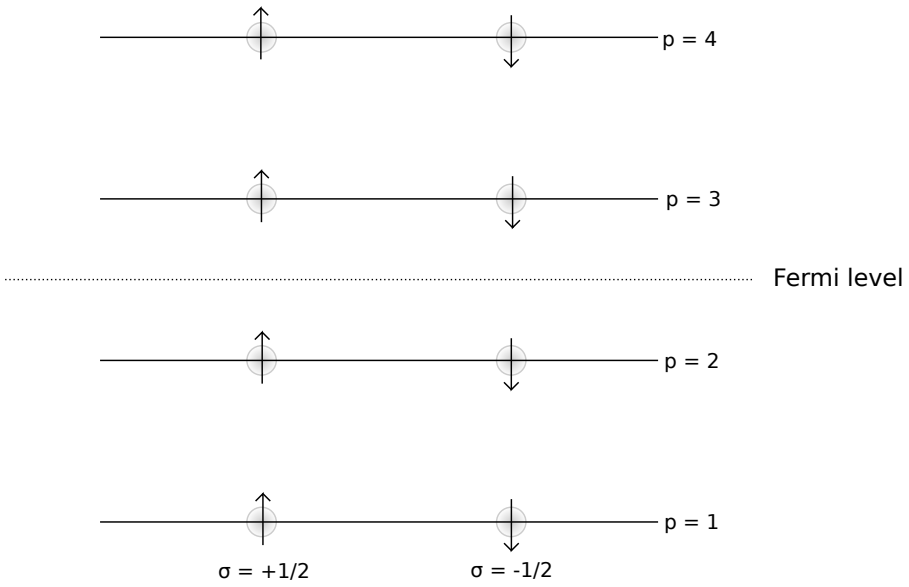

Figure 6.1: A figure depicting a 4 particles-4 holes state. The system consists of occupied particle states below the Fermi level and unoccupied hole states above Fermi level.

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.

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

$$a^\dagger_p a^\dagger_q a_s a_r = \left\{a^\dagger_p a^\dagger_q a_s a_r\right\} + \left\{a^\dagger_p a_r\right\} \delta_{qs\in i} - \left\{a^\dagger_p a_s\right\} \delta_{qr\in i} \tag{6.9}$$

$$+ \left\{a^\dagger_q a_s\right\} \delta_{pr\in i} \; - \left\{a^\dagger_q a_r\right\} \delta_{ps\in i} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i} \tag{6.10}$$

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.

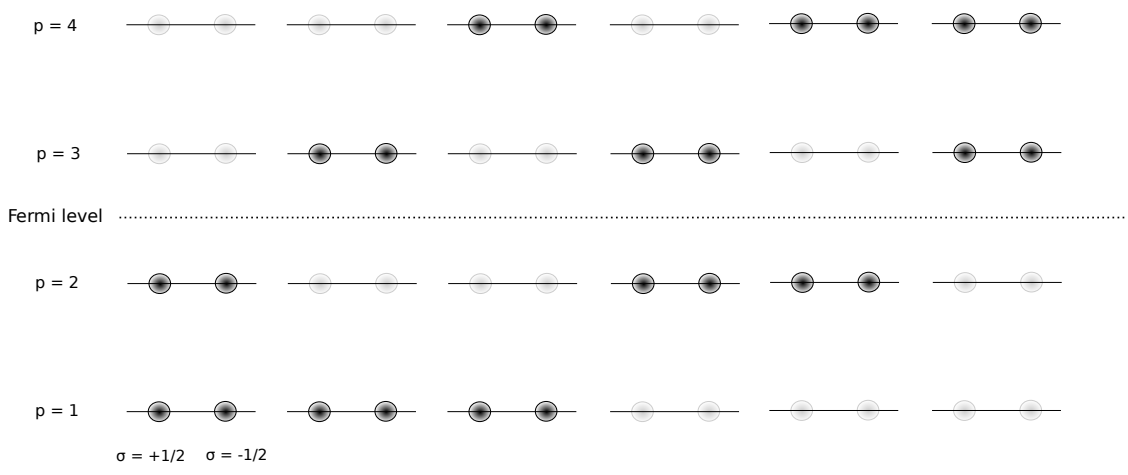

Figure 6.2: Configuration space for given pairing model showing all possible distributions of electrons

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

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

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

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

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

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

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

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

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

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

We split the basis aswell

$$\left|\Psi_0\right\rangle = \left|\Phi_0\right\rangle + \sum_{i}^{\infty} c_i \left|\phi_i\right\rangle \tag{6.25}$$

Assuming intermediate normalization

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

We can calculate the total exact energy

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

Where we know that

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

And we get the corrolation energy

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

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

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

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

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

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

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

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

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

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

Giving

$$\left|\Phi_0\right\rangle = \hat{P}\left|\Psi_0\right\rangle \quad \chi = \hat{Q}\left|\Psi_0\right\rangle \tag{6.35}$$

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

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

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

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

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

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

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

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

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

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

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.

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

Variational principle ensures that

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

We now introduce a change of basis

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

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

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

We get the short hand equations to be solved

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

6.4.5 RSPT to for Pairing model

Given that our Hartree-Fock basis is canonical, $\hat{F}_N^0 = 0$, 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

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

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, $hatT$ as

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

Chapter 8

Implementation

Chapter 9

Results

Chapter 10

Appendix