

UNIVERSITY OF OSLO

FYS4480 Oral Exam

Quantum mechanics for many-particle
systems

August Femtehjell

august.femtehjell@fys.uio.no

16th December, 2024



Introduction

Contents

- ① Introduction
- ② Full Configuration Interaction
- ③ Hartree-Fock
- ④ Many-Body Perturbation Theory
- ⑤ Coupled-Cluster Theory

Notation

Here, we follow the notation of having states $ijk \dots$ refer to occupied states, and $abc \dots$ refer to unoccupied states, typically below and above the Fermi level, respectively. From a reference state $|\Phi_0\rangle$ with N particles, we write a 1-particle-1-hole ($1p-1h$) excitation as

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle, \quad (1)$$

and similarly for $2p-2h$, $3p-3h$, etc.

We write a state Φ as a Slater determinant

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \gamma) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\beta(x_1) & \cdots & \psi_\gamma(x_1) \\ \psi_\alpha(x_2) & \psi_\beta(x_2) & \cdots & \psi_\gamma(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_\alpha(x_N) & \psi_\beta(x_N) & \cdots & \psi_\gamma(x_N) \end{vmatrix} \quad (2)$$

for a set of single-particle functions $\{\psi_\alpha\}$.

Motivation

We are, in essence, interested in finding the ground state energy of a many-body system, that is, solving the eigenvalue problem

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (3)$$

where \hat{H} is the Hamiltonian operator and $|\Psi_0\rangle$ is the ground state wave function, such that the ground state energy E_0 is minimized.

The complexity arises from the fact that the exact solution cannot typically be found for systems with more than a few particles, and we must resort to approximations.

The Pairing Model

As an illustration of the various methods, we consider the pairing model, defined by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} = \xi \sum_{p\sigma} (p-1) a_{p\sigma}^\dagger a_{p\sigma} - \frac{1}{2} g \sum_{pq} a_{p+}^\dagger a_{p-}^\dagger a_{q-} a_{q+}. \quad (4)$$

ξ denotes the spacing between the single-particle levels, and we set $\xi = 1$. \hat{V} only allows for pairing, with a constant strength g .

Slater Determinants for Pairing Model

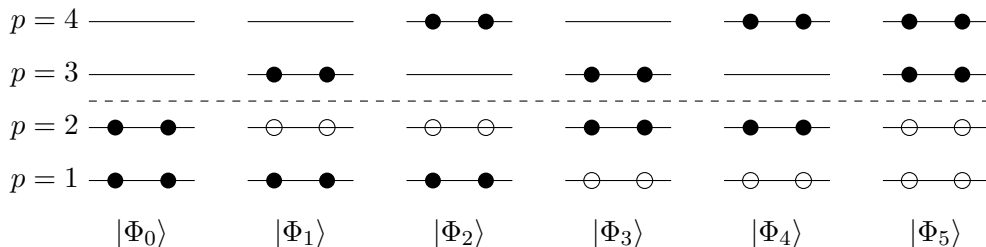


Figure 1: Schematic representation of the six possible Slater determinants for a system with four particles, under the constraint of no broken pairs, total spin $S = 0$, considering only the four lowest levels $p = 1, 2, 3, 4$.

Full Configuration Interaction

Contents

- ① Introduction
- ② Full Configuration Interaction
 - Configuration Interaction
- ③ Hartree-Fock
- ④ Many-Body Perturbation Theory
- ⑤ Coupled-Cluster Theory

Full Configuration Interaction Theory

In full configuration interaction (FCI) theory, we seek to write the wave function as a linear combination of all possible Slater determinants, that is, all possible configurations of the system, truncated at some level.

That is, we wish to write the wave function as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ia} C_i^a |\Phi_i^a\rangle + \sum_{ijab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots, \quad (5)$$

where the coefficients C are determined by solving the eigenvalue problem.

Solving the Problem

In solving the system, one first has to set up the Hamiltonian matrix, with elements

$$H_{i,j} = \langle \Phi_i | \hat{H} | \Phi_j \rangle, \quad (6)$$

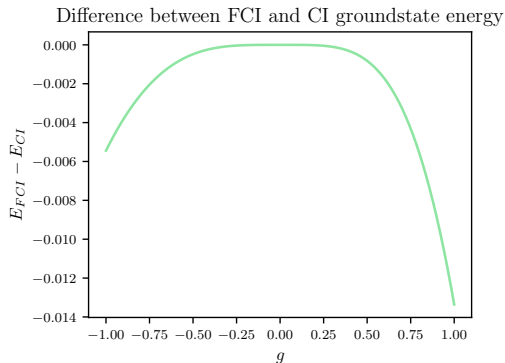
and then diagonalize the matrix to find the eigenvalues and eigenvectors. The ground state energy can then be found as the lowest eigenvalue, with the corresponding eigenvector giving the coefficients C .

FCI is exact, but computationally expensive, as the number of possible configurations grows factorially as $\binom{n}{N}$. Approximative methods are therefore required.

Configuration Interaction in the Pairing Model

A first approximative method is configuration interaction (CI) theory. Here, we limit the types of excitations included in Eq. (5) at some level. For example, in the pairing model, we can limit the excitations to $2p-2h$ excitations, that is, we include all configurations except $|\Phi_5\rangle$ in Fig. 1.

CI has the benefit of being a variational method, but the number of configurations can still grow rapidly.



Hartree-Fock

Contents

- ① Introduction
- ② Full Configuration Interaction
- ③ Hartree-Fock
- ④ Many-Body Perturbation Theory
- ⑤ Coupled-Cluster Theory

Hartree-Fock Theory

In Hartree-Fock (HF) theory, we assume that the system can be approximated by a single Slater determinant Φ , and we seek to find the wavefunctions $|\psi_\alpha\rangle$ that minimize the energy

$$E_0 = \langle \Phi | \hat{H} | \Phi \rangle. \quad (7)$$

This gives rise to the HF equations

$$\hat{h}^{\text{HF}} |\psi_\alpha\rangle = \varepsilon_\alpha |\psi_\alpha\rangle, \quad (8)$$

where $\hat{h}^{\text{HF}} = \hat{t} + \hat{u}_{\text{ext}} + \hat{u}^{\text{HF}}$, called the Fock operator, is an effective one-body operator. Here, \hat{u}^{HF} is the mean potential from the other particles, of the form

$$\langle p | \hat{u}^{\text{HF}} | q \rangle = \sum_i \langle pi | V | qi \rangle_{AS}. \quad (9)$$

Varying the Wave Functions

As Eq. (9) depends on the eigenfunctions, Eq. (8) is nonlinear. We can therefore solve it iteratively, until convergence is reached¹. Varying the wave functions directly lead to a set of coupled integro-differential equations, wherein the integrals need to be computed at each iteration.

Another, more computationally efficient approach, is to expand the wave functions in a basis of known functions, and vary the coefficients of the expansion. We do this by a unitary transformation to a new basis p ,

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \quad (10)$$

where we now vary the coefficients $C_{p\alpha}$.

¹If it converges at all.

The HF Equations

Varying the coefficients, we find

$$\sum_{\gamma} h_{\alpha\gamma}^{\text{HF}} C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}, \quad (11)$$

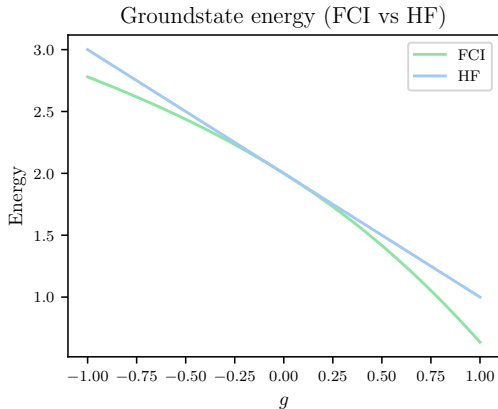
where

$$h_{\alpha\gamma}^{\text{HF}} = \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\beta\delta} \rho_{\beta\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (12)$$

Here, $\rho_{\beta\delta}$ is the density matrix, defined as $\rho_{\beta\delta} = \sum_i \langle \beta | i \rangle \langle i | \delta \rangle = \sum_i C_{i\beta} C_{i\delta}^*$. Eq. (11) is in effect nothing more than an eigenvalue problem, and the HF equations are solved by diagonalizing the matrix h^{HF} repeatedly. The efficiency comes from the fact that the integrals in Eq. (12) need only be computed once, and the density matrix is updated at each iteration from the eigenvectors.

Hartree-Fock with the Pairing Model

Returning to the pairing model, we can derive the HF energy estimate as $E^{\text{HF}} = 2 - g$. As the HF method is variational, we know that $E^{\text{HF}} \geq E_0$.



Many-Body Perturbation Theory

Contents

- ① Introduction
- ② Full Configuration Interaction
- ③ Hartree-Fock
- ④ Many-Body Perturbation Theory
 - Brillouin-Wigner
 - Rayleigh-Schrödinger
- ⑤ Coupled-Cluster Theory

Many-Body Perturbation Theory

In many-body perturbation theory (MBPT), we seek to find the ground state energy by expanding the wave function in a series of perturbations to the Hamiltonian. We assume that the exact solution can be written as

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m |\Phi_m\rangle, \quad (13)$$

and that the ground state is dominated by the unperturbed problem

$$\hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle. \quad (14)$$

Correlation Energy

The Schrödinger equation is then

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle, \quad (15)$$

which gives

$$\langle \Phi_0 | \hat{H} | \Psi_0 \rangle = E. \quad (16)$$

Combining this with

$$\langle \Psi_0 | \hat{H}_0 | \Phi_0 \rangle = W_0, \quad (17)$$

and using the fact that \hat{H}, \hat{H}_0 are Hermitian, we find

$$\langle \Phi_0 | \hat{H}_I | \Psi_0 \rangle = E - W_0 = \Delta E, \quad (18)$$

where ΔE is the correlation energy.

Perturbed Expression

Introducing the energy variable ω , we can derive

$$\Delta E = \sum_{i=0}^{\infty} \left\langle \Phi_0 \left| \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i \right| \Phi_0 \right\rangle. \quad (19)$$

This is in reality nothing more than a rewrite of Eq. (18), but serves as a starting point for the perturbation expansion. It contains the unknown energy E , as well as the variable ω , and hence we need further assumptions to solve it.

Brillouin-Wigner Perturbation Theory

In Brillouin-Wigner perturbation theory (BWPT), we set $\omega = E$ in Eq. (19), and we find

$$\begin{aligned}\Delta E &= \sum_{i=0}^{\infty} \left\langle \Phi_0 \left| \hat{H}_I \left\{ \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \right\}^i \right| \Phi_0 \right\rangle \\ &= \left\langle \Phi_0 \left| \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \dots \right) \right| \Phi_0 \right\rangle.\end{aligned}\tag{20}$$

The equations then become rather simple, as compared with Eq. (19), with the exception on the unknown energy E . It can however be solved iteratively, for an initial guess of E .

Rayleigh-Schrödinger Perturbation Theory

In Rayleigh-Schrödinger perturbation theory (RSPT), we set $\omega = W_0$ in Eq. (19), and we find

$$\begin{aligned}\Delta E &= \sum_{i=0}^{\infty} \left\langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} (W_0 - E + \hat{H}_I) \right\}^i | \Phi_0 \right\rangle \\ &= \sum_{i=0}^{\infty} \left\langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) \right\}^i | \Phi_0 \right\rangle.\end{aligned}\tag{21}$$

As $\hat{Q}\Delta E|\Phi_0\rangle = 0$, we can write

$$\Delta E = \left\langle \Phi_0 | \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \dots | \Phi_0 \right\rangle.\tag{22}$$

Order by Order Contributions

Eq. (22) allows us to define the recursive formula

$$\Delta E = \sum_{i=1}^{\infty} \Delta E^{(i)}, \quad (23)$$

where the first few terms are, writing $\langle \hat{A} \rangle = \langle \Phi_0 | \hat{A} | \Phi_0 \rangle$,

$$\Delta E^{(1)} = \langle \hat{H}_I \rangle \quad (24)$$

$$\Delta E^{(2)} = \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle \quad (25)$$

$$\Delta E^{(3)} = \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle - \left\langle \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \hat{H}_I \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \right\rangle. \quad (26)$$

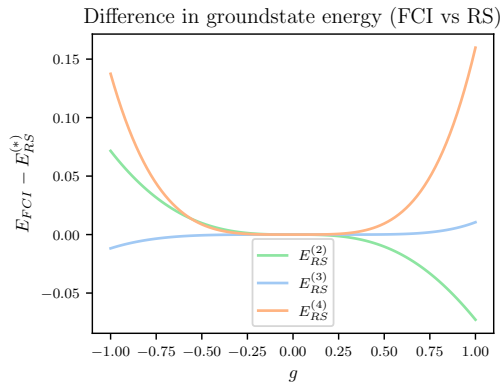
Order by Order Contributions

With the previous formula, we can find the correlation energy up to a given order of contributions. This method is however not without its drawbacks. For one, there is no guarantee that the series will converge, and the method is not variational. This entails that we will not necessarily get an improved estimate from including more terms in the series.

RSPT Results for the Pairing Model

Returning again to the pairing model, we have the ground state energy difference for the RSPT method, as a function of the interaction strength g .

As we see, the estimates diverge from the exact energy from both above and below, as the method is non-variational. In addition, adding additional terms to the series does not guarantee a better estimate.



Coupled-Cluster Theory

Contents

- ① Introduction
- ② Full Configuration Interaction
- ③ Hartree-Fock
- ④ Many-Body Perturbation Theory
- ⑤ Coupled-Cluster Theory**

Coupled-Cluster Theory

In coupled-cluster (CC) theory, we seek to write the wave function as

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (27)$$

where \hat{T} is the cluster operator, defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots, \quad (28)$$

with \hat{T}_n being the n -body cluster operator. The first two such operators are

$$\hat{T}_1 = \frac{1}{(1!)^2} \sum_{ai} t_i^a a_a^\dagger a_i, \quad \text{and} \quad \hat{T}_2 = \frac{1}{(2!)^2} \sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \quad (29)$$

With this, we also define the similarity transformed Hamiltonian $\overline{H}_N = e^{-\hat{T}} \hat{H} e^{\hat{T}}$.

Determining the Cluster Amplitudes

We determine the cluster amplitudes $t_{i_1 \dots i_n}^{a_1 \dots a_n}$ by solving the equations

$$\left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \overline{H_N} | \Phi_0 \right\rangle = 0, \quad (30)$$

which is derived from the equations

$$\left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \hat{H} e^{\hat{T}} | \Phi_0 \right\rangle = E_0 \left\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | e^{\hat{T}} | \Phi_0 \right\rangle. \quad (31)$$

If we were to solve this exactly without truncations, i.e. by including up to $np-nh$ excitations, we would have the same complexity as FCI. We therefore need to truncate the series, and the most common truncation is at CCSD, where we include up to $2p-2h$ excitations.

Truncated Couple-Cluster

In order to make the method computationally feasible, we truncate the series at some level. By doing this, the method is non-variational.

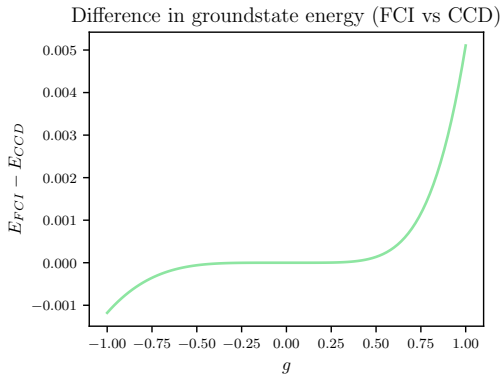
We solve the equations iteratively, and in this case we need an initial guess for the cluster amplitudes. A common choice in CCD is then to use the first order wave operator from MPBT, setting

$$(t_{ij}^{ab})^{(0)} = \frac{\langle ab|V|ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (32)$$

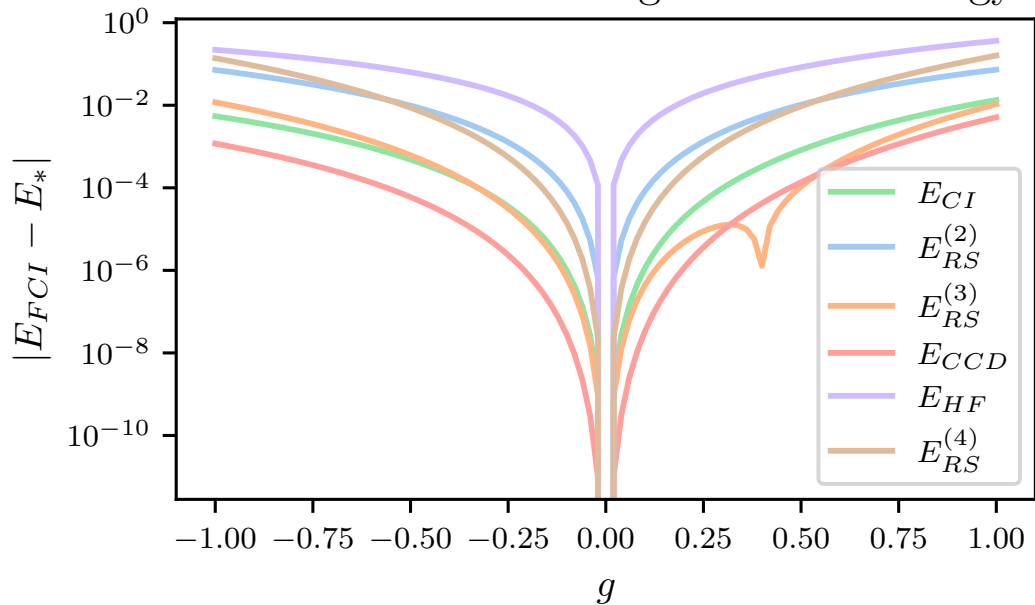
CCD Results for the Pairing Model

Returning to the pairing model, we have the ground state energy difference for the CCD method, as a function of the interaction strength g .

The pairing model is dominated by pairing correlations, and the CCD method is able to capture this.



Absolute difference in groundstate energy



Derivation of the HF Equations

Contents

⑥ Derivation of the HF Equations

⑦ Derivation of MBPT

⑧ Pauli Exclusion Principle

⑨ Wick's Theorem

⑩ Thouless' Theorem

Derivation of the HF Equations

In the original basis α we have the energy functional

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{\alpha} \langle \alpha | \hat{h}_0 | \alpha \rangle + \frac{1}{2} \sum_{\alpha\beta} \langle \alpha\beta | V | \alpha\beta \rangle_{AS}. \quad (33)$$

By way of varying the coefficients, the HF equations are found by introducing the new basis p defined by the unitary transformation

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \quad (34)$$

and minimizing the energy functional

$$E[\Phi^{\text{HF}}] = \langle \Phi^{\text{HF}} | \hat{H} | \Phi^{\text{HF}} \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | V | ij \rangle_{AS} \quad (35)$$

with respect to the coefficients $C_{p\alpha}$.

Introducing Lagrange Multipliers

Defining the functional in Eq. (35) as a functional of the coefficients $C_{p\alpha}$, we have

$$E_0[C] = \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (36)$$

As we have orthonormal basis functions, we have

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}, \quad (37)$$

so we introduce the functional

$$F[C] = E_0[C] - \sum_i \lambda_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}, \quad (38)$$

where λ_i are the Lagrange multipliers enforcing orthonormality.

Minimizing F

Minimizing F with respect to $C_{i\alpha}^*$, we wish to solve

$$\frac{dF}{dC_{i\alpha}^*}[C] = \frac{d}{dC_{i\alpha}^*} \left[E_0[C] - \sum_j \lambda_j \sum_{\alpha} C_{j\alpha}^* C_{j\alpha} \right] = 0. \quad (39)$$

Term by term we have

$$\frac{d}{dC_{i\alpha}^*} \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle = \sum_{\beta} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \quad (40)$$

$$\frac{d}{dC_{i\alpha}^*} \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} = \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}, \quad (41)$$

Minimizing F , cont.

and finally

$$\frac{d}{dC_{i\alpha}^*} \sum_i \lambda_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} = \lambda_i C_{i\alpha}. \quad (42)$$

Combining these terms, we have

$$\sum_{\beta} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} - \lambda_i C_{i\alpha} = 0. \quad (43)$$

Recognizing λ_i as the eigenvalues $\varepsilon_i^{\text{HF}}$, we can write this as

$$\sum_{\gamma} \left[\langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_j \sum_{\beta\delta} C_{j\beta}^* C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} \right] C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}. \quad (44)$$

Hartree-Fock Equations Found

This finally results in the HF equations

$$\sum_{\gamma} h_{\alpha\gamma}^{\text{HF}} C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}. \quad (45)$$

Derivation of MBPT

Contents

- ⑥ Derivation of the HF Equations
- ⑦ Derivation of MBPT**
- ⑧ Pauli Exclusion Principle
- ⑨ Wick's Theorem
- ⑩ Thouless' Theorem

Derivation of Many-Body Perturbation Expansion

We have

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle \quad (46)$$

$$(\hat{H}_0 + \hat{H}_I)|\Psi_0\rangle = E|\Psi_0\rangle \quad (47)$$

$$-\hat{H}_0|\Psi_0\rangle = (-E + \hat{H}_I)|\Psi_0\rangle \quad (48)$$

$$(\omega - \hat{H}_0)|\Psi_0\rangle = (\omega - E + \hat{H}_I)|\Psi_0\rangle, \quad (49)$$

where ω is an energy variable dependent on the expansion method. Assuming the resolvent of $(\omega - \hat{H}_0)$ exists, we can then rewrite the Schrödinger equation as

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) |\Psi_0\rangle. \quad (50)$$

Combining with Projection Operators

With the projection operators

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0| \quad \text{and} \quad \hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|, \quad (51)$$

we can then write

$$\begin{aligned} |\Psi_0\rangle &= (\hat{P} + \hat{Q}) |\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle \\ &= |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) |\Psi_0\rangle. \end{aligned} \quad (52)$$

Solving this in an iterative fashion, with an initial guess for $|\Psi_0\rangle = |\Phi_0\rangle$, we have

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i |\Phi_0\rangle. \quad (53)$$

Pauli Exclusion Principle

Contents

- ⑥ Derivation of the HF Equations
- ⑦ Derivation of MBPT
- ⑧ Pauli Exclusion Principle**
- ⑨ Wick's Theorem
- ⑩ Thouless' Theorem

Pauli Exclusion Principle

The Pauli principle states that no two fermions can be in the same place, and they cannot have the same quantum numbers. This is achieved through representing the states Φ as Slater determinants, as if one of the requirements is violated, we would have linearly dependent rows or columns in the determinant respectively. Thus the determinant would vanish.

The Pauli principle is also enforced through the creation operators, by requiring that

$$\{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0, \quad (54)$$

as this gives us that $a_i^\dagger a_i^\dagger = 0$.

Wick's Theorem

Contents

- ⑥ Derivation of the HF Equations
- ⑦ Derivation of MBPT
- ⑧ Pauli Exclusion Principle
- ⑨ Wick's Theorem**
- ⑩ Thouless' Theorem

Wick's Theorem

Wick's theorem is based on two main principles, *normal ordering* and *contractions*.

Normal ordering is the process of moving all creation operators to the left of all annihilation operators, specifically

$$\{\hat{A}\hat{B}\cdots\hat{X}\hat{Y}\} = (-1)^P [\text{creation operators}] \cdot [\text{annihilation operators}], \quad (55)$$

where P is the number of permutations needed to move all creation operators to the left of all annihilation operators.

A contraction is defined as the vacuum expectation value of two operators, and is denoted by

$$\overline{\hat{A}\hat{B}} = \langle 0 | \hat{A}\hat{B} | 0 \rangle. \quad (56)$$

Wick's Theorem

The theorem then states that any product of annihilation and creation operators can be written as a sum of normal ordered products, with all possible contractions. For example, a string of N operators can be written as

$$\begin{aligned}
 \hat{A}\hat{B}\cdots\hat{X}\hat{Y}\hat{Z} = & \{\hat{A}\hat{B}\cdots\hat{X}\hat{Y}\hat{Z}\} + \sum_{[1]} \{\overset{\frown}{\hat{A}\hat{B}}\cdots\hat{X}\hat{Y}\hat{Z}\} \\
 & + \sum_{[2]} \{\overset{\frown}{\hat{A}\hat{B}}\cdots\overset{\frown}{\hat{X}\hat{Y}}\hat{Z}\} + \dots + \sum_{[\frac{N}{2}]} \{\overset{\frown}{\hat{A}\hat{B}}\cdots\overset{\frown}{\hat{X}\hat{Y}}\hat{Z}\}.
 \end{aligned} \tag{57}$$

This can then be utilized to reduce the number of terms which need to be computed, as a number of the terms typically vanish.

Wick's Theorem

This is especially the case when computing vacuum expectation values, as a normal ordering of operators which is not fully contracted will vanish. We are then simply left with

$$\langle 0 | \hat{A} \hat{B} \cdots \hat{X} \hat{Y} \hat{Z} | 0 \rangle = \sum_{[\frac{N}{2}]} \langle 0 | \{ \overbrace{\hat{A} \hat{B} \cdots \hat{X} \hat{Y} \hat{Z}}^{\text{fully contracted}} \} | 0 \rangle = \sum_{[\frac{N}{2}]} \overbrace{\hat{A} \hat{B} \cdots \hat{X} \hat{Y} \hat{Z}}^{\text{fully contracted}}. \quad (58)$$

Then for instance, when there is an odd number of operators, or a different number of creation and annihilation operators, we can immediately read off the vacuum expectation value as zero.

Thouless' Theorem

Contents

- ⑥ Derivation of the HF Equations
- ⑦ Derivation of MBPT
- ⑧ Pauli Exclusion Principle
- ⑨ Wick's Theorem
- ⑩ Thouless' Theorem

Thouless' Theorem

Thouless' theorem states that any state $|\Psi\rangle$ not orthogonal to a determinant $|\Phi\rangle$ can be written as

$$|\Psi\rangle = \exp \left\{ \sum_{ai} C_{ai} a_a^\dagger a_i \right\} |\Phi\rangle. \quad (59)$$

From this we derive

$$|\Psi\rangle = \prod_i \left\{ 1 + \sum_a C_{ai} a_a^\dagger a_i + \left(\sum_a C_{ai} a_a^\dagger a_i \right)^2 + \dots \right\} |\Phi\rangle, \quad (60)$$

and as the higher-order terms include operators of the form $(a_i)^n$, all but the first two terms vanish. With $|\Phi\rangle = a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_n}^\dagger |0\rangle$, we can then derive

$$|\Psi\rangle = \prod_i \left\{ 1 + \sum_a C_{ai} a_a^\dagger a_i \right\} a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_n}^\dagger |0\rangle = \prod_i \left\{ a_i^\dagger + \sum_a C_{ai} a_a^\dagger \right\} |0\rangle. \quad (61)$$