

Summary of lectures FYS4480 autumn 2018

October 24, 2018

Disclaimer

The purpose of this note is to summarize what has been covered so far in the course and provide a general overview over important results and methods. Statements are given without proof and one should consult the lecture notes for more in depth discussion of the various topics.

1 Introduction

1.1 Particle statistics

The fact that elementary particles are identical, or indistinguishable is expressed by demanding that the probability density $|\Psi(x_1, x_2, \dots, x_N)|^2$ must be permutation invariant. That is, if we exchange any coordinates we must get the same probability

$$|\Psi(x_1, x_2, \dots, x_N)|^2 = |\Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)})|^2. \quad (1)$$

Here σ is any permutation of coordinate indices.

To make this somewhat precise we write down the definition of permutations and define the so-called permutation operator.

Definition 1 (Permutation). Let \mathcal{I} be the finite set $\mathcal{I} = \{1, 2, 3, \dots, N\}$. A permutation is a function, $\sigma : \mathcal{I} \rightarrow \mathcal{I}$, that takes every number in \mathcal{I} and maps it to another unique number in \mathcal{I} . Informally, a permutation is any reordering of N indices.

The collection of all permutations of \mathcal{I} is denoted S_N and is called the symmetric group on N letters. In particular S_N has $N!$ elements, i.e there are $N!$ possible reorderings of N indices. We write $\sigma \in S_N$ for an arbitrary permutation.

Definition 2 (Transposition). A transposition is a permutation $\sigma \in S_N$, where only a single pair of indices (i, j) in $\{1, 2, \dots, i, \dots, j, \dots, N\}$ are exchanged. That is to say, $\sigma(i) = j$ and $\sigma(j) = i$, while $\sigma(k) = k$ for all $k \neq i, j$.

Theorem 1. Any permutation $\sigma \in S_N$ can be obtained by a series of transpositions. The sign of the permutation is given by $(-1)^{|\sigma|}$, where $|\sigma|$ is the number of transpositions needed to obtain the permutation.

Example 1 (A permutation). Let $\mathcal{I} = \{1, 2, 3\}$. Then $\sigma(1) = 3, \sigma(2) = 1, \sigma(3) = 2$ is a permutation. In other words, we have a reordering of three indices given by $\{\sigma(1), \sigma(2), \sigma(3)\} = \{3, 1, 2\}$.

Note that in terms of transpositions we could perform the reordering as follows

$$\{1, 2, 3\} \xrightarrow{\text{transpose 3 and 2}} \{1, 3, 2\} \xrightarrow{\text{transpose 1 and 3}} \{3, 1, 2\}.$$

Here we needed two transpositions so $|\sigma| = 2$.

Definition 3 (The permutation operator). The permutation operator \hat{P}_σ is defined as the operator that evaluates a wavefunction at permuted coordinates

$$\hat{P}_\sigma \Psi(x_1, \dots, x_N) = \Psi(x_{\sigma(1)}, \dots, x_{\sigma(N)}). \quad (2)$$

Now, the condition

$$|\Psi(x_1, x_2, \dots, x_N)|^2 = |\Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)})|^2$$

is equivalent to

$$\Psi(x_1, x_2, \dots, x_N) = e^{i\alpha(\sigma)} \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)}) \quad (3)$$

which again is equivalent to saying that $\Psi(x_1, x_2, \dots, x_N)$ must be an eigenfunction of the permutation operator 2

$$\hat{P}_\sigma \Psi(x_1, x_2, \dots, x_N) = e^{i\alpha(\sigma)} \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)}). \quad (4)$$

One can show that either $\hat{P}_\sigma \Psi = \Psi$ for every $\sigma \in S_N$, or $\hat{P}_\sigma \Psi = (-1)^{|\sigma|} \Psi$ for every $\sigma \in S_N$ and $|\sigma|$ is the number of transpositions. In the former case, Ψ is "totally symmetric with respect to permutations", and in the latter case, "totally anti-symmetric". Bosons have totally symmetric wavefunctions only, and fermions have totally anti-symmetric wavefunctions only.

In this course, we will restrict our attention to fermions, i.e we must look for anti-symmetric wavefunctions.

1.2 Slater Determinants

Definition 4 (Slater determinant). Let $\psi_{\alpha_1}, \psi_{\alpha_2}, \dots, \psi_{\alpha_N}$ be arbitrary single-particle functions (not necessarily orthonormal). The Slater determinant defined by these functions is denoted $\Phi(x_1, \dots, x_N; \alpha_1, \dots, \alpha_N)$, and is defined by the formula

$$\Phi(x_1, \dots, x_N; \alpha_1, \dots, \alpha_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(x_1) & \psi_{\alpha_1}(x_2) & \dots & \dots & \psi_{\alpha_1}(x_N) \\ \psi_{\alpha_2}(x_1) & \psi_{\alpha_2}(x_2) & \dots & \dots & \psi_{\alpha_2}(x_N) \\ \dots & \dots & \dots & \dots & \dots \\ \psi_{\alpha_N}(x_1) & \psi_{\alpha_N}(x_2) & \dots & \dots & \psi_{\alpha_N}(x_N) \end{vmatrix}$$

where x_i stand for the coordinates and spin values of a particle i and $\alpha_1, \alpha_2, \dots, \alpha_N$ are quantum numbers needed to describe remaining quantum numbers.

It is common to use the notation

$$\Phi(x_1, \dots, x_N; \alpha_1, \dots, \alpha_N) = |\alpha_1 \alpha_2 \dots \alpha_N\rangle \quad (5)$$

for the Slater determinant.

A useful way to express the Slater determinant is via the antisymmetrization operator \hat{A} .

Definition 5 (Antisymmetrization operator). The antisymmetrization operator \hat{A} is defined as

$$\hat{A} = \frac{1}{N!} \sum_{\sigma \in S_N} (-1)^{|\sigma|} \hat{P}_\sigma \quad (6)$$

where the notation $\sum_{\sigma \in S_N}$ means that we sum over all possible permutations of N indices.

The expression for the Slater determinant given above, can now be written in terms of the antisymmetrization operator as follows

$$\begin{aligned} \Phi(x_1, \dots, x_N; \alpha_1, \dots, \alpha_N) &= \frac{1}{\sqrt{N!}} \underbrace{\sum_{\sigma \in S_N} (-1)^{|\sigma|} \hat{P}_\sigma (\psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \dots \psi_{\alpha_N}(x_N))}_{= \hat{A}} \\ &= \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} (-1)^{|\sigma|} \psi_{\alpha_1}(x_{\sigma(1)}) \psi_{\alpha_2}(x_{\sigma(2)}) \dots \psi_{\alpha_N}(x_{\sigma(N)}) \\ &= \sqrt{N!} \hat{A} \Phi_H(x_1, \dots, x_N) \end{aligned} \quad (7)$$

where $\Phi_H(x_1, \dots, x_N) \equiv \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \dots \psi_{\alpha_N}(x_N)$.

2 Second quantization

2.1 Creation and annihilation operators

Definition 6 (Vacuum state). The state $|0\rangle$ represents the state containing no particles and is referred to as the vacuum state. Another common notation is to use $|-\rangle$. The vacuum state satisfies $\langle 0|0\rangle = 1$. It should be noted that $|0\rangle \neq 0$.

Definition 7 (The creation operator). We define the fermion creation operator a_α^\dagger , creating a particle in the single-particle state ϕ_α , as

$$a_\alpha^\dagger |0\rangle \equiv |\alpha\rangle \quad (8)$$

and

$$a_\alpha^\dagger |\alpha_1 \alpha_2 \dots \alpha_n\rangle = |\alpha \alpha_1 \alpha_2 \dots \alpha_n\rangle, \quad (9)$$

if $\alpha \neq \alpha_i$ for all single-particle states in the determinant. Furthermore, insertion of α at position $j+1$ will induce a sign change $(-1)^j$

$$a_\alpha^\dagger |\alpha_1 \alpha_2 \dots \alpha_j \alpha_{j+1} \dots \alpha_n\rangle = (-1)^j |\alpha_1 \alpha_2 \dots \alpha_j \alpha \alpha_{j+1} \dots \alpha_n\rangle. \quad (10)$$

If $\alpha = \alpha_i$ for some single-particle state, then

$$a_\alpha^\dagger |\alpha_1 \alpha_2 \dots \alpha_n\rangle = |\alpha \alpha_1 \alpha_2 \dots \alpha_n\rangle = 0 \quad (11)$$

Definition 8 (The annihilation operator). The annihilation operator, a_α , is the Hermitian adjoint of a_α^\dagger , i.e

$$a_\alpha \equiv (a_\alpha^\dagger)^\dagger. \quad (12)$$

The annihilation operator gives the zero result when acting on the vacuum state

$$a_\alpha |0\rangle = 0. \quad (13)$$

If $|\Phi\rangle = |\alpha_1\alpha_2\cdots\alpha_{i-1}\alpha_i\alpha_{i+1}\cdots\alpha_n\rangle$ is an arbitrary Slater determinant and $\alpha = \alpha_i$

$$a_\alpha |\alpha_1\alpha_2\cdots\alpha_{i-1}\alpha_i\alpha_{i+1}\cdots\alpha_n\rangle = (-1)^{i-1} |\alpha_1\alpha_2\cdots\alpha_{i-1}\alpha_{i+1}\cdots\alpha_n\rangle, \quad (14)$$

i.e it removes particle i from the determinant. Otherwise $a_\alpha |\Phi\rangle = 0$, that is if $\alpha \neq \alpha_i$ for all single-particle states in the determinant.

Definition 9 (Anticommutator of operators). The anticommutator of two operators \hat{A} and \hat{B} is defined as

$$\{\hat{A}, \hat{B}\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}. \quad (15)$$

Theorem 2 (The fundamental anticommutator relations). The creation and annihilation operators satisfy the so-called "fundamental anticommutator" relations

$$\{a_p^\dagger, a_q^\dagger\} = 0 \quad (16)$$

$$\{a_p, a_q\} = 0 \quad (17)$$

$$\{a_p, a_q^\dagger\} = \delta_{pq}. \quad (18)$$

$$(19)$$

2.2 Representation of operators

The matrix representation of a one-body operator, relative to a single particle basis $\{\phi_i\}_{i=1}$, is given by

$$\langle\phi_p|\hat{h}|\phi_q\rangle \equiv \int \phi_p^*(\mathbf{r})\hat{h}\phi_q(\mathbf{r})d\mathbf{r}. \quad (20)$$

Common notations are $\langle\phi_p|\hat{h}|\phi_q\rangle = \langle p|\hat{h}|q\rangle = h_q^p$. The second quantized form a one-body operator is given by

$$\hat{H}_0 = \sum_{pq} \langle p|\hat{h}|q\rangle a_p^\dagger a_q. \quad (21)$$

Likewise the matrix representation of a two-body operator, typically the coulomb interaction, is given by

$$\langle\phi_p\phi_q|\hat{v}|\phi_r\phi_s\rangle = \int \phi_p^*(\mathbf{r}_1)\phi_q^*(\mathbf{r}_2)\hat{v}(\mathbf{r}_1, \mathbf{r}_2)\phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \quad (22)$$

It is common to write $\langle\phi_p\phi_q|\hat{v}|\phi_r\phi_s\rangle = \langle pq|\hat{v}|rs\rangle = v_{rs}^{pq}$. Furthermore, it is customary to introduce the *anti-symmetric* matrix element

$$\langle pq|\hat{v}|rs\rangle_{AS} \equiv \langle pq|\hat{v}|rs\rangle - \langle pq|\hat{v}|sr\rangle. \quad (23)$$

Here it should be noted that many sources drop the AS subscript, which can be a source of confusion. The second quantized form a two-body operator is given by

$$\hat{H}_I = \frac{1}{2} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r \quad (24)$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{AS} a_p^\dagger a_q^\dagger a_s a_r \quad (25)$$

Thus, the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$, using anti-symmetric matrix elements is given by

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{AS} a_p^\dagger a_q^\dagger a_s a_r. \quad (26)$$

2.3 Wicks theorem and related concepts

Definition 10 (Operator string). A sequence of creation and annihilation operators is called an operator string. Generally an operator string of n creation and annihilation operators are on the form

$$A_1 A_2 \cdots A_n, \quad A_i \in \{a_p, a_p^\dagger\}. \quad (27)$$

For example

$$A_1 A_2 A_3 A_4 = a_p a_q^\dagger a_r a_s^\dagger,$$

where $A_1 = a_p$, $A_2 = a_q^\dagger$, $A_3 = a_r$ and $A_4 = a_s^\dagger$.

Definition 11 (Vacuum expectation value). The number

$$\langle -|A_1 A_2 \cdots A_n| - \rangle \quad (28)$$

is referred to as a vacuum expectation value, where $A_1 A_2 \cdots A_n$ is an operator string.

Definition 12 (Normal ordered product). The normal-ordered product form of an operator string $A_1 A_2 \cdots A_n$ is defined as a rearrangement,

$$\{A_1 A_2 \cdots A_n\} \equiv (-1)^{|\sigma|} A_{\sigma(1)} A_{\sigma(2)} \cdots A_{\sigma(n)}, \quad (29)$$

where σ is a permutation such that all the creation operators in the operator string is to the left of all the annihilation operators, i.e.,

$$\{A_1 A_2 \cdots A_n\} \equiv (-1)^{|\sigma|} [\text{creation operators}] \cdot [\text{annihilation operators}]. \quad (30)$$

The permutation σ is in general not unique, since we may permute the creation and annihilation operators separately without affecting the total expression. For example,

$$\{a_p a_q^\dagger a_r^\dagger a_s\} = a_q^\dagger a_r^\dagger a_p a_s = -a_r^\dagger a_q^\dagger a_p a_s = a_r^\dagger a_q^\dagger a_s a_p = -a_q^\dagger a_r^\dagger a_s a_p \quad (31)$$

To find the permutation σ that normal-orders an operator product, it is usually simplest to count the number f of anticommutations necessary to achieve the rearrangement, and set $(-1)^{|\sigma|} = (-1)^f$. Note that the string $A_1 \cdots A_n \neq \{A_1 \cdots A_n\}$ in general, since by reordering creation and annihilation operators we neglect the extra terms arising from the Kronecker delta in the anti-commutator relation $\{a_p, a_q^\dagger\} = \delta_{pq}$.

Definition 13 (Contraction). A contraction between two arbitrary creation and annihilation operators X and Y , is the number defined by

$$\overline{XY} \equiv \langle -|XY|-\rangle. \quad (32)$$

We list the possible contractions, relative to the vacuum state $|-\rangle$,

$$\overline{a_p^\dagger a_q^\dagger} = \langle -|a_p^\dagger a_q^\dagger|-\rangle = 0 \quad (33)$$

$$\overline{a_p a_q} = \langle -|a_p a_q|-\rangle = 0 \quad (34)$$

$$\overline{a_p^\dagger a_q} = \langle -|a_p^\dagger a_q|-\rangle = 0 \quad (35)$$

$$\overline{a_p a_q^\dagger} = \langle -|a_p a_q^\dagger|-\rangle = \delta_{pq} \quad (36)$$

Wick's theorem states that every string of creation and annihilation operators can be written as a sum of normal-ordered products where we perform every possible contraction.

Theorem 3 (Wicks theorem). Let $A_1 \cdots A_n$ be an operator string of creation and annihilation operators. Then,

$$\begin{aligned} A_1 A_2 \cdots A_n &= \{A_1 A_2 \cdots A_n\} + \sum_{(1)} \{A_1 \overline{} \cdots A_n\} + \sum_{(2)} \{A_1 \overline{\overline{}} \cdots A_n\} + \cdots \\ &+ \sum_{\lfloor \frac{n}{2} \rfloor} \{A_1 \underbrace{\overline{\overline{\overline{\overline{}}}} \cdots A_n}_{\lfloor \frac{n}{2} \rfloor \text{ contractions}}\} \end{aligned}$$

The notation $\sum_{(m)}$ signifies that we sum over all combinations of m contractions. When n is even, the last sum signifies that we sum over $n/2$ contractions, i.e., all operators are contracted. If n is odd, there is one uncontracted operator left in each term of the last sum.

Evaluation of vacuum expectation values are greatly simplified by Wicks theorem. First note that for any string with at least one factor

$$\langle -|\{A_1 \cdots A_n\}|-\rangle = 0, \quad (37)$$

because in the normal-order product, the annihilation operators are to the right, and the creation operators are on the left.

Theorem 4 (Wicks theorem for vacuum expectation values). For odd n , Wicks theorem gives

$$\langle -|A_1 \cdots A_n|-\rangle = 0, \quad (38)$$

while for even n ,

$$\langle -|A_1 \cdots A_n|-\rangle = \sum_{\lfloor \frac{n}{2} \rfloor} \{A_1 \underbrace{\overline{\overline{\overline{\overline{}}}} \cdots A_n}_{\text{all contracted}}\}. \quad (39)$$

Fact 1. A useful fact is that the sign of a fully contracted operator product is $(-1)^k$, where k is the number of contraction line crossings.

Consider an operator string on the form

$$\{A_1 A_2 \cdots A_p\} \{B_1 B_2 \cdots B_q\} \cdots \{Z_1 Z_2 \cdots Z_r\} \quad (40)$$

where each substring is normal ordered. Then the generalized Wicks theorem states that we only have to consider contractions between different substrings. That is, contractions involving two operators from the same substring -referred to as self contractions- do not contribute.

Theorem 5 (The generalized Wicks theorem). Let

$$\{A_1 A_2 \cdots A_p\} \{B_1 B_2 \cdots B_q\} \cdots \{Z_1 Z_2 \cdots Z_r\}$$

be an operator string consisting of normal ordered substrings. Then,

$$\begin{aligned} \{A_1 A_2 \cdots A_p\} \{B_1 B_2 \cdots B_q\} \cdots \{Z_1 Z_2 \cdots Z_r\} &= \{A_1 A_2 \cdots A_p \dot{B}_1 B_2 \cdots B_q \dot{\cdots} \dot{Z}_1 Z_2 \cdots Z_r\} \\ &+ \sum_{(1)}' \{A_1 A_2 \cdots A_p \dot{B}_1 B_2 \cdots B_q \dot{\cdots} \dot{Z}_1 Z_2 \cdots Z_r\} \\ &+ \sum_{(2)}' \{A_1 A_2 \cdots A_p \dot{B}_1 B_2 \cdots B_q \dot{\cdots} \dot{Z}_1 Z_2 \cdots Z_r\} \\ &+ \cdots \\ &+ \sum_{\lfloor \frac{n}{2} \rfloor}' \underbrace{\{A_1 A_2 \cdots A_p \dot{B}_1 B_2 \cdots B_q \dot{\cdots} \dot{Z}_1 Z_2 \cdots Z_r\}}_{\lfloor \frac{n}{2} \rfloor \text{ contractions}} \end{aligned}$$

The notation $\sum_{(m)}'$ signifies that we sum over all combinations of m contractions that each involve operators from different substrings. The vertical dots are only a bookkeeping device to remind ourselves which operators belong to which substrings.

2.4 Particle-hole formalism

Consider a N -particle system and the single-particle functions $\{\phi_p\}_{p=1}^L$, with L denoting the number of single-particle functions. In particle-hole formalism we divide the single-particle functions into two sets. The first N single-particle functions, $\{\phi\}_{i=1}^N$, are referred to as particle/occupied-states/functions while the $N+1, \cdots, L$ states, $\{\phi\}_{a=N+1}^L$, are referred to as hole/unoccupied/virtual states. The indices i, j, k, \cdots are reserved for particle states and indices a, b, c, \cdots are reserved for hole states. General states, particle or hole, are indexed by p, q, r, \cdots .

Definition 14 (The reference state). We define the reference Slater determinant $|c\rangle$ to be the determinant constructed from the hole states, i.e

$$|c\rangle = \prod_{i=1}^N a_i^\dagger |0\rangle = |\phi_1 \phi_2 \cdots \phi_N\rangle. \quad (41)$$

Other common notations for the reference state are $|c\rangle = |\Phi_0\rangle = |\Phi\rangle_{\text{ref}}$.

Definition 15 (Excited determinants). From the reference determinant, we can construct excited determinants using the creation and annihilation operators, substituting one or more particle states with hole states.

$$\begin{aligned} |\Phi_i^a\rangle &= a_a^\dagger a_i |c\rangle, \quad \text{single excitation} \\ |\Phi_{ij}^{ab}\rangle &= a_b^\dagger a_j a_a^\dagger a_i |c\rangle, \quad \text{double excitation,} \\ &\vdots \end{aligned}$$

Definition 16 (Quasiparticle creation and annihilation operators). Quasiparticle creation and annihilation operators b_p, b_p^\dagger are defined as follows

$$b_i = a_i^\dagger, \quad b_a = a_a \quad (42)$$

$$b_i^\dagger = a_i, \quad b_a^\dagger = a_a^\dagger. \quad (43)$$

Thus, for hole indices, quasiparticle creation operators are the ordinary creation operators, but for particle states, creating a quasiparticle is the same as destroying a particle in a particle state. One says that b_i^\dagger creates a hole, while b_a^\dagger creates a particle.

Furthermore, the fundamental anticommutator relations are preserved for quasiparticle creation and annihilation operators

$$\{b_p^\dagger, b_q^\dagger\} = 0, \quad (44)$$

$$\{b_p, b_q\} = 0, \quad (45)$$

$$\{b_p, b_q^\dagger\} = \delta_{pq}. \quad (46)$$

Definition 17 (The new vacuum state). Making the observation that

$$b_p |c\rangle = 0 \text{ for all } p, \quad (47)$$

we see that the reference acts for quasiparticle creation/annihilation as the vacuum did for the ordinary creation/annihilation operators. Thus, we define the reference $|c\rangle$ to be vacuum state for the quasiparticle operators. We will often refer to $|c\rangle$ as the new vacuum state in the following.

Fact 2. The definition of normal-ordering, contractions, and ultimately Wick's theorem, depended only on the anticommutator relations and the property

$$a_p |0\rangle = 0$$

Thus, Wick's theorem is valid also for quasiparticles.

Notice that relative to the new vacuum state, there are now two non-zero contractions

$$\overline{b_a b_b^\dagger} = \overline{a_a a_b^\dagger} = \langle c | a_a a_b^\dagger | c \rangle = \delta_{ab} \quad (48)$$

$$\overline{b_i b_j^\dagger} = \overline{a_i^\dagger a_j} = \langle c | a_i^\dagger a_j | c \rangle = \delta_{ij}. \quad (49)$$

$$(50)$$

2.5 Normal ordering relative to the new vacuum state

If we normal order relative to the new vacuum $|c\rangle$ the one-body Hamiltonian can be written

$$\hat{H}_0 = H_0^{(1\text{-body})} + H_0^{(0\text{-body})} \quad (51)$$

where we have defined

$$H_0^{(0\text{-body})} \equiv \sum_i \langle i | \hat{h} | i \rangle \quad (52)$$

$$H_0^{(1\text{-body})} \equiv \sum_{pq} \langle p | \hat{h} | q \rangle \{a_p^\dagger a_q\}. \quad (53)$$

The notation $H^{n\text{-body}}$ means that the operator acts as a n -body operator, with 0-body being the same as a constant.

The two-body Hamiltonian can be written as

$$\hat{H}_I = \hat{H}_I^{(2\text{-body})} + \hat{H}_I^{(1\text{-body})} + \hat{H}_I^{(0\text{-body})} \quad (54)$$

$$(55)$$

where

$$\hat{H}_I^{(2\text{-body})} = \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle_{\text{AS}} \{a_p^\dagger a_q^\dagger a_s a_r\}, \quad (56)$$

$$\hat{H}_I^{(1\text{-body})} = \sum_{pqi} \langle pi | \hat{v} | qi \rangle_{\text{AS}} \{a_p^\dagger a_q\}, \quad (57)$$

$$\hat{H}_I^{(0\text{-body})} = \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \quad (58)$$

We now define

$$\begin{aligned} E_0^{\text{ref}} &\equiv H_0^{(0\text{-body})} + \hat{H}_I^{(0\text{-body})} = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \\ \{\hat{F}\} &\equiv H_0^{(1\text{-body})} + \hat{H}_I^{(1\text{-body})} = \sum_{pq} \langle p | \hat{f} | q \rangle \{a_p^\dagger a_q\} \\ \{\hat{H}_I\} &\equiv \hat{H}_I^{(2\text{-body})} \end{aligned}$$

where we defined the so-called fock matrix element

$$\langle p | \hat{f} | q \rangle = \langle p | \hat{h} | q \rangle + \sum_i \langle pi | \hat{v} | qi \rangle_{\text{AS}} \quad (59)$$

E_0^{ref} is referred to as the reference energy and $\{\hat{F}\}$ is the Fock-operator.

Thus, we can write the full Hamiltonian normal ordered relative to the new vacuum as

$$\hat{H} = E_0^{\text{ref}} + \{\hat{F}\} + \{\hat{H}_I\}. \quad (60)$$

When computing expectation values using the normal ordered Hamiltonian we can now use Wicks generalized theorem, considering only contractions between normal ordered substrings. Recall carefully, that there are two possible non-zero contractions relative to the new vacuum state.

Example 2. Consider the computation of the matrix element $\langle c|\{\hat{F}\}|\Phi_i^a\rangle$. By Wicks generalized theorem we have

$$\langle c|\{\hat{F}\}|\Phi_i^a\rangle = \sum'_{\lfloor \frac{n}{2} \rfloor} \langle c| \left(\sum_{pq} \langle p|\hat{f}|q\rangle \{a_p^\dagger a_q\} a_a^\dagger a_i \right) |c\rangle,$$

With $\sum'_{\lfloor \frac{n}{2} \rfloor}$ meaning that we sum over all possible contractions between different normal ordered substrings.

Note that $a_a^\dagger a_i$ already is on normal order form. The computation is also simplified by noting that there is only one possible way of contracting all operators and get a non-zero result, that is

$$\overbrace{\{a_p^\dagger a_q\} a_a^\dagger a_i} = \delta_{pi} \delta_{qa} \quad (61)$$

with a positive sign since there are two line crossings. Thus,

$$\begin{aligned} \langle c|\{\hat{F}\}|\Phi_i^a\rangle &= \langle c| \left(\sum_{pq} \langle p|\hat{f}|q\rangle \delta_{pi} \delta_{qa} \right) |c\rangle \\ &= \langle i|\hat{f}|a\rangle \langle c|c\rangle \\ &= \langle i|\hat{f}|a\rangle. \end{aligned}$$

3 Many-body methods

3.1 Configuration Interaction Theory

3.2 Hartree-Fock theory

3.2.1 The Hartree-Fock equations

In Hartree-Fock theory the underlying idea is to approximate the true wavefunction of a N -particle system $|\Psi\rangle$ by a **single** Slater determinant

$$|\Phi\rangle = |\psi_1 \psi_2 \dots \psi_N\rangle \quad (62)$$

where the ψ_i 's are orthonormal single-particle functions.

In Hartree-Fock we know the form of the wavefunction which by assumption is a single Slater determinant. The unknowns are the single-particle functions ψ_i .

How do we go about finding these single-particle functions? The idea is to expand the ψ_i 's in a fixed known (finite in practice) basis $\{\phi_\lambda\}_{\lambda=1}^L$ which we take to be orthonormal for simplicity ($\langle \phi_p | \phi_q \rangle = \delta_{pq}$)

$$\psi_p = \sum_{\lambda} C_{p\lambda} \phi_{\lambda}. \quad (63)$$

Typically the basis functions ϕ_λ are chosen as the eigenfunctions of the single-particle operator \hat{h}_0 such that

$$\hat{h}_0 \phi_\lambda = \epsilon_\lambda \phi_\lambda. \quad (64)$$

Now, the unknowns are the expansion coefficients $\{C_{p\lambda}\}$ which determines ψ_i in terms of the ϕ_λ 's. The constraint that the ψ_i 's must be orthonormal gives that we must have

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \sum_{\alpha} C_{i\alpha}^* C_{j\alpha}. \quad (65)$$

The equation for the expansion coefficients is obtained by minimizing the energy of a single Slater determinant

$$\begin{aligned} E[\Phi] &= \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle_{AS} \\ &= \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \phi_\alpha | \hat{h}_0 | \phi_\beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \phi_\alpha \phi_\beta | v | \phi_\gamma \phi_\delta \rangle_{AS}, \end{aligned}$$

with respect to the expansion coefficients subject to the constraint that the ψ_i 's must be orthonormal. Here the notation $\langle \phi_\alpha | \hat{h}_0 | \phi_\beta \rangle$ and $\langle \phi_\alpha \phi_\beta | v | \phi_\gamma \phi_\delta \rangle_{AS}$ are meant as a reminder that matrix elements are with respect to the fixed basis functions ϕ_λ .

The constraint is incorporated via so-called Lagrange multipliers such that in order to minimize $E[\Phi]$ we have to solve

$$\frac{d}{dC_{i\alpha}^*} \left[E[\Phi] - \underbrace{\sum_j \epsilon_j \sum_{\alpha} C_{j\alpha}^* C_{j\alpha}}_{\text{The constraint}} \right] = 0. \quad (66)$$

Taking derivatives one obtains

$$\sum_{\beta} \left\{ \langle \alpha | \hat{h} | \beta \rangle + \sum_j \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \right\} C_{i\beta} = \epsilon_i C_{i\alpha}. \quad (67)$$

Defining the so-called Fock matrix

$$h_{\alpha\beta}^{\text{HF}} \equiv \langle \alpha | \hat{h} | \beta \rangle + \sum_j \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \quad (68)$$

we can rewrite 67 as

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{i\beta} = \epsilon_i^{\text{HF}} C_{i\alpha}. \quad (69)$$

Now let C be the matrix that consists of the $C_{i\beta}$'s. By definition $[C^\dagger]_{\beta i} = [C]_{i\beta}$, i.e element (β, i) of the **matrix** C^\dagger is equal to the matrix element $C_{i\beta}$. Then 69 can be written as

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} [C^\dagger]_{\beta i} = [C^\dagger]_{\alpha i} \epsilon_i^{\text{HF}} \quad (70)$$

$$(71)$$

where we recognize the left-hand side as a matrix-matrix product $h^{\text{HF}} C^\dagger$ where h^{HF} is the matrix having $h_{\alpha\beta}^{\text{HF}}$ as its elements. If we define $\mathcal{E} = \text{diag}(\epsilon_1, \epsilon_2, \dots, \epsilon_N)$

to be the diagonal matrix containing ϵ_i along its diagonal the right-hand side is the matrix-matrix product $C^\dagger \mathcal{E}$. Thus, Eq. 69 can be expressed as the non-linear eigenvalue problem

$$h^{\text{HF}}(C)C^\dagger = C^\dagger \mathcal{E}. \quad (72)$$

The above equation is commonly referred to as the Roothan-Hall equations. Thus we can solve for C , which are the unknowns we are interested in, by diagonalizing h^{HF} . However, the fact that the equation is non-linear due to the fact that h^{HF} depends on C , means that we must solve the Roothan-Hall equations iteratively. We will give a outline of one common approach to solve the Roothan-Hall equations.

3.2.2 Outline of how to write a Hartree-Fock program

3.3 Many-body Perturbation Theory

3.4 Coupled Cluster Theory