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Teil I

Fundamentals

Kapitel 1

Quantum Mechanics

1.1 Classical Mechanics

The formalism used in quantum mechanics largely stems from William Rowan Hamilton's formulation of classical mechanics. Through the process of canonical quantisation any classical model of a physical system is turned into a quantum mechanical model.

In Hamilton's formulation of classical mechanics, a complete description of a system of N particles is described by a set of canonical coordinates $q = (\vec{q}_1, \ldots, \vec{p}_N)$ and corresponding conjugate momenta $p = (\vec{p}_1, \ldots \vec{p}_N)$. Together, each pair of coordinate and momentum form a point $\xi = (q, p)$ in phase space, which is a space of all possible states of the system. Moreover, pairs of generalised coordinates and conjugate momenta are canonical if they satisfy the Poisson brackets so that $\{q_i, p_k\} = \delta_{ij}$. The Poisson bracket of two functions is defined as

$$\{f, g\} = \frac{\partial f}{\partial q}\frac{\partial g}{\partial g} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial q}. \tag{1.1}$$

The governing equations of motion in a classical system is Hamilton's equations,

$$\dot{q} = \frac{\partial}{\partial p}\mathscr{H}(q, p) \tag{1.2}$$

$$\dot{p} = -\frac{\partial}{\partial q}\mathscr{H}(q, p) \tag{1.3}$$

where $\mathscr{H}(q, p)$ is the Hamiltonian, a function for the total energy of the system. Hamilton's equations may also be stated in terms of the Poisson brackets,

$$\frac{dp_i}{dt} = \{p_i, \mathscr{H}\}, \ \frac{dq_i}{dt} = \{q_i, \mathscr{H}\}. \tag{1.4}$$

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A system consisting of N of equal mass m, subject forces caused by an external potential, as well as acting on each other with forces stemming from a central potetntial $w(q_i j)$ has the following Hamiltonian,

$$\mathscr{H}(q,p) = \mathscr{T}(q) + \mathscr{V}(p) + \mathscr{W}(p) = \frac{1}{2m}\sum_i |\vec{p_i}|^2 + \sum_i v(\vec{r_i}) + \frac{1}{2}\sum_{i<j} w(\vec{r_{ij}}). \qquad (1.5)$$

This Hamiltonian conveniently contains several parts - the kinetic energy, the external potential energy and the interaction energy; denoted by $\mathscr{T}$, $\mathscr{V}$ and $\mathscr{W}$ respectively.

1.2   Canonical Quantisation

In order to transition from a classical system to a quantum system, we move from the classucal phase space to the Hilbert space, through the procedure known as canonical, or first[1]-, quantisation. Whilst the state of a classical system is a point in phase space, a quantum state is a complex-valued state vector in discrete, infinite dimensional, Hilbert space, that is a complete vector space equipped with an inner product. This space is most commonly chosen to be the space of square-integrable functions Ψ, dependent on all coordinates

$$\Psi = \Psi(x_1, x_2, \ldots, x_N). \qquad (1.6)$$

These functions are dubbed wavefunctions and are maps from a point $(x_1, \ldots, x_N)$ in configuration space to the complex vector space,

$$\Psi : X^N \to \mathbb{C}. \qquad (1.7)$$

It has been widely discussed how such an object can represent the state of a particle. The answer is provided by Max Born's probabilistic interpretation, which says that $|\Psi(x_1, \ldots, x_N)|^2$, gives the probability of finding the particle at a certain position. For a situation with one particle in one dimension we have,

$$\int_a^b |\Psi(x)|^2 dx = \left\{ \begin{array}{l} \text{probability of finding the} \\ \text{particle between } a \text{ and } b \end{array} \right\} \qquad (1.8)$$

while $|\Psi(x_1, x_2, \ldots, x_N)|^2$ is the probability density for locating all particles at the point $(x_1, \ldots x_N) \in X^N$. Since the total probability must be 1, we are provided with a normalisation condition for the wavefunction,

$$\int_{X^N} |\Psi(x_1, x_2, \ldots, x_N)|^2 dx_1 dx_2 \ldots dx_N = \mathbb{1}. \qquad (1.9)$$

1.2.1   The Dirac-von Neumann Postulates

The following postulates, or axioms, provide a precise and concise description of quantum mechanics in terms of operators on the Hilbert space. There are many variations of these postulates, introduced both by their namesakes Paul Adriene Maurice Dirac[7] and John von Neumann[25].

Hilbert Space   A quantum state of an isolated physical system is described by a vector with unit norm in a Hilbert space, a complex vector space quipped with a scalar product.

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[1]Second quantisation comes later.

Observables   Each physical observable of a system is accociated with a *hermitian* operator acting on the Hilbert space. The eigenstates of each such operator define a *complete, orthonormal* set of vectors.

With $\hat{O}$ an operator, hermiticity means,

$$\langle\phi|\,\hat{O}\psi\rangle = \langle\hat{O}\phi\,|\psi\rangle \equiv \langle\phi|\,\hat{O}\,|\psi\rangle. \tag{1.10}$$

Completeness means,

$$\sum_i |i\rangle\,\langle i| = \mathbb{1}. \tag{1.11}$$

Orthonormal means,

$$\langle i|j\rangle = \delta_{ij}. \tag{1.12}$$

Time Evolution   The time evolution of the state vector, $|\psi\rangle = |\psi(t)\rangle$, is given by the Schrödinger equation[2].

$$i\hbar\frac{d}{dt}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle. \tag{1.13}$$

Measurements   Physically measurable values, associated with an obeservable $\hat{O}$ are defined by the eigenvalues o_n of the observable,

$$\hat{O}\,|n\rangle = o_n\,|n\rangle. \tag{1.14}$$

The probability for finding a particular eigenvalue in the measurement is

$$p_n = |\langle n|\psi\rangle|^2, \tag{1.15}$$

with the system in state $|\psi\rangle$ before the measurement, and $|n\rangle$ as the eigenstate corresponding to the eigenvalue o_n.

1.3   The Many-Body Quantum Hamiltonian

The full Hamiltionian for a quantum many-body system can be a large and unwieldy thing. In this study we will constrain ourselves to the study of electronic systems. Purely on a phenomenological basis, one would include nuclear terms in the Hamiltonian as well. In this study however, we will stay within the Born-Oppenheimer approximation and treat the nuclei as stationary particles, thereby refraining from introducing terms that involve the motion of nuclei. Here we introduce the molecular electronic Breit-Pauli Hamiltionian, throrougly described in Helgaker et al.[17],

$$\hat{H}_{\text{mol}}^{\text{BP}} = \begin{cases} \hat{H}_{\text{kin}} & \leftarrow \text{kinetic energy} \\ +\hat{H}_{\text{cou}} & \leftarrow \text{Coulomb interactions} \\ +\hat{H}_{\text{ee}} & \leftarrow \text{external electric field interaction} \\ +\hat{H}_Z & \leftarrow \text{Zeeman intercations} \\ +\hat{H}_{\text{so}} & \leftarrow \text{spin-orbit interactions} \\ +\hat{H}_{\text{ss}} & \leftarrow \text{spin-spin interactions} \\ +\hat{H}_{\text{oo}} & \leftarrow \text{spin-spin interactions} \\ +\hat{H}_{\text{dia}} & \leftarrow \alpha^4\text{diamagnetic interactions} \end{cases} \tag{1.16}$$

---

[2]In the Schrödinger picture.

Kinetic energy   The Breit-Pauli kinetic energy term in Equation 1.16 is

$$\hat{H}_{\text{kin}} = -\frac{1}{2}\sum_i \nabla_i^2 - \frac{\alpha^2}{8}\sum_i \nabla_i^4, \qquad (1.17)$$

where the first term is the common classical kinetic energy operator and the second term is the relativistic mass-velocity term. This term arises because of the dependence of mass on velocity. This is one of the larger relativistic corrections for slow electrons. The mass-velocity term is unbounded from below and should not be included in variational calculations[22].

Coulomb interactions   Coulomb interaction terms in the Breit-Pauli Hamiltonian (Equation 1.16) are the following,

$$\begin{aligned}
\hat{H}_{\text{cou}} = & -\sum_{iK} \frac{Z_K}{r_{iK}} + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{K\neq L}\frac{Z_k Z_L}{R_{KL}} \\
& + \frac{\alpha^2\pi}{2}\sum_{iK}Z_K\delta(\mathbf{r}_{iK}) - \frac{\alpha^2\pi}{2}\sum_{i\neq j}\delta(\mathbf{r}_{ij}) \\
& + \frac{2\pi}{3}\sum_{iK}Z_K R_K^2\delta(\mathbf{r}_{iK}) - \frac{1}{3}\sum_{iK}\frac{\text{tr}\,\Theta_K(3\mathbf{r}_{iK}\mathbf{r}_{iK}^T - r_{iK}^2 I_3)}{r_{ik}^5}.
\end{aligned} \qquad (1.18)$$

The first three terms are the nonrelativistic Coulomb point-charge interactions between nucles and electron, electron and electron and nucleus and nucleus, respectively. The fourth and fifth terms are the Darwin corrections caused by the Zitterbewegung of the electrons. Because the nuclear point-charge model is not always adequate, the second-to-last and last term correct errors from this approximation. Here, R_K is the nuclear extent and Θ_K is the nuclear quadropole moment. These terms are important in nuclear resonance studies[22] and nucllear quadropole resonance studies[1].

External electric field interactions   The Breit-Pauli Hamiltonian includes terms that model the effects of an externally applied scalar potential $\phi(\mathbf{r})$,

$$\hat{H}_{\text{ef}} = -\sum_i \phi_i + \sum_K Z_K\phi_K + \frac{\alpha^2}{\phi_K}\sum_i(\nabla_i \cdot \mathbf{E}_i). \qquad (1.19)$$

It is often safe to assume that the applied field are quite uniform on the molecular scale, and one therefore often expands Equation 1.19 in multipoles,

$$\hat{H}_{\text{ef}} = Q_{\text{tot}}\phi_0 - \mu_{\text{tot}} \cdot \mathbf{E}_0 - \frac{1}{2}\text{tr}\,\mathbf{Q}_{\text{tot}}\mathbf{V}_0 + \dots, \qquad (1.20)$$

where q_{tot} is the total charge of the molecule, μ_0 is the dipole moment, $\mathbf{Q}_{\text{tot}}$ is the second moment, and $\mathbf{V}_0$ is the electric field gradient. Higher-order terms are only necessary for fields that vary greatly in time.

Zeeman interactions   Paramagnetic interactions of the molecule with an externally applied magnetic field $\mathbf{B}$ are described by the Zeeman term in the Breit-Pauli Hamiltonian (Equation 1.16),

$$\hat{H}_Z = -\mathbf{B}\cdot\sum_i\left(-\frac{1}{2}\mathbf{l}_{iO} - \mathbf{s}_i + \frac{1}{2}\alpha^2\mathbf{s}_i\nabla_i^2\right) - \mathbf{B}\cdot\sum_K \mathbf{M}_K. \qquad (1.21)$$

The nuclear part, here represented by the last term in Equation 1.21, are on the order of 10^{-3} in atomic units. This is much smaller than the electronic part, given by the first sum in

Equation 1.21, but the nuclear part is very important in nuclear magnetic resonance (NMR) computations, where it determines the unshielded resonance lines in the spectra.

The first term inside the parenthesis in Equation 1.21 corresponds to Zeeman interaction with the magnetic moment generated by the orbital angular momentum of the electrons, $\mathbf{l}_{iO} = \mathbf{r}_{iO} \times \mathbf{p}_i$. The second and third terms in the paranthesis are electronic contributions to Zeeman effect from the spin of the electrons. The relativistic correction constituted in the third term is important in electron paramegnetic resonance (EPR) spectroscopy.

Spin-orbit interactions Up to second order in the fine-structure constant, the terms that couple motion of eletrons to particle spins in Equation 1.16 are

$$
\begin{aligned}
\hat{H}_{\text{so}} = & \frac{\alpha^2}{2} \sum_{iK} \frac{Z_K \mathbf{s}_i \cdot \mathbf{l}_{iK}}{r_{iK}^3} - \frac{\alpha^2}{2} \sum_{i \neq j} \frac{\mathbf{s}_i \mathbf{l}_{ij}}{r_{ij}^3} - \alpha^2 \sum_{i \neq j} \frac{\mathbf{s}_j \mathbf{l}_{ij}}{r_{ij}^3} \\
& + \alpha^2 \sum_{iK} \frac{\mathbf{M}_K \cdot \mathbf{l}_{iK}}{r_{iK}^3} + \frac{\alpha^2}{4} \sum_i (\mathbf{E}_i \times \mathbf{p}_i - \mathbf{p}_i \times \mathbf{E}_i)
\end{aligned}
\tag{1.22}
$$

When electron spin coupled to magnetic filed induced by other charges i motion we have spin-orbit interaction. The first term in Equation 1.22 models nuclear spin-orbit effect, the second term models interaction between the spin of a particle with its own orbit, the third is interaction with other orbits. The fourth term is known as the orbital hyperfin operator and couples magnetic moments to the orbital motion of electrons, while the fifth and last term is modles coupling of electric fields and orbits.

Spin-psin interaction All terms that arises in the Breit-Pauli Hamiltionian (Equation 1.16) due to coupling between magnetic momenta or spin of two particles are

$$
\begin{aligned}
\hat{H}_{\text{ss}} &= \frac{\alpha^2}{2} \sum_{i \neq j} \left[\frac{r_{ij}^2 \mathbf{s}_i \cdot \mathbf{s}_j - 3\mathbf{s}_i \cdot \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \mathbf{s}_j}{r_{ij}^5} - \frac{8\pi}{3} \delta(\mathbf{r}_{ij}) \mathbf{s}_i \cdot \mathbf{s}_j \right] \\
&= \alpha^2 \sum_{iK} \left[\frac{r_{iK}^2 \mathbf{s}_i \cdot \mathbf{M}_K - 3\mathbf{s}_i \cdot \mathbf{r}_{iK} \mathbf{r}_{iK} \cdot \mathbf{M}_K}{r_{iK}^5} - \frac{8\pi}{3} \delta(\mathbf{r}_{iK}) \mathbf{s}_i \cdot \mathbf{M}_k \right] \\
&= \frac{\alpha^2}{2} \sum_{K \neq L} \left[\frac{r_{KL}^2 (\mathbf{M}_K \mathbf{M}_L - 3(\mathbf{M}_K \cdot \mathbf{R}_{KL})(\mathbf{R}_{KL} \cdot \mathbf{M}_L)}{R_{KL}^5} \right]
\end{aligned}
\tag{1.23}
$$

Diamagnetic Interactions The magnitude of effects from diamagnetic interaction in the Breit-Pauli Hamiltonian (Equation 1.16) are terms of order α^4 or smaller. Most of these effects are only important in some cases where strong external magnetic fields are applied (NMR, EPR).

1.3.1 Atomic Units

In the Hamiltionian above (Equation 1.16), we have grown up and set $\hbar = m_e = e = \cdots = 1$. This is a result of using atomic units, a form of commonly used dimensionless units. To see how these units arise, consider the time-independent Schrödinger equation for a Hydrogen atom,

$$
\left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \phi = E\phi,
\tag{1.24}
$$

where $\hbar$ is the reduced Planck constant, equal to Planck's constant divided by 2π; m_e is the mass of the electron, $-e$ is the charge of the electron and ϵ_0 is the permitivity of free space. We make this equation dimensionless by letting $r \to \lambda r'$,

<div align="center">Tabelle 1.1: Conversion of atomic units to SI units.</div>

Physical quantity	Conversion factor	Value
Length	a_0	$5.2918 \times 10^{-11} m$
Mass	m_e	$9.1095 \times 10^{-31} kg$
Time	$\hbar/E_a$	$2.4189 \times 10^{-17} s$
Charge	e	$1.6022 \times 10^{-19} C$
Energy	E_a	$4.3598 \times 10^{-18} J$
Velocity	$a_0 E_a/\hbar$	$2.1877 \times 10^6 ms^{-1}$
Angular momentum	$\hbar$	$1.0546 \times 10^{-34} Js$
Electric dipole moment	ea_0	$8.4784 \times 10^{-30} Cm$
Electric polarizability	$e^2 a_0^2/E_a$	$1.6488 \times 10^{-41} C^2 m^2 J^{-1}$
Electric field	$E_a/(ea_0)$	$5.1423 \times 10^{11} Vm^{-1}$
Wave function	$a_0^{-3/2}$	$2.5978 \times 10^{15} m^{-3/2}$

$$\left(-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0\lambda r'}\right)\phi' = E\phi'. \tag{1.25}$$

We can factor out the constants in front of the operators, if we choose λ so that,

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = E_a \rightarrow \lambda\frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 \tag{1.26}$$

where E_a is the atomic unit of energy that chemists call Hartree. Incidently, we see that λ is just the Bohr radius, a_0. If we let $E' = E/E_a$, we obtain the dimensionless Schrödinger equation,

$$\left(-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right)\phi' = E'\phi'. \tag{1.27}$$

Some conversion factors between atomic units and SI units can be found in Table 1.1.

1.4   Indistinguishable Particles

In classical mechanics, although particles are indistinguishable, one typically regards particles as individuals because a permutation of particles is counted as a new arrangement and something different than the initial configuration. This was called "Transcedental Individuality" by Heinz Post[30]. In quantum mechanics, on the other hand, a permutation is not regarded as giving rise to a new arrangement. It follows that quantum objects are very different from anything else we know from everyday life, and must be considered "non-individual". By taken this idea to it's extreme one may postulate that all particles of a given type are one and the same. Here from a telephone call betwwen John Wheeler and Richard Feynman[8],

> I received a telephone call one day at the graduate college at Princeton from Professor Wheeler, in which he said, "Feynman, I know why all electrons have the same charge and the same mass" "Why?" "Because, they are all the same electron!"

Following the brief discussion above one may conclude that, the probability density for the location of particles in a system must be permutation invariant,

$$|\Psi(x_1, x_2, \ldots, x_i, x_j, \ldots, x_N)|^2 = |\Psi(x_1, x_2, \ldots, x_j, x_i, \ldots, x_N)|^2. \tag{1.28}$$

For any arbitrary permutation, this is equivalent to

$$\Psi(x_1, \ldots x_N) = e^{i\alpha(\sigma)} \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}), \tag{1.29}$$

where $\sigma \in S_N$ is some permutation of N indices and α is some real number that may be dependent on σ. The same relation can be written by way of a linear permutation operator,

$$(\hat{P}_\sigma \Psi)(x_1, \ldots, x_N) = \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}). \tag{1.30}$$

The 'indistinguishability postulate" states that if a permutation P is applied to a state representing an assembly of particles, there is no way of distinguishing between the permuted state and the original, by means of an observation at any time.

One can show (Difficult to show? exercise 2.2 in FYS-KJM4480) that

$$\hat{P}_\sigma \Psi = \begin{cases} \Psi \\ (-1)^{|\sigma|}\Psi \end{cases} \quad \forall \sigma \in S_N \tag{1.31}$$

where $|\sigma|$ is the number of transpositions in σ and the sign will be $(-1)^{|\sigma|} = \pm 1$. In the former case, when the sign is $+$, the wavefunction is "totally symmetric with respect to permutations"; while in the latter case, when the sign is $-$, the wavefunction is "totally anti-symmetric."

This leads us to another postulate in quantum theory that we have only two types of basic particles, *bosons* have totally symmetric wavefunctions only, while *fermions* have totally anti-symmetric wavefunctions only. "The physical consequences of this postulate seems to be in good agreement with experimental data" [23]. Moreover, all particles with integer spin are bosons, and all particles with half-integer spin are fermions [9, 28]. This can be proved in relativistic quantum mechanics, but must be accepted as an axiom in nonrelativistic theory[18]. Boson follow Bose-Einsten statistics and fermions follow Fermi-Dirac statistics.

To this day, particles with no other spin has been found, but norwegian physicists Jon Magne Leinaas and Jan Myrheim discovered that in one- and two dimensions, more general permutations symmetries are possible. The dubbed this third class of fundamental particles änyons"[23].

1.5 Representation of the Wavefunction

We have already invested some time in what the wave-function is, but some more time is necessary in order to build a nomenclature for writing down wavefunctions that actually describe many-electron systems with which we are concerned. For some smaller systems it can be satisfactory or even provident to use a single, special function to describe the entire system. Here however, we introduce the Slater determinant as we will only consider many-electron wavefunctions that can be written as a single Slater determinant or as a linear combination of several Slater determinants.

We define an *orbital*[3] which is the wavefunction for a single particle, or more precicely a single electron. The wavefunction a larger group of electrons, for instance those electrons surround an atom or molecule, we call the *molecular orbital*. We also discriminate between spatial orbitals which are functions of spatial coordinates; and spinorbitals, which are functions of the space and spin coordinates (typically a product of a spatial orbital and a spin function). A very complete description and thorough discussion of all things concerning electronic sructure wavefunctions is given by Szabo and Ostlund[40].

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[3]Sometimes also called a single-particle function, a single-particle orbital, a single-electron orbital or similar. There is a chance that these terms will be used interchangably throughout this text without warning.

1.5.1 Slater Determinants

The best description for a multiple-electron wavefunction, given by the independent-particle approximation is the Slater determinant,

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix} = \mathscr{A}\psi_1\psi_2\dots\psi_N, \tag{1.32}$$

where $\psi_i(\mu)$ is a spinorbital and $\mathscr{A}$ is the antisymmetriser. The spinorbitals, are single-particle functions in $L^2(X)$, not necessarily orthonormal.

To illustrate why this is a good approximation of the electronic wave function, condiser first the two-electron case,

$$\Phi_{N=2} = \frac{1}{\sqrt{(2)}}(\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)). \tag{1.33}$$

We see from this relatively simple expression that if the electrons where to occupy the same state. This ensures that the Pauli exclusion principle for fermions[29]. Moreover, if we switch coordinates of any two single-particle functions (spinorbitals), corresponding to the interchange of rows in Equation 1.32, the result is a change of sign. This attribute accomodates the total anti-symmetry necessary for a fermionic wavefunction.

Kapitel 2

Second Quantisation

Some Slater determinant is written,

$$|\Phi\rangle = |\phi_i \phi_j \phi_k \ldots \phi_z\rangle = |ijk \ldots z\rangle. \tag{2.1}$$

2.1 Creation and Annihilation Operators

The notation of creation and annihilation operators vary,

creation operator for spinorbital ϕ_i, $\hat{X}_i^\dagger, \hat{a}_i^\dagger, \hat{c}_i^\dagger, \hat{i}^\dagger$;

annihilation operator for spinorbital ϕ_i, $\hat{X}_i, \hat{a}_i, \hat{c}_i, \hat{i}$.

Herein, $\hat{a}_i^\dagger$, $\hat{a}_i$ is used and, if there is no change of confusion, $\hat{i}^\dagger$, $\hat{i}$.

The Creation Operator . For every single-particle index q, we define the creation operator $c_q^\dagger$ acting on the vacuum state by

$$\hat{a}_i^\dagger |0\rangle = |q\rangle. \tag{2.2}$$

For any slater determinant with $N > 0$, the action is defined by

$$\hat{a}_i^\dagger |jk \ldots z\rangle = |ijk \ldots z\rangle, \tag{2.3}$$

$$\hat{a}_i^\dagger |ijk \ldots z\rangle = 0 \tag{2.4}$$

The Annihilation Operator . It i sufficient to state that the annihilation c_i operator is the hermitian adjoint of the creation operator $\hat{c}_i$, but to specify we have

$$\hat{a}_i |0\rangle = 0, \tag{2.5}$$

as there is no particle in the vacuum state to annihilate.

For any arbitrary Slater determinant, we have

$$\hat{a}_i |ijk \ldots z\rangle = |ij \ldots z\rangle, \tag{2.6}$$

$$\hat{a}_i |jk \ldots z\rangle = 0 \tag{2.7}$$

SOMETHING MORE ABOUT THE DIFFERENT PERMUTATIONS.

We can now build a Slater determinant as the result of successive operation of several creation operators $\hat{a}_q^\dagger$ on the vacuum state,

$$\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \ldots \hat{a}_z^\dagger |0\rangle = |ijk \ldots z\rangle. \tag{2.8}$$

It is convenient to arrange the spinorbitals in a Slater determinant in alphabetical order, as in Equation 2.8. This makes it necessary to ascertain the effects a creation or annihilation operator will have on a Slater determinant when the affected orbital is not at the beginning of the string of orbitals in the Slater determinant. Generally we have,

$$\hat{P} |ijk \ldots z\rangle = (-1)^{\sigma(\hat{P})} |ijk \ldots z\rangle, \tag{2.9}$$

where $\hat{P}$ permutes the string of orbitals and $\sigma(\hat{P})$ is the parity of the permutation $\hat{P}$. we have

$$\hat{a}_p^\dagger |ijk \ldots z\rangle = (-1)^{\eta_p} |ijk \ldots p \ldots z\rangle, \tag{2.10}$$

$$\hat{a}_p |ijk \ldots p \ldots z\rangle = (-1)^{\eta_p} |ijk \ldots z\rangle, \tag{2.11}$$

where η_p is the number of orbitals preceeding the orbital ϕ_p, pertaining to the creation (annihilation) operator, in the Slater determinant.

2.2 Anticommutator Relations

Consider some creation operators acting on a Slater determinant,

$$\begin{aligned}
\hat{a}_p^\dagger \hat{a}_q^\dagger |ijk \ldots\rangle &= |pqijk \ldots\rangle \\
\hat{a}_q^\dagger \hat{a}_p^\dagger |ijk \ldots\rangle &= |qpijk \ldots\rangle = - |pqijk \ldots\rangle.
\end{aligned} \tag{2.12}$$

We demand that these two opartions be equivalent, or that

$$\begin{aligned}
\hat{a}_p^\dagger \hat{a}_q^\dagger &= -\hat{a}_q^\dagger \hat{a}_p^\dagger \\
\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} &\equiv \hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = \hat{0}.
\end{aligned} \tag{2.13}$$

This is one of several important anti-commutator relations for creation and annihilation operators.

Similarly, for annihilation operators we have

$$\begin{aligned}
\hat{a}_p \hat{a}_q |qpijk \ldots\rangle &= \hat{a}_p |pijk \ldots\rangle = |ijk \ldots\rangle \\
\hat{a}_q \hat{a}_p |qpijk \ldots\rangle &= -\hat{a}_q \hat{a}_p |pqijk \ldots\rangle = -\hat{a}_q |qijk \ldots\rangle = - |ijk \ldots\rangle.
\end{aligned} \tag{2.14}$$

These two operations must also be equivalent,

$$\begin{aligned}
\hat{a}_p \hat{a}_q &= -\hat{a}_q \hat{a}_p \\
\{\hat{a}_p, \hat{a}_q\} &\equiv \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = \hat{0}.
\end{aligned} \tag{2.15}$$

One case remains, when a creation operator and an annihilation operator is applied together on a Slater determinant,

$$\hat{a}_p^\dagger \hat{a}_q |qijk \ldots\rangle = \hat{a}_p^\dagger |ijk \ldots\rangle = |pijk \ldots\rangle. \tag{2.16}$$

This operation will replace ϕ_q by ϕ_p even if ϕ_p would have been somewhere else in the interior of the Slater determinant. Any sign change as an effect of moving the orbital to the front of the string would be negated when the orbital is moved back to the original position. Exchanging the order of the operators however,

$$\hat{a}_q \hat{a}_p^\dagger |qijk \ldots\rangle = \hat{a}_q |pqijk \ldots\rangle = -\hat{a}_q |qpijk \ldots\rangle = - |pijk \ldots\rangle. \tag{2.17}$$

We again see a sign change and have,

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \hat{0} \quad (p \neq q). \tag{2.18}$$

If, on the other hand, $p = q$ we have

$$\hat{a}_p^\dagger \hat{a}_p \left| pijk\ldots \right\rangle = \left| pijk\ldots \right\rangle,$$
$$\hat{a}_p \hat{a}_p^\dagger \left| pijk\ldots \right\rangle = 0, \tag{2.19}$$

and if the orbital ϕ_p in question does not appear in the Slater determinant,

$$\hat{a}_p^\dagger \hat{a}_p \left| ijk\ldots \right\rangle = 0,$$
$$\hat{a}_p \hat{a}_p^\dagger \left| ijk\ldots \right\rangle = \hat{a}_p \left| pijk\ldots \right\rangle = \left| ijk\ldots \right\rangle. \tag{2.20}$$

For all cases we have that,

$$\left(\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger \right) \left| \ldots \right\rangle = \left| \ldots \right\rangle, \tag{2.21}$$

or

$$\{\hat{a}_p^\dagger, \hat{a}_p\} = \{\hat{a}_p, \hat{a}_p^\dagger\} = \hat{1}. \tag{2.22}$$

In conclusion, the anti-commutator relations of the creation and annihilation operators are,

$$\{\hat{a}_p, \hat{a}_q\} = \hat{0}, \tag{2.23}$$
$$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \hat{0}, \tag{2.24}$$
$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \{\hat{a}_p, \hat{a}_q^\dagger\} = \hat{\delta}_{pq}. \tag{2.25}$$

2.3 Representation of Operators

A second-qunatised one-body operator is written like

$$\hat{h} = \sum_{i=1}^N \hat{h}(i) = \sum_{ij} \left\langle i \right| \hat{h} \left| j \right\rangle \hat{a}_i^\dagger \hat{a}_j, \tag{2.26}$$

where in general, $\left\langle p \right| \hat{h} \left| q \right\rangle$ is the matrix element of the single-particle operator $\hat{h}$ in a given one-particle basis,

$$\left\langle p \right| \hat{h} \left| q \right\rangle = \int dx \phi_p(x)^* \hat{h} \phi_q(x). \tag{2.27}$$

More accurately, we see from Equation 2.26, that $\hat{h}$ weighs each occupied orbital of a Slater determinant with the appropriate matrix element.

A second-quantised two-body operator is written like

$$\hat{w} = \sum_{i,j}^N \hat{w}(i,j) = \frac{1}{2} \sum_{ijkl} \left\langle ij \right| \hat{w} \left| kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k = \frac{1}{4} \sum_{ijkl} \left\langle ij \| kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k, \tag{2.28}$$

where

$$\left\langle ij \right| \hat{w} \left| kl \right\rangle \equiv \left\langle i(1)j(2) \right| \hat{w}_{12} \left| k(1)l(2) \right\rangle \tag{2.29}$$

and the antisymmetric two-eletron integral for $\hat{u}$ is abreviated,

$$\left\langle ij \right| \hat{w} \left| kl \right\rangle - \left\langle ij \right| \hat{w} \left| kl \right\rangle = \left\langle ij \right| \hat{w} \left| kl \right\rangle \equiv \left\langle ij \| kl \right\rangle. \tag{2.30}$$

Similarly to the one-particle operator, the two-particle operator assigns the correct matrix element to pairs of single particle functions.

The second-quantised Hamiltonian can therefore be written,

$$\hat{H} = \hat{h} + \hat{w} = \sum_{ij} \hat{h}_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{4} \left\langle ij \| kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k. \tag{2.31}$$

2.4 Normal Order and Wick's Theorem

We have built the foundations necessary to describe wavefunctions in terms of creation- and annihilation operators as well as a simple way of writing a general electronic Hamiltionian in the second-quantised manner. The following is a necessety to be able to compute vacuum expectation values ($\langle -| \hat{A}\hat{B} \ldots |-\rangle$) of products of creation- and annihilation operators. Such expectation values are very important for several computational methods, see Harris, Monkhorst and Freeman (1992)[12].

2.4.1 Normal ordering and contractions

The normal-ordered product of a string of operators $\hat{A}_1$, $\hat{A}_2$, $\hat{A}_3$, ..., is defined as the rearranged product of operators such that all the creation operators are the left of all the annihilation operators, including a phase factor corresponding to the parity of the permutation producing the rearrangent

$$
\begin{aligned}
n[\hat{A}_1\hat{A}_2 \ldots \hat{A}_n] &\equiv (-1)^{|\sigma|} \hat{A}_{\sigma(1)}\hat{A}_{\sigma(2)} \ldots \hat{A}_{\sigma(n)} \\
&= (-1)^{\sigma(\hat{P})} \hat{P}(\hat{A}_1\hat{A}_2 \ldots \hat{A}_n) \\
&= (-1)^{|\sigma|} [\text{creation operators}] \cdot [\text{annihilation operators}] \\
&= (-1)^{|\sigma|} \hat{a}^\dagger \hat{b}^\dagger \ldots \hat{u}\hat{v},
\end{aligned} \tag{2.32}
$$

where $\hat{P}$ is a permutation operator actiing on the product of operators, and σ is the parity of the permutation. One should bear in mind that this definition is by no means unique. Here are some examples,

$$
n[\hat{a}^\dagger \hat{b}] = \hat{a}^\dagger \hat{b} \quad n[\hat{b}\hat{a}^\dagger] = -\hat{a}^\dagger \hat{b}
$$

$$
n[\hat{a}\hat{b}] = \hat{a}\hat{b} = -\hat{b}\hat{a}
$$

$$
n[\hat{a}^\dagger \hat{b}^\dagger] = \hat{a}^\dagger \hat{b}^\dagger = -\hat{b}^\dagger \hat{a}^\dagger
$$

$$
n[\hat{a}^\dagger \hat{b}\hat{c}^\dagger \hat{d}] = -\hat{a}^\dagger \hat{c}^\dagger \hat{b}\hat{d} = \hat{c}^\dagger \hat{a}^\dagger \hat{b}\hat{d} = \hat{a}^\dagger \hat{c}^\dagger \hat{d}\hat{b} = -\hat{c}^\dagger \hat{a}^\dagger \hat{d}\hat{b}.
$$

Note that the second quantised Hamiltonian in Equation 2.31 is already on normal-ordered form.

For two arbitrary creation and annihilation operators, we define their contraction as

$$
\overset{\frown}{\hat{A}\hat{B}} \equiv \langle -| \hat{A}\hat{B} |-\rangle , \tag{2.33}
$$

equivalently,

$$
\overset{\frown}{\hat{A}\hat{B}} \equiv \hat{A}\hat{B} - n[\hat{A}\hat{B}]. \tag{2.34}
$$

For a creation- and annihilation operator there are four possible contractions,

$$
\begin{aligned}
\overset{\frown}{\hat{a}^\dagger \hat{b}^\dagger} &= \langle -| \hat{a}^\dagger \hat{b}^\dagger |-\rangle = \hat{a}^\dagger \hat{b}^\dagger - n[\hat{a}^\dagger \hat{b}^\dagger] = 0 \\
\overset{\frown}{\hat{a}\hat{b}} &= \langle -| \hat{a}\hat{b} |-\rangle = \hat{a}\hat{b} - n[\hat{a}\hat{b}] = 0 \\
\overset{\frown}{\hat{a}^\dagger \hat{b}} &= \langle -| \hat{a}^\dagger \hat{b} |-\rangle = \hat{a}^\dagger \hat{b} - n[\hat{a}^\dagger \hat{b}] = 0 \\
\overset{\frown}{\hat{a}\hat{b}^\dagger} &= \langle -| \hat{a}\hat{b}^\dagger |-\rangle = \hat{a}\hat{b}^\dagger - n[\hat{a}\hat{b}^\dagger] = \hat{a}\hat{b}^\dagger - (-\hat{b}^\dagger \hat{a}) = \{\hat{a}, \hat{b}^\dagger\} = \delta_{ab}.
\end{aligned} \tag{2.35}
$$

We see that all contractions between creation- and annihilation operators are a number, most of them are zero and only those with a annihilation operator to the left and a creation operator to the right can be one.

Contrations inside a normal ordered product is definded as follows,

$$n[\hat{A}\hat{B}\hat{C}\ldots\overbrace{\hat{R}\ldots\hat{S}\ldots\hat{T}}\ldots\hat{U}\ldots] = (-1)^\sigma \hat{R}\hat{T}\hat{S}\hat{U}\ldots n[\hat{A}\hat{B}\hat{C}\ldots], \tag{2.36}$$

where all contracted operator pairs are moved to the front of the normal ordered product, and σ is the parity of the permutations required for this relocation. The result will be zero, or plus or minus the normal ordred product without the contracted operator pairs.

2.4.2 Wick's Theorem

Wick's theorem states that every string of creation and annihilation operators can be written as a sum of normal-ordered products with all possible contractions,

$$\hat{A}\hat{B}\hat{C}\hat{D}\cdots = n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots]$$
$$+ \cdots + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \cdots + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \cdots + \tag{2.37}$$
$$+ n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \ldots,$$

where eventually all possible contractions of one, two pairs etc, are included.

Especially when computing vacuum expectation values of normal-ordred products is Wick's theorem very important. The reason for this is that each contraction will not contribute to the result, unless it is a fully contracted operator string,

$$\langle| \hat{A}\ldots\hat{B}\ldots\hat{C}\ldots\hat{D}\ldots |\rangle = \sum_{\substack{\text{all possible} \\ \text{contractions}}} \langle| n[\hat{A}\ldots\hat{B}\ldots\hat{C}\ldots\hat{D}\ldots] |\rangle. \tag{2.38}$$

Most vacuum expectation values contain operators strings already have substrings that are already normal-ordered. This warrants a very useful generalisation of Wick's theorem for such strings,

$$n[\hat{A}_1\hat{A}_2\ldots]n[\hat{B}_1\hat{B}_2\ldots]\ldots n[\hat{Z}_1\hat{Z}_2\ldots] = n[\hat{A}_1\hat{A}_2\cdots:\hat{B}_1\hat{B}_2\cdots:\cdots:\hat{Z}_1\hat{Z}_2\ldots]$$
$$+ \sum_{(1)} n[\hat{A}_1\hat{A}_2\cdots:\hat{B}_1\hat{B}_2\cdots:\cdots:\hat{Z}_1\hat{Z}_2\ldots] + \cdots + \sum_{(n)} n[\hat{A}_1.\ldots\ldots\ldots\hat{Z}_N], \tag{2.39}$$

where we sum over all combinations of contractions that each involce operators from different substrings, starting with one contractions and up to when all opertors, or as many as possible, are contracted.

2.4.3 Particle-Hole Formalism

We see that a Slater determinant can be built recursively with creation operators,

$$\hat{I} = i_1 i_2 \hat{.}\ldots i_N = \hat{i}_1^\dagger \hat{i}_2^\dagger \ldots \hat{i}_N^\dagger |\rangle. \tag{2.40}$$

Instead of rewriting Slater determinants with operators applied to the vacuum state in this manner we will introduce the convenient reference state, or Fermi vacuum, Slater determinant,

$$|0\rangle = |\Phi_0\rangle = |ijk\ldots n\rangle. \tag{2.41}$$

We will define other Slater determinants relative to this reference state. For instance,

$$|\Phi_i^a\rangle \equiv \hat{a}^\dagger\hat{i}\,|\Phi_0\rangle = |ajk\ldots n\rangle \tag{2.42}$$

$$|\Phi_{ij}^{ab}\rangle \equiv \hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\,|\Phi_0\rangle = |abk\ldots n\rangle \tag{2.43}$$

$$|\Phi_i\rangle \equiv \hat{i}\,|\Phi_0\rangle = |jk\ldots n\rangle \tag{2.44}$$

$$|\Phi^a\rangle \equiv \hat{a}^\dagger\,|\Phi_0\rangle = |aijk\ldots n\rangle \tag{2.45}$$

where equations 2.42, 2.43 2.44 and 2.45 constitues a single excitation, a double excitation, an electorn removal and an electron attachment, respectively. Note that these reference relative Slater determinants have the following properties,

$$\left|\Phi_{ij}^{ab}\right\rangle = \left|\Phi_{ji}^{ba}\right\rangle = -\left|\Phi_{ij}^{ba}\right\rangle = -\left|\Phi_{ji}^{ab}\right\rangle. \tag{2.46}$$

Take note of the specific letters used for creating and annihilating electrons in the example above. $i, j, k, l, \ldots$ are letters restricted to indices of *hole* states, $a, b, c, d, \ldots$ are letters restriced to indices of *particle* states and the $p, q, r, \ldots$ are for general use, indicating any state. Notice that

$$\begin{aligned} \hat{i}^\dagger\,|0\rangle &= 0 \quad \hat{a}\,|0\rangle = 0, \\ \langle 0|\,\hat{i} &= 0 \quad \langle 0|\,\hat{a}^\dagger = 0. \end{aligned} \tag{2.47}$$

Whenever we try to insert an electron where there already is one, or when we try to remove an electron that is not there, we get zero as result.

2.4.4 Wick's theorem relative to the Fermi vacuum

Now we will modify the concepts of normal-ordering, contractions and Wick's theoreom so that the work better in conjunction with the Fermi vacuum, instead of the physical vacuum.

First we introduce pseudo-operators,

$$\begin{aligned} \hat{b}_i &= \hat{i}^\dagger, \quad \hat{b}_i^\dagger = \hat{i} \\ \hat{b}_a &= \hat{a}^\dagger, \quad \hat{b}_i^\dagger = \hat{a}^\dagger, \end{aligned} \tag{2.48}$$

where $\hat{b}_i^\dagger$ is a hole creation operator and $\hat{b}_i$ is a particle creation operator, but only for vacant spaces below the fermi level. The reasoning for introducing such operators is to be able to work with the fermi vacuum in the same manner as regular operators work with the physical vacuum.

We introduce a new type of normal ordering for the pseudo-operators (and for the actual operators that the represent),

$$\{\hat{A}\hat{B}\hat{C}\} = (-1)\hat{b}_p^\dagger\hat{b}_q^\dagger\ldots\hat{b}_u\hat{b}_v. \tag{2.49}$$

We write a contraction in the same manner,

$$\overset{\frown}{\hat{A}\hat{B}} = \hat{A}\hat{B} - \{\hat{A}\hat{B}\}. \tag{2.50}$$

A normal-ordered product with contractions inside is also definede the same way.

For contractions we see that the only non-zero contractions are

$$\overset{\frown}{\hat{b}_i\hat{b}_j^\dagger} = \overset{\frown}{\hat{i}^\dagger\hat{j}} = \delta_{ij}, \quad \overset{\frown}{\hat{b}_a\hat{b}_b^\dagger} = \overset{\frown}{\hat{a}\hat{b}^\dagger} = \delta_{ab}. \tag{2.51}$$

Here we are also made aware the first benefit of pseudo-operators. More generally we have the anticommutator relations

$$\{\hat{b}_p, \hat{b}_q^\dagger\} = \delta_{pq}, \quad \{\hat{b}_p, b_q\} = 0 \tag{2.52}$$

Excited Slater determinants can be written using pseudo-operators,

$$|\Phi_i^a\rangle \equiv \hat{b}_a^\dagger \hat{b}_i^\dagger |\Phi_0\rangle \tag{2.53}$$

$$\left|\Phi_{ij}^{ab}\right\rangle \equiv \hat{b}_b^\dagger \hat{b}_j^\dagger \hat{b}_a^\dagger \hat{b}_i^\dagger |\Phi_0\rangle \tag{2.54}$$

Teil II

Quantum Many-Body Approximations

Kapitel 3

Hartree-Fock Theory

In 1927, soon after the discovery of the Schrödinger equation in 1926, Douglas R. Hartree introduced a procedure which he called the self-consistent field method[13]. Hartree sought to do without empirical parameters and to solve the many-body time-independent Schrödinger equation from fundamental principles, *ab initio*. A year later John C. Slater and John A. Gaunt provided a sounder theoretical basis for the Hartree method by applying the variational principle to a trial wave function as a product of single-particle functions[38][11]. Slater later pointed out, with support from Vladimir A. Fock, that the method merely applied the Pauli exclusion principle in its older, incorrect formulation; forbidding presence of two electrons in the same state, but neglecting quantum statistics[37][10]. It was shown that a Slater determinant satisfies the antisymmetric property of the exact solution and would be a suitable ansatz for applying the variational principle. Later, Hartree reformulated the method for calculation[14].

The Hartree-Fock methods makes the following simplications to the multi-electron atomic (molecular) problem,

- The full molecular wavefunction is contrained to a function of the coordinates of only the electrons in the molecule. In not so many words, the Born-Oppernheimer approximation is inerent in the method.

- Any relativistic effects are completely ignored, i.e. the momentum operator is assumed to be completely non-relativistic.

- A variational solution is assumed to be a linear combination of a basis set, which is assumed to be approximately complete. This set of basis functions is usually orthogonal, but may not be.

- Some electron correlation effects are ignored, as the methods implies a mean-field approximation. Coulomb correlation is fully incorporated in the Hartree-Fock method, but it ignores Fermi Correlation and is therefore inable to describe some effects, like London dispersion[1].

- Any energy eigenfunction is assumed to be describable by a single Slater determinant.

Relaxation of the last two simplifications give rise to the large group of many-body methods commonly referred to as post-Hartree-Fock methods.

---

[1]Named after Fritz London; London dispersion forces (LDF) are a type of force between atoms and molecules[15]

3.1   Deriving the Hartree-Fock Equations

Consider a Hamiltionian for some system

$$\hat{H} = \hat{H}_0 + \hat{W}, \quad \hat{H}_0 = \sum_i^N \hat{h}(i), \tag{3.1}$$

where the ground state of $\hat{H}_0$ is a Slater determinant consisting of N single-particle functions,

$$\Phi = \mathscr{A}\phi_1\phi_2\ldots\phi_N, \quad \langle\phi_i|\phi_j\rangle = \delta_{ij}. \tag{3.2}$$

If $\hat{W}$ is only a limited perturbation to the system, it is reasonable to assume that the actual ground state of the full system can also be represented by a Slater determinant. Because the Hartree-Fock theory includes a mean-field approximation, each particle moves independently of the others interacting with the remainding electrons only idirectly through an average potential $\hat{v}^{\mathrm{HF}}$.

The expectation value of the Hamiltionian in Equation 3.1 is

$$\langle\Phi|\,\hat{H}\,|\Phi\rangle = \sum_i \langle\phi_i|\,\hat{h}\,|\phi_i\rangle + \frac{1}{2}\sum_{ij} \langle\phi_i\phi_k|\,\hat{w}\,|\phi_i\phi_j - \phi_j\phi_i\rangle\,, \tag{3.3}$$

where

$$\langle\phi_i\phi_j|\,\hat{w}\,|\phi_k\phi_l\rangle = \int\int \bar{\phi}_i(1)\bar{\phi}_j(2)\hat{w}(1,2)\phi_k(1)\phi_l(2)d1d2$$

Now we want to minimise the energy (Equation 3.1) under the contraint of orthonormal single-particle functions, id est $\langle\phi_i|\phi_k\rangle = \delta_{ij}$. The minimum solution is called the Hatree-Fock state, $|\Phi_{\mathrm{HF}}\rangle$. An optimisation problem with a constraint begs the formualtion of a Lagrangian functional with a Lagrange multiplier for each constraint,

$$\begin{aligned}
\mathscr{L}(\phi_1,\ldots,\phi_n,\lambda) &= \langle\Phi|\,\hat{H}\,|\Phi\rangle - \sum_{ij}\lambda_{ij}(\langle\phi_i|\phi_j\rangle - \delta_{ij}) \\
&= \sum_i \langle\phi_i|\,\hat{h}\,|\phi_i\rangle + \frac{1}{2}\sum_{ij}\langle\phi_i\phi_j|\,\hat{w}\,|\phi_i\phi_j - \phi_j\phi_i\rangle - \sum_{ij}\lambda_{ij}(\langle\phi_i|\phi_j - \delta_{ij}\rangle).
\end{aligned} \tag{3.4}$$

The constraints can always be treated separately, $\partial\mathscr{L}/\partial\lambda_{ij}\langle\phi_i|\phi_j\rangle - \delta_{ij}$, as this demand will be fullfilled by finding that the solutions ϕ_i are orthonormal.

In order to find the optimum of the Lagrangian in (Equation 3.4), we choose a $k \in \{1,\ldots,N\}$ and compute the directional derivative of ϕ_k^*, by varying this single particle function and leaving all others fixed,

$$\delta\phi_k = \epsilon\eta, \quad \delta\phi_l = 0, k \neq l, \tag{3.5}$$

where ϵ is some small number, and η is a normalized single-particle function. We define a function representing this variation,

$$f(\epsilon) = \mathscr{L}(\phi_1,\ldots,\phi_k + \epsilon\eta,\ldots,\phi_N,\lambda), \tag{3.6}$$

expanded to first order in ϵ,

$$f(\epsilon) = f(0) + \epsilon f'(0) + \mathscr{O}(\epsilon^2). \tag{3.7}$$

For an optimum we must have

$$f'(0) = 0, \quad \forall\eta, \tag{3.8}$$

which means that the directional derivative of $\mathscr{L}$ at $\{\phi_i\}_{i=1}^N$, in the direction η vanishes.

We compute the Taylor expansion of the varied Lagrangian (Equation 3.6),

$$f(\epsilon) = \sum_i \langle \phi_i + \delta_{ki}\epsilon\eta | \, \hat{h} \, | \phi_i \rangle + \frac{1}{2} \sum_{ij} \langle (\phi_i + \delta_{ki}\epsilon\eta)(\phi_j + \delta_{kj}\epsilon\eta) | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle$$
$$- \sum_{ij} \lambda_{ij}(\langle \phi_i + \delta_{ik}\epsilon\eta | \phi_j \rangle - \delta_{ij}) + \mathcal{O}(\epsilon^2) \tag{3.9}$$

$$= \sum_i \langle \phi_i | \, \hat{h} \, | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle + \epsilon \langle \eta | \, \hat{h} \, | \phi_k \rangle$$
$$+ \frac{1}{2} \sum_{ij} \langle \phi_i\delta_{kj}\epsilon\eta | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle$$
$$+ \frac{1}{2} \sum_{ij} \langle \delta_{ki}\epsilon\eta\phi_j | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle \tag{3.10}$$
$$- \sum_{ij} \lambda_{ij}(\langle \phi_i|\phi_j \rangle - \delta_{ij}) - \sum_{ij} \lambda_{ij}(\langle \delta_{ik}\epsilon\eta|\phi_j \rangle - \delta_{ij}) + \mathcal{O}(\epsilon^2)$$

$$= \sum_i \langle \phi_i | \, \hat{h} \, | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle + \epsilon \langle \eta | \, \hat{h} \, | \phi_k \rangle - \sum_{ij} \lambda_{ij}(\langle \phi_i|\phi_j \rangle - \delta_{ij})$$
$$+ \frac{1}{2}\epsilon \sum_i \langle \phi_i\eta | \, \hat{w} \, | \phi_i\phi_k \rangle - \frac{1}{2}\epsilon \sum_i \langle \phi_i\eta | \, \hat{w} \, | \phi_k\phi_i \rangle$$
$$+ \frac{1}{2}\epsilon \sum_j \langle \eta\phi_j | \, \hat{w} \, | \phi_k\phi_j \rangle - \frac{1}{2}\epsilon \sum_j \langle \eta\phi_j | \, \hat{w} \, | \phi_j\phi_k \rangle \tag{3.11}$$
$$- \epsilon \sum_j \lambda_{jk} \langle \eta|\phi_j \rangle + \mathcal{O}(\epsilon^2)$$

$$= \sum_i \langle \phi_i | \, \hat{h} \, | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \, \hat{w} \, | \phi_i\phi_j - \phi_j\phi_i \rangle - \sum_{ij} \lambda_{ij}(\langle \phi_i|\phi_j \rangle - \delta_{ij})$$
$$+ \epsilon \langle \eta | \, \hat{h} \, | \phi_k \rangle + \epsilon \sum_i \langle \eta\phi_i | \, \hat{w} \, | \phi_k\phi_i \rangle - \epsilon \sum_i \langle \eta\phi_i | \, \hat{w} \, | \phi_i\phi_k \rangle \tag{3.12}$$
$$- \epsilon \sum_j \lambda_{jk} \langle \eta|\phi_j \rangle + \mathcal{O}(\epsilon^2)$$

Notice that the zeroth term, represented by the first line in Equation 3.12, is simply the original Lagrangian in Equation 3.4. We equate all the first-order terms to zero,

$$\langle \eta | \, \hat{h} \, | \phi_k \rangle + \sum_i \langle \eta\phi_i | \, \hat{w} \, | \phi_k\phi_i \rangle - \sum_i \langle \eta\phi_i | \, \hat{w} \, | \phi_i\phi_k \rangle - \sum_i \lambda_{ik} \langle \eta|\phi_i \rangle = 0. \tag{3.13}$$

This must be valid for any choice η, meaning

$$\hat{h} \, | \phi_k \rangle + \sum_i \langle \cdot \, \phi_i | \, \hat{w} \, | \phi_k\phi_i \rangle - \sum_i \langle \cdot \, \phi_i | \, \hat{w} \, | \phi_i\phi_k \rangle - \sum_i \lambda_{ik} \, | \phi_i \rangle = 0, \tag{3.14}$$

where $\langle \cdot \, \phi_1 | \, \hat{w} \, | \phi_2\phi_3 \rangle \in L_1^2$ is interpreted as an integral over only the second particle in the matrix element. We define,

$$\hat{v}_{\text{HF}} = \hat{v}_{\text{direct}} + \hat{v}_{\text{exchange}} = \sum_i \langle \cdot \, \phi_i | \, \hat{w} \, | \phi_k\phi_i \rangle - \sum_i \langle \cdot \, \phi_i | \, \hat{w} \, | \phi_i\phi_k \rangle \tag{3.15}$$

$$\hat{f} = \hat{h} + \hat{v}_{\text{HF}}, \tag{3.16}$$

and can then rewrite Equation 3.14 to

$$\hat{f} \left| \phi_i \right\rangle = \sum_j \lambda_{ij} \left| \phi_j \right\rangle, \tag{3.17}$$

which are the non-canonical Hartree-Fock equations.

It so happends that the Slater dertminant $|\Phi\rangle$ is invariant under unitary transformation of the single particle functions. Consider

$$\tilde{\phi}_k = \sum_j \phi_j U_{jk}, \tag{3.18}$$

where U is a unitary matrix. This implies that $\left| \tilde{\Phi} \right\rangle = \det(U) |\Phi\rangle$, is the same state and the energy must be the same as well. We choose a particular unitary transformation U, rotating the single particle functions in a certain manner so that $\lambda = UEU^H$, where $E_{jk} = \delta_{jk}\epsilon_k$ are the elemnets of a diagonal matrix (the eigenvalues of λ). This provides us with a new set of eigenvalue equations,

$$\hat{f}(\tilde{\phi}_1, \ldots, \tilde{\phi}_N) \left| \tilde{\phi}_i \right\rangle = \epsilon_i \left| \tilde{\phi}_i \right\rangle, \tag{3.19}$$

which are the canonical Hartree-Fock equations. From now on we will stick with these equations and suppress the tilde notations.

3.2   The Roothan-Hall Equations

In order to solve the Hartree-Fock equations (Equation 3.19) we render the equations in a finite, fixed basis $\{\chi_p\}_{p=1}^L$ of a finite size L. It is not a necessity for this basis to be orthonormal, and we therefore define the overlap matrix,

$$S_{pq} \equiv \langle \chi_p | \chi_q \rangle. \tag{3.20}$$

The Hartree-Fock single-particle functions are expanded in this basis,

$$\left| \phi_p \right\rangle = \sum_q \left| \chi_q \right\rangle U_{qp}, \tag{3.21}$$

where U is not necessarily unitary, because the basis is not necessarily orthongonal. However, we do have $U^H S U = \hat{1}$.

We insert the expansion from Equation 3.21 into the expression for the canonical Hatree-Fock equations from Equation 3.19,

$$\hat{f} \sum_r \left| \chi_r \right\rangle U_{rp} = \epsilon_p \sum_r \left| \chi_r \right\rangle U_{rp}. \tag{3.22}$$

Then we left project with an arbitrary function from our new basis,

$$\begin{aligned} \langle \chi_q | \hat{f} \sum_r |\chi_r\rangle U_{rp} &= \epsilon_r \langle \chi_q | \chi_r \rangle \sum_r U_{rp} \ \forall q, p \\ \sum_r F_{qr} U_{rp} &= \epsilon_r \sum_r S_{qr} U_{rp} \ \forall q, p \\ F(D)U &= SU\epsilon. \end{aligned} \tag{3.23}$$

where the last line is the Roothan-Hall equations.

Elaborating on the computation of the Fock matrix element,

$$F_{qp} = \langle \chi_q | \hat{f} | \chi_p \rangle = \langle \chi_q | \hat{h} | \chi_p \rangle + \langle \chi_q | \hat{v}_{\text{direct}} | \chi_p \rangle - \langle \chi_q | \hat{v}_{\text{exchange}} | \chi_p \rangle, \tag{3.24}$$

where

$$
\begin{aligned}
\langle \chi_q | \hat{v}_{\text{direct}} | \chi_p \rangle &= \sum_j \langle \chi_q \phi_j | \hat{w} | \chi_p \phi_j \rangle = \sum_{p'q'j} U_{jq'} U_{jp'}^* \langle \chi_q \chi_{q'} | \hat{w} | \chi_p \chi_{p'} \rangle \\
&= \sum_{p'q'} D_{p'q'} \langle \chi_q \chi_{q'} | \hat{w} | \chi_p \chi_{p'} \rangle
\end{aligned}
\tag{3.25}
$$

$$
\begin{aligned}
\langle \chi_q | \hat{v}_{\text{exchange}} | \chi_p \rangle &= \sum_j \langle \chi_q \phi_j | \hat{w} | \phi_j \chi_p \rangle = \sum_{p'q'j} U_{jq'} U_{jp'}^* \langle \chi_q \chi_{q'} | \hat{w} | \chi_{p'} \chi_p \rangle \\
&= \sum_{p'q'} D_{p'q'} \langle \chi_q \chi_q' | \hat{w} | \chi_p' \chi_p \rangle,
\end{aligned}
\tag{3.26}
$$

giving us,

$$F_{qp} = \langle \chi_q | \hat{h} | \chi_p \rangle + \sum_{p'q'} D_{p'q'} (|\chi_q \chi_{q'}\rangle \hat{w} | \chi_p \chi_{p'} \rangle - |\chi_q \chi_{q'}\rangle \hat{w} | \chi_{p'} \chi_p \rangle), \tag{3.27}$$

where $D = UU^H$, is the density matrix.

The benefit of the Roothan-Hall equations (Equation 3.21), is that they are represented by matrices, and therefore easy to implement on a computer. The Roothan-Hall equations are solved iterably, starting from an initial guess for U. This guess can be used to compute the density matrix, $D^{(}k) = \sum_i u_i^{(k)} (u_i^{(k)})^*$, where k denotes the iteration. The density matrix is used to compute the Fock matrix. This provides us with a general eigenvalue problem, from which a new U and ϵ can be found. This formula is then repeated until the the iterations converge. At this point we say that we have self-consitency in the mean field, and this method is usually called the method of self-constistent field (SCF) iterations.

3.3   [UNFINISHED] Restricted Hartree-Fock Theory

3.4   [UNFINISHED] Unrestricted Hartree-Fock Theory

Kapitel 4

Perturbation Theory

Perturbation theory is a very powerful method and a generic method applicable to all matrix problems. Additionally, perturbation theory is relatively cheap in terms of computing time especially compared with coupled cluster theory. As the method provides a different route to the solution of the Schrödinger equation, by approaching the exact solution systematically, based on an order-by-order expansion of the energy and wave function. Therefore, perturbation theory is often used to improve the results from other computation schemes. What is more, the exponential form of the wave function in coupled cluster theory stems from the non-degenerate Rayleigh-Schrödinger perturbation theory (RSPT) expansion.

4.1 Formal perturbation theory

We split the Hamiltonian into a known part and a perubed part,

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{4.1}$$

Sometimes it is convenient to write

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \tag{4.2}$$

where we have included an örder parameter"λ. This parameter is used to categorise the contributions of different order. The exact solution is given by

$$\hat{H} \Psi_n = E_n \Psi_n$$
$$(\hat{H}_0 + \hat{V}) \Psi_n = E_n \Psi_n, \quad \Psi_n = \Phi_n + \chi_n \tag{4.3}$$

while the solvable and simple zero order problem is given by

$$\hat{H}_0 \Phi_n = E_n^{(0)} \Phi_n \tag{4.4}$$

By projecting Equation 4.3 with $\langle \Phi_0 |$ we get

$$\langle \Phi_n | \hat{H}_0 | \Psi_n \rangle + \langle \Phi_n | \hat{V} | \Psi_n \rangle = E_n \langle \Phi_n | \Psi_n \rangle$$
$$\rightarrow E_n = \langle \Phi_n | \hat{H} | \Psi_n \rangle \tag{4.5}$$
$$\rightarrow \Delta E_n = E_n - E_n^0 = \langle \Phi_n | \hat{V} | \Psi_n \rangle$$

where we have used that

$$\langle \Phi_m | \Phi_n \rangle = \delta_{mn} \tag{4.6}$$
$$\langle \Psi_n | \Phi_n \rangle = \langle \Phi_n + \chi_n | \Phi_n \rangle = 1 \tag{4.7}$$
$$\langle \Psi_n | \Psi_n \rangle = 1 + \langle \chi_n | \chi_n \rangle. \tag{4.8}$$

This is called the intermediate normalisation assumption.

4.1.1   Energy- and Wavefunction Expansion

We now have need for the order parameter from λ Equation 4.2 as we expand the wavefunction and energy,

$$\Psi_n = \Phi_n + \chi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \dots \quad (\Psi_n^{(0)} \equiv \Phi_n)$$
$$E_n = E_n^{(0)} + \Delta E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{4.9}$$

We insert these expansions into the Schrödinger equation,

$$(\hat{H} - E_n)\Psi_n = 0$$
$$(\hat{H}_0 + \lambda\hat{V})\Psi_n = 0, \tag{4.10}$$

resulting in

$$(\hat{H}_0 + \lambda\hat{V} - E_n^{(0)} - \lambda E_n^{(1)} - \lambda^2 E_n^{(2)} - \dots)(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda\Psi_n^{(2)} + \dots) = 0. \tag{4.11}$$

Now we gather the coefficients of different powers of λ,

$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(0)} = 0 \tag{4.12}$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(1)} = (E_n^{(1)} - \hat{V})\Psi_n^{(0)} \tag{4.13}$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(2)} = (E_n^{(1)} - \hat{V})\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)} \tag{4.14}$$
$$\dots$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(m)} = (E_n^{(1)} - \hat{V})\Psi_n^{(m-1)} + \sum_{l=0}^{m-2} E_n^{(m-l)}\Psi_n^{(l)}. \tag{4.15}$$

Where the last line gives a general mth-order equation. This equation can be simplified somewhat,

$$(E_n^{(0)} - \hat{H}_0)\Psi_n^{(m)} = \hat{V}\Psi_n^{(m-1)} - \sum_{l=0}^{m-1} E_n^{(m-l)}\Psi_n^{(l)}. \tag{4.16}$$

By applying $\langle\Phi_n|$ to each of the equations, we get expressions for $E_n^{(m)}$. For λ^1 (Equation 4.13) we get,

$$\langle\Phi_n|\,\hat{H}_0 - E_n^{(0)}\,\big|\Psi_n^{(1)}\big\rangle = \langle\Phi_n|\,E_n^{(1)} - \hat{V}\,|\Phi_n\rangle$$
$$\big\langle(\hat{H}_0 - E_n^{(0)})\Phi_n\big|\Psi_n^{(1)}\big\rangle = \langle\Phi_n|\,E_n^{(1)} - \hat{V}\,|\Phi_n\rangle \tag{4.17}$$
$$\rightarrow E_n^{(1)} = \langle\Phi_n|\,\hat{V}\,|\Phi_n\rangle = \hat{V}_{nn}$$

Since we have an expression for $E_n^{(1)}$, we can solve the inhomogeneous differential equation for $\Psi_n^{(1)}$, by also requiring the intermediate normalisation condition $\big\langle\Phi_n\big|\Psi_n^{(1)}\big\rangle = \delta_{l0}$. For the general mth-order expression (Equation 4.15),

$$\langle\Phi_n|\,E_n^0 - \hat{H}_0\,\big|\Psi_n^{(m)}\big\rangle = \langle\Phi_n|\,\hat{V}\,\big|\Psi_n^{(m-1)}\big\rangle - \sum_{l=0}^{m-1} E_n^{(m-l)}\big\langle\Phi_n\big|\Psi_n^{(l)}\big\rangle$$
$$E_n^{(m)} = \big\langle\Phi_n^{(m)}\big| = \langle\Phi_n|\,\hat{V}\,\big|\Psi_n^{(m-1)}\big\rangle. \tag{4.18}$$

In principle, we can obtain every next-order energy contribution $E_n^{(m)}$ from the previous-order wavefunctions $\Psi_n^{(m-1)}$ and then solve for $\Psi_n^{(m)}$.

4.1.2 The $2n+1$ Wigner Rule

4.1.3 Projection Operators

We define the projection operators in terms of the zero-order wave functions,

$$\hat{P} = |\Phi_0\rangle \langle \Phi_0|$$

$$\hat{Q} = \hat{1} - \hat{P} = \sum_{i=1}^{N} |\Phi_i\rangle \langle \Phi_i| . \tag{4.19}$$

The projecton operators have the following conventient properties,

$$\hat{P}^2 = |\Phi_0\rangle \langle \Phi_0|\Phi_0\rangle \langle \Phi_0| = |\Phi_0\rangle \langle \Phi_0| = \hat{P}$$

$$\hat{Q}^2 = (1 - \hat{P})^2 = \hat{1} - \hat{P} - \hat{P} + \hat{P} = \hat{1} - \hat{P} = \hat{Q}$$

$$\hat{P}\hat{Q} = \hat{Q}\hat{P} = 0$$

$$[\hat{P}, \hat{H}_0] = [\hat{Q}, \hat{H}_0] = 0 \tag{4.20}$$

If we write the wavefunction as a linear expansion in terms of Φ_i,

$$\Phi = \sum_i a_i \Phi_i, \tag{4.21}$$

acting on it with the projection operators will yield

$$\hat{P}\Psi = \sum_i a_i |\Phi_0\rangle \langle \Phi_0|\Phi_i\rangle = \sum_i a_i |\Phi_0\rangle \delta_{0i} = a_0 \Phi_0. \tag{4.22}$$

In not so many greek letters, the operator $\hat{P}$ will extract Φ_0 from Ψ, while $\hat{Q}$ annihilates $\hat{Q}$,

$$\hat{Q}\Psi = (\hat{1} - \hat{P}) = \Psi - a_0 \Phi_0 = \sum_{i=1}^{N} a_i \Phi_i, \tag{4.23}$$

meaning we can write

$$\Psi = \hat{P}\Psi + \hat{Q}\Psi. \tag{4.24}$$

4.1.4 The Resolvent

Now follows what some considers a more elegant derivation of the perturbation equations, including the introduction of the *resolvent* of the unperturbed part of the Hamiltonian $\hat{H}_0$.

Starting from a rearrangment of the Schrödinger equation,

$$(\hat{H}_0 + \hat{V})\Psi = E\Psi,$$

$$\rightarrow -\hat{H}_0\Phi = (\hat{V} - E)\Psi, \tag{4.25}$$

we introduce a seemingline arbirary parameter ζ by adding $\zeta\Phi$ to both sides,

$$(\xi - \hat{H}_0)\Phi = (\hat{V} - E + \xi)\Phi. \tag{4.26}$$

Next, we apply $\hat{Q}$ to both sides,

$$\hat{Q}(\zeta - \hat{H}_0)\Psi = \hat{Q}(\hat{V} - E + \zeta)\Psi. \tag{4.27}$$

The right-hand side of this expression can be rewritten as,

$$\hat{Q}(\zeta - \hat{H}_0)\Psi = \hat{Q}^2(\zeta - \hat{H}_0) = \hat{Q}(\zeta - \hat{H}_0)\hat{Q}\Psi$$
$$= \sum_{i \neq 0} \sum_{j \neq 0} |\Phi_i\rangle \langle\Phi_i| \zeta - \hat{H}_0 |\Phi_j\rangle \langle\Phi_j|, \tag{4.28}$$

Equation 4.27 is now

$$\hat{Q}(\zeta - \hat{H}_0)\hat{Q}\Psi = \hat{Q}(\hat{V} - E + \zeta)\Psi. \tag{4.29}$$

By restricting to choice of ζ, so they do not coincide with the eigenvalues of $\hat{H}_0$ in $\hat{Q}$-space, we ensure that the inverse of $\hat{Q}(\zeta - \hat{H}_0)\hat{Q}$ exists. This inverse is the *resolvent* of $\hat{H}_0$,

$$\hat{R}_0(\zeta) = \frac{\hat{Q}}{\zeta - \hat{H}_0} \equiv \sum_{i \neq 0} \sum_{j \neq 0} |\phi_i\rangle \langle\Phi_i| (\zeta - \hat{H}_0)^{-1} |\Phi_j\rangle \langle\Phi_j|. \tag{4.30}$$

The resolvent simplifies in the diagonal case to

$$\hat{R}_0(\zeta) = \sum_{i \neq 0} |\Phi_i\rangle \langle\Phi_i| (\zeta - E_j^{(0)})^{-1} |\Phi_j\rangle \langle\Phi_j| = \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle\Phi_i|}{(\zeta - E_i^{(0)})}. \tag{4.31}$$

It is somewhat straightforward to prove that $\hat{R}_0(\zeta)$ is the inverse of $\hat{Q}(\zeta - \hat{H}_0)\hat{Q}$ in $\hat{Q}$-space,

$$\frac{\hat{Q}}{\zeta - \hat{H}_0}\hat{Q}(\zeta - \hat{H}_0)\hat{Q}$$

$$= \left(\sum_{i,j \neq 0} |\Phi_i\rangle \langle\Phi_i| (\zeta - \hat{H}_0)^{-1} |\Phi_j\rangle \langle\Phi_j| \right) \left(\sum_{k,l \neq 0} |\Phi_k\rangle \langle\Phi_k| (\zeta - \hat{H}_0) |\Phi_l\rangle \langle\Phi_l| \right)$$

$$= \sum_{i,l \neq 0} |\Phi_i\rangle \langle\Phi_i| (\zeta - \hat{H}_0)^{-1} \left(\sum_{j \neq 0} |\Phi_j\rangle \langle\Phi_j| \right) (\zeta - \hat{H}_0) |\Phi_l\rangle \langle\Phi_l| \tag{4.32}$$

$$= \sum_{i,l \neq 0} |\Phi_i\rangle \langle\Phi_i| (\zeta - \hat{H}_0)^{-1}(1 - |\Phi_0\rangle \langle\Phi_0|)(\zeta - \hat{H}_0) |\Phi_l\rangle \langle\Phi_l|$$

$$= \sum_{i \neq 0} |\Phi_i\rangle \langle\Phi_i| = \hat{Q}.$$

Applying the resolvent to both sides of Equation 4.29,

$$\hat{Q}\Psi = \hat{R}_0(\zeta)(\hat{V} - E + +\zeta)\Psi$$
$$\rightarrow \Psi = \Phi_0 + \hat{R}_0(\zeta)(\hat{V} - E + \zeta)\Psi, \tag{4.33}$$

which can be interpreted as a recursive relation for Ψ. Substituting the right-hand side into Ψ on the right-hand side repeatedly yields,

$$\Psi = \sum_{m=0}^{\infty} \{\hat{R}_0(\zeta)(\hat{V}) - E + \zeta\}^m \Phi_0. \tag{4.34}$$

The problem with this equation is that E, which is unknown, appears on the right-hand side. A question also arises regarding what to do with ζ. There are two common choices for ζ that give rise to two important theories,

$$\zeta = E \leftarrow \text{Brillouin-Wigner Perturbation}$$

$$\zeta = E_0^{(0)} \rightarrow -E + \zeta = -\Delta E \leftarrow \text{Rayleigh-Schrödinger Perturbation}$$

4.2 [UNFINISHED] Brillouin-Wigner Perturbation Theory

Set $\zeta = E$ and get BWPT[3, 42].

4.3 [UNFINISHED] Rayleigh-Schrödinger Perturbation Theory

set $\zeta = E_n^{(0)}$ and get RSPT[32, 34].

Kapitel 5

Coupled Cluster

In the late 1950s Fritz Coester constructed a rigorous formal solution of the bound state Schrödinger equation as a set of single particle wave functions[5]. He wanted to find an expression for the wave operator ω, which transforms a zero-order wavefunction to the exact wave function,

$$\Psi = \Omega \Phi_0. \tag{5.1}$$

From Coester's solutions it would become apparent that the Rayleigh-Schrödinger perturbation expansions of the energy does not contain matrix elements representing the products of so-called unlinked diagram. In other words, one form of Ω is given a "linked-diagram expansion",

$$\Omega \left| \Phi_0 \right\rangle = \left| \Phi_0 \right\rangle = \sum_{k=1}^{\infty} \left((\hat{R}_0 \hat{W})^k \left| \Phi_0 \right\rangle \right)_L. \tag{5.2}$$

a This is further underlined in discussions by John Hubbard[19] and Nicolaas Marinus Hugenholtz[20].

Conveniently, Ω may be written quite generally as

$$\Omega = e^{\hat{T}}, \quad \Psi = e^{\hat{T}} \Phi_0. \tag{5.3}$$

This exponential form has been come to be known as the Coupled Cluster ansatz, even though it is much more than a simple guess for the form of the exact wavefunction. To underline this point we quote Herman Kümmel: "Strange as it may be, in spite of the many successes of the coupled cluster method there is still a widespread belief that the underlying exponential structure is something artificial, accidental or an approximation only. This is why I want to make it clear that this feature is extremely natural - even necessary - on a very fundamental level, not necessarily connected with many-body theory"[21].

Throughout the 1950s and early 1960s, Coester and Kümmel developed the coupled cluster method together and proposed using the exponential-form wave operator as coupling between the shell-model state and the correct state vector for nuclear matter[6]. At the time, the method proved too computationally intensive. Specifically, the hard core potenatials of nuclear physics leaves no freedom in truncating the set of coupled cluster equations. However, the method was picked up by Jiří Čížek who in 1966 reformulated the method for modelling of electron correlation in atoms and molecules[4]. Further development with Josef Paldus made the coupled cluster method one of the most succesfull[1] methods in quantum chemistry. Together with Isaiah Shavitt, Čížek and Paldus did the first *ab initio* comutations with the method, which they called the coupled-pair many-electron-theory (MET)[26], as it can be intepreted as the perturbative variant of the many-electron-theory of Oktay Sinanoğlu[36].

---

[1] At least one of the most prevalent

5.1   The Cluster Operator

Having established the form of the coupled cluster wavefunction as

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle , \tag{5.4}$$

we now take a closer look at the cluster operator, which is divided into sub-operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_2 + \hat{T}_3 + \dots, \tag{5.5}$$

where the one-, two- and three-body operators are defined thusly,

$$\hat{T}_1 = \sum_{ai} t_i^a \{\hat{a}^\dagger \hat{i}\} \tag{5.6}$$

$$\hat{T}_2 = \frac{1}{(2!)^2} \sum_{ijab} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \tag{5.7}$$

$$\hat{T}_3 = \frac{1}{(3!)^2} \sum_{ijkabc} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \hat{c}^\dagger \hat{k}\}, \tag{5.8}$$

where the coefficients $t_{ijk\dots}^{abc\dots}$ are commonly referred to as the coupled cluster *amplitudes*, and are coefficients to be determined. The strings of operators are automatically normal-ordered. The general m-body cluster operator is given by

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ij\dots \\ ab\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \dots\}, \tag{5.9}$$

which produces an m-fold excitation. It is not necessary to include cluster-operators up to a infinite-fold excitation. Logically, the maximum excitation order is dictated by the number of electrons in the system n, such that $n \geq m$. Any higher-order excitation operator would eventually annihilate an unoccupied orbital, resulting in a zero-contribution. The prefactor $1/(m!)^2$ accounts for the redundancy created by unrestricted summations, as a permutation of any of the m hole or m particle indices will not produce a distinct contributions. Indeed, we have for example that

$$\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} = -\hat{a}^\dagger \hat{j} \hat{b}^\dagger \hat{i} = -\hat{b}^\dagger \hat{i} \hat{a}^\dagger \hat{j} = \hat{b}^\dagger \hat{j} \hat{a}^\dagger \hat{j}, \tag{5.10}$$

and therefore we must also have that

$$t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}. \tag{5.11}$$

Hence, the $(2!)^2 = 4$ contributions of two hole indices, ab, and two particle indices, ij, will produce four equal terms, which is offset by the prefactor $1/4$.

The exponential wave operator $e^{\hat{T}}$ may be expanded as a Taylor series,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots. \tag{5.12}$$

By including only single- and double excitations, $\hat{T}_{\text{CCSD}} = \hat{T}_1 + \hat{T}_2$, this expressions becomes

$$e^{\hat{T}_{\text{CCSD}}} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \dots \tag{5.13}$$

Contributions to the wave function containing only a single cluster operator, $\hat{T}_m$, are called connected cluster contributions, while those containing products of cluster operators, $\hat{T}_{m_1}^\alpha \hat{T}_{m_2}^\beta$, are called disconnected cluster contributions.

This inclusion of only sigle- and double excitations is called "Coupled Cluster Singles Doubles", elucidating the subscript CCSD[31]. The most common approximation in coupled cluster theory is the CCSD model. Here, the operator $\hat{T}_2$ describes the important electron-pair interaction and the $\hat{T}_1$ operator carries out the orbital relaxations induced by the field set up by electron-pair interactions.

Importance of different parts of the cluster operator

The most important contribution to the wave-function in quantum chemistry is undoubtedlty $\hat{T}_2$, because of the two-electron nature of the Hamiltonian. It describes the most important interaction of quantum chemistry, the electron-pair interaction. The inclusion of $\hat{T}_1$ and its products are relatively insensitive to the choice of basis set, as the operators $e^{\hat{T}_1}$ has the effect of transforming thereference state $|\Phi_0\rangle$ to another Slater determinant. This is known as Thouless theorem[41]. With very high electron-density, the three-particle operator $\hat{T}_3$ becomes important. Higher-order terms are usually of less and decreasing importance, but they can be of concern in special situations. For instance, the four-particle operator $\hat{T}_4$ is very important in nuclear physics. See for instance Helgaker et ali[16] or Shavitt & Bartlett[35] for further discussion on this topic.

5.2 Coupled-Cluster Doubles (CCD)

As a good starting point for understanding the coupled cluster scheme and especially where the coupled-cluster equations come from, we now constrain the cluster operator to

$$\hat{T}_{\text{CCD}} = \hat{T}_2, \tag{5.14}$$

and completely derive the coupled cluster equations for this case. The CCD wave function includes all connected and disconnected clusters involving $\hat{T}_2$ only,

$$\Psi_{\text{CCD}} = e^{\hat{T}_2} = \Phi_0 + \hat{T}_2\Phi_0 + \frac{1}{2}\hat{T}_2^2\Phi_0 + \frac{1}{3!}\hat{T}_2^3\Phi_0 + \dots \tag{5.15}$$

There are several methods with which to arrive at the coupled-cluster equations and here we employ two of them for the coupled cluster doubles truncation. First, we use configuration-interaction techniques and the Slater-Condon rules (Appendix A) and second, we use the "algebraic method", employing second quantisation and Wick's theorem. A third way is with the aid of diagrams. A brief note on such diagrams can be found in Appendix B.

5.2.1 Configuration space derivation

We start from the CCD-constrained time-independent Schrödinger equation,

$$\hat{H}\Psi_{\text{CCD}} = E_{\text{CCD}}\Psi_{\text{CCD}}, \tag{5.16}$$

which we left project with the reference state,

$$\langle\Phi_0|\,\hat{H}\,|\Psi_{\text{CCD}}\rangle = \langle\Phi_0|\,E_{\text{CCD}}\,|\Psi_{\text{CCD}}\rangle$$
$$\rightarrow E_{\text{CCD}} = \langle\Phi_0|\,\hat{H}\,|\Psi_{\text{CCD}}\rangle,$$

where we have taken advandage of the intermediate normalisation, $\langle \Phi_0 | \Psi_{\text{CCD}} \rangle = 1$. We then insert the exponential expansion from the coupled cluster ansatz,

$$
\begin{aligned}
E_{\text{CCD}} &= \langle \Phi_0 | \, \hat{H} (1 + \hat{T}_2) \, | \Phi_0 \rangle \\
&= E_{\text{ref}} + \sum_{\substack{i>j \\ a>b}} \langle \Phi_0 | \, \hat{H} \, \big| \Phi_{ij}^{ab} \big\rangle \, t_{ij}^{ab} \\
&= E_{\text{ref}} + \sum_{\substack{i>j \\ a>b}} \langle ij | ab \rangle \, t_{ij}^{ab}.
\end{aligned}
\tag{5.17}
$$

The energy expression will truncate here because no higher order terms will contribute. It is common to substract E_{ref} to get,

$$
\hat{H}_N \Psi_{\text{CCD}} = \Delta E_{\text{CCD}} \Psi_{\text{CCD}},
\tag{5.18}
$$

where $\hat{H}_N = \hat{H} - E_{\text{ref}}$. Now follows a bunch of expressions intended to show the correspondence between coupled cluster- and perturbation theory,

$$
\hat{H}_N = \hat{F} - \hat{U} + \hat{H}_2 - E_{\text{ref}} = \hat{H}_0 + \hat{F}^0 - \hat{U} + \hat{H}_2 - E_{\text{ref}},
\tag{5.19}
$$

where,

$$
\hat{H}_0 = \hat{F}^d = \sum_\mu \hat{f}_\mu^d, \quad \langle p | \, \hat{f}_\mu^d \, | q \rangle = \epsilon_p \delta_{pq}
\tag{5.20}
$$

$$
\hat{F}^0 = \sum_\mu \hat{f}_\mu^0, \quad \langle p | \, \hat{f}^0 \, | q \rangle = (1 - \delta_{pq}) \langle p | \, \hat{f} \, | q \rangle
\tag{5.21}
$$

$$
\hat{U} = \sum_\mu \hat{u}_\mu, \quad \langle p | \, \hat{u}_\mu \, | q \rangle = \sum_i \langle pi | qi \rangle
\tag{5.22}
$$

$$
\hat{H}_2 = \sum_{\mu > \nu} \frac{1}{r_{\mu\nu}}, \quad E_{\text{ref}} = E_0 + E^{(1)},
\tag{5.23}
$$

$$
E_0 = \sum_i \epsilon_i, \quad E^{(1)} = -\frac{1}{2} \sum_{ij} \langle ij | ij \rangle.
\tag{5.24}
$$

In the canonical HF case we have $\hat{F}^0 = 0$ and $\hat{F}^d = \hat{F}$.

In order to compute the energy of the system we need the amplitudes t_{ij}^{ab}. Starting from the modified Schrödinger equation,

$$
\hat{H}_N \Psi_{\text{CCD}} = \Delta E_{\text{CCD}} \Psi_{\text{CCD}}.
\tag{5.25}
$$

We left project with a doubly-excited Slater determinant, and insert for the CC ansatz,

$$
\big\langle \Phi_{ij}^{ab} \big| \, \hat{H}_N e^{\hat{T}_2} \, | \Phi_0 \rangle = \Delta E_{\text{CCD}} \big\langle \Phi_{ij}^{ab} \big| \, e^{\hat{T}_2} \, | \Phi_0 \rangle
\tag{5.26}
$$

$$
\big\langle \Phi_{ij}^{ab} \big| \, \hat{H}_N \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right) | \Phi_0 \rangle = \Delta E_{\text{CCD}} t_{ij}^{ab}.
\tag{5.27}
$$

Here we have only expanded the exponential function up to the quadratic term. The next term in the series will triple-excite the bra Slater determinant, which will give a zero-contribution according to the Slater-Condon rules, because of two noncoincidences. Next we apply the Slater-Condon rules to the rest of the terms on the right-hand side, starting with just the normal-ordered Hamiltonian,

$$
\big\langle \phi_{ij}^{ab} \big| \, \hat{H}_N \, | \Phi_0 \rangle = \langle ab | ij \rangle,
\tag{5.28}
$$

where only $\hat{H}_2$ contributes.

Next we look at the linear term,

$$
\begin{aligned}
\left\langle \Phi_{ij}^{ab} \middle| \hat{H}_N \hat{T}_2 \middle| \Phi_0 \right\rangle &= \sum_{klcd} \left\langle \phi_{ij}^{ab} \middle| \hat{H}_N \middle| \phi_{kl}^{cd} \right\rangle \\
&= \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_0 - E_{\text{ref}} \middle| \Phi_{ij}^{ab} \right\rangle t_{ij}^{ab} + \sum_{\substack{k>l \\ c>d}} \left\langle \Phi_{ij}^{ab} \middle| \hat{F}^0 - \hat{U} \middle| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd} \\
&\quad + \sum_{\substack{k>l \\ c>l}} \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_2 \middle| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd} = L_0 + L_1 + L_2.
\end{aligned}
\tag{5.29}
$$

We are going to evaluate these terms one-by-one, starting with L_0,

$$
\begin{aligned}
L_0 &= \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_0 - E_{\text{ref}} \middle| \Phi_{ij}^{ab} \right\rangle = \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_0 - E_0 - E^{(1)} \middle| \Phi_{ij}^{ab} \right\rangle \\
&= \left(-\varepsilon_{ij}^{ab} + \frac{1}{2} \sum_{kl} \langle kl|kl \rangle \right) t_{ij}^{ab} \cdot,
\end{aligned}
\tag{5.30}
$$

where $\varepsilon_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$.

The next term,

$$
L_1 = \sum_{\substack{k>l \\ c>d}} \left\langle \Phi_{ij}^{ab} \middle| \hat{F}^0 - \hat{U} \middle| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd},
\tag{5.31}
$$

yields contributions if at least three of the indices k, l, c, d are equal to the indices i, j, a, b (we want one or zero noncoincidences). All the possible terms are,

$$
L_1 = \begin{cases}
-\sum_k u_{kk} t_{ij}^{ab} & \text{all indices equal} \\[2mm]
-\sum_k (f_{jk}^0 - u_{jk}) t_{ik}^{ab} & \text{one hole index unequal} \\[2mm]
+\sum_k (f_{ik}^0 - u_{ik}) t_{jk}^{ab} & \text{the other hole index unequal} \\[2mm]
-\sum_c (f_{ac}^0 - u_{ac}) t_{ij}^{bc} & \text{one particle index unequal} \\[2mm]
+\sum_c (f_{bc}^0 - u_{bc}) t_{ij}^{zc} & \text{the other particle index unequal.}
\end{cases}
\tag{5.32}
$$

For the last linear term,

$$
L_2 = \sum_{\substack{k>l \\ c>d}} \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_2 \middle| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd},
\tag{5.33}
$$

we require that at least two of the indices k, l, c, d are equal to the indices i, j, a, b, as we can do with at most two noncoincidences in the bra and the ket. For equality in both the hole indices or both the particle indices we have

$$
cd = ab \quad \rightarrow \quad \sum_{k>l} \langle ij|kl \rangle t_{kl}^{ab}
\tag{5.34}
$$

$$
kl = ij \quad \rightarrow \quad \sum_{c>d} \langle ab|cd \rangle t_{ij}^{cd}.
\tag{5.35}
$$

For one equality in both hole and particle index we have

$$
-\sum_{kl} \left(\langle bk|cj \rangle t_{ik}^{ac} - \langle bk|ci \rangle t_{jk}^{ac} - \langle ak|cj \rangle t_{ik}^{bc} - \langle bk|ci \rangle t_{jk}^{ac} \right),
\tag{5.36}
$$

where the sign stems from the maximum coincidence permutations as dictated by the Slater-Condon rules. Most of the three- and four euqal index terms are accounted for by the expression above, the remaining three-index equality terms are

$$-\sum_{kl} \left(\langle jl|kl \rangle t_{ik}^{ab} - \langle il|kl \rangle t_{jk}^{ab} \right) \tag{5.37}$$

$$+\sum_{cl} \left(\langle bl|cl \rangle t_{ij}^{ac} - \langle al|cl \rangle t_{ij}^{bc} \right), \tag{5.38}$$

and there is one term for the case where all indices are equal,

$$\sum_{k>l} \langle kl|kl \rangle t_{ij}^{ab} = \frac{1}{2} \sum_{kl} \langle kl|kl \rangle t_{ij}^{ab}. \tag{5.39}$$

These last three- and four-index equality terms are expressible in terms of $\hat{u}$, and will cancel the first term in L_1 together with the $\hat{u}$ term from L_0. All terms so far are the same as in a CID computation. The difference between CCD and CID as the following extra quadratic terms,

$$Q = \frac{1}{2} \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_N \hat{T}_2^2 \middle| \Phi_0 \right\rangle = \frac{1}{2} \sum_{\substack{k>l \\ c>d}} \sum_{\substack{m>n \\ e>f}} \left\langle \phi_{ij}^{ab} \middle| \hat{H}_N \middle| \Phi_{klmn}^{cdef} \right\rangle t_{kl}^{cd} t_{mn}^{ef}. \tag{5.40}$$

From this expression we will have a contrition only when four of the indices k, l, m, n, c, d, e, f are equal to i, j, a, b, and only $\hat{H}_2$ can contribute. After some algebraic acrobatics we'll find that this becomes

$$Q = \sum_{\substack{k>l \\ c>d}} \langle kl|cd \rangle \left[(t_{ij}^{ab} t_{kl}^{cd} + t_{ij}^{cd} t_{kl}^{ab}) - 2(t_{ik}^{ac} t_{jl}^{cd} + t_{ij}^{bd} t_{ij}^{bd}) \right.$$
$$\left. -2(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \right]. \tag{5.41}$$

From Equation 5.17 we see that

$$\Delta E_{\text{CCD}} = \sum_{\substack{i>j \\ a>b}} \langle ij|ab \rangle t_{ij}^{ab}, \tag{5.42}$$

and because the indices in Equation 5.41 are dummy variables we see that the first term here cancels with the right-hand side of Equation 5.27. Some algebraic massage after the initial acrobatic exercises leads to,

$$\varepsilon_{ij}^{ab} t_{ij}^{ab} = \langle ab|ij \rangle + \frac{1}{2} \sum_{cd} \langle ab|cd \rangle t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \langle ij|kl \rangle t_{kl}^{ab}$$
$$- \sum_{kl} \left(\langle bk|cj \rangle t_{ik}^{ac} - \langle bk|ci \rangle t_{jk}^{ac} - \langle ak|cj \rangle t_{ik}^{bc} + \langle ak|ci \rangle t_{jk}^{bc} \right)$$
$$- \sum_{k} \hat{f}_{jk}^0 t_{ik}^{ab} + \sum_{k} \hat{f}_{ik}^0 t_{jk}^{ab} + \sum_{c} \hat{f}_{bc}^0 t_{ij}^{ac} - \sum_{c} \hat{f}_{ac}^0 t_{ij}^{bc} \tag{5.43}$$
$$+ \sum_{klcd} \langle kl|cd \rangle \left[\frac{1}{4} t_{ij}^{cd} t_{kl}^{ab} - \frac{1}{2} (t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac}) \right.$$
$$\left. - \frac{1}{2} (t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + (t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \right],$$

which is the CCD amplitude equations. This equation contains simultaneous algebraic expressions, contrary to CI. The equations must be solved iteratively, substituting t_{ij}^{ab} obtained in each iteration, into the quadratic terms for the next iteration.

5.2.2 Algebraic Derivation

In this derivation we make great use of second quantisation formalism and Wick's theorem. We start with the normal-ordered Hamiltonian,

$$\hat{H}_N = (\hat{H}_0)_N + \hat{F}_N^0 + \hat{W}$$
$$= \sum_p \varepsilon_p \{\hat{p}^\dagger \hat{p}\} + \sum_{p \neq q} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq|rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}. \tag{5.44}$$

The one-particle terms $(\hat{H}_0)_N$ and $\hat{F}_N^0$ can be combined by setting $\varepsilon_p = f_{pp}$, reducing the normal-ordered Hamilionian to

$$\hat{H}_N = \hat{F}_N + \hat{W}$$
$$= \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq|rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}. \tag{5.45}$$

First we want to find an expression for the energy,

$$\Delta E_{\text{CCD}} = \langle 0| \hat{H}_N (1 + \hat{T}^2) |0\rangle = \langle 0| \hat{H}_N \hat{T}_2 |0\rangle , \tag{5.46}$$

where only the vacuum expectation value of the product of the Hamiltonian and the doubles cluster operators gives a contributions, because the vacuum expectation value of just the Hamiltonian is zero. Inserting for the operators,

$$\Delta E_{\text{CCD}} = \sum_{\substack{i>j \\ a>b}} \langle 0| \left[\sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq|rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} \right] \{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle t_{ij}^{ab}. \tag{5.47}$$

Here the one-particle part will vanish as there is no manner one can contract all the operators in this term without using an internal contraction in the normal-ordered product. It is also useful to convert the first sum to an unrestricted sum,

$$\Delta E_{\text{CCD}} = \frac{1}{16} \sum_{ijab} \sum_{pqrs} \langle pq|rs \rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle t_{ij}^{ab}. \tag{5.48}$$

We contract the operators in the normal-ordered products,

$$\langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\}$$
$$+ \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle \tag{5.49}$$
$$= \delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb}$$
$$- \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra} + \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rn}. \tag{5.50}$$

All these products of delta functions give us a reduction in the sums and the CCD energy becomes,

$$\Delta E_{\text{CCD}} = \frac{1}{4} \sum_{ijab} \langle ij|ab \rangle t_{ij}^{ab}. \tag{5.51}$$

The natural next step is to find the amplitude equations,

$$\langle \Phi_{ij}^{ab}| \hat{H}_N \left(1 + \hat{T}_2 + \frac{1}{2}\hat{T}^2 \right) |0\rangle = \Delta E_{\text{CCD}} t_{ij}^{ab}. \tag{5.52}$$

We compute this expression in steps, starting with the lone normal-ordred Hamiltonian,

$$\left\langle \Phi_{ij}^{ab} \right| \hat{H}_N \left| 0 \right\rangle = \frac{1}{4} \sum_{pqrs} \left\langle 0 \right| \{\hat{a}\hat{b}\hat{j}^\dagger \hat{i}^\dagger\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} \left| 0 \right\rangle \left\langle pq | rs \right\rangle, \tag{5.53}$$

here we also have to compute a few contractions,

$$\langle 0 | \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}$$

$$+ \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} | 0 \rangle \tag{5.54}$$

$$\begin{aligned} =& \delta_{ir}\delta_{js}\delta_{bq}\delta_{ap} - \delta_{ir}\delta_{js}\delta_{bp}\delta_{aq} \\ & - \delta_{is}\delta_{jr}\delta_{bq}\delta_{ap} + \delta_{is}\delta_{jr}\delta_{bp}\delta_{aq}. \end{aligned} \tag{5.55}$$

This will leave us with a similar expression as the one in the energy equation,

$$\left\langle \Phi_{ij}^{ab} \right| \hat{H}_N \left| 0 \right\rangle = \left\langle ab | ij \right\rangle. \tag{5.56}$$

Now for the linear terms,

$$\begin{aligned} \left\langle \phi_{ij}^{ab} \right| \hat{H}_N \hat{T}_2 \left| 0 \right\rangle &= \sum_{\substack{k>l \\ c>d}} \left\langle \phi_{ij}^{an} \right| \hat{H}_n \{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \left| 0 \right\rangle t_{kl}^{cd} \\ &= \frac{1}{4} \sum_{klcd} \left\langle \Phi_{ij}^{ab} \right| \hat{F}_N + \hat{W} \left| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd} \end{aligned} \tag{5.57}$$

Starting with the first term,

$$\begin{aligned} L_1 &= \frac{1}{4} \sum_{klcd} \left\langle \phi_{ij}^{ab} \right| \hat{F}_N \left| \phi_{kl}^{cd} \right\rangle t_{kl}^{cd} \\ &= \frac{1}{4} \sum_{klcd} \sum pq f_{pq} \left\langle \phi_{ij}^{ab} \right| \{\hat{p}^\dagger \hat{q}\} \left| \phi_{kl}^{cd} \right\rangle t_{kl}^{cd} \\ &= \frac{1}{4} \sum_{klcd} \sum_{pq} f_{pq} \left\langle 0 \right| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \left| 0 \right\rangle t_{kl}^{cd} \end{aligned} \tag{5.58}$$

The product of normal-ordered operators must be contracted in such a way that tree and three operators in the first and last operators string are contracted with one another, and the two operators in the middle string is contracted with one operator in the last and first one. This provides us with $3 \times 3 \times 2 = 16$ possible contractions. Here are the first four contractions,

$$\{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\}$$

$$+ \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \tag{5.59}$$

$$\begin{aligned} =& \delta_{ik}\delta_{jl}\delta_{bd}\delta_{ap}\delta_{cq} + \delta_{ik}\delta_{jl}\delta_{ac}\delta_{bp}\delta_{dq} \\ & - \delta_{ik}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pl} - \delta_{iq}\delta_{pk}\delta_{jl}\delta_{bd}\delta_{ac}. \end{aligned} \tag{5.60}$$

The last 12 contractions will be equivalent to these four, and thus we rid ourselves of the $\frac{1}{4}$-prefactor, yielding

$$L_1 = \sum_c (f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc}) + \sum_k (f_{ik} t_{jk}^{ab} - f_{jk} t_{ik}^{ab}). \tag{5.61}$$

Proceeding to the second linear term,

$$
\begin{aligned}
L_2 &= \frac{1}{4} \sum_{klcd} \left\langle \Phi_{ij}^{ab} \right| \hat{W} \left| \Phi_{kl}^{cd} \right\rangle t_{kl}^{cd} \\
&= \frac{1}{16} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{j}^\dagger \hat{b}\hat{i}^\dagger \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\hat{l}\} |0\rangle t_{kl}^{cd}
\end{aligned}
\tag{5.62}
$$

Here there are many possible ways to contract the operators string, so it is convenient to label the different kinds of contractions. Subscript a-term consist of two hole-hole contractions, subscript b-terms consist of two particle-particle contractions and subscript c-terms consist of one particle-hole and one hole-particle contractions,

$$
\begin{aligned}
L_{2a} &= \frac{1}{8} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\hat{l}\} |0\rangle t_{kl}^{cd} \\
&= \frac{1}{8} \sum_{pqrs} \sum_{cd} \langle pq|rs \rangle \langle 0| \{\hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger\} |0\rangle t_{kl}^{cd}
\end{aligned}
\tag{5.63}
$$

$$
\begin{aligned}
L_{2b} &= \frac{1}{8} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} |0\rangle t_{kl}^{cd} \\
&= \frac{1}{8} \sum_{pqrs} \sum_{kl} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{l}\hat{k}\} |0\rangle t_{kl}^{cd}
\end{aligned}
\tag{5.64}
$$

$$
\begin{aligned}
L_{2c} &= \frac{1}{4} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \\
&\quad + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \\
&\quad + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \\
&\quad + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} |0\rangle t_{kl}^{cd} \\
&= \frac{1}{4} \sum_{pqrs} \sum_{kc} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{k}\} \\
&\quad - \{\hat{j}^\dagger \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{k}\} \\
&\quad - \{\hat{i}^\dagger \hat{b}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{k}\} \\
&\quad + \{\hat{j}^\dagger \hat{b}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{k}\} |0\rangle .
\end{aligned}
\tag{5.65}
$$

The vacuum expectation value in L_{2a} can be evaluated as,

$$
\begin{aligned}
&\langle 0| \{\hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger\} + \{\hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger\} \\
&+ \{\hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger\} + \{\hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger\} |0\rangle
\end{aligned}
\tag{5.66}
$$

$$
\begin{aligned}
&= \delta_{bq}\delta_{ap}\delta_{sd}\delta_{rc} - \delta_{bq}\delta_{ap}\delta_{sc}\delta_{rd} \\
&\quad - \delta_{aq}\delta_{bp}\delta_{sd}\delta_{rc} + \delta_{aq}\delta_{bp}\delta_{sc}\delta_{rd}
\end{aligned}
\tag{5.67}
$$

Inserting this result into the original expression and substituting to similar indicies will yield,

$$
L_{2a} = \frac{1}{2} \sum_{cd} \langle ab|cd \rangle t_{ij}^{cd}.
\tag{5.68}
$$

A very similar computation will yield the following result for the next linear term,

$$L_{2b} = \frac{1}{2} \sum_{kl} \langle kl|ij \rangle \, t_{kl}^{ab}. \tag{5.69}$$

The last linear term is very different, however. INSERT SOMETHING HERE!

After long last, we have only the quadratic term to deal with,

$$Q = \frac{1}{8} \sum_{pqrs} \sum_{\substack{k>l \\ c>d}} \sum_{\substack{m>n \\ e>f}} \langle pq|rs \rangle \, \langle 0| \, \{\hat{i}^\dagger \hat{j}^\dagger \hat{b} \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l} \hat{k}\}\{\hat{e}^\dagger \hat{f}^\dagger \hat{n} \hat{m}\} \, |0\rangle \, t_{kl}^{dc} t_{mn}^{ef}. \tag{5.70}$$

In this expression there are no non-zero contractions between the third and fourth normal ordered operator string. We therefore need to contract operators in the first normal-ordered string with operators either in the third or four string, and the operator in the second string with the rest.

We start by contracting all operators in the first normal-ordered string with all the operators in the fourth normal-ordered string,

$$\frac{1}{8} \sum_{pqrs} \sum_{\substack{k>l \\ c>d}} \sum_{\substack{m>n \\ e>f}} \langle pq|rs \rangle \, \langle 0| \, \{\hat{i}^\dagger \hat{j}^\dagger \hat{b} \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l} \hat{k}\}\{\hat{e}^\dagger \hat{f}^\dagger \hat{n} \hat{m}\} \, |0\rangle \, t_{kl}^{cd} t_{mn}^{ef}$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{\substack{k>l \\ c>d}} \langle pq|rs \rangle \, \langle 0| \, \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l} \hat{k}\} \, |0\rangle \, t_{kl}^{cd} t_{ij}^{ab}. \tag{5.71}$$

There are four possible ways to contract this last term, resulting in

$$\frac{1}{2} \sum_{\substack{k>l \\ c>d}} \langle kl|cd \rangle \, t_{kl}^{cd} t_{ij}^{ab}. \tag{5.72}$$

We get the same result by contracting the four operators in the first string with the four operators in the third string, cancelling the factor $\frac{1}{2}$, eventually yielding a result equal to $\Delta E_{\text{CCD}} t_{ij}^{ab}$, which we see by comparing this result to Equation 5.42.

There are four remaining reasonable classes in which to sort the permutations of contractions that remain;

    a the two hole operators in the first string are contracted with the third or fourth operator string, yielding equal results;

    b one hole and one particle operators in the first string are contracted with operators in the third string, the rest of the operators in the first string are contracted with operators in the fourth string;

    c two particle operators and one hole operator from the first string are contracted with operators in the third string, the last hole operator is contracted with an operator in the fourth string;

    d one particle operator and two hole operators are contracted with operators in the third string and the last particle operator with an operator in the fourth string.

The results for class a and class b are somewhat straight-forward to compute, giving the following,

$$Q_a = \frac{1}{16} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{l}\hat{k}\}\{\hat{c}^\dagger \hat{d}^\dagger\} |0\rangle t_{ij}^{cd} t_{kl}^{ab}$$

$$= \frac{1}{4} \sum_{klcd} \langle kl|rs \rangle t_{ij}^{cd} t_{kl}^{ab} \tag{5.73}$$

$$Q_b = \frac{1}{4} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{k}\}\{\hat{d}^\dagger \hat{l}\} |0\rangle (t_{ik}^{ac} t_{jl}^{bd} - t_{ik}^{bc} t_{jl}^{ad})$$

$$= \sum_{klcd} \langle kl|cd \rangle (t_{ik}^{ac} t_{jl}^{bd} - t_{ik}^{bc} t_{jl}^{ad}) = \sum_{klcd} \langle kl|cd \rangle (t_{ik}^{ac} t_{jl}^{bd} - t_{ik}^{bd} t_{jl}^{ac}) \tag{5.74}$$

The sets of terms for class c and d can each be generated in two distinct ways, dependent on the choice of the tree operators from the first operator string ($\hat{i}^\dagger \hat{a}\hat{b}$ or $\hat{j}^\dagger \hat{a}\hat{b}$ for c and $\hat{i}^\dagger \hat{j}^\dagger \hat{a}$ or $\hat{i}^\dagger \hat{j}^\dagger \hat{b}$ for d). In each case there are 16 possibilities; the three operators from the first string can be contracted with operators in both the third or fourth string in four ways and the remaining operators can be then be contracted in two ways. All these possibilities lead to equivalent results. For example, here is the first Q_c term,

$$\frac{1}{8} \sum_{pqrs} \sum_{klcd} \sum_{mnef} \langle pq|rs \rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\}\{\hat{e}^\dagger \hat{f}^\dagger \hat{n}\hat{m}\} |0\rangle t_{kl}^{cd} t_{mn}^{ef}$$

$$= -\frac{1}{8} \sum_{pqrs} \sum_{klcd} \langle pq|rs \rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\}\{\hat{l}\} |0\rangle t_{kj}^{cd} t_{li}^{ab} |0\rangle \tag{5.75}$$

The remaining operators in this expression can be contracted in four ways,

$$\langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\}\{\hat{l}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\}\{\hat{l}\}$$

$$+ \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\}\{\hat{l}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger \hat{d}^\dagger \hat{k}\}\{\hat{l}\} |0\rangle \tag{5.76}$$

$$= \delta_{pl}\delta_{qk}\delta_{rd}\delta_{sc} - \delta_{pk}\delta_{ql}\delta_{rd}\delta_{sc} - \delta_{pl}\delta_{qk}\delta_{rc}\delta_{sd} + \delta_{pk}\delta_{ql}\delta_{rc}\delta_{sd} \tag{5.77}$$

Algbra eventually leads to,

$$-\frac{1}{2} \sum_{klcd} \langle kl|cd \rangle t_{ik}^{ab} t_{jl}^{cd}. \tag{5.78}$$

A similar computations provides the second Q_c term,

$$-\frac{1}{2} \sum_{klcd} \langle kl|cd \rangle t_{ik}^{cd} t_{jl}^{ab} \tag{5.79}$$

These two terms give us,

$$Q_c = -\frac{1}{2} \sum_{klcd} \langle kl|cd \rangle (t_{ik}^{ab} t_{jl}^{cd} - t_{ik}^{cd} t_{jl}^{ab}) \tag{5.80}$$

Treating the class d terms gives,

$$Q_d - \frac{1}{2} \sum_{klcd} \langle kl|cd \rangle (t_{ij}^{ac} t_{kl}^{bd} - t_{ij}^{bd} t_{kl}^{ac}). \tag{5.81}$$

Combining all the quadratic terms will now yield the same as in Equation 5.41, and we can conclude that an algebraic derivation of the coupled cluster method is equivalent to the configuration space derivation.

5.3   [UNFINISHED] The Coupled Cluster Equations

5.4   [UNFINISHED] The Lagrangian Formulation

s

5.5   [UNFINISHED] Genererealisation in Time

Teil III

Implementation and Results

Kapitel 6

Implementation: Quantum Systems

For a quantum system to be studied on the computer it is necessary to make a distinction for what defines the system. One must therefore undergo the mathematical procedure of defining a finite basis sets that defines the quantum system under scrutiny when dealing with the electronic problem.

Here we present the `quantum_system` python module, designed to provide basis sets for one- and two-dimensional quantum dots. The two-dimensional quantum dot can also be modelled with a constant, homogeneous magnetic field; and as a double quantum dot. Moreover, the module includes an option for constructing a custom system which can be interfaced with popular quantum chemistry packages `PySCF`[39] and `Psi4`[27].

The `quantum_system` module can installed from github with `pip` by the following command,

```
pip install git+https://github.com/Schoyen/quantum-systems.git
```

The same task can of course be accomplished by more commands,

```
git clone https://github.com/Schoyen/quantum-systems.git
cd quantum-systems
pip install .
```

NOTE: not sure the part below here is necessary. Maybe just link to web page documentation? If it is done, that is..

It can be useful to install the module to a separate environment. We have made this possible through `conda`,

```
conda environment create -f environment.yml
conda activate quantum-systems
```

6.1   Quantum Dots [TODO: dipole moments]

In reality, quantum dots are nanometre-sized structures made of semiconductor materials. Theoretically, quantum dots are easy to model by harmonic oscillator potential and in practice they are relativelty easy to manufacture in a laboratory. This doubly theoretical-experimental benefit has made quantum dots a popular area of study. Moreover so because of their wide area of apllications.

The possible applications of quantum dots are many. Coupled single-electron quantum dots could potentially be used as harware elements in quantum computers, i.e. qubits[24]; quantum dots also promise to increase the efficiency of photvoltaic solar cells; and they have already found use in cellular imaging in biology. Reimann and Manninen[33] has written an outstandingly thorough review on quantum dots, covering their varied types of fabrication, theoretical methods common in their study and vast ocean of applications.

The usefulness and relative theoretical ease of modelling warrants the study of quantum dots. Herein, several classes have been implemented in order to construct basis sets modelling quantum dots in both one and two dimensions. These basis sets models *bound* systems as the common harmonic oscillator-type potentials that are used have the characteristics of infinite quantum wells.

6.1.1   One Dimension

This is perhaps one of the simplest of all quantum mechanical models, being studied ad nauseum in everyones introductory quantum mechanics course. The one-body part of the Hamiltonian for the one-dimensional quantum harmonic oscillator is,

$$\hat{h} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \tag{6.1}$$

The potential, $\hat{v} = \frac{1}{2}m\omega^2\hat{x}^2$, forms the well known parabolig curve. In a general one-dimensional system, this potenation could readily be exchanged for something else. For instance that of the *double well*,

$$\hat{v} = \frac{1}{2}m\omega^2\left(\hat{x}^2 + \frac{1}{4}l^2 - l|\hat{x}|\right), \tag{6.2}$$

where l is the width of a barrier in the middle of the parabolic potential.

In atomic units we can set $\hbar = m = 1$. Substituting for the momentum operator, $\hat{p} = -i\hbar(\hat{\partial}/\partial x)$, gives us

$$\hat{h} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \hat{v}. \tag{6.3}$$

The second-order derivate can be approximated by the central difference formula for some function $f(x)$, yielding

$$f''(x) = \frac{f(x+dx) - 2f(x) + f(x-dx)}{dx^2}, \tag{6.4}$$

for some small dx. This means that we approximate the Hamilton operator of the system (Equation 6.3) by a matrix,

$$h_q^p = \begin{pmatrix} 1/dx^2 + v_1 & -1/2dx^2 & \ddots & & & \\ -1/2dx^2 & 1/dx^2 + v_2 & -1/2dx^2 & \ddots & & \\ \ddots & -1/2dx^2 & 1/dx^2 + v_3 & -1/2dx^2 & \ddots & \\ & \ddots & \ddots & \ddots & \ddots & \ddots \\ & & \ddots & -1/2dx^2 & 1/dx^2 + v_{n-1} & -1/2dx^2 \\ & & & \ddots & -1/2dx^2 & 1/dx^2 + v_n \end{pmatrix}, \tag{6.5}$$

and we have thus transformed the time-independent Schrödinger equation

$$\hat{h}\left|n\right\rangle = \epsilon\left|n\right\rangle, \tag{6.6}$$

into a matrix equation which is easily representable and solvable on a computer, where n is the number of points used to numerically represent the wavefunciton and Hamiltonian mateix representation. This is done with some generic eigenvalue solver, for instance `numpy.linalg.eigh`. The eigen functions provide the foundations for the single-particle functions.

Since we would like to model interaction between particles we need something more, than just a numerical representation of the one-body operator. We therefore need to compute coulomb interaction, in the form of an integral. This is done in several steps, starting with an "inner intergral" over all all space and two and two single-particle functions,

$$u_s^q = \int \phi_q(x_1) \frac{\alpha}{(x_1 - x_2)^2 + 2a^2} \phi_s(x_2) dx, \tag{6.7}$$

where a and α are parameters that are necessary to include for this integral to be calculable. Numerically, this part is divided into two functions in our python implementation,

```python
def _shielded_coulomb(x_1, x_2, alpha, a):
    return alpha / np.sqrt((x_1 − x_2) ** + a ** 2)


def _compute_inner_integral(spf, l, num_grid_points, grid, alpha, a):
    inner_integral = np.zeros((l, l, num_grid_points), dtype=np.complex128)

    for q in range(l):
        for s in range(l):
            for i in range(num_grid_points):
                inner_integral[q, s, i] = _trapz(
                    spf[q]
                    * _shielded_coulomb(grid[i], grid, alpha, a)
                    * spf[s],
                    grid,
                )

    return inner_integral
```

The inner orbital is then used in the computation in the orbial integral,

$$w_{rs}^{pq} = \int \phi_p u_s^q \phi_r dx, \tag{6.8}$$

which numerically is implemented as follows,

```python
def _compute_orbital_integrals(spf, l, inner_integral, grid):
    u = np.zeros((l, l, l, l), dtype=np.complex128)

    for p in range(l):
        for q in range(l):
            for r in range(l):
                for s in range(l):
                    u[p, q, r, s] = _trapz(
                        spf[p] * inner_integral[q, s] * spf[r], grid
                    )

    return u
```

Each integral is solved by the trapezoidal scheme,

```
def _trapz(f, x):
    n = len(x)
    delta_x = x[1] − x[0]
    val = 0

    for i in range(1, n):
        val += f[i − 1] + f[i]

    return 0.5 * val * delta_
```

Needless to say, computing the coulomb integrals is one of the more compute-heave tasks, and we therefore make great use of just-in-time compulation from the `numba` module for python.

A full representation of the one-dimensional quantum dot (oscillator) class is provided below,

---

class quantum_systems.**OneDimensionalHarmonicOscillator**
  (*n*, *l*, *grid_length*, *num_grid_points*, *omega=0.25*, *mass=1*, *a=0.25*, *alpha=1.0*)

Create One-Dimensional Quantum Dot basis set.

Parameters
  n(*int*) Number of electrons
  l(*int*) Number of spinorbitals
  grid_length(*int or float*) Space over which to construct wavefunction.
  num_grid_points(*int of float*) Number of points for construction of wavefunction.
  omega(*float, default* 0.25) Angular frequency of harmonic oscillator potential.
  mass(*int or float, default* 1.0) Mass of electrons. Atomic units is used as default.
  a(*float, default* 0.25) Necessary in Coulomb integral computation.
  alpha(*float, default* 1.0) Necessary in Coulomb integral computation.

Attributes
  h One-body matrix **Type** np.array
  f Fock matrix **Type** np.array
  u Two-body matrix **Type** np.array

Methods
  setup_system(*Potential=None*)
      Must be called in order to compute basis functions. The method will revert to regular harmonic oscillator potential if no potential has been provided. Optional potentials include one-dimensional double well potentials.
  contruct_dipole_moment()
      Constructs dipole moment. This method is called by **setup_system**(). Necessary when constructing custom systems with time development.

6.1.2 Two Dimensions

The one-body part of the Hamiltonian for a two-dimensional quantum dots is almost identical to the one-body part for a one-dimensional quantum dot. In cartesian coordinates we simple include a y in the potential as well as an x, but mostly because we have analytical expressions for the Coulomb integrals in polar coordinates[2], we write the one-body operators in polar
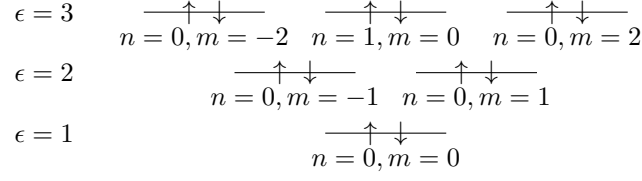
$$\epsilon = 3 \quad \overline{\uparrow \; \downarrow} \quad \overline{\uparrow \; \downarrow} \quad \overline{\uparrow \; \downarrow}$$
$$n = 0, m = -2 \quad n = 1, m = 0 \quad n = 0, m = 2$$

$$\epsilon = 2 \quad \overline{\uparrow \; \downarrow} \quad \overline{\uparrow \; \downarrow}$$
$$n = 0, m = -1 \quad n = 0, m = 1$$

$$\epsilon = 1 \quad \overline{\uparrow \; \downarrow}$$
$$n = 0, m = 0$$

Abbildung 6.1: In this plot we see the energy degeneracy of the lowest three energy levels in the two-dimensional quantum dot. Each arrow represents a spin up or a spin down state with the quantum numbers n and m as listed below. This pattern goes on indefinitely with the addition of one bar (two oscillators) per level.

coordinates as well with $\hat{r}^2 = \hat{x}^2 + \hat{y}^2$,

$$\hat{h} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{r}^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right) + \frac{1}{2}m\omega^2\hat{r}^2. \tag{6.9}$$

The wavefunctions for a two-dimensional harmonic oscillator can be written

$$\phi(r,\theta) = N_{nm}(ar)^{|m|}L_n^{|m|}(a^2r^2)e^{-a^2r^2/2}e^{im\theta}, \tag{6.10}$$

where $a = \sqrt{m\omega/\hbar}$ si the Bohr radius, $L_n^{|m|}$ is the associated Laguerre polynomials, n and m are the principal and the azimutal quantum numbers respectively, and N_{nm} is a normalisation factor given by,

$$N_{nm} = a\sqrt{\frac{n!}{\pi(n+|m|)!}}. \tag{6.11}$$

The energy eigenvalues of a two-dimensional harmonic oscillator is given by

$$\epsilon_{nm} = \hbar\omega(2n + |m| + 1). \tag{6.12}$$

An important difference between the one-dimensional quantum dot and a two-dimensional quantum dot is that in the latter we have energy degeneracies of the eigenstates. This is illustrated in Figure 6.1. In this figure we have included a spin-up and a spin-down state for each n, m-state. This spin feature is not in any way included in Equation 6.10, but we may represent the spin condition by including it in the orthonormality conditions of the wavefunctions,

$$\langle n_1 m_1 \sigma_1 | n_2 m_2 \sigma_2 \rangle = \delta_{n_1 n_2}\delta_{m_1 m_2}\delta_{\sigma_1 \sigma_2}, \tag{6.13}$$

where σ is the spin.

Because of the energy degeneracy present in two-dimensional quantum dots and for a more computer-friendly labelling of basis functions, it is necessary to make a mapping from the three quantum numbers n, m, to a single (quantum) number p. This functionality $(n, m) \mapsto p$ is achieved by the following python function

```python
def get_index_p(n, m):
    num_shells = 2 * n + abs(m) + 1

    previous_shell = 0
    for i in range(1, num_shells):
        previous_shell += i
```

```python
    current_shell = previous_shell + num_shells

    if m == 0:
        if n == 0:
            return 0

        p = previous_shell + (current_shell − previous_shell) // 2

        return p

    elif m < 0:
        return previous_shell + n

    else:
        return current_shell − (n + 1)
```

It will also be necessary to map back $p \mapsto (n, m)$,

```python
def get_indices_nm(p):
    n, m = 0, 0
    previous_shell = 0
    current_shell = 1
    shell_counter = 1

    while current_shell <= p:
        shell_counter += 1
        previous_shell = current_shell
        current_shell = previous_shell + shell_counter

    middle = (current_shell − previous_shell) / 2 + previous_shell

    if (current_shell − previous_shell) & 0x1 == 1 and abs(
        p − math.floor(middle)
    ) < 1e−8:
        n = shell_counter // 2
        m = 0

        return n, m

    if p < middle:
        n = p − previous_shell
        m = −((shell_counter − 1) − 2 * n)

    else:
        n = (current_shell − 1) − p
        m = (shell_counter − 1) − 2 * n

    return n, m
```

The analytical formula for the Coulomb integrals, provided by Anisimovas and Matulis[2]

is

$$
\begin{aligned}
\langle \phi_1\phi_2|\hat{W}|\phi_3\phi_4\rangle = {} & \delta_{s_1,s_4}\delta_{s_2,s_3}\delta_{m_1+m_2,m_3+m_4}\Big[\prod_{i=1}^{4}\frac{n_i!}{(|m_i|+n_i)}\Big]^{1/2}\sum_{(4)j=0}^{n}\frac{(-1)^{j_1+j_2+j_3+j_4}}{j_1!j_2!j_3!j_4!} \\
& \times \Big[\prod_{i=1}^{n}\binom{n_i+|m_i|}{n_i+j_i}\Big]\frac{1}{2^{(G+1)/2}}\sum_{(4)l=0}^{\gamma}(-1)^{\gamma_2+\gamma_3-l_2-l_3} \\
& \times \delta_{l_1+l_2,l_3+l_4}\Big[\prod_{i=1}^{4}\binom{\gamma_i}{l_i}\Big]\Gamma\Big(1+\frac{L}{2}\Big)\Gamma\Big(\frac{G-L+1}{2}\Big).
\end{aligned}
\tag{6.14}
$$

The symbols j_i are integer summation indices (regular indices) running from 0 to n_i. The symbols γ_i stand for numbers,

$$
\gamma_1 = j_1 + j_4 + (|m_1| + m_1)/2 + (|m_4| - m_4)/2
$$
$$
\gamma_4 = j_1 + j_4 + (|m_1| - m_1)/2 + (|m_4| + m_4)/2
$$

γ_2 and γ_3 can be obtained by replacing indices $1 \to 2$ and $4 \to 3$. Moreover,

$$
\sum_{(4)j=0}^{n} = \sum_{j_1=0}^{n_1}\sum_{j_2=0}^{n_2}\sum_{j_3=0}^{n_3}\sum_{j_4=0}^{n_4}, \quad G = \sum_i \gamma_i, \quad L = \sum_i l_i
$$

For the implementation of this expression for the purpose of computing the two-dimensional quantum dot basis sets, we refer the reader to the appendices (Appendix C).

The final specification of the two-dimensional harmonic oscillator basis set class, which is everything the user sees is the following,

---

class quantum_systems.**TwoDimensionalHarmonicOscillator**
  (*n, l, radius_length, num_grid_points, omega*=0.25, *mass=1*)

Create Two-Dimensional Quantum Dot basis set.

Parameters
  n(*int*) Number of electrons
  l(*int*) Number of spinorbitals
  grid_length(*int or float*) Space over which to construct wavefunction.
  num_grid_points(*int of float*) Number of points for construction of wavefunction.
  omega(*float, default* 0.25) Angular frequency of harmonic oscillator potential.
  mass(*int or float, default* 1.0) Mass of electrons. Atomic units is used as default.

Attributes
  h One-body matrix **Type** np.array
  f Fock matrix **Type** np.array
  u Two-body matrix **Type** np.array

Methods
  setup_system()
      Must be called in order to compute basis functions.
  contruct_dipole_moment()
      Constructs dipole moment. This method is called by **setup_system**().

Double well

class quantum_systems.**TwoDimensionalDoubleWell**
  (*n*, *l*, *radius_length*, *num_grid_points*, *barrier_strength*=1.0, *l_ho_factor*=1.0, *omega*=0.25, *mass*=1)

Create Two-Dimensional Quantum Dot with double well potential, i.e. the Double Dot. This class inherits from **TwoDimensionalHarmonicOscillator**.

Parameters
    n(*int*) Number of electrons
    l(*int*) Number of spinorbitals
    grid_length(*int or float*) Space over which to construct wavefunction.
    num_grid_points(*int of float*) Number of points for construction of wavefunction.
    barrier_strength(*float, default* 1.0) Barrier strength in double well potential.
    l_ho_factor(*float, default* 1.0) Normal HO vs double well basis function multiple.
    omega(*float, default* 0.25) Angular frequency of harmonic oscillator potential.
    mass(*int or float, default* 1.0) Mass of electrons. Atomic units is used as default.

Attributes
    h One-body matrix **Type** np.array
    f Fock matrix **Type** np.array
    u Two-body matrix **Type** np.array

Methods
    setup_system(*axis*=0)
        Must be called in order to compute basis functions. Parameter *axis* decices to which axis the well barrier is aligned. $(0, 1) = (x, y)$.

Magnetic field

> **class** quantum_systems.**TwoDimHarmonicOscB**
>   (*n*, *l*, *radius_length*, *num_grid_points*, *omega_0*=1.0, *mass*=1, *omega_c*=0)
>
> Create Two-Dimensional Quantum Dot with constant homogenous magnetic field. This class inherits from **TwoDimensionalHarmonicOscillator**.
>
> **Parameters**
>   **n**(*int*) Number of electrons
>   **l**(*int*) Number of spinorbitals
>   **grid_length**(*int or float*) Space over which to construct wavefunction.
>   **num_grid_points**(*int of float*) Number of points for construction of wavefunction.
>   **omega_0**(*float, default* 1.0) Part of harmonic osc. not dep. on magnetic field.
>   **mass**(*int or float, default* 1.0) Mass of electrons. Atomic units is used as default.
>   **omega_c**(*float, default* 0) Frequency corresponding to strenght of magnetic field.
>
> **Attributes**
>   **h** One-body matrix **Type** np.array
>   **f** Fock matrix **Type** np.array
>   **u** Two-body matrix **Type** np.array
>
> **Methods**
>   **setup_system**()
>   Must be called in order to compute basis functions.
>   **construct_dipole_moment**()
>   Constucts dipole moment. This method is called by setup_system().

6.2 Constructing a Custom System

6.3 Time Evolution

Kapitel 7

Validation

7.1 1D

Testing against Zanghellini[43], see Figure 7.1

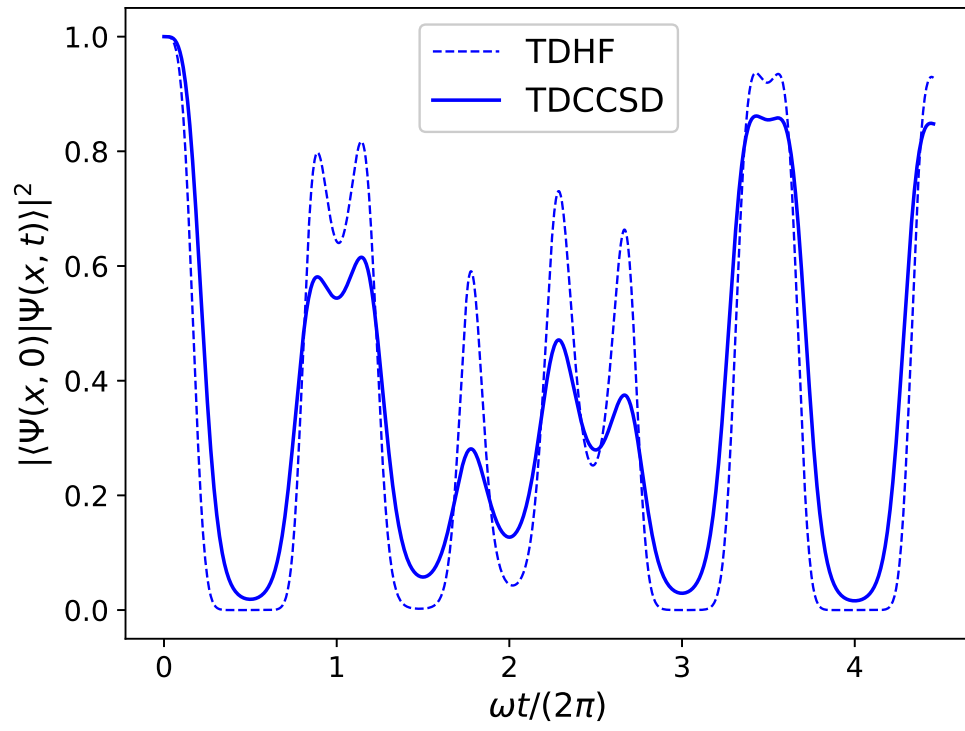Abbildung 7.1: Same as figure two in [43].

Anhang A

Slater-Condon Rules

The Slater-Condon rules are ways to express integrals over operators in terms of single-particle orbitals. Here is an outline of a proof for these rules.

Consider first some Slater determinants,

$$|I\rangle = |i_1 i_2 \ldots i_N\rangle = \hat{i}_1^\dagger \hat{i}_2^\dagger \ldots \hat{i}_N^\dagger |\rangle \tag{A.1}$$

$$|J\rangle = |j_1 j_2 \ldots j_N\rangle = \hat{j}_1^\dagger \hat{j}_2^\dagger \ldots \hat{j}_N^\dagger |\rangle . \tag{A.2}$$

To get started, we want to compute the inner product $\langle I | J \rangle$ of these two Slater determinants,

$$\langle I | J \rangle = \langle | \, \hat{i}_N \ldots \hat{i}_2 \hat{i}_1 \hat{j}_1^\dagger \hat{j}_2^\dagger \ldots \hat{j}_N^\dagger |\rangle . \tag{A.3}$$

In order to evaluate this expression, we move every annihilation operater $\hat{i}_p$ to the right. Starting with $\hat{i}_1$, for instance, we have two possible outcomes. If there is no $\hat{j}_q$ that is the same as $\hat{i}_1$ we get

$$\langle I | J \rangle = \langle | \, \hat{i}_N \ldots \hat{i}_2 \hat{j}_1^\dagger \hat{j}_2^\dagger \ldots \hat{j}_N^\dagger \hat{i}_1 |\rangle \, (-1)^N = 0, \tag{A.4}$$

because $\hat{i}_1 |\rangle = 0$. The other possibility that may arise is that $\hat{i}_1 = \hat{j}_q$, so that

$$\hat{i}_1 \hat{j}_q^\dagger = \{\hat{i}_1, \hat{j}_q^\dagger\} - \hat{j}_q^\dagger \hat{i}_1 = \hat{\delta}_{i_1 k_q} - \hat{j}_p^\dagger \hat{i}_1 = \hat{1} - \hat{j}_q^\dagger \hat{i}_1, \tag{A.5}$$

and

$$\langle I | J \rangle = \langle | \, \hat{i}_N \ldots \hat{i}_2 \hat{j}_1^\dagger \hat{j}_2^\dagger \ldots \hat{j}_{p-1}^\dagger \hat{j}_{p+1}^\dagger \ldots \hat{j}_N^\dagger \hat{i}_1 |\rangle \, (-1)^{p-1} - 0. \tag{A.6}$$

We continue in this manner, moving all $\hat{i}$ to the right and the final result will be zero if there are any $\hat{i}_p$ without a matching $\hat{j}_q$ or $(-1)^\tau$ if the two operator strings are identical to a permutation τ.

Next, consider a symmetric one-body operator

$$\hat{F} = \sum_{\mu=1}^{N} \hat{f}_\mu, \tag{A.7}$$

where μ is the identity of the electron on which the identical $\hat{f}_\mu$ operate. Computing a matrix element of this one-body operator between two Slater determinants will yield three possible

results,

$$
\begin{aligned}
\langle I| \hat{F} |J\rangle &= \langle i_1 i_2 \dots i_N| \hat{F} |j_1 j_2 \dots j_N\rangle \\
&= \sum_{\mu} \langle i_1 i_2 \dots i_N| \hat{f}_{\mu} |j_1 j_2 \dots j_N\rangle \\
&= \sum_{\mu} \langle \phi_{i_1} \phi_{i_2} \dots \phi_{i_N}| \hat{f}_{\mu} \sum_{\hat{P}} (-1)^{\sigma(\hat{P})} \left| \hat{P} \phi_{j_1} \phi_{j_2} \dots \phi_{j_N} \right\rangle = \begin{cases} \sum_k \langle i_k| \hat{f} |i_k\rangle (-1)^{\sigma(\hat{P})} & \text{I} \\ \langle i_k| \hat{f} |i'_k\rangle (-1)^{\sigma(\hat{P})} & \text{II} \\ 0 & \text{III} \end{cases}
\end{aligned}
$$

$$(A.8)$$

In the last line, the integral is written with spinorbitals instead of Slater determinants. The result will be the first case (I), if the operators needed to construct the Slater determinants are the same, up to a permutation with permutation parity σ associated with the permutation operator $\hat{P}$ needed to permute the product of spinorbitals. If there exists excactly one noncoincidence in the string of operators so that $\hat{P} j_1 j_2 \dots j_N = i_1 i_2 \dots i'_k \dots i_N$ where $i_k \neq i'_k$, we get the result in the second case (II). If there are two or more noncoincidences, the result is zero (III).

With second quantisation we might write a one-electron operators differently,

$$
\sum_{kl} \langle k| \hat{f} |l\rangle \hat{a}_k^{\dagger} \hat{a}_l = \sum_{kl} f_{kl} \hat{a}_k^{\dagger} \hat{a}_l. \tag{A.9}
$$

It is possible to show that the results are the same in this representation. First, consider the case where the two Slater determinants are equal,

$$
\begin{aligned}
\langle I| \sum_{kl} f_{kl} \hat{a}_k^{\dagger} \hat{a}_l |I\rangle &= \sum_{kl} f_{kl} \langle I| \hat{a}_k^{\dagger} \hat{a}_l |I\rangle \\
&= \sum_{kl} f_{kl} \delta_{kl} n_l(I) = \sum_{k \in I} f_{kk} = \sum_{k=1}^{N} \langle i_k| \hat{f} |i_k\rangle .
\end{aligned}
\tag{A.10}
$$

Second, we look at the case where we have one noncoincidence, $i_p \neq j_p$,

$$
\begin{aligned}
\langle I| \sum_{kl} f_{kl} \langle I| \hat{a}_k^{\dagger} \hat{a}_l |J\rangle &= \sum_{kl} f_{kl} \langle I| \hat{a}_k^{\dagger} \hat{a}_l |J\rangle \\
&= \sum_{kl \neq p} f_{kl} \langle I| \hat{a}_k^{\dagger} \hat{a}_l |J\rangle + f_{i_p j_p} \langle I| \hat{i}_p^{\dagger} \hat{j}_p |J\rangle \\
&= 0 + f_{i_p j_p} \langle I'|I'\rangle = \left\langle \hat{i}_p \left| \hat{f} \right| \hat{i}_p \right\rangle .
\end{aligned}
\tag{A.11}
$$

Lastly, there is no pair of operators $\hat{a}_k^{\dagger} \hat{a}_l$ that will give a non-zero result. Consequently, we see that the second-quantised form of the one-body operator gives the same result.

Similarly, consider a symmetric two-body operator,

$$
\hat{G} = \sum_{\mu < \nu}^{N} \hat{g}_{\mu\nu} = \frac{1}{2} \sum_{\mu \neq \nu}^{N} \hat{g}_{\mu\nu} = \frac{1}{2} \sum_{ijkl} \langle ij| \hat{g} |kl\rangle \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k. \tag{A.12}
$$

We would like to show that the second-quantized form is correct, and therefore firstly consider the case where the two Slater determinants are equal, i.e. zero noncoincidences;

$$
\langle I| \hat{G} |I\rangle = \frac{1}{2} \sum_{ijkl} \langle ij| \hat{G} |kl\rangle \langle I| \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k |I\rangle . \tag{A.13}
$$

We must have $k = i_p$ and $l = i_q$ appear in $|I\rangle$, so that

$$\langle I| \hat{G} |I\rangle = \frac{1}{2} \sum_{ij} \langle ij| \hat{g} |i_p i_q\rangle \langle I| \hat{a}^\dagger \hat{a}^\dagger \hat{a}_{i_p} \hat{a}_{i_q} |i_1 i_2 \ldots i_p \ldots i_q \ldots\rangle$$
$$= \frac{1}{2} \sum_{ij} \langle ij| \hat{g} |i_p i_q\rangle \langle I| \hat{a}_i^\dagger \hat{a}_j^\dagger |i_1 i_2 \ldots\rangle (-1)^{(p-1)+(q-2)}. \tag{A.14}$$

From this point we have two possibilities for the values of i and j, because the creation operators must put the same values back into the ket,

$$\begin{aligned} \langle i_p i_q| \hat{g} |i_p i_q\rangle \langle I|i_1 i_2 \ldots i_p \ldots i_q \ldots\rangle (-1)^{(p-1)+(q-2)}(-1)^{(p-1)+(q-2)} \\ = \langle i_p i_q| \hat{g} |i_p i_q\rangle \end{aligned} \qquad (i = i_p, \ j = i_q); \quad \text{(A.15)}$$

$$\begin{aligned} \langle i_q i_p| \hat{g} |i_p i_q\rangle \langle I|i_1 i_2 \ldots i_p \ldots i_q \ldots\rangle (-1)^{(p-1)+(q-2)}(-1)^{(p-1)+(q-1)} \\ = -\langle i_q i_p| \hat{g} |i_p i_q\rangle = -\langle i_p i_q| \hat{g} |i_q i_p\rangle \end{aligned} \qquad (i = i_q, \ j = i_p). \quad \text{(A.16)}$$

By starting in the reverse order, we obtain the same contributions. The total matrix element is therefore,

$$\langle I| \hat{G} |I\rangle = \frac{1}{2} \sum_{i \in I} \sum_{j \in J} (\langle ij| \hat{g} |ij\rangle - \langle ij| \hat{g} |ji\rangle) = \sum_{\substack{i<j \\ i,j \in I}} \langle ij| \hat{g} |ij\rangle_{\text{AS}}. \tag{A.17}$$

Next, we consider a single noncoincidence in $|I\rangle$, $i_p \neq i_p'$,

$$|I\rangle = |i_1 i_2 \ldots i_p \ldots\rangle, \tag{A.18}$$
$$|I'\rangle = |i_1 i_2 \ldots i_p' \ldots\rangle. \tag{A.19}$$

We get contributions to $\langle I| \hat{G} |I'\rangle$ from the operator string $\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k$ in the following cases,

$$i = i_p', \ k = i_p, \ j = l = i_q \rightarrow \langle i_p' i_q |i_p i_q\rangle \tag{A.20}$$
$$i = i_p', \ l = i_p, \ j = k = i_q \rightarrow -\langle i_p' i_q |i_q i_p\rangle \tag{A.21}$$
$$j = i_p', \ l = i_p, \ i = k = i_q \rightarrow \langle i_q i_p' |i_q i_q\rangle \tag{A.22}$$
$$j = i_p', \ k = i_p, \ i = l = i_q \rightarrow -\langle i_q i_p' |i_p i_q\rangle, \tag{A.23}$$

where the two first terms are equal to the last terms, respectively. This leaves us with,

$$\langle I'| \hat{G} |I\rangle = 2 \times \frac{1}{2} (\langle i_p' j| \hat{g} |i_p j\rangle - \langle i_p' j| \hat{g} |j i_p\rangle) = \sum_{j \in I} \langle i_p' j| \hat{g} |i_p j\rangle_{\text{AS}}. \tag{A.24}$$

After a while we see a pattern emerges. For two noncoincidences ($i_p \neq i_p'$, $i_q \neq i_q'$) we have,

$$\langle I'| \hat{G} |I\rangle = \langle i_p' i_q'| \hat{g} |i_p i_q\rangle, \tag{A.25}$$

while for three or more noncoincidences,

$$\langle I'| \hat{G} |I\rangle = 0. \tag{A.26}$$

Anhang B

Diagrammatic Notation

B.1 Slater determinants

Drawing the reference state will result in a drawing of nothing. A single-excited reference state is two vertical arrows

$$\Phi_i^a = \quad \text{i} \uparrow \quad \downarrow \text{a} \;, \tag{B.1}$$

while the double-excited Slater determinant consists of four vertical arrows,

$$\Phi_{ij}^{ab} = \quad \text{i} \uparrow \quad \downarrow \text{a} \quad \text{j} \uparrow \quad \downarrow \text{b} \;. \tag{B.2}$$

The horizontal positions of the lines have no significance. If we want to indicate a bra or ket form we draw a couple of horizontal lines,

$$\left|\Phi_i^a\right\rangle = \{\hat{a}^\dagger \hat{i}\}\left|0\right\rangle = \quad \text{i} \uparrow \quad \downarrow \text{a} \;, \quad \left\langle\Phi_i^a\right| = \left\langle 0\right| \{\hat{i}^\dagger \hat{a}\} = \quad \text{i} \uparrow \quad \downarrow \text{a} \;, \tag{B.3}$$

where $\{ABC\dots\}$ is a normal ordered product relative to the Fermi vacuum. A double-excited ket state could be drawn like

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\}\left|0\right\rangle = \{(\hat{a}^\dagger \hat{i})(\hat{b}^\dagger \hat{j})\}\left|0\right\rangle = \quad \text{i} \uparrow \quad \downarrow \text{a} \quad \text{j} \uparrow \quad \downarrow \text{b} \tag{B.4}$$

This drawing could, however, also mean $\left|\phi_{ij}^{ba}\right\rangle$. The use of diagrams will be independent of this ambiguity, as long as one remains consistent. To be precise one can introduce dotted/dashed

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lines,

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\}\left|0\right\rangle = \{(\hat{a}^\dagger\hat{i})(\hat{b}^\dagger\hat{j})\}\left|0\right\rangle = \quad \text{(B.5)}$$

These indicate what index letters should be above and below one another.

B.2   One-Body Operator

The one-electron operator on normal-ordered from is given by

$$\hat{U}_N = \sum_{pq} \left\langle p\right|\hat{u}\left|q\right\rangle \{\hat{p}^\dagger\hat{q}\}, \tag{B.6}$$

acting on a singly excited Slater determinant

$$\left|\Phi_i^a\right\rangle = \{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle, \tag{B.7}$$

id est

$$\sum_{pq} \left\langle p\right|\hat{u}\left|q\right\rangle \{\hat{p}^\dagger\hat{q}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle. \tag{B.8}$$

There are four different terms arising from this expression, depending on whether p and q represents particles or holes. Beginning with a *particle-particle* term,

$$\begin{aligned}
\left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\hat{c}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle &= \left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\hat{c}\hat{a}^\dagger\hat{i}\}\left|0\right\rangle + \left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\overset{\sqcap}{\hat{c}\hat{a}^\dagger}\hat{i}\}\left|0\right\rangle \\
&= \left\langle b\right|\hat{u}\left|c\right\rangle \hat{b}^\dagger\hat{a}^\dagger\hat{i}\hat{c}\left|0\right\rangle + \left\langle b\right|\hat{u}\left|c\right\rangle \delta_{ac}\{\hat{b}^\dagger\hat{i}\} \\
&= 0 + \left\langle b\right|\hat{u}\left|c\right\rangle \delta_{ac}\left|\Phi_i^a\right\rangle,
\end{aligned} \tag{B.9}$$

giving non-zero contributions of the type

$$\left\langle b\right|\hat{u}\left|a\right\rangle \{\hat{b}^\dagger\hat{a}\}\left|\Phi_i^a\right\rangle = \left\langle b\right|\hat{u}\left|a\right\rangle \left|\Phi_i^b\right\rangle. \tag{B.10}$$

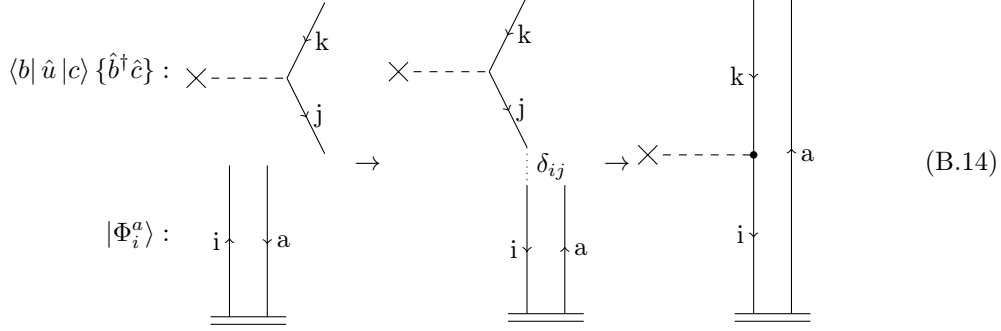We can draw a graphical representation of this contraction process,

$$\tag{B.11}$$

Now, let's consider a *hole-hole* term acting on the same single-excited Slater determinant,

$$\begin{aligned}
\left\langle j\right|\hat{u}\left|k\right\rangle \{\hat{j}^\dagger\hat{k}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle &= \left\langle j\right|\hat{u}\left|k\right\rangle \{\hat{j}^\dagger\hat{k}\hat{a}^\dagger\hat{i}\}\left|0\right\rangle + \left\langle j\right|\hat{u}\left|k\right\rangle \{\overset{\sqcap}{\hat{j}^\dagger\hat{k}\hat{a}^\dagger}\hat{i}\}\left|0\right\rangle \\
&= -\left\langle j\right|\hat{u}\left|k\right\rangle \{\hat{k}\hat{a}^\dagger\hat{i}\hat{j}^\dagger\}\left|0\right\rangle + \delta_{ij}\left\langle i\right|\hat{u}\left|k\right\rangle \{\hat{k}\hat{a}^\dagger\}\left|0\right\rangle \\
&= 0 - \delta_{ij}\left\langle i\right|\hat{u}\left|j\right\rangle \{\hat{a}^\dagger\hat{k}\}\left|0\right\rangle \\
&= -\delta_{ij}\left\langle i\right|\hat{u}\left|j\right\rangle \left|\Phi_k^a\right\rangle,
\end{aligned} \tag{B.12}$$

meaning we are only left with non-zero contributions of the type,

$$\langle i | \hat{u} | j \rangle \{\hat{i}^\dagger \hat{k}\} | \Phi_i^a \rangle = - \langle i | \hat{u} | k \rangle | \Phi_k^a \rangle . \tag{B.13}$$

One can make a diagrammatic representation of this contraction as well,

$$\tag{B.14}$$

Next, we look at the *particle-hole* term,

$$\begin{aligned} \langle b | \hat{u} | j \rangle \{\hat{b}^\dagger \hat{j}\}\{\hat{a}^\dagger \hat{i}\} | 0 \rangle &= \langle b | \hat{u} | j \rangle \{\hat{b}^\dagger \hat{j}\hat{a}^\dagger \hat{i}\} | 0 \rangle \\ &= \langle b | \hat{u} | j \rangle \, \hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i} | 0 \rangle \\ &= \langle b | \hat{u} | j \rangle \, \big| \Phi_{ij}^{ab} \big\rangle , \end{aligned} \tag{B.15}$$

with no contraction in this case. This expression is represented by

$$\tag{B.16}$$

showing the resulting determinant is $\big| \Phi_{ij}^{ab} \big\rangle$. Holes and particles joined at the same vertex, on the same path, are in the same vertical position in the excited Slater determinant. This representation may appear to leave out the cases where $i = j$ and/or $a = b$, but these diagrams will give a vanishing Slater determinant.

The *hole-particle* term is

$$\begin{aligned} \langle j | \hat{u} | b \rangle \{\hat{j}^\dagger \hat{b}\}\{\hat{a}^\dagger \hat{i}\} | 0 \rangle &= \langle j | \hat{u} | b \rangle \{\hat{j}^\dagger \hat{b}\hat{a}^\dagger \hat{i}\} | 0 \rangle + \langle j | \hat{u} | b \rangle \{\overbrace{\hat{j}^\dagger \hat{b}\hat{a}^\dagger \hat{i}}\} | 0 \rangle \\ \hat{U}_N = \qquad &+ \langle j | \hat{u} | b \rangle \{\hat{j}^\dagger \overbrace{\hat{b}\hat{a}^\dagger} \hat{i}\} | 0 \rangle + \langle j | \hat{u} | b \rangle \{\overbrace{\hat{j}^\dagger \hat{b}\hat{a}^\dagger \hat{i}}\} | 0 \rangle \\ &= \delta_{ij}\delta_{ab} \langle j | \hat{u} | b \rangle | 0 \rangle = \langle i | \hat{u} | a \rangle | 0 \rangle , \end{aligned} \tag{B.17}$$

which is represented by

$$\tag{B.18}$$

which shows that the result of the operation involved the vacuum state.

The full one-body operator becomes,

$$
\sum_b \underbrace{\quad}_{\langle b| \, \hat{u} \, |a \rangle \, \left| \Phi_i^b \right\rangle} + \sum_j \underbrace{\quad}_{-\langle i| \, \hat{u} \, |j \rangle \, \left| \Phi_j^a \right\rangle} + \sum_{bj} \underbrace{\quad}_{\langle b| \, \hat{u} \, |j \rangle \, \left| \Phi_{ij}^{ab} \right\rangle} + \underbrace{\quad}_{\langle i| \, \hat{u} \, |a \rangle \, |0\rangle} \tag{B.19}
$$

Anhang C

2D Coulomb elements

Implementation of two-body matrix elements for the two-dimensional quantum dots[2]. Note that Anisimovas and Matulis uses the chemist's convention $\langle ij| \hat{u} |lk \rangle$ which is $\langle ij| \hat{u} |kl \rangle$ in the physcist's notation. That is, the last two indices are interchanged.

```python
def coulomb_ho(n_i, m_i, n_j, m_j, n_l, m_l, n_k, m_k):
    element = 0

    if m_i + m_j != m_k + m_l:
        return 0

    M_i = 0.5 * (abs(m_i) + m_i)
    dm_i = 0.5 * (abs(m_i) - m_i)

    M_j = 0.5 * (abs(m_j) + m_j)
    dm_j = 0.5 * (abs(m_j) - m_j)

    M_k = 0.5 * (abs(m_k) + m_k)
    dm_k = 0.5 * (abs(m_k) - m_k)

    M_l = 0.5 * (abs(m_l) + m_l)
    dm_l = 0.5 * (abs(m_l) - m_l)

    n = np.array([n_i, n_j, n_k, n_l], dtype=np.int64)
    m = np.array([m_i, m_j, m_k, m_l], dtype=np.int64)
    j = np.array([0, 0, 0, 0], dtype=np.int64)
    l = np.array([0, 0, 0, 0], dtype=np.int64)
    g = np.array([0, 0, 0, 0], dtype=np.int64)

    for j_1 in range(n_i + 1):
        j[0] = j_1
        for j_2 in range(n_j + 1):
            j[1] = j_2
            for j_3 in range(n_k + 1):
                j[2] = j_3
                for j_4 in range(n_l + 1):
                    j[3] = j_4
```

```python
                g[0] = j_1 + j_4 + M_i + dm_l
                g[1] = j_2 + j_3 + M_j + dm_k
                g[2] = j_3 + j_2 + M_k + dm_j
                g[3] = j_4 + j_1 + M_l + dm_i

                G = np.sum(g)
                ratio_1 = log_ratio_1(j)
                prod_2 = log_product_2(n, m, j)
                ratio_2 = log_ratio_2(G)

                temp = 0
                for l_1 in range(g[0] + 1):
                    l[0] = l_1
                    for l_2 in range(g[1] + 1):
                        l[1] = l_2
                        for l_3 in range(g[2] + 1):
                            l[2] = l_3
                            for l_4 in range(g[3] + 1):
                                l[3] = l_4

                                if l_1 + l_2 != l_3 + l_4:
                                    continue

                                L = np.sum(l)

                                temp += (
                                    -2
                                    * (int(g[1] + g[2] - l[1] - l[2]) & 0x1)
                                    + 1
                                ) * np.exp(
                                    log_product_3(l, g)
                                    + math.lgamma(1.0 + 0.5 * L)
                                    + math.lgamma(0.5 * (G - L + 1.0))
                                )

                element += (
                    (-2 * (int(np.sum(j)) & 0x1) + 1)
                    * np.exp(ratio_1 + prod_2 + ratio_2)
                    * temp
                )

    element *= log_product_1(n, m)

    return element
```

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