Unternehmen Taifun

by

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Contents

Part I

Fundamentals

Chapter 1

Quantum Mechanics

> Hierzu ist es notwendig, die Energy nicht als eine stetige unbeschränkt teilbare, sondern als eine discrete, ause einer ganzen Zahl von endlichen gleichen Teilen zusammengesetzte Grösse aufzufassen.
>
> — Max Planck

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,

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

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,

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

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

$$\Psi = \Psi(x_1, x_2, \ldots, x_N). \tag{1.6}$$

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

$$\Psi : X^N \to \mathbb{C}. \tag{1.7}$$

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,

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

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,

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

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[1] and John von Neumann[8].

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.

[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. Electronic systems are

Free particle in one dimension,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{1.16}$$

Introduce potential.
Many particles in many dimenions.
Interaction.
Nuclear interaction (molecule).
There is other stuff as well.
In atomic units, the Hamiltonian for N electrons and M nuclei is [3],

$$\hat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_iA} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_AZ_B}{R_{AB}}, \tag{1.17}$$

[2] In the Schrödinger picture.
[3] Often referred to as the electronic Hamiltonian

Table 1.1: Conversion of atomic units to SI units THIS IS FROM SZABO AND OSTLUND.

Physical quantity	Conversion factor	Value
Length	a_0	$5.2918 \times 10^{-11} m$
Mass	m_e	$9.1095 \times 10^{-31} kg$
Charge	e	$1.6022 \times 10^{-19} C$
Energy	E_a	$4.3598 \times 10^{-18} J$
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	$E_a/(ea_0)$	$5.1423 \times 10^{11} V m^{-1}$
Wave function	$a_0^{-3/2}$	$2.5978 \times 10^{15} m^{-3/2}$

where M_A si the ratio of the mass of nucleus A to the mass of an electron, and Z_A is the atomic number of nuclus A. The first term in Equation 1.17 is the operator for the kinetic energy of the electrons, the second term is the operator for the kinetic energi of the nuclei, the third term represents the Coulomb attraction between the electrons and the nuclei, the fourth term is the Coulomb repulsion between electrons and the fifth and last term is the Coulomb repulsion between nuclei.

PERHAPS FIGURE OF GENERAL SYSTEM HERE?

1.3.1 Atomic Units

In the Hamiltionian above (Equation 1.17), 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,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \phi = E\phi, \tag{1.18}$$

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 $r \to \lambda r'$,

$$\left(-\frac{\hbar^2}{2m_e\lambda^2} \nabla'^2 - \frac{e^2}{4\pi\epsilon_0 \lambda r'} \right) \phi' = E\phi'. \tag{1.19}$$

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

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = E_a \to \lambda \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 \tag{1.20}$$

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,

$$\left(-\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right) \phi' = E'\phi'. \tag{1.21}$$

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

1.3.2 The Born-Oppenheimer Approximation

1.4 Indistinguishable Particles and Pauli

In a quantum system the particles are identical and impossible to tell apart, as indicated by several studies (KILDE!!). Feynman: In fact, all electrons are one and the same. The probability density for the location of particles in a system must therefore be permutation invariant,

$$|\Psi(x_1, x_2, \ldots, x_i, x_j x_N)|^2 = |\Psi(x_1, x_2, \ldots, x_j, x_i x_N)|^2. \tag{1.22}$$

For any arbitrary permutation, this is equivalent to

$$\Psi(x_1, \ldots x_N) = e^{i\alpha(\sigma)}\Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}), \tag{1.23}$$

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,

$$(\hat{P}_\sigma \Psi)(x_1, \ldots, x_N) = \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}). \tag{1.24}$$

1.5 Representation of the Wavefunction

1.6 Orbitals

1.6.1 Hartree Products

1.6.2 Slater Determinants

1.7 The Harmonic Oscillator System

Chapter 2

Second Quantisation

Some Slater determinant is written,

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

2.1 Creation and Annihilation Operators

I SHOULD PROBABLY CHANGE TO Qs HERE...?

The notation of creation and annihilation operators vary,

$$\text{creation operator for spinorbital } \phi_i,\ \hat{X}_i^\dagger, \hat{a}_i^\dagger, \hat{c}_i^\dagger, \hat{i}^\dagger;$$
$$\text{annihilation operator for spinorbital } \phi_i,\ \hat{X}_i, \hat{a}_i, \hat{c}_i, \hat{i}.$$

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

$$\hat{a}_i^\dagger |jk \dots z\rangle = |ijk \dots z\rangle \,, \tag{2.3}$$
$$\hat{a}_i^\dagger |ijk \dots z\rangle = 0 \tag{2.4}$$

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

$$\hat{a}_i |ijk \dots z\rangle = |ij \dots z\rangle \,, \tag{2.6}$$
$$\hat{a}_i |jk \dots z\rangle = 0 \tag{2.7}$$

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,

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

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,

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

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

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

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

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,

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

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

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

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,

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

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,

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

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

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

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

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

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

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

where

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

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

$$\langle ij|\,\hat{u}\,|kl\rangle - \langle ij|\,\hat{u}\,|kl\rangle = \langle ij|\,\hat{u}\,|kl\rangle \equiv \langle ij|kl\rangle\,. \tag{2.30}$$

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,

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

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)[4].

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

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

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,

$$\begin{gathered}
\{\hat{a}^\dagger\hat{b}\} = \hat{a}^\dagger\hat{b} \quad \{\hat{b}\hat{a}^\dagger\} = -\hat{a}^\dagger\hat{b} \\
\{\hat{a}\hat{b}\} = \hat{a}\hat{b} = -\hat{b}\hat{a} \\
\{\hat{a}^\dagger\hat{b}^\dagger\} = \hat{a}^\dagger\hat{b}^\dagger = -\hat{b}^\dagger\hat{a}^\dagger \\
\{\hat{a}^\dagger\hat{b}\hat{c}^\dagger\hat{d}\} = -\hat{a}^\dagger\hat{c}^\dagger\hat{b}\hat{d} = \hat{c}^\dagger\hat{a}^\dagger\hat{b}\hat{d} = \hat{a}^\dagger\hat{c}^\dagger\hat{d}\hat{b} = -\hat{c}^\dagger\hat{a}^\dagger\hat{d}\hat{b}.
\end{gathered}$$

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

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

equivalently,

$$\overbrace{\hat{A}\hat{B}} \equiv \hat{A}\hat{B} - \{\hat{A}\hat{B}\}. \tag{2.34}$$

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

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

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.

CONTRACTIONS INSIDE A NORMAL ORDERED PRODUCT HERE.

2.4.2 Wick's Theorem

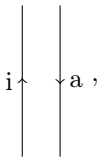
2.4.3 Generalized Wick's Theorem

2.4.4 Particle-Hole Formalism

2.5 Diagrammatic Notation

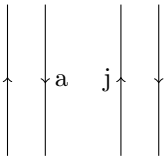
2.5.1 Slater determinants

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

$\Phi_i^a =$ 

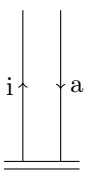
, (2.36)

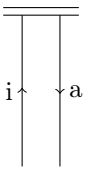
while the double-excited Slater determinant consists of four vertical arrows,

$\Phi_{ij}^{ab} =$ 

. (2.37)

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,

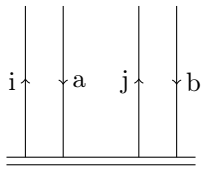
$|\Phi_i^a\rangle = \{\hat{a}^\dagger\hat{i}\}\,|0\rangle =$ 

, $\langle\Phi_i^a| = \langle 0|\,\{\hat{i}^\dagger\hat{a}\} =$ 

, (2.38)

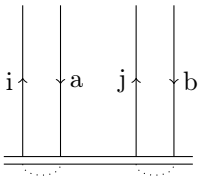
where $\{ABC\dots\}$ is a normal ordered product relative to the Fermi vacuum. A double-excited ket state could be drawn like

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\}\left|0\right\rangle = \{(\hat{a}^\dagger\hat{i})(\hat{b}^\dagger\hat{j})\}\left|0\right\rangle = \tag{2.39}$$



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 lines,

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\}\left|0\right\rangle = \{(\hat{a}^\dagger\hat{i})(\hat{b}^\dagger\hat{j})\}\left|0\right\rangle = \tag{2.40}$$



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

2.5.2 One-Body Operator

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

$$\hat{U}_N = \sum_{pq}\left\langle p\right|\hat{u}\left|q\right\rangle\{\hat{p}^\dagger\hat{q}\}, \tag{2.41}$$

acting on a singly excited Slater determinant

$$\left|\Phi_i^a\right\rangle = \{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle, \tag{2.42}$$

id est

$$\sum_{pq}\left\langle p\right|\hat{u}\left|q\right\rangle\{\hat{p}^\dagger\hat{q}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle. \tag{2.43}$$

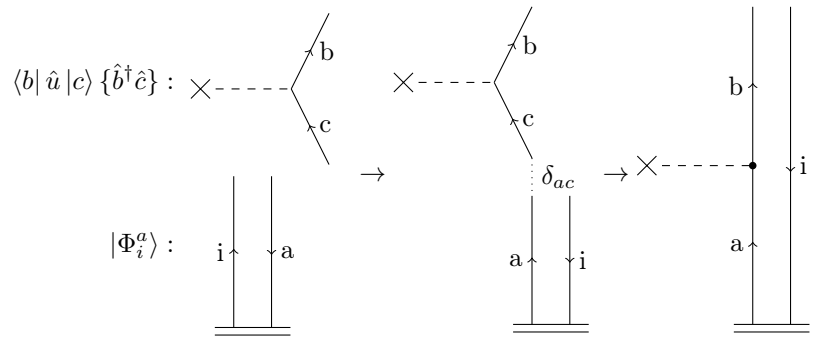
There are four different terms arising from this expression, depending on whether p and q represents particles or holes. Beginning with a *particle-particle* term,

$$\begin{aligned}\left\langle b\right|\hat{u}\left|c\right\rangle\{\hat{b}^\dagger\hat{c}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle &= \left\langle b\right|\hat{u}\left|c\right\rangle\{\hat{b}^\dagger\hat{c}\hat{a}^\dagger\hat{i}\}\left|0\right\rangle + \left\langle b\right|\hat{u}\left|c\right\rangle\{\hat{b}^\dagger\overset{\sqcap}{\hat{c}}\hat{a}^\dagger\hat{i}\}\left|0\right\rangle \\ &= \left\langle b\right|\hat{u}\left|c\right\rangle\hat{b}^\dagger\hat{a}^\dagger\hat{i}\hat{c}\left|0\right\rangle + \left\langle b\right|\hat{u}\left|c\right\rangle\delta_{ac}\{\hat{b}^\dagger\hat{i}\} \\ &= 0 + \left\langle b\right|\hat{u}\left|c\right\rangle\delta_{ac}\left|\Phi_i^a\right\rangle,\end{aligned} \tag{2.44}$$

giving non-zero contributions of the type

$$\left\langle b\right|\hat{u}\left|a\right\rangle\{\hat{b}^\dagger\hat{a}\}\left|\Phi_i^a\right\rangle = \left\langle b\right|\hat{u}\left|a\right\rangle\left|\Phi_i^b\right\rangle. \tag{2.45}$$

We can draw a graphical representation of this contraction process,



(2.46)

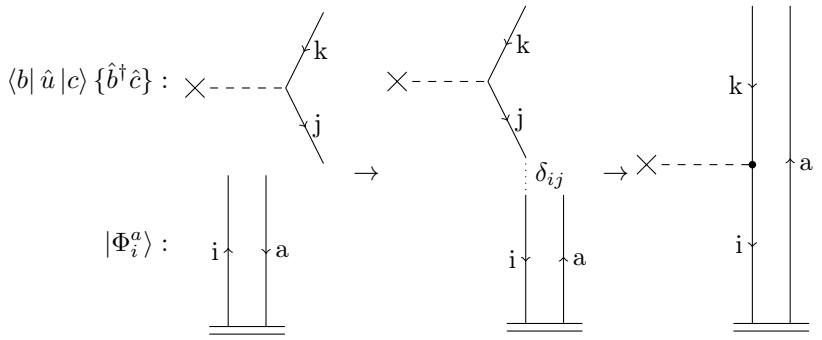
Now, let's consider a *hole-hole* term acting on the same single-excited Slater determinant,

$$\begin{aligned}
\langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\
&= -\,\langle j|\,\hat{u}\,|k\rangle\,\{\hat{k}\hat{a}^\dagger\hat{i}\hat{j}^\dagger\}\,|0\rangle + \delta_{ij}\,\langle i|\,\hat{u}\,|k\rangle\,\{\hat{k}\hat{a}^\dagger\}\,|0\rangle \\
&= 0 - \delta_{ij}\,\langle i|\,\hat{u}\,|j\rangle\,\{\hat{a}^\dagger\hat{k}\}\,|0\rangle \\
&= -\delta_{ij}\,\langle i|\,\hat{u}\,|j\rangle\,|\Phi^a_k\rangle\,,
\end{aligned} \tag{2.47}$$

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

$$\langle i|\,\hat{u}\,|j\rangle\,\{\hat{i}^\dagger\hat{k}\}\,|\Phi^a_i\rangle = -\,\langle i|\,\hat{u}\,|k\rangle\,|\Phi^a_k\rangle\,. \tag{2.48}$$

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

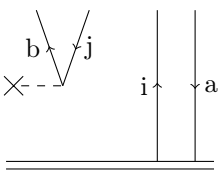


(2.49)

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

$$\begin{aligned}
\langle b|\,\hat{u}\,|j\rangle\,\{\hat{b}^\dagger\hat{j}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle b|\,\hat{u}\,|j\rangle\,\{\hat{b}^\dagger\hat{j}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\
&= \langle b|\,\hat{u}\,|j\rangle\,\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\,|0\rangle \\
&= \langle b|\,\hat{u}\,|j\rangle\,\left|\Phi^{ab}_{ij}\right\rangle,
\end{aligned} \tag{2.50}$$

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



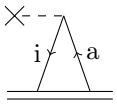
(2.51)

showing the resulting determinant is $\left|\Phi_{ij}^{ab}\right\rangle$. 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

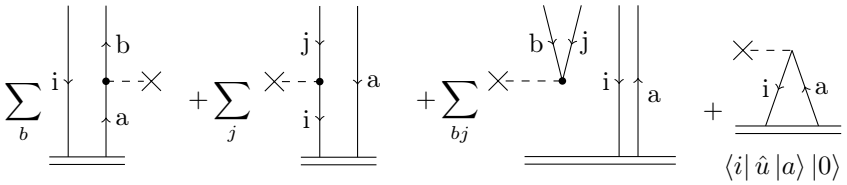
$$\begin{aligned}\langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\ &+ \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\ &= \delta_{ij}\delta_{ab}\,\langle j|\,\hat{u}\,|b\rangle\,|0\rangle = \langle i|\,\hat{u}\,|a\rangle\,|0\rangle\,,\end{aligned} \tag{2.52}$$

which is represented by



(2.53)

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



$\langle b|\,\hat{u}\,|a\rangle\,\left|\Phi_i^b\right\rangle \qquad -\langle i|\,\hat{u}\,|j\rangle\,\left|\Phi_j^a\right\rangle \qquad \langle b|\,\hat{u}\,|j\rangle\,\left|\Phi_{ij}^{ab}\right\rangle \qquad \langle i|\,\hat{u}\,|a\rangle\,|0\rangle$

(2.54)

Part II

The Quantum Many-Body Problem

Chapter 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[5]. 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[10][3]. 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[9][2]. 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[6].

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 assumet 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 eigen function 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[7]

3.1 Deriving the Hartree-Fock Equations

Consider a Hamiltonian for some system

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