Unternehmen Taifun

by

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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[3] and John von Neumann[16].

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. 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.[12],

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

[2] In the Schrödinger picture.

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

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

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[14].

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

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

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[14] 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 $\phi(\mathbf{r})$,

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

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,

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

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),

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

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 $r \to \lambda r'$,

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	$a_0^{-3/2}$	$2.5978 \times 10^{15} m^{-3/2}$

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

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[19]. 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[4],

> 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" [15]. Moreover, all particles with integer spin are bosons, and all particles with half-integer spin are fermions [5, 17]. This can be proved in relativistic quantum mechanics, but must be accepted as an axiom in nonrelativistic theory[13]. 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 "anyons"[15].

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[24].

[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[18]. 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.

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

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,

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

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,

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

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

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

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

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,

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

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

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

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,

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

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

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

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 Hamiltonian 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)[8].

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,

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

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,

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

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

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

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,

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

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,

$$\begin{aligned}\hat{A}\hat{B}\hat{C}\hat{D}\cdots =& n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\overbrace{\hat{A}\hat{B}}\hat{C}\hat{D}\ldots] + n[\overbrace{\hat{A}\hat{B}\hat{C}}\hat{D}\ldots] + n[\overbrace{\hat{A}\hat{B}\hat{C}\hat{D}}\ldots] \\ &+\cdots + n[\hat{A}\overbrace{\hat{B}\hat{C}}\hat{D}\ldots] + n[\hat{A}\overbrace{\hat{B}\hat{C}\hat{D}}\ldots] + \cdots + n[\hat{A}\hat{B}\overbrace{\hat{C}\hat{D}}\ldots] + \cdots + \\ &+ n[\overbrace{\hat{A}\hat{B}}\overbrace{\hat{C}\hat{D}}\ldots] + n[\overbrace{\hat{A}\overbrace{\hat{B}\hat{C}}\hat{D}}\ldots] + n[\overbrace{\hat{A}\hat{B}\overbrace{\hat{C}\hat{D}}}\ldots] + \ldots,\end{aligned} \tag{2.37}$$

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,

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

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,

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

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

Part II

Quantum Many-Body Approximations

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[9]. 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[23][7]. 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[22][6]. 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[10].

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[11]

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,

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

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,

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

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 $k \in \{1,\dots,N\}$ 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,

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

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),

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

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

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

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

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 $\langle \cdot\ \phi_1 | \hat{w} | \phi_2\phi_3 \rangle \in L^2_1$ 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.

Chapter 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 "order parameter" λ. This parameter is used to categorise the contributions of different order. The exact solution is given by

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

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

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

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,

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

We insert these expansions into the Schrödinger equation,

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

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,

$$\begin{aligned} \langle\Phi_n|\,\hat{H}_0 - E_n^{(0)}\,\left|\Psi_n^{(1)}\right\rangle &= \langle\Phi_n|\,E_n^{(1)} - \hat{V}\,|\Phi_n\rangle \\ \left\langle(\hat{H}_0 - E_n^{(0)})\Phi_n\right|\left.\Psi_n^{(1)}\right\rangle &= \langle\Phi_n|\,E_n^{(1)} - \hat{V}\,|\Phi_n\rangle \\ \rightarrow E_n^{(1)} &= \langle\Phi_n|\,\hat{V}\,|\Phi_n\rangle = \hat{V}_{nn} \end{aligned} \tag{4.17}$$

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 $\left\langle\Phi_n\middle|\Psi_n^{(1)}\right\rangle = \delta_{l0}$. For the general mth-order expression (Equation 4.15),

$$\begin{aligned} \langle\Phi_n|\,E_n^0 - \hat{H}_0\,\left|\Psi_n^{(m)}\right\rangle &= \langle\Phi_n|\,\hat{V}\,\left|\Psi_n^{(m-1)}\right\rangle - \sum_{l=0}^{m-1} E_n^{(m-l)}\left\langle\Phi_n\middle|\Psi_n^{(l)}\right\rangle \\ E_n^{(m)} = \left\langle\Phi_n^{(m)}\right| &= \langle\Phi_n|\,\hat{V}\,\left|\Psi_n^{(m-1)}\right\rangle. \end{aligned} \tag{4.18}$$

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,

$$\begin{aligned} \hat{P} &= |\Phi_0\rangle \langle\Phi_0| \\ \hat{Q} &= \hat{1} - \hat{P} = \sum_{i=1}^{N} |\Phi_i\rangle \langle\Phi_i| . \end{aligned} \tag{4.19}$$

The projecton operators have the following conventient properties,

$$\begin{gathered} \hat{P}^2 = |\Phi_0\rangle \langle\Phi_0|\Phi_0\rangle \langle\Phi_0| = |\Phi_0\rangle \langle\Phi_0| = \hat{P} \\ \hat{Q}^2 = (1-\hat{P})^2 = \hat{1} - \hat{P} - \hat{P} + \hat{P} = \hat{1} - \hat{P} = \hat{Q} \\ \hat{P}\hat{Q} = \hat{Q}\hat{P} = 0 \\ [\hat{P}, \hat{H}_0] = [\hat{Q}, \hat{H}_0] = 0 \end{gathered} \tag{4.20}$$

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,

$$\begin{aligned} (\hat{H}_0 + \hat{V})\Psi &= E\Psi, \\ \rightarrow -\hat{H}_0\Phi &= (\hat{V} - E)\Psi, \end{aligned} \tag{4.25}$$

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,

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

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,

$$\begin{aligned}&\frac{\hat{Q}}{\zeta - \hat{H}_0}\hat{Q}(\zeta - \hat{H}_0)\hat{Q} \\ &\quad= \left(\sum_{i,j\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta - \hat{H}_0)^{-1} \, |\Phi_j\rangle \langle\Phi_j|\right)\left(\sum_{k,l\neq 0} |\Phi_k\rangle \langle\Phi_k| \, (\zeta - \hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l|\right) \\ &\quad= \sum_{i,l\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta - \hat{H}_0)^{-1} \left(\sum_{j\neq 0} |\Phi_j\rangle \langle\Phi_j|\right) (\zeta - \hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l| \\ &\quad= \sum_{i,l\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta - \hat{H}_0)^{-1}(1 - |\Phi_0\rangle \langle\Phi_0|)(\zeta - \hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l| \\ &\quad= \sum_{i\neq 0} |\Phi_i\rangle \langle\Phi_i| = \hat{Q}.\end{aligned} \tag{4.32}$$

Applying the resolvent to both sides of Equation 4.29,

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

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 Brillouin-Wigner Perturbation Theory

Set $\zeta = E$ and get BWPT[2, 25].

4.3 Rayleigh-Schrödinger Perturbation Theory

set $\zeta = E_n^{(0)}$ and get RSPT[20, 21].

Part III

Results

Chapter 5

Validation

5.1 1D

Testing against Zanghellini[26], see Figure 5.1

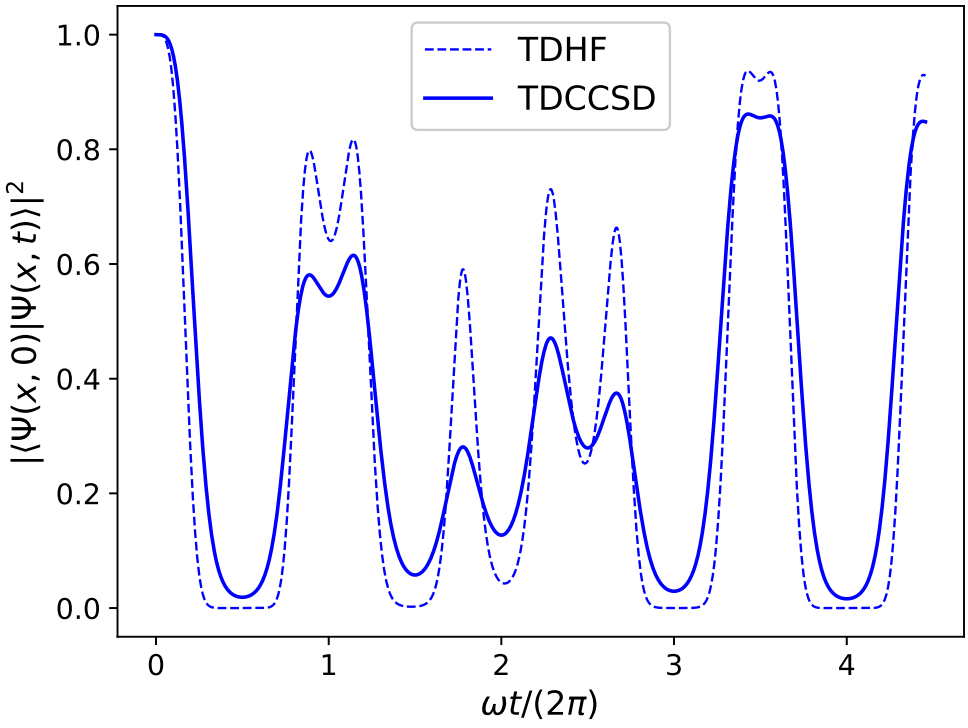


Figure 5.1: Same as figure two in [26].

Appendix 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,

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

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

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

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

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

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

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

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

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,

$$\begin{aligned}\langle I|\,\hat{F}\,|J\rangle &= \langle i_1 i_2 \dots i_N|\,\hat{F}\,|j_1 j_2 \dots j_N\rangle \\ &= \sum_{\mu} \langle i_1 i_2 \dots i_N|\,\hat{f}_\mu\,|j_1 j_2 \dots j_N\rangle \\ &= \sum_{\mu} \langle \phi_{i_1}\phi_{i_2}\dots\phi_{i_N}|\,\hat{f}_\mu \sum_{\hat{P}} (-1)^{\sigma(\hat{P})} \left|\hat{P}\phi_{j_1}\phi_{j_2}\dots\phi_{j_N}\right\rangle = \begin{cases} \sum_k \langle i_k|\,\hat{f}\,|i_k\rangle\,(-1)^{\sigma(\hat{P})} & \text{I} \\ \langle i_k|\,\hat{f}\,|i'_k\rangle\,(-1)^{\sigma(\hat{P})} & \text{II} \\ 0 & \text{III} \end{cases}\end{aligned} \tag{A.8}$$

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, $i_p \neq j_p$,

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

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

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

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,

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

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

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

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

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,

$$i = i'_p,\ k = i_p,\ j = l = i_q \to \langle i'_p i_q|i_p i_q\rangle \tag{A.20}$$

$$i = i'_p,\ l = i_p,\ j = k = i_q \to -\langle i'_p i_q|i_q i_p\rangle \tag{A.21}$$

$$j = i'_p,\ l = i_p,\ i = k = i_q \to \langle i_q i'_p|i_q i_q\rangle \tag{A.22}$$

$$j = i'_p,\ k = i_p,\ i = l = i_q \to -\langle i_q i'_p|i_p i_q\rangle\,, \tag{A.23}$$

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

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

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,

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

Appendix 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

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

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

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

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,

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

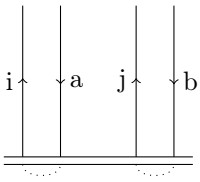
where $\{ABC\dots\}$ is a normal ordered product relative to the Fermi vacuum. A double-excited ket state could be drawn like

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

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

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,

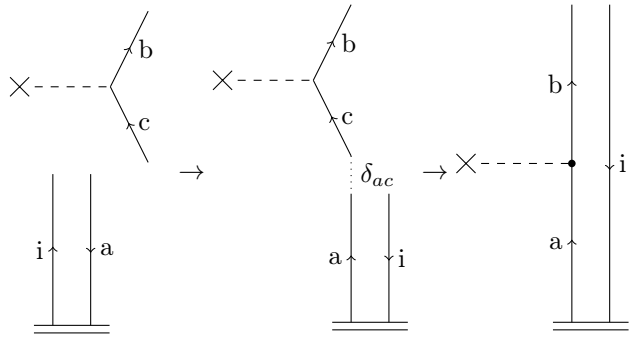
$$\begin{aligned}
\left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\hat{c}\}\{\hat{a}^\dagger\hat{i}\}\left|0\right\rangle &= \left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\hat{c}\hat{a}^\dagger\hat{i}\}\left|0\right\rangle + \left\langle b\right|\hat{u}\left|c\right\rangle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

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,

$\left\langle b\right|\hat{u}\left|c\right\rangle \{\hat{b}^\dagger\hat{c}\}:$ $\left|\Phi_i^a\right\rangle:$ (B.11)



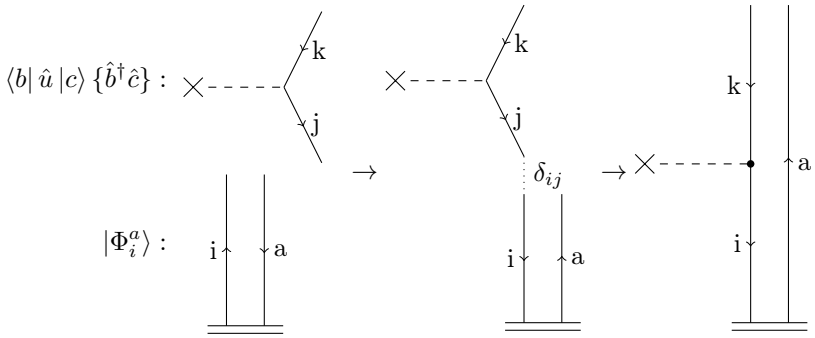
Now, let's consider a *hole-hole* term acting on the same single-excited Slater determinant,

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

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,

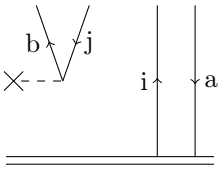


(B.14)

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

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

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



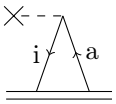
(B.16)

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

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

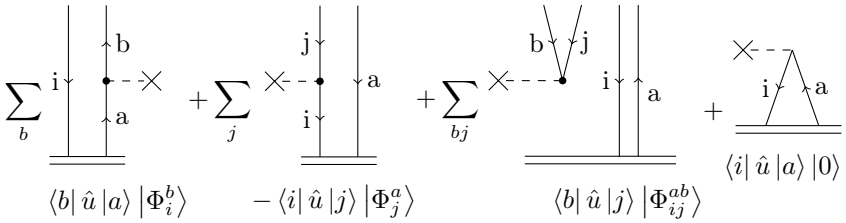
which is represented by



(B.18)

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

The full one-body operator becomes,



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

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