

UNTERNEHMEN TAIFUN

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Part I

Fundamentals

Chapter 1

Quantum Mechanics

Hierzu ist es notwendig, die Energy nicht als eine stetige unbeschränkt teilbare, sondern als eine discrete, aus 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 $q = (\vec{q}_1, \dots, \vec{q}_N)$ and corresponding conjugate momenta $p = (\vec{p}_1, \dots, \vec{p}_N)$. 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

$$\{f, g\} = \frac{\partial f}{\partial q} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q}. \quad (1.1)$$

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

$$\dot{q} = \frac{\partial}{\partial p} \mathcal{H}(q, p) \quad (1.2)$$

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

where $\mathcal{H}(q, p)$ 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,

$$\frac{dp_i}{dt} = \{p_i, \mathcal{H}\}, \quad \frac{dq_i}{dt} = \{q_i, \mathcal{H}\}. \quad (1.4)$$

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 potential $w(q_{ij})$ has the following Hamiltonian,

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

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

1.2 Canonical Quantisation

In order to transition from a classical system to a quantum system, we move from the classical phase space to the Hilbert space, through the procedure known as canonical, or first¹-, 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

$$\Psi = \Psi(x_1, x_2, \dots, x_N). \quad (1.6)$$

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

$$\Psi : X^N \rightarrow \mathbb{C}. \quad (1.7)$$

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 $|\Psi(x_1, \dots, x_N)|^2$, gives the probability of finding the particle at a certain position. For a situation with one particle in one dimension we have,

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

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

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

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[2] and John von Neumann[11].

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 equipped with a scalar product.

¹Second quantisation comes later.

Observables Each physical observable of a system is associated 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,

$$\langle \phi | \hat{O} \psi \rangle = \langle \hat{O} \phi | \psi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle. \quad (1.10)$$

Completeness means,

$$\sum_i |i\rangle \langle i| = \mathbf{1}. \quad (1.11)$$

Orthonormal means,

$$\langle i | j \rangle = \delta_{ij}. \quad (1.12)$$

Time Evolution The time evolution of the state vector, $|\psi\rangle = |\psi(t)\rangle$, is given by the Schrödinger equation².

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

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

$$\hat{O} |n\rangle = o_n |n\rangle. \quad (1.14)$$

The probability for finding a particular eigenvalue in the measurement is

$$p_n = |\langle n | \psi \rangle|^2, \quad (1.15)$$

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 Hamiltonian 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 Hamiltonian, thoroughly described in Helgaker et al.[9],

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

²In the Schrödinger picture.

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

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

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[10].

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

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

The first three terms are the nonrelativistic Coulomb point-charge interactions between nucleus 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 quadrupole moment. These terms are important in nuclear resonance studies[10] and nuclear quadrupole resonance studies[1].

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

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

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

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

where q_{tot} is the total charge of the molecule, μ_0 is the dipole moment, \mathbf{Q}_{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),

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

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 parenthesis are electronic contributions to Zeeman effect from the spin of the electrons. The relativistic correction constituted in the third term is important in electron paramagnetic resonance (EPR) spectroscopy.

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

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

When electron spin coupled to magnetic field induced by other charges in 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 hyperfine operator and couples magnetic moments to the orbital motion of electrons, while the fifth and last term is modes coupling of electric fields and orbits.

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

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

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 Hamiltonian above (Equation 1.16), we have grown up and set $\hbar = m_e = e = \dots = 1$. 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,

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

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 permittivity of free space. We make this equation dimensionless by letting $r \rightarrow \lambda r'$,

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

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

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

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

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

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

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

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,

$$|\Psi(x_1, x_2, \dots, x_i, x_j x_N)|^2 = |\Psi(x_1, x_2, \dots, x_j, x_i x_N)|^2. \quad (1.28)$$

For any arbitrary permutation, this is equivalent to

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

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,

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

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,

$$|\Phi\rangle = |\phi_i \phi_j \phi_k \dots \phi_z\rangle = |ijk\dots z\rangle. \quad (2.1)$$

2.1 Creation and Annihilation Operators

I SHOULD PROBABLY CHANGE TO Qs HERE...?

The notation of creation and annihilation operators vary,

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

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

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

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

$$\hat{a}_i^\dagger |ijk\dots z\rangle = |ijk\dots z\rangle, \quad (2.3)$$

$$\hat{a}_i^\dagger |ijk\dots z\rangle = 0 \quad (2.4)$$

The Annihilation Operator . It is 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

$$\hat{a}_i |0\rangle = 0, \quad (2.5)$$

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

For any arbitrary Slater determinant, we have

$$\hat{a}_i |ijk\dots z\rangle = |ij\dots z\rangle, \quad (2.6)$$

$$\hat{a}_i |ijk\dots z\rangle = 0 \quad (2.7)$$

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,

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

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

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

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

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

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

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

2.2 Anticommutator Relations

Consider some creation operators acting on a Slater determinant,

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

We demand that these two operations be equivalent, or that

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

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

Similarly, for annihilation operators we have

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

These two operations must also be equivalent,

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

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

$$\hat{a}_p^\dagger \hat{a}_q |qijk\dots\rangle = \hat{a}_p^\dagger |ijk\dots\rangle = |pijk\dots\rangle. \quad (2.16)$$

This operation will replace ϕ_q by ϕ_p even if ϕ_p would have been somewhere else in the interior of the Slater determinant. Any sign change as an effect of moving the orbital to the front of the

string would be negated when the orbital is moved back to the original position. Exchanging the order of the operators however,

$$\hat{a}_q \hat{a}_p^\dagger |qijk\dots\rangle = \hat{a}_q |pqijk\dots\rangle = -\hat{a}_q |qpijk\dots\rangle = -|pijk\dots\rangle. \quad (2.17)$$

We again see a sign change and have,

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

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

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |pijk\dots\rangle &= |pijk\dots\rangle, \\ \hat{a}_p \hat{a}_p^\dagger |pijk\dots\rangle &= 0, \end{aligned} \quad (2.19)$$

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

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |ijk\dots\rangle &= 0, \\ \hat{a}_p \hat{a}_p^\dagger |ijk\dots\rangle &= \hat{a}_p |pijk\dots\rangle = |ijk\dots\rangle. \end{aligned} \quad (2.20)$$

For all cases we have that,

$$(\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger) |\dots\rangle = |\dots\rangle, \quad (2.21)$$

or

$$\{\hat{a}_p^\dagger, \hat{a}_p\} = \{\hat{a}_p, \hat{a}_p^\dagger\} = \hat{1}. \quad (2.22)$$

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

$$\{\hat{a}_p, \hat{a}_q\} = \hat{0}, \quad (2.23)$$

$$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \hat{0}, \quad (2.24)$$

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \{\hat{a}_p, \hat{a}_q^\dagger\} = \hat{\delta}_{pq}. \quad (2.25)$$

2.3 Representation of Operators

A second-quantised one-body operator is written like

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

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

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

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

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

where

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

and the antisymmetric two-electron integral for \hat{u} is abbreviated,

$$\langle ij | \hat{u} | kl \rangle - \langle ij | \hat{u} | kl \rangle = \langle ij | \hat{u} | kl \rangle \equiv \langle ij | kl \rangle. \quad (2.30)$$

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,

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

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 necessity to be able to compute vacuum expectation values ($\langle - | \hat{A} \hat{B} \dots | - \rangle$) of products of creation- and annihilation operators. Such expectation values are very important for several computational methods, see Harris, Monkhorst and Freeman (1992)[5].

2.4.1 Normal ordering and contractions

The normal-ordered product of a string of operators $\hat{A}_1, \hat{A}_2, \hat{A}_3, \dots$, 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 rearrangement

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

where \hat{P} is a permutation operator acting 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,

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

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

$$\overline{\hat{A} \hat{B}} \equiv \langle - | \hat{A} \hat{B} | - \rangle, \quad (2.33)$$

equivalently,

$$\overline{\hat{A} \hat{B}} \equiv \hat{A} \hat{B} - \{\hat{A} \hat{B}\}. \quad (2.34)$$

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

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

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

$$\Phi_i^a = \begin{array}{c} | \\ \text{i} \uparrow \\ | \\ \text{a} \downarrow \\ | \end{array}, \tag{2.36}$$

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

$$\Phi_{ij}^{ab} = \begin{array}{c} | \\ \text{i} \uparrow \\ | \\ \text{a} \downarrow \\ | \\ \text{j} \uparrow \\ | \\ \text{b} \downarrow \\ | \end{array}. \tag{2.37}$$

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,

$$|\Phi_i^a\rangle = \{\hat{a}^\dagger \hat{i}\} |0\rangle = \begin{array}{c} | \\ \text{i} \uparrow \\ | \\ \text{a} \downarrow \\ | \end{array}, \quad \langle \Phi_i^a| = \langle 0| \{\hat{i}^\dagger \hat{a}\} = \begin{array}{c} \overline{\overline{|}} \\ \text{i} \uparrow \\ | \\ \text{a} \downarrow \\ | \end{array}, \tag{2.38}$$

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

$$|\phi_{ij}^{ab}\rangle = \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\} |0\rangle = \{(\hat{a}^\dagger \hat{i})(\hat{b}^\dagger \hat{j})\} |0\rangle = \begin{array}{c} \uparrow \quad \downarrow \quad \uparrow \quad \downarrow \\ \text{i} \quad \text{a} \quad \text{j} \quad \text{b} \end{array} \quad (2.39)$$

This drawing could, however, also mean $|\phi_{ij}^{ba}\rangle$. 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,

$$|\phi_{ij}^{ab}\rangle = \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\} |0\rangle = \{(\hat{a}^\dagger \hat{i})(\hat{b}^\dagger \hat{j})\} |0\rangle = \begin{array}{c} \uparrow \quad \downarrow \quad \uparrow \quad \downarrow \\ \text{i} \quad \text{a} \quad \text{j} \quad \text{b} \end{array} \cdot \quad (2.40)$$

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 form is given by

$$\hat{U}_N = \sum_{pq} \langle p | \hat{u} | q \rangle \{\hat{p}^\dagger \hat{q}\}, \quad (2.41)$$

acting on a singly excited Slater determinant

$$|\Phi_i^a\rangle = \{\hat{a}^\dagger \hat{i}\} |0\rangle, \quad (2.42)$$

id est

$$\sum_{pq} \langle p | \hat{u} | q \rangle \{\hat{p}^\dagger \hat{q}\} \{\hat{a}^\dagger \hat{i}\} |0\rangle. \quad (2.43)$$

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,

$$\begin{aligned} \langle b | \hat{u} | c \rangle \{\hat{b}^\dagger \hat{c}\} \{\hat{a}^\dagger \hat{i}\} |0\rangle &= \langle b | \hat{u} | c \rangle \{\hat{b}^\dagger \hat{c} \hat{a}^\dagger \hat{i}\} |0\rangle + \langle b | \hat{u} | c \rangle \{\hat{b}^\dagger \hat{c} \hat{a}^\dagger \hat{i}\} |0\rangle \\ &= \langle b | \hat{u} | c \rangle \hat{b}^\dagger \hat{a}^\dagger \hat{i} \hat{c} |0\rangle + \langle b | \hat{u} | c \rangle \delta_{ac} \{\hat{b}^\dagger \hat{i}\} \\ &= 0 + \langle b | \hat{u} | c \rangle \delta_{ac} |\Phi_i^a\rangle, \end{aligned} \quad (2.44)$$

giving non-zero contributions of the type

$$\langle b | \hat{u} | a \rangle \{\hat{b}^\dagger \hat{a}\} |\Phi_i^a\rangle = \langle b | \hat{u} | a \rangle |\Phi_i^b\rangle. \quad (2.45)$$

We can draw a graphical representation of this contraction process,

$$\langle b | \hat{u} | c \rangle \{ \hat{b}^\dagger \hat{c} \} : \times \text{---} \text{---} \text{---} \rightarrow \text{---} \text{---} \text{---} \rightarrow \text{---} \text{---} \text{---} \quad (2.46)$$

$|\Phi_i^a\rangle :$

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

$$\begin{aligned} \langle j | \hat{u} | k \rangle \{ \hat{j}^\dagger \hat{k} \} \{ \hat{a}^\dagger \hat{i} \} | 0 \rangle &= \langle j | \hat{u} | k \rangle \{ \hat{j}^\dagger \hat{k} \hat{a}^\dagger \hat{i} \} | 0 \rangle + \langle j | \hat{u} | k \rangle \{ \hat{j}^\dagger \hat{k} \hat{a}^\dagger \hat{i} \} | 0 \rangle \\ &= - \langle j | \hat{u} | k \rangle \{ \hat{k} \hat{a}^\dagger \hat{i} \hat{j}^\dagger \} | 0 \rangle + \delta_{ij} \langle i | \hat{u} | k \rangle \{ \hat{k} \hat{a}^\dagger \} | 0 \rangle \\ &= 0 - \delta_{ij} \langle i | \hat{u} | j \rangle \{ \hat{a}^\dagger \hat{k} \} | 0 \rangle \\ &= - \delta_{ij} \langle i | \hat{u} | j \rangle | \Phi_k^a \rangle, \end{aligned} \quad (2.47)$$

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

$$\langle i | \hat{u} | j \rangle \{ \hat{i}^\dagger \hat{k} \} | \Phi_i^a \rangle = - \langle i | \hat{u} | k \rangle | \Phi_k^a \rangle. \quad (2.48)$$

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

$$\langle b | \hat{u} | c \rangle \{ \hat{b}^\dagger \hat{c} \} : \times \text{---} \text{---} \text{---} \rightarrow \text{---} \text{---} \text{---} \rightarrow \text{---} \text{---} \text{---} \quad (2.49)$$

$|\Phi_i^a\rangle :$

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

$$\begin{aligned} \langle b | \hat{u} | j \rangle \{ \hat{b}^\dagger \hat{j} \} \{ \hat{a}^\dagger \hat{i} \} | 0 \rangle &= \langle b | \hat{u} | j \rangle \{ \hat{b}^\dagger \hat{j} \hat{a}^\dagger \hat{i} \} | 0 \rangle \\ &= \langle b | \hat{u} | j \rangle \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i} | 0 \rangle \\ &= \langle b | \hat{u} | j \rangle | \Phi_{ij}^{ab} \rangle, \end{aligned} \quad (2.50)$$

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

$$\quad (2.51)$$

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

The *hole-particle* term is

$$\begin{aligned} \langle j | \hat{u} | b \rangle \{ \hat{j}^\dagger \hat{b} \} \{ \hat{a}^\dagger \hat{i} \} | 0 \rangle &= \langle j | \hat{u} | b \rangle \{ \hat{j}^\dagger \hat{b} \hat{a}^\dagger \hat{i} \} | 0 \rangle + \langle j | \hat{u} | b \rangle \overbrace{\{ \hat{j}^\dagger \hat{b} \hat{a}^\dagger \hat{i} \}}^{\text{---}} | 0 \rangle \\ &+ \langle j | \hat{u} | b \rangle \overbrace{\{ \hat{j}^\dagger \hat{b} \hat{a}^\dagger \hat{i} \}}^{\text{---}} | 0 \rangle + \langle j | \hat{u} | b \rangle \overbrace{\{ \hat{j}^\dagger \hat{b} \hat{a}^\dagger \hat{i} \}}^{\text{---}} | 0 \rangle \\ &= \delta_{ij} \delta_{ab} \langle j | \hat{u} | b \rangle | 0 \rangle = \langle i | \hat{u} | a \rangle | 0 \rangle, \end{aligned} \quad (2.52)$$

which is represented by

$$\begin{array}{c} \times \text{---} \diagup \\ \diagdown \text{---} \times \\ i \quad a \end{array} \quad (2.53)$$

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

$$\begin{aligned} \sum_b \underbrace{\begin{array}{c} i \downarrow \quad \uparrow b \\ \bullet \text{---} \times \\ \uparrow a \end{array}}_{\langle b | \hat{u} | a \rangle |\Phi_i^b\rangle} + \sum_j \underbrace{\begin{array}{c} \times \text{---} \downarrow j \\ \bullet \text{---} \uparrow a \\ i \downarrow \end{array}}_{-\langle i | \hat{u} | j \rangle |\Phi_j^a\rangle} + \sum_{bj} \underbrace{\begin{array}{c} \times \text{---} \diagdown \quad \diagup \times \\ \diagdown \quad \uparrow \\ b \quad j \end{array}}_{\langle b | \hat{u} | j \rangle |\Phi_{ij}^{ab}\rangle} + \underbrace{\begin{array}{c} \times \text{---} \diagup \\ \diagdown \text{---} \times \\ i \quad a \end{array}}_{\langle i | \hat{u} | a \rangle | 0 \rangle} \end{aligned} \quad (2.54)$$

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[6]. 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[13][4]. 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[12][3]. 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[7].

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

- The full molecular wavefunction is constrained to a function of the coordinates of only the electrons in the molecule. In not so many words, the Born-Oppernheimer approximation is inherent 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 method implies a mean-field approximation. Coulomb correlation is fully incorporated in the Hartree-Fock method, but it ignores Fermi Correlation and is therefore unable to describe some effects, like London dispersion¹.
- 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.

¹Named after Fritz London; London dispersion forces (LDF) are a type of force between atoms and molecules[8]

3.1 Deriving the Hartree-Fock Equations

Consider a Hamiltonian for some system

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,

$$|I\rangle = |i_1 i_2 \dots i_N\rangle = \hat{i}_1^\dagger \hat{i}_2^\dagger \dots \hat{i}_N^\dagger | \rangle \quad (\text{A.1})$$

$$|J\rangle = |j_1 j_2 \dots j_N\rangle = \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_N^\dagger | \rangle. \quad (\text{A.2})$$

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

$$\langle I|J\rangle = \langle \hat{i}_N \dots \hat{i}_2 \hat{i}_1 \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_N^\dagger | \rangle. \quad (\text{A.3})$$

In order to evaluate this expression, we move every annihilation operator \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

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

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

$$\hat{i}_1 \hat{j}_q^\dagger = \{\hat{i}_1, \hat{j}_q^\dagger\} - \hat{j}_q^\dagger \hat{i}_1 = \delta_{i_1 k_q} - \hat{j}_p^\dagger \hat{i}_1 = \hat{1} - \hat{j}_q^\dagger \hat{i}_1, \quad (\text{A.5})$$

and

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

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

$$\hat{F} = \sum_{\mu=1}^N \hat{f}_\mu, \quad (\text{A.7})$$

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

results,

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

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 exactly 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,

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

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,

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

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

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

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,

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

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;

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

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

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

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,

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

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

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

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

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

$$|I\rangle = |i_1 i_2 \dots i_p \dots \rangle, \quad (\text{A.18})$$

$$|I'\rangle = |i_1 i_2 \dots i'_p \dots \rangle. \quad (\text{A.19})$$

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

$$i = i'_p, k = i_p, j = l = i_q \rightarrow \langle i'_p i_q | i_p i_q \rangle \quad (\text{A.20})$$

$$i = i'_p, l = i_p, j = k = i_q \rightarrow -\langle i'_p i_q | i_q i_p \rangle \quad (\text{A.21})$$

$$j = i'_p, l = i_p, i = k = i_q \rightarrow \langle i_q i'_p | i_q i_q \rangle \quad (\text{A.22})$$

$$j = i'_p, k = i_p, i = l = i_q \rightarrow -\langle i_q i'_p | i_p i_q \rangle, \quad (\text{A.23})$$

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

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

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

$$\langle I' | \hat{G} | I \rangle = \langle i'_p i'_q | \hat{g} | i_p i_q \rangle, \quad (\text{A.25})$$

while for three or more noncoincidences,

$$\langle I' | \hat{G} | I \rangle = 0. \quad (\text{A.26})$$

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