

Many Electron Systems

Permutations:

Consider a system of n identical particles. By identical particles we mean that all intrinsic properties of the particles are the same, such as mass, spin, charge, etc.

In classical mechanics we can in principle follow the trajectory of each individual particle. They are, therefore, distinguishable even though they are identical. In quantum mechanics the particles are not distinguishable if they are close enough or if they interact strongly enough. The quantum mechanical wave function must reflect that.

When the particles are indistinguishable, the act of labeling the particles is an arbitrary operation without physical significance. Therefore, all observables must be unaffected by interchange of particle labels. The operators are said to be symmetric under interchange of labels. The Hamiltonian, for example, is symmetric, since the intrinsic properties of all the particles are the same. Let $\psi(1, 2, \dots, n)$ be a solution to the Schrödinger equation, (Here n represents all the coordinates, both spatial and spin, of the particle labeled with n). Let P_{ij} be an operator that permutes (or ‘exchanges’) the labels i and j :

$$P_{ij}\psi(1, 2, \dots, i, \dots, j, \dots, n) = \psi(1, 2, \dots, j, \dots, i, \dots, n).$$

This means that the function $P_{ij}\psi$ depends on the coordinates of particle j in the same way that ψ depends on the coordinates of particle i . Since H is symmetric under interchange of labels:

$$H(P_{ij}\psi) = P_{ij}H\psi, \quad \text{i.e.,} \quad [P_{ij}, H] = 0.$$

Therefore, $P_{ij}\psi$ is also a solution of the Schrödinger equation with the same eigenvalue as ψ .

Exchange Degeneracy: There are $n!$ different permutations of n labels and all the $n!$ wave functions have the same energy. Some linear combination of the $n!$ functions gives the proper description of the system. Since $[P_{ij}, H] = 0$, i.e. P_{ij} is a constant of the motion, the linear combination that describes the system initially, is the proper linear combination for all time.

The density (i.e. probability distribution) must be unaffected by P

$$|P_{ij}\psi|^2 = |\psi|^2$$

but that is not the case with the wavefunction, which is not an observable. Therefore, the functions ψ and $P_{ij}\psi$ can differ in phase

$$P_{ij}\psi = e^{i\alpha}\psi$$

where α is a real number. Applying P_{ij} again will undo the permutation, so we must have

$$P_{ij}(P_{ij}\psi) = P_{ij}^2\psi = \psi$$

that is

$$(e^{i\alpha})^2 = 1.$$

There are only two distinct solutions $\alpha = 0$ and $\alpha = \pi$ corresponding to

$$P_{ij}\psi = \begin{cases} +\psi & \text{symmetric under interchange} \\ -\psi & \text{antisymmetric under interchange} \end{cases}.$$

It turns out that both solutions are found in nature. For some particles, called *Fermions*, the wavefunction should be *antisymmetric* ($\alpha = \pi$). Examples are electrons, protons and neutrons. For other particles, called *Bosons*, the wavefunction should be *symmetric* ($\alpha = 0$). Examples are photons (particles with integral spin).

The behavior of the wavefunction when composite particles (not elementary), such as atoms, are interchanged can be deduced by counting the number of Fermions. For example: When two ${}^4\text{He}$ atoms are interchanged

2 Electrons:	Pick up factor	$(-1)(-1) = +1$
2 Protons:	Pick up factor	$(-1)(-1) = +1$
2 Neutrons:	Pick up factor	$(-1)(-1) = +1$.

So the wavefunction should not change sign, i.e. ${}^4\text{He}$ atoms behave as Bosons.

When two ${}^3\text{He}$ atoms are interchanged:

2 Electrons:	Pick up factor	$(-1)(-1) = +1$
2 Protons:	Pick up factor	$(-1)(-1) = +1$
1 Neutron:	Pick up factor	(-1) .

So the wavefunction should change sign, ${}^3\text{He}$ atoms are Fermions.

Since hydrogen atoms are very light, one often needs to use a quantum mechanical description of the motion of the nuclei as well as the electrons. The wave function changes sign if we interchange labels of two electrons (electrons are Fermions) and it changes sign if we interchange the labels of two nuclei (the nuclei consist of one proton which is a Fermion), but if we interchange two H atoms (both electron and proton), then we pick up

a factor of $(-1)(-1) = +1$, i.e., the wavefunction does not change sign. Hydrogen atoms behave as Bosons.

Therefore, given a function $\psi(1, 2, \dots, n)$ that satisfies the Schrödinger equation but does not have the right exchange symmetry, we must construct a linear combination of permutations that is symmetric when we are dealing with Bosons and antisymmetric when we are dealing with Fermions. Let P be any one of the $n!$ permutations. It can be constructed from a sequence of pairwise permutations. Let the number of pairwise permutations required be r_P . For example:

$$\begin{array}{rcccl}
 & (1, 3, 2) & r = 1 & \text{odd} & \\
 & \downarrow P_{13} & & & \\
 (1, 2, 3) & (2, 3, 1) & r = 2 & \text{even} & \\
 & \downarrow P_{12} & & & \\
 & (2, 1, 3) & \left\{ \begin{array}{l} r = 3 \\ \text{or } r = 1 \end{array} \right. & \text{odd} &
 \end{array}$$

The normalized symmetric linear combination appropriate for Bosons is

$$\psi^+ = \frac{1}{\sqrt{n!}} \sum_p P_p \psi(1, 2, \dots, n) .$$

The index p runs over all the $n!$ permutations. Similarly, the normalized antisymmetric linear combination appropriate for Fermions is:

$$\psi^- = \frac{1}{\sqrt{n!}} \sum_p (-1)^{r_p} P_p \psi(1, 2, \dots, n) .$$

We can define operators that perform the required linear combination. The *symmetrizer*, S , is

$$S \equiv \frac{1}{\sqrt{n!}} \sum P$$

and the *antisymmetrizer*, A , is

$$A \equiv \frac{1}{\sqrt{n!}} \sum (-1)^{r_p} P .$$

Then $\psi^+ = S\psi$ and $\psi^- = A\psi$.

Non-Interacting Electrons: (the simplest case)

The total Hamiltonian of the system is a sum of terms, each acting only on a single electron:

$$H = H_1 + H_2 + \dots H_n .$$

Since the Hamiltonian separates, a solution to the Schrödinger equation can be found that is a product of one electron functions:

$$\chi(1, 2, \dots, n) = \chi_a(1)\chi_b(2) \dots \chi_0(n) .$$

The one electron functions are called *spin-orbitals* and depend both on spin and spatial coordinates and the product function, $\chi(1, 2, \dots, n)$, is called a *Hartree Product*. The properly antisymmetrized many electron wavefunction is:

$$\begin{aligned} \psi(1, 2, \dots, n) &= A \chi(1, 2, \dots, n) \\ &= \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_a(1) & \chi_b(1) & \dots & \chi_0(1) \\ \chi_a(2) & \chi_b(2) & \dots & \chi_0(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_a(n) & \chi_b(n) & \dots & \chi_0(n) \end{vmatrix} . \end{aligned}$$

Applying some general rules about determinants, we can see that this wavefunction has the required properties: When the determinant is expanded out there are $n!$ terms half of which have a $-$ sign. A permutation P_{ij} corresponds to interchanging the rows i and j , which causes the determinant to change sign. Therefore the antisymmetry is built in. We will frequently be dealing with determinantal wave functions in this section. It is therefore essential to have a convenient short hand notation for such functions. Following Szabo et. al we will use the notation

$$\psi(1, 2, \dots, n) = |\chi_a(1)\chi_b(2) \dots \chi_0(n) \rangle .$$

The pointed bracket will therefore have a different meaning in this section than it had previously.

If two spin orbitals are equal, for example $\chi_a = \chi_b$ then two columns are the same and the determinant vanishes, $\psi = 0$. That is, two electrons cannot be in the same spin-orbital. This is referred to as *Pauli exclusion*.

Assuming the hamiltonian does not couple spatial coordinates and spin, the spin-orbitals can be written as a product of spatial and spin functions. For example, if electron 1 is in spatial orbital a and has spin up, the spin-orbital is

$$\chi_a(1) = \phi_a(\vec{r}_1)\alpha(\omega_1) .$$

Since we have used the symbols of the ket notation to mean a determinantal wave function in this section, we will be explicitly dealing with functions rather than kets. To deal with the spin, we therefore imagine having functions $\alpha(\omega)$ for spin up and $\beta(\omega)$ for spin down and introduce, purely for convenience, a hypothetical variable, ω . Eventually, we will always integrate over expressions involving the functions α and β and the important thing to remember is that they are orthonormal

$$\int d\omega \alpha^*(\omega) \beta(\omega) = 0$$

and

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = 1.$$

The Hartree product is truly an independent electron wavefunction. But the antisymmetrizer introduces some correlation between electrons with parallel spin. This is called the *exchange correlation*. The effect can be seen by looking at the electron density in configuration space. Consider a two electron Slater determinant:

$$\psi(1, 2) = A \chi_a(1)\chi_b(2) = |\chi_a(1)\chi_b(2) \rangle .$$

First assume the two electrons have opposite spins and occupy different spatial orbitals

$$\chi_a(1) = \phi_a(\vec{r}_1)\alpha(\omega_1)$$

and

$$\chi_b(2) = \phi_b(\vec{r}_2) \beta(\omega_2) .$$

(α means spin up and β spin down). Expanding the determinant we get:

$$\psi(1, 2) = \phi_a(\vec{r}_1)\alpha(\omega_1)\phi_b(\vec{r}_2)\beta(\omega_2) - \phi_a(\vec{r}_2)\alpha(\omega_2)\phi_b(\vec{r}_1)\beta(\omega_1) .$$

The simultaneous probability of finding electron 1 within \vec{r}_1 and $\vec{r}_1 + d\vec{r}_1$ and electron 2 within \vec{r}_2 and $\vec{r}_2 + d\vec{r}_2$ is obtained from $|\psi(1, 2)|^2$ by ‘integrating out’ the ‘spin variables’:

$$\begin{aligned} P(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 &= \int d\omega_1 \int d\omega_2 |\psi(1, 2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \left[|\phi_a(\vec{r}_1)|^2 |\phi_b(\vec{r}_2)|^2 + |\phi_a(\vec{r}_2)|^2 |\phi_b(\vec{r}_1)|^2 \right] d\vec{r}_1 d\vec{r}_2 . \end{aligned}$$

The first term is the product of the probability of finding electron 1 within \vec{r}_1 and $(\vec{r}_1 + d\vec{r}_1)$ times the probability of finding electron 2 within \vec{r}_2 and $(\vec{r}_2 + d\vec{r}_2)$ given that electron 1 occupies ϕ_a and electron 2 occupies ϕ_b . The second term has electron 2 occupying ϕ_a and electron 1 occupying ϕ_b . Since the electrons are indistinguishable, the correct probability is the average of the two terms. Therefore the electrons are still fully uncorrelated if their spin is opposite.

Alternatively, assume the two electrons have the same spin, say spin down. Then

$$\begin{aligned} \chi_a(1) &= \phi_a(\vec{r}_1)\beta(\omega_1) \\ \chi_b(2) &= \phi_b(\vec{r}_2)\beta(\omega_2) . \end{aligned}$$

Then the probability distribution becomes:

$$\begin{aligned} P(\vec{r}_1, \vec{r}_2) &= \frac{1}{2} \left[|\phi_a(\vec{r}_1)|^2 |\phi_b(\vec{r}_2)|^2 + |\phi_a(\vec{r}_2)|^2 |\phi_b(\vec{r}_1)|^2 \right. \\ &\quad \left. - 2\text{Re} \left\{ \phi_a^*(\vec{r}_1)\phi_b(\vec{r}_1)\phi_b^*(\vec{r}_2)\phi_a(\vec{r}_2) \right\} \right] . \end{aligned}$$

The extra term makes the probabilities *correlated*. In particular $P(\vec{r}_1 = \vec{r}, \vec{r}_2 = \vec{r}) = 0$, i.e., two electrons with parallel spin cannot be found at the same point in space. A *Fermi hole* is said to exist around each electron.

Calculation of Matrix Elements using Slater Determinants:

Let $\psi(1, 2, 3, \dots, N)$ be a normalized Slater determinant

$$\psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(1) & \chi_j(1) & \dots & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \dots & \chi_k(2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_i(N) & \chi_j(N) & \dots & \chi_k(N) \end{vmatrix}$$

where the χ_i are spin-orbitals. We will use the shorthand notation

$$\psi(1, 2, \dots, N) = |\chi_i \chi_j \dots \chi_k \rangle$$

where it is understood that the electron labels are in the order $1, 2, \dots, N$. Because of the antisymmetry we have, for example:

$$|\dots \chi_m \dots \chi_n \dots \rangle = -|\dots \chi_n \dots \chi_m \dots \rangle.$$

Given an operator O and two N -electron determinants $|K \rangle$ and $|L \rangle$, the problem now is to evaluate the matrix element $\langle K | O | L \rangle$. We need to obtain an expression involving integrals over the individual spin-orbitals. In particular we need to evaluate the energy, $\langle H \rangle$.

There are two types of operators that are relevant:

One electron operators:

$$O_1 = \sum_{i=1}^N h(i)$$

where $h(i)$ only involves the i -th electron and the summation index, i , runs over all electrons. For example

$$h(i) = -\frac{\hbar^2}{2m} \nabla_i^2.$$

Two electron operators:

$$O_2 = \sum_{i=1}^N \sum_{j>i}^N v(i, j) \equiv \sum_{i<j} v(i, j)$$

where $v(i, j)$ is an operator that depends on the coordinates of both electrons, i and j . An important example is the Coulomb interaction e^2/r_{ij} and we will be using that example in the discussion that follows.

Regarding the determinants $|K \rangle$ and $|L \rangle$, there are three different situations:

Case 1: The two determinants are equal, i.e.,

$$|L \rangle = |K \rangle = |\dots \chi_m \chi_n \dots \rangle.$$

Case 2: The two determinants differ by one spin-orbital: For example, replacing χ_m by χ_p in $|L \rangle$

$$|K \rangle = |\dots \chi_m \chi_n \dots \rangle$$

$$|L \rangle = |\dots \chi_p \chi_n \dots \rangle .$$

Case 3: The two determinants differ by two spin-orbitals: For example, replacing χ_m by χ_p and χ_n by χ_q in $|L \rangle$

$$|K \rangle = |\dots \chi_m \chi_n \dots \rangle$$

$$|L \rangle = |\dots \chi_p \chi_q \dots \rangle .$$

It can easily be shown that the matrix elements of O_1 are zero if $|K \rangle$ and $|L \rangle$ differ by more than one spin-orbital, and that the matrix elements of O_2 are zero if $|K \rangle$ and $|L \rangle$ differ by more than two spin-orbitals.

It is essential to use some convenient shorthand notation for the various integrals. Unfortunately there are two different notations in common use, that are sometimes referred to as ‘chemists notation’ and ‘physicists notation’. We will use square brackets, $[\]$, for the former and pointed brackets, $\langle \ \rangle$, for the latter. The definitions are as follows:

$$\begin{aligned} [ij|k\ell] &\equiv \int dx_1 \int dx_2 \chi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \chi_k^*(2) \chi_\ell(2) \quad \text{‘chemists notation’} \\ &= \langle ik|j\ell \rangle \quad \text{‘physicists notation’} \end{aligned}$$

and

$$\begin{aligned} [i|h|j] &\equiv \int dx_1 \chi_i^*(1) h(\vec{r}_1) \chi_j(1) \quad \text{‘chemists notation’} \\ &= \langle i|h|j \rangle \quad \text{‘physicists notation.’} \end{aligned}$$

The integration variable x_i denotes both the spatial and spin coordinates of electron i . We will also use a short hand notation for the difference between two integrals in the ‘physicists notation’:

$$\langle ij||k\ell \rangle \equiv \langle ij|k\ell \rangle - \langle ij|\ell k \rangle .$$

The following table gives the matrix elements of *one-electron* operators in terms of the spin-orbitals of the determinants.

$$O_1 = \sum_{i=1}^N h(i)$$

Case 1: $|K \rangle = |\dots mn \dots \rangle$

$$\langle K|O_1|K \rangle = \sum_m^N [m|h|m] = \sum_m^N \langle m|h|m \rangle$$

$$\begin{aligned} \text{Case2: } |K\rangle &= |\dots mn\dots\rangle \\ |L\rangle &= |\dots pn\dots\rangle \end{aligned}$$

$$\langle K|O_1|L\rangle = [m|h|p] = \langle m|h|p\rangle$$

$$\begin{aligned} \text{Case3: } |K\rangle &= |\dots mn\dots\rangle \\ |L\rangle &= |\dots pq\dots\rangle \end{aligned}$$

$$\langle K|O_1|L\rangle = 0$$

The following table gives the matrix elements of the *two-electron* operator representing Coulomb interaction of N electrons in terms of the spin-orbitals of the determinants.

$$O_2 = \sum_{i=1}^N \sum_{j>i}^N r_{ij}^{-1}$$

$$\text{Case 1: } |K\rangle = |\dots nm\dots\rangle$$

$$\langle K|O_2|K\rangle = \frac{1}{2} \sum_m^N \sum_n^N [mm|nn] - [mn|nm] = \frac{1}{2} \sum_m^N \sum_n^N \langle mn||mn\rangle$$

$$\begin{aligned} \text{Case2: } |K\rangle &= |\dots mn\dots\rangle \\ |L\rangle &= |\dots pn\dots\rangle \end{aligned}$$

$$\langle K|O_2|L\rangle = \sum_n^N [mp|nn] - [mn|np] = \sum_n^N \langle mn||pn\rangle$$

$$\begin{aligned} \text{Case3: } |K\rangle &= |\dots mn\dots\rangle \\ |L\rangle &= |\dots pq\dots\rangle \end{aligned}$$

$$\langle K|O_2|L\rangle = [mp|nq] - [mq|np] = \langle mn||pq\rangle$$

Example: To illustrate how the rules in the table come about we will work out the matrix elements for a determinant (case 1) made up of two spin-orbitals:

$$|\psi\rangle = |\chi_1\chi_2\rangle$$

One Electron Operator:

$$\begin{aligned}
\langle \psi | h(1) | \psi \rangle &= \int d\vec{x}_1 \int d\vec{x}_2 \frac{1}{\sqrt{2}} \left(\chi_1(\vec{x}_1) \chi_2(\vec{x}_2) - \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \right)^* \\
&\quad h(\vec{r}_1) \frac{1}{\sqrt{2}} \left(\chi_1(\vec{x}_1) \chi_2(\vec{x}_2) - \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \right) \\
&= \frac{1}{2} \int d\vec{x}_1 \int d\vec{x}_2 \left(\chi_1^*(\vec{x}_1) \chi_2^*(\vec{x}_2) h(\vec{r}_1) \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \right. \\
&\quad + \chi_2^*(\vec{x}_1) \chi_1^*(\vec{x}_2) h(\vec{r}_1) \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \\
&\quad - \chi_1^*(\vec{x}_1) \chi_2^*(\vec{x}_2) h(\vec{r}_1) \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \\
&\quad \left. - \chi_2^*(\vec{x}_1) \chi_1^*(\vec{x}_2) h(\vec{r}_1) \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \right) .
\end{aligned}$$

Since the operator $h(1)$ does not involve coordinates of electron 2 we can easily carry out the \vec{x}_2 integration. In the first two terms, \vec{x}_2 only appears in the same spin-orbital within each term. Therefore using the fact that both χ_1 and χ_2 are normalized, the integration over \vec{x}_2 gives 1 in the first two terms. However, in the last two terms \vec{x}_2 appears in both χ_1 and χ_2 within each term. The integration over \vec{x}_2 then gives zero because the spin-orbitals are orthogonal. We are left with

$$\begin{aligned}
\langle \psi | h(1) | \psi \rangle &= \frac{1}{2} \int d\vec{x}_1 \chi_1^*(\vec{x}_1) h(\vec{r}_1) \chi_1(\vec{x}_1) \\
&\quad + \frac{1}{2} \int d\vec{x}_1 \chi_2^*(\vec{x}_1) h(\vec{r}_1) \chi_2(\vec{x}_1) \\
&= \frac{1}{2} \sum_m^2 \langle m | h | m \rangle .
\end{aligned}$$

Similarly

$$\langle \psi | h(2) | \psi \rangle = \frac{1}{2} \sum_m^2 \langle m | h | m \rangle .$$

Adding the two gives case 1 in the table for the one-electron operator, O_1 .

Two Electron Operator: $O_2 = 1/r_{12}$

$$\begin{aligned}
\langle \psi | \frac{1}{r_{12}} | \psi \rangle &= \frac{1}{2} \int d\vec{x}_1 \int d\vec{x}_2 \left(\chi_1^*(\vec{x}_1) \chi_2^*(\vec{x}_2) \frac{1}{r_{12}} \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \right. \\
&\quad + \chi_2^*(\vec{x}_1) \chi_1^*(\vec{x}_2) \frac{1}{r_{12}} \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \\
&\quad - \chi_1^*(\vec{x}_1) \chi_2^*(\vec{x}_2) \frac{1}{r_{12}} \chi_2(\vec{x}_1) \chi_1(\vec{x}_2) \\
&\quad \left. - \chi_2^*(\vec{x}_1) \chi_1^*(\vec{x}_2) \frac{1}{r_{12}} \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \right)
\end{aligned}$$

Since $1/r_{12} = 1/r_{21}$ we can interchange the indices on the dummy integration variables. Therefore the first term is the same as the second, and the third term is the same as the fourth. Using the ‘physicists’ notation for two electron integrals:

$$\langle \psi | \frac{1}{r_{12}} | \psi \rangle = \langle 12|12 \rangle - \langle 12|21 \rangle \equiv \langle 12||12 \rangle .$$

Using the ‘chemists’ notation instead

$$[11|22] = \langle 12|12 \rangle$$

and

$$[12|21] = \langle 12|21 \rangle ,$$

the matrix element can be written as

$$\langle \psi | \frac{1}{r_{12}} | \psi \rangle = [11|22] - [12|21] .$$

This illustrates case 1 in the table for the two-electron operator, O_2 .

Example: Evaluate matrix elements for determinants that differ by one spin-orbital (case 2). Again use two spin-orbitals and choose different ones for the two determinants:

$$|\psi_A \rangle = |\chi_1 \chi_2 \rangle$$

and

$$|\psi_B \rangle = |\chi_3 \chi_4 \rangle .$$

We clearly have

$$\langle \psi_A | h(1) | \psi_B \rangle = 0$$

because the \vec{x}_2 integration gives zero in all terms,

$$0 = \int d\vec{x}_2 \chi_i(\vec{x}_2) \chi_j(\vec{x}_2) \text{ when } i \neq j.$$

This illustrates case 3 in the table for the one electron operator, O_1 .

The two-electron matrix element is, by definition,

$$\langle \psi_A | \frac{1}{r_{12}} | \psi_B \rangle = [13|24] - [14|23] = \langle 12||34 \rangle .$$

The energy of a determinantal wavefunction:

Using the tables, we can readily find the expectation value of the total energy in a single determinant state $|K\rangle$ of N electrons

$$\begin{aligned}\langle H \rangle &= \langle K|H|K \rangle = \langle K|O_1 + O_2|K \rangle \\ &= \sum_m^N \langle m|h|m \rangle + \frac{1}{2} \sum_m^N \sum_n^N \langle mn||mn \rangle\end{aligned}$$

The sums run over all the occupied spin-orbitals. The one electron operator h includes the kinetic energy of the electron and the interaction with all the nuclei

$$h(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

The summation index A runs over all nuclei that electron i interacts with. Here the electron charge has been set to one, $e = 1$, and Z_A is the nuclear charge in units of the electron charge, e . Each occupied spin-orbital χ_i in $|K\rangle$ contributes $\langle i|h|i \rangle$ to the energy and every unique pair of occupied spin-orbitals χ_i, χ_j contributes $\langle ij||ij \rangle$. Note that

$$\frac{1}{2} \sum_m \sum_n \langle mn||mn \rangle = \sum_m \sum_{n>m} \langle mn||mn \rangle$$

since

$$\langle mn||mn \rangle = \langle nm||nm \rangle$$

and

$$\langle mm||mm \rangle = 0.$$