Systems of of many electrons

Exchange of particle labels

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.

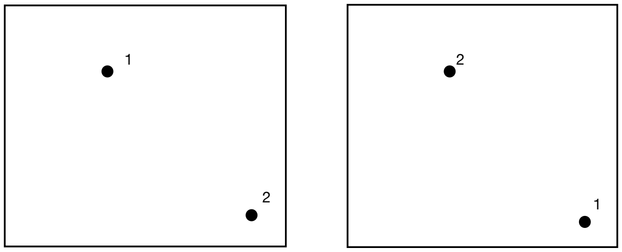

Figure 3. A pairwise permutation of the labels on identical particles.

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 this fact.

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 $\psi(1, 2, \ldots, N)$ 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:

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

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 lables 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

$$\begin{aligned} P_{ij}\psi = &+ \psi \qquad \text{symmetric under interchange} \\ &- \psi \qquad \text{antisymmetric under interchange.} \end{aligned} \tag{1}$$

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 ^4He atoms are interchanged

$$\begin{aligned} \text{2 electrons give factor} &\quad (-1)(-1) = +1 \\ \text{2 protons give factor} &\quad (-1)(-1) = +1 \\ \text{2 neutrons give factor} &\quad (-1)(-1) = +1 \end{aligned}$$

So the wavefunction should not change sign, i.e. ^4He atoms behave as Bosons.

When two ^3He atoms are interchanged:

$$\begin{aligned} \text{2 electrons give factor} &\quad (-1)(-1) = +1 \\ \text{2 protons give factor} &\quad (-1)(-1) = +1 \\ \text{1 neutron gives factor} &\quad -1 \end{aligned}$$

So the wavefunction should cange sign, ^3He 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 elecrons. The wave function changes sign if we interchange labels of two electrons (electrons are Fermions) and it changes sign if we interchange the lables 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.

When a stationary state wave function is being constructed for a system, for example to evaluate possible values of the energy, it is not enough to just solve for eigenfunctions of the Hamiltonian operator, one also needs to build in the right symmetry with respect to the exchange of labels on the particles. For example, if a given a function $\psi(1, 2, \ldots, N)$ is found to satisfy the Schrödinger equation but does not have the right exchange symmetry, it is necessary to construct a linear combination of permutations of the labels to obtain a function that is symmetric under the exchange of labels when dealing with Bosons or antisymmetric when 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:

$$\begin{tikzcd}
 & (1,3,2) \arrow[d, "P_{13}"'] & r_P = 1 & \text{odd} \\
(1,2,3) \arrow[ur, "P_{23}"] \arrow[dr, "P_{12}"'] & (2,3,1) \arrow[d, "P_{23}"'] & r_P = 2 & \text{even} \\
 & (2,1,3) & r_P = 3 \text{ or } 1 & \text{odd}
\end{tikzcd}$$

The normalized symmetric linear combination appropriate for Bosons is

$$\psi^+ = \frac{1}{\sqrt{N!}} \sum_p P_p \phi(1, 2, \ldots, N) \ .$$

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

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

The difference in the energy that is obtained from ϕ and that obtained from ψ^- is called the *exchange energy.* That is

$$E_{exch} \ = < \psi^-|H|\psi^- > \ - \ < \phi|H|\phi > \ .$$

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

Independent electrons: (the simplest system containing several electrons)

If the Hamiltonian of the system separates, i.e. can be written as a sum of terms, each term acting only on a single electron

$$H = H_1 + H_2 + \dots H_N$$

then a solution to the Schrödinger equation can be found that is a product of one electron functions

$$\phi(1, 2, \dots, N) = \chi_a(1)\chi_b(2)\dots\chi_0(N) \ .$$

The one electron functions are called *spin-orbitals* (this is the terminology in chemistry but in physics they are called single particle wavefunctions). Spin-orbitals depend both on spin and spatial coordinates and the product function, $\chi(1, 2, 3, \dots, N)$, is called a *Hartree Product.* The properly antisymmetrized many electron wavefunction is:

$$\psi^-(1, 2, \dots, N) = A \ \phi(1, 2, 3, \dots, N)$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_a(1) & \chi_b(1) & \chi_c(1) & \dots & \chi_0(1) \\ \chi_a(2) & \chi_b(2) & \chi_c(2) & \dots & \chi_0(2) \\ \chi_a(3) & \chi_b(3) & \chi_c(3) & \dots & \chi_0(3) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \chi_a(N) & \chi_b(N) & \chi_c(N) & \dots & \chi_0(N) \end{vmatrix}$$

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 minus 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. We will use the notation

$$\psi^-(1, 2, \dots, N) = |\chi_a(1)\chi_b(2)\dots\chi_0(N) > \ .$$

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 twof 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

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

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 antisymmetrized wavefunction obtained by constructing the Slater determinant has introduced some, limited correlation between any pair of lelectrons that have parallel spin. This is called the *exchange correlation* (not to be confused with the 'correlation energy' which is the difference between the Hartree-Fock estimate of the energy and the exact value of the energy). The effect can be seen by looking at the electron density in configuration space. Consider a two electron Slater determinant:

$$\psi^-(1,2) = A\{\chi_a(1)\chi_b(2)\} = |\chi_a(1)\chi_b(2)> .$$

Example a. First, assume the two electrons have opposite spins and occupy different spatial orbitals

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

and

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

(α means spin up and β spin down). By expanding the determinant, we get:

$$\psi^-(1,2) = \frac{1}{\sqrt{2}}\left(\phi_I(\vec{r}_1)\alpha(\omega_1)\phi_{II}(\vec{r}_2)\beta(\omega_2) - \phi_I(\vec{r}_2)\alpha(\omega_2)\phi_{II}(\vec{r}_1)\beta(\omega_1)\right)\ .$$

The simultaneous probability of finding one of the two electron near a point $\vec{r}_1$ and the other near a point $\vec{r}_2$ (that is, one of the electrons is in an interval between $\vec{r}_1$ and $\vec{r}_1 + d\vec{r}$ and the other electron in an interval between $\vec{r}_2$ and $\vec{r}_2 + d\vec{r}$ is obtained from the magnitude squared of the wave function $|\psi(1,2)|^2$ by integrating out the 'spin variables':

$$\begin{aligned} P(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 &= \int d\omega_1 \int d\omega_2\ |\psi(1,2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2}\Big[|\phi_I(\vec{r}_1)|^2|\phi_{II}(\vec{r}_2)|^2 + |\phi_I(\vec{r}_2)|^2|\phi_{II}(\vec{r}_1)|^2\Big] d\vec{r}_1 d\vec{r}_2\ . \end{aligned}$$

By setting $\vec{r}_1 = \vec{r}_s$ and $\vec{r}_2 = \vec{r}_t$, the first term is the product of the probability of finding electron 1 within $\vec{r}_s$ and $(\vec{r}_s + d\vec{r})$ times the probability of finding electron 2 within $\vec{r}_t$ and $(\vec{r}_t + d\vec{r})$ as electron 1 occupies orbital ϕ_I and electron 2 occupies orbital ϕ_{II}. The second term has electron 2 occupying ϕ_I and electron 1 occupying ϕ_{II}. Since the electrons are indistinguishable, the correct probability is the average of the two terms. Therefore, two electrons with opposite spin are fully uncorrelated at this level of theory.

Example b. Secondly, assume the two electrons have the same spin, say spin up. Then

$$\begin{aligned} \chi_a(1) &= \phi_I(\vec{r}_1)\alpha(\omega_1) \\ \chi_b(2) &= \phi_{II}(\vec{r}_2)\alpha(\omega_2)\ . \end{aligned}$$

Then, the probability distribution becomes:

$$\begin{aligned} P(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\Big[&|\phi_I(\vec{r}_1)|^2|\phi_{II}(\vec{r}_2)|^2 + |\phi_I(r_2)|^2|\phi_{II}(\vec{r}_1)|^2 \\ &- 2Re\Big\{\phi_I^*(\vec{r}_1)\phi_{II}(\vec{r}_1)\phi_{II}^*(\vec{r}_2)\phi_I(\vec{r}_2)\Big\}\Big]\ . \end{aligned}$$

The extra term that has appeared as compared with example *a* introduces *correlation* in the distribution of the two electrons. 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, a region from which other electrons of the same spin are excluded. The presence of the Fermi hole is an important consideration. It results, for example, in a substantial difference in the accuracy of the Hartree-Fock approximation for singlet states and for triplet states, since the presence of the extra Fermi hole in the triplet tends to keep the electrons apart and, thereby, lower the Coulomb repulsion between them.

Calculation of Matrix Elements using Slater Determinants:

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

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

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

$$\psi(1,2,\ldots,N)=|\chi_i\chi_j\ldots\chi_k>$$

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

$$|\ldots\chi_m\ldots\chi_n\cdots>=-|\ldots\chi_n\ldots\chi_m\cdots>.$$

Various calculations in quantum mechanics involve the evaluation of matrix elements of an operator with the wavefunction. It, therefore, becomes important to develop expressions for matrix elements of various types of operators when the wavefunction is of the form of a Slater determinant. Given an operator O and two N-electron determinants $|K>$ and $|L>$, the problem now is to evaluate the matrix element $<K|O|L>$. We need to obtain an expression involving integrals over the individual spin-orbitals. In particular, we need to evaluate the energy, $<H>=<K|H|L>$.

There are two types of operators that are relevant:

One electron operators are of the form

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

where $h(i)$ only involves the $i-th$ electron and the summation index, i, runs over all electrons. For a molecule, the one electron part of the Hamiltonian is (in atomic units)

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

Two electron operators are of the form

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

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 which has the form of $1/r_{ij}$ and will be used in the following discussion.

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

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

$$|L>=|K>=|\ldots\chi_m\chi_n\cdots>.$$

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

$$|K>=|\ldots\chi_m\chi_n\cdots>$$

$$|L>=|\dots\chi_p\chi_n\cdots> \quad .$$

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 $|L>$

$$|K>=|\dots\chi_m\chi_n\cdots>$$

$$|L>=|\dots\chi_p\chi_q\cdots> \quad .$$

It can easily be shown that the matrix elements of O_1 are zero if $|K>$ and $|L>$ differ by more than one spin-orbital, and that the matrix elements of O_2 are zero if $|K>$ and $|L>$ 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 the former and denote integrals over spin-orbitals with square brackets, [ ]. The definitions are as follows:

$$[i|h|j] \equiv \int dx_1 \chi_i^*(1) h(\vec{r}_1) \chi_j(1)$$

and

$$[ij|k\ell] \equiv \int dx_1 \int dx_2 \; \chi_i^*(1)\chi_j(1)\frac{1}{r_{12}}\chi_k^*(2)\chi_\ell(2)$$

The integration variable x_i denotes both the spatial and spin coordinates of electron i (note, we assume the Hamiltonian does not depend on spin and therefore denote the variable there as $\vec{r}_1$).

The following table gives the matrix elements of *one-electron* operators for determinant wave functions in terms of the integrals over spin-orbitals.

Table 1 : Matrix elements of one electron operators of the form $O_1 = \sum_{i=1}^{N} h(i)$

Case1 :	$\vert K>=\vert\dots mn\cdots>$	$<K\vert O_1\vert K>=\sum_m^N\,[m\vert h\vert m]$
Case 2 :	$\vert K>=\vert\dots mn\cdots>$ $\vert L>=\vert\dots pn\cdots>$	$<K\vert O_1\vert L>=[m\vert h\vert p]$
Case 3 :	$\vert K>=\vert\dots mn\cdots>$ $\vert L>=\vert\dots pq\cdots>$	$<K\vert O_1\vert L>=0$

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.

$$Table\ 2:\quad Matrix\ elements\ of\ two\ electron\ operators\ of\ the\ form\quad O_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1}$$

Case1 : $|K>=|\ldots nm\cdots>$

$$<K|O_2|K>=\tfrac{1}{2}\ \textstyle\sum_m^N\ \sum_n^N\ [mm|nn]-[mn|nm]$$

Case 2 : $|K>=|\ldots mn\cdots>$
$|L>=|\ldots pn\cdots>$

$$<K|O_2|L>=\textstyle\sum_n^N\ [mp|nn]-[mn|np]$$

Case 3 : $|K>=|\ldots mn\cdots>$
$|L>=|\ldots pq\cdots>$

$$<K|O_2|L>=[mp|nq]-[mq|np]$$

To illustrate how the rules in the table come about, calculations of some of the matrix elements are presented below for some of the possible choices of Slater determinants.

Example 1: The simplest case is when the same Slater determinant appears on the left and right hand side of the matrix element (case 1)

$$|\psi>=|\chi_1\chi_2>$$

1.a For a one-electron operator:

$$\begin{aligned}<\psi|h(1)|\psi> &= \int d\vec{x}_1\int d\vec{x}_2\ \frac{1}{\sqrt{2}}\Big(\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)-\chi_2(\vec{x}_1)\chi_1(\vec{x}_2)\Big)^*\\ &\qquad h(\vec{r}_1)\frac{1}{\sqrt{2}}\Big(\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)-\chi_2(\vec{x}_1)\chi_1(\vec{x}_2)\Big)\\ &= \frac{1}{2}\int d\vec{x}_1\int d\vec{x}_2\Big(\chi_1^*(\vec{x}_1)\chi_2^*(\vec{x}_2)h(\vec{r}_1)\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\\ &\qquad +\chi_2^*(\vec{x}_1)\chi_1^*(\vec{x}_2)h(\vec{r}_1)\chi_2(\vec{x}_1)\chi_1(\vec{x}_2)\\ &\qquad -\chi_1^*(\vec{x}_1)\chi_2^*(\vec{x}_2)h(\vec{r}_1)\chi_2(\vec{x}_1)\chi_1(\vec{x}_2)\\ &\qquad -\chi_2^*(\vec{x}_1)\chi_1^*(\vec{x}_2)h(\vec{r}_1)\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\Big)\ .\end{aligned}$$

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

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

Similarly

$$<\psi|h(2)|\psi>=\frac{1}{2}\ \sum_m^2\ [m|h|m].$$

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

1.b For the two-electron operator $O_2 = 1/r_{12}$:

$$\begin{aligned}
<\psi|\ \frac{1}{r_{12}}\ |\psi> = \frac{1}{2}\ \int d\vec{x}_1 \int d\vec{x}_2 \Big(& \chi_1^*(\vec{x}_1)\chi_2^*(\vec{x}_2)\ \frac{1}{r_{12}}\ \chi_1(\vec{x}_1)\chi_2(\vec{x}_2) \\
& + \chi_2^*(\vec{x}_1)\chi_1^*(\vec{x}_2)\ \frac{1}{r_{12}}\ \chi_2(\vec{x}_1)\chi_1(\vec{x}_2) \\
& - \chi_1^*(\vec{x}_1)\chi_2^*(\vec{x}_2)\ \frac{1}{r_{12}}\ \chi_2(\vec{x}_1)\chi_1(\vec{x}_2) \\
& - \chi_2^*(\vec{x}_1)\chi_1^*(\vec{x}_2)\ \frac{1}{r_{12}}\ \chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\Big)
\end{aligned}$$

Since $1/r_{12} = 1/r_{21}$, the indices can be interchanged 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.

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

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

Example 2: Now use determinants that differ by two spin-orbitals (case 3). Again, the Slater determinants are constructed by using two spin-orbitals but different spin-orbitals are chosen for the two determinants:

$$|\psi_A>=|\chi_1\chi_2>$$

and

$$|\psi_B>=|\chi_3\chi_4> \quad .$$

We clearly have

$$<\psi_A|h(1)|\psi_B>=0$$

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,

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

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 $|K>$ of N electrons

$$\begin{aligned}
<H> =< K|H|K> &=< K|O_1 + O_2|K> \\
&= \sum_m^N [m|h|m] + \frac{1}{2}\ \sum_m^N \sum_n^N [mm|nn] - [mn|nm]
\end{aligned}$$

The sums run over all the occupied spin-orbitals. The one electron operator h inclues 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 $|K>$ contributes $[i|h|i]$ to the energy and every unique pair of occupied spin-orbitals χ_i, χ_j contributes $[ii|jj] - [ij|ji]$. Note that

$$\frac{1}{2} \sum_{m}^{N} \sum_{n}^{N} [mm|nn] - [mn|nm] \; = \; \sum_{m} \sum_{n>m} [mm|nn] - [mn|nm]$$

since

$$[ij|ji] = [ji|ij] \;\; \text{and} \;\; [\mathrm{ii}|\mathrm{jj}] = [\mathrm{jj}|\mathrm{ii}]$$

and terms with $n = m$ cancel out.