Matrix Elements Between Slater Determinants

Expressing the wavefunction in terms of Slater Determinants means that at some point we will have to evaluate matrix elements of the Hamiltonian and other operator between these determinants. The rules for doing so where worked out some time ago by Slater and Condon and are appropriately enough called the Slater-Condon rules which we will now derive.

Consider the Slater determinant

$$\Psi(1,2,3,\cdots,N) = \hat{\mathcal{A}}\, a(1)b(2)c(3)\cdots d(N)$$

where the elements are orthonormal spin-orbitals,

$$\langle a|a\rangle = \langle b|b\rangle = \langle c|c\rangle = \cdots = \langle d|d\rangle = 1$$

and

$$\langle a|b\rangle = \langle a|c\rangle = \langle a|d\rangle = \langle b|c\rangle = \langle b|d\rangle = \cdots = \langle c|d\rangle = 0$$

Let's first consider the overlap integral

$$\langle \Psi|\Psi\rangle = \left\langle \hat{\mathcal{A}}a(1)b(2)c(3)\cdots d(N)\middle|\hat{\mathcal{A}}a(1)b(2)c(3)\cdots d(N)\right\rangle$$

Because $\hat{\mathcal{A}}$ is self adjoint ($\hat{\mathcal{A}} = \hat{\mathcal{A}}^{+}$), and satisfies $\hat{\mathcal{A}}^2 = \sqrt{N!}\,\hat{\mathcal{A}}$ we have

$$\langle \Psi|\Psi\rangle = \left\langle \hat{\mathcal{A}}abc\cdots d\middle|\hat{\mathcal{A}}abc\cdots d\right\rangle = \left\langle abc\cdots d\middle|\hat{\mathcal{A}}^{+}\hat{\mathcal{A}}abc\cdots d\right\rangle = \left\langle abc\cdots d\middle|\hat{\mathcal{A}}^2 abc\cdots d\right\rangle$$

and

$$\langle \Psi|\Psi\rangle = \sqrt{N!}\left\langle abc\cdots d\middle|\hat{\mathcal{A}}abc\cdots d\right\rangle = \left\langle abc\cdots d\middle|\sum_P \varepsilon_P \hat{P}abc\cdots d\right\rangle$$

where we have used the definition of $\hat{\mathcal{A}}$. We may expand the sum over permutations into classes consisting of zero transpositions (the identity), single transpositions (ST), double transpositions (DT), triple transpositions (TT), up to N fold transpositions (NT).

$$\sum_P \varepsilon_P \hat{P}abc\cdots d = a(1)b(2)c(3)\cdots d(N) + ST + DT + TT + \cdots + NT$$

The identity or zero transposition contributes

$$\langle abc \cdots d \,|\, abc \cdots d \rangle = \langle a|a\rangle \langle b|b\rangle \langle c|c\rangle \cdots \langle d|d\rangle = 1$$

A particular ST, say $\hat{P}_{12}$ contributes the term

$$\langle abc \cdots d \,|\, bac \cdots d \rangle = \langle a|b\rangle \langle b|a\rangle \langle c|c\rangle \cdots \langle d|d\rangle = 0$$

Indeed all ST, DT, etc will not contribute because a mismatch between the order on the right and on the left will result in an overlap between two orthogonal orbitals. So if the orbitals are orthonormal the Slater Determinant is normalized to 1.

Now consider the matrix element of the Hamiltonian

$$\langle \hat{H} \rangle = \langle \Psi | \hat{H} | \Psi \rangle = \langle \hat{\mathcal{A}} abc \cdots d \,|\, \hat{H} \,|\, \hat{\mathcal{A}} abc \cdots d \rangle$$

where

$$\hat{H} = \sum_{i=1}^{N} \hat{f}(i) + \sum_{i<j}^{N} g(i,j) = \hat{F} + \hat{G}$$

Once again, because $\hat{\mathcal{A}}$ is self adjoint ($\hat{\mathcal{A}} = \hat{\mathcal{A}}^{+}$), commutes with $\hat{H}$, $\left[\hat{H}, \hat{\mathcal{A}} \right] = 0$ and satisfies $\hat{\mathcal{A}}^2 = \sqrt{N!}\,\hat{\mathcal{A}}$ we have

$$\langle \hat{H} \rangle = \langle abc \cdots d \,|\, \hat{\mathcal{A}}\hat{H} \,|\, \hat{\mathcal{A}} abc \cdots d \rangle = \langle abc \cdots d \,|\, \hat{H} \,|\, \hat{\mathcal{A}}^2 abc \cdots d \rangle = \sqrt{N!} \langle abc \cdots d \,|\, \hat{H} \,|\, \hat{\mathcal{A}} abc \cdots d \rangle$$

Using $\sqrt{N!}\,\hat{\mathcal{A}} = \sum_{P} \varepsilon_P \hat{P}$ we have

$$\langle \Psi | \hat{H} | \Psi \rangle = \left\langle abc \cdots d \,\middle|\, \hat{H} \,\middle|\, \sum_{P} \varepsilon_p \hat{P} abc \cdots d \right\rangle$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \left\langle abc \cdots d \,\middle|\, \hat{F} \,\middle|\, \sum_{P} \varepsilon_p \hat{P} abc \cdots d \right\rangle + \left\langle abc \cdots d \,\middle|\, \hat{G} \,\middle|\, \sum_{P} \varepsilon_p \hat{P} abc \cdots d \right\rangle$$

We will first evaluate the matrix element of the sum of one particle operators $\hat{F}$. As above, we expand the sum over permutations into classes of transpositions

$$\langle \Psi | \hat{F} | \Psi \rangle = \langle abc \cdots d \,|\, \hat{F} \,|\, abc \cdots d + ST + DT + TT + \cdots + NT \rangle$$

and consider the zero transposition term

$$\langle abc \cdots d \,|\, \sum_{i=1}^{N} \hat{f}(i) \,|\, abc \cdots d \rangle = \langle a|\hat{f}|a \rangle \langle b|b \rangle \langle c|c \rangle \cdots \langle d|d \rangle +$$

$$\langle a|a \rangle \langle b|\hat{f}|b \rangle \langle c|c \rangle \cdots \langle d|d \rangle + \langle a|a \rangle \langle b|b \rangle \langle c|\hat{f}|c \rangle \cdots \langle d|d \rangle + \langle a|a \rangle \langle b|b \rangle \langle c|c \rangle \cdots \langle d|\hat{f}|d \rangle$$

$$\langle abc \cdots d \,|\, \sum_{i=1}^{N} \hat{f}(i) \,|\, abc \cdots d \rangle = \langle a|\hat{f}|a \rangle + \langle b|\hat{f}|b \rangle + \langle c|\hat{f}|c \rangle + \cdots + \langle d|\hat{f}|d \rangle$$

Now consider one of the single transposition terms, say $\hat{P}_{12}$.

$$\langle abc \cdots d \,|\, \sum_{i=1}^{N} \hat{f}(i) \,|\, bac \cdots d \rangle = \langle a|\hat{f}|b \rangle \langle b|a \rangle \langle c|c \rangle \cdots \langle d|d \rangle +$$

$$\langle a|b \rangle \langle b|\hat{f}|a \rangle \langle c|c \rangle \cdots \langle d|d \rangle + \langle a|b \rangle \langle b|a \rangle \langle c|\hat{f}|c \rangle \cdots \langle d|d \rangle + \langle a|b \rangle \langle b|a \rangle \langle c|c \rangle \cdots \langle d|\hat{f}|d \rangle$$

Clearly there is always a mismatch and since the overlap $\langle a|b \rangle = 0$, the contribution of $\hat{P}_{12}$ vanishes. In a similar fashion all matrix elements involving ST, DT, etc vanish. So the expectation value of the sum of one particle operators $\hat{F} = \sum_{i=1}^{N} \hat{f}(i)$ is given by

$$\langle abc \cdots d \,|\, \sum_{i=1}^{N} \hat{f}(i) \,|\, abc \cdots d \rangle = \langle a|\hat{f}|a \rangle + \langle b|\hat{f}|b \rangle + \langle c|\hat{f}|c \rangle + \cdots + \langle d|\hat{f}|d \rangle$$

In general the expectation value of a sum of one particle operators is the sum of the expectation values of the individual operators with respect to the elements of the Slater Determinant.

To evaluate the matrix element of $\hat{G} = \sum_{i<j}^{N} g(i,j)$ we note

$$\langle \Psi |\hat{G}|\Psi \rangle = \langle abc \cdots d \,|\, \hat{G} \,|\, abc \cdots d + ST + DT + TT + \cdots + NT \rangle$$

and consider the zero transposition term

$$\langle abc \cdots d \,|\, \sum_{i<j}^{N} g(i,j) \,|\, abc \cdots d \rangle =$$

$$\langle abc \cdots d \,|\, g(1,2) \,|\, abc \cdots d \rangle + \langle abc \cdots d \,|\, g(1,3) \,|\, abc \cdots d \rangle + \cdots + \langle abc \cdots d \,|\, g(1,N) \,|\, abc \cdots d \rangle +$$

$$\langle abc \cdots d \,|\, g(2,3) \,|\, abc \cdots d \rangle + \cdots + \langle abc \cdots d \,|\, g(2,N) \,|\, abc \cdots d \rangle +$$

$$\langle abc \cdots d \,|\, g(3,N) \,|\, abc \cdots d \rangle$$

$$\langle abc\cdots d|\sum_{i<j}^{N}g(i,j)|abc\cdots d\rangle=$$

$$\langle a(1)b(2)|g(1,2)|a(1)b(2)\rangle+\langle a(1)c(3)|g(1,3)|a(1)c(3)\rangle+\cdots+\langle a(1)d(N)|g(1,N)|a(1)d(N)\rangle+$$

$$\langle b(2)c(3)|g(2,3)|b(2)c(3)\rangle+\cdots+\langle b(2)d(N)|g(2,N)|b(2)d(N)\rangle+$$

$$\langle c(3)d(N)|g(3,N)|c(3)d(N)\rangle$$

and since the electron labels are dummy indices this may be rewritten as

$$\langle abc\cdots d|\sum_{i<j}^{N}g(i,j)|abc\cdots d\rangle=$$

$$\langle a(1)b(2)|g(1,2)|a(1)b(2)\rangle+\langle a(1)c(2)|g(1,2)|a(1)c(2)\rangle+\cdots+\langle a(1)d(2)|g(1,2)|a(1)d(2)\rangle+$$

$$\langle b(1)c(2)|g(1,2)|b(1)c(2)\rangle+\cdots+\langle b(1)d(2)|g(1,2)|b(1)d(2)\rangle+$$

$$\langle c(1)d(2)|g(1,2)|c(1)d(2)\rangle$$

Further, if we agree to always label the electron coordinates as 1 and then 2 we may rewrite this sum as

$$\langle abc\cdots d|\sum_{i<j}^{N}g(i,j)|abc\cdots d\rangle=$$

$$\langle ab|g(1,2)|ab\rangle+\langle ac|g(1,2)|ac\rangle+\cdots+\langle ad|g(1,2)|ad\rangle+$$

$$\langle bc|g(1,2)|bc\rangle+\cdots+\langle bd|g(1,2)|bd\rangle+$$

$$\langle cd|g(1,2)|cd\rangle$$

Lets now determine the contribution of the single transpositions by considering the $\hat{P}_{12}$ term.

$$\langle abc\cdots d|\sum_{i<j}^{N}g(i,j)|bac\cdots d\rangle=$$

$$\langle abc\cdots d|g(1,2)|bac\cdots d\rangle+\langle abc\cdots d|g(1,3)|bac\cdots d\rangle+\cdots+\langle abc\cdots d|g(1,N)|bac\cdots d\rangle+$$

$$\langle abc\cdots d|g(2,3)|bac\cdots d\rangle+\cdots+\langle abc\cdots d|g(2,N)|bac\cdots d\rangle+$$

$$\langle abc\cdots d|g(3,N)|bac\cdots d\rangle$$

The first term becomes

$$\langle abc\cdots d|g(1,2)|bac\cdots d\rangle=\langle ab|g(1,2)|ba\rangle\langle c|c\rangle\cdots\langle d|d\rangle=\langle ab|g(1,2)|ba\rangle$$

while the second is

$$\langle abc\cdots d\,|\,g(1,3)\,|\,bac\cdots d\rangle = \langle ac\,|\,g(1,3)\,|\,bc\rangle\langle b\,|\,a\rangle\cdots\langle d\,|\,d\rangle = 0$$

because $\langle b\,|\,a\rangle = 0$. Indeed the only contribution from the $\hat{P}_{12}$ term is $\langle ab\,|\,g(1,2)\,|\,ba\rangle$. Examining the remaining ST terms shows that each ST contributes one integral and the total contribution of these ST terms is

$$\langle abc\cdots d\,|\,\hat{G}\,|\,ST\rangle = -\langle ab\,|\,g(1,2)\,|\,ba\rangle - \langle ac\,|\,g(1,2)\,|\,ca\rangle - \cdots - \langle ad\,|\,g(1,2)\,|\,da\rangle$$
$$-\langle bc\,|\,g(1,2)\,|\,cb\rangle - \cdots - \langle bd\,|\,g(1,2)\,|\,db\rangle - \cdots - \langle cd\,|\,g(1,2)\,|\,dc\rangle$$

The negative sign is a result of the odd partity of the ST terms. Continuing this analysis shows that

$$\langle abc\cdots d\,|\,\hat{G}\,|\,DT+TT+\cdots+NT\rangle = 0$$

Note that we can write the ST contribution as

$$\langle abc\cdots d\,|\,\hat{G}\,|\,ST\rangle = -\langle ab\,|\,g(1,2)\hat{P}_{12}\,|\,ab\rangle - \langle ac\,|\,g(1,2)\hat{P}_{12}\,|\,ac\rangle - \cdots - \langle ad\,|\,g(1,2)\hat{P}_{12}\,|\,ad\rangle$$
$$-\langle bc\,|\,g(1,2)\hat{P}_{12}\,|\,bc\rangle - \cdots - \langle bd\,|\,g(1,2)\hat{P}_{12}\,|\,bd\rangle - \cdots - \langle cd\,|\,g(1,2)\hat{P}_{12}\,|\,cd\rangle$$

and so the total two electron contribution is

$$\langle\Psi\,|\,\hat{G}\,|\,\Psi\rangle = \langle abc\cdots d\,|\,\sum_{i<j}^{N}g(i,j)\,|\,abc\cdots d+ST\rangle =$$
$$\langle ab\,|\,g(1,2)(1-\hat{P}_{12})\,|\,ab\rangle + \langle ac\,|\,g(1,2)(1-\hat{P}_{12})\,|\,ac\rangle + \cdots + \langle ad\,|\,g(1,2)(1-\hat{P}_{12})\,|\,ad\rangle +$$
$$\langle bc\,|\,g(1,2)(1-\hat{P}_{12})\,|\,bc\rangle + \cdots + \langle bd\,|\,g(1,2)(1-\hat{P}_{12})\,|\,bd\rangle +$$
$$\langle cd\,|\,g(1,2)(1-\hat{P}_{12})\,|\,cd\rangle$$

If we write the Slater Determinant using a general set of ortonormal spin orbitals $\{\varphi_i\}$

$$\Psi(1,2,3,\cdots,N) = \hat{\mathcal{A}}\varphi_1(1)\varphi_2(2)\varphi_3(3)\cdots\varphi_N(N)$$

The matrix element of the Hamiltonian becomes

$$\langle\Psi\,|\,\hat{H}\,|\,\Psi\rangle = \sum_{i=1}^{N}\langle\varphi_i\,|\,\hat{f}\,|\,\varphi_i\rangle + \sum_{i<j}^{N}\langle\varphi_i(1)\varphi_j(2)\,|\,g(1,2)(1-\hat{P}_{12})\,|\,\varphi_i(1)\varphi_j(2)\rangle$$

Off-Diagonal Matrix Elements

Determinants differ by one spin orbital

We often need to evaluate matrix elements of one and two electron operators when the determinants are different. For example we made need

$\langle \Psi | \hat{H} | \Omega \rangle$ where Ψ & Ω are Slater Determinants composed of different spin orbitals. We will restrict ourselves here to the special, but very useful case, where the spin orbitals in Ψ & Ω orthogonal and of course normalized. Lets first consider the case where Ψ & Ω differ by one spin orbital and lets take them as

$$\Psi(1,2,3,\cdots N) = \hat{A}\phi\varphi_2\varphi_3\cdots\varphi_N \text{ and } \Omega(1,2,3,\cdots N) = \hat{A}\chi\varphi_2\varphi_3\cdots\varphi_N .$$

Consider first the matrix element of the one electron operator $\hat{F}(1,2,3,\cdots,N)$. As above we have

$$\langle \Psi | \hat{F} | \Omega \rangle = \langle \phi\varphi_2\varphi_3\cdots\varphi_N | \hat{F} | \sum_P \varepsilon_P \chi\varphi_2\varphi_3\cdots\varphi_N \rangle = \langle \phi\varphi_2\varphi_3\cdots\varphi_N | \hat{F} | \chi\varphi_2\varphi_3\cdots\varphi_N + ST + DT + \cdots + NT \rangle$$

The zero transposition term contributes

$$\langle \phi | \hat{f} | \chi \rangle$$

while all other contributions vanish. For the two electron operator the zero transposition term contributes

$$\langle \phi\varphi_2\varphi_3\cdots\varphi_N | \sum_{i<j}^{N} g(i,j) | \chi\varphi_2\varphi_3\cdots\varphi_N \rangle = \sum_{i=2}^{N} \langle \phi(1)\varphi_i(2) | g(1,2) | \chi(1)\varphi_i(2) \rangle$$

and the ST term contributes

$$\langle \phi\varphi_2\varphi_3\cdots\varphi_N | \sum_{i<j}^{N} g(i,j) | ST \rangle = \sum_{i=2}^{N} \langle \phi(1)\varphi_i(2) | g(1,2) | \varphi_i(1)\chi(2) \rangle$$

All other contributions vanish and we may write the matrix element of the Hamiltonian as

$$\langle \Psi | \hat{H} | \Omega \rangle = \langle \phi | \hat{f} | \chi \rangle + \sum_{i=2}^{N} \langle \phi(1)\varphi_i(2) | g(1,2)(1-\hat{P}_{12}) | \chi(1)\varphi_i(2) \rangle$$

Note that this formula presupposes that the spin orbitals in Ψ & Ω that do not match are in the first position following $\hat{A}$ and that those that are common to both determinants are

are in the same order in both Ψ & Ω. If this is not the case one simply rearranges the orbitals to bring them into this standard order and keeps track of the resulting phase difference with the result that this matrix element might be multiplied by a minus sign.

Determinants differ by two spin orbitals

Suppose $\Psi = \hat{\mathcal{A}}\phi(1)\rho(2)\varphi_3(3)\cdots\varphi_N(N)$ & $\Omega = \hat{\mathcal{A}}\chi(1)\eta(2)\varphi_3(3)\cdots\varphi_N(N)$

Using the techniques detailed previously one can show that the matrix element of the one electron operator $\hat{F}$ between these two determinants vanishes and the two electron operator contributes

$$\left\langle \Psi \left| \hat{H} \right| \Omega \right\rangle = \left\langle \Psi \left| \sum_{i<j}^{N} g(i,j) \right| \Omega \right\rangle = \left\langle \phi(1)\rho(2) \left| g(1,2)(1-\hat{P}_{12}) \right| \chi(1)\eta(2) \right\rangle$$

Where once again the orbitals have been brought into coincidence.

Determinants differ by three or more spin orbitals

When Ψ & Ω differ by three or more spin orbitals $\left\langle \Psi \left| \hat{H} \right| \Omega \right\rangle = 0$