6.6: The Slater-Condon Rules

To form Hamiltonian matrix elements $H_{K,L}$ between any pair of Slater determinants constructed from spin-orbitals that are orthonormal, one uses the so-called Slater-Condon rules. These rules express all non-vanishing matrix elements involving either one- or two- electron operators. One-electron operators are additive and appear as

$$F = \sum_i \phi(i); \tag{6.6.1}$$

two-electron operators are pairwise additive and appear as

$$G = \sum_{i<j} g(i,j) = \frac{1}{2}\sum_{i \neq j} g(i,j). \tag{6.6.2}$$

The Slater-Condon rules give the matrix elements between two determinants

$$|\rangle = |\phi_1 \phi_2 \phi_3 \ldots \phi_N| \tag{6.6.3}$$

and

$$|'\rangle = |\phi'_1 \phi'_2 \phi'_3 \ldots \phi'_N| \tag{6.6.4}$$

for any quantum mechanical operator that is a sum of one- and two- electron operators ($F+G$). It expresses these matrix elements in terms of one-and two-electron integrals involving the spin-orbitals that appear in $|\rangle$ and $|'\rangle$ and the operators f and g.

As a first step in applying these rules, one must examine $|\rangle$ and $|'\rangle$ and determine by how many (if any) spin-orbitals $|\rangle$ and $|'\rangle$ differ. In so doing, one may have to reorder the spin-orbitals in one of the determinants to achieve maximal coincidence with those in the other determinant; it is essential to keep track of the number of permutations (N_p) that one makes in achieving maximal coincidence. The results of the Slater-Condon rules given below are then multiplied by $(-1)^{N_p}$ to obtain the matrix elements between the original $|\rangle$ and $|'\rangle$. The final result does not depend on whether one chooses to permute $|\rangle$ or $|'\rangle$ to determine N_p.

The Hamiltonian is, of course, a specific example of such an operator that contains both one- and two-electron components; the electric dipole operator $\sum_i e\mathbf{r}_i$ and the electronic kinetic energy $-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2$ are examples of one-electron operators (for which one takes $g=0$); the electron-electron coulomb interaction $\sum_{i<j} e^2/r_{ij}$ is a two-electron operator (for which one takes $f=0$).

The two Slater determinants whose matrix elements are to be determined can be written as

$$|\rangle = \frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P\phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N) \tag{6.6.5}$$

$$|'\rangle = \frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^q Q\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N) \tag{6.6.6}$$

where the spin-orbitals $\{\phi_j\}$ and $\{\phi'_j\}$ appear in the first and second determinants, respectively, and the operators P and Q describe the permutations of the spin-orbitals appearing in these two determinants. The factors $(-1)^p$ and $(-1)^q$ are the signs associated with these permutations as discussed earlier in Section 6.1.1. Any matrix element involving one- and two-electron operators

$$\langle |F+G|'\rangle = \frac{1}{\sqrt{N!}}\sum_{P,Q}(-1)^{p+q} \tag{6.6.7}$$
$$\langle P\phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|F+G|Q\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle$$

needs to be expressed in terms of integrals involving the spin-orbitals in the two determinants and the one- and two-electron operators.

To simplify the above expression, which contains $(N!)^2$ terms in its two summations, one proceeds as follows:

a. Use is made of the identity $\langle P\psi|\psi'\rangle = \langle y|P\psi'\rangle$ to move the permutation operator P to just before the $(F+G)$

$$\begin{aligned}&\langle P\phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|F+G|Q\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle \\ &= \langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|P(F+G)|Q\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle\end{aligned} \tag{6.6.8}$$

b. Because F and G contain sums over all N electrons in a symmetric fashion, any permutation P acting on $F+G$ leaves these sums unchanged. So, P commutes with F and with G. This allows the above quantity to be rewritten as

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|F+G|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle \tag{6.6.9}$$

c. For any permutation operator Q, the operator PQ is just another permutation operator. Moreover, for any Q, the set of all operators PQ runs over all $N!$ permutations, and the sign associated with the operator PQ is the sign belonging to P times the sign associated with Q, $(-1)^{p+q}$. So, the double sum (i.e., over P and over Q) appearing in the above expression for the general matrix element of $F+G$ contains $N!$ identical sums over the single operator PQ of the sign of this operator $(-1)^{p+q}$ multiplied by the effect of this operator on the spin-orbital product on the right-hand side

$$\langle |F+G|' \rangle = \frac{1}{\sqrt{N!}} N! \tag{6.6.10}$$

$$\sum_{P,Q} (-1)^{p+q} \langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|F+G|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle$$

By assumption, as explained earlier, the two Slater determinants have been compared and arranged in an order of maximal coincidence and the factor $(-1)^{N_p}$ needed to bring them into maximal coincidence has been determined. So, let us begin by assuming that the two determinants differ by three spin-orbitals and let us first consider the terms arising from the identity permutation $PQ = E$ (i.e., the permutation that alters none of the spin-orbitals' labels). These terms will involve integrals of the form

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_j(j)\cdots\phi_N(N)|F+G|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_j(j)\cdots\phi'_N(N)\rangle \tag{6.6.11}$$

where the three-spin orbitals that differ in the two determinants appear in positions k, n, and j. In these $4N$-dimensional (3 spatial and 1 spin coordinate for each of N electrons) integrals:

a. Integrals of the form (for all $i \neq k$, n, or j)

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_j(j)\cdots\phi_N(N)|f(i)|\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_j(j)\cdots\phi'_N(N)\rangle \tag{6.6.12}$$

and (for all i and $l \neq k$, n, or j)

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_j(j)\cdots\phi_N(N)|g(i,l)|\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_j(j)\cdots\phi'_N(N)\rangle \tag{6.6.13}$$

vanish because the spin-orbitals appearing in positions k, n, and j in the two determinants are orthogonal to one another. For the F-operator, even integrals with $i = k$, n, or j vanish because there are still two spin-orbital mismatches at the other two locations among k, n, and j. For the G-operator, even integrals with i or $l = k$, n, or j vanish because two mismatches remain; and even with both i and $l = k$, n, or j, the integrals vanish because one spin-orbital mismatch remains. The main observation to make is that, even for $PQ = E$, if there are three spin-orbital differences, neither the F nor G operator gives rise to any non-vanishing results.

b. If we now consider any other permutation PQ, the situation does not improve because any permutation cannot alter the fact that three spin-orbital mismatches do not generate any non-vanishing results.

If there are only two spin-orbital mismatches (say in locations k and n), the integrals we need to evaluate are of the form

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|f(i)|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle \tag{6.6.14}$$

and

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_n(n)\cdots\phi_N(N)|g(i,l)|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_n(n)\cdots\phi'_N(N)\rangle \tag{6.6.15}$$

c. Again, beginning with $PQ = E$, we can conclude that all of the integrals involving the F-operator (i.e., $\phi(i)$, $\phi(k)$, and $\phi(n)$) vanish because the two spin-orbital mismatch is too much even for $\phi(k)$ or $\phi(n)$ to overcome; at least one spin-orbital orthogonality integral remains. For the G-operator, the only non-vanishing result arises from the $i = k$ and $l = n$ term $\langle \phi_k(k)\phi_n(n)|g(k,n)|\phi'_k(k)\phi'_n(n)\rangle$.

d. The only other permutation that generates another non-vanishing result is the permutation that interchanges k and n, and it produces $-\langle \phi_k(k)\phi_n(n)|g(k,n)|\phi'_n(k)\phi'_k(n)\rangle$

, where the negative sign arises from the $(-1)^{p+q}$ factor. All other permutations would interchange other spin-orbitals and thus generate orthogonality integrals involving other electrons' coordinates.

If there is only one spin-orbital mismatch (say in location k), the integrals we need to evaluate are of the form

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_N(N)|f(i)|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_N(N)\rangle \tag{6.6.16}$$

and

$$\langle \phi_1(1)\phi_2(2)\cdots\phi_k(k)\cdots\phi_N(N)|g(i,l)|PQ\phi'_1(1)\phi'_2(2)\cdots\phi'_k(k)\cdots\phi'_N(N)\rangle. \tag{6.6.17}$$

e. Again beginning with $PQ = E$, the only non-vanishing contribution from the F-operator is $\langle \phi_k(k)|f(k)|\phi'_k(k)\rangle$. For all other permutations, the F-operator produces no non-vanishing contributions because these permutations generate orthogonality integrals. For the G-operator and $PQ = E$, the only non-vanishing contributions are

$$\langle\phi_k(k)\phi_j(j)|g(k,j)|\phi'_k(k)\phi_j(j)\rangle \tag{6.6.18}$$

where the sum over j runs over all of the spin-orbitals that are common to both of the two determinants.

f. Among all other permutations, the only one that produces a non-vanishing result are those that permute the spin-orbital in the kth location with another spin-orbital, and they produce

$$-\langle\phi_k(k)\phi_j(j)|g(k,j)|\phi'_j(k)\phi_k(j)\rangle. \tag{6.6.19}$$

The minus sign arises from the $(-1)^{p+q}$ factor associated with this pair wise permutation operator.

Finally, if there is no mismatch (i.e., the two determinants are identical), then

g. The identity permutation generates

$$-\langle\phi_k(k)|f(k)|\phi_k(k)\rangle. \tag{6.6.20}$$

from the F-operator and

$$\frac{1}{2}\sum_{j\neq k=1}^{N}\langle\phi_j(j)\phi_k(k)|g(k,j)|\phi_j(j)\phi_k(k)\rangle \tag{6.6.21}$$

from the G-operator.

h. The permutation that interchanges spin-orbitals in the kth and jth location produces

$$-\frac{1}{2}\sum_{j\neq k=1}^{N}\langle\phi_j(j)\phi_k(k)|g(k,j)|\phi_k(j)\phi_j(k)\rangle. \tag{6.6.22}$$

The summations over j and k appearing above can, alternatively, be written as

$$\sum_{j<k=1}^{N}\langle\phi_j(j)\phi_k(k)|g(k,j)|\phi_j(j)\phi_k(k)\rangle \tag{6.6.23}$$

and

$$-\sum_{j<k=1}^{N}\langle\phi_j(j)\phi_k(k)|g(k,j)|\phi_k(j)\phi_j(k)\rangle. \tag{6.6.24}$$

So, in summary, once maximal coincidence has been achieved, the Slater-Condon (SC) rules provide the following prescriptions for evaluating the matrix elements of any operator $F+G$ containing a one-electron part $F=\sum_i\phi(i)$ and a two-electron part $G=\sum_{i<j}g(i,j)$.:

i. If $|\rangle$ and $|'\rangle$ are identical, then

$$\langle|F+G|\rangle=\sum_i\langle\phi_i|f|\phi_i\rangle+\sum_{i\rangle j}[\langle\phi_i\phi_j|g|\phi_i\phi_j\rangle-\langle\phi_i\phi_j|g|\phi_j\phi_i\rangle], \tag{6.6.25}$$

where the sums over i and j run over all spin-orbitals in $|\rangle$;

ii. If $|\rangle$ and $|'\rangle$ differ by a single spin-orbital mismatch ($\phi_p\neq\phi'_p$),

$$\langle|F+G|'\rangle=(-1)^{N_p}\langle\phi_p|f|\phi'_p\rangle+\sum_j[\langle\phi_p\phi_j|g|\phi'_p\phi_j\rangle-\langle\phi_p\phi_j|g|\phi_j\phi'_p\rangle], \tag{6.6.26}$$

where the sum over j runs over all spin-orbitals in $|\rangle$ except ϕ_p;

iii. If $|\rangle$ and $|'\rangle$ differ by two spin-orbitals ($\phi_p\neq\phi'_p$ and $\phi_q\neq\phi'_q$),

$$\langle|F+G|'\rangle=(-1)^{N_p}\langle\phi_p\phi_q|g|\phi'_p\phi'_q\rangle-\langle\phi_p\phi_q|g|\phi'_q\phi'_p\rangle \tag{6.6.27}$$

(note that the F contribution vanishes in this case);

iv. If $|\rangle$ and $|'\rangle$ differ by three or more spin orbitals, then

$$\langle|F+G|'\rangle=0; \tag{6.6.28}$$

v. Φ or the identity operator I, the matrix elements $\langle|I|'\rangle=0$ if $|\rangle$ and $|'\rangle$ differ by one or more spin-orbitals (i.e., the Slater determinants are orthonormal if their spin-orbitals are).

In these expressions,

$$\langle \phi_i | f | \phi_j \rangle \tag{6.6.29}$$

is used to denote the one-electron integral

$$\int \phi_i^*(r) f(r) \phi_j(r) dr \tag{6.6.30}$$

and

$$\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle \tag{6.6.31}$$

(or, in short hand notation, $\langle ij|kl\rangle$) represents the two-electron integral

$$\int \phi_i^*(r) \phi_j^*(r') g(r,r') \phi_k(r) \phi_l(r') dr dr'. \tag{6.6.32}$$

The notation $\langle ij|kl\rangle$ introduced above gives the two-electron integrals for the $g(r,r')$ operator in the so-called Dirac notation, in which the i and k indices label the spin-orbitals that refer to the coordinates r and the j and l indices label the spin-orbitals referring to coordinates r'. The r and r' denote r, θ, ϕ, σ and $r', \theta', \phi', \sigma'$ (with σ and σ' being the α or β spin functions).

If the operators f and g do not contain any electron spin operators, then the spin integrations implicit in these integrals (all of the ϕ_i are spin-orbitals, so each ϕ is accompanied by an α or β spin function and each ϕ^* involves the adjoint of one of the α or β spin functions) can be carried out using $\langle a|a\rangle = 1$, $\langle a|b\rangle = 0$, $\langle b|a\rangle = 0$, $\langle b|b\rangle = 1$, thereby yielding integrals over spatial orbitals.

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