

11.3: The Slater-Condon Rules

The Slater-Condon rules express integrals of one- and two-body operators over wavefunctions constructed as Slater determinants of orthonormal orbitals in terms of the individual orbitals. In doing so, the original integrals involving N-electron wavefunctions are reduced to sums over integrals involving at most two molecular orbitals

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

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

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 ($\phi_p \neq \phi'_p$),

$$\langle |F + G|' \rangle = \langle \phi_p | f | \phi'_p \rangle + \sum_j [\langle \phi_p \phi_j | g | \phi'_p \phi_j \rangle - \langle \phi_p \phi_j | g | \phi_j \phi'_p \rangle],$$

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 $\phi_q \neq \phi'_q$),

$$\langle |F + G|' \rangle = \langle \phi_p \phi_q | g | \phi'_p \phi'_q \rangle - \langle \phi_p \phi_q | g | \phi'_q \phi'_p \rangle$$

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

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

$$\langle |F + G|' \rangle = 0;$$

v. For 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).

Recall that each of these results is subject to multiplication by a factor of $(-1)^{N_p}$ to account for possible ordering differences in the spin-orbitals in $|\rangle$ and $|\rangle$.

In these expressions,

$$\langle \phi_i | f | \phi_j \rangle$$

is used to denote the one-electron integral

$$\int \phi_i^*(r) f(r) \phi_j(r) dr$$

and $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ (or in short hand notation $\langle ij | kl \rangle$) represents the two-electron integral

$$\int \phi_i^*(r) \phi_j^*(r') g(r, r') \phi_k(r) \phi_l(r') dr dr'$$

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). The fact that r and r' are integrated and hence represent 'dummy' variables introduces index permutational symmetry into this list of integrals. For example,

$$\langle ij | kl \rangle = \langle ji | lk \rangle = \langle kl | ij \rangle^* = \langle lk | ji \rangle^*;$$

the final two equivalences are results of the Hermitian nature of $g(r, r')$.

It is also common to represent these same two-electron integrals in a notation referred to as Mulliken notation in which:

$$\int \phi_i^*(r) \phi_j^*(r') g(r, r') \phi_k(r) \phi_l(r') dr dr' = (ik | jl).$$

Here, the indices i and k , which label the spin-orbital having variables r are grouped together, and j and l , which label spin-orbitals referring to the r' variables appear together. The above permutational symmetries, when expressed in terms of the Mulliken integral list read:

$$(ik|jl) = (jl|ik) = (ki|lj)^* = (lj|ki)^*.$$

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 as $\langle \alpha|\alpha \rangle = 1$, $\langle \alpha|\beta \rangle = 0$, $\langle \beta|\alpha \rangle = 0$, $\langle \beta|\beta \rangle = 1$, thereby yielding integrals over spatial orbitals. These spin integration results follow immediately from the general properties of angular momentum eigenfunctions detailed in Appendix G; in particular, because α and β are eigenfunctions of S_Z with different eigenvalues, they must be orthogonal $\langle \alpha|\beta \rangle = \langle \beta|\alpha \rangle = 0$.

The essential results of the Slater-Condon rules are:

1. The full $N!$ terms that arise in the N -electron Slater determinants do not have to be treated explicitly, nor do the $N!(N! + 1)/2$ Hamiltonian matrix elements among the $N!$ terms of one Slater determinant and the $N!$ terms of the same or another Slater determinant
2. All such matrix elements, for **any** one- and/or two-electron operator can be expressed in terms of one- or two-electron integrals over the spin-orbitals that appear in the determinants.
3. The integrals over orbitals are three or six dimensional integrals, regardless of how many electrons N there are.
4. These integrals over mo's can, through the LCAO-MO expansion, ultimately be expressed in terms of one- and two-electron integrals over the primitive atomic orbitals. It is only these ao-based integrals that can be evaluated explicitly (on high speed computers for all but the smallest systems).

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