11.2: The Slater-Condon Rules Give Expressions for the Operator Matrix Elements Among the CSFs

To form the $H_{K,L}$ matrix, one uses the so-called **Slater-Condon rules** which express all non-vanishing determinental matrix elements involving either one- or two- electron operators (one-electron operators are additive and appear as

$$F = \sum_i f(i);$$

two-electron operators are pairwise additive and appear as

$$G = \sum_{ij} g(i,j).$$

Because the CSFs are simple linear combinations of determinants with coefficients determined by space and spin symmetry, the $H_{I,J}$ matrix in terms of determinants can be used to generate the $H_{K,L}$ matrix over CSFs.

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

$$| >= |\phi_1\phi_2\phi_3 \ldots \Phi_N|$$

and

$$|' >= |\phi'_1\phi'_2\phi'_3 \ldots \phi'_N|$$

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 | > and | '> and the operators f and g.

As a first step in applying these rules, one must examine | > and | '> and determine by how many (if any) spin-orbitals | > and | '> 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 | > and | '>. The final result does not depend on whether one chooses to permute | > or | '>.

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 $F = \sum_i f(i)$ and a two-electron part $G = \sum_{ij} g(i,j)$ (the Hamiltonian is, of course, a specific example of such an operator; 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 $\sum_{i>j}\frac{e^2}{r_{ij}}$ is a two-electron operator (for which one takes f = 0)):

> *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, or in other words, the original 3N dimensional integral is expressed in terms of many three- and six-dimensional integrals.*