To form the \( \langle H_{K,L} \rangle \) 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 \( \langle H_{I,J} \rangle \) matrix in terms of determinants can be used to generate the \( \langle H_{K,L} \rangle \) matrix over CSFs.

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

\[
|>=|\phi_1\phi_2\phi_3...\Phi_N|
\]

and

\[
|'>=|\phi_1'\phi_2'\phi_3'...\phi_N'|
\]

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 \(|'\rangle\) and the operators \(f\) and \(g\).

As a first step in applying these rules, one must examine \(|>\) and \(|'\rangle\) and determine by how many (if any) spin-orbitals \(|>\) 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 \(\langle(N_p)\rangle\) that one makes in achieving maximal coincidence. The results of the Slater-Condon rules given below are then multiplied by \(\langle(-1)^{N_p}\rangle\) to obtain the matrix elements between the original \(|>\) and \(|'\rangle\). The final result does not depend on whether one chooses to permute \(|>\) or \(|'\rangle\).

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 \(\langle F = \sum_i f(i) \rangle\) and a two-electron part \(\langle G = \sum_{ij} g(i,j) \rangle\) (the Hamiltonian is, of course, a specific example of such an operator; the electric dipole operator \(\langle \sum_i e r_i \rangle\) and the electronic kinetic energy \(\langle \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 \rangle\) are examples of one-electron operators (for which one takes \(g = 0\)) and the electron-electron coulomb interaction \(\langle \sum_i \sum_j \frac{e^2}{r_{ij}} \rangle\) 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.
Contributors

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