

11.1: Configuration State Functions can Express the Full N-Electron Wavefunction

It has been demonstrated that a given electronic configuration can yield several space- and spin- adapted determinantal wavefunctions; such functions are referred to as configuration state functions (CSFs). These CSF wavefunctions are **not** the exact eigenfunctions of the many-electron Hamiltonian, H ; they are simply functions which possess the space, spin, and permutational symmetry of the exact eigenstates. As such, they comprise an acceptable set of functions to use in, for example, a [linear variational treatment](#) of the true states.

In such variational treatments of electronic structure, the N-electron wavefunction Ψ is expanded as a sum over **all** CSFs that possess the desired spatial and spin symmetry:

$$\Psi = \sum_J C_J \Phi_J.$$

Here, the Φ_J represent the CSFs that are of the correct symmetry, and the C_J are their expansion coefficients to be determined in the variational calculation. If the spin-orbitals used to form the determinants, that in turn form the CSFs $\{\Phi_J\}$, are orthonormal one electron functions (i.e., $\langle \phi_k | \phi_j \rangle = \delta_{k,j}$), then the CSFs can be shown to be orthonormal functions of N electrons

$$\langle \Phi_J | \Phi_K \rangle = \delta_{J,K}.$$

In fact, the Slater determinants themselves also are orthonormal functions of N electrons whenever orthonormal spin-orbitals are used to form the determinants.

The above expansion of the full N-electron wavefunction is termed a "[configuration-interaction](#)" (CI) expansion. It is, in principle, a mathematically rigorous approach to expressing Ψ because the set of **all** determinants that can be formed from a complete set of spin-orbitals can be shown to be complete. In practice, one is limited to the number of orbitals that can be used and in the number of CSFs that can be included in the CI expansion. Nevertheless, the CI expansion method forms the basis of the most commonly used techniques in quantum chemistry.

In general, the optimal variational (or perturbative) wavefunction for any (i.e., the ground or excited) state will include contributions from spin-and space-symmetry adapted determinants derived from all possible configurations. For example, although the determinant with $L = 1, S = 1, M_L = 1, M_S = 1$ arising from the $1s^2 2s^2 2p^2$ configuration may contribute strongly to the true ground electronic state of the Carbon atom, there will be contributions from all configurations which can provide these L, S, M_L , and M_S values (e.g., the $1s^2 2s^2 2p^1 3p^1$ and $2s^2 2p^4$ configurations will also contribute, although the $1s^2 2s^2 2p^1 3s^1$ and $1s^2 2s^1 2p^2 3p^1$ will not because the latter two configurations are odd under inversion symmetry whereas the state under study is even).

The mixing of CSFs from many configurations to produce an optimal description of the true electronic states is referred to as configuration interaction (CI). Strong CI (i.e., mixing of CSFs with large amplitudes appearing for more than one dominant CSF) can occur, for example, when two CSFs from different electronic configurations have nearly the same Hamiltonian expectation value. For example, the $1s^2 2s^2$ and $1s^2 2p^2$ configurations of Be and the analogous ns^2 and np^2 configurations of all alkaline earth atoms are close in energy because the ns-np orbital energy splitting is small for these elements; the π^2 and π^{2*} configurations of ethylene become equal in energy, and thus undergo strong CI mixing, as the CC π bond is twisted by 90° in which case the π and π^* orbitals become degenerate.

Within a variational treatment, the relative contributions of the spin-and space symmetry adapted CSFs are determined by solving a secular problem for the eigenvalues (E_i) and eigenvectors (C_i) of the matrix representation H of the full many-electron Hamiltonian \mathbf{H} within this CSF basis:

$$\sum_L H_{K,L} C_{i,L} = E_i C_{i,K}.$$

The eigenvalue E_i gives the variational estimate for the energy of the i^{th} state, and the entries in the corresponding eigenvector $C_{i,K}$ give the contribution of the K^{th} CSF to the i^{th} wavefunction Ψ_i in the sense that

$$\Psi_i = \sum_K C_{i,K} \Phi_K,$$

where Φ_K is the K^{th} CSF.

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