

19.1: Introduction to Multi-Determinant Wavefunctions

Much of the development of the previous chapter pertains to the use of a single Slater determinant trial wavefunction. As presented, it relates to what has been called the unrestricted Hartree-Fock (UHF) theory in which each spin-orbital ϕ_i has its own orbital energy ϵ_i and LCAO-MO coefficients $C_{\nu,i}$; there may be different $C_{\nu,i}$ for α spin-orbitals than for β spin-orbitals. Such a wavefunction suffers from the *spin contamination* difficulty detailed earlier.

To allow for a properly spin- and space- symmetry adapted trial wavefunction and to permit Ψ to contain more than a single CSF, methods which are more flexible than the single-determinant HF procedure are needed. In particular, it may be necessary to use a combination of determinants to describe such a proper symmetry function. Moreover, as emphasized earlier, whenever two or more CSFs have similar energies (i.e., Hamiltonian expectation values) and can couple strongly through the Hamiltonian (e.g., at avoided crossings in configuration correlation diagrams), the wavefunction must be described in a multiconfigurational manner to permit the wavefunction to evolve smoothly from reactants to products. Also, whenever dynamical electron correlation effects are to be treated, a multiconfigurational Ψ must be used; in this case, CSFs that are **doubly excited** relative to one or more of the essential CSFs (i.e., the dominant CSFs that are included in the so-called reference wavefunction) are included to permit polarized-orbital-pair formation.

Multiconfigurational functions are needed not only to account for electron correlation but also to permit orbital readjustments to occur. For example, if a set of SCF orbitals is employed in forming a multi-CSF wavefunction, the variational condition that the energy is stationary with respect to variations in the LCAO-MO coefficients is no longer obeyed (i.e., the SCF energy functional is stationary when SCF orbitals are employed, but the MC-energy functional is generally not stationary if SCF orbitals are employed). For such reasons, it is important to include CSFs that are **singly excited** relative to the dominant CSFs in the reference wavefunction.

That singly excited CSFs allow for orbital relaxation can be seen as follows. Consider a wavefunction consisting of one CSF $|\phi_1 \dots \phi_i \dots \phi_N|$ to which singly excited CSFs of the form $|\phi_1 \dots \phi_m \dots \phi_N|$ have been added with coefficients $C_{i,m}$:

$$\Psi = \sum_m C_{i,m} |\phi_1 \dots \phi_m \dots \phi_N| + |\phi_1 \dots \phi_i \dots \phi_N|.$$

All of these determinants have all of their columns equal except the i^{th} column; therefore, they can be combined into a single new determinant:

$$\Psi = |\phi_1 \dots \phi'_i \dots \phi_N|,$$

where the relaxed orbital ϕ'_i

$$\phi'_i = \phi_i + \sum_m C_{i,m} \phi_m.$$

The sum of CSFs that are singly excited in the i^{th} spin-orbital with respect to $|\phi_1 \dots \phi_i \dots \phi_N|$ is therefore seen to allow the spin-orbital ϕ_i to relax into the new spin-orbital ϕ'_i . It is in this sense that singly excited CSFs allow for orbital reoptimization.

In summary, doubly excited CSFs are often employed to permit polarized orbital pair formation and hence to allow for electron correlations. Singly excited CSFs are included to permit orbital relaxation (i.e., orbital reoptimization) to occur.

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