

Finding symmetry-broken SCF solutions: Accurate modeling of SCF electronic energy surfaces

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Spontaneous symmetry breaking signals the onset of strong electron correlation. The symmetry-broken wavefunction, if it exists, is lower in energy than the standard Restricted Hartree-Fock one, and often offers a better approximation to potential energy surfaces. Its other main use is that it allows the identification the *active* orbitals participating in strong correlation. These orbitals can then be treated at a higher theoretical level, e.g., MC-SCF. Symmetry breaking has received much interest from the 1960s to the present.

Most important is the spontaneous breaking of the total spin (S^2) symmetry (*triplet instability* in singlet systems). It approximates the singlet state with different orbitals for α and β spins. This leads to contamination by higher (mainly triplet) states, hence its name. A *singlet unstable* SCF wavefunction is simply a saddle point on the SCF energy surface as a function of orbital rotations between occupied and virtual orbitals. It becomes important if the minimum has lower spatial symmetry than the Hamiltonian. Other instabilities include energy lowering if the orbitals are made complex, general spin functions (linear combinations of α and β spin functions), and a combination these, as classified by Fukutome. However, triplet instability is sufficient in most cases. E.g., complex instability in a two-orbital model, and probably generally, implies triplet instability. In systems which have multiple low-lying SCF solutions, the fractionally occupied natural orbitals of the *average density* span the active space.

The calculation of a UHF wavefunction for an unstable singlet system may be difficult. SCF convergence, for reasons which are understandable, is generally poor in these cases, and convergence to saddle points is common. Instability is indicated by negative eigenvalues of the electronic Hessian. Most stability analyses stop at this point. However, at least a *quartic* expansion is needed to model the SCF energy as a function of orbital rotations in unstable systems. The calculation of higher derivatives, and the solution of the resulting equations if there is more than one instability, appear difficult.

We have found, first numerically and then analytically, that mixed higher derivatives of the SCF energy with odd powers in an orbital rotation angle vanish in the eigenfunction basis of the Hessian. This allows the location of minima to fifth order by a linear system of equations in the squared orbital rotation angles. Only real solutions are physical.

Orbital selection for MC-SCF will be discussed and compared to the UHF natural orbital criterion. Examples include nitrobenzene, ozone, Li_2 , linear polyenes and polyacenes, azulene, porphine, m-benzyne, the transition state of the Bergman cyclization, non-planar π systems like corannulene, C_{60} , and Thiele's hydrocarbon, as well as transition metal systems: Cr_2 , ferrocene, and Hieber's anion $[\text{Fe}(\text{CO})_3\text{NO}]^-$.