

# Best practices for non-Aufbau configurations



**Aufbau principle:** a maximum of two electrons are put into orbitals in the order of increasing orbital energy, i.e., the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals, – leading to a low-spin state.

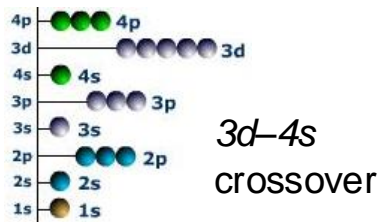
*Niels Bohr, 1923*

## Assumptions:

- electrons exist in sharp stationary states
- these states are preserved upon addition of an electron and a proton to the system

**Ehrenfest's adiabatic principle:** if a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions.

*Paul Ehrenfest, 1917*



*WIREs Comput. Mol. Sci.* **2015**, *5*, 440.  
*Br. J. Philos. Sci.* **1991**, *42*, 309.

**Pauli exclusion principle (modern):** under the exchange of two identical particles, the total (many-particle) wave function is antisymmetric for fermions and symmetric for bosons.

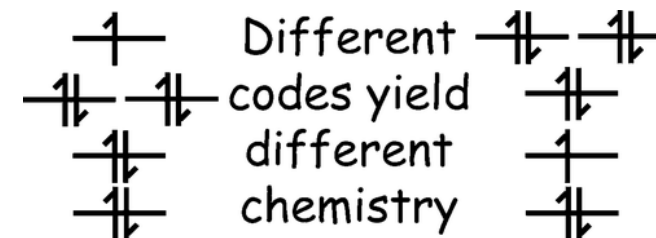
**Modern quantum mechanics:** in the stationary states, the quantum numbers of individual electrons do not commute with the Hamiltonian, only the total angular momentum does.

**Pauli exclusion principle (original):** it should be forbidden for more than one electron with the same value of the main quantum number  $n$  to have the same value for the other three quantum numbers  $k$ ,  $j$  and  $m$ .

*Wolfgang Pauli, 1925*

## In silico

The total high-spin ROHF Fock matrix is constructed from UHF alpha and beta Fock matrices using *arbitrary* canonicalisation parameters.



*J. Phys. Chem. A* **2010**, *114*, 8772.

Some electronic structure codes allow *manually* setting occupations and thus comparing aufbau and non-aufbau configurations, e.g. in ADF

OCCUPATIONS IntegerAufbau

IrrepOccupations

irrep orbitalnumbers

irrep orbitalnumbers

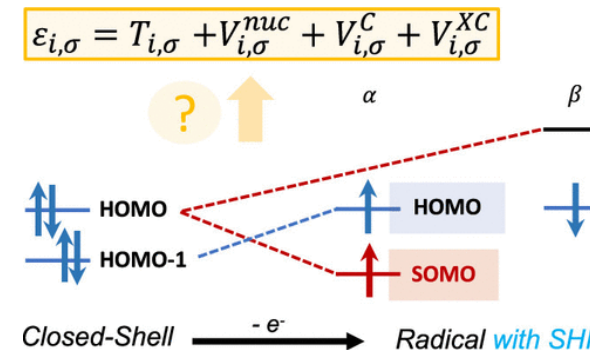
...

End

[Similar can be done with CAS]

## In experiment

The formation of a SOMO-HOMO inverted (quasi-closed-shell) radical from a closed-shell parent compound (*i.e.*, with an even number of electrons) is likely to occur when the electrons in the highest molecular orbital (HOMO) of the closed-shell parent repel each other strongly, while at the same time, the repulsion between the HOMO and other occupied frontier MOs is much weaker.



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