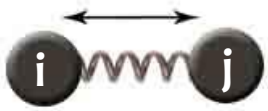
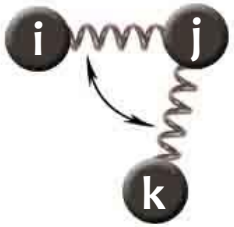
Answers to simple (but important!) quantum chemical questions.

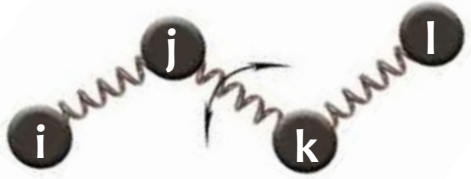
Zero energy

* AB-initio: All particles (including electrons) are at infinity.
* Molecular mechanics: Each term has it own zero energy "spring is fully relaxed".



$$\Delta E_{Stretch} = \sum_{Bonds} k_{Stretch}\left(r_{ij} - r_{eq}\right)^2$$





$$\Delta E_{Dihedral} = \sum_{Dihedral}\left[k_0 + \sum_{r=1}^{n} k_r\left(1+\cos\left(r\theta_{ijkl}\right)\right)\right]$$

$$\Delta E_{Valance} = \sum_{Valance} k_{Valance}\left(\alpha_{ijk} - \alpha_{eq}\right)^2$$

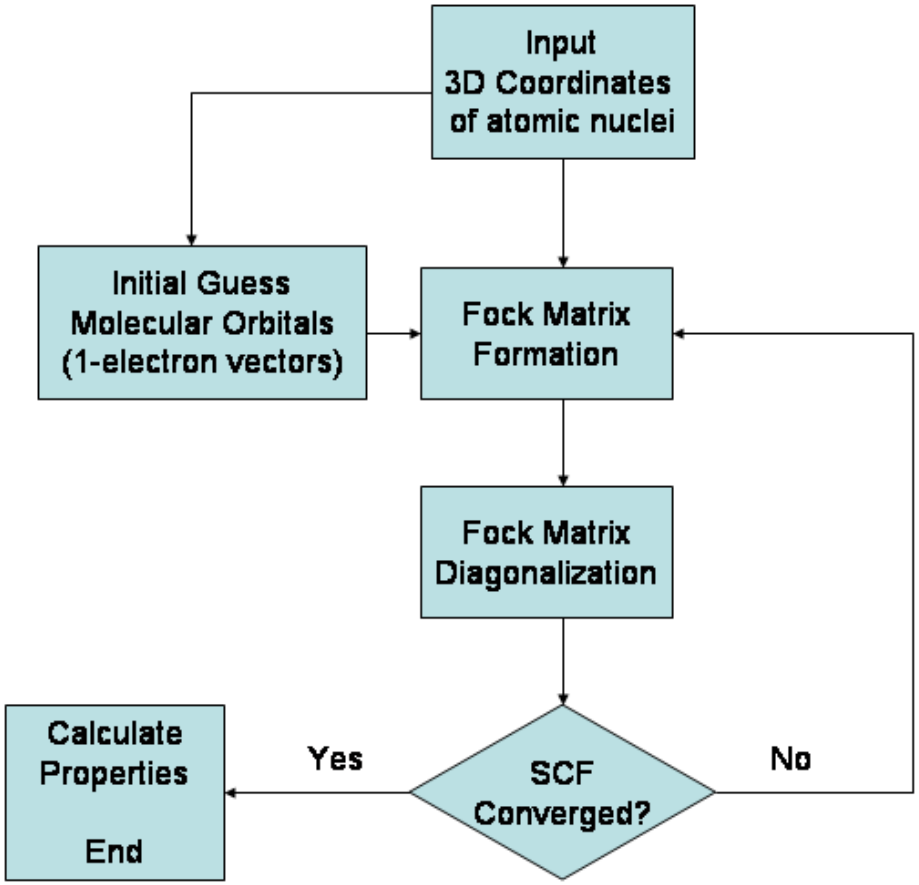
Born-Oppenheimer

* Due to the high ratio between the mass of the nuclei and electrons the wave function can be broken to its electron and nuclear components:

$$\Psi = \psi_{electrons} \cdot \psi_{nuclear}$$

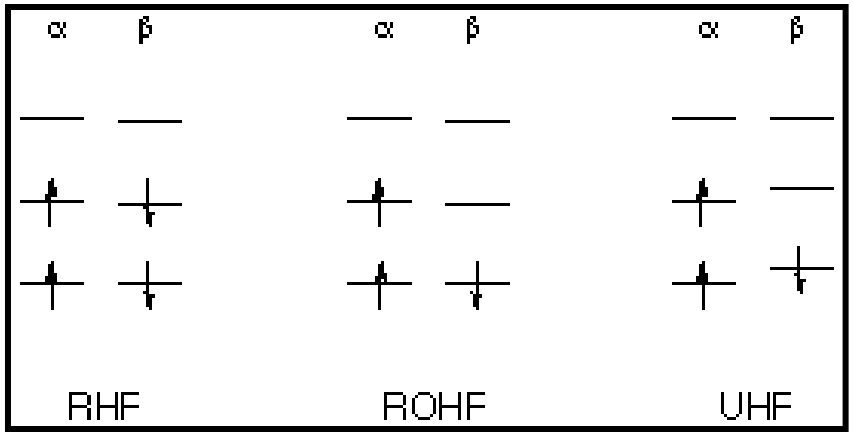
* First the electronic Schrödinger equation is solved with fixed nuclei.
* In the next step the Schrödinger equation for the nuclei is solved in the potential of the electrons.

Self consistent field (SCF) Solution to HF



RHF/ROHF/UHF

* RHF Restricted HF: allows only for calculating closed shell systems, multiplicity =1.
* ROHF Restricted Open Shell HF: allows open shell calculations.
* UHF Unrestricted HF: allows open shell calculations, α and β have different spatial coordinates.



MO-LCAO

* Molecular orbitals are approximated as linear combinations of atomic orbitals.

Molecular orbital i

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n$$

Atomic orbital n

or

$$\phi_i = \sum_r c_{ri}\chi_r$$

* The atomic orbitals are expressed as a basis set of functions.
* The c coefficients are determined throughout the HF calculation.

Chemical precision

* In this lab we report precisions of 0.1%
* Energy: ~ 10KJ/mole ⟹ ΔE=0.01 KJ/mole
  ~ 0.01 hartree ⟹ ΔE=10^{-5} hartree
  ~ 1 eV ⟹ ΔE=0.001 eV
  ~ 10 Kcal/mole ⟹ ΔE=0.01 Kcal/mole

* Length: ~ 1 Å ⟹ Δl=0.001 Å
* Angle: ~ 1-10° ⟹ Δθ= 0.01°
* Charge: ~1e ⟹ Δq=0.001 e
* Dipole: ~1Debye ⟹ Δμ=0.001 Debye

* The convergence parameters are the same