# Code YOCKO

geometrY Hartree-FOCK Optimisation

By Lauriane Pierrot Deseilligny & Côme Cattin

The problem

- Find a way to optimise geometry of simple compounds

- *Via* common quantum chemistry techniques
  - Density Functional Theory (DFT)
  - **Hartree Fock**

  (CG < MM < MM polarisable < semi-empiriques < HF < DFT < post Hartree-Fock)

- Ultimate goal: compare geometry criteria with experimental
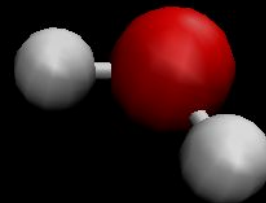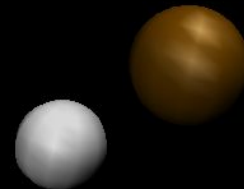
Hartree Fock method

$$\mathcal{H}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) = \mathcal{E}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\})$$

$$\boxed{\mathcal{H} = \mathcal{T}_n + \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee} + \mathcal{V}_{nn}}$$

- Slater Type Orbital (STO) = Gaussian Type Orbital
- Wave function = Slater determinant

$$\Psi_{HF}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- Minimise HF energy

$$\boxed{E_{HF} = \langle \Psi_{HF} | \mathcal{H}_{elec} + \mathcal{V}_{nn} | \Psi_{HF} \rangle} \quad \text{where} \quad \mathcal{H}_{elec} = \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee}$$

Derivative	Property
$\partial E/\partial R_i$	Forces on the nuclei (i component); equilibrium geometry; transition state geometry; rotational contributions to the molecular entropy
$\partial E/\partial F_\alpha$	Dipole moment component
$\partial E/\partial G_k$	Generalized multipole moment corresponding to the k wave vector component of an external electric field[2]
$\partial^2 E/\partial R_i \partial R_j$	Force constant matrix component; harmonic vibrational frequencies; signature of a stationary point on the energy hypersurface (minimum, first order saddle point, etc.)
$\partial^2 E/\partial R_i \partial F_\alpha$	Infrared intensities (in the doubly harmonic approximation)
$\partial^2 E/\partial F_\alpha \partial F_\beta$	(Static) dipole polarizability component
$\partial^2 E/\partial G_k \partial G_{k'}$	Generalized multipole polarizability (k, k' component)[2]
$\partial^2 E/\partial B_\alpha \partial u_{j\beta}$	NMR shielding constants
$\partial^2 E/\partial u_{k\alpha} \partial u_{j\beta}$	Indirect NMR spin–spin coupling constants
$\partial^2 E/\partial B_\alpha \partial B_\beta$	(Static) dipole magnetizability ($\alpha\beta$ component)
$\partial^2 E/\partial F_\alpha \partial B_\beta$	Optical rotatory power and (optical) circular dichroism
$\partial^3 E/\partial R_i \partial R_j \partial R_k$	Cubic force constants; cubic anharmonic corrections to vibrational frequencies
$\partial^3 E/\partial F_\alpha \partial F_\beta \partial F_\gamma$	(Static) dipole hyperpolarizability
$\partial^3 E/\partial R_i \partial F_\alpha \partial F_\beta$	Polarizability derivatives; Raman intensities in the harmonic approximation (at low excitation frequency)
$\partial^3 E/\partial R_i \partial B_\alpha \partial u_{j\beta}$	NMR chemical shift derivatives with respect to molecular geometry
$\partial^3 E/\partial R_i \partial R_j \partial F_\alpha$	Electrical anharmonicity; intensity of infrared transitions forbidden in the harmonic approximation (mechanical anharmonicity also has a contribution)
$\partial^4 E/\partial R_i \partial R_j \partial R_k \partial R_l$	Quartic force constants; quartic anharmonic corrections to vibrational frequencies
$\partial^4 E/\partial Q_i{}^2 \partial Q_j{}^2$	Dominant quartic anharmonicity corrections to vibrational frequencies
$\partial^3 E/\partial R_i \partial F_\alpha \partial B_\beta$	Vibrational optical rotatory power
$\partial^4 E/\partial R_i \partial R_j \partial R_k \partial R_l$	Quartic force constants; quartic anharmonic corrections to vibrational frequencies
$\partial^4 E/\partial Q_i{}^2 \partial Q_j{}^2$	Dominant quartic anharmonicity corrections to vibrational frequencies

Abbreviations: R_i is a general nuclear coordinate, Q_j is a normal coordinate, F_α is the α component of the external homogeneous electric field, B_α is the α component of the external magnetic induction (field), G_k is the k component of a spatially modulated electric field Ge^{ikr}, and $u_{j\beta}$ is the β component of the magnetic moment of nucleus j.

H_{elec} 's eigen vectors: Molecular orbitals ϕ (1,...,n electrons: 1 electrons vs the n-1 left)

$$H_{elec} \phi = \varepsilon \phi$$

Molecules= atoms and their electrons : Atomic orbitals

LCAO : "chemical interpretation"

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

Pb if dimension = ∞ : "Solution"= truncate the AO basis

$$\hat{H}_e = \sum_i \hat{h}_1(\vec{x}_i) + \sum_{i,j} \hat{h}_2(\vec{x}_i, \vec{x}_j)$$ $\hat{H}_e \, \phi = \varepsilon \phi$ becomes "SCF" convergence FC= ε SC
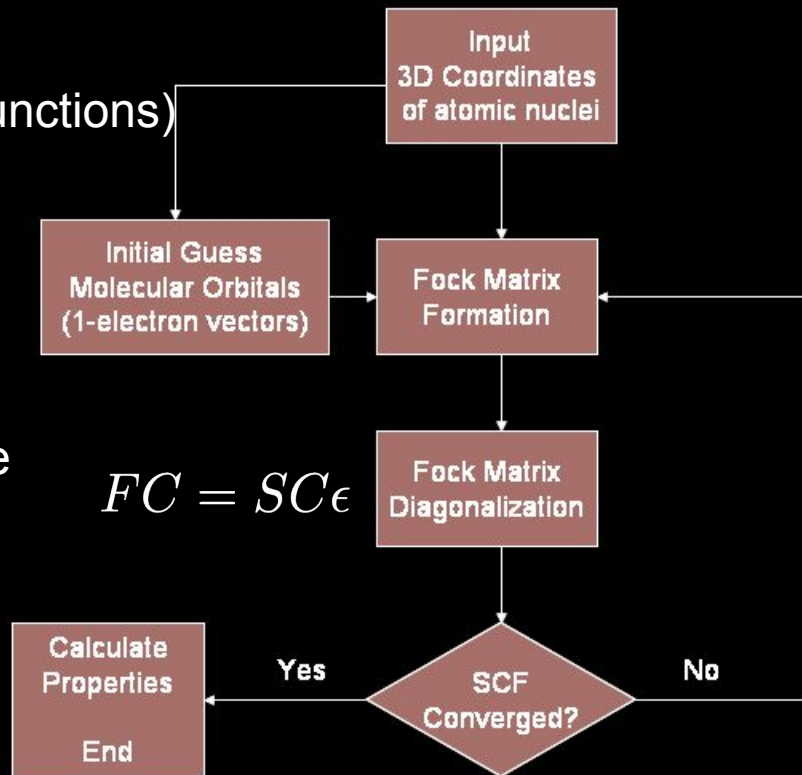
For the curious ones…

$$\hat{F} = \sum_{i=1}^{N} \sum_{m,n}^{N_b} c_{mi}^\star c_{ni} \langle \chi_m | \hat{h}_1 | \chi_n \rangle + \frac{1}{2} \sum_{i,j}^{N} \sum_{m,np,q}^{N_b} c_{mi}^\star c_{pi} c_{nj}^\star c_{qj} \left[\langle \chi_m \chi_p | \hat{h}_2 | \chi_n \chi_q \rangle - \langle \chi_p \chi_m | \hat{h}_2 | \chi_n \chi_q \rangle \right]$$

$$- \sum_i^N \varepsilon_i \left[\sum_{n,m}^{N_b} c_{mi}^\star c_{ni} \langle \chi_m | \chi_n \rangle - 1 \right]$$

Computational

- Integral (for non-gaussian basis functions)

- Eigenvalue problem

- Self Consistent Field convergence

$$FC = SC\epsilon$$

Input
3D Coordinates
of atomic nuclei

Initial Guess
Molecular Orbitals
(1-electron vectors)

Fock Matrix
Formation

Fock Matrix
Diagonalization

SCF
Converged?

Yes

No

Calculate
Properties

End

DFT: ρ, $\nabla\rho$, $\nabla^2\rho$

Wavefunction, ket, basis, matrix (3N-6) $\rightarrow$ functional equations on electronic density ρ (3 dim)

- More efficient, more elegant

- Bigger system

- But more empirical, various functional possibilities,
  cf. Jacob's scale :)
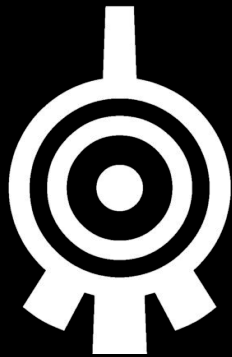
Soon available

github.com/sequoia-dev/YOCKO