by Roman Čurík

Roothaan equations

Introduction of 1-electron basis set $b_\alpha(\vec{r}) = \langle \vec{r} | b_\alpha \rangle$ $\{b_\alpha\}_{\alpha=1}^{K}$

$$\varphi_i(\vec{r}) = \sum_\alpha c_{\alpha i}\, b_\alpha(\vec{r})$$

$$\langle \vec{r} | \varphi_i \rangle = \sum_\alpha c_{\alpha i} \langle \vec{r} | b_\alpha \rangle$$

Hartree-Fock equations

$$(\hat{h} + \hat{J} - \hat{K}) | \varphi_i \rangle = \varepsilon_i | \varphi_i \rangle$$

$\langle b_\alpha |$ /

$$\sum_\beta c_{\beta i} (\hat{h} + \hat{J} - \hat{K}) | b_\beta \rangle = \varepsilon_i \sum_\beta c_{\beta i} | b_\beta \rangle$$

$$\sum_\beta (h_{\alpha\beta} + J_{\alpha\beta} - K_{\alpha\beta}) c_{\beta i} = \sum_\beta S_{\alpha\beta} c_{\beta i} \varepsilon_i$$

In matrix form:

$$(h + J - K)\, C = S C \varepsilon$$

Fock matrix

$$F C = S C \varepsilon$$

C = (different eigenstates i; α; $\ldots$)

overlap matrix

Generalized eigenvalue problem - typical for non-orthogonal basis

Orthogonal basis: $S_{\alpha\beta} \to \delta_{\alpha\beta}$ → ordinary eigenvalue problem

How to solve the generalized eigenvalue prob.?

A) Naive

$F C = S C \varepsilon$ (after $S^{-1} F C = C \varepsilon$, non-Hermitian)

$$S^{-1/2} F S^{-1/2} S^{1/2} C = S^{1/2} C \varepsilon$$

$$\bar{F}\, \bar{C} = \bar{C} \varepsilon$$

ordinary eigenvalue problem gives the same orbital energies

then

$$C = S^{-1/2} \bar{C}$$

S is Hermitian, positive definite matrix. Numerics may be problematic for nearly + linear-dependent basis $|b_\alpha\rangle$ → lowest eigenvalues of $S_{\alpha\beta}$ are close to zero (10^{-15}) and even negative ($\sim -10^{-15}$)

B.) More stable Cholesky factorization

Symmetric, positive-definite matrix S can be factorized to (LU decomposition)

$$S = LL^+$$

(L is lower-diagonal)
(reduced "square root" of S)

$$F C = L L^+ C \varepsilon$$

$$F (L^+)^{-1} L^+ C = L L^+ C \varepsilon$$

$$L^{-1} F (L^+)^{-1} L^+ C = L^+ C \varepsilon$$

$$\bar{F}\ \bar{C} = \bar{C}\ \varepsilon$$

H ... Hermitian
$\Downarrow$
H^{-1} ... Hermitian

$$\left[L^{-1} F (L^+)^{-1} \right]^+ = L^{-1} F (L^+)^{-1}$$

is $[\,]^{-1}$ and $[\,]^+$ interchangable?

$$L^{-1} L = 1 \Rightarrow L^+ \underbrace{(L^{-1})^+}_{(L^+)^{-1}} = 1$$

CASE 1: (OPEN-SHELL) UHF $\hat{K}$ operator is constructed from spin-orbitals with an identical spin and acts only on spinorbitals with the same spin

We get coupled set of 2 equations:

$$\begin{aligned} (h + J - K^\alpha)\, C^\alpha &= S\, C^\alpha \varepsilon^\alpha \\ (h + J - K^\beta)\, C^\beta &= S\, C^\beta \varepsilon^\beta \end{aligned}$$

Pople-Nesbet equations

$$J_{\alpha\beta} = \sum_{\gamma,\delta}^{K} \sum_{i=1}^{N^\alpha} C^{\alpha *}_{\gamma i} C^{\alpha}_{\delta i} [\alpha\beta|\gamma\delta] + \sum_{\gamma,\delta} \sum_{i=1}^{N^\beta} C^{\beta *}_{\gamma i} C^{\beta}_{\delta i} [\alpha\beta|\gamma\delta]$$

$$K^\alpha_{\alpha\beta} = \sum_{\gamma,\delta}^{K} \sum_{i=1}^{N^\alpha} C^{\alpha *}_{\gamma i} C^{\alpha}_{\delta i} [\alpha\delta|\gamma\beta] \; ; \; K^\beta_{\alpha\beta} = \sum_{\gamma,\delta}^{K} \sum_{i=1}^{N_\beta} C^{\beta *}_{\gamma i} C^{\beta}_{\delta i} [\alpha\delta|\gamma\beta]$$

CASE 2: (CLOSED-SHELL) RHF We restrict spatial components of α and β electrons to be equal.

Typical run of HF codes

1.) For fixed geometry and fixed basis set $\{b_\alpha\}_{\alpha=1}^{K}$ ←

compute 1-electron and 2-electron integrals:

1 electron: $h_{\alpha\beta} = \langle \alpha | h | \beta \rangle$; 2-electron: $I_{\alpha\rho\gamma\delta} = [\alpha\rho | \gamma\delta]$ (four-index)

2.) Use a semiempirical method to guess $C_{\alpha i}$; IF you lack one, use $C_{\alpha i} = \delta_{\alpha i}$

3.) Build the Fock matrix $F = h + J - K$ ←

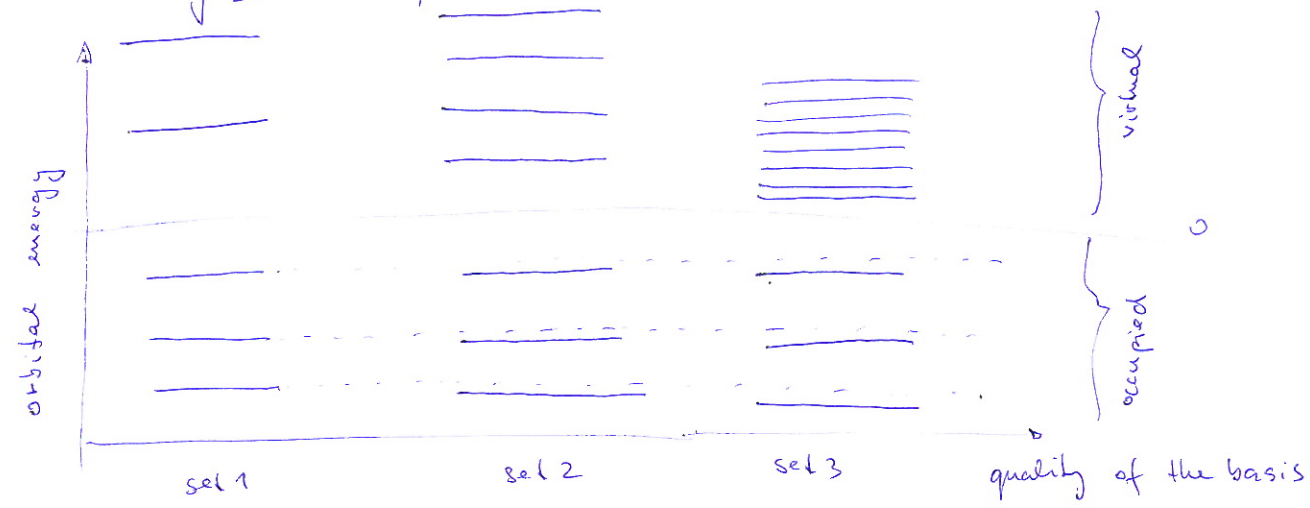
4.) Diagonalize, obtain ε_i and $C_{\alpha i}$

5.) Convergence test, ΔE_0^{it}, $\Delta D_{\alpha\rho}^{it}$ — not converged

6.) During geometry optimization you change the geometry and start from 1.)

Notes on the orbitals

- Dimension of Roothaan equations is K → the dimension of the basis
- Diagonalization of Fock matrix will give K orbitals and K energies
- J and K matrices are constructed from the first N spinorbitals →
  → occupied spinorbitals or doubly occupied orbitals
- Remaining 2K − N spinorbitals are called virtual orbitals



→ 2 sets of Pople-Nesbet equations become identical.

$$(h + J - K)\,C = S\,C\,\varepsilon$$

Roothaan 1951
Clemens

$$J_{\nu\beta} = 2 \sum_{\gamma,\delta}^{K} \sum_{i=1}^{N/2} C^{*}_{\gamma i}\, C_{\delta i}\, [\alpha\beta\,|\,\gamma\delta]$$

The factor "2" is sometimes put into the Roothaan eq.

CASE 3: (OPEN-SHELL) ROHF

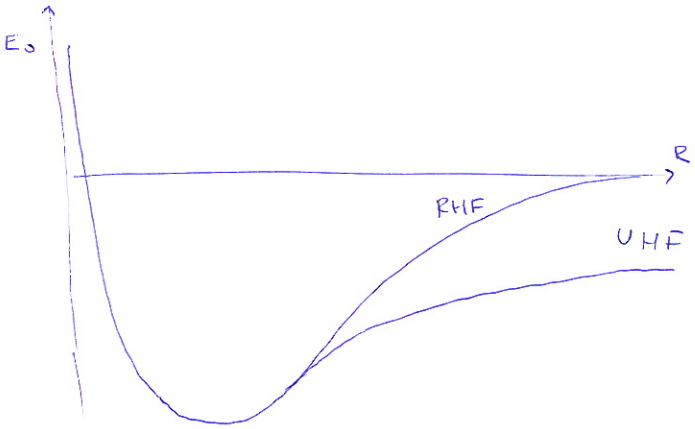
closed-shell part is kept restricted. (Singly) occupied open-shell part is then forced to be orthogonal to the doubly-occupied closed-shell part. Roothaan 1960.

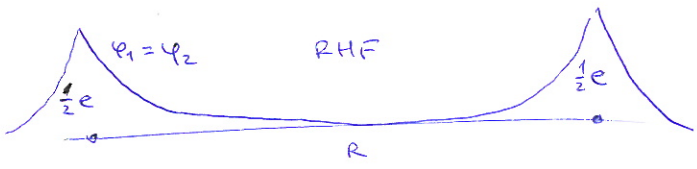
- Not so simple, theory must be built with the orthogonality constraints $N/2 + 1$ spinorbitals.

Example RHF vs UHF and H_2 dissociation

In RHF approach the asymptotic energy contains self-repulsion of half-an-electron with itself, twice

$$\varepsilon_0 = 2\langle\varphi_1|h|\varphi_1\rangle + \tfrac{1}{2}[\varphi_1\varphi_1|\varphi_1\varphi_1]$$





For closed shell UHF there is always one RHF solution that is valid UHF solution.