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Roothaan equations

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

$$\psi_i(\vec{r}) = \sum_{\alpha} c_{\alpha i} b_{\alpha}(\vec{r}) \quad \{b_{\alpha}\}_{\alpha=1}^K$$

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

Hartree-Fock equations

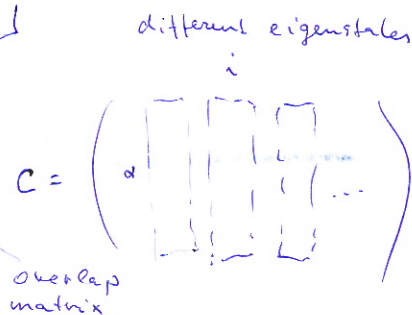
$$(\hat{h} + \hat{J} - \hat{K}) |\psi_i\rangle = \epsilon_i |\psi_i\rangle$$

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

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

In matrix form:

$$\left( \begin{array}{l} (\hat{h} + \hat{J} - \hat{K}) \mathbf{c} = \mathbf{S} \mathbf{c} \epsilon \\ \mathbf{F} \mathbf{c} = \mathbf{S} \mathbf{c} \epsilon \end{array} \right)$$



overlap matrix

Generalized eigenvalue problem - typical for non-orthogonal basis

orthogonal basis:  $S_{\alpha\beta} \rightarrow \delta_{\alpha\beta} \rightarrow$  ordinary eigenvalue problem

How to solve the generalized eigenvalue prob.?

A) Naive

$$\mathbf{F} \cdot \mathbf{c} = \mathbf{S} \mathbf{c} \epsilon$$

(after  $\mathbf{S}^{-1} \mathbf{F} \mathbf{c} = \epsilon \mathbf{c}$ , non-Hermitian)

$$\mathbf{S}^{-1/2} \mathbf{F} \mathbf{S}^{-1/2} \mathbf{S}^{1/2} \mathbf{c} = \mathbf{S}^{1/2} \mathbf{c} \epsilon$$

$$\left( \begin{array}{l} \bar{\mathbf{F}} \\ \bar{\mathbf{c}} \end{array} \right) = \bar{\mathbf{c}} \epsilon$$

ordinary eigenvalue problem gives the same orbital energies

then

$$\left( \mathbf{c} = \mathbf{S}^{-1/2} \bar{\mathbf{c}} \right)$$

S is Hermitian, positive definite matrix. Numerics may be problematic for nearly linear-dependent basis  $|b_{\alpha}\rangle \rightarrow$  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)

$$S = LL^T \quad (L \text{ is lower-diagonal})$$

(reduced square root of  $S$ )

$$Fc = LL^T c \epsilon$$

$$F(L^T)^{-1}L^T c = LL^T c \epsilon$$

$$\underbrace{L^{-1}F(L^T)^{-1}}_{\bar{F}} \underbrace{L^T c}_{\bar{c}} = \underbrace{L^T c \epsilon}_{\bar{\epsilon}}$$

$$\boxed{\bar{F} \bar{c} = \bar{\epsilon}}$$

$H \dots$  Hermitian  
 $\downarrow$   
 $H^{-1} \dots$  Hermitian

$$[L^{-1}F(L^T)^{-1}]^+ = L^{-1}F(L^T)^{-1}$$

is  $[J]^{-1}$  and  $[J]^+$  interchangeable?

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

$(L^T)^{-1}$

CASE 1: (OPEN-SHELL) UHF

$\hat{K}^{\uparrow}$  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:

$$\begin{cases} (h + J - K^{\alpha}) c^{\alpha} = S c^{\alpha} \epsilon^{\alpha} \\ (h + J - K^{\beta}) c^{\beta} = S c^{\beta} \epsilon^{\beta} \end{cases}$$

Pople-Nesbet equations

$$J_{\alpha\beta} = \sum_{\gamma\delta}^k \sum_{i=1}^{N_{\alpha}} C_{\gamma i}^{\alpha*} C_{\delta i}^{\alpha} [\alpha\beta | \gamma\delta] + \sum_{\gamma\delta}^{N_{\beta}} \sum_{i=1}^{N_{\beta}} C_{\gamma i}^{\beta*} C_{\delta i}^{\beta} [\alpha\beta | \gamma\delta]$$

$$K_{\alpha\beta}^{\alpha} = \sum_{\gamma\delta}^k \sum_{i=1}^{N_{\alpha}} C_{\gamma i}^{\alpha*} C_{\delta i}^{\alpha} [\alpha\delta | \gamma\beta] \quad ; \quad K_{\alpha\beta}^{\beta} = \sum_{\gamma\delta}^k \sum_{i=1}^{N_{\beta}} C_{\gamma i}^{\beta*} C_{\delta i}^{\beta} [\alpha\delta | \gamma\beta]$$

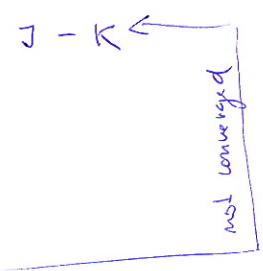
CASE 2: (CLOSED-SHELL) RHF

We restrict spatial components

of  $\uparrow$  and  $\downarrow$  electrons to be equal.

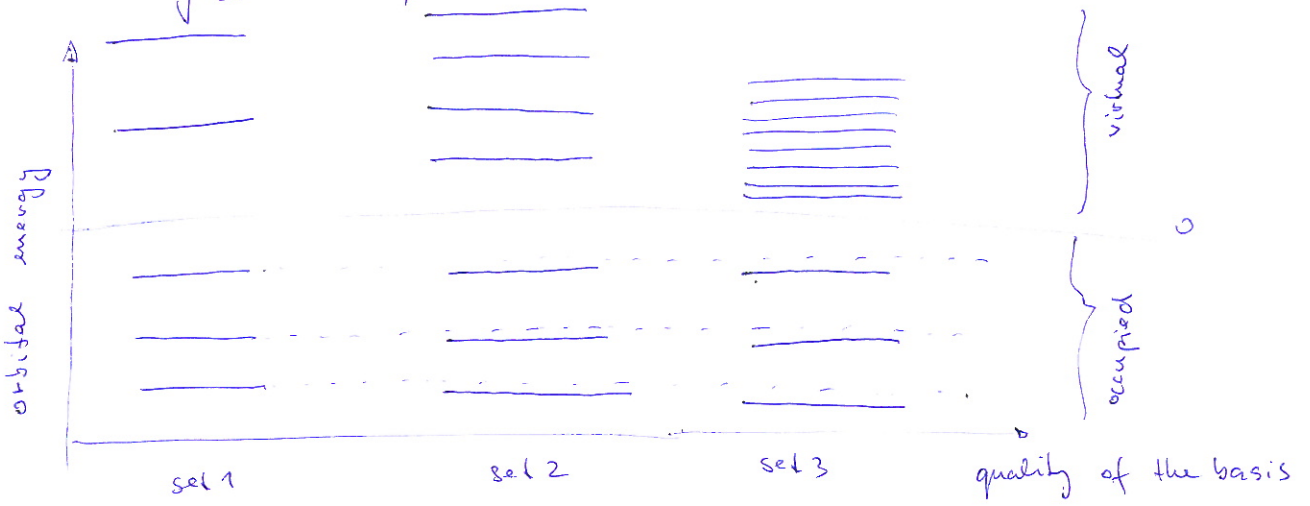
Typical run of HF codes

- 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:  $J_{\alpha\beta\gamma\delta} = \langle \alpha\beta | \gamma\delta \rangle$  (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  $\epsilon_i$  and  $c_{\alpha i}$
- 5.) Convergence test,  $\Delta E_0^{it}$ ,  $\Delta D_{\alpha\beta}^{it}$
- 6.) During geometry optimization you change the geometry and start from 1.)



Notes on the orbitals

- Dimension of Roothaan equations is  $K \rightarrow$  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  $\rightarrow$  occupied spinorbitals or doubly-occupied orbitals
- Remaining  $2K - N$  spinorbitals are called virtual orbitals



→ 2 sets of Pople-Nesbet equations become identical.

$$(h + J - K) c = S c \epsilon$$

Roothaan 1957  
Clemens

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

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

CASE 3: (OPEN-SHELL) ROHF

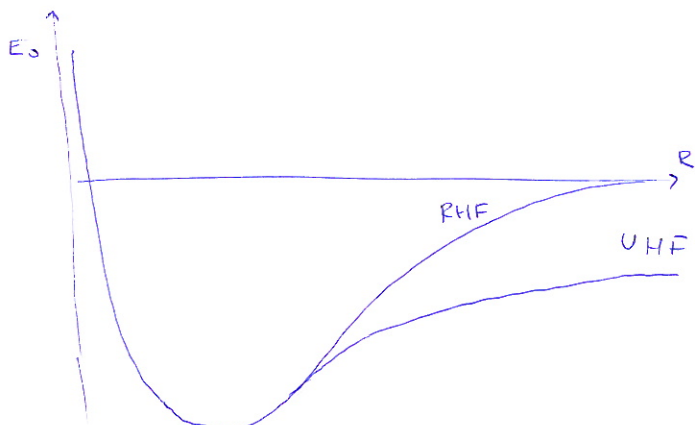
closed-shell part is kept restricted, (singly) occupied

open-shell part is then forced to be orthogonal to the doubly-occupied closed-shell part. Roothaan 1960.

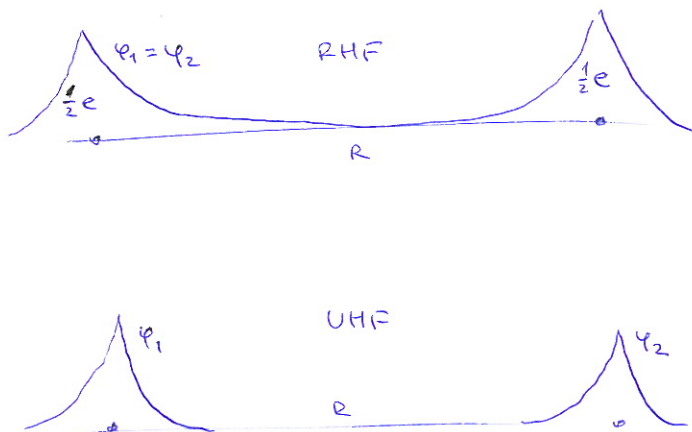
- Not so simple, theory must be built with the orthogonality constraints.  $N/2 + 1$  spinorbitals.

Example RHF vs. UHF and  $H_2$  dissociation

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



$$E_0 = 2 \langle \varphi_1 | h | \varphi_1 \rangle + \frac{1}{2} [\varphi_1 \varphi_1 | \varphi_1 \varphi_1]$$



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