Unrestricted HF (UHF)

How to model open-shell systems?

- RHF is made to describe closed-shell systems and we have used restricted spin orbitals:

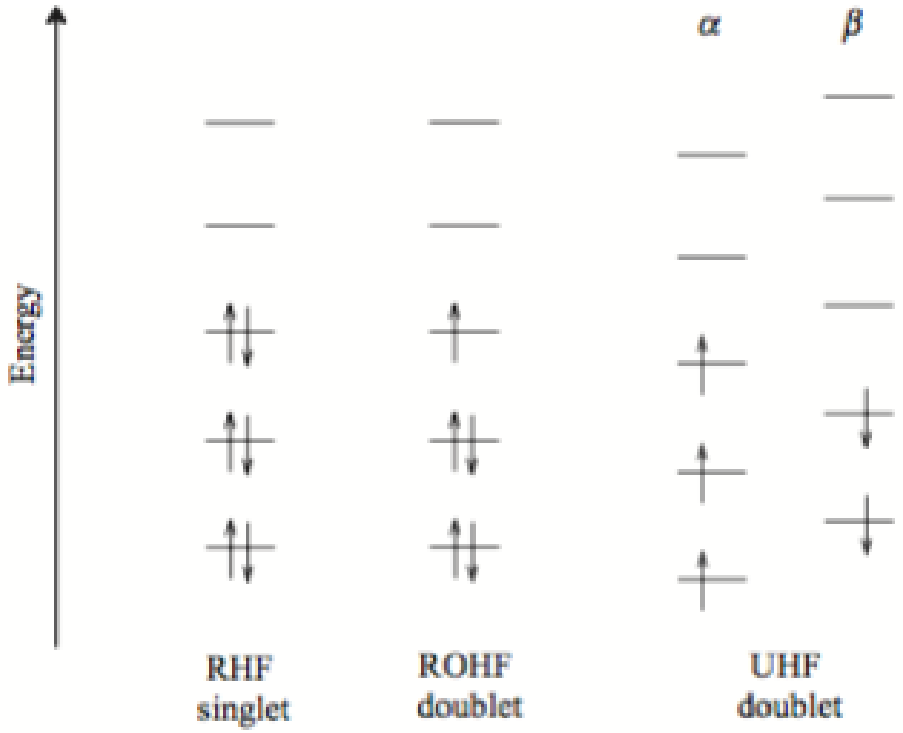
$$\chi_i^{\text{RHF}}(\boldsymbol{x}) = \begin{cases} \alpha(\omega)\,\psi_i(\boldsymbol{r}) \\ \beta(\omega)\,\psi_i(\boldsymbol{r}) \end{cases}$$

- It does **not** described open-shell systems
- For open-shell systems we can use unrestricted spin orbitals

$$\chi_i^{\text{UHF}}(\boldsymbol{x}) = \begin{cases} \alpha(\omega)\,\psi_i^{\alpha}(\boldsymbol{r}) \\ \beta(\omega)\,\psi_i^{\beta}(\boldsymbol{r}) \end{cases}$$

- RHF = Restricted Hartree-Fock $\leftrightarrow$ Roothaan-Hall equations
- UHF = Unrestricted Hartree-Fock $\leftrightarrow$ Pople-Nesbet equations
- Restricted Open-shell Hartree-Fock (ROHF) do exist but we won't talk about it

RHF, ROHF and UHF



- RHF = Restricted Hartree-Fock
- UHF = Unrestricted Hartree-Fock
- ROHF = Restricted Open-shell Hartree-Fock

The UHF wave function

Slater determinants for UHF

$$\Psi_{\text{UHF}} = \underbrace{\frac{1}{\sqrt{N^\alpha!}} \begin{vmatrix} \psi_1^\alpha(\boldsymbol{r}_1) & \cdots & \psi_{N^\alpha}^\alpha(\boldsymbol{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_1^\alpha(\boldsymbol{r}_{N^\alpha}) & \cdots & \psi_{N^\alpha}^\alpha(\boldsymbol{r}_{N^\alpha}) \end{vmatrix}}_{\Psi^\alpha(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{N^\alpha})} \underbrace{\frac{1}{\sqrt{N^\beta!}} \begin{vmatrix} \psi_1^\beta(\boldsymbol{r}_{N^\alpha+1}) & \cdots & \psi_{N^\beta}^\beta(\boldsymbol{r}_{N^\alpha+1}) \\ \vdots & \ddots & \vdots \\ \psi_1^\beta(\boldsymbol{r}_N) & \cdots & \psi_{N^\beta}^\beta(\boldsymbol{r}_N) \end{vmatrix}}_{\Psi^\beta(\boldsymbol{r}_{N^\alpha+1},\ldots,\boldsymbol{r}_N)}$$

- The UHF wave function is a product of two determinants
  - One for the spin-up electrons $\Psi^\alpha(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{N^\alpha})$
  - One for the spin-down electrons $\Psi^\beta(\boldsymbol{r}_{N^\alpha+1},\ldots,\boldsymbol{r}_N)$
- The Pauli exclusion principle only requires the wave function to be antisymmetric wrt the exchange of two same-spin electrons

Unrestricted Hartree-Fock Equations

UHF equations for unrestricted spin orbitals

To minimize the UHF energy, the unrestricted spin orbitals must be eigenvalues of the α and β Fock operators:

$$\boxed{f^{\alpha}(1)\,\psi_j^{\alpha}(1) = \varepsilon_j^{\alpha}\,\psi_j^{\alpha}(1)} \qquad \boxed{f^{\beta}(1)\,\psi_j^{\beta}(1) = \varepsilon_j^{\beta}\,\psi_j^{\beta}(1)}$$

where

$$f^{\alpha}(1) = h(1) + \sum_i^{N^{\alpha}} [J_i^{\alpha}(1) - K_i^{\alpha}(1)] + \sum_i^{N^{\beta}} J_i^{\beta}(1)$$

The Coulomb and Exchange operators are

$$J_i^{\alpha}(1) = \int \psi_i^{\alpha}(2) r_{12}^{-1} \psi_i^{\alpha}(2) d\boldsymbol{r}_2 \quad K_i^{\alpha}(1)\psi_j^{\alpha}(1) = \left[\int \psi_i^{\alpha}(2) r_{12}^{-1} \psi_j^{\alpha}(2) d\boldsymbol{r}_2\right] \psi_i^{\alpha}(1)$$

Unrestricted Hartree-Fock Equations (Take 2)

UHF energy

The UHF energy is composed by three contributions:

$$E_{\text{UHF}} = E^{\alpha\alpha}_{\text{UHF}} + E^{\beta\beta}_{\text{UHF}} + E^{\alpha\beta}_{\text{UHF}}$$

which yields

$$\boxed{E_{\text{UHF}} = \sum_{i}^{N^\alpha} h_i^\alpha + \frac{1}{2}\sum_{ij}^{N^\alpha}(J_{ij}^{\alpha\alpha} - K_{ij}^{\alpha\alpha}) + \sum_{i}^{N^\beta} h_i^\beta + \frac{1}{2}\sum_{ij}^{N^\beta}(J_{ij}^{\beta\beta} - K_{ij}^{\beta\beta}) + \sum_{i}^{N^\alpha}\sum_{j}^{N^\beta} J_{ij}^{\alpha\beta}}$$

The matrix elements are given by

$$h_i^\sigma = \langle \psi_i^\sigma | h | \psi_i^\sigma \rangle \qquad J_{ij}^{\sigma\sigma'} = \langle \psi_i^\sigma \psi_j^{\sigma'} | \psi_i^\sigma \psi_j^{\sigma'} \rangle \qquad K_{ij}^{\sigma\sigma} = \langle \psi_i^\sigma \psi_j^\sigma | \psi_j^\sigma \psi_j^\sigma \rangle$$

Note that $K_{ij}^{\alpha\beta} = 0 \Leftrightarrow$ there is no exchange between opposite-spin electrons

UHF energy of the Li atom

Problem

"Write down the UHF wave function of the doublet state of the lithium atom, and find its energy."

UHF energy of the Li atom

Problem

"Write down the UHF wave function of the doublet state of the lithium atom, and find its energy."

Solution

The UHF wave function for the doublet state of Li is

$$\Psi_{\text{UHF}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1^\alpha(\boldsymbol{r}_1) & \psi_2^\alpha(\boldsymbol{r}_1) \\ \psi_1^\alpha(\boldsymbol{r}_2) & \psi_2^\alpha(\boldsymbol{r}_2) \end{vmatrix} \psi_1^\beta(\boldsymbol{r}_3)$$

while the corresponding energy is

$$E_{\text{UHF}} = h_1^\alpha + h_1^\beta + h_2^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$$

The Pople-Nesbet Equations

Expansion of the unrestricted spin orbitals in a basis

$$\psi_i^\alpha(\boldsymbol{r}) = \sum_{\mu=1}^{K} C_{\mu i}^\alpha \, \phi_\mu(\boldsymbol{r}) \qquad \psi_i^\beta(\boldsymbol{r}) = \sum_{\mu=1}^{K} C_{\mu i}^\beta \, \phi_\mu(\boldsymbol{r})$$

The Pople-Nesbet equations

$$\mathbf{F}^\alpha \, \mathbf{C}^\alpha = \mathbf{S} \, \mathbf{C}^\alpha \, \mathbf{E}^\alpha \qquad \mathbf{F}^\beta \, \mathbf{C}^\beta = \mathbf{S} \, \mathbf{C}^\beta \, \mathbf{E}^\beta$$

$$F_{\mu\nu}^\alpha = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^\alpha [(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_{\lambda\sigma} P_{\lambda\sigma}^\beta (\mu\nu|\sigma\lambda)$$

$$F_{\mu\nu}^\beta = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^\beta [(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_{\lambda\sigma} P_{\lambda\sigma}^\alpha (\mu\nu|\sigma\lambda)$$

$\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ are both functions of $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ $\Rightarrow$ There's a coupling between α and β MOs!

Unrestricted Density Matrices

Spin-up and spin-down density matrices

$$P^{\alpha}_{\mu\nu} = \sum_{i=1}^{N^{\alpha}} C^{\alpha}_{\mu} C^{\alpha}_{\nu i} \quad \Leftrightarrow \quad \mathbf{P}^{\alpha}$$

$$P^{\beta}_{\mu\nu} = \sum_{i=1}^{N^{\beta}} C^{\beta}_{\mu i} C^{\beta}_{\nu i} \quad \Leftrightarrow \quad \mathbf{P}^{\beta}$$

Properties of the density ($\sigma = \alpha$ or β)

$$\rho^{\sigma}(\boldsymbol{r}) = \sum_{\mu\nu} P^{\sigma}_{\mu\nu} \phi_{\mu}(\boldsymbol{r}) \phi_{\nu}(\boldsymbol{r})$$

$$\int \rho^{\sigma}(\boldsymbol{r}) d\boldsymbol{r} = N^{\sigma}$$

Total and Spin density matrices

$$\underbrace{\mathbf{P}^{\mathrm{T}}}_{\text{Charge density}} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta}$$

$$\underbrace{\mathbf{P}^{\mathrm{S}}}_{\text{Spin density}} = \mathbf{P}^{\alpha} - \mathbf{P}^{\beta}$$

How to perform a UHF calculation in practice?

The SCF algorithm

1. Specify molecule $\{\boldsymbol{R}_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$ (same as RHF)
2. Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle\mu\nu|\lambda\sigma\rangle$ (same as RHF)
3. Diagonalize $\mathbf{S}$ and compute $\mathbf{X}$ (same as RHF)
4. Obtain guess density matrix for $\mathbf{P}^\alpha$ and $\mathbf{P}^\beta$
   - 1a. Calculate $\mathbf{G}^\alpha$ and then $\mathbf{F}^\alpha = \mathbf{H} + \mathbf{G}^\alpha$
   - 1b. Calculate $\mathbf{G}^\beta$ and then $\mathbf{F}^\beta = \mathbf{H} + \mathbf{G}^\beta$
   - 2. Compute $(\mathbf{F}^\alpha)' = \mathbf{X}^\dagger \mathbf{F}^\alpha \mathbf{X}$ and $(\mathbf{F}^\beta)' = \mathbf{X}^\dagger \mathbf{F}^\beta \mathbf{X}$
   - 3a. Diagonalize $(\mathbf{F}^\alpha)'$ to obtain $(\mathbf{C}^\alpha)'$ and $\mathbf{E}^\alpha$
   - 3b. Diagonalize $(\mathbf{F}^\beta)'$ to obtain $(\mathbf{C}^\beta)'$ and $\mathbf{E}^\beta$
   - 4. Calculate $\mathbf{C}^\alpha = \mathbf{X}\,(\mathbf{C}^\alpha)'$ and $\mathbf{C}^\beta = \mathbf{X}\,(\mathbf{C}^\beta)'$
   - 5. Form the new new density matrix $\mathbf{P}^\alpha$ and $\mathbf{P}^\beta$, and compute $\mathbf{P}^\mathsf{T} = \mathbf{P}^\alpha + \mathbf{P}^\beta$
   - 6. Am I converged? If not go back to 1.
5. Calculate stuff that you want, like E_{UHF} for example

Congratulations!

You have survived Part II of Chem3208!

Next time, we will talk about

Electronic correlation methods