

Chem 3430 - Additional Notes on SCF (1)

$$\begin{array}{ccc} \phi_i = & \sum_{\alpha}^m c_{i\alpha} \chi_{\alpha} & \text{LCAO approx.} \\ \uparrow & \uparrow & \\ \text{MO} & \text{AO} & \end{array}$$

HF equations in AO basis set \equiv Roothaan eqs.

$$\underline{F} \cdot \underline{C} = \underline{S} \cdot \underline{C} \cdot \underline{\epsilon}$$

$$F_{\alpha\beta} = \langle \chi_{\alpha} | F | \chi_{\beta} \rangle - \text{Fock matrix}$$

$$S_{\alpha\beta} = \langle \chi_{\alpha} | \chi_{\beta} \rangle - \text{Overlap matrix}$$

$$D_{\gamma\delta} = \sum_j^{\text{occ MO}} c_{\gamma j} c_{\delta j} - \text{density matrix}$$

$$\underline{F} = \underline{h} + \underline{G} \underline{D}$$

↑ KE, nucl attr.

coul. + exch S's

Direct SCF

Single point

integrals to 10^{-6} accuracy

convg to 10^{-4} on E, ρ or 10^{-5} on E^-

Other jobs

use by default tight convg.

10^{-8} on ρ

conv = N, converge density matrix to 10^{-N} (2)

maxcycle = N

Lots of other options to address convergence in difficult cases.

guess = read, reads orbitals from checkpoint file

Comments on symmetry

By default Fock matrix is symmetrized

By default the density matrix is not symmetrized.

⇒ Electronic wavefunction can break symmetry

This could not happen if G03 used symmetry-adapted basis functions!

Even when G03 uses symmetry, it is using at most the symmetry of the largest abelian subgroup.

There are lots of keywords dealing with symmetry
Can turn off totally, or remove certain symmetry elements.

Types of HF

- RHF $\rightarrow |a\bar{a} b\bar{b} \dots n\bar{n}|$, closed-shell
- VHF $\rightarrow |a\bar{a}' b\bar{b}' \dots n\bar{n}'|$, closed- or open shell
- ROHF $\rightarrow |a\bar{a} b\bar{b} \dots n|$, open-shell

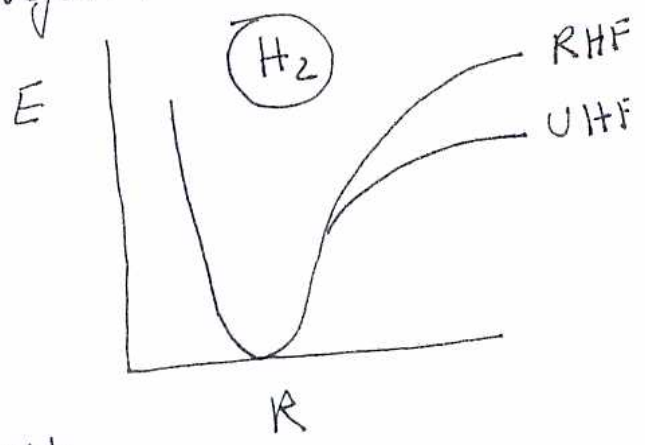
Li atom $\psi^{\text{ROHF}} = |1s \bar{1s} 2s|$

$\psi^{\text{OHF}} = |1s \bar{1s}' 2s|$

Easier to code OHF than ROHF and easier to code MP2 corrections for OHF wavefunction.

Symmetry-breaking OHF wavefunctions can be energetically below RHF wavefunction

Consider H_2 as described by a minimal basis set.



$$\left. \begin{aligned} \sigma_u &= 1s_A + 1s_B \\ \sigma_g &= 1s_A - 1s_B \end{aligned} \right\} \text{leaving out normalization}$$

$$\psi^{\text{RHF}} = |\sigma_g \bar{\sigma}_g|$$

$$\psi^{\text{OHF}} = |\sigma \bar{\sigma}'|$$

σ and σ' must be linear combinations of σ_g and σ_u

$$\begin{cases} \sigma = c\sigma_g + s\sigma_u \\ \sigma' = c\sigma_g - s\sigma_u \end{cases} \begin{cases} c = \cos\theta \\ s = \sin\theta \end{cases}$$

$$|\sigma \bar{\sigma}| = [c^2 \sigma_g^2 - s^2 \sigma_u^2] (\alpha\beta - \beta\alpha) \leftarrow \text{singlet}$$

$$- cs [\sigma_g \sigma_u - \sigma_u \sigma_g] (\alpha\beta + \beta\alpha) \leftarrow \text{triplet}$$

The price of recovering correlation in a single determinant, is that the triplet is mixed in.

$$\langle S^2 \rangle = 2S + 1$$

For a singlet $\langle S^2 \rangle = 0$

For the above UHF wavefunction $\langle S^2 \rangle > 0$

If $\langle S^2 \rangle \gtrsim 1.2$, results cannot be trusted.

Need a multiconfigurational method or DFT

Stable - checks for lower energy solutions

Stable = opt, checks and reoptimizes

** Certain types of instability invalidates frequency or MP2 calculations.