PROBLEMS

1. Helium Hartree-Fock

Wavefunction anzats:

$$\varphi(\vec{r}) = \sum_{p=1}^{4} C_p \chi_p(\vec{r}) \qquad \chi_p(\vec{r}) = e^{-\alpha_p r^2}$$

According to Thijssen, C_p satisfy

$$\boxed{\sum_{pq}\left(h_{pq} + \sum_{rs} C_r C_s Q_{prqs}\right) C_q = E' \sum_{pq} S_{pq} C_q}$$

We need h_{pq}, Q_{prqs} and S_{pq}.

$$h_{pq} := \langle \chi_p | -\frac{1}{2}\nabla^2 - \frac{2}{r} | \chi_q \rangle =$$

$$= \int d\vec{r}\, \chi_p(\vec{r}) \left(-\frac{1}{2}\nabla^2 - \frac{2}{r}\right) \chi_q(\vec{r}) =$$

$$= \left\{ \begin{aligned} \nabla^2 e^{-\alpha r^2} &= \frac{1}{r}\partial_r^2 \left(r e^{-\alpha r^2}\right) = \\ &= \frac{1}{r}\partial_r \left(e^{-\alpha r^2} - 2\alpha r^2 e^{-\alpha r^2}\right) = \\ &= \frac{1}{r}\left(-2\alpha r - 4\alpha r + 4\alpha^3 r^3\right) e^{-\alpha r^2} = \\ &= \left(4\alpha^3 r^2 - 6\alpha\right) e^{-\alpha r^2} \end{aligned} \right\} =$$

$$= \int d\vec{r}\, e^{-\alpha_p r^2} \left(3\alpha_q - 2\alpha_q^3 r^2 - \frac{2}{r}\right) e^{-\alpha_q r^2}$$

$$= 4\pi \int_0^\infty dr\, r^2 \left(3\alpha_q - 2\alpha_q^3 r^2 - \frac{2}{r}\right) e^{-(\alpha_q + \alpha_p) r^2}$$

Standard integrals:

$$\boxed{\begin{aligned} \int_0^\infty r e^{-\alpha r^2} dr &= \frac{1}{2}\frac{1}{\alpha} \\ \int_0^\infty r^2 e^{-\alpha r^2} dr &= \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}} \\ \int_0^\infty r^4 e^{-\alpha r^4} dr &= \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}} \end{aligned}}$$

Use these to evaluate h_{pq}:

$$h_{pq} = 4\pi \int_0^\infty dr \left(3\alpha_q r^2 - 2\alpha_q^3 r^4 - 2r\right) e^{-(\alpha_q+\alpha_p)r^2} =$$

$$= 4\pi\left[3\alpha_q\left(\frac{1}{4}\sqrt{\frac{\pi}{(\alpha_p+\alpha_q)^3}}\right) - \right.$$

$$\left. - 2\alpha_q^3\left(\frac{3}{8}\sqrt{\frac{\pi}{(\alpha_p+\alpha_q)^5}}\right) - 2\left(\frac{1}{2}\frac{1}{\alpha_p+\alpha_q}\right)\right] =$$

$$= 3\pi\alpha_q\sqrt{\frac{\pi}{(\alpha_p+\alpha_q)^3}} - 3\pi\alpha_q^3\sqrt{\frac{\pi}{(\alpha_p+\alpha_q)^5}} - \frac{4\pi}{\alpha_p+\alpha_q}$$

Similarily:

$$S_{pq} := \langle \chi_p | \chi_q \rangle = \int d^3r\, e^{-(\alpha_p+\alpha_q)r^2} =$$

$$= 4\pi\int_0^\infty dr\, r^2 e^{-(\alpha_p+\alpha_q)r^2} = \pi\sqrt{\frac{\pi}{(\alpha_p+\alpha_q)^3}}$$

Thijssen gives Q_{prqs} as

$$Q_{prqs} = \frac{2\pi^{5/2}}{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)\sqrt{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}$$

(from difficult integral)

Solution algorithm

Let $\vec{C} = (C_0 \;\; C_1 \;\; C_2 \;\; C_3)^T$.

Given: h_{pq}, S_{pq}, Q_{pqrs}

1. Pick arbitrary initial $\vec{C}$
2. Normalize $\vec{C}$:

   2b. Compute $\|C\|^2 = \sum_{p,q} C_p S_{pq} C_q$

   2b. Scale $\vec{C} \longmapsto \frac{\vec{C}}{\sqrt{\|C\|^2}}$

3. Compute matrix F:

$$F_{pq} = h_{pq} + \sum_{rs} Q_{prqs} C_r C_s$$

4. Solve generalized eigenvalue problem

$$F\vec{C} = E' S \vec{C}$$

Pick the solution with lowest E' as new $\vec{C}$. Repeat from 2.

Generalized Eigenvalue problem

$$F\vec{c} = E' S \vec{c}$$

Assume S real symmetric

$$\Rightarrow \exists U: \quad U^{+} S U = D$$

where D is diagonal. $D^{-1/2}$ is well defined (operate elementwise).
If $V = U D^{-1/2}$, then

$$V^{+} S V = I$$

Let $\vec{c} = V \vec{c}' \Leftrightarrow \vec{c}' = V^{+} \vec{c}$
Now note that

$$F\vec{c} = E' S \vec{c}$$

$$\Leftrightarrow V^{T} F V \vec{c}' = E' V^{T} S V \vec{c}' = E' \vec{c}',$$

so $\vec{c}'$ is given by solving

$$(V^{T} F V) \vec{c}' = E' \vec{c}'.$$

This is the normal eigenvalue problem!

$\vec{c}$ is then given by $\vec{c} = V \vec{c}'$.