SCF Calculation for Two Electron Atoms and Ions

Trial Wave Function: $\Psi(r,\beta) := \sqrt{\frac{\beta^3}{\pi}} \cdot \exp(-\beta \cdot r)$

Calculate kinetic energy: $T_e(\beta) := \int_0^{\infty} \Psi(r,\beta) \cdot \left[-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} (r \cdot \Psi(r,\beta)) \right] \cdot 4 \cdot \pi \cdot r^2 \, dr \;\Big|\; \begin{matrix} \text{assume}, \beta > 0 \\ \text{simplify} \end{matrix} \rightarrow \frac{1}{2} \cdot \beta^2$

Calculate electron-nucleus potential energy:

$$V_{ne}(\beta, Z) := \int_0^{\infty} \Psi(r,\beta) \cdot \frac{-Z}{r} \cdot \Psi(r,\beta) \cdot 4 \cdot \pi \cdot r^2 \, dr \;\Big|\; \begin{matrix} \text{assume}, \beta > 0 \\ \text{simplify} \end{matrix} \rightarrow (-\beta) \cdot Z$$

Calculation of electron-electron potential energy:

a. Calculate the electrostatic potential due to the β electron:

$$\Phi(\beta, r) := \frac{1}{r} \cdot \int_0^{r} \Psi(x,\beta)^2 \cdot 4 \cdot \pi \cdot x^2 \, dx \ldots \;\Big|\; \begin{matrix} \text{assume}, \beta > 0 \\ \text{simplify} \end{matrix} \rightarrow \frac{-\left[e^{(-2) \cdot r \cdot \beta} \cdot \beta \cdot r + e^{(-2) \cdot r \cdot \beta} - 1 \right]}{r}$$

$$+ \int_r^{\infty} \frac{\Psi(x,\beta)^2 \cdot 4 \cdot \pi \cdot x^2}{x} \, dx$$

b. Calculate the electron-electron potential energy of the α and β electrons using result of part a:

$$V_{ee}(\alpha, \beta) := \int_0^{\infty} \Psi(r,\alpha)^2 \cdot \Phi(\beta, r) \cdot 4 \cdot \pi \cdot r^2 \, dr \;\Big|\; \begin{matrix} \text{assume}, \beta > 0, \alpha > 0 \\ \text{simplify} \end{matrix} \rightarrow \alpha \cdot \beta \cdot \frac{\alpha^2 + 3 \cdot \beta \cdot \alpha + \beta^2}{\left(\alpha^2 + 2 \cdot \beta \cdot \alpha + \beta^2 \right) \cdot (\beta + \alpha)}$$

SCF Calculation

1. Supply nuclear charge and an input value for β: $Z := 2$ $\beta := 2.0$ $\alpha := Z$

2. Define orbital energies of the electrons in terms of the variational parameters:

Orbital energy of the α electron: $\varepsilon_{1s\alpha}(\alpha,\beta) := T_e(\alpha) + V_{ne}(\alpha,Z) + V_{ee}(\alpha,\beta)$

Orbital energy of the β electron: $\varepsilon_{1s\beta}(\alpha,\beta) := T_e(\beta) + V_{ne}(\beta,Z) + V_{ee}(\alpha,\beta)$

3. Minimize orbital energies with respect to α and β:

Given $\frac{d}{d\alpha}\varepsilon_{1s\alpha}(\alpha,\beta) = 0$ $\alpha := \text{Find}(\alpha)$ $\alpha = 1.5999$ $\varepsilon_{1s\alpha}(\alpha,\beta) = -0.8116$

Given $\frac{d}{d\beta}\varepsilon_{1s\beta}(\alpha,\beta) = 0$ $\beta := \text{Find}(\beta)$ $\beta = 1.7126$ $\varepsilon_{1s\beta}(\alpha,\beta) = -0.9250$

4. Calculate the energy of the atom:

$E_{atom} := T_e(\alpha) + V_{ne}(\alpha,Z) + T_e(\beta) + V_{ne}(\beta,Z) + V_{ee}(\alpha,\beta)$ $E_{atom} = -2.8449$

5. Record results of the SCF cycle and return to step 1 with the new and improved input value for β.

6. Continue until self-consistency is achieved.

7. Verify the results shown below for He. Repeat for Li^+, Be^{2+} and B^{3+}.

β (input)	α	$\varepsilon_{1s\alpha}$	β	$\varepsilon_{1s\beta}$	E_{atom}
2.0000	1.5999	−0.8116	1.7126	−0.9250	−2.8449
1.7126	1.6803	−0.8887	1.6895	−0.8987	−2.8476
1.6895	1.6869	−0.8959	1.6877	−0.8967	−2.8477
1.6877	1.6874	−0.8964	1.6875	−0.8965	−2.8477
1.6875	1.6875	−0.8965	1.6875	−0.8965	−2.8477