2.51: Outline of the SCF Method for Two Electrons

Trial Wave Function:

$$\Psi(r,\ \beta) = \sqrt{\frac{\beta^3}{\pi}}\exp(-\beta r)$$

Calculate kinetic energy:

$$T_e(\beta) = \int_0^\infty \Psi(r,\ \beta)\left[-\frac{1}{2r}\frac{d^2}{dr^2}(r\Psi(r,\ \beta))\right]4\pi r^2 dr \ \left|\ \begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array}\right. \rightarrow (-\beta)Z$$

Calculate electron-nucleus potential energy:

$$V_{ne}(\beta,\ Z) = \int_0^\infty \Psi(r,\ \beta)\frac{-Z}{r}4\pi r^2 dr \ \left|\ \begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array}\right. \rightarrow (-\beta)Z$$

Calculation of electron-electron potential energy:

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

$$\Phi(\beta,\ r) = \begin{array}{l}\frac{1}{r}\int_0^\tau \Psi(x,\ \beta)^2 4\pi x^2 dx \ldots \\ \quad + \int_r^\infty \frac{\Psi(x,\ \beta)^2 4\pi x^2 dx}{x} dx\end{array} \left|\ \begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array}\right. \rightarrow \frac{-\left[e^{(-2)r\beta}\beta r + e^{(-2)r\beta} - 1\right]}{r}$$

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

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

SCF Calculation

1. Supply nuclear charge and an input value for β:

$$Z = 2 \quad \beta = 2.0 \quad \alpha = Z$$

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

$$\begin{array}{ll}\text{Orbital energy of the } \alpha \text{ electron:} & \varepsilon_{1s\alpha}(\alpha,\ \beta) = T_e(\alpha) + V_{ne}(\alpha,\ Z) + V_{ee}(\alpha,\ \beta)\\ \text{Orbital energy of the } \beta \text{ electron:} & \varepsilon_{1s\beta}(\alpha,\ \beta) = T_e(\beta) + V_{ne}(\beta,\ Z) + V_{ee}(\alpha,\ \beta)\end{array}$$

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

$$\begin{array}{llllll}\text{Given} & \frac{d}{d\alpha}\varepsilon_{1s\alpha}(\alpha,\ \beta) = 0 & \alpha = \text{Find}(\alpha) & \alpha = 1.5999 & \varepsilon_{1s\alpha}(\alpha,\ \beta) = -0.8116\\ \text{Given} & \frac{d}{d\beta}\varepsilon_{1s\beta}(\alpha,\ \beta) = 0 & \beta = \text{Find}(\beta) & \beta = 1.7126 & \varepsilon_{1s\beta}(\alpha,\ \beta) = -0.9250\end{array}$$

4. Calculate the energy of the atom:

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

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+}

$$\begin{pmatrix}\beta\text{ (input)} & \alpha & \varepsilon_{1s\alpha} & \beta & \varepsilon_{1s\beta} & E_{atom}\\ 2.000 & 1.5999 & -0.8116 & 1.7126 & -0.9250 & -2.8449\\ 1.7126 & 1.6803 & -0.8887 & 1.6895 & -0.8987 & -2.8476\\ 1.6895 & 1.6869 & -0.8959 & 1.6877 & -0.8967 & -2.8477\\ 1.6877 & 1.6874 & -0.8964 & 1.6875 & -0.8965 & -2.8477\\ 1.6875 & 1.6875 & -0.8965 & 1.6875 & -0.8965 & -2.8477\end{pmatrix}$$