2.52: The SCF Method for Two Electrons Using a Gaussian Wave Function

Gaussian Trial Wave Function:

$$\Psi(r,\ \beta) = \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}} \exp\left(-\beta r^2\right)$$

Calculate kinetic energy:

$$\int_0^\infty \Psi(r,\ \beta)\left[-\frac{1}{2r}\frac{d^2}{dr^2}(r\Psi(r,\ \beta))\right] 4\pi r^2 dr \quad \left|\begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array}\right. \rightarrow \frac{3}{2}\beta$$

Calculate electron-nucleus potential energy:

a. Calculate the electric potential of one of the electrons in the presence of the other:

$$\frac{1}{r}\int_0^r \Psi(x,\ \beta)^2 4\pi x^2 dx + \int_r^\infty \frac{\Psi(x,\ \beta)^2 4\pi x^2}{x} dx \quad \left|\begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array}\right. \rightarrow \frac{\operatorname{erf}\left(r 2^{\frac{1}{2}} \beta^{\frac{1}{2}}\right)}{r}$$

b. Calculate the electron-electron potential energy using the result of part a:

$$\int_0^\infty \Psi(r,\ \beta)^2 \left(\frac{\operatorname{erf}\left(r 2^{\frac{1}{2}} 2^{\frac{1}{2}}\right)}{r}\right) 4\pi r^2 dr \quad \begin{array}{l}\text{assume, } \beta>0\\ \text{simplify}\end{array} \rightarrow \frac{2}{\pi}(\beta\pi)^{\frac{1}{2}}$$

SCF Calculation

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

$$Z = 2 \quad \beta = 0.767 \quad \alpha = Z$$

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

$$\text{Orbital energy of the } \alpha \text{ electron:} \quad \varepsilon_{1s\alpha}(\alpha,\ \beta) = \frac{3\alpha}{2} - Z\sqrt{\frac{8\alpha}{\pi}} + \sqrt{\frac{8\alpha\beta}{\pi(\alpha+\beta)}}$$

$$\text{Orbital energy of the } \beta \text{ electron:} \quad \varepsilon_{1s\beta}(\alpha,\ \beta) = \frac{3\beta}{2} - Z\sqrt{\frac{8\beta}{\pi}} + \sqrt{\frac{8\alpha\beta}{\pi(\alpha+\beta)}}$$

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

$$\text{Given} \quad \frac{d}{d\alpha}\varepsilon_{1s\alpha}(\alpha,\ \beta) = 0 \quad \alpha = \text{Find}(\alpha) \quad \alpha = 0.7670 \quad \varepsilon_{1s\alpha}(\alpha,\ \beta) = -0.6564$$

$$\text{Given} \quad \frac{d}{d\beta}\varepsilon_{1s\beta}(\alpha,\ \beta) = 0 \quad \beta = \text{Find}(\beta) \quad \beta = 0.7670 \quad \varepsilon_{1s\beta}(\alpha,\ \beta) = -0.6564$$

4. Calculate the energy of the atom:

$$E_{atom} = \frac{3\alpha}{2} \quad \frac{3\beta}{2} - Z\sqrt{\frac{8\alpha}{\pi}} - Z\sqrt{\frac{8\beta}{\pi}} + \sqrt{\frac{8\alpha\beta}{\pi(\alpha+\beta)}} \quad E_{atom} = -2.3010$$

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+}.

$$\begin{pmatrix} \beta(\text{input}) & \alpha & \varepsilon_{1s\alpha} & \beta & \varepsilon_{1s\beta} & E_{atom} \\ 2.000 & 0.4514 & -0.4988 & 0.9303 & -0.8031 & -2.2703 \\ 0.9303 & 0.6943 & -0.6117 & 0.8023 & -0.6816 & -2.2996 \\ 0.8023 & 0.7504 & -0.6454 & 0.7749 & -0.6618 & -2.3009 \\ 0.7749 & 0.7633 & -0.6539 & 0.7688 & -0.6576 & -2.3010 \\ 0.7688 & 0.7661 & -0.6588 & 0.7674 & -0.6567 & -2.3010 \\ 0.7674 & 0.7668 & -0.6563 & 0.7671 & -0.6564 & -2.3010 \\ 0.7671 & 0.7669 & -0.6564 & 0.7670 & -0.6564 & -2.3010 \\ 0.7670 & 0.7670 & -0.6564 & 0.7670 & -0.6564 & -2.3010 \end{pmatrix}$$

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