

## SCF Calculation for Two Electron Atoms and Ions Using a Gaussian Wave Function

Gaussian Trial Wave Function:

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

Calculate kinetic energy:

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

Calculate electron-nucleus potential energy:

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

Calculation of electron-electron potential energy:

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

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

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

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

## SCF Calculation

1. Supply nuclear charge and an input value for  $\beta$ :  $Z := 2$      $\beta := 0.7670$      $\alpha := Z$

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

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

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

3. Minimize orbital energies with respect to  $\alpha$  and  $\beta$ :

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

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

4. Calculate the energy of the atom:

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

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

6. Continue until self-consistency is achieved.

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

$\beta$ (input)	$\alpha$	$\varepsilon_{1s\alpha}$	$\beta$	$\varepsilon_{1s\beta}$	$E_{\text{atom}}$
2.0000	0.4514	-0.4988	0.9303	-0.8031	-2.2703
0.9303	0.6946	-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	-0.6558	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