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

Gaussian Trial Wave Function:

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

Calculate kinetic energy:

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

Calculate electron-nucleus potential energy:

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

Calculation of electron-electron potential energy:

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

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

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

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

SCF Calculation

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

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

Orbital energy of the α electron:

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

Orbital energy of the β 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 α and β:

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

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4. Calculate the energy of the atom:

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

$E_{atom} = -2.3010$

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+}.

β (input)	α	$\varepsilon_{1s\alpha}$	β	$\varepsilon_{1s\beta}$	E_{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