Variational Calculation on the Helium Atom Using a Trigonometric Trial Wave Function

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Trigonometric Trial Wave Function:

$$\Psi(r,\beta) := \sqrt{\frac{3\cdot\beta^3}{\pi^3}}\cdot\operatorname{sech}(\beta\cdot r)$$

Demonstrate the wave function is normalized.

$$\int_0^\infty \Psi(r,\beta)^2\cdot 4\cdot\pi\cdot r^2\, dr \quad \begin{array}{l} \text{assume},\beta > 0 \\ \text{simplify} \end{array} \to 1$$

The terms contributing to the total electronic energy of the helium atom are the kinetic energy of each electron, each electron's interaction with the nucleus, and the interaction of the electrons with each other.

Calculate kinetic energy:

$$2\cdot\int_0^\infty \Psi(r,\beta)\cdot\left[-\frac{1}{2\cdot r}\cdot\frac{d^2}{dr^2}(r\cdot\Psi(r,\beta))\right]\cdot 4\cdot\pi\cdot r^2\, dr \quad \begin{array}{l} \text{assume},\beta > 0 \\ \text{simplify} \end{array} \to \frac{1}{3}\cdot\beta^2\cdot\frac{12+\pi^2}{\pi^2}$$

Calculate electron-nucleus potential energy:

$$2\cdot\int_0^\infty \Psi(r,\beta)\cdot\frac{-2}{r}\cdot\Psi(r,\beta)\cdot 4\cdot\pi\cdot r^2\, dr \quad \begin{array}{l} \text{assume},\beta > 0 \\ \text{simplify} \end{array} \to (-48)\cdot\beta\cdot\frac{\ln(2)}{\pi^2}$$

Calculate electron-electron potential energy:

$$\int_0^\infty \Psi(r,\beta)^2\cdot\left(\frac{1}{r}\cdot\int_0^r \Psi(x,\beta)^2\cdot 4\cdot\pi\cdot x^2\, dx + \int_r^\infty \frac{\Psi(x,\beta)^2\cdot 4\cdot\pi\cdot x^2}{x}\, dx\right)\cdot 4\cdot\pi\cdot r^2\, dr$$

Write the equation for the total electronic energy in terms of the variational parameter β:

$$E(\beta) := \frac{1}{3}\cdot\beta^2\cdot\frac{12+\pi^2}{\pi^2} + (-48)\cdot\beta\cdot\frac{\ln(2)}{\pi^2} + \int_0^\infty \Psi(r,\beta)^2\cdot\left(\frac{1}{r}\cdot\int_0^r \Psi(x,\beta)^2\cdot 4\cdot\pi\cdot x^2\, dx + \int_r^\infty \frac{\Psi(x,\beta)^2\cdot 4\cdot\pi\cdot x^2}{x}\, dx\right)\cdot 4\cdot\pi\cdot r^2\, dr$$

Minimize the energy with respect to the variational parameter β.

$$\beta := 1 \qquad \beta := \text{Minimize}(E, \beta) \qquad \beta = 1.902 \qquad E(\beta) = -2.672$$

Compare the variational calculation to the Hartree-Fock limit: $\qquad E_{HF} := -2.8617$

$$\frac{E_{HF} - E(\beta)}{E_{HF}} = 6.614\ \%$$

Compare optimized trial wave function with the Hartree-Fock wave function (see McQuarrie and Simon, page 283) by plotting the radial distribution functions.

$$\Phi(r) := .75738 \cdot \exp(-1.430 \cdot r) + .43658 \cdot \exp(-2.4415 \cdot r) + .17295 \cdot \exp(-4.0996 \cdot r) - .02730 \cdot \exp(-6.4843 \cdot r) + .06675 \cdot \exp(-7.97$$