

Approximate Methods: Gaussian Trial Wave Function for Hydrogen

A Gaussian function, $\exp(-\alpha r^2)$, is proposed as a trial wavefunction in a variational calculation on the hydrogen atom. Determine the optimum value of the parameter α and the ground state energy of the hydrogen atom. Use atomic units: $\hbar = 2\pi$, $m_e = 1$, $e = -1$.

$$\Psi(r, \beta) := \left(\frac{2 \cdot \beta}{\pi}\right)^{\frac{3}{4}} \cdot \exp(-\beta \cdot r^2) \quad T = -\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2}(r \cdot \Psi) \quad V = -\frac{1}{r} \quad \int_0^\infty 4 \cdot \pi \cdot r^2 dr$$

a. Demonstrate the wave function is normalized.

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

b. Evaluate the variational integral.

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

c. Minimize the energy with respect to the variational parameter β .

$$\beta := 1 \quad \beta := \text{Minimize}(E, \beta) \quad \beta = 0.283 \quad E(\beta) = -0.424$$

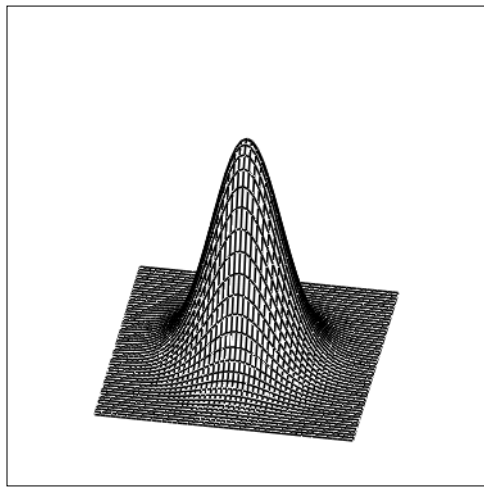
d. The exact ground state energy for the hydrogen atom is $-5 E_h$. Calculate the percent error.

$$\frac{-5 - E(\beta)}{-5} \cdot 100 = 15.117$$

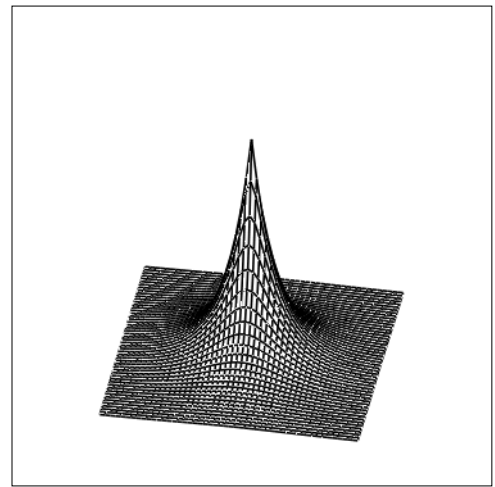
e. The differences between the Gaussian and Slater type wavefunctions are illustrated with the surface plots show below.

$$N := 50 \quad b := 5 \quad i := 0..N \quad j := 0..N \quad y_i := -b + \frac{2 \cdot b \cdot i}{N} \quad x_j := -b + \frac{2 \cdot b \cdot j}{N}$$

$$\text{Gauss}_{i,j} := \left(\frac{2 \cdot \beta}{\pi}\right)^{\frac{3}{4}} \cdot \exp\left[-\beta \cdot \left[\left(x_i\right)^2 + \left(y_j\right)^2\right]\right] \quad \text{Slater}_{i,j} := \frac{1}{\sqrt{\pi}} \cdot \exp\left[-\sqrt{\left(x_i\right)^2 + \left(y_j\right)^2}\right]$$



Gauss



Slater

f. These wavefunctions can also be compared by plotting their radial distribution functions:

$r := 0, .1..6$

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

$$S(r) := \frac{1}{\sqrt{\pi}} \cdot \exp(-r)$$

