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: $h = 2\pi$, $m_e = 1$, $e = -1$.

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

a. Demonstrate the wave function is normalized.

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

b. Evaluate the variational integral.

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

$$+\int_0^{\infty}\Psi(r,\beta)\cdot-\frac{1}{r}\cdot\Psi(r,\beta)\cdot 4\cdot\pi\cdot r^2\,dr$$

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

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

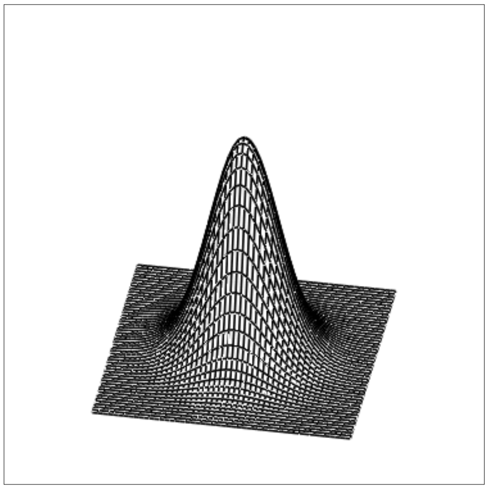
d. The exact ground state energy for the hydrogen atom is -.5 E_h. Calculate the percent error.

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

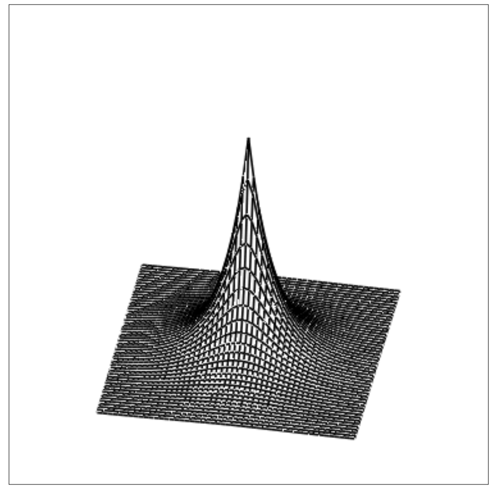
e. The differences between the Gaussian and Slater type wavefunctions are illustrated with the surface plots show below.

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

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



Gauss



Slater

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

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

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

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