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 \( \alpha \) and the ground state energy of the hydrogen atom. Use atomic units: \( h = 2\pi, m_e = 1, e = -1 \).

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

\( a. \) Demonstrate the wave function is normalized.

\[
\int_0^\infty \Psi^2(r, \beta) \cdot 4 \pi r^2 dr \quad \text{assume } \beta > 0 \quad \text{simplify} \quad \rightarrow 1
\]

\( b. \) Evaluate the variational integral.

\[
E(\beta) := \int_0^\infty \Psi^2(r, \beta) \cdot \left[ -\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \Psi(r, \beta)) \right] \cdot 4 \pi r^2 dr \quad \text{assume } \beta > 0 \quad \text{simplify} \quad \rightarrow \frac{1}{2} \cdot \frac{3}{2} \pi \beta - \frac{4}{2} \cdot \frac{1}{2} \beta^2
\]

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

\( c. \) Minimize the energy with respect to the variational parameter \( \beta \).

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

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

\[
\frac{-0.5 - E(\beta)}{-0.5} \cdot 100 = 15.117
\]

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

\[
Gauss_{i,j} := \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}} \exp\left[-\beta \left( x_i^2 + y_j^2 \right) \right] \quad \text{Slater}_{i,j} := \left(\frac{1}{\sqrt{\pi}}\right) \exp\left[-\left( x_i^2 + y_j^2 \right) \right]
\]
These wavefunctions can also be compared by plotting their radial distribution functions:

\[ r := 0, 1, \ldots, 6 \]

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

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