10.20: Gaussian Trial Wavefunction for the Hydrogen Atom

A Gaussian function, exp(-αr^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 = 2π, m_e = 1, e = -1.

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

$$T = \frac{-1}{2r}\frac{d^2}{dr^2}(r\blacksquare)$$

$$V = \frac{1}{r}$$

$$\int_0^\infty \blacksquare 4\pi r^2 dr$$

a. Demonstrate the wave function is normalized.

$$\int_0^\infty \Psi(r,\beta)^2 4\pi r^2 dr|_{simplify}^{assume,\ \beta>0} \rightarrow 1$$

b. Evaluate the variational integral.

$$E(\beta) := \int_0^\infty \Psi(r,\beta)\left[\frac{-1}{2r}\frac{d^2}{dr^2}(r\Psi(r,\beta))\right]4\pi r^2 dr \ldots |_{simplify}^{assume,\ \beta>0} \rightarrow \frac{1}{2}\frac{3\pi^{\frac{1}{2}}\beta - (4)2^{\frac{1}{2}}\beta^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} + \int_0^\infty \Psi(r,\beta)\frac{-1}{r}\Psi(r,\beta)4\pi r^2 dr$$

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

β := 1 β := Minimize (E, β) β = 0.283 E(β) = -0.424

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

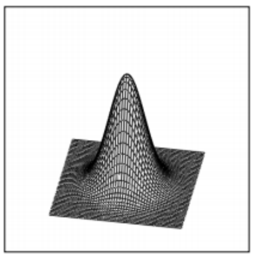
$$\frac{-.5 - E(\beta)}{-.5} = 15.117$$

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

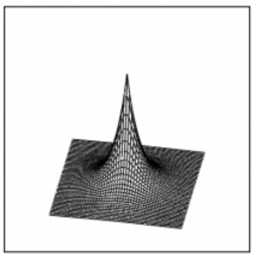
N := 50 b := 5 i := 0..N j := 0..N $y_i := -b + \frac{2bi}{N}$ $x_j := -b + \frac{2bj}{N}$

$$Gauss_{i,j} := \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}} exp[-\beta[(x_i)^2 + (y_j)^2]]$$

$$Slater_{i,j} := \frac{1}{\sqrt{\pi}} exp[-\sqrt{(x_i)^2 + (y_j)^2}]$$



Gauss



Slater

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

r := 0, .1 .. 6

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

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