14. Consider the Gaussian function e^{-cr^2} as a variational function for the ground state of the H atom. Normalise this function. Obtain the optimum value of the variational constant c. Calculate the ground state energy.

$$\int_0^\infty x^{2n} e^{-bx^2} dx = \frac{1\cdot 3 \cdots (2n-1)}{2^{n+1}} \left(\frac{\pi}{b^{2n+1}}\right)^{1/2} \quad n = 1, 2, \ldots$$

Normalisation of e^{-cr^2}

$$N^2 \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-2cr^2} r^2 dr \sin\theta \, d\theta \, d\phi = N^2 4\pi I = 1$$

$$I = \int_0^\infty r^2 e^{-2cr^2} dr = \frac{\sqrt{\pi}}{8\sqrt{2}\, c^{3/2}}$$

$$\therefore N = \frac{1}{2\sqrt{\pi}\,\dfrac{\pi^{1/4}}{8^{1/2}\, 2^{1/4}\, c^{3/4}}} = \left(\frac{2c}{\pi}\right)^{3/4}$$

Variational integral $= \langle N e^{-cr^2} | \hat{\mathcal{H}} | N e^{-cr^2} \rangle$

$(\hat{\mathcal{H}} = -\frac{1}{2}\hat{\nabla}^2 - \frac{1}{r})$

$$= N^2 4\pi \left\{ -\left[\frac{1}{2}\int_0^\infty \left(e^{-cr^2} \frac{\partial^2}{\partial r^2} e^{-cr^2}\right) r^2 dr + \int_0^\infty \frac{1}{r}\left(e^{-cr^2} \frac{\partial}{\partial r} e^{-cr^2}\right) r^2 dr \right] + - \int_0^\infty e^{-cr^2} \frac{1}{r} e^{-cr^2} r^2 dr \right\}$$

Show how, by expanding $\hat{\nabla}^2$ ..

$$= 4\pi N^2 \left\{ -(I_1 + I_2) - I_3 \right\}$$

$$\frac{\partial}{\partial r} e^{-cr^2} = -2rc\, e^{-cr^2}$$

$$\frac{\partial^2}{\partial r^2} e^{-cr^2} = 4c^2 r^2 e^{-cr^2} - 2c\, e^{-cr^2}$$

$$\therefore I_1 + I_2 = 2c^2 \int_0^\infty r^4 e^{-2cr^2} dr - 3c \int_0^\infty r^2 e^{-2cr^2} dr$$

$$= 2c^2 \frac{3}{8} \frac{\pi^{1/2}}{2^{5/2} c^{5/2}} - 3c \frac{1}{4} \frac{\pi^{1/2}}{2^{3/2} c^{3/2}}$$

$$= \frac{-3\sqrt{\pi}\, c^{-\frac{1}{2}}}{2 \cdot 4 \cdot 2^{3/2}}$$

$$\therefore K.E. = -4\pi N^2 (I_1 + I_2) = 4\pi \frac{2^{3/2} c^{3/2}}{\pi^{3/2}} \cdot \frac{3 \pi^{1/2} c^{-\frac{1}{2}}}{2 \cdot 4 \cdot 2^{3/2}}$$

$$= \frac{3}{2} c$$

$$I_3 = \int_0^\infty e^{-2cr^2} r\, dr = \frac{1}{2} \int_0^\infty e^{-2cu} du = \frac{1}{4c}$$

$$\therefore P.E. = -I_3 \cdot 4\pi N^2 = -\frac{1}{4c} 4\pi \frac{2^{3/2} c^{3/2}}{\pi^{3/2}}$$

$$= -2\sqrt{2}\, \pi^{-1/2} c^{1/2}$$

$\therefore$ Variational energy $\mathcal{E} = \frac{3}{2} c - \frac{2\sqrt{2}}{\sqrt{\pi}} \sqrt{c}$

$$\frac{\partial \mathcal{E}}{\partial c} = 0 \quad \Rightarrow \quad \frac{2\sqrt{2}}{2\sqrt{\pi}} c^{-\frac{1}{2}} = \frac{3}{2}$$

$$c = \frac{8}{9\pi}$$

G.S. energy $= \frac{3}{2} \frac{8}{9\pi} - \frac{2\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{8}}{3\sqrt{\pi}} = \underline{-0.424 \text{ a.u}}$

(About 15% higher than the exact value)

What is the exact value ?!

The optimised wave function is $\frac{8}{\sqrt{27}\, \pi^{3/2}} e^{-\frac{8}{9\pi} r^2}$

Does this wave function satisfy the Virial Theorem?