Introduction

In this problem, I will use the variational principle to compute the ground state energy for four trial wavefunctions.

Variational Principle:

$$\langle\psi|H|\psi\rangle \geq E_{gs}; \qquad \textit{For any trial wavefunction } \psi$$

Step 1: $\langle\psi|\psi\rangle = 1$

Step 2: $\langle\psi|H|\psi\rangle = \langle\psi|T|\psi\rangle + \langle\psi|V|\psi\rangle = \langle E(\alpha_1, \alpha_2, \ldots, \alpha_N)\rangle$

Step 3: $\frac{dE(\alpha_1,\alpha_2,\ldots,\alpha_i,\ldots,\alpha_N)}{d\alpha_i} = 0$

Step 4: $E(\alpha_1^*, \alpha_2^*, \ldots, \alpha_N^*) \geq E_{gs}$

Where $\alpha_1, \alpha_2, \ldots, \alpha_N$ are parameters to be minimized into $\alpha_1^*, \alpha_2^*, \ldots, \alpha_N^*$

Problem 8.19[1]

$$\psi_1(r) = Ae^{-\alpha r} \qquad \psi_2(r) = Ae^{-\alpha r^2} \qquad \psi_3(r) = \begin{cases} A(R-r) & 0 \leq r \leq R \\ 0 & \text{elsewhere} \end{cases} \qquad \psi_4(r) = \frac{1}{1+(\alpha r)^2}$$

Trial wavefunction: $\psi_1(r) = Ae^{-\alpha r}$

$$\langle\psi_1|\psi_1\rangle = 4\pi A^2 \int_0^\infty e^{-2\alpha r} r^2 dr = 1$$

Using the fact that $I(\beta) = \int_0^\infty e^{-\beta r} dr = \frac{1}{\beta}$; Then taking the second derivative of $I(\beta)$

$$\frac{d^2 I(\beta)}{d\beta^2} = \int_0^\infty e^{-\beta r} r^2 dr = \frac{2}{\beta^3}$$

$$4\pi A^2 \frac{2}{(2\alpha)^3} = 1 \implies A = \sqrt{\frac{\alpha^3}{\pi}}$$

$$E(\alpha) = \langle\psi_1|H|\psi_1\rangle = \langle\psi_1|T|\psi_1\rangle + \langle\psi_1|V|\psi_1\rangle$$

$$\langle\psi_1|T|\psi_1\rangle = -\frac{2\hbar^2\pi}{m} A^2 \int_0^\infty e^{-\alpha r} \nabla^2 e^{-\alpha r} r^2 dr$$

Using integration by parts, we can simplify the Laplacian

$$\int \Psi^*(\mathbb{R}) \nabla^2 \Psi(\mathbb{R}) d^3\mathbb{R} = -\int |\nabla\Psi(\mathbb{R})|^2 d^3\mathbb{R}$$

$$\langle\psi_1|T|\psi_1\rangle = \frac{2\hbar^2\pi\alpha^2}{m} A^2 \int_0^\infty e^{-2\alpha r} r^2 dr$$

[1] Griffith's Introduction to Quantum Mechanics, 3rd ed.

$$\langle\psi_1|T|\psi_1\rangle = \frac{2\hbar^2\pi\alpha^2}{m}\frac{\alpha^3}{\pi}\frac{2}{(2\alpha)^3} = \frac{\hbar^2\alpha^2}{2m}$$
$$\langle\psi_1|V|\psi_1\rangle = -4\pi ke^2A^2\int_0^\infty e^{-\alpha r}\frac{1}{r}e^{-\alpha r}r^2dr = -4\pi ke^2A^2\int_0^\infty e^{-2\alpha r}rdr$$
$$\frac{dI(\beta)}{d\beta} = -\int_0^\infty e^{-\beta r}rdr = -\frac{1}{\beta^2}$$
$$\langle\psi_1|V|\psi_1\rangle = -4\pi ke^2A^2\frac{1}{4\alpha^2} = -\alpha ke^2$$
$$\langle\psi_1|H|\psi_1\rangle = E(\alpha) = \frac{\hbar^2\alpha^2}{2m} - \alpha ke^2$$
$$\frac{dE(\alpha)}{d\alpha} = 0 \implies \frac{\hbar^2\alpha}{2m} - ke^2 = 0 \implies \alpha^* = \frac{e^2km}{\hbar^2}$$
$$E(\alpha^*) = -\frac{e^4k^2m}{2\hbar^2} = -\frac{e^4m}{8\epsilon_0^2h^2} = -Ry = E_{gs}$$

Trial wavefunction: $\psi_2(r) = Ae^{-\alpha r^2}$

$$\langle\psi_2|\psi_2\rangle = 4\pi A^2\int_0^\infty e^{-2\alpha r^2}r^2dr = 1$$

Using the fact that $I(\beta) = \int_0^\infty e^{-\beta r^2}dr = \frac{1}{2}\sqrt{\frac{\pi}{\beta}}$; Then taking the first derivative of $I(\beta)$

$$\frac{dI(\beta)}{d\beta} = -\int_0^\infty e^{-\beta r^2}r^2dr = -\frac{1}{4}\sqrt{\frac{\pi}{\beta^3}}$$
$$\pi A^2\sqrt{\frac{\pi}{(2\alpha)^3}} = 1 \implies A = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$
$$E(\alpha) = \langle\psi_2|H|\psi_2\rangle = \langle\psi_2|T|\psi_2\rangle + \langle\psi_2|V|\psi_2\rangle$$
$$\langle\psi_2|T|\psi_2\rangle = -\frac{2\hbar^2\pi}{m}A^2\int_0^\infty e^{-\alpha r^2}\nabla^2e^{-\alpha r^2}r^2dr = \frac{8\hbar^2\pi\alpha^2}{m}A^2\int_0^\infty e^{-2\alpha r^2}r^4dr$$
$$\frac{d^2I(\beta)}{d\beta^2} = \int_0^\infty e^{-\beta r^2}r^4dr = \frac{3}{8}\sqrt{\frac{\pi}{\beta^5}}$$
$$\langle\psi_2|T|\psi_2\rangle = \frac{3\hbar^2\pi\alpha^2}{m}\sqrt{\frac{8\alpha^3}{\pi^3}}\sqrt{\frac{\pi}{32\alpha^5}} = \frac{3\hbar^2\alpha}{2m}$$
$$\langle\psi_2|V|\psi_2\rangle = -4\pi ke^2A^2\int_0^\infty e^{-\alpha r^2}\frac{1}{r}e^{-\alpha r^2}r^2dr = -4\pi ke^2A^2\int_0^\infty e^{-2\alpha r^2}rdr$$

Using u-substitution technique, $u = e^{-\alpha r^2}; \quad du = 2\alpha re^{-\alpha r^2}dr$

$$\langle\psi_2|V|\psi_2\rangle = -\pi ke^2\sqrt{\frac{8\alpha^3}{\pi^3}}\frac{1}{\alpha} = -2ke^2\sqrt{\frac{2\alpha}{\pi}}$$
$$\langle\psi_2|H|\psi_2\rangle = E(\alpha) = \frac{3\hbar^2\alpha}{2m} - 2ke^2\sqrt{\frac{2\alpha}{\pi}}$$
$$\frac{dE(\alpha)}{d\alpha} = 0 \implies \frac{3\hbar^2}{2m} - ke^2\sqrt{\frac{2}{\pi\alpha}} = 0 \implies \alpha^* = \frac{8e^4k^2m^2}{9\pi\hbar^4}$$
$$E(\alpha^*) = \frac{e^4k^2m}{2\hbar^2}\left[\frac{8}{3\pi} - \frac{16}{3\pi}\right] = -\frac{8}{3\pi}Ry > E_{gs}$$

Trial wavefunction: $\psi_3(r) = \begin{cases} A(R-r) & 0 \le r \le R \\ 0 & \textbf{elsewhere} \end{cases}$

$$\langle\psi_3|\psi_3\rangle = 4\pi A^2 \int_0^R (R-r)^2 r^2 dr = 4\pi A^2 \int_0^R r^4 - 2r^3 R + r^2 R^2 dr \implies A = \sqrt{\frac{15}{2\pi R^5}}$$

$$\langle\psi_3|T|\psi_3\rangle = \frac{2\hbar^2\pi}{m} A^2 \int_0^R \left|\frac{d}{dr}(R-r)\right|^2 r^2 dr = \frac{2\hbar^2\pi}{m} A^2 \frac{R^3}{3} = \frac{5\hbar^2}{mR^2}$$

$$\langle\psi_3|V|\psi_3\rangle = -4\pi ke^2 A^2 \int_0^R (R-r)^2 r dr = -\pi ke^2 A^2 \frac{R^4}{3} = -\frac{5ke^2}{2R}$$

$$\langle\psi_3|H|\psi_3\rangle = E(R) = \frac{5\hbar^2}{mR^2} - \frac{5ke^2}{2R}$$

$$\frac{dE(R)}{dR} = 0 \implies \frac{5ke^2}{2R^2} - \frac{10\hbar^2}{mR^3} = 0 \implies R^* = \frac{4\hbar^2}{ke^2 m}$$

$$E(R^*) = -\frac{5e^4k^2m}{16\hbar^2} = -\frac{5}{8}Ry > E_{gs}$$

More & Comparison

Using this Mathematica code:

```
ψ[r_] := 1/(1 + α^2 r^2)
Normalization = Solve[4 Pi A^2 Integrate[ψ[r]^2 * r^2, {r, 0, ∞}] == 1, A, Reals][[2]] // Normal;
T = A^2 (2 ℏ^2 Pi)/m Integrate[D[ψ[r], r]^2 * r^2, {r, 0, ∞}] // Normal;
V = -A^2 4 Pi k e^2 Integrate[ψ[r]^2 * r, {r, 0, ∞}] // Normal;
En = T + V /. Normalization;
astar = Assuming[{α > 0, m > 0, ℏ > 0, k > 0, e > 0}, Solve[D[En, α] == 0, α, Reals]][[1]] // Normal;
"E(α*)=" <> ToString[(Assuming[{α > 0, m > 0, ℏ > 0, k > 0, e > 0}, (En /. astar) // FullSimplify] // Quiet), TraditionalForm] // TraditionalForm
"E(α*)=" <>
  ToString[Assuming[{α > 0, m > 0, ℏ > 0, k > 0, e > 0}, (En /. astar) // FullSimplify] * 1/e /. ℏ → 1.054571817 * 10^-34 /. k → 9 * 10^9 /. e → 1.6 * 10^-19 /.
    m → 9.1093837 × 10^-31, TraditionalForm] <> "eV" // TraditionalForm
```

Figure 1: Mathematica code used to obtain the results for ψ_4

Using the code to obtain the results for ψ_4, then making a table of comparison:

ψ_{trial}	$e^{-\alpha r}$	$e^{-\alpha r^2}$	$(R-r)$	$\frac{1}{1+(\alpha r)^2}$
$E(\alpha^*)$	$-Ry$	$-\frac{8}{3\pi}Ry$	$-\frac{5}{8}Ry$	$-\frac{8}{\pi^2}Ry$
%Difference	0%	15.1%	37.5%	18.9%

Table 1: Results