PROBLEM 5: Variational Method

In the x-basis, the Hamiltonian for a hydrogen atom is

$$\begin{aligned} H &= \frac{P^2}{2m} - \frac{e^2}{r} \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{e}{r}. \end{aligned}$$

Let us choose

$$\psi_\alpha(r) = e^{-\alpha r^2}, \quad \alpha > 0$$

as a trial wave function for the ground state.

(a) [2 points] Find $\langle \psi_\alpha | \psi_\alpha \rangle$. (**N.B.** This wave function is not normalized.)

(b) [4 points] Find the expectation value of the Hamiltonian $\langle H \rangle$.

(c) [4 points] Determine the best bound on the energy for the ground state of this system using the variational method and the trial wave function given above.

(a)

Our Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e}{r}$$

and the trial wavefunction is

$$\psi_\alpha(r) = e^{-\alpha r^2},$$

where α is the variational parameter. Then

$$\langle\psi_\alpha|\psi_\alpha\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}|e^{-\alpha r^2}|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 e^{-2\alpha r^2} dr \sin\theta \, d\theta \, d\phi$$

$$= \int_0^{2\pi}\int_0^{\pi} \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} \sin\theta \, d\theta \, d\phi$$

$$= \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} \cdot 4\pi$$

$$= \frac{\pi}{2\alpha}\sqrt{\frac{\pi}{2\alpha}}$$

$$\boxed{\langle\psi_\alpha|\psi_\alpha\rangle = \left(\frac{\pi}{2\alpha}\right)^{3/2}}$$

Normalizing ...

$$A^2\left[\left(\frac{\pi}{2\alpha}\right)^{3/2}\right] = 1$$

$$A = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

so

$$\boxed{\psi_\alpha = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}}.$$

(b)

$$\langle H\rangle = \langle \Psi_\alpha | H | \Psi_\alpha\rangle$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-\alpha r^2}\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{e}{r}\right)\left(e^{-\alpha r^2}\right) r^2 dr \sin\theta \, d\theta d\phi$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 e^{-\alpha r^2}\sin\theta\left[\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-\alpha r^2}\right)-\frac{e}{r}e^{-\alpha r^2}\right]dr\,d\theta\,d\phi$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 e^{-\alpha r^2}\sin\theta\left[\frac{-\hbar^2}{2m}\left(4\alpha^2 r^2 e^{-\alpha r^2}-6\alpha e^{-\alpha r^2}\right)-\frac{e}{r}e^{-\alpha r^2}\right]dr\,d\theta\,d\phi$$

$$= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\int_0^{\infty}\left[\frac{-\hbar^2}{2m}\left(4\alpha^2 r^4 e^{-2\alpha r^2}\right)-\frac{\hbar^2}{2m}\left(-6\alpha r^2 e^{-2\alpha r^2}\right)-e\,r\,e^{-2\alpha r^2}\right]dr$$

$$= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\left[-\frac{4\alpha^2\hbar^2}{2m}\left(\frac{3}{4\alpha^3}\right)+\frac{6\alpha\hbar^2}{2m}\left(\frac{1}{4\alpha^3}\right)-e\left(\frac{1}{4\alpha^2}\right)\right]$$

$$= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\left[-\frac{3\hbar^2}{2m}\frac{1}{\alpha^3}+\frac{3\hbar^2}{4m}\frac{1}{\alpha^2}-\frac{e}{4\alpha^2}\right]$$

$$\boxed{\langle H\rangle = \pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\left[-\frac{6\hbar^2}{m\alpha^3}+\frac{3\hbar^2}{m\alpha^2}-\frac{e}{\alpha^2}\right]}$$

or

$$\langle H\rangle = \sqrt{\frac{8}{\pi}}\left[-\frac{6\hbar^2}{m\alpha^{3/2}}+\frac{3\hbar^2}{m\alpha^{1/2}}-\frac{e}{\alpha^{1/2}}\right].$$

(c)

We know

$$\langle \psi_\alpha | H | \psi_\alpha \rangle \geq E_0 ,$$

where E_0 is the actual ground state energy. We want to minimize $\langle H \rangle$ with respect to the variational parameter α,

$$\frac{d\langle H \rangle}{d\alpha} = 0 .$$

So

$$\frac{d\langle H\rangle}{d\alpha} = \sqrt{\frac{8}{\pi}}\left[-\frac{6\hbar^2}{m}\left(-\frac{3}{2\alpha^{5/2}}\right) + \frac{3\hbar^2}{m}\left(-\frac{1}{2\alpha^{3/2}}\right) - e\left(-\frac{1}{2\alpha^{3/2}}\right)\right]$$

$$= \sqrt{\frac{8}{\pi}}\left[\frac{9\hbar^2}{m\alpha^{5/2}} - \frac{3\hbar^2}{2m\alpha^{3/2}} + \frac{e}{2\alpha^{3/2}}\right],$$

and

$$\frac{d\langle H\rangle}{d\alpha} = 0$$

$$\sqrt{\frac{8}{\pi}}\left[\frac{9\hbar^2}{m\alpha^{5/2}} - \frac{3\hbar^2}{2m\alpha^{3/2}} + \frac{e}{2\alpha^{3/2}}\right] = 0$$

$$\frac{9\hbar^2}{m\alpha^{5/2}} - \frac{1}{2\alpha^{3/2}}\left(-e + \frac{3\hbar^2}{m}\right) = 0$$

$$\frac{9\hbar^2}{m\alpha^{5/2}} = \frac{1}{2\alpha^{3/2}}\left(\frac{3\hbar^2}{m} - e\right)$$

$$\frac{9\hbar^2}{m} = \frac{\alpha}{2}\left(\frac{3\hbar^2}{m} - e\right)$$

(c), cont'd...

$$\frac{\alpha}{2} = \frac{9\hbar^2}{3\hbar^2 - em}$$

$$\alpha = \frac{18\hbar^2}{3\hbar^2 - em}$$

or

$$\alpha = \frac{18}{3 - \frac{em}{\hbar^2}}.$$

Plugging back into $\langle H \rangle$ gives us an expression for the upper bound on the ground state energy.

$$\langle H \rangle = \sqrt{\frac{8}{\pi}}\left[-\frac{6\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2} + \left(\frac{3\hbar^2}{m} - e\right)\left(\frac{3 - em/\hbar^2}{18}\right)^{1/2}\right]$$

$$= \sqrt{\frac{8}{\pi}}\left[-\frac{6\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2} + \frac{\hbar^2}{m}\left(3 - \frac{em}{\hbar^2}\right)\left(\frac{3 - em/\hbar^2}{18}\right)^{1/2}\right]$$

$$= \sqrt{\frac{8}{\pi}}\left[\frac{18\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2} - \frac{6\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2}\right]$$

$$= \sqrt{\frac{8}{\pi}}\left[\frac{12\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2}\right]$$

$$\boxed{\langle H \rangle = \frac{24\sqrt{2}}{\sqrt{\pi}}\frac{\hbar^2}{m}\left(\frac{3 - em/\hbar^2}{18}\right)^{3/2} \geq E_0}$$