PH423 Assignment 3

Parth Sastry
180260026

Sahas Kamat
180260030

Sankalp Gambhir
180260032

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Question 2.

The Hamiltonian for an electron in the Hydrogen atom is

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \tag{1}$$

obtained from

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + P(\vec{r}) = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

and then expressing the Laplacian in spherical coordinates and setting Z = 1. Here μ is the reduced mass of the system.

The only undetermined parameter in our trial wavefunction is α. We'll have to minimize the expectation value of the Hamiltonian of an electron in a Hydrogen atom (1) with respect to this undetermined parameter by solving

$$\frac{d\langle H\rangle(\alpha)}{d\alpha} = 0 \tag{2}$$

So the first thing to do is to solve for $\langle H\rangle$, and then minimize this value with respect to α

$$\langle H\rangle = \frac{\langle\psi|\, H\, |\psi\rangle}{\langle\psi|\psi\rangle}$$

in wave function formalism, this takes the form of an integral over all space.

$$\langle H\rangle = \frac{\iiint_{allspace}(r^2 sin(\theta))\psi^*(r,\theta,\phi)\hat{H}\psi(r,\theta,\phi)\,dr\,d\theta\,d\phi}{\iiint_{allspace}(r^2 sin(\theta))\psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\,dr\,d\theta\,d\phi} \tag{3}$$

Our trial wave function, as given in the question, is real-valued, and spherically symmetric.
We first calculate the norm of the wave function. Our trial wave function is

$$\psi_\alpha(r) = \begin{cases}\left(1 - \frac{r}{\alpha}\right) & r \leqslant \alpha, \\ 0 & r \geqslant \alpha\end{cases}$$

$$
\begin{aligned}
therefore\, \langle\psi|\psi\rangle &= \iiint_{allspace} (r^2 sin(\theta))\psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, dr\, d\theta\, d\phi \\
&= 4\pi \int_0^\infty r^2\psi^2(r)\, dr \\
&= 4\pi \int_0^\alpha r^2 \left(1-\frac{r}{\alpha}\right)^2 dr \\
&= 4\pi \int_0^\alpha \left(r^2 - \frac{2r^3}{\alpha} + \frac{r^4}{\alpha^2}\right) dr \\
&= 4\pi \frac{\alpha^3}{30}
\end{aligned}
$$

Due to the symmetries in the system, the numerator in 3 takes the form

$$
\langle\psi| H |\psi\rangle = 4\pi \int_0^\infty r^2\psi(r)\hat{H}\psi(r)\, dr
$$

We need to find out what the action on the Hamiltonian operator on our trial wavefunction is.

$$
\begin{aligned}
\hat{H}\psi(r) &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r)}{\partial r}\right)\right] - \frac{e^2}{4\pi\varepsilon_0}\frac{\psi(r)}{r} \\
&= -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(\frac{-r^2}{\alpha}\right)\right] - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}-\frac{1}{\alpha}\right) \\
&= -\frac{\hbar^2}{2\mu r^2}\left[\frac{-2r}{\alpha}\right] - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}-\frac{1}{\alpha}\right) \\
&= \frac{\hbar^2}{\mu r\alpha} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}-\frac{1}{\alpha}\right)
\end{aligned}
$$

The above derivation for $\hat{H}\psi(r)$ is for $r \leqslant \alpha$. For $r \geqslant \alpha$, our wavefunction is zero, and this $\hat{H}\psi(r)$ also evaluates to zero.
Thus, for $\langle\psi| H |\psi\rangle$, we have

$$
\begin{aligned}
\langle\psi|\,H\,|\psi\rangle &= 4\pi \int_0^\infty r^2 \psi(r)\hat{H}\psi(r)\,dr \\
&= 4\pi \int_0^\alpha r^2 \left(1 - \frac{r}{\alpha}\right) \left[\frac{\hbar^2}{\mu r \alpha} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{1}{\alpha}\right)\right] dr \\
&= 4\pi \int_0^\alpha \left(1 - \frac{r}{\alpha}\right) \left[\frac{\hbar^2 r}{\mu \alpha} - \frac{e^2}{4\pi\varepsilon_0}\left(r - \frac{r^2}{\alpha}\right)\right] dr \\
&= 4\pi \int_0^\alpha \left[\left(\frac{\hbar^2}{\mu\alpha} - \frac{e^2}{4\pi\varepsilon_0}\right) r + \left(-\frac{\hbar^2}{\mu\alpha^2} + \frac{e^2}{2\pi\varepsilon_0\alpha}\right) r^2 - \left(\frac{e^2}{4\pi\varepsilon_0\alpha^2}\right) r^3\right] dr \\
&= 4\pi \left[\left(\frac{\hbar^2}{\mu\alpha} - \frac{e^2}{4\pi\varepsilon_0}\right) \frac{\alpha^2}{2} + \left(-\frac{\hbar^2}{\mu\alpha^2} + \frac{e^2}{2\pi\varepsilon_0\alpha}\right) \frac{\alpha^3}{3} - \left(\frac{e^2}{4\pi\varepsilon_0\alpha^2}\right) \frac{\alpha^4}{4}\right] \\
&= 4\pi \left[\frac{\hbar^2}{\mu}\left(\frac{\alpha}{2} - \frac{\alpha}{3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{\alpha^2}{2} + \frac{2\alpha^2}{3} - \frac{\alpha^2}{4}\right)\right] \\
&= 4\pi \left(\frac{\hbar^2\alpha}{6\mu} - \frac{\alpha^2 e^2}{48\pi\varepsilon_0}\right)
\end{aligned}
$$

Using this result, and our result for the norm of ψ, we have

$$
\begin{aligned}
\langle H\rangle &= \frac{4\pi\left(\frac{\hbar^2\alpha}{6\mu} - \frac{\alpha^2 e^2}{48\pi\varepsilon_0}\right)}{4\pi\frac{\alpha^3}{30}} \\
&= 30\left(\frac{\hbar^2}{6\mu\alpha^2} - \frac{e^2}{48\pi\varepsilon_0\alpha}\right)
\end{aligned}
$$

Substituting this in 2, we have

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

$$
\begin{aligned}
\therefore \frac{d}{d\alpha}\left(\frac{\hbar^2}{6\mu\alpha^2} - \frac{e^2}{48\pi\varepsilon_0\alpha}\right) &= 0 \\
\implies \left(-\frac{\hbar^2}{3\mu\alpha_{min}^3} + \frac{e^2}{48\pi\varepsilon_0\alpha_{min}^2}\right) &= 0 \\
\implies \alpha_{min} &= \frac{16\pi\varepsilon_0\hbar^2}{\mu e^2}
\end{aligned}
$$

The variational bound on the ground state energy is given by

$$
\begin{aligned}
\langle H\rangle_{min} &= 30\left(\frac{\hbar^2}{6\mu\alpha_{min}^2} - \frac{e^2}{48\pi\varepsilon_0\alpha_{min}}\right) \\
&= 30\left(\frac{\mu e^4}{6*256\pi^2\varepsilon_0^2\hbar^2} - \frac{\mu e^4}{3*256\pi^2\varepsilon_0^2\hbar^2}\right) \\
&= 30\left(-\frac{\mu e^4}{6*256\pi^2\varepsilon_0^2\hbar^2}\right) \\
&= -\frac{5\mu e^4}{256\pi^2\varepsilon_0^2\hbar^2}
\end{aligned}
$$

This value of α_{min} that we obtained is 4 times the reduced Bohr radius.

$$
\begin{aligned}
\alpha_{min} &= \frac{16\pi\varepsilon_0\hbar^2}{\mu e^2} \\
a_0^* &= \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \\
\therefore\ \alpha_{min} &= 4a_0^*
\end{aligned}
\tag{4}
$$

Question 7.

The expectation value of the hamiltonian using this trial wavefunction may be written as:

$$
\frac{\langle\psi_\alpha|\,H\,|\psi_\alpha\rangle}{\langle\psi_\alpha|\psi_\alpha\rangle} \tag{5}
$$

In the position basis, this expression becomes:

$$
\frac{\int_{-\infty}^{\infty}\frac{1}{x^2+\alpha^2}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{Kx^2}{2}\right)\frac{1}{x^2+\alpha^2}dx}{\int_{-\infty}^{\infty}\frac{1}{(x^2+\alpha^2)^2}dx} \tag{6}
$$

Simplifying, we get the following integral for the Kinetic part of the numerator:

$$
\langle T\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\frac{1}{x^2+\alpha^2}\frac{\partial^2}{\partial x^2}\frac{1}{x^2+\alpha^2}dx \tag{7}
$$

Integrating by parts and using the fact that $\frac{1}{(x^2+\alpha^2)^2}$ falls to zero faster than x at $\pm\infty$ we get:

$$\begin{aligned}\langle T\rangle &= \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}(\frac{\partial}{\partial x}\frac{1}{x^2+\alpha^2})^2 dx \\ &= \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\frac{4x^2}{(x^2+\alpha^2)^4}dx\end{aligned} \tag{8}$$

Using the substitution $x = \alpha \tan\theta$ we get

$$\langle T\rangle = \frac{2\hbar^2}{m\alpha^5}\int_{-\pi/2}^{+\pi/2}\cos^4\theta\sin^2\theta d\theta \tag{9}$$

This can be written in terms of the beta function:

$$\langle T\rangle = \frac{2\hbar^2}{m\alpha^5}B(3/2,5/2) = \frac{\pi\hbar^2}{8m\alpha^5} \tag{10}$$

Now we calculate the potential energy term in the numerator:

$$\langle V\rangle = \int_{-\infty}^{\infty}\frac{Kx^2}{2}\frac{1}{(x^2+\alpha^2)^2}dx \tag{11}$$

We use the same substitution as above to get:

$$\langle V\rangle = \frac{K}{2\alpha}\int_{-\pi/2}^{+\pi/2}\sin^2\theta d\theta = \frac{K\pi}{4\alpha} \tag{12}$$

The denominator is the following integral:

$$\int_{-\infty}^{\infty}\frac{1}{(x^2+\alpha^2)^2}dx \tag{13}$$

Again using the same $x = \alpha\tan\theta$ substitution:

$$\int_{-\pi/2}^{+\pi/2}\frac{1}{\alpha^3}\cos^2\theta d\theta = \frac{\pi}{2\alpha^3} \tag{14}$$

Finally, we get for the expectation value of H:

$$\langle H\rangle = \frac{\hbar^2}{4\alpha^2 m} + \frac{k\alpha^2}{2} \tag{15}$$

We use the AM-GM inequality to find a lower bound for $\langle H\rangle$:

$$\langle H \rangle_{min} = \hbar\sqrt{\frac{k}{2m}} \tag{16}$$

The value of α that gives us this minumum value will be the one for which both terms are equal:

$$\alpha_0 = \sqrt[4]{\frac{\hbar^2}{2km}} \tag{17}$$

Question 8.

(a) Writing matrices for the Hamiltonians $\hat{\mathbf{H}}_0$ and $\hat{\mathbf{H}}'$ with ψ_a and ψ_b as basis

$$\hat{\mathbf{H}}_0 = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix}, \tag{18}$$

$$\hat{\mathbf{H}}' = \begin{pmatrix} E_a & h \\ h & E_b \end{pmatrix} \text{ , and} \tag{19}$$

$$\begin{aligned} \hat{\mathbf{H}} &= \hat{\mathbf{H}}_0 + \hat{\mathbf{H}}' \\ &= \begin{pmatrix} 2E_a & h \\ h & 2E_b \end{pmatrix} . \end{aligned} \tag{20}$$

The eigenvalues for this combined Hamiltonian are easily calculated by considering the eigenvalue equation and taking a determinant to get $\det(E \cdot \hat{\mathbf{1}} - \hat{\mathbf{H}}) = 0$. The eigenvalues E which solve this equation are thus given by

$$(E - 2E_a) \cdot (E - 2E_b) - h^2 = 0 \tag{21}$$

$$E = (E_a + E_b) \pm \sqrt{(E_a + E_b)^2 + h^2} \tag{22}$$

We can also obtain the eigenvectors (c_1, c_2) from the same equation, obtaining easily the relation

$$\frac{c_1}{c_2} = \frac{(E_b - E_a) \pm \sqrt{(E_b - E_a)^2 + h^2}}{h} \tag{23}$$

We note that the two summands on the right side can be split using the familiar trigonometric identity between the tangent and secant to get

$$\frac{c_1}{c_2} = \tan\alpha \pm \sec\alpha \tag{24}$$

(b) To obtain an estimate of the ground state energy, we assume the trial wavefunction of the form $\psi = \cos\theta \cdot \phi_a + \sin theta \cdot \phi_b$. Notably, the state is assumed to be normalized. Hence, the energy eigenvalues are obtained simply by calculating the expectation value of the Hamiltonian $\hat{\mathbf{H}}$ and minimizing it with respect to the parameter θ

$$\langle\psi|\,\hat{\mathbf{H}}|\psi\rangle = \begin{pmatrix}\cos\theta & \sin\theta\end{pmatrix}\begin{pmatrix}2E_a & h \\ h & 2E_b\end{pmatrix}\begin{pmatrix}\cos\theta \\ \sin\theta\end{pmatrix} \tag{25}$$

$$= 2E_a\cos^2\theta + 2E_b\sin^2\theta + 2h\cos\theta\sin\theta \tag{26}$$

and minimizing

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\langle\psi|\,\hat{\mathbf{H}}|\psi\rangle = 0$$

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left(2E_a\cos^2\theta + 2E_b\sin^2\theta + 2h\cos\theta\sin\theta\right) = 0$$

$$-4E_a\cos\theta\sin\theta + 4E_b\sin\theta\cos\theta + 2h\cos^2\theta - 2h\sin^2\theta = 0\ . \tag{27}$$

Observing that this can be converted to an equation in $\cos 2\theta$ and $\sin 2\theta$, and finally dividing by $\cos 2\theta$ we get an equation solely in the tangent

$$\tan 2\theta = \frac{h}{E_a - E_b} \tag{28}$$

Recognizing this as the tangent substitution we performed in part a, we get

$$\tan 2\theta = -\cot\alpha\ . \tag{29}$$

Using the tangent double-angle formula and solving the resultant quadratic equation, we obtain the ratio

$$\tan\theta = \frac{\sin\theta}{\cos\theta} = \tan\alpha \pm \sec\alpha \tag{30}$$

which are precisely the eigenvectors we got in part a! So the expectation values corresponding to these are given by the eigenvalues themselves.

The variational principle is accurate in this case because the trial wavefunction spans the entire state space, so minimizing over it, we guarantee a global minima.