VARIATIONAL PRINCIPLE AND L=1 STATES OF THE HYDROGEN ATOM

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Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Section 16.1; Exercise 16.1.5.

Here we'll apply the variational principle to the hydrogen atom. In the problem, Shankar asks us to look at the $l=1$ states but does not specify the principal quantum number n, so I'll assume he wants us to solve the problem for the lowest value of n for which we can have an $l=1$ state, which is $n=2$.

To review, the wave function for hydrogen is given as

$$\begin{aligned}
\psi_{nlm}(r,\theta,\phi) &= R_{nl}(r)Y_l^m(\theta,\phi) &(1)\\
u_{nl}(\rho) &= \rho^{l+1}e^{-\rho}v_{nl}(\rho) &(2)\\
u_{nl}(r) &\equiv rR_{nl}(r) &(3)\\
\rho &= \kappa r &(4)\\
\rho_0 &= \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} &(5)\\
\kappa &= \frac{\sqrt{-2mE}}{\hbar} &(6)
\end{aligned}$$

The solution was expressed as a series:

$$v_{nl}(\rho)=\sum_{j=0}^{\infty}c_j\rho^j \tag{7}$$

with the coefficients c_j satisfying a recursion relation:

$$c_{j+1}=\frac{2(j+l+1)-\rho_0}{(j+1)(j+2(l+1))}c_j \tag{8}$$

To keep the wave function finite as $r\to\infty$, the series for v_{nl} must terminate, which gives rise to the quantization condition $n=j+l+1$. If we specify n and l, then we get the maximum value of $j_{max}=n-l-1$ that appears in the series 7. If we take $n=2$ and $l=1$, then $j_{max}=0$, which means that v_{21} is a constant. The wave function therefore has the form

$$\psi_{21m}(r,\theta,\phi) = R_{21}(r)\,Y_1^m(\theta,\phi) \tag{9}$$

$$= \frac{u_{21}(r)}{r}Y_1^m(\theta,\phi) \tag{10}$$

$$= Are^{-ar}Y_1^m(\theta,\phi) \tag{11}$$

for constants A (determined by normalization) and a. Since the quantum number m (for the z component of angular momentum) appears only in the form $e^{im\phi}$ in the spherical harmonic $Y_1^m(\theta,\phi)$, it will disappear when we calculate matrix elements.

The trial function given by 11 incorporates the required limiting behaviour of the wave function, since it behaves as r as $r\to 0$ and as e^{-ar} as $r\to\infty$. The number of nodes in the wave function is determined by the degree of the polynomial v_{nl} and since this is constant, there are no nodes. (If we wanted to solve the system for, say, $n=3$ and $l=1$, then $j_{max}=1$ in 7 and we would have a single node.)

To apply the variational principle, we first need to find $\langle\psi|\psi\rangle$. Since the spherical harmonics are normalized already and are the only place where the angular variables occur, we can ignore them in what follows and just concentrate on the radial bits. Our trial function is therefore

$$R = Are^{-ar} \tag{12}$$

Therefore

$$\langle\psi|\psi\rangle = \int_0^\infty \left(Are^{-ar}\right)^2 r^2 dr \tag{13}$$

$$= \frac{3A^2}{4a^5} \tag{14}$$

where as usual I'm using Maple to do the integrals.

The function $R(r)$ satisfies the radial equation which is

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V(r)\right)R = ER \tag{15}$$

In our case, $l=1$ and $V=-\frac{e^2}{r}$ so we have

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{\hbar^2}{m}\frac{1}{r^2}-\frac{e^2}{r}\right)R = ER \tag{16}$$

If we call the operator on the LHS H_R then the matrix element is

$$\langle H_R\rangle = \langle R|H_R|R\rangle \tag{17}$$

The derivative term is (Maple again):

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{\hbar^2}{2m}A\frac{e^{-ar}}{r}\left(a^2r^2-4ar+2\right) \tag{18}$$

Therefore (again, remember that the angular integral comes out to 1):

$$\langle\psi|H_R|\psi\rangle = A^2\int_0^\infty re^{-ar}\left[-\frac{\hbar^2}{2m}\frac{e^{-ar}}{r}\left(a^2r^2-4ar+2\right)+\right. \tag{19}$$

$$\left.\left(\frac{\hbar^2}{m}\frac{1}{r^2}-\frac{e^2}{r}\right)re^{-ar}\right]r^2dr \tag{20}$$

$$= \frac{3}{8}A^2\frac{a\hbar^2-me^2}{ma^4} \tag{21}$$

Our estimate for the energy is therefore

$$\langle E\rangle = \frac{\langle\psi|H_R|\psi\rangle}{\langle\psi|\psi\rangle} \tag{22}$$

$$= \frac{\left(\hbar^2a-me^2\right)a}{2m} \tag{23}$$

To find the bound on the energy, we take the derivative and solve

$$\frac{d\langle E\rangle}{da} = \frac{\hbar^2a}{m}-\frac{e^2}{2} = 0 \tag{24}$$

$$a_0 = \frac{me^2}{2\hbar^2} \tag{25}$$

Plugging this back into 23 we find

$$E_0 \le -\frac{me^4}{8\hbar^2} \tag{26}$$

This is, in fact, the exact answer for $n=2$, which isn't terribly surprising, since our choice for the trial function is in fact the correct form of the exact equation.