

WKB APPROXIMATION AND THE HYDROGEN ATOM

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 8.14.

As another example of applying the WKB approximation to a 3-d problem with a spherically symmetric potential, we'll look at the radial equation for the hydrogen atom.

The general wave function can be written as the product of a radial function $R(r)$ and a spherical harmonic $Y(\theta, \phi)$.

With the substitution $u(r) \equiv rR(r)$ the radial equation for hydrogen can be written

$$(1) \quad -\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left(-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right) u = Eu$$

The effective potential is the term in parentheses:

$$(2) \quad V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

and has the form of a well with sloping sides on both sides, at points r_1 and r_2 defined by the roots of

$$(3) \quad E = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

In this case, the WKB equations satisfy the condition

$$(4) \quad \int_{r_1}^{r_2} p(r) dr = \left(n - \frac{1}{2} \right) \pi \hbar$$

Plugging in the formulas for the hydrogen atom we get

$$(5) \quad \int_{r_1}^{r_2} p(r) dr = \sqrt{2m} \int_{r_1}^{r_2} \sqrt{E + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}} dr$$

$$(6) \quad = \sqrt{-2mE} \int_{r_1}^{r_2} \frac{1}{r} \sqrt{-r^2 - \frac{e^2}{4\pi\epsilon_0 E} r + \frac{\hbar^2}{2mE} l(l+1)} dr$$

where we've factored out $-E$ (since for a bound state, $E < 0$). We can simplify the notation by defining the positive quantities

$$(7) \quad B \equiv -\frac{e^2}{4\pi\epsilon_0 E}$$

$$(8) \quad C \equiv -\frac{\hbar^2}{2mE} l(l+1)$$

The turning points r_1 and r_2 can be found from the roots of the term inside the square root in 6:

$$(9) \quad r_1 = \frac{B - \sqrt{B^2 - 4C}}{2}$$

$$(10) \quad r_2 = \frac{B + \sqrt{B^2 - 4C}}{2}$$

so we can factor the quadratic to get

$$\begin{aligned}
(11) \quad \int_{r_1}^{r_2} p(r) dr &= \sqrt{-2mE} \int_{r_1}^{r_2} \frac{1}{r} \sqrt{(r-r_1)(r_2-r)} dr \\
(12) \quad &= \sqrt{-2mE} \frac{\pi}{2} (\sqrt{r_2} - \sqrt{r_1})^2 \\
(13) \quad &= \sqrt{-2mE} \frac{\pi}{2} (r_1 + r_2 - 2\sqrt{r_1 r_2}) \\
(14) \quad &= \sqrt{-2mE} \frac{\pi}{2} (B - 2\sqrt{C}) \\
(15) \quad &= \sqrt{-2mE} \frac{\pi}{2} \left(-\frac{e^2}{4\pi\epsilon_0 E} - 2\sqrt{-\frac{\hbar^2}{2mE} l(l+1)} \right) \\
(16) \quad &= \frac{\pi}{2} \left(-\frac{e^2 \sqrt{2m}}{4\pi\epsilon_0 \sqrt{-E}} - 2\hbar \sqrt{l(l+1)} \right) \\
(17) \quad &= \left(n - \frac{1}{2} \right) \pi \hbar
\end{aligned}$$

where we've used the integral given in Griffiths's question to get the second line, and the last line uses 4. Solving 16 for E gives the WKB energy levels:

$$\begin{aligned}
(18) \quad E &= - \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar^2 \left(n - \frac{1}{2} + \sqrt{l(l+1)} \right)^2} \\
(19) \quad &= \frac{-13.6 \text{ eV}}{\left(n - \frac{1}{2} + \sqrt{l(l+1)} \right)^2}
\end{aligned}$$

since the ground state of hydrogen is given by the Bohr formula

$$(20) \quad E_0 = - \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar^2} = -13.6 \text{ eV}$$