Ground State Hydrogen Energy via Variational Principles

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To demonstrate the how the variational principle is used, we can estimate the ground state energy of hydrogen including relativistic fine structure corrections. We will use an exponential as our wavefunctional form,

$$\psi_{var} = Ae^{-br} \tag{1}$$

since it is a very popular choice due to making the integrals rather easy to evaluate. The ground state of hydrogen 'happens' to actually be of this form, specifically

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \tag{2}$$

which means that our estimate of the ground state energy should be very close to the actual value. We can also check the optimal parameter value of b and make sure that it comes out to be $1/a$ as further evidence of the validity of the method.

The first step is to determine the normalization of our form:

$$\int d^3\vec{r}|\psi_{var}(r)|^2 = 1 = |A|^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta e^{-2br} dr d\theta d\phi \tag{3}$$

The angular integral is very easy to evaluate since we assume our wavefunction has no dependence on θ or ϕ:

$$|A|^2 4\pi \int_0^\infty r^2 e^{-2br} dr \tag{4}$$

Using integration by parts, we get that our r integral is

$$\int_0^\infty r^2 e^{-2br} dr = \left(\frac{-r}{2b} - \frac{r}{b^2} - \frac{1}{4b^3} \right) e^{-2br} \Bigg|_0^\infty \tag{5}$$

We can show using L'Hopital's rule that the first two terms are zero when plugging in ∞, leaving us with only the last term evaluated at 0.

$$|A|^2 4\pi \left(\frac{1}{4b^3} \right) = 1 \rightarrow A = \sqrt{\frac{b^3}{\pi}} \tag{6}$$

$$\psi_{var} = \sqrt{\frac{b^3}{\pi}} e^{-br} \tag{7}$$

Now that we have our variational ansatz, we need to put the Hamiltonian in a form where we can easily evaluate the expectation value $\langle\psi_{var}| \hat{H} |\psi_{var}\rangle$. Beginning with just the Bohr Hamiltonian:

$$\hat{H}_{Bohr} = \frac{-\hbar^2}{2m} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{8}$$

Since our wavefunction is assumed to be spherically symmetric, we can simplify the Laplacian to:

$$\hat{H}_{Bohr} = \frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r} \tag{9}$$

When considering fine structure corrections, there are two new terms in the Hamiltonian: the relativistic term and the spin-orbit coupling term.

$$\hat{H}_r = \frac{-p^4}{8m^3c^2}, \quad \hat{H}_{so} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2c^2r^3} \vec{S} \cdot \vec{L} \tag{10}$$

We can put the relativistic term into a good form using the definition of p:

$$\hat{H}_r = \frac{-(-i\hbar\vec{\nabla})^4}{8m^3c^2} = \frac{-\hbar^4\nabla^4}{8m^3c^2} = \frac{-\hbar^4}{8m^3c^2}\vec{\nabla}^4 \tag{11}$$

Spin-orbit coupling is a little harder to put in a form that is convenient to work with, due both to the $\vec{S}\cdot\vec{L}$ and the $\frac{1}{r^3}$. Due to these reasons, we will ignore this term, and just compare the relativistic correction to the ground state energy.

With this in mind, our final Hamiltonian is

$$\hat{H} = \hat{H}_{Bohr} + \hat{H}_r = \frac{-\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} + \frac{-\hbar^4}{8m^3c^2}\vec{\nabla}^4 \tag{12}$$

We now want to evaluate the expectation value $\langle\hat{H}\rangle$:

$$\langle\hat{H}\rangle = \langle\psi_{var}|\,\hat{H}\,|\psi_{var}\rangle = \frac{-\hbar^2}{2m}\int\left(\sqrt{\frac{b^3}{\pi}}e^{-br}\right)\left(\vec{\nabla}^2\sqrt{\frac{b^3}{\pi}}e^{-br}\right)d^3\vec{r} \tag{13}$$

$$-\frac{e^2}{4\pi\epsilon_0}\int\left(\sqrt{\frac{b^3}{\pi}}e^{-br}\right)\frac{1}{r}\left(\sqrt{\frac{b^3}{\pi}}e^{-br}\right)d^3\vec{r} - \frac{\hbar^4}{8m^3c^2}\int\left(\sqrt{\frac{b^3}{\pi}}e^{-br}\right)\left(\vec{\nabla}^4\sqrt{\frac{b^3}{\pi}}e^{-br}\right)d^3\vec{r}$$

Let's evaluate each of these terms separately, since they are reasonably complicated. Starting with the first:

$$\frac{-\hbar^2b^3}{2m\pi}\int e^{-br}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}e^{-br}\right)d^3\vec{r} = \frac{-\hbar^2b^3}{2m\pi}(4\pi)(-b)\int_0^\infty e^{-br}\frac{d}{dr}\left(r^2e^{-br}\right)dr \tag{14}$$

$$= \frac{2\hbar^2b^4}{m}\int_0^\infty e^{-2br}\left(2r - br^2\right)dr \tag{15}$$

We can evaluate these two integrals using integration by parts:

$$\int_0^\infty re^{-2br}dr = \left(\frac{-r}{2b} - \frac{1}{4b^2}\right)e^{-2br}\Big|_0^\infty = \frac{1}{4b^2} \tag{16}$$

$$\int_0^\infty r^2e^{-2br}dr = \left(\frac{-r^2}{2b} - \frac{r}{2b^2} - \frac{1}{4b^3}\right)e^{-2br}\Big|_0^\infty = \frac{1}{4b^3} \tag{17}$$

Plugging back into the first term, we have

$$\frac{2\hbar^2b^4}{m}\left(\frac{2}{4b^2} - \frac{b}{4b^3}\right) = \frac{\hbar^2b^2}{2m} \tag{18}$$

Next up, we can evaluate the second term, where we will be able to reuse one of the results from integration by parts above.

$$-\frac{e^2}{4\pi\epsilon_0}\frac{b^3}{\pi}(4\pi)\int_0^\infty re^{-2br}dr = -\frac{e^2}{4\pi\epsilon_0}\frac{b^3}{\pi}(4\pi)\frac{1}{4b^2}dr = \frac{-e^2b}{4\pi\epsilon_0} \tag{19}$$

Now the last term will be a bit more involved than the previous two, but we can follow the same general procedure.

$$-\frac{\hbar^4}{8m^3c^2}\frac{b^3}{\pi}\int\left(e^{-br}\right)\left(\vec{\nabla}^4e^{-br}\right)d^3\vec{r} = -\frac{\hbar^4}{8m^3c^2}\frac{b^3}{\pi}(4\pi)\int_0^\infty\left(e^{-br}\right)\left(\vec{\nabla}^2\vec{\nabla}^2e^{-br}\right)r^2dr \tag{20}$$

$$= \frac{-\hbar^4}{8m^3c^2}\frac{b^3}{\pi}(4\pi)\int_0^\infty\left(e^{-br}\right)\vec{\nabla}^2\left[\left(2r - br^2\right)e^{-br}\right]r^2dr \tag{21}$$

$$= \frac{-\hbar^4}{8m^3c^2}\frac{b^3}{\pi}(4\pi)\int_0^\infty\left(e^{-br}\right)\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\left(2r - br^2\right)e^{-br}\right]r^2dr \tag{22}$$

$$= \frac{-\hbar^4}{8m^3c^2}\frac{b^3}{\pi}(4\pi)\int_0^\infty b^3e^{-2br}\left[-4r + br^2\right]dr \tag{23}$$

This will be evaluated using integration by parts (which we have already done), and gives the following result:

$$= \frac{-\hbar^4}{8m^3c^2}\frac{b^3}{\pi}(4\pi)\frac{-3b}{4} = \frac{3\hbar^4 b^4}{8m^3c^2} \tag{24}$$

Putting all 3 terms back together (equations 18, 19, 24) we have a final parameterized energy of

$$\langle\hat{H}\rangle = \frac{\hbar^2 b^2}{2m} - \frac{e^2 b}{4\pi\epsilon_0} + \frac{3\hbar^4 b^4}{8m^3c^2} \tag{25}$$

Since we are interested in finding a minimum value of this expression, it is also helpful to take the first derivative with respect to our parameter, b:

$$\frac{d}{db}\langle\hat{H}\rangle = \frac{\hbar^2 b}{m} - \frac{e^2}{4\pi\epsilon_0} + \frac{3\hbar^4 b^3}{2m^3c^2} \tag{26}$$