b. Solution of the radial equation - the energy eigenvalues

For the hydrogen atom, the potential is the familiar Coulomb potential

\[ V(r) = -\frac{e^2}{r} \]

where \( e \) is the electronic charge and, as in most texts, we use cgs units. In atomic units \( e = 1 \).

In addition to using the Coulomb potential, we also make the substitution

\[ r = \sqrt{-\frac{\hbar^2}{8\mu E} \rho} \]

where \( E \) is the binding energy of the electron to the proton, a negative number. Also, we have temporarily dropped the \( n \) and \( \ell \) subscripts on \( E \) since we do not as yet even know that \( E \) is quantized.

With these substitutions the radial equation for the hydrogen atom becomes

\[
\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR(\rho)}{d\rho} \right) + \left[ \frac{\lambda_c}{\rho} - \frac{1}{4} - \frac{\ell(\ell + 1)}{\rho^2} \right] R(\rho) = 0
\]

where

\[ \lambda_c = \frac{e^2}{\hbar} \sqrt{\frac{\mu}{2|E|}} = \sqrt{\frac{1}{2|E|}} \quad \text{(au)} \]

and

\[ \alpha^2 = \frac{8\mu|E|}{\hbar^2} = 8|E| \quad \text{(au)} \]

By examining the asymptotic behavior of the wave function we are led to specify that
\[ \lim_{\rho \to \infty} R(\rho) = \rho^n \exp[\pm \left( \frac{\ell}{2} \right) \rho] \]

As usual, we must discard the plus sign on physical grounds.

We try the solution

\[ R(\rho) = F(\rho) \exp\left[ -\frac{1}{2} \rho \right] \]

where

\[ F(\rho) = \rho^s \left( a_0 + a_1 \rho^1 + a_2 \rho^2 + \ldots \right) = \rho^s L(\rho) \]

Substitution gives

\[ \rho^2 L''(\rho) + \rho \left[ 2(s + 1) - \rho \right] L'(\rho) + \left[ \rho(\lambda - s - 1) + s(s + 1) - \ell (\ell + 1) \right] L(\rho) = 0 \]

If \( \rho = 0 \) then

\[ s(s + 1) = \ell (\ell + 1) \quad \Rightarrow \quad s = \ell, -\ell + 1 \]

But, since the wave function must be finite at the origin, we must discard the solution \( s = -\ell + 1 \).

We have then

\[ \rho L''(\rho) + \left[ 2(\ell + 1) - \rho \right] L'(\rho) + (\lambda - \ell - 1) L(\rho) = 0 \]

Now assume that \( L(\rho) \) is given by an infinite power series in \( \rho \) and make the substitution

\[ L(\rho) = \sum_{j=1}^{\infty} a_j \rho^j \]

Notice that \( j \) is merely an index and therefore an integer. Inserting this power series in the differential equation for \( L(\rho) \) we obtain a recursion relation for the coefficients \( a_j \).
\[ a_{j+1} = \frac{j + \ell + 1 - \lambda}{(j + 1)(j + 2\ell + 2)} a_j \]

Now, examine the convergence of the series in the recursion relation

\[ \lim_{j \to \infty} \left[ \frac{a_{j+1}}{a_j} \right] \to 1 \]

This series diverges! The only way to obtain a physical solution is to force the series to terminate, that is, we drop the requirement that \( L(\rho) \) be an infinite power series. In order for the series to terminate, the numerator of the recursion relation must vanish for some value of \( \lambda \) equal to a positive integer. Recall that \( j \) is, by definition, an integer. This is a very important step. To this point there was no hint that the energy, which is contained in \( \lambda \), had to be "quantized". It is seen then that it is the necessity of convergence of the series, the requirement that the wave function be bounded, that forces quantized levels upon the hydrogen atom.

For the series to converge \( \lambda \) must be an integer that is equal to the rest of the numerator. We designate this value of \( \lambda \) by \( n \) which will, of course, turn out to be the usual principal quantum number. We also replace \( j \), the index, by \( n_r \), the "radial" quantum number. We have then

\[ \lambda = n = n_r + \ell + 1 \]

so that, going back to the definition of \( \lambda \) we have

\[ E_n = -\left| E \right| = -\frac{\mu e^4}{2\hbar^2 n^2} = -(\mu c^2) \alpha^2 \cdot \frac{1}{2n^2} = \frac{1}{2n^2} \text{ (a. u.)} = \frac{13.6 \text{ eV}}{n^2} \]

where \( \alpha = 1/137 \), the fine structure constant, and \( n \) may take on any value in the range \( 1 \leq n \leq \infty \). The last three forms of the hydrogen energy levels given above

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are particularly useful in certain circumstances. The form containing $\alpha$ is useful if it is recalled that the rest mass of the electron, $\mu c^2$, is $\sim 0.5 \text{ MeV}$. It is readily calculated that the ground state energy of the hydrogen atom is $-13.6 \text{ eV}$. Moreover, this expression explicitly shows the difference in magnitudes between nuclear and atomic binding energies. The utility of the last two forms is obvious. The expression for the energy in atomic units immediately give the conversion from electron volts to au, i.e. 1 au of energy is equivalent to twice the ground state binding energy of the hydrogen atom, 27.2 eV.

Thus, the potential well provided by the effective potential $V_{\text{eff}}(r)$ of the Coulomb potential supports an infinite number of energy levels. This is in contrast to other cases, e.g. a three dimensional square well, in which there are only a finite number of levels. The reason for the infinite number of levels is that the Coulomb is a very long range potential, i.e. $1/r$ falls off very slowly with increasing $r$.

The figure below is a schematic energy level diagram of the hydrogen levels.

![Energy level diagram of hydrogen](image-url)

The energy levels of hydrogen superimposed on a graph of the Coulomb potential.